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UNIVERSITY OF SOUTHAMPTON

New Liquid Crystals For Display Mixtures

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MA (Oxon)

A thesis submitted for the degree of Doctor of Philosophy

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ABSTRACT

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NEW LIQUID CRYSTALS FOR DISPLAY MIXTURES

by Frederick Holden Boardman

This thesis is concerned with the design, synthesis and properties of thermotropic liquid crystals based on the fluorene and 9,10-dihydrophenanthrene core units. Derivatives of 9,10-dihydrophenanthrene were found to be both expensive to prepare and difficult to purify, and attention was concentrated on fluorene derivatives. Simple 2,7-disubstituted fluorenes are either monotropic or exhibit enantiotropic smectic phases. Accordingly a third benzene ring was directly coupled to the fluorene core to give a 2-phenylfluorene.

The homologous series of 2-(4-cyanophenyl)-7-alkylfluorenes from ethyl to nonyl was prepared *via* a five step convergent synthesis, and the compounds were isolated as white crystalline solids. All the compounds exhibited enantiotropic nematic phases, and the heptyl, octyl and nonyl homologues also exhibited a smectic A phase. The parent compound 2-(4-cyanophenyl)fluorene with no alkyl chain was prepared by a similar route, but did not exhibit an enantiotropic mesophase.

Some physical properties of 2-(4-cyanophenyl)-7-pentylfluorene were measured, and many values (*e.g.* dielectric anisotropy and birefringence) were similar to those for the commercially successful 4-pentyl-4'-cyano-*p*-terphenyl. However 2-phenylfluorene material had a higher viscosity. These properties could be related to the crescent shape of the 2-phenylfluorene core, which is dictated by the bridging methylene group.

Lateral substitution of the fluorene core was investigated in an attempt to prepare low melting point derivatives. Four C9 alkylated compounds were prepared, and these were found to be oils. However no mesophases were detected.

Some 2-(4-alkoxyphenyl)-7-alkylfluorenes were prepared as low birefringence analogues, but these were found to exhibit smectic phases at high temperatures.

The analogous alkoxy compound 2-pentoxy-7-(4-cyanophenyl)fluorene was prepared but could not be satisfactorily purified. Preliminary investigations into partial reduction of the fluorene core were carried out, but these did not progress beyond an early stage.

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This thesis and the work described within it are entirely my own, except where I have *either* acknowledged help from a named person *or* when a reference is given to a published source or thesis. Text taken from another source will be enclosed in quotation marks or written in italics and a reference will be given.

ABBREVIATIONS

5CB	4-Pentyl-4'-cyanobiphenyl
5CT	4-Pentyl-4''-cyano- <i>p</i> -terphenyl
BP-DEF	9,9-Diethyl-2,7-bis(pyrrol-2-yl)fluorene
DLS	Dynamic light scattering
DSC	Differential scanning calorimetry
GCMS	Gas chromatography mass spectroscopy
IPS	In-plane switching
LEP	Light emitting polymer
MBBA	<i>N</i> -(4-methoxybenzylidene)-4-butaniline
PAA	Bis(4-methoxyphenyl)-diazene- <i>N</i> -oxide
PET	Petroleum ether (boiling range (°C) stated in parentheses)
PFPV	Poly(9,9-dihexylfluorene-2,7-diylvinylene- <i>alt</i> -2,6-pyridinylenevinylene)
PFV	Poly(fluorenylenevinylene)
POM	Polarized optical microscopy
PPV	Poly(phenylenevinylene)
rt	room temperature
TMS	Tetramethylsilane
TN	Twisted nematic

1. INTRODUCTION

1.1 OVERVIEW

The mention of *liquid crystals* conjures up images of pocket calculators and digital watches. The advent of the liquid crystal display opened up new possibilities, satisfying a demand for lightweight, affordable, low power consumption devices and creating a market for portable computers and flat screen televisions. There is a strong commercial drive for new liquid crystal materials to make improved devices. The search has been given added urgency in the face of competition from emerging display technologies, such as light emitting polymers (Section 1.11).



Fig. 1: (i) Flat screen computer; (ii) calculator; (iii) digital watch.

The invention of the liquid crystal display represents one of the most important technological achievements of the twentieth century. It resulted from many years of research, and was made possible by co-operation between chemists, physicists, mathematicians and device engineers. There are now over seventy thousand reported liquid crystalline materials, in a world market worth around ten billion pounds per year. However only a fraction of these compounds are suitable for use in display devices, and there is still plenty of room for improvement.

1.2 HISTORICAL PERSPECTIVE

The history of liquid crystals began in the late nineteenth century with an Austrian botanist and his studies into the natural product cholesterol.¹ Reinitzer derivatized cholesterol as the benzoate ester **1**, but, despite numerous attempts at purification, he could not obtain a sharp transition from the crystalline solid to an isotropic liquid.

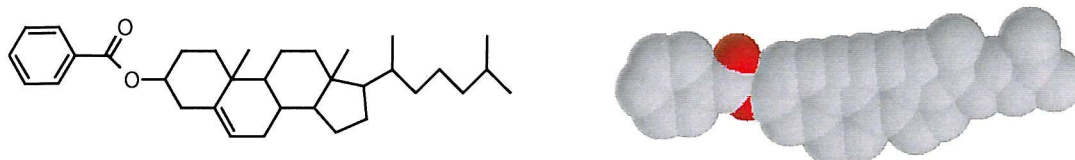


Fig. 2: (i) Cholesteryl benzoate 1; (ii) space filled model.

On heating, the material first melted sharply at 146 °C to give a cloudy fluid. At a higher temperature (179 °C) the fluid abruptly cleared to give a conventional transparent liquid. Reinitzer also observed that the material exhibited a range of colours, particularly near to the clearing point. He could not explain these observations and passed his findings and a sample of the unusual material to Lehmann, an authority on crystals working in Germany. Lehmann had adapted a microscope by the addition of a heated stage, which allowed the temperature of the sample under observation to be precisely controlled. He used this microscope to carry out detailed studies into the phase transitions of a number of compounds by monitoring changes in optical appearance. Lehmann's experimental setup was the forerunner of the polarized optical microscope and heated stage shown in Figure 3.

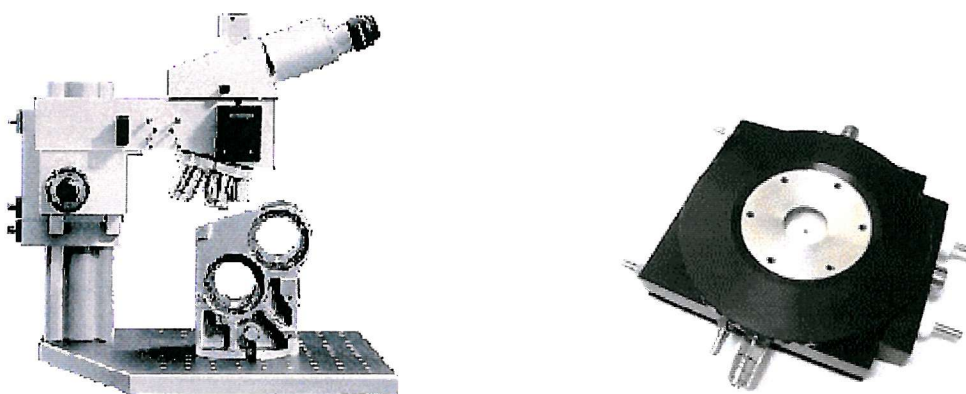


Fig. 3: (i) Polarized optical microscope; (ii) heated stage.

After many studies Lehmann was convinced that he was observing a new state of matter.² He coined the description *fliessende krystalle!* (flowing crystals) to describe the region between the melting and clearing points. However this term did not last, and the materials became known as *liquid crystals*. It is this combination of the flow properties of liquids and the birefringence associated with solids that make liquid crystals a distinct state of matter.

1.3 STRUCTURED FLUIDS

A solid has a fixed size and shape. The molecules which make up the solid librate about a fixed position within a lattice array. This is positional order *i.e.* there is a correlation

between their centres of mass. The molecules in a solid also have orientational order, as they are arranged such that their axes lie along specific directions. Both the positional and orientational order are long range, giving rise to a periodic structure. Most crystalline solids (Cr) are anisotropic *i.e.* their physical properties vary according to the axis of measurement. In some cases the bulk solid is isotropic.

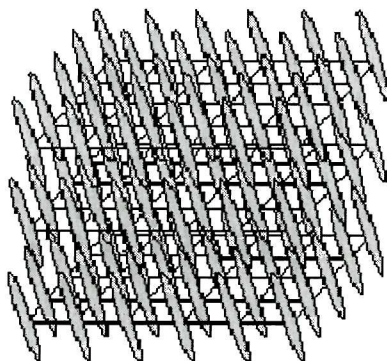


Fig. 4: Molecular organization in a crystalline solid.

When a solid is heated to give a liquid the periodic structure is lost. The molecules in liquids are no longer constrained to occupy fixed positions, but are free to move around relative to one another. There is no positional or orientational order (except at short range), and the physical properties of the liquid are the same in all directions. The material is said to be isotropic (I).

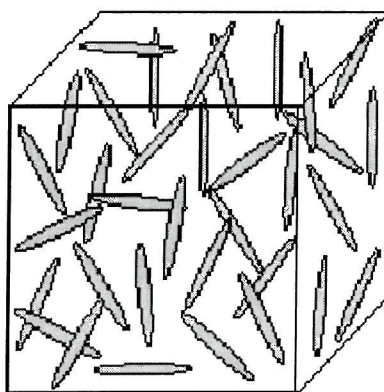


Fig. 5: Molecular organization in an isotropic liquid.

Liquid crystals occupy the middle ground between crystalline solids and isotropic liquids. For this reason, materials which are capable of forming a liquid crystal phase (or mesophase) are known as mesogens (from *meso*, meaning middle). However the properties are not simply an average of the properties of a solid and a liquid. Liquid crystals are

anisotropic fluids, exhibiting the anisotropic properties of a solid, *e.g.* birefringence, but having the flow characteristics of a liquid. The mesogenic molecules retain a degree of long range orientational (and sometimes positional) ordering.

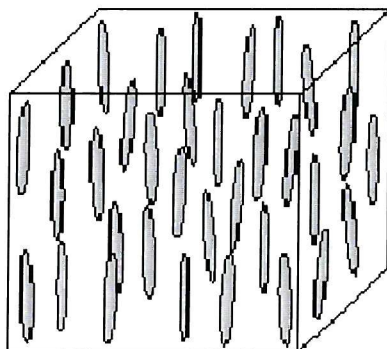


Fig. 6: Molecular organization in a nematic liquid crystal.

Many thousands of compounds exhibit a mesophase region. It is to be found on the phase diagram between the solid and liquid states. The size of the mesophase region is mainly determined by the molecular structure; however it also depends on the temperature and pressure. Most studies of phase behaviour are made at atmospheric pressure, and the mesophase region is therefore usually quoted as the temperature range between the melting and clearing points.

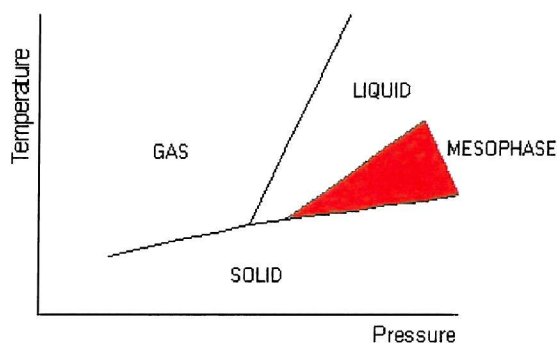


Fig. 7: Phase diagram.

When a liquid crystalline material is heated the first transition is the melting of the solid to give a cloudy fluid. This is the melting point, the lower temperature boundary of the mesophase. The degree of opacity depends on the magnitude of the birefringence, hence some mesophases may only be very slightly cloudy. On further heating there may be transitions between different types of mesophases, until finally the cloudy fluid clears to give an isotropic liquid. This is the clearing point, the upper temperature boundary of the mesophase. For pure materials these are sharp transitions, *i.e.* occur across a narrow

temperature range. The mesogenic range is the region between the melting and clearing points. A knowledge and understanding of the factors which influence the melting and clearing points are of key importance in the study and application of liquid crystals.

1.4 LYOTROPICS AND THERMOTROPICS

There are two extreme types of liquid crystal, lyotropics and thermotropics.

1.4.1 Lyotropics

Lyotropics are important in many biological systems, where they are an important constituent of cell membranes. They are formed when materials such as detergents are added to water. Lyotropic phases are formed by amphiphilic molecules, *i.e.* those which possess both polar and non-polar regions. The polar region is hydrophilic (water loving) whereas the non-polar region is hydrophobic (water hating). When amphiphilic molecules are added to water they dissolve to give a solution. Above a certain concentration (the critical micelle concentration) the molecules aggregate to form micelles.

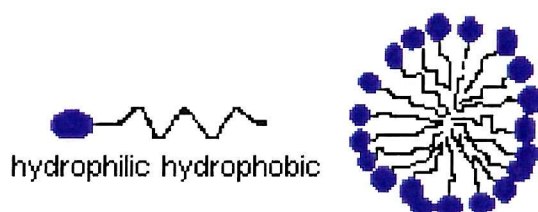


Fig. 8: (i) Amphiphilic molecule; (ii) micelle.

By forming a micelle the hydrophobic “tails” are kept away from the water. The surfactants found in washing powders work on this principle, trapping particles of oil or dirt inside the micelle. The outer surface of the micelle is hydrophilic, so the hydrophobic oil or dirt is in effect made water soluble.

At very high concentrations of amphiphile the micelles interact to form more complex structures, such as lamellar phases. In some of these phases the molecules are inverted, with the hydrophilic regions inside the micelles. Aqueous solutions are then trapped inside the structure. If the aqueous solution contains a metal then the micelles provide the template for a structured material.

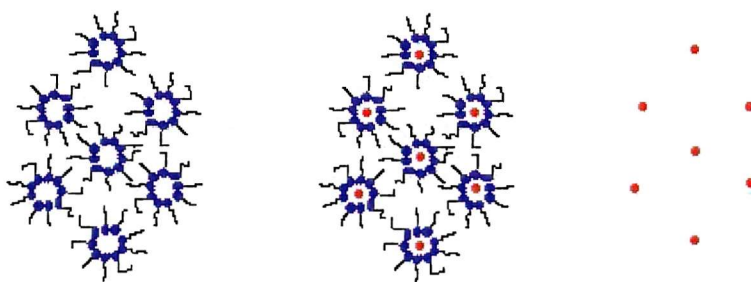


Fig. 9: (i) Lamellar phase; (ii) trapped metal atoms; (iii) structured material.

1.4.2 Thermotropics

This thesis is concerned with the development of thermotropic materials for use in liquid crystal displays, and lyotropic materials were not studied. Thermotropics are pure materials which exhibit liquid crystal phases across a given temperature range. Phases which can be observed reversibly on heating and cooling are enantiotropic, whereas those which may only be observed on supercooling are said to be monotropic.

As early studies into liquid crystals progressed, it became apparent that different types of mesogenic materials existed. These materials were classified according to their properties, and in particular the optical textures they exhibited when studied by polarized optical microscopy. Initially there were thought to be two classes: nematics and smectics. Later, subdivisions were introduced as more materials were prepared and studied. Developments in both the theory and physical structure of mesophases increased the understanding of the arrangement of molecules within the phase. The phases may be classified more formally by relating the observed macroscopic properties to the molecular organization within the phase.

1.5 PHASE MODIFICATIONS

1.5.1 Nematic

A nematic (N) is the least ordered phase. The molecules align with their long axes approximately parallel. This preferred alignment is called the director, \mathbf{n} . There is no correlation between the centres of mass, and at short range the nematic is similar to an isotropic liquid.

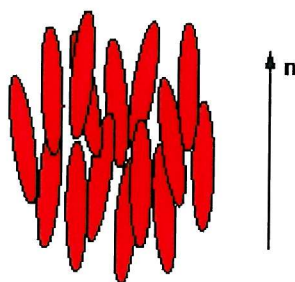


Fig. 10: Nematic phase and director \mathbf{n} .

When studied using a polarized optical microscope and white light, a nematic material exhibits a variety of colours and patterns, particularly near to the clearing point *i.e.* the nematic to isotropic transition. When the sample is physically manipulated with a spatula it shears easily, and produces bright birefringent flashes when compressed. The word nematic is derived from *nematos*, meaning “thread-like,” which describes fluid defects observed in some conditions. The director in the bulk non-aligned sample normally varies in a uniform way, which give the nematic schlieren texture its characteristic appearance. There are also abrupt changes, giving rise to disinclinations, and when viewed in a polarizing microscope the defects are seen as black brushes, which have 2 or 4 arms, like a Maltese cross.

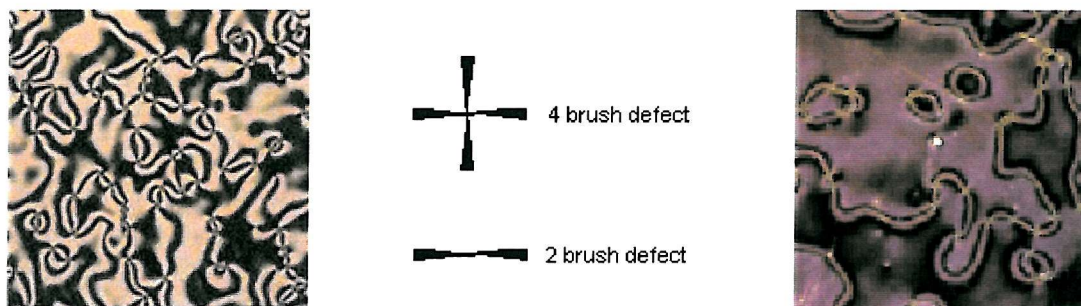


Fig. 11: Nematic Schlieren texture.

1.5.2 Chiral nematic

The nematic phase has a chiral analogue (N^*) in which the director varies in a helical fashion. This phase is exhibited by optically active mesogens, such as Reinitzer's cholesteryl benzoate **1**. They were therefore known originally as cholesterics. However they are more correctly termed chiral nematics, because the essential feature is chirality and not the presence of a cholesterol structure. The local arrangement of molecules is also the same as in the nematic phase. Chiral nematic phases are usually highly coloured, as the pitch (repeat length) of the helix is of the order of the wavelength of visible light and therefore reflects certain frequencies strongly.

The pitch length of the helix is a function of temperature, and it decreases on heating as the helix becomes more tightly wound. Shorter wavelengths are therefore reflected, and there is a blue shift on heating. This unexpected behaviour arises from a strong pretransitional effect at the low temperature end of the chiral nematic phase, just above the smectic A to nematic transition. At the transition from ordered smectic phase to chiral nematic the molecular ordering must be similar to avoid a sudden change in structure. The smectic A phase has no distortion, so the helix must be unwound (*i.e.* infinite pitch length) at the transition. As the temperature is increased the helical pitch length decreases. If the material does not exhibit a smectic A phase then there is no pretransitional effect, and the pitch length does not necessarily decrease on heating.

Chiral nematics are used in strip thermometers, which consist of a series of segments of mesogenic mixtures on a backing sheet of black light-absorbent material. These segments of material are carefully formulated so as to have a helical pitch length of the order of the wavelength of visible light across a number of sequential narrow temperature ranges. When a given temperature is reached the pitch length of the corresponding segment is of the order of the wavelength of visible light. The incident light is reflected, and the segment appears highly coloured. Above or below this temperature no light of visible wavelengths is reflected and the segment appears black, as light is transmitted through the mixture where it is absorbed by the backing layer. The red segment in Figure 12 has a helical pitch length of the order of the wavelength of visible light, and therefore reflects the incident light.

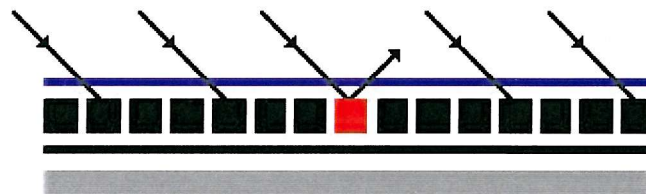


Fig. 12: Strip thermometer.

Chiral nematic materials are also used for more sophisticated thermal imaging. The object under study, *e.g.* a section of aerofoil in a wind tunnel, is coated with a chiral nematic mixture. The mixture is formulated such that the helical pitch length varies linearly with temperature. The wavelength of light which is reflected changes as the pitch length alters, therefore a given colour corresponds to a particular temperature. A photograph of the aerofoil section allows patterns of airflow to be determined from the colour and hence the temperature at various points.

1.5.3 Smectic A

Smectic phases have some positional ordering, with the molecules forming loosely layered structures. The name smectic is derived from *smectos*, meaning soap-like, as early observations noted that the materials were similar to soaps, *i.e.* slippery. The least ordered modification is the smectic A (SmA) phase. The molecules are arranged in layers with the director perpendicular to the layer. The positions of the molecules in adjacent layers bear no relationship to one another.



Fig. 13: Smectic A phase and director \mathbf{n} .

The smectic A phase is much more viscous than a nematic, and samples behave as gummy solids when studied by polarized optical microscopy. If the director is perpendicular to the microscope slide, *i.e.* homeotropically aligned (Section 1.8.1), a black, optically extinct texture is observed. Physical manipulation with a spatula usually results in shearing to give the characteristic focal conic fan texture because the alignment is no longer homeotropic. Focal conics arise from arrangement of the molecules in a series of curved layers.

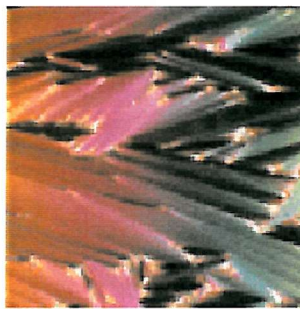


Fig. 14: Smectic A focal conic fan texture.

1.5.4 Smectic C

The smectic C (SmC) phase is similar to the smectic A, with the molecules arranged in layers. The difference is that the director is no longer perpendicular to the layers, but is tilted by an angle θ to the layer normal.

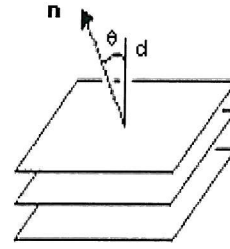
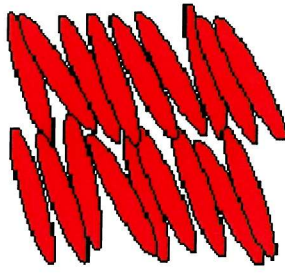


Fig. 15: Smectic C phase and director \mathbf{n} .

Because of the tilt angle θ , it is not possible for the sample to be homeotropically aligned. Focal conics are seen, and a schlieren texture with four brush defects only is exhibited.



Fig. 16: Smectic C focal conic texture.

1.5.5 *Smectic B*

In the smectic B (SmB) phase the director is perpendicular to the layer, as in the smectic A phase. However there is positional ordering within the layer, as at short range the molecules are loosely packed in a hexagonal arrangement. There is additional ordering of these hexagons over a long range.

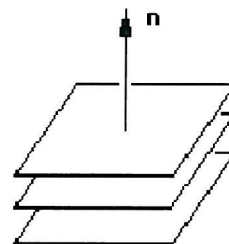
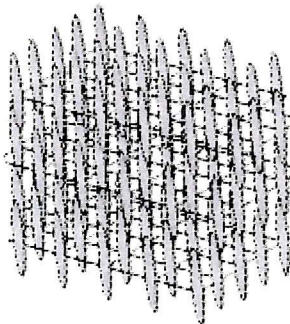


Fig. 17: Smectic B phase and director \mathbf{n} .

When studied by optical microscopy, there are three possible textures: optically extinct, resulting from homeotropic alignment, focal conics and mosaic.

1.5.6 Crystal phases

Other ordered phases are known. They are much closer to crystals, and are not as frequently encountered.

1.6 PHYSICAL CHARACTERIZATION

When confronted with a new material the primary task is to place it in one of the classes outlined above (Section 1.5). To do this the macroscopic properties of the material must be related to the molecular organization. Three techniques can assist with this task: polarized optical microscopy, differential scanning calorimetry and X-ray analysis.

1.6.1 Polarized optical microscopy

A liquid crystal phase is usually identified experimentally by the optical texture observed when the material is studied using a polarized optical microscope (POM). This is similar to a conventional microscope, but the sample is placed on a heated stage between a pair of crossed plane polaroids. White light passes through the first polaroid to give plane polarized light, which is incident on the sample. If the material under study is isotropic then the plane of polarization of the light is unchanged by passage through the sample. In this case no light can pass through the second polaroid, as it is perpendicular to the plane of polarization. The sample therefore appears black.

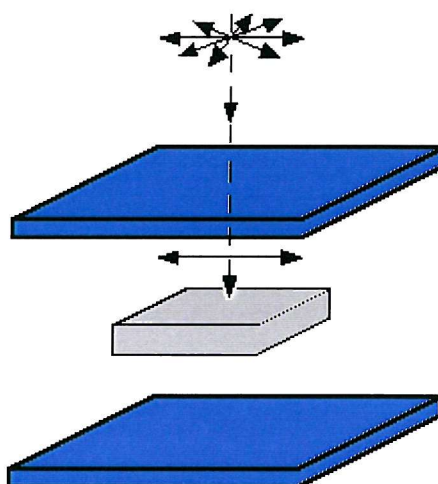


Fig. 18: POM: isotropic sample – no light transmitted.

If the sample under study is birefringent, the plane of polarization is changed as it is transmitted through the sample. A single crystal of a solid appears transparent, as the plane of polarization of the transmitted light is no longer perpendicular to the second polaroid,

and some of it is transmitted. Liquid crystalline materials are birefringent, therefore some of the incident light is transmitted. The manner in which the light is transmitted is dependent on the liquid crystal phase and the orientation of the director \mathbf{n} .

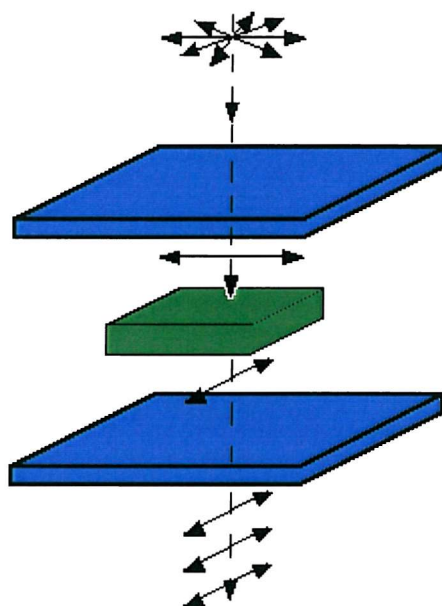


Fig. 19: POM: birefringent sample – light transmitted.

However, within the sample the director changes, giving rise to a series of patterns indicative of the director orientation. This characteristic defect texture often allows the phase to be identified (Section 1.5).

1.6.2 Differential scanning calorimetry

Differential scanning calorimetry is used to locate phase transitions and study their thermodynamics. At a first order phase transition there is a change in enthalpy and entropy. These changes may be very small, and a sensitive technique is needed to detect and measure them. DSC very accurately monitors the heat input required to increase the temperature of the sample under study.

A small amount of material (≈ 5 mg) is placed in an aluminium sample pan, the pan is sealed and then placed in an oven. An identical empty container (the reference pan) is also placed in the oven. The oven is heated at a controlled rate, usually $10^{\circ}\text{C min}^{-1}$, and the sample and reference pans are maintained at the same temperature. Heat is applied to the sample pan in order to keep it at the same temperature as the reference. The heat supplied is monitored by the instrument as a function of temperature.

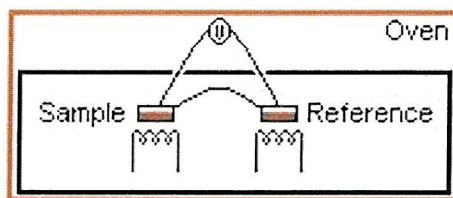


Fig. 20: Differential scanning calorimeter.

Both a heating and a cooling curve are recorded. This first cycle is used simply to anneal the sample, and it is the second heating curve which is used for calculations. The resulting DSC trace is a plot of heat input vs. temperature. For most materials the transitions are endothermic, *i.e.* an input of heat is required to effect a phase transition. At the melting point a relatively large input of heat is required, as the change in molecular organization from a solid to a fluid is large. Other phase transitions, *e.g.* liquid crystal to isotropic, only require a small input, as the molecular organizations are similar.

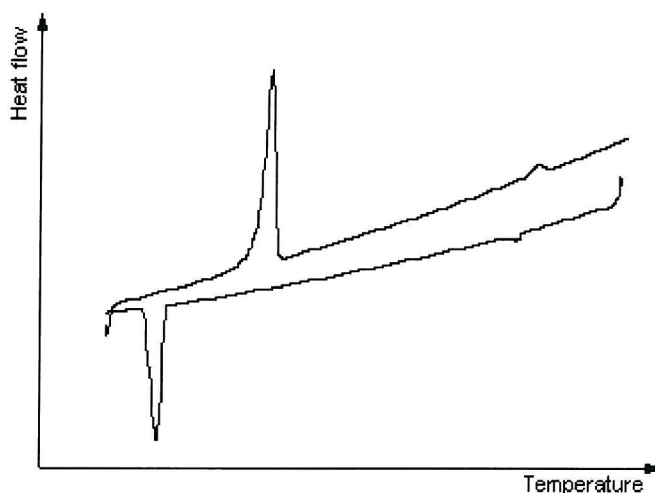


Fig. 21: DSC trace.

The sample has a heat capacity, therefore a small input of heat is required to keep the pan isothermal with the reference, and the DSC trace slopes up from left to right. The area under a peak is proportional to the enthalpy of transition. The instrument is calibrated using a standard material, enabling the area under the peak to be converted into the energy for the transition. The mass of sample is known, and the molar enthalpy of transition (ΔH_{trans}) can be calculated.

At the phase transition the two phases are in equilibrium and must therefore have the same free energy (G). Consequently the change in free energy (ΔG) is zero at any phase transition.

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G_{\text{trans}} = 0 \quad (\text{at a phase transition})$$

$$\therefore \Delta H_{\text{trans}} = T_{\text{trans}}\Delta S_{\text{trans}} \quad (\text{by substitution})$$

$$\therefore \Delta S_{\text{trans}} = \Delta H_{\text{trans}}/T_{\text{trans}} \quad (\text{rearranging})$$

The temperature of the phase transition (T_{trans}) is obtained from the DSC trace, and the molar entropy of transition (ΔS_{trans}) can then be calculated. This is usually then divided by the gas constant R to give the dimensionless quantity $\Delta S_{\text{trans}}/R$.

DSC gives transition temperatures and calorimetric data for a material. It cannot identify the mesophases exhibited by the material. However the magnitudes of the values (especially $\Delta S_{\text{trans}}/R$) do give an indication of the likely identity of the phase involved.

Table 1: Calorimetric values for 4-octyl-4'-cyanobiphenyl **2h**.

Transition	T_{trans}/K	$\Delta H_{\text{trans}}/kJmol^{-1}$	$\Delta S_{\text{trans}}/R$
Cr \rightarrow SmA	294 ³	25.1 ³	10.3 *
SmA \rightarrow N	305 ³	0.18 ³	0.07 *
N \rightarrow I	313 ³	0.84 ³	0.32 *

* Calculated using $\Delta S_{\text{trans}} = \Delta H_{\text{trans}}/T_{\text{trans}}$

1.6.3 X-ray diffraction

Liquid crystalline materials can be studied by X-ray diffraction. The director is aligned by applying a uniform magnetic field. This is usually done in the fluid nematic phase, as alignment of the more viscous smectic phases is not usually so easy. When the aligned sample is placed in an X-ray diffractometer, signals are scattered by the ordered phase. Different phases produce characteristic scattering patterns which reflect the molecular ordering within the phase.

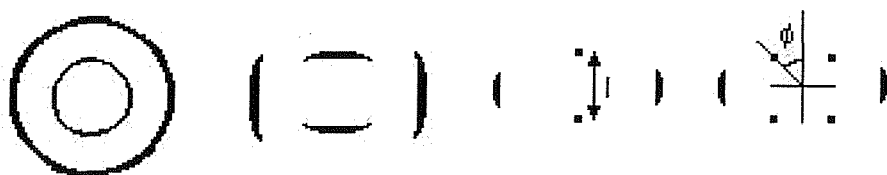


Fig. 22: X-ray diffraction: (i) isotropic; (ii) nematic; (iii) smectic A; (iv) smectic C.

An isotropic sample gives the diffuse rings, whereas a nematic material gives two pairs of bands. The smectic A material has a layered structure, and reflections from these layers

give a single pair of bands and two dots. The pair of bands are less diffuse than those of the nematic molecule, and the gap between the two dots corresponds to the layer spacing l . A smectic C material is more ordered, and gives a single pair of bands and four dots. The tilt angle ϕ can be measured from the scattering pattern.

1.6.4 Joint application of techniques

Differential scanning calorimetry and X-ray diffraction are important complementary techniques for the study of liquid crystals. However, for initial phase identification the microscope is the most popular and powerful tool due to its low cost and ease of use. Calorimetric studies can then be carried out by DSC, giving important information about phase transitions. X-ray studies are used to unambiguously identify a phase, but a combination of techniques is needed in order to gather a range of information.

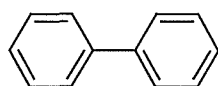
1.7 ANATOMY OF A LIQUID CRYSTAL

The main structural requirement for a mesogenic molecule is shape anisotropy. The molecules should be rod-shaped, with a length-to-breadth ratio of at least 3:1. These are known as calamitic molecules.

1.7.1 The liquid crystal core

Normally, a carbocyclic moiety forms the central part of the molecule, defining the molecular architecture and imparting some structural rigidity. Traditional core units are unsaturated, providing for delocalization of π electrons over the molecule. The most widely used of these is the benzene ring, although many others are known.

One or more of these units may be joined together by a linking group to give a larger core. Typical groups include esters and imines, although a direct carbon-carbon bond may be used, *e.g.* two benzene rings are directly linked by an aryl-aryl bond to give biphenyl **3**.

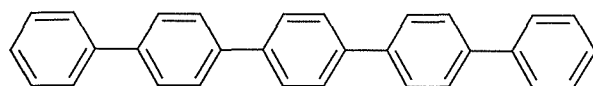


Cr 71 I

Fig. 23: Biphenyl **3**.

Although biphenyl itself is rod-like it does not form a mesophase, as its length-to-breadth ratio is too small. Linking together five benzene rings give quinquephenyl **3**, which has a much larger length-to-breadth ratio. The increased molecular length makes **3** mesogenic, forming an nematic phase.⁴ These transition temperatures are very high, reflecting the

efficient packing in the solid state.

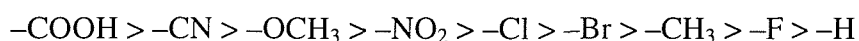


Cr 380 N 431 I

Fig. 24: Quinquephenyl **4**.

1.7.2 Polar end groups

Polar substituents have a strong role in influencing phase formation. From empirical studies it has been shown that the following order reflects the relative ability of an end group to promote a nematic phase:



An early report⁵ studied the *phase promoting efficiency* of various terminal groups, and concluded that *the order is the order of decreasing polarity regardless of sign; and so evidently the main factor is the magnitude of the group dipole*. This seems to hold for the above list, apart from fluorine, which forms a very polar bond to carbon but shows a poor nematic promoting efficiency. Clearly the role of polar substituents is more subtle than at first thought.

Carboxylic acids are a special case, as they form hydrogen bonded dimers. This doubles the effective length of the molecule, which leads to a larger than expected length-to-breadth ratio and therefore makes the molecule mesogenic. In this case the cyano groups of adjacent molecules preferentially align parallel to one another, with the dipoles paired, *i.e.* with the molecules pointing in opposite directions. The overall effect of this is to loosely order the molecules into pairs, similar to the dimers formed by carboxylic acids. The result is a nematic phase, with the long axes of the molecules aligned approximately parallel.

The polar cyano group is a strong nematic promoter, and is often used as an end group. Cyano-containing materials have had a great impact on the development of materials for display devices.

1.7.3 Flexible chains

A small increase in molecular weight generally results in a slightly higher melting point (T_{trans}), as the enthalpy of transition (ΔH_{trans}) is greater, because of stronger intermolecular forces. However this is not always the case, as addition of a saturated alkyl or alkoxy chain actually lowers the melting point of the compound, *e.g.* 4-butylbiphenyl **5d** (17 °C)⁶ has a lower melting point than biphenyl **3** (71 °C).⁷ The reduction in melting point stems from the

important role played by another factor, the entropy of transition (ΔS_{trans}). In the solid state the chain is held in a fixed conformation, and the atoms can only librate about fixed points. On melting, rotational degrees of freedom are realized as the conformational restraints on the chain are lost.

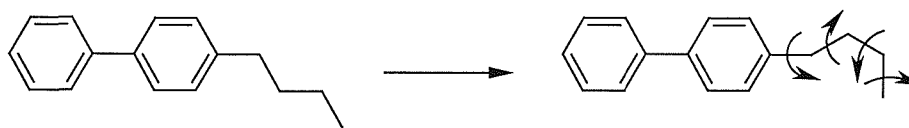


Fig. 25: 4-Butylbiphenyl **5d**: (i) solid state; (ii) after melting.

There is a large gain in entropy, as the chain now adopts many different conformations. The changes in Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) are related by the thermodynamic equation:

$$\Delta G = \Delta H - T\Delta S$$

At a phase transition (*e.g.* solid to liquid) the two phases are in equilibrium and must therefore have the same free energy. Consequently the change in free energy is zero at any phase boundary.

$$\Delta G_{\text{trans}} = 0$$

$$\therefore \Delta H_{\text{trans}} = T_{\text{trans}}\Delta S_{\text{trans}} \quad (\text{by substitution})$$

$$\therefore T_{\text{trans}} = \Delta H_{\text{trans}}/\Delta S_{\text{trans}} \quad (\text{rearranging})$$

As the chain length is increased there is a small increase in the enthalpy of melting, ΔH_{trans} . However a longer chain has a much greater number of possible conformations, and consequently a much larger entropy change on melting, ΔS_{trans} . Moving up a homologous series ΔS_{trans} increases more rapidly than ΔH_{trans} . Therefore ΔH_{trans} may be considered to be approximately constant.

$$\Delta H_{\text{trans}} \approx \text{constant}$$

$$\therefore T_{\text{trans}} \propto 1/\Delta S_{\text{trans}}$$

Longer chains have a greater number of degrees of freedom, so they have a larger entropy gain on melting. The temperature at the transition (*e.g.* the melting point T_{trans}) is therefore inversely proportional to the chain length n . This derivation explains the decrease in melting point observed as n is increased moving up a homologous series, *e.g.* the 4-alkyl-4'-cyano-*p*-terphenyls **6** (Section 3.4).

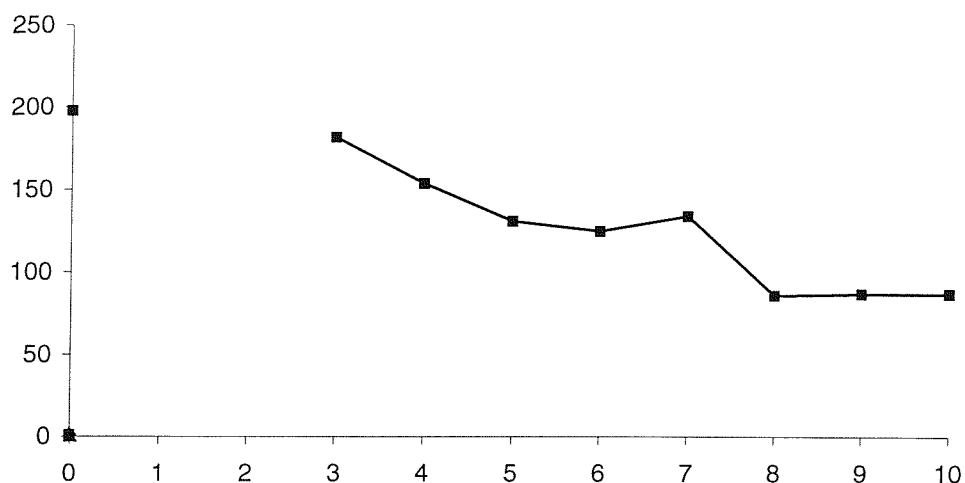


Fig. 26: Variation in melting point for the 4-alkyl-4'-cyano-*p*-terphenyls **6**.

1.7.4 Odd-even effect

Superimposed on the trend of decreasing melting points is the odd-even effect. Assuming that the lowest energy all trans conformation is adopted, molecules having chains with an odd number of carbon atoms (*e.g.* 4-pentylbiphenyl **5e**) pack more efficiently than those with even lengths (*e.g.* 4-butylbiphenyl **5d**).

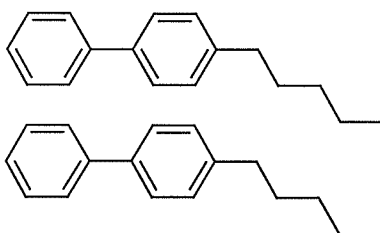


Fig. 27: (i) 4-Pentylbiphenyl **5e**; (ii) 4-butylbiphenyl **5d**.

The solid state structure is therefore more stable, so the melting point for the material is generally higher. There is therefore a saw tooth variation in the melting point (—), which can be pronounced in some homologous series, *e.g.* the 4-alkoxy-4'-cyanobiphenyls **7**.^{8,9}

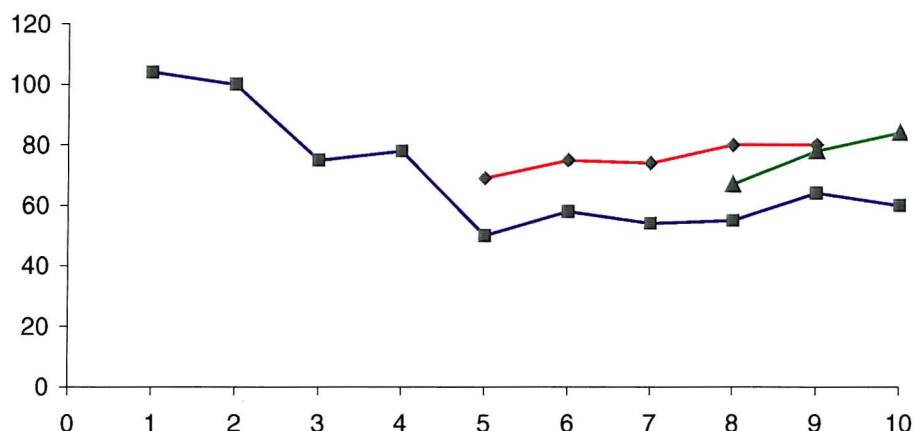


Fig. 28: Odd-even effect for the 4-alkoxy-4'-cyanobiphenyls **7**.

The clearing point (—) also tends to decrease as the chain length is increased. However the decrease is often less pronounced, resulting in a wider mesogenic range for the higher homologues. The clearing point can also show an odd-even effect.

A smectic phase often occurs at longer chain lengths, and the injection of a smectic to nematic transition (—) is observed. The smectic phase is favoured by long chain homologues, which stabilize the layered arrangement of the molecules.

1.7.5 Calamitic liquid crystals

A simple mesogenic molecule consists of three sections: a rigid core, a polar end group and a flexible chain. These rod-like molecules are known as calamitic liquid crystals.



Fig. 29: Calamitic liquid crystal.

It was thought that a fully polarizable core was a prerequisite for mesophase formation, and consequently most early work was directed towards conjugated aromatic systems.

However, later work showed that partially saturated cores often have enhanced properties.

Compared to 5CB **2e**, *trans*-1-(4-cyanophenyl)-4-pentylcyclohexane **8** (PCH-5) is less conjugated and more flexible. This confers a lower birefringence and viscosity on the material, which also shows an increased clearing point and therefore wider mesophase range than 5CB **2e**.¹⁰ Even a fully saturated core can still be liquid crystalline, providing

that the necessary rod-like architecture is retained, *e.g.* *trans*-1-(*trans*-4-cyanocyclohexyl)-4-pentylcyclohexane **9**.¹⁰

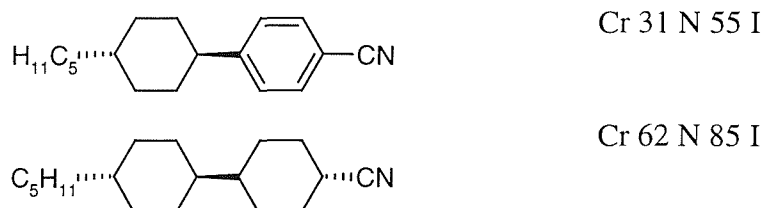


Fig. 30: (i) *trans*-1-(4-Cyanophenyl)-4-pentylcyclohexane (PCH-5) **8**; (ii) *trans*-1-(*trans*-4-cyanocyclohexyl)-4-pentylcyclohexane **9**.

However systems with alternating polarizable and non-polarizable regions do not usually form enantiotropic liquid crystal phases. The clearing point of *trans*-1-(4-cyanocyclohexyl)-4-pentylbenzene **10** is considerably lower than that of 5CB **2e**, and consequently the material forms a monotropic phase only on careful supercooling.¹⁰

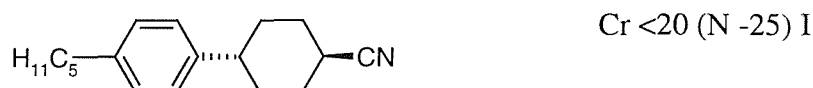


Fig. 31: *trans*-1-(4-Cyanocyclohexyl)-4-pentylbenzene **10**.

The primary requirement for a molecule to be mesogenic is the shape anisotropy, and it may be that **10** adopts an unfavourable conformation which causes the dramatic lowering in the clearing point.

1.7.6 Structure-property relations

The challenge is to tailor the structures of molecules to generate specific liquid crystal phases with the desired properties over a given range of temperature.¹¹ In order to accomplish this task, the constituent parts of the target molecule must be carefully chosen, as the outcome is a subtle interplay of many factors. The effects that changing the constituent parts of a molecule produce have been discussed previously, but another important aspect of choosing a target molecule is the ease of synthesis.

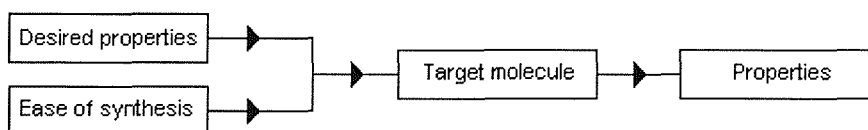


Fig. 32: Molecular engineering.

1.7.7 Discotic liquid crystals

Another type of mesogen was predicted by Vörländer. In the 1970s (relatively recent in the history of liquid crystals), this novel class of mesogenic materials was finally discovered. These are the discotics, or columnar phases, and are formed by disc shaped molecules such as 1,2,3,4,5,6-hexapentanoyloxybenzene **11**.¹²

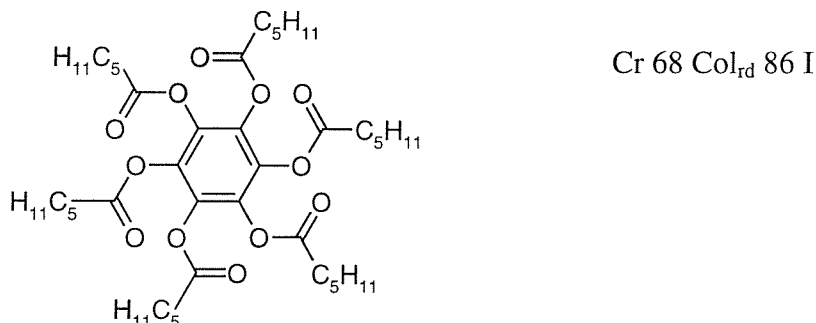


Fig. 33: 1,2,3,4,5,6-Hexapentanoyloxybenzene **11**.

The molecules have a diameter-to-thickness ratio of at least 3:1, and form stacks (columns) of discs. A number of different phases are possible, and these are classified according to the degree of ordering within the stacks.

1.8 DISPLAY DEVICES

In the hundred years following Reinitzer's work, many liquid crystals have been made. Vörländer and many others made outstanding contributions to the field.¹³ Later, Gray and others carried out much work towards the understanding of the link between chemical structure and mesogenic properties, establishing many rules for future generations of molecular engineers.¹⁴ But it was not until relatively recently that liquid crystals began to find commercial applications.¹⁵

Display devices rely on changing the appearance of a liquid crystalline material by the application of an electric field. The change in appearance is caused by altering the arrangement of molecules in the sample. The molecular arrangement is controlled by surface forces and applied electric fields.

1.8.1 Surface forces

By surface treatment of a substrate, *e.g.* glass, the director can be induced to lie parallel (uniform planar alignment) or perpendicular (homeotropic alignment) to the cell surface.



Fig. 34: (i) Uniform planar alignment; (ii) homeotropic alignment.

A display device works by being able to change the alignment of the director and hence the optical properties by the application of an electric field. The nematic phase is both fluid and anisotropic, and nematics form the basis of the highly successful liquid crystal display industry. Their high degree of fluidity allows the director orientation to be rapidly altered by an electric field. There is competition between surface induced alignment and the alignment by an applied electric field.

1.8.2 Dielectric anisotropy

In order to be used in display devices a liquid crystal must respond to an electric field. The presence of a polar substituent and polarizable electron density creates an anisotropy in the dielectric constant. It is this dielectric anisotropy that determines the alignment of the liquid crystal in an external electric field. The dielectric anisotropy ($\Delta\epsilon$) is the difference between the relative permittivity measured parallel (ϵ_{\parallel}) and perpendicular (ϵ_{\perp}) to the director.

$$\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$$

The relative permittivity depends on two factors, the permanent polarization arising from dipole moments created by polar substituents and the polarizability arising from redistribution of electron density when the molecule is placed in an electric field. It is therefore a combination of the magnitude and direction of permanent dipoles and polarizability that dictate the sign and magnitude of the dielectric anisotropy. It is usually the permanent dipoles that have the greater effect.

A permanent dipole may be established by the addition of a polar substituent, or by the incorporation of a polarized bond within the structure. Bis(4-methoxyphenyl)-diazene-*N*-oxide **12** (PAA) consists of two *p*-methoxybenzene rings linked by an azoxy group. The azoxy linking group contains a large polar bond at an angle of $\approx 60^\circ$ to the long axis of the molecule. Additionally the terminal methoxy groups each have a dipole, but it is the charged azoxy group that has the overriding effect. Consequently ϵ_{\perp} is larger than ϵ_{\parallel} , and the material has a small negative dielectric anisotropy.¹⁰

In the case of *N*-(4-ethoxybenzylidene)-4-aminobenzonitrile **13** the polar cyano group has a large dipole parallel to the molecular long axis. The Schiff's base linkage and the terminal

ethoxy groups also have dipoles. The overall outcome is a large dipole parallel to the molecular axis, and the molecule therefore has a large positive dielectric anisotropy.¹⁰

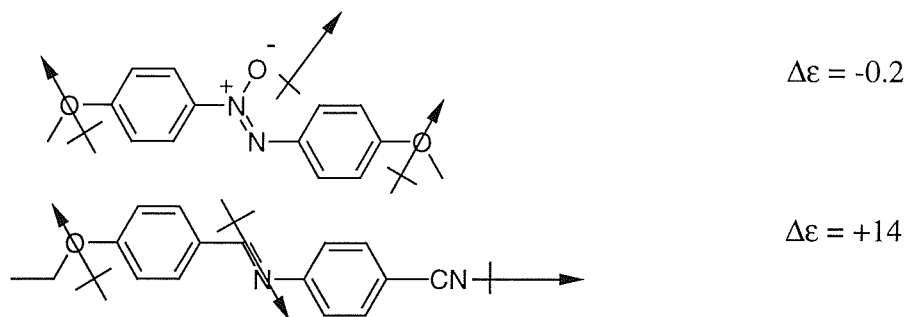


Fig. 35: (i) Bis(4-methoxyphenyl)-diazene-*N*-oxide **12**; (ii) *N*-(4-ethoxybenzylidene)-4-aminobenzonitrile **13**.

The sign and magnitude of the dielectric anisotropy determine the type of display device to which the material is suited.

1.8.3 Dynamic Light Scattering display

The first liquid crystal display devices appeared towards the end of the 1960s. These were the Dynamic Light Scattering displays, which relied on a conductive effect. The devices used compounds with a Schiff's base linkage such as *N*-(4-methoxybenzylidene)-4-butylaniline **14** (MBBA) and higher homologues.

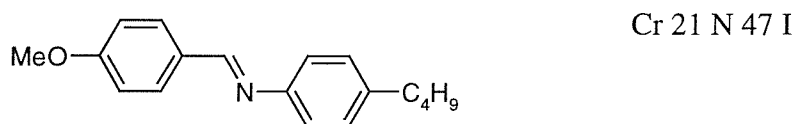


Fig. 36: *N*-(4-Methoxybenzylidene)-4-butylaniline **14**.

MBBA **14** has a negative dielectric anisotropy (Section 1.8.2). By suitable surface treatment the director is aligned parallel to the substrate. An electric field is applied across the cell, but because the material has a negative dielectric anisotropy the director still lies parallel to the substrate. This would be expected to give no change in appearance. However ionic impurities such as tetraalkylammonium halides are added, and these want to move parallel to the applied electric field. Movement parallel to the field is hindered by the uniform planar alignment of the director, and as a result it randomizes. This gives a turbid “on” state, which contrasts with the transparent “off” state. The essential requirement for the display mixture is that it has a positive conductivity anisotropy and a negative dielectric anisotropy, which results in electrohydrodynamic motion.



Fig. 37: Dynamic light scattering device: (i) transparent off state; (ii) turbid on state.

The advantage of the DLS display is that no polarizers are needed. Unfortunately the early devices had short lifetimes, as any trace of moisture hydrolyzed the Schiff's base linkage of MBBA **14**, resulting in a loss of liquid crystallinity.

1.8.4 Twisted Nematic display

To make durable devices more robust materials were needed. Accordingly Gray and colleagues designed and synthesized the 4-alkyl-4'-cyanobiphenyls, such as 5CB **2e**.¹⁶ These molecules are typical calamitic liquid crystals. They are composed of a rod-like core (biphenyl) with a small polar substituent at one end (the strongly nematic promoting cyano group) and an alkyl chain at the other end (to lower the melting point).

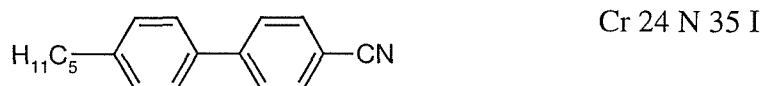


Fig. 38: 4-Pentyl-4'-cyanobiphenyl **2e**.

Such mesogens have a positive dielectric anisotropy and high birefringence, coupled with reasonable viscosity and high chemical and thermal stability, making them ideal for use in the early display devices. The drawback of these compounds is their limited mesogenic range. Adding a third 1,4-disubstituted benzene ring gives a terphenyl. 4-Alkyl-4''-cyano-*p*-terphenyls such as 5CT **6e** have similar properties to the alkylcyanobiphenyls, but have a much larger mesophase range.¹⁷ Unfortunately they have much higher melting points.

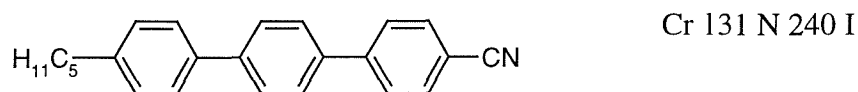


Fig. 39: 4-Pentyl-4''-cyano-*p*-terphenyl **6e**.

Neither 5CB **2e** or 5CT **6e** are mesogenic across a suitable temperature range. A device needs to operate over a wide temperature range, from around -20 to +60 °C.¹⁸ But the design and synthesis of a single compound which combines all the desired physical properties is not usually possible. However simply mixing **2e** and **6e** gave a eutectic mixture with a large nematic range.¹⁹

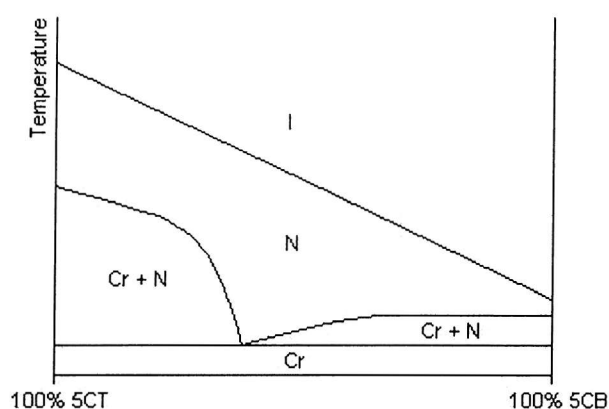


Fig. 40: Phase diagram for a mixture of 5CT **6e** and 5CB **2e**.

Several other components are added to the mixture to fine tune physical properties such as viscosity, elastic constants and birefringence. These mixtures are used in seven segment twisted nematic displays, such as those found in digital watches for three decades. A thin layer of nematic mixture ($\approx 10\mu\text{m}$) is sandwiched between a pair of transparent electrodes to make a cell. The cell is placed between a pair of crossed polaroids. Suitable treatment of the cell surface makes the director line up in a quarter turn spiral. The cell thickness is selected to give a spiral with a pitch length much longer than the wavelength of visible light. The spiral acts as a waveguide, light is transmitted, and the cell appears transparent. This is the "off" state. When an electric field is applied, the director aligns parallel to the electric field. The spiral is lost, and there is no longer a waveguiding effect. No light is transmitted and the cell appears black. This is the "on" state.

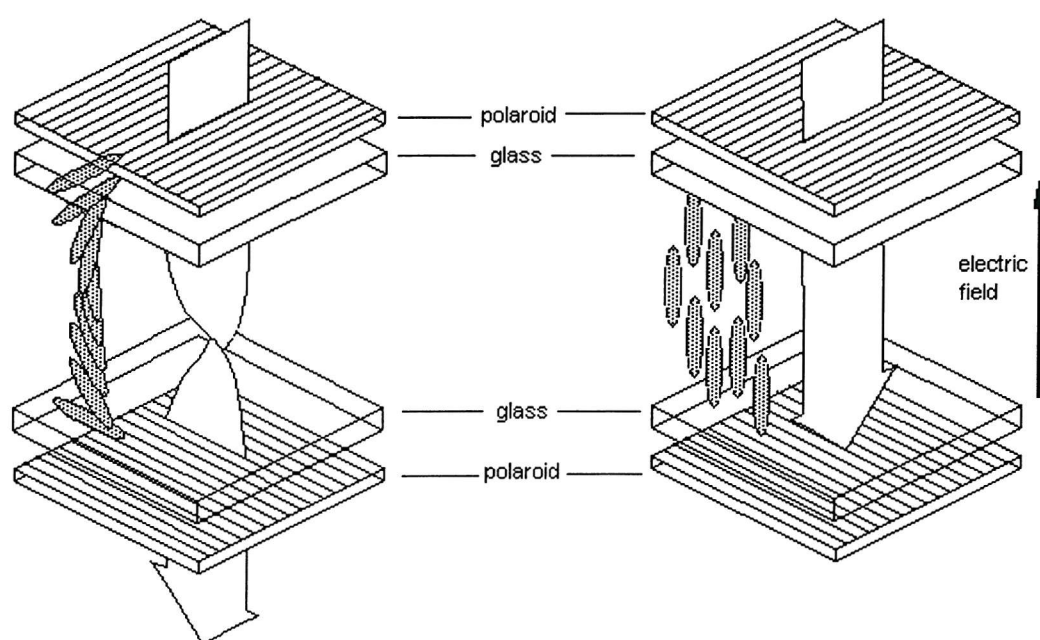


Fig. 41: The twisted nematic device: (i) off state; (ii) on state.

Despite its success the twisted nematic device does have limitations. The switching time between the off and on states is slow and the maximum display size is relatively small. The devices of the future will incorporate complex larger displays where higher resolution (smaller pixels) and faster switching is required. Rather than having individually addressed electrodes as in a seven segment display, multiplexing is used. The electrodes on one side of the cell are arranged in rows and those on the other side are arranged in columns. To “switch on” a pixel it must receive a suitable electrical signal to both its row *and* column. This requires materials of exceptionally low conductivity, or charge leakage occurs giving a transient on state. There must be a clear visible difference between the on and off states in order to give high contrast. There is therefore a need for new mesogenic materials, which combine the properties needed for a new generation of display devices.

1.9 NEW NEMATOGENS

The project is concerned with the development of new nematogens based on fused carbocyclic cores, in particular 6,5,6- and 6,6,6- biphenyl analogues. When two aromatic rings of biphenyl are linked with an alkyl bridge a more structurally rigid core unit results. Linking with a methylene bridge gives fluorene **15**, whereas an ethane unit gives 9,10-dihydrophenanthrene **16**.



Fig. 42: (i) Fluorene **15**; (ii) 9,10-dihydrophenanthrene **16**.

These structural constraints result in lower flexibility and a different packing arrangement. The conformation of 9,10-dihydrophenanthrene **16** is similar to that of biphenyl. The rings do not lie in the same plane, but are twisted through *ca.* 20°. ²⁰ The two conformers of 9,10-dihydrophenanthrene, **16a** and **16b**, are identical in the unsubstituted material. The energy barrier is low and interconversion between the conformers is rapid.

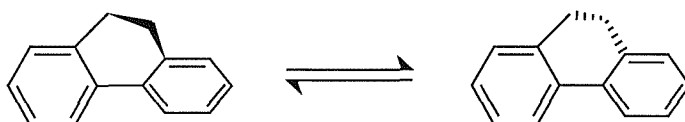


Fig. 43: Two conformers of 9,10-dihydrophenanthrene **16a** and **16b**.

9,10-Dihydrophenanthrene is prepared by catalytic hydrogenation of phenanthrene. The

resulting material is commercially available, but in a relatively impure form. The material has a low melting point, 34 °C,²¹ which appears to make it an ideal core for the formation of room temperature mesogens (biphenyl has a higher melting point, 71 °C).⁷ However the increased molecular width of 9,10-dihydrophenanthrene reduces the length-to-breadth ratio, which disfavours the formation of mesophases.

Bridging with a methylene group to give fluorene **15** imposes much greater structural constraints, as a rigid cyclopentane ring is formed. By simple geometric constraints this forces the aromatic rings to become coplanar, and turns the *para* axes through 24° to accommodate the 5-membered ring. Solid state studies produced an X-ray structure which confirms the bent structure of the molecule.²²

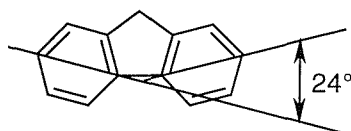


Fig. 44: Molecular structure of fluorene **15**.

Fluorene is a white solid with a melting point of 115 °C.²³ It is a by-product of coal tar distillation, and is available inexpensively and in a high state of purity. The advantages of fluorene are (i) coplanar rings leading to a better overlap and greater delocalization of π electrons, and; (ii) the C9 position as a site for lateral substitution. A delocalized π system is not a prerequisite for mesophase formation, but is advantageous for potential luminescence properties. Lateral substitution provides an additional weapon in the synthetic armoury. The great deal of recent interest in fluorene-based materials makes them worthy of serious consideration (Section 1.11).

1.10 SYNTHETIC TRANSFORMATIONS

The synthesis of a target compound may not be straightforward, especially if it has to be repeated several times to make a homologous series. There needs to be an important balance between design and synthesis, enabling the identification of compounds that are both promising targets and reasonably straightforward to synthesize.

Many commercially successful liquid crystals are based on biphenyl. The aromatic rings of biphenyl are relatively easy to substitute, as one phenyl group leads to activation of the other ring. The phenyl group displays an *ortho*, *para* directing effect, so substitution can occur in the 2- or 4- positions. The *ortho* position is disfavoured on steric grounds, so

substitution occurs *para* to the phenyl ring, *i.e.* in the 4- position. By suitable choice of substituent the *para* substituted phenyl group can activate the unsubstituted aromatic ring. A second substitution then occurs at the 4'- position, to give a 4,4'-disubstituted biphenyl **17**. Therefore by design biphenyl is predisposed to form compounds which give calamitic liquid crystals.

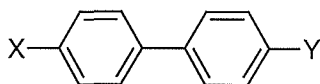


Fig. 45: 4,4'-Disubstituted biphenyl **17**.

Fluorene and 9,10-dihydrophenanthrene show similar orientation and reactivity towards electrophilic aromatic substitution. The presence of the alkyl bridge physically blocks one of the *ortho* positions in each ring, but otherwise has little effect. Fluorene and 9,10-dihydrophenanthrene are therefore both ideal systems for the formation of rod-shaped molecules.

1.11 POLYFLUORENES

There is currently a great deal of interest in fluorene-containing polymers such as the poly(9,9-dialkylfluorene)s **18** and poly(9,9-diethyl-2,7-bis(pyrrol-2-yl)fluorene) (BP-DEF) **19**.

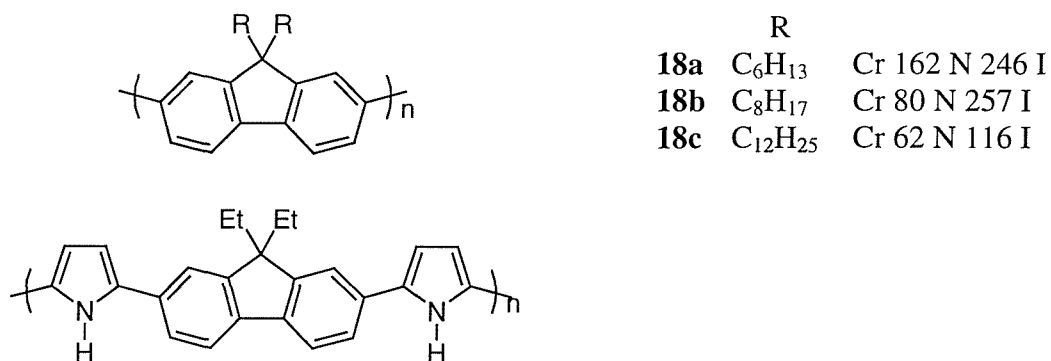


Fig. 46: (i) poly(9,9-Dialkylfluorene) **18**; (ii) poly(9,9-diethyl-2,7-bis(pyrrol-2-yl)fluorene) **19**.

Polyfluorenes such as **18**, where $n \approx 50$, have been shown to fluoresce both in solution and as thin films on a glass substrate.²⁴ These materials are liquid crystalline *e.g.* poly(9,9-dihexylfluorene) **18a** exhibits a nematic phase from 162 to 246 °C. The transition temperatures are lower for poly(9,9-dialkylfluorene)s with longer alkyl chains. BP-DEF **19** and related fluorene-heterocycle hybrid polymers show interesting

electroactive properties.²⁵ Copolymers such as poly(9,9-di-*n*-hexylfluorene-2,7-diylvinylene-*alt*-2,6-pyridinylene vinylene) (PFPV) **20**, which combine the electrochemical characteristics of poly(pyridine-2,5-diyl) **21** and PFV show superior electro-optic properties to established light-emitting polymers (LEPs) such as poly(phenylenevinylene) (PPV) **22**.²⁶

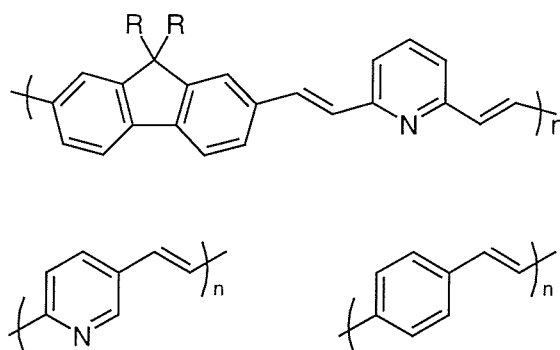


Fig. 47: (i) poly(9,9-di-*n*-Hexylfluorene-2,7-diylvinylene-*alt*-2,6-pyridinylene vinylene) **20**; (ii) poly(pyridine-2,5-diyl) **21**; (iii) poly(phenylenevinylene) **22**.

Several functional organic display devices based on polyfluorenes and on fluorene-containing copolymers have been reported.²⁷ Polyfluorenes are fast becoming important constituents of electroluminescent devices.²⁸

1.12 AIMS AND OBJECTIVES

The aim of this project was to generate new liquid crystals based on the fluorene and 9,10-dihydrophenanthrene core units. These novel mesogens would show enantiotropic nematic phases, making them possible candidates for commercial display mixtures.

As the project progressed it became apparent that the fluorene core held more promise than the 9,10-dihydrophenanthrene unit. The latter was considerably more expensive, and simple derivatives proved to be difficult to purify. In contrast fluorene derivatives were readily synthesized and recrystallized from high purity low cost fluorene. The fluorene system became increasingly topical as many literature reports of polyfluorenes and related materials were published. Consequently attention was focussed on the fluorene core at an early stage.

1.13 FLUORENE LIQUID CRYSTALS

Many reports have shown that fluorene is a poor core unit for making nematogens. Almost all the reported 2,7-disubstituted fluorenes exhibit only smectic or monotropic nematic phases.²⁹ Early work concluded that incorporation of a fluorene core in place of biphenyl

led to a reduction of the mesogenic range. For 2,7-disubstituted fluorenes: ...it is found that the melting points are higher [and the] clearing points slightly lower than those of the biphenyl analogues.³⁰ 2-Pentyl-7-cyanofluorene **23e** exhibits a monotropic nematic phase,³⁰ whereas the analogous biphenyl (5CB, **2e**) forms an enantiotropic nematic (Section 1.8.4).

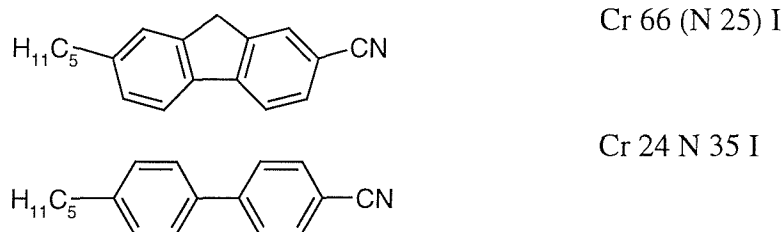


Fig. 48: (i) 2-Pentyl-7-cyanofluorene **23e**; (ii) 4-pentyl-4'-cyanobiphenyl **2e**.

A database search³¹ yielded 147 simple fluorene compounds. These could be divided into three classes, according to the phase behaviour exhibited:

(a) Simple melting point (no mesophase observed)

This class had 51 compounds, including some monosubstituted fluorenes. There were also several simple disubstituted fluorenes *e.g.* 2-bromo-7-octylfluorene **24h**. Some of these compounds were intermediates in the synthesis of other fluorenes.

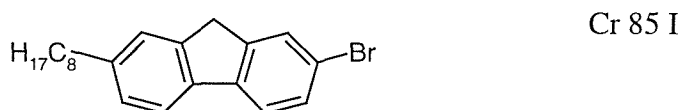


Fig. 49: 2-Bromo-7-octylfluorene **24h**.

(b) Monotropic

This class had 26 compounds, including the 2-alkyl-7-cyanofluorenes **23**. The compounds showed mainly smectic A phases, but there were a few nematics, *e.g.* 2-butanoyl-7-nonylfluorene **25**.

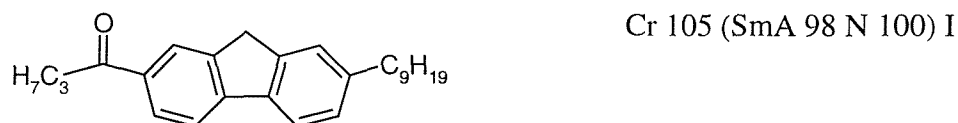
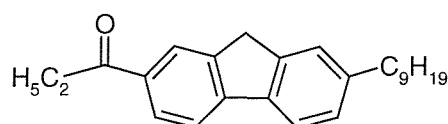


Fig. 50: 2-Butanoyl-7-nonylfluorene **25**.

(c) Enantiotropic

This class had 70 compounds, the vast majority of which only exhibit smectic A phases. Only one nematic (2-propionyl-7-nonylfluorene **26**) was found. It was later discovered that reports of its mesophase behaviour were greatly exaggerated.³² The material actually exhibited a smectic A phase,³³ and the misunderstanding arose from incorrectly reported results.

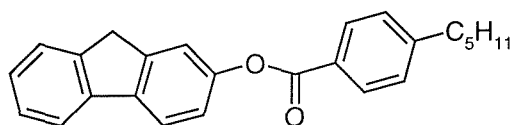


Cr 95 SmA 114 I

Fig. 51: 2-Propionyl-7-nonylfluorene **26**.

The preponderance of smectics arises from the structural rigidity of the fluorene core, and the ability to have strong face to face interactions, which leads to the formation of layers. The bent geometry leads to an increase in molecular width over that of biphenyl, leading to a reduction in the length-to-breadth ratio, which reduces mesogenicity. Long alkyl chain substituents are therefore required to generate stable mesophases, but these favour the formation of smectics.

The database search and literature reports indicated that simple 2,7-disubstituted fluorenes were not promising candidates for the formation of enantiotropic nematic phases. A fluorene-based liquid crystal with a large mesogenic range was needed. The mesogenic range can be increased by extending the molecular length. Addition of a third benzene ring gives a larger length-to-breadth ratio, giving an increased mesogenic range, *e.g.* 5CB **2e** *versus* 5CT **6e** (Section 1.8.4). A database search³¹ revealed that a number of fluorenyl benzoate materials had been prepared. These materials showed enantiotropic nematic phases, *e.g.* 2-fluorenyl-4'-pentylbenzoate **27**.³⁴

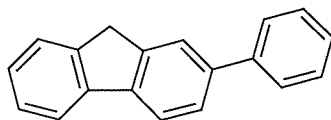


Cr 120 N 139 I

Fig. 52: 2-Fluorenyl-4'-pentylbenzoate **27**.

As the fluorene esters form enantiotropic nematic phases, it was reasoned that linking the third benzene ring directly to the fluorene core would also give a stable nematic liquid crystal. The direct linkage *via* an aryl-aryl bond would give a 2-phenylfluorene **28**.

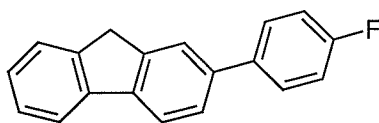
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**Fig. 53:** 2-Phenylfluorene **28**.

Unsubstituted 2-phenylfluorene **28** has been prepared,³⁵ and was found to have a considerably higher melting point than fluorene (115 °C). This is similar to the increase in melting point going from biphenyl (71 °C) to *p*-terphenyl (212 °C). The evidence from the 2-fluorenyl-4'-alkylbenzoates and similar reported compounds suggests that 2-phenylfluorene-based materials should show a large mesophase range. However this would be at the expense of higher transition temperatures.

1.14 2-PHENYLFLUORENES

Despite extensive literature and database searches,³⁶ no references to *mesogenic* 2-phenylfluorenes were found. In addition to unsubstituted 2-phenylfluorene **28**, a small number of derivatives had been prepared, *e.g.* 2-(4-fluorophenyl)fluorene **29**.³⁷ These compounds were synthesized in order to investigate their luminescence properties. There is no evidence that the potential mesogenic properties were studied or even considered. The synthesis of 2-phenylfluorene-based liquid crystals was therefore a novel and potentially rewarding area for research.

**Fig. 54:** 2-(4-Fluorophenyl)fluorene **29**.

1.15 SUMMARY AND CONCLUSIONS

In the last century liquid crystals had changed from an interesting area for academic research into a multi-billion pound industry. A great deal of information and theory was built up over many years of research. This was then put into practice as successive liquid crystal devices revolutionized the display industry. The challenge is synthesize new liquid crystals which combine all the desired properties *e.g.* dielectric anisotropy, birefringence, a suitable mesogenic range *etc.*

Knowledge of structure-property relations allows the design of a suitable target. However

the synthesis of the target molecule often proves time consuming, and several syntheses may be needed before a molecule with the desired properties is made. It is therefore important to make a compromise between the ideal target molecule and the ease of synthesis.

Fluorene-based materials do not exhibit enantiotropic nematic phases. It was therefore necessary to add a third benzene ring to fluorene, giving 2-phenylfluorene **28** as a core unit. Incorporation of the strongly nematic promoting cyano group would favour the formation of wide nematic mesophases. Accordingly the 2-(4-cyanophenyl)-7-alkylfluorenes **30** were chosen as the initial synthetic targets. These compounds are closely related to the commercially successful 4-alkyl-4''-cyano-*p*-terphenyls **6**, *e.g.* 4-pentyl-4''-cyanoterphenyl **6e**, which exhibits an enantiotropic nematic phase. The target compound 2-(4-cyanophenyl)-7-pentylfluorene **30e** was expected to show similar phase behaviour.

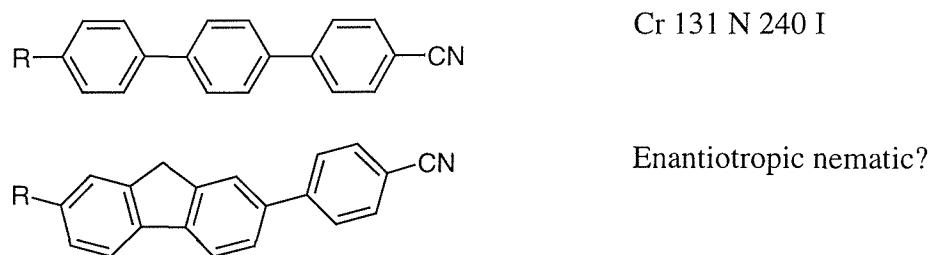


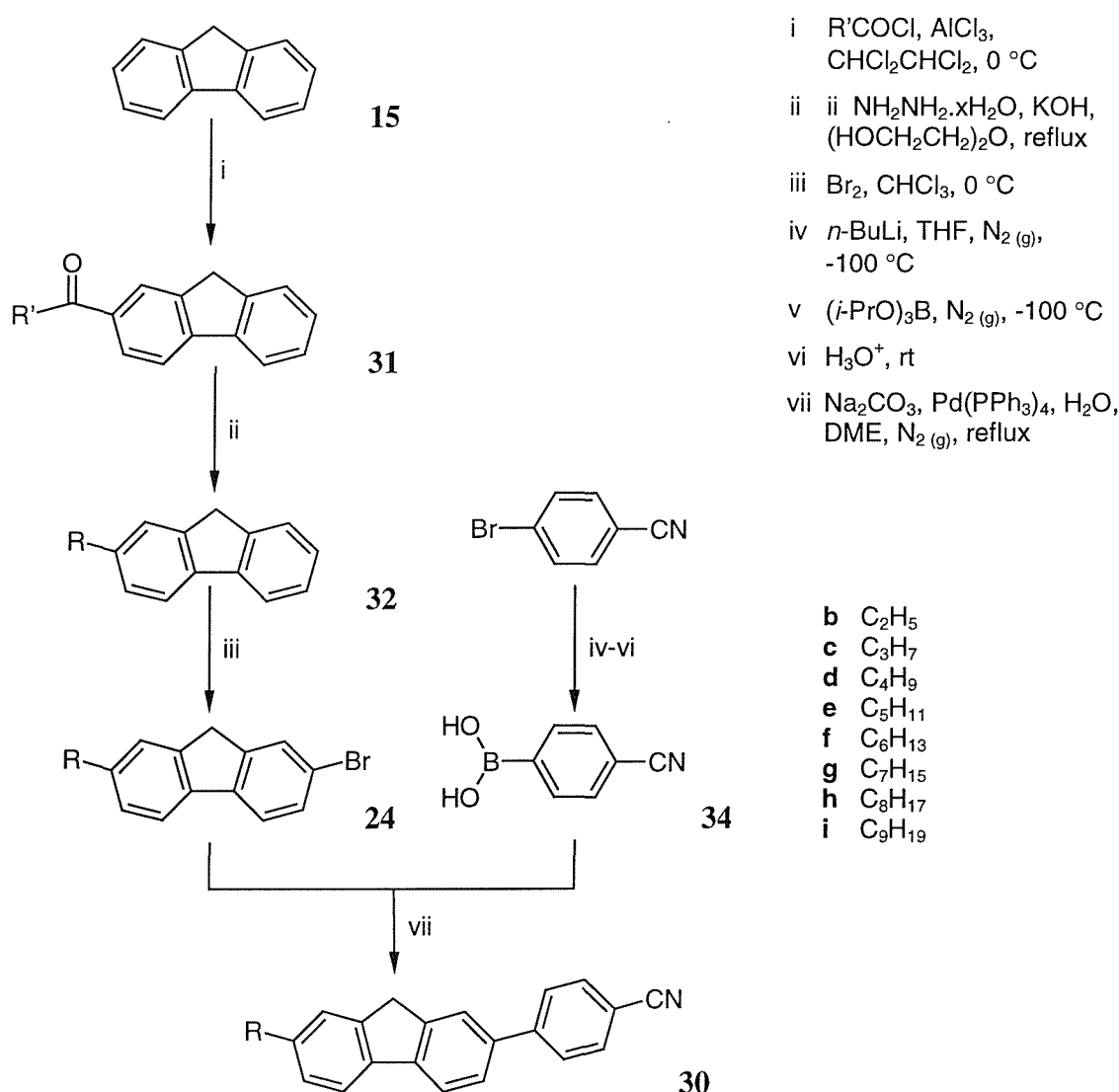
Fig. 55: (i) 4-Pentyl-4''-cyanoterphenyl **6e**; (ii) 2-(4-cyanophenyl)-7-pentylfluorene **30e**.

2. SYNTHESIS OF 2-(4-CYANOPHENYL)-7-ALKYLFLUORENES

2.1 OVERVIEW

In order to generate enantiotropic nematogens a third benzene ring was added to the fluorene core to give 2-phenylfluorene **28**. The strongly nematic promoting cyano group was added to favour the formation of a nematic mesophase. Accordingly the 2-(4-cyanophenyl)-7-alkylfluorenes **30** were chosen as the initial synthetic targets.

The homologous series of 2-(4-cyanophenyl)-7-alkylfluorenes **30** was synthesized *via* the five step convergent route shown in Scheme 1.

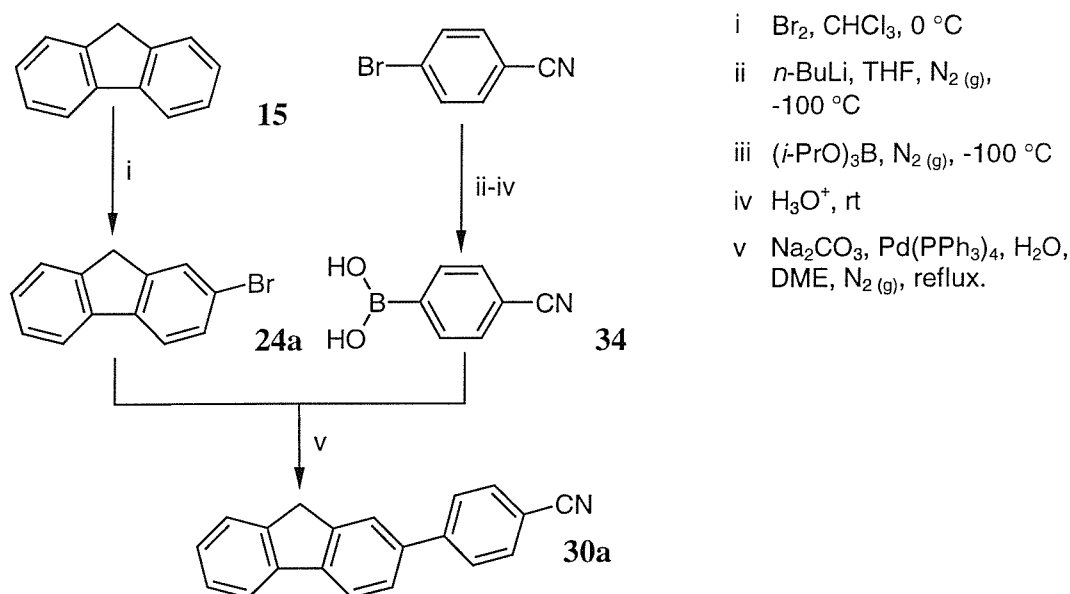


Scheme 1: Synthesis of 2-(4-cyanophenyl)-7-alkylfluorenes **30**.

The first step, a Friedel-Crafts acylation of fluorene **15**, was optimized to give consistently high yields (57-83%) of pure material **31**. Reduction, using the Huang-Minlon modification

of the Wolff-Kishner reduction gave the product **32** in 28-89% yield. In some cases an unexpected side reaction occurred, and the 9-ethylated material **33** was isolated as the major product. This problem was alleviated by changing the base to the milder sodium carbonate. The third step was bromination of **32** using a solution of bromine in chloroform. Crude yields were high, but the yield of pure isolated material **24** varied from less than 1% to 70%. The boronic acid **34** was prepared in 66% yield, but the procedure was not reproducible and often gave impure material. The final step was a Suzuki coupling of the aryl bromide **24** and boronic acid **34**. Yields varied from 4 to 46%.

The parent compound 2-(4-cyanophenyl)fluorene **30a**, with no alkyl chain, was prepared *via* a similar three step convergent route, as shown in Scheme 2.



Scheme 2: Synthesis of 2-(4-cyanophenyl)fluorene **30a**.

Monobromination of fluorene **15** was accomplished using a solution of bromine in chloroform. Following recrystallization 2-bromofluorene **24a** was isolated in 32% yield. The boronic acid **34** was isolated in 66% yield as described previously. The Suzuki coupling step gave 2-(4-cyanophenyl)fluorene **30a** in 9% yield.

Preparation of 2-methylfluorene **35** was attempted by direct coupling of lithium dimethyl copper to 2-bromofluorene **30a**. The reaction was unsuccessful, and consequently the methyl homologue 2-(4-cyanophenyl)-7-methylfluorene **36** could not be prepared.

2.2 ELECTROPHILIC AROMATIC SUBSTITUTIONS – A DISCUSSION

In the synthesis of calamitic liquid crystals the target is a rod shaped molecule. In biphenyl, the directing effects of the first benzene ring dictates that substitution occurs in the *para* position of the second benzene ring, *e.g.* at the 4- position. This behaviour is paralleled by fluorene, where substitution also occurs in the *para* position of the second benzene ring *e.g.* at the 2- position. Suitable choice of functional group enables a second substitution to be made at the opposite end of the molecule, *e.g.* in the *para* position of the remaining unsubstituted benzene ring. This is the 4'- position in biphenyl and the 7- position in fluorene. The result is the desired rod-shaped architecture that is needed for the formation of liquid crystalline phases.

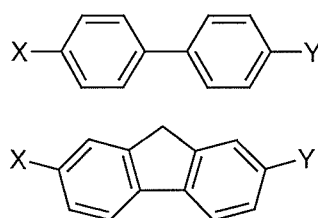
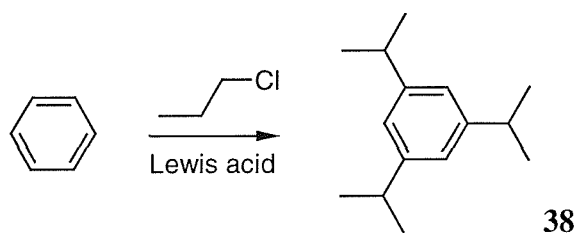
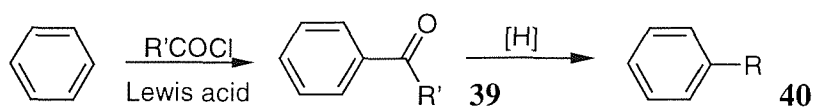


Fig. 56: (i) 4,4'-Disubstituted biphenyl **17**; (ii) 2,7-disubstituted fluorene **37**.

In the synthesis of the 2-(4-cyanophenyl)-7-alkylfluorenes **30** the first task was to introduce an alkyl group into the 2-position. The Friedel-Crafts alkylation process is of limited use in this situation, as polyalkylation and rearrangement are competing side reactions.³⁸ In the presence of a Lewis acid catalyst, straight chain alkyl halides can undergo rearrangement to give the more stable branched chain intermediates. Polyalkylation to give **38** may also occur, as the mono-substituted product is activated and is therefore more reactive than the starting material.

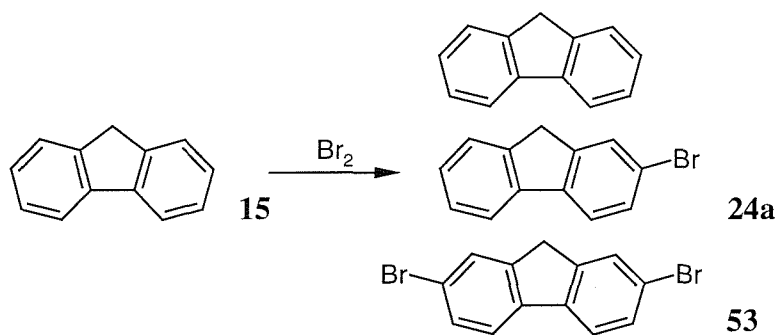


To alleviate these problems, a two step approach was employed. The Friedel-Crafts acylation³⁹ was used to regioselectively introduce a single acyl chain at the 2-position. The carbonyl moiety in **39** was then reduced to methylene, to give the desired 2-alkyl compound **40**.

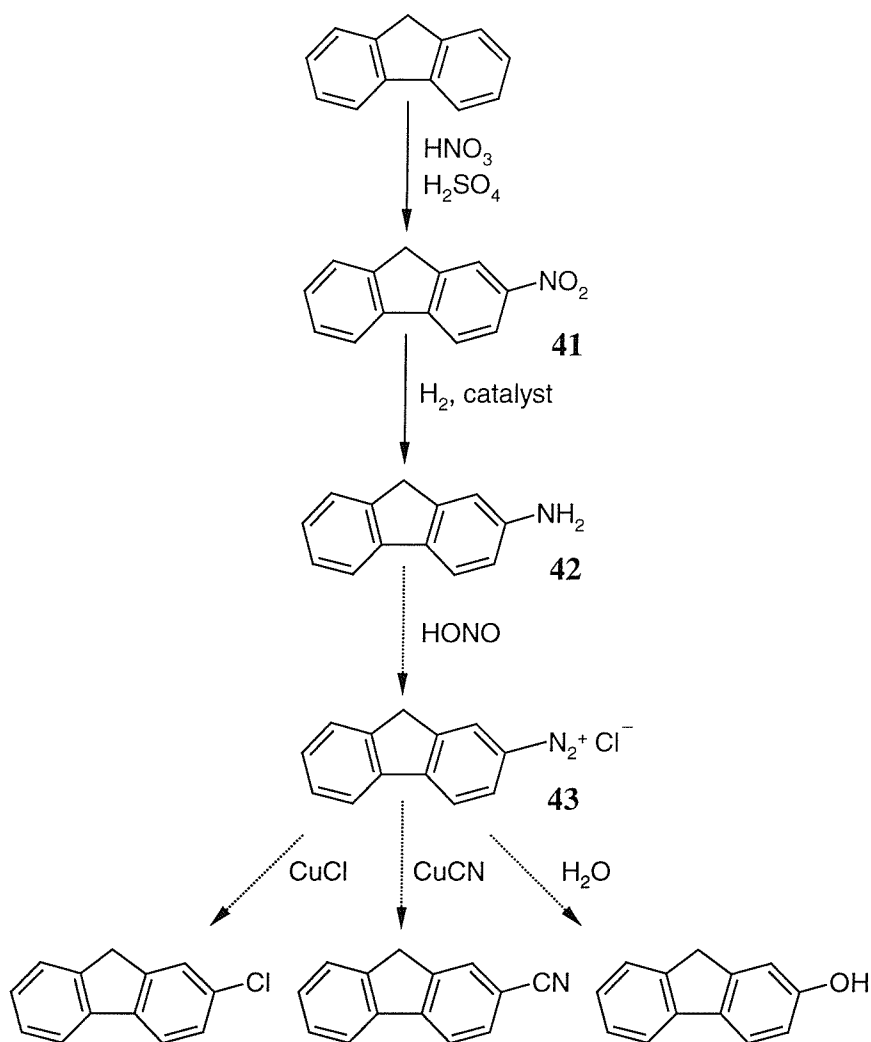


Friedel-Crafts acylation was carried out on fluorene using a range of different commercially available straight chain acid chlorides. The 2-acetyl derivative **31b** is a key intermediate in the synthesis of related fluorene-based liquid crystals, as suitable functional group interconversions will allow access to a range of compounds.

Halogenation was explored as an alternative means of introducing a substituent to the 2-position. Many procedures exist for the monobromination of fluorene. A number of these were attempted, but the results were somewhat variable. No satisfactory method was found, as reactions invariably gave a mixture of unreacted fluorene, the desired monobrominated product **24a** and polybrominated compounds. The monobrominated product **24a** could be isolated by repeat recrystallizations, but at the expense of a satisfactory yield.



In a literature report,⁴⁰ treatment of fluorene with a mixture of nitric and sulphuric acids gave 2-nitrofluorene **41** in 79% yield. Conversion to 2-aminofluorene **42** was accomplished in 80% yield by reduction. In this way nitration can provide an excellent route to a number of important intermediates, as diazotization of 2-aminofluorene **42** to give fluorene-2-diazonium chloride **43** would give access to a range of monosubstituted fluorenes, *e.g.* the halo, cyano, and hydroxy derivatives (Scheme 3).⁴¹



Scheme 3: Postulated route to 2-substituted fluorenes *via* a diazonium salt **43**.

Materials related to the analogous biphenyl compounds 4-nitrobiphenyl **44** and 4-aminobiphenyl **45** and were once popular intermediates in the synthesis of liquid crystals. They are now classed as “zero manufacture” materials.⁴² Although the nitro **41** and amino **42** fluorene derivatives are not banned, they are classed as “experimental carcinogens.”⁴³ Nitration was not therefore carried out and alternative routes were pursued.

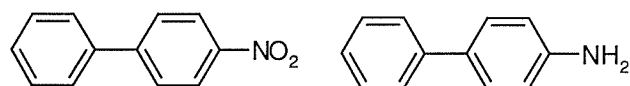
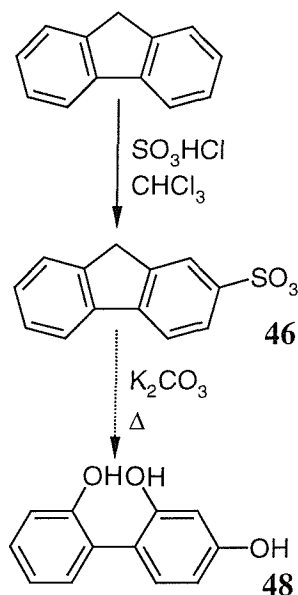


Fig. 57: (i) 4-Nitrobiphenyl **44**; (ii) 4-aminobiphenyl **45**.

Sulphonation of an aromatic compound to give a sulphonic acid is the first step of a standard route to phenols. The sulphonic acid is then fused with a base to give the phenol.⁴⁴ A literature preparation of fluorene-2-sulphonic acid **46** was reported as being

straightforward.⁴⁵ Fluorene-2-sulphonic acid **46** was then converted to the potassium sulphonate derivative **47**, which was then fused with potassium carbonate. However partial degradation of **47** was found to occur, and a compound thought to be 2,4,2'-trihydroxybiphenyl **48** was isolated as the major product.⁴⁵ In view of these reported results sulphonation was not attempted.

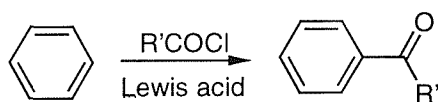


Scheme 4: Attempted literature route to 2-hydroxyfluorene **49**.

A large number of fluorene derivatives are known.⁴⁶ Many of the compounds described below have been prepared previously and reported in the literature. Although the transformations employed to synthesize these molecules follow well established general procedures, full spectroscopic data was not generally available. The synthetic methodology was therefore developed using model compounds, which would be less costly to use and more straightforward to characterize. Once developed, the chemistry was applied to systems of real interest.

2.3 ACYLATION

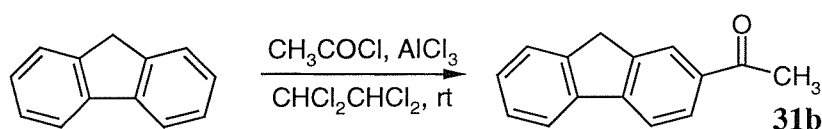
The Friedel-Crafts acylation⁴⁷ was chosen to introduce functionality into the aromatic system. This procedure employs an acyl halide as electrophile and requires the presence of a Lewis acid as catalyst.



Friedel-Crafts reactions are traditionally carried out using either nitrobenzene or carbon disulphide as the solvent.⁴⁸ Nitrobenzene has an exceptionally high boiling point and is toxic.⁴² Consequently it is difficult to remove during the workup. Since carbon disulphide is somewhat unpleasant to handle and has a very low flash point,⁴⁹ an alternative solvent was sought.

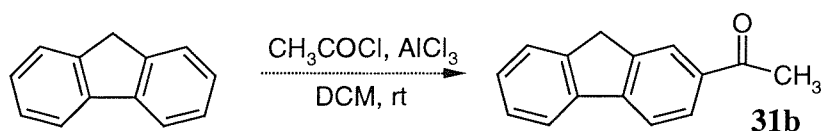
A literature acylation procedure using 1,1,2,2-tetrachloroethane was followed.⁵⁰ Although having a high boiling point,⁴⁹ this solvent was relatively easy to remove *in vacuo*. Careful purification of the solvent was necessary.⁵⁰ 1,1,2,2-Tetrachloroethane was dried by stirring over anhydrous calcium chloride, then distilled at reduced pressure. The distillate was then filtered through a plug of alumina. In the early stages of the project aluminium chloride was purified by sublimation at reduced pressure.⁵¹ Only small amounts of catalyst (≈ 1 g) could be purified by this method. Commercially available high purity aluminium chloride was used in later work. This had no detrimental effect on the reaction and removed limitations on the scale of the process.

A mixture of fluorene, acetyl chloride and dry 1,1,2,2-tetrachloroethane was stirred at room temperature. Aluminium chloride was added, and the reaction mixture was stirred at room temperature.



Following workup the crude product was dissolved in a mixture of hot dichloromethane and 80-100 petroleum ether, then left to cool. After recrystallization, 2-acetylfluorene **31b** was isolated in 82% yield. No evidence for the formation of diacylated derivatives was found.

Acetylation of fluorene was also attempted using dichloromethane as solvent. Dichloromethane has a much lower boiling point than 1,1,2,2-tetrachloroethane, and would be easier to remove during the workup procedure. A mixture of fluorene, acetyl chloride and dichloromethane was stirred at room temperature. Aluminium chloride was added, and the reaction mixture was stirred at room temperature.



On workup the crude reaction mixture formed an emulsive jelly. Following exhaustive extractions and an extended workup, no product was isolated. Other workers have reported similar results when using dichloromethane as solvent in Friedel-Crafts acylations.⁵²

Friedel-Crafts acylation of fluorene was extended to the synthesis of the propionyl and pentanoyl homologues. A mixture of fluorene, the appropriate acid chloride and 1,1,2,2-tetrachloroethane was stirred at room temperature. Aluminium chloride was added, and the reaction mixture was stirred at room temperature. Following recrystallization from hot dichloromethane-80-100 petroleum ether, 2-propionylfluorene **31c** and 2-pentanoylfluorene **31e** were isolated in yields of 57 and 71% respectively.

All the acylfluorenes from acetyl **31a** to nonanoyl **31i** were synthesized cleanly and in good yields. In a refinement to the procedure the reaction mixture was initially stirred at 0 °C. A solution of fluorene, acid chloride and 1,1,2,2-tetrachloroethane was stirred in an ice bath. Aluminium chloride was added, and the stirred reaction mixture was allowed to warm to room temperature. The recrystallization procedure was also improved. The crude residue was dissolved in hot chloroform. Hot 60-80 petroleum ether was added, and the mixture was heated with activated charcoal. The mixture was filtered whilst hot and then left to cool. The recrystallized material was isolated in high yield.

Table 2: Synthesis of 2-acylfluorenes **31**.

Compound	Conditions and purification	Yield
31b 2-Acetylfluorene	1.01 eq R'COCl; rt*	82%
31c 2-Propionylfluorene	1.00 eq R'COCl; rt*	57%
31d 2-Butyrylfluorene	1.00 eq R'COCl; 0 °C [†]	83%
31e 2-Pentanoylfluorene	1.00 eq R'COCl; rt*	71%
31f 2-Hexanoylfluorene	1.00 eq R'COCl; 0 °C [†]	79%
31g 2-Heptanoylfluorene	0.99 eq R'COCl; 0 °C [†]	82%
31h 2-Octanoylfluorene	1.00 eq RCOCl; 0 °C [†]	81%
31i 2-Nonanoylfluorene	0.99 eq RCOCl; rt*	66%

* recrystallized from hot dichloromethane-80-100 petroleum ether

[†] recrystallized from hot chloroform-60-80 petroleum ether (charcoal)

Many of the acylation reactions were later repeated, and the yield of isolated product was often higher than reported in Table 2. It was possible to carry out the procedure on a large scale (up to 50 g of fluorene) to give a high yield of pure material.

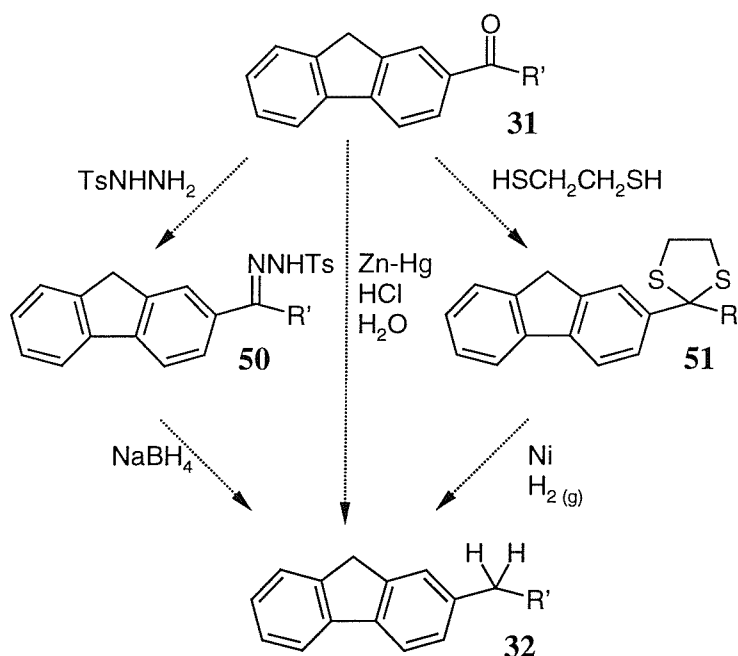
2.4 REDUCTION

There are several different procedures available for the reduction of an aryl ketone to a methylene group.

In the Clemmenson reduction the ketone is heated with zinc amalgam and aqueous hydrochloric acid.⁵³ The presence of the acid means that the procedure is not tolerant of ether linkages, although this was not a problem for the synthesis of the 2-(4-cyanophenyl)-7-alkylfluorenes **30**.

The ketone can be converted to the tosylhydrazone derivative **50** by condensing with tosylhydrazine. This is then reduced using sodium borohydride.⁵⁴ This procedure is not suitable for the short chain compounds, as solubility would become a problem.

A malodorous alternative is the Muzingo reduction.⁵⁵ The ketone is converted to the thioacetal **51** by reaction with 1,2-ethanedithiol. The thioacetal **51** is then reduced by hydrogenation with a nickel catalyst.

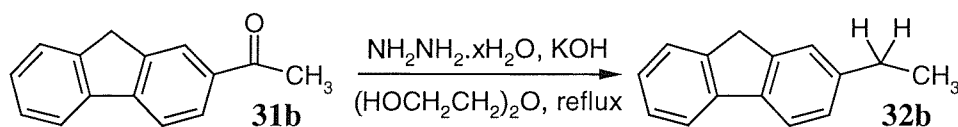


Scheme 5: Postulated routes to 2-alkylfluorenes **32**.

In the event none of these three procedures were used, as the conversion of 2-acetylfluorene **31b** to 2-ethylfluorene **32b** was accomplished using two complementary procedures. In the Huang-Minlon modification⁵⁶ of the Wolff-Kishner reduction⁵⁷ a mixture of the ketone, hydrazine hydrate, potassium hydroxide and diethylene glycol is heated strongly. The ketone **31** condenses with hydrazine hydrate to give a hydrazone intermediate **52**. The hydrazone is not isolated, but is decomposed by strong heating with potassium hydroxide.

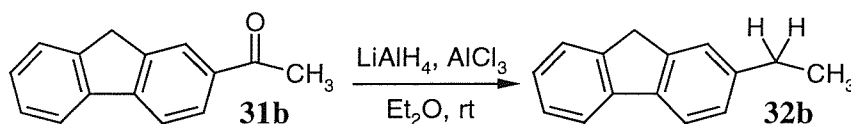
Nitrogen is evolved, and water is distilled out of the reaction vessel to drive the reaction to completion. The process is both enthalpically and entropically favoured.

A mixture of 2-acetylfluorene **31b**, hydrazine hydrate, potassium hydroxide and diethylene glycol was heated, first at reflux, then strongly to distil out water.



After workup, 2-ethylfluorene **32b** was obtained in a reasonably pure form. Further purification was achieved by recrystallization, and 2-ethylfluorene **32b** was isolated in 28% yield.

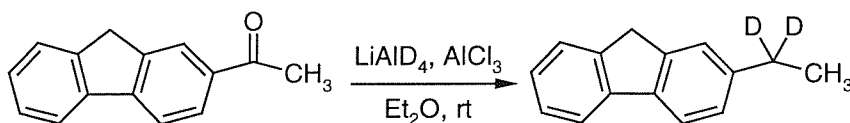
In the second procedure the ketone was reduced using a mixture of lithium aluminium hydride and aluminium chloride.⁵⁸ A mixture of 2-acetylfluorene **31b**, lithium aluminium hydride, aluminium chloride and dry diethyl ether was stirred at room temperature.



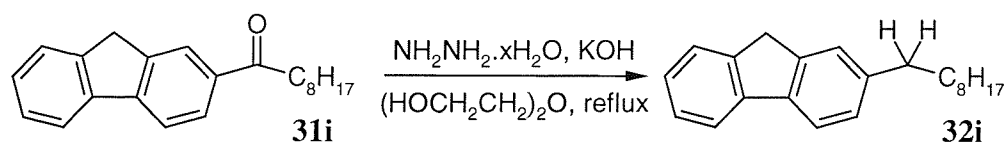
Following column chromatography impure 2-ethylfluorene **32b** was obtained in *ca.* 75% yield. The hydride reduction method is more expensive and time consuming than the Huang-Minlon modification of the Wolff-Kishner reduction. Anhydrous conditions were required for the reaction and column chromatography was needed to obtain any product. The 2-acylfluorene starting material was not wholly soluble in the reaction mixture, and the procedure could not be carried out on a large scale.

The Wolff-Kishner procedure was the method of choice, as it was found to be cheaper and more straightforward. It was also possible to carry out the procedure on a large scale.

The hydride reduction method gives a potential route to deuteriated mesogens. By using lithium aluminium deuteride in place of lithium aluminium hydride two deuterium atoms can be introduced into the alkyl chain.



The Wolff-Kishner procedure was successfully applied to the reduction of 2-nonanoylfluorene **31i**. A mixture of 2-nonanoylfluorene **31i**, hydrazine hydrate, potassium hydroxide and diethylene glycol was heated, first at reflux, then strongly to distil out water.



Following filtration through a plug of silica, 2-nonylfluorene **32i** was isolated in 89% yield. Using the Huang-Minlon modification of the Wolff-Kishner reduction it was possible to isolate most of the desired 2-alkylfluorenes **32** in good yields (Table 3).

Table 3: Synthesis of 2-alkylfluorenes **32** (caustic base).

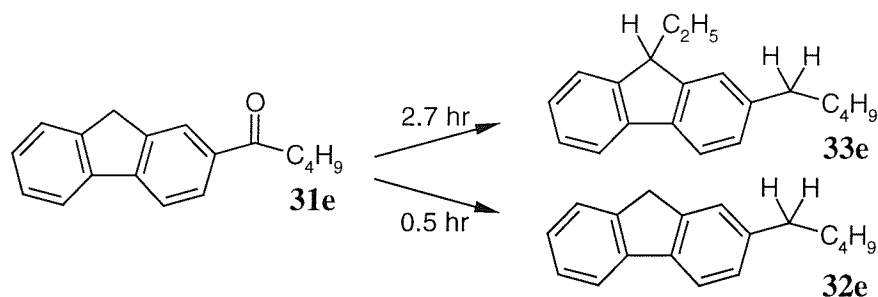
Compound	Conditions and purification	Yield
32b 2-Ethylfluorene	reflux 2.6 hr; strong heat 1.6 hr*	28%
32d 2-Butylfluorene	reflux 3.7 hr; strong heat 0.2 hr [†]	51%
32e 2-Pentylfluorene	reflux 1.8 hr; strong heat 0.5 hr [†]	57%
32g 2-Heptylfluorene	reflux 1.3 hr; strong heat 0.3 hr [†]	63%
32i 2-Nonylfluorene	reflux 2.3 hr; strong heat 0.5 hr [‡]	89%

* recovered from ethanol-hexane solution following hot filtration

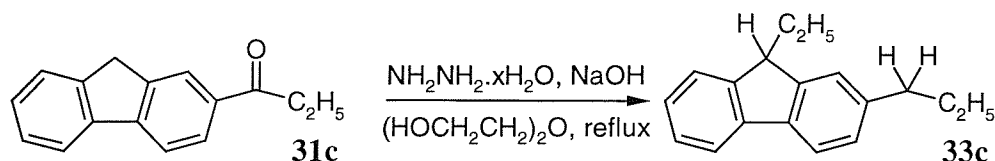
[†] recrystallized from hot ethanol

[‡] solution in dichloromethane-60-80 petroleum ether filtered through silica plug

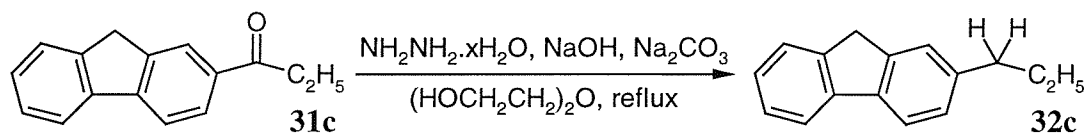
However in some cases a 2-alkyl-9-ethylfluorene **33** was obtained as the major product. A mixture of 2-pentanoylfluorene **31e**, hydrazine hydrate, potassium hydroxide and diethylene glycol was heated, first at reflux, then strongly to distil out water. The reaction gave a mixture of products. Following separation by column chromatography the crude oil 2-pentyl-9-ethylfluorene **33e** was obtained in *ca.* 54% yield. The procedure was repeated on a second sample of 2-pentanoylfluorene **31e**. The reaction time was shortened and the expected product 2-pentylfluorene **32e** was isolated in 57% yield.



Several attempts to reduce 2-propionylfluorene **31c** to 2-propylfluorene **32c** were unsuccessful. Even with a greatly reduced reaction time 2-propyl-9-ethylfluorene **33c** was the major product. The solvent was distilled and the base was purified in an attempt to prevent the occurrence of 9-substitution. **33c** was still obtained as the major product.



Changing the base from an alkali metal hydroxide to the milder sodium carbonate was found to alleviate the problem. A mixture of 2-propionylfluorene **31c**, hydrazine hydrate, sodium hydroxide, sodium carbonate and diethylene glycol was heated, first at reflux, then strongly to distil out water.



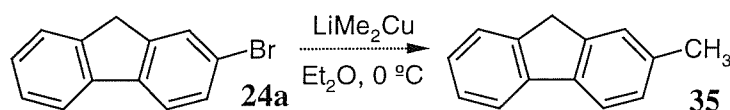
2-Propylfluorene **32c** was isolated in 73% yield. 2-Hexanoylfluorene **31f** was reduced using sodium carbonate as base, to give 2-hexylfluorene **32f** in 66% yield. In both cases no other products were detected.

Table 4: Synthesis of 2-alkylfluorenes **32** (carbonate base).

Compounds	Conditions and purification	Yield
32c 2-Propylfluorene	Reflux 3.0 hr; strong heat 3.0 hr*	73%
32f 2-Hexylfluorene	Reflux 3.0 hr; strong heat 1.3 hr*	66%
32h 2-Octylfluorene	Reflux 5.0 hr; strong heat 2.0 hr*	83%

* recrystallized from hot ethanol (charcoal)

The modified Wolff-Kishner procedure, using sodium carbonate as base, gave good results. However longer reaction times were needed to decompose the hydrazone intermediate, especially when the procedure was carried out on a large scale. A series of reactions were carried out aimed at unravelling this significant and unusual side reaction (Section 5.4). Preparation of 2-methylfluorene **35** was attempted by direct coupling of lithium dimethyl copper to 2-bromofluorene **24a**.^{59, 60} A solution of methyllithium in diethyl ether⁶¹ was added to a mixture of copper(I)iodide and diethyl ether to give the Gilman reagent. A solution of 2-bromofluorene **24a** was then added.

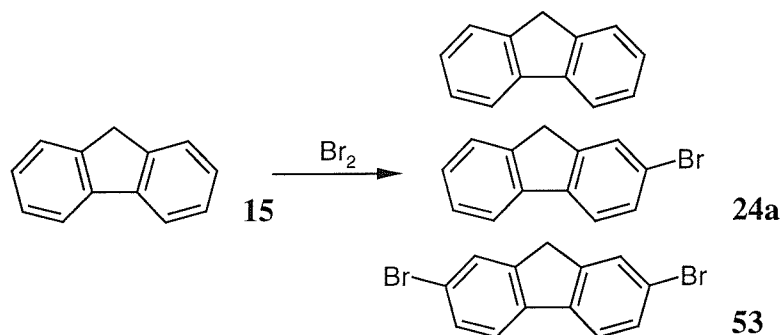


Following recrystallization, *ca.* 35% unreacted 2-bromofluorene **24a** was recovered. There was no indication that any coupled product was formed.

2.5 BROMINATION

The next step in the synthesis of the 2-(4-cyanophenyl)-7-alkylfluorenes **30** was the introduction of a bromine atom into the second ring of the molecule to give a 2-bromo-7-alkylfluorene **24**. Before this was attempted, bromination methodology was explored using unsubstituted fluorene as a model system. The target product of these reactions was 2-bromofluorene **24a**, which was an intermediate in the synthesis of 2-(4-cyanophenyl)fluorene **30a**.

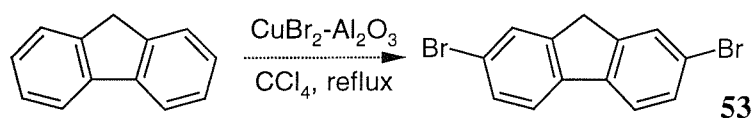
Many procedures exist for the monobromination of fluorene. Several routes to 2-bromofluorene **24a** were attempted, but no wholly satisfactory method was found. Non-brominated fluorene and polybrominated compounds (*e.g.* 2,7-dibromofluorene **53**) were obtained in addition to the desired monobrominated product.



In some cases it was possible to isolate the monobrominated product **24a**, but several recrystallizations were needed. However the yields were greatly reduced. Several literature procedures for the monobromination of fluorene were followed.

(a) Copper(II)bromide on alumina

Copper(II)bromide on alumina was prepared by a literature method.⁶² A mixture of copper(II)bromide, water and aluminium oxide (Brockmann II) was swirled to mix. The solvent was removed, and the residue was dried *in vacuo* to give copper(II)bromide on alumina. A literature procedure was followed.⁶³ The report states that by varying the reaction time either 2-bromofluorene **24a** or 2,7-dibromofluorene **53** can be prepared. A mixture of fluorene, copper(II)bromide on alumina and carbon tetrachloride was heated at reflux.

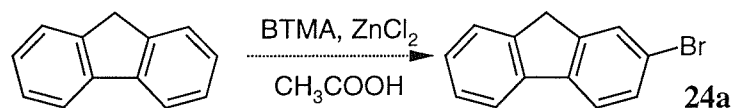


Following recrystallization, impure 2,7-dibromofluorene **53** was obtained in *ca.* 11% yield. It appeared that dibromination occurred somewhat more readily than reported in the literature.

(b) Benzyltrimethylammonium tribromide

Benzyltrimethylammonium tribromide was prepared from benzyltrimethylammonium chloride by a literature method.⁶⁴ A mixture of benzyltrimethylammonium chloride, sodium bromate, water and dichloromethane was treated with hydrobromic acid. Recrystallization gave benzyltrimethylammonium tribromide. A literature procedure which reported clean conversion to 2-bromofluorene **24a** was followed.⁶⁴

A mixture of fluorene, benzyltrimethylammonium tribromide, zinc(II)chloride and glacial acetic acid was stirred at room temperature.

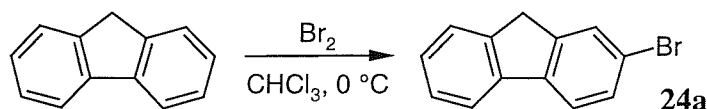


Following recrystallization, impure 2-bromofluorene **24a** was obtained in *ca.* 15% yield. The procedure was repeated with a greatly increased reaction time to give impure 2-bromofluorene **24a** in *ca.* 25% yield. When the procedure was repeated with the reaction mixture heated at reflux, impure 2-bromofluorene **24a** was obtained in *ca.* 28% yield. In all three cases the material obtained contained *ca.* 10% non-brominated fluorene. Both

increasing the reaction time and raising the temperature led to small improvements in the yield, but no pure material was isolated, and the yield was still very low.

(c) Bromine (chloroform)

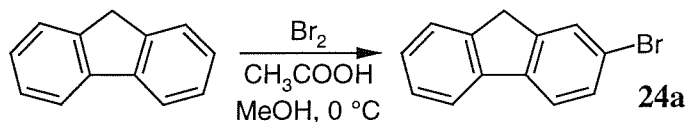
In a literature procedure, direct treatment of fluorene with bromine gave, after several recrystallizations, the desired monobrominated product.⁴⁵ A solution of bromine in chloroform was added slowly to a cold stirred solution of fluorene in chloroform.



Following recrystallization from hot ethanol-water, 2-bromofluorene **24a** was isolated in 32% yield.

(d) Bromine (methanol-acetic acid)

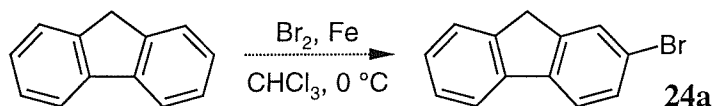
The direct bromination approach was employed using a different solvent system. A solution of bromine in glacial acetic acid was added slowly to a cold stirred solution of fluorene in methanol.



Following recrystallization from hot ethanol-water, 2-bromofluorene **24a** was isolated in 27% yield.

(e) Bromine and iron(III)chloride

The addition of a Lewis acid is known to catalyse electrophilic bromination reactions.⁶⁵ A solution of bromine in chloroform was added slowly to a cold stirred mixture of fluorene, iron(II)chloride and chloroform.



Following recrystallization from hot ethanol-water, impure 2-bromofluorene **24a** was obtained in *ca.* 27% yield.

None of these reactions proceeded to completion, and the crude brominated product(s) always contained unreacted fluorene. Partial purification was achieved by recrystallization from hot ethanol-water to give impure 2-bromofluorene in low yields. Pure material was

obtained by methods (c) and (d), although the yields were low. No pure material was isolated from any of the other methods. Fluorene and the brominated products co-eluted by TLC and so it was not possible to follow the progress of the reactions by chromatography. These results are summarized in Table 5.

Table 5: Synthesis of 2-bromofluorene **24a**.

Method	Conditions and purification	Yield
Copper(II)bromide on alumina	4.51 eq Br ₂ ; reflux 2.0 hr*	- [†]
Benzyltrimethylammonium tribromide	1.00 eq Br ₂ ; rt, 2.7 hr*	ca. 15% [‡]
Benzyltrimethylammonium tribromide	1.00 eq Br ₂ ; rt, 46.8 hr*	ca. 25% [‡]
Benzyltrimethylammonium tribromide	1.00 eq Br ₂ ; reflux, 0.2 hr*	ca. 28% [‡]
Bromine (chloroform)	0.99 eq Br ₂ ; 0 °C*	32%
Bromine (methanol-acetic acid)	1.00 eq Br ₂ ; 0 °C*	27%
Bromine and iron(III)chloride	1.00 eq Br ₂ ; 0 °C*	ca. 27% [§]

* recrystallized from hot ethanol-water

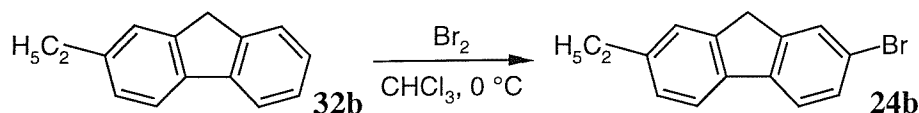
[†] impure 2,7-dibromofluorene **53** was obtained in ca. 11% yield

[‡] contained ca. 10% non-brominated fluorene

[§] contained ca. 20% non-brominated fluorene

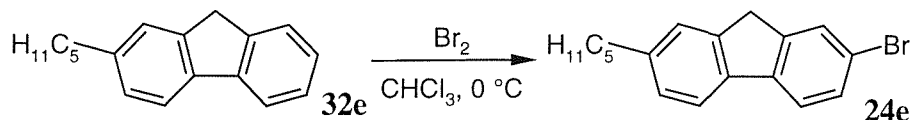
Direct bromination using chloroform as solvent was therefore the method of choice, although only small amounts of pure material were isolated.

The bromination procedure was extended to the 2-alkylfluorenes **32**. The alkyl group is both activating and *ortho*, *para* directing.⁶⁶ Substitution was expected to occur in the unhindered *para* position of the unsubstituted ring. The weak activating effect of the alkyl group was expected to increase the rate of reaction and therefore the reaction yield. A solution of bromine in chloroform was added slowly to a cold stirred solution of 2-ethylfluorene **32b** in chloroform.



Following recrystallization from hot ethanol, 2-bromo-7-ethylfluorene **24b** was isolated in 27% yield. In an attempt to improve the yield, an excess of bromine was used, and, after stirring at room temperature overnight, the reaction mixture was briefly heated at reflux. A solution of bromine in chloroform was added slowly to a cold stirred solution of 2-

pentylfluorene **32e** in chloroform. After warming to room temperature over 16.3 hours, the reaction mixture was heated at reflux for 0.3 hours.



Following recrystallization from hot ethanol, 2-bromo-7-pentylfluorene **24e** was isolated in 49% yield. This procedure was extended to the synthesis of the homologous series of 2-bromo-7-alkylfluorenes **24** with mixed results. Following recrystallization from hot ethanol, the pure propyl **24c**, hexyl **24f** and octyl **24h** homologues were isolated in yields of 28-70%. Under the same conditions the impure butyl **24d**, heptyl **24g** and nonyl **24i** compounds were obtained in *ca.* 52-57% yield. These three materials all contained *ca.* 10% of the non-brominated 2-alkylfluorene **32**. The presence of non-brominated material was found to have no effect on the subsequent Suzuki coupling reaction. To provide samples for characterization, small portions of the three impure materials were recrystallized from hot chloroform-hexane. Small amounts of the pure 2-bromo-7-alkylfluorene **24** were isolated.

Table 6: Synthesis of 2-bromo-7-alkylfluorenes **24**.

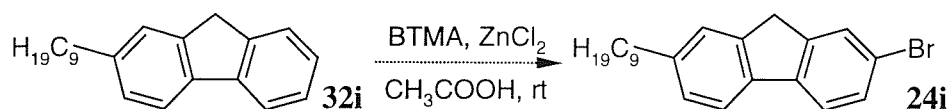
Compounds	Conditions and purification	Yield
24b 2-Bromo-7-ethylfluorene	1.00 eq Br ₂ ; 0 °C*	27%
24c 2-Bromo-7-propylfluorene	1.11 eq Br ₂ ; 0 °C→reflux 1.0 hr*	70%
24d 2-Bromo-7-butylfluorene	1.06 eq Br ₂ ; 0 °C→reflux 1.0 hr*	<1% [†]
24e 2-Bromo-7-pentylfluorene	1.10 eq Br ₂ ; 0 °C→reflux 0.3 hr*	49%
24f 2-Bromo-7-hexylfluorene	1.09 eq Br ₂ ; 0 °C→reflux 0.6 hr*	65%
24g 2-Bromo-7-heptylfluorene	1.20 eq Br ₂ ; 0 °C→reflux 0.3 hr*	<1% [†]
24h 2-Bromo-7-octylfluorene	1.09 eq Br ₂ ; 0 °C→reflux 1.0 hr*	28%
24i 2-Bromo-7-nonylfluorene	1.01 eq Br ₂ ; 0 °C→reflux 0.5 hr*	1% [†]

* recrystallized from hot ethanol

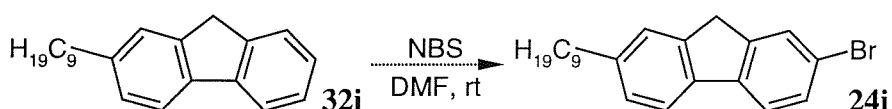
[†] second recrystallization from hot chloroform-hexane

Bromination of 2-nonylfluorene **32i** was attempted using benzyltrimethylammonium tribromide.⁶⁴ A mixture of 2-nonylfluorene **32i**, benzyltrimethylammonium tribromide, zinc(II)chloride and glacial acetic acid was stirred at room temperature. Following recrystallization from hot ethanol, impure 2-bromo-7-nonylfluorene **24i** was obtained in *ca.*

34% yield. The material contained *ca.* 40% non-brominated 2-nonylfluorene **32i**.

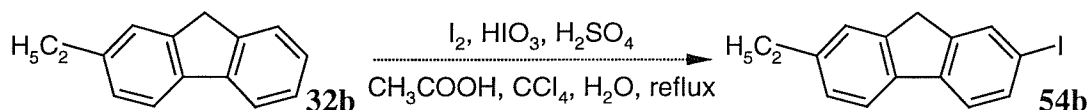


Bromination of 2-nonylfluorene was attempted using *N*-bromosuccinimide in a polar solvent system.⁶⁷ A mixture of 2-nonylfluorene **32i**, *N*-bromosuccinimide and *N,N*-dimethylformamide was stirred at room temperature. Following recrystallization from hot ethanol, impure 2-bromo-7-nonylfluorene **24i** was obtained in *ca.* 30% yield. The material contained *ca.* 25% non-brominated 2-nonylfluorene **32i**.

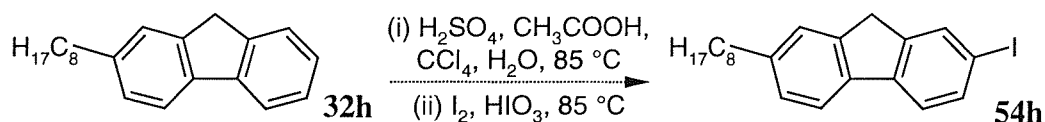


Neither benzyltrimethylammonium tribromide nor *N*-bromosuccinimide gave good results, and direct bromination using bromine and chloroform remained the most effective route to 2-bromo-7-alkylfluorenes **24**.

Iodide is a better leaving group than bromide, and it was found that aryl iodides generally gave better results in Suzuki coupling reactions.⁶⁸ However aromatic iodination is more difficult than bromination. Preparation of a 2-iodo-7-alkylfluorene **54** was attempted according to a literature procedure.⁶⁹ A mixture of 2-ethylfluorene **32b**, iodine, iodic acid, sulphuric acid, acetic acid, carbon tetrachloride and water was heated at reflux.



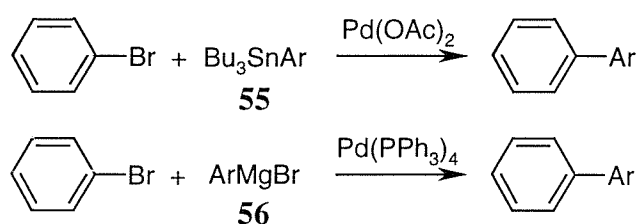
Following recrystallization, 2-iodo-7-ethylfluorene **54b** was obtained in *ca.* 17% yield. A mass spectrum indicated that the isolated material contained *ca.* 10% diiodinated material. A similar method was applied to the iodination of 2-octylfluorene **32h**.⁷⁰ A mixture of 2-octylfluorene **32h**, concentrated sulphuric acid, glacial acetic acid, carbon tetrachloride and water was heated at 85 °C. Iodine and iodic acid were added, and the reaction mixture was heated at 85 °C.



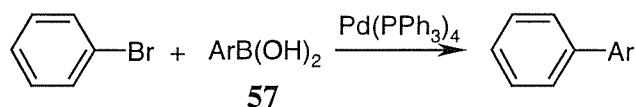
Following recrystallization, impure 2-iodo-7-octylfluorene **54h** was obtained in *ca.* 50% yield. A mass spectrum indicated that the material contained *ca.* 20% non-iodinated 2-octylfluorene **32h**. No other iodination reactions were attempted.

2.6 ARYL-ARYL COUPLINGS

It is possible to make a direct aryl-aryl bond using a transition metal-catalyzed coupling of an aryl bromide to an electron deficient species. Procedures such as the Stille coupling⁷¹ (aryl stannane **55** and palladium acetate) and Grignard reaction⁷² (aryl Grignard **56** and tetrakis(triphenylphosphine)palladium(0)) have found wide synthetic utility.



Many parameters may be varied, *i.e.* solvent, nature of transition metal and ligands, nature of electron deficient species *etc.* The Suzuki coupling was chosen for this work. An aryl bromide is coupled with a boronic acid **57** in the presence of tetrakis(triphenylphosphine)palladium(0) catalyst.⁷³

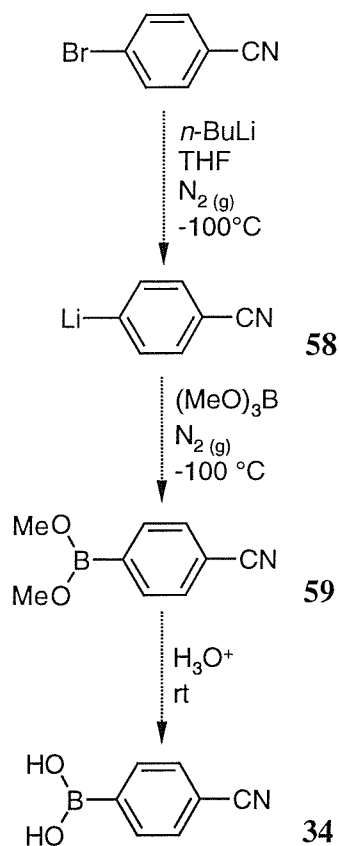


The Suzuki coupling is tolerant of most functional groups, and has been used in the preparation of many mesogenic compounds. Unlike many other coupling reactions, anhydrous conditions are not necessary, indeed the presence of aqueous base is essential if any reaction is to occur at all.⁷⁴

Tetrakis(triphenylphosphine)palladium(0) was prepared by a literature method from palladium(II)acetate.⁷⁵ A mixture of palladium(II)chloride, triphenylphosphine and dimethylsulphoxide was heated at 165 °C. Hydrazine hydrate was added, and the reaction mixture was stirred at 150 °C. After cooling, the precipitate formed was filtered and dried *in vacuo* to give tetrakis(triphenylphosphine)palladium(0) in 84% yield. The catalyst rapidly degraded in air, but was found to be effective after several months if stored under a nitrogen atmosphere in the freezer.

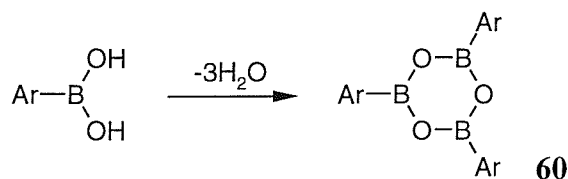
2.7 BORONIC ACIDS

4-Cyanobenzoboronic acid **34** was prepared from 4-bromobenzonitrile according to an established procedure.⁷⁶ Addition of butyllithium to 4-bromobenzonitrile effected transmetallation to give the aryllithium intermediate **58**. Quenching with trimethylborate gave the borate ester **59**. Addition of dilute acid cleaved the borate ester **59** to give the boronic acid **34**. After workup impure 4-cyanobenzoboronic acid **34** was obtained in *ca.* 56% yield.



Scheme 6: Attempted synthesis of 4-cyanobenzoboronic acid **34**.

The material contained an unknown component, which was thought to be the boroxine **60**. Boroxines are formed when boronic acids spontaneously dehydrate in air.⁷⁷

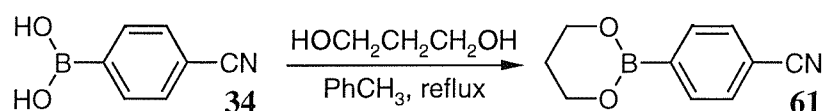


The free acid **34** and the boroxine **60** are synthetically equivalent, therefore boroxine formation complicates the characterization process, but is not detrimental to the coupling

reaction. However the spectral data was not consistent with the formation of the boroxine **60**, and the identity of the second component was not known.

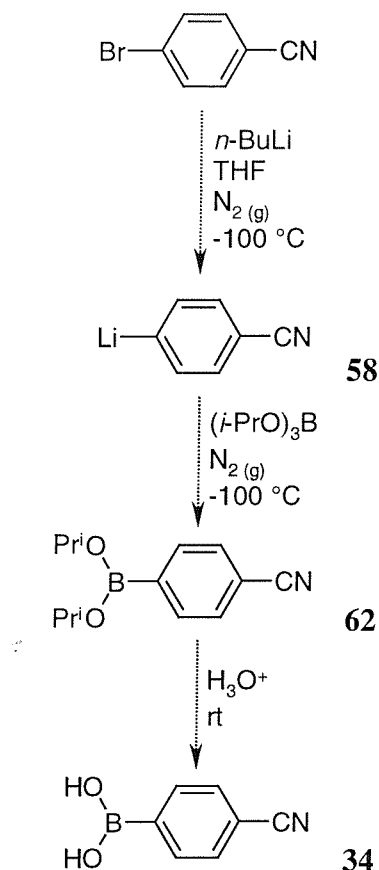
Purification of the material were attempted using a literature procedure.⁷⁸ The crude material was dissolved in hot sodium hydroxide solution. The aqueous layer was washed with diethyl ether to remove non-ionic compounds, then aqueous hydrochloric acid was added to precipitate the boronic acid, which was extracted into diethyl ether. This procedure was only partially successful, and the 4-cyanobenzoboronic acid **34** still contained unknown impurities.

In an attempt to obtain pure material, 4-cyanobenzoboronic acid **34** was converted to 4-cyanobenzoboronic acid, 1,3-propanediol cyclic ester **61**. A mixture of 4-cyanobenzoboronic acid **34**, 1,3-propanediol and toluene was heated at reflux.⁷⁹



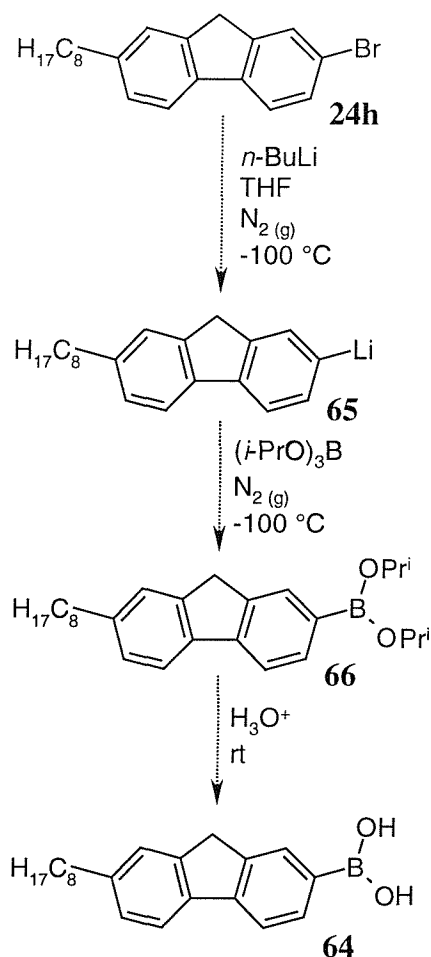
After recrystallization, 4-cyanobenzoboronic acid, 1,3-propanediol cyclic ester **61** was isolated in 63% yield.

In an improved procedure, the aryllithium intermediate **58** was quenched with trisopropylborate to give the borate ester **62**. Trisopropylborate has given better results in similar reactions. Trimethylborate often contains traces of methanol.⁸⁰ The borate ester **62** was then stirred with dilute acid. Following workup and precipitation from alkaline solution 4-cyanobenzoboronic acid **34** was isolated in 66% yield.



Scheme 7: Synthesis of 4-cyanobenzoboronic acid **34**.

An unsymmetric target can be synthesized by either of two possible combinations of transition metal intermediate and electron deficient species. In the present study, 2-(4-cyanophenyl)-7-alkylfluorenes **30** were obtained by coupling of a 2-bromo-7-alkylfluorene **24** with a 4-cyanobenzoboronic acid **34**. Since use of the alternative “reverse” coupling of 4-bromobenzonitrile to 7-alkylfluorene-2-boronic acid **63** might give an improved yield,⁶³ preparation of the boronic acid **64** was also attempted. Butyllithium was added to 2-bromo-7-octylfluorene **24h** to effect transmetalation to give the aryllithium intermediate **65**. Triisopropylborate was added to quench the intermediate, and the resulting borate ester **66** was cleaved by stirring with dilute acid.



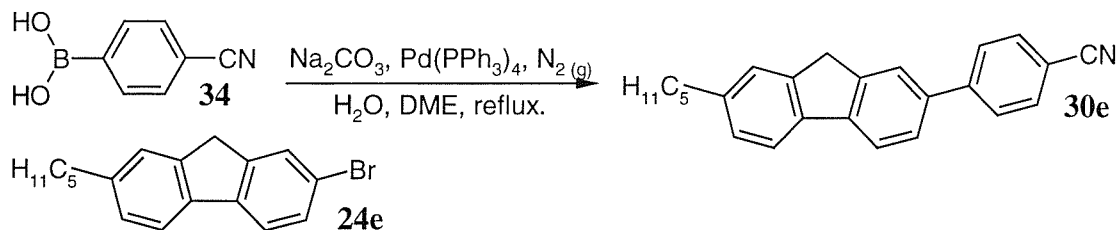
Scheme 8: Attempted synthesis of 7-octylfluorene-2-boronic acid **64**.

Following workup, unreacted 2-bromo-7-octylfluorene **24h** was recovered. A ^1H NMR spectrum indicated the presence of *ca.* 10% unknown reaction products. The spectrum suggested that these were 9-substituted compounds, although only unreacted 2-bromo-7-octylfluorene **24h** was detected by GCMS. There was no evidence that transmetallation occurred, and it appears that deprotonation at the methylene bridge occurred preferentially. On workup any 9-fluorenyl intermediates formed would be protonated to regenerate the starting material. There are many reported fluorene-2-boronic acids, but these are all 9,9-disubstituted compounds, where there are no acidic protons to interfere with the transmetallation step.

2.8 SUZUKI COUPLING

The 2-(4-cyanophenyl)-7-alkylfluorenes **30** mesogens were synthesized by a palladium catalyzed Suzuki coupling of a 2-bromo-7-alkylfluorene **24** to 4-cyanobenzoboronic acid **34**. A mixture of the aryl bromide **24e**, the boronic acid **34**, aqueous sodium carbonate

solution and 1,2-dimethoxyethane was deoxygenated using a stream of nitrogen gas. Tetrakis(triphenylphosphine)palladium(0) catalyst was added, and the reaction mixture was heated at reflux.



Following workup, the crude residue was dissolved in dichloromethane and filtered through a plug of silica. Further purification was effected by dissolving the products in hot 40-60 petroleum ether and heating the mixture with activated charcoal. The mixture was filtered whilst hot and then left to cool. Following recrystallization, 2-(4-cyanophenyl)-7-pentylfluorene **30e** was isolated in 21% yield.

It was hoped that optimization of the process would lead to an increase in yield. However when the process was extended to the other homologues the yields were disappointingly low (4-16%). The 2-(4-cyanophenyl)-7-alkylfluorenes **30** were all isolated as white crystalline solids which exhibited sharp transition temperatures.

Because of synthetic problems detailed in Sections 2.5 and 2.7, pure materials for the Suzuki coupling procedure were not always available. The 2-bromo-7-alkylfluorenes **24** often contained low levels of the non-brominated 2-alkylfluorene **32**, and 4-cyanobenzoboronic acid **34** often contained low levels of unidentified impurities. However the outcome of the reaction did not appear to be adversely affected by the use of impure materials, as the yields were consistently low regardless of the quality of the reagents used. The exception was 2-(4-cyanophenyl)-7-propylfluorene **30c**, which was isolated as a white solid in 46% yield. This dramatic increase in yield was made possible by using a larger excess of boronic acid in the coupling reaction. The solvent system for recrystallization was also modified. A solution of the crude product in dichloromethane was filtered through a plug of silica as before. The crude residue was dissolved in hot chloroform. Hot 60-80 petroleum ether was added, and the mixture was heated with activated charcoal. The mixture was filtered whilst hot and then left to cool. The combined use of a larger excess of boronic acid and the two solvent recrystallization system resulted in a higher yield.

Table 7: Synthesis of 2-(4-cyanophenyl)-7-alkylfluorenes **30**.

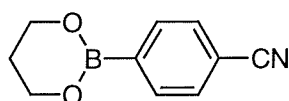
	Compound	Conditions and purification	Yield
30a	2-(4-Cyanophenyl)fluorene	1.10 eq ArB(OH) ₂ ; reflux 3.1 hr*	9%
30b	2-(4-Cyanophenyl)-7-ethylfluorene	1.20 eq ArB(OH) ₂ ; reflux 5.5 hr*	16%
30c	2-(4-Cyanophenyl)-7-propylfluorene	1.48 eq ArB(OH) ₂ ; reflux 3.4 hr*	46%
30d	2-(4-Cyanophenyl)-7-butylfluorene	1.21 eq ArB(OH) ₂ ; reflux 7.3 hr [†]	4%
30e	2-(4-Cyanophenyl)-7-pentylfluorene	1.18 eq ArB(OH) ₂ ; reflux 5.3 hr [†]	21%
30f	2-(4-Cyanophenyl)-7-hexylfluorene	1.21 eq ArB(OH) ₂ ; reflux 6.0 hr [†]	8%
30g	2-(4-Cyanophenyl)-7-heptylfluorene	1.17 eq ArB(OH) ₂ ; reflux 7.0 hr [†]	12%
30h	2-(4-Cyanophenyl)-7-octylfluorene	1.17 eq ArB(OH) ₂ ; reflux 2.2 hr [†]	4%
30i	2-(4-Cyanophenyl)-7-nonylfluorene	1.17 eq ArB(OH) ₂ ; reflux 5.0 hr [†]	16%

* recrystallized from hot chloroform-60-80 petroleum ether (charcoal)

[†] recrystallized from hot 40-60 petroleum ether (charcoal)

The synthesis of the mesogens 2-(4-cyanophenyl)-7-octylfluorene **30h** and 2-(4-cyanophenyl)-7-nonylfluorene **30i** was repeated using a larger excess of boronic acid and the modified purification procedure. The yields were greatly increased: 51% for **30h** and 57% for **30i**. These improvements to the final step made it possible to synthesize multigram quantities of the 2-(4-cyanophenyl)-7-alkylfluorene **30** mesogens.

Purification of 4-cyanobenzoboronic acid **34** by conversion to the cyclic ester derivative **61** was carried out. Following recrystallization, 4-cyanobenzoboronic acid, 1,3-propanediol cyclic ester **61** was isolated in 63% yield (Section 2.7).

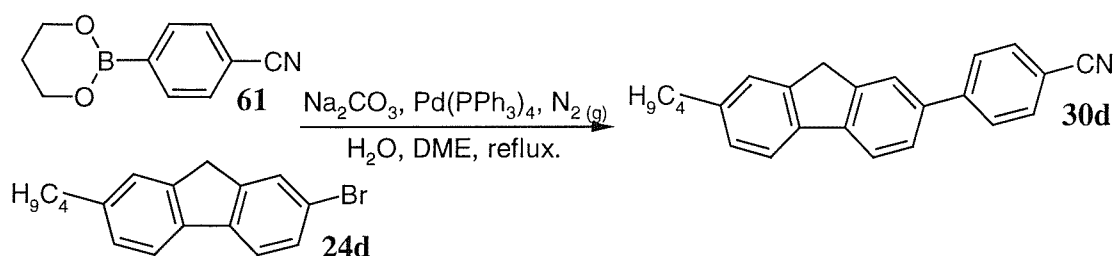
**Fig. 58:** 4-Cyanobenzoboronic acid, 1,3-propanediol cyclic ester **61**.

Similar boronic acids have been successfully prepared and used in literature Suzuki coupling procedures.⁷⁹ These compounds have a greater solubility in organic solvents, and can therefore be more readily purified by recrystallization. Their greater solubility also means that they are easier to use in reactions.

The coupling procedure was carried out using 4-cyanobenzoboronic acid, 1,3-propanediol cyclic ester **61**. It was hoped that this would lead to an increase in yield. A mixture of the

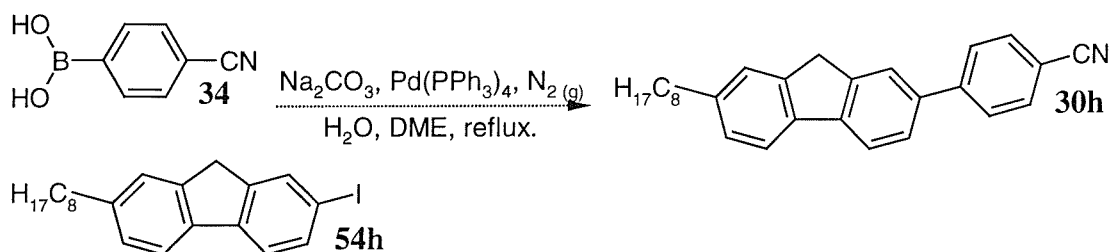
impure aryl bromide **24d**, the boronic acid **61**, aqueous sodium carbonate solution and 1,2-dimethoxyethane was deoxygenated using a stream of nitrogen gas.

Tetrakis(triphenylphosphine)palladium(0) catalyst was added, and the reaction mixture was heated at reflux.



Following recrystallization 2-(4-cyanophenyl)-7-butylfluorene **30d** was isolated in 63 % yield. This was a slight improvement over the 57% yield of 2-(4-cyanophenyl)-7-nonylfluorene **30i** obtained from the repeat synthesis. However, when the extra synthetic step needed to prepare 4-cyanobenzoboronic acid, 1,3-propanediol cyclic ester **61** is taken into account, the overall yield is actually lower.

Optimization of both the Suzuki coupling reaction and the purification procedure had led to an improvement in yield from 21% to 57%. However, the reported yields for similar Suzuki couplings were higher.⁸¹ Aryl iodides generally give higher yields than aryl bromides in Suzuki coupling reactions as iodide is a better leaving group than bromide. However preparation of the aryl iodide is usually more difficult than preparation of the analogous aryl bromide. Attempts to make 2-iodo-7-alkylfluorenes **54** were only partially successful, and no pure material was available (Section 2.5). A coupling reaction was attempted using a sample of impure 2-iodo-7-octylfluorene **54h**, which contained *ca.* 20% non-iodinated 2-octylfluorene **32h**. A mixture of the impure aryl iodide **54h**, the boronic acid **34**, aqueous sodium carbonate solution and 1,2-dimethoxyethane was deoxygenated using a stream of nitrogen gas. Tetrakis(triphenylphosphine)palladium(0) catalyst was added, and the reaction mixture was heated at reflux. Following workup, impure 2-(4-cyanophenyl)-7-octylfluorene **30h** was isolated in *ca.* 6% yield.



This disappointing result may be attributed in part to the small scale of the reaction.

However no pure material was obtained.

The reverse coupling reaction between of 4-bromobenzonitrile and a 7-alkylfluorene-2-boronic acid **64** was considered, but attempts to prepare **64** were unsuccessful (Section 2.7).

2.9 SUMMARY AND CONCLUSIONS

The five step convergent route described above gave access to the homologous series of 2-(4-cyanophenyl)-7-alkylfluorenes **30**. The first step, a Friedel-Crafts acylation, was very successful, giving the desired 2-acylfluorenes **31** in excellent yields of up to 82%. Results for the second step varied. Reduction of the 2-acylfluorene **31** using the Huang-Minlon modification of the Wolff-Kishner reduction gave either the desired 2-alkylfluorene **32** or the unwanted 2-alkyl-9-ethylfluorene **33**. When the desired product was obtained the yield ranged from low (28%) to excellent (89%). Changing the base from potassium hydroxide to sodium carbonate suppressed the side reaction, and the desired product could be isolated in 66-83% yield.

The 2-alkylfluorenes **32** were brominated by addition of a solution of bromine in chloroform. The reaction rarely proceeded to completion, and the aryl bromide product **24** often contained non-brominated 2-alkylfluorene **32**. Pure material could be isolated by subsequent recrystallizations. The yields varied from <1 to 70%, and the procedure showed poor reproducibility.

Preparation of 4-cyanobenzoboronic acid **34** from 4-bromobenzonitrile was fraught with difficulties. The material obtained often contained low levels of impurities. However the presence of these impurities was not found to be detrimental to the Suzuki coupling step. 4-Cyanobenzoboronic acid **34** could be purified by conversion to the cyclic ester **61**, but this extra synthetic step outweighed the small increase in yield in the subsequent Suzuki coupling reaction.

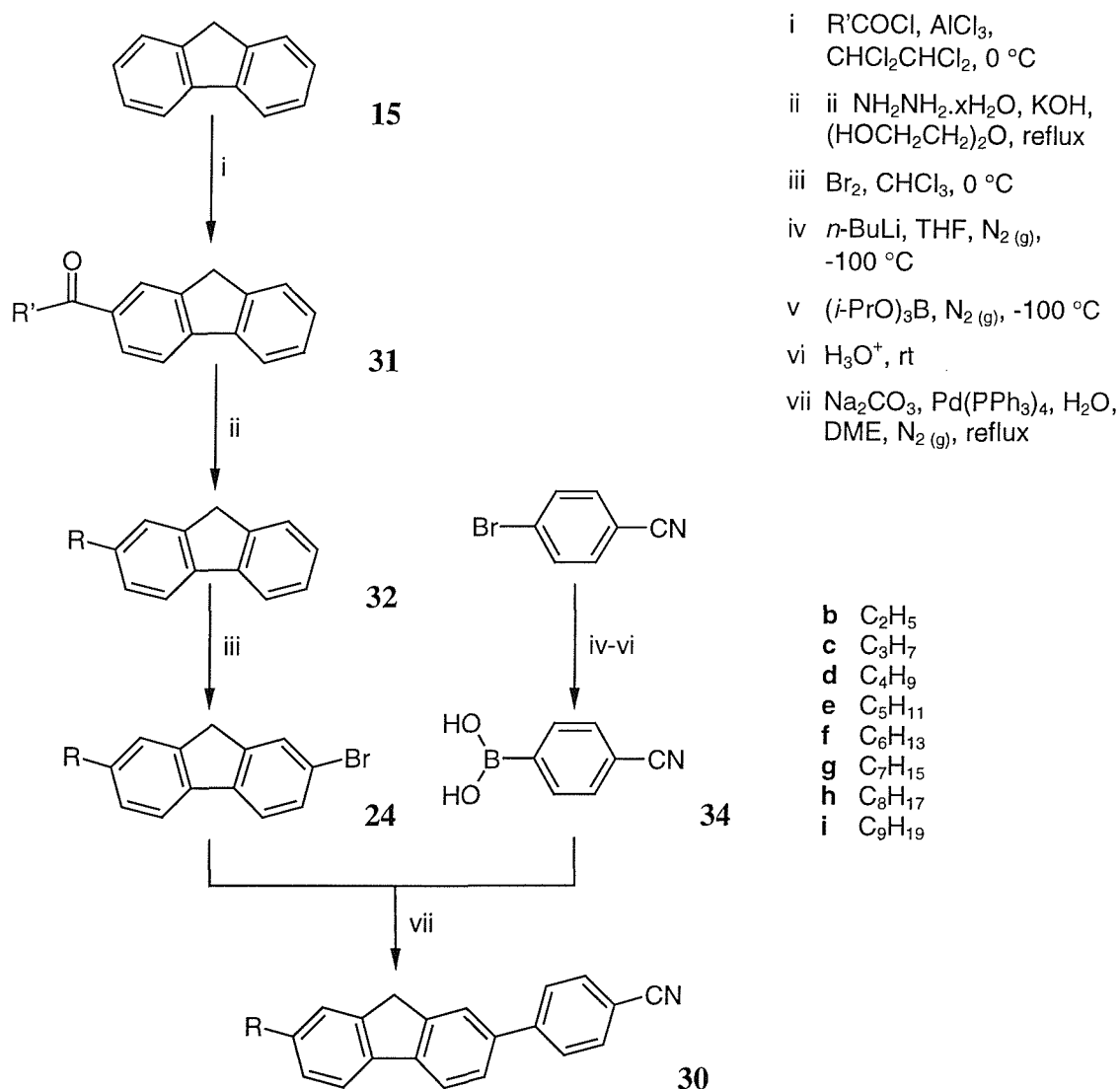
Suzuki coupling of the 2-bromo-7-alkylfluorenes **24** to 4-cyanobenzoboronic acid **34** proceeded in low yields of 4-21%. Refinements in the process enabled the isolation of the desired 2-(4-cyanophenyl)-7-alkylfluorenes **30** in up to 63% yield.

The synthetic route to the 2-(4-cyanophenyl)-7-alkylfluorenes **30** was successful, as all of the desired products were isolated in a high state of purity. However there is scope for improvement, particularly in the bromination step. The major drawback of the route is that the alkyl chain is introduced in the first synthetic step. This means that a large number of duplicate reactions are needed to synthesize the entire homologous series.

3. PROPERTIES OF 2-(4-CYANOPHENYL)-7-ALKYLFLUORENES

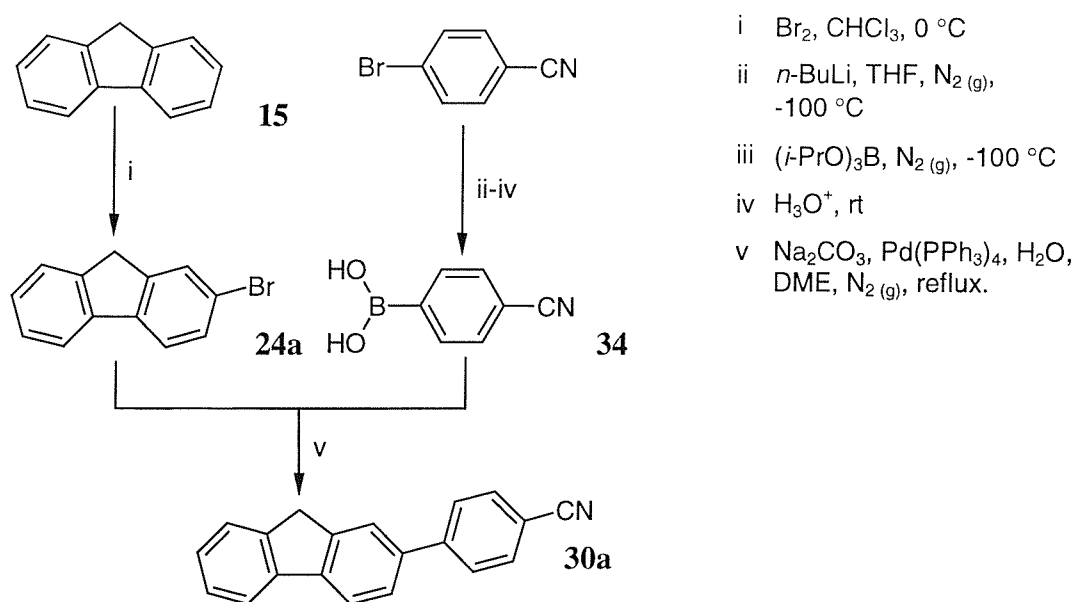
3.1 OVERVIEW

The 2-(4-cyanophenyl)-7-alkylfluorenes from C₂ **30b** to C₉ **30i** were prepared *via* the five step convergent route outlined in Scheme 9.



Scheme 9: General synthetic route to 2-(4-cyanophenyl)-7-alkylfluorenes **30**.

The compounds were isolated as white crystalline solids, and were all found to exhibit nematic mesophases across a wide temperature range. The heptyl **30g**, octyl **30h** and nonyl **30i** homologues also exhibited smectic A phases. The parent compound, with no alkyl chain, was prepared by a similar route (Scheme 10). 2-(4-Cyanophenyl)fluorene **30a** was also isolated as a white crystalline solid.



Scheme 10: Synthesis of 2-(4-cyanophenyl)fluorene **30a**.

2-(4-Cyanophenyl)fluorene **30a** did not exhibit an enantiotropic mesophase. A monotropic phase was detected by DSC studies, but only a simple melting point was observed by polarized optical microscopy. This result could not be replicated in later DSC studies. Calculation of energy minimized structures and measurement of physical properties and device characteristics was undertaken by Hitachi, Ltd.⁸² X-ray analysis was carried out at the University of Sheffield.⁸³ These results are clearly indicated at the beginning of the appropriate section.

Throughout this chapter comparisons are made with the 4-alkyl-4''-cyano-*p*-terphenyls **6**.

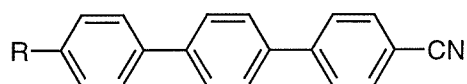


Fig. 59: 4-Alkyl-4''-cyano-*p*-terphenyls **6**.

These materials were important constituents of early display devices (Section 1.8.4). In many areas (*e.g.* dielectric anisotropy and birefringence) the 2-(4-cyanophenyl)-7-alkylfluorenes **30** had similar properties to the commercially successful 4-alkyl-4''-cyano-*p*-terphenyls **6**. However the greater rigidity and crescent shape of the 2-phenylfluorene core resulted in some disadvantageous values, most notably a high viscosity.

Many fluorene containing materials are used as electroluminescent materials for a new generation of flat panel displays (Section 1.11). The 2-(4-cyanophenyl)-7-alkylfluorenes **30** were found to show interesting luminescence properties, and may offer new possibilities for

light emitting elements in flat panel displays.

3.2 STRUCTURAL CHARACTERIZATION

The novel mesogens were fully characterized using a range of complementary spectroscopic and physical techniques. The purity of each compound was initially checked by thin layer chromatography. In all cases the compound eluted as a single component which was visualized using long wavelength (350 nm) light. Because of the fluorescent nature of the compounds (Section 3.9), nothing was visualized using 254 nm light.

^1H and ^{13}C NMR spectra were recorded on solutions of the compounds in deuteriochloroform, and the spectra for 2-(4-cyanophenyl)-7-pentylfluorene **30e** are reproduced in Figure 60.

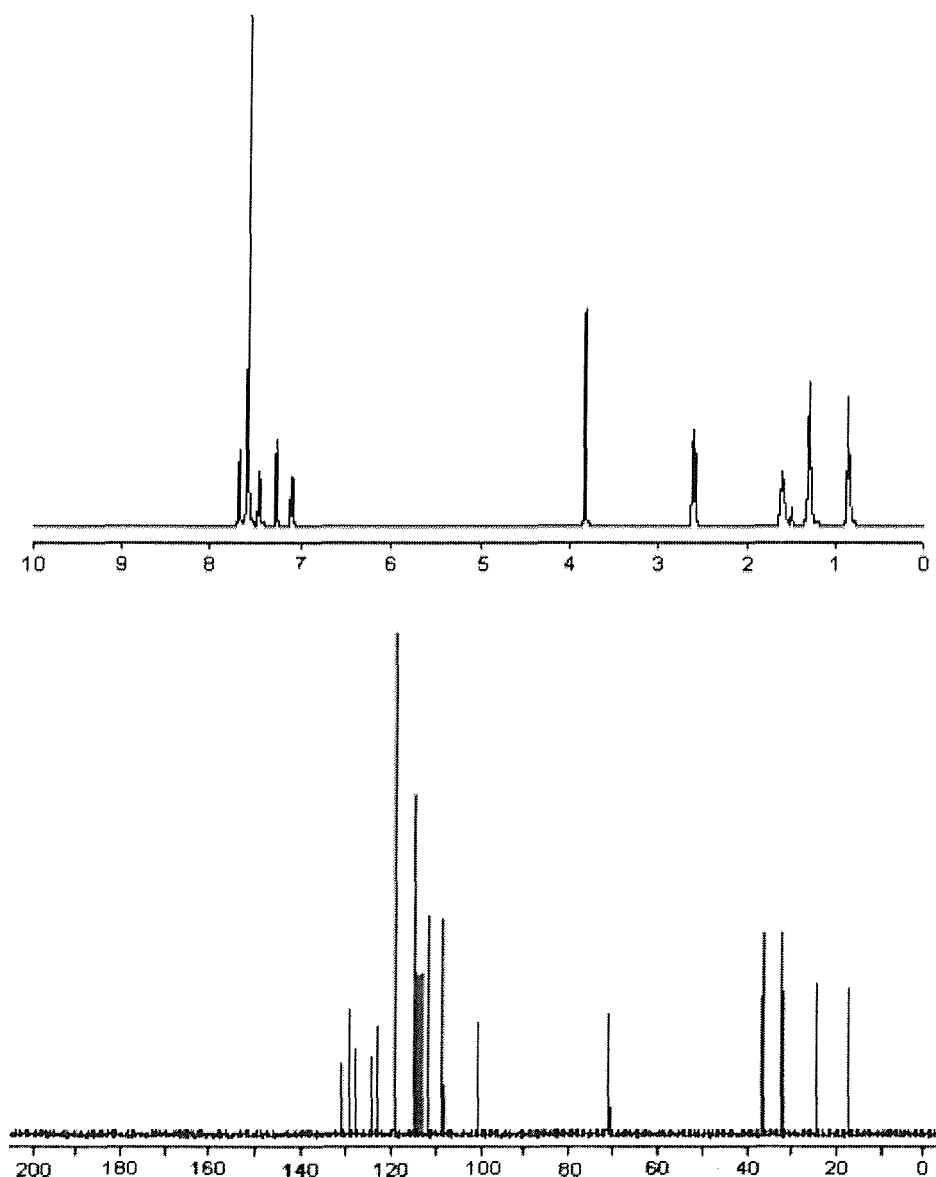


Fig. 60: 2-(4-Cyanophenyl)-7-pentylfluorene **30e** spectra: (i) ^1H NMR; (ii) ^{13}C NMR.

There was very little change in chemical shift moving up the homologous series, although the alkyl regions of both the ^1H and ^{13}C spectra necessarily became more complicated as signals began to overlap. The aromatic region of the ^1H NMR spectrum was more complicated than expected, as several signals overlapped to give a five proton multiplet. The C9 methylene singlet ($\delta_{\text{H}} \approx 4$) was a diagnostic signal, and it served as a useful, if imprecise, criterion of purity. The presence of a second component in levels of 5% or more was detectable as a shoulder on the singlet signal.

Melting points were initially measured on a sample in an open capillary tube. The liquid crystal phase transitions could also be observed using this method. Accurate determination of the transition temperatures was then carried out by polarized optical microscopy (Section 3.4). Using POM it was possible to control precisely the rate of heating, and the phase transitions could be clearly observed by monitoring the changes on optical texture.

Infra red spectra were obtained on samples prepared by making a mull with nujol. Later work with solutions of the mesogens in chloroform gave much better results. The diagnostic cyanide stretch at $\nu_{\text{max}} = 2228 \text{ cm}^{-1}$ was clearly observed in all cases.

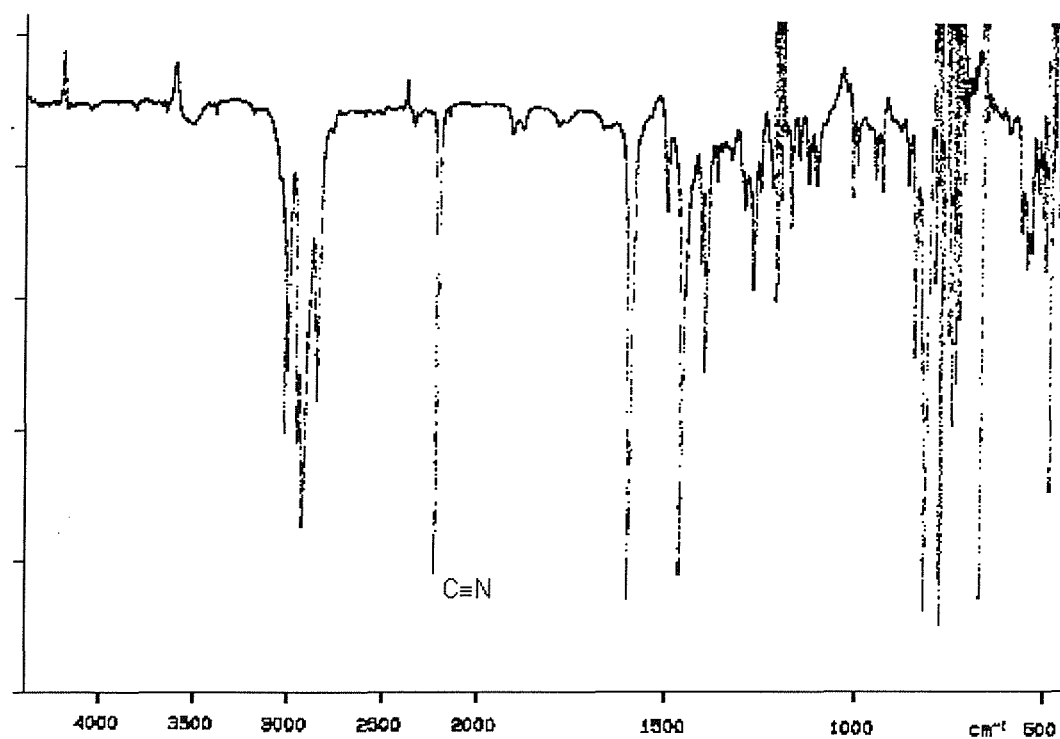


Fig. 61: 2-(4-Cyanophenyl)-7-pentylfluorene **30e**: IR spectrum.

Gas chromatography mass spectroscopy (GCMS) proved to be an invaluable technique for the analysis of the mesogens and intermediates (Section 9.1). However, limitations on the operating temperature of the instrumentation meant that higher melting point compounds

could not be analyzed in this way. The technique gave a good qualitative indication of purity. However, an internal reference was not used, and the separated components were detected by a total ion count. The method could therefore not be used to determine the quantitative purity of the compounds.

UV-Visible spectroscopy gave important insights into the delocalization of the π -electrons throughout the structure. UV-Visible and luminescence spectra are discussed below (Section 3.9).

Satisfactory combustion analyses (within 0.3% of the theoretical values) were obtained for all the compounds.

Many of the intermediates were already reported in the literature. However comprehensive spectroscopic data was rarely available, and these compounds were therefore also characterized using a range of techniques.

3.3 MOLECULAR GEOMETRY

This work was carried out by Hitachi, Ltd.⁸²

The molecule structures of 4-pentyl-4'-cyanobiphenyl **2e**, 4-pentyl-4''-cyano-*p*-terphenyl **6e** and 2-(4-cyanophenyl)-7-pentylfluorene **30e** were optimized using MOPAC97.⁸⁴

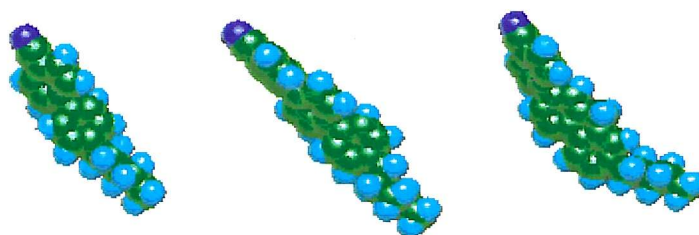
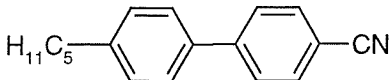
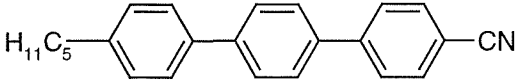
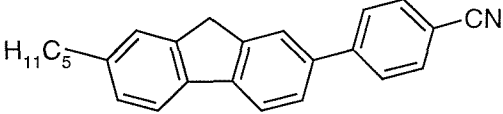


Fig. 62: MOPAC97 structures: (i) 4-pentyl-4'-cyanobiphenyl **2e**; (ii) 4-pentyl-4''-cyano-*p*-terphenyl **6e**; (iii) 2-(4-cyanophenyl)-7-pentylfluorene **30e**.

The energy minimized structures of the biphenyl **2e** and the terphenyl **6e** were as expected, with the benzene rings twisted but retaining colinearity along their 1,4- axes. These molecules have the classic rod-shape of a calamitic liquid crystal. In the case of the 2-phenylfluorene **30e**, the two rings which make up the fluorene core are coplanar. The third *p*-cyanophenyl ring is twisted in a similar manner to the rings in **2e** and **6e**. The bent geometry of the fluorene core is accentuated by the pentyl chain at one end of the molecule and the *para* substituted benzene ring at the other, which gives a crescent shaped molecule. The molecular dimensions of **2e**, **6e** and **30e** were measured on the energy minimized structures using MOPAC97. These measurements represent the length and width of a box

just large enough to enclose the molecular core. The dimensions are for the core only, *i.e.* the pentyl chain is not included in the calculation.

Table 8: Molecular dimensions from MOPAC97.

		Core length*/nm	Core width*/nm
2e		0.97	0.43
6e		1.39	0.43
30e		1.37	0.53

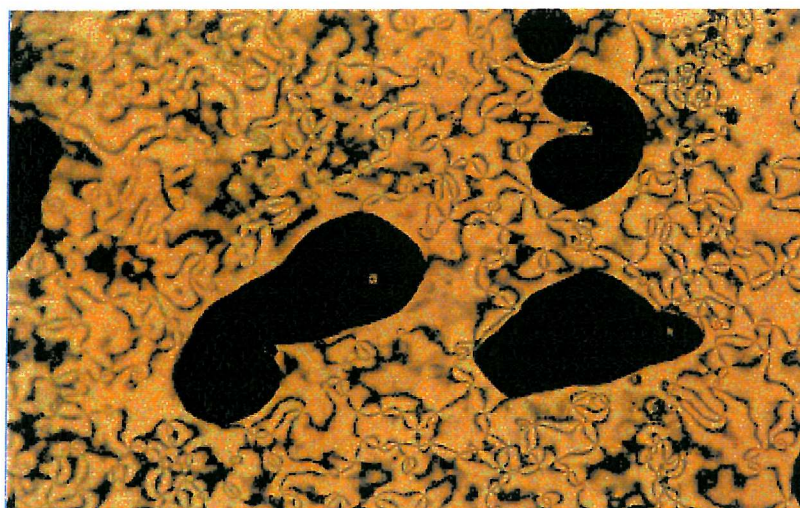
* These dimensions are for the core only, *i.e.* the pentyl chain is not included in the measurement.

The molecular width of **2e** and **6e** was the same, as it is determined by the size of a benzene ring. Because of its crescent shape, the 2-phenylfluorene **30e** is slightly shorter than the terphenyl **6e**. However **30e** is $\approx 20\%$ wider. Many of the physical properties of 2-(4-cyanophenyl)-7-pentylfluorene **30e** may be explained in terms of its crescent shape.

3.4 POLARIZED OPTICAL MICROSCOPY

The liquid crystal phases were identified by the characteristic optical textures observed by polarized optical microscopy. The materials all exhibited sharp transitions ($\approx 1^\circ\text{C}$). The parent compound **30a** showed a simple melting point, although a metastable phase was detected by differential scanning calorimetry. However, no evidence of a mesogenic phase could be found by polarized optical microscopy. The other members of the series **30b-30i** all exhibited enantiotropic nematic phases. These were identified from the characteristic Schlieren texture, examples of which are shown in Figure 63.

The first photograph (Figure 63a) shows a biphasic sample generated by cooling a sample from the isotropic. A nematic Schlieren texture with four brush defects and optically extinct isotropic regions coexist in the same sample. A different sample gave more varied optical textures. Just below the clearing point (Figure 63b) a colourful Schlieren texture was observed. On further heating the sample became brighter (Figure 63c). Optically extinct isotropic regions are visible at the edges of the photograph.



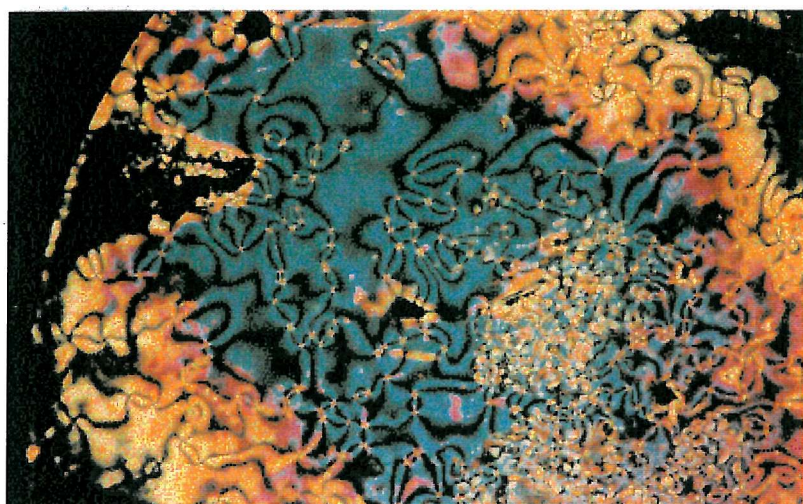
(a) Biphasic sample on cooling from the isotropic.

30f (203 °C)



(b) On heating to just below clearing point.

30g (202 °C)



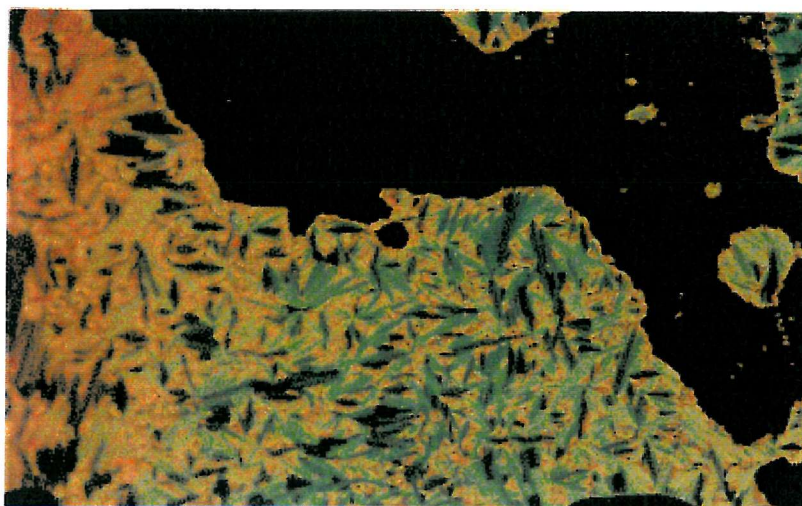
(c) At the clearing point.

30g (205 °C)

Fig. 63: Schlieren textures of 2-(4-cyanophenyl)-7-alkylfluorenes **30**.

In addition to the nematic, the heptyl (**30g**) octyl (**30h**) and nonyl (**30i**) homologues also exhibited a smectic phase. The optical textures generated contained large grey regions arising from homeotropically aligned molecules. These regions did not extinguish fully on

rotation, which suggested that the phase was biaxial. It was thought to be a smectic C, but no four brush defects were observed. However X-ray analysis of 2-(4-cyanophenyl)-7-octylfluorene **30h** proved that the phase was actually a smectic A (Section 3.6). In most cases the textures were disappointing, and only oily streaks and homeotropically aligned areas were seen. However, Figure 64 shows focal conics which were generated by cooling the sample from the nematic.



On cooling from nematic.

30i (187 °C)

Fig. 64: Focal conic texture of 2-(4-cyanophenyl)-7-nonylfluorene **30i**.

The POM transition temperatures for the 2-(4-cyanophenyl)-7-alkylfluorenes **30** are shown in Figure 65. As the alkyl chain length is increased, the melting and clearing points both decrease steadily. There is no significant odd-even effect. The pentyl homologue **30e** had a mesogenic range of 80 °C (Cr 130 N 218 I). The longer chains compounds (heptyl **30g**, octyl **30h** and nonyl **30i**) form a smectic A phase.

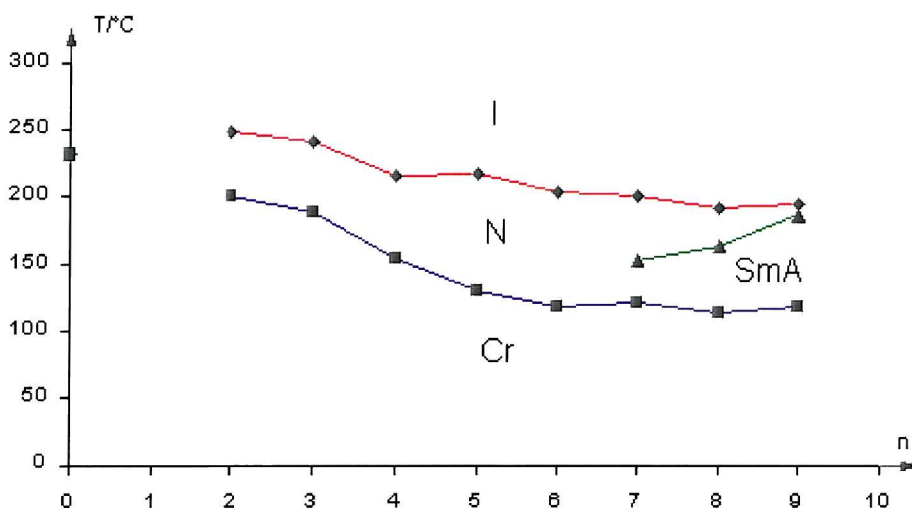


Fig. 65: Transition temperatures for the 2-(4-cyanophenyl)-7-alkylfluorenes **30**.

Table 9 shows the transition temperatures for the 2-(4-cyanophenyl)-7-alkylfluorenes **30**. The reported values for the 4-alkyl-4''-cyano-*p*-terphenyls **6** are included for comparison (column 5).

Table 9: POM data for the 2-(4-cyanophenyl)-7-alkylfluorenes **30**.

	R	Transition	Temperature* /°C	CT Temperature /°C	
30a	H	Cr → I	232	198	85
30b	C ₂ H ₅	Cr → N N → I	201 248	- -	
30c	C ₃ H ₇	Cr → N N → I	188 241	182 258	86
30d	C ₄ H ₉	Cr → N N → I	154 220	154 242	87
30e	C ₅ H ₁₁	Cr → N N → I	130 218	131 240	88
30f	C ₆ H ₁₃	Cr → N N → I	118 203	125 228	89
30g	C ₇ H ₁₅	Cr → SmA SmA → N N → I	122 152 201	134 (126) 222	90
30h	C ₈ H ₁₇	Cr → SmA SmA → N N → I	114 160 187	86 197 214	90
30i	C ₉ H ₁₉	Cr → SmA SmA → N N → I	118 186 194	87 206 212	90

* Corrected by calibration with standard materials.

These values compare favourably with the analogous terphenyls. The melting points are broadly similar, but the 2-phenylfluorenes have lower clearing points. The heptyl **6g**, octyl **6h** and nonyl **6i** terphenyls form both smectic A and E phases. The lower clearing points of the 2-(4-cyanophenyl)-7-alkylfluorenes **30** are a consequence of the crescent shape of the fluorene core, which leads to a smaller length-to-breadth ratio.

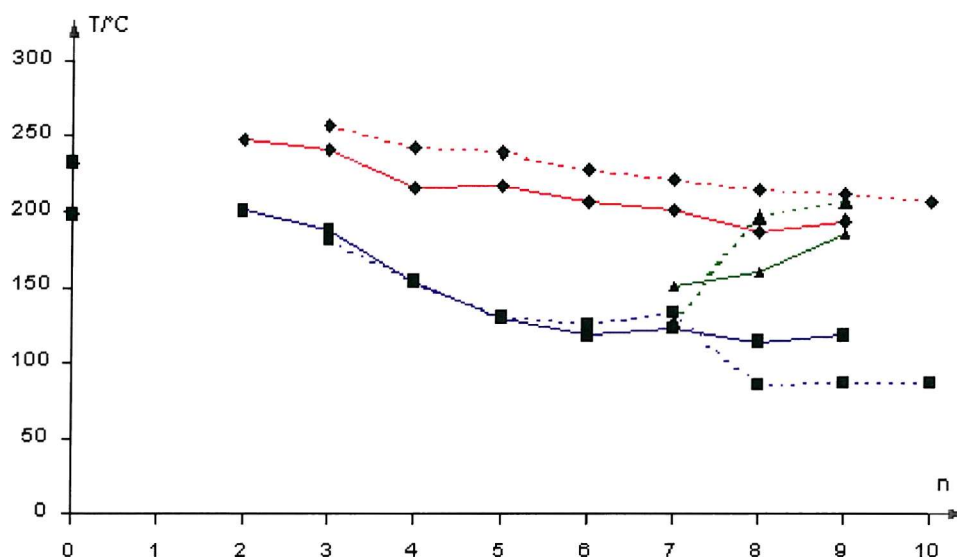


Fig. 66: Transition temperatures: (i) 2-(4-cyanophenyl)-7-alkylfluorenes **30** (—); (ii) 4-alkyl-4''-cyano-*p*-terphenyls **6** (-----).

3.5 DIFFERENTIAL SCANNING CALORIMETRY

Calorimetric data on the materials was obtained by differential scanning calorimetry. POM analysis of 2-(4-cyanophenyl)fluorene **30a** indicated a simple melting point, even when the sample was carefully supercooled. However a DSC trace clearly indicated that the compound was monotropic. A mesophase, probably a nematic was detected on supercooling, although this result could not be replicated in subsequent experiments.

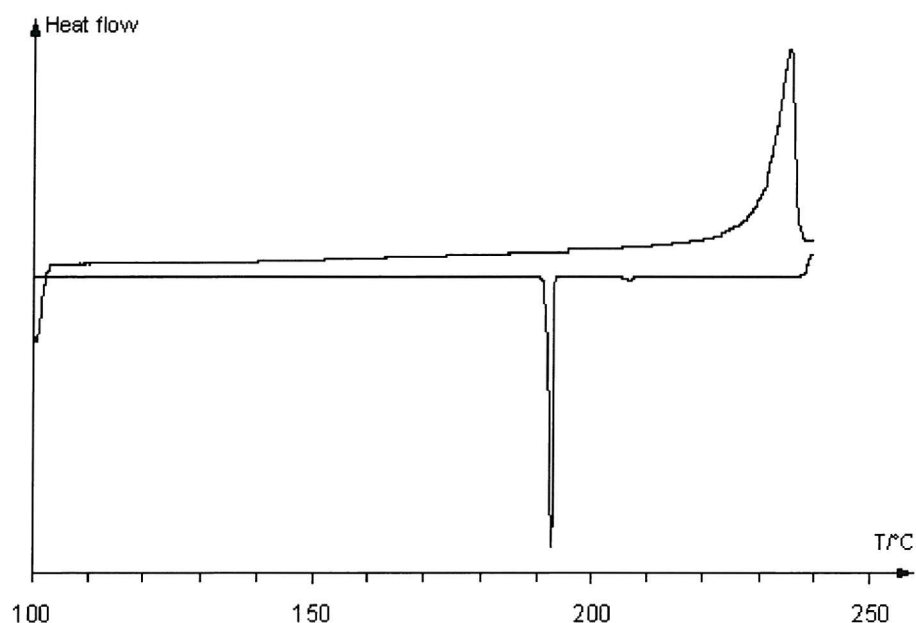


Fig. 67: DSC trace for 2-(4-cyanophenyl)fluorene **30a**.

Further DSC studies were not straightforward. The first cycle of heating and cooling was carried out to anneal the sample. The second heating curve was then recorded, but the observed transitions were broader than expected. Indeed in many cases the first heating curve had narrower transitions than those for the annealed sample. This was totally unexpected, as there was no evidence that the materials were unstable, and all the phase transitions observed by POM were sharp and reversible.

An investigation was carried out into this unexpected problem. A sample of 2-(4-cyanophenyl)-7-ethylfluorene **30b** was heated and cooled successively five times.

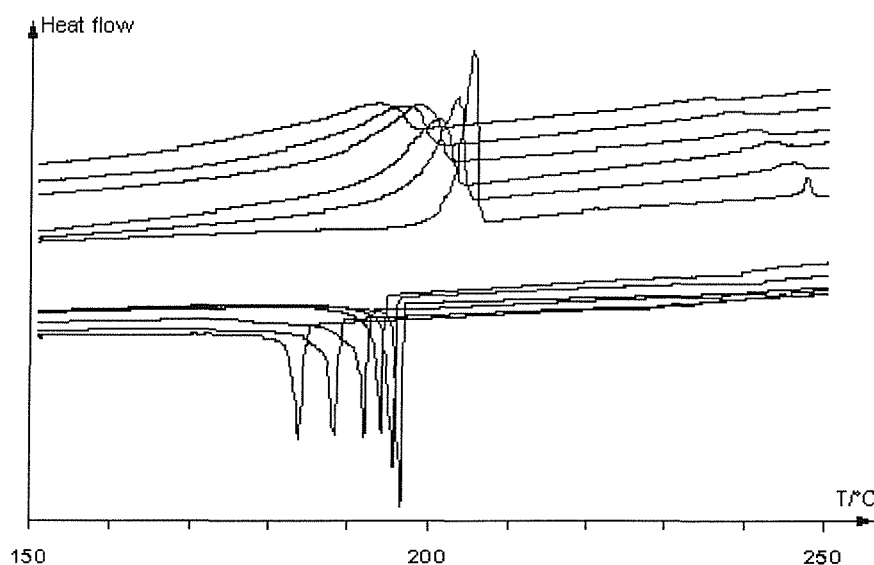


Fig. 68: Successive DSC traces for 2-(4-cyanophenyl)-7-ethylfluorene **30b**.

The first cycle showed reasonably sharp transitions, but the peaks broadened on successive cycles of heating and cooling. The peak positions also shifted to lower temperatures, *i.e.* the transition temperatures were reduced. The integrated area under the melting peak (solid \rightarrow nematic) was also found to decrease on successive cycles.

The sample of 2-(4-cyanophenyl)-7-ethylfluorene **30b** was recovered from the sample pan following the experiment, and ^1H and ^{13}C NMR spectra were recorded. The ^{13}C NMR spectrum showed no change. The ^1H NMR spectrum had additional signals at δ_{H} 2.64, 3.98, 4.92 and 7.10-8.12. No degradation products could be detected by GCMS analysis. From analysis of the ^1H NMR integrals, the amount of degradation product present after six cycles of heating and cooling was estimated at *ca.* 10%.

A identical set of heating and cooling cycles was carried out by POM on a fresh sample of 2-(4-cyanophenyl)-7-ethylfluorene **30b**. The transition temperatures were found to show the same decrease as found by DSC, and the transitions became less distinct on successive

cycles. The optical textures were often biphasic, showing optically extinct regions alongside nematic schlieren texture.

The problem appeared to be degradation of the sample. This was strongly temperature dependent, as samples of the material stored at room temperature showed not change over several years. Also, the peak broadening on DSC analysis was much less pronounced for the lower melting point homologues.

This problem of partial degradation was circumvented by annealing the sample at a low temperature, then recording the heating curve. The sample was heated to a few degrees above the melting point to give a homogenous mesogenic phase, with all the sample in thermal contact with the sample pan. The sample was cooled to give the annealed solid, then the heating curve was recorded across the entire mesogenic range. Values were obtained from this trace, the second heating curve.

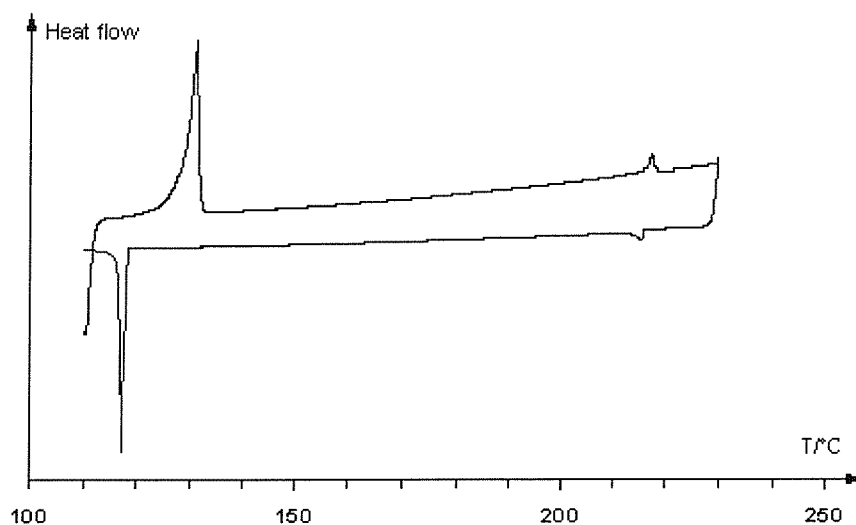


Fig. 69: DSC traces for 2-(4-cyanophenyl)-7-pentylfluorene **30e**.

Using this method it was possible to obtain calorimetric data for the 2-(4-cyanophenyl)-7-alkylfluorenes **30** (Table 10). However the weak smectic A to nematic transition in 2-(4-cyanophenyl)-7-heptylfluorene **30g** could not be detected. The low entropy changes for the nematic to isotropic transitions are consistent with the crescent shape of the molecules, which may have a tendency for local biaxial ordering. The ethyl homologue has lower values of ΔH and $\Delta S/R$ than the other materials, which may be a consequence of slight sample degradation. The other values are self consistent.

Table 10: Calorimetric data for the 2-(4-cyanophenyl)-7-alkylfluorenes **30**.

	R	Transition	Temperature /°C	ΔH /kJmol ⁻¹	$\Delta S/R$
30a	H	Cr → I	229.6	19.53	4.68
30b	C ₂ H ₅	Cr → N	201.3	11.20	2.79
		N → I	247.1	0.46	0.11
30c	C ₃ H ₇	Cr → N	186.6	15.77	4.13
		N → I	239.6	0.40	0.09
30d	C ₄ H ₉	Cr → N	157.9	18.92	5.28
		N → I	219.6	0.41	0.10
30e	C ₅ H ₁₁	Cr → N	128.6	14.54	4.35
		N → I	216.3	0.43	0.11
30f	C ₆ H ₁₃	Cr → N	114.2	18.50	5.70
		N → I	203.3	0.41	0.10
30g	C ₇ H ₁₅	Cr → SmA	117.5	19.85	6.07
		SmA → N	-	-	-
		N → I	201.8	0.49	0.12
30h	C ₈ H ₁₇	Cr → SmA	114.5	21.14	6.56
		SmA → N	177.9	0.55	0.15
		N → I	193.3	0.41	0.11
30i	C ₉ H ₁₉	Cr → SmA	113.0	21.87	6.77
		SmA → N	181.9	0.93	0.11
		N → I	189.4	1.72	0.21

3.6 X-RAY ANALYSIS

This work was carried out by David Dunmur and Goran Ungar at Sheffield University.⁸³ Measurements were made on 2-(4-cyanophenyl)-7-octylfluorene **30h**. The sample was placed in a Lindemann tube then heated to give the nematic phase. On cooling to the smectic phase the sample partially aligned as concentric cylinders in the sample tube. The diffraction pattern was then recorded using a Marr Research Image Plate Detector and a standard Cu K α X-ray source.

At 130°C, the measured layer spacing was 39Å. There was an additional very weak scattering feature at an angle corresponding to a spacing of 22.8Å along the smectic layer normal. The molecular length for the all trans extended chain conformation of 2-(4-

cyanophenyl)-7-octylfluorene **30h** was calculated as 23.2 Å using Cerius².⁹¹ Comparison of the measured layer spacing with the molecular length suggests an interdigitated smectic A phase. The crescent shaped molecules may adopt the arrangement shown in Figure 70, where bilayers are formed in order to maximize favourable overlaps between the *p*-cyanophenyl rings.



Fig. 70: Interdigitated smectic A phase of 2-(4-cyanophenyl)-7-octylfluorene **30h**.

The weak scattering feature detected is consistent with an incommensurate periodicity of about one molecular length, showing that not all the molecules are paired in the interdigitated layers. Similar interdigitated SmA_d phases are observed for the 4-alkyl-4'-cyanobiphenyls **2**. The analogous terphenyl compounds also exhibit smectic A phases.

3.7 MIXTURE WORK

The high melting points of the series of 2-(4-cyanophenyl)-7-alkylfluorenes **30** prevented the direct measurement of many physical properties, as the mesogenic ranges of the materials were above the permissible operating temperatures of the instruments.

Accordingly, mixtures of the mesogens were prepared in an attempt to form a eutectic and therefore depress the melting point sufficiently to allow useful data to be obtained. The results are summarized in Table 11.

Odd chain length compounds were chosen for the study. The pure propyl **30c**, pentyl **30e** and heptyl **30g** and nonyl **30i** homologues all form a nematic phase (i-iv). The heptyl and nonyl homologue also form a smectic A phase (iii-iv).

Initially C₃/C₅/C₇ ternary mixtures were studied (v-viii). The four mixtures prepared all formed a nematic phase only. However only a slight lowering of the melting point was achieved. The most effective mixture (vii) had a mesogenic range only slightly larger than that of the pure pentyl material (ii).

The C₃ component was replaced with the nonyl homologue **30i**, and two ternary C₅/C₇/C₉

mixtures were prepared (ix-x). The mixtures exhibited both a smectic and a nematic phase. Again only a small reduction in the melting point was achieved, and the smectic to nematic transition temperatures were high. The samples supercooled to a small extent.

Table 11: Transition temperatures for 2-(4-cyanophenyl)-7-alkylfluorenes **30** mixtures.

*	30c (C ₃)	30e (C ₅)	30g (C ₇)	30i (C ₉)	Transition temperatures [†]
i	PURE	-	-	-	Cr 192 N 245 I
ii	-	PURE	-	-	Cr 130 N 222 I
iii	-	-	PURE	-	Cr 122 SmA 156 N 205 I
iv	-	-	-	PURE	Cr 118 SmA 190 N 198 I
v	65%	35%	0%	-	Cr 164 N 228 I
vi	32%	34%	34%	-	Cr 118 N 210 I
vii	16%	34%	50%	-	Cr 105 N 204 I
viii	0%	33%	67%	-	Cr 109 N 195 I
ix	-	33%	34%	33%	Cr 103 SmA 148 N 195 I
x	-	50%	34%	16%	Cr 103 SmA 125 N 197 I

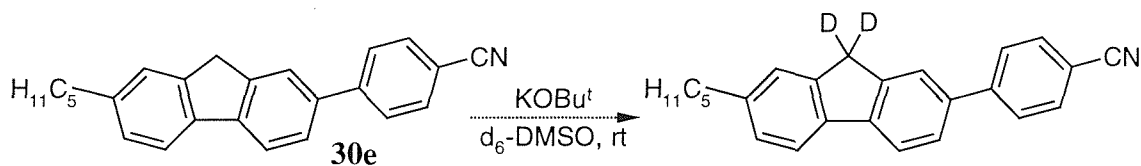
* Mixtures of mesogens were prepared by combining 2 mmol solutions of the pure compounds in chloroform in the required proportions. The solvent was then allowed to evaporate, and the resulting solids were dried thoroughly *in vacuo* before analysis

[†] Transition temperatures were determined by polarizing optical microscopy and are uncorrected

3.8 DEUTERIATION STUDIES

²H NMR studies on deuteriated liquid crystal samples can provide important information about molecular orientational ordering within the phase. It is not necessary to fully deuteriate the mesogen and selective deuteration at a specific site is often preferred.⁹² Complete exchange is not required, but a high percentage of exchange ensures an adequate signal to noise ratio for the ²H NMR spectrum.

The C9 methylene bridge of fluorene provides an excellent site for deuteration. Several literature methods describe the synthesis of 9,9-d₂-fluorene **67**.⁹³ A preliminary exchange experiment was carried out on a sample of 2-(4-cyanophenyl)-7-pentylfluorene **30e** according to a procedure adapted from literature reports.⁹⁴ A solution of **30e** and d₆-dimethylsulphoxide was left to stand at room temperature. Potassium *tert*-butoxide was added, and the colourless solution turned dark green.



The experiment was carried out in an NMR tube, and the exchange process was monitored by recording ^1H NMR spectra at convenient intervals. The spectra suggested that partial exchange at the 9-position had occurred, but that the compound had to some extent degraded. The alkyl signals remained fairly constant, but there were significant changes in the aryl region. This was unexpected, especially given the literature precedents for labelling *unsubstituted* fluorene at the 9-position under similar conditions.^{93, 94}

In an attempt to understand the process, the spectra were analyzed for changes in chemical shift and integrals. Each spectrum was divided into three sections: (i) the C9 methylene signal; (ii) the alkyl region; and (iii) the aryl region. The integral for each section was normalized relative to the *t*-butanol signal (Table 12).

Table 12: Chemical shifts and integral ratios for the attempted deuteriation of 2-(4-cyanophenyl)-7-pentylfluorene **30e**.

Time/hr	$\delta_{\text{H}(\text{rel})}$ (C9) *	\int_{rel} (C9) †	\int_{rel} (Alkyl H) †	\int_{rel} (Aryl H) †
0 ‡	(4.05)	(2H, 2)	(11H, 10.3)	(10H, 8.9)
4.6	3.39	1.00	19.5	13.5
53.3	3.25	0.64	24.7	21.0
90.2	3.27	0.88	26.7	22.0
114.8	3.26	1.30	25.2	21.3
236.7	3.25	2.00	26.7	21.8

* $\delta_{\text{H}(\text{rel})}$ (C9) taking δ_{H} (Bu^tOH) as 1.14

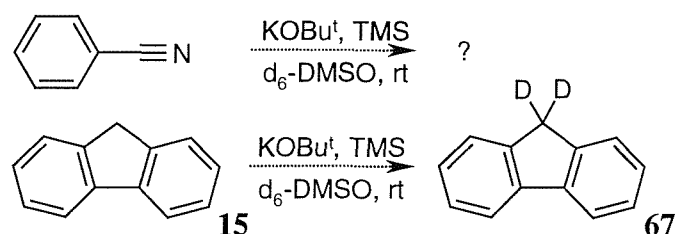
† \int_{rel} is the integral relative to $\int(\text{Bu}^t\text{OH})$

‡ values for $t = 0$ are for unadulterated **30e** before any KOBU^t was added

These results are inconclusive, suggesting that initially partial deuteriation occurred at the C9 position, but that these deuterons were gradually exchanged for protons. The likely source of these protons was water from the atmosphere, as the tube was not hermetically sealed. At the end of the experiment the material in the NMR tube (by now a yellow solution) was quenched with deuterium oxide, then extracted into chloroform. However, because of the small scale of the experiment and the presence of residual solvent, the

identity of the products could not be determined.

To discover the nature of the unexpected products of the attempted deuteration, similar experiments were carried out on samples of benzonitrile and fluorene. As they are commercially available it was possible to use larger amounts of these materials, which allowed good quality ^{13}C NMR spectra to be recorded. Samples of benzonitrile and fluorene were each placed in an NMR tube with d_6 -dimethylsulphoxide. Potassium *tert*-butoxide was added, and the colourless fluorene sample changed to an orange-brown solution. The benzonitrile solution remained colourless throughout the experiment. Tetramethylsilane was added as an internal standard, and ^1H and ^{13}C NMR spectra were recorded at convenient intervals.



After several weeks the sample of benzonitrile was unchanged. No exchange or degradation was observed, showing that the cyano group can withstand the basic conditions. The sample of fluorene had partially degraded, and the spectra were analyzed as described above (Table 12). In this case changes in both the proton and carbon chemical shifts were monitored relative to TMS.

Table 13: Chemical shifts and integral ratios for the attempted deuteration of fluorene.

Time/hr	$\delta_{\text{H}(\text{rel})} (\text{C9})^*$	$\delta_{\text{C}(\text{rel})} (\text{C9})^\dagger$	$\int_{\text{rel}} (\text{C9})^\ddagger$	$\int_{\text{rel}} (\text{Aryl H})^\ddagger$
0 §	(3.91)	(36.3)	(2H, 2)	(8H, 4.7)
4.6	3.91	36.3	3.93	10.3
53.3	3.91	36.3	3.93	9.9
90.2	3.91	36.3	3.93	10.0
114.8	3.91	36.3	3.93	9.9
236.7	3.91	36.3	3.73	10.0

* $\delta_{\text{H}(\text{rel})} (\text{C9})$ taking $\delta_{\text{H}} (\text{TMS})$ as 0.00

† $\delta_{\text{C}(\text{rel})} (\text{C9})$ taking $\delta_{\text{C}} (\text{TMS})$ as 0.0

‡ \int_{rel} is the integral relative to $\int (\text{Bu}^t\text{OH})$

§ values for $t = 0$ are for unadulterated **15** before any KOtBu was added

There was a dramatic change in the carbon spectrum, from six peaks for fluorene (0 hours) to thirteen peaks (236.7 hours). However the chemical shift of the C9 signal remained constant throughout. A mass spectrum of the adulterated material showed peaks at δ_c 180 and 182, consistent with the formation of both 9-hydroxyfluorene **68** and fluorenone **69**.

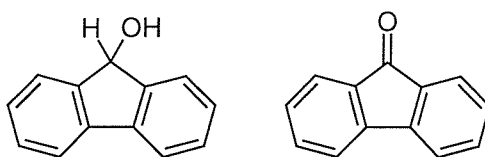


Fig. 71: (i) 9-Hydroxyfluorene **68**; (ii) fluorenone **69**.

The presence of these compounds was consistent with the aerial oxidation of fluorene. These conditions were therefore too harsh for the fluorene core. No deuteriated product was detected.

3.9 UV-VIS AND LUMINESCENCE STUDIES

The luminescence properties of the 2-(4-cyanophenyl)-7-pentylfluorene **30e** were of particular relevance in the light of recent interest in fluorene containing materials (Section 1.11). Several materials based on poly(dialkylfluorene)s have been incorporated in commercial display devices, where they are used as visible light emitters.²⁴ By suitable chemical modification, these materials can be made to luminesce at red, green and blue wavelengths.²⁷ Liquid crystalline luminescent materials are the subject of current research, since they may offer new possibilities for light emitting elements in flat panel displays.²⁸ The 2-(4-cyanophenyl)-7-alkylfluorenes **30** are important materials, as they are mesogens which show strong fluorescence. They are part of a new class of materials which may combine the increased charge mobilities of liquid crystalline monomers with the light emitting properties of polymers.

Unsubstituted fluorene absorbs at λ_{max} 266 nm, whereas the 2-(4-cyanophenyl)-7-alkylfluorenes **30** absorbed strongly at around 320 nm. The addition of the *p*-cyanophenyl ring extends the π -electron system by conjugation, shifting the absorption to longer wavelengths. The extinction coefficients for the 2-phenylfluorene compounds were considerably higher than for unsubstituted fluorene, which is also consistent with greater delocalization of electrons throughout the structure.

The 2-(4-cyanophenyl)-7-alkylfluorenes **30** were observed to fluoresce on a silica plate when irradiated with 350 nm light. More detailed luminescence analysis was carried out on

2-(4-cyanophenyl)fluorene **30a** and the pentyl and nonyl homologues **30e** and **30i**. The materials were studied as dilute solutions in dichloromethane. The solution was excited at the absorption maximum as determined by UV-VIS spectroscopy, and the luminescence spectrum was recorded. In all three cases, strong fluorescence was observed.

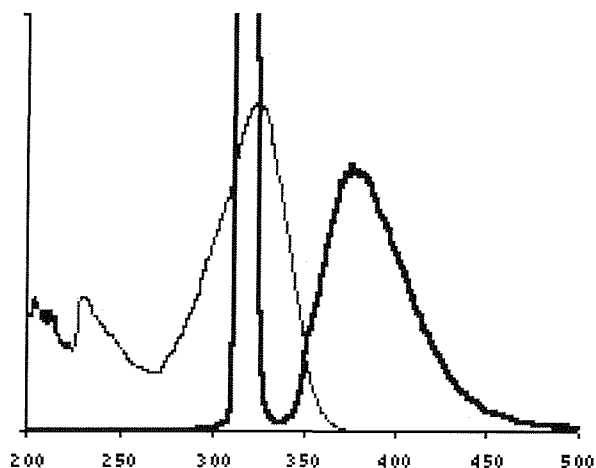


Fig. 72: UV-VIS (—) and luminescence (—) spectra for 2-(4-cyanophenyl)-7-pentylfluorene **30e**.

When 2-(4-cyanophenyl)-7-pentylfluorene **30e** was irradiated with light at 324 nm, light was emitted at 391 nm. This represents a red shift of 67 nm, which is not much smaller than the shift of 82 nm measured for poly(9,9-dihexylfluorene) **18a**.²⁴

The luminescence spectra of unsubstituted fluorene **15** and 4-pentyl-4''-cyano-*p*-terphenyl **6** were also recorded. Both these compounds also showed strong fluorescence, and the results are summarized in Table 14.

Table 14: Luminescence data for the 2-(4-cyanophenyl)-7-alkylfluorenes **30**.

	R	R'	$\lambda_{\text{ex}}/\text{nm}$	$\lambda_{\text{em}}/\text{nm}$	$\Delta\lambda/\text{nm}$
15	H	H	266	304	38
30a	H	<i>p</i> -NCC ₆ H ₄	318	376	58
30e	C ₅ H ₁₁	<i>p</i> -NCC ₆ H ₄	324	391	67
30i	C ₉ H ₁₉	<i>p</i> -NCC ₆ H ₄	324	395	71
6e	<i>p</i> -NC(C ₆ H ₄) ₃ C ₅ H ₁₁		303	378	75

The addition of a methylene bridge to 5CT **6e** to give 2-(4-cyanophenyl)-7-pentylfluorene **30e** results in a bathochromic shift of 21 nm for the absorption maximum. The extinction

coefficient for **30e** is also larger ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 61400 vs 42900 for 5CT **6e**). 5CT **6e** was found to show a red shift of 75 nm on fluorescence, which is slightly larger than the 67 nm observed for **30e**. However the emission maximum for **30e** is still at a longer wavelength, *i.e.* closer to visible light, than 5CT **6e**. These results are consistent with the greater delocalization of electrons over the two coplanar aromatic rings of the 2-phenylfluorene system.

3.10 PHYSICAL PROPERTIES

This work was carried out by Hitachi, Ltd.⁸²

The success of a liquid crystalline material depends on many factors, *e.g.* long term stability, ease of synthesis and the temperature range across which it is mesogenic. However it is anisotropic properties that determine the suitability of the material for use in commercial display devices. Three properties are of paramount importance: (i) optical appearance – the contrast between the on and off states; (ii) electrical response – its response to an applied field; and (iii) viscosity – how long it takes to switch between the on and off states. In view of their high melting points and rigid core structure, the 2-(4-cyanophenyl)-7-alkylfluorenes **30** were not expected to be ideal candidates for incorporation in display devices. However full evaluation of this new class of materials was carried out in order to provide important information about the structure-property relations for the novel 2-phenylfluorene liquid crystal core.

The high melting point of the 2-(4-cyanophenyl)-7-alkylfluorenes **30** dictated that physical measurements had to be carried out in a nematogenic solvent. Accordingly 2-(4-cyanophenyl)-7-pentylfluorene **30e** was dissolved in ZLI-4792, a commercially available nematic host mixture. ZLI-4792 has a very large nematic range (from -40 to +91 °C).

Many of its properties have been measured previously, and it is a standard choice of nematogenic solvent. The solubility of **30e** in the host mixture was low, so measurements were carried out on a 5wt% solution of **30e** in ZLI-4792.

The birefringence Δn was determined by measuring $d\Delta n$ for a homogeneous alignment cell with a gap of d between glass plates. The dielectric anisotropy $\Delta\epsilon$ was determined from the relationship between the voltage and the capacitance of a homogeneous alignment cell operating at 1 kHz. The viscosity η was measured using an E-type viscometer.

Measurements were also made on similar solutions of 4-pentyl-4'-cyanobiphenyl **2e** and 4-pentyl-4"-cyano-*p*-terphenyl **6e**.

The measurements on the host mixture were then extrapolated to 100% to give the desired

physical parameters, which are reported in Table 15.

Table 15: Birefringence, dielectric anisotropy and viscosity data.

		$\Delta\epsilon$ (1 kHz)	Δn (589 nm)	$\eta/\text{mPa s}$
2e	<i>p</i> -NC(C ₆ H ₄) ₂ C ₅ H ₁₁	14.4	0.19	17.6
6e	<i>p</i> -NC(C ₆ H ₄) ₃ C ₅ H ₁₁	20.4	0.37	45.9
30e	<i>p</i> -NCC ₆ H ₄ (C ₁₃ H ₁₀)C ₅ H ₁₁	20.7	0.38	207.0

Measurements were made on the host mixture then extrapolated to 100%

The value of $\Delta\epsilon$ obtained for 4-pentyl-4"-cyano-*p*-terphenyl **6e** was smaller than the literature value of 22. This may be explained by the use of a different technique (in the literature method, ϵ_{\parallel} and ϵ_{\perp} were measured separately). The measured birefringences for **2e** and **6e** also differed slightly from the literature values. A discrepancy may also arise from the need to carry out the measurements on dilute solutions of the material under test. Large errors can therefore occur on extrapolation of the results.

3.10.1 Birefringence

In order to differentiate between the off and on states, the change in the director alignment must produce a change in optical appearance. The molecules are optically anisotropic, *i.e.* the refractive index depends on the angle of viewing. The birefringence or optical anisotropy (Δn) is the difference between the refractive index measured parallel (n_{\parallel}) and perpendicular (n_{\perp}) to the director.

$$\Delta n = n_{\parallel} - n_{\perp}$$

Δn for the 2-phenylfluorene **30e** was high, as expected for a cyano-containing compound. The value was, however, only slightly larger than Δn for 5CT **6e**. This reflects the slightly larger π -electron conjugation in **30e**

3.10.2 Dielectric anisotropy

2-(4-Cyanophenyl)-7-pentylfluorene **30e** and 4-pentyl-4"-cyano-*p*-terphenyl **6e** both had large positive dielectric anisotropies. As discussed earlier (Section 1.8.2), $\Delta\epsilon$ depends on the induced polarization when the material is placed in an electric field and the permanent polarization arising from dipole moments. The cyano group is a strong dipole, and it is this that dictates the sign and magnitude of $\Delta\epsilon$. It is therefore unsurprising that the 2-

phenylfluorene **30e** and 5CT **6e** were found to have similar dielectric anisotropies.

3.10.3 Rotational viscosity

Several different viscosities are defined for a nematic, depending on how the molecular orientation is changed.¹⁵ For several of these viscosities there is no change in the director orientation. In these studies the rotational viscosity γ_l was measured. Here there is a change in the director orientation, as it is the long axis of the molecule which is turned. The measured viscosity η was almost proportional to the rotational viscosity γ_l .

Viscosities can be greatly influenced by subtle changes in molecular structure. The crescent shape of the 2-(4-cyanophenyl)-7-pentylfluorene **30e** and the possibility of stronger core interactions may be expected to increase the viscosity. The 2-phenylfluorene **30e** had a much larger rotational viscosity than the terphenyl **6e**.

3.11 DEVICE CHARACTERISTICS

This work was carried out by Hitachi, Ltd.⁸²

Response time and driving voltage were measured in the in-plane switching (IPS) mode. In this mode, the director alignment is uniform planar, *i.e.* parallel to the substrate, in both the on and off states. Switching between the two states is carried out by applying an electric field parallel to the substrate.

Measurements were made on a 5wt% solution of 2-(4-cyanophenyl)-7-pentylfluorene **30e** in the nematic host mixture ZLI-4792. Similar 5wt% solutions of 4-pentyl-4'-cyanobiphenyl **2e** and 4-pentyl-4'-cyano-*p*-terphenyl **6e** were prepared and studied using the same experimental setup. The dielectric anisotropy and viscosity were measured for all three mixtures.

Table 16: Response time and driving voltage.

Cell mixture	$\Delta\epsilon$	$\eta/\text{mPa s}$	$\tau_{\text{off}}/\text{ms}$	V_{max}/V
5% 2e in ZLI-4792	5.51	13.0	20.6	11.2
5% 6e in ZLI-4792	5.56	13.6	23.2	11.1
5% 30e in ZLI-4792	5.55	14.7	24.2	11.1

The dielectric anisotropies of the terphenyl and the 2-phenylfluorene mixtures were similar, and these were slightly higher than the equivalent value for the biphenyl mixture. The 2-phenylfluorene mixture had a significantly higher viscosity.

The variation of transmittance with applied voltage was studied, and the response time τ_{off} and driving voltage V_{max} (the voltage at the transmittance maximum) were determined.

3.11.1 Response time

The response time τ_{off} depends strongly on both the rotational viscosity and the twist elastic constant k_{22} :

$$\tau_{\text{off}}/d^2 \propto \eta/k_{22}$$

The 2-phenylfluorene mixture had a viscosity approximately 10% higher than the terphenyl mixture, but this translated into a smaller (*ca.* 5%) increase in the response time τ_{off} . It therefore follows that **30e** must have a larger twist elastic constant k_{22} than **6e**. The twist elastic constant is of key importance for the IPS mode, and the relationship between the crescent shaped core and physical properties such as η and τ_{off} is interesting.

3.11.2 Driving voltage

The driving voltage for the IPS mode is the applied field required to realign the director to give maximum transmittance. V_{max} was found to be similar for all three mixtures. V_{max} depends on the twist elastic constant k_{22} and the dielectric anisotropy $\Delta\epsilon$:

$$V_{\text{max}}^2 \propto k_{22}/\Delta\epsilon$$

As $\Delta\epsilon$ is similar for **6e** and **30e**, this suggests that the materials have similar twist elastic constants. However further studies are needed to confirm this.

3.12 SUMMARY AND CONCLUSIONS

The 2-(4-cyanophenyl)-7-alkylfluorenes **30** are in many respects similar to the 4-alkyl-4"-cyano-*p*-terphenyls **6**. The melting points are virtually identical, and the 2-phenylfluorenes have slightly lower clearing points. The dielectric anisotropy and birefringence of 2-(4-cyanophenyl)-7-pentylfluorene **30e** and 4-pentyl-4"-cyano-*p*-terphenyl **6e** were measured, and were found to be almost identical. However, the crescent shaped 2-phenylfluorene **30e** had a much higher rotational viscosity than the terphenyl **6e**.

The properties shown by 2-(4-cyanophenyl)-7-pentylfluorene **30e** do not make it suitable for incorporation in conventional display devices. However, the luminescence properties of the molecule proved interesting, especially in the light of recent interest in fluorene containing molecules as light emitters for flat panel displays.

4. SYNTHESIS OF 2-ALKOXY-7-(4-CYANOPHENYL)FLUORENES

4.1 OVERVIEW

One problem with the synthetic route to 2-(4-cyanophenyl)-7-alkylfluorenes **30** (Section 2.1) is that the alkyl chain is introduced in the first step, the Friedel-Crafts acylation of fluorene. Introduction of the chain at a later stage is much more desirable, as it would greatly reduce the number of repetitive steps needed to synthesize a homologous series. One option for circumventing the problem would be the use of the related alkoxy derivatives, since in this case the alkyl chain can be introduced at a later stage in the synthesis, by alkylation of a hydroxy group.

Replacement of an alkyl group with alkoxy group has been shown to raise both the melting and clearing points.⁸ Often the clearing point is increased by a greater margin, giving a larger mesogenic range, *cf.* 2-pentanoyl-7-nonylfluorene **70** vs. 2-octoxy-7-pentanoylfluorene **71**.⁹⁵

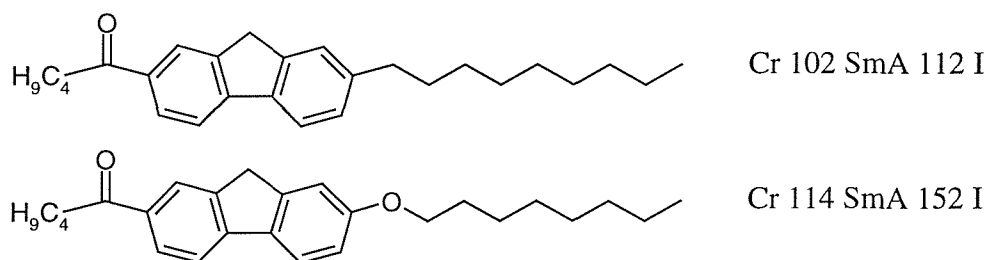
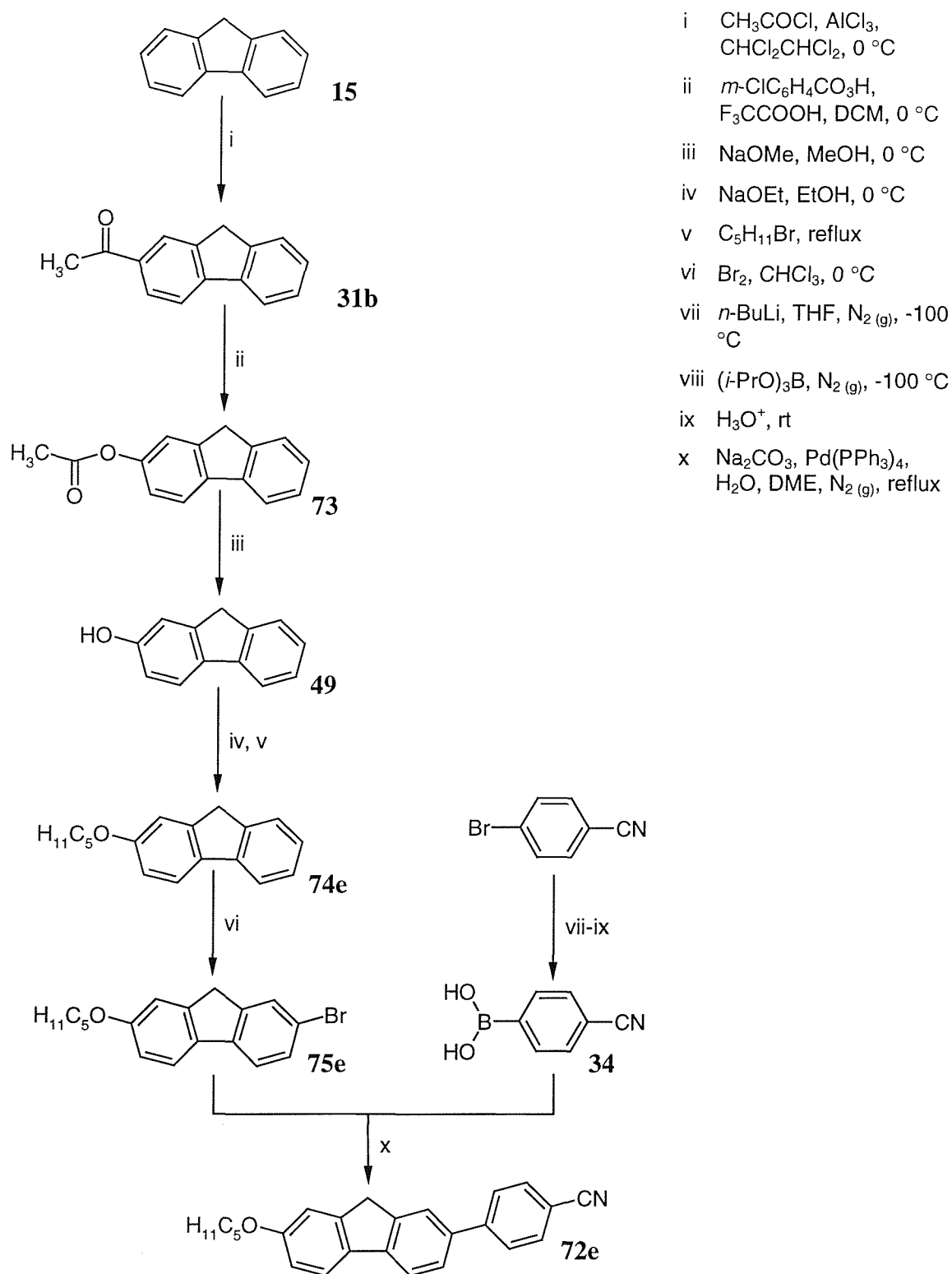


Fig. 73: (i) 2-Pentanoyl-7-nonylfluorene **70**; (ii) 2-octoxy-7-pentanoylfluorene **71**.

The octoxy and nonyl groups are sterically equivalent, as the oxygen atom simply replaces a methylene group in the chain. Comparisons should therefore be made between the alkyl compound and the isostructural alkoxy compound with one less methylene group in the carbon chain. The lone pairs on the oxygen atom can conjugate with the aromatic system, with the result that the first carbon-oxygen bond lies in the same plane as the benzene rings. This overlap increases the effective length of the core, which slightly increases the induced polarizability therefore giving a larger positive dielectric anisotropy (Section 1.8.2).

The physical properties of an alkoxy compound are usually very similar to those of the analogous alkyl compound. The 2-alkoxy-7-(4-cyanophenyl)fluorenes **72** were therefore expected to show the same phase behaviour as the 2-(4-cyanophenyl)-7-alkylfluorenes **30**. A seven step convergent route (Scheme 11) to 2-pentoxo-7-(4-cyanophenyl)fluorene **72e** was developed, with introduction of the alkyl chain occurring in the fourth step.



Scheme 11: Synthesis of 2-pentoxo-7-(4-cyanophenyl)fluorene **72e**.

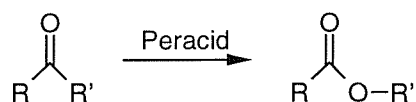
Treatment of 2-acetylfluorene **31b** with *m*-chloroperoxybenzoic acid effected a Baeyer-Villiger rearrangement to give 2-acetoxyfluorene **73** in 86% yield. The ester linkage was then cleaved using sodium methoxide to give 2-hydroxyfluorene **49** in 79% yield. These two steps, and the initial Friedel Crafts acetylation to give **31b**, were carried out on a large scale

to give multi-gram quantities of 2-hydroxyfluorene **49**.

In an modified Williamson ether synthesis,⁹⁶ treatment of 2-hydroxyfluorene **49** with sodium ethoxide followed by pentyl bromide gave 2-pentoxyfluorene **74e** in 61% yield. Bromination of 2-pentoxyfluorene **74e** was then accomplished by addition of a solution of bromine in chloroform. This step was problematic, and several recrystallizations were needed to isolate 2-bromo-7-pentoxyfluorene **75e** in 11% yield. The final step was a Suzuki coupling reaction similar to those described earlier (Section 2.8). 4-Cyanobenzoboronic acid **34** was made using the route developed in the synthesis of the 2-(4-cyanophenyl)-7-alkylfluorenes **30** (Section 2.7). Using impure 2-bromo-7-pentoxyfluorene **75e** it was possible to synthesize a small amount of impure 2-pentoxy-7-(4-cyanophenyl)fluorene **72e**. The route has seven synthetic steps, as opposed to five steps for the 2-(4-cyanophenyl)-7-alkylfluorenes **30**. However the first three steps are common to all the homologues, as introduction of the alkyl chain does not occur until the fourth step. The major drawback to this route was the unpredictability of the bromination step. An improved route was needed, and work was carried out to investigate a number of alternative synthetic strategies.

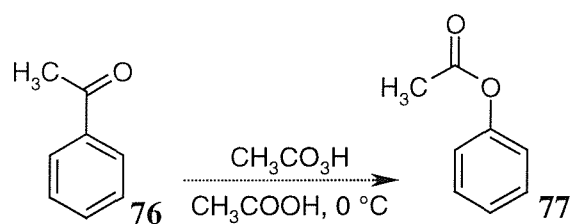
4.2 BAEYER-VILLIGER REARRANGEMENT

The Baeyer-Villiger rearrangement of a ketone to an ester was developed as a route to phenols.⁹⁷ The product formed from the reaction of an unsymmetrical substrate, *e.g.* a phenyl ketone, depends on the relative migratory aptitudes of the aryl and alkyl groups.

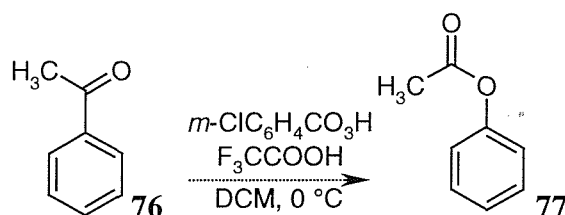


An aryl group is expected to migrate preferentially, though an early report suggested otherwise, citing a mixture of products.⁹⁸ No evidence of alkyl group migration was observed in this work.

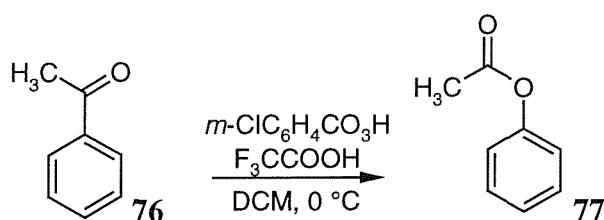
The commercially available compound, acetophenone **76** was used as a model for the reaction. The rearrangement was attempted using peracetic acid,⁹⁹ which was generated *in situ* from a mixture of sulphuric acid, aqueous hydrogen peroxide and acetic acid. The solution was assumed to be $\approx 10\%$ active.¹⁰⁰ Distillation was not attempted, as peracetic acid is reported as being prone to violent decomposition at elevated temperatures.¹⁰¹ Acetophenone was added to the solution, and the reaction mixture was stirred at room temperature. Following column chromatography only starting material was recovered.



m-Chloroperbenzoic acid is often used to effect Baeyer-Villiger rearrangements.¹⁰² mCPBA is a commercially available solid, which greatly simplifies the handling procedure. In a literature procedure,¹⁰³ a mixture of acetophenone, commercial *m*-chloroperbenzoic acid, trifluoroacetic acid and dry dichloromethane was stirred at room temperature.



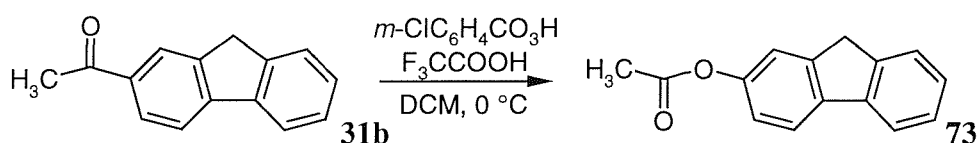
Complete conversion did not occur, and a (1:1) mixture of product and starting material was obtained. As the product and starting material have similar boiling points and polarities, separation by distillation or column chromatography was not attempted. The crude *m*-chloroperbenzoic acid contained *m*-chlorobenzoic acid and water. The peracid was purified by removal of water followed by recrystallization from warm dichloromethane. Material purified in this way contained *m*-chlorobenzoic acid, and was assumed to be $\approx 70\%$ active. The reaction was then repeated using the purified mCPBA.



Under these conditions the conversion of acetophenone to phenyl acetate **77** was achieved in 58% yield.

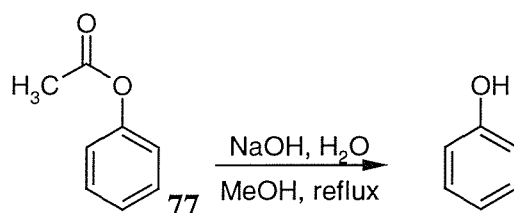
Having developed the chemistry successfully on the model compound acetophenone, the procedure was extended to the substrate of interest, 2-acetylfluorene **31b**. Fluorene was acetylated in a Friedel-Crafts procedure to give 2-acetylfluorene **31b** in 82% yield (Section 2.3). The Baeyer-Villiger rearrangement was effected by stirring a mixture of 2-acetylfluorene **31b** with purified *m*-chloroperbenzoic acid, trifluoroacetic acid and dry

dichloromethane. This gave 2-acetoxyfluorene **73** in 86% yield. An excess of mCPBA was needed to favour conversion to the ester product. When the reaction was repeated using only one equivalent of mCPBA complete conversion did not occur. The material produced contained *ca.* 25% unreacted 2-acetylfluorene **31b**. However it was possible to remove the unreacted 2-acetylfluorene **31b** along with other non polar contaminants following the ester cleavage step (Section 4.3).

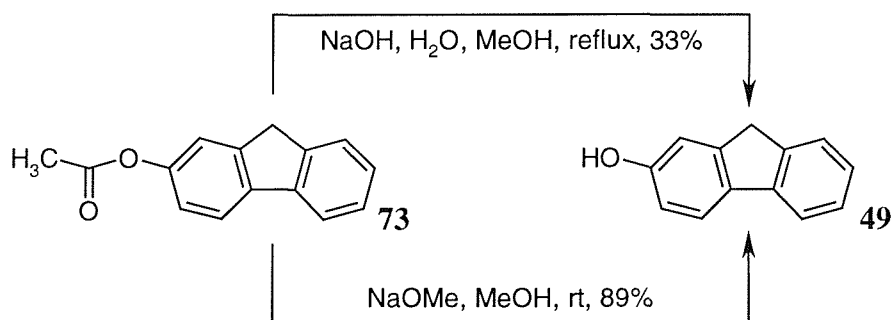


4.3 ESTER CLEAVAGE

Commercially available phenyl acetate **77** was used as a model for this step. A mixture of **77**, aqueous sodium hydroxide and methanol was heated at reflux. Workup gave impure phenol in *ca.* 83% yield.



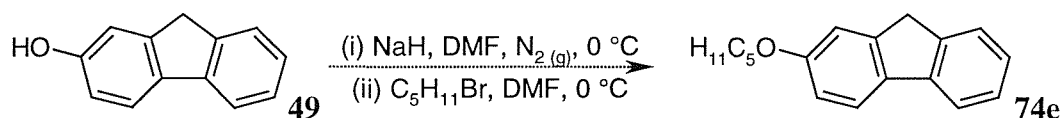
This procedure was extended to 2-acetoxyfluorene **73**. A mixture of **73**, aqueous sodium hydroxide and methanol was heated at reflux. After workup the crude product was dissolved in aqueous alkaline solution, and the non-polar contaminants were removed with organic washes. Following this procedure, 2-hydroxyfluorene **49** was isolated in 33% yield. In an improved procedure, a mixture of 2-acetoxyfluorene **73** and methanol was treated with a freshly prepared solution of sodium methoxide in methanol. The reaction was carried out at room temperature.



Following workup, clean 2-hydroxyfluorene **49** was isolated in an excellent yield of 89%. Using the three step route of acetylation, Baeyer-Villiger rearrangement and alkaline ester hydrolysis it was possible to prepare multigram quantities of 2-hydroxyfluorene **49**. The overall yield was 55% for the three steps from fluorene.

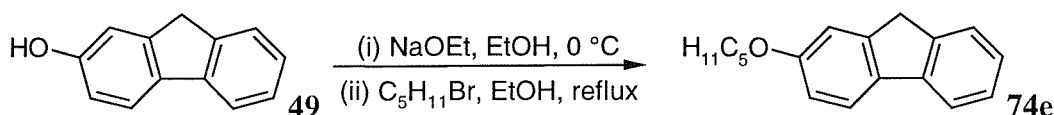
4.4 O-ALKYLATION

Alkylation of 2-hydroxyfluorene **49** was attempted using a modified literature procedure.¹⁰⁴ 2-Hydroxyfluorene **49** was deprotonated using sodium hydride in *N,N*-dimethylformamide. Pentyl bromide was then added, and the reaction mixture was stirred overnight at room temperature.



Workup gave a crude oil. A combination of column chromatography and recrystallization gave impure 2-pentoxyfluorene **74e** in *ca.* 9% yield. Deprotonation of the acidic methylene bridge was a competing process. With this reactive species present a number of unwanted products were formed. Lateral alkylation was an inconvenient side reaction, and explains the lengthy purification procedure necessary to obtain even a small amount of impure product. Milder conditions were needed to selectively deprotonate at oxygen and eliminate this problem.

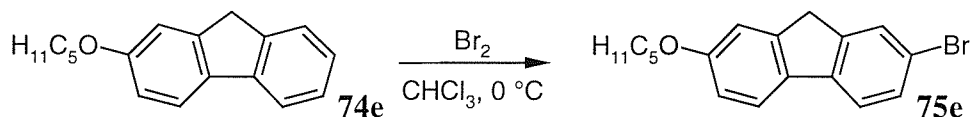
In an modified Williamson ether synthesis,¹⁰⁵ 2-hydroxyfluorene **49** was first deprotonated using a freshly prepared solution of sodium ethoxide in ethanol. Pentyl bromide was then added, and the reaction mixture was heated at reflux. After recrystallization, 2-pentoxyfluorene **74e** was isolated in 61% yield.



4.5 BROMINATION

Direct bromination of 2-pentoxyfluorene **74e** was problematic, as the alkoxy substituent activated the substituted ring towards bromination, giving a number of potential brominated products. There was also the possibility that the alkoxy group would be cleaved by hydrobromic acid formed in the reaction mixture.

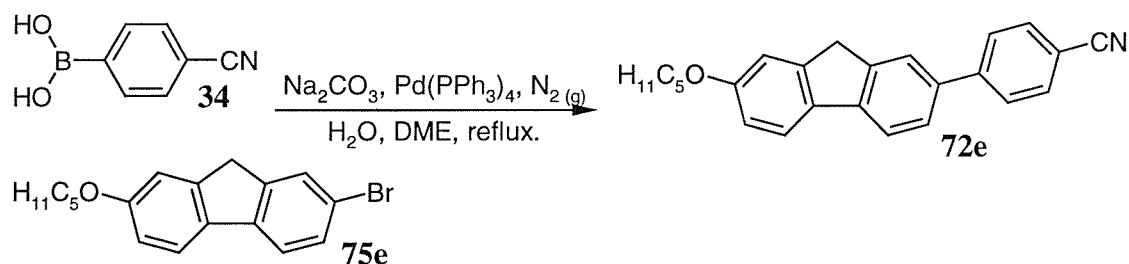
Nevertheless, direct bromination was attempted. A solution of bromine in chloroform was added to 2-pentoxyfluorene **74e**, and the reaction mixture was stirred at room temperature.



Several recrystallizations were needed to isolate the desired isomer 2-bromo-7-pentoxyfluorene **75e** in 11% yield. On a larger scale a mixture of brominated compounds was produced, and it was not possible to isolate **75e**.

4.6 SUZUKI COUPLING

The final step in the synthesis of 2-pentoxy-7-(4-cyanophenyl)fluorene **72e** was the Suzuki coupling of 2-bromo-7-pentoxyfluorene **75e** to 4-cyanobenzoboronic acid **34**. The boronic acid was prepared from benzonitrile in a one pot process as described earlier (Section 2.7). The coupling procedure was the same as that developed for the synthesis of 2-(4-cyanophenyl)-7-alkylfluorenes **30** (Section 2.8). A mixture of the aryl bromide **75e**, the boronic acid **34**, aqueous sodium carbonate and 1,2-dimethoxyethane was deoxygenated by a stream of nitrogen gas. Tetrakis(triphenyl)phosphinepalladium(0) catalyst was added, and the reaction mixture was heated at reflux.



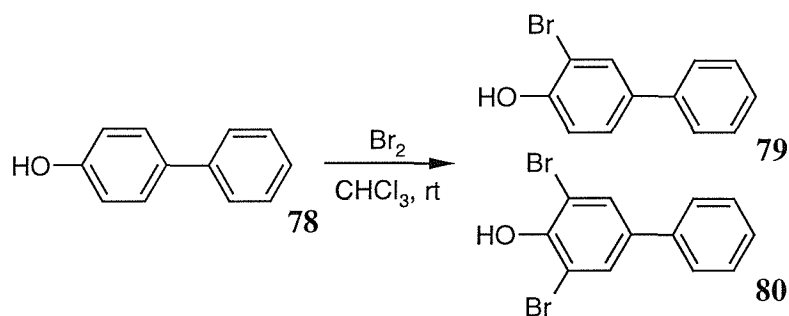
Following workup and two recrystallizations, impure 2-pentoxy-7-(4-cyanophenyl)fluorene **72e** was obtained in *ca.* 9% yield. The material produced was a white crystalline solid, but a mass spectrum indicated that it contained *ca.* 10% brominated 2-pentoxy-7-(4-cyanophenyl)fluorene. The position of the bromine atom could not be determined, but it must have originated from the presence of a dibrominated impurity in the aryl bromide **75e** used in the coupling reaction.

Limited analysis by polarizing optical microscopy indicated that the impure material exhibited a nematic phase. The transitions were sharp, and the impure material had a large mesogenic range (Cr 127 N 229 I). This compares well with the isostructural compound 2-

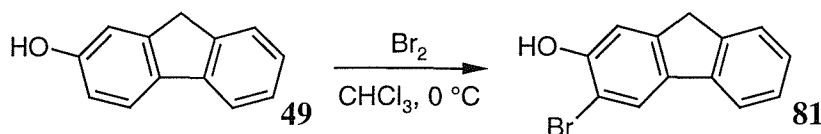
(4-cyanophenyl)-7-hexylfluorene **30f** (Cr 118 N 207 I, Section 3.4). This behaviour was as predicted, but clearly a source of clean product was required before any detailed studies could be undertaken.

4.7 BROMINATION OF 2-HYDROXYFLUORENE

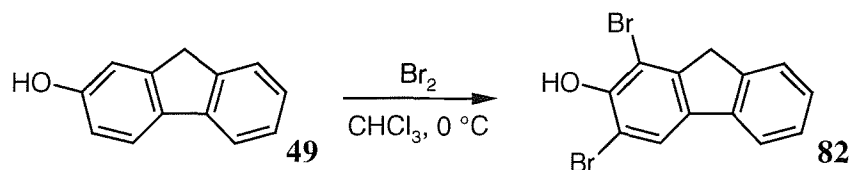
The hydroxy group is strongly activating and *ortho*, *para* directing.⁶⁶ Literature work¹⁰⁶ reported that direct bromination of 4-hydroxybiphenyl **78** gave the *ortho* brominated products 3-bromo-4-hydroxybiphenyl **79** and 3,5-dibromo-4-hydroxybiphenyl **80**. The relative proportions of **79** and **80** could be controlled by varying the amount of bromine added.



2-Hydroxyfluorene **49** was brominated by slow addition of a solution of bromine in chloroform. Bromination was found to occur in the 3- position. There are two *ortho* positions, and the sterically less hindered 3- position was clearly favoured over the 1- position. The reaction proceeded more rapidly than the bromination of a 2-alkylfluorene **32**, and this was attributed to the activating effect of the hydroxy group.



After recrystallization, 2-hydroxy-3-bromofluorene **81** was isolated in 32% yield. The presence of a small amount of dibrominated material (<5%) was detected by GCMS. This procedure was carried out on a larger scale. Following column chromatography and recrystallization, 2-hydroxy-3-bromofluorene **81** was isolated in 42% yield. In addition, 1,3-dibromo-2-hydroxyfluorene **82** was isolated in 6% yield.

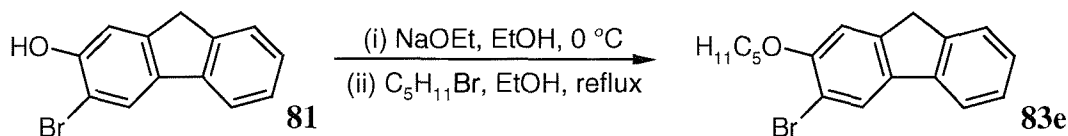


The position of the bromine atoms in 1,3-dibromo-2-hydroxyfluorene **82** was proved by a single crystal X-ray structure (R-factor 4.2%) (Section 9.2).



Fig. 74: X-ray structure of 1,3-dibromo-2-hydroxyfluorene **82**.

However it was not possible to obtain good quality crystals of the monobrominated product 2-hydroxy-3-bromofluorene **81**. A sample of the material was converted to the alkoxy derivative **83** using the procedure developed for *O*-alkylation of 2-hydroxyfluorene **49** (Section 4.4). 2-Hydroxy-3-bromofluorene **81** was deprotonated using a freshly prepared solution of sodium ethoxide in ethanol. Pentyl bromide was added, and the reaction mixture was heated at reflux.



After recrystallization, 2-pentoxo-3-bromofluorene **83e** was isolated in 60% yield. Good quality crystals were obtained, and a single crystal X-ray structure (R-factor 6.9%) proved the position of the bromine atom in 2-pentoxo-3-bromofluorene **83e** (Section 9.3).

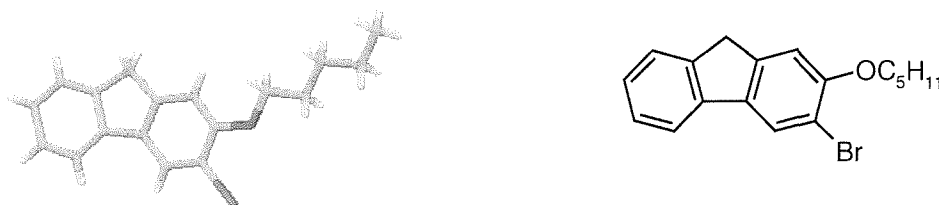


Fig. 75: X-ray structure of 2-pentoxo-3-bromofluorene **83e**.

In an analogous *O*-alkylation reaction, 2-hydroxy-3-bromofluorene **81** was converted to 2-heptoxo-3-bromofluorene **83g** in 80% yield. This improvement in yield was made possible by using an excess of sodium ethoxide and heptyl bromide in the reaction.

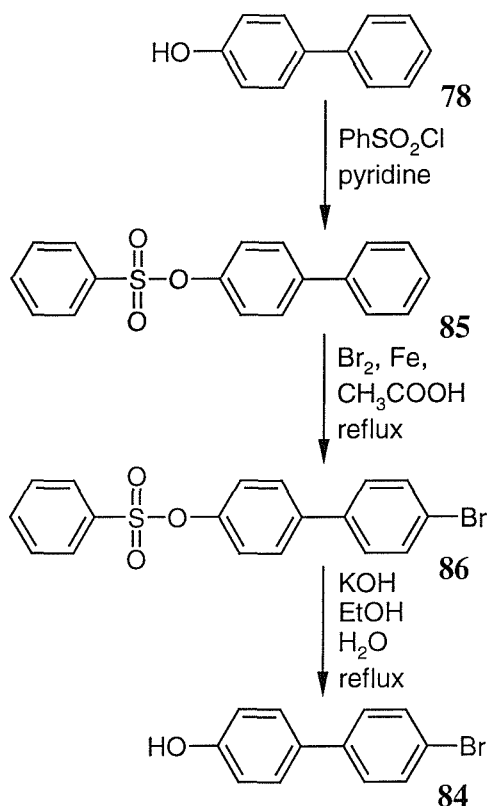
4.8 SULPHONATE ESTERS

Direct bromination of 4-hydroxybiphenyl **78** led to the formation of the *ortho* brominated products 3-bromo-4-hydroxybiphenyl **79** and 3,5-dibromo-4-hydroxybiphenyl **80**.

Similarly, direct bromination of 2-hydroxyfluorene **49** gave the *ortho* brominated products 2-hydroxy-3-bromofluorene **81** and 1,3-dibromo-2-hydroxyfluorene **82** (Section 4.7).

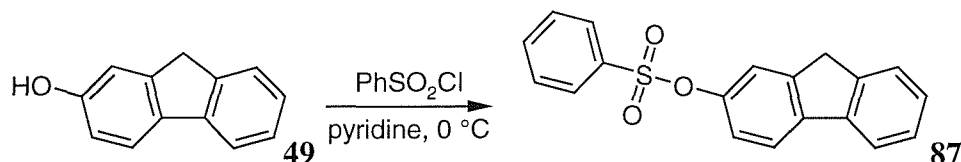
Therefore it was not possible to synthesize the desired 4,4'-biphenyl or 2,7-fluorene derivatives by direct bromination of the hydroxy compound.

The literature solution to this problem involved a three step route to 4-bromo-4'-hydroxybiphenyl **84** (Scheme 12).¹⁰⁷ 4-Hydroxybiphenyl **78** was converted to biphenyl-4-phenylsulphonate **85** by reaction with benzenesulphonyl chloride in pyridine. The product was isolated in 66% yield. The sulphonate group is electron withdrawing, and therefore deactivates the aromatic system, thus favouring *para* bromination in the unsubstituted ring at the other end of the molecule. Bromination was accomplished by heating a mixture of the sulphonate ester **85**, bromine, powdered iron and acetic acid at reflux. 4-Bromobiphenyl-4'-phenylsulphonate **86** was isolated in 97% yield. Heating **86** at reflux with a mixture of potassium hydroxide, ethanol and water cleaved the sulphonate group to give 4-bromo-4'-hydroxybiphenyl **84** in 55% yield.

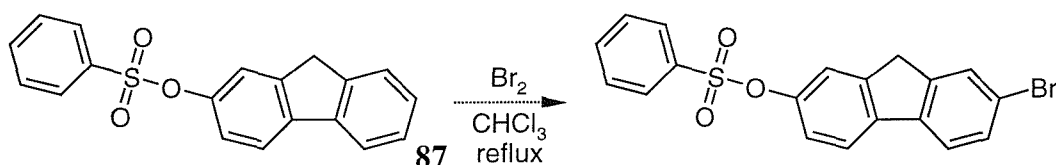


Scheme 12: Synthesis of 4-bromo-4'-hydroxybiphenyl **84**.

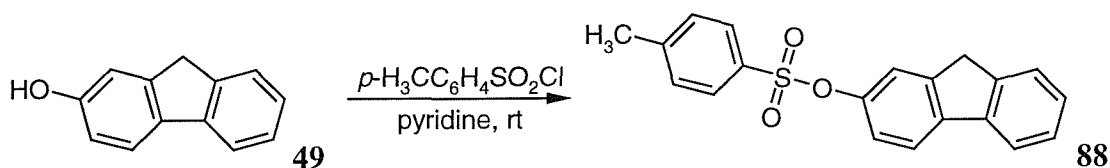
This literature procedure was extended to 2-hydroxyfluorene **49**. A mixture **49** and pyridine was treated with benzenesulphonyl chloride. Following recrystallization, fluorene-2-phenylsulphonate **87** was isolated in 47% yield.



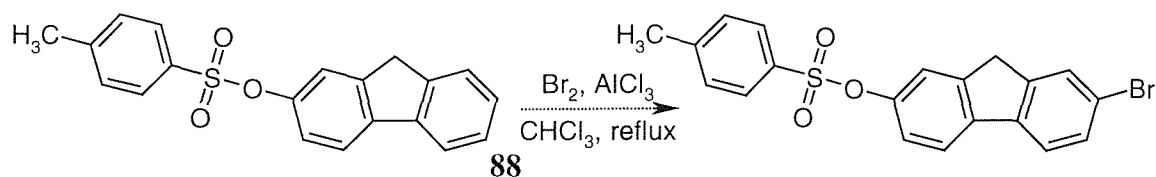
Bromination of fluorene-2-phenylsulphonate **87** was then attempted. A mixture of the sulphonate ester **87**, bromine and chloroform was heated at reflux. Following workup, unreacted fluorene-2-phenylsulphonate **87** starting material was recovered. No brominated product was detected.



Toluenesulphonic acid derivatives are often easier to prepare, as toluenesulphonyl chloride is a solid and can therefore be purified by recrystallization, whereas benzenesulphonyl chloride is a liquid.¹⁰⁸ In an attempt to improve the yield of sulphonate ester, preparation of the tosylate derivative **88** was attempted. A mixture of 2-hydroxyfluorene **49** and pyridine was treated with toluenesulphonyl chloride. Following recrystallization, fluorene-2-tolylsulphonate **88** was isolated in 42% yield. This low yield was somewhat disappointing.



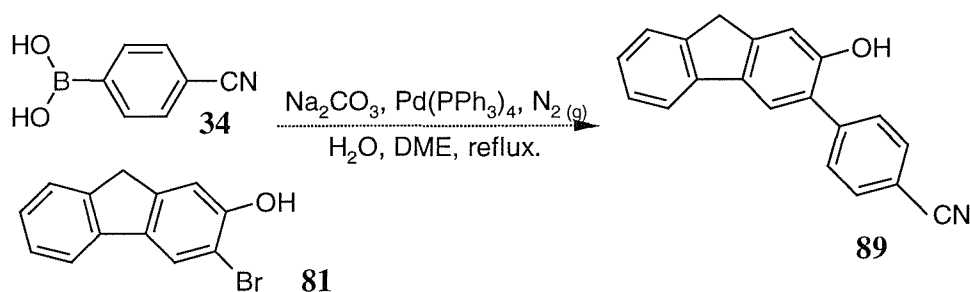
Bromination of fluorene-2-tolylsulphonate **88** was then attempted. A Lewis acid catalyst was added to promote electrophilic bromination. A mixture of the sulphonate ester **88**, bromine, aluminium chloride and chloroform was heated at reflux. Following workup, unreacted fluorene-2-tolylsulphonate **88** starting material was recovered. No brominated product was detected.



It is clear from this work that more rigorous conditions are needed to effect bromination. No further work was carried out in this area.

4.9 DIRECT COUPLING APPROACH

In order to investigate the scope of the Suzuki procedure, the direct coupling of 2-hydroxy-3-bromofluorene **81** to 4-cyanobenzoboronic acid **34** was attempted under the conditions used previously (Section 2.8). A mixture of the aryl bromide **81**, the boronic acid **34**, aqueous sodium carbonate and 1,2-dimethoxyethane was deoxygenated with a stream of nitrogen gas. Tetrakis(triphenylphosphine)palladium(0) catalyst was added, and the reaction mixture was heated at reflux.

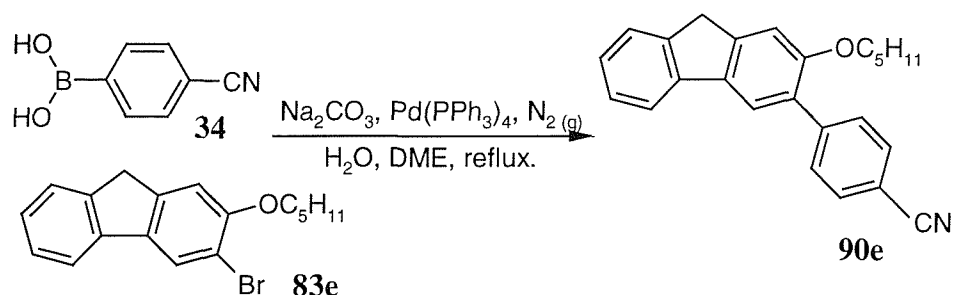


A multi-component mixture was obtained after workup. Following column chromatography, ^1H and ^{13}C NMR spectra of the least polar component appeared to be consistent with the formation of the coupled product, 2-hydroxy-3-(4-cyanophenyl)fluorene **89**, in 9% yield. An IR spectrum had a signal indicative of a hydroxy group at 3519 cm^{-1} and a characteristic cyanide stretch at 2229 cm^{-1} . However GCMS analysis clearly indicated a mixture of unreacted 2-hydroxy-3-bromofluorene **81** and a second unknown compound (m/z 179) at shorter retention time. No further purification was attempted.

4.10 WEDGE SHAPED MESOGENS

2-Pentoxy-3-(4-cyanophenyl)fluorene **90e** was prepared by coupling 2-pentoxy-3-bromofluorene **83e** to 4-cyanobenzoboronic acid **34** under Suzuki conditions (Section 2.8). A mixture of the aryl bromide **83e**, the boronic acid **34**, aqueous sodium carbonate, and 1,2-dimethoxyethane was deoxygenated using a stream of nitrogen gas.

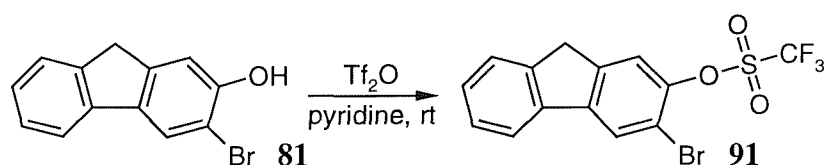
Tetrakis(triphenyl)phosphine palladium(0) catalyst was added, and the reaction mixture was heated at reflux.



Following purification, impure 2-pentoxymethyl-7-(4-cyanophenyl)fluorene **90e** was obtained in *ca.* 45% yield. A small amount (<5%) of unreacted aryl bromide **83e** was detected by GCMS. The reaction was repeated on a larger scale, and 2-pentoxymethyl-7-(4-cyanophenyl)fluorene **90e** was isolated in a slightly improved yield of 51%.

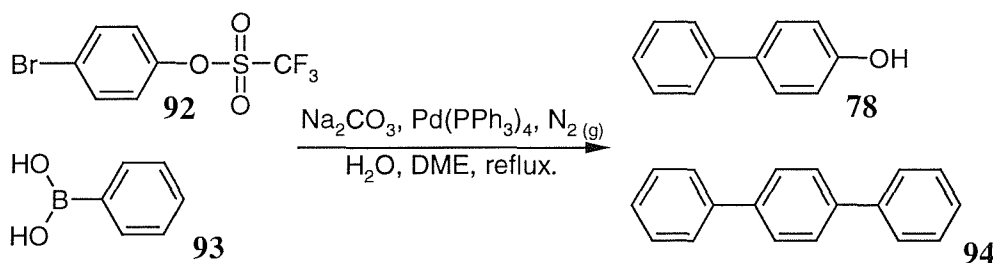
When studied using polarized optical microscopy, **90e** was found to melt at 125 °C. However a monotropic crystal phase could be accessed by careful supercooling of the isotropic fluid to *ca.* 75 °C, then heating the sample slightly. On further heating there was a transition to the isotropic fluid at 105 °C. The nonoxy homologue 2-nonoxymethyl-7-(4-cyanophenyl)fluorene **90i** was prepared in 10% yield by the same route. This procedure was carried out by a co-worker.¹⁰⁹ **90i** was found to show similar monotropic phase behaviour to **90e**. On heating, the sample melted at 90 °C to give an isotropic liquid. On supercooling, a crystal phase formed at *ca.* 57 °C. The longer alkoxy chain stabilized the phase, and it was found to coexist with the crystalline solid across a wide temperature range from ambient to 90 °C.

In an attempt to make some progress in the exploitation of the *ortho* bromination products, the Suzuki coupling of a triflate and a boronic acid was explored.¹¹⁰ Conversion of 2-hydroxy-3-bromofluorene **81** to 3-bromofluorene-2-trifluoromethylsulphonate **91** was carried out.¹¹¹ A mixture of the hydroxy compound **81**, trifluoromethanesulphonic anhydride and dry pyridine was stirred at room temperature. Following workup, 3-bromofluorene-2-trifluoromethylsulphonate **91** was obtained as a crude oil in *ca.* 96% yield. The oil solidified on standing.



A direct aryl-aryl bond may be formed between an aryl triflate and an electron deficient species *via* a transition metal-catalyzed coupling reaction (Section 2.6). There are some examples where an aryl triflate is coupled to an aryl stannane (Stille coupling).¹¹² In several cases the aryl triflate is cited as being more reactive than the analogous aryl bromide.¹¹³ Lithium chloride may be added to the reaction mixture to prevent decomposition of the catalyst.¹¹²

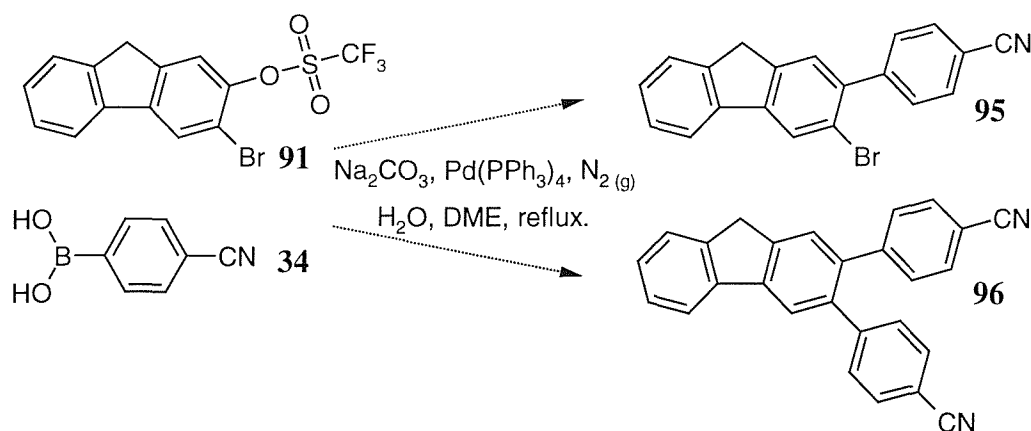
In a literature report,¹¹³ a mixture of 4-bromophenyltrifluoromethylsulphonate **92**, phenylboronic acid **93**, aqueous sodium carbonate solution, 1,2-dimethoxyethane and tetrakis(triphenylphosphine)palladium(0) was heated to give a mixture of 4-hydroxybiphenyl **78** (22%) and *p*-terphenyl **94** (37%).



This result suggested that it was not straightforward to selectively couple to a triflate moiety. In the present work, two reactions were carried out using 3-bromofluorene-2-trifluoromethylsulphonate **91**, and lithium chloride was added in an attempt to promote coupling to the triflate. The purpose of these investigations was to establish the selectivity of the Suzuki coupling towards aryl bromides and aryl triflates, and thereby potentially provide access to a new class of compounds.

In both reactions a mixture of 3-bromofluorene-2-trifluoromethylsulphonate **91**, 4-cyanobenzoboronic acid **34**, lithium chloride, aqueous sodium carbonate solution and 1,2-dimethoxyethane was deoxygenated using a stream of nitrogen gas.

Tetrakis(triphenylphosphine)palladium(0) catalyst was added, and the reaction mixture was heated at reflux. The first reaction used one equivalent of boronic acid, which was hoped would give the monocoupled product 2-(4-cyanophenyl)-3-bromofluorene **95**, and the second used an excess in an attempt to form 2,3-bis(4-cyanophenyl)fluorene **96**.



In the event the product of both reactions was 3-(4-cyanophenyl)fluorene-2-trifluoromethylsulphonate **97** in *ca.* 18%, and no coupling of the triflate moiety was observed. This result suggests that it is not easy to couple aryl triflates to boronic acids under standard Suzuki conditions.

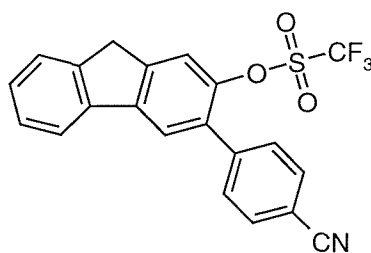
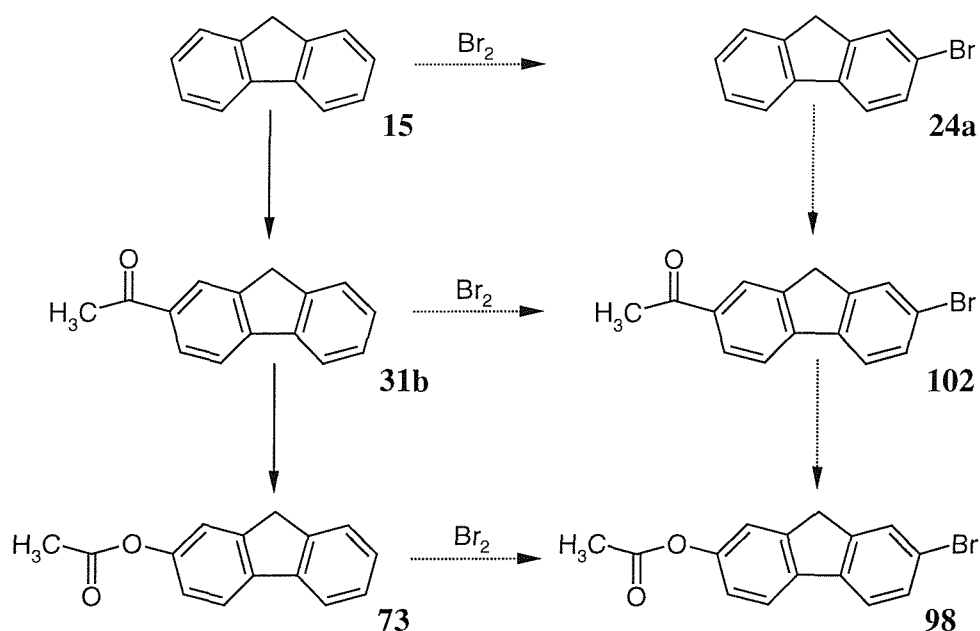


Fig. 76: 3-(4-Cyanophenyl)fluorene-2-trifluoromethylsulphonate **97**.

4.11 OTHER STRATEGIES

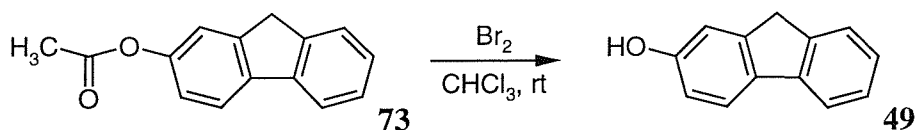
The work described above had not succeeded in developing a reliable route to 2-bromo-7-alkoxyfluorenes **75**. Direct bromination of a 2-alkoxyfluorene **74** was problematic, giving a mixture of brominated products. Bromination of 2-hydroxyfluorene **49** gave the unwanted isomer 2-hydroxy-3-bromofluorene **81**. The alternative strategy of conversion to a sulphonate ester followed by bromination was unsuccessful, as it was not possible to brominate either the phenylsulphonate **87** or the tosylate **88** under the conditions used. To develop an efficient synthetic route to 2-alkoxy-7-(4-cyanophenyl)fluorenes **72**, bromination was explored at various stages in the existing synthetic route (Scheme 13). A literature precedent¹¹⁴ for the bromination of 2-acetoxyfluorene **73** looked promising, and other possibilities were the bromination of 2-acetylfluorene **31b** or starting the synthesis with 2-bromofluorene **24a**.



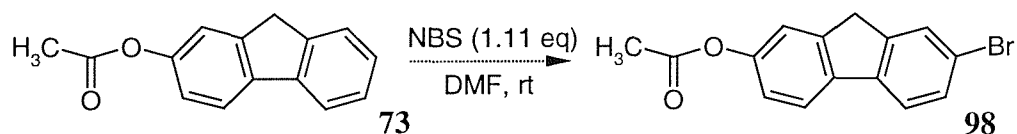
Scheme 13: Alternative routes to 2-alkoxy-7-(4-cyanophenyl)fluorenes **72**.

4.12 BROMINATION OF 2-ACETOXYFLUORENE

A solution of 2-acetoxyfluorene **73** (0.60 g, 2.7 mmol) in chloroform was treated with bromine. The reaction gave a mixture of products, separation of which was attempted by column chromatography. A small amount (*ca.* 6%) of impure 2-hydroxyfluorene **49** was obtained, indicating that cleavage of the ester had occurred. No brominated products were detected by GCMS.

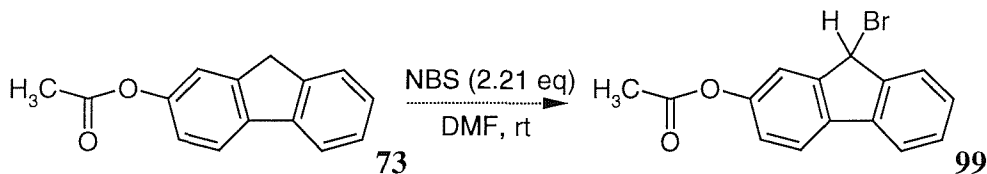


Bromination of 2-acetoxyfluorene **73** was then attempted using *N*-bromosuccinimide.¹¹⁴ A mixture of **73**, *N*-bromosuccinimide and dry *N,N*-dimethylformamide was stirred at room temperature. Following workup, a (1:1) mixture of 2-acetoxyfluorene **73** and 2-bromo-7-acetoxyfluorene **98** was obtained.



This reaction was repeated using a large excess of NBS, in an attempt to favour greater conversion of 2-acetoxyfluorene **73** to the brominated product. A mixture of 9-brominated

material and non-brominated 2-acetoxyfluorene **73** was obtained. A ^1H NMR spectra had a signal at δ_{H} 5.91, consistent with the formation of 2-acetoxy-9-bromofluorene **99**.



These results are summarized in Table 17.

Table 17: Bromination of acetoxyfluorene **73**.

Reagents	Conditions	Product	Yield
Br_2 , CHCl_3	0.98 eq Br_2 , 0°C^*	2-Hydroxyfluorene 49	ca. 6%
NBS, DMF	1.11 eq Br, rt^*	2-Bromo-7-acetoxyfluorene 98	- [†]
NBS, DMF	2.21 eq Br, rt^\ddagger	2-Acetoxy-9-bromofluorene 99	- [§]

* chromatographed (silica gel, chloroform) then recrystallized from hot chloroform-60-80 petroleum ether

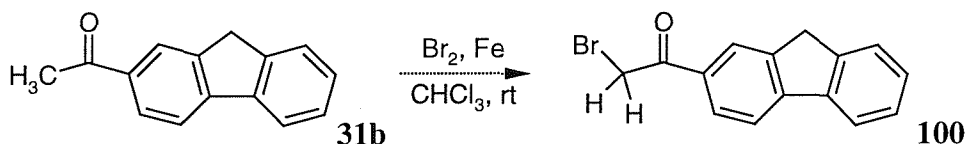
[†] (1:1) mixture of acetoxyfluorene **73** and 2-bromo-7-acetoxyfluorene **98**

[‡] recrystallized from hot chloroform-60-80 petroleum ether (charcoal)

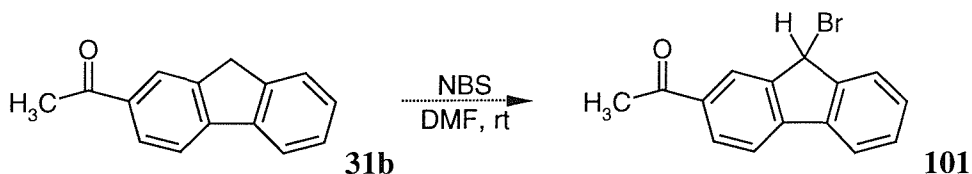
[§] mixture of acetoxyfluorene **73** and 2-acetoxy-9-bromofluorene **99**

4.13 BROMINATION OF 2-ACETYLFLUORENE

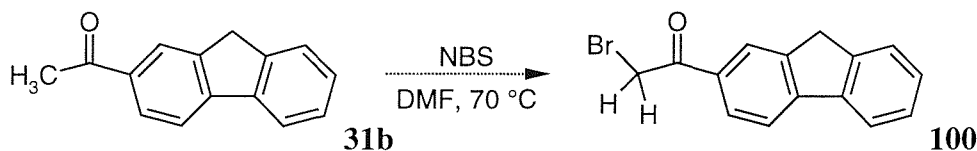
Bromination of 2-acetylfluorene **31b** using a solution of bromine in chloroform with added iron filings resulted in the formation of α -bromo-2-acetylfluorene **100** in 91% yield. This procedure was carried out by a co-worker.¹¹⁵



A mixture of 2-acetylfluorene **31b**, *N*-bromosuccinimide and dry *N,N*-dimethylformamide was stirred at room temperature. In this case a mixture of unreacted 2-acetylfluorene **31b** and 2-acetyl-9-bromofluorene **101** was obtained. A ^1H NMR spectra had a signal at δ_{H} 6.01, consistent with the formation of 2-acetyl-9-bromofluorene **101**.



This procedure was repeated, but the reaction mixture was stirred at 70 °C. The unexpected product α -bromo-2-acetylfluorene **100** was isolated in 9% yield.



These results are summarized in Table 18.

Table 18: Bromination of 2-acetylfluorene **31b**.

Reagents	Conditions	Product	Yield
Br ₂ , Fe, CHCl ₃	1.02 eq Br ₂ , rt*	α -Bromo-2-acetylfluorene 100	91%
NBS, DMF	1.13 eq Br, rt [†]	2-Acetyl-9-bromofluorene 101	- [‡]
NBS, DMF	1.57 eq Br, 70 °C [§]	α -Bromo-2-acetylfluorene 100	9%

* recrystallized from hot chloroform-60-80 petroleum ether

[†] recrystallized from hot chloroform-60-80 petroleum ether (charcoal)

[‡] (1:1) mixture of 2-acetylfluorene **31b** and 2-acetyl-9-bromofluorene **101**

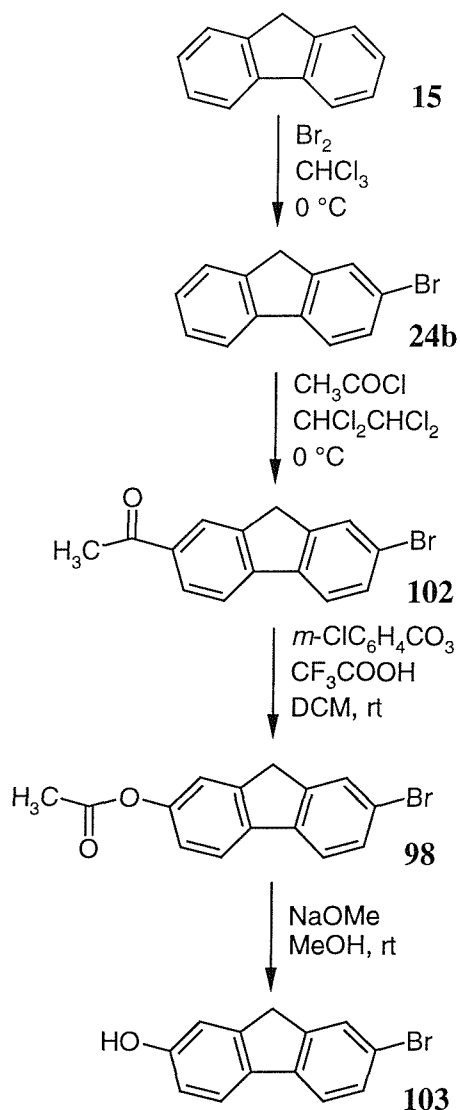
[§] chromatographed (silica gel, chloroform) then recrystallized from hot chloroform-60-80 petroleum ether

4.14 BROMINATION OF FLUORENE

An alternative approach was to start the synthesis using 2-bromofluorene **24a** (Scheme 14). The problem with this approach was that the initial bromination step did not proceed to completion, and a mixture of 2-bromofluorene **24a** and non-brominated fluorene was obtained (Section 2.5). The bromination of fluorene, and the subsequent Friedel-Crafts acetylation and Baeyer-Villiger rearrangement was carried out by a co-worker.¹¹⁵

Direct bromination of fluorene was achieved using a solution of bromine in chloroform, and impure 2-bromofluorene **24a** was obtained in 52% yield (Section 2.5). This material contained *ca.* 10% non-brominated fluorene. A subsequent Friedel-Crafts acetylation (Section 2.3) on the impure material gave 2-bromo-7-acetylfluorene **102** in 19% yield, and the Baeyer-Villiger rearrangement (Section 4.2) of **102** gave 2-bromo-7-acetoxyfluorene **98** in 61% yield. These three steps were carried out by a co-worker.¹¹⁵

A mixture of 2-bromo-7-acetoxyfluorene **98** and dry methanol was treated with freshly prepared sodium methoxide. The reaction mixture was stirred at room temperature. Following workup slightly impure 2-bromo-7-hydroxyfluorene **103** was obtained in *ca.* 91% yield.

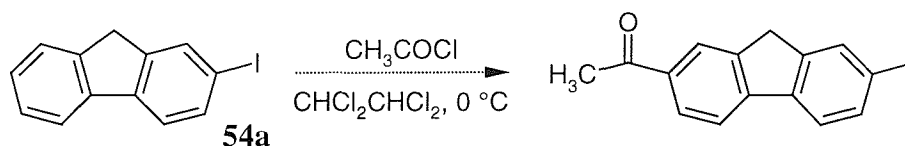


Scheme 14: Synthesis of 2-bromo-7-hydroxyfluorene **103**.

This provides a potential reliable route to 2-alkoxy-7-(4-cyanophenyl)fluorenes **72**, although some optimization of the reaction conditions is needed. No further work was carried out on this synthesis.

This sequence was attempted on the analogous iodine compounds. Impure 2-iodofluorene **54a** was prepared by iodination of fluorene. A mixture of iodine, iodic acid, sulphuric acid, water and carbon tetrachloride was heated at reflux. Following workup, impure 2-iodofluorene **54a** was obtained in *ca.* 69% yield. The 2-iodofluorene **54a** obtained contained *ca.* 10% non-iodinated fluorene. This procedure was carried out by a co-worker.¹¹⁵

2-Iodofluorene **54a** was acetylated using the Friedel-Crafts procedure (Section 2.3) to give a mixture of acetylated products. These products co-eluted and could not be separated by recrystallization.



4.15 SUMMARY AND CONCLUSIONS

The 2-alkoxy-7-(4-cyanophenyl)fluorenes **72** were expected to show similar properties to the 2-(4-cyanophenyl)-7-alkylfluorenes **30**. The synthesis of 2-pentoxy-7-(4-cyanophenyl)fluorene **72e** was attempted *via* a seven step route. Acetylation of fluorene on a large scale gave 2-acetylfluorene **31b** in up to 82% yield (Section 2.3). This was then treated with *m*-chloroperbenzoic acid in a Baeyer-Villiger rearrangement to give 2-acetoxyfluorene **73** in up to 86% yield. The ester linkage was then cleaved using sodium methoxide to give 2-hydroxyfluorene **49** in 79% yield. In this way it was possible to isolate multigram quantities of the valuable intermediate 2-hydroxyfluorene **49**.

The pentyl chain was introduced *via* an adapted Williamson ether synthesis to give 2-pentoxyfluorene **74e** in 61% yield. **74e** was brominated using a solution of bromine in chloroform. This step was problematic, and several recrystallizations were needed to isolate 2-bromo-7-pentoxyfluorene **75e** in 11% yield. The final step was the Suzuki coupling of the aryl bromide to 4-cyanobenzoboronic acid **34** (Section 2.7). By this method it was possible to synthesize impure 2-pentoxy-7-(4-cyanophenyl)fluorene **72e** in *ca.* 9% yield.

Preliminary studies on the impure material indicated that it exhibited a nematic phase across a large range.

This route introduced the alkyl chain in the fourth synthetic step, but was unsatisfactory because of the inefficient bromination step. Bromination was explored at several earlier points in the synthetic scheme. Of these alternative schemes, introduction of bromine in the first step showed promise, although the reaction conditions need to be optimized in order to ensure the success of this approach.

5. LATERAL SUBSTITUTION

5.1 OVERVIEW

The properties of a rod-shaped molecule may be subtly altered by the addition of a substituent perpendicular to the molecular axis.¹¹⁶ Addition of a small polar atom can create a dipole orthogonal to the major axis of the molecule, fluorine being an ideal substituent. Replacement of a hydrogen atom with fluorine has a small effect on the molecular architecture, as the steric bulk is only slightly increased.¹¹⁷ However the loss of symmetry operations and presence of a new dipole moment have consequences that go far beyond the modest increase in molecular width. Altering a mesogen by lateral substitution can change the phase behaviour and lead to enhanced physical properties, *e.g.* a lower viscosity.¹¹⁷ The symmetric mesogen 4,4''-dipentyl-*p*-terphenyl **104** has a high temperature smectic A phase across a relatively narrow range.¹¹⁸ Modification of the structure to give the laterally fluorinated terphenyl 4-pentyl-1',2'-difluoro-4''-pentyl-*p*-terphenyl **105** results in a much larger mesogenic range at a considerably lower temperature.¹¹⁹

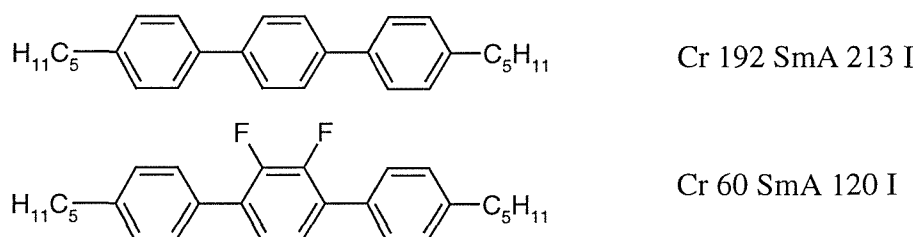


Fig. 77: (i) 4,4''-Dipentyl-*p*-terphenyl **104**; (ii) 4-pentyl-1',2'-difluoro-4''-pentyl-*p*-terphenyl **105**.

Mesogens such as 4-pentyl-1',2'-difluoro-4''-pentyl-*p*-terphenyl **105** are assembled from the appropriate 1,4-disubstituted benzene “building blocks” *via* a series of transition metal coupling reactions.¹²⁰ They are used in chiral smectic C devices, where the dipole created by the polar fluorine atom allows the director alignment to be changed.¹⁵

Lateral substitution discourages the formation of ordered smectic phases by disrupting the packing arrangement, nematics being therefore favoured. Once again the small fluorine atom is an ideal substituent, as it only slightly alters the structure of the molecule.

The fluorene core has an attractive structural feature in the methylene bridge, which provides an excellent site for lateral substitution. Indeed 9-substituted fluorenes are a commonly occurring class of compounds, for example as a component of Fmoc protecting groups, *e.g.* *N*-(9-fluorenylmethoxycarbonyl)glycine **106**.

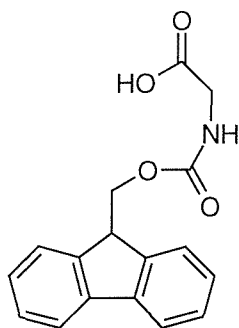


Fig. 78: *N*-(9-Fluorenylmethoxycarbonyl)glycine **106**.

The C9 bridge is relatively acidic, as it is a benzylic position stabilized by two benzene rings. Fluorene is considerably more acidic than diphenylmethane, as its conjugate base the fluorenyl anion **107** is a 14 π electron aromatic system, the negative charge being delocalized over all three rings.

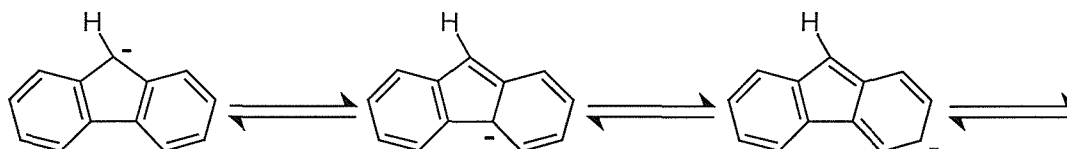


Fig. 79: Fluorenyl anion **107**.

Indeed fluorenyllithium **108** was one of the first known organolithium compounds, being prepared in 1928 by the addition of ethyllithium to a solution of fluorene.¹²¹ Compounds such as η^5 -cyclopentadienyl- η^6 -fluorenyliron **109**, a metallocene similar to ferrocene, have been prepared,¹²² reflecting the relative stability of the fluorenyl anion **107**.

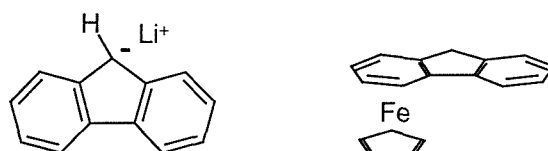


Fig. 80: (i) Fluorenyllithium **107**; (ii) η^5 -cyclopentadienyl- η^6 -fluorenyliron **109**.

5.2 STRATEGIES FOR LATERAL SUBSTITUTION

5.2.1 Conversion to fluorenone

Fluorene is readily oxidized to fluorenone **69**.¹²³ The presence of a carbonyl moiety on the methylene bridge creates a dipole moment in the plane of the aromatic rings and orthogonal to the long axis of the molecule.

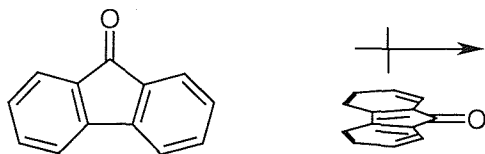


Fig. 81: (i) Fluorenone **69**; (ii) orthogonal dipole moment.

The presence of this dipole is detrimental to mesophase formation, and 2,7-disubstituted fluorenones tend to form monotropic liquid crystal phases.¹²⁴ Increasing the molecular width is detrimental to mesophase formation, as it decreases the length-to-breadth ratio, making the molecule less rod-like. A database search³¹ has yielded nine simple fluorenone compounds, only two of which, 2-octoxy-7-dodecanoylfluorenone **110** and 2-dodecanoyl-7-pentanoylfluorenone **111**, exhibit an enantiotropic phase.

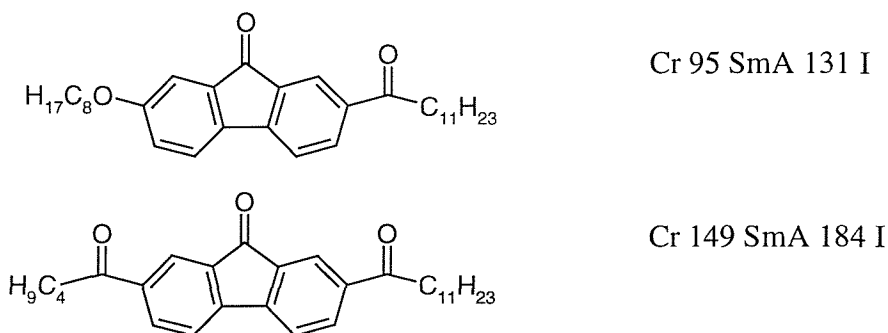
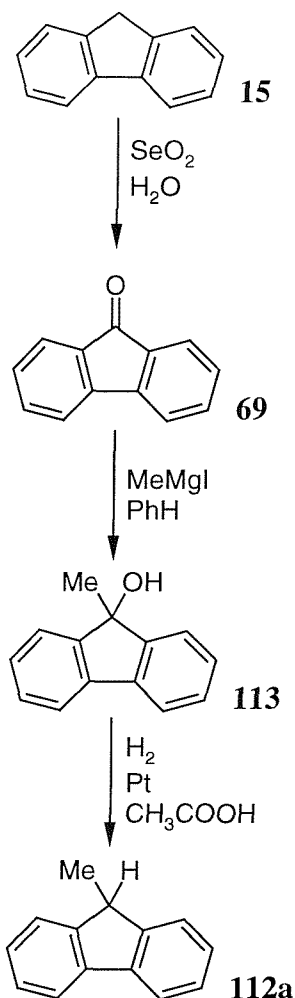


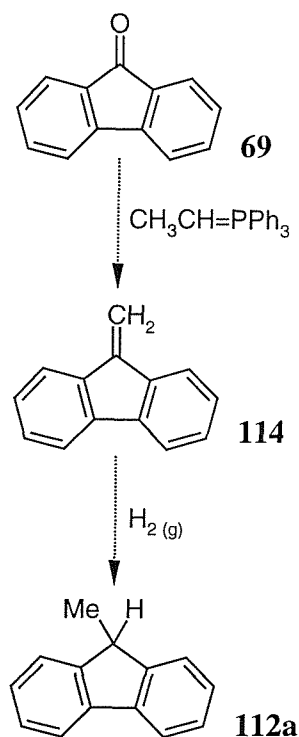
Fig. 82: (i) 2-Octoxy-7-dodecanoylfluorenone **110**; (ii) 2-pentanoyl-7-dodecanoylfluorenone **111**.

5.2.2 Routes to 9-alkylfluorenes

Many synthetic transformations can be carried out on fluorenone, providing potential routes to a range of 9-substituted derivatives. For example, addition of a Grignard reagent gives a tertiary alcohol, which is prone to dehydration, but can be reduced to a 9-alkylfluorene **112**. In one literature procedure¹²⁵ (Scheme 15) fluorene was oxidized to fluorenone **69** in 69% yield by strong heating with selenium dioxide and water in a sealed tube. Addition of methylmagnesium iodide gave 9-hydroxy-9-methylfluorene **113** in 85% yield, which was subsequently reduced to 9-methylfluorene **112a** by catalytic hydrogenation in 76% yield. A possible alternative procedure is the Wittig methylenation or alkenylation of fluorenone **69** to give a dibenzofulvalene **114** (Scheme 16). Catalytic hydrogenation of **114** would then give the 9-alkylfluorene **112**. No references to the use of this method on fluorenone were found.



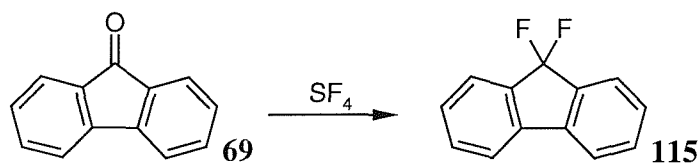
Scheme 15: Literature route to 9-methylfluorene **112a** – Grignard.



Scheme 16: Postulated route to 9-methylfluorene **112a** – Wittig.

5.2.3 Routes to 9,9-difluorofluorene

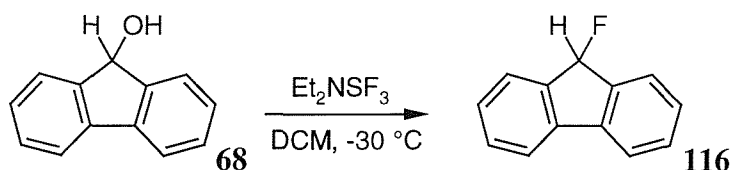
Treatment of fluorenone (**69**) with a fluorinating agent such as sulphur tetrafluoride¹²⁶ would be expected to give 9,9-difluorofluorene (**115**).



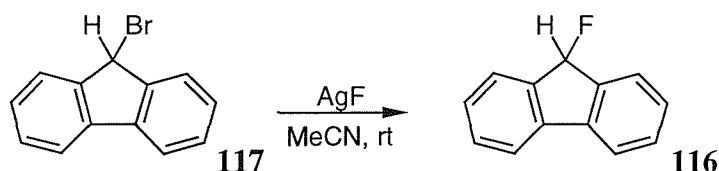
Unfortunately sulphur tetrafluoride is toxic and corrosive.¹²⁷ However the mild fluorinating agent diethylaminosulphur trifluoride (DAST) effects the same transformation,¹²⁸ but yields are low for diarylketones such as fluorenone (**69**).¹²⁹

5.2.4 Routes to 9-fluorofluorene

DAST may also be used to replace a hydroxyl group with a fluorine atom.¹³⁰ In a literature method, treatment of a solution of 9-hydroxyfluorene **68** in dichloromethane with DAST gave 9-fluorofluorene **116** in a crude yield of 48%.¹³¹



However the report notes that *9-hydroxyfluorene is unstable to storage and purification*. In an alternative method¹³² a solution of 9-bromofluorene **117** in acetonitrile was stirred with silver fluoride, to give 9-fluorofluorene **116**. The yield for this procedure was not stated.



This report states that *the compound [116] is unstable at room temperature and decomposes rapidly to polymers and hydrofluoric acid. A methanol solution was found to be stable*.

Because of the reported instability of 9-fluorofluorene **116** no work on monofluorination was attempted in this project. Difluorinated derivatives such as 9,9-difluorofluorene **115** were promising targets, but ketones require more forcing conditions to fluorinate with DAST. In the event for the present study 9-alkylation was chosen as the protocol of choice.

5.3 LATERAL ALKYLATION OF THE FLUORENE CORE

Adding a lateral alkyl chain greatly reduces the melting point of a compound, as the packing efficiency of the crystalline solid is decreased. Unfortunately it also leads to a lower clearing point, as the molecular width is greater (Section 1.7.6). A database search³¹ yielded only five 9-methylfluorenes compounds. All of these were monotropic, showing that lateral methylation reduced the clearing point more than the melting point, leading to a loss of the enantiotropic mesophase range. The simple fluorene mesogen 2-dodecanoyl-7-pentanoylfluorene **118** exhibits an enantiotropic smectic phase. Modification of the structure by lateral methylation to give 2-dodecanoyl-7-pentanoyl-9-methylfluorene **119**

reduced the melting point and promoted the formation of a nematic phase.¹⁶⁰ However the reduction in the clearing point was much greater, giving a monotropic liquid crystal.

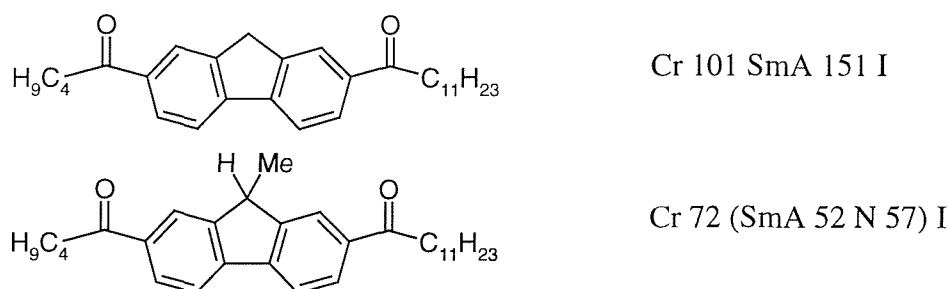


Fig. 83: (i) 2-Dodecanoyl-7-pentanoylfluorene **118**; (ii) 2-dodecanoyl-7-pentanoyl-9-methylfluorene **119**.

The methylene bridge protons of fluorene ($\text{pK}_a \approx 23$)¹³³ can be readily removed with a strong base such as butyl lithium. (Simple benzylic protons have a typical pK_a of ≈ 40 (*e.g.* toluene) whereas diphenylmethane has a pK_a of ≈ 34).

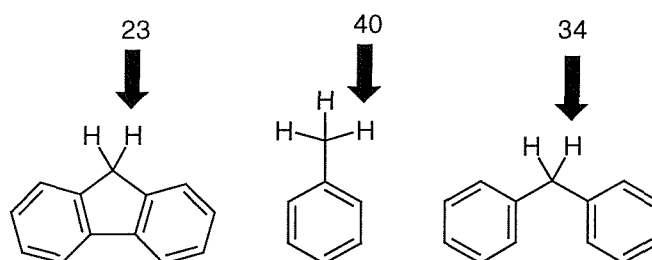
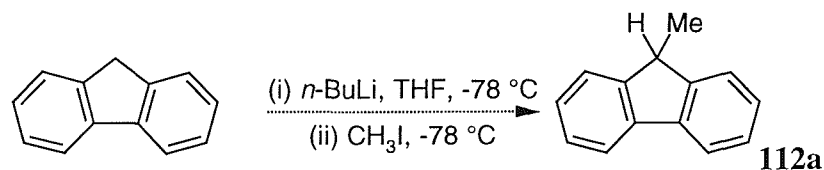


Fig. 84: (i) Fluorene; (ii) toluene; (iii) diphenylmethane.

In the present work unsubstituted fluorene was used as a model for development of 9-substitution methodology. There are several literature procedures for monoalkylation of fluorene which involve deprotonation with a base followed by quenching with an alkyl halide.¹³⁴ Preparation of 9-methylfluorene **112a** was attempted. A solution of fluorene in dry tetrahydrofuran was treated with *n*-butyllithium then quenched with methyl iodide.



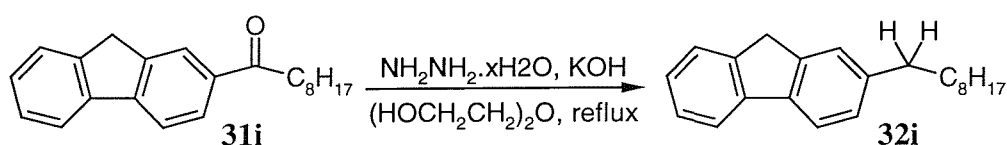
The reaction did not proceed to completion, giving a mixture of products and starting material. As fluorene and 9-methylfluorene **112a** are very similar compounds, separation is

not straightforward. Following column chromatography and two recrystallizations, a small amount of a mixture of 9-methylfluorene **112a** and 9,9-dimethylfluorene **120a** was obtained.

In view of the poor selectivity and low efficiency of this conversion other approaches were considered. A number of 9-ethylatedfluorenes were obtained as a result of other investigations.

5.4 UNUSUAL WOLFF-KISHNER REDUCTIONS

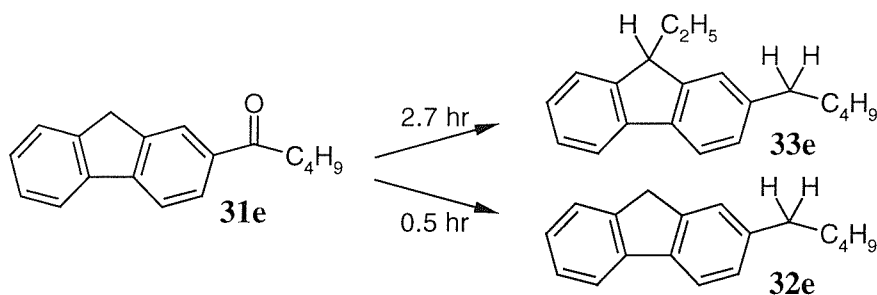
In the synthesis of 2-(4-cyanophenyl)-7-alkylfluorenes **30** it was necessary to reduce 2-acylfluorenes **31** to the corresponding 2-alkylfluorenes **32** (Section 2.1). Using the Huang-Minlon modification of the Wolff-Kishner reduction (Section 2.4) it was possible to isolate the desired 2-alkylfluorenes **32** in excellent (>80%) yield. The procedure was successfully applied to the reduction of 2-nonanoylfluorene **31i**. A mixture of **31i**, hydrazine hydrate, potassium hydroxide and diethylene glycol was heated, first at reflux, then strongly to distil out water. Following filtration through a plug of silica 2-nonylfluorene **32i** was isolated in 89% yield (Section 2.4).



5.4.1 Unexpected byproducts

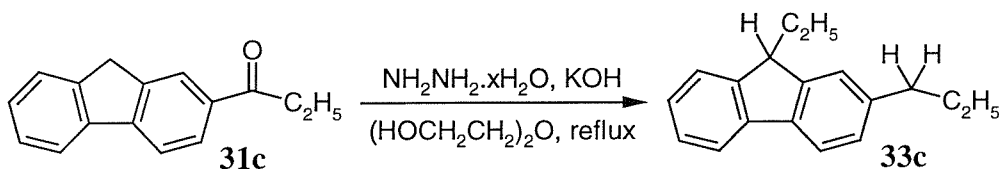
In some cases the reduction of 2-acylfluorenes **31** by this method led to the formation of 2-alkyl-9-ethylfluorenes **33** as the major products. This unusual side-reaction was investigated with a view to (i) suppressing it so that it would be possible to isolate the desired 2-alkylfluorenes **32** and (ii) to see if could offer a novel route to 9-alkylated fluorenes **33**.

Reduction of 2-pentanoylfluorene **31e** gave a mixture of products. Following column chromatography, impure 2-pentyl-9-ethylfluorene **33e** was obtained in *ca.* 54%. The procedure was repeated on a second sample of 2-pentanoylfluorene **31e**, but with a shortened reaction time. Following recrystallization, the expected product 2-pentylfluorene **32e** was isolated in 57% yield.

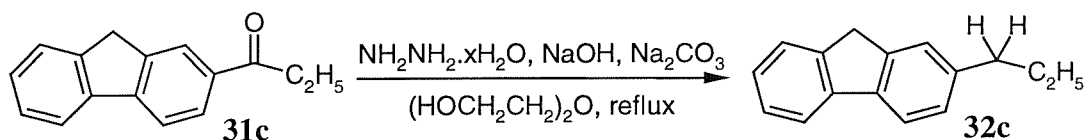


Scheme 17: Reduction of 2-pentanoylfluorene **31e**.

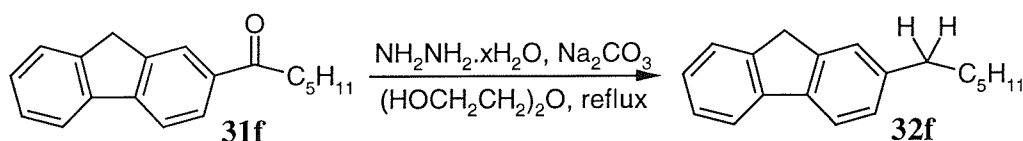
Several attempts to reduce 2-propionylfluorene **31c** to 2-propylfluorene **31c** under these conditions were unsuccessful. Following column chromatography, impure 2-propyl-9-ethylfluorene **33c** was obtained in *ca.* 47%. Even using a greatly reduced reaction time **33c** was still obtained as the major product in *ca.* 20% yield. In an attempt to prevent the occurrence of 9-substitution and produce the desired 2-alkylfluorene product **32**, the solvent was distilled prior to use and the base was purified.¹³⁵ However 2-propyl-9-ethylfluorene **33c** was still the major product (*ca.* 64% yield).



Changing the base to a mixture of sodium hydroxide and sodium carbonate was found to alleviate the problem. Following recrystallization, 2-propylfluorene **32c** was isolated in 73% yield.



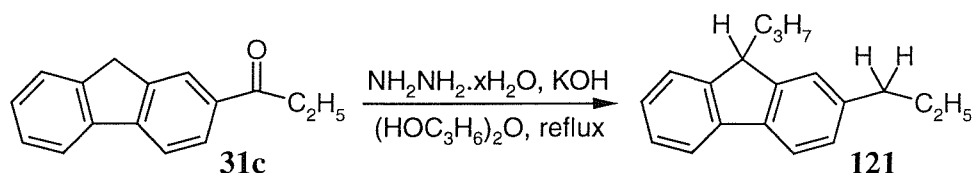
Replacement of all the sodium hydroxide with the milder sodium carbonate was also successful when applied to the reduction of 2-hexanoylfluorene **31f**. Following recrystallization, 2-hexylfluorene **32f** was isolated in 67% yield.



5.4.2 Mechanistic investigations

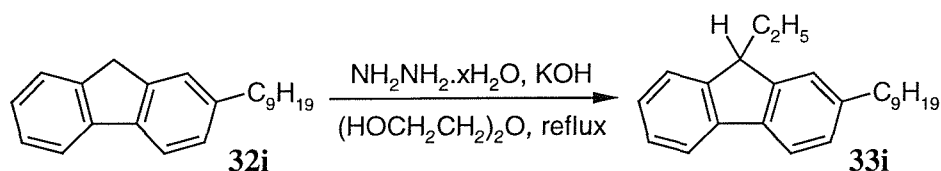
A series of reactions were devised and carried out with the aim of gaining further insight into this unexpected side reaction.

The origin of the alkyl group was unclear, as the solvent diethylene glycol is not a conventional source of an ethyl group. The reaction was carried out using dipropyleneglycol as solvent. The dipropylene glycol used contained a number of isomers. Following column chromatography, impure 2-propyl-9-propylfluorene **121** was obtained in *ca.* 44% yield.



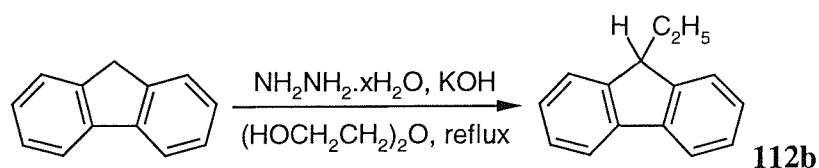
This result suggested that the solvent was the source of the alkyl group. The material contained a number of isomers, but separation of these was not attempted.

When a sample of authentic 2-nonylfluorene **32i** was heated with hydrazine hydrate, potassium hydroxide and diethylene glycol, impure 2-nonyl-9-ethylfluorene **33i** was obtained in *ca.* 75% yield after column chromatography.



This observation suggested that the reaction proceeds *via* the reduced product and does not involve either the carbonyl moiety or the hydrazone intermediate **52**.

Unsubstituted fluorene was then subjected to the same reaction conditions, to give impure 9-ethylfluorene **112b** in *ca.* 4% yield after column chromatography.



This demonstrated that the process only involves the C9 bridge, and does not require the presence of an alkyl, acyl or hydrazone functionality.

This series of experiments showed that, under the harsh alkaline conditions of the Wolff-

Kishner reaction, it was possible to alkylate at the acidic C9 bridge of fluorene. The presence of a functional group, acyl, alkyl or the tosylate intermediate, was not necessary for the reaction to occur. The unlikely source of the alkyl group was the solvent.

In all the reactions described above the 9-alkylated product **33** was obtained as the major component. However the materials always contained impurities. ^1H and ^{13}C NMR spectra clearly showed that 9-alkylation had occurred, but there were also unidentified ^{13}C NMR signals and discrepancies in the ^1H NMR integrals. When the reaction products were analyzed by gas chromatography mass spectroscopy it was possible to resolve these minor components. In some cases the impurities could then be tentatively identified from their mass spectra. Often a component with a $(M - 28)^+$ peak or a $(M + 28)^+$ peak was present. These correspond to the non-ethylated **32** and diethylated **122** compounds and their retention times and estimated yields are listed in Table 19.

Table 19: 9-Alkylated Wolff-Kishner products.

Major component		M^+		$(M - 28)^+$		$(M + 28)^+$	
		RT*	Yield [†]	RT*	Yield [‡]	RT*	Yield [‡]
i	9-Ethylfluorene 112b	5.16	ca. 4%	-	-	5.56	< 1%
ii	2-Ethyl-9-ethylfluorene 33b	5.58	ca. 42%	-	-	-	-
iii	2-Propyl-9-ethylfluorene 33c	5.75	ca. 47%	-	-	6.07	< 1%
iv	2-Propyl-9-ethylfluorene 33c	5.78	ca. 20%	5.65	ca 5%	-	-
v	2-Propyl-9-ethylfluorene 33c	5.77	ca. 64%	-	-	-	-
vi	2-Propyl-9-propylfluorene 121	5.91	ca. 44%	5.63	ca. 25%	-	-
vii	2-Pentyl-9-ethylfluorene 33e	6.18	ca. 54%	-	-	-	-
viii	2-Hexyl-9-ethylfluorene 33f	6.37	ca. 50%	6.29	< 1%	6.64	ca. 5%
ix	2-Nonyl-9-ethylfluorene 33i	6.90	ca. 75%	-	-	-	-

* Retention time in minutes from gas chromatogram

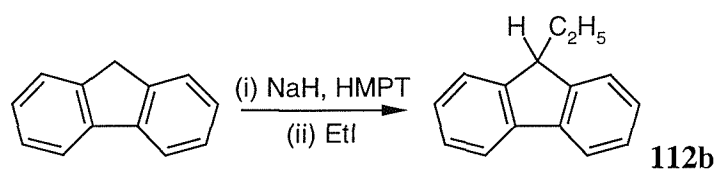
[†] Overall reaction yield

[‡] Estimated yield from gas chromatogram

5.4.3 Mechanisms

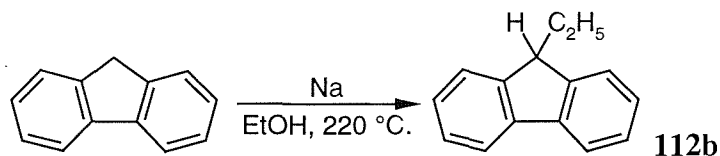
Despite extensive searching of the literature no reference to the unexpected 9-alkylfluorene Wolff-Kishner products could be found. It appears that there is no precedent for this process, which effects reduction and alkylation in a single pot process.

There are many routes to 9-alkylfluorenes, normally *via* initial deprotonation of fluorene by a base followed by quenching with an alkyl halide. For example in a literature procedure,¹³⁶ described as “très exothermique”, a mixture of fluorene and hexamethylphosphorus triamide was treated first with sodium hydride then quenched with ethyl iodide. Following workup, 9-ethylfluorene **112b** was obtained in 67% yield.



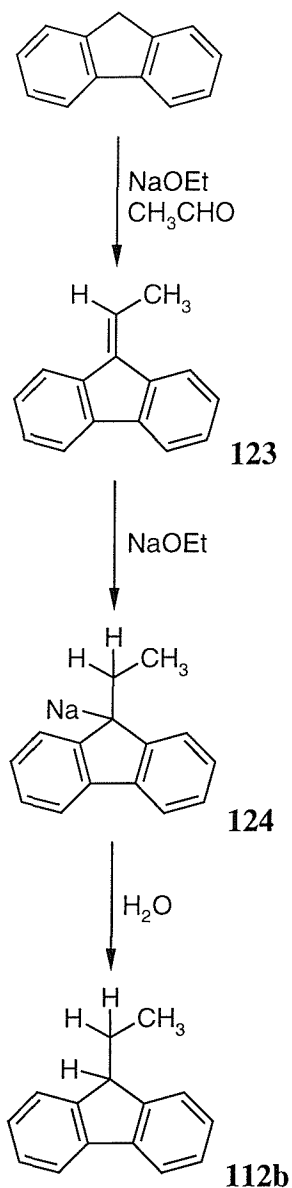
The procedure was repeated¹³⁷ using isopropylmagnesium chloride as base, and 9-ethylfluorene **112b** was obtained in a slightly increased yield of 72%.

There are several examples where an alcohol acts as the source of the alkyl group *e.g.* a mixture of fluorene, sodium and ethanol was heated in a sealed tube to give 9-ethylfluorene **112b** in a crude yield of 92%.¹³⁸



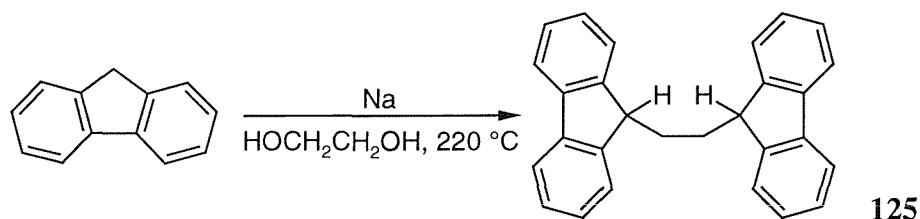
This procedure was successfully applied to the synthesis of other homologous 9-alkylfluorenes.

The proposed mechanism for this process has several stages (Scheme 18). Under the reaction conditions a small amount of acetaldehyde is present resulting from aerial oxidation of the alcohol. Sodium ethoxide is formed by the reaction between ethanol and sodium. Acetaldehyde reacts with fluorene in a Knoevenagel type condensation to give the dibenzofulvalene **123**. Sodium ethoxide adds across the double bond *via* a six membered ring transition state (*cf.* Meerwein-Ponndorf-Verley reduction) to give **124**, which, on workup, is protonated to give 9-ethylfluorene **112b**.



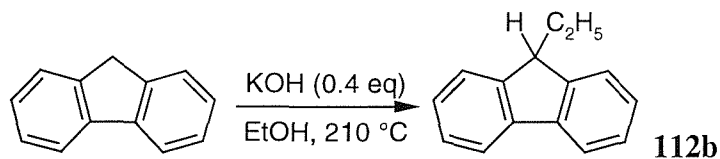
Scheme 18: Synthesis of 9-ethylfluorene **112b** – dibenzofulvalene mechanism.

This mechanism neatly explains the fact that only mono alkylated material is formed in these reactions. The procedure was carried out using ethylene glycol to give the bridged bisfluorenyl species 1,2-bis(9-fluorenyl)ethane **125** in 56% yield.¹³⁹



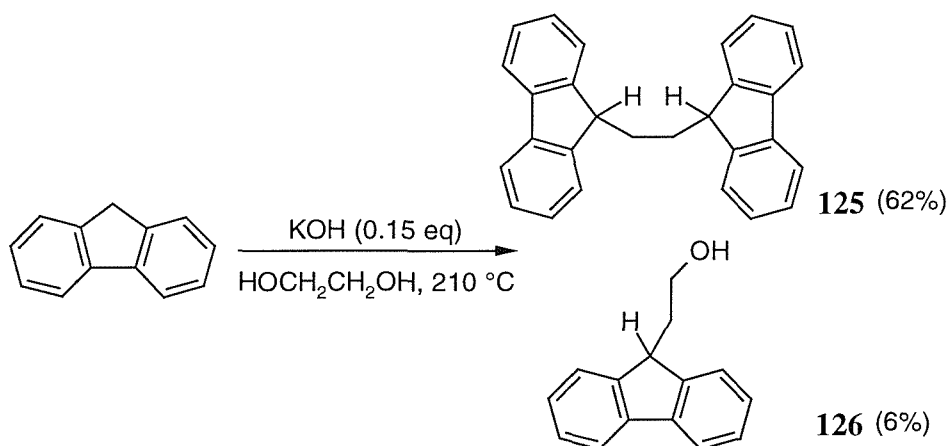
It is reported that a excess of alkali metal alkoxide is not needed to effect the reaction. In a modified procedure a mixture of fluorene, potassium hydroxide (0.4 equivalents) and

ethanol was heated in an autoclave to give 9-ethylfluorene **112b** in 84% yield.



This procedure was also carried out using methanol, butanol and 2-ethylhexanol. In all three cases the 9-alkylfluorene **112** was obtained in high yield.

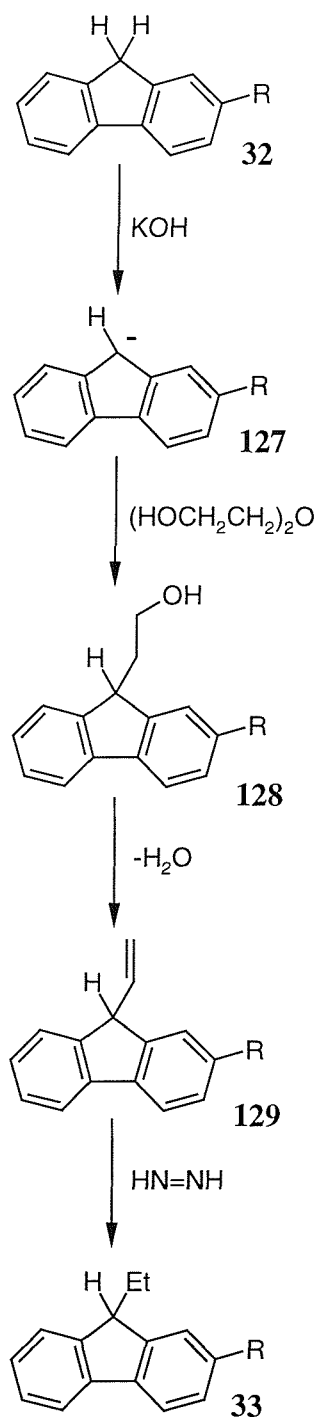
Reaction with ethylene glycol under similar conditions¹⁴⁰ gave a mixture of bis(9-fluorenyl)ethane **125** and 9-(2-hydroxyethyl)fluorene **126**.



This mechanism seems unlikely for the Wolff-Kishner, as it cannot explain the formation of diethylated material. Aerial oxidation of diethylene glycol to give an aldehyde seems unlikely, given that the reaction is carried out under a nitrogen atmosphere generated by the degradation of the hydrazone intermediate. With no aldehyde present a Knoevenagel type condensation to give a dibenzofulvalene cannot occur.

It is postulated that the side reaction proceeds *via* the following pathway:

- (i) The reduction of the carbonyl moiety to a methylene group occurs, giving the expected 2-alkylfluorene **32**.
- (ii) Under the harsh alkaline conditions of the reaction a proton is removed from the methylene bridge to give the fluorenyl ion **127**. This ion is rapidly quenched by an S_N2 attack on the solvent to give 2-alkyl-9-(2-hydroxyethyl)fluorene **128**;
- (iii) The 9-(2-hydroxyethyl)fluorene then undergoes elimination of water to give 2-alkyl-9-vinylfluorene **129**;
- (iii) **129** is hydrogenated by diimide to give the 2-alkyl-9-ethylfluorene **33**.

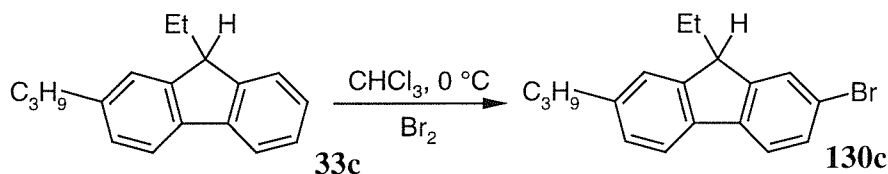


Scheme 19: Synthesis of 9-ethylfluorenes – proposed reaction pathway.

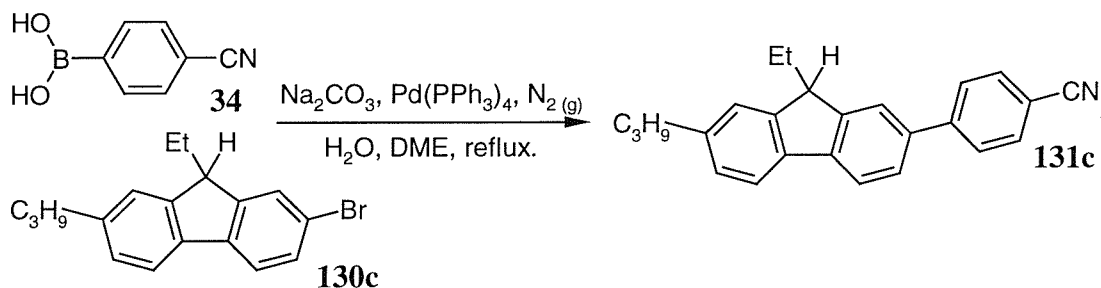
From the experiments that have been carried out it is known that the reaction proceeds *via* the expected 2-alkylfluorene **32**. The methylene bridge of fluorene is acidic ($\text{pK}_a \approx 23$), and can be deprotonated by caustic bases. In the Wolff-Kishner reaction nitrogen is evolved and water is distilled out, giving an anhydrous, oxygen free environment. If water were present then the fluorenyl anion **127** would be rapidly reprotonated.

5.5 9-ALKYL MESOGENS

The work described above (Section 5.4) had produced a sample of 2-propyl-9-ethylfluorene **33c**. The material contained impurities including 2-propyl-9,9-diethylfluorene **122c** (< 1%). Despite these impurities conversion of the material to a laterally substituted mesogen was attempted. A solution of impure **33c** in chloroform was treated with bromine to give impure 2-bromo-7-propyl-9-ethylfluorene **130c** in *ca.* 107% yield. This material contained low levels of impurities, including non-brominated 2-propyl-9-ethylfluorene **33c** (*ca.* 10%).



A mixture of impure 2-bromo-7-propyl-9-ethylfluorene **130c**, impure 4-cyanobenzoboronic acid **34**, sodium carbonate, water and 1,2-dimethoxyethane was deoxygenated with a stream of nitrogen gas. Tetrakis(triphenyl)phosphinepalladium(0) catalyst was added, and the reaction mixture was heated at reflux.



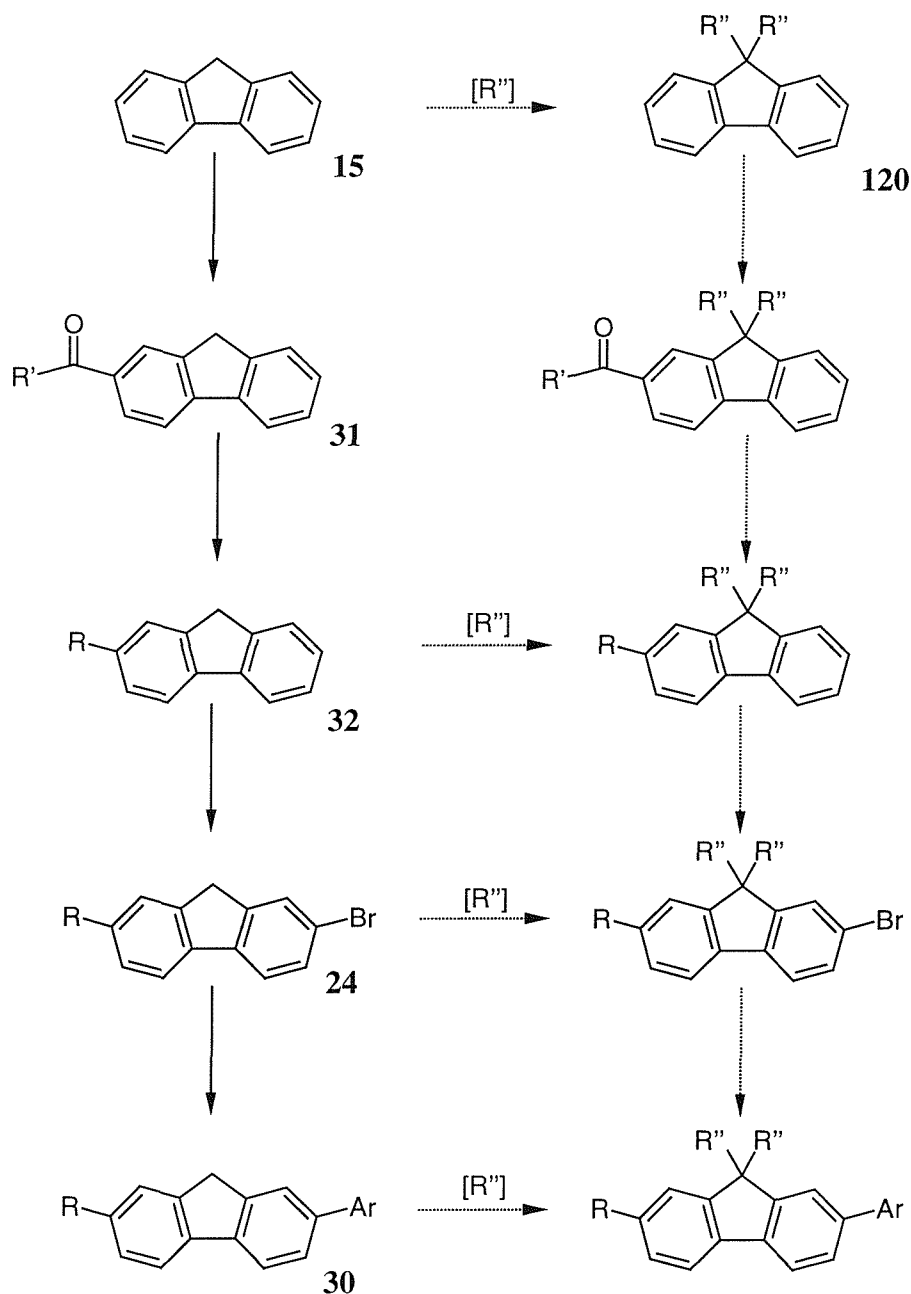
Following column chromatography and reduced pressure distillation, impure 2-(4-cyanophenyl)-7-propyl-9-ethylfluorene **131c** was obtained in *ca.* 32 % yield. A ^1H NMR spectrum indicated the presence of low levels (*ca* 5%) of unknown impurities.

Recrystallization was attempted with various solvent systems, but no pure material was obtained. During these attempts at purification the material had decomposed to give several components. Following column chromatography, impure 2-(4-cyanophenyl)-7-propyl-9-ethylfluorene **131c** was obtained in *ca.* 2% yield. A ^1H NMR spectrum indicated the presence of low levels (*ca* 5%) of unidentified impurities.

5.6 9,9-DIALKYLFLUORENES

A report¹⁴¹ states that *9-alkylfluorenes are unstable to oxygen...[and can be] oxidized to 9-hydroxy-9-alkylfluorene*. If a small amount of 9,9-dialkylfluorene **120** were formed it would

be difficult to isolate pure product. Therefore because of difficulties encountered in their preparation and doubts about their stability, no further work on 9-alkylfluorenes was carried out. Accordingly, 9,9-dialkylfluorenes were pursued as stable target compounds. There are several stages in the synthesis of 2-(4-cyanophenyl)-7-alkylfluorenes **30** where alkyl groups can be introduced into the 9-position.



Scheme 20: Routes to 2-(4-cyanophenyl)-7-alkyl-9,9-dialkylfluorenes.

Whilst the methylene bridge protons of fluorene are acidic ($pK_a \approx 23$) and can be readily removed with a strong base such as butyl lithium, protons alpha to a ketone group are also acidic, with a typical pK_a of ≈ 19 . Therefore addition of a strong base would preferentially

deprotonate the ketone of a 2-acylfluorene. Alkylfluorenes are not as base sensitive, as benzylic protons have a typical pK_a of ≈ 40 . It should therefore be possible to selectively deprotonate a 2-alkylfluorene at the 9-position.

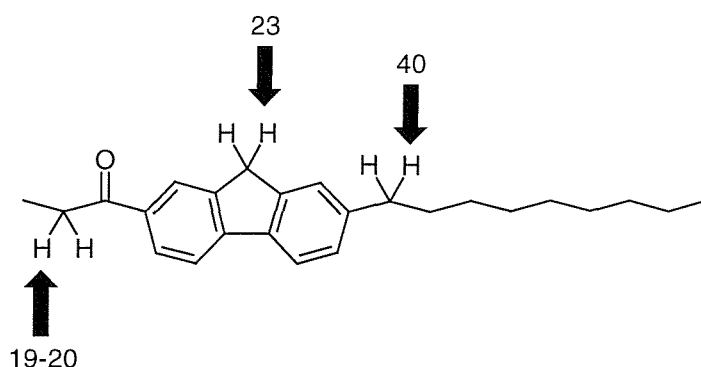
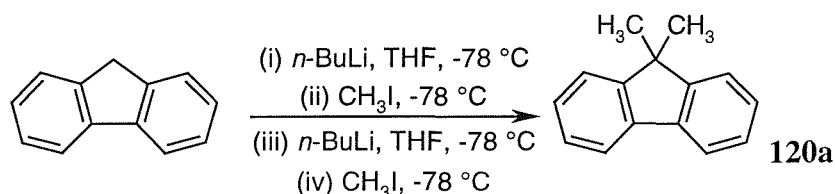


Fig. 85: 2-Propionyl-7-nonylfluorene **26**.

Attention therefore turned to the preparation of a 9,9-dialkylfluorenes **120**. Deprotonation of fluorene followed by quenching with an alkyl halide, further deprotonation and quenching gives a 9,9-dialkylfluorene **120**. It is desirable to laterally alkylate at the latest possible stage in the synthetic scheme. Ideally therefore alkylation would be carried out directly on the mesogen. Unfortunately large amounts of mesogen were not available and the methodology was developed on the intermediates.

Initially dialkylation of fluorene was explored. A solution of fluorene in dry tetrahydrofuran was treated with *n*-butyllithium then quenched with methyl iodide. The reaction mixture was again treated with *n*-butyllithium then finally quenched with a second portion of methyl iodide. Following recrystallization, impure 9,9-dimethylfluorene **120a** was obtained in *ca.* 37 % yield.



Analysis by gas chromatography mass spectroscopy indicated the presence of <1% 9-methylfluorene **112a**, indicating that the reaction did not proceed to completion. GCMS analysis also indicated the presence of *ca.* 5% 9-methyl-9-butylfluorene **132**. A possible explanation for the formation of this unexpected product was that transmetallation between *n*-butyllithium and methyl iodide produced butyl iodide, which then quenched the 9-methylfluorenyl ion intermediate.

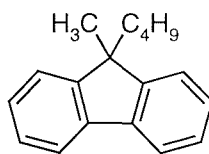


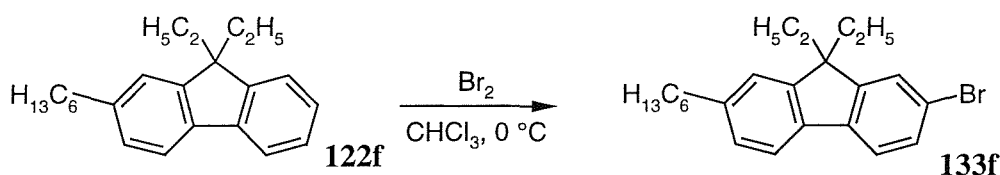
Fig. 86: 9-Methyl-9-butylfluorene **132**.

5.7 9,9-DIALKYL MESOGENS

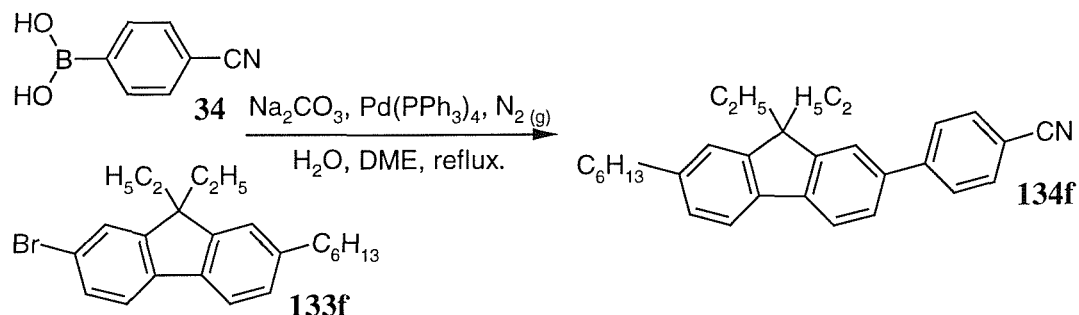
Transmetallation and deprotonation were competing reactions. Therefore, in order to discourage transmetallation, use of the sterically hindered base lithium diisopropylamide was explored.

5.7.1 Bromination of a laterally alkylated fluorene

A solution of impure 2-hexyl-9,9-diethylfluorene **122f** in chloroform was treated with bromine. After workup, impure 2-bromo-7-hexyl-9,9-diethylfluorene **133f** was obtained in *ca.* 100% yield.

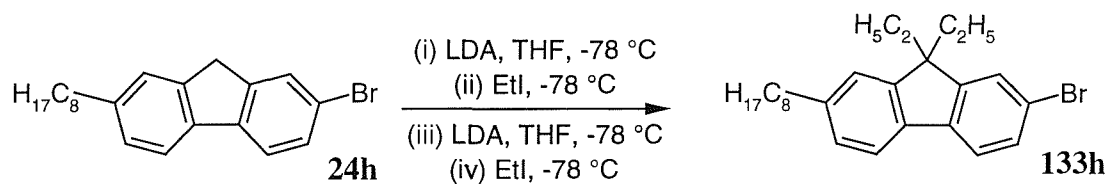


A mixture of this impure 2-bromo-7-hexyl-9,9-diethylfluorene **133f**, 4-cyanobenzoboronic acid **34**, sodium carbonate, water and 1,2-dimethoxyethane was deoxygenated with a stream of nitrogen gas. Tetrakis(triphenylphosphine)palladium(0) catalyst was then added, and the reaction mixture was heated at reflux. Following column chromatography and reduced pressure distillation, impure 2-(4-cyanophenyl)-7-hexyl-9,9-diethylfluorene **134f** was obtained in *ca.* 4 % yield. ^1H and ^{13}C NMR spectra indicated the presence of unknown impurities in this material.

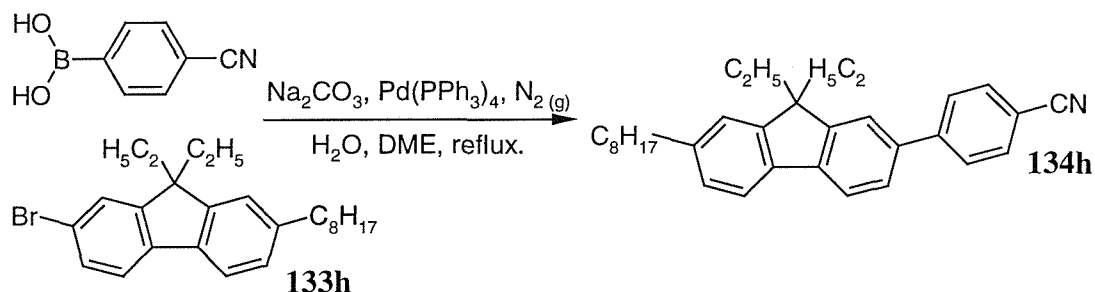


5.7.2 Alkylation of an aryl bromide

A solution of 2-bromo-7-octylfluorene **24h** in dry tetrahydrofuran was treated with lithium diisopropylamide then quenched with ethyl iodide. The reaction mixture was again treated with lithium diisopropylamide and finally quenched with a second portion of ethyl iodide. Following workup, 2-bromo-7-octyl-9,9-diethylfluorene **133h** was isolated in 98 % yield.



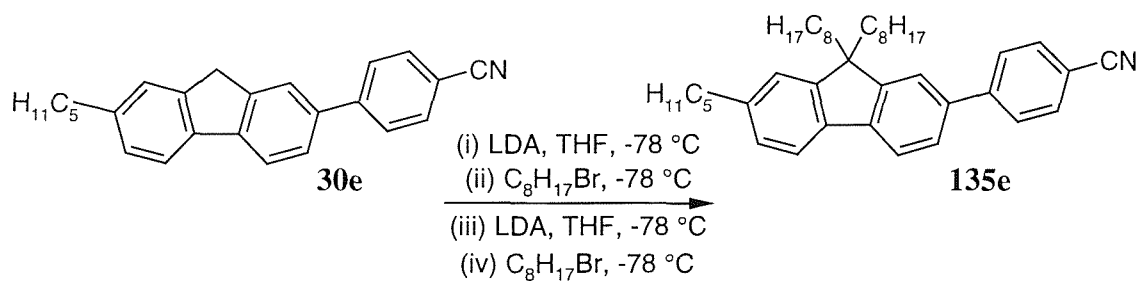
The C9 dialkylated aryl bromide **133h** was then coupled with 4-cyanobenzoboronic acid to give a laterally alkylated mesogen. A mixture of 2-bromo-7-octyl-9,9-diethylfluorene **133h**, 4-cyanobenzoboronic acid **34**, sodium carbonate, water and 1,2-dimethoxyethane was deoxygenated with a stream of nitrogen gas. Tetrakis(triphenyl)phosphinepalladium(0) catalyst was added, and the reaction mixture was heated at reflux. After workup, impure 2-(4-cyanophenyl)-7-octyl-9,9-diethylfluorene **134h** was obtained in *ca.* 85 % yield.



^1H and ^{13}C NMR spectra indicated the presence of unknown impurities in this material.

5.7.3 Direct alkylation of a mesogen

Direct alkylation was carried out on 2-(4-cyanophenyl)-7-pentylfluorene **30e**. A solution of **30e** in dry tetrahydrofuran was treated with lithium diisopropylamide, then quenched with octyl bromide. The reaction mixture was again treated with lithium diisopropylamide and finally quenched with a second portion of octyl bromide. Following workup and column chromatography, 2-(4-cyanophenyl)-7-pentyl-9,9-dioctylfluorene **135e** was isolated in 30% yield.



Four laterally substituted mesogens were prepared by the different routes described above.

Table 20: Laterally substituted mesogens.

Compound	Details	Yield
131c 2-(4-cyanophenyl)-7-propyl-9-ethylfluorene	Suzuki coupling*	ca. 32%
134f 2-(4-cyanophenyl)-7-hexyl-9,9-diethylfluorene	Suzuki coupling [†]	ca. 4%
134h 2-(4-cyanophenyl)-7-octyl-9,9-diethylfluorene	Suzuki coupling [†]	ca. 85%
135e 2-(4-cyanophenyl)-7-pentyl-9,9-dioctylfluorene	Direct alkylation	30%

*unstable (degraded on attempted recrystallization)

[†]contained low levels of unidentified impurities

The C9 monoalkylated product **131c** was found to be both difficult to purify and unstable. No other monoalkylated products were prepared. Two compounds, **134f** and **134h**, were prepared by a Suzuki coupling of a boronic acid to a 9,9-dialkylated fluorene. Both compounds were found to be difficult to satisfactorily purify. In contrast direct alkylation of a mesogen gave the pure desired product 2-(4-cyanophenyl)-7-pentyl-9,9-dioctylfluorene **135e**.

5.8 PROPERTIES OF LATERALLY ALKYLATED MESOGENS

Four laterally alkylated mesogens were prepared, but three of these contained low levels of impurities. Impure 2-(4-cyanophenyl)-7-propyl-9-ethylfluorene was an oily solid, but attempts to purify the sample by recrystallization were unsuccessful (Section 5.5). The other three compounds were oils, therefore purification by recrystallization was not possible. Pure 2-(4-cyanophenyl)-7-pentyl-9,9-dioctylfluorene **135e** was prepared by direct alkylation of 2-(4-cyanophenyl)-7-pentylfluorene **30e**, and was successfully purified by column chromatography.

2-(4-Cyanophenyl)-7-pentyl-9,9-dioctylfluorene **135e** was studied by polarized optical microscopy. At room temperature, the bulk material was a clear pale yellow oil. On the microscope this material gave an optically extinct isotropic texture. Despite cooling, no

changes was observed, and no mesophases were generated.

The three slightly impure materials were also studied by POM. The oily solid 2-(4-cyanophenyl)-7-propyl-9-ethylfluorene **131c** was amorphous, and gave no textures. The impure oils 2-(4-cyanophenyl)-7-hexyl-9,9-diethylfluorene **134f** and 2-(4-cyanophenyl)-7-octyl-9,9-diethylfluorene **134h** were isotropic, and no mesophases could be generated.

5.9 SUMMARY AND CONCLUSIONS

Lateral substitution is a powerful technique for altering the properties of a mesogen.

Alkylation of the fluorene core was explored in detail, and four C9 alkylated 2-(4-cyanophenyl)-7-alkylfluorenes were prepared. These materials were all oils and were difficult to purify satisfactorily. The exception to this was 2-(4-cyanophenyl)-7-pentyl-9,9-dioctylfluorene **135e**, which was prepared cleanly by dialkylation of 2-(4-cyanophenyl)-7-pentylfluorene **30e**.

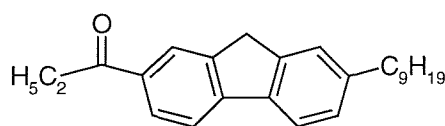
These fact that these materials were oils proves that lateral alkylation dramatically lowers the melting point of the compounds. However, the materials were found to be isotropic and no mesophases were detected.

In some cases the Wolff-Kishner reduction of a 2-acylfluorene **31** resulted in the formation of a 2-alkyl-9-ethylfluorene **33**. A series of studies established that the ethyl group originated from the solvent, diethylene glycol, and postulated a mechanism for the process. The side-reaction could be suppressed by using sodium carbonate in place of the caustic base, but could not be controlled to give a clean route to 2-alkyl-9-ethylfluorenes **33**.

6. OTHER SYNTHESSES

6.1 OVERVIEW

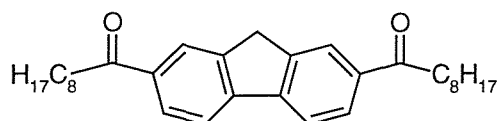
In the early stages of this project, attention was focussed on simple fluorene-based mesogens. All the reported 2,7-disubstituted fluorenes were either monotropic or exhibited enantiotropic smectic phases (Section 1.13). There was only one reported enantiotropic nematic compound, 2-propionyl-7-nonylfluorene **26**.³² Close examination of the literature revealed a second conflicting report of the same molecule.³³ 2-Propionyl-7-nonylfluorene **26** was prepared in three steps from fluorene, and was found to exhibit a smectic A phase. No nematic phase was detected, and the observed transition temperatures were in good agreement with one of the reports.³³



Cr 95 SmA 114 I

Fig. 87: 2-Propionyl-7-nonylfluorene **26**.

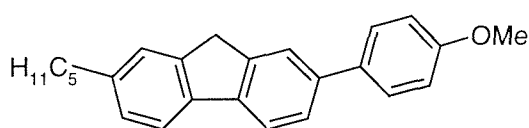
Several symmetrically substituted 2,7-diacylfluorenes were reported as exhibiting an enantiotropic smectic phase (Section 1.13). Such compounds can be prepared from fluorene in a single step. 2,7-Dinonanoylfluorene **136h** was prepared and was found to exhibit both smectic A and smectic C phases, with the observed transition temperatures in good agreement with a literature report.¹⁴²



Cr 121 SmC 146 SmA 148 I

Fig. 88: 2,7-Dinonanoylfluorene **136h**.

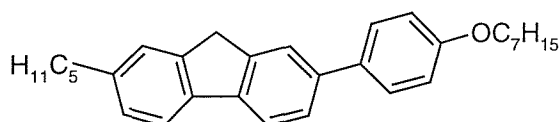
The three 2-(4-methoxyphenyl)-7-alkylfluorenes **137e**, **137g** and **137i** were prepared as low birefringence analogues of the cyano-containing 2-(4-cyanophenyl)-7-alkylfluorenes **30**. The methoxy group is not as strongly nematic promoting as the cyano group (Section 1.7.2), and the 2-(4-methoxyphenyl)-7-alkylfluorenes **137** were found to exhibit ill defined smectic phases at elevated temperatures, *e.g.* 2-(4-methoxyphenyl)-7-pentylfluorene **137e** (Figure 89).



Cr 223 SmX 226 SmX 235 I

Fig. 89: 2-(4-Methoxyphenyl)-7-pentylfluorene **137e**.

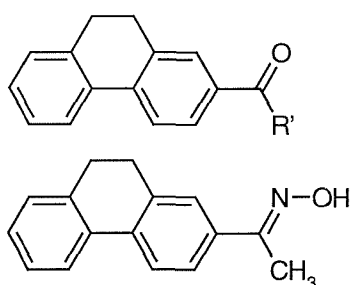
Replacement of the methoxy group with a longer alkoxy chain was expected to lower the melting point and therefore give a larger mesophase region (Section 1.7.3). Accordingly 2-(4-heptoxyphenyl)-7-pentylfluorene **138e** was prepared, and was found to exhibit a stable smectic A phase.



Cr 205 SmA 234 I

Fig. 90: 2-(4-Heptoxyphenyl)-7-pentylfluorene **138e**.

Some work was also carried out on the related 9,10-dihydrophenanthrene core unit (Section 1.9). The preparation of three 2-acyl-9,10-dihydrophenanthrenes **139b**, **139c** and **139e** was attempted, but no pure materials could be isolated. Conversion of **139b** to the oxime derivative produced a small amount of 2-acetoxime-9,10-dihydrophenanthrene **140b**.

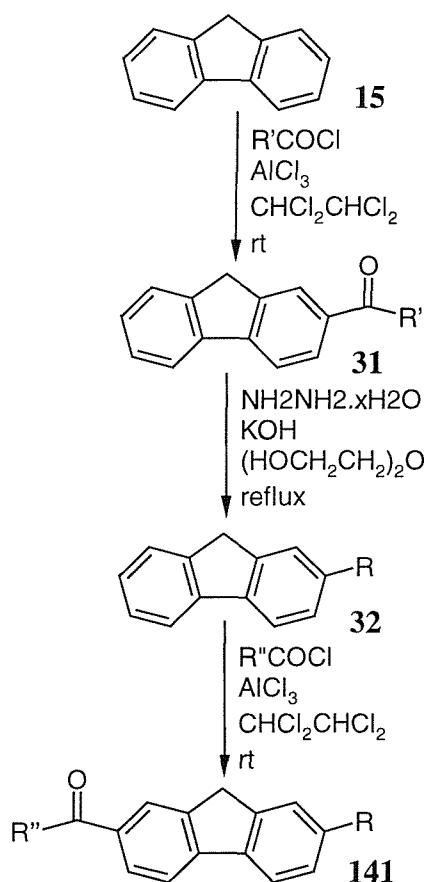
**139b**, R' = CH₃**139c**, R' = C₂H₅**139e**, R' = C₄H₉**Fig. 91:** (i) 2-Acyl-9,10-dihydrophenanthrenes **139**; (ii) 2-acetoxime-9,10-dihydrophenanthrene **140**.

Partial reduction of the carbocyclic core was a potentially valuable method of modifying the properties of a compound. Carboxylic acid derivatives were required in order to explore this technique using the Birch Reduction. Preparation of fluorene carboxylic acids was attempted, but was only partially successful.

6.2 2-ACYL-7-ALKYLFLUORENES

The initial targets of the project were simple disubstituted mesogens. Friedel-Crafts acylation (Section 2.3) of fluorene with the appropriate acid chloride gave the 2-

acylfluorene **31**. This was then followed by the Huang-Minlon modification of the Wolff-Kishner reduction (Section 2.4) to give the 2-alkylfluorene **32**. These two steps are identical to those used in the synthesis of the 2-(4-cyanophenyl)-7-alkylfluorenes **30** (Chapter 2). A second Friedel-Crafts acylation was used to introduce an acyl group at the other end of the molecule.

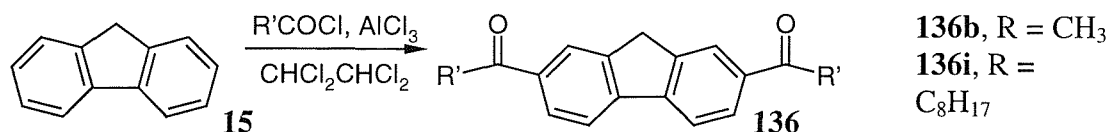


Scheme 21: Synthesis of 2-acyl-7-alkylfluorenes **141**.

The second acylation step was initially explored using 2-ethylfluorene **32b** as a model compound, and was found to give lower than expected yields. When 2-ethylfluorene **32b** was treated with two equivalents of acetyl chloride, a small amount (*ca.* 10%) of impure 2-acetyl-7-ethylfluorene **142** was obtained. However, repetition of the reaction but with only one equivalent of acetyl chloride allowed the isolation of 2-acetyl-7-ethylfluorene **142** in 52% yield. The short molecule 2-acetyl-7-ethylfluorene **142** did not show any mesophases. The literature compound 2-propionyl-7-nonylfluorene **26** was prepared in 42% yield by the acylation of 2-nonylfluorene **32h**. 2-Propionyl-7-nonylfluorene **26** exhibited a smectic A phase (Cr 95 SmA 114 I), with transition temperatures in good agreement with the reported values.³³

6.3 2,7-DIACYLFLUORENES

Symmetric disubstituted derivatives can be made by a Friedel-Crafts reaction using an excess of the relevant acid chloride. Because the acyl substituent is electron withdrawing it deactivates the system towards aromatic electrophilic substitution (Section 2.2). An excess of acyl halide is therefore required in order to produce 2,7-diacylfluorenes **136**.



In the present work reaction of fluorene with a five fold excess of nonanoyl chloride gave a mixture of products. Separation by column chromatography followed by recrystallization gave 2,7-dinonanoylfluorene **136h** in 7% yield. From this low yield and the observation that no unreacted starting material or monosubstituted product were isolated, it is clear that such forcing conditions are not actually required.

Treatment of fluorene with two equivalents of acetyl chloride gave a mixture of 2-acetylfluorene **31b** and 2,7-diacetylfluorene **136b**. A subsequent reaction with 2.5 equivalents led to the isolation of 2,7-diacetylfluorene **136b** in 7% yield. Clearly the amount of acyl chloride required to effect disubstitution must be carefully optimized in order to produce high yields.

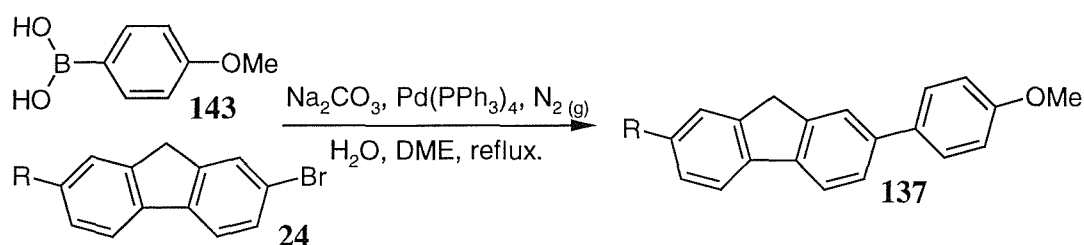
2,7-Diacetylfluorene **136b** did not show any mesophases, whereas 2,7-dinonanoylfluorene **136h** exhibited both smectic A and smectic C phases (Cr 121 SmC 146 SmA 148 I). These transition temperatures were slightly lower than the reported literature values.¹⁴²

6.4 2-(4-ALKOXYPHENYL)-7-ALKYLFLUORENES

Early liquid crystal devices were only effective when viewed from a position perpendicular to the screen, and the display appeared grey if viewed from the side.¹⁴³ This narrow viewing angle arose from the use of highly birefringent cyano-containing mesogens in the display mixtures. Modification of these compounds by replacement of the terminal cyano moiety with an alkoxy group lowered the birefringence, which made the devices more effective by greatly increasing the viewing angle.¹⁴³

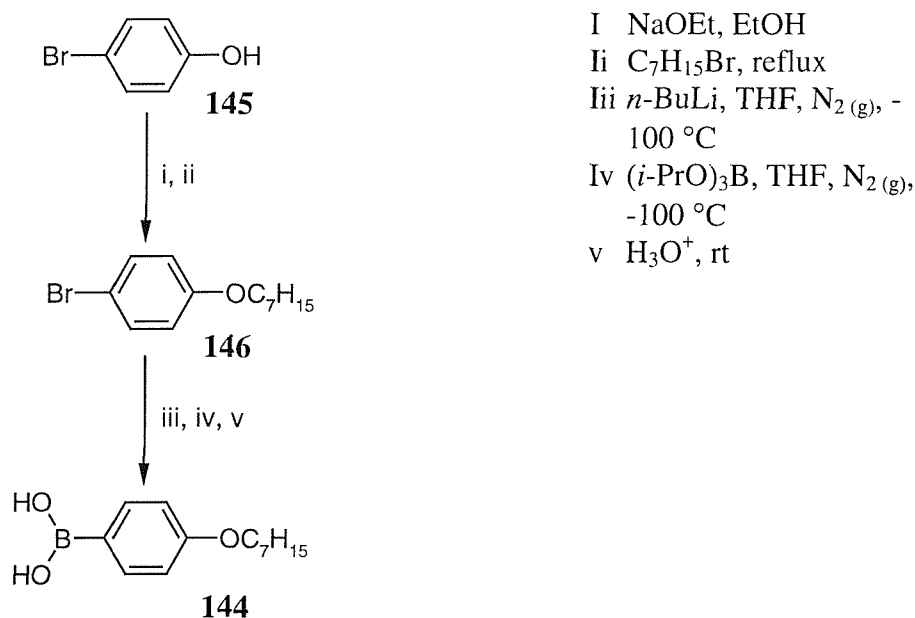
The homologous series of 2-(4-cyanophenyl)-7-alkylfluorenes **30** was prepared (Chapter 2), and, as expected, these cyano-containing mesogens were found to be highly birefringent (Section 3.10.1). Cyanides are strong nematic promoters, whereas the methoxy group does not encourage the formation of nematic phases (Section 1.7.2). Consequently replacement

of the cyano group with a methoxy group can result in the loss of a nematic phase. The three 2-bromo-7-alkylfluorenes **24e**, **24g** and **24h** were coupled with commercially available 4-methoxybenzoboronic acid **143** under Suzuki conditions (Section 2.8). These aryl bromides were intermediates in the synthesis of the 2-(4-cyanophenyl)-7-alkylfluorenes **30**, so no duplication of synthetic steps was required (Section 2.5). A mixture of the aryl bromide **24**, 4-methoxybenzoboronic acid **143**, aqueous sodium carbonate solution and 1,2-dimethoxyethane was deoxygenated using a stream of nitrogen gas. Tetrakis(triphenylphosphine)palladium(0) catalyst was added, and the reaction mixture was heated at reflux.



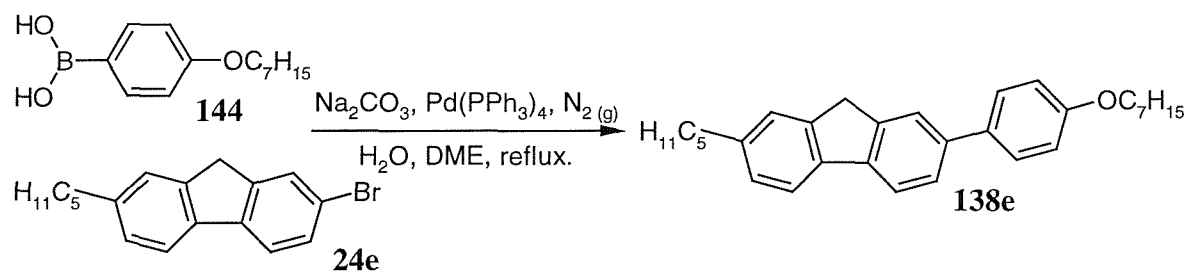
Following recrystallization, the 2-(4-methoxyphenyl)-7-alkylfluorenes **137** were isolated as amorphous solids in 11 to 12% yield. Preliminary investigations were carried out by polarized optical microscopy. The 2-(4-methoxyphenyl)-7-alkylfluorenes **137** were found to show ill defined smectic phases at high temperatures (Table 21). No other data on the physical properties of these compounds was collected.

Lengthening the alkoxy chain should help to stabilize the mesophase and lower the transition temperatures. In order to investigate this, 4-heptoxybenzoboronic acid **144** was made from 4-bromophenol **145** in two steps. In an adapted Williamson ether synthesis (Section 4.4), 4-bromophenol **145** was deprotonated with a solution of sodium ethoxide in ethanol. Heptyl bromide was then added to give 1-bromo-4-heptoxybenzene **146** in *ca.* 90% yield. **146** was an oil which contained low levels of unidentified impurities. The material was carried forward to the next stage of the synthesis without attempting further purification. The boronic acid **144** was prepared in a similar manner to 4-cyanobenzoboronic acid **34** (Section 2.7). Transmetalation of **146** was effected by addition of butyllithium to give the aryllithium intermediate **147**. This was quenched with triisopropyl borate to give the borate ester **148**. Hydrolysis was achieved by stirring in dilute acid, and recrystallization gave 4-heptoxybenzoboronic acid **144** in 49% yield.



Scheme 22: Synthesis of 4-heptoxybenzoboronic acid **144**.

4-Heptoxybenzoboronic acid **144** was coupled to 2-bromo-7-pentylfluorene **24e** under Suzuki conditions to give 2-(4-heptoxyphenyl)-7-pentylfluorene **138e** in 20% yield.



This material was unusual in that it could not be visualized on a TLC plate, despite using a range of staining agents.¹⁴⁴ The material showed a stable smectic phase, but at an unexpectedly high temperature.

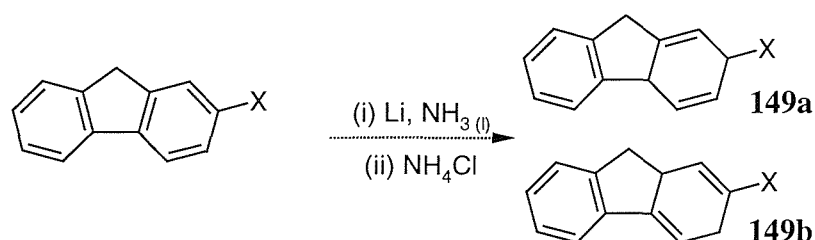
Table 21: 2-(4-Alkoxyphenyl)-7-alkylfluorenes.

	Compound	Transition Temperatures*	Yield
137e	2-(4-Methoxyphenyl)-7-pentylfluorene	Cr 223 SmX 226 SmX 235 I	12%
137g	2-(4-Methoxyphenyl)-7-heptylfluorene	Cr 217 SmX 221 SmX 229 I	12%
137i	2-(4-Methoxyphenyl)-7-nonylfluorene	Cr 211 SmX 215 SmX 221 I	11%
138e	2-(4-Heptoxyphenyl)-7-pentylfluorene	Cr 205 SmA 234 I	20%

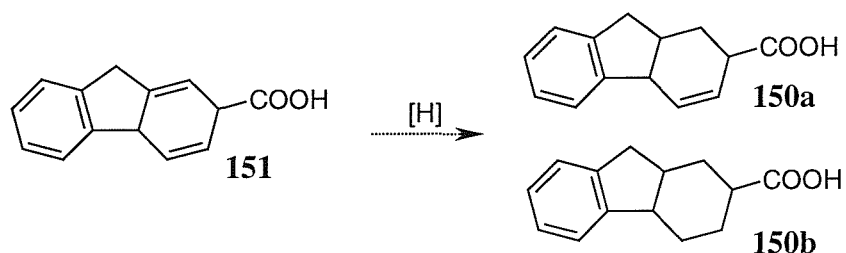
* The identity of these smectic phases was uncertain

6.5 PARTIAL REDUCTION METHODOLOGY - CARBOXYLIC ACIDS

An interesting and potentially valuable strategy for modifying the properties of a compound is partial reduction of the carbocyclic core. The preparation of compounds with partially saturated fluorene cores provides significant scope for altering mesogenic properties, and such an approach is novel within this field. Partial reduction may be accomplished by a two electron Birch reduction,¹⁴⁵ which provides an excellent method for converting an aromatic ring to a 1,4-dihydrobenzene. Reduction is effected by a mixture of alkali metal (usually lithium) and liquid ammonia.



Much work has been carried out into the effect of substituents on the product from reduction of a variety of aromatic systems.⁵⁰ A mixture of products is normally expected, but the product distribution can be influenced by the choice of reagents and conditions.⁵⁰ Birch reductions have been explored on fluorene and 9,10-dihydrophenanthrene substrates.⁵⁰ It is anticipated that employing an electron withdrawing group such as carboxylic acid will favour **149a** as the major product. However compounds such as **149a** are unstable and unless crystalline tend to rearomatize on standing in air. Hydrogenation with a suitable catalyst could be used to give stable products such as **150a** and **150b**.

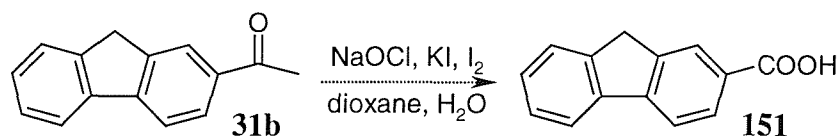


Several strategies were employed to make fluorene carboxylic acids. Preparation of fluorene-2-carboxylic acid **151** was attempted *via* three complementary procedures.

6.5.1 Haloform Reaction

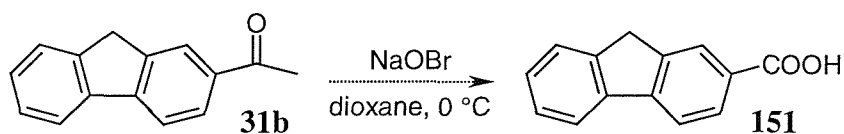
The haloform reaction converts methyl ketones to acids. Many combinations of reagents have been successfully employed, but the basic requirements are a base and a source of

halide ions.¹⁴⁶ In a test scale iodoform oxidation,⁵⁰ a mixture of 2-acetylfluorene **31b**, aqueous sodium hypochlorite and dioxane was treated with a solution of potassium iodide and iodine.



No precipitate of iodoform was observed during the reaction or workup. A mass spectrum of the crude material had a peak at $m/z = 209$, corresponding to the carboxylate anion of **151**, but a ^{13}C NMR spectrum had peaks at δ_{C} 198 and 207, suggesting a mixture of carbonyl products. In view of the small scale of the reaction no further work was carried out.

In a literature bromoform procedure¹²⁴ a mixture of 2-acetylfluorene **31b** and 1,4-dioxane was stirred in an ice bath. A freshly prepared aqueous solution of sodium hypobromite was added.



Recrystallization from hot glacial acetic acid gave a mixture of products. A ^{13}C NMR spectrum of the mixture had carbonyl peaks at δ_{C} 166.4, 167.6 and 192.1, and a mass spectrum had peaks at m/z 210 and 224. The spectra were consistent with the formation of a (1:1) mixture of fluorene-2-carboxylic acid **151** and fluorenone-2-carboxylic acid **152**.

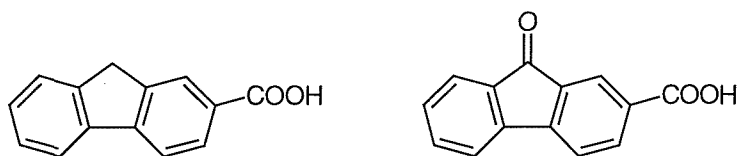
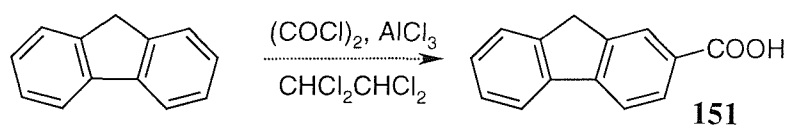


Fig. 92: (i) Fluorene-2-carboxylic acid **151**; (ii) fluorenone-2-carboxylic acid **152**.

Such oxidation of the methylene bridge has been reported as a competing side reaction.¹²⁴

6.5.2 Oxalyl chloride

Fluorene was treated with oxalyl chloride^{147, 148} in a procedure analogous to the Friedel-Crafts acylation (Section 2.3). A mixture of fluorene, aluminium chloride and 1,1,2,2-tetrachloroethane was treated with oxalyl chloride.



The reaction produced a mixture of unknown compounds. A mass spectrum had peaks at m/z 358 and 386, suggesting the presence of the benzophenone and benzil analogues **153** and **154**. These are possible products, as the oxalyl chloride molecule can react with two fluorenes to form a bridged species. Similar results were reported when biphenyl was treated with oxalyl chloride.¹⁴⁹

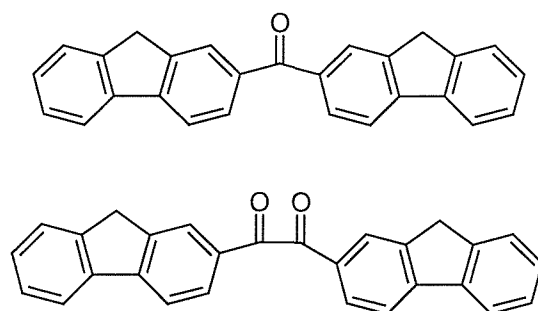
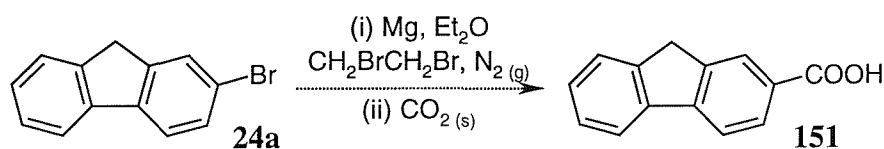


Fig. 93: (i) Difluorenylketone **153**; (ii) di(fluorenylcarbaldehyde) **154**.

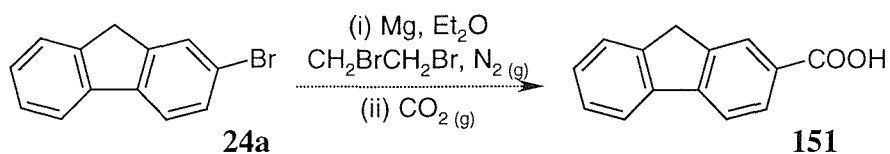
6.5.3 Grignard

Carboxylic acids may be prepared by the reaction of a Grignard reagents with carbon dioxide.¹⁵⁰ Preparation of fluorene-2-magnesium bromide from 2-bromofluorene **24a** was attempted. A mixture of magnesium turnings and dry diethyl ether was stirred at room temperature. A solution of 2-bromofluorene **24a** and 1,2-dibromoethane in dry diethyl ether was added, and the reaction mixture was then stirred at room temperature. The Grignard intermediate was then quenched by pouring onto dry ice.



No products were isolated. Unreacted 2-bromofluorene **24a** was recovered from the reaction mixture, suggesting that conversion to the Grignard intermediate did not proceed to completion. The presence of fluorene in the reaction mixture suggested that the Grignard intermediate was quenched by water (probably in the “dry” ice).

This reaction was repeated using more rigorously anhydrous conditions. A stream of freshly prepared carbon dioxide¹⁵¹ was bubbled through Grignard solution.



Following workup, and recrystallization 10% unreacted 2-bromofluorene **24a** was recovered. None of the expected product was isolated suggesting that conversion to the Grignard intermediate did not proceed to completion. No more attempt was made to prepared fluorene-2-carboxylic acid **151**.

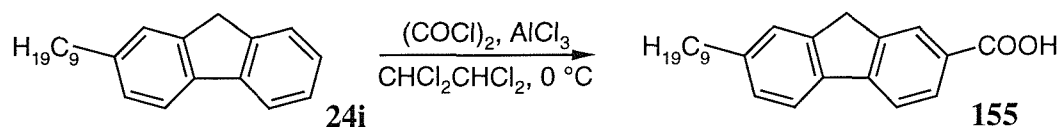
Table 22: Attempted synthesis of fluorene-2-carboxylic acid **151**.

	Conditions	Result	Yield
i	NaOCl, KI/I ₂ , dioxane, H ₂ O, reflux	Mixture of products, possibly 151	-
ii	NaOBr, dioxane, 0 °C*	(1:1) mixture of 151 and 152	-
iii	(COCl) ₂ , AlCl ₃ , CHCl ₂ CHCl ₂ , rt	Mixture of products, 153 and 154	-
iv	24a → Grignard then CO ₂ (s) [†]	Mixture of 24a and fluorene	-
v	24a → Grignard then CO ₂ (g)*	2-Bromofluorene 24a	10%

* recrystallized from hot glacial acetic acid (charcoal)

[†] recrystallized from hot glacial acetic acid-water

Preparation of 7-nonylfluorene-2-carboxylic acid **155** was attempted using oxalyl chloride. A mixture of 2-nonylfluorene **32i**, oxalyl chloride and 1,1,2,2-tetrachloroethane was stirred in an ice bath. Aluminium chloride was added, and the stirred reaction mixture was allowed to warm to room temperature. Following recrystallization, 7-nonylfluorene-2-carboxylic acid **32i** was isolated in 14% yield.



No bridged species were detected. Because of the small amount of **32i** available no further work was carried out on partial reduction methodology.

6.6 9,10-DIHYDROPHENATHRENE DERIVATIVES

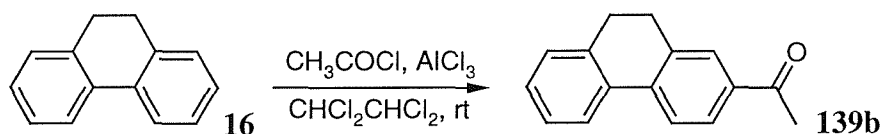
Many liquid crystals based on the 9,10-dihydrophenanthrene core have been reported. A database search³¹ yielded 91 simple 2,7-disubstituted 9,10-dihydrophenanthrenes. Some of these compounds formed enantiotropic nematic phases, in contrast to the smectic phases

exhibited by the analogous 2,7-disubstituted fluorenes (Section 1.13).

The structure of 9,10-dihydrophenanthrene **16** is close to that of biphenyl **3** (Section 1.9).

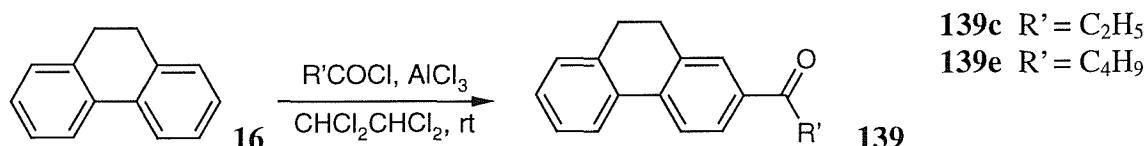
The two benzene rings are coaxial and retain a degree of flexibility. The material has a low melting point, 34 °C,²¹ which appears to make it an ideal core for the formation of room temperature mesogens (*cf.* biphenyl, mp 71 °C⁷ and fluorene, mp 115 °C²³). Unfortunately 9,10-dihydrophenanthrene is around 20 times as expensive as fluorene, and is not available in as high a state of purity.⁴⁹ As difficulties were encountered in the purification of simple 2-acyl derivatives only limited work was undertaken. Five Friedel-Crafts acylations were carried out (Table 23).

A literature preparation of 2-acetyl-9,10-dihydrophenanthrene **139b** was followed.⁵⁰ A mixture of 9,10-dihydrophenanthrene **16**, acetyl chloride and 1,1,2,2-tetrachloroethane was stirred at room temperature with aluminium chloride catalyst.



The crude product was an oil, whereas the authentic material was a low melting point solid. Following column chromatography and recrystallization, impure 2-acetyl-9,10-dihydrophenanthrene **139b** was obtained as a solid in *ca.* 21% yield. TLC analysis indicated a single component, but a ¹H NMR spectrum had additional signals at δ_H 8.20, 8.50 and 8.70. The nature of the impurities was not known. This reaction was repeated, and in this case the oil was triturated with 40-60 petroleum ether to give impure 2-acetyl-9,10-dihydrophenanthrene **139b** as an oily solid. An attempted recrystallization from hot dichloromethane-60-80 petroleum ether was unsuccessful. The oily solid contained a large amount of residual 1,1,2,2-tetrachloroethane.

The Friedel-Crafts acylation procedure was also carried out with propionyl chloride and pentanoyl chloride giving crude samples of **139c** and **139e**.



Purification of these two compounds was also attempted by recrystallization, but no pure material was isolated. ¹H NMR spectra of **139c** and **139e** indicated the presence of unknown impurities at δ_H 8.23, 8.52 and 8.75, similar to the signals observed for the impure

2-acetyl-9,10-dihydrophenanthrene **139b**.

The acetylation procedure was repeated on a larger scale, and, after workup, residual 1,1,2,2-tetrachloroethane was removed by trituration with 40-60 petroleum ether. Impure 2-acetyl-9,10-dihydrophenanthrene **139b** was obtained in *ca.* 31% yield. A mass spectrum had a peak at *m/z* 222, corresponding to the expected product. However a ^1H NMR spectrum had additional signals at δ_{H} 7.70, 8.20, 8.50 and 8.70, and a ^{13}C NMR spectrum had an extra 16 minor peaks. The spectral evidence suggested the formation of a small amount (*ca.* 10%) of isomeric material.

Table 23: Synthesis of 2-acyl-9,10-dihydrophenanthrenes **139**.

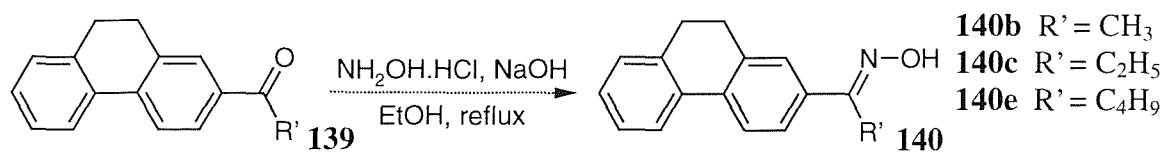
	Compound	Conditions	Yield
i	2-Acetyl-9,10-dihydrophenanthrene 139b	1.27 eq $\text{R}'\text{COCl}$; rt*	<i>ca.</i> 21%
ii	2-Acetyl-9,10-dihydrophenanthrene 139b	1.19 eq $\text{R}'\text{COCl}$; rt [†]	-
iii	2-Propionyl-9,10-dihydrophenanthrene 139c	1.00 eq $\text{R}'\text{COCl}$; rt	-
iv	2-Pentanoyl-9,10-dihydrophenanthrene 139e	1.05 eq $\text{R}'\text{COCl}$; rt	-
v	2-Acetyl-9,10-dihydrophenanthrene 139b	1.01 eq $\text{R}'\text{COCl}$; 0 °C [†]	<i>ca.</i> 31%

* chromatographed (silica gel, dichloromethane-40-60 petroleum ether) then recrystallized from hot dichloromethane-80-100 petroleum ether

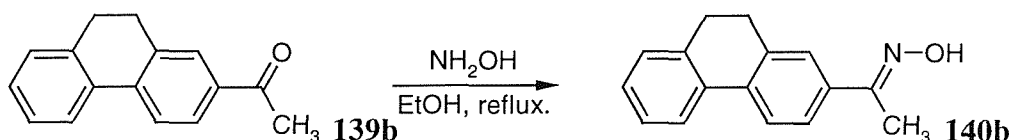
[†] trituated with 40-60 petroleum ether

In the reactions described above (Table 24, entries i-v) it was not possible to isolate any pure monoacylated 9,10-dihydrophenanthrene **139**. A potential method for the purification of these compounds is the conversion of the ketone moiety to an oxime. Oximes are high melting point crystalline compounds which are generally readily purified by recrystallization.¹⁵² This approach has been used in a literature preparation of 2-acyl-9,10-dihydrophenanthrene **139b**.¹⁵³

Accordingly, conversion of the crude 2-acyl-9,10-dihydrophenanthrenes **139** to the oxime derivatives **140** was attempted (Table 24). A mixture of the crude 2-acyl-9,10-dihydrophenanthrene **139**, sodium hydroxide, hydroxylamine hydrochloride and ethanol was heated at reflux. Following workup, a combination of recrystallization and column chromatography failed to isolate any pure material. It is possible that the presence of residual 1,1,2,2-tetrachloroethane promoted side reactions which led to the formation of impurities.



The attempted conversion of 2-acetyl-9,10-dihydrophenanthrene **139b** to the oxime derivative **140b** was repeated using a slightly modified procedure. Hydroxylamine was freshly prepared by the addition of sodium hydroxide to hydroxylamine hydrochloride.¹⁵⁴ The free base was added to a mixture of **139b** and ethanol, which was then heated at reflux. Following recrystallization from hot dichloromethane-60-80 petroleum ether, 2-acetoxime-9,10-dihydrophenanthrene **140b** was isolated in 29% yield.



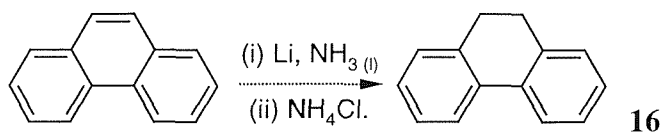
The oxime **140b** was crystalline and heating with dilute sulphuric acid should regenerate pure 2-acetyl-9,10-dihydrophenanthrene **139b**. However only a small amount of material was available and no further work was carried out.

Table 24: Preparation of oxime derivatives.

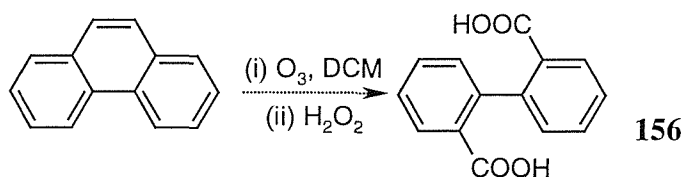
	Compound	Conditions	Yield
i	2-Acetoxime-9,10-dihydrophenanthrene 140b	NH_4OCl , NaOH; reflux	-
ii	2-Propionyloxime-9,10-dihydrophenanthrene 140c	NH_4OCl , NaOH; reflux	-
iii	2-Pentanoyloxime-9,10-dihydrophenanthrene 140e	NH_4OCl , NaOH; reflux	-
iv	2-Acetoxime-9,10-dihydrophenanthrene 140b	NH_2OH , reflux*	29%

* Recrystallized from hot dichloromethane-60-80 petroleum ether (charcoal)

Work into 9,10-dihydrophenanthrene derivatives was curtailed by the high cost and low state of purity of the starting material relative to fluorene. Some work on an alternative route to 9,10-dihydrophenanthrene was undertaken by a co-worker.¹⁵⁵ Using the Birch reduction it was possible to selectively reduce the reactive ethylene bridge of phenanthrene to give 9,10-dihydrophenanthrene **16**.



In the limited work carried out an inseparable mixture of starting material and **16** was produced. With fine tuning of the reaction conditions it should be possible to increase the proportion of the desired reduced product **16**. Using ozonolysis it may be possible to convert unreacted **16** to the base extractable diphenic acid **156**. However there is a possibility that ozone may reoxidize 9,10-dihydrophenanthrene. Optimization of the procedure could make available a plentiful source of high purity 9,10-dihydrophenanthrene, enabling further work to be carried out.



6.7 SUMMARY AND CONCLUSIONS

The reported 2,7-disubstituted fluorenes exhibited only smectic phases, and it was found that a third benzene ring was needed to give an enantiotropic nematic phase (Section 1.14). Replacement of the cyano group in a 2-(4-cyanophenyl)-7-alkylfluorene **30** with a methoxy group was carried out in an attempt to reduce the birefringence of the mesogens. Three 2-(4-methoxyphenyl)-7-alkylfluorenes **137** were prepared. The three compounds were found to be weakly mesogenic, and exhibited ill-defined smectic phases across a narrow range at an elevated temperature. Replacing the methoxy group with a long alkoxy chain was expected to stabilize the formation of mesophases. 2-(4-Heptoxyphenyl)-7-pentylfluorene **138e** was prepared and was found to exhibit a stable smectic A phase. Friedel-Crafts acylation of 9,10-dihydrophenanthrene did not progress beyond an early stage. The simple 2-acyl-9,10-dihydrophenanthrenes **139** were found to be difficult to purify. 2-Acetyl-9,10-dihydrophenanthrene **139b** was successfully converted to the oxime derivative 2-acetoxime-9,10-dihydrophenanthrene **140b**. 9,10-Dihydrophenanthrene derivatives were expensive to prepare and purify. In contrast fluorenes were cheaper to prepare and considerably easier to purify, and work concentrated on fluorene-based mesogens. Work on partial reduction methodology was curtailed by problems in making fluorene carboxylic acids. This area has considerable scope for novel research.

7. CONCLUSIONS AND FUTURE WORK

Many mesogens based on the biphenyl and terphenyl core units have been made, and their properties evaluated. The 4-alkyl-4'-cyanobiphenyls and 4-alkyl-4"-cyano-*p*-terphenyls have been used extensively as components of liquid crystal display mixtures. The fluorene moiety differs from a biphenyl unit in being flat and slightly bent in the plane of the rings, but it has been investigated only to a limited extent as a possible mesogenic core. Previous work on fluorene containing mesogens showed them to exhibit mainly smectic phases. This work concluded that simple fluorene-based materials do not exhibit enantiotropic nematic phases.

Addition of a third benzene ring gave the 2-phenylfluorene core unit. To favour the formation of a nematic phase, a cyano group was added to the *para* position of the benzene ring and a suitable alkyl chain to the fluorene core. The homologous series of 2-(4-cyanophenyl)-7-alkylfluorenes was successfully prepared *via* a five step convergent route. This route gave pure materials, but there is scope for improvement, particularly in the bromination step, which showed poor reproducibility, and in the Suzuki coupling, which was low yielding.

The novel 2-phenylfluorene compounds were found to exhibit enantiotropic nematic phase across a broad range. Their melting points were virtually identical to the analogous 4-alkyl-4"-cyano-*p*-terphenyls, and the 2-phenylfluorenes have slightly lower clearing points. Some physical properties of 2-(4-cyanophenyl)-7-pentylfluorene and 4-pentyl-4"-cyano-*p*-terphenyl were measured. Both compounds had almost identical birefringences and dielectric anisotropies. However, the crescent shaped 2-phenylfluorene had a much higher rotational viscosity than the terphenyl. The luminescence properties of the 2-phenylfluorene proved to be interesting, especially in the light of recent interest in fluorene containing molecules as light emitters for flat panel displays. 2-(4-Cyanophenyl)-7-pentylfluorene showed strong fluorescence, and has a higher extinction coefficient and emits light at a longer wavelength than the analogous terphenyl.

The properties shown by 2-(4-cyanophenyl)-7-pentylfluorene do not make it suitable for incorporation in conventional display devices. However, the 2-(4-cyanophenyl)-7-alkylfluorenes may be considered as model systems for luminescent mesogens, which have potential interest as new display materials.

It is surprising that there have been no reports of 2-phenylfluorenes liquid crystals in the

literature. This omission is remarkable, in view of the huge amount of research carried out on biphenyl and terphenyl based materials. The 2-phenylfluorene liquid crystals are comparable with the terphenyls, but the opportunity to functionalize at the fluorene bridgehead, together with the crescent-shaped coplanarity of the fluorene core is expected to change their properties significantly.

Lateral substitution is a powerful technique for altering the properties of a mesogen.

Alkylation of the fluorene core was explored, and four C₉ alkylated 2-(4-cyanophenyl)-7-alkylfluorenes were prepared. These materials were all oils and were difficult to satisfactorily purify. The exception to this was 2-(4-cyanophenyl)-7-pentyl-9,9-dioctylfluorene, which was prepared cleanly by dialkylation of 2-(4-cyanophenyl)-7-pentylfluorene. The fact that these materials were oils proves that lateral alkylation dramatically lowers the melting point of the compounds. However, the materials were found to be isotropic and no mesophases were detected. This is an area that should be studied in more detail, as pure 2-(4-cyanophenyl)-7-alkyl-9,9-dialkylfluorenes with suitable chain lengths are almost certain to be mesogenic.

An alternative strategy for modifying the properties of the 2-(4-cyanophenyl)-7-alkylfluorenes is partial reduction of the aromatic core. In order to accomplish this it was first necessary to explore the Birch reduction of fluorene carboxylic acids. This was not possible, as attempts to synthesize the carboxylic acids were only partially successful. Partial reduction is a powerful technique, and future work in this area may well prove to be extremely rewarding.

Synthesis of the 2-alkoxy-7-(4-cyanophenyl)fluorenes was explored. These compounds were expected to show similar properties to the 2-(4-cyanophenyl)-7-alkylfluorenes, but it was possible to introduce the alkyl chain at a later stage in the synthesis, thus avoiding the need to carry out many duplicate reactions. A small amount of impure 2-pentoxy-7-(4-cyanophenyl)fluorene was prepared, and preliminary studies on this material indicated that it exhibited a nematic phase across a large range. This early work on the 2-alkoxy-7-(4-cyanophenyl)fluorenes was promising, but the synthetic route requires modification to make it efficient and high yielding.

2-(4-Alkoxyphenyl)-7-alkylfluorenes were prepared as low birefringence analogues of the 2-(4-cyanophenyl)-7-alkylfluorenes. The methoxy compounds exhibited ill-defined smectic phases across a narrow range at an elevated temperature. Using a longer alkoxy chain was expected to produce stable mesophases, and 2-(4-heptoxyphenyl)-7-pentylfluorene was found to exhibit a smectic A phase, but at high temperature.

Use of the Wolff-Kishner reduction to convert a 2-acylfluorene to a 2-alkylfluorene gave, in some cases, the unexpected 2-alkyl-9-ethylfluorene product. This side-reaction could be avoided by the use of sodium carbonate in place of the caustic base. Some studies into this reaction were carried out, and it was found that the unlikely source of the ethyl group was the solvent, diethylene glycol. However the process could not be controlled to give a clean route to 2-alkyl-9-ethylfluorenes.

In summary, 2-phenylfluorene mesogens offer much scope for further research, because of the possibilities for modification of the core unit. The current interest in fluorene containing materials means that this work is of direct relevance.

8. EXPERIMENTAL

8.1 SPECTROSCOPIC DATA

Melting points were determined on an Electrothermal melting point apparatus and are uncorrected.

Combustion (CHN) analyses were carried out by Jill Maxwell or Alan Stones at UCL.

Samples were thoroughly dried *in vacuo* prior to submission.

Ultra-Violet spectra were recorded on a Shimadzu 1601 UV-Visible spectrophotometer.

Samples were prepared as a solution in a quartz cell.

Infra-Red spectra were recorded on a Perkin Elmer 1600 FTIR spectrometer. Samples were prepared as either (i) a solution in an NaCl cell; or (ii) a thin film or nujol mull on a KBr disc.

^1H NMR and ^{13}C NMR spectra were routinely recorded on a Bruker AC300 spectrometer at 300 MHz and 75.42 MHz respectively. Spectra were also recorded on a Bruker AC400 spectrometer at 400 MHz and 100.56 MHz respectively. ^{13}C NMR spectra were fully decoupled. Peaks are quoted in p.p.m. (δ) and are referenced to residual solvent.

Multiplicities are quoted as s-singlet, d-doublet, t-triplet, q-quartet, m-multiplet. Coupling constants (J) are quoted in Hz.

Mass spectra were carried out by John Langley or Julie Herniman in the Department, using a VG 70-SE spectrometer. GCMS analysis was carried out using a ThermoQuest TraceMS gas chromatography spectrometer (Section 9.1). The mode of ionization is indicated in parentheses (EI-electron impact, ES-electrospray).

Polarizing Optical Microscopy was carried out using an Zeiss microscope with a Linkam temperature controller. Transition temperatures were corrected by calibration with standard materials.

Differential Scanning Calorimetry was carried out using a Perkin Elmer DSC 7 Calorimeter.

Luminescence spectra were recorded on a Perkin Elmer LS 50B luminescence spectrometer. Samples were prepared as a solution in a quartz cell.

X-ray analysis was carried out by David Dunmur and Goran Ungar at the University of Sheffield.⁸³ The diffraction pattern was recorded on a partially aligned sample in a Lindemann tube using a Marr Research Image Plate Camera and a standard Cu K α X-ray source.

Single crystal X-ray analysis was carried out by Peter Horton using a Nonius KappaCCD diffractometer and Nonius FR591 rotating anode X-ray generator. The structures were solved using WinGX¹⁵⁶ and refined using SHELX-97.¹⁵⁷

Measurement of birefringence, electric anisotropy, viscosity, response time and driving voltage was undertaken by Hitachi Research Laboratories in Japan.⁸² The measurements were made on 5wt% solutions in the nematic host mixture ZLI-4792.

Energy minimizations were carried out by Hitachi using MOPAC97⁸⁴ or by David Dunmur using Cerius^{2,91}.

Thin layer chromatographic analysis was performed using aluminium microplates coated with silica GF₂₅₄. Plates were visualized using 254 nm light, unless otherwise stated.

Column chromatography was performed over silica gel.

8.2 GENERAL METHODS

Unless otherwise stated all reagents were obtained from a commercial source and were used without further purification.

Benzyltrimethylammonium tribromide was prepared from benzyltrimethylammonium chloride according to a literature procedure.⁶⁴

N-Bromosuccinimide was recrystallized from hot water.

n-Butyllithium in hexanes was titrated against borneol in dry tetrahydrofuran using fluorene as an indicator.

Carbon dioxide was prepared by adding aqueous hydrochloric acid to calcium carbonate.

The gas was dried by bubbling through concentrated sulphuric acid.¹⁵¹

m-Chloroperbenzoic acid was dissolved in diethyl ether, then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was recrystallized from warm dichloromethane. mCPBA purified in this way was free from water, but contained residual *m*-chlorobenzoic acid. The reagent was assumed to be 70% active.

Copper(II)bromide on alumina was prepared from copper(II)bromide according to a literature procedure.⁶²

Sodium hydroxide was purified according to a literature procedure.¹³⁵

Tetrakis(triphenylphosphine)palladium(0) was prepared from palladium(II)chloride according to a literature procedure.⁷⁵

All solvents for column chromatography, recrystallizations, IR, UV-Visible and luminescence analysis were distilled.

Carbon tetrachloride was dried by continuous reflux over phosphorus pentoxide, and

freshly distilled before use.

Dichloromethane was dried by continuous reflux over calcium hydride, and was freshly distilled before use.

Diethyl ether was dried over sodium wire, and was freshly decanted before use.

Alternatively, diethyl ether was dried by continuous reflux over sodium wire using benzophenone as an indicator, and was freshly distilled before use.

N,N-Dimethylformamide was dried over activated 4 Å molecular sieves, and was freshly decanted before use.

Ethanol was dried by continuous reflux over calcium sulphate, and was freshly distilled before use.

Methanol was dried by continuous reflux over calcium sulphate, and was freshly distilled before use.

1,1,2,2-Tetrachloroethane was dried over calcium chloride, and was freshly distilled then filtered through a plug of alumina before use.

Tetrahydrofuran was dried by continuous reflux over sodium wire using benzophenone as an indicator, and was freshly distilled before use.

8.3 SYNTHESIS OF 2-(4-CYANOPHENYL)-7-ALKYLFLUORENES

8.3.1 2-Acylfluorenes

2-Acetylfluorene

A solution of fluorene (0.95 g, 5.7 mmol) and acetyl chloride (0.41 ml, 5.8 mmol) in dry 1,1,2,2-tetrachloroethane (25 ml) was stirred at room temperature. Aluminium chloride (1.14 g, 8.5 mmol) was added, and the reaction mixture was stirred at room temperature for 19.8 hours. Further aluminium chloride (0.39 g, 2.9 mmol) was added, and the reaction mixture was stirred at room temperature for 23.2 hours. Water (15 ml) and concentrated hydrochloric acid (15 ml) were added and the products were extracted into dichloromethane (3 x 20 ml). The combined organic extracts were washed with sodium bicarbonate solution (aq, 10%, 2 x 20 ml) and water (20 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was recrystallized twice from hot dichloromethane-80-100 petroleum ether to give a pale yellow solid, 2-acetylfluorene **31b** (0.98 g, 82%, mp 126-127 °C (from DCM-PET (80-100), lit.,¹⁵⁸ 130-131 °C)). (Found: C, 86.0; H, 5.7. C₁₅H₁₂O requires C, 86.5; H, 5.8%); $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 227 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 3000), 295sh, 307sh, 316 (7100); $\nu_{\max}(\text{nujol})/\text{cm}^{-1}$ 1680s (C=O), 1609w,

1567w, 1464m, 1422w, 1400w, 1360m, 1292m, 1267m, 1229m ; δ_{H} (300 MHz; CDCl_3) 2.69 (3H, s, COCH_3), 3.97 (2H, s, CH_2 (C9)), 7.37-7.46 (2H, m, ArH), 7.60 (1H, d, $J = 6.6$, ArH), 7.83-7.90 (2H, m, ArH), 8.02 (1H, d, $J = 8.1$, ArH), 8.16 (1H, s, ArH); δ_{C} (75.42 MHz; CDCl_3) 26.8, 36.9, 119.7, 120.9, 125.0, 125.3, 127.1, 127.8, 128.0, 135.6, 140.5, 143.3, 144.5, 146.4, 198.1 (C=O); m/z (EI) 208 (M^+ , 71%), 193 (ArCO^+ , 100), 165 (Ar^+ , 83).

2-Propionylfluorene

A solution of fluorene (0.93 g, 5.6 mmol) and propionyl chloride (0.49 ml, 5.6 mmol) in dry 1,1,2,2-tetrachloroethane (25 ml) was stirred at room temperature. Aluminium chloride (1.12 g, 8.4 mmol) was added, and the reaction mixture was stirred at room temperature for 19.8 hours. Further aluminium chloride (0.38 g, 2.8 mmol) was added, and the reaction mixture was stirred at room temperature for 23.2 hours. Water (15 ml) and concentrated hydrochloric acid (15 ml) were added and the products were extracted into dichloromethane (2 x 20 ml). The combined organic extracts were washed with sodium bicarbonate solution (aq, 10%, 3 x 20 ml) and water (20 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was recrystallized from hot dichloromethane-80-100 petroleum ether to give a brown solid, 2-propionylfluorene **31c** (0.71 g, 57%, mp 114-116 °C (from DCM-PET (80-100), lit.,¹⁵⁹ 118-119 °C)).

(Found: C, 86.2; H, 6.1. $\text{C}_{16}\text{H}_{14}\text{O}$ requires C, 86.45; H, 6.35%); $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 225 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 4900), 294sh, 307sh, 315 (11600); $\nu_{\text{max}}(\text{nujol})/\text{cm}^{-1}$ 1676s (C=O), 1609w, 1560w, 1223m; δ_{H} (300 MHz; CDCl_3) 1.28 (3H, t, $J = 7.4$, COCH_2CH_3), 3.07 (2H, q, $J = 7.4$, COCH_2CH_3), 3.96 (2H, s, CH_2 (C9)), 7.36-7.45 (2H, m, ArH), 7.60 (1H, d, $J = 7.4$, ArH), 7.82-7.87 (2H, m, ArH), 8.03 (1H, d, $J = 8.1$, ArH), 8.16 (1H, s, ArH); δ_{C} (75.42 MHz; CDCl_3) 8.5, 31.9, 36.9, 119.7, 120.8, 124.7, 125.2, 127.0, 127.3, 127.9, 135.4, 140.6, 143.3, 144.5, 146.2, 200.7 (C=O); m/z (EI) 222 (M^+ , 38%), 193 (ArCO^+ , 100), 165 (Ar^+ , 50).

2-Butyrylfluorene

A solution of fluorene (9.97 g, 60 mmol) and butyryl chloride (6.2 ml, 60 mmol) in dry 1,1,2,2-tetrachloroethane (250 ml) was stirred in an ice bath. Aluminium chloride (12.01 g, 90 mmol) was added, and the reaction mixture was allowed to warm to room temperature, with stirring, over 20.0 hours. Further aluminium chloride (4.02 g, 30 mmol) was added, and the reaction mixture was stirred at room temperature for 49.7 hours. Water (150 ml) and concentrated hydrochloric acid (150 ml) were added, and the products were extracted

into dichloromethane (3 x 200 ml). The combined organic extracts were washed with sodium bicarbonate solution (aq, 10%, 2 x 200 ml) and water (200 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was recrystallized from hot chloroform-60-80 petroleum ether (charcoal) to give a yellow solid, 2-butyrylfluorene **31d** (10.11 g, 71 %, mp 116-118 °C (from CHCl₃-PET (60-80), lit.,¹⁵⁹ 118-119 °C)).

$\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 228 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 11200), 239sh, 295sh, 308sh, 315 (28200); $\nu_{\max}(\text{CHCl}_3 \text{ soln.})/\text{cm}^{-1}$ 2965m, 2875w, 1673vs (C=O), 1610s, 1571w, 1466m, 1421m, 1403m, 1365m, 1274m, 1143m, 1094w, 1007w, 958w, 837w; δ_{H} (300 MHz; CDCl₃) 1.05 (3H, t, $J = 7.4$, COCH₂CH₂CH₃), 1.74-1.90 (2H, m, COCH₂CH₂CH₃), 3.00 (2H, t, $J = 7.4$, COCH₂CH₂CH₃), 3.95 (2H, s, CH₂ (C9)), 7.84-7.97 (2H, m, ArH), 7.58 (1H, d, $J = 6.6$, ArH), 7.79-7.88 (2H, d, $J = 6.6$, ArH), 8.02 (1H, d, $J = 8.1$, ArH), 8.14 (1H, s, ArH); δ_{C} (75.42 MHz; CDCl₃) 14.1, 18.2, 37.1, 40.8, 119.8, 121.0, 124.9, 125.4, 127.2, 127.6, 128.1, 135.7, 140.7, 143.4, 144.6, 146.3, 200.4 (C=O); m/z (EI) 236 (M^+ , 36%), 208 (ArCOCH₃⁺, 6), 193 (ArCO⁺, 100), 165 (Ar⁺, 55).

A second crop of 2-butyrylfluorene **31d** (off-white solid (1.65 g, 12%)) was isolated from the mother liquor. This co-chromatographed ($R_f = 0.64$ in DCM) and had ¹H and ¹³C NMR spectra identical to those obtained for the authentic material described above.

2-Pentanoylfluorene

A solution of fluorene (0.96 g, 5.8 mmol) and pentanoyl chloride (0.70 ml, 5.8 mmol) in dry 1,1,2,2-tetrachloroethane (25 ml) was stirred at room temperature. Aluminium chloride (1.11 g, 8.3 mmol) was added, and the reaction mixture was stirred at room temperature for 19.8 hours. Further aluminium chloride (0.40 g, 3.0 mmol) was added, and the reaction mixture was stirred at room temperature for 23.2 hours. Water (15 ml) and concentrated hydrochloric acid (15 ml) were added and the products were extracted into dichloromethane (3 x 20 ml). The combined organic extracts were washed with sodium bicarbonate solution (aq, 10%, 2 x 20 ml) and water (20 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was recrystallized from hot dichloromethane-80-100 petroleum ether to give a yellow green solid, 2-pentanoylfluorene **31e** (1.02 g, 71%, mp 107-108 °C (from DCM-PET (80-100), lit.,¹⁶⁰ 106 °C)).

(Found: C, 86.3; H, 7.2. C₁₈H₁₈O requires C, 86.4; H, 7.25%); $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 224 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 10400), 295sh, 307sh, 315 (23000); $\nu_{\max}(\text{nujol})/\text{cm}^{-1}$ 1665s (C=O), 1610m, 1464s, 1375m, 1337w, 1274w, 1217w, 1145w; δ_{H} (300 MHz; CDCl₃) 0.99 (3H, t, $J = 7.4$,

COCH₂CH₂CH₂CH₃), 1.42-1.52 (2H, m, COCH₂CH₂CH₂CH₃), 1.73-1.82 (2H, m, COCH₂CH₂CH₂CH₃), 3.03 (2H, t, J = 7.4, COCH₂CH₂CH₂CH₃), 3.96 (2H, s, CH₂ (C9)), 7.35-7.45 (2H, m, ArH), 7.60 (1H, d, J = 6.6, ArH), 7.82-7.87 (2H, m, ArH), 8.02 (1H, d, J = 8.1, ArH), 8.16 (1H, s, ArH); δ_C (75.42 MHz; CDCl₃) 14.0, 22.6, 26.7, 36.9, 38.5, 119.6, 120.8, 124.7, 125.2, 127.0, 127.4, 127.9, 135.6, 140.6, 143.3, 144.5, 146.1, 200.5 (C=O); m/z (EI) 250 (M⁺, 27%), 193 (ArCO⁺, 100), 165 (Ar⁺, 55).

2-Hexanoylfluorene

A solution of fluorene (9.99 g, 60 mmol) and hexanoyl chloride (8.4 ml, 60 mmol) in dry 1,1,2,2-tetrachloroethane (250 ml) was stirred in an ice bath. Aluminium chloride (12.17 g, 91 mmol) was added, and the reaction mixture was allowed to warm to room temperature, with stirring, over 20.0 hours. Further aluminium chloride (4.14 g, 31 mmol) was added, and the reaction mixture was stirred at room temperature for 49.5 hours. Water (150 ml) and concentrated hydrochloric acid (150 ml) were added, and the products were extracted into dichloromethane (3 x 200 ml). The combined organic extracts were washed with sodium bicarbonate solution (aq, 10%, 2 x 200 ml) and water (200 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was recrystallized from hot chloroform-60-80 petroleum ether (charcoal) to give a yellow solid, 2-hexanoylfluorene **31f** (11.17 g, 70 %, mp 115-117 °C (from CHCl₃-PET (60-80), lit.,³⁰ 117-118 °C)).

λ_{\max} (CH₂Cl₂)/nm 228 (ϵ /dm³mol⁻¹cm⁻¹ 11600), 240sh, 295sh, 307sh, 315 (28400); ν_{\max} (CHCl₃ soln.)/cm⁻¹ 2958s, 2891s, 2871m, 1671vs (C=O), 1610vs, 1571m, 1467m, 1421m, 1403m, 1364m, 1296m, 1250m, 1141m, 1096m, 1006m, 958m, 831m; δ_H (300 MHz; CDCl₃) 0.95 (3H, t, J = 7.0, COCH₂CH₂(CH₂)₂CH₃), 1.35-1.48 (4H, m COCH₂CH₂(CH₂)₂CH₃), 1.72-1.85 (2H, m, COCH₂CH₂(CH₂)₂CH₃), 3.00 (2H, t, J = 7.4, COCH₂CH₂(CH₂)₂CH₃), 3.94 (2H, s, CH₂ (C9)), 7.35-7.47 (2H, m, ArH), 7.60 (1H, d, J = 7.4, ArH), 7.80-7.90 (2H, d, J = 6.3, ArH), 8.02 (1H, d, J = 8.1, ArH), 8.16 (1H, s, ArH); δ_C (75.42 MHz; CDCl₃) 14.1, 22.8, 24.5, 31.8, 37.1, 38.9, 119.8, 121.0, 124.9, 125.4, 127.2, 127.6, 128.1, 135.7, 140.7, 143.4, 144.6, 146.3, 200.6 (C=O); m/z (EI) 264 (M⁺, 23%), 221 (ArCOC₂H₄⁺, 10), 208 (ArCOCH₃⁺, 90), 193 (ArCO⁺, 100), 165 (Ar⁺, 65).

A second crop of 2-hexanoylfluorene **31g** (off-white solid (1.39 g, 9%)) was isolated from the mother liquor. This co-chromatographed (R_f = 0.69 in DCM) and had ¹H and ¹³C NMR spectra identical to those obtained for the authentic material described above.

2-Heptanoylfluorene

A solution of fluorene (6.53 g, 39 mmol) and heptanoyl chloride (6.0 ml, 39 mmol) in dry 1,1,2,2-tetrachloroethane (150 ml) was stirred in an ice bath. Aluminium chloride (7.78 g, 58 mmol) was added, and the reaction mixture was allowed to warm to room temperature, with stirring, over 29.6 hours. Further aluminium chloride (2.61 g, 20 mmol) was added, and the reaction mixture was stirred at room temperature for 39.5 hours. Water (100 ml) and concentrated hydrochloric acid (100 ml) were added, and the products were extracted into dichloromethane (3 x 150 ml). The combined organic extracts were washed with sodium bicarbonate solution (aq, 10%, 2 x 50 ml) and water (150 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was recrystallized from hot chloroform-60-80 petroleum ether (charcoal) to give a yellow solid, 2-heptanoylfluorene **31g** (7.67 g, 70 %, mp 105-107 °C (from CHCl₃-PET(60-80), lit.,³⁰ 110-112 °C)).

$\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 228 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 13400), 261sh, 271 (26500), 277sh, 294 (9100), 306 (11700); $\nu_{\max}(\text{CHCl}_3 \text{ soln.})/\text{cm}^{-1}$ 2930vs, 2856s, 1515w, 1467m, 1404m, 1298w, 1005w, 955w, 831w; δ_{H} (300 MHz; CDCl₃) 0.92 (3H, t, $J = 7.0$, COCH₂CH₂(CH₂)₃CH₃), 1.25-1.50 (6H, m, COCH₂CH₂(CH₂)₃CH₃), 1.78-1.85 (2H, m, COCH₂CH₂(CH₂)₃CH₃), 3.02 (2H, t, $J = 7.4$, COCH₂CH₂(CH₂)₃CH₃), 3.91 (2H, s, CH₂ (C9)), 7.27-7.46 (2H, m, ArH), 7.58 (1H, d, $J = 7.4$, ArH), 7.71-7.88 (2H, d, $J = 6.3$, ArH), 8.01 (1H, d, $J = 8.1$, ArH), 8.13 (1H, d, $J = 8.1$, ArH); δ_{C} (75.42 MHz; CDCl₃) 14.3, 22.7, 24.7, 29.3, 31.9, 37.0, 38.9, 119.8, 121.0, 124.9, 125.4, 127.2, 127.6, 128.1, 135.7, 140.7, 143.4, 144.6, 146.3, 200.6 (C=O); 278 (M⁺, 33%), 221 (ArCOCH₂CH₃⁺, 11), 208 (ArCOCH₂⁺, 99), 193 (ArCO⁺, 100), 165 (Ar⁺, 66).

A second crop of 2-heptanoylfluorene **31g** (yellow solid (1.28 g, 12%)) was isolated from the mother liquor. This co-chromatographed ($R_f = 0.60$ in DCM) and had ¹H and ¹³C NMR spectra identical to those obtained for the authentic material described above.

2-Octanoylfluorene

A solution of fluorene (10.48 g, 63 mmol) and octanoyl chloride (10.8 ml, 63 mmol) in dry 1,1,2,2-tetrachloroethane (250 ml) was stirred in an ice bath. Aluminium chloride (12.50 g, 94 mmol) was added, and the reaction mixture was allowed to warm to room temperature, with stirring, over 25.2 hours. Further aluminium chloride (4.31 g, 32 mmol) was added, and the reaction mixture was stirred at room temperature for 51.9 hours. Water (150 ml) and concentrated hydrochloric acid (150 ml) were added, and the products were extracted into dichloromethane (3 x 200 ml). The combined organic extracts were washed with

sodium bicarbonate solution (aq, 10%, 2 x 200 ml) and water (200 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was recrystallized from hot chloroform-60-80 petroleum ether (charcoal) to give a pale yellow solid, 2-octanoylfluorene **31h** (12.95 g, 70 %, mp 99-101 °C (from CHCl₃-PET (60-80), lit.,³⁰ 99-100 °C)).

$\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 229 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 12800), 240sh, 293sh, 308sh, 315 (32200); $\nu_{\max}/\text{cm}^{-1}$ (CHCl₃ soln.) 2929vs, 2856s, 1673vs (C=O), 1610s, 1571w, 1467m, 1421m, 1403m, 1366w, 1302w, 1269m, 1140m, 1096w, 1006w, 958w, 831w; δ_{H} (300 MHz; CDCl₃) 0.92 (3H, t, J = 6.6, COCH₂CH₂(CH₂)₄CH₃), 1.24-1.50 (8H, m, COCH₂CH₂(CH₂)₄CH₃), 1.72-1.85 (2H, m, COCH₂CH₂(CH₂)₄CH₃), 3.00 (2H, t, J = 7.4, COCH₂CH₂(CH₂)₄CH₃), 3.92 (2H, s, CH₂ (C9)), 7.34-7.47 (2H, m, ArH), 7.58 (1H, d, J = 6.6, ArH), 7.83 (2H, d, J = 7.0, ArH), 8.01 (1H, d, J = 8.1, ArH), 8.16 (1H, s, ArH); δ_{C} (75.42 MHz; CDCl₃) 14.4, 23.0, 24.9, 29.5, 29.7, 32.1, 37.2, 39.1, 119.9, 121.1, 125.0, 125.5, 127.3, 127.7, 128.2, 135.8, 140.8, 143.6, 144.8, 146.5, 200.8 (C=O); m/z (EI) 292 (M⁺, 23%), 221 (ArCOC₂H₄⁺, 11), 208 (ArCOCH₃⁺, 100), 193 (ArCO⁺, 79), 165 (Ar⁺, 60).

A second crop of 2-octanoylfluorene **31h** (pale yellow solid (1.91 g, 11%)) was isolated from the mother liquor. This co-chromatographed ($R_f = 0.70$ in DCM) and had ¹H and ¹³C NMR spectra identical to those obtained for the authentic material described above.

2-Nonanoylfluorene

A solution of fluorene (2.51 g, 15 mmol) and nonanoyl chloride (2.7 ml, 15 mmol) in dry 1,1,2,2-tetrachloroethane (60 ml) was stirred at room temperature. Aluminium chloride (3.08 g, 23 mmol) was added, and the reaction mixture was stirred at room temperature for 18.7 hours. Further aluminium chloride (1.00 g, 7.5 mmol) was added, and the reaction mixture was stirred at room temperature for a further 15.3 hours. Water (40 ml) and concentrated hydrochloric acid (40 ml) were added and the products were extracted into dichloromethane (3 x 60 ml). The combined organic extracts were washed with sodium bicarbonate solution (aq, 10%, 2 x 60 ml) and water (60 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was recrystallized from hot dichloromethane-60-80 petroleum ether give an off white solid, 2-nonanoylfluorene **31i** (3.05 g, 66%, mp 106-108 °C (from DCM-PET (60-80), lit.,¹⁶¹ 106 °C)).

(Found: C, 85.9; H, 8.6. C₂₂H₂₆O requires C, 86.2; H, 8.55%); $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 227 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 13900), 295sh, 307sh, 315 (32800); $\nu_{\max}(\text{nujol})/\text{cm}^{-1}$ 1672m (C=O),

1610w; δ_{H} (300 MHz; CDCl_3) 0.90 (3H, t, $J = 6.6$, $\text{COCH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 1.23-1.48 (10H, m, $\text{COCH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 1.78 (2H, m, $\text{COCH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 3.03 (2H, t, $J = 7.7$, $\text{COCH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 3.97 (2H, s, CH_2 (C9)), 7.36-7.46 (2H, m, ArH), 7.60 (1H, d, $J = 6.6$, ArH), 7.83-7.88 (2H, m, ArH), 8.02 (1H, d, $J = 8.1$, ArH), 8.16 (1H, s, ArH); δ_{C} (75.42 MHz; CDCl_3) 14.1, 22.7, 24.6, 29.2, 29.5, 31.9, 36.9, 38.8, 119.6, 120.8, 124.7, 125.2, 127.0, 127.4, 127.9, 135.6, 140.6, 143.3, 144.5, 146.2, 200.5 (C=O); m/z (EI) 306 (M^+ , 18%), 208 (ArCOCH_3^+ , 100), 193 (ArCO^+ , 93), 165 (Ar^+ , 54).

8.3.2 2-Alkylfluorenes

2-Methylfluorene (attempted synthesis)

A mixture of copper(I)iodide (9.98 g, 52.4 mmol) and dry diethyl ether (50 ml) was stirred in an ice bath under nitrogen. A solution of methyllithium in diethyl ether (1.6 M, 65 ml, 104 mmol) was added over 25 minutes. The resulting solution of lithium dimethyl copper was stirred in an ice bath for 30 minutes. A solution of impure 2-bromofluorene (4.26 g, *ca.* 17.4 mmol) in dry diethyl ether (100 ml) was added over 10 minutes. The stirred reaction mixture was allowed to warm to room temperature over 22.7 hours. The reaction mixture was poured onto vigorously stirred hydrochloric acid (aq, 2 M, 250 ml). Hydrochloric acid (aq, 2 M, 100 ml) and water (100 ml) were added, and the organic layer was separated. The aqueous layer was extracted with diethyl ether (2 x 100 ml). The combined organic extracts were washed with hydrochloric acid (aq, 2 M, 100 ml) and water (100 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was recrystallized from hot ethanol (charcoal) to give an orange solid, impure 2-bromofluorene **24a** (1.51 g, *ca.* 35% recovery).

TLC analysis indicated a single component which co-chromatographed with the starting material. The solid had ^1H and ^{13}C NMR spectra identical to those obtained for the starting material.

2-Ethylfluorene

METHOD I

A mixture of 2-acetylfluorene **31b** (3.62 g, 17.4 mmol), hydrazine hydrate (8.5 ml, 175 mmol), potassium hydroxide (9.82 g, 175 mmol) and diethylene glycol (60 ml) was heated at reflux for 2.6 hours. The reaction mixture was then heated strongly for 1.6 hours to distil out water. After cooling, water (150 ml) and concentrated hydrochloric acid (20 ml) were added, and the products were extracted into dichloromethane (3 x 150 ml). The combined organic extracts were washed with water (100ml), then dried over anhydrous sodium

sulphate and filtered. The solvent was removed. A portion of the residue (1.00 g) was dissolved in hot ethanol-hexane. The solution was filtered whilst hot. After cooling, the solvent was removed from the filtrate to give a yellow solid, 2-ethylfluorene **32b** (0.95 g, 28 %, mp 98-100 °C (from filtrate, EtOH-hexane, lit.,¹⁶¹ 99-100 °C)).

$\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 261sh, 270 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 26500), 276sh, 294 (8500), 306 (11100); $\nu_{\max}(\text{nujol})/\text{cm}^{-1}$ 952w, 828w, 767w, 732m; δ_{H} (300 MHz; CDCl_3) 1.31 (3H, t, $J = 7.6$, CH_2CH_3), 2.75 (2H, q, $J = 7.6$, CH_2CH_3), 3.89 (2H, s, CH_2 (C9)), 7.23 (1H, d, $J = 8.1$, ArH), 7.26-7.31 (1H, m, ArH), 7.36 (1H, d, $J = 8.1$, ArH), 7.41 (1H, s, ArH), 7.54 (1H, d, $J = 7.4$, ArH) 7.72 (1H, d, $J = 8.1$, ArH), 7.77 (1H, d, $J = 7.4$, ArH); δ_{C} (75.42 MHz; CDCl_3) 16.0, 29.1, 36.8, 119.6, 119.7, 124.5, 124.9, 126.2, 126.5, 126.6, 139.4, 141.8, 143.1, 143.5; m/z (EI) 194 (M^+ , 83), 179 (ArCH_2^+ , 100), 165 (Ar^+ , 74).

METHOD II

A mixture of aluminium chloride (3.16 g, 23.7 mmol), lithium aluminium hydride (0.94 g, 24.8 mmol) and dry diethyl ether (60 ml) was stirred in an ice bath under nitrogen. A mixture of 2-acetylfluorene **31b** (0.98 g, 4.7 mmol) and dry diethyl ether (50 ml) was added over 4 minutes. Further diethyl ether (20 ml) was added, and the stirred reaction mixture was allowed to warm to room temperature over 42.2 hours. Water (50 ml) and concentrated sulphuric acid (10 ml) were added, and the organic layer was separated. The aqueous layer was extracted with diethyl ether (2 x 50 ml). The combined organic extracts were washed with water (2 x 100 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was chromatographed on silica gel using dichloromethane as eluent to give a yellow solid, impure 2-ethylfluorene **32b** (0.73 g, *ca.* 75%).

TLC analysis indicated a single component which co-chromatographed ($R_f = 0.80$ in DCM) with the authentic material described in METHOD I.

^1H and ^{13}C NMR spectra were similar to those obtained for the authentic material described in METHOD I, but showed low levels of unidentified impurities.

2-Propylfluorene

METHOD I

A mixture of 2-propionylfluorene **31c** (1.09 g, 4.9 mmol), hydrazine hydrate (2.4 ml, 49 mmol), sodium hydroxide (0.98 g, 25 mmol), sodium carbonate (2.60 g, 25 mmol) and diethylene glycol (25 ml) was heated at reflux for 3.0 hours. The reaction mixture was then heated strongly for 3.0 hours to distil out water. After cooling, water (75 ml) and

concentrated hydrochloric acid (10 ml) were added, and the products were extracted into dichloromethane (3 x 75 ml). The combined organic extracts were washed with water (75 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was recrystallized from hot ethanol (charcoal) to give a white solid, 2-propylfluorene **32c** (0.18 g, 18 %, mp 57-59 °C (from EtOH)).

$\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 258sh, 270 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 21000), 277sh, 294 (7100), 306 (9100); $\nu_{\max}(\text{CHCl}_3 \text{ soln.})/\text{cm}^{-1}$ 3672w, 2931s, 2872m, 1898w, 1614w, 1456s, 1406m, 1298w, 1134w, 1098w, 1004w, 954w, 831w; δ_{H} (300 MHz; CDCl_3) 1.03 (3H, t, $J = 7.4$, $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.67-1.82 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.72 (2H, t, $J = 7.7$, $\text{CH}_2\text{CH}_2\text{CH}_3$), 3.91 (2H, s, CH_2 (C9)), 7.24 (1H, d, $J = 7.4$, ArH), 7.21-7.37 (1H, m, ArH), 7.37-7.45 (2H, m, ArH), 7.56 (1H, d, $J = 7.4$, ArH), 7.73 (1H, d, $J = 8.1$, ArH), 7.80 (1H, d, $J = 7.4$, ArH); δ_{C} (75.42 MHz; CDCl_3) 14.1, 25.1, 37.0, 38.4, 119.7, 125.1, 125.3, 126.4, 126.8, 127.3, 139.6, 141.7, 142.0, 143.3, 143.6; m/z (EI) 208 (M^+ , 49%), 179 (ArCH_2^+ , 100), 165 (Ar^+ , 13).

A second crop of 2-propylfluorene **32c** (yellow solid (1.56 g, 55%)) was isolated from the mother liquor. This co-chromatographed ($R_f = 0.86$ in DCM) and had ^1H and ^{13}C NMR spectra identical to those obtained for the authentic material described above.

METHOD II

A mixture of aluminium chloride (18.71 g, 0.14 mol), lithium aluminium hydride (5.31 g, 0.13 mol) and dry diethyl ether (300 ml) was stirred in an ice bath under nitrogen. A mixture of 2-propionylfluorene (6.23 g, 28 mmol), dry diethyl ether (300 ml) and dichloromethane (50 ml) was added over 45 minutes. The stirred reaction mixture was allowed to warm to room temperature over 25.0 hours. Water (300 ml) and concentrated sulphuric acid (50 ml) were added, and the organic layer was separated. The aqueous layer was extracted with diethyl ether (2 x 300 ml). The combined organic extracts were washed with water (500 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was chromatographed on silica gel using dichloromethane-40-60 petroleum ether (1:1) as eluent followed by recrystallization to give an off-white solid, impure 2-propylfluorene **32c** (0.46 g, *ca.* 8%).

TLC analysis indicated a single component which co-chromatographed ($R_f = 0.82$ in DCM) with the authentic material described in METHOD I.

^1H and ^{13}C NMR spectra were similar to those obtained for the authentic material described in METHOD I, but showed low levels of unidentified impurities.

2-Butylfluorene

A mixture of 2-butyrylfluorene **31d** (10.61 g, 45 mmol), hydrazine hydrate (21.9 ml, 450 mmol), sodium hydroxide (18.04 g, 450 mmol) and diethylene glycol (180 ml) was heated at reflux for 3.7 hours. The reaction mixture was then heated strongly for 0.2 hours to distil out water. After cooling, water (500 ml) and concentrated hydrochloric acid (70 ml) were added, and the products were extracted into dichloromethane (2 x 500 ml). The combined organic extracts were washed with water (500 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was recrystallized from hot ethanol (charcoal). The recrystallized material was dissolved in dichloromethane-40-60 petroleum ether (1:1, 20 ml). The solution was filtered through a plug of silica then rinsed with dichloromethane-40-60 petroleum ether (100 ml). The solvent was removed. The residue was recrystallized from hot ethanol (charcoal) to give an off-white solid, 2-butylfluorene **32d** (3.78 g, 38%, mp 65-67 °C (from EtOH), lit.,¹⁶² 65-67 °C).

λ_{max} (CH₂Cl₂)/nm 260sh, 271 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 20400), 277sh, 294 (7000), 306 (8900); ν_{max} (CHCl₃ soln.)/cm⁻¹ 2930vs, 2859m, 1616w, 1456m, 1405m, 1134w, 1102w, 1004w, 955w; δ_{H} (300 MHz; CDCl₃) 1.02 (3H, t, J = 7.4, CH₂CH₂CH₂CH₃), 1.38-1.53 (2H, m, CH₂CH₂CH₂CH₃), 1.64-1.78 (2H, m, CH₂CH₂CH₂CH₃), 2.75 (2H, t, J = 7.7, CH₂CH₂CH₂CH₃), 3.91 (2H, s, CH₂ (C9)), 7.21-7.37 (2H, m, ArH), 7.37-7.45 (2H, m, ArH), 7.57 (1H, d, J = 7.4, ArH), 7.74 (1H, d, J = 7.7, ArH), 7.81 (1H, d, J = 7.4, ArH); δ_{C} (75.42 MHz; CDCl₃) 14.2, 22.6, 34.2, 36.1, 37.0, 119.8, 125.1, 125.3, 126.4, 126.8, 127.2, 139.5, 141.9, 142.0, 143.3, 143.6; m/z (EI) 222 (M⁺, 44%), 179 (ArCH₂⁺, 100), 165 (Ar⁺, 14).

A second crop of 2-butylfluorene **32d** (off-white solid (1.32 g, 13%)) was isolated from the mother liquor. This co-chromatographed (R_f = 0.82 in DCM) and had ¹H and ¹³C NMR spectra identical to those obtained for the authentic material described above.

2-Pentylfluorene

A mixture of 2-pentanoylfluorene **31e** (1.98 g, 7.9 mmol), hydrazine hydrate (3.9 ml, 80 mmol), potassium hydroxide (4.35 g, 78 mmol) and diethylene glycol (40 ml) was heated at reflux for 1.8 hours. The reaction mixture was then heated strongly for 0.5 hours to distil out water. After cooling, water (100 ml) and concentrated hydrochloric acid (10 ml) were added, and the products were extracted into dichloromethane (3 x 100 ml). The combined organic extracts were washed with water (100 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was dissolved in diethyl ether-

40-60 petroleum ether (1:1, 10 ml). The solution was filtered through a plug of silica and rinsed with diethyl ether-40-60 petroleum ether (1:1, 50 ml). The solvent was removed. The residue was recrystallized from hot ethanol to give a pale yellow solid, 2-pentylfluorene **32e** (1.07 g, 57%, mp 60-63 °C (from EtOH, lit.,³⁰ 61-63 °C)).

$\nu_{\max}(\text{nujol})/\text{cm}^{-1}$ 761w, 734m; δ_{H} (300 MHz; CDCl_3) 1.00 (3H, t, $J = 6.6$, $\text{CH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 1.38-1.48 (4H, m, $\text{CH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 1.67-1.78 (2H, m, $\text{CH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 2.73 (2H, t, $J = 7.7$, $\text{CH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 3.90 (2H, s, CH_2 (C9)), 7.21-7.37 (2H, m, ArH), 7.37-7.45 (2H, m, ArH), 7.57 (1H, d, $J = 7.4$, ArH), 7.73 (1H, d, $J = 8.1$, ArH), 7.80 (1H, d, $J = 7.4$, ArH); δ_{C} (75.42 MHz; CDCl_3) 14.3, 22.8, 31.7, 31.8, 36.3, 37.0, 119.7, 125.1, 125.3, 126.4, 126.8, 127.2, 139.5, 142.0, 143.3, 143.6; m/z (EI) 236 (M^+ , 60%), 179 (ArCH_2^+ , 100), 165 (Ar^+ , 16).

2-Hexylfluorene

A mixture of 2-hexanoylfluorene **31f** (3.19 g, 12.1 mmol), hydrazine hydrate (5.9 ml, 121 mmol), sodium carbonate (12.80 g, 121 mmol) and diethylene glycol (100 ml) was heated at reflux for 3.0 hours. The reaction mixture was then heated strongly for 1.3 hours to distil out water. After cooling, water (150 ml) and concentrated hydrochloric acid (20 ml) were added, and the products were extracted into dichloromethane (3 x 150 ml). The combined organic extracts were washed with water (150 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was dissolved in diethyl ether-40-60 petroleum ether (1:1, 50 ml). The solution was filtered through a plug of silica and rinsed with diethyl ether-40-60 petroleum ether (1:1, 3 x 50 ml). The solvent was removed. The residue was recrystallized from hot ethanol (charcoal) to give a pale green solid, 2-hexylfluorene **32f** (1.83 g, 61%, mp 63-65 °C (from EtOH, lit.,³⁰ 64-65 °C)).

$\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 227 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 9300), 261sh, 270 (23500), 276sh, 294 (8000), 306 (10300); $\nu_{\max}(\text{CHCl}_3 \text{ soln.})/\text{cm}^{-1}$ 2929vs, 2856m, 1615w, 1456m, 1425w, 1405w, 1378w, 1298w, 1176w, 1134w, 1005w, 955w, 881w, 830w; δ_{H} (300 MHz; CDCl_3) 0.97 (3H, t, $J = 7.1$, $\text{CH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 1.29-1.50 (6H, m, $\text{CH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 1.64-1.78 (2H, m, $\text{CH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 2.73 (2H, t, $J = 7.7$, $\text{CH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 3.91 (2H, s, CH_2 (C9)), 7.24 (1H, t, $J = 7.0$, ArH), 7.32 (1H, t, $J = 7.4$, ArH), 7.37-7.45 (2H, m, ArH), 7.57 (1H, d, $J = 7.4$, ArH), 7.73 (1H, d, $J = 7.4$, ArH), 7.80 (1H, d, $J = 7.4$, ArH); δ_{C} (75.42 MHz; CDCl_3) 14.3, 22.8, 29.3, 32.0, 36.4, 37.0, 119.7, 125.1, 125.3, 126.4, 126.8, 127.2, 139.5, 142.0, 143.3, 143.6; m/z (EI) 250 (M^+ , 23%), 179 (ArCH_2^+ , 100), 165 (Ar^+ , 14).

A second crop of 2-hexylfluorene **32f** (pale green solid (0.18 g, 6%)) was isolated from the

mother liquor. This co-chromatographed ($R_f = 0.74$ in DCM) and had ^1H and ^{13}C NMR spectra identical to those obtained for the authentic material described above.

2-Heptylfluorene

A mixture of 2-heptanoylfluorene **31g** (7.75 g, 28 mmol), hydrazine hydrate (13.5 ml, 0.28 mol), potassium hydroxide (15.60 g, 0.28 mol) and diethylene glycol (150 ml) was heated at reflux for 1.3 hours. The reaction mixture was then heated strongly for 0.3 hours to distil out water. After cooling, water (500 ml) and concentrated hydrochloric acid (50 ml) were added, and the products were extracted into dichloromethane (2 x 500 ml). The combined organic extracts were washed with water (500 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was dissolved in dichloromethane-40-60 petroleum ether (1:1, 20 ml). The solution was filtered through a plug of silica and rinsed with dichloromethane-40-60 petroleum ether (1:1, 2 x 50 ml). The solvent was removed. The residue was recrystallized from hot ethanol (charcoal) to give a white solid, 2-heptylfluorene **32g** (3.87 g, 53%, mp 54-56 °C (from EtOH, lit.,³⁰ 58-60 °C)).

λ_{max} (CH₂Cl₂)/nm 228 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 13400), 261sh, 271 (26500), 277sh, 294 (9100), 306 (11700); ν_{max} (CHCl₃ soln.)/cm⁻¹ 2928vs, 2856s, 1615w, 1467m, 1404m, 1298w, 1005w, 955w, 831w; δ_{H} (300 MHz; CDCl₃) 0.80 (3H, t, $J = 6.6$, CH₂CH₂(CH₂)₄CH₃), 1.12-1.45 (8H, m, CH₂CH₂(CH₂)₄CH₃), 1.50-1.65 (2H, m, CH₂CH₂(CH₂)₄CH₃), 2.60 (2H, t, $J = 7.7$, CH₂CH₂(CH₂)₄CH₃), 3.76 (2H, s, CH₂ (C9)), 7.24 (1H, t, $J = 7.4$, ArH), 7.31 (1H, t, $J = 7.4$, ArH), 7.41 (2H, t, $J = 7.4$, ArH), 7.57 (1H, d, $J = 7.4$, ArH), 7.74 (1H, d, $J = 8.1$, ArH), 7.79 (1H, d, $J = 7.4$, ArH); δ_{C} (75.42 MHz; CDCl₃) 14.3, 22.9, 29.4, 29.6, 32.1, 36.4, 37.0, 119.7, 125.1, 125.3, 126.4, 126.8, 127.2, 139.5, 142.0, 143.3, 143.6; m/z (EI) 264 (M^+ , 24%), 179 (ArCH_2^+ , 100), 165 (Ar^+ , 17).

A second crop of 2-heptylfluorene **32g** (white solid (0.75 g, 10%)) was isolated from the mother liquor. This co-chromatographed ($R_f = 0.85$ in DCM) and had ^1H and ^{13}C NMR spectra identical to those obtained for the authentic material described above.

2-Octylfluorene

A mixture of 2-octanoylfluorene **31h** (7.96 g, 27 mmol), hydrazine hydrate (13.2 ml, 270 mmol), sodium carbonate (29.13 g, 280 mmol) and diethylene glycol (150 ml) was heated at reflux for 5.0 hours. The reaction mixture was then heated strongly for 2.0 hours to distil out water. After cooling, water (500 ml) and concentrated hydrochloric acid (100 ml) were added, and the products were extracted into dichloromethane (2 x 500 ml). The combined

organic extracts were washed with water (500 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was recrystallized from hot ethanol (charcoal) to give a pale yellow green solid, 2-octylfluorene **32h** (5.65 g, 75 %, mp 58-60 °C (from EtOH)).

$\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 227 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 9100), 259sh, 270 (22300), 276sh, 294 (7700), 306 (9800); $\nu_{\max}(\text{CHCl}_3 \text{ soln.})/\text{cm}^{-1}$ 2928vs, 2855s, 1615w, 1467m, 1456s, 1404w, 1298w, 955w, 831w; δ_{H} (300 MHz; CDCl_3) 0.95 (3H, t, $J = 6.6$, $\text{CH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 1.26-1.51 (10H, m, $\text{CH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 1.64-1.80 (2H, m, $\text{CH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 2.73 (2H, t, $J = 7.7$, $\text{CH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 3.91 (2H, s, CH_2 (C9)), 7.25 (1H, d, $J = 7.4$, ArH), 7.28-7.37 (1H, m, ArH), 7.37-7.47 (2H, m, ArH), 7.58 (1H, d, $J = 7.4$, ArH), 7.74 (1H, d, $J = 7.4$, ArH), 7.80 (1H, d, $J = 7.4$, ArH); δ_{C} (75.42 MHz; CDCl_3) 14.3, 22.9, 29.5, 29.6, 29.8, 32.1, 32.1, 36.4, 37.0, 119.8, 125.1, 125.3, 126.4, 126.8, 127.2, 139.5, 142.0, 143.3, 143.6; m/z (EI) 278 (M^+ , 52%), 178 (ArCH_2^+ , 100), 165 (Ar^+ , 25).

A second crop of 2-octylfluorene **32h** (yellow solid (0.60 g, 8%)) was isolated from the mother liquor. This co-chromatographed ($R_f = 0.77$ in DCM) and had ^1H and ^{13}C NMR spectra identical to those obtained for the authentic material described above.

2-Nonylfluorene

A mixture of 2-nonanoylfluorene **31i** (2.49 g, 8.1 mmol), hydrazine hydrate (4.0 ml, 82 mmol), potassium hydroxide (4.50 g, 80 mmol) and diethylene glycol (40 ml) was heated at reflux for 2.3 hours. The reaction mixture was then heated strongly for 0.5 hours to distil out water. After cooling, water (150 ml) and concentrated hydrochloric acid (10 ml) were added, and the products were extracted into dichloromethane (2 x 150 ml). The combined organic extracts were washed with water (150 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was dissolved in dichloromethane-40-60 petroleum ether (1:1, 10 ml). The solution was filtered through a plug of silica and rinsed with dichloromethane-40-60 petroleum ether (1:1, 50 ml). The solvent was removed to give an off white solid, 2-nonylfluorene **32i** (2.10 g, 89 %, mp 61-63 °C (silica plug, DCM-PET (40-60), lit., ¹⁶⁰ 67 °C)).

(Found: C 90.3; H, 9.8. $\text{C}_{22}\text{H}_{26}$ requires C, 90.35; H, 9.65%); $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 226 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 10600), 261sh, 267sh, 270 (28300), 278sh, 294 (10200), 306 (12900); $\nu_{\max}(\text{CHCl}_3 \text{ soln.})/\text{cm}^{-1}$ 2927s, 2855m, 1615w, 1456m, 1405w, 1298w, 1005w, 955w, 831w; δ_{H} (300 MHz; CDCl_3) 0.91 (3H, t, $J = 6.6$, $\text{CH}_2\text{CH}_2(\text{CH}_2)_6\text{CH}_3$), 1.20-1.45 (12H, m, $\text{CH}_2\text{CH}_2(\text{CH}_2)_6\text{CH}_3$), 1.60-1.75 (2H, m, $\text{CH}_2\text{CH}_2(\text{CH}_2)_6\text{CH}_3$), 2.70 (2H, t, $J = 7.7$,

$\text{CH}_2\text{CH}_2(\text{CH}_2)_6\text{CH}_3$), 3.89 (2H, s, CH_2 (C9)), 7.22 (1H, d, $J = 7.4$, ArH), 7.27-7.32 (1H, m, ArH), 7.35-7.40 (2H, m, ArH), 7.55 (1H, d, $J = 7.4$, ArH), 7.71 (1H, d, $J = 8.1$, ArH), 7.77 (1H, d, $J = 7.4$, ArH); δ_{C} (75.42 MHz; CDCl_3) 14.1, 22.7, 29.4, 29.4, 29.6, 31.9, 31.9, 36.2, 36.8, 119.6, 119.6, 124.9, 125.1, 126.2, 126.6, 127.0, 139.3, 141.8, 143.1, 143.4; m/z (EI) 292 (M^+ , 78%), 179 (ArCH_2^+ , 100), 165 (Ar^+ , 14).

8.3.3 2-Bromo-7-alkylfluorenes

Benzyltrimethylammonium tribromide

A mixture of benzyltrimethylammonium chloride (9.31 g, 50 mmol), sodium bromate (3.92 g, 26 mmol), water (80 ml) and dichloromethane (50 ml) was stirred in an ice bath. Hydrobromic acid (aq, 47%, 20 ml, 174 mmol) was added over 14 minutes. The reaction mixture was allowed to warm to room temperature over 40 minutes. The organic layer was separated, and the aqueous layer was extracted with dichloromethane (3 x 20 ml). The combined organic extracts were dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was recrystallized from hot dichloromethane-diethyl ether to give an orange solid, benzyltrimethylammonium tribromide (15.8 g, 81%, mp 100-102 °C (from DCM-Et₂O) (lit.,⁶⁴ 100-101 °C))

Copper(II)bromide on alumina

Copper(II)bromide (13.2 g, 59 mmol), water (30 ml) and aluminium oxide (Brockmann II, 20.95 g) were swirled to mix. The solvent was removed. The residue was dried (>100 °C, 0.6 mbar) for 3 hours to give a black solid, copper(II)bromide on alumina (29.9 g).

2-Bromofluorene

METHOD I

A mixture of fluorene (1.03 g, 6.2 mmol), copper (II) bromide on alumina (15.99 g, 56 mmol (as Br)) and dry carbon tetrachloride (50 ml) was heated at reflux under nitrogen for 2.0 hours. After cooling, the reaction mixture was filtered. The solvent was removed from the filtrate. The residue was recrystallized from hot ethanol-water (9:1) to give a pale yellow solid, impure 2,7-dibromofluorene **53** (0.23 g, *ca.* 11%).

δ_{H} (300 MHz; CDCl_3) 3.87 (2H, s, CH_2 (C9)), 7.51 (2H, m, ArH), 7.61 (2H, m, ArH), 7.68 (2H, s, ArH); (75.42 MHz; CDCl_3) 36.7, 121.1, 121.4, 128.5, 130.3, 139.8, 144.9.

TLC analysis indicated a single component which co-chromatographed with the starting material. A ^1H NMR spectrum showed low levels of impurities at δ_{H} 7.30-7.43 and 7.72-7.78.

METHOD II

A mixture of fluorene (1.00 g, 6.0 mmol), benzyltrimethylammonium tribromide (2.35 g, 6.0 mmol), zinc chloride (0.93 g, 6.8 mmol) and glacial acetic acid (40 ml) was stirred at room temperature for 46.8 hours. Water (30 ml) and sodium sulphite solution (aq, 5%, 15 ml) were added, and the products were extracted into 40-60 petroleum ether (4 x 60 ml). The combined organic extracts were dried over anhydrous sodium sulphate and filtered through a plug of alumina. The solvent was removed. The residue was recrystallized from hot ethanol-water (9:1) to give a white solid, impure 2-bromofluorene **24a** (0.22 g, *ca.* 15%).

TLC analysis indicated a single component which co-chromatographed with the starting material. A ^1H NMR spectrum indicated the presence of *ca.* 10% non-brominated fluorene.

METHOD III

A solution of fluorene (2.51 g, 15 mmol) in chloroform (80 ml) was stirred in an isopropyl alcohol-solid carbon dioxide bath. A solution of bromine (0.77 ml, 15 mmol) in chloroform (20 ml) was added over 2.7 hours, with the reaction mixture was stirred in an ice bath. The reaction mixture was then allowed to warm to room temperature over 16.5 hours. Sodium carbonate solution (aq, 10%, 100 ml) was added, and the products were extracted into dichloromethane (2 x 50 ml). The combined organic extracts were washed with sodium metabisulphite solution (aq, 5%, 20 ml) and water (20 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was recrystallized from hot ethanol-water (9:1) to give a white solid, 2-bromofluorene **24a** (1.17 g, 32%, mp 106-110 °C (from EtOH-H₂O, lit.,¹⁶³ 110-111 °C)).

(Found: C, 63.4; H, 3.5; Br, 32.2. C₁₃H₉Br requires C, 63.7; H, 3.7; Br, 32.6%);

λ_{max} (CH₂Cl₂)/nm 268sh, 272 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 31000), 285sh, 296 (10800), 307 (12400); ν_{max} (nujol)/cm⁻¹ 763w, 726w; δ_{H} (300 MHz; CDCl₃) 3.90 (2H, s, CH₂ (C9)), 7.32-7.43 (2H, m, ArH), 7.50-7.57 (2H, m, ArH), 7.64-7.69 (2H, m, ArH), 7.77 (1H, d, J = 8.1, ArH); δ_{C} (75.42 MHz; CDCl₃) 36.8, 119.9, 121.1, 125.1, 127.0, 127.1, 128.3, 129.9, 140.7; *m/z* (EI) 246 (M⁺ (^{81}Br), 20%), 244 (M⁺ (^{79}Br), 20), 165 (Ar⁺, 100).

METHOD IV

A solution of fluorene (2.50 g, 15 mmol) in methanol (70 ml) was stirred in an ice bath. A solution of bromine (0.77 ml, 15 mmol) in glacial acetic acid (30 ml) was added over 1.8 hours, with the reaction mixture stirred in an ice bath. The reaction mixture was then allowed to warm to room temperature over 20.3 hours. The reaction mixture was

concentrated by removing approximately half the solvent *in vacuo*. Sodium carbonate solution (aq, 10 %, 100 ml) was added, and the products were extracted into dichloromethane (2 x 50 ml). The combined organic extracts were washed with sodium metabisulphite solution (aq, 5%, 20 ml) and water (20 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was recrystallized from hot ethanol-water (9:1) to give a white solid, 2-bromofluorene **24a** (1.01 g, 27%, mp 101-106 °C (from EtOH-H₂O, lit.,¹⁶³ 110-111 °C)). The material co-chromatographed (R_f = 0.82 in DCM) had ¹H and ¹³C NMR spectra identical to those obtained for the authentic material described above in METHOD III.

METHOD V

A mixture of fluorene (2.51 g, 15 mmol), iron(III)chloride (2.98 g, 18 mmol) and chloroform (80 ml) was stirred in an ice bath. A solution of bromine (0.77 ml, 15 mmol) in chloroform (20 ml) was added over 1.0 hours, with the reaction mixture stirred in an ice bath. The reaction mixture was allowed to warm to room temperature over 20.4 hours. Sodium carbonate solution (aq, 10 %, 100 ml) was added and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 x 50 ml). The combined organic extracts were washed with sodium metabisulphite solution (aq, 5%, 2 x 20 ml) and water (20 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was recrystallized from hot ethanol-water (9:1) to give a pale yellow solid, impure 2-bromofluorene **24a** (1.06 g, *ca.* 27%).

TLC analysis indicated a single component which co-chromatographed with the starting material. A ¹H NMR spectrum indicated the presence of *ca.* 20% non-brominated fluorene.

2-Bromo-7-ethylfluorene

A solution of 2-ethylfluorene **32b** (0.98 g, 5.1 mmol) in chloroform (25 ml) was stirred in an ice bath. A solution of bromine (0.26 ml, 5.1 mmol) in chloroform (10 ml) was added over 5.3 hours, with the reaction mixture stirred in an ice bath. The reaction mixture was then allowed to warm to room temperature over 66.0 hours. Sodium carbonate solution (aq, 10 %, 40 ml) was added, and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 x 20 ml). The combined organic extracts were washed with sodium metabisulphite solution (aq, 5%, 2 x 10 ml) and water (10 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was recrystallized from hot ethanol to give a yellow solid, 2-bromo-7-ethylfluorene **24b** (0.37 g, 27%, mp 139-142 °C (from EtOH)).

(Found: C, 66.3; H, 4.7; Br, 29.4. C₁₅H₁₃Br requires C, 65.95; H, 4.8; Br, 29.95%);

$\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 272sh, 276 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 30100), 289sh, 300 (11100), 311 (12400); $\nu_{\max}(\text{nujol})/\text{cm}^{-1}$ 814w, 724w; δ_{H} (300 MHz; CDCl_3) 1.32 (3H, t, $J = 7.4$, CH_2CH_3), 2.75 (2H, q, $J = 7.4$, CH_2CH_3), 3.85 (2H, s, CH_2 (C9)), 7.24 (1H, d, $J = 7.4$, ArH), 7.39 (1H, s, ArH), 7.50 (1H, d, $J = 8.1$, ArH), 7.60 (1H, d, $J = 8.1$, ArH), 7.67 (2H, d, $J = 7.4$, ArH); δ_{C} (75.42 MHz; CDCl_3) 16.0, 29.1, 36.7, 119.8, 120.8, 124.6, 126.8, 128.2, 129.8, 138.4, 140.8, 143.2, 143.7, 145.2; m/z (EI) 274 (M^+ (^{81}Br), 52%), 272 (M^+ (^{79}Br), 50), 259 ($\text{Ar}(\text{CH}_2)^{81}\text{Br}^+$, 40), 257 ($\text{Ar}(\text{CH}_2)^{79}\text{Br}^+$, 42), 193 ($\text{ArCH}_2\text{CH}_3^+$, 31), 178 (ArCH_2^+ , 17), 165 (Ar^+ , 5).

2-Bromo-7-propylfluorene

A solution of 2-propylfluorene **32c** (0.80 g, 3.8 mmol) in chloroform (25 ml) was stirred in an ice bath. A solution of bromine (0.22 ml, 4.3 mmol) in chloroform (10 ml) was added over 0.3 hours, with the reaction mixture stirred in an ice bath. The reaction mixture was then allowed to warm to room temperature, with stirring, over 10.7 hours. The reaction mixture was heated at reflux for 1.0 hours. After cooling, sodium carbonate solution (aq, 10%, 30 ml) was added, and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 x 20 ml). The combined organic extracts were washed with sodium metabisulphite solution (aq, 5%, 2 x 10 ml) and water (10 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was recrystallized from hot ethanol (charcoal) to give an off-white solid, 2-bromo-7-propylfluorene **24c** (0.77 g, 70%, mp 117-120 °C (from EtOH)).

$\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 270sh, 276 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 28200), 300 (10700), 312 (11800); $\nu_{\max}(\text{CHCl}_3 \text{ soln.})/\text{cm}^{-1}$ 3684w, 2932m, 2872m, 1602m, 1460s, 1407s, 1273m, 1170m, 1135w, 1062m, 1006m; δ_{H} (300 MHz; CDCl_3) 1.00 (3H, t, $J = 7.4$, $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.63-1.80 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.69 (2H, t, $J = 7.4$, $\text{CH}_2\text{CH}_2\text{CH}_3$), 3.86 (2H, s, CH_2 (C9)), 7.21 (1H, d, $J = 7.4$, ArH), 7.36 (1H, s, ArH), 7.50 (1H, d, $J = 8.1$, ArH), 7.60 (1H, d, $J = 8.1$, ArH), 7.68 (2H, m, ArH); δ_{C} (75.42 MHz; CDCl_3) 14.1, 25.0, 36.8, 38.4, 119.8, 120.1, 121.0, 125.3, 127.5, 128.3, 129.9, 138.5, 141.0, 142.2, 143.3, 145.3; m/z (EI) 288 (M^+ (^{81}Br), 46%), 286 (M^+ (^{79}Br), 48), 259 ($\text{Ar}(\text{CH}_2)^{81}\text{Br}^+$, 92), 257 ($\text{Ar}(\text{CH}_2)^{79}\text{Br}^+$, 96), 207 (ArC_3H_7^+ , 22), 178 (ArCH_2^+ , 100), 164 (Ar^+ , 10).

2-Bromo-7-butylfluorene

A solution of 2-butylfluorene **32d** (4.07 g, 18.3 mmol) in chloroform (140 ml) was stirred in an ice bath. A solution of bromine (1.0 ml, 19.5 mmol) in chloroform (40 ml) was added over 1.0 hours, with the reaction mixture stirred in an ice bath. The reaction mixture was

then allowed to warm to room temperature, with stirring, over 15.3 hours. The reaction mixture was heated at reflux for 1.0 hours. After cooling, sodium carbonate solution (aq, 10%, 140 ml) was added, and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 x 100 ml). The combined organic extracts were washed with sodium metabisulphite solution (aq, 5%, 2 x 50 ml) and water (50 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was recrystallized from hot ethanol (charcoal) to give a white solid, impure 2-bromo-7-butylfluorene **24d** (2.80 g, *ca.* 57%).

A portion of this material (0.25 g) was recrystallized from hot chloroform-hexane to give a white solid, 2-bromo-7-butylfluorene **24d** (0.04 g, <1%, mp 108-110 °C (from CHCl₃-hexane)).

λ_{\max} (CH₂Cl₂)/nm 228 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 9500), 271sh, 277 (24600), 300 (9200), 312 (10400); ν_{\max} (CHCl₃ soln.)/cm⁻¹ 2928s, 2856m, 1602w, 1459s, 1407m, 1274w, 1170w, 1061w, 1006w, 858w; δ_{H} (300 MHz; CDCl₃) 0.96 (3H, t, $J = 7.4$, CH₂CH₂CH₂CH₃), 1.33-1.48 (2H, m, CH₂CH₂CH₂CH₃), 1.60-1.73 (2H, m, CH₂CH₂CH₂CH₃), 2.70 (2H, t, $J = 7.7$, CH₂CH₂CH₂CH₃), 3.86 (2H, s, CH₂ (C9)), 7.22 (1H, d, $J = 8.1$, ArH), 7.38 (1H, s, ArH), 7.50 (1H, d, $J = 8.1$, ArH), 7.61 (1H, d, $J = 8.1$, ArH), 7.67 (2H, d, $J = 7.4$, ArH); δ_{C} (75.42 MHz; CDCl₃) 14.2, 22.6, 34.1, 36.0, 36.8, 119.8, 120.0, 121.1, 125.3, 127.4, 128.3, 129.9, 138.5, 141.0, 142.5, 143.3, 145.3; m/z (EI) 302 (M⁺ (⁸¹Br), 45), 300 (M⁺ (⁷⁹Br), 47), 259 (Ar(CH₂)⁸¹Br⁺, 94), 257 (Ar(CH₂)⁷⁹Br⁺, 100), 178 (ArCH₂⁺, 93), 165 (Ar⁺, 19), 152 (32).

2-Bromo-7-pentylfluorene

A solution of 2-pentylfluorene **32e** (1.00 g, 4.2 mmol) in chloroform (30 ml) was stirred in an ice bath. A solution of bromine (0.24 ml, 4.7 mmol) in chloroform (10 ml) was added over 2.9 hours, with the reaction mixture stirred in an ice bath. The reaction mixture was then allowed to return to room temperature, with stirring, over 16.3 hours. The reaction mixture was heated at reflux for 0.3 hours. After cooling, sodium carbonate solution (aq, 10%, 35 ml) was added, and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 x 20 ml). The combined organic extracts were washed with sodium metabisulphite solution (aq, 5%, 2 x 10 ml) and water (10 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was recrystallized from hot ethanol (charcoal) to give a white solid, 2-bromo-7-pentylfluorene **24e** (0.65 g, 49 %, mp 93-95 °C (from EtOH, lit.,³⁰ 95-96 °C)).

λ_{\max} (CH₂Cl₂)/nm 227 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 10300), 271sh, 277 (25400), 300 (9600), 312

(10800); $\nu_{\max}(\text{nujol})/\text{cm}^{-1}$ 857w, 814m; δ_{H} (300 MHz; CDCl_3) 0.92 (3H, t, $J = 6.6$, $\text{CH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 1.30-1.47 (4H, m, $\text{CH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 1.78 (2H, m, $\text{CH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 2.68 (2H, t, $J = 7.7$, $\text{CH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 3.68 (2H, s, CH_2 (C9)), 7.22 (1H, d, $J = 7.4$, ArH), 7.37 (1H, s, ArH), 7.50 (1H, dd, $J = 8.8$, 2.2, ArH), 7.60 (1H, d, $J = 8.1$, ArH), 7.65 (2H, m, ArH); δ_{C} (75.42 MHz; CDCl_3) 14.2, 22.8, 31.7, 36.3, 36.8, 119.8, 120.0, 121.0, 125.3, 127.4, 128.3, 129.9, 138.5, 141.0, 142.5, 143.3, 145.3; m/z (EI) 394 ($\text{M}^{+81}\text{Br}^{+}$, *ca.* 1%), 316 ($\text{ArC}_5\text{H}_{11}^{81}\text{Br}^{+}$, 76), 314 ($\text{ArC}_5\text{H}_{11}^{79}\text{Br}^{+}$, 77), 259 ($\text{ArCH}_2^{81}\text{Br}^{+}$, 99), 257 ($\text{ArCH}_2^{79}\text{Br}^{+}$, 100), 178 (ArCH_2^{+} , 48), 165 (Ar^{+} , 7).

A Mass spectrum indicated the presence of a small amount (*ca.* 1%) of dibrominated material.

2-Bromo-7-hexylfluorene

A solution of 2-hexylfluorene **32f** (1.29 g, 5.2 mmol), and chloroform (40 ml) was stirred in an ice bath. A solution of bromine (0.29 ml, 5.6 mmol) in chloroform (10 ml) was added over 0.5 hours, with the reaction mixture stirred in an ice bath. The reaction mixture was then allowed to return to room temperature, with stirring, over 13.2 hours. The reaction mixture was heated at reflux for 0.6 hours. After cooling, sodium carbonate solution (aq, 10%, 50 ml) was added, and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 x 40 ml). The combined organic extracts were washed with sodium metabisulphite solution (aq, 5%, 20 ml) and water (20 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was recrystallized from hot ethanol to give a white solid, 2-bromo-7-hexylfluorene **24f** (1.10 g, 65%, mp 94-96 °C (from EtOH, *lit.*,³⁰ 90-92 °C)).

$\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 228 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 10900), 271sh, 277 (27400), 300 (10700), 312 (11800); $\nu_{\max}(\text{CHCl}_3 \text{ soln.})/\text{cm}^{-1}$ 2929s, 2856m, 1602w, 1459m, 1407m, 1294w, 1273w, 1170w, 1135w, 1062w, 1006w, 935w, 858w, 815m; δ_{H} (300 MHz; CDCl_3) 0.93 (3H, t, $J = 6.3$, $\text{CH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 1.37-1.48 (6H, m, $\text{CH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 1.61-1.75 (2H, m, $\text{CH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 2.72 (2H, t, $J = 7.7$, $\text{CH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 3.86 (2H, s, CH_2 (C9)), 7.23 (1H, d, $J = 7.4$, ArH), 7.38 (1H, s, ArH), 7.49 (1H, d, $J = 8.1$, ArH), 7.60 (1H, d, $J = 8.1$, ArH), 7.63-7.70 (2H, m, ArH); δ_{C} (75.42 MHz; CDCl_3) 14.3, 22.8, 29.2, 32.0, 36.4, 36.8, 119.8, 120.1, 121.1, 125.3, 127.4, 128.3, 129.9, 138.5, 141.0, 142.5, 143.3, 145.3. m/z (EI) 330 (M^{+81}Br , 40%), 328 (M^{+79}Br , 40), 259 ($\text{Ar}(\text{CH}_2)^{81}\text{Br}^{+}$, 100), 257 ($\text{Ar}(\text{CH}_2)^{79}\text{Br}^{+}$, 100), 178 (ArCH_2^{+} , 90), 165 (Ar^{+} , 15), 152 (20).

2-Bromo-7-heptylfluorene

A solution of 2-heptylfluorene **32g** (3.38 g, 12.8 mmol) in chloroform (100 ml) was stirred in an ice bath. A solution of bromine (0.79 ml, 15.4 mmol) in chloroform (30 ml) was added over 0.4 hours, with the reaction mixture stirred in an ice bath. The reaction mixture was then allowed to return to room temperature, with stirring, over 18.5 hours. The reaction mixture was heated at reflux for 0.3 hours. After cooling, sodium carbonate solution (aq, 10%, 100 ml) was added, and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 x 60 ml). The combined organic extracts were washed with sodium metabisulphite solution (aq, 5%, 2 x 30 ml) and water (30 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was recrystallized from hot ethanol (charcoal) to give a white solid, impure 2-bromo-7-heptylfluorene **24g**, (2.29 g, *ca.* 52 %). A portion of this material (0.25 g) was recrystallized from hot chloroform-hexane to give a white solid, 2-bromo-7-heptylfluorene **24g** (0.01 g, <1%, mp 90-91 °C (from CHCl₃-hexane, lit.,³⁰ 87-89 °C)).

λ_{max} (CH₂Cl₂)/nm 228 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 9700), 271sh, 277 (23800), 300 (9100), 312 (10100); ν_{max} (CHCl₃ soln.)/cm⁻¹ 2928s, 2856m, 1602w, 1459s, 1407m, 1274w, 1170w, 1061w, 1006w, 858w; δ_{H} (300 MHz; CDCl₃) 0.92 (3H, t, *J* = 6.6, CH₂CH₂(CH₂)₄CH₃), 1.23-1.48 (8H, m, CH₂CH₂(CH₂)₄CH₃), 1.60-1.75 (2H, m, CH₂CH₂(CH₂)₄CH₃), 2.69 (2H, t, *J* = 7.7, CH₂CH₂(CH₂)₃CH₃), 3.88 (2H, s, CH₂ (C9)), 7.22 (1H, d, *J* = 7.4, ArH) 7.37 (1H, s, ArH), 7.49 (1H, d, *J* = 8.1, ArH), 7.61 (1H, d, *J* = 8.1, ArH), 7.65-7.72 (2H, m, ArH); δ_{C} (75.42 MHz; CDCl₃) 14.3, 22.9, 29.4, 29.5, 32.0, 36.3, 36.8, 119.8, 120.0, 121.0, 125.3, 127.4, 128.3, 129.9, 138.5, 141.0, 142.5, 143.3, 145.3; *m/z* (EI) 344 (M⁺ (⁸¹Br), 44%), 342 (M⁺ (⁷⁹Br), 45), 259 (Ar(CH₂)⁸¹Br⁺, 93), 257 (Ar(CH₂)⁷⁹Br⁺, 96), 178 (ArCH₂⁺, 100), 165 (Ar⁺, 15), 152 (17).

2-Bromo-7-octylfluorene

A solution of impure 2-octylfluorene **32h** (1.93 g, *ca.* 6.9 mmol) in chloroform (50 ml) was stirred in an ice bath. A solution of bromine (0.39 ml, 7.5 mmol) in chloroform (20 ml) was added over 1.0 hours, with the reaction mixture stirred in an ice bath. The reaction mixture was then allowed to warm to room temperature, with stirring, over 18.6 hours. The reaction mixture was heated at reflux for 1.0 hours. After cooling, sodium carbonate solution (aq, 10%, 60 ml) was added, and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 x 40 ml). The combined organic extracts were washed with sodium metabisulphite solution (aq, 5%, 2 x 20 ml) and water (20 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was

recrystallized from hot ethanol (charcoal) to give a pale yellow solid, 2-bromo-7-octylfluorene **24h** (0.70 g, 28%, mp 79-81 °C (from EtOH, lit.,³⁰ 80-81 °C)).

$\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 270sh, 277 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 28200), 300 (10700), 312 (11800); $\nu_{\max}(\text{CHCl}_3 \text{ soln.})/\text{cm}^{-1}$ 2958vs, 2855s, 1602w, 1459s, 1407m, 1273w, 1170w, 1135w, 1061w, 1006w, 857w; δ_{H} (300 MHz; CDCl_3) 0.91 (3H, t, $J = 6.2$, $\text{CH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 1.21-1.50 (10H, m, $\text{CH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 1.61-1.77 (2H, m, $\text{CH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 2.69 (2H, t, $J = 7.7$, $\text{CH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 3.85 (2H, s, CH_2 (C9)), 7.22 (1H, d, $J = 7.4$, ArH) 7.37 (1H, s, ArH), 7.49 (1H, d, $J = 8.1$, ArH), 7.61 (1H, d, $J = 8.1$, ArH), 7.65-7.72 (2H, m, ArH); δ_{C} (75.42 MHz; CDCl_3) 14.3, 22.9, 29.5, 29.6, 29.7, 32.0, 32.1, 36.4, 36.8, 119.8, 120.1, 121.0, 125.3, 127.4, 128.3, 129.9, 138.5, 141.0, 142.5, 143.3, 145.3; m/z (EI) 358 (M^+ (^{81}Br), 36%), 356 (M^+ (^{79}Br), 36), 259 ($\text{Ar}(\text{CH}_2)^{81}\text{Br}^+$, 74), 257 ($\text{Ar}(\text{CH}_2)^{79}\text{Br}^+$, 74), 178 (ArCH_2^+ , 100), 165 (Ar^+ , 13).

2-Bromo-7-nonylfluorene

METHOD I

A mixture of 2-nonylfluorene **32i** (0.53 g, 1.8 mmol), zinc chloride (0.27 g, 2.0 mmol), benzyltrimethylammonium tribromide (0.72 g, 1.8 mmol) and glacial acetic acid (5 ml) was shielded from light and stirred at room temperature for 22.3 hours. Water (15 ml) and sodium sulphite solution (aq, 5%, 10 ml) were added, and the products were extracted into 40-60 petroleum ether (4 x 30 ml). The combined organic extracts were dried over anhydrous sodium sulphate and filtered through a plug of alumina. The solvent was removed. The residue was recrystallized from hot ethanol to give a white solid, impure 2-bromo-7-nonylfluorene **24i** (0.23 g, *ca.* 34%).

TLC analysis indicated a single component ($R_f = 0.80$ in DCM) which co-chromatographed with the starting material. A ^1H spectrum indicated the presence of *ca.* 40% non-brominated 2-nonylfluorene **32i**.

METHOD II

A mixture of 2-nonylfluorene **32i** (0.53 g, 1.8 mmol) and *N*-bromosuccinimide (0.32 g, 1.8 mmol) in dry *N,N*-dimethylformamide (10 ml) was shielded from light and stirred at room temperature for 22.8 hours. The solvent was removed. Water (25 ml) and dichloromethane (25 ml) were added to the residue, and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 x 25 ml). The combined organic extracts were washed with sodium carbonate solution (aq, 10%, 25 ml), sodium metabisulphite solution (aq, 5%, 25 ml) and water (25 ml), then dried over anhydrous sodium sulphate and filtered.

The solvent was removed. The residue was recrystallized from hot ethanol to give a white solid impure 2-bromo-7-nonylfluorene **24i** (0.20 g, *ca.* 30%).

TLC analysis indicated a single component ($R_f = 0.80$ in DCM) which co-chromatographed with the starting material. A ^1H spectrum indicated the presence of *ca.* 25% non-brominated 2-nonylfluorene **32i**.

METHOD III

A solution of 2-nonylfluorene **32i** (1.01 g, 3.5 mmol) in chloroform (25 ml) was stirred in an ice bath. A solution of bromine (0.18 ml, 3.5 mmol) in chloroform (10 ml) was added over 1.5 hours, with the reaction mixture stirred in an ice bath. The reaction mixture was then allowed to return to room temperature, with stirring, over 20.8 hours. The reaction mixture was heated at reflux for 0.5 hours. After cooling, sodium carbonate solution (aq, 10%, 40 ml) was added, and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 x 20 ml). The combined organic extracts were washed with sodium metabisulphite solution (aq, 5%, 2 x 10 ml) and water (10 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was recrystallized from hot ethanol to give a white solid, impure 2-bromo-7-nonylfluorene **24i** (0.67 g, *ca.* 52%). A portion of this material (1.00 g) was recrystallized from hot chloroform-hexane to give a white solid, 2-bromo-7-nonylfluorene **24i** (0.15 g, 1%, mp 83-85 °C (from CHCl_3 -hexane)).

λ_{max} (CH_2Cl_2)/nm 227 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 11900), 271sh, 277 (27600), 300 (10500), 312 (11700); ν_{max} (CHCl_3 soln.)/ cm^{-1} 2927s, 2855m, 1602w, 1459m, 1407m, 1294w, 1273w, 1170w, 1135w, 1061w, 1006w, 857w, 815m; δ_{H} (300 MHz; CDCl_3) 0.92 (3H, t, $J = 6.2$, $\text{CH}_2\text{CH}_2(\text{CH}_2)_6\text{CH}_3$), 1.23-1.48 (12H, m, $\text{CH}_2\text{CH}_2(\text{CH}_2)_6\text{CH}_3$), 1.60-1.75 (2H, m, $\text{CH}_2\text{CH}_2(\text{CH}_2)_6\text{CH}_3$), 2.72 (2H, t, $J = 7.7$, $\text{CH}_2\text{CH}_2(\text{CH}_2)_6\text{CH}_3$), 3.87 (2H, s, CH_2 (C9)), 7.22 (1H, d, $J = 8.1$, ArH) 7.38 (1H, s, ArH), 7.50 (1H, d, $J = 8.1$, ArH), 7.61 (1H, d, $J = 8.1$, ArH), 7.65-7.72 (2H, m, ArH); δ_{C} (75.42 MHz; CDCl_3) 14.3, 22.9, 29.6, 29.8, 32.0, 32.1, 36.4, 36.8, 119.8, 120.1, 121.0, 125.3, 127.4, 128.3, 129.9, 138.5, 141.0, 142.5, 143.3, 145.3; m/z (EI) 372 (M^+ (^{81}Br), 42%), 370 (M^+ (^{79}Br), 44), 259 ($\text{Ar}(\text{CH}_2)^{81}\text{Br}^+$, 99), 257 ($\text{Ar}(\text{CH}_2)^{79}\text{Br}^+$, 100), 178 (ArCH_2^+ , 94), 165 (Ar^+ , 12), 152 (12).

8.3.4 2-Iodo-7-alkylfluorenes

2-Iodofluorene

2-Iodofluorene **54a** was successfully prepared by iodination of fluorene. This procedure was carried out by a co-worker.

2-Iodo-7-ethylfluorene

A mixture of 2-ethylfluorene **32b** (0.75 g, 3.9 mmol), iodine (0.35 g, 1.4 mmol), iodic acid (0.14 g, 0.8 mmol), concentrated sulphuric acid (0.15 ml), water (7 ml), glacial acetic acid (25 ml) and carbon tetrachloride (3 ml) was heated at reflux for 20.5 hours. After cooling, sodium metabisulphite solution (aq, 10%, 10 ml) was added and the solution stirred at room temperature for 30 minutes. The solvent was removed. The residue was recrystallized from hot methanol to give a pale yellow solid, impure 2-iodo-7-ethylfluorene **54b** (0.24 g, *ca.* 19 %, mp 160-163 °C (from MeOH)).

δ_{H} (300 MHz; CDCl_3) 1.30 (3H, t, $J = 7.5$, CH_2CH_3), 2.74 (2H, q, $J = 7.5$, CH_2CH_3), 3.85 (2H, s, CH_2 (C9)), 7.23 (1H, d, $J = 7.4$, ArH), 7.39 (1H, s, ArH), 7.50 (1H, d, $J = 8.1$, ArH), 7.69 (2H, d, $J = 7.4$, ArH), 7.87 (1H, s, ArH); δ_{C} (75.42 MHz; CDCl_3) 15.9, 29.1, 36.5, 119.8, 121.2, 124.5, 126.7, 134.1, 135.7, 141.4, 143.0, 143.9, 145.4; m/z (EI) 446 (MI^+ , 9%), 320 (M^+ , 100), 305 ($\text{Ar}(\text{CH}_2)\text{I}^+$, 44), 193 ($\text{ArCH}_2\text{CH}_3^+$, 52), 178 (ArCH_2^+ , 44), 164 (Ar^+ , 11). TLC analysis indicated a single component which co-chromatographed with the starting material. A Mass Spectrum indicated that the product contained *ca.* 10% diiodinated material.

2-Iodo-7-octylfluorene

A mixture of 2-octylfluorene **32h** (0.50 g, 1.8 mmol), concentrated sulphuric acid (0.1 ml), water (1 ml), carbon tetrachloride (2 ml) and glacial acetic acid (10 ml) was heated at 85 °C. Iodine (0.19 g, 0.7 mmol) and iodic acid (0.07 g, 0.4 mmol) were added, and the reaction mixture was heated at 85 °C for 4.0 hours. After cooling, sodium metabisulphite solution (aq, 5%, 10 ml) was added. Dichloromethane (25 ml) was added, and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 x 25 ml). The combined organic extracts were washed with sodium carbonate solution (aq, 10%, 10 ml), sodium metabisulphite solution (aq, 5%, 10 ml) and water (10 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was recrystallized from hot ethanol to give a white solid, impure 2-iodo-7-octylfluorene **54h** (0.36 g, *ca.* 50%).

δ_{H} (300 MHz; CDCl_3) 0.94 (3H, t, $J = 6.6$, $\text{CH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 1.22-1.51 (10H, m, $\text{CH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 1.61-1.75 (2H, m, $\text{CH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 2.71 (2H, t, $J = 7.7$,

$\text{CH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 3.81 (2H, s, CH_2 (C9)), 7.21 (1H, d, $J = 8.1$, ArH), 7.37 (1H, s, ArH), 7.49 (1H, d, $J = 8.1$, ArH), 7.68 (2H, t, $J = 6.6$, ArH), 7.87 (1H, s, ArH); δ_{C} (75.42 MHz; CDCl_3) 14.3, 22.9, 29.5, 29.6, 29.7, 32.0, 32.1, 36.4, 36.7, 91.3, 119.9, 121.4, 125.2, 127.4, 134.2, 135.8, 138.5, 141.6, 142.7, 143.1, 145.6; m/z (EI) 404 (M^+ , 45%), 305 ($\text{Ar}(\text{CH}_2)\text{I}^+$, 92), 278 ($\text{ArC}_8\text{H}_{17}^+$, 7), 178 (ArCH_2^+ , 100), 165 (Ar^+ , 16).

TLC analysis indicated a single component which co-chromatographed with the starting material. A ^1H NMR spectrum indicated the presence of *ca.* 20% non-iodinated 2-octylfluorene.

8.3.5 Boronic acids

4-Cyanobenzoboronic acid

A solution of 4-bromobenzonitrile (10.58 g, 58 mmol) in dry tetrahydrofuran (200 ml) was stirred in a diethyl ether-liquid nitrogen bath under nitrogen. A solution of *n*-butyllithium in hexanes (2.5 M, 24 ml, 60 mmol) was added over 25 minutes. The reaction mixture was stirred in a diethyl ether-chloroform-liquid nitrogen bath for 44 minutes. Triisopropylborate (14 ml, 61 mmol) was added over 8 minutes. The reaction mixture was allowed to warm to room temperature, with stirring, over 8.8 hours. Concentrated hydrochloric acid (20 ml) and water (100 ml) were added, and the resulting cloudy solution was stirred at room temperature for 30 minutes. The products were extracted into dichloromethane (3 x 100 ml). The combined organic extracts were washed with water (3 x 100 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was dissolved in sodium hydroxide solution (aq, 2M, 50 ml). The aqueous layer was washed with diethyl ether (2 x 50 ml). Hydrochloric acid (aq, 1 M, 100 ml) was added to the aqueous layer to give a precipitate. The precipitate was filtered and dried to give a pale orange solid, 4-cyanobenzoboronic acid **34** (5.64 g, 66%, mp >345 °C (ppt from H_2O)). (Found: C, 64.1; H, 3.05; N, 10.5. $\text{C}_7\text{H}_6\text{NO}_2\text{B}$ requires C, 57.2; H, 4.1; N, 9.5%); $\lambda_{\text{max}}(\text{MeCN})/\text{nm}$ 233 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 18300), 240 (16200), 278 (1200), 285 (1100); $\nu_{\text{max}}(\text{nujol})/\text{cm}^{-1}$ 3510m, 3337m, 2229m ($\text{C}\equiv\text{N}$), 1937w, 1682w, 1610w, 1556m, 1415m, 1274m, 1157m, 1065m, 1006m, 834m, 774m, 735m, 586m; δ_{H} (300 MHz; d_6 -DMSO) 7.78 (2H, d, $J = 8.1$, ArH), 7.93 (2H, d, $J = 8.1$, ArH), 8.45 (2H, s, $\text{B}(\text{OH})_2$); δ_{C} (75.42 MHz; d_6 -DMSO) 112.5, 119.1, 131.1, 134.7, 140.0; m/z (EI) 147 (M^+ , 46%), 103 (PhCN^+ , 100), 76 (Ph^+ , 14).

4-Cyanobenzoboronic acid, 1,3-propanediol cyclic ester

A mixture of impure 4-cyanobenzoboronic acid **34** (1.39 g, *ca.* 9.5 mmol), 1,3-propanediol (6.8 ml, 94 mmol) and toluene (25 ml) was heated at reflux for 1.0 hours. After cooling, the solvent was removed. Water (50 ml) and dichloromethane (50 ml) were added, and the aqueous layer was separated. The aqueous layer was extracted with dichloromethane (2 x 50 ml). The combined organic extracts were washed with water (50 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was recrystallized from hot chloroform-60-80 petroleum ether to give an off-white solid, 4-cyanobenzoboronic acid, 1,3-propanediol cyclic ester **61** (1.11 g, 63%, mp 89-91 °C (from CHCl₃-PET(60-80))).

λ_{max} (CH₂Cl₂)/nm 237 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 22500), 245 (20200), 279 (1600), 287 (1500); ν_{max} (CHCl₃ soln.)/cm⁻¹ 3531w (br), 2961m, 2999m, 2230s (C≡N), 1607m, 1552m, 1483vs, 1430vs, 1344vs, 1308vs, 1274vs, 1226s, 1153vs, 1129vs, 1008m, 924m, 839vs; δ_{H} (300 MHz; CDCl₃) 1.95-2.07 (2H, m, OCH₂CH₂CH₂O), 4.12 (4H, t, J = 6.6, OCH₂CH₂CH₂O), 7.78 (4H, s, ArH); δ_{C} (75.42 MHz; CDCl₃) 26.8, 61.9, 113.0, 118.9, 131.1, 131.3, 134.0, 134.7; *m/z* (EI) 187 (M⁺, 86%), 157 (Ph(CN)BOCH₂CH₂⁺, 23), 129 (Ph(CN)BO⁺, 100), 116 (Ph(CN)CH₂⁺, 17), 102 (PhCN⁺, 38), 76 (Ph⁺, 44).

7-Octylfluorene-2-boronic acid (attempted synthesis)

A solution of 2-bromo-7-octylfluorene **24h** (0.99 g, 2.8 mmol) in dry tetrahydrofuran (25 ml) was stirred in a acetone-solid carbon dioxide bath under nitrogen. A solution of *n*-butyllithium in hexanes (2.5 M, 1.1 ml, 2.8 mmol) was added over 10 minutes. The reaction mixture was stirred in a acetone-solid carbon dioxide bath for 30 minutes.

Triisopropylborate (0.65 ml, 2.8 mmol) was added over 5 minutes. The reaction mixture was allowed to warm to room temperature, with stirring, over 7.0 hours. Concentrated hydrochloric acid (2 ml) and water (40 ml) were added, and the resulting cloudy solution was stirred at room temperature for 30 minutes. Dichloromethane (40 ml) was added, and the organic layer was separated. The organic extracts were washed with water (3 x 20 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed to give a yellow solid, impure 2-bromo-7-octylfluorene **24h** (0.78 g, *ca.* 79% recovery).

TLC analysis indicated a single component (*R_f* = 0.82 in DCM) which co-chromatographed with the starting material. ¹H and ¹³C NMR spectra indicated the presence of unknown impurities.

8.3.6 2-(4-Cyanophenyl)-7-alkylfluorenes

Tetrakis(triphenylphosphine)palladium(0)

A mixture of palladium(II)chloride (1 g, 5.6 mmol), triphenylphosphine (7.46 g, 28 mmol) and dimethylsulphoxide (70 ml) was heated at 165 °C. Hydrazine hydrate (1.8 ml, 37 mmol) was added, and the reaction mixture was stirred at 150 °C for 20 minutes. After cooling, the precipitate formed was filtered (sintered glass) and rinsed with diethyl ether (2 x 50 ml) and ethanol (2 x 50 ml). The precipitate was dried to give a green solid, tetrakis-(triphenylphosphine)palladium(0) (5.45 g, 84%, mp 108-114 °C, dec. (lit.,⁷⁵ 116 °C)).

2-(4-Cyanophenyl)fluorene

Nitrogen gas was bubbled through a stirred mixture of impure 2-bromofluorene **24a** (1.36 g, *ca.* 5.55 mmol), impure 4-cyanobenzoboronic acid **34** (0.90 g, *ca.* 6.12 mmol), sodium carbonate solution (aq, 2M, 6 ml) and 1,2-dimethoxyethane (60 ml) for 30 minutes.

Tetrakis(triphenylphosphine)palladium(0) (0.19 g, 160 µm) was added, and the reaction mixture was heated at reflux for 3.1 hours. After cooling, dichloromethane (150 ml) and water (150 ml) were added, and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 x 150 ml). The combined organic extracts were washed with water (150 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was dissolved in dichloromethane (50 ml). The solution was filtered through a plug of silica and rinsed with dichloromethane (2 x 50 ml). The solvent was removed. The residue was recrystallized from hot chloroform-60-80 petroleum ether (charcoal) to give a white solid, 2-(4-cyanophenyl)fluorene **30a** (0.13 g, 9 %, mp 228-230 °C (from CHCl₃-PET(60-80))).

(Found: C, 89.5; H, 4.9; N, 5.1. C₂₀H₁₃N requires C, 89.9; H, 4.9; N, 5.2%);

$\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 229 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 16600), 318 (35900); $\nu_{\max}(\text{CHCl}_3 \text{ soln.})/\text{cm}^{-1}$ 2228s (C≡N), 1606s, 1483w, 1456m, 1408m, 1016w, 956w; δ_{H} (300 MHz; CDCl₃) 3.98 (2H, s, CH₂ (C9)), 7.33-7.47 (2H, m, ArH), 7.60 (2H, m, ArH), 7.72-7.80 (5H, m, ArH), 7.81-7.91 (2H, m, ArH); δ_{C} (75.42 MHz; CDCl₃) 37.1, 110.7, 119.2, 120.4, 120.6, 124.0, 125.3, 126.3, 127.2, 127.4, 127.8, 132.8, 137.7, 141.1, 142.5, 143.7, 144.3, 146.1; m/z (EI) 267 (M⁺, 100), 165 (Ar⁺, 35).

A Mass spectrum indicated the presence of <1% 2,7-di(4-cyanophenyl)fluorene.

2-(4-Cyanophenyl)-7-ethylfluorene

Nitrogen gas was bubbled through a stirred mixture of impure 2-bromo-7-ethylfluorene **24b** (0.99 g, *ca.* 3.6 mmol), impure 4-cyanobenzoboronic acid **34** (0.64 g, *ca.* 4.4 mmol), sodium carbonate solution (aq, 2M, 3.6 ml) and 1,2-dimethoxyethane (43 ml) for 30

minutes. Tetrakis(triphenyl)phosphinepalladium(0) (0.13 g, 112 μm) was added, and the reaction mixture was heated at reflux for 5.5 hours. After cooling, dichloromethane (100 ml) and water (100 ml) were added, and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 x 100 ml). The combined organic extracts were washed with water (100 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was dissolved in dichloromethane (20 ml). The solution was filtered through a plug of silica and rinsed with dichloromethane (3 x 50 ml). The solvent was removed. The residue was recrystallized from hot chloroform-60-80 petroleum ether (charcoal) to give a white solid, 2-(4-cyanophenyl)-7-ethylfluorene **30b** (0.17 g, 16 %, mp 200 °C (from CHCl_3 -PET(60-80))).

(Found: C, 89.2; H, 6.0; N, 4.5. $\text{C}_{22}\text{H}_{17}\text{N}$ requires C, 89.5; H, 5.8; N, 4.7%);

$\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 235 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 10600), 324 (31400). $\nu_{\text{max}}(\text{CHCl}_3 \text{ soln.})/\text{cm}^{-1}$ 3684w, 2967m, 2228s ($\text{C}\equiv\text{N}$), 1605vs, 1511w, 1470s, 1408m, 1280w; δ_{H} (300 MHz; CDCl_3) 1.32 (3H, t, $J = 7.7$, CH_2CH_3), 2.78 (2H, q, $J = 7.7$, CH_2CH_3), 3.95 (2H, s, CH_2 (C9)), 7.26 (1H, d, $J = 7.4$, ArH) 7.43 (1H, s, ArH), 7.60 (1H, d, $J = 8.1$, ArH), 7.70-7.81 (6H, m, ArH), 7.85 (1H, d, $J = 8.1$, ArH); δ_{C} (75.42 MHz; CDCl_3) 16.1, 29.3, 37.0, 110.6, 119.3, 120.2, 124.0, 124.8, 126.2, 127.0, 127.8, 132.7, 137.2, 138.7, 142.6, 144.0, 144.1, 144.3, 146.2; m/z (EI) 295 (M^+ , 100%), 280 ($\text{Ar}(\text{CH}_2)\text{PhCN}^+$, 78), 266 (ArPhCN^+ , 48).

2-(4-Cyanophenyl)-7-propylfluorene

Nitrogen gas was bubbled through a stirred mixture of 2-bromo-7-propylfluorene **24c** (0.54 g, 1.9 mmol), impure 4-cyanobenzoboronic acid **34** (0.41 g, *ca.* 2.8 mmol), sodium carbonate solution (aq, 2M, 1.9 ml) and 1,2-dimethoxyethane (23 ml) for 30 minutes.

Tetrakis(triphenyl)phosphinepalladium(0) (0.07 g, 61 μm) was added, and the reaction mixture was heated at reflux for 3.4 hours. After cooling, dichloromethane (50 ml) and water (50 ml) were added, and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 x 50 ml). The combined organic extracts were washed with water (100 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was dissolved in dichloromethane (10 ml). The solution was filtered through a plug of silica and rinsed with dichloromethane (3 x 25 ml). The solvent was removed. The residue was recrystallized from hot chloroform-60-80 petroleum ether (charcoal) to give a white solid, 2-(4-cyanophenyl)-7-propylfluorene **30c** (0.27 g, 46 %, mp 183 °C (from CHCl_3 -PET(60-80))).

(Found: C, 89.1; H, 5.2; N, 4.5. $\text{C}_{23}\text{H}_{19}\text{N}$ requires C, 89.3; H, 6.2; N, 4.5%);

$\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 324 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 14900); $\nu_{\max}/\text{cm}^{-1}$ (nujol mull) 3684w, 2931vs 2872s, 2228vs ($\text{C}\equiv\text{N}$), 1920w, 1798w, 1605vs, 1510w, 1470s, 1407m, 1280m; δ_{H} (300 MHz; CDCl_3) 1.00 (3H, t, $J = 7.4$, $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.65-1.80 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.70 (2H, t, $J = 7.7$, $\text{CH}_2\text{CH}_2\text{CH}_3$), 3.95 (2H, s, CH_2 (C9)), 7.25 (1H, d, $J = 7.4$, ArH), 7.41 (1H, s, ArH), 7.60 (1H, d, $J = 8.1$, ArH), 7.70-7.80 (6H, m, ArH), 7.84 (1H, d, $J = 8.1$, ArH); δ_{C} (75.42 MHz; CDCl_3) 14.1, 25.0, 37.0, 38.4, 110.6, 119.3, 120.1, 120.2, 123.9, 125.4, 126.2, 127.5, 127.8, 132.7, 137.2, 142.4, 142.6, 144.0, 144.2, 146.2. m/z (EI) 309 (M^+ , 47%), 280 ($\text{Ar}(\text{CH}_2)\text{PhCN}^+$, 100), 266 (ArPhCN^+ , 8).

2-(4-Cyanophenyl)-7-butylfluorene

METHOD I

Nitrogen gas was bubbled through a stirred mixture of impure 2-bromo-7-butylfluorene **24d** (1.00 g, *ca.* 3.3 mmol), impure 4-cyanobenzoboronic acid **34** (0.59 g, *ca.* 4.0 mmol), sodium carbonate solution (aq, 2M, 3.3 ml) and 1,2-dimethoxyethane (40 ml) for 32 minutes. Tetrakis(triphenylphosphine)palladium(0) (0.12 g, 104 μm) was added, and the reaction mixture was heated at reflux for 7.3 hours. After cooling, dichloromethane (100 ml) and water (100 ml) were added, and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 x 100 ml). The combined organic extracts were washed with water (100 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was dissolved in dichloromethane (20 ml). The solution was filtered through a plug of silica and rinsed with dichloromethane (3 x 50 ml). The solvent was removed. The residue was recrystallized from hot 40-60 petroleum ether (charcoal) to give a white solid, 2-(4-cyanophenyl)-7-butylfluorene **30d** (0.03 g, 3 %, mp *ca.* 155 °C (from PET(40-60))).

(Found: C, 88.8; H, 6.4; N, 4.2. $\text{C}_{24}\text{H}_{21}\text{N}$ requires C, 89.1; H, 6.55; N, 4.3%);

$\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 238 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 11000), 324 (34800); $\nu_{\max}(\text{CHCl}_3 \text{ soln.})/\text{cm}^{-1}$ 3684w, 2931m, 2858w, 2228s ($\text{C}\equiv\text{N}$), 1605vs, 1469s, 1407m, 1280w; δ_{H} (300 MHz; CDCl_3) 0.97 (3H, t, $J = 7.4$, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.34-1.48 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.62-1.74 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.71 (2H, t, $J = 7.7$, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 3.95 (2H, s, CH_2 (C9)), 7.25 (1H, d, $J = 7.4$, ArH), 7.41 (1H, s, ArH), 7.51 (1H, d, $J = 8.1$, ArH), 7.70-7.80 (6H, m, ArH), 7.85 (1H, d, $J = 7.4$, ArH); δ_{C} (75.42 MHz; CDCl_3) 14.2, 22.6, 34.1, 36.0, 37.0, 110.6, 119.3, 120.1, 120.2, 123.9, 125.4, 126.2, 127.5, 127.8, 132.7, 137.2, 138.7, 142.6, 144.0, 144.2, 146.2; m/z (EI) 323 (M^+ , 76%), 280 ($\text{Ar}(\text{CH}_2)\text{PhCN}^+$, 100), 266 (ArPhCN^+ , 7).

A second crop of 2-(4-cyanophenyl)-7-butylfluorene **30d** (white solid (0.01 g, 1%)) was isolated from the mother liquor. This co-chromatographed ($R_f = 0.71$ in DCM) and had ^1H and ^{13}C NMR spectra identical to those obtained for the authentic material described above.

METHOD II

Nitrogen gas was bubbled through a stirred mixture of impure 2-bromo-7-butylfluorene **24d** (1.00 g, *ca.* 3.3 mmol), 4-cyanobenzoboronic acid, 1,3-propanediol cyclic ester **61** (0.94 g, 5.0 mmol), sodium carbonate solution (aq, 2M, 3.3 ml) and 1,2-dimethoxyethane (40 ml) for 20 minutes. Tetrakis(triphenylphosphine)palladium(0) (0.12 g, 104 μm) was added, and the reaction mixture was heated at reflux for 3.7 hours. After cooling, dichloromethane (100 ml) and water (100 ml) were added, and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 x 100 ml). The combined organic extracts were washed with water (100 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was dissolved in dichloromethane (20 ml). The solution was filtered through a plug of silica and rinsed with dichloromethane (3 x 50 ml). The solvent was removed. The residue was recrystallized from hot chloroform-60-80 petroleum ether (charcoal) to give a white solid, 2-(4-cyanophenyl)-7-butylfluorene **30d** (0.49 g, 46 %).

A second crop of 2-(4-cyanophenyl)-7-butylfluorene **30d** (pale yellow solid (0.18 g, 17%)) was isolated from the mother liquor.

Both the first and second crop co-chromatographed ($R_f = 0.60$ in DCM) and had ^1H and ^{13}C NMR spectra identical to those obtained for the authentic material described in METHOD I.

2-(4-Cyanophenyl)-7-pentylfluorene

Nitrogen gas was bubbled through a stirred solution of impure 2-bromo-7-pentylfluorene **24e** (0.58 g, *ca.* 1.84 mmol), impure 4-cyanobenzoboronic acid **34** (0.32 g, *ca.* 2.18 mmol), sodium carbonate solution (aq, 2M, 2 ml) and dimethoxyethane (20 ml) for 39 minutes. Tetrakis(triphenylphosphine)palladium(0) (0.07 g, 61 μm) was added, and the reaction mixture was heated at reflux for 5.3 hours. After cooling, dichloromethane (60 ml) and water (60 ml) were added, and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 x 60 ml). The combined organic extracts were washed with water (60 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was dissolved in dichloromethane (10 ml). The solution was filtered through a plug of silica and rinsed with dichloromethane (3 x 50 ml). The solvent was removed. The residue was recrystallized from hot 40-60 petroleum ether (charcoal) to

give a white solid, 2-(4-cyanophenyl)-7-pentylfluorene **30e** (0.13 g, 21 %, mp *ca.* 123 °C (from PET(40-60))).

(Found: C, 88.8; H, 6.9; N, 4.0. C₂₅H₂₃N requires C, 89.0; H, 6.9; N, 4.15%);

$\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 230 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 25200), 324 (61400); $\nu_{\max}(\text{CHCl}_3 \text{ soln.})/\text{cm}^{-1}$ 3675w, 2958w, 2930m, 2857w, 2228s (C \equiv N), 1605s, 1509w, 1470s, 1407w, 1280w; δ_{H} (300 MHz; CDCl₃) 0.93 (3H, t, J = 6.6, CH₂CH₂(CH₂)₂CH₃), 1.32-1.47 (4H, m, CH₂CH₂(CH₂)₂CH₃), 1.64-1.77 (2H, m, CH₂CH₂(CH₂)₂CH₃), 2.70 (2H, t, J = 7.7, CH₂CH₂(CH₂)₂CH₃), 3.94 (2H, s, CH₂ (C9)), 7.25 (1H, d, J = 8.1, ArH) 7.41 (1H, s, ArH), 7.60 (1H, d, J = 8.1, ArH), 7.70-7.79 (6H, m, ArH), 7.84 (1H, d, J = 7.4, ArH); δ_{C} (75.42 MHz; CDCl₃) 14.3, 22.8, 31.7, 31.7, 36.3, 37.0, 110.6, 119.3, 120.1, 120.2, 123.9, 125.4, 126.2, 127.5, 127.7, 132.7, 137.2, 138.7, 142.7, 142.7, 144.0, 144.2, 146.2; m/z (EI) 337 (M⁺, 76%), 280 (Ar(CH₂)PhCN⁺, 100), 266 (ArPhCN⁺, 7), 178 (ArCH₂, 4).

2-(4-Cyanophenyl)-7-hexylfluorene

Nitrogen gas was bubbled through a stirred mixture of impure 2-bromo-7-hexylfluorene **24f** (1.02 g, *ca.* 3.1 mmol), impure 4-cyanobenzoboronic acid **34** (0.55 g, *ca.* 3.7 mmol), sodium carbonate solution (aq, 2M, 3.1 ml) and 1,2-dimethoxyethane (40 ml) for 30 minutes. Tetrakis(triphenylphosphine)palladium(0) (0.11 g, 100 μm) was added, and the reaction mixture was heated at reflux for 6.0 hours. After cooling, dichloromethane (100 ml) and water (100 ml) were added, and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 x 100 ml). The combined organic extracts were washed with water (100 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was dissolved in dichloromethane (20 ml). The solution was filtered through a plug of silica and rinsed with dichloromethane (3 x 50 ml). The solvent was removed. The residue was recrystallized from hot 40-60 petroleum ether (charcoal) to give a white solid, 2-(4-cyanophenyl)-7-hexylfluorene **30f** (0.08 g, 7 %, mp 112 °C (from PET(40-60))).

(Found: C, 88.9; H, 7.2; N, 3.9. C₂₆H₂₅N requires C, 88.8; H, 7.2; N, 4.0%);

$\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 235 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 11500), 324 (35800); $\nu_{\max}(\text{CHCl}_3 \text{ soln.})/\text{cm}^{-1}$ 2929s, 2856m, 2228s (C \equiv N), 1605s, 1510w, 1470s, 1407m, 1281w; δ_{H} (300 MHz; CDCl₃) 0.91 (3H, t, J = 6.6, CH₂CH₂(CH₂)₃CH₃), 1.26-1.45 (6H, m, CH₂CH₂(CH₂)₃CH₃), 1.62-1.75 (2H, m, CH₂CH₂(CH₂)₃CH₃), 2.70 (2H, t, J = 7.7, CH₂CH₂(CH₂)₃CH₃), 3.95 (2H, s, CH₂ (C9)), 7.24 (1H, d, J = 7.4, ArH), 7.41 (1H, s, ArH), 7.61 (1H, d, J = 8.1, ArH), 7.70-7.80 (6H, m, ArH), 7.84 (1H, d, J = 7.4, ArH); δ_{C} (75.42 MHz; CDCl₃) 14.3, 22.8, 29.2, 31.9,

36.4, 37.0, 110.6, 119.3, 120.1, 120.2, 123.9, 125.3, 126.2, 127.5, 127.8, 132.7, 137.2, 138.7, 142.7, 142.7, 144.0, 144.2, 146.2; m/z (EI) 351 (M^+ , 83%), 280 ($Ar(CH_2)PhCN^+$, 100), 266 ($ArPhCN^+$, 7).

A second crop of 2-(4-cyanophenyl)-7-hexylfluorene **30f** (white solid (0.01 g, 1%)) was isolated from the mother liquor. This co-chromatographed ($R_f = 0.71$ in DCM) and had 1H and ^{13}C NMR spectra identical to those obtained for the authentic material described above.

2-(4-Cyanophenyl)-7-heptylfluorene

Nitrogen gas was bubbled through a stirred solution of impure 2-bromo-7-heptylfluorene **24g** (1.36 g, *ca.* 3.97 mmol), impure 4-cyanobenzoboronic acid **34** (0.68 g, *ca.* 4.63 mmol), sodium carbonate solution (aq, 2M, 4 ml) and 1,2-dimethoxyethane (40 ml) for 30 minutes. Tetrakis(triphenylphosphine)palladium(0) (0.14 g, 120 μm) was added, and the reaction mixture was heated at reflux for 7.0 hours. After cooling, dichloromethane (100 ml) and water (100 ml) were added, and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 x 100 ml). The combined organic extracts were washed with water (100 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was dissolved in dichloromethane (15 ml). The solution was filtered through a plug of silica, rinsed with dichloromethane (3 x 50 ml) and the solvent was removed. The residue was recrystallized from hot 40-60 petroleum ether (charcoal) to give a white solid, 2-(4-cyanophenyl)-7-heptylfluorene **30g** (0.18 g, 12 %, mp 115 °C (from PET(40-60))).

(Found: C, 88.65; H, 7.5; N, 3.7. $C_{27}H_{27}N$ requires C, 88.7; H, 7.45; N, 3.8%);

$\lambda_{max}(CH_2Cl_2)/nm$ 230 ($\epsilon/dm^3 mol^{-1} cm^{-1}$ 20600), 324 (48500); $\nu_{max}(CHCl_3 soln.)/cm^{-1}$ 3687w, 2928s, 2856m, 2228 ($C\equiv N$), 1605s, 1508w, 1469s, 1407w, 1280w; δ_H (300 MHz; $CDCl_3$) 0.90 (3H, t, $J = 6.6$, $CH_2CH_2(CH_2)_4CH_3$), 1.25-1.45 (8H, m, $CH_2CH_2(CH_2)_4CH_3$), 1.62-1.75 (2H, m, $CH_2CH_2(CH_2)_4CH_3$), 2.72 (2H, t, $J = 7.7$, $CH_2CH_2(CH_2)_4CH_3$), 3.94 (2H, s, CH_2 (C9)), 7.25 (1H, d, $J = 7.4$, ArH) 7.42 (1H, s, ArH), 7.61 (1H, d, $J = 8.1$, ArH), 7.71-7.80 (6H, m, ArH), 7.83 (1H, d, $J = 8.1$, ArH); δ_C (75.42 MHz; $CDCl_3$) 14.3, 22.9, 29.4, 29.5, 32.0, 36.4, 37.0, 110.6, 119.3, 120.1, 120.2, 123.9, 125.3, 126.2, 127.5, 127.8, 132.7, 138.7, 142.7, 144.0, 144.2, 146.2; m/z (EI) 365 (M^+ , 63%), 280 ($Ar(CH_2)PhCN^+$, 100), 266 ($ArPhCN^+$, 7), 178 ($ArCH_2$, 4).

2-(4-Cyanophenyl)-7-octylfluorene

METHOD I

Nitrogen gas was bubbled through a stirred mixture of 2-bromo-7-octylfluorene **24h** (0.50

g, 1.4 mmol), impure 4-cyanobenzoboronic acid **34** (0.24 g, *ca.* 1.6 mmol), sodium carbonate solution (aq, 2M, 1.4 ml) and 1,2-dimethoxyethane (17 ml) for 81 minutes. Tetrakis(triphenylphosphine)palladium(0) (0.05 g, 43 μ m) was added, and the reaction mixture was heated at reflux for 2.2 hours. After cooling, dichloromethane (40 ml) and water (40 ml) were added, and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 x 40 ml). The combined organic extracts were washed with water (40 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was dissolved in dichloromethane (10 ml). The solution was filtered through a plug of silica and rinsed with dichloromethane (3 x 25 ml). The solvent was removed. The residue was recrystallized from hot 40-60 petroleum ether (charcoal) to give a white solid, 2-(4-cyanophenyl)-7-octylfluorene **30h** (0.02 g, 4 %, mp *ca.* 105 °C (from PET(40-60))).

(Found: C, 88.3; H, 7.3; N, 3.4. C₂₈H₂₉N requires C, 88.6; H, 7.7; N, 3.7%);

λ_{max} (CH₂Cl₂)/nm 324 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 36600); ν_{max} (CHCl₃ soln.)/cm⁻¹ 3684w, 2928vs, 2855s, 2228s (C \equiv N), 1605vs, 1511w, 1469s, 1407m, 1280w; δ_{H} (300 MHz; CDCl₃) 0.89 (3H, t, J = 6.6, CH₂CH₂(CH₂)₅CH₃), 1.23-1.48 (10H, m, CH₂CH₂(CH₂)₅CH₃), 1.61-1.72 (2H, m, CH₂CH₂(CH₂)₅CH₃), 2.70 (2H, t, J = 7.7, CH₂CH₂(CH₂)₅CH₃), 3.95 (2H, s, CH₂(C9)), 7.23 (1H, d, J = 8.1, ArH), 7.41 (1H, s, ArH), 7.61 (1H, d, J = 8.1, ArH), 7.70-7.80 (6H, m, ArH), 7.85 (1H, d, J = 8.1, ArH); δ_{C} (75.42 MHz; CDCl₃) 14.3, 22.8, 29.4, 29.6, 29.7, 32.0, 32.1, 36.4, 37.0, 110.6, 119.3, 120.1, 120.2, 124.0, 125.4, 126.2, 127.5, 127.8, 132.7, 137.2, 138.7, 142.7, 144.0, 144.2, 146.2; *m/z* (EI) 379 (M⁺, 80%), 280 (Ar(CH₂)PhCN⁺, 100), 266 (ArPhCN⁺, 6).

METHOD II

Nitrogen gas was bubbled through a stirred mixture of impure 2-iodo-7-octylfluorene **54h** (0.19 g, *ca.* 470 μ mol), 4-cyanobenzoboronic acid **34** (0.10 g, 680 μ mol), sodium carbonate solution (aq, 2M, 0.5 ml) and 1,2-dimethoxyethane (6 ml) for 15 minutes.

Tetrakis(triphenylphosphine)palladium(0) (0.02 g, 17 μ m) was added, and the reaction mixture was heated at reflux for 1.2 hours. After cooling, dichloromethane (20 ml) and water (20 ml) were added, and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 x 20 ml). The combined organic extracts were washed with water (20 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was dissolved in dichloromethane (25 ml). The solution was filtered through a plug of silica and rinsed with dichloromethane (3 x 50 ml). The solvent

was removed. The residue was recrystallized from hot chloroform-60-80 petroleum ether (charcoal) to give an off-white solid, impure 2-(4-cyanophenyl)-7-octylfluorene **30h** (0.01 g, *ca.* 6%).

TLC analysis indicated a single component which co-chromatographed ($R_f = 0.70$ in DCM) with the authentic material described above in METHOD I.

^1H and ^{13}C NMR spectra were similar to those obtained for the authentic material described above in METHOD I, but showed low levels of unidentified impurities.

2-(4-Cyanophenyl)-7-nonylfluorene

Nitrogen gas was bubbled through a stirred solution of impure 2-bromo-7-nonylfluorene **24i** (0.71 g, *ca.* 1.91 mmol), impure 4-cyanobenzoboronic acid **34** (0.33 g, *ca.* 2.24 mmol), sodium carbonate solution (aq, 2M, 2 ml) and dimethoxyethane (20 ml) for 29 minutes. Tetrakis(triphenylphosphine)palladium(0) (0.08 g, 69 μm) was added, and the reaction mixture was heated at reflux for 5.0 hours. After cooling, dichloromethane (60 ml) and water (60 ml) were added, and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 x 60 ml). The combined organic extracts were washed with water (60 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was dissolved in dichloromethane (20 ml). The solution was filtered through a plug of silica and rinsed with dichloromethane (3 x 50 ml). The solvent was removed. The residue was recrystallized from hot 40-60 petroleum ether (charcoal) to give a white solid, 2-(4-cyanophenyl)-7-nonylfluorene **30i** (0.12 g, 16 %, mp *ca.* 110 °C (from PET(40-60))).

(Found: C, 88.2; H, 8.0; N, 3.45. $\text{C}_{29}\text{H}_{31}\text{N}$ requires C, 88.5; H, 7.9; N, 3.6%);

$\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 231 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 21300), 324 (54200); $\nu_{\text{max}}(\text{CHCl}_3 \text{ soln.})/\text{cm}^{-1}$ 3688w, 2927vs, 2855s, 2228s ($\text{C}\equiv\text{N}$), 1605vs, 1508w, 1469s, 1420w, 1407w, 1280w; δ_{H} (300 MHz; CDCl_3) 0.91 (3H, t, $J = 6.6$, $\text{CH}_2\text{CH}_2(\text{CH}_2)_6\text{CH}_3$), 1.24-1.48 (12H, m, $\text{CH}_2\text{CH}_2(\text{CH}_2)_6\text{CH}_3$), 1.64-1.77 (2H, m, $\text{CH}_2\text{CH}_2(\text{CH}_2)_6\text{CH}_3$), 2.72 (2H, t, $J = 7.7$, $\text{CH}_2\text{CH}_2(\text{CH}_2)_6\text{CH}_3$), 3.95 (2H, s, CH_2 (C9)), 7.25 (1H, d, $J = 7.4$, ArH) 7.42 (1H, s, ArH), 7.60 (1H, d, $J = 8.1$, ArH), 7.70-7.79 (6H, m, ArH), 7.84 (1H, d, $J = 8.1$, ArH); δ_{C} (75.42 MHz; CDCl_3) 14.3, 22.9, 29.5, 29.6, 29.8, 32.0, 32.1, 36.4, 37.0, 110.6, 119.3, 120.1, 120.2, 123.9, 125.3, 126.2, 127.5, 127.7, 132.7, 137.2, 138.7, 142.7, 142.7, 144.0, 144.2, 146.2; m/z (EI) 393 (M^+ , 94%), 280 ($\text{Ar}(\text{CH}_2)\text{PhCN}^+$, 100), 266 (ArPhCN^+ , 7), 178 (ArCH_2 , 3).

8.4 SYNTHESIS OF 2-ALKOXY-7-(4-CYANOPHENYL)FLUORENES

8.4.1 *Synthesis of 2-pentoxy-7-(4-cyanophenyl)fluorene***Phenyl acetate**

METHOD I

Concentrated sulphuric acid (239 mg, 2.4 mmol) was added to a mixture of hydrogen peroxide (aq, 30%, 14.4 g, 0.13 mol) and glacial acetic acid (8.51 g, 0.14 mol). The reaction mixture was stirred at room temperature for 23.2 hours. A solution of acetophenone **76** (0.50 g, 4.2 mmol) in dry dichloromethane (10 ml) was added with caution, and the reaction mixture was stirred at room temperature for 168 hours. Dichloromethane (30 ml) was added, and the organic layer was washed with sodium bicarbonate solution (aq, 5%, 4 x 50 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was chromatographed on silica gel using dichloromethane to give a pale yellow oil, acetophenone **76** (0.33 g, 66% recovery).

The oil co-chromatographed ($R_f = 0.56$ in DCM) and had a ^1H NMR spectrum identical to that obtained for the starting material.

METHOD II

A solution of acetophenone **76** (1.0 ml, 8.5 mmol) in dry dichloromethane (25 ml) was stirred at room temperature. A mixture of *m*-chloroperbenzoic acid (70%, 3.40 g, 14 mmol) and dry dichloromethane (5 ml) was added. Trifluoroacetic acid (0.70 ml, 9.1 mmol) was added over 1 minute, and the reaction mixture was stirred at room temperature for 3.8 hours. Further *m*-chloroperbenzoic acid (70%, 2.36 g, 9.6 mmol) was added, and the reaction mixture was stirred at room temperature for 95.2 hours. Dichloromethane (25 ml) was added, and the organic layer was washed with sodium metabisulphite solution (aq, 20%, 25 ml), potassium carbonate solution (aq, saturated, 25 ml) and water (25 ml), then dried over anhydrous sodium sulphate and filtered. The solvent removed to give a pale yellow oil, impure phenyl acetate **77** (0.67 g, *ca.* 58%).

TLC analysis indicated a single component ($R_f = 0.48$ in DCM) which co-chromatographed with the starting material. A ^{13}C NMR spectrum indicated unknown impurities.

$\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$ 3064w, 2361w, 1765vs (C=O), 1594s, 1493s, 1371s, 1216vs, 1194vs, 1013m, 925s, 815m, 749s, 692s; δ_{H} (300 MHz; CDCl_3) 2.32 (3H, s, CH_3), 7.13 (2H, m, ArH), 7.23-7.29 (1H, m, ArH), 7.39-7.24 (2H, m, ArH); δ_{C} (75.42 MHz; CDCl_3) 21.1, 121.6, 125.9, 129.5, 150.7, 169.5; m/z (EI) 136 (M^+ , 9%), 94 (PhOH^+ , 100), 77 (Ph^+ , 3).

Phenol

A mixture of phenyl acetate **77** (0.40 g, 2.9 mmol), methanol (60 ml) and sodium hydroxide solution (aq, 10%, 10 ml) was heated at reflux for 16 hours. After cooling, the solvent was removed. The residue was dissolved in water (50 ml), and the aqueous layer was washed with diethyl ether (50 ml). Hydrochloric acid (aq, 2M, 50 ml) was added, and the aqueous layer was extracted with diethyl ether (50 ml). The organic layer was dried over anhydrous sodium sulphate and filtered. The solvent was removed to give a pale yellow oil, impure phenol (0.23 g, *ca.* 83%).

($\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3332br (O-H), 3046w, 2848w, 2722w, 2616w, 2480w, 1933w, 1842w, 1711m, 1595s, 1499s, 1472s, 1366m, 1225s, 1168m, 1071m, 1024w, 1000w, 887m, 826m, 810m, 751s, 690s; δ_{H} (300 MHz; CDCl_3) 6.25 (1H, br s, OH), 6.92 (2H, d, $J = 7.4$, ArH), 7.01 (1H, t, $J = 7.4$, ArH), 7.31 (2H, m, ArH); δ_{C} (75.42 MHz; CDCl_3) 115.5, 121.0, 129.8, 155.2; m/z 94 (M^+ , 100%).

The oil co-chromatographed ($R_f = 0.26$ in DCM) and had ^1H and ^{13}C NMR spectra identical to those obtained for a sample of commercial material. The ^{13}C NMR spectrum had very low intensity peaks δ_{C} 115-134 which could not be assigned.

2-Acetoxyfluorene

A mixture of 2-acetylfluorene **31b** (0.98 g, 4.7 mmol), *m*-chloroperbenzoic acid (70%, 4.35 g, 18 mmol) and dry dichloromethane (25 ml) was stirred at room temperature.

Trifluoroacetic acid (0.40 ml, 5.2 mmol) was added over 1 minute, and the reaction mixture was stirred at room temperature for 113 hours. Dichloromethane (25 ml) was added, and the organic layer was washed with sodium metabisulphite solution (aq, 20%, 25 ml), water (25 ml), potassium carbonate solution (aq, saturated, 25 ml) and water (25 ml). The organic extracts were dried over anhydrous sodium sulphate and filtered. The solvent was removed to give a brown solid, 2-acetoxyfluorene **73** (0.91 g, 86%, mp 125 °C (from removal of solvent, DCM, lit.,¹⁶⁴ 128 °C)).

$\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 227 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 3600), 266 (10300), 293 (3600), 304 (4200); $\nu_{\max}(\text{nujol mull})/\text{cm}^{-1}$ 1754m (C=O), 1581w, 1197m, 1129w, 1005w, 940w, 898w, 842w, 775w, 741m; δ_{H} (300 MHz; CDCl_3) 2.35 (3H, s, OCOCH_3), 3.92 (2H, s, CH_2 (C9)), 7.10 (1H, d, $J = 7.4$, ArH), 7.28-7.42 (3H, m, ArH), 7.53 (1H, d, $J = 8.1$, ArH), 7.75 (2H, d, $J = 7.4$, ArH); δ_{C} (75.42 MHz; CDCl_3) 21.4, 37.0, 118.7, 120.0, 120.3, 120.5, 125.2, 126.8, 127.0, 139.7, 141.1, 143.4, 144.7, 149.9, 170.1; m/z (EI) 224 (M^+ , 13%), 182 (ArOH^+ , 100), 165 (Ar^+ , 14).

2-Hydroxyfluorene**METHOD I**

A mixture of 2-acetoxyfluorene **73** (0.63 g, 2.8 mmol), methanol (60 ml) and sodium hydroxide solution (aq, 10%, 10 ml) was heated at reflux for 19.3 hours. After cooling, the solvent was removed. The residue was dissolved in water (50 ml), and the aqueous layer was washed with diethyl ether (50 ml). Hydrochloric acid (aq, 2M, 50 ml) was added, and the aqueous layer was extracted with diethyl ether (50 ml). The organic layer was washed with water (50 ml) then dried over anhydrous sodium sulphate and filtered. The solvent was removed to give a pale orange solid, 2-hydroxyfluorene **49** (0.17 g, 33%, mp 158-160 °C (from silica plug, Et₂O, lit.,¹⁴⁷ 169-170 °C).

ν_{max} (nujol mull)/cm⁻¹ 1703w, 1615w, 1302w, 1267w, 853w, 824w, 764w, 728w; δ_{H} (300 MHz; CDCl₃) 3.86 (2H, s, CH₂ (C9)), 6.87 (1H, dd, J = 8.1, 2.2, ArH), 7.04 (1H, d, J = 2.2, ArH), 7.25 (1H, m, ArH), 7.36 (1H, t, J = 7.0, ArH), 7.51 (1H, d, J = 7.4, ArH), 7.64 (1H, d, J = 8.1, ArH), 7.69 (1H, d, J = 7.4, ArH); δ_{C} (75.42 MHz; CDCl₃) 36.9, 112.2, 114.1, 119.0, 120.7, 124.9, 125.6, 126.7, 134.8, 141.6, 142.6, 145.3, 155.1; m/z (EI) 182 (M⁺, 100%), 165 (Ar⁺, 12).

METHOD II

Sodium (7.17 g, 310 mmol) was added to dry methanol (75 ml) over 2.0 hours. The resulting solution was added to a mixture of 2-acetoxyfluorene **73** (6.69 g, 300 mmol) and dry methanol (250 ml). The reaction mixture was stirred at room temperature for 2.0 hours. The solvent was removed. The residue was dissolved in water (500 ml) and the aqueous layer was washed with diethyl ether (250 ml). Hydrochloric acid (aq, 2 M, 250 ml) was added to give a light brown precipitate. The precipitate was extracted into diethyl ether (2 x 500 ml). The organic layer was washed with water (500 ml), dried over anhydrous sodium sulphate, then filtered through a plug of silica and rinsed with diethyl ether (4 x 100 ml). The solvent was removed to give a pale orange solid, 2-hydroxyfluorene **49** (4.31 g, 79%). The solid co-chromatographed (R_f = 0.27 in DCM) and had ¹H and ¹³C NMR spectra identical to those obtained for the authentic material described above in METHOD I.

2-Pentoxyfluorene**METHOD I**

A solution of 2-hydroxyfluorene **49** (3.04 g, 16.7 mmol) in dry *N,N*-dimethylformamide (50 ml) was stirred in an ice bath under nitrogen. Sodium hydride (60% dispersion, 1.00 g, 25.0 mmol) in dry *N,N*-dimethylformamide (10 ml) was added, and the reaction mixture was

stirred in an ice bath under nitrogen for 1.1 hours. A solution of 1-bromopentane (2.5 ml, 20.2 mmol) in dry *N,N*-dimethylformamide (10 ml) was added over 13 minutes. The stirred reaction mixture was then allowed to warm to room temperature under nitrogen over 23.1 hours. The solvent was removed. Sodium hydroxide solution (aq, 5%, 100 ml) and diethyl ether (100 ml) were added to the residue. The organic layer was separated. The aqueous layer was extracted with diethyl ether (50 ml). The combined organic extracts were washed with sodium hydroxide solution (aq, 5%, 50 ml). Methanol (50 ml) was added, and the organic mixture was washed with water (100 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was chromatographed on silica gel using dichloromethane-40-60 petroleum ether (1:1) as eluent to give five fractions. The least polar fraction was recrystallized from hot ethanol (charcoal) to give a white solid, impure 2-pentoxyfluorene **74e** (0.38 g, *ca.* 9%).

A ^1H NMR spectrum showed unknown impurities, especially in the alkyl region. ^1H and ^{13}C NMR spectra of the less polar fractions suggested the presence of unknown compounds substituted at the 9-position.

METHOD II

Sodium (0.13 g, 5.7 mmol) was added to dry ethanol (50 ml). The resulting solution was added to a mixture of 2-hydroxyfluorene **49** (1.02 g, 5.6 mmol) and dry ethanol (50 ml). The reaction mixture was stirred at room temperature for 1.5 hours. A solution of 1-bromopentane (0.76 ml, 6.1 mmol) in dry ethanol (10 ml) was added over 5 minutes. The reaction mixture was stirred at room temperature for 9.3 hours, then heated at reflux for 11.6 hours. After cooling, the solvent was removed. Sodium hydroxide solution (aq, 20%, 100 ml) and dichloromethane (100 ml) were added to the residue, and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 x 50 ml). The combined organic extracts were washed with sodium hydroxide solution (aq, 20%, 50 ml) and water (50 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was recrystallized from hot ethanol to give a pale orange solid, 2-pentoxyfluorene **74e** (0.84 g, 59%, mp 90-92 °C (from EtOH)).

$\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 225 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 12500), 275 (24600), 306 (8300), 316 (8000);
 $\nu_{\text{max}}(\text{CHCl}_3 \text{ soln.})/\text{cm}^{-1}$ 2958m, 2872m, 1612s, 1581m, 1490s, 1456vs, 1389m, 1306s, 1141s, 1109s, 1031s, 1000m, 951m; δ_{H} (300 MHz; CDCl_3) 0.88 (3H, t, $J = 7.4$, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 1.25-1.46 (4H, m, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 1.68-1.81 (2H, m, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 3.78 (2H, s, CH_2 (C9)), 3.92 (2H, t, $J = 6.6$, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$),

6.85 (1H, d, $J = 7.4$, ArH), 7.01 (1H, s, ArH), 7.15 (1H, t, $J = 7.0$, ArH), 7.26 (1H, t, $J = 7.4$, ArH), 7.42 (1H, d, $J = 7.4$, ArH), 7.59 (2H, t, $J = 7.0$, ArH); δ_{C} (75.42 MHz; CDCl_3) 14.2, 22.7, 28.4, 29.3, 37.2, 68.4, 111.3, 113.7, 119.2, 120.7, 125.0, 125.6, 126.9, 134.7, 141.9, 142.9, 145.2, 159.0; m/z (EI) 252 (M^+ 47%), (ArO^+ , 100), 165 (Ar^+ , 41), 152 (75).

A second crop of 2-pentoxylfluorene **74e** (orange solid (0.02 g, 2%)) was isolated from the mother liquor. This had ^1H and ^{13}C NMR spectra identical to those obtained for the authentic material described above.

2-Bromo-7-pentoxylfluorene

A solution of 2-pentoxylfluorene **74e** (0.60 g, 2.4 mmol) in chloroform (16 ml) was stirred in an ice bath. A solution of bromine (0.12 ml, 2.3 mmol) in chloroform (6 ml) was added over 30 minutes, with the reaction mixture was stirred in an ice bath. The reaction mixture was then allowed to return to room temperature, with stirring, over 2.0 hours. Sodium carbonate solution (aq, 10%, 20 ml) was added, and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 x 15 ml). The combined organic extracts were washed with sodium metabisulphite solution (aq, 5%, 2 x 10 ml) and water (10 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was recrystallized from hot ethanol (charcoal) followed by hot chloroform-60-80 petroleum ether to give a white solid, 2-bromo-7-pentoxylfluorene **75e** (0.09 g, 11 %, mp 112-114 °C (from CHCl_3 -PET (60-80)).

(Found: C, 65.3; H, 5.55; Br, 24.6. $\text{C}_{18}\text{H}_{19}\text{OBr}$ requires C, 65.3; H, 5.8; Br, 24.1%).

$\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 229 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 13400), 285 (30400), 310 (12000), 321 (11300); $\nu_{\text{max}}(\text{CHCl}_3 \text{ soln.})/\text{cm}^{-1}$ 2933m, 2873m, 1611m, 1583w, 1488w, 1462s, 1438m, 1408w, 1340w, 1295m, 1264s, 1177m, 1107m, 1062w, 1027w, 1000w, 948w, 856m, 815m; δ_{H} (300 MHz; CDCl_3) 0.98 (3H, t, $J = 7.0$, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 1.36-1.58 (4H, m, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 1.78-1.93 (2H, m, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 3.83 (2H, s, $\text{CH}_2(\text{C9})$), 4.02 (2H, t, $J = 6.6$, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 6.93 (1H, dd, $J = 8.1, 2.2$, ArH), 7.08 (1H, s, ArH), 7.42-7.57 (2H, m, ArH), 7.59-7.70 (2H, m, ArH); δ_{C} (75.42 MHz; CDCl_3) 14.2, 22.7, 28.4, 29.2, 37.0, 68.5, 111.3, 113.9, 119.3, 120.4, 120.8, 128.2, 129.9, 133.6, 140.9, 144.9, 159.3; m/z (EI) 332 (M^+ (^{81}Br), 29%), 230 (M^+ (^{79}Br), 29), 262 ($\text{Ar}(\text{OH})^{81}\text{Br}^+$, 42), 260 ($\text{Ar}(\text{OH})^{79}\text{Br}^+$, 44), 181 (ArOH^+ , 100), 152 (86).

2-Pentoxyl-7-(4-cyanophenyl)fluorene

Nitrogen gas was bubbled through a stirred mixture of impure 2-bromo-7-pentoxylfluorene **75e** (1.58 g, *ca.* 4.8 mmol), 4-cyanobenzoboronic acid **34** (1.07 g, 7.3 mmol), sodium

carbonate solution (aq, 2M, 5 ml) and 1,2-dimethoxyethane (60 ml) for 20 minutes. Tetrakis(triphenylphosphine)palladium(0) (0.20 g, 133 μmol) was added, and the reaction mixture was heated at reflux for 6.8 hours. After cooling, water (150 ml) and dichloromethane (150 ml) were added, and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 x 150 ml). The combined organic extracts were washed with water (150 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was dissolved in dichloromethane (50 ml) and the solution was filtered through a plug of silica and rinsed with dichloromethane (3 x 50 ml). The solvent was removed. The residue was recrystallized twice from hot chloroform-60-80 petroleum ether (charcoal) to give a white solid, impure 2-pentoxo-7-(4-cyanophenyl)fluorene **72e** (0.16 g, *ca.* 9%, mp 125 °C (from CHCl_3 -PET(60-80))). TLC analysis indicated a single component (R_f = 0.62 in DCM). A mass spectrum indicated the presence of *ca.* 10% brominated product.

(Found: C, 81.0; H, 6.2; N, 3.6. $\text{C}_{25}\text{H}_{23}\text{NO}$ requires C, 84.95; H, 6.6; N, 4.0%);

$\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 230 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 21500), 333 (44500); $\nu_{\text{max}}(\text{CHCl}_3 \text{ soln.})/\text{cm}^{-1}$ 2957m, 2934m, 2872w, 2228s ($\text{C}\equiv\text{N}$), 1604vs, 1510w, 1467vs, 1407m, 1335w, 1280s, 1263s, 1169w, 1040m, 1101m, 1016w, 847m, 819s; δ_{H} (300 MHz; CDCl_3) 0.97 (3H, t, J = 7.0, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 1.45-1.59 (4H, m, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 1.79-1.95 (2H, m, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 3.93 (2H, s, CH_2 (C9)), 4.05 (2H, t, J = 6.6, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 6.97 (1H, dd, J = 8.8, 2.2, ArH) 7.13 (1H, s, ArH), 7.58 (1H, d, J = 7.4, ArH), 7.67-7.81 (7H, m, ArH); δ_{C} (75.42 MHz; CDCl_3) 14.2, 22.7, 28.4, 29.2, 37.2, 68.5, 110.5, 111.4, 114.0, 119.3, 119.7, 121.1, 123.8, 126.3, 127.7, 132.7, 133.8, 136.5, 142.6, 143.8, 145.8, 146.2, 159.4; m/z (EI) 353 (M^+ , 37%), 283 ($\text{Ar}(\text{PhCN})\text{OH}^+$, 100), 266(Ar^+ , 9).

8.4.2 Direct bromination of 2-hydroxyfluorene

2-Hydroxy-3-bromofluorene

A solution of 2-hydroxyfluorene **49** (1.02 g, 5.6 mmol) in chloroform (50 ml) was stirred in an ice bath. A solution of bromine (0.29 ml, 5.6 mmol) in chloroform (10 ml) was added over 26 minutes, with the reaction mixture stirred in an ice bath. The reaction mixture was allowed to warm to room temperature, with stirring, over 1.1 hours. The organic layer was washed with sodium carbonate solution (aq, 10%, 2 x 40 ml). The solvent was removed. The residue was recrystallized from hot ethanol to give an off-white solid, 2-hydroxy-3-bromofluorene **81** (0.47 g, 32%, mp 152-154 °C (from EtOH)).

$\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 228 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 14600), 271 (17700), 278sh, 311sh, 319 (8300);
 $\nu_{\max}(\text{CHCl}_3 \text{ soln.})/\text{cm}^{-1}$ 3518s (O–H), 3262w br, 2901w, 2793w, 1611m, 1576m, 1482m, 1451vs, 1404s, 1342vs, 1314vs, 1130s, 1034m, 959m, 872m; δ_{H} (300 MHz; CDCl_3) 3.83 (2H, s, CH_2 (C9)), 5.58 (1H, s, OH), 7.21 (1H, s, ArH), 7.24-7.32 (1H, m, ArH), 7.32-7.42 (1H, t, $J = 7.4$, ArH), 7.51 (1H, d, $J = 8.1$, ArH), 7.67 (1H, d, $J = 7.4$, ArH), 7.85 (1H, s, ArH); δ_{C} (75.42 MHz; CDCl_3) 36.9, 109.2, 112.9, 119.4, 123.1, 125.2, 126.5, 127.1, 136.3, 140.6, 142.9, 145.0, 151.3; m/z (EI) 262 (M^+ (^{81}Br), 70%), 260 (M^+ (^{79}Br), 71), 181 (ArO^+ , 80), 151 (100), 126 (31), 90 (75), 76 (61), 63 (25).

A gas chromatogram indicated the presence of a second component at slightly longer retention time. A mass spectrum of the second component suggested the presence of dibrominated material. The level of contamination was estimated at <5%.

m/z (EI) 342 ($(\text{M}^{(81}\text{Br})+^{81}\text{Br})^+$, 18%), 340 ($(\text{M}^{(81}\text{Br})+^{79}\text{Br})^+$ and $(\text{M}^{(79}\text{Br})+^{81}\text{Br})^+$, 37), 338 ($(\text{M}^{(79}\text{Br})+^{79}\text{Br})^+$, 18).

1,3-Dibromo-2-hydroxyfluorene

A solution of 2-hydroxyfluorene **49** (18.4 g, 0.10 mol) in chloroform (1200 ml) was stirred in an ice bath. A solution of bromine (5.1 ml, 0.10 mol) in chloroform (200 ml) was added over 3.0 hours, with the reaction mixture stirred in an ice bath. The reaction mixture was allowed to warm to room temperature, with stirring, over 3.2 hours. Sodium carbonate solution (aq, 10%, 800 ml) was added, and the organic layer was separated. The organic layer was washed with sodium metabisulphite solution (aq, 5%, 2 x 300 ml) and water (300 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was recrystallized from hot ethanol to give an off-white solid, 2-hydroxy-3-bromofluorene **81** (6.39 g, 24%). A second crop was isolated from the mother liquor. This was chromatographed on silica gel using dichloromethane-40-60 petroleum ether (1:1) as eluent to give three fractions. The least polar fraction was an off-white solid, 2-hydroxy-3-bromofluorene **81** (4.77 g, 18%). The most polar fraction was recrystallized from hot ethanol to give a white solid, 1,3-dibromo-2-hydroxyfluorene **82** (2.10 g, 6%, mp 151-153 °C (from EtOH)).

(Found: C, 46.1; H, 2.15; Br, 48.7. $\text{C}_{13}\text{H}_8\text{OBr}_2$ requires C, 45.9; H, 2.4; N, 47.0%).

$\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 229 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 23300), 272 (20000), 307 (6600), 318 (7500);
 $\nu_{\max}(\text{CHCl}_3 \text{ soln.})/\text{cm}^{-1}$ 3505s (O–H), 3060w, 1602w, 1560m, 1434vs, 1338s, 1312vs, 1250s, 1163vs, 1103w, 1048m, 978m, 948w, 871m, 838w; δ_{H} (300 MHz; CDCl_3) 3.79 (2H, s, CH_2 (C9)), 5.91 (1H, s, OH), 7.27-7.43 (2H, m, ArH), 7.53 (1H, d, $J = 7.4$, ArH), 7.62

(1H, d, $J = 7.4$, ArH), 7.81 (1H, s, ArH); δ_C (75.42 MHz; CDCl₃) 39.0, 108.0, 108.7, 119.9, 122.8, 125.2, 127.0, 127.3, 136.4, 140.5, 142.1, 144.7, 148.1; m/z (EI) 342 (M^+ ($^{81}\text{Br}^{81}\text{Br}$), 18%), 340 (M^+ ($^{79}\text{Br}^{81}\text{Br}$), 37), 338 (M^+ ($^{79}\text{Br}^{79}\text{Br}$), 20), 261 (Ar(OH) $^{81}\text{Br}^+$, 76), 259 (Ar(OH) $^{79}\text{Br}^+$, 79), 181 (ArO $^+$, 8), 151 (100).

Fluorene-2-phenylsulphonate

A solution of 2-hydroxyfluorene **49** (0.25 g, 1.4 mmol) in dry pyridine (10 ml) was stirred in an ice bath. Benzene sulphonyl chloride (0.20 ml, 1.6 mmol) was added, and the reaction mixture was allowed to warm to room temperature, with stirring, over 15.0 hours. Diethyl ether (25 ml), dichloromethane (25 ml) and sodium hydroxide solution (aq, 20%, 25 ml) were added, and the organic layer was separated. The organic layer was washed with hydrochloric acid (aq, 2M, 25 ml), sodium hydroxide solution (aq, 20%, 25 ml), hydrochloric acid (aq, 2M, 25 ml) and water, then dried over anhydrous sodium sulphate and filtered. The residue was recrystallized from hot ethanol (charcoal) to give an off-white solid, fluorene-2-phenylsulphonate **87** (0.21 g, 47%, mp 109-110 °C (from EtOH)).

(Found: C, 70.6; H, 4.5; S, 9.7. C₁₉H₁₄SO₃ requires C, 70.8; H, 4.4; S, 9.95%).

λ_{max} (CH₂Cl₂)/nm 228 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 9000), 267 (22300), 292 (8400), 304 (9900); ν_{max} (CHCl₃ soln.)/cm⁻¹ 1586w, 1483m, 1454vs, 1374vs, 1283m, 1092vs, 934vs, 873m; δ_H (300 MHz; CDCl₃) 3.84 (2H, s, CH₂ (C9)), 6.93 (1H, dd, $J = 8.1, 2.2$, ArH), 7.25 (1H, s, ArH), 7.28-7.42 (2H, m, ArH), 7.54 (3H, t, $J = 6.3$, ArH), 7.61-7.77 (3H, m, ArH), 7.89 (2H, d, $J = 8.1$, ArH); δ_C (75.42 MHz; CDCl₃) 37.1, 119.6, 120.2, 120.5, 121.1, 125.3, 127.2, 127.3, 128.7, 129.3, 134.4, 135.5, 140.5, 140.9, 143.5, 144.9, 148.6; m/z (EI) 322 (M^+ , 17%), 181 (ArO $^+$, 100), 152 (58).

2-Bromofluorene-7-phenylsulphonate (attempted synthesis)

A solution of fluorene-2-phenylsulphonate **87** (0.12 g, 373 μmol) and bromine (0.05 ml, 973 μmol) in chloroform (10 ml) was heated at reflux for 2.5 hours. After cooling, sodium carbonate solution (aq, 10%, 10 ml) was added and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 x 10 ml). The combined organic layers were washed with sodium metabisulphite solution (aq, 5%, 10 ml) and water (10 ml), then dried over anhydrous sodium sulphate and filtered. The residue was recrystallized from hot ethanol to give an off-white solid, fluorene-2-phenylsulphonate **87** (0.05 g, 42% recovery).

The solid co-chromatographed ($R_f = 0.63$ in DCM) and had ^1H and ^{13}C NMR spectra identical to those obtained for the starting material.

Fluorene-2-tolylsulphonate

A solution of 2-hydroxyfluorene **49** (0.88 g, 4.8 mmol) and *p*-toluene sulphonyl chloride (1.37 g, 7.2 mmol) in dry pyridine (40 ml) was stirred at room temperature for 20.4 hours. Hydrochloric acid (aq, 2M, 100 ml) was added to give an off white precipitate. The precipitate was filtered under suction (glass disc), then rinsed with hydrochloric acid (aq, 2M, 2 x 25 ml) and dried. The residue was recrystallized from hot chloroform-ethanol (charcoal) to give a white solid, fluorene-2-tolylsulphonate **88** (0.69 g, 42%, mp 185-187 °C (from CHCl₃-EtOH)).

(Found: C, 71.4; H, 4.65; S, 9.4. C₂₀H₁₆SO₃ requires C, 71.4; H, 4.8; S, 9.5%). λ_{\max} (CH₂Cl₂)/nm 229 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 16300), 269 (21600), 292 (8100), 304 (9800); ν_{\max} (CHCl₃ soln.)/cm⁻¹ 2924w, 1598w, 1484w, 1454s, 1403w, 1373s, 1307w, 1238w, 1175vs, 1091s, 1020w, 934s, 873m, 836s; δ_{H} (300 MHz; CDCl₃) 2.47 (3H, s, C₆H₄CH₃), 3.87 (2H, s, CH₂ (C9)), 6.93 (1H, dd, J = 8.5, 2.2, ArH), 7.22-7.45 (5H, m, ArH), 7.55 (1H, d, J = 7.4, ArH), 7.65 (1H, d, J = 8.1, ArH), 7.73 (3H, d, J = 8.8, ArH); δ_{C} (75.42 MHz; CDCl₃) 21.9, 37.1, 119.6, 120.1, 120.5, 121.1, 125.2, 127.1, 127.2, 128.8, 129.9, 132.5, 140.6, 140.8, 143.5, 144.8, 145.5, 148.7; *m/z* (EI) 336 (M⁺, 15%), 181 (ArO⁺, 100), 152 (61), 91 (PhCH₃⁺, 16).

2-Bromofluorene-7-tolylsulphonate (attempted synthesis)

A mixture of fluorene-2-tolylsulphonate **88** (0.27 g, 804 μmol), aluminium chloride (0.04 g, 300 μmol) and chloroform (10 ml) was stirred at room temperature. Bromine (0.1 ml, 973 μmol) was added, and the reaction mixture was heated at reflux for 11.2 hours. After cooling, sodium carbonate solution (aq, 10%, 20 ml) was added and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 x 20 ml). The combined organic layers were washed with sodium metabisulphite solution (aq, 5%, 20 ml) and water (20 ml), then dried over anhydrous sodium sulphate and filtered. The residue was recrystallized from hot chloroform-ethanol (charcoal) to give an off-white solid, impure fluorene-2-tolylsulphonate **88** (0.12 g, *ca.* 44% recovery).

TLC analysis indicated a single component (*R_f* = 0.65 in DCM) which co-chromatographed with the starting material. ¹H and ¹³C NMR spectra indicated the presence of unknown impurities.

2-Hydroxy-3-(4-cyanophenyl)fluorene (attempted synthesis)

Nitrogen gas was bubbled through a stirred mixture of 2-hydroxy-3-bromofluorene **81** (1.17 g, 4.5 mmol), impure 4-cyanobenzoboronic acid **34** (0.99 g, *ca.* 6.7 mmol), sodium

carbonate solution (aq, 2M, 4.5 ml) and 1,2-dimethoxyethane (56 ml) for 23 minutes. Tetrakis(triphenylphosphine)palladium(0) (0.16 g, 138 μ mol) was added, and the reaction mixture was heated at reflux for 2.6 hours. After cooling overnight, dichloromethane (100 ml) and water (100 ml) were added, and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 x 100 ml). The combined organic extracts were washed with water (100 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was chromatographed on silica gel using dichloromethane as eluent to give six fractions. GCMS analysis of the least polar fraction indicated a mixture of two components, one of which was unreacted aryl bromide starting material **81**. The identity of the second component was not known.

Data for least polar fraction:

(Found: C, 60.5; H, 3.4; N, 0.0. $C_{20}H_{13}NO$ requires C, 84.8; H, 4.6; N, 4.9%); $\nu_{\max}(\text{CHCl}_3 \text{ soln.})/\text{cm}^{-1}$ 3519m (O–H), 2902w, 2229m ($C\equiv N$), 1608m, 1576m, 1486m, 1451vs, 1404m, 1342s, 1314m, 1283m, 1201m, 1130m, 1034m, 959m, 871m, 843m; δ_{H} (300 MHz; CDCl_3) 3.72 (2H, s, CH_2 (C9)), 5.50 (1H, s, OH), 7.10 (1H, s, ArH), 7.12–7.21 (1H, m, ArH), 7.21–7.30 (1H, t, $J = 7.4$, ArH), 7.30–7.45 (3H, m, ArH), 7.45–7.67 (4H, m, ArH), 7.72 (1H, s, ArH); δ_{C} (75.42 MHz; CDCl_3) 36.9, 109.2, 112.9, 119.4, 123.1, 125.2, 126.5, 127.1, 127.4, 127.9, 128.8, 129.3, 132.8, 136.3, 139.3, 140.6, 143.0, 145.0, 145.8, 151.3; m/z (EI) 262 (M^+ (^{81}Br), 70%), 260 (M^+ (^{79}Br), 71), 181 (ArO^+ , 80), 151 (100), 126 (31), 90 (75), 76 (61), 63 (25).

A gas chromatogram indicated the presence of a second unknown component at shorter retention time.

m/z (EI) 179 (100%), 151 (33).

2-Pentoxy-3-bromofluorene

Sodium (0.09 g, 3.9 mmol) was added to dry ethanol (50 ml). The resulting solution was added to a mixture of 2-hydroxy-3-bromofluorene **81** (0.99 g, 3.8 mmol) and dry ethanol (50 ml). The reaction mixture was stirred at room temperature for 1.5 hours. A solution of 1-bromopentane (0.52 ml, 4.2 mmol) in dry ethanol (10 ml) was added over 3 minutes. The reaction mixture was stirred at room temperature for 10.2 hours, then heated at reflux for 11.6 hours. After cooling, the solvent was removed. Sodium hydroxide solution (aq, 20%, 100ml) and dichloromethane (100 ml) were added to the residue, and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 x 50 ml). The combined organic extracts were washed with sodium hydroxide solution (aq, 20%, 50 ml)

and water (50 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was recrystallized from hot ethanol to give a white solid, 2-pentoxo-3-bromofluorene **83e** (0.72 g, 57%, mp 69-70 °C (from EtOH)).

$\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 228 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 21000), 276 (20600), 313 (8100), 321 (8500); $\nu_{\max}(\text{CHCl}_3 \text{ soln.})/\text{cm}^{-1}$ 2959m, 2934m, 2837w, 1603m, 1570w, 1487m, 1450vs, 1406m, 1388m, 1332m, 1276vs, 1139m, 1035m, 877w, 838w; δ_{H} (300 MHz; CDCl_3) 1.00 (3H, t, $J = 7.0$, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 1.48-1.61 (4H, m, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 1.82-1.95 (2H, m, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 3.81 (2H, s, CH_2 (C9)), 4.08 (2H, t, $J = 6.6$, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 7.10 (1H, s, ArH), 7.26 (1H, t, $J = 8.1$, ArH), 7.45 (1H, t, $J = 7.4$, ArH), 7.51 (1H, d, $J = 7.4$, ArH), 7.66 (1H, d, $J = 7.4$, ArH), 7.92 (1H, s, ArH); δ_{C} (75.42 MHz; CDCl_3) 14.3, 22.6, 28.4, 29.1, 37.1, 69.7, 110.3, 111.3, 119.4, 124.6, 125.0, 126.2, 127.1, 135.9, 140.9, 142.9, 144.1, 154.7; m/z (EI) 332 (M^+ (^{81}Br) 43%), 330 (M^+ (^{79}Br) 44), 262 ($\text{Ar}^{(81}\text{Br})\text{OH}^+$, 70), 260 ($\text{Ar}^{(79}\text{Br})\text{OH}^+$, 89), 181 (ArOH^+ , 89), 165 (Ar^+ , 22), 152 (100).

A second crop of 2-pentoxo-3-bromofluorene **83e** (white solid (0.04 g, 3%)) was isolated from the mother liquor. This had ^1H and ^{13}C NMR spectra identical to those obtained for the authentic material described above.

2-Heptoxo-3-bromofluorene

Sodium (0.13 g, 5.7 mmol) was added to dry ethanol (50 ml). The resulting solution was added to a mixture of 2-hydroxy-3-bromofluorene **81** (1.39 g, 5.3 mmol) and dry ethanol (50 ml). The reaction mixture was stirred at room temperature for 1.1 hours. A solution of 1-bromoheptane (1.0 ml, 6.4 mmol) in dry ethanol (10 ml) was added over 5 minutes. The reaction mixture was heated at reflux for 10.0 hours. After cooling, the solvent was removed. Sodium hydroxide solution (aq, 20%, 150 ml) and dichloromethane (150 ml) were added to the residue, and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 x 75 ml). The combined organic extracts were washed with sodium hydroxide solution (aq, 20%, 75 ml) and water (75 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was recrystallized from hot ethanol to give a white solid, 2-heptoxo-3-bromofluorene **83g** (1.41 g, 80%, mp 84-86 °C (from EtOH)).

(Found: C, 66.6; H, 6.3; Br, 22.9. $\text{C}_{20}\text{H}_{23}\text{OBr}$ requires C, 66.85; H, 6.45; Br, 22.2%).

$\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 229 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 19300), 276 (20800), 313 (8800), 321 (9000); $\nu_{\max}(\text{CHCl}_3 \text{ soln.})/\text{cm}^{-1}$ 2930s, 2872m, 1604m, 1570w, 1486., 1450vs, 1406m, 1382m, 1276s, 1139m, 1035m, 950w, 877w; δ_{H} (300 MHz; CDCl_3) 0.95 (3H, t, $J = 6.6$,

OCH₂CH₂(CH₂)₄CH₃), 1.30-1.65 (8H, m, OCH₂CH₂(CH₂)₄CH₃), 1.83-1.98 (2H, m, OCH₂CH₂(CH₂)₂CH₃), 3.83 (2H, s, CH₂ (C9)), 4.07 (2H, t, J = 6.3, OCH₂CH₂(CH₂)₂CH₃), 7.09 (1H, s, ArH), 7.27 (1H, t, J = 7.4, ArH), 7.37 (1H, t, J = 7.4, ArH), 7.51 (1H, d, J = 7.4, ArH), 7.66 (1H, d, J = 8.1, ArH), 7.92 (1H, s, ArH); δ_C (75.42 MHz; CDCl₃) 14.3, 22.8, 26.2, 29.2, 29.4, 32.0, 37.1, 69.7, 110.3, 111.3, 119.4, 124.6, 125.0, 126.2, 127.1, 135.9, 140.9, 142.9, 144.1, 154.7; *m/z* (EI) 360 (M⁺ (⁸¹Br) 14%), 358 (M⁺ (⁷⁹Br) 14), 262 (Ar(⁸¹Br)OH⁺, 52), 260 (Ar(⁷⁹Br)OH⁺, 54), 181 (ArOH⁺, 100), 165 (Ar⁺, 12), 152 (64).

2-Pentoxo-3-(4-cyanophenyl)fluorene

Nitrogen gas was bubbled through a stirred mixture of 2-pentoxo-3-bromofluorene **83e** (0.44 g, 1.3 mmol), impure 4-cyanobenzoboronic acid **34** (0.29 g, *ca.* 2.0 mmol), sodium carbonate solution (aq, 2M, 1.3 ml) and 1,2-dimethoxyethane (16 ml) for 24 minutes. Tetrakis(triphenylphosphine)palladium(0) (0.05 g, 43 μ mol) was added, and the reaction mixture was heated at reflux for 7.0 hours. After cooling overnight, dichloromethane (40 ml) and water (40 ml) were added, and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 x 40 ml). The combined organic extracts were washed with water (40 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was dissolved in dichloromethane (10 ml). The solution was filtered through a plug of silica and rinsed with dichloromethane (3 x 50 ml). The solvent was removed. The residue was recrystallized from hot chloroform-60-80 petroleum ether (charcoal) to give a pale yellow solid, impure 2-pentoxo-3-(4-cyanophenyl)fluorene **90e** (0.21 g, *ca.* 45 %, mp *ca.* 110 °C (from CHCl₃-PET(60-80))).

(Found: C, 83.8; H, 6.5; N, 3.75. C₂₅H₂₃NO requires C, 84.95; H, 6.6; N, 4.0%); λ_{\max} (CH₂Cl₂)/nm 229 (ϵ /dm³mol⁻¹cm⁻¹ 24200), 271 (45800), 295sh, 331 (9800); ν_{\max} (CHCl₃ soln.)/cm⁻¹ 2958s, 2872m, 2228s (C \equiv N), 1606s, 1454vs, 1401s, 1340s, 1275s, 1136s, 1031m, 843vs; δ_H (300 MHz; CDCl₃) 0.93 (3H, t, J = 7.8, OCH₂CH₂(CH₂)₂CH₃), 1.30-1.46 (4H, m, OCH₂CH₂(CH₂)₂CH₃), 1.71-1.82 (2H, m, OCH₂CH₂(CH₂)₂CH₃), 3.94 (2H, s, CH₂ (C9)), 4.05 (2H, t, J = 6.6, OCH₂CH₂(CH₂)₂CH₃), 7.22 (1H, s, ArH) 7.25-7.32 (1H, m, ArH), 7.38 (1H, t, J = 7.4, ArH), 7.55 (1H, d, J = 7.4, ArH), 7.65-7.77 (6H, m, ArH); δ_C (75.42 MHz; CDCl₃) 14.2, 22.5, 28.4, 29.0, 37.3, 69.0, 109.6, 110.3, 119.3, 119.5, 121.8, 125.1, 126.1, 127.1, 128.0, 130.6, 131.8, 134.9, 141.5, 142.8, 144.2, 145.6, 155.7; *m/z* (EI) 353 (M⁺, 65%), 283 (Ar(PhCN)OH⁺, 100), 253(40), 226 (19), 181 (ArO⁺, 20), 152 (9).

A gas chromatogram indicated the a small amount of a second component at shorter

retention time. This component had an identical mass spectrum to the aryl bromide starting material.

3-Bromofluorene-2-trifluoromethylsulphonate

A solution of 2-hydroxy-3-bromofluorene **81** (1.12 g, 4.7 mmol) in dry pyridine (40 ml) was stirred at room temperature. Trifluoromethanesulphonic anhydride (1.2 ml, 7.3 mmol) was added, and the mixture was stirred at room temperature for 12.8 hours. Hydrochloric acid (aq, 2 M, 100 ml) and diethyl ether (100 ml) were added, and the organic layer was separated. The aqueous layer was extracted with diethyl ether (2 x 100 ml). The combined organic extracts were washed with hydrochloric acid (aq, 2 M, 50 ml) and water (50 ml), then dried over anhydrous sodium sulphate and filtered. The residue was chromatographed on silica gel using chloroform as eluent to give a yellow oil, impure 3-bromofluorene-2-trifluoromethylsulphonate **91** (1.75 g, *ca.* 96%).

TLC analysis indicated a single component ($R_f = 0.75$ in DCM). ^1H and ^{13}C NMR spectra indicated the presence of unknown impurities.

λ_{max} (CH_2Cl_2)/nm 229 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 17300), 268 (21800), 297 (9000), 309 (10700); ν_{max} (CHCl_3 soln.)/ cm^{-1} 1425s, 1332w, 1290w, 1230w, 1139s, 1034w, 954s, 847s, 816m; δ_{H} (300 MHz; CDCl_3) 3.80 (2H, s, CH_2 (C9)), 7.32-7.45 (2H, m, ArH), 7.48 (1H, s, ArH), 7.56 (1H, d, $J = 6.6$, ArH), 7.68 (1H, d, $J = 6.6$, ArH), 7.93 (1H, s, ArH); δ_{C} (75.42 MHz; CDCl_3) 36.9, 114.6, 116.7, 119.6, 120.6, 125.1, 125.4, 127.4, 128.3, 139.0, 143.3, 143.8, 144.1, 145.4; m/z (EI) 394 (M^+ (^{81}Br), 6%), 392 (M^+ (^{79}Br), 6), 261 (Ar (^{81}Br) O^+ , 39), 259 (Ar (^{79}Br) O^+ , 40), 181 (ArO^+ , 3), 152 (100).

3-(4-Cyanophenyl)fluorene-2-trifluoromethylsulphonate

Nitrogen gas was bubbled through a mixture of 3-bromofluorene-2-trifluoromethylsulphonate **91** (0.47 g, 1.2 mmol), 4-cyanobenzoboronic acid **34** (0.52 g, 3.5 mmol), lithium chloride (0.08 g, 1.3 mmol), sodium carbonate solution (aq, 2M, 1.2 ml) and 1,2-dimethoxyethane (15 ml) for 35 minutes. Tetrakis(triphenylphosphine)palladium(0) (0.05 g, 43 μmol) was added, and the reaction mixture was heated at reflux for 3.7 hours. After cooling, water (50 ml) and dichloromethane (50 ml) were added, and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2x 50 ml). The combined organic extracts were washed with water (50 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was dissolved in dichloromethane (25 ml). The solution was filtered through a plug of silica and rinsed with dichloromethane (3 x 50 ml). The solvent was removed. The residue was chromatographed

on silica gel using dichloromethane-hexane (1:1) as eluent to give a pale yellow solid, impure 3-(4-cyanophenyl)fluorene-2-trifluoromethylsulphonate **97** (0.09 g, *ca.* 18%). TLC analysis indicated a single component ($R_f = 0.63$ in DCM). ^1H and ^{13}C NMR spectra indicated the presence of unknown impurities.

λ_{max} (CH_2Cl_2)/nm 228 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 18300), 261 (43800), 306 (8800); ν_{max} (CHCl_3 soln.)/ cm^{-1} 2232m ($\text{C}\equiv\text{N}$), 1608w, 1481w, 1452m, 1424vs, 1340w, 1292w, 1244s, 1204s, 1140vs, 1098m, 1022w, 951s, 842vs; δ_{H} (300 MHz; CDCl_3) 3.92 (2H, s, CH_2 (C9)), 7.26-7.54 (2H, m, ArH), 7.56-7.61 (4H, m, ArH), 7.68-7.85 (4H, t, $J = 4.0$, ArH); δ_{C} (75.42 MHz; CDCl_3) 37.2, 112.3, 118.8, 119.3, 120.6, 122.3, 124.8, 125.5, 127.5, 128.2, 130.5, 132.0, 132.5, 139.6, 141.1, 142.6, 143.7, 145.2, 145.4; m/z (EI) 415 (M^+ 10%), 282 (Ar(O)PhCN^+ , 100), 253 (20).

8.4.3 Other strategies for bromination

2-Bromo-7-acylfluorene

METHOD I

A mixture of 2-acetylfluorene **31b** (0.30 g, 1.4 mmol), *N*-bromosuccinimide (0.29 g, 1.6 mmol) and dry *N,N*-dimethylformamide (10 ml) was stirred at room temperature for 14.0 hours. The solvent was removed. Water (20 ml) and dichloromethane (20 ml) were added, and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 x 20 ml). The combined organic extracts were washed with sodium carbonate solution (aq, 10%, 20 ml), sodium metabisulphite solution (aq, 5%, 20 ml) and water (20 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was recrystallized from hot chloroform-60-80 petroleum ether (charcoal) to give a (1:1) mixture of 2-acetylfluorene **31b** and 2-acetyl-9-bromofluorene **101**.

TLC analysis indicated a single component ($R_f = 0.46$ in DCM).

Selected spectral data: δ_{H} (300 MHz; CDCl_3) 6.01 (1H, s, CHBr (C9)); m/z (EI) 286 (M^+ (^{81}Br), 5%), 284 (M^+ (^{79}Br), 5).

METHOD II

A mixture of 2-acetylfluorene **31b** (1.07 g, 5.1 mmol), *N*-bromosuccinimide (1.44 g, 8.1 mmol) and dry *N,N*-dimethylformamide (30 ml) was heated at 70 °C for 14.5 hours. After cooling, the solvent was removed. Water (75 ml) and dichloromethane (75 ml) were added, and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 x 75 ml). The combined organic extracts were washed with sodium carbonate solution

(aq, 10%, 75 ml), sodium metabisulphite solution (aq, 5%, 75 ml) and water (75 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was chromatographed on silica gel using chloroform as eluent to give five fractions.

Fraction 2 was recrystallized from hot chloroform-60-80 petroleum ether (charcoal) to give a yellow-orange solid α -bromo-2-acetylfluorene **100** (0.13g, 9%).

The solid co-chromatographed ($R_f = 0.74$ in DCM) and had ^1H and ^{13}C NMR spectra identical to those obtained for the authentic material prepared by a co-worker.

METHOD III

2-Bromo-7-acylfluorene **102** was successfully prepared by acetylation of 2-bromofluorene **24a**. This procedure was carried out by a co-worker.

2-Bromo-7-acetoxyfluorene

METHOD I

A solution of 2-acetoxyfluorene **73** (0.60 g, 2.7 mmol) in chloroform (18 ml) was stirred in an ice bath. A solution of bromine (0.14 ml, 2.7 mmol) in chloroform (7 ml) was added over 30 minutes, with the reaction mixture stirred in an ice bath. The reaction mixture was allowed to warm to room temperature, with stirring, over 19.0 hours. Sodium carbonate solution (aq, 10%, 20 ml) was added, and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 x 15 ml). The combined organic extracts were washed with sodium metabisulphite solution (aq, 5%, 2 x 10 ml) and water (10 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was chromatographed on silica gel using chloroform as eluent to give three fractions. The most polar fraction was recrystallized from hot chloroform-60-80 petroleum ether to give a yellow-brown solid, impure 2-hydroxyfluorene **49**.

TLC analysis indicated a single component ($R_f = 0.18$ in DCM). ^1H and ^{13}C NMR spectra indicated the presence of unknown impurities.

METHOD II

A mixture of 2-acetoxyfluorene **73** (0.34 g, 1.5 mmol), *N*-bromosuccinimide (0.30 g, 1.7 mmol) and dry *N,N*-dimethylformamide (10 ml) was stirred at room temperature for 14.0 hours. The solvent was removed. Water (20 ml) and dichloromethane (20 ml) were added, and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 x 20 ml). The combined organic extracts were washed with sodium carbonate solution (aq, 10%, 20 ml), sodium metabisulphite solution (aq, 5%, 20 ml) and water (20 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was chromatographed on silica gel to give four fractions. The least polar fraction was

recrystallized from hot chloroform-60-80 petroleum ether to give a (1:1) mixture of 2-acetoxyfluorene **73** and 2-bromo-7-acetoxyfluorene **98**.

TLC analysis indicated a single component ($R_f = 0.58$ in DCM).

METHOD III

A mixture of 2-acetoxyfluorene **73** (0.50 g, 2.2 mmol), *N*-bromosuccinimide (0.88 g, 4.9 mmol) and dry *N,N*-dimethylformamide (15 ml) was stirred at room temperature for 11.5 hours. The solvent was removed. Water (30 ml) and dichloromethane (30 ml) were added, and the organic layer was separated. The aqueous layer was extracted with dichloromethane (30 ml). The combined organic extracts were washed with sodium carbonate solution (aq, 10%, 30 ml), sodium metabisulphite solution (aq, 5%, 30 ml) and water (30 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was recrystallized from hot chloroform-60-80 petroleum ether (charcoal) to give impure 2-acetoxy-9-bromofluorene **99**.

TLC analysis indicated a single component ($R_f = 0.63$ in DCM). ^1H and ^{13}C NMR spectra indicated the presence of unknown impurities.

METHOD IV

2-Bromo-7-acetoxyfluorene **98** was successfully prepared by a Baeyer-Villiger rearrangement of 2-bromo-7-acetylfluorene **102**. This procedure was carried out by a co-worker.

2-Bromo-7-hydroxyfluorene

Sodium (0.27 g, 11.7 mmol) was added to dry methanol (10 ml) over 15 minutes. The resulting solution was added to a mixture of 2-bromo-7-acetoxyfluorene **98** (0.36 g, 1.2 mmol) and dry methanol (10 ml). The reaction mixture was stirred at room temperature for 2.0 hours. The solvent was removed. The residue was dissolved in water (20 ml) and the aqueous layer was washed with diethyl ether (10 ml). Hydrochloric acid (aq, 2M, 10 ml) was added to give an orange precipitate. The precipitate was extracted into diethyl ether (2 x 20 ml). The combined organic extracts were washed with water (20 ml), then dried over anhydrous sodium sulphate and filtered through a plug of silica. The solvent was removed to give a orange solid, impure 2-bromo-7-hydroxyfluorene **103** (0.28 g, *ca.* 91%, mp 171-174 °C (lit.,¹¹⁴ 175-178 °C).

TLC analysis indicated a single component ($R_f = 0.20$ in DCM). ^1H and ^{13}C NMR spectra indicated the presence of unknown impurities.

λ_{max} (CH_2Cl_2)/nm 228 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 9000), 278 (19900), 308 (6600), 319

(6500); ν_{\max} (CHCl₃ soln.)/cm⁻¹ 3595m, 3309m (br), 1614s, 1586m, 1486m, 1463vs, 1408m, 1343m, 1274s, 1170m, 1101m, 1061w, 1038w, 933m, 857m, 814s; δ_{H} (300 MHz; d₆-DMSO) 3.72 (2H, s, CH₂ (C9)), 6.80 (1H, dd, J = 8.5, 2.6, ArH), 6.95 (1H, s, ArH), 7.30-7.47 (1H, m, ArH), 7.47-7.53 (3H, m, ArH), 9.02 (1H, s, OH); δ_{C} (75.42 MHz; d₆-DMSO) 36.2, 111.9, 114.2, 118.1, 119.6, 120.3, 127.5, 129.2, 131.8, 140.7, 144.2, 144.4, 157.0; m/z (EI) 262 (M⁺ (⁸¹Br), 32%), 260 (M⁺ (⁷⁹Br), 34), 181 (ArO⁺, 100), 152 (58).

2-Iodo-7-acetylfluorene (attempted synthesis)

A mixture of impure 2-iodofluorene **54a** (0.50 g, *ca.* 1.7 mmol), acetyl chloride (0.12 ml, 1.7 mmol) and dry 1,1,2,2-tetrachloroethane (20 ml) was stirred in an ice bath. Aluminium chloride (0.65 g, 4.9 mmol) was added, and the stirred reaction mixture was allowed to warm to room temperature over 25.0 hours. Further aluminium chloride (0.22 g, 1.6 mmol) was added and the reaction mixture was stirred at room temperature for 11.8 hours. Water (10 ml) and concentrated hydrochloric acid (10 ml) were added, and the products were extracted into dichloromethane (3 x 10 ml). The combined organic extracts were washed with sodium bicarbonate solution (aq, 10%, 2 x 10 ml) and water (10 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was recrystallized from hot chloroform-hexane (charcoal) to give a yellow solid (0.18 g), a mixture of acetylated products.

TLC analysis indicated a single component (R_f = 0.40 in DCM).

8.5 SYNTHESIS OF LATERALLY SUBSTITUTED FLUORENES

8.5.1 9-Alkyl and 9,9-dialkylfluorenes

9-Methylfluorene

A solution of fluorene (1.66 g, 10 mmol) in dry tetrahydrofuran (25 ml) was stirred in an acetone-solid carbon dioxide bath under argon. A solution of *n*-butyllithium in hexanes (1.5 M, 7.0 ml, 10.5 mmol) was added, and the reaction mixture was stirred in an acetone-solid carbon dioxide bath under argon for 1.8 hours. Methyl iodide (0.75 ml, 12.0 mmol) was added over 5 minutes, and the reaction mixture was stirred in an acetone-solid carbon dioxide bath under argon for 30 minutes. The reaction mixture was allowed to warm to room temperature over 2.6 hours. Further methyl iodide (0.50 ml, 8.0 mmol) was added, and the reaction mixture was stirred at room temperature under argon for 19.3 hours. Ammonium chloride solution (aq, 4%, 25 ml) was added, and the products were extracted into diethyl ether (3 x 30 ml). The combined organic extracts were washed with sodium

thiosulphate solution (aq, 10%, 30 ml) and water (2 x 30 ml) then dried over anhydrous sodium sulphate and filtered through a plug of alumina. The solvent was removed. The residue was chromatographed on silica gel using dichloromethane-40-60 petroleum ether (1:1) as eluent, then recrystallized from hot ethanol-methanol-water followed by hot methanol-water to give a mixture of 9-methylfluorene **112a** and 9,9-dimethylfluorene **120a** (pale yellow solid, 0.04 g).

Selected spectral data: δ_{H} (300 MHz; CDCl_3) 1.59 (3H, d, $J = 5.6$, CHCH_3), 3.98 (1H, t, $J = 5.6$, CHCH_3).

9,9-Dimethylfluorene

A solution of fluorene (4.02 g, 24 mmol) in dry tetrahydrofuran (50 ml) was stirred in an acetone-solid carbon dioxide bath under nitrogen. A solution of *n*-butyllithium in hexanes (2.5 M, 13 ml, 33 mmol) was added over 10 minutes. The reaction mixture was stirred in an acetone-solid carbon dioxide bath under nitrogen for 15 minutes. Methyl iodide (2.3 ml, 37 mmol) was added over 20 minutes. The reaction mixture was stirred in an acetone-solid carbon dioxide bath under nitrogen for 1.1 hours. A solution of *n*-butyllithium in hexanes (2.5 M, 13 ml, 33 mmol) was added over 10 minutes. The reaction mixture was stirred in an acetone-solid carbon dioxide bath under nitrogen for 15 minutes. Methyl iodide (2.3 ml, 37 mmol) was added over 20 minutes. The reaction mixture was allowed to warm to room temperature with stirring, over 15.6 hours. Ammonium chloride (aq, 5%, 50 ml) was added, and the products were extracted into diethyl ether (3 x 100 ml). The combined organic extracts were washed with sodium thiosulphate solution (aq, 10%, 75 ml) and water (75 ml), then dried over anhydrous sodium sulphate and filtered through a plug of alumina. The solvent was removed. The residue was recrystallized from hot methanol to give an off-white oily solid, impure 9,9-dimethylfluorene **120a** (1.75 g, *ca.* 37 %, mp 60-63 °C (from MeOH, lit.,⁵⁰ 94-95 °C)).

TLC analysis indicated a single component ($R_f = 0.77$ in DCM) which co-chromatographed with the starting material. ^1H and ^{13}C NMR spectra indicated the presence of unknown impurities. GCMS analysis indicated the presence of <1% 9-methylfluorene **112a** and *ca.* 5% 9-methyl-9-butylfluorene **132**.

δ_{H} (300 MHz; CDCl_3) 1.60 (6H, s, CH_3), 7.38-7.48 (4H, m, ArH), 7.51-7.56 (2H, m, ArH), 7.78-7.85 (2H, m, ArH); δ_{C} (75.42 MHz; CDCl_3) 27.4, 47.1, 120.2, 122.8, 127.2, 127.5, 139.4, 152.4; m/z (EI) 194 (M^+ , 46%), 179 (ArCH_3^+ , 100), 152 (15).

9-Ethylfluorene

A mixture of fluorene (1.09 g, 6.6 mmol), hydrazine hydrate (3.2 ml, 66 mmol), potassium hydroxide (3.68 g, 66 mmol) and diethylene glycol (25 ml) was heated at reflux for 3.0 hours. The reaction mixture was then heated strongly for 3.0 hours to distil out water. After cooling, water (75 ml) and concentrated hydrochloric acid (10 ml) were added, and the products were extracted into dichloromethane (3 x 75 ml). The combined organic extracts were washed with water (75 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was chromatographed on silica gel using dichloromethane-40-60 petroleum ether (1:1) as eluent to give a green oil, impure 9-ethylfluorene **112b** (0.05 g, *ca.* 4%).

TLC analysis indicated a single component ($R_f = 0.82$ in DCM). ^1H and ^{13}C NMR spectra indicated the presence of unknown impurities.

δ_{H} (300 MHz; CDCl_3) 0.62 (3H, t, $J = 7.4$, CH_2CH_3), 1.93-2.04 (2H, m, CH_2CH_3), 3.85 (1H, t, $J = 5.5$, CH (C9)), 7.18-7.31 (4H, m, ArH), 7.41 (2H, d, $J = 6.6$, ArH), 7.66 (2H, d, $J = 7.4$, ArH); δ_{C} (75.42 MHz; CDCl_3) 9.9, 25.9, 48.7, 112.0, 124.5, 127.0, 127.1, 141.5, 147.4; m/z (EI) 194 (M^+ , 33%), 165 (Ar^+ , 100).

8.5.2 2-Alkyl-9-alkylfluorenes

2-Ethyl-9-ethylfluorene

A mixture of 2-acetylfluorene **31b** (1.01 g, 4.9 mmol), hydrazine hydrate (2.4 ml, 49 mmol), potassium hydroxide (2.73 g, 49 mol) and diethylene glycol (25 ml) was heated at reflux for 3.0 hours. The reaction mixture was heated strongly for 3.0 hours to distil out water. After cooling, water (75 ml) and concentrated hydrochloric acid (10 ml) were added, and the products were extracted into dichloromethane (2 x 75 ml). The combined organic extracts were washed with water (75 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was chromatographed on silica gel using chloroform as eluent to give an orange-brown oil, impure 2-ethyl-9-ethylfluorene **33b** (0.45 g, *ca.* 42%).

TLC analysis indicated a single component ($R_f = 0.76$ in DCM). ^1H and ^{13}C NMR spectra indicated the presence of unknown impurities.

δ_{H} (300 MHz; CDCl_3) 0.80 (3H, t, $J = 7.4$, CH_2CH_3 (C9)), 1.36 (3H, t, $J = 7.4$, CH_2CH_3 (C2)), 2.08-2.21 (2H, m, CH_2CH_3 (C9)), 2.81 (2H, q, $J = 7.4$, CH_2CH_3 (C2)), 3.98 (1H, t, $J = 5.4$, CH (C9)), 7.22-7.38 (2H, m, ArH), 7.40-7.48 (2H, m, ArH), 7.55 (1H, d, $J = 7.4$, ArH), 7.72 (1H, d, $J = 8.1$, ArH), 7.77 (1H, d, $J = 8.1$, ArH); δ_{C} (75.42 MHz; CDCl_3) 10.1,

16.2, 26.0, 29.4, 48.6, 119.6, 119.7, 124.0, 124.4, 126.5, 126.8, 127.0, 139.2, 141.6, 143.4, 147.4, 147.7; m/z (EI) 222 (M^+ , 34%), 207 ($Ar(CH_2)CH_2CH_3^+$, 7), 193 ($ArCH_2CH_3^+$, 100), 178 ($ArCH_2^+$, 81), 165 (Ar^+ , 13).

2-Propyl-9-ethylfluorene

A mixture of 2-propionylfluorene **31c** (7.05 g, 32 mmol), hydrazine hydrate (15.5 ml, 320 mmol), potassium hydroxide (17.8 g, 320 mol) and diethylene glycol (150 ml) was heated at reflux for 1.5 hours. The reaction mixture was heated strongly for 42 minutes to distil out water. After cooling, water (500 ml) and concentrated hydrochloric acid (50 ml) were added, and the products were extracted into dichloromethane (2 x 500 ml). The combined organic extracts were washed with water (500 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was chromatographed on silica gel using dichloromethane-40-60 petroleum ether (1:1) as eluent to give an orange oily solid, impure 2-propyl-9-ethylfluorene **33c** (3.55 g, *ca.* 47%).

TLC analysis indicated a single component (R_f = 0.85 in DCM). 1H and ^{13}C NMR spectra indicated the presence of unknown impurities.

δ_H (300 MHz; $CDCl_3$) 0.83 (3H, t, J = 7.4, $CH_2CH_2CH_3$), 1.08 (3H, t, J = 7.4, CH_2CH_3), 1.78 (2H, m, CH_2CH_3), 2.12-2.25 (2H, m, $CH_2CH_2CH_3$), 2.76 (2H, t, J = 7.4, $CH_2CH_2CH_3$), 4.01 (1H, t, J = 5.5, CH (C9)), 7.28 (1H, d, J = 8.1, ArH), 7.32-7.46 (3H, m, ArH), 7.58 (1H, d, J = 7.4, ArH), 7.75 (1H, d, J = 8.7, ArH), 7.81 (1H, d, J = 8.1, ArH); δ_C (75.42 MHz; $CDCl_3$) 10.1, 14.1, 25.2, 26.0, 38.6, 48.6, 119.6, 119.7, 124.5, 124.7, 126.4, 127.0, 127.4, 139.2, 141.7, 141.8, 147.4, 147.6; m/z (EI) 236 (M^+ , 56%), 207 ($ArCH_2CH_2CH_3^+$, 100), 178 ($ArCH_2^+$, 81).

2-Propyl-9-propylfluorene (mixture of isomers)

A mixture of 2-propionylfluorene **31c** (1.11 g, 5.0 mmol), hydrazine hydrate (2.4 ml, 49 mmol), potassium hydroxide (2.99 g, 53 mmol) and di(propylene glycol) (25 ml) was heated at reflux for 3.0 hours. The reaction mixture was heated strongly for 3.0 hours to distil out water. After cooling, water (75 ml) and concentrated hydrochloric acid (10 ml) were added, and the products were extracted into dichloromethane (3 x 75 ml). The combined organic extracts were washed with water (75 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was chromatographed on silica gel using dichloromethane-40-60 petroleum ether (1:1) as eluent to give a yellow oil impure 2-propyl-9-propylfluorene **121** (0.55 g, *ca.* 44%).

TLC analysis indicated a single component (R_f = 0.86 in DCM). 1H and ^{13}C NMR spectra indicated the presence of unknown impurities.

δ_{H} (300 MHz; CDCl_3) 0.85 (t, $J = 7.4$) and 1.02 (t, $J = 7.0$) (3H, CH_3 s (Pr)), 1.12 (3H, t, $J = 7.4$, $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.31-1.49 (m) and 1.65 (d, $J = 7.4$) (2H, $\text{CH} + \text{CH}_2$ (Pr)), 1.77-1.92 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.02-2.16 (2H, m, CH_2 (Pr)), 2.80 (2H, t, $J = 7.7$, $\text{CH}_2\text{CH}_2\text{CH}_3$), 4.00-4.14 (1H, m, CH (C9)), 7.30 (1H, d, $J = 7.4$, ArH), 7.35-7.52 (3H, m, ArH), 7.62 (1H, d, $J = 6.6$, ArH), 7.78 (1H, d, $J = 7.4$, ArH), 7.84 (1H, d, $J = 7.4$, ArH); δ_{C} (75.42 MHz; CDCl_3) 14.2, 14.7, 19.4, 25.2, 35.8, 38.6, 47.6, 119.7, 124.6, 124.8, 126.5, 127.0, 127.4, 139.0, 141.5, 141.8, 148.1, 149.5; m/z (EI) 250 (M^+ , 87%), 221 ($\text{Ar}(\text{CH}_2)\text{CH}_2\text{CH}_2\text{CH}_3^+$, 54), 207 ($\text{ArCH}_2\text{CH}_2\text{CH}_3^+$, 100), 193 ($\text{ArCH}_2\text{CH}_3^+$, 19), 178 (ArCH_2^+ , 73), 165 (Ar^+ , 19).

2-Pentyl-9-ethylfluorene

A mixture of 2-pentanoylfluorene **31e** (1.77 g, 7.1 mmol), hydrazine hydrate (3.5 ml, 72 mmol), potassium hydroxide (4.14 g, 74 mmol) and diethylene glycol (30 ml) was heated at reflux for 1.6 hours. The reaction mixture was then heated strongly for 2.7 hours to distil out water. After cooling, water (100 ml) and concentrated hydrochloric acid (10 ml) were added, and the products were extracted into dichloromethane (3 x 100 ml). The combined organic extracts were washed with water (100 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was chromatographed on silica gel using dichloromethane-40-60 petroleum ether as eluent to give a yellow oil, impure 2-pentyl-9-ethylfluorene **33e** (1.00 g, *ca.* 54%).

TLC analysis indicated a single component ($R_f = 0.84$ in DCM). ^1H and ^{13}C NMR spectra indicated the presence of unknown impurities.

δ_{H} (300 MHz; CDCl_3) 0.77 (3H, t, $J = 7.4$, CH_2CH_3), 0.97 (3H, t, $J = 7.0$, $\text{CH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 1.34-1.49 (4H, m, $\text{CH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 1.64-1.80 (2H, m, $\text{CH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 2.05-2.18 (2H, m, CH_2CH_3), 2.72 (2H, t, $J = 8.1$, $\text{CH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 3.97 (1H, t, $J = 5.9$, CH (C9)), 7.21 (1H, d, $J = 7.4$, ArH), 7.26-7.42 (3H, m, ArH), 7.53 (1H, d, $J = 7.4$, ArH), 7.70 (1H, d, $J = 8.1$, ArH), 7.76 (1H, d, $J = 7.4$, ArH); δ_{C} (75.42 MHz; CDCl_3) 10.0, 14.3, 22.8, 26.0, 31.8, 36.4, 48.5, 119.6, 124.4, 124.6, 126.5, 127.0, 127.3, 139.1, 141.6, 142.0, 147.3, 147.6; m/z (EI) 250 (M^+ , 30%), 193 ($\text{ArCH}_2\text{CH}_3^+$, 100), 178 (ArCH_2^+ , 6), 165 (Ar^+ , 29).

2-Hexyl-9-ethylfluorene

A mixture of 2-hexanoylfluorene **31f** (9.62 g, 36 mmol), hydrazine hydrate (17.7 ml, 360 mmol), potassium hydroxide (20.20 g, 360 mmol) and diethylene glycol (250 ml) was heated at reflux for 7.0 hours. The reaction mixture was then heated strongly for 2.1 hours to distil out water. After cooling, water (500 ml) and concentrated hydrochloric acid (50

ml) were added, and the products were extracted into dichloromethane (2 x 500 ml). The combined organic extracts were washed with water (500 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was chromatographed on silica gel using dichloromethane-40-60 petroleum ether (1:1) as eluent to give an orange red oil, impure 2-hexyl-9-ethylfluorene **33f** (5.06 g, *ca.* 50%).

TLC analysis indicated a single component ($R_f = 0.85$ in DCM). ^1H and ^{13}C NMR spectra indicated the presence of unknown impurities.

δ_{H} (300 MHz; CDCl_3) 0.63 (3H, t, $J = 7.7$, CH_2CH_3), 0.82 (3H, m, $\text{CH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 1.14-1.44 (6H, m, $\text{CH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 1.50-1.68 (2H, m, $\text{CH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 1.91-2.03 (2H, m, CH_2CH_3), 2.61 (2H, t, $J = 7.7$, $\text{CH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 3.82 (1H, t, $J = 5.5$, CH (C9)), 7.08 (1H, d, $J = 6.6$, ArH), 7.12-7.28 (3H, m, ArH), 7.38 (1H, d, $J = 7.4$, ArH), 7.55 (1H, d, $J = 8.1$, ArH), 7.62 (1H, d, $J = 7.4$, ArH); δ_{C} (75.42 MHz; CDCl_3) 10.0, 14.4, 22.9, 26.0, 29.3, 32.0, 36.5, 48.6, 119.6, 125.3, 125.4, 127.0, 127.2, 127.3, 139.1, 141.7, 142.1, 147.4, 147.6; m/z (EI) 278 (M^+ , 69%), 249 ($\text{ArC}_6\text{H}_{13}^+$, 28), 207 ($\text{Ar}(\text{CH}_2)\text{CH}_2\text{CH}_3^+$, 86), 193 ($\text{ArCH}_2\text{CH}_3^+$, 70), 178 (ArCH_2^+ , 100), 165 (Ar^+ , 17).

2-Nonyl-9-ethylfluorene

A mixture of 2-nonylfluorene **32i** (0.94 g, 3.2 mmol), hydrazine hydrate (1.6 ml, 33 mmol), potassium hydroxide (1.82 g, 32 mmol) and diethylene glycol (20 ml) was heated at reflux for 3.0 hours. The reaction mixture was heated strongly for 3.0 hours to distil out water. After cooling, water (50 ml) and concentrated hydrochloric acid (5 ml) were added, and the products were extracted into dichloromethane (3 x 50 ml). The combined organic extracts were washed with water (50 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was chromatographed on silica gel using dichloromethane-40-60 petroleum ether (1:1) as eluent to give a yellow oil, impure 2-nonyl-9-ethylfluorene **33i** (0.77 g, *ca.* 75%).

TLC analysis indicated a single component ($R_f = 0.87$ in DCM). ^1H and ^{13}C NMR spectra indicated the presence of unknown impurities.

δ_{H} (300 MHz; CDCl_3) 0.81 (3H, t, $J = 7.4$, CH_2CH_3), 0.99 (3H, t, $J = 6.6$, $\text{CH}_2\text{CH}_2(\text{CH}_2)_6\text{CH}_3$), 1.30-1.52 (12H, m, $\text{CH}_2\text{CH}_2(\text{CH}_2)_6\text{CH}_3$), 1.78-1.83 (2H, m, $\text{CH}_2\text{CH}_2(\text{CH}_2)_6\text{CH}_3$), 2.10-2.22 (2H, m, CH_2CH_3), 2.77 (2H, t, $J = 7.7$, $\text{CH}_2\text{CH}_2(\text{CH}_2)_6\text{CH}_3$), 4.01 (1H, t, $J = 5.5$, CH (C9)), 7.25 (1H, d, $J = 7.4$, ArH), 7.31-7.46 (3H, m, ArH), 7.56 (1H, d, $J = 7.4$, ArH), 7.72 (1H, d, $J = 8.1$, ArH), 7.78 (1H, d, $J = 8.1$, ArH); δ_{C} (75.42 MHz; CDCl_3) 10.0, 14.4, 22.9, 26.0, 29.6, 29.8, 32.1, 32.2, 36.5, 48.6,

119.6, 119.7, 124.4, 124.6, 126.5, 127.0, 127.3, 139.1, 141.7, 142.1, 147.4, 147.6; m/z (EI) 320 (M^+ , 100%), 291 ($ArC_9H_{19}^+$, 4), 207 ($Ar(CH_2)CH_2CH_3^+$, 62), 193 ($ArCH_2CH_3^+$, 35), 178 ($ArCH_2^+$, 34), 165 (ArH^+ , 5).

8.5.3 Synthesis of 2-(4-cyanophenyl)-7-alkyl-9-alkylfluorenes

2-Bromo-7-propyl-9-ethylfluorene

A solution of impure 2-propyl-9-ethylfluorene **33c** (2.29 g, *ca.* 9.7 mmol) in chloroform (50 ml) was stirred in an ice bath. A solution of bromine (0.5 ml, 9.7 mmol) in chloroform (10 ml) was added over 12 minutes, with the reaction mixture stirred in an ice bath. The reaction mixture was then allowed to warm to room temperature, with stirring, over 21.9 hours. After cooling, sodium carbonate solution (aq, 10%, 100 ml) was added, and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 x 50 ml). The combined organic extracts were washed with sodium metabisulphite solution (aq, 5%, 2 x 20 ml) and water (20 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed to give a red oily solid, 2-bromo-7-propyl-9-ethylfluorene **130** (3.25 g, *ca.* 107%).

TLC analysis indicated a single component (R_f = 0.85 in DCM) which co-chromatographed with the starting material. 1H and ^{13}C NMR spectra indicated the presence of unknown impurities.

δ_H (300 MHz; $CDCl_3$) 0.58 (3H, t, J = 7.4, $CH_2CH_2CH_3$), 0.85 (3H, t, J = 7.4, CH_2CH_3), 1.57 (2H, m, CH_2CH_3), 1.88-2.01 (2H, m, $CH_2CH_2CH_3$), 2.56 (2H, t, J = 7.4, $CH_2CH_2CH_3$), 3.78 (1H, t, J = 5.5, CH (C9)), 6.94-7.57 (6H, m, ArH); δ_C (75.42 MHz; $CDCl_3$) 9.8, 14.0, 25.1, 25.8, 38.5, 48.5, 119.7, 120.3, 120.9, 124.6, 127.6, 127.7, 130.1, 138.1, 140.7, 142.3, 147.2, 149.4; m/z (EI) 316 (M^+ (^{81}Br), 46%), 314 (M^+ (^{79}Br), 48), 285 (100), 256 (48), 235 ($Ar(CH_2CH_3)CH_2CH_2CH_3^+$, 21), 193 ($ArCH_2CH_3^+$, 62), 165 (Ar^+ , 10).

2-(4-Cyanophenyl)-7-propyl-9-ethylfluorene

Nitrogen gas was bubbled through a stirred mixture of impure 2-bromo-7-propyl-9-ethylfluorene **130** (2.86 g, *ca.* 9.1 mmol), impure 4-cyanobenzoboronic acid **34** (1.35 g, *ca.* 9.2 mmol), sodium carbonate solution (aq, 2M, 9.0 ml) and 1,2-dimethoxyethane (100 ml) for 50 minutes. Tetrakis(triphenylphosphine)palladium(0) (0.30 g, 260 μ m) was added, and the reaction mixture was heated at reflux for 5.0 hours. After cooling, dichloromethane (200 ml) and water (200 ml) were added, and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 x 200 ml). The combined organic extracts were washed with water (100 ml), then dried over anhydrous sodium sulphate and filtered.

The solvent was removed. The residue was dissolved in dichloromethane (50 ml). The solution was filtered through a plug of silica and rinsed with dichloromethane (3 x 50 ml). The solvent was removed. The residue was chromatographed on silica gel using dichloromethane-40-60 petroleum ether (1:1) as eluent to give three fractions. The second fraction was distilled at reduced pressure (>250 °C, 0.3 mbar) to give a yellow oily solid, impure 2-(4-cyanophenyl)-7-propyl-9-ethylfluorene **131c** (0.97 g, *ca.* 32 %).

TLC analysis indicated a single component ($R_f = 0.57$ in DCM). ^1H and ^{13}C NMR spectra indicated the presence of unknown impurities.

Recrystallization was attempted with various solvent systems, but no pure material was obtained. The residue was chromatographed on silica gel using chloroform as eluent to give a pale yellow oil, impure 2-(4-cyanophenyl)-7-propyl-9-ethylfluorene **131c** (0.05 g, *ca.* 2 %).

TLC analysis indicated a single component ($R_f = 0.57$ in DCM). ^1H and ^{13}C NMR spectra indicated the presence of unknown impurities.

δ_{H} (300 MHz; CDCl_3) 0.78 (3H, t, $J = 7.4$, CH_2CH_3), 1.02 (3H, t, 7.4, CH_2CH_3), 1.66-1.82 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.10-2.22 (2H, m, CH_2CH_3), 2.71 (2H, t, $J = 7.7$, $\text{CH}_2\text{CH}_2\text{CH}_3$), 4.01 (1H, t, $J = 5.5$, CH (C9)), 7.23 (1H, d, $J = 8.1$, ArH), 7.38 (1H, s, ArH), 7.59 (1H, d, $J = 8.1$, ArH), 7.68-7.83 (7H, m, ArH); δ_{C} (75.42 MHz; CDCl_3) 10.0, 14.1, 25.1, 25.9, 38.5, 48.6, 110.6, 119.3, 120.0, 120.1, 123.2, 124.7, 126.4, 127.6, 127.8, 132.7, 137.3, 138.3, 142.4, 142.5, 146.3, 147.9, 148.3; m/z (EI) 337 (M^+ , 86%), 308 ($\text{Ar}(\text{C}_3\text{H}_7)\text{PhCN}^+$, 100), 294 ($\text{Ar}(\text{C}_2\text{H}_5)^+$, 26), 279 ($\text{Ar}(\text{CH}_2)^+$, 84), 264 (Ar^+ , 9).

8.5.4 Synthesis of 2-(4-cyanophenyl)-7-alkyl-9,9-dialkylfluorenes

2-Bromo-7-hexyl-9,9-diethylfluorene

A solution of impure 2-hexyl-9,9-diethylfluorene **122f** (1.84 g, *ca.* 6.0 mmol) in chloroform (40 ml) was stirred in an ice bath. A solution of bromine (0.34 ml, 6.6 mmol) in chloroform (10 ml) was added over 2.0 hours, with the reaction mixture stirred in an ice bath. The reaction mixture was then allowed to warm to room temperature, with stirring, over 17.4 hours. Sodium carbonate solution (aq, 10%, 50 ml) was added, and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 x 30 ml). The combined organic extracts were washed with sodium metabisulphite solution (aq, 5%, 2 x 25 ml) and water (25 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was purified by reduced pressure distillation to give a brown oil (>250 °C, 0.2 mbar), impure 2-bromo-7-hexyl-9,9-diethylfluorene **133f** (2.32 g,

ca. 100%).

TLC analysis indicated a single component ($R_f = 0.80$ in DCM) which co-chromatographed with the starting material. ^1H and ^{13}C NMR spectra indicated the presence of unknown impurities. GCMS analysis indicated the presence of <1% 2-bromo-7-hexanoyl-9-ethylfluorene, *ca.* 5% 2-bromo-7-hexyl-9-ethylfluorene and *ca.* 5% 2-bromo-7-(α -ethylhexyl)-9,9-diethylfluorene.

δ_{H} (300 MHz; CDCl_3) 0.26 (6H, t, $J = 7.4$, CH_2CH_3), 0.75-0.91 (3H, m, $\text{CH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 1.18-1.37 (6H, m, $\text{CH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 1.49-1.65 (2H, m, $\text{CH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 1.85-2.01 (4H, m, CH_2CH_3), 2.61 (2H, t, $J = 7.7$, $\text{CH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 7.00-7.15 (2H, m, ArH), 7.32-7.55 (4H, m, ArH); δ_{C} (75.42 MHz; CDCl_3) 8.6, 14.2, 22.8, 29.1, 31.9, 32.9, 36.4, 56.4, 119.6, 120.5, 120.8, 123.1, 126.3, 127.4, 130.0, 138.2, 140.9, 142.8, 149.8, 152.3; m/z (EI) 386 (M^+ (^{81}Br), 44%), 384 (M^+ (^{79}Br), 45%), 357 ($\text{Ar}(\text{CH}_2\text{CH}_3)\text{C}_6\text{H}_{11}^{81}\text{Br}^+$, 31%), 355 ($\text{Ar}(\text{CH}_2\text{CH}_3)\text{C}_6\text{H}_{11}^{79}\text{Br}^+$, 32), 315 ($\text{Ar}(\text{CH}_2)(\text{CH}_2\text{CH}_3)^{81}\text{Br}^+$, 15),), 313 ($\text{Ar}(\text{CH}_2)(\text{CH}_2\text{CH}_3)^{79}\text{Br}^+$, 16), 276 ($\text{Ar}(\text{C}_6\text{H}_{11})\text{CH}_2\text{CH}_3^+$, 55), 205 ($\text{Ar}(\text{CH}_2)\text{CH}_2\text{CH}_3^+$, 67), 192 ($\text{ArCH}_2\text{CH}_3^+$, 38), 165 (Ar^+ , 8).

2-Bromo-7-octyl-9,9-diethylfluorene

A solution of 2-bromo-7-octylfluorene **24h** (1.01 g, 2.8 mmol) in dry tetrahydrofuran (25 ml) was stirred in an acetone-solid carbon dioxide bath under nitrogen. A solution of lithium diisopropylamide in tetrahydrofuran/*n*-heptane (2 M, 1.7 ml, 3.4 mmol) was added over 10 minutes. The reaction mixture was stirred in an acetone-solid carbon dioxide bath under nitrogen for 1.4 hours. Ethyl iodide (0.3 ml, 3.7 mmol) was added over 10 minutes. The reaction mixture was stirred in an acetone-solid carbon dioxide bath under nitrogen for 1.0 hours. A solution of lithium diisopropylamide in tetrahydrofuran/*n*-heptane (2 M, 1.7 ml, 3.4 mmol) was added over 5 minutes. The reaction mixture was stirred in an acetone-solid carbon dioxide bath under nitrogen for 1.0 hours. Ethyl iodide (0.3 ml, 3.7 mmol) was added over 10 minutes. The reaction mixture was allowed to warm to room temperature, with stirring, over 13.1 hours. Ammonium chloride (aq, 5%, 10 ml) was added, and the products were extracted into diethyl ether (3 x 20 ml). The combined organic extracts were washed with sodium thiosulphate solution (aq, 10%, 15 ml) and water (15 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed to give an orange oil, 2-bromo-7-octyl-9,9-diethylfluorene **133h** (1.15 g, 98 %).

λ_{max} (CH_2Cl_2)/nm 228 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 28300), 272sh, 281 (42800), 302 (21400), 314 (25600); ν_{max} (CHCl_3 soln.)/ cm^{-1} 2927s, 2855m, 1600w, 1456w, 1404w, 1378w, 1257w,

1131w, 1061w, 1006w, 877w, 817m; δ_{H} (300 MHz; CDCl_3) 0.36 (6H, t, $J = 7.4$, CH_2CH_3), 0.91 (3H, t, $J = 6.6$, $\text{CH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 1.22-1.47 (10H, m, $\text{CH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 1.60-1.77 (2H, m, $\text{CH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 2.02 (4H, q, $J = 7.4$, CH_2CH_3), 2.71 (2H, t, $J = 7.4$, $\text{CH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 7.13 (1H, s, ArH), 7.18 (1H, d, $J = 8.1$, ArH), 7.42-7.50 (2H, m, ArH), 7.55 (1H, d, $J = 8.1$, ArH), 7.60 (1H, d, $J = 7.4$, ArH); δ_{C} (75.42 MHz; CDCl_3) 8.7, 14.3, 22.9, 29.4, 29.5, 29.7, 32.0, 32.0, 32.9, 36.5, 56.4, 119.6, 120.5, 120.8, 123.1, 126.3, 127.4, 130.0, 138.2, 140.9, 142.8, 149.8, 152.3; m/z (EI) 414 (M^+ (^{81}Br), 67%), 412 (M^+ (^{79}Br), 68%), 385 ($\text{Ar}(\text{CH}_2\text{CH}_3)\text{C}_8\text{H}_{17}^{81}\text{Br}^+$, 42%), 383 ($\text{Ar}(\text{CH}_2\text{CH}_3)\text{C}_8\text{H}_{17}^{79}\text{Br}^+$, 41), 304 ($\text{Ar}(\text{CH}_2\text{CH}_3)\text{C}_8\text{H}_{17}^+$, 72), 271 ($\text{Ar}(\text{CH}_2\text{CH}_3)^{81}\text{Br}^+$, 33), 269 ($\text{Ar}(\text{CH}_2\text{CH}_3)^{79}\text{Br}^+$, 31), 205 ($\text{Ar}(\text{CH}_2)\text{CH}_2\text{CH}_3^+$, 100), 192 ($\text{ArCH}_2\text{CH}_3^+$, 41), 165 (Ar^+ , 8).

2-(4-Cyanophenyl)-7-hexyl-9,9-diethylfluorene

Nitrogen gas was bubbled through a stirred mixture of impure 2-bromo-7-hexyl-9,9-diethylfluorene **133f** (1.84 g, *ca.* 4.8 mmol), 4-cyanobenzoboronic acid **34** (1.05 g, 7.1 mmol), sodium carbonate solution (aq, 2M, 4.8 ml) and 1,2-dimethoxyethane (60 ml) for 10 minutes. Tetrakis(triphenylphosphine)palladium(0) (0.20 g, 173 μm) was added, and the reaction mixture was heated at reflux for 2.6 hours. After cooling, dichloromethane (150 ml) and water (150 ml) were added, and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 x 150 ml). The combined organic extracts were washed with water (150 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was dissolved in dichloromethane (50 ml). The solution was filtered through a plug of silica and rinsed with dichloromethane (3 x 100 ml). The solvent was removed. The residue was chromatographed on silica gel using chloroform as eluent to give five fractions. The third fraction was distilled at reduced pressure (243 $^{\circ}\text{C}$, 0.2 mbar) to give a pale yellow oil, impure 2-(4-cyanophenyl)-7-hexyl-9,9-diethylfluorene **134f** (0.08 g, *ca.* 4 %).

TLC analysis indicated a single component ($R_f = 0.66$ in DCM). ^1H and ^{13}C NMR spectra indicated the presence of unknown impurities.

$\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 229 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 16700), 329 (32300); $\nu_{\text{max}}(\text{CHCl}_3\text{ soln.})/\text{cm}^{-1}$ 2960vs, 2926s, 2854vs, 2226vs ($\text{C}\equiv\text{N}$), 1604vs, 1511w, 1468s, 1404m, 1376m, 1258w, 1179w, 1134w, 1016w, 889w, 817vs, 744m; δ_{H} (300 MHz; CDCl_3) 0.41 (6H, t, $J = 7.4$, CH_2CH_3), 0.92 (3H, t, $J = 6.6$, $\text{CH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 1.28-1.47 (6H, m, $\text{CH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 1.62-1.77 (2H, m, $\text{CH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 2.02-2.16 (4H, m, CH_2CH_3), 2.73 (2H, t, $J = 8.9$, $\text{CH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 7.21 (2H, d, $J = 8.8$, ArH), 7.58 (2H, d, $J = 8.1$,

ArH), 7.67 (1H, d, $J = 8.1$, ArH), 7.72-7.85 (5H, m, ArH); δ_C (75.42 MHz; $CDCl_3$) 8.8, 14.3, 22.8, 29.1, 31.9, 31.9, 33.0, 36.5, 56.3, 110.5, 119.3, 119.9, 120.0, 121.6, 123.2, 126.3, 127.5, 127.8, 132.7, 137.5, 138.4, 142.7, 143.0, 146.4, 150.6, 151.1; m/z (EI) 407 (M^+ , 64%), 378 ($Ar(C_6H_{13})(C_2H_5)PhCN^+$, 41), 336 ($Ar(C_2H_5)_2PhCN^+$, 15), 294 ($Ar(CH_2)_2PhCN^+$, 57).

2-(4-Cyanophenyl)-7-octyl-9,9-diethylfluorene

Nitrogen gas was bubbled through a stirred mixture of 2-bromo-7-octyl-9,9-diethylfluorene **133h** (0.40 g, 1.0 mmol), 4-cyanobenzoboronic acid **34** (0.21 g, 1.4 mmol), sodium carbonate solution (aq, 2M, 1.0 ml) and 1,2-dimethoxyethane (12 ml) for 20 minutes. Tetrakis(triphenyl)phosphinepalladium(0) (0.03 g, 26 μ m) was added, and the reaction mixture was heated at reflux for 3.0 hours. After cooling, dichloromethane (40 ml) and water (40 ml) were added, and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 x 40 ml). The combined organic extracts were washed with water (40 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was dissolved in dichloromethane (25 ml). The solution was filtered through a plug of silica and rinsed with dichloromethane (3 x 50 ml). The solvent was removed to give a yellow oil, impure 2-(4-cyanophenyl)-7-octyl-9,9-diethylfluorene **134h** (0.36 g, *ca.* 85 %).

TLC analysis indicated a single component ($R_f = 0.67$ in DCM). 1H and ^{13}C NMR spectra indicated the presence of unknown impurities.

λ_{max} (CH_2Cl_2)/nm 228 ($\epsilon/dm^3 mol^{-1} cm^{-1}$ 25600), 328 (48500); $\nu_{max}(CHCl_3 soln.)/cm^{-1}$ 2927vs, 2854s, 2228s ($C\equiv N$), 1604s, 1511w, 1467s, 1404w, 1378w, 1046w, 909m, 820m; δ_H (300 MHz; $CDCl_3$) 0.41 (6H, t, $J = 7.4$, CH_2CH_3), 0.92 (3H, t, $J = 6.6$, $CH_2CH_2(CH_2)_5CH_3$), 1.22-1.47 (10H, m, $CH_2CH_2(CH_2)_5CH_3$), 1.63-1.76 (2H, m, $CH_2CH_2(CH_2)_5CH_3$), 2.10 (4H, q, $J = 7.4$, CH_2CH_3), 2.72 (2H, t, $J = 7.4$, $CH_2CH_2(CH_2)_2CH_3$), 7.13-7.25 (2H, m, ArH), 7.53-7.62 (2H, m, ArH), 7.67 (1H, d, $J = 7.4$, ArH), 7.71-7.85 (5H, m, ArH), δ_C (75.42 MHz; $CDCl_3$) 8.8, 14.3, 22.9, 29.5, 29.7, 32.0, 32.0, 33.0, 36.5, 56.3, 110.5, 119.3, 119.9, 120.0, 121.6, 123.2, 126.3, 127.5, 127.8, 132.7, 137.5, 138.4, 142.7, 143.0, 146.4, 150.5, 151.2; m/z (EI) 435 (M^+ , 100%), 407 ($Ar(C_8H_{17})(C_2H_5)PhCN^+$, 27), 336 ($Ar(CH_2)(C_2H_5)_2PhCN^+$, 11), 294 ($Ar(CH_2)_2PhCN^+$, 23).

2-(4-Cyanophenyl)-7-pentyl-9,9-dioctylfluorene

A solution of 2-(4-cyanophenyl)-7-pentylfluorene **30e** (0.26 g, 0.77 mmol) in dry tetrahydrofuran (10 ml) was stirred in an acetone-solid carbon dioxide bath under nitrogen.

A solution of lithium diisopropylamide in tetrahydrofuran/*n*-heptane (2M, 0.45 ml, 0.9 mmol) was added over 10 minutes. The reaction mixture was stirred in an acetone-solid carbon dioxide bath under nitrogen for 1.0 hours. Octyl bromide (0.17 ml, 0.98 mmol) was added over 10 minutes. The reaction mixture was stirred in an acetone-solid carbon dioxide bath under nitrogen for 1.0 hours. A solution of lithium diisopropylamide in tetrahydrofuran/*n*-heptane (2M, 0.45 ml, 0.9 mmol) was added over 10 minutes. The reaction mixture was stirred in an acetone-solid carbon dioxide bath under nitrogen for 1.0 hours. Octyl bromide (0.17 ml, 0.98 mmol) was added over 10 minutes. The reaction mixture was allowed to warm to room temperature with stirring, over 20.4 hours. Ammonium chloride (aq, 5%, 10 ml) was added, and the products were extracted into diethyl ether (3 x 10 ml). The combined organic extracts were washed with sodium thiosulphate solution (aq, 10%, 10 ml) and water (10 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was chromatographed on silica gel using dichloromethane-hexane as eluent to give a pale yellow oil, 2-(4-cyanophenyl)-7-pentyl-9,9-dioctylfluorene **135** (0.18 g, 30 %).

λ_{\max} (CH₂Cl₂)/nm 229 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 18700), 330 (37600); ν_{\max} (CHCl₃ soln.)/cm⁻¹ 2928s, 2855m, 2228m (C≡N), 1604m, 1467m, 820m; δ_{H} (300 MHz; CDCl₃) 0.83 (6H, t, J = 6.6, CH₂CH₂(CH₂)₅CH₃), 0.93 (3H, t, J = 6.6, CH₂CH₂(CH₂)₂CH₃), 1.01-1.32 (24H, m, CH₂CH₂(CH₂)₂CH₃ and CH₂CH₂(CH₂)₅CH₃), 1.32-1.47 (4H, m, CH₂CH₂(CH₂)₅CH₃), 1.64-1.77 (2H, m, CH₂CH₂(CH₂)₂CH₃), 1.94-2.08 (4H, m, CH₂CH₂(CH₂)₅CH₃), 2.72 (2H, t, J = 7.4, CH₂CH₂(CH₂)₂CH₃), 7.15-7.23 (2H, m, ArH), 7.52-7.60 (2H, m, ArH), 7.66 (1H, d, J = 8.1, ArH), 7.72-7.83 (5H, m, ArH), δ_{C} (75.42 MHz; CDCl₃) 14.2, 22.8, 23.9, 29.3, 30.1, 31.6, 31.6, 31.9, 36.4, 40.5, 55.2, 110.5, 119.3, 119.9, 120.0, 121.5, 123.2, 126.3, 127.4, 127.8, 132.7, 137.4, 138.0, 142.2, 142.9, 146.4, 151.4, 151.9; m/z (EI) 561 (M⁺, 100%), 448 (Ar(C₅H₁₁)(C₈H₁₇)PhCN⁺, 19), 349 (Ar(C₅H₁₁)(CH₂)PhCN⁺, 13), 336 (Ar(C₅H₁₁)PhCN⁺, 18), 292 (Ar(CH₂)₂PhCN⁺, 25), 279 (Ar(CH₂)PhCN⁺, 23).

8.6 OTHER SYNTHESSES

8.6.1 2-(4-Alkoxyphenyl)-7-alkylfluorenes

4-Bromoanisole

A mixture of 4-bromophenol **145** (1.97 g, 11 mmol) in *N,N*-dimethylformamide (30 ml) was stirred in an ice bath under nitrogen. Sodium hydride (60%, 0.44 g, 11 mmol) and *N,N*-dimethylformamide (5 ml) were added, and the reaction mixture was stirred in an ice bath

under nitrogen for 0.9 hours. Further sodium hydride (60%, 0.30 g, 7.5 mmol) and *N,N*-dimethylformamide (5 ml) were added, and the reaction mixture was stirred in an ice bath under nitrogen for 1.3 hours. A solution of methyl iodide (0.8 ml, 13 mmol) in *N,N*-dimethylformamide (10 ml) was added over 8 minutes, and the stirred reaction mixture was allowed to warm to room temperature under nitrogen over 20.2 hours. The solvent was removed. Diethyl ether (25 ml) and sodium hydroxide solution (aq, 5%, 25 ml) was added to the residue, and the organic layer was separated. The aqueous layer was extracted with diethyl ether (25 ml). The combined organic extracts were washed with sodium hydroxide solution (aq, 5%, 25 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed to give a pale yellow oil, impure 4-bromoanisole (1.02 g, *ca.* 48%). The oil co-chromatographed ($R_f = 0.70$ in DCM) and had ^1H and ^{13}C NMR spectra identical to those obtained for a commercial sample.

The ^1H NMR spectrum showed unknown impurities at δ_{H} 0.9 and 1.3 and the ^{13}C NMR spectrum showed unknown impurities at δ_{C} 14.2-37.1.

1-Bromo-4-heptoxybenzene

Sodium (0.29 g, 13 mmol) was added to dry ethanol (50 ml). The resulting solution was added to a mixture of 4-bromophenol **145** (1.02 g, 5.6 mmol) and dry ethanol (50 ml). The reaction mixture was stirred at room temperature for 0.7 hours. A solution of 1-bromoheptane (2.2 ml, 14 mmol) in dry ethanol (10 ml) was added over 2 minutes. The reaction mixture was heated at reflux for 10.0 hours. After cooling, the solvent was removed. Sodium hydroxide solution (aq, 20%, 250 ml) and dichloromethane (250 ml) were added to the residue, and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 x 125 ml). The combined organic extracts were washed with sodium hydroxide solution (aq, 20%, 125 ml) and water (125 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed to give a pale brown liquid, impure 1-bromo-4-heptoxybenzene **146** (2.83 g, *ca.* 90%).

$\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 232 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 11800), 283 (1600), 291sh; $\nu_{\text{max}}(\text{CHCl}_3 \text{ soln.})/\text{cm}^{-1}$ 2930vs, 2871s, 1871w, 1591s, 1489s, 1469s, 1389w, 1286s, 1242s, 1171s, 1102w, 1072m, 1023m, 1002m, 823s; δ_{H} (300 MHz; CDCl_3) 0.94 (3H, t, $J = 6.6$, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_4\text{CH}_3$), 1.27-1.55 (8H, m, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_4\text{CH}_3$), 1.73-1.87 (2H, m, $\text{CH}_2\text{CH}_2(\text{CH}_2)_4\text{CH}_3$), 3.92 (2H, t, $J = 6.6$, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_4\text{CH}_3$), 6.79 (2H, d, $J = 8.8$, ArH), 7.38 (2H, d, $J = 8.8$, ArH); δ_{C} (75.42 MHz; CDCl_3) 14.3, 22.8, 26.1, 29.2, 29.4, 32.0, 68.4, 112.7, 116.4, 132.3, 158.4; m/z (EI) 272 (M^+ (^{81}Br), 17%), 270 (M^+ (^{79}Br), 17), 174 ($\text{Ph}(\text{OH})^{81}\text{Br}^+$, 100), 172

(Ph(OH)⁷⁹Br⁺, 100), 93 (PhOH⁺, 8).

4-Heptoxybenzoboronic acid

A solution of 1-bromo-4-heptoxybenzene **146** (2.47 g, 9.1 mmol) in dry tetrahydrofuran (50 ml) was stirred in an acetone-solid carbon dioxide bath under nitrogen. A solution of *n*-butyllithium in hexanes (2.5 M, 3.6 ml, 9.0 mmol) was added over 15 minutes. The reaction mixture was stirred in an acetone-solid carbon dioxide bath under nitrogen for 1.0 hours. Triisopropylborate (2.1 ml, 9.1 mmol) was added over 2 minutes. The reaction mixture was allowed to warm to room temperature, with stirring, over 21.1 hours. Water (20 ml) and concentrated hydrochloric acid (4 ml) were added, and the resulting cloudy solution was stirred at room temperature for 30 minutes. Dichloromethane (40 ml) was added, and the organic layer was separated. The combined organic extracts were washed with water (3 x 20 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. Sodium hydroxide solution (aq, 2 M, 20 ml) and diethyl ether (10 ml) were added to the residue. The organic layer was separated. The aqueous layer was extracted with diethyl ether (10 ml). To the combined organic extracts were added hydrochloric acid (aq, 1 M, 50 ml), diethyl ether (50 ml) and dichloromethane (150 ml). The organic layer was separated and washed with water (50 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was recrystallized from hot chloroform-60-80 petroleum ether to give a white solid, 4-heptoxybenzoboronic acid **144** (1.05 g, 49%, mp 96-98 °C (from CHCl₃-PET (60-80))).

(Found: C, 71.0; H, 8.9. C₁₃H₂₁BO₃ requires C, 66.1; H, 9.0%). $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 230 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 21500), 333 (44500); $\nu_{\max}(\text{CHCl}_3 \text{ soln.})/\text{cm}^{-1}$ 3661w, 3556w, 2930s, 2858s, 1602s, 1568m, 1513m, 1468m, 1415s, 1375s, 1346s, 1246s, 1179s, 1112s, 1010m, 835m; δ_{H} (300 MHz; CDCl₃) 0.97 (3H, t, J = 6.6, OCH₂CH₂(CH₂)₄CH₃), 1.27-1.60 (8H, m, OCH₂CH₂(CH₂)₄CH₃), 1.78-1.93 (2H, m, CH₂CH₂(CH₂)₄CH₃), 4.05 (2H, t, J = 6.3, OCH₂CH₂(CH₂)₄CH₃), 7.02 (2H, d, J = 8.1, ArH), 8.15 (2H, d, J = 8.1, ArH); δ_{C} (75.42 MHz; CDCl₃) 14.3, 22.8, 26.2, 29.3, 29.4, 32.0, 68.0, 114.1, 122.2, 137.6, 162.9; *m/z* (EI) 236 (M⁺, 36%), 208 (Ph(OH)OC₇H₁₅⁺, 27), 192 (PhOC₇H₁₅⁺, 22), 164 (13), 138 (PhOCH₂CH₂⁺, 71), 110 (Ar(OH)₂⁺, 100), 99 (ArOH⁺, 63), 77 (Ar⁺, 16).

2-(4-Methoxyphenyl)-7-pentylfluorene

Nitrogen gas was bubbled through a stirred solution of impure 2-bromo-7-pentylfluorene **24e** (0.30 g, *ca.* 0.95 mmol), 4-methoxybenzoboronic acid **143** (0.16 g, 1.05 mmol), sodium carbonate solution (aq, 2M, 1 ml) and dimethoxyethane (10 ml) for 25 minutes.

Tetrakis(triphenylphosphine)palladium(0) (0.03 g, 26 μmol) was added, and the reaction mixture was heated at reflux for 21.5 hours. After cooling, dichloromethane (30 ml) and water (30 ml) were added, and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 x 30 ml). The combined organic extracts were washed with water (30 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was dissolved in dichloromethane (10 ml). The solution was filtered through a plug of silica and rinsed with dichloromethane (2 x 50 ml). The solvent was removed. The residue was recrystallized from hot ethanol (charcoal) to give a silver solid, 2-(4-methoxyphenyl)-7-pentylfluorene **137e** (0.04 g, 12 %, mp 215-219 °C (from EtOH)).

(Found: C, 87.65; H, 7.6. $\text{C}_{25}\text{H}_{26}\text{O}$ requires C, 87.7; H, 7.65%). $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 229 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 4300), 304 (9100), 316 (9000); $\nu_{\text{max}}(\text{CHCl}_3 \text{ soln.})/\text{cm}^{-1}$ 2929m, 2858w, 1608m, 1518s, 1469s, 1043w, 1026w; δ_{H} (300 MHz; CDCl_3) 0.93 (3H, t, $J = 6.6$, $\text{CH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 1.34-1.45 (4H, m, $\text{CH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 1.64-1.77 (2H, m, $\text{CH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 2.72 (2H, t, $J = 7.7$, $\text{CH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 3.89 (3H, s, OCH_3), 3.93 (2H, s, CH_2 (C9)), 7.02 (2H, m, ArH), 7.24 (1H, d, $J = 8.1$, ArH), 7.40 (1H, s, ArH), 7.55-7.66 (3H, m, ArH), 7.71 (2H, d, $J = 7.4$, ArH), 7.80 (1H, d, $J = 8.1$, ArH); δ_{C} (75.42 MHz; CDCl_3) 14.3, 22.8, 31.7, 31.8, 36.3, 37.1, 55.5, 114.4, 119.7, 119.9, 123.5, 125.3, 125.6, 127.3, 128.3, 134.3, 139.1, 139.3, 140.7, 141.9, 143.8, 144.0, 159.1; m/z (EI) 342 (M^+ , 100%), 285 ($\text{Ar}(\text{CH}_2)\text{PhOMe}^+$, 89), 270 ($\text{Ar}(\text{CH}_2)\text{PhO}^+$, 11), 242 (ArPh^+ , 17).

2-(4-Methoxyphenyl)-7-heptylfluorene

Nitrogen gas was bubbled through a stirred solution of impure 2-bromo-7-heptylfluorene **24g** (0.60 g, *ca.* 1.75 mmol), 4-methoxybenzoboronic acid **143** (0.30 g, 1.97 mmol), sodium carbonate solution (aq, 2M, 2 ml) and 1,2-dimethoxyethane (20 ml) for 33 minutes.

Tetrakis(triphenylphosphine)palladium(0) (0.06 g, 52 μmol) was added, and the reaction mixture was heated at reflux for 11.3 hours. After cooling, dichloromethane (60 ml) and water (60 ml) were added, and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 x 60 ml). The combined organic extracts were washed with water (60 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was dissolved in dichloromethane (10 ml). The solution was filtered through a plug of silica and rinsed with dichloromethane (3 x 50 ml). The solvent was removed. The residue was recrystallized from ethanol (charcoal) to give an off-white

lustrous solid, 2-(4-methoxyphenyl)-7-heptylfluorene **137g** (0.08 g, 12 %, mp 203-208 °C (from EtOH)).

(Found: C, 86.2; H, 8.1. $C_{27}H_{30}O$ requires C, 87.5; H, 8.2%). $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 229 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 14500), 303 (29900), 316 (29400); $\nu_{\max}(\text{CHCl}_3\text{ soln.})/\text{cm}^{-1}$ 2929s, 2856m, 1608w, 1518s, 1469s, 1042w, 1026w; δ_{H} (300 MHz; CDCl_3) 0.77-0.86 (3H, t, $J = 6.6$, $\text{CH}_2\text{CH}_2(\text{CH}_2)_4\text{CH}_3$), 1.13-1.45 (8H, m, $\text{CH}_2\text{CH}_2(\text{CH}_2)_4\text{CH}_3$), 1.52-1.65 (2H, m, $\text{CH}_2\text{CH}_2(\text{CH}_2)_4\text{CH}_3$), 2.61 (2H, t, $J = 7.7$, $\text{CH}_2\text{CH}_2(\text{CH}_2)_4\text{CH}_3$), 3.77 (3H, s, OCH_3) 3.81 (2H, s, CH_2 (C9)), 6.92-7.05 (2H, m, ArH), 7.14 (1H, d, $J = 7.4$, ArH), 7.30 (1H, s, ArH), 7.47-7.56 (3H, m, ArH), 7.64 (2H, d, $J = 8.1$, ArH), 7.71 (1H, d, $J = 8.1$, ArH); δ_{C} (75.42 MHz; CDCl_3) 14.3, 22.9, 29.4, 29.5, 32.0, 36.4, 37.0, 55.5, 114.4, 119.7, 119.9, 123.5, 125.2, 125.6, 127.3, 128.3, 134.3, 139.1, 139.2, 140.7, 141.9, 143.8, 144.0, 159.1; m/z (EI) 370 (M^+ , 100%), 285 (94), 242 (12); m/z (EI) 370 (M^+ , 100%), 285 ($\text{Ar}(\text{CH}_2)\text{PhOMe}^+$, 94), 270 ($\text{Ar}(\text{CH}_2)\text{PhO}^+$, 6), 242 (ArPh^+ , 12).

2-(4-Methoxyphenyl)-7-nonylfluorene

METHOD I

Nitrogen gas was bubbled through a stirred solution of impure 2-bromo-7-nonylfluorene **24i** (0.35 g, *ca.* 0.94 mmol), 4-methoxybenzoboronic acid **143** (0.16 g, 1.05 mmol), sodium carbonate solution (aq, 2M, 1 ml) and dimethoxyethane (10 ml) for 22 minutes.

Tetrakis(triphenylphosphine)palladium(0) (0.03 g, 26 μm) was added, and the reaction mixture was heated at reflux for 68.9 hours. After cooling, dichloromethane (30 ml) was added, and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 x 30 ml). The combined organic extracts were washed with sodium bicarbonate solution (aq, 10%, 30 ml) and water (30 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was chromatographed on silica gel using diethyl ether-40-60 petroleum ether (19:1) as eluent to give four fractions. ^1H and ^{13}C NMR spectra of the material which was insoluble in the eluent were consistent with the formation of a single product, 2-(4-methoxyphenyl)-7-nonylfluorene **137i** (<0.01 g).

δ_{H} (300 MHz; CDCl_3) 0.90 (3H, t, $J = 6.6$, CH_3), 1.22-1.43 (12H, m, CH_2s), 1.60-1.73 (2H, m, CH_2), 2.70 (2H, t, $J = 7.7$, CH_2), 3.88 (3H, s, OCH_3), 3.92 (2H, s, CH_2 (C9)), 7.01 (2H, d, $J = 8.8$, ArH) 7.22 (1H, d, $J = 8.1$, ArH), 7.39 (1H, s, ArH), 7.54-7.65 (3H, m, ArH), 7.71 (2H, d, $J = 8.1$, ArH), 7.80 (1H, d, $J = 8.1$, ArH); δ_{C} (75.42 MHz; CDCl_3) 14.3, 22.9, 29.5, 29.6, 29.7 (2 peaks), 32.0 (2 peaks) 36.4, 37.0, 55.5, 114.3 (2 peaks), 119.7, 119.9, 123.4, 125.2, 125.6, 127.2, 128.3 (2 peaks), 134.3, 139.1, 139.2, 140.7, 141.9, 143.8, 144.0, 159.1;

m/z (EI) 398 (M^+ , 100%), 285 (60), 242 (Ar^+ , 11).

METHOD II

Nitrogen gas was bubbled through a stirred solution of impure 2-bromo-7-nonylfluorene **24i** (0.68 g, *ca.* 1.83 mmol), 4-methoxybenzoboronic acid **143** (0.36 g, 2.37 mmol), sodium carbonate solution (aq, 2M, 2 ml) and dimethoxyethane (20 ml) for 25 minutes.

Tetrakis(triphenylphosphine)palladium(0) (0.06 g, 52 μ m) was added, and the reaction mixture was heated at reflux for 7.0 hours. After cooling overnight, dichloromethane (60 ml) and water (60 ml) were added, and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 x 60 ml). The combined organic extracts were washed with water (60 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was dissolved in dichloromethane (20 ml). The solution was filtered through a plug of silica and rinsed with dichloromethane (3 x 50 ml). The solvent was removed. The residue was recrystallized from hot ethanol (charcoal) to give an off-white lustrous solid, 2-(4-methoxyphenyl)-7-nonylfluorene **137i** (0.08 g, 11 %, mp *ca.* 202 °C (from EtOH)).

(Found: C, 86.8; H, 8.7. $C_{29}H_{34}O$ requires C, 87.4; H, 8.6%). $\lambda_{max}(CH_2Cl_2)/nm$ 228 ($\epsilon/dm^3 mol^{-1} cm^{-1}$ 18700), 304 (37000), 316 (36300); $\nu_{max}(CHCl_3 soln.)/cm^{-1}$ 2927s, 2854m, 1608w, 1518s, 1469s, 1042w, 1026w; δ_H (300 MHz; $CDCl_3$) 0.80 (3H, t, $J = 6.6$, $CH_2CH_2(CH_2)_6CH_3$), 1.14-1.35 (12H, m, $CH_2CH_2(CH_2)_6CH_3$), 1.52-1.66 (2H, m, $CH_2CH_2(CH_2)_6CH_3$), 2.60 (2H, t, $J = 7.7$, $CH_2CH_2(CH_2)_6CH_3$), 3.78 (3H, s, OCH_3), 3.84 (2H, s, CH_2 (C9)), 6.91 (2H, m, ArH), 7.13 (1H, d, $J = 7.4$, ArH), 7.29 (1H, s, ArH), 7.44-7.54 (3H, m, ArH), 7.62 (2H, d, $J = 8.1$, ArH), 7.70 (1H, d, $J = 7.4$, ArH); δ_C (75.42 MHz; $CDCl_3$) 11.3, 22.9, 29.5, 29.6, 29.7, 32.0, 36.4, 37.0, 55.5, 114.3, 119.7, 119.9, 123.4, 125.2, 125.6, 127.2, 128.3, 134.3, 139.1, 139.2, 140.6, 141.9, 143.8, 144.0, 159.1; m/z (EI) 398 (M^+ , 100%), 285 ($Ar(CH_2)PhOMe^+$, 49), 270 ($Ar(CH_2)PhO^+$, 4), 242 ($ArPh^+$, 7).

2-(4-Heptoxyphenyl)-7-pentylfluorene

Nitrogen gas was bubbled through a stirred solution of impure 2-bromo-7-pentylfluorene **24e** (0.51 g, *ca.* 1.6 mmol), 4-heptoxybenzoboronic acid **144** (0.58 g, *ca.* 2.5 mmol), sodium carbonate solution (aq, 2M, 1.6 ml) and dimethoxyethane (20 ml) for 20 minutes. Tetrakis(triphenylphosphine)palladium(0) (0.06 g, 52 μ m) was added, and the reaction mixture was heated at reflux for 1.5 hours. After cooling, dichloromethane (50 ml) and water (50 ml) were added, and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 x 50 ml). The combined organic extracts were washed

with water (50 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was dissolved in dichloromethane (50 ml). The solution was filtered through a plug of silica and rinsed with dichloromethane (3 x 50 ml). The solvent was removed. The residue was recrystallized from hot chloroform-60-80 petroleum ether (charcoal) to give a white solid, 2-(4-heptoxyphenyl)-7-pentylfluorene **138e** (0.10 g, 14 %, mp 205 °C (from CHCl₃-PET (60-80))).

(Found: C, 87.3; H, 9.25. C₃₁H₃₈O requires C, 87.3; H, 9.0%). λ_{\max} (CH₂Cl₂)/nm 229 (ϵ /dm³mol⁻¹cm⁻¹ 16000), 307 (34000); ν_{\max} (CHCl₃ soln.)/cm⁻¹ 2930s, 2857m, 1607m, 1516s, 1468vs, 1246s, 1178m, 820s; δ_{H} (300 MHz; CDCl₃) 0.90-1.01 (6H, m, CH₂CH₂(CH₂)₂CH₃ and OCH₂CH₂(CH₂)₄CH₃), 1.28-1.55 (12H, m, CH₂CH₂(CH₂)₂CH₃ and OCH₂CH₂(CH₂)₄CH₃), 1.63-1.77 (2H, m, CH₂CH₂(CH₂)₂CH₃), 1.84 (2H, m, OCH₂CH₂(CH₂)₄CH₃), 2.61 (2H, m, CH₂CH₂(CH₂)₂CH₃), 3.95 (2H, s, CH₂ (C9)), 4.04 (2H, t, J = 6.6, OCH₂CH₂(CH₂)₄CH₃), 7.02 (2H, d, J = 8.8, ArH), 7.25 (1H, t, J = 7.4, ArH), 7.40 (1H, s, ArH), 7.62 (3H, t, J = 7.4, ArH), 7.72 (2H, d, J = 8.1, ArH), 7.80 (1H, d, J = 8.1, ArH); δ_{C} (75.42 MHz; CDCl₃) 14.3, 14.3, 22.8, 26.2, 29.3, 29.5, 31.7, 31.8, 32.0, 36.3, 37.1, 68.3, 114.9, 119.7, 119.9, 123.4, 125.3, 125.6, 127.3, 128.2, 134.1, 139.2, 139.3, 140.6, 141.8, 143.8, 144.0, 158.7; m/z (EI) 426 (M⁺, 100%), 382 (9), 369 (12), 330 (Ar(C₅H₁₁)PhOH⁺, 21), 271 (Ar(CH₂)PhOH⁺, 42).

A second crop of 2-(4-heptoxyphenyl)-7-pentylfluorene **138e** (white solid (0.04 g, 6%)) was isolated from the mother liquor. This had ¹H and ¹³C NMR spectra identical to those obtained for the authentic material described above.

8.6.2 2-Acyl-7-alkylfluorenes

2-Acetyl-7-ethylfluorene

A solution of 2-ethylfluorene **32b** (0.69 g, 3.6 mmol) and acetyl chloride (0.25 ml, 3.5 mmol) in dry 1,1,2,2-tetrachloroethane (20 ml) was stirred in an ice bath. Aluminium chloride (0.72 g, 5.4 mmol) was added, and the reaction mixture was allowed to warm to room temperature over 31.5 hours. Further aluminium chloride (0.24 g, 1.8 mmol) was added, and the reaction mixture was stirred at room temperature for 40.0 hours. Water (20 ml) and concentrated hydrochloric acid (20 ml) were added and the products were extracted into dichloromethane (3 x 30 ml). The combined organic extracts were washed with sodium bicarbonate solution (aq, 10%, 2 x 20 ml) and water (20 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was recrystallized

from hot chloroform-60-80 petroleum ether to give a yellow solid, 2-acetyl-7-ethylfluorene **142** (0.44 g, 52%, mp 107 °C (from CHCl₃-PET (60-80), lit.,¹⁶⁵ 125.5-126.5 °C).

$\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 229 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 17000), 298sh, 320 (34900); $\nu_{\max}(\text{CHCl}_3 \text{ soln.})/\text{cm}^{-1}$ 2968m, 1672s (C=O), 1609s, 1565w, 1420m, 1359m, 1272s, 1163w, 1136w, 957w, 822m; δ_{H} (300 MHz; CDCl₃) 1.30 (3H, t, $J = 7.4$, CH₂CH₃), 2.67 (3H, s, COCH₃), 2.77 (2H, q, $J = 7.4$, CH₂CH₃), 3.91 (2H, s, CH₂ (C9)), 7.26 (1H, d, $J = 7.4$, ArH), 7.44 (1H, s, ArH), 7.72-7.81 (2H, m, ArH), 8.00 (1H, d, $J = 8.1$, ArH), 8.12 (1H, s, ArH); δ_{C} (75.42 MHz; CDCl₃) 16.0, 26.9, 29.3, 36.9, 119.5, 120.9, 124.9, 125.0, 127.1, 127.9, 135.3, 138.3, 143.4, 144.9, 145.1, 146.8, 198.2; m/z (EI) 236 (M⁺, 77%), 221 (Ar(C₂H₅)CO⁺, 100), 193 (ArCO⁺, 39), 178 (ArCH₂⁺, 41), 165 (Ar⁺, 12).

2-Propionyl-7-nonylfluorene

A solution of 2-nonylfluorene **32i** (1.48 g, 5.1 mmol) and propionyl chloride (0.45 ml, 5.2 mmol) in dry 1,1,2,2-tetrachloroethane (30 ml) was stirred at room temperature.

Aluminium chloride (1.05 g, 7.9 mmol) was added, and the reaction mixture was stirred at room temperature for 19.4 hours. Further aluminium chloride (0.37 g, 2.8 mmol) was added, and the reaction mixture was stirred at room temperature for 23.5 hours. Water (15 ml) and concentrated hydrochloric acid (15 ml) were added and the products were extracted into dichloromethane (2 x 20 ml). The combined organic extracts were washed with sodium bicarbonate solution (aq, 10%, 3 x 20 ml) and water (20 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was recrystallized from hot ethanol to give an off-white solid, 2-propionyl-7-nonylfluorene **26** (0.75 g, 42%, mp 94-95 °C (from EtOH, lit.,³³ 91 °C)).

(Found: C, 86.1; H, 9.5. C₂₅H₃₂O requires C, 86.15; H, 9.3%); $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 229 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 17200), 319 (38300); $\nu_{\max}(\text{nujol})/\text{cm}^{-1}$ 1674 (C=O), 1608; δ_{H} (300 MHz; CDCl₃) 0.80 (3H, t, $J = 7.0$, CH₂CH₂(CH₂)₆CH₃), 1.15-1.40 (15H, m, CH₂CH₂(CH₂)₆CH₃ and COCH₂CH₃), 1.57-1.62 (2H, m, CH₂CH₂(CH₂)₆CH₃), 2.61 (2H, t, $J = 7.7$, CH₂CH₂(CH₂)₆CH₃), 2.98 (2H, q, $J = 7.1$, COCH₂CH₃), 3.83 (2H, s, CH₂ (C9)), 7.14 (1H, d, $J = 8.1$, ArH), 7.32 (1H, s, ArH), 7.68 (2H, m, ArH), 7.92 (1H, d, $J = 8.1$, ArH), 8.05 (1H, s, ArH); δ_{C} (75.42 MHz; CDCl₃) 8.7, 14.3, 22.8, 29.5, 29.7, 31.9, 32.0, 32.1, 36.4, 36.9, 119.4, 120.7, 124.8, 125.4, 127.5, 127.6, 135.1, 138.3, 143.3, 143.5, 144.9, 146.6, 200.9 (C=O); m/z (EI) 348 (M⁺, 41%), 319 (Ar(CO)C₉H₁₉⁺, 100), 235 (Ar(COCH₂CH₃)CH₂⁺, 19), 178 (ArCH₂⁺, 21).

8.6.3 2,7-Diacylfluorenes

2,7-Diacetylfluorene

A solution of fluorene (4.01 g, 24 mmol) and acetyl chloride (4.3 ml, 61 mmol) in dry 1,1,2,2-tetrachloroethane (125 ml) was stirred in an ice bath. Aluminium chloride (4.90 g, 37 mmol) was added, and the reaction mixture was allowed to warm to room temperature over 53.9 hours. Further aluminium chloride (5.06 g, 38 mmol) was added, and the reaction mixture was stirred at room temperature for 17.8 hours. Water (100 ml) and concentrated hydrochloric acid (100 ml) were added and the products were extracted into dichloromethane (3 x 100 ml). The combined organic extracts were washed with sodium bicarbonate solution (aq, 10%, 2 x 100 ml) and water (100 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was recrystallized from hot chloroform-60-80 petroleum ether (charcoal) to give a pale brown solid, 2,7-diacetylfluorene **136b** (0.43 g, 7%, mp 177-180 °C (from CHCl₃-PET (60-80), lit.,¹⁶⁶ 179.5-180 °C).

$\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 228 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 8100), 235sh, 244sh, 302sh, 317 (34100), 329 (35600); $\nu_{\max}(\text{CHCl}_3 \text{ soln.})/\text{cm}^{-1}$ 1878vs (C=O), 1610s, 1577m, 1485w, 1433m, 1416m, 1401w, 1359s, 1295s, 1257vs, 1155m, 1005w, 958w, 867w, 822m; δ_{H} (300 MHz; CDCl₃) 2.66 (6H, s, COCH₃), 3.96 (2H, s, CH₂ (C9)), 7.87 (2H, d, J = 8.1, ArH), 8.01 (2H, d, J = 8.1, ArH), 8.14 (2H, s, ArH); δ_{C} (75.42 MHz; CDCl₃) 27.0, 37.0, 120.8, 125.2, 128.0, 136.6, 144.7, 145.1, 198.0 (C=O); m/z (EI) 250 (M⁺, 55%), 236 (Ar(COCH₃)CO⁺, 100), 207 (ArCOCH₃⁺, 7), 192 (ArCO⁺, 27), 163 (Ar⁺, 28).

2,7-Dinonanoylfluorene

A solution of fluorene (0.97 g, 5.8 mmol) and nonanoyl chloride (5.5 ml, 31 mmol) in dry 1,1,2,2-tetrachloroethane (30 ml) was stirred at room temperature. Aluminium chloride (6.12 g, 46 mmol) was added, and the reaction mixture was stirred at room temperature for 16.3 hours. Further aluminium chloride (1.97 g, 15 mmol) was added, and the reaction mixture was stirred at room temperature for 96.4 hours. Water (50 ml) and concentrated hydrochloric acid (50 ml) were added and the products were extracted into dichloromethane (3 x 30 ml). The combined organic extracts were washed with sodium bicarbonate solution (aq, 10%, 2 x 30 ml) and water (30 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was chromatographed twice on silica gel, first using dichloromethane-40-60 petroleum ether (1:1) then using dichloromethane as eluent, then recrystallized from hot ethanol to give a white solid, 2,7-dinonanoylfluorene

136i (0.17 g, 7%, mp 106-108 °C (from EtOH, lit., ¹⁴² 121 °C)).

(Found: C, 83.6; H, 9.5. C₃₁H₄₂O₂ requires C, 83.4; H, 9.5%. $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 303sh, 318 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 41300), 329 (43600); $\nu_{\text{max}}(\text{nujol})/\text{cm}^{-1}$ 1680w (C=O), 830w, 724w; δ_{H} (300 MHz; CDCl₃) 0.88 (6H, t, J = 6.3, COCH₂CH₂(CH₂)₅CH₃), 1.30 (20H, m, COCH₂CH₂(CH₂)₅CH₃), 1.77 (4H, m, COCH₂CH₂(CH₂)₅CH₃), 3.01 (4H, t, J = 7.4, COCH₂CH₂(CH₂)₅CH₃), 4.01 (2H, s, CH₂ (C9)), 7.90 (2H, d, J = 8.1, ArH), 8.05 (2H, d, J = 8.1, ArH), 8.18 (2H, s, ArH); δ_{C} (75.42 MHz; CDCl₃) 14.3, 22.8, 24.7, 29.4, 29.6, 32.0, 37.1, 39.0, 120.8, 125.0, 127.7, 136.6, 144.7, 145.0, 200.6 (C=O); m/z (EI) 446 (M⁺, 16%), 348 (Ar(COCH₃)COC₈H₁₇⁺, 90), 333 (Ar(CO)COC₈H₁₇⁺, 100), 250 (Ar(COCH₃)₂⁺, 100), 192 (ArCO⁺, 41), 164 (Ar⁺, 14).

8.6.4 Carboxylic acids

Fluorene-2-carboxylic acid (attempted synthesis)

METHOD I

A solution of 2-acetylfluorene **31b** (0.05 g, 0.3 mmol) in dioxane (10 ml) was stirred at room temperature. A solution of potassium iodide (0.20 g, 1.2 mmol) and iodine (0.11 g, 0.42 mmol) in water (1 ml) was added and the reaction mixture was stirred at room temperature. After 30 minutes, no change was apparent. Sodium hypochlorite solution (aq, 10 ml) was added, giving a white precipitate after 1 minute. The reaction mixture was heated at reflux overnight. After cooling, the reaction mixture was extracted with diethyl ether (2 x 25 ml). The combined organic extracts were washed with sodium metabisulphite solution (aq, 5%, 25 ml) and water (25 ml), dried over anhydrous sodium sulphate, filtered and the solvent was removed to give an orange solid (0.03 g).

TLC analysis indicated a single component (R_f = 0.00 in DCM). ¹H and ¹³C NMR spectra suggested a mixture of compounds. A mass spectrum suggested the presence of fluorene-2-carboxylic acid **151**. The presence of the acid could not be conclusively demonstrated.

Selected spectral data: δ_{C} (75.42 MHz; CDCl₃) 198 (C=O), 207 (C=O); m/z (ES) 209 (C₁₃H₉COO⁻).

METHOD II

Bromine (0.8 ml, 16 mmol) was added to a solution of sodium hydroxide (2.21 g, 55 mmol) in water (11 ml). The resulting sodium hypobromite solution was added to a mixture of 2-acetylfluorene **31b** (0.70 g, 3.4 mmol) and 1,4-dioxane. The reaction mixture was stirred in an ice bath, then allowed to warm to room temperature over 16.1 hours. Sodium

metabisulphite solution (aq, 5%, 60 ml) and concentrated hydrochloric acid (3 ml) were added. The resulting precipitate was filtered, then rinsed with hydrochloric acid (aq, 2 M, 2 x 10 ml) and dried. The residue was recrystallized from hot glacial acetic acid (charcoal) to give a yellow solid, a (1:1) mixture of fluorene-2-carboxylic acid **151** and fluorenone-2-carboxylic acid **152**.

METHOD III

A mixture of fluorene (1.04 g, 6.3 mmol) and aluminium chloride (1.25 g, 9.4 mmol) in dry 1,1,2,2-tetrachloroethane (25 ml) was stirred at room temperature. A solution of oxalyl chloride (0.50 ml, 5.8 mmol) in dry 1,1,2,2-tetrachloroethane (5 ml) was added over 6 minutes. The reaction mixture was stirred at room temperature for 12.6 hours. Further aluminium chloride (0.42 g, 3.1 mmol) was added, and the reaction mixture was stirred at room temperature for 24.6 hours. Water (15 ml) and concentrated hydrochloric acid (15 ml) were added, and the products were extracted into dichloromethane (3 x 20 ml). The combined organic extracts were washed with sodium bicarbonate solution (aq, 10%, 2 x 20 ml) and water (20 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed to give a light brown solid (1.14 g, mp *ca.* 200 °C).

TLC analysis of the residue indicated a single component ($R_f = 0.67$ in DCM). A ^{13}C NMR spectrum suggested a mixture of two or more products. A Mass spectrum was inconclusive, but showed peaks of low intensity consistent with the formation of the dimeric fluorene compounds **153** and **154**.

m/z (EI) 386 (ArCOCOAr^+ , <1%), 358 (ArCOAr^+ <1%), 210 (ArCOOH^+ , 8), 193 (ArCO^+ , 100), 165 (Ar^+ , 44).

METHOD IV

Magnesium turnings (0.21 g, 8.6 mmol) were dry stirred under nitrogen for 15 minutes. Dry diethyl ether (10 ml) was added. A solution of 2-bromofluorene **24a** (1.00g, 4.1 mmol) and 1,2-dibromoethane (0.35 ml, 4.1 mmol) in dry diethyl ether (40 ml) was added over 10 minutes. After stirring at room temperature under nitrogen for 3.1 hours, the resulting solution was poured onto dry ice and stirred for 15 minutes. Further dry ice (50 g) was added, and the reaction mixture stirred for 20 minutes. Further dry ice (50 g) was added, and the reaction mixture stirred for 1.9 hours. Water (25 ml) and concentrated hydrochloric acid (5 ml) were added, and the organic layer was separated. The aqueous layer was extracted with diethyl ether (25 ml). The combined organic extracts were washed with water (25 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. Sodium hydroxide solution (aq, 1M, 40 ml) was added, and the mixture was

heated to give a colourless solution and orange solid. After cooling, the aqueous layer was washed with diethyl ether (50 ml). Hydrochloric acid (aq, *ca.* 1M, 100 ml) was added, and the aqueous layer extracted with diethyl ether (100 ml). The organic layer was dried over anhydrous sodium sulphate, filtered and the solvent removed to give a white-yellow oil (0.02 g). The solvent was removed from the diethyl ether wash. The residue was recrystallized from hot acetic acid-water to give a pale yellow solid, impure 2-bromofluorene **24a** (0.17 g, *ca.* 17%).

The solid co-chromatographed ($R_f = 0.80$ in DCM) and had ^1H and ^{13}C NMR spectra identical to those obtained for the starting material.

7-Nonylfluorene-2-carboxylic acid

A solution of 2-nonylfluorene **32i** (1.02 g, 3.5 mmol) and oxalyl chloride (0.30 ml, 3.5 mmol) in dry 1,1,2,2-tetrachloroethane (50 ml) was stirred in an ice bath. Aluminium chloride (0.77 g, 5.8 mmol) was added, and the reaction mixture was allowed to warm to room temperature over 25.0 hours. Further aluminium chloride (0.22 g, 1.6 mmol) was added, and the reaction mixture was stirred at room temperature for 11.7 hours. Water (20 ml) and concentrated hydrochloric acid (20 ml) were added and the products were extracted into dichloromethane (3 x 20 ml). The combined organic extracts were washed with sodium bicarbonate solution (aq, 10%, 2 x 50 ml) and water (50 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was dissolved in dichloromethane (50 ml). The solution was filtered through a plug of silica and rinsed with dichloromethane (2 x 50 ml). The solvent was removed. The residue was recrystallized from hot chloroform-hexane (charcoal) to give a pale yellow solid 7-nonylfluorene-2-carboxylic acid **155** (0.17 g, 14%, mp 150 °C (from CHCl_3 -hexane)).

λ_{max} (CH_2Cl_2)/nm 230 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 12600), 349 (26600); ν_{max} (CHCl_3 soln.)/ cm^{-1} 2927s, 2855m, 1662m, 1606vs, 1562w, 1467w, 1421w, 1346w, 1307w, 1255w, 1107w, 1006w, 942w, 827w; δ_{H} (300 MHz; CDCl_3) 0.90 (3H, t, $J = 6.6$, $\text{CH}_2\text{CH}_2(\text{CH}_2)_6\text{CH}_3$), 1.20-1.47 (12H, m, $\text{CH}_2\text{CH}_2(\text{CH}_2)_6\text{CH}_3$), 1.61-1.77 (2H, m, $\text{CH}_2\text{CH}_2(\text{CH}_2)_6\text{CH}_3$), 2.71 (2H, t, $J = 7.7$, $\text{CH}_2\text{CH}_2(\text{CH}_2)_6\text{CH}_3$), 3.94 (2H, s, CH_2 (C9)), 7.27 (1H, d, $J = 8.1$, ArH), 7.42 (1H, s, ArH), 7.78 (1H, d, $J = 8.1$, ArH), 7.85 (1H, d, $J = 8.1$, ArH), 8.06 (1H, d, $J = 8.1$, ArH), 8.18 (1H, s, ArH); δ_{C} (75.42 MHz; CDCl_3) 14.3, 22.9, 29.5, 29.7, 31.9, 32.1, 36.4, 36.9, 120.0, 121.2, 125.5, 126.6, 127.8, 129.7, 131.2, 138.0, 143.7, 144.3, 145.3, 148.6, 195.2; m/z (EI) 336 (M^+ , 67%), 223 ($\text{Ar}(\text{CH}_2)\text{COOH}^+$, 100), 178 (ArCH_2^+ , 21).

8.6.5 9,10-Dihydrophenanthrene derivatives

2-Acetyl-9,10-dihydrophenanthrene

METHOD I

A solution of 9,10-dihydrophenanthrene (1.01 g, 5.6 mmol) and acetyl chloride (0.56 g, 7.1 mmol) in dry 1,1,2,2-tetrachloroethane (25 ml) was stirred at room temperature.

Aluminium chloride (1.06 g, 7.9 mmol) was added, and the reaction mixture was stirred at room temperature for 15.0 hours. Further aluminium chloride (0.33 g, 2.5 mmol) was added, and the reaction mixture was stirred at room temperature for 24.0 hours. Water (15 ml) and concentrated hydrochloric acid (15 ml) were added and the products were extracted into dichloromethane (3 x 20 ml). The combined organic extracts were washed with sodium bicarbonate solution (aq, 5%, 2 x 20 ml) and water (20 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was chromatographed on silica gel using dichloromethane-40-60 petroleum ether as eluent followed by recrystallization from hot dichloromethane-80-100 petroleum ether to give a pale yellow-orange solid, impure 2-acetyl-9,10-dihydrophenanthrene **139b** (0.26g, *ca.* 21%).

TLC analysis indicated that the solid eluted as a single component. ^1H and ^{13}C NMR spectra indicated the presence of unknown impurities.

METHOD II

A solution of 9,10-dihydrophenanthrene (4.51 g, 25 mmol) and acetyl chloride (1.8 ml, 25 mmol) in dry 1,1,2,2-tetrachloroethane (120 ml) was stirred in an ice bath. Aluminium chloride (5.08 g, 38 mmol) was added, and the reaction mixture was allowed to warm to room temperature over 19.3 hours. Further aluminium chloride (1.87 g, 14 mmol) was added, and the reaction mixture was stirred at room temperature for 50.3 hours. Water (100 ml) and concentrated hydrochloric acid (100 ml) were added and the products were extracted into dichloromethane (3 x 100 ml). The combined organic extracts were washed with sodium bicarbonate solution (aq, 10%, 2 x 100 ml) and water (100 ml), dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was triturated with 40-60 petroleum ether (70 ml) to give a brown solid, impure 2-acetyl-9,10-dihydrophenanthrene **139b** (1.73 g, *ca.* 31%).

TLC analysis indicated a single component ($R_f = 0.50$ in DCM). ^1H and ^{13}C NMR spectra indicated the presence of unknown impurities.

δ_{H} (300 MHz; CDCl_3) 2.64 (3H, s, COCH_3), 2.85-2.97 (4H, m, CH_2CH_2), 7.26-7.40 (3H, m, ArH), 7.77-7.96 (4H, m, ArH); δ_{C} (75.42 MHz; CDCl_3) 26.8, 29.0, 29.1, 123.9, 124.6,

127.3, 127.4, 128.1, 128.2, 128.8, 133.6, 135.9, 137.7, 138.2, 139.3, 198.0 (C=O); m/z (EI) 222 (M^+ , 46%), 207 ($ArCO^+$, 100), 179 (Ar^+ , 38).

2-Propionyl-9,10-dihydrophenanthrene

A solution of 9,10-dihydrophenanthrene (0.95 g, 5.3 mmol) and propionyl chloride (0.49 g, 5.3 mmol) in dry 1,1,2,2-tetrachloroethane (25 ml) was stirred at room temperature.

Aluminium chloride (1.07 g, 8.0 mmol) was added, and the reaction mixture was stirred at room temperature for 18.6 hours. Further aluminium chloride (0.38 g, 2.8 mmol) was added, and the reaction mixture was stirred at room temperature for 27.5 hours. Water (15 ml) and concentrated hydrochloric acid (15 ml) were added and the products were extracted into dichloromethane (3 x 20 ml). The combined organic extracts were washed with sodium bicarbonate solution (aq, 5%, 3 x 20 ml) and water (20 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was recrystallized from hot chloroform-60-80 petroleum ether to give a yellow solid, impure 2-propionyl-9,10-dihydrophenanthrene **139c** (0.11 g, *ca.* 9%).

TLC analysis indicated that the solid eluted as a single component. 1H and ^{13}C NMR spectra indicated the presence of unknown impurities.

2-Pentanoyl-9,10-dihydrophenanthrene

A solution of 9,10-dihydrophenanthrene (0.87 g, 4.8 mmol) and pentanoyl chloride (0.61 g, 5.1 mmol) in dry 1,1,2,2-tetrachloroethane (25 ml) was stirred at room temperature.

Aluminium chloride (0.98 g, 7.3 mmol) was added, and the reaction mixture was stirred at room temperature for 18.6 hours. Further aluminium chloride (0.32 g, 2.4 mmol) was added, and the reaction mixture was stirred at room temperature for 29.2 hours. Water (15 ml) and concentrated hydrochloric acid (15 ml) were added and the products were extracted into dichloromethane (3 x 20 ml). The combined organic extracts were washed with sodium bicarbonate solution (aq, 5%, 3 x 20 ml) and water (20 ml), then dried over anhydrous sodium sulphate and filtered. The solvent was removed. The residue was recrystallized from hot chloroform-80-100 petroleum ether to give a yellow solid, impure 2-pentanoyl-9,10-dihydrophenanthrene **139e** (0.02 g, *ca.* 2%).

TLC analysis indicated that the solid eluted as a single component. 1H and ^{13}C NMR spectra indicated the presence of unknown impurities.

2-Acetoxime-9,10-dihydrophenanthrene

METHOD I

A mixture of impure 2-acetyl-9,10-dihydrophenanthrene **139b** (1.46 g, *ca.* 5.7 mmol), hydroxylamine hydrochloride (1.98 g, 28 mmol), sodium hydroxide (1.22 g, 31 mmol),

ethanol (25 ml) and dichloromethane (7 ml) was heated at reflux for 17.5 hours. After cooling, water (30 ml) was added. The solvent was removed. The residue was chromatographed on silica gel using dichloromethane as eluent to give a pale yellow solid (0.08 g).

TLC analysis indicated that the solid eluted as a single component. ^1H and ^{13}C NMR spectra indicated a mixture of two components.

METHOD II

A mixture of hydroxylamine hydrochloride (3.84 g, 55 mmol), sodium hydroxide (2.00g, 50 mmol) and ethanol (40 ml) was stirred in an ice bath for 2.0 hours. The resulting hydroxylamine solution was filtered into a mixture of impure 2-acetyl-9,10-dihydrophenathrene **139b** (1.56 g, 7.0 mmol) and ethanol (10 ml). The reaction mixture was heated at reflux for 17.2 hours. After cooling, water (65 ml) was added, and the reaction mixture was stirred at room temperature. The resulting precipitate was filtered, rinsed and dried. The residue was recrystallized from hot dichloromethane-60-80 petroleum ether (charcoal) to give a yellow solid, 2-acetoxime-9,10-dihydrophenathrene **140b** (0.49g, 29%, mp 143-145 °C (from DCM-PET (60-80), lit.,¹⁵³ 144 °C).

$\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 293 ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ 20800), 271 (17400), 316 (12200); $\nu_{\text{max}}(\text{CHCl}_3 \text{ soln.})/\text{cm}^{-1}$ 3673w, 3582s, 3311s (br, OH), 1602w, 1481s, 1439m, 1369m, 1292m, 1004s, 936s, 889m, 832m; δ_{H} (300 MHz; CDCl_3) 2.37 (3H, s, CH_3), 2.93 (4H, s, CH_2CH_2), 7.28 (2H, d, $J = 4.4$, ArH), 7.30-7.39 (1H, m, ArH), 7.55 (1H, d, $J = 1.5$, ArH), 7.59 (1H, dd, $J = 8.1, 1.5$, ArH), 7.78 (2H, d, $J = 8.1$, ArH); δ_{C} (75.42 MHz; CDCl_3) 12.4, 29.1, 29.3, 124.0, 124.9, 125.9, 127.2, 127.9, 128.4, 134.1, 135.4, 135.7, 137.7, 156.1; m/z (EI) 237 (M^+ , 17%), 221 ($\text{ArC}(\text{NH})\text{CH}_3^+$, 88), 206 (ArCNH^+ , 100), 178 (Ar^+ , 43).

2-Propionyloxime-9,10-dihydrophenathrene

A mixture of impure 2-propionyl-9,10-dihydrophenathrene **139c** (0.81 g, *ca.* 5.3 mmol), hydroxylamine hydrochloride (1.98 g, 28 mmol), sodium hydroxide (1.14g, 29 mmol) and ethanol (25 ml) was heated at reflux for 14.5 hours. After cooling, water (30 ml) was added, and the resulting precipitate filtered and dried. The solvent was removed to give a yellow solid (0.50 g).

TLC analysis indicated that the solid eluted as a single component. ^1H and ^{13}C NMR spectra indicated the presence of unknown impurities.

2-Pentanoyloxime-9,10-dihydrophenanthrene

A mixture of impure 2-pentanoyl-9,10-dihydrophenanthrene **139e** (1.19 g, *ca.* 4.8 mmol), hydroxylamine hydrochloride (2.00 g, 29 mmol), sodium hydroxide (1.14 g, 29 mmol) and ethanol (25 ml) was heated at reflux for 13.8 hours. After cooling, water (30 ml) was added, and the resulting precipitate filtered and dried. The residue was recrystallized from hot hexane then chromatographed on silica gel to give an off-white solid (0.15 g). TLC analysis indicated that the solid eluted as a single component. ^1H and ^{13}C NMR spectra indicated the presence of unknown impurities.

8.6.6 Deuteriated compounds**9,9-d₂-2-(4-Cyanophenyl)-7-pentylfluorene** (attempted synthesis)

A mixture of 2-(4-cyanophenyl)-7-pentylfluorene **30e** (10 mg) and d₆-dimethylsulphoxide (*ca.* 0.6 ml) was placed in an NMR tube at room temperature. An NMR spectrum was recorded. Potassium *tert*-butoxide (*ca.* 1 mg) was added, and NMR spectra were recorded at intervals of 4.6, 53.3, 90.2, 114.8 and 236.7 hours. The mixture was quenched with deuterium oxide (*ca.* 1 ml). Water (10 ml) was added, and the mixture was extracted with chloroform (5 x 10 ml). The combined organic layers were dried over anhydrous sodium sulphate and filtered. The solvent was removed to give a yellow solid (4 mg).

^1H and ^{13}C NMR spectra suggested that the compound had partially degraded.

Benzonitrile (attempted deuteration)

A mixture of benzonitrile (21 mg, 0.2 mmol) and d₆-dimethylsulphoxide (1 ml) was placed in an NMR tube at room temperature. ^1H and ^{13}C NMR spectra were recorded. Potassium *tert*-butoxide (*ca.* 15 mg) was added, and NMR spectra were recorded at intervals of 7.6, 36.8, 48.4, 150.8 and 343.1 hours. The mixture was quenched with deuterium oxide (*ca.* 1 ml). Chloroform (10 ml) and water (10 ml) were added. The organic layer was separated, then dried over anhydrous sodium sulphate and filtered. The solvent was removed to give a colourless liquid, benzonitrile.

^1H and ^{13}C NMR spectra were identical to those of unadulterated benzonitrile.

9,9-d₂-Fluorene (attempted synthesis)

A mixture of fluorene (33 mg, 0.2 mmol) and d₆-dimethylsulphoxide (1 ml) was placed in an NMR tube at room temperature. ^1H and ^{13}C NMR spectra were recorded. Potassium *tert*-butoxide (*ca.* 15 mg) was added, and NMR spectra were recorded at intervals of 6.5, 35.5, 47.1, 149.5 and 341.9 hours. The mixture was quenched with deuterium oxide (*ca.* 1 ml). Chloroform (10 ml) and water (10 ml) were added. The organic layer was separated, then

dried over anhydrous sodium sulphate and filtered. The solvent was removed to give a yellow oily solid.

^1H and ^{13}C NMR suggested a mixture of fluorene and an unknown second component. A mass spectrum suggested the presence of 9-hydroxyfluorene **68** and fluorenone **69** in addition to unadulterated fluorene.

m/z (EI) 182 (ArOH^+) 180 (ArO^+), 166 (Ar^+).

9. APPENDIX

9.1 THERMOQUEST TRACE MS GAS CHROMATOGRAPHY MASS SPECTROMETER

Sample volume	1.0 µl
Initial oven temperature	60 °C
Initial time	2.00 min
Ramp rate	50 °C min ⁻¹
Final temperature	300 °C
Hold time	4.00 min
Injection	Splitless
Scans per second	2
Scan range	35-560 Daltons
Column	Rtx-5 (15 m) 5% diphenyl-95% dimethyl polysiloxane
Detector	Total ion count

9.2 X-RAY DATA FOR 1,3-DIBROMO-2-HYDROXYFLUORENE

Empirical formula	$C_{13}H_8Br_2O$	
Formula weight	340.01	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	$a = 14.562(3)$ Å $b = 3.9760(10)$ Å $c = 19.222(4)$ Å	$\alpha = 90^\circ$ $\beta = 100.02(3)^\circ$ $\gamma = 90^\circ$
Volume	$1095.9(4)$ Å ³	
Z	4	
Calculated density	2.061 Mg m ⁻³	
Absorption coefficient	7.368 mm ⁻¹	
F(000)	656	
Crystal size	0.4 x 0.05 x 0.025 mm	
θ range for data collection	1.93 to 27.49°	
Limiting indices	-17 ≤ h ≤ 18, -5 ≤ k ≤ 5, -23 ≤ l ≤ 23	
Reflections collected / unique	7649 / 2358 [R(int) = 0.0658]	
Completeness to $\theta = 27.49^\circ$	94.0%	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2358 / 0 / 177	
Goodness-of-fit on F ²	0.971	
Final R indices [I > 2σ(I)]	R1 = 0.0415, wR2 = 0.1008	
R indices (all data)	R1 = 0.0583, wR2 = 0.1118	
Coordinates and bond angles	(CDROM D:\XRAY\)	

9.3 X-RAY DATA FOR 2-PENTOXY-3-BROMOFLUORENE

Empirical formula	$C_{18}H_{19}BrO$	
Formula weight	331.24	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	$a = 7.563(2)$ Å $b = 9.711(2)$ Å $c = 11.715(2)$ Å	$\alpha = 72.61(3)^\circ$ $\beta = 74.07(3)^\circ$ $\gamma = 76.01(3)^\circ$
Volume	$777.5(3)$ Å ³	
Z	2	
Calculated density	1.415 Mg m ⁻³	
Absorption coefficient	2.637 mm ⁻¹	
F(000)	340	
Crystal size	0.15 x 0.05 x 0.025 mm	
θ range for data collection	3.04 to 29.41°	
Limiting indices	$-9 \leq h \leq 8$, $-12 \leq k \leq 10$, $-15 \leq l \leq 12$	
Reflections collected / unique	6939 / 3336 [R(int) = 0.0928]	
Completeness to $\theta = 29.41^\circ$	77.0%	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3336 / 0 / 182	
Goodness-of-fit on F^2	0.913	
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0694, wR2 = 0.1456	
R indices (all data)	R1 = 0.1565, wR2 = 0.1768	
Coordinates and bond angles	(CDROM D:\XRAY\)	

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