THE SYNTHESIS AND CHARACTERISATION OF LIQUID CRYSTAL OLIGOMERS

BY

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UNIVERSITY OF SOUTHAMPTON

ABSTRACT

FACULTY OF SCIENCE

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Master of Philosophy

The Synthesis and Characterisation of Liquid Crystal Oligomers.

by Peter Jeremy Barnes

The liquid-crystalline state has been known for just over 100 years [1], but it is really the last 25 years that have brought about the wealth of present day knowledge concerning this fascinating state of matter. Much of our knowledge has resulted because of the use of liquid crystals in electro-optic devices which have revolutionised the display industry [2]. The investigation of such systems has caused a major expansion in the fundamental science and has proved an intellectual challenge to our understanding of molecular interactions necessary for liquid crystal formation. Many new techniques have been developed and adapted specifically for the analysis, characterisation and utilisation of liquid-crystalline systems.

The majority of molecules that exhibit liquid crystal phases are long and rod-like, typically they contain rigid groups to which are attached either one or two alkyl chains. This can be extended to polymeric systems where many such rigid groups are joined together via alkyl chains. As an aid to the understanding and

rationalisation of the behaviour of polymeric liquid crystals, and particularly the role of the alkyl chain within the system, oligomeric molecules which consist of rigid groups connected via flexible alkyl chains can be synthesised and their behaviour examined. Such molecules have proved to be good models for certain properties of the polymeric systems, they are easier to study experimentally, and they present fewer difficulties when developing molecular theories with which to understand their behaviour. Here we describe the synthesis and investigation of some specifically deuteriated 'dimers' and 'trimers' using NMR spectroscopy in an attempt to explain some of the differences in liquid-crystalline properties observed between oligomeric molecules containing alkyl chains of different length.

Chapter one provides an introduction to liquid crystals; their phases, their molecular structure and how this relates to their physical properties, and also how NMR spectroscopy can be used to provide information their structure. In chapter two the odd-even effect, observed in oligomers, is investigated using NMR spectroscopy and unusual conclusions concerning the molecular organisation are drawn.

CONTENTS

CHAPTER ONE

AN INTRODUCTION TO LIQUID CRYSTALS, THEIR PROPERTIES AND CHARACTERISATION

1.1 Introduction

Some solids, mainly organic in nature, do not have a well defined solid to isotropic liquid transition temperature, they melt first to form a turbid liquid which is birefringent, a property typically exhibited by crystals, but they flow under shear, a property typically exhibited by liquids. Such phases are termed liquid crystals.

This fascinating class of materials was discovered by Reinitzer and Lehmann just over 100 years ago but it is only in recent years that their potential applications has stimulated an interest in their behaviour at a fundamental level. In this thesis the work is concerned with thermotropic liquid crystals i.e. those which are formed by thermal effects; either by heating a solid or by cooling a liquid phase in contrast to lyotropic liquid crystals [3]. These are usually composed of two or more components e.g. soap and water where the solute molecule contains different functional groups with hydrophobic and hydrophillic properties, so that the mixture forms aggregates when the solvent is added. On altering the composition of the mixture, different aggregates will be formed which interact to give the lyotropic liquid crystal phases.

The thermotropic class of liquid crystals can be further broken down according to the long range spatial and angular arrangements of the molecules with respect to one another. Three basic types of mesophase exist: nematic, cholesteric and smectic, however, the nematic and cholesteric phases are very closely linked and cannot be distinguished on the molecular scale. All three types have the

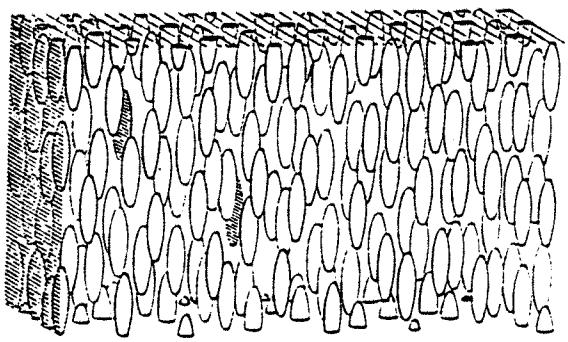
fundamental requirement of anisotropy in the molecular shape. In most liquid crystals this means rod-like molecules whose long axes tend to lie parallel over large molecular distances. However, discotic liquid crystals are also known [4]. Discotic mesophases are formed by molecules with a disc-like structure, they exhibit nematic phases although the discs can also stack together in columns which then arrange themselves to form additional liquid crystalline phases.

The symmetry of these phases varies, thus most nematic phases have uniaxial symmetry although biaxial nematics have been reported. The less ordered smectic phases are arranged in layers and many of these have biaxial symmetry, except for the smectic A phase which is uniaxial. The highly ordered crystalline smectic phases have symmetry of the same order as some crystalline solids.
The majority of the work described on this thesis was carried out in the uniaxial nematic phase.

1.2 Liquid-Crystalline Phases

Nematic Mesophase

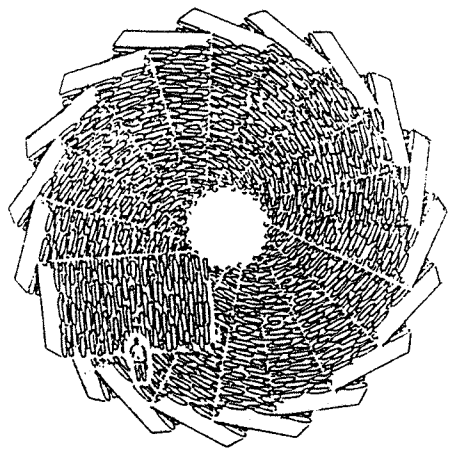
The nematic phase is the most disordered of the liquid crystal phases and is commonly bounded by a smectic or crystalline phase at low temperature and an isotropic liquid at high temperature. It is distinguished from an isotropic liquid by the long range orientational ordering of the constituent rod-like molecules which tend to lie parallel to a common axis called the director, n. In contrast the molecular positions show only short range order as in a normal liquid. The director is randomly arranged in the bulk but a small electric or magnetic field is sufficient to give true macroscopic order of director orientation. It is this property which is utilised in most of the electro-optic display devices currently available [5].



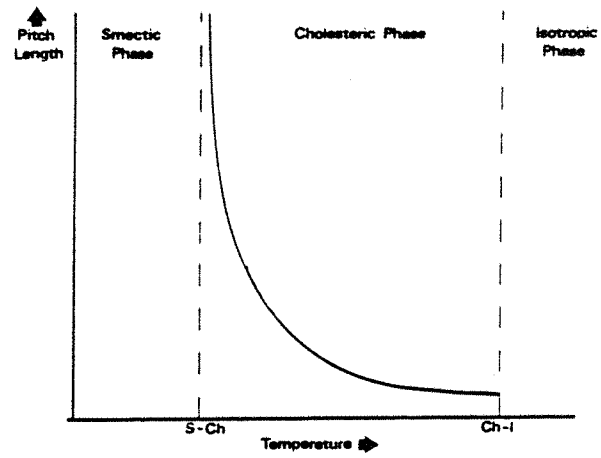
Schematic representation of nematic mesophase.

Cholesteric Mesophase

The cholesteric mesophase is exhibited only by chiral molecules and is not discernable from the nematic phase on a molecular scale, but differs significantly in that the director is not randomly arranged in space but undergoes a helical distortion. The structure may be simplistically envisaged as composed of regions of nematic liquid crystal, the director of an individual region is rotated through a microscopic angle with respect to the director in adjacent regions. As a succession of regions is passed through, the director turns through 360° and the distance traversed represents the pitch length for the helix. When the pitch is of the order of the wavelength of visible light Bragg scattering occurs and the phase becomes coloured. Changing the temperature when the system is coloured will alter the pitch of the helix, and hence the colour; this thermochromic property has found numerous applications [6]. The pitch is much longer than the molecular length and it can be removed by the action of an electric or magnetic field which aligns the director parallel to the field. Since the cholesteric phase is formed only by optically active species, a racemic mixture of both isomers will give a nematic mesophase conversely a nematic phase may be converted into a cholesteric phase by the addition of small amounts of optically active material.



cholesteric



Temperature dependence of cholesteric helical pitch (and colour play) in the region of a smectic A transition.

Smectic Mesophase

From a structural point of view, all smectics are layered structures, with a well-defined interlayer spacing, which can be measured by X-ray diffraction. The three main types in this classification are identified by the letters A, B and C; this is a purely chronological nomenclature with no structural implications.

A smectic mesophase is classified as having some degree of long range translational order as well as long range orientational order. This extra degree of freedom gives rise to at least nine recognised polymorphic smectic modifications with several more variations observed but not fully characterised or documented.

Smectic A

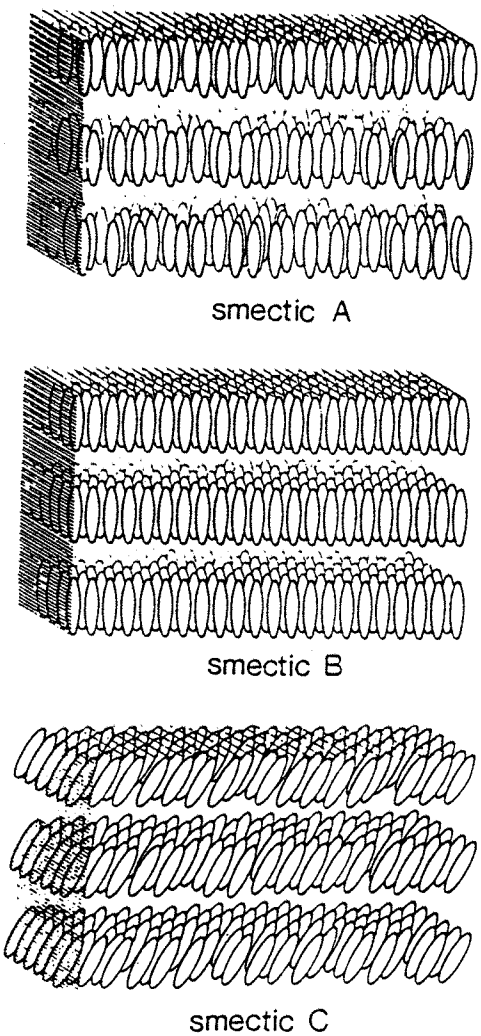
This is the simplest smectic structure with a layer thickness close to the full length of the constituent molecules first recognised by Friedel [7]. Inside each layer, the centres of mass of the molecules show no long range order, and each layer can be regarded as a two dimensional nematic. The system is optically uniaxial with the optical axis normal to the plane of the layers.

Smectic C

The smectic C phase contrasts with the smectic A phase by being optically biaxial, this feature can be interpreted by regarding the director as being tilted with respect to the normal of the layers. These layers are free to slide over one another as in the smectic A phase, i.e. there is no long range correlation, even of the tilt direction, between the layers. The tilt angle in the smectic C phase has been shown to vary with temperature in a uniform way, for example, in TBBA (a di-Schiffs base) the tilt angle, θ, changes gradually from 0° to 25° within the smectic C range because the phase is formed from a smectic A. In contrast when the smectic C is formed from a nematic the tilt angle jumps to a large (~30°) value which is insensitive to temperature.

Smectic B

The smectic B phase has the constituent molecules arranged within the layers in a hexagonally close-packed array with the molecular long axes perpendicular to the layer planes. In some cases the close-packed arrangement within a given layer has been shown to be very long range with the hexagonal net extending over a large number of layers thus making it structurally solid-like and not a true liquid crystal phase. However, the phase exhibits shear and flow properties under stress, precisely reversible phase transitions, does not undergo supercooling and, for homologous series, shows regular trends, all of the characteristics usually observed when dealing with true liquid crystals.

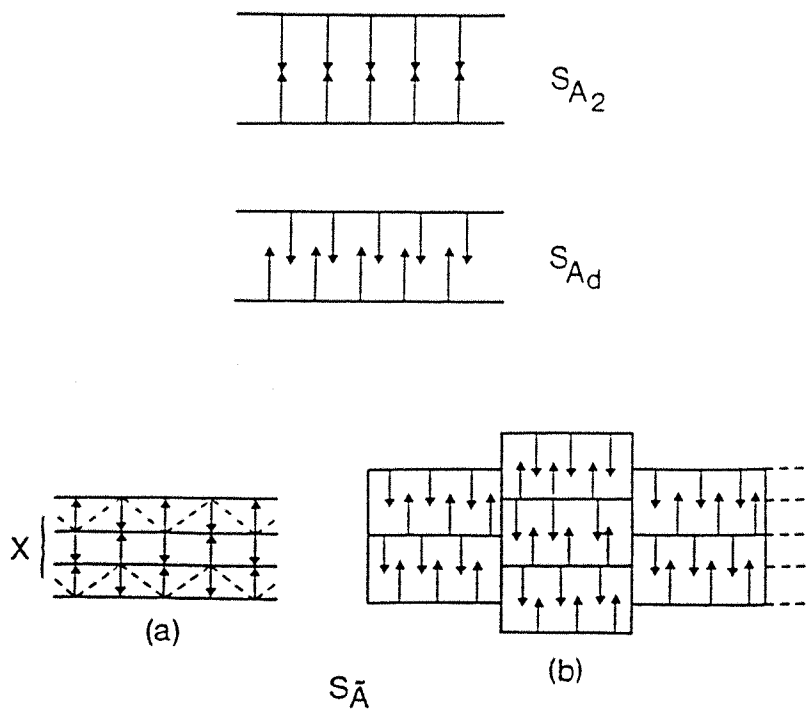


Schematic representation of smectic A,B and C phases.

'Exotic' Smectics

The thermotropic smectics include more complex structures with the further designations D-J. Most of these may be envisaged as a combination of one or more of the characteristics of the A, B and C phases with the careful distinction between a crystal smectic and a hexatic smectic. A crystal smectic phase has a hexagonal close-packing of molecules within the layers with long range spatial correlation of the hexagonal net between layers whereas a hexatic smectic has no such long range spatial correlation between layers. For example, the F and I phases are the tilted analogues of the hexatic smectic B phase, the difference between them is defined by the direction of tilt of the director. Similarly, the G and J phases are the tilted analogues of the crystal smectic B phase.

Further sub-divisions within the smectic phases have also been recognised. For example, some smectic A variations are, S_{A2}, S_{Ad} and $S_{\tilde{A}}$, these structures are usually exhibited by polar molecules. They result from specific molecular interactions which can mean that the basic structural unit within the smectic A phase is a dimer.



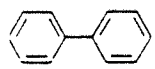
Schematic representation of some smectic A variations.

1.3. Liquid Crystal Structure-Property Relationships

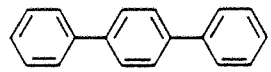
The anisotropy of molecular shape is a fundamental requirement for the formation of liquid crystals which, up until the mid 1970's, when Chandrasekhar [4] discovered that disc-shaped molecules also form stable mesophases, meant that the molecule had to be long and rod-like for mesomorphism to occur. This section outlines basic thermotropic liquid-crystalline behaviour of rod-like molecules in relation to their molecular structure.

Typically, the simplest rod-like mesogenic molecules have a structure of the form,

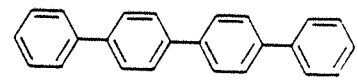
where X and Y may be hydrocarbon chains, or X a small group like -CN, -NO_2, -Br etc. and Y an alkyl chain. The middle portion of the molecule is a more or less rigid aromatic core. In general, any terminal group X or Y which extends the molecule along the molecular axis without increasing the molecular breadth too much increases the ability of the molecule to form a stable mesophase and/or increases the thermal stability of that mesophase. For example, the phenyl ring systems,



C 71°C I,



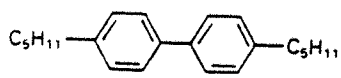
C 212°C I,



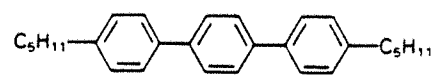
C 300°C I.

where the melting points are very high.

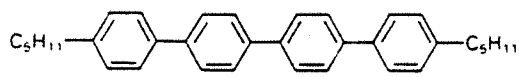
The addition of flexible chains to either end lowers the melting point enough to access the liquid crystal phase,



C 26°C S 47.6°C S 52.2°C I,

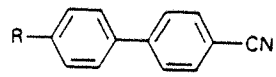


C 192°C S 213°C I,

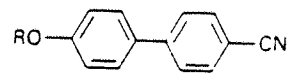


C 297°C S_A 352°C I.

Elongating a semi-rigid molecule is not the only factor conducive to liquid crystal mesophase stability, consider the two series,

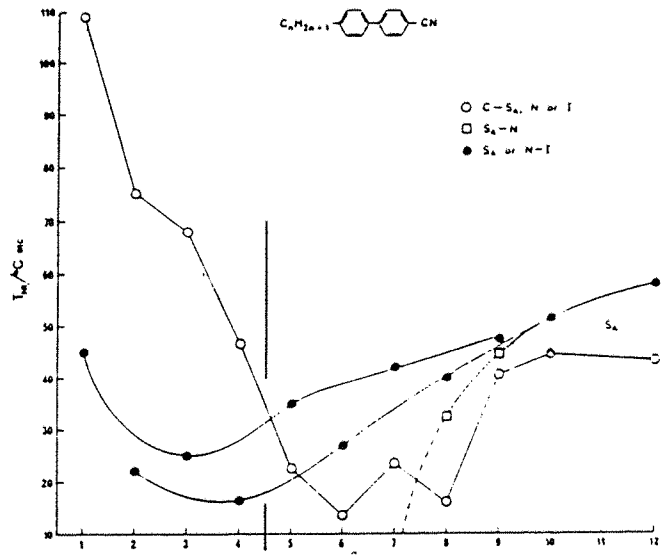


Series 1.

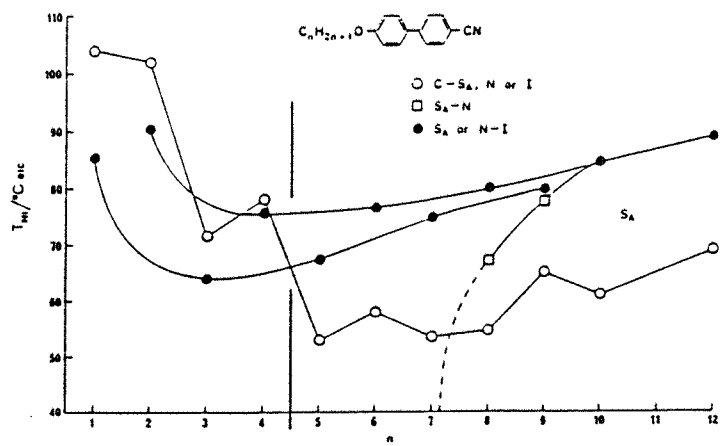


Series 2.

where although both molecules have the same number of atoms in their terminal chains, their mesogenic properties differ considerably.



1. Transition temperatures for the 4-n-alkyl-4'-cyanobiphenyls.



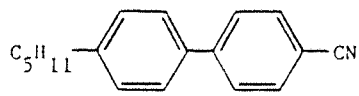
2. Transition temperatures for the 4-n-alkyloxy-4'-cyanobiphenyls.

This difference is probably not wholly explained simply by the small differences in bond angles and bond lengths relating to the C-O-ring and C-C-ring situations, although recent theoretical studies on ring-chain bond angles do predict a significant transition temperature difference between the two systems. The major reason is usually attributed to the conjugative interactions between the lone pair on the oxygen in series 2 and the aromatic rings considerably enhancing the anisotropy in molecular polarisability thus raising the clearing points. With this reasoning we should expect that any electron rich group connected to the ring system would have a similar effect on the clearing points, and indeed, replacing the oxygen in series 2 with an amino (-NH-) group does this [8]. Conversely an electrophilic group such as perfluoroalkyl chain would oppose any conjugation and probably give reduced thermal stability [9], but minimal rotation within such a chain disguises any electronic effects and can actually raise the transition temperatures [10].

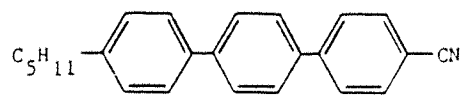
An efficiently conjugated aromatic group is not, however, a prerequisite for useful nematogenic properties, indeed, the first liquid crystal studied was largely alicyclic [1]. Replacing one of the phenyl rings in series 1 or 2 with its saturated analogue not only maintains a useful nematic range [11] but produces a lower viscosity and birefringence Δn while maintaining a relatively large dielectric anisotropy $\Delta\epsilon$. These properties make the materials suitable for use in phase change displays since low viscosity enhances response times, moderate to low Δn reduces the thickness and uniformity constraints while a large $\Delta\epsilon$ ensures strong interaction between the liquid crystal and the applied electric field. Here perhaps it is more plausible to think of the cyclohexane ring not as a central linking unit but as a terminal group because the cyano group can adopt an axial or equatorial conformation. Furthermore, replacing the second phenyl ring with cyclohexane gives a molecule with an enantiotropic nematic phase at around room temperature. This gives lower Δn and a negative permittivity anisotropy $\Delta\epsilon$ both

of which are useful for producing high contrast guest-host and cholesteric-nematic phase change displays [12].

The thermal stability of the liquid crystal is frequently enhanced by incorporating a third aromatic ring, for example,

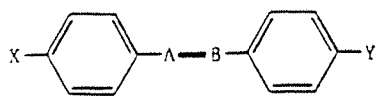


C-N, 22.5°; N-I, 35°

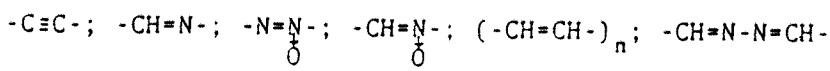


C-N, 130°; N-I, 239°

or a linking unit thus,

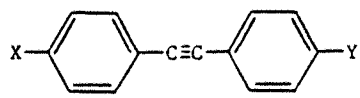


The linking unit A-B usually contains multiple bonds about which freedom of rotation is restricted so preserving the rigidity and elongation of the molecule. These multiple bonds can also conjugate with the phenyl rings enhancing the anisotropic polarisability; such linking units include,

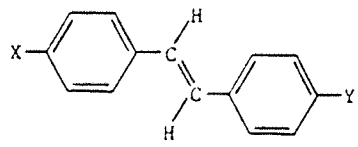


The ester linkage is also effective since resonance confers double bond character on the C-O linkage thus restricting rotation.

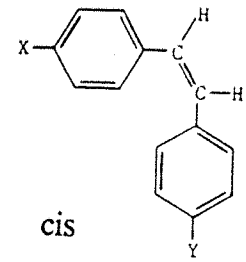
It should be noted however that apart from the tolanes,



molecules containing a linking group are not completely linear and in some cases the possibility of isomerisation can reduce the ability of a molecule to form a liquid crystal. For example, only trans stilbene exhibits a liquid-crystalline phase whereas the cis isomer does not,

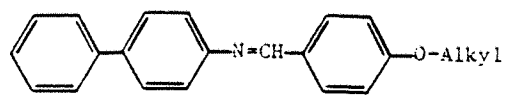


trans

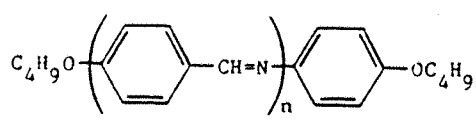


cis

Increasing the length of the terminal alkyl/alkoxy chains increases the smectic tendencies relative to the nematic tendencies of a system. Eventually a stage is reached when nematic properties are extinguished and the compounds are purely smectic, for example, the 4-(4'-n-alkoxy-benzilidene)aminobiphenyls, see fig.1.

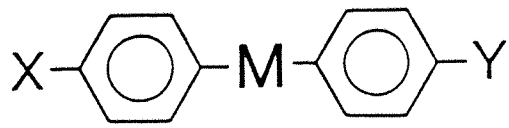


Increasing the number of rings and linking units has a similar effect resulting in a much greater thermal persistence of the phase. For the system,

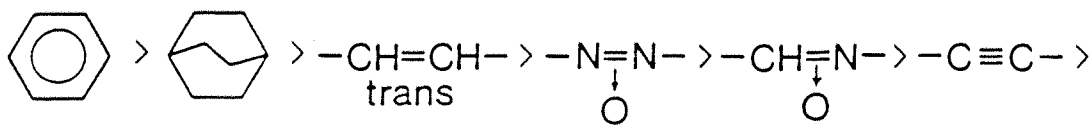


when n is 1 the nematic phase is monotropic the nematic-isotropic transition temperature, T_{NI}, is 121°C and when n=2, T_{NI}=298°C. It is generally accepted that to enhance thermal stability both molecular elongation and rigidity need to

increase, although a liquid crystal phase may be obtained at lower temperatures by the introduction of some flexibility into the molecule,
For the molecules of general structure,



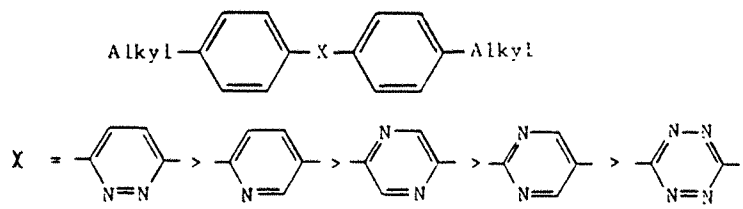
it is possible to construct an average order of efficiency for the central groups M in increasing the nematic-isotropic transition temperatures [13]. The general order is,



−N=N− > −CH=N− > −CO.O− > none.

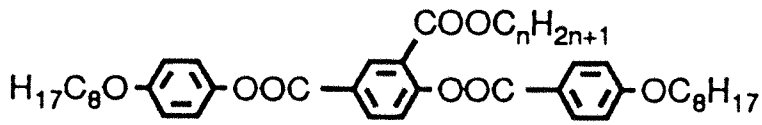
Stereochemical considerations are important and affect the position in the order e.g. stilbenes are planar, azoxybenzenes are slightly twisted, Schiffs' bases are considerably twisted and the aromatic rings in tolanes lie orthogonal to one another. It should be noted that most linking groups bend the molecule thus reducing the tendency to form liquid crystal phases and possibly the melting point also.
It is interesting to note although not directly relevant to this project that the inclusion of heteroatoms into the molecule has been studied and a recent review of heteroatomic rings as linking groups has been given [14]. It was found that the general order for T_{NI} enhancement in the system,

is

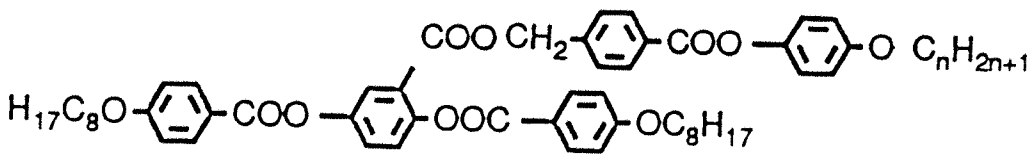


The order of effectiveness of terminal heteroatomic rings varies from system to system and a clear picture does not result from these studies, but in some cases conjugative interactions and twisting of the structure do follow an expected pattern.

The addition of lateral substituents onto the rigid aromatic rings and linking groups serves to broaden the molecule thus lessening the length to breadth ratio and causing T_{NI} to fall. The extent of the lowering of the transition temperature can be related to the size of the substituent. However, for alkyl chains the effect is not so dramatic as might have been anticipated presumably because the lateral chain lies more or less parallel to the long axis of the basic molecule. For example,



in this series, as n increases, a nematic phase is maintained for all n studied from 1 to 12, and for,



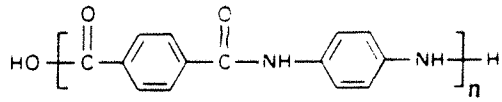
the clearing temperatures are nearly independent of the length of the alkoxy chain [15].

n	T_{CN}/°C	T_{NI}/°C
1	121	152
2	120	153
3	110	153
4	108	152
5	99	151
6	99	149
7	103	148

General accounts of the effects of lateral substituents have been well documented by Gray [13] and by Demus [17].

1.3.1 Oligomers

The liquid-crystalline materials previously described have all had a common structural make-up; an essentially rigid aromatic group to enhance the liquid crystal to isotropic liquid transition temperatures, with terminal groups/chains to extend the mesogenic range by lowering the melting point. In consequence it is not immediately obvious that a system with rigid groups linked by a flexible spacer unit should be mesogenic. However, it has been demonstrated by a number of investigators [18-21] that the introduction of flexible polymethylene groups between mesogenic moieties in a polymer backbone not only lowers the melting and clearing temperatures but can produce improved liquid-crystalline properties. In fact polymeric liquid crystals are of considerable current interest because their transition temperatures are considerably lower than those in which the mesogenic groups are bound directly to one another, for example Kevlar,



or through a non-mesogenic group [22], but because they have great potential as high strength fibres and plastics such systems are of considerable interest and importance. Mouldings made from liquid crystal polymers have shown some degree of self-reinforcement by displaying a definite layer (composite like) structure which enhances their mechanical properties.

Polymeric mesogens possessing a regularly altering $(\text{rigid-flexible})_n$ structure, for example, the polyester,

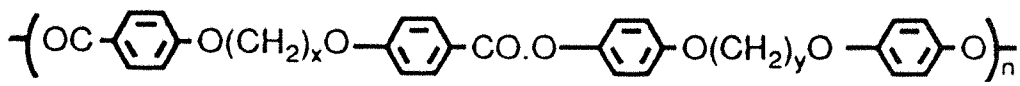
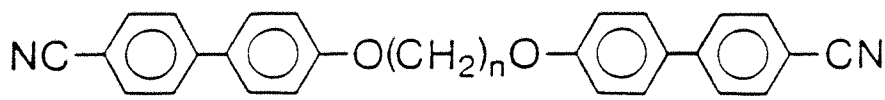


exhibit significant variations in certain liquid crystalline properties. These variations or rather alternations depend on the nature of the flexible spacer [23] and the number of bonds which make up that spacer, odd or even [24]. Chains with an odd number of bonds have markedly higher transition temperatures than their even counterparts, this odd-even effect gradually falls off with increasing n and could be attributable to the increased number of gauche conformations possible for longer chains which may well tend to reduce the difference in the anisotropy for conformers with odd and even spacers.In order to provide a firm basis for the interpretation of the effect of spacer groups it is valuable to study small molecule systems which possess the full chemical structure of the repeating unit and also have non-reactive end groups at the molecular termini analogous to the chemical nature of the polymer. Recently liquid-crystalline compounds having a rigid-flexible-rigid structure have been studied as models for liquid-crystalline polymers [25].

These so-called dimeric liquid crystals retain the basic structural component of many main chain thermotropic polymers i.e. a flexible spacer between two rigid mesogenic groups,

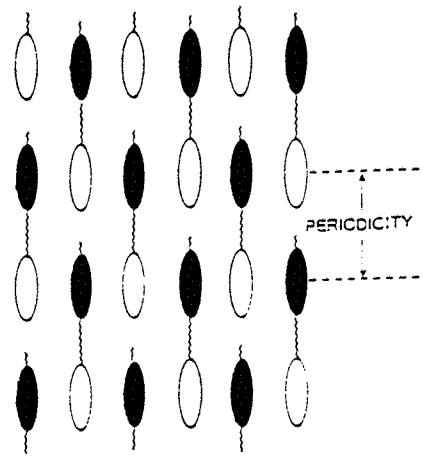
However their properties have the merit of being relatively straightforward to interpret since they are monodisperse and as such their behaviour is not complicated by a molecular weight distribution. In order to demonstrate whether such dimeric molecules are good models for their analogous polymeric systems Emsley et al. [25] synthesised the α,ω-bis(4-cyanobiphenyl-4'-oxy)alkanes,



and found that, as with their polymeric counterparts, their properties exhibit a pronounced alteration upon varying the length of the spacer, see figs.2 and 3. Thus the alternation in the nematic-isotropic transition temperatures is attenuated gradually on increasing the spacer length whereas that of the entropy of transition does not, a trait very similar to that exhibited by semi-flexible main chain polymers. The effect of terminal substituents upon the properties of dimeric liquid crystals has been investigated and is found to be similar to the behaviour of analogous nematogens with a single mesogenic group [26]. In fact structure-property relationships in dimers, where applicable, are similar to those developed for monomeric compounds [27], for example, a lateral methyl substituted on the mesogenic group reduces T_{NI} in both monomeric and dimeric liquid crystals, but for alkyl chains this reduction levels off as the lateral chain length increases [28]. It is interesting to note that Demus [29] had previously concluded that a lateral

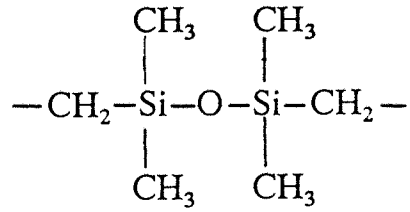
chain substituent attached to the centre of a rigid group strongly suppresses smectic behaviour whereas an equivalent chain at the end actually promotes smectic tendencies, this is thought to be because lateral chains affect the uniform packing arrangement desirable for smectic behaviour.

Asymmetric dimers, molecules with two dissimilar rigid groups connected via a flexible spacer, have been synthesised as a natural progression from previous symmetric studies. Attard et al. [30] following Hogan et al. [31] have synthesised two homologous series of asymmetric dimers each with an electron acceptor group at one end and an electron donor group at the other. They observed analogous variations in T_{NI} in relation to their symmetric parents but noted strange smectic behaviour and phase structure. It had previously been proposed by Hogan et al. [31] that the unusual phase behaviour and layer spacings, obtained from X-ray data, for such systems was due to an intercalated structure resulting from charge transfer interactions between the different units.



Changing the nature of the spacer has also been investigated as a means of lowering the crystal to liquid crystal transition temperatures. It has been found that the use of an oligosiloxane spacer has the desired effect of lowering the transition temperatures, because of its high flexibility and low crystallinity whilst maintaining the useful characteristics of the resultant liquid crystals [32,33].

Apparently the low temperature fluidity of these materials can be attributed to the effect of the bulky structure, flexibility and the irregular conformations of the oligodimethylsiloxane spacer between the rigid mesogenic groups.



The methyl groups in these dimethylsiloxane units rotate with unusual ease around the Si-O bond even at temperatures as low as -195°C [34].

From the evidence described here it appears that there may be a continuum of liquid-crystalline behaviour from dimers to polymers through low molar mass oligomeric structures. In order to investigate this further Attard and Imrie [35] prepared, as a continuation of Abe's earlier work, mesogens containing three anisotropic units linked by flexible spacers and described these as trimers. They prepared a series of compounds in which cyanobiphenyloxy groups were joined through flexible spacers to a phenyl unit with a lateral alkyl chain which was necessary to improve the solubility and to lower their melting points. They found that for these symmetric trimers T_{NI} decreased with little or no alternation on increasing the number of methylene groups in the lateral chain. This expected result is analogous to the behaviour found in both monomeric and polymeric mesogens possessing lateral alkyl chains. Hence it may be concluded that oligomeric molecules containing rigid mesogenic groups connected through flexible spacers provide an interesting class of mesogens both as models for polymeric systems and as useful liquid crystals in their own right.

Figure 1.

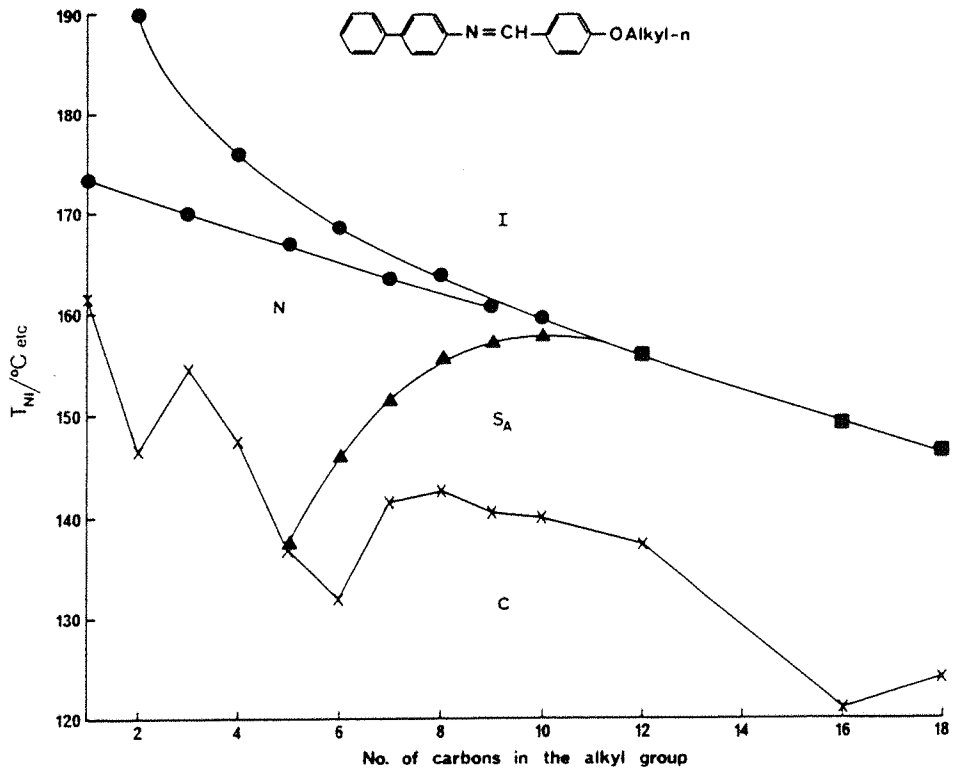


Fig. 1 Transition temperatures for the 4-(4'-n-alkyloxybenzilidene)aminobiphenyls.

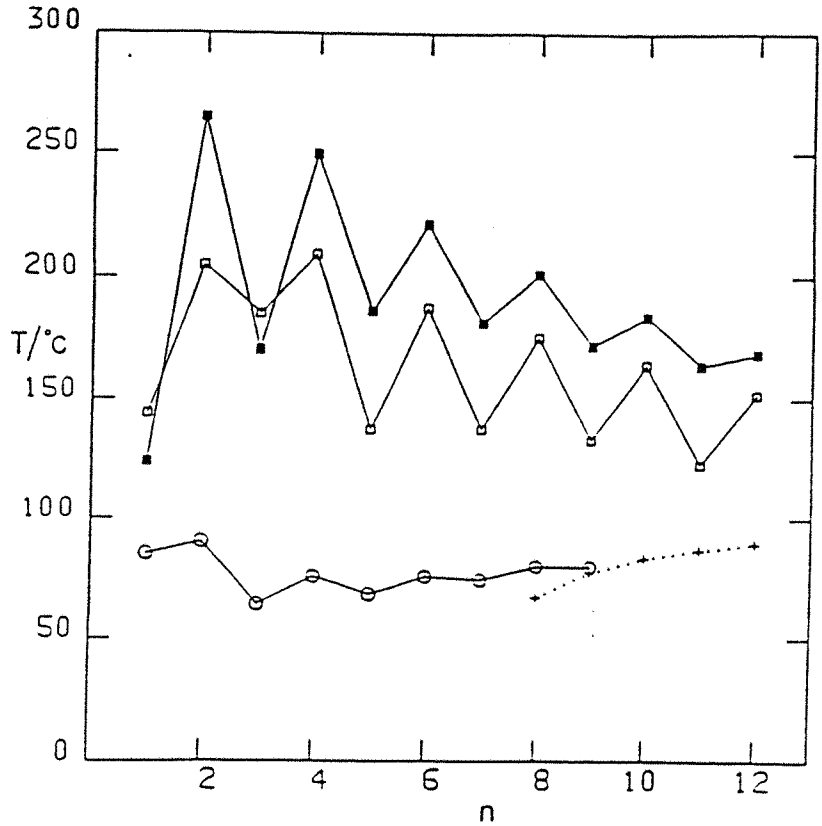


Figure 2a The dependence of the transition temperatures for the α,ω-bis4,4'-cyanobiphenyloxy)alkanes on the number of methylene groups in the flexible core; □ indicates C-N or C-I while ■ denotes N-I transition. The nematic-isotropic (⊖) or smectic A-isotropic (+) transition temperatures for the 4-n-alkyloxy-4'-cyanobiphenyls are also known where n now gives the number of carbon atoms in the alkyloxy chain.

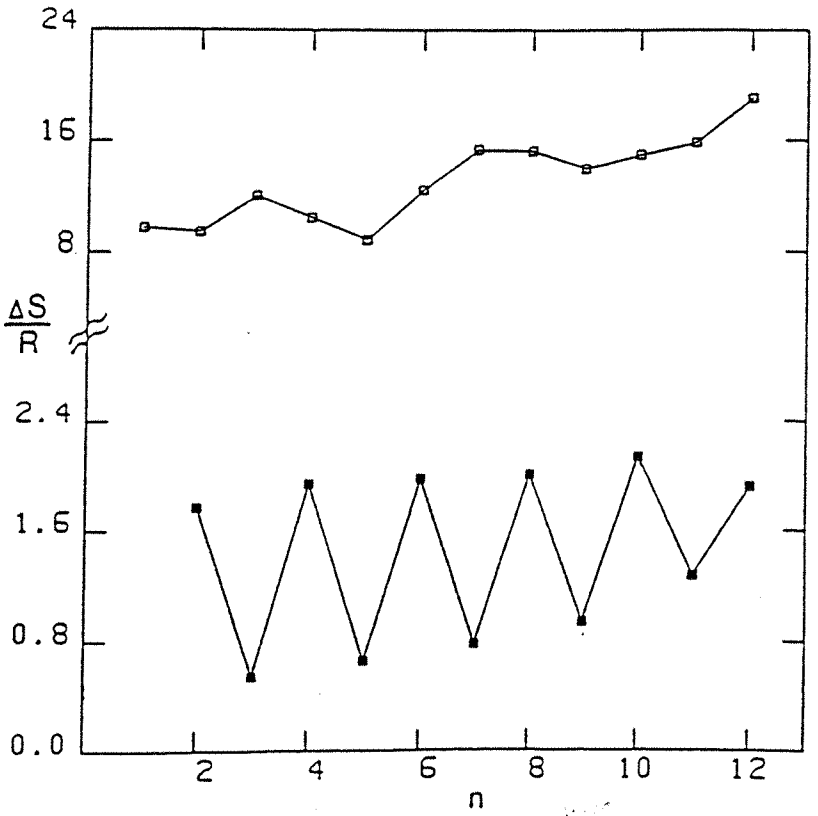
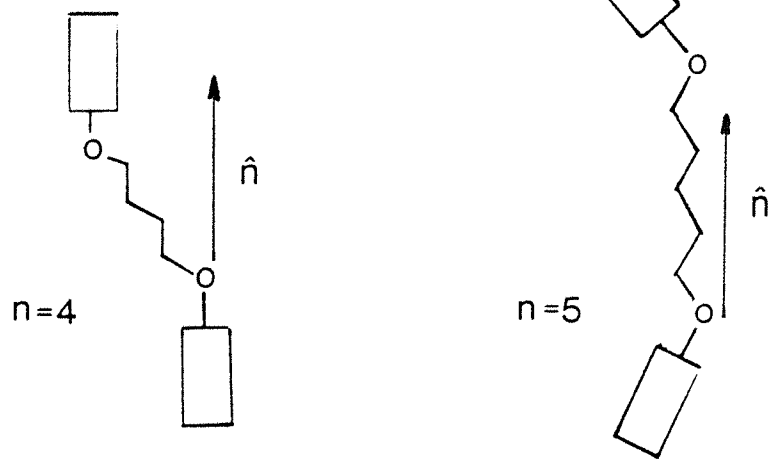


Figure 2b The entropy of melting (■) and the entropy change (□) at the nematic-isotropic tranition for the α,ω-bis(4,4'-cyanobiphenyloxy)alkanes as a function of the number of methylene groups in the flexible core.

1.4 A Qualitative Interpretation of the 'Odd-Even'Effect

It is found that the liquid-crystalline properties of oligomers and polymers containing a flexible alkyl chain depend critically on the length of that chain. For example the nematic-isotropic transition temperatures, T_{NI}, for members of a homologous series of dimers with an even number of methylene groups fall on one smooth curve while T_{NI} for those with an odd number fall on another (fig.2a) This odd-even effect is also exhibited by other properties which include the entropy change at the nematic-isotropic transition $\Delta S/R$ (fig.2b), and the orientational order at the transition. The entropy exhibits a continuous alternation which is not attenuated, unlike T_{NI} the strong alternation in $\Delta S/R$ implies a dramatic variation in the orientational order of the mesogenic groups with the number of methylene groups in the alkyl chain, such a variation has been observed using deuterium NMR spectroscopy. All of these alternations are reduced quite dramatically when the chain is terminal. The dramatic odd-even effects can, perhaps, be understood qualitatively by considering two members of a dimeric series, one with an odd number of methylene links the other even.



The tetrahedral character of the sp^3 carbon atoms dictates that consecutive methylene units within a chain are bent with respect to one another. When the

lowest energy all-trans conformations of the dimers are considered the mesogenic groups lie collinear in even membered spacers but are always at an angle to one another for odd spacers. Even allowing for some gauche links, which are thermally populated at temperatures close to T_{NI}, the major axes of the rigid mesogenic groups for odd n are not expected to be parallel and the molecule is, on average, more bent than its even counterpart. Since the order in the liquid-crystalline phase is favoured by the ability of the component molecules to pack efficiently, the pentamethylene spacer in the angular all-trans conformation prevents formation of an extended, rod-like structure with favourable steric packing. This theory is apparently supported up by the higher order parameters of nematogens with even membered alkyl chains.

1.5 Order Parameters

To characterise the orientational order of liquid crystal systems under specified thermodynamic conditions it is convenient to identify a set of orientational order parameters. With thermotropic liquid crystals the primary thermodynamic variable is temperature (at constant pressure) and it is expected that as temperature increases then the values of the order parameters will decrease from 1 in the crystalline state through a decimal figure in the liquid-crystalline phase(s) to become zero in the isotropic state provided the order parameter is correctly defined.

For rigid, cylindrically symmetric molecules we have the probability of finding a molecule pointing along the director as a function of ß, this singlet orientational distribution function is normalised and satisfies the symmetry constraint. (See fig.3)

$$f(ß) = f(\pi - ß), \qquad -(1)$$
$$\int f(ß)\cos ß\, dß = 1,$$

where ß is the angle between the director and the molecular symmetry axis. To identify a set of acceptable order parameters we can expand the singlet orientational distribution function in a basis set of orthogonal functions. Such a set is the Legendre polynomials $P_L(\cos ß)$ [32], and their orthogonality is defined by,

$$\int_0^{\pi} dß \sin ß P_L(\cos ß) P_N(\cos ß) = \frac{2}{(2L+1)} \delta_{LN}. \qquad -(2)$$

The explicit forms of the first few Legendre polynomials are;

$$P_0(\cos ß) = 1,$$
$$P_1(\cos ß) = \cos ß,$$
$$P_2(\cos ß) = {}^{3}/_{2}\cos^2 ß - {}^{1}/_{2},$$
$$P_3(\cos ß) = {}^{5}/_{2}\cos^3 ß - {}^{3}/_{2}\cos ß,$$
$$P_4(\cos ß) = {}^{35}/_{8}\cos^4 ß - {}^{30}/_{8}\cos^2 ß + {}^{3}/_{8},$$

Since $\cos(\pi - ß) = -\cos ß$, then $P_L(\cos ß) = (-)^L P_L(\cos \pi - ß)$, and so we only need retain even terms of P_L when expanding f(ß).

Thus,

$$f(ß) = \sum_{L\,(even)}^{\infty} f_L P_L(\cos ß). \qquad -(3)$$

The J^{th} coefficient in the expansion can be obtained by using the orthogonality of the basis set together with the definition of the order parameters. Multiplying both sides of equation (3) by $P_J(\cos ß)$ and integrating over $\sin ß dß$ gives,

$$\int dß \sin ß f(ß) P_J(\cos ß) = \Sigma f_L \int dß \sin ß P_L(\cos ß) P_J(\cos ß)$$

and so

$$f_J = (2J+1)\bar{P}_J, \qquad -(4)$$

where

$$\bar{P}_J = \int dß \sin ß P_J(\cos ß) f(ß).$$

The Legendre polynomial averages, P_J, thus represent our set of orientational order parameters and the expansion of f(ß)is,

$$f(ß) = {}^1/_2 + {}^5/_2 \bar{P}_2 . P_2(\cos ß) + {}^9/_2 \bar{P}_4 . P_4(\cos ß) + \ldots\ldots \quad -(5)$$

The first non-trivial term contains the second rank order parameter

$$\bar{P}_2 = \frac{\overline{(3\cos^2 ß - 1)}}{2}, \qquad -½ \le P_2 \le 1$$

where the bar denotes an average over the orientational fluctuations of a molecule. This corresponds to the order parameter introduced by Zwetkoff in 1939 [33].

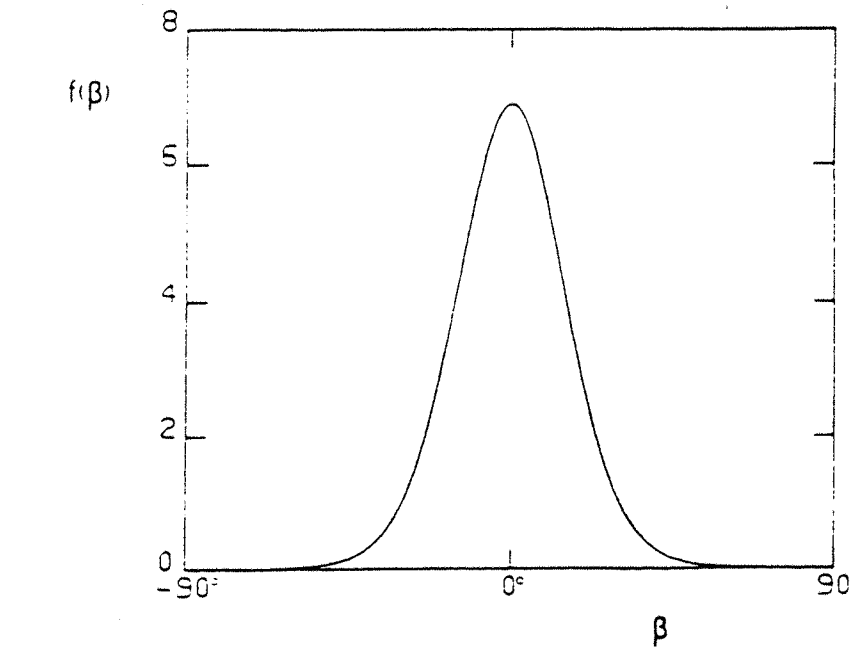
When the molecular structure cannot be assumed to be cylindrically symmetric, even though the phase is, $\bar{P}_2$ is insufficient to describe the orientational order of a molecule even at the second rank level. It must be replaced by an ordering matrix whose diagonal elements give the order parameters for three orthogonal axes set in the molecule. Saupe [34] defined such an ordering matrix $S_{\alpha\beta}$ by,

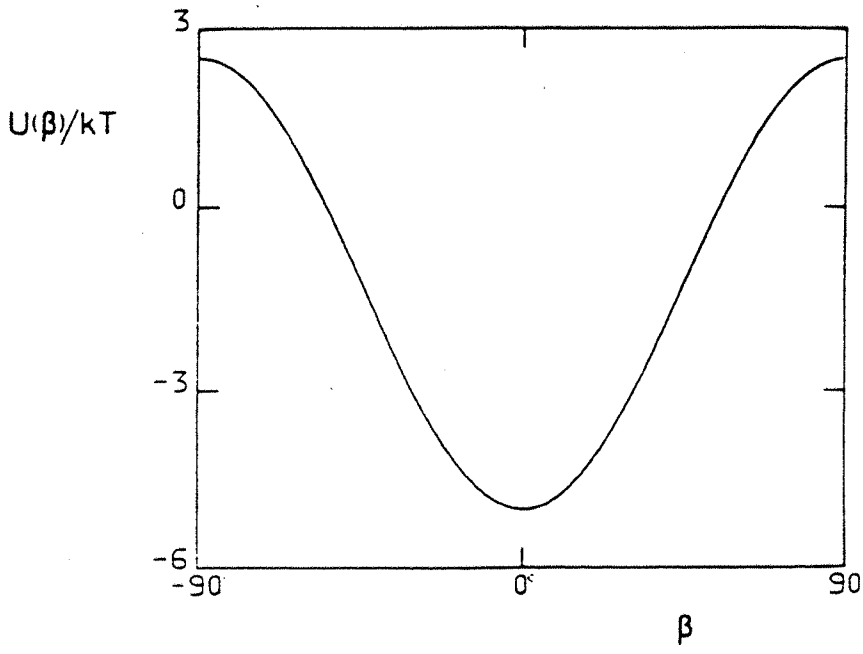
$$S_{\alpha\beta} = \frac{\overline{(3\cos\Theta_\alpha \cos\Theta_\beta - \delta_{\alpha\beta})}}{2},$$

where α and ß are the molecular axes x,y,z, Θ_α and Θ_β are the angles between the molecular α and ß axes and the director, $\delta_{\alpha\beta}$ is the Kronecker delta which is 1 if α=ß and 0 if different. The matrix is real, symmetric ($S_{\alpha\beta}$-$S_{\beta\alpha}$) and traceless

($S_{xx}+S_{yy}+S_{zz}=0$). Since the elements are all real $S_{\alpha\beta}$ can be diagonalised to give a matrix with only two independent non-zero elements, S_{zz} and $(S_{xx}-S_{yy})$ where $S_{zz}=\bar{P}_2$, the major order parameter and $S_{xx}-S_{yy}$ is the biaxial order parameter related to the biaxiality in the molecular interactions. By convention the axes x,y and z are defined such $|S_{zz}|>(S_{xx}-S_{yy})$ and $(S_{xx}-S_{yy})>0$.

Figure 3. The singlet orientational distribution function f(ß). The potential of mean torque U(ß)/kT for a rod-like molecule is also shown.





1.6 NMR Spectroscopy

NMR is a powerful tool in the investigation of interactions in a molecular environment. In the isotropic liquid, a wealth of information on the structure of the molecules in the liquid can be obtained. In liquid crystals, as well as the structural information, the anisotropy of the fluid can also be explored. Here we sketch those features of NMR spectroscopy necessary to understand the experiments described in the following chapter. Certain nuclei possess a characteristic property called spin denoted by the letter I. I exists in multiples of ½, for example for hydrogen I=½, and for deuterium I=1. These nuclei have (2I+1) spin states and so deuterium will have 3 spin states characterised by the nuclear magnetic spin quantum number m_I = -1, 0 ,+1. In the absence of an external field these spin states are degenerate, when a magnetic field is applied the nuclear spins interact with the field to remove their degeneracy.Transitions between these Zeeman levels occur with selection rules $\Delta m_I = \pm 1$ and so for a single deuteron there is a maximum of two spectral lines. The static information available from the deuterium magnetic resonance (DMR) spectra of a molecule comes from the following factors: chemical shift, direct and indirect coupling (or spin-spin coupling) and, because it is a nucleus with I>½, quadrupole splitting. Thus the full static spin hamiltonian for a molecule containing more than one type of magnetic nucleus is made up of the following terms

$$H = H_Z + H_{JZ} + H_D + H_Q,$$

where H_Z is the Zeeman spin hamiltonian, H_J is the indirect spin-spin coupling hamiltonian, H_D is the dipolar spin hamiltonian, H_Q is the quadrupolar spin hamiltonian.

The Zeeman term in the static hamiltonian is the result of the spin interaction between the magnetic dipole moment of the nucleus and the magnetic flux density B_o at the nucleus. In a DMR experiment the flux density is large enough to ensure that the nuclear spins are quantised only along the direction of the

magnetic field. This direction is chosen to be the z-axis of a laboratory frame of reference.

The quadrupolar term comes from the interaction between the nuclear spin I and the quadrupolar interaction tensor Q. For a single crystal or a monodomain liquid crystal a combination of the Zeeman and quadrupolar terms gives, for a single deuteron in a magnetic field B,

$$H_z + H_Q = -\nu I_z + \tilde{q}_{\parallel}(3I_z^2-2),$$

where ~ denotes a partially averaged quantity, and ν is the resonance frequency in the absence of the quadrupolar interaction. For a uniaxial liquid crystal $\tilde{q}_{\parallel}$ is the component of the partially averaged quadrupolar tensor parallel to the director taken to be parallel to the field, I_z is the z component of I, the spin operator. The eigenvalue of the spin operator I_z is m_I, and in general m_I has the values I, I-1, -I+1, -I. The spin levels have energy Em_I given by,

$$Em_I = -\nu m_I + \tilde{q}_{\parallel}(3m_I^2 - I(I+1))/4.$$

The energy of the three spin levels of the deuteron are,

$$E_1 = -\nu + \tilde{q}_{\parallel}/4,$$
$$E_0 = -\tilde{q}_{\parallel}/2,$$
$$E_{-1} = +\nu + \tilde{q}_{\parallel}/4.$$

According to the selection rule for the allowed transitions, the two spectral lines will occur at,

$$\nu_1 = \nu - 3\tilde{q}_{\parallel}/4,$$
$$\nu_2 = \nu + 3\tilde{q}_{\parallel}/4,$$

the measured splitting between the two lines, $\Delta\nu$, is

$$\Delta\nu = 3\tilde{q}_{\parallel}/2,$$

where $\tilde{q}_{\parallel}$ is given by,

$$\tilde{q}_{\parallel} = {}^2/_3 \Sigma q_{\alpha\beta} S_{\alpha\beta};$$

where $S_{\alpha\beta}$ is the Saupe ordering matrix and $q_{\alpha\beta}$ is the total quadrupolar tensor.

This can be written in terms of the principal components of q, as

$$\tilde{q}_{\parallel} = \frac{2(q_{zz}S_{zz} + q_{xx}S_{xx} + q_{yy}S_{yy})}{3},$$

which reduces to,

$$\tilde{q}_{\parallel} = \frac{q_{zz}[S_{zz} + \eta(S_{xx} - S_{yy})]}{3},$$

where $\eta = (q_{xx} - q_{yy})/q_{zz}$.

To a good approximation, the asymmetry η in the quadrupolar tensor is negligible, i.e. q has cylindrical symmetry about the C-D bond and so determination of $\tilde{q}_{\parallel}$ gives the order parameter for the C-D bond direction S_{CD} since $q_{zz} = q_{CD}$.

The dipolar spin hamiltonian describes the through-space spin-spin interaction between two magnetic moments and can be expressed, in tensor form, as,

$$H_D = \underset{\sim}{I}\underset{\sim}{D}^{ij}.\underset{\sim}{I}j.,$$

where D^{ij} is the symmetric and traceless second rank dipolar interaction tensor whose components are,

$$D^{ij}_{\alpha\beta} = \frac{\nu_i\nu_j h}{4\pi^2 r_{ij}^3}(\delta_{\alpha\beta} - 3\cos\theta_{ij\alpha}\cos\theta_{ij\beta})/2.$$

Here r_{ij} is the length of the internuclear vector, $\theta_{ij\alpha}$ is the angle between the α axis and the internuclear vector. The molecular reorientational motion averages the direction cosines which are expressed in the laboratory frame and the components of the dipolar coupling tensor in a principal axis system reduces to simple multiples of the z component.

$$\tilde{D}^{ij}_{B} = \frac{\nu_i\nu_j h}{4\pi^2 r_{ij}^3} S_{zz},$$

i.e. $\tilde{D}^{ij}_{s}$ has cylindrical symmetry and the splitting of the fine structure gives the order parameter for the symmetry axis i.e. the line joining the nuclei.

The figures show the typical quadrupolar splitting observed for equivalent deuterons in a molecule in the absence of any dipolar (H--D) interaction fig.4, and fig.5 shows the quadrupolar lines now split with a dipolar interaction.

fig.4

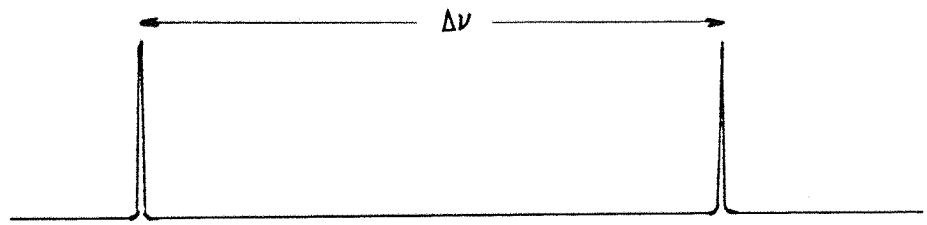
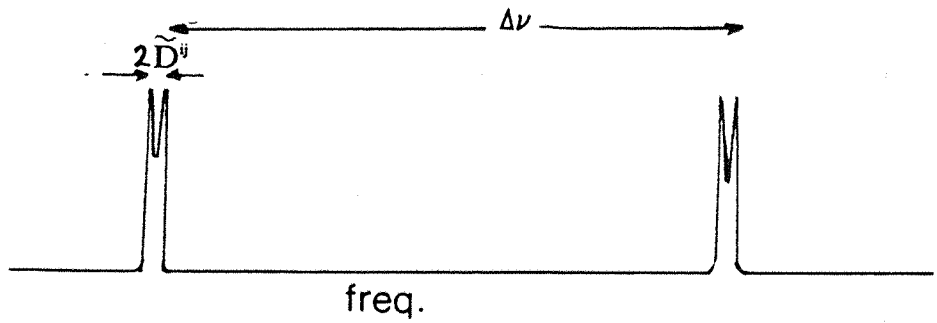


fig.5

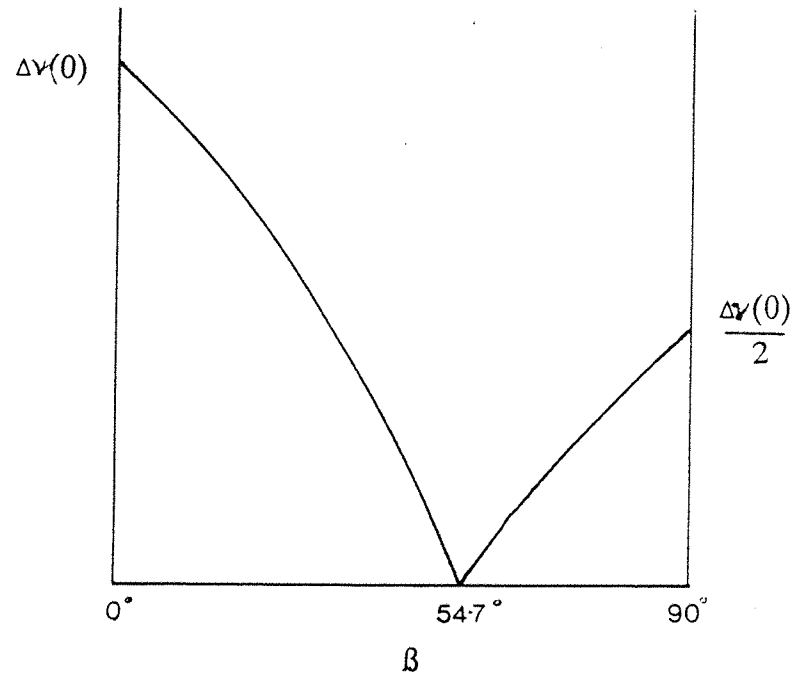


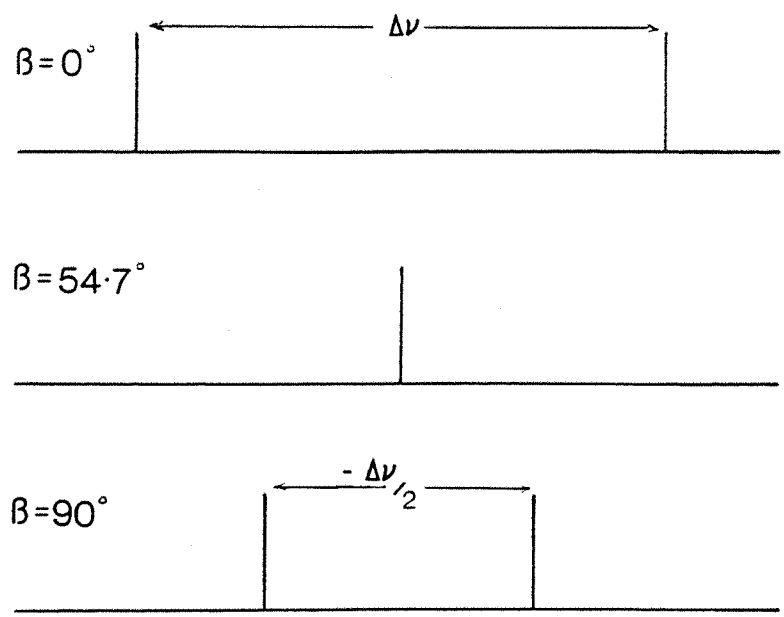
For nematogens with a positive anisotropic magnetic susceptibility the director, n, lies parallel to the applied magnetic field, B, provided the field is larger than about 0.3T, a condition which is easily met by most NMR spectrometers. For this director orientation the maximum quadrupolar splitting is observed. However, if the sample is now rotated with respect to the magnetic field the quadrupolar splitting is reduced according to the relationship,

$$\Delta\nu(ß) = \Delta\nu(0)\frac{(3\cos^2ß-1)}{2}$$

where ß is the angle between the director and the magnetic field. The splitting is reduced until the so-called magic angle of ~54.7° is reached when just a single line is observed as the peaks superimpose corresponding to the degeneracy of the two allowed transitions. As ß increases further the line splits again and the splitting continues up to a minimum value of - $\Delta\nu(0)/2$ when the director is

orthogonal to the field. In such experiments only the modulus of the splitting is observed and so when ß=90° the two quadrupolar peaks are observed at $\Delta\nu(0)/2$.





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CHAPTER TWO

2.1 INTRODUCTION

The primary characteristic of a liquid crystal is its long range orientational order and so the determination of this is an important task in understanding the behaviour of liquid crystals, especially at the molecular level. As we have seen NMR spectroscopy may be used to study the orientational behaviour of liquid crystals by measuring the quadrupolar and dipolar splittings of strategically placed deuterium atoms within the molecule. For the vast majority of liquid crystals, especially those containing a flexible alkyl chain, this is a formidable task since to characterise completely the orientational order of a molecule oriented in a liquid crystal, even at the second rank level, a Saupe ordering matrix is required for each rigid sub-unit [1]. An alternative approach with which to investigate the orientational order is to use a probe molecule, that is a rigid solute with high symmetry which is aligned with respect to the director due to the intrinsic order of the liquid crystal solvent combined with the anisotropy in the solute-solvent interaction. Such a method also has the practical advantage that the liquid crystal solvent under investigation need not be deuteriated, which can often be a difficult and expensive task. Typical rigid probe molecules with D_{2h} symmetry frequently used are, for example, anthracene-d_{10}, 1,4-dinitrobenzene-d_4, anthraquinone-d_8 [2]. For such symmetric probes just two pieces of information are needed to determine the two independent elements of the Saupe ordering matrix, the major order parameter, S_{zz} and the biaxial order parameter (S_{xx}-S_{yy}). However, such studies cannot, of necessity, provide direct information about the orientational order of the solvent molecule, although the ordering of the solute will certainly depend on that of the solvent.

Here we shall use a combination of these two approaches to study the orientational order in a novel class of liquid crystals in which mesogenic groups are linked together via flexible spacers. In particular we shall investigate the

molecular organisation for such oligomeric liquid crystals containing odd and even numbered spacers. We wish to see if the difference in the orientational order observed for dimers [3] and for solutes dissolved in them [4] is due to a geometric factor or, as is widely believed, due simply to the higher order of molecules with even spacers. To test the validity of either model the orientational order of an odd and an even symmetric dimer, dissolved in a liquid crystal solvent, was determined from the DMR spectra of suitably deuteriated dimers. In this way any difference in the observed order must result from a difference in the solute-solvent interactions and not in the orientational order of the environment which will be the same for both dimers. In order to demonstrate which if either hypothesis is correct two deuteriated dimers were synthesised, α,ω-bis(3,5-d_2-4'-cyanobiphenyl-4-oxy)butane, (CBO4OCB), and α,ω-bis(3,5-d_2-4'-cyanobiphenyl-4-oxy)pentane, (CBO5OCB); they were examined in the pure state and dissolved in the nematogen para-azoxyanisole, PAA. In this way we are able to probe the molecular organisation within the common nematogenic solvent and more importantly within the pure nematogens. As we shall see the results turn out to have fundamental implications for our understanding of the ordering of such dimers.

As we have seen in the first chapter dimeric liquid crystals have proved to be good models for polymeric systems as well as being interesting mesogens in their own right. In an attempt to pursue the role of the flexible spacer in determining the orientational order of oligomeric systems, a natural progression from the dimers would be to study molecules with three mesogenic groups connected by flexible spacers, i.e. trimers. Two members from the symmetric trimeric series, 4,4'-bis(4'-cyanobiphenyloxyalkyloxy)-biphenyls, specifically deuteriated were synthesised and their orientational order was investigated using DMR. Strictly these compounds are not trimers for the middle biphenyl group is not identical to the end cyanobiphenyl group; however the difference is not sufficiently great to change from this convenient terminology to something which while more

accurate would inevitably be more cumbersome. The physical properties of this trimeric series have been investigated and were found to be very similar qualitatively to those observed for the analogous dimeric CBOnOCB series although the magnitude of the odd-even effects for both the nematic-isotropic transition temperature and the entropy of transition are consistently more accentuated [15], see figure 6. In an attempt to further our understanding of this fascinating behaviour in terms of the molecular organisation within the nematic phases we have studied the orientational order of the end and middle mesogenic groups, again by using deuterium NMR spectroscopy.

The diagram below shows a simplistic representation of the all-trans geometry of two members of the trimeric series and where the deuterium was incorporated into the structure. Such structures emphasise the difference in shape between the odd and even trimers however it is important not to forget there are many more conformations available to the trimers than for the dimers with the same spacers. Four trimers were prepared, two for each spacer length, 8 and 9, deuteriated in the 3,5 positions of the end and middle mesogenic groups. By the measurement of the DMR spectra for these deuteriated trimers we are able to say something about the preferred geometry within the system and the alignment of the mesogenic groups with respect to the director and hence with respect to each other.

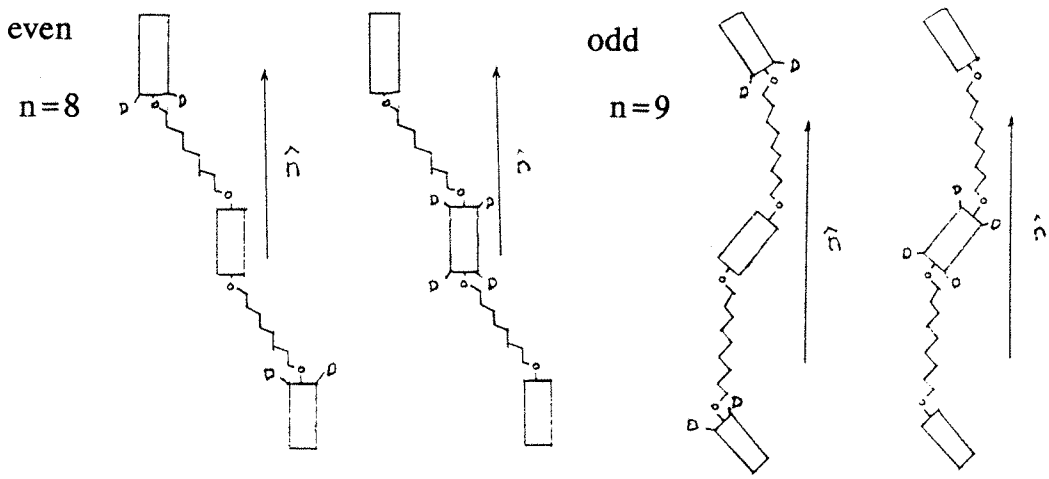
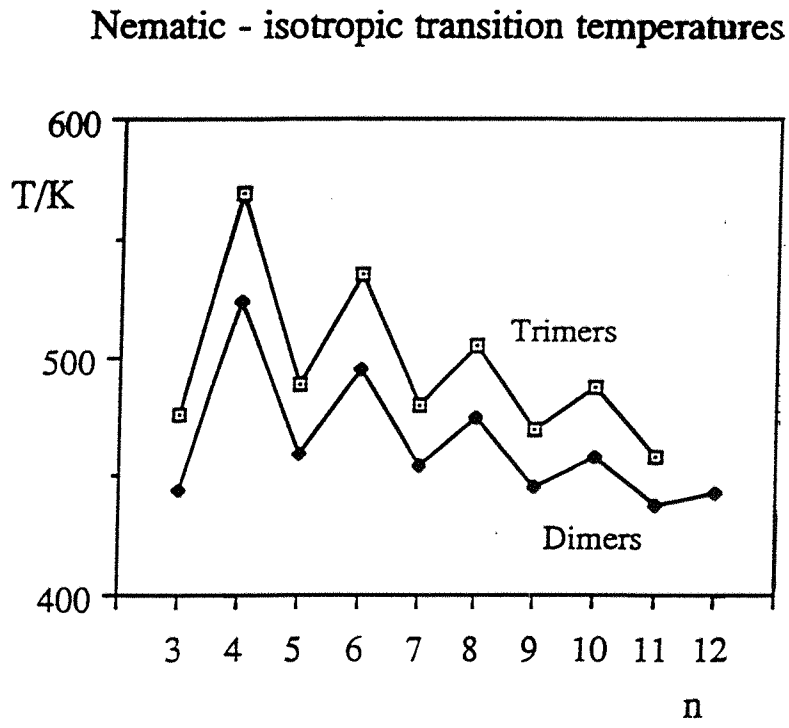
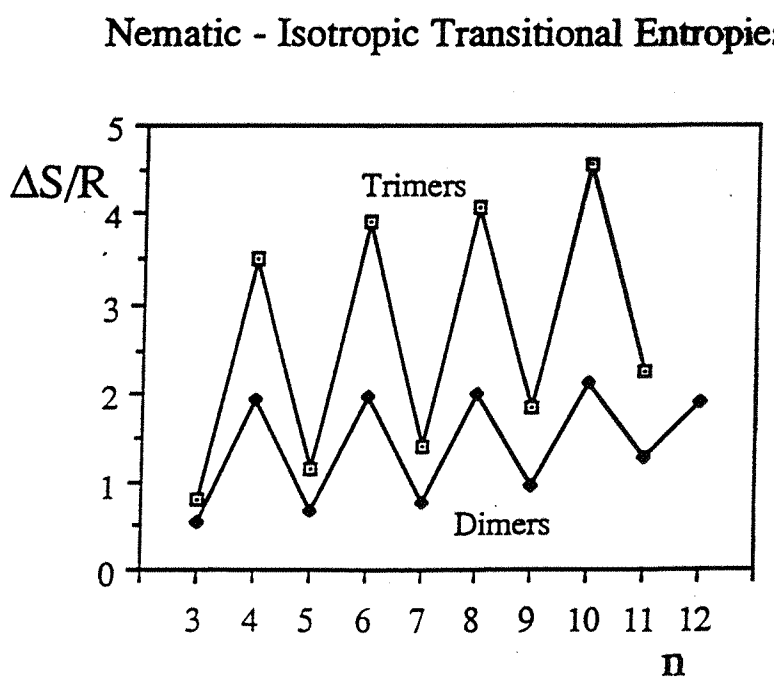


Figure 6. Graphs showing some physical properties of the dimers and trimers.





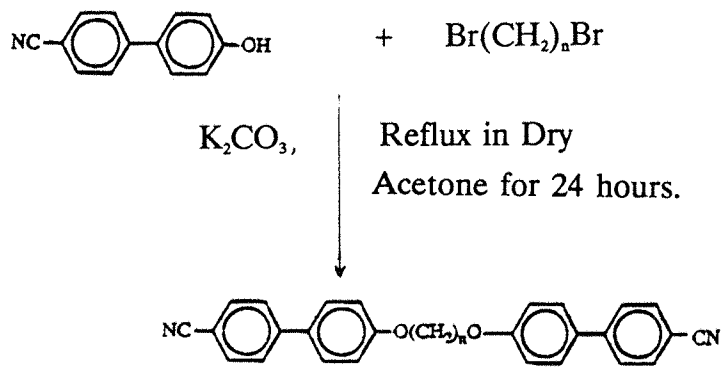
2.2 Experimental

In order to investigate the odd-even effect for dimeric molecules it was convenient to study symmetric materials that is with the same mesogenic groups, materials that are relatively straightforward to prepare, and those for which previous extensive experimental and theoretical work has already been done. Hence the α,ω,bis(4-cyanobiphenyl-4'-oxy)alkanes were chosen, the physical properties are well documented and some DMR studies on the orientational order of certain groups within the molecules have been carried out [5]. These dimers were deuteriated in the 3,5 positions of the inner phenyl rings because of the ease of synthesis; nonetheless this is not an ideal position because the angle between the C-D bond and the molecular long-axis is approximately 60° i.e. very close to the so-called magic angle which makes the extraction of the ordering tensor very sensitive to assumptions concerning the molecular geometry.

The synthesis of the dimers and trimers was generally based on the synthesis of the 4-n-alkyloxy-4'-cyanobiphenyl liquid crystals described by Gray et al.[6] and uses hydroxycyanobiphenyl kindly supplied by BDH Ltd. In all of the synthetic experiments, the non-deuteriated material was prepared and characterised first to ensure an efficient technique and adequate yields before the deuteriated analogue was made. The deuteriation in all cases was performed on the biphenyl precursors, rather than the final oligomeric materials, to ensure selectivity and because the solubility of the dimers and trimers in the solvents used for deuteriation was far greater for the starting materials.

α,ω-bis(4-cyanobiphenyl-4'-oxy)alkanes; n=4,5

These particular dimers with alkyl chains containing 4 and 5 methylene groups were chosen because they have both been thoroughly examined experimentally and they also have large differences in their transition temperatures; such differences are less marked for the molecules with longer chains. Both members of the series were prepared in the following way.



4-hydroxy-4'-cyanobiphenyl (1g, 2.1 equiv.) was dissolved in dry acetone and anhydrous potassium carbonate (3.7g, 5 equiv.) was added. The α,ω-dibromoalkane (1.2g, 1 equiv.) was added and the mixture stirred under reflux for 24 hours. After cooling, the mixture was shaken thoroughly with water and the off-white solid filtered off, washed well with water and dried. The solid was dissolved in the minimum amount of boiling ethyl acetate (~150 ml g^{-1}) and the hot solution was filtered. The filtrate was allowed to stand at room temperature overnight when the product crystallised as a white solid (yield 70%).

The transition temperatures for these dimers were,

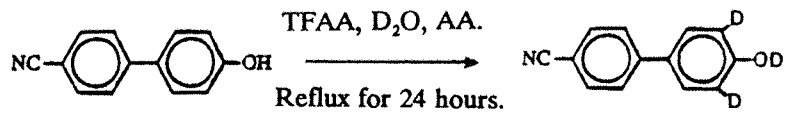
n=4, T_{CN} = 210°C (209°C), T_{NI} = 253°C (253°C).

n=5, T_{CN} = 139°C (136°C), T_{NI} = 196°C (197°C).

The literature values, given in parentheses, are in good agreement with our results, thus supporting the purity of these materials.

Deuteriation of 4-hydroxy-4'-cyanobiphenyl

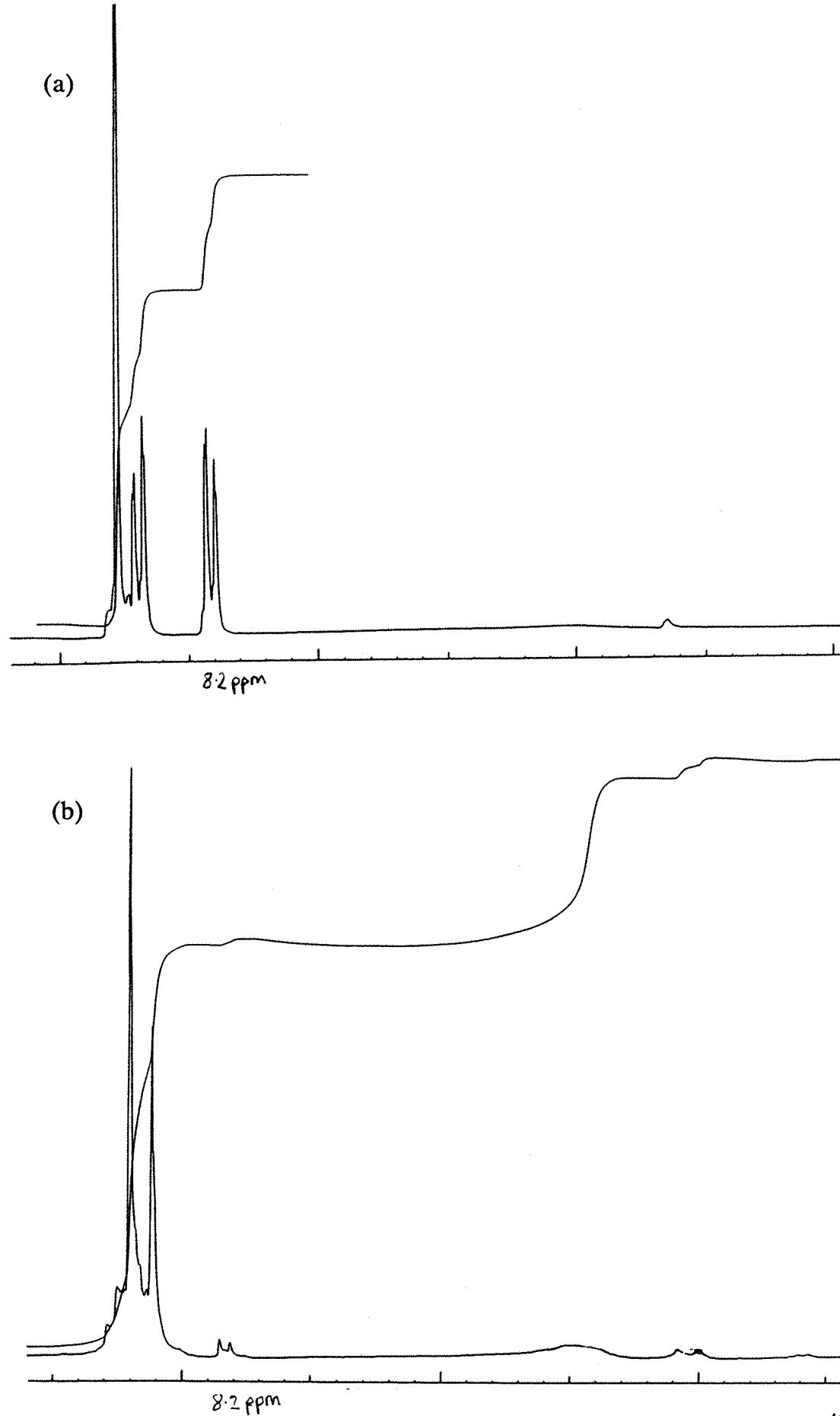
Deuteriation of the 4-hydroxy-4'-cyanobiphenyl, (OCB), was achieved by employing the following procedure described by Emsley et al.[7].



Trifluoroacetic anhydride (20ml) was added slowly with cooling to D_2O (10ml) this produces the strongly acidic trifluoroacetic acid-d_1, to this acetic anhydride (15ml) and 4-hydroxy-4'-cyanobiphenyl (2.0g) were added and the mixture refluxed for 24 hours. The reaction mixture was allowed to cool and then shaken with water (200ml), the white solid thus precipitated was filtered off, washed well with water and dried. The major component (~70%) of the crude product was 4-(3,5-d_2-4-hydroxyphenyl)benzamide which results from hydrolysis of the cyano group. This unwanted component was removed by refluxing the solid in dichloromethane (400ml) and methanol (4ml) for 2 hours, standing overnight and filtering off the insoluble amide. After evaporation of the solvent the solid was found to be very soluble in ethyl acetate so the product was recrystallised from

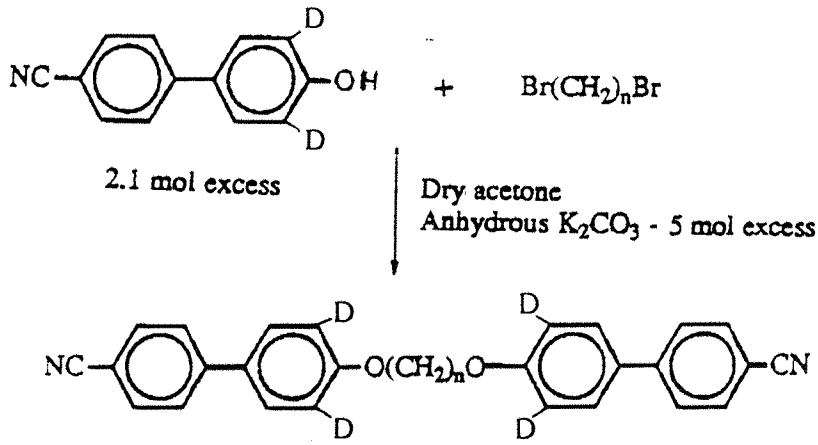
20% v/v aq. methanol (150ml) with decolorising charcoal to give pure 4-hydroxy-4'-cyanobiphenyl-d_2, (OCB-d_2), as white crystals with a yield of 30%.
Comparison between the ^{1}H NMR spectra of OCB and OCB-d_2 showed a virtual disappearance of the peaks at 8.2ppm attributed to the 3,5-hydrogens for OCB. By comparing the integrals of the peaks the product was estimated to have >90% incorporation of deuterium; see figure 7.
The use of 4-hydroxy-4'-bromobiphenyl can be substituted for the OCB in the deuteriation stage without the disadvantage of hydrolysis, however, the subsequent cyanation that is necessary gives a relatively poor yield of ~50%. This would be an overall gain but it is not clear if the acidic conditions in the cyanation process would promote back exchange of the deuterons. In addition the nitrile can be recovered to some extent from the amide. The amide produced from the cyano hydrolysis may be converted back to the nitrile by refluxing in chlorosulphonyl isocyanate [8]. This technique involves dissolving the amide (20 mmol) in dry triethylamine (10 ml) and dry dichloromethane, (DCM), this was added to a solution of chlorosulphonyl isocyanate (15 mmol) in DCM at 0°C. The mixture was stirred for 8 hours at room temperature and then refluxed for 1 hour. After allowing the mixture to cool, it was poured into water, the DCM layer was separated and the aqueous layer extracted three times with DCM. The combined organics were dried over anhydrous Na_2SO_4 and filtered, evaporation of the solvent left the crude nitrile which was purified by recrystallisation and characterised by the comparison of the ^{1}H NMR spectrum with that of the original materials.

Figure 7. ^1H NMR Spectra of (a) OCB, and (b) OCB-d_2.



Preparation of α,ω-bis(3,5-d_2-4'-cyanobiphenyl-4-oxy)alkanes: n=4,5

These were prepared according to the reaction scheme,



A mixture of OCB-d_2 (0.5g, 2.1 equiv.), α,ω-dibromoalkane (0.5g, 1 equiv.), and potassium carbonate (1.83g, 5 equiv.) was refluxed in dry acetone for 24 hours. The mixture was filtered while hot and the acetone removed under vacuum. Recrystallisation from ethyl acetate gave white crystals in 40% yield, ^{1}H NMR, ^{13}C NMR spectra as well as the transition temperatures showed these to be the desired products obtained with a high purity. The transition temperatures were

n=4, T_{CN} = 212°C (209°C), T_{NI} = 255°C (253°C).

n=5, T_{CN} = 140°C (136°C), T_{NI} = 197°C (197°C).

These values are slightly higher (~1-2°C) than for the non-deuteriated dimers but this is not very significant when the experimental error is taken into account, although the higher T_{NI} normally means an improved purity. All of the readings measured on the hot-stage of the polarising microscope at temperatures >150°C are frequently ±1-2°C in error because of the large temperature gradient across the sample.

^{1}H NMR shows ~90% incorporation of deuterium for both dimers, as is apparent from the spectra shown in figures 8 and 9.

Figure 8. ^{1}H NMR Spectra of (a) CBO4OCB, and (b) CBO4OCB-d_4.

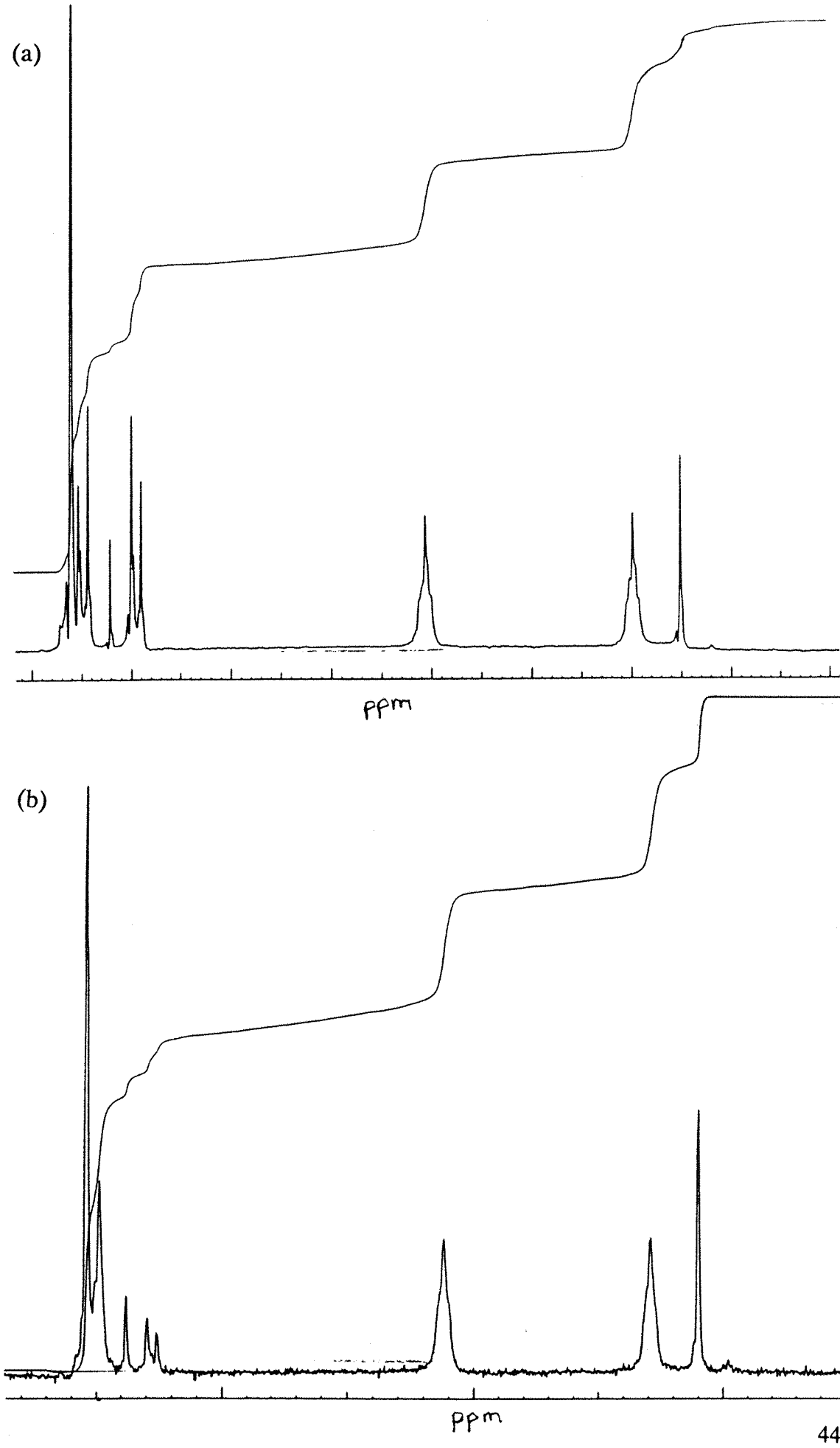
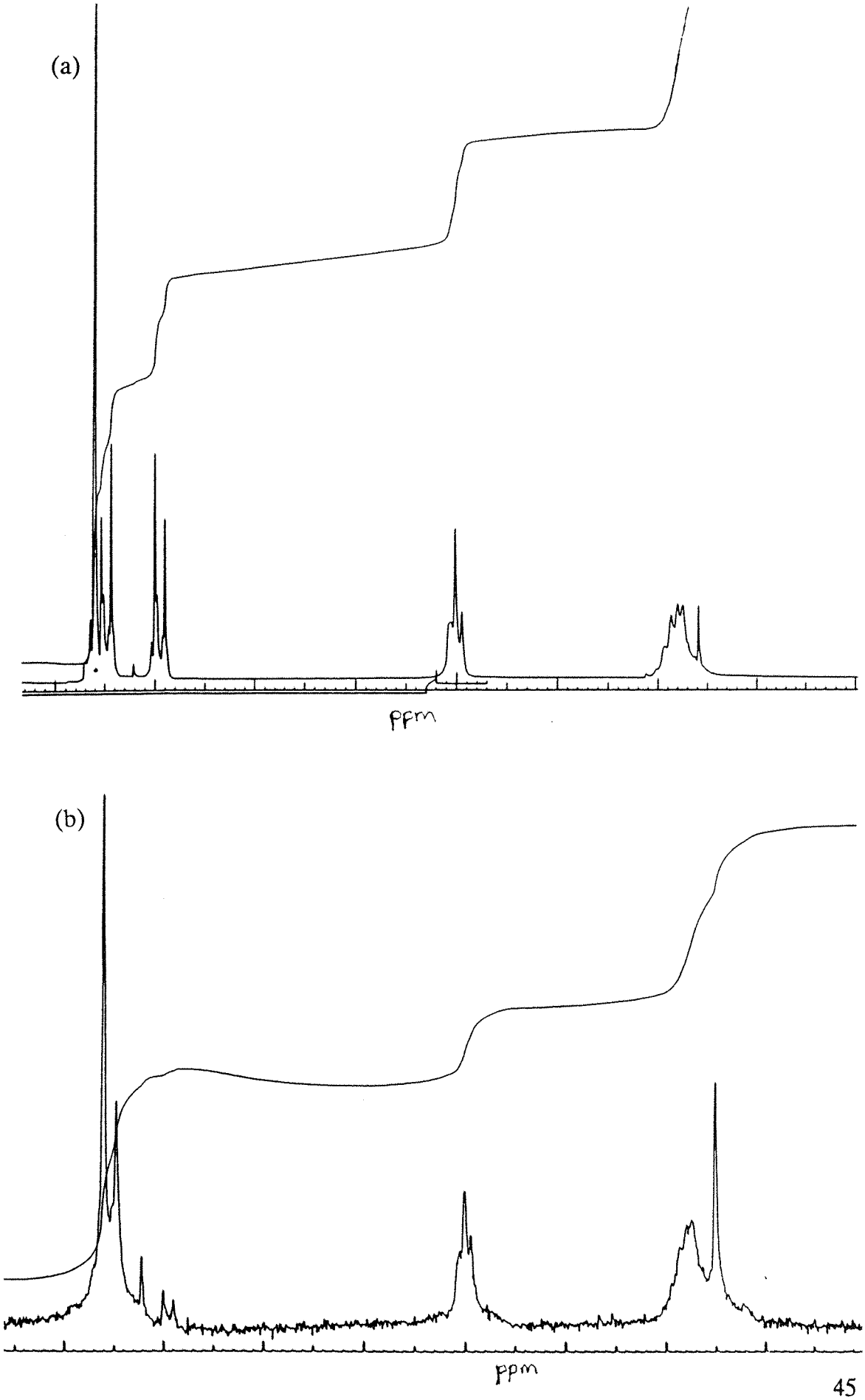
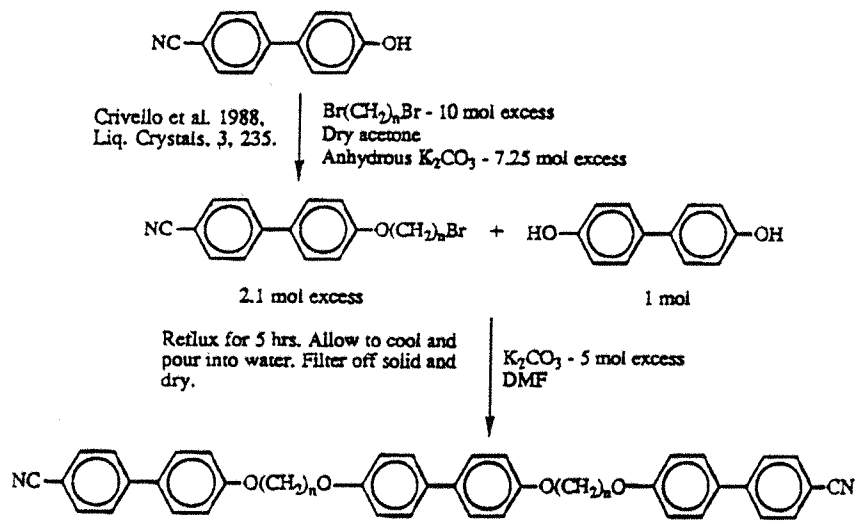


Figure 9. ^{1}H NMR Spectra of (a) CBO5OCB, and (b) CBO5OCB-d_4.



Preparation of 4,4'-bis(4'-cyanobiphenyloxyalkyloxy)-biphenyls, n=8,9.

These particular trimers were chosen because they are similar both in structure and in physical properties to the dimers; in addition they have the merit that they have been synthesised previously and so are reasonably well characterised [14]. The 8 and 9 length spacer chains were selected because they have similar transition temperatures to the dimers studied which ensures that they are less liable to thermal decomposition than the homologues with shorter spacers in addition,because of their higher solubility, they are also easier to purify than the trimers with shorter spacers. These trimers are usually referred to as symmetric because the two chains linking the three mesogenic groups have the same length. Both trimers were prepared in the following way according to the reaction scheme,



4-hydroxy-4'-cyanobiphenyl (1g, 1 equiv.) was dissolved in dry acetone and anhydrous K_2CO_3 (5.5g, 7.25 equiv.) was added. The α,ω-dibromoalkane (14.6g, 10 equiv. excess) was added and the mixture was stirred under reflux for 18 hours. The mixture was filtered while hot and the acetone removed under reduced pressure. The excess α,ω-dibromoalkane was distilled under vacuum and

the crude 4-bromo-n-alkyloxy-4'-cyanobiphenyl was recrystallised from methanol and dried. Yield 85%. 4-n-bromoalkyloxy-4'-cyanobiphenyl (1g, 2.1 equiv.) and biphenol (0.22g, 1 equiv.) were dissolved in dry dimethyl formamide (30 ml) and K_2CO_3 (1.7g, 5 equiv.) was added, this was heated under reflux for 5 hours, allowed to cool and then poured into water (200 ml). The white precipitate was filtered off and dried. The high molecular weight of the product drastically reduces the solubility and increases the melting point. After drying, the sparingly soluble symmetric trimer was recrystallised using toluene and refluxing for several hours; somewhat surprisingly boiling ethyl acetate was found to be an ineffective solvent. Yield 50%. Characterisation was effected by comparison of the transition temperatures and entropies of transition with previously prepared samples using optical microscopy and differential scanning calorimetry.

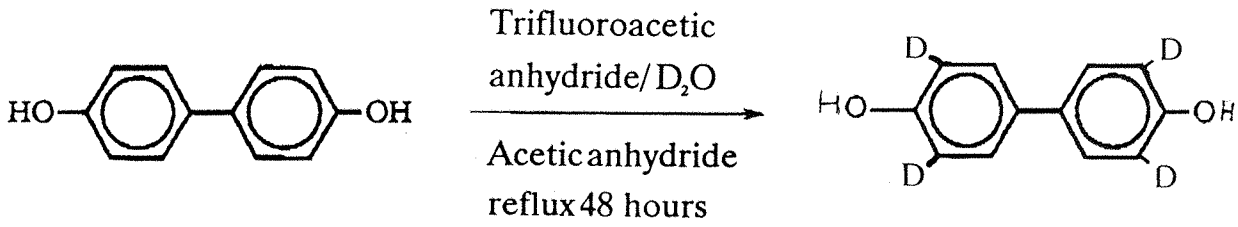
n=8 T_{CN} = 200°C (201°C), T_{NI} = 236°C (235°C).

n=9 T_{CN} = 152°C (154°C), T_{NI} = 200°C (200°C).

The literature values given in brackets are in good agreement with our results thus supporting the purity of these materials.

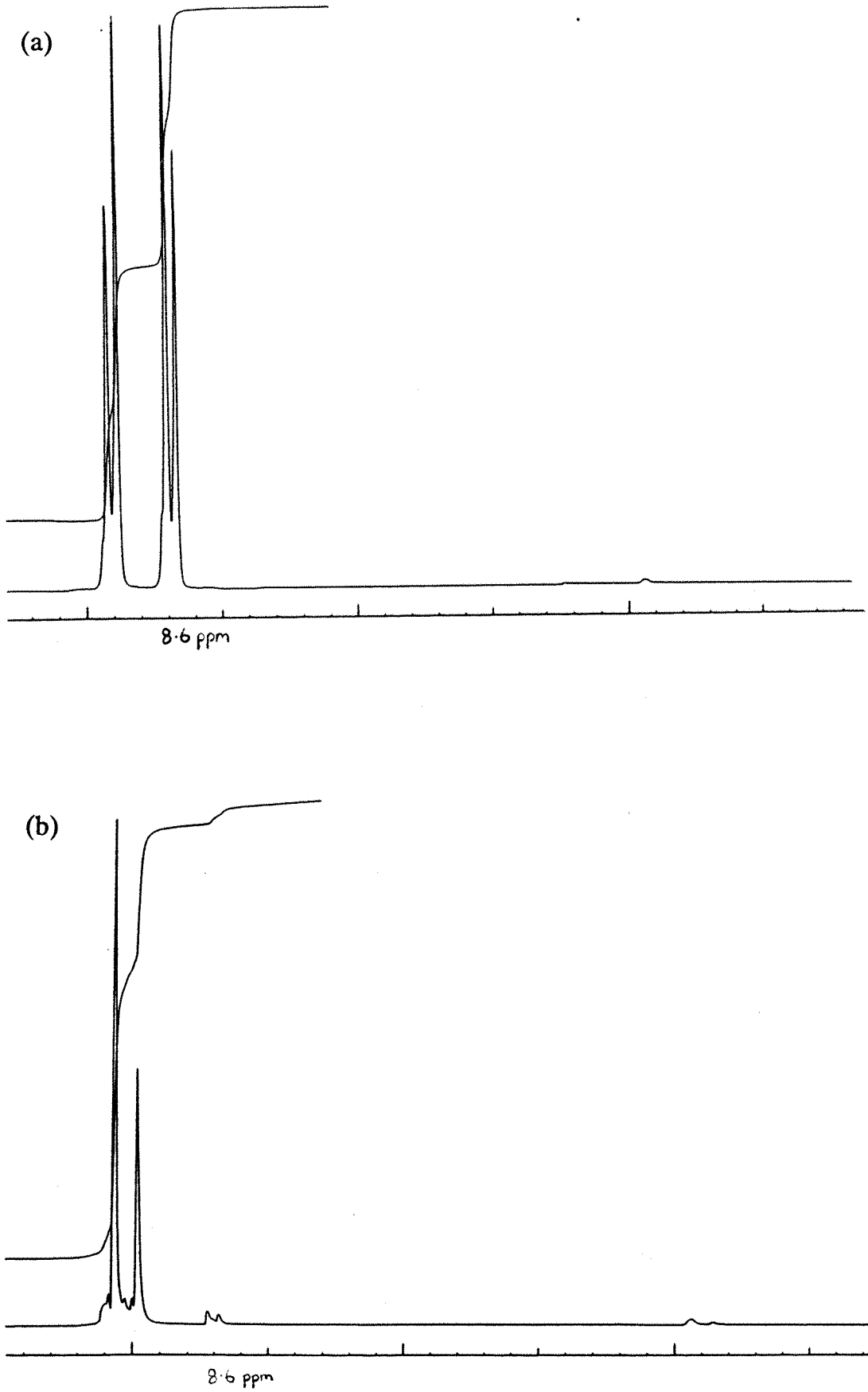
Deuteriation of Biphenol

The partial deuteriation of biphenol was achieved using a similar method to that described for 4-hydroxy-4'-cyanobiphenyl.



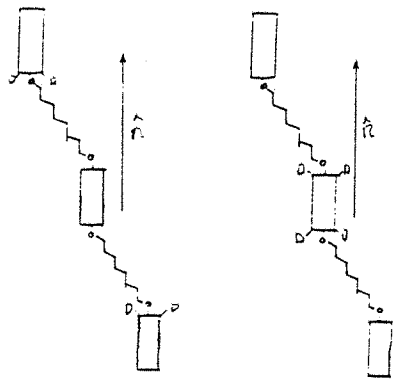
Trifluoroacetic anhydride (40ml) was added slowly with cooling and shaking to D_2O (15ml). Acetic anhydride (25ml) and biphenol (5g) were then added and the mixture refluxed for 48 hours. After shaking the cooled reaction mixture with water (200ml), the white solid was filtered off, washed well with water, and dried. The solid is readily recrystallised from ethanol to give 3,3',5,5'd_4-biphenol in 90% yield. ^1H NMR showed a decrease in peak area of ~90% for the 3,5-H's at 8.6ppm, see the spectra in figure 10.

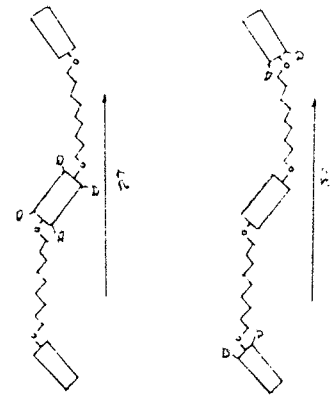
Figure 10. ^{1}H NMR Spectra of (a) Biphenol, and (b) Biphenol-d_4.



Deuteriation of trimers

The specific incorporation of the deuterium was achieved by using OCB-d_2 and biphenol-d_4, in place of their non-deuteriated analogues, in the manner described previously. The simple figures given below show the trimers and the position of deuterium incorporation within them.

n=8 

n=9 

Characterisation of the deuteriated trimers was difficult because of their extremely low solubility in conventional solvents, however, they all showed transition temperatures to within 1.5°C of their previously prepared non-deuteriated homologues. Yields ~50%.

Middle deuteriated,

n=8 T_{CN} = 198°C (201°C), T_{NI} = 236°C (235°C).

n=9 T_{CN} = 149°C (154°C), T_{NI} = 199°C (200°C).

End deuteriated,

n=8 T_{CN} = 196°C (201°C), T_{NI} = 236°C (235°C).

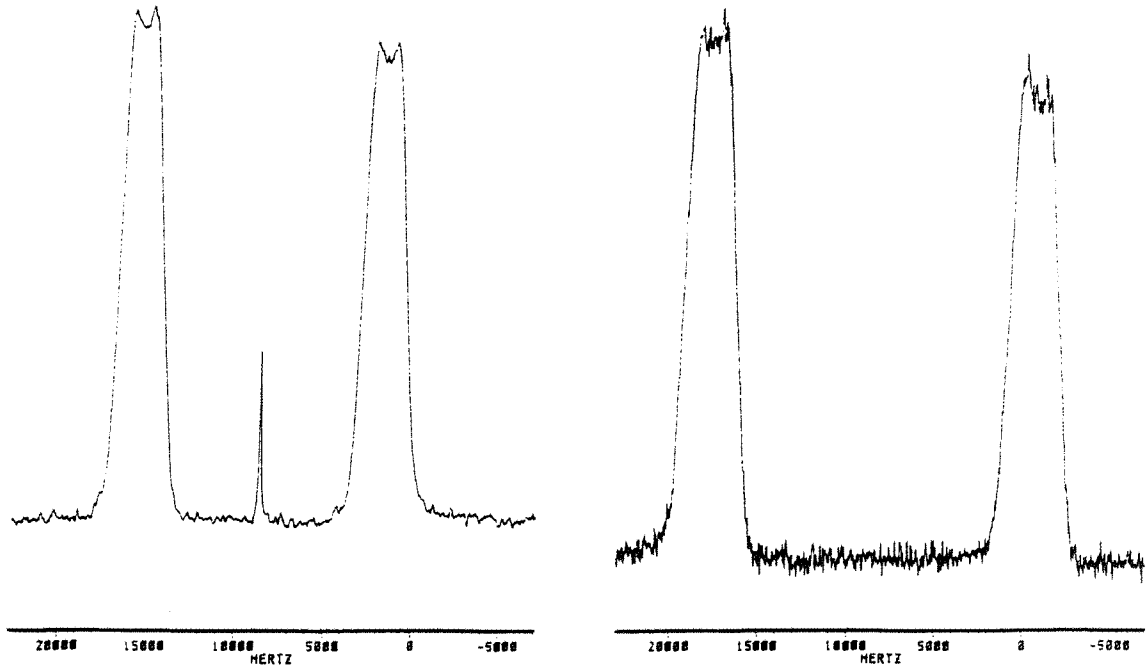
n=9 T_{CN} = 148°C (154°C), T_{NI} = 196°C (200°C).

The literature values given in brackets are in good agreement with our results thus supporting the identity and purity of these materials.

2.3 Deuterium NMR measurements

The deuterium NMR spectra of all of the compounds were measured using a Bruker MSL 200 spectrometer operating at 30.7 MHz. The probe head had a 10mm diameter solenoid coil mounted horizontally and the samples were contained in a 5mm o.d. tubes. Since the transition temperatures of the materials are so high, up to 260°C, it was necessary to use a pre-heated air supply which was exhausted from the bore of the superconducting magnet by means of a glass tube connected to a small suction pump. The spectra were obtained typically by averaging 15,000 transients following 90° pulses of 5.5 μs duration, a delay between pulses of 0.15s was used with a spectral width of 20 kHz accumulated into 8K of computer memory; this gives a resolution of 2.5 Hz which is well within the accuracy to which peak definition estimates could be made ($\sim \pm 50$ Hz) because of the large spectral linewidths.

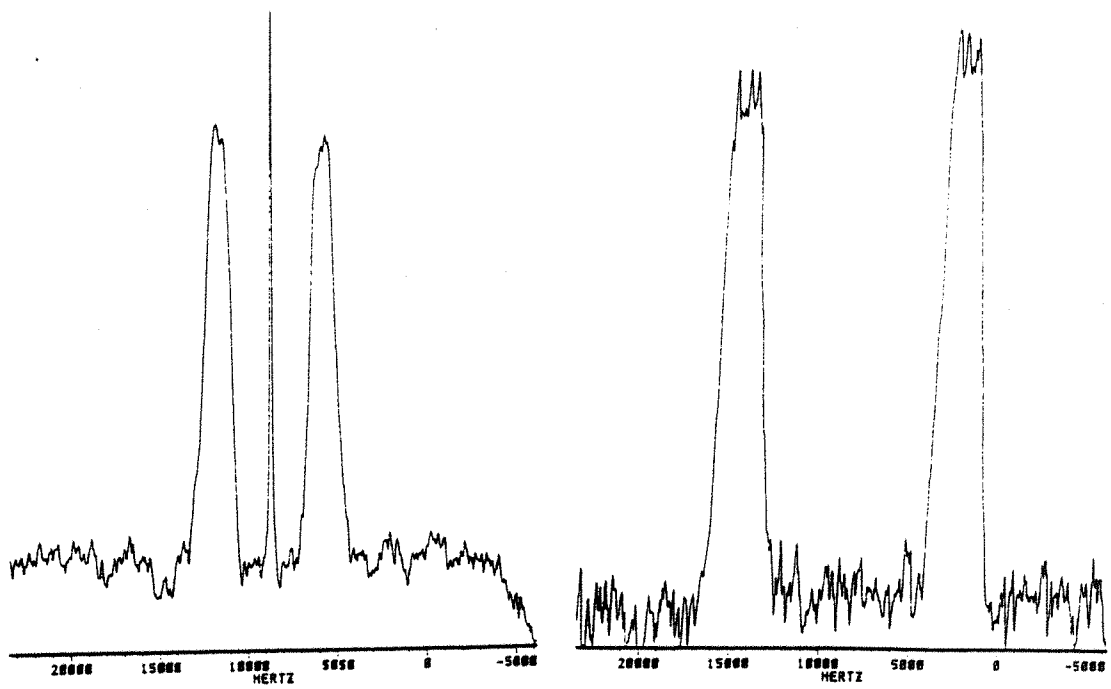
Sample preparation was based on a total of ~200 mg of material contained in an NMR tube, this was heated until the contents were just isotropic then flicked to ensure thorough mixing of the components. About 5% of the deuteriated dimer was used in each case, i.e. in itself and in PAA, this was considered to be low enough to ensure that solute-solute interactions were negligible and yet sufficiently high to provide spectra with an acceptable signal to noise ratio. The spectra for the dimers deuteriated in the cyanobiphenyl groups did not vary significantly in form and two examples of each compound are shown in figures 11 and 12, one at the nematic-isotropic transition temperature, T_{NI}, and one near the crystal-nematic transition temperature which gives the highest order possible. For the T_{NI} spectra the broad outer lines are associated with the nematic phase while the narrow, central peak originates from the co-existing isotropic phase. The large width of the spectral lines in the nematic phase results from the unresolved dipolar couplings which are completely averaged in the isotropic phase. Since there are two co-existing phases the transition occurs over a range of temperatures, this is to be expected for a nematogenic solvent exhibiting a first order phase transition. On lowering the temperature the transition starts at T_I



Pure CBO4OCB at T_{NI}

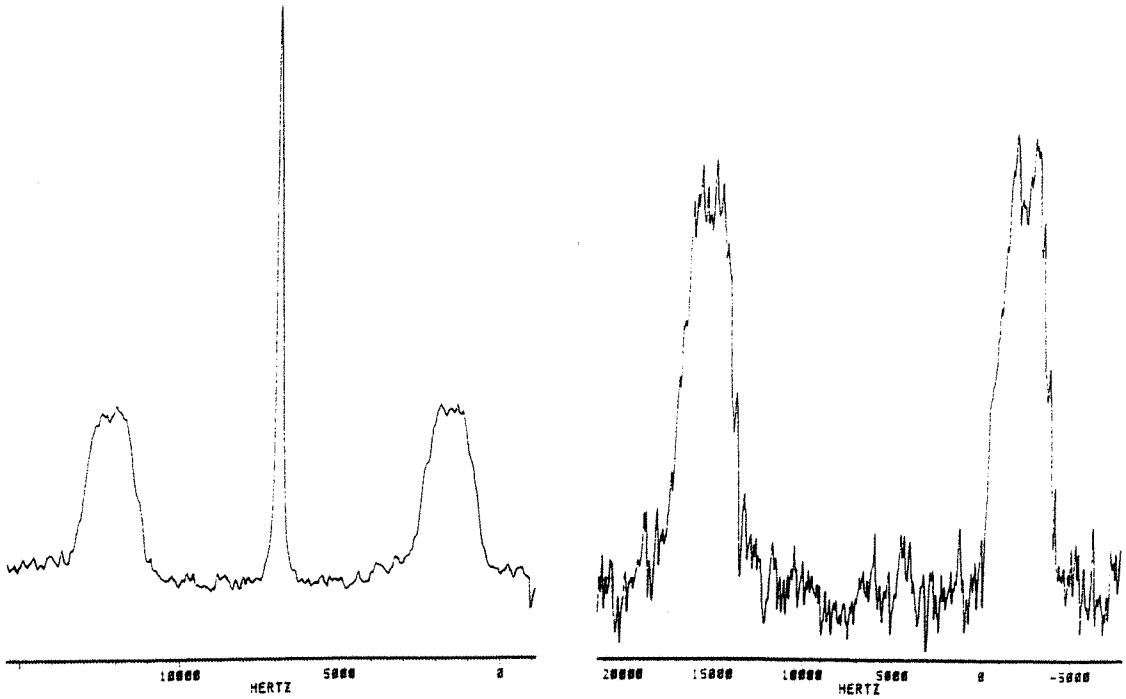
Pure CBO4OCB at T_{NI} - 43°C

Figure 11. Deuterium NMR Spectra of pure dimers at T_{NI} and at T_{NI}-43°C.



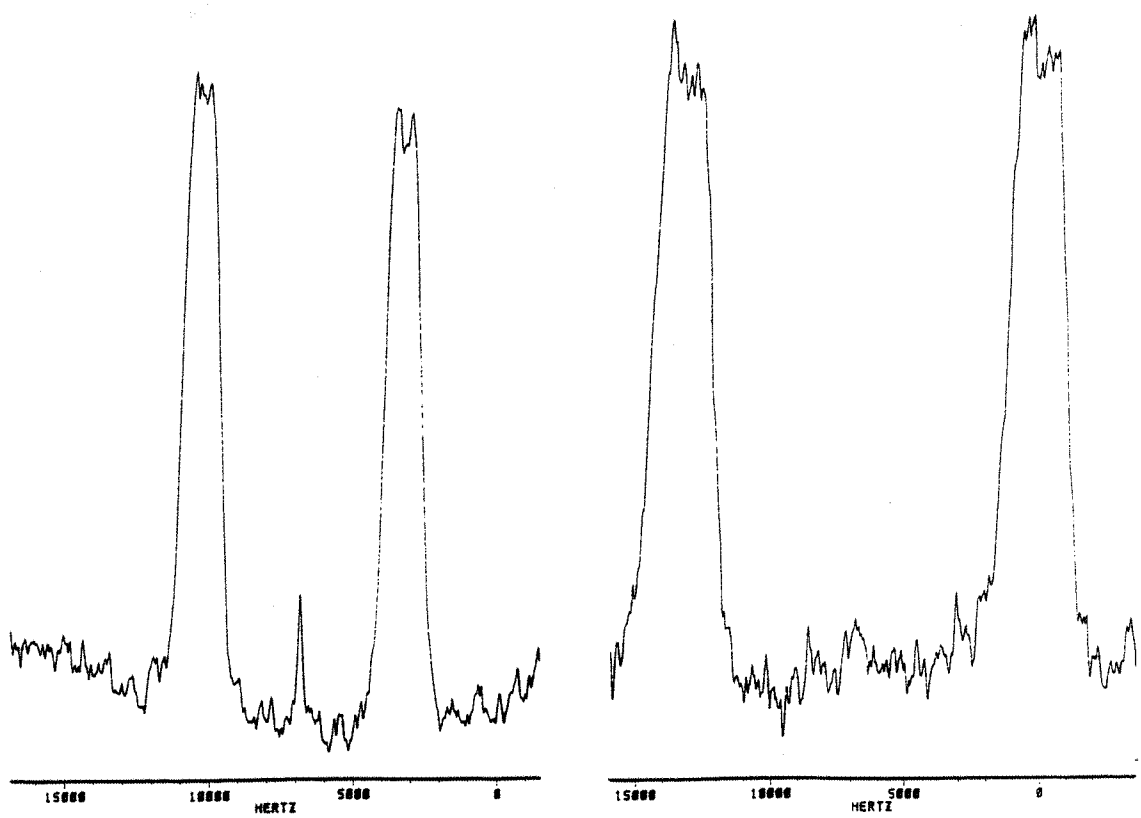
Pure CBO5OCB at T_{NI}

Pure CBO5OCB at T_{NI} - 43°C



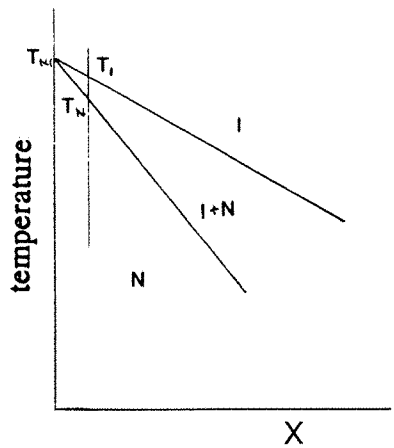
CBO4OCB in PAA at T_{NI} CBO4OCB in PAA at T_{NI} - 20°C

Figure 12. Deuterium NMR Spectra of dimers in PAA at T_{NI} and at T_{NI}-20°C.



CBO5OCB in PAA at T_{NI} CBO5OCB in PAA at T_{NI} - 20°C

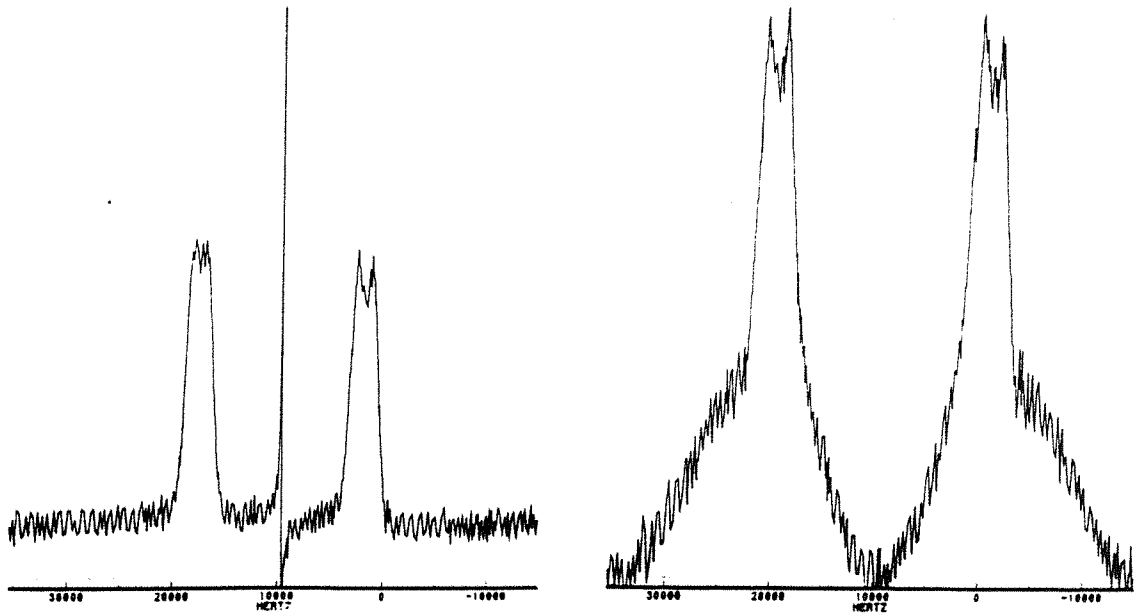
when the nematic phase first appears and is complete at T_N when the isotropic phase disappears; however, this biphasic region appears over a narrow region of 1-2°C because of the low solute concentration. Co-existing spectra were also observed for the notionally pure systems. Again the width of the biphasic regime was small and may also result from a small amount of impurity or as seems more likely from a temperature gradient existing across the sample.



2.4 Spectral Analysis

The deuterium spectra shown in figures 11 to 14 from the nematic phase of the oligomers, both dimers and trimers, contain just one quadrupolar doublet from the four equivalent aromatic deuterons each line of which is split into a much smaller doublet by the dipolar interaction with the neighbouring 2,6 protons. The dipolar doublet is clearly apparent on the spectra for the even dimer CBO4OCB especially at T_{NI};at the lower shifted temperature of 43°C the noise masks the splitting to a certain extent. For the odd dimer CBO5OCB the dipolar splitting is far less apparent presumably because of its lower orientational order and the greater spectral noise. Similarly the dipolar splittings can just be observed for the even trimer (see figure 13) with the deuteron on either the end or the middle mesogenic groups. In addition the dipolar splitting could not be observed for the odd trimer presumably because of its lower orientational order. This is certainly in accord with the significantly smaller quadrupolar splitting found for the odd

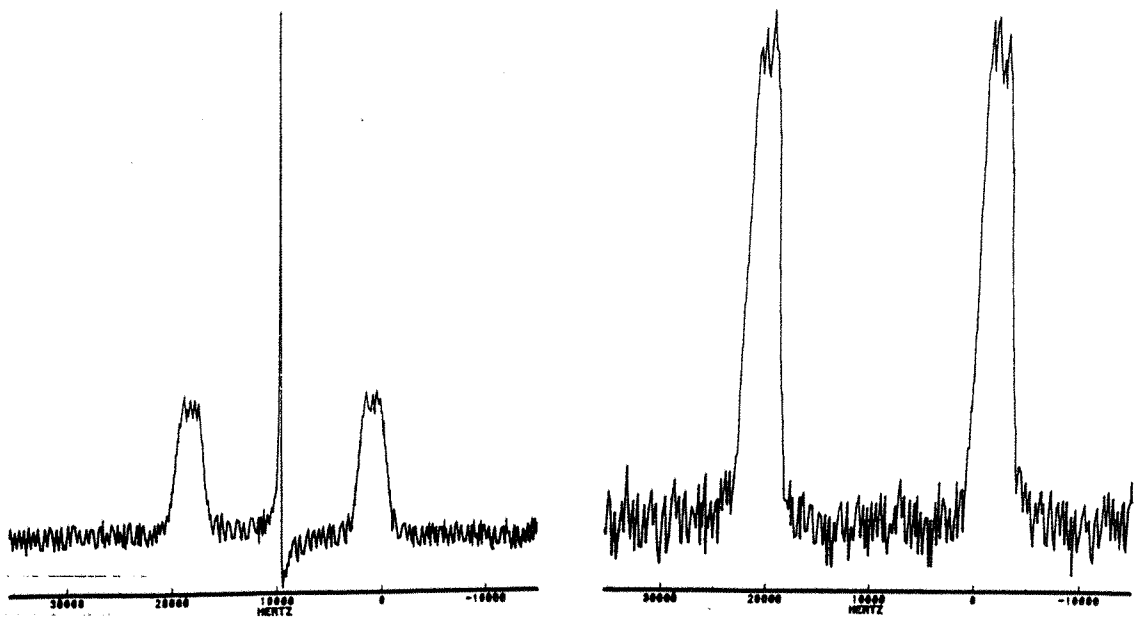
trimer in comparison with that for the even. Simulation of the lineshapes to take account of the unresolved dipolar coupling would be desirable in order to obtain accurate estimates of the partially resolved H-D dipolar splittings; however, suitable software was unavailable at the time of the analysis. It is estimated that the dipolar couplings were determined, for the odd and the even spectra, with a precision of approximately ± 50Hz , i.e. ±5% in a typical dipolar splitting of 1 kHz. This error estimate is not absolute however, a number of factors may limit the accuracy with which the dipolar splittings can be determined. These include the fluctuations in the splittings caused by variations in the temperature at the high settings necessarily used in these experiments. In addition, the routine employed to reduce the spectral noise also reduces the resolution, however for the settings used we do not expect these to make a major contribution to the uncertainty in measuring the splittings.



Trimer 8 d_4^{ends} at T_{NI}.

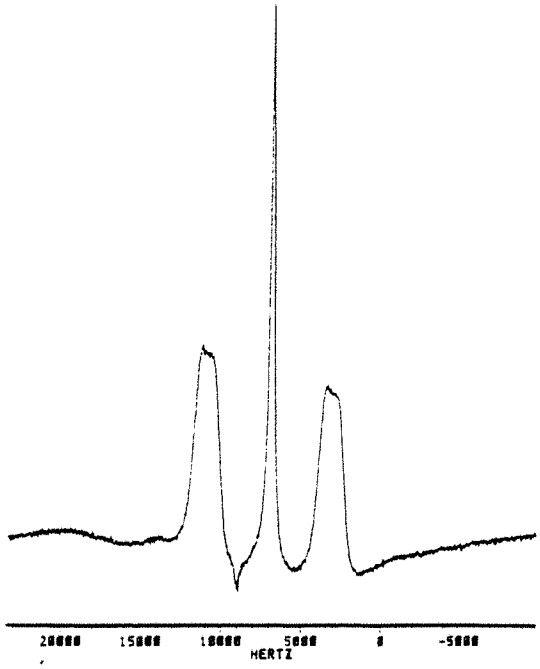
Trimer 8 d_4^{ends} at T_{NI}-36°C.

Figure 13. Deuterium NMR Spectra of trimer 8 at T_{NI} and at T_{NI}-36°C.

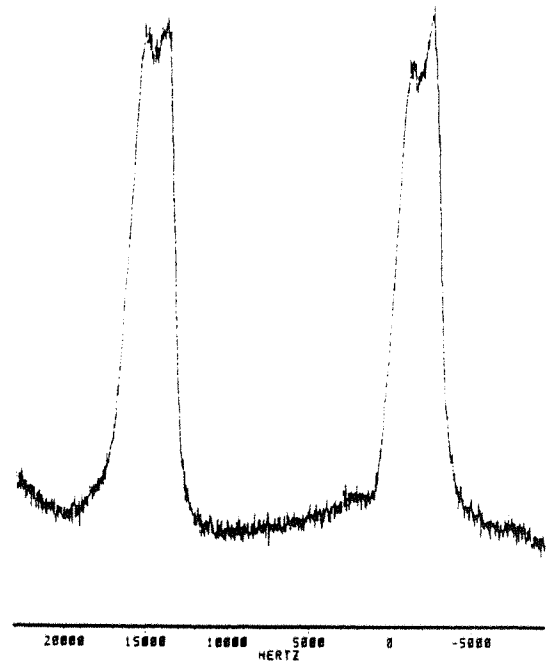


Trimer 8 d_4^{middle} at T_{NI}.

Trimer 8 d_4^{middle} at T_{NI}-36°C.

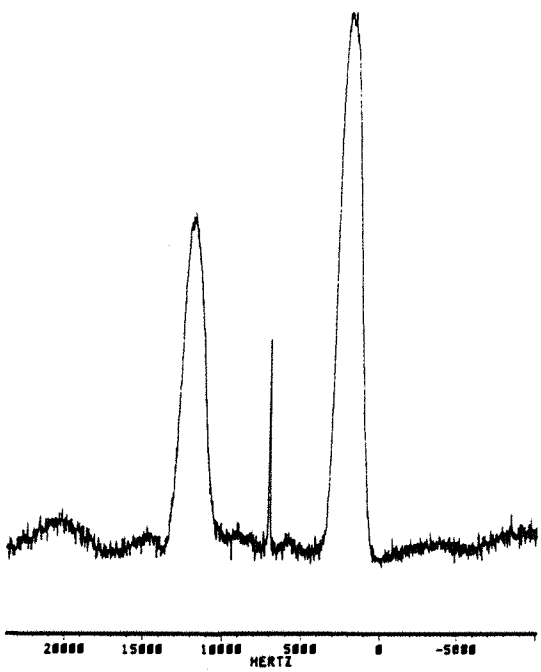


Trimer 9 d_4^{ends} at T_{NI}.

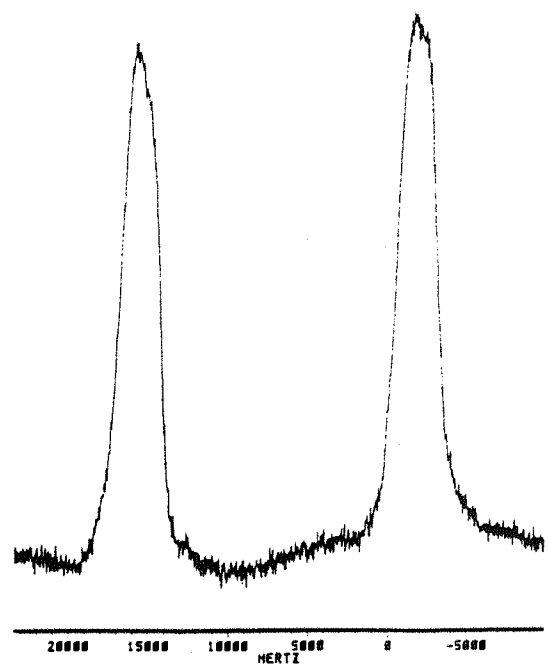


Trimer 9 d_4^{ends} at T_{NI}-36°C.

Figure 14. Deuterium NMR Spectra of trimer 9 at T_{NI} and at T_{NI}-36°C.



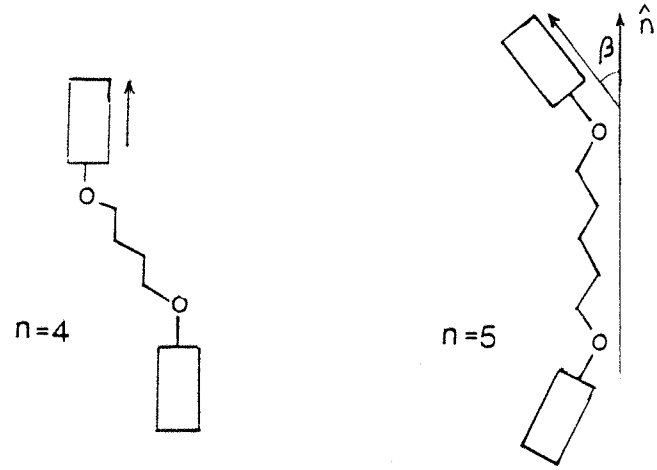
Trimer 9 d_4^{middle} at T_{NI}.



Trimer 9 d_4^{middle} at T_{NI}-36°C.

2.5 Results for the Dimers

As we have seen the determination of the orientational order for a non-rigid molecule containing many rigid sub-units is a formidable task. However, for oligomeric molecules with mesogenic groups linked by flexible chains evaluation of the order parameters for just the mesogenic parts of the oligomers is of special importance. For the dimers the major order parameter along the direction of the long axis of the mesogenic group is obtained by measuring the dipolar splittings



where ß is the angle between the para axis of the mesogenic group and the director of the nematic phase. The quadrupolar splittings which are obtained with far higher precision give the order parameter of the C-D bond direction, S_{CD}. Relating this to the ordering matrix for the phenyl ring to which the deuteron is attached is a difficult task requiring a detailed knowledge of the molecular geometry and the intramolecular motion [7]. Fortunately we need not attempt such an analysis here in order to make significant comments on the molecular organisation of the oligomers.

The splittings observed are a direct measure of the orientational order within the systems and so we shall deal with these rather than the order parameters themselves. The values of the dipolar and quadrupolar splittings for the dimers in the pure state and in solution are plotted in figure 15 against the shifted temperature (T_{NI}-T); this allows comparisons to be made readily between the

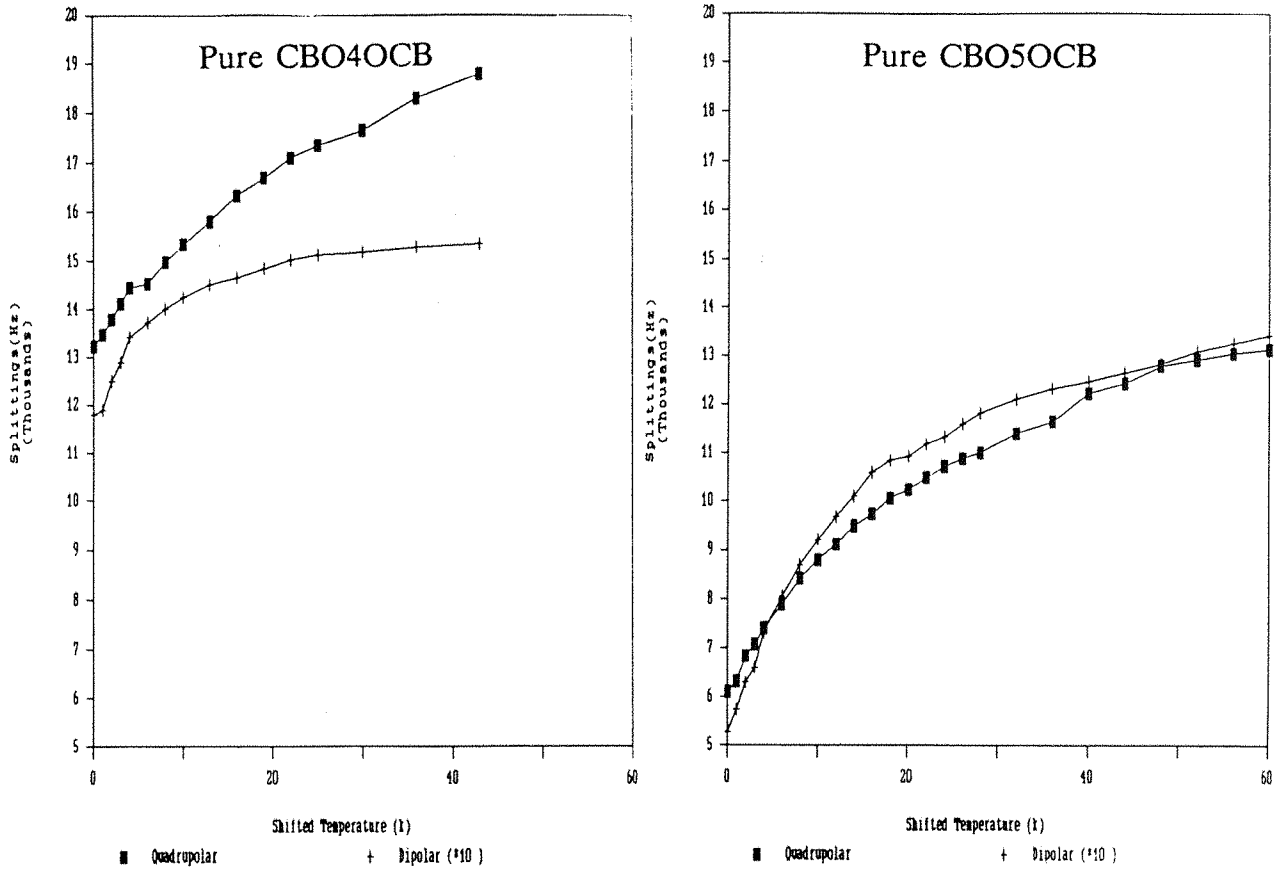
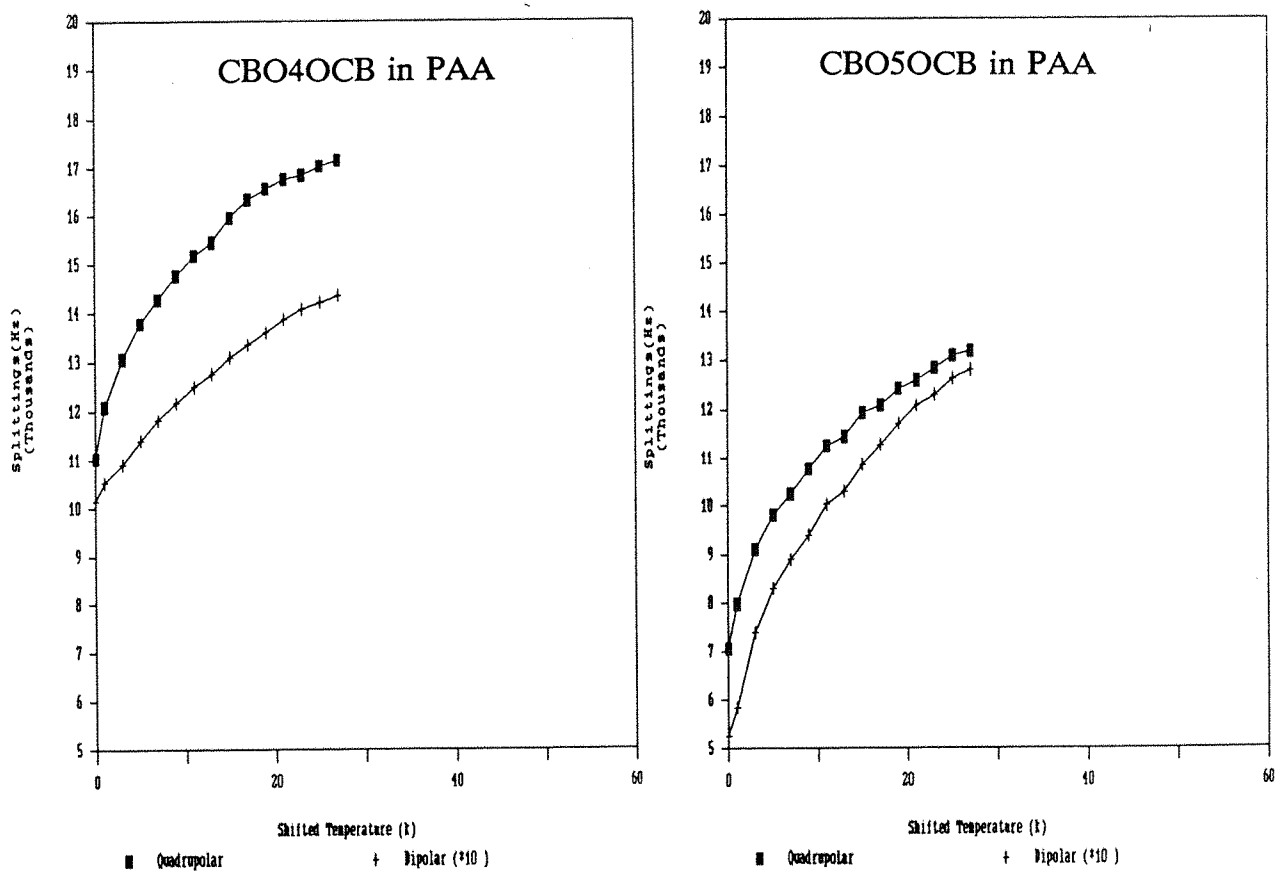


Figure 15. Graphs of dipolar and quadrupolar splittings against shifted temperature for the dimers in the pure state and dissolved in PAA.



systems using a common temperature scale throughout. The following observations can be made concerning these results.

1. It is seen that in the pure states for the odd and even dimers the splittings are significantly greater for the even dimer at a given shifted temperature, in agreement with previous studies [3,9].

2. If the spectra of each dimer dissolved in the nematogen PAA are now compared it is seen that the splittings for the even dimer are greater than those for the odd.

3. By comparing the spectra of pure CBO5OCB and of CBO5OCB in PAA the dipolar and quadrupolar splittings are very similar, indeed any difference is well within experimental error.

4. The comparison of spectra for CBO4OCB and for CBO4OCB in PAA shows similar quadrupolar splittings but the dipolar splittings in the pure state appear to increase at a smaller rate to those in solution.

5. The gradients of the dipolar and the quadrupolar splittings with respect to temperature are larger in both the pure state and in solution for the odd dimer than for the even dimer.

We will now attempt to rationalise these observations.

1. This is an expected result, in that odd members of homologous oligomeric series containing flexible alkyl chains have been found to display lower splittings than the even members [3,9], see figure 2 for example. This has previously been thought to be because odd oligomers are intrinsically less ordered orientationally than even oligomers, in other words their bent structure does not allow the mesogenic groups to align so parallel with the director, that is the bent structure is not so compatible with the liquid-crystalline organisation and so the intrinsic packing is less efficient and a more disordered system is thought to exist.

2. This result again tallies with the odd-even effect observed in oligomers. The difference between the dipolar and quadrupolar splittings or the nematic-isotropic transition of the even over that of the odd dimer is of the same

magnitude as that observed in the pure systems i.e. ~500 Hz for the dipolar splittings and ~6 kHz for the quadrupolar splittings.

3. The similarity between the two spectra indicates that the ordering in the pure state is almost the same as the ordering of the dimers when dissolved in the nematic solvent. The ordering within a liquid crystal system is decided by the orientational order of the environment and the anisotropy in the molecular interactions, it can be assumed that with only 5% dimer in the CBO5OCB/PAA system, the dimer molecules interact virtually exclusively with the solvent and not with themselves. The fact that the splittings are so similar for the two systems is consistent with the view that the ordering of the solute is decided by the geometry of the solute molecules and is not an intrinsic property of the system as a whole. In other words the orientational order of the two environments, pure CBO5OCB and PAA, are essentially the same.

4. The hypothesis that the order in the oligomeric systems is due to a geometric factor is consolidated when the spectra of pure CBO4OCB and CBO4OCB in PAA are compared. The quadrupolar splittings for both are very similar as for the odd dimer, however, the dipolar splittings for pure CBO4OCB initially increase more rapidly than for CBO4OCB in PAA although they do converge as the temperature decreases. This initial steep rise in the splittings is consistent with the idea of the flexible dimer molecules becoming more anisometric on cooling as the orientational order increases; there is then a synergism between the conformational distribution for the dimer and its orientational order. This is not observed in PAA because the orientational ordering of the solvent is decided by solvent-solvent interactions and not by that of the dimer which is present in such low concentrations. This does not occur for the odd dimer because there are so few conformations with a high anisotropy and so the conformational distribution cannot change significantly in response to variations in the orientational order.

5. The observation that for the odd dimer the gradients of the dipolar and the quadrupolar splittings are larger in both the pure state and in solution can be

explained by the bent structure of the CBO5OCB molecule. The system is less ordered near T_{NI} than for the CBO4OCB system and so the CBO5OCB molecules need to order themselves faster than the more ordered CBO4OCB molecules before reaching the limiting value of perfect order at low temperature which necessarily creates a steeper rise in the splittings.

These results for the odd and even liquid crystal dimers allow us to propose a new model for the molecular organisation within the nematic phase of these materials. The starting point for this is the quite different molecular shapes of the odd and even dimers in the all-trans configuration. As we saw in the first chapter the mesogenic groups are parallel for the even dimer while for the odd dimer the mesogenic groups are inclined to one another. This simple picture of the different molecular shapes is preserved even when allowance is made for the molecules to exist in a wide variety of conformational states. The requirement for the two mesogenic groups to be equivalent constrains the way in which the dimers must pack in the uniaxial nematic phase. For the even dimers the mesogenic groups will be arranged so that on average they are parallel to the director, as is shown in figure 16. In contrast for the odd dimers the bent shape requires that, on average, the mesogenic groups are tilted with respect to the director; this organisation is sketched in figure 17.
The quadrupolar and dipolar splittings will necessarily reflect this difference in the molecular organisation. In both cases the director is aligned parallel to the magnetic field used in the NMR experiment. Thus for the even dimers the mesogenic groups are, on average, parallel to the field whereas for the odd dimer the groups are, on average, tilted with respect to the magnetic field by an angle ß. This tilting of a director away from the global director is equivalent to having rotated the sample by an angle ß and in consequence the splittings would all be reduced by a factor $P_2(\cos\beta)$. It is this reduction which is believed to be primarily responsible for the smaller order parameters observed for the odd dimers in comparison with their even counterparts. We should note however that the

Figure 16. Diagram showing the packing arrangement for an even dimer.

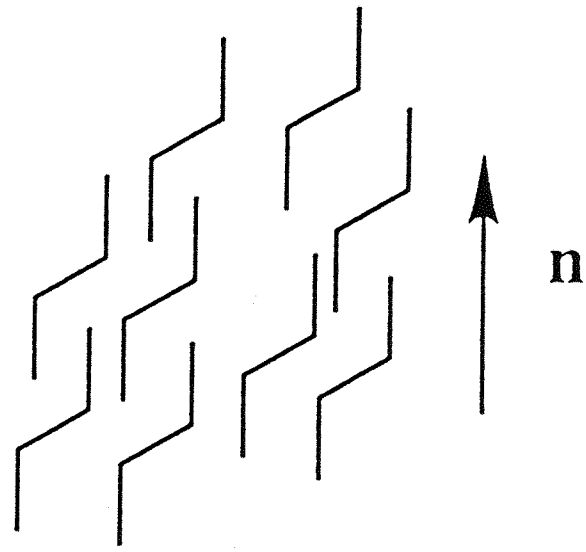
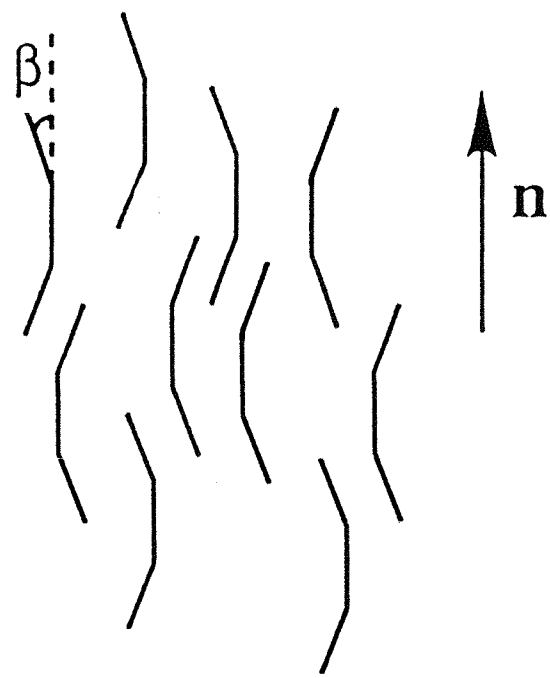


Figure 17. Diagram showing the packing arrangement for an odd dimer.



reduction by the simple $P_2(\cos\beta)$ factor is only strictly valid if the symmetry with respect to the local director is uniaxial as it is for the global director.

To test this interpretation further it is necessary to know what the splittings would have been for the odd dimers when the magnetic field was parallel to the local rather than the global director. To a first approximation these splittings might be identified with those of the even dimer if the orientational order of the environment, with respect to the local director, was the same for both the even and the odd dimers. This seems likely to be the case as the results obtained from the dimers dissolved in the nematogenic solvent seem to show. Here the orientational order of the environment to which the dimers are subjected is clearly identical since it originates from the common solvent. However the quadrupolar and dipolar splittings, especially at the nematic-isotropic transition, are essentially identical to those for the pure dimers. It seems reasonable to assume, therefore, that the splittings for the odd dimers if the magnetic field was oriented along the local director would equal those for the even dimer. With this assumption the splittings for the odd and even dimers are predicted to be related by

$$\Delta\nu_q^{odd} = \Delta\nu_q^{even} P_2(\cos\beta),$$

and

$$\Delta\nu_d^{odd} = \Delta\nu_d^{even} P_2(\cos\beta),$$

where the subscripts q and d denote the quadrupolar and dipolar splittings, respectively. The validity of these equations and hence this rather simple model, can be explored via the ratios $\Delta\nu_q^{odd}/\Delta\nu_q^{even}$ and $\Delta\nu_d^{odd}/\Delta\nu_d^{even}$. These should be identical to each other at the same shifted temperature and essentially independent of temperature provided the angle between the local and global directors for the odd dimers do not change. In addition we expect this angle, from the molecular geometry, to be about 25° and this can be determined from the ratios of the splittings. The ratios are shown in figures 18 and 19 for the quadrupolar and dipolar splittings, respectively.

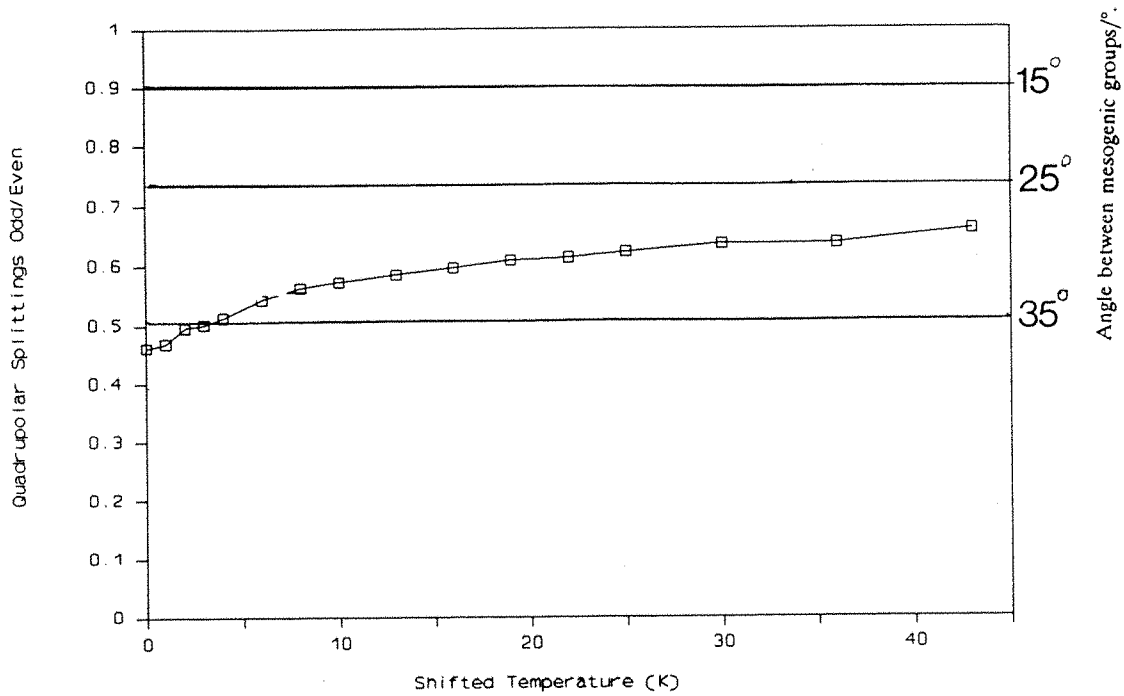


Figure 18. Graph of quadrupolar splitting ratio against shifted temperature for the pure dimers.

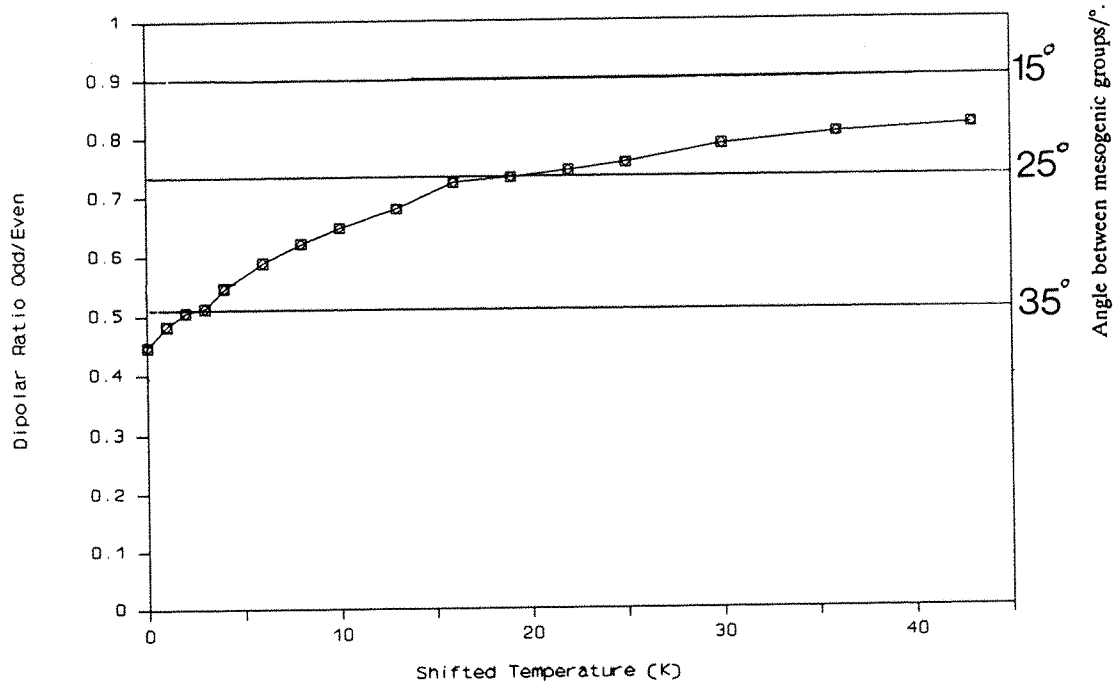


Figure 19. Graph of dipolar splitting ratio against shifted temperature for the pure dimers.

As we can see from the graphs, the ratios are not strictly independent of temperature, the splitting ratios increase with temperature for both the dipolar and quadrupolar splittings. This change is especially noticeable for the dipolar splitting ratio and it is tempting to attribute this to the larger uncertainty of determining the dipolar splittings. We shall, therefore, confine our attention to the quadrupolar ratio. Again this is seen, in figure 18, to increase with decreasing temperature although the change is far smaller than that for the dipolar splitting. Indeed for the temperature range from 10 to 40°C below the nematic-isotropic transition the ratio is essentially constant as predicted by the simple model. To indicate the associated values of ß the angle through which the local director is tilted away from the global director we show, on both figures, the values of $P_2(\cos ß)$ calculated for the angles 15°, 25°, and 35°. From the results in figure 18 we can see that ß varies between 27 and 37° over a wide temperature range of 40°. The quadrupolar splitting ratio seems to be in accord with the model in that the ratio is insensitive to temperature and the average value of ß is about 30° which is close to that estimated from the molecular geometry for the odd dimer in the all-trans conformation. Finally it would seem that the small decrease in the angle ß with decreasing temperature would be consistent with the tendency of the mesogenic groups in the odd dimer to become more parallel as the orientational order of the nematic phase increases.

The model does not, of course, apply for the dimers dissolved in a nematic solvent such as PAA because here there is just a global director. Nonetheless it is of some interest to see how the corresponding quadrupolar and dipolar ratio plots behave; they are shown in figures 20 and 21, respectively.

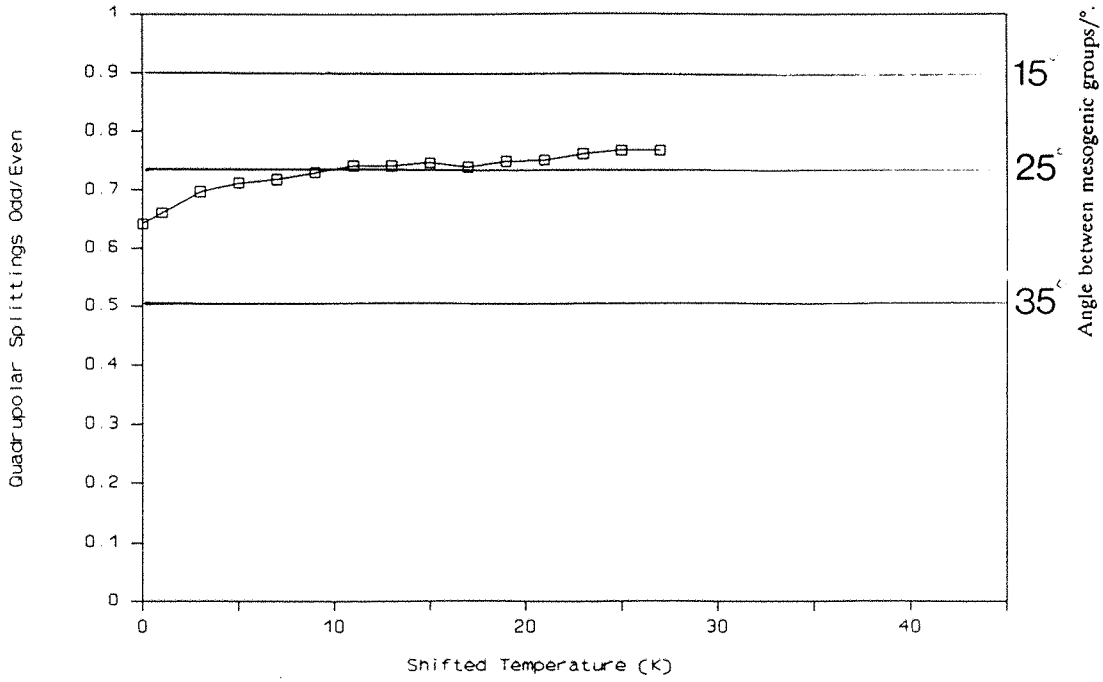


Figure 20. Graph of quadrupolar splitting ratio against shifted temperature for the dimers in PAA.

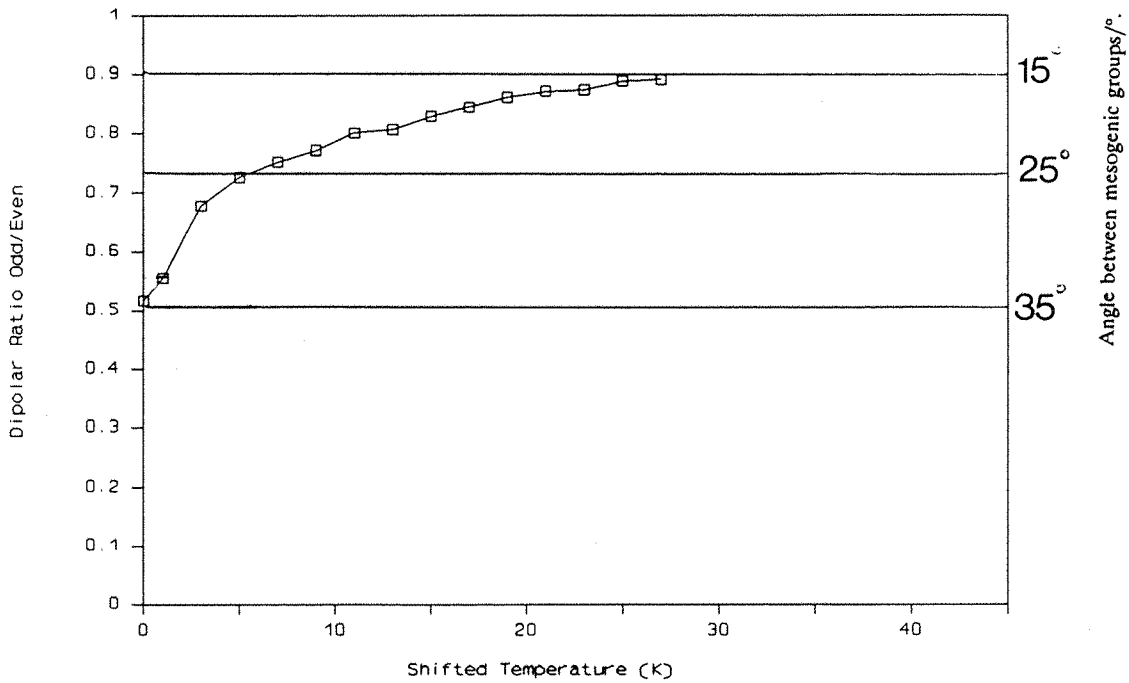


Figure 21. Graph of dipolar splitting ratio against shifted temperature for the dimers in PAA.

Somewhat surprisingly the behaviour is reminiscent of that found for the pure dimers. Thus the dipolar ratio increases quite markedly with decreasing temperature while the change for the quadrupolar ratio is far less marked. To understand these changes in terms of the ordering matrix for the odd and even dimers existing as they do in their many conformations is a difficult task and one which we shall not attempt here. However a simplistic explanation might have its origins in the angular correlations between the two mesogenic end groups. For example, in the limit that the groups are uncorrelated then the ordering of the groups might be expected to be independent of the flexible spacer. This might be the case for the even dimers but not for the odd where there is a geometrical constraint determining the correlation coefficient for the end groups even when the conformational distribution is essentially uniformly populated. We shall explore this sort of model in slightly more detail for the trimers.

2.6 Results for the Trimers.

As the NMR spectra in figures 13 and 14 show the quadrupolar splittings for the deuterons in the end mesogenic groups are slightly larger than for those in the middle group for both the odd and the even trimers. As these splittings depend on both the molecular geometry and the orientational order it is not possible to see whether the difference implies a greater order for the end mesogenic groups. However we can estimate just how sensitive the quadrupolar splittings are to the molecular geometry in the following way. It is assumed that the orientational order for the end and middle mesogenic groups are the same.It is further assumed that the ordering matrix for the phenyl rings to which the deuterons are attached can be taken to be cylindrically symmetric about the para axis. Then the quadrupolar splittings are given by

$$\Delta\nu_q^{end} = (3/2)q_{CD}S\ P_2(\cos\beta^{end}),$$

and

$$\Delta\nu_q^{middle} = (3/2)q_{CD}S\ P_2(\cos\beta^{middle}),$$

where ß is the angle made by the C-D bond with the para axis of the phenyl ring. The ratio of the splittings is then determined by purely geometric factors

$$\Delta\nu_q^{end}/\Delta\nu_q^{middle} = P_2(\cos\beta^{end})/P_2(\cos\beta^{middle}).$$

There is insufficient information to determine both of these angles but if we make the reasonable assumption that one of them is 60° then the other can be determined. The results obtained from the quadrupolar splittings in figure 22, with the previous assumptions with in addition β^{middle} taken to be 60° are given in the table for the odd and even trimers for temperatures at the nematic-isotropic transition and for T_{NI}-36°.

	β^{end} / °	
$(T_{NI}-T)$/°C	Odd	Even
0	59.70	59.46
36	59.72	59.57

As we can see the values of ß for the end groups differ by very small amounts (from 0.3° to 0.5°) from the value of 60° assumed for the middle mesogenic groups. In addition the deviation from the perfect geometry seems to be essentially independent of temperature over the entire nematic range. It would seem therefore that the different quadrupolar splittings for the end and middle mesogenic groups observed for both odd and even trimers can be understood simply in terms of quite modest geometric differences. It further suggests that the mesogenic groups are ordered to essentially the same extent in both trimers. As we shall now see these results are in accord with theory.

The results for the quadrupolar splittings and hence the order parameters for the end and middle mesogenic groups found for the trimers with odd and even spacers turn out to be in good agreement with a theory for mesogens composed of flexible molecules. The foundations of the theory were laid by Marcelja [10] and then extended by Luckhurst [11] in order to reduce the computational complexity. Within the theory the molecules are allowed to exist in different conformations according to Flory's rotameric state model [12]. The intricate anisotropic molecular interactions are replaced by a molecular field which has an angular variation defined by the second rank modified spherical harmonics. The strength of the molecular field varies from conformer to conformer in a way which depends on the geometry of the conformer. In addition the conformational interaction tensors are assumed to be the sum of segmental contributions. For the trimers the fundamental segments are taken to be the mesogenic groups and the carbon-carbon bonds in the flexible spacers. Finally the strength of the segmental contributions are assumed to be linear in the orientational order parameters of both the mesogenic groups and the alkyl chains.
Given these approximations it is then possible to calculate the nematic-isotropic transition temperature and the order parameters as a function of the spacer length. The input parameters required for these calculations are E_{tg}/RT and X_c/X_a. Here E_{tg} is the energy difference between a trans and a gauche link while

X_c and X_a are the interaction tensors for a carbon-carbon bond and a mesogenic group, respectively; for simplicity the interaction parameters for the end and middle mesogenic groups are taken to be the same. This appears to be a reasonable assumption for the trimers which have been studied. The ratio X_c/X_a was set equal to 0.2, which is a value obtained by fitting the order parameter profiles for 4-n-alkyloxy-4'-cyanobiphenyls to the theory [13]. Finally E_{tg}/RT was given the value of 1.0 which is reasonable and gives a good fit to the order parameter profiles.

These values were used to obtain the results given in the table for the scaled nematic-isotropic transition temperature (T_{NI}^*) and the order parameters for the para axes of the end (P_2^e) and middle (P_2^m) mesogenic groups at the transition. The results have been obtained for spacers containing 1 to 7 methylene groups. Naturally it would have been desirable to have values for the spacers with 8 and 9 methylene groups to make more direct contact with experiment. However, these calculations proved to be prohibitively expensive because of the enormous number of conformations all of which are included in the calculations. Nonetheless the general trends are readily discernable and are seen to be in agreement with experiment. Thus for the spacers with an even number of methylene groups in the spacer the order parameters for the end and middle groups are essentially the same; in fact the order of the middle group is predicted to be slightly larger than for the end group. In contrast there is a marked difference for the early odd spacers with the ordering of the end mesogenic group being greater than for the middle. This can be visualised in the following way; the end groups tend to be parallel to the director but because of the geometrical constraint imposed by the spacers the middle mesogenic group tends to be inclined with respect to the end groups and hence to the director. As the length of the odd spacer increases so the predicted difference between the order parameters of the end and the middle mesogenic groups decreases. Indeed extrapolation of the results suggest that for the nine spacer the difference would be negligible. This suggests that as the chain length is increased the angular

correlations between the three mesogenic groups are lost and all three of them will now tend to be parallel to the director. The theory also predicts that the order parameters for the para axes of the mesogenic groups are larger for the even than the odd spacers, again in agreement with experiment, see table 1.

Table 1. The predicted nematic-isotropic transition temperatures (T_{NI}^{*}), and order parameters for the end (P_2^e) and middle (P_2^m) mesogenic groups for symmetric trimers with n methylene groups in the spacers.

n	T*	P_2^e	P_2^m	P_2^e-P_2^m
1	0.1645	0.3351	0.0313	0.3035
2	0.3153	0.5746	0.6203	-0.0457
3	0.1574	0.4116	0.1661	0.2455
4	0.2595	0.6874	0.7258	-0.0358
5	0.1650	0.5068	0.3387	0.1681
6	0.2303	0.7392	0.7672	-0.0280
7	0.1708	0.5814	0.4800	0.1014

Due to the poor quality of the spectra for the odd trimer and its smaller order, the dipolar splittings were only discernable for the even trimer, hence a comparison cannot be made between the odd and even trimers. However the same theory is expected to hold although the comparison might be less conclusive because of the large relative error for the much smaller dipolar splittings. These are shown in figure 23 for the end and middle mesogenic groups of the even trimer. They show very little difference between them indeed they are probably equal to within the experimental error in accord with the quadrupolar results and theory.

Figure 22. Quadrupolar splittings for trimer 8.

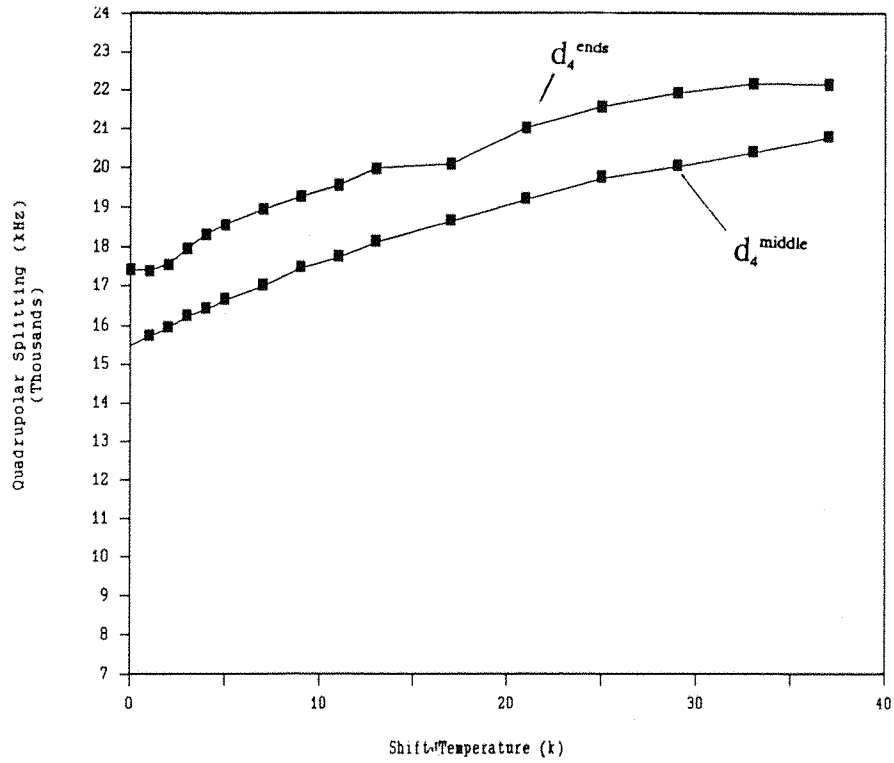


Figure 23. Quadrupolar splittings for trimer 9.

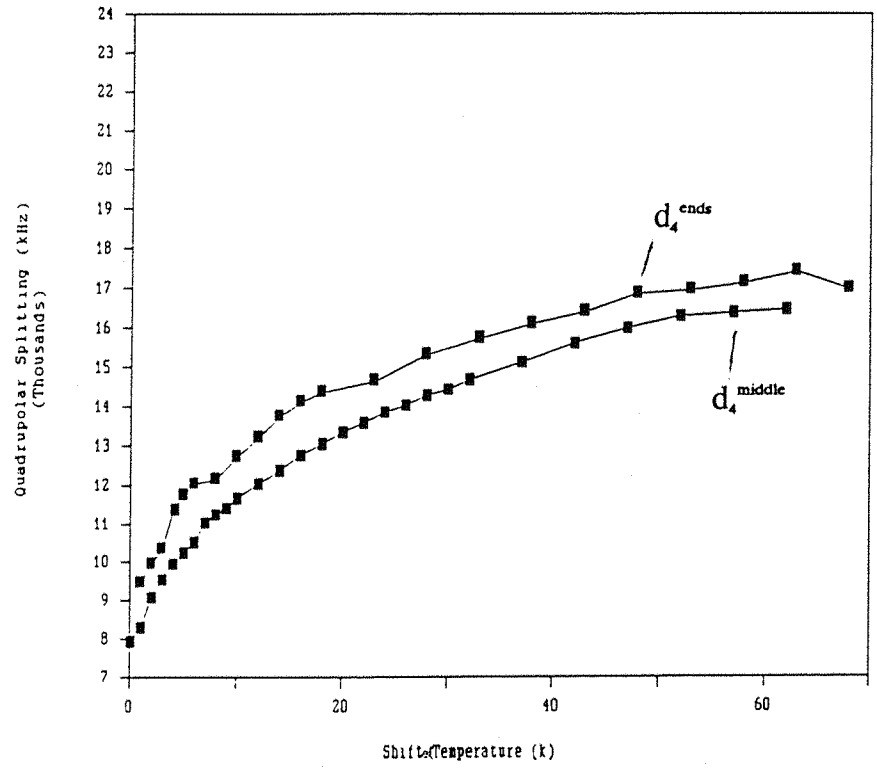
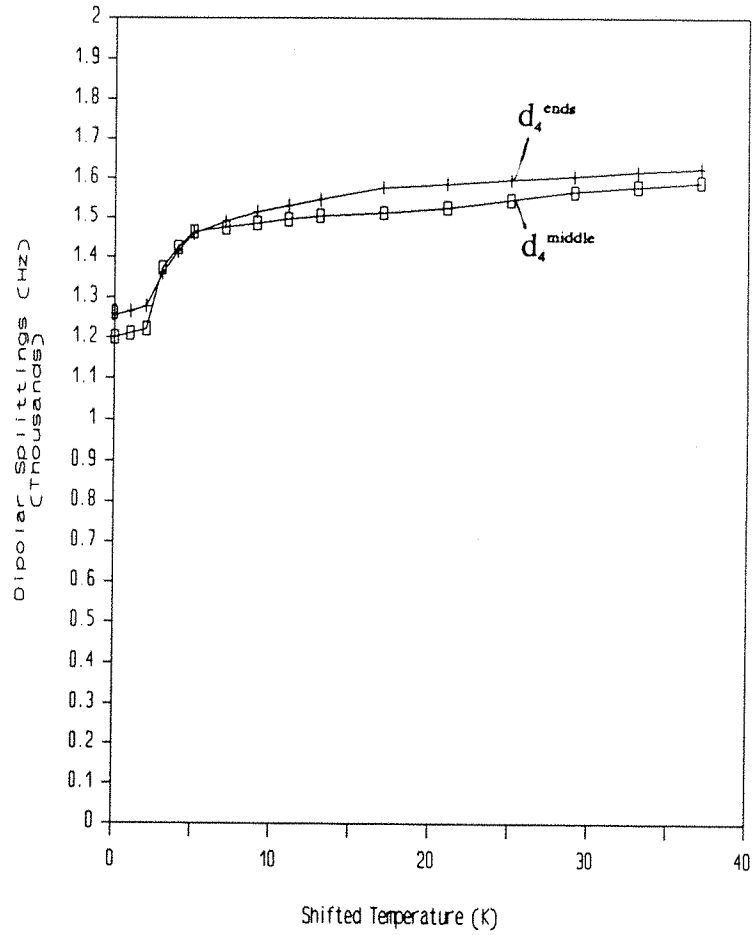


Figure 23. Dipolar splittings for trimer 8.



2.7 Conclusions

This project has shown how important deuterium NMR spectroscopy can be in studying the orientational order and molecular organisation in two classes of liquid crystal oligomers, the so-called dimers and trimers. For the dimers the orientational order, as reflected by both quadrupolar and dipolar splittings, is found to be significantly greater for the even than for the odd dimers. This difference appears to be independent of the nature of the environment, that is the pure liquid crystal or a common nematogenic solvent. These results can be understood semi-quantitatively in terms of a novel model for the molecular organisation in the nematic phase. For the odd dimer there is a local director which is tilted with respect to the global director. It is this tilt resulting from the bent geometry of the odd dimer which causes the apparent reduction of the orientational order with respect to the even. Indeed the intrinsic order with respect to the local director would seem to be essentially the same for the even and odd dimers. Such a conclusion is in marked contrast to the commonly held view that the orientational order in the nematic phase of an even dimer is greater than that for an odd.

In principle the same ideas might be expected to hold for the trimers. However, the deuterium NMR results for these give a different picture. Thus for both the even and the odd trimers the quadrupolar splittings for the end mesogenic groups are essentially identical to those for the middle group. While this might be expected for the even trimer it is not in accord with the anticipated bent conformation of the odd trimer. It would appear that the mesogenic groups are essentially uncorrelated for the long spacers used in these experiments and that the geometric constraint found for the dimers is no longer obtained for the trimers. Such qualitative conclusions based on the observed splittings are supported by the predictions of a molecular field theory of nematics composed of flexible molecules. This theory is also able to account for the larger quadrupolar splittings found for the even trimers in comparison to the odd.

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