UNIVERSITY OF SOUTHAMPTON

New hybrid Discotic/Calamitic Liquid Crystals

by Andrew Gordon Douglass

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Chapter 2 The Preparation and Properties of the Benzene-1,3,5-tri-(4-carboxyalkoxy-benzylidene-4'-n-alkylanilines)

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ABSTRACT

FACULTY OF SCIENCE

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New hybrid Discotic/Calamitic Liquid Crystals

by Andrew Gordon Douglass

This thesis discusses the investigation of the transitional behaviour of the benzene-1,3,5-tri-(4-carboxyalkoxy-benzylidene-4'-n-alkylanilines) in which three rod-like mesogenic units are attached to a disc-like core with flexible spacer chains. Four homologous series are synthesised varying the lengths of both the linking and terminal aliphatic chains. The spacer chain lengths employed consist of three to six methylene units, while those of the terminal alkyl chains consist of 1-10, 12 units. Both optical microscopy and differential scanning calorimetry are employed to investigate the mesomorphic properties of these materials. It is found that a progression from nematic to smectic behaviour occurs as a function of terminal chain length, this crossover occurs as the terminal chain length exceeds the spacer chain length. In addition, for spacing chains consisting of an even number of carbon atoms smectic C phases are found in the proximity of this crossover point, these then giving way to smectic A phases at higher terminal chain lengths. For all the series a number of more highly ordered phases with textures typical of calamitic systems were noted. However, the possibility that some or all of these phases may be columnar is not excluded.

CHAPTER ONE

INTRODUCTION

It is little more than 100 years since the discovery of liquid crystals. While studying cholesteryl benzoate, Reinitzer noted a turbid mesophase between the melting point at 145°C and the transition to a clear liquid at 179°C [1]. This mobile intermediate phase was investigated by Lehmann [2] who demonstrated its birefringent properties and coined the name liquid crystal. The kind of mesophase present in cholesteryl benzoate which is brought about by a change in temperature is termed thermotropic. The interest in thermotropic liquid crystals has increased dramatically over the past twenty years, principally as a result of their use in wristwatches and other display systems.

Mesophases can also be formed from solvent induced aggregation of certain amphiphilic molecules. These phases are termed lyotropic. It is worth noting that the distinction between these two sub-classes of liquid crystals is useful, but is by no means absolute in that some materials exhibit both lyotropic and thermotropic mesomorphism. A number of differing structures and packing arrangements have been distinguished within these systems, some of which have analogues in thermotropic liquid crystals. An understanding of the function and properties of lyotropic mesophases is of great importance, for example surfactants and biological membranes are both lyotropic liquid crystalline phases.

The work presented in this thesis considers only thermotropic systems, in particular the relationship between mesogenic behaviour and molecular structure.

1.1 Thermotropic Liquid Crystals

For the vast majority of compounds (>99%) heating the crystal will effect the transition to the isotropic liquid. However, for an enantiotropic liquid crystal it is found that on heating the crystal a transition to a fluid phase maintaining a degree of order occurs. An enantiotropic mesophase is one that is formed by heating the crystal or cooling the isotropic liquid. Alternatively, thermodynamically unstable mesophases can be formed by supercooling from the isotropic liquid: these are termed monotropic phases. Translational ordering is reduced or even lost within this mesophase but orientational order is present in all liquid crystal phases. This can be understood when considering the kinds of molecules that will form liquid crystalline phases. The key feature is molecular anisometry. This can be achieved by synthesising structures of an elongated, rod-like shape. It is then possible for these molecules to have a tendency to lie with their long axes parallel after the crystal structure has been destroyed, thereby maintaining a degree of order. Recently more exotic forms of anisometry have been found to lead to thermotropic mesomorphism, by creating for example disc- and bowl-shaped mesogenic moieties.

The long range orientational ordering retained within a liquid crystal phase is described by a unit vector, $\hat{n}$, known as the director [3]. In an uniaxial phase composed of rod like molecules, plotting the distribution function, $f(\beta)$, for the molecular long axes will give an axial array about the preferred director alignment as shown in figure 1. This distribution occurs as a result of molecular random motions due to thermal energy. The function $f(\beta)$ is in general unknown and is therefore expanded as an infinite series in the Legendre polynomials, $P_L(\cos\beta)$,

$$f(\beta) = \sum_L f_L \, P_L(\cos\beta)\,, \qquad 1.1$$

where f_L are the expansion coefficients. The mesophase has a plane of symmetry perpendicular to the director, $f(\beta) = f(\pi-\beta)$. Therefore $f(\beta)$ is an even function and odd rank polynomials vanish. To obtain an expression for the expansion coefficients f_L, equation 1.1 is multiplied by $P_N(\cos\beta)$, and integrated with respect to β

$$\int_0^{\pi} P_N(\cos\beta)\, f(\beta) \sin\beta \, d\beta = \sum_L f_L \int_0^{\pi} P_N(\cos\beta)\, P_L(\cos\beta) \sin\beta \, d\beta. \qquad 1.2$$

The Legendre polynomials are orthogonal allowing 1.2 to be written in the form

$$\bar{P}_N = \sum_L f_L \frac{2}{2L+1} \delta_{LN} . \qquad 1.3$$

δ_{LN} is the Kronecker delta which is unity for L=N and zero otherwise. It is possible to rewrite 1.3 as

$$f_L = [(2L+1)/2] \ \bar{P}_L \quad , \qquad 1.4$$

therefore,

$$f(\beta) = \sum [(2L+1)/2] \bar{P}_L P_L(\cos\beta) \qquad 1.5$$

where P_L are the order parameters of rank L. There are an infinite number of order parameters

$$f(\beta) = 0.5 + 5/2 \bar{P}_2 P_2(\cos\beta) + 9/2 \bar{P}_4 P_4(\cos\beta) + \ldots \quad . \qquad 1.6$$

In practice a good approximation of mesophase orientational order may be obtained by considering only $\bar{P}_2$,the second rank order parameter. Values of $\bar{P}_2$ may be evaluated experimentally by deuterium magnetic resonance spectroscopy.

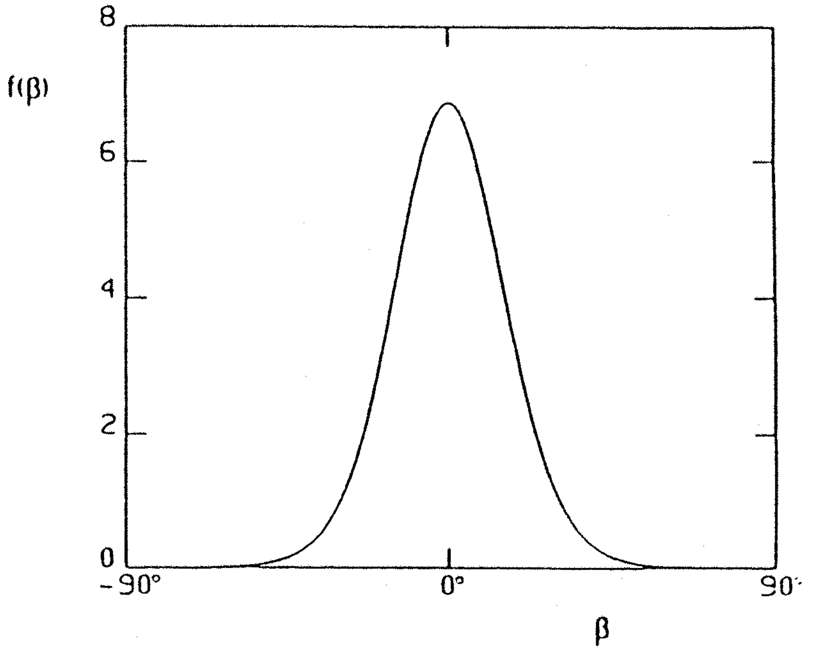


Figure 1. Singlet orientational distribution $f(\beta)$ for a rod-like molecule as a function of the angle between the molecular symmetry axis and the director.

1.2 Liquid Crystal Phases

The different kinds of liquid crystal phase can be distinguished by the types and degree of molecular organisation involved. Phases formed by calamitic systems will be described in this section and phases formed by discotic systems in the following section. Different liquid crystalline phases exhibit characteristic textures when viewed optically through crossed polarizers. The general features of these textures are outlined within this section. A more detailed discussion and photographs of textures are given by Gray and Goodby [4] and Demus and Richter [5].

1.2.1 Nematic

This represents the most disordered of the mesophases. There is no correlation between the molecular centres (i.e. the molecules do not lie on lattice points) but there is a tendency for the molecular long axes to lie parallel to the director axis. This form of molecular order is illustrated schematically in figure 1.2.1. In the absence of any external constraints the director axis will vary continuously throughout the phase. Two other kinds of nematic phase also exist, referred to as the normal cybotactic and skewed cybotactic nematics [6,7].

When viewed through crossed polarizers the nematic phase exhibits a thread-like, schlieren texture. The low degree of molecular ordering is reflected in the high mobility of the phase and if a sample is subjected to mechanical stress flashes may be observed. Point singularities exist from which black bands, or schlieren brushes originate. Two variations of this point singularity are possible, one having four associated brushes, the other only two.

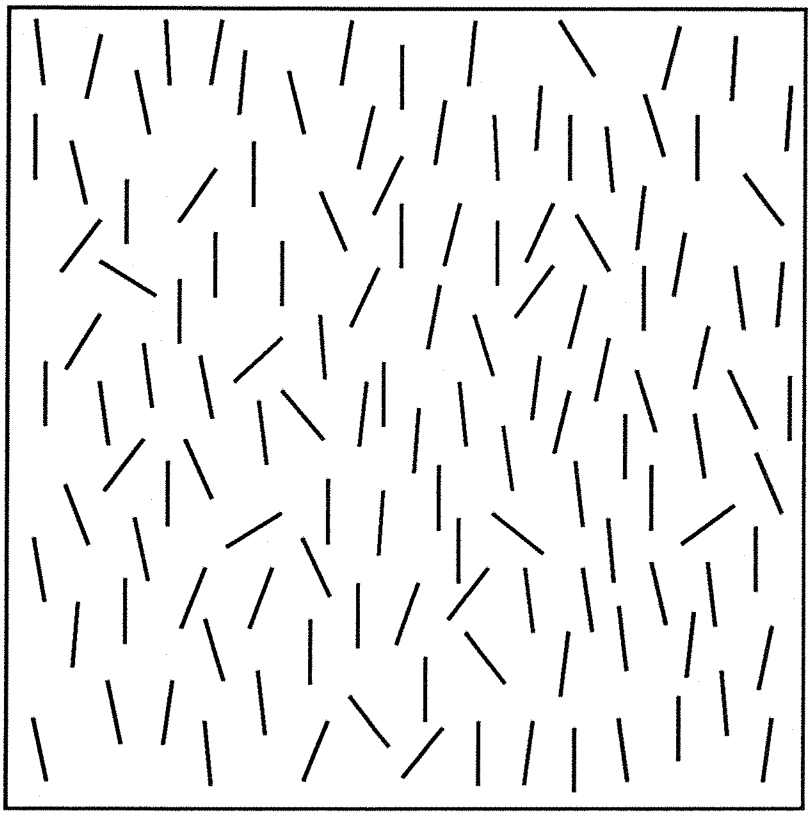


Figure 1.2.1 Molecular organisation within the nematic phase (idealised)

1.2.2 Cholesteric

This is a helical phase formed either by a chiral compound or by the addition of a chiral material to a nematic phase. The director does not lie parallel everywhere throughout the phase as in an aligned nematic, but rather is rotated through a constant angle on passing through the phase. The specific rotation of the molecules present will dictate the sense of the helix. This phase is also referred to as the chiral nematic.

1.2.3 Smectic Phases

This more viscous state has an ordering of the molecular long axes in common with the nematic phase. It also has an ordering associated with the molecular centres giving a layered structure. Different kinds of smectic phase have been discovered reflecting a variance in molecular arrangements within layers. These have been classified as S_A, S_B, S_C etc.

Before discussing these differing morphologies it is necessary to introduce the concept of bond-orientational order. It should be noted that in this context the word 'bond' does not relate to the conventional chemical bond, but rather the to a unit vector describing the lattice axis. If one considers an imaginary line drawn between two neighbouring centres of mass, relative to a fixed direction, an angle will be defined. It is then possible to conceive of a form of molecular ordering where the value of this angle remains constant throughout the phase, without necessitating the invocation of any actual positional long range order of the molecular centres.

Smectic phases exhibit two kinds of optical texture. A natural texture is formed when a smectic phase occurs on cooling from either the isotropic liquid or the nematic phase. If the smectic phase derives from another smectic then the resulting paramorphotic texture will be modified by the characteristics of the preceding phase.

Smectic A

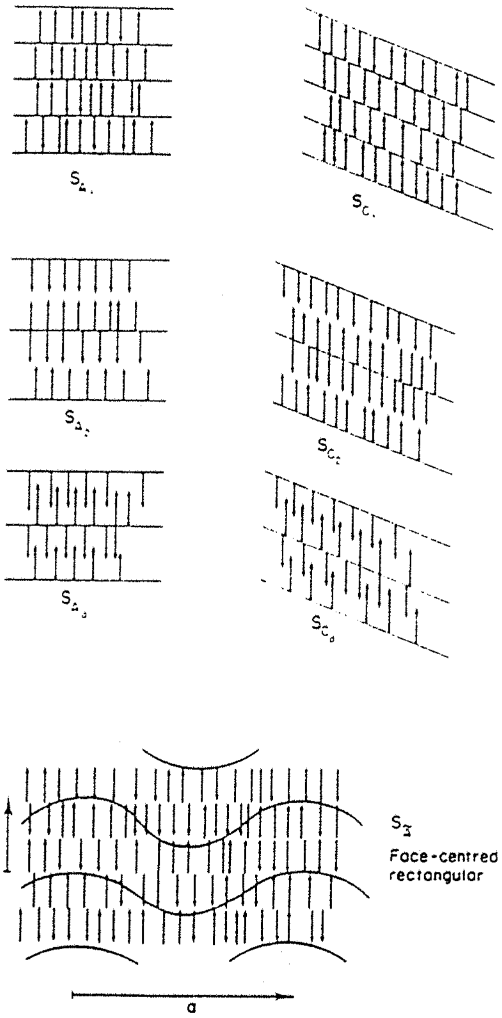
This is the least ordered of the smectic phases. The molecules lie within well defined layers. However, within the layers there is no correlation of the molecular centres of mass. The molecules lie approximately parallel to each other with the director lying perpendicular to the layer normal. Free rotation occurs about the molecular long axes and the phase is uniaxial in nature. Closer studies of the smectic A phase have revealed four differing modifications to the phase structure; namely the S_{A1}, S_{A2}, S_{Ad} and $S_{\tilde{A}}$. These are illustrated schematically in figure 1.2.3.1.

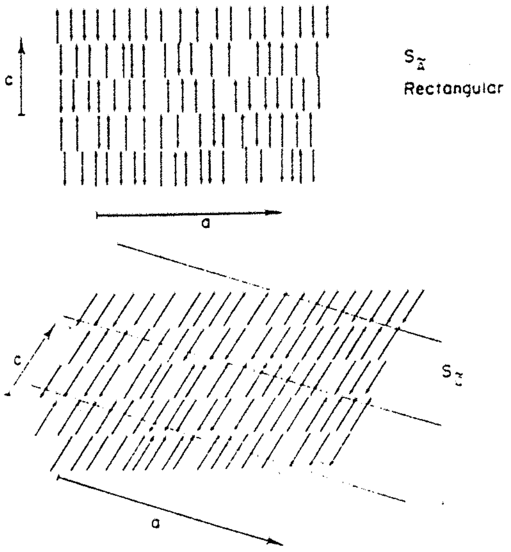
Molecules without strongly polar groups will tend to form the S_{A1} phase where no head to tail ordering of the molecules occurs. Layer spacings measured by X-ray diffraction give values equalling about 0.8 the length of the constituent molecules considered in their all-trans conformation. This may be attributed to two effects. Firstly, a conformational distribution of molecular configurations exists and secondly, as individual molecular axes deviate from the director alignment so the layer spacing will be decreased.

The S_{A2} phase has favourable head to tail correlations giving an antiferroelectric ordering. This results in a bilayer structure. The S_{Ad} is a semi-bilayer phase where only partial molecular associations occur.

The smectic A antiphase ($S_{\tilde{A}}$) can be regarded as having a ribbon structure where antiferroelectric ordering similar to that in the S_{A2} phase is modulated through the layer giving a two-dimensional molecular polarisation ordering.

The simplest natural texture of the smectic A phase is exhibited when the layer structure lies parallel to the slide surface giving a homeotropic alignment. Such alignment can be effected by, for example, chemically treating or cleaning the slide surfaces. Alternatively, a second texture may develop, initially by the formation of bâtonnets which merge to give a focal-conic fan texture.





1.2.3.1 Schematic representations of the differing smectic A and C phases.

Smectic C

This is analogous to the smectic A phase in having an associated one dimensional density wave describing molecular positional correlations. However, the preferred orientation of the molecular long axes is no longer perpendicular to the layer normal. The molecules lie at an angle, known as the tilt angle, which is measured with respect to the layer normal. There is a long range correlation of the tilt directors and free rotation about the molecular long axes. The smectic C phase is biaxial in nature and modifications of the structure similar to those in the smectic A phase are possible, giving rise to the S_{C1}, S_{C2}, S_{Cd}, $S_{\tilde{C}}$ phases (see figure 1.2.3.1).

The most commonly observed texture is the schlieren. This can be easily distinguished from the nematic schlieren by the absence of point singularities having two associated brushes. In addition the smectic C phase is more viscous than the nematic and will not 'flash' when stressed mechanically. The schlieren texture may appear sanded due to the point singularities and brushes being small and therefore blurred. The areas between the schlieren brushes may be lined. The focal-conic texture may occur either naturally or paramorphotically, the former being quite rare. The texture may appear broken and sanded, particularly when paramorphotic. A paramorphotic focal-conic texture will always be formed when preceded by a focal-conic smectic A texture.

Smectic B

In common with the smectic A phase the molecular long axes of the constituent molecules are oriented orthogonal to the layer planes giving a uniaxial phase. There is a two-dimensional ordering present; within a given layer a hexagonally close packed structure is formed, as illustrated in figure 1.3.3.2. The molecules move rapidly about their long axes. However, studies have shown [8] that the molecules lie too closely packed for free rotation to occur and so rotations occur cooperatively within the layer. There are no positional correlations between the layers, correlations within a layer are medium range, but three–dimensional long range bond-orientational ordering is present. This phase is often referred to as the hexatic B to distinguish it from the crystal B phase.

As with the other untilted phases the smectic B may exhibit a homeotropic texture. Additionally, natural mosaic or paramorphotic focal-conic fan textures may be formed. The mosaic texture appears as platelets or disks, which may have a uniquely identifiable 'H' shape. Generally these form within a homeotropic texture. The focal-conic texture has forms that are very smooth and defect free (c f. S_A, S_C). If the phase is formed from a preceding smectic A then at the transition between the phases bars appear across the backs of the fans. These transition bars also occur on heating the smectic B phase to the smectic A.

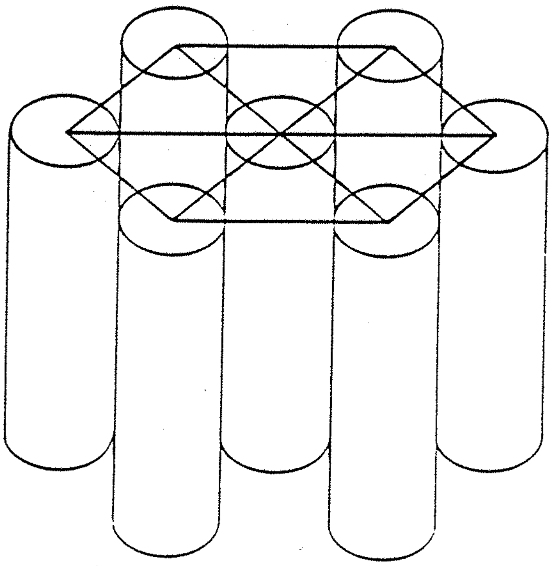


Figure 1.2.3.2 Schematic representation of the smectic B phase.

Smectics F and I

These two phases are very similar in nature. The molecules are arranged in a pseudo-hexagonal manner; the positional correlations within layers of the smectic F are only of the order of 100-150Å. There is a certain amount of debate as to whether the positional correlations within the layers of the smectic I phase are short range [9] or long range [10]. However both phases lack long range order between layers while retaining three-dimensional long range bond-orientational order. As shown in figure 1.2.3.3 the molecular long axes are tilted towards the edge of the quasi-hexagonal lattice in the smectic F and tilted towards the apex of the quasi-hexagonal lattice in the smectic I phase. Both phases are C-centred monoclinic with the smectic F having a>b and the smectic I a<b. As these phases are both tilted incorporation of chiral centres in constituent molecules will create a helical phase.

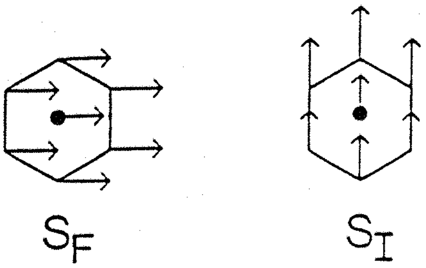


Figure 1.2.3.3 Schematic representation of smectics F and I illustrating the director tilt direction.

Natural textures of these phases are very uncommon, however both have distinctive paramorphotic phases. The focal-conic fan texture has broken fans with 'L' shaped dark patches. A schlieren texture is exhibited by both phases; the smectic F texture is crossed with mosaic lines.

1.2.4 Crystal Phases

These phases were originally classed as smectics and have only recently been described as crystal phases, the nomenclature reflecting their three-dimensional positional ordering.

Crystal B

This phase has long range layer correlations and positional long range order within a layer giving three-dimensional positional order. It is possible to distinguish differing stacking arrangements of these layers as in conventional crystallography.

Textures of this phase are similar to those of the smectic B phase.

Crystal G and J

Just as the smectics F and I may be regarded as tilted analogues of the smectic B phase then the crystal G and J phases may be regarded as analogues of the crystal B phase. The G phase has molecular long axes tilting towards the edge of the hexagonal net and in the H phase the molecular long axes tilt towards the apex of the hexagonal net. Close packing of the molecules prevents free rotation occuring about the molecular long axes but a reorientational motion about this axis is permitted [11]. Although the phase appears macroscopically to be hexagonal in nature, microscopically the structure is of a herring bone type with molecular dynamic reorientations about a six-fold axis giving rise to an average hexagonal array. Chiral molecules forming G and J phases have low optical activity, probably due to strong layer correlations [4].

Natural textures are of mosaic platelets, while focal-conic textures are either broken fan or arced broken fan in nature, depending on the texture of the preceding phase. A number of paramorphotic mosaic textures can be formed depending on the phase sequence leading to their formation.

Crystal E

The contraction of one six-fold axis of a smectic B hexagonally close packed layer structure gives rise to a 'herring bone' arrangement. This modification, illustrated in figure 1.2.4.1, gives rise to the crystal E phase. The phase is biaxial in nature, has three-dimensional long range bond-orientational order, two-dimensional long range positional order and correlations between up to 1000 layers. Experiments have shown that layer spacings are similar to molecular lengths, indicating an orthogonal arrangement of the molecular long axes. The molecules continue to move rapidly about their long axes, but rotations are less than 180°, producing a flapping motion. This rotational constraint is a result of molecular close packing. The E phase is therefore highly ordered with an orthorhombic cell structure.

Three paramorphotic crystal E structures have been noted, these being mosaic, focal-conic and platelet. The focal-conic is also described as the arced paramorphotic focal-conic fan texture as a result of the distinctive lines or arcs which cross the backs of the fans. This particular texture will form from a focal-conic smectic A or B texture. Cooling a homeotropic smectic A or B phase will give a platelet E texture, these platelets frequently appearing transparent. The mosaic texture will follow a mosaic smectic B texture with the mosaic platelets being crossed with parallel lines.

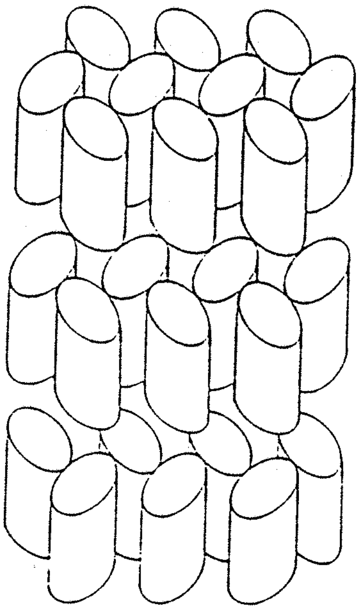


Figure 1.2.4.1 Schematic of herring bone packing in the E phase.

Crystal H and K

These phases both have a herring bone type structure, the molecules being tilted with respect to the layer normal. As such they are tilted analogues of the E phase (see figure 1.2.4.1). The H phase has the director tilted towards the edge of the pseudo-hexagonal lattice (a>b) and the K phase has the director tilted towards the apex of the pseudo-hexagonal lattice (a<b). In common with the E phase disordering is by rotation of π around the molecular long axes. Both phases form a monoclinic unit cell with two dimensional long range positional order, three-dimensional long range bond-orientational order, and long range correlations between layers. The last property diminishes the likelyhood of chiral phases exhibiting more than a modicum of optical activity.

Focal-conic textures may appear to be be of a broken or clear type. The mosaic textures formed by these two phases are more informative with respect to phase identification, despite the platelets formed varying greatly in appearance. As yet no natural textures have been reported for these phases.

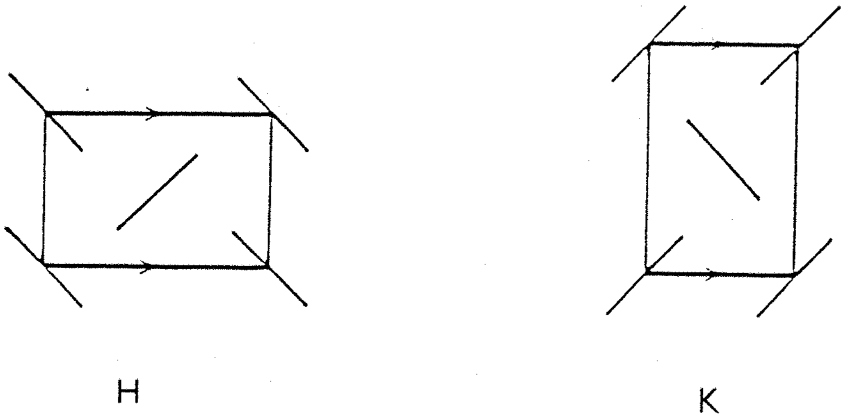


Figure 1.3.4.2 Director tilt in the Crystal H and K phases.

1.2.5 D Phase

Originally named the smectic D. This phase is thought to consist of three dimensional cubic networks of molecules similar to those postulated in lyotropic systems [12]. Very few examples of this phase have been reported and at least two differing modifications of this phase have been recognised [13,14]. Cubic phases are optically isotropic and therefore do not exhibit any textures. They are generally identifiable by their occurrence between other mesophases.

1.3 Discotic Phases

Discotic mesogens have been shown to exhibit a number of mesophases, reflecting the various degrees of ordering possible in these molecules. Two kinds of morphology can be distinguished, nematic and columnar.

1.3.1 Nematic

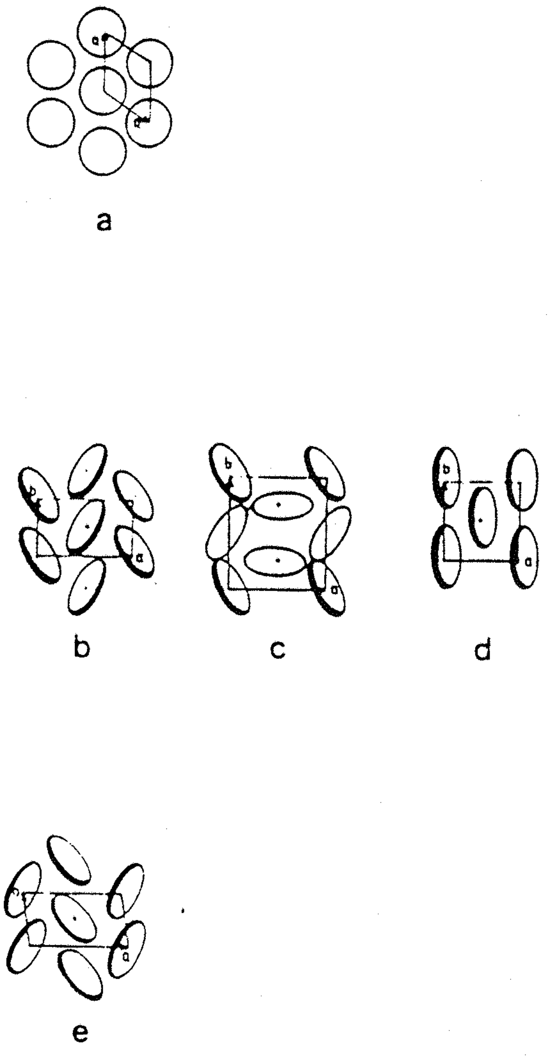
The disc-like molecules have a tendency to lie parallel, their short axes (the disc normal) lying parallel to the director. There is no positional or long range bond-orientational ordering in common with the calamitic nematic phase. Re-entrant behaviour has been noted [15] for discotic nematic compounds. Chiral discotic nematic phases have also been reported.

Optically, the discotic nematic, denoted N_D, exhibits a schlieren texture. Point singularities with both four and two associated brushes are present.

1.3.2 Columnar Phases

These phases have stacked columns of molecules, packed to give a two-dimensional array. Columnar discotic phases are labelled D [16], the different structures are characterised by the subscripts o representing ordered and d representing disordered. This order/disorder defines the stacking within a column. Further distinction is made by use of the subscripts h, hexagonal, r, rectangular and ob, oblique. All the columnar phases possess three-dimensional long range bond-orientational order. The symmetries of these phases are illustrated in figure 1.3.2.

It should be noted that columnar phases exhibited by polycatenar and phasmidic mesogens are denoted by the symbol ø to distinguish these phases from those formed by discotic liquid crystals.


a

b c d

e

Figure 1.3.1 Molecular organisation in the discotic columnar phases. a is hexagonal, b rectangular $D_{rd(P2_1/a)}$, c rectangular $D_{rd(P2/a)}$, d rectangular $D_{rd(C2/m)}$ and e oblique $D_{ob.d}$.

Hexagonal

Molecules forming these phases have two-dimensional positional long range order: the columns lie on a hexagonal lattice. The phase is uniaxial and both D_{ho} and D_{hd} phases have been identified. The D_{ho} is the most ordered of all the discotic phases having positional order in three dimensions.

Both phases give homeotropic textures optically. The D_{ho} phase occurs by the formation of digitated stars from homeotropic hexagons, finally coalescing into a mosaic of domains. [17]. The D_{hd} gives a natural texture that will grow in a similar manner to a crystal, with no mosaic domains. However, focal-conic textures are more frequently observed.

Rectangular

There are three structural modifications of this phase, denoted by the use of the following two-dimensional space groups; $P2_1/a$ (the most common), P2/a and C2/m. These are all tilted biaxial phases.

Textures of these phases are not easily distinguished, however the D_{rd} phase exhibits a texture similar to that of the calamitic crystal G phase.

Oblique

This phase is rarely observed and no general features of the optical textures have been reported.

1.4 Phase Transitions

Any phase transition can be classified according to its order. This concept is derived from consideration of the Gibbs free energy equation

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

At a transition the Gibbs free energy is zero and a first order transition displays a discontinuity in first derivative properties associated with this, see figure 1.4.1. Therefore the entropy and enthalpy of transition are non-zero and the heat capacity, a second derivative, will be infinite at the transition. These observations indicate that energy is being used to disorder the system while at the transition temperature (i.e a latent heat). The vast majority of transitions are first order in nature. A nematic-isotropic transition is weakly first order, i.e. there is a small change in entropy and enthalpy at the transition a reflection of the relatively low difference in molecular ordering between these two phases. In contrast a crystal-isotropic transition is strongly first order. The two phases have very different degrees of molecular ordering at the transition.

Second order transitions are continuous with respect to their first order derivative properties, having zero enthalpies and entropies of transition. This indicates a continuous changes in the ordering of the system during the transition. The S_C to S_A transition is usually second order; upon heating a sample in its S_C phase a continuous change in the tilt of the directors occurs until at the transition temperature the directors have aligned themselves perpendicular to the layer normal forming the smectic A phase. Second order quantities are discontinuous, i.e. the heat capacity changes at the transition.

The thermodynamic properties of a liquid crystal can be investigated by differential scanning calorimetry (DSC) which permits the determination of transition temperatures, enthalpies and entropies.

The differential scanning calorimeter supplies energy to two samples; one being that under study and the second a reference. An average temperature circuit in response to a preset time-temperature program controls this heating rate keeping the temperature of the two samples equal. However, when one sample undergoes a phase transition a temperature difference will develop between the sample and reference holders. A temperature difference circuit is employed to alter the power to the two heaters in order to maintain the temperatures equal. This power difference may be plotted with respect to time generating a peak if a first order transition is crossed. In effect, the machine measures the heat capacity of the material under study. By measuring the peak area (A), the enthalpy (H) of transition can be calculated using the equation

$$H = \frac{KRA}{WS}$$

where W= sample weight, K= machine calibration constant , R= range sensitivity and S represents the chart speed. Use of a calibrated standard (generally indium) allows K to be eliminated from the equation and thus the sample transition enthalpy can be calculated.

Empirically first order transition temperatures can be measured either by extrapolation of the leading edge of the peak to the baseline, or if the peak is broad, then by simply using the peak maximum. Strictly by definition, second order transitions have no enthalpy of transition but they do show a change in heat capacity evidenced by a step in the baseline of the DSC plot. The point at which the step reaches its half height is generally used to determine the transition temperature.

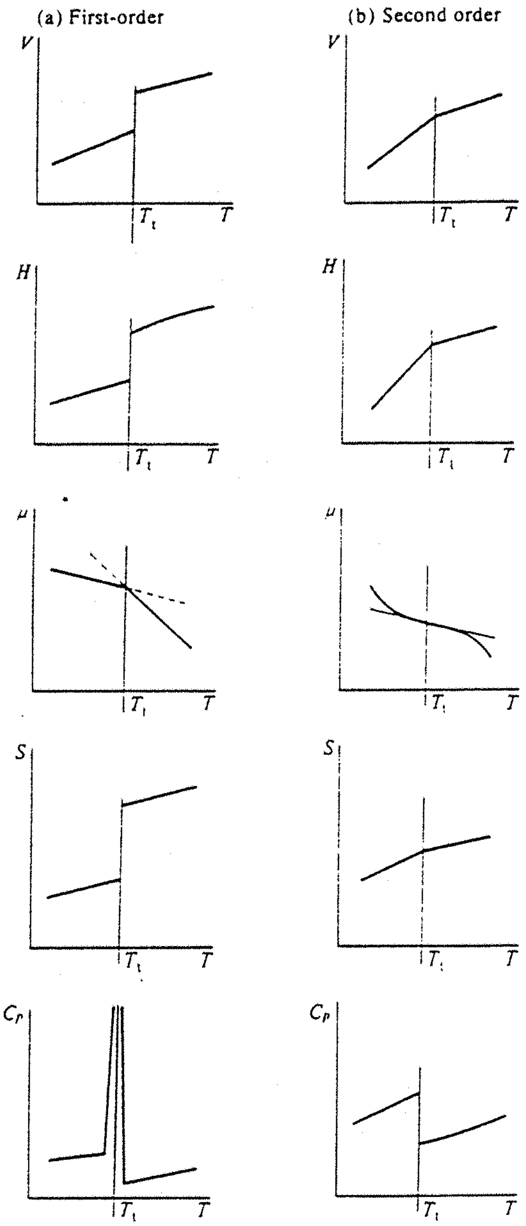


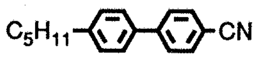
Figure 1.4.1 Changes in thermodynamic properties at first and second order phase transitions.

1.5 Structure-Property Relationships

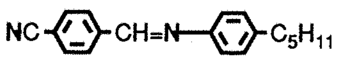
It has been estimated that about 20000 thermotropic liquid crystal compounds have been synthesised and that this number is increasing by around 1000 each year [17]. This vast amount of data has allowed empirical rules to be established on the structure-property relationships determining liquid crystalline behaviour. Due to a combination of early discovery and the relatively simple molecules involved the effects of structural modification are best understood in low molar mass rod-like mesogens. This information has more recently been complemented by the evolution of similar rules in polymeric and other, less conventional, mesogenic systems.

1.5.1 Low Molar Mass

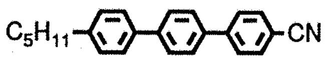
The conventional approach to the design of a calamitic liquid crystal is to have two terminally substituted aromatic rings linked by a rigid unit. The central joining unit generally consists of a multiply bonded system which extends the aromatic nature of the molecule. The advantages of such a linkage are twofold; firstly the anisotropic polarisability of the molecule is increased by conjugation, thereby promoting the tendency for the molecules to lie in a parallel direction. Secondly, this multiply bonded unit is unable to rotate freely, constraining the molecule in an extended semi-rigid linear form.



N-I 35°C.

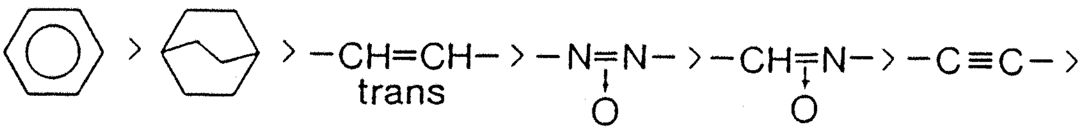


N-I 77°C.



N-I 239°C.

It is found that the use of these multiply bonded linkages will increase the temperature at which the mesophase-isotropic transition occurs. Similarly, increasing the number of aromatic rings increases the thermal stability of the mesophase. The relative abilities of these units to encourage mesogenic phase stability have been investigated by Gray [19] with the following sequence (greatest ability to stabilise a mesophase first) being generally followed.

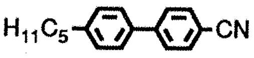


$-N{=}N- > -CH{=}N- > -CO.O- >$ none.

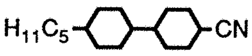
It may also be noted that carboxylic acid groups are capable of dimerisation by hydrogen bonding and so can also be regarded as semi-rigid linking groups. It is not necessary to incorporate aromatic units into a molecule in order to induce mesogenic behaviour, for example

C 53°C N 110.6°C I

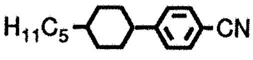
A comparison of the effects of non-aromatic ring incorporation in 4-n-alkyl-4'-cyano two ring systems has been carried out [20]. Considering the four mesogens



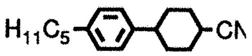
N-I 35°C.



N-I 85°C.



N-I 55°C.



N-I -25°C.

illustrates that in these systems use of cyclohexane rings increases mesophase stability. It is also found that use of the bicyclo[2.2.2]octane confers even greater mesophase stability than that exhibited by the illustrated examples. The relative stability of 4-cyano-(trans-4'-n-pentylcyclohexyl)-benzene relative to 4-n-pentyl-(trans-4'-cyanocyclohexyl)-benzene led to the suggestion that alternating regions of high and low polarisability along a mesogenic unit decreases liquid crystal stability compared to a mesogen having only one area of each polarisability.

Differing terminal substituents can have dramatic effects on the thermal stability of liquid crystal phases. Substituents which interact well with the aromatic system in the molecule by conjugation, for example the CN group, have the greatest effect as they further enhance the polarisability anisotropy of the molecule and so increase dispersion forces. Gray [19] has compiled a table showing the relative ability of a terminal group to increase the nematic-isotropic transition temperature.

Ph > $NHCOCH_3$ > CN > OCH_3 > NO_2 > Br > $N(CH_3)_2$ > CH_3 > F > H

The terminal groups which attract most interest are the alkyl and alkoxy chains. These tend to be incorporated in at least one of the terminal positions as they reduce the melting point of a crystal, producing an extension in or the appearance of a mesophase region. The most striking factor exhibited when studying the effect of such chains is seen in the alternation of the nematic-isotropic transition temperatures with respect to increasing chain length. This alternation attenuates with increasing chain length until it becomes a negligible effect. Figure 1.5.1 illustrates this effect for the homologous series the 4-alkyloxy-4'-n-cyanobiphenyls.

Nematic-isotropic transition temperatures of alkyl-substituted mesogens generally lie on two smooth curves. Members of a series having an even number of carbon atoms in an alkyl chain lie on a curve at lower temperatures than that drawn for odd members. Consideration of the distributions of alkyl chain conformers provides an explanation of this phenomenon. Conformations which increase the length to breadth ratio of a molecule will increase the stability of the nematic phase. For an n-alkyl mesogen, those members having an odd number of methylene units can adopt a greater number of conformations in which the molecular anisometry is increased. More importantly, these conformers are favoured by the nematic environment. Therefore when the transition to the isotropic liquid occurs the conformational entropy change would be greatest for alkyl chains having an odd number of constituent methylene units. This implies that nematic-isotropic transition temperatures increase with increasing chain length. However, it is found that for high clearing point nematogens the transition temperature decreases with increasing chain length and for low clearing point mesogens, below 100°C, increasing chain length increases transition temperatures. In the case of high clearing point mesogens the effect of core-core dilution by the hydrocarbon chains is most important.

Alkoxy groups demonstrate similar properties to alkyl groups with two differences. One is that odd members show the lower transition temperatures In comparison to the even members. The inclusion of the oxygen causes the terminal chain to begin at an angle to the core rather than the first methylene bond being along the molecular long axis.

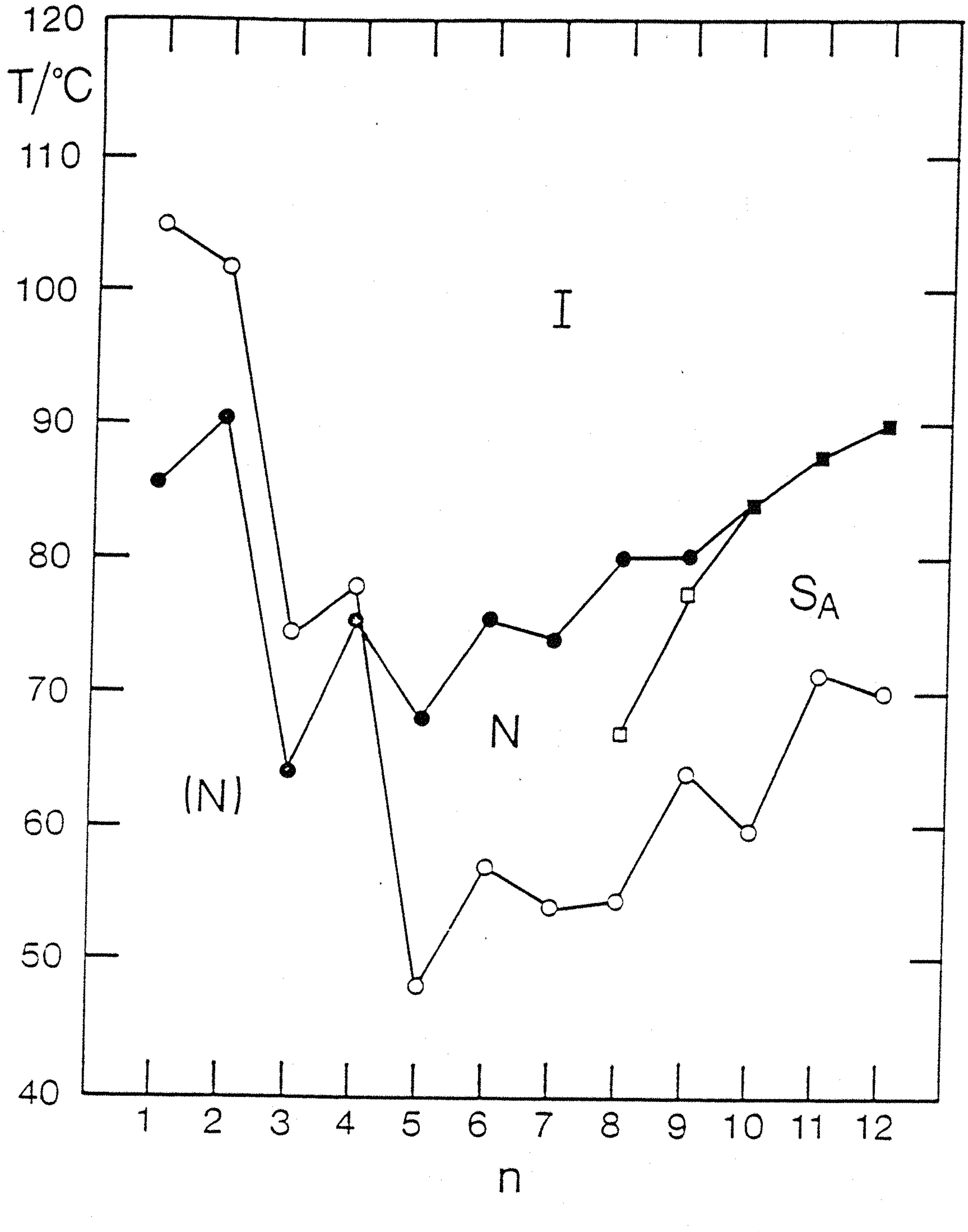
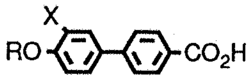


Figure 1.5.1 Transition temperature dependence on the number of methylene units in the terminal chain of the 4-cyano-4'-n-alkoxybiphenyls. Monotropic phases are shown in parentheses. ○ denotes the melting point, ● nematic-isotropic transition, ■ smectic A-isotropic transition and □ the smectic A-nematic transition.

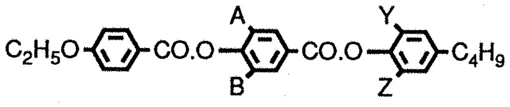
Secondly, for comparative systems alkoxy groups have nematic-isotropic transition temperatures some 30-40°C higher than alkyl terminal groups. This occurs due to the ability of the oxygen atom to interact with the conjugated aromatic system increasing the polarisability anisotropy of the molecule and therefore the stability of the mesophase.

An increase in alkyl or alkoxy chain length will tend to favour smectic behaviour in preference to nematic and will cause the eventual disappearance of the latter. This effect can be attributed to the interactions between the delocalised electron systems, these being energetically more stable than those between the aromatic systems and the alkyl chains.

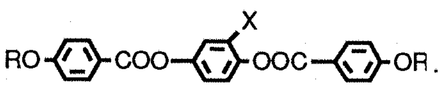
Lateral substitution of the mesogenic core in monomeric systems has been extensively studied. For example [21] in



it has generally been found that substituent size is the dominant factor: the larger the lateral substituent the greater the depression in clearing temperature that is effected. It is worth noting that the polarisability and polarity of the substituent group did not appear to be a significant factor in this respect. Exceptions to this rule have been reported. It has been shown [22] that in certain positions on the molecule

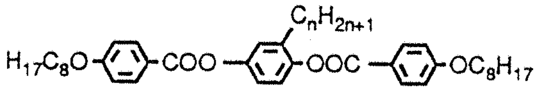


a methyl group could actually increase mesophase stability. This may be due to the lateral substituent having an 'interlocking' effect, thereby increasing mesophase order. Dewar et al. [23] reported similar findings for substitution on the mesogen



A lateral substituent may also promote mesogenic phase stability by an intramolecular interaction [24] which enhances the molecular anisometry. When considering systems having aromatics such as naphthalene incorporated then it may be that the substituent does not alter the molecular length to breadth ratio [19].

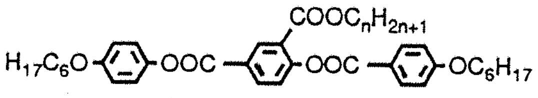
The effect of incorporating larger lateral substituents has also been investigated. For the series of 1,4-bis-(4-n-octyloxybenzoyloxy)-2-n-alkylbenzenes



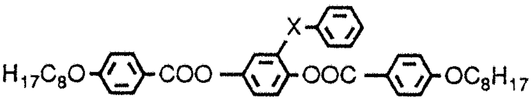
n= 1-16

varying n [25] showed that enantiotropic nematic phases could be formed even when lateral chains of up to 16 carbon atoms were incorporated. Further studies on these and other similar compounds [26] further confirmed that long chain substitution did not prevent mesogenic behaviour. These results were rationalised by the suggestion that the lateral chain adopts conformations which maintain a high length to breadth ratio in the nematic phase.

Imrie and Taylor [27] synthesised the series of 2,5-bis-(4-n-hexyloxybenzoyloxy)-benzoates



for n=1-12. It was also found that mesogenic behaviour could be maintained with long lateral chains. It was suggested that, although the results could be explained by postulating a conformational distribution favouring the lateral chain lying parallel to the molecular axis, such an assumption was not necessary. The reduction in nematic-isotropic transition temperature upon increasing chain length could be attributed to a dilution in core-core interactions. The effects of incorporating aromatic units [28,29] in the lateral chain of the diester



have been studied. For X=OOC$(CH_2)_n$ it was found that incorporation of the first methylene unit increased the nematic thermal stability by 33°C. Increasing n from 1-6 produced an odd-even effect (n=odd more stable) in the clearing temperatures (see figure 1.5.2). By using X=$COOCH_2$ and substituting the pendant aromatic unit smectic phases were formed for pBr, mNO_2, pNO_2 and pCN. Clearing temperatures for the latter two examples, and for the molecule X=$COOCH_2CHOH$ and pNO_2, were all greater than

150°C ; significantly higher than for unsubstituted pendant aromatic mesogens.

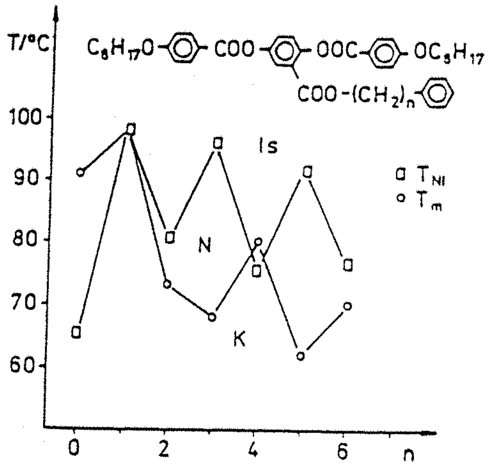


Figure 1.5.2 Transition temperature dependence on the spacer length for the homologous series the ω-alkylphenyl-2,5-bis-(4-n-octyloxybenzoyloxy)-benzoates.

It was also shown for the series X=$COOCH_2$ having p-alkoxy chains attached to the pendant ring enantiotropic nematic (n=1-10) and monotropic smectic C phases (n=4-10) could be formed. Clearing temperatures were essentially constant for all ten homologues (figure 1.5.3).

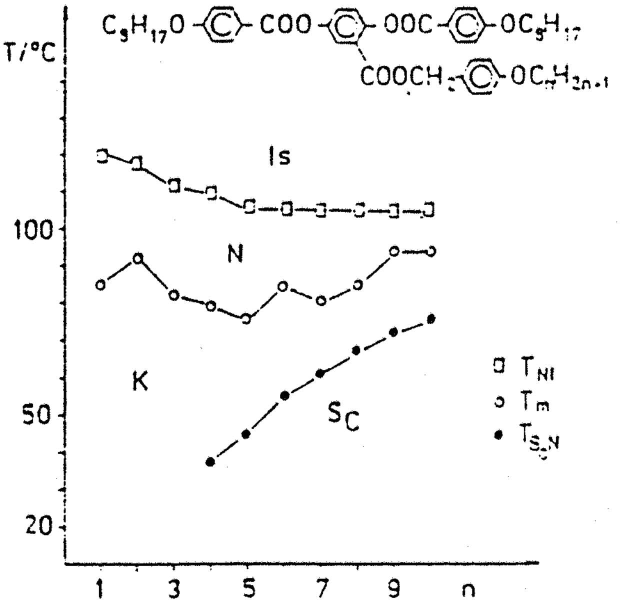
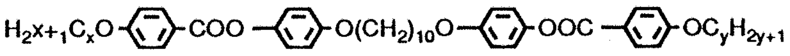


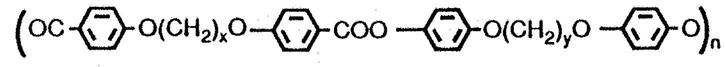
Figure 1.5.3 Transition temperatures versus alkyl chain length for the homologous series the 4-n-alkyloxybenzyl-2,5-bis-(4-n-octyloxybenzoyl-oxy)-benzoates.

1.5.2 Dimeric and Trimeric Liquid Crystals

Dimeric liquid crystals consist of two rigid units linked by a flexible chain. The mesogenic units utilised are identical to those in monomeric systems. The flexible linking units are most frequently aliphatic in nature. Such dimers were first synthesised by Vorlander in 1928 [30] and shown to be mesogenic. It was not until the technological importance of main-chain liquid crystalline polymers began to emerge that the impetus to investigate oligomeric systems developed. These oligomers could be used as model compounds in the investigation of properties of more complex polymeric analogues. Griffin and Britt [31] conducted the first such study, synthesising the symmetric dimers



The properties of these molecules were compared with those of the nematogenic polymers



and the monomers having the identical mesogenic core which had been previously reported.

Figure 1.5.2 shows clearly that the dimeric materials exhibit clearing temperatures significantly higher than those of the monomers and lower than those of the polymers. All three series exhibited an alternation in transition temperatures with respect to the aliphatic chain parity, even members being thermodynamically more stable than odd.

Jin et al. [32] synthesised a series of 1, 10-bis-(4,4'-disubstituted phenyloxy-carboxyphenyloxy)decanes in order to investigate the degree to which differing terminal substituents stabilised mesogenic phases. The terminal groups used were H, CH_3, Cl, CN, Ph and CHO and the results compared with those of analogous monomers [19]. The results gave excellent agreement in relative stabilising ability in comparison with monomers. Further studies into the effects of alkyl and alkoxy terminal chains have been

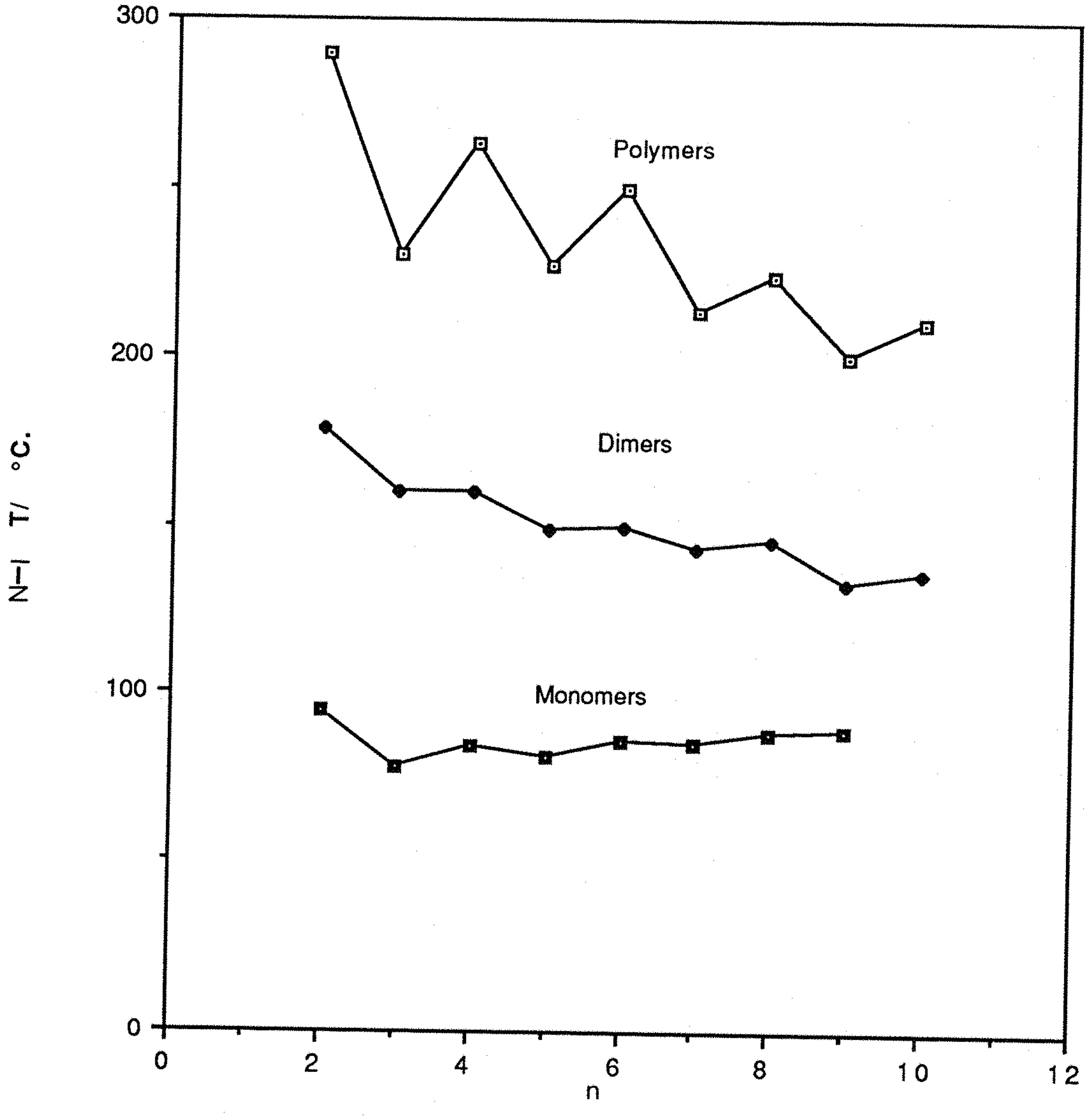
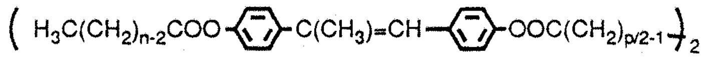


Figure 1.5.2 Transition temperature dependence on chain length of the alkoxy tail segment in analogous monomers, dimers and polymers [31].

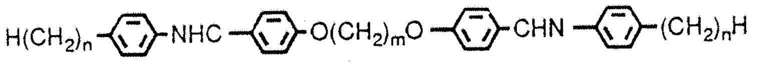
carried out. Jin et al. [33] studied the effect of terminal alkoxy chains on three sets of dimers, the α,ω-bis-(alkoxyphenyloxycarboxyphenyloxy)alkanes using pentane, hexane and decane central spacers. These compounds were compared with those of analogous polymers synthesised by the same group. The results revealed a very strong dependence of thermodynamic properties on spacer length for the polymers having n=10 and a less pronounced dependence for analogous dimers. Although transition temperatures for the dimers did not exhibit an obvious dependence on parity of the spacer, the enthalpies and entropies did show an odd even effect. It appeared that such a dependence was more pronounced for mesogenic dimers having a longer central spacer.

An analysis of the dependence of mesogenic properties on central spacer length was conducted by Emsley et al [34]. They studied the series of α, ω-bis-(4-cyanobiphenyl-4'-oxy)alkanes for the first twelve members. They found that all members were nematogenic, although the first and third members were monotropic. Nematic-isotropic transition temperatures, enthalpies and entropies of transition all exhibited a strong dependence on the parity of the central spacer chain. Members with an even number of carbon atoms in the spacer showed higher clearing temperatures and greater entropies/ enthalpies than odd members.

Homologous series having variations in both terminal and spacing chains have been synthesised. For the series [35]

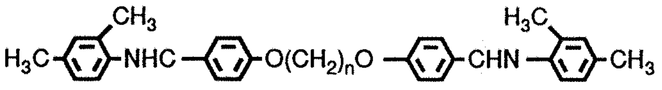


it was found that terminal chain parity had little effect on the thermodynamic properties at the liquid crystal-isotropic liquid transition, whereas the parity of the spacer had a significant effect. In common with monomeric materials increasing terminal chain length favoured smectic phase formation, conversely increasing spacer chain length favoured nematic phases. Studies on the series [36,37]



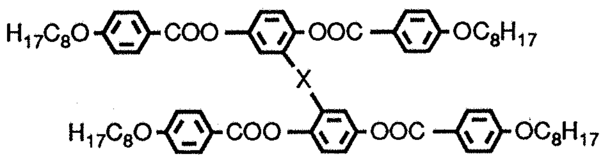
n=1-12, m=1-12

showed that both the terminal and spacer chain parities had significant effects on thermodynamic properties at the liquid crystal-isotropic transition. In these compounds only smectic phases were formed when the terminal length exceeded half that of the spacer chain. For the series having m=1, n=3-12 lateral methyl substitution



caused an average reduction in nematic-isotropic transition temperature of 57°C compared with unsubstituted analogues. Odd n members showed a greater $T_{N\text{-}I}$ reduction than even members, thereby accentuating the odd-even effect for these materials.

Dimeric materials have also been synthesised by lateral linkage, rather than terminally. This has been effected by the use of fused aromatics [39], rigid linkages [40] or by flexible linkages [41]. The latter compounds, based on the same parent system as the laterally substituted monomers described in 1.5.1 are of the form



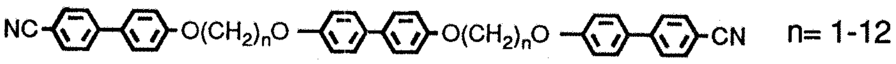
For X=CONH$(CH_2)_n$NHCO where n=1-12 all members were nematic, the first three exhibiting monotropic smectic C phases. Melting points and clearing temperatures both showed a dependence on chain parity.

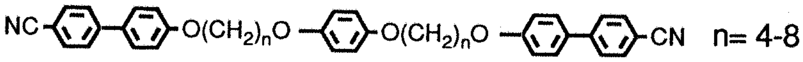
Compounds having aromatic units incorporated in the lateral linkage were also synthesised e.g.

X= $COOCH_2CH_2O$-(--)$_n$-OCH_2CH_2OOC n=1,2

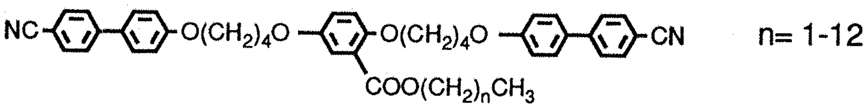
These molecules could be described as trimers, enantiotropic nematic phases being exhibited by both members. Nematic phases could also be formed when the linking aromatic unit (n=1) was substituted with Cl, Me, or C_2H_5, transition temperatures being depressed by ~15°C for the first two and by 29°C for the ethyl substituent.

More conventionally shaped trimers have also been synthesised. Two series [44,45] of the form





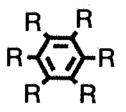
demonstrated that a central biphenyl unit increased transition temperatures by 50°C over a central phenyl unit. Nematic-isotropic transition entropy changes were strongly dependent on linking chain lengths. Attachment of a lateral chain [46] to the trimer

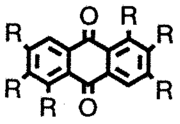


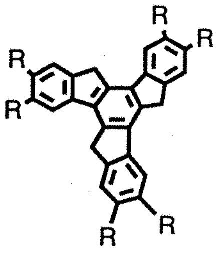
gave nematic-isotropic transition temperatures that were not dependent on lateral chain parity. Transition temperatures decreased with increasing chain length and entropy changes at the nematic-isotropic transition were found to be virtually independent of chain length.

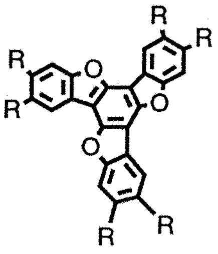
1.5.3 Discotic Liquid Crystals

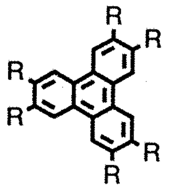
Discotic mesogens were first reported in 1977 [46] when Chandrasekhar et al. synthesised the benzene hexa-n-alkanoates using from butyl to nonyl chain lengths. All but the first and last members exhibited mesophases having the columnar structure identified as D_{hd}. This synthesis actually represented the rediscovery of these systems, the same compounds having been synthesised some 50 years earlier [47]. Since 1977, extensive research into the structure and properties of this new form of mesogenic system has been undertaken. The most commonly reported materials consist of a flat, rigid core; benzene, triphenylene, truxene, trioxatruxene or anthraquinone being the usual choice. To this unit are attached six flexible aliphatic chains, normally via an ether or ester linkage.











These compounds generally require at least three carbon atoms in each of the aliphatic chains to effect mesogenic behaviour. These flexible units, by reducing melting points increase mesophase accessibility, a phenomenon well established in calamitic systems. Materials that do not require this dense paraffinic crown are the scyllo-inositol hexaesters which exhibit mesogenic behaviour for the acetyl, propionyl and butyroyl derivatives [48].

Investigations into the conformations of the pendant chains of discotic materials synthesised to this stage has produced interesting results. Generally no dependence on chain parity is evidenced. X-ray diffraction studies [49,50] suggest high conformational freedom in the chains. It has been suggested [51] that for the hexa(hexylthio)triphenylene compounds the D_{hd}->D_{ho} transition is driven by increased chain stiffness in the latter phase. Studies on a number of truxene derivatives suggest that on average chains lie in a plane perpendicular to the column axis [52]. In contrast to this are studies [53] on the hexaalkoxytriphenylenes, results of which led to the postulation of a 'diabolo' type structure for short chain homologues and a 'tubular' structure, see figure 1.5.3.1, for longer chain members. Deuterium magnetic resonance spectroscopy investigations carried out on members of this series [54] showed evidence for the etheric COC bond lying normal to the disk plane.

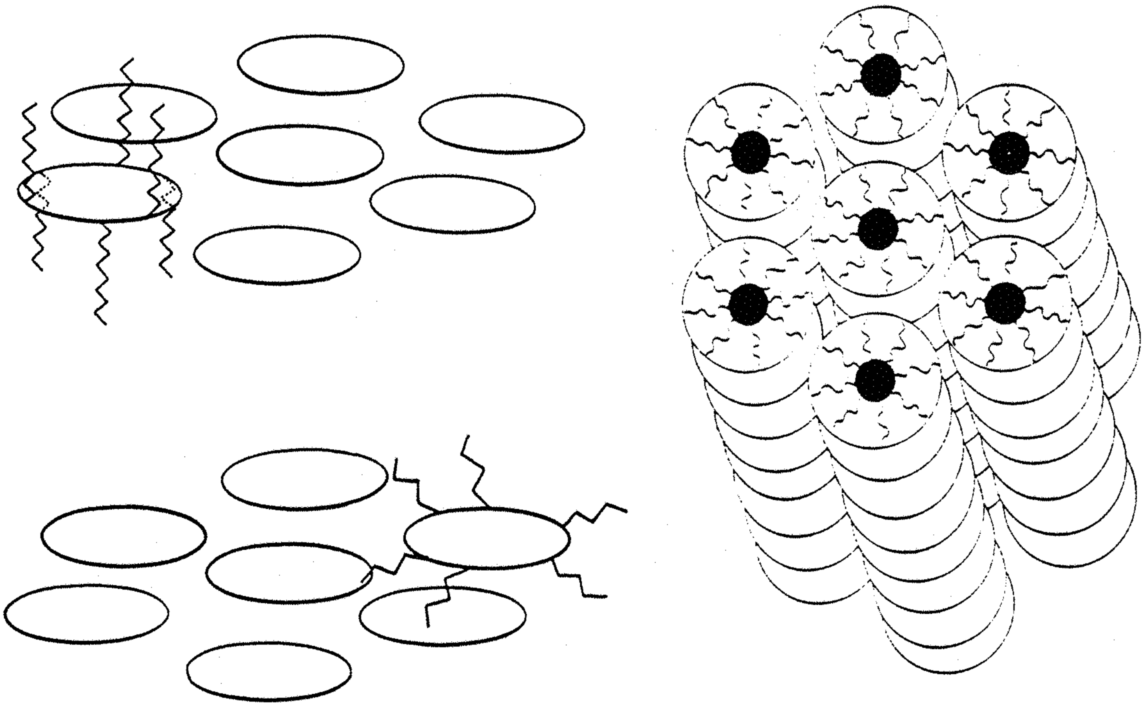
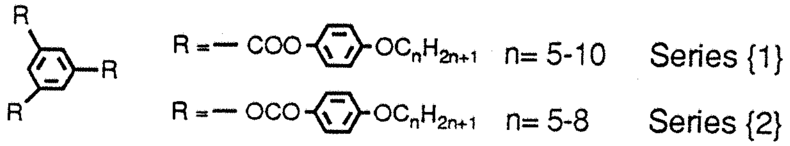


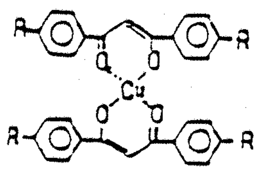
Figure 1.5.3.1 Tubular and diabolo type structures postulated for the hexasubstituted triphenylenes (left) and schematic of discotic mesophase having pendant chains in plane (right).

A number of 1,3,5-trisubstituted benzenes have been synthesised. The 1,3,5-tris-(3',4',5'-tri-n-decyloxybenzoyloxy)benzene [55] exhibits a monotropic columnar phase D_{ho} and an analogous compound using a central cyclohexane ring forms an enantiotropic D_{ho} phase between 31 and 61°C. The series of 1,3,5-tris-(4-n-alkyloxy-benzoyloxy)benzenes {1} have been shown to be mesogenic exhibiting discotic nematic phases [56], reaffirming the observation that the absence of a dense paraffinic region around a mesogenic core does not preclude mesogenic behaviour.

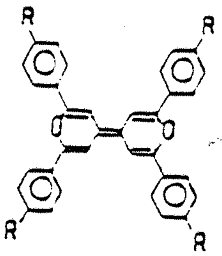


The nematic phases are all monotropic in nature. Reversing the ester linkages by using a 1,3,5-benzene triol derivative {2} gave a series of non-mesogenic homologues (n=5-8). This was attributed both to the greater flexibility of the side chain aryl groups in {2} and to increased population of the dissymmetric conformer compared with {1}. Discotic cholesteric phases have been exhibited by tri-substituted benzenes having cholesteryl and ß-sitosteryl as attached units [57].

Heterocyclic systems [58] and organometallic complexes [59] have both been used to produce discotic mesophases.



R = n- $C_{10}H_{21}$ -



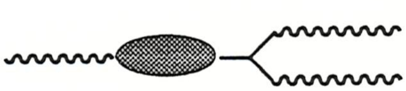
R = n - C_nH_{2n+1} -

1.5.4 Unconventional Structures

The existence of two very different forms of mesogenic material (discotic and calamitic) has prompted investigations into molecular structures that deviate from the classical rod- or disc-like shape. A number of novel liquid crystalline materials have arisen from such investigations, some of which have proved capable of forming both lamellar and columnar phases at varying temperatures.

One form of architectural change investigated has been the number of aliphatic chains attached to a mesogenic core.

Swallowtailed [60] and forked mesogens [61] of the general shape



have both been shown to form lamellar phases. X-ray diffraction studies [62] on the homologous series, the di-n-alkyl-4-[-4-(4-n-octyloxy-benzoyloxy)-benzoyloxy]benzylidenemalonates [63] gave evidence for strings of interdigitated molecules within the smectic phase (figure 1.5.4.1).

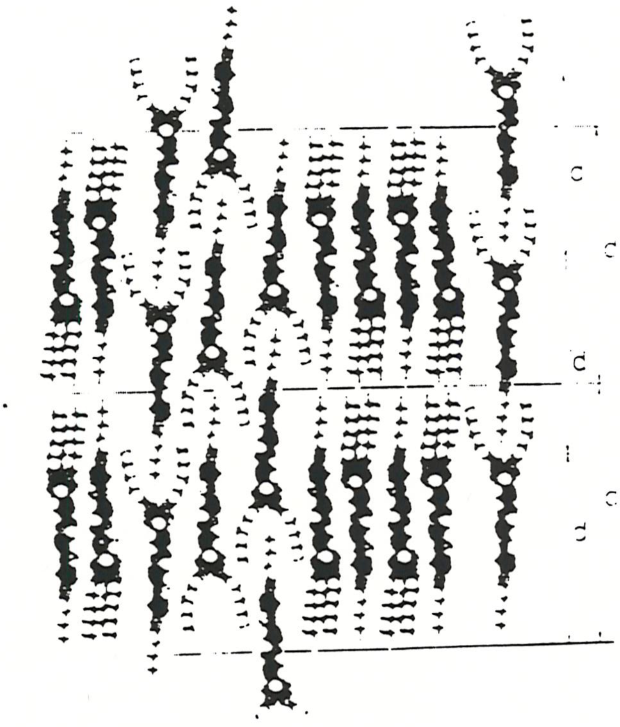
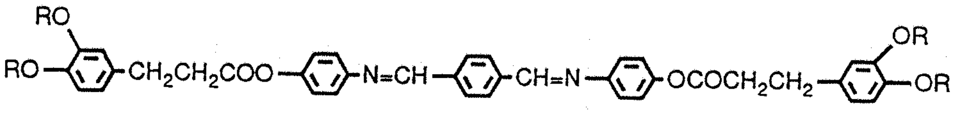
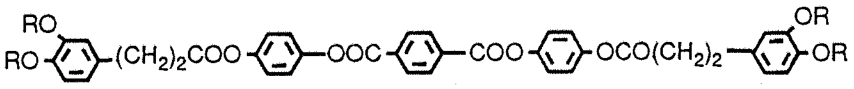


Figure 1.5.4.1 Interdigitated molecules within the smectic A phase of the di-n-alkyl-4-[-4-(4-n-octyloxy-benzoyloxy)benzoyloxy]benzylidenemalonates.

The introduction of an additional terminal chain, giving biforked or bi-swallowtailed molecules leads to a much more complex polymorphism where members of a series can form lamellar, cubic and columnar phases, for example, the following series:



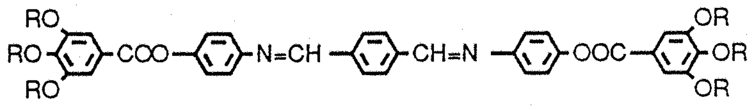
Series One



Series Two

The lamellar phases formed by these molecules were smectic C in nature. In the case of the second series it was found that the first two members (n=7,8) exhibited smectic C phases. The remaining homologues exhibited either $Ø_{ob}$ or $Ø_{h}$ phases suggesting that increasing aliphatic chain length promoted columnar phases. Increasing chain lengths had little effect on the melting (121-125°C) and clearing temperatures (137-139.5°C). Similar trends were exhibited in series one.

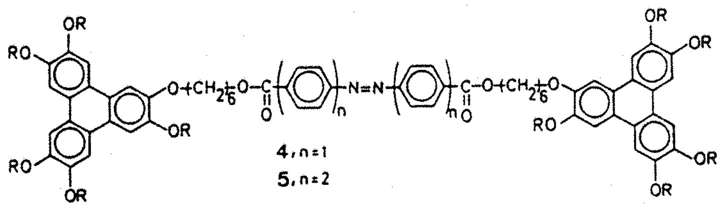
Phasmidic mesogens having a rod-like 5 ring core and 3',4',5'-trialkoxy-substituted end groups have been synthesised [64].



These molecules can be considered as having half-disk end groups. For the two mesophases exhibited a lamello-columnar structure was postulated for the $Ø_{ob}$ phase and a hexagonal columnar structure for the $Ø_{h}$ phase. Praefke et al. [65] synthesised the 2,3,4-trihexyloxycinnamic acid, which exhibits a biaxial nematic phase. A number of derivatives of the 3,4,5-tris-(4-n-dodecyloxybenzoyloxy)benzoyloxy molecule have been shown to exhibit discotic phases [66].

Alterations to the mesogenic core structure have also been investigated. A cross-shaped molecule, 1,2,4,5-tetra-(4-n-butyloxyphenylcarboxyoxy)-benzene [67] exhibits a monotropic nematic phase. Three members of the series, the tetra-(4-n-alkoxyphenyl)tetrathiafulvenes [68] having pendant, butyl, octyl or decyl aliphatic chains were found to be non-mesogenic.

Several compounds having both discotic and rod-like cores linked by flexible spacers have been reported [69]. One example is the molecule



4, n=1
5, n=2

which gives a mesophase having the rod-like segments ordered in a smectic like manner and the discs in a hexagonal columnar array. When the discotic units were bound laterally to the rod-like core, rather than terminally, no liquid crystal phases were formed.

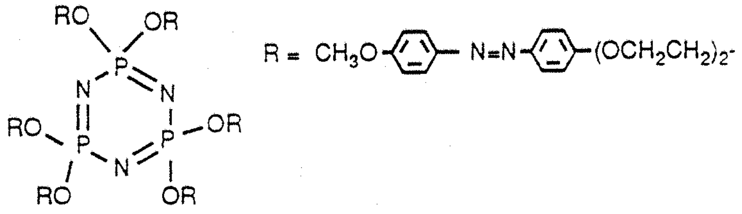
CHAPTER TWO

2.1 Introduction

Since the discovery of discotic mesogens in 1977 interest has arisen into the differing kinds of molecular architectures that are capable of stabilising liquid crystal phases. In the present work novel series of mesogens are synthesised and their mesogenic properties investigated.

Discotic phases can be formed by benzene rings having six pendant paraffinic chains attached by various linking groups. Discotic phases may also be formed by a number of benzene-1,3,5-trisubstituted derivatives. The 3',4',5'-trialkoxy(benzoyloxy)benzenes form monotropic D_{ho} phases. Takenaka et al. [56] have shown the 1,3,5-tri-(4-alkoxyphenoxycarbonyl)-benzenes to exhibit discotic nematic phases.

The cyclic trimer, polymer precursor [70] having six rod-like mesogenic units linked to a cyclic core by flexible spacers

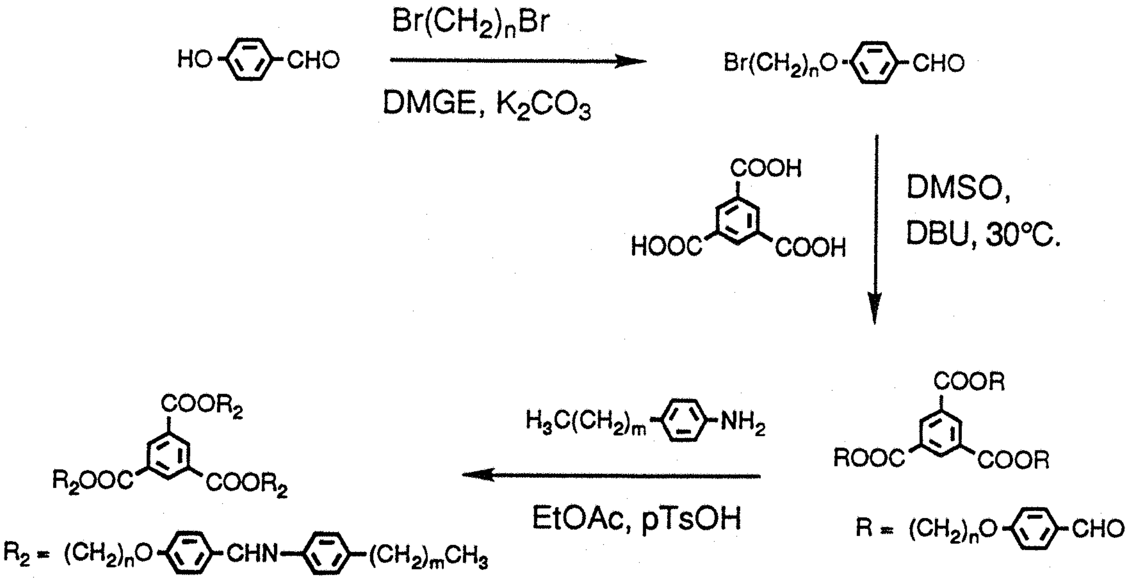


exhibits a monotropic nematic phase, although it was not stated whether this was calamitic or discotic in nature. Recently, a molecule having a tetrahedral centre and four pendant mesogenic units has been shown to exhibit smectic A phases [71]. The authors suggested conformational distributions of the linking aliphatic chains that preserved a high length to breadth ratio.

It was therefore proposed to take a 1,3,5-benzenetricarboxylic acid unit and attach to this three benzylidene-p-n-alkylaniline units via flexible aliphatic spacers of varied length. This preserves a structure of high symmetry (three fold axis), a feature suggested to be important in the formation of discotic phases, although the flexible spacers between the rigid units will permit a large number of conformers, very few of these being of high symmetry. The benzylidene-p-n-alkylanilines are chosen as they have been shown to be effective rod-like mesogenic units [72]. The spacer chain between the core and the pendant mesogenic units allows the possibility for the molecule to adopt conformations which give a high length to breadth ratio. This form of conformational distribution has been suggested as the reason for mesogenic behaviour in liquid crystals possessing a rod-like core and large lateral substituents.

2.2 Experimental

The reaction scheme for the synthesis of the benzene-1,3,5-tri-(4-carboxy-alkoxybenzylidene-4'-n-alkylanilines) involves three steps:



4-n-Bromoalkoxybenzaldehyde

A mixture of α, ω-dibromoalkane (0.4mol), 4-hydroxybenzaldehyde (.04mol, 5g) and anhydrous potassium carbonate (0.28mol, 39.6g) were refluxed with stirring for six hours in dry diethylene glycol dimethyl ether[1] [DMGE] (50ml). (The DMGE was dried by standing over sodium hydroxide and then refluxing with calcium hydride).The hot mixture was then filtered and washed with (4x50ml) portions of hot absolute ethanol. The ethanol was subsequently removed on a rotary evaporator. Both the diethylene glycol dimethyl ether and dibromoalkane were removed by distillation using a Kugelrohr short path distillation apparatus. The product was then distilled and purified by column chromatography (50/ 50 diethyl ether: 60:80 petroleum ether). Yields were in the range 60-70%.

[1] Absolute ethanol was used as solvent initially. However, it was found that alkylation of the ethanol occurred during reaction.

n	Bp. °C./ 5mm Hg.
3	100
4	130
5	155
6	180

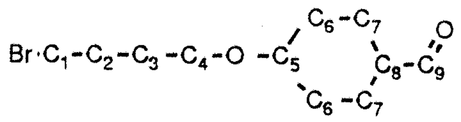
Table 2.1 Boiling points of the 4-n-bromoalkoxybenzaldehydes.

The products were characterised by infra-red and n.m.r. spectroscopy.

1-Bromobutyloxybenzaldehyde

I.R. υ 1690 cm^{-1}.

^{1}H-n.m.r. ($CDCl_3$) δ 1.7-2.2 (4H, m), 3.4 (2H, t), 4.0 (2H, t) 7.0 (2H, d), 7.8 (2H, d), 9.8 (1H, s) ppm.



Carbon	δ (ppm).
1	33.10
2	27.26
3	28.93
4	66.89
5	163.37
6	114.32
7	131.37
8	129.52
9	189.95

Table 2.2 ^{13}C-n.m.r. assignment of 1-bromobutyloxybenzaldehyde ($CDCl_3$).

Benzene-1,3,5-tri-(4-carboxyalkoxybenzaldehyde).

The reaction was carried out using a method adapted from that of Nishikubo et al. [73]. Benzene-1,3,5-tricarboxylic acid (.01mol, 2.36g) was dissolved in dry dimethyl sulphoxide (50ml) and 1,8-diazabicyclo-(5.4.0)-undec-7-ene (0.034mol, 5.13g) added. The solution was stirred for ten minutes and then the 4-n-bromoalkoxybenzaldehyde (0.037mol) added. The reaction was stirred for 8 hours at 30 °C, poured into ethyl acetate (200ml), washed with water (4x100ml), sodium carbonate solution (3x100ml) and dried over magnesium sulphate. The ethyl acetate was removed on a rotary evaporator and the unreacted 4-n-bromoalkoxybenzaldehyde removed by vacuum distillation. The product, generally a viscous oil, was characterised by infra-red and n.m.r. spectroscopy.

Benzene-1,3,5-tri-(4-carboxypentyloxybenzaldehyde)

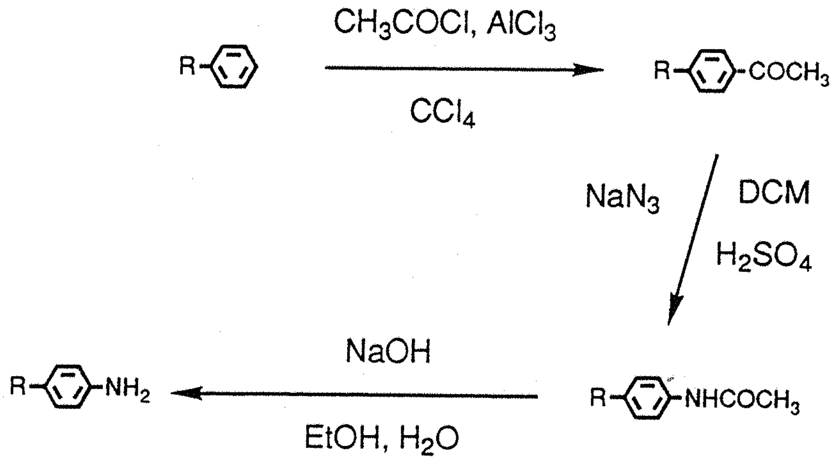
I.R. υ 1690, 1726 cm^{-1}.

^{1}H-n.m.r. ($CDCl_3$) δ 1.6-1.9 (18H, m), 4.0 (6H, t), 4.2 (6H, t) 7.2 (6H, d), 7.8 (6H, d), 8.9 (3H,s) 9.8 (3H, s) ppm.

^{13}C- n.m.r. ($CDCl_3$) δ 190.8, 165.0, 164.2, 134.6, 132.1, 131.5, 130.0, 114.9, 68.1, 65.7, 28.8, 28.6, 22.8 ppm.

4-n-Alkylanilines

These were all available commercially from either Aldrich or Lancaster Chemical Companies, excepting 4-n-nonylaniline. This was synthesised via the route



using the method described by Keller and Liebert [74].

2.3.2 Benzene-1,3,5-tri-(4-carboxyalkoxybenzylidene-4'-n-alkylanilines)

The benzene-1,3,5-tri-(4-carboxyalkyloxybenzaldehyde) (0.001mol) was dissolved in dry ethyl acetate (20ml). Freshly distilled 4-n-alkylaniline (0.004mol) and catalytic amounts of p-toluenesulphonic acid were added and the solution stirred for 9 hours at room temperature. The resulting precipitate was filtered off. The product was purified by heating under reflux in ethanol, followed by filtration to remove insoluble impurities and recrystallisation from toluene/ ethanol. Products formed using benzene-1,3,5-tri-(4-carboxybutyloxybenzaldehyde) and anilines of terminal chain length greater than three carbons could not be recrystallised due to gel formation. A number of solvent and solvent/ non-solvent mixtures were tested (e.g. ethyl acetate, ethyl acetate/ dichloromethane, toluene, toluene/ hexane, toluene/ acetonitrile, dichloromethane/ ethanol.) with similar results. Yields were in the range 50-75%. The products were characterised by n.m.r. spectroscopy.

Benzene-1,3,5-tri-(4-carboxypentyloxybenzylidine-4'-n-butylaniline)

^{1}H-n.m.r. ($CDCl_3$) δ 0.9 (9H, t) 1.2-2.1 (30H, m), 2.6 (6H, t), 4.0 (6H, t) 4.5 (6H, t) 7.0 (6H, d), 7.3 (12H, m) 7.8 (6H, d), 8.4 (3H, s) 8.9 (3H, s) ppm.

^{13}C- n.m.r. ($CDCl_3$) δ 165.0, 161.6, 158.7, 149.9, 140.4, 134.5, 131.5, 130.4, 129.4, 129.0, 120.8, 114.7, 67.8, 65.6, 35.2, 33.7, 28.9, 28.5, 22.7, 22.4, 14.0 ppm.

Thermal Characterisation of the Benzene-1,3,5-tri-(4-carboxyalkoxybenzylidine-4'-n-alkylanilines)

The thermal behaviour of the products was investigated using a Perkin-Elmer DSC-2 differential scanning calorimeter calibrated with an indium standard. The optical textures of the mesophases were studied using an Olympus BH-2 polarising optical microscope equiped with a Linkam hot stage.

2.3 Results and Discussion

For simplicity the homologous series of compounds discussed in the remainder of this report will be referred to in the form [n,m] where n represents the number of methylene units in each spacer chain and m represents the number of methylene units in each terminal chain.

Series [3,m]

The transition temperatures and thermal data for this series are given in table 2.3.1. The first three members exhibit monotropic nematic phases, these being assigned by their characteristic highly mobile, schlieren texture which flashes when mechanically stressed. Higher homologues are all smectic in nature; [3,4] and [3,5] exhibit smectic A phases, identified by the focal-conic fan and homeotropic texture. The remaining members of the series form smectic A phases and a second unidentified smectic phase, denoted S_1. The texture of this latter phase shows heavily broken and lined focal conics and grey broken platelet regions in areas that were previously homeotropic, indicating a tilted or E phase.

m	C-/ °C	N-I/ °C	S_A-I		S_1-S_A	
			T/ °C	ΔS/ R	T/ °C	ΔS/ R
1	153	(124)				
2	153	(113)				
3	160	(125)				
4	156		(130)			
5	158		(154)	4.29		
6	153		161	4.90	(135)	
7	151		170	5.47	(138)	1.40
8	146		174	5.49	(140)	1.45
9	145		176	5.70	(141)	1.42
10	141		177	5.72	142	1.60
12	135		179	5.73	143	1.72

Table 2.3.1 Transition temperatures and entropies of the [3,m] series, ( ) denotes a monotropic transition. The uncertainties in the entropy readings are ±10% and in the transition temperatures ±1.5°C.

Figure 2.3.1a shows the dependence of the transition temperatures on the terminal chain length. The cross-over from nematic to smectic behaviour with increasing terminal chain length is in accord with general observations [19] and can be attributed to increased molecular inhomogeneity favouring a layered structure. The thermal stability of the smectic phases increases rapidly and then levels off with increasing m. This behaviour is similar to that found in monomeric systems having low transition temperatures but anomalous for high transition temperature liquid crystals. This point will be discussed more fully later. The S_1 phase shows a slight increase in transition temperatures on increasing the terminal chain length. Melting points initially show little dependence on terminal chain length and then gradually decrease on ascending the series.

Figure 2.3.1b shows the dependence of the entropies of transition on the terminal chain length. These values could not be obtained for the first four homologues due to the onset of crystallisation, but for the remaining members the trends of the transition temperatures are followed. The S_1-S_A transition entropies increase gradually. Those for the S_A-I transition rise and then stabilise at around 5.7. These values would appear to be high and an explanation for this will be given later.

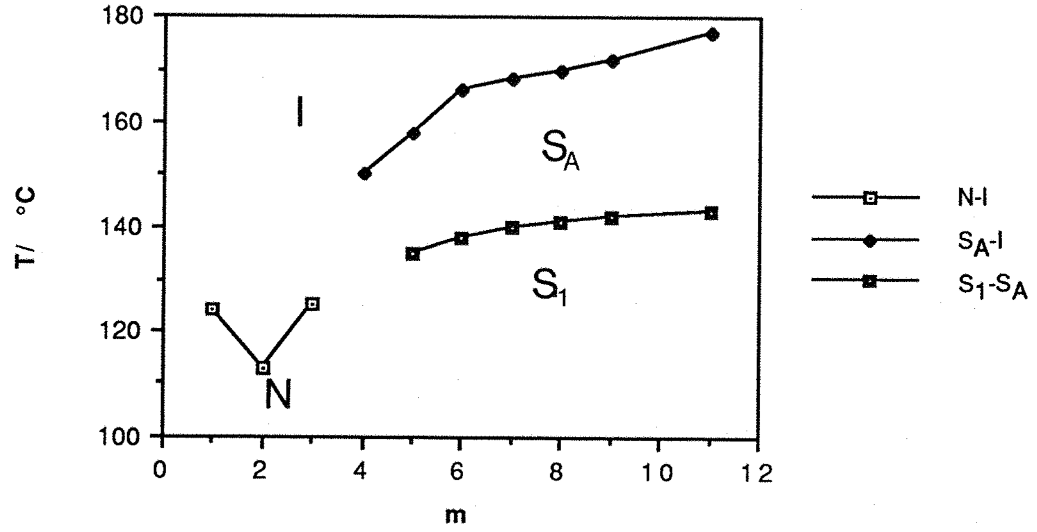


Figure 2.3.1a Transition temperature dependence on terminal chain length for the [3,m] series.

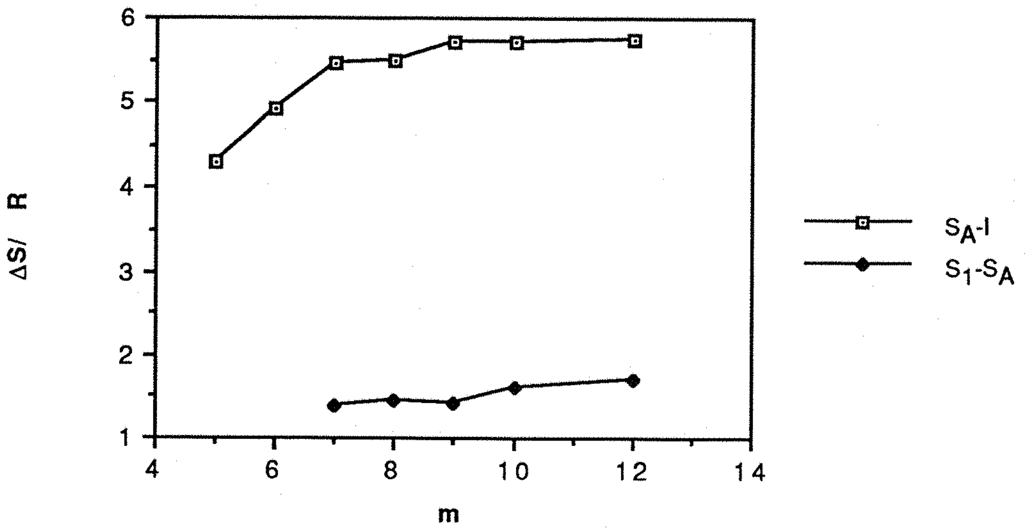


Figure 2.3.1b Entropy of transition dependence on terminal chain length for the [3,m] series.

Series [4,m]

The transition temperatures and thermal data for this series are shown in table 2.3.2. The first four homologues exhibit monotropic nematic phases, [4,3] and [4,4] also exhibiting monotropic smectic C phases. The S_C phases were identified on the basis of their focal conic and schlieren texture, only schlieren textures having four associated brushes were present, in contrast to the nematic phases which exhibited schlieren textures having both two and four associated brushes. [4,5] and [4,6] were solely smectic C, [4,7] and [4,8] displayed smectic A, smectic C and an unidentified smectic phase, denoted S_2, at temperatures below those for the S_C. In the S_2 phase texture the focal-conics exist merely as broken remnants. In addition regions of well defined grey platelets are present (formed in previously schlieren areas), possibly suggesting a S_F phase. However, this is a only a very tentative assignment. Higher homologues exhibit the S_A and S_2 phases and in addition a low temperature smectic phase denoted S_3. This was recognised by a break up of the platelet texture which became less well defined.

The transition temperature dependence on terminal chain length is shown in figure 2.3.2a. The nematic phase temperatures of transition rise slightly and are superceded by smectic phases which rise rapidly in stability and then stabilise. It would appear that the smectic C phase stability rises to a maximum and then begins to decrease; this trend is masked somewhat by the appearance of the S_2 phase, the transition temperatures of which rise rapidly and then level out on ascending the homologous series.

The transition entropy dependence on aliphatic chain length is plotted in figure 2.3.2b. The S_C-N transition entropies are significantly higher than those for the S_A-N entropies in the [3,m] series and indeed higher than the S_A-N entropies for the two other series, as will become apparent. This reflects the greater degree of ordering in the tilted phase as compared with the analogous untilted phase. However, comparing the S_C-I and the S_A-I entropies for this series shows the latter to be greater. At first sight this may seem anomalous, but it may be reasonable to assume that very different kinds of molecular packing are involved in these two phases. Further consideration will be given to this point later.

The smectic C to smectic A transitions are second order and not discernable in the DSC data. Likewise the S_2-S_C transitions would appear to be second order with the S_2-S_A transitions being very weakly first order (approximately

m	C- /°C	N-I		S_C-N		S_C-I*, S_C-S_A		S_{A}-I		S_2-S_C*, S_2-S_A	S_3-S_2	
		T/ °C	ΔS/R	T/ °C	ΔS/R	T/ °C	ΔS/R	T/ °C	ΔS/R	T/ °C	T/ °C	ΔS/R
1	146	(104)										
2	141	(105)										
3	130	(111)	0.25	(92)	1.43							
4	128	(110)	0.38	(104)	2.50							
5	133					(127)*	4.16					
6	116					135*	4.31					
7	114					138		143	5.66	112*		
8	111					134		150	5.88	123*		
9	99							154	5.95	131	(86)	0.70
10	99							157	5.96	132	(84)	1.03
12	107							158	6.00	131	(87)	1.30

Table 2.3.2 Transition temperatures and enthalpies for the [4,m] series. Monotropic transitions are shown in brackets. The uncertainties in the transition temperatures are ±1.5° and in the entropies ±10%.

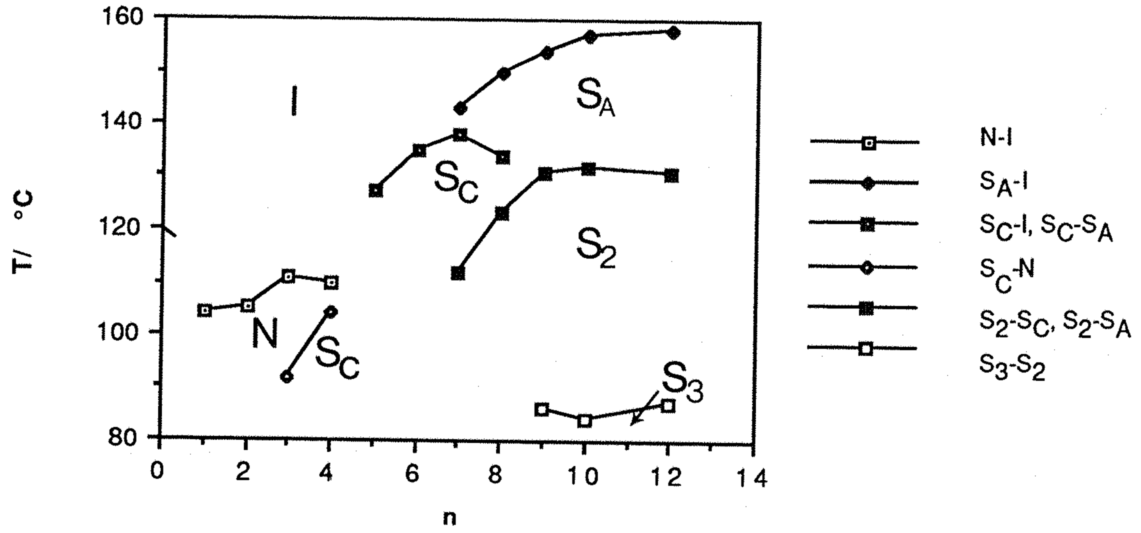


Figure 2.3.2a Transition temperature dependence on terminal chain length for the [4,m] series.

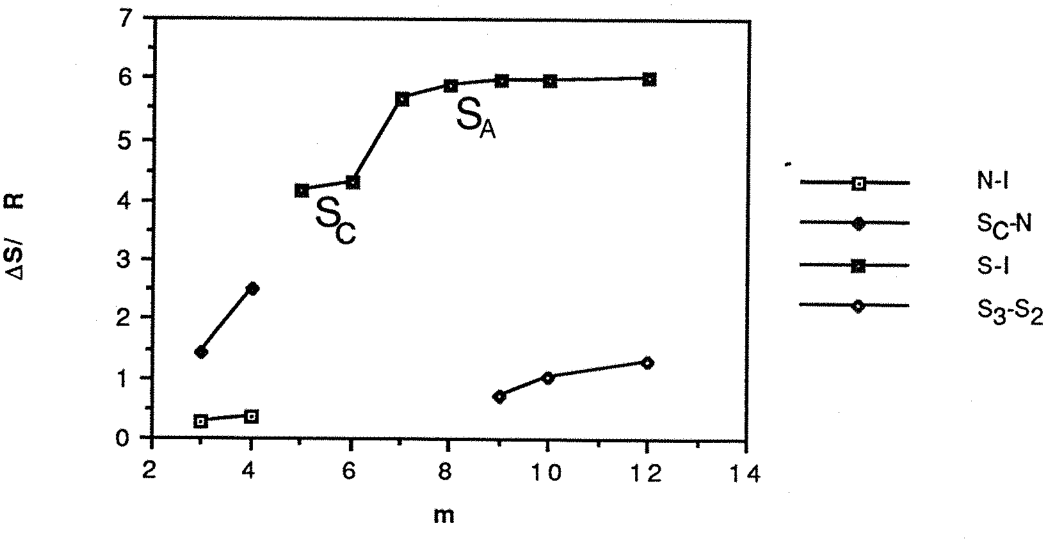


Figure 2.3.2b Entropy of transition dependence on terminal chain length for the [4,m] series.

0.1-0.2ΔS/ R). The S_3-S_2 transition is first order, increasing in entropy with increasing terminal chain length.

Series [5,m]

The transition temperatures and thermal data for this series are shown in table 2.3.3 and the transition temperature dependence on terminal chain length shown in figure 2.3.3a. Members of the series having terminal chains of up to five methylene units all exhibit monotropic nematic phases which generally rise in stability with increasing m. Smectic A phases are shown for all but the first member of the series, the transition temperatures of which increase and then level off. The tilted smectic phase behaviour of this series is quite different to that of the other series. Smectic C phases are exhibited by all homologues having m greater than 5. It is worth noting that the temperatures for the S_C-S_A transition increase and do not level off or decrease in contrast to the behaviour in the [4,m] series. Additionally the smectic phase that appears below the smectic C phase for the homologues having eight or more methylene units in the terminal chain bears no resemblance to any of the phases exhibited in the other series. The texture for this phase, denoted S_4, is composed of both sanded focal-conics (these were also present in the S_C texture) and an ill-defined platelet texture. The platelets were unbroken, being larger and more brightly coloured than those of the other platelet textures described in the results leading to the conclusion that this phase is not equivalent to the S_1, S_2 or S_3 phases.

The transition entropy dependence on terminal chain length is shown in figure 2.3.3b. The nematic-isotropic transition entropies increase gradually with increasing m. The smectic A-isotropic transition entropies are significantly higher than those of the smectic A-nematic transition, as would be expected. The S_4-S_C transition is first order, the entropies associated with this gradually increasing on ascending the series.

m	C- /°C	N-I		S_A-N*, S_A-I		S_C-S_A	S_4-S_C	
		T/ °C	ΔS/R	T/ °C	ΔS/R	T/ °C	T/ °C	ΔS/R
1	130	(93)						
2	130	(105)	0.47	(90)*	0.32*			
3	120	(118)	0.61	(100)*	0.54*			
4	111	(115)	0.77	(100)*	0.74*			
5	126	(119)	1.09	(109)*	0.75*			
6	116			128	5.25	(80)		
7	107			140	5.85	(84)		
8	110			144	5.95	(102)	(81)	1.48
9	103			148	7.20	110	(85)	2.01
10	117			149	7.06	(116)	(92)	2.15
12	100			153	7.25	(128)	(93)	2.70

Table 2.3.3 Transition temperatures and enthalpies for the [5,m] series. Monotropic transitions are shown in brackets. The uncertainties in the transition temperatures are ±1.5° and in the entropies ±10%.

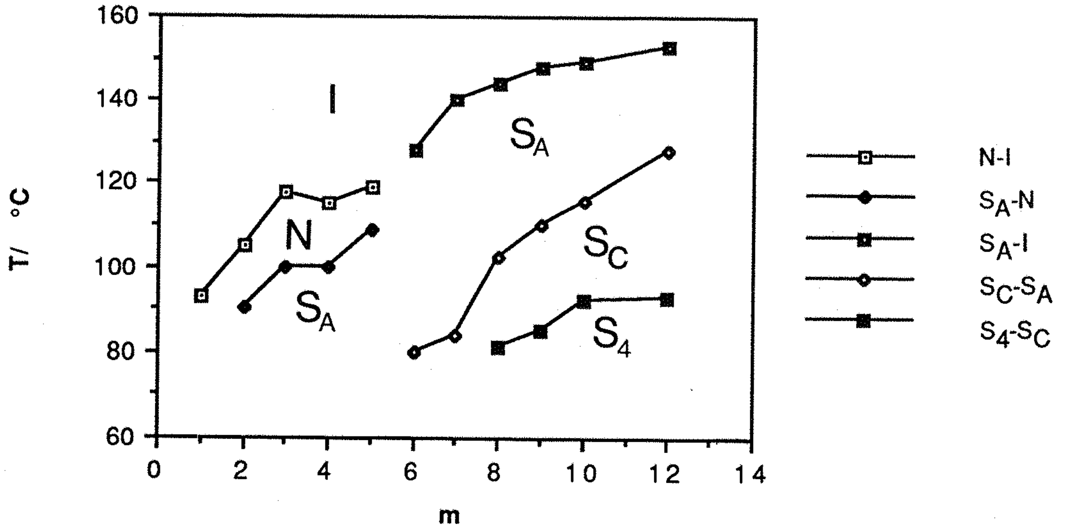


Figure 2.3.3a Transition temperature dependence on terminal chain length for the [5,m] series.

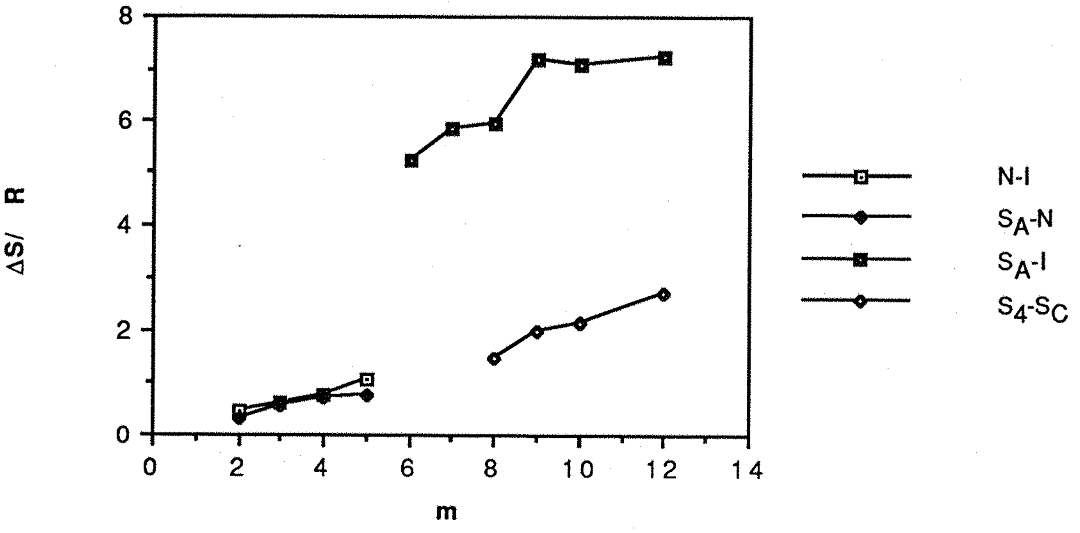


Figure 2.3.3b Entropy of transition dependence on terminal chain length for the [5,m] series.

Series [6,m]

The transition temperatures and thermal data for this series are shown in table 2.3.4 and the transition temperature dependence on terminal chain length shown in figure 2.3.4a. The first homologue exhibits a monotropic nematic phase, the next five members show both nematic and smectic A phases the transition temperatures of which rise gradually on ascending the series. The mesophase behaviour of the remaining homologues is similar to that found in the higher members of the [4,m] series. Smectic C phases appear for the seventh to ninth homologues. The S_2 phase appears at m=7 and increases in thermal stability with increasing terminal chain length, thereby becoming more favoured than the smectic C phases which disappear. In common with the [4,m] series smectic A phases are formed as the high temperature modification and S_3 phases as the low temperature modification for long terminal chain homologues.

The transitional entropy change dependence on terminal chain length is shown in figure 2.3.4b. Nematic-isotropic entropy changes show a slight odd-even effect, odd members being more stable than even. This is in accord with observations in calamitic systems [19], although the small number of data points prohibits any inferences being made. The smectic A transition entropies show a dramatic increase at the point where the crossover between nematic-isotropic and smectic-isotropic transitions occurs. The S_4-S_2 transition entropies increase with increasing terminal chain length in common with the [4,m] series, this phase first appearing for the same homologue (nonyl) in both series. The S_2-S_A transition entropies are approximately of the order 0.1-0.2 $\Delta S/R$.

m	C- /°C	N-I		S_A-N*, S_A-I		S_C-I*, S_C-S_A		S_2-S_C*, S_2-S_A	S_3-S_2	
		T/ °C	ΔS/R	T/ °C	ΔS/R	T/ °C	ΔS/R	T/ °C	T/ °C	ΔS/R
1	147	(100)								
2	115	(105)		(96)*						
3	87	106	0.80	97 *	0.70*					
4	107	109	0.66	(98)*	0.61*					
5	96	113	0.97	101*	0.64*					
6	105	112	0.74	(102)*	0.75*					
7	96					121*	6.25*	111		
8	116			129	6.60	126		116		
9	95			134	7.42	127		120	(80)	0.80
10	96			137	7.67			125	(82)	1.25
12	102			140	8.29			127	(87)	2.20

Table 2.3.4 Transition temperatures and enthalpies for the [6,m] series. Monotropic transitions are shown in brackets. The uncertainties in the transition temperatures are ±1.5° and in the entropies ±10%.

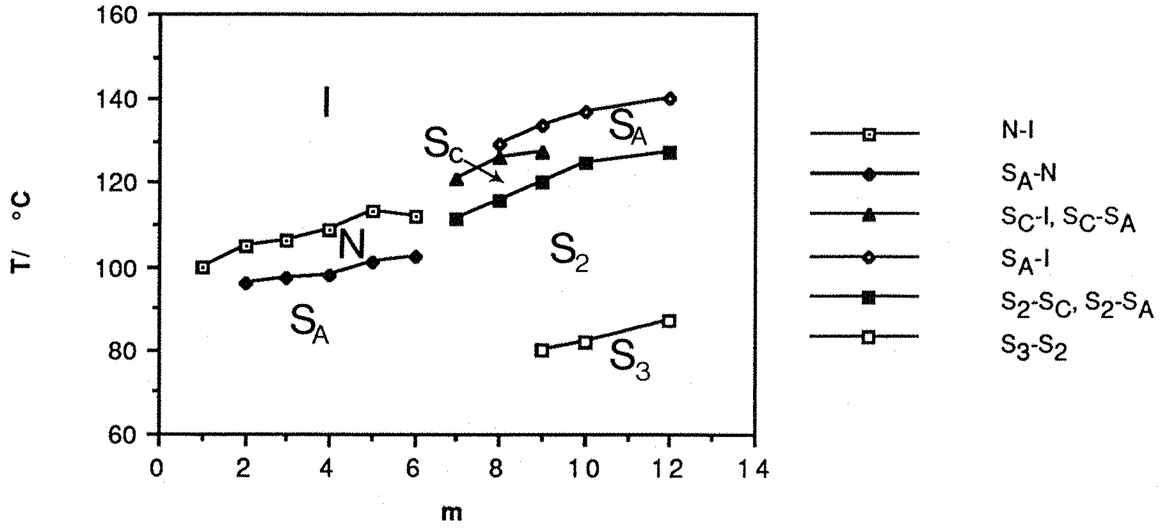


Figure 2.3.4a Transition temperature dependence on terminal chain length for the [6,m] series.

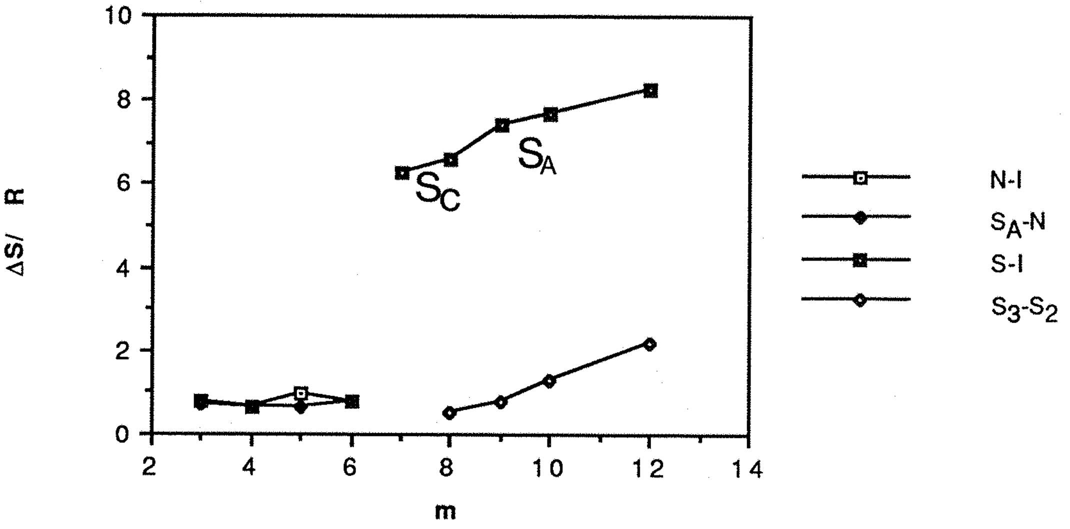


Figure 2.3.4b Entropy of transition dependence on terminal chain length for the [6,m] series.

General trends on increasing terminal chain length

When considering the effects of the terminal chain length that are common to all four series a number of interesting features can be found. Perhaps the most prominent feature is the relation between the terminal chain length and spacer chain length in determining the crossover between nematic and smectic mesomorphism. For all the series nematic phases do not occur for homologues having terminal chains consisting of more methylene units than the spacing chains, yet all other homologues do exhibit nematic phases. It is worth noting a feature found in terminally linked dimeric liquid crystals; that is, for smectic phases to be formed the terminal chain length must be greater than half the spacer chain length. In this relation ether linkages are regarded as part of the flexible spacer. Unfortunately, there has not been a large number of studies on such systems, but the trend is none the less significant. By these criteria in the system presented here nematic phases are only formed by molecules having a smaller number of flexible units in the terminal chain than in the spacer chain. However, a degree of flexibility would also be anticipated in the oxygen linkage of the ester function. Smectic transition entropies also show a change at this crossover point, namely that a marked increase in these occur on moving from the smectic-nematic to the smectic-isotropic transitions, this is shown in figure 2.3.5. This difference can be attributed to the presence of an ordered intermediate nematic phase in the former. However, the large smectic-isotropic transition entropy may indicate a greater degree of ordering in this smectic A phase as compared with the smectic A phases formed from preceding nematic phases. By plotting the nematic-isotropic transition temperature dependence on the difference between the terminal and spacing chain lengths for these series further trends may be noted, as shown in figure 2.3.6. It would appear that the odd spacer members exhibit a short parity dependence ([5,1] excepted). Both even spacer series give similar trends with a possibly reversed parity dependence in comparison with the odd spacer series.

Figure 2.3.7 shows the smectic-isotropic transition temperature dependence on terminal chain length for the four series. It should be noted that [4,5], [4,6] and [6,7] all relate to smectic C-isotropic transitions, the others being smectic A-isotropic. (The fact that these S_C-I transitions are exhibited by even spacer compounds occuring near the 'crossover' point is itself an important indication of the dependence on spacer chain parity of the mesogenic properties.) The figure depicts clearly the increase in transition temperatures on ascending the series which levels off. The smectic-isotropic transition entropies show a similar trend, this is shown in figure 2.3.8. It has already

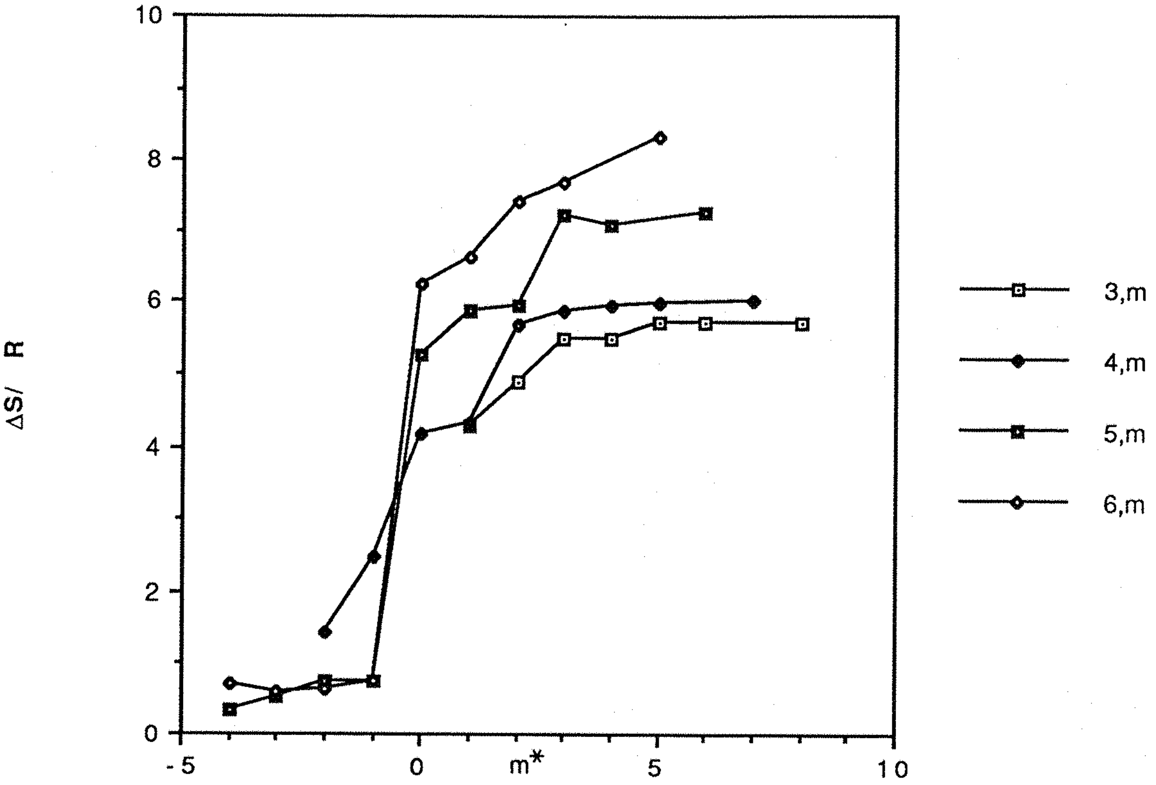


Figure 2.3.5 Smectic-nematic and Smectic-isotropic transition entropies. m* is zero when the number of terminal methylene units exceeds the number of central methylene units by one. Note that the first four points for the [4,m] series and the [6,m*=0] relate to smectic C phases, all others being transitions from smectic A phases.

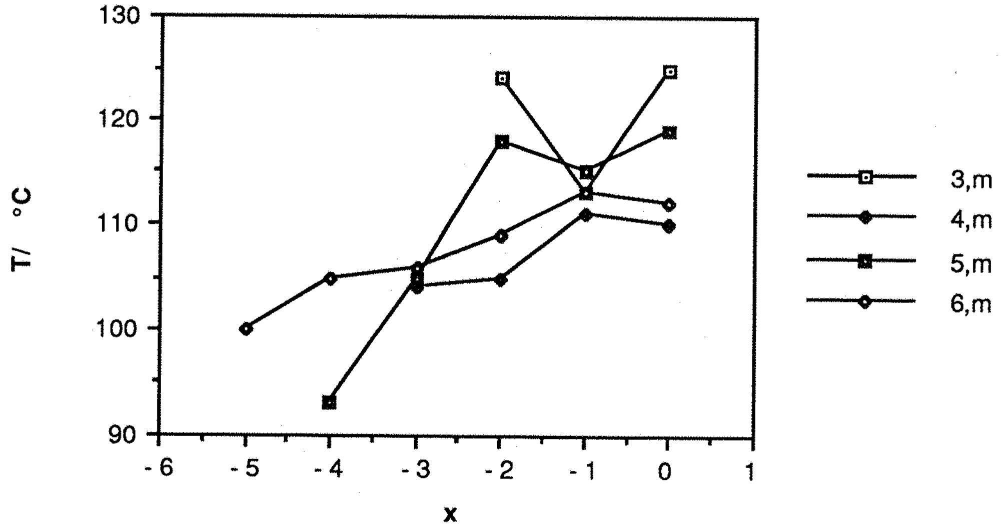


Figure 2.3.6 Nematic-isotropic transition temperatures; x=0 when m=n.

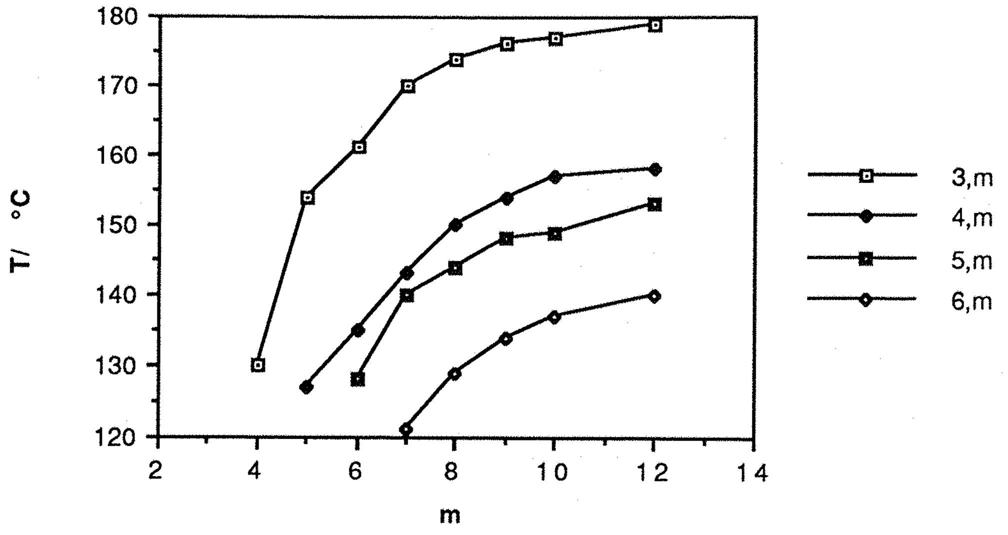


Figure 2.3.7 Smectic A-isotropic transition temperature dependence on terminal chain length. The smectic C-isotropic transitions for [4,5], [4,6] and [6,7] are also included.

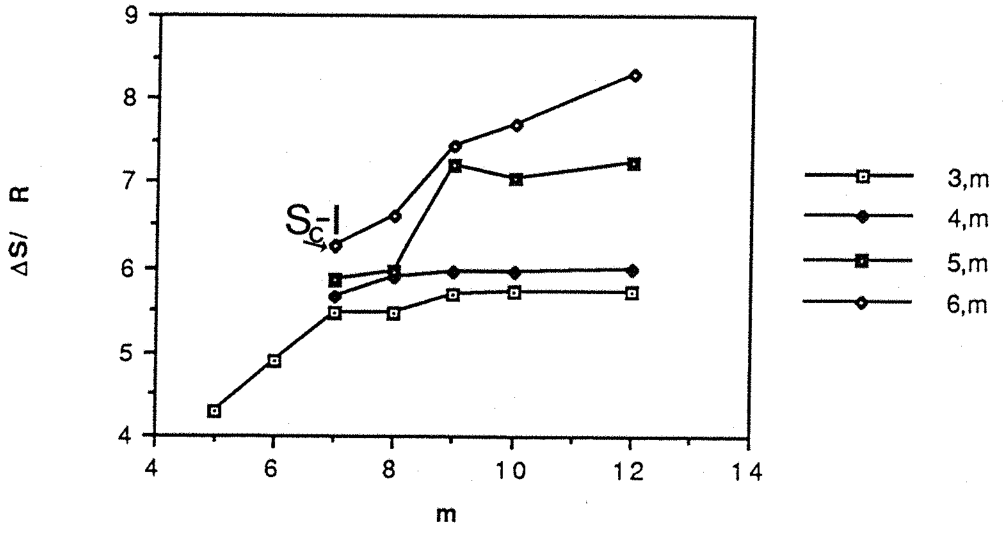


Figure 2.3.8 Smectic A-isotropic entropy of transition dependence on terminal chain length. The smectic C-isotropic transition entropy has been included for [6,7].

been stated that this rising stability is commonly found in monomeric systems having low transition temperatures. This feature has also been found for a series of dimeric liquid crystals the α, ω-bis-(4-n-alkylphenyliminobenzylidene-4'-oxy)alkanes (m.OnO.m's) [36,37]. In series having an odd number of methylene units in the spacing chain it is found that smectic-isotropic transition temperatures rise as shown in figure 2.3.9. This effect is particularly noticeable for homologues having short spacer lengths. This trend shows that the terminal chains play an important role in stabilising liquid crystal phases. In the dimeric materials short spacer chain lengths restrict the number of conformations available to a particular molecule and in the case of an odd spacer length dimer very few of these conformers permit an elongated structure. Increasing terminal chain length therefore increases the number of possible conformers having a high length to breadth ratio. These conformers will be favoured by the liquid crystal environment and so increase mesophase stability. This argument can be used to explain the trends found in the [n,m] series. The 1,3,5-substitution on the central benzene ring will give a molecule with a discotic type symmetry in a significant number of conformations. However, the flexible spacer chains also permit conformers which give an elongated molecule. We have already seen that these molecules form phases having textures characteristic of calamitic systems. It is therefore reasonable to assume that conformations which give a high length to breadth ratio are favoured in the liquid crystal phases formed by these materials. Due to the bulky nature of the pendant groups, the average length to breadth ratios of these materials are assumed to be smaller than those of the odd spacer dimers, in which case the contributions of the terminal chains to mesophase stability are anticipated to be of greater importance in the [n,m] materials. This provides a possible explanation of the rapid rise in transition temperatures on increasing terminal chain length and its stabilisation.

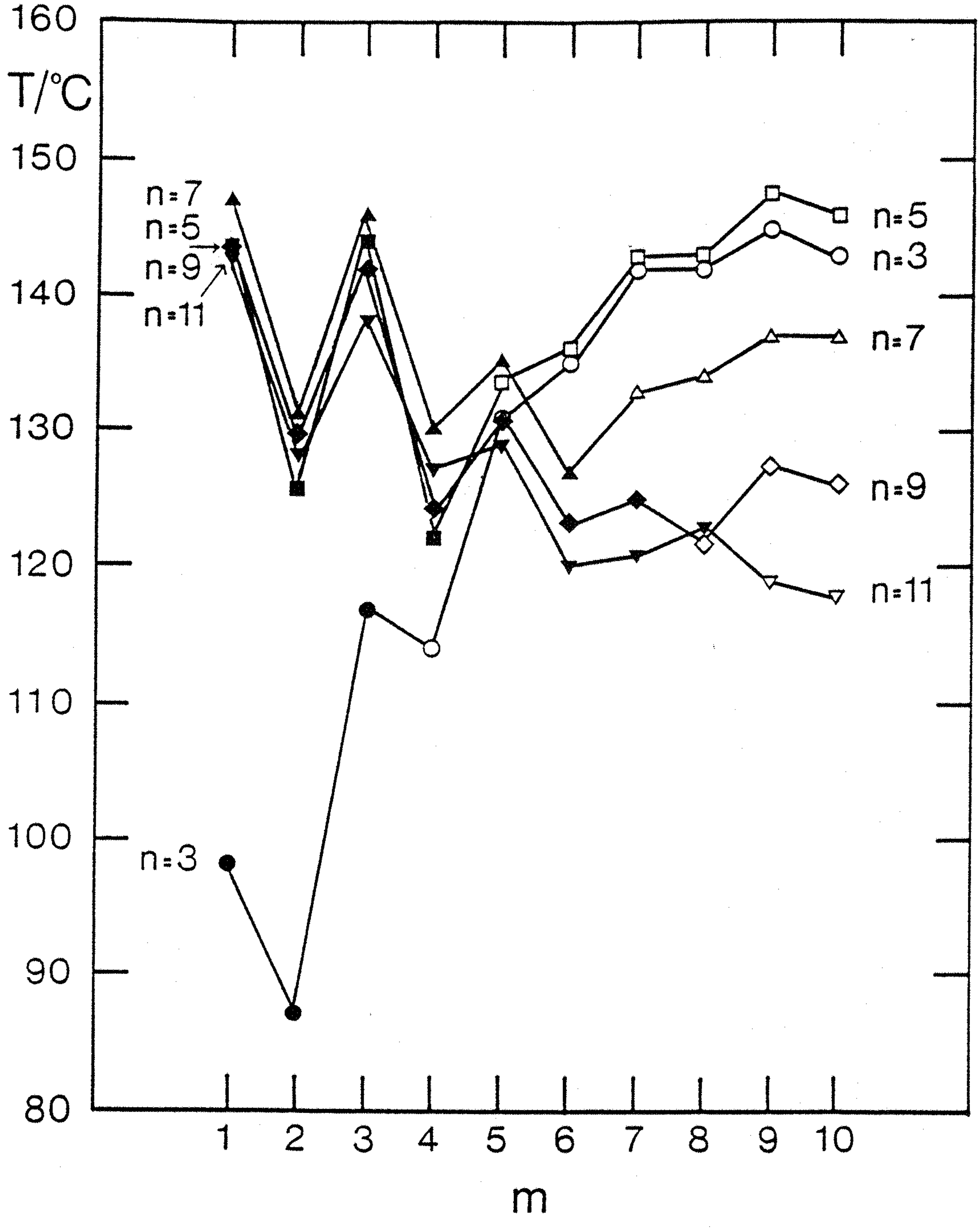


Figure 2.3.9 The dependence of the liquid crystal-isotropic transition temperature on the length of the terminal alkyl chains for m.OnO.m series having an odd number of methylene units in the alkyl core. Filled symbols indicate a nematic-isotropic transition and open symbols represent a smectic-isotropic transition.

Effects of varying spacer chain length

Figure 2.3.10 shows the dependence of the smectic-isotropic transition temperatures on spacer chain length. The transition temperatures show a large decrease on increasing n, this is attributed to a dilution in core-core interactions. An obvious odd-even effect can be seen, although the series only includes four homologues this is evident for a large variation in m. Odd members are more stable than even members, these being able to adopt a greater number of conformations that preserve a more linear shape. The smectic-isotropic entropies are shown in figure 2.3.11, these increase with increasing n again reflecting the greater number of conformations available to higher homologues which give a high length to breadth ratio, these being favoured in the liquid crystal environment. The mesomorphic behaviour of the even spacer compounds is similar, and dissimilar to that found in the odd spacer compounds.

General points

The trends shown by these compounds can be rationalised by suggesting that the molecules adopt a shape in which a high length to breadth ratio is maintained. However, this opens the question as to whether or not the increased packing ability offsets the entropy loss in introducing gauche linkages into the structure. It is possible to envisage other kinds of packing in the mesophases. One form, having a structure analogous to the tubular discotic phases as described in 1.3.5 can be discounted as it is not anticipated that the ester linkages would lie orthogonal to the benzene ring core, as is possible with an etheric linkage or even a reversed ester linkage. A structure similar to those found with cone-shaped liquid crystals having molecules stacked in a column, neighbouring columns being stacked in the opposite direction may be possible. However, no conclusions can be drawn about the molecular packing until X-ray diffraction studies have been carried out on the mesophases.

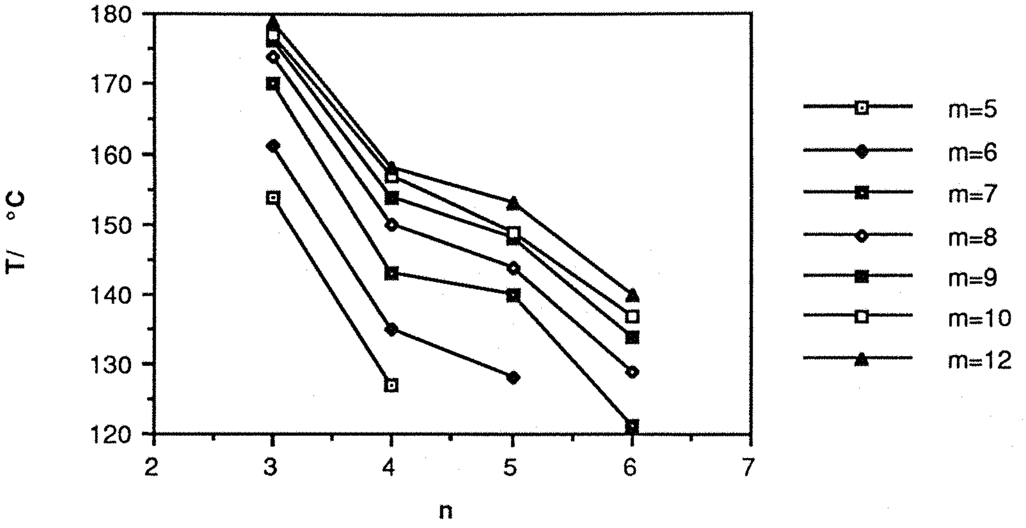


Figure 2.3.10 Smectic-isotropic transition temperature dependence on the spacer chain length. Note that [4,5], [4,6] and [6,7] relate to S_C phases, all other values relate to S_A phases.

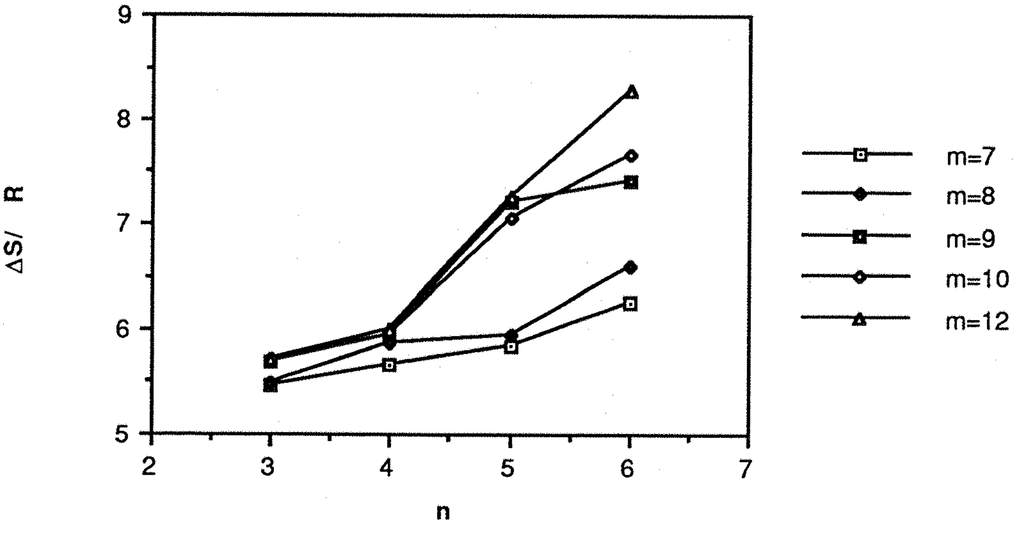


Figure 2.3.11Smectic-isotropic transition entropy dependence on the spacing chain length. Note that [6,7] relates to a smectic C-isotropic transition.

2.4 Conclusions

It has been shown that the four [n,m] series, which at first sight might appear to have a discotic type symmetry, exhibit optical textures characteristic of calamitic phases. This may be due to the ability of the molecules to adopt conformations that give a high length to breadth ratio, these being preferentially selected in the liquid crystal phases. However, this does not exclude the possibility that some or all of the phases may be columnar or discotic nematic in nature. X-ray diffraction studies are required to resolve this question. The mesomorphic behaviour has a dependence not only on the spacer and terminal chain lengths but also on the ratio between these. All homologues having a greater number of methylene units in the terminal chain than in the flexible spacer exhibited smectic phases only. Smectic-isotropic transition temperatures and entropies increase with increasing terminal chain length. This has been rationalised by consideration of the conformational distributions of the flexible units in these compounds.

REFERENCES

1. Reinitzer, F., 1888, Mh. Chem., 9, 421.
2. Lehmann, O., 1900, Vernhandl. d. Deutschen Phys. Ges., Sitzung v. 16.3, 12.
3. Frank, F.C., 1958, Disc. Faraday Soc., 25, 19.
4. Gray, G.W., and Goodby, J.W.G., 1984, Smectic Liquid Crystals, Leonard Hill, London.
5. Demus, D., and Richter, L., 1978, Textures of Liquid Crystals, Verlag Chemie, Weinheim, New York.
6. De Vries, A., 1970, Mol. Cryst. Liq. Cryst., 10, 219.
7. Chistyakov, I.G., and Chaikowsky, W.M., 1969, Mol. Cryst. Liq. Cryst., 7, 269.
8. Levelut, A.M., and Lambert, M., 1971, Compt. Rend. Acad. Sci. (Paris), 272, 1018.
9. Budai, J., Davey, S.C., Pindak, R., and Goodby, J.W., 1984, J. Phys. (Paris) Lett., 45, L-1053.
10. Bennatar, J.J., Moussa, F., and Lambert, M., 1980, J. Phys. (Paris), 41, 1371.
11. Leadbetter, A.J., Mazid, M.A., and Richardson, R.M., 1980, Liquid Crystals, Chandrasekhar, S., (ed.), Heydon, London, Philadelphia and Rheine.
12. Tardieu, A., and Billard, J., 1976, J. Phys. (Paris), 37, 79.
13. Etherington, G., Leadbetter, A.J., Wang, X.J., Gray, G.W., and Tajbakhsh, A.R., 1986, Liquid Crystals, 1, 3, 209.
14. Demus, D., Gloza. A., Hartung, H., Rapthel, I., and Wiegaleben, A., 1981, Cryst. Res Techn., 16, 1445.
15. Tinh, N.H., Foucher, P., Destrade, C., Levelut, A.M., and Malthete, J., 1984, Mol. Cryst. Liq. Cryst., 111, 277.
16. Destrade, C., Tinh, N.H., Gasparoux, H., Malthete, J., and Levelut, A.M., 1981, Mol. Cryst. Liq. Cryst., 71, 111.
17. Bougliand, Y., 1981, J. Phys. Lett., 42, 1461.
18. Demus, D., 1989, Liquid Crystals, 5, 1, 75.
19. Gray, G.W., 1979, The Molecular Physics of Liquid Crystals, Luckhurst, G.R., and Gray., G.W., (eds.), Academic Press, Ch. 1.
20. Toyne, K.J., 1987, Thermotropic Liquid Crystals, Gray, G.W., (ed.), John Wiley and Sons.
21. Gray, G.W., 1974, Liquid Crystals and Plastic Crystals, Gray G.W., and Windsor, P.A., (eds.), 1, Ellis Horwood, England.
22. Young, W.R., Haller, I., and Green, D.C., 1972, J. Org. Chem., 37, 3707.
23. Dewar, M.J.S., and Griffin, A.C., 1975, J. Am. Chem. Soc., 97, 6662.

24. Hirata, H., Waxman, S.M., Teucher, I., and Labes, M.M., 1973, Mol. Cryst. Liq. Cryst., 20, 343.
25. Demus, D., Hauser, Isenberg, A., Pohl, M., Selbmann, Ch., Weissflog, W., and Wieczorek, S., 1985, Cryst. Res. Techn., 20, 10, 1413.
26. Weissflog, W., and Demus, D., 1985, Mol. Cryst. Liq. Cryst., 129, 235.
27. Imrie, C.T., and Taylor, L., 1989, Liquid Crystals, 8, 1, 1.
28. Weissflog, W., and Demus, D., 1988, Liquid Crystals, 3, 2, 275.
29. Diele, S., Weissflog, W., Pelzl, G., Manke, H., and Demus, D., 1986, Liquid Crystals, 1, 1, 101.
30. Vorlander, D., 1927, Z. Phys. Chem., 126, 449.
31. Griffin. A.C., and Britt, T.R.,1981, J. Am. Chem. Soc., 103, 4957.
32. Jin, J-I, Chung, J-S, Kang, J-S, and Lenz, R.W., 1982, Mol. Cryst. Liq. Cryst. Lett., 82, 261.
33. Jin, J-I, Oh, H-T, and Park, J-H, 1986, J. Chem. Soc. Perkin. Trans. II, 343.
34. Emsley, J.W., Luckhurst, G.R., Shilstone, G.N., and Sage, I., 1985, Mol. Cryst. Liq. Cryst. Lett., 129, 235.
35. Centore. R., Roviello, A., and Sirigu, A., 1988, Liquid Crystals, 3, 11, 1525.
36. Imrie, C.T., 1988, Ph.D Thesis, University of Southampton.
37. Date, R.W., Imrie, C.T., and Luckhurst, G.R., (in preparation).
38. Imrie, C.T., 1989, Liquid Crystals, 6, 4, 391.
39. Kelker, H., and Scheurle, B., 1969, Molec. Crystals, 7, 381.
40. Griffin, A.C., Thames, S.F., and Bonner, M.S., 1977, Mol. Cryst. Liq. Cryst. Lett., 43, 135.
41. Dehne, H., Roger, A., Demus, D., Diele, S., Kresse, H., Pelzl, G., Wedler, W., and Weissflog, W., 1989, Liquid Crystals, 6, 47.
42. Weissflog, W., Demus, D., Diele, S., Nitschke, P., and Wedler. W., 1989, 5, 1, 111.
43. Furuya, H., Koichi, A., and Abe, A., 1986, Polmer J., 18, 10, 779.
44. Luckhurst, G.R., and Sundholm, F., (unpublished work).
45. Attard, G.S., and Imrie, C.T., 1989, Liquid Crystals, 6, 4, 387.
46. Chandrasekhar, S., Sadashiva, B.K., and Suresh, K.A., 1977, Pramana, 9, 471.
47. Backer, H.J., and Van Der Baan, S., 1937, Rec. Trav. Chem. Pays-Bays, 56, 1161.
48. Kohne, B., and Praefke, K., 1986, Z. Naturf., 41b, 1036.
49. Carfagna, C., Iannelli, P., Roviello, A., and Sirigu, A., 1987, Liquid Crystals, 2, 5, 611.
50. Levelut, A.M., 1979, J. Phys. (Paris) Lett., 40, L-81.
51. Heiney, P.A., Fontes, E., de Jeu, W.H., Riera, P.C., and Smith, A.B., 1989, J. Phys. France, 50, 461.

52. Destrade, C., Gasparoux, H., Foucher, P., Tinh, N.H., Malthete, J., and Jacques, J., 1983, J.Chim.Phys., 80, 137.
53. Destrade, C., Mondon, M.C., and Malthete, J., 1979, J. Phys. Colloq., 40, C3.
54. Cheng, G.Q., and Dong, R.Y., 1988, J. Chem. Phys., 89, 5, 3308.
55. Guillon, D., Skoulios, A., Piechocki, C., Simon, J., and Weber, P., 1983, Mol. Cryst. Liq. Cryst., 100, 275.
56. Takenaka, S., Nishimura, K., and Kusabayashi, S., 1984, Mol. Cryst. Liq. Cryst., 111, 227.
57. Nishimura, K., Takenaka, S., and Kusabayashi, S., 1984, Mol. Cryst. Liq. Cryst., 104, 347.
58. Giroud-Godquin, A.M., and Billard, J., 1981, Mol. Cryst. Liq. Cryst., 66, 137.
59. Malthete, J., Canciell, J., Gabard, J., and Jacques, J., 1981, Tetrahedron, 37, 16, 2283.
60. Tinh, N.H., Gasparoux, H., Malthete, J., and Destrade, C., 1984, Mol. Cryst. Liq. Cryst., 114, 19.
61. Diele, S., Manke, S., Weissflog, W., Demus, D., 1988, Liquid Crystals,
62. Weissflog, W., Wiegeleben, A., Diele, S., and Demus, D., 1984, Cryst. Res. Techn., 19, 583.
63. Destrade, C., Nguyen, H.T., Alstermark, C., Lindsten, G., Nilsson, M., and Otterholm, B., 1990, Mol. Cryst. Liq. Cryst., 180b, 265.
64. Malthete, J., Levelut, A.M., and Tinh, N.H., 1985, J. Phys (Paris) Lett., 46, L-875.
65. Praefke, K., Kohne, B., Gundogan, B., Demus, D., Diele, S., and Pelzl, G., 1990, Mol. Cryst. Liq. Cryst. Lett., 7, 1, 27.
66. Malthete, J., Collet, A., and Levelut, A.M., 1989, Liquid Crystals, 5, 1, 123.
67. See reference [18]
68. Babeau, A., Tinh, N.H, Gasparoux, H., Polycarpe, C., Torrielles, and Giral, L., 1982, Mol. Cryst. Liq. Cryst. Lett., 72, 171.
69. Allcock, H.R., Kim, C., 1989, Macromolecules, 22, 2596.
70. Kreuder, W., Ringsdorf, H., Herrmann-Schonner, O., and Wendorf, J., 1987, Angew. Chem. Int. Ed. Engl., 26, 12, 1249.
71. Eidenschink, R., Kreuser, F.-H., and De Jeu, W.H., 1990, Liquid Crystals, 8, 6, 879.
72. Demus, D., and Zaschke, H., 1984, Flussige Kristalle in Tabellen II, Veber, Leipzig.
73. Nishikubo, T., Iizawa, T., Takahashi, A., and Shimokawa, T., 1990, J. Polym. Sci. Part A: Polym. Chem., 28, 105.
74. Keller, P., and Liebert, L., 1978, Sol. Stat. Phys. Supp., 14, 20.