CHAPTER I

INTRODUCTION

LIQUID CRYSTALS

Liquid crystals are states of matter in which the molecular order is intermediate between the ordered crystals and the disordered liquids. Liquid crystals are divided into two classes, viz., the lyotropic and the thermotropic liquid crystals. In lyotropic liquid crystals the change in the molecular ordering is brought about by varying the concentration of a solute in a solvent or a mixture of solvents. In thermotropic liquid crystals this is achieved by variation of temperature. Liquid crystalline phases are also called mesomorphic phases or mesophases and the compounds exhibiting such phases are known as mesogens.

Thermotropic liquid crystals

The first recorded observation of thermotropic liquid crystals has been attributed to Reinitzer.[1] He noticed that, cholesteryl benzoate at 145°C "melted not into a clear transparent but always into a cloudy only translucent liquid" and on further heating at 178°C "the clouding suddenly vanishes".[1] It has now been established that all such intermediate phases are characterised by an orientational order of the molecules. Orientational order can only be defined with respect to anisotropic properties of molecules. Geometrical anisotropy of molecules has been found to be a necessary but not a sufficient condition for a compound to exhibit liquid crystalline phases. Thus, most of the mesogens have a lath-like structure, and the mesophases exhibited by these are called calamitic mesophases. A mesophase existing above the melting point is called enantiotropic and that which exists below the melting point is known as monotropic. The calamitic mesophases are divided into following categories.

The nematic phase (N)

The molecules in the nematic phase tend to be parallel to a common axis called the director and possess a long range orientational order (Figure 1).

The cholesteric or the chiral nematic phase (N*)

If the molecules are chiral then the nematic mesophase has a helical twist of the director. The screw axis is normal to the molecular long axes (Figure 2). The nematic phase can be considered as a cholesteric with an infinite pitch and the cholesteric phase can be regarded simply as a spontaneously twisted nematic.

The smectic mesophases (S)

The molecules in the smectic phases possess an orientational and a lamellar order. In smectic A (S_A) phase the molecules lie parallel to the layer normal. The smectic C (S_C) phase is the tilted analogue of the S_A phase. The molecular long axes are tilted with respect to the layer normal. This tilt direction is maintained through the layers. In the chiral smectic C (S_{C*}) phase this tilt precesses around the layer normal, thus forming a helical structure. The compounds exhibiting this phase have to

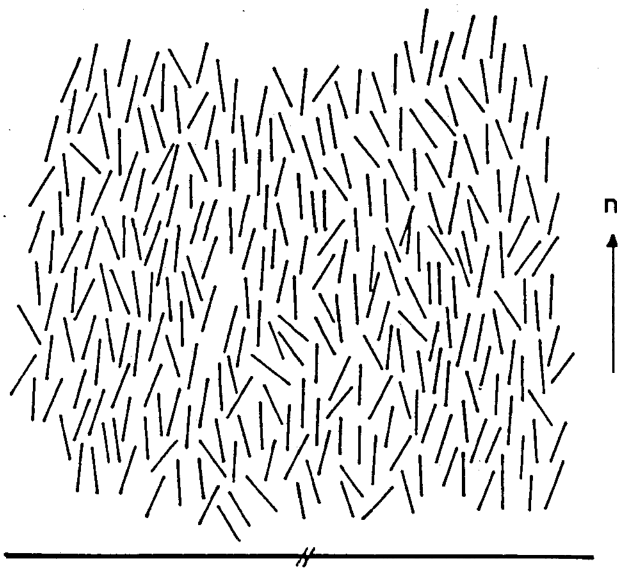


Figure 1: Schematic representation of the molecular arrangement in nematic phase (after Leadbetter[3]).

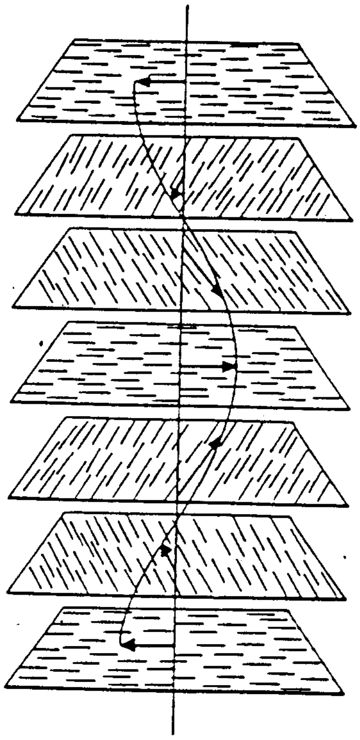


Figure 2: Schematic representation of the molecular arrangement in chiral nematic phase. (after Chandrasekhar[2]).

be chiral. In S_A, S_C and S_{C*} phases the centres of mass of molecules are randomnly distributed in each layer. These layers are not well defined and are best considered in terms of a sinusoidal density wave (Figures 3 and 4). The molecules have only a quasi- long range order and the dephasing length beyond which the layers cannot be distinguished is of the order of a centimeter.[2] The N* and the S_{C*} phases can also be obtained by introducing a small amount of chiral impurity in the N and the S_C phases respectively.

In recent years increasing number of higher order smectic phases have been discovered. These are classified according to the positional ordering of molecules present within the layers. To make a clear distinction between liquid crystal and a true (but disordered) crystal, Leadbetter[3] has suggested the following nomenclature: "when a structure has long-range order of molecular positions in three dimensions it is a crystal, despite the presence of various other kinds of disorder, and structures having less than this degree of positional order, but retaining some aspects of order above that possessed by an isotropic liquid, are properly called liquid crystals." The principal phase types which have been established are summarised in Table 1. And the possible order in which mesophases can occur is shown in Table 2.

Blue phases

Blue phases appear in a narrow range of temperature (typically less than 0.5°C) between the N* phase and the

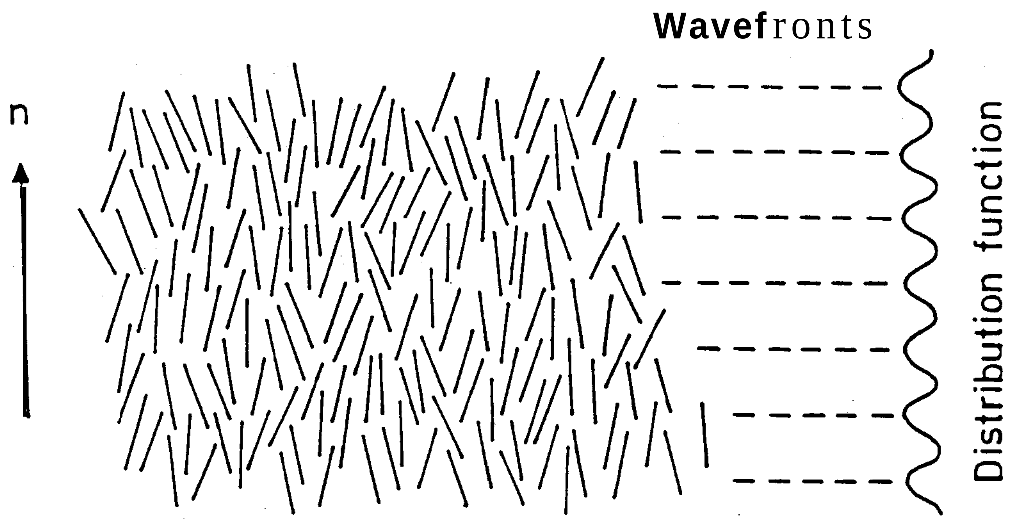


Figure 3: Schematic representation of the molecular arrangement in smectic A phase (after Leadbetter[3]).

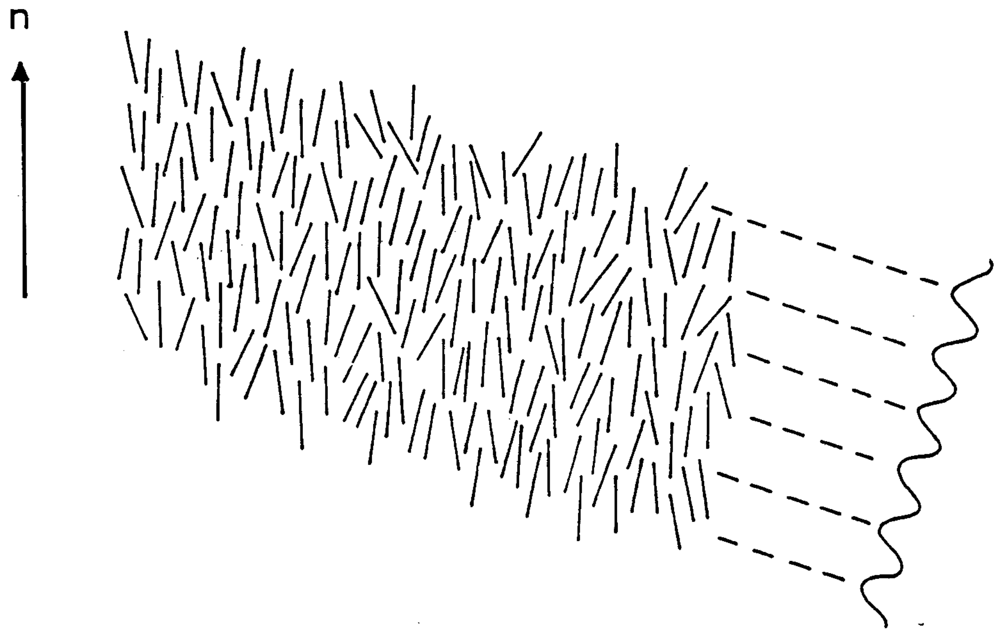


Figure 4: Schematic representation of the molecular arrangement in smectic C phase (after Leadbetter[3]).

Table 1

Principal calamitic mesophases (after Leadbetter[3])

<table>
<tr><td rowspan="8">Ordered crystal</td><td colspan="4">Disordered crystal</td><td colspan="3">Liquid crystal</td><td rowspan="6">Isotropic liquid</td></tr>
<tr><td colspan="4">Layer structures</td><td colspan="2">Smectic</td><td>Nematic</td></tr>
<tr><td colspan="4"></td><td>Based on weakly coupled ordered layers - 'two-dimensional' systems</td><td>Based on one-dimensional density wave (liquid layers)</td><td rowspan="4">N</td></tr>
<tr><td colspan="2">Orthogonal: molecules parallel to c, perpendicular to ab plane</td><td>E</td><td>B</td><td>S_B^h</td><td>S_A
$(S_{A_1}, S_{A_2}, S_{A_d}, S_{\tilde{A}})$</td></tr>
<tr><td rowspan="2">Tilted: molecules parallel to c, at angle <π/2 to ab plane</td><td>a >b</td><td>H</td><td>G</td><td>S_F</td><td>C</td></tr>
<tr><td>a < b</td><td>K</td><td>J</td><td>I</td><td>$(S_{C_1}, S_{C_2}, S_{C_d}, S_{\tilde{C}})$</td></tr>
<tr><td colspan="4">Cubic structures</td></tr>
<tr><td colspan="4">D
other</td></tr>
</table>

Table 2

Polymorphic variants (after Sackmann[86])

Monomorphic	Dimorphic	Trimorphic
N	$S_A N$	$S_B S_A N$
S_A	$S_B N$	$S_C S_A N$
S_B	$S_C N$	$S_G S_A N$
S_C	$S_G N$	$S_E S_A N$
S_E	$S_B S_A$	$S_G S_B N$
S_I	$S_C S_A$	$S_I S_C N$
	$S_E S_A$	$S_E S_B S_A$
	$S_G S_C$	$S_B S_C S_A$
	$S_I S_C$	$S_E S_C S_A$
	$S_E S_B$	$S_I S_C S_A$
	$S_G S_I$	$S_G S_C S_A$
	$S_G S_F$	$S_G S_B S_A$
		$S_G S_F S_A$
		$S_F S_I S_C$
		$S_G S_I S_C$

Tetramorphic	Pentamorphic	Hexamorphic
$S_G S_B S_A N$	$S_G S_B S_C S_A N$	$S_G S_F S_B S_C S_A N$
$S_E S_B S_A N$	$S_H S_G S_C S_A N$	$S_G S_F S_I S_C S_A N$
$S_B S_C S_A N$	$S_G S_I S_C S_A N$	$S_K S_J S_I S_C S_A N$
$S_G S_C S_A N$	$S_G S_F S_C S_A N$	$S_H S_G S_F S_C S_A N$
$S_I S_C S_A N$	$S_K S_J S_I S_C N$	
$S_H S_G S_C N$	$S_G S_F S_I S_C S_A$	
$S_E S_B S_C S_A$	$S_H S_G S_F S_C S_A$	
$S_G S_B S_C S_A$		
$S_G S_F S_C S_A$		
$S_H S_G S_C S_A$		
$S_G S_I S_C S_A$		
$S_K S_I S_C N$		

Temperature →

isotropic liquid (I) phase, provided the pitch of the N* phase is relatively short (<3000 A). Three blue phases have been identified, viz., BPI, BPII and BPIII respectively. These differ in their lattice structure. BPIII is also known as 'blue fog' and no structural symmetry has been identified.

Discotic liquid crystals

In 1977, Chandrasekhar et al.[4] reported disc shaped molecules, benzene hexa-n-alkanoates, which exhibited thermotropic mesophases. Since then a variety of discotic liquid crystals have been synthesised. The mesophases obtained with disc-like molecules are shown in table 3. There are two fundamental types, nematics (N_D) and columnar (D). The N_D phase is characterised by only a single order parameter associated with the tendency of the discs to align parallel to each other. In the columnar phsse, the discs are stacked one on top of the other in columns. The stacking within a column can be ordered (D_o) or disordered (D_d). The columns in turn can possess a hexagonal (D_{ho}, D_{hd}) or a rectangular (D_{ro}, D_{rd}) symmetry.

Metallomesogens

Probably the first known thermotropic metal containing liquid crystals were the alkali metal salts of the carboxylic acids,[5] which form lamellar phases characteristic of soaps and the diaryl mercury derivatives[5] which form smectic phases. The first transition metal complex exhibiting a mesophase was reported by Giroud and Billard.[6] Ohta et al.[7] have synthesised a

Table 3

Principal discotic mesophases (after Leadbetter[3])

	Columnar structures	Nematic	
Ordered crystal	Based on columns of molecules stacked in ordered (o) or disordered (d) manner; columns form two-dimensional lattice	N_D	Isotropic liquid
	Hexagonal: D_{ho}, D_{hd} Rectangular: D_{rd}; $P2_1/a$, $P2/a$, $C2/m$ Oblique: D_{obd}		

number of copper β-diketonates and based on optical and Xray studies have identified the mesophases as discotic lamellar phsses.

Chandrasekhar et al.[8] have reported paramagnetic nematic phases in a number of copper chelates. They[8] have also reported a biaxial nematic phase in a copper complex. Metallomesogens are gaining importance because they offer useful optical, magnetic and electrical properties.[9]

Chiral smectic C (S_{C*}) phase and ferroelectricity

In 1969, Saupe[10] predicted that the **tilt** direction in S_C phase would spiral about the direction normal to the layer planes on passing through the layers if the molecules were to be chiral. Helfrich and Oh[11] synthesised an optically active molecule which exhibited such a phase. Meyer et al.[12] advanced symmetry arguments for the existence of ferroelectricity in tilted smectic phases comprised of chiral molecules. The S_C phase has (i) two-fold rotation axis perpsndicular to the plane containing the molecule (director) and the layer normal and (ii) a reflection plane normal to this two-fold axis. When the medium consists of chiral molecules the reflection plane is eliminated. Thus within each layer the S_{C*} phase has only a two-fold rotation axis. This allows the existence of a non-zero polarisation parallel to this axis. Since the plane defined by the director and the layer normal rotates on passing through the layers in S_{C*} phase, the polarisation vector which is perpendicular to this plane also rotates through the layers and the net polarisation is zero for the helical structure (Figures 5 and **6**). However, when the helix is unwound a non-zero value for the polarisation is obtained. The direction of the polarisation vector can be defined as follows. A right hand screw acting along the two-fold axis, when turned in the direction of the molecular tilt moves in the direction of positive polarisation[13] (Figure 7).

In 1980, Clark and Lagerwall[14] demonstrated an electro-optical effect that utilised the ferroelectric property. Since then ferroelectric liquid crystalline phases have shown a potential as electrically active media in a variety of applications such as displays,[15] light valves,[16] spatial light modulators,[17] optical processing[18] and pyroelectric detectors.[19] Ferroelectricity can also be exhibited by other tilted smectic phases composed of chiral molecules. The S_{C*} phase is the most fluid phase to offer such a property and therefore gives the greatest potential for electrooptic device applications.

Influence of molecular structure on mesomorphism

The association between molecular structure and the mesomorphic properties has been very rigorously studied by Gray.[20] Most of the mesogens have a characteristic geometrical shape described as rod-like or lath-like giving rise to anisotropic cohesive forces. However, if the intermolecular attractions are too strong the melting point of the crystals will be higher. And upon melting, the thermal motions may prevent an existence of any ordering of the molecules. Similarly, weak intermolecular forces can lower the melting point but the cohesive forces may be

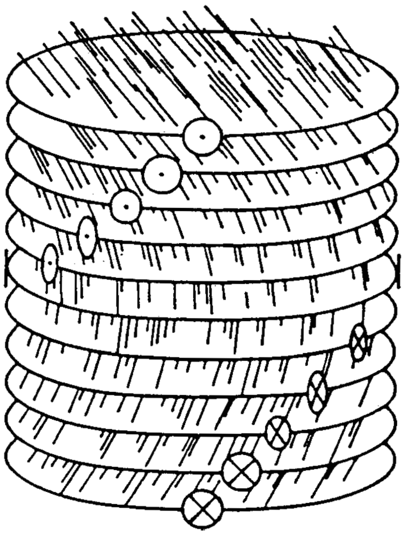


Figure 5: Schematic representation of the molecular arrangement in chiral smectic C phase with the direction of spontaneous polarisation (after Escher[76]).

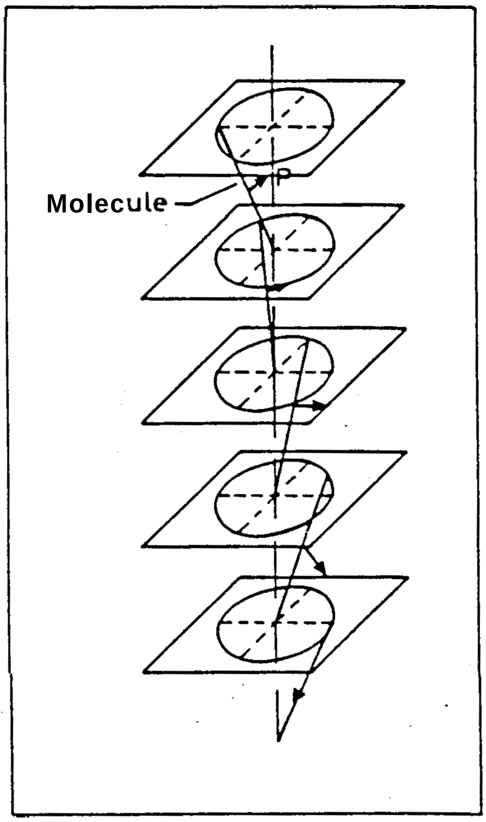


Figure. *6:* Alignment of the long axis and the average dipole vector of a molecule in chiral smectic C phase (after Escher[76]).

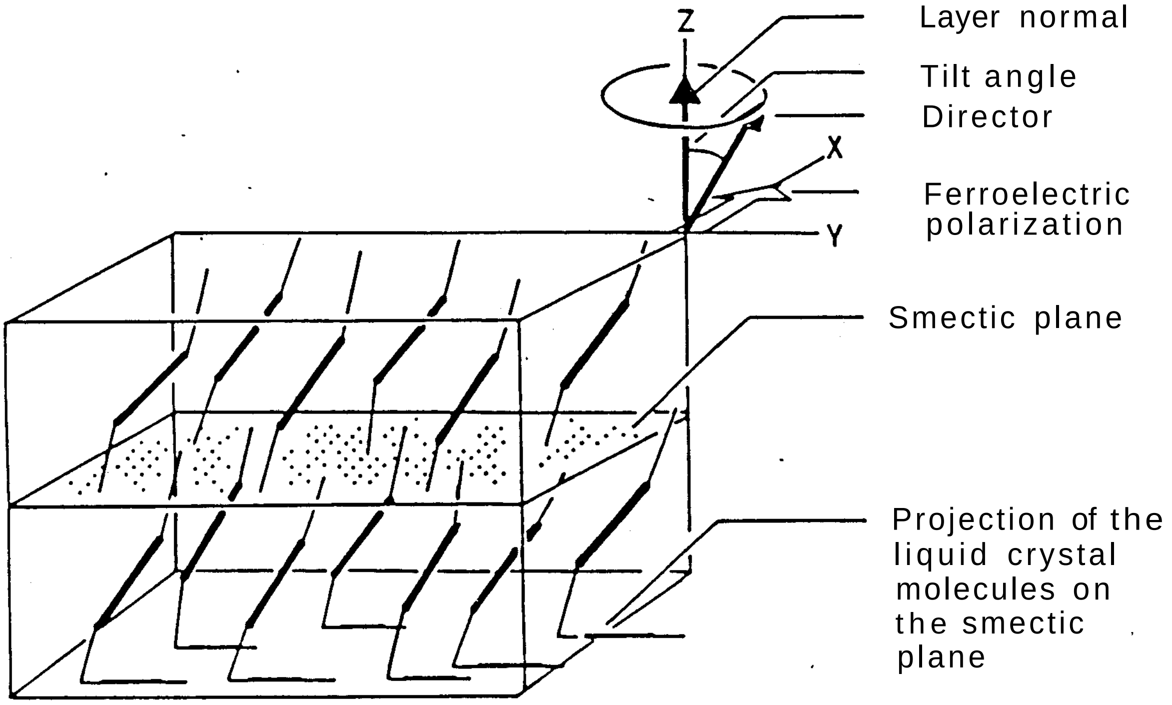
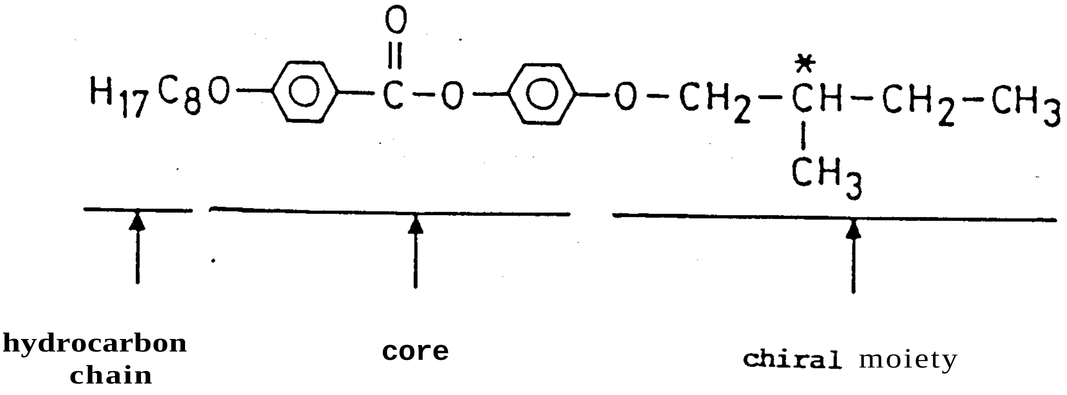


Figure 7: (after Walba et al.[58]).

inadequate to maintain order in the fluid state. In both the cases crystal will directly melt into an isotropic liquid phase. Thus, for a liquid crystal to be formed, cohesive forces operating between elongated molecules must be both anisotropic and of suitable magnitude. While correlating the structure to the mesophase some of the parameters to be taken into consideration are: the overall shape of the molecules, the packing efficieny, the balance between the length and the breadth, the rigidity, the linearity, the anisotropy of polarisability and the directions as well as the magnitude of dipole moments of various groups within the molecules. Due to the rapidly increasing variety in the structures of mesogens[21] and only a qualitative understanding of intermolecular interactions, no concrete generalisations seem to be possible. For convenience, while discussing the structure-mesophase relationships a molecule such as shown below can be divided into three parts, viz., the hydrocarbon chain, the core and the chiral moiety.



Effects on mesophases, in particular the S_{C^*} phase, due to variations in each part have been discussed separately.

Variations in the hydrocarbon chain

These include increasing or reducing the number of methylene units in the chain. Gray and his co-workers[20] have shown that plots of the mesomorphic transition temperatures versus the alkyl chain length for a very large number of homologous series show smooth curve relationship of one kind or another. The melting points however show no regularity. The compounds exhibiting the S_{C*} phase are generally the higher homologues. In many series of compounds the thermal stability of the S_{C*} phase is found to increase with increasing carbon atoms in the chain.[22-29] The increase per methylene unit becomes less and less as the chain length increases. However, there are examples of some homologous series in which this trend is not followed.[26,28,30] Kelly et al.[26] introduced a double bond at the terminal end of the chain. This resulted not only in the depression in the melting points but also in the reduction of thermal stability of the SC* phase. Janulis et al.[31] replaced the hydrogen atoms in the chain by fluorine atoms and observed an increase in the melting points and a reduction in the thermal stability of the S_{C*} phase.[32] There are examples reported in the literature[28,33,34] wherein the value of the spontaneous polarisation increases in some cases and decreases in others along a homologous series.

Variations in the core

When the hydrocarbon chain is linked to the core through an oxygen atom the thermal stability of the S_{C*} phase has been found to increase.[35,36] However, little change in the value of spontaneous polarisation is observed.[37] The enhancement of the thermal stability due to oxygen linkage could be attributed to the increased lateral dipole moment. And this being distant from the chiral centre, the value of spontaneous polarisation is unaffected. Kitamura et al.[38] have reported an example wherein a monotropic S_{C*} phase and an enantiotropic S_A phase observed in the alkoxy compound are totally suppressed in the analogous alkyl compound which is found to be non-mesogenic. When an alkoxy group in a compound exhibiting a monotropic S_{C*} and an enantiotropic S_A phase was replaced by an alkanoyloxy group,[36] the latter exhibited enantiotropic S_{C*} phase with an increased thermal stability and an additional ferroelectric phase below the S_{C*} phase. The S_A phase vanished. This change generally brings about an increase in the thermal stability of the S_{C*} phase.[36] A biphenyl group in place of a phenyl ring[22,28,37] offers more rigidity and polarisability to the core. The thermal stability of the S_{C*} phase is found to increase. However at times the value of the spontaneous polarisation is lowered.[32,39] In an ester containing phenyl and biphenyl rings, the thermal stability of the S_{C*} phase is enhanced when the biphenyl moiety can participate in the conjugation. The value of spontaneous polarisation also increases in this case.[37]

Introduction of benzoyloxy group[28,40,41] increases the mesophase transition temperatures. Inversion of centrally situated ester linkage has dramatic effects upon the phase sequences.[22,23,36,37,42,43] It is observed that whenever the chiral moiety is in conjugation with the ester group, the S_{C*} phase goes over to the N* phase and when it is not, the S_{C*} phase goes over to the S_A phase on increasing the temperature. This observation holds good even when the chiral moiety is attached to the core by an ester linkage.[36] The reversal of -CH=N- linkage has little effect on the mesomorphic behaviour.[38] When an ester is replaced by a thioester, the thermal stability of the S_{C*} phase has been found to increase.[31] The replacement of an ester group by an azomethane linkage[25,38,44] does not show any definite trend in the thermal stability. Taniguchi et al.[45] have studied the effect of replacing central -COO- linkage unit by a $-CH_2O-$ group. Upon this change the S_{C*} thermal stability as well as the value for spontaneous polarisation seem to decrease. They have also reported an exception where the value of spontaneous polarisation has doubled by bringing about the same change.

When an aromatic ring from the core is substituted by a cyclohexane ring[22,26] the polarisability reduces and often the S_{C*} phase disappears altogether. A change from cinnamoyloxy to a-methylcinnamoyloxy moiety lowers the mesophase transition temperatures.[46] In some cases the value of spontaneous polarisation has also been reduced considerably.[53] Similarly a-chlorocinnamoyloxy group reduces the mesophase temperatures and the a-cyano group increases the melting point, however reducing the thermal stability of the S_{C*} phase.[48] Introduction of a nitrogen atom in the phenyl ring affects the S_{C*} phase thermal stability depending on the position of the nitrogen atom in the ring.[20,49] A lateral substituent on benzene ring can affect the breadth as well as the lateral dipole of the molecule. Hence it can play a major role in determining the thermal stability as well as the spontaneous polarisation of the S_{C*} phase. If the polar groups are accommcdated within the rotational volume of the molecule so that they do not increase the breadth then they tend to stabilise the smectic phases.[50] Thus, when a hydroxyl group is substituted on the benzene ring in such a way that it can form an intra-molecular hydrogen bond with a carbonyl group[5,] or nitrogen atoms of the benzylideneamino[49,52] or benzalazine group[47] it is found to favour the S_{C*} phase as well as increase the value of spontaneous polarisation. Sakurai et al.[53] have reported an example in which a lateral hydroxyl group in a Schiff's base introduced the S_{C*} and the S_A phases in place of the N* phase present in the unsubstituted parent compound. Introduction of two lateral cyano groups[43] in the phenyl ring increases the melting point as well as the thermal stability of the S_{C*} phase. When a halogen is introduced in the phenyl ring,[37,43] the value of spontaneous polarisation increases. However, if this halogen is present at the ortho position to a carbonyl group the value is found to decrease.[37,54] This is attributed to the fact that the carbonyl and the halogen groups are likely to lie in opposite directions due to electrostatic repulsion. The effect of introduction of a fluorine atom at various positions in compounds exhibiting the S_C phase has been studied by Gray et al.[55] Chambers et al.[56] have investigated the effect of mono-, di-, and tri-fluorination in phenyl biphenyl carboxylates. The S_C phase is seen to be a predominant phase in these compounds.

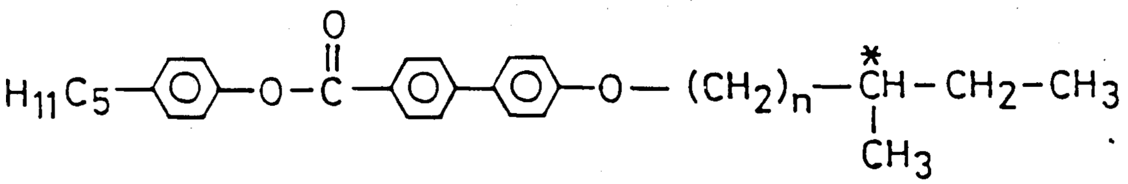
Variations in the chiral moiety

Variations in the chiral moiety are mainly directed towards enhancement of spontaneous polarisation. An increase in the dipole at the chiral carbon atom is found to result in an increase in the value of the spontaneous polarisation. This has been observed in compounds in which a methyl group is replaced by a chlorine atom.[57] An epoxy group is also found to enhance the value of spontaneous polarisation and, an ethoxy group is not as effective.[58,59] When methylene groups are introduced in between the chiral centre and the core the value of spontaneous polarisation is found to decrease.[52,60] This is attributed to the weakening of the interactions between the core and the chiral centre. This however has little effect on mesomorphism.[61] The helical twist present in the S_{C*} phase flips from one handedness to the other along a homologous series obtained by introduction of methylene units between the chiral centre and the core.[62] The sign of optical rotation and the direction of spontaneous polarisation also alternates. However, Otterholm et al.[24] have synthesised some compounds where this odd-even effect on the sign of polarisation related to the chiral centre moving away from the core of the molecule is not observed. Reducing the distance between the core and the chiral centre results in the reduction of the pitch.[63] This is disadvantageous because higher field is necessary to unwind the helix. Goodby et al.[64] have studied the damping motion of the chiral centre and its effect on polarisation. They observe that as the terminal chain is extended on the external side of the chiral centre the rotational motion of the chiral group is resticted which results in an increase of polarisation. This damping also enhances the steric repulsive effects and depresses the liquid crystal phase. Yoshino et al.[65]

have synthesised compounds in which the chiral moiety is flanked by two ester groups and by an ester and an ether linkage respectively. The value of spontaneous polarisation in the latter compound was found to be four times the value of the former. This has been explained by considering the relative orientation of bond moments around the chiral carbon atom. Geelhaar[66] has reported some optically active 4-cyanocyclohexyl-4"-alkoxybiphenyls. As the 2-methylbutyl group attached to the cyclohexane ring is replaced by methyl isopropyl ether, isopropyl acetate and isopropyl pentanoate, the value of spontaneous polarisation is found to increase. For the last compound the melting point gets considerably depressed and a wide range of S_{C*} phase is observed.

Bone et al.[67] have synthesised compounds using a-pinene and R-menthol as the optically active groups. The spontaneous polarisation has been measured by using these as dopants. For the compound containing a-pinene moiety enantiotropic S_{C*} phase is observed, whereas menthol substituted compound is non-mesomorphic. The lack of mesophase is attributed to the bulky isopropyl group. However this is responsible for enhancing the value of the spontaneous polarisation due to increased steric hindrance. Thiranes and oxiranes have also been used as optically active groups in compounds exhibiting S_{C*} phase.[41] From the analysis of C^{13} NMR and the relaxation times of the carbon atoms. Yoshizawa et al.[68] observe that the rotational frequency of the chiral carbon atom does not change much during transition from S_A to S_{C*} phase. However, the mobility of the polar group adjacent to the chiral carbon atom (carbonyl in this case) decreases remarkably during the phase transitions. Enantiomers have identical melting points.[69] The same appears to be true for mesomorphic transitions.[61,70] In S_{C*} phase the compounds of opposite absolute configurations form helices of opposite twists (handedness) and have polarisation vectors pointing in opposite directions but of same magnitude.[62] The racemates differ by a few degrees in the mesomorphic transition temperatures from the enantiomers and have non-helical and non-ferroelectric phases. Goodby and Chin[71] have reported that chirality can apparently induce additional ferroelectric phases to occur in pure compounds which need not be present in the racemic mixture.

There have been attempts to understand the origin of polarisation in S_{C*} phase at the molecular level.[58,72-76] Polarisation is dipole moment per unit volume, however the spontaneous polarisation observed in the S_{C*} phase is two orders of magnitude less than the sumnation of dipole moments of individual molecules. This could be because it is only on an average that the dipoles orient in the direction of the polarisation vector. The molecular rotation about the molecular long axis, i.e., the director is anisotropic in the S_{C*} phase. Because of this rotational bias some orientations of a molecule are preferred over others. Therefore, a dipolar ordering takes place. The extent of ordering is determined by the molecular structure and specifically by the rigid coupling between molecular dipoles and the chiral centre.[72,74,75] However, this is only an assumption and there is not sufficient body of experimental data to ensure a firm relationship between molecular structure and the magnitude of polarisation.[77] Walba et al.58 have proposed a model which suggests that polarisation originates from a novel kind of molecular recognition related to a diastereomeric host-guest complexation. They also show how the sign of the polarisation can be predicted using the proposed model.' The director here is considered as "the axis of minimum rotational inertia for each conformation" which implies a zig-zag model where the core is more tilted than the chains. Gray and McDonnell[78] proposed a rule relating molecular structure, absolute configuration and twist sense for the cholesteric phase. Goodby et al.[73] in addition to the above factors consider the inductive effect at the chiral centre and relate it to the sign of polarisation as shown in the tables 4 and 5. Position of the chiral centre is determined by the number of atoms it is removed from the aromatic ring structure of the central core of the compound, e.g., in the homolgous series



the chiral carbon atom is n+2 atoms from the core. About thirty examples have been given which follow these rules. In their next paper Goodby et al.[73] present compounds for which there is inversion of rules to a certain extent. The twist sense of the helix, the rotation of the plane polarised light are now associated with the direction of polarisation as follows.

Table 4

dipolar inductive effect at chiral center	abs. config.	position of chiral center	rotation of plane-polarised light	helix twist sense	spontaneous polarisation direction
+I	S	e	d	LH	Ps(-)
+I	R	o	d	LH	Ps(-)
+I	R	e	l	RH	Ps(+)
+I	S	o	l	RH	Ps(+)
-I	S	e	l	RH	Ps(+)
-I	R	o	l	RH	Ps(+)
-I	R	e	d	LH	Ps(-)
-I	S	o	d	LH	Ps(-)

(**After** Goodby et al.[73])

Table 5

dipolar inductive effect at chiral center	abs. config.	position of chiral center	spontaneous polarisation direction
+I	S	e	Ps(-)
+I	S	o	Ps(+)
+I	R	e	Ps(+)
+I	R	o	Ps(-)
-I	S	e	Ps(+)
-I	S	o	Ps(-)
-I	R	e	Ps(-)
-I	R	o	Ps(+)

(After Goodby et al.[73])

Ps(-) ≡ l(-)   R.H helix
Ps(+) = d(+) = L.H helix

The angle made by the core is the optic angle (α) and that made by the chains is the steric angle (θ). Two tilt orientations are possible in the S_{C*} phase of the zig-zag structure (Figure 8). "One hypothesis for inversion of initial guidelines lies in the change in the tilt orientation of the molecules. The rigid aromatic core in this case may be packed in a more upright orientation relative to the layer planes than the molecule as a whole ($\alpha < \theta$), i.e., reverse of that postulated previously ($a > \theta$)."

There have been reports of inversion of sign of polarisation on cooling the ferroelectric phase.[65,79-82] This behaviour has been attributed to a change in the conformation of the molecule at certain temperature. Also "a change of intermolecular interaction when the tilt exceeds some critical value which may induce a change of the molecular interaction (conformation) and reversal of the sign of polarisation.[65] This change has also been brought about by doping a liquid crystal exhibiting an S_C phase.[79] The temperature at which the polarisation changes sign is dependent upon the concentration of the chiral material in the non-chiral host.

Brand and Cladis[83] reported a new 'truly ferroelectric phase-smectic X' which possesses a net permanent polarisation and can be switched in a bistable way in an electric field. Unlike

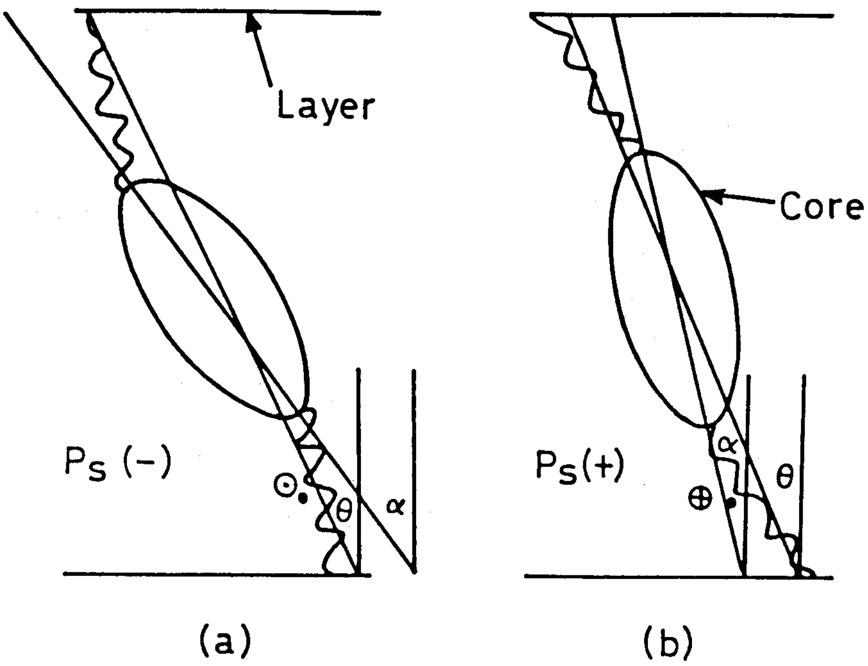


Figure 8: Two possible **tilt** orientations of a molecule in chiral smectic C phase (after Goodby et al.[73]).

S_{I^*}, S_{G^*} and S_{C^*} the orientation of the director does not change in the S_X phase when the field is turned off. This phase was observed in S(+)-4-(2'-methylbutyl)phenyl 4-n-octylbiphenyl-4-carboxylate. They further suggested 'helielectric' as a more appropriate name for those phases which are normally called 'ferroelectric phases' since that describes the zero field ground state and distinguishes them from the 'truly ferroelectric phases' like the smectic X. Chandani et al.[84] reported an 'anti-ferroelectric phase' in 4-(1-methylheptyloxycarbonyl)phenyl 4'-octyloxybiphenyl 4"-carboxylate. They designated it as $S_{C^*_A}$. Perhaps this is similar to the phase observed by Levelut et al.85 in 1(methyl)heptyl terephthalidene bis aminocinnamate which was designated as 'smectic O'.

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