

Chapter 1

Introduction

Liquid Crystals

Many organic compounds exhibit a variety of intermediate phases between their ordered crystalline phase and disordered isotropic liquid phase. These intermediate phases are called liquid crystalline phases as they exhibit both crystal-like as well as liquid-like properties.¹⁻³ The molecules exhibiting liquid crystalline phases are geometrically anisotropic, i.e., they are rod-like or disk-like in shape. The phase transition in these compounds can be brought about by changing the temperature and this class of materials is known as thermotropic liquid crystals. Liquid crystalline phases may also be obtained by adding a solvent or a mixture of solvents to appropriate solutes. These are called lyotropic liquid crystals. Liquid crystalline phases are also called mesomorphic phases or mesophases and the compounds exhibiting such phases are known as mesogens. This thesis deals only with thermotropic liquid crystals.

Thermotropic liquid crystals

The first recorded observation of thermotropic liquid crystals has been attributed to Reinitzer.³ He noticed that, cholesteryl benzoate at 145.0°C melted not into a clear transparent but always into a cloudy translucent liquid and on further heating at 178.0°C that clouding suddenly vanished. The cloudy phase existing between 145.0°C and 178.0°C is the liquid crystalline phase. A mesophase existing above the melting point is called enantiotropic and that which exists below the melting point is known as monotropic. The thermotropic liquid crystalline phases are classified according to the positional and

orientational ordering in their molecular arrangement. Here, we describe the structure of some of the liquid crystalline phases that are discussed in this thesis.

The nematic phase (N)

The simplest of the liquid crystalline phases is the nematic phase. It is a fluid in which the long molecules have orientational order but no positional order in the centre of masses of the various molecules. A schematic molecular arrangement of this phase is shown in figure 1.1.a. This phase is cylindrically symmetric, i.e., optically uniaxial and centrosymmetric. The average orientation of the molecules can be represented by an apolar vector $\overset{A}{n}$ called director. Recently, the existence of the biaxial nematic phase has been reported.⁴

The smectic mesophases (S)

The molecules in the smectic phases possess an orientational and a lamellar order. Several modifications of the smectic phase are known.

The smectic A (S_A) phase

In this phase there is a layered arrangement of the long molecules. Within the layers the molecules have short range order but there is no positional order and the average orientation of the molecules is parallel to the layer normal. This phase can be looked upon as liquid in two dimensions and crystal in the third dimension. A schematic diagram of this phase is shown in figure 1.1.b.

The smectic C (S_C) phase

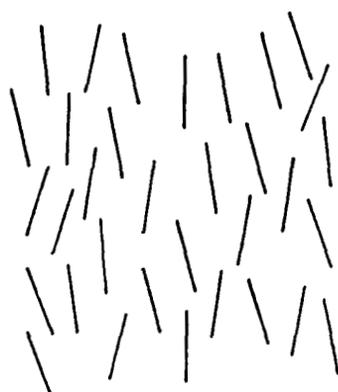
This phase is similar to smectic A phase except that the molecules in the layers are tilted uniformly at an angle with respect to the layer normal. The projection of the molecules into the layer plane is defined by a polar vector called the C director. A schematic diagram of smectic C phase is given in figure 1.1.c.

The cholesteric or the chiral nematic (N*) phase

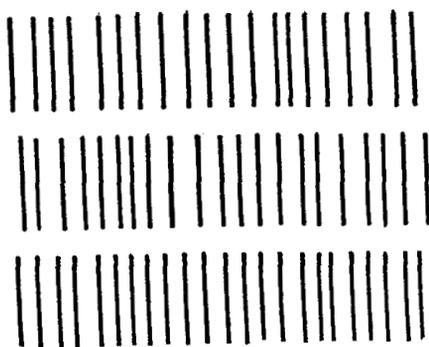
This phase is exhibited by compounds composed of non-centrosymmetric (chiral) molecules. In this phase the molecules arrange themselves in a helical structure. The phase can be described as being made up of nematic planes helically piled over one another so that the director is rotating uniformly about the director normal. Figure 1.2.a shows the molecular arrangement in the cholesteric phase. This phase can also be obtained by doping a nematic liquid crystal with a small amount of a chiral compound. The distance P over which the director rotates by 2π is called the pitch of the medium. Since the nematic director is apolar, the cholesterics have a 2 fold screw axis. Hence the optical periodicity of the medium is P/2. In general this period is of the order of wavelength of light. Therefore this phase exhibits some remarkable optical properties.^{2,5} Also light can be used as a probe to investigate the structure of the this phase.⁶

The blue phases

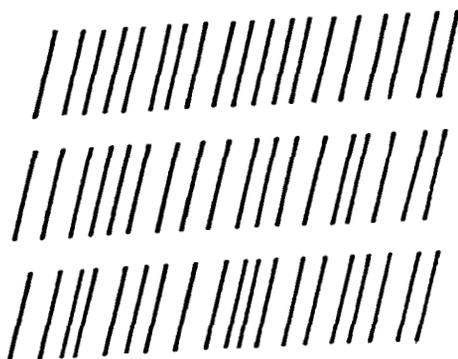
It has been found that cholesteric phase with a very small pitch ($< 1\mu\text{m}$) can under go phase transition to thermodynamically stable phases before transforming to the isotropic liquid over a very short temperature range ($\sim 1^\circ\text{C}$). These phases are known as blue



a



b



c

Figure 1.1. Schematic representation of the molecular arrangement in the (a) nematic, (b) smectic **A** and (c) smectic **C** liquid crystalline phases.

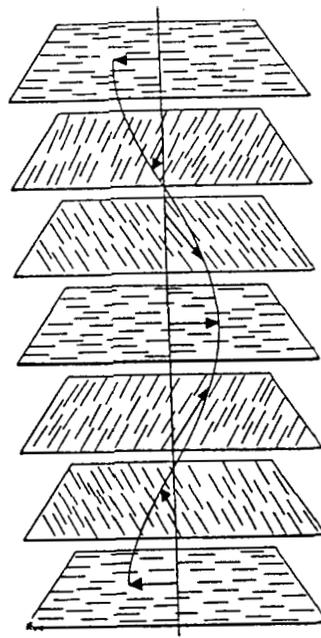
phases.⁵ There are three types. The blue phase I and the blue phase II have body centered cubic and simple cubic structures respectively. The structure of the blue phase III is not yet very well established.

The chiral smectic C (S_C^*) phase and ferroelectricity

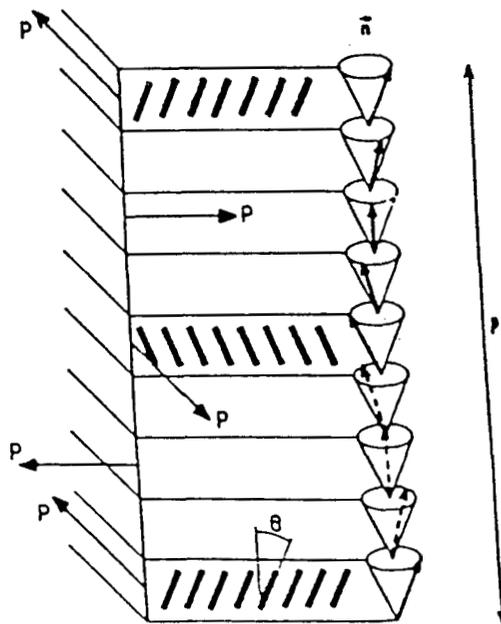
If compounds made up of chiral molecules exhibit smectic C phase then that phase is chiral smectic C (S_C^*). The molecular arrangement in chiral smectic C phase is shown in figure 1.2.b. The azimuth of the tilted molecules precesses from one layer to another giving rise to a helical structure similar to the cholesteric liquid crystals, and which shows ferroelectricity.⁷ Clark and Lagerwall⁸ demonstrated an electro-optical effect that utilised the ferroelectric property.

The antiferroelectric (S_{CA}^*), ferrielectric ($S_{C\gamma}^*$) and the chiral smectic C_α ($S_{C\alpha}^*$) phases

The antiferroelectric phase (S_{CA}^*) was discovered by Chandani *et al.*⁹ in 4-(1-methylheptyloxycarbonyl)phenyl-4'-octyloxybiphenyl-4-carboxylate (MHPOBC). Later they identified sub-phases such as ferrielectric and $S_{C\alpha}^*$ phases in the same compound.^{10, 11} In antiferroelectric phase the molecules are tilted in opposite directions in adjacent layers, whereas in ferrielectric phase the molecules are tilted in opposite directions randomly. As a result of this ordering the spontaneous polarisation is averaged to zero for the bulk unwound antiferroelectric phase in a zero electric field. The schematic diagram of this phase is given in figure 1.3.a. There is residual spontaneous polarisation for the ferrielectric phase. The mesophase observed by Levelut *et al.*¹² in 1-methylheptyl



a



b

(after Fukuda et al.¹³)

Figure 1.2. Schematic representation of the molecular arrangement in the (a) cholesteric, and (b) chiral smectic C liquid crystalline phases.

terephthalidene bis aminocinnamate which was designated as "smectic O" phase is in fact antiferroelectric. Antiferroelectric phase shows tristable switching from antiferroelectric phase to ferroelectric phase in an electric field and this effect is shown schematically in figure 1.3.b. Ferroelectric phase exhibits tetrastable switching under an electric field and this is shown diagrammatically in figure 1.3.c. As a consequence of this, these materials can be utilised in fast switching display device applications." The structure of $S_{C\alpha}^*$ phase appears to be a competitive one between the structures of the antiferroelectric and ferroelectric phases. There are contradicting proposals for the structure of this phase, but a group of Japanese scientists proposed twelve possible structures for this. The real structure of this phase has not yet been clearly established.

The swallow-tailed achiral antiferroelectric phase ($S_{C_{alt}}$)

The existence of zig-zag ordered smectic C phase ($S_{C_{alt}}$) in non-chiral compounds has been known for many years. This type of compounds were first reported by Levelut *et al.*¹² and also occur as dimers and in some polymers. More recently Nishiyama and Goodby¹⁴ prepared a non-chiral swallow-tailed compound which showed complete miscibility with the $S_{C_A}^*$ phase. They proposed that the incidence of the $S_{C_{alt}}$ phase was due to the formation of molecular pairs which was due to the overall molecular geometry and not necessarily as a direct result of the chirality of the species. Goodby *et al.*¹⁵ found that as the length of the off-axis alkyl substituent is increased in chiral propiolates, the incidence of antiferroelectric phase also increases. When they lengthened the off-axis lateral alkyl substituent until it equalled that of the terminal chain length, it resulted in a

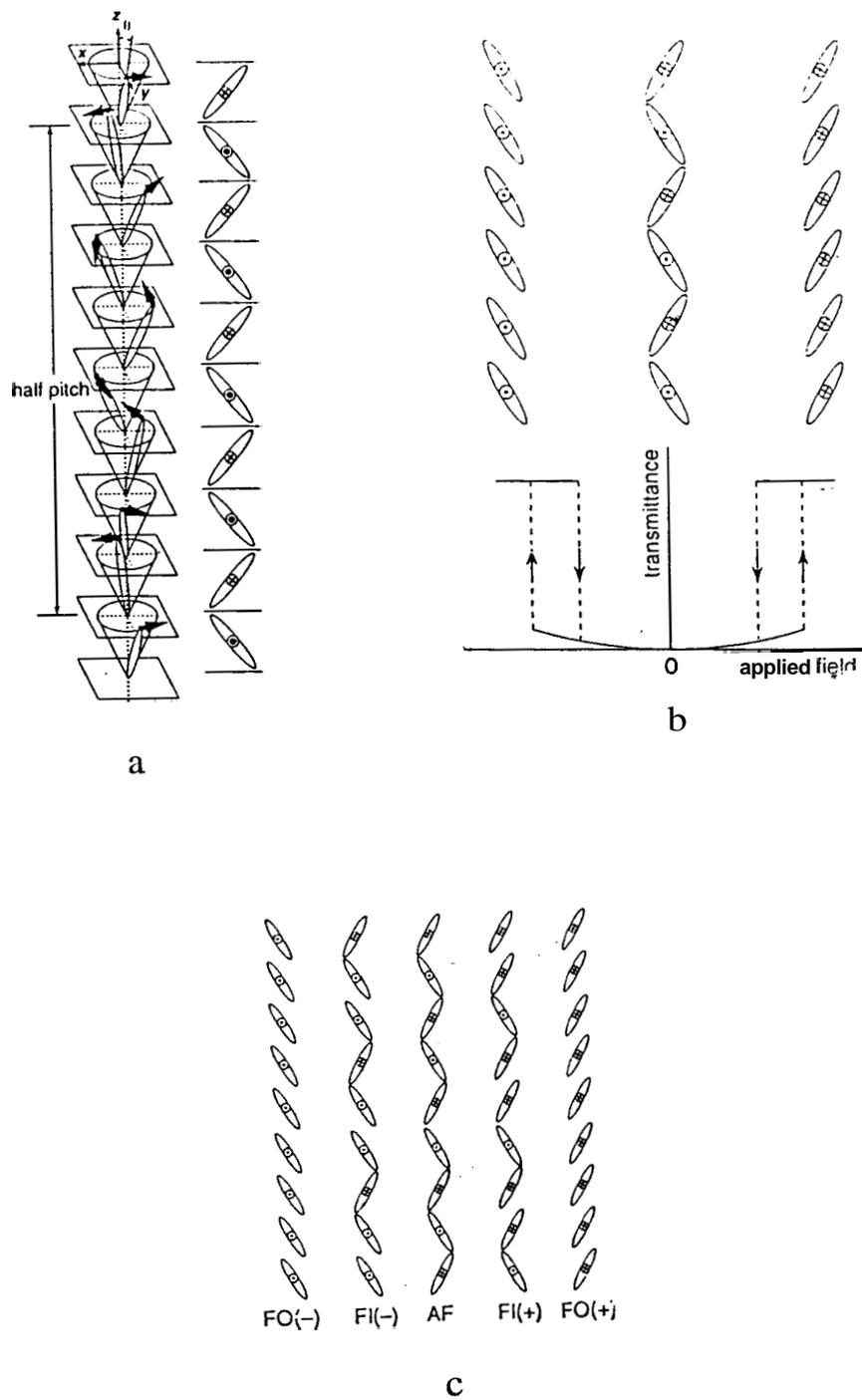


Figure 1.3. Schematic representation of the arrangement of molecules in the (a) antiferroelectric phase, (b) tristable states of antiferroelectric and (c) tetrastable states of ferroelectric phases (after Fukuda *et al.*¹³).

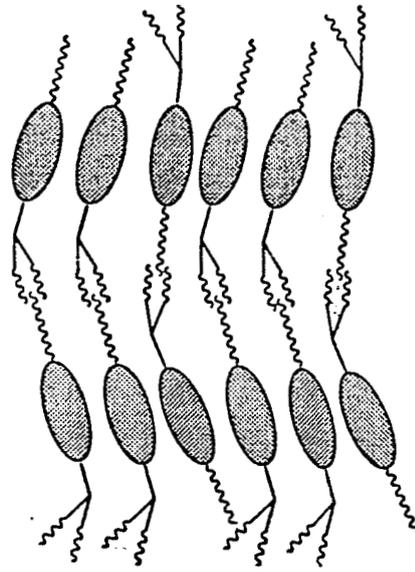
achiral swallow-tailed compound which possesses a smectic C phase which has an antiferroelectric-like structure and this is shown in figure 1.4.a.

The twist grain boundary smectic A (TGB_A) phase

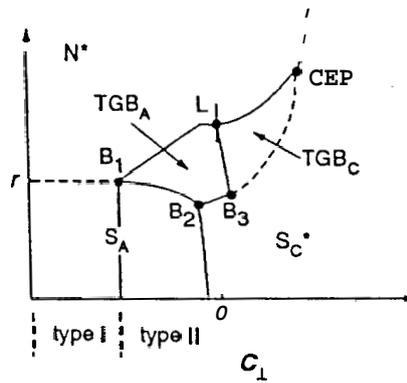
It was de Gennes¹⁶ who predicted that twist or bend distortions can be incorporated into a layered smectic A structure by the presence of an array of screw or edge dislocations. A model for such an array of dislocations for chiral molecules was proposed by Renn and Lubensky¹⁷ and the existence of this phase was discovered by Goodby *et al.*¹⁸ in some propiolate derivatives. The phase diagram proposed by Renn and Lubensky is shown in figure 1.4.b. In the TGB_A phase small blocks of smectic A layers rotate with respect to one another, thereby forming a helical structure. The axis of the helix is perpendicular to the long axis of the molecules. The blocks are separated from one another by screw dislocations. This type of defect allows the blocks to be rotated through a small angle with respect to one another. As a helix is formed with the aid of screw dislocations, the dislocations themselves are periodic. It was predicted that rows of screw dislocations will form grain boundaries in the phase. The pitch of the helix is of the order of wavelength of visible light, and hence it reflects light selectively. A schematic representation of this phase is shown in figure 1.4.c. Renn and Lubensky extended their theory for the existence of TGB_C phase.¹⁹ This phase was discovered recently in some fluoro substituted tolane derivatives.²⁰

Influence of molecular structure on mesomorphism

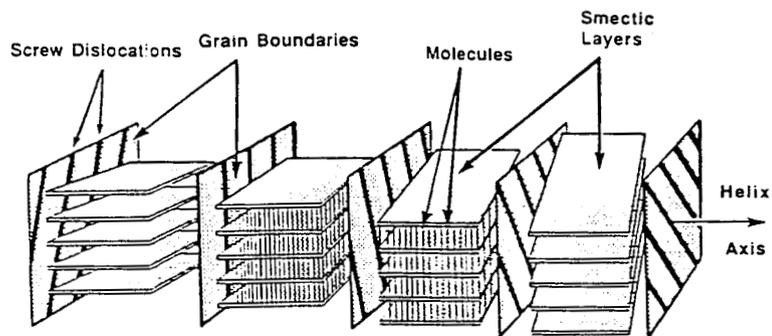
The association between molecular structure and the mesomorphic properties of calamitic liquid crystals has been very rigorously studied by Gray.²¹ Most of the mesogens



a (after Goodby *et al.*¹⁴)



b (after Renn and Lubensky¹⁷)

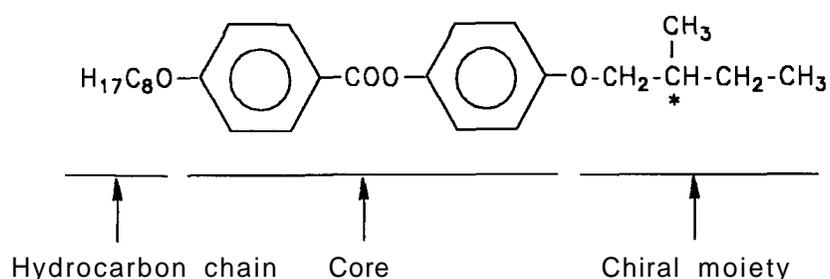


c (after Goodby *et al.*¹⁸)

Figure 1.4. Schematic representation of the molecular arrangement in the (a) swallow-tailed achiral antiferroelectric phase, (b) theoretical phase diagram of TGB_A phase proposed by Renn and Lubensky, and (c) twist grain boundary smectic A phase.

Chapter 1

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 high, 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 inadequate to maintain order in the fluid state. In both cases the crystal will directly melt to 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 efficiency, the balance between the length and the breadth, the rigidity, the linearity, the anisotropy of polarisability and the direction 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 ²² 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.



Effect on mesophases, in particular chiral mesophases, due to variation in each part have been discussed separately.

Variation in the hydrocarbon chain

These include increasing or reducing the number of methylene units in the chain. Gray and his co-workers²¹ 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.²³⁻³⁰ 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.^{27,29,31} Kelly *et al.*²⁷ 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 S_C^* phase. Janulis *et al.*³² 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. There are examples reported in the literature^{29,33,34,35} wherein the value of the spontaneous polarisation increases in some cases and decreases in others along a homologous series.

Variation 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**.^{36,37} However, little change in the value of spontaneous polarisation is observed. The enhancement of the thermal stability due to oxygen linkage could be attributed to the increased lateral dipole moment. This being distant from the chiral centre, the value of spontaneous polarisation is

unaffected. Kitamura *et al.*³⁹ 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^* phase and an enantiotropic S_A phase was replaced by an alkanoyloxy group³⁷ 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 had vanished. This change generally brings about an increase in the thermal stability of the S_C^* phase.³⁷ A biphenyl group in place of a phenyl ring^{23,29,38} 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.^{33,40} In an ester containing phenyl and biphenyl moities, the thermal stability of the S_C^* phase is enhanced due to the biphenyl moiety participating in the conjugation. The value of spontaneous polarisation also increases in this case.³⁸

Introduction of benzoyloxy group^{29,41,42} increases the mesophase transition temperatures. Inversion of centrally situated ester linkage has dramatic effect upon the phase sequences.^{23,24,37,38,43,44} 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.³⁷ The reversal of $-\text{CH}=\text{N}-$ linkage has little effect on the mesomorphic behaviour.³⁷ When an ester is replaced by a thioester, the thermal stability of the S_C^* phase has been found to increase.³⁷ The replacement of an ester group by an azomethine linkage^{26,39,45} does not show any definite trend in the thermal stability. Taniguchi *et al.*⁴⁶

have studied the effect of replacing central -COO- linkage unit by a -CH₂O- group. Upon this change the S_C* thermal stability as well as the value for spontaneous polarisation seem to decrease.

When an aromatic ring from the core is substituted by a cyclohexane ring^{23,27} the polarisability gets reduced and often the S_C* phase disappears altogether. A change from cinnamoyloxy to *o*-methylcinnamoyloxy moiety lowers the mesophase transition temperatures.⁴⁷ In some cases the value of spontaneous polarisation also gets reduced considerably.⁴⁸ Similarly α -chlorocinnamoyloxy group reduces the mesophase temperatures and the *o*-cyano group increases the melting point, while reducing the thermal stability of the S_C* phase.⁴⁹ 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.^{21,50} A lateral substituent on a phenyl 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 accommodated within the rotational volume of the molecule so that they do not increase the breadth then they tend to stabilise the smectic phases.⁵¹ Thus, when a hydroxyl group is substituted on the benzene ring in such a way that it can form an intramolecular hydrogen bond with a carbonyl group⁵² or nitrogen atom of the benzylideneamino^{50,53} or benzalazine group⁴⁸ it is found to favour the S_C* phase as well as increase the value of spontaneous polarisation. Sakurai *et al.*⁵⁴ have reported an example in which a lateral hydroxy 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 groups⁴⁴ on the phenyl ring increases the melting point as well as the thermal stability of

the S_C^* phase. When a halogen is introduced on the phenyl ring, ^{38,44} 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.^{38,55} 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 fluoro group at various positions in compounds exhibiting the S_C phase has been studied by Gray *et al.*⁵⁶ Chambers *et al.*⁵⁷ have investigated the effect of mono-, di- and tri-fluorination in many phenyl-biphenylcarboxylates. The S_C^* phase is seen to be a predominant phase in these compounds.

Variation in the chiral moiety

Variation in the chiral moiety is mainly directed towards enhancement of spontaneous polarisation. An increase in the dipole moment 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 chloro group.⁵⁸ It has been observed that the thermal range of the $S_{C_A}^*$ phase increases in compounds in which a methyl group is replaced by a trifluoromethyl or pentafluoroethyl groups.¹³ In this case there is a direct transition from S_A phase to $S_{C_A}^*$ phase. An epoxy group is also found to enhance the value of spontaneous polarisation and, an ethoxy group is not as effective.^{59,60} When methylene groups are introduced between the chiral centre and the core the value of spontaneous polarisation is found to decrease.^{53,61} This is attributed to the weakening of the interactions between the core and the chiral centre. This however has little effect on mesomorphism.⁶² 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.” The sign of optical rotation and the direction of spontaneous polarisation also alternate. However, Otterholm et al.²⁵ 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.⁶⁴ This is disadvantageous because higher field is necessary to unwind the helix. Goodby et al.⁶⁵ have studied the damping motion of the chiral centre and its effect on polarisation. They observed that as the terminal chain is extended on the external side of the chiral centre, the rotational motion of the chiral group is restricted which results in an increase of the value of polarisation. This damping also enhances the steric repulsive effects and depresses the liquid crystal phase. Yoshino et al.⁶⁶ have synthesised compounds in which the chiral moiety is flanked by two ester groups and by an ester and an ether linkage groups 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. Geelhaar⁶⁷ has reported some optically active trans-1-(4''-alkoxybiphenyl)-4-(2-methylbutyl)-4-cyanocyclohexanes. When the 2-methylbutyl group attached to the cyclohexane ring is replaced by methyl isopropyl ether, isopropyl acetate or isopropyl pentanoate group, the value of spontaneous polarisation increases gradually. For the last compound the melting point gets considerably depressed and a wide range of S_C^* phase is observed.

Bone et al.⁶⁸ have synthesised materials using α -pinene and menthol as the optically active compounds and S_C^* phase has been obtained by using these as dopants in a S_C host. Enantiotropic S_C^* phase was observed for the compound containing α -pinene, whereas menthol containing compound was non-mesomorphic. The lack of mesophase has been

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.⁴² From the analysis of ^{13}C NMR and the relaxation times of the carbon atoms, Yoshizawa *et al.*⁶⁹ observed 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. Generally the enantiomers have identical melting points⁷⁰ and the same appears to be true for mesomorphic transitions as well.^{62,71} 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.⁶³ The racemates differ by a few degrees in the mesomorphic transition temperatures as compared to the enantiomers and have non-helical and non-ferroelectric phases. Goodby and Chin⁷² have reported that chirality can induce additional ferroelectric phases in pure chiral 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.^{59,73-77} Polarisation is dipole moment per unit volume, although the spontaneous polarisation observed in the S_C^* phase is two orders of magnitude less than the summation 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 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.^{73,75,76} 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.⁷⁸ Walba *et al.*⁵⁹ 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 tilted more than the chains. Gray and McDonnell⁷⁹ proposed a rule relating molecular structure, absolute configuration and twist sense for the cholesteric phase. Goodby *et al.*⁷⁴ 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 tables 1.1 and 1.2. 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 shown below.



For example in the homologous series, the chiral carbon atom is $n+2$ atoms from the core. More than thirty examples are known which follow these rules. Goodby *et al.*⁷⁴ prepared compounds for which there is violation of these 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.

Ps (-) \equiv l (-) \equiv R.H. helix

Ps (+) \equiv d (+) \equiv L.H. helix

Table 1.1

Dipolar inductive effect at chiral centre	Abs. config.	Position of chiral centre	Rotation of plane polarised light	Helix twist sense	Spontaneous polarisation direction
+I	S	e	d	LH	P _S (-)
+I	R	o	d	LH	P _S (-)
+I	R	e	l	RH	P _S (+)
+I	S	o	l	RH	P _S (+)
-I	S	e	l	RH	P _S (+)
-I	R	o	l	RH	P _S (+)
-I	R	e	d	LH	P _S (-)
-I	R	o	d	LH	P _S (-)

(after Goodby *et al.*⁷⁴)

Table 1.2

Dipolar inductive effect at chiral centre	Abs. config.	Position of chiral centre	Spontaneous polarisation direction
+I	S	e	P_S(-)
+I	S	o	P_S(+)
+I	R	e	P_S(+)
+I	R	o	P_S(-)
-I	S	e	P_S(+)
-I	S	o	P_S(-)
-I	R	e	P_S(-)
-I	R	o	P_S(+)

(after Goodby *et al.*⁷⁴)

Two tilt orientations are possible in the S_C^* phase of the zig.-zag structure as shown in figure 1.5. The angle made by the core is the optic angle α and that made by the chains is the steric angle(θ). 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 ($\alpha > \theta$).

There have been reports of inversion of sign of polarisation on cooling the ferroelectric phase.^{66,80-83} This behaviour has been attributed to a change in the conformation of the molecule at a 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.⁶⁶ This change has also been brought about by doping a liquid crystal exhibiting an S_C phase.⁸⁰ The temperature at which the polarisation changes sign is dependent upon the concentration of the chiral material in the non-chiral host.

Brand and Cladis⁸⁴ 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 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 of 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.

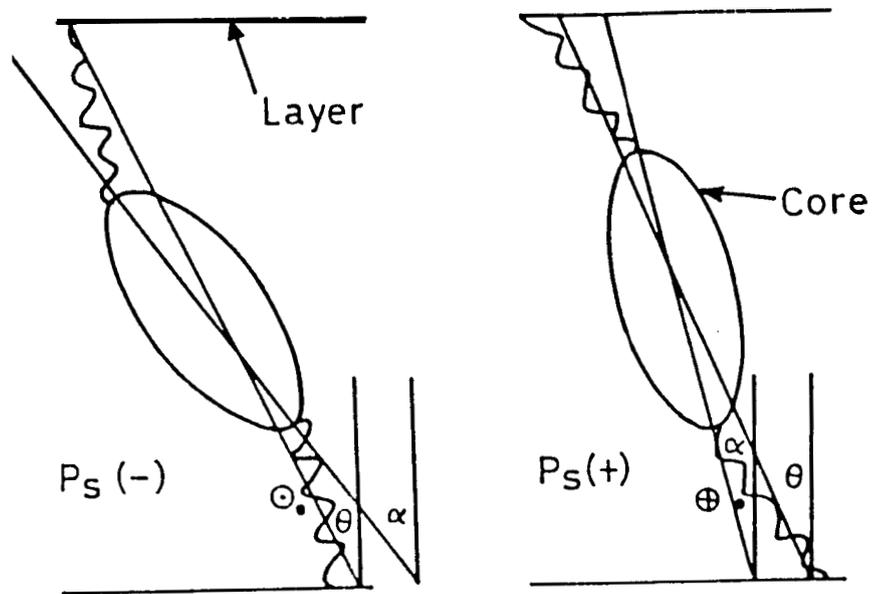


Figure 1.5. Two possible zig-zag tilt orientations of S_C^* phase (after Goodby *et al.*⁷⁴).

The effect of molecular chirality on antiferroelectric and twist grain boundary phases are shown in figures 1.6.a and 1.6.b respectively.

Applications

The main application of liquid crystals is in electronic displays. Nematic liquid crystals are widely used for these purposes. Cholesteric liquid crystals are used as temperature sensors in disposable thermometers, aerodynamic testing⁸⁵ *etc.* Another important use of cholesteric liquid crystals is in the medical field.⁸⁶ They have also been used to produce panels that exhibit an optical memory effect.⁸⁷

Chromatography is of great importance in modern chemical analysis and physico-chemical investigations. Liquid crystals are among the materials used in chromatography. The use of liquid crystals as stationary phases in gas chromatography was described for the first time in 1963 by Kelker⁸⁸ and later by Dewar and Schroeder.⁸⁹ Ever since, liquid crystal stationary phases have been applied successfully for separation of composite mixtures, chiefly isomers, including those of polycyclic hydrocarbons.

Liquid crystals are used to control or alter the chemical reactivity of dissolved solutes.^{90,91} Liquid crystals do alter reactivity as a result of their ability to control solute diffusion, orient reactants and discriminate between stable solutes and transition states according to their sizes and shapes. This ability depends on the degree of order present in the liquid crystal and the structure of the reactants in relation to that of the mesogen.

Thus, the electric field induced antiferroelectric - ferroelectric phase transition is applicable to display devices.⁹¹ Two main characteristics are the sharp threshold behaviour under a DC field between antiferroelectric and ferroelectric (AF-F) states and the

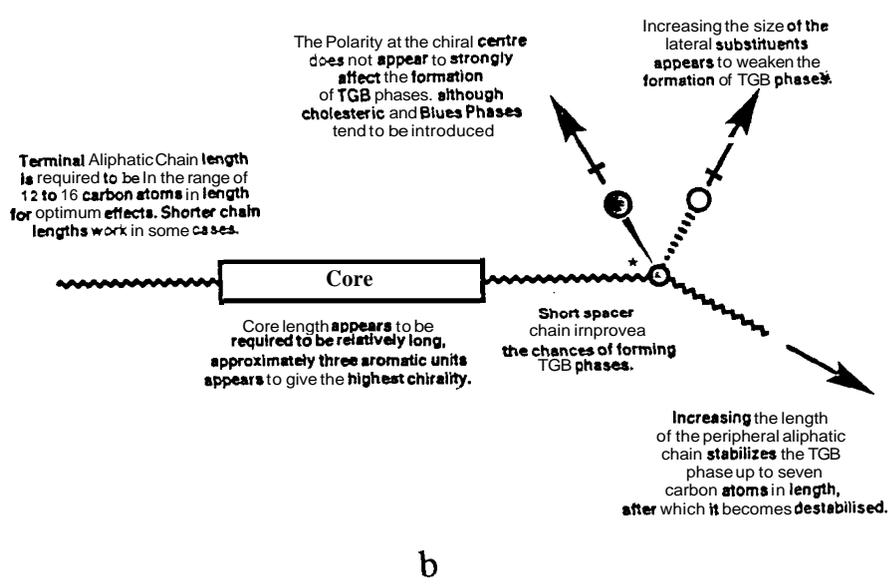
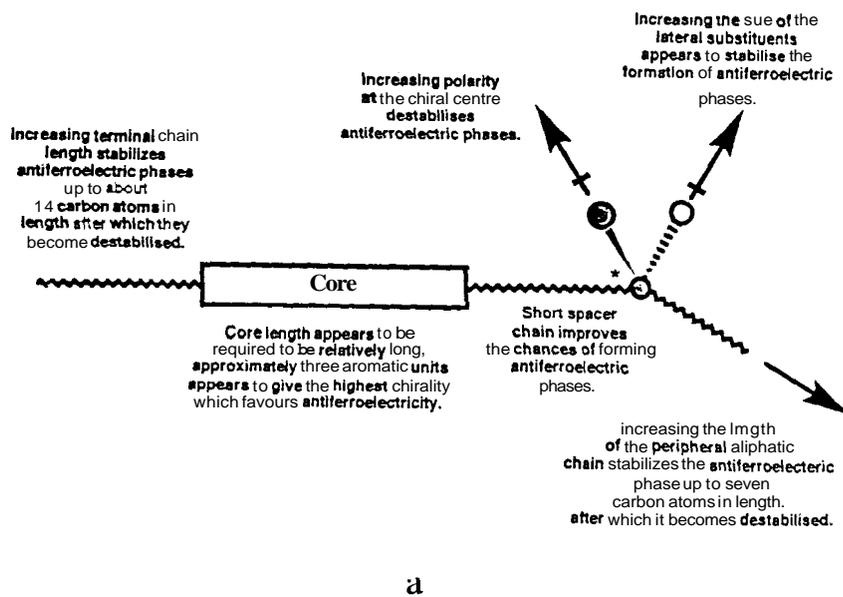


Figure 1.6. Schematic representation of effect of molecular chirality on (a) antiferroelectric and (b) TGB_A liquid crystalline phases.

hysteresis in the switching, bringing about a bistable device. The switching current peaks are observed at the voltages of the F-AF and AF-F switching and are equivalent to the double hysteresis in a D-E loop, which is characteristic to antiferroelectricity.

The AFLC display (AFLCD) utilises both F states, as clearly noticed by two driving frames. Two states give the same transmittance, so that one can use them alternatively. The AFLCD is not affected by ghost effect which is a serious problem in FLC. Another problem in FLC is the weakness against mechanical shock because of the smectic layer structure. AFLC cells have a remarkable feature of self alignment recovery during an operation from damage caused by mechanical and thermal shocks. Also the non-chevron structure gives rise to an additional advantage and relatively high contrast ratio.

The AFLC-SLM may not be suited for image storage devices, since a constant voltage has to be applied to the cell in order to memorise addressing images. This may be applicable for real time holography. Work is going on in many laboratories around the world at the present time not only to have a clear understanding of the complex nature of these mesophases but also to use them advantageously in many devices.

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