Chapter-1 Introduction

Liquid Crystals

The credit for the discovery of the liquid crystalline state has been attributed to Reinitzer [1]. Broadly, liquid crystals can be classified into (1) Thermotropic Liquid Crystals - which are obtained by the action of heat on certain pure compounds or their mixtures and (2) Lyotropic Liquid Crystals - which are generated by the action of a solvent on suitable substrates. In this thesis, we are concerned with thermotropic liquid crystals and excellent reviews are available on this topic, particularly those concerning calamitic and discotic liquid crystals[2,3,4]. However, a brief description of some of the well known mesophases exhibited by rod-like molecules (calamitic) which are encountered during the investigations carried out and described in this thesis are given below.

Nematic (N) phase

Nematic phase is the least ordered and simplest of the liquid crystalline phases known. On cooling the isotropic liquid to the nematic phase, the medium gains some amount of orientational ordering but no positional ordering and the molecules can easily slide past one another. On an average all the molecules point in a particular direction (orientational ordering) defined as a director and is denoted by a vector **n**. As a consequence, the mesophase is anisotropic and shows interesting optical properties. Nematic liquid crystals are the most commonly used materials in electro-optic displays. A perfectly aligned nematic liquid crystal is optically uniaxial and the structure is characterized by a point group D_{exh} .

The smectic (Sm) phases

The molecules in smectic phases exist in layers with a well defined periodicity. Depending on the arrangement of molecules within the smectic layers (in-plane order), these can be further classified into different types of smectic phases. The alphabetical suffixes used to identify different smectic phases simply indicate the order of their discovery. The arrangement of molecules in smectic A and smectic C phases are described below.

1

The smectic A (SmA) phase

The constituent molecules of smectic A phase lie parallel to one another with the long molecular axis parallel to the layer normal and the center of molecular mass have no long range positional order. Hence, smectic A phase can be considered as a two-dimensional liquid (freedom of molecular motion within the smectic layer) and a quasi one-dimensional crystal (hindered translation between the layers). The mesophase is optically uniaxial, the structure has D_{eeh} symmetry (due to the rotation around the long axis). This is the highest temperature smectic phase and hence it exhibits higher ordered symmetry. The X-ray experiments clearly reveal the orthogonal arrangement of the molecules with respect to the layer planes. Hence, the layer spacing (d) obtained from X-ray diffraction is comparable to the calculated length (L) of the molecule.

The smectic C (SmC) phase

This is an analog of SmA phase, except that the molecules tilt with respect to the layer normal. Hence the phase is optically biaxial. The tilt direction may be random between the layers. The smectic C phase shows the monoclinic symmetry and the point group symbol is C_{2h} . The observed layer spacing from X-ray experiments show a tilt of the molecules within the layer. The layer spacing may or may not vary with temperature which sometimes depends on the chemical nature of the material.

The cholesteric (N^*) phase

If the nematic phase is made up of chiral molecules or is doped with a suitable chiral material, then a spontaneous precession of molecular director **n** about the Z-axis gives rise to a helical structure for the mesophase. The helical twist axis is perpendicular to the preferred direction of the molecules. The chemical structure and the nature of chiral group present in the molecule determine the handedness of the mesophase. This mesophase exhibits unique optical properties due to selective reflection of light and this concept has been made use of in many applications.

The blue phases (BP)

The name blue phase is historically derived from the optical Bragg reflection of blue light, but blue phases can also exhibit the visible light of longer wavelengths due to the large lattice constants. If the pitch of the cholesteric phase is relatively short (< 7000 Å) then the

blue phases (BP I, BP II and BP III) appear over a short range of temperature (< 1° C) between the cholesteric phase and the isotropic liquid. There are three blue phases, out of which two (BP I, BP II) have cubic symmetry and the third one (BP III) has an amorphous structure. Several other blue phases also exist with a different cubic symmetry only in the presence of external fields.

The chiral smectic C (SmC^{*}) phase



Fig. 1.1. (a) Schematic representation of the arrangement of molecules in helical fashion in the chiral smectic C phase (E=0), (b) the bistable switching of the unwound state of chiral smectic C phase by the application of an electric field (above the threshold voltage). (After Fukuda *et al.*[6])

The discovery of ferroelectricity in liquid crystals was not accidental. Based on symmetry arguments, Meyer *et al.* [5] not only predicted the existence of ferroelectricity in liquid crystals, but also demonstrated the same experimentally. The structure of chiral smectic C phase is similar to that of achiral smectic C phase, except that the precession of the director of the chiral molecules from layer to layer produces a helical structure for the mesophase as shown in figure **1.1a**. Since the mirror plane symmetry has been eliminated by introduction of a chiral molecule or by doping the SmC phase with a suitable chiral material (point group symmetry reduces from the C_{2h} to C₂) the medium becomes chiral. As a consequence, there exists a spontaneous polarization parallel to the two-fold axis and perpendicular to the tilt direction of the molecules which is stabilized by the formation of helical structures. The tilt direction is unique for a given material and hence the medium becomes homochiral. The handedness of the mesophase is determined by the nature of the chiral group present in the molecule.

The layer polarization can be stabilized by the formation of helix and hence the net polarization in the mesophase becomes zero. However, the helical structure can be unwound by the application of a sufficiently high electric field perpendicular to the helical axis. Then the medium can have a net polarization that can be reversed by reversing the polarity of the applied electric field as shown in figure **1.1b**. Thus, the structure is bistable and can take one of the two different states of opposite polarization in the absence of any external electric field. These materials are useful in rapidly switching electro-optic shutters, with the response time in microseconds.

The antiferroelectric smectic (SmC^{*}_A) phase

The antiferroelectric smectic C phase was discovered accidentally by Chandani *et al.* [7] in 1989 while conducting conoscopic experiments on 4-(1-methylheptyloxycarbonyl)phenyl- 4^{1} -octyloxybiphenyl-4-carboxylate (MHPOBC). The structure of the antiferroelectric phase is similar to that of the ferroelectric phase except for the fact that the molecules tilt in opposite directions in adjacent layers. As a consequence, the dipoles oppose in alternate layers there by cancelling each other as shown schematically in figure **1.2a**. Hence, the net polarization is zero for a given medium as in the case of a ferroelectric phase. The tilt of the molecules in opposite directions in adjacent layers was confirmed by using a freely suspended film of the mesophase. This mesophase has a helical structure macroscopically due to the alternate tilt of the molecules in adjacent layers.

unwound by the application of a sufficiently high electric field to induce a ferroelectric state. By reversing the polarity of the applied electric field, this can be switched to another ferroelectric state and on switching off the field, this relaxes to the antiferroelectric ground state. This is shown schematically in figure **1.2b**. The tristable switching for this mesophase is also clearly demonstrated in this figure.



Fig. 1.2. A schematic representation of (a) arrangement of the molecules in the antiferroelectric phase (E=0), (b) unwound state exhibiting tristable switching by the application of electric field (above the threshold voltage). (After Fukuda *et al.*[6])

Later, Chandani *et al.* [8] also found a few sub-phases while carrying out careful electrooptical switching characteristics for MHPOBC and these are designated as SmC^*_{α} , SmC^*_{γ} etc.

Twist grain boundary (TGB) phases

In 1972, de Gennes predicted [9] that a defect stabilized mesophase can be created when a smectic A phase is subjected to twist or bend distortions. The bend and twist distortions can be stabilized by an array of screw or edge dislocations. The possible structural model for such a phase was proposed by Renn and Lubensky [10a], who called this mesophase as twist grain boundary A (TGB_A) phase. A schematic representation of this phase structure is shown in figure **1.3**. The first practical example of a compound exhibiting TGB_A phase was provided by Goodby *et al.* [10b].



Fig. 1.3. Schematic representation of rotation of blocks of smectic layers which are separated by grain boundaries in TGB phase and the length of the individual block is l_b . The helical axis is perpendicular to the smectic layer normal. (After Goodby *et al.*[10])

In certain compounds composed of chiral molecules, small blocks of the SmA phase rotate with respect to one another by screw dislocations forming the helical structure of the TGB_A phase. This phase generally appears while cooling directly from the isotropic liquid or a cholesteric phase. The TGB_C phase is the analog of TGB_A phase except that the molecules tilt within the smectic blocks. The TGB_C^* phase has blocks of helical structures as in the SmC^* phase. The helical axis of the blocks is perpendicular to the twist axis of the TGB phase.

Columnar mesophases from disk-like molecules

Until 1977, it was believed that only rod-like molecules exhibit liquid crystalline phases. However, Chandrasekhar *et al.* [11] discovered a new class of liquid crystals in which compounds composed of disk-like molecules (benzene hexa-n-alkanoates) are stacked one above the other to form columns. These columns further arrange in a hexagonal lattice to exhibit a new type of mesophase namely, the columnar mesophase.

Chiral phases from achiral molecules (Banana liquid crystals)

During the early part of this century, Vorlander and his coworkers synthesized more than 2000 mesogenic compounds to examine the relationship between chemical structure and the effective mesomorphic behaviour. They synthesized the first homologous series of compounds to study the effect of chain length on the mesomorphic properties [12]. Vorlander also pointed out that the occurrence of mesophase in compounds depends on the shape or geometry of the constituent molecules. Later, a variety of compounds were synthesized which included a polar terminal group and exhibiting a nematic phase, siamese twins, mesogenic dimers, metallomesogens, polymers etc. [13]. In addition, the credit for the synthesis of the first compound with a nonlinear molecular shape and exhibiting mesomorphic properties has also been attributed to Vorlander and Apel [14]. They had named these molecules as "Bad Rods". The chemical structure and the transition temperatures (°C) of a few such compounds are given on the following page.

Compounds **1a**, **1b** and **1c** are derived from catechol, resorcinol and isophthalic acid respectively. Though they synthesized these compounds in the 1930's, they could not characterize the mesophases [M] exhibited by them. It was only in 1989, the mesophase exhibited by compound **1a** was identified as a nematic phase by Demus [16] and he classified these molecules as fused twins. However, there was no further activity of synthesis of such nonlinear mesogenic compounds. In 1991, Kuboshita *et al.* [17] started examining the thermal behaviour of 1, 2-phenylene bis[4-(4-n-alkoxybenzylideneamino) benzoates] and their derivatives. With the passage of time, a number of series of such



p: nematic phase is monotropic; clearing temperature could not be determined as the sample crystallizes immediately.

compounds [18], viz., 1, 2-phenylene bis[4-(4-n-alkoxyphenyliminomethyl)benzoates] (1d), 2, 3-naphthylene bis [4-(4-n-alkoxyphenyliminomethyl)benzoates] (1e) and 1, 2, 3-tris[4-(4-n-alkoxybenzylideneamino)benzoyloxy]benzene (1f) were synthesized and their mesomorphic properties investigated.



1d

1e

n=1,2.....12,14,16 N, SmA and SmB phases n=1,2.....12,14 N and SmA phases



The mesophases exhibited by these compounds (1d, 1e, 1f) are nematic (N), Smectic A (SmA) and Smectic B (SmB) phases which have been characterized by classical techniques such as textural observations under a polarizing microscope, X-ray diffraction measurements and finally miscibility studies using suitable compounds. It was found [18] that the linear three-ring part of the molecule tilts with respect to the layer normal by about 37°. It was also speculated that the SmA phase obtained in these compounds may form a partial bilayer structure at the layer center by the overlap of V-shaped five-ring system and

the alkyl chains making a large tilt angle with respect to the layer normal. In addition, Akutagawa *et al.* [19] reported the synthesis and the mesomorphic properties of achiral nonlinear mesogenic materials derived from resorcinol viz. 1,3-phenylene bis [4-(4-nalkoxyphenyliminomethyl) benzoates] (**1g**) and related compounds. They identified the mesophase obtained for the n-octyloxy homologue as a smectic C phase based on textural observations, enthalpy values, X-ray diffraction measurements and finally by miscibility studies. No electro-optical switching measurements were carried out for these materials simply because the mesophase obtained was from achiral molecules.



However, till 1995 it was believed that the ferro- and / or antiferro-electric properties of mesophases could be obtained only from compounds composed of chiral molecules. Molecular chirality and a tilt of the molecules in a smectic layer reduces the overall symmetry of the mesophase and are essential to exhibit ferroelectricity [21]. The real breakthrough was made by Niori *et al.*[20] in 1996 who reported ferroelectric switching behaviour in a compound (**1h**) composed of achiral banana-shaped molecules.

The origin of ferroelectricity in these compounds is mainly due to the efficient packing of bent-core molecules into smectic layers, which restrict the rotation around the long molecular axis and hence there is an induced polarization along the bent direction. This inlayer induced polarization can be reversed by the application of an external electric field. They identified the high temperature phase (S_1) of compound **1h** as smectic and ferroelectric by X-ray diffraction studies as well as by the observation of a single polarization current peak for each half cycle in the triangular wave electric field. experiments. The net macroscopic polarization in the ground state was found to be zero because of the formation of a helical structure along the cone-axis (molecular precession). From the textural observations, they found that the molecules do not tilt with respect to the layer normal. Hence this mesophase was designated as SmA_b [22, 23]. A large number of compounds with bent molecular shape have been synthesized since then and, though reported to exhibit ferroelectric properties [22, 23, 24, 25, 26, 27], all these were proved to be antiferroelectric in nature and these aspects will be discussed later.

In 1997 Link *et al.* [28] conducted several experiments using freely suspended films of compounds **1g** and **1h**. They proved that the molecules tilt about the layer normal and hence the earlier report of orthogonal molecular organization should be excluded. Careful observations using depolarized reflected light microscopy (DRLM) revealed that the mesophase of compound **1g** should have the antiferroelectric ground state due to the fact that only odd- or even-number layers respond to the applied electric field confirming the alternation of polarity in successive layers. This beautiful demonstration attracted several research groups around the world to investigate the mesophases exhibited by such compounds. Around the same time, Heppke *et al.* [29] and Weissflog *et al.* [30] also observed the two polarization current peaks for each half cycle in the electro-optical experiments for the mesophases of compounds **1g** and **1h**, which supported the existence of ground state antiferroelectricity.

The smectic phases exhibited by banana-shaped compounds are not miscible with any of the known smectic phases of calamitic compounds. Hence a different nomenclature was required to describe the special features of liquid crystalline phases formed by compounds composed of achiral banana-shaped molecules. The symbol B was accepted to be used to differentiate banana-phases from others, which was suggested at the workshop on Banana-Shaped Liquid Crystals: " Chirality by Achiral Molecules" held in Berlin in December 1997. The symbol B stands for Banana- or Bent- or Bow-shaped mesogens. Depending on the molecular structure as well as the special molecular packing of these bent-core (BC) molecules [31] into smectic or two-dimensional structures (C_{2v} , C_2 , C_{1h} and C_1 symmetry of the mesophases), they give rise to ferro-, ferri- or antifero-electric properties. There are atleast eight different B-phases reported so far and are designated as B_1 , B_2 ,..... B_7 , B_8 . The suffix numbers of B indicate the order of the discovery [32] of different B-phases and has nothing to do with the phases themselves. However, the phases designated as B_3 and B_4 were later characterized as crystalline phases based on careful X-ray diffraction studies.

The **B**₁ mesophase

The B₁ mesophase has also been designated as SmA_b^{1} [23, 33], X_{B1} [29] and Col_r [34] in the literature. Normally, this phase is observed for the lower homologues of a homologous series of compounds.

On slow cooling of the isotropic liquid, this mesophase appears as dendritic nuclei which coalesce into a mosaic texture. Sometimes this mesophase grows as colourful spherulites



[35] as seen under a polarizing microscope. The mesophase is viscous and difficult to align using either a magnetic or electric field. The clearing enthalpy obtained is indicative of a first order phase transition and is in the range of 14-20 kJmol⁻¹ depending on the chemical nature of the constituent molecules. The measured order parameter value is about 0.84 which is independent of temperature. This is a high temperature phase with respect to the B₂ phase [34] and a low temperature phase with respect to the B₆ phase [36]. The B₆ to B₁ phase transition occurs through minimal changes in the texture and a small change in enthalpy value (weakly first order)[36]. As of now atleast five phenyl rings are required for a bent-core compound to exhibit this mesophase.

X-Ray diffraction studies of a B_1 mesophase show atleast two or more reflections in the small angle region. None of these reflections correspond to the layer thickness of the molecules and hence a simple layer structure can be excluded. The reflection corresponding to less than half molecular length is an evidence for the intercalated structure of the mesophase and also a small tilt of the bent-core (BC) molecules. The additional reflections are indicative of a two-dimensional ordering for the mesophase and a proposed model for this mesophase is shown in figure 1.4. A diffuse wide-angle peak shows a liquid-like order of the bent-core molecules within the frustrated layers. In 1998, Watanabe *et al.* [33] obtained a monodomain of the B_1 phase by sandwiching a thin film

($\approx 50 \ \mu m$) of the sample between two glass plates. The diffraction pattern clearly revealed the existence of a two-dimensional rectangular cell with well defined lattice parameters **a** and **b**. Here, **b** corresponds to the layer thickness of the rectangular lattice which is the full molecular length of BC molecules and **a** represents approximately the number of molecules existing in the lattice. It appears that 6-10 molecules can exist in a lattice and each cluster can have 3-4 molecules. On increasing the n-alkyl chain length, the number of molecules in the clusters increase [34] and as a result the values of the lattice parameters **a** and **b** also increase. The pronounced odd-even effect of the alkyl chains over the lattice parameters has also been observed. Stability of the B₁ phase may also depend on the ratio of the core length of the arm of the banana molecule and the length of the alkyl chain (length of the alkyl chain should be less than the core length of the arm of the molecule). However, the proposed model shown in figure **1.4**, may not satisfy all the B₁ phases exhibited by different compounds of various homologous series reported in the literature.





The clusters of the BC molecules arrange in a two-dimensional lattice such that they can reduce the dipolar interactions and increase the packing efficiency as shown in figure 1.4. Since the number of molecules (2, 3 or 4) are less in a cluster, the net polarization is also less, which is cancelled by the adjacent cluster. Therefore no electro-optical switching could be expected in such a structure even at a high electric field.

The B₂ mesophase

This is the most commonly observed mesophase in different homologous series of compounds. This phase has also been designated as $SmA_b[22, 23]$, S_{X1} [24], $SmX_1[25]$, $M_1[30, 37]$, X_{B2} [29] or SmCP_A[28]. The B_2 to isotropic phase transition enthalpy value is in the range of 20-25 kJmol⁻¹. This is a less viscous and electro-optically switchable mesophase and hence more attention has been paid to understand the basic structure of this mesophase. In this regard, Link et al. [28] conducted several experiments and established the complete structure of the mesophase. Perhaps this is the most well-understood banana phase. On slow cooling of a thin film of the isotropic liquid, B₂ phase appears in different forms as observed under a polarizing microscope. Sometimes it shows a finger print pattern, a grainy fan-shaped texture, schlieren texture and chiral domains of opposite handedness. A well-oriented monodomain sample of the B_2 phase shows layer reflections in the small angle region (meridian). The wide-angle diffuse peak indicates the absence of in-plane order and is located out of equator [30, 37, 38]. The calculated tilt angle is about 30-45° depending on the chemical nature of the compound and the temperature. The measured order parameter value is about 0.8 which is almost temperature independent unlike SmA or SmC phase of calamitic compounds.

Link *et al.* [28] conducted some experiments on compounds 1g (n=9) and 1h. Results from these revealed the existence of tilted layers (SmC-like) and the plane containing these tilted layers are referred to as a tilt plane. The molecules pack along a bent direction, to constitute a polar plane which is perpendicular to the tilt plane. In addition, the tilted molecules exist in layers and produce a layer plane. These three different planes (assumed to be three co-ordinates) exist for a given layer as shown in figure 1.5. If these three coordinates form a particular handedness (depending on tilt direction with respect to the other two co-ordinates), the mirror image of this shows the opposite handedness as shown in figure 1.6. In other words, these two are non-superimposable mirror images. Hence, the layer becomes chiral though the individual molecules are achiral.

Finally, The origin of chirality is due to

 (i) The sterically packed bent-core molecules along the bent direction in a layer restrict the rotation about the layer normal which produces polarization in each layer.



Fig. 1.5. A schematic representation of the arrangement of bent-core molecules in the B_2 phase showing the origin of layer chirality from achiral molecules; z smectic layer normal; n: director of BC molecules; b: layer polar direction; c tilt direction of BC molecules. (After Link e al.[28])

(ii) The tilt of the bent-core molecules within the smectic layer reduces the symmetry *cf* the structure of the mesophase.

The BC molecules pack along the bent direction and exist in an antiparallel configuration in successive layers such that the polarization cancels out. Hence the net polarization becomes zero for alternate layers. Since molecular chirality is absent, depending on the tilt direction of achiral bent-core molecules in alternate layers produces two antiferroelectric ground state structures as shown in figure 1.7.



Fig. 1.6. A demonstration of the origin of layer chirality from achiral molecules. The layer normal, tilt direction and the polar axis produces a right-handed co-ordinate system as shown at the left bottom, the mirror image of these co-ordinates produces a left-handed system which clearly represents the layer chirality. (After Heppke *et al.*[39])

- (i) A racemic structure in which the polarization alternates from layer to layer and the BC molecules tilt in the same direction $(SmC_SP_A: synclinic smectic C, polarization antiferroelectric)$. In such a structure the alternate layers will have opposite handedness and hence macroscopically it forms racemic domains. However, cn application of an electric field, the induced polar ferroelectric states also become racemic $(SmC_AP_F: anticlinic smectic C, polarization ferroelectric)$. Hence, two optically equivalent (extinction cross) ferroelectric states will be generated. The extinction cross obtained (resulted from the equidistant circular smectic layers) is independent of the polarity of the applied electric field.
- (ii) A homochiral structure is one in which the polarization as well as the tilt direction of the BC molecules alternate from layer to layer (SmC_AP_A : anticlinic smectic C, polarization antiferroelectric). Since the successive layers have the same handedness, macroscopically it forms chiral domains. The resultant ferroelectric state obtained on application of an electric field is also chiral (SmC_SP_F : synclinic



Fig. 1.7. A schematic representation of the arrangement of molecules in racemic (SmC_SP_A) as well as in homogeneous chiral states (SmC_AP_A) of antiferroelectric ground state (at zero electric field). The origin of corresponding racemic (SmC_AP_F) and homochiral (SmC_SP_F) ferroelectric states by the application of electric field (above the threshold voltage) are also shown.

smectic C, polarization ferroelectric) and optically different ferroelectric states could be obtained by the reversal of polarity of the applied electric field. In other words, the ferroelectric states obtained switches from one to the other by reversal of polarity of the applied field. This is followed by the rotation of extinction cross with respect to the directions of the crossed polarizers. In general, the polarization measurements were carried out using a triangular-wave method and this will be described in detail in appropriate chapters. The calculated polarization value for this mesophase varies from 100 to 1000 nC cm⁻² and even more. The P_S value completely depends on the chemical nature of the compounds, mainly the position and orientation direction of lateral polar substituents with respect to the polar axis and also the type of packing in the mesophase. However, the temperature dependence of P_S value cannot be excluded which is minimal.

The possible existence of spontaneous polarization in achiral molecules was pointed out theoretically by Brand *et al.* [40] in 1992 and it was experimentally proved in 1996 by Niori *et al.* [20].

The B₃ phase

This mesophase has also been designated as SmX_2 [22, 25], Hex B_b [23] or X_{B3} [29] in the literature. This is a low temperature phase with respect to a B₂ phase and high temperature phase with respect to a B₄ phase. This phase also appears at a lower temperature with respect to a B₁ Phase. The X-ray diffraction measurements carried out for the powder sample shows many sharp reflections in the small angle as well as in the wide-angle regions. This clearly suggests a crystalline structure for the phase.

The B₄ phase

This is a low temperature phase with respect to a B_2 and / or a B_3 phase. This phase appears directly from a B_2 phase or via a B_3 phase. This phase has also been designated as SmX₃ [22] in the literature. The X-ray diffraction pattern of this phase shows many sharp reflections in the small angle as well as in the wide-angle regions, which point towards a crystalline structure. One of the textural features of this phase is the intense blue colour that it exhibits. Hence this phase is also designated as Sm Blue phase [23, 29]. On slow cooling of either a B_2 phase or a B_3 phase, this phase appears as large domains of opposite chirality which are weakly birefringent. The atomic force microscopic experiments revealed that this phase has a helical superstructure. Sekine *et al.* [23] proposed a TGB-like structure for this mesophase. A more interesting feature of this phase is that it exhibits a second harmonic generation (SHG) without external fields indicating that the medium is spontaneously chiral. The nonlinear coefficient is about 0.5 pm V which is of the same order of magnitude as that of crystalline quartz. Hence this phase may be useful in practical applications [23].

The B₅ mesophase

This phase was first observed in three homologues of the same series of compounds (compound **1j**) derived from 2-methylresorcinol [32, 37]. This phase normally appears as a lower temperature phase with respect to a B_2 phase. The textural changes between B_2 and B_5 phases are minimal with a small transition enthalpy (weakly first order) change. Sometimes it may not be possible to differentiate the textures of B_2 and B_5 phases under a polarizing microscope. However, the X-ray diffraction patterns for the two mesophases are different. Layer reflections obtained in the small angle region is similar to those of the B_2 phase whereas the wide-angle region shows additional reflections for a lower temperature B_5 phase. The wide-angle reflections of an oriented pattern of the B_5 phase can be indexed for a rectangular lattice. This shows the existence of a short range order within the smectic layers. The bending angle and the torsion angle in the molecules remain unchanged at the transition from a B_2 to a B_5 phase. Hence the symmetry is retained. In addition, B_5 phase also shows an antiferroelectric switching behaviour like a B_2 phase.



Cr 161 B₅ 165 B₂ 172 I

The B₆ mesophase

This mesophase has also been designated as $S_{intercal}$ phase in the literature [42]. This mesophase was first observed in a Schiff's base compound **1k** [32]. On slow cooling of the isotropic liquid, this mesophase exhibits a fan-shaped texture similar to the one which is normally seen for a SmA phase. However, this phase cannot be aligned homeotropically. Hence the possibility of a simple SmA phase like structure can be excluded. On shearing the fan-shaped texture of a B₆ phase, sometimes schlieren texture is obtained.





Fig. 1.8. The proposed intercalated structure of bent-core molecules in the B_6 phase. The tail and the core interactions seem to be dominant than the core-core interactions for shorter chain lengths. (After Weissflog *et al.*[30])

The mesophase to isotropic transition enthalpy value is in the range of 10-15 kJmol⁻¹ depending on the chemical nature of the constituent BC molecules. The X-ray diffraction pattern for the B_6 phase shows layer reflections in the small angle region and a diffuse peak in the wide-angle region which is indicative of the absence of in-plane order. The first order layer reflection obtained in the small angle region is slightly less than half-molecular length, which is calculated by assuming an all *trans* conformation of the n-alkyl chain. This indicates the existence of an intercalated structure in the mesophase as shown schematically in figure **1.8**. Also, there is an indication that molecules tilt with respect to the layer normal and the estimated tilt angle is about 20-30°. A monodomain sample of the

 B_6 phase exhibits slightly diffuse reflection peaks in the small angle region which are oriented perpendicular to the wide-angle diffuse spots indicating that the rows of molecules are non-correlated to each other [32]. This mesophase normally appears for the shorter homologues in a series. The stability of the intercalated structure has been further explained by Rouillon *et al.* [43] using a Monte-Carlo simulation. According to them, it is possible to build an intercalated structure by allowing an alternation of high and low potentials. The electro-positive alkyl chains can be accommodated between the arms of the aromatic parts (electro-negative) of the bent-core molecules for the system to be stable.

The **B**₇ mesophase

This mesophase was first observed in compounds derived from 2-nitroresorcinol (compound 11) [32]. Among all the known eight B-phases, only B₄ and B₇ phases are known to exhibit helical superstructures. While the B₄ phase is truly crystalline, the B₇ phase is liquid crystalline. This mesophase exhibits several beautiful optical-textures. Pelzl et al. [44] have reported some microscopic textures for this mesophase. On slow cooling of the isotropic liquid, the mesophase exhibits textures such as elongated germs, straight lancets or irregular thread-like patterns and frequently these germs are spiral or doublespiral which are typically 2-3 μm in thickness and about 20 μm in length [45]. The handedness of the screw-like germs can be identified by careful observation under a polarizing microscope. It has been found that equal number of right- and left-handed spiral germs are present indicating the achiral nature of the molecules. Sometimes, this mesophase grows as oval or circular domains with equidistant stripes indicating the chiral nature and appearance of myelinic textures are similar to those observed for lyotropic liquid crystals. In addition, this mesophase exhibits many extraordinary textures like twoor three-dimensional periodic patterns. The observation of single- and double-twisted germs indicate the achiral symmetry breaking of the smectic layers and the circular concentric arcs give evidence for the helicoidal periodicity. Probably the helical



Cr 116 B₇ 177 I

superstructures are due to the twist of chiral smectic layers [45]. However, the existence of lancet-like ribbons are an indication for a racemic structure of the mesophase. It should be noted that the mesophase to isotropic enthalpy (25-30 kJmol⁻¹) is quite high when compared to other banana phases and sometimes the melting enthalpy cannot be determined [32]. Probably the B₇ phase has a C₁ symmetry [31, 46] and recently, based on theoretical models Cladis *et al.* [47] have also suggested the same.

The X-ray powder pattern of a B_7 phase shows many sharp reflections in the small angle region. Hence it excludes the possibility of a simple smectic structure. However, there are reflections which can account for a layered structure and the additional reflections indicate the existence of two- or three-dimensional ordering of the molecules [48,49]. In addition, the wide-angle diffuse peak shows the absence of in-plane order. Till now, no oriented X-ray pattern could be obtained for the B_7 mesophase. Though some studies have been initiated to determine the structure [45] the exact structure of the B_7 mesophase is still not clear. The synthesis and other aspects concerning this interesting phase is discussed in Chapter-5.

The B₈ mesophase

Recently, Bedel *et al.* [50] reported a bilayer structure for the mesophase of a bent-core compound derived from isophthalic acid containing terminal alkanoate end groups. Perhaps this is the first example of a BC compound exhibiting a bilayer structure. In addition, this mesophase exhibits an antiferroelectric switching behaviour. This mesophase also exhibits various optical textures which are not observed for other B-phases. Since this mesophase with a new structure was not seen in a BC compound, the symbol B_8 was assigned to the same.

Variants of the B-phases

Bedel *et al.* [51] reported a mesophase in compounds (for shorter terminal chains) containing a fluorine substituent on the outer phenyl ring which is *ortho* to the n-alkoxy chain. Though the textural features observed were similar to a B_1 phase, based on miscibility and X-ray diffraction studies they have assigned a symbol B_{1X} to the mesophase. No electro-optical switching could be observed for this phase even at high electric field. Recently, this B_{1X} phase has also been reported in a different homologous series of compounds [38].

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Nguyen *et al.* [52] reported some achiral banana-shaped compounds which exhibit four smectic phases without in-plane order and all of them are antiferroelectric. They have designated these mesophases as X_1 , X_2 , X_3 and X_4 . Recently, Weissflog *et al.* [48, 53] also reported some smectic B-phases which exhibit an antiferroelectric switching behaviour. They have assigned the symbol B_2^{1} and B_2^{10} for these mesophases. The exact structure of all these smectic phases and how these phases are different from a B_2 phase are yet to be understood.

Bedel *et al.* [51] reported a two-dimensional banana phase exhibiting ferroelectric switching behaviour. Perhaps this is the first example of a BC compound known to exhibit a ferroelectric phase and assigned the symbol B_{7bis} . Walba *et al.* [54] reported a second example of chiral molecules (racemic mixture) exhibiting ferroelectric properties and assigned the symbol B_7 to this mesophase. Based on textural similarity with a B_7 mesophase [32], Heppke *et al.* [55], Lee *et al.* [56], Dierking *et al.* [57] and Jakli *et al.* [58] also reported smectic phases exhibiting helical structures and claimed that the mesophases in each case to be B_7 . These aspects will be discussed in more detail in Chapter-5.

Recently, Nadasi *et al.* [41] reported different B_5 phases based on electro-optical switching characteristics and careful X-ray diffraction measurements in a single compound containing a fluorine substituent on the central as well as outer phenyl rings. For a compound with n-dodecyl chain, the high temperature B_5 mesophase exhibits two polarization current peaks for each half cycle indicating the antiferroelectric switching bahaviour (B_{5A}) whereas the lower temperature B_5 phase shows only one polarization current peak indicating the ferroelectric switching behaviour (B_{5F}). However, for the compound with n-octyloxy terminal chain, five different B_5 phases are reported in addition to a B_2 phase out of which four of them are antiferroelectric and the lowest temperature phase is ferroelectric.

In order to understand the effect of molecular structure on the occurrence of mesomorphic properties, several hundred compounds have been synthesized by various groups and their physical properties investigated. These have been synthesized by (i) the variation of the alkyl chain length, (ii) variation in the core, (iii) different linking groups and (iv) different lateral substituents in all available positions. These studies have resulted in some new mesophase structures in Banana Liquid Crystals.

Variation in the hydrocarbon chain

One of the most successful exercises in liquid crystal chemistry is the study of the effect of chain length on the mesomorphic properties. Most of the compounds composed of bentcore molecules and exhibiting mesophases contain two terminal chains [32]. The synthesis and characterization of complete homologous series of bent-core compounds so far appear to be very limited [32, 36, 43, 52, 59, 60, 61]. However, Sadashiva *et al.*[36] carried out systematic studies and reported the first homologous series of compounds exhibiting B₆, B₁and B₂ phases on ascending the series. Normally, homologues with short chain length exhibit nematic, smectic A, B₆ or B₁ phases. In general, the higher homologues exhibit electro-optically switchable mesophases. The mesophase structures and their sequence in banana-shaped mesogens are shown in figure 1.9. The introduction of perfluoroalkyl fragments on the terminal chain can stabilize the mesophases but they increase the clearing temperatures [34, 62].

General structure of banana-shaped mesogens



Variation in the core

The core in general can be defined as the rigid part, which is constructed from phenyl rings (in most cases) via linking groups like, -COO-, -OCO-, -CH=N-, -N=N- etc. The stability



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Fig. 1.9. A schematic representation of the effect of terminal chain length on the occurrence of the different types of mesophases.

of the mesophase also depends on the number of phenyl rings present in the bent-core. Most of the compounds reported in the literature contain five phenyl rings [32]. However, compounds containing three, six and seven phenyl rings have also been reported. For example, Kovalenko *et al.*[62] reported bent-core compounds containing only three phenyl rings and perfluorinated alkyl terminal chains. They exhibit only a SmA phase and no banana phase was obtained.

Compounds containing six phenyl rings have been reported by several groups [32]. Shen *et al.* [34, 42] reported different BC compounds containing six phenyl rings exhibiting B-phases. In addition, Thisayukta *et al.* [63, 64, 65] also reported six-ring BC compounds and the mesophases observed in these compounds have not been completely characterized. Several series of compounds containing seven phenyl rings were mainly reported by Sadashiva *et al.* [35, 36, 61, 66] and Shen *et al.* [34, 42]. On increasing the number of phenyl rings, the thermal range of the mesophases as well as the clearing temperatures increase.

Effect of lateral substituents

In calamitic and columnar liquid crystals, the lateral substituents are incorporated mainly to disrupt the close-packing of the molecules in the crystal lattice as well as in the mesophase. This is particularly advantageous for inducing mesophases as well as to modify the melting and clearing temperatures. The effect of lateral substituents on the mesomorphic properties depends on the following three factors, (i) size, (ii) polarity and (iii) substituted position. It is known that in bent-core compounds the bend angle in the core is one of the important factors to generate the banana phases. By choosing suitable lateral substituents at required positions of the molecule one can generate different phases apart from reducing the melting as well as the clearing temperatures. But the substitution on the central phenyl ring seems to affect more, because the bend angle between the two arms gets altered [32]. Also, polar lateral substituents can change the electron density distribution around the molecule leading to a change in the mesomorphic behaviour. Since, lateral substituents in BC compounds have profound effect on the mesomorphic behaviour, it is worthwhile making a systematic study of the same.

Weissflog *et al.*[32] have investigated a number of compounds substituted on the central phenyl ring as well as on the outer phenyl rings. It was found that on the central phenyl

ring, a methyl group at the obtuse angle induced a new phase namely B_5 , a nitro group at the same position induces a different phase which is B_7 when compared to the unsubstituted compound, which exhibits a B_2 phase. Substitution at *ortho* position to the carboxylate group of the outer phenyl rings of compounds derived from 4-cyanoresorcinol seems to increase the bend angle. Such a compound is known to exhibit rich polymesomorphism viz. nematic, smectic A, smectic C and B₂ phases when compared to the unsubstituted parent compound [67]. Sadashiva et al. [36, 61, 66] carried out systematic investigations in order to understand the effect of lateral substituents by varying the polarity, namely fluoro, chloro, methyl, methoxy etc., substituted on the middle rings of the arms of the BC molecules. Though chloro and methyl groups have approximately the same size, they show a completely different mesomorphic behaviour to that which has been seen in calamitic liquid crystals. Lateral substitution on the outer phenyl rings of fivering banana-shaped compounds have also been reported by several groups namely, Heppke et al. [68], Lee and Chien et al. [69,70], Bedel et al. [38, 59] and Eremin et al. [71]. One of the most interesting effects observed is that the introduction of fluorine at *ortho* position to the terminal n-alkoxy chain of the outer phenyl ring induces ferroelectric properties.

Applications of liquid crystals

After the discovery of liquid crystalline state, the synthesis of liquid crystals was of academic interest and a laboratory curiosity. The unique optical, magnetic and electrical properties in these materials have been made use of in applications. Cholesteric liquid crystals have been used as thermochromic materials. The colour changes in cholesteric liquid crystals indicate small changes in temperature due to a property called selective reflection. Hence it has been used for thermal mapping [72], aerodynamic testing [72] etc. Cholesteric liquid crystals are also widely used in medical applications. In 1964, commercially available disposable thermometers made up of cholesteric liquid crystals have been used to detect the body temperature [72]. They have also been used in many fancy items, toys and decorative materials.

One of the most important and practical applications of liquid crystals is in electronic display devices such as watches, clocks, calculators, panel meters, computers and other digital displays. They have also been used for many laboratory experiments such as solvents for NMR spectroscopy, as stationary phases for gas liquid chromatography etc. Ionic liquid crystals have also been used as solvents in some organic reactions (for

example Friedel-Crafts alkylation and acylation etc.), which will enhance the rate of reaction as also the yield when compared to the other usual solvents.

The discovery of ferro- and antiferro-electricity in compounds composed of achiral bentcore molecules are begining to find their way into display devices. It has been found that the antiferroelectric racemic and the ferroelectric chiral states are opaque, whereas the ferroelectric racemic and the antiferroelectric chiral states are transparent. On the basis of these observations, Jakli *et al.* [73] demonstrated the possibility of a display using bananashaped mesogens. They exhibit two distinct states namely, racemic and chiral. The racemic structure scatters light and hence it is OFF state and is optically clear under electric fields. The chiral structure is transparent at zero fields and is scattering in the ON state. These two structures can be reversibly interchanged and hence they can be used in devices. They require energy only to switch from one stable state to the other. One of the major problems in these materials is the existence of synclinic domains (racemic) along with the homochiral domains unlike in chiral rod-like molecules. However, this problem can be solved by doping these materials with 1% of a SmC^{*} material [28]. As a result, the whole medium will be homochiral which can be used in display devices.

Due to the large number of packing possibilities in these biaxial bent-core molecules into smectic as well as two-dimensional phases, they will have a broad range of economically viable applications [74]. The value added features of these materials over others are (a) a faster electro-optic response than other liquid crystals with helical structure; (b) the steric packing of the materials allowing possible rotations about an arrow axis with a small change in the layer spacing and (c) ambidextrous chirality. However, all these are at an infancy level and much more work has to be carried out before they could be used in practical devices.

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