Chapter 1

Introduction

Liquid crystals are a thermodynamically stable state of matter, which exist between the three-dimensionally ordered crystal and the completely disordered isotropic liquid. One of the important factors required for an organic compound to exhibit a liquid crystalline phase is the shape or geometric anisotropy of the constituent molecules. Liquid crystals have imperfect long-range orientational and / or positional order. Thus, they have some properties of liquids and have anisotropic properties of crystals like birefringence. The discovery of the liquid crystalline state has been attributed to Reinitzer [1].

If the liquid crystalline state is achieved by the action of heat, they are classified as thermotropic liquid crystals and if they are obtained by the action of a solvent, they are termed as lyotropic liquid crystals. In this thesis, the synthesis and characterization of thermotropic liquid crystals are discussed. A brief description of a few well-known thermotropic liquid crystalline phases are given below.

Nematic (N) phase

A nematic liquid crystal is a turbid liquid, and possesses only orientational ordering of the constituent molecules. The nematic phase belongs to the point group $D_{\infty h}$. The direction of preferred molecular orientation is defined by a vector quantity namely, the director. The distribution function is rotationally symmetric around the director and hence the nematic phase is uniaxial in nature. The characteristic feature of a nematic liquid crystal is the thread-like texture it exhibits when viewed under a polarizing microscope. Nematic liquid crystals are widely used in display applications.

Smectic (Sm) phases

Smectic (soap-like) phases have stratified structures, with a well defined interlayer spacing. The constituent molecules possess some correlation in their position in addition to orientational ordering. The molecules in smectic mesophases are fluid in two directions and can rotate about the long molecular axis. Further, these can be classified into different types of smectics depending on the ordering of the molecules within the layers (in-plane order). The suffixes, which are used to differentiate smectic phases, indicate the chronological order of their discovery. Two simple smectic phases namely SmA and SmC are described below.

Smectic A (SmA) phase

Smectic A is the simplest among the smectic liquid crystals and belongs to the symmetry group $D_{\infty h}$. In SmA phase, the average long molecular axes lie normal to the layer plane, but within the layers the molecular distribution is still random and liquid-like. Thus, smectic A phase can be considered as one-dimensional crystal in the direction normal to the layers and a two-dimensional liquid within the layers. Since the molecules rotate about their long molecular axis and are orthogonal to the layer planes the mesophase is uniaxial. Smectic **A** phase exhibits two kinds of optical textures namely, a focal-conic and a homeotropic texture which can be seen under a polarizing microscope. The X-ray diffraction pattern of SmA phase reveals that the obtained layer spacing (d) is of the order of full molecular length (L) of the molecule.

Smectic C (SmC) phase

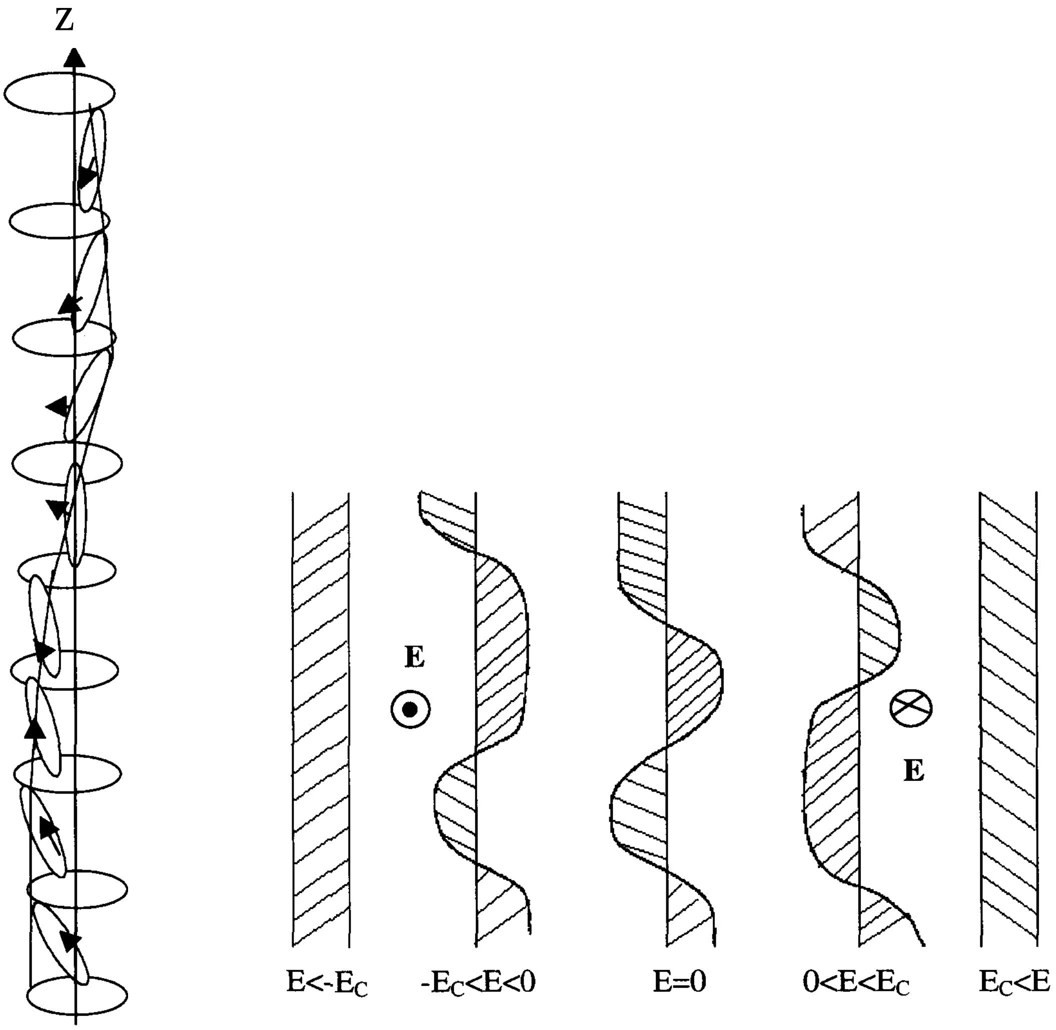
In SmC phase, the long molecular axis of constituent molecules are tilted with respect to the layer normal. Further, the molecules are packed in an unstructured way within the layers. Thus smectic C is a tilted analog of smectic A phase and belongs to C_{2h} point group. The tilt direction of the molecules in one homogeneous domain of a SmC phase is aligned in the same direction. However the tilt direction may change continuously over an area of the sample. The layer spacing (d) obtained from X-ray diffraction is less than the measured molecular length (L) indicating a tilt of the constituent molecules. Broken focal-conic as well as schlieren textures are observed for this mesophase under a polarizing microscope. Conoscopic experiments reveal the biaxial nature of the mesophase.

Cholesteric (N*) phase

The cholesteric (or chiral nematic) liquid crystal is composed of optically active molecules or can be obtained by doping a nematic phase with chiral compounds. In the cholesteric mesophase the long molecular axis varies its direction in a regular way such that a continuous twist along the optic axis takes place leading to a helical structure. Cholesteric mesophase exhibits interesting optical properties, which have been made use of in practical applications as thermochromic materials.

Chiral Smectic C (SmC*) phase

In 1975, Meyer ***et*** al. [2] based on symmetry arguments showed that ferroelectricity could be achieved in smectic C liquid crystal made of chiral compounds. Introducing chirality into the molecules breaks the mirror plane symmetry, thus the point group symmetry reduces from C_{2h} to C_2. As a consequence of the presence of a chiral center, the director precesses from layer to layer leading to a helical structure and hence the polarization (P,) in the mesophase. Handedness of the chiral center will decide the helical twist sense of the mesophase. A pictorial representation of SmC* phase as proposed by Meyer [2] is shown in figure **1.1 (a).** The macroscopic chirality in SmC* phase is compensated by the formation of helical structure in the mesophase.



(a) **(b)**

Figure 1.1(a): A structure of the chiral ferroelectric smectic C*phase as proposed by Meyer *et al.* [2]; (b) response of the helix of a ferroelectric smectic C* phase with an external electric field (after Meyer [3]).

When an electric field is applied in a direction parallel to the smectic planes, the molecules slowly orient themselves towards the electric field. This causes distortion in the helical periodicity as shown schematically in figure **1.1 (b).** When the applied field crosses the threshold voltage, the structure gets completely unwound and will have a polar ferroelectric structure. By reversing the polarity of applied field, the direction of polarization can be reversed which results in the other ferroelectric state. On switching off the field the orientation of dipoles remains in either of the two ferroelectric states. Thus SmC* mesophase has a bistable structure.

Antiferroelectric Smectic C (SmC$_A^*$) phase

Antiferroelectricity in liquid crystals was first reported by Chandani ***et al.*** *[5]*in 4-(1-methylheptyloxycarbonyl)phenyl-4-*n*-octyloxybiphenyl-4-carboxylate (MHPOBC) in 1989. In an antiferroelectric smectic C phase the constituent molecules tilt in opposite directions in successive layers.

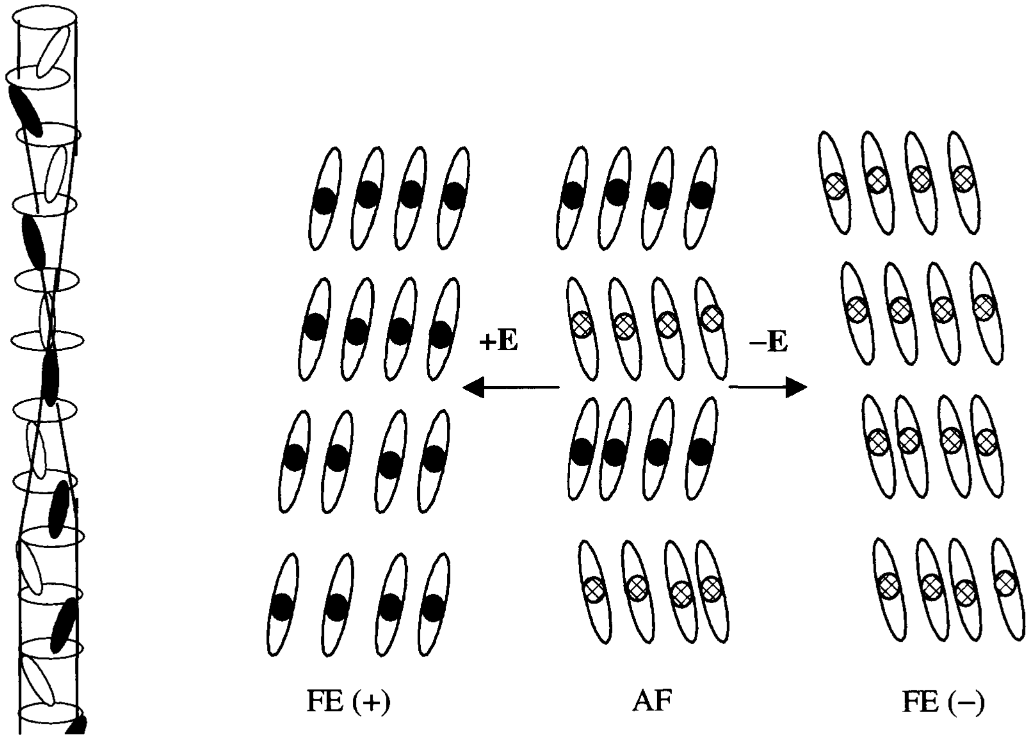


Figure 1.2 (a): A pictorial representation of the double winded helix of the antiferroelectric smectic C*phase; (b) the tristable state of the antiferroelectric mesophase (after Fukuda *et al.* [4]).

In 1998, Mach ***et*** al. [6] gave the final proof of the alternating tilt of molecules in adjacent layers of the antiferroelectric smectic C mesophase by resonant X-ray scattering experiments. Thus, the basic structural unit of SmC_A^* phase comprises two neighbouring layers in which the molecules are tilted in opposite directions. One can imagine the SmC_A^* phase as double twisted helicoidal structure formed by two identical ferroelectric SmC^* helices gearing into each other as shown schematically in figure **1.2(a)**.

On applying a sufficiently high electric field, the helix of SmC_A^* phase can be unwound which will result in one of the ferroelectric states. However, on reversing the polarity of the applied field it switches to the other ferroelectric state. On switching off the field the dipoles relax to an antiferroelectric ground state. This tristable switching of SmC_A^* phase is shown schematically in figure **1.2(b)**.

Twist Grain Boundary (TGB) phases

In 1974, de Gennes [7] predicted a topologically defect-stabilized mesophase in analogy with superconductors. When the intrinsic twisting power of the material is high, the smectic **A** structure breaks down into periodic stacks of layers, with a finite twist distortion. These layers are mediated by regular array of screw dislocations. Renn and Lubensky [8] proposed a model for this mesophase and named it as TGB_A phase. Similarly a SmC phase can give rise to a TGB_C phase.

Columnar mesophases

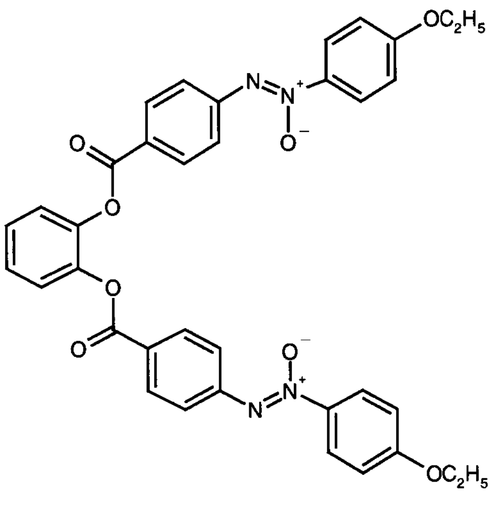
Till 1977, only rod-like molecules provided the shape anisotropy required for the formation of liquid crystals. However, exception for this principle came from the discovery by Chandrasekhar ***et*** al. [9a]. of columnar mesophases formed by disk-like molecules The disk-like molecules are stacked one above the other aperiodically to form the columns. These columns are arranged on a hexagonal lattice such that the columns can slide. Thus this columnar mesophase is a two-dimensional solid and a one-dimensional liquid. Several variants of the columnar structure have also been found [9b].

Banana mesophases (B-phases)

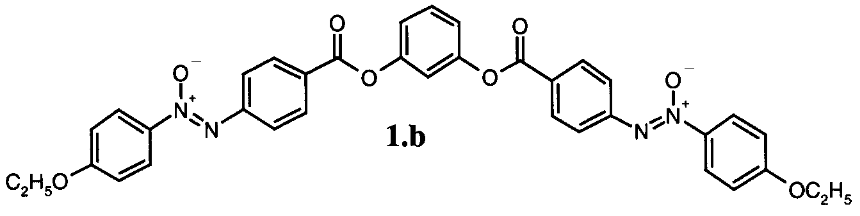
The symmetry concept is an integral part of liquid crystalline phases, a reduction of which leads to various new mesophase structures. In banana liquid crystals reduction of symmetry was achieved by connecting the two rods through a bend.

The credit for the synthesis of unconventional compounds exhibiting liquid crystalline properties can be attributed to Vorlander and his group [10]. They explored the structure-property relationships of rod-like molecules by synthesizing various types of compounds. These include liquid crystals with heterocycles and alicyclic rings, hydrogen bonded liquid crystals, terminal polar nematics, siamese twins, mesogenic dimers with flexible spacers, metallomesogens and main chain polymers. Most of these compounds represent the first examples in their respective categories exhibiting mesomorphic behaviour.

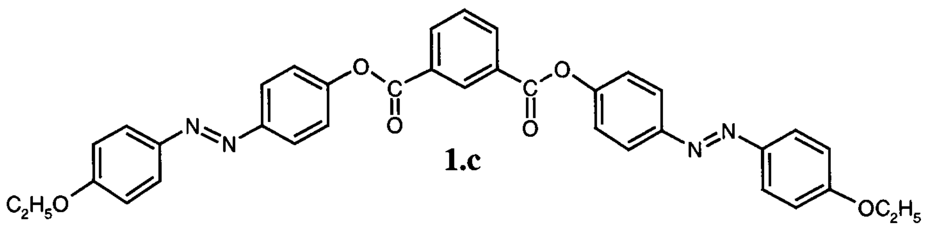
Three bent-shape compounds, which were synthesized by Vorlander et al. [10] are derivatives of catechol, resorcinol and isophthalic acid and the structures of these compounds (**1.a**, **1.b**, and **1.c** respectively) are given below. The characterization of the mesophases exhibited by these compounds was not carried out.



1.a

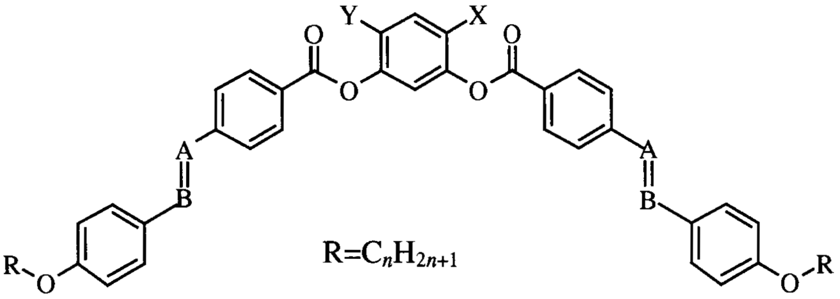


1.b



1.c

The study of the mesomorphic properties exhibited by bent-shaped compounds was renewed in 1991. Kuboshita *et al.* [11] synthesized dimers, derived from 1, 2-dihydroxybenzene and 2, 3-dihydroxynaphthalene. The mesophases obtained were characterized as N, SmA and SmB. However, in 1994 Akutagawa *et al.* [12] synthesized four homologous series of compounds derived from resorcinol. The general structure of these compounds is shown below.



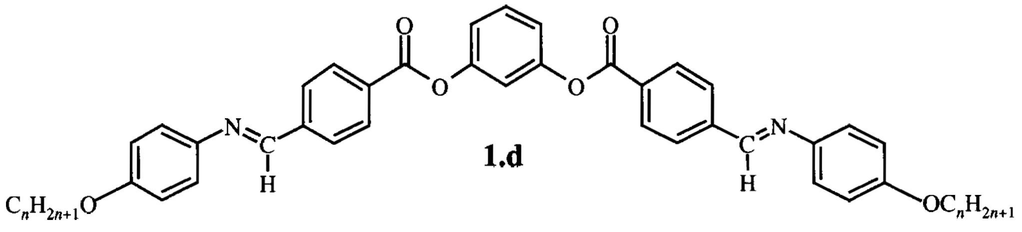
I -A=B- = -CH=N-, X= Y= H

II -A=B- = -N=CH-, X= Y =H

III -A=B- = -N=CH-, X= Cl, Y =H

IV -A=B- = -N=CH-, X= Y = Cl

From the microscopic textural observations, enthalpy values, XRD and miscibility studies they concluded that the mesophases exhibited by these compounds as N and SmC. From XRD studies they argued that the tails are nearly normal to the layers whereas the cores are tilted by about 48°. Later, some of the compounds, which have this general structure, were synthesized by Pelzl *et al.* [28] who showed that they exhibit B-phases. However, the real breakthrough came from Niori *et al.* [15] who reported ferroelectric properties in the achiral compound, namely 1, 3-phenylene bis[4-(4-*n*-octyliminomethyl)benzoate] (**1.d**, n=8).



1.d

Thus, the observation of switchable mesophases from achiral molecules opened a new sub-field of thermotropic liquid crystals.

Their results can be summarized as follows:

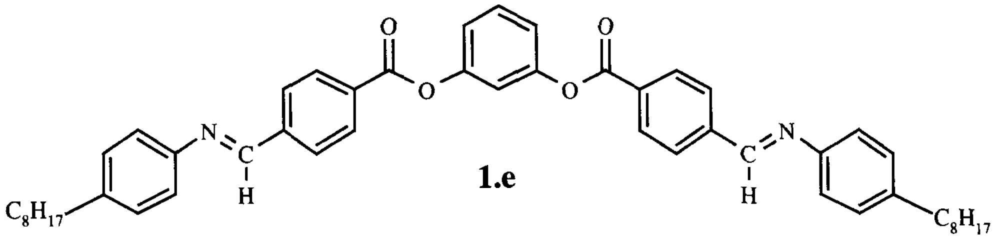
I. The ferroelectricity in achiral compounds can be ascribed to C_{2V} symmetry of the molecular packing.

II. Because of their shape, these compounds form a peculiar smectic phase in which the molecules are closely packed along the bend direction. Due to this, there exists a spontaneous polarization along the bend direction. This polarization direction can be reversed by applying an electric field.

III. The observation of a single current peak in the triangular-wave electric field experiment point towards a ferroelectric ordering of the molecules in the ground state.

IV. X-Ray diffraction studies on this compound showed SmA type arrangement of the molecules within the layers. (No tilt in the core as pointed out by Akutagawa *et al.*[12]).

In 1997, Weissflog *et* al. [16] reported an antiferroelectric current response with untilted cores in the same octyl homologue of **1.d** (*n*=8). At the same time Heppke *et* al. [17] reported ferroelectric switching current dynamics in several homologues of **1.d** and **1.e**.



1.e

All these contradictory results were put to an end by the beautiful experiments carried out by Link *et* al. [18]. They carried out depolarized reflected light microscopy (DRLM) experiments, on compounds **1.d** (*n*=9) and **1.e** with an oblique incidence and slightly uncrossed polarizers. They observed that in the smectic phases of these compounds the optic axis is tilted with respect to the layer normal. This ruled out the possibility of an orthogonal arrangement of the molecules in the smectic phase. The study of free standing films of the mesophases of these compounds gave strong odd-even effect by the application of weak electric field. This led them to conclude that the ground state structure of these mesophases is antiferroelectric in nature.

In the same year, an International Workshop on Banana-shaped mesogens: "Chirality by Achiral Molecules", was organized in Berlin to recommend a nomenclature for the different mesophases exhibited by banana-shaped compounds. Since these mesophases were not miscible with any of the known thermotropic liquid crystalline phases, the symbol B was assigned to signify the shape of the molecules. Seven mesophases were identified and assigned the symbols B_1, B_2...B_7. Recently, another mesophase designated as B_8 [20] has been added to the above list. The suffixes indicate the chronological order of the discovery of the mesophases.

Symmetry in banana-phases

According to the theoretical predictions of Brand ***et*** al. [21], there are four possible ways of arranging the bent-core molecules within the smectic layers. They predicted the possible ferro- antiferro- and ferri-electric phases based on symmetry arguments. Vectors **n, l** and **m** have been used to represent the long molecular axis, tilt direction and polar direction respectively. **A** schematic representation of the possible arrangements of bent-core molecules in smectic layers is shown in figure **1.3.**

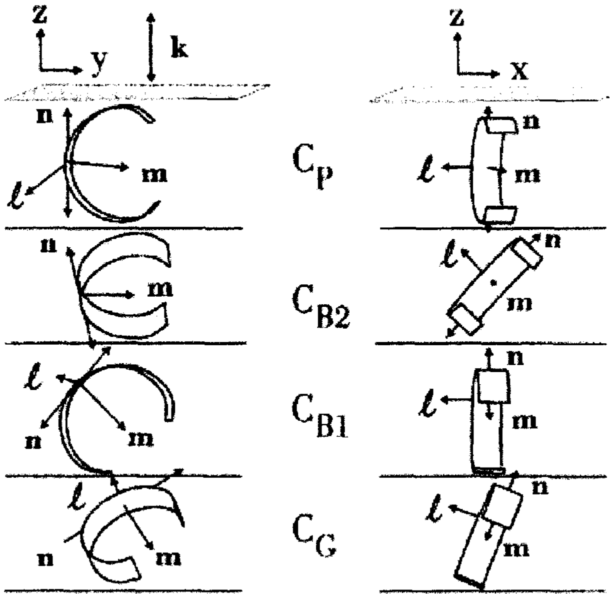


Figure 1.3: Possible arrangements of bent molecules in smectic layers (x-y:layer plane; z:layer normal; n:molecular long axis) (after Brand *et* al. [21]).

The possible scenarios are

1. Orthogonal alignment of n, while 1 and m are parallel to layer plane indicated by symmetry notation C_P.
2. The director n is tilted with respect to layer normal and is indicated by symmetry notation C_{B2}.
3. Both n and m are tilted, so that two-fold rotation axis is absent, and there exists only horizontal mirror plane, indicated by symmetry notation C_{B1}.
4. If all the three-principle axes (n, 1, and m) enclose an angle of 0° or 90" then the molecules will have C_1 symmetry.

Such a phase (phase with C_1 symmetry) was predicted by de Gennes and is indicated by symmetry notation C_G where G stands for "Generalized. The B-phases namely B_2 and B_5 comes under the symmetry of C_{B2}. B_1 and B_6 mesophases are variants of symmetry C_{B2}. While B_7 mesophase comes under the category of symmetry C_G.

As pointed out by Tschierske and Dantlgraber [22] the macroscopic chirality in banana-shaped compounds can be compensated in three different ways.

i. Collapse of the layers or frustrated phases: B_1 and B_6 mesophases.
ii. Antiferroelectric ordering of the dipoles in adjacent layers: B_2 and B_5 mesophases
iii. Formation of helical structures: B_7 mesophase / SmC_G phase.

General observations in banana liquid crystals

a. The banana-shaped compounds are biaxial in nature because of their intrinsic shape.
b. The mesomorphic behaviour is strongly dependent on the bending angle. Typical angle is ≈120°, and if the bending angle increases to ≈145° one would expect calamitic mesophases in addition to banana phases.
c. The mesophase behaviour also depends on chain length. The commonly observed phase sequence is B_6-B_1-B_2 as a function of n-alkyl chain length on ascending the series.
d. The high value of mesophase to isotropic transition temperature indicates the high rigidity of molecular packing.
e. The value of spontaneous polarization is rather high when compared with those of calamitic liquid crystals and varies generally from about 300 to 1000 $nC\ cm^{-2}$.
f. Antiferroelectric mesophases are commonly observed when compared to ferroelectric mesophases in banana-shaped compounds. On the contrary, in the case of calarnitics, a majority of compounds show a ferroelectric mesophase (SmC*). The comparison and

layer fluctuations involving ferro- and antiferro-electric properties in calamitic and banana-shaped compounds was given by Nadasi ***et*** al. [23] and a pictorial representation of this is shown in figure 1.4 **(a-d).**

Because of out of layer fluctuations which are allowed in the ferroelectric phase of calamitics and antiferroelectric mesophase of banana-shaped compounds, their structures are thermodynamically and entropically stable. Whereas in the case of antiferroelectric phase of calamitics and ferroelectric mesophase of banana-shaped compounds they have to sustain the entropical penalty, as out of layer fluctuations are absent and hence are less commonly observed.

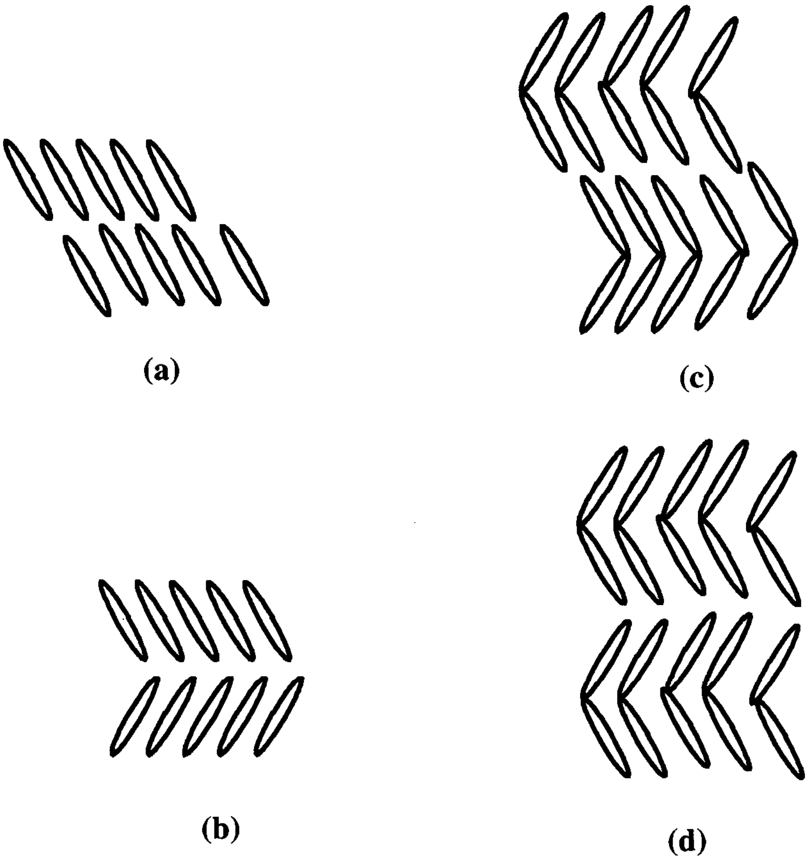
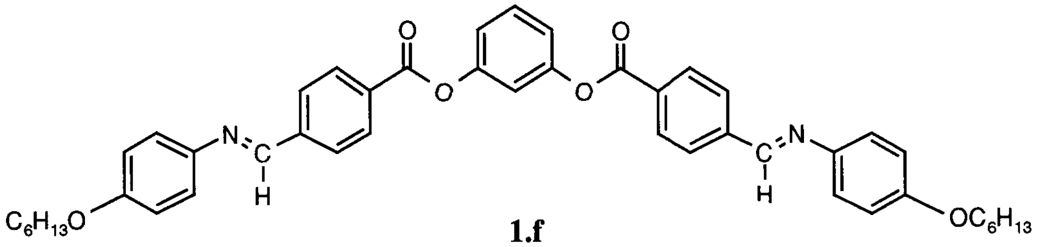


Figure 1.4 (a) and (b):The molecular arrangement in ferroelectric and antiferroelectric mesophases of calamitic liquid crystals; (c) and (d): the molecular arrangement in antiferroelectric and ferroelectric mesophase of banana liquid crystals (after Nadasi *et al.* [23]).

B_1 meophase

This mesophase was designated differently in the initial stages, for eg ; SmA'$_b$, [24, 25] X_{B1}, [26] and Col$_r$ [27]. The first compound (**1.f**) exhibiting the B_1 mesophase was reported by Watanabe ***et*** al. [25] and has the following chemical structure.



1.f

B_4 143.6 B_3 159.1 B_1 173.4 I [25]

The B_1 mesophase is commonly observed for middle members of a homologous series of compounds. When a sample is cooled from the isotropic phase and observed under a polarizing microscope, the mesophase appears in two different forms. Either a mosaic texture or colourful spherulitic pattern can be observed. The viscosity of the mesophase is rather high and difficult to shear the cover slip. The textures are highly birefringent because of the two-dimensional ordering of the molecules in the mesophase. The mesophase to isotropic transition enthalpy is in the range of 10-20 kJ mol^{-1}. Sometimes B_6 to B_1 mesophase transition could be seen in banana-shaped compounds [29]. In such a transition if the B_6 mesophase shows a schlieren texture, then at the transition mosaic texture starts to appear. If the B_6 mesophase has a focal-conic texture then the change in the texture is minimal. The associated enthalpy change at the B_6 to the B_1 mesophase transition is also rather small.

The B_1 mesophase can be considered as a columnar mesophase with a rectangular lattice built up by ribbons with parallel alignment of bent-core molecules. The bending direction in successive ribbons is antiparallel, so that the macroscopic chirality is subdued. Each repeating rectangular unit consists of cluster of molecules. The polarization due to these clusters is small and is nullified by the adjacent clusters and hence no net polarization is observed for this mesophase. The confirmation of the structure of this mesophase is from XRD studies. Typically, for a B_1 mesophase two or more reflections are observed in the small angle region of a diffraction pattern. One of the reflections corresponds to half the molecular length, which indicates the intercalated layered structure of the mesophase. A diffuse wide-angle reflection indicates the liquid-like ordering of the molecules within the layers.

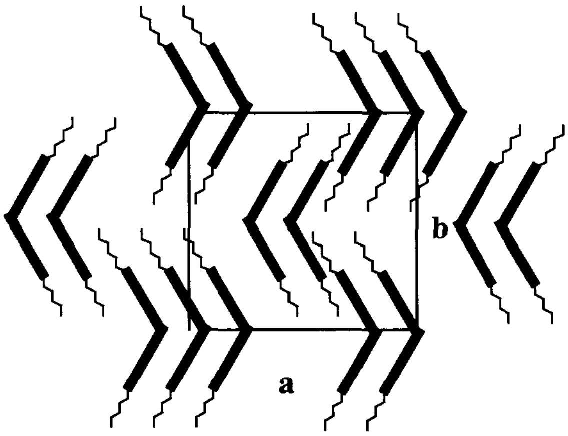


Figure 1.5: A schematic representation of bent-core molecules in a two-dimensional columnar B_1 mesophase (after Watanabe *et al.* [25]).

Watanabe ***et al.*** [25] obtained a monodomain of this mesophase, which clearly confirms the rectangular lattice with the lattice parameters **a** and **b** for the mesophase. Based on this observation they proposed a model for this mesophase. The model for the mesophase is shown in figure 1.5. The lattice parameter **a** is related to the number of molecules which exist in the rectangular lattice. Typically 3-4 molecules exist in each cluster and about 8-10 molecules can be accommodated in the lattice. The parameter **a** is alkyl chain dependent in a homologous series. The other parameter **b** indicates the actual length of the molecule. Core-core interactions in this mesophase is effective and depends on the length of the arms of the core and the n-alkyl / n-alkoxy chain length. On increasing the alkyl chain length, the core-core interactions are reduced. These unfavorable chain-core interactions on increasing the alkyl chain length disturb the two-dimensional rectangular lattice and yield a lamellar mesophase.

Variants of B_1 mesophase

Bedel ***et*** al. [30] reported a variant of a B_1 mesophase in the lower homologues of a series of compounds which contain a fluorine *ortho* to the n-alkoxy chain. XRD studies gave four reflections in the small angle region; the corresponding unsubstituted compounds show only two reflections. However, those four reflections could be indexed to a rectangular lattice. The miscibility studies of the fluoro substituted compound with the unsubstituted compound revealed the non-ideal behaviour. Therefore, they labeled that as Bx phase. Similar kind of mesomorphic behaviour was also reported for another series of compounds by Bedel ***et al.*** [31]. Recently, from our laboratory [32] a B_1 phase with an unusually large tilt angle in bent-core compounds derived from 2-cyanoresorcinol has been reported. Two columnar phases (B, and B_{1rev}) having a two-dimensional modulated structure with spontaneous polarization was recently reported by Szydlowska ***et al.*** [33, 34].

B_2 mesophase

Among all the banana phases, the electro-optically switchable B_2 mesophase has been studied in detail. This mesophase has also been designated as a $SmCP_A$ phase by Link ***et al.*** [18]. Although different symbols have been assigned for this mesophase, the accepted nomenclature is either to call it as B_2 or a $SmCP_A$ phase. This mesophase is less viscous than a B_1 phase and is generally observed for the higher homologues in a series. The mesophase to isotropic transition enthalpy value is in the range of 18-25 kJ mol^{-1}. The mesophase appears in different forms under a polarizing microscope. The commonly observed textures are fingerprint or fringe pattern, schlieren and focal-conic textures. XRD studies on oriented samples of this mesophase have been reported [31, 35,361. The reflections in the small angle region are in the ratio of 1:1/2:1/3, indicating a lamellar periodicity. The wide-angle diffuse peak indicates the absence of in-plane ordering within the smectic layers. The first order reflection obtained is less than the full molecular length indicating a tilt of the molecules within the layer. The measured tilt angle from XRD studies varies between 35 to 50° depending on the chemical nature of the constituent molecules and the temperature. A lot of attention has been paid to this mesophase mainly because of its response to an applied electric field. Link ***et al.*** [18] carried out a series of experiments on compounds **1.d** (*n*=9) and **1.e**. These include free standing film of the sample, which has been imaged with depolarized reflected light microscopy (DRLM) using oblique laser illumination. They interpreted their results in the following way.

The molecules in a smectic layer are tilted thus reducing the symmetry from C_{2h} to C_2. All the molecules in the layer tilt in the same direction constituting the tilt plane. Because of the shape, the molecules are packed in a bend direction, which is responsible for generating the in-layer ferroelectric polar order, which is normal to the tilt plane. Since the molecules are stacked in layers, a layer plane is obtained. A pictorial representation of all the three planes is shown in figure 1.6. These three planes can be considered as three co-ordinates of a chiral system and the mirror image is non-superimposable. Hence the layer becomes chiral even though the molecules are achiral.

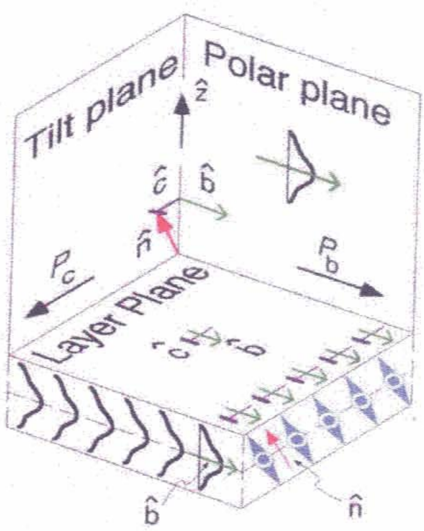


Figure 1.6: A pictorial representation of origin of layer chirality by achiral molecules; z: layer normal, n: director of the bent-core molecules, b: polar direction, c:tilt direction of the molecules(after Link *et al.* [18]).

Heppke and Moro [19] have further substantiated the layer chirality pictorially and this is shown in figure 1.7.

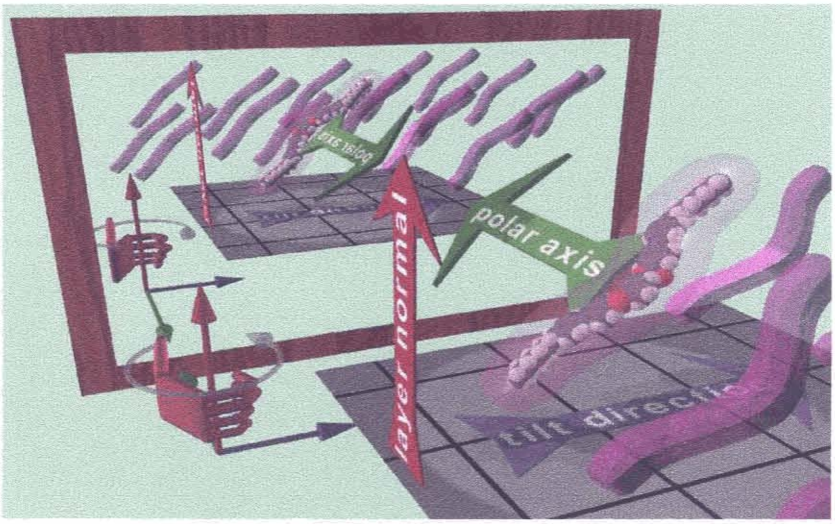


Figure 1.7: The mirror images of bent-core molecules demonstrating the chirality; the three components, layer normal, polar axis and tilt direction form the non-superimposable mirror images (after Heppke and Moro [19]).

The tilting of dipoles in opposite directions in successive layers compensates the layer polarization as well as the macroscopic polarization in this mesophase. Depending on the tilt sense in adjacent layers there are two distinct possibilities namely SmC_SP_A (synclinic Smectic C, Polarization antiferroelectric) and SmC_AP_A (anticlinic Smectic C, Polarization antiferroelectric). The synclinic tilt of the molecule in adjacent layers, results in a racemic structure and is thermodynamically a more stable state. On application of an electric field, the ferroelectric phase is induced and has a SmC_AP_F structure. On reversing the polarity of the applied field, no change in the orientation directions of the dark brushes could be seen under crossed polarizers. If the tilt sense is in the opposite direction in adjacent layers, it results in a homochiral (SmC_AP_A) structure.

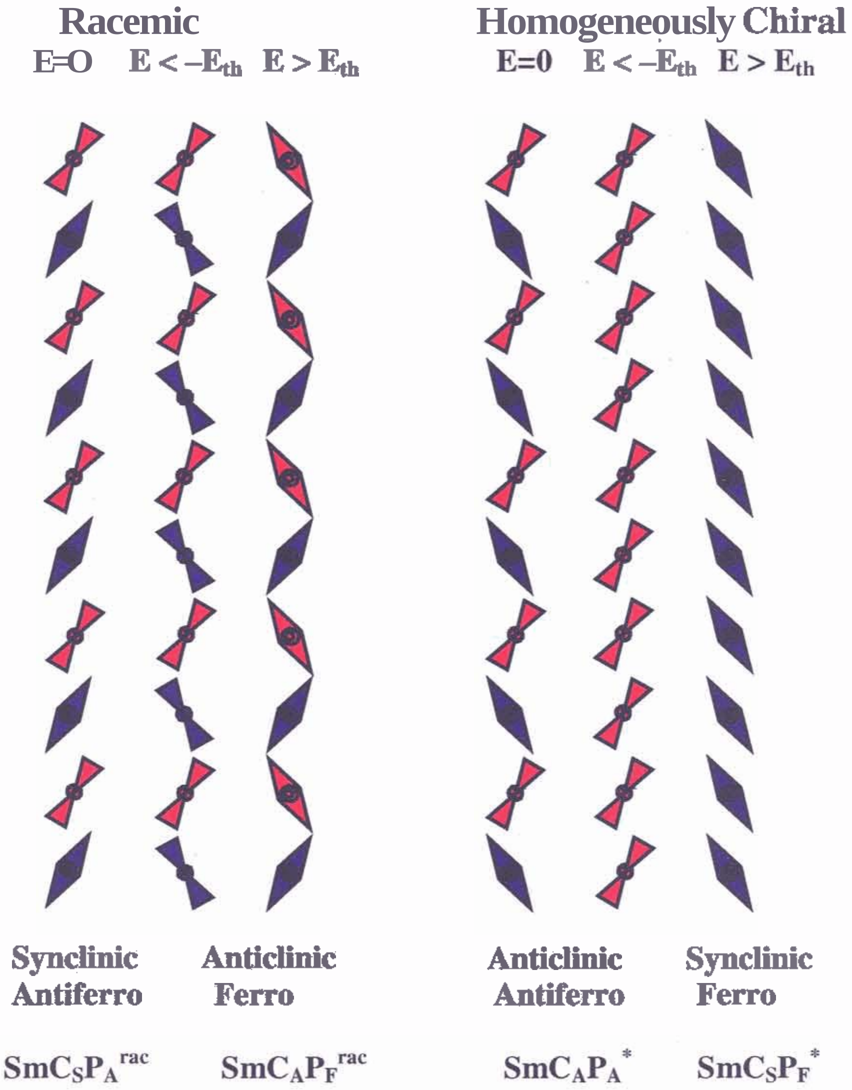


Fig. 1.8: A schematic representation of the arrangement of the molecules in racemic (SmC_SP_A) and chiral states (SmC_AP_A) of antiferroelectric mesophase and the corresponding field induced ferroelectric states racemic (SmC_AP_F) and chiral (SmC_SP_F) (after Link et *al.* [18]).

The field induced ferroelectric state, SmC_SP_F has two distinct orientations. The tilt direction in successive layers and their response to an applied electric field is shown schematically in figure **1.8.**

The spontaneous polarization was measured by triangular-wave method and the observation of two current peaks per half cycle indicates the antiferroelectric ground state structure for the mesophase.

Variants of B_2 mesophase

Nguyen *et al.* [37] reported four smectic antiferroelectric mesophases and named them as X1, X2, X3, X4. Recently Eremin *et al.* [38] also reported two mesophases which are designated as B′ and B''. The detailed structures of these mesophases are not known and therefore regarded as variants of a B_2 mesophase. Recently Svoboda *et al.* [39] also reported two lamellar antiferroelectric phases and designated them as B' and B''.

B_3 mesophase

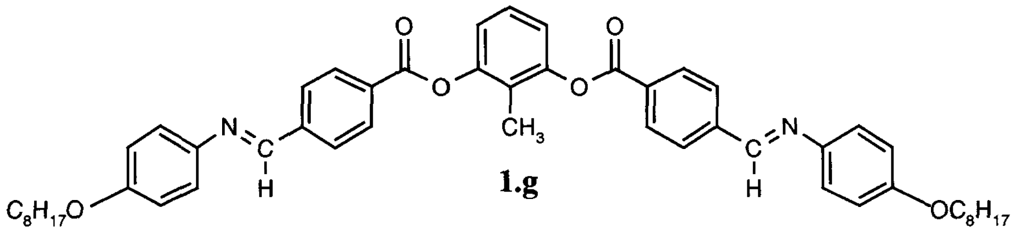
Although this phase was considered under B-phases, careful XRD studies on this phase revealed the crystalline nature. This phase is a lower temperature phase w.r.t. the B_2 mesophase [28].

B_4 mesophase

Detailed XRD studies on this phase revealed the crystalline structure and it exhibits some interesting optical features. This phase was observed on cooling from either a B_2 or a B_3 phase [28]. The unique textural feature of this phase was the observation of a blue colour with domains of opposite handedness. Hence this phase has also been named as smectic blue phase [24, 26]. The atomic force microscope experiments show that the phase has a helical superstructure. Sekine *et al.* [24] have reported a TGB-like structure for this phase.

B_5 mesophase

This mesophase was first observed in a derivative 2-methylresorcinol1.g [28, 36].



1.g

Cr 161 B_5 165 B_2 172 I

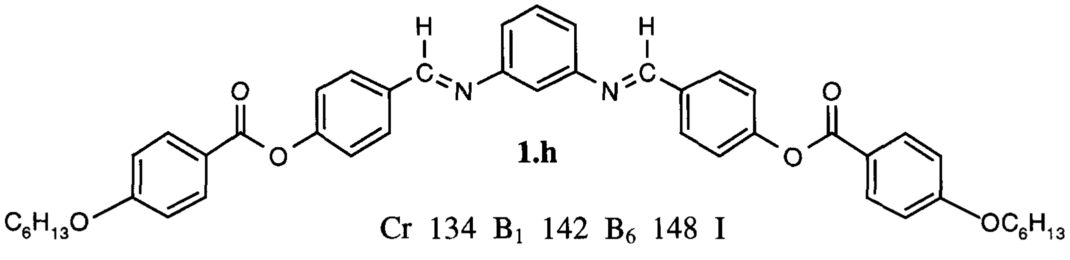
Always, this mesophase was observed on cooling the B_2 mesophase and has only a paramorphotic texture. The transition from B_2 to B_5 mesophase is first order. XRD studies on the mesophase show lamellar periodicity in the small angle region. However, in the wide-angle region some additional reflections were observed. This means that this mesophase has in-plane periodicity within the layers and reflections in the wide-angle region can be indexed to a centered rectangular lattice. Electro-optical experiments point towards an antiferroelectric ground state structure for the mesophase. Thus, the only difference between B_2 and B_5 mesophases is the presence of an additional short-range order within smectic layers in the latter case.

Variants of B_5 mesophase

Nadasi *et* al. [23] have reported five new variants of a B_5 phase in five-ring compounds containing fluorine in the central as well as outer phenyl rings *ortho* to the *n*-alkoxy chain. When a B_2 mesophase was cooled from the isotropic phase, they observed four different antiferroelectric B_5 sub-phases with a small change in the enthalpy for each transition. They also observed a transition from an antiferroelectric phase to a ferroelectric mesophase. The exact structures of these mesophases have not been determined. Around the same time Eremin *et* al. [38] also observed a B_5 mesophase below a B_2 and B_2 sub-phases (B' and B'') and B_5 mesophase subsequently transformed to a B_X mesophase. These compounds are derivatives of 2-methylresorcinol containing a fluorine substituent *ortho* to the *n*-alkoxy chain.

B_6 mesophase

This mesophase was first observed in compound **1.h**. [28]



1.h

Cr 134 B_1 142 B_6 148 I

This mesophase can be observed normally for homologues with shorter alkyl chain. This phase has also been designated as $Sm_{intercal}$ [40].

On cooling the isotropic liquid, this mesophase appears as batonnets and coalesces to a smooth focal-conic texture. These textural features are reminiscent of a SmA phase, but can never be aligned homeotropically. The enthalpy of mesophase to isotropic transition is about 10-15 kJ mol^{-1}. The proposed model for the mesophase is shown in figure **1.9.**

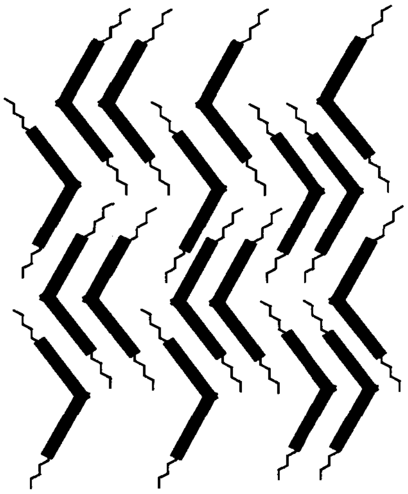


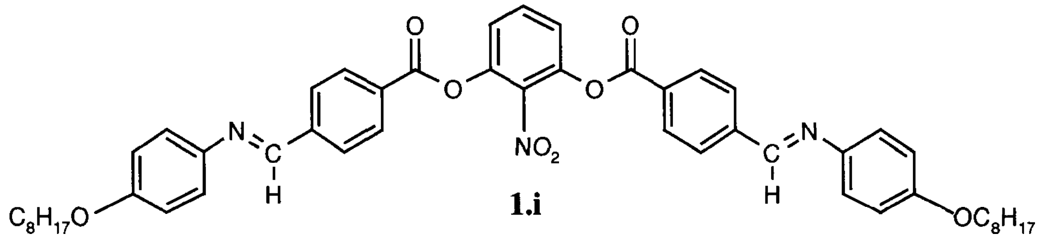
Figure 1.9: A schematic representation of bent-core molecules in the B_6 mesophase (after Weissflog *et al.* [35]).

The first order reflection in the small angle region of a X-ray diffraction pattern corresponds to less than half the molecular length. This implies an interdigitation of the molecules. The oriented pattern reveals the tilt of the molecule and the measured tilt angle is about 25-30". In some compounds a direct transition from B_6 to B_1 mesophase could be observed. On cooling the sample from B_6 to B_1 phase, the molecules start to aggregate to form clusters. These clusters arrange into a two-dimensional lattice to form a B_1 phase.

Rouillon ***et** al.* [41] have carried out Monte-Carlo simulation studies on the B_6 mesophase and reported the molecular model allowing the high and low potentials. In such a periodical structure, there exists some vacant gaps which must be filled by the electropositive alkyl chain. Due to the constraint in the packing of the aromatic cores, only short chains can fill up the voids. Hence the mesophase is stable for compounds having shorter alkyl chains.

B_7 mesophase

The B_7 mesophase phase shows the most beautiful and unique optical textures. It was first observed in 2-nitroresorcinol derivatives (Compound **1.i** [42]).



1.i

Cr 116 B_7 177 I

The mesophase has C_1 symmetry and exhibits helical superstructure. Pelzl *et al.* [42] reported four compounds derived from 2-nitroresorcinol and exhibiting the B_7 mesophase. The mesophase to isotropic transition enthalpy value is rather high and sometimes more than the melting enthalpy values. Strangely, sometimes the melting points could not be determined. Pelzl *et al.* [42] reported various beautiful optical textures exhibited by the B_7 mesophase. On slow cooling the isotropic phase, B_7 mesophase appears in different forms in the same sample preparation. The characteristic feature is observation of single-, double- and triple-winded helices. They also observed various other textural variants such as elongated germs with lancet-like or irregular thread-like germs, circular domains with equidistant concentric arcs etc. On further cooling various two-dimensional periodic patterns were also observed. The occurrence of spiral germ points to a helical structure and concentric lines on the circular domains is a result of helical periodicity. This periodicity is probably due to twisted distribution of molecular tilt, which corresponds to pitch of the helical structures as in the case of a SmC^* phase.

The XRD studies of this mesophase gave several reflections in the small angle region ruling out the possibility of a simple layered structure. The wide-angle diffuse peak indicates the liquid-like in-plane order. Recently, from our laboratory two homologous series of compounds exhibiting the B_7 mesophase have been reported [32, 43]. All the characteristic features observed in the standard materials could also be seen in these materials.

Variants of B_7 mesophase

One of the characteristic features of B_7 mesophase is the growth of spirals. Such textures have been seen in a number of different systems and, although the XRD patterns of these compounds are different, the same symbol B_7 has been assigned to them [45-50]. Recently, the structure of the mesophase exhibited by compound MHOBOW [47] which exhibits various textural patterns including spirals has been solved by Coleman *et al.* [44], who have proposed a modulated smectic structure but assigned the symbol B_7 to this mesophase. The occurrence of B_7 phase in different systems will be discussed in detail in Chapter **3.**

B_8 mesophase

Bedel ***et al.*** [20] reported a bilayer structure for the mesophase of compounds derived from isophthalic acid containing n-alkanoate terminal group. Interestingly this mesophase exhibits antiferroelectric switching behaviour. Since the mesophase textures as well as structure were different from the known B-phases, the symbol B_8 was assigned for this mesophase.

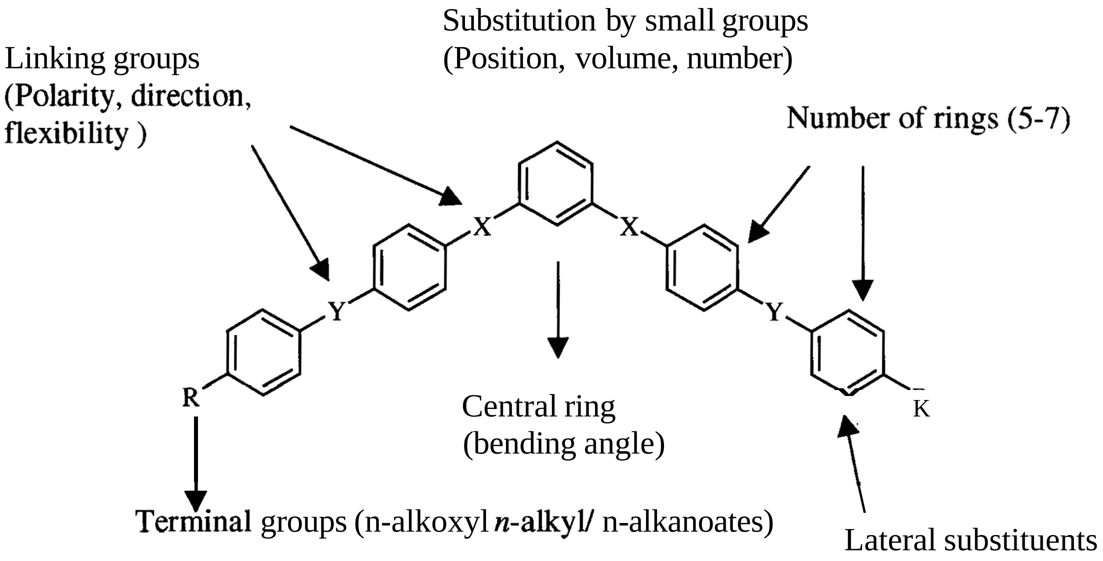
Ferroelectric mesophases in banana-shaped compounds

As pointed by Nadasi ***et al.*** [23] ferroelectric mesophases are thermodynamically not favorable in banana-shaped compounds. Only a few compounds exhibiting ferroelectric mesophases have been reported so far. The first report of ferroelectricity in banana-shaped compounds was from Walba ***et al.*** [47] who designed and synthesized compounds showing conglomerates. Extending the idea of anticlinic arrangement of molecules from calamitics, they synthesized an unsymmetrical compound with racemic 2-octanol as one of the terminal chains. The ferroelectricity in the mesophase was proved by bistability in the electro-optical experiment. Based on microscopic observations they labeled the mesophase as B_7.
Bedel ***et al.*** [30] observed ferroelectric switching properties for compounds containing fluorine substitent *ortho* to the n-alkoxy chains. They labeled the mesophase as $B7_{bis}$. The fluorine at this position favors the formation of ferroelectric mesophases. Two more examples of compounds exhibiting ferroelectric properties were reported [23, 51]. These compounds also contain fluorine *ortho* to the n-alkoxy chains. Interestingly, in one such case [51] both smectic and two-dimensional ferroelectric mesophases were observed on ascending the homologous series.

To understand the occurrence of ferroelectric mesophases in the bent-core compounds, polyphilic bent-core compounds were designed and synthesized [22, 52]. The authors suggested that the occurrence of ferroelectricity in these compounds is a result of decoupling of the layers.

General remarks on structure-property relationships in bent-core compounds

The bent-core compounds can be represented by the following general structural formula.



The bent-core compounds synthesized, characterized and reported so far can be categorized as having

i) different central rings
ii) different linking groups
iii) different n-alkoxy / n-alkyl chain lengths
iv) various polar lateral substituents

Most of the compounds reported so far contain five phenyl rings and are basically derived from 1, 3-dihydroxybenzene [15, 28, 29, 45, 53]. 2, 7-Dihydroxynaphthalene [55, 101], 3, 4-dihydroxybiphenyl [22] have also been used as a central unit. Six or seven-ring compounds have also been reported [27, 29]. On increasing the number of phenyl rings in the core, the thermal range as well as the clearing temperature of the mesophase will also increase.

Normally used linking groups are iminomethyl, ester, azo and ethylene units. Compounds containing Schiff's base linkage group show rich polymorphism when compared with other systems.

Most of the compounds composed of bent-core molecules contain two n-alkoxy or *n*-alkyl chains as terminal groups. The synthesis of a homologous series of compounds gives a trend of the occurrence of different mesophases on ascending the series. The commonly observed trend in a homologous series of banana-shaped compounds is B_6-B_1-B_2 phase on ascending the series [29, 41].

Influence of lateral substituents

The study of lateral substitution is an important exercise in liquid crystal research. It has been found that the mesomorphic behaviour is greatly influenced by the position of substitution, as well as by the size and polarity of the substituents. A substitution on the central phenyl ring has significant influence on the bend angle. The compounds containing substituents like chloro- and cyano- at 4-position of central phenyl ring were reported by Weissflog ***et al.*** [28, 53]. In these compounds, along with banana phases classical calamitic phases were also observed. Substitution at 2- or 5- position of 1, 3-phenylene central unit resulted in different phase behaviour [28, 38, 42]. Suitable substitution on the outer phenyl ring of the bent-core has also a significant effect on mesomorphic behaviour. Interesting examples are compounds containing fluorine *ortho* to the n-alkoxy chain exhibiting ferroelectric behaviour [23, 30, 51].

The following two techniques were used extensively to investigate the nature of the mesophases exhibited by various compounds studied in this thesis.

I) X-Ray diffraction studies

II) Electro-optical investigations

X-Ray diffraction studies

X-Ray diffraction gives adequate evidence in arriving at the structure of the different mesophases. Generally powder samples and in a few cases oriented samples have been used to obtain diffraction patterns of bent-core compounds. This technique has been used extensively to examine the different mesophases obtained and discussed in this thesis.

Rigaku, Ultrax 18 rotating anode generator was used as a X-ray source. X-Rays thus produced were monochromated by using a graphite crystal, which has a characteristic wavelength of 1.54Å (Cu-K_∞ radiation). These X-rays were collimated through a double-slit arrangement and made to fall on the sample, which was taken in a sample holder. The temperature of the sample holder was controlled by a computer to an accuracy of ± 0.1°C. The diffraction pattern obtained from the sample was recorded on a two-dimensional image plate detector. **A** block diagram of the X-ray set-up used is shown in figure **1.10.**

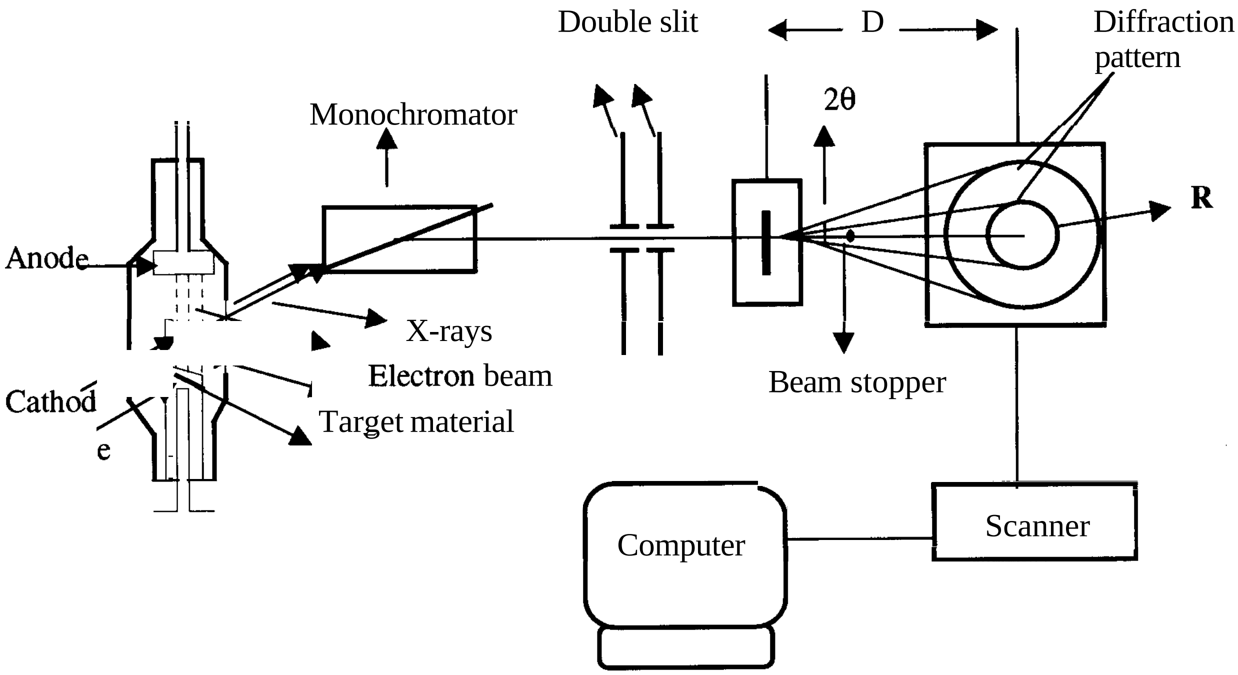


Figure 1.10: A block diagram of X-ray diffraction experimental set-up used in the studies.

The layer spacing of the mesophase was calculated using Bragg's equation, d= nh / 2 sin0

Where n= 1, (for first order reflection)

d= determined layer spacing

λ= 1.54Å (characteristic wavelength of Cu-$K_{\propto}$ radiation)

θ= Bragg's angle and can be calculated as θ= ½ x $\tan^{-1}$(R/D)

R= Radius of the diffraction pattern, D= Distance between the sample and the detector.

The tilt angle of the molecules in the mesophase can be calculated as $\theta = \cos^{-1}$ (d/L), where L is the measured molecular length.

Electro-optical investigations

In order to study the effect of electric field on the banana mesophases and to measure the spontaneous polarization in appropriate cases, the standard triangular-wave method was used. The experimental set-up used is shown in figure **1.11.** For the electro-optical experiments the cell was constructed using indium tin oxide (ITO) coated glass plates separated by Mylar spacers. The inner surfaces of these conducting glass plates were coated with polyiirnide and unidirectionally rubbed. The thickness of the cell was measured by interferometric technique. The sample was filled in to the cell in the isotropic phase and cooled slowly to get good alignment of the sample. The triangular waves of definite amplitude and frequency were produced by using a WAVETEK GENERATOR, MODEL 39 and were amplified hundred times using an amplifier TREK MODEL 601-B. The output from the amplifier was split into two channels CH1 and CH2. Channel CH1 was directly connected to the oscilloscope, which acted as a reference signal; CH2 was connected to the oscilloscope via a 10 kΩ resistance. The resultant curve obtained on the oscilloscope screen was a plot of switching current Vs time. To confirm the tilt sense of the mesophases dc field experiments were carried out using a Regulated Dual Power Supply (Model 6401).

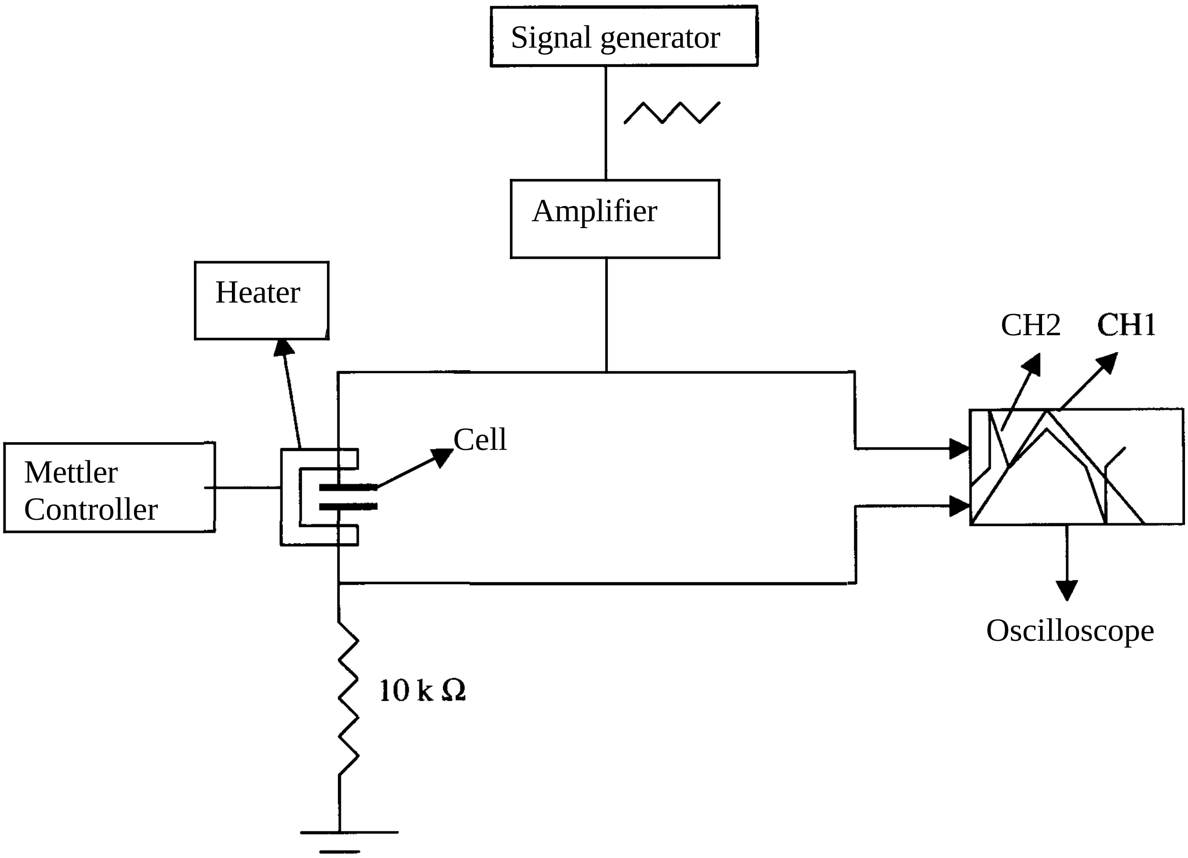


Figure 1.11: The block diagram of a circuit used for the measurement of saturated polarization.