

Chapter 1

Introduction

The liquid crystalline state was first observed by Reinitzer [1] in 1888. Liquid crystals are intermediate states between the ordered crystalline phase and the disordered isotropic liquid phase. They possess a long-range order as in crystals and mobility as in liquids, which give rise to anisotropic physical properties. The fundamental requirement for any substance to exhibit a liquid crystalline state is the shape anisotropy of the constituent molecules. On the basis of this property, three types of thermotropic liquid crystals have been realized which are obtained by the action of heat.

- (i) Calamitic liquid crystals: formed by rod-like molecules
- (ii) Discotic liquid crystals: formed by disc-like molecules
- (iii) Banana liquid crystals: formed by banana-shaped or bent-core (BC) molecules

In calamitic and discotic liquid crystals a free rotation of the molecules along the long molecular axis and disc normal respectively, is allowed (figure **1.1a and b**) reducing the symmetry of the molecules to D_{∞} . The phase symmetry in these systems can be reduced by introducing chirality into constituent molecules [2, 3]. A tilted smectic phase of such chiral rod-like molecules (SmC^*) has the polar symmetry C_2 and exhibits spontaneous electric polarization in each layer, leading to ferro-, ferri- and antiferro-electric switching behaviour [4].

In banana-shaped liquid crystals reduction of symmetry is achieved by linking two rigid-rod segments through a bend. In contrast to the rod- and disc-shaped mesogens, bent-shaped molecules possess a strong lateral steric moment, which restricts the rotation about the long molecular axis (figure **1.1c**). Further, the molecular structure allows an organization of these molecules into layers. This compact packing of bent-molecules in the layers and high rotational hindrance along the long molecular axis results in an in-layer polarization (P) along the bend direction.

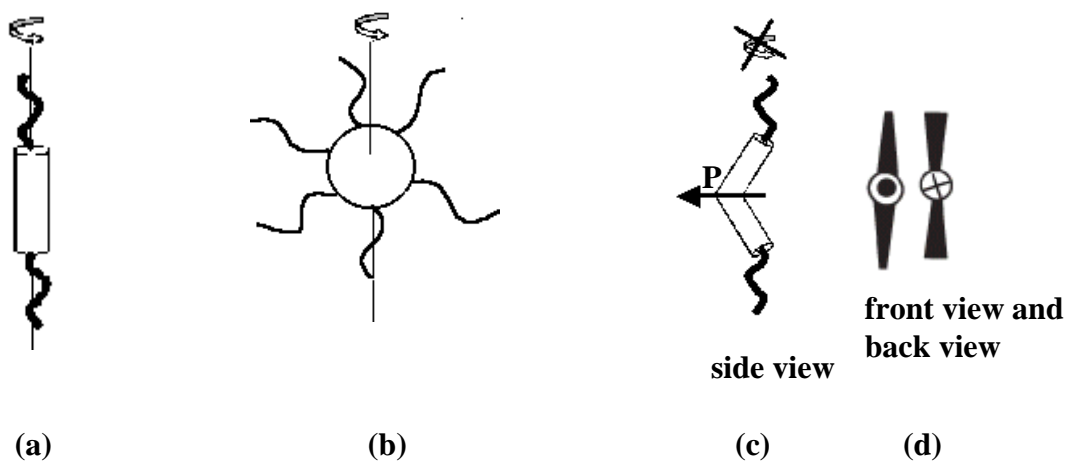
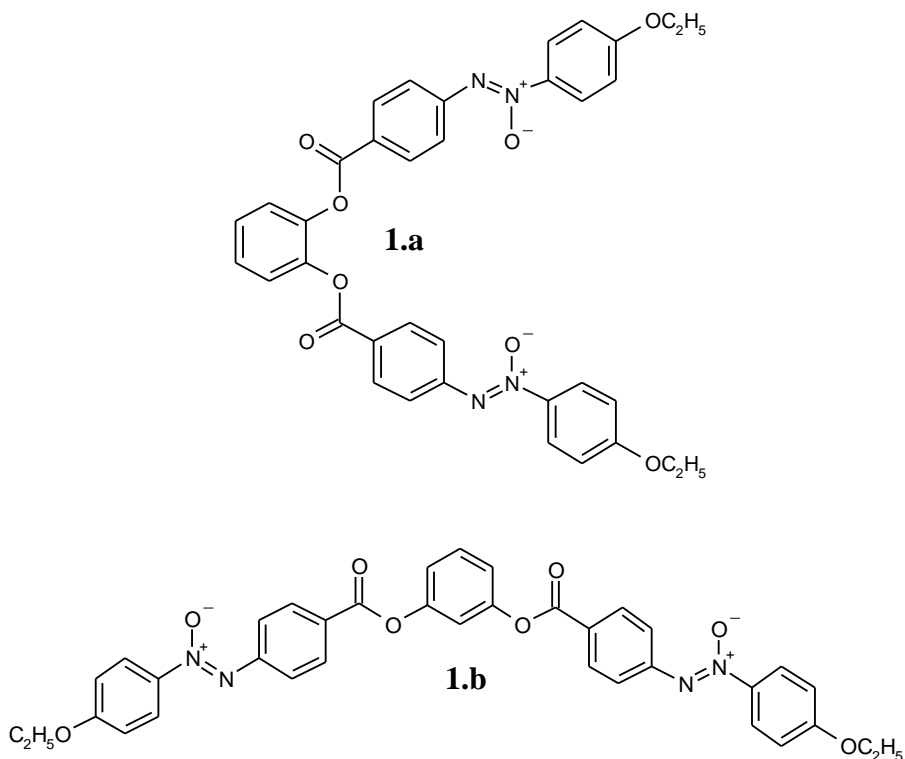
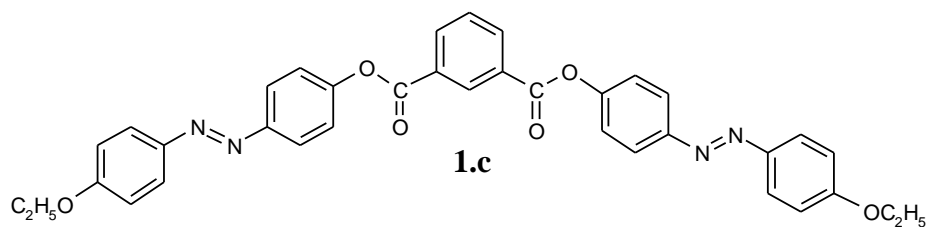


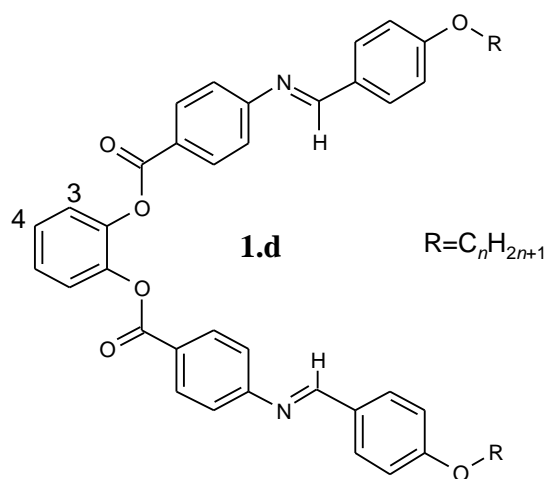
Figure 1.1: (a), (b) and (c), A schematic representation of a rod, a disc and a bent-shaped molecule respectively; (d) front view and back view of a bent-shaped molecule.

The first bent-shaped liquid crystalline materials were synthesized by Vorlander and his group in 1932 [5]. However, the mesophases were not characterized. Two isomeric bent-shaped five-ring mesogens derived from catechol (**1.a**), resorcinol (**1.b**) and a five-ring mesogen derived from isophthalic acid (**1.c**) reported by Vorlander are shown below.

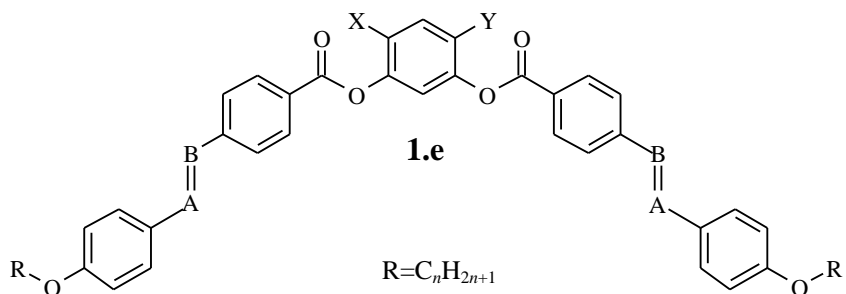




In 1991, Kuboshita *et al.* [6] synthesized and studied the mesomorphic properties of a series of 1,2-phenylene bis [4-(4-*n*-alkoxybenzylideneamino)benzoates] (**1.d**) and also the corresponding 3- and 4-methyl-1,2-phenylene compounds. On the basis of microscopic observations, X-ray powder diffraction measurements and miscibility studies, the mesophases exhibited by these compounds were characterized as N, SmA and SmB. In 1993, Matsuzaki and Matsunaga reported [7] the 2,3-naphthylene analogues and the mesophases were identified as N and SmA. All these compounds have an acute-angle configuration.

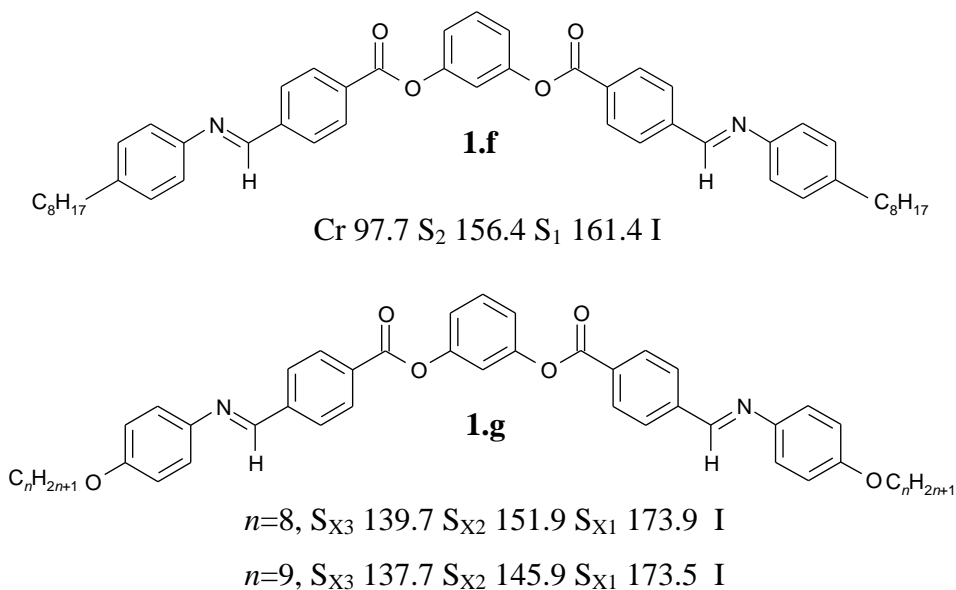


However, they extended the work to compounds with an obtuse angle configuration and in 1994, Akutagawa *et al.* reported [8] synthesis and mesomorphic properties of four homologous series of compounds derived from resorcinol (**1.e**). The mesophases shown by these compounds were identified as N and SmC. From XRD studies, they argued that the tails are nearly normal to the layers whereas the cores are tilted.



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

A real breakthrough in bent-core liquid crystals came in 1996, when Niori *et al.* [9] reported ferroelectricity in a smectic phase formed by an achiral banana-shaped compound (**1.f**).



The ferroelectricity in the mesophase of these compounds is attributed to the C_{2v} symmetry resulting from the packing of banana-shaped molecules into layers. Because of the intrinsic shape,

these molecules adopt dense packing in the layers and are all aligned in the bend direction. Each layer has biaxiality that is in-layer anisotropy exists and the refractive indices are different in the bend direction and in the direction normal to the y-axis (figure 1.2). This corresponds to a C_{2v} symmetry. There exists a two-fold axis along y-axis and there are mirror planes perpendicular to the x- and z-axes. Since there is no mirror plane perpendicular to the two-fold axis, a polarization can be expected to arise along the y-axis (bend direction).

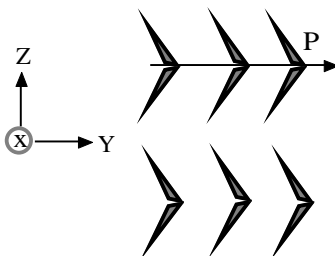


Figure 1.2: A possible smectic structure formed by the banana-shaped molecules (after Niori *et al.* [9]).

X-Ray diffraction studies on the higher temperature phase of compound **1.f** indicated a layered arrangement of molecules in the mesophase. The switching current measurements employing a triangular-wave electric field showed a single current peak per half period of the applied voltage indicating ferroelectric nature of the mesophase.

In 1997, Sekine *et al.* reported [10] a spontaneous helix formation in the smectic phase of an achiral bent-core compound **1.g** ($n=8$). The origin of the helix (macroscopic chirality) was discussed in view of the twisted molecular conformation (conformational chirality) and the escape from macroscopic polarization.

In the same year, Link *et al.* [11] carried out several experiments on freely suspended films drawn in the mesophase of compounds **1.f** and **1.g** ($n=9$). They employed depolarized reflected light microscopic (DRLM) techniques to probe electric dipole density in the smectic phases of these compounds. The DRLM observations with oblique laser incidence and slightly uncrossed polarizers showed that the optic axis in the smectic phase of these compounds is tilted relative to the layer normal. By applying a small electric field to the freely suspended films in the mesophase,

they observed that odd-N (N-number of layers) regions were ferroelectric (FE), whereas even-N regions did not react to the field. This observation indicated that the ground state structure of these mesophases is antiferroelectric (AF) with the layer polarization alternating from layer to layer. They designated the mesophase as “SmCP_A”, where “SmC” stands for tilted smectic, “P” represents polar and “A” stands for antiferroelectric.

However, in the same year, in an International Workshop on “Banana-Shaped Liquid Crystals: Chirality by Achiral Molecules” held in Berlin, it was suggested to use the general symbol “B” for the mesophases exhibited by banana-shaped compounds, since they were not miscible with any of the known phases of calamitic/discotic compounds. A total of seven phases were identified initially and assigned the symbol B₁, B₂,.....B₇. Another phase was discovered later which was designated as B₈ [12]. The letter B signifies the shape of the constituent molecules, viz. banana, bow, etc. and the suffixes indicate the sequence of discovery of the mesophases.

Considering the different possibilities for the packing of the bent-shaped molecules, Brand *et al.* [13] predicted four classes of fluid biaxial phases.

- (i) A transversely polarized non-tilted structure with C_{2v} symmetry (proposed by Niori *et al.* [9])
- (ii) A tilted phase with a monoclinic chiral symmetry C₂ (B₂ phase proposed by Link *et al.* [11])
- (iii) An achiral layer structure with a monoclinic symmetry C_s
- (iv) A triclinic configuration with chiral C₁ symmetry (SmC_G, where G stands for generalized proposed by de Gennes [14])

A schematic representation of these possibilities is shown in figure **1.3a, b, c** and **d** respectively.

In bent-core molecules, there exists a polar order, which results from the directed organization of these molecules in the layers. Such systems with macroscopic polarization are unstable and the molecules try to rearrange in such a way that the net polarization of the system becomes zero. Thus, in many of the mesophases formed by bent-core compounds, the phase structure is determined by a strong desire to escape from macroscopic polarization. It has been suggested [15, 16] that there are four ways to avoid this bulk polarization namely,

- (i) layer modulation: B_1 and B_6 phases
- (ii) antiferroelectric correlation of dipoles in the adjacent layers: B_2 phase
- (iii) helix formation: B_4 phase
- (iv) splay modulation: B_7 type phases

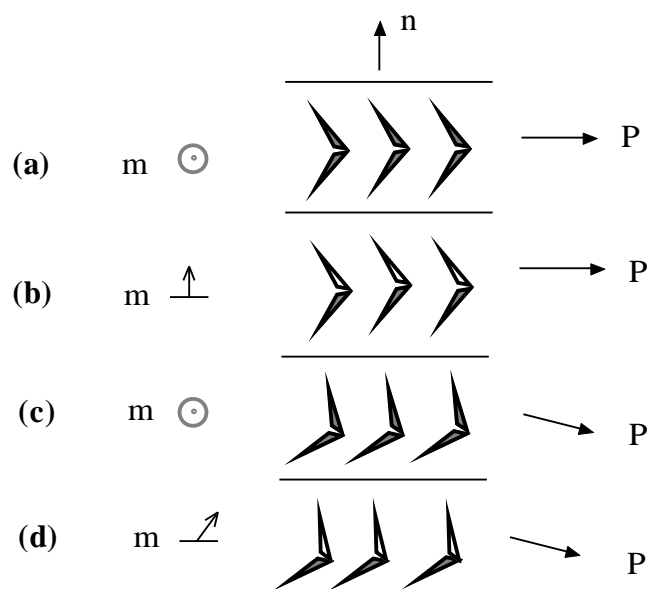


Figure 1.3: Different possibilities of packing of bent-core molecules within the layers.

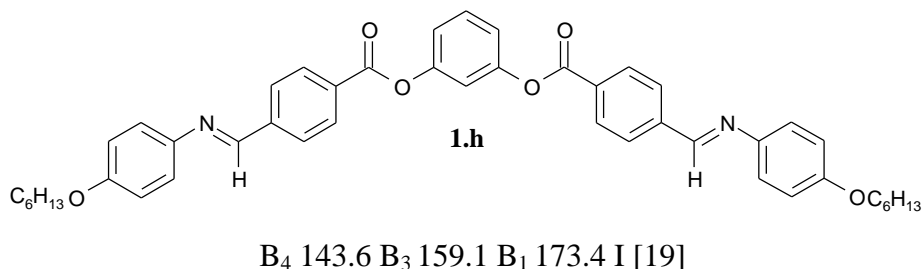
n:Smectic layer normal, **m:** molecular plane normal, **P:** layer polarization; (a) **n** is normal to both **m** and **P**; (b) **n** is normal to **P**, but not to **m**; (c) **n** is perpendicular to **m**, but not to **P**; (d) **n** is neither perpendicular to **P** nor to **m** (after Jakli *et al.* [17]).

In the following section, a brief description of the structures of the different mesophases exhibited by bent-core compounds is presented.

B_1 mesophase

The first compound (**1.h**) exhibiting a B_1 phase was reported [18] by Sekine *et al.* who designated the mesophase as SmA_b' . On the basis of XRD measurements made on the mesophase

of this compound, the authors speculated a frustrated antiphase structure. However, in 1998, Watanabe *et al.* [19] showed the existence of a two-dimensional (2D) rectangular lattice structure in the B₁ phase, using microbeam X-ray diffraction of a monodomain sample.



B₁ mesophase is commonly observed in bent-core compounds with short terminal alkyl chains. In a homologous series, this phase occurs between the non-polar B₆ phase and the polar B₂ phase on ascending the series. On slow cooling from the isotropic liquid, the B₁ mesophase develops as dendritic pattern, which eventually leads to a mosaic-like texture. Sometimes the mesophase shows spherulitic pattern, when the isotropic liquid is cooled slowly. The B₆ to B₁ phase transition has been reported [20-26] in a few bent-core compounds. At this phase transition the textural changes are minimal. The B₁ phase obtained on cooling the schlieren texture of a B₆ phase exhibits a mosaic texture when sheared. The enthalpy accompanying the B₆ to B₁ transition is rather low indicating a weak first order transition. The B₁ to B₂ transition is rather rare and has been observed only in very few systems [27-30]. Among the four reports of such a transition, in two systems [27, 30] the transition has been seen only on cooling whereas in the other two reports [28, 29] the transition has been observed both on heating and cooling. As reported by Shen *et al.* [27] during the transition, the mosaic texture of the B₁ phase changes to a schlieren texture.

The X-ray diffraction pattern of the B₁ mesophase is indicative of a two-dimensional rectangular lattice as suggested by Watanabe *et al.* [19]. Two or more reflections are observed in the small angle region besides a diffuse wide-angle reflection. One of the small angle reflections corresponds to half the molecular length, which indicates an intercalation in the structure. The diffuse peak in the wide-angle region indicates a liquid-like in-plane order. The 2D modulated structure for the B₁ phase proposed by Watanabe *et al.* is shown in figure 1.4.

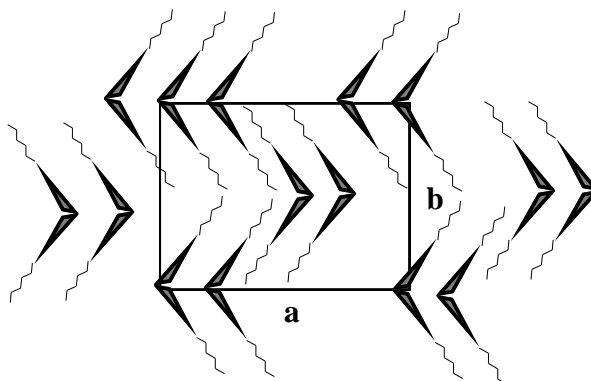


Figure 1.4: A schematic representation of the frustrated structure of B_1 mesophase.
(after Watanabe *et al.* [19]).

According to this model, the phase is built of columns formed by layer fragments. The molecules in layer fragments are organized in such a way that the polarization direction in adjacent clusters is antiparallel. The polarization direction is perpendicular to the column axis and the molecules are non-tilted. The lattice parameter a provides an approximate number of molecules in the lattice and the parameter b corresponds to the length of the molecule.

In this structure, there is some overlap between the aromatic parts of the molecules at the interfaces of neighboring domains, which contributes to stabilizing the phase. However, there also exists an unfavourable overlap of the aromatic cores and the aliphatic chains of the neighboring molecules at the boundaries between the domains. If the chain length is shorter this unfavourable interaction is reduced and the molecules can move across the domains. This causes a collapse of the 2D lattice and gives rise to an intercalated smectic B_6 phase. If the chain length is sufficiently long, the unfavourable chain-core interaction increases and there is a segregation of the aromatic cores and aliphatic chains resulting in a monolayer structure (B_2). Thus, in a homologous series, B_6 , B_1 and B_2 phases appear in that sequence on increasing the chain length [21, 22, 24].

The B_1 phase does not show any response to an applied electric field. This is because the rotation of the molecules is restricted due to the steric hindrance arising from the interactions between column boundaries.

Variants of B_1 mesophase

Bedel *et al.* reported [31, 32] a two-dimensional phase with a rectangular lattice, which is different from the conventional B_1 phase. This phase was observed in a series of compounds, which contain a fluoro substituent *ortho* to the terminal *n*-alkoxy chain. The XRD data obtained for this mesophase could be indexed to a rectangular lattice and the phase did not respond to an applied electric field. However, miscibility studies of this mesophase with the B_1 phase of the unsubstituted compound showed a strong non-ideal behaviour. Hence they designated the mesophase as B_x . However, they have not proposed any structure for this mesophase.

Szydłowska *et al.* reported [33] two new modulated phases, which they initially called as B_x and B_{x1} . These phases are switchable under an electric field, which is in contrast to the commonly observed B_1 phase. On the basis of XRD studies and electro-optical behaviour, they suggested that, in the B_x phase, the polarization direction is parallel to the column axis and the density modulation is in the plane perpendicular to the polarization vector. Hence, they assigned the symbol B_{1rev} for the B_x phase and $B_{1revtilt}$ for B_{x1} phase, which is the tilted analogue of B_{1rev} . Pelz *et al.* also reported [34] such phases in two new compounds. Similar columnar phases were also reported by Reddy *et al.* [35].

Recently, Takanishi *et al.* [36] carried out X-ray microbeam diffraction measurements on the B_1 phase of a prototype bent-core compound **1.h**, in order to investigate the local layer structure and intralayer molecular orientation. Their results indicate that, the molecular bending plane is normal to the frustrated plane (parallel to the column axis) (figure 1.5) and this is different from the model proposed earlier for the B_1 phase [19], but the same as B_{1rev} phase.

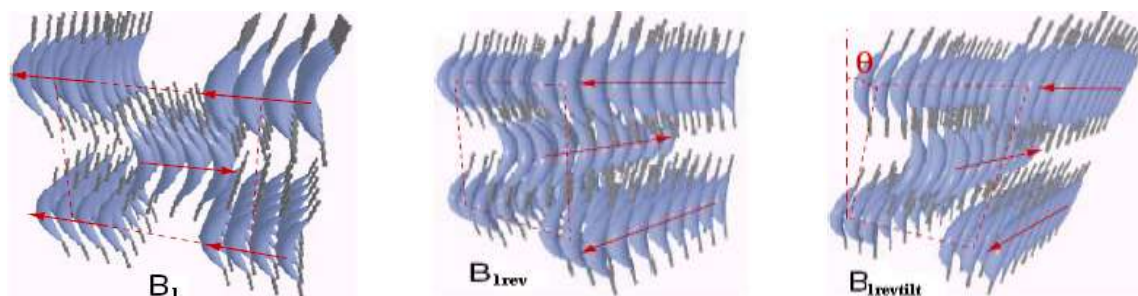


Figure 1.5: Proposed structures of B_1 , B_{1rev} and $B_{1revtilt}$ phases (after Takanishi *et al.* [36]).

B₂ mesophase

The B₂ mesophase is the most commonly observed and most extensively studied among all the banana mesophases. This mesophase was first observed in compound **1.f** by Niori *et al.* [9]. This mesophase is generally observed in bent-core compounds with long terminal alkyl chains and it exhibits a variety of textures. A fingerprint or fringe pattern, schlieren and focal-conic textures are quite often observed. Sometimes chiral domains of opposite handedness are also observed on slow cooling from the isotropic phase.

The X-ray diffraction pattern of this mesophase exhibits layer reflections, up to third or even fourth order in the small angle region and a diffuse peak in the wide-angle region. In a well-oriented sample [32, 37, 38], the layer reflections are situated along the meridian and wide-angle diffuse scattering peak is inclined with respect to the meridian and the equator, indicating a tilt of the molecules. The measured first order spacing is less than the calculated full molecular length, which further supports the tilt of the molecules in the layers. Local layer structure in the circular domains in this phase has also been studied using X-ray microbeam [39] and several types of layer structures have been suggested.

A clear understanding of the structure of this mesophase was given by Link *et al.* [11]. They carried out careful electro-optical investigations on freely suspended films and transparent electro-optic cells filled with samples of compounds **1.f** and **1.g** ($n=9$). Their experimental results revealed that the optic axis is tilted relative to the layer normal and the layer polarization, in the plane normal to the tilt direction, alternates from layer to layer. The layer polarization is due to the steric packing of bent-core molecules in the layers along the bend direction. Their observations of the mesophase also suggest a strong biaxiality and ordering of molecular planes normal to the tilt direction of the optic axis. They designated the mesophase as SmCP_A.

On the basis of these results they considered three distinct planes, a tilt plane, a polar plane and a layer plane associated with a given layer, as shown in figure **1.6**. If these three planes are assumed to be three co-ordinates of a system, then the mirror image is non-superimposable. Thus, the layer becomes chiral, although the individual molecules are achiral.

A pictorial representation of the layer chirality as proposed by Heppke and Moro [40] is shown in figure **1.7**.

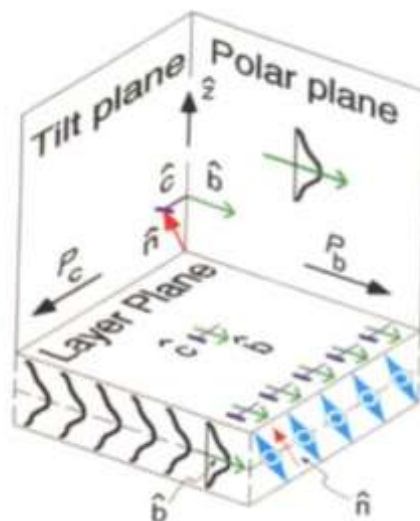


Figure 1.6: A pictorial representation of the geometry of a smectic layer in the B_2 ($SmCP_A$) phase; z : layer normal, n : director of the bent-core molecules, b : polar direction, c : tilt direction of the molecules (after Link *et al.* [11]).

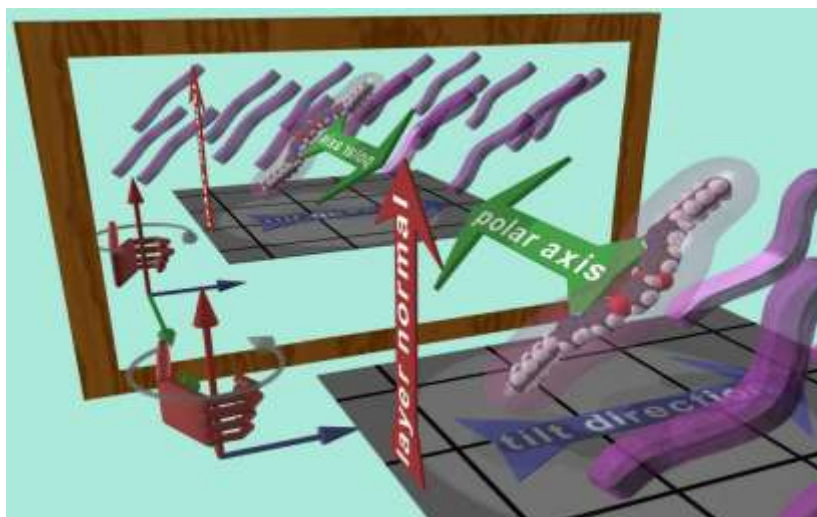


Figure 1.7: A pictorial representation of origin of layer chirality from achiral molecules; the layer normal, tilt direction and the polar axis define a coordinate system, which forms non-superimposable mirror images (after Heppke and Moro [40]).

The combination of polar order and tilt direction gives the layer a chiral structure in the SmCP_A phase. Depending on the tilt direction and polar direction of the molecules in adjacent layers, two ground state structures can be considered, namely SmC_sP_A (synclitic antiferroelectric) and SmC_aP_A (anticlitic antiferroelectric). The chirality of the layers is the same in SmC_aP_A and hence it represents a homochiral structure whereas chirality alternates from layer to layer in SmC_sP_A resulting in a racemic structure. On application of an electric field, a switching from antiferroelectric to ferroelectric state is observed. A schematic representation of the molecular arrangements in the chiral and racemic states at zero electric field and after the application of the field is shown in figure 1.8. The switching process takes place by a collective rotation of the molecules around a cone. This switching process reverses the polar direction as well as tilt direction, but preserves the layer chirality. Thus the SmC_sP_A and SmC_aP_A switch to SmC_aP_F (racemic) and SmC_sP_F (chiral) structures.

However, there are a few reports in which switching between the antiferroelectric and ferroelectric states take place *via* rotation around a long molecular axis, which results in inversion of layer chirality. This process is slower than the motion around a cone and takes place only if the faster switching around a cone is hindered for any reason. Therefore, this type of switching is observed in undulated smectic phases [41-43] and in SmCP_A phases with a small tilt ($< 20^\circ$) of the molecules and a large bend angle [42, 44].

Variants of B_2 mesophase

Infact, there are a few reports of the existence of B_2 -like phases, which show lamellar XRD pattern and antiferroelectric behaviour under the field. Eremin *et al.* reported [45] two mesophases below a B_2 phase on cooling from the isotropic phase in a compound containing a CH_3 group in the angular position of the central ring and a fluorine atom *ortho* to the each of the terminal alkyl chains. The mesophases were designated as B_2' and B_2'' . Svoboda *et al.* also reported [46] two B_2 -like phases, which were labelled as B_2' and B_2'' in compounds derived from 1-cyanonaphthalene-2,7-diol. The detailed structures of these mesophases are not yet established.

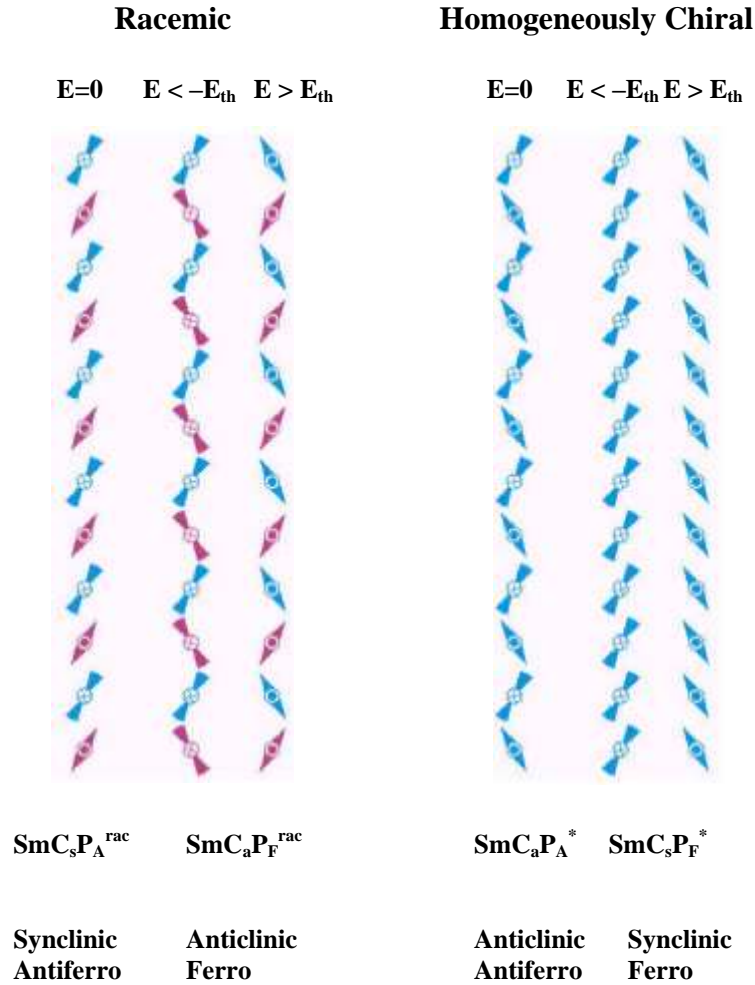


Fig. 1.8: A schematic representation of the arrangement of BC molecules in racemic and chiral states of an antiferroelectric mesophase and the corresponding field induced ferroelectric states (after Link *et al.* [11]) ; rac: racemic, * chiral.

B₃ mesophase

The B₃ phase is a low temperature phase with respect to a B₂ phase and appears above a B₄ phase [20]. On rapid cooling from the B₂ phase, no textural change could be observed in the B₃ phase. However, on slow cooling, a slight change in the form of breaking of domain is observed. The XRD pattern of a non-oriented sample shows a number of reflections in the small angle as well as wide-angle regions, which suggests a crystalline structure. However, the dielectric [47] and terahertz spectroscopic results [48] indicate that the dynamics in the B₃ phase is similar to that in

the B₂ phase and therefore cannot be a crystal. On the basis of these results, B₃ phase is characterized as a higher-order smectic phase.

B₄ mesophase

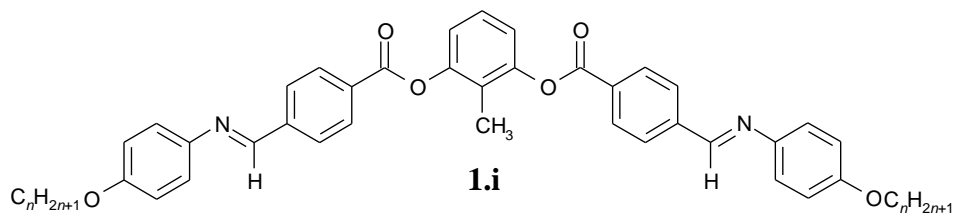
This mesophase appears below a B₂ phase or a B₃ phase. The mesophase exhibits dark blue coloured domains under crossed polarizers. However, domains of different brightness are observed on slightly decrossing one of the polarizers [49]. A circular dichroism (CD) spectrum clearly shows domains with opposite sense and this indicates that the domains are chiral [50]. The mesophase is also named as smectic blue phase [18, 51] because of the characteristic blue colour exhibited by this phase.

XRD pattern of a powdered sample shows several reflections in the small angle as well as in the wide-angle regions, suggesting a crystalline order. However, dielectric studies for a low-frequency relaxation suggested that the B₄ phase is not crystalline [47, 52]. Simple harmonic generation was observed in this mesophase even in the absence of electric field [53], which indicates the existence of a spontaneous non-centrosymmetric order.

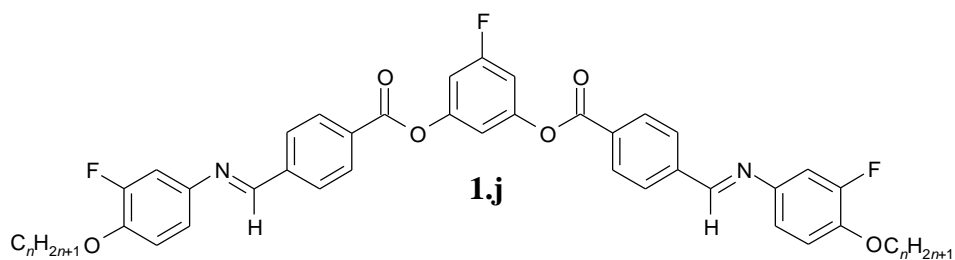
A TGB-like structure has been proposed for this phase by Sekine *et al.* [18]. The X-ray microbeam experiments are consistent with the proposed TGB-like structure.

B₅ mesophase

The B₅ mesophase is reported in only a few systems so far. This phase was first observed [38] in a BC compound derived from 2-methylresorcinol (**1.i**). Later this phase was observed in derivatives of 2-methyl- [45] and of 5-fluororesorcinol [54], which contain a fluoro substituent *ortho* to the terminal *n*-alkoxy chain on the both the arms (**1.j**). In these compounds, B₅ phase occurs below a B₂ phase. The transition enthalpy is small and the textural changes at the transition are also minimal.



$n=8$ Cr 161 B₅ 165 B₂ 172 I
 $n=9$ Cr 157 B₅ 163 B₂ 168 I
 $n=10$ Cr 153 B₅ 158 B₂ 167 I



$n=12$ Cr 112 B_{5F} 122.5 B_{5A} 128 B₂ 157 I

XRD pattern of this mesophase shows layer reflections up to sixth order in the small angle region and some additional reflections in the wide-angle region. From an oriented pattern, the reflections in the wide-angle region have been indexed to a rectangular lattice [38, 54] and in-plane molecular packing in the B₅ phase was proposed [20, 38], as shown in figure 1.9. An antiferroelectric behaviour was observed in the B₅ phase on application of an electric field. However, a ferroelectric switching is also reported [54] for the lower temperature B₅ phase of compound 1.j.

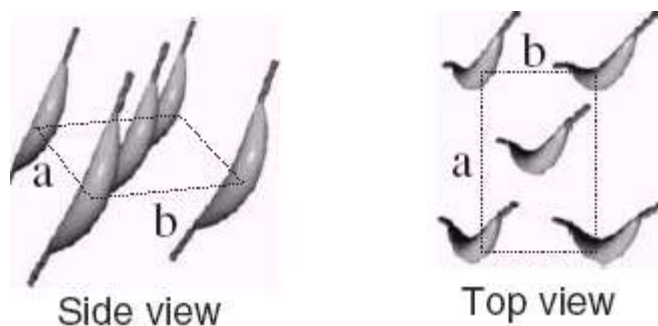


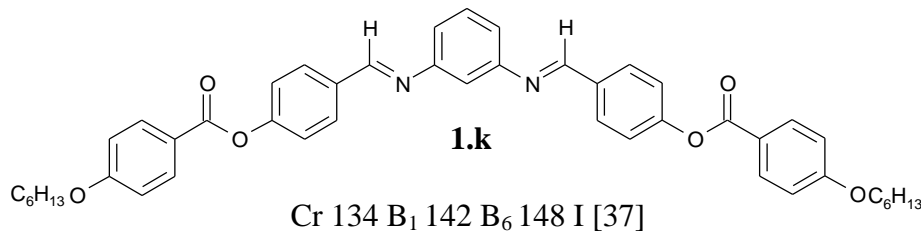
Figure 1.9: A pictorial representation of in-plane molecular packing in the B₅ phase.

Variants of B₅ mesophase

Five new variants of B₅ phase are reported [54] by Nadasi *et al.* for compound **1.j** ($n=8$). On cooling the isotropic liquid of compound **1.j**, they observed five B₅ sub-phases below a B₂ phase with a small enthalpy value for each transition. Among these, four exhibited antiferroelectric behaviour and a transition from an antiferroelectric phase to a ferroelectric phase was also observed. The exact structures of these sub-mesophases have not been determined.

B₆ mesophase

This mesophase was first observed [37] in compound **1.k**. This phase is also designated as SmA_c, SmC_c or SmC_{int}.



The B₆ phase exhibits a fan-shaped texture similar to SmA phase. However, it is difficult for this phase to be aligned homeotropically, which rule out the possibility of a SmA like structure. Sometimes, schlieren texture could be obtained on shearing the fan-shaped texture of B₆ phase. A transition from B₆ to B₁ phase is observed [20-26] in some compounds.

XRD pattern of the B₆ phase shows lamellar reflections in the small angle region along with a diffuse wide-angle reflection. The first order layer spacing in the small angle region is smaller than half the calculated molecular length. This indicates an intercalated structure. An oriented pattern of this mesophase indicates tilt of the molecules and the estimated tilt angle is about 20-30° [20]. A schematic representation of the molecular arrangement in the B₆ phase is shown in figure **1.10**.

In a homologous series, on increasing the chain length, B₆, B₁ and B₂ phases appear in that sequence [21]. Rouillon *et al.* [22] carried out Monte-Carlo conformational search to obtain the lowest energy conformations of BC molecules exhibiting B₆ phase and subjected them to semi-

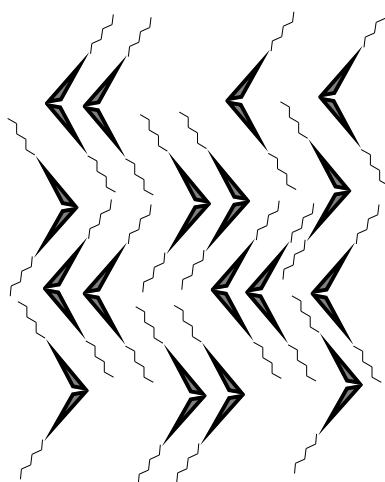


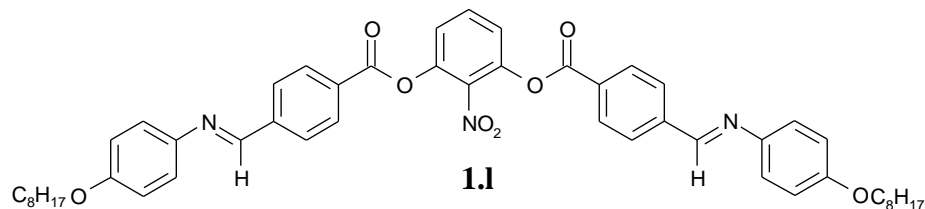
Figure 1.10: A schematic representation of the arrangement of BC molecules in the B₆ phase (after Pelzl *et al.* [20]).

empirical quantum mechanical charge calculation. The electrostatic potential maps were drawn and on the basis of analysis of these, they proposed a molecular arrangement with an alternation of high and low potentials. In such a periodic structure, the electro-positive aliphatic chains fill up the vacant gaps between the aromatic (electronegative) parts. Due to the constraints in packing of aromatic cores, only short chains can fill the space. Hence, the B₆ phase is observed for lower members of the series with short alkyl chains.

B₇ mesophase

The B₇ phase was first observed [55] in a compound derived from 2-nitroresorcinol (**1.1**). Later this phase was also observed in a number of compounds derived from 2-cyanoresorcinol [56-59]. There is also a report [60] of the observation of this phase in compounds derived from 5-fluoresorcinol.

Among all the mesophases exhibited by BC compounds, the B₇ phase shows the most beautiful and fascinating textures. One such texture is the helical nuclei that appear on slow cooling the isotropic liquid, resembling that of telephone wires. Jakli *et al.* [61] showed that left and right-handed helices occur in equal numbers and these screw-like domains consist of smectic filaments, which form single, double or triple coils. The other textural variants observed for the B₇ phase include lancet-like or thread-like germs, circular domains with equidistant concentric rings,



Cr 116 B₇ 177 I

myelinic-like, checker-board-like and banana-leaf-like textures. It was considered that the helical filaments are indicative of chirality [61]. However, Coleman *et al.* [62] showed that polarization modulation is the essential element stabilizing the filament structure. They pointed out that the helical winding of polarization modulation within the filament, with the helix sense established by the nucleation event and remain fixed during growth provides an explanation for the twist deformation of filaments. Based on this they argue that helical filament formation neither relies on, nor is indicative of supramolecular chirality. It has also been pointed [16] out that any layer instability can induce helical filaments during the growth process, even if the resulting phase is a modulated, undulated, or even a simple smectic mesophase.

XRD pattern of B₇ mesophase shows several reflections in the small angle region besides a wide-angle diffuse reflection. One characteristic feature of all the XRD patterns of B₇ phases exhibited by compounds derived from 2-nitro-, 2-cyano- and 5-fluoro-resorcinol is the presence of a medium angle reflection at a distance corresponding to 7-8 Å. Coleman *et al.* [62] carried out synchrotron X-ray studies on compound **1.1**. On the basis of experimental results they proposed an interdigitated 2D lattice for the mesophase. The proposed model will be discussed in Chapter 5. A similar 2D lattice has been proposed for the B₇ phase exhibited by a compound derived from 2-cyanoresorcinol, on the basis of synchrotron X-ray diffraction studies [63]. It has been pointed out [16] that, the distance corresponding to the medium angle reflection is in a range of typical value of face-to-face packed dimers and if such a face-to-face packing takes place in the B₇ phase, then the medium angle reflection might correspond to some order between these dimers.

Earlier reports [55] indicate that, no electro-optical switching could be observed in a B₇ phase at least upto 40 V μm⁻¹. However, in 2003 a transition from a non-switchable B₇ phase to two antiferroelectric sub-phases (B_{7AF1} and B_{7AF2}) in higher homologues of nitro-substituted

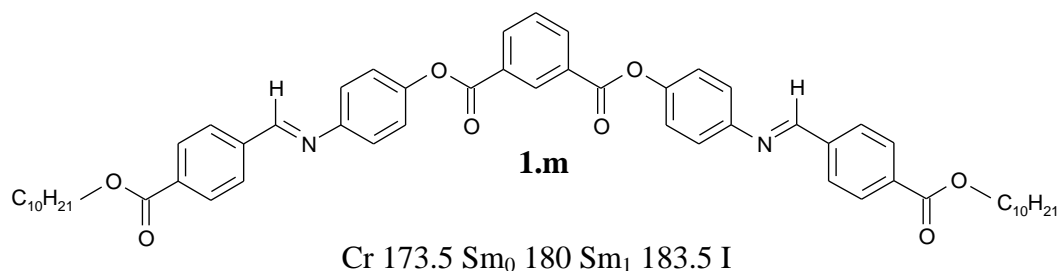
compounds has been reported [59]. Also, in compounds derived from 5-fluoro-resorcinol, a transition from an antiferroelectric SmCP_A phase to a ferroelectrically switchable B₇ phase has been observed [60]. So far, these two represent examples of a switchable B₇ phase obtained from compounds with a substituted central phenyl unit.

Variants of B₇ phase

There are a number of compounds the mesophases of which exhibit spiral filaments and other textural variants, on slow cooling the isotropic liquid. These mesophases have also been designated as B₇ [32, 64-68] despite the fact that their XRD patterns are different from that of the original B₇ phase [55]. These mesophases exhibit layer reflections in the small angle region and a few of them show satellites of weak intensities behind layer reflections [66, 67] that indicate a modulation. Importantly, the medium angle reflection is absent in the XRD pattern of these mesophases. Coleman *et al.* [62] carried out several experiments on the mesophase exhibited by compound MHOBOW [66], which shows ferroelectric characteristics. They proposed a polarization modulated/undulated layer stripe structure stabilized by splay of polarization for this phase, but assigned the symbol B₇. The phase structure proposed by Coleman *et al.* will be discussed in detail in Chapter 5. A SmC_G structure has also been discussed for these mesophases [17, 69]. Recently, it has been suggested [16] to use the symbol B₇' for these mesophases, which exhibit the textural variants of B₇ phase and their XRD patterns are different from classical B₇ phase [55].

B₈ mesophase

In 2001, Bedel *et al.* reported [12] a few BC compounds derived from isophthalic acid and containing terminal *n*-alkyl carboxylate groups. In a homologue with *n*=10 (**1.m**), for the higher temperature phase (Sm₁), they observed a bilayer structure and an antiferroelectric behaviour. The



textures exhibited by this phase are also different from those observed for other B-phases. Since this mesophase has a new structure, the authors suggested the symbol B₈. Later [41], the phases Sm₀ and Sm₁ were characterized as SmC_sP_A (polar SmC phase, subscripts s and A refer to synclitic and antiferroelectric) and SmC_sG₂P_A (subscript 2 refers to bilayer structure made of SmC_G layers, G stands for general).

SmC_G phase

SmC_G phase has a triclinic configuration with chiral C₁ symmetry. The possibility of such a smectic phase with lowest possible symmetry was proposed by de Gennes [14], who coined the name SmC_G, where G stands for general. Later, Brand *et al.* [13] gave theoretical model for the realization of such a phase in a system composed of BC molecules. In SmC_G phase, in addition to the tilt of the molecules, a leaning of the molecules in the tilt plane is considered. An orientation of the BC molecules where all three principal axes make an angle with the smectic layer different from 0° or 90° leads to a SmC_G structure. The other aspects concerning this phase are discussed in Chapter 4.

Ferroelectric mesophases in bent-core compounds

Ferroelectric mesophases are thermodynamically not favourable in banana-shaped compounds. This is because, ferroelectric structure in such compounds involves anticlinic interlayer interfaces, in which the out-of-layer fluctuations are suppressed and thus carries an entropic penalty (figure **1.11a**) [54]. The penetration of the layers is favourable in an AF arrangement of the molecules (figure **1.11b**) and hence AF phases are preferable. Thus in order to obtain ferroelectric switching materials the basic idea is to stabilize the anticlinic interlayer interfaces within this type of organization.

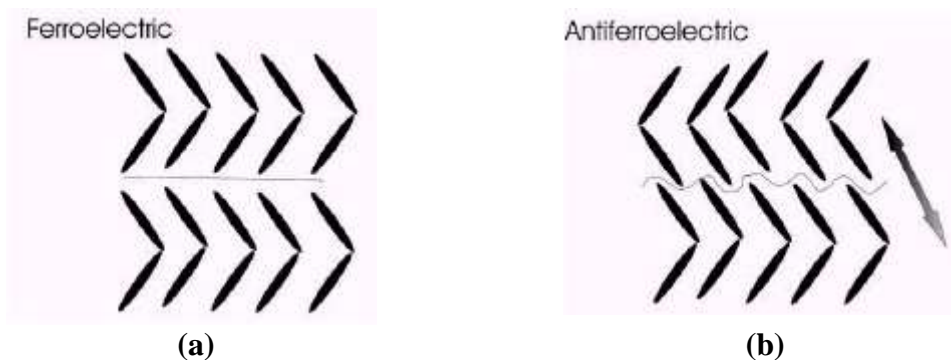


Figure 1.11: The molecular organization in FE and AF phases in bent-core molecules (after Nadasi *et al.* [54])

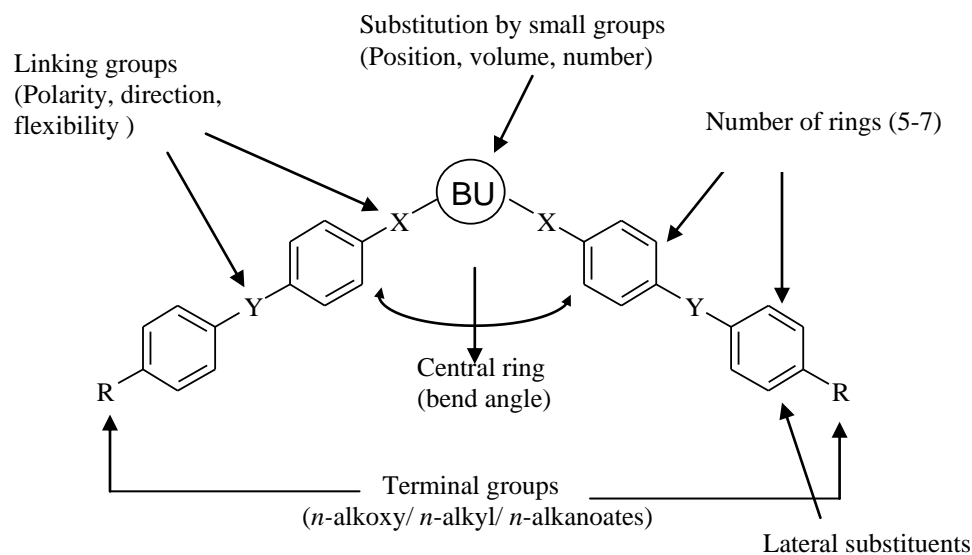
The first approach to obtain a FE switching material was made by Walba *et al.* [66]. They synthesized an unsymmetrical compound with a chiral terminal chain, the same as used for chiral rod-like materials showing SmC_a^* phase (chiral anticlinic SmC) at one end. The mesophase exhibited by this compound is characterized to have a polarization modulation, which leads to undulated layer structure [62]. However, under a high electric field, the polarization modulation defects get eliminated which in turn removes the undulation resulting in a ferroelectric switching (SmC_sP_F) structure.

Bedel *et al.* reported [31] ferroelectric-switching behaviour for a mesophase exhibited by compounds, which contain two fluoro substituents *ortho* to each of the two terminal *n*-alkoxy chains. There are a few more reports [32, 35, 54, 70, 71], which also describe ferroelectric switching and in these compounds also, two fluoro substituents *ortho* to each of the two terminal *n*-alkoxy chains are incorporated.

In a few cases where ferroelectric switching in BC compounds has been reported, the molecules contain branched (chiral) alkyl chains [72, 73], achiral oligosiloxane [74], oligocarbosilane terminal chains [75] or terminal *n*-alkyl carboxylate groups [12, 41].

Structure property relationships in bent-core mesogens

A general structure of the bent-shaped mesogens is shown below.



Most of the BC compounds reported up to now contain five phenyl rings [16, 20, 76]. However, compounds containing three [77], six [32] and seven [16, 32, 76] phenyl rings have also been reported. On increasing the number of phenyl rings, the thermal range of the mesophases as well as the clearing temperatures also increase. In most cases, the central unit is a rather rigid, 1,3-disubstituted benzene ring, a 2,6-disubstituted pyridine ring, a 2,7-disubstituted naphthalene unit or a 4,3'-disubstituted biphenyl unit. In BC molecules the bend angle is about 120° . However, the bend angle may vary between 105° and 140° depending on the chemical structure of the molecule [78]. Lateral substituents near the linking groups of the central unit strongly influence this bend angle.

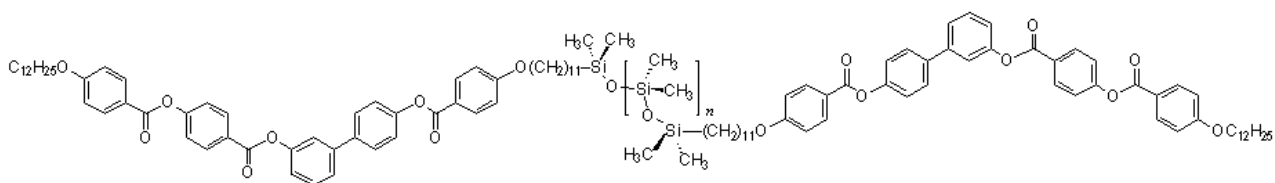
Normally used linking groups are Schiff's base (azomethine, $-\text{CH}=\text{N}-/ -\text{N}=\text{CH}-$) and ester ($-\text{OCO}-/ -\text{COO}-$) units. In addition, azo ($\text{N}=\text{N}$), ethylene ($-\text{C}=\text{C}-$), acetylene ($-\text{C}\equiv\text{C}-$) have also been incorporated as linking groups. Often Schiff's base derivatives show rich polymorphism when compared with the other systems.

n-Alkyl or *n*-alkyloxy chains are used as terminal groups in most of the bent-shaped mesogens. However, there are a couple of reports in which terminal carbon-hydrogen chain is linked by sulfur [65], carbonyl or carboxylic groups [12, 41]. Perfluoroalkyl fragments are used as terminal chains in some cases [27, 77], in which a strong increase in the transition temperature is observed.

Lateral substituents in bent-core compounds have profound effect on the mesomorphic behaviour. 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 can alter the bend angle. Also, polar lateral substituents can change the electron density distribution around the core leading to a change in the mesomorphic behaviour. Suitable substitution on the outer phenyl ring of the bent-core has also a significant effect on mesomorphic behaviour. A variety of lateral substituents such as fluoro, chloro, iodo, bromo, methyl, ethyl, nitro, cyano and trifluoromethyl groups in different positions of the bent-core molecules have been used [16, 20, 24, 79-81]. A detailed account of the effect of different lateral substituents on mesomorphic properties is given in Chapter 3.

Mesogenic dimers

Mesogenic dimers contain two mesogenic units connected by a flexible spacer. The first mesogenic dimer made of rod-like units was reported [82] by Vorlander long ago. Although there are a large number of mesogenic dimers made up of rod-like units as well as a few made up of disc-like units [83], only a few examples are known in which a bent-shaped unit is used [84, 85]. The first liquid crystalline dimers composed of two banana-shaped mesogenic units connected by a dimethylsiloxane unit (**1.n**) were reported by Dantlgraber *et al.* [86]. In these dimers, either FE or



1.n

$n=1$: Cr 64 SmCP_F* 132 I

$n=2$: Cr 92 SmCP_A 132 I

AF switchable polar smectic C phases were observed depending on the number of flexible dimethylsiloxane units.

Very recently, Kosata *et al.* reported [87] symmetric dimers where several bent-core mesogenic units are terminally linked with different flexible spacers, such as a siloxane, a tetraethylene glycol and an alkylene spacer. They did not observe any mesophase when a flexible alkylene spacer was used. However, a columnar phase could be obtained when the ester linking groups between the “inner” rings were reversed. A detailed account of these are presented in the last chapter.

Experimental techniques

The following two techniques were employed to examine the structure and polar properties of the mesophases exhibited by various BC compounds investigated and reported in this thesis.

- (a) X-Ray diffraction
- (b) Electro-optical measurements

X-Ray diffraction measurements

X-Ray diffraction measurements were carried out in order to investigate the structure of the mesophase. Generally powder samples and in a few cases oriented samples were used to obtain diffraction patterns of the mesophases of bent-core compounds. The powder samples held in sealed Lindemann capillaries (diameter: 0.7 mm; wall thickness: 0.01 mm) were cooled from the isotropic state to the mesophase and irradiated. Oriented patterns were obtained by slow cooling of a drop of sample on a glass plate from the isotropic state.

The X-rays were generated by a 4 kW rotating anode generator (Rigaku Ultrax 18). The beam was monochromated to obtain a radiation of wavelength 1.54Å (Cu-K_α radiation) by using a graphite crystal. A double slit arrangement was used to collimate the beam, which subsequently interacted with the sample 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 of the mesophase was collected on a two-dimensional image plate detector. A schematic representation of the X-ray set-up used is shown in figure 1.12.

The layer spacing of the mesophase was calculated using Bragg's equation, $n\lambda = 2d\sin\theta$

Where, $n= 1$ (for first order reflection)

$\lambda= 1.54\text{Å}$ (wavelength of Cu-K_α radiation)

$d=$ measured layer spacing

$\theta=$ Bragg's angle and can be calculated as $\theta = \frac{1}{2} \tan^{-1} \frac{R}{D}$

$R=$ 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

$$\theta = \cos^{-1} \frac{d}{l} \text{ where, } l\text{-calculated molecular length.}$$

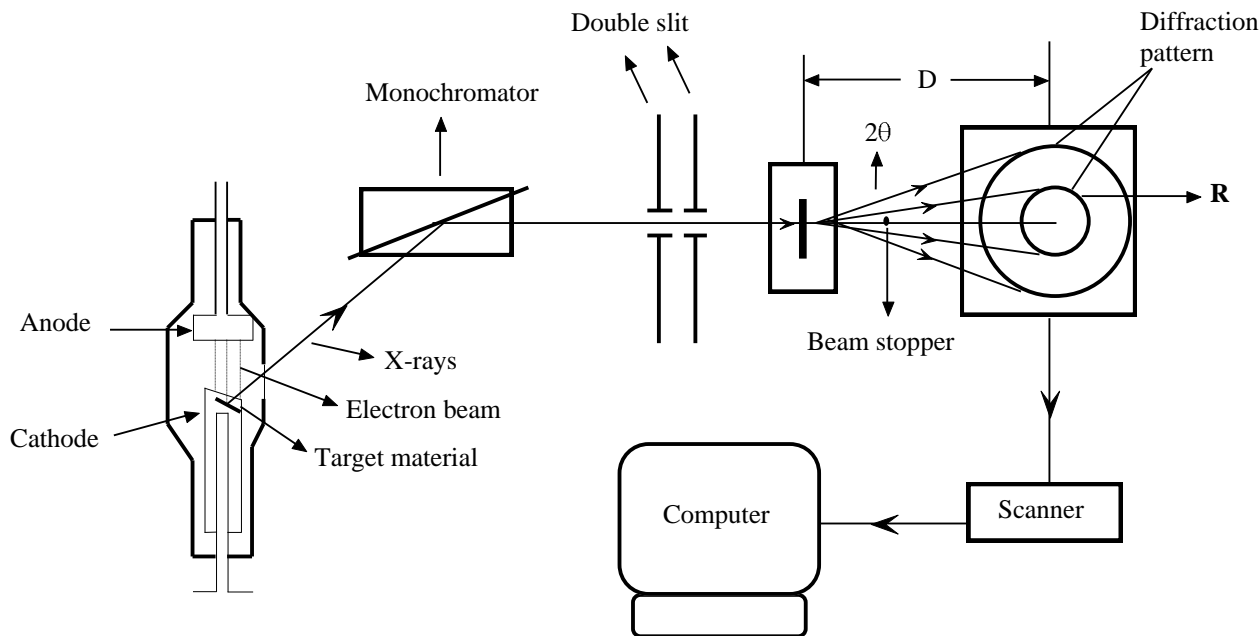


Figure 1.12: A block diagram showing the X-ray diffraction experimental set-up.

Electro-optical investigations

In order to study the polar properties of the banana mesophases and to measure the polarization value for the mesophase, the standard triangular-wave method [88] was used. A block diagram of the experimental set-up used is shown in figure 1.13.

The electro-optical experiments were carried out using sample cells made up of transparent glass plates, coated with indium tin oxide (ITO). In order to obtain a planar alignment of the sample, the inner surfaces of these conducting glass plates were coated with polyimide and unidirectionally rubbed. The thickness of the cell was controlled by using Mylar spacers and the thickness was measured by interferometric technique. In some experiments, the commercially obtained (EHC, Japan) cells were also used. The sample was filled in to the cell in the isotropic phase and cooled slowly to get a good alignment of the sample. The triangular wave of definite amplitude and frequency was produced by using a wave from generator (Wavetek model 39) which was amplified hundred times using an amplifier (Trek model 601-B). The output from the amplifier was divided into two channels CH1 and CH2. The waveform Channel CH1 was directly

connected to the oscilloscope, which acted as a reference signal; CH2, the output signal from the sample was connected to the oscilloscope (Agilent 54621A) *via* a 10 (or 1) kΩ resistance. The resultant curve obtained on the oscilloscope screen was a plot of switching current *versus* time. The polarization value was calculated by integrating the area under the peaks obtained in the experiment using the relation

$$P \approx \frac{I \times t}{A} \quad \text{where, } I - \text{current, } t - \text{time, } A - \text{cell area}$$

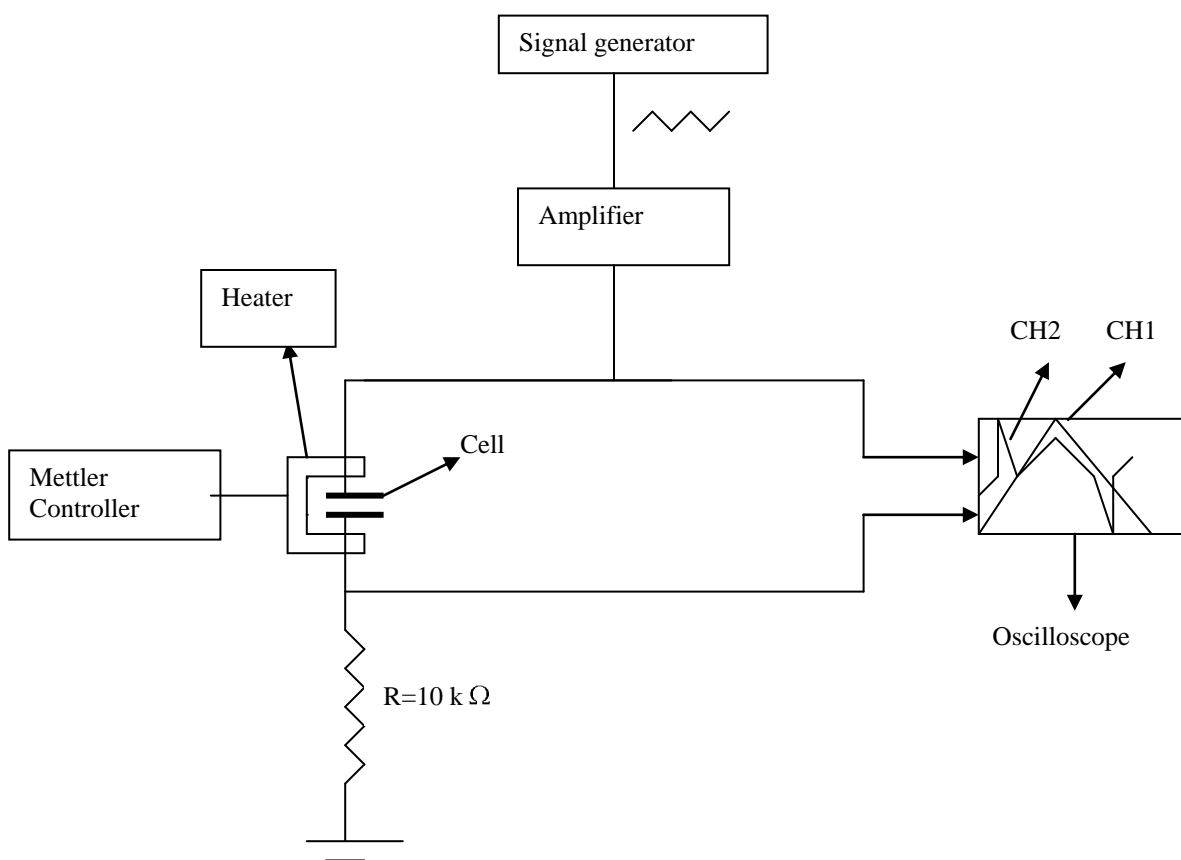


Figure 1.13: The block diagram of a circuit used for the measurement of polarization.

To find the tilt sense of the molecules in the mesophase, dc field experiments were carried out using a regulated dual dc power supply (Aplab, Model LD 6401)

Dielectric measurements on mesophases of some of the compounds were carried out by A. Jakli, Kent State University, Kent, USA.

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