Chapter 1

Introduction

Liquid crystals are a state of matter in which the degrees of molecular order lie intermediate between the ordered crystalline state and the completely disordered isotropic liquid. The combination of long range order as in crystals and mobility as in liquids gives rise to materials with anisotropic physical properties such as birefringence, viscosity and other properties not associated with either crystals or liquids. The molecules in the liquid crystal state have long-range orientational order and partial positional order. Thus, they have some properties of liquids and have anisotropic properties of crystals like birefringence as mentioned earlier.   The discovery of the liquid crystalline state has been attributed to Reinitzer [1].   One of the fundamental requirements for a substance to exhibit a mesophase is geometrical or shape anisotropy of the constituent molecules. Thermotropic liquid crystals are obtained by the action of heat and these may be further classified into three broad types and they are,

(i)   Calamitic liquid crystals: which are formed by rod-like molecules

(ii)   Discotic liquid crystals: which are formed by disc-like molecules

(iii)   Banana liquid crystals: which are formed by banana-shaped or bent-core (BC) molecules.

The bent-core compounds are composed of a rigid central unit and two semi-rigid rods with chains at the end. The symmetry of liquid crystalline phases shown by these compounds is sometimes broken as a result of simultaneous director tilt and polar order perpendicular to the long molecular axis. Hence these liquid crystalline phases exhibit chiral phases. A schematic representation of side view, front view and back view of such a bent-shaped molecule is shown in figure **1.1.** Because of the intrinsic shape of the molecule, the rotation of the molecule along its long axis is hindered.

The first bent-core liquid crystalline materials were synthesized by Vorlander *et al.* [2] in 1932. However, the mesophases were not characterized. Bent-shaped compounds can be synthesized by introducing suitable groups in the *meta* or *ortho* positions of a central phenyl ring. For example, three bent-shaped compounds derived from catechol, resorcinol and isophthalic acid whose structures (**1.a**, **1.b**, and **1.c** respectively) are given below can be considered as bent-

core compounds. The credit for the synthesis of the first compound with a non-linear molecular shape and exhibiting mesomorphic properties has also been attributed to Vorlander and Apel. They had named these molecules as "Bad Rods".

side view   front view and back view
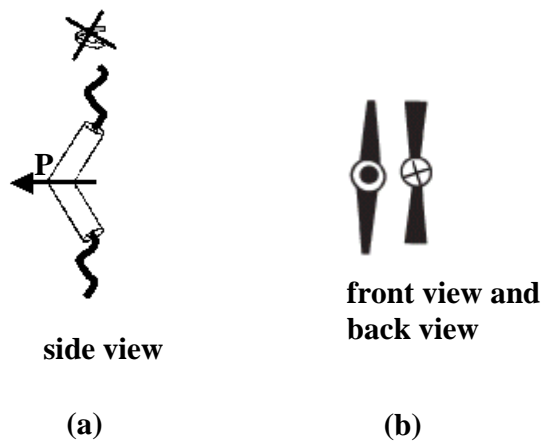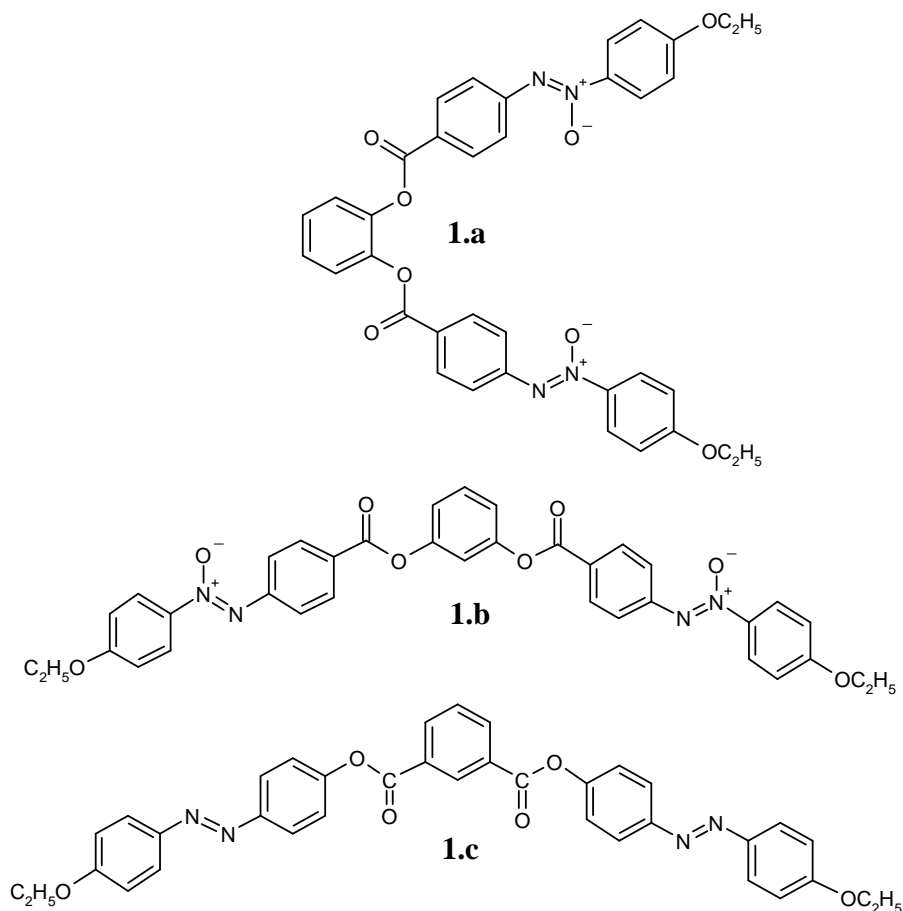
(a)   (b)

Figure 1.1: A schematic representation of a bent-shaped molecule (a) side view and (b) front view and back view of a bent-shaped molecule.


2

Later in 1991, Kuboshita *et al*. [3] 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. The mesophases exhibited by these compounds were characterized as nematic (N), smectic A (SmA) and smectic B (SmB) on the basis of microscopic observations, X-ray powder diffraction measurements and miscibility studies. In 1993, Matsuzaki and Matsunaga reported [4] the 2,3-naphthylene analogues and the mesophases were identified as nematic and SmA. All these compounds have an acute-angle configuration.
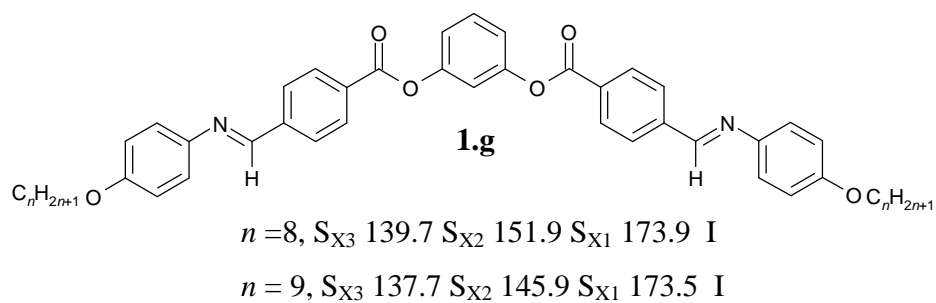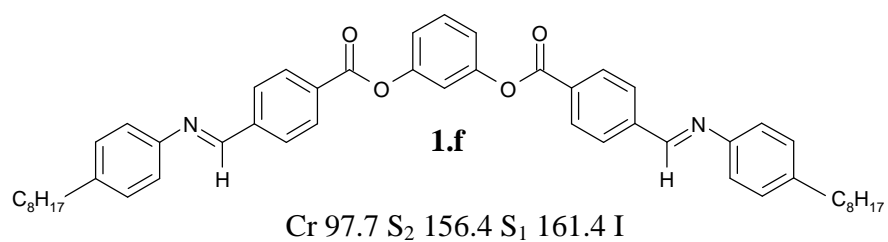
.

1.d   R=C$_n$H$_{2n+1}$
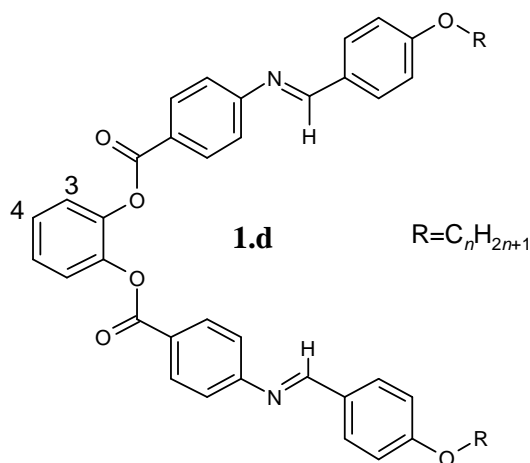
In 1994, Akutagawa *et al*. reported [5] the synthesis and mesomorphic properties of four homologous series of compounds derived from resorcinol (**1.e**). The mesophases shown by these compounds were identified as N and SmC. From XRD studies, they argued that the tails are nearly normal to the layers whereas the cores are tilted. No electro-optical switching measurements were carried out for these materials simply because the mesophases obtained were from compounds composed of achiral molecules.

However, a real breakthrough in bent-core liquid crystals came in 1996, when Niori *et al*. [6] reported ferroelectricity in a smectic phase formed by an achiral banana-shaped compound (**1.f**).

1.e

$R = C_nH_{2n+1}$
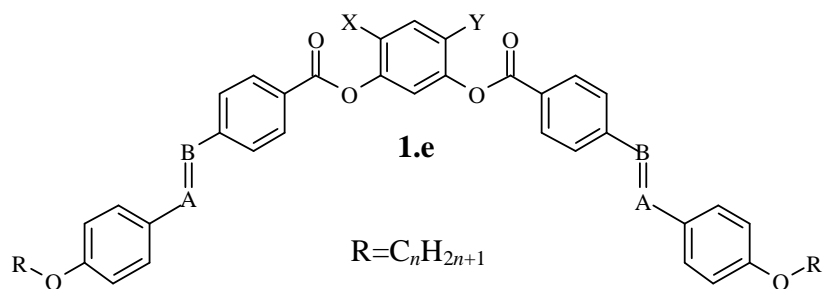
I   -A=B-   =   -N=CH-,   X= Y= H

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

1.f

Cr 97.7 S_2 156.4 S_1 161.4 I

1.g

n =8, S_{X3} 139.7 S_{X2} 151.9 S_{X1} 173.9 I

n = 9, S_{X3} 137.7 S_{X2} 145.9 S_{X1} 173.5 I

The ferroelectricity in the mesophase of these compounds was 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 viz. 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).
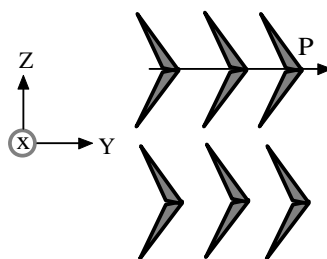

Figure 1.2: A possible smectic structure formed by the banana-shaped molecules (after
        Niori *et al*. [6]).

The layered structure of the higher temperature phase of compound **1.f** was confirmed by X-Ray diffraction studies. 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 [7] 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 1997 Link *et al.* [8] conducted several experiments using freely suspended films of compounds **1.f** and **1.g**. They proved that the molecules tilt about the layer normal and hence the earlier report of orthogonal molecular organization should be excluded. Careful observations using depolarized reflected light microscopy (DRLM) revealed that the mesophase of compound

1.f should have the antiferroelectric ground state due to the fact that only odd- or even-number layers respond to the applied electric field confirming the alternation of polarity in successive layers. They designated the mesophase as "SmCP$_A$", where "SmC" stands for tilted smectic, "P" represents polar and "A" stands for antiferroelectric.

This beautiful demonstration attracted several research groups around the world to investigate the mesophases exhibited by such compounds. Around the same time, Heppke *et al*. [9] and Weissflog *et al*. [10] also observed the two polarization current peaks for each half cycle in the electro-optical experiments for the mesophases of compounds **1.f** and **1.g,** which supported the existence of ground state antiferroelectricity.

In the meantime a large number of bent-core compounds were synthesized and their mesomorphic properties investigated. Interestingly, an International Workshop on "Banana-Shaped Liquid Crystals: Chirality by Achiral Molecules" was held in Berlin, in December 1996, and 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 B$_1$, B$_2$......B$_7$. Another phase was discovered later which was designated as B$_8$ [11]. 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*. [12] predicted four classes of fluid biaxial phases.

A transversely polarized non-tilted structure with C$_{2v}$ symmetry (proposed by Niori *et al*. [6])

1. A tilted phase with a monoclinic chiral symmetry C$_2$ (B$_2$ phase proposed by Link *et al*. [8])
2. An achiral layer structure with a monoclinic symmetry C$_S$
3. A triclinic configuration with chiral C$_1$ symmetry (SmC$_G$, where G stands for generalized proposed by de Gennes [13])

A schematic representation of these possibilities is shown in figures **1.3.a, 1.3.b, 1.3.c** and **1.3.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 [14, 15] 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
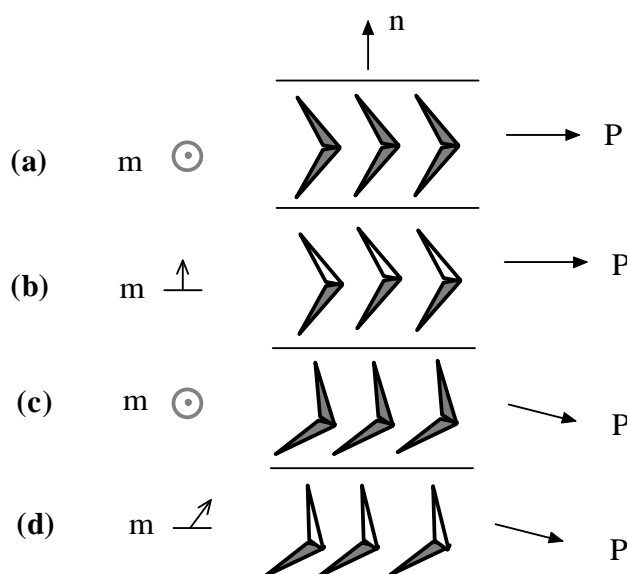

Figure 1.3: Different possibilities of packing of bent-core molecules within the layers.
    n:Smectic layer normal, m: molecular plane normal, P: layer polarization; (a) n
    is normal to both m and P; (b) n is normal to P, but not to m; (c) n is
    perpendicular to m, but not to P; (d) n is neither perpendicular to P nor to m
    (after Jakli *et al.* [16]).

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 B_1 phase can be regarded as a rectangular columnar phase (Col_r). The first bent-core compound (**1.h**) exhibiting a B_1 phase was reported by Sekine *et al*.[17] who designated the mesophase as SmA_b' on the basis of XRD measurements made on the mesophase of this compound. Later, in 1998, Watanabe *et al*. [18] showed the existence of a two-dimensional (2D) rectangular lattice structure in the B_1 phase, using microbeam X-ray diffraction of a monodomain sample.

1.h

B_4 143.6 B_3 159.1 B_1 173.4 I [19]
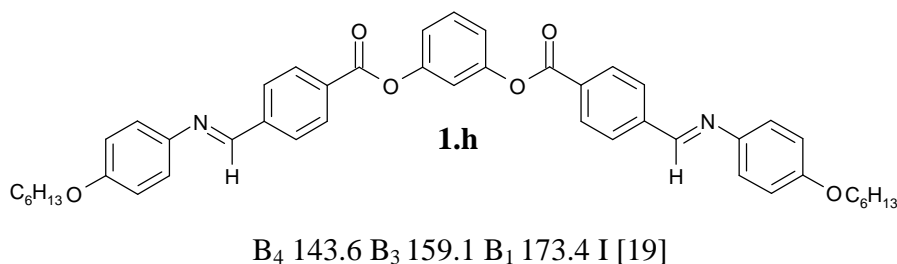
B_1 mesophase is commonly observed in BC compounds with short terminal alkyl chains. In a homologous series, this phase occurs between the non-polar B_6 phase and the polar B_2 phase on ascending the series. The B_1 mesophase develops as dendritic pattern, which coalesce to a mosaic-like texture and sometimes the mesophase shows spherulitic pattern, when the isotropic liquid is cooled slowly. The B_6 to B_1 phase transition has been reported [19-25] in a few bent-core compounds. At this phase transition the textural changes are minimal. The B_1 to B_2 transition is rare and it has been observed only in very few systems [26-29].

In the X-ray diffraction pattern of a B_1 mesophase, two or more reflections are observed in the small angle region in addition to 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. On

the basis of this, Watanabe *et al.* [18] proposed a 2D modulated structure for the B_1 phase as shown in figure **1.4**. 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. 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. Generally in a homologous series, B_6, B_1 and B_2 phases appear in that sequence on increasing the chain length [20, 21, 23].
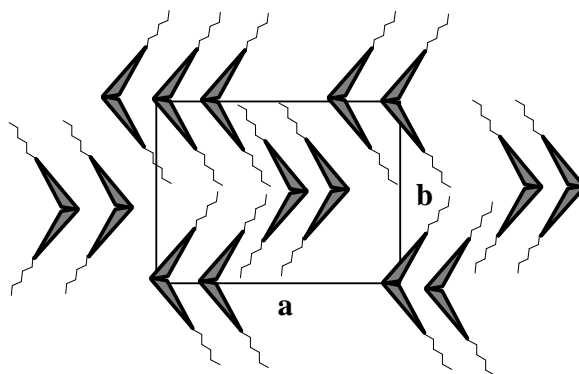
Figure 1.4: A schematic representation of the frustrated structure of B_1 mesophase. (after Watanabe *et al.* [18]).

Variants of B_1 mesophase

Bedel *et al.* reported [30, 31] 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.

Szydlowska *et al*. reported [32] 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 [33] such phases in two new compounds. Similar columnar phases were also reported by Reddy *et al*. [34].

Recently, Takanishi *et al*. [35] carried out microbeam X-ray 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 [18], but the same as B_{1rev} phase.
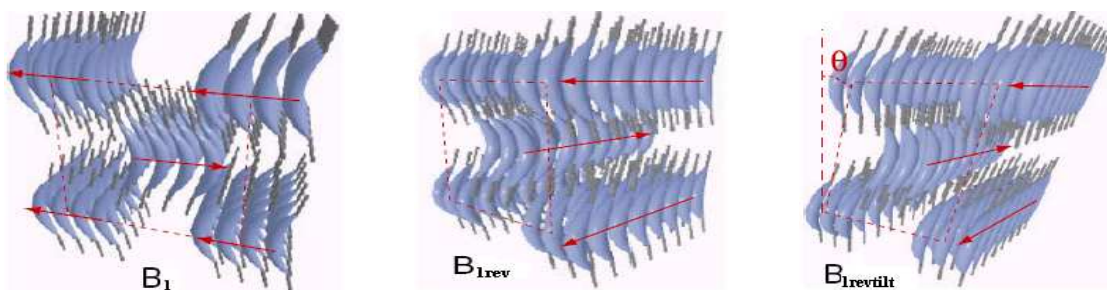

Figure 1.5: Proposed structures of B_1, B_{1rev} and $B_{1revtilt}$ phases (after Takanishi *et al*. [35]).

B$_2$ mesophase

Among all the banana mesophases the B$_2$ mesophase is the most commonly observed and most extensively studied. This mesophase was first observed in compound **1.f** by Niori *et al.* [6]. 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 B$_2$ to isotropic phase transition enthalpy value is in the range of 20-25 kJ mol^{-1}. This is a less viscous and electro-optically switchable mesophase and hence more attention has been paid to understand the basic structure of this mesophase.

In this regard, Link *et al.* [7] conducted several experiments such as 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 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.

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 [37] is shown in figure **1.7**.

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$_s$P$_A$ (synclinic antiferroelectric) and SmC$_a$P$_A$ (anticlinic antiferroelectric). The chirality of the layers is the same in SmC$_a$P$_A$ and hence it represents a homochiral structure whereas chirality alternates from layer to layer in SmC$_s$P$_A$ resulting in a racemic structure. On application of an electric field, a
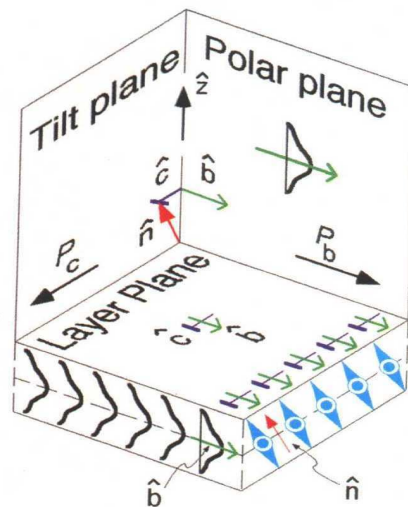
Figure 1.6: A pictorial representation of the geometry of a smectic layer in the B_2 (SmCP$_A$) phase; z: layer normal, n: director of the bent-core molecules, b: polar direction, c: tilt direction of the molecules (after Link *et al*. [11]).
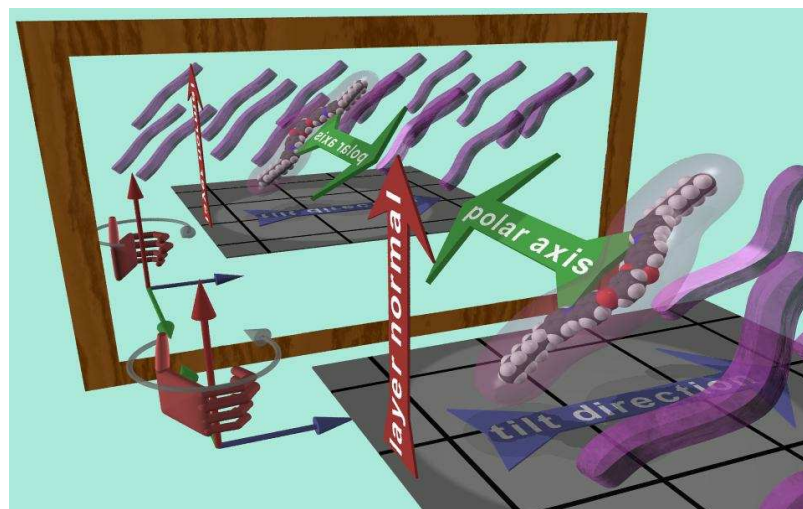

Figure 1.7: A pictorial representation of origin of layer chirality from achiral molecules; the layer normal, tilt direction and the polar axis define a coordinate system, which forms non-superimposable mirror images (after Heppke and Moro [37]).

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.

Racemic   **Homogeneously Chiral**

$E=0$ $E < -E_{th}$ $E > E_{th}$ $E=0$ $E < -E_{th}$ $E > E_{th}$

$SmC_sP_A{}^{ra}$ $SmC_aP_F{}^{ra}$ SmC_aP_A SmC_sP_F

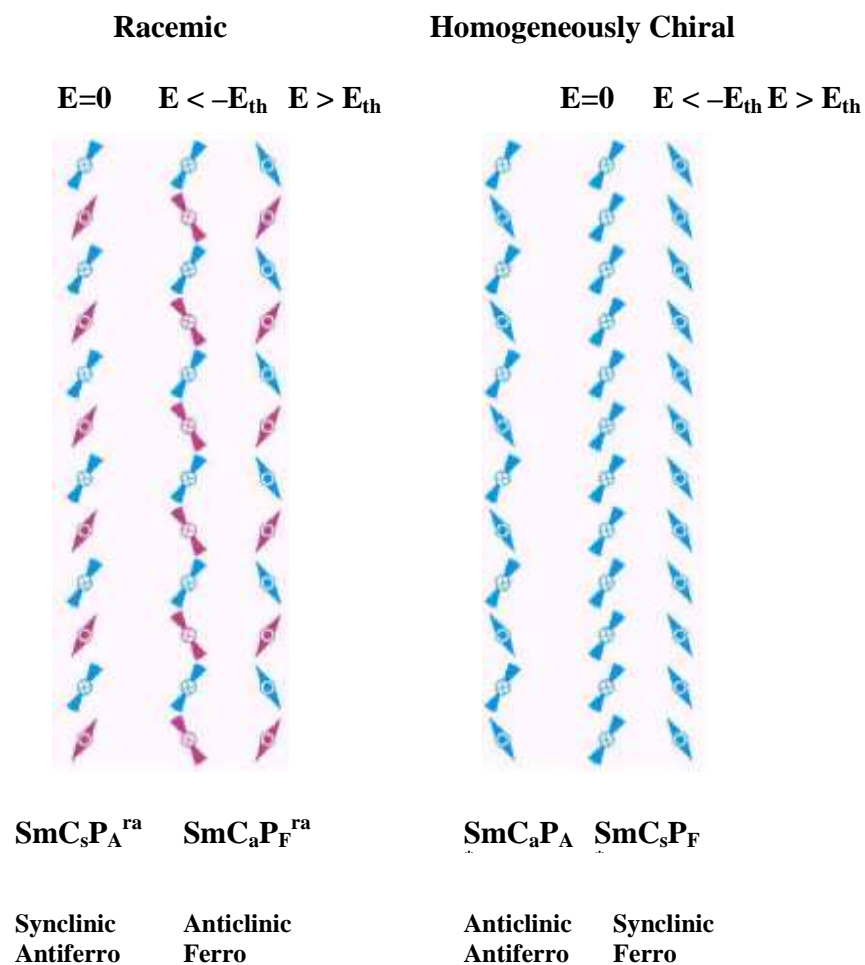| **Synclinic** | **Anticlinic** | | **Anticlinic** | **Synclinic** |
| **Antiferro** | **Ferro** | | **Antiferro** | **Ferro** |

Figure 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*. [7]) ; rac: racemic, * chiral.

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 [38-40] and in $SmCP_A$ phases with a small tilt ($< 20°$) of the molecules and a large bend angle [39, 41].

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 [42] 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 [43] 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 structure of these mesophases are not yet established.

B_3 mesophase

The B_3 phase always appears below B_2 phase and above a B_4 phase [19]. On rapid cooling from the B_2 phase, no textural change could be observed in the B_3 phase. However, on slow cooling, a slight change in the form of breaking of domain is observed. The XRD pattern of a powder sample shows a number of reflections in the small angle as well as wide-angle regions, which indicate a crystalline structure. On the basis of the dielectric [44] and terahertz spectroscopic results [45], B_3 phase is characterized as a higher-order smectic phase.
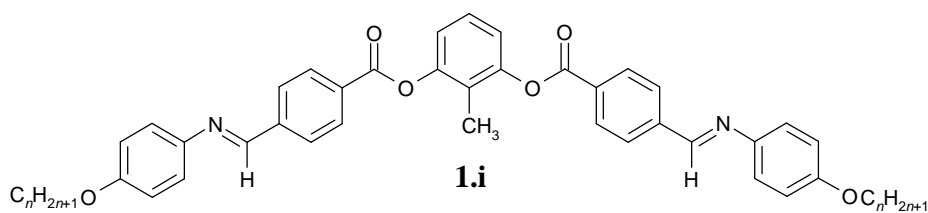
B_4 mesophase

The B_4 phase is a crystalline phase and always appears below a B_2 phase or a B_3 phase. The mesophase exhibits dark blue coloured domains under crossed polarizers. Hence, this mesophase is also named as smectic blue phase [17, 48]. However, domains of opposite

brightness are observed on decrossing either polarizer or analyzer [46]. A circular dichroism (CD) spectrum clearly shows domains with opposite sense and this indicates that the domains are chiral [47].

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 B_4 phase is not crystalline [44, 49]. A more interesting feature of this phase is that it exhibits a second harmonic generation (SHG) without external fields indicating that the medium is spontaneously chiral. The atomic force microscope experiments show that the phase has a helical superstructure. Sekine *et al.* [17] have proposed a TGB-like structure for this phase. The X-ray microbeam experiments are consistent with the proposed TGB-like structure. Usually, the B_4 phase is formed as a low temperature phase in compounds exhibiting B_2 phase [49, 50] although B_4-B_7 transitions have also been observed [51].

B_5 mesophase

This mesophase was first observed in a derivative of 2-methylresorcinol **1.i** [27, 35]. Later this phase was observed in derivatives of 2-methyl- [42] and of 5-fluororesorcinol [52], which contain a fluoro substituent *ortho* to the terminal *n*-alkoxy chain on the both the arms (**1.j**).

$n = 8$ Cr 161 B_5 165 B_2 172 I
$n = 9$ Cr 157 B_5 163 B_2 168 I
$n = 10$ Cr 153 B_5 158 B_2 167 I

$n = 12$ Cr 112 B_{5F} 122.5 B_{5A} 128 B_2 157 I
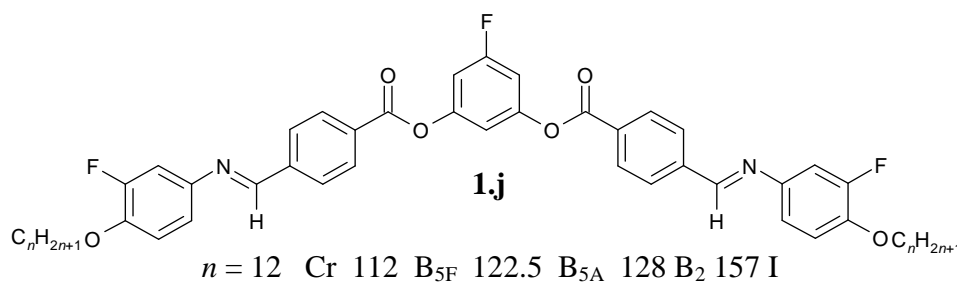
Always, this mesophase was observed below B_2 mesophase and has only a paramorphotic texture. The transition from B_2 to B_5 mesophase is first order. XRD studies on the mesophase show lamellar periodicity in the small angle region. However, in the wide-angle region some additional reflections were observed. From an oriented pattern, the reflections in the wide-angle region have been indexed to a rectangular lattice [52, 53] and in-plane molecular packing in the B_5 phase was proposed [19, 53], as shown in figure **1.9**. 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. B_5 phase also shows an antiferroelectric switching behaviour like B_2 phase. 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.
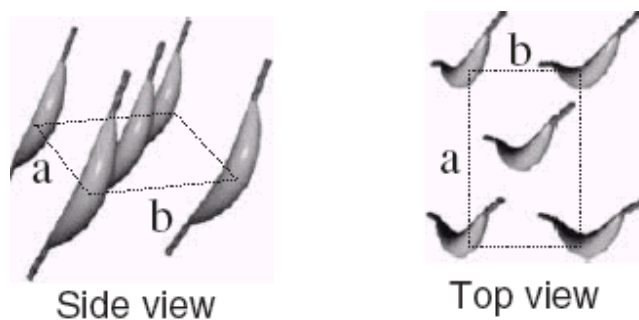

Side view   Top view

Figure 1.9: A pictorial representation of in-plane molecular packing in the B_5 phase. (after Pelzl *et al*. [19]).

Variants of B_5 mesophase

Nadasi *et al*. [52] 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*. [42] 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 [10] in compound **1.k**. This phase is generally exhibited by compounds with short terminal chains. On slow cooling of the isotropic liquid, this mesophase exhibits a fan-shaped texture similar to the one which is normally seen for a SmA phase. However, this phase cannot be aligned homeotropically. Hence the possibility of a simple SmA phase like structure can be excluded. On shearing the fan-shaped texture of a B_6 phase, sometimes a schlieren texture is obtained. A transition from B_6 to B_1 phase is observed [19-25] in some compounds.

1.k

Cr 134 B_1 142 B_6 148 I [10]
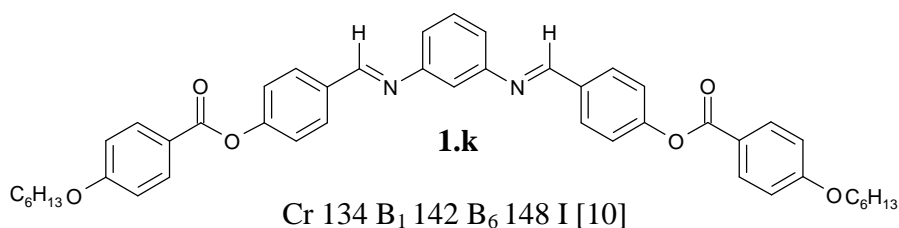
XRD pattern of a B_6 phase shows lamellar reflections in the small angle region along with a diffuse wide-angle reflection. The first order layer spacing in the small angle region is smaller than half the calculated molecular length. This indicates an intercalated structure. Hence, this mesophase has been designated as SmA_c, SmC_c or SmC_{int}. An oriented pattern of this mesophase indicates tilt of the molecules and the estimated tilt angle is about 20-30° [19]. Rouillon *et al.* [22] have carried out Monte-Carlo simulation studies on the B_6 mesophase and reported a 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. A schematic representation of the molecular arrangement in the B_6 phase is shown in figure **1.10.**
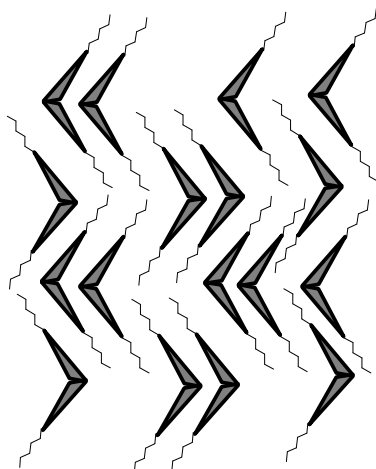
Figure 1.10: A schematic representation of the arrangement of BC molecules in the B$_6$ phase (after Pelzl *et al*. [19]).

B$_7$ mesophase

The B$_7$ phase was first observed [54] in a compound derived from 2-nitroresorcinol (**1.l**). 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-fluroresorcinol.

1.l

Cr 116 B$_7$ 177 I
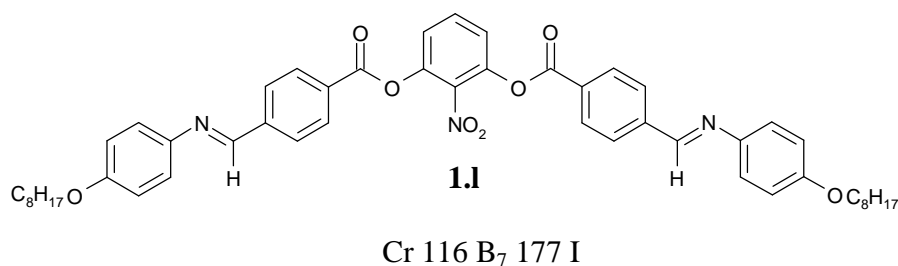
Among all the mesophases exhibited by BC compounds, the B$_7$ phase shows the most beautiful and fascinating textures such as the helical nuclei that appear on slow cooling the isotropic liquid, resembling that of telephone wires. Jakli *et al*. [61] showed that left and right-handed helices occur in 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 B_7 phase include lancet-like or thread-like germs, circular domains with equidistant concentric rings, 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 [15] 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. On the basis of these results they proposed a polarization modulated/undulated layer structure associated with splay defects for such a mesophase. The proposed model is shown in figure **1.11.**
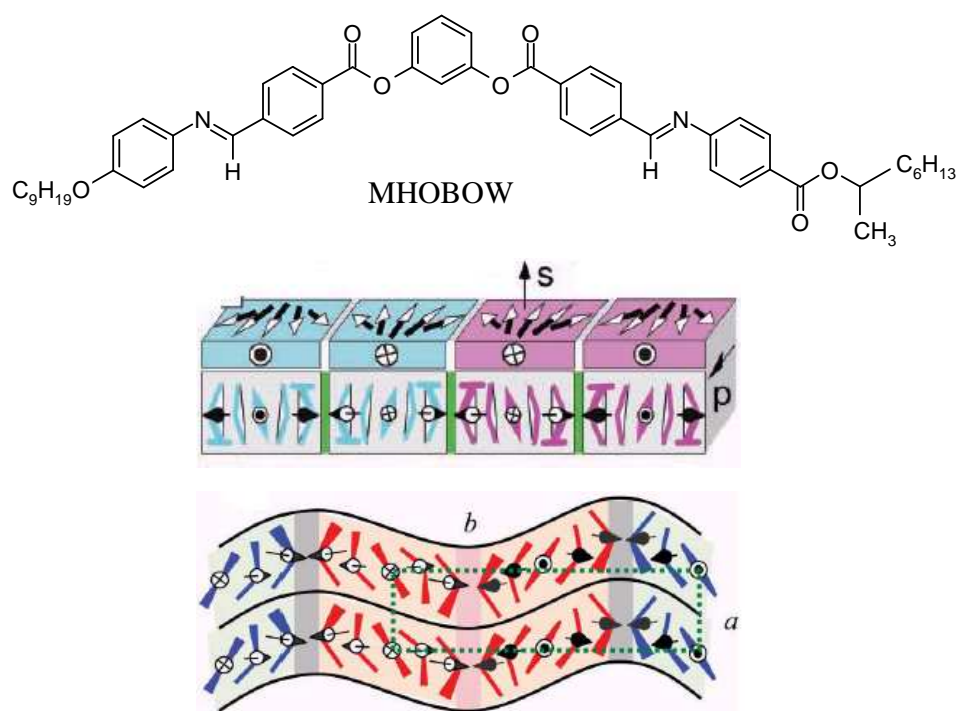

Figure 1.11: The proposed model of a polarization modulated/undulated layer stripe structure for the B_7 phase of compound MHOBOW [62].

Coleman *et al.* also carried out experiments on the mesophase exhibited by compound **1.l,** in which the B_7 phase was first observed. XRD studies indicate an oblique 2D reciprocal lattice for this mesophase. They propose a polarization modulated and an interdigitated 2D lattice structure for this mesophase, which is the lattice structure of the B_1 phase. The authors suggest that in such a structure, the orientation frustration at the splay defect planes might be relieved by interdigitation of the layers, which accommodates the opposite orientation of the bent-core molecules on opposite sides of the defect lines. A schematic representation of the model proposed for compound **1.l** [62] is shown in figure **1.12.**
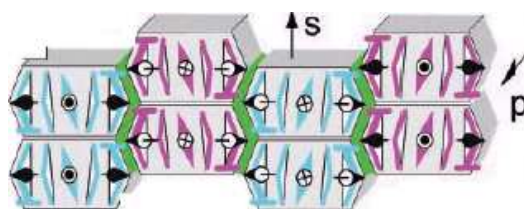

Figure 5.2: The proposed model for the B_7 mesophase of compound 1.1 [62].

XRD pattern of B_7 mesophase shows several reflections in the small angle region besides a wide-angle diffuse reflection. One characteristic feature of all the XRD patterns of B_7 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.l**. On the basis of experimental results they proposed an interdigitated 2D lattice for the mesophase. It has been pointed out [15] 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 B_7 phase, then the medium angle reflection might correspond to some order between these dimers.

Earlier reports [54] indicate that, no electro-optical switching could be observed in a B_7 phase at least upto 40 V μm^{-1}. However, in 2003 a transition from a non-switchable B_7 phase to

two antiferroelectric sub-phases (B_{7AF1} and B_{7AF2}) in higher homologues of nitro-substituted compounds has been reported [60]. Also, in compounds derived from 5-fluororesorcinol, a transition from an antiferroelectric $SmCP_A$ phase to a ferroelectrically switchable B_7 phase has been observed [61]. So far, these two represent examples of a switchable B_7 phase obtained from compounds with a substituted central phenyl unit.

Variants of B_7 phase

There are a number of compounds the mesophases of which exhibit spiral filaments and other textural variants, on slow cooling of the isotropic liquid. These mesophases have also been designated as B_7 [31, 64-68] despite the fact that their XRD patterns are different from that of the original B_7 phase [54]. 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 B_7. Recently, it has been suggested [15] to use the symbol B_7' for these mesophases, which exhibit the textural variants of B_7 phase and their XRD patterns are different from classical B_7 phase [54].

B_8 mesophase

Bedel *et al*. reported [11] a few BC compounds derived from isophthalic acid and containing terminal *n*-alkanoate groups. In a homologue with $n = 10$ (**1.m**), for the higher temperature phase (Sm_1), 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 B_8. Later [38], the phases Sm_0 and Sm_1 were characterized as SmC_sP_A (polar SmC phase, subscripts s and A refer to synclinic and antiferroelectric) and $SmC_sG_2P_A$ (subscript 2 refers to bilayer structure made of SmC_G layers, G stands for general). Perhaps this is the first and only report on the B_8 phase thus far.

1.m

Cr 173.5 Sm$_0$ 180 Sm$_1$ 183.5 I
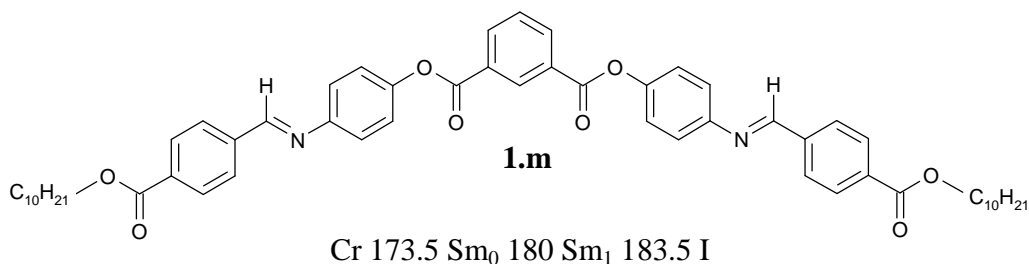
Ferroelectric mesophases in bent-core compounds

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 **1.13.a**) [52]. The penetration of the layers is favourable in an AF arrangement of the molecules (figure **1.13.b**) 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.

(a)   **(b)**
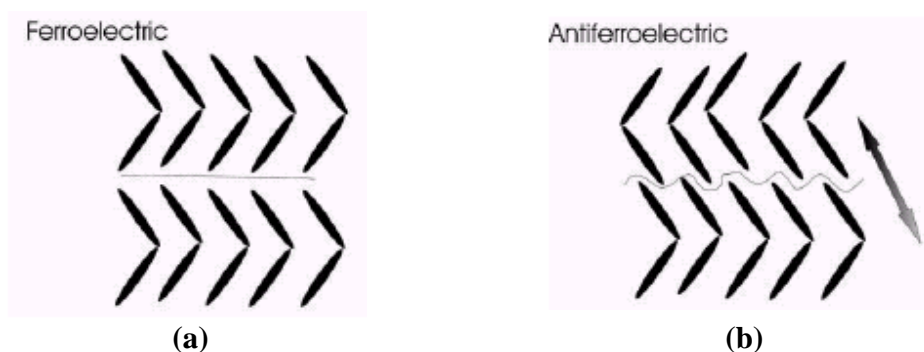
Figure 1.13: The molecular organization in FE and AF phases in bent-core molecules
(after Nadasi *et al*. [52])

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
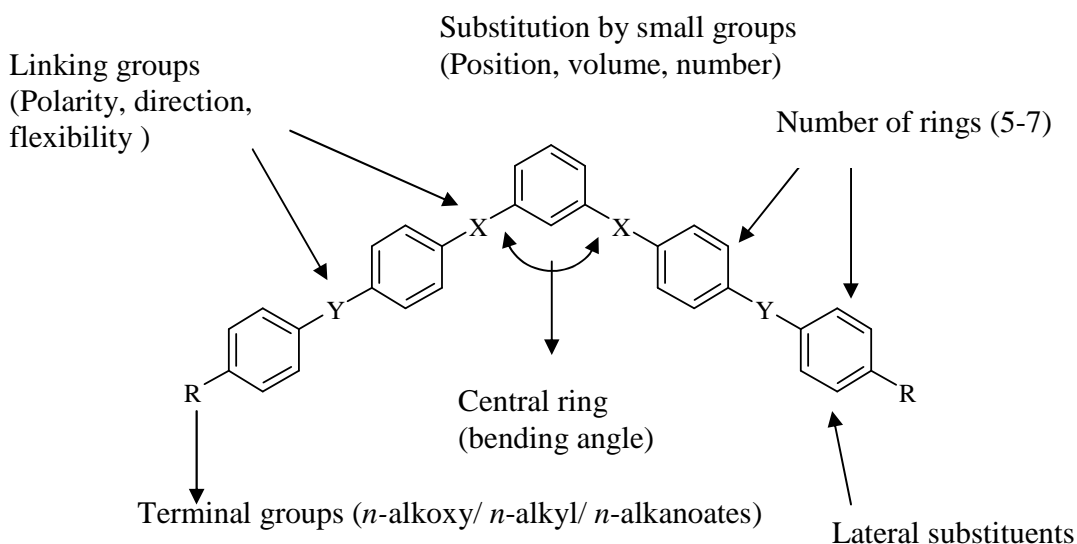
chiral rod-like materials showing SmC_a^* phase (chiral anticlinic SmC) at one end. The mesophase exhibited by this compound is characterized to have a polarization modulation, which leads to undulated layer structure [62]. However, under a high electric field, the polarization modulation defects get eliminated which in turn removes the undulation resulting in a ferroelectric switching (SmC_sP_F) structure.

Bedel *et al*. reported [30] 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 [31, 34, 52, 69, 70], 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 [71, 72], achiral oligosiloxane [73], oligocarbosilane terminal chains [74] or terminal *n*-alkyl carboxylate groups [11, 38].

Structure property relationships in bent-core mesogens

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

Linking groups
(Polarity, direction,
flexibility)

Substitution by small groups
(Position, volume, number)

Number of rings (5-7)

Central ring
(bending angle)

Terminal groups (*n*-alkoxy/ *n*-alkyl/ *n*-alkanoates)

Lateral substituents

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 BC compounds reported up to now contain five phenyl rings [15, 19, 75]. However, bent-core compounds containing three [76, 77], four [78], six [31] and seven [15, 31, 75] 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 resorcinol, derivatives of resorcinol, isophthalic acid, 5-methoxyisophthalic acid, 2,7-dihydroxynaphthalene and 3,4′-disubstituted biphenyl moiety. Generally, banana phases are obtained only when the bend angle is between 110º and 140º. This can be greatly influenced by nature of the chemical structure of the central unit and lateral substituents on the central unit.

Generally, Schiff's base (azomethine, -CH=N-/ -N=CH-) and ester (-OCO-/-COO-) units are used as linking groups. In addition, azo (N=N), ethylene (-C=C-), acetylene (-C≡C-) have also been used. Often, compounds containing Schiff's base linkage group show rich polymorphism when compared with 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 [64], carbonyl or carboxylic groups [11, 38]. Perfluoroalkyl fragments are used as terminal chains in some cases [26, 76], in which a strong increase in the transition temperature is observed.

**Influence of lateral substituents**

The influence of lateral substituents on the mesophases of bent-core compounds were studied extensively. Generally, fluoro, chloro, ethyl, methyl, cyano, nitro and trifluoro lateral substituents [15, 19, 23, 79-81] have been used. 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. Generally lateral substituents reduce the melting as well as clearing temperatures. 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 the mesomorphic behaviour. A detailed account of the effect of different lateral substituents in the middle and terminal ring on the mesomorphic properties are described in Chapters **6** and **7** of this thesis.

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 dimethysiloxane unit (**1.n**) were reported by Dantlgraber *et al*. [86]. In these dimers, either FE or AF switchable polar smectic C phases were observed depending on the number of flexible dimethylsiloxane units.
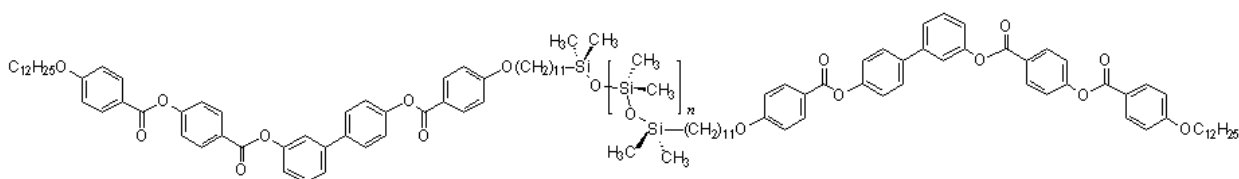
1.n

$n = 1$: Cr 64 SmCP$_F^*$ 132 I

$n = 2$: Cr 92 SmCP$_A$ 132 I

Later, 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. Simultaneously, the first polar symmetric mesogenic dimers composed of bent-core molecules and linked by an alkylene spacer were reported by Umadevi *et al.* [88] by reversing the ester linking groups between the "inner" rings. The mesophase of these dimers has been designated as a $Col_{ob}P_F$ phase.

The design and synthesis of new type of dimers in which the individual monomers are connected at the apex positions via flexible alkylene spacers are described here in chapter **5.** These types of dimers are apolar as the polarity of the dipolar groups cancel with each other.

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