Chapter 1
General Introduction: Liquid Crystals
1.1 Introduction:
The foundation of liquid crystal science is traditionally set in the year 1888, an Austrian botanist Reinitzer observed a cloudy intermediate phase in the melt of cholesteryl benzoate [1], which is later known as a cholesteric liquid crystal. Since then, thousands of molecules that exhibit liquid crystal (LC) phases were synthesized. The discovery of spontaneous polarity [2], and chirality [3] in smectic liquid crystal phases exhibited by bent-shaped molecules has stimulated the liquid crystal community as well as condensed matter scientists [4-8], because of their distinct characteristics viz, spontaneous supramolecular chirality, ferro- and anti-ferroelectricity, electro-optic switching and exotic phases. The synthesis of bent-core molecules is reported for the first time in 1929-32 at Halle University [9, 10], and only recently they are confirmed to exhibit a banana phase, B6 or a nematic phase [11]. However, at that time LC phases exhibited by the bent-shaped molecules were not paid much attention due to lack of understanding of these phases. In literature, majority of the bent-core compounds reported till date contain five or more aromatic rings [4, 5]. Very few reports appeared on bent-core systems containing four aromatic rings exhibiting mesophases [12], while majority of them either exhibit calamitic type liquid crystalline phases or non-mesomorphic. So, it is a challenging task to design, synthesize and tune the four-ring bent-core or banana shaped molecules to obtain banana liquid crystalline phases. In this thesis a new class of achiral unsymmetrical four-ring bent-core mesogens possessing different linking moieties viz., azo-ester-imine, imine-ester-imine, and having different substituents at distinct positions of the central core of the molecule are designed, successfully synthesized and characterized. These compounds exhibit particularly nematic, smectic and polarization modulated layer undulated B7/B1_{RevTiled} phases and the results are discussed in the light of current literature reports.

1.2 Liquid crystal:
Three states of matter, namely solid, liquid and gas differ mainly by the type of positional and orientational order and different degree of order. As most substances are heated, they usually melt at a fixed temperature and transforms
into an isotropic liquid. However there are also some substances which have no direct transition between the solid and the isotropic liquid. Intermediate state between solid and liquid states can be found for these substances which are called mesophases. These mesophases can be plastic crystals or liquid crystalline phases [13]. In solid state, the molecules have a long range positional and orientational order whereas in liquid state the molecules have only a short range order and the individual molecules are mobile. In liquid crystalline phases, the molecules have lost some degree of order of the solid state, and have got some degree of mobility, so they have some characteristics of the solid state and of the liquid state (Figure 1.1), for example, anisotropic physical properties and mobility [14].

![Molecular arrangements in (a) crystals, (b) liquid crystals and (c) Isotropic liquid.](image)

**Figure 1.1:** Molecular arrangements in (a) crystals, (b) liquid crystals and (c) Isotropic liquid.

### 1.3 Classification of liquid crystals:

Liquid crystalline materials have developed to a large family and they have quite different structures, usually they are divided into two groups, thermotropic and lyotropic liquid crystals [15]. Materials which form liquid crystalline phase as pure materials in dependence on the temperature are thermotropic liquid crystals and the mesophases which are induced by solvent in a certain temperature interval are called lyotropic liquid crystals. Both thermotropic and lyotropic liquid crystals are broken into groups depending on their macroscopic structure. Usually, thermotropic liquid crystalline phases are formed by rod-like (calamitic) and disc-like (discotic) molecules. Both of them
can form nematic phase. In the nematic liquid crystal phases, nematic (N), chiral nematic (N* or Ch), and blue phases (BPs), molecules have long-range orientational order, but no positional order.

Lyotropic liquid crystals can be formed by amphiphilic molecules, in (mostly protic) solvent. Here we can distinguish lamellar, columnar and different cubic mesophases, nematic phases are quite rare in lyotropic systems (Figure 1.2).

![Diagram of liquid crystal phases](image)

**Figure 1.2:** Examples of liquid crystalline molecules and phases.

Calamitic molecules can exhibit additional smectic phase where molecules are ordered in layers. More than ten smectic liquid crystal phases have been known and were named using alphabets like ‘smectic-A’ (SmA) to Smectic Q. Examples of smectic liquid crystal phases are shown in Figure 1.3. Compounds of disc like molecules can exhibit columnar phase, in which
molecules are stacked one on top of another to build up columns. Bent-shaped mesogens also exhibit the nematic, smectic and columnar phases. Details about liquid crystal phases of bent-shaped mesogens are introduced and discussed in following section.

Figure 1.3: Examples of layer structure of smectic phases. (a) Sm-A, (b) Sm-C, (c) Sm-CA, (d) Sm-B, (e) Sm-I and (f) Sm-IA. In the phases, (a)-(c), molecules have no in-plane positional order in a smectic layer, while in the hexatic phases on (d)-(f) molecules have the short range positional order even in a plane of smectic layer.

1.4 Ferroelectricity and Antiferroelectricity in Liquid Crystals:

The concept of ferroelectricity first comes from solid state physics. It is found that some crystals have spontaneous polarization even without an external electric field. If the direction of this spontaneous polarization can be changed with a change of the direction of an external field, the material has ferroelectricity [16]. Mayer reported that introduction of chirality to the Sm-C phase lowers its symmetry from $C_{2h}$ to $C_2$ and allows spontaneous polarization
normal to the tilt plane. However, in bulk, the chirality of molecules forces the tilt direction rotating from layer to layer so that the molecules forms helical structures (Figure 1.4) and spontaneous polarization is usually cancelled out macroscopically. To observe the spontaneous polarization, the helix in the Sm-C* phase should be unwound. In bulk, the helix usually does not unwind (in some particular material the helix unwinds only at one temperature) and hence the bulk spontaneous polarization is not easy to be observed.

Figure 1.4: Helical super structure in the Sm-C* phase.

By surface alignment Clark and Lagerwall solved this problem [17]. In a thin cell in which smectic layers align perpendicular to the substrates i.e. smectic layer normal is parallel to the substrates, the helix in the Sm-C* phase is unwound when the cell thickness is smaller than the helical pitch. Domains in which spontaneous polarization is not cancelled out are observed in such cells and the polarization switches by application of an external electric field as shown in Figure 1.5.
Figure 1.5: The helical structure and the surface stabilized state of ferroelectric Sm-C* phase. In a thick planar cell, molecules wind helix with its axis parallel to the surface. (a) top-view and (b) side view of the deformed-helical ferroelectric liquid crystal cell (DHFLC). However the cell thickness is thin around the helical pitch, the helix is unwound by surface interactions and molecules uniformly align as shown in (c) and (d) or (e) and (f); (c) and (e) are top view and (d) and (f) are side view of the surface stabilized ferroelectric liquid crystal cell (SSFLC).

In the antiferroelectric phases the polarization cancels out from layer to layer, whereas in ferrielectric phases the polarization in subsequent layers is only partially compensated. Antiferroelectric chiral smectic-CA phase i.e. Sm-CA* phase found by Chandani et al. [18, 19] and Galerne et al. [20], in which spontaneous polarization in two adjacent layers alters the direction without external fields and aligns uniformly as in the Sm-C* phase when a strong external electric field are applied [18, 19] (Figure 1.6). Because the field induced transition from Sm-CA* to Sm-C* state is usually first order and switching between two states occurs at a certain field strength (threshold field) and exhibits hysteresis, i.e. the threshold field is different whether the process is switching from Sm-CA* to Sm-C* or vice-versa. In these phases, the molecular tilt direction changes repeatedly in a short period around three to four layers [21-27]. In terms of molecular orientation in these phases two models had been proposed, Ising model and Clock model [24, 28-32]. The origin of these various Sm-C* sub-phases is still under discussion though the detailed molecular orientation in these sub-phases had been investigated by means of conoscopy, resonant x-ray scattering and optical polarized ellipsometry.
Figure 1.6: Molecular orientation in the antiferroelectric Sm-CA* phase. (a) top-view and (b) side view of the antiferroelectric Sm-CA* phase in a planar cell. Spontaneous polarization in each smectic layers is canceled out because of anticlinic orientation of molecules. However the spontaneous polarization re-orientates and uniformly aligns along an external electric field direction when the electric field is applied ((c) and (d) or (e) and (f)). These two states (d) and (f) are having the same molecular orientation which observed in the Sm-C* phase and only stable under application of an external field, so that these states are called as field-induced Sm-C* state.

1.5 Chirality in achiral banana shaped molecule:
In the tilted polar smectic phases (Sm-CP phases) of achiral bent-core molecules, two types of layers exist, and one of which is the mirror image of the other (Figure 1.7(a)). As in the case of the Sm-C* phase of rod-like molecules, the spontaneous polarization of each layers is uniquely defined. However, the situation is little complicated because molecules in each layer have a bent-direction $\mathbf{b}$, $\mathbf{P}$ and $\mathbf{b}$ are assumed to be parallel but their directions are not always the same. For this case, the layer chirality, instead of the sign of spontaneous polarization, is defined by Link et al. [3] using the molecular
direction \( \mathbf{n} \) making an angle \( \theta \) with the layer normal \( \mathbf{Z} \), molecular tilt direction along \( \mathbf{X} \) and polar direction \( \mathbf{b} \) along \( \mathbf{Y} \).

**Figure 1.7:** (a) Geometry for smectic layers and layer stacking in tilted smectic phase of bent-core molecules. (b) In one smectic layer with layer normal along the \( \mathbf{z} \)-axis composed of bent-core molecules with polar order along \( \mathbf{b} \) parallel to the \( \mathbf{y} \)-axis, two possible layer structures one of which is mirror image of the other, are defined by the director \( \mathbf{n} \) tilting by \( \theta \) either along the positive or negative to \( \mathbf{x} \)-axis.

Banana molecules represent the first achiral molecules forming super-structural chirality in the fluid liquid crystalline state [15]. It arises due to the tilted organisation of the molecules within the polar layers. In this configuration the layer normal, the tilt direction and the polar axis define a chiral system which is either right-handed or left-handed as shown in **Figure 1.7**. Changing either polarisation direction (indicated by crosses or dots in circles) or tilt direction changes the chirality sense of the layer (indicated by red (+) vs. blue (-) colour) [3]. There are four possible combinations of the layers. In SmC_AP_A and SmC_SPF structures, all the layers of a macroscopic domain have the same chirality sense. These phase structures are homogeneous chiral and occur in both enantiomeric forms (as conglomerates). In the SmC_SPF_A and SmC_APF structures there are equal numbers of layers with (+) and (-) chirality and hence these superstructures are racemic on a macroscopic scale [3]. During the switching process, rotation usually takes place on a cone, which changes tilt
direction and polar direction simultaneously and therefore chirality is maintained. This means that switching under electric fields occurs either between the two chiral states SmC\textsubscript{A}P\textsubscript{A} and SmC\textsubscript{3}P\textsubscript{F} or between the two racemic states SmC\textsubscript{3}P\textsubscript{A} and SmC\textsubscript{A}P\textsubscript{F}[33, 34] (Figure 1.8).

![Figure 1.8: Microphotographs in B2 phase of P-8-O-PIMB. A variety of colored domains are observed, which indicates that the homochiral, racemic, and partial mixing of homochiral and racemic domains coexist.](image)

This type of chirality is observable during the switching process. Further the intrinsic super-structural chirality of these polar smectic and modulated smectic phases due to the combination of tilt and polar order, which is manifested in the switching process (rotation of extinction crosses) there is also a spontaneous desymmetrisation [35], observed as chiro-optical effect in some of these mesophases. These mesophases exhibit chirality characterised by the spontaneous formation of a conglomerate composed of macroscopic domains of opposite chirality. Between crossed polarisers the textures appear as nearly uniformly blue or dark areas. By slight decrossing of the polarisers, domains become visible and the brightness of the domains is exchanged by decrossing the polarisers i.e. rotation of polarizer either in clockwise or anticlockwise direction, indicating the optical activity (rotation of polarised light) of these domains. Different domains have opposite sense of chirality.

Beside the intrinsic superstructural chirality of these polar smectic and modulated smectic phases due to the combination of tilt and polar order, which is manifested in the switching process (rotation of extinction crosses) there is also a spontaneous desymmetrisation [36, 37] (deracemisation), observed as
chirooptical effect in some of these mesophases. These mesophases show a chirality characterised by the spontaneous formation of a conglomerate composed of macroscopic domains of opposite chirality. The typical appearance of these mesophases is shown in Figure 1.9. From the crossed polarisers the textures appear as nearly uniformly blue or dark areas. By slight decrossing of the polarisers, domains become visible and the brightness of the domains is exchanged by decrossing the polarisers either in one or the other direction, indicating the optical activity (rotation of polarised light) of these domains. Different domains have opposite sense of chirality. Such mesophases, formed by achiral molecules (or racemic mixtures), i.e., where the optical activity is not derived from a robust molecular (usually configurational) chirality, are indicated herein by the superscript \(^{(*)}\). In contrast, the superscript \(^{(*)}\) without brackets is used for LC phases derived from chiral molecules in their nonracemic form. This phenomenon is found for the B4\(^{(*)}\) phases, which are higher ordered mesophases and for some polar smectic phases (‘dark conglomerate phases’, SmCPA/FE \(^{(*)}\)), but also in some nematic phases assigned as N\(^{(*)}\).

**Figure 1.9:** Features of supramolecular chirality in LC phases of bent-core molecules: (a,b) Optical photomicrographs of chiral domains of opposite handedness as seen under a polarising microscope upon slightly decrossing (5–10\(^{\circ}\)) polariser and analyser either in one or the other direction (SmC\(_a\)P\(_A\) \(^{(*)}\) phase [38]).

Sometimes, on slow cooling from the isotropic liquid state the growth of LC phases i.e. helical filaments and single or double-winded patterns are observed in achiral bent-core molecules (Figure 1.10). These helical superstructures can in exceptional cases also be formed at the transition from the isotropic liquid state to smectic and columnar phases, but most importantly they represent the characteristic feature of the B7-type mesophases. These helical filaments are
formed with both handedness in a ratio 1:1 and represent an expression of macroscopic chirality. This chirality does not necessarily depend on the superstructural or any supramolecular chirality of banana mesophases.

**Figure 1.10:** (a) helical filaments formed at the transition from the isotropic phase to the B7 phase of the compound (b) [39].

### 1.6 Liquid Crystal Phases and their Structures of Bent-core Molecules:

Bent-core or banana-shaped liquid crystals refer to the liquid crystals whose molecular shape resemble the bananas or a bow with a bend at the centre of the molecules and exhibiting the optical textures similar to banana leaf like. Majority of the bent-core molecules link through an aromatic 1,3-disubstituted phenyl ring (**Figure 1.11**) or 2,7-disubstituted naphthalene moiety derivatives. The angle between two linking arms ranges from 100° to 140°. Because of the molecular shape with no Cₐ symmetry along the molecular axis, bent-core mesogens produce unique smectic phases that rod-like molecules never form.

1997 after the Berlin workshop [40], liquid crystal phases of bent-core molecules have been named as the ‘Bi’ (i is an integer number) phase in the chorological order of their discovery. After the B1-B7 phases were defined [8], however, people realized that there were several different structures or states in one phase and also the detailed structure of new phases was gradually investigated, people found that there were a lot of phases having very similar but slightly different structure. The nomenclature of these liquid crystal phases were discussed in the Boulder workshop on 2002 and people were agreed to make another rule of naming the phases of the bent-core mesogens using the same name used for the rod-like mesogens, for example Sm-A or Sm-C and additional characters and suffixes. Also the space group of the phase will be added for a detailed definition. Structures and properties of smectic phases of the bent-core molecules are summarized on **Table 1.1**.
Figure 1.1: General structure of bent core molecule.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Structure</th>
<th>Polar</th>
<th>Tilting in a layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>Frustation (columnar)</td>
<td>Usually not</td>
<td>Tilted, non-tilted</td>
</tr>
<tr>
<td>B2</td>
<td>SmCP</td>
<td>Polar</td>
<td>Tilted</td>
</tr>
<tr>
<td>B3</td>
<td>Sm (crystal-like)</td>
<td>Non-polar</td>
<td>Non-tilted</td>
</tr>
<tr>
<td>B4</td>
<td>TGB (chiral domain)</td>
<td>Non-polar</td>
<td>Non-tilted</td>
</tr>
<tr>
<td>B5</td>
<td>SmCP (hexatic order)</td>
<td>Polar</td>
<td>Tilted</td>
</tr>
<tr>
<td>B6</td>
<td>Interdigitation</td>
<td>Non-polar</td>
<td>Tilted, non-tilted</td>
</tr>
<tr>
<td>B7</td>
<td>SmCP (modulation)</td>
<td>Polar</td>
<td>Tilted</td>
</tr>
<tr>
<td>B8</td>
<td>SmCP</td>
<td>Polar</td>
<td>Tilted</td>
</tr>
</tbody>
</table>

Table 1.1: Liquid crystal phases of bent-core molecules. “Polar” indicates that the phase shows responses to an applied electric field or not. “Tilting in a layer” indicates that the average molecular long axis in a smectic layer is tilted with respect to the smectic layer normal direction or not tilted.

1.6.1 B1 phase:

The B1 phase is categorized as a columnar (Col) phase because of the arrangement of molecules in a columnar structure [41-45]. Typical mosaic textures are observed from the crossed polarizers position which are similar to those observed in a columnar phase exhibited by discotic liquid crystals. Dendritic like growth of domains in B1 was discussed [46] while the NMR measurements [47] revealed that orientational order parameter (0.84) and molecular bending angle (120°) are independent of temperature. The molecular
structures and observed textures exhibited by these compounds in the B1 phase are shown in **Figure 1.12.**

**Figure 1.12:** (a) & (b) Microphotograph of characteristic texture of B1 phase (c) Several compounds exhibiting B1 phase.

From X-ray diffraction measurements, diffuse broad scattering peaks are observed at wide angles, indicates intralayer liquid like order. In contrast, several sharp peaks are observed at small angles \[48\]. Since the smallest- and next smallest- angle peaks have no relation to the first- and second-order diffractions corresponding to the smectic layer, a two-dimensional (2D) frustrated layer structure was also proposed to explain the results \[41-45\].

**Figure 1.13:** Proposed layer structures of (a) B1, (b) B1rev, and (c) B1revtilt. Red arrows indicate the polar direction

Different modulated phase structures are also reported which are different from conventional B1 phase \[41-45\]. In contrast, some of these modulated phases are switchable under the application of an electric field, exhibit irreversible
enhanced optical birefringence in fan-shaped textures which remains even when the field is turned off. This behaviour is same as that in the frustrated phase of the bent-shaped dimer [49]. This behaviour is the same as that in the frustrated phase of the bent-shaped dimer [27]. On the other hand, by the application of a significantly high field (>15 V/mm), a single switching current peak is observed at a frequency as low as 1 Hz. Considering this electrooptic switching behaviour and X-ray study, Szydlowska et al. [48] concluded that Bx forms the new modulated structure (B1_{rev}) shown in Figure 1.13(b) and that Bx₁ is the tilted version. Almost at same time, Pelz et al. also reported the same modulated structures as B1_{rev} and B1_{revtilt} in different compounds based on X-ray diffraction measurements [50]. The switching process in B1_{revtilt} is very complicated, depending on the field form, amplitude, and frequency [50] and also suggested the existence of a 3D modulated structure, although decisive evidence has not been obtained. Complete classification of the B1-related phases is a subject for future research.

### 1.6.2 B2 phase:

The B2 phase is the most extensively studied because of its polar switching properties despite the molecule is achiral. Niori et al. first observed the ferroelectric-like switching current due to spontaneous polarization and explained the polar order based on close packing of molecules in a smectic layer with a unique bending direction along a C_{2v} symmetry axis. The existence of a helical structure [51] is reported in the absence of a field because of the striped texture resembling the texture observed in chiral SmC* phase of rod-like molecules. However, antiferroelectric-like switching current [52] and molecular tilting with respect to the layer normal by electro-optic investigations on freely suspended films and sandwich cells, proposing different model structure [3]. In the B2 phase, a molecular long axis n tilts by θ from the smectic layer normal z, as shown in Figure 1.14. Because of the existence of a third axis, i.e., bent direction b, each layer, where the bent-core molecules are closely packed with uniform bent and tilt senses and possesses chirality.
a) Definition of chirality in tilted smectic phase of bent-core molecules. b) Four possible polar structures in B2 phase. The combination of the interlayer polar and clinicity correlations specifies the layer chirality as homo-chiral or racemic. Blue and red coloured molecules specify (+) and (-) layer chiralities, respectively. According to the interlayer correlations of polarization, which is assumed to be parallel to \( \mathbf{b} \), and tilt direction, four states as shown in Figure 1.14 are possible: SmC\(_{S,A}P_{F,A}\) [35]. In this nomenclature, subscripts \( S \) and \( A \) abbreviates for synclinic and anticlinic arrangement of molecules in adjacent layers, and subscripts \( F \) and \( A \) abbreviates ferroelectric and anti-ferroelectric nature of the adjacent layers. The layer chirality alters from layer to layer in SmC\(_{S}P_{A}\) and SmC\(_{A}P_{F}\), and hence is racemic. In contrast, the layer is homo-chiral in SmC\(_{A}P_{A}\) and SmC\(_{S}P_{F}\). One important difference from the polar order in SmC\(^*\) and SmC\(^*_A\) phases is that the tilt and polarization senses are not correlated. Therefore, a racemic layer is possible, and there exist two homo-chiral domains of equal probability. In P-8-OPIMB, SmC\(_{A}P_{A}\) and SmC\(_{S}P_{A}\) were first discovered. Although ferroelectric SmC\(_{S}P_{F}\) structures were first observed in the B7 phase [35], later SmC\(_{S}P_{F}\) [53] and SmC\(_{A}P_{F}\) [54, 55] in B2 phase were confirmed one after another. Moreover, field-induced polarization reversal with the unchanged long molecular axis was observed in some distinct samples and conditions. In this switching, chirality switching is also associated with the polarization reversal. In powder X-ray diffraction measurements, the SmA or
SmC like diffraction patterns, i.e., small-angle sharp layer reflections and wide-angle broad diffuse scattering were observed. Using oriented samples, wide-angle diffuse scattering peaks appear out of the direction normal to layer reflections and the deviation angle is between 35° and 40° [51,56], which is same as the apparent molecular tilt angle determined optically. Although X-ray resonant scattering measurements were performed in the B2 phase in order to clarify the molecular tilting direction, a quantitative analysis is yet to be reported [57]. Local layer structures in circular domains were investigated using an X-ray micro-beam [58] and several types of layer structures such as mono-tilted and chevron depending on the layer chirality and the position of the domains were observed without a field. The layer structure change from cylindrical to onion-like was confirmed by high-field application and termination. Recently different B2-like phases which are not identical with earlier B2 phase were also reported [59-65] with typical characteristics; B7-like textures such as spiral [59-61, 63] and chiral separated microscopic domains [58, 61, 62] in the virgin state (Figure 1.15), and a simple lamellar X-ray pattern, different from that of the modulated structures [59-63]. This phase seems to form a homo-chiral SmC_{AP}A or SmC_{SP}F structure.

Figure 1.15: (Color online) Microphotographs of (a) spiral texture [66] and (b) and (c) chiral separated domains in B2-like phase, which can be recognized as bright and dark domains from the decrossing polarizers.

Compound with a CH_{3} substituent in the central core and fluorine moieties in the terminal chains, four mesophases similar to B2 are observed by DSC [62]. Among them, three mesophases in a higher temperature region are identified as B2 phases, although the polar structures have not yet been clarified. The mesomorphic classifications of these compounds will be a subject of future research.
1.6.3 B3 phase:
The structure and properties of B3 phase, which frequently appears between B2 and B4 phase. Paramorphotic texture of B2 phase appeared in B3 phase by rapid cooling as shown in Figure 1.16, but the domains are broken on slow cooling when the same is observed. Although a ferroelectric-like switching current indicating large spontaneous polarization up to 150 nC/cm² was reported, no electro-optic response was reported [51]. The SHG (second-harmonic generation) activity initially reported [67] was not confirmed [68] and the dielectric constant was low.
The 2D X-ray diffraction pattern shows the layer spacing in B3 is the same as that in the crystal, longer than that in B2 [42, 44, 45] and shorter than that in B4 [3]. Since the layer spacing in B3 is shorter than the molecular length of all trans-conformation and a texture with high optical birefringence was observed in the homeotropic alignment, molecules are expected to be tilted away from the layer normal. The B3 phase might be a crystalline phase since several sharp diffraction peaks are observed in wide angle x-ray scattering.

![Figure 1.16: a) Microphotograph of B3 phase of P-8-OPIMB. b) X-ray intensity profiles in B2, B3, and B4 of P-8-OPIMB.](image)

1.6.4 B4 phase:
The lowest temperature banana phase, B4, has been extensively studied because of its chiral characteristics. Textures in the B4 phase under a polarizing microscope appear as transparent dark-blue coloured domains, as shown in Figure 1.17. This blue colour was first considered to be caused by selective reflection due to the helical structure [69, 70] like a twist-grain-boundary (TGB) phase [71]. The absorption of molecules in the near-UV
region had been assumed that the origin of the bluish colour is not simple. When crossed polarizers are decrossed, two adjacent domains with different brightness are observed, and the brightness of each domain is interchanged by the rotation of the polarizers either clockwise or counterclockwise [Figure 1.17 (a) and (c)] [72]. The CD spectrum reflected each domain with an opposite sense [73]. Hence, this change in brightness in adjacent regions is attributed to the optical rotation, suggesting that the B4 phase has a chiral structure. From X-ray experiments, there is the smectic layer ordering and molecules are thought to be not tilted from the layer normal because the layer spacing is comparable to the molecular length. Molecules in the B4 phase are not switchable and the dielectric constant is low, SHG was observed even without the electric field. This indicates the existence of a spontaneous non-centrosymmetric order. The effective nonlinear optical coefficient is large [66, 67, 74] are characteristic chiral nonlinear optic effects such as SHG, CD and electrogyration are observed.

Figure 1.17: Microphotographs of B4 phase of P-8-OPIMB [75] (b) obtained under crossed polarizers, by rotating one of polarizers (a) clockwise and (c) counterclockwise.

1.6.5 B5 phase:
The B5 phase was first observed in 1998, only a few reports have appeared [61, 76, 77]. The compounds exhibiting B5 phases are shown in Figure 1.18. The B5 phase is the Sm-CP phase with the in-plane positional ordering. Electro-optic response in this phase is similar to that in the B2 phase [76, 78]. From x-ray scattering measurements, the phase is known to have a positional ordering in the smectic layer. Weissflog et al. reported three distinct B5 phases in which electro-optic response and x-ray scattering profile were the same but distinguishable only in DSC measurements [79].
1.6.6 B6 phase:

This phase was first reported in the compound as shown in Figure 1.19 [8]. Only a few compounds showing this B6 phase have been identified. Also, the B6 phase is similar to the B1 phase in terms of interdigitation of molecules each other for the half molecular length, but this phase does not exhibit 2D ordering which easily determined by x-ray scattering experiments. Also, the phase exhibits a reflection corresponding to the half molecular length (002) while the reflection corresponding to the molecular length (001) is cancelled out and not observed. The B6 phase is sometimes observed in an upper temperature range of the B1 phase [80]. Because dipole moments of molecules are cancelled out each other, no electro-optic response is observed except a dielectric response.

Figure 1.18: a) Optical texture of the B$_{5_A}$ phase b) Molecular structures exhibiting B5 phase

Figure 1.18: (a) Typical texture observed for B6 phase. (b) Chemical structure of compound in which B6 phase was first observed. (c) The model for B6 phase.
1.6.7 B7 phase:
The B7 phase has attracted considerable attention because of its beautiful and distinctive optical textures, the molecular tilt and polarization directions are the same from layer to layer. The B7 phase typically appears on cooling from the isotropic liquid, forming a variety of beautiful optical textures, including chessboard, banana-leaf, and ribbon-like patterns [39, 81-86] (Figure 1.20) X-ray scattering from the B7 phase shows multiple satellite peaks above the first order layer reflection peak, pointing to periodicity in two directions [87-89]. The B7 microstructure is revealed by freeze-fracture transmission electron microscopy (FFTEM) images, which confirm that the smectic layers have undulations [81, 90] (Figure 1.21(a)). The ground state of B7 phase is a stack of synclinic, ferroelectric layers that lower their free energy by adopting a configuration with periodically splayed polarization, [81, 91-94] shown in Figure 1.21(b). This splayed structure is the local preferred state by symmetry, and appears as macroscopic undulations if the energy of the required defect boundaries between modulation stripes is sufficiently low. Because of the larger layer fluctuations that occur near the stripe boundaries, the layers are thicker there [10]. Layer expansion near the stripe boundaries alone, however, would produce a frustrated state, with empty space between the smectic layers (Figure 1.21(c)). In order to fill space and maintain a uniform layer pitch along $\hat{z}$, the layers at the center of each stripe tilt. Depending on molecular tilt and polarization direction, the elemental polarization splay stripes are shown in [Figure 1.21(d)-(g)]. In an applied electric field of sufficient strength, the polarization-modulated state can be transformed into a state with uniform polarization and flat layers [81, 95].

Figure 1.20: Typical textures observed in B7 phase (a), (b) Chiral MHOBOW in a 8-micron thick cell. (c) In a 4-micron thick cell.
Topological defects of the B7 layer undulation are homochiral (either left-handed or right-handed) over macroscopic distances. The chirality of the layers couples with the layer undulations, causing them to form either clockwise or anticlockwise spiral patterns, an example of chirality transfer from the molecular to the mesoscopic scale.

**Figure 1.21:** The B7 bent-core liquid crystal phase. (a) FFTEM image of the compound (i) quenched at $T = 112^\circ$C and then fractured in the bulk, showing smectic layer edges and B7 layer undulations. (b–g) Model of layer modulations driven by polarization splay: (b) the tendency for the polarization within the layers to be splayed can be accommodated globally by the formation of a periodic array of locally-splayed stripes. (c) Layer expansion at the stripe boundaries produces a frustrated state, which is relieved by layer undulations. The undulations allow the layer thickness at the center of each stripe to be smaller than at the boundaries, while the layer pitch is uniform along $\hat{z}$. Pairs of elemental polarization modulation stripes with alternating molecular tilt and polarization orientation are shown, the layers being right-handed in (d) and (e) (cyan, $2 \times \hat{z}$ parallel to $\hat{\rho}$) and left-handed in (f) and (g) (magenta, $2 \times \hat{z}$ antiparallel to $\hat{\rho}$). Tees indicate the ends of the rotated bent-core molecules closest to the reader. [39(b)]
References:


