Chapter I

General Introduction
1.1. Introduction:

The term Liquid Crystal (LC) itself suggests that it has the properties of both solid as well as liquid. Liquid crystals form a unique state of matter. Between the solid (crystalline) and liquid (isotropic) phases some compounds display a distinctly different intermediate state, also referred to as the *fourth state of matter*, or the *mesophase*. As such, these materials display properties common to both solids and liquids. Due to anisotropic weak intermolecular interactions, the molecules [1] in such a liquid crystalline assembly possess some kind of either positional or orientational order, but with a much lower degree of organization than in a crystalline solid. Therefore, the LC phase shows a liquid-like flowing behavior and as a result of the higher degree of organization compared to ordinary liquids these materials are much more viscous and often turbid. Because of this combination of dynamic behavior and high degree of organization, liquid crystals tend to be sensitive to various stimuli such as temperature, electric and magnetic fields and non-mesogenic molecules dissolved in the liquid crystalline matrix. Combined with their self-assembling behavior, this makes them extremely interesting for researchers of both chemistry and physics. Due to their unique properties these materials have found widespread applications in displays (LCDs).

The mesophase was first discovered in 1888 by the Austrian botanist Reinitzer, who was intrigued by the observation that cholesteryl benzoate has two melting points [2]. Together with Lehmann, a German physicist, this phenomenon was further investigated [3]. Much later it was found that liquid crystals are ubiquitous in nature as cell membranes of phospholipids as well as myelin, a lipid material protecting the nerves are liquid crystalline. The same holds for some DNA and protein solutions, like for instance the secretion of a spider that is used to generate silk. Although a rich variety of molecules are known that are prone to form liquid crystalline phases showing large differences in the degree and kind of orientation, they all have a strongly anisotropic shape in common.

Liquid crystals can be divided from the chemical standpoint into:

(i) Thermotropic liquid crystals and (ii) Lyotropic liquid crystals.

Thermotropic liquid crystals are those, which show mesomorphic behaviour in a definite temperature range. On the other hand, lyotropic liquid crystalline phases
show mesomorphic behaviour by the change in the concentration of the solute in a solution. Calamitic and discotic molecules are the most common forms in which both thermotropic as well as lyotropic liquid crystals exist [3]. Liquid crystalline systems can be classified in many ways [4]. Apart from the distinction between calamitic and discotic; another important type- banana-shaped or bent-core molecule is an intermediate between the rod like and the disc like molecules. One can discriminate between amphiphilic or non amphiphilic, metal containing or non-metal containing and low molecular weight or polymeric liquid crystals. Moreover, most LC materials described above show thermotropic behaviour, meaning that they are solvent free systems, that are liquid crystalline in a limited temperature range. Below this range a thermotropic liquid crystalline substance will form a crystalline phase and above this temperature an isotropic liquid phase exists (Figure 1.1).

Figure: 1.1: Thermotropic liquid crystal phase transition behaviour.

However, there are also solvent-solute type systems, where the aggregation of the solutes results in liquid crystallinity (lyotropic behaviour). The work presented in
this thesis will focus on low molecular weight banana-shaped or bent-core thermotropic liquid crystals. These liquid crystals can be divided into several types of sub-phases that differ in the degree of orientational ordering. Three important sub-phases are smectic (Sm), nematic (N) and cholesteric (N*) (or chiral nematic) (Figure 1.2).

1.2. Molecular Order
In the crystalline (solid) state, molecules usually have near-perfect orientational order. In the mesophase this degree of order is partially lost though not completely, as the molecules show highly dynamic behavior and on an average point in the same direction. In fact, the molecules point preferably along a common orientation axis than in any other direction sufficient enough to create orientational order. This preferred direction is called the director (Figure 1.3). The degree of order is described by the order parameter ($S$), which is a measure for the average angle $\theta$ between the director and the long axes of the mesogens. For an isotropic sample, $S = 0$, whereas for a perfectly aligned crystal $S = 1$. For a typical liquid crystal, the value of $S$ lies between 0.3 and 0.8, and this value generally decreases due to higher mobility and disorder as the temperature is raised.

$$S = \frac{3\cos^2 \theta - 1}{2}$$

Figure: 1.3: Model structure of the nematic phase and definition of the nematic director $n$. The angle $\theta$ denotes the deviation of the long axis of an individual mesogens from the director.

1.3. Smectic Liquid Crystals
The smectic LC phase is of enormous importance for modern liquid crystal research [4]. Originally, discovered with amphiphilic molecules, the phase was named after
the Greek word σμεκτός (smektos meaning soap-like). In this phase the molecules apart from possessing orientational order; they are organized in layers which can slide relative to each other resulting in highly viscous liquid-like behavior. Many different smectic phases are known, each one differing in orientation and position of the mesogenic molecules [5]. They are distinguished by a letter and denoted as SmA, SmB, SmC and etc in alphabetical order with their order of occurrence or discovery. A chiral version of the SmC phase also exists and is designated as SmC*. In the SmC phase, the molecules in the layered structure are tilted and in the SmC* phase the average orientation of these tilted molecules exhibits a helical propagation going from layer to layer resulting in a structure that is not superimposable on its mirror image. As a result of ferroelectric properties associated with this phase, it is considered highly promising for future applications in materials science and display technology. Further, these can be classified into different types of smectics depending on the ordering of the molecules within the layers (in-plane order). The suffixes which are used to differentiate smectic phases indicate the chronological order of their discovery. Two simple smectic phases namely SmA and SmC are described below.

**Smectic A (SmA) phase**

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

**Smectic C (SmC) phase**

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

**Chiral Smectic C (SmC*) phase**

In 1975, Meyer et al. [6] based on symmetry arguments showed that ferroelectricity could be achieved in smectic C liquid crystal made of chiral compounds. Introducing chirality into the molecules breaks the mirror plane symmetry, thus the point group symmetry reduces from $C_{2h}$ to $C_2$. As a consequence of the presence of a chiral centre, the director processes from layer to layer leading to a helical structure and hence the polarization ($P$), in the mesophase. Handedness of the chiral centre will decide the helical twist sense of the mesophase. A pictorial representation of SmC* phase is shown in *(Figure 1.4 (a) and (b)).* The macroscopic chirality in SmC* phase is compensated by the formation of helical structure in the mesophase. When an electric field is applied in a direction parallel to the smectic planes, the molecules slowly orient themselves towards the electric field.

![Figure 1.4:](image)

**Figure: 1.4:** (a) Spiraling of the director in SmC* phase. (b) Basic geometry of the SmC* phase showing layer normal $Z$, tilt angle $\theta(T)$, molecular director $n$, director $C$, polarization $P$ along $(z \times n)$ and azimuthal angle $\Phi$ of $P$ about $z$. Directions of both $n$ and $P$ vary spatially in a helical manner.
This causes distortion in the helical periodicity. When the applied field crosses the threshold voltage, the structure gets completely unwound and will have a polar ferroelectric structure. By reversing the polarity of applied field, the direction of polarization can be reversed which results in the order ferroelectric state. On switching off the field the orientation of dipoles remains in either of the two ferroelectric states. Thus, SmC* mesophase has a bistable structure.

**Antiferroelectric Smectic C (SmC_A*) phase**

Antiferroelectricity in liquid crystals was first reported by Chandani *et al* [7] in 4-(1-methylheptyloxy carbonyl)phenyl-4-n-octyloxy biphenyl-4-carboxylate (MHPOBC) in 1989. In an Antiferroelectric smectic C phase the constituent molecules tilt in opposite directions in successive layers. In 1998, Mach *et al.* [8] gave the final proof of the alternating tilt of molecules in adjacent layers of the Antiferroelectric Smectic C mesophase by resonant X-ray scattering experiments. Thus, the basic structural unit of SmC_A* phase comprises two neighboring layers in which the molecules are tilted in opposite directions. One can imagine the SmC_A* phase as double twisted helicoidal structure formed by two identical ferroelectric SmC* helices gearing into each other (Figure 1.5).

On applying a sufficiently high electric field, the helix of SmC_A* phase can be unwound which will result in one of the ferroelectric state. However, on reversing the polarity of the applied field it switches to the other ferroelectric state. On switching off the field the dipoles relax to an antiferroelectric ground state.

![Figure 1.5: the arrangement of molecules in (a) ferro (b) anti-ferro and (c) chiral smectic C.](image)

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*Figure: 1.5:* the arrangement of molecules in (a) ferro (b) anti-ferro and (c) chiral smectic C.
Other types of Smectic Liquid Crystals are -

1. **Smectic D**: Cubic lattice with micelle type molecular arrangement. This phase is usually observed between SmA and SmC or between SmC and Isotropic phase.

2. **Smectic E**: 3-D orthorhombic crystal with interlayer herringbone structure.

3. **Smectic F**: Titled hexatic structure with C centered monoclinic with in-plane short-range positional correlation and weak or no interlayer positional correlation.

4. **Smectic G**: 3-D crystal with C-centered monoclinic.

5. **Smectic H**: 3-D crystal with C-centered monoclinic and having herringbone structure.

6. **Smectic I**: Titled hexatic C-centered monoclinic with slightly greater in-plane correlation than SmF.

7. **Smectic J**: 3-D crystal with C centered mono clinic structure.

8. **Smectic K**: 3-D monoclinic structure with herringbone structure.

**1.4. Twist Grain Boundary (TGB) phase**

In 1974, de Gennes [9] predicted a topologically defect-stabilized mesophase in analogy with superconductors. When the intrinsic twisting power of the material is high, the smectic A structure breaks down into periodic stacks of layers, with a finite twist distortion. These layers are mediated by regular array of screw dislocation. Renn and Lubensky [10] proposed a model for this mesophase and named it as TGB\(_A\) phase. Similarly a SmC phase can give rise to a TGB\(_C\) phase.

**1.5. Nematic Liquid Crystals**

The simplest liquid crystalline phase possible is the nematic phase (N), as it has only a slight orientational order of the individual mesogens. The molecules can translate freely and can rotate around their long axis, leading to a much lower viscosity than observed for smectic phases. The nematic phase is named after the Greek word νεμα (nema meaning thread) as it often appears to have miniscule threads when observed through a microscope.
1.6. Cholesteric Liquid Crystals

The cholesteric (or chiral nematic, N*) liquid crystalline phase is essentially a nematic phase with an additional helical change in orientation of the director.

Figure: 1.6: Schematic representation of chiral nematic or cholesteric phase and definition of the cholesteric pitch.

Whereas the director in an ordinary nematic liquid crystal has a constant direction, in a cholesteric phase it changes direction in a helical fashion throughout the sample, perpendicular to the helix axis. The orientation of the director describes a helical propagation along the cholesteric helix axis that is non-superimposable on its mirror image, making it chiral. The resulting supramolecular chirality is indicated by the sign and magnitude of the cholesteric pitch $p$, which is the distance, in the material across which the director rotates a full 360° (Figure 1.6). The name of the cholesteric phase originates from the cholesterol derivatives for which this phenomenon was first observed [2, 3], but in principle any chiral nematic phase is referred to as cholesteric.

1.7. Banana Mesophase

The symmetry concept is an integral part of liquid crystalline phases, a reduction of which leads to various new mesophase structures. In banana liquid crystal reduction of symmetry was achieved by connecting the two rods through a bend. The credit for the synthesis of unconventional compounds exhibiting liquid crystalline properties can be attributed to Vorlander and his group [17]. They explored the structure property relationships of rod-like molecules by synthesizing various types of compounds. These include liquid crystal with heterocyclic and alicyclic rings, hydrogen bonded liquid crystals, terminal polar nematics and mesogenic dimers.
with flexible spacers, metallomesogens and main chain polymers. Most of these compounds represent the first examples in their respective categories exhibiting mesomorphic behaviour.

Three bent-shaped compounds which were synthesized by Volander et al. [17], are derivatives of catechol, resorcinol and isophthalic acid and the structures of these compounds (1a, 1b and 1c respectively) are given below. The characterization of the mesophase exhibit by these compounds was not carried out at that time.

The study of the mesomorphic properties exhibited by bent-shaped compounds was renewed in 1991. Kuboshita et al. [18] synthesized dimers, derived from 1,2-dihydroxy-benzene and 2,3-dihydroxynaphthalene. The mesophase obtained were characterized as N, SmA and SmB. However, in 1994 Akutagawa et al. [19] synthesized four homologous series of compounds derived from resorcinol. The general structure of these compounds is shown below.
From the microscopic texture observations, enthalpy values, XRD and miscibility studies they concluded that mesophases exhibit by these compounds are N and SmC. From XRD studies they argued that the tails are nearly normal to the layers whereas the cores are tilted by about 48°C. Later, some of the compounds, which have the general structure, were synthesized by Pelzl et al. [21] who showed that they exhibit B-phases. However, the real breakthrough came from Niori et al. [20] who reported ferroelectric properties in the achiral compound, namely 1,3-phenylene bis[4-(4-n-octyliminomethyl)benzoate] (1d, n=8).

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

Their result can be summarized as follows:

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

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

III. The observation of a single current peak in the tri-angular current electric field experiment point towards a ferroelectric ordering of the molecules in the ground state.
IV. X-ray diffraction studies on these compounds showed SmA type arrangement of the molecules within the layers (no tilt in the core as pointed out by Akutagawa et al. [19]).

In 1977, Weissflog et al. [22] reported an antiferroelectric current response with untilted cores in the same octyl homologue of 1d (n=8). At the same time Heppke et al. [23] reported ferroelectric switching current dynamics in several homologues of 1d and 1e.

All these contradictory results were put to an end by the beautiful experiments carried out by Link et al. [24]. They carried out depolarized reflected light microscopy (DRLM) experiments, on compounds 1d (n=9) and 1e with an oblique incidence and slightly uncrossed polarizers. They observed that in the smectic phases of these compounds the optic axis is tilted with respect to the layer normal. This ruled out the possibility of an orthogonal arrangement of the molecules in the smectic phase. The study of free standing films of the mesophases of these compounds gave strong odd-even effect by the application of weak electric field. This led them to conclude that the ground state structure of these mesophases is antiferroelectric in nature.

In the same year, an International Workshop on Banana-shaped mesogens: “Chirality by Achiral molecules”, was organized in Berlin to recommend a nomenclature for the different mesophases exhibited by banana-shaped compounds. Since these mesophases were not miscible with any of the known thermotropic liquid crystalline phases, the symbol B was assigned to signify the shape of the molecules. Seven mesophases were identified and assigned the symbols B1, B2, B3, B4, B5, B6, and B7. Recently, another mesophase was assigned as B8 [25] has been added to the above list. The suffixes indicate the chronological order of the discovery of the mesophases.
General observations in Banana liquid crystals

a. The banana-shaped compounds are biaxial in nature because of their intrinsic shape.

b. The mesomorphic behaviour is strongly dependent on the bending angle. Typical angle is $\sim 120^0$, and if the bending angle increases to $\sim 145^0$ one would expect calamitic mesophases in addition to banana phase.

c. The mesophase behaviour also depends on chain length. The commonly observed phase sequence is $B_6$-$B_1$-$B_2$ as a function of $n$-alkyl chain length on ascending the series.

d. The high value of mesophase to isotropic transition temperature indicates the high rigidity of molecular packing.

e. The value of spontaneous polarization is rather high when compared with those of calamitic liquid crystals and varies generally from about 300 to 1000 nC cm$^{-1}$.

f. Antiferroelectric mesophases are commonly observed when compared with ferroelectric mesophase in banana-shaped compounds. On the contrary, in the case of calamitics, a majority of compounds show a ferroelectric mesophase (SmC*). The comparison and layer fluctuations involving ferro-and antiferroelectric properties in calamitic and banana-shaped compounds were given by Nadasi et al. [26]. Because of out of layer fluctuations which are allowed in the ferroelectric phase of calamitics and antiferroelectric mesophase of banana-shaped compounds, their structures are thermodynamically and entropically stable. Whereas in the case of antiferroelectric phase of calamitics and ferroelectric mesophase of banana-shaped compounds they have to sustain the entropically penalty, as out of layer fluctuations are absent and hence are less commonly observed.

**B$_1$ mesophase**

This mesophase was designated differently in the initial stages, for e.g. $SmA_b$ [27, 28] $X_{B1}$ [29] and columnar [30]. The first compound (1f) exhibiting the $B_1$ mesophase was reported by Watanabe et al. [28] and has the following chemical structure.
The B₁ mesophase is commonly observed for middle members of a homologous series of compounds. When a sample is cooled from the isotropic phase and observed under a polarizing microscope, the mesophase appears in two different forms. Either a mosaic texture or colorful spherulitic pattern can be observed. The viscosity of the mesophase is rather high and difficult to shear the cover slip. The textures are highly birefringent because of the two-dimensional ordering of the molecules in the mesophase. The mesophase to isotropic transition enthalpy is in the range 10-20 kJmol⁻¹. Sometimes B₆ to B₁ mesophase transition could be seen in banana-shaped compounds [31]. In such a transition if the B₆ mesophase shows a schlieren texture, then at the transition mosaic texture starts to appear. If the B₆ mesophase has a focal-conic texture then the change in the texture is minimal. The associated enthalpy change at the B₆ to the B₁ mesophase transition is also rather small.

The B₁ mesophase can be considered as a columnar mesophase with a rectangular lattice built up by ribbons with parallel alignment of bent-core molecules. The bending direction in successive ribbons is antiparallel, so that the macroscopic chirality is subdued. Each repeating rectangular unit consists of cluster of molecules. The polarization due to these clusters is small and is nullified by the adjacent clusters and hence no net polarization is observed for this microscope. The confirmation of the structure of this mesophase is from XRD studies. Typically, for a B₁ mesophase two or more reflections are observed in the small angle region of a diffraction pattern. One of the reflections corresponds to half the molecular length, which indicates the intercalated layered structure of the mesophase. A diffuse wide-angle reflection indicates the liquid-like ordering of the molecules within the layers.
Watanabe et al. [28] proposed a model for the mesophase. The model for the mesophase is shown in Figure 1.7. Core-core interaction in this mesophase is effective and depends on the length of the arms of the core and n-alkyl/ n-alkoxy chain length. On increasing the alkyl chain length, the core-core interactions are reduced. These unfavorable chain–core interactions on increasing the alkyl chain length disturb the two dimensional rectangular lattice and yield a lamellar mesophase.

**B<sub>2</sub> mesophase**

Among all the banana phases, the electro-optically switchable B<sub>2</sub> mesophase has been designated as a SmCP<sub>A</sub> phase by Link et al. [24]. Although different symbols have been assigned for the mesophase, the accepted nomenclature is either to call it as B<sub>2</sub> or SmCP<sub>A</sub> phase. This mesophase is less viscous than B<sub>1</sub> phase and is generally observed for the higher homologue series. The mesophase to isotropic transition enthalpy value is in the range of ~18-25 kJmol<sup>-1</sup>. The mesophase exhibits different optical textures under polarizing microscope. The commonly observed textures are fingerprint or fringe pattern, schlieren and focal-conic textures. XRD studies on oriented samples of this mesophase have been reported [31, 35and 36].

The reflections in the small angle region are in the ratio of 1:1/2:1/3, indicating a lamellar periodicity. The wide-angle diffuse peak indicates the absence of in-plane ordering within the smectic layers. The first order reflection obtained is less than the full molecular length indicating a tilt of the molecules within the layer. The measured tilt angle from XRD studies varies between 35 to 50° depending on the chemical nature of the constituent molecules and the temperature. A lot of attention has been paid to this mesophase mainly because of its response to an applied electric...
field. Link et al. [24] carried out a series of experiments on compounds 1d (n=9) and 1e. These include free standing film of the sample and depolarized reflected light microscopy (DRLM) using oblique laser illumination. They interpreted their results in the following way.

The molecules in a smectic layer are tilted, thus reducing the symmetry from C_{2h} to C_2. All the molecules in the layer tilt in the same direction constituting the tilt plane. Because of the shape, the molecules are packed in a bend direction, which is responsible for generating the in-layer ferroelectric polar order, which is normal to the tilt plane. Since the molecules are stacked in layers, a layer plane is obtained. The tilting of dipoles in opposite directions in successive layers compensates the layer polarization as well as macroscopic polarization in this mesophase. Depending on the tilt sense in adjacent layers there are two distinct possibilities namely SmC_{S} P_{A} (Synclinic smectic C, polarization antiferroelectric) and SmC_{A} P_{A} (anticlinic smectic C, polarization antiferroelectric). The synclinic tilt of the molecule in adjacent layers results in a racemic structure and is thermodynamically a more stable state. On application of an electric field, the ferroelectric phase is induced and has a SmC_{A} P_{A} structure. On revering the polarity of the applied field, no change in the orientation directions of the dark brushes could be seen under crossed polarizers. If the tilt sense is in the opposite direction in adjacent layers, it results in a homochiral (SmC_{A} P_{A}) structure. A pictorial representation of the molecules in non tilted SmA phase cause SmAP_{F} and SmAP_{A} and tilted SmC and SmC_{A} result in racemic (SmC_{S} P_{A}) and chiral states (SmC_{A} P_{A}) of antiferroelectric mesophase and the corresponding field induced ferroelectric states racemic (SmC_{A} P_{F}) and chiral (SmC_{S} P_{F}) is shown in Figure 1.8.
The field induced ferroelectric state, SmC_{3}P_{r} has two distinct orientations. The tilt direction in successive layers and their response to an applied electric field is shown schematically in figure 1.8. The spontaneous polarization was measured by triangular-wave method and the observation of two current peaks per half cycle indicates the antiferroelectric ground state structure of the mesophase.

**B\textsubscript{3} mesophase**

Although this phase was considered under B-phases, careful XRD studies on this phase revealed the crystalline nature. This phase is a lower temperature phase with respect to the B\textsubscript{2} mesophase [21].
B₄ mesophase
Detailed XRD studies on this phase revealed the crystalline structure and it exhibits some interesting optical features. This phase was observed on cooling from either a B₂ or a B₃ phase [21]. The unique textural feature of this phase was the observation of a blue colour with domains of opposite handedness. Hence this phase has been named as smectic blue phase [27, 29]. The atomic force microscope experiments show that the phase has a helical superstructure. Sekine et al. [27] have reported a TGB-like structure for this phase.

B₅ mesophase

This mesophase was first observed in a derivative 2-methylresorcinol (1g) [21, 32]. Always, this mesophase was observed on cooling the B₂ mesophase and has only a paramorphotic texture. The transition from B₂ to B₅ mesophase is first order. XRD studies on the mesophase show lamellar periodicity in the small angle region. However, in the wide angle region some additional reflections were observed. This means that, this mesophase has in-plane periodicity within the layers and reflections in the wide-angle region can be indexed to a centered rectangular lattice. Electro-optical experiments towards an antiferroelectric ground state structure for the mesophase. Thus, the only difference between B₂ and B₅ mesophases is the presence of an additional short-range order within smectic layers in the latter case.

B₆ mesophase
This mesophase was first observed in 1h [21]. This mesophase can be observed normally for homologues with short alkyl chain. This phase has also been designated as intercalated smectic phase (Sm_intercal) [33].
On cooling the isotropic liquid, this mesophase appears as batonnets and coalesces to a smooth focal-conic texture. These textural features are reminiscent of a SmA phase, but can never be aligned homeotropically. The enthalpy of mesophase to isotropic transition is about 10-15 kJmol$^{-1}$. The proposed model for the mesophase is shown in Figure 1.9. The first order reflection in the small angle region of an X-ray diffraction pattern corresponds to less than half the molecular length. This implies an interdigitation of the molecules. The oriented pattern reveals the tilt of the molecule and the measured tilt angle is about $\sim 25^\circ-30^\circ$. In some compounds a direct transition from B$_6$ to B$_1$ mesophase could be observed. On cooling the sample from B$_6$ to B$_1$ phase, the molecules start to aggregate to form clusters. These clusters arrange into a two-dimensional lattice to form a B$_1$ phase.

**Figure: 1.9:** A schematic representation of bent-core molecules in the B$_6$ mesophase

Rouillon *et al.* [34] have carried out Monte-Carlo simulation studies on the B$_6$ mesophase and reported the molecular model allowing the high and low potentials. In such a periodical structure, there exist 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 chain can be filled up by the voids. Hence the mesophase is stable for compounds having shorter alkyl chains.
**B₇ mesophase**

The B₇ mesophase phase shows the most beautiful and optical unique textures. It was first observed in 2-nitroresorcinol derivatives \[1i\] [35]. Also a schematic representation of the molecules in tilt plane (xz), layer plane (xy) and polar plane (yz) and synclinically or anticlinically in the tilt plane and the polar plane is shown in Figures 1.10 (a) and (b) and undulated smectic B₇ phase is shown in Figure 1.11.

![Chemical structure of B₇ mesophase](image)

The mesophase has C₁ symmetry and exhibits helical superstructure. Pelzl *et al.* [35] reported four compounds derived from 2-nitroresorcinol and exhibiting the B₇ mesophase. The mesophase to isotropic transition enthalpy value is rather high and sometimes more than the melting enthalpy values. Strangely, sometimes the melting point could not be determined. Pelzl *et al.* [35] reported various beautiful optical textures exhibited by the B₇ mesophase. On slow cooling from the isotropic phase, B₇ mesophase appears in different forms in the same sample preparation. The characterization feature is observation of single, double and triple-winded helices. They also observed various other textural variants such as elongated germs with lancet-like or irregular thread-like germs, circular domains with equidistant concentric arcs etc. On further cooling various two-dimensional periodic patterns were also observed. The occurrence of spiral germ points to a helical structure and concentric lines on the circular domains is a result of helical periodicity. This periodicity is probably due to twisted distribution of molecular tilt, which corresponds to pitch of the helical structures as in the case of a SmC* phase.

The XRD studies of this mesophase gave several reflections in the small angle region ruling out the possibility of a simple layered structure. The wide-angle diffuse peak indicates the liquid-like plane order. B. K. Sadashiva *et al.* two homologous series of compounds exhibiting the B₇ mesophase have been reported.
[36, 37]. All the characteristic features observed in the standard materials could also be seen in these materials.

Figure: 1.10: The four Sm-CP structures give four different conditions to end-chains of molecules at the interface of adjacent layers.

In the Sm-CP phase, three planes, tilt plane (xz), layer plane (xy) and polar plane (yz) are defined as shown in (a). End-chains at the interface tilted synclinically (or anticlinically) in the tilt plane and the polar plane as shown in (b). The polar order of one Sm-CP state is described using the relative tilt in polar plane i.e., end chains tilted synclinically (or anticlinically) in two antiferroelectric states (or two ferroelectric states).

Figure: 1.11: Structure of the undulated smectic phase proposed as a model of layer structure of the B\textsubscript{7} phase.

\textbf{B\textsubscript{5} mesophase}\n
Bedel \textit{et al.} [25] reported a bilayer structure for the mesophase of compounds derived from isophthalic acid containing n-alkanoate terminal group. Interestingly this mesophase exhibits antiferroelectric switching behaviour. Since the mesophase
textures as well as structure were different from the known B-phases, the symbol \( B_g \) was assigned for this mesophase.

1.8. General remarks in bent-core compounds
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 length
iv) Various polar lateral substituents

Most of the compounds reported so far contain five phenyl rings and basically derived from 1,3-dihydroxybenzene [20, 21, 31, 38, 39]. 2,7-dihydroxynaphthalene [40, 41], 3,4-dihydroxybiphenyl [42] have also been used as a central unit. Six or seven ring compounds have also been reported [30, 31]. On increasing the number of phenyl rings in the core, the thermal range of the mesophase as well as the clearing temperature increases.

Commonly used linking groups are imine, ester, azo and ethylene units. Compounds containing Schiff’s base linking group show rich polymorphism when compared with other systems. Most of the compounds of bent-core molecules contain two n-alkoxy or n-alkyl chains as terminal groups. The synthesis of a homologous series of compounds gives a trend of the occurrence of different mesophases on ascending the series. The commonly observed trend in a homologous series of banana-shaped compounds is \( B_6-B_1-B_2 \) phase on ascending the series [31, 34].

1.9. Discotic Mesophase
Thermotropic liquid crystal derived from rod-like molecules were only known until Chandrasekhar et al. [43] and Billard et al. [44] discovered liquid crystalline phases in molecules of discotic shape. There was evidence that mesomorphic phases were formed from disk-like molecules in the year 1960 (Brooks and Taylor, 1968); however the first identification of a discotic phase was by Chandrasekhar et al. in 1977 with benzene-hexa-n-alkanoates compounds [43]. Since then, a large number of discotic compounds have been synthesized and a variety of discotic mesophases discovered. Structurally, most of them fall into two distinct categories; nematic and
the columnar. Both the phases of the disk-like molecules are shown in Figures 1.12.

Nematic phase is the simplest discotic phase, because there is orientational order of the discs without any long-range translational order. The molecules move around quite randomly, but on average the axis perpendicular to the plane of each molecule tends to orient along the director. Unlike the classical nematic phase of rod-like molecules, this phase is optically negative.

Chiral nematic discotic liquid crystals also exist. In this phase the director rotates in a helical fashion throughout the sample just as in the case of rod-like chiral nematic liquid crystal. A smectic-like lamellar phase has been reported but the disposition of the molecules in the layers has not yet been resolved.

General and attractive features:
1. Relatively easy synthesis.
2. Easy processing within the mesophase.
3. Self-organization within their LC phase, leading to highly organized materials
4. High anisotropy of specific properties (i.e., refraction of light).
5. Discotic mesogens have been considered as attractive candidates for application in organic devices such as photovoltaic solar cells, light emitting diodes and field effect transistor.

Discotic LC's are unique nano structure with remarkable electronic and optoelectronic properties. Due to the axial stacking of aromatic cores, disk-like molecules organized themselves into 1-D columnar wire and these columns in turn arrange themselves in various 2-D lattices. The transport along the columnar axis is much faster than between the columns. This stacking is based on extensive and highly stabilizing overlap of molecular π-orbital of rigid aromatic moieties that are ~ 3.5 Å apart. This central aromatic core represents the rigid part of the molecule, and is surrounded by long alkyl or other peripheral substituents, which provide the flexibility to the molecule. Variation of either the core or these peripheral substituents yields new materials with mesomorphic properties that can be varied in a controllable fashion. Due to their relatively high charge carrier mobility, they tend to form highly ordered films of various thicknesses and self healing of defects owing to their dynamic nature.
Most frequently, disk-like molecules with a flexible periphery organize into a “molecular wires” which are interconnected through their long alkyl substituents [43]. It is rather important to realize that the main interaction between the aromatic cores is $\pi-\pi$ interaction, which is the result of a combination of dipole-dipole (electrostatic), Vander Waals, and dipole-induced attractive forces, and Pauli repulsion (short range repulsion), none of them being predominant.

![Diagram](image)

**Figure: 1.12:** Columnar phases of disc-like molecules: (a) upright columnar structure (b) its hexagonal and (c, d) rectangular modifications (e) tilted columnar structure (f) its face-centered rectangular lattice and (g) Nematic phase of disc-like molecules.

1.10. Application of Liquid Crystals:

Liquid crystals are beautiful and extremely useful, one of the most active and fascinating fields of scientific and industrial research. Their dual nature and easy response to electric, magnetic and surface forces have generated innumerable applications, which continue to grow both in money and diversity. Besides the familiar numeric displays and temperature sensors one now finds liquid crystals in high-resolution TV displays, projection systems, optical computing, and fibres with tensile strength greater than steel and even in painting. They are a tool for fundamental and basic research in physics, chemistry, space, engineering, mathematics, and biology.
Nematics are the ones that have been deployed in most of the applications. But as research progressed and the advantages of cholesteric, smectics and FLCs came to be known, they are being used in place of nematics and for a number of other applications. Nematics and smectics are used in liquid crystal displays (LCD), digital watches, pocket calculators, information displays, computer monitors, television displays etc. Despite the rather slow response speed, liquid crystal displays are the technology of choice for reasons such as flexibility, low voltage, low power operation and its ease of fabrication. Twisted nematic displays are still dominating the LCD field, as most of the displays produced today are either twisted nematic [45] or super-twisted [46] nematic displays. The FLC displays are a fast emerging field as new alignment techniques as well as new addressing techniques are being developed [47]. The usage of electroclinic effect as well as deformed helix ferroelectric effect [48] has been utilized to get fast FLC displays with grey scale capability.

Cholesteric liquid crystals are also used in a number of ways. They are used in temperature sensitive devices, medical applications, thermometers, thermographs, tumor testing, vein and artery location, infections, battery testers, cosmetic art (liquid crystal paints), mood rings, decoration and advertising. Understanding of lyotropic Liquid Crystals is important because of their role in biological membranes. Other uses of Lyotropic Liquid Crystals are in emulsions, detergents, food industry, and oil recovery.

Liquid crystal droplets are currently being worked on at NASA, USA to combine beams of light from multiple telescopes, which is a good way to search for distant planets around other stars. Thus, liquid crystals have number of potential uses besides being used in display applications.
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