

CHAPTER 1

Introduction

1.1. A brief introduction to liquid crystals

Liquid crystals (LCs) are an intriguing class of soft condensed matter, thermodynamically located between the three dimensionally ordered crystals and the completely disordered liquids. As the name imply, they share properties of both isotropic liquid (as fluidity) and crystalline solid (as orderedness). A number of organic substances are found to demonstrate different liquid crystalline phases as intermediate between the solid and liquid phases. Such transitional phases are also designated as ‘mesophases’ with the prefix ‘meso-’ (greek, ‘μεσο’) signifying ‘in between’. The fundamental requirement for an organic compound to exhibit a liquid crystalline phase is the molecular shape anisotropy (anisometric molecules) with the length in one dimension being several times than that in the other dimensions, thereby enhancing the probability of obtaining an aligned fluid phase. Furthermore, there must be some flexible molecular part (as the alkyl chain) in order to introduce some structural disorder. It is the delicate balance between the structural anisotropy and flexibility which helps in deciding the stability of the mesophases. Due to the presence of such a high degree of geometrical anisotropy, the LC molecules possess some sort of orientational order, however, the translational order of the molecules, which is a characteristic of crystalline solid, is either partially or completely absent. There are also exceptions where one or more rules, to be satisfied for being a general liquid crystalline phase, are found to be violated, for example, the lack of fluidity in

‘soft crystal’ smectic *G* phase [1] or the nonexistence of optical anisotropy in dark conglomerate phase involving chiral conglomerate domains [2], even though both of them are considered as liquid crystalline phases.

The discovery of liquid crystal is in general attributed to an Austrian botanist Friedrich Reinitzer, although there are several evidences of liquid crystalline behavior in a number of organic samples in past, however, without any proper identification of them. In 1888, while investigating cholesteryl benzoate, Reinitzer, first observed that during melting, for a specific temperature interval (between 145.4 °C and 178.5 °C), the compound remains in a cloudy fluid state between the crystalline solid and isotropic liquid and then transforms into the clear liquid [3]. The discovery of Reinitzer stimulated further research effort and Otto Lehmann, a German physicist, employing his polarizing optical microscope subsequently confirmed the presence of two melting points in between which the crystal could exist in a liquid-like state [4], which also led him to introduce the term ‘liquid crystals’ for this class of compounds. A further milestone in the history of liquid crystal was the nomenclature of different mesophases by George Friedel in 1922 [5], which are still in use today. Since then, thousands of such compounds displaying variety of phases between the solids and liquids with distinct characteristic behavior have been synthesized.

Ever since the discovery of liquid crystals, they have appeared as a field of considerable interest from both the theoretical and experimental point of view. Whereas the theoretical branch is chiefly concerned in manifesting the structure-property correlation as well as the impact of the inter-molecular interactions on the mesomorphic behavior on a macro-level to obtain a better understanding about this class of substances, the experimental branch is particularly engaged in finding out new compounds and their characterization to obtain useful materials for technological applications. It is the unmatched advantage of order and fluidity in a single system and also their unique capability to be able to response to an external perturbing field (i.e., electric,

magnetic or surface force field) which divulges them as a candidate of unparalleled significance in vast areas of modern science and technology. The field-induced switchable optical operation of them has been widely employed in achieving their greatest technological application – liquid crystal displays (LCDs). Apart from that, they are also extensively employed in other technological applications as optical switches, temperature sensors, optical imaging and recording, medical applications, non-destructive mechanical testing of materials under stress, beam steering, tweezers, laser projection, dynamic holography and so on. Furthermore, such versatile materials also serve as excellent systems for investigating the phenomena of phase transitions and critical phenomena. They as well form the basis of understanding of several soft material and biological systems. There are plenty of books and review articles available in the literature, which give in detail the fundamentals as well as advancement in this field up to now [1, 6–21].

This dissertation is primarily focused on the study of physical properties of a few bent-core or banana-shaped liquid crystals and their mixtures with calamitic molecules. In an attempt to achieve an essence of the effect of bent mesogenic molecules on the phase behavior of rod-like LCs, the critical behavior at different phase transitions has also been studied. The following introductory section is principally devoted to a few relevant LC systems of interest, and their mesomorphism, physical properties and phase transitions.

1.2. Classification of liquid crystals

Depending on the mechanism that induces the transitions among the different liquid crystalline phases, they can be categorized into two broad classes: Thermotropic and Lyotropic liquid crystals. For thermotropic liquid crystals, the transitions among the intermediate phases can be brought about solely by thermal process (i.e., by varying the temperature of the compound). Furthermore, depending on the fact that whether the transition is uni- or bi-directional, such compounds are referred to as monotropic and enantiotropic respectively. For lyotropic liquid crystals, the transition among the various

mesophases are accomplished under the influence of the solvent, i.e., by varying the relative concentrations of the components of the system (multi-component solution). The lyotropic liquid crystals are particularly of importance in studying biological systems while thermotropic liquid crystals find their applications in technological field.

1.2.1. Lyotropic liquid crystals

Lyotropic liquid crystals are anisotropic solution of rod-like molecules in an isotropic solvent. In general they are made up of amphiphilic molecules (surfactant) having a polar (hydrophilic) head and one or more non-polar (hydrophobic) tails [figure 1.1(a)] dissolved in water. In appropriate solvent, they self-assemble in various ways with their polar head oriented towards the polar solvent (water) and the non-polar chains towards one another, forming small aggregates, called micelles [figure 1.1(b)]. At low surfactant concentration the micelles are more or less spherical. While at higher concentrations they rearrange themselves, forming dissimilar structures and hence, the different lyotropic mesophases as lamellar, hexagonal, cubic phases

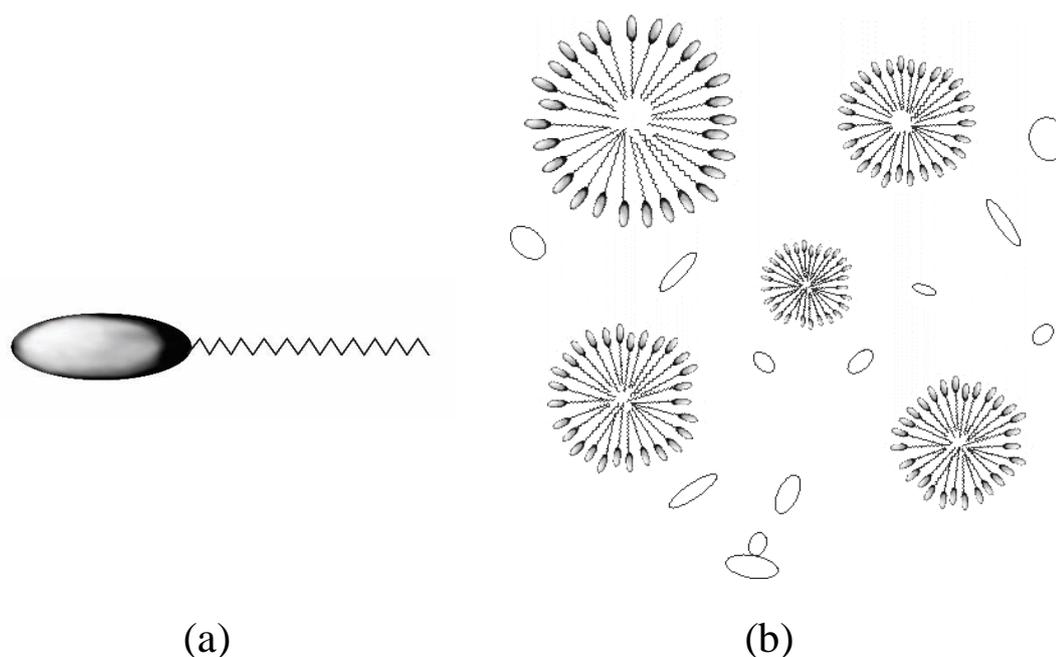


Figure 1.1. Schematic diagram of (a) an amphiphilic molecule and (b) a micellar phase.

etc. Moreover, for this class of liquid crystals one of the most striking fact is that the interaction between the solute molecules is secondary while that between the solute and polar part of the solvent is the primary one which decides the stability of a lyotropic mesophase. Soap solution is a very common example of lyotropic liquid crystal. Since, this dissertation is not concerned with lyotropic liquid crystals, further details on lyotropic systems are not being discussed here.

1.2.2. Thermotropic liquid crystals

The term ‘thermotropic’ arises because here the variation of the resultant molecular ordering in the LC medium and hence, the transitions among the different LC phases, are brought about through the variation of temperature. In this case the molecular orientations and ordering of the self-assembled molecular association are the key factors which determine the different mesophases.

The necessity of high structural anisotropy of the basic molecular unit (also known as ‘mesogen’) of thermotropic LCs leads to the synthesis of molecules with numerous characteristic shapes such as rod-like or calamitic LCs [figure 1.2(a)], disc-shaped or discotic LCs [figure 1.2(b)] and LCs with other exotic geometries such as banana-shaped or bent-core LCs [figure 1.2(c)],

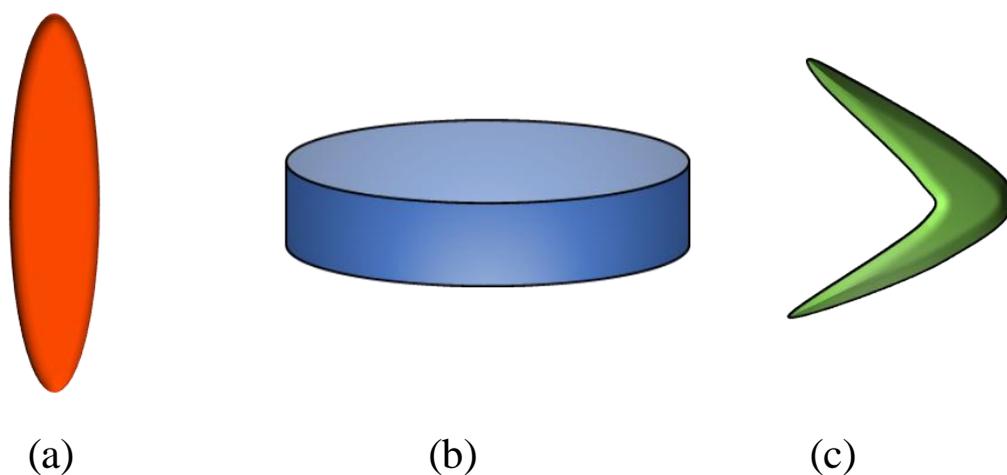


Figure 1.2. Schematic diagram of three different types of thermotropic liquid crystal molecules: (a) calamitic, (b) discotic and (c) bent-core.

hockey stick-shaped, T-shaped, pyramid-shaped, star-shaped and so on. The following section is limited to the discussion on the general features and mesomorphisms of two of the most widely studied LCs – the calamitic and bent-core ones, which are relevant to this work.

1.2.3. Calamitic liquid crystals

The fundamental structural unit of calamitic LCs generally consists of a rigid straight aromatic core of phenyl rings with one or more flexible alkyl terminal chains. So far, a variety of liquid crystalline phases with diverse phase structure and mesomorphic properties have been revealed in them. A few of them, which are most frequent, are discussed here in a nutshell.

1.2.3.1. Nematic (*N*) phase

The simplest of all the liquid crystal phases is the nematic (*N*) phase. As one cools a thermotropic LC from its isotropic state, the mesophase into which it usually first transforms is the *N* phase. The *N* phase differs from the isotropic phase by the fact that due to the minimization of the excluded volume, it is characterized by a long range orientational order of the molecular long axis, i.e., although the centers of mass of the nematic molecules are randomly distributed across the volume, they still have an affinity to align themselves parallel to a favored direction, known as the ‘director’ (\hat{n}) [figure 1.3(a)]. However, no positional ordering is observed within this mesophase and that is why they exhibit a high degree of fluidity. Due to the head-tail symmetry (i.e., absence of polarity) of the molecules, the director is considered to be an axial vector, i.e., \hat{n} and $-\hat{n}$ are equivalent. Although in a nematic phase there is a local variation of the preferred direction across the volume, a uniformly aligned monodomain nematic sample is in general optically uniaxial with the molecules being free to rotate about their long molecular axis. Thus, the molecules in the nematic phase are usually characterized by a cylindrical symmetry. However, for molecules with relatively lower symmetry, there are also evidences of the existence of a second director \hat{m} giving rise to a biaxial nematic phase [22–28],

where \hat{m} is along the preferred direction of orientation of the short molecular axis and is at right angle to \hat{n} [figure 1.3(b)]. Furthermore, there are also examples of nematic phases comprising short range domains with smectic-like layered structures termed as ‘cybotactic nematic phase’ [29–38].

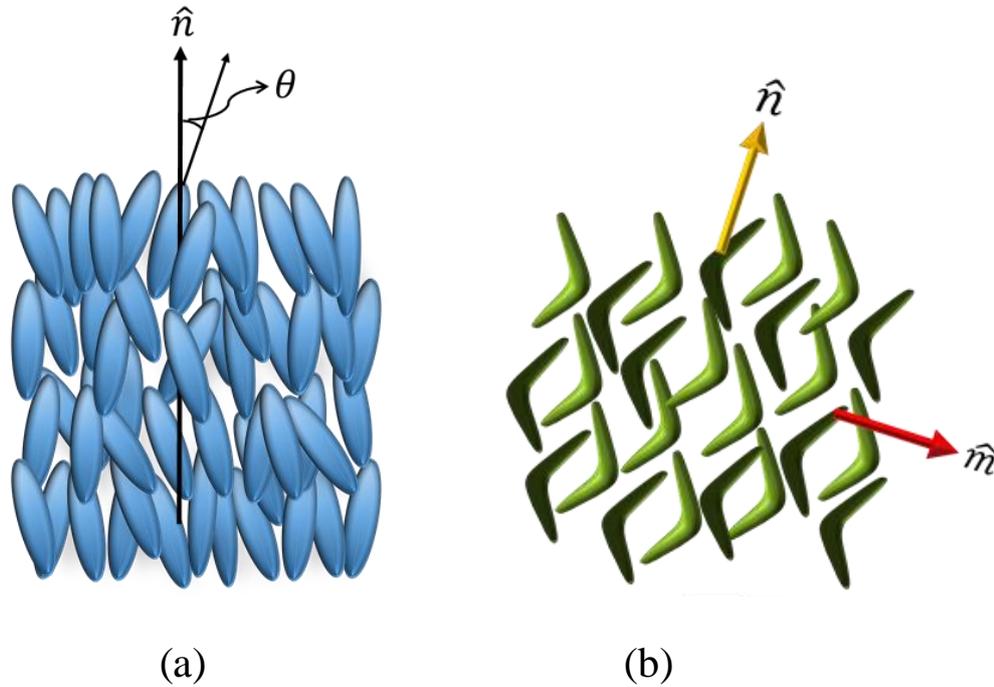


Figure 1.3. Schematic representation of molecular ordering in (a) uniaxial nematic phase and (b) biaxial nematic phase.

For a uniaxial nematic phase with cylindrical symmetry, the resultant molecular ordering in the medium can be described by an order parameter,

$$S = \langle P_2(\cos \theta) \rangle = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle \quad (1.1)$$

where θ represents the angle between the nematic director \hat{n} and the molecular long axis and the angled bracket indicates the local average over all the molecules. The quantity S gives the average degree of alignment of the molecules relative to the director. Theoretically, S can assume values in between -0.5 to 1 but experimental values are found to range between 0.3 and 0.8.

1.2.3.2. Cholesteric or chiral nematic (N^*) phase

Nematic phases are observed for LCs either containing achiral molecules or for those which are racemic mixtures. Materials with chiral centre in their molecular structure or those consisting of chiral dopant, favor the alignment of the molecules at an angle to each other and hence, lead to the formation of a modified phase-structure where in addition to the long range orientational order, the molecules gradually twist in a periodic manner about an axis perpendicular to their director thereby giving rise to a macroscopic helical

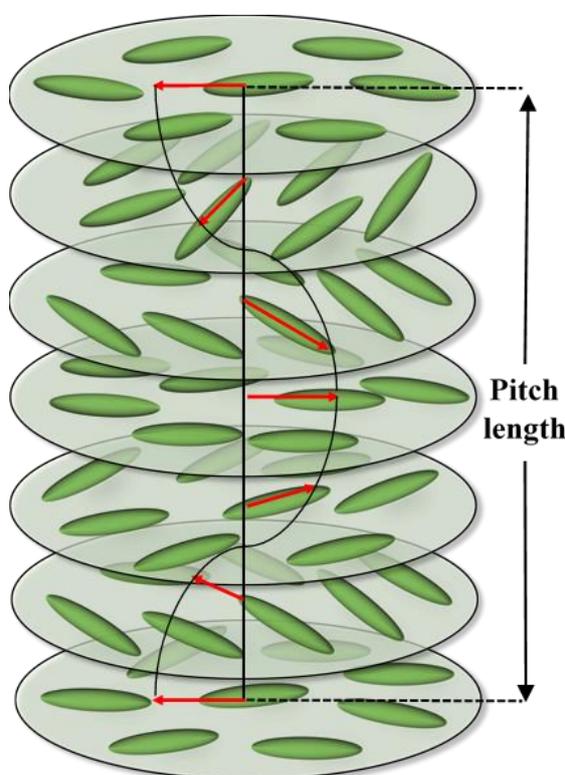


Figure 1.4. Schematic representation of molecular ordering in cholesteric or chiral nematic phase.

structure [figure 1.4]. The handedness of such helices again depends on the molecular conformation. These phases are termed as chiral nematic or cholesteric (N^*) phases because of their preliminary observations in cholesterol derivatives. In cholesteric mesophase, the longitudinal distance in which a full rotation of the molecular director about the helix axis is completed, is termed as the pitch (p) of the helix and in fact an infinite pitch of this mesophase leads to

the nematic phase. Furthermore, the helix-pitch is found to be rather sensitive to temperature. The cholesteric mesophase shows many unique optical properties like selective reflection (Bragg reflection) of circularly polarized light having wave lengths similar to their pitch and high optical rotatory power. Such exclusive features and also the temperature dependence of the pitch-length make them suitable for a number of optical applications.

1.2.3.3. Smectic (Sm) phase

The Smectic (Sm) phase possesses some degree of positional ordering in addition to the orientational ordering of the constituent molecules. In this phase, the centers of mass of the molecules are on the average arranged in equidistant layers with a well-defined interlayer separation. In each of these layers, the molecular long axis can either be along the direction of the layer normal or tilted relative to it. Due to the strong correlation between the molecular size and layer thickness, smectics can be regarded as a two dimensional material within a single layer. In some of the smectic phases, molecules are mobile within the layer plane and also can rotate about the molecular long axis. Moreover, due to lack of interlayer attraction, the smectic layers can slide over one another and thereby this phase exhibits fluid like characteristics even though with a viscosity much higher compared to that in the nematic phase. On the basis of structural dissimilarity and ordering of the molecules within the layers, smectic mesophase again can be categorized into various sub-phases, some of which in the sequence of decreasing symmetry are as follows: Smectic *A*, Smectic *C*, Smectic *B* and so on. In the following section, a brief introduction to a few of the smectic phases related to this thesis is presented.

Smectic A (Sm-A) phase

The least ordered layered liquid crystalline phase is the smectic *A* (Sm-*A*) phase. In this phase, the molecules on the average align themselves normal to the layer planes with no positional correlation among the molecular centre of

mass within a layer [figure 1.5]. Such a configuration can be described by considering a one-dimensional mass density wave along the layer normal. However, this modulation is quasi long range in character, i.e., it ceases on a relatively large scale due to the presence of thermal agitations. Moreover, the molecules are mobile within the layers and also can rotate freely about the molecular long axis. Thus, Sm-A phase can be regarded as a two dimensional

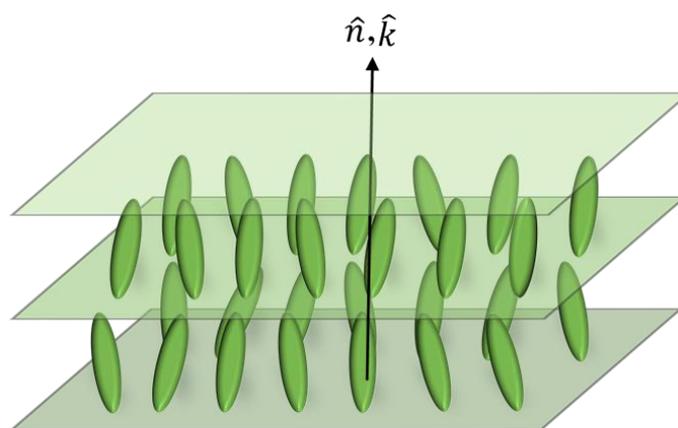


Figure 1.5. Schematic representation of molecular ordering in smectic A phase. The director \hat{n} is parallel to the smectic layer normal \hat{k} .

fluid. This phase is optically uniaxial with the optic axis being along the direction of the molecular long axis. Depending on the correlation between the interlayer spacing (d) and molecular length (l), the smectic A phase again can be classified into various sub-phases as monolayer smectic A (Sm-A₁) with $d = l$, bilayer smectic A (Sm-A₂) with $d = 2l$, partially bilayer smectic A (Sm-A_d) with $l < d < 2l$ and the smectic antiphase (Sm- \tilde{A}) [39–42].

Smectic C (Sm-C) phase

On lowering the temperature of Sm-A phase, the smectic C (Sm-C) phase is often formed which possesses a structure much similar to that of Sm-A phase, i.e., consisting of fluid-like layers with no positional correlation within the layers but in this case the molecular long axis and hence, the director is tilted relative to the layer normal at an angle θ , which is again common for all the molecules [figure 1.6]. This angle is referred to as the tilt angle and is

usually found to be dependent on temperature. The fact that the molecules are tilted with respect to the layering direction in the Sm-C phase causes the breaking of the infinite-fold rotational symmetry of the molecules about their long axis, as occurs in the Sm-A phase and hence, the Sm-C phase exhibits optical biaxiality and a relatively greater viscosity than that in the Sm-A phase. Furthermore, the tilted molecular arrangement in the Sm-C phase is also energetically more favorable than the orthogonal molecular organization in the Sm-A phase. Depending on the relative arrangement of the molecules in the neighboring layers, the Sm-C phase can be categorized into two distinct classes – the synclonic smectic C (Sm-C_s) phase and the anticlinic smectic C (Sm-C_a) phase. In the Sm-C_s phase, the direction of the tilt is the same in adjacent smectic layers, whereas it alternates between the layers of the Sm-C_a phase.

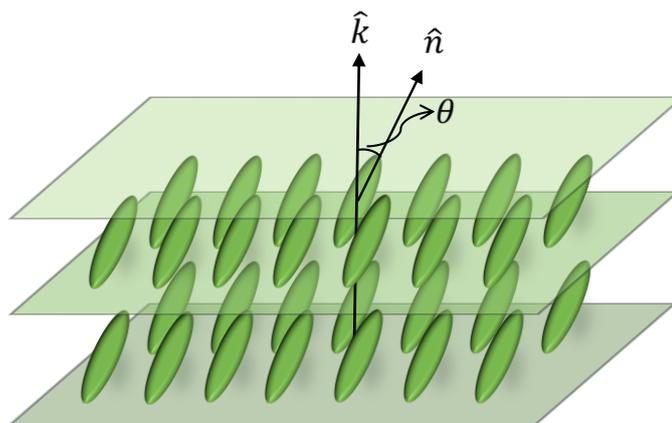


Figure 1.6. Schematic representation of molecular ordering in smectic C phase. The director \hat{n} is tilted with respect to the smectic layer normal \hat{k} by an angle θ .

Moreover, in addition to the above smectic phases, if the molecules are optically active (having no reflection symmetry), the chiral analogue of the Sm-A and Sm-C phases known as the chiral smectic A (Sm-A*) and chiral smectic C (Sm-C*) phases respectively, are formed.

Chiral Smectic A (Sm A*) phase

In this phase the molecules are packed in layers with their molecular long axis being parallel to the layer normal and at the same time also rotate in a

liquid-like fashion around the layer normal [43–45]. As there is no correlation among the molecules in a smectic layer, the net transverse polarization vanishes. Hence, in spite of being made up of chiral molecules, the Sm-A* is apolar in nature.

Chiral Smectic C (Sm C*) phase

The smectic C* phase is similar to the smectic C phase except for the fact that due to the presence of chirality in the molecular structure, the tilt direction of the molecules precesses around the layer normal from one layer to another [figure 1.7], giving rise to a helicoidal structure [46–50]. The pitch of this helical deformation is relatively greater than the interlayer spacing. The chirality present here, suppresses symmetry and R. B. Meyer *et al.* on the basis of symmetry considerations, first argued and demonstrated that the layers of the Sm-C* phase are ferroelectric in nature [46], i.e., there exists a non-zero spontaneous polarization (\hat{P}_S) for each layer in a direction perpendicular to the tilt plane and the layer normal. However, because of the presence of the helix as the direction alters from one layer to another, there exists no net macroscopic polarization. To facilitate a non-zero macroscopic polarization, the helix must have to be unwound by means of an external electric field or via surface interactions [51–54]. The Sm-C* phase again can be grouped under the following headings: Sm-C _{α} *, Sm-C*, Sm-C _{γ} * and Sm-C _{β} * in order of decreasing temperature [55–57]. Here, except for Sm-C _{α} * phase, in all other phases the helicoidal structure is formed because of the presence of chirality while in the Sm-C _{α} * phase non-chiral interactions are responsible for the formation of helices while chirality helps only in deciding their sense of twist [58]. There is also an antiferroelectric variant of the chiral smectic C phase – Sm-C_A* phase. In the Sm-C_A* phase, the direction of tilt alternates in adjacent layers and hence, the direction of spontaneous polarization also alternates from one layer to the next, canceling out the total polarization. However, the polarization can be aligned uniformly between the layers on applying a strong

external field. One intriguing fact is that in LCs the antiferroelectric Sm- C_A^* phase appears at a lower temperature than that of the ferroelectric Sm- C^* phase while an opposite trend is detected in solid state materials.

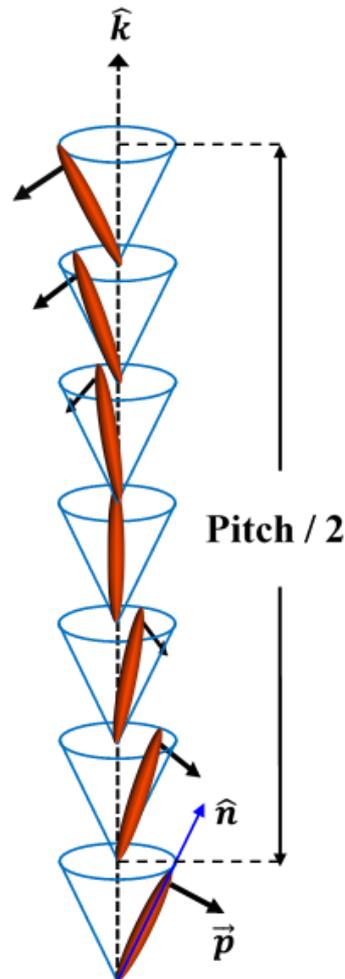


Figure 1.7. Schematic representation of the helical structure of chiral smectic C (Sm- C^*) phase with the helix axis parallel to the smectic layer normal \hat{k} . The molecular dipole moment \vec{p} is always perpendicular to the director \hat{n} .

There are also many other smectic variants with a variety of ordering as the hexatic smectic phases – Hex- B , Sm- F , Sm- I and Sm- L with a long range bond orientational order but short range positional order within the smectic layers; the crystal- B or Sm- B_{cry} and crystal E or Sm- E with a true 3D crystalline arrangement (long range positional and bond ordering) and the related tilted phases – smectic G (Sm- G), smectic H (Sm- H), smectic J (Sm- J), smectic K (Sm- K) [1, 7, 17].

1.2.4. Bent-core liquid crystals

The basic molecular structure of liquid crystalline materials can be modified in number of ways to give rise to new mesogenic features. An excellent example of which is the bent-core or banana-shaped or bow-like mesogens, representing a relatively new sub-field of liquid crystals. In calamitic and discotic LCs, a free rotation of the molecules about their long molecular axis or normal to the disc respectively is permissible without requiring any special symmetry consideration. This fact reduces the possibility for bent-shaped molecules to be a ‘good’ candidate for forming liquid crystal phases as in this case a free rotation of molecules about their long axis leads to a large excluded volume. D. Vorländer and his group were successful to report the first ever synthesis of several bent-core liquid crystals [59, 60]. However, their work had not paid much attention until the seminal work of Matsunaga *et al.* in the early 1990s [61–64] and the subsequent discovery of polar switching in one of the smectic phases (B_2 phase) in an achiral bent-core compound by Niori *et al.* [65]. The discovery of exceptional mesogenic properties and also the occurrence of exotic mesophase sequences in the bent-shaped compounds have brought them at the focus of scientific attention, unveiling a fascinating new domain in the branch of thermotropic liquid crystals.

The banana-shaped molecules are usually achiral, consisting of a rigid, non-linear core of aromatic rings with meta-substituted central ring; side linking groups and terminal chains [figure 1.8]. Here the meta-substituted central aromatic ring serves as the origin of the shape non-linearity of the molecular structure. Furthermore, such molecules may also consist of odd numbered non-cyclic spacer units, forming the twin mesogens. It has been found that in such twins, the phase characteristics are strongly dependant on the relative length of the spacer and terminal chains. Depending on the position of the structural bend, the banana-shaped molecules again may be symmetric or asymmetric and it is usually the nature of the substituents as well as their

location in the structure, which play a key role in determining the basic structural and mesogenic features of these compounds.

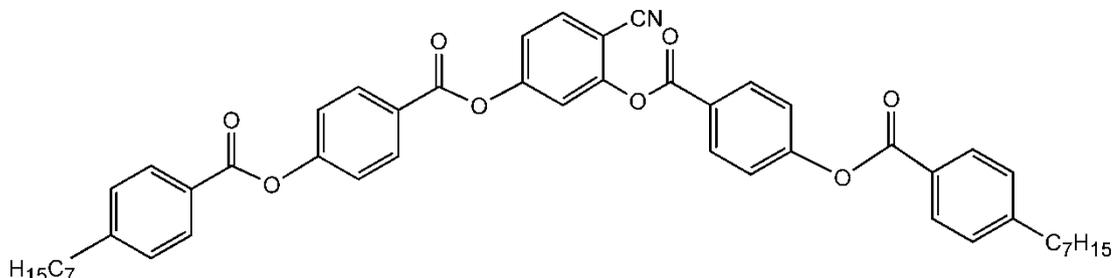


Figure 1.8. Molecular structure of one of the bent-core compounds under study [compound **1/7** (described in chapter 3)].

These unique structural characteristics as well as the related interaction among the bent mesogenic molecules give rise to a number of new mesophases, finding no counterpart in the field of calamitic LCs. The most remarkable of them are a group of columnar and smectic phases, termed as the *B* phases – the series B_1 to B_8 in the chronological order of their discovery [18, 19, 66]. These names were proposed at the workshop on banana-shaped liquid crystals held in Berlin in 1997. However, later, as some of these *B* phases have been appeared to embrace a variety of structures and symmetries, this nomenclature has been discarded being rather confusing. Then it has been decided to use the same terminology for bent-core mesophases as those used for calamitic liquid crystals along with further characters and suffixes and as well mentioning the space group of those phases for incurring the detailed information. It has also been observed that despite the presence of bend in these molecules, carefully chosen delicate modifications in molecular structure may yield calamitic like polymorphisms involving classical smectic *C*, smectic *A* and even nematic phases [26–28, 32, 67–76]. Besides, in recent years, a rich variety of exotic mesophases with diverse molecular ordering as the dark conglomerate phase [2], polar smectic *A* (*Sm-AP*) phase [77–80] etc., have also been revealed in them.

The reasons behind the formation of such group of exceptional mesophases with outstanding phase-structure and related mesophase sequences are primarily two-fold:

First, for bent-core molecules one can define two directors – one \hat{n} , along the long molecular axis and another one in the direction of the bow, \hat{m} [figure 1.9]. Under steric conditions and also owing to the kinked shape of the bent-molecules, they undergo a periodic potential while translating through the neighboring molecules, causing breaking of the translational symmetry along the molecular long axis. At the same time, there also exists a rotational hindrance about the director \hat{n} to reduce the excluded volume effect. Hence, the molecules tend to arrange themselves into planes in a smectic like manner with the ‘bow-axis’ \hat{m} aligned along a common direction. Since, the layer normal \hat{k}

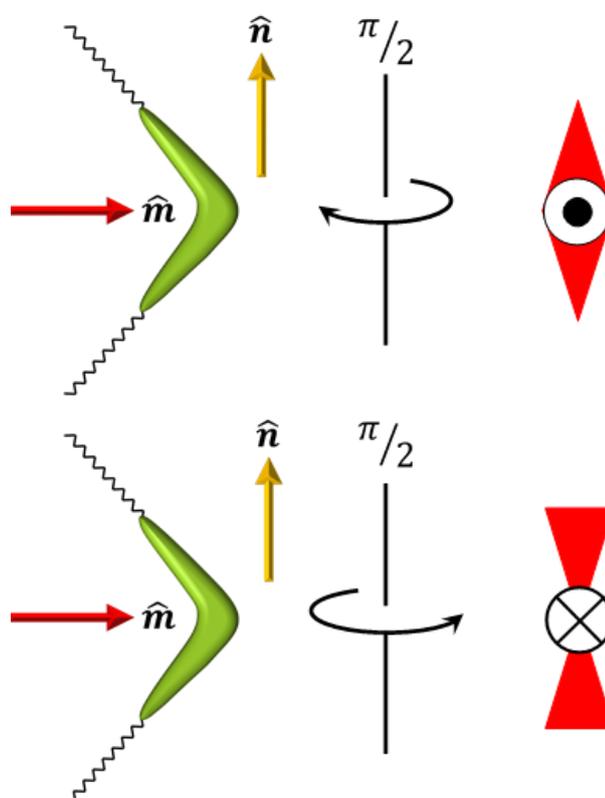


Figure 1.9. Schematic diagram of a bent-core molecule and its symbolic representation for observation from front and back sides. \hat{n} represents the unit vector along the direction of the molecular long axis, \hat{m} denotes the unit vector along the molecular kink-direction.

defines a direction independent of \hat{n} and \hat{m} , a large variety of mesophases (e.g., B_1 – B_8 phases) with dissimilar symmetries result.

Secondly, if the molecule possesses a dipole moment along the bend-direction, the lateral correlation of the molecular dipoles yields a polar order within the layers, which can be switched on applying an electric field. This in effect leads to the formation of molecular monodomains with a significant macroscopic spontaneous polarization. Additionally, if the molecules are tilted within the layers, a combination of tilt direction and polar vector can give rise to layer chirality even though the individual molecules are not optically active themselves [18–20, 81–83]. Thus, by utilizing the structural feature, i.e., the angular non-linearity existing in the central molecular unit, the bent molecules may give rise to a number of unusual smectic modifications with ferroelectric, antiferroelectric or ferrielectric properties and even unique chiral mesophase morphologies regardless of the occurrence of molecular domains of equal numbers of opposite handedness.

In the following section, the structural aspects of few of the liquid crystal phases appearing in bent-core compounds will be discussed in brief.

Fundamental mesophases of bent-core liquid crystals

Mesogenic molecules with symmetrical geometries enjoy the advantage of free rotation around their long molecular axis and related reduction in their free energy. Conversely, for bent-core molecules, because of the excluded volume effect, such a decrease in free energy is usually manifested by hindering their rotation in terms of their unique packing capabilities. In accordance with the theory developed by Brand *et al.* [84], there are four possible ways of organizing the bent-core molecules within the layers of

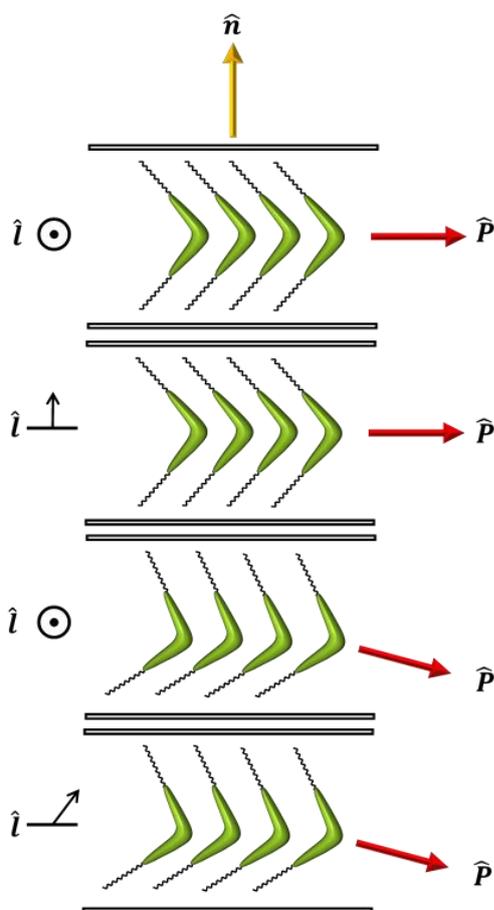


Figure 1.10. Schematic representation of different possibilities of packing of bent-core molecules within the layers. \hat{n} : Smectic layer normal, \hat{l} : molecular plane normal, \hat{P} : layer polarization; (a) \hat{n} is perpendicular to both \hat{l} and \hat{P} ; (b) \hat{n} is perpendicular to \hat{P} , but not to \hat{l} ; (c) \hat{n} is perpendicular to \hat{l} , but not to \hat{P} ; (d) \hat{n} is neither perpendicular to \hat{P} nor to \hat{l} [85].

smectic phase. They are-

- i. An orthogonal arrangement of smectic layer normal (\hat{n}) with the molecular plane normal (\hat{l}) and polarization direction (\hat{P}) being parallel to the layers. This corresponds to C_{2v} symmetry.
- ii. The molecular long axis is tilted relative to the layer normal (\hat{n}), indicating the appearance of monoclinic chiral symmetry C_2 .
- iii. Both the molecular long axis and molecular layer plane are tilted leading to a monoclinic symmetry C_s .

- iv. Appearance of a triclinic arrangement with all the three principal directions being tilted, the corresponding symmetry being chiral C_1 .

These four possibilities are schematically depicted in figure 1.10. Phase corresponding to case (iv) was first predicted by de Gennes [1] and the related symmetry is often termed as C_G , where G means generalized. In the following section, few of the basic liquid crystal phases exhibited by bent-core molecules are discussed.

1.2.4.1. Smectic phases of bent-core liquid crystals

B_1 phase

The B_1 phase consists of a rectangular lattice with two periodicities, in the plane and perpendicular to the polarization (\hat{P}_z) direction and hence, can be regarded as a columnar mesophase [figure 1.11]. This phase can be considered as made up of columns of fragments, formed from parallel aligned bent-core molecules in such a way that the direction of polarization in the neighboring fragments is antiparallel to one another. Hence, the net polarization in this

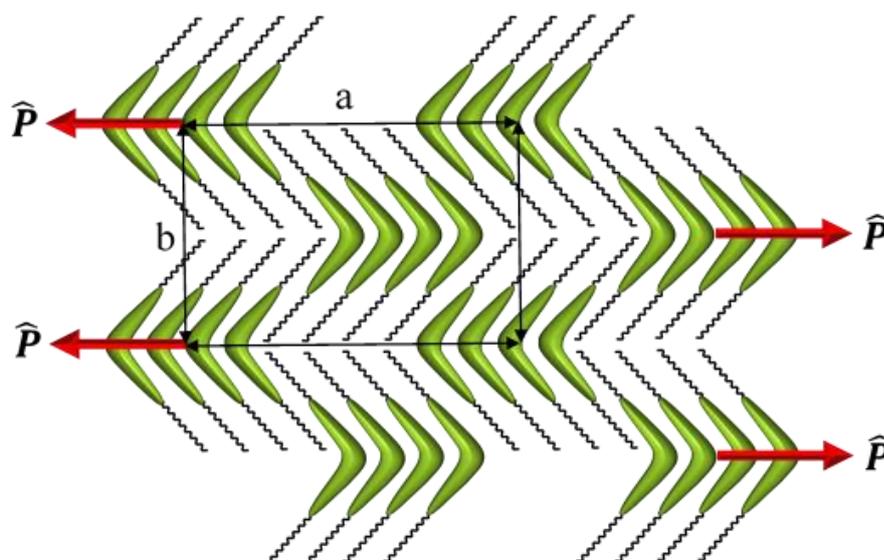


Figure 1.11. Schematic representation of molecular organization in B_1 mesophase. a and b give the measure of periodicities in the two perpendicular directions.

phase vanishes and no field-induced switching behavior is observed in the usual B_1 phase. The conventional X-ray diffraction pattern in this phase consists of a diffuse wide-angle scattering, implying liquid-like intralayer order. Several sharp reflections have also been observed in the small angle region, indicating the existence of a 2D frustrated layer structure [18, 19]. There are also reports of novel 2D modulated variants of B_1 mesophase with a structure varying much from the conventional one [86–89]. They are designated as the $B_{1\text{rev}}$ and $B_{1\text{revtilt}}$ phases, where the second one is the tilted version of the former. Unlike the normal B_1 phase, both of these phases can be switched by applying an electric field.

B_2 phase

The B_2 phase, which is also termed as the Sm- CP phase, is the most widely investigated among the mesophases formed by the banana-shaped molecules. Here, the molecules are uniformly arranged within layers and tilted with respect to the smectic-layer normal, leading to a structure with C_{2v} symmetry, wherein a spontaneous polarization emerges along the direction of the two-fold symmetry axis. Hence, the smectic layers in B_2 phase demonstrates macroscopic spontaneous polarization normal to the molecular tilt plane, which again can be switched on reversal of an applied electric field.

On entering the B_2 phase from the disordered isotropic liquid, actually there are three simultaneous breaking of symmetries, leading to the appearance of smectic layering, polar order and clinicity [82]. Now, depending on the structure of polar order in the adjacent smectic layers, i.e., whether they are ferroelectric (corresponding notation being P_F) or antiferroelectric (P_A) and clinicity of molecules, i.e., whether molecular arrangement is synclinic (C_S) or anticlinic (C_A), four different variants of Sm- CP or B_2 phase may appear [figure 1.12]. Following the notations introduced by Link *et al.* [82], they are Sm- $C_S P_F$, Sm- $C_A P_F$, Sm- $C_S P_A$, and Sm- $C_A P_A$ [28–30]. Here, Sm- $C_S P_F$ and Sm- $C_A P_F$ are ferroelectric in nature while Sm- $C_S P_A$ and Sm- $C_A P_A$ are

antiferroelectric. Moreover, the two structures, $\text{Sm-C}_S P_F$ and $\text{Sm-C}_S P_A$ possess synclinic molecular arrangement while the rest two possess anticlinic molecular arrangement. One intriguing difference between calamitic and bent-core chiral smectic phases is that in case of bent-core molecules, the polarization and tilt directions are not interrelated [19]. In bent-core molecules, an alteration in polarization or tilt direction indicates corresponding change in layer chirality, where the chirality of the successive layers may either be identical (homogeneously chiral) or alternating (racemic). Among the stated four Sm-CP phases, $\text{Sm-C}_S P_F$ and $\text{Sm-C}_A P_A$ consist of layers of same chirality while the other two, i.e., $\text{Sm-C}_A P_F$ and $\text{Sm-C}_S P_A$ are racemic in nature. The ground state of Sm-CP or B_2 phases of banana-shaped molecules is usually antiferroelectric in nature.

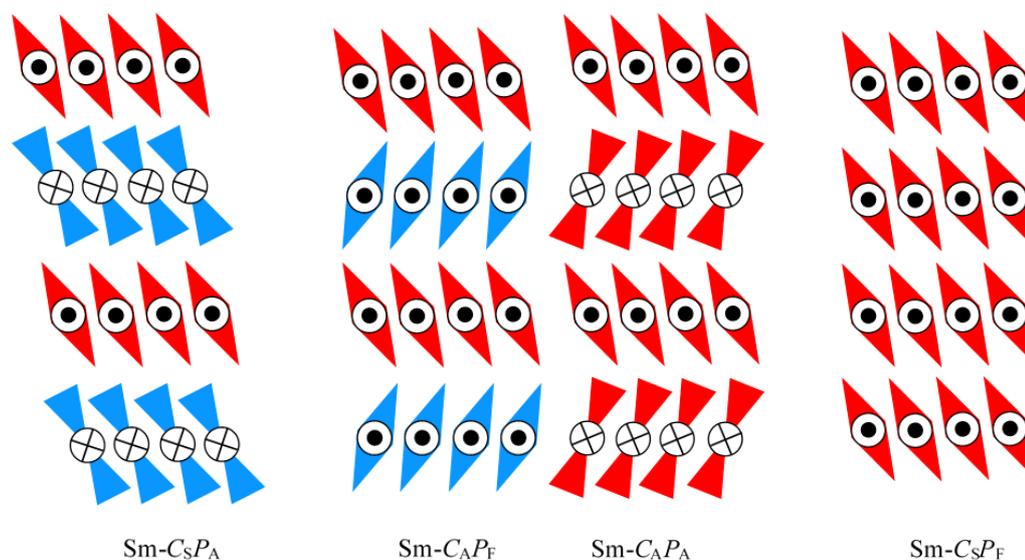


Figure 1.12. Schematic representation of molecular arrangements in the four fundamental variants of Sm-CP phase. From the left the first two structures are racemic in nature while the rest two are homogeneously chiral.

The X-ray diffraction pattern of a well-aligned B_2 sample consists of sharp layer reflections, up to third or fourth order on the meridian and a diffused wide angle scattering, suggesting the absence of in-plane order [18, 19]. Moreover, the maxima in the wide angle scattering are inclined relative to

the meridian and the equator, which indicate the tilted configuration of molecules in the B_2 phase.

B_3 phase

B_3 phase generally appears on cooling the B_2 phase and above the B_4 phase. It possesses textural similarity to B_2 phase on rapid cooling from the same. However, on slow cooling, difference appears between the two textures in the form of breaking of domains. The X-ray diffraction pattern of a non-oriented B_3 sample exhibits a number of sharp reflections in the wide-angle as well as in the small angle region, suggesting a crystalline structure of this phase [18]. However, outcomes from dielectric [90] and terahertz spectroscopy [91] reveal that the dynamics in B_3 phase is similar to that in B_2 phase, indicating a higher-ordered smectic like nature of B_3 phase. Furthermore, from an analysis of the X-ray diffraction pattern of oriented planar domain of B_3 sample, the layer spacing in this phase has found to be shorter than the molecular length of all *trans*-conformation [19]. This fact and also the appearance of texture with high optical birefringence in the homeotropic alignment, indicate a probable tilted molecular arrangement in this phase.

B_4 phase

The B_4 phase is also termed as the smectic blue phase because of the appearance of dark blue colored domain texture when viewed under crossed polarizing optical microscope [92, 93]. On decrossing the polarizers, domains of different brightness appear which again interchange their brightness on rotating any of the polarizers in clockwise and anticlockwise directions [94]. Such a brightness exchange is due to the optical activity of the medium, indicating a chiral structure of this phase.

The B_4 phase generally appears on cooling the B_3 or B_2 phase. X-ray diffraction patterns in this phase indicate the existence of smectic-like layering and an in-plane order with correlation length smaller than that in the B_3 phase

[19]. Moreover, the layer spacing has been found to be comparable to the molecular length suggesting a non-tilted organization of molecules in this phase [92]. Despite the fact that B_4 phase is non-switchable, simple harmonic generation (SHG) signal was detected in this phase even in the absence of any external electric field, implying the molecules are non-centrosymmetrically ordered [95, 96]. Furthermore, recent freeze-fracture transmission electron microscopy (FFTEM) studies shows that the B_4 phase is made up of twisted layers of molecules which are again assembled to form chiral nano-bundles [97]. For the presence of such structures, this phase is also frequently designated as the helical nano-filament (HNF) phase. This HNF phase is also much attractive because of its unique nanostructure in which the further self-organization of the filaments leads to the formation of oriented arrays of filaments that are phase coherent relative to their twist [98, 99]. During the growth of such arrays, the chirality of the filaments has found to be preserved, the filaments those are already present controls the handedness of the new-born filaments [100].

B_5 phase

The B_5 phase is much similar to the B_2 phase, except for the appearance of an additional in-plane positional ordering in the former case [figure 1.13]. The B_5 phase appears on cooling the B_2 phase and the related transition enthalpy is small [18, 83, 101]. Both the B_2 and B_5 phases demonstrate similar textural appearance and electro-optical response. However, the wide-angle region of X-ray diffraction pattern in the B_5 phase is more complex than that in the B_2 phase. For an oriented B_5 sample, the X-ray diffraction profile consists of additional scattering peaks at wide-angle region perpendicular to the small-angle layer-reflection, indicating the appearance of in-plane density waves within the smectic layers, which again has been described by considering the existence of a 2D rectangular lattice within the layers [18, 83, 101].

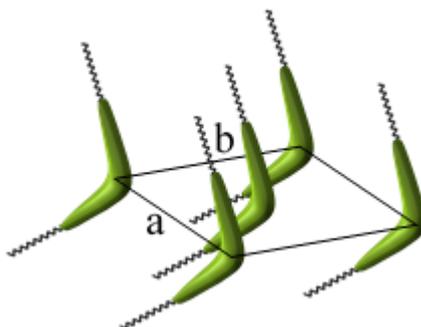


Figure 1.13. Schematic representation of the in-plane molecular packing in the B_5 phase [19]. Vectors **a** and **b** suggest the presence of in-plane order.

B_6 phase

The B_6 phase consists of an intercalated smectic structure along with the absence of any in-plane correlation among the molecules within a layer [figure 1.14]. In general, B_6 phase has been found to exhibit a fan-shaped texture reminiscent of the texture in the Sm-A phase of calamitic molecules [71]. However, it is much difficult to obtain a homeotropic alignment in this phase. X-ray diffraction measurements in an aligned B_6 sample reveals the existence of only first order reflection in the small angle region in the diffraction pattern, indicating the presence a periodicity less than half the molecular length i.e., an

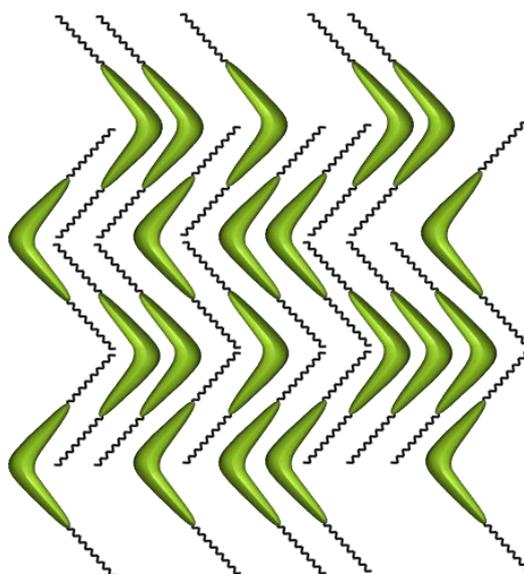


Figure 1.14. Schematic representation of molecular ordering in the B_6 phase.

interdigitation of the molecules [18, 102]. Furthermore, the X-ray diffraction profile at the wide-angle region has been found to comprise four broad diffuse peaks, suggesting the presence of an in-plane liquid-like order while the inclination between the neighboring diffuse peaks corresponds to a tilted arrangement of molecules in this phase [18, 102].

B_7 phase

The B_7 phase appears below the isotropic phase during cooling and is much attractive for the occurrence of a rich variety of textures in this mesophase. The textural appearance of B_7 phase includes a variety of spiral domains, twisted helical filaments with single, double or triple coils, high- and low-birefringence focal conics, lancet-like or thread-like germs, Chiral micromosaic domains, checker-board-like domains, banana-leaf-like domains, circular domains and many more [103–109]. The appearance of the helical filaments suggests the presence of chirality in this phase [104].

X-ray diffraction studies in B_7 phase reveals a diffraction profile consisting of diffuse broad scattering at the wide-angle region, indicating lack of in-plane order and several sharp reflections in the small-angle region [103, 107, 110, 111]. Such unique profile has been accounted for by considering a 2D ordered modulated layer structure caused by the polarization splay [110]. Moreover, Small Angle X-Ray Studies (SAXS) in this phase suggests a B_1 like columnar structure comprising a 2D rectangular lattice [18, 86, 112, 113].

On application of an electric field, the B_7 phase usually exhibits a ferroelectric-like bistable switching a few degrees below the B_7 –isotropic transition, which again has been found to convert into a tristable process on lowering the temperature [103].

B_8 phase

The B_8 mesophase is relatively newer among all the B phases and was first reported by Bedel *et al.* in 2001 [66]. Upon slow cooling from isotropic

phase, the textures of B_8 phase grows as spiral domains and may convert into fan-shaped texture on further lowering of temperature. X-ray diffraction studies in B_8 phase suggests a bilayer structure of this mesophase [66]. This phase demonstrates an antiferroelectric switching behavior.

Sm-A, Sm-C and Sm-AP phases

Depending on the structural features, bent-core molecules are usually found to possess a bending angle ranging between 105° and 140° [114]. Molecules for which this bending angle resides in the neighborhood of the stated upper limit, tends to form the traditional Sm-A and Sm-C phases as appeared in rod-like liquid crystals. In the Sm-A and Sm-C phases of bent-core mesogens, the molecular long axis is parallel to the layer-normal and inclined at an angle to it respectively along with the absence of any in-plane periodicity or polar order. The textural appearance of a Sm-A bent-core sample consists of a fan-shaped texture or a homeotropic texture while for a Sm-C compound it comprises a broken fan-shaped texture or a schlieren texture. Due to the absence of any in-plane polar order, no ferroelectric switching can be realized in the bent-core Sm-A phase [114, 115]. However, dielectric studies in the bent-core Sm-C phase reveal the existence of short range ferroelectric clusters in the medium, leading to a weak switching response on application of an external field [114, 115].

The polar smectic A (Sm-AP) phase in bent-core liquid crystals may be treated as the orthogonal complement of the B_2 or Sm-CP phase. This phase is similar to the Sm-A phase as observed in rod-like liquid crystals except the appearance of an in-plane polar order owing to the close packing of the bent-core molecules [77–80]. Depending on the relative orientation of the polarization \vec{P}_s in subsequent smectic layers in Sm-AP phase, two possible situations may arise: a parallel orientation of \vec{P}_s in successive layers leading to the ferroelectric polar smectic A (Sm-AP_F) phase, while a repeated alteration of

alignment of \vec{P}_s in consecutive layers leads to its antiferroelectric counterpart, i.e., the Sm- AP_A phase [figure 1.15]. The Sm- AP_A has usually been found to form the stable ground state [77–79] whereas the Sm- AP_F phase has appeared to be a metastable one which can be induced by applying an electric field and reverts to the Sm- AP_A phase on removal of the field. However, recently a stable Sm- AP_F phase has also been reported by Reddy *et al.* [80]. For a homogeneously aligned Sm- AP sample, a fan-shaped texture typical for the Sm- A phase appears while homeotropically aligned Sm- AP samples are found to exhibit schlieren textures because of the presence of phase-biaxiality [78, 79]. The X-ray diffraction pattern of this phase consists of layer reflections on the meridian in small-angle region and diffuse wide-angle scattering centered on the equator, confirming the orthogonal configuration of the molecules within the smectic layers [20]. Furthermore, the switching process in the Sm- AP phase is quite slow because of the presence of steric hindrance to the rotation of molecules around their long molecular axes by the adjacent molecules.

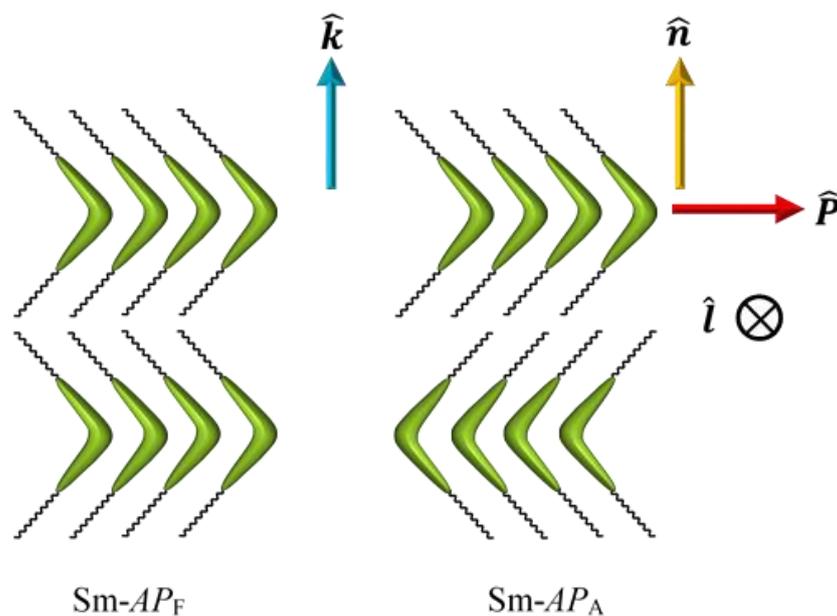


Figure 1.15. Schematic representation of molecular arrangements in the ferroelectric Sm- AP_F and antiferroelectric Sm- AP_A phases.

1.2.4.2. Nematic phase of bent-core liquid crystals

Nematic (N) phases are relatively scarce among the mesophases formed by banana-shaped compounds. This is because the translational symmetry required for the formation of N phases, is strongly frustrated by the kinked shape of the banana molecules. Hence, in order to restrict the molecules from aggregating into smectic layers, molecules with special structural characteristics have to be synthesized. This can be achieved in bent-core molecules with a rather extended aromatic core and shorter terminal chains as in different bent oligophenyleneethylenes [116, 117], *m*-terphenyls [71], and naphthalene derivatives [72–75], or by reducing the molecular-bend as obtained in 5-membered heterocycles, like oxadiazoles [26–28, 32, 67] or dimesogens composed of rod-like and bent-units [68, 118–120].

The most noteworthy difference between the nematic phases formed by the calamitic and bent-core molecules is the existence of short-range ‘cybotactic’ clusters with smectic-like layered structure [figure 1.16] in the later case [31–38]. The evidence of such clustering has also been detected in nematic phase formed by calamitic molecules [30], but, here they appear only before the smectic–nematic transition as a part of the pretransitional modification in the concerned mesogenic medium. In bent-core nematics, where the high lateral correlation among the bent-molecules favors the formation of such structural aggregates, they persist as an inherent part of the nematic phase structure. In some cases they are even found to exist in the isotropic phase as well [37]. X-ray diffraction studies in bent-core nematic phase have conclusively validated the presence of such clusters [32, 35, 36]. Furthermore, although the clusters are biaxial in nature, on a macroscopic scale their effect average out, resulting in a uniaxial nematic medium.

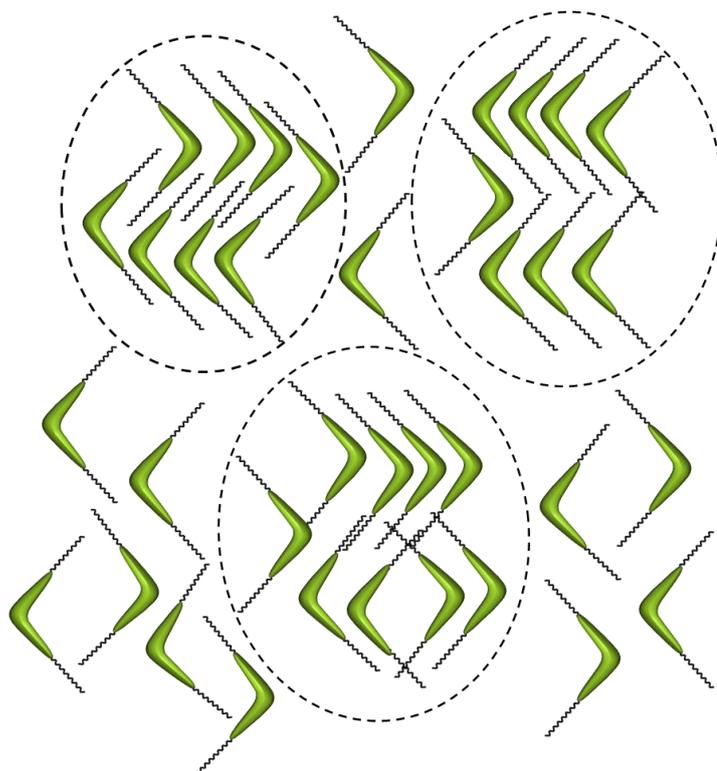


Figure 1.16. Schematic representation of molecular arrangement in the nematic phase of bent-core liquid crystals comprising smectic-like clusters.

Such a clustering again possesses a pronounced influence on the phase characteristics of bent-core nematics. As in some bent-core nematics the clustering was assumed to be responsible for the emergence of dramatically higher rotational viscosity values than that for usual calamitics [121, 122]. Actually, the unique molecular conformation of the bent-core molecules and also the appearance of the smectic-like aggregates in the nematic phase, endows the bent-core nematics with a number of unique properties such as great flexoelectricity [123, 124], extraordinary electroconvection patterns [125–127], a considerable Kerr effect [128], unique rheological properties [34, 121, 122] etc., none of which are observed in normal nematic phases formed by rod-like molecules. Recently, intense research work is focused on the quest for the elusive biaxial nematic phase in bent-core molecules, which holds promising technological answers in the field of high end display devices. Another important feature of the bent-core liquid crystal which is also at the center of attention in the liquid crystal research, is the twist-bend nematic phase [129–

136]. This twist-bend structure can find potential applications in tunable diffraction grating and in reflective display etc. Such a rich set of characteristics explores the potential for new applications in the area of electro-optic device technology. Some of the major issues and challenges for researchers in this field include a deeper insight into the origin of ferroelectric-like switching behavior in cybotactic nematic phase of bent-core liquid crystals, conclusive experimental proof of the existence of the biaxial nematic phase in bent-core molecules, realization of room temperature cybotactic nematic phase in bent-core liquid crystals with a potential for practical application. Thus further studies of cybotaxis in bent-core nematics in conjunction with the possibility of tuning the nano-scale polar ordering, could possibly lead to new liquid crystal based applications.

1.2.5. Hockey stick-shaped liquid crystals

In recent years, an interesting class of mesogenic compounds with a shape intermediate between the classical rod-like molecules and the conventional banana-shaped mesogens, the ‘hockey stick-shaped’ compounds [figure 1.17], has emerged as a field of significant interest. This class of molecules is asymmetric in relation to the position of bend in their molecular structure, i.e., the two arms of the bent-structure are significantly different with respect to their lengths. In hockey stick-shaped molecules having a bent aromatic core, the angle of the molecular long axis results from a 1,3-phenylene fragment or 2,5-disubstituted heterocyclic five-membered ring in strongly non-symmetric four or five-ring aromatic systems [137–142]. In another type of hockey-stick mesogens – which is in relation to the type presented in this dissertation – the bend is introduced by an alkyl or alkyloxy chain attached in the *meta*-position of a terminal phenyl ring [143–150]. Depending on the sizes of the segments and constituents of the moiety presents in the segments, these molecules are again able to form a number of distinct mesophase morphologies [147, 150]. Some of these compounds are of

considerable interest due to the occurrence of two polymorphic tilted smectic phases – the synclonic smectic *C* (*Sm-C_s*) as well as the anticlinic smectic *C* (*Sm-C_a*) phase [138, 144]. This dimorphism is only rarely observed for mesogens having no asymmetric carbon atom except for the case wherein the terminal chain is a branched chain (swallow tailed) [151, 152]. From NMR investigations it has been confirmed that in hockey stick-shaped compound the *Sm-C_s*–*Sm-C_a* phase transition is accompanied by a conformational change in the overall molecular shape from a more rod-like one in the *Sm-C_s* phase to a hockey stick like shape in the *Sm-C_a* phase and leads to a different packing of the molecules within the layers of the *Sm-C_a* phase. Recent discovery of a rich set of exotic phenomena in such asymmetric bent-shaped molecules, such as the occurrence of nematic phase displaying both calamitic and bent-core-like features [153], the macroscopically chiral nematic and dark conglomerate phases [154], a dark conglomerate phase consisting of randomly oriented smectic blocks, called the random grain boundary (RGB) phase [155], the coexistence of two different molecular tilts at the *N*–*Sm-C* transition [156], a layer thinning transition [157] etc., also makes them potential candidate for designing future noble materials with desirable functional characteristics and obtaining further insight into the phenomena of self-organization in liquid crystals.

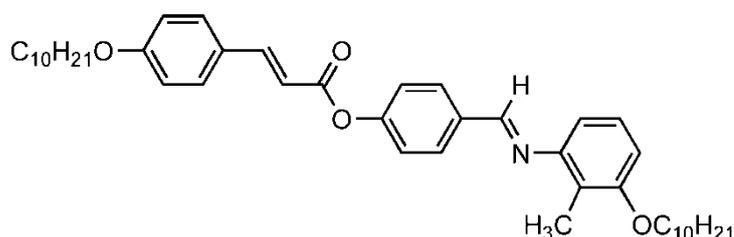


Figure 1.17. Molecular structure of one of the hockey stick-shaped compounds under study [compound **4** (described in chapter 4)].

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