CHAPTER I

Introduction to liquid crystals: phase types, structures and applications

I. 1 Introduction

Liquid crystal (LC) phases represent a unique state of matter characterized by both mobility and order on a molecular and at the supramolecular levels. This behaviour appears under given conditions, when phases with a characteristic order intermediate to that of a three dimensionally ordered solid and a completely disordered liquid are formed. Molecules in the crystalline state possess orientational and three dimensional positional orders. That is the constituent molecules of highly structured solids occupy specific sites in a three dimensional lattice and points their axes in fixed directions as illustrated in Fig.1.1a. Liquid crystal phases possess orientational order (tendency of the molecules to point along a common direction called the director **n**) and in some cases positional order in one or two dimensions as shown in Fig I.1b and I.1c. On the other hand, in the isotropic liquid state, the molecules move randomly and rotate freely about all possible directions (see Fig. I.1d). Thus, liquid crystals (LCs) have been defined as "orientationally ordered liquids" or "positionally disordered crystals" that combine the properties of both the crystalline (optical and electrical anisotropy) and the liquid (molecular mobility and fluidity) states [1]
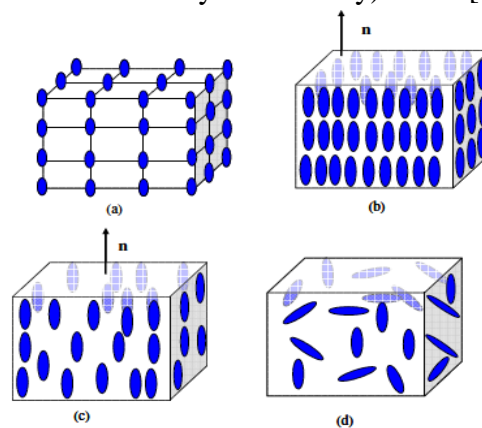
Figure I. 1 Schematic representation of molecular packing in the a) crystals b & c) liquid crystals and d) liquid state.

1. 2. Classification of liquid crystals

The liquid crystal state(s) can be attained either by the action of heat on mesogens or by action of solvent on amphiphilic systems. The mesophases obtained by temperature variation are called *thermotropic*. Thermodynamically stable mesophases which appear both on heating and cooling are termed *enantiotropic*, while the thermotropic mesophases that appear only on cooling are *monotropic*. On the other hand, LC phases formed by dissolving the compound in an appropriate solvent (under given concentration and temperature conditions) are known as *lyotropic*. Besides, there are some molecules that exhibit LC phases under the influence of both heat and solvent; such systems have been referred to as amphotropic. Lyotropic LC phases are frequently encountered in everyday life, and most importantly, life itself is critically based on such ordered fluids. Despite the significance of lyotropic LCs, thermotropic LCs have claimed a relatively greater attention, firstly because they are simple to realize and handle and secondly they serve as an important medium in fabricating low-power display devices. Notably both kinds of LCs, in part, have facilitated to improve our understanding of the supra molecular chemistry driven by secondary interactions [2]. The classification of mesogens and mesophases has been always a complicated task; this is because over the last two decades a rich variety of mesophases have been discovered through conventional or nonconventional or new molecular architecture. Nonethless, some basic principles are followed to categorize them. First and foremost, as mentioned above, they are fundamentally classified as being either *thermotropic* or *lyotropic* given the fact that the method of their realization and therefore, the resulting mesomorphism differs

significantly. In particular, the mode of mesophase formation in thermotropics is by the organization of the individual molecules in contrast to the lyotropics, wherein the constituent (solute) molecules firstly aggregate and these fine structures then form different mesophases that generally depend on the temperature and concentration [3,4]. Besides, there are different ways to classify these materials: for example in terms of their structure (into amphiphilic and non-amphiphilic molecules), molecular shape (calamitic, discotic and banana mesogens etc.), molecular size (as low-and high molecular weight compounds) and with respect to the type of mesophase formed (nematic, cholesteric, smectic, columnar, and cubic mesophase etc.). Since the thesis is concerned with thermotropic LCs only a very brief discussion is provided on lyotropic LCs.

1. 3. Lyotropic liquid crystal

Compounds forming lyotropic mesophases usually consist of a flexible lipophilic chain (the tail) and a polar (ionic or non-ionic) head group.
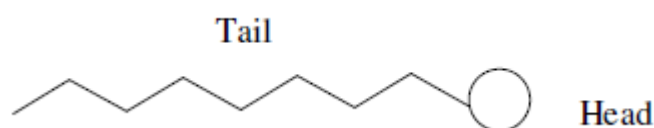
Tail

Head

Tail is an alkyl chain in most cases with 6 to 20 methylene groups;

Head can be:

(a) Ionic

(b) zwitterionic
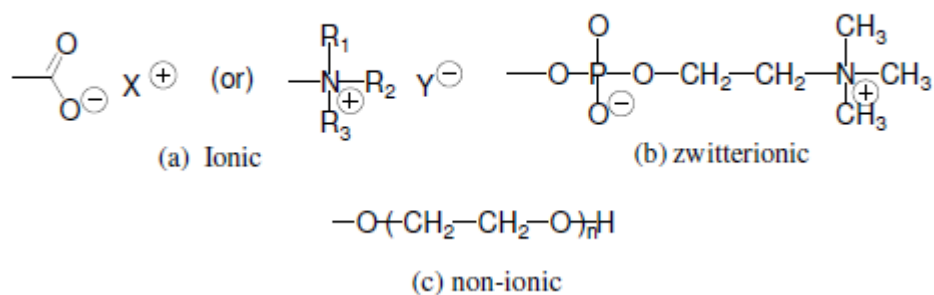
$-O(CH_2-CH_2-O)_n H$

(c) non-ionic

Figure I. 2. Examples for amphiphilic molecules composed of polar hydrophilic head group and a hydrophobic tail.

Depending on the molecular structure, solvent, concentration of the amphiphile in the solvent and temperature different mesophases can be observed. Their formation is caused by the separation of incompatible (hydrophilic polar and hydrophobic non-polar) parts of the individual molecules. When amphiphilic molecules which are surfactants are added into a polar solvent, true molecular mixtures exist at low surfactant concentration. After exceeding a critical concentration, they form small aggregates with finite size called micelles so that the polar groups occupy the interface towards polar solvent. It is spherical in shape and the size is normally comparable to a few molecular lengths. When the surfactant concentration is further increased, micelles can turn to disc like, cylindrical and platelike supramolecular aggregates which organize themselves into different nematic, cubic, hexagonal columnar and lamellar lyotropic mesophases [5]. Typical example of a lyotropic phase is formed by dissolution of soap in water. It is ubiquitous in living matter and some of the examples include the biological membranes, DNA etc. Apart from its importance in biological systems, the lyotropic mesophases are also of significant interest as evident from the first experimental observation of a biaxial nematic phase in a lyotropic system [6].

1. 4. Thermotropic liquid crystals

Most of the crystals on heating transform into the isotropic liquid phase by simultaneous loss of the long range positional and orientational orders. If the molecules possess certain amount of shape anisotropy, then the disappearance in one, two or three dimensions of long-range translational periodicity in the crystal may precede the collapse of the long range orientational order. Such compounds

do not show a single transition from solid to liquid but rather a cascade of transitions involving LC phases with the mechanical and symmetry properties intermediate between those of liquid and a crystal. The temperature at which the crystal transforms into mesophase is called *melting point* while that from the mesophase to isotropic state is called *clearing point*.

Materials displaying thermotropic LC property are mostly organic or metal containing organic compounds. Among the enormous number of organic compounds known, only a small fraction shows this LC behaviour. Such types of compounds usually comprise of hard (rigid) and soft (flexible) regions. The aromatic cores and some non-aromatic cores account for the rigidity while paraffinic chains are the soft regions of the molecule. However these two distinct parts are combined in a specific way so as to attain a particular anisotropic shape of the molecule. The mobility in these systems are provided by large amplitude motions of molecules or molecular parts, namely the flexible chains. The orientational order arises from the parallel alignment of anisometric molecules and positional order is mainly the consequence of specific attractive forces and amphiphilicity. The existence of permanent dipole moments and their magnitude or the anisotropy of the molecular polarizability is determinant in the efficacy of these molecular interactions. Thus molecular shape anisotropy plays a very important role in determining the formation and type of the liquid crystalline phases.

1. 4. 1. Conventional liquid crystals

Rod-like and disc-shaped mesogens exhibit thermotropic mesomorphism; they are popularly known as calamitics and discotics respectively. For many years

it was believed that the molecule has to be long or rod-shaped (Fig. I. 3a) such as 4-methoxybenzylidene-4'-n-butylaniline, MBBA (**I**) [5]. However, in 1977 Chandrasekhar *et al*. demonstrated that disk-like molecules (Figure. 1. 3b) such as benzene-1, 2, 3, 4, 5, 6-hexayl hexaoctanoate (**II**) display mesomorphism [7].
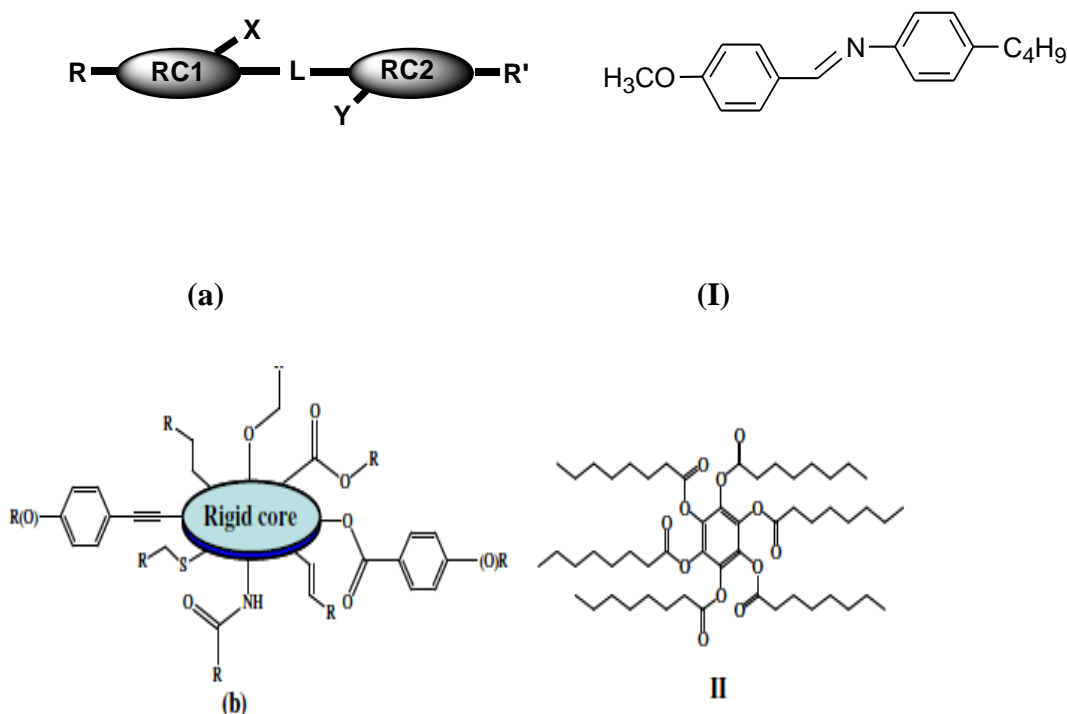

(a)   (I)

(b)   II

Figure 1. 3. General templates for the rod-like (a) and disc-shaped (b) mesogens and their respective representative examples **I** and **II**.

RC1 and **RC2** are the rigid cores that are often aromatic in nature (e. g. , 1, 4-phenyl, 2, 5-pyrimidinyl, 2, 6-naphthyl etc.) but can also be alicyclic (e. g. , trans-4-cyclohexyl, cholesteryl etc.). In many examples these two cores are connected via a covalent bond and in some cases they are connected by linking unit **L** (e. g., -COO-, -CH$_2$-CH$_2$, -CH=N-, -N=N- etc.). The terminal substituents **R** and **R'** are usually either alkyl or alkoxy chains. In many cases one of the terminal units is a polar substituent (e. g., CN, F, NCO, NCS, NO$_2$, etc). In some special cases the lateral units **X** and **Y** (e. g. , F, Cl, CN, CH$_3$ etc.) are incorporated in the main

molecular structure. A typical example of achiral rod-like mesogen is 4-methoxybenzylidene-4'-n-butylaniline (MBBA) [6]. By employing rod-like mesogenic segments, two types of liquid crystalline polymers (LCPs) have been reported [7]. They are the main chain and side chain LCPs. Main chain LCPs consist of rod-like anisotropic repeating units that form a long chain. In side chain LCPs, rod-like mesogenic units are attached to the side of the polymer backbone. Inclusion of molecular chirality in rod-like molecules furnishes chiral LCs and is known to exhibit various chiral structures [8].

1. 4. 2. Non conventional liquid crystals

In recent times a great deal of attention has been given to the generation of self-organized systems with complex mesophase morphologies. This is achieved by tailoring the shape of rigid segments by increasing the number of incompatible units in the molecules or by changing the volume fractions of the incompatible segments. These molecules with anisometric shape that deviates from the conventional rod or disc shape are collectively termed as 'non-conventional liquid crystals' [9]. The general feature of majority of such materials is the molecular structural contrast within a molecule i.e., these molecules are made up of chemically different molecular parts that are incompatible with each other. Some of the important examples of non-conventional systems (see Fig I. 4) are oligomers (**III**) [10], polycatenars (**IV**) [11], bent-core molecules (**V**) [12,9d], polyhydroxy amphiphiles (**VI**) [13], octahedral complexes (**VII**) [14], star shaped molecules (**VIII**) [15], rodcoil molecules (**IX**) [16].
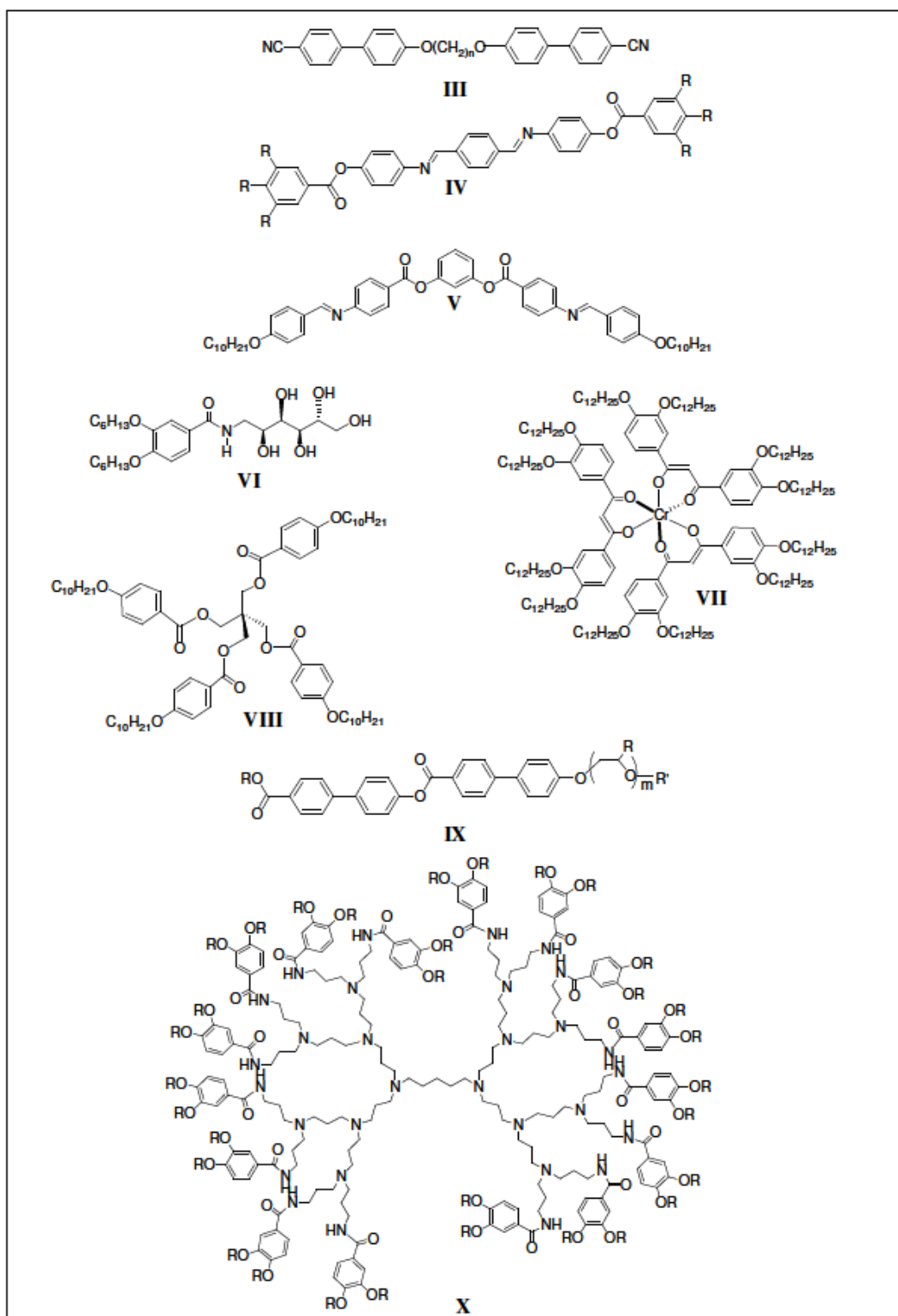
Figure 1. 4. Molecular structures of different types of non-conventional LCs. and dendrimers (X) [17]. In this thesis the research work on non-conventional LCs is focused on dimeric and bent core molecules.

1. 4. 3. Mesophase morphologies of thermotropic liquid crystals

Depending on the chemical structure and the shape of the constituent molecules and external parameters such as temperature and pressure, a rich variety of LC phases have been observed. In this section, mesomorphism exhibited by conventional calamitic molecules is discussed. The mesomorphism of discotic molecules and dimers is described briefly in section 1. 6. Some of the non-conventional molecular structures mentioned in the previous section which show a distinctive phase behavior are discussed in the recent review articles [10].

1. 4. 3. 1. Calamitic liquid crystals: phases and structures

In calamitic mesogens, there are three types of mesophases namely the *nematic*, *cholesteric* and *smectic* originally classified by Friedel [7] based on the degree of positional and orientational order. The discovery of new phases in liquid crystals turns to be often associated with an increase of complexity. Examples include the formation of chirality induced helical supermolecular structures like TGB and Blue phases. In the following sections brief description about the structures of the above mentioned phases are given.

(a)Nematic (N) phase:

The simplest LC phase is the nematic and it generally occurs just below the isotropic phase with a viscosity comparable to those of isotropic liquids. Depending on the surface conditions, N phase exhibits schlieren, marble and pseudoisotropic textures. In this phase the constituent molecules have no positional order but are on an average, oriented about a particular direction called the director, **n** [18]. The molecular organization in the nematic phase is illustrated in Fig. I. 5. Even though the preferred direction of molecules varies from point to

point in the medium, a uniformly aligned sample is optically uniaxial (N_u) and birefringent. However, the biaxial modification of this phase abbreviated as N_b, is also known [18 d-g]. The orientational order of the phase is quantified by the order parameter **S** and the values increase from, about 0.3 near the clearing temperature to 0.6-0.7 at temperatures below the clearing point. Because of the parallel alignment of the molecules along their long axes they exhibit anisotropic physical properties.

Figure 1. 5. Schematic representation of the molecular organization in the N phase of the calamitic LCs

(b)Cholesteric (N*) mesophase

Cholesteric mesophase is the chiral variant of the nematic mesophase and therefore it is also called chiral nematic phase. It occurs in systems where constituent molecules are chiral [8]. It can also be obtained by doping the nematic LC with optically active molecules. The name cholesteric has a historical origin i.e., this particular type of liquid crystalline organization was observed in esters of cholesterols [18c]. In these systems, there is a weak tendancy for neighboring

molecules to allign at a slight angle at one another. This leads a local director to form a helix in space with a well-defined pitch that is much longer than the size of a single molecule. Helical twist may be right handed or left handed depending on the molecular conformation. The cholesteric state is illustrated in Fig. I. 6. This helical arrangement is responsible for the unique optical properties of the phase, such as selective reflection [1,10e, f]. When plane-polarised light interacts with this chiral macroscopic structure, its plane of polarization is rotated along the direction of the helix. When the pitch of the helix corresponds to a wavelength in the visible region of the spectrum (~400-800 nm) the chiral mesophase is colored. Importantly, the pitch of the helix is temperature-sensitive and therefore, the reflected wavelength. Furthermore; helical structures can be unwound by the application of an electric field, which drives the reorientation of the molecular axis along the field direction. Depending on the surface conditions, N* phase exhibits schlieren and oily streak textures.
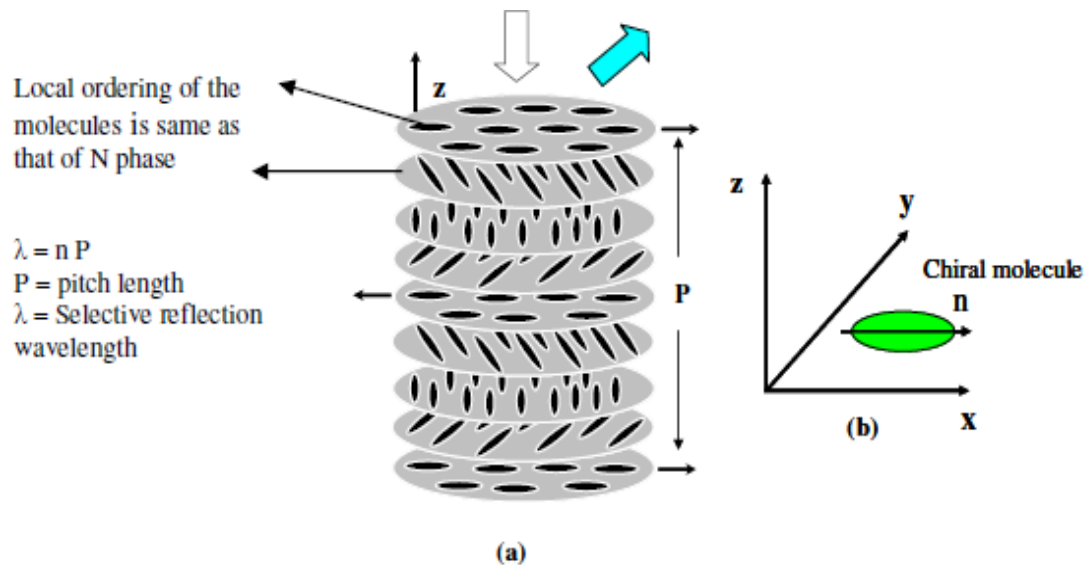
Local ordering of the molecules is same as that of N phase

$\lambda = n\,P$
P = pitch length
λ = Selective reflection wavelength

Chiral molecule

(b)

(a)

Figure 1. 6 (a) Helical structure of the chiral nematic phase, (b) The director lies in the xy plane, perpendicular to the direction of the helix (z), and rotates in the plane that defines the helical structure.

(c)Smectic (Sm) mesophases:

In some phases the molecular center of gravity is on an average arranged in equidistant planes, so that in addition to orientational order, positional order is also present which leads to a layered structure: such phases have been called smectics. Depending on the molecular arrangements within the layer and the extent of inter-layer correlations smectic mesophases are classified into different types [1, 19, 20] according to the chronological order of their detection the smectic phases have been designated with code letters A,B,C…etc. Fluidity of the layer is an essential characteristic of all smectic phases. A more rigorous way to treat the layering arrangement is to consider an one-dimensional mass density wave [21], the different smectic LC phases discovered hitherto are smecticA (SmA), smectic B (SmB, also known as hexatic B), smectic C (SmC), smectic F (SmF) and smectic I (SmI). Further, these smectic LC phases can be divided into two categories depending upon whether the constituent molecules are tilted or not, with respect to the layer normal. The SmA and SmB phases are orthogonal (non-tilted) phases whereas SmC, SmF and SmI are tilted phases. The chiral smectic mesophases are formed when the constituent molecules are chiral. These are chiral SmA, chiral smectic C (SmC*), chiral smectic I (SmI*) and chiral smectic F (SmF*) phases. SmA and SmC are the two most commonly observed and extensively investigated among the various smectic phases. In the following section the structural details of some of the important smectic phases have been discussed briefly.

Smectic A (SmA) and chiral SmA phases:

  In the smectic A phase the director lies along the layer normal. The molecular packing within the layers is liquid-like and has no long-range positional correlation. Likewise, there is no correlation between the lateral positions of the molecules in successive layers. Because of the disorder within the layers, the layers are not well defined and in formal terms the SmA phase can be described as a one-dimensional mass density wave [21]. Thus the idealized picture of the SmA phase shown in Fig. I. 1b is far from accurate. The sub-phases of SmA such as SmA_2 (a bilayer phase), SmA_d (a partially-bilayer. Thus the idealized picture of the SmA phase shown in Fig. I. 1b is far from accurate. The sub-phases of SmA such as SmA_2 (a bilayer phase), SmA_d (a partially-bilayer phase) and $Sm\tilde{A}$ (a modulated phase) are also known. Like biaxial nematic phase, SmA can also possess biaxial symmetry that has been termed biaxial smectic A (SmA_b) phase wherein the molecules are along the layer normal, but have an additional director in the plane of the layers. Though the chiral version of the smectic A phase (observed with optically active molecules) is structurally the same as that of achiral SmA, owing to molecular chirality the symmetry is reduced from $D_{\infty h}$ to D_{∞}.

          As a consequence, in the SmA phase (Fig. I. 7a), when an electric field is applied orthogonal to the layer normal direction there will be a coupling of the electroclinic susceptibility to the field and the long molecular axes of the molecules will tilt with respect to the layer planes (Fig. I. 7b) for relatively low applied fields, the tilt angle varies linearly with the field. This linear electrooptic phenomenon is called electroclinic effect [22]. Both SmA and chiral SmA phases

exhibit characteristic focal-conic texture in slides treated for planar orientation and a dark field of view in slides treated for homeotropic orientation.
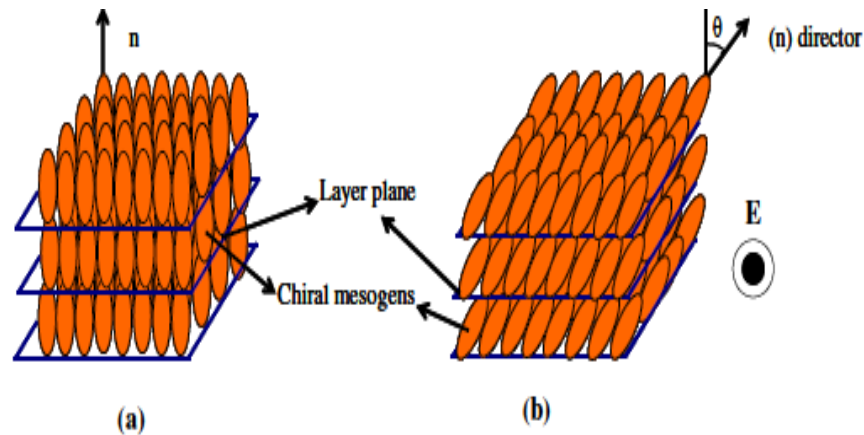

Figure 1. 7 Schematic representation of the SmA phase formed by chiral rod-like anisometric molecules: (a) orthogonal layered geometry; (b) tilted layered structure (electroclinic effect) obtained by the application of electric field along the layer planes of geometry (a)

Smectic C (SmC) and chiral smectic C (SmC*) phases:

The smectic C phase differs from the SmA phase in that the director of each layer is inclined at an angle to the layer normal and this angle being identical for all layers (Fig. I. 8a) [23]. While the SmA phase is generally optically uniaxial, the SmC phase is optically biaxial. The tilt angle in this phase has been shown to vary with temperature and it often increases monotonically with decreasing temperature. X-ray studies indicate that the layer thickness in this phase is considerably less than the molecular length. The symmetry elements of this phase correspond to the point group C_{2h} (Fig. I. 8a and I. 9a). In the chiral smectic C (SmC*) phase, formed by optically active molecules a macroscopic molecules exist. The helix occurs as a result of a gradual change in molecular tilt direction (**n**) from layer to layer, about an axis perpendicular to the layer planes (Fig. I. 9b). Due to the presence of chiral molecules, the SmC* phase has reduced C_2

symmetry (Fig. I. 8b) which creates in equivalence in the dipole moment along the
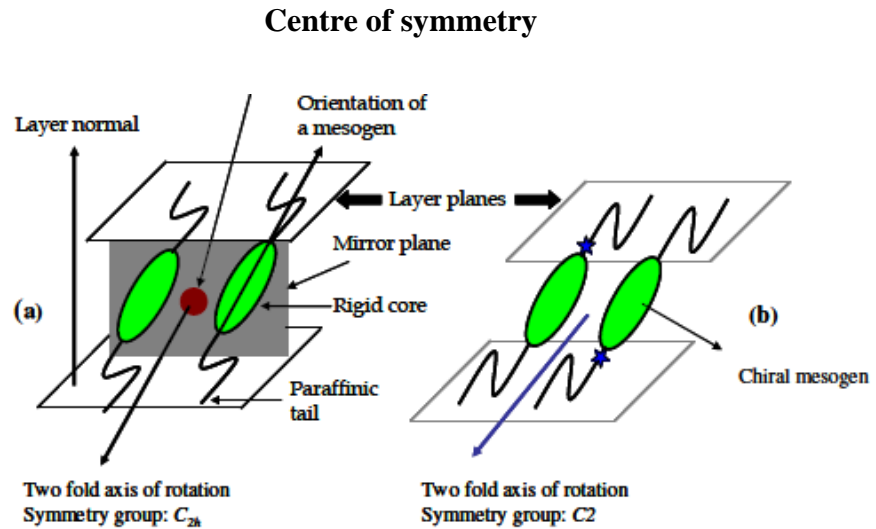
C_2 axis normal to the tilt

Centre of symmetry

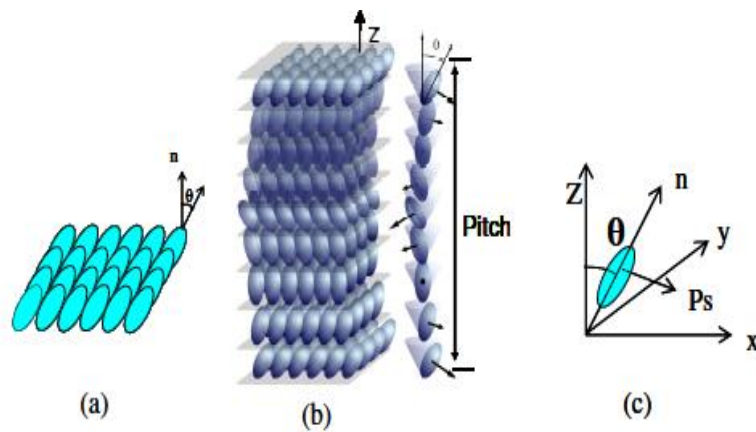**Figure 1. 8.** Symmetry in the (a) SmC and (b) SmC* mesophases

Figure 1. 9. (a) Structure of the SmC phase, (b) LHS: helical macroscopic structure of the SmC* phase in which the consecutive layers precess around the layer normal (z); RHS: the representation of the precession of a single chiral molecule in the consecutive layers; (c) a chiral molecule represented in its layer plane (xy) with its polarisation (*Ps*) (due to the inherent form chirality in the SmC* phase) (LHS: Left hand side; RHS: right hand side)

direction (Figure. I. 9c), resulting in spontaneous polarization (Ps) in each layer. However the presence of helix averages out the Ps to zero [23]. Nevertheless, to

obtain a macroscopic Ps (ferroelectric behavior) the helix can be unwound by surface interactions or by the application of an electric field [24].

(d)Chiral frustrated phases:

Chirality efficiently reduces the molecular symmetry which in turn can significantly modify the mesomorphic behaviour. Chiral molecules prefer to pack in a certain manner, but such a structure cannot be adopted everywhere due to molecular constraints. Such a situation leads to the stabilization of what are called as frustrated phases [25]. Examples include blue phases (BP) and twist grain boundary (TGB) phases and the structures of which are briefly described below.

Blue phases (BP):

These are distinct thermodynamic phases that appear over a narrow temperature range between chiral nematic and isotropic liquid phases in short pitch (<5000 Å), BPII a simple cubic lattice and BPIII is probably achiral nematic LCs [26-33] which are usually single component optically active rod-like mesogens or mixtures composed of achiral and optically active mesogens [30b]. Recently, they have been also reported to occur in discotics [29] and LC dimers [10i]. The first observation of the blue phase has been attributed to Reinitzer [28]. Three distinct blue phases have been identified i.e., BPI, BPII and BPIII that occur in the same order with increasing temperature. The naming of these phases as blue is due to their Bragg reflections in the blue wavelengths indicating a partially periodic structure with lattice parameters of several hundred nanometers. However, blue phases are now known to reflect other colors in the visible range. Saupe was the first to suggest a chiral cubic structure from the optical activity of the BPs and their lack of birefringence [24, 28]. Bragg reflection studies indicate

that BPI has a body centered cubic lattice amorphous one. The structure of the BPs involves a radial twist of the director called a double cylinder. However, this double twisted structure cannot extend perfectly into three-dimensional space. Figure 1. 10 shows the schematic representation of the spaghetti model of BPIII, having randomly oriented squirming double twist cylinders, while geometrical models of cubic blue phases (BPI and BPII) consist of cubic net works of double twist cylinders separated by disclination lines (Fig. I. 11) [30]. (see below for details).
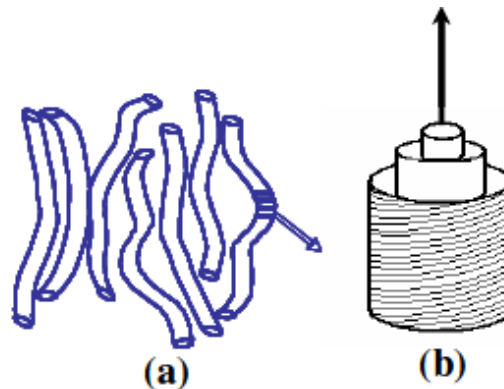

Figure 1. 10. Schematic representation of the theoretical spaghetti model of BPIII (a) having randomly oriented squirming double twist tubes (b).
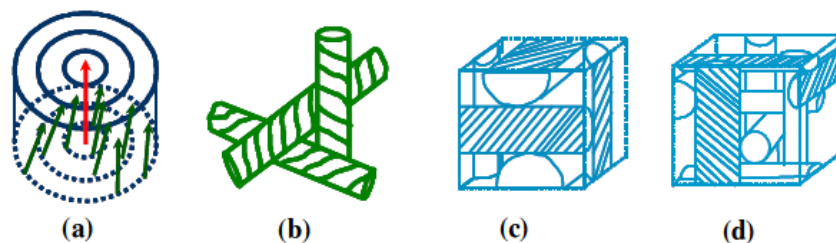
Figure 1. 11. (a) Schematic illustration of a double twist cylinder. At the core the director is oriented parallel to the cylinder axis. Moving outwards, the local director twists along any radius until the twist is approximately 45° at the edge of the double twist cylinder; (b) local arrangement of three double twist cylinders forming a defect region; (c) spatial arrangement of double twist cylinders that lead to the simple cubic structure of BPII and (d) spatial arrangement of double twist cylinders that lead to body centred cubic structure of BPI.

Cubic blue phases BPI and BPII are built up of double-twist cylinders as schematically shown in fig. I. 10a, which represent a local structure of minimum energy within a double twist cylinder the local director rotates around any given radius of the cylinder. The double twist cylinders spatially arrange perpendicular to each other, the arrangement eventually leading to the three dimensional cubic lattice of topological defects [32] observed in blue phases (Figure. I. 11c, d). Combined interpretation of various experimental investigations on the structure of these phases has revealed that the BPII phase has a simple cubic unit cell of lattice defects, while the BPI phase is body centered cubic, both with lattice parameters in the order of several hundred nanometers (the wavelength of visible light). The blue phases are thus optically isotropic, i.e. linear birefringence is absent. The optical texture of the cubic blue phases is quite characteristic, generally with a platelet texture. Amorphous BPIII is characterized by its foggy appearance.

The twist grain boundary (TGB) phases:

These phases usually appear at the transition from SmA or SmC* phase to N* or isotropic phase. For short pitch chiral materials there can be a competition between the need for the molecules to form abhelical structure due to their chiral packing requirements and the need for the phase to form a layered structure. Molecules relieve this frustration by forming twist grain boundary phase that consists of blocks of smectic layers, the successive layers being rotated by a constant angle to give a helical structure with helix axis orthogonal to the layer normal direction. Since the smectic layers cannot be continuously twisted, they are separated from one another by screw dislocations to form grain boundaries which themselves are periodic, leading to the presence of layering as well as

helical twist. Further, depending upon whether the smectic blocks are of smectic A or smectic C or smectic C*, three different types of TGB phases such as TGBA, TGBC and TGBC* are possible [43] and are observed experimentally [34-36] (Fig. I. 12). The structure of the TGBC* phase is more complicated than the TGBA and TGBC phases. Experimentally it has been observed that this phase exhibits a regular (square or hexagonal) grid pattern superimposed on the planar structure. To explain the structure of TGBC* phase, Galerne proposed an improved model based on the original model by Renn [46d]. According to this model, in addition to the tilt of the molecules with respect to the smectic layer normal as in TGBC phase, the molecular tilt itself undergoes a twist around the SmC* helix axis, which lies in a plane perpendicular to the TGB helix axis. Thus each of the smectic blocks has a smectic C* structure with its helix axis orthogonal to that of the TGB helix. The model retains the concept of helislabs, which leads to an additional type of coarse grain boundary whose size could be larger than the size of the smectic slabs. Like the smectic slabs, helislabs are also separated by parallel sets of defect lines (with defects now being disclinations) and the grids are consequence of this. According to another model proposed [36e], the appearance of the square grid in this TGBC* phase is supposed to be due to the undulation of the smectic slabs, which means that the grain boundaries are not flat. Thus, in TGB phases, as in blue phases, the frustration is relieved by the presence of defects. The model retains the concept of helislabs, which leads to an additional type of coarse grain boundary whose size could be larger than the size of the smectic slabs. Like the smectic slabs, helislabs are also separated by parallel sets of defect lines (with defects now being disclinations) and the grids are

consequence of this. According to another model proposed [36e], the appearance of the square grid in this TGBC* phase is supposed to be due to the undulation of the smectic slabs, which means that the grain boundaries are not flat. This is referred as undulated TGBC* (UTGBC*) phase. Recently, Clark et al. , have proposed that the square grid pattern arises from a common structure: 'giant' smectic blocks of planar layers terminated by grain boundaries [36g].
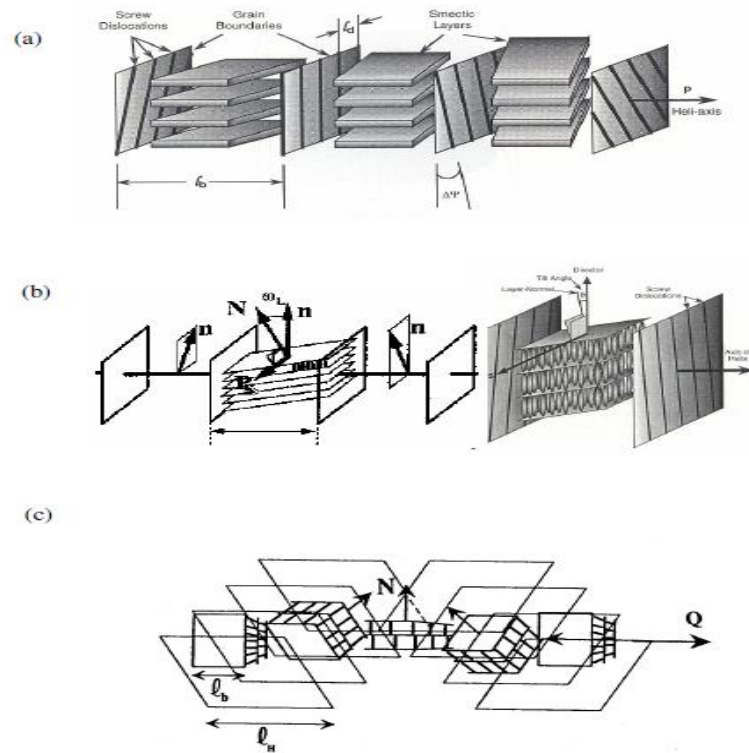
Figure 1. 12. (a) Structure of TGBA phase, where d = smectic layer spacing, lb = thickness of the smectic slabs, ld = distance between neighboring screw dislocation and p = pitch of the director field, (b) structure of TGBC phase where $\_L$ = tilt angle of the layers, **n** = director, N = layer normal, PS = spontaneous polarization, lb = thickness of the smectic slabs, (c) structure of TGBC* phase where Q = main helical wave vector, N = layer normal, lb = distance between the two neighboring grain boundaries, lH = thickness of helislab

1. 5. Sequence rule and reentrant behaviour in calamitic liquid crystals

A thermotropic LC can exhibit one to several LC phases between the crystal and isotropic liquid states. Materials which exhibit two or more LC phases are said to be *polymesomorphic* and the process is known as *polymesomorphism*. By systematic observation of different phases in polymorphic compounds a rule for the phase sequences was derived [46]. According to this general rule smectic phases are the low temperature phases while the nematic phase occurs at higher temperatures. Considering all structures known in calamitic LCs a hypothetical sequence was derived: *Isotopic (I) - N - SmA - SmC - SmB - SmI - SmF - Crystal B - J - G - E - K - H- Crystal* for achiral materials and *I - BP- N*- TGB - SmA - SmC* - SmI* -SmF** for chiral LCs. Till date, there is no single material is reported to exhibit all these phases. However, there are many real phase sequences that can be considered as parts of the above given hypothetical full sequence. Remarkable exceptions to this hypothetical sequence have been detected in *reentrant transitions* [47]. A system is said to undergo a reentrant phase transition, if a variation of any thermodynamic field such as temperature or pressure results in two (or sometimes more) phase changes and finally attains a state which is macroscopically similar to the initial state.

1. 6. Discotic liquid crystals: phase types and structures

It was believed for a long time that mesomorphism could be shown only by molecules with rod-like structure. However, in 1977 Chandrasekhar *et al.* showed that disc-like molecules such as hexa-*n*-alkanoyloxybenzenes (see **II** in Fig. I. 3) exhibit mesomorphic behavior [6]. In general such compounds are called "discotics" and here the rigidity at the centre of the molecules is an essential

structural requirement [34]. In general a discotic molecular structure can be shown as in figure1. 2b. Achiral discotic LCs exhibit two different types of mesophases namely nematic (N), lamellar and columnar (Col) phases. The nematic phase is similar to the nematic phase of the rod-like molecules in possessing the orientational order (Fig. I. 13a). Another variant of nematic phase is known in which the nematic structure is formed by columns (Fig. I. 13b) and has been called columnar nematic phase (Ncol).
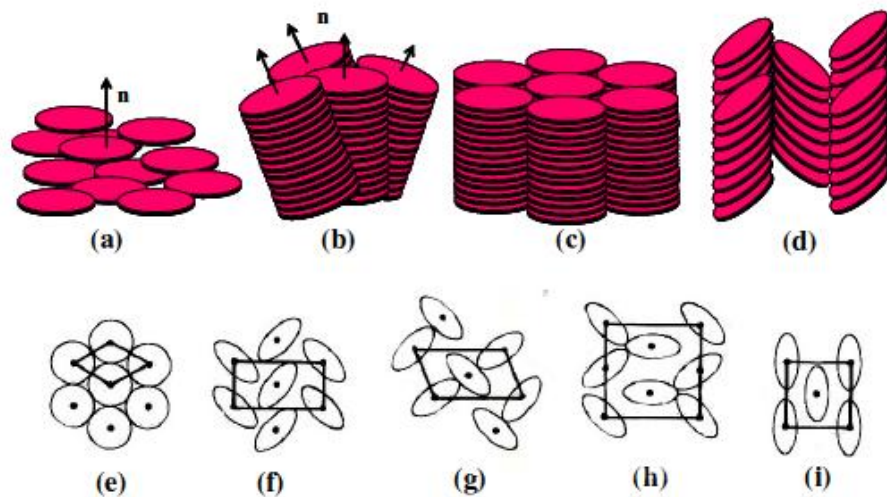
Figure 1. 13. (a) The nematic phase, (b) columnar nematic phase, (c) columnar hexagonal phase, (d) columnar rectangular phase, (e)-(i) plan views of the two-dimensional lattice: (e) hexagonal symmetry,(f) rectangular symmetry, (g) oblique symmetry (h) rectangular symmetry, (i) rectangular face-centered symmetry

The most common phase exhibited by disc-like molecules is the columnar phase, in which the discs stack into columns (Fig. I. 13c, d). Columnar LCs shows a rich polymorphism and is normally classified at three levels; according to the symmetry of the two-dimensional array, the orientation of the core with respect to the column axis and the degree of order within the column. The stacking of discs within the columns can be ordered or disordered.

However, based on the symmetry of two dimensional (2D) array of the columnar mesophases they may be classified into three classes namely, hexagonal, rectangular and oblique [34b]. In columnar hexagonal phase the constituent molecules can have either an aperiodic arrangement (liquid-like) or long-range positional order within the column. Columnar rectangular (Colr) and columnar oblique (Col_{ob}) phases are characterized by a liquid-like molecular order along the columns, in which the columns are arranged either in a rectangular or oblique packing respectively. Fig1. 13-e-i show plan view of the two-dimensional lattice of columns in different columnar mesophases [1a]. The workhorses of discotic liquid crystal research have been derivatives of triphenylene and pthalocyanines [37a]. Many derivatives of anthraquinone, ethynyl benzene, hexabenzocoronens, tricycloquinazolines, macrocycles with a large cavity at the centre, metallo-discogens containing copper, molybdenum, nickel and palladium etc are added to the list of new discogens [37]. The guidelines framed for the formation of mesophases in achiral discotics have been followed to realize chiraldiscotic systems by introducing one or several chiral chains around the periphery of discotic core which are known to exhibit either a chiral nematic (N*) or columnar phases. The blue phase has been rarely observed in discotics [37d]. The discotic chiral nematic phase has a structure analogous to that of the chiral nematic phase exhibited by calamitics. Interestingly, a certain columnar phase formed by chiral discotics exhibits ferroelectric switching properties, which appear to have some advantages over its tilted smectic counterpart in electro-optical displays. The discotic nematic is now considered to be a better medium for display applications especially with respect to viewing angle problems [38]. Added to this the recent

commercialization of discotic nematic in the production of optical compensation films by Fuji Film Company [39] has created an immense interest in this area. The potential use of discotic materials, especially those exhibiting columnar phases, as quasi-one dimensional conductors, photoconducting systems, ferroelectrics, light emitting diodes, photovoltaic solar cells, optical storage devices, hybrid computer chips for molecular electronics etc. , are attracting considerable attention [37c].

1. 7. Identification of thermotropic mesophases

As discussed in previous sections, till date a number of liquid crystalline phases have been discovered. The structural differences between these phases are quite narrow and therefore the precise characterization of LC phases generally requires the use of different techniques. The most commonly used device to identify the LC phases is the polarizing optical microscope (POM) which reveals the characteristic optical texture of a mesophase. The optical textures are usually observed in thin layers of the sample between two glass plates, pretreated for either homogeneous or homeotropic alignment of the molecules. Calorimetric study using differential scanning calorimetry (DSC) is a complementary tool to microscopic studies to know the precise phase transition temperature and the enthalpy change associated with the transition. However there are limitations in mesophase characterization by either of these methods as the optical textures of different smectic or columnar phases are difficult to distinguish and the enthalpy values can not be so characteristic for different phase transitions. Sometimes miscibility studies, in which a well known liquid crystal phase are physically mixed with an unknown phase to ascertain the nature of the phase is carried out

based on the criterion of complete miscibility of identical phases [40]. For unambiguous identification of mesophases, structural information such as relative molecular positions, the presence of long-range positional order, the quality of preferred molecular orientation etc. , can be obtained from diffraction studies. X-ray, electron and neutron radiations are suitable for diffraction studies. X-rays are probably the most convenient and widely used whereas electrons and neutrons have advantages in particular situations. Other experimental techniques such as electro-optic measurements, nuclear magnetic resonance (NMR) spectroscopy etc. , are also in use for the characterization of mesophase.

I. 8. Physical properties of liquid crystals

Since liquid crystals are anisotropic fluids, various physical properties measured in different directions will not be the same. In other words, the parallel alignment of anisotropic molecules gives rise to the anisotropy of various physical properties that are the basis of a number of practical applications known for LCs. Some of the important anisotropic properties directly relevant to various liquid crystal applications [1c, 56] are discussed below.

(a)Optical anisotropy (Birefringence)

All crystal types other than cubic are optically anisotropic or birefringent. The free rotation in liquids averages out any asymmetry of molecular shape and the medium becomes optically isotropic. Mesogens due to their shape and polarization anisotropy are birefringent, exhibiting different properties for light traveling with the electric vector propagating parallel and perpendicular to the director or optic axis. The electric vector of incident plane polarized light entering a liquid crystalline phase is split into two components called ordinary (o) and

extraordinary (e) rays. The electric field of the o-ray is always perpendicular to the optic axis, so its refractive index 'n_o'is a constant independent of propagation direction. The electric field of e- ray lies in a plane that contains the optic axis, so its refractive index n_e (θ) varies with the ray propagation angle with respect to the optic axis. Thus the birefringence of the medium, Δn (θ), depends on the propagation direction and is defined as Δn (θ) = n_e (θ) - n_o. Most nematic liquid crystals have positive birefringence ($\Delta n > 0$), meaning that the e-ray is delayed with respect to the o-ray on passage through the LC phase. Interference between the e-ray and the o-ray that travel through the medium with different velocities gives rise to the coloured appearance of these thin films.

(a) Dielectric anisotropy

The interaction between a liquid crystal and an electric field is dependent on the magnitude of the dielectric permittivity (ε) measured parallel ($\varepsilon\|$) and perpendicular ($\varepsilon\perp$) to the director and to the difference between them (i.e. , the dielectric anisotropy $\Delta\varepsilon = \varepsilon\| - \varepsilon\perp$). The dielectric permittivity of a material is defined as the ratio of the capacitance of the material C_{mat} to that in vacuum C_{vac} ($\varepsilon = C_{mat}/C_{vac}$). The dielectric constants are dependent on the frequency of the applied field up to transition to the isotropic liquid. Above the clearing point, the dielectric constants measured along all the three axes are equal due to the isotropic nature of a liquid and therefore, $\Delta\varepsilon$ decreases to zero. The sign and magnitude of the $\Delta\varepsilon$ are attributable to the resultant permanent dipole moments.

(b) Elastic constants

The elastic behaviour of a liquid crystal phase under a distorting force such as an electric field or at an interface with a solid surface is determined by the three

elastic constants k_1, k_2, k_3 that are associated with splay, twist and bend deformations respectively. The elastic constants are molecular parameters and describe the restoring forces on a molecule within a liquid crystalline phase in response to an external force that distorts the medium from its lowest energy configuration. The elastic constants co-determine the spatial and temporal response of the director to the applied external electric and magnetic fields. The equilibrium position is then restored upon removal of the field by elastic forces that originate at the interface between the LC and the orientation layers that cover the device substrates.

(c) Viscosity

The viscosity of any material is a collective property resulting from the interaction of the molecules with one another. The flow velocity in the liquid crystalline state is also an anisotropic property that depends on the direction of flow of individual molecule with respect to the director at any one point within the medium. Three parameters are required to characterize the nematic state as the constituent molecules are anisotropic. These are η_1, which is perpendicular to the direction of flow, but parallel to the velocity gradient; η_2, which is parallel to the direction of flow, but perpendicular to the velocity gradient and η_3 which is perpendicular to the direction of flow and to the velocity gradient. Individual viscosity coefficients influence the optical response times in an electro-optic display device.

I. 9. Applications and prospects of liquid crystals

(a) Display applications

By virtue of their fluid nature, LCs can be easily processed into thin films, yet they retain the optical properties of crystalline materials such as the ability to rotate plane polarized light. In addition, the orientation of the molecules in liquid crystal films can be modulated on a relatively short time scale using a low electric field. Because the birefringence in a liquid crystal phase is a function of the angle formed by plane-polarized light and the director '**n**', it can effectively function as an ON/OFF light shutter between crossed polarizers under the influence of an electric field. Most LC applications are indeed based on this simple concept of an ON/OFF light shutter [29d]. Majority of the liquid crystals displays (LCDs) fabricated today use either the twisted nematic (TN) [1c] or super twisted nematic (STN) [43] displays. The nematic phase formed by discotic mesogens has recently been reported to be useful for wide viewing angle LCDs because of their negative birefringence [42, 44].

(b)Temperature sensors

Chiral nematic (cholesteric) liquid crystals reflect light with a wavelength proportional to the magnitude of pitch. Because the pitch is dependent upon temperature, the colour reflected also is dependent upon temperature. Thus, cholesteric LCs make it possible to accurately gauge temperature just by looking at the colour. By mixing different cholesteric LCs, a device for practically any temperature range can be built. This property has been exploited for practical applications [45] in diverse areas including medicine, packing industry and electronics. Cholesteric liquid crystals as 'fever strips' are in use as disposable

thermometers. LC thermal sensors can be attached to skin to show a thermal map. This is useful because often physical problems such as tumors have a different temperature than the surrounding tissue. LC temperature sensors can also be used to find bad connections on a circuit board by detecting the characteristic higher temperature.

(d) Columnar fluid phases as a promising media for modern applications

As discussed earlier, the preferential self-organizing ability of discotic mesogens to form columnar (Col) mesophases is driven by favourable π-π interactions between the aromatic cores. Columnar mesophase offers a one-dimensional pathway for the electronic charge migration, where the central aromatic core is the conducting unit, with external peripheral chains as the insulating mantle [46,1i]. This LC state is of great importance because it allows the possibility to combine different physical properties (optical, conductive) with orientational control of the molecular order, self healing of structural defects and ease of processability. Most importantly all these properties can be tailored by careful molecular engineering. Thus, Col LC phases can be used as promising media for various device applications as shown in (fig. I. 15). Currently the solar cells used for the direct conversion of light into electricity by the photovoltaic effect are fabricated from inorganic semiconductors; in particular they are based on the single or polycrystalline silicon cells. On the other hand, organic thin-film solar cells having single crystalline material are also promising flat-plate photovoltaic technology. However, the flat-plate technology based on either of these two materials is rather difficult and expensive. Most importantly, the large quantity of inorganic semiconductors used in such a technology is hazardous to
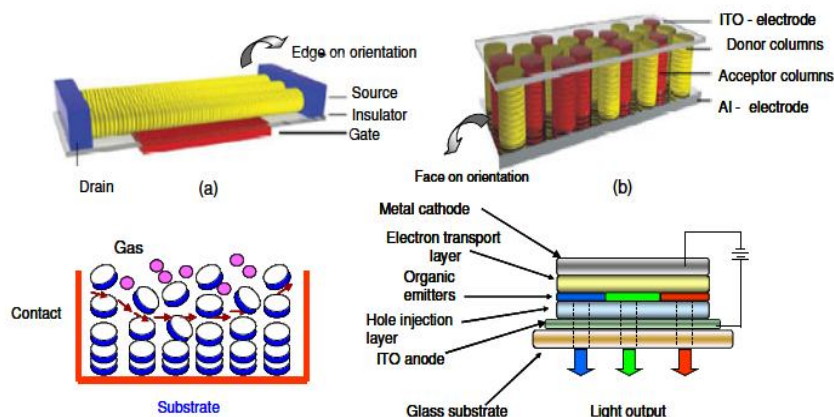
Figure1. 15. Schematic representations of molecular electronic devices from columnar mesophases [adopted from ref. 49]: (a) field effect transistor; (b) Photovoltaic or solar cells; (c) gas sensors and (d) organic light emitting diodes.

the environment. Thus, for the solar cell applications, new organic materials with low cost and good processability, large absorption coefficient, efficient photo generation of charge and good charge carrier mobility are needed. In this context, the Col phases formed by the electron rich/poor discotic mesogens appear to be promising given the fact that their structure resembles the aromatic stacking in single crystalline conductors. In particular, segregated stacks of columnar mesophases made up of donor and acceptor type discotics in their "face on" orientation imitate the same morphology of solar cells (Fig. I. 15b). The "edge on" orientation of the Col phases can be translated into field effect transistors (FET) which are the vital components in molecular electronic devices (Fig. I. 15a). The high mobility for photo induced charge carriers in the Col phases also make them suitable for their use as the active charge transport layer in fast and high resolution xerographic and laser printing applications [47]. The Col phase has a unique conductive surface layer due to the fluctuations along the lengths of the column.

The carrier mobility along the surface is fluctuation assisted and the tunneling rates are exponentially dependent on the molecular core spacings. The core separation fluctuates with the surface and changes as soon as the surface is disturbed. The electrical conductivity of this surface layer is, therefore, very sensitive to the absorption of molecules. Thus columnar liquid crystals can be used as sensitive gas sensors for both polar and nonpolar molecules (Fig. I. 15c) [48]. Recently Col phases gaining importance in the construction of organic light emitting diodes (OLEDs) as they can act as good emitting and conductive layers with proper structural design. Columnar phases with a combination of hol/electron transporting and luminescence properties are an ideal media for the fabrication of OLEDs (Fig. 1. 15d) [46].

(e) Other applications

Liquid crystals have other applications also. Polymers form an important subclass of liquid crystal materials and occur in nature as solutions of some biopolymers and are important in the processing of advanced high-modulus engineering materials like Kevlar [49]. Liquid crystals are employed as anisotropic solvents for the study of various physiochemical properties [50]. The nematic phase, in which the molecules can be homogeneously oriented by a magnetic field such that the optic axis lies parallel to the field, is employed as anisotropic solvent in NMR spectroscopy. This technique provides information regarding the anisotropy of the chemical shifts and molecular geometry [51]. Liquid crystals are used as solvents to alter the rates of uni- or bi-molecular thermal and photochemical reactions [52]. This technique is based on the ability of the mesophase to control the orientation of solutes, impart constraints on their

mobility and remove the randomness of molecular motions and orientations. A combination of the analytical strengths of gas chromatography and the unique structure and shape selective properties of the LC phase has led to the wide spread use of LCs as stationary phases in chromatography. Effective and selective separation of positional and geometric isomers can be brought about by the interaction of the solute with the orientational order provided by the anisotropy of the LC stationary phase. Cholesteric LCs are also used for chiral recognition [53]. Lyotropic LCs are exploited for applications in commercial detergents and cosmetics [54] and for the simulation of bio membranes [55]. Recently, another important application of LCs as a medium for controlled drug release has been envisaged [56].

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