Chapter I

INTRODUCTION

LIQUID CRYSTALS

Liquid crystal refers to the intermediate phases between crystalline solid and isotropic liquid. A liquid crystal can flow like a liquid, and can even form a drop as liquid and at the same time exhibit anisotropic properties of crystalline solid. Liquid crystalline phase was first observed by an Austrian Botanist Friedrich Reinitzer [1,2] in 1888 with a substance related to cholesterol. Otto Lehmann [3,4] in 1890 gave the name Liquid Crystal to these compounds. Georges Friedel [5,6] in 1922, described these phases as mesomorphic phase or mesophase since these phases are observed in between the isotropic liquid and crystalline solid. Many organic, organometallic, inorganic and biological compounds show these thermodynamically stable states in which the substance retain the anisotropic properties such as dielectric, optical, magnetic and others, inherent in a crystal besides simultaneously having the liquid properties. In Liquid Crystal Database, 262869 properties of 85526 liquid crystal compounds have been enumerated [7]. Moreover, in the four volumes of Handbook of Liquid Crystal by D. Demus *et al.* [8] physical properties of many different types of liquid crystalline compounds have been described.

To understand liquid crystals in terms of order of molecules, we recall that in a crystalline solid the molecules have fixed orientation and the centres of mass of the molecules are distributed on a 3-dimensional periodic lattice. The crystal, therefore, possess long range ordering in both position and orientation of the molecules. On the other hand, in isotropic liquid the molecules do not have positional or orientational order. Their positions and the directions they point are randomly distributed. In liquid crystals the molecules exhibit a certain degree of orientational order and they may have some degree of positional order in addition giving rise to many different types of liquid crystalline phases.

The molecules of liquid crystals are mostly rigid non-spherical and rod like or disc like in shape. **Figures 1.1 and 1.2** illustrate the shape of the molecules. However, the constituent molecules may be even banana, Y-, H-, T- etc shaped, an interesting review has recently been given by D. Demus [9] on this aspect. Several

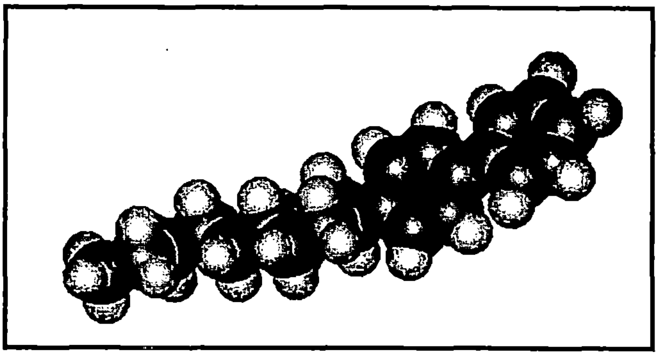


Figure 1.1. Rod-shaped liquid crystal molecule.

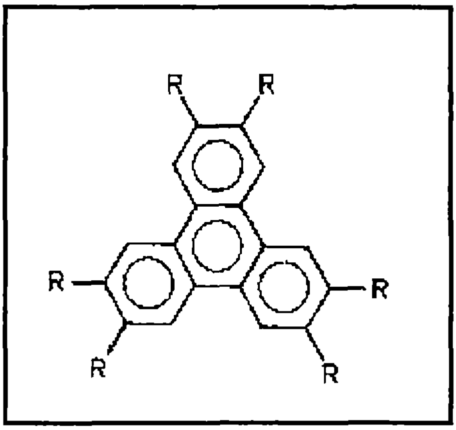


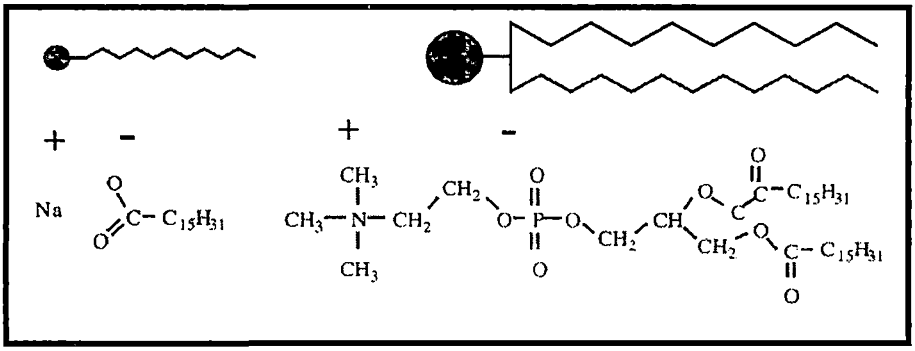
Figure 1.2. Disc-shaped liquid crystal molecule (R=$C_nH_{2n+1}O$ or $C_nH_{2n+1}CO.O$)

books, monographs and review articles [10-22] discuss at length the molecular structure and physical properties of liquid crystals.

Liquid crystals are widely used in various scientific and technical applications due to their distinctive physical properties. For example, optical birefringence, dielectric anisotropy and elastic constants and viscosity coefficients are sensitive to weak external stimuli. External perturbations such as electric and magnetic fields, heat energy and acoustical energy can all be used to induce optical effects. Presently most of the display related research is centered on the application of electro-optic effects because of relative ease and efficiency of excitation with an external electric or magnetic field as compared to other means of excitation. Liquid crystal electro-optic effects are important because they do not require emission of light, but they modify the passage of light through the liquid crystal by either light scattering, modulation of optical density or colour changes. Based on the principle of dynamic light scattering or twisted nematic (TN) mode, liquid crystals are used for making display devices (LCDs) such as watches, pocket calculators, note books, personal digital assistants, cellular phones, desktop monitors, laptops and TVs [23-25]. The advantage of LCDs is the relative low input power consumption per unit area, wide-angle viewing, fast switching time, large area display by small volume, design flexibility, high resolution, wide temperature range and high contrast ratio. Recently ferroelectric liquid crystals are used for new generation of fast versatile liquid crystal devices [26]. The other material that are used for display devices are the polymer dispersed liquid crystals (PDLC) [27-28].

Certain cholesterol liquid crystals show color changes from red to violet when its helical pitch changes due to change in temperature and are therefore used in medicine for the diagnosis of diseases. For example cholesteric liquid crystals are used in thermal mapping of human skin for diagnosis of circulatory system diseases or for the detection of tumors etc [29].

The liquid crystalline solutions with non-mesogenic guest molecules are easily oriented in electric or magnetic field and the bulk sample of highly oriented solute molecules can be prepared. Liquid crystals are therefore used as solvent for organic molecules in nuclear magnetic resonance (NMR) measurements and



(a) (b)

Figure 1.3. The molecular structure and model of two lyotropic liquid crystals (a) soap and (b) phospholipid.

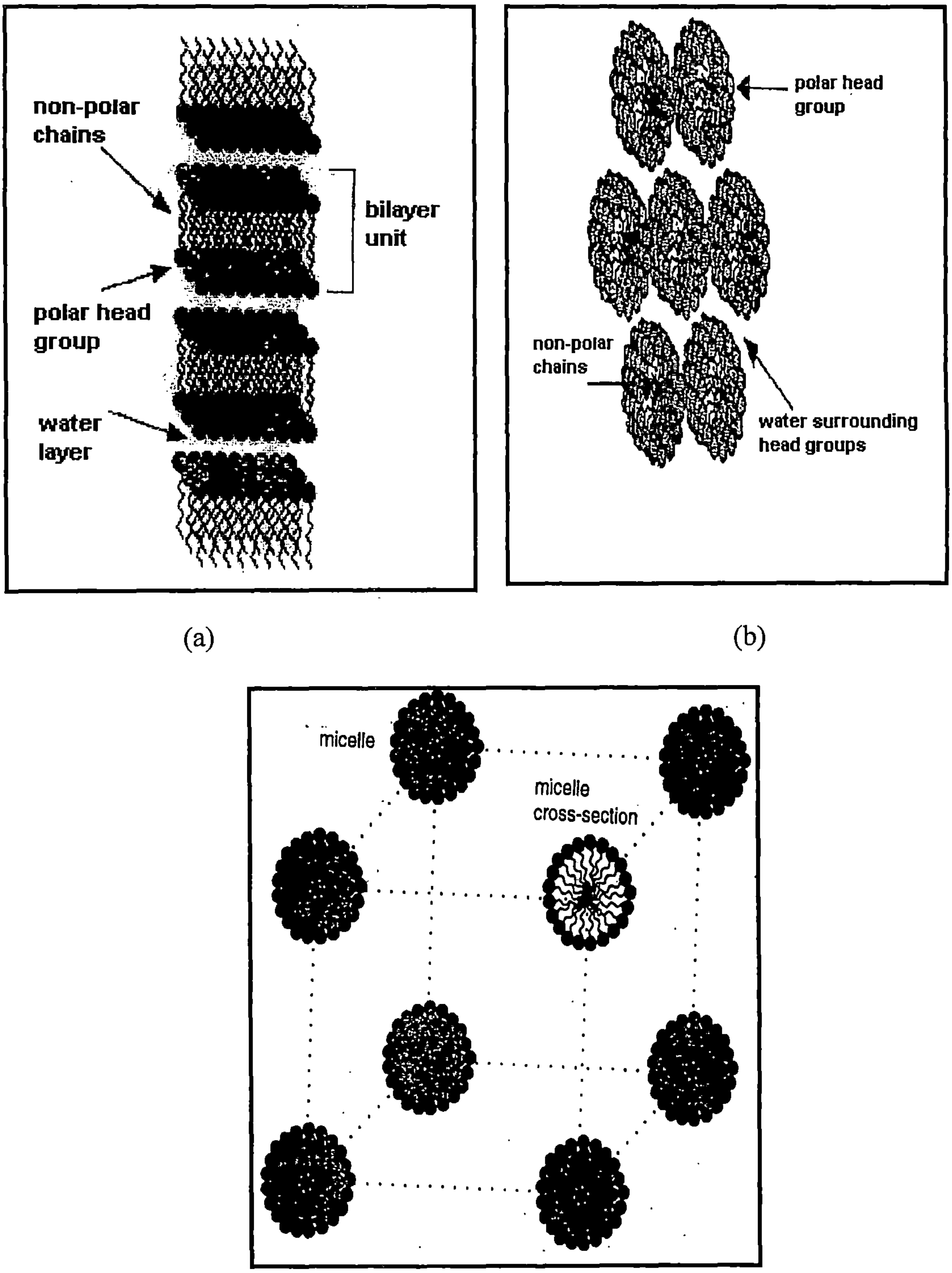
infrared (IR) spectroscopy to perform polarization studies. Liquid crystals are also used as solvents in gas-liquid chromatography (GLC) for the separation of two geometric isomers such as m- and p-xylene. There are many books and articles where different types of applications of liquid crystals and various aspects of those applications have been discussed in details [30-50].

TYPES OF LIQUID CRYSTAL

There are two basic groups of liquid crystal viz. thermotropic and lyotropic liquid crystals. A thermotropic liquid crystal exhibits thermally stable mesomorphic phases in a certain temperature range and shows phase transitions by changing temperature. A lyotropic liquid crystal, in contrary, shows mesomorphic behavior in a certain range of concentration of the solute in a suitable solvent.

Lyotropic liquid crystals

Lyotropic liquid crystals are anisotropic solutions of two or more components being composed of large organic molecules dissolved in a polar solvent, usually water [51-61]. The temperature range in which liquid crystalline phases exist is mainly determined by the solute concentration. The constituent unit forming mesophases are anisotropic molecules or associated groups of many molecules. These molecules combine with a hydrophobic group at one end and hydrophilic group at the other end. Lyotropic liquid crystals molecules form ordered structure in both polar and non-polar solvent. Solutions of soap and water and various phospholipids are typical example of lyotropic liquid crystals (**Figure 1.3**). In soap and water solution the hydrophobic tails assemble together and hydrophilic heads attracts water. The resulting soap molecule is called a miscelle and vesicle in case of phospholipids. The principle interaction resulting in long range order in lyotropic liquid crystals is the interaction of the organic molecules with aqueous solvent. The intermolecular interaction between the organic molecules is of secondary importance. There are three different types of mesophases a lyotropic liquid crystals can have viz. lamellar, hexagonal and cubic phases [59-61] as shown



(a) (b)

(c)

Figure 1.4. The structure of lyotropic liquid crystal phases (a) lamellar (b) hexagonal and (c) cubic phases.

in **Figure 1.4**. Lyotropic mesophases are found in various biological systems. Many synthetic polypeptides, cell membranes of living organisms, tobacco mosaic virus (TMV), deoxyribonucleic acid (DNA) molecules shows lyotropic behavior when dissolved in suitable solvents, often water, in appropriate concentration. The biological aspects of liquid crystals have recently been reviewed by J. W. Goodby [62]. Lyotropic liquid crystals will not be discussed any more since this dissertation concerns only with the thermotropic liquid crystals.

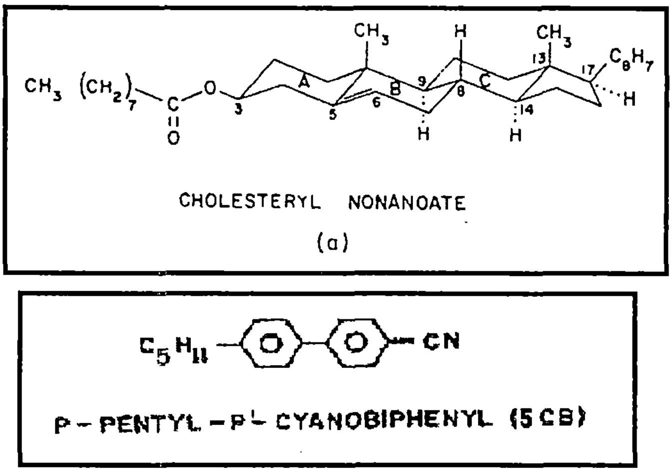
Thermotropic liquid crystals

Thermotropic liquid crystals exhibit mesophases and phase transitions with change in temperature. These are usually organic substances with molecular structures typified by those of cholesteryl nanonoate and p-pentyl-p'-cyanobiphenyl (5CB) as shown in **Figure 1.5**. Depending on the molecular structure these liquid crystals are grouped into calamatic, discotic and polymeric types.

Mesophases shown by thermotropic liquid crystals with rod like molecular structures are called calamatic liquid crystals. From detail optical and x-ray studies, Friedel [5] classified thermotropic liquid crystals broadly into three types: nematic, cholesteric and smectic.

Nematic liquid crystals

The nematic phase is a one dimensional ordered elastic fluid. This phase has no long range translational ordering of the molecules, thus showing the fluid character of the phase. However, the molecules in this phase have long range orientational order. The molecules tend to align parallel to each other with their long axes all pointing roughly in the same direction [64], **Figure 1.6**. The average direction along which the molecules point is called the director and is usually denoted by a unit vector **n**. The direction of **n** is arbitrary in space. The director **n** and –**n** are indistinguishable i.e. in a bulk nematic phase, there are as many molecules pointing in one direction with respect to the director, as they are pointing in the opposite direction. Nematic phase occurs when the constituent molecules are achiral i.e. they must be identical to its mirror image or the molecules must be



(b)

Figure 1.5. Molecular structures of compounds giving rise to thermotropic mesophases.

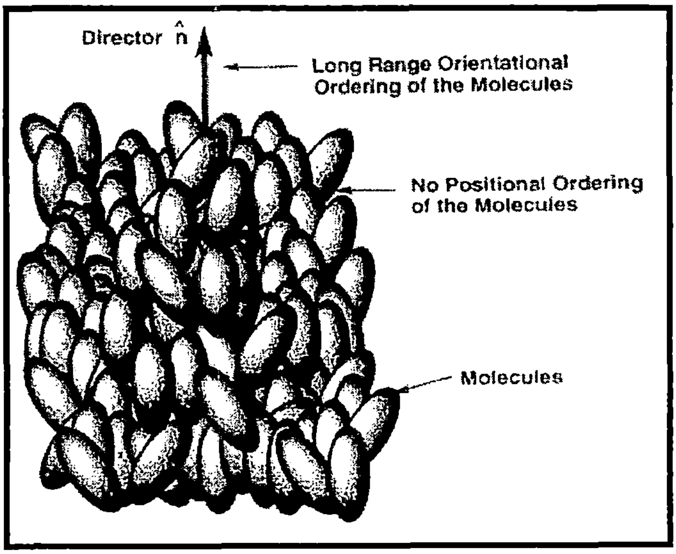


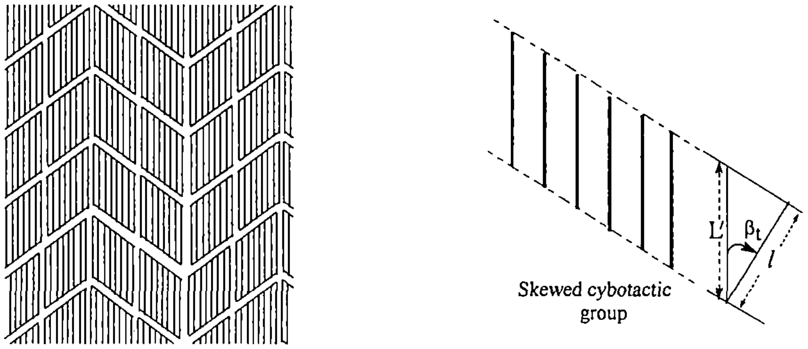
Figure 1.6. The molecular arrangement in the nematic phase.

present in racemic (1:1) mixture of the right and left handed species. The rod like molecules in nematic phase is rotationally and orientationally disordered relative to their short axes and the phase is uniaxial and therefore it has strong positive birefringence also with respect to all other physical properties. When the molecules have board shape the degree of rotational freedom about their long axes is restricted. As such there could be an ordering of such molecules giving rise to a biaxial nematic phase. The biaxial modification of the nematics has also been discovered [64-73]. Nematic phase are very sensitive to external fields, electric or magnetic and mechanical stress, which it translate into visible optical effects, for which they find wide application in display devices.

X-ray studies [74-77] indicate that in certain nematic liquid crystals, there are molecules arranged in groups. In each group the molecules are parallel to each other and the center of the molecules lie in a plane, **Figure 1.7**. These groups or clusters of molecules therefore possess short range order and are called cybotactic groups. The molecules in the cybotactic groups may either be arranged normal or tilted to the plane. The resulting phases are respectively called normal or skewed cybotactic nematic.

Cholesteric liquid crystals

A nematic liquid crystal when mixed with chiral (optically active) molecules, the structure undergoes a helical distortion about an axis normal to the preferred molecular direction **n, Figure 1.8**. The twist may be right or left handed depending on the molecular conformation. Locally a colesteric phase is similar to a nematic phase and the molecular centre of mass have no long range order. Racemic mixture of optically active cholesterics results in nematic phase. Therefore the nematic phase is a cholesteric of infinite pitch of the helix. The energy of twist form a small part (10^{-5}) of the total energy associated with the parallel alignment of the molecules [78] so that even when small amount of cholesteric substance or a non-mesogenic optically active substance is added to nematic the mixture adopts helical conformation. The pitch of the spiral is temperature dependent and comparable to an optical wavelength. The cholesteric-nematic transition is found to be absent [79]



(a) (b)

Figure 1.7. (a) Model showing the molecular arrangement in cybotactic nematic phase (b) schematic representation of sweked cybotactic group (full lines indicates the molecules, the broken lines shows the boundary planes. β_t is the tilt angle.

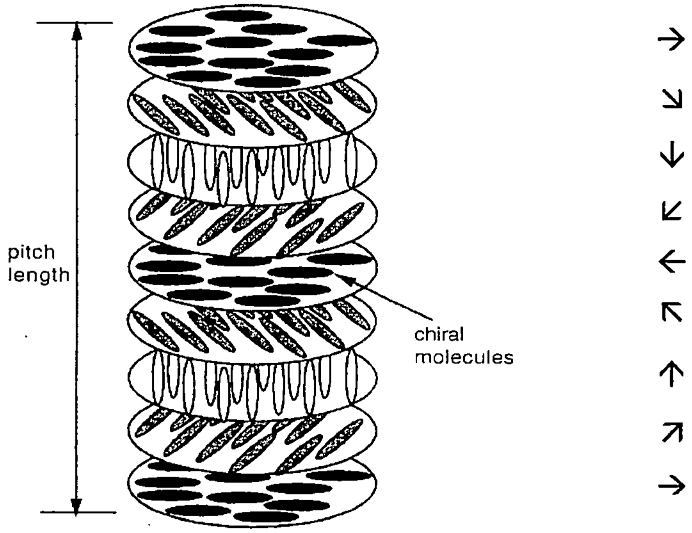


Figure 1.8. The molecular arrangement in the cholesteric phase. The imaginary planes have been drawn for convenience, and do not imply the layered structure.

when the temperature of the cholesteric is changed and also by a strong magnetic field applied normal to the helical axis [80,81].

Cholesterics with pitch less than 5000Å, exhibit what are known as **blue phases.** The blue phases exist over a small temperature range (~1^0C) between the mesophase and isotropic liquid transition [82, 83]. Three distinct blue phases (I, II and III) have been identified and occur in that order with increasing temperature.

Smectic liquid crystals

Smectic liquid crystals have layered structures, are characterized by both orientational order of the long molecular axes and by a reduced positional order than the crystals. Smectics are therefore ordered phases than nematics. Normal to the layers the molecule are arranged in a one dimensional density wave and within the layers the molecules are either randomly distributed or have some ordering. The inter layer interactions are weak as compared with the intermolecular lateral forces, as such the layers can slide over one another, thereby promoting fluidity, though it is much viscous than the nematic phase. The in plane positional ordering of the constituent molecules and the orientational order relative to the layer planes give rise to four sub-groups of smectic mesophases. The first two groups can be defined where the molecules have their long axes on an average normal to the layers. The two groups are distinguished by the degree of positional ordering of the constituent molecules. For example smectic A and hexatic B have short range positional ordering [84]. Where as the crystal B and crystal E phases are smectic like soft crystal modification [85,86] with the constituent molecules having long range positional ordering in 3-dimension [87]. The other two sub groups have their constituent molecules tilted relative to the layer planes. In smectic C, smectic I and smectic F phases the molecule have short range positional ordering [88,89] while in crystal G, crystal H, crystal J and crystal K phases the molecules have long range 3-dimensional ordering [85,89]. Smectic A, C, C_{alt}, B_{hex}, I and F are smectic liquid crystals while B, E, G, H, J and K are crystal phases. The latter phases however have properties different from normal crystals. The structures of smectic modifications have been investigated by x-ray diffraction techniques [90-95].

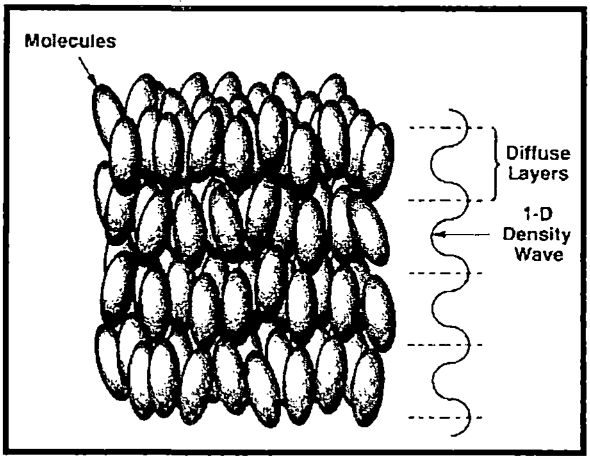


Figure 1.9. Molecular arrangement of the orthogonal smectic A phase.

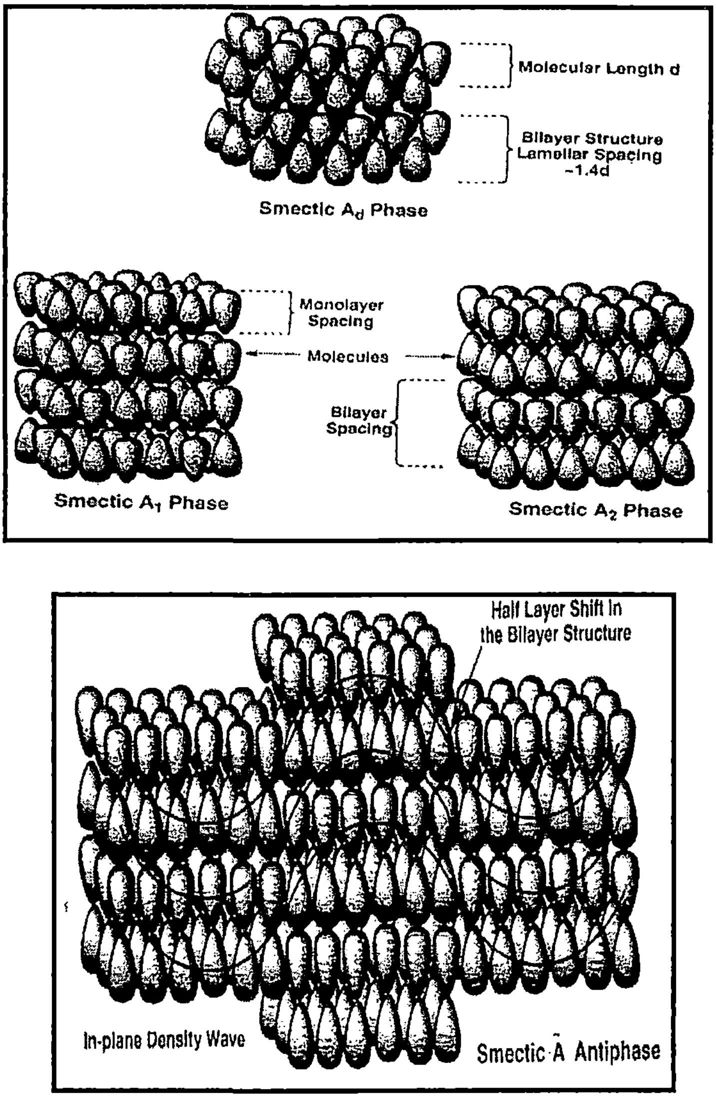


Figure 1.10. Sub-phases of smectic A showing the bilayer and monolayer structures- semi bilayer SmA_d, monolayer SmA_1, bilayer SmA_2 and ribbon $Sm\tilde{A}$.

Smectic A

In smectic A (SmA) phase the molecular long axes have long range orientational order within the smectic layers while the molecular center of mass inside each layer have no long range order, **Figure 1.9**. The director is normal to the layer planes. The layers can slide over one another thus forming a two dimensional liquid system. The molecules are free to rotate about their long axes [96,97]. SmA has infinite fold rotational symmetry about the axis parallel to the director, for which this phase is uniaxial [95]. The SmA layer spacing 'd' is close to full length 'L' of the constituent molecules. If the molecules have strong longitudinal dipole moment the anti parallel nearest neighbour correlations will result in the modification of the structure of SmA [98,99]. Thus SmA can further be divided into subphases viz., SmA_1 which is a conventional smectic A phase, where the molecules have random head to tail orientations, SmA_2 is a bilayer phase with antiferroelectric ordering of the constituent molecules [100], SmA_d is a semi bilayer phase with partial molecular overlapping due to associations [98,99] and $Sm\tilde{A}$ is called ribbon or antiphase phase [101-103], **Figure 1.10**. The last phase is a modulated antiferroelectric ordering of the molecules within the layer giving a ribbon like structure. Polymorphism of SmA phase have been discussed in detail by several authors [103-118]. Biaxial SmA ($Sm\ A_b$) phase has also been reported [119,120].

Smectic C

In smectic C (SmC) phase the constituent molecules are arranged in layers with the molecules tilted relative to the layer plane (**Figure 1.11**) at a temperature dependent angle. The layer spacing 'd' of the SmC phase is less than the molecular length. The layer thickness $d=L\cos\beta$ where L is the molecular length and β is the tilt angle. The SmC phase is optically biaxial [121,122]. There is no long range positional ordering of the molecules, however orientational ordering appears to be long range. A sub phase of SmC phase also exist called alternating smectic C (SmC_{alt}) or SmO[123-125]. The other sub phases of smectic C are SmC_1 which is a conventional smectic C phase, where the molecules have random head to tail

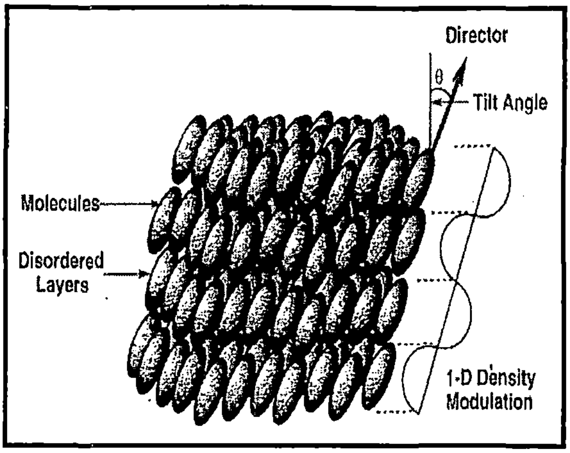
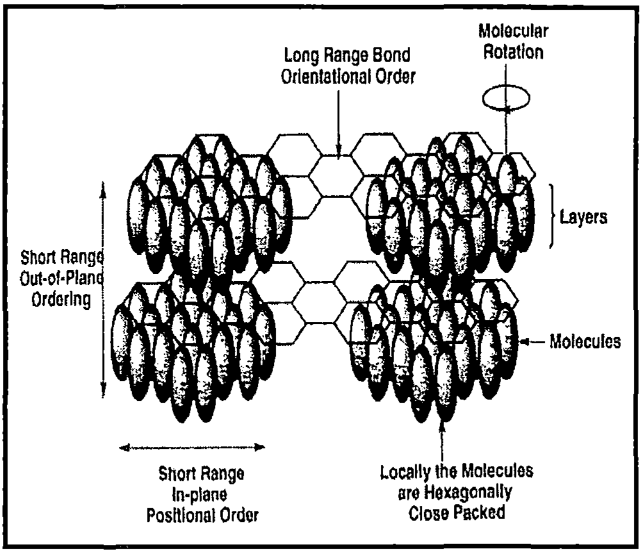
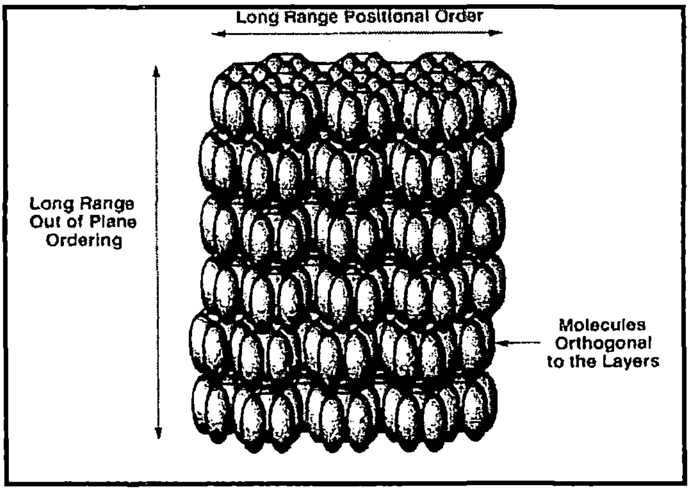


Figure 1.11. The molecular arrangement of tilted smectic C phase.



(a)



(b)

Figure 1.12. Structure of (a) smectic B and (b) crystal B phases.

orientations, SmC_2 is a bilayer phase with antiferroelectric ordering of the constituent molecules, SmC_d is a semi bilayer phase with partial molecular overlapping due to associations and $Sm\tilde{C}$ is called ribbon or antiphase phase. Thus, the smectic C_1, C_2, C_d and $\tilde{C}$ phases are the analogues of A_1, A_2, A_d and $\tilde{A}$ phases respectively [92,126].

Smectic B

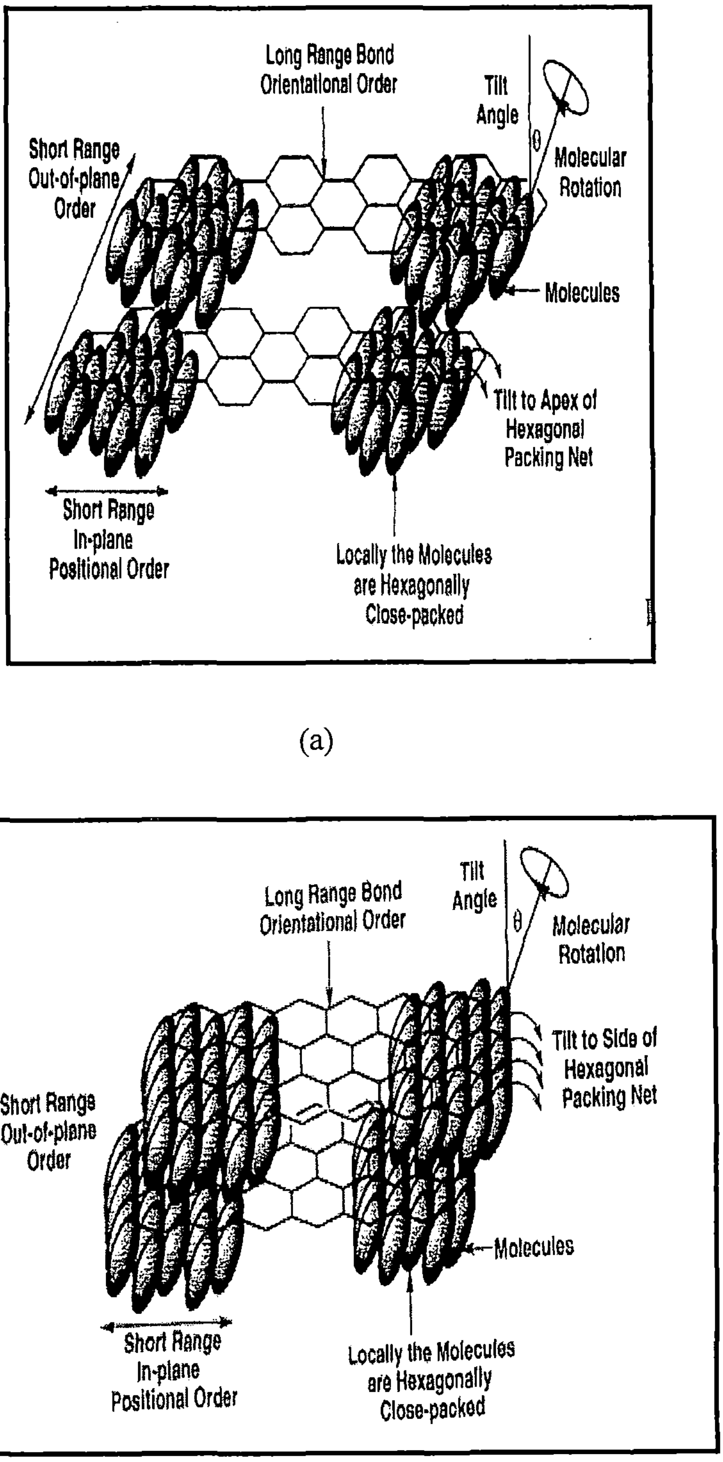
Smectic B (SmB) or Hexatic B phase is more ordered than the SmA phase. The constituent molecules having their long axis normal to the layer plane and the center of mass of the molecules are arranged in a hexagonal symmetry [19,84,87,127,128] as shown in **Figure 1.12(a)**. It is optically uniaxial or biaxial. The molecules are free to rotate about their long axis however the rotational freedom about their short axes are restricted, due to the close packing of the molecules. Under a microscope the SmB phase usually shows a mosaic texture. This phase has long range bond orientational order. Thus the SmB is most ordered of the three major smectic phase A, B and C. The sequence of phase transition in a material possessing all the above three phases is always SmB ↔ SmC ↔ SmA.

Smectic I

The hexagonal nature of the SmB phase generates two tilted analogues called the smectic I (SmI) and smectic F (SmF) phases where the molecules are tilted. In SmI phase molecules are arranged in a similar fashion as in SmC phase, **Figure 1.13(a)**. The positional ordering of molecules is short range in nature [88,93,130-133]. Out of plane correlation of the molecular position are weak [87]. The phase however, has long range bond orientational order. The tilt in the molecular long axis in SmI phase is directed towards an apex of the hexagonal packing net.

Smectic F

Smectic F phase is almost identical to SmI phase [131]. The only difference between the two phases is the tilt direction, which in the SmI phase is directed



(a)

(b)

Figure 1.13. Structure of (a) smectic I and (b) smectic F phases.

towards the apex of the hexagonal net whereas in the SmF phase it is directed towards an edge of the net [132], **Figure 1.13(b)**. SmI and SmF phases differ in the extent of in plane ordering, the SmF have slightly longer correlation length than SmI [134,135].

Crystal B

The molecules in this state [87,136-138] are arranged in layers with their long axes normal to the layer planes as in smectic A phase as shown in **Figure 1.12(b)**. The molecules have long range translational order in 3-dimension as well as long range bond orientational order as in smectic B phase. X-ray studies indicate that molecules are not laterally separated to allow free rotation about their long axes to occur. The molecules undergo reorientational motion about their long axes on a time scale of 10^{11} times per second. The inter layer packing of molecules in crystal B shows some variations in the inter-layer stacking, as such mono-, bi- and tri-layer unit cell are obtained. The layers are hexagonally close packed and the layer stacking could be (i) AAA..... type of layer packing (ii) there is a shift in the adjacent layers to give an ABAB.... type of packing (iii) the adjacent layers are shifted in opposite directions to give ABCABC....type of layer stacking [139]. The layers of B and C are not necessarily in the trigonal positions relative to A. The transition between different packing structures can occur by changing temperature, though no enthalpy change could be detected.

Crystal E

In crystal E phase the molecules are also arranged with long axes normal to the layer planes. The molecules are arranged locally in orthorhombic array [140] as shown in **Figure 1.14** and so this phase is biaxial [141]. The rotation of the molecules about their long axes is not free [90] and therefore the molecules are arranged in a herringbone array. The molecules undergo oscillatory motion in the time scale of 10^{11} times per second. The molecules have long range periodic order

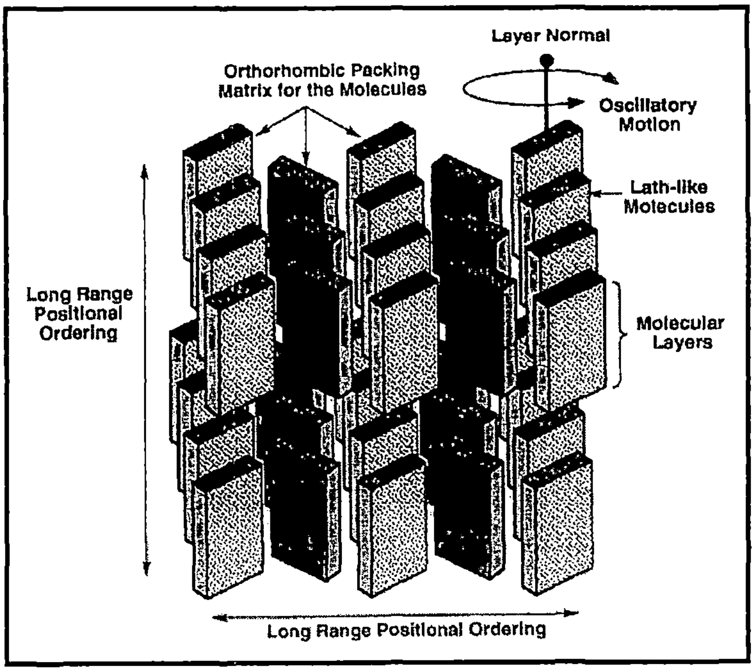


Figure 1.14. Molecular arrangement in crystal E phase.

both inside the layers and out of planes. Bilayer structure of crystal E as in crystal B is also found [97].

Crystal J and G phases

The crystal J and G phases [140,142,] are the crystalline analogues to smectic I and F phases [87,136]. The molecules in the J phase are arranged in layer with their molecular long axes tilted relative to the layer planes. There is long range positional ordering within the layers and also between the layers [143]. The molecules are packed in a pseudo-hexagonal structure when viewed down the tilt direction. The packing of molecules in the layers is of AAA... type [90,132]. The crystal G phase has similar structure as the J phase except that the tilt of the molecules is directed towards the edge of the hexagonal packing array whereas in J phase the tilt is towards the apex of the hexagonal net. The molecules undergo rapid reorientational motion about their long axes [87,136, 139].

Crystal H and K phases

The molecules of these phases are arranged in layers and possess long range positional ordering inside and between the layers. The molecular packing is monoclinic with the tilt being towards the short edge of the packing net in H phase and to the longer edge of the packing array in the K phase [87,132,136,139]. These phases are analogous with the crystal E except that the molecules are tilted with respect to the layer planes [96,97].

Variants of H and K phases are possible with the tilt making an angle with edges of the monoclinic unit cell [144]. The motion of molecules about their long axes is assumed to be oscillatory in nature just as in E phase [96,97].

Essentially the phases B(cryst), J, G, E, K, and H are crystalline. However, the molecular dynamics are quite different from those observed in crystals. For example, the molecules are undergoing rapid reorientational motion about their long axes [139]. Also many internal molecular rotations like trans-gauche conformational

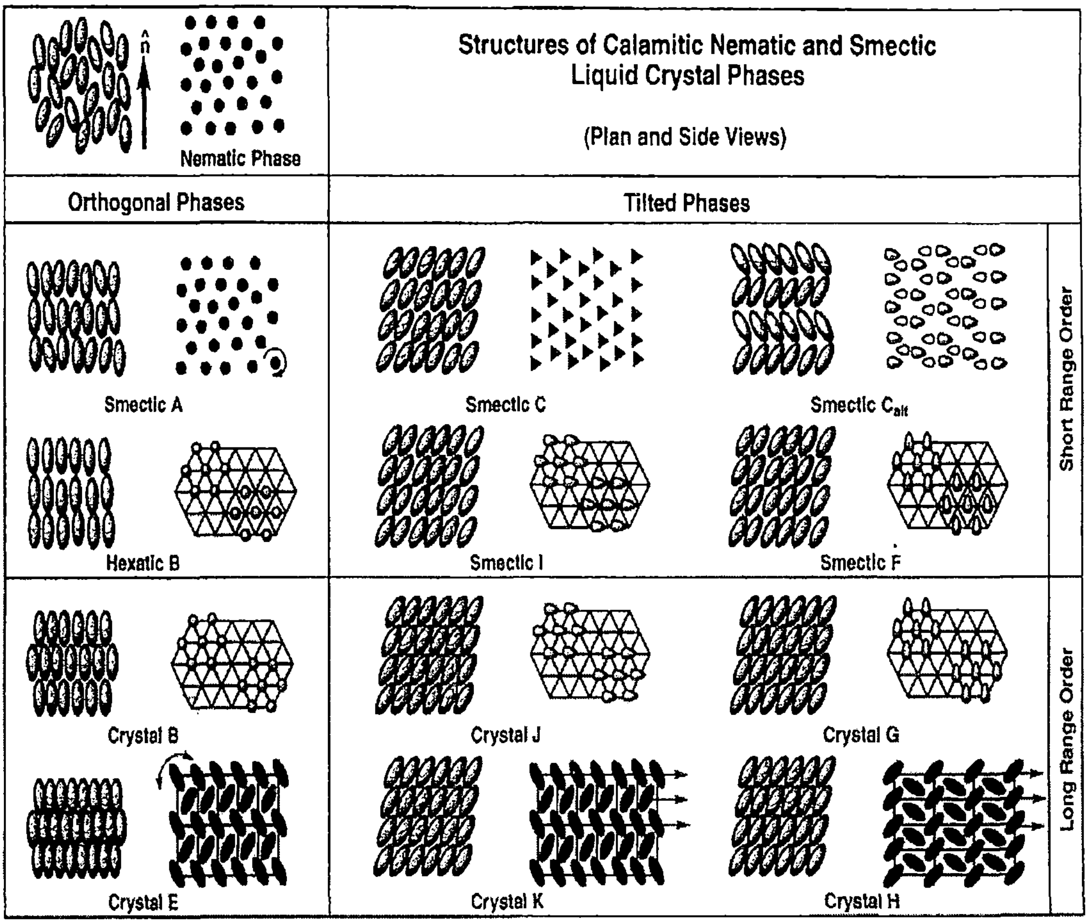


Figure 1.15. Plan and side view of the structures and molecular order in liquid crystalline phases. The rod –like molecules, represented as ellipses show the layer ordering and circles, dots, triangles or ellipses, show the plan view of the layers.

Figures 1.3,1.4,1.8,1.16 from [198]

Figures 1.6,1.7,1.9-1.15 from [8].

changes, takes place at the same time. The rapid reorientational motion of the molecules about their long axes, has led to describe these phases as soft crystals.

The molecular structure with ordering in various phases of calamitic liquid crystals and isotropic liquid is summarized in **Table 1.1** and the comparative plan and side view of the mesophases are shown in **Figure 1.15**.

In smectic mesophases the alphabets were assigned to different phases simply in chronological order in which these phases were discovered. From the current knowledge the sequence of liquid crystalline phases in decreasing ordering or with increasing temperature may be written as follows [8]:

Crystal→H →K →E →G →J → SmF → B(cryst)→[B(hex), SmI] →SmC →SmA→N(or Ch) → Isotropic Liquid.

Table 1.1 Molecular arrangements and ordering in liquid crystalline phases.

Phase type	**Molecular orientation**	**Molecular packing**	**Molecular orientational ordering**	**Bond orientational ordering**	**Positional ordering**	
					Normal to the layer	**Within the layer**
Isotropic	random	random	SRO	SRO	SRO	SRO
N	Parallelism of long molecular axis	random	LRO	SRO	SRO	SRO
SmA	orthogonal	random	LRO	SRO	QLRO	SRO
SmC	tilted	random	LRO	SRO	QLRO	SRO
SmB hex	orthogonal	hexagonal	LRO	LRO	QLRO	SRO
SmI	Tilt to apex of hexagon	pseudo hexagonal	LRO	LRO	QLRO	SRO
SmF	tilt to side of hexagon	pseudo hexagonal	LRO	LRO	QLRO	SRO
B	orthogonal	hexagonal	LRO	LRO	LRO	LRO
J	Tilt to apex of hexagon	pseudo hexagonal	LRO	LRO	LRO	LRO
G	tilt to side of hexagon	pseudo hexagonal	LRO	LRO	LRO	LRO
E	orthogonal	orthorhombic	LRO	LRO	LRO	LRO
K	tilted to longer side of cell	monoclinic	LRO	LRO	LRO	LRO
H	tilted to shorter side of cell	monoclinic	LRO	LRO	LRO	LRO

SRO→ short range order, LRO→ long range order, QLRO→ quasi-long range order

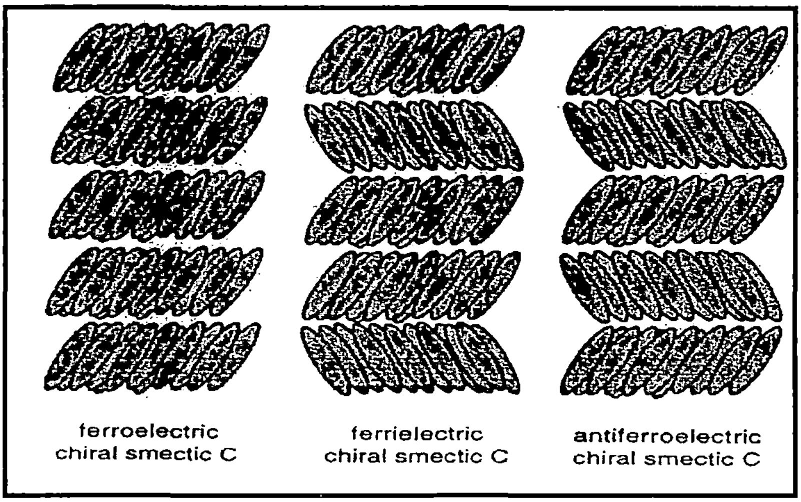
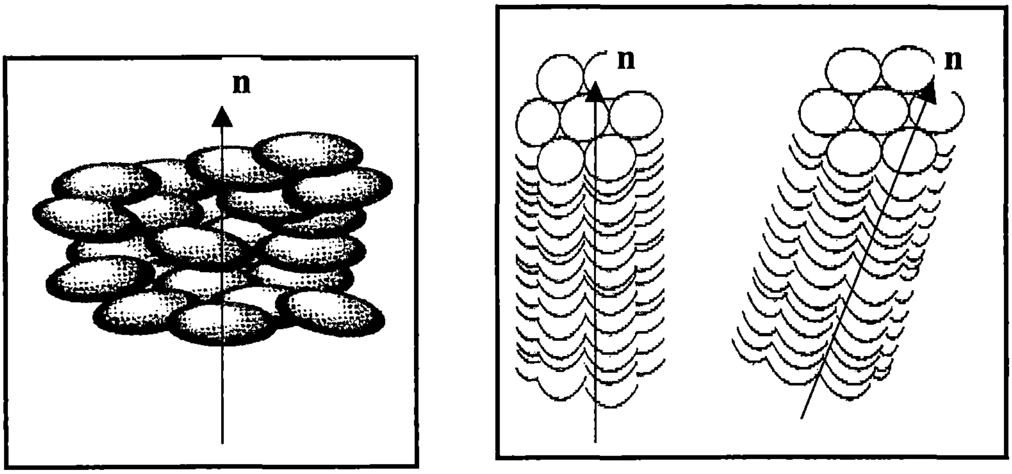


Figure 1.16. The structures of chiral smectic phases, SmC*, SmC$^*_{\text{ferri.}}$ and SmC$^*_{\text{anti.}}$



(a) (b) (c)

Figure 1.17. The schematic representation of discotic (a) nematic and columnar structures of (b) upright columns, (c) tilted columns. (the arrows show the director **n**).

Ferroelectric liquid crystals

There are different types of smectic liquid crystal phases SmC*, SmI* and SmF* and crystal smectic phases J*, G*, K* and H* in which the constituent molecules are chiral (optically active) and their long axes are tilted with respect to the layer planes. Chiral compounds with tilted structures exhibit ferroelectric properties. Ferroelectric liquid crystals (FLCs) have been the subject of intense investigation over the last two decades, not only with respect to their intriguing properties for fundamental condensed matter research, being the only known intrinsic polar fluid materials, but also for applications in fast switching flat panel displays or optical light modulators. Excellent review articles, books and monographs on FLCs are available such as in [46, 145-150].

The chiral smectic mesophases takes the form of a helical structure, which is different from the helix in chiral nematic phase. The most commonly exhibited tilted chiral smectic phase is the SmC*. Due to its reduced symmetry (lack of mirror symmetry in SmC^* than in SmC) the phase can be spontaneously polarized.

There are other chiral smectic phases viz., antiferroelectric chiral smectic C (SmC^*_{anti}) phase, the ferrielectric chiral smectic C ($SmC^*_{ferri.}$) phase. The structures of SmC*, $SmC^*_{anti.}$ and $SmC^*_{ferri.}$ are shown in **Figure 1.16**. In $SmC^*_{anti.}$ phase the constituent molecules have tilted lamellar structure of the ferroelectric SmC* phase but the tilt direction of the molecular long axes alternates from layer to layer. As such the spontaneous polarization of SmC^*_{anti} is zero. The SmC^*_{ferri} phase also has alternating tilted structure, however the alteration is not symmetrical and more layers are tilted in one direction than the other. This phase generates spontaneous polarization, the magnitude of which depends on the degree of alternation of tilt direction.

Three subphases – SmC^*_α, SmC^*_β and SmC^*_γ - have also been found in many antiferroelectric liquid crystal materials [151]. In 1996 Nirori *et al.* [152] observed ferroelectric switching even in achiral banana-shaped molecules as predicted by Watanabe *et al.* [153] and many such systems are found to have ferroelectric properties.

Various applications of FLCs have been discussed in references [26,46,154-158] including the commercial 15 inch FLC panel with 1280x1024 pixels, each pixels being capable of displaying 16 colours.

Discotic liquid crystals

Disc like molecules, with one molecular axis much shorter than the other two, as shown in **Figure 1.2**, also exhibit liquid crystal phases. [159-163]. There are two basic types of discotic mesophases that have been recognized viz., columnar and nematic. The disc are stacked one on top of the other to form columns, different columns forming a two dimensional lattice. In some cases the columns are liquid like where the molecular centers are arranged aperiodically within each columns, while in others the molecules are regularly stacked. Columnar and nematic discotic phases are shown in **Figure 1.17**. A number of variants of this structure have been identified viz., hexagonal, rectangular, oblique, etc. The polymorphism in columnar phases is analogous in many ways to the polymorphism in smectic mesophases exhibited by calamatic materials. The nematic phase N_D exhibited by discotic materials shows similar optical textures as that of calamatic nematic phase N and has orientationally ordered arrangement of the disc without any long range positional order. This phase is optically negative. Recently, few disc shaped materials have been discovered that exhibit columnar nematic N_C phase [164,165]. Present state of research in discotic mesophases have been reviewed by A. N. Cammidge and R J Bushby [166] and very recently by S. Kumar [167]. In the later reference some commercial applications of triphenylene based discotic liquid crystals have also been mentioned.

Polymer liquid crystals

Polymers are substances whose molecules are built up of a large number of chemically bonded repeating structural units. With a suitable mesogenic building units (monomers) the substance exhibits liquid crystalline properties. These mesogenic units, (usually calamatic but many discotic types exist) should be

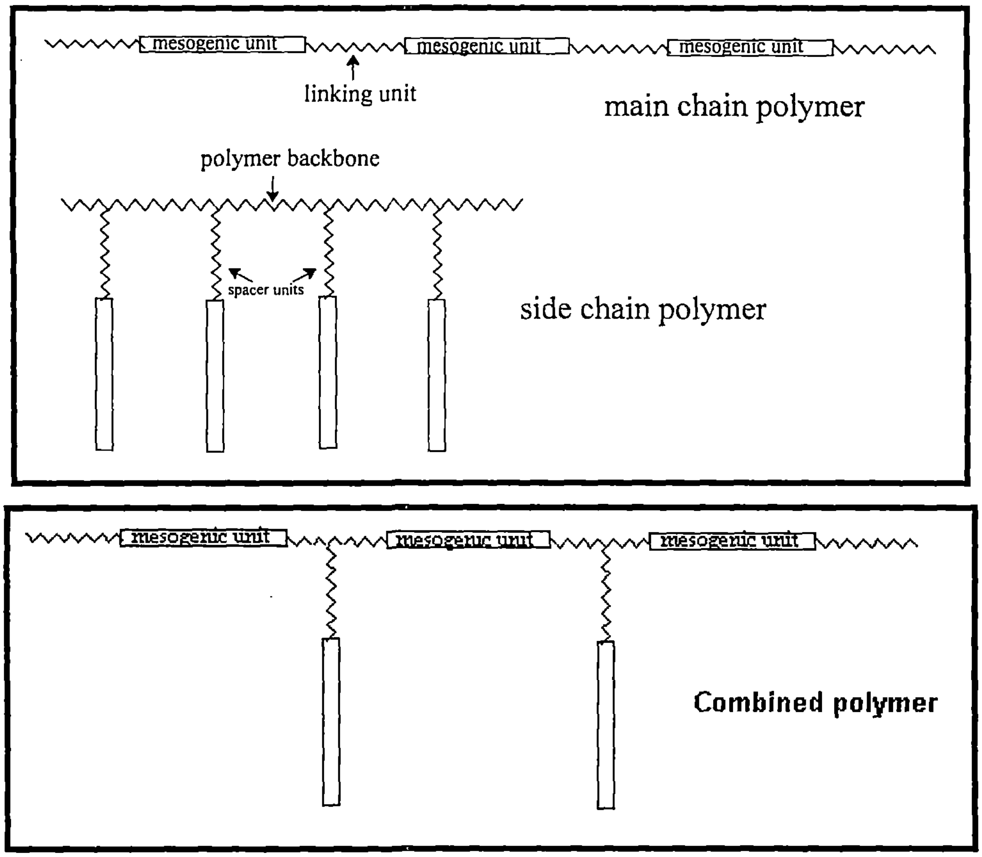


Figure 1.18. The main types of liquid crystal polymers.

attached with appropriate functional end groups in order to obtain a polymer. There are two types of polymer liquid crystals viz., main chain and side chain. In the main chain polymer liquid crystals the mesogenic group repeats via the linking unit. The nature of the mesophase depends rather sensitively on the backbone, the mesogenic unit and the linking unit [168]. When the mesogenic repeating unit are rod-like, the mesophases similar to the nematic, cholesteric, smectic types of calamatic liquid crystals are observed [169-172] and with discotic mesogenic unit other new kinds of mesophases are generated [173-177] viz., sanidic (or board like) nematic and columnar nematic phases. The flexible linking unit between the functional groups and the rigid mesogenic groups provides the flexibility of the polymer main chain. Side chain polymer liquid crystals consist of mesogenic groups fixed as side chain to the polymer backbone. The large number of possible mesogenic units together with the different structural alternatives gives rise to enormous number of side chain polymer liquid crystals compounds. The third class of polymer liquid crystals is called combined polymer liquid crystals which has the combined features of main chain and side chain polymer liquid crystals. The structural features of the three types are shown in **Figure 1.18**. Polymer liquid crystals exhibit the same liquid crystalline phases as exhibited by low molar mass mesogens. However the identification of the mesophases exhibited by the polymers are usually far more difficult than for low molar mass liquid crystals. Low molar mass liquid crystals show first order phase transitions from the crystalline phase at lower and from isotropic liquid phase at higher temperatures. However the latter transition is found in polymers, but former transition is not exhibited. On cooling the polymer liquid crystals is transformed to polymer glass since the orientation order is frozen in without any changes.

Induced Smectic and Re-entrant Nematic phases

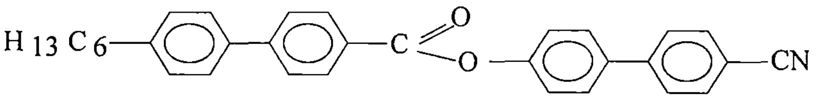
An interesting feature of binary or multi-component liquid crystals mixtures is the formation of relatively more ordered phase, the so called induced smectic phase from components which show only nematic phase in their pure state [178-

189]. It is now established that the induced phases occur in binary mixtures with one component having a strong terminal polar group and another component with weak or non-polar terminal groups. Mixtures of two cyano compounds have been found to induce smectic C phase [188]. The dipole-induced dipole interactions is thought to play major part in the induce phase stabilization. Charge transfer complex is formed with polar molecules acting as acceptors [179,183,187]. Re-entrant phenomena of less ordered nematic phase (N_R) below the more ordered smectic phase are also observed by Cladis [190] in binary mixtures of certain mesogenic compounds containing a terminal cyano group. Later Cladis and co-workers [191,192] also observed this phenomenon in pure single component systems at higher pressures. Since then, this interesting phase transition has been observed at atmospheric pressure in a few pure compounds containing a terminal cyano group[193-196]. Even the spectacular re-entrant polymorphism viz. Isotropic $\rightarrow$ N $\rightarrow$ SmA_d $\rightarrow$ N_R $\rightarrow$ SmA_d $\rightarrow$ N_R $\rightarrow$ SmA_1 $\rightarrow$ $\tilde{C}$ $\rightarrow$ $SmA_2$$\rightarrow$ SmC2 $\rightarrow$ Crystal, has also been observed [197]. The occurrence of this phenomenon is evidently of considerable importance from the theoretical point of view.

List of the compounds investigated

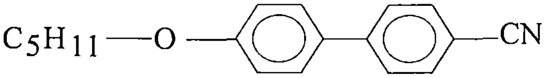
The names and structural formulae of the compounds studied in the present thesis are given below. Abbreviated names are given within parentheses.

1. **4-Cyanobiphenyl-4'- hexylbiphenyl carboxylate. (6CBB)**

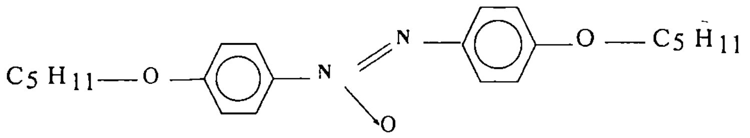


2. **Binary mixtures of compounds 4, 5 and 6 with 3 along with some properties of these pure compounds**

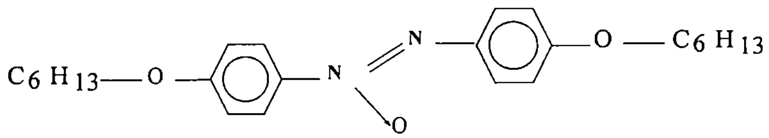
3. **4,4'- Pentyloxy cyanobiphenyl (5OCB)**



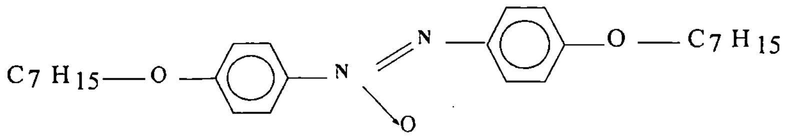
4. **4,4'-bis(Pentyloxy) azoxybenzenes (5OAB)**



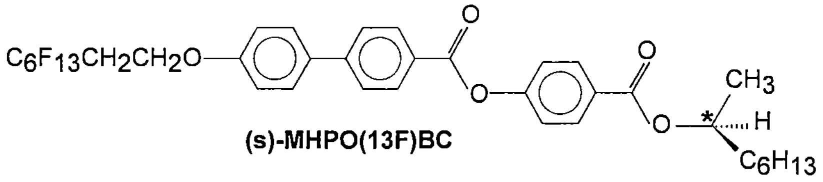
5. **4,4'-bis(Hexyloxy) azoxybenzenes (6OAB)**



6. **4,4'-bis(Heptyloxy) azoxybenzenes (7OAB)**



7. **Ferroelectric compound [MHPO(13C)BC]**



(s)-MHPO(13F)BC

Aim and Scope

During the last few decades interest in liquid crystals has increased due to its immense possibilities for practical applications as well as its role in biological systems. These materials have unusual structural, physicochemical and thermophysical properties: the fine balance of the structure and its dependence on the temperature, pressure and external fields; the existence of unusual phase transitions and so on. Thus the study of liquid crystals is of great significance for the further development of the theory and for increasing the depth of understanding the nature, structure and properties of possible aggregate states and of corresponding phase transitions. Studies on different macroscopic and microscopic properties viz. optical birefringence, static and frequency dependent dielectric constants, elastic constants, order parameters etc.; crystal and molecular structure analysis for finding structure-property relationship are, therefore, very important. Since, in commercial liquid crystal display devices multi-component mixtures are always used to optimize the relevant physical parameters, studies on mixtures, in addition to the pure components, are also important.

Keeping this in view in the present dissertation **5OCB and nOAB (n=5-7) and their binary mixtures** have been studied by employing different experimental techniques like – Optical microscopy for texture studies, Differential scanning calorimetry for phase transitions, Dilatometry for density measurement, Thin prism technique for optical birefringence measurement, X-ray diffraction for identification of phases and finding different molecular parameters, Freedericksz transition for elastic constant measurement, Capacitance measurement technique for dielectric constant measurements.

The **ferroelectric liquid crystal compound MHPO(13C)BC** was studied by optical microscopy and DSC. The spontaneous polarization measurement and frequency domain dielectric spectroscopy study have also been done on this compound.

The **3-D crystal structure of 6CBB** has been determined by direct methods from single crystal X-ray intensity data and attempts have been made to explain mesophase formation and stability in the light of the packing of the molecules in the crystalline state.

In addition, the observed results have been interpreted and tried to explain in the light of existing ideas and theories. Results obtained on the present systems have also been compared with those of structurally similar compounds to get better idea about the structure property relationship.

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