Chapter I

INTRODUCTION

1.1 LIQUID CRYSTALS

The term **liquid crystal** stands for a state of condensed matter that is intermediate between the crystalline solid and amorphous liquid state. A liquid crystal is strongly anisotropic in some of its properties like ordinary crystals and yet exhibits a certain degree of fluidity, which in some cases, is comparable to that of an ordinary liquid. The molecules in a crystal have both positional and orientational ordering whereas in liquids their arrangement is random. In liquid crystals, however, the molecules are more ordered than in liquids but are less ordered than that observed in a typical crystal.

The liquid crystalline state was first discovered in 1888 by an Austrian botanist Friedrich Reinitzer [1] while studying cholesterols in plants. He observed a cloudy liquid between two melting points in cholesteryl benzoate and cholesteryl acetate. Remarkable iridescent colours were also observed between the two melting points. Otto Lehmann, a German Physicist, reaffirmed the observations [2,3] made by Renitzer and termed such materials as **flowing crystals** in 1889, **crystalline liquids** in 1890 and **liquid crystals** in 1900 [4]. Since the liquid crystal phase is observed between the isotropic liquid and crystalline solid phase it is also called **mesophase** or **mesomorphic phase**, as suggested by Georges Friedel [5,6]. Materials, which undergo transition to liquid crystal phase or mesophase, are known as **liquid crystalline materials** or **mesogens**. The historical perspective of the liquid crystal research is found in the refernces [7-10].

Liquid crystal is currently an important phase of matter both from the viewpoint of basic sciences and technological applications. Thousands of compounds — mainly organic, and some organometallic, inorganic and bio-molecules, are now known to form mesophases [10-18]. Molecules of various shapes and nature form liquid crystalline phases. But the common features among them are that the molecules are geometrically anisotropic in shape and highly anisotropic intermolecular forces hold them together. Depending upon the detailed molecular structure, a compound may exhibit one or more mesophases before it is transformed into the isotropic liquid from the solid phase. Transitions to these intermediate states may be brought about by thermal processes or by the influence of solvents. Though first observed more than a century ago resurgence in liquid crystal research took place in 1960s and at present, members of the scientific community all over the world are working in this fascinating interdisciplinary field. As a result many excellent books and monographs have appeared on all aspects of the liquid crystals ranging from the fundamentals to the forefront of research. Some of these have been referred [12,14,17-57].

1.2 CLASSIFICATION OF LIQUID CRYSTALS

Liquid crystals may be divided into two main categories viz. **lyotropic** and **thermotropic.** A lyotropic liquid crystalline material forms mesophases in a certain range of concentration of the solution of the substance in some solvent. On the other hand, a thermotropic mesogen exhibits a liquid crystalline phase in a certain temperature range and undergoes phase transitions when temperature changes.

1.2.1 Lyotropic liquid crystals

Lyotropic liquid crystals [33,46,57-73] are made up of two or more components. Generally a lyotropic molecule contains a hydrophilic polar head group and one or more long hydrophobic alkyl chains (Figure 1.1). Such amphiphilic molecules form ordered structure in both polar and non-polar solvents. A typical example of this type of liquid crystal is soap and water system where mesomorphic phases appear as a function of concentration. The water molecules penetrate the space between the layers formed by polar groups of the soap molecules and weaken the attractive forces between them to cause transition from solid phase to lyotropic phase. Mainly three different types lyotropic phases viz. lamellar (or neat), hexagonal (or middle) and cubic (or viscous isotropic) are possible. In Figure 1.2 lamellar lyotropic phase structure is illustrated. Temperature range of a lyotropic phase depends upon the concentration. Lyotropic liquid crystals occur abundantly in nature, being ubiquitous in living systems. For example, the tobacco mosaic virus (TMV), many synthetic polypeptides, cell membranes of all

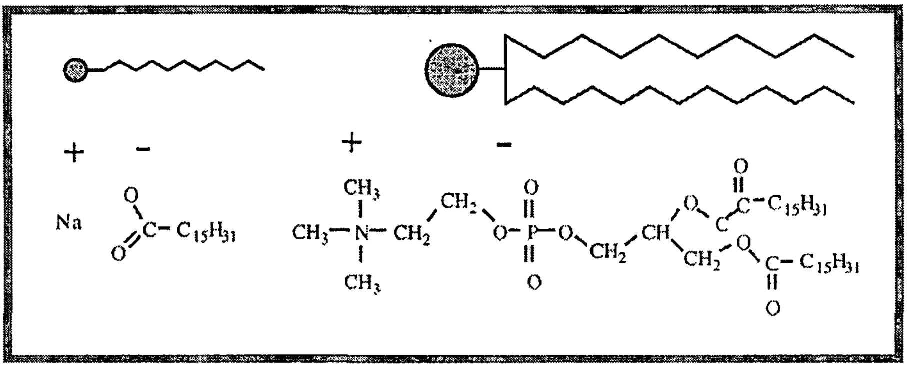

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Figure 1.1 Lyotropic liquid crystal molecules: Soap (left) and Phospholipid (right)

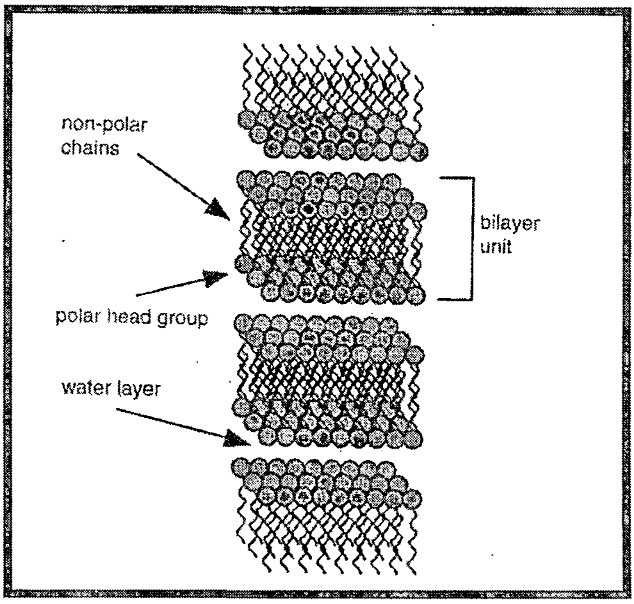

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Figure 1.2 Structure of the lamellar lyotropic liquid crystal phase.

living organism and some organic fluids like blood, deoxyribonucleic acid (DNA) molecules exhibit lyotropic behaviour when dissolved in an appropriate solvent (usually water) in suitable concentration. Also there is a well-defined family of lyotropic mesogens embracing a range of drugs, dyes, nucleic acids, antibiotics, carcinogens and anti-cancer agents. Since the present thesis contains results of only the thermotropic liquid crystalline systems, no further discussion will be made on lyotropic mesophases.

1.2.2 Thermotropic Liquid crystal

As mentioned earlier, thermotropic liquid crystals are those in which phase transitions occur due to change in temperature. The vast majority of thermotropic liquid crystals are composed of rod-like molecules (one molecular axis is much longer than the other two) and they are known as calamitic liquid crystals. A typical calamitic liquid crystal is shown in Figure 1.3. Following the nomenclature proposed by Friedel [5], they are classified into three main types: **nematic, cholesteric and smectic.**

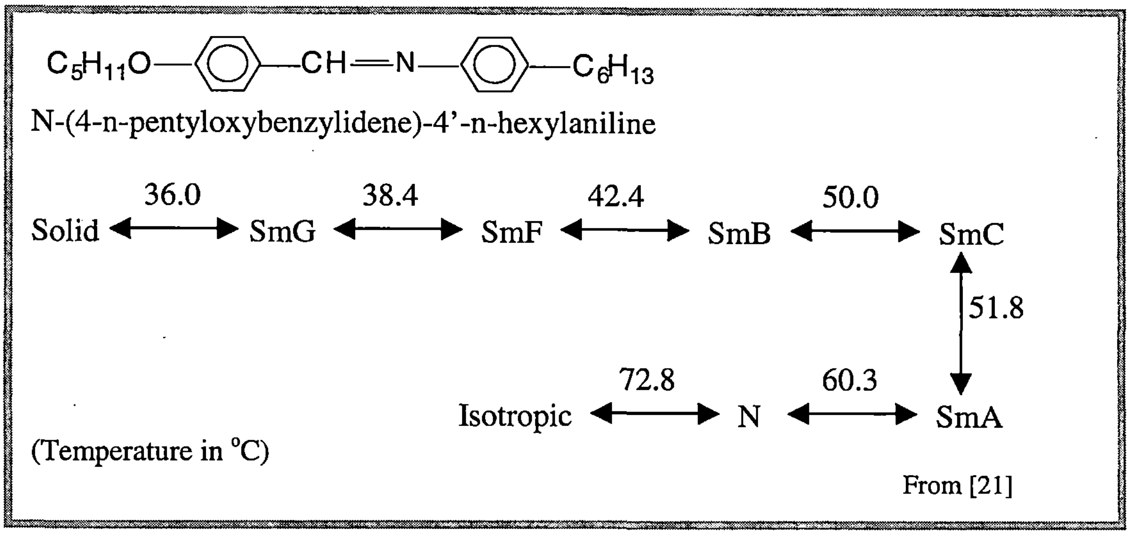

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Figure 1.3 A typical calamitic liquid crystal with transition temperatures.

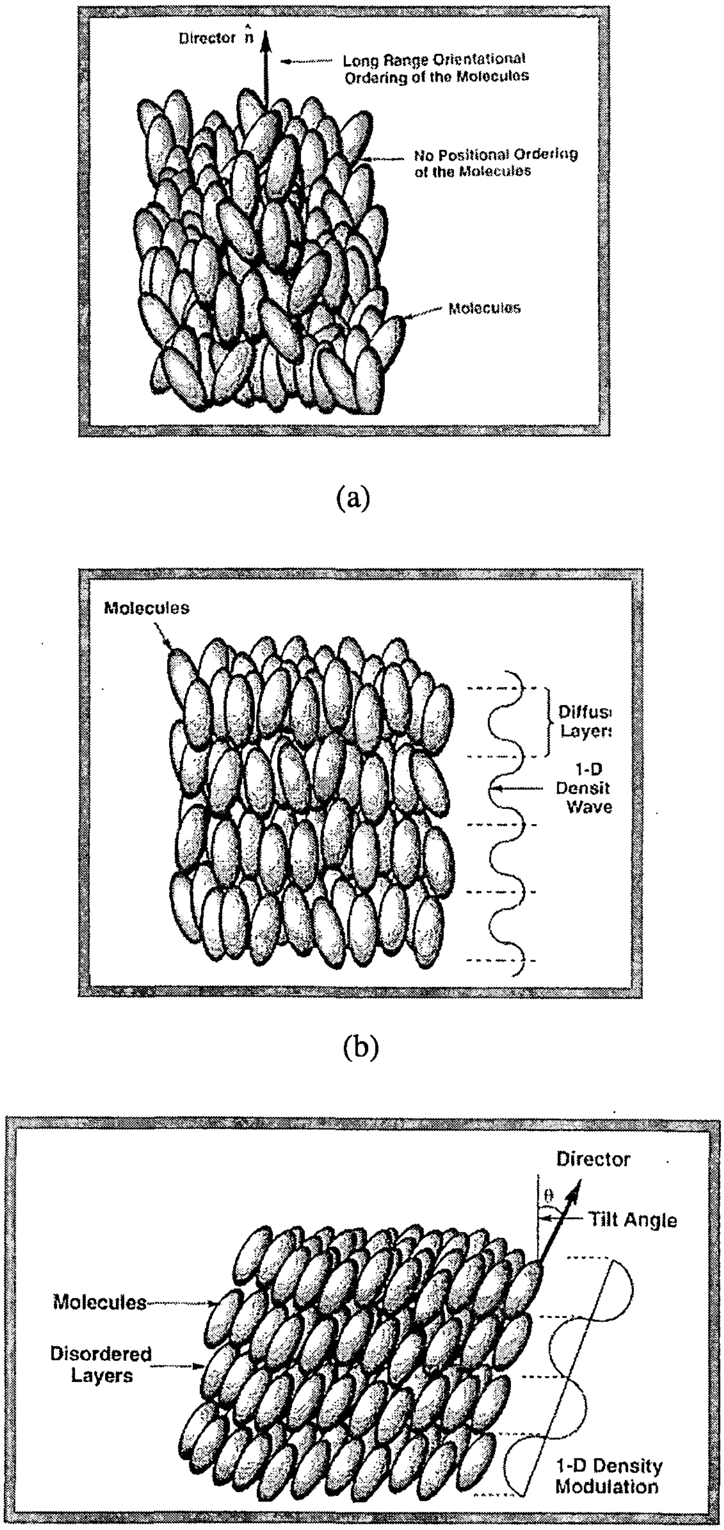
1.2.2.1 *Nematic (N) liquid crystal*

The nematic liquid crystals have a high degree of long-range orientational order of the molecules but no long-range translational order i.e., the long axes of the molecules tend to be parallel to a particular direction, called the **director** (designated by a unit vector **n**), and their centres are distributed at random. This is shown in Figure 1.4(a). This phase is optically uniaxial but a biaxial modification has also been discovered [74-84]. It is easy to disturb the alignment of the molecules of nematic liquid crystals by external influences. So nematics are able to translate weak external signals (electrical, magnatic, mechanical) into visible optical effects for which they are extremely useful in various display devices.

Adriaan de Vries [85-87] from X-ray studies first proposed the existence of another type of nematic called **cybotactic nematic** where small clusters of molecules are arranged in layers. If the molecules of cybotactic groups are normal to the layers then it is called a **normal cybotactic nematic** (N_{OC}) and if the molecules are titled to the cybotactic layers then it belongs to **skewed cybotactic nematic** (N_{SC}) variety.

1.2.2.2 *Cholesteric (Ch) liquid crystals*

Cholesteric mesophase is also a nematic type of liquid crystal except that the constituent molecules are chiral i.e. optically active. As a result the director is not fixed in space but rotates in helical fashion about an axis perpendicular to the director [23,88-93] as shown in Figure 1.5. The helix may be right handed or left handed depending on the molecular conformation. The pitch of the helix is usually of the order of the wave length of visible range of electromagnatic spectrum and is highly temperature dependent. Optically inactive molecules or racemic mixtures of cholesterics result in a cholesteric of infinite pitch which is nothing but a true nematic. Also, when a small quantity of a cholesteric substance [5], or even a non-mesogenic optically active substance [94], is added to a nematic the mixture adopts a helical configuration like a cholesetric. So, the cholesetric phase may be regarded as a twisted nematic phase [95] or conversely, a nematic phase as a cholesetric phase of infinite pitch. The absence of Ch-N phase transition by variation of temperature [96] and Ch-N transition (rather transformation) by application of strong magnetic field normal to the helical axis [97,98] confirm this fact. The spiral arrangement of the molecules in the cholesteric phase is responsible for the selective



(a)

(b)

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(c)

Figure 1.4 The structure of the (a) nematic phase (b) orthogonal smectic A phase and (c) tilted smectic C phase.The arrow indicates the director **n**.

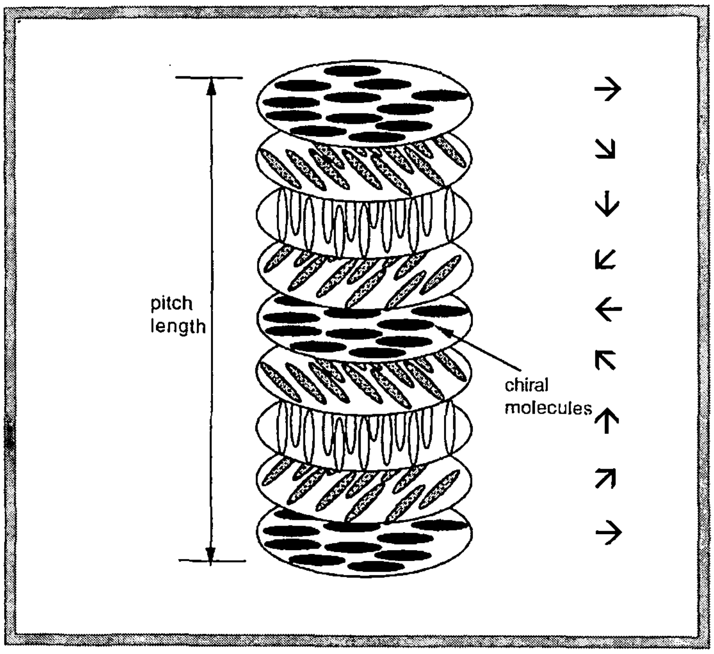

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Figure 1.5 Schematic representation of the helical structure of the cholesteric liquid crystals. The views represent imaginary slices through the structure and do not imply any type of layered structure. The arrows indicate the director **n**.

reflection of circularly polarised light and a rotatory power about a thousand times greater than that of an ordinary optically active substance [21]. Cholesterics of low pitch (less than about 0.5 μm) exhibit what are known as **blue phases** [99,100]. These phases exist over a small temperature range (~1°C) between the liquid crystal phase and the isotropic liquid. Three distinct blue phases (I, II and III) have been identified and occur in that order with increasing temperature.

1.2.2.3 *Smectic liquid crystal*

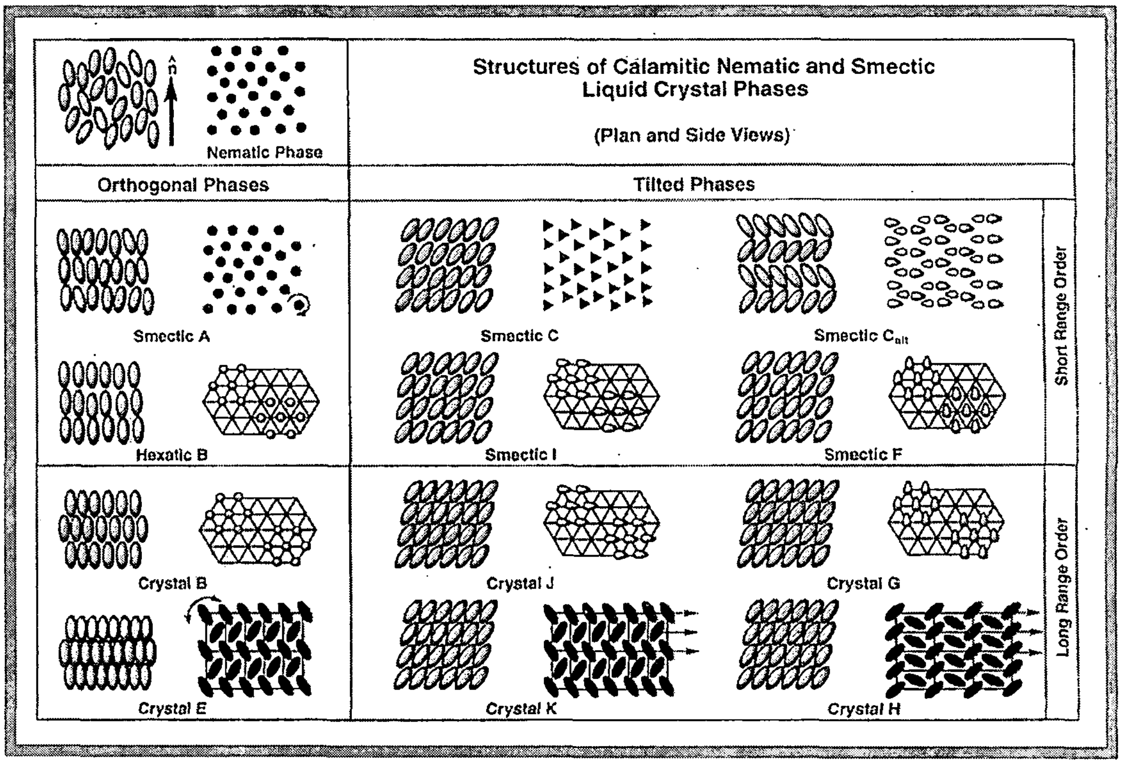
The smectic phase of a liquid crystal represents a higher state of ordering than nematics. In addition to the orientational ordering the molecules are arranged in layers. A great variety of smectic phases can be observed depending on the molecular arrangements in the layers[14, 17,18,24,25,101-108]. The molecules may be upright or inclined to the layers and may or may not have long range positional ordering in each layer, but long range orientational ordering is always present in all layers of the smectic liquid crystal. Some of the smectic liquid crystals have three dimensional long range positional order as in a crystal while some others have three dimensional long range **'bond orientational order'** without any long range positional order [109,110]. The interlayer attractions are weaker than the lateral forces between molecules and hence the layers can easily slide over one another. Hence smectics have fluidity though these are much more viscous than nematics.

The stratified smectic phase is divided into four subgroups by considering first the extent of the in-plane positional ordering of the constituent molecules and then considering the tilt orientational ordering of the long axes of the molecules relative to the layer planes. Firstly, the two groups can be classified where the molecules on average are normal to the layers. The difference between these two groups is in the extent of positional ordering. For example, in the smectic A and hexatic B phases the molecules have only short range positional order [110], whereas the crystal B and crystal E phases are 'smectic-like' soft crystal modifications [111,112] where the molecules have long range positional ordering in three dimensions [101]. Secondly, in the two other classes the molecules are tilted with respect to the layer planes. In the smectic C, smectic I and smectic F phases the molecules have short range positional ordering [113,114], but in the crystal G, crystal H, crystal J and crystal K phases the molecules have long range three dimensional ordering [111,114]. X-ray diffraction techniques have been used to investigate the structures of the smectic modifications [111,115-119] and have been shown in Figure 1.6.

It may be mentioned here that previously all the above phases were termed as smectics. Some of these are now termed as crystals because of their long range orientational as well as long range 3-D positional ordering. These phases, however, have somewhat different properties from normal crystals, for example, their constituent molecules are reorientating on a time scale of 10^{11} times per second about their long axes[120,121].

Smectic A (SmA) phase:

In this phase the long axes of the molecules on average are perpendicular to the layer planes and within each layer the centres of mass of the molecules are



From [17]

Figure 1.6 The structures of the various liquid crystal mesophases. For each phase the side view is shown to the left and the plan view to the right. The rod-like molecules are shown as ellipses, their cross-sectional areas as circles, triangles or ellipses. The triangles and arrows are used to represent molecular tilt directions.

irregularly spaced in a liquid like fashion. Normal to the layers the molecules are essentially arranged in a one-dimensional density wave [101]. In this phase usually the layer spacing (d) is approximately equal to the molecular length (L). However, other modifications are also possible. The sub-phases of smectic A are described as monolayer smectic A (SmA_1), bilayer smectic A (SmA_2), partially bilayer smectic A (SmA_d) [101]. Partial bilayer ordering is typically caused either by interdigitation or pairing of the molecules with partial overlap [122,123] and found to happen in materials where the molecules have terminal polar groups. Another smectic modification called 'ribbon' or antiphase ((Sm~A) has also been reported [124,125] where an undulating bilayer is observed. Sub-structures of SmA phases is shown in Figure 1.7. Details regarding these polymorphism of smectic A have been reported by many authors [124-144].

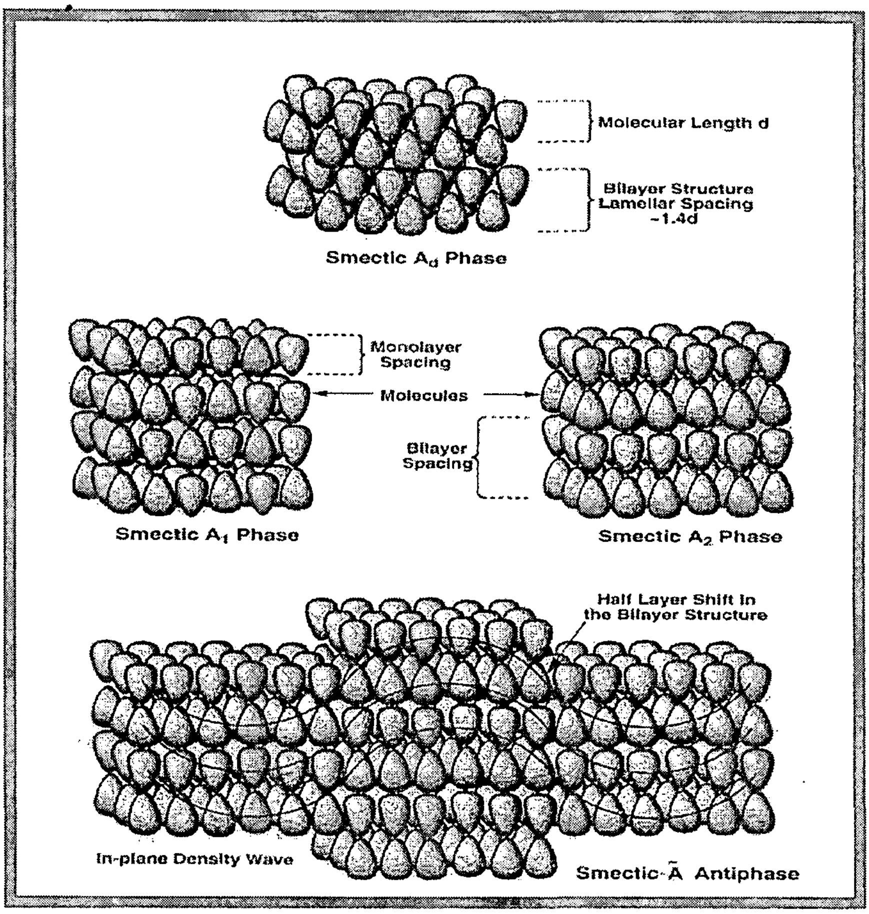


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Figure 1.7 Bilayer and monolayer structures of the smectic A phase.

Smectic C (SmC) phase:

The smectic C phase is a tilted form of the smectic A phase, i.e., the molecules are inclined with respect to the layer normal. The layer spacing (d) of this phase is less than the molecular length (L) due to this tilt. If β_t is the tilt angle with respect to the layer normal then the layer spacing is $d = L\cos\beta_t$. Depending upon the temperature dependence of the tilt angles attempts have been made to divide Sm_C phase in three subgroups [102,145]. The smectic C phase is optically biaxial [146,147]. A quadrupolar charge distribution in the molecules helps the formation of this phase, because the intermolecular electrostatic interaction is repulsive when the molecules are parallel to the layer normal, whereas it is reduced much when the molecules are tilted. From the consideration of the packing of the hydrocarbon chains of the molecules it can be seen that tilted arrangement of molecules within the layers is energetically more favourable.

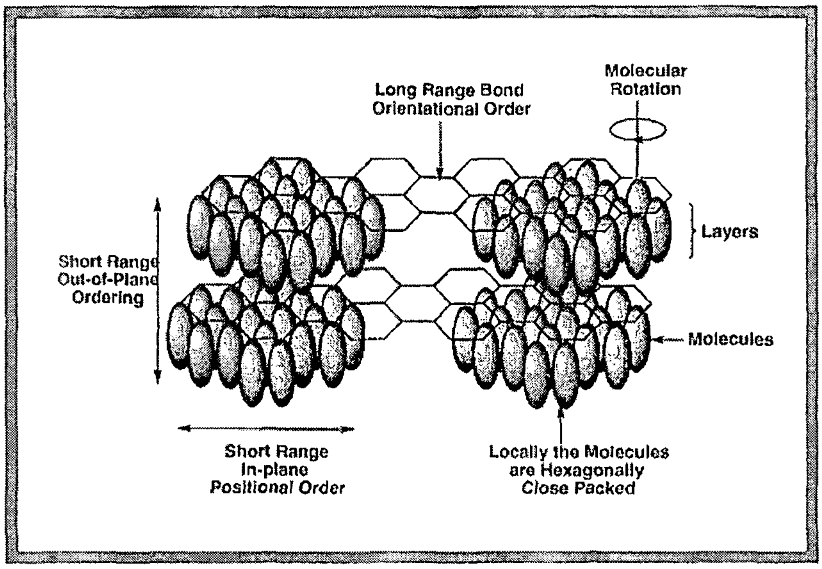
In SmC phase, when the constituent molecules are strongly axially polar, four sub phases are observed [119,148] identical to those of the SmA phase, except that the molecules are tilted with respect to the layer planes. In this case an additional subgroup has been found where the tilt direction appears to flip as one moves from one layer to the other and is called alternating smectic C (SmC_{alt}) [149-151].

Smectic B (SmB) phase:

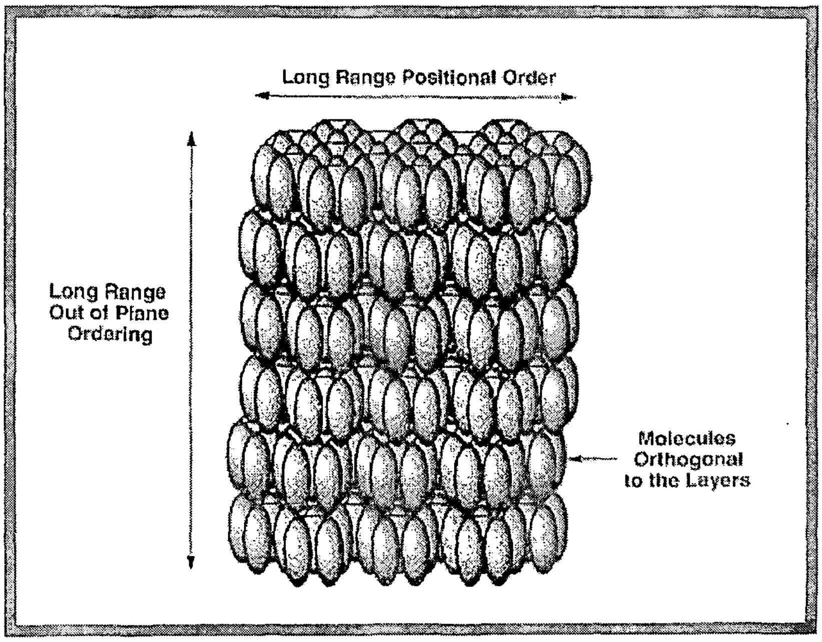
Two distinct types of smectic B phase have been identified, one is called Hexatic B (SmB_{hex}) and the other one is Crystal B (B). In SmB_{hex} phase the molecular arrangement is close to that of the SmA phase, however, within a layer the molecules are arranged in close packed hexagonal symmetry [25,101, 110,152,153]. Although the positional ordering within the layer is short range, there is long range bond orientational order [109,154] in this phase. If the line joining the centres of mass of a molecule and its nearest neighbour is called a 'bond' then by 'long range bond orientational order' it is meant that the orientation of the hexagonal packing array is of long range. In Crystal B phase, additionally the molecules have long range positional order within the layers as well as along the layer normals [25,101,112,115]. However, in Crystal B phase the inter-layer stacking sequence may be of mono- (AAAA type), bi- (ABAB type) and tri- (ABCABC type) layers [155]. Even random ABCABC type packing is also reported[156]. Structures of SmB_{hex} and B phases have been shown in Figure 1.8.

Smectic E (SmE) phase:

The Smectic E phase is now designated as Crystal E (E) phase since it can also be considered as a 'soft' crystal like the B phase [157-160]. Doucet et al [158, 161] concluded that within the layers the molecules are packed in herringbone array with orthorhombic symmetry. The phase is, therefore, biaxial. The lath-like molecules rotate cooperatively about their long axes on a time scale of 10^{11} times



(a)



(b) From [17]

Figure 1.8 Structure of the (a) hexatic Smectic B phase, (b) Crystal B phase showing ABC packing.

per second [153,162] but unlike in B phase the motion is not full free rotation rather of an oscillatory nature. E phase is also found to have bilayer structure as in B phase [121].

Smectic I (SmI) and Smectic F (SmF) phases:

The structures of Smectic I phase is similar to SmB_{hex} but the molecules in this case are tilted within the layers, direction of tilt being towards an apex of the hexagonal packing net [113,118,163-166]. Thus it has short range in-plane and quasi-long range out-of-plane positional order as well as long-range bond orientational order in three dimension. The only difference in the molecular arrangement of Smectic F phase is that the tilt of the molecules is towards an edge of the hexagonal packing net [164,165]. In addition slightly longer correlation has been observed in the in-plane positional ordering than that found in Smectic I phase [167,168].

Smectic G, Smectic G′, Smectic H and Smectic H′ phases:

All these smectic phases are now termed respectively as Crystal G, Crystal J, Crystal H and Crystal K phase since they have long range three dimensional order [25,101,116,155,161,164,165,169,170] and they are like 'soft' crystals. In these cases the molecules are tilted with respect to the layer planes. The crystal J and G modifications are like the tilted Crystal B phase, direction of the tilt being that in SmI and SmF phases respectively (Figure 1.9). On the other hand the crystal H and K phases are like tilted Crystal E phase, the tilt direction is like that of SmI and SmF phases respectively. Thus the packing structure is pseudo-hexagonal in J and G whereas it is of monoclinic nature in H and K phases. Molecules are undergoing rapid reorientational motion about their long axes in J and G phases [25,101,155]. However, this motion is cooperative and oscillatory in nature in H and K phases like in the E phase [120,121].

The structural features of the phases observed in calamitic thermotropic type of liquid Crystals has been summarized in Table 1.1. No single liquid crystal

TABLE 1.1

Structural features of calamitic thermotropic liquid crystal 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

material is found to exhibit all the phases but many compounds are found to exhibit complex polymorphism, for example, the compound N-(4-n-pentyloxybenzylidene)-4'-n-hexylaniline possess the phases N, SmA, SmC, SmB, SmF and SmG phases (Figure 1.3). Current knowledge of phase sequencing with respect to temperature is found to be as follows [171]:

Isotropic, N_O, N_{SC} (or Ch), SmA, SmC, SmB_{hex}, SmI, SmF, B, J, G, E, K, H, Crystal

Decreasing temperature

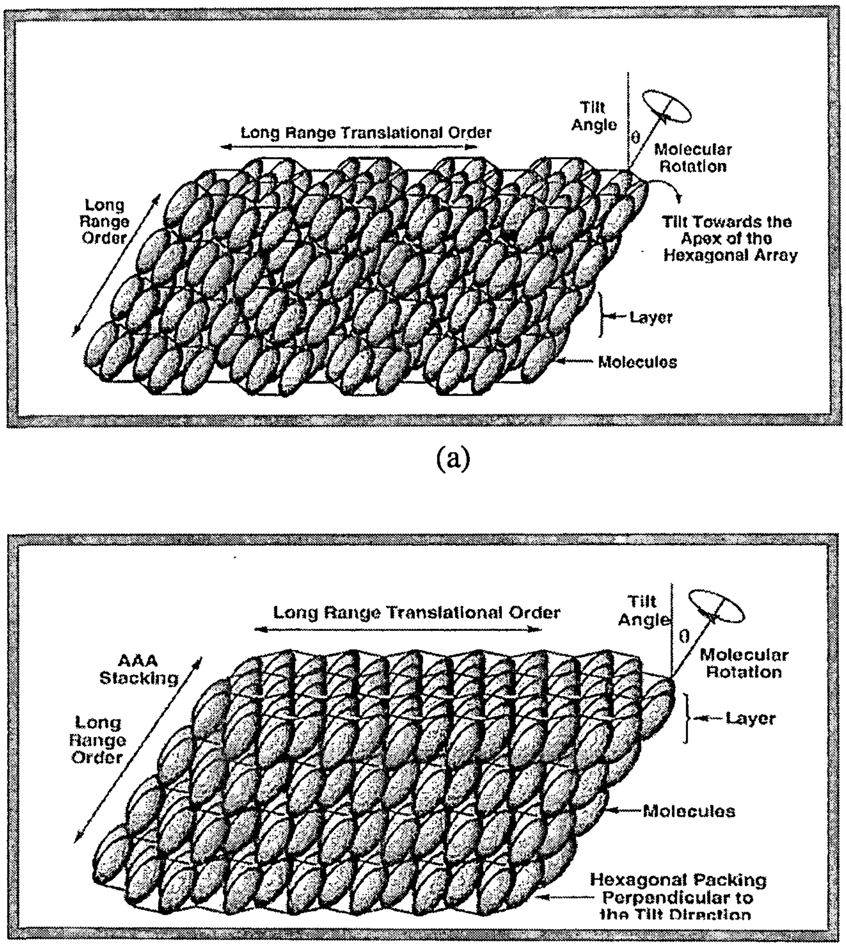
Increasing order →

1.2.2.4 *Ferroelectric Liquid Crystals*

The seven liquid crystal classes SmC, SmI, SmF, J, G , K and H are characterised by a tilt between the director and the normal to the smectic layers. If, additionally, the molecules are chiral, the material become optically active and show ferroelectric properties [42,45,172,173]. These phases are denoted by SmC*, SmI*, SmF*, J*, G* , K* and H*. By virtue of their symmetry, ferroelectric liquid crystals are piezoelectric too, because polarisation in these materials can be induced by mechanical stress. Antiferroelectric and ferrielectric liquid crystals phases have also been found. The constituent molecules of the antiferroelectric chiral smectic C (SmC^*_{anti}) phase have the tilted lamellar structure of the ferroelectric SmC* phase but the tilt direction alternates from layer to layer to give a zig-zag structure. Therefore, the spontaneous polarization of the phase is zero. The ferrielectric chiral smectic C (SmC^*_{ferri}) also has alternating tilted structure except that the alteration is not symmetrical and more layers are tilted in one direction than the other. Accordingly, the ferrielectric phase generates a spontaneous polarization which depends upon the degree of alternation of tilt directions. The study of ferroelectric liquid crystals has become important for their variety of applications such as in large area, high information content colour display devices and compounds having SmC* phase (both ferro and antiferro type) are mainly used for this purpose[174-178].

1.2.2.2 *Discotic Liquid Crystal*

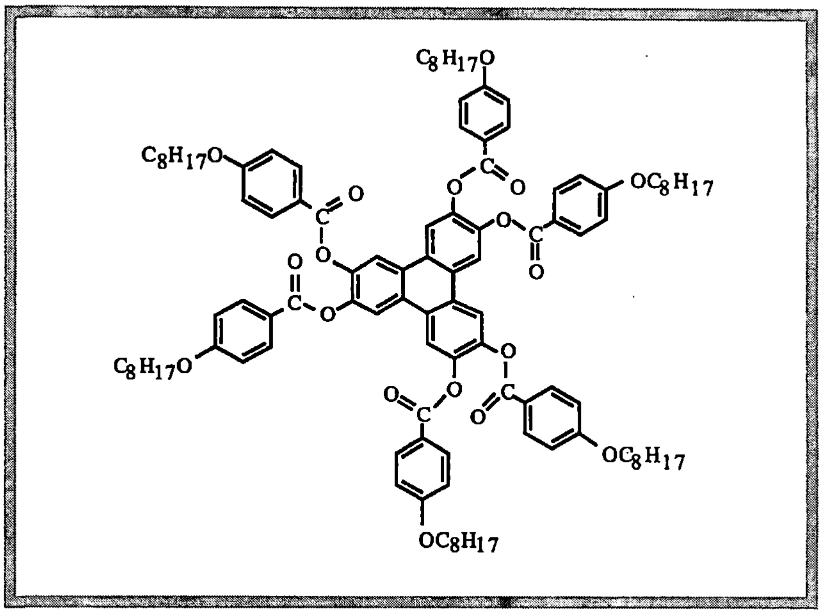
Thermotropic mesomorphism has also been observed [179-181] in pure compounds consisting of simple disc-shaped molecules (one molecular axis is much shorter than the other two) and the mesophases formed by such compounds are called **discotic liquid crystals.** A large number of discotic compounds (also called **discogens**) have been synthesized and a variety of mesophases have been discovered [182-186]. A typical discotic liquid crystal molecule has been shown in Figure 1.10. Structurally most of the discotic liquid crystals fall into two distinct categories – the **columnar** and the **nematic.** In columnar phase, the disc-like molecules are stacked one on top of the other aperiodically to form liquid like



(a)

(b) From [17]

Figure 1.9 Structure of (a) crystal J phase and (b) crystal G phase.



From [39]

Figure 1.10 Typical discotic liquid crystal molecule.

columns, the different columns constituting a two dimensional lattice. A number of variants of this structure have been identified: **hexagonal, rectangular** and **oblique** etc. The nematic discotic phase has an orientationally ordered arrangement of the discs without any long range translational order. This phase is optically negative. A cholesteric phase with disc-like molecules has also been identified [187,188]. A smectic-like lamellar phase of discotic liquid crystal has been reported [189-191] in the literature.

1.2.2.3 *Polymer Liquid Crystal*

Thermotropic liquid crystalline phases are also exhibited by some polymers [36,48,55,56]. The basic monomer units are lower molecular weight mesogens with rod-like or disc-like molecules, which are attached to the polymer backbone in the main chain, or as side groups (Figure 1.11). The nature of the mesophase depends rather sensitively on the backbone, the mesogenic unit and the spacers [192]. With rod-shaped repeating units in the polymers, mesophases similar to the nematic, cholesteric, smectic types of calamitic liquid crystals are observed [193-197],

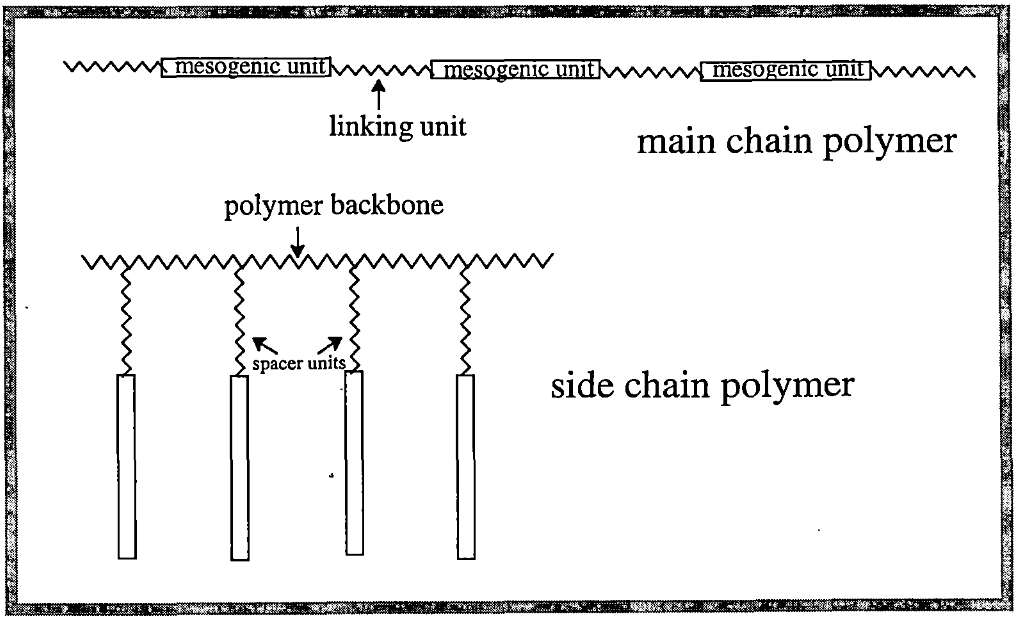


Figure 1.11 Schematic Polymer liquid crystal molecule (main and side chain).

whereas, with disc-shaped repeating units some new kinds of mesophase structures have been found [198-202] like **'sanidic'** (or board-like) nematic and **'columnar'** nematic phases.

Liquid crystals are also found to form with molecules other than the aforesaid molecular types viz. calamitic, chiral calamitic, discotic and polymeric . D. Demus has recently shown [10] in a review article that many different types of molecules can exhibit liquid crystallinity. For example, it has been shown that molecular shape may even be bowl-, sofa-, banana-, U-, H-, Y- and T-shaped[203-209]. A detailed discussion on liquid crystals in non-conventional materials like dimers, oligomers, dendrimers, plasmids, polycatenar, metallomesogens, charge-transfer systems, supramolecular hydrogen bonded systems have been made in reference [210]. Many other interesting liquid crystal phases have also been reported like frustrated chiral smectic A* or twist-grain boundary phase[211,212], reentrant phase [213-216], induced smectic phases [216-219] etc.

1.3 APPLICATIONS OF LIQUID CRYSTALS

Liquid crystals have got a wide range of scientific and technical applications due to their unique physical properties. There are several books and articles[28,30,42,48,49,50,220-240] which give an account of the applications of liquid crystals. General discussions on the principles of applications of liquid crystals have been given in references [232 - 240]. However, a brief outline of some of the applications of liquid crystals have been given here.

Since liquid crystals are very sensitive to even weak external perturbations they are used in measurement of temperature, pressure and chemical contamination. The helical pitch of cholesteric liquid crystals is highly sensitive to temperature and hence a slight change in temperature changes colour of the sample. Thus cholesteric liquid crystals have got interesting sensing applications[225, 226, 228,235]. One of these is the so called thermal mapping of components of electronic devices. The use of cholesteric liquid crystals as an investigative and diagnostic tool in medicine has become widespread. For example skin infections and malignant skin tumours may

From [39]

Plate 1 Privacy window using a polymer dispersed liquid crystal film.

From [39]

Plate 2 Portable computer with an active matrix colour liquid crystal display.

be detected and located by the use of cholesteric liquid crystals. It is possible due to the fact that the portion of the infected skin or tumour has higher temperature than the surrounding uninfected area.

The discovery of dynamic scattering mode in nematic liquid crystals [233,237-239] has opened a new area of electronic display technology. In thin layers nematic liquid crystals change their transmission properties for normal or polarised light when subjected to an electric field. This property is utilised for alphanumeric and analog display image converters and matrix type picture screens. Recently, ferroelectic liquid crystals (S_C*) are being used for a new generation of fast versatile liquid crystal devices [227,229,236]. Polymer dispersed liquid crystals (PDLC) form a relatively new class of materials which are used in many types of displays[227,231]. In practice liquid crystals are widely used in displays for watches, clocks, calculators, various digital panel meters, televisions, laptop computer monitors, note-book computers, mobile phone set, switchable windows and other light shutter devices [plate 1 and plate 2]. The relatively low optical contrast, low power consumption, light weight, etc. are the main advantages of liquid crystal displays (LCD's) over other types of displays. These facts have dramatically popularised the liquid crystal displays [240]. This trend will go up with the advent of better LC materials and improved technology paving a revolution in electronic communication system.

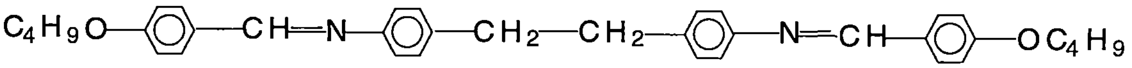
As the molecules of liquid crystals are oriented in magnetic field with optic axis parallel to the field, they are used as anisotropic solvents for nuclear magnetic resonance (NMR) measurements[227,234]. Liquid crystals are also used as solvents for the studies of infra red (IR) and ultra violet (UV) spectra of solute molecules in the form of liquid crystal films [231,234].

Liquid crystals are also used as solvents with stationary phases in gas liquid chromatography (GLC). Separation of compounds on the basis of molecular shape is the most promising practical application of liquid crystals in GLC [241,242]. The wider is the stationary mesophase range with higher molecular ordering the more effective is the liquid crystal in GLC.

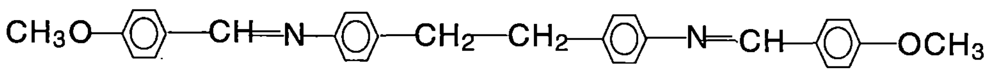
1.4 NAME AND STRUCTURE OF THE INVESTIGATED COMPOUNDS

The name and structural formula of the nine compounds studied in the present work are given bellow. Abbreviated names are given within parentheses.

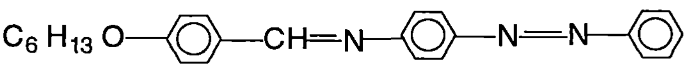
1. **N, N′ –Bis (p-butoxybenzylidine)-α,α′ -bi-p-toluidine (BBBT)**



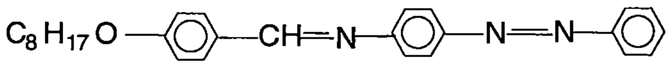
2. **N, N′ –Bis (p-methoxybenzylidine)-α,α′ -bi-p-toluidine (BMBT)**



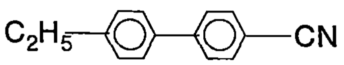
3. **N-(4-n-hexyloxybenzylidene)-4′- phenylazoaniline (6OBPAA)**



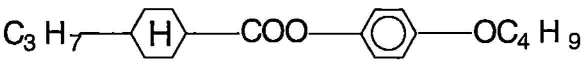
4. **N-(4-n-octyloxybenzylidene)-4′- phenylazoaniline (8OBPAA)**



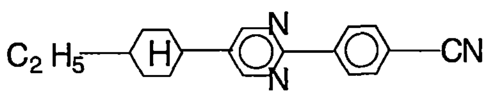
5. **4-n-ethyl 4′cyanobiphenyl (2CB)**



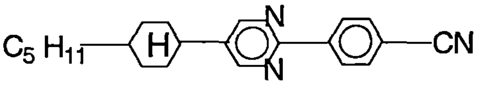
6. **p-butoxyphenyl *trans*-4- propylcyclohexane carboxylate (BPPCC)**



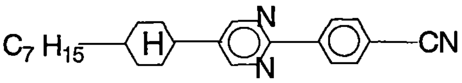
7. **5-(4-ethylcyclohexyl) -2- (4-Cyanophenyl) pyrimidine (ECCPP)**



8. 5-(trans-4-pentylcyclohexyl)-2- (4-cyanophenyl) pyrimidine (PCCPP)



9. 5-(trans-4-heptylcyclohexyl)-2- (4-cyanophenyl) pyrimidine (HCCPP)



1.5 SCOPE AND AIM OF THE WORK

Liquid crystals have widespread scientific and technological applications for which identification of different phases, their different macroscopic and microscopic properties (like order parameters, dielectric constants, intermolecular interactions, etc.), crystal and molecular structure analysis are very important. Since, in commercial liquid crystal display devices multicomponent mixtures are always used to optimize the relevant physical parameters, studies on mixtures, in addition to the pure components, are also important. In view of this, texture studies by optical microscopy, DSC studies, X-ray diffraction studies, static dielectric anisotropy studies as well as crystal and molecular structural analysis and intermolecular interaction energy calculation on the above compounds and some binary mixtures are undertaken in the present dissertation. 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 structure-property relationship.

Texture and X-ray studies on, (a) BMBT and BBBT, (b) 6OBPAA, 8OBPAA and their equimolar mixture and (c) three binary mixtures of BPPCC and 2CB, are made for phase identification and determination of apparent molecular length, layer spacing, intermolecular distance, orientational order parameters of magnetically aligned samples. Temperature variation of some of the physical parameters have also been studied. The orientational order parameter values at different temperatures have been compared with those obtained from Maier-Saupe theory (for nematic phase) and McMillan's theory (for smectic A phase). D.S.C. studies on BBBT and BMBT have also been carried out for evaluation of transition temperatures, transition enthalpies and entropies. Static dielectric studies on BPPCC and its mixtures with 2CB have also been made to determine the principal dielectric constants ($\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$), dielectric anisotropy ($\Delta\varepsilon$) and mean dielectric constant ($\bar{\varepsilon}$) at different temperatures. Effective values of the molecular dipole moments in the mesophase have been calculated using Maier and Meier theory. Dipole-dipole correlation factors ($g_{\parallel}$ and $g_{\perp}$) for BPPCC have also been calculated.

The crystal and molecular structures of 2CB and BPPCC have 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.

The pair intermolecular interaction energies of ECCPP, PCCPP and HCCPP have been calculated by atom-atom potential method taking into account the Van der Waals' and electrostatic interactions. The minimum energy configuration of dimers of these mesogens have been compared with the previous data obtained from crystal structure analysis and X-ray scattering studies in mesophases.

A brief review on different types of liquid crystal phases exhibited by different types of molecules has been made at the outset. Theoretical aspects relevant to the present work in brief and the experimental techniques and data analysis procedures in detail have also been described before presenting the results.

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