CHAPTER I

Mesogens and the purpose of the present investigation

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Abstract

In this chapter the salient features of the mesogens, their classifications and structures have been delineated. The classifications of mesophases exhibited by thermotropic mesogens have also been described. The scope and purpose of the present work have also been discussed.

I. 1 Introduction

Liquid crystals form a state of matter intermediate between the solid and the liquid. The terms 'mesomorph' (Greek *mesos morphe*, between two states, forms) and 'mesophase' are also used. A mesogen is the molecule which gives rise to a mesophase. The terms *mesogen* and *liquid crystals* are used synonymously.

Crystal and liquid are the most common condensed matter phases. The difference is that in a crystal the molecules are ordered both positionally and orientationally, where the molecules are constrained both to occupy specific sites in a lattice and to point their molecular axes in specific directions, whereas in a liquid both are distributed randomly. In nature, interestingly many phases with more order than present in liquids but less than that of crystals also exists. These materials grouped together are called *mesogens* or *liquid crystals*, since they share properties of both liquids and crystals.

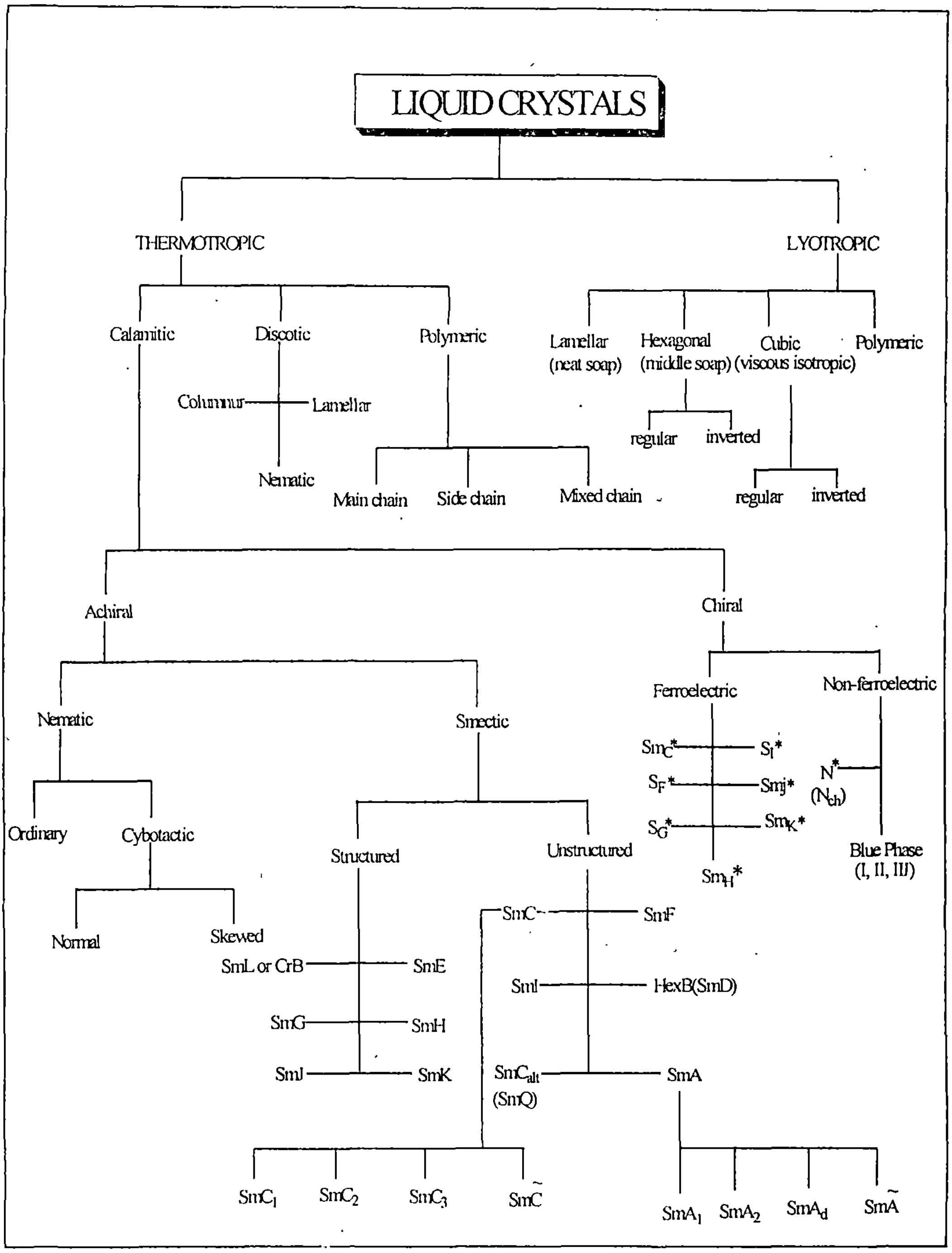
The first discovery of liquid crystals or mesogens is often ascribed to Austrian botanist Friedrich Reinitzer's work with cholesteryl ester published in 1888 [1], but it can be traced back to 1850s with the observation of birefringent textures in nerve myelin by Virchow [2] and to Heinz's work on magnesium tetradecanoate [3]. In the initial stage, the contribution of German physicist Otto Lehmann [4] to the field of mesogens is remarkable. Since then, a large variety of materials have been synthesized and now the total number of registered synthesized mesogens exceeds eight million [5].

Mesogens or liquid crystals constitute an important phase of matter both from the viewpoint of basic sciences and technological applications. The advancement of liquid crystal science and technology has been a truly interdisciplinary effort, which combines basic principles of physics, chemistry and engineering. The field of liquid crystals covers a wide area of chemical structures, physical properties and technical applications. Research on liquid crystals exploded during the years of 1970 and 1980, still it continues to command as one of the frontier areas of science and technology.

People are familiar with the soap foam since a long ago, without knowing about its liquid crystalline nature. At present, technological applications of liquid crystal have made it an essential part of our daily life. Now it is being used for displays in all sorts of instrumentation, particularly it finds extensive applications in domestic appliances and office automation. The success of mesogenic materials in flat panel displays and electro-optical applications can be credited to the collaborations of scientists in various fields and unique interface between academia and industry. The success of the liquid crystal display (LCD) over the other display technologies is attributed to the following advantages:

1. Non-emissive display with extremely low voltage and power consumption;
2. Enhanced lifetime operation;
3. Size and design flexibility, compactness;
4. Flatness, wider viewing angle;
5. Higher resolution;
6. Faster response time;
7. Wider operation temperature range;
8. A negligible incoherent colonization and a high contrast ratio;
9. Small capital investment.

Table I. 1 Classification of Liquid crystals



Many other uses of liquid crystals are found in optical devices, thermography, as solvent for spectroscopy, chemical reaction, gas chromatography, non-destructive testing, electro–magnetic radiation detectors, sound wave and pressure detectors etc. It also finds applications in medical science, such as diagnosis of vascular diseases, cancer diagnosis and pharmaceutical tests. The various applications of liquid crystals have been discussed in details in the literature [6-9]. The historical progress and perspectives in liquid crystal research are found in the references [6, 10-16].

This remarkable development in the LCD science and technology is closely linked with specific physical properties. The electro-optical parameters of LCD like threshold voltage, response times, contrast ratio and multiplexity are strongly dependent on the anisotropy in optical, electrical, magnetic and elastic properties of liquid crystal materials [17].

Liquid crystals or mesogens are unique condensed matter systems for theoreticians specially to study the thermodynamics of phase transitions and critical phenomena. Liquid crystal synthesis is a field in its own right, especially in investigating structure-property relationships.

I. 1. 1 *Classifications of mesogens*

Mesogens exhibit a variety of phases, which differ from one another by their structure and physical properties. Mesogens are broadly divided into two groups (Table I.1) viz. *thermotropics* and *lyotropics*, based on the two different ways of taking a crystal into a mesophase. Thermotropic mesogens have gained a relevant place in the field of material science, where as lyotropic mesogens are of fundamental importance in life science.

Thermotropic mesogens or liquid crystals change phases with temperature; the crystals melt to the mesophase (at the melting point) and then clear to the isotropic liquid at a higher temperature. When the thermotropic mesophase appears both in the heating and cooling process (when it is thermodynamically stable) it is called *enantiotropic*. The thermodynamically unstable mesophases, which only appear on cooling process due to the hysteresis in the crystallization point are referred as *monotropic*. Some compounds show several mesophases i.e. they exhibit polymorphism.

Another way of taking a crystal into a mesophase by dissolving the compound in an adequate solvent under given concentration and temperature conditions. These are known as *lyotropic* mesogens..

A number of compounds can behave as both thermotropic and lyotropic mesogens. They are called *amphotropic* mesogens. The alkali salts of long chain aliphatic acids are well known examples [18].

In the mesogenic materials, the intermolecular forces responsible for the molecular arrangement are essentially the same as those operating in molecular solids. However only certain molecules exhibit meogenic behaviour. Mesogenic molecules need to satisfy a number of structural and electronic requirements [19] so that a satisfactory packing of molecules is achieved with appropriate interactions between neighbouring molecules. The existence of permanent dipole moments and their magnitude or the anisotropy of the molecular polarizability are determinant in the effectiveness of these molecular interactions. Thermotropics are held by together by weak dipole-dipole and dispersion forces. Their magnitude is critical; when they are too weak or when they are too strong, the mesogenic character is lost. Hence the molecular features which optimize thermotropic behaviour are very important. Molecular shape [14, 17, 20] is an important governing factor for the formation of a mesophase. To exhibit mesogenic properties organic compounds require strongly polarizable groups such as aromatic rings, ester, or other oxy- or nitrile functions. A number of different types of geometrically anisotropic molecules form mesophases.

Classifications of thermotropic mesogens

The classifications of thermotropic mesogens are made on the basis of the structure and shape of the constituent molecules. The most common type is a long rod-shaped molecule wherein one molecular axis is much more longer than the other two axes, as shown in Figure I.1. The basic structural requirements of a thermotropic mesogen molecule are shown in Figure I.2.

Calamitic mesogen

Rodlike thermotropic mesogens require a long rigid group (often phenyl rings which form a core; two or more rigid parts linked directly or via linking groups) with several long flexible *n*-alkyl- (or *n*-alkoxy-) tails. The rodlike shape, together with the polarizable groups, increase the molecular anisotropy and facilitate the formation of mesophases. Such a molecule can be represented in the first approximation, as a solid rod or spherocylinder or ellipsoid of revolution (Figure I.3). These compounds are called *calamitic mesogens* and they can exhibit different phases.

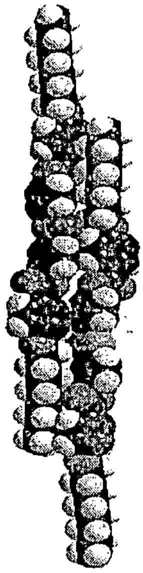


Figure I. 1 Space filling model of a typical rod shaped liquid crystal molecule.

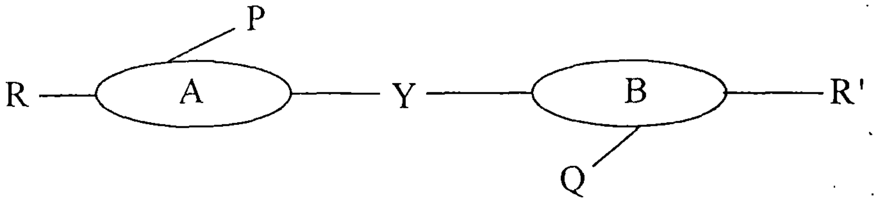


Figure I. 2 Basic structural requirements of thermotropicliquid crystal molecule. A and B → rigid core units often aromatic or alicyclic linked by a linking group Y (e.g., -CO_2-, -C≡C-, -CH_2CH_2-). R, R′ → terminal chain often alkyl or alkyloxy chains or polar substituent group (e. g., CN, F, NCS, NO_2). P and Q → lateral constituents (polar of alkyl groups).

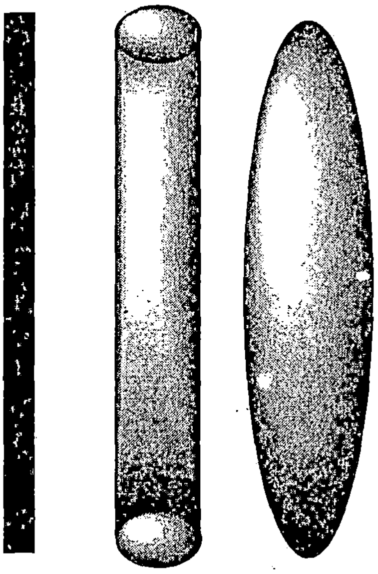


Figure I. 3 Model for liquid crystal molecules as solid rod or spherocylinder or ellipsoid.

Discotic mesogen

Disc-like molecules, as distinguished from the rod-like molecules, which have one molecular axis much shorter than the other two, also form liquid crystalline phase, thereby calling them *discotic* mesogens. However, the mesophase is not itself discotic but may be columnar, nematic or lamellar. Typical molecular arrangements are shown in Figure I .4.

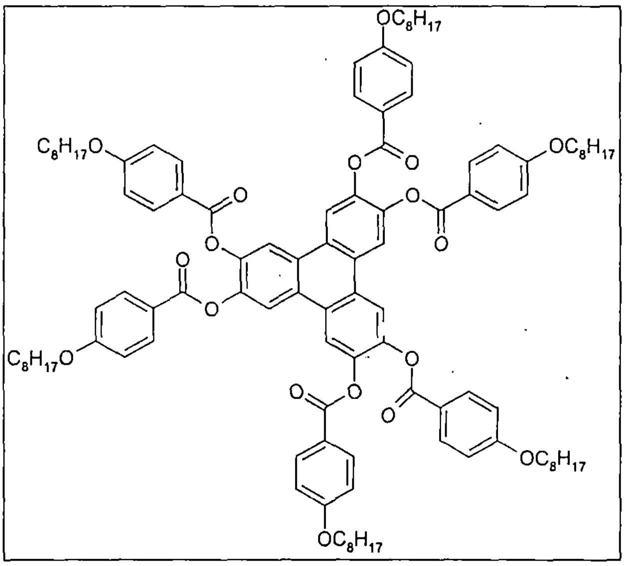


Figure I. 4 Typical discotic liquid crystal molecule.

Polymeric mesogen

Polymeric molecules with both side chains and main chain (Figure I.5) form mesophases [14,15] and are called polymeric mesogens. Here also, segments of polymer must be rigid in order to be liquid crystalline. In main chain polymer, rigid structural units resembling calamitic mesogens are separated by flexible hydrocarbon chains. The rigid part develops the orientational and sometimes positional order characteristics of liquid crystals over a certain temperature range.

Although most of the thermotropic mesogens possess rod-type structure, a wide range of molecular shapes like bowl-, sofa-, banana- or bent-core, Y-, H-, T-, crooked-shaped are observed for thermotropic mesogens [16,18, 21, 22]. An extensive review has been made by D. Demus [16] on different types of mesogenic molecules.

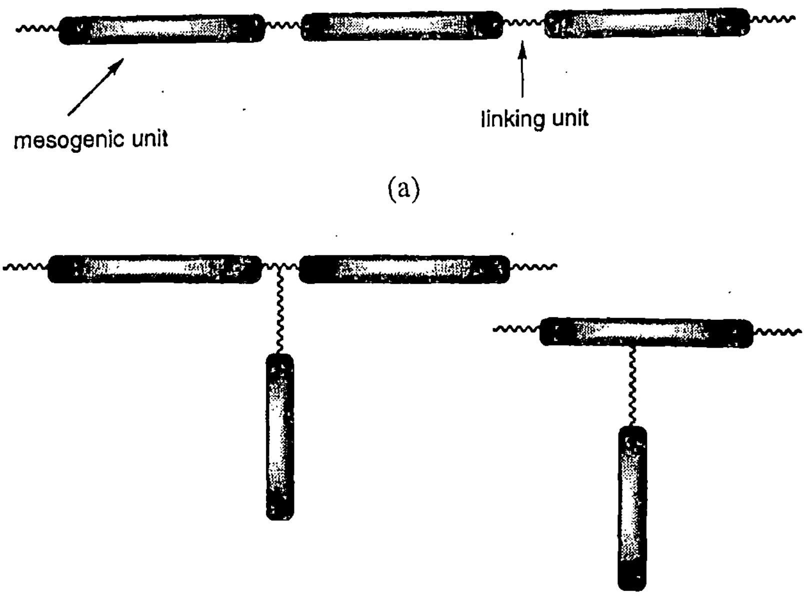


Figure I. 5 Schematic representation of Polymer liquid crystal (main and side chain)

Star-like mesogen

Star-like mesogens are basically oligomers. At a glance they seem to be discotic type due to their star-like molecular structure [16]. The presence of the flexible spacers in the compounds ensures the observance of smectic and nematic phases.

Glassy mesogen

A number of compounds with molecular structures deviating substantially from the rod-like shape form glassy liquid crystalline phases at low temperatures [16]. These are considered as unconventional mesogens.

When the constituent molecules are chiral all the tilted smectic phases exhibit dipolar ordering i.e. they can behave as ferroelectric, ferrielectric and antiferroelectric materials [14, 16, 23, 24]. Molecules with bent-core may also behave as ferroelectric, ferrielectric and antiferroelectric materials [21].

Ferroelectric mesogen or Ferroelectric liquid crystal (FLC)

Smectic C mesogens having chiral centres (S_{c^*} phase), which have a twist axis normal to the layers, exhibit ferroelectric behaviour [23]. The optical properties of this structure are similar to those of the cholestic liquid crystals despite some differences. The earliest study was performed on p-decycloxybenzylidene-p'-amino-2-methylbutyl cinnamate. Smectic C* is of great importance for its application in fast electro-optical switching. Detailed properties of smectic C* phase are available in literature [18, 25].

Antiferroelectric and *Ferrielectric mesogen*

The assembly of the molecules in the antiferroelectric chiral smectic C (S_{C^*anti}) phase has the tilted, lamellar structure of the ferroelectric S_{c^*} phase; but the tilt direction altermates from layer to layer give a zig-zag structure. The ferrielectric chiral smectic C (S_{C^*ferri}) phase also has an alternating tilted structure but the alteration is not symmetrical and more layers are tilted in direction than the other. The antiferroelectric phase is currently the subject of much research because of the great potential in display devices, particulaly for fast switching displays [5, 26].

Supramolecular hydrogen bonded mesogen

Van Romburg [16] found that 4-methoxycinnamic acid between 169°C and 185°C is in the liquid crystalline state, which is now called 'supramolecular' compounds containing hydrogen bonds. Such associated systems constitute an important area of liquid crystal research for last two decades. Detailed information is available in review [27].

Polyols mesogen

Compounds with a number of hydroxy groups (polyols) may form complicated associates, depending on the whole molecular structure. Depending on the number of free OH groups, single molecule or associates of two to five molecules form the discs [16].

Polymer dispersed mesogen or liquid crystal (PDLC)

Polymer dispersed mesogens are made of small liquid crystal droplets embedded into a polymeric matrix. They are good materials suitable for applications such as smart windows, shutters, optical displays, temperature sensors etc. The detailed discussions are available in the review articles [14, 28].

Dendrimer

Dendrimers having their regular highly branched molecular structure with terminal rigid rod-like mesogenic groups are capable of anisotropic mesophase formation [16, 22].

Metallomesogen

Meatallomesogens are metal containing liquid crystalline compounds with charge-transfer complexes [29-32]. They are usually organometallic or conventional coordination compounds. They combine the physical properties exhibited by liquid crystals with the variety and range of metal-based coordination chemistry. They exhibit thermotropic calamitic, discotic and cubic phases as well as lyotropic phases of different structures. Due to the presence of metal atom possessing large and polarizable concentration of electron density, the physical properties (e.g. birefringence) of the compounds is enhanced and many interesting possibilities regarding optical, magnetic and electrical properties exist.

Lyotropic mesogens

A different type of molecules form mesophases, only at sufficiently high solute concentration, when mixed with a normally isotropic solvent of some kind, we call them *lyotropic mesogens*. The salient features of such molecules are (i) they posses a hydrophobic group, highly soluble in hydrocarbon or nonpolar solvents, at one end and (ii) hydrophilic group, highly soluble in water or other polar solvents, at the other end. Such *amphiphilic* molecules from ordered structures in both polar and non-polar solvents. Good examples are the soaps and various phospholipids, both the classes of compounds have a polar 'head' group attached to a hydrocarbon 'tail' group (Figure I.6). When dissolved in water, the resulting structure for soap molecules is called a micelle and for phospholipids is called a vesicle. The temperature range of the mesophase of an lyotropic liquid crystal is determined by its concentration. At low concentration the solute molecules are distributed randomly throughout the solvent. Above a certain concentration lyotropic mesophase is formed. Solute-solvent interaction plays a major role to maintain long-range ordering in lyotropic mesophase and solute-solute interaction is secondary. Three different mesophases viz. lamellar, hexagonal and cubic phases, are possible. The lamellar lyotropic liquid crystal phase

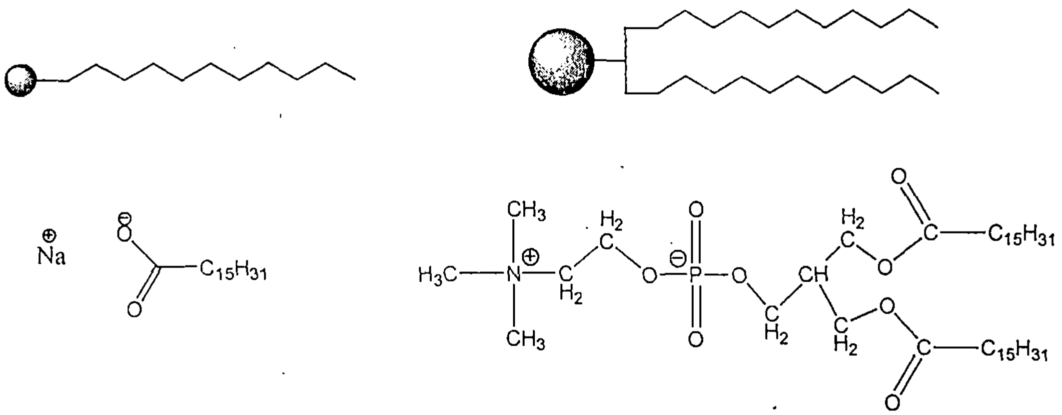


Figure I. 6 Lytropic liquid crystal molecules: Soap (left) and Phospholipid (right)

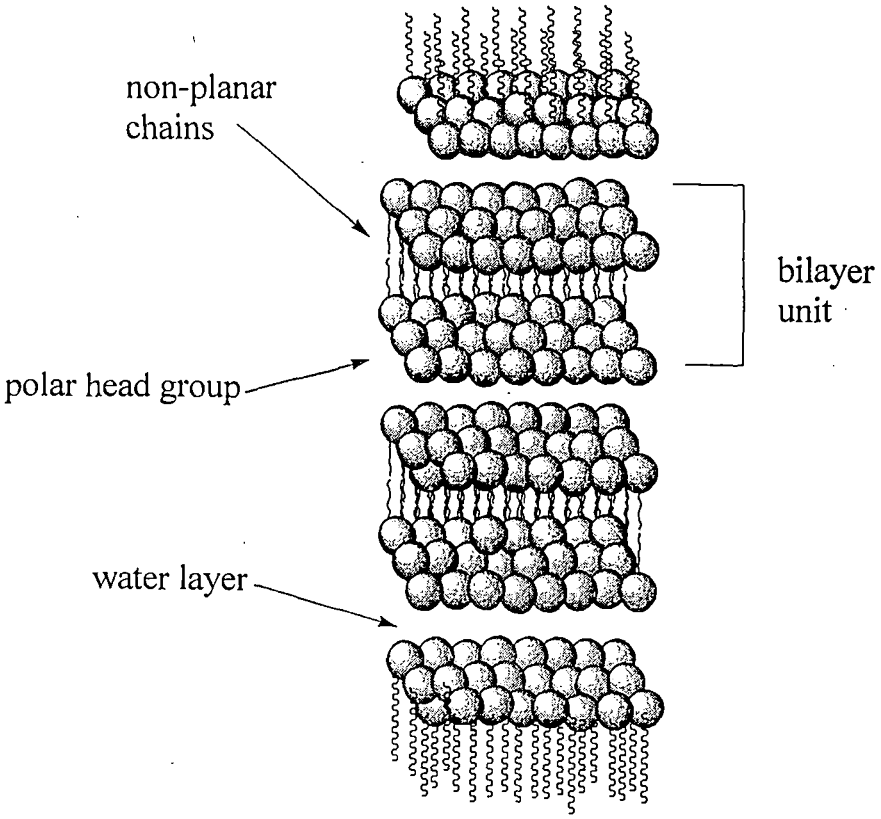


Figure I. 7 Structure of the lamellar lyotropic liquid crystal phase.

structure is illustrated in Figure I.7. Lyotropic liquid crystals have been extensively reviewed by Winsor [33], Brown, Doane and Neff [34] and Brown and Walkon [35].

The lyotropic mesophases have important relevance to the biological system. Many polypeptides, deoxyribonucleic acid (DNA) molecules, cell membranes of all living organism and organic fluids like blood exhibit lyotropic behaviour when dissolved in an appropriate solvent (usually water) in suitable concentration. There is also a well-defined family of lyotropic mesogens encompassing a range of drugs, dyes, nucleic acids, antibiotics, carcinogens and anti-cancer agents. These *chromonic* materials [36] do not generally have significant surfactant properties in contrast to the conventional amphiphile mesogens, such as soaps, detergents and biological lipids. Their molecular structures are characterized by (i) shapes are disk-like or plank-like as opposed to rod-like, (ii) they are aromatic rather than aliphatic and (iii) the hydrophilic ionic or hydrogen-bonding solubilizing groups are arranged around the peripheries of the molecules, not at the ends.

I. 1. 2 *Classification of thermotropic mesophases*

In the melting process of a solid the constituent molecules undergo large and rapid simultaneous changes in rotational, positional and orientational order at the melting point. However, in the melting processes of mesogens, there are stepwise breakdown of these orders. The mesophase is made up of a number of orientationally ordered phases which occur between the breakdown of translational positional ordering of the molecules in a crystal and the formation of the orientationally disordered state of liquid. Thus a variety of thermodynamically stable, intermediate states between the solid and the liquid are produced. A typical melting sequence on heating for rod-like molecules of a liquid crystal is shown in Figure I.8.

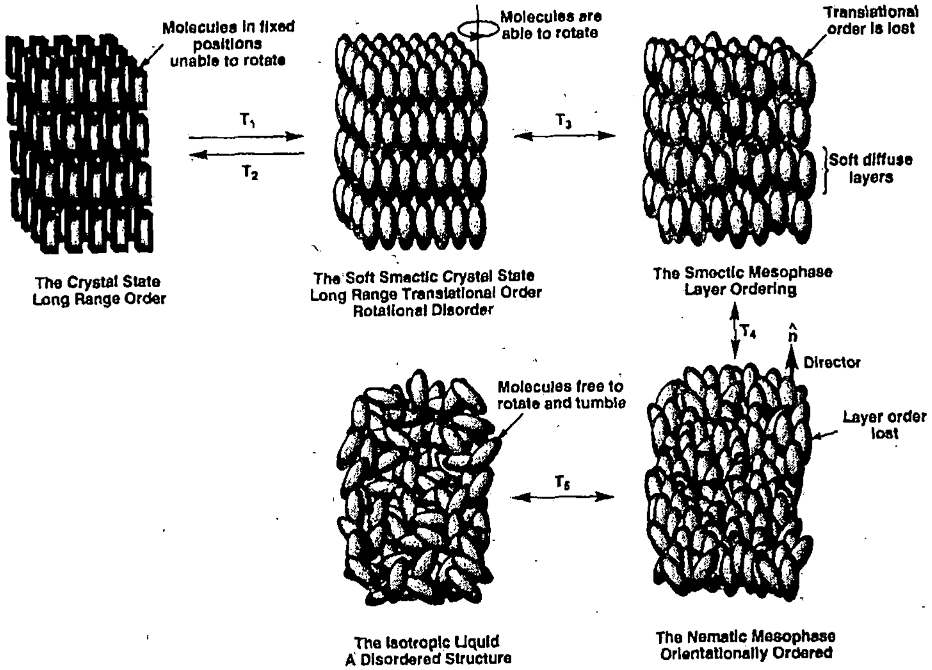


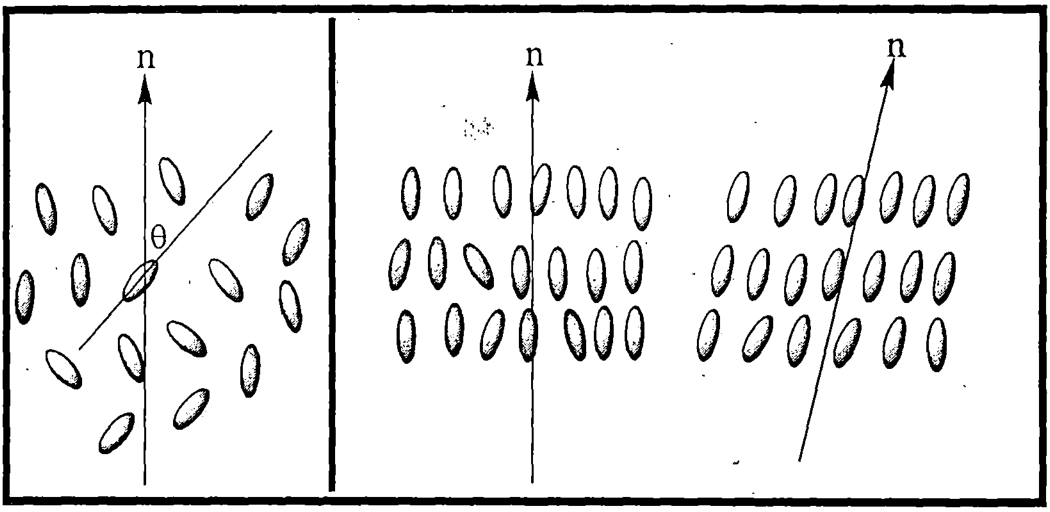
Figure I. 8 Molecular arrangement in calamitic (rod-like) liquid crystals with possible melting and recrystallisation sequences.

On heating a hypothetical calamitic, rod-like thermotropic liquid crystalline material, where all of the mesophases are possible, can go through the following sequence:

Crystal-H-K-E-G-J-SmF-B(cryst.)-SmI-SmC-SmA-N-Isotropic liquid.

Decreasing Order -->

The classifications of thermotropic mesogenic phases are primarily based on symmetry consideration and the two main categories are *nematic* and *smectic*. The early names of the different liquid crystalline phases are based on optical observations



(a) (b) (c)

Figure I. 9 Molecular order in a nematic liquid crystal, **n** is the director making an angle θ with the long axis of a molecule (a) and two liquid crystal phases with positional order: smectic A (b), smectic C (c).

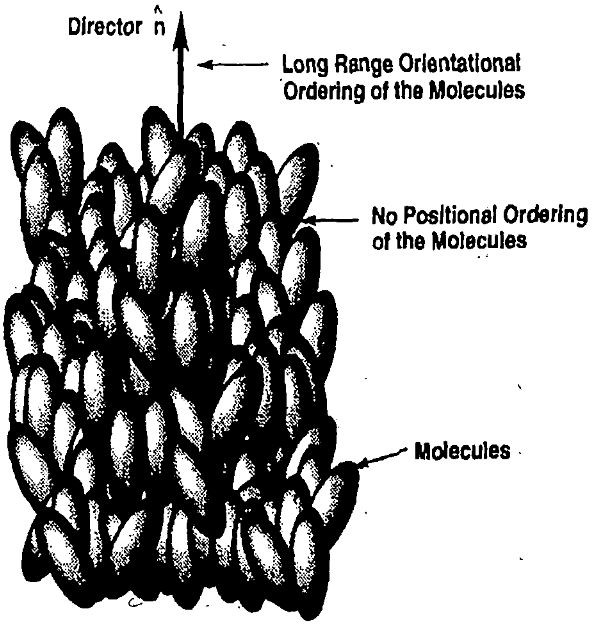


Figure I. 10 The structure of the nematic phase (broad view).

and finally confirmed by X-ray investigations. G. Friedel [37] introduced the terms *nematic*, *cholestic* and *smectic*, which are still in use. *Nematic* was taken from a Greek word *nematos* (thread-like), the defect seen under crossed polariser. *Smectics* term is also taken from a Greek word *smectos* (soap-like).

In macroscopic approach, the structure of a mesophase is usually characterized by the so-called director **n**, a unit vector which shows an average orientation of the long molecular axes in some macroscopic bulk (Figure I.9).

I. 1. 2. 1 *Nematic*

The nematic phase (N) is the most disordered type of liquid crystal mesophase. Nematic phase ($\propto$ /mm symmetry) is the simplest measophase shown in the Figure I.9. Broad view is given in Figure I.10. The salient features of this phase are:

1. Nematic liquid crystals have long-range orientational order about the molecular long-axis.
2. They have no positional long-range order in the arrangement of the center of molecules as in isotropic liquid.
3. There exist some preferential orientation of the molecules, characterized by the axis of nematic order denoted by the unit vector **n**,
4. The direction of **n** of the bulk sample may be determined by surface force or externally applied field.
5. They exhibit schlieren; threaded marbled; homogeneous textures.
6. Most nematics are optically uniaxial medium of positive birefringence.

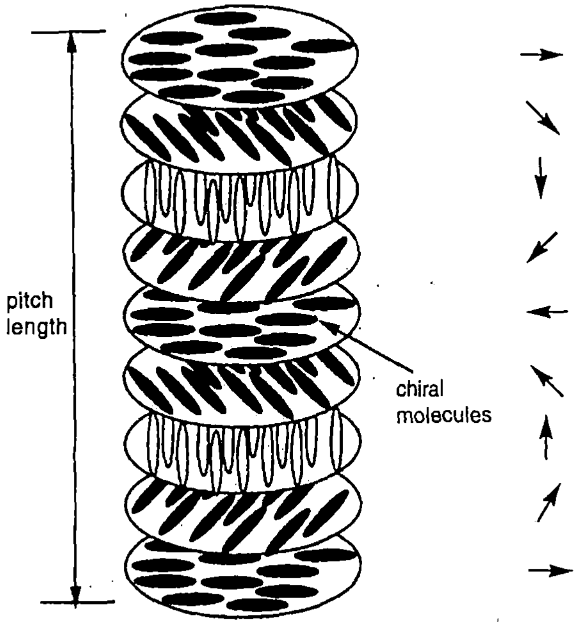
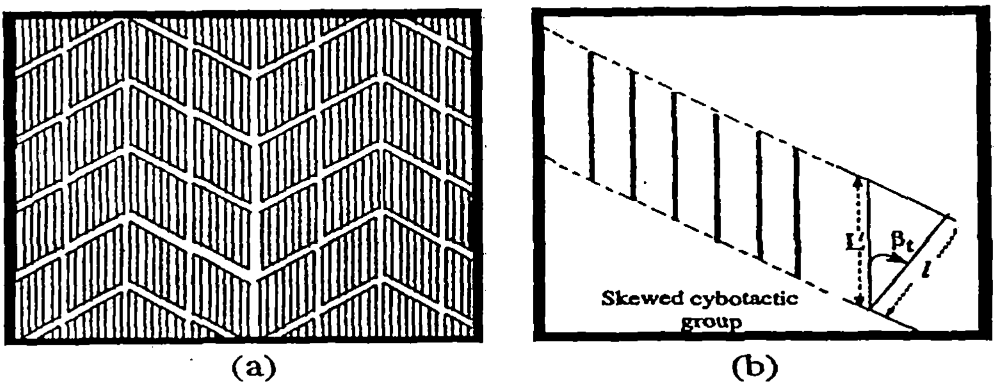


Figure I. 11 Schematic representation of the helical structure of the cholesteric liquid crystals. The views represent imaginary slices through the structure. The arrows indicate the director **n**.



(a) (b)

Figure I. 12 (a) Structural model and the scheme for the molecular orientation in cybotactic nematic phase. (b) Schematic representation of a skewed cybotactic group. The heavy full lines indicate the molecules, the broken lines gives positions of the boundary planes. β_t is the tilt angle.

7. The molecular properties of nematic are such that the left-handed and right-handed forms are indistinguishable (*achirality*). In the opposite case, the system must be racimic (1:1) mixture of right- and left-handed molecules.
8. Anti-parallel dipolar association is found between nearest neighbour molecules possessing permanent dipole moment.
9. Molecular rotation about long axis is unhindered.
10. Nematics are sensitive to external electric and magnetic fields and many different electro- (magneto-) optical effects occur in them.

The cholesteric mesophase is also a nematic type of liquid crystal except that it is composed of optically active molecules (Figure I.11). As a consequence the structure requires a spontaneous twist about an axis normal to the preferred molecular directions ($\infty 2$ symmetry); the twist may be right-handed or left handed depending on the molecular conformation.

X-ray studies [38-41] show that some nematics posses a lamellar type of short-range order, i.e., they consist of molecules, called cybotactic groups, the molecular centers in each cluster are arranged in layers (Figure I.12) When molecular long-axis is arranged perpendicular to the plane or tilted with respect to the plane, the phases are respectively called normal cybotactic or skewed cybotactic nematic phase respectively.

I. 1. 2. 2 *Smectic phase*

Mesophases exhibiting, in addition to orientational order, also a certain degree of positional order, are called smectic phases, Sm in short. In the smectic state, the molecules tend to be arranged within layers or planes. Considering possible arrangements within layers and between the layers, a variety of molecular arrangements are possible, which give rise to a large number phases. For smectics, the director has a slightly different definition than for nematics. In theis case, **n** is a unit vector, which shows the average orientation of the long molecular axes in each layer. Followings are the significant features of smectic phases.

1. Mesophase has a layered structure. It exhibits one-dimensional positional order, so that the structure is formed by parallel molecular monolayers or bilayers.
2. Molecules are mobile in two directions within each layer and can rotate about one axis in some cases.
3. The interlayer attractions are weak as compared with the lateral forces between molecules and in consequence the layers are able to glide over one another easily.
4. Molecules may be normal to the plane of the layers or inclined to it.
5. This phase is more viscous than nematic.
6. For a given material usually it occurs at temperatures below the nematic domain.

Polymorphism is much more obvious in smectic phases. The lamellar smectic state is readily divided into four subgroups by considering first, the extent of the in-plane positional ordering of the constituent molecules and second, the tilt orientational ordering of the long axis of the molecules relative to the layer planes. These two groups are distinguished from each other by the extent of the positional ordering of the constituent molecules. Thus smectic A, C, C_{alt}, B_{hex}, I and F are essentially smectic liquid crystals, whereas B, E, G, H, J and K are crystal phases, which are distinguished from normal crystals that their constituent molecules are reorienting rapidly about their long axes. So a large number of different smectic phases have been identified [16, 17, 42-47].

SmecticA
SmecticD
SmecticC
SmecticB
SmecticE
SmecticF
SmecticG
SmecticH
SmecticI
SmecticK
mecticL
mecticM
SmecticO
SmecticQ

In the above scheme (A, D, C, B, E,…………, Q), the lower temperature modifications stand farther to the right. The alphabetic order merely indicates the chronological order of discovery. The sub-phase of the smectic C phase viz. smecticO or $\mathrm{SmC_{alt}}$ and smectic Q were discovered by Levelut et al. [16, 48]. The plan view of the polymorphs is shown in Figure I.13. Some of them (e.g., S_B, S_E, S_G, S_H, S_J and S_K) have three-dimensional long-range positional order as in a crystal, though with weak interlayer forces, while some others, referred to as hexatic phases, have three-dimensional long range bond-orientational order, but without any long-range positional order. SmA, HexB, CrystalE are orthogonal whereas SmC, I, F, Crystal J, G, H, K are tilted in nature. The smectic D phase has a cubic structure [48] and would appear to be an exemption to the rule that smectics have layered structures. The cubic phases of thermotropic liquid crystals display an independent class of liquid crystalline phases of thermotropic liquid crystals display an independent class of liquid crystalline phases besides the smectic and columnar ones [49]. The great

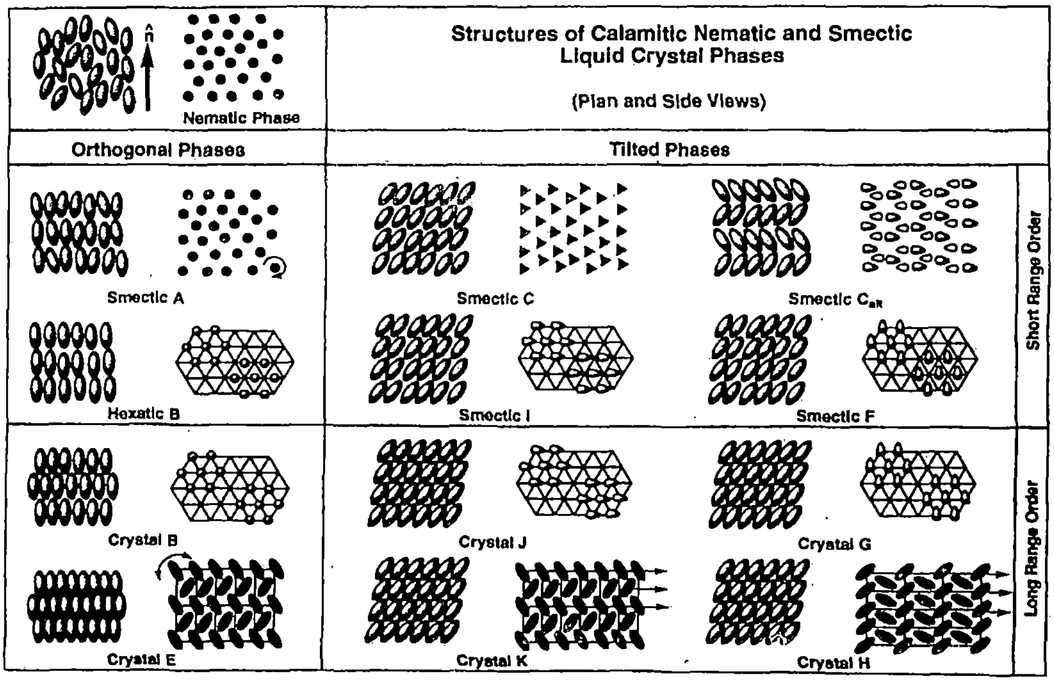


Figure I. 13 The structure of the various liquid crystal phases. For each phase the side view is shown to the left and the plan view to the right. The rod-like molecules are shown as ellipses, their cross-sectional areas as circles, triangles of ellipses. The triangles and arrows are used to represent molecular tilt directions.

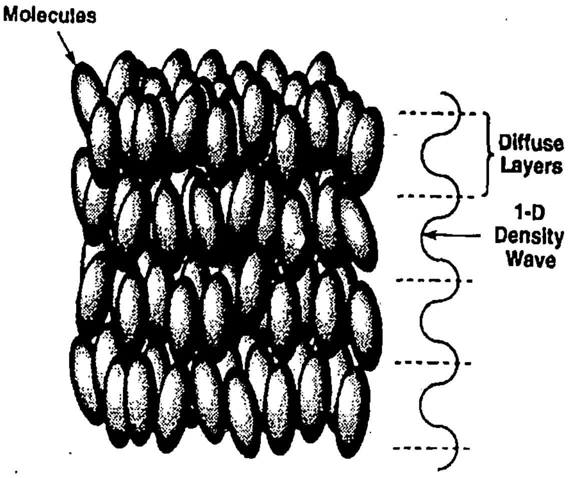


Figure I. 14 Orthogonal smectic A phase (broad view).

variety of chemical structures leads to different cubic phases, which can be expected to be molecular aggregates of different characters.

Out of all the above polymorphism smectic A, smectic C and smectic B occur very frequently.

I. 1. 2. 3 *Smectic A (Sm A)*

Features of this phase (Fig.I.9) and broad view in Fig.I.14 are as follows:

1. The director **n** is perpendicular to the plane of the layer.
2. No positional order within the layer i.e., inside each layer nematic ordering exists (∞/mm symmetry).
3. Within each layer molecules have only orientational ordering.
4. The centers of mass of the molecules possess quasi long-range translational periodicity along the layer normal.
5. They exhibit focal conic (fan-shaped or polygonal); stepped drops; homogeneous; textures.
6. Phase is optically uniaxial in character.
7. The rotation around the short molecular axes is more or less hindered depending on the degree of order.

A number of polymorphic types of SmA phase [14, 43, 44, 49, 50, 51] have been discovered, viz. SmA_1 (monolayer phase), SmA_2 (bilayer phase), SmA_d (pertiallybilayer phase), $Sm\tilde{A}$ (antiphase) and SmA_{ic}.(phase intermediate between SmA_d and SmA_2) [52].

The smectic A liquid crystals, constituting of biaxial rod-like molecules, can have biaxial symmetry and the medium is then characterized by three directors. Recently a polymorphic system has been found to exhibit the biaxial SmA (SmA_b) phase [53, 54].

I. 3. 2. 2 *Smectic C (SmC)*

The properties of SmC phase (Fig. I.9 and broad view in Fig. I.15) are as follows:

1. Smectic C is a tilted form of smectic A, i.e., the director n is tilted with respect to the layer normal (2/m symmetry). Each layer is a two dimensional liquid.
2. Tilt angle may be constant or temperature dependent.
3. It exhibits broken focal conic; schlieren; homogeneous textures.
4. Due to the presence of pronounced tilt angles the phase is optically biaxial.
5. Few of them can show chirality with twist axis normal to the layers.
6. The rotation around the molecular long axes is not strongly hindered. The rotation around the short molecular axes is more or less hindered depending of the degree of order.

It shows polymorphism into three subgroups, viz., C_1, C_2 and C_3 depending on the nature of tilt angles [49]. However for system of molecules possessing terminal polar groups other sub-phases pf Smectic C phases, which are direct analogues of smectic A_1, A_2, A_d and Sm$\tilde{A}$ phases [48]. Chiral smectic (SmC*) liquid crystals [18,23,53] exhibit the same molecular organization inside each layer as smectic C. However, in this case the molecules bear electric dipoles oriented perpendicularly to the layer normal. Thererfore, each layer possesses a macroscopic polarization. Usually the smectic C* structure as a whole is helical (the molecules are chiral) and the polarization rotates as one moves from one layer to another (∞2 symmetry). To polarize a smectic C*, one should unscrew the spiral structure by applying the external electric field.

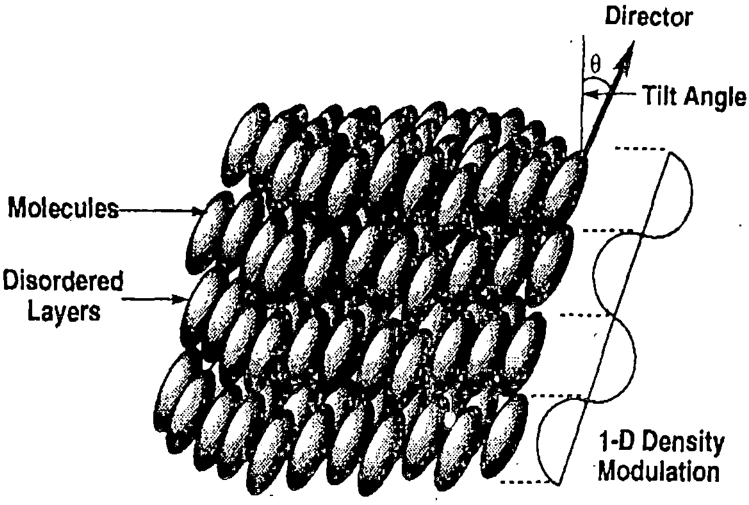


Figure I. 15 The structure of tilted Smectic C phase (broad view)

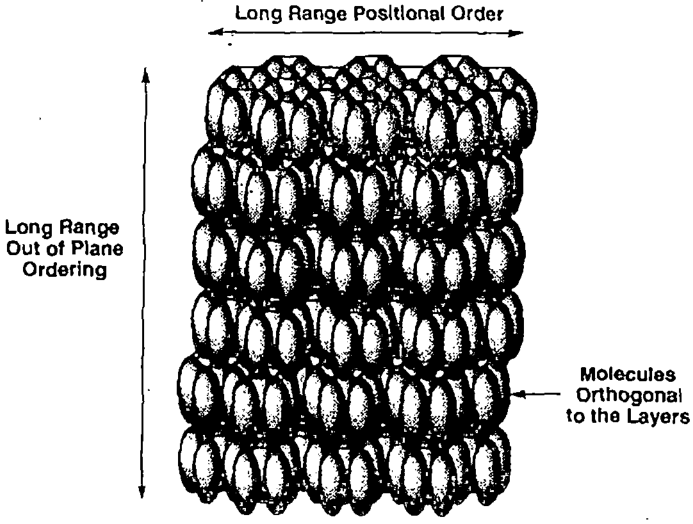


Figure I. 16 Structure of the crystal B phase.

Table I.2 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	Nil	Nil	Nil	Nil
N	Parallelism of long molecular axis	Random	LRO	Nil	Nil	Nil
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

I. 1. 2. 4 *Smectic B (SmB)*

Smectic B phase shows following properties:

1. Within a layer molecular long axes are perpendicular to the plane of the layer and the centers of mass of the molecules are arranged in hexagonal symmetry (6/mm symmetry).
2. It exhibits mosaic; stepped drops; pseudo-isotropic; homogeneous; schlieren textures.
3. It is optically uniaxial or biaxial.
4. Molecular rotation is hindered. String hindrance of the rotation around the shory molecular axes due to the higher packing density; only small hindrance of the rotation around the molecular long axes.

Two distinct types of SmB have been identified: (a) Crystal B- (CrB or L) and (b) Hexatic-B phase. Both the phases exhibit long-range bond orientational order but CrB (or L) shows inter and intra layer long range translational order whereas hexatic B exhibits quasi long range inter layer and short range intra layer translational order. Structure of crystal B phase is shown in Figure I.16.

The broad structural features and ordering [17, 24, 55, 56] of the liquid crystal phases are summarized in the Table I.2 and different classes [24, 35, 47, 57, 58] of liquid crystals are given in TableI.1.

Other than the phases described above, a rich variety of phases have been discovered like frustrated nematic chiral or Blue Phases (BPI, II, TGB) [59,60], Re-entrant phase [61-63], Induced and Enhanced smectic phases [62, 63, 64-70]. Details are given in the respective references indicated. I have not discussed about these interesting phases since these are not relevant to the present work.

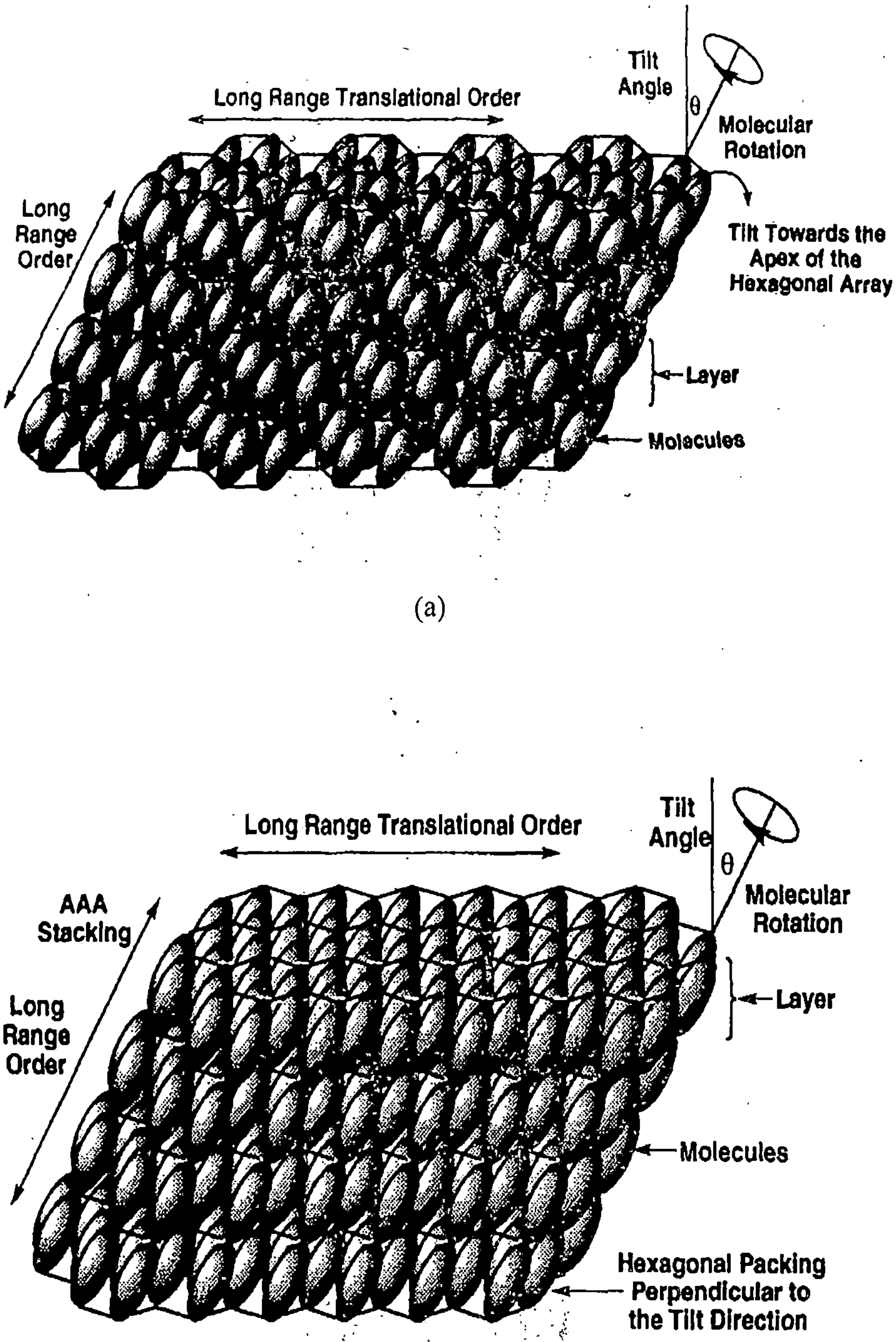
The structure and several physical properties of all the numerous liquid crystalline phases are given in details by de Gennes [42], de Jeu [71], Vertogen and de Jeu [72], Brown [73], Sonin [74], Pershan [45], Tsykalo [47], Chandrasekhar [18], de Gennes [42], Blinov and Chigrinov [75].

I. 1. 2. 5 *Smectic E (SmE)*

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 [76-78]. Doucet et al [77, 79] 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 per second [80, 81] 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 [82].

I. 1. 2. 6 *Smectic I (SmI) and Smectic F (SmF) phases*

The structures of Smectic I phase is similar to $\mathrm{SmB_{hex}}$ but the molecules in this case are tilted within the layers, direction of tilt being towards an apex of the hexagonal packing net [83-88]. Thus it has short range in-plane and quasi-long range out-of-plane positional order as well as long-range bond orientional order in three dimensions. 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 [86, 87]. In addition slightly longer correlation has been observed in the in-plane positional ordering than that found in Smectic I phase [89,90].



(a)

(b)

Figure I.17 Structure of (a) crystal J phase and (b) crystal G phase.

I. 1. 2. 7 *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 [79, 86, 87, 91-95] 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 phases, direction of the tilt being that in SmI and SmF phases respectively (Figure I.17). 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 like in the E phases [82,96].

I. 2 Purpose of the present work

Aryl azene oxides, particularly bis(aryl)diazene oxides or azoxybenzenes, are well known for their meosgenic behaviour [97]. The earliest report of mesogenic 4-azoxyanisole appeared in 1890 [98]. Kast investigated the single crystal structure of 4-azoxyanisole [99], whereas Herrmann and Krummacher made X-ray studies on its powder form [100]. In 1902, Vorländer found the mesomorphic behaviour of diethyl ester of azoxybenzoic acid. A large number of mesogenic bis(aryl)diazene oxides were synthesized and studied by the famous school of Vorländer at Halle, Germany [97, 101-103]. Synthesis of another important class of azoxy mesogens, esters of 4-azoxycinnamic acids, was also reported by Vorländer [103]. At present those compounds are considered as early ferroelectric materials [104]. Furthermore, the first V-shaped azoxy compound was also reported by Vorländer [105]. Interestingly, the mesogenic behaviour of aryl azene oxides is mainly confined within the group of bis(aryl)diazene oxides only. Among bis(aryl)diazene oxides, bis(4-*n*-alkoxyphenyl)diazene oxides and bis(4-*n*-alkyphenyl)diazene oxides are two important groups for meosgens [106-123].

The common synthetic route to prepare the mesogenic symmetrical or unsymmetrical bis(4-*n*-alkyl/alkoxyphenyl) diazene oxides involves the oxidation of corresponding bis(4-*n*-alkyl/alkoxyphenyl) diazene [124]. The other reported methods are summerized as follow:

(i) Synthesis of symmetrical bis(4-*n*-alkyl/alkoxyphenyl)diazene oxides by electrochemical reduction of 4- *n*-alkyl/alkoxynitrobenzenes [125].

(ii) The reduction of p-alkoxynitrobenzenes by lithium aluminium hydride in the ether medium at -70°C to produce azo compounds, followed by oxidation of the azo compound to the corresponding azoxy compound by H_2O_2 in the acetic acid medium at 65°C (36 h.) [126].

(iii) Synthesis of mesogenic bis-(n-alkyl)azoxybenzenes by oxidation of the 4-alkyl anilines using 30% hydrogen peroxide. [127].

(iv) Preparation of 4,4'-di-*n*-alkoxyazoxybenzene by chemical reduction of nitrophenyl ethers with sodium methoxide [128].

(v) Synthesis of 4,4'-*n*-dialkoxyazobenzenes by the reductive coupling of 4-alkoxynitrobenzene with metallic bismuth pellets in a stainless steel ball mill [129].

On detailed scrutiny of the above methods for the synthesis of 4,4′-di-*n*-alkoxyazoxybenzenes, it appears that the existing methods suffer one or more of the following limitations.

1. Multiple steps.
2. Prolonged reaction time.
3. Multiple products.
4. Special set-up like electrochemical reductor, ball-mill etc.
5. Reaction conditions are not always friendly to the environment.

Objectives of the present work

The objectives of the present investigation are to address the above-mentioned problems and attempts would be made to achieve the followings.

(i) To develop a convenient synthetic route for mesogenic azoxy compounds.

(ii) The synthetic procedure should be chemoselective.

(iii) The method should be environment friendly, economic and rapid.

(iv) Designing of new group of compounds by modifying the 4,4′ positions of azoxyarenes with suitable substituents for tuning the mesogenic behaviour.

(v) The new areas of aryl azene oxides, particularly triazene-1-oxides, would be explored for their mesogenic behaviour.

(vi) General synthetic routes would be designed and developed for the new group of triazene-1-oxide compounds.

(vii) Mesogenic behaviour of the proposed group of triazene-1-oxides would be regulated by using different types of spacers and substituents.

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