CHAPTER-I

GENERAL INTRODUCTION

INTRODUCTION

There exist crystals which are of such considerable softness that one could almost call them liquid. These are liquid crystals. Liquids that exhibit crystal like anisotropy are called liquid crystals. G. Friedel[1] argued that the term mesomorphs should be used to describe them since the substances are neither true crystals nor true liquids.

Following the discovery of liquid crystals almost a century ago[2,3], it was established that liquid crystals can be formed by heating certain crystalline solids above their melting points (thermotropic) or by dissolving certain compounds in polar solvents (lyotropic). From X-ray diffraction studies G.Friedel classified them as smectic (soap like) and nematic (thread like)[4]. The early history as well as subsequent developments of liquid crystals through 1956 have been reviewed thoroughly by Brown and Shaw[5]. The present discussion will be limited to thermotropic mesophase only.

Nematic Mesophase

Progression from the completely symmetric isotropic liquid through the mesomorphic phases into the crystalline phases can be described in terms of three separate types of order. The first, or the molecular orientational order, describes the fact that the molecules have some preferential orientation analogous to the spin orientational order of ferromagnetic materials. Nematic liquid crystals have this type of order only.

The molecular order of nematic liquid crystals is shown in Figure 1.1. Two features are immediately apparent from the Figure 1.1.

(i) There is long range orientational order, i.e., the molecules tend to align parallel to each other.

(ii) The nematic phase is fluid, i.e., there is no long range correlation of the molecular center of mass positions.

In the state of thermal equilibrium the nematic phase has symmetry ∞/mm and is therefore uniaxial. The direction of the prrincipal axis $\bar{n}$ (the director) is arbitrary in space.

Nematic liquid crystals are very responsive to their environment and external forces have pronounced effect in their behaviour. A small orienting field (e.g. 0.02 Tesla) is sufficient to give true long range order of director orientation.

de Vries[6] found another type of nematic phase called cybotactic nematic in which the molecules group themselves into isolated planar arrays.

Smectic Mesophase

The rigid rod-like molecules believed to be the building blocks of all liquid crystals can array themselves in parallel layers to form a smectic mesophase[1,4] . The molecules may be normal to the planes of the layers (Figure 1.2a) or tilted within them (Figure 1.2b). The arrangement of centers of gravity within the planes may be at random or regular. The interlayer attractions are small in comparison to the lateral forces and the layers are able to slide one another. Initially, liquid crystals were classified according to their optical anisotropies[7] . Smectic A mesophase (SmA) is optically uniaxial because the molecules are assumed to normal to the layers and randomly distributed within them. The molecular arrangements become increasingly more ordered in SmB , SmC etc. as given in Table 1.1. SmD is no longer considered to be liquid crystal. The progression of order through the sequence of mesomorphic phase (nematic, smectics) is given in table 1.2.

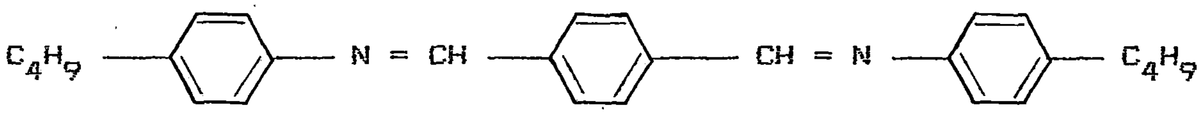
Thermotropic mesomorphism (discotic mesomorphism) has been observed[8] in pure compounds consisting of simple disc-like molecules in which discs are stacked one on top of the other in columns. These columns constitute a hexagonal arrangement, but the spacing between the discs in each column is irregular. Thus the structure has translational periodicity in two dimensions and liquid-like disorder in the third.

Cholesteric Mesophase

Cholesteric liquid crystals (Figure 1.3) have a two dimensional nematic structure. There is no long range order in the centers of mass of the molecule and the molecules are aligned along a preferred axis $\bar{n}$ which has a helical symmetry. The pitch of the helix is temperature and concentration dependent. The constituent molecules are optically active. Periodicity along the helical axis results in Bragg scattering.

A liquid crystalline compound may possess more than one mesomorphic phases. The example of such a compound is given below:

N, N′-terephthalyli-bis(4-n-butylaniline) (TBBA in short)



According to the literatures[9-11] the following phase transitions are observed

$$C \underset{}{\overset{112.5^{o}C}{\rightleftharpoons}} SmB \overset{144.0^{o}C}{\rightleftharpoons} SmC \overset{172.5^{o}C}{\rightleftharpoons} SmA \overset{198.5^{o}C}{\rightleftharpoons} N \overset{235.5^{o}C}{\rightleftharpoons} I$$

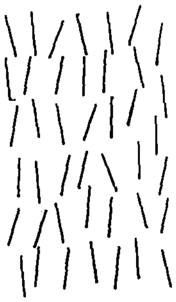
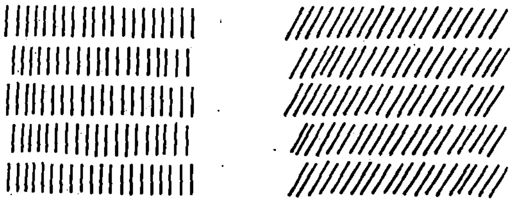


Figure: 1.1. Schematic representation of molecules in nematic state.



(a) (b)

Figure : 1·2. Schematic representation of (a) Smectic-A and (b) Smectic-C.

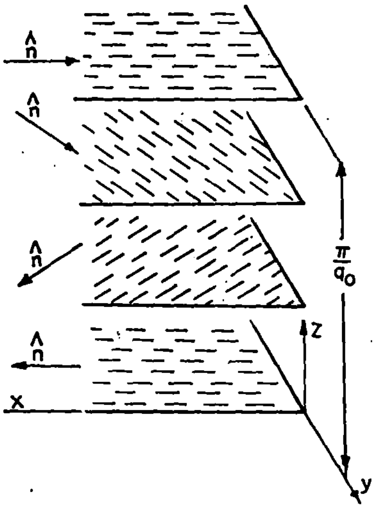


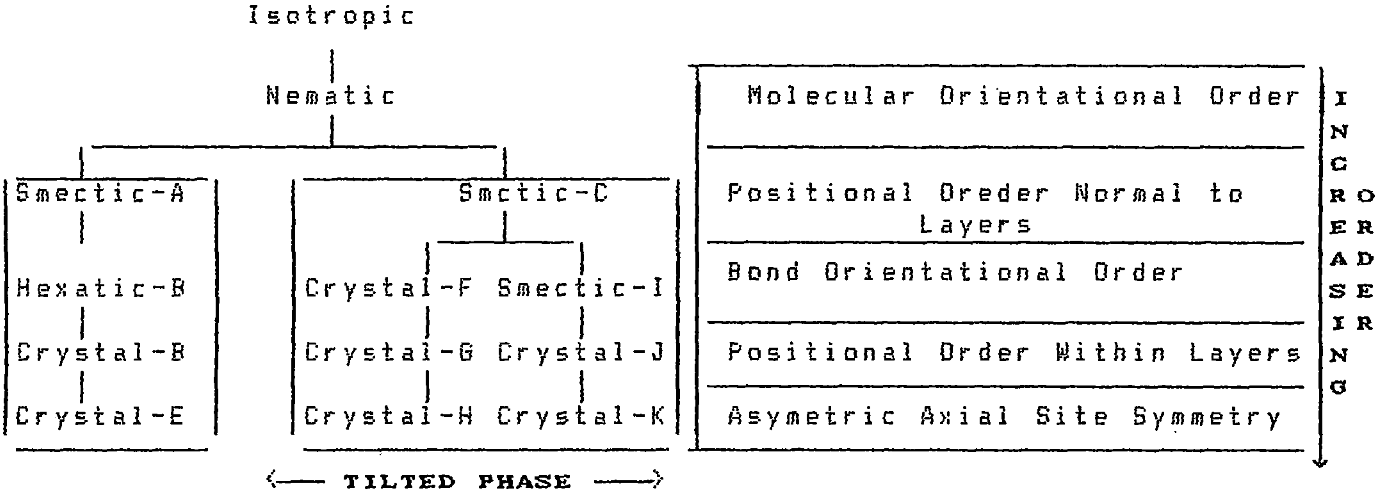
Figure: 1·3. Schematic representation of cholesteric order.

TABLE 1.1

Liquid crystal arrays

Symbol	Name	Molecular alignment
N	Nematic	Strong tendency to parallel a single director and, sometimes, to form nearly periodic molecular rings.
SmA	Smectic- A	Molecular layering in which the molecules within each layer tend to be parallel, but uncorrelated, with long axis normal or nearly normal to plane
SmB	Smectic-B	Molecular ordering within each layer into a regular hexagonal packing.
SmC	Smectic-C	Uncorrelated but nearly parallel molecules that are tilted raletive to plane of layer.
SmD	Smectic-D	Believed to have isotropic (cubic) molecular array.
SmE SmH	Smectic-E to Smectic-H	More highly ordered molecular arrays within parallel layers with molecular correlations within layers and between layers possible.

TABLE 1.2


Isotropic
Nematic
Smectic-A
Hexatic-B
Crystal-B
Crystal-E
Smctic-C
Crystal-F
Smectic-I
Crystal-G
Crystal-J
Crystal-H
Crystal-K
TILTED PHASE
Molecular Orientational Order
Positional Oreder Normal to Layers
Bond Orientational Order
Positional Order Within Layers
Asymetric Axial Site Symmetry
INCREASING
ORDER

For a material having only smectic phase with the increase of temperature, the sequence of phase will be

$$C \rightleftharpoons Sm \rightleftharpoons I$$

With cholesterics and smectics, it has been observed that

(i) $C \rightleftharpoons Ch \rightleftharpoons I$

(ii) $C \rightleftharpoons Sm \rightleftharpoons CH \rightleftharpoons I$

No substances have been found to exhibit both nematic and cholesteric phases, though cholesteric can undergo to nematic phase under the action of external electric and magnetic fields.

Cladis[12] found that binary mixtures of some mesogenic cyano compounds followed on cooling the scheme

$$I \longrightarrow N \longrightarrow SmA \longrightarrow N$$

The abbreviations used are defined as

C — Crystal mesophase
SmA — Smectic A mesophase
SmB — Smectic B mesophase
SmC — Smectic C mesophase
Ch — Cholesteric mesophase
N — Nematic mesophase
I — Isotropic liquid

The low temperature nematic below the smectic phase is called the re-entrant nematic phase. This phenomenon has also been observed afterwards by Cladis et al at elevated pressure[13,14] and by others at atmospheric pressure[15-17] in pure compounds.

Molecular Structure of Thermotropic Mesogens

The presence of common structural features in the majority of thermotropic liquid crystal mesogens makes possible certain generalizations regarding the types of molecules to show liquid crystalline behaviour. The structural features that appear essential are

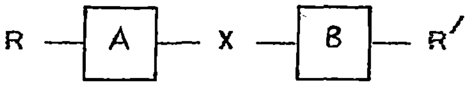
(i) The molecules should be long relative to its width. Due to the geometrical anisotropy of the molecules, the intermolecular forces are anisotropic giving rise to different anisotropic properties in mesophase. The relatively weak forces in certain directions may break on heating so that different mesophases are formed.

(ii) Rigidity along the long axis is another important feature so that parallel orientation may not be broken.

(iii) The molecules should possess strong dipolar (permanent or induced) and easily polarizable groups. The forces responsible for the mesophases are primarily dipole-dipole and dispersive forces.

(iv) The melting point must not be too high, lest only supercooled metastable mesophases be formed monotropically. However, polarity of the terminal part frequently gives rise to very strong intermolecular attractions resulting in the rise of melting point.

The most general structure of liquid crystals consists of two rigid aromatic groups (A,B) coupled with a central linkage group (–X–). R, R$'$ may be alkyl, alkoxy, aceloxy, nitro, amino, hydroxy, bromo, chloro, iodo, etc. groups.



In most cases the two aromatic groups are benzene rings but in some cases either one or both of the rings are cyclohexane, pyrimidine, bicyclooctane etc. groups[18,19]. The name of the liquid crystal is generally termed on the central linkage group such as Schiff bases, esters, azoxy compounds etc.[19-21].

1.1 THEORY

The liquid crystal molecules do possess a quasi long range orientational order of their long axes which tend to be parallel to a common axis called the director $\bar{n}$. When speaking of phase transitions in liquid crystals it is necessary to describe the way the molecular order changes as a function of temperature. The efficiency of the molecular orientation along $\bar{n}$ can be described by a single order parameter $[\langle P_2(\cos\theta)\rangle]$ where θ is the angle between the long molecular axis and the director, being experiment dependent.

The order parameter $\langle P_2\rangle$ can be determined by optical, NMR, X-ray diffraction or magnetic susceptibility studies.

Nematic Phase

The existence of nematic oredr can be understood in terms of mean field theory by Maier and Saupe[22-24]. By mean field approximation we mean that the interaction between the individual molecules is represented by a potential of average force. This theory, therefore, ignores fluctuations in the short range order. Maier and Saupe developed a statistical theory to describe the liquid crystalline state and the molecular ordering for the nematic phase. In analogy to the treatment of ordering phenomenon in ferromagnetics or ferroelectrics this theory describes the intermolecular orientation forces by a mean field method. Each individual molecule feels a nematic potential which is given by

$$U = -A/V^2 \langle P_2(\cos\theta)\rangle P_2(\cos\theta) \qquad (1)$$

where V is the mean molecular volume and A is a constant characteristic of the molecule, independent of pressure, volume and temperature. The derivation is based on the model that the molecule alignment is caused by dispersion forces. Here only the induced dipole-dipole contribution is concerned. The anisotropy of the molecular polarizability caused an angular dependence of the intermolicular dispersion forces and therefore is responsible for mesomorphic phase.

Humphries et al [25] have, however, shown that the assumption of the anisotropic dispersion forces for the formation of nematic phase was not essential. A Single molecule potential (mean field) can be set up to have the correct orientation dependence. (i) U should be minimum when the molecule is parallel to the director and maximum when the molecule is perpendicular to the director. Thus U may be chosen to be proportional to $-P_2(\cos\theta)$. (ii) U must be proportional to $\langle P_2(\cos\theta)\rangle$, the average degree of orientation. This potential which is responsible for nematic phase formation should vanish when $\langle P_2\rangle=0$ and be maximum when the molecules are highly ordered. Finally, U should contain a factor v to describe the overall strength of the intermolecular interactions; the difference between various materials will be accounted for by allowing the strength v to vary from one substance to another. Putting all the requirements together we arrive at mean field approximation to the orientational potential energy of a single molecule

$$U(\cos\theta)= -v \langle P_2(\cos\theta)\rangle P_2(\cos\theta) \qquad (2)$$

This version of the theory has been shown to provide qualitative picture of the nematic phase and its transition.

Humphries et al[25] developed a more comprehensive concept by including higher order terms in the mean field potential for cylindrically symmetric molecules. Their result is

$$U_1(\cos\theta) = \sum_L v_L \langle P_L(\cos\theta)\rangle P_L(\cos\theta) \qquad (3)$$

U_1 is the single molecule potential in the mean field approximation.

It has been found the terms with L= 0 in (3) may be dropped since it is nearly an additive constant. Then

$$U_1(\cos\theta) = v_2\langle P_2\rangle P_2(\cos\theta) + v_4\langle P_4\rangle P_4(\cos\theta) + \text{------} \qquad (4)$$

retention of only first term of equation (4) gives the Maier-Saupe theory.

Orientational Distribution Function

Orientational distribution function $\rho(\cos\theta)$ gives the probability of finding a molecule whose axis makes an angle θ with the director $\bar{n}$. With this function we can compute the average values of various quantities of interest pertaining to the nematic phase.

Orientational distribution function corresponding to the single molecule potential has the form

$$\rho\ (\cos\theta) = Z^{-1}\ \exp.\left[-\beta\ U\ (\cos\theta)\right]$$

$$Z = \int_0^1 \exp.\left[-\beta\ U\ (\cos\theta)\right]\ d(\cos\theta) \tag{5}$$

where Z is the single molecule partition function. $\beta = 1/kT$, k is the Boltzmann's constant, T is the temperatre in absolute unit. Order parameter $\langle P_2\rangle$ can be expressed in terms of $\rho(\cos\theta)$ which is given by

$$\langle P_2\rangle = \int_0^1 P_2\ (\cos\theta)\ \rho\ (\cos\theta)\ d(\cos\theta) \tag{6}$$

Using equation (5) in equation (6) we get

$$\langle P_2\rangle = \frac{\int_0^1 P_2\ (\cos\theta)\ \exp.\ \left[\beta\ v\ P_2(\cos\theta)\ \langle P_2\rangle\right]\ d(\cos\theta)}{\int_0^1 \exp\left[\beta\ v\ P_2(\cos\theta)\ \langle P_2\rangle\right]\ d(\cos\theta)} \tag{7}$$

This is the self consistent equation for the determination of the temperature dependence of $\langle P_2\rangle$.

Theories of Smectic A Liquid Crystals

Contributions to the theory of Smectic A liquid crystals have been made by a number of investigators[26-30]. In all cases the treatments are an extension of the Maier-saupe mean field model of nematics.

McMillan[28,29] developed the theory of smectic-A liquid crystals for the single molecule potential starting from the Kobayashi form of potential[26,27]. The smectic-A liquid crystals possess both orientational and translational orders. The molecular distribution function must therefore describe both the tendency of the molecules to orient along $\bar{n}$ and to form layers perpendicular to $\bar{n}$. The distribution function is thus a function of both $\cos\theta$ and z, and can be expanded in a double series:

$$f(\cos\theta,z) = \sum_{\substack{L=0\\(\text{even})}} \sum_{n=0} A_{LN}\, P_L(\cos\theta)\cos(2\pi nz/d) \qquad (8)$$

$$\int_{-1}^{1}\int_{0}^{d} f(\cos\theta,z)\, dz\, d(\cos\theta) = 1 \qquad (9)$$

where d is the layer spacing along z-direction and θ is the angle made by the molecular long axis with the director, assumed to be in the z-direction.

In addition to the purely orientational and translational order parameters, the $\langle P_L(\cos\theta)\rangle$ and $\langle\cos(2\pi nz/d)\rangle$, we find the set of mixed-order parameters, $\langle P_L(\cos\theta)\cos(2\pi nz/d)\rangle$. These describe the correlation or coupling between the degrees of orientational and translational order. The three order parameters of lowest degree appear in all published theories[26-30] of the smectic-A phase and have given speacial symbols:

$$\begin{aligned} \eta &\equiv \langle P_2(\cos\theta)\rangle, \\ \tau &\equiv \langle \cos(2\pi z/d)\rangle, \\ \sigma &\equiv \langle P_2(\cos\theta)\ \cos(2\pi z/d)\rangle \end{aligned} \tag{10}$$

In the isotropic phase, $\eta = \tau = \sigma = 0$; in the nematic phase, $\eta \neq 0$, $\tau = \sigma = 0$; in the smectic-A phase, $\eta \neq 0$, $\tau \neq 0$, $\sigma \neq 0$. For perfect order all three tend to unity.

According to McMillan the potential function for smectic-A phase is of the form

$$V_M(\cos\theta, z) = -v\left[\delta\nu\tau\ \cos(2\pi z/d) + \left\{\eta + \nu\sigma\ \cos(2\pi z/d)\right\}P_2(\cos\theta)\right] \tag{11}$$

v, δ and ν are three constants which depend on the characteristic of the molecules. Lengthening the alkyl chains in a homologous series increases the spacing d and hence is expected to increase the parameter ν.

1.2 CRYSTAL STRUCTURE OF THERMOTROPIC LIQUID CRYSTALS

It is now well established that for proper understanding and interpretation of several physical properties of liquid crystalline phases a knowledge of the molecular structure in the crystalline phase is very useful. The molecular conformation in the crystalline state predetermines the molecular organisation in the mesomorphic state. The first attempt to correlate the molecular arrangement in the mesophases with the crystal structure of the mesogenic material was undertaken by Bernal and Crowfoot[31] in the early 1930's. With the advent of computer program in the late 1970's, a large number of structures have been determined, most of them possess nematic phase.

Preliminary survey of the present knowledge regarding solid mesophase relationship was given by Bryan[32] . On the basis of the evidence obtained it can be stated that

(i) The molecules of the organic crystals when heated to the liquid crystalline state adopt an arrangement somewhat similar to that in the crystals[31] .

(ii) In nematic crystals the long narrow molecules are found to be more or less parallel and interleave one another to form an "imbricated packing". The transformation from the solid to the nematic phase is characterised by the breakdown of the positional order of the molecules but not of the orientational oredr[33] .

(iii) For smectic compounds the molecules are found to be packed in parallel arrays[34] .

This is true at least for the majority of cases so far known, but at this stage we must be careful to generalise it[34] . Brown[35] found an imbricated packing for a nematogenic compound with the non-planar molecules arranged in herringbone fashion in planes perpendicular to the long axis. Brown and his co-workers[36] also found a herrinbonic compound with a tilt relative to the layers. Bryan et al[37-39] discussed the role of hydrogen bond in the formation of mesogenic compounds.

1.3 MONOLIQUID CRYSTALS

According to the classification of liquid crystals some of the smectic phases possess a highly ordered lattice. This raises the inquiry of differtiating between a crystalline solid and a smectic liquid crystal. By raising the temperature gradually a single crystal can be converted to the smectic phases, giving a well oriented mono-liquid crystal. Since it started as a single crystal, the mono-liquid crystal should in general be comparable with respect to the molecular orientation and alignment with that formed by the effect of magnetic field. X-ray diffraction experiments performed on crystals allow us to determine the structures at the atomic level whereas in ordered smectic phases only information at the molecular level is available. By studying the structures of mesogenic single crystals it may be possible to establish rules concerning the relation between solid phases and mesomorphic phases which appear on melting.

1.4 APPLICATIONS

Liquid crystals have got a wide range of scientific applications. The colour of cholesteric liquid crystals changes sharply with small changes in temperature. This feature can be used in a number of unique temperature sensitive applications. As a result, applications to medical diagnostics, electronic component testing and aerodynamic structure analysis became feasible.

Nematic and cholesteric liquid crystals have already found wide applications in display devices, as many of their physical properties such as birefringence, optical activity etc. are sensitive to weak external perturbations. The remarkable electro-optic effects have rendered it possible to prepare liquid crystal displays whose main advantage over the other types is that they do not require emissions of light, and so consume very low power.

When nematic liquid crystals are arranged in thin layers, their ability to transmit scattered or polarised light changes by applying an electric field. This phenomenon can be utilised for alphanumeric and analog displays, image converters and matrix type picture screens. Recently, ferroelectric liquid crystals (SmC^{*}) have been used for a new generation of fast versatile liquid crystal devices.

Although liquid crystalline materials have been known for 100 years large scale applications for the materials in the form of electronic displays did not occur until the mid 1970 when compact, attractive calculators and watches with liquid crystal displays (LCD) reached market place and soon became house hold items. Now some 12 years later low cost LCD's are being made by hundreds. Today, we see more sophisticated LCD's appearing in such products as portable computers and hand held colour TV sets, the fabled liquid crystal colour TV on a wall, appear to be only a few years in the future. Another major applications for LCD's could be the electronic window shade which has been around for more than 20 years.

1.5 SCOPE AND AIM OF THE WORK

The Liquid crystals have widespread applications. In view of this, study of electro optic properties, phase transitions by different experimental methods, molecular and crystal structural analysis of the liquid crystalline compounds have appeals to the research workers.

I have undertaken the study of liquid crystalline compounds belonging to the homologous series of alkoxy cyanobiphenyl alkyl ether and alkyl cyclohexyl cyanophenyl pyrimidine.

For the alkoxy cyanobiphenyl alkyl ether series order parameter values have been determined at different temperatures from refractive index measurements. Pronounced odd-even effect is exhibited in the results.

Order parameters from both X-ray and optical studies have been determined for the compounds belonging to the other series. From X-ray diffraction photographs orientational distribution function, apparent molecular length and lateral intermolecular distance at different temperatures have been calculated.

The X-ray diffraction study of the monoliquid crystals of the compounds of the alkoxy cyanobiphenyl alkyl ether series possesing smectic phases have been undertaken by me. Diffraction patterns exhibit order disorder phenomena when I slowly cool the monoliquid crystal down to the room temperature.

Crystal structure has been solved for one of the compounds of the second series by direct methods.

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