CHAPTER-I

GENERAL INTRODUCTION

1.1 What is liquid crystal

The term liquid crystal indicates a state of matter which is intermediate between the crystalline solid and the isotropic liquid. The honour of discovery of liquid crystalline phase goes to F.Reinitzer[1,2] and O.Lehmann[3-5]. Observing an unusual melting behaviour in certain organic compounds they drew conclusion that these compounds must possess an intermediate phase between liquid and solid. Since liquid crystals flow like ordinary liquids and exhibit anisotropic properties like solid crystals, O.Lehmann, in 1890, designated the name "Liquid Crystals" to these compounds. Of course, following Friedel's[6,7] suggestions the term 'mesomorphic state', meaning, 'intermediate state' is much in use, along with the term 'liquid crystals'. Many thousands of organic compounds are now found to form liquid crystals[8,9]. According to Brown[10] about 5% of the known organic compounds have one or more liquid crystal phases. A few organometalic compounds exhibit liquid crystallinity[10,11]. Zocher[12] has noted that some inorganic compounds show liquid crystalline phases.

In the liquid crystalline state the three dimensional translational symmetry of the centres of mass of the molecules, which characterize crystalline solid, is absent, partially or fully. But since the molecules of liquid crystals are highly non-spherical (rod like or disc like), some degree of orientational order is still present in the mesophases, as observed in the anisotropic physical properties of these materials. At a higher temperature, known as clearing temperature (T_c), all sort of order disappears and the substance forms isotropic liquid. These changes take place in reverse order on cooling for most of the liquid crystalline substances.

1.2 Classification of liquid crystals

There are broadly two types of liquid crystalline mesophases, viz. 'Lyotropic' and 'Thermotropic'.

LYOTROPIC MESOPHASES : Lyotropic liquid crystals are anisotropic solution of rod like molecules (often of biological origin) in an isotropic solvent[13-16]. Deoxyribonucleic acid (DNA), certain viruses and many synthetic polypeptides all form mesophases when dissolved in an appropriate solvent (usually water) in suitable concentration. Most important point is that the intermolecular interaction between the solute molecules is secondary but the primary interaction is between the solute and polar part of solvent molecules, which is the most crucial in providing the stability of these ordered phases. A very common example of lyotropic liquid crystal is soap solution. Concentration of the solution is the main controlling parameter to form several mesophases. Abundant lyotropic liquid crystals are found mostly in living systems. Since this dissertation is not concerned with lyotropic liquid crystals, it shall not be discussed any further.

THERMOTROPIC MESOPHASE : The term 'thermotropic' arises because transition of mesophases occurs due to the change of temperature. In 1922 G.Friedel[17] classified the thermotropic liquid crystals into three types : nematic, cholesteric and smectic.

Nematic mesophase

The word nematic has come from the Greek word νῆμα which means 'thread'. When a thin layer of nematic sample is observed between crossed polarizers under a microscope, a characteristic pattern known as texture is seen, which is usually thread-like. The nematic liquid crystals do not possess long range translational order, thus showing the fluid character of the nematic phase, but they have long range orientational order of the long axis of the molecules. Although the centres of mass of the molecules are randomly distributed still the molecules have a tendency to align themselves in a preferred direction, known as the 'director' denoted by $\overleftrightarrow{n}$. This phase is uniaxial due to the fact that the molecules are generally rotating freely around their long molecular axes. The axis of uniaxial symmetry has no polarity i.e. $\overleftrightarrow{n}$ and $-\overleftrightarrow{n}$ are equivalent. Figure 1.1 shows the schematic diagram of molecular order of nematic and isotropic phases. The preferred direction usually varies from point to point, but in an aligned sample the director points to the same direction throughout the sample. According to the molecular statistical theory of Maier and Saupe[18] the anisotropy of the molecular polarizability is responsible

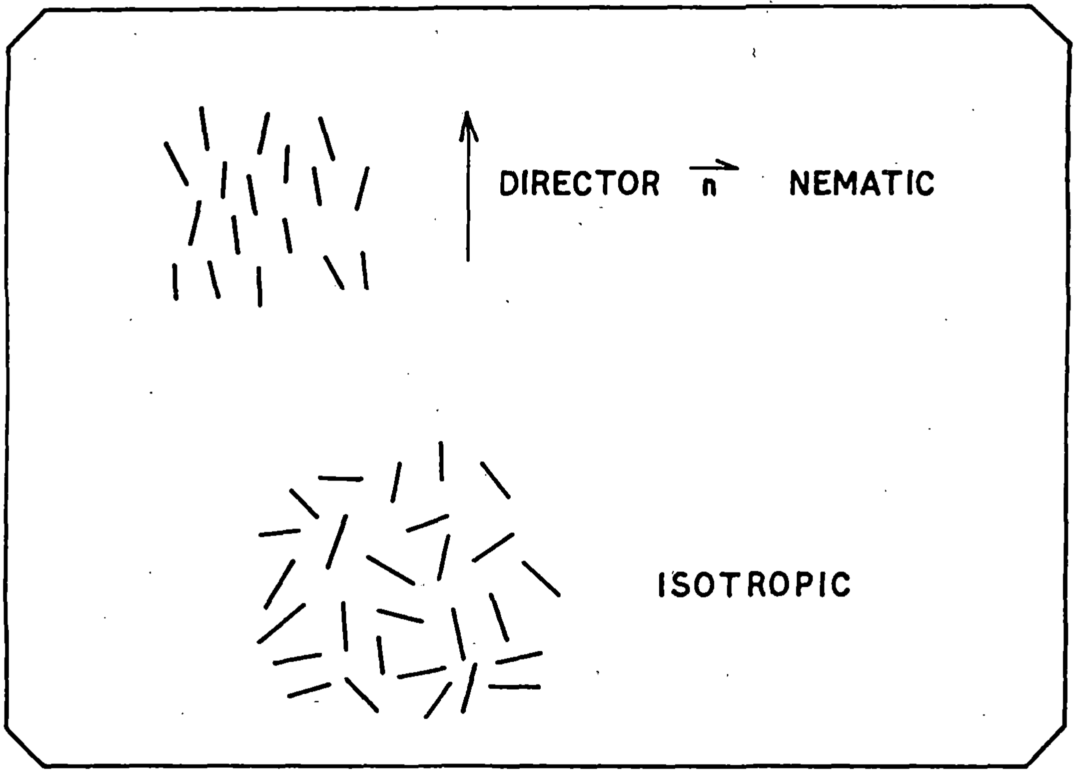


FIG. I.I. SCHEMATIC REPRESENTATION OF MOLECULES IN NEMATIC AND ISOTROPIC STATES.

for the occurance of the liquid crystalline phase. Recent X-ray studies[19,20] seems to indicate that in certain nematic liquid crystals a substantial part of the molecules are arranged in groups known as cybotactic group[21]; in each group the molecules are parallel to each other, and the centres of the molecules lie in a fairly well defined plane. There are two types of cybotactic nematic groups. When the long axis of the molecules makes a considerable angle with the normal to the boundary planes, the phase is know as skewed cybotactic nematic phase. On the other hand when the molecular axis is approximately normal to the boundary planes, the phase is normal cybotactic nematic. So nematic phase may be classified into three types :

(i) Classical nematic phase
(ii) Normal cybotactic nematic phase
(iii) Skewed cybotactic nematic phase.

Cholesteric mesophase

The term cholesteric arises because of the original association of cholesterol derivatives with this mesophase. In 1888 what Reinitzer discovered from the synthesis of cholesteryl esters is nothing but cholesteric liquid crystals. The cholesteric mesophase is basically a nematic type liquid crystal except that it is composed of optically active molecules. In addition to the long-range orientational order there exists a spatial variation of the director leading to the helical structure due to presence of optically active molecules[22]. The helical structure can be best described by an variable intrinsic director (Fig.1.2) :

$$n_x = \cos(q_o z + c),$$
$$n_y = \sin(q_o z + c),$$
$$n_z = 0,$$

c being a constant.

The sign of q_o distinguishes between left-handed ('leavo' type) and right-handed ('dextro' type) chiral nematics. The longitudinal distance in which a full rotation of director is completed is known as pitch L of the helix, nominally defined as

$$L = \frac{2\pi}{|q_0|}$$

However, since $\overleftrightarrow{n}$ and $-\overleftrightarrow{n}$ are equivalent,

$$L = \frac{\pi}{|q_0|}$$

when $q_o = 0$ i.e. L is infinite leads to the nematic phase. Because of this, the cholesteric mesophase is often called a twisted nematic mesophase[23-25]. Two cholesterics, one with left-handed and the other with right-handed helicity produce a nematic, i.e. a cholesteric with infinite pitch[17,26,27].

No liquid crystalline sample has been found so far possessing nematic and cholesteric phases together. Electric

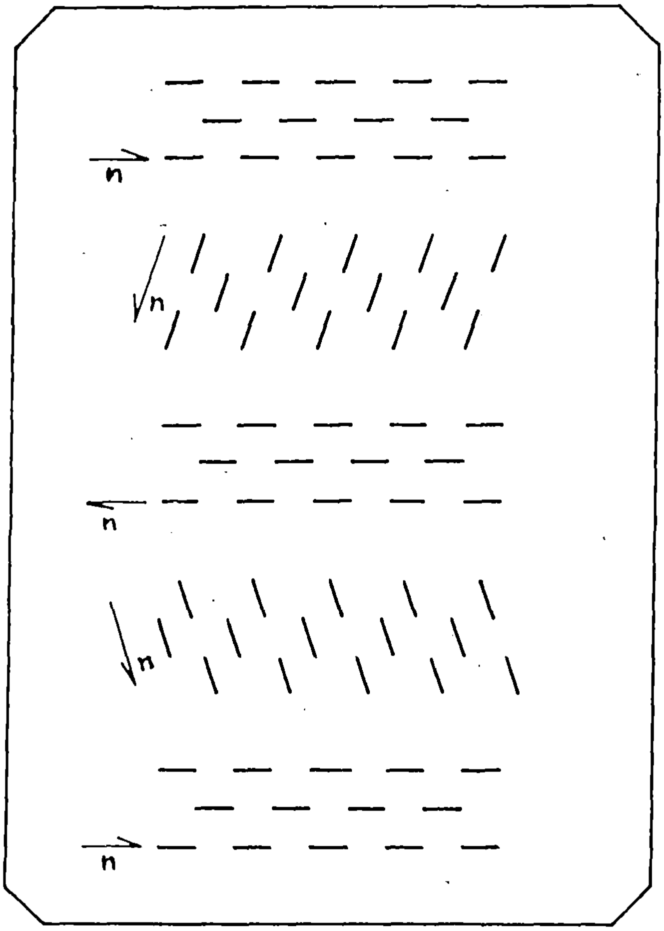
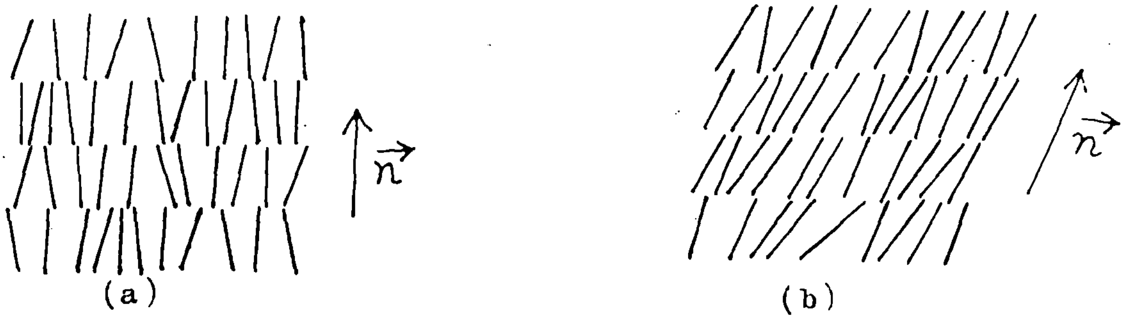


FIG. 1.2. SCHEMATIC REPRESENTATION OF CHOLESTERIC STRUCTURE.



(a) (b)

Fig. 1.3 Schematic representation of two types smectic order: (a) smectic A order, (b) smectic C order.

or magnetic field may cause cholesteric to nematic transition.

Smectic mesophases

Smectic liquid crystals are more viscous than the nematic. In addition to the orientational ordering of elongated molecules, the smectic phases possess some positional order. The centres of molecules are, on average, arranged in equidistant layers. In some smectic phases, the molecules are mobile in two directions (in the layer plane) and can rotate about its long axis. The interlayer attractions are weaker than in lateral forces between the molecules, and the layers can slide over one another relatively easily thus showing fluid behaviour though with greater viscosity than nematics. The various types of smectic phases have been identified by miscibility, texture and X-ray diffraction studies. At least eight thermotropic smectic phases have been identified[28-37]. Smectic phases have been designated as follows[38].

$$S_A, S_B, S_C, S_D, S_E, S_F, S_G, S_H \ldots$$

Some other smectic phases such as $S_{G'}$, $S_{H'}$, and S_I have been discovered recently[39-42]. Since in the present work is mostly concerned with S_A, S_B and S_C phases, only these phases will be described in more detail.

Smectic A mesophase (S_A)

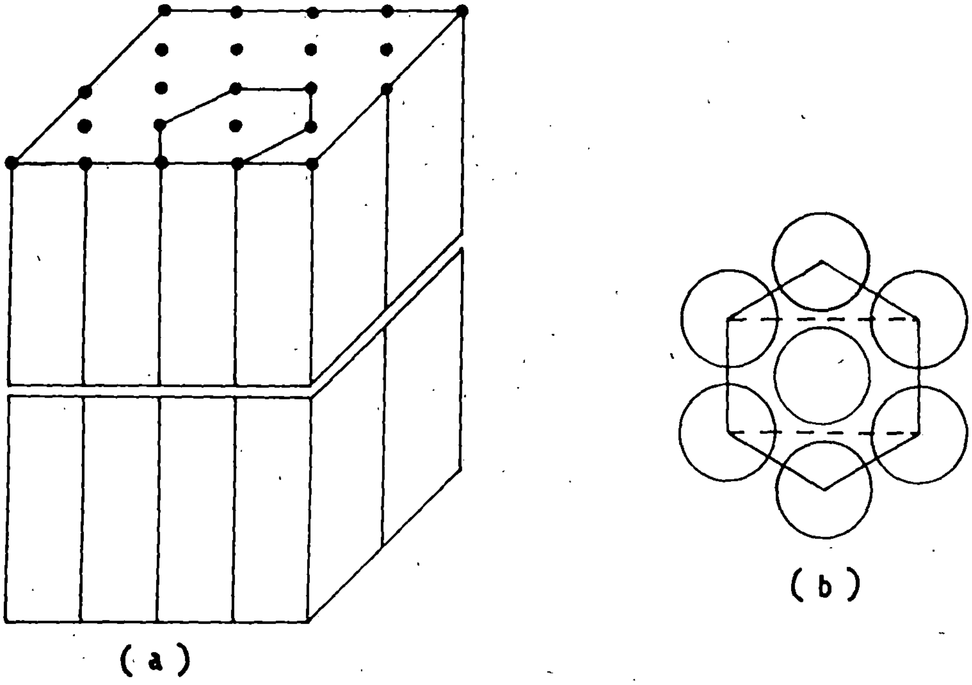
Smectic A phase is the simplest member of the smectic group. The long axes of the molecules lie almost parallel to one another within the smectic layers, the director being normal to the layer plane. The layers can slide over one another. The molecules are generally free to rotate about their long axes and the distribution of the molecular centres in the layer plane is random[31,43,44]. The molecular arrangement is illustrated schematically in Figure 1.3. As a consequence of infinite fold rotational symmetry about an axis parallel to the direction normal to the layer, smectic A phase at thermal equilibrium are optically uniaxial[45]. Smectic A polymorphism has been now an established fact. Recent works[46-52] have revealed that smectic A phase can be subdivided into several distinct phases, such as, monolayer S_{A_1}, bilayer S_{A_2}, partially bilayer S_{A_d} and smectic antiphase $S_{\tilde{A}}$. To have more information regarding bilayer-monolayer transitions, undulation structures and co-existent density waves of incommensurate wave lengths some recent publications on the subject may be consulted[53-61].

Smectic C mesophase (S_C)

The structure of the smectic C phase is very similar to that of smectic A phase except that the director is not normal to the planes of the layer[45,62-64] (Fig.1.3). The layer spacing of the smectic C phase is less than that of the corresponding A phase due to the tilt angle, the angle between the director and the layer normal. The tilt angle of the smectic C phase may be constant or temperature dependent[63]. Depending upon the temperature dependence of tilt angle de Vries[65] tried to subdevide smectic C phase into three groups. Experimental evidences of these modifications are available elsewhere[19,20,66-71]

Smectic B mesophase (S_B)

The molecules in the smectic B phase are also arranged in layers with their long axes almost parallel to each other. There is no long range translational order in the direction of the molecular axis. However, the layers are similar to two-dimensional crystals because the centres of mass of the molecules are arranged in a close-packed hexagonal pattern in the plane of the layers[19,45,72,73]. A correlated rotational motion of the molecules about the long axis exists[72,74,75]. Lambert et al[72] identified two S_B modification. The first one is of positive optical uniaxial character. The long axes of the molecules in a hexagonal layer structure are orthogonal to the plane of the layer[72]. The second type of S_B phase is optically positive biaxial character, in which the long axes of the molecules are tilted relative to the plane of the monoclinic or pseudohexagonal structured layer. The papers[62,66] support the existence of this type of S_B phase. Of course, the two smectic B modifications are classified by Sackmann and Demus[30] as one type.



(a) TWO LAYERS (b) SECTIONS IN THE BASIC PLANE, THE ROTATING MOLECULES HAVE CIRCULAR CROSS SECTIONS.

FIG. 1.4 STRUCTURE OF HEXAGONAL SMECTIC B.

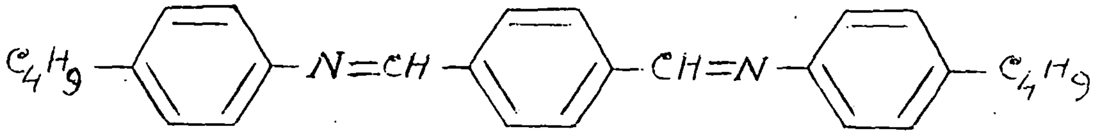
Fig.1.4 shows the schematic diagram of the molecular arrangement in a layer of uniaxial smectic B phase.

The layers in the hexagonal S_B phase are stacked so as to give bilayer (ABABAB ... packing), trilayer (ABCABCA ...), random (ABCBCA...) or (rarely) correlated monolayer (AA ...) structures and enthalpyless transition from one to another may occur[42,75]. In the present dessertation such smectic B - smectic B transition has been reported for the first time in one liquid crystalline substance (MBAC)[100].

Typical example of a liquid crystalline sample

A liquid crystalline sample may possess more than one mesomorphic phases.

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



According to the literatures[30,62,66] the following phase transitions are observed

$$C \underset{}{\overset{112.5^{\circ}C}{\rightleftarrows}} S_B \overset{144.0^{\circ}C}{\rightleftarrows} S_C \overset{172.5^{\circ}C}{\rightleftarrows} S_A \overset{198.5^{\circ}C}{\rightleftarrows} N \overset{235.5^{\circ}C}{\rightleftarrows} I$$

The abbreviations used are defined as[76]

C - Crystal
S_A - Smectic A mesophase
S_B - Smectic B mesophase
S_C - Smectic C mesophase
Ch - Cholesteric mesophase
N - Nematic mesophase
I - Isotropic liquid

Molecular structure of thermotropic mesogens

The pioneer workers regarding the typical structural properties of the liquid crystalline molecules are D.Vorländer, C.Weygand, C.Weigand and G.W.Gray[77]. According to their investigations the general structural features of a molecule forming liquid crystal are as follows :

(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.

New liquid crystalline phases

In addition to the liquid crystalline phases discussed above, fundamentally a new type of mesophase has been recently discovered. Chandrasekhar et al[78] have synthesized and investigated the properties of the new type of molecules which are disc-like and they form a mesophase known as 'discotic phase'. The molecules stack like coins to form a hexagonal close-pack array. Previously, very similar disc-like mesogens had been identified in petrolium and coal tar[79,80]. In recent years significant amount of research have been performed with disc-like molecules[81-85].

Normally organic compounds that show liquid crystallinity on heating give a series of mesophases, with order being lost stepwise over a range of temperature[30,68]. But Cladis[86] was the first to observe a counter example where less ordered nematic phase reappeared at a lower temperature than the more ordered smectic phase. This new phase is termed as re-entrant nematic phase[86,87].

According to Cladis binary mixtures of certain mesogenic cyano compounds exhibit the following path during cooling.

Isotropic —— Nematic —— Smectic —— Nematic

At elevated pressure Cladis et al[88,89] have observed this phenomenon. The mechanism of the formation of the nematic phase at lower temperature has been explained by Cladis[90]. The re-entrant nematic phase has been observed in some pure compounds[91-97] and their mixtures at atmospheric pressure. Re-entrant smectic phases have also been reported[97,98]. Melthete et al[99] has got re-entrant cholesteric phase in pure compounds recently.

Objective and scope of this work

Although the first of the numerous liquid crystalline phases was discovered almost a century ago, these mesophases are still not very well understood, the anisotropy of the shape of the molecules and of the intermolecular potential play major roles in determining the stability of the various liquid crystalline phases. Several theories on mesophases have been developed and one of the easiest ways to test a theory is to compare the predicted order parameters with those obtained from experimental methods. Moreover, technical application of liquid crystals is mostly in display devices, whose efficiency depends upon order parameter. Hence, experimental order parameter determination is necessary and important from both theoretical and technical considerations. In view of these implications, in the liquid crystal research laboratory at University of North Bengal orientational order parameters are being determined from X-ray diffraction and refractive index measurements for last eight years. However, due to the approximations involved during analysis of the data, there remains some uncertainty in the calculated values obtained from these experiments. To overcome this difficulty it was decided to set up an apparatus for measuring the magnetic susceptibility of monodomain liquid crystal samples, since in this case, order parameters can be obtained directly from experimental data without involved calculations and approximations. A Curie torsian balance was set up for measuring magnetic susceptibilities. Four nematic compounds of a homologous series were used for refractive index, X-ray diffraction and magnetic susceptibility measurements and the orientational order parameters obtained from these data are compared with each other as well as with the theoretical predictions from Maier-Saupe theory.

During the setting up of the Curie torsion balance, refractive index measurements were done on some Schiff's base compounds, but unfortunately due to either paucity of the sample or its chemical decomposition, magnetic susceptibility measurements could not be performed on these. However, these experimental data and their analysis have been included in this dessertation.

Finally, in trying to determine the orientational order parameters in the smectic B phase of a compound (MBAC), an enthalpyless SmB⟷SmB transition was observed, which has also been included in this thesis.

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