CHAPTER I

GENERAL INTRODUCTION

1.1. What Liquid Crystals are:

The Austrian botanist F. Reinitzer[1] and the German chemist O. Lehmann[2,3], as early as 1888, observed that certain compounds, e.g. cholesteryl acetate and cholesteryl benzoate, when heated did not pass directly to the liquid state but adopt a structure which had both the anisotropic optical, electrical and magnetic properties of true crystals and the hydrodynamic properties of true liquids. On reaching a certain temperature, called melting point, the solid undergoes transformation into a turbid condition and at still higher temperature, called clearing point, the turbidity disappears and isotropic liquid state is formed. On cooling these changes take place in reverse order. The result of their pioneering research work led Lehmann to name this kind of substance as "Liquid Crystals" even though the term seems to be misnomer. Because of their intermediate nature between liquid and solid state these compounds are also termed by Friedel[4] as mesophases.

The two major categories of liquid crystals are identified as thermotropic and lyotropic. Thermotropic liquid crystals are obtained, as described earlier, by heating certain chemical compounds. On the other hand, lyotropic liquid crystals are obtained by mixing two or more compounds, one of which is a polar solvent. These systems occur in both inanimate and animate matter, the most common example being aqueous soap solution. We will not discuss about lyotropic liquid crystals further, since, in this dissertation we are concerned only with thermotropic liquid crystals. Reviews on lyotropic liquid crystals are given in references[5-8].

As proposed by G.Friedel[9], in 1922, thermotropic liquid crystals are generally divided according to their structures, into two major groups, namely, nematics and smectics. In nematic phase (the term is coined from the Greek wor~~l~~d νημα meaning thread) there is no correlation between the molecular centres of mass, but the direction of the molecular long axes do statistically have preferred direction of orientation, called the director. This is schematically shown in Fig. 1.1. Since there is no restriction regarding the positions of the centres of mass, the molecules have a high degree of mobility and the nematic phase is markedly affected by external fields. Within this group fall another category, namely the cholesteric phase (so called due to the presence of optically active cholesterol group in its molecule) which have the same structure as the nematics but with an additional twist about an axis perpendicular to the long axes of the molecules. That is the cholesterics are nothing but twisted nematics (Fig.1.2). The cholesterics display colour due to Bragg reflection. Smectic liquid crystals (this term is also coined from a Greek word σμηγμα meaning soap) again have the long axes of the molecules orientated in a certain direction, but here the centres of mass of the molecules are arranged in

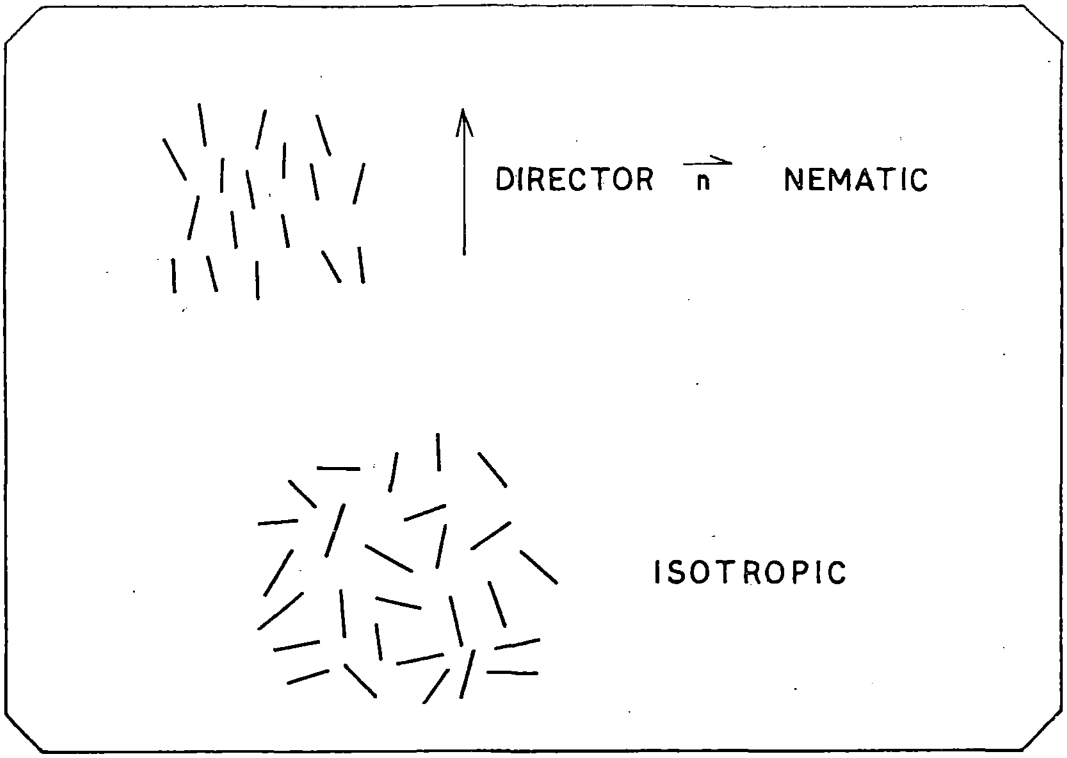


FIG. 1.1. SCHEMATIC REPRESENTATION OF MOLECULES IN NEMATIC AND ISOTROPIC STATES.

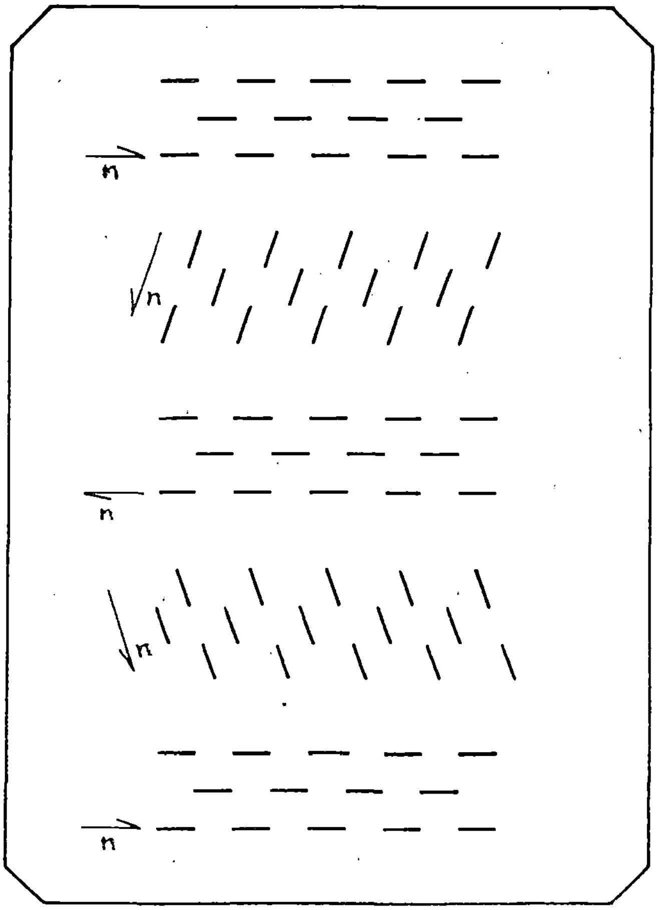


FIG. 1.2. SCHEMATIC REPRESENTATION OF CHOLESTERIC STRUCTURE.

equidistant planes. The molecules are generally free to move within smectic planes and also across the planes. There are many sub-divisions of the smectic state depending upon the arrangement of the molecules within the layers. Another type of liquid crystal was discovered by Chandrasekhar and co-workers[10,11], and was termed as columnar phase, where the flat disc-like molecules are stacked in columns and so the plane of the molecules are perpendicular to the director contrary to the former types where the molecules are parallel to the director. We shall, however, describe different phases in detail in the next chapter.

A liquid crystalline sample may posses more than one mesomorphic phase i.e. different smectic phases and nematic or cholesteric phase with the following transition sequence.

$$\text{Solid} \rightleftharpoons \text{Smectic} \rightleftharpoons \text{Nematic} \rightleftharpoons \text{Isotropic}$$

No such substance has been found that exhibits both nematic and cholesteric phases even though cholesterics can undergo a transition to nematics under influence of external field. All most all the mesomorphic phase transitions are enantiomorphic i.e. they take place reversibly on heating and cooling, the reversal to the solid phase is usually accompanied by supercooling as in the case of ordinary crystallization. Monotropic transition may also occur, e.g. smectic phase, occurs only on cooling in cholesteryl nonanoate[12].

Most of the liquid crystalline materials are organic compounds. According to Brown[13] approximately five percent of the known organic compounds have one or more liquid crystal phases. A few organometallic compounds of mercury, tin and germanium[13] and silicon, nickel and palladium[14] exhibit liquid crystallinity. Some salts of aliphatic acid also possess this property. Zocher[15] has noted that inorganic compounds such as silicates vanadium pentoxide, γ-aluminium hydroxide and β-iron (III) hydroxide also exhibit liquid crystalline super phases.

1.2. Molecular structure of Thermotropic Mesogens:

At present there is no way of predicting with certainity whether a given molecule will exhibit liquid crystalline phase. However, D. Vorländer, C. Weygand, C.Weigand and G.W. Gray[16], discovered four general criteria that indicate a molecule's predisposition to forming a liquid crystal. It should be born in mind that these are only generalization and exceptions do exist.

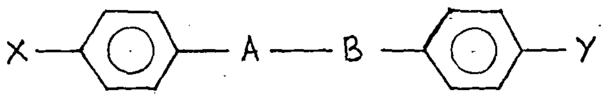
1. The molecule will be long relative to its width. Because of this geometrical anisotropy, the intermolecular forces are also likely to be anisotropic, a fact responsible for maintaining order in liquid crystals. The relatively weak forces in certain directions may break on heating giving rise to different mesophases before going to the isotropic liquid state.

2. The molecules will have some rigidity along the long axes, otherwise flexibility would break the parallel orientation in the molten state.

3. The molecules may have simultaneous existence of strong dipole (permanent and induced) and easily polarisable groups. The existence of easily polarizable groups (such as aromatic groups) as well as dipoles in a suitable direction enhance the anisotropy of cohesive forces. A permanent dipole along the molecular axis results in most pronounced liquid crystalline effect.

4. The melting point must not be too high (when thermal motion of the molecules prevent ordering of the molecules required to form a mesophase), lest only supercooled metastable mesophases be formed monotropically. High polarity on the terminals of the molecules results a very strong intermolecular attraction thus raises the melting point.

The vast majority of liquid crystalline substances are thus based on the following structure:



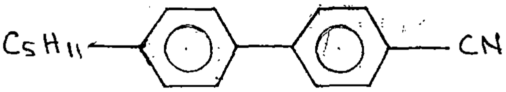
They posses:

1. Two or more aromatic (or more rarely, heteroaromatic and/or cycloaliphatic) rings, called core, usually benzene rings, as shown; these are easily polarizable and planer.

2. One or more bridging groups, A – B, that bind the rings together; usually the core and bridging group(s) are rigid.

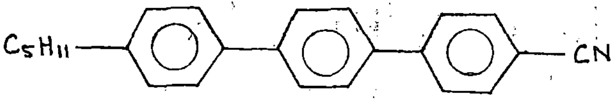
3. Two terminal groups, X and Y, usually attached to the 'para' positions of the aromatic rings and may be same or different.

The aromatic rings may also be directly connected as in p-cyano-p'-pentylbiphenyl.



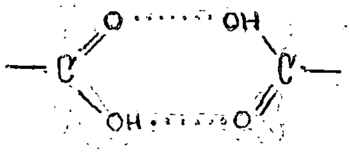
Crystal 22.5°C Nematic 35°C Isotropic

The mesomorphic behaviour is greatly influenced if the length of the rigid core is increased by introducing additional aromatic rings as bridging group as in p-cyano-p'-n-pentyl terphenyl[17]



Crystal 130°C Nematic 239°C Isotropic.

Very often the bridging group contain multiple bonds to maintain rigidity and linearity. Most commonly encountered bridging groups are listed below[18] and more detail description on this will be found in reference[16].



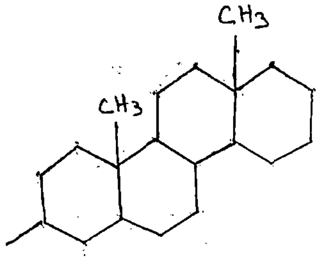
acid dimer

$-CH = CH-$

olefin

$-C \equiv C-$

acetyline

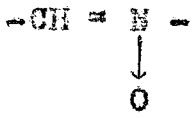


Δ^5 -steroid

$-CH = N-$

azomethine

(Schiff's base)

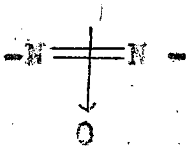


$-CH = N(\rightarrow O)-$

nitrone

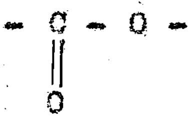
$-N = N-$

azo



$-N = N(\rightarrow O)-$

azoxy



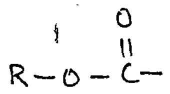
$-C(=O)-O-$

ester

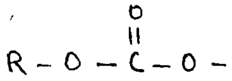
Terminal groups vary widely in chemical nature and determines which mesophase will be observed. Most frequently encountered terminal groups are listed below[18]:

$CH_3-(CH_2)_2-$ - Alkyl may be branched

$RO-$ - Alkoxy, also internal ethers



$R-O-C(=O)-$ - Carboalkoxy



$R-O-C(=O)-O-$ - Alkylcarbonato

F, Cl, Br, I - Halogen

$-CN$ - Cyano

$-NO_2$ - Nitro

R_2N- - Amino R may be H.

Chemical constitution of different mesophases are listed by Kelker and Hatz[19]. Gray[20,21] by studying the seventy homologous series available at that time observed that certain general types of curves, relating the transition temperatures to the number of carbon atoms in the series, might be obtained and this could be used to correlate all the members of the series. Recently reported homologous series[22] can also be approximately correlated by one or another of general curves of Gray. He found -

1. The different phase transition temperatures (Nematic-Isotropic, Smectic-Isotropic, Smectic-Nematic) give smooth curve though the melting point do not show any regularity.

2. The clearing points of nematic phasedecrease with increasing chain length. The observed exceptions to this rule have also been explained[22].

3. The Nematic-Isotropic transition temperatures fit in two curves, one for even and the other for odd number of carbon atoms in alkylchain, giving rise to the so called "odd-even" effect. The transition temperatures decrease with a distinct alternation, the amplitude of the alternation, ~~the amplitude of the~~ also being reduced with increasing chain length.

4. The plot of clearing point of smectics and the smectic-nematic transition temperatures usually reaches a maximum at a moderate chain length and decreases gradually with further elongation of the chain. This plot normally shows no distinct "odd-even" effect[23].

5. When more than one phase is possible the smectic state increases in thermal stability, at the expense of the nematic or cholesteric phase as chain length increases. It is often seen that, while the lower homologous are purely nematic, the higher are purely smectic and the intermediate homologoues, exhibit both mesophases. Smectic states are stabilized by multiple dipoles acting transverse to the molecular axis (lateral attractions), while terminal attractions appear to be more important in determining nematic thermal stability.

The effect of broadoning of a molecule by introducing one or more substituents in place of hydrogens along the side of the core structure is given in detail by Gray[20]. The broadening reduces the anisotropic polarisability and consequently the intermolecular attractions. Young and his co-workers[24] studied the following compound

and found a systematic decrease in Nematic-Isotropic temperature as the number of CH_3 group introduced at positions A, B or Y, Z was increased.

1.3. Crystal structures of thermotropic mesogens:

It is now well established that for a proper understanding and interpretation of several physical properties of liquid crystalline phases, a knowledge of the molecular structure in the crystalline state is very useful, as the molecular conformation in the crystalline state predetermines the molecular organisation in the mesomorphic state. From the previous section it is obvious that since the discovery of liquid crystallinity a great number of useful rules concerning their chemical constitution have been stated. But so far, much less is known about the relationships between molecular packing in the solid and the possible occurence of thermal mesomorphism after melting. Though the first attempt to correlate the molecular arrangement in the mesophase with the crystal structure of the mesogenic material was undertaken by Bernal and Crowfoot[25] in the early 1930's, further studies had for many years been very few. Upto 1974, only seven crystal structures had been determined[26]. The situation, changed drastically with the advent of computer program in the late 1970's. Now a large number of structures have been determined, most of them being nematic, a few with different types of smectic precursors[26-30]. A preliminary survey of the present knowledge with respect to the solid-mesophase relationships was given by Bryan[31]. On the basis of the meagre evidence at hand it is stated:

1. The molecules of the organic crystals when heated to the liquid crystalline state adopt an arrangement somewhat similar to that in the crystals[25].

2. In nematogens the long narrow molecules are found to be more of less parallel and interleave one another to form what was described by Bernal and Crowfoot as 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 order[32].

3. For smectogenic compounds the molecules are found to be packed in parallel array, again as predicted[27,33].

Certainly this is true of at least the majority of the small number of cases so far known - but at this stage we must be cautious to generalise it[28]. Brown[34] 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[35] also found a herringbone packing in stratified structure for a smectogenic compound with a tilt relative to the layers. Bryan, Forcier and Miller[36-38] also discussed the role of hydrogen bond in the formation of mesogenic compounds.

1.4. Applications of liquid crystals:

In his pioneering work more than fifty years ago, Dr. Vörländer[39] had already considered the idea of technical applications of liquid crystals without, however, finding a possibility. Only in the last two decades intensive study began to make technological use of the unique properties of liquid crystals. An account of technical application have been given in some books[18, 40-46]. References of series of review articles havebeen given by Kelker and Hatz[47]. We shall, however, give here only a brief outline.

Since liquid crystals are very sensitive to weak external perturbations, they are used in detection of temperature, pressure and chemical contamination. The helical pitch of the cholesteric liquid crystals is highly temperature sensitive and so a slight change in temperature changes colour of the sample. In some cases it is found that a rise of less 3°C is adequate to change the colour of reflected light from red over the entire visible spectrum to blue (Table 1.1).

Table 1.1

Colour change as a function of temperature (^{o}C) in a cholesteric liquid crystal[43].

Human body temperature			36.9
Colourless	-	Red	39.5
Red	-	Orange	37.7
Orange	-	Yellow	40.0
Yellow	-	Green	40.2
Green	-	Cyan	40.6
Cyan	-	Blue	41.2
Blue	-	Violet	42.0
Violet	-	Colourless	43.0

At the expense of the indicator range[48], the temperature resolution can even reach .007°C. Thus cholesteric liquid crystals have interesting sensing applications[49]. One of these is the so-called thermal mapping of electronic components. Two prime purposes for thermal mapping in the electronics industry are to obtain temperature distributions of operating devices and to identify heat-producing malfunctions.

Cholesteric liquid crystals have been found useful also in the measurement of surface temperatures in aerodynamic designs[13]. The remarkable sensitivity to temperature change has made it possible, for the first time, to observe some of the finer details in boundary layer flow such as occur in transition regions from laminar to turbulent. Small shock waves impinging on the surface can also be detected. The use of cholesteric liquid crystals as an investigative and diagnostic tool in medicine has become rather widespread in the past several years. For example skin infections and malignant skin tumour may be detected and located by use of cholesteric liquid crystals. The tumour is located in that the temperature of the skin in the vicinity of a tumour is higher than that of the surrounding area.

The discovery of dynamic scattering mode in nematic liquid crystals[50] 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 phenomena can be utilised for alphanumeric and analog display image converters and matrix-type picture screens. In practice, liquid crystals are now widely used in displays for watches, clocks, calculators and various digital pannel meters. The relatively low optical contrast than LED's in dynamic scattering mode has been dramatically improved in field effect mode[51] display devices.

As the liquid crystal molecules are orientated in magnetic field with optic axis parallel to the field, they can be used as anisotropic solvents for nuclear magnetic resonance measurements. Liquid crystals have also been used as solvents for the studies of NIR and UV spectra of solute molecules in liquid crystal films.

1.5. Scope and aim of the work:

It is evident from the last section that liquid crystals have enormous remarkable applications. For this purpose, identification of different phases, their electro-optic properties and molecular and crystal structure analysis are important. In the present work we have chosen five liquid crystalline substances -

BBBA, APAPA, OOBPD, 5OCB and CPHB -

for X-ray diffraction studies. Taking powder and aligned X-ray diffraction photographs of BBBA, APAPA and OOBPD their phases have been identified. Also orientational distribution functions $f(\beta)$ and order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ of magnetically aligned samples have been calculated. These are described in chapters II to V. X-ray diffraction studies in liquid crystalline phases of 5OCB and CPHB were made earlier in our laboratory. In the present work we have determined their crystal and molecular structures by X-ray diffraction technique and tried to find out correlation between crystalline and mesomorphic phases. These have been reported in chapters VI to VIII.

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