CHAPTER 1

Introduction

INTRODUCTION :

Anisotropic fluid or liquid crystals are mysterious in their properties and are extremely useful, thus providing scientists and engineers with one of the most active and fascinating fields of scientific and industrial research.

The liquid crystalline state had been discovered in 1888 by Austrian botanist Reinitzer[1,2] and Lehman[3,4,5] while investigating the properties of some easters of cholesterol.The properties of liquid crystalline phases are intermediate between those of crystalline solids and isotropic liquids, so they are referred to as mesophases or mesomorphic phases by Friedel[6,7]. Nowadays thousands of organic chemicals are known to form mesophases[8,9,10]. Few organo-metallic and some inorganic chemicals also show liquid crystalline properties.

Liquid crystals have some-what asymmetric shape of molecules. The molecules in the form of rods are held together by highly anisotropic forces due to dipole and quadrupole interactions. These anisotropic intermolecular forces, taken together with the asymmetric shape of the molecules can give a turbid mobile liquid, exhibiting some degree of long range orientational or translational ordering of the molecules not present in an ordinary isotropic liquid. Many excellent books and review articals on liquid crystals regarding detail molecular structures and physical properties of mesogenic compounds have already been published and only a few of them[11-23] have been listed.

CHARACTERISTICS OF MOLECULES WHICH FORM LIQUID CRYSTALS.

The molecular features of compounds which form thermotropic liquid crystals may be described as follows :

1. The molecules will be long relative to its width.
2. The molecules will have some rigidity along the axis.
3. The molecules may have simultaneous existence of strong dipoles

and easily polarizable groups. The most pronounced liquid crystalline effect is most likely to occur if the strong dipole is on the molecular axis.

4. The molecule may have weak polar groups at its extremities. This property appears to have sub-ordinate importance.

These general characteristics serve only as guide lines and that some molecules without them, or may be only some of them, will form liquid crystal systems.

Along with the architecture of the molecule, one is interested in molecular interactions which produce the liquid crystalline state. Some of these interactions are as follows :

(1) Dipole-dipole interactions.

(2) Ion-dipole interactions.

(3) Induced dipole interactions.

(4) Hydrogen bonding in large molecules.

1. CLASSIFICATION OF LIQUID CRYSTALS.

Liquid crystals can be divided into two distinct types, known as lyotropic and thermotropic liquid crystals.

1.1 Lyotropic mesophase.

The lyotropic liquid crystals[24-30] are prepared by mixing two or more compounds, one of which has a rather large polar character. A typical system of this type is soap and water system where mesomorphic phase appears as a function of either concentration or temperature. In this soap water system, the polar water molecules penetrates between the layers of the polar groups of the soap molecules and accomplish the weakening of the attractive forces between them to cause transition from the solid phase to the liquid crystal phase. This solid - liquid system behaves as a mobile liquid and show many of the anisotropic physical properties chacteristics of the solid phase. However no technical application of lyotropic system for display devices are known as yet[31]. Since this dissertation is concerned only with thermotropic liquid crystals, I will not discuss this lyotropic phase in detail.

1.2 Thermotropic mesophase :

Thermotropic liquid crystals are those where phase transitions occur due to the change of temperature. Now these thermotropic mesogens are divided into three classes distinguished by their different degrees of orientational and translational orders. Friedel[32] recognized three main classes of thermotropic liquid crystals known as nematic, smectic and cholesteric. A diagrammatic representation of the molecular structure in each of these is shown in figure 1.1.

1.2a Nematic mesophase

The nematic mesophase consists of elongated molecules and have long range orientational order. The centres of the molecules are distributed at random but their long axis tends to be parallel to one particular direction, the director. This phase is uniaxial with respect to all physical properties but a biaxial modification has been discovered recently. It is very easy to deform the aligned nematic liquid crystals by external agents. Nematics are able to translate weak external signals (electrical, magnetic, mechanical) into visible optical effects. This has made them very useful for certain display applications.

X-ray studies[34,35] indicate that some nematics possess a lamellar type of short-range order i.e.,they consists of clusters of molecules called cybotactic groups[36]- the molecular centres in each clusters arranged in layers. The cybotactic nematics may be either normal or skewed depending on the condition whether the molecules in the cybotactic group are arranged orthogonal to or tilted with respect to the layers. Those phases which are neither

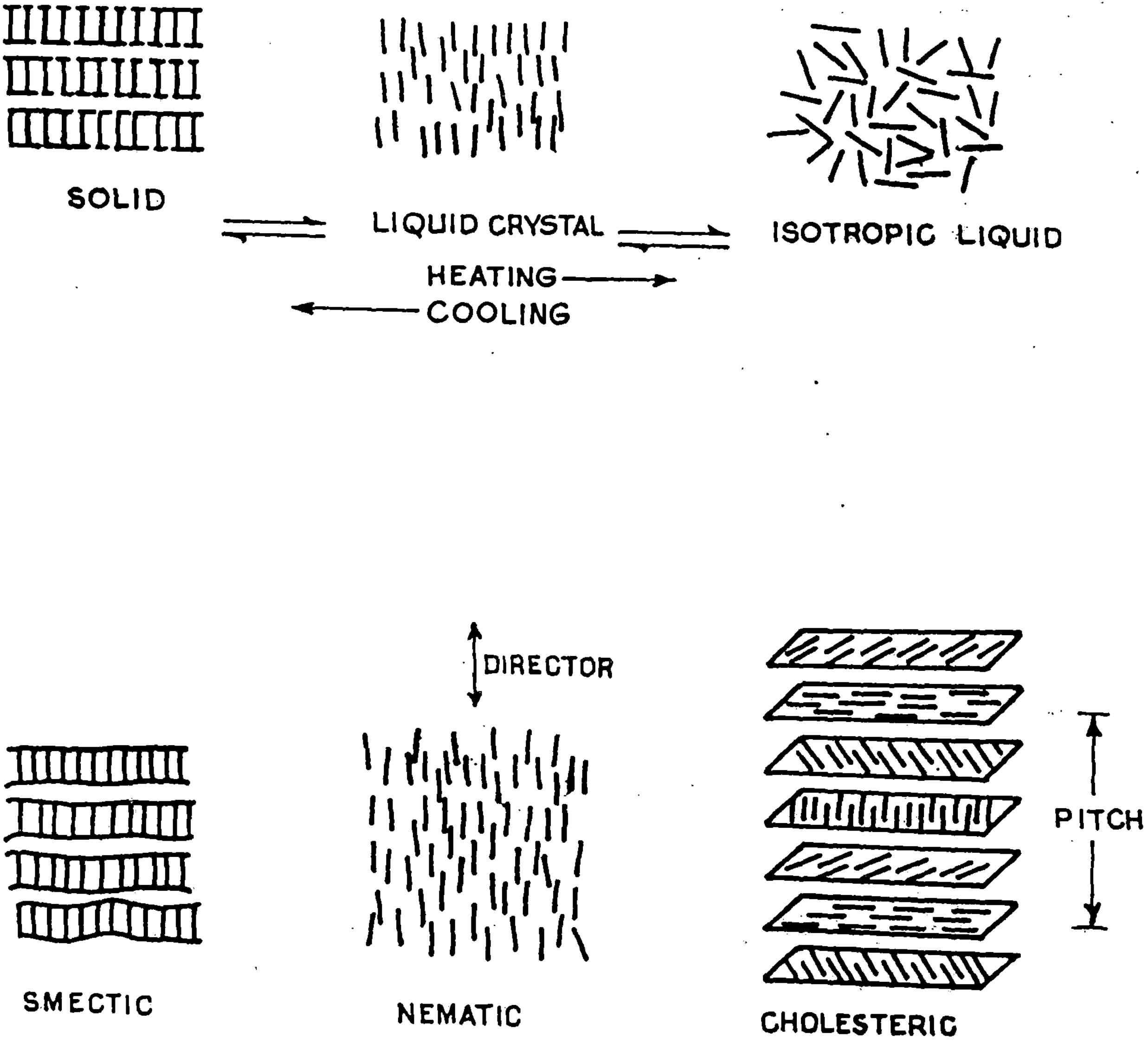


Figure 1.1 : Molecular arrangement in various type of liquid crystals.

distinctly cybotactic nor completly normal nematic, have been placed in a group known as intermediate nematic.

1.2b Cholesteric or chiral nematic phase

The cholesteric mesophase is also a nematic type of liquid crystal except that it is composed of optically active molecules. Indeed, it can be said that a nematic is simply a cholesteric with an infinite helical pitch. Cholesteric phase has an inherent chirality associated with them. This causes them to pack with a sense of helical twist imparted to the preferred direction of molecular alignment giving rise to a natural repeat or pitch in the structure[37-40] which is characteristic of the pure cholesteric material. Typical values of this natural pitch are in the range 0.2 to 1μm for pure material and many of them exhibit diffraction colours since they selectively reflect one sense of circularly polarised light. Due to this colour effect, cholesterics are used in liquid crystal thermometers. Cholesterics of low pitch less than about 0.5μm exhibit what are known as blue phases. These phases exist over a small temperature range (~1°C) between the liquid crystal phase and the isotropic liquid.

1.2c Smectic mesophase.

The smectic phase represents a higher state of order and have always layer structures. A variety of molecular arrangement is possible within each layer. Molecules may be upright in the layer or may be inclined with respect to the normals to the layers. Some of them have three dimensional long range positional order as in a crystal, while some others, referred to as hexatic phases, have three dimensional long-range "bond orientational" order, but without any long range positional order. The interlayer attractions are weaker than the lateral forces between the molecules and hence the layers can slide over one another thus showing fluid behaviour.

A large number of smectic polymorphs have been indentified[41-50]

S_A, S_B, S_C, S_D, S_E, S_F, S_G, S_H, S_I, S_J, S_K, S_L

The main features of the smectic are presented in table 1.1

TABLE - 1.1

Sm. Phase type	Molecular orientation	Molecular packing	Orientational ordering	Positional ordering	Optical activity
A	Orthogonal	random	short range	short range	uniaxial
C	Tilted	random	short range	short range	biaxial
$B_{\text{(hexatic)}}$	Orthogonal.	hexagonal	long range	short range	uniaxial
I	Tilt to apex of hexagon	pseudo-hexagonal	long range	short range	biaxial
F	Tilt to side of hexagon	pseudo-hexagonal	long range	short range	uniaxial
$L_{\text{(B crys)}}$	Orthogonal	hexagonal	long range	long range	uniaxial or biaxial
J (G')	Tilt to apex of hexagon	pseudo-hexagonal	long range	long range	biaxial
G	Tilt to side of hexagon	pseudo-hexagonal	long range	long range	biaxial
E	Orthogonal	Orthorhombic.	long range	long range	uniaxial or biaxial
K (H')	Tilted to side a	Monoclinic	long range	long range	biaxial
H	Tilted to side b	Monoclinic	long range	long range	biaxial

The compounds which have been studied by me have mainly nematic phases, except one which has got SmecticA phase over very small range of temperature.

SmecticA phase :

In the classical smecticA, the layer spacing (d) is approximately equal to molecular length (l). However, if the molecules have strong longitudinal dipole moment, there will be near neighbour antiparallel correlations and this can result in subtle changes[51,52] in the structure of smecticA. Recent works[53-59] have revealed that smecticA phase can be subdivided into several distinct phases such as monolayer smectic A_1, bilayer smectic A_2, partially bilayer smectic A_d, and smectic antiphase smectic A. Details regarding this polymorphism on smecticA are given in references[60-68].

1.3 NEW LIQUID CRYSTALLINE PHASES

1.3a. Discotic Phase.

Thermotropic mesomorphism has also been observed[69] in pure compounds consisting of simple disc like molecules and is termed as discotic liquid crystals. Structurally, most of them fall into two distinct categories, the columnar and the nematic. In columnar phase discs are stacked one on top of the other aperiodically to form liquid-like columns, the different columns constituing a two dimensional lattice. A number of variants of this structure have been identified : hexagonal, rectangular, tilted etc. The nematic phase has an orientationally ordered arrangement of the disc without any long range translational order. This phase is optically negative. A cholesteric phase has also been identified. In recent years significant amount of research have been performed with disc like molecules[70-74].

1.3b Re-entrant nematic and injected smectic phase.

Re-entrant nematic phase is a phenomenon first observed by Cladis[75-77] in a binary mixture of two strongly polar cyano-compounds. Over a range of composition, the sequence of transition on the mixture from the isotropic phase was as follows

$$\text{Iso} \longrightarrow \text{N} \longrightarrow \text{SmA} \longrightarrow \text{N}_R \longrightarrow \text{Solid}$$

where N stands for the usual nematic and N_R for a second nematic, called the re-entrant nematic phase, which appears at a lower temperature. In certain polar compounds this behaviour is readily induced either by the application of elevated pressure or by making appropriate binary mixtures[78]. Based on the molecular point of view, S. Chandrasekhar[79] has discussed qualitatively the re-entrant phenomenon.

One of the fascinating features of binary liquid crystal mixture is the formation of so-called injected (or induced) smectic phases from components which show only nematic phases in their pure states[80,81]. Induced smectic phases are often formed in binary mixtures of one compound having a strong terminal polar group and another compound having non-polar terminal group. Evidently, dipole-induced dipole interactions play a major part in this phase stabilization. A molecular model of the induced smectic phase has been discussed by de Jeu et al.[82]

1.3c Ferroelectric liquid crystal.

All smectic phases with tilted structure derived from chiral compounds exhibit ferroelectric properties.[83] The seven liquid crystal classes (C, I ,F, G, H, J, and K) are characterised by a tilt between the director and normal to the smectic layer. If additionaly the constituent molecules are optically active, these smectic phases are denoted by C^*, I^*, F^*, G^*, H^*, J^* and K^* and they show ferroelectric properties. By virtue of their symmetry, ferroelectric smectics are piezoelectric (polarization can be induced by mechanical shear). The study of ferroelectric liquid crystals have become important for their variety of application such as in display devices.

An anti-ferroelectric smectic phase has been identified recently.The structure is expected to have an interlayer herringbone arrangement.

1.3d Polymer liquid crystal.

Thermotropic liquid crystalline phases are also exhibited by some polymers and this is the subject of much recent research nowa -days. The polymeric liquid crystals usually reveal a wider range of mesophase than the corresponding monomeric ones. The polymers show a high thermal resistance and chemical stability. Biphenylcarboxylic esters of polysiloxanes constitute a large group of liquid crystal polymers.

1.4 APLLICATIONS :

Liquid crystals have got a wide range of scientific applications. Nematic and cholesteric liquid crystals have already found wide applications in display devices, as many of their physical properties such as birefringence , optical activity ect. 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 emission of light and so consume very low power.

Although liquid crystalline materials have been known for 100 years, large scale applications of 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 and soon became household items. The applications for liquid crystal displays are rapidly moving well beyond the early simple watches and calculators to a new level of sophistication, which is far more demanding and therefore is forcing rapid advances in the technology. Nowadays liquid crystals are used in optical computing, nonlinear optics, decorative and visual arts, spectroscopy , chromatography and others indicating that there is a relatively broad future potential for this technology.

Recently ferro-electric liquid crystals ($Sm\ C^*$) have been used for a new generation of fast versatile liquid crystal devices. Polymer dispersed liquid crystals[84] (PDLC) form a relatively new class of materials which are used in many types of displays, switchable windows and other light shutter devices.

1.5 OBJECTIVE AND SCOPE OF THIS WORK.

The subject of liquid crystals has grown enormousely to become a fascinating interdisciplinary field of study. A variety of new thermotropic phases have been discovered including over a dozen of different smectic modifications, discotic, biaxial nematics which have opened up new field of research for the condensed matter physicists. Technological advances are also spectacular. In view of these, study of the physical properties of some liquid crystals by different experimental techniques have been undertaken by me.

It is well known that stuctures of the rigid core of liquid crystal molecules strongly affect their physical properties. It has been found that the introduction of a double bond at specific side chain positions also markedly affect the material properties of liquid crystals. I have undertaken the study of six alkenyl liquid crystalline compounds which have nematic phase over a wide range of temperature. Order-parameter determination is very important from both theoretical and technical consideration, because efficiency of liquid crystal material in display devices depends on its order paranmeter values. By means of small-angle x-ray diffraction studies the compounds have been characterised, order parameters have been determined from aligned samples. Order parameters have also been determined by optical birefringence study.

The investigation of the crystal stucture of mesogenic compounds may provide clues for the formation and stability of liquid crystalline phases. If certain interactions or properties play an important role in the liquid crystalline as well as in the crystalline state, an investigation of the crystal structure may lead to a better understanding of the packing of molecules in the liquid crystalline phase. In view of this I have undertaken the study of crystal structure analysis of some nematogens and successfully solved two crystal structures by direct method.

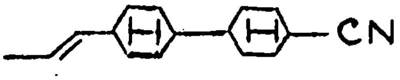
Experimental determination of dipole moments of polar liquid crystalline samples dissolved in non-polar p-xylene solution has been done by me. These experimental values are compared with the dipole moments calculated from atomic charge distribution.

STRUCTURE OF THE LIQUID CRYSTALS STUDIED.

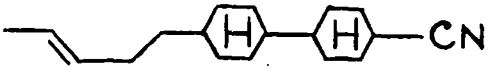
The liquid crystals studied in the present investigations were obtained from Hoffman - La Roche, Bassel , Switzerland as gift. These samples were used fresh from the package without further purification.

A list of the liquid crystals and their structural formula is given below :

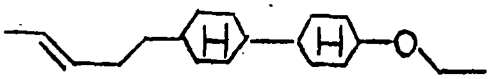
(1) $C_3H_5-C_6H_{10}-C_6H_{10}-CN$



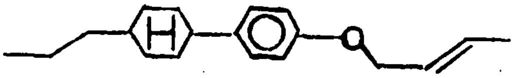
(2) $C_5H_9-C_6H_{10}-C_6H_{10}-CN$



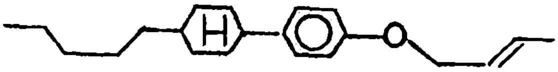
(3) $C_5H_9-C_6H_{10}-C_6H_{10}-OC_2H_5$



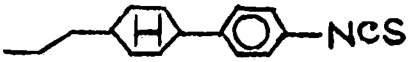
(4) $C_3H_7-C_6H_{10}-C_6H_6-OC_4H_7$



(5) $C_5H_{11}-C_6H_{10}-C_6H_6-OC_4H_7$



(6) $C_3H_7-C_6H_{10}-C_6H_6-NCS$



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