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CHAPTER I

GENERAL INTRODUCTION

Introduction

Certain long organic molecules can exist in phases intermediate between liquid and solid. These phases have some of the properties of a liquid, such as fluidity and inability to support a shear. They have also some properties of a crystal. Lehmann[1] named this phase as 'Liquid Crystals'. Friedel[2,3] suggested the term 'Mesomorphic State'.

Liquid crystals exhibit anisotropic properties as do solid crystals. The mesophase can be identified visually by its characteristic turbidity or by a polarising microscope by its optical birefringence.

Liquid crystals in general can be formed by two processes, by "solvent" effect (lyotropic mesomorphism) and by thermal processes (thermotropic mesomorphism). In this study we are only concerned with the latter, where compounds exhibit liquid crystal phases on heating from the solid.

The macroscopic anisotropy of liquid crystal is attributed to long range molecular orientational order with possible additional one or two dimensional positional order. In general, liquid crystal molecules are highly elongated with a fairly rigid long axis and thus have an energetic advantage in cooperative alignment, the position of benzene rings and polar groups on the molecule determines the range and type of the phase, by influencing the form of the intermolecular potential. The measurement of suitably defined order parameters related to orientational and positional molecular order, provides valuable information on the nature of the intermolecular forces responsible for phase transitions and other thermodynamic properties of liquid crystal.

Classification and Nomenclature

There are three basic type of thermotropic liquid crystals. Following the classification of Friedel^3 they are named as Smectic, Nematic and Cholesteric.

1. **Nematic:**

i) Nematic liquid crystals have no translational order (Fig. 1.A).

ii) The molecules have free rotational motions about their long axis, but they have orientational order,

iii) The molecules tend to align parallel to some direction, $\vec{n}$.

iv) The molecules are assumed either to lack, or the dipoles are equally distributed in opposite directions. Statistically speaking, this means that the states of $+\vec{n}$ and $-\vec{n}$ are indistinguishable.

v) The nematic liquid crystals are optically uniaxial.

vi) The lattice space groups is $C_{\infty v}$

vii) The molecules are either optically inactive or, if they are optically active, there is a (1:1) mixture of right and left handed species in the nematic crystal.

de Vries[4] found another type of nematic phase called cybotactic nematic in which molecules group themselves into isolated planar arrays.

2. Smectic Liquid Crystals

i) All smectic liquid crystals have a layered structure (Fig. 1.2). The centre of gravity of the elongated molecules are arranged in equidistant planes.

ii) The long axes of the molecules are parallel to a preferred direction $\vec{n}$ which may be normal to the planes or tilted by a certain angle.

iii) The arrangement of the centre of gravity within the planes may be at random or regular.

iv) The inter layer attractions are small in comparison to the lateral forces and the layers are able to slide over one another. There are several types of smectic phases, Smectic A is the one in which the director is perpendicular to the plane of the layers, while in smectic C phase the director is tilted with respect to normal to the plane of the layers. The classification and characterisation of smectic phases are mainly done by Hermann[5], Sackmann[6] and Demus, Annold[7].

The classifications were done by different workers by different methods, such as miscibility criterion, texture studies, X-ray datas. The smectic phases can be

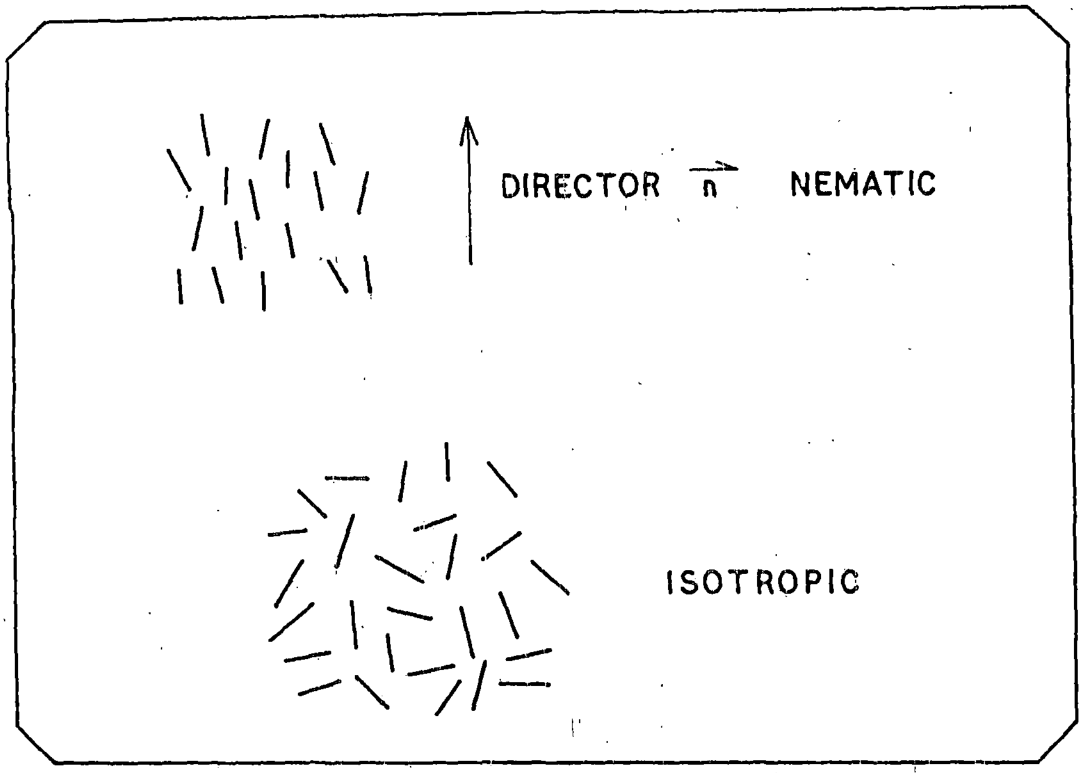


FIG. 1.1. SCHEMATIC REPRESENTATION OF MOLECULES IN NEMATIC AND ISOTROPIC STATES.

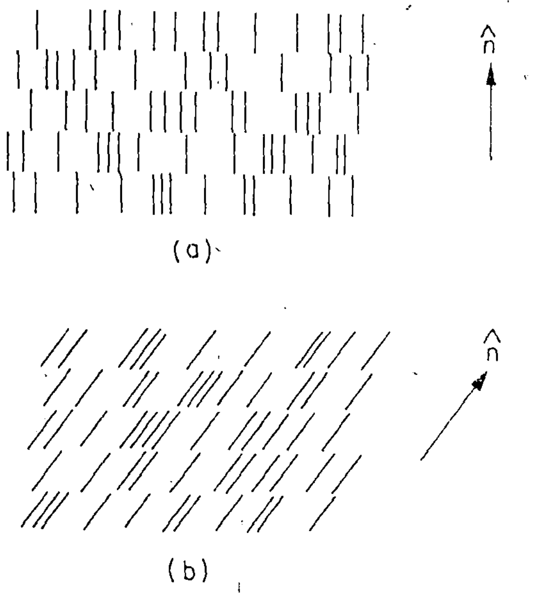


Fig 1.2. Schematic representation of two types of smectic order: (a) smectic A order; (b) smectic C order.

arranged sequentially as smect, A, D, C, B, E, F, G, H......, where lower temperature phases stand further to the right.

3. Cholesteric Structure

i) The structure is a two dimensional nematic (Fig. 1.3).

ii) There is no long range order in the centres of gravity.

iii) The molecules are aligned along a perferred axis $\vec{n}$.

iv) $\vec{n}$ is not a constant in space and has a helical symmetry.

v) The pitch of the helix is temperature and concentration dependent.

Another type of liquid crystals was discovered by S.Chandrasekhar and Co-workers[8] a few years ago, called columner phase or canonic phase, where the flat disc like molecules are stacked in columns and so the plane of the molecules are perpendicular to the direction contrary to the former types where the molecules are parallel to the directors[9], (Fig. 1.4).

If a substance has both the phases, smectic and nematic, then on heating the crystalline solid phase melts into a smectic phase which subsequently transforms to the nematic isotropic phases.

$$C \rightleftharpoons S \rightleftharpoons N \rightleftharpoons I$$

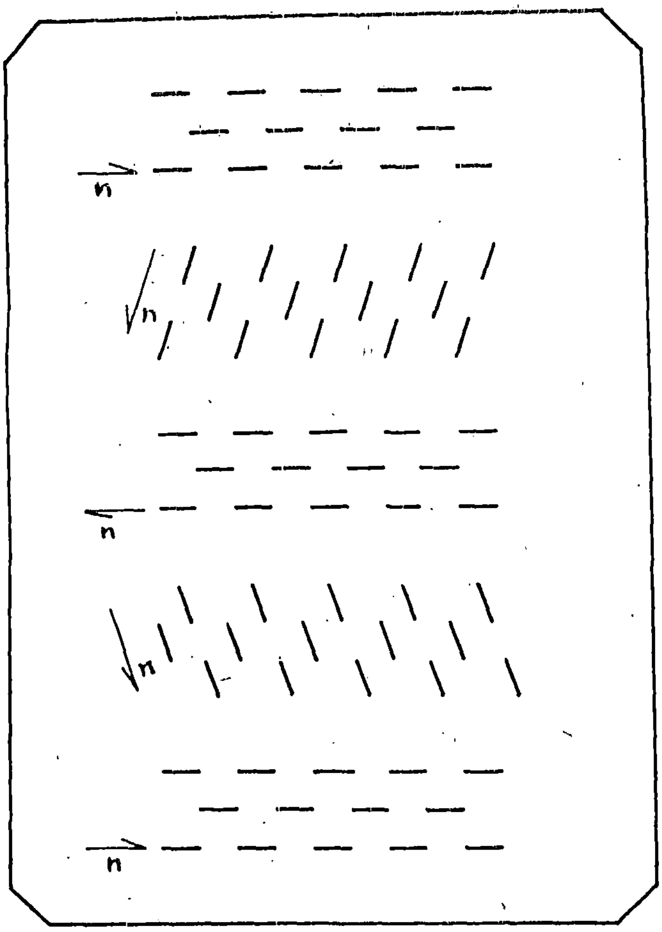


FIG. 1.3. SCHEMATIC REPRESENTATION OF CHOLESTERIC STRUCTURE.

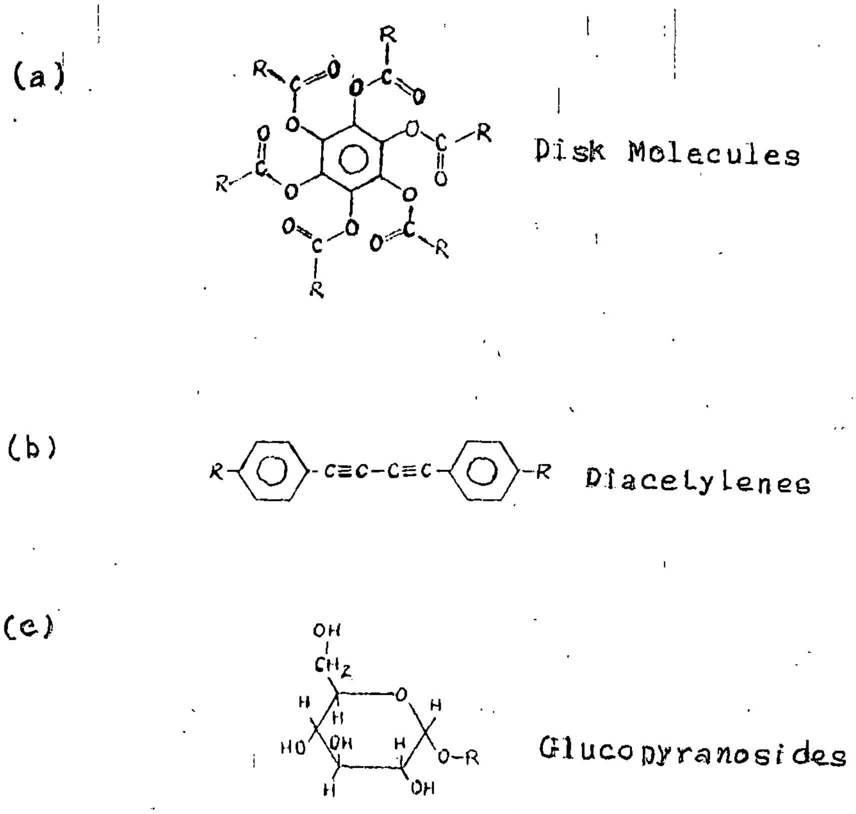
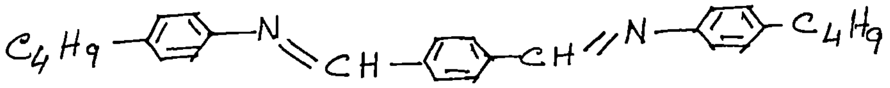


Fig. 1.4. New Liquid Crystals

For example, terepthal-bis-(-p-butyl aniline) TBBA which has the chemical structure[10]



has the phases and transition temperature (°C) as given below:

$$C \underset{113^\circ C}{\rightleftharpoons} S_B \underset{144^\circ C}{\rightleftharpoons} S_C \underset{172^\circ C}{\rightleftharpoons} S_A \underset{200^\circ C}{\rightleftharpoons} N \underset{236^\circ C}{\rightleftharpoons} I$$

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

$$C \rightleftharpoons S_n \rightleftharpoons I$$

With cholesterics and smectics, it has been observed experimentally that

(i) $S \longrightarrow Ch \longrightarrow I$

(ii) $S \longrightarrow$ Smectic A $\longrightarrow Ch \longrightarrow I$

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

Cladis[11] found in binary mixtures of some mesogenic cyano compounds, that they followed on cooling the scheme:- isotropic $\longrightarrow$ nematic $\longrightarrow$ smectic A nematic. The low temperature nematic, below the smectic phase, is called the re-entrant nematic phase. This phenomenon has also been observed by Cladis et al at elevated pressure[12,13] and by others at atmospheric pressure[14-16] in pure compounds.

Molecular Structure:-

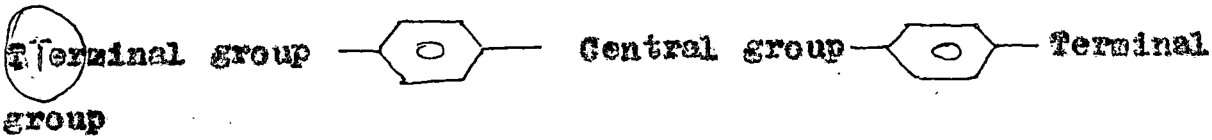
Molecules showing mesomorphism possesses the following structure -

(i) The molecules are geometrically anisotropic, they are either rod-shaped, flat or lath shaped.

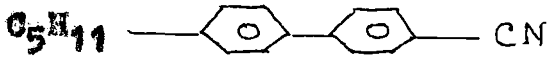
(ii) The molecules have some rigidity along the long axes so that parallel orientation may not be broken. The molecules should possess strong dipolar (Permanent or induced) and easily polarisable groups. The forces responsible for the mesophases are primarily dipole-dipole interactions and dispersive forces.

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.

Most of the thermotropic mesogens can be represented by

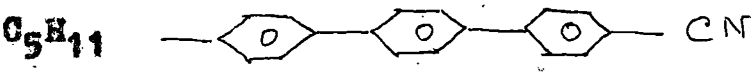


The terminal groups may be same or different. The central core is usually attached to the para positions of the benzene ring. These are easily polarisable and planqr. The aromatic rings may also be connected directly[17] as in p-cyano-p'-pentyl biphenyl.



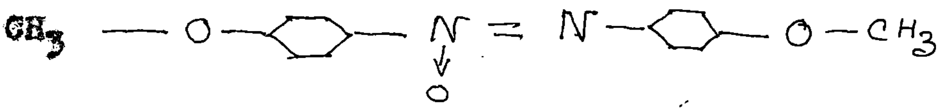
$$C \xrightarrow{22.5^\circ C} N \xrightarrow{35^\circ C} I$$

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



$$C \xrightarrow{130^\circ C} N \xrightarrow{239^\circ C} I$$

Often the central group certain multiple bonds to maintain rigidity and linearity as in P-azoxyanisole (PAA)



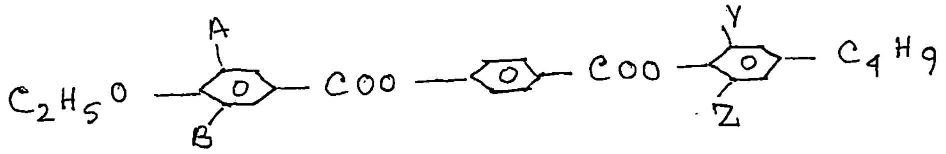
By studying the homologous series Gray[18,19] observed that certain general types of curves relating the transition temperatures to the number of carbon atoms in the series might be obtained and this could be used to correlate all the members of the series. He found – (i) The different phase transition temperatures (N — I, S — I, S — N) give smooth curve though the melting point do not show any uniformity. (ii) The clearing points of nematic phase decreases with increasing chain length. (iii) The N-I temperatures fit in two curves one for even and other for odd number of carbon atoms in n-alkyl chain, giving rise to the so-called 'Odd-even' effect. The N - I temperature decreases with a distinct alternation and the amplitude of the alternation also reduces with increasing chain length.

(iv) The plot of clearing points of smectics and the S - N transition temperatures usually reaches a maximum of a moderate chain-length and decreases gradually with further elongation of the chain. This plot normally shows no distinct odd-even effect[21].

(v) In a homologous series, shorter chains exhibit purely or predominantly nematic phases, while smectic phases dominate in longer chain molecules, at the expense of nematic thermal stability[18-21].

The effect of broadening 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[18].

The broadening reduces the anisotropic polarisability and consequently the intermolecular attractions. Young and his co-worker[22] studied the following compounds -



and found a systematic decrease in N —— I temperatures as the number of CH_3 group inserted at positions A, B or Y, Z was increased.

Theories of Nematic Liquid Crystals

In a macroscopic volume of a nematic liquid crystal, the preferential direction n is in general not uniform, but changes from place to place under the action of disturbing forces such as convection, flow, wall x effects, etc. However, even large samples can be aligned by both magnetic and electric fields.

In a homogeneously ordered liquid crystal sample the long axes of the molecules are parallel to the preferred direction. This holds only in a time or space average. In reality, due to their thermal energy, the individual molecules or small groups of molecules tumble about the preferred direction. The efficiency of the molecular orientation along $\vec{n}$ can be described by a single order parameter $\langle P_2 \rangle$

$$\langle P_2 \rangle = \frac{1}{2}\langle 3\cos^2\theta - 1 \rangle$$

where the brackets mean the time or space average and θ is the angle between the long molecular axis and the preferred direction. This ideal nematic order will be possible near the absolute zero point of the temperature only if material would not freeze. For an isotropic liquids $\langle P_2 \rangle = 0$.

The order parameter $\langle P_2 \rangle$ can be determined by measuring the principal refractive indices or the diamagnetic susceptibilities or X-ray diffraction. Other methods use the ultraviolet or infrared dichroism or nuclear magnetic resonance spectra.

Molecular Statistical Theory.

Maier and Saupe[23-25] 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

$$U = -\frac{A}{V^2} \langle P_2 \cos\theta \rangle P_2 (\cos\theta)$$

where V is the molar volume, and A is a constant characteristic of the molecule, related to its polarizability.

The derivation is based on the model that the molecule alignment is caused by dispersion forces.

Only the induced dipole-dipole contribution is considered. The anisotropy of the molecular polarizability causes an angular dependence of the intermolecular dispersion forces and therefore is responsible for mesomorphic phase.

Humphries[26] have, however, shown that the assumption of the anisotropic dispersion forces for the formation of nematic phase was not essential. Thus a single molecule potential (mean field) can be set up to give particular 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

$$- P_2(\cos\theta) = -(3\cos^2\theta - 1)/2 \qquad \ldots(2)$$

(ii) U must be proportional to $\langle P_2\rangle$ the average degree of orientation. This potential which is responsible for nematic phase formation should vanish when $\langle P_2\rangle = 0$ and be minimum when the molecules are highly ordered. Thus

$$U(\cos\theta) = -\vartheta\langle P_2\rangle \cos\theta\rangle\theta\} \, P_2(\cos\theta) \qquad \ldots(3)$$

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 $\vec{n}$.

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

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

$$Z = \int_0^1 \exp[-\beta U(\cos\theta)]\, d(\cos\theta) \qquad \ldots(4)$$

where Z is the single molecule partition function $\beta = \frac{1}{KT}$, K is the Boltzmann's constant. T is the temperature in absolute unit. The limit of integration has been restricted within 0 and 1 because $\vec{n}$ and $-\vec{n}$ are indistinguishable. The dependence of the order parameter $\langle P_2 \rangle$ on the temperature T can be found by solving the self-consistency equation

$$\langle P_2 \rangle = \int_0^1 P_2(\cos\theta)\, f(\cos\theta)\, d(\cos\theta) \qquad \ldots(5)$$

using equation (4) in equation (5)

$$\langle P_2 \rangle = \frac{\int_0^1 P_2(\cos\theta) \exp[\beta \vartheta P_2(\cos\theta) \langle P_2 \rangle]\, d(\cos\theta)}{\int_0^1 \exp[\beta \vartheta P_2(\cos\theta) \langle P_2 \rangle]\, d(\cos\theta)} \qquad \ldots(6)$$

A computer programs has been used to obtain the value or values of $\langle P_2 \rangle$ (for any particular T (or β) that satisfies equation (6). $\langle P_2 \rangle = 0$ is a solution at all T, below certain temperature determined by $KT/\vartheta = 0.22284$, two other solutions appear. Of the three solutions below the critical temperature the one which satisfies the thermodynamic condition of minimum free energy will give the stable phase.

<u>Extension of the Maier-Saupe Theory.</u>

Humphries, James and Luckhurst[26] developed a more comprehensive concept by including higher order terms in the mean field potential for cylindrically symmetric molecules.

Their result is

$$U_1(\cos\theta) = \sum_L \upsilon_L \langle P_L \rangle (\cos\theta) \qquad \ldots(7)$$

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

$$\langle P_L \rangle = \int_0^1 P_L(\cos\theta)\, P_1(\cos\theta)\, d(\cos\theta) \qquad \ldots(8)$$

where $P_1(\cos\theta)$ is the orientational distribution function and P_L's are the Lth. order terms of the Legendre Polynomial (L takes only even values). It has been the terms with L = 0 in (7) may be dropped since it is merely an additive constant. Then

$$U_1(\cos\theta) = \upsilon_2 \langle P_2 \rangle P_2(\cos\theta) + \upsilon_4 \langle P_4 \rangle P_4(\cos\theta) \qquad \ldots(9)$$

retention of only first term of equation (9) gives the Maier-Saupe theory.

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[27] in the nearly 1930's. Upto 1974 only seven crystal structures had been determined[28]. This situation changed drastically with the advent of computer program in the late 1970s'. Now a large number of structures have been determined, most of them being nematic.

Preliminary survey of the present knowledge regarding solid mesophase relationships was given by Bryan[29]. On the basis of the evidence at hand it can be stated -

i) The molecules of the organic crystals when heated to the liquid crystalline state adopt an arrangement somewhat similar to that in the crystals[27].

ii) In nematic crystals the long narrow molecules are found to be more of less parallel and interleave one another to form an 'imbricated packing' (described by Bernal and Crowfock). 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[30].

iii) For smectic compounds the molecules are found to be packed in parallel array, as predicted[31].

This is true at least the majority of cases, so far known but at this stage we must be cautious to generalise it[31]. Brown[32] found an imbricated packing for a nematogenic compound with the non-planner molecules arranged in herringbone fashion in planes perpendiculer to the long axis. Brown and his co-workers[33] also found a herringbonic compound with a tilt relative to the layers. Bryan, Focier and Miller[34-36] also discussed the role of hydrogen bond in the formation of mesogenic compounds.

Applications:

Considerable basic research on the optical and electrical characteristics of liquid crystal was carried out during the later half of the this century to develop the applications of liquid crystals. It has been found that liquid crystals have got a wide range of scientific application.

The sharp changes in the color of x cholesteric liquid crystals with small changes in temperature have resulted in a number of unique temperature sensing applications[37]. As a result, applications to medical diagnostics, electronic component testing and aerodynamic structure analysis became feasible.

Nematic and cholesteric liquid crystals have already is found wide application 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. Liquid crystals are used in displays for watches, clocks, calculators, panel meters and other digital displays.

The x extremely low power requirements of the display coupled with further improvements in complimentary symmetry metal oxide semiconductor integrated circuits has made possible the development of pocket computer.

Liquid crystal displays are gaining acceptance in the digital instrument field, replacing light-emitting displays in applications where portability is of prime interest.

Liquid crystals are used in the flat pannel television displays. The progress of electronics, especially semiconductor electronics directs microtechnology which requires low voltage and low current devices. In this point of view LCD is most promising among various devices.

Recently, ferroelectric liquid crystals (S_c^*) have been used for a new generation of fast versatile liquid crystal devices.

Scope and Aim of the Work

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 f present work six liquid crystalline substances namely PCCPP, PCTP, PBBA, EBBA, BPCPP and 5OCB have been chosen.

From X-ray diffraction photographs of magnetically aligned samples PCCPP, PCTP, PBBA and EBBA, orientational distribution function f(β), order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$, have been calculated. X-ray diffraction studies in liquid crystalline phases of the samples BPCPP and 5OCB were done earlier in our laboratory. In the present work, optical birefringence studies of the samples PCCPP, PCTP, PBBA, BPCPP and 5OCB are done. The crystal and molecular structure of the sample PCCPP have been determined from X-ray diffraction. All the experimental works are reported in Chapter III and IV.

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