CHAPTER 1

INTRODUCTION TO LIQUID CRYSTALS.
Certain materials show not a single transition but rather a cascade of transitions on going from solid to liquid phase. These new phases are found to possess mechanical and symmetrical properties intermediate between those of a liquid and those of a crystal. Although the existence of liquid crystals have been known for comparatively a long time, the meteoric rise in interest recently, has occurred for several reasons. Liquid crystals have revolutionised the display industry. The liquid crystalline state is ubiquitous in biologically active system including the human anatomy. Also the physical behavior of liquid crystals turns out to be remarkably subtle. Lehmann was the first to suggest the name 'liquid crystals' to identify these new states of matter or mesomorphic phases.

A crystal is a three dimensional periodic array of atoms or group of atoms. The centres of gravity of the various groups are arranged on a lattice. On the other hand the molecules in an isotropic liquid has no positional and orientational order. The liquid state of matter differs most obviously from the solid state by the property of fluidity.

Mesophases lack the perfect order of crystalline state, but are more ordered than a liquid phase. Liquid crystals are partially ordered, showing X-ray diffraction pattern from Bragg reflection, but are assumed to be liquid in the sense that a shear stress is not opposed by permanent forces.
Several books and review articles on liquid crystals have been published by eminent authors. The names of a few are included in the references.

II Types of Liquid Crystals and their molecular arrangements:

Liquid crystals can be classified somewhat loosely into two types, thermotropic and lyotropic. Those which can be formed by thermal effects, that is by heating a solid or by cooling a liquid phase are termed as thermotropic. Lyotropic liquid crystals are usually obtained by dispersing a compound with another compound, one of which is solvent say water. Being biologically important, these lyotropic liquid crystals possess in their molecular structure an ionic group that is water soluble, and an organic part that is insoluble in water.

Amphiphilic compounds are those which behave as lyotropic while non-amphiphilic compounds are thermotropic, in nature.

The kind of molecules which form thermotropic liquid crystals generally have a common geometry. These organic molecules will be elongated and possess a fairly rigid core structure. The general formula for these compounds is as follows:

```
Terminal group -- O-- Linkage group -- O-- Terminal group
```
Polymorphism in thermotropic Liquid Crystals.

Thermotropic liquid crystals are usually divided into three classes; nematic, cholesteric and smectic.

1. Nematics.

In the nematic phase the centres of gravity of molecules have no long range order. However the long axis of the molecule tends to align in a particular direction, \( \langle n \rangle \) (Fig 1). So we have a statistically parallel orientation of the long axis of the molecule along the director. This ensures that all macroscopic tensor properties of the phase display one set of values along the unique axis and another set is exhibited at all directions perpendicular to it. Hence optically a nematic is a uniaxial medium showing positive birefringence with the optical axis along \( \langle n \rangle \). This phase has a cylindrical symmetry about \( n \). Except for the ferroelectric 22 crystals, the states of the director \( \langle n \rangle \) and \( \langle -n \rangle \) are thought to be indistinguishable.

The director is the most probable and the most populated direction of the molecule. At finite temperatures however the thermal motion of the molecules prevents perfect alignment.

The word nematic comes from a Greek word "Nema" meaning "thread" as a thin film of nematic liquid crystal show thread like pattern, called the "Schliern texture"
FIG 1: SCHEMATIC REPRESENTATION OF TWO TYPES OF SMECTIC ORDER (a) SMECTIC A ORDER AND (b) SMECTIC C ORDER
when observed under microscope (Plate 1). These patterns are due to the stable defects that characterise the phases.

Two different theories of liquid crystalline structures have been proposed by various researchers. The Swarm theory assumes that the interior of a nematic liquid crystal in the absence of any external forces other than the orienting surfaces is composed of clusters of molecules with definite boundaries. A cluster or 'swarm' contains $10^4$ to $10^6$ molecules arranged approximately parallel so that a unique axis is determined for the swarm.

The continuum theory suggests that the orientation direction of the liquid crystals can vary slowly from point to point (except at singularities), and is determined by orienting influence of the container walls and external forces and fields.

Different nematic texture other than the classical nematic phase has been presented by de Vries. He proposed that in skewed cybotactic phase the molecules are arranged in groups in such a way that the centres of molecules in each group lie in a phase making an angle significantly different from 90 degree with the mean direction of the long axis of the molecules in that group. Another texture
which de Vries identifies as the normal cybotactic phase is similar to these skewed one but with close to 90 degrees.

Because of thermal motion the molecules in a nematic phase are not all exactly parallel but the extent of parallelism is measured by the order parameter \( S \). Nematic liquids are easily oriented by a magnetic field with the optical axis becoming parallel to the field axis. It can also be oriented by surface treatment.

2. **Cholesterics.**

Molecules in the cholesteric state essentially lies in planes of a few angstrom thick. Very many such planes stack upon one another to form a several thousand angstrom thick layer. The direction of the long axis of a molecule in a given phase is slightly and systematically rotated from the direction of the axis of the molecules in the adjacent planes (Fig. 1).

The result is a helical structure which shows great optical activity because the layer distance of several angstroms corresponds to the optical wavelength.

A nematic phase is converted into a chlorellastic phase by the addition of a small amount of optically active (Chiral) material. Again two chlorellastics of opposite helical senses give a nematic mesophase at some finite composition. Hence the chlorellastic phase may be
regarded as twisted nematic phase.

Locally a cholesteric is very similar to a nematic material, there being no long range order of the centres of gravity of the molecules. The order parameter in the cholesteric phase is assumed to be the same as in the nematics.

The ideal spiral arrangement in cholestrics is easily distorted and focal conic texture is obtained when viewed under a microscope between two parallel glass plates (plate 2). Grandjean structure is observed when the cholestric liquid is confined in a wedge shaped space. Grandjean planes are actually singular lines. It is assumed that the undistorted helix structure is realized only in region where the gap width is an integral multiple of the half pitch.


In smectic liquid crystals the molecules are arranged in layers with their long axis approximately normal to the plane of the layers. The molecules can move in two directions in their own plane and can rotate about one axis. The molecules within a layer may be regularly spaced as in a crystal or may be randomly distributed. The planes can slide easily over one another.

The smectic textures always occur as expected from their higher order at lower temperatures than the nematic
and cholesteric liquids. If a substance shows both nematic and smectic states, then the for the gradual decrease in temperature the following phases are obtained:—

Isotropic Liquid $\rightarrow$ Nematic $\rightarrow$ Smectic $\rightarrow$ solid crystal.

Several possible structural modifications in the smectic phase have been discussed by various workers including Sackmann and Demus, Saupe, Fergason et al. Smectic polymorphism can be identified using the polarising microscope, thermal analysis, miscibility studies and X-ray investigations. Sackmann and Demus studied in detail and reported various smectic phases from smectic A to smectic H. They are identified by miscibility studies. However de Varies has classified the smectics into three main classes as and on the basis of X-ray studies.

III Physical investigations with liquid crystals.

1. Thermodynamic measurements.

Barrel, Porter and Johnson, and various other workers have used the differential scanning calorimetry and differential thermal analysis method for calorimetric measurements. From the adiabatic calorimetry studies Arnold has determined the heat capacities and latent heats. It has been found that the entropy changes of nematic - isotropic and
Cholesteric - isotropic transitions are of the same order of magnitude. This is in agreement with the interpretation regarding the similarity of these phases. In compounds of a homologous series a progressive alteration in the clearing point temperature has been found with increasing chain length. Maier and Saupe has described this odd-even regularity due to the dipole - dipole dispersion forces.

The heat capacity curves for liquid crystal components exhibiting several mesomorphic phases has been determined and compared with the heat capacity data from the statistical theory of Maier and Saupe.

Phase characterization, enthalpies and entropies of transition of some substituted benzyamines has been estimated and a relationship between these parameters and molecular weight was found by Palacios. Navard and Cox has studied the Smectic A Nematic transition from the measurement of the height of the DSC transition peak. They have found that the SA-N transition for octyle cyanobiphenyl was second order but for nonyl cyanophenyl it was first order. Takahash measured the temperature dependance of specific volumes for N-(4-n-pentyloxybenzilidene)-4-n-alkylaniline, 50, n (from n=4 to 14). They found that
the compounds with odd numbered carbons in the alkyl chain exhibit larger volume changes than those with the even numbered carbons at the I-N transition whereas at the N-S transition an opposite alternation is found. A Chandra and Jaiswal studied the phase transition behaviour of highly purified cholesteryl acetate by DTA and thermal optical microscopy. They found that the appearance of the cholesteric phase depends on both the time period and the temperature at which annealing is performed. They have detected a new solid phase S and its formation is linked with nucleation rate.

A fast new didatometric method for locating phase transitions in liquid crystals has been listed by Domenico.

2. Infrared Raman Spectra and Fluorescent Measurement with Liquid Crystals.

Polarized infrared radiation interacts with a molecular vibrational transition moment according to the expression $(\mathbf{M \cdot E})$. If the transition moment $\mathbf{M}$ is perpendicular to the field vector $\mathbf{E}$, no light is absorbed. Using polarized infrared radiation Maier and Englert have studied the degree of orientation in nematic liquid crystals oriented by surface forces. Neff Gulrich and Brown have studied the orientation in
a d.c. electric field by infrared dichroic methods. Bhide et al have observed the Raman Spectra for different phases of TBBA.

Photo Kinematical approach has been utilised for investigation of solid – smectic – isotropic phase transition in some P-P', di substituted biphenyl molecules by Maiti. Davies has studied the liquid crystalline polymorphism from Raman Spectroscopy.

The Raman Spectrum of 4 - n - butyloxy benzoic acid has been studied in a longitudinal and transverse magnetic field by Koller, Lorenzen, and Schwab. They found that certain vibrations become active in a magnetic field and that the activity depends on the orientation of the vibrational polarizability tensor with respect to the electric vector of the scattered light. Percheve found the S2 and S4 order parameter of some liquid crystals through fluorescent measurements. With polarized fluorescence of dyes oriented in room temperature nematic liquid crystals Baur et al found the order parameters. Fluorescence spectra of 3 COB S4 and 8 COB in solution have been studied by David.


A large fraction of research work is being conducted in this field as the magnetic resonance studies give information on the process at the
molecular level.

a. **Nuclear Magnetic Resonance.**

Spence and his coworkers were the first to observe the NMR, spectrum of PAA in the nematic phase and they interpreted the spectrum in terms of order resulting from parallel orientation.

Lippmann, and Weber found that the spectrum in the liquid crystal phase depends upon the degree of molecular order and the configuration of the molecule which comprised this state of matter. On conducting NMR studies of solutes in nematic liquid crystals Englert recognized that highly resolved spectrum of a solute molecule can be observed on top of the broad unresolved spectrum of liquid crystal solvent. Plenty of information could be obtained about the ordered solute molecule including the precise relative bond lengths and angles, signs of spin spin coupling constants and anisotropic chemical shifts.

NMR spectra has been used to measure the order \( \langle P^2 \rangle \) in thermotropic systems and of ordered solutes. Shashidhara has obtained the orientational order parameter \( S \) for a nematic liquid crystal 4-4'-bis (pentyloxy) azoxy benzene
from wideline N M R spectra using the doublet splitting arising from dipole dipole interaction of the adjacent rings protons. By deuton magnetic resonance technique Bos et al have measured the order parameter $S_{zz}$ and $(S_{xx} - S_{yy})$ and their temperature dependance in nematic and smectic C phases of $P^-\text{-}(\text{Heptyloxy})\text{-azoxybenzene (HOAB)}$.

Pretransitional phenomena in the isotropic phase of a liquid crystal have been observed by N M R spectroscopy in presence of an electric field. Rai et al have reported spin probe in isotropic, nematic and smectic A phases of NPOOB. They have studied the angular variation of the spectra in smectic A phase and determined the order parameter S, the rotation correlation time $T_\text{R}$ and the anisotropic diffusion parameter ($\langle N \rangle$) at different temperatures.

b. **Electron Paramagnetic Resonance.**

Luckhurst has used EPR to distinguish between the swarm and continuum theories of nematic liquid crystal. He found that the two models are identical E.P.R measurements being more sensitive than N M R, requires less solute also it is effective in the study of viscous liquid crystals.
c. **Mossbauer Effects.**

Uhrich et al observed the Mossbauer effect from the quadrupole split Fe Spectrum of 1, 1'-diacetylferrocenes dissolved in 4, 4'-di-heptyloxyazoxy benzene in the S texture. The structure of the smectic phase can be studied by measurements of recoil free fraction. Also Mossbauer studies can be made of ordered molecules which do not form single crystal in the solid state.

4. **X-ray and neutron Scattering Measurement.**

The first X-ray study of liquid crystal were performed long back in 1913 by Van lingen. Laue and Debye Scherrer patterns of liquid crystalline textures can be analyzed to establish information on the intermolecular arrangements, strata packing of this structural facts. X-ray techniques have a very practical use in relation to the classification and the degree of ordering in smectic phases. For these experiments the sample has to be in monodomain. Bryan et al studied the crystal structure of P-N-alkoxy benzoic acids and P-N-alkoxy cinnamic acids with X-ray measurements. Goodbey et al by using free standing liquid crystal film technique found that the non crystalline B phase has short range, in plane position.
at correlations but long range, three dimensional, six fold bond orientational order. The structural phase transition of MBBA and DOBAMBC have been studied by 69 energy dispersion X-ray diffraction.

5. **Ultrasonic Investigations.**

The measurement of the absorption and velocity of the ultrasonic longitudinal sound waves in several liquid crystals near the phase transition has been carried out by several researchers. They have found that the absorption passes through a maximum at the isotropic - liquid crystal transition. Also the velocity changes discontinuously at the transition passing through a minimum at that point. Edmonds and 70 Orr have applied the theory of Maier and Saupe to explain the absorption in the nematic phase near the isotropic transition, based on the theories used for absorption near the critical point in rare gases. A review of the work done in ultrasonic investigations is given in the chapter four.

6. **Optical Properties.**

a. **Birefringence.**

Microscopic observation of nematic liquid crystals between crossed polarizers show that it behaves optically like uniaxial crystals and show 71 positive birefringence Chatelain has contributed
much to the knowledge concerning the refractivity and light scattering properties of the nematic phase. At the nematic isotropic transition temperature a discontinuity in the refractive index is observed.

Measurements of infrared birefringence of some liquid crystal mixtures are reported by Shin Tson et al. Saupe was the first to measure the birefringence of liquid crystals by conoscopic method. A nematic slab with planar alignment placed between crossed polarizers such that the polarizer and analyser are at 45 degrees to the preferred direction of alignment shows a typical interference pattern.

b. **Optical rotation and scattering.**

Linearly polarized light when transmitted perpendicular to the molecular layer is found to have direction of its electrical vector rotated progressively along a helical path. The light scattering effect in liquid crystals is reported by Porter. Chandrasekhar et al have measured the optical rotatory power of liquid crystals by interferometric method. Sackmann has studied the effect of electric field induced orientation of liquid crystals and their optical absorption. The
study of the circular vibration propagation in cholesteric liquid crystals has been carried out by Chaletain, Heilmer, and Derick has used the dynamic scattering mode in a nematic liquid crystal in order to determine the performance of nematic liquid crystal displays.

7. Viscosity
Viscosity measurements in a nematic liquid crystal showed that the quantity is anisotropic, which is expected from the very nature of the liquid crystals. A review work on the rheological data available for mesomorphic states is given by Porter.

The distortion of a nematic slab in a magnetic field first observed by Freedricksz has found application in liquid crystals display devices. The transition is essentially due to the magnetic alignment of the bulk sample directors at sufficiently high field strength. A homeotropic cell containing an insulating nematic slab is uniaxial in the undistorted state and becomes birefringent above the threshold voltage. This electrically controllable birefringence is interesting for device applications and has been studied by several workers. The electric field induced cholesteric to nematic phase transition was observed by Wysocki et al.
IV. Application of liquid crystals.

Liquid crystals are found to exhibit different optical properties such as reflection, birefringence, circular dichroism, optical rotation and colour. All these properties being very sensitive to the change in the environment such as temperature, pressure, electric or magnetic field or chemical vapours are exploited to practical advantage.

The colour sensitivity of cholesteric liquid crystals is used to measure the temperature. In the liquid phase these materials are colourless but on cooling gradually they go through a range of colours in the mesophase. With the cholesteric sample, a detector that displays colour as a function of microwave intensity has been developed. The cholesteric structure might soon be used for the detection of infrared radiation. The cholesteric materials are also used in the electronic industries as non destructive testing tools. The use of cholesteric liquid crystals for thermal mapping of the surfaces of aircraft models in wind tunnel tests has been explored. The quantity of bonding the laminates (those used in aircraft structures) can be established by applying a film of cholesteric liquid crystal to one side of the laminate and observing the pattern of heat flow to the other surface.

Liquid crystals are currently being employed for wrist watch faces, disposable thermometers, tumor detection,
digital readout for many instruments and microcomputers, optical filters, solvents for N M R, E S R, infrared and ultraviolet spectroscopy, and for many toys and decorative purposes. They are also used in thin screen television display. As these systems require a very low voltage and power they are desirable for use in integrated circuits and complex addressing schemes.

Liquid crystals may be used as stationary phases in vapour phase chromatography for improved separation of certain isomers and of substance from a multi component system. Thermodynamic data such as heats of solution and activity coefficients of solutes in liquid crystals using the chromatographic technique can be readily determined. On obtaining these thermodynamic data on solutes in liquid crystalline phases good separations of position isomers – e.g xylenes cis-trans isomers and may be optical isomers can be developed.

Smectics shows potential for use as storage media. New uses for liquid crystals are rapidly emerging in different areas of applications.
REFERENCES

1. Reinitzer, F. Montsh, 9, 421 (1888).


23 Bose, E., Physik Z., 8, 513 (1907), 10, 230 (1909).
24 Ornstein, L.S., Z., Kristallogi., 79, 10 (1931).
31 Grandjian, F., Compt. Rend., 172, 71 (1921).
                                      Pramane supplement 1, 93, (1975).
46 Maier, W and Englert, G., Z Electro Chem. 64, 689 (1960).
64 Luckhurst, G.R. Mol. Crystl. 2, 363, (1964)
81 Friedericksz V. and Repiewa A, Z., Physk 42, 532 (1927).