INTRODUCTION

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1.a. General

With almost a century old history behind it, the field of the fourth state of existence of matter, commonly known as the "mesomorphic state" is very well known to scientists and technologists because of its versatile technological as well as commercial applications. Interest in this field springs not only because of their unusual physical and optical properties, but also due to recent development of a number of instrumental techniques such as nuclear magnetic resonance, electron paramagnetic resonance and differential scanning calorimetry enabling scientists to establish beyond any doubt the incredible fourth state of existence.

It is a matter of common experience that liquids and crystals are quite different forms of matter, having nothing in common. A crystal, on one hand, is a rigid state of matter consisting of regularly spaced particles in a three dimensional matrix. These particles move but only within the region of their sites in the crystal lattice. A liquid, on the other hand, is known as a free flowing substance that takes the shape of its container. Particles in a liquid move in a totally random manner. In addition particles in a liquid flow around and over each other quite easily, while in a crystal they do not as they are held in place by forces within the solid.

So solids seem to be opposite of liquids.

Compounds, when heated melt to clear liquids sharply at definite temperature. The thermal energy received by the molecules or atoms of a compound in a solid state makes their bonds loosened imparting them the freedom of freely flowing isotropic liquids. However, in certain compounds while thermal energy is being received, there appears to be a range where the properties of liquids and those of crystals overlap. The thermal energy induces flow, making the domain structure loosened to an extent, yet it is not enough to shatter the order of crystallinity completely. A sort of residual orderly orientation of molecules persists until another temperature is reached which totally eliminates regularity of structure altogether. This state of existence, between these two definite transitions, is independent within the definite temperature range and is neither totally crystalline nor completely liquid, but has properties of both. The state is known as "mesophase" or "mesomorphic state" and the phenomenon as "mesomorphism"; the compounds that exhibit this unique property are called 'liquid crystals' or 'mesomorphs' or 'mesogens'.

Liquid crystals flow, take the shape of any container and can be poured into, but their particles behave we ordinarily think of only in solids. These particles tend to form within the liquid state loosely ordered three-dimensional arrays rather like the lattice structure of a crystalline substance. Optically they exhibit properties usually associated only with crystalline solids. They display anisotropy, that is, they scatter light in symmetrical patterns and reflect different colours depending on the viewing angle. This indicates that the liquid crystal state is a liquid form of matter with an internal structure much like that of crystalline solids, that is, a region in which properties of liquids and crystalline solids overlap.

Reinitzer (1) and Lehman (2) have shown this strange phenomenon, giving the name 'fluid crystals' or 'liquid crystals' to the substances exhibiting the intermediate state of existence.

1.b. Nomenclature

Though the forms 'liquid crystals' and 'crystalline liquids' have been widely used from early times, Friedel (3) and Friedel and Friedel (4) proposed the name 'mesomorphic state' meaning the intermediate state (Greek : mesor-intermediate, morph-form), between the crystalline solid on the one hand and isotropic liquid on the other. The widely used other terms in literature are 'mesomorph', 'mesoform', 'mesophase' and 'mesomorphism'.

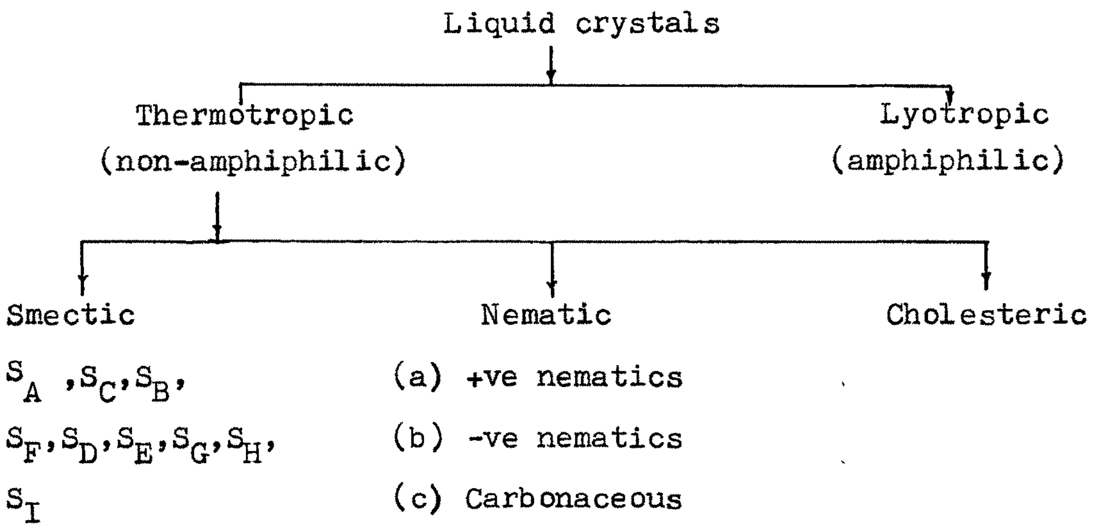
Brown and Shaw (5) have used the term 'mesomorphism' for the title of their first review. However, the term 'liquid crystals' is still prevalent.

'Thermotropic mesomorphism' (3,6,7) refers to production of the mesomorphic state by application of heat in contrast to 'lyotropic mesomorphism' which means formation of liquid crystals by solvation, the solvent generally being water.

Gray and Winsor (8) suggested the use of the terms 'amphiphilic' comparable with 'lyotropic' and 'non-amphiphilic' comparable with 'thermotropic'. Liquid crystals at high pressure are reported by Cladis and coworkers (9).

1.c. Classification of mesomorphs

Liquid crystals fall into two main classes which in turn are classified into subclasses as presented below:



1.d. Thermotropic Liquid Crystals: (Nonamphiphilic Mesogens)

After the first discovery of the phenomenon by Reinitzer (1), Gattermann and Ritschcke (10) in 1890 observed a similar behaviour of the compounds p-azoxyanisole and p-azoxyphenetole.

Vorlander (11) prepared hundreds of compounds exhibiting the same phenomenon in a short period of time. One important generalization concerning the structure of the compounds forming mesophase was evidently visualised without much effort, viz. the molecules were quite long. Despite synthesis of a large number of substances showing liquid crystallinity in a relatively short duration, its acceptance as an 'intermediate state' came much later.

Various views are expressed by different research workers. Tamman (12), Nernst (13) and Quincke (14) held the view that the mesophase was a two phase system owing to suspension of small crystals in the isotropic liquid or presence of impurities in the compounds resulting into formation of an emulsion of two liquids. Bredig and Schukowsky (15) and Cohen (16) tried without success to separate the emulsion into two constituents by electrostatic and centrifugal processes. Schencke (17) and Vorlander (18) critisizing the emulsion theory have argued in favour of the liquid crystalline state. de Kock (19) studied mixed liquid crystals and suggested that crystalline liquid state was a homogeneous state and not an emulsion of two liquids. He also repeated Tamman's sedimentation experiments and did not support the theory of two phase emulsion advanced by Tamman. Pawloff (20), Wulff (21) and Voight (22) have also discussed the nature of liquid crystals. The impurity theory is viewed as normally untenable,since the compounds exhibiting liquid crystallinity are with simple chemical constitution, the theory was ruled out when it was found that mesophase gives a clear field of view in the ultramicroscope.

Thermotropic liquid crystals are formed by heating crystalline solids consisting of long, rodlike molecules with polar terminal groups which are responsible for parallel alignment of the molecules. In an ordered crystalline state of mesogens, binding forces between the structural units exist. Thermal agitation causes disturbance in the domain structure. On gradual heating, weaker forces break down first giving the molecules a relative degree of movement causing a fluid condition. Yet at this stage, the energy acquired by the molecules is insufficient to overcome the forces responsible to maintain an ordered structure. The turbidity is due to the different orientation of the individual crystals which scatters the light to a more or less extent. Due to a preferred parallel orientation of the molecules in partially fluid state, scattering of the light gives rise to birefringence under polarizing microscope. On further heating, a stage is reached when sufficient energy is acquired by the molecules with the result that the preferred parallel orientation is altogether lost and an isotropic liquid is formed. Thus from solid to liquid, the transitions in case of mesogens can be written as follows:

$$\begin{array}{c}\text{Crystalline}\\\text{state}\end{array} \overset{t_1}{\rightleftharpoons} \begin{array}{c}\text{Liquid crystalline}\\\text{state}\end{array} \overset{t_2}{\rightleftharpoons} \begin{array}{c}\text{Isotropic}\\\text{liquid}\end{array}$$

$$\xrightarrow{\text{increasing temperature}}$$

These transitions take place at definite temperatures (t_1 and t_2) and are reversible. The reversible change from liquid crystal to crystalline solid is generally accompanied by supercooling. The transition in which t_2 is at a higher temperature than t_1 is termed as 'enantiotropic' transition' and the phase obtained is known as 'enantiotropic mesophase'.

Sometimes a mesogen may melt to an isotropic liquid at t_1°C. On gradual cooling the isotropic liquid, super cooling may occur and temperature may fall considerably below t_1°C before crystallization occurs. If a mesophase has a stable range of existence just below the melting point, then under supercooling the mesophase may appear at t_2°C before crystallization occurs. In this case t_2 will be lower than t_1 and the mesophase is essentially metastable and designated as monotropic with respect to the solid phase. The monotropic temperature t_2 is reversible; without permitting it to crystallize, on raising the temperature again the monotropic mesomelt is changed into isotropic liquid at t_2 itself. The above change can be represented as under:

$$\begin{tikzcd}
\text{Crystalline state} \arrow[r, "t_1"] & \text{Isotropic liquid} \arrow[d, shift left, "t_2"] \\
 & \begin{array}{c}\text{Liquid crystalline state}\\ \text{(monotropic)}\end{array} \arrow[u, shift left] \arrow[ul]
\end{tikzcd}$$

Based on the molecular arrangement which gives rise to textures and other optical characteristics of the mesophase, Friedel (23) classified mesogens into three categories (i) smectic (ii) nematic and (iii) cholesteric. Birefringent patterns of mesophases are referred to as 'textures' a term which he considers preferable to 'structures'. Most of the compounds exhibit smectic or nematic mesophases.

The word smectic originates from the Greek word "Smectos" meaning soap-like as one of the very first liquid crystalline compounds synthesized, ammonium oleate, a soap salt, exhibited this type of texture. Many common soaps exhibit smectic phases at elevated temperatures (~200°C) or in the presence of water.

The word nematic means 'thread like ' and significant in that the molecules when examined under polarized light in a microscope show characteristics threaded lines.

The cholesteric phase is so called as these compounds are mostly derivatives of cholesterol.

1.d(i) Smectic Liquid Crystals

The smectic mesophase is a liquid crystal having the highest order and is stratified. In this phase, the molecules are arranged in parallel layers. The arrangement within the layers may be either random or ordered. In either case, the long axis of the molecules in a given layer is parallel to one another and perpendicular to the plane of the layer. Each stratum is one molecule thick or at most a few molecules thick. These layers can slide back and forth over one another because the molecules are free to move from side to side or forward and backward but not up and down. It is so because the temperature is just enough to break bonds between

Not always

layers of molecules, but not enough to break up the layers themselves. It is a highly viscous, turbid fluid and an ordinary soap bubble is an example of a smectic liquid crystal. Soap molecules arranged side by side at the inner and outer surfaces of a soap bubble constitute smectic layers.

Certain substances such as paraffins, fatty acids, etc. which possess three dimensional crystalline layer structure do not pass through a two dimensional smectic mesophase on heating. Perhaps, lateral cohesions of the chains are not sufficient to form smectic layers; hence on heating, the molecules directly give isotropic liquid. In the smectic phase the layers of molecules are quite flexible. If a single sheet could be suspended in space free from gravity it would take a form of a perfectly flat surface and side to side attractions of the molecules in the sheet would be the strongest on it (Fig.1).

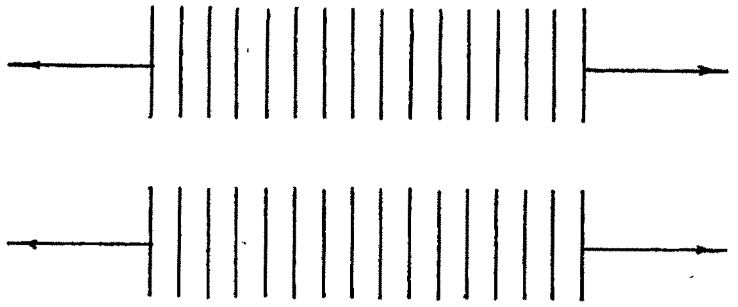


Fig.1

A section representing the molecular arrangement in two plane smectic strata.

A smectogenic solid when melted on a very clear slide gives rise to terraced texture. These 'many molecular thick' strata are called 'grandjean plates' (24). If the coverslip is moved, gliding of layers over one another is clearly marked, but displacement in any other direction is restricted. This leads to the view that the molecules lie in two dimensional layers with long axes parallel to one another and perpendicular to the plane of terraces.

The cohesions between these layers are relatively weak which account for the characteristic layer flow observed in the stepped drops. A number of such smectic sheets laid on top of one another, like the leaves of a book, will tend to adjust further so as to let ends of the molecules in one sheet fit in some characteristic way to ends of the molecules in the adjacent sheet. While in a solid crystal there is three dimensional order, in the smectic phase the temperature is just sufficient to break up the sheets only, leaving a two dimensional order.

On further heating, the smectic phase may yield directly isotropic liquid. The change may be represented as under:

$$\begin{matrix}\text{Crystalline}\\ \text{solid}\end{matrix} \xrightleftharpoons{t_1} \begin{matrix}\text{Smectic}\\ \text{mesophase}\end{matrix} \xrightleftharpoons{t_2} \begin{matrix}\text{Isotropic}\\ \text{liquid}\end{matrix}$$

Many compounds, however, exhibit both smectic and nematic or cholesteric mesophases, in which case the changes may be represented as follows:

$$\text{Crystalline solid} \overset{t_1}{\rightleftharpoons} \text{Smectic mesophase} \overset{t_2}{\rightleftharpoons} \text{Nematic or cholesteric mesophase} \overset{t_3}{\rightleftharpoons} \text{Isotropic liquid}$$

A good number of mesogens show more than one type of smectic phase besides nematic or cholesteric phase. This is called polymorphism in smectic mesophase.

$$\text{Crystalline solid} \overset{t_1}{\rightleftharpoons} \text{Smectic II} \overset{t_2}{\rightleftharpoons} \text{Smectic I} \overset{t_3}{\rightleftharpoons} \text{Nematic or cholesteric mesophase} \overset{t_4}{\rightleftharpoons} \text{Isotropic liquid}$$

The smectic phase when formed on cooling the isotropic liquid, first appears frequently in the form of non-spherical characteristic elongated birefringent particles which are known as batonnets. These increase in number as the temperature falls, coalesce and show evidence of a focal conic structure, so named after their shape. The focal conic structure was an important means of detecting the smectic mesophase.

The focal conic texture is the most common of the smectic textures. Under microscope the smectic phase looks quite immobile unlike the nematic one. The focal conic smectic texture shows a number of fine dark lines. The shape and arrangement of these lines are like those of ellipses and hyperbolae. Bragg (25) has given an excellent account of focal conic structure and the geometry involved. This furnishes further evidence for the layer theory of the smectic structure.

Herramann (26) differentiated smectic phases into two types, one with unstructured layers and other with structured layers. In the first group the distribution of the molecular centres within the layers corresponds to that of a two dimensional liquid. It is without long range order. In the second group the layers are built up regularly so that the positions of the molecular centres lie on a two dimensional lattice. The most common smectics are in the first group which includes the phases classified as smectic A and smectic C. A representative of the second group is classified as smectic B. Sackmann and Demus (27) classified smectic phases according to the textures observed in microscope. They studied in detail and reported seven smectic phases from smectic A to smectic G. The four smectic phases of N-(p-heptyloxybenzylidene)-p'-pentylaniline were classified by x-ray diffraction as S_H (tilted B), S_B (normal B), S_C and S_A in order of increasing temperature (28). The large molecular axes are probably normal to the layers in S_A, S_C and S_H and perpendicular to the layers in S_B.

Table : 1

Classification of Smectic liquid crystals (27)

Types of phases	Types of textures
Smectic A (Unstructured layers)	(a) Simple fan shaped (b) Simple polygon (focal conic)
Smectic C (Unstructured layers)	(a) Broken fan shaped (b) Broken polygon (focal conic)

Table : 1 (contd)

Types of phases	Types of textures
Smectic B	(a) Mosaic texture
(structured layers)	(b) Fan shaped (c) Polygon } with decreased number of line - Schlieren texture

Trimorphous smectic substances exhibit liquid crystalline phases with decreasing temperature in the following succession :

Isotropic liquid → Nematic → Smectic A → Smectic C → Smectic B

It is obvious that smectic A is more ordered than the nematic, since it has an additional one-dimensional translational order. In compounds which exhibit both smectic A and nematic phases, the former occurs at low temperatures.

de Vries (29) has classified the smectic into three main classes as α, β and γ on the basis of x-ray studies. The class α contains smectic A, C , F and D; the class β contains smectic B and class γ contains smectic E, G and H. de Vries has also reported two classification systems for smectic phases based on symmetry and order (30).

1. Smectic α Phases

These are the least ordered smectics, although the layer structure corresponds to a certain degree of positional order, the degree of order within the plane is low.

a. S_A (α_1) :

This structure is well known, the molecules in the layered structure stand perpendicular to the layers and are disordered, corresponding to a two dimensional liquid (31,32). The degree of order in S_A is not much different from that in S_C (33) suggesting there by that S_A and S_C transition may be second order. There is a chaotic distribution of the centres of gravity of the molecules inside the layer.

H.T. Nguyen (34) has reported a new homologous series in which three S_A phases i.e. S_{A1}, S_{Ad} and S_{A2} are identified by small angle x-ray scattering. Three derivatives exhibit the novel smectic phase made of ribbons. Madhusudana et al (35) have reported S_A - S_A transition.

b. S_C (α_2) :

This structure is a tilted form of smectic A, that is, the molecules are disordered within the layers but tilted. It is more ordered than smectic A and occurs at low temperatures in compounds exhibiting both the states. The tilt angle gradually decreases to zero as the sample is heated and there occurs a second order (continuous) C-A transition which does not involve any latent heat or volume change.

NMR studies (32) indicate that smectic C is very much like smectic A possessing fast molecular reorientational and translational diffusion.

The chiral S_C phase is discussed by using a simple molecular model (36). The helix is expressed in terms of the tilt angle and smectic order parameter. A comparison is made with the cholesteric phase.

Nguyen et al (37) reported S_C-S_{C2} transition with the N - S_A - S_C - S_{C2} sequence and also a new S_{Ad} - S_{C2} sequence in pure mesogens by x-ray measurements.

c. S_F (α_3):

No exact structural description is available except reported by Sackmann and Demus (27). It has a layered structure closely related to that of S_C and falls below S_C on temperature scale and more ordered. A new series exhibiting this phase is reported by Billard et al (38, 39).

X-ray diffraction (40) patterns of single domain samples of this phase of terephthal bis(4-pentylaniline) were used to study the nature of the phase. S_F phase is intermediate between the S_B and S_C phases. Recently S_F and S_I are reported to be characteristic of new stages between the 3-dimensionally ordered S_B and S_G and the 2-dimensionally S_C phase (41). The structures and phase transitions of the tilted hexatic phases (S_F and S_I) were studied by x-ray diffraction (42).

Two novel phase sequences involving S_F phase namely (i) S_H-S_F-S_A-Iso and (ii) S_H-S_F-S_B-S_C-S_A-N-Iso, have been reported (43).

d. S_D (α_D):

In terms of order this phase should be intermediate between S_A (α_1) and S_C (α_2). It has a strong tendency to assume an optically isotropic texture, which has been supposed to be the pecularity of amphiphilic compounds only. Probably the presence of long paraffin tails stabilize the micelle structure in the absence of a solvent. X-ray diffraction study of the phase is done by Billard et al (44).

2. Smectic β Phases:

de Vries' classification contains only one smectic that is, smectic B, S_B (β_1). It is an ordered layered structure with molecules aligned normal to the layers. All workers seem to agree that there is a high degree of order in the layers and that the molecules conform to a hexagonal arrangement in the layers (45), in contrast to S_A where there is a chaotic distribution of the centres of gravity of molecules inside the layer. It is more crystal like compared to either A or C phase.

Sakagami et al (46) have reported two S_B modifications, the transition heat of which is very small.

3. Smectic γ phases

There are three phases in this classification.

a. S_E (γ_1)

There are two varieties of this layered phase - normal (27) and tilted (27,29). de Vries suggests the existence of a three dimensional lattice, a view which contrasts with that of Diele et al (47).

b. S_G (Γ_2)

This is also a layered phase with a nonrandom molecular arrangement within the layers. Billard (39) reports this phase in a binary system. Sorai et al (48) report unusual glassy state of this phase.

This phase is reported during the x-ray diffraction study of the homologous azobenzene derivative series by Pelzl et al (49). The textures and the structures of the phase are described and discussed. S_G phase is also reported by Nguyen et al (50).

c. S_H (Γ_3)

The structure of S_H is approximately that of a tilted S_B. NMR studies (51,52) have proved molecular arrangement to be three dimensional monoclinic lattice. de Vries (52) classified this phase as a separate phase and not tilted S_B as done by Sackmann and Demus (27). Gray and Goodby synthesized pure esters giving S_B and S_H phases separately and distinctly (54).

The existence is reported of a novel thermotropic smectic mesophase built with ribbons forming a two dimensional oblique lattice, by Hardouin et al (55,56). A new type of smectic phase

(S_j) has been reported by virtue of the x-ray diffraction study (57).

No hypothesis or theory has been proposed to explain the smectic structure.

1.d.(ii) Nematic Liquid Crystals

The term nematic is derived from the Greek word 'nema' meaning 'thread like' as the mobile thread like lines are observed under polarizing microscope. The nematic state is less ordered as compared to the smectic as there is no layered arrangement of the molecules. The long axes of molecules are oriented in a parallel fashion with the centre of gravity of molecules being randomly distributed. Such arrangements of the molecules are referred to as an imbricated structures as shown in Fig.2.

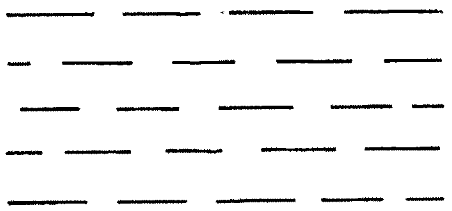


Fig.2

Molecular arrangement in nematic phase

The arrangement of the molecules in nematic mesophase can be compared with a long box of round pencils. The molecules exist in the form of groups, each group containing about 100,000 parallel molecules. These groups are referred to as swarms. The 'Swarm Theory' was first proposed by E. Bose (58) in 1909 to explain the molecular arrangement and order in the nematic phase. Optical properties indicate that the molecules are in a constant state of movement, that is why swarms do not remain constant in size but are continually exchanging molecules with one another. The arrangement of the swarms is not a rigid one and is subject to mechanical deformation.

The swarm theory accounts for the turbidity which is associated with the nematic mesophase, the light scattering properties of the swarms explaining the opalescence. Evidences in support of the swarm theory are provided by properties such as electromagnetic field (59,60), Viscosities (61), transparency (62), refractive index (63) magnetic and electric properties (64, 65) of the phases, summary of such measurements is given by Ornstein and Kast (66).

Zocher (67) in 1927 critised the above theory and proposed a new theory known as 'distortion hypothesis' which is based on the concepts of a continuum for the nematic phase such that the orientation of the molecules changes in a continuous fashion throughout the bulk of the mesophase, now referred to as the 'Continuum theory' of liquid crystals.

Zocher (67) made the following assumptions:

1. The sample will tend to adopt a condition such that the axial direction of the molecules is the same throughout.

2. If any external force disturbs this condition of uniform orientation, the axial direction will change continuously until a restorting force of an elastic nature balances the external force.

3. On solid surface, such as glass or metal, the molecular positions originally adopted are almost unchangeable.

The continuously changing molecular orientation in a nematic mesophase explains the magnetic and electric properties of the nematic mesophase in a better way than the swarm hypothesis.

X-ray studies have thrown some light on the structure of nematic mesophase. This technique is less fruitful because of the much lesser degree of molecular organization. The earliest (68) work does not indicate any essential difference between the x-ray diffraction patterns of the nematic phase and of the isotropic liquid. X-ray diffraction patterns for the nematic phase and the isotropic liquids were indistinguishable diffuse halos, which indicate the absence of layer structure in nematic phase.

Bernal and Crowfoot (69) reported x-ray investigation of the crystalline state of some nematic compounds like p-azoxyanisole, p-azoxyphenetole etc. The study indicated that in the crystalline state the molecules were arranged parallel to one another but inseparable in layers. They used the word 'imbricated' meaning overlapping like a scale of a fish to describe the shape of the molecules (Fig.2). It is not necessary that nematogenic compounds have always imbricated structure in their crystalline state. In some cases the molecules are arranged in layers, but such compounds may exhibit both smectic and nematic mesophases (70). The imbricated structure of a compound in its crystalline state does not necessarily mean that a nematic mesophase will be formed on melting the crystals. For instance, if the intermolecular forces in the crystals are very strong, the melting point of the compound may be so high that the parallel orientation of the molecules does not persist when the lattice disintegrates and the isotropic liquid may be produced. On the other hand, even if the melting point is low, the dimensions of the molecules and the strength of intermolecular attractions may be quite unstable for maintenance of any molecular order on heating. Therefore isotropic liquid would be formed.

Mayer and Saupe (71) have given a simple molecular theory of the nematic liquid crystals. They have mentioned that nematic-isotropic transition temperatures can be determined by calculation of free enthalpies of the phases involved at the transition.

Recently Gelbart has discussed molecular theories of nematic liquid crystals (72).

Disc like mesophases:
(Columnar phases)

Since the first paper (73) reporting the existence of a mesophase for a pure disc-like molecule, several series of plate-like molecules have been synthesized (74, 75, 76, 77). Some of these compounds exhibit several mesophases and in one case a complete miscibility between the mesophases of molecules belonging to two distinct series have been observed. Thus, the disc-like compounds seem to exhibit a rich polymorphism of their mesophases similar to the polymorphism of classical liquid crystalline phases of elongated molecules. Disc-like mesophase is one of the two most thoroughly discussed topics at the recent liquid crystal meetings.

Most of these phases correspond to a tubular or better, column arrangement of discs (73, 78), a structure in which the flat molecules are stacked in infinite columns (D phase). With respect to a regular (O) or irregular (d) stacking of discs and considering the symmetry of the two dimensional lattice of columns, hexagonal (h) or rectangular (r), classification of these columnar phases has been proposed.

A systematic study of all these series by means of optical texture observations, calorimetric measurements, binary phase diagram studies and x-ray measurements show clearly the existence of only three different mesophases, namely D_{ho}, D_{hd} and D_{rd} (79).

Disc-like mesogens exhibit two different mesomorphic phases : a columnar mesophase (D) and a lamellar nematic phase (N_D). The D_t tilted columnar phase is the fifth identified mesophase found in disc-like mesogens (D_{rd}, D_{hd}, D_{ho}, D_t and N_D) (79). The analogies between these two condensed states of matter and the classical liquid crystals are very great as regards optical textures and molecular structure. The only but fundamental difference is that in one case the molecules are parallel to the general director while in the other case they are perpendicular to it.

Disc-like mesogens exhibit interesting mesophases which are similar to liquid crystals but seem to contradict the accepted picture of liquid crystals: (i) The molecules have two dimensional, disk-like structure, as opposed to one-dimensional, rod-like structure. (ii) Since the discogenic molecules have high symmetries such as six fold (73, 80), a three fold (74, 75,76, 78,79,81) or a two fold symmetry (77), the molecules have no net permanent electric dipole moment. (iii) Although the available optical data are scare, the disc-like mesogens are known to be characterized by optically uniaxial mesophases with an optical negative sign (74). Nematic and smectic mesogens usually exhibit uniaxially (or biaxially for some of the smectic subclasses) positive optical properties, while cholesteric mesogen shows uniaxial negative sign (82). Although observation of optical activity of the disc-like mesogens has not been reported, it is not likely that they are optically active and belong to the cholesteric mesophase,(iv) The x-ray diffraction patterns (73, 78, 80) prove that the disc-like mesophases are a new kind of condensed state (columnar arrangement with hexagonal packing). The polymorphism can be attributed to the conformational meltings of the n-paraffinic moieties and thus a series of the transitions should be regarded as a kind of successive phase transition. Various nomenclatures proposed to describe the new kind of mesophase are disc-like mesophase, discotic mesophase (74), planar mesophase (83) or columnar liquid crystal (84).

As discussed earlier, normal nematic compounds consist of rod-like molecules whose longest axes tend to be parallel in the nematic phase. Alben (85), Onsagar (86) and Dreyer (87) suggested, in addition to these positive nematics, it is expected that there might be 'negative' nematics with planar molecules aligned with their shortest axes parallel. Alben (85) proposed a possible phase diagram for mixtures of such 'positive' and 'negative' nematic liquid crystals.

Chandrasekhar et al (73,88) supported the above idea and reported thermotropic mesomorphism in pure compounds consisting of simple disc like molecules e.g. benzene hexa-n-alkanoate. The mesophase is indicated to be highly ordered lamellar type by thermodynamic, optical and x-ray studies. Based on the x-ray data a structure is proposed in which the discs are stacked one on top of the other in columns that constitute a hexagonal arrangement, but the spacing between the discs in each column is irregular.

Thus the structure has transitional periodicity in two dimensions and liquid like disorder in the third.

Several compounds (74, 75, 76, 80, 81, 83, 84, 89, 90) of disc-like mesophase have been reported. Some of them exhibit two or three discotic mesophases but the hexa-alkanoyloxy derivatives (90) exhibit a large diversity of columnar phases (six different phases). The different phases are described on the basis of optical textures (79), binary phase diagrams (77), and x-ray measurements (78, 91). Chandrasekhar et al (92) have reported disc-like mesogens with lowest molecular weight synthesized so far. Till date only about 100 different mesogenic disc shaped molecules are reported to have been synthesized and yet 7 different columnar phases are clearly identified (90).

Recently Akopova et al have reported synthesis and discotic mesomorphism of tetraoctanoyl hydroquinone (93). Reentrant N_D nematic and D_r columnar mesophases are also described at atmospheric pressure in a pure disc-like compound (94).

In view of the recent results from various research groups the relation of molecular structure to liquid crystal properties of disc-like compounds is discussed by Kohne et al (95). Columnar mesophases from metal (like Cu, Zr or Mn) and metal-free derivative of phthalocyanine (96), in some transition metal complexes (97,98) and nickel complexes (99) have been reported. Columnar liquid crystals consisting of macrocyclic units are also reported (100).

Carbonaceous Mesophases:

Zimmer and White (101) reported this new type of nematic mesophase transformation usually occuring in the range of 400°C to 500°C during the process of cocking and carbonization. The mesophase formed at this temperature by condensation of molecules is termed carbonaceous mesophase. Plate-like molecule in contrast to the rod-like molecules of nematic liquid crystal is the distinctive feature of this mesophase. Thus, carbonaceous mesophase appears to be a lamellar liquid crystal in which space is filled by plate-like molecules which may vary in size and shape but tend to pack in parallel arrays. These arrays are free to bend and twist. Electron microscope and optical microscope studies of the size and structure of the phase are reported (102). The molecular structure of the carbonaceous liquid crystals is studied by electron diffraction and the optical properties are also reported (103). Mesophase pitches derived from petroleum, coal tar and naphthalene were separated into their isotropic and anisotropic phases by high temperature centrifugation and were characterised by elemental constitutions, densities, solubilities, molecular weight distributions, x-ray and EPR spectra (104).

Smectic Reentrant

Reentrant phenomena is one of the two most thoroughly discussed topics at the recent liquid crystal meetings. Reentrant smectic phase along with reentrant nematic have been reported (105, 106, 107). A systematic comparative study of several series of structurally neighbouring compounds has been made giving reentrant smectic and reentrant nematic mesomorphism.

Experimental data concerning the various reentrant phases are summed up revealing the various factors favourable to the occurence of the reentrance. The chemical composition and location of dipoles in the molecules, reduced temperatures and length of the rigid core are discussed as relevant parameters. New phase sequence N- S_A - S_C - N - S_A was found with decreasing temperature.

Nematic Reentrant:

Normally in phase transitions, the higher temperature phase is less well ordered (more symmetric) than the lower temperature phase (108). This is not a law of thermodynamics (109), however, and although counter-intuitive, the reentrant nematic phase (110), is one more example of a more symmetric phase reoccuring at a lower temperature than the less symmetric smectic phase (111).

Cladis (110) first reported metastable reentrant nematic phase below smectic mesophase on cooling. Certain cyano compounds with alkyl or alkoxy end groups exhibiting the bilayer smectic A phase exhibit this typical phase (110, 112, 113, 114, 115). N-S_A- reentrant N phenomenon has been found to occur in cyano compounds which form anti-parallel molecular associations

(116, 117, 118, 119) perhaps even in the isotropic liquid phase, due to the very large dipole associated with the nitrile bond ($\sim$ 4.5 debye). The number of associations and their lifetime increase as the temperature decreases and results in a S_A layering which is not commensurate with a molecular length (120) (as is the usual case) but rather the length of an associated pair. Sufficiently long-lived at lower temperature, it is postulated that such pairing neutralizes the long range attractive electrostatic forces necessary to stabilize layering so that only the shorter range repulsive interactions remain. These latter can only stabilize a nematic phase and not a smectic phase for which some kind of attractive interaction is necessary to localize the molecules in layers. The reentrant nematic is believed to be composed of relatively long-lived associated molecular pairs packed into a tight but mobile configuration. Very polar molecules stabilize the layering better resulting in a higher T_{NA}, N to S_A transition temperature.

It is found that density increases monotonically with decreasing temperature. In the vicinity of the re-entrant nematic transition, the density in the S_A phase increases by a tiny amount above an extrapolated value from a trend established in the S_A phase. Re-entrant behaviour might be due to expansion of the layer spacing.

It is known that the reentrant nematogens form bilayers in the S_A phase, the neighbouring molecules in each bilayer being antiparallel and it is believed that subtle changes in the bilayer structure are responsible for their re-entrant behaviour. Studies have shown that the molecular associations in the two nematic phases are different, this difference being unobservable in either the elastic constant (110) or orientational order determinations (121).

The enantiotropic reentrant compounds (113,122,123,124) as well as binary mixtures showing reentrant nematic phase are also reported (124,125,126). X-ray and high pressure investigations of this phase is reported (118, 125,127,128). The reentrant polymesomorphism is reported by Nguyen et al (124, 129,130,131), and the influence of the length of the conjugated system on the reentrant phenomenon is studied (131). Demus et al (129, 132) studied the influence of the polar terminal group and the length of the conjugated system in exhibition of this phase. The polar terminal group is a favourable condition after the formation of the reentrant nematic phase. It is not important that the polar group be directly connected with the benzene ring. The linkage group between the two benzene rings seems only to influence the conditions for the detection of the reentrant phase (133). Highly polar groups induce more polarizability, which in turn increase the long range attractive electrostatic forces necessary to stabilise layering, hence ratio of lateral to terminal attractions is higher.

Urs et al (134) studied the effect of a lateral substituent on the reentrant nematic phenomenon and discussed phase diagrams of binary mixtures of compounds with a reentrant phase with a compound exhibiting no reentrant phase. The binary mixtures exhibit stable enantiotropic reentrant behaviour over a range of composition though the pure compounds themselves are monotropic reentrants. Sadashiva (135) reports that the lateral substituent, depending on its location, seems to have varying degrees of influence on the reentrant nematic phase.

Nguyen et al (136) reported the relation between alkoxy chain length and the core size, to give reentrant smectic and nematic phases. On the basis of these results a thermodynamic model for this phase is presented by Clark et al (137). Microscopic one particle model of reentrant behaviour in nematogens is given by Longa et al (138).

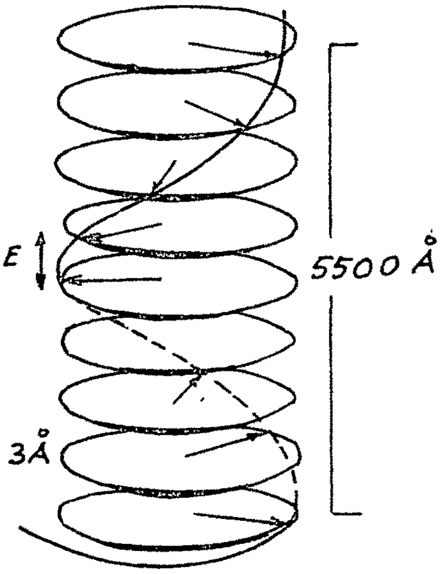
Nematic Textures :

On cooling the isotropic liquid of a nematogen, circular birefringent areas or droplets are first obtained. After transition has occured completely, the texture would often depend upon the layer thickness. Relatively thicker nematic layers may show the typical threaded texture, the well defined thread like structures may move and float around the nematic liquid. In thinner layers the threaded texture transforms to the 'Schlieren texture' with point like disclinations. Between crossed polarizers, the appearance of schlieren forms is characterized by dark brushes which originate from points, in which the direction of extinction is not defined. Usually points with two or four dark brushes can be observed. By suitable surface treatment possibly films with uniform molecular alignment can be obtained. Sometimes in extreme cases, with untreated surfaces, an irregular texture resembling appearance of polished marble can be obtained due to surface effect - the texture being known as 'marble texture'. In some cases the uniformly aligned films get their optic axis normal to the surface rendering the mesophase to adopt a homeotropi texture, also called 'pseudo-mesophase'.

1.d.(iii) Cholesteric Liquid Crystals

The cholesteric phase is so named because its molecular structure is characteristic of a large number of compounds derived from cholesterol. One of the very first compounds discovered exhibiting mesomorphism was cholesterol benzoate - a sterol derivative (1). Non-sterol derivatives possessing the general requirements of typical nematic structure, also exhibit cholesteric phase (139). These are known as 'chiral nematics'.

It is essentially a nematic type of liquid crystal except that it is composed of optically active (with the ability to rotate the plane of vibration of polarized light) molecules. Cholesteric mesogens resemble smectic phase in that the molecules are arranged in layers. Within a given layer, the molecules are parallel to each other. This is reminiscent of the nematic phase, but the direction of the long axis in each layer is displaced slightly from the corresponding direction, in the next layer giving appearance of a 'twisted nematic'. The overall effect is that of a helix. It is this pecularity of structure that



SUGGESTED ORGANIZATION
OF THE CHOLESTERIC PHASE

FIG. 3

accounts for many of the interesting properties of cholesteric liquid crystals. The molecular structure of a cholesteric mesogen is delicately balanced and is easily disturbed. These small disturbances interfere with the weak forces between molecules and have the effect of slightly changing the molecular structure of the substances. But such a structural change also changes the optical properties of liquid crystals which give them potentials of technical applications. The twisted structure may also be obtained by dissolving a few percent of an optically active compound in any nematic liquid crystal. The helical arrangement can be either right or left handed and gives rise to some specular optical effects.

Friedel (23) noted a somewhat close resemblances between the cholesteric and nematic phases. No substance was found exhibiting both phases viz. cholesteric and nematic, whereas each commonly occured in association with smectic phase. Also as seen in the previous para, nematic phase can be transformed into cholesteric phase by dissolving an optically active compound in it. Again the transitions from a smectic to a nematic mesophase as well as from a smectic to a cholesteric mesophase are discontinuous. All these facts lead to suggest cholesteric phase as a special variation of nematic mesophase (23).

It is observed that the mobility of cholesteric mesophase is much greater than that of the smectic phase (140). It exhibits the most reasonable properties of intense iridescent colours and high optical rotatory power due to Grandjean plane texture. The property is dependent upon nature of the compound and temperature and angle of incidence of the beam. Gray (141) reported that cholesteric phase could be regarded as an individual phase and that it was more similar to smectic phase rather than nematic mesophase. The fluidity and orientation by electric and magnetic fields of this phase is like the nematic phase (142). Vorlander and Janecke (143), Leclercq et al (144) and Gray (145) have shown that the optically active compounds were cholesteric whereas the inactive racemic varieties were nematic. Electric and magnetic fields can force a cholesteric mesophase into nematic arrangement (142).

Stumpf (146), Gray (70), Mathieu (147), Oseen (148) and Fergason (149) have explained mathematically the optical rotatory power of the cholesteric mesophase. Goossens (150) has put forward the molecular theory of the cholesteric phase.

Mathieu (151) has summarized the optical properties. Cholesteric liquid phase can show different textures (152) such as focal conic, planar or plane texture and blue phase. Hydrodynamic and optical properties of cholesteric depend on textures, and many differ strongly from those of nematics. Certain cholesteric compounds, although colorless themselves, are able to scatter light selectively into different colours. The most striking features of the phase is the strong optical activity and the selective light reflection which is due to the twisted helical structure. Physical effects such as temperature, pressure, shear and traces of organic vapour result in various colour changes due to winding or unwinding of the helix. Malthete reports reentrant cholesteric phase in some pure compounds (153).

Several compounds with three benzene rings and with a cyano end group having a cholesteric reentrant phase are prepared and their liquid crystal properties described (154). In another series with a nitro end group and not having reentrant phenomena, one compound exhibits a blue phase.

Textures of cholesteric phase :

Cholesteric liquid crystals can show textures such as focal conic and planar which can originate from optically isotropic texture originally formed (152). Certain cholesteric compounds, on cooling the isotropic liquid, exhibit a phase which is visible to the eyes in reflected light but not in polarized light. This is known as "blue phase". Experimental studies of the blue phase of cholesteric liquid crystals have revealed two cubic phases (BP I and BP II) and a possible amorphous 'fog' phase (BP III) (155). Fong et al (156) reported at least two monotropic BP phases in pure compounds. Recent papers (157, 158) reported transformation of blue phases into the unwound cholesteric phase by applying an electric field. The possible structure of the blue phase was determined by NMR studies (159, 160).

1.e. Lyotropic Liquid Crystals:
(Amphiphilic Mesogens)

Another important group of liquid crystals which are formed by the influence of solvents, generally water, is called lyotropic mesogens (3,6,7). Gray and Winsor (8) suggest the use of the term 'amphiphilic mesogens' or 'amphiphiles'. The classification of these is somewhat difficult from that of the Thermotropic group.

Lehmann (161) was the first to recognise this mesophase in aqueous solution of ammonium oleate. Amphiphiles are compounds possessing two groups with large solubility differences viz. (a) hydrophilic (having affinity for water) such as -COOH, $-SO_3K$, -COONa, $-O(CH_2-CH_2-O-)_nH$, -OH, and $N(Me)_3Br$ are water soluble and hydrocarbon insoluble and (b) long hydrophobic (water repellent) or liophilic groups such as $-C_nH_{2n+1}$ and $-C_nH_{2n+1}.C_6H_4-$ which are hydrocarbon soluble and water insoluble. Compounds in which these two opposing tendencies are strong and fairly balanced form mesophases with water within ranges of concentration and temperature which depend on the compound. Because of this dual character such compounds are called amphiphiles.

Lyotropic substances are strongly birefringent. The gradual breakdown of the crystal lattice by addition of water or in general solvent may be represented as :

$$\begin{array}{c}\text{Crystalline}\\ \text{substance}\end{array} \underset{\text{dehydration}}{\overset{\begin{array}{c}\text{solvent}\\ \text{(water)}\end{array}}{\rightleftharpoons}} \text{Liquid crystal} \underset{\text{Evaporation}}{\overset{\begin{array}{c}\text{Excess}\\ \text{solvent}\\ \text{(water)}\end{array}}{\rightleftharpoons}} \begin{array}{c}\text{Solution}\\ \text{or}\\ \text{colloidal}\\ \text{solution}\end{array}$$

The mesophases formed by typical amphiphiles may be regarded as based on the arrangement of multimolecular units termed as 'aggregates' or 'micelles' which are themselves commonly 'liquid' or 'fused' in character. Many amphiphiles form mesophases in the pure state, whereas for others micellar units and intermicellar liquid constitute jointly the amphiphilic mesophases representing single, thermodynamically stable or sometimes metastable phases. The formation of the amphiphilic mesophases depends on intramicellar (short ranged) and intermicellar (long ranged) interactions.

Mesophases in binary systems of amphiphiles and water may be classified as (A) the neat phase (G phase), (B) the middle phase (M_1 phase), (C) the viscous isotropic phase (V_1 phase), (D) the isotropic phase (S_1C phase) and the inverse phase (V_2 and M_2 phases) (162). If all the above mesophases occured at a given time in a binary system, the sequence of appearance with increasing concentration of amphiphilic compound would be

$$S_1C \longrightarrow M_1 \longrightarrow V_1 \longrightarrow G \longrightarrow V_2 \longrightarrow M_2$$

The complete series does not appear to have been found in any single system.

A precise knowledge of the phase diagram of the soap-water systems is very important to the soap industry. The study of lyotropics has also significance since several biological systems are known to form such mesophases. One example is the bile acid.

Table 2

Classification of mesophases in binary systems of amphiphiles and water (162)

Name of the phase	Nomenclature
The neat phase	G phase
The middle phase	M_1 phase
The viscous isotropic phase	V_1 phase
The isotropic phase	S_1C phase
The inverse phase	V_2 and M_2 phase

The formation of the different phases of lyotropic liquid crystals is considered as a function of the relative importance of cohesive forces and affinity forces for water (163).

Recently an interesting account of the composition, properties and structure of liquid crystalline phase in systems of amphiphilic compounds is given by Ekwall (164). DuPre et al (165) reported reentrant isotropic phase of concentrated solutions of poly-p-benzyl-L-glutamate, in a mixed solvent system containing a denaturant acid. Robinson (166) reports an interesting observation that viscous solutions of poly-γ--benzal-L-glutamate in certain organic solvents are anisotropic. Small et al (167, 168) have studied lyotropic mesomorphism of ternary and quarternary systems of bile salts, lecithin, cholesterol and water. Lawson and Flautt (169) have studied NMR spectroscopy of smectic and waxy mesophases in surfactant systems such as sodium palmitate-water system. Influence of the lengths and conformation states of hydrocarbon chains, on the stability of lyotropic phases, has been reported (170).

Soap, (soap like alkali salts of naphthenic and resin acids, 9-chloro and 9-bromo-phenanthrene-3-sulphonic acid), substituted phenanthrene sulphonic acids, certain naphthyl amine disulphonic acids etc. show mesomorphic property under controlled action of water (171, 172, 173). Alcoholic solutions of these compounds do not show mesomorphic property. Certain dyes also exhibit this property (174, 175, 176). Marsden and McBain (177) and McBain (178) have studied the x-ray diffraction patterns of aqueous non-ionic detergents. Sheppard's work (179) on 1-1'-diethyl-2-2'-cyanine salts and diethyl- ψ -cyanine proposes a new type of nematic molecular phase that of pluri molecular filaments rather than elongated molecules. It has been asserted (6) that the action of water or in general any other solvent and heat are not dissimilar in regard to the effect of breaking the bonds holding the molecules in their crystalline orientations in one or possibly two directions.

Lyotropic liquid crystal property produced by the dissolution of benzene hexamine derivative in $CHCl_3$ or aliphatic and aromatic solvents have been reported (180). Alkylated sugars are known to form smectic-like phases which are thermotropic, however, these substances are surfactants (181).

1.f. Plastic crystals : Amphiphilic and non-amphiphilic cubic mesophases:

A crystalline solid possesses both three dimensional long range positional order and orientational order, a liquid crystal has orientation order and zero (or reduced) positional order, a plastic crystal possesses long range positional order but it is orientationally completely disordered and an isotropic liquid possesses neither. Plastic crystal molecules are usually compact and globular whereas liquid crystal molecules are generally long and rigid. In plastic crystals orientational disorder occurs at a lower temperature than positional disorder, in liquid crystals the reverse is true. In other words in liquid crystals, the fluidity comes first on heating but in plastic crystals isotropy comes first. In short, liquid crystals are solid like liquids and plastic crystals are liquid like solids. Thus plastic crystals are neither true liquid nor true solids but constitute a further mesomorphic state of matter. Plastic crystals have now been accepted as an integral part of the wide mesomorphic range with two extremes of crystalline solids and isotropic liquids on either side and which are optically isotropic (8). Plastic crystal lattice is less rigid which is reflected in the softness and volatility of plastic crystals.

Timmermanns (182, 183, 184) first recognised plastic crystals as typically containing 'globular' molecules and showing a low entropy of liquefaction. The formation of plastic crystals is due to the capacity of the constituent molecules, over a particular range of temperature, to arrange themselves in a cubic array while at the same time undergoing thermal rotatory displacements so that there is no long range orientational order between the molecules.

Typical examples of plastic crystals are tetramethyl methane, cyclohexane, carbon tetrahalides, hexamethyl ethane, 2-2-dimethyl butane, camphor, neopentane, cyclobutane, perfluorocyclohexane etc. Plastic crystals almost always contain globular molecules, but all molecules that are globular do not give rise to plastic crystals. Methane, silane, Germane and carbontetrachloride all form plastic crystals, Silicon tetrachloride does not. This may be because the longer Si-Cl bonds produce greater molecular inter-locking and thus hinder rotatory displacements.

Because of the less rigidity of the plastic crystal lattice, it is easily deformed or extruded. It may flow under its own weight and is likely to be tacky to touch.

Investigations of thermal properties, x-rays (82), dielectric properties, nuclear magnetic resonance (185) and diffusion have been employed to understand motion in plastic crystals. Plastic crystals at high pressure are reported by Cladis and coworkers (9).

1.g. Mesomorphic Polymers

History of mesomorphic organic compounds is more than a century old but that of mesomorphic polymers is only about 35 years old. Oster (186) reported polymers with liquid crystalline order in aqueous solutions of tobacco mosaic virus in 1950 and in 1956 Robinson (166) reported polymeric liquid crystal solution of poly-(p-benzyl-L-glutamate) in various solvents. Number of synthetic polymers are reported (187, 188, 189). The polymerisation of non-mesogenic monomer within liquid crystalline solvents is reported by Amerik and coworkers (190), Tanaka et al (191) and Blumstein et al (192). Organisation of monomer within the mesomeric solvent has a considerable influence on the kinetics of polymerization and the molecular weight (193). Polymerization of non-mesogenic monomers having mesophase inducive side chain results in polymer with the monotropic liquid crystal properties (194, 195, 196).

Polymerization of mesogenic monomers were studied in mesomorphic state and in isotropic solutions and the polymers obtained were found to be thermotropic in nature. Perplies et al (197, 198) and Wondorff et al (199) studied polymerization of liquid crystal monomers, their structure and the thermotropic liquid crystalline behaviour.

Various types of liquid crystal polymers have been reported. For example (1) Comb-like enantiotropic liquid crystalline polymers (200),(2) rod-like condensation polymers (201),(3) Stiff chain polymer lyotropic liquid crystals (202),(4) poly-(n-alkyl isocyanates) with alkyl side chain length between four and twelve carbon atoms exhibiting both lyotropic and thermotropic mesomorphism (203). Bhadani et al (204) investigated highly substituted cellulose derivatives to study the effect of side chain structure on the mesogenic properties of these polymers. Vora et al (205) studied the effect of solvent and temperature on mesomorphic properties of polymer of p-hydroxybenzoic acid.

A number of patents and reports claiming the production of fibres (Kevlar fibres) from polymer solution existing in the liquid crystalline state are now known (206,207,208). These fibres have tenacities which on weight basis are greater in magnitude than those reported for steel. Kevlar fibres have been shown to be useful as tire cords, as a replacement for glass and steel belts in bias-belted and radial belted tyres. Kevlar 49 has been shown to be competitive with the lower modulus types of graphite fibres in rigid composites. Other applications include conveyor belts, V-belts, roper, cables, body armor, structural parts in aircrafts, circuit boards, fan blades and sporting goods (i.e. golf sticks, skis etc). The p-oriented fibres are used in flame resistant clothing. A detailed account is given in literature (209).

1.h. Biological Systems:

Virchow (210) in 1854 first reported mesomorphic property in the form of Myelin. Biological systems are multicomponent and contain numerous types of macro-molecules, organic ions etc.

Liquid crystalline matter, mostly lyotropic mesophases, favour the formation of complex macromolecules from simple precursor organic molecules (211, 212, 213, 214). Bernal and Faukuchen (215) gave one of the first demonstrations of liquid crystalline phenomenon in a well characterized biological system using x-ray diffraction to investigate solutions of tobacco mosaic virsus. Muralt and Edsall (216) noted birefringence in the case of muscles in 1930. Liquid crystallinity in the case of tissues was reported by Pearse (217). From the study of the structure of haemoglobin, M. Perutz et al (218) concluded that it could assume liquid crystalline form in the red cell. The brilliant work by Engstrom and Finean (219) on the structure of nervous tissues shows the presence of two components in optical opposition in the concentric multilayers of lipid or lipoproteins forming the myelin sheath. It was shown conclusively by Robinson (166) in 1956 that polypeptide-poly-γ-benzene-L-glutamate existed in organic solvents as a cholesteric liquid crystalline spiral. A definite claim that liquid crystals entered the structure of living cells and tissues was made in 1959 (213) when it was shown that complex lipids present in adrenal cortex, ovaries, myelin and in a thermomatous arteries existed at body temperature in a cholesteric mesophase. Detailed study of the mesomorphism in biological systems was done by Stewart (220) and gave reasons why mesomorphism is observed in biological systems. He gave the preparation of artificial mesophase by ternary systems of cholesterol, amphiphilic (lecithin or polyoxyethylene ester) substance and solvent (water). Ambrose (221) studied liquid crystallinity in muscle filaments and has reported the factors controlling liquid crystalline states and their biological interactions.

Knapp and Nicholas (222) reported the isolation of tetracyclic triterpene ester exhibiting smectic and cholesteric mesophase from banana peels and from the seeds of strychnine producing plants in 1968. Evdokinov et al (223) proved a mesomorphic state of nucleic acids.

Recently a review, with forty references, of the properties of cholesteric proteins present in biological systems as cholesteric liquid crystals is being done by Neville (224).

Effect of drugs on liquid crystalline behaviour of model biological membrane is studied by Phadke et al (225). The role of liquid crystal characteristics in the process of biological adaptation is discussed by Panda (226).

1.i. Structural Characteristics of Liquid Crystals:

The two factors influencing to a great extent the liquid crystalline properties are

(A) Molecular geometry and
(B) Intermolecular forces

(A) Though thermotropic mesogens vary in chemical constitution, molecular geometry is a very important factor which influences to a great extent the liquid crystalline properties. Generally molecules of mesogens are elongated and rod or lath-like in shape. They tend to pack in a regular manner, giving rise to a parallel arrangement in crystalline state along their major axis. In such long molecules, presence of polar terminal, middle or lateral groups and polarizable units in p-p' positions along with benzene rings, play an important role in imparting the mesogens with liquid crystalline properties.

(B) Intermolecular forces also play very important role. They are of three types:

(i) dipole-dipole attraction - the direct interaction between permanent dipoles in the molecules,

(ii) induced dipole attraction - arising from the mutual polarization of the molecules by their permanent dipole moments and

(iii) dispersion forces - the interaction between instantaneous dipoles produced by spontaneous oscillations of the electron clouds of the molecules.

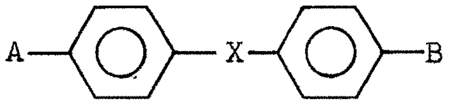
The greater the rigidity of a molecule, the greater is the anisotropy of molecular geometry and the greater is the tendency of the molecule to exhibit mesomorphism.

The non-polar though long molecules of normal paraffins do not possess attractions of type (i) and (ii) and the polarizability of the alkyl chain is not sufficiently high for the dispersion forces i.e. of the type (iii) to be strong. The net result is quite low molecular attractions which are incapable of resisting the thermal breakdown on heating. Hence these turn out to be low melting substances without exhibiting mesomorphic property.

The monomeric molecules of a carboxylic acid possess dipole moment, but its effective packing unit in the lattice is a dimer; the resultant dipole thus should be zero. Naturally in such cases dipole-dipole and induced-dipole attraction will be of little significance. To constitute a potentially mesomorphic system, the long narrow molecules must contain groups of atoms with which are associated permanent dipole moment and the molecule itself must be highly polarizable.

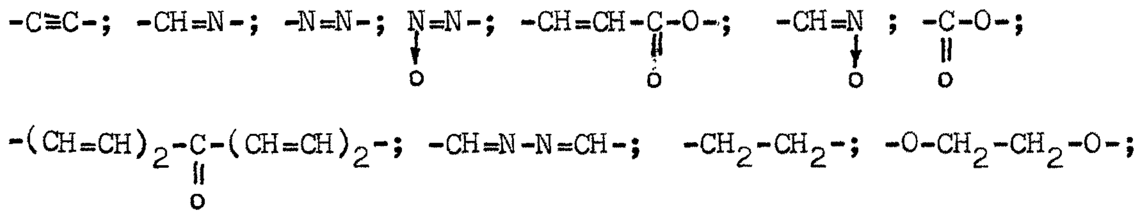
Aromatic Type Compounds

Aromatic Type compounds make up the largest group of known compounds exhibiting mesomorphism. Aromatic nucleii are polarizable, planar and rigid and suitable substituents in correct positions give rise to mesomorphism. For benzene nucleii, substituents should occupy p-positions and be of such a kind that they link up at least one other benzene ring which also carries a p-substituent. It is desirable that the central group which joins the two rings is of a rigid nature, that is the two rings and the central group should constitute a lath or rod-like core of the molecule. Central groups usually contain a multiple bond or systems of conjugated double bonds. It is represented as :



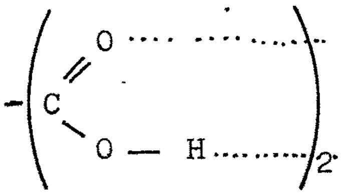
where X is central linkage, A and B are terminal substituents.

The well known central linkages are $-CH=CH-$; $-(CH=CH)_{2-3}$;

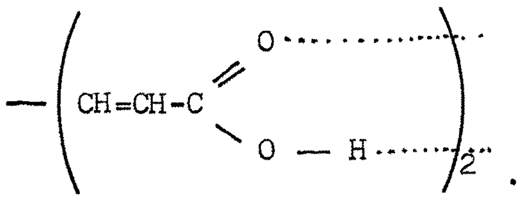


$-C\equiv C-$; $-CH=N-$; $-N=N-$; $\underset{\underset{O}{\downarrow}}{N}=N-$; $-CH=CH-\underset{\underset{O}{\|}}{C}-O-$; $-CH=\underset{\underset{O}{\downarrow}}{N}$; $-\underset{\underset{O}{\|}}{C}-O-$;

$-(CH=CH)_2-\underset{\underset{O}{\|}}{C}-(CH=CH)_2-$; $-CH=N-N=CH-$; $-CH_2-CH_2-$; $-O-CH_2-CH_2-O-$;

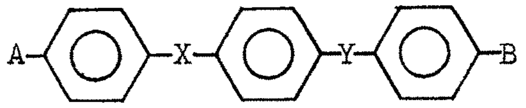


;



Influence of the central group on the mesomorphic property is reported by H.T.Nguyen et.al.(227).

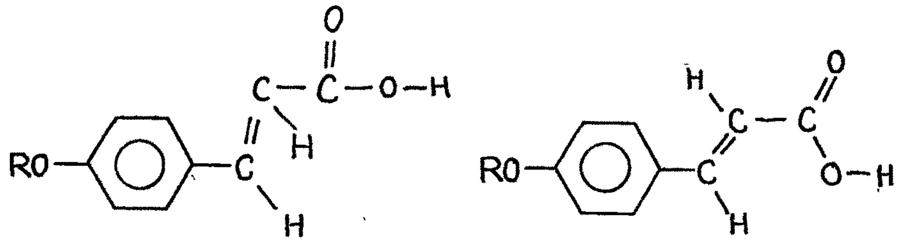
When more than two benzene rings are linked through more than one central linkage, the liquid crystalline properties are enhanced, the effect being the most when all the rings are conjugated. It can be represented as



The linkage of benzene rings with ortho and meta position and introduction of a bulky group or atom at ortho or meta position of benzene rings broadens the molecules forcing them further apart from the parallel orientation (228, 229). Interaction energy falls off rapidly as it is inversely proportional to the distance between the attracting centres. The introduction of dipolar groups into the parent molecules will increase the intermolecular attractions but only if the separation of the molecular axes is not increased too greatly. Thus the introduction of dipolar group into the side of the molecule usually decreases, the thermal stabilities of the mesophases of the parent compound because of the broadening effect (230, 231).

The substitution of fluoro, chloro and bromo atoms in p-decyloxy benzoic acid explains the influence of the dipolar group upon mesomorphism. The fluoro and chloro-substituted compounds exhibit mesomorphism while bromo substituent eliminates the mesomorphic behaviour (230, 231).

Though trans-p-n-alkoxy cinnamic acids (232) and p-n-alkoxy benzoic acids (233) have the same molecular length, the cinnamic acids exhibit more thermally stable smectic and /or nematic mesophases. The cis-p-n-alkoxy cinnamic acids are non-mesomorphic as they do not form linear dimers.



cis-

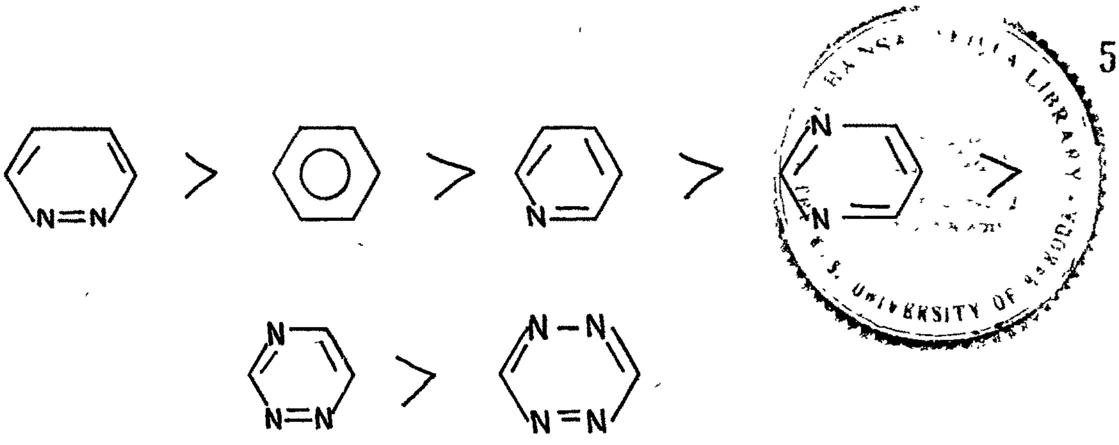
trans-

Fig.4

The greater mesomorphic thermal stability of the cinnamic acids is not attributed to the greater molecule length resulting from the -CH=CH- units, but to the greater polarizability which is conferred on the dimeric molecule by the double bonds.

The greater mesomorphic thermal stabilities of the biphenyl acids (234) than those of the benzoic acids (219) are because of the four aromatic rings in each biphenyl acid molecule (dimeric) versus only two in each benzoic acid molecule (dimeric). Dimers of biphenyl acids will possess more polarizability besides length as compared to the dimers of benzoic acids. Thus not length alone but greater polarizability will be responsible for the enhanced thermal stabilities. Replacement of aromatic rings by saturated alicyclic rings gives reductions in thermal stabilities of mesophases indicating that linearity is an important part of a compound to exhibit mesomorphism (235).

Certain cyclohexane derivatives (236, 237, 238) as well as heterocyclic ring systems (239-242) have been reported to show mesomorphism. The mesophases of 4-trans-4-alkyl-cyclohexane carboxylic acids and 1,4 bis (4'-heptylcyclohexyl) cyclohexane, identified as nematic and S_B phases, confirms the existence of mesogenic molecules without permanent dipolar moment or a delocalized electron. Gray and Nash discussed their mesomorphic behaviour (243). A range of related compounds containing different heterocyclic rings 'X' as the central ring and having either two alkyl or alkoxy groups in the terminal positions is examined by Schubert et al (244, 245). From this data they have given the order of efficiency for the smectic phase. Certain results quoted by Dewar et al (246, 247, 248) are also relevant in this context.



The effect of terminal substituents:

The terminal hydroxyl and amino groups are not usually favourable to liquid crystal formation because of the polymeric hydrogen bonding raising the melting points and favouring a non-parallel arrangements of the molecules (249-250). However, some homologous series with phenolic end substituent showing mesomorphism are reported (251). Study of a range of pure mesogens (252) and mixtures of mesomorphic and non-mesomorphic compounds (253, 254) make it clear that the substituents selected at the p-positions were more efficient than a terminal hydrogen in promoting nematic mesogenic property. Gray (252) gives an average terminal group efficiency order as

$$-\mathrm{Ph} > -\mathrm{NHCOCH_3} > -\mathrm{CN} > -\mathrm{OCH_3} >$$
$$-\mathrm{No_2} > -\mathrm{Cl} > -\mathrm{Br} > -\mathrm{N(CH_3)_2} >$$
$$-\mathrm{CH_3} > -\mathrm{F} > -\mathrm{H}$$

It is noted that $-NO_2$ and $-OCH_3$ substituents which lie high in nematic order are low in smectic order. The same order is maintained for cholesteric systems (254).

Alicyclic compound rings if subjected to certain constraints to diminish its flexibility, give rise to mesogens (255). The flexibility of cyclohexane ring placed centrally in a molecule is very critical, whereas more terminally, this has less serious effects.

Alternation of nematic-isotropic transition or its absence in the case of smectic-nematic transitions, with odd or even number of carbon atoms of the alkyl chain of the terminal substituent has been explained on the basis of zig-zag conformation (256) or on the basis of the considerations advanced by Flory (257) and Marcelja (258).

Most of the terminal alkyl groups found in mesogenic compounds are unbranched but few examples of mesogenic compounds with branched terminal alkyl groups are reported (255). Branching of the terminal alkyl group produces a decrease in the thermal stability of the mesophases (250-255, 259-261). The effect on liquid crystal thermal stability is the greatest when the branching occurs at the first carbon atom of the chain. Movement of the point of branching away from the first carbon atom of the chain towards the end of the chain causes the transition temperature to rise again (260). Branching at any point appears to have greater effect on the nematic than on the smectic thermal stability.

The effect of lateral substituents:

The effects of lateral substituents into the elongated mesogens molecules have been reported (234, 262). The substituents induce two opposite effects : (i) they force apart the molecules and reduce intermolecular lateral cohesions but at the same time (ii) they may increase the molecular polarizability which in turn increases the intermolecular attractions. When the first effect predominates the lateral substituents have three pronounced effects on liquid crystallinity:

(1) lower the temperature at which mesophase appears
(2) decrease the stability of mesophase
(3) destroy any smectogenic property regardless of alkoxy or alkyl group chain length.

But due the second force, liquid crystal thermal stability enhances particularly that of the smectic mesophase (263). O-hydroxy substituted mesogens are exceptions to the above general rule, due to intermolecular hydrogen bonding which increases the overall polarizability of the molecule. Gray (252) gave the order of the substituent effect for the lateral substituents:

Smectic order : $-H < -F < -Cl < -Br < -No_2 < -CH_3 < -I$
Nematic order : $-H < -F < -CH_3 < -Cl < -Br < -I < -No_2$

Gardlund et al (264) studied the effect of lateral methyl group on benzylidene anilines. Several new series are studied for the effect of the lateral long chain, unbranched or branched, substituents (265). Griffin et al (266) investigated the effect of lateral trifluoromethyl group on mesomorphism and correlated it with a lateral methyl group. The effect of a lateral methyl group on the transition temperatures in series of phenylene esters have been studied by Arora and coworkers (267). The introduction of the lateral methyl group decreases the transition temperatures of all phases due to change in molecular conformation as well as broadening of the molecule. The increased dissymmetry, resulting from methyl group leads to less effective packing in crystal lattices and lowering the transition temperatures.

Mesomorphic properties of 2:5, 1:5 and 1:4 substituted naphthalene derivatives have been studied by Gray and Jones (263), Wiegand (268) and Dave et al (269,270) giving the order of stability of compounds as

$$2:6 > 1:5 > 1:4$$

The effects of lateral substitution of the type, which in addition to broadening the molecule, increases its thickness by imposing its steric effect on the system i.e. by causing a twisting about one of the bonds so that parts of the molecule are rotated out of the plane of the remainder of the molecule, are also reported (271, 272). A combination of both breadth and steric effects greatly reduces the thermal stabilities of the ordered arrangement of molecules in the liquid crystal and as expected smectic thermal stability is affected more than nematic thermal stability. Study of compounds with lateral long chain substituents indicate that the nematic state is mainly stabilized by steric repulsions and that the attractive forces play only a secondary role (273).

A.Hauser reports a decrease in the melting and clearing temperatures, deminishing of the optical anisotropy and order parameter but increase in viscosity during the study of the influence of lateral branches on the mesomorphic properties (274).

J.E.Fearon et al have studied the effect of lateral fluoro-substitution on the liquid crystalline properties of some alkylcyanobiphenyls and related compounds (275). They reported that 2-F-substituent causes a greater depression of T_{N-I} than 2'-fluorosubstituent. In non-cyano systems, 2- and 2'-F-substituents in biphenyl derivatives give similar depression in T_{N-I} which are larger than those found in CN systems and the different depressions for the F-substituted CN compounds probably arise because of the effect of the F on the antiparallel correlations of the parent systems. The effects on smectic and nematic thermal stabilities are qualitatively similar but are usually greater for smectic transitions.

1(j) Specific properties and defects

Various techniques like x-ray diffraction, IR spectra, NMR etc. are used to determine properties and structure of mesogens. X-ray studies (276, 277, 278) reveal that the true crystalline packing below the solid-smectic transition, between solid-smectic and smectic-isotropic transition, the diffraction patterns showed evidence for a regular arrangement of layers. The isotropic liquid phase gave no diffraction patterns at all. X-ray examination of nematic mesogens (69) reveal that the molecules in the unit cells are arranged in parallel orientation with their ends imbricated and that nematic liquids and isotropic liquids have similar diffraction patterns (271,279, 280). Diffraction study supported by polarizing microscopy (29) divide nematics into four types, cholesterics into two and smectic E and G into several subtypes.

UV absorption spectroscopy (281) as applied to nematic and isotropic phases failed to give any valuable information regarding molecular interactions but IR spectra of mesophases and isotropic liquids are more or less identical (282). D.Grasso has described a simple method for detecting the phase transitions in liquid crystals by UV absorption spectroscopy (283). IR spectra (284) also indicate the difference between twisted nematic phase and ordinary nematic phase.

Raman spectroscopy of cholesteric liquid crystals (285, 286, 287) and smectic liquid crystals (288) clearly spelt out the structural characteristics (289).

NMR studies (290-295) are also quite interesting and show (296-301) that nematic liquids could be used as solvents to study the NMR spectra of oriented molecules. A number of reviews (302-308) of this types of study have been published.

The technique of E.P.R. is not much applicable to the study of liquid crystalline compounds due to the fact that mesogens are generally not paramagnetic. However, some work (309-314) in this field is noteworthy.

Viscosity measurements (315-319) of nematogenic mesogens indicate a steady fall of viscosity with rising temperature, however, at temperatures close to the mesomorphic-isotropic transition, a sudden rise in viscosity showing a maximum has been observed, followed by a steady fall once again. For smectogens (320) a sudden fall in viscosity exactly at the smectic-isotropic transition without any rise to a maximum preceding the transition has been reported. More studies for pure mesogens (321-322) and their mixtures (323) as well as the study of pre-freezing phenomenon (324) in relation to liquid crystals have been reported.

Surface tension measurements of liquid crystals by different techniques have been carried out by a number of researchers (325-330). While some of the results confirm and support mutually, some are contradictory.

Kast (280) provided a critical review of the work done in the field of dielectric constant measurements of mesogens. Abrupt changes in dielectric constant as the mesophase is transferred to isotropic liquid were observed (331). The dielectric properties were found to vary with the velocity of flow, strength of the applied magnetic field and temperature (332). Changes in dielectric constant in longitudinal and transverse magnetic fields, up to 5,000 gauss (333) and effect of shear on dielectric constant of mesophases (334) have been reported. The effect of dielectric field on molecular alignment in the mesomorphic state (335) and exhibition of negative dielectric anisotropy (336) are some of the more recent studies. Recently, dielectric studies of n-OBCAB in the S_A, reentrant nematic and reentrant S_A phases is carried out by Shashidhar et al (337). Effect of smectic ordering on the dielectric properties of reentrant nematic mixture was carried out by Ratna et al (338).

DSC technique has been used to measure specific heats of nematic, smectic and cholesteric liquid crystals (339) and relationship of the transition enthalpies with some specialities of molecular structure by calorimetric investigation have been shown (340). Glassy states of smectic mesophase have been established by the DTA studies of a series of anils (341) for the first time. That the changes in nematic-isotropic transition temperatures arise from changes in the entropy of transition and not in the heat of transition (342) have been shown. Heat capacities of a disc like mesogen (343) have also been reported. Miyajima et al (344) revealed complex phase relation of p-n-hexyloxybenzylidene-p'-toluidine by DTA. Crystal-crystal phase transitions are revealed by Tsuji et al (345). The effect of heating rates on transition temperatures and the shape of DTA curves was correlated by Fodor et al (346). Semendyaeva et al (347) investigated binary systems forming liquid crystals by DTA. Smectic polymesomorphism of some liquid crystalline compounds, in mixture, upto 3 Kbars by DSC is investigated by Spratte et al (348).

Mössbauer effect (349, 350) and Ultrasonics (351-355) effect of pressure on mesomorphic phases (356-357) have been studied in details.

It is only logical to think of defects in liquid crystals as well known since long in solid crystals. The polarizing microscope has been from the start the favoured instrument to study the defects in liquid crystals. Lehmann (358) described defects and textures though a large number of them may have to be rediscovered. Friedel and Grandjean (23) imparts character to the defects and indicates clearly how the study of defects throws light on structural properties of the phase in which they exist. Such a study classified liquid crystals into nematic, cholesteric and smectic phases. Defects such as of smectic textures, linear elasticity and dislocations, confocal domains etc. have been studied in good details (359). Orientation defects in the smectic C phase (360) have been studied. Dialatometric technique was used by Guillon et al (361), stimpfle et al (362) and Armitage et al (363) to study smectic polymesomorphism or phase change in mesogens.

1.k. Mixed mesomorphism

When mesomorphs are mixed, their melting points as well as transition temperatures depress in the usual way following more or less the law of mixtures. Different types of mixtures where none, one or both components are mesomorphs have been investigated. Tamman (12), Lehmann (358), Smiths (364) and Vorlander and Ost (360) showed the depression of melting points and transition points in the phase diagrams of the mixtures showing liquid crystalline property. Schenck (365) and Schenck and Schneider (366) reported that nematic-isotropic temperature of p-azoxyanisole is lowered by the addition of other substances. The extent of mixed mesophase and the effect of terminal substituents in the exhibition of mixed mesomorphism have been studied in greater details by Dave and Dewar (367), Dave and Lohar (368), Dave and Vasanth (369), Lohar and Shah (370), Lohar and Patel (371), Lohar and Mashru (372) and Lohar and Dave (Jr.) (373).

If two mesogens are totally miscible in a mesomorphic state the corresponding mesophases of the two pure components are of the same type. With more than thousand binary phase diagrams studied no exception is found to the five following miscibility rules:

(1) Two compounds each exhibiting a mesophase of the same type are not everytime totally miscible in this mesomorphic state (the reciprocal to the definition does not exist).

(2) If two mesophases can form a two phase system in equilibrium these two mesophases are of different types.

(3) Till now we know only ten different types of calamitic (smectic and nematic) mesophases.

(4) Except for the reentrant nematic and reentrant smectic the succession order for the calamitic mesophases versus temperature is constant for pure compounds.

(5) Two enantiomers are totally miscible in all the non-solid states.

Bogojawlenslay and Winogrodow (374) deduced from their study of mixed mesomorphism the latent transition temperatures of non-mesomorphic substances by extrapolation method much earlier. Walter (375) reported similar cases, however,Dave and Dewar (367) critised the extrapolation method since they obtained different values for latent transition temperatures of a non-mesomorphic substance depending upon whether the liquid crystalline component was p-azoxyanisole or p-azoxyphenetole. Later on better evidence in favour of the accuracy of the extrapolation method was found by Dave and Lohar (368). More evidences in support of the extrapolation method prescribing certain definite conditions for better reliability have been brought out by Lohar and Shah (370), Dewar and Goldberg (376), Lohar and Patel (371) and Lohar and Mashru (372).

de Kock's (377) contention that there should exist a range of temperature over which two liquid phases - one isotropic and another anisotropic co-exist was questioned by Dave and Dewar (367) who after reexamining the system studied by de Kock reported that the mixed liquid crystalline region is a single homogeneous phase.

Quite interesting results have been obtained by mixing p-azoxyanisole with different schiff bases by Dave and Dewar (367) and Dave and Lohar (368) and deduced an order of efficiency of the terminal groups for exhibiting nematic mixed mesophases. Margerum et al (378) studied the effect of molecular length on nematic mixtures.

On the basis of miscibility criteria and texture phenomena Demus (27) and Sackmann, Demus and Gray (379,380) have identified smectic mesophases. A numerical technique has been used by Domon and Billard (381) and Hulme and Raynes (382) to predict the eutectic composition of some liquid crystalline mixtures.

Lohar and Dave (Jr.) (373) and Labes et al (383) have reported an induced smectic mesophase in some binary mixtures recently. Waclawek (384) and Wagner (385) have discussed intermolecular forces operating in induced smectics. Derfel (386) has discussed pre-transitional effects in nematic mixtures exhibiting induced smectic phase. Iida (387) reported induction of a nematic phase by intermolecular charge transfer interaction and application of solid solution model. The ferroelectricity in the mixtures of chiral with non-chiral smectic C is discussed by Matsumara (388). Binary mixture method was used to ascertain that nematic-smectic A transitions were of second order (389). Isobaric phase diagrams, by contact method, of smectic phase are reported recently which exhibit non-ideal behaviour (390).

Phase diagrams of some mixtures of nematic liquid crystal and ordinary liquid or normal aliphatic alcohols was studied by Gidley et al (391) and Trostina et al (392) respectively. Effect of isomerism of butyl alcohol on the mesomorphic properties of a binary system was studied by Pirogov et al (393). A method is proposed for calculating the transition temperature of a two component mixture of nematic liquid crystals by D. chen and

G.Huang which is also suitable for a many component mixture (394). The transition temperatures of mixtures were calculated and agree well with experimental values.

Mixed mesomorphism is made use of in electrical appliances. The mesomorphic compounds when mixed with other non-mesomorphic or mesomorphic substances in proper proportions, give rise to a stable room temperature mesomorph which may find many useful applications (395-396).

1.(1) Applications of Liquid Crystals:

Optical and physical properties of liquid crystals are mainly made use of in their practical applications. The applications of liquid crystals can be classified in three major groups viz.

(a) Thermographic measurements
(b) Display devices
(c) GLC techniques

(a) Thermographic Measurements

Thermography is, perhaps, the earliest application developed in 1965. Thermography or surface temperature mapping is based on the fact that some of the mesogens reflect different colors at different temperatures. The pitch of a cholesteric liquid crystal decreases as the temperature is increased. If the consequent change in the wavelength of reflection spans the visible range between say temperature t_1 and t_2, any temperature within these limits can be read off simply by noting the reflected color. Temperature sensitivities of the order of 0.5°C for entire visible range are easily achieved by mixing two or more compounds in different ratios. It is proved useful in medicine.

Cholesteric mesogens in mixtures are normally used for preparing suitable films. In the thermal mapping of the human body, liquid crystals are applied to the surface of the skin to locate veins, arteries and other internal structures that transmit heat at a different rate from that of the surrounding tissues. Area of skin lying over veins and arteries are slightly warmer than other areas and the thermal map provided by a film of cholesteric mixture clearly indicates in color the paths of these veins and arteries. The application of skin thermography in the medical field (397-399) are therefore concerned with the detection and response to treatment of vascular diseases and subcutaneous tumours. Suspected cancer is also indicated by the local color change as a result of higher temperature (400, 401). Because of their unique color properties, cholesteric liquid crystals can be employed to indicate temperature field patterns and for color picture screens (402,403). Liquid crystal containing device for measuring and displaying temperature has been reported (404). Liquid crystal display devices have also been reported (405-409). Bicyclic- , tricyclic- and tetracyclic ethanes, pyridazines and tetracyclic chloro-diesters exhibit distinct physical characteristics, such as low viscosities, low elastic ratios, large mesomorphic range, large negative dielectric anisotropies and/or low dielectric relaxation frequencies, for use, in displays for automobile (410).

The cholesteric liquid crystals incorporated in polymer rods or foils can be used to measure temperatures. It is very useful for the rapid detection of fever especially by oral temperature measurements (411).

Liquid crystals can be used to find cracks in metal surfaces and coatings (thermographical analysis). They can also be used for testing metallic joints, insulation in refrigeration and cooling units.

Cholesteric liquid crystals can also be used to monitor temperature distributions in active electronic circuits, high resistance connections, surfaces and sub-surface films (412).

They also find use as analytical tool to detect the presence of small amounts of gases or of solvent vapours by means of color changes (413). The color of liquid crystals is not dependent upon temperature alone. Both chemical and mechanical changes can bring about color changes. For example, extremely small amounts of certain chemical vapours produce color change in liquid crystals. If liquid crystals merely serve as a solvent for the vapour, their color change will be reversible. On the other hand, if they react chemically with the vapour, the color change will be permanent. Usually only a few ppm of the chemical vapour can produce an immediate color change. The use of liquid crystals for the detection of traces of toxic chemical vapours in air shows great promise. For instance, the unburnt hydrocarbons usually found along with carbonmonoxide could be detected. Air pollution monitoring devices have been developed based on this principle. Recently Chilaya et al report a new nematic-chiral mixture for application in thermography (414).

In short, liquid crystal thermal devices are used for (i) measuring the temperature of the body and room (ii) non-destructive testing of electronics component composites and bonded structures (iii) protective devices (iv) monitoring the temperature of milk in baby feeder bottle, bath tubs, hot water taps etc. and (v) detecting microwaves and displaying their intensity through holography.

(b) Display devices:

The most important technological application of liquid crystals, however, is in digital display devices. Liquid crystal display devices are made by sandwiching a thin film of liquid crystal between two sheets of glass. The inner surface of each sheet is coated with a transparent, electrical conducting material such as tin oxide. When a small positive charge is applied to one sheet and negative charge to the other, liquid crystal film turns opaque instantaneously, The electrodes can be arranged in different segments or elements of the display device so that, when energised they produce either a number, a letter or image as in digital wrist watch or calculator readout.

They may be used in certain types of light valves, memory circuits, rear projection screens and display panels. Liquid crystal display (LCD) devices at present consist of digital read outs on several instruments and watch faces. Nematic liquid crystals, together with cholesteric liquid crystals are used in storage mode liquid crystal devices. The storage mode materials may find application in devices that display information which does not change frequently, for example, highway signs, arrival and departure boards at airports and railways. Such display systems also hold the key to graphic displays and flat TV receivers. Small experimental models of such TV sets have been made in Japan and USA. There are two advantages of such devices over other electronic devices. First, they reflect light instead of generating it. So they can be viewed in full light without being 'washed out' by the incident light and under a wide range of lighting conditions including direct sunlight and flood lighting. Second, they do not emit light and therefore draw much less power than light emitting diodes and are inexpensive to operate.

In thin layers, nematic liquid crystals change their transmission properties for normal or polarized light when subjected to an electric field. This phenomenon can be utilized for alphanumeric and analog displays, image converters and matrix type picture screen (415-417), Hareng et al (418) have summarized this work. Liquid crystals are used in flat screen TV and storage displays (419). Reflective type of LCD is reported (420) which is more readable than the conventional one. Cholesteric liquid crystals are used with nematic liquid crystals to give systems capable of storing information. Recently, some display devices using nematic and cholesteric liquid crystals were reported (421, 422, 423).

LCDs are advantageous due to low operating voltages, low power consumption, ability to withstand high levels of light (as liquid crystals scatter light) and low cost. Disadvantages are difficulty in cell fabrication, life time, response time and viewing angle considerations. The applications of smectic and cholesteric liquid crystals to electrooptical and thermooptical display devices are reported (424).

An intriguing possible application of liquid crystals is their use as anisotropic solvent to study the influence of the partial orientation on the reaction rate of chemical reactions. The rate of thermal decomposition of picric acid in azoxyanisole was studied by Svedberg (425). Orientation of nematic phase by a magnetic field decreased the rate of decomposition. Moreover, a sudden increase in the rate of picric acid decomposition was observed at the nematic to isotropic transition. Brown (426) studied the reaction rate of the Claisen rearrangement in a nematic state and Barnett and Sohn (427) studied the pyrolysis of xanthate in nematic solvents. W.J. Leigh has investigated the use of liquid crystal solvents to effect stereochemical control in the Diels-Alder reaction (428). Nematic liquids may serve as good solvents for many molecular rearrangements and polymerization reactions. More applications in the field of liquid crystals are from Japan (429,430).

(c) GLC techniques:

Number of research papers are being published illustrating the unique property of liquid crystals in separation of structural isomers (431,432,433). Liquid crystals provide better separation of isomers than the conventional stationary phases.

Kelkar (431) and Dewar and Schroder (433) showed that meta- and para-disubstituted benzene may be separated much better by using liquid crystals as stationary phase than with conventional column packing materials. The work of Martire et al (434) supports this view. The para isomer is more soluble and is retained longer. This behaviour is interpreted in the light of the current theories of nematic solutions and a separation mechanism is proposed. The extent to which this mechanism may be extended to other geometric isomers is also proposed (434).

Panse et al (435-438) used laterally substituted liquid crystals as stationary phase in GLC. Authors found that lateral substitution on the middle ring has a profound influence on the relative retentions of isomers. Liquid crystals coated glass microbeads were used in GLC columns, which have high efficiency and wide temperature range (439). Sojak et al (440,441) and De Leone et al (442) reported separation of hydrocarbon isomers on cholesteric mesophase.

Liquid crystals are reported in separation of mixtures of disubstituted benzene isomers (443,444).

Binary and ternary mixed liquid crystal stationary phases of eutectic composition are also studied for the selectivity of the isomers (445,446). The selectivity of the mixed phases can be predicted at any temperature if the properties of the single phases are known. At the melting point, the selectivity of the mixed phases is usually higher than that of the single phases. The efficiencies of columns with mixed phases are reported to be usually higher than expected from the additivity principle (447). A.Ziolek et al (448-449) have reported the effect of lateral substituents on the properties of liquid crystal as stationary phases in gas chromatography. Laterally substituted liquid crystals with high potential for the separation of positional and geometric isomers of various aromatic compounds when used as stationary phase in gas chromatography has been reported (450). A method is proposed for evaluating liquid crystal stationary phases for gas chromatograph by analyzing the thermodynamic functions of sorbate solutions (451). The ordering of the liquid crystal phase affects essentially the chromatographic separation.

Disc-like liquid crystals belonging to the triphenylene derivative group are also tested as stationary phases (452). Differences are found in the behaviour of disc-like and rod-like liquid crystal phases. On disc-like liquid crystals, compounds with a linear molecular structure are easily separated from those with a cyclic structure having similar boiling temperatures.

So far mostly nematogenic compounds and to some extent cholesteric compounds are studied for gas-liquid chromatography. Smectogenic and reentrant liquid crystals are also proposed and used as stationary phases for the gas chromatographic separation of disubstituted benzene, naphthalene deri.; biphenyl deri. etc. (453). These isomers could not be separated sharply by the S_B state, whereas they were separated completely by both S_A and S_C states. It is suggested that the unique selectivity of the S_A and S_C states can be explained by the difference in the mode of molecular packing between S_B and S_A or S_C.

These are by no means all the possible applications of liquid crystals. These are for instance, well-developed academic applications. The structure of anisotropic molecules can be studied by dissolving them in liquid crystals and then studying the spectra (NMR, optical etc.) of the oriented solute molecules. Suffice it to say that research in the area of liquid crystals has been growing rapidly in the past few years.