INTRODUCTION

CHAPTER - 1

INTRODUCTION

1.A.1 - GENERAL

Earlier, it was a belief beyond doubt that matter exists in three forms only Viz - solid, liquid and gases. But now, another intermediate state is also known which is in between solid and liquid states of matter but still much more important from application point of view that it cannot be ignored, though intermediate in character. The intermediate state is known as 'meso-phase' or 'mesomorphic state' or simply 'mesomorphism' and the compounds exhibiting this unique phenomena are termed as 'mesogens', mesomorphs' or 'liquid crystals'.

The study of mesomorphism gained momentum only during the last two decades because of the expanding horizons of applications of Liquid crystals to a variety of fields including medicine and electronic industries. Though not every new liquid crystal has turned out to be useful but the potential utility value cannot be denied since more and more usages are being explored thoroughly.

Reinitzer (1) first observed a cloudy melting point at 145°C and then another clear melting point at 176°C while studying the nature of cholesteryl benzoate. Only a year later, Lehmann (2) confirmed this unique property of some compounds and gave the name 'fluid crystals' or 'liquid crystals'.

A simple explanation may suggest the formation of liquid crystals. It is a matter of common experience that compounds when heated melt to clear liquids sharply at a definite temperature characteristic of every compound. The external thermal energy received by the molecules or atoms make their bonds loosened imparting them a kind of freedom which results in the attainment of liquid state. The temperature at which the transformation takes place being definite. As solids are regarded to be as orderly domain structure, the intake of thermal energy disturbs the inertia bearing rigidity which disappears to give rise to fluid characters. However, in certain compounds while the domain structure gets loosened enough to cause flow at a certain temperature, the thermal energy received at this level is not enough to shatter the crystallanity completely. Consequently, a sort of residual orderly orientation of molecules persists until another temperature is reached that causes the molecules to be deprived of the regularity of structure altogether. Between these two temperatures, the molecule displays unique properties characteristic of neither true solid state nor liquid state. Thus, it may be regarded as an independent state of existance appearing within a definite temperature range.

The liquid crystals are non-isotropic turbid and viscous fluid having optical properties such as birefringence, the property usually associated with crystalline solids.

1.A.2- NOMENCLATURE

First objection to the name liquid crystal was raised by Friedel (3) and then by Friedel and Friedel (4), on the basis that the actual state is neither completely solid nor really liquid. Thus came the name 'mesomorphic state' (3) some other terms frequently used are mesogens, mesoforms, mesophase, crystalline liquids, eutactites (5), and para crystals (4), but the more accepted term for the phenomenon is mesomorphism (6).

1.A.3 - CLASSIFICATION

Lawrence (7) and then Jelly (8) classified the mesomorphic state on the basis of the manner in which it is prepared in two classes - (1) thermotropic mesomorphism - mesophase induced by means of heat and (2) lyotropic mesomorphism - mesophase induced by means of solvation, the solvent generally is water.

A comparatively new classification was propounded by Gray and Winsor (9) using the terms amphiphilic and non-amphiphilic mesogens.

The amphiphilic mesogens are called lyotropic and non-amphiphilic mesophases are commonly called as thermotropic and can be represented by Fig.1.

Liquid Crystals

Thermotropic (non-amphiphilic)	Lyotropic (amphiphilic)

(i) --- Smectic: S_A, S_C, S_B, S_F, S_D, S_E, S_G, S_H.

(ii) --- Nematic:- +ve nematics
-ve nematics (Discotic)
carbonaceous.

(iii) --- Cholesteric

Fig.1.

Timmermanns (10) classified the mesomorphic compounds into two major groups - (i) Plastic crystals and (ii) Liquid crystals. The basic difference between two classes is the molecular shape and geometry. The plastic crystals are globular and compact molecules undergoing sharp transition on heating first to the cubic optically isotropic plastic crystal and then to amorphous liquid. While the liquid crystals are long, rigid, and rod-like molecules. Gray and Winsor (11) have reviewed some rare cases of emergence of plastic crystal mesophase as a further mesophase of the series of liquid crystalline phases at high temperatures.

1.A.4 - MESOMORPHIC STATE

The first explanation regarding the emergence of liquid crystalline phase was given by Tamman(12), Nernst (13) and Quincke (14) also supported the view of Tamman that the mesophase is actually a two phase system owing to suspension of small crystals in the isotropic liquid or presence of impurities in the compound resulting into formation of an emulsion of two liquids. But attempts to separate the emulsion into its constituents by electrostatic methods (15) and centrifugal methods (16) failed. Schenke (17) and Vorlander (18) critisized the emulsion theory and argued in favour of liquid crystalline state. A.C.de Kock (19) repeated Tamman's experiment but his results did not support the theory presented by Tamman.

Thus, it was established (20, 21) that liquid crystalline state is truely a physical state which is intermediate between isotropic liquid and crystalline solid state, and the transitions in case of mesogens can be written as follows -

$$\text{crystalline state} \xrightarrow[t_1]{\text{temp}} \text{Liquid crystalline stage} \xrightarrow[t_2]{\text{temp}} \text{Isotropic liquid.}$$

Thus, the states of existance of matter may well be represented as follows -

$$\text{crystal} \underset{t_2}{\overset{t_1}{\rightleftharpoons}} \text{liquid crystal} \overset{t_2}{\rightleftharpoons} \begin{array}{c}\text{Isotropic}\\ \text{liquid}\end{array} \xrightarrow{t_3} \text{gas}$$

As the transitions t_1 and t_2 take place at definite temperature, the states are reversible, but normally this reversible change from L.C. to C is achieved by supercooling, though no such supercooling is observed during cooling the isotropic liquid to liquid crystalline state. This type of transition where t_2 is the higher temperature than t_1 is termed as "enantiotropic transition" and the phase obtained is known as enantiotropic mesophase.

But sometimes on heating a mesogen may melt to an isotropic liquid at t_1° directly and on gradual cooling, temperature may fall below t_1, before crystallization occurs. If a mesophase has a stable range just below the melting point then during supercooling, it may appear before crystallisation. In this case t_2 temperature will be lower than t_1. This type of mesophase is termed as monotropic mesophase. The above changes may be represented as --

$$\begin{tikzcd}
\text{Crystalline state} \arrow[rr, "t_1"] & & \text{Isotropic liquid} \arrow[dl, "t_2"] \\
& \text{Liquid crystal} \arrow[ul, "t_3"] &
\end{tikzcd}$$

1.A.5 THERMOTROPIC MESOPHASES

Liquid crystalline compounds are long rod shaped molecules having polar terminal groups, in their crystalline state, the structural units are tied together with a strong binding force. On gradual heating, the thermal energy breaks down the weaker forces of the molecule allowing restricted movement causing a fluid condition. But at this stage the thermal energy is not sufficient enough to break down all the binding forces, or to overcome the forces responsible to maintain an ordered structure. Due to a preferred parallel orientation of the molecules in partially fluid state, light is scattered giving rise to birefringence under polarising microscope. These birefringent patterns of mesophases as 'textures' (22) and the mesogens in three categories on the basis of molecular arrangement which gives rise to those textures. The three categories are:

(i) Smectic - (gk - Smectos = soap like)

(ii) Nematic - showing thread like texture under polarising microscope.

(iii) Cholesteric - named as cholesteric as these mesogens are mostly derivatives of cholesterol.

Though Vorlander (23) criticised this nomenclature for lack of proper significance, no other nomenclature is suggested and the above nomenclature is now universally accepted.

(i) Smectic mesophase

Smectic mesophase is the most ordered one exhibited by organic solids which are already stratified molecules. The thermal energy received at the temperature in which the smectic phase exists is not sufficient enough to break down lateral cohesions, but it disrupts end to end molecular cohesions only. Thus the molecule get loosened and acquires a little flow, the lateral adhesion and layers remain intact retaining a two dimensional order.

The Smectic mesophase appears in the forms of terraced textures under polarising microscope. These terraced texture or strata are called as 'grandjean plates' (24). The glidening of these plates over one another can be observed clearly if the coverslip is disturbed slightly, but the movement is restricted to one direction only. This leads to the view that the molecules lie in dimensional layers with their long axes parallel to one another and perpendicular to the plane of terraces. Obviously, the cohesion between two layers is quite weak which account for the characteristic layer flow.

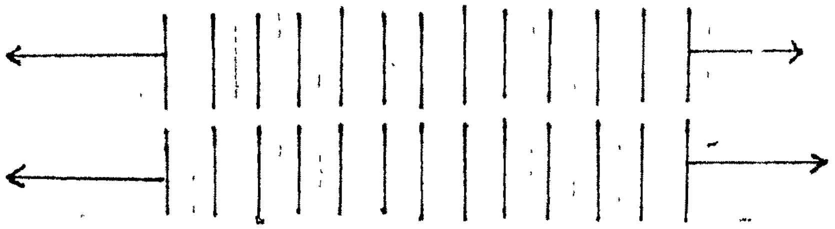


fig-2 Molecular arrangement in smectic mesophase.

On further heating, the smectic mesophase may pass into isotropic liquid phase as depicted below -

$$\text{Crystalline solid} \overset{t_1}{\rightleftharpoons} \text{Smectic mesophase} \overset{t_2}{\rightleftharpoons} \text{Isotropic liquid}$$

There is a large number of compounds, however which exhibits both smectic and nematic or cholesteric mesophases, the changes may be depicted as -

$$\begin{array}{c}\text{Crystalline}\\\text{Solid}\end{array} \xrightleftharpoons{t_1} \begin{array}{c}\text{Smectic}\\\text{mesophase}\end{array} \xrightleftharpoons{t_2} \begin{array}{c}\text{Nematic or}\\\text{cholesteric}\\\text{mesophase}\end{array} \xrightleftharpoons{t_3} \begin{array}{c}\text{Isotropic}\\\text{liquid}\end{array}$$

The emergence of more than one type of mesophase is called "polymorphism." Many compounds of mesogens show polymorphism in smectic mesophase also, where more than one smectic phase appears besides nematic or cholesteric phase. The changes may follow the path---

$$\begin{array}{l}\text{Crystalline}\\\text{solid}\end{array} \xrightleftharpoons{t_1} \begin{array}{c}\text{smectic}\\\text{II}\end{array} \xrightleftharpoons{t_2} \begin{array}{c}\text{smectic}\\\text{I}\end{array} \xrightleftharpoons{t_3} \begin{array}{l}\text{nematic}\\\text{or cho-}\\\text{lesteric}\end{array} \xrightleftharpoons{t_4} \begin{array}{l}\text{isotropic}\\\text{liquid.}\end{array}$$

- On cooling the isotropic liquid, the smectic phase appears in the form of small drop like birefringent particles which are known as batonnets. These batonnets increasing in number with the fall of temperature, coalesce and shows a focal conic texture characteristic of smectic mesophase. The texture gives a fan-shaped appearance under polarised light. The study of focal conic structure is largely due to Friedel (22). Drago (25) has given an excellent account of focal conic structure and the geometry involved which provides sufficient evidence for the layer theory of the smectic structure.

Smectic phases can be differentiated into two types (26), one with unstructured layers and the other with structural layers. The most common smectics are in the first group which includes the phase defined as Smectic-A and Smectic-C. The most common representation of the second group is classified as smectic B.

Sackmann and Demus (27) and their co-workers (31) have examined a number of smectic compounds and their mixtures with one another in order to assign structures to the smectic mesophase from the rule of miscibility in mixed liquid crystal formation. They have classified smectic phase according to the textures observed in microscope.

TABLE - 1

Texture classification of Smectic Mesophase (31).

Type of smectic mesophase	structure		Texture
Smectic A	Planar	(i)	Stepped drops
		(ii)	Oily streaks
		(iii)	Homeotropic
	Non-planar (Dupin cyclides)	(i)	Simple polygonal
		(ii)	Simple fan-shaped
		(iii)	Batonnets
		(iv)	Bubble texture
Smectic C	Cylinders planar	(i)	Myelinic texture
		(ii)	Homogenous
		(iii)	Stepped drops
		(iv)	Schlieren textures
	Non-planar (Dupin cyclides)	(i)	Broken polygonal
		(ii)	Broken fan shaped
		(iii)	Batonnets
	Twisted	(i)	Planar
		(ii)	Schlieren
		(iii)	Striated fan shaped.
Smectic F	Planar	(i)	Schlieren
		(ii)	Stepped drops
	Non-planar (Dupin cyclides)	(i)	Stripped, broken, fan shaped texture

Contd.

Smectic B	Hexagonal planar	(i)	Mosaic texture
		(ii)	Homeotropic
		(iii)	Stepped drops Batonnets Ovals Lancets
	Non-planar (Dupin cyclides)	(i)	Focal conic textures paramorphosis
	Tilted	(i)	Mosaic texture
		(ii)	Planar texture (optically active)
Smectic E	Planar	(i)	Mosaic
		(ii)	Stepped drops
	Non-planar	(i)	Striated
		(ii)	Stripped fan shaped
Smectic G	Planar	(i)	Mosaic
		(ii)	Stepped drops
Smectic D	Cubic	(i)	Isotropic
	Bands	(i)	Mosaic texture

The sequence of emergence of these smectic mesophase in a polymesomorphic compound is as follows ---

Isotropic ---► Nematic ---► Smectic ---► Smectic ---► smectic
liquid A C B

Herrmann (28) and Chistyakov (29) reported after studying the X-ray diffraction pattern by smectic A mesophase that the molecules are arranged in parallel layers, their distribution with respect to lateral direction is statistical.

Sackmann and Demus (30) reported several smectic phases and named them from smectic A to smectic G. These forms of smectic mesophases can be distinguished clearly by miscibility studies. However, de Vries (32) classified the smectic mesophases into three main classes on the basis of X-ray studies and referred to them as α, β, and γ smectic mesophases.

It is clear thus that two notations exists for distinguishing smectic mesophases. One that of Sackmann and Demus (30) named smectics according to the order of their discovery and differentiate them on the basis of their texture and the other that of de Vries (32) who lists them according to increased order in molecular packing. Sackmann and Demus (30) do not consider smectic H as a separate phase where as de Vries (32) and MCMillan (33-34) do.

Smectic α

These are the least ordered smectics, according to de Vries classification, though the layer structure corresponds to a certain degree of positional order, the degree of order within the plane is low. This class contains smectic A, C, F and D phases of Sackmann and Demus (30).

(i) S_A (α_1) - This is the most frequent smectic and is obtained at high temperatures. The molecules in the layered structure stand perpendicular to the layer and are disordered, corresponding to a two dimensional liquid (36, 35). The degree of order is quite similar to that of S_C (37) indicating that the S_A-S_C transition may be of second order.

Amer and Shen (38) studied the raman spectra of α_1 mesophase and stated that rapid reorientation about the long molecular axis occurs in this mesophase. Their study also indicate that the interlayer interaction is weaker in the solid. NMR studies (39) also supports the view.

(ii) $S_C(\alpha_2)$ - The molecules exhibiting this phase are disordered with the layers but tilted thus, this phase is regarded as a tilted smectic A. There may be three types of smectic C phases -

(a) Smectic C with a temperature dependent tilt angle which does not exhibit smectic phase at a high temperature (36).

(b) Though tilt angle is found to temperature dependant, it exhibits smectic A mesophase at higher temperatures (36, 40).

(c) Recently a new twisted smectic A structure has also been reported (41-44). The phase was classified as a type of cholesteric by de Vries (32). He also suggested reclassifying smectic into four types.

NMR studies by wise (36) clearly indicate the similarity between smectic A and smectic C possessing fast molecular reorientational and translational diffusion.

(iii) S_F (α_3) - The information about this phase is mainly due to the Sackmann and Demus (30). The Smectic F has a layered structure quite similar to that of Smectic C, but the phase is much more ordered and thus exists at a lower temperature only. Not much structural description is available.

(iv) S_D (α_D) - In terms of order, this phase is an intermediate to SA (α1) and Sc (α2) between which it may exist at temperature scale. However as deVries (32) states there is some doubt as to the way to classify this phase.

2. Smectic β phases - This class of de Vries classification contains only one smectic phase so far that is smectic B. Though de Vries (32) cites evidence in favour of the presence of another type of mesophase i.e. Smectic H, Sackmann and Demus (30) reject the idea on miscibility ground and classify it as a tilted Smectic B giving it the notation BC. de Vries (45) suggested SB phase as an ordered layered structure with molecules aligned normal to the layers. Levelut (46) suggested this phase is having a high degree of order in the layers and the molecules conform to a hexagonal arrangement in the layers. However, if Smectic B is a crystal or a liquid crystal is still a question.

3. Smectic γ phases - There are three phases in this classification -

(a) SE (γ_1) : The SE mesophase may appear as a normal SE mesophase (30) or tilted SE mesophase (30, 32). de Vries suggests the existence of a three dimensional lattice in this dimensional order is largely removed.

(b) SG (γ2) - The X-ray patterns of SG and SH are found to be quite similar (32). The arrangement of molecules within the layers is also regarded as non-random.

(c) SH (γ3) - The phase is regarded as tilted Smectic B structurally but the molecular arrangement is found to be of a three dimensional monoclinic lattice (43).

Interdigitated Smectics

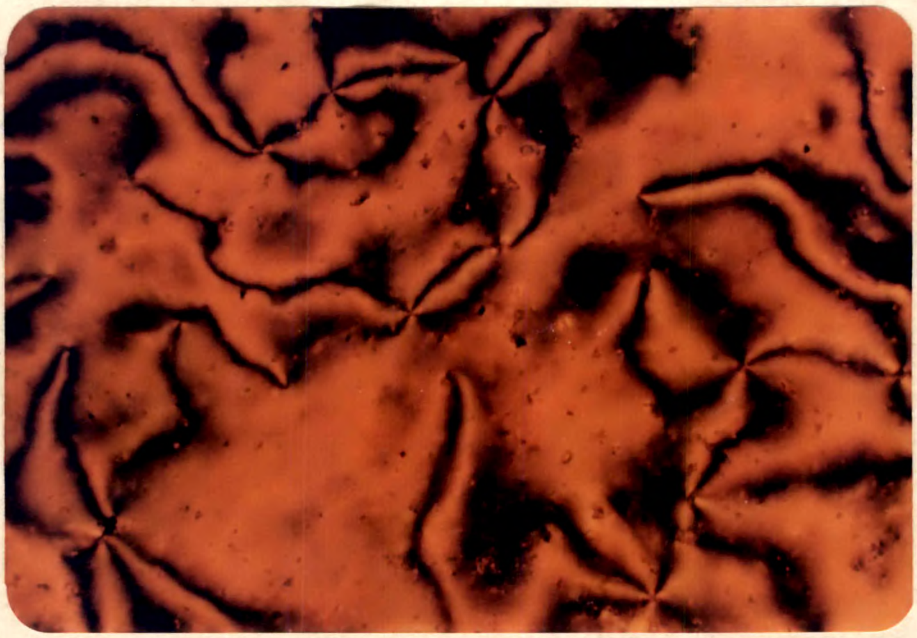
This new family with the structure of a highly ordered smectic like phase is recently reported by de Vries (49). The molecules are arranged in layers with their alkyl tails are fully interdigitated with the tails of molecules of adjacent layers. The currently known smectic phases are therefore suggested to be called as segragated Smectics.

Recently, a new mesomorphic sequence with reentrant smectic phases is also observed (50).

Nematic Liquid Crystals

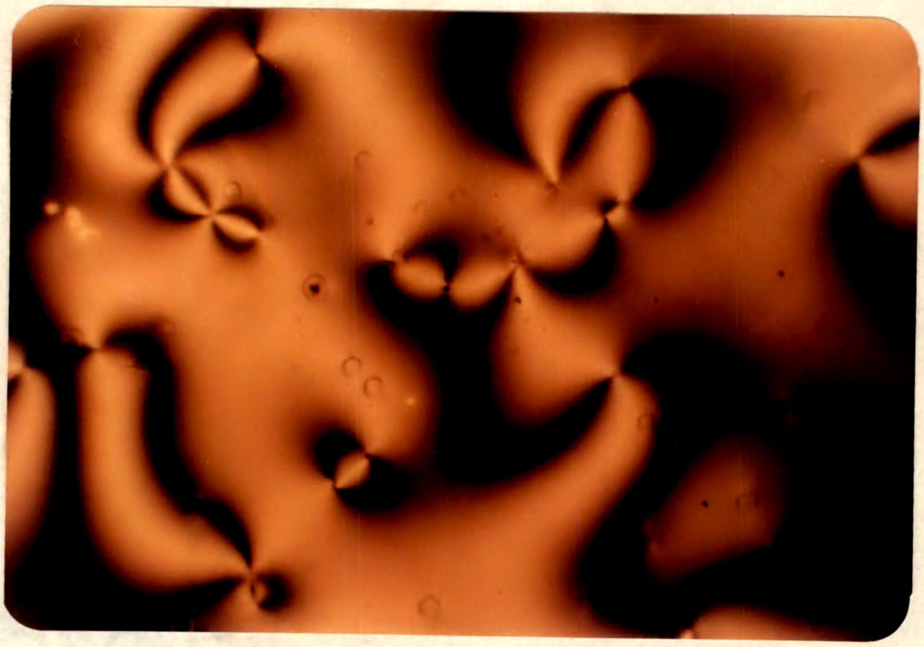
The nematics show a mobile threaded structure under polarized light. The state is less ordered as compared to the smectic as molecules are not arranged in a layered structure, but they lie parallel to each one another, without any regular organization at the

NEMATIC MESOPHASE :



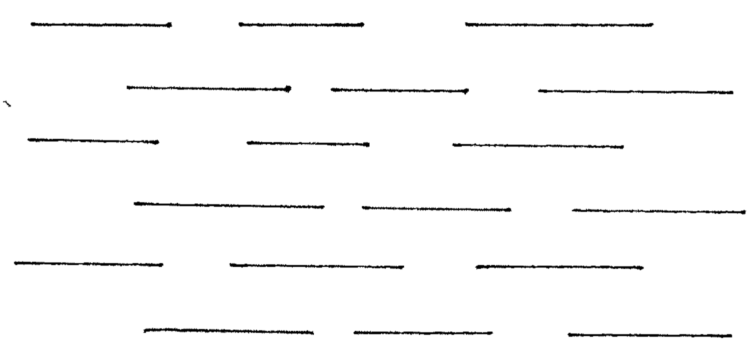
NEMATIC MESOPHASE – THREADED TEXTURE FILM BETWEEN GLASS SLIDES. CROSSED POLARIZERS. MAGNIFICATION X96.

NEMATIC MESOPHASE.



NEMATIC MESOPHASE – THREADED TEXTURE 'SCHLIEREN TYPE' WITH DISCLINATION POINTS. FILM BETWEEN CROSSED POLARIZERS. MAGNIFICATION X96.

ends of the molecules. Such arrangement of the molecules is called as imbricated structure is shown below -



Molecular Arrangement In Nematic Mesophase
Fig - 3

Nematic - Various theories have been put forth to explain the phenomenon.

(i) The Swarm theory proposed by E. Bose (51)

(ii) The continnum theory proposed by Zocher (52)

(iii) Simple molecular theory by Maier (53).

Nematic Textures

On cooling the isotropic liquid of a nematogen, the nematic mesophase appears in the form of small circular birefringent areas or droplets, which coalsce to form a threaded structure. The exact texture of the nematic phase depends upon the layer thickness. Relatively thicker layers show the typical threaded struc-

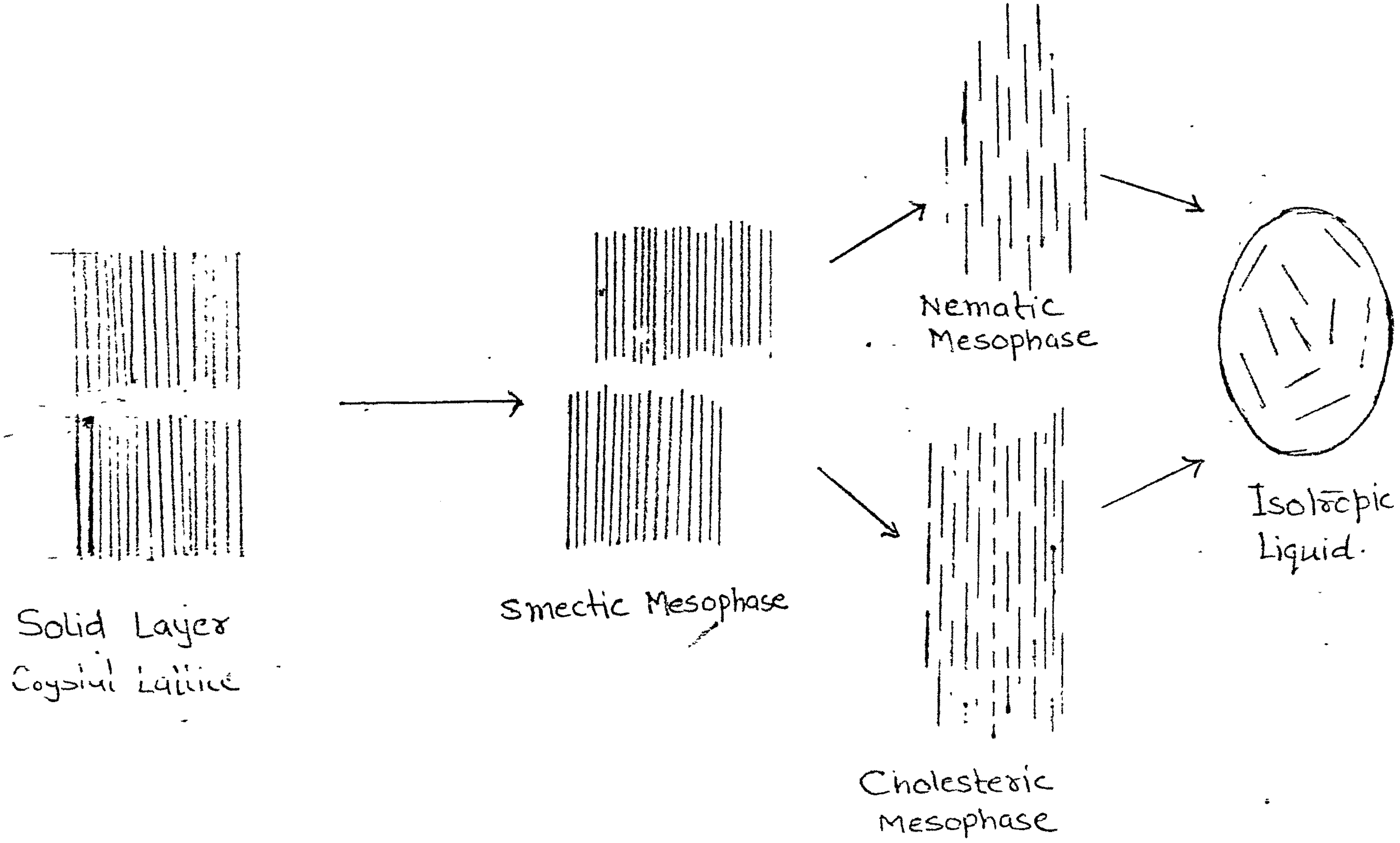


FIG. 7. Schematic Representation of Phase Transitions.

ture, whereas, in thinner layers, the texture is of 'Schlieren Type' with point like disclinations between crossed polarizers, the appearance of Schlieren forms is characterised 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. Sometimes, in extreme cases, with untreated surfaces, an irregular texture resembling appearance of polished marble can be obtained due to surface effect, the exture being called as marble texture.

Three types of nematic phases, based on their X-ray diffraction patterns are proposed (32). These phases are (i) Skewed cybotactic nematic (ii) normal cybotactic nematic (iii) the classical nematic phase.

Nematic reentrant -

The first report regarding a monotropic nematic reentrant phase under pressure was made by Cladis(54). After this, some enantiotropic reentrant phases in pure compounds and binary mixtures are also reported (55 - 60). X-ray and high pressure investigations of the reentrant nematic transitions are also carried out (61 - 64). On the basis of these results a thermodynamic model for this phase is presented by Clark et al (65).

Disc like Mesophase

Normal nematic compounds consist of rigid lath-like molecules whose longer axes are parallel to each other. In addition to these positive nematics, some negative nematics with shorter axes parallel to each other are also reported (66 - 67). Alben (68) proposed a possible phase diagram for mixtures of such positive and negative liquid crystals. Till date only 70 different mesogenic disc-shaped molecules are reported to have been synthesized and yet 7 different columnar phases are clearly identified (69). These phases are described on the basis of optical textures (70), binary phase diagrams (71) and X-ray measurements (72).

Carbonaceous Mesophases

Zimmen and White (73) discovered this new mesophase during the process of coking and carbonization. At a high temperature the molecule condenses to form a liquid crystal which is termed as 'Carbonaceers mesophase'. The mesophase appears to be a lameller one in which space is filled by plate like molecules of different size and shape arranged parallel to each other but free to bend and twist.

Cholesteric Mesophase

The first compound exhibiting mesomorphism was cholesteryl benzoate - a sterol derivative as reported by Reinitzer (1) in 1888. The mesophase is given the name 'Cholesteric mesophase' after the fact that the compounds exhibiting this mesophase were mostly cholesterol derivative though cholesterol itself does not show any liquid crystallanity. Now some non-sterol compounds are also known to exhibit this type of mesophase, the criterian being optical activity, the nomenclature is still used.

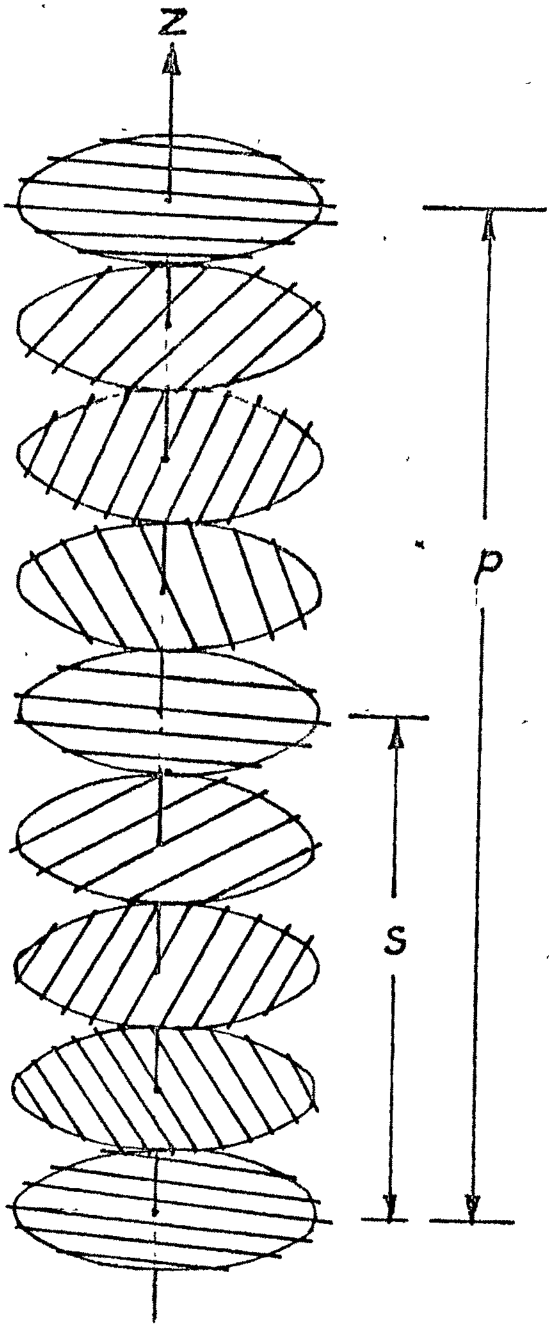
The close relationship between cholesteric and nematic was noted by Friedel (22). While polymesomorphism with a sequence of smectic and nematic mesophase occurring in the same compound is known to exist, no compound exhibiting both nematic and cholesteric mesophase is known. Only Smectic-nematic or Smectic-Cholesteric transition combinations are reported when Polymesophases are formed. Again the transition from a Smectic to nematic as well as from a Smectic to a

Cholesteric mesophase are discontinuous, naturally Friedel considered cholesteric mesophase as a special viariation of nematic mesophase but not an independent variety. Friedel (22) also observed that mixtures of certain cholesteric substance give nematic mesophases and that the addition of certain optical active compound to the nematic mesophase of p.azoxy anisole gives rise to cholesteric properties. Chatelain (55) has found that the amount of light diffused by the nematic mesophase is similar to that diffused by the cholesteric mesophase. The mobility of cholesteric mesophase is also found to be greater than that of smectic mesophase. Though, the cholesteric mesophase is quite similar to nematic as well as smectic phase in some aspects, it exhibits the most remarkable properties like producing intense, iridescent colours and high optical rotatory power due to Grandjean plane texture.

Gray (74) has regarded the cholesteric mesophase as an individual phase and stated it to be more similar to smectic phase rather than nematic phase. But various other studies suggest it to be more similar to nematic mesophase. Cholesteric mesophase has fluidity like the nematic mesophase, the phase can be oriented by electric

FIG.

A SCHEMATIC DRAWING OF THE CHOLESTERIC STRUCTURE



and magnetic fields (75). Vorlander and Janecke (76), Laclercq et. al (77) and Gray (78) have shown that the optically active compounds were cholesteric whereas the inactive racemic varieties were nematic. Stumpf (79), Gray (80), Mathieu (81), Oseen (82), and Fergason (83) have explained mathematically the optical rotatory power of the cholesteric mesophase.

The most interesting optical property of this mesophase is its display of indescent colours due to the scattering of light. The property is dependent upon nature of the compound, temperature and angle of incidence of the light beam. The optical properties summarized by Mathieu (84) are as follows :

1. The cholesteric structure is uniaxial and optically negative thus there is a single optic axis normal to the surface along which the index of refraction is a minimum.
2. The cholesteric structure is optically active with rotatory powers many times that of common optically active materials. The plane of linearly polarized light is rotated through an angle several hundred times that of the usual optically active materials.

3. When illuminated with white light, the cholesteric structure scatters the light to give an indescent colour, which varies with substance temperature and angle of incident beam.

4. The cholesteric structure is circularly dichoric for some wave length region, that is one circularly polarized component of the incident beam is transmitted without attenuation, whereas the other is scattered. Either the right or the left hand circular polarized component will be affected.

The optical properties depend on a delicately balanced molecular arrangement. A slight disturbance in the form of change in shape of molecule or change in dipole which interferes with the weak forces between molecules may result in a dramatic change. All optical properties like reflection, transmission, birefringence, optical rotation, colour intensity may undergo marked transformation.

Re-entrant Mesophases

Previously, it was a general belief that nematic mesophase being less ordered one than smectic mesophase should be obtained at higher temperatures. But Cladis (85) obtained nematic mesophase at lower temperature than the smectic mesophase in a binary mixture. The nematic phase obtained at a lower temperature is called the reentrant nematic mesophase. The phenomenon is explained by assuming that the anti-parallel associations responsible for the formation of bilayer smectic A mesophase provide some kind of rearrangement which accounts for the re-appearance of the nematic mesophase before the commencement of smectic A mesophase. Now this re-entrant behaviour is reported in Nematic, smectic, Cholesteric, Discotic and Isotropic phases.

Most of the cases of mesogens exhibiting re-entrant behaviour are reported in last three years. Destrade et al (85 - 88) have studied a number of mesogenic series with terminal substituent as a highly polar group as $-NO_2$, -CN, -Br, which are showing reentrant nematic or smectic mesophase. They have discussed the relation between molecular geometry, influence of the Central Group, influence of the terminal substituent on the re-entrant mesophase.

Pelzi (89) suggested that a strongly Polar Group at one terminal end offers a favourable condition for the emergence of reentrant nematic mesophase, but reentrant nematic mesophase was predicted to appear in mixtures of two non-polar compound, provided that one molecule should have long aliphatic chains at both the ends, whereas the other should have an alkyl chain at one end only (90). The system which agrees well with this prediction actually exhibited reentrant nematic mesophase (91).

Recently a reentrant nematic system having end formyl group in naphthalene ring system is also reported by Trivedi and Thakar (97). Number of theories are proposed to explain reentrant phenomenon (98 - 99).

Reentrant isotropic phase is also reported now (92 - 94) and reentrant cholesteric mesophase in Polar mesogens are also reported (95 - 96).

An unique phenomenon of quadruple reentrance of mesophases is also reported recently (100). The microscopic Spin-gas model of a mesogen reproduced mesophases four times.

Lyotropic Mesomerphism and Amphiphilic Mesophases

Presence of a solvent may also induce the formation of a mesophase by amphiphilic compounds. Generally water is the most common solvent, hence thename lyotropic mesomorphism, though more appropriate term - amphiphilic mesophase is now widely used.

Ammonium oleate was the first amphiphilic compound reported by Lehmann (101). The mesophase formation can be represented as follow -

$$\begin{array}{c}\text{Crystalline}\\ \text{Ammonium Oleate}\end{array} \underset{\text{Dehydration}}{\overset{\text{Water}}{\rightleftarrows}} \begin{array}{c}\text{Liquid}\\ \text{crystal}\end{array} \underset{\text{Evaporation}}{\overset{\text{Excess of water}}{\rightleftarrows}} \begin{array}{c}\text{Solution}\\ \text{(Clear or}\\ \text{colloidal)}\end{array}$$

The mesophase is exhibited by compounds possessing two main groups in the same molecules which greatly differ in their solubility relationship (102). The hydrophilic groups such as - COOH, $-SO_3K$, - COONa, $-O(CH_2CH_2O)_nH$, $-N(Me)_3Br$ possessed by an ampripnilic compound, tend to be hydrophilic and hydrocarbon insoluble but lipophilic groups such as - CnH2n + 1, CnH2n + 1 C6H4 - contained in the same molecule tend to behave exactly oppositely by being hydrophobic and hydrocarbon soluble.

Various compounds like soap, soap like alkali salts of naphthenic acid etc. have been reported to exhibit mesomorphic property under controlled action of water (103 - 105). Alcoholic solutions of such compounds do not show mesomorphic property, rather a high degree of dehydration is the necessary criterion for the formation of a mesophase. The solvents, other than water, used for producing mesophase are liquid paraffin (106) glycerol, isopropanol and diethylene glycol (107). A number of cationic and non-ionic detergents when treated with water and other solvents exhibit anisotropic phases (108-113).

Lyotropic mesophases analogous to smectic and nematic thermotropic mesophases have been reported, the change from smectic to nematic state being brought about by further addition of solvent.

Mcbain (114) distinguished two forms of mesomorphism in soal solutions.

Lawrence (115) showed that the action of water or in general any other solvent is similar to that of temperature which breaks down the bonds holding the molecules in their crystalline orientations in one or two directions. In solution, this permits the entrance of solvent molecules into the lattice with a relative swelling of the molecule. The phase rule study also shows how narrow are some of the limits of the mesophase which in turn help in explaining some of the contradictory statements concerning these phases.

Marsden and McBain (116) have studied the X-ray diffraction patterns of aqueous non-ionic detergents and have discussed the smectic property. Palit, Moghe and Biswas (117) reported the appearance of lyotropic mesophase during their study of solubilization of water by cationic detergents. Zocher and Copper (118) have reported that the methylene blue, neutral red and some other dyes also show lyotropic mesophase, since then many dyes have been tested for mesomorphic characters.

Sheppard's work (119) on 1.1'-diethyl-2.2' cyanine salts (diethyl- -cynanine) proposes a new type of nematic molecular phase, that of pluri-molecular filaments rather than elongated molecules.

Robinson (120) has reported an interesting observation that viscous solution of poly- - benzal-L. glutamate in certain organic solvents are anisotropic and show a number of characteristic properties similar to thermotropic cholesteric mesophase. Small et al (121) have studied lyotropic mesomorphism of ternary and quarternary systems of bile salts, lecithin, cholesterol and water. Lawson and Flault (122) have studied NMR spectroscopy of smectic and waxy mesophases in various surfactant systems such as sodium palmitate-water system.

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) viscous isotropic phase (V_1 phase) (D) isotropic phase (S_1C phase) and the inverse phase (V_2 and M_2 phases) (123).

The sequence of emergence of these phase in a system with increasing concentration of amphiphile compound is as follows-

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

But not a single system showing the complete series of mesophases is reported so far.

Recently Etwall (124) has given an interesting account of composition, properties and structure of liquid crystalline phases in systems of amphiphilic compound.

Plastic crystals - amphiphilic cubic mesophases -

A crystalline solid can be characterised by having both three dimensional long range positional order and orientational order, whereas an isotropic liquid possesses neither. A liquid crystal has orientational order and zero or reduced positional order whereas a plastic crystal possesses long range positional order but completely disordered orientationally. Liquid crystal molecules are long and rigid pastic crystal molecules are globular and compact. In plastic crystals orientational disorder occurs at a lower temperature than positional disorder, in liquid crystals the reverse true. In short, while liquid crystals are solid like liquids, the plastic crystals are liquid like solids. Thus plastic crystals may constitute another mesomorphic state of matter.

The plastic crystals are first recognized by Timmermann's (125-127) as characteristically 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 cubic array while at the same time undergoing thermal rotatory displacements so that there is no long range orientational order between the molecules.

Though plastic crystals contain globular molecules, not all the globular molecules can give rise to plastic crystals. Some typical plastic crystals are formed by tetramethyl methane, cyclohexane, carbon tetrachloride, camphor, cyclobutane, neopentane, hexamethyl ethane, 2,2,dimethyl butane etc.

A plastic crystal is easily deformed, it may flow under its own weight and is likely to be tacky to touch.

Investigation of various physical properties such as thermal properties, X-ray (128), dielectric properties, N.M.R. spectroscopy (129) and diffusion have been employed to explain motion in plastic crystals.

Mesomorphic Polymers

The study of mesogenic compounds dates as far back as 1879, but polymeric mesogens are investigated only in recent years. And now the study of mesomorphic mesogens is gaining momentum as these are very significant from application point of view. Recently a number of synthetic mesomorphic polymers are reported (130-132).

Polymerization of mesomorphic monomers, their structures and the thermotropic liquid crystalline behaviour of the resulting polymers are studied (133-135). Some non-mesomorphic monomers having mesophase - inclusive side-chain also exhibit monotropic mesomorphic properties on polymerization

(136 - 138).

Various types of mesomorphic polymers have been reported. Shiber et al (139) reported comb-like enantiotropic liquid crystalline polymer with side groups modelling smectic type liquid crystals. Preston (140) reported rod like condensation polymers. A review on stiff-chain polymer showing lyotropic mesomorphism is given by Miller (141). Recently polymers exhibiting both lyotropic and thermotropic mesomorphism are also reported (142).

The effect of side-chain structure on the mesomorphic properties of substituted cellulose derivatives was studied by Bhadani et al (143). The effect of solvent and temperature on mesomorphic characteristics of polymer of p-hydroxy benzoic acid have been studied by Vora et al (144). The effect of the order of linkage between mesogenic units on thermal properties of main chain thermotropic polymers have also been studied (145).

Biological systems

In biological system, the mesomorphic properties were first shown by Virchow (149) in the form of myelin, but the first demonstration of this phenomenon in a well characterised biological system was given by Bernal and Faukuchen (150) who used X-ray diffraction to investigate solutions of tobacco mosaic virus. Liquid crystallanity in the case of muscle was reported by Muralt and Edsall (151) and in the case of tissues by Pearse (152).

While studying the structure of haemoglobin, Perutz et al (153) reported that it may assume liquid crystalline form in the red cell. Robinson (154) showed conclusively that a polypeptide - poly 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 by Stewart (155) when it was shown that complex lipids present in adrenal cortex, ovaries and myelin existed at body temperature in a characteristic mesophase. Stewart (156) and Ambrose (157) studied the mesomorphism in biological systems in details and gave reasons and factors controlling mesomorphic states and then biological interaction.

Structural characteristics of liquid crystals

The thermotropic mesogens vary in chemical constitution but there are certain definite factors which are responsible for the occurence of their mesomorphic properties. Molecular geometry is a very important factor which influence to a great extent the liquid crystalline properties. Generally the molecules of mesogens are elongated and rod or lath-like in shape. They are closely packed in a regular manner giving rise to parallel arrangement in crystalline state along the major axis. In such long molecules, presence of polar groups at terminal, central or lateral position and polarizable units in p. p'- positions along with benzene rings play important role in endowing the mesogens with liquid crystalline properties.

Even, the presence of ideal structural geometry may not turn the compound to behave as a liquid crystal. Some intermolecular forces also play important role. The intermolecular forces are of three types -

(1) dipole - dipole attractions - the direct interaction between permanent dipoles in the molecules.

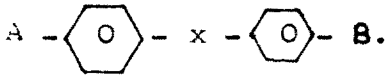
(2) induced dipole attractions arising from the

mutual polarization of the molecules by their permanent dipole moments.

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

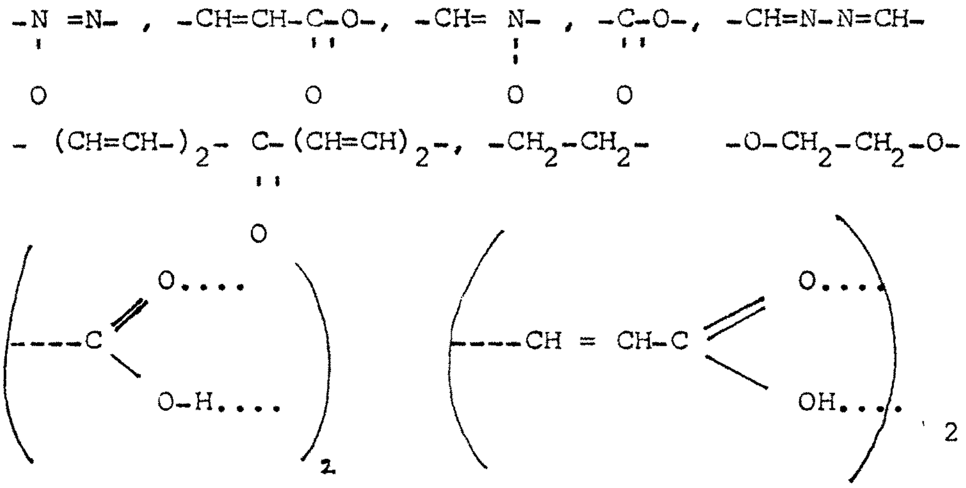
For a mesogen, to constitute a potentially mesomorphic system, the long, rod like molecule must contain groups of atoms with which are associated permanent dipole moment, and the molecule itself should be highly polarizable.

As most of the thermotropic liquid crystals are aromatic in nature, aromatic nuclei being polarizable thus if suitable substituents are placed in appropriate positions, they can give rise to mesomorphism. For benzene nuclei, substituents should occupy p-positions and be of such a kind that at least one other benzene ring, also carrying a p-substituent should be present. It is desirable that the central group which joins the ring is of a rigid nature, that is the two rings and the central group should constitute a lath - or rod - like core of the moleaules. It can be represented, thus



Where A and B are the terminal substituents and x is the central group. Central groups normally contain a multiple bond or conjugated double bend system. The common central linkages are -

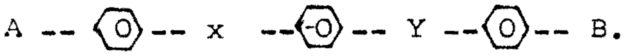
$-CH=CH-$, $(-CH=CH-)_{2-3}$, $-C\equiv C$, $-CH=N-$, $-N=N-$



$-\underset{O}{N}=N-$, $-CH=CH-\underset{O}{C}-O-$, $-CH=\underset{O}{N}-$, $-\underset{O}{C}-O-$, $-CH=N-N=CH-$

$-(CH=CH-)_2-\underset{O}{C}-(CH=CH)_2-$, $-CH_2-CH_2-$ $-O-CH_2-CH_2-O-$

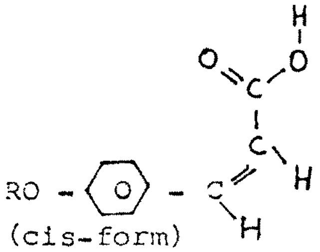
The liquid crystalline properties are enhanced with the addition of one more benzene ring, the effect being most when all the ring are conjugates. It can be represented as below

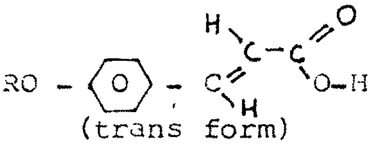


The linkage of benzene rings with O- and m-positions and introduction of a bulky atom or group in a position other than at the end of the molecule will appreciably broaden the geometry of molecule. The molecules which are oriented parallel to one other are therefore forced to fall apart as a result the interaction energy decreases rapidly. Since it is inversely proportional to the distance between the attracting centres. The introduction of dipolar group into the parent molecules will increase the inter molecular attractions but only if the separation of the molecular axes is not increased too greatly. Thus the introduction of dipolar group into the sides of the molecule usually decreases the thermal stability of the mesophases of the parent compound because of the broadening effect (158-159).

The effect of broadening the molecule is very well explained by the introduction of fluoro, chloro and bromo atoms in p.decryloxy benzoic acid (158-159). The fluoro and chloro-substituted compounds exhibit mesomorphism while bromo substituent eliminates the mesomorphic behaviour.

Similarly, cis-p.n. alkoxy cinnamic acids are non-mesomorphic because they do not form lintar dimers. Of the two, trans-p.n.alkoxy cinnamic acids (160) and p.n. alkoxy benzoic acids (161) both of them are of same molecular length, the cinnamic acid exhibits more thermally stable smecticand/or nematic mesophase.


(cis-form)


(trans form)

- (p.n. Alkoxy cinnamic acids)

The greater mesomorphic thermal stability of the cinnamic acid is possibly due to the greater polarizability of the double bonds and greater molecular length due to the presence of $-CH = CH-$ chain. Thus not length alone but greater polarizability will be responsible for the enhanced thermal stabilities. Gray (162) confirmed the concept when he showed that the greater mesomorphic stability of biphenyl acids than those of benzoic acids are because of the four aromatic rings in each biphenyl acid molecule, (dimeric), when there are two aromatic rings present in each benzoic acid (dimeric).

Dewar and Goldberg (163) have also shown that the replacement of aromatic rings by saturated alicryclic rings gives reductions in the thermal stabilities of mesophase indicating that linearity is our important part of a compound to exhibit mesomorphism.

The presence of groups capable of giving polymeric hydrogen bonding such as hydroxyl and amino group at terminal end is also not favourable for liquid crystallanity, the hydrogen bending favours non-parallel arrangement and also increases melting point thus reducing the thermal stability (164-165). Though, recently some homologous series with phenolic end substituent have been found to be mesomorphic (166). Gray (167) has given an efficiency order of the terminal substituents for mesomorphic states. It is pointed out that $-NO_2$ and -OME, substituents which lie high in nematic order are low in smectic order.

Alteration of nematic-isotropic transitions with odd or even number of carbon atoms of the alkyl chain of the terminal substituent - odd-even effect, and its absence in case of smectic-nematic transitions has been explained on the basis of zig-zag conformation (168) or on the basis of concepts advanced by Flory (169) and Marcelja (170).

It was noted that branching of the terminal alkyl groups also decreases the termal stability of the mesophase (171 - 174). When the branching occurs at the first carbon atom of the chain, the effect on liquid crystals thermal stability is the greatest. Branching at any other point appears to have greater effects on the nematic than on the smectic thermal stability. Movement of the point of branching away from the first carbon atom towards the end of the chain causes the transition temperature to rise again (173).

Certain cyclohexane derivatives (175) and hetero-cyclic ring systems (176) have also been reported to show liquid crystallanity, their mesomorphic behaviour is discussed by Gray and Nash (174).

The effect of lateral substituent upon the mesomorphic state have also been widely studied (177 - 180). The substituent will have two effects -

(a) The introduction of a lateral substituent will invariably broaden the molecular geometry, thus the long molecular axes may be forced apart by the substituent, reducing intermolecular forces of attraction and thus lowering the thermal stability of mesophase. Since lateral attractions will be most affected, the thermal stability of the smectic mesophase will decrease more than that of a nematic phase.

(b) The change from a ring -H to ring -K (Laterial substituent) bend with increase the molecular polarizability and possibly the molecular dipolarity. This should increase lateral intermolecular attractions enhancing liquid crystal thermal stability specially that of the smectic mesophase.

Though, both effects operating are opposite in nature, it has been established (181) that effect (a) always predominates, the thermal stabilities of mesophase are decreased.

The effects of lateral substitution in which the substituent in addition to broadening the molecule, also increases its thickness by imposing its steric effects on the system i.e. by causing a twist around one of the bends, so that parts of the molecule are rotated out of the plane of the remainder of the molecule are also studied (182-184). A combination of both breadth and steric effects greatly reduces the thermal stabilities of the ordered arrangement of molecules and as expected, smectic thermal stability is affected more than nematic thermal stability (184).

Physical properties and defects

Various modern techniques are being used to ascertain the molecular structure and to determine properties of liquid crystals.

Application of X-rays to the study of smectic mesomorphs (185 - 188) reveal the true crystalline packing below the solid smectic transition, between solid-smecticand smectic-isotropic transition, the diffraction patterns showed evidence for a regular arrangement of layers.

X-rays examination of nematic mesomorph showed the imbricated arrangement of molecules and that the diffraction patterns shows that nematic and isotropic liquids show indistinguishable halos (177, 185, 186,188). It has been shown (187) that while large groups or swarms are absent in isotropic liquids, small crypotactic groups of molecules do exist in isotropic melts.

I.R. spectra (189) also indicated the difference between twisted nematic phase and ordinary nematic phase.

The structural characteristics of cholesteric (190 - 193) and smectic liquid crystals (194) are also explained by Raman Spectroscopy (195).

NMR studies of some meogens is also proved to be of great significance (162 - 202) as it can provide clues regarding molecular geometry and orientation of the oriented molecules. Some nematic liquids are also suggested to be used as solvents to study the NMR spectrum of oriented molecules (203 - 209).

UV absorption spectroscopy when applied to nematic and isotropic phases could not provide any valuable information.

The e.p.r. technique is also not much significant as the mesogens are normally not the paramagnetic compounds. However, some work in this field is available (210 - 215).

The viscosity measurements for cholesteric (216) nematic (217) and smectic (218) mesomorphic compounds indicate the change in viscosity at various transition temperatures. More study in this field for pure liquid crystalline solids (219), their binary mixtures (220) as well as the study of prefreezing phenomenon (221) have been reported.

The surface tension studies of liquid crystalline compounds are carried out by various methods techniques

(222 - 226). However, while some of the results confirm and support mutually, some are contradictory.

The study of dielectric constant measurement of mesomorphic compounds is also carried out (227 - 228). The dielectric properties were found to vary with belocity of flow, strength of applied magnetic field, and temperature (229). Changes in dielectric constants under various conditions (230 - 231) and the effect of dielectric field on molecular alognment in the mesomorphic state (232) are studied. Exhibition of negative dielectric anisotropy (233) and dielectric studies in reentrant smectic and nematic mesophase (234) are also reported recently.

DSC and DTA technique are also being used to determine some characteristics of molecular structures of mesogens (235 - 240) and their binary mixtures (241 - 243).

It is logicalto think defects in liquid crystals as in solid crystals. It was Lehmann (244) who described defects and textures, which may have to be rediscovered. Orientational defects in smectic (phase (245) have been studied.

Dilatometric Studies (246 - 248), Mossbauer effect (249 - 250), ultrasonics (251 - 255), effect of pressure on mesomorphic phases (256 - 257) have been studied in good details.

MIXED MESOMORPHYSM

The transition temperatures of pure mesogens are greatly depressed in the presence of another substance, mesomorphic or non-mesomorphic, in the usual way following more or less the law of mixtures.

Different types of mixtures where none, one or both the components were mesogens have been investigated (258-261). The extent of mixed mesophase and the effect of terminal substituents in the exhibition of mixed mesomorphism have been studied recently in good details by Dave and Dewar (262), Dave and Lohar (263), Dave and Vasanth (264), Lohar and Shah (265), Lohar and Patel (266), Lohar and Mashru (267), Lohar and Dave Jr. (268).

Much earlier the latent transition temperatures of non-mesomorphic compounds are determined by extrapolation method (269). Inspite of initial criticism (270), the methods have been proved to be adequately accurate (263) under certain definite conditions (265-266).

Dave and Dewar (262) and Dave and Lohar (263) have deduced an order of efficiency of the terminal groups for exhibiting nematic mixed mesophase. Effect of molecular length on nematic mistures is studied by Margerum et a.(270).

The mesomorphic compounds when mixed with other non-mesomorphic or mesomorphic compounds in proper proportions give rise to a stable room temperature mesomorph which may find many useful applications (271).

The textures of various smectic mesophases have been identified on the basis of miscibility studies (272 - 273).

Induced smectic mesophases in some binary mixtures are also reported (267, 274). Pretransitional effects in nematic mixtures exhibiting induced smectic phase are also discussed (275).

Applications of Liquid Crystals

Liquid crystals are finding a good field of varied application as the days pass by. The last decade has seen a sudden spate in the demand of mesogens for industrial use, which is evergrowing.

The applications of liquid crystals can be classified in three main classes viz -

(1) Thermographic measurements
(2) Display devices
(3) GLC Techniques

(1) Thermographic Measurements -

Certain cholesteric liquid crystals selectively reflect light in visible region depending on the pitch of helix. The pitch of the helix is temperature dependent and therefore these cholesteric liquid crystals may be used to control the temperature by showing colour changes. Similar colour shifts are also obtained by changing electric or magnetic fields and the pressure and concentration of gases. As some cholesteric liquids are thermally very sensitive, they are widely used for detection of vascular diseases and subcutaneous tumors (276 - 281) and alergies to chemical substances introduced in the blood stream (282). Liquid crystal thermography assisted in the difficult diagnosis of various intra-abdominal abscessesl, and some other diseases (283 - 285).

Liquid crystals are also used in non-destructive testing as to detect cracks in metallic surfaces and coating (286), to locate stress areas and potential fracture sites in metal (287), in testing insulation in refrigeration and cooling units.

Now, liquid crystals are also used for coating decorative fabric. The colour of this fabric changed from yellow to various shades of green at temperature ranging from 6° to 38°C (288)

(2) Display Devices

Cholesteric liquid crystals encapsulated or incorporated in a thin sheet are used to make some very interesting and useful devices. Some common devices simple liquid crystal thermometer (289) temperature limit indicator (290), voltage and current meters (291 -292) to flat screen televisions and storage displays (293).

Mixtures of cholesteric with nematic liquid crystals are also used in some display devices (294-296).

(3) GLC Techniques

Recently, some cholesteric and nematic liquid crystals are used as a stationery phase in glas liquid chromatography (GLC) (297 - 300). Liquid crystal coated glass micro beads were used in GLC columns which have high efficiency and wide temperature range (301).

Nematic liquid crystals may serve as good solvents for many molecular rearrangements and polymerization reactions. Thus Claisen rearrangement (302), pyrolysis of xanthates (303), decomposition of picric acid (304) and determination of polycyclic aromatic hydro-carbons (305) are studied using nematic liquid crystals as solvents.

Mesomorphic Polymers

The first liquid crystalline compound investigated in biological system was a polymer (306). Now a number of synthetic mesomorphic polymers are reported (307 - 309).

Polymerization of liquid crystal monomers, their structures and thermotropic liquid crystalline behaviour of the resulting polymers were studied by Perplies et al (310) and by Wondorff et al (311).

A detailed account of applications of these mesomorphic polymers has been given (312). A number of

patents and reports claiming the production of fibres-kevlar fibres from polymer solution existing in the liquid crystalline state are known (313 - 315). These fibres have been shown to be useful as tire cords, as a replacement for glass and steel belts in radial belted tyres, conveyor belts, V-Belts and circuit-boards.
The p-oriented fibres are also used in flame resistant clothing.