I N T R O D U C T I O N

INTRODUCTION

1. Definition and Nomenclature.

Majority of substances may be obtained in one or more crystalline phases, a liquid phase and a vapour phase. But certain substances form one more liquid phase which is turbid and shows mechanical properties of a true liquid and optical properties of a true crystal. When such solids are heated they do not pass directly into the liquid state but first adopt a turbid structure which shares the properties of a true crystal and a true liquid showing both birefringence and fluidity, the consistency varying with different compounds from that of a paste to that of a freely flowing liquid. At a higher temperature this turbid phase passes into a clear isotropic liquid. The process is reversible although some supercooling may occur when mesomorphic-solid temperatures are reached as in the case of ordinary crystallization. Such an intermediate state has been described as Liquid Crystal Phase since the time of its discovery.

Towards the end of the nineteenth century, in 1888, Reinitzer (1)- an Austrian botanist, for the first time observed the phenomenon of liquid crystallinity in the case of cholesteryl benzoate. However, Lehmann (2)- a German physicist was the first to make a systematic study and coined the term Liquid Crystal or Crystalline Liquid to describe this intermediate state.

Although the term Liquid Crystal is simple and suggestive and has been freely used since the time it was first suggested by Lehmann, objections have been raised to this nomenclature.As more of the properties of this phase became known, Friedel (3) stressed that, though this phase exhibits some of the properties of crystalline matter and some of the properties of an isotropic liquid, the liquid crystals were neither genuinely crystalline nor liquid and proposed that it would be preferable to refer liquid crystalline state as a mesophase (mesos = intermediate; phasis = phase), meaning a state intermediate between a crystalline solid and an amorphous liquid. This term and the associated terms mesomorph, mesoform, mesomorphism and mesomorphic are widely used in the literature.

Rinne (4) criticized both these terminologies on the basis that they had no structural meaning. He classified matter as exhibiting either ataxy (a disordered or amorphous structure) or eutaxy (an ordered structure). The mesomorphis and crystalline states will belong to the class of eutactites, since they possess ordered structures. To describe the mesomorphic state he subdivided this class and proposed the term paracrystals. Here the word crystal significantly emphasizes the natural proximity of the state to the crystalline condition, while the prefix para- signifies that many of the organic compounds which possess this type of eutaxy are para-substituted benzene derivatives. Thus, the classification is :

(1) Atactites - isotropic liquids, gases and amorphous matter.

(2) Eutactites -(a) Crystals - three dimensional order.

(b) Paracrystals - one - or two - dimensional order.

Brown and Shaw (5) consider the related term mesomorphic state preferable and have used it as the title of their recent review. However, the name liquid crystal is still frequently employed and will be used in this thesis.

Classification of the mesomorphic state on the basis of the manner in which it is obtained is also discussed in the literature. Using the nomenclature of Friedel (6), Lawrence (7) and Jelly (8), thermotropic mesomorphism refers to the formation of the mesophase by means of heat in contrast to lyotropic mesomorphism which has been defined as the process of forming the mesophase by solvation, the solvent generally being water.

As a result of detailed optical studies, Friedel (3) was able to distinguish clearly three different types of mesophases. These are :

(a) The smectic mesophase - a turbid, viscous state, with certain properties reminiscent of those found for soaps. The term smectic is derived from the Greek word, smectos meaning soap-like.

(b) The nematic mesophase - a turbid but mobile state. The word nematic again stems from the Greek word, nematos meaning thread-like.

(c) The cholesteric mesophase - a turbid and mobile mesophase exhibiting some unique optical properties, quite different from those of the smectic and nematic mesophases. The majority of compounds exhibiting this type of mesophase are cholesterol derivatives.

Soon after Reinitzer's observation of apparently double melting points in cholesteryl benzoate, Gattermann (9), in 1890 found similar behaviour in the case of p-azoxyanisole and p-azoxyphenetole. These discoveries were soon followed by synthesis of compounds of like character in hundreds, mainly by Vorlander (10). It became immediately evident that all these substances had one common feature - a very long molecule, and this has always been accepted as a necessary criterion of a mesomorphic substance.

The theoretical interpretation of the mesomorphic state has intrigued many physicists and chemists. Tamman (11), Nernst (12) and Quincke (13) described these melting phenomena as arising from the colloidal effect of minute crystals held in suspension in the isotropic liquid or from the presence of impurities in the compounds, giving an emulsion of two liquids. All attempts to separate the alleged emulsion into its constituents by G.Bredig and G.Von.Schukowsky (14) and Coehn (15) by electrostatic and centrifugal processes were futile. Schenck (16) and Vorlander (17) have also criticized the emulsion theory and argued in favour of the existence of crystalline liquids. A.C.de Kock (18) on the basis of his work on liquid mixed cyrstals, has supported the view that crystalline liquid is a homogeneous phase and not an emulsion of two liquids. He also repeated Tamman's sedimentation experiments without success. Pawloff (19), Wulff (20) and Voigt (21) have also discussed the nature of liquid crystals. The mesomorphic behaviour being observed in large number of compounds, often in a compound of simple chemical constitution, the attempts to explain the origin of mesophases in terms of impurity became untenable and were ruled out completely when it was found that a mesophase gives a clear field of view in the ultramicroscope. So far no proof of heterogeneity has been reported and the homogeneity of liquid crystals has been generally accepted.

Lehmann (22) carried out a large number of experiments to illustrate the properties and formation of liquid crystals from the isotropic liquid. He considered that the phenomenon was due to the formation of crystals in the liquid condition, which appeared perfectly transparent under the microscope. The turbidity which usually accompanies the phenomenon, he attributed to the different orientation of the individual crystals which scatters the light to a more or less extent. Vorlander believed that the substances were truly liquid crystals and had a fixed space lattice (23). However, further microscopic examination of liquid crystals carried out by Mauguin (24), Friedel and Grandjean (25,26) soon dispelled these ideas and established that the liquid crystal state is a truly physical state, intermediate between the crystalline solid and the isotropic liquid.

The three states of matter may be expressed as Solid $\rightleftharpoons$ Liquid $\rightleftharpoons$ Vapour or gas; liquid crystalline compounds however, form one more intermediate state between the solid and the liquid. In the crystalline state, the molecules lie parallel to one another and are held together by attraction through the polar groups and also by unspecific Van der Waals attraction. When the solid is heated, the weaker bonds break first leaving the solid with some degree of relative movement before sufficient thermal energy has been acquired to overcome in any great degree the tendency for them to set themselves parallel to one another. Thus the solid melts to a fluid but remains birefringent because of the preferred orientation of the molecules. The gradual thermal breakdown may be represented as:

$$\underset{\text{state}}{\text{Crystalline}} \overset{t_1}{\rightleftharpoons} \underset{\text{state}}{\text{Liquid crystalline}} \overset{t_2}{\rightleftharpoons} \underset{\text{state}}{\text{Amorphous liquid}}$$

$$\xrightarrow{\text{Increasing temperature}}$$

These transitions take place at definite temperatures and are precisely reversible. Generally, due to the application of heat, the solid crystal is disordered and directly passes over to the amorphous liquid state at its melting point, but if the conditions are favourable for mesomorphism, the order breaks down in stages, first passing into liquid crystalline state at temperature t_1. This state has certain degree of order and hence acquires anisotropic properties. Further heating to t_2 destroys the orientation of the mesophase and finally gives amorphous liquid. Thus the action of controlled heat is responsible for breaking down the alignment and is similar to the action of solvent in lyotropic mesomorphism.

The mesomorphic transitions so far discussed occur on heating the substance, and reverse in the opposite order on cooling. Such a mesophase is called the enantiotropic mesophase. Quite frequently, however, the solid melts normally to give a liquid at T_1, but when the isotropic liquid is cooled, supercooling may occur and a mesophase appears (at T_2) below the melting point and before crystallization occurs. Such a mesophase is given the name monotropic mesophase. The sequence of changes of state for a compound exhibiting monotropic mesophase may be represented as:

$$\begin{tikzcd}
\text{Crystals} \arrow[rr, dashed, "T_1"] & & \text{Isotropic liquid} \arrow[dl, "T_2"] \\
& \text{Mesophase} \arrow[ul] &
\end{tikzcd}$$

Thus, a monotropic phase is observed only on cooling but if the temperature can be raised before crystallization occurs, the isotropic liquid will be obtained at T_2.

2. <u>Smectic, Nematic and Cholesteric mesophases:</u>

Based on the findings of the detailed microscopic examination by Friedel, liquid crystals are conveniently divided into three types- Smectic, Nematic and Cholesteric. Of the three, smectic and nematic are the most common types of mesophases and the study of their optical properties has made possible to assign structures to them. These structures do not, however, extend uniformly throughout the melt but the whole melt is composed of the random orientations of groups or swarms of molecules as proposed by Bose's swarm theory. Vorlander (27) has, however, criticized this nomenclature but he has not suggested any satisfactory alternative and these names have been generally accepted.

Some examples of the organic compounds which show one or the other of these phases are given in Table 1.

TABLE - 1

Smectic compounds.	M.P. °C	T.P. °C
4,4'-Diethyl azoxybenzoate	114.0	122.5
4,4'-Diethyl azoxycinnamate	140.0	249.0
p-n-Octadecyloxybenzoic acid	102.0	131.0
Ammonium oleate	smectic at ordinary temperature.	
Nematic compounds.		
p-Azoxyanisole	118.0	136.0
p-Azoxyphenetole	137.0	168.0
Anisaldazine	169.0	182.0
p-Methoxycinnamic acid	173.5	190.0
Cholesteric compounds.		
Cholesteryl benzoate	145.5	178.5
n-Amyl p-(4-cyanobenzylidineamino)cinnamate	92.0	105.0

Ammonium oleate shows a smectic phase at ordinary temperature, but it being a lyotropic mesomorph, no transition temperature can be given for it. Most of the liquid crystalline substances which have been studied are exclusively either smectic or nematic. However, many compounds are known which display both types of mesophases. The change with increasing temperature may be represented as :

$$\text{Solid crystal} \xrightarrow{t_1} \text{Smectic} \xrightarrow{t_2} \text{Nematic} \xrightarrow{t_3} \text{Isotropic liquid}$$

A few substances have been found to possess more than one phase of the same type and even here the temperature range of stability of the different phases is sharply defined. Such an example is that of 4'-n-hexoxy-3'-nitrodiphenyl-4-carboxylic acid which possesses two smectic phases and one nematic phase.

$$\text{Crystal} \overset{136.0}{\rightleftharpoons} \text{Smectic}_1 \overset{158.0}{\rightleftharpoons} \text{Smectic}_2 \overset{213.5}{\rightleftharpoons} \text{Nematic} \overset{218.0}{\rightleftharpoons} \text{Isotropic liquid}$$

Lyotropic mesomorphs (7) also exhibit a similar behaviour as exhibited by thermotropic liquid crystals. The most notable example is Sandquist's 10-bromophenanthrene-6-sulphonic acid (28) which shows both smectic and nematic phases. With sufficient water to be a paste, it appears to be a typical smectic phase and with more water it changes to nematic and finally passes to a true solution with excess of water.

$$\text{Solid} \xrightarrow{\text{water}} \underset{\text{(smectic)}}{\text{Thick paste}} \xrightarrow[\text{water}]{\text{more}} \underset{\text{(nematic)}}{\text{Thin paste}} \xrightarrow[\text{water}]{\text{excess of}} \text{True solution}$$

It is thus clear that the crystal space-lattice breaks down in stages by thermal agitation or solvent effect and transforms finally into isotropic liquid or a true solution respectively. The change from ordered solid crystal to smectic to nematic takes place with increasing breakdown of orientation until finally a completely disordered state is reached. These transitions may be outlined as follows:

(a) Three-dimensional crystal.-Apart from vibration, the centres of gravity of all lattice units are fixed; rotations are not possible.

(b) Crystal with rotating molecules.-The centres of gravity of all lattice units are fixed; rotation about one or more axes is possible. e.g. Butyl halides.

(c) Smectic structure.- The centres of gravity of all the units (molecules) are mobile in two directions; rotation about one axis is permitted.

(d) Nematic structure.- The centres of gravity of the units (molecules) are mobile in three directions; rotation about one axis is permitted.

(e) True liquid.-The centres of gravity of the units are mobile in three directions; rotation about three axes perpendicular to one another is possible.

This brings home the idea that the smectic phase possesses a more highly ordered structure than the nematic one. A very convenient nomenclature for transitions representing equilibrium between phases, suggested by Brown and Shaw (5) is given in Table 2.

TABLE 2

Equilibrium between structures	Abbreviated nomenclature.
Crystal $\rightleftharpoons$ Mesomorphic state (smectic or nematic)	C - M point
Crystal $\rightleftharpoons$ smectic structure	C - S point
Crystal $\rightleftharpoons$ Nematic structure	C - N point
$Smectic_1 \rightleftharpoons Smectic_2$	$S_1 - S_2$ point
$Smectic_2 \rightleftharpoons Smectic_3$	$S_2 - S_3$ point
Smectic $\rightleftharpoons$ Nematic	S - N point
Mesomorphic $\rightleftharpoons$ Liquid	M - L point
Smectic $\rightleftharpoons$ Liquid	S - L point
Nematic $\rightleftharpoons$ Liquid	N - L point

2a. <u>Smectic phase.</u>:

The smectic phase has a stratified structure, the long molecules being arranged in layers with their long axis approximately normal to the plane of the layers. Though, this is a highly ordered phase, the spacing of the molecules within each layer is, however, not uniform as it would be in the true crystal. The fluidity of the phase is attributed to the fact that the layers can glide over one another in hundreds like individual units in a pack of cards. Substances forming three-dimensional crystalline layer structures such as the paraffinic compounds, fatty acids etc, do not pass through a smectic mesophase on heating. It seems that the lateral adhesion of the chains is not sufficient to form smectic layers. 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 the form of a perfectly flat surface and side to side attractions of the molecules (Fig.1) in the sheet would be the strongest forces acting on it. Obviously, the cohesions between these layers will be relatively weak, thus accounting for the characteristic layer flow observed in the stepped drops.

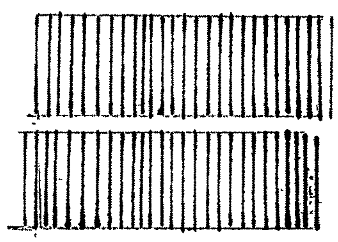


Fig.1 - A section representing the molecular arrangement in two plane smectic strata.

Imagine a number of such smectic sheets laid on top of one another like the leaves of a book. They would now tend to adjust themselves still further, so that the ends of the molecules in one sheet would fit in some characteristic way to the ends of the molecules in the adjacent sheets. Thus a solid crystal would be formed in which there would be order and repetition in every direction in space. In the smectic phase, the temperature is just high enough to ease the bonds between sheets but not high enough to break up the sheets themselves. In some cases, the crystalline structure within a sheet may even break down to give the nematic phase.

A film of a smectic phase stretched over a small hole in a plate gives the condition of parallel sheets. The resulting structure is optically homogeneous and is said to be homeotropic. This homeotropy is formed when the smectic phase is formed on a surface with which it does not form strong local attachments. An interesting feature of the homeotropic structure is the formation of a series of strata or terraces. These terraces are called Grandjean terraces after their discoverer Grandjean (29) and can be seen very clearly when thallium stearate is heated to the first transition point. The stratified structure of the smectic phase was inferred from the formation of stepped drops observed under microscope and has been further confirmed by X-ray analysis (30). The smectic layer structure provides a regular periodicity normal to the layers so that this mesoform gives an X-ray diffraction pattern from which the thickness can be calculated. The layers are homogeneous and when observed in ordinary light, they resemble an isotropic liquid but between crossed nicols the layers appear as homogeneous birefringent patches.

When the smectic structure is formed from cooling the isotropic liquid, it frequently first appears in the form of non-spherical characteristic elongated birefringent bodies known as batonnets. As the temperature falls, these batonnets coalesce and form a focal conic mosaic pattern. Thus, this characteristic focal conic structure has become an important means of detecting the smectic mesophase. It extends all over the specimen and when examined in the polarized light, gives a fan-like appearance and has its origin in the lack of common orientation of the smectic sheets as they form. Friedel has studied the optics of this structure and Bragg (31) has given an excellent account of the focal conic structure and geometry involved, which furnish a further evidence of the layer theory of the smectic structure. The smectic mesophase behaves as a positive uniaxial crystal and remains unaffected by magnetic and electric fields.

2b. Nematic phase :

The nematic phase is not as highly ordered as the smectic phase. The molecules in the nematic phase are arranged with their long axes parallel but they are not separated into layers. They form groups or swarms, each swarm containing hundreds of molecules. E.Bose (32) in 1909 proposed swarm theory to explain the molecular arrangement and order in the nematic phase.

The majority of mesomorphic compounds are comprised of long rod-shaped molecules having dipolar groups situated either centrally or terminally. Because of the elongated molecular shape and the rotation moments existing between neighbouring dipolar molecules, there will be a tendency for the molecules to arrange themselves parallel to one another. These molecules, on the basis of swarm theory, are not oriented in the same direction throughout the whole medium, but are grouped in aggregates or swarms. The molecules within each swarm lie parallel or approximately so, but in a direction that is random to the molecules of the other swarm in the medium. This would mean that the liquid crystalline structure resembles a mass of small crystals rather than a single crystal. However, unlike the mass of small crystals, the swarms do not remain static but are continually exchanging molecules with one another and with the optically isotropic liquid. Thus, the swarms may in fact be considered as the basic particles used to build up the nematic mesophase, particles which are capable of changing their axial directions, and which are, therefore, subject to orientation effects and even Brownian movement.

The Swarm Hypothesis accounts satisfactorily for the turbidity associated with the nematic phase, the light-scattering properties of the swarms explaining the opalescence. Each swarm will be clear and transparent but owing to the reflection and diffusion of light between them turbidity arises to a great or less extent. At higher temperatures, the molecular motion increases with the result that the average size of the swarm gradually decreased and when it becomes smaller than the wavelength of light, turbidity disappears giving a very sharp transition to the isotropic liquid. The effect could occur so rapidly that observations carried out using different wavelengths of illuminating light would detect no difference in the transition temperature. Above this temperature, the liquid is to all intents and purposes singly refracting.

The results of the X-ray analysis carried out by Van der Lingen (33) definitely ruled out Vorländer's assumption that the liquid crystals are endowed with a space-lattice structure which is an important criterion of a true crystal. The regularity of structure producing double refraction and other optical effects simulative of crystals appear to be due to the similar orientation of the flat elongated molecules, the swarm theory of Bose thus being varified. Further, considerable amount of evidence in favour of swarm theory has been provided by the investigation of the optical behaviour of these anisotropic liquids under the influence of a magnetic field (34,35) and by the determination of their viscosity at different temperatures (36). The first mathematical treatment of the swarm theory was given by Ornstein and Zernicke (37).

However, the swarm theory did not pass without criticism; Zocher (38) in particular questioned the validity of the deductions made by Ornstein and proposed the distortion hypothesis in place of the swarm theory. The ideas of the distortion hypothesis have been expressed in highly mathematical terms and are based on the study of the distortion of the nematic structure in the magnetic field.

Though this hypothesis explains some of the properties of nematic structure, especially its behaviour in the magnetic field, it has its own limitations when one attempts to explain the properties of light extinction and wall effects. Increasing evidence in support of the swarm theory is available from the researches like transparency (39), refractive index (37) and magnetic and electric properties (40,41) of mesophases; a summary of such measurements is given by Ornstein and Kast (42).

The properties of the nematic structure indicate that the molecules are parallel or nearly parallel to one another but are not in layers (Fig.2). This phase is very

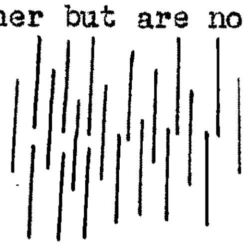


Fig.2.- Molecular arrangement in the nematic phase.

much similar to a true liquid state and has been compared with the cybotactic structure of liquids (43) but compared with the latter, the former has a low internal energy. The X-ray study by Bernal and Crowfoot (30) reveals that the molecules lie parallel to one another and in an imbricated arrangement in the nematic mesophase. The phase owes its mobility to the facility with which the molecules can be drawn past one another while retaining a strong tendency to acquire a parallelism between the long dimensions of the molecules and the direction of drawing. Unlike the smectic mesoforms, the nematic mesoforms are orientated by electric and magnetic fields indicating a greater freedom of movement of the molecules in the nematic phase.

In an electric field, the molecules set themselves with their axes at right angles to the lines of force and in the magnetic field they lie with their long axes parallel to the lines of force.

A notable difference between the smectic and the nematic mesophases lies in the way in which the two mesophase types separate from the isotropic liquid. While the smectic mesophase appears as batonnets, the nematic mesophase separates as tiny, spherical droplets which coalesce to give a nematic threaded texture. The optical effect of the nematic threads has been studied by Zocher and Birstein (44). It seems that the threads are the lines of discontinuities in the structure, i.e. they correspond to the ellipses and hyperbolae in smectic phase but their being no stratification in the medium like the one in smectic phase, no definite geometrical law can be applied.

Zocher and Ungar (45) investigated the sections of nematic structure in converging polarized light and at thickness upto 1 mm., and arrived at the conclusion that the parallel arrangement of the molecules extends from one glass surface to the other, right through the preparation in these thin sections.

Maier and Saupe (46) have given a simple molecular theory of the nematic liquid crystalline state by which it is shown that the nematic-isotropic transition temperature may be determined by calculation of the free enthalpies of the phases involved at the transition. Later, they (47) derived a formula for the average inner field acting on a single molecule in a nematic molecular order. More recently, they (48) have improved their theory by the introduction of close range order parameters and have calculated constituents of thermodynamic energy functions corresponding to the nematic molecular order.

2c. Cholesteric phase :

The cholesteric phase is found in the melt of several compounds mainly those possessing sterol type of skeleton. In many ways, the properties of this phase resemble to those of the smectic and nematic phases. Friedel (3), noted a somewhat closer resemblance between the cholesteric phase and the nematic phase. No substances were found exhibiting both phases viz. cholesteric and nematic, whereas it commonly occured in association with the smectic phase. Based on this argument Friedel considered the cholesteric phase as a special case of the nematic phase. Friedel emphasised his arguments by his observation that mixtures of certain cholesteric substances give nematic mesophase, and that the addition of certain optically active compounds to the nematic mesophase of p-azoxyanisole gives rise to cholesteric properties. Chatelain (49) observed that the amount of light diffused by the nematic mesophase is similar to that diffused by the cholesteric mesophase. More recently Gray (50) on the basis of his study of the mesomorphic behaviour of the fatty esters of cholesterol has expressed the opinion that the cholesteric phase may be best regarded as an individual phase type, though it is more similar to the smectic than to the nematic phase.

When the isotropic liquid of cholesteric compounds is cooled to give the cholesteric mesophase, the texture adopted is focal-conic which is always optically negative and uniaxial unlike the smectic and nematic mesophases which have the properties of positive uniaxial crystals. When a cover slip displacement is made to the homeotropic texture before the focal-conic groups appear, the entire preparation adopts the plane texture. As soon as the plane texture is obtained, the iridescent colours become visible in white light, depending upon the compounds.

Friedel (3) has described the extremely high optical rotatory power of the Grandjean plane texture; however, Stumpf (51) was the first to observe that the direction of rotation of the plane of polarization of the light depends upon the wavelength of the incident light. Mathieu (52) demonstrated that the scattered radiations from the plane texture of cholesteric mesophase form a narrow spectral band, of width 0.02μ, which separates the two spectral regions of opposite optical rotatory sign. De Vries (53) has attempted to relate the physical characteristics of the texture to the arrangement of the layers in cholesteric mesophase.

3. Lyotropic Mesomorphism :

Liquid crystallinity formed by solvation is referred to as lyotropic mesomorphism. The action of a solvent on a solid also involves a disruption of the crystal lattice by the attraction of solute molecules from the ordered crystal lattice into the disordered state of solution. Most of the compounds quite normally pass into solution. Certain compounds, however, on treatment with solvent give a state which is neither a true solid nor a true solution but which is intermediate in character between these two and is found to possess liquid crystalline properties. Since the effect of solvent is responsible for this type of mesophase occurrence, the phenomenon is termed as lyotropic mesomorphism. One of the first liquid crystalline substances discussed by Lehmann (54) was ammonium oleate which belongs to the category of lyotropic liquid crystals. An excess of solvent will of course cause a lyotropic mesophase to pass over into a true solution and the evaporation of such a solution will give first the liquid crystalline state followed by a solid mass. The lyotropic mesophases are always strongly birefringent, although their physical nature may vary widely from that of a waxy substance to that of a clear gel.

Substances like soaps, the soap like alkali salts of nephthenic acids, resin acids, 9-chloro and 9-bromo-phenanthrene-3-sulfonic acids (55) and certain naphthylamine disulfonic acids (56) show mesomorphic state under the controlled action of water. Alcoholic solutions of these compounds do not generally show anisotropic behaviour, so a high degree of hydration appears to be a necessary prerequisite for the occurrence of many lyotropic mesophases. McBain (57) has discussed the forms of mesomorphism in soap solutions. Some of the soap systems have been studied with solvents other than water, e.g. liquid paraffin (58), glycerol, isopropanol and diethylene glycol (59) and in these cases also lyotropic mesophases are found to occur.

A number of cationic and non-ionic detergents have also been reported to give anisotropic phases when they are treated with solvents, in particular with water (60-65). Elliot and Ambrose (66) observed birefringent solutions when poly-γ-benzyl-L-glutamate was dissolved in chloroform. Rinne (4) showed that 10-bromophenanthrene-6-sulfonic acid (55) passes successively through the smectic and nematic stages and finally becomes isotropic while adding increasing quantity of water. A close relationship obviously existing between these liquid crystalline states and the truly colloidal states has been discussed by Ostwald (67). Recently Palit, Moghe and Biswas (68) during their study of solubilization of water by cationic detergents have come across liquid crystalline phases particularly in systems which are close to the solubilization maximum.

Zocher and Coper (69) have shown that methylene blue, neutral red and also other dyes give orientation on rubbed surfaces. Dreyer (70) has discussed the behaviour of films from aqueous solution of amaranth yellow S and naphthol yellow S as well as the dyes of the other classes which exhibit a mesomorphic phase. Sheppard's work (71) on diethyl-Ψ-cyanine proposes a new type of nematic molecular phase, that of plurimolecular filaments rather than elongated molecules. The structure proposed involves intermolecularly co-ordinated water molecules between opposite terminal nitrogen atoms along parallel resonance chains.

More recently, Robinson (72) has reported the interesting observation that viscous solutions of poly-γ-benzyl-L-glutamate are anisotropic in certain organic solvents and show a number of characteristic properties similar to these observed in the thermotropic cholesteric mesophase.

4. Structural requirments for mesomorphism :

As Vorlander has pointed out, liquid crystallinity is no more a rare phenomenon. It is connected with the molecular structure of the compound displaying this behaviour. Vorlander, who has prepared a large number of liquid crystalline compounds has stated that the synthesis of liquid crystalline substances is no more a matter of great difficulty, provided certain conditions are fulfilled. The compounds possessing these properties vary widely in chemical constitution, but all possess the common feature of molecular geometric anisotropy. Generally speaking the molecules of mesomorphic compounds are elongated, rod- or lath- like in shape and terminating in polar groups. Cholesteryl molecules which possess liquid crystalline properties are considerably broad but here also length predominates over breadth and thickness.

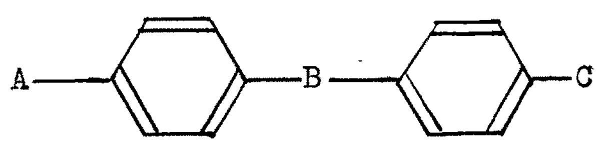
To synthesise a potentially mesomorphic system, long narrow molecules must contain groups of atoms with which are associated permanent dipole moments and the molecule itself must be highly polarizable. To ensure a high polarizability for the rod-like molecule would be to incorporate in it, polarizable aromatic rings and unsaturated linkages. In aromatic compounds, it is necessary to maintain the linearity of the system as Vorlander (73) calls it and hence most of the benzene derivatives which exhibit mesomorphism are para-substituted; 4,4'-di(benzylideneamino) biphenyl is a well-known example. This molecular complexity also prevails in the amorphous liquid state (74).

The shape of these elongated rod-like molecules facilitates to set themselves parallel to one another leading to the closest possible packing in the crystalline or liquid crystalline state, the molecules being held together by local attachments due to the polar groups and unspecific Van der Waals attraction. On raising the temperature, the cohesion between the molecules previously holding them together in the crystal arrangement does not break down uniformly in all directions; there may be a lateral cohesion still operating which will tend to hold the molecules together in groups. The transition to the disordered arrangement found in true liquid phase due to the collapse of three-dimensional order and geometrical arrangement of the molecules in the solid state, therefore, takes place in stages, i.e. the weaker linkages break first, leaving the molecules with some freedom of relative movement before they acquire sufficient thermal energy to overcome the tendency of parallel arrangement. Thus the medium acquires a flow movement and it is birefringent because of the preferred orientation of the molecules.

However, it is frequently found that many long and narrow or lath-shaped molecules do not give rise to liquid crystalline phase and so due consideration should be given to the other factors which assist this phenomenon.

In addition to the linearity of the molecules, the compound should not be very high melting to cause thermal agitation sufficient to bring disorder in the melt and that the intermolecular forces should be strong enough so that some order may be preserved in the melt when the crystal lattice breaks down, but strong intermolecular forces bring about high melting point. These two conditions are in opposition to one another and therefore, all compounds with long molecules do not form liquid crystals. For example, the long and narrow molecules of n-decane and n-dodecane fulfil the requirment of geometric anisotropy, yet these compounds are not mesomorphic. Therefore, it may be concluded that, the compounds such as normal paraffins and the homologues of acetic acid possessing favourable geometrically suitable conditions for mesophase formation, exhibit no mesomorphic properties for the simple reason that the attractive forces operating between the molecules are not sufficiently strong to maintain a parallel arrangement for the molecules after the crystal lattice has melted. Therefore, in predicting whether a compound will be mesomorphic or not, the nature and the probable strength of the intermolecular attractions must enter into our considerations together with the purely geometric aspects of the molecule. Thus, a compound to form a liquid crystal should possess long molecules capable of giving cohesive forces to attract the neighbouring molecules. Normal Van der Waals forces may not be strong enough to bring about such attractions and cohesion must result from the intermolecular forces of a polar nature.

The compounds studied for liquid crystallinity reveal that liquid crystalline compounds are characterised by long chain molecules often possessing mildly active groups like $-C \equiv C-$, $-CH = CH-$, $-N=NO-$, $-CH=N-$, $-CH=N-N=HC-$ in the middle of the molecule and generally terminating in active groups like $-OR$, $-COOR$ where R is a normal alkyl chain. In fact, the minimum structural requirements for a compound to exhibit mesomorphism have been summarised by Brown and Shaw (5) by the general formula:



where A and C are polar end groups and B is a mildly polar central group. The terminal polar groups increase cohesion between the molecules in an end-to-end fashion while the central group gives lateral adhesion. As a matter of fact, these dipolar groups impart dipole moment to the molecule as a result of which the molecules will exert rotation moments on one another. This will orientate the molecules in parallel and the attractive forces between the molecules being effective over short ranges, the molecules will attach preferably end-to-end. Thus the swarm will be anisotropic and the long axis of the molecules will lie parallel to the long axis of the swarm. However, the polar attraction should not be very great to raise the melting point of the compound very high when the thermal agitation at this temperature will cause spontaneous disorder in the melt.

The benzene ring also plays a similar role in mesomorphism. The increase in the number of aromatic rings increases the stability of the mesophases. For example, p-n-propoxybenzoic acid having one benzene ring melts at 145°C to give a nematic melt which clears at 154°C, thus giving a phase length of 9°C only. 4'-n-Propoxydiphenyl-4-carboxylic acid with one more benzene ring than the previous acid, melts at 260°C and clears at 287°C, thus exhibiting liquid crystallinity for 27°C. Here, the increase of one ring has resulted in rising the nematic thermal stability from 154°C to 287°C. In many cases, it has been found that the liquid crystalline substances sublime or distil before they change to isotropic liquid, e.g. 4:4'-di-(p-methoxybenzylideneamino)diphenyl, N:N'-di-(p-methoxybenzylidene)-p-phenylenediamine etc.

The normal fatty acids are not mesomorphic but their ammonium and thallous salts show either thermotropic or lyotropic mesomorphism. These salts should be more polar than the free acid and so give more cohesion. Ammonium myristate melts to a smectic phase which persists over some 30°C to 35°C before giving the isotropic liquid. Thallous stearate shows a phase length of 45°C from 118°C to 163°C.

Bernal and Crowfoot (30) have generalised the conditions for smectic and nematic liquid crystals. Smectic substances should have either one active group as in the case of ammonium oleate or a fairly strongly active group at each end as in para-azoxy esters of benzoic and cinnamic acids. This will induce layer formation which is often found in solid crystals. Such crystals are known as smectogenic. In the case of nematic substances, the molecules contain weakly active groups at the centre as well as at the ends as in para-azoxy ethers. This may lead to imbricated crystal structure as found in p-azoxyanisole and p-azoxyphenetole which give nematic mesophase only. Such crystals are known as nematogenic. p-Methoxycinnamic acid may at the first sight be expected to be smectic but in the melt the molecules are associated in pairs by the carboxyl groups forming a double molecule of the type giving rise to a nematic mesophase rather than smectic (75).

p-n-Alkoxybenzoic acids are the simplest molecules known to form liquid crystals (76-80). In these acids the length of the rod-shaped molecules is increased by the hydrogen bond formation and the mesomorphism arises from the association of the acids forming a dimer through carboxylic groups. Thus, p-n-propoxybenzoic acid which has the simplest molecular structure known to form liquid crystals, acquires a structure which is linear and similar in shape and size to the typical nematic substance - p-azoxyanisole. This is supported by the fact that methyl ester of this acid is not mesomorphic, though the ester group is dipolar but does not compensate for the shortness of the ester molecule and hence the carboxylic group plays an important role in increasing the length of the molecule. p-Methoxy- and p-ethoxybenzoic acids are not mesomorphic which may be attributed to their high melting points. However, the mixtures of the two acids over a range of temperature and concentration show the nematic mesophase as a result of the lowering of their melting points.

As it has been pointed out by Vorlander (81), a definite axis of symmetry in long chain molecules plays a decisive role in liquid crystal formation. The introduction of groups which destroy the symmetry of the molecule either reduces the mesomorphic stability or results in total elimination of liquid crystalline properties. The introduction of $-CH_2$ group between two benzene nuclei in a highly stable liquid crystalline benzidine derivative causes the disappearance of enantiotropic form. Similar effect is observed when -CO, -CS, -S- etc., groups are introduced and -NH- group reduces the range of mesomorphic stability practically to zero though sometimes monotropic mesomorphism is observed. Vorlander explains this phenomenon by the departure of the molecule from the straight line arrangement.

The replacement of alkoxy group by an alkyl group either destroys the mesomorphic properties or reduces mesomorphic thermal stabilities.

Effect of molecular breadth on mesomorphism is interesting. Vorlander (82) was the first to report the existence of mesomorphism in certain naphthalene derivatives, which are considerably broader than benzene derivatives. Later Gray and Jones (83, 84) have found that 6-n-alkoxy-2-naphthoic acids are mesomorphic and halogen substitution in

5-position results in decreasing the stability of the mesophases in the higher members and elimination of mesomorphism in the lower members. Even 2-p-n-alkoxybenzylideneaminophenanthrenes (85) are mesomorphic.

The substantial increase in breadth destroys mesomorphism of a parent compound, e.g. a nematic phase of 27^{o}C in p-n-pentyloxybenzoic acid is eliminated by 3:5-dichlorination. Therefore, it is evident that the breadth of a molecule cannot be increased greatly without destroying mesomorphism. To investigate precisely the effect of the breadth and molecular dimensions on mesomorphism Gray and Jones (86) extended their study to the influence of substituents in the 3-position of p-n-alkoxybenzoic acids and in the 5-position of 6-n-alkoxy-2-naphthoic acids. They found that 3-bromo-4-n-alkoxybenzoic acids do not exhibit mesomorphism whereas less broad fluoro- and chloro- derivatives show short mesophases.

Gray (87) also studied the effect of replacement of n-alkyl group by a branched alkyl group in 6-n-alkoxy-2-naphthoic acids and found that the mesomorphic characteristics are greatly reduced or destroyed. He comments that the effect of branching in the alkyl group will have a greater effect than halogen- or nitro-substitution in the 5-position, since the branching will force the molecules apart by preventing the close packing of the alkyl groups which is possible in the normal ethers.

5. <u>Physical Properties</u> :

Compared to the optical and chemical properties much less work has been done on the study of physical properties of liquid crystalline substances.

5a. <u>X-ray studies of the mesomorphic state</u> :

Hückel (88) and de Broglie and Friedel (89) were the first to examine liquid crystals by means of X-rays. Huckel (88), Katz (90) and Kast (91) concluded that the X-ray diffraction patterns of the nematic structure are similar to those of the liquid. de Broglie and Friedel showed that the molecules in the smectic structure are in equidistant parallel strata. However, Glamann, Herrmann and Krummacher (92) reported a small difference in the X-ray patterns in the nematic and the liquid structure. Herrmann (93) made a useful contribution to the X-ray study of mesophases; his findings were that the X-ray diffraction patterns for the isotropic liquids and the nematic mesophases were diffuse halos which could not be distinguished while for the smectic mesophases two types of diffraction pattern were observed, one showing a halo and a narrow inner ring, and the other a sharp ring and an inner ring. Herrmann attributes the new type of interference giving the sharp inner and outer rings to a hexagonal cylindrical packing of the molecule within the smectic planes. This is also a possible explanation of polymesomorphic behaviour of smectic phases.

Kast (94) in his X-ray studies of the nematic phase observed that the diffraction halos of the nematic phase change and become crescent shaped perpendicular to either a magnetic or an electric field. Herrmann, Krummacher and May (95) concluded that in anisaldazine and p-azoxyanisole, the long molecular axes are orientated perpendicular to the applied field and in methyl p-(4-ethoxybenzylideneamino) cinnamate parallel to the field. Stewart (96) carried out an X-ray study on p-azoxyanisole in the presence and the absence of the magnetic field. He has compared the X-ray patterns of the nematic and the isotropic liquids and indicated that the relatively large agglomerates of the molecules (swarms) in the nematic mesophase do not persist in the isotropic liquid, but that smaller, cybotactic groups of the molecules do exist in the isotropic liquid. Brown and Shaw (97) have studied X-ray diffraction patterns of the mesophases of azines.

Bernal and Crowfoot (30) carried out X-ray analysis of the nematic liquid crystalline compounds in crystalline state and found that in the case of p-azoxyanisole the molecules do not lie in the layers but they are parallel to each other in an imbricated fashion. They concluded that an imbricated arrangement of the parallel molecules will occur in the nematic mesophase itself. Recently Bryan (98) has done X-ray work on p-n-alkoxybenzoic acids in solid states.

Nordsieck, Ferguson and Rosevear (99) have used X-ray methods to study the transformations of sodium palmitate. The subwaxy, waxy and superwaxy phases exhibit two diffuse short spacing rings, while the subneat and neat phases exhibit one diffuse short spacing ring.

5b. Ultra Violet and Infra Red Spectroscopic studies :

Ultra violet and infra red spectroscopic studies of mesophases have not so far yielded any vital information about the molecular orientation and the degree of molecular aggregation in the mesophases. Rawlins and Taylor (100) reported that the spectra of the mesophases and the isotropic liquids are more or less identical. Freymann and Servant (101) studied the Raman spectra of solid, nematic and isotropic phases of p-azoxyanisole.

More recently Maier and Saupe (102) examined ultra violet absorption characteristics of the nematic and the isotropic phases of p-azoxyanisole and concluded that ultra violet spectroscopy offers little hope of giving any information about the nature of the molecular interactions in the nematic melt. Maier and Englert (103) have also published the results of their very detailed infra red study on 4,4'-disubstituted azo- and azoxy-benzenes and suggested that the work may eventually make it possible to use infra red spectroscopy to compare the molecular orientation of the crystalline and the mesomorphic states of the compounds.

5c. Proton Magnetic Resonance studies :

Spence, Moses and Jain (104) have reported that the proton resonance line changes markedly in character on passing from the isotropic liquid which gives a single narrow line to the nematic mesophase of p-azoxyanisole. In the nematic structure, the amplitude of the signal decreases greatly compared to the liquid state and the line splits into three components. Later, Jain, Lee and Spence (105) showed that the character of the signal from p-azoxyanisole remains virtually unaltered as the temperature is increased from the solid-nematic point. The decrease in the spearation of satellite peaks occurs just before the nematic-isotropic transition temperature at which the separation into the three peaks suddenly vanishes, and a single line characteristic of the isotropic liquid is obtained.

Spence, Moses and Jain (104) tried to explain these effects by a very strong hindering of the methyl groups in p-azoxyanisole, but Spence, Gutowsky and Holm (106) explained these effects in terms of the magnetic non-equivalence of the protons of the aromatic rings in the mesophases of p-azoxyanisole. Jain, Moses, Lee and Spence (107) extended their study to p-azoxyphenetole and anisaldazine.

Ewing and Lee (108) found a triplet signal similar to those found for p-azoxyanisole and anisaldazine in the highest temperature mesomorphic phase of ethyl p-(4-methoxybenzylideneamino)cinnamate which exhibits three mesomorphic phases. For this compound a radical change in line shape was observed with decreasing temperature until only a single narrow line on a broad plateau resulted. The limited available data on the signal from smectic phases by Moses (109) indicates that in general a single structureless line is observed which is intermediate in width between that of the liquid and the crystalline phase. Grant, Hedgecock and Dunell (110) determined the transition temperature of anhydrous sodium stearate by nuclear magnetic resonance and found that they agree well with the temperatures obtained by conventional methods. Jain et al (107) have also observed a single structureless line in cholesteric mesophase of cholesteryl benzoate.

5d. Viscosity :

Schenk (111) determined the change of viscosity with temperature for cholesteryl benzoate and p-azoxyanisole by using the capillary flow method. He found that the viscosity of the mesophase fell off with increasing temperature, but at temperature close to the mesomorphic-isotropic transition, there was in each case a sudden break in the viscosity against temperature curve, the viscosity rising steeply to a maximum at the transition temperature and then falling again. Eichwold (112), Bacherer and Kast (113) have confirmed Schenk's observation.

Vorlander (82) determined the viscosity changes in the smectic phase of ethyl p-azoxybenzoate over the temperature range 114^{o}C to about 133^{o}C and showed that the trends were unlike those obtained with cholesteric or nematic systems. There was a very sudden fall in the viscosity exactly at the smectic-isotropic transition, but no rise to maximum preceded the transition. He (27) also studied the changes in viscosity with increasing temperature for ethyl p-(4-ethoxybenzylideneamino)-α-methylcinnamic acid and p-(4-methoxybenzylideneamino)cinnamate both of which show mesomorphic-mesomorphic transitions. He observed that the polymesomorphic changes between smectic mesophases and mesomorphic changes between different mesophase types (smectic-nematic) are accompanied by sudden decrease in the viscosity as the temperature rises.

5e. Surface Tension :

Ferguson and Kennedy (114) found that the surface tension of the mesophases increases with rising temperature. Naggiar (115) by his modified experimental technique showed that, for p-azoxyanisole the surface tension decreased from about 39.5 dyn/cm at a temperature just above the melting point of about 116 °C to just below 37.4 dyn/cm at the nematic-isotropic transition at 133-134 °C thus contradicting Ferguson and Kennedy's observation. Schwartz and Moseley (116) confirmed Naggiar's results on p-azoxyanisole by studying p-azoxyphenetole (nematic) and ethyl p-azoxybenzoate (smectic) using the ring method on a du Nouy tensiometer.

5f. Dielectric constant of the nematic structure :

Kast (117) has given a critical summary of the work done in this field on liquid crystals upto 1931. Kast's survey is concerned with substances having the nematic structure which from their dielectric characters fall into two groups, i.e. symmetrical and asymmetrical molecules. Symmetrical molecules (e.g. anisaldazine) show a reduction in dielectric constant when a magnetic field is perpendicular to the plates of the condenser and a small increase when parallel. There is a small increase in the dielectric constant of unsymmetrical molecules (e.g. ethyl p-ethoxybenzylideneamino-α-methylcinnamate) when they are acted on by a magnetic field parallel to the electrical field.

Bhide and Bhide (118) measured dielectric constant and absorption of p-azoxyanisole by the resonance method at frequencies of 1000, 3855 and 6480 kilocycles. There were abrupt changes in the dielectric constant as the mesomorphic phase changed to the isotropic liquid, with the changes being more pronounced at the higher frequencies. The values of the dielectric constant for rising and falling temperatures below the nematic-isotropic point were not coincident. Cholesteryl benzoate showed comparable effects on the change in dielectric constant but showed no absorption. Ornstein, Kast and Bouma (119) from the study of the dielectric constant measurements of benzophenone and p-azoxyanisole, calculated the degree of orientation of the swarms obtaining a maximum value of about 80 percent.

Marinin and Tsvetkov (120) by means of the suspension method studied the dielectric properties of p-azoxyanisole in motion through capillary. The dielectric properties were found to vary with the velocity of flow, the strength of the applied magnetic field and the temperature. Maier (121) observed the change in dielectric constant in longitudinal and transverse magnetic field upto 5000 gauss. He found that a horizontal temperature gradient of 0.1 ^{o}C per centimeter produces almost complete orientation of the swarms. Funt and Mason (122) found no effect of shear on the dielectric constant of the mesomorphic state by the usd of a rotating cylindrical condenser.

Recently Maier, Barth and Wiehl (123) studied the dielectric constants of 4,4'-dipentoxy-azoxybenzene. Tsvetkov and Marinin (124) evaluated the Kerr constant for p-azoxyanisole, p-azoxyphenetole, dibenzalbenzidine, anisal-p-aminoazobenzene, ethyl p-azoxybenzoate, anisaldazine and p-acetoxybenzalazine.

5g. Magnetic Susceptibility :

Comparatively much less work has been done on the magnetic properties of substances in the mesomorphic state, although there have been several studies of the phenomenon discovered by Mauguin (125) that the optic axis of substances in this state tends to set itself parallel to the lines of force of a magnetic field of sufficient intensity. Foex (126) found that the average susceptibility of powdered p-azoxyanisole is -0.565×10^{-6}; at the mesomorphic (nematic) transition temperature (116 °C) the susceptibility falls rapidly to -0.457×10^{-6}. As the temperature rises, the dimagnetism also increases slowly until above 133 °C when the substance becomes an isotropic liquid for which $X = -0.545 \times 10^{-6}$. If now the temperature is lowered, the reverse changes occur except that the nematic phase may persist considerably below 116 °C. Analogous behaviour was found in the case of p-azoxyphenetole and anisaldazine. The reason for this type of behaviour is that the long dimension of the molecule is the least dimagnetic and hence orientates to lie in the direction of the lines of force. If the substance is crystallised in a magnetic field, a strong anisotropy exists with the smallest diamagnetism along the lines of force. Foex also reports on measurements of principal susceptibilities over a temperature range.

Substances such as ethyl p-azoxybenzoate which occur in the smectic phase show in general only a small and irregular increase of diamagnetism on passing from solid to liquid. If, however, a field is present during cooling to the smectic phase, orientation sets in with a strong decrease of diamagnetism. Some further studies of magnetic anisotropy in liquid crystals have been reported by Tsvetkov and Sosnovskii (127).

5h. Chromatography :

Very recently, applications of liquid crystals as stationary phases in gas-liquid chromatography are described by Dewar and Schroeder (128). The use of nematic phase of p-azoxyanisole led to excellent separations of a number of meta-para pairs of disubstituted benzene derivatives; mixtures of m-xylene and p-xylene were easily separated by using smectic phases of 4,4'-dihexoxyazoxybenzene and 4,4'-diheptoxyazoxybenzene. The retention times vary in an interesting manner with temperature showing a marked decrease at the transition point to normal liquids; as anticipated, the effect is less for the more nearly linear p-isomers.

6. Mesomorphism in Homologous Series:

It has been observed earlier that there is a close relationship between mesomorphism and molecular constitution of organic substances. With a view to correlate the effect of the structural modifications on mesomorphism, the researchers in this field centred their attention around the study of mesomorphic properties of different series of organic compounds. Vorlander (129) examined the variation in the mesomorphism in the Schiff's bases obtained by the condensation of aromatic aldehydes with trans p-aminocinnamic acid esters. Friedel (3), Jaeger (130) and Gray (131) have studied the phase transitions in the homologous series of cholesteryl esters of the saturated fatty acids. When various transition points are plotted against the number of carbon atoms in the side chain, Gray (131) finds that all the smectic-cholesteric points lie on one curve which rises at first and then falls gradually with the maximum at cholesteryl laurate. The cholesteric - isotropic transition points lie on two curves, of which, the lower one falls steeply at first and then more gradually through the points for esters with an even number of carbon atoms in the alkyl chain; however, the upper curve representing homologues having odd number of carbon atoms in the alkyl chain rises steeply from the acetate to the butyrate and then falls gradually through the points for the hexanoate, octanoate, decanoate, laurate, myristate, palmitate and stearate. Bennett and Jones (78) and later Gray and Jones (80,132) examined the mesomorphic trends in p-n-alkoxybenzoic and trans p-n-alkoxycinnamic acids. The study indicates that, when the alkyl chains are short, the systems are either non-mesomorphic or nematic; as the chain length increases, the smectic properties begin to appear. The smectic phase length increases at the expense of the nematic phase length with each successive chain increment until finally in the higher homologues only the smectic phases are found. Weygand and Gabler (133) examined homologous series of p-azo- and p-azoxy compounds and Schiff's bases. Their observations are similar to those of Bennett, Jones and Gray, though several of their compounds display monotropic mesophases.

Recently, Gray and co-workers (83-85, 131, 134-141) studied various homologous series of organic compounds to investigate the effect of alkyl chain length and substitution in the aromatic nucleus on mesomorphism. Generally, when the mesomorphic transition temperatures for the compounds of a homologous series are plotted against the number of carbon atoms in the alkyl chain, the upper transition points lie on two smooth curves; the upper curve corresponds to the compounds with an even number of carbon atoms in the alkyl chain and the lower one to those with an odd number of carbon atoms. The smectic-nematic transition points lie on a smooth rising curve which merges with the falling nematic-isotropic curve for the homologues having even number of carbon atoms in the alkyl chain.

Gray et al. extended their studies to the influence of substituents (86, 137, 138) in the 3-position of p-n-alkoxybenzoic acids and trans p-n-alkoxycinnamic acids, in the 5-position of 6-n-alkoxy-2-naphthoic acids and in the 3'-position of 4'-n-alkoxydiphenyl-4-carboxylic acids and their alkyl esters and have correlated the effects of substituents with mesomorphic thermal stabilities. The

3-substitution in p-n-alkoxybenzoic acids and trans p-n-alkoxycinnamic acids introduces an additional dipole moment into the molecule. Such an introduction in a mesomorphic molecules has two opposing effects : (i) the substituent will decrease the smectic and nematic thermal stabilities by increasing the separation of the long axes of the molecules and (ii) the substituent will increase both the smectic and nematic thermal stabilities because of its polarization effects which will enhance the intermolecular cohesions. 3-Bromo-4-n-alkoxybenzoic acids do not show any mesomorphism while the less broad fluoro- and chloro-derivatives show short mesophases. In the case of trans p-n-alkoxycinnamic acids the breadth and polarization are increased by halogen substitution and the thermal stabilities of the mesophases are altered. The presence of chlorine or bromine however does not completely eliminate the mesomorphic properties though in the broader bromo-derivatives, the long chain dodecyl, hexadecyl and octadecyl ethers alone exhibit monotropic mesophases. In the case of 5-substituted 6-n-alkoxy-2-naphthoic acids, effect (ii) predominates and the mesomorphic thermal stabilities are frequently higher than those of the parent unsubstituted acids. Generally, in most of the systems, the substituent exerts its full breadth-increasing effect on the molecule which results in the increase in the separation of the long axes of the molecules and there is a remarkable decrease in the smectic and nematic thermal stabilities when compared to the unsubstituted parent molecule.

Brown and Shaw (5) and recently Gray (142a) have given vivid account of the mesomorphic behaviour of various homologous series which throw good light on molecular structure and mesomorphism. More details regarding the effect of structural changes on phase transitions in certain homologous series and factors governing them will be discussed later in the discussion section.

7. Mesomorphism in Biological Systems :

Until recently mesomorphism in biological systems has been virtually ignored, although the first observation of a mesomorphic state in biological systems seems to be the mention of myelin forms in 1854 (143). It has now been known that several biological systems exhibit liquid crystalline properties and some possess properties analogous to those observed in mesomorphic systems. Many living tissues like muscles, nerves, tendons and bones show the optical property of double refraction (144). The degree of double refraction in such fibrous systems increases on stretching and decreases on contraction.

It has been found by Rinne (4) that merely moistening sphingomyelin, kerasin and lecithin preparations with water or aqueous glycerol and heating causes the formation of a smectic phase. Phrenosin and kerasin were separated from galactosides of the brain by the use of cold pyridine and mesomorphic forms were obtained (145). Massive deposits of mesomorphic compounds are found in kidneys, liver, spleen marrow and aorta walls, through the utilization of cholesterol compounds.

Living sperms, composed in part of protein, nucleoproteins and albumins have been shown to possess a mesomorphic phase (146, 147). The anisotropy occuring very commonly in the sperms is exhibited in the extended form of sperm head. This double refraction can be destroyed by the artificial swelling of the sperm heads.

A recent discussion of the structure of chromosomes is given by Ambrose (148). Aqueous solutions of certain viruses e.g. tobacco mosaic virus exhibit lyotropic mesomorphic properties (149-151).

Brown and Shaw (5) have pointed out that mesomorphic state is singularly well fitted to provide complex forms in which organization and lability can be combined to a unique degree. Compounds can be found in the biological systems whose molecular structure and orientation represent every intermediate degree of orientation, plasticity and viscosity between crystalline substances on the one hand and mesomorphism or even isotropic substances on the other hand. The mesomorphic modifications are of important biological significance; slight changes in composition and in physical and chemical properties can materially affect the formation, continuation or cessation of the mesomorphic state, a delicate balance characteristic of many biological processes. As Bowden (152) has put it, this state seems to be especially suited to biological functions and may possibly be the basis of vital activity.

8. Mixed-Mesomorphism :

The purity of an organic compound is many times commonly judged by the mixed melting point. When an organic compound is mixed with some other organic compound, the mixed melting point is found to be lower than the individual melting points of the pure components. Similarly, if a mesomorphic compound is mixed with another mesomorphic or non-mesomorphic component, the solid-mesomorphic and mesomorphic-isotropic transition points may get depressed and the degree of depression will depend upon the concentration of the added component in the mixture.

Schenck (153) showed that the isotropic-nematic transition temperature of p-azoxyanisole is lowered by the addition of other substances. He also pointed out that p-azoxyanisole and p-azoxyphenetole in the liquid crystalline state form isomorphous mixtures. Kock (18), with a view to explore the possibility of the use of this transition in the cryoscopic work and to study the effect of the addition of another substance on the mesomorphic state of a liquid crystalline substance, investigated a number of binary systems of the mixtures of substances, one or both of which were liquid crystalline. He found that inthe binary systems where one component is liquid crystalline and the other non-liquid crystalline, mixed liquid crystals were formed but only upto a certain concentration of the second component, the nematic-isotropic temperature being lowered. He discussed the general problem in terms of the phase rule.

Bogojawlensky and Winogradow (154) have examined mixtures of isomorphous substances and have reported the formation of mixed liquid crystals from pairs of substances one or even both of which were not giving normal liquid crystals. They also determined the latent or labile transition points (isotropic-nematic points) of the non-mesomorphic substances in many cases by the extrapolation of the nematic-isotropic transition curve which was linear in the majority of cases. Vorlander and Gahren (155) and Bennett and Jones (78) also observed that binary mixtures of the components which were non-mesomorphic gave rise to liquid crystals when they were melted. Walter (156) has given an explanation to the observation of Vorlander and Gahren. He said that the compounds which yield such mixtures are generally very well crystallized and are not readily supercooled. Consequently, a monotropic liquid crystal phase which might be anticipated for them remains latent. If two such chemically similar substances are mixed, it may happen that the melting point of the mixed solid phase which is usually lower than the melting point of the individual components, falls below the mixed melting point of the crystalline liquid phase which with chemically related substances should lie between the two latent crystalline liquid melting points of pure components. Such a mixture which should form mixed liquid crystals, exhibits enantiotropic liquid crystalline properties. Walter supported his views by studying a binary mixture of anisic acid and anisylidene-propionic acid which themselves are non-mesomorphic but their mixtures yield mixed liquid crystals within certain limits of concentration. Dave and Lohar (157) have described enantiotropic nematic liquid crystalline properties of mixtures of p-anisylidene-p-phenetidine (monotropic nematic) and p-nitrobenzylidene-p-phenetidine (non-mesomorphic). Prins (158) studied the binary mixtures of p-azoxyphenetole with p-azophenetole, cholesteryl isobutyrate, cholesteryl propionate, cholesteryl benzoate, p-methoxycinnamic acid and p-azoxyanisole and discussed the problem in terms of phase rule. He observed that p-azoxyphenetole and p-azoxyanisole form a continuous series of mixed liquid crystals throughout, the linear clearing point curve falling regularly from the upper melting point of the former to that of the latter component. Cholesteryl propionate also shows a similar behaviour.

It seems Kock and Prins have studied the problem from the standpoint of phase rule but no satisfactory explanation seems to be available as to the nature of mixed liquid crystals and the mode of their formation. Dave and Dewar (159) investigated a number of binary systems in which one component was liquid crystalline and the other non-mesomorphic. In all the cases studied, the liquid phase is apparently a homogeneous single phase which may or may not be anisotropic. They found no evidence for the two distinct liquid phases, one isotropic and the other anisotropic, existing side by side over a range of temperature, for a binary mixture of a given composition. From their experimental results they have tried to deduce the effect of the terminal groups of a non-mesomorphic component on mixed mesomorphism. They state that the transition lines of binary systems in the phase diagrams stand as a measure of the tendency of the non-mesomorphic component towards mixed mesomorphism;

consequently they obtained different values of group slopes for various end groups. The lower slope value indicates the greater tendency of the non-mesomorphic component towards mixed liquid crystal formation and vice versa. The binary systems studied by them comprise of p-azoxyanisole as the nematic mesomorphic component and p-substituted Schiff's bases as the non-mesomorphic components (160). From the slope of the transition lines of the phase diagrams, they have deduced the following order of efficiency of the end groups of the non-mesomorphic components towards mixed liquid crystal formation:

$$NO_2 > OM_e > Me_2N > Me > Cl > Br > H$$

Later, Dave and Lohar (161) studied more systems of this type and found the following extended order of group efficiency in the descending sequence:

$$NO_2 > OC_2H_5 > OCH_3 > O.CO.C_2H_5 > O.CO.CH_3 > Me_2N > CH_3 = Cl$$
$$Cl \quad Br > I > OH > H$$

This order is the order of decreasing polarity of the groups regardless of sign; and so evidently the main factor is the magnitude of the group dipole moment and not its direction.

Binary mixtures with nematic liquid crystal as one of the components have been studied but such mixtures with the smectic liquid crystalline component do not seem to have been studied so far. It was, therefore, thought worthwhile and interesting to study binary systems with smectic liquid crystals as one of the components. The behaviour of such mixtures will be discussed in detail later on in the discussion section.