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

INTRODUCTION

Definition and Nomenclature :

A crystal is generally thought of as being a rigid solid. Solids, in general melt to give isotropic liquid on heating. The molecules in a crystal are fixed in a regular three dimensional array whereas, molecules in a liquid , if not as randomly distributed as those in a gas, are not arranged in any order that extends over a distance greater than a few molecules across.

Yet, there do exist substances which form one more liquid phase possessing some of the properties of both liquids and crystals.

Thus, when certain solids e.g. p-azoxyanisole, are heated, they do not pass directly into the liquid state, but adopt a structure which has properties intermediate between those of a true crystal and those of a true liquid. At a certain temperature the solid undergoes transformation to a turbid condition that is both birefringent and fluid, the consistency varying with different compounds from that of a paste to a freely flowing liquid. At a higher temperature, the turbid phase melts sharply to a clear isotropic liquid. On cooling, the changes take place in the reverse direction, although some supercooling may occur when mesomorphic-solid transition temperatures are reached, as in the case of ordinary crystallization. Such an intermediate state has been given the name liquid crystal since the

time of its discovery.

The phenomenon of liquid crystallinity was first observed in 1888 by the Austrian botanist F. Reinitzer (1) who noted that solid cholesteryl benzoate melts at 145.5°C to a cloudy liquid and at 178.5°C the liquid becomes clear. Shortly thereafter, the German Physicist O.Lehmann (2) after a systematic study of such substances, showed that the cloudy intermediate phase seemed to have a crystal-like structure. He suggested the name liquid crystal or crystalline liquid in order to describe this intermediate state of substances, which is liquid in its mobility and crystalline in its optical properties. The first property (liquid) suggests that the substances in this phase are readily disturbed though the mesophase may be readily renewed, while the latter property (crystal) suggests some degree of arrangement of the component molecules. Although the term 'liquid crystal' is simple and suggestive and has been used since its inception by Lehmann, objections have been raised to this nomenclature ; there have been many controversial discussions regarding the relative advantages of the names liquid crystal and crystalline liquid. However, both the names are unsatisfactory, as the state is neither crystalline nor liquid in the true sense of the words. Crystals have a three dimensional order, whereas phases may have one or two dimensional order. The word liquid is also not very appropriate as the phase in some cases may be crystalline in hardness as in the case of lecithin.

Owing to the birefringence of the turbid liquid

observed through crossed nicols, the terms 'anisotropic liquid' or 'anisotropic melt' are also used.

As more and more properties of these liquid crystals became established which obviously, supported for a new state of matter, Friedel (3,4) in particular stressed that though this state possesses some of the properties of a liquid as well as of a crystal, liquid crystals were neither genuinely crystalline nor liquid. He described this state as a mesomorphic state (Greek- mesos, intermediate ; morphe, form) which means the intermediate state between the crystalline and the amorphous states. This term and the associated terms 'mesomorph','mesophase' and 'mesoform' are also generally used today.

Rinne (5) has criticized both the terminologies on the basis that they do not convey any structural meaning. He classified matter as exhibiting either ataxy (a disordered or amorphous structure) or eutaxy (an ordered structure). The mesomorphic and crystalline states will belong to the class of eutactites, since they possess ordered or regular structures. Amorphous matter like isotropic liquids and gases will fall into the category of atactites. Rinne suggested the term 'para crystals' for substances exhibiting mesomorphism. The term 'crystal' emphasizes the natural proximity of the state to the crystalline condition of the turbid state and the prefix 'para' reminds us that most 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 other amorphous matter.
2. Eutactites - (a) Crystals - Three dimensional order.
   (b) Para Crystals - one or two dimensional order.

However, Rinne's nomenclature has not been adopted to any significant extent.

Brown and Shaw (6) consider the term 'mesomorphic state' preferable and have used it as the title for their recent review. Inspite of many subsequent arguments about nomenclature, the name liquid crystal is still ffequently employed and will be used in this thesis.

The mesomorphic state has been further classified considering the way in which it is obtained. The formation of the mesomorphic state by virtue of heating is referred to as thermotropic mesomorphism by Friedel (3), Lawerence (7) and Jelly (8), while lyotropic mesomorphism has been defined as that type of mesomorphism obtained by solvation, the solvent generally being water. Further, as a result of his detailed optical studies, Friedel was able to distinguish clearly three different types of mesophases. They are :

1. The smectic mesophase..... a turbid, viscous state, with certain properties reminiscent of those found for soap. The term smectic (soap-like) was coined by Friedel (9) from Greek σμεγμα meaning grease or slime.

2. The nematic mesophase..... a turbid but mobile state. The term nematic is also coined by Friedel (9) from the Greek νημα meaning thread. On surfaces like glass this mesophase frequently adopts a characteristic threaded texture which can be clearly observed by a microscope.
3. The cholesteric mesophase ..... a turbid and mobile phase, having unique optical characteristics different from those of smectic and nematic mesophases. The majority of compounds exhibiting this type of mesophase are derived from cholesterol or other sterol systems and hence the name.

Mesomorphic State :

Reinitzer (10) was the first person to discover that the crystals of cholesteryl benzoate melted sharply at 145.5°C to a turbid liquid which is birefringent and it remained so until the temperature was increased to 178.5°C when the turbidity disappeared suddenly giving a clear isotropic liquid. Two years later in 1890, Gattermann (11) observed that, very similar phenomenon occured in the case of p-azoxyanisole and p-azoxyphenetole which possessed double melting points. The discovery of these mesomorphic states attracted the attention of a number of chemists in the early 20th century. Notable among these were O.Lehmann (12) and Vorlander (13,14) who, in a short period,prepared over 250 compounds exhibiting this phenomenon. It soon became evident that all these substances possessed one common feature - a very long molecule - which has been attributed as a property most favourable for this

phenomenon of mesomorphism.

Despite the number of cases of mesomorphic behaviour which were soon reported, many years passed before it was universally accepted that the mesomorphic state is a true state of matter intermediate between the normal solid and normal liquid state. Tamman (15), Nernst (16) and Quincke (17) 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 Bredig and von Schukowsky (18) and A.Coehn (19) by electrostatic and centrifugal processes were futile. Schenck (20) and Vorlander (21) have also criticised the emulsion theory and argued in favour of the existence of crystalline liquids. A.C. de Kock (22) on the basis of his work on 'liquid mixed crystals' has supported ~~to~~ 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 (23), Wulff (24) and Voigt (25) 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 (26) conducted a large number of experiments in order 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, just as marble appears opaque when observed en masse, eventhough it is really composed of a mass of transparent crystals of calcite. Vorlander believed that the substances were truly liquid crystals and had a fixed space lattice (27). However, further microscopic examination of the liquid crystals, carried out by Mauguin (28), Friedel and Grandjean (29,30) soon dispelled these ideas and established that the liquid crystalline state is a truly physical state intermediate between the crystalline solid and the isotropic liquid.

Generally, the three states of matter may be expressed as under :

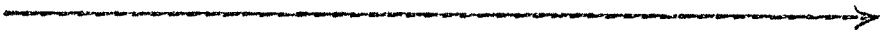
Solid $\rightleftharpoons$ Liquid $\rightleftharpoons$ Vapour or Gas

On the basis of structural orderliness the matter may broadly be said to exist in two common states - crystalline and amorphous. Solids in general, belong to

the category of crystalline substances while liquids and gases are put under the category of amorphous substances. Glasses, however, form an intermediate state giving a gradual transition from one to the other. Liquid crystals will form another such intermediate state. They consist of molecules that are elongated and in some cases flattened as well, possessing one or more polar groups. This shape of the molecules favours a parallel alignment to one another like a bundle of short tooth picks or pencils. In the crystalline state of a mesomorph the molecules lie parallel to one another and are held together by attraction through the polar groups and also by the 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 fluid but remains birefringent because of the preferred orientation of the molecules. The gradual thermal breakdown may be represented as :

Crystalline $\overset{t_1}{\rightleftharpoons}$	Liquid $\overset{t_2}{\rightleftharpoons}$	Amorphous
State	Crystalline	Liquid
	State	State

Increasing temperature



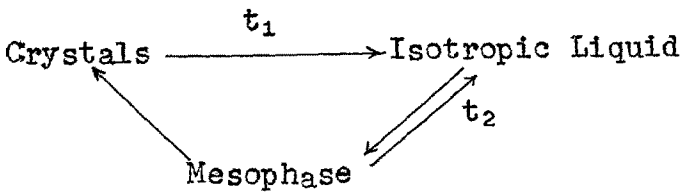
These transitions take place at definite temperatures and are precisely reversible. Owing to the application of heat the perfect orientation of the solid crystal is disordered and if molecular conditions are suitable, the solid crystalline state, at the melting point directly passes over to the amorphous liquid state. If, however, conditions are favourable to mesomorphism, the order breaks down in stages, first passing into liquid crystalline state at temperature $t_1\,^{o}C$. This state has certain degrees of freedom and hence acquires anisotropic properties. Further heating to $t_2\,^{o}C$ 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 representation of matter into three states in the case of such anisotropic melts is inadequate and hence a modified way may be as follows :

$$\underset{\text{(Crystal)}}{\text{Solid}} \rightleftarrows \underset{\text{Crystal}}{\text{Liquid}} \rightleftarrows \underset{\text{Liquid}}{\text{Isotropic}} \rightleftarrows \underset{\text{Gas}}{\text{Vapour or}}$$

(Mesophase)

The mesomorphic transitions so far discussed occur on heating the substances and these transitions reverse in the opposite direction on cooling. Such a mesophase is called the enantiotropic mesophase. Quite

frequently, however, the solid melts normally to give liquid at t_1 °C, but when the isotropic liquid is cooled, supercooling may occur and a mesophase appears just below the melting point at t_2 °C and before crystallisation 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 :



Thus, a monotropic mesophase is observed only on cooling but, if the temperature can be raised before crystallisation occurs, the isotropic liquid will be obtained at t_2 °C.

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. Just as most compounds melt, the majority of the compounds pass quite normally into solution. However, certain compounds on treatment with the solvent give a state which is neither a true solid nor a true solution, but which is intermediate in character between

these two extremes. Such states are found to have liquid crystalline properties and since the effect of solvent is responsible for their occurence, the phenomenon is termed as lyotropic mesomorphism. One of the first liquid crystalline substances discussed by Lehmann (31), ammonium oleate, belongs to the category of lyotropic liquid crystals. An excess of solvent will of course cause the 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 the solid mass. 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. Taking the example of ammonium oleate the gradual breakdown of the crystal lattice by the addition of water or in general a solvent, may be represented as :

Crystalline....	Water ⟶	Liquid....	Excess ⟶	Solution or
Ammonium	(solvent)	Crystal	Water	Colloidal
Oleate ⟵	Dehydration..	State ⟵	Evaporation...	Solution

Substances like soaps, soap-like alkali salts of naphthenic acids, resin acids, 9-chloro- and 9-bromo-phenanthrene-3-sulphonic acids show mesomorphic state under the controlled action of water (32). Alcoholic solutions of these compounds do not generally show anisotropic behaviour and a high degree of hydration appears to be a necessary prerequisite for the occurence of many lyotropic mesophases. McBain (33) 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 (34), glycerol, isopropanol and diethylene glycol (35) and in these cases also lyotropic mesophases are found to occur.

A number of cationic and non-ionic detergents have also been shown to give anisotropic phases when they are treated with solvents and in particular with water (36,37). A close relationship obviously existing between these liquid crystalline states and the truly colloidal states, has been discussed by Ostwald (38). Recently, Palit, Moghe and Biswas (39) have during their study of solubilization of water by cationic detergents, come across liquid crystalline phases, particularly in systems which are close to the solubilization maximum.

Zocher and Coper (40) have shown that methylene blue, neutral red and also other dyes gave orientation on rubbed surfaces. Dreyer (41) has discussed the behaviour of films from the aqueous solutions of amaranth and naphthol yellow S, as well as the dyes of the other classes which exhibit a mesomorphic phase. Sheppard's work (42) on 1,1'-diethyl-2,2'-cyanine salts (diethyl-ψ-cyanine) proposes a new type of nematic molecular phase, that of pluri-molecular filaments rather than elongated molecules. The structure proposed involves intermolecularly coordinated water molecules between opposite terminal nitrogen atoms along parallel resonance chains,

Lyotropic liquid crystalline states analogous

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

More recently, Robinson (43) 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 those observed in the thermotropic cholesteric mesophase.

Smectic, Nematic and Cholesteric Mesophases :

As a result of the detailed microscopic examination by Friedel, liquid crystals are conveniently divided into three types - smectic, nematic and cholesteric (9). Of the three, smectic and nematic are the most common types of mesophases and based on their optical properties structures have been assigned 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 (44) has, however, criticised this nomenclature but he has not suggested any satisfactory alternative and these names have been generally accepted.

Many compounds are known to show one or the other of these mesophases. Some examples are given in the table 1.

Table 1

Type	Melting Point °C	Transition Point °C
Smectic :		
Ethyl p-azoxybenzoate	114.0	122.5
Ethyl p-azoxycinnamate	140.0	249.0
n-Octyl-p-azoxycinnamate	94.0	175.0
Ammonium oleate	Smectic at ordinary temperature.	
Nematic :		
p-Azoxyanisole	118.0	136.0
p-Azoxyphenetole	137.0	168.0
Anisaldazine	169.0	182.0
p-Methoxycinnamic acid	173.5	190.0
Dibenzalbenzidine	234.0	260.0
Cholesteric :		
Cholesteryl benzoate	145.5	178.5
Amylcyanobenzalaminocinnamate	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, some can exist as both types of phases and in these cases there are always definite transition temperatures defining the stability of different phases. The change with increasing

temperature may be represented as :

$$\text{Crystal} \xrightarrow{t_1} \text{Mesophase I} \xrightarrow{t_2} \text{Mesophase II} \xrightarrow{t_3} \text{Amorphous Liquid}$$

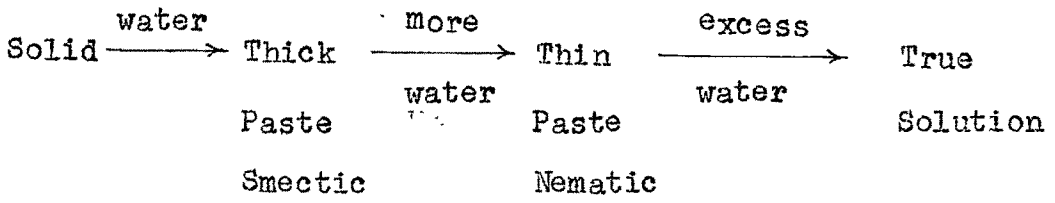
A few substances have been found to possess more than one phase of the same type and even here the temperature range of stability of the different phases is sharply defined. Such an example is that of ethyl p-aminocinnamate which possesses two smectic phases and one nematic phase.

$$\text{Crystal} \underset{}{\overset{83^{\circ}C}{\rightleftharpoons}} \text{Smectic} \underset{}{\overset{91^{\circ}C}{\rightleftharpoons}} \text{Smectic} \underset{}{\overset{118^{\circ}C}{\rightleftharpoons}} \text{Nematic} \underset{}{\overset{139^{\circ}C}{\rightleftharpoons}} \text{Isotropic}$$

Phase I Phase II Phase Liquid

The situation in this particular case, however, is complicated because the stable modification of the solid melts at $108^{\circ}C$ and so forms smectic phase II directly, thus keeping smectic phase I in metastable condition.

Lyotropic mesomorphs (7) also exhibit a similar behaviour as exhibited by thermotropic liquid crystals. The most notable example is Sandquist's 10-bromo-phenanthrene-6-sulphonic acid (45) 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.



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 and then to nematic, takes place with increasing breakdown of orientation until finally a completely disordered state is reached. These transitions may be outlined as follows :

1. Three-dimensional crystal. Apart from vibration, the centres of gravity of all lattice units are fixed ; rotations are not possible.
2. Crystal with rotating molecules. The centres of gravity of all lattice units are fixed ; rotation about one or more axes is possible.
3. Smectic structure. The centres of gravity of the units (molecules) are mobile in two directions ; rotation about one axis is permitted.
4. Nematic structure. The centres of gravity of the units (molecules) are mobile in three directions ; rotation about one axis is permitted.
5. 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 phase. A very convenient nomenclature for the transitions representing equilibrium between phases has been suggested by Brown and Shaw (6) and is given below in table 2.

Table 2

Equilibrium Between Structures	Nomenclature	Abbreviated Nomenclature
Crystal $\rightleftharpoons$ Mesomorphic state (Smectic or Nematic)	Crystal-Mesomorphic Point	C-M Point
Crystal $\rightleftharpoons$ Smectic structure	Crystal-Smectic Point	C-S Point
Crystal $\rightleftharpoons$ Nematic structure	Crystal-Nematic Point	C-N Point
Smectic structure I $\rightleftharpoons$ Smectic structure II.	Smectic I-Smectic II Point	S_1-S_2 Point
Smectic structure II $\rightleftharpoons$ Smectic structure III	Smectic II - Smectic III Point	S_2-S_3 Point
Smectic structure $\rightleftharpoons$ Nematic	Smectic-Nematic Point	S-N Point

Table 2 (Contd.)

Mesomorphic $\rightleftharpoons$ Liquid state	Mesomorphic-Liquid Point	M-L Point
Smectic structure $\rightleftharpoons$ Liquid	Smectic-Liquid Point	S-L Point
Nematic structure $\rightleftharpoons$ Liquid	Nematic-Liquid Point	N-L Point

The details of mesomorphic structure was established by Friedel. The smectic phase has a stratified structure, the long molecules being arranged in layers with their long axes approximately normal to the plane of layers. The structure greatly resembles the layer structure of long chain substances except that in the smectic phase the layers glide over each other as liquids. Substances forming three-dimensional crystalline layer structures such as the paraffinic substances, fatty acids etc., do not pass through a smectic mesoform 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 attraction of the molecules in

the sheet would be the strongest on it (fig.1).

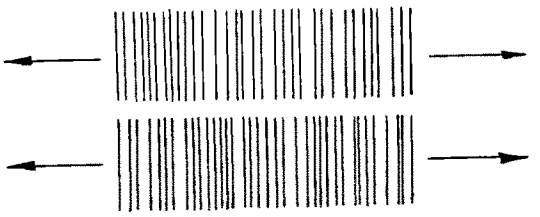


Fig 1 : A section representing the molecular arrangement in two plane smectic strata.

Obviously, the cohesions between these layers will be relatively weak thus accounting for the characteristic layer flow observed in the stepped drops.

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 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.

Nematic phase is not so highly ordered as the smectic phase. Although the molecules in the nematic phase are arranged with their long axes parallel they are not separated into layers. A helpful analogy, here, would

be a long box of short tooth picks or pencils which are all free to roll around and slide back and forth but, which remain parallel to the long axis of the box. However, this structure does not extend throughout the whole melt. The molecules exist in the nematic phase, in the form of parallel groups or swarms, each swarm containing thousands of molecules. The name swarms and the theory, called the 'swarm theory' were first proposed by E.Bose (46) in 1909, in order to explain the molecular arrangement and order in the nematic phase.

The majority of the mesomorphic compounds are comprised of long, rod-shaped molecules, frequently carrying 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. Howevery there is difference in that 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 swarms consisting of such parallelwise arranged molecules in a perfect fluid condition and without any suspicion of a space-lattice arrangement will evidently assume the symmetry of a rotation figure and be likely to behave optically like a uniaxial crystal. The swarm hypothesis explains satisfactorily for the turbidity associated with the nematic mesophase ; the light scattering properties of swarms explain 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 decreases and when it becomes smaller than the wavelength of light, the turbidity disappears giving a very sharp transition to the isotropic liquid. The effect occurs so rapidly that the observations carried out using different wavelengths of illuminating light could 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 J.S.Van der Lingen (47) definitely ruled out the views of Vorlander, who asserted that the liquid crystals are endowed with a space-lattice structure, an important

criterion of a true crystal. As Tamman's emulsion theory is out of question Vorlander's contention of space-lattice structure is absolutely out of any consideration. The regularity of structure producing double refraction and other optical effects simulative of crystals appears to be due to the similar orientation of the flat elongated molecules themselves, the swarm theory of Bose thus being verified. 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 an electromagnetic field (48,49) and by the determination of their viscosity at different temperatures (50). The first mathematical treatment of the swarm theory was given by Ornstein and Zernicke (51). However, the swarm theory did not pass without criticism and Zocher (52) in particular, questioned the validity of the deductions made by Ornstein and proposed the distortion hypothesis in place of swarm theory. The ideas of the distortion hypothesis have been expressed in highly mathematical terms and are based on the study of distortion of the nematic structure in a 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 (53), refractive index (54),

magnetic and electric properties (55,56) of the mesophases and a summary of such measurements is given by Ornstein and Kast (57).

The cholesteric phase is found in the melts of several compounds mainly those containing cholesteryl ring system. In many ways the properties of the cholesteric phase resemble those of the smectic and nematic phases. It has been difficult to assign these compounds to one of the two main types of mesophases and several workers have regarded it as belonging to a third type of mesophase. Friedel, noted a somewhat closer resemblence between the cholesteric phase and the nematic phase. No substances were found exhibiting both phases viz. cholesteric and nematic whereas each commonly occured in association with the smectic phase. Based on these arguments Friedel considered the cholesteric phase as a special case of the nematic phase. Further, when certain mixtures of dextro and laevo cholesteric substances are heated, the typical cholesteric properties gradually disappear and are replaced by nematic properties without any disontinuity in the change. This points out the nearness of the cholesteric phase to the nematic phase.

More recently Gray (58) 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 best be regarded as an individual phase type, though it is more similar to the smectic than to the nematic phase. However, unlike the smectic and

nematic substances which are optically positive, the cholesteric liquid crystals are optically negative. This makes the assignment of the cholesteric phase to any of the two main classes, rather difficult.

Some of the characteristic features of the smectic, nematic and cholesteric phases will now be described.

Smectic Phase :

The essential feature of the structure of a smectic phase is that the molecules are arranged in layers with their long axis approximately normal to the planes of the layers. The spacing of the molecules within each layer is, however, not uniform as it would be in a 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.

A film of smectic phase stretched over a small hole in a plate gives the condition of parallel sheets. The resulting structure is optically homogeneous and said to be homoeotropic. This homoeotropy is formed only on a surface with which it does not form strong local attachments. An interesting feature of the homoeotropic structure is the formation of a series of strata or terraces. These terraces are called Grandjean terraces after their discoverer Grandjean (59) and can be seen very clearly when thallium(I) 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 the microscope and which has been further confirmed by X-ray analysis.

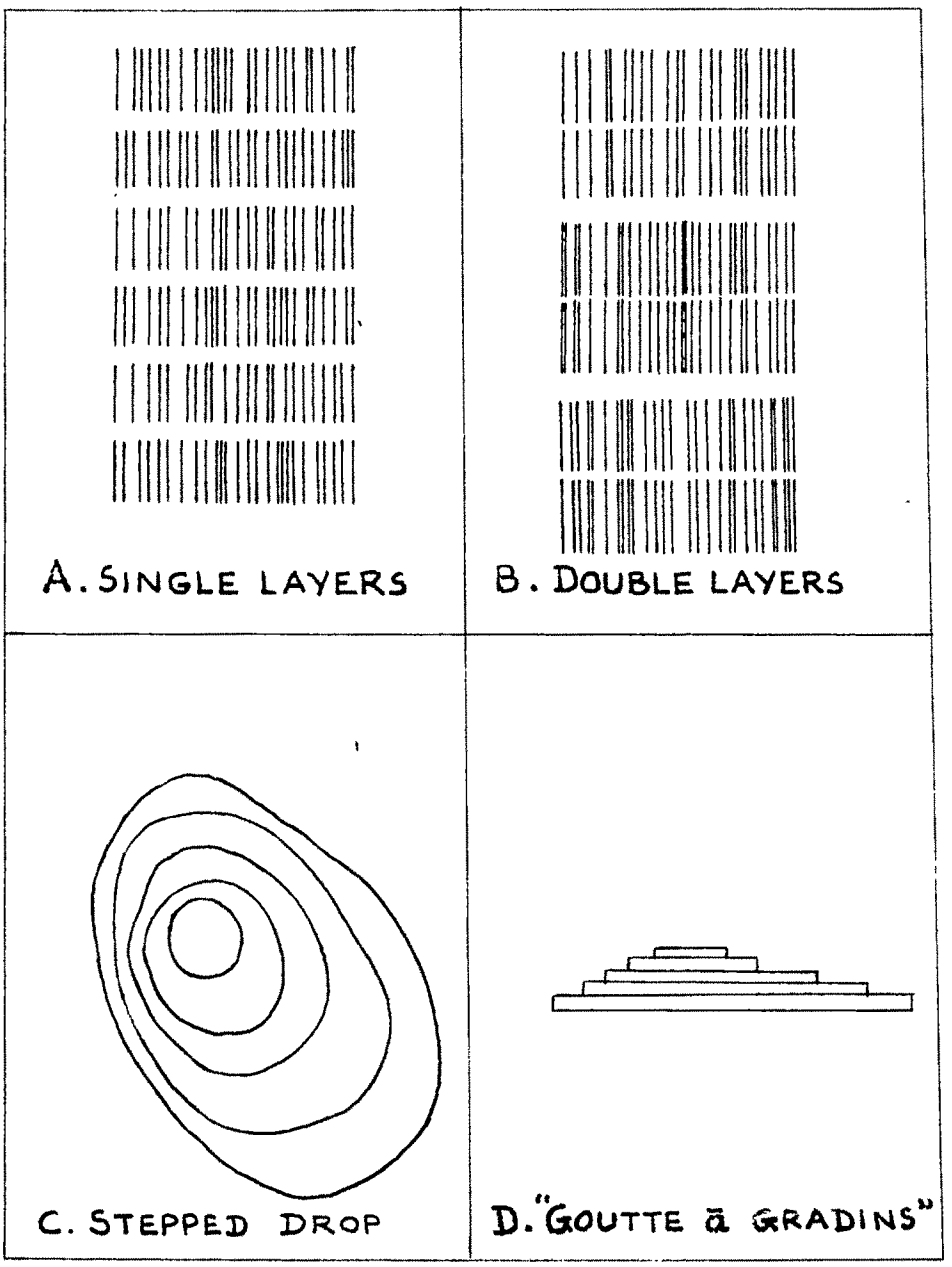

A. SINGLE LAYERS
B. DOUBLE LAYERS
C. STEPPED DROP
D. "GOUTTE à GRADINS"

FIG. 2

The smectic layer structure provides a regular periodicity normal to the layers so that this mesomorphic state gives an X-ray diffraction pattern from which, the layer thickness can be calculated. The distance between the layers approximates to the length of a molecule but deviations in this distance arise if the molecules are tilted ; for example, for ethyl p-azoxybenzoate, the spacing is more in the mesomorphic state compared to that in the crystalline state probably because the molecules are tilted. The layers are homogeneous and show the optical character of a positive uniaxial crystal. When observed in ordinary light they resemble an isotropic liquid but between crossed nicols the layers appear as homogeneous birefringent patches.

When smectic structure is formed from cooling the isotropic liquid, it first appears frequently in the form of non-spherical, characteristic elongated birefringent bodies. These increase in number as the temperature falls and show evidence of a focal-conic structure. These particles are known as batonnets, so named, after their shape. These batonnets are seen to coalesce just as the drops of an ordinary liquid merge into one another. The surfaces of these batonnets are interlaced with minute focal-conic groups and as the batonnets grow in size, coalesce and finally fill the entire field of view, the focal-conic structure is produced.

Thus, the characteristic focal-conic structure has become an important means of detecting the smectic mesoform. It extends all over the specimen and when

examined in polarised light it gives a fan-like appearance and has its origin in lack of common orientation of the smectic sheets as they form. Friedel has studied the optics of this structure and Sir William Bragg (60) has given an excellent account of the focal-conic structure and the geometry involved, which furnish further evidence for the layer theory of the smectic structure. Whatever be the structure, the smectic mesophase behaves as a positive uniaxial crystal. It remains unaffected by magnetic and electric fields. The solid crystalline form of the substances exhibiting smectic mesophase is designated as 'smectogenic' crystals.

Nematic Phase :

The properties of the nematic structure indicate that the molecules are parallel or nearly parallel to one another, but are not in layers. The nematic phase is very much similar to a true liquid state and has been compared with the cybotactic structure of liquids (61), but compared with the latter, the former has a low internal energy. Like true liquids the nematic liquids give only diffusion haloes with X-rays confirming the absence of a layer structure of the smectic phase. The optical behaviour of the phase which is uniaxial and positive, is indicative of the parallel arrangement of the molecules and the absence of periodicity in the structure by X-ray diffraction rules out the layer structure. It can be concluded that the substance owes its mobility to the facility with which the molecules can be drawn past one another while retaining a strong tendency

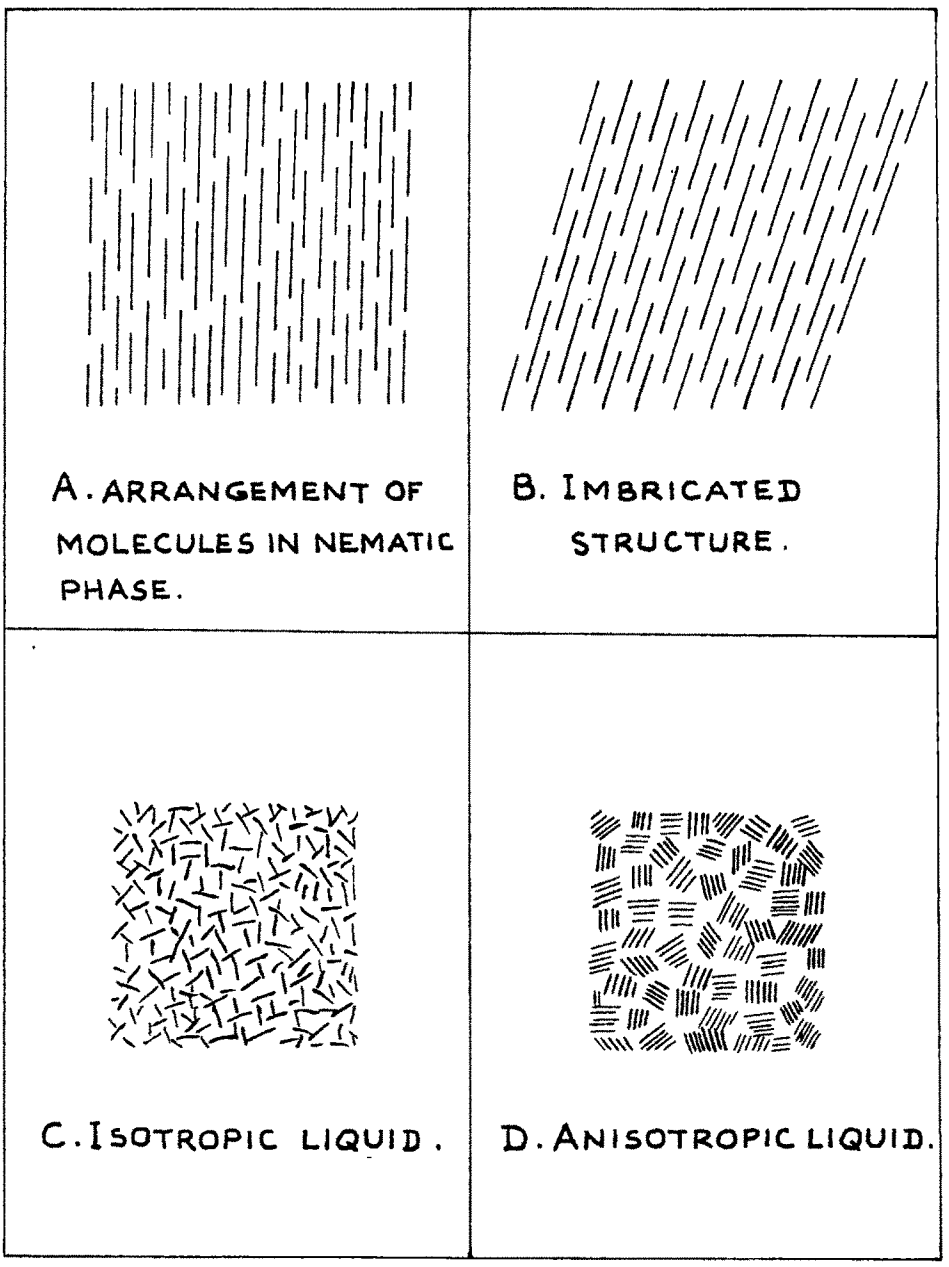

A. ARRANGEMENT OF MOLECULES IN NEMATIC PHASE.
B. IMBRICATED STRUCTURE.
C. ISOTROPIC LIQUID.
D. ANISOTROPIC LIQUID.

FIG. 3

to acquire a parallelism between the long dimensions of the molecules and the direction of drawing. Unlike immobile smectic phase, the particles of dust can move freely in a nematic mesophase without destroying its structure. Further, unlike the smectic mesoforms, the nematic mesoforms are orientated by electric and magnetic fields indicating a greater freedom of movement of the molecules. In an electric field the molecules set themselves with their axis at right angles to the lines of force and in the magnetic field they lie with their long axis parallel to the lines of force.

A nematic mesophase has no stratification but does possess some interesting optical properties and has some degree of molecular arrangement. The nematic phase lacking a stratified structure has none of the focal-conic structures or gouttes-à-gradins. A notable difference between the smectic and nematic mesophases lies in the way in which the two mesophase types separate from the isotropic liquid. Whilst the smectic phase appears as batonnets, the nematic mesophase separates as tiny, spherical droplets which coalesce to give a nematic texture. Bernal and Crowfoot (62) studied the crystal structure of solid p-azoxyanisole, p-azoxyphenetole and anisal-1:5-diamino-naphthalene, which form nematic phases. Their X-ray analysis shows that the molecules in the solid state lie parallel to one another but cannot be clearly separated into layers. This crystal pattern has been described as imbricated ; however, it cannot be inferred that all

nematic substances possess an imbricated structure in the crystalline state for, in some, the molecules are arranged in layers. It appears that with a layer arrangement of molecules in the crystalline state, the substance can exhibit a smectic phase, as well as a nematic phase.

When the nematic preparation is placed between glass surfaces, the molecules in contact with the glass tend to be attached sideways to the surfaces. The orientation of the molecules in the bulk of the phase appears to be governed by those sticking to the glass surface. If a nematic substance is heated to convert it into the mesomorphic state, the phase is seen in patches or plates with defined outlines. Each patch has its own special orientation derived from that of the original crystal. The preparation is fluid, birefringent and uniform in optical properties. If the cover slip is moved sideways carefully and the preparation of the nematic structure observed under a microscope, there appears an effect which indicates that the boundaries of the uniform plates are doubled. This is because the molecules in the top layer are attached to the coverslip and move with it while those on the bottom layer remain attached to the lower slide ; the molecules in the bulk of the preparation adjust themselves to the shearing effect. Turning of the coverslip gives a hellicoidal or twisted transition from one plate orientation to the other. The plates in the nematic phase, however, possess an extraordinary permanence. If the nematic structure is heated just inside

the isotropic liquid state and cooled again to the nematic structure, the pattern of nematic plates almost remains the same as before. This may be explained by the reasoning that the molecules at the glass surfaces remain oriented in the liquid state and that when the system is cooled, they direct the molecules in the preparation into their original arrangements.

When a mesomorphic substance is cooled suddenly from the liquid state to the nematic phase, the preparation becomes full of complicated vortices and interwinnings. Among these are the fine lines or threads from which the structure derives its name. The optical effects of the nematic threads have been studied by Zocher and Birstein(63). It seems that the threads are the lines of discontinuities in the structure, i.e., they correspond to the ellipses and hyperbolae in smectic phases but there being no stratification in the medium like the one in the smectic phase, no definite geometrical law can be applied. The nature of discontinuity is a matter of some doubt. It may be that the long axes of the molecules are directed in a radial manner ; the lines may denote the presence of vortices, perhaps hollow and vacuous, around which the molecules are circulating. In such a case the long axes of the molecules would be tangential to circles centered on the threads. The discontinuity may be due to both structural patterns. In any case, the lines can be looked upon as axes about which the medium is structurally built. Zocher and Ungar(64) investigated the nematic structure in converging polarized

light and at thickness up to 1 mm. They concluded that the parallel orientation of the molecules extends from one glass surface to the other, right through the preparation in these thin sections.

W.Maier and A.Saupe (65) have given a simple molecular theory of the nematic liquid crystalline state and have further derived a formula for the inner field acting on a single molecule of a nematic order (66).

Cholesteric Phase :

The cholesteric mesophase is formed by a number of cholesteryl esters and substituted derivatives of cholesterol and the mesophase derives its name from this fact. However, a few other optically active substances not belonging to the cholesteryl ring system also show this type of phase. For example, active amyl-p-(4-cynobenzylideneamino)-cinnamate (I), a cholesteric substance, wherein the molecules do not contain the sterol type of skeleton, shows this type of phase. The cholesteric phase resembles both nematic and smectic phases to some extent. The higher fatty acid esters of cholesterol which have marked paraffinic properties show clearly the characteristics of a smectic mesophase, which are generally found absent in the lower members. Here, the ring system predominates and the system is cholesteric.

The cholesteric mesophase displays certain additional properties. The mesophase shows brilliant iridescent colours in polarized light as it cools towards its setting point. There is a variety of colours, varying

from bright blue-violet to green or pink. The cholesteric phase shows the optics of a negative uniaxial crystal. These properties in the case of cholesteryl derivatives are attributed to the flat shape of the molecule. The cholesterol compounds are all optically active, sometimes very strongly ; the rotation amounting to several turns per millimeter of thickness. The optical activity is dextro in majority of the cases. The various colours displayed by a thin cholesteryl film are due to the scattering of rays and to the circular polarization of the scattered light. Another characteristic of this phenomenon is that, if the incident light is already circularly polarized in the same sense as normally scattered by the substance, the scattering takes place without change of sense. In other cases, polarized light is reflected, the sense of rotation being reversed. If the incident circularly polarized light is of opposite sense, then the light will be transmitted without any change of sense. The optical rotation of the cholesteric structure has been studied recently by Mathieu (67) and Levy (68). The orientation of the cholesteric structure of cholesteryl esters on ionic salts has been studied by Grandjean (69).

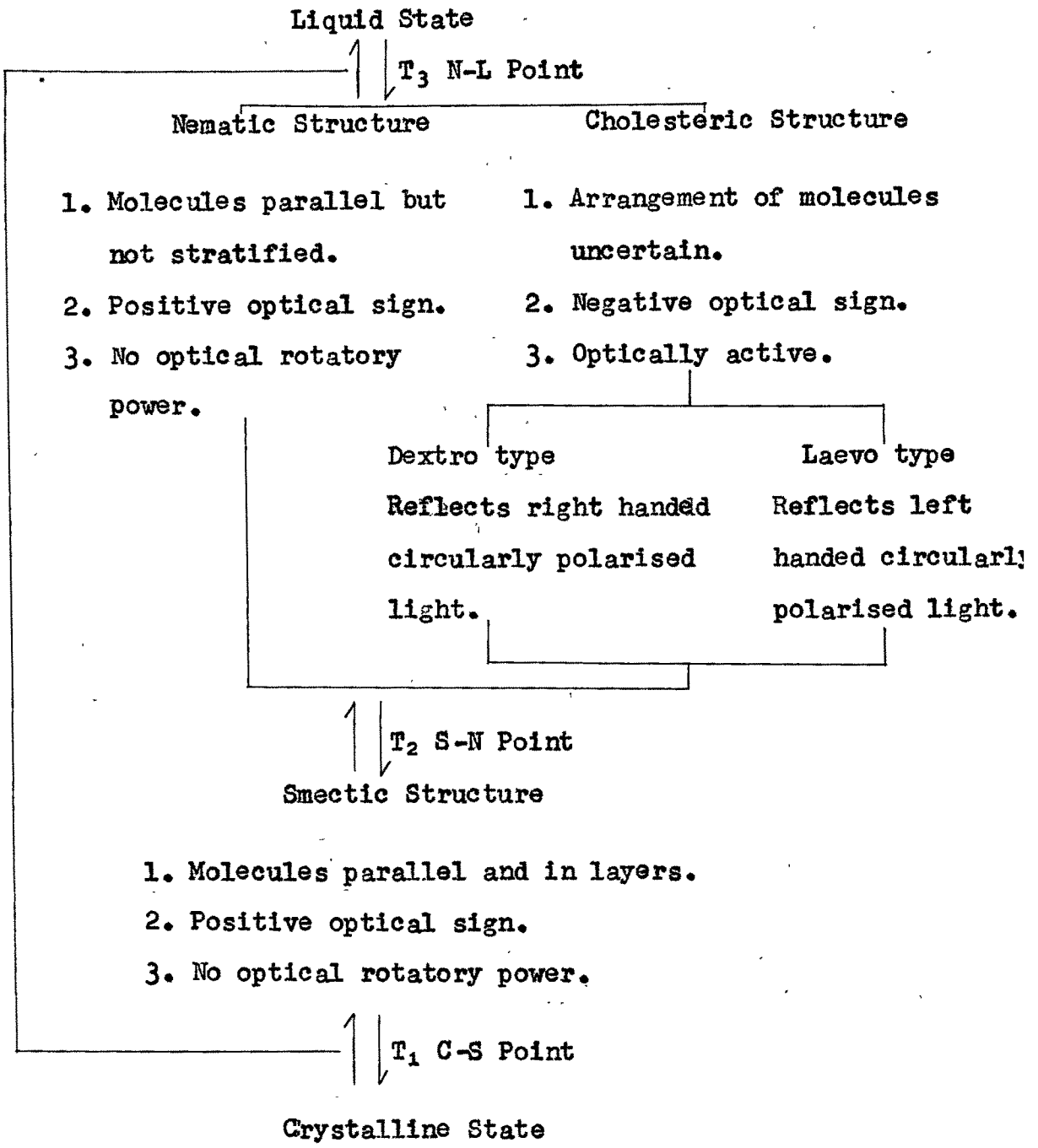
Cooling of a cholesteric melt first produces a confused focal-conic structure, which state neither exhibits brilliant colours nor optical rotatory power. But, a slight mechanical disturbance produces the Grandjean planes which reflect the light of brilliant colours. The colour is temperature dependent, being a

vivid green at higher temperatures and golden-bronze at lower temperatures. The planes are seen as equally spaced strata separated by regions of discontinuity analogous to the stepped drops in smectic phase, but the layer is much greater and varies from 2000 to 80,000 A^{o} in different cases.

The similarity between smectic and cholesteryl substances particularly in their layer structure is due to the shape of cholesterol molecule. However, these two mesophases possess different optical signs. The cholesteric phase has a negative sign whereas the smectic phase has a positive sign. The cholesteryl molecule would therefore, be perpendicular to the axis of rotation. The packing of the broad flat molecules will produce a series of planes similar to those in the smectic phase.

Some esters of β-hydrocholesterols of the allo series are reported to be mesomorphic (70) while the corresponding esters of α-dihydrocholesterols of the epi series show no mesomorphism at all in their melts.

After having discussed the three different types of mesophases, the relation of the mesophase to the isotropic liquid on the one hand and to the true crystalline state on the other, alongwith a few important characteristics may be represented diagrammatically as under :



Physical Properties of Liquid Crystals :

X-ray examination of the mesomorphic compounds has helped a great deal in explaining the mesomorphic structure. Bernal and Crowfoot (62) who carried out the X-ray

examination of the crystalline states of several mesomorphic compounds have shown that in the nematic compounds the molecules in the unit cells are arranged parallelwise with their ends imbricated. From this it is inferred that such an imbricated arrangement of parallel molecules will occur in the nematic mesophase. The smectic and cholesteric substances contain the molecules in parallel arrangement with their ends in a line, which is suggestive of a layer structure. Thus, on the basis of X-ray examination it is possible to predict whether a compound will be smectic or nematic and correspondingly such substances are called smectogenic or nematogenic.

Smectic mesomorphs give good X-ray pattern providing evidence for layer structure. In some cases layer spacings have been measured in which layer thickness has been found as equal to the length of a molecule except when the molecules are tilted. Herrmann's (71) X-ray study of thallium stearate and oleate has shown that the molecules are two-layers thick and arranged at an angle of inclination to smectic planes, which is greater in the crystalline fluid phase than in the crystal solid phase. Nematic substances do not give X-ray spacings.

Brown and Shaw (72) have recently studied X-ray patterns of the mesomorphic and liquid states of some alkoxybenzalazines. They confirm that the diffraction patterns for the nematic and liquid states are quite similar in regard to shape but positively mention that, the diffraction intensity showing up at the principal maximum is

a few percent greater for the nematic structure than for the liquid state. The principal peak in the case of nematic state in relation to the liquid state, is more clearly defined. The greater sharpness and its steeper slope indicate a more orderly structure of the mesomorphic state compared to that of a true liquid.

X-ray studies on nematic melts which were orientated by magnetic and electric fields have also been carried out. Herrmann, Krummacher and May (73) concluded that in certain cases like p-azoxyanisole and anisaldazine the long molecular axes are orientated perpendicular to the applied electric field and in other cases, e.g., methyl p-(4-ethoxybenzylideneamino)cinnamate, parallel to the field. H.Zocher (74) has given a mathematical treatment of the orienting effects of a magnetic field on the swarms.

Ultraviolet and infrared spectroscopic studies of mesophases have so far not given any vital information about either the molecular orientation or the degree of molecular aggregation in the mesophases. The early spectroscopic studies reported by Rawlins and Taylor (75) lead to the conclusion that the spectra of the mesophases and the isotropic liquids are more or less identical. Similarly, a more recent examination of Raman spectra of solid, nematic and isotropic phases of p-azoxyanisole by Freymann and Servant (76) revealed only one difference between the spectra of the anisotropic melt and the solid state and that of the isotropic liquid, namely the presence of a line at 1247 cm^{-1} in the spectra of the two anisotropic

states. Maier and Englert (77) have given an account of their infrared studies on 4,4'-disubstituted azo- and azoxybenzenes. They are of the opinion that it may be possible to use infrared spectroscopy for the comparison of the molecular orientations of the crystalline and the mesomorphic states of compounds.

In recent years, a few papers have been published which throw light on proton magnetic resonance in the mesomorphic state. Spence, Moses and Jain (78) have shown that proton resonance line changes markedly in character on passing from the isotropic liquid of p-azoxyanisole, which gives a single narrow line, to the nematic phase. Here, the amplitude of the signal is decreased and the single line broadens greatly and splits into three peaks. The amplitude of the central peak is the greatest and the two satellite peaks have equal intensity. Spence et al (78) attempted to explain these effects as due to a very strong hindering of the methyl groups present in p-azoxyanisole and has also given an alternative explanation in terms of the magnetic non-equivalence of the protons of the aromatic rings in the nematic melt of p-azoxyanisole.

Jain et al (79) have summarised the work of Moses (80) on smectogenic compounds by saying that the smectic mesophases of a limited number of systems such as sodium oleate and sodium stearate show a single structureless line intermediate in width between that of the isotropic liquid and the solid state.

Becherer and Kast (81) determined the viscosity of

liquid crystalline substances using the Helmholtz method. They report that the increase in viscosity just before the nematic-isotropic or cholesteric-isotropic transition always appears to be very sudden and the viscosity reaches a maximum, exactly at the transition temperature. With increasing temperature above the transition point, the fall in viscosity appears to occur at a variable rate. Ostwald (82) reports that the nematic and cholesteric mesophases possess a state of dispersion which is typical of colloids and also refers to the marked structural viscosity of the smectic and cholesteric phases which can be taken as evidence for regarding the mesophases as similar to gelatine or rubber sols. Bose (83) studied the nematic melt of anisaldazine and showed that the mesophase disobeys the Hagen-Poiseuille relationship between viscosity and rate of shear.

Vorlander (84) determined the viscosity of ethyl p-azoxybenzoate, over the temperature range of 114^{0}C to 133^{0}C and showed that there is a sudden fall in viscosity exactly at the smectic-isotropic transition, without any rise to a maximum as observed with cholesteric or nematic systems.

The dielectric properties of the nematic mesophase are important because of the supporting evidence which they give for the existence of swarms. Foex (85) showed that the magnetic rotation moment of a swarm can be calculated from the measurements of dielectric constant as a function of the magnetic field strength. Jezewski (86) and Foex (85) have found the same value of 10^{6} mols, for the size of the swarm. Bhide and Bhide (87) measured the dielectric constant

and absorption of p-azoxyanisole by resonance method and found abrupt changes in dielectric constant as the phase changed from mesomorphic to the isotropic liquid. Marinin and Tzvetkov (88) examined the dielectric properties of p-azoxyanisole under the influence of magnetic field. Their results indicate that the dielectric constant varies with the magnetic field strength, with temperature and also with the rate of flow.

Chatelain and Pellet (89) showed that it is possible to measure the two indexes of refraction of the mesophase, the ordinary index (n_o) and the extraordinary index (n_e). Their experiments showed that the difference between n_e and n_o decreases with temperature and that at the nematic-isotropic transition there is a discontinuity in refractive index giving a value for the isotropic liquid. These results illustrate the extremely high birefringence of the nematic mesophase, and the rapid way in which it varies with increasing temperature. Riwlin (54) has found that there is a good agreement between transparency for varying light and thickness of mesophase. She made use of Ornstein and Zernicke's (55) relationship between refractive index and transparency. These results agree well with those of Moll and Ornstein (56) and show the evidence for the existence of swarms.

The data obtained from measurements of the surface tension of mesophases so far, seem to be conflicting. Ferguson and Kennedy (90) found that the surface tension of the mesophase increases with rising temperature which is

exactly opposite to the behaviour of isotropic liquids for which the surface tension decreases with rising temperature. Naggiar (91) and more recently Schwartz and Moseley (92) have shown that the surface tension of a mesophase decreases with increasing temperature.

Foex (85,93) determined the principal magnetic susceptibility of crystalline p-azoxyanisole and found that the susceptibility value is much less than for substances like naphthalene which do not occur in mesomorphic state. The average susceptibility of powdered p-azoxyanisole is -0.565×10^{-6} ; at 116°C when the nematic phase is formed, he found a rapid fall in the susceptibility to -0.457×10^{-6}. As the temperature rises, the diamagnetism also increases slowly until above 133°C when the substance becomes isotropic liquid, for which the susceptibility value is -0.545×10^{-6}. On cooling, the changes are reversible 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 diamagnetic 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 has also reported on the measurements of principal magnetic susceptibilities over a range of temperature.

Smectic mesophases exhibited by substances like ethyl p-azoxybenzoate in general, show 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 state, orientation sets in with a strong decrease of diamagnetism. Some further studies of magnetic anisotropy in liquid crystals have been reported by Tzvetkov and Sosnovskii (94).

Very recently, Dewar and Schroeder (95) have described the application of liquid crystals as stationary phases in gas-liquid chromatography. The use of the 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 liquid ; as anticipated, the effect has been found to be less for the more nearly linear p-isomers.

Chemical Constitution and Mesomorphism :

Compounds which exhibit thermotropic mesomorphic properties vary widely in chemical constitution, but all possess a common feature of molecular geometrical anisotropy. Generally speaking, the molecules of mesomorphic compounds are elongated, rod or lath-like in shape and this seems to be a necessary requirement. However, it cannot be said that because the molecules are elongated the compound will necessarily be mesomorphic. Compounds such as the normal paraffins and the homologues of acetic acid though they

possess geometrical requirements suitable for mesophase formation do not exhibit liquid crystalline properties for the simple reason that the attractive forces operating between the molecules are so weak that they are unable to maintain a parallel arrangement of molecules after the crystal lattice has melted. Hence, in addition to the geometrical aspect of the molecules, the nature and probable strength of the intermolecular attractions must be given due consideration. In order to constitute a potentially mesomorphic system, the long molecules must possess groups of atoms having permanent dipole moments and the molecule as a whole must be polarizable. A high polarizability for the molecule may be ensured by incorporating polarizable aromatic rings and unsaturated linkages. In the aromatic compound it is necessary to maintain the linearity of the system. A para-para substitution in the benzene rings helps to maintain the criterion of linearity. Dibenzylidenebenzidine is a good example.

A compound comprised of molecules which are long, narrow and linear and in which there are dipolar groups, should give strong intermolecular attractions. If, however, the intermolecular attractions are too strong, selective weakening of the cohesive forces may not occur until high temperatures are reached and when the melting starts, the thermal vibrations may be too great to allow an ordered arrangement of molecules to persist. This shows that the melting points of the compounds should not be too high and this may be attributed as one of the reasons where the

compounds although possessing linearity fail to exhibit mesomorphic properties. The long chain fatty acids however, having rod-shaped molecules apparently suitable for mesomorphism do not exhibit it although their melting points are low enough to favour the existence of mesophase. The absence of mesophase in such cases can be attributed to the lack of cohesive forces between the carbon chains. In the absence of cohesive forces, the molecules after the breakdown of the crystal lattice will take up random orientation and no mesophase can be obtained. Therefore, the presence of polar groups in the molecule which are capable of enhancing the intermolecular forces is necessary.

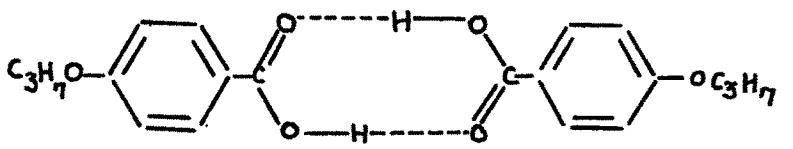
In general the mesomorphic compounds consist of long chain molecules often possessing mildly polar groups like -C = C-, -C = N-, -N = NO-, -CH = N-, -CH = N-N = CH-, in the middle of the molecule and an active group like -OR, -COOR where R stands for a normal alkyl chain, at the end. The middle groups will give lateral adhesion whereas the end groups do so in an end to end manner. The dipole moments imparted by the groups cause the molecules to exert rotation moments on one another. The result is a parallel orientation of the molecules. The molecules lie in such a way that their long axis will lie parallel to the long axis of the swarm.

Besides the presence of the polar groups, the structural alteration has a good deal of effect on the thermal stabilities of the mesomorphic compounds. It has been found that addition of a unit such as an aromatic ring to the molecule of a mesomorphic compound increases the

thermal stability of the mesophases provided that the molecule is not broadened. Thus the thermal mesomorphic stabilities of a biphenyl compound are higher than those of the corresponding benzene compound. For example, the compound $CH_3O.CO.C_6H_4.CO.C_6H_4.CO.C_6H_4.CO.OC_2H_5$ having three benzene rings has a phase length of 140°C (142-282°C), whereas the ester, $CH_3O.CO.C_6H_4.CO.C_6H_4.CO.C_6H_4.CO.C_6H_4.CO.OC_2H_5$, with an additional benzene ringhas a greatly increased region of stability from 187°C to red heat at which the substance decomposes. Many mesomorphic compounds like dianisalbenzidine, $CH_3O.C_6H_4.CH:N.C_6H_4.C_6H_4.N:CH.C_6H_4.OCH_3$, prepared by Vorlander evaporate or distil over before they transform to isotropic liquid. Vorlander (96) points out that these substances with this behaviour, remarkably exhibit mesomorphism. Brown and Shaw (6) have summarised the minimum structural requirements for a compound to show a mesophase as two benzene rings with a mildly polar group at the centre and p-p-substituted fairly polar terminal groups. The increase in the thermal stabilities of the mesophases as explained above should be due to the combination of enhanced cohesive forces and the geometric anisotropy of the molecules.

It is worthwhile considering the question if it is possible to outline the molecular features which are likely to determine whether the mesophase of a compound will be smectic or nematic, or both. A generalisation of

the conditions that give rise to these structures has been made by Bernal and Crowfoot (62). Smectic substances have either one active group e.g., in ammonium oleate, or a fairly strong active groups at the ends as in p-azoxy esters. This will induce layer formation and is often found in solid crystals. Such crystals are known as smectogenic. On the other hand molecules having weakly active groups at the centre as well as at the ends as in p-azoxy ethers lead to imbricated structures characteristic of nematic mesophases. Such crystals are known as nematogenic. p-Methoxycinnamic acid may at the first sight be expected to be smectic but in its melt the dimerisation of carboxylic groups takes place forming a double molecule of the type which favours nematic mesophase rather than a smectic one (97). Dimerisation as well as hydrogen bonding give rise to conditions favourable to mesomorphism. p-n-Alkoxybenzoic acids (98-101) are the simplest examples exhibiting mesomorphism because of dimerisation of their two molecules. Here, the dimerisation of carboxylic acids by intermolecular hydrogen bonding of the carboxyl groups preserves the linearity and increases the molecular length, maintaining the intermolecular attractions at a suitably high level favouring the mesomorphism to occur. Thus, p-n-propoxybenzoic acid has the simplest molecular structure to form liquid crystal.



A further proof in support of the effect of dimerisation and hydrogen bonding is afforded by the fact that the corresponding methyl ester of p-n-propoxy-benzoic acid is non-mesomorphic, eventhough it has a low melting point and possesses a dipolar ester group, as the ester has no tendency to association. Gray (102) has also given few generalisations about the molecular characteristics which are likely to lead to mesomorphic behaviour. The molecules of mesomorphic compound should preferably have a high length : breadth ratio and it is necessary that the long molecule should be made up of a sufficient number of groups of atoms which are either permanently dipolar or readily polarizable, so that the intermolecular attractions are sufficiently great to maintain the parallel anisotropic arrangement of the molecules. On the other hand, if the molecule contains groups which lead to very strong intermolecular attractions or to intermolecular hydrogen bonding of a polymeric nature, such that the melting point of the compound is very high then, irrespective of the molecular shape, mesomorphism will not occur. Culling, Gray and Lewis (103) have substantiated this aspect of high melting points as being unfavourable for mesomorphism. They report that 4-cyano- and 4-methoxy-4''-nitro-p-terphenyl and 4-acetamido-and 4-amino-3,4''-dinitro-p-terphenyl exhibit nematic mesophases while 4,4''-dinitro-p-terphenyl and 4-acetamido-4''-nitro-p-terphenyl do not exhibit mesomorphism owing to their very high melting points.

The shape of the molecule and the axis of symmetry play an important role in determining the mesomorphic behaviour. The increase in the molecular breadth leads to decreased mesomorphic properties. Introduction of certain groups which destroy the symmetry of the molecule (104) either reduces the range of mesomorphic stability or results in complete extinction of the mesophase. For example, introduction of CH_2 group between two benzene nuclei in a highly stable liquid crystalline benzidine derivative causes the disappearance of enantiotropic mesophase. Similar is the effect of groups like -CO, -CS, -S etc. In the same way, the introduction of a non-polar alkyl group in place of a polar alkoxy group destroys the mesomorphic properties on account of reduction in the end to end cohesion in the melt.

Gray (102) has summarised the effect of alkyl chain length on mesomorphism. He reports that increase in the alkyl chain length increases the ratio of the lateral to the terminal attractions between the molecules, so making the probability greater that the layer arrangement will persist after melting, when the terminal attractions are weakened. Smectic properties are therefore most likely to be observed in the long chain members of a homologous series of mesomorphic compounds. The observations of Bennett and Jones (100) for the homologous series of p-n-alkoxybenzoic acid and trans -p-n-alkoxycinnamic acid substantiate the above conclusion. They report that

non-mesomorphic or nematic behaviour is observed in the case of the members of short alkyl chain length. Smectic properties followed by nematic begin to appear as the alkyl chain length increases and finally in the higher members a pure smectic phase is observed. Weygand and Gabler (105) found similar observations in the case of p-azo and p-azoxyanisole series. Thus, a general pattern of behaviour is that the lower homologues are nematic, the middle members exhibit a smectic mesophase followed by nematic and the long chain members are purely smectic.

Lateral intermolecular attractions are therefore helpful in determining the smectic properties, but only in relation to the weakness of the accompanying terminal attractions. These lateral attractive forces between elongated molecules would be enhanced by the presence of strong dipole moments operating across the major axes of the molecules, because a dipole-dipole reinforcement takes place with a suitable layer arrangement. Substitution of a molecule normally decreases the thermal stabilities of both the smectic and nematic mesophases owing to the broadening effect. But in cases like 6-n-alkoxy-2-naphthoic acids (106), 5-substitution leads to quite a small increase in the molecular breadth, because of the projection of the 4-hydrogen atom. This means that substituents like chloro- and bromo- instead of decreasing the thermal stabilities of the mesophases increase them because of their dipolar and polarizability effects. Vorlander (107) has reported certain naphthalene derivatives which are

considerably broader than benzene ring as exhibiting mesomorphism. In spite of their extended surface, certain anils of 2:6-diaminonaphthalene are mesomorphic. Vorlander has shown that the naphthalene anils are less mesomorphic compared to the corresponding more linear anils derived from diaminodiphenyl. These facts point out that the nature of mesomorphism decreases with increasing breadth of the molecules. It is known that 3:5-dichlorination of p-n-pentyloxybenzoic acid completely destroys the nematic mesomorphism of 27 ^{0}C phase length in p-n-pentyloxybenzoic acid although the melting point is 22 ^{0}C lower than its parent acid. The total destruction of mesomorphism is due to the broadening effect of the two chlorine atoms (108). This shows that the breadth of a molecule cannot be increased above a certain limit without destroying mesomorphism. If a dipolar group increases the molecular breadth, the smectogenic tendencies will be reduced, unless the dipole is strong enough to counterbalance the decrease in thermal stability arising from the increased molecular separation. However, it may be said that for a system of elongated molecules to be smectic, the ratio of the lateral to the terminal attractions should be high.

If a molecule is structurally suitable for mesomorphism but contains short alkyl chain and no strong dipole moments operating across the long axis, then the compound is most likely to exhibit the nematic properties (102). Considering two different molecules of almost identical length and shape e.g., p-n-octyloxybenzoic

acid (109) and p-n-nonylbenzoic acid (101), there are two dipoles acting at an angle across the long axis of each molecule, in the dimeric molecules of the ether, while there are no such strong dipoles present in the alkyl acid. Thus the octyloxy acid exhibits both nematic and smectic phases and the nonyl acid as a result of the weaker lateral attractions between the molecules is purely nematic in its behaviour. It has also been observed that the dipolar substituents are much more likely to enhance the thermal stability of a smectic mesophase than that of a nematic mesophase.

3-Chloro derivatives (110) of the dimeric p-n-alkoxybenzoic acids contain molecules which are substantially broader than the p-n-alkoxybenzoic acid molecule. This causes two effects : (a) the enhancement of the lateral intermolecular attractions arising from the increased polarity and polarizability of the substituted molecules and (b) the decrease in the intermolecular lateral attractions because of the increased separation of the long axes of the molecules. In fact, the 3-chloro substituent decreases both the nematic and smectic thermal stabilities of the parent acid and the larger 3-bromo- and 3-iodo- substituents completely eliminate the mesomorphic properties. Gray, Hartley and Jones (111) studied the mesomorphic properties of 4'-n-alkoxydiphenyl-4-carboxylic acids and their simple alkyl esters and a comparison is made with those of 4-n-alkoxybenzoic acids. These acids exhibit mesophases

of greater thermal stability than the simple benzoic acids ; this is attributed to the enhanced intermolecular cohesion arising from the second benzene ring and also to the greater molecular length of the diphenyl compounds. Gray (112) has studied the mesomorphic properties of thirteen anils derived from p-n-alkoxybenzaldehydes and 2-aminophenanthrene and found more evidence for the planar configuration of diphenyl ring in the mesomorphic state.

When the mesomorphic transition temperatures for a homologous series of compounds 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 (109,113). This common behaviour in many homologous series is attributed to the packing of the molecules with their long axes parallel. The alternation for odd and even numbers is believed to be due to variations in the packing of the terminal methyl groups (114). It has been observed that in general, the nematic-isotropic transition temperatures fall with increasing alkyl chain length with a regular alternation of the temperatures occuring between homologues containing odd and even number of carbon atoms in the alkyl chain. If the series also exhibits smectic properties, then the smectic-nematic transition temperatures will be found to rise steeply at first and then more gradually as the alkyl

chain lengthens. In most cases, the smectic-nematic curve coincides with the falling nematic-isotropic curve before the former has reached its maximum. After the merging of these two curves, no nematic properties are observed in the series, and the smectic mesophases pass direct to the isotropic liquid. This common behaviour of the smooth curves may be explained by a typical example as that of the 4'-n-alkoxybiphenyl-4-carboxylic acids.

Gray, Jones and Marson further extended their studies to the influence of substituents particularly halogens (115,116) in the 3-position of p-n-alkoxybenzoic acids, in the 5-position of 6-n-alkoxy-2-naphthoic acids, in the 3-position of p-n-alkoxycinnamic acids and 3'-position of 4'-n-alkoxydiphenyl-4-carboxylic acids and their alkyl esters and have correlated the effects of substituents on mesomorphic thermal stabilities. 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 the 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 entirely eliminate the mesomorphic properties, although in the broader bromo derivatives the long chain dodecyl, hexadecyl and octadecyl ethers alone exhibit mesophases and these are monotropic . In most 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 marked decrease in smectic and nematic thermal stabilities on passing from unsubstituted to substituted system.

Therefore, substitution leading to an increase in molecular breadth will decrease the smectic and nematic thermal stabilities i.e. the smectic-nematic, smectic-isotropic and nematic-isotropic transition temperatures.

Brown and Shaw (6) and recently Gray (102) have given a detailed account of the mesomorphism with respect to the chemical constitution of the compounds and thereby have assigned minimum structural requirements for a compound to be mesomorphic. The molecules must be elongated and rod or lath-like shaped, with an essentially linear structure and must possess active central groups to provide the intermolecular lateral cohesion and terminal groups to produce terminal attractions.

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 (117). 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 the muscles, nerves, tendons and bones

show the optical property of double refraction (118). The degree of double refraction in such fibrous systems increases on stretching and decreases on contraction.

It has been found by Rinne (5) 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 (119). 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 (120,121). The anisotropy occuring very commonly in the sperms is exhibited in the extended form of the 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 (122). Aqueous solutions of certain viruses e.g. tobacco mosaic virus exhibit lyotropic mesomorphic properties (123-125). Brown and Shaw (6) have pointed out that the mesomorphic state is singularly well fitted to provide complex forms in which organisation 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.

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 (126) has put it this state seems to be especially suited to biological functions and may possibly be the basis of vital activity.

Mixed Liquid Crystals :

From the above description it can be said that the liquid crystalline state is a stable intermediate state having marked transition temperatures which separate it from the true solid state and the isotropic liquid state. This mesophase possesses some of the mechanical properties of a liquid and some of the optical properties of a crystal. Any foreign substance dissolved in such a liquid finds itself in an anisotropic environment and its properties are affected to a considerable extent.

When two mesomorphic compounds are mixed, the melting points and the mesomorphic transition temperatures are depressed. If both the components of the mixture are enantiotropic mesomorphs by themselves, then the mixture will give an enantiotropic mesophase depending on the temperature ranges over which the mesophases of the two

components are thermally stable. Binary mixtures of certain non-mesomorphic compounds with a mesomorphic compound frequently exhibit mesomorphism. Cases of liquid crystallinity in mixtures of two non-mesomorphic components have also been reported. Gaubert obtained mesomorphic systems by mixing molten cholesterol in turn with succinimide, the tartaric acids, malic,maleic,malonic,succinic,anisic, cinnamic and lactic acids (127). He also examined liquid crystalline mixtures obtained by heating ergosteryl acetate, propionate or butyrate with glycollic acid, glycerol and orcin (128) and on melting certain cholesterol and ergosterol derivatives with urea (129). Kravchenko and Pastukhova (130) have reported liquid crystallinity in mixtures of non-mesomorphic compounds such as the hydrocarbons indene and naphthalene.

Schenck (131) has shown that the transition temperature of isotropic liquid-crystalline liquid for p-azoxyanisole is lowered by the addition of other substances. He calculated the molecular lowering of the transition temperature in the case of p-azoxyanisole from which he calculated the heat of transition. He further showed that p-azoxyanisole and p-azoxyphenetole form isomorphous mixture in the mesomorphic state.

The depression of the transition temperatures observed in the mesomorphic substances by the presence of another substance is just similar to the lowering of the freezing points of true solids by the addition of other substances. The transition from liquid to mesomorphic

state can be made use of in cryoscopic work in just the same way as the transition from liquid to solid, but in the case of liquid — liquid crystalline transition, the thermal changes being comparatively much small, the molecular depression reaches a high value.

With a view to find out the extent of the utility of the transition in cryoscopic work and also to study the effect of the addition of another substance on the mesomorphic state of a mesomorphic compound, de Kock (22) investigated the binary mixtures of substances, one or both the components of which were liquid crystalline substances. When p-azoxyanisole (114-135.2^{o}C) and p-methoxycinnamic acid (170-185.5^{o}C) both of which are nematic mesomorphs, are mixed, their melting points as well as the transition points are lowered and the upper transition temperature-concentration curve exhibits a rounded minimum. As the temperature decreases, varying with the composition of the mixture, one or the other pure solid substance is deposited. The temperature - concentration curve obtained in these cases resembles an ordinary freezing point curve with a eutectic at 107-8^{o}C. de Kock said that between these two curves the two substances are in liquid crystalline state and form a continuous series of homogeneous mixed liquid crystals. He further studied some binary systems where only one component is a liquid crystal, viz : (1) p-azoxyanisole and quinol (2) p-methoxycinnamic acid and quinol and (3) p-azoxyanisole and benzophenone.

In all these cases, he observed that mixed liquid crystals are formed but only to a certain concentration of the non-liquid crystalline component, the transition temperatures of the mesomorphic - isotropic liquid state being lowered by the addition of quimol or benzophenone. He also calculated the molecular depression in the case of p-azoxyanisole with quimol or benzophenone as solute and obtained the same value in both the cases, approximately 4900. The corresponding latent heat of the change liquid crystalline — amorphous liquid state for p-azoxyanisole was found to be 0.68 Cal. He discussed the general problem in terms of the phase rule.

Bogojawlensky and Winogradow (132) studied binary mixtures of isomorphous substances and have reported the formation of mixed liquid crystals from pairs of substances one or even both of which were non-mesomorphic. A complete series of mixed liquid crystals was discovered in the case of p-azoxyphenetole and p-azophenetole mixture, where the former is a liquid crystal (137-167.5^{o}C) and the latter melts at 160.2^{o}C but possesses a metastable monotropic liquid crystalline form which lies 4 degrees below its normal melting point, at 156.1^{o}C. The freezing point curve and the melting point curve in this case are both straight lines and they intersect each other so that in the temperature - concentration diagram there exists a region of stable and a region of metastable mixed liquid crystals. In all the cases the clearing point curve is a linear one and from this linearity of the curve they deduced that the

other apparently non-liquid crystalline substance should have a potent or latent liquid crystal form, but this cannot be observed as the transition to isotropic liquid lies below the normal melting point and could not be ascertained owing to the impossibility of supercooling. The latent or labile transition point of the non-liquid crystalline substance was determined in a number of cases by extrapolation of the clearing point curve which is linear in the majority of the cases. This should provide an explanation to the observation of Vorlander and Gahren (133) that substances which themselves are not liquid crystalline, form liquid crystals when they are melted together.

Walter obtained enantiotropic mixed liquid crystals within limits of concentration using a mixture of anisic acid and anisalpropionic acid which themselves are non-mesomorphic substances. He determined the latent melting points of the liquid crystalline phase of these acids from the behaviour of their mixtures with p-methoxycinnamic acid by the extrapolation of the clearing point curve and found that the melting point curve joining the latent melting points of the two non-liquid crystalline compounds, so obtained is a straight line. Tamman's view (135) that formation of liquid crystals from a mixture of non-liquid crystalline substances is a matter of emulsion formation is thus disproved.

The extents of the melting point depressions

and the phase diagrams for mixtures showing liquid crystalline properties are discussed in the early publications of Tamman (15), Lehmann (136), Smits (137) and in the later work of Vorlander and Ost (138). Contradictory views have been expressed by different workers concerning the nature of the change from the anisotropic state of a mixture of a mesomorphic and non-mesomorphic component to the true isotropic liquid state of the mixture. de Kock (22) and Prins (139) maintained that phase rule theory did not allow a direct transition at a fixed temperature, from the two-component mesophase to the two-component isotropic melt and that there must be a temperature range over which a series of mixtures of different composition of the two liquids, one anisotropic and the other isotropic, coexist.

Recently Dave and Dewar (140) re-examined this problem by studying the behaviours of binary mixtures of varying composition, each mixture comprising a nematic mesomorphic compound and a non-mesomorphic substance. They repeated the system- mixture of p-azoxyanisole (nematic) and quinol (non-mesomorphic), the two-component system for which de Kock (22) claimed that he had obtained evidence for a range of temperature over which two liquid phases of different composition coexisted. Dave and Dewar have clearly shown that the transition from the anisotropic to isotropic state is sharp and have concluded in general terms that the liquid phase produced by heating the mixture of solids, is a homogeneous single phase, whether it is

mesomorphic or not. They opine that the experimental evidence on which de Kock based his results seems to be scanty, the transitions being followed mainly by observing the change in the liquid region from cloudy to clear without careful temperature control and without proper stirring. Dave and Dewar (140,141) and later Dave and Lohar (142) studied a number of binary mixtures where one component is a liquid crystal by itself and deduced a slope value of the transition curve which has been attributed to the polarity of the end groups present in the non-liquid crystalline molecule. Further, they conclude from their observations that any substance, with anisotropic molecular structure would form a liquid crystal provided it can be obtained in a liquid form at a sufficiently low temperature. Dave and Dewar have also refuted the suggestion of de Kock (22) that the depression of the transition point by solutes might be used as a method for determining molecular weights.

Mixed liquid crystal formation has been reported in mixtures of non-liquid crystalline substances. With a view to find if mixed liquid crystals can be obtained in such mixtures Dave and Dewar studied a few binary systems of substances which from the structural point of view, furnish the minimum requirements of exhibiting mesomorphism, but are apparently non-mesomorphic ; they did not observe any mixed liquid crystal formation in these cases. Dave and Lohar (143) have, however, reported mixed mesomorphism

in certain mixtures of non-liquid crystalline Schiff's bases.

The foregoing description arouses several interesting points which demand further investigation. Further studies from this point of view have been carried out in this investigation and it is hoped that this will throw further light on the subject.