INTRODUCTION

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Definition and Nomenclature :

It is common knowledge that solids, in general, when heated, melt to isotropic liquid. The physical and the optical properties of a true crystal are different from those of a true liquid. However, it has been observed that in the case of certain chemical compounds, some of the wellknown properties of true crystals and true liquids coexist over a range of temperature.

Thus, when certain solids, e.g., p-azoxyanisole, are heated they do not directly pass into the liquid state, but first adopt a structure which has properties intermediate between those of a true crystal and those of a true liquid. On reaching a certain temperature the solid undergoes transformation into 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 this phase finally melts to form a clear isotropic liquid. On cooling the liquid, these changes take place in the reverse order, although some supercooling may occur when transition temperatures are reached, as in the case of ordinary crystallisation. Such an intermediate state has been described by the name ' liquid crystal ' since the time its first discovery was made.

The phenomenon of liquid crystallinity was first observed by Reinitzer (1) in the year 1888. O. Lehmann (2) was, however, the first to make a systematic study of such substances and he proposed the name ' liquid crystal ' or ' crystalline liquid ' to describe this intermediate state of substances which are liquid in their mobility and crystalline in their optical properties. The first property (liquid) suggests that the substances in this phase are readily disturbed though the phase 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 most widely used since the time it was first suggested by Lehmann, objections have been raised to this nomenclature. There have been fruitless discussions regarding the relative advantages of the names ' liquid crystal ' and ' crystalline liquid '. In fact, both the names are unsatisfactory, as the state is neither crystalline nor liquid in the true sense of these words. Crystals have a three dimensional order, whereas phases may have one or two dimensional order. The word liquid is also not much proper as the phase may in some cases be crystalline in hardness, as for example in lecithin. On account of the turbid liquid being birefringent when examined through crossed nicols, the terms ' anisotropic liquid ' or ' anisotropic melts ' are also used.

A more satisfactory nomenclature has been proposed by Friedel (3,4), who is of the opinion that the name liquid

crystal is not a good one as the substances are neither perfect crystals nor perfect liquids. He described this state as a ' mesomorphic state ' (Greek-mesos, intermediate ; morphe, form), meaning a state intermediate between the crystalline and the amorphous state. From this are derived the terms ' mesomorphs ', ' mesoforms ', and ' mesophase ', which are more logical since the properties to be described are intermediate between other properties that are well defined.

Rinne (5) has argued that the adjective ' mesomorphous ' proposed by Friedel (3, 4) expresses only an intermediate character and does not carry any structural meaning. The expression liquid crystal introduces, by the adjective, a property which is not typical of the whole material. Accordingly matter can be classified either as ' ataxy ' (irregular or amorphous structure) or as ' eutaxy ' (regular or ordered structure). Mesomorphic and crystalline substances which possess an ordered structure will belong to the class of eutactites whereas amorphous matter, isotropic liquids and gases will fall into the category of atactites. He, therefore, proposed the name ' para crystals ' for substances exhibiting mesomorphism. Here the word crystal significantly emphasises the connotation of the crystalline condition of the turbid state, while the prefix para carries home the idea that most of the organic compounds exhibiting the phenomenon are para substituted benzene derivatives. Thus

the classification is :

1. Atactites - Isotropic liquids, gases and other amorphous matter.
2. Eutactites - (a) Crystals - 3-dimensional order.
   (b) Para Crystals - 1- or 2-dimensional order.

Brown and Shaw (6) consider the related term ' mesomorphic state ' prefarable and have used it as the title of their recent review. Nonetheless, the name liquid crystal is still frequently employed and will be used throughout this thesis.

Classification of the mesomorphic state on the basis of the manner in which it is prepared is also discussed in the literature. Using the nomenclature of Friedel (3), Lawrence (7) and Jelly (8) ' thermotropic mesomorphism ' refers to the production of the mesomorphic state by means of heat in contrast to ' lyotropic mesomorphism ' which has been defined as the process for preparation of the mesomorphic state by solvation, the solvent generally being water.

Again, compounds exhibiting mesomorphism have been classified chiefly by two structures which have been designated as ' smectic ' and ' nematic '. The term smectic (soap like) was coined by Friedel (9) from the Greek σμεγμα, meaning grease or slime. The smectic structure

is stratified, the molecules being arranged in layers with their long axis approximately normal to the plane of the layers. The term nematic, is also coined by Friedel (9) from the Greek νημα , meaning thread. This literally describes the thread like lines which are seen in the nematic structure on microscopic observation. In the nematic structure the molecules preserve a parallel or nearly parallel orientation. A third structure viz. cholesteric, so called because it is mainly shown by cholesteryl derivatives, is also described in literature. No attempt, however, is made to discuss these structures here as these will be detailed later.

The Mesomorphic State :

The originating discovery of Reinitzer (10) in the year 1888 was that cholesteryl benzoate after melting at its fusion point 145°C, changes to a turbid liquid, which is doubly refractive and remains so on further heating until it reaches the temperature 179°C, when it suddenly becomes isotropic. In 1890, Gattermann (11) observed that a similar phenomenon occurred in the case of p-azoxyanisole and p-azoxyphenetole, which possessed the same property of having apparently double melting points. These discoveries were soon followed by preparation of compounds of like character in hundreds, chiefly by Vorlander (12). This phenomenon, then became a topic of vigorous investigation and remained so for a number of years.

Various research workers have expressed different views in respect to the formation and properties of liquid crystals. The theoretical interpretation of the mesomorphic state has intrigued many a physicist and chemist. Tammann (13) and others held the view that the crystalline liquids are two phase systems resembling somewhat emulsions, and not homogeneous ones. Bredig and Schukowsky (14) and Coehn (15) attempted in vain by electrostatic and centrifugal processes to separate the alleged emulsion into its constituents. Schenck (16) and Vorlander (17) have also criticised 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 crystals ' has supported the view that crystalline liquid is a homogeneous phase and not an emulsion of two liquids. He also repeated without success Tammann's sedimentation experiments. No clear proof of heterogeneity has been provided and the homogeneity of crystalline liquids has now been generally accepted. Quincke (19), Pawloff (20), Wulff (21) and Voigt (22) have also discussed the nature of liquid crystals.

Lehmann (23) has described a number of experiments in order to illustrate the properties and formation of liquid crystals from isotropic liquids. 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 is attributed to different orientation of the individual crystals which scatters the light to a great or less extent, just as marble appears opaque when observed enmass, 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 (24). However, Mauguin (25), Friedel and Grandjean (26, 27) carried out further microscopic examination of liquid crystals. They could not find any basis for these ideas and established the liquid crystal state as a truly physical state intermediate between the crystalline solid and isotropic liquid.

The most rational explanation of the phenomenon of liquid crystals has been provided by the swarm theory first proposed by E. Bose (28). This is based on the fact discovered by Vorlander that the molecules concerned in the formation of mesomorphic state are of exceptional length. In all theoretical discussions of the molecular theory of liquids, it is presupposed for purposes of simplicity that the molecule is spherical. This supposition, of course, holds good for liquified monoatomic elements only ; it can scarcely be said to be valid for a compound such as anisaldazine, $CH_3O.C_6H_4.CH:N-N:CH.C_6H_4.OCH_3$, one of the liquid crystalline substances.

If two such elongated molecules approach each other so closely that the mean distances of their centers

of gravity are less than half the length of the molecule, all free rotation must cease except about the direction of elongation, and the molecules will take up more or less a parallel position. These molecules, on the basis of the 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, there is a difference in that the swarms do not remain static but are continually exchanging molecules with one another and with the optically isotropic liquid. The arrangement of the swarms is not a rigid one and is subject to mechanical deformation.

A bundle or swarm of such parallelwise arranged molecules in a perfectly 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 uniaxial crystal. Each swarm will be clear and transparent, but owing to the reflection and diffusion of light between the swarms, turbidity will arise to a great or less extent. As heating continues to higher temperatures, the molecular motion increases, with the result that the average size of the swarm gradually becomes smaller and smaller, and when it becomes smaller than the

wavelength of light, turbidity disappears transforming the whole medium into a clear liquid. Above this temperature the liquid is to all intents and purposes singly refracting.

Vorlander's (24) assertion that the liquid crystals are endowed with a space-lattice structure, an important criterion of a true crystal, stood in the way of the general acceptance of the Bose's swarm theory. In order to arrive at some plausible conclusion, J.S. Vander Lingen (29) carried out the X-ray analysis of anisotropic liquids. The result was definitely against the assertion made by Vorlander, as no evidence for space-lattice structure was revealed by the X-ray examination. As Tammann'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 appear to be due merely to the similar orientation of the flat elongated molecules themselves, the swarm theory of Bose thus being verified. Further, considerable evidence of much importance 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 (30, 31) and by determination of their viscosity at different temperatures (32). As these highly interesting anisotropic liquids lack in the fixed space-lattice structure- an essentially must be property

of a true and perfectly organised solid crystal, one may be inclined to think that these are not liquid crystals as they are called. However, the parallel arrangement of the molecules brought about largely by their inordinate length, and assisted in most cases by their degree of viscosity and the unusual play of the molecular forces when the molecules are so elongated, would appear to constitute these remarkable bodies as a connecting link between ordinary liquids and true solid crystals.

Some of the physical characteristics of these mesomorphic substances have been well examined and it appears that the X-ray analysis of these substances may prove to be useful in enhancing the present understanding of the mesomorphic structure. Before a brief account of this is given, it would be quite appropriate to give first some account at this stage of the theories relevent to this study.

The transformation of the wellknown three states of matter may be expressed as follows :

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

From the point of view of structural orderliness, the matter may broadly be said to exist in two common states- crystalline and amorphous. It has already been pointed out in the previous section that solid substances are classified under 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. Almost a similar type of

intermediate transition state may be conferred upon the substances discovered by Lehmann and others and so commonly known as liquid crystals. It can be stated that compounds exhibiting mesomorphism 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 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 as well as 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 system becomes fluid but remains birefringent because of the preferred orientation of some of the molecules. The gradual thermal break down may be represented as follows :

Crystalline state	$\underset{\longleftarrow}{\xrightarrow{t_1}}$	Liquid Crystalline state	$\underset{\longleftarrow}{\xrightarrow{t_2}}$	Amorphous Liquid state

Increasing temperature

$\longrightarrow$

The transitions take place at definite temperatures. Application of heat causes the perfect orientation of the solid crystal to be disordered and if the molecular conditions are not as stated above, the solid crystalline state directly

passes over to the amorphous liquid state at the melting point of the solid. If however, the conditions are favourable to a mesophase, the order breaks down in stages, first passing into liquid crystalline state at temperatures t_1. At this stage the fluid acquires anisotropic properties. Further heating finally destroys this ' residual crystallinity ' transforming it at t_2 temperatures into an isotropic or amorphous liquid. The action of controlled heat is responsible for breaking down the alignment and is similar to the action of solvent in lyotropic mesomorphism. The system of representing matter into three states being inadequate in the case of such anisotropic melts, a modified way may be as follows :

Solid ⟶ Liquid ⟶ Isotropic ⟶ Vapour or
(Crystal) ⟵ Crystal ⟵ Liquid ⟵ Gas
(Mesophase)

Lyotropic Mesomorphism :

Liquid crystallinity formed by solvation is referred to as lyotropic mesomorphism. Although as compared to the thermotropic mesomorphic systems, lyotropic mesomorphism is less extensively discussed in the literature, it is interesting to note that one of the first liquid crystalline substances discussed by Lehmann (33) was ammonium oleate which falls in the category of lyotropic liquid crystals. Ammonium oleate is deposited from alcoholic solution in what appear to be definite geometrical forms. However, a closer

examination shows that the contours are somewhat rounded and the so called crystals can flow into one another when they touch each other. Lehmann was naturally inclined to name this intermediate state as liquid crystal. This kind of mesomorphism is profoundly modified in its formation by the amount of water that is allowed to be present. It is water, or in general the solvent, which gradually breaks down the crystal lattice passing through the liquid crystalline state.

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

Substances like the soaps, the soap like alkali salts of naphthenic and resin acids and bromophenanthrene-sulphonic acid show mesomorphic state under the controlled action of water (34). McBain (35) has tried to discuss the forms of mesomorphism in soap solutions. He distinguished the neat and the middle soap mesomorphic phases and has discussed them.

It has been discussed (7) that the action of water or in general any other solvent and heat are not dissimilar in regard to the effect of breaking the bonds holding the molecules in their crystalline orientations in one or possibly two directions. In solution, this permits the entrance of ' solvent ' molecules into the lattice, with a corresponding swelling of the structure. The phase rule has been applied to the soap systems by many workers. This study

shows how narrow are some of the limits of the mesomorphic phases, which in turn helps in explaining some of the contradictory statements concerning these phases.

Marsden and McBain (36) have even studied the aqueous systems of non-ionic detergents by the use of X-ray diffraction and have given a discussion of the smectic phase. Recently Palit, Moghe and Biswas (37) 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.

It was shown by Zocher and Coper (38) that Methylene Blue and Neutral Red as well as other dyes gave orientation on rubbed surface. Since then many dyes have been tested for mesomorphic character. Dreyer (39) has discussed the behaviour of films from the aqueous solutions of amaranth and Naphthol Yellow S, as well as dyes of other classes which exhibit a mesomorphic phase. Sheppard's work (40) 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 co-ordinated water molecules between opposite terminal nitrogen atoms along parallel resonance chains.

Smectic, Nematic and Cholesteric Phases of Liquid Crystals :

Friedel made a detailed microscopic examination of the mesomorphic substances available in sufficiently large

number at the time, and classified the mesomorphic compounds into three main types (i) smectic, (ii) nematic and (iii) cholesteric (9). A study of the optical properties of these states made it possible to assign structures to the first two of these phases but even now little is known about the cholesteric phase. 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 amplified by Bose's swarm theory.

Most of the organic compounds exhibiting mesomorphism may be ascribed to possess either smectic or nematic structure. This clearly indicates the importance of these two types. The word smectic having a greek origin meaning soap like does not bear any special significance except that the liquid crystalline ammonium oleate, a soap salt, and one of the first liquid crystalline substances discovered belongs to the smectic structure. Hence, perhaps, the name. The word nematic means thread like and is significant in that the molecules belonging to this category, when examined in polarised light under microscope emerge in the form of characteristic threaded appearance. The third type of phase, the cholesteric phase, is so called because it is shown mainly by cholesteryl derivatives. Eventhough Vorlander (41) has criticised this nomenclature for lack of proper significance, he has not proposed any alternative satisfactory designation for the various phases. These names have now been generally accepted.

Some of the wellknown compounds which exhibit one or the other mesomorphic phase are listed in Table 1.

Table 1

Type	Melting Point °C	Transition Point °C
Smectic		
1. Ethyl-p-azoxybenzoate	114.0	121.0
2. Ethyl-p-azoxycinnamate	140.0	249.0
3. n-Octyl-p-azoxycinnamate	94.0	175.0
4. Ammonium oleate	smectic at ordinary temperature.	
Nematic		
1. p-Azoxyanisole	118.0	136.0
2. p-Azoxyphenetole	137.0	168.0
3. Anisaldazine	165.0	180.0
4. p-Methoxycinnamic acid	172.0	188.0
5. 6-Methoxy-2-naphthoic acid	213.0	224.0
6. Dibenzalbenzidine	234.0	260.0
Cholesteric		
1. Cholesteryl benzoate	146.0	178.5
2. 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 mesomorphic substances which have been studied are either exclusively smectic or exclusively nematic, but some have been found to exhibit both the types of mesophases. In such cases as well there are definite transition temperatures defining the stability of different phases. The symbolic change may be represented as follows :

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

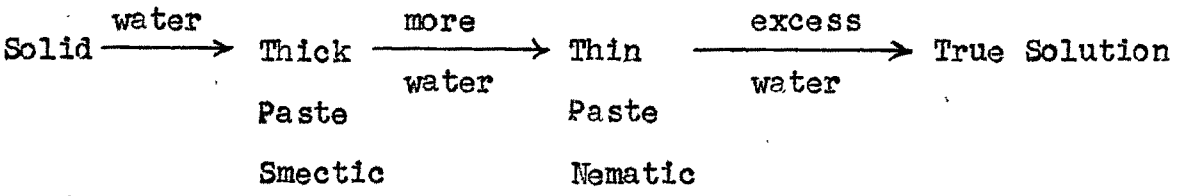
6-n-Decyloxy-2-naphthoic acid is one such mesomorphic compound exhibiting both smectic and nematic phases. This compound melts to smectic phase at 139°C and remains so till it reaches the temperature 147°C, when it begins exhibiting a nematic phase. On raising the temperature to 181°C, it changes to isotropic liquid (42). These transition temperatures are completely reproducible for a pure compound. A few compounds have been found to exhibit more than one phase of the same type, the transition temperatures of which are also sharp defining the stability of the different phases. Such an example is that of ethyl-p-aminocinnamate which possesses two smectic phases and one nematic phase. However, a complication in this case should

$$\text{Crystal} \underset{83^\circ\text{C}}{\rightleftharpoons} \text{Smectic Phase I} \underset{91^\circ\text{C}}{\rightleftharpoons} \text{Smectic Phase II} \underset{118^\circ\text{C}}{\rightleftharpoons} \text{Nematic Phase} \underset{139^\circ\text{C}}{\rightleftharpoons} \text{Isotropic Liquid}$$

be noted, and that is that the stable modification of this

solid melts at 108°C, and so forms smectic phase II directly, smectic phase I remaining in metastable condition.

Very closely resembling the behaviour of thermotropic liquid crystals are also lyotropic mesomorphs (7). The most notable example is Sandquist's (43) 10-bromophenanthrene-6-sulphonic acid which shows both smectic and nematic mesophases. With sufficient water to form a paste it appears to be a typical smectic body and with more water it changes to nematic, finally passing 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 crystal to smectic to nematic takes place with increasing break down 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 centers of gravity of all lattice units are fixed ; rotations are not possible.
2. Crystal with rotating molecule. The centers of gravity of all lattice units are fixed ; rotation about one or more

axes is possible. Example : butyl halides (44).

3. Smectic structure. The centers of gravity of the units (molecules) are mobile in two directions ; rotation about one axis is permitted.

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

5. The true liquid. The centers of gravity of the units are mobile in three directions ; rotation about three axes perpendicular to one another is possible.

This shows that the smectic phase possesses a more ordered structure than the nematic one. A very convenient nomenclature for 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
A. 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 structure	Smectic-Nematic Point	S-N Point
B. 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 idea of mesomorphic structure was first introduced by Friedel, who gave a classification based on his studies of the mesomorphic compounds. The smectic state has a stratified structure, the long molecules being arranged in layers with their long axis approximately normal to the plane of layers. The smectic phase is more highly ordered and is equivalent to a one-dimensional liquid. This structure may be compared to the familiar layer structure of long chain substances with the difference that in the smectic structure

the layers flow 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, probably because the lateral cohesion of the chains is not sufficient to form smectic layers. In the smectic phase there is a strong lateral adhesion along the direction of the molecules which gives it a layer flow. As the temperature is raised this lateral adhesion gradually diminishes and the layer structure breaks down to give the nematic phase which is a two-dimensional liquid. A parallel orientation of rod-shaped molecules has been found to exist in the nematic phase. However, there is no repeating spacing between the rods as regular as that in the smectic phase which gives good X-ray interference. This structure does not extend throughout the whole melt. As has been stated earlier, it exists in the form of small groups or aggregates or swarms, each comprising of some hundred thousand molecules. While the arrangement of molecules within each swarm consists of a definite orientation, one swarm is not necessarily set parallel to another.

Hence, for many purposes a swarm may be considered an independent elementary particle capable of giving Brownian movement of the swarm as a whole. This theory not only explains the turbid appearance of a liquid crystal as being due to the scattering of light by the swarms but it also accounts for the fact that the orienting effects produced by electric and magnetic fields are much larger than would be

expected if the field acted on the molecules individually. The first exact mathematical treatment of the swarm was given by Ornstein and Zernicke (45). A brief reference to Zocher's (46) distortion theory may be made over here. His suggestion and derivation of equations are based on his study of distortion of the nematic structure in a magnetic field. Although the hypothesis advanced by him did explain 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 (47), refractive index (48), magnetic and electric properties (49, 50) of the mesophases and a summary of such measurements is given by Ornstein and Kast (51).

The cholesteric phase is less known and chiefly found in compounds containing cholesteryl ring system. Some of the properties of this phase resemble those of the smectic and the nematic phases with some more additional properties. It has been a difficult problem to assign this phase to either type of structure viz. smectic or nematic, and several investigators are in favour of regarding it as a distinct third type of phase. Friedel has however, suggested that cholesteric phase is a special case of nematic phase. His main arguments are that certain substances are known to exist in both smectic and nematic phases, the sequence being always a smectic phase followed by a nematic phase. Others are

known to have both a smectic and a cholesteric phase, here also smectic is followed by cholesteric. But no substance has been found to possess both a nematic and a cholesteric phase together. 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 discontinuity in the change. On this basis, therefore, cholesteric phase should be equivalent to nematic phase.

More recently Gray (52) on the basis of his study of the mesomorphic behaviour of the fatty esters of cholesterol expresses his opinion that cholesteric phase may best be regarded as an individual phase type, nonetheless it is more similar to the smectic than to the nematic mesophase.

However, optically the cholesteric compounds are negative, whereas the nematic and smectic mesophases are positive. This makes the assignment of the cholesteric phase to any of the two classes rather difficult.

Smectic :

The smectic type of mesophase is much more oily in consistency and has limited internal mobility. A very essential feature of this structure 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 should be in a true crystal.

The smectic phase has a very complicated internal structure, and when allowed to spread over a flat surface tends to form a series of strata or terraces. These terraces are called Grandjean planes after their discoverer Grandjean (53), and can be seen very plainly when thallium stearate is heated to the first transition point. Each layer is seen to glide between its upper and lower neighbours. It is due to these gliding layers that the phase possesses its fluidity. The stratified structure of the smectic phase was inferred from the formation of stepped drops observed under the microscope. The X-ray analysis confirms this stratified structure. 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 layer thickness can be calculated. The distance between the layers approximates to the length of a molecule. Deviations in this distance arise if the molecules are tilted ; as is in the case of ethyl-p-azoxybenzoate where the spacing is more in the mesomorphic state as compared to that in the crystalline state, probably because the molecule is tilted. The layers are homogeneous in appearance and show the optical character of a positive uniaxial crystal. They resemble an isotropic liquid when viewed in ordinary light, but under polarised light the layers appear as homogeneous birefringent patches.

When the smectic phase is tried to be obtained from an isotropic melt or from a solution by cooling, it appears frequently first in the form of particles having characteristic elongated shapes which appear as bright discs under polarised

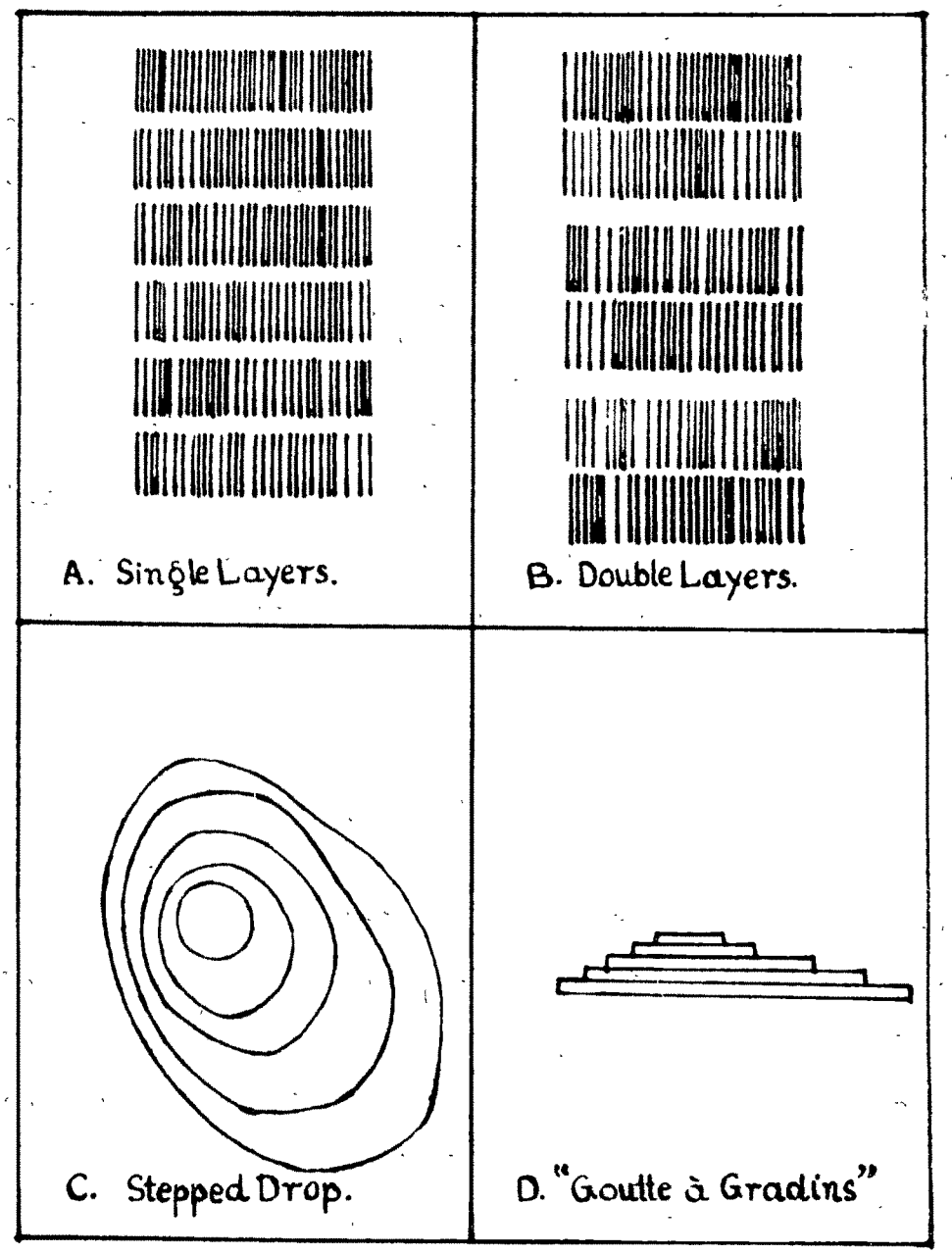

A. Single Layers.
B. Double Layers.
C. Stepped Drop.
D. "Goutte à Gradins"

Fig. 1.

light. This is characteristic of a smectic phase. These elongated particles increase in number and show an evidence of focal conic structure. After their shape, they are known as batonnets. They resemble crystals but have rounded edges and fuse together when two such particles meet each other. A clear focal conic structure is seen when the whole of it is transformed into the smectic state.

Thus this characteristic focal conic structure has become an important means of detecting 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 (54) has given an excellent account of the focal conic structure and the geometry involved, which furnish a further evidence of 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 are designated as ' smectogenic ' crystals.

Nematic :

In nematic phase, the molecules get themselves arranged in parallel or approximately parallel orientation to one another. The similarity of this phase to true liquids in certain aspects is striking and hence it has been compared

with the cybotactic structure of liquids (55), though as compared to the latter, the former has a low internal energy. The optical behaviour of the phase which is uniaxial and positive indicates the parallel arrangement of the molecules, while the X-ray analysis, which gives only diffusion haloes without periodicity, just as in the case of true liquids, indicates the absence of layer structure in the nematic phase. As there exists a strong attraction between the ends of the molecules in a smectic phase, the smectic phase is less fluid, but as compared to this, the molecules in a nematic phase are drawn past one another in the direction of their long axis and therefore the nematic phase is more fluid. Unlike the immobile smectic phase, the particles of dust can move about quite freely in a nematic phase without destroying its structure. Further, unlike the smectic mesoforms, the nematic mesoforms are oriented by electric and magnetic fields indicating a greater freedom of movement of the molecules in the nematic type of the phase. 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.

Nematic mesophase does not show any stratified structure, and hence it does not exhibit a focal conic structure or give rise to ' gouttes-a-grandins '. In contrast to the formation of batonnets in a semectic phase, the nematic substances separate as spherical drops from their melts or solutions. The crystal structure of p-azoxyanisole,

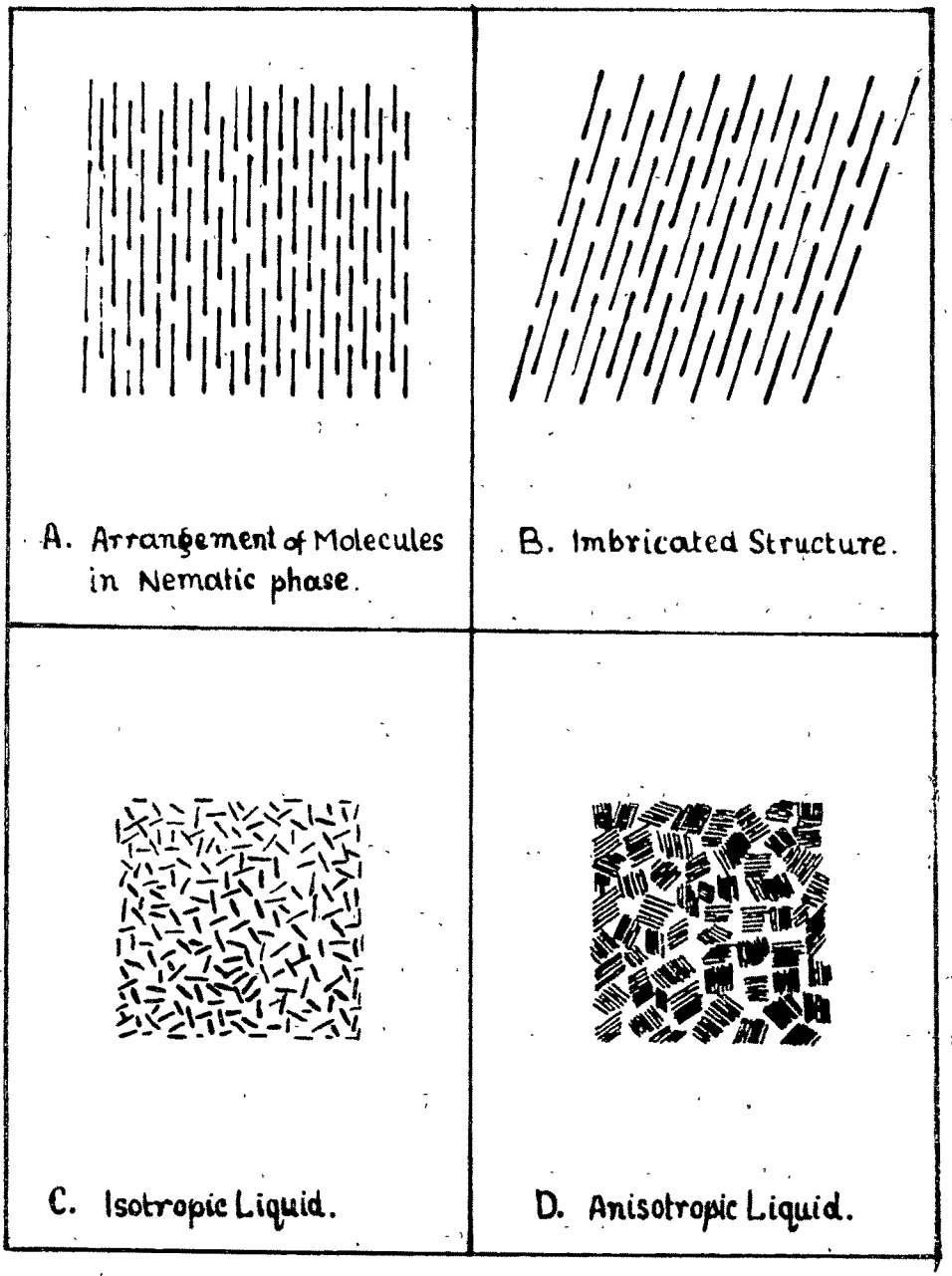

A. Arrangement of Molecules in Nematic phase.
B. Imbricated Structure.
C. Isotropic Liquid.
D. Anisotropic Liquid.

Fig. 2.

p-azoxyphenetole and anisal-1:5-diaminonaphthalene, all of which form nematic phases has been studied by Bernal and Crowfoot (56). Their X-ray analysis shows that the molecules lie parallel to one another but cannot be clearly separated into layers. They are interlocked or imbricated. But all nematic substances do not show imbricated structure in the crystalline state, and in some, the molecules are arranged in layers. It appears that where this is the case the substance can exist as a smectic 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 into the mesomorphic state, the phase is seen in patches or plates with defined outline. Each patch has its own special orientation derived from that of the original crystal. The preparation is fluid and birefringent and uniform in optical properties. A slight shifting of the coverslip causes the borders of the uniform plates become doubled, the molecules in the top layer moving with the coverslip while those in the bottom layer remaining stuck to the slide. Turning the cover slip gives a hellicoidal or twisted transition from one plate orientation to the other. The plates in the nematic phase possess an extraordinary permanance. If the nematic structure is heated just inside

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

The optical effects of nematic threads have been studied by Zocher and Birstein (57). It appears that the lines are due to 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 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 axis of the molecules are directed towards the lines in a radial manner ; the lines may denote the presence of vortices, perhaps hollow, around which the molecules are circulating . In this case the long axis of the molecules would be tangential to circles centered on the threads. Possibly both types of discontinuities exist and in either case the lines may be regarded as axes round which the medium is structurally rolled up. Zocker and Ungar (58) studied the nematic structure in converging polarised light and at thickness up to 1 mm. A conclusion has been drawn 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 (59) 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 (60).

Cholesteric :

Although the cholesteric structure in certain aspects resembles the smectic and the nematic structures, it has certain additional characteristics of its own that are markedly different from both these structures. Cholesteric structure is chiefly exhibited by cholesterol and its derivatives. The higher fatty acid esters of cholesterol which have marked paraffinic properties show clearly the characteristics of a smectic phase, which are generally found absent in the lower members. Here the ring system predominates. A few other substances not belonging to the cholesteryl ring systems, e.g. amylcyanobenzal-aminocinnamate also exhibit cholesteric mesophase but the structure of this substance also is found to be similar to the cholesteryl system.

Some of the additional properties displayed by the cholesteric mesophases are interesting. The mesophase shows brilliant irridiscent colours in polarised light as it cools towards its setting point. There is a variety of colours, ranging 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 generally optically active, some times very strongly so ; the rotation amounting to several

turns per millimeter of thickness. In majority of the cases the optical activity is of the dextro variety.

According to Friedel (3), who has summarised the optical rotation of the cholesteric phase, a dextro structure will rotate the plane of polarisation of the incident light to the right when the wavelength is less than that of the light scattered at maximum intensity, and to the left when its wavelength is greater than this. For substances with laevo structure, laevo rotation takes place when the incident light is of shorter wavelength than that scattered at maximum intensity and dextro rotation when the wavelength is greater.

The fine display of colours by a thin cholesteryl film is the result of the scattering of rays. This scattered light is circularly polarised. A further interesting property is that if the incident light is circularly polarised in the same sense as that normally scattered by the substance, then no change in the sense takes place, which is contrary to what is normally found for the reflection of circularly polarised light. If the incident circularly polarised light is of opposite sense, the light is then transmitted without change of sense. The optical rotation of the cholesteric structure has been studied recently by Mathieu (61) and Levy (62). Grandjean (63) has studied the orientation of the cholesteric structure of cholesteryl esters on ionic salts.

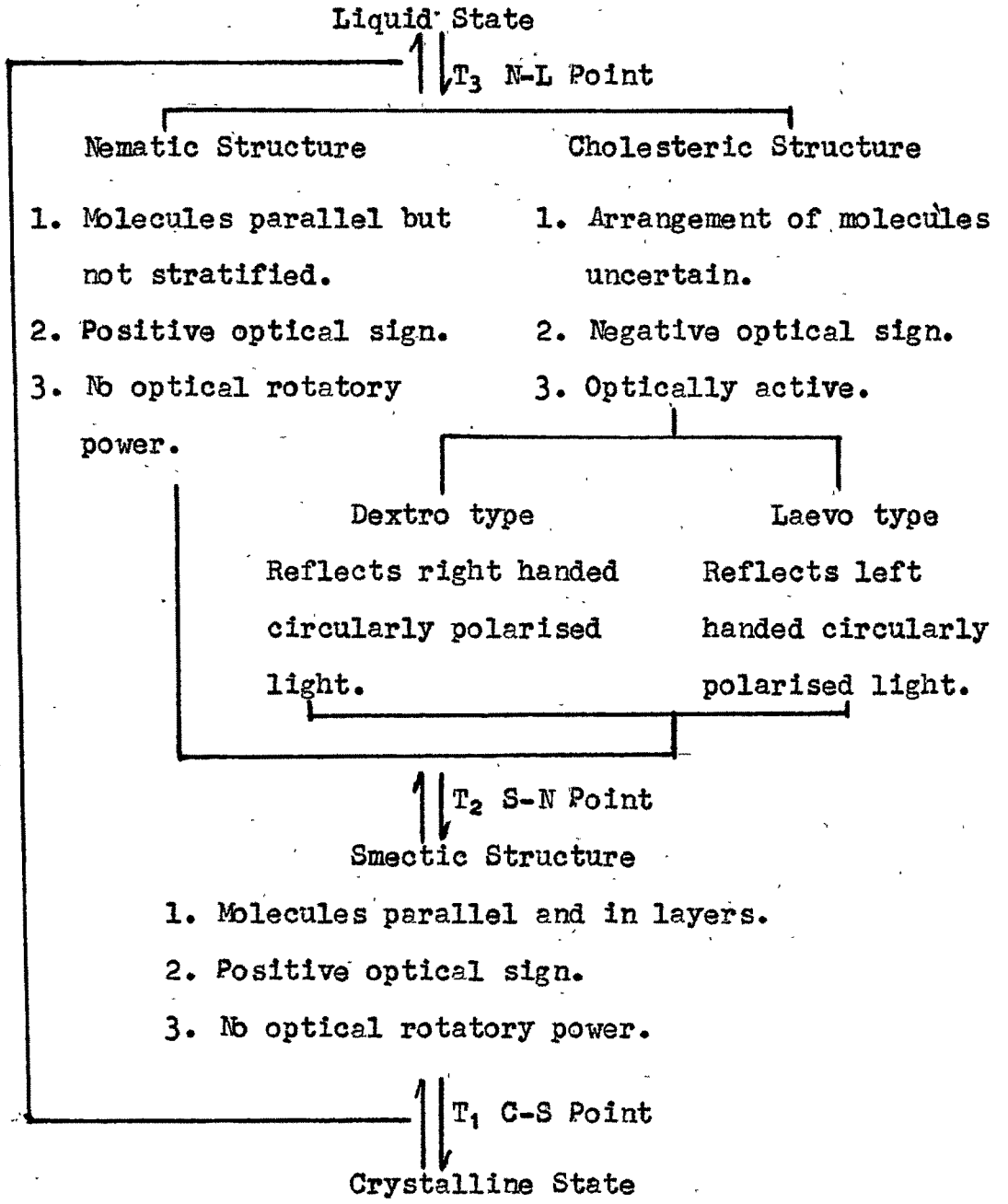
On cooling the cholesteric melt, there appears at first a confused focal conic structure, in which state it does not exhibit the brilliant colours or optical rotatory

power. However, with a slight mechanical disturbance, the medium assumes the form of Grandjean planes which reflect 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° in different cases.

It is due to the shape of the cholesteryl molecule that certain similarities, particularly the layer structure, are found in the cholesteric and smectic types of mesophases. However, these two mesophases differ in their optical signs. The cholesteric phase has a negative sign while the smectic phase has a positive one. 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 found in the smectic mesoform.

Some esters of β-hydrocholesterols of the allo series are reported to be mesomorphic (64) whereas the corresponding esters of α-dihydrocholesterols of the epi series show no mesomorphism at all in the melts.

With the above discussion of the different types of mesophases, now the relation of the intermediate state to the isotropic liquid on the one hand and to the true crystalline state on the other, along with a few important characteristics may be diagramatically represented as follows :



Physical Properties :

The X-ray study of the mesomorphic compounds has helped a great deal in revealing the structure of the mesophase. X-ray examination of the crystalline state of

several mesomorphic compounds was carried out by Bernal and Crowfoot (56), who have shown that in the nematic compounds the molecules in the unit cells are arranged in parallel formation with their ends imbricated. This is the structure suggested as existing in nematic phases. The smectic and cholesteric substances contain the molecules in parallel arrangement with the ends of the molecules in line, which suggests a layer type of structure. The X-ray examination, thus, provides the data which may help in predicting whether a compound will be smectic or nematic. It is on this basis that such substances have been named as ' smectogenic ' or ' nematogenic ' in their crystalline state.

Smectic mesomorphs give good X-ray pictures 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.

Herman's (65) X-ray examination 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.

X-ray study of nematic substances has also been carried out by a number of workers. A comparision of the nematic structure and the liquid state of p-azoxyanisole by means of X-ray analysis has been done by Huckel (66), Kast

(67), Katz (68) and others. It has been reported that the X-ray diffraction patterns for the two structures are similar. More recently some small but definite differences in the X-ray patterns of nematic and liquid structures of this compound are reported in the literature (69-72). Nematic substances do not give X-ray spacings. Very recently Shaw and Brown (73) have carried out the study of 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 in a microphotometer trace of the diffraction pattern 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. According to these workers, the greater sharpness found for the principal peak of the nematic structure as well as its steeper inner slope, undoubtedly indicate more regularity of structure in the mesomorphic state than in the liquid state. Recently Bryan (74) also has carried out X-ray study of the p-n-alkoxybenzoic acids, from p-methoxy to p-n-decyloxybenzoic acids. Phototropy and mesomorphism in certain compounds has been studied by Brown and Shaw (75).

Nematic substances have been studied more closely from the point of view of their physical properties. Their structure has been ascribed to the existence of swarms in the mesophase. The swarms are loosely held together with the

molecular axis parallel but with no other regularity. Substantiating proofs for the swarm theory of the nematic mesophase have further been provided by some other optical and physical measurements. Riwlin (47) has found that there is good agreement between transparency for varying light and thickness of mesophase. She made use of Ornstein and Zernickes' (48) relationship between refractive index and transparency. This is good evidence that the mesophase consists of aggregates or swarms. These results are in agreement with the experiments of Moll and Ornstein (49) in a magnetic field. H.Zocher (76) has given a mathematical treatment of the orienting effects of a magnetic field on the swarms. The behaviour of liquid crystals in electric and magnetic fields has been observed by Freedericksz and Zolina (77).

Studies on viscosity of nematic phases have been done by Herzog and Kudar (78), Ostwald (79) and D.Vorlander (41). They have found that the viscosity for the amorphous state is smaller than for the anisotropic state. The nematic melts show a marked structural viscosity in the mesomorphic region and also there appears a marked increase in viscosity in the region of transition point, clearly indicating thereby that they do not obey the Hagenpoiseiulle law connecting viscosity with rate of shear. As far as viscosity is concerned, the substances in this region behave like gelatin or rubber sols.

Magnetic properties specially in regard to

orientation have been studied by Foex (80) who has shown that the magnetic rotation moment of a swarm can be calculated from the measurements of dielectric constants as a function of the magnetic field strength. According to this, the size of the swarm is found to be 10^6 mols. Dielectric measurements of Jezewski (81) also suggest the same value for the size of the swarm. Bhide and Bhide (82) also measured the dielectric constant and absorption of p-azoxyanisole by resonance method and found abrupt changes in dielectric constant as the mesomorphic state changes to the isotropic liquid. Kast (83) has observed a similar behaviour. Some study regarding surface tension is also done. Generally, the surface tension of liquids decreases with increasing temperature but in the case of mesomorphic state the surface tension increases abruptly at the transition temperature and then again falls regularly (84). Bragg (85), Bernal and Wooster (86) and Lawrence (87) give valuable information on the subject of liquid crystals. Brown and Shaw (6) have nicely depicted various aspects of the mesomorphic state.

Recently, studies of proton magnetic resonence have been extended to anisotropic molecules by Spence, Moses and Jain (88). They report that in the nematic structure the amplitude of the signal decreases greatly compared to the liquid state and the line splits into three components. The splitting of the peak is interpreted by them as arising possibly from a very strong hindering of the rotations of the

methyl groups or, as an alternative suggestion, the protons in the benzene rings may be magnetically non-equivalent in the nematic structure. Further work has shown that the extent of orientation in 4,4'-diethoxyazoxybenzene was greater than in 4,4'-dimethoxyazoxybenzene and 4,4'-dimethoxy-d_3-azoxybenzene (89).

Maier and Englert have made some infra red spectroscopic investigations on substances having crystalline liquid phases. Spectra of seven different 4,4'-di-n-alkoxyazoxybenzenes (methoxy- to heptoxy-) and of 4,4'-dihexoxyazobenzene were determined with a Perkin-Elmer double beam spectrometer. The spectrum of the crystalline liquid phase was found to be identical with respect to number and frequency positions of the bonds as well as to intensity and half value width with that of the normally liquid phase (90). The infra red spectra of some 4,4'-derivatives of azobenzene and azoxybenzene are also studied by them (91).

Chemical Properties :

The phenomenon of liquid crystallinity has been found to be deeply connected with the structure of the compounds exhibiting mesomorphism. Vorlander has contributed a great deal to the understanding of the basic structure required for showing mesomorphism by synthesising compounds in hundreds and he holds it no longer difficult to synthesise such compounds provided certain conditions are well observed.

A study of the properties and formulae of such

compounds capable of existing in mesomorphic state should make it clear what conditions ought to be observed. The molecules of all such compounds possess a striking common feature in having a great length relative to the other two dimensions. These molecules are elongated chainlike which may be flattened as well in some cases, generally terminating in polar groups. Cholesteryl molecules are considerably broad, but here also length predominates over breadth and thickness. A long, narrow and rod-shaped molecule should provide the conditions required for a mesophase. A para-para substitution in the benzene ring is also an essential criterion for a mesophase to exist, is shown by Vorlander (92). He calls this as the ' criterion of linearity ', which should be observed in the synthesis of liquid crystalline substances. Dibenzylidene benzidine is a good example. This molecular complexity also prevails in the amorphous liquid state (93).

The rod-like shape of these molecules helps them in having a parallel alignment, leading to the closest possible packing in the crystalline or mesomorphic state, the molecules being held together by local attachments due to the polar groups, as well as by the unspecific Van der Waals attraction. There is a cohesion which keeps the molecules together but as the temperature is raised the cohesion force will be weakened. However, it does not break down uniformly in all directions on account of the parallel alignment of the molecules, and a lateral cohesion may still persist which

has a tendency to hold the molecules together in bundles. The transition from an orderly state to a random one, characteristic of a true liquid, should therefore, take place in stages i.e. the weaker linkages should break first attributing to the molecules a degree of relative freedom of movement before sufficient thermal energy is acquired for the complete break down of the parallel arrangement. Consequently where this is the case, the medium acquires a flow movement and remains birefringent due to the preferred orientation of the molecules.

Many a compound the molecular structures of which will plead for their showing a mesophase, however, do not do so when heated. A clear cut explanation speaking for their inability of showing a mesophase may not readily be available. Beyond doubt, the criterion of linearity is an essential, however, this alone may not be sufficient and several other factors may play their own role in adorning the substance with a mesophase. The melting point of the compound should not be too high to cause enough thermal agitation to bring about disorder in the melt as also the intermolecular forces should be strong enough to resist the breaking down process of the crystal lattice, in order to maintain some degree of orderliness. But strong intermolecular forces bring about high melting points. These two conditions stand vis-a-vis each other, and therefore, all compounds with long molecules do not show a mesomorphic phase. Sometimes, the melting point may result in thermal agitation to bring about spontaneous

disorder in the melt or the cohesive forces may not be strong enough to preserve order even at low temperatures at which a mesophase can exist. Thus the long chain fatty acids having rod-shaped molecules apparently suitable for mesomorphism do not exhibit it although their melting points are low enough for a liquid crystalline state to exist, and indicate packing of the linear molecules with only a little difference in the arrangement of the terminal groups for odd and even carbon chains. The absence of mesomorphism can be attributed to the lack of cohesion between the carbon chains. In absence of a cohesive force, once the crystal lattice breaks down, the molecules will take up random orientation and no mesophase can be seen. It is clear enough that should a compound tend to exhibit liquid crystallinity, it must possess long molecules capable of giving rise to cohesive forces to attract the neighbouring molecules. Therefore, there must exist intermolecular forces of a polar nature to give rise to enough cohesion, as normal Van der Waals attractions may not be strong enough to bring about such effect.

Generally liquid crystalline compounds are found to consist of long chain molecules often possessing mildly polar groups e.g. -C = C-, -C = N, -N = NO-, -CH = N-, -CH = N-N = CH-, in the middle and an active group e.g. -OR, -COOR, where R stands for a normal alkyl chain, at the end. The middle groups will give lateral adhesion whereas the end groups will also do this but in an end to end manner. The

groups function to attribute dipole moment to the molecule as a result of which the molecules will exert rotation moments on one another. The result is a parallel orientation of the molecules and as the attractive forces between the molecules being effective over short ranges the molecules will preferentially be attached end to end. An aggregate of molecules thus will be anisotropic and the long axis of the molecules will lie parallel to the long axis of the swarm. However, it should be noted that the polar attraction should not be too great to cause the melting point of the compound go so high as to facilitate a spontaneous disorder in the melt due to high thermal agitation at that temperature.

Besides the above consideration of polar forces the benzene ring plays a very important role in the exhibition of mesomorphism. That a majority of organic compounds exhibiting a mesophase are aromatic compounds speaks volumes for the important place of benzene ring in liquid crystallinity. With the increase in the number of aromatic rings, the stability and phase length of the liquid crystal are also increased. The compound $CH_3O.CO.C_6H_4.CO.C_6H_4.CO.C_6H_4.CO.OC_2H_5$ has three benzene rings and is an enantiotropic liquid crystal with a phase length of 140°C (142°C - 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 one more benzene ring added, has a greatly increased region of stability from 187°C to red heat at which the substance decomposes. With four aromatic rings now, the phase length is about 300°C. Also, it is interesting to note that many

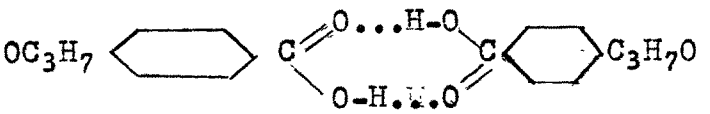
mesomorphic compounds evaporate or distill over before they transform to isotropic liquid. The compound dianisalbenzidine $CH_3O.C_6H_4.CH:N.C_6H_4.C_6H_4.N:CH.C_6H_4.OCH_3$, prepared by Vorlander, containing four benzene rings distills directly from the mesophase and isotropic state cannot be reached. Vorlander (94) here points out that these substances with this behaviour remarkably exhibit mesomorphism. Apparently the stability of the phases should be due to the lateral adhesions in the mesophase. 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 central group and p-p-substituted fairly polar terminal groups.

Both thermotropic and lyotropic mesomorphisms are shown by the salts of fatty acids, e.g. ammonium myristate, thallous salts etc., whereas fatty acids do not show any. Naturally, these salts should be more polar than the free acids, and so are capable of giving greater cohesion. Ammonium myristate gives a smectic phase with 30°C to 35°C phase length and thallous stearate shows a phase length of about 45°C.

A generalisation of conditions that give rise to a smectic or a nematic mesophase has been done on the basis of X-ray analysis. Smectic substances have either one active group e.g. in ammonium oleate or a fairly strongly active group at each end as in p-azoxy esters. This will cause layer formation and is often found in solid crystals. Such crystals

are called smectogenic. On the other hand molecules of substances melting directly to nematic liquid are found to possess weakly active groups near the middle as well as at the end as in p-azoxy ethers. Such groups lead to imbricated structure, a characteristic of nematic phase and the crystals are called nematogenic.

p-Methoxycinnamic acid may at the first sight be expected to be smectic but in the melt, the molecules get associated in pairs by the carboxyl groups, forming a double molecule of the type required for nematic mesophase rather than for smectic (95). Dimerisation as well as hydrogen bonding give rise to conditions favourable to mesomorphism. p-n-Alkoxybenzoic acids (96 - 99) are the simplest examples exhibiting liquid crystallinity by way of dimerisation of their two molecules. In these acids the length of the rod-shaped molecules is increased by the hydrogen bond formation and the liquid crystallinity arises from the association of molecules forming a dimer through carboxyl groups. Thus p-n-propoxybenzoic acid having a simplest molecular structure known to form liquid crystal acquires a structure which is linear and similar to the typical nematic substance say, p-azoxyanisole.



That the corresponding methyl ester of p-n-propoxy benzoic acid, eventhough having a low melting point, does not show a mesophase because the ester has no tendency to such

association is a further proof of the effect of dimerisation and hydrogen bonding in yielding mesomorphism. The carboxyl group helps in getting the association and thus increases the length of the molecule. p-Methoxy and p-ethoxy benzoic acids, however, do not form liquid crystals, which is attributed to their high melting points but the mixture of the two acids when melted yields nematic liquid crystals due to the lowering of their melting points. This should provide an evidence in support of the statement that high melting point will cause thermal agitation resulting into spontaneous disorder in the melt. Recent work of Culling, Gray and Lewis (100) will also substantiate this aspect of high melting points being unfavourable for exhibition of 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 because these are very high melting substances.

A certain axis of symmetry plays a definite role in the formation of liquid crystals (101). Such groups which function to destroy the symmetry of the molecule if introduced damage the liquid crystallinity by way of either reducing the range of stability or complete extinction of the phase. Thus introduction of CH_2 group between two benzene nuclei in a highly stable liquid crystal benzidine derivative causes the disappearance of enantiotropic form. The effects of CO, CS, S etc. groups are similar. The NH group reduces the range of

stability practically to zero although montropy is sometimes observed. An explanation for this phenomenon is, according to Vorlander, that the molecule in such conditions departs from its straight line arrangement. In the same way, introduction of a non-polar alkyl group in the place of a polar alkoxy group destroys the mesomorphic properties on account of reduction in the end to end cohesion in the melt.

Mesomorphism and chemical constitution appear to be very closely related and it seems that very few investigators like Vorlander, and more recently Brynmor Jones, Gray and co-workers have attempted to find a relationship between these two aspects. Friedel (9), however, has discussed the variation of mesomorphism in the homologous series of cholesteryl esters of the saturated fatty acids. He found that the first four members from formate to butyrate give a cholesteryl phase, which is monotropic in the fist two. With the increase of chain length the smectic properties begin to appear, the phase length of the smectic type increasing and that of the nematic type decreasing with the ascending series. The stearate gives only a smectic form which is monotropic. With a short chain, the cholesteryl structure predominates, but with a long chain only a smectic phase appears, because now the determining factor of the properties is the fatty acid molecule itself. However, when it is of an intermediate length, both parts of the molecule influence the mesomorphic behaviour, a smectic phase appearing first and a cholesteric phase at higher temperatures.

Investigations of Bennett and Jones (98) throw some light on the effect of alkyl chain length on mesomorphism. They examined homologous series of p-n-alkoxybenzoic acid and trans-p-n-alkoxycinnamic acid and reported that with the alkyl chains short in length, the systems are either non-mesomorphic or nematic. As the alkyl chain length increases, the smectic properties begin to appear and the increase in smectic phase length is at the cost of nematic phase length. With each successive chain increment, the smectic phase length increases and nematic phase length decreases, until finally in the higher members, smectic phase alone is found. These observations reveal that smectic characteristics depend on the predominance of the aliphatic properties in the molecule and the greater length of the long chain ethers. Weygand and Gabler (102), who examined the homologous series of p-azo- and p-azoxyanisole, found their observations to be in agreement with those of Bennett and Jones (98), although several of their compounds showed monotropic mesomorphism.

Linearity of the structure appears to be the inseparable and essential criterion of liquid crystallinity and yet some broad molecules such as cholesteryl esters distinctly exhibit mesomorphism, which certainly invites the attention of investigators to establish relationship between the length and breadth of the molecules showing mesophase. Only a few molecules broader than benzene have been found to be mesomorphic. Vorlander (103) has reported certain

naphthalene derivatives which are considerably broader than benzene ring as exhibiting mesomorphism. The 2:6-substitution in naphthalene can provide certain degree of linearity. Inspite of their extended surface, certain anils of 2:6-diaminonaphthalene are mesomorphic compounds. Vorlander has shown that the naphthalene anils are less mesomorphic than the corresponding more linear anils derived from diaminodiphehyl. The 1:4-substituted naphthalene derivatives are found to exhibit monotropic mesomorphism. All these facts point to the diminishing nature of mesomorphism with increasing breadth of the molecules. Further 3:5-dichlorination of p-n-pentyloxybenzoic acid destroys the nematic mesomorphism of 27°C in p-n-pentyloxybenzoic acid in spite of the fact that the melting point of the former is 22°C lower than the parent acid. The total disappearance of the mesophase results from the broadening effect of the two chlorine atoms (104). Even lowering of the melting point does not help in keeping at least some mesophase in view. Evidently it should be said that the breadth of a molecule cannot be increased beyond a certain limit without destroying mesomorphism.

Gray and Jones (104, 105) report that 4- and 5-n- alkoxy-1-naphthoic acids and 7-n-alkoxy-2-naphthoic acids do not show mesomorphism whereas 6-n-alkoxy-2-naphthoic acids alone are mesomorphic in behaviour. They attribute the absence of mesomorphism to the fact that either the molecules of these acids are not linear or they are very broad. The mesomorphism in 6-n-alkoxy-2-naphthoic acids is explained in that the

molecules although broader than the alkoxybenzoic acids, are long and rod-shaped forming dimers very similar in shape and size as the alkoxycinnamic acids. They have shown that despite their molecular breadth, the naphthoic acids are more mesomorphic than the corresponding alkoxybenzoic or alkoxycinnamic acids. Gray, Hartley and Jones (106) studied the mesomorphic properties of 4'-n-alkoxydiphenyl-4-carboxylic acids and their simple alkyl esters and compared their mesomorphic behaviour with that of 4-n-alkoxybenzoic acids. These acids exhibit mesophases of much greater relative thermal stability than the simpler benzoic acids ; this is attributed to the enhanced intermolecular cohesion arising from the second benzene ring and to the greater molecular length of the diphenyl compounds. This is further confirmed by the mesomorphic behaviour of the anils from 4-aminodiphenyl, and much more stability of the dianils of benzidine than those of p-phenylenediamine (107). Gray (108) 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 states (109).

When constants 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 acids with an even number of carbon atoms in the alkyl chain and lower to those with an odd number of carbon atoms

(110). This common behaviour in many homologous series is attributed to the packing together of the molecules with their long axis parallel. The alternation for odd and even numbers is believed to be due to variations in the packing of the terminal methyl groups (111).

With a view to corelate the effects of molecular dimensions on mesomorphism Gray, Jones and Marson further extended their studies to the influence of substituents, particularly halogens (112 - 114) in the 3-position of p-n-alkoxybenzoic acids, in the 5-position of 6-n-alkoxynaphthoic acids, in 3-position of p-n-alkoxycinnamic acid and 3'-position of 4'-n-alkoxydiphenyl-4-carboxylic acids and their alkyl esters. 3-Bromo-4-n-alkoxybenzoic acids do not exhibit mesomorphism whereas in the corresponding less broad fluoro and chloro derivatives short phases are found. The thermal stabilities of the phases of the broader chloro acids are lower than those for the corresponding fluoro acids (113). The effect of substituents in 6-n-alkoxy-2-naphthoic acids is similar, the point of appearance of mesomorphism in the series depending upon the substituent atom or group. The breadth and polarisation of the trans-p-n-alkoxycinnamic acids are increased by halogen substitution and the thermal stabilities of the mesophases are altered. The presence of chlorine or bromine 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. On the other hand all trans-4-n-alkoxy-3-iodocinnamic acids are non-mesomorphic. The relative thermal stabilities of the mesophases of 4'-n-alkoxy-diphenyl-4-carboxylic acids and their alkyl esters are decreased by chloro-, bromo-, and nitro-substituents in the 3'-position. All these results point to a similar conclusion. The mesomorphism decreases with the increasing molecular breadth.

Vorlander (115) has summarised the molecular requirements for mesomorphism. The molecules must be either rod-shaped, flat or lath-shaped, with a predominantly linear structure and active central groups to provide lateral cohesion and terminal groups to give an end to end cohesion.

Mesomorphism in Biological Systems :

Much less attention appears to have been paid to the study of mesomorphism in biological systems. It may appear to be somewhat surprising that the first observation of mesomorphic state in biological systems, although not reported as such, seems to be the mention of myelin forms in 1854 (116), much earlier than the first discovery of a liquid crystalline substance was made by Reinitzer in 1888 (1). Brown and Shaw (6) emphasise the importance of this study by pointing out that the mesomorphic state is significantly 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.

It is obvious that the biological systems exhibiting mesomorphism should be systems of two or more components, at least one of it being a substance tending to para-crystallinity and another in general being water (117). This variable permeability of liquid crystals enables them to be as effective for chemical reactions as true liquids or gels, as against the relative impenetrability of solid crystals. Bernal (117) holds the view that on account of liquid crystals possessing an internal structure lacking in liquids, and directional properties not found in gels, a liquid crystal in a cell through its own structure becomes a proto-organ for mechanical or electrical activity and in association with others in specialised cells in higher animals gives rise to true organs as muscles and nerves. He further emphasises the role of liquid crystals in biological systems in furnishing, with its oriented molecules, an ideal medium for catalytic action, particularly of the complex type needed to account for growth and reproduction.

It has been pointed out by Wald (118) that very little of a living cell is highly fluid, most of it consisting of molecules having varying degrees of orientation to one another, that is to say most of the cell represents various degrees of approach to crystallinity. He points out that much of the dynamic plastic quality of cellular

structure, the capacity for constant change of shape and interchange of material, are derived from the property of liquid crystallinity. Recently Kacser (119) has expressed the view that native protein and nucleic acid in genetic material are para-crystalline. Feughelman et al. (120) have given experimental evidence to this effect.

As is already mentioned above, the biological mesomorphism first observed was in the myelin forms. A few years after this original report in 1854, minute fatty globules from the juice of the suprarenal gland were found to exhibit double refraction under polarised light and to exhibit a small black cross in each drop when observed between crossed nicols (121). An important feature of these myelin bodies as well as of the acid esters of cholesterol, ammonium stearate and palmitate and others, seems to be the power of dissolving other substances while maintaining their mesomorphic character. These compounds can dissolve other mesomorphic type substances in large proportions and can even dissolve substances of entirely different molecular character, in contrast to many ordinary crystalline substances which can only dissolve isomorphous components. Therefore, these myelin bodies play a significant role in certain microbiological reactions, where this dissolving power is of high importance. Diffused myelin or myelins of lacithin like nature are probably essential constituents of the cells of most tissues. Indeed, the lecithin present in significant amounts in the red corpuscles probably fits

these bodies to be the common carriers of the organism (122).

It may be said that the mesomorphic modifications are of important biological significance, for 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 also of many biological processes. The structure of the mesomorphic state may provide a favourable environment for the catalytic biological processes. One can compare the extended molecules with fairly strong dipoles and easily polarised groups so characteristic of biological fluids to the molecules of inanimate nature exhibiting mesomorphism. As Bowden has put it (123), indeed this state seems to be especially suited to biological functions and may possibly be the basis of vital activity.

Mixed Liquid Crystals :

It can be said from the aforegoing description of the liquid crystalline state that the limits of its stability are well marked by sharp transition temperatures which separate it from the amorphous liquid state stable at higher temperatures and the solid crystal state stable at lower temperatures. The liquid crystalline state exists between these two sharp transitions and exhibits properties which are similar to those of solid crystals excepting those qualities depending upon the rigidity inherent in a true crystal, as for example, the fixed space lattice structure. If any other

substance is dissolved in such a liquid, the dissolved substance will be in an anisotropic environment and its properties are likely to be affected to a considerable extent. The modifying action of a foreign substance on mesomorphic structure has been discussed in general terms by Gaubert (124).

Kast (125) has shown that various samples of p-azoxyanisole containing different amounts of impurities gave different values for the critical frequency of the applied electrical field at which the orientation of the mesomorphic phase disappeared with the addition of foreign substances (126). It has been shown that the addition of minute quantities of a circularly polarising compound to an optically inactive nematic structure can transform it into a strongly active and pleochroic one, the rotatory power of such a system will then be proportional to the amount of asymmetric substance present (127). The addition of a substance that showed a large tendency to set uniaxially e.g. p-ethoxybenzal-amino-α-methylcinnamic acid brings randomly arranged mesomorphic compounds into an uniaxial arrangement. The structure of the planes noted in amylcyanobenzalamino cinnamate may be observed in mixed cholesteryl salts and mixtures of cholesteryl salts with liquids such as p-azoxyphenetole (128, 129).

Mesomorphic compounds were obtained by melting cholesterol in turn with succinimide, the tartaric acids, malic, maleic, lactic, malonic, succinic, cinnamic and

anisic acids (130, 131), by melting ergosterol propionate, acetate and butyrate with glycolic acid, glycerol, and orcin (132), and by melting compounds of cholesterol and ergosterol with urea (133). Mixtures of two liquid crystalline substances were prepared by Tammann (13) who studied them under microscope. His observation was that many of the mixtures were mesomorphic. Mixtures of optically negative cholesteryl propionate and optically positive ethyl anisalaminocinnamate were prepared by Gaubert (134), and he determined the refractive indices at different concentrations.

Just as the freezing points of true solids are lowered by the addition of other substances, so also are the transition temperatures of liquid crystals lowered by the presence of foreign substances. The transition from liquid to liquid crystalline state can be made use of in cryoscopic work 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.

That the transition temperature of isotropic-liquid-crystalline liquid for p-azoxyanisole is lowered by the addition of other substances has been shown by Schenck (135). He also calculated the molecular lowering of the transition temperature in the case of p-azoxyanisole from which he calculated the heat of transition. He has further shown that p-azoxyanisole and p-azoxyphenetole in the liquid crystalline

state form isomorphous mixtures.

Binary mixtures of substances, one or both the components of which were liquid crystalline substances, were investigated by de Kock (18), with a view to find out how far the transition can be made use of in cryoscopic work and to study the effect of the addition of another substance on the mesomorphic state of a liquid crystalline substance. When p-azoxyanisole (114-135.2°C) and p-methoxycinnamic acid (170.6-185.5°C) both of which are nematic liquid crystals, are mixed, their melting points as well as transition points are lowered and the upper transition temperature - concentration curve exhibits a rounded minimum. At lower temperatures, varying with the composition of the mixture, one or other of the pure solid substances is deposited. The temperature - concentration curve obtained on these observations resembles an ordinary freezing point curve with a eutectic at 107-8°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 also studied binary systems where only one component is a liquid crystal viz. (i) p-azoxyanisole and quinol, (ii) p-methoxycinnamic acid and quinol, (iii) p-azoxyanisole and benzophenone and (iv) ethyl p-azoxybenzoate and ethyl p-azobenzoate. He observed that mixed liquid crystals are formed but only to a certain concentration of the second component, the transition temperatures of the liquid crystalline -amorphous liquid state being lowered by

the addition of quinol-or benzophenone. He also calculated the molecular depression in the case of p-azoxyanisole with quinol 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 phase rule.

Lehmann (136) also studied binary mixtures of substances, one or both of which exhibited mesomorphism and measured the transformation temperatures. Bogojawlensky and Winogradov (137) studied binary mixtures of isomorphous substances, one or both of which were non-liquid crystalline substances, and reported the formation of mixed liquid crystals in both of them. 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°C) and the latter melts at 160.2°C, but possesses a metastable monotropic mesomorphic state which lies four degrees below its normal melting point at 156.1°C. In this case both the freezing point curve and the melting point curve are straight lines intersecting each other showing a region of stable and a region of metastable mixed liquid crystals in the temperature - concentration diagram. 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 because the transition to isotropic liquid lies below the normal melting point and could not be ascertained owing to the impossibility of cooling. This latent transition was determined in a number of cases by extrapolation of the clearing point curve which is linear in majority of the cases. This should provide an explanation to the observation of Vorlander and Gahren (138) that substances which themselves are not liquid crystalline, form liquid crystals when they are melted together.

Walter (139) has tried to explain the observation made by Vorlander and Gahren. According to him, the substances, binary mixtures of which exhibit such mixed liquid crystallinity are generally very well crystallised and are not readily supercooled. Therefore, a monotropic liquid crystal phase which may be anticipated for them by reason of their chemical constitution remains latent. If two such chemically similar substances are mixed, it may happen that the melting point of the solid phase of the mixture, which is generally lower than the melting point of the individual components, falls below the mixed melting point of the liquid crystalline phase, which with chemically related substances should lie between the two latent crystalline liquid melting points of pure components. Such a mixture exhibits enantiotropic liquid crystal properties. This was experimentally shown by him in a mixture of anisic acid and anisal-propionic acid which themselves are not liquid crystals. He obtained enantiotropic mixed liquid crystals in this case within

certain limits of concentration. 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 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. Tammann's (140) view that formation of liquid crystals from a mixture of non-liquid crystalline substances is a matter of emulsion formation thus stands disproved.

Binary mixtures of p-azoxyphenetole with p-azophenetole, cholesteryl isobutyrate, cholesteryl propionate, cholesteryl benzoate, p-methoxycinnamic acid and p-azoxyanisole have been studied by Prins (141) who discussed the problem in terms of phase rule. He observed that p-azoxyphenetole and p-azoxyanisole form a continuous series of mixed liquid crystals, the linear clearing point curve falling regularly from the upper melting point of the former to that of the latter component. Cholesteryl propionate shows a similar behaviour. The binary mixtures of p-methoxycinnamic acid and cholesteryl benzoate with p-azoxyphenetole also behave similarly except for the minimum shown by the mixed liquid crystal curves. In the case of binary mixtures of p-azoxyphenetole with p-azophenetole and cholesteryl isobutyrate, a series of mixed liquid crystals are reported to be formed in each case up to the point where the clearing point curve intersects the freezing point curve, while in the

case of cholesteryl isobutyrate the mixed liquid crystals become metastable below 110°C. Lehmann (142) has however, criticised this work but Prins (143) has emphasised the importance of quantitative observations as opposed to qualitative microscopic observations.

Vorlander and Ost (144) have made a detailed qualitative study of the crystal-mesomorphic point lowering caused by mixing several pairs of mesomorphic substances. In some cases the crystal-mesomorphic point of the hybrid was calculated empirically and compared with the observed value.

Kock and Prins and even Vorlander seem to have studied the problem from the stand point of phase rule, but no satisfactory explanation seems to be available as to the nature of the mixed liquid crystals and the mode of their formation. Recently an attempt in this direction has been made by Dave and Dewar (145). De Kock (18) who studied the binary mixture of p-azoxyanisole and quinol suggested that the transition from anisotropic to isotropic does not occur very sharply. He thought that as a rule there should exist a range of temperature over which two liquid phases - one isotropic and another anisotropic coexist. However, Dave and Dewar (145) after repeating the observations very carefully of the mixture studied by de Kock, have distinctly shown that the transition from the anisotropic to isotropic is sharp and the liquid crystalline region is a homogeneous single phase without any indication of the

existence of the two phase liquid system at the anisotropic-isotropic liquid transition. 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 from cloudy to clear without careful temperature control and without stirring. Dave and Dewar (145, 146) 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 by them to the polarity of the end groups of the admixed molecule. Further, they conclude from their observations that any substance with anisotropic molecular structure would form a liquid crystal if it could be obtained in a liquid form at a sufficiently low temperature. They have also refuted the suggestion advanced by de Kock (18) that the depression of the transition point by solutes might be used as a method of determining molecular weights. Dave and Dewar (146) also studied some binary mixtures of substances which furnish from the structural point of view, the minimum requirements of exhibiting mesomorphism, but are apparently non-liquid crystalline by themselves, with a view to find if mixed liquid crystals can be obtained over a range of temperature and concentration, but they could not observe any such mixed liquid crystal formation in such non-liquid crystalline mixtures. They also expressed their apprehension at the method of extrapolation in predicting latent transition temperatures.

Several points of interest arise from this description which require an adequate explanation. Further studies from these points of views have been carried out in this investigation, with a hope to arrive at some plausible conclusions.