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

INTRODUCTION.

1. Definition and Nomenclature.

The common states of matter are gas, liquid and solid. The particles in a gas are randomly distributed and the space in the system is sparsely occupied. In a liquid the molecules are packed close enough to be in contact with one another and lie at all times within mutual fields of attraction of their neighbours. The intermolecular distances are about the size of the molecules themselves. A primary property of a liquid is that it assumes the shape of its container and bounds itself at the top by its own free surface.

The dominant feature of the solid - crystalline state, in contrast to gaseous or liquid state, is that strong bonding forces exist between its molecules and give orderly arrangement to this state. Thermal agitation disturbs this order so that, when temperature is high enough and average thermal energy of a molecule exceeds its bonding energy, the molecules escape from one another's influence and solid melts to isotropic liquid, whose state of order shows no preferred direction.

But there exists a series of compounds which behave differently when they melt. The crystal first, at a well defined temperature, loses its three dimensional arrangement and gives a turbid melt comprising layers of molecules which can be displaced relative to each other, and this gives the melt some anisotropic properties. This intermediate turbid state is called liquid crystal or mesophase. Because of the movability of its molecules the mesophase has no crystalline

appearance any more. Mechanically it is a liquid. On the other hand, as the molecules are still subject to arrangement, the mesophase has anisotropic optical properties, and thus optically it is a crystal. Finally as the temperature increases still further, the last molecular aggregates break down, so that, at a definite temperature, the turbid anisotropic melt becomes isotropic, The consistency of the turbid fluid formed varies from a paste to a free flowing liquid, and at a higher temperature the turbid condition is converted into the true 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.

F.Reinitzer (1), an Austrian botanist, for the first time observed the phenomenon of liquid crystallinity in the case of cholesteryl benzoate. He observed that cholesteryl benzoate melts at 145.5°C to a cloudy liquid giving colours, and becomes transparent at 178.5°C. O.Lehmann (2) was the first to carry out the systematic study of such compounds and he coined the term liquid crystal or crystalline liquid to describe this phenomenon. Although this name is still commonly used, objections have been raised to this nomenclature.

The detailed study of the properties of liquid crystals supported the view that it is a new state of matter. Friedel (3,4) studied liquid crystals in more detail and he proposed that as this phase is neither a true liquid nor a true solid, the term mesomorphic state (Greek - mesos, intermediate;

morphe, form) would be more appropriate meaning a state intermediate between a crystalline solid and an amorphous liquid. This term and the associated terms mesomorphy, mesoform, mesomorphism and mesomorphic are widely used in the literature.

Rinne (5) has criticised both these terminologies on the basis that they did not carry 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, whereas amorphous matter, isotropic liquids and gases will fall into the category of atactites. He, therefore, proposed the name paracrystals. Here the word crystal significantly emphasizes the natural proximity of the state to the crystalline condition, while the prefix para signifies that many of the organic compounds which possess this type of eutaxy are parasubstituted benzene derivatives. Thus, the classification is :

1. Atactites - Isotropic liquids, gases and other amorphous matter.
2. Eutactites - (a) Crystals - three dimensional order.
   (b) Paracrystals - one or two dimensional order.

Brown and Shaw (6) consider the term mesomorphic state preferable and have used it as the title for their review. However, the name liquid crystal is still frequently employed.

Liquid crystals are classified into two major groups on the basis of the manner in which they are obtained. (7-9). One of these is identified as thermotropic indicating that this class is obtained by heating. Lyotropic liquid crystals constitute the second major group and are obtained by mixing two or more components. In two-component systems involving water, the second component is generally an amphiphile. Lyotropic systems can be large in number and varied in composition.

Friedel carried out optical studies of a number of mesomorphic compounds, and clearly distinguished three different types of mesophases. They are :

1. The smectic mesophase ..... a turbid, viscous state, with certain properties reminiscent of those found for soaps. The term smectic (soaplike) is coined by Friedel from the Greek word, smectos meaning grease or slime.
2. The nematic mesophase ..... the term nematic, coined by Friedel from the Greek word meaning thread, describes the threadlike lines which are seen under the microscope.
3. The cholesteric mesophase ..... a turbid and mobile phase, having certain characteristics of its own which are markedly different from the smectic and nematic mesophases. The cholesteric mesophase is mainly exhibited by the derivatives of cholesterol or other sterol systems and hence the name.

Mesomorphic State :

Reinitzer (1) first reported the phenomenon of double melting point in cholesteryl benzoate in 1888, while

Lehmann (2) was the first to describe the property of liquid crystallinity. Soon after this initial discovery Lehmann (10) found that ammonium oleate and p-azoxyphenetole were examples of substances that may exist in the mesomorphic state. Gattermann and Ritschke (11) in 1890 found similar behaviour in the case of p-azoxyanisole and p-azoxyphenetole. In the begining the discovery of these mesomorphic states aroused curiosity in some of the chemists and after that it attracted the attention of a number of chemists in the early 20th century. Lehmann (12) and Vorländer (13) prepared hundreds of compounds exhibiting this phenomenon in a short period. It became immediately evident that all these substances had one common feature - a very long molecule, and this has always been accepted as a necessary criterion of a mesomorphic substance.

Despite the number of cases of mesomorphic behaviour which were soon reported, a number of years passed before it was universally accepted that the mesomorphic state is a true state of matter intermediate between normal solid and the normal liquid state. In their early papers Tammann (14), Nernst (15) and Quincke (16) described these melting phenomena as arising from the colloidal effect of minute crystals held in the isotropic liquid, or from the presence of impurities in the compounds, giving an emulsion of two liquids. All attempts to separate the alleged emulsion into its constituents by G.Bredig and von Schukowsky (17) and Coehn (18) by electrostatic and

centrifugal processes were futile. Schenck (19) and Vorländer (20) have also criticized the emulsion theory and argued in favour of the existence of crystalline liquids. A.C. de Kock (21) 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 Tammann's sedimentation experiments without success. Pawloff (22), Wulff (23) and Voight (24) 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 mesophase 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 (25) carried out a large number of experiments to illustrate the properties and formation of liquid crystals from the isotropic liquid. He considered that the phenomenon was due to the formation of crystals in the liquid condition, which appeared perfectly transparent under the microscope. The turbidity which usually accompanies the phenomenon, was attributed by him to the different orientation of the individual crystals which scatters the light to a more or less extent. Vorländer (20), (26) believed that these substances were truly liquid crystals

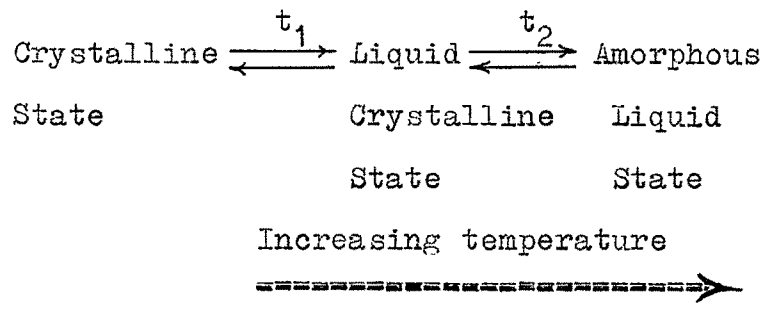
and had a fixed space lattice. However, further microscopic examination of liquid crystals carried out by Mauguin (27), Friedel and Grandjean (28,29) soon dispelled these ideas and established that the liquid crystal state is a truly physical state, intermediate between the crystalline solid and the isotropic liquid.

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

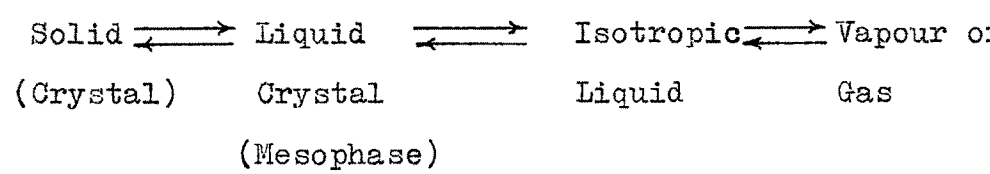
Solid $\rightleftharpoons$ Liquid $\rightleftharpoons$ Vapour or Gas

The common state of matter may broadly be classified into two main groups : Crystalline and amorphous. Solids in general, belong to the category of crystalline substances while liquids and gases come in the second category i.e., amorphous. Mesomorphic substances form the intermediate state between the crystalline and amorphous states. They consist of molecules which are long and rod shaped, possessing one or more dipolar groups. This type of structure favours the parallel alignment of the molecules similar to a long box of round pencils. In the crystalline state of a mesomorph, bonding forces exist between the molecules. Thermal agitation disturbs this order and on heating 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 break-down may be presented

as :

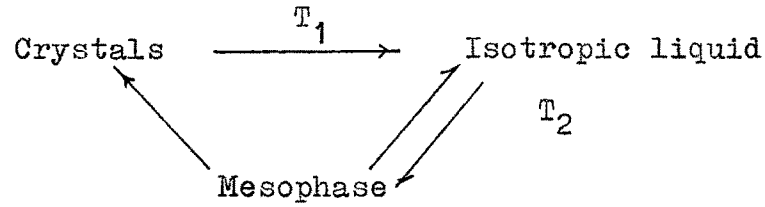


These transitions take place at definite temperatures and are precisely reversible. In most of the solid crystalline substances, heating breaks down their ordered structure and the solid is transformed into an isotropic liquid, whose state of order shows no preferred direction at its melting point, but if the conditions are favourable for mesomorphism, the order breaks down in stages, first passing into liquid crystalline state at temperature t_1. This state has certain degree of order and hence acquires anisotropic properties. Further heating to t_2 destroys the orientation of the mesophase and finally gives amorphous liquid. Thus the action of controlled heat is responsible for breaking down the alignment in stages and is similar to the action of solvent in lyotropic mesomorphism. The ~~representation~~ classification of matter into three states in the case of such anisotropic melts is inadequate and hence a modified way may be as follows :



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 a liquid at T_1, but when the isotropic liquid is cooled, supercooling may occur and a mesophase appears below the melting point at T_2 and before crystallization occurs. Such a mesophase is given the name monotropic mesophase. The sequence of changes of state for a compound exhibiting monotropic mesophase may be represented as :



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

2. Smectic, Nematic and Cholesteric mesophases :

Friedel carried out detailed optical studies of mesomorphic compounds and as a result liquid crystals are conveniently divided into three types - Smectic, Nematic and Cholesteric. Smectic and nematic are the most common types of mesophases and the study of their optical properties has made it possible to assign structures to them. These structures do not 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. Vorländer (30) has, however, criticized this nomenclature but he has not suggested any satisfactory alternative and these names have been generally accepted.

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

Table - 1

Type of compounds	Melting Point °C	Transition Point °C
Smectic :		
4,4' -Diethyl azoxybenzoate	114.0	122.5
4,4' -Diethyl azoxycinnamate	140.0	249.0
p-n-Octadecyloxybenzoic acid	102.0	131.0
Ammonium oleate	Smectic at ordinary temperature.	
Nematic :		
p-Azoxyanisole	118.0	136.0
p-Azoxyphenetole	137.0	168.0
Anisaldazine	169.0	182.0
p-Methoxycinnamic acid	173.5	190.0
Cholesteric :		
Cholesteryl benzoate	149.0	187.0
Cholesteryl cinnamate	160.0	215.0
Active α-amyl-p-(4-cyanobenzylideneamino) cinnamate.	92.0	105.0

Ammonium oleate shows a smectic phase at ordinary temperature, but it being a lyotropic mesomorph, no transition temperature can be given for it. Most of the liquid crystalline substances which have been studied are exclusively either smectic or nematic. Some compounds, however, exhibit both types of mesophases and there are always definite transition temperatures defining the stability of different mesophases. The change with increasing temperature may be represented as :

$$\text{Crystalline solid} \xrightarrow{t_1} \text{Smectic} \underset{\leftarrow}{\xrightarrow{t_2}} \text{Nematic} \underset{\leftarrow}{\xrightarrow{t_3}} \text{Isotropic liquid}$$

Number of compounds are known possessing more than one mesophase of the same type. Polymorphism in smectic mesophase is more common. Here also the temperature range and the stability of the different mesophases is sharply defined. Such an example is that of 4' -n-hexyloxy-3' - nitrodiphenyl-4-carboxylic acid which possesses two smectic phases and one nematic phase.

$$\text{Crystalline solid} \xrightarrow{136.0^{\circ}C} \text{Smectic}_{II} \underset{\leftarrow}{\xrightarrow{158.0^{\circ}C}} \text{Smectic}_{III} \underset{\leftarrow}{\xrightarrow{213.5^{\circ}C}} \text{Nematic} \underset{\leftarrow}{\xrightarrow{218.0^{\circ}C}} \text{Isotropic liquid} \quad (31)$$

Recently Demus et al. (32) have reexamined number of above type of substances including the one given here and have designated different phases of the smectic mesophase as smectic A, smectic B, smectic C etc. The above compound should thus be designated as :

$$\text{Crystalline solid} \xrightarrow{133.4^\circ C} \text{Smectic C} \underset{}{\overset{163.3^\circ C}{\rightleftharpoons}} \text{Smectic A} \overset{213.5^\circ C}{\rightleftharpoons} \text{Nematic} \overset{218.3^\circ C}{\rightleftharpoons} \text{Isotropic liquid}$$

Lyotropic mesomorphs (8) also show a similar behaviour as exhibited by thermotropic liquid crystals. The most notable example is Sandquist's (33) 10-bromo-phenanthrene-6-sulphonic acid which shows both smectic and nematic phases. With sufficient water to be a paste, it appears to be a typical smectic phase and with more water it changes to nematic and finally passes to a true solution with excess of water.

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

It is thus clear that the crystal space-lattice breaks down in stages by thermal agitation or solvent effect and transforms finally into isotropic liquid or a true solution respectively. The transition from the completely ordered solid crystal through the smectic and nematic structures to the true liquid may be outlined as follows (6) :

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. e.g. Butyl halides.

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 A $\rightleftharpoons$ Smectic structure B	Smectic A - Smectic B point	S_A- S_B Point
Smectic structure B $\rightleftharpoons$ Smectic structure C	Smectic B - Smectic C point	S_B- S_C Point

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

2a. Smectic Mesophase :

The smectic mesophase has a stratified structure, the long molecules being arranged in layers with their long axes approximately normal to the plane of layers. Though, the smectic phase is a highly ordered phase, the spacing of the molecules within each layer is, however, not uniform as it would be in the true crystal. The fluidity of the phase is attributed to the fact that the layers can glide over one another like individual units in packs of cards. Substances forming three-dimensional crystalline layer structure such as the paraffinic substances, fatty acids etc., do not pass through a smectic mesophase on heating. It seems that lateral cohesion of the chains is not sufficient to form smectic layers; hence on heating the molecules directly give isotropic liquid. In the smectic phase the layers of molecules are quite flexible. If a single sheet could be suspended in space, free from gravity, it would take the form of a perfectly flat surface and side to side

attractions of the molecules in the sheet would be the strongest on it (Fig.1).

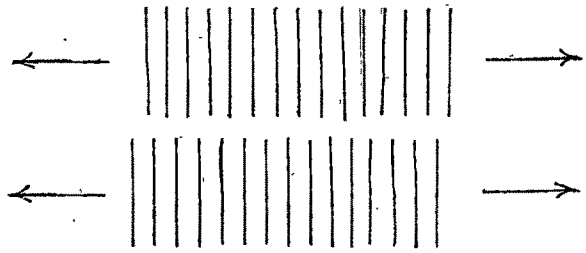


Fig 1 : A section representing the molecular arrangement in two plane smectic strata.

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 molecules in the adjacent sheets. Thus a solid crystal would be formed in which there would be order and repetition in every direction in space. In the smectic phase, the temperature is just high enough to break up the sheets themselves. In some cases, the crystalline structure within a sheet may even break down to give the nematic phase.

A film of a smectic phase stretched over a small hole in a plate gives the condition of parallel sheets. The resulting structure is optically homogeneous and is said to be homeotropic. This homeotropy arises when the surface exerts no orienting effects, i.e. when contact between the mesophase and the surface is imperfect. An interesting

feature of the homeotropic structure is the formation of series of strata or terraces. These terraces are called Grandjean terraces after their discoverer Grandjean (34) 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 microscope and has been further confirmed by X-ray analysis (35). The smectic layer structure provides a regular periodicity normal to the layers so that this mesoform gives an X-ray diffraction pattern from which the thickness can be calculated. The thickness of the layer approximates to the length of a molecule but deviations in this 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 when observed in ordinary light, they resemble an isotropic liquid but between crossed nicols the layers appear as homogeneous birefringent patches.

When the smectic structure is formed from cooling the isotropic liquid, it first appears frequently in the form of non-spherical, characteristic elongated birefringent bodies. These increase in number as the temperature falls, coalesce and show evidence of a focal-conic structure. These particles are known as bâtonnets, so named, after their shape. The focal-conic structure has become an important means of detecting the smectic mesophase. It extends all over the specimen and when examined in polarized 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 Bragg (36) 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 low magnetic and electric fields.

Polymorphism in the smectic mesophase is extensively studied by Sackmann and Demus (37). They examined about 120 such pure compounds and their mixtures with one another and assigned structures to the smectic mesophase from the rule of miscibility in mixed liquid crystal formation. They could observe different textures of the smectic phase by means of a micro-heating stage and classify different smectic phases according to the textures observed in the mesophase (table 3).

Table - 3

Scheme of texture groups of Smectic liquid crystals.

1. Smectic A :	(a) simple fanshaped texture.		
	(b) simple polygon texture.		
2. Smectic C :	(a) broken fanshaped texture.		Schlieren texture
	(b) broken polygon texture.		
3. Smectic B :	(a) fanshaped texture.	with decreased number of lines	
	(b) polygon texture.		
	(c) mosaic texture.		

The solid crystalline form of the substances exhibiting smectic mesophases is designated as " Smectogenic " crystals.

Nematic Mesophase :

The nematic mesophase is not as highly ordered as the smectic mesophase. The molecules in the nematic phase are arranged with their long axes parallel but they are not separated in layers. Optical properties of the nematic mesophase indicate that the molecules are in a constant state of movement, such that any parallel arrangement must become distorted and twisted, particularly in parts of the mesophase which are away from the orienting influences of surfaces. The molecules in the nematic phase exist in the form of groups, each group containing about 100,000 parallel molecules. These groups are referred to as swarms, and the theory known as the swarm theory was first proposed by E.Bose (38) in 1909, to explain the molecular arrangement and order in the nematic phase.

The majority of mesomorphic compounds are comprised of long, rod-shaped or lath-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 swarms in the medium. This would mean that the liquid crystalline structure resembles a mass of small crystals rather than a single crystal. However, unlike the mass of small crystals, the swarms do not remain static but are continually exchanging molecules with one another and with the optically isotropic liquid. Thus, the swarms may in fact be considered as the basic particles used to build up the nematic mesophase - particles which are capable of changing their axial directions, and which are, therefore, subject to orientation effects and even Brownian movement.

The swarm hypothesis accounts satisfactorily for the turbidity associated with the nematic mesophase; the light scattering properties of the 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 wavelenth 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 (39) definitely ruled out the views of Vorländer that the liquid crystals are endowed with a space-lattice structure, an important criterion of a true crystal. The regularity of structure producing double refraction and other optical effects simulative of crystals appear to be due to the similar orientation of the flat elongated molecules 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 electro-magnetic field (40,41) and by the determination of their viscosity at different temperatures (42). The first mathematical treatment of the swarm theory was given by Ornstein and Zernicke (43). Evidence in support of the swarm theory is available from the researches like transparency (44), refractive index (45) and magnetic and electric properties (46,47) of mesophases; a summary of such measurements is given by Ornstein and Kast (48).

However, the swarm theory did not pass without criticism and Zocher (49) in particular questioned the validity of the deductions made by Ornstein and the experimental techniques employed. In place of the swarm theory he proposed the distortion hypothesis which is based on the concept of a continuum for the nematic mesophase such that the orientation of the molecules changes in a continuous fashion throughout the bulk of the mesophase, now referred to as the continuum theory of liquid crystals.

The ideas of distortion hypothesis have been expressed in highly mathematical terms and are based on the study of distortion of nematic structure in a magnetic field.

Zocher made the following assumptions to derive equations for his theory of distortion in a magnetic field:

1. The entire nematic structure under observation tends to take up such a position that the axial direction at every point is the same;
2. Any force acting so as to disturb the state (under 1) where the directions are uniform causes a distortion in the nematic structure in which the direction changes continuously until a restoring force of an elastic nature holds the applied force in equilibrium; and
3. the position of the units in the nematic structure initially assumed at the surface of solid bodies (e.g.glass) are almost unchangeable by application of an external force (magnetic field).

Zocher claimed that his concept of a continuously changing molecular orientation in the nematic mesophase explains the magnetic and electric properties of the mesophase better than does the swarm theory. Bernal (50), however, by reviewing the experimental facts has compared the merits of the two theories and has pointed out that the orientating effects of surfaces on the nematic mesophase could be explained by either theory. Although, a number of many interesting properties of nematic mesophase may be explained on the basis of the swarm concept, it would not be proper to forget the distortion hypothesis of Zocher. For instance, Chatelain (51)

has shown that his studies on the diffusion of light from the sections of nematic mesophases indicate the existance of swarms of 10^7 molecules, but in his review of liquid crystals he points out that the true structure of the nematic mesophase is without doubt more continuous than indicated by swarm theory.

Brown et al. (52) in their recent review suggest that continuum theory is well suited to the treatment of anisotropic liquids. They point out that the real objection to the swarm theory is not the fact that it is in some way opposed to the continuum theory. It is simply that swarms as defined originally do not exist. This implies that a compromise between the swarm theory and distortion hypothesis may in fact be nearer to the truth and it is interesting to note that Furth and Sitte (53) as back as in 1937 sought to show that the two theories are not imcompatible. Luckhurst (54) applied both the swarm and distortion theories of the nematic mesophase to the study of magnetic resonance experiments and has shown that they lead to isomathematical conclusions.

The properties of nematic structure indicate that the molecules are parallel or nearly parallel to one another but are not in layers (fig.2). This phase is very similar to a true liquid state and has been compared with the cybotactic structure of liquids (55), but compared with the latter, the former has a low internal energy. Like true liquids the nematic liquids give only diffusion haloes with

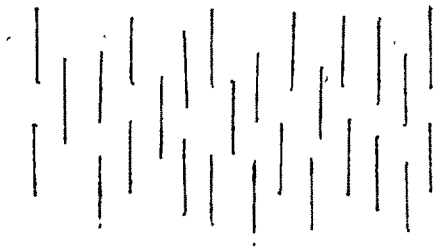


Fig. 2 : Molecular arrangement in the nematic phase.

X-rays confirming the absence of 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. The X-ray study of Bernal and Crowfoot (35) of some solid nematogenic compounds which form nematic phase on heating, reveals 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. The nematic mesophase owes its mobility to the facility with which the molecules can be drawn past one another while retaining a strong tendency to acquire a parallelism between the long dimensions of the molecules and the direction of drawing. Unlike the smectic mesoforms, the nematic mesoforms are oriented by low electric and magnetic fields indicating a greater freedom of movement of the

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

A notable difference between the smectic and nematic mesophases lies in the way in which the two mesophase types separate from the isotropic liquid. While the smectic phase appears as bâtonnets, the nematic mesophase separates as tiny, spherical droplets which coalesce to give a nematic threaded texture. The optical effect of the nematic threads has been studied by Zocher and Birstein (56). It seems that the threads are the lines of discontinuities in the structure, i.e. they correspond to the ellipses and hyperbolae in smectic phase but there being no stratification in the medium like the one in the smectic phase, no definite geometrical law can be applied. These discontinuities may be due to a line about which the whole medium is circulating. If we imagine circles having the thread as an axis passing through their centres, and with their planes normal to the thread, the molecules may then lie with their long axes tangential to these circles. The circles would then be equivalent to vortex rings in the circulating medium, and the molecules would be carried round the centre of the vortex, i.e. the threads, with their long axes in the direction of circulating flow. In such a system, the thread would again be equivalent to the centre of spherulite, and would be visible. It is possible that both interpretations are correct, and that the threads mark both kinds of optical

discontinuity.

Zocher and Ungar (57) investigated the sections of nematic structure in converging polarized light and at thickness upto 1 mm and arrived at the conclusion that the parallel arrangement of the molecules extends from one glass surface to the other, right through the preparation in these thin sections.

Maier and Saupe (58) have given a simple molecular theory of the nematic liquid crystalline state by which it is shown that the nematic-isotropic transition temperature may be determined by calculation of the free enthalpies of the phases involved at the transition. Later, they derived a formula for the average inner field acting on a single molecule in a nematic molecular order. More recently, they have improved their theory by the introduction of close range order parameters and have calculated constituents of thermodynamic energy function corresponding to the nematic molecular order.

2c. Cholesteric Mesophase :

The cholesteric mesophase is found in the melts of several compounds mainly those containing the sterol type skeleton. In many ways the properties of the cholesteric phase resemble those of the smectic and nematic phases. Friedel, noted a somewhat closer resemblance between the cholesteric phase and the nematic phase. No substance was found exhibiting both the 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. Friedel emphasized his arguments by his observation that mixtures of dextro and laevo rotatory cholesteric substances give nematic mesophase, and that the addition of certain optically active compounds to the nematic mesophase of p-azoxyanisole gives rise to cholesteric properties. Chatelain (51) observed that the amount of light diffused by the nematic mesophase is similar to that diffused by the cholesteric mesophase. Gray (59) on the basis of his study on the mesomorphic behaviour of the fatty esters of cholesterol had expressed the opinion that the cholesteric phase may be regarded as an individual phase type, and that it is more similar to the smectic than to the nematic phase. It can be seen from the above discussion that opinions were divided whether cholesteric mesophase is a nematic or a smectic type.

It would be interesting to note that, though, first mesomorphic compound observed was a cholesteric one with characteristic properties, practically this mesophase remained almost neglected for forty years or so. Recent technical development in non-destructive testing where cholesteric materials are being used attracted the attention of physicists and chemists to study the properties of cholesteric mesophase in detail and their work within last few years has proved beyond doubt that cholesteric mesophase is nematic in type. Cholesteric compounds have fluidity like nematic mesophase. They can be oriented by electric and magnetic fields like the

nematic mesophase (60). When two cholesteric compounds with opposite optical rotatory power are mixed in different proportions a stage comes when that mixture exhibits a nematic mesophase (61). As early as in 1914 Vorländer and Janecke (62) reported that the racemic amyl p-anisalamino-α-methyl cinnamate exhibits nematic mesophase, whereas, both active forms of the ester exhibit all the properties of cholesteric mesophase. Recently similar experiments on a number of racemic compounds exhibiting the mesophase have been carried out by Billard and co-workers (63) and Gray (64). They prepared alkoxybiphenyl carboxylic acids having asymmetric centre in the ether chain and p-(arylideneamino)-cinnamic acids esterified with an alcohol containing an asymmetric centre. In all these compounds the nematic phases were observed in the cases of racemic derivatives and cholesteric phases in the cases of enantiomers.

Billard et. al. (63) also studied the mixtures of two enantiomers and showed that when both are exactly in 50 percent composition the nematic phase is exhibited. Friedel (7) in his paper has devoted fifty pages in explaining the similarity of the cholesteric and nematic mesophases. All this clearly indicates that the cholesteric mesophase is nematic in type and Gray (64) has recently concluded as under :

" The great weight of evidence now suggests strongly that cholesteric and nematic liquid crystals are very closely related. Until this evidence accumulated in the last three years, I preferred to consider the cholesteric

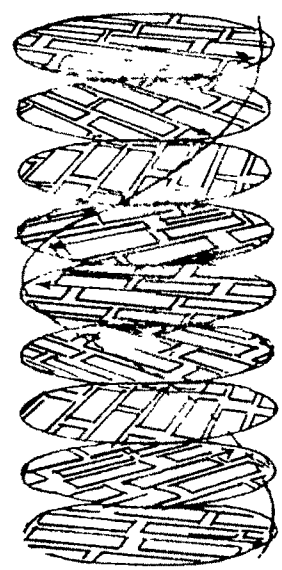
liquid crystal as a third distinct type of liquid crystal, and indeed, some of the properties of cholesteric liquid crystals are still difficult to rationalize in terms of a nematic system, e.g. the apparent focal-conic texture of the cholesteric state. However, it now seems preferable to regard the cholesteric state as closely akin to the nematic state, but exhibiting additional and unique optical properties stemming from the optical asymmetry of the molecules. The general conclusions reached by Friedel about the cholesteric state seem therefore to be vindicated by these results obtained some 45 years later."

Cholesteric mesophase has certain characteristic properties of its own which are markedly different from the smectic and nematic mesophases. It is optically active and shows extremely high rotatory power of the Grandjean plane texture. When illuminated with white light the most stri king property of the cholesteric structure is that of scattering the light to give vivid colours. The colour of the scattered light at a particular angle to the surface of the film is dependent on (a) the substance, (b) the temperature and (c) the angle of the incident beam. The optical properties described above depend on a delicately balanced molecular arrangement. A change in shape or dipole moment or any other disturbance which interferes with the weak forces between the molecules, results in a dramatic change, reflexion, transmission, birefringence, optical rotation and colour - all undergo marked

transformations.

Friedel (7), Stumpf (65), Mathieu (66) and Gray (67) have tried to explain the optical rotatory power of the plane cholesteric texture. They could explain some of the behaviour of the cholesteric mesophase but the arrangement of the molecules in the cholesteric mesophase was not clear. Oseen (68) has given mathematical equations to explain the high optical rotatory power and transmission of different colours of plane texture. Recently Fergason (69) has explained optical properties of cholesteric mesophase on the basis of the model suggested by Oseen. It explains almost all the properties of the plane texture.

High optical activity of cholesteric mesophase is indicative of a helical arrangement of the molecules in the mesophase, the observed periodicity being equal to half the pitch. De Vries (70) developed a theory, based on such a helical arrangement, to explain the optical properties of the cholesteryl compounds and derived an equation relating the optical rotation to the pitch of the helix. He could not test the theory for lack of accurate data; however, he says qualitatively the agreement is complete. After that, the theory is quantitatively verified by Chandrasekhar et al. (71). Cano and Chatelain (72), and Chatelain et al. (73,74) have also verified the theory and found in good agreement. Robinson (75) used this equation to verify the properties of polypeptide solutions which were giving cholesteric properties. With the help of this equation he developed some new compounds which exhibited all the



PROBABLE ORGANIZATION OF THE CHOLESTERIC PHASE

FIG. 3

properties of cholesteric mesophase. Daniel Berg (76) is of the opinion that in cholesteric liquid crystals the molecules are aligned to each other within the planes but with respect to the next plane there is a slight twist so, as one goes up the axis from one cholesteric plane to the next, the cholesteric molecules are spiral. The repeat distance is of the order of 1000 A° (Fig.3). This repeat distance gives the cholesteric phase its peculiar optical properties of scattering the light and appearing highly iridescent. Recently Goossens (77) has put forth molecular theory of the cholesteric phase. The molecular properties of optically active molecules are used to extend the molecular statistical theory of the nematic phase in order to explain the helical structure of the cholesteric phase.

When the isotropic liquid of a cholesteric compound is cooled to give the cholesteric mesophase, usually the texture adopted is focal-conic. Even a little disturbance brings about a change to plane texture. Sometimes on cooling, instead of focal-conic texture a homeotropic texture is observed. The cholesteric mesophase is always optically negative and uniaxial.

3. Lyotropic Mesomorphism :

Liquid crystallinity formed by solvation is referred to as lyotropic mesomorphism. In the case of thermotropic systems the transition from the solid crystal to the liquid crystal and from liquid crystal to istropic liquid is stepwise during gradual heating. In the same manner

large number of compounds having amphiphilic molecules when treated with a gradual addition of the solvent do not directly form a clear isotropic solution. Instead, they first give rise to a system with properties of the liquid crystalline structures, and then with excess of the solvent pass to a true solution state. The process is reversible. Evaporation of the solution first gives rise to a liquid crystalline state followed by a solid mass. Similarly if a hot saturated solution of a compound capable of forming a lyotropic liquid crystal is cooled, liquid crystals often develop, indicating that lyotropic systems are also thermotropic and it is the cooperative action of the temperature and of the solvent which enables them to pass successively from the solid crystalline state to the liquid crystalline state and to the isotropic liquid or the dissolved state.

In his recent review, Winsor (78) has defined amphiphilic compounds as follows : Amphiphilic compounds are characterised by possessing in the same molecule two groups which differ greatly in their solubility relationships. These are (1) a hydrophilic group which tends to be water soluble and hydrocarbon insoluble and (2) a lipophilic group which tends to be hydrocarbon soluble and water insoluble. Typical hydrophilic groups are -OH, $-O(CH_2CH_2O)_nH$, -COONa, $-SO_3K$, $-NMe_3Br$; typical lipophilic groups are

$-C_nH_{2n+1}$, $-C_{17}H_{33}$ and $C_8H_{17}O_2C-\underset{|}{CH}-CH_2COOC_8H_{17}$.

According to the relative magnitudes of the hydrophilic and lipophilic functions of the two groups, amphiphilic compounds may range from predominantly hydrophilic, water soluble and hydrocarbon insoluble (e.g. $C_nH_{2n+1}COOK$, where n = 1 to 3), to predominantly lipophilic, hydrocarbon soluble and water insoluble (e.g. $C_nH_{2n+1}OH$ where $n > 12$). The most striking amphiphilic properties of micelle formation, liquid crystal solution formation and solubilization etc. are shown most markedly by amphiphilic compounds, or mixtures of amphiphilic compounds, in which both the hydrophilic and lipophilic functions are strong and not too unequally matched (e.g. $C_nH_{2n+1}COONa$ where n = 8-20).

The first lyotropic substance, ammonium oleate was reported by Lehmann (79). Lyotropic substances are always strongly birefringent, although their physical nature may vary from a turbid, free flowing fluid to a waxy substance. 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 $\longrightarrow$ Liquid.... Excess $\longrightarrow$ Solution or
Ammonium (solvent) Crystal Water Colloidal
Oleate $\longleftarrow$ Dehydration..State $\longleftarrow$ 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 controlled action of water (80-82). Alcoholic solutions of

these compounds do not generally show anisotropic behaviour, so a high degree of hydration appears to be a necessary prerequisite for the occurrence of many lyotropic mesophases. McBain (83) 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 (84), glycerol, isopropanol and diethylene glycol (85) 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 (86, 87). A close relationship obviously existing between these liquid crystalline states and the truly colloidal states, has been discussed by Ostwald (88). Recently, Palit, Moghe and Biswas (89) have during their study of solubilization of water by cationic detergent, come across liquid crystalline phases, particularly in systems which are close to the solubilization maximum.

Zocher and Coper (90) have shown that methylene blue, neutral red and also other dyes gave orientation on rubbed surfaces. Dreyer (91) has discussed the behaviour of films from the aqueous solutions of amaranth yellow S and naphthol yellow S, as well as the dyes of the other classes which exhibit a mesomorphic phase. Sheppard's (92) work 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; however, these are not as simple as in the case of thermotropic mesophases. Number of other mesophases are also reported in lyotropic systems which do not fit in nematic and smectic structures. The change from one lyotropic phase to another phase can be obtained by the alteration of lipophilic-hydrophilic balance and the solvent. For instance (93), cholesterol and sodium lauryl sulphate in 1:1 mixture gave myelin figures, whereas, on increasing the sodium lauryl sulphate to 1:2 or 1:3, bâtonnets of Friedel are formed.

Robinson (94) has reported the interesting observation that viscous solutions of poly-γ-benzyl-L-glutamate are anisotropic in certain organic solvents and show number of characteristic properties similar to those observed in the thermotropic cholesteric mesophase. It has high optical rotation and exhibits iridescent colours. Recently (75) he reports that like thermotropic cholesteric mesophase lyotropic mesophases are obtained having opposite twist of helix in different solvents (e.g. dioxane and methylene chloride). When the mixture of these solvents is taken to dissolve poly-γ-benzyl-L-glutamate, the definite proportion of the solvent mixture

gives a nematic mesophase, just as two cholesteric compounds with opposite rotatory power are mixed a stage comes when they exhibit a nematic mesophase.

Small et al. (95,96) have studied lyotropic mesomorphism of ternary and quaternary systems of bile salts, lecithin, cholesterol and water. These studies have thrown some light on biological processes.

4. Chemical Constitution and Mesomorphic State :

Vorländer from his study of a large number of organic compounds pointed out that close relationship exists between the symmetry of the molecule and its capacity to form liquid crystals. These compounds vary widely in chemical constitution. In general the molecules of mesomorphic compounds are elongated, rod or lath-shaped and possess middle and terminal polar groups.

The shape of these elongated rod-like molecules facilitates to set themselves parallel to one another leading to the closest possible packing in the crystalline or liquid crystalline state, the molecules being held together by local attachments due to the polar groups and unspecific Van der Waals attraction. On raising the temperature, the cohesions between the molecules previously holding them together in the crystal arrangement does not break down uniformly in all directions; there may be a lateral cohesion still operating which will tend to hold the molecules together in groups. The transition to the disordered arrangement found in true

liquid phase due to the collapse of three-dimensional order and geometrical arrangement of the molecules in the solid state, therefore, takes place in stages, i.e., the weaker linkages break first, leaving the molecules with some freedom of relative movement before they acquire sufficient thermal energy to overcome the tendency of parallel arrangement. Thus the medium acquires a flow movement and it is birefringent because of the preferred orientation of molecules.

However, it is frequently found that many long and narrow or lath-shaped molecules do not give rise to mesomorphism. The normal paraffins and the homologues of acetic acid though they possess geometrical requirements suitable for mesophase formation do not exhibit mesomorphism 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 the molecules after the crystal lattice has melted. Hence, in addition to the geometrical aspect of the molecules, the nature and the 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, as Vorländer has pointed out; hence the benzene derivatives with 1,4-(p,p') substitution would be the ideal model for a compound to exhibit mesomorphism. p-Azoxyanisole is a well-known example.

A compound comprised of molecules which are long, narrow and linear, with dipolar groups, should provide 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 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 and polarizability fail to exhibit mesomorphic properties.

Besides the presence of the polar groups, the structural alteration has a good deal of effect on the thermal stabilities of the mesomorphic compounds. The addition of a unit such as an aromatic ring to the molecule of a mesomorphic compound increases the thermal stability of the mesophase provided that it does not increase the breadth. For example, p-n-propoxybenzoic acid melts at 145°C to be a nematic melt which clears at 154°C. 4'-n-Propoxybiphenyl-4-carboxylic acid with one more benzene ring than the previous acid, melts at 260°C and

clears at 287°C. Here the increase of the benzene ring resulted not only in increased length of the mesophase, but the nematic thermal stability is also increased from 154°C to 287°C. In many cases compounds having more benzene rings are thermally stable even when they sublime or distil before they change to isotropic liquid, e.g. 4,4'-di(p-methoxybenzylideneamino) diphenyl, N,N'-di(p-methoxybenzylidene)-p-phenylene diamine etc.

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

Bernal and Crowfoot (35) have generalized the conditions for smectic and nematic liquid crystals. Smectic substances should have either one active group as in the case of ammonium oleate or a fairly strongly active group at each end as in para- azoxy esters of benzoic and cinnamic acids. This will induce layer formation which is often found in solid crystals. Such crystals are known as smectogenic. In the case of nematic substances, the molecules contain weakly active groups at the centre as well as at the ends as in para- azoxy ethers. This may lead to imbricated crystal structure as found in p-azoxyanisole and p-azoxyphenetole which give nematic mesophase only. Such crystals are known as nematogenic.

p-n-Alkoxybenzoic acids are the simplest molecules

known to form liquid crystals (97-101). As such the length of the simple acid molecule is not long enough to exhibit mesomorphism but the length of the acid molecule is increased by the hydrogen bond formation and the mesomorphism arises from the association of the acids forming a dimer through carboxylic groups. Thus, p-n-propoxybenzoic acid which has the simplest molecular structure to form liquid crystals, acquires a structure which is linear and similar in shape and size to the typical nematic substance, p-azoxyanisole.

p-Methoxycinnamic acid may at the first sight be expected to be smectic but in the melt the molecules are associated in pairs by the carboxylic groups forming a dimer molecule of the type giving rise to a nematic mesophase rather than smectic (102). The proof in support of the effect of dimerisation and hydrogen bonding is afforded by the fact that the corresponding methyl esters of p-n-propoxybenzoic acid and p-methoxy-cinnamic acid are non-mesomorphic, eventhough they have a low melting point and possess a dipolar ester group.

As has been pointed out by Vorländer (103), 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. The introduction of certain groups which destroy the symmetry of the molecule either reduces the thermal stability of the mesophase or

results in complete extinction of the mesophase. The 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 -CO- , -CS- , etc. groups. In the same way, the introduction of a non-polar alkyl group in place of a polar alkoxy group either destroys the mesomorphic properties or reduces mesomorphic thermal stabilities.

Effect of molecular breadth on mesomorphism is interesting. Vorländer (103) was the first to report the existence of mesomorphism in certain naphthalene derivatives which are considerably broader than benzene derivatives. Later Gray and Jones (101) found that 6-n-alkoxy-2-naphthoic acids are mesomorphic, whereas, 4-n-alkoxy-1-naphthoic acids are non-mesomorphic. Gray (104) reports that 2-p-n-alkoxybenzylideneamino phenanthrenes are mesomorphic. Recently Dave et al. (105). have reported that Schiff's base compounds comprising naphthalene nuclei are mesomorphic but thermally less stable than the corresponding benzylidene Schiff's base compounds. According to Gray (67) the mesomorphic compound should have a high length to breadth ratio and the molecule should contain groups which are permanently dipolar or readily polarizable. In the naphthalene compounds if the length can be increased to balance the length to breadth ratio, molecules would exhibit

mesomorphism as is evinced by above examples.

Recently Dewar and Goldberg (106) have shown that the replacement of p-phenylene groups in the compound exhibiting mesomorphism by a saturated ring like cyclohexane or bicyclo[2.2.2.] octane either reduces the thermal stability or destroys the mesomorphism, indicating that linearity and polarizability are essential for a compound to exhibit mesomorphism. Gray (67) has pointed out that a substituent in a mesomorphic compound will affect the mesophase in the following ways :

(a) by broadening the molecule. This will tend to decrease the thermal stabilities of the smectic and nematic mesophases, as a result of the increased lateral separation and the decreased lateral attractions;

(b) by increasing the polarity and polarizability of the molecule. This will tend to increase the smectic and nematic thermal stabilities because of the resulting increase in the lateral attractions.

Of these two opposing effects, the first always predominates, unless the substituent does not exert its full breadth increasing effect. Only when a substituent occupies some pocket in the side of a molecule, has substitution been observed to increase mesomorphic thermal stability; the 5-halogen-6-n-alkoxy-2-naphthoic acids (101) and 4-p-n-alkoxybenzylideneamino-3'-fluoro-biphenyls provide examples of this kind. In the normal case as observed in the p-n-alkoxybenzoic acids,

substitution in the 3- position by halogens either reduces the thermal stability or eliminates mesomorphism.

Mesomorphism in Homologous Series :

It has been observed earlier that there is a close relationship between mesomorphism and molecular constitution of organic compounds. With a view to correlate the effect of the structural modifications on mesomorphism, the researchers in this field centred their attention around the study of mesomorphic properties of different series of organic compounds. Gray and co-workers have prepared about 70 homologous series exhibiting mesomorphism. Gray has summarized the results of these series in his book (67). It has been observed that when the alkyl chains are short, the systems are either non-mesomorphic or nematic, as the chain length increases, smectic properties begin to appear and as the smectic phase increases, the nematic phase decreases with each successive chain increment, till in the higher homologues like hexadecyl and octadecyl ethers only smectic phases are found. Generally, when the mesomorphic transition temperatures are plotted against the number of carbon atoms in the alkyl chain, the transition points lie on two smooth curves, the upper curve corresponding 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 in the alkyl chain. In a homologous series exhibiting smectic and nematic mesophases, smectic-nematic transition points generally lie on a smooth rising curve which merges with the falling

nematic-isotropic curve at dodecyl or hexadecyl ether. However, in some of the homologous series (107,108a,b) smectic-nematic transition point curve does not merge with the falling nematic-isotropic curve and the last members of the series exhibit nematic mesophase alongwith the smectic mesophase. In the case of the cholesteryl fatty acid ester series (59), the smectic-cholesteric transition point curve does not merge with the falling cholesteric-isotropic curve and the cholesteric mesophase persists upto the last member of the series.

5. Physical Properties :

Compared to the optical and chemical properties much less work had been done on the study of physical properties of liquid crystalline substances; however, in recent years, considerable work is being done on physical properties and applications of liquid crystals.

5a. X-ray Studies of the Mesomorphic State :

The first attempt to study the liquid crystals by X-ray structural analysis followed immediately after the discovery of X-ray diffraction. Van der Lingen (109) obtained Laue diffraction patterns of p-azoxyanisole and p-azoxyphenetole in the liquid crystalline state. Hückel (110) and de Broglie and Friedel (111) studied X-ray diffraction patterns of the liquid crystals. Hückel (110), Katz (112) and Kast (113) concluded that the X-ray diffraction patterns of the nematic structure are similar to those of the liquid. de Broglie and Friedel showed that

the molecules in the smectic structure are in equidistant parallel strata. However, Glamann, Herrmann and Krumacher (114) reported a small difference in the X-ray patterns in the nematic and the liquid structure. Herrmann (115) made a useful contribution to the X-ray study of mesophases; his findings were that the X-ray diffraction patterns for the isotropic liquids and the nematic mesophases were diffuse halos which could not be distinguished. For the smectic mesophases two types of diffraction pattern were observed, one showing a halo and a narrow inner ring, and the other a sharp ring and an inner ring. Herrmann attributes the new type of the interference giving the sharp inner and outer rings to a hexagonal cylindrical packing of the molecule within the smectic phases. This is also a possible explanation of polymesomorphic behaviour of smectic phases.

Kast (116) in his X-ray studies of the nematic phase observed that the diffraction halos of the nematic phase change and become crescent shaped perpendicular to either a magnetic field or an electric field. Herrmann, Krumacher and May (117) concluded that in anisaldazine and p-azoxyanisole, the long molecular axes are oriented perpendicular to the applied field and in methyl p-(4-ethoxy-benzylideneamino) cinnamate parallel to the field. Stewart (118) carried out an X-ray study on p-azoxyanisole in the presence and the absence of the magnetic field. He has compared the X-ray patterns of the nematic and the isotropic liquids and indicated that the relatively large

agglomerates of the molecules (swarms) in the nematic mesophase do not persist in the isotropic liquid, but that smaller cybotactic groups of the molecules do exist in the isotropic liquid. Shaw and Brown (119) have studied X-ray diffraction patterns of the mesophases of azines.

Bernal and Crowfoot (35) carried out X-ray analysis of the nematogenic compounds and found that in the case of p-azoxyanisole the molecules do not lie in the layers but they are parallel to each other in an imbricated fashion. They concluded that an imbricated arrangement of the parallel molecules will occur in the nematic mesophase itself. Recently Bryan (120) has done X-ray work on p-n-alkoxybenzoic acids in solid states.

Nordsieck, Ferguson and Rosevear (121) have used X-ray methods to study the transformations of sodium palmitate. The subwaxy, waxy and superwaxy phases exhibit two diffuse short spacing rings, while the subneat and neat phases exhibit one diffuse short spacing ring. Falqueirettes (122) using modern apparatus, obtained new interesting data for p-azoxyanisole. An oriented liquid crystalline film of p-azoxyanisole was obtained by the Chatelain method (123) with the simultaneous action of a magnetic field. The patterns had a pair of equatorial diffuse arcs and three pairs of weak meridional arcs.

Recently Chistyakov and Vainshtein (124) studied the structure of α-benzeneazo-(anisal-α-naphthylamine) in the vitrified liquid crystalline state. Chistyakov (125,126),

studied the structure of 4,4'-nonyloxybenzaltoluidine and cholesteryl caprate in the liquid crystal state by using a controlled temperature camera for X-ray investigation. The mode of orientation adopted by the molecules of 4,4'-nonyloxybenzaltoluidine and cholesteryl caprate in the liquid crystal state has been determined. He also studied the structure of N-(p-dimethylaminobenzylidene)-4(p-carbethoxy-phenylazo)-1-naphthylamine and a mixture of cholesteryl acetate and benzoate with the help of X-ray diffraction in the supercooled state. Gusakova and Chistyakov (127) studied the structural properties of liquid crystalline mixtures of isobutyl and isoamyl derivatives of 1-[(p-isoalkoxybenzylidene) amino] naphthalene-4-azobenzenes. The structure changes related to the variation of composition as obtained by X-ray analysis and distribution function were detected. Delord and Falqueirettes (128) studied the X-ray scattering of nematic liquid single crystal of p-azoxyanisole and calculated the linear distribution of atoms for the nematic phase.

Gulrich and Brown (129) carried out X-ray diffraction study of N-(p-methoxybenzylidene) p-cyanoaniline in nematic liquid crystalline and isotropic liquid states. They compared experimental intensities obtained from X-ray pattern in the liquid crystalline state with calculated intensities of a number of models of molecular packings.

De Vries (130) obtained evidence for the existence of more than one type of nematic phases with the help of X-ray diffraction studies, supported by polarizing

microscopy and the type of the preceding smectic phase. De Vries (131) in his X-ray photographic studies of liquid crystals has determined the apparent molecular length and thickness in three phases of ethyl p-[(p-ethoxybenzylidene) amino] benzoate. A general theory is developed for the relation between the molecular length and the position of a diffraction maxima, with the help of which are detected the molecular parameters for the three phases of ethyl p-[(p-ethoxybenzylidene)amino] bezoate. He reports that the nematic phase appears to be a classical nematic phase. There is no significant ordering of the molecules apart from near parallelism of the long axis of neighbouring molecules.

Sackmann and co-workers (132a,b), have done some interesting work on classifying smectic textures. They found that smectic A, smectic B, and smectic C phases have certain intensity versus angle diffraction profiles which are similar. De Vries (130) and Chistyakov et al. (133) have shown by X-ray studies that smectic C has a tilted arrangement of molecules within a stratum. Pohl and Steinstraesser (134) have indicated by X-ray diffraction study and NMR measurements that in the nematic phase of the binary mixtures of p,p'-disubstituted benzylidene anilines with each other or with structurally related compounds there exists nematic secondary structure. This consists of freely intermobile molecular strands of different lengths in which three each molecular chains twisted towards each other by 180° have combined, each showing head-to-tail sequence.

5b. Ultraviolet and Infra-Red Spectroscopic Studies :

Ultraviolet and infra-red spectroscopic studies of mesophases have not so far yielded any vital information about the molecular orientation and the degree of molecular aggregation in the mesophases. Rawlins and Taylor (135) reported that the spectra of the mesophases and the isotropic liquids are more or less identical. Freymann and Servant (136) studied the Raman spectra of solid, nematic and isotropic phases of p-azoxyanisole.

More recently Maier and Saupe (137) examined ultraviolet absorption characteristics of the nematic and the isotropic phases of p-azoxyanisole and concluded that ultraviolet spectroscopy offers little hope of giving any information about the nature of the molecular interactions in the nematic melt. Maier and Englert (138) have also published the results of their very detailed infra-red study of 4,4'-disubstituted azo and azoxy-benzenes and suggested that the work may eventually make it possible to use infra-red spectroscopy to compare the molecular orientation of the crystalline and the mesomorphic states of the compounds.

L'vova and Suschinskii (139) studied the infra-red spectra of p-methoxyphenyl azoxyphenetole, 4,4'-azoxyanisole and cholesteryl propionate as solids, liquid crystals and isotropic liquids at 3-15μ . They report that the transition of the solids to liquid crystals were accompanied by sharp changes of the spectra, whereas the transitions from liquid crystals to isotropic liquids did not cause qualitative changes of spectra. The results were explained by the

action of several factors, e.g. degree of orientation of the molecules and situation of the centres of gravity. Ceasar, Levenson and Gray (140) reported the infra-red spectra of p-(p'-ethoxybenzoxy) phenyl butyl carbonate. They report that polarizations of electronic absorption bands can be obtained by orienting the molecules of interest in a nematic liquid crystal host. Khodzhaeva and co-workers (141-143) studied the infra-red absorption spectra of the liquid crystalline state of p-n-alkoxybenzoic acids. The curve plotting the relation between infra-red dichroism of the absorption bands and temperature contains jumps close to the transition points isotropic-liquid crystal phase, nematic-smectic phase, liquid crystal-solid crystal phase, which indicates the jump-like change in the position of the molecules close to these points. Baessler and Labes (144) determined the pitch of cholesteric liquid crystal by infra-red transmission measurement.

Neff, Gulrich and Brown (145) have studied the orientation in a d.c. electric field by infra-red dichroic methods. Koller, Lorenzen and Schwab (146) studied the Raman spectrum of 4-n-butoxybenzoic acid in a longitudinal and transverse magnetic field. They find that certain vibrations become active in a magnetic field and that the activity depends on the orientation of the vibrational polarizability tensor with respect to the electric vector of the scattered light. Zhanova et al. (147) studied the Raman spectra of p-azoxyanisole, anisaldazine and p,p'-azoxybenzoic acid ethyl ester at phase transitions

solid crystal--liquid crystal--isotropic liquid. The shift of frequences and changes of relative intensities were observed for several lines. Bulkin and Prochoska (148) studied the Raman spectra of p,p'-azoxyanisole in the crystal, nematic and isotropic phases.

5c. Magnetic Resonance :

(I) Proton Magnetic Resonance Studies :

Spence, Moses and Jain (149) observed that the proton resonance line changes markedly in character on passing from the isotropic liquid which gives a single narrow line to the nematic mesophase of p-azoxyanisole; the amplitude of the signal decreases and the single line broadens greatly and splits into three peaks. Spence et al. (150-152) correctly interpreted this spectrum in terms of order resulting from parallel orientation. A detailed analysis of this spectrum came later when Lippmann (153), Lippmann and Weber (154) and Weber (155,156) used a method of moments to show that the shape of the spectrum in liquid crystal phase depended upon the degree of molecular order and the configuration of the molecule which comprised this state of matter. Magnetic resonance studies of states in nematic liquid crystals began with Saupe and Englert (157) who first recognized that it should be possible to observe the highly resolved spectrum of a simple solute molecule on top of the broad, unresolved spectrum from the liquid crystal solvent. They found that ~~the~~ a wealth of information could be obtained about the ordered solute molecule including relative bond lengths

and angles to a precision unequaled by other techniques, signs of spin-spin coupling constants and anisotropic chemical shifts. In addition, their research work opened a new avenue in which to probe the liquid crystalline state. A number of workers have become interested in this aspect of liquid crystals. A number of review papers on N.M.R. of ordered solutes have appeared in the literature (158-161).

The success of N.M.R. in liquid crystalline systems is due to the rapid translational diffusion of the molecules in many of these phases. As a result, the nuclear magnetic dipole interactions between spins belonging to different molecules average to zero. The spectrum then depends only upon the interacting spins within the molecule. The fact that a broad N.M.R. spectrum exists at all is a consequence of the partial molecular order exhibited by these compounds. The molecules on the average are parallel to some preferred direction. As a result of the anisotropy of the diamagnetic susceptibility, the preferred direction is established by the direction of an external magnetic field and made uniform over the whole sample.

A complication arises in determining degree of order of the liquid crystal molecules, as they are large and contain large number of proton spins. As a consequence under the high resolution a complex spectrum of lines is observed. To measure the degree of order for the liquid crystal molecule, it is, therefore, necessary to use a small liquid crystal molecule which shows simple enough spectrum to be evaluated. Rowell *et al.* (162) selectively deuterated *p*-azoxyanisole to

simplify the spectrum. In the nematic phase, p-azoxyanisole shows a spectrum of three unresolved lines. When the methyl groups were deuterated, they obtained two completely resolved lines, which they assigned to the interaction between the ortho protons in the phenyl ring. For cases where there is no resolved structure on a wide line spectrum, the method of moments has been used. The protons do not provide a good means for the determination of the degree of order in a Schiff's base because of uncertainities in the configuration of the molecule. The fluorine resonance could then be used to obtain a value of degree of order. Fergason et al. (163) studied the molecular configuration by using fluorine resonance. In order to determine the relative significance of permanent electrical dipole moments and dispersion type forces, Saupe (164) and later, Nehring and Saupe (165) performed some experiments and they observed little variation indicating dipole-dipole forces are of minor importance. Nehring and Saupe have studied the orientation of several selectively fluorinated benzenes in a common solvent. They observed differences in the orientation of different fluorobenzenes. Regarding dispersion type forces, these differences could be attributed to localized contributions of the fluorine substituted bonds.

Recently, several workers have been interested in orientational studies. One of the most interesting methods for orientation is the use of smectic materials. Yannoni (166) has succeeded in ordering a solute molecule in a smectic A

texture. Fluorine spectra were recorded of 20 mole percent solution of 1,1,1,-trifluorotrichloroethane in the smectic phase of 4-(2-n-propoxyethoxybenzylideneamino) acetophenone. From the splitting, the degree of order for the smectic phase was determined. Carr and co-workers (167a,b) have extensively studied the effect of a.c.electric field on nematic liquid crystals. Recently Diehl et al. (168) reported uniform alignment of the nematic phase with d.c.electric fields. They Studied the high resolution spectra of cis-1,2-dichloroethylene dissolved in n-propyl (4-methoxybenzylidene)-4-amino-α-methyl cinnamate at 27°C and aligned with an external d.c.electric field. In their sample they report small conductance effects.

Sackmann et al. (61,160,169,170) have performed some interesting experiments with the cholesteric phase. They have shown that it is possible to observe the spectrum of a solute molecule when dissolved in a cholesteric liquid crystal that orients with its pitch axis parallel to the external magnetic field. This appears to be particularly true for compensated mixtures of cholesteryl derivatives of opposing helicities. They were also able to show that in the case of compensated mixtures, that is, no macroscopic helicity, a solute molecule may still experience a local helical environment since the solute spectra in the mixed cholesteric solvents differs from that seen in nematic solvents. When the pitch axis is aligned perpendicular to the field, they were able to induce a cholesteric-nematic

transition with the applied magnetic field. Lyotropic liquid crystal phases have also been studied by N.M.R. (171-175).

(II) Electron Paramagnetic Resonance :

A technique which has been gaining increasing interest in liquid crystal studies is that of electron paramagnetic resonance (epr). The compounds which show liquid crystallinity are not, in general, paramagnetic. Therefore, this technique is limited to solute studies where the solute molecule contains an unpaired electron spin. The concentration of the solute required for epr study is considerably less than that needed for nmr work. Mole fractions less than 10^{-3} give observable spectra, the ultimate reason for the increased sensitivity being the large value of the Bohr magneton. This sensitivity is advantageous in probing liquid crystals since many of the properties of this state of matter are strongly dependent on dissolved foreign substances. EPR studies of the nematic phase typically show that required concentrations of the paramagnetic probe do not significantly alter such properties as the nematic-isotropic phase transition temperature or the width of the transition. The first reported work of epr in liquid crystals was that of Carrington and Luckhurst (176), who observed diphenyl-picrylhydrazly (DPPH) and the tetracyanoethylene anion ($TCNE^-$) dissolved in p-azoxyanisole. At temperatures above the nematic-isotropic transition they observed five and nine line spectra respectively, which were characteristic of that seen in any nonviscous isotropic liquid crystal. Upon

lowering the temperature into the nematic phase, the splittings between the lines were observed to decrease abruptly at the transition, then continue to decrease continuously as the temperature was further lowered through the nematic phase. This observation was predicted by Carrington and Luckhurst and correctly interpreted in terms of the partial alignment of the solute molecules induced by host nematic. The Vanadyl acetyl acetonate (VAAC) contains VO^{++} radical and has been the most popular probe in recent investigations (177-183). Fryberg and Gelerinter (177) have studied VAAC in a long temperature range nematic, N,N'-(di-n-octyloxybenzylidene)-2-chloro-1,4-phenylenediamine, having a temperature range from 179°C to a supercooled temperature near 40°C. The spectra above the nematic range are typical of that seen in isotropic liquids. In the nematic phase just below the clearing point the spectrum is characteristic of moderate order, whereas just above the solidification point the spectrum is characteristic of apparent high order.

Luckhurst and Chen (181) have studied the effect of solute concentration on the order of the nematic phase. They measured the order with a paramagnetic solute of low concentration, then introduced other solutes with varying concentration. They report that the presence of the solute does not seriously disturb the order of the nematic phase. The epr experiments mentioned so far have all used a vanadyl complex for the unpaired spin. Other paramagnetic probes (184-188) which have been used include the tetracyanoethylene

anion (176), Coppinger's radical, perinaphthenyl, bis(2,2-6,6-tetramethylpiperidyl oxide-4-yl)glutamate and bis(2,2,6,6-tetramethylpiperidyl oxide-4-yl) terephthalate. Sackmann and Krebs (189) have reported electron spin resonance spectra of the chargetransfer complexes oriented in the nematic liquid crystalline phase obtained by the 1.85:1 by weight mixture of cholesteryl chloride and cholesteryl laurate.

(III) Mössbauer Effects :

The Mössbauer effect is studied in the smectic liquid crystal state for the first time by Uhrich et al. (190). They observed the quadrupole split ^{57}Fe spectrum of 1,1'-diacetylferrocene dissolved in 4,4'-di-n-heptyloxy-azoxybenzene in the smectic C texture. In the smectic C phase the molecules are bound within planes with the spacing between the planes being less than the length of the molecule; the molecules are tilted in the layers. The motion of the molecules, on the other hand, is more fluid-like within the planes. This property is characterized by a rather large anisotropy in the viscosity. Mössbauer spectra for 1,1'-diacetylferrocene ordered by the smectic phase of 4,4'-di-n-heptyloxyazoxybenzene is recorded and the splittings between the lines are determined by the value of the quadrupole coupling constant. The sum of the areas under the peaks is proportional to the recoil-free fraction. This quantity was observed to decrease sharply to a non-zero value as the sample was heated from the solid state into the smectic phase,

then remain relatively constant as the temperature continued to rise through the smectic range. As the smectic-nematic transition was approached, it would then rapidly decrease to zero. The preferred direction of the solute molecules is uniform throughout the sample.

The implications of these experiments are that it is possible to study the structure of the smectic phase by measurements of recoil-free fraction and to make Mössbauer studies of ordered molecules which do not form single crystals in the solid state.

5d. Viscosity :

Schenk (191) determined the change of viscosity with temperature for cholesteryl benzoate and p-azoxyanisole by using the capillary flow method. He found that the viscosity of the mesophase fell off with increasing temperature, but at temperature close to the mesomorphic-isotropic transition, there was in each case a sudden break in the viscosity against temperature curve, the viscosity rising steeply to a maximum at the transition temperature and then falling again. Eichwold (192) and Becherer and Kast (193) have confirmed Schenk's observation. Vorländer (103) determined the viscosity changes in the smectic phase of ethyl p-azoxybenzoate over the temperature range 114°C to about 133°C and showed that the trends were unlike those obtained with cholesteric or nematic systems. There was a very sudden fall in the viscosity exactly at the smectic-isotropic transition, but no rise to a maximum preceded the transition. Many of the conventional

methods used for measuring viscosity in normal liquids cannot be used for liquid crystals because of surface orientation effects. Porter and Johnson (194) studied the viscosity of cholesteryl esters by using low-shear capillary viscometer and high-shear rotational concentric cylinder instrument. All cholesteryl esters studied show newtonian flow in their isotropic state and non-newtonian flow in their respective cholesteric phases. Shakspear and Ubbelohde (195) studied the viscosity of the nematic and isotropic phases of p-azoxyanisole and its mixtures with phenanthrene. Porter et al. (196) have studied the viscosity of cholesteryl myristate in cholesteric, smectic and isotropic phases by using cone-and-plate viscometer. Results are similar to the earlier ones. A prominent viscosity maximum is observed near the cholesteric-isotropic transition which depends on shear rate. Surface effects on viscosity have been clearly demonstrated by Fisher and Fredrickson (197). Recently Kartha and Padmini studied (198,199) the viscosity of cholesteryl esters by using cone-and-plate type viscometer. They report that there is noticeable abrupt change in the viscosity at the transition temperature in the case of cholesteryl acetate and cholesteryl benzoate, whereas very slight variation is observed in the case of cholesteryl formate. In the case of cholesteryl stearate a plot of η vs (1000/T) exhibits changes in slopes at the smectic-cholesteric and cholesteric-isotropic transitions.

5e. Surface Tension :

Ferguson and Kennedy (200) found that the surface tension of the mesophases increases with rising temperature. Naggiar (201) by his modified experimental technique showed that, for p-azoxyanisole the surface tension decreased from about 39.5 dyn./cm. at a temperature just above the melting point of about 116°C to just below 37.4 dyn./cm. at the nematic-isotropic transition at 133-134°C, thus contradicting Ferguson and Kennedy's observations. Schwartz and Moseley (202)confirmed Naggiar's results on p-azoxy-anisole by studying p-azoxyphenetole(nematic) and ethyl p-azoxybenzoate (smectic) using the ring method on a du Nõuy tensiometer. Churchill and Bailey (203) measured the surface tension of cholesteryl myristate as a function of continuous varying temperature. On cooling into the cholesteric phase, the surface tension exhibits a steep rise of upto 10 dyn./cm. and then falls back abruptly before the cholesteric-smectic transition. In the heating mode, the surface tension of the cholesteric phase was relatively independent of temperature. Neumann and Sell (204) measured the temperature dependence of the surface tension of fatty acid esters of cholesterol. The temperature coefficient of the surface tension often varies strongly during the conversions from one phase to another.

5f. Dielectric Constant :

Kast (205) has given a critical summary of the work done in this field on liquid crystals upto 1931. Kast's survey is concerned with substances having the nematic structure which

from their dielectric characters fall into two groups, i.e., symmetrical and asymmetrical molecules. Symmetrical molecules (e.g. anisaldazine) show a reduction in dielectric constant when a magnetic field is perpendicular to the plates of the condenser and a small increase when parallel. There is a small increase in the dielectric constant of unsymmetrical molecules (e.g. ethyl p-ethoxybenzylideneamino-α-methyl cinnamate) when they are acted on by a magnetic field parallel to the electrical field.

Bhide and Bhide (206) measured dielectric constant and absorption of p-azoxyanisole and cholesteryl benzoate by the resonance method at different frequencies. There were abrupt changes in the dielectric constant as the mesomorphic phase changed to the isotropic liquid, the changes being more pronounced at the higher frequencies. The values of the dielectric constant for rising and falling temperatures below the nematic-isotropic point were not coincident. Cholesteryl benzoate showed comparable effects on the change in dielectric constant but showed no absorption. Ornstein, Kast and Bouma (207) from the study of the dielectric constant measurements of benzophenone and p-azoxyanisole, calculated the degree of orientation of the swarms obtaining a maximum value of about 80 percent.

Marinin and Tsvektov (208) used suspension method to study the dielectric properties in motion through capillary. The dielectric properties were found to vary with the velocity of flow, the strength of the applied magnetic field

and the temperature. Maier (209) observed the change in dielectric constant in longitudinal and transverse magnetic field upto 5000 gauss. He found that a horizontal temperature gradient of 0.1°C per centimeter produces almost complete orientation of the swarms. Funt and Mason (210) found no effect of shear on the dielectric constant of the mesomorphic state by the use of a rotating cylindrical condenser.

Recently Maier, Barth and Wiehl (211) studied the dielectric constants of 4,4'-dipentoxy-azoxybenzene. Marinin and Tsvektov (212) evaluated the Kerr constant for p-azoxy-anisole, p-azoxyphenetole, dibenzalbenzidine, anisal-p-amino-azobenzene, ethyl p-azoxybenzoate, anisaldazine and p-acetoxy-benzalazine. Recently Gopalkrishna et al. (213) have studied the dielectric properties of eight cholesteryl derivatives at 1 MC/S. The transition temperature showed marked supercooling of the liquid crystal phase. Hysteresis in the values of dielectric constant is reported in the liquid crystal state. Phase transformations in the solid cholesteryl bromide are detected. Gopalkrishna et al. (214) also studied the influence of magnetic and electric fields on the dielectric constant of the liquid crystal phase of anisal p-aminoazobenzene.

Axmann (215) studied the dielectric constant in an oriented nematic liquid crystal and Baessler et al. (216) measured dielectric constant in a mixture of cholesteric liquid crystals.

5g. Magnetic Susceptibility :

Comparatively much less work has been done on the

magnetic properties of substances in the mesomorphic state, although there have been several studies of the phenomenon discovered by Mauguin (27) that the optic axis of substances in this state tends to set itself parallel to the lines of force of a magnetic field of sufficient intensity. Foex (217) found that the average susceptibility of powdered p-azoxyanisole is -0.565×10^{-6} ; at the nematic transition temperature (116°C) the susceptibility falls rapidly to -0.457×10^{-6}. As the temperature rises, the diamagnetism also increases slowly until above 133°C when the substance becomes an isotropic liquid for which $x = -0.545 \times 10^{-6}$. Now, if cooling is started, the reverse change occurs except that the nematic phase may persist considerably below 116°C. p-Azoxyphenetole and anisaldazine also show similar behaviour. 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. Substances such as ethyl p-azoxybenzoate which occur in the smectic phase show in general only a small and irregualr increase of diamagnetism on passing from solid to liquid. If, however, a field is present during cooling to the smectic phase, orientation sets in with a strong decrease of diamagnetism. Some further studies of magnetic anisotropy in liquid crystals have been reported by Tsvektov and Sosnovskii (218).

5h. Chromatography :

Dave and Dewar (219,220) studied the effect of addition

of a second component on a liquid crystalline compound p-azoxyanisole. They observed that the addition of second component depresses the transition temperature of p-azoxyanisole and reduces the range over which the mixture is anisotropic. As might have been expected, the effect was smaller (219) the more nearly the solute molecules resembled those of p-azoxyanisole in size, shape and polarity. Evidently the energetically favourable arrangement of molecules in the nematic phase is disturbed by a foreign material, but to a lesser extent the more closely the two resemble one another. One obvious consequence of this is that foreign substances should dissolve more easily in liquid crystals, the more easily their molecules fit into the liquid crystal " lattice "; different position isomers in particular should show different solubilities in liquid crystals, owing to the differences in shape between their molecules. The linear isomers should dissolve more easily, their molecules resembling more closely the rod-shaped molecules of the solvent. With this view Dewar and Schroeder (221) used liquid crystals as stationary phases in gas liquid chromatography. At about the same time Kelker (222) initiated a similar investigation. Preliminary results were encouraging. Dewar and Schroeder (221.) could separate position isomers by using nematic liquid crystals as solvents. They further extended their work to smectic liquid crystals (223). They observe that the smectic phases are more effective than nematic phases as stationary phases in gas chromatography. Dewar, Schroeder

and Schroeder (224) indicate that the selectivity of mesomorphic liquids toward solute molecules on the basis of shape is an excellent tool for estimating mesophase molecular order. Barrall et al. (225) recommend gas chromatography for general detection of liquid crystal transition temperatures. Kastev and Shapov (226) determined the stability constant of an olefin-liquid crystal system by means of gas liquid chromatography. Kelker and Von Schivizhoffen (227) have reviewed the use of liquid crystal in gas chromatography. They have discussed the properties of liquid crystalline phases which are important in gas chromatography. Thermodynamic aspects and practical applications are discussed. Martire et al. (228) studied thermodynamics of solutions with liquid crystal solvents in gas liquid chromatography. They used cholesteryl myristate as solvent. They obtained infinite dilution solute activity coefficients at several temperatures in the smectic, cholesteric and isotropic liquid phases. A possible reason for the unusual solvent behaviour of the cholesteric phases is offered. Chow and Martire (229) also studied thermodynamics of solutions with nematogenic liquid crystal solvents. Kelker and Verhelst (230) studied the pretransformation behaviour of nematic phase in relation to retention of volumes. Recently Vigdergauz and Vigalok (231) have reported chromatographic analysis on columns with liquid crystal fixed phases. The chromatographic characteristics of nematic liquid crystals and their mixtures were investigated for the

analysis of paraffinic and aromatic hydrocarbons and their derivatives. Dimethyl naphthalenes were separated within the liquid crystal temperature range of p,p'-azoxyphenetole. The mixed liquid crystal phase, forming eutectic mixture has sorption properties not complying with the additivity principle, increasing the possibilities of chromatographic analysis. Chow and Martire (232) have described the use of gas liquid chromatography in determination of the degree of order in a nematic mesophase and potential utility of this approach to study the order within the cholesteric mesophase is also described. Kelker et al. (233) have reported new applications of nematic phase in gas chromatography.

5I. Calorimetry of Mesomorphic Substances :

When a mesomorphic compound is cooled from isotropic liquid phase, it passes through various mesophase transitions and solidifies. In the transition change isotropic liquid to mesophase, and the change from one mesophase to another mesophase, the latent heats and entropy changes are generally quite small compared to the final transition from mesophase to crystalline solid. For example, the transition heats (K cal/mole) for the phase transitions of 4,4'-di-n-heptyloxyazoxybenzene (52) are

$$\text{Isotropic} \overset{0.243}{\longleftrightarrow} \text{Nematic} \overset{0.381}{\longleftrightarrow} \text{Smectic} \overset{9.78}{\longleftrightarrow} \text{Crystalline solid.}$$

Such small changes are difficult to measure accurately.

Additional problems arise due to difficulties in purification and decomposition of compounds at the high temperatures required for most mesophase transitions. Hence, systematic thermodynamic studies have been made on only a few of the many liquid crystalline compounds. Recent calorimetry studies have been reviewed and discussed by Porter, Barrall and Johnson (234). Most of the compounds studied are nematic or cholesteric.

Calorimetric measurements using the method of differential thermal analysis and differential scanning calorimetry have been reported recently by Barrall, Porter and Johnson (234) and by Ennulat (235). The most significant studies have been reported in an important series of papers by Arnold et al. (236). Arnold uses the method of adiabatic calorimetry for the determination of heat capacities and latent heats. Arnold has also studied the latent heats of series of cholesteryl esters of saturated fatty acids by the methods of differential thermal analysis. Brown et al. (52) have compared the results of Arnold et al. and Barrall et al. They state that the large discrepancy in these values is an indication of the uncertainty of the differential thermal analysis method and suggests that caution should be exercised in the interpretation of the results based on this method. They summarize the results in terms of general statements. The entropy changes of nematic-isotropic and cholesteric-isotropic transitions are of the same order of magnitude in agreement with accepted interpretation regarding the

similarity of these phases. In homologous series, aside from the small odd-even alternations, there is a general tendency for the transition entropy to increase with increasing molecular weight. A general correlation is observed in which the mesomorphic-isotropic transition entropy is roughly 2 percent of the total for all transitions from solid to isotropic liquid; smectic-isotropic transition entropies are usually much larger, roughly by a factor of ten. For intermediate transitions the smectic B to smectic C is larger than that for smectic C to smectic A (236).

Arnold has also obtained heat capacity data for number of mesomorphic compounds. Arnold has compared his heat capacity data with the statistical theory of Maier and Saupe. In general, the details of the heat capacity curve are not well determined by the theory. Arnold emphasizes the effect of impurity on the shape of the heat capacity curves.

6. 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 (237). It has now been ~~known~~ shown that several biological systems exhibit liquid crystalline properties and some possess properties analogous to those observed in mesomorphic systems. Many living tissues like muscle, nerves, tendons and bones show the optical property of double refraction (238). The degree of double refraction in such fibrous systems increases on streching and decreases

on contraction.

Living sperms, composed in part of protein, nucleo-proteins, and albumins, have been shown to possess a mesomorphic phase.(239,240). Aqueous solutions of certain viruses e.g. tobacco mosaic virus exhibit lyotropic mesomorphism (241-243).

Brown and Shaw (6) have pointed out that it seems probable 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. Catalytic processes in biological systems could readily find a favourable environment in the structure of the mesomorphic state. As Bowden (244) has put it, this state seems to be especially suited to biological functions and may possibly be the basis of vital activity.

Chapmann (245) points out in his recent review that not a great deal of work has been done with pure, carefully characterized systems, despite many comments and speculations over several years about the importance of liquid crystalline behaviour in biology. He further reports that pure phospholipids and phospholipids obtained from brain exhibit liquid crystallinity. Some of them are liquid crystals at room temperature. They also give lyotropic mesomorphism. Fergason and Brown (246) have also recently published a

review on the liquid crystals and living systems.

Robinson (75) has studied mesomorphism of polypeptide solutions and he obtained nematic and cholesteric pahses in these solutions. He has discussed the biological structures and mesomorphism.

Stewart (247) mentions that there are several good theoretical reasons why matter in the liquid crystalline state should play a part in the structure of living tissues. He gives a number of examples where mesomorphism is observed in biological systems. He also describes the preparation of artificial mesophase by ternary systems of cholesterol, amphiphile (lecithin or polyoxyethylene ester) and solvent (water).

Small and co-workers (95,96,248) have studied ternary and quaternary systems of amphiphilic substances in water. This study throws light in the cholesterol gallstone formation. They state that the composition of gallbladder bile, especially in pathological cases, has been shown to vary widely. They mention that, indeed, from an examination of phase diagrams it is possible to predict that a change in the percentage of any of the components (cholesterol, lecithin, bile salt and water) may lead to the formation of crystals of cholesterol or one of the paracrystalline phase.

7. Mixed Mesomorphism :

Just as the freezing points of the solids are depressed by the addition of other substances, so also are the transition temperatures of liquid crystals lowered

by the presence of foreign substances. When a mesomorphic compound is mixed with another mesomorphic or non-mesomorphic component, the solid-mesomorphic and mesomorphic-isotropic transition points may get depressed and the degree of depression will depend upon the concentration of the added component in the mixture. The phenomenon of liquid crystallinity is known as mesomorphism, so also the formation of mixed liquid crystals may be called mixed mesomorphism.

Schenck (249) showed that the nematic-isotropic transition temperature of p-azoxyanisole is lowered by the addition of other substances. He also pointed out that p-azoxyanisole and p-azoxyphenetole in the liquid crystalline state form isomorphous mixtures. de Kock (21) investigated a number of binary systems of mixtures of substances, one or both of which were liquid crystalline. He found that in the binary systems where one component is liquid crystalline and the other non-liquid crystalline, mixed liquid crystals were formed but only upto a certain concentration of the second component, the mesomorphic isotropic temperature being lowered.

Bogojawlensky and Winogradow (250) have examined mixtures of isomorphous substances and have reported the formation of mixed liquid crystals from pairs of substances one or even both of which were not giving normal liquid crystals. They also determined latent or labile transition points (isotropic-nematic points) of the non-mesomorphic substances in many cases by the extrapolation of the

nematic-isotropic transition curve which was linear in the majority of cases. Vorländer and Gahren (251) and Bennett and Jones (99) also observed that binary mixtures in which both the components were non-mesomorphic, gave rise to liquid crystals within a certain concentration range when they were melted. Walter (252) has given an explanation to the observation of Vorländer and Gahren. He said that the compounds which yield such mixtures are generally very well crystallized and are not readily supercooled. Consequently, a monotropic liquid crystal phase which might be anticipated for them remains latent. If two such chemically similar substances are mixed, it may happen that the melting point of the mixed solid phase which is usually lower than the melting point of the individual components, falls below the mixed melting point of the crystalline liquid phase which with chemically related substances should lie between the two latent crystalline liquid melting points of pure components. Such a mixture which should form mixed liquid crystals, exhibits enantiotropic liquid crystalline properties. Walter studied the binary system of anisic acid and anisylidene-propionic acid which themselves are non-mesomorphic but their mixtures yield mixed liquid crystals within certain limits of concentration. Prins (253) studied a number of binary systems of nematic and cholesteric compounds and discussed the problem in terms of phase rule. de Kock and Prins concluded that in two-component systems the mesomorphic-isotropic liquid transition temperatures should not in general occur

sharply but that, as a rule, there should be a range of temperature over which the two liquid phases of different composition could co-exist. Dave and Dewar (219,220) repeated de Kock's work with great care and obtained a phase diagram which does not show any indication of the two-phase liquid system observed by de Kock. They investigated a number of binary systems in which one component was mesomorphic and the other non-mesomorphic. In all the cases studied, the liquid phase is apparently a homogeneous single phase which may or may not be anisotropic. From their experimental results they have tried to deduce the effect of the terminal groups of a non-mesomorphic component on mixed mesomorphism. They state that the transition lines of binary systems in the phase diagrams stand as a measure of the tendency of the non-mesomorphic component towards mixed mesomorphism; consequently they obtained different values of group slopes for various end groups. The lower slope value indicates the greater tendency of the non-mesomorphic component towards mixed mesophase formation and vice versa. They studied binary systems comprised of p-azoxyanisole a nematic component and p-substituted Schiff's bases as the non-mesomorphic components. From the slope of the transition lines of the phase diagrams, they have deduced an order of efficiency of the end groups of the non-mesomorphic components toward mixed mesophase formation.

$$NO_2 > OMe > Me_2N > Me \geqslant Cl > Br > H$$

Dave and Lohar (254) and Dave and Vasanth (255) studied more systems of this type and found an extended order of group efficiency in the descending sequence.

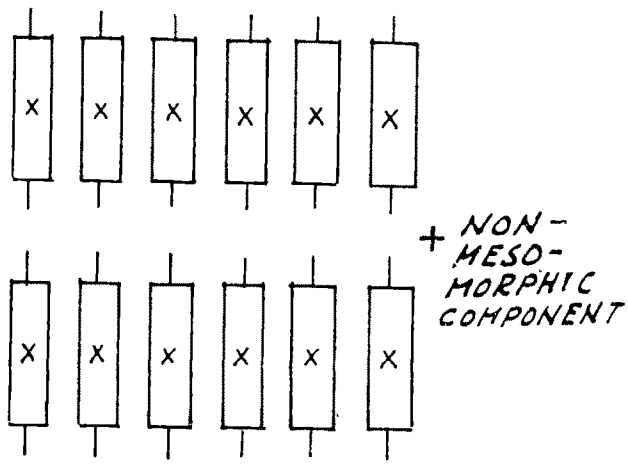
$NO_2 > OEt > OMe > O\cdot CO\cdot Et = OPr > O\ CO\ Me > NMe_2$
$Me = Cl > F = Br > I > OH > NEt_2 > H$ (256)

They consider that this order is the order of decreasing polarity of the groups regardless of sign and so evidently the main factor is the magnitude of the group dipole moment and not its direction. Group efficiency order should, however, be a cumulative effect of many factors like dipole interactions, the over-all polarizability of the system, size of the groups, shape of the molecules and even hydrogen bonding and mutual conjugative effects (67). Gray (67) has pointed out that the group efficiency orders for nematogenic systems will not hold good to smectogenic systems whose thermal stabilities are governed by quite different factors.

The binary systems reported so far mainly comprise of componets one or both of which may be nematic mesomorphs or non-mesomorphs. Demus and Sackmann (37) identified smectic mesophases on the basis of miscibility criteria and texture phenomena. Probably no systematic studies have been made for mixed mesomorphism in the smectic phase. Dave, Patel and Vasanth (257) studied binary systems comprising ethyl p-azoxybenzoate (a smectic mesomorph) and Schiff's bases as non-mesomorphic solutes. A continuous series of mixed smectic mesomorphism is formed over a range

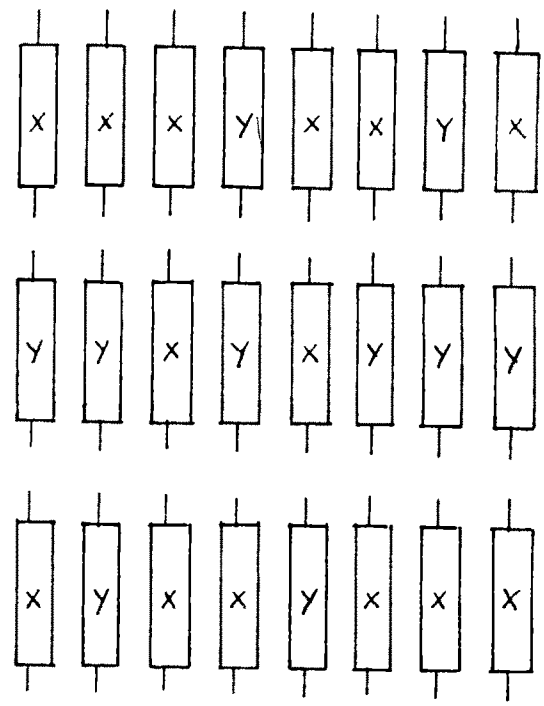
of temperature and concentration. The transition lines are as usual depressed except in the case of nitro and in some cases chloro-substituted Schiff's bases where the smectic-isotropic transition curve exhibits a maximum. Dave, Patel and Vasanth (258) also studied binary mixtures comprising p-n-dodecyloxybenzal-p-n-butoxyaniline, a polymesomorph exhibiting smectic and nematic mesophases and other non-mesomorphic Schiff's base compounds. In these cases mixed polymesomorphism is observed over a range of temperature and concentration. The smectic-nematic and nematic-isotropic transition lines are as usual depressed regularly with increasing concentration of the non-mesomorphic component, the range of temperature over which the nematic phase exists increasing at the cost of the smectic mesophase. However, the binary mixtures comprising Schiff's bases with NO_2- group show a peculiar behaviour; the nematic phase is completely eliminated and the smectic phase shows an enhanced thermal stability, the smectic-isotropic transition curve showing a maximum in the phase diagram. Dave and Patel (259) studied binary mixtures comprising p-n-octyloxy-benzoic acid, a polymesomorph exhibiting smectic and nematic mesophases and other non-mesomorphic p-substituted benzoic acids. They report that smectic-nematic and nematic-isotropic transition lines are as usual depressed regularly with increasing concentration of the non-mesomorphic component, the range over which the nematic phase exists increasing at the cost of the smectic mesophase, However, in the binary mixtures comprising NO_2- group in the

FIG. 4



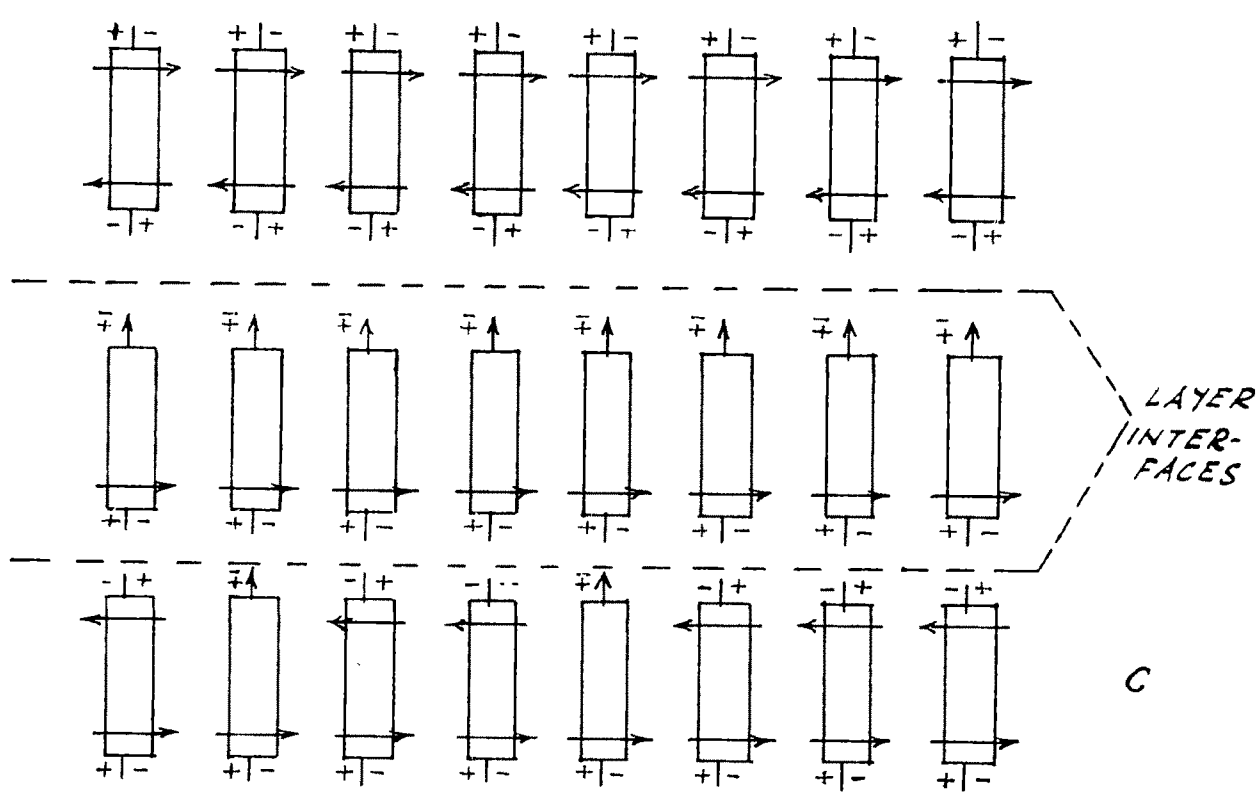
A

SMECTIC PHASE (PURE COMPOUND)



B

SMECTIC PHASE (MIXTURE)



C

non-mesomorphic component both smectic and nematic mesophases show an enhancement in the thermal stability. Dave and Dewar (219,220) in their study of nematic mixed mesomorphism report that the presence of NO_2- group enhances the thermal stability of the mixed nematic mesophase, its group slope value being the lowest. They have ascribed this to the high polarity of NO_2- group. Schroeder and Schroeder (260) in their study of the mixtures of a polymesomorph - 4,4'-di-n-hexyloxyazoxybenzene with 4-nitro-substituted anils report the enhancement in the thermal stabilities of both the mesophases. They have tried to explain these enhanced thermal stabilities of their mixtures by invoking a head to head arrangement of nitrosubstituted molecules in the layer structure of the mixed smectic mesophase with the nitro groups adjacent to one another in the middle of each layer. They have postulated a dimeric species of the nitro anils analogous to the dimeric carboxylic acids which are liquid crystals.

Dave and Vora (256) have commented on this postulate of dimer formation; they state that if this is the case, nitro anils themselves could be expected to exhibit mesomorphism which is not the case. An explanation for the enhanced thermal stabilities due to such groups is given by Byron and Gray (67) in pure mesomorphic systems. Dave et al. (257) have explained mixed smectic mesomorphism by giving the tentative possible picture of such a melt (fig.4 A and B) where X represents the molecules of

the mesomorphic component and Y represents the molecules of the non-mesomorphic component and their mode of packing (fig. 4c). Normally with this arrangement, the presence of NO_2 or Cl end group in the non-mesomorph would cause a reduction in the thermal stability by decreasing lateral cohesive forces. However, it is observed that the presence of these end groups bring about an enhancement in the smectic thermal stability. They have tried to explain this behaviour by assuming the tilting of the molecular strata in the melt. It may be pointed out here that the transition lines being curved no order for the tendency of the non-mesomorphic component toward mixed smectic mesomorphism could be derived.

Mlodzeevskii (261) observed that mixtures of cholesterol and cetyl alcohol and cholesterol and glycerol give rise to mesomorphic phases. A.S.C. Lawrence (262) has recently reported mixed liquid crystal formation in C_{12}, C_{13}, C_{14}, C_{16} and C_{18} alkanol systems with the formation of 2:1 alkanol:cholesterol complex. Chistyakov and Usol'tseva (263) have reported monotropic mesomorphism in cholesterol-cetyl alcohol systems. They have also reported mesomorphism in cholesterol-glycerol systems. Gaubert (264) obtained mesomorphic systems by mixing molten cholesterol in turn with succinimide, tartaric acids, malic, maleic, malonic, succinic, anisic, cinnamic and lactic acids. He also studied liquid crystalline mixtures obtained by heating ergosteryl acetate, propionate or butyrate with glycollic acid, glycerol, orcin and on melting certain cholesterol and

ergosterol derivatives with urea (265).

Liquid crystalline mixtures have been studied to examine the effect on the textures of various mesophases. Friedel (7) observed that addition of a very small amount of cholesteryl compounds to a nematic substance such as p-azoxyanisole imparts to the latter the characteristic properties of cholesteric mesophase. Vorländer (62) also has studied the effect of optically active substances for liquid crystallinity by mixing them with optically inactive substances. He reports that optically active compounds exhibit cholesteric mesophase whereas the racemic form is nematic. Luckhurst and Smith (266) report that addition of an optically active solute to a nematogen brings about profound changes in the structure of the mesophase which in fact becomes cholesteric. Billard and co-workers (63) and Gray (64) have recently reported that racemic nematic compounds on resolution exhibit a cholesteric mesophase. Sackmann et al. (61) have reported that when two cholesteryl compounds with opposite optical rotatory power are mixed in different proportions, a stage comes when that mixture exhibits a nematic mesophase. Reference should be made to the study of optical rotatory power in the mixtures of cholesteric and nematic substances by Cano and Chatelain (72), Chatelain and Martin (73), Buckingham et al. (267) and Stegemeyer and Mainusch (268).

It is rather difficult to explain the role of the terminally situated groups and their dipole moments on mesomorphic characteristic of mixtures as these systems are fairly complex and any attempt to relate molecular

structure to liquid crystalline properties of the mixtures will be on a qualitative basis.

8. Application of Liquid Crystals :

8a. Cholesteric Liquid Crystals :

When illuminated with white light the cholesteric liquid crystal scatters light to give iridescent colours (269). With changes in temperature or pressure new colours are produced. For each compound there is a characteristic temperature range it passes through, when heated, in the entire colour spectrum from red to violet; the process is reversible. The colours are due to the double refraction as well as circular polarization of the light by the cholesteric liquid crystal. The cholesteric liquid crystals are thermally very sensitive and can be used in thermal tests in place of radiometers. Cholesteric liquid crystals may provide a simple method of (a) measuring surface temperatures, (b) measuring temperature difference by means of difference of colours and (c) following certain dynamic processes visually such as thermal expansion.

(i) Thermographic Measurements of Human Skin Temperature (270) :

The skin over subcutaneous lesions and tumors is warmer than the normal surrounding skin. Thermotopographic measurement by liquid crystals forms an important test for the measurement of size and response to treatment. Cholesteric liquid thermography permits immediate visualization of surface temperature. The thermogram can be recorded photographically also. The cost in time and

equipment is minimal.

(ii) Testing Materials :

Cholesteric liquid crystals can be used for the non-destructive testing of materials, such as to reveal blockages in heat conducting systems or local over-heating of the metal surfaces caused by eddy currents in wind tunnel experiments.

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

They show variation in heat transfer between well-bonded and poorly bonded areas on honey comb structure. To find the hot spots as small as one thousandth of an inch in integrated circuits cholesteric liquid crystals can be used. These compounds can be used to map out the heating element in the heating pad to show the position of the element after it has been moulded in rubber pad.

Cholesteric liquid crystals can be used to monitor temperature distributions in active electronic circuits, high resistance connections, surfaces and subsurface films (271).

They can be used as analytical tool to detect the presence of any small amounts of gases or of solvent vapours by means of colour changes (272).

(iii) The Liquid Crystal Thermometers (273) :

The cholesteric liquid crystals incorporated in polymer rods or foils can be used to measure temperature.

It is very useful for the rapid detection of fevers especially by oral temperature measurements.

(iv) Publicity Materials and Toys :

Cholesteric liquid crystals incorporated in plastic sheets can be used to make some very interesting temperature or pressure sensitive publicity materials and toys.

A new electrophotographic imaging process using mixed cholesteric liquid crystal and a xerographic plate is recently reported (274).

8.b. Nematic Liquid Crystals (275) :

(i) In electronics :

Liquid crystals can be used for display devices. A liquid crystal device differs fundamentally from an electronic display device such as a cathode ray tube. A liquid crystal device generates no light of its own but it scatters light. A liquid crystal device has got two main advantages : (1) since it reflects light instead of generating light, it can be viewed under a wide range of lighting conditions including direct sun light or a flood light, (2) since the liquid crystal device does not emit light, it should require relatively little power.

Electronic Window :

The electronically controlled window is perhaps the simplest device. Basically, it is a parallel plate capacitor with transparent electrodes (tin oxide on glass). With no voltage applied the window is clear. When approximately 50 volts is applied the window becomes

opalescent. It is possible that this opalescent effect could be used to provide glass door panels and windows that could be frosted at the touch of a button to insure privacy for the users. A step away from that is the possibility that liquid crystals can be used to provide electronic curtains that will automatically control the amount of sun light admitted into our homes.

All Electronic Clock :

The liquid crystal display concept could lead to quite different approaches for some fairly conventional commercial products. One such product is the familiar time indicator or clock. The construction of such clock is reported, which has no mechanical moving parts. The basis of this clock is the seven-segment liquid crystal numeric display cell. Four of these cells arranged in a row can then be used to present the time in hours and minutes or, with two additional cells, the seconds can be displayed. Lloyd's have recently put a liquid crystal calculator on the market.

(ii) Television :

In years to come, the liquid crystal display concept may yield a practical thin screen competitor to the cathode ray tube used in radar and TV displays.