# PART - 2

## AZOMESOGENS

# INTRODUCTION

# INTRODUCTION

## 1. Liquid Crystals-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 the temperature is high enough and the average thermal energy of a molecule exceeds its bonding energy, the molecules escape from one another's influence and solid melts to an isotropic liquid, whose state of order shows no preferred direction.

There exists a series of compounds known as liquid crystals which behave differently when they melt. Liquid crystals are highly associated liquids that occur over various temperature ranges in melts or solutions of certain organic molecules and some polymers. Liquid crystallanity is an intermediate state of matter, existing in a peculiar twilight zone between the boundries of the usual crystalline solids and isotropic liquids.

The melting of normal solids is associated with the collapse of overall positional order of the lattice array and marks the onset of essentially free rotation of the particles. Two intermediate phases of matter have been identified where only one or the other of these two freedoms (freedom of position and freedom of rotation) has been at least partially obtained. These are termed liquid crystals and plastic crystals. These mesophases do not satisfy all the criteria for either a true solid or a true liquid and in fact exhibit many physical properties that are characteristic of both; for example, liquid crystals flow, but their optical properties such as birefrigence, are those usually expected of regular solids. Molecules within plastic crystals have rotational and diffusional mobilities approaching that of the liquid phase although the solid condition is maintained. In liquid crystals molecules are free to move but their rotational mobility is restricted; in plastic crystals the molecules are free to rotate in place and to some extent change lattice sites, but they still form a regular crystalline superstructure.

The phenomenon of mesomorphism is essentially a consequence of molecular shape. A general condition for the formation of a mesophase is that the molecules comprising the system be either (a) elongated and in some cases also flat(possibility of liquid crystallanity) or (b) approximately spheroidal (possibility of plastic crystallanity). A rough determining factor for mesomorphism is therefore, the length to breadth ratio of the molecular frame, which may be denoted by R. When $R \geq 1$ there is a possibility of liquid crystal formation and if $R \simeq 1$, a plastic crystal may occur.

F. Reinitzer(1), an Austrian botonist, for the first time observed the phenomenon of liquid crystallanity 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. A German physicist Otto Lehmann was the first one to carry out systematic study of this phenomenon(2). In his papers Lehmann used the terms"Fluiessende Krystalle" and "Flussige Krystalle" meaning flowing or fluid crystals for these states. Thus he coined the term liquid crystal or crystalline liquid. Although this term 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 form mesomorphic state(Greek-mesos,intermediate: morphs-form) would be more appropriate,meaning a state intermediate between a crystalline solid and an amorphous liquid. This term and the associated terms mesomorph, mesomorphism, mesomorphic, mesogenic 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 either ataxy(a disordered or amorphous structure ) or eutaxy(an ordered structure), the mesomorphic and crystalline state will belong to the class of eutactites, since they possess ordered or regular structures, whereas amorphous matter, isotropic liquid and gases will fall into the category of atactites. He, therefore, proposed the name paracrystals. The word crystal significantly emphasizes the natural proximity of the state to the crystalline condition, while the prefix para signifies that many of the organic compounds which possess this type of eutaxy are para substituted benzene derivatives. Thus the classification is:

1. Atectites - 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) have used the term mesomorphism 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 liquid crystals indicating that this class is obtained by the application of heat. Lyotropic liquid crystals constitute the second major group and are obtained by mixing two or more components. Even-though the terms thermotropic and lyotropic are widely used, Gray and Winsor(10) prefer the terms amphiphilic and non-amphiphilic. The lyotropic mesogens frequently form mesophases either at room temperature or at higher temperature, where an amphiphile incorporates considerable amount of water and/or organic liquids into their structure so they have been called lyotropic i.e. solvent induced mesophases. The thermotropic mesogens have mainly been studied as pure compounds with emphasis on the transition temperatures for the mesomorphic and non-mesomorphic states.

Soon after the initial discovery by Reinitzer(1), Lehmann(11) found that ammonium oleate and p-azoxy phenetole were the examples of the substances that may exist in the liquid crystalline state. Following and concurrently with Lehmann's studies, synthetic work was done by organic chemists in Germany to ascertain whether effects efforts such as those observed by Reinitzer and Lehmann were due to impurities and later, to unravel the relationship between chemical constitution and the capacity to form liquid crystals.(12-17)

The liquid crystalline compounds consist of molecules which are long and rod shaped, possessing polarizable middle parts and one or more dipolar end groups. This type of structure favours the parallel alignment of the molecules. In the crystalline state of a mesogen the bonding forces exist between the molecules. However, 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 a fluid but remains birefringent because of the prefered orientation of the molecules. On further heating the thermal vibrations are increased to a greater extent and the isotropic liquid is obtained. The gradual thermal breakdown in liquid crystalline compounds may be expressed as under:

$$\begin{array}{c}\text{Crystalline}\\ \text{State}\end{array} \overset{t_1}{\rightleftharpoons} \begin{array}{c}\text{Liquid}\\ \text{Crystalline}\\ \text{State}\end{array} \overset{t_2}{\rightleftharpoons} \begin{array}{c}\text{Amorphous}\\ \text{Liquid}\\ \text{State}\end{array}$$

$$\overrightarrow{\text{increasing}}\ \text{temperature}$$

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. However, 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 molecules and the mesophase finally changes to amorphous liquid. Thus the action of controlled heat is responsible for breaking down the alignment in stages. The representation of matter into three states in the case of such anisotropic melts is inadequate and hence a modified way may be as follows:

$$\begin{array}{c}\text{Crystalline}\\\text{Solid}\end{array} \xrightleftharpoons{t_1} \begin{array}{c}\text{Liquid}\\\text{Crystal}\\\text{(Mesophase)}\end{array} \xrightleftharpoons{t_2} \begin{array}{c}\text{Isotropic}\\\text{Liquid}\end{array} \xrightleftharpoons{t_3} \begin{array}{c}\text{Vapour}\\\text{or gas}\end{array}$$

The transitions $t_1$ and $t_2$ take place at definite temperatures and are reversible. But the reversal from the liquid crystalline state into the crystalline state is usually accompanied by supercooling. This type of transition in which $t_2$ is at higher temperature than $t_1$ is termed enantiotropic transition and the phase is known as an 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 termed monotropic mesophase.

The sequence of changes of state for a compound exhibiting monotropic mesophase may be represented as:

$$\begin{tikzcd}
\text{Crystaline Solid} \arrow[rr, "t_1"] & & \text{Isotropic liquid} \arrow[dl, shift left] \\
& \text{Mesophase} \arrow[ul] \arrow[ur, shift left, "t_2"'] &
\end{tikzcd}$$

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 Liquid Crystals:

Friedal(7) carried out detailed optical studies of liquid crystals, on the basis of which the liquid crystals are conviniently 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. Vorlander(18) 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 chart-1.

## Chart- 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-Azoxy phenetole | 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 isoamyl 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:

Crystalline Solid $\xrightarrow{t_1}$ smectic $\xrightarrow{t_2}$ Nematic $\xrightarrow{t_3}$ Isotropic Liquid

Number of compounds are known possessing more than one mesophase of the same type. Polymorphism in the 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 possess two smectic phases and one nematic phase.

Crystalline Solid $\xrightarrow{136.0^\circ C}$ Smectic$_{II}$ $\xrightarrow{158.0^\circ C}$ Smectic$_{III}$ $\xrightarrow{213.5^\circ C}$
Nematic $\xrightarrow{218.0^\circ C}$ Isotropic liquid (19)

Demus et.al(20) have examined number of above type of substances including the one given here and have designated different phases of the smectic mesophases as smectic A, smectic B, smectic C etc. The above compound should thus be designated as:

Crystalline Solid $\xrightarrow{133.4^\circ C}$ Smectic C $\xrightarrow{163.3^\circ C}$ Smectic A $\xrightarrow{213.5^\circ C}$
Nematic $\xrightarrow{218.3^\circ C}$ Isotropic liquid.

Lyotropic mesomorphs (8) also show a similar behaviour as exhibited by thermotropic liquid crystals. The most notable example is Sandquist's (21) 10-bromophenanthrene-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.

Solid $\xrightarrow{\text{water}}$ Thick paste (Smectic) $\xrightarrow[\text{Water}]{\text{More}}$ Thin paste (Nematic) $\longrightarrow$

$\xrightarrow[\text{Water}]{\text{Excess of}}$ 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):

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

(ii) 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.

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

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

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

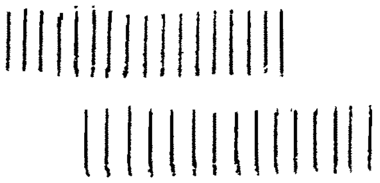
This brings home the idea that the smectic phase possesses a more highly ordered structure than the nematic phase.

## 2. a. Smectic Mesophase:

Smectic mesophase is a turbid, viscous state, with certain properties reminiscent of those found for soaps. The term'smectic' is in fact derived from the Greek word "Smectos" meaning soap like and has no special significance. Itwas first used for ammonium oleate, it being the first smectic substance known.

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 molecule 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.



A section representing the molecular arrangement in two plane strata.

Fig. 1.

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 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(22). 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(23).

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 batonnets, 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(24) 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.

It is generally assumed that smectic mesophase has a laminar structure which is developed in addition to an orientational long range order similar to that in nematics. A laminar structure means that the density of distribution of the molecular centres has its highest value along equidistant surfaces. The molecular centres have to be suitably defined for this purpose in relation to the molecular shape and molecular interactions. They coincide only for symmetrical molecules with the centres of mass.

Based on the proposal of Hermann(25),Saupe(26) proposed a subdivision of smectic into two groups -smectic phases with unstructured layers and smectic phases with structured layers. In the first group the distribution of the molecular centres within the layers corresponds to that of a two-dimensional liquid. It is without long range order. In the second group the layers are built up regularly so that the positions of the molecular centres lie on a two dimensional lattice. The most common smectics are in the first group which includes the Phases classified as smectic A and smectic C. A representative of the second group is classified as smectic 'B'. Much work on the classification of smectic mesophases has been done by Sackmann and Demus(27). They examined a number of 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 classified smectic phase according to the textures observed in the mesophases(Chart2).

## Chart.2

Scheme of texture groups of smectic liquid crystals:

1. Smectic A : (a) Simple fan-shaped texture
   (b) Simple polygon texture
2. Smectic C : (a) Broken fan-shaped texture
   (b) Broken polygon texture
3. Smectic B : (a) Fan-shaped texture
   (b) Polygon texture
   (c) Mosaic texture

3. (a), (b): with decreased number of lines.

2. and 3.: Schlieren texture

Recently Sackmann and Demus(27) proposed seven smectic phases, A through G. These are classified by miscibility studies, However, smectic mesophases are classified into three main classes called $\alpha$, $\beta$ and $\gamma$ by de Vries(28) based on X-ray studies. The class $\alpha$ contains smectic type A, C, F and D, class $\beta$ contains the smectic B and class $\gamma$ contains the smectic E, G and H. The solid crystalline form of the substance exhibiting smectic mesophases is designated as "Smectogenic" crystals.

2. b. <u>Nematic Mesophase</u> :

The term 'nematic' means threadlike (Greek-nema, thread) and is used because of the mobile thread like lines which are observed in 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 and can be compared to a long box of round pencils. Electric and magnetic fields orientate the molecules in a nematic phase, but have no effect on a smectic phase once it is established. However, the molecules in a smectic phase are influenced by these effects in the process of formation from the melt. 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 influence of surface. 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(29) in 1909, to explain the molecular arrangement and order in the nematic phase. The majority of the 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 rotational movements 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 oreiented in the same direction throughout the whole medium, but are grouped in aggregates or swarms. The molecules within each swarm lie parallel or approximately so, but in a direction that is random to the molecules of the other swarm in the medium. This would mean that the liquid crystalline structure resembles a mass of small crystals rather than a single crystal. However, unlike the mass of small crystals the swarms do not remain static but are continually exchanging molecules with one another. 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 for the turbidity associated with the nematic mesophase; the light scattering properties of the swarm 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 more or less extent. At higher temperatures the molecular motion increases, with the result that the average size of the swarm gradually decreases and when it becomes smaller than the wavelength of light the turbidity disappears giving a very shapp transition to the isotropic liquid. The effect occurs so rapidly that the observations carried out using different wave lengths of illuminating light could detect no difference in the transition temperatures. Above this temperature, the liquid is to all intents and purposes singly refracting. The results of X-ray study of Van der Lingen(30) rated out the views of Vorlander 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 characteristic of crystals, in liquid crystals appear to be due to the similar orientation of the molecules, the Bose's swarm theory thus being varified. Further, a 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(31,32) and by the determination of their viscosities at different temperatures(33). The first mathematical treatment of the swarm theory was given by Ornstein and Zernicke(34). Evidence in support of the swarm theory is available from the researches like transparency(35), refractive index(36) and magnetic and electric properties(37,38) of mesophases; a summary of such measurements is given by Ornstein and Kast(39).

However, the Swarm theory did not pass without criticism. Zocher(40) 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 mathematical terms and are based on the study of distortion of nematic structure in a magnetic field.

Zocher(40) made the following assumptions to derive equations for his theory of distortion in a magnetic field:

(i) The entire nematic structure under observation tends to take up such position that the axial direction at every point is the same.

(ii) Any force acting so as to disturb the state(under i) where the directions are uniform causes a distortion in the nematic structure in which the direction changes continuously until a restoring forces of an elastic nature holds the applied force in equilibrium.

(iii) 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(40) 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(41),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.

Chatelain(42) has shown that his studies on the diffusion of light from the sections of nematic mesophases indicate the existence of swarms of 107 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.(43) in their review suggest that the 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 the continuum theory may in fact be nearer to the truth and it is interesting to note that Furth and Sitte(44) as long back as in 1937 sought to show that the two theories are not incompatible. Luckhurst(45) 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. A schematic representation of the order in a nematic phase is shown in Fig.2.

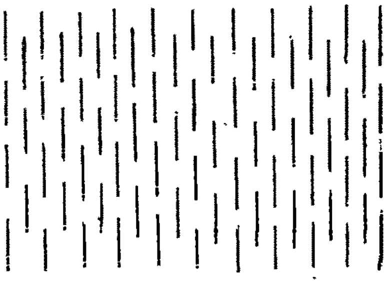


Fig.2:
Molecular arrangement in the nematic phase.

The nematic phase is very similar to a true liquid state and has been compared with the cybotactic structure of liquids(46), but compared with the latter, the former has a low internal energy. Like true liquids the nematic liquids give only diffusion haloes with X-rays confirming the absence of 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 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.

The response of nematic liquid to electric fields involves a process of orientation of the rod-like molecules in same direction with respect to that of the field. An external electric field makes a molecule orient with its dipolar axis parallel to that field. If that axis is more or less in the direction of the major molecular axis, then that molecule is said to have positive dielectric anisotropy; conversely molecules with negative dielectric anisotropy tend to align with their major axes perpendicular to the field.

Maier and Saupe(47) have given a simple molecular theory of the nematic liquid crystalline state by which it is shown that the nematic - isotropic transition temperatures may be determined by calculations of the free enthalpies of the phases involved in the transitions. 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 order parameoters and have calculated constituents for thermodynamic molecular order(47 a).

The nematic liquid to amorphous isotropic liquid transition is a first order transition. The transition energies are generally small but vary considerably.

In homologous series the transition energy increases with increasing molecular length. No apparent change in viscosity is noticeable at the isotropic-nematic transition; nematic can be poured just as easily as normal liquids.

A notable difference between the smectic and nematic mesophase lies in the way in which the two mesophases types separate from the isotropic liquid. While the smectic phase appears as batonnets, the nematic mesophase separates as tiny, spherical droplets. The appearance of the textures that form after the completed transition often depends considerably on the layer thickness. Thicker nematic layers may show the typical threaded texture. The well defined thread-like structures may move and float around in the nematic liquid. The term nematic refers to this structure.

In thin layers the threaded texture changes to the Schlieren texture with point-like disclinations. By suitable surface treatment it is possible to obtain films with uniform molecular alignment. With untreated surfaces, the surface effect may produce an irregular texture reminding one of polished marble (the marble texture).

## 2 C. New types of Nematic Phases:

Common nematogenic materials consist of rod-like molecules whose longest axes tend to be parallel in the nematic phase as discussed earlier. As suggested by Alben(48), Onsagar(49) and Dryer(50), in addition to such positive nematics, it is reasonable to expect that there might be 'negative' nematics with planar molecules aligned with their shortest axes parallel. Alben(48) has proposed a possible phase diagrams for mixtures of such 'positive' and 'negative' nematic liquid crystals.

The recent results of Chandrasekher et.al(51), have vindicated the idea of 'negative' nematic mesophase. They report that Thermotropic mesomorphism has been observed in pure compounds consisting of simple disc like molecules, viz. benzenehexa-n-alkanoates. Thermodynamic, optical and X-ray studies indicate that the mesophase is a highly ordered lamallar type of liquid crystal. Based on the X-ray data, a structure is proposed in which the discs are stacked one on top of the other in columns that constitute a hexagonal arrangement, but the spacing between the discs in each column is irregular. Thus the structure has transitional periodicity in two dimensions and liquid like disorder in the third. Another new type of nematic mesophase has been discussed by Zimmer and White(51A) obtained during the process of coking and carbonization. The mesophase transformation usually occurs in the range of 400 to 500° C. At this temperature the molecules condense to form a liquid crystal which has been termed the carbonaceous mesophase (Fig.3). The distinctive feature of the carbonaceous mesophase is the plate-like molecule in contrast to the rod-like molecule of nematic liquid crystals. The carbonaceous mesophase thus appears to be a lamellar liquid crystal in which space is filled by plate like molecules which may vary in size and shape but tend to pack in parallel arrays.These arrays are free to bend and twist.

## 2.d. Cholesteric Mesophase:

The cholesteric mesophase is found in the melts of several compounds mainly those containing the sterol type skeleton, from which it derives the name. All the compounds which exhibit cholesteric mesomorphism are found to be optically active. Non-sterol derivatives can, however, also exist in a cholesteric liquid crystalline state, the only necessary condition being optical activity of the compounds.

In many ways the properties of the cholesteric phase resemble those of the smectic and nematic phases. Friedel(7) noted a somewhat closer resemblance between the cholesteric phase and the nematic phase. No substance was found to exhibit both the phases viz. cholesteric and nematic, whereas each commonly occured in association with the

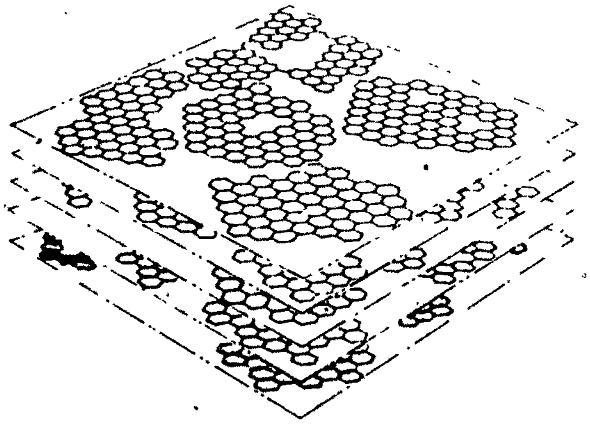


FIGURE 3 Model of the carbonaceous mesophase—a lamellar liquid crystal.

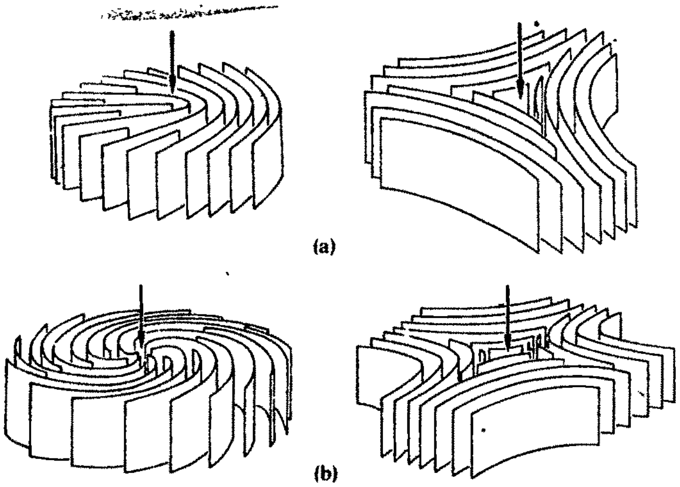


FIGURE 3 Layer-stacking wedge disclinations of rotation (a) $+\pi$ and $-\pi$ and (b) $+2\pi$ and $-2\pi$.

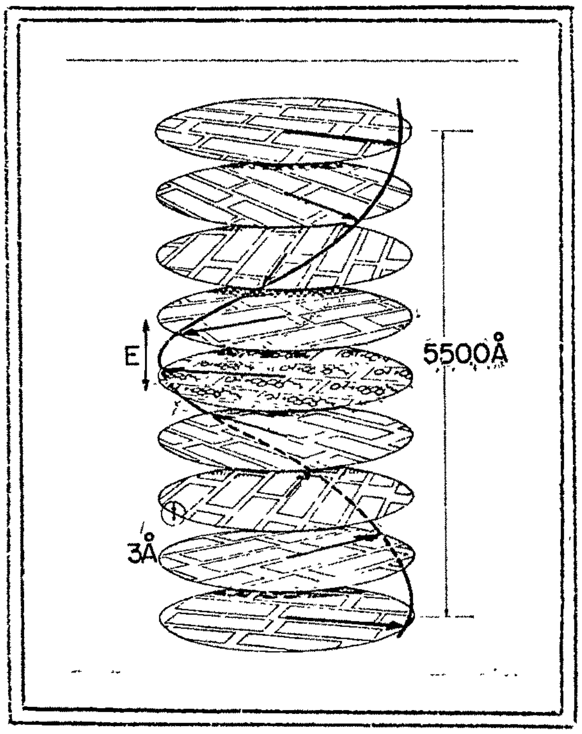
smectic phase. Based on these arguments Friedel considered the cholesteric phase as a special case of the nematic phase. Friedel emphasized his arguments by his observation that mixtures of dextro and laevo rotatory cholesteric substances give the nematic mesophase. Similarly a nematic liquid crystal can be transformed to a cholesteric liquid crystal by dissolving an optically active compound in it. Chatelain(42) observed that the amount of light diffused by the nematic phase is similar to that diffused by the cholesteric mesophase. Gray on the basis of his study of the fatty esters of cholesterol(52) 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.

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(53). As early as in 1914 Vorlander and Janeoke(10) reported that the racemic amyl-p-anisal-amino-$\alpha$- methyl cinnamate exhibits nematic mesophase, whereas the active forms(d and l 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 Leclercq et.al.,(54) and Gray(55). In these cases the optically active compounds were cholesteric wheareas the inactive racemic varieties were nematic.

All this clearly indicate that the cholesteric mesophase is nematic in type. Cholesteric mesophase has certain characteristic properties of its own which are markedly different from the smectic and nematic mesophases. When illuminated by white light the most striking property of the cholesteric mesophase 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-reflection, transmission, birefringence, optical rotation, and colour - all undergo marked transformations. Friedel(7) Stumpf(56), Mathieu(57) and Gray(58) have tried to explain the optical rotatory power of the plane cholesteric texture. Oseen(59) has explained mathematically the high optical rotatory power and transmission of different colours of plane texture. Fergason(60) has explained optical properties of the cholesteric mesophase on the basis of the model suggested by Oseen.

High optical activity of the cholesteric mesophase is indicative of a helical arrangement of the molecules in the mesophase, the observed periodicity along the cholesteric axis being equal to half the pitch. de vries(61) developed a theory, based on such helical properties of the cholesteryl compounds and derived an equation relating the optical rotation to the pitch of the helix. Chandrasekhar and Co-workers(62,63) and Chetalain and Coworkers(64-66) have tried to verify this theory and found in good agreement. Robinson(67) 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 properties of cholesteric mesophase. Daniel Berg(68) 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 phase to the next, the cholesteric molecules are spiral, the repeat distance being of the order of 1000 A° (Fig.4). This repeat distance gives the cholesteric phase its peculiar optical properties of scattering the light and

FIG. 4



PROBABLE ORGANIZATION OF THE CHOLESTERIC PHASE appearing highly iridescent, Recently Goossens(69) has put forward the 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. The focal-conic texture nucleates in discrete points from which it grows in all directions forming circular areas, until finally the whole film is covered. In the plane texture the sample is uniformly aligned with the twist axis perpendicular to the plane of the film. There are, however, often alignment discontinuties which can show reflection colours. The wave length of the light at the centre of the reflection band is, for perpendicular incidences, equal to the length of the pitch multiplied by the refractive index.

The cholesteric mesophase is always optically negative and uniaxial.

### 3. Plastic Crystals(Molecular Crystals or Isotropic Cubic Mesophases.)

In contrast to liquid crystals, which are solid like liquids, plastic crystals are liquid-like solids. Plastic crystal molecules are approximately spheroidal in shape and therefore, the molecules that make up this intermediate phase (notable examples being Camphor and adamantane) are able to attain a large degree of rotational freedom before passing into a true liquid condition. However, the phase is not amorphous. A definite crystal structure is maintained although it appears that intersite diffusion occurs rather readily. As a result of this high microscopic mobility these solids are quite easily deformed. They can be extruded at relatively by low pressures and some even have the consistency of butter (e.g. perfluorocyclohexane flows by its own weight). For these reasons the mesophase is termed plastic although the condition has nothing to do with high polymers, for which the name is usually used. Plastic crystals are thus neither true liquids nor true crystalline solids, but constitute a further mesomorphic state of matter equivalent in status to the liquid crystals(70).

The liquid crystals are typically formed by relatively elongated and rather rigid lath-like molecules which have restricted rotational freedom. The plastic crystals on the other hand are typically constituted by rather compact globular molecules, which when undergoing rotatory displacements acquire close to spherical symmetry.

The non-liquid crystalline cubic, optically isotropic mesophases formed by globular molecules known as plastic crystals, were discovered by Timmermanns(71). They show low entropy of liqueffaction. The formation of plastic crystals is due to the capacity of the constituent molecules over a particular temperature to arrange themselves in a cubic array at the same time undergoing thermal rotatory displacement so that there is no long range orientational order between the molecules. At the upper limit of this temperature range liquefaction occurs with breakdown of the cubic arrangement but with only a small increase in entropy and little increase in volume. At a lower temperature limit a transition occurs(Crystal I - Crystal-II) typically to an ordered anisotropic solid crystal. In this case there is a large decrease in entropy. Occasionally, however, there is a transition with only a small entropy decrease to a second (and some times even to a third) plastic crystalline form which undergoes a transition at a still lower temperature with a large decrease in entropy to an ordinary solid crystal.

The experimental evidence concerning the degree of molecular motion in plastic crystals is based on investigations of thermal properties, X-ray diffraction,dielectric properties, NMR and diffusion. It was the peculiar thermal behaviour of plastic crystals which led Timmermanns to the recognition of plastic crystals as a mesomorphic substance(71) Similar to liquid crystals, in this case also, the transition, crystalline solid to mesophase, is accompanied by a high entropy increase while the entropy increase for the change mesophase to amorphous liquid is relatively small. The X-ray diffraction studies indicate that the molecules in plastic crystals have considerable mobility but they do not have literally free rotation.

Gray and Winsor(10) have discussed the optically isotropic cubic mesophases exhibited by liquid crystaline substances in their recent review.

Sackmann and Coworkers have shown the formation of cubic mesophases in 4'-n-hexadecyloxy-and 4'-n-octadecyloxy (20,72) 3'-nitrobiphenyl-4-carboxylic acids at higher temperatures(20,73). In the cubic phase, the lattice spacing corresponds to about twice the molecular length. It therefore seems probable that the rotating units are here composed of globular assemblies("Cybotactic complexes") of parallel lath-like molecules, the optical isotropy of the phase arising from the statistically random orientation of the individually highly anisotropic units.

Winsor has further suggested that the high temperature coloured "Modifications" formed by certain cholesterol derivatives known as 'bluephase'(1,73,74-78) may also possess related constitutions. These phases are usually much more fluid and may show marked flow birefringence(75).

In these phases it would seem that the individual units must consist of small molecular assemblies each with a twist as cholesteric plane texture. These units will be orientated at random but those suitably orientated in relation to the direction of vision should give a colour effect anqlogous to that of the plane texture itself. This would equally be possible whether the coloured phase represented an amorphous liquid or a plastic mesophase.

## 5. Lyotropic Mesomorphism(Mesomorphism formed by amphiphilic compounds).

Liquid crystallanity formed by the effect of water or organic compound on amphiphilic compounds is referred to as lyotropic mesomorphism. In his review, Winsor (76) has defined amphiphilic compounds as follows: Amphiphilic compounds are characterized by possessing in the same molecule two groups which differ greatly in their solubility relationships. These are(a) a hydrophilic group which tends to be water soluble and hydrocarbon insoluble and (b) a lipophilic group which tends to be hydrocarbon soluble and water insoluble. Typical hydrophilic groups are OH, $-O(CH_2CH_2O)n$ $-COONa$ $-SO_3K$, $-NMe_3Br$, $PO_4-CH_2-CH_2-\overset{+}{N}H_3$, and typical lipophilic groups are $C_n\,H_{2n+1}$, $-C_{17}H_{33}$ and $C_8H_{17}O_2C-\underset{|}{C}H-CH_2-COOC_8H_{17}$

Lyotropic substances are always strongly birefringent, their physical nature varying from a turbid free flowing fluid to a waxy solid. The first lyotropic substance ammonium oleate was reported by Lehmann(11). The gradual break down of ammonium oleate in the presence of water(solvent) may be represented as:

$$\begin{array}{c}\text{Crystalline}\\ \text{Ammonium}\\ \text{Oleate}\end{array} \underset{\text{Dehydration}}{\overset{\text{Water}}{\rightleftarrows}} \begin{array}{c}\text{Liquid}\\ \text{Crystalline}\\ \text{State}\end{array} \underset{\text{Evaporation}}{\overset{\text{Excess water}}{\rightleftarrows}} \begin{array}{c}\text{Solution}\\ \text{or}\\ \text{Colloid}\end{array}$$

Substances like soap, Soap-like alkali salts of naphthenic acids, resin acids, substituted phenanthrene sulphonic acids etc., show mesomorphic state under controlled action of water(71-79). Alcoholic solutions of these compounds do not generally show anisotropic behaviour,so a high degree of hydration appears to be necessary prerequisite for the occurence of many lyotropic mesophases. McBain(80) has discussed the forms of mesomorphism in soap solution.Some of the soap systems have been studied with solvents other than water(81,82). A number of cationic and nonionic detergents have also been shown to give anisotropic phases when they are treated with solvents and in perticular with water(83,84). A close relationship obviously existing between these liquid crystalline states and the truly colloidal states, has been discussed by Ostwald(85). Palit et.al,

(86) during their study of solubilization of water by cationic detergents have come across liquid crystalline phases.

Zocher and Coper(87) have shown that methylene blue, neutral red and also other dyes give orientation on rubbed surfaces.

Lyotropic liquid crystalline states analogous to the smectic and nematic thermotropic liquid crystals 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 alteration of lipophilic-hydrophilic balance and the solvent. For instance, cholesterol and sodium lauryl sulphate in 1:1 mixture give myelin figures, whereas on increasing the sodium lauryl sulphate to 1:2 or 1:3 batonnets of Friedel were obtained(88).

Robinson(89) has reported the interesting observation that viscous solutions of poly-$\gamma$- benzyl-L-glutamate(PB GL) are anisotropic in certain organic solvents, and show a number of characteristic properties similar to those observed in the thermotropic cholesteric phase. It has high optical rotation and exhibits iridescent colours. He, also reports that like thermotropic cholesteric mesophase, lyotropic mesophases are obtained having opposite twist of helix in different solvents(67), when the mixture of these solvents is used to dissolve PBGL the definite proportion of the solvent mixture gives a nematic mesophase just as two cholesteric compounds with opposite rotatory power when mixed give a nematic mesophase.

A fundamental feature of all amphiphilic phases is the tendency for the mutual orientation of the amphiphile molecules with the their hydrocarbon and polar moieties grouped like-to-like. In solid crystalline phases, this leads to the long-range arrangement of the molecules in parallel sheets with alternate orientation of the sheets. For example, in the one or more crystalline phases formed by the alkali metal soaps at room temperatures, the extended hydrocarbon chains are arranged in three-dimensional crystalline order either normal to or inclined at an angle to the sheets. At higher temperatures a crystalline form is sometimes found in which the hydrocarbon chains undergo thermal rotation about their long axes. In this form the hydrocarbon chains lie normal to the sheets in two dimensional hexagonal array. At still higher temperature and/or through the effect of solvents, a mesophase is formed which is termed the fused mesophase. It is the most familiar lyotropic mesophase(90)

Lyotropic systems are also thermotropic and it is the coöperative 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.

Mesophases in binary systems of amphiphiles and water are of cubic isotropic and liquid crystalline type and may be classified as(a) the neat phase(G phase), (b) the middle phase(M,phase), (c) the viscous isotropic phase($V_1$ phase) and (d) the inverse phase($V_2$ and $M_2$ phase) (91)

## 4. Analogies between plastic crystals, Thermotropic liquid Crystals and Lyotropic liquid crystals:

It has been suggested by Gray and Winsor(92) that constitutional analogies exist between the thermodynamically stable cubic mesophase formed by globular molecules, by globular transitional groupings of molecules derived from certain non-amphiphilic mesogens, and by globular micelles in amphiphilic(lyotropic) systems.

Further, constitutional analogies have been noted between the thermodynamically stable lyotropic $M_1$ and $M_2$ phases and the non-amphiphilic nematic/cholesteric phases and between the lyotropic G phase and the non-amphiphilic smectic phase.

Recent findings have also suggested that even the compounds with spherical molecules exhibits nematic mesophase and with long lath like molecules exhibit cubic isotropic plastic crystalline phases as discussed earlier.

Much more work in this direction can bring out number of such systems exhibiting above mentioned mesophases having structural analogies.

5. Mesomorphism in Biological systems:

Liquid crystals play an important role in nature. Brown and shaw(6) have pointed out that it seems probable that the mesomorphic modifications are of important biological significance, for, slight changes in composition and in physical and chemical properties can materially affect the formation, continuation or cessation of the mesomorphic state, 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(93) has put it, this state seems to be especially suited to biological functions and may possibly be the basis of vital activity.

Living sperms, composed in part of protein, nucleo proteins and albumins, have been shown to possess a mesomorphic state(94,95). Ferguson and Brown(96) have reviewed the liquid crystals in living systems.

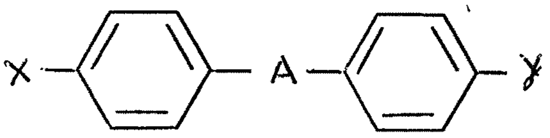
Stewart(97) mentions that there are several good theoretical reasons why matter in the liquid crystalline state should play a part in the structure of living tissues and gives a number of examples where mesomorliphism is observed in biological systems. Chapman(98) describes the essential components of membranes of living cells and connective tissues and the significance of liquid crystals in them.

6. Chemical constitution and Mesomorphic State:

Vorlander 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 a liquid crystalline compound 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 attractions. On raising the temperature the cohesions between the molecules previously holding them together in the crystalline arrangement do not break down uniformly in all directions. There may be some residual cohesions still operating which will tend to hold the molecules together in groups. The transition to the dis-ordered 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.

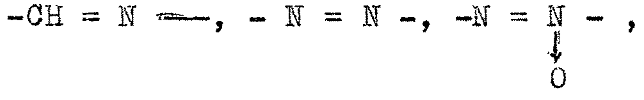
Intermolecular cohesive forces between the molecules ~~is~~ are a requirement for the formation of liquid crystals. However, the intermolecular attractions should not be strong that the melting point of the compound is very high. At high temperature the thermal motion may prevent the existence of an ordered phase. If the intermolecular forces are very weak, the crystals may melt at lower temperature but the cohesive forces may be again weak to maintain the molecules in the ordered state. Thus for a liquid crystal to be formed the cohesive forces operating between elongated molecules must be both anisotropic and of suitable magnitude(99). Another criterion for the formation of liquid crystals is the rigidity of the elongated molecules. If the molecules lack rigidity, flexing may occur along its length and this may prevent the formation of liquid crystal. For example, long chain n-alkanoic acids are non-mesomorphic because the alkyl chains are flexible and these may coil and bend. However, the introduction of unsaturation in the chain makes the molecules more rigid due to $Sp^2$ hybridization and thus 2,4-dienoic acids are mesomorphic.

The majority of the thermotropic type of liquid crystals are aromatic in nature. Aromatic nuclei are polarizable, planar, rigid and if the substituents are placed at proper positions can give rise to mesomorphism. For benzene nuclei the substituents must occupy p, p'-position and be of such kind that they link up at least one other benzene ring which also carries a p-substitutent. It is preferable that the linking group between the two benzene nuclei should also be of rigid nature. This can be represented as follows:

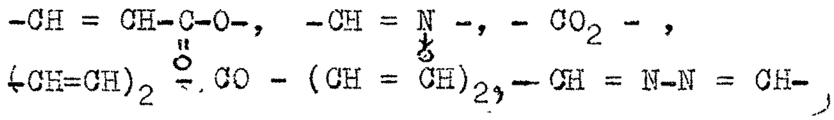


where X and y are the terminal substituents and A the central linkage. The usual central linkages are

$-CH = CH -, -(CH = CH)_n, -C \equiv C-$



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



$-CH = CH-\underset{\overset{\|}{O}}{C}-O-, -CH = \underset{\downarrow O}{N} -, - CO_2 - ,$

$-(CH=CH)_2 .CO - (CH = CH)_2, -CH = N-N = CH-$

$-CH_2-CH_2 -, - O - CH_2-CH_2 - O -, -(CO_2H)_2-$ etc.

The linkage of benzene rings through the O and m-positions is not favourable to the liquid crystal formation because the molecules then become non-linear. However, linearity and rigidity are increased by linking up the benzene rings directly and thus biphenyl provide a rich source of liquid Crystals which are thermally more stable than those of the benzene substituted analogues. It is observed that the benzene ring plays an important role in the formation of liquid crystals. With the increase in the number of aromatic rings, the stability and phase length of the mesophase are increased.

Dewar and Goldberg(100) in their studies have shown that replacement of aromatic rings by saturated alicyclic rings give marked reduction in thermal stabilities of the mesophase indicating that linearity is essential for a compound to exhibit mesomorphism.

Dewar and Riddle(101) studied a number of potentially mesomorphic esters and thioesters in which the central p-phenylene ring of bis(p-methoxyphenyl) terephthalate, or dithioterephthalate, is replaced by mono cyclic, bicyclic saturated, partly saturated and Nitrogen heterocyclic and oxoheterocyclic rings. From these studies they suggest that the geometry is the most important factor in determining the stabilities of the nematic mesophase, the essential requirement being a linear rod-shaped molecule of more or less uniform cross section.

Dewar and Griffin(102) in their thermodynamic study of the role of the central group on the stability of nematic liquid crystals suggest that polarity in the central part of the linear molecule may reduce the nematic-isotropic transition temperature through a reduction in the effective symmetry number, even though polarity in the terminal groups favours the nematic stability. They suggest that the ideal structure for a nematic molecule seems to be a linear non-polar cylinder of uniform cross section with polar ends. They attribute the superiority of the ester(-COO-) and azoxy($-N=\underset{\underset{O}{\downarrow}}{N}-$) linking groups over vinylene(-CH = CH -) or azo(-N=N-) groups to their greater width rather than to their greater polarity.

Mesomorphic compounds containing a heterocyclic ring have been reported by a number of authors(103-107). Gray et. al.(108) have studied some heterocyclic mesogens and ~~has~~ compared with other heterocyclic mesogens. They state~~s~~ that the limited number of heterocyclic mesogens strongly suggests that the dominant effect of the hetero-atom is to produce changes in conjugative interactions within the molecule which affect factors such as polarizability and dipolarity. Intermolecular effects produced by the lone pair of electrons are apparent, in certain cases, also significant.

## 7. The effect of terminal and Lateral Substitutents on Liquid Crystalline Behaviour:

Early reviews state that the molecules of mesogenic compounds should contain moderately dipolar terminal groups. In majority of the cases the substituted compounds exhibit more stable mesophase compared to unsubstituted mesogenic compounds. only for smectic liquid crystals do certain terminal substituents reduce thermal stability.

Gray(99) studied the influence of terminal substituents in pure mesogenic compounds and obtained group efficiency orders in nematic and smectic systems. Wiegand(109) studied the influence of the substituents in alkyl group and modified sterol Skeleton on cholesteric mesophase. Gray(58) and Dave and Vora(110) have studied the effect of substitution in cholesteryl benzoates; they have obtained group efficiency orders for the different substituents in the cholesteric systems.

Most of the terminal alkyl groups found in mesogenic compounds are unbranched. However, a few examples of mesogenic compounds with branched terminal alkyl groups are of course known. It is observed that branching produces a decrease in the thermal stability of the mesophases. When the branching occurs at the first carbon atom of the chain, the effect on thermal stability is the greatest.

The commencement of the smectic or a nematic mesophase in a mesogenic compound often depends on the terminal substituents.

The effects of introducing lateral substituents into elongated molecules of mesogenic compounds are of interest.

The side substituent may force apart the molecules and this may reduce the intermolecular lateral cohesions but at the same time the side substituents may increase the molecular polarizability which in turn may increase the intermolecular attractions. Thus the liquid crystallanity of a mesogen depends upon these effects. An order of the substituent effect for the lateral substituent is given by Gray(99).

Smectic order: $H < F < Cl < Br = NO_2 < Me < I$

Nematic order: $H < F < Me < Cl \leq Br < I = NO_2$

When these transition temperatures are plotted against the breadth of the substituent, the nematic-isotropic transitions fit a good curve whereas the smectic-isotropic transitions do not. The reason for the difference is that the nematic thermal stability is influenced primarily by the breadth effect and the smectic thermal stability by a combination of breadth and dipolar effects.

However, if the substituent occupy certain pockets in the molecule so that the breadth effect is not manifested, it is found to increase the thermal stabilities. 5-Halogeno-6-n-alkoxy-2-naphthoic acids and 4-p-n-alkoxybenzylidene-3'-fluoro-biphenyls provide examples of this type.

Wiegand(110), Gray(99), Dave and co-workers(111,112) studied number of compounds comprising naphthalene nucleus and have found that 2,6 and 1,5-naphthalene derivatives are more mesogenic compared to 1,4 derivatives.

## 8. Mesomorphism in Homologous Series :

To correlate the effect of the structural modifications on mesomorphism the researchers in this field centred their attention around the study of mesomorphism properties of different homologous series of organic compounds. A number of series exhibiting mesomorphism have been synthesized by various workers in the field. When the mesomorphic transition temperatures e.g., nematic-isotropic, smectic-isotropic, cholesteric-isotropic, smectic-cholesteric or smectic-smectic, for the homologous series are plotted against the number of carbon atoms in the n-alkoxy groups, smooth curves may be drawn through points for like related transitions. Usually solid to mesomorphic or isotropic points do not exhibit the regular trends. The mesomorphic-isotropic transition temperatures alternate typically, these lie on two falling curves, the upper one for even and lower one for odd number of carbon atoms in the n-alkoxy chain. For system with n-alkoxy group attached directly to the ring, the reverse situation arises because the oxygen of the ether link in the alkoxy group is equivalent stereochemically to a methylene unit(99).

The odd-even effect becomes less marked as the series is ascended and the two curves merge later in the series. The smectic-nematic temperatures usually do not alternate and lie on a smooth curve which rises steeply at first, then levels out and merges with the falling nematic-isotropic curve. However, there are cases in which the smectic-nematic transition curve does not merge with the following nematic-isotropic transition curve and the last members of the series exhibit nematic mesophase alongwith the smectic mesophase. There are also cases in which the smectic-cholesteric temperatures alternate. These are dealt with in greater detail in the discussion part.

## 9. Mixed Mesomorphism :

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

Schenck et. al.(113,114) showed that a nematic-isotropic transition temperatures of p-azoxyanisole is lowered by the addition of other substances. De kock(115) and Bogojawlensky and Winogradow(116) have examined mixtures of isomorphous substances and have reported the formation of mixed crystals from pairs of substances, one or even both of which are not giving normal liquid crystals. Bogojawlensky et. al., also determined latent or labile transition points (isotropic-nematic) of the non-mesomorphic substances in many cases by extrapolation of the nematic-isotropic transition temperature curve which was linear in most of the cases. Varlander and Gahren(117) also observed that binary mixtures in which the components were non-mesomorphic gave rise to liquid crystals within a certain concentration range when they were melted. Walter(118) has given an explanation to the observation of Varlander and Gahren. He said that the compounds which yield such mixtures are generally very highly crystalline and are not readily super cooled. Consequently a monotropic liquid crystal phase which might be anticipated for them remains latent. If 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 points of the individual components falls below the mixed melting point of the crystalline liquid phase which with chemically related substances should be between the two latent crystalline melting points of pure components. Such a mixture which should form mixed liquid crystals exhibits enantiotropic liquid crystalline properties. Walter studied the binary systems of anisic acid and anisylidene propionic acid (118) which themselves are non-mesomorphic but their mixtures yield mixed liquid crystals within certain limits of concentration. de Kock(115) and Prins(119) 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 transtion temperatures should not in general occur sharply but that as a rule there should be a range of temperatures over which the two liquid phases of different compositions could co-exist, Dave and Dewar(120) reported de Kock's work and obtained a phase diagram which does not show any indication of the two phase liquid system observed by de Kock. They investigated 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 homogenous 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. Dave and co-workers(121, 122,122a) studied number of such systems where one of the component was a nematogen and derived the group efficiency orders. In their review on mixed mesomorphism, Dave and Vora(123) have given the combined group efficiency order for the end groups in the nematic mesophase as follows:

$NO_2 > OEt > OMe > OCOEt = n\text{-}OPr \;\; \phi COMe > NMe_2 > Me =$
$Cl > F > Br > I > OH > NEt_2 > H$.

They considere that the 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 overall polarizability of the system, size of the group, shap of the molecules and even hydrogen bonding and mutual conjugation effects. Gray(58) pointed out that the group efficiency order for nematogenic systems will not hold good for smectogenic systems whose thermal stabilities are governed by quite different factors.

Lohar and co-workers(124,125) recently studied the reliability of extrapolation method for determining latent transition temperatures of non-mesogenic compounds mixed with a nematogen.

Sackmann and Demus(27) identified smectic mesophases on the basis of miscibility criteria and texture phenomena.

Dave et. al(126) studied binary systems comprising a smectic/polymesomorphic (smectic-nematic) substance and non-mesogenic components. They have observed that non-mesogenic component containing-$NO_2$ group enhanced the smectic mesophases thermal stability and in the poly-mesomorphic compound such non-mesogens not only showed an enhancement in smectic phase but completely eliminated nematic mesophase.

Domon and Billard have (127) shown that it is possible to predict the phase diagrams of mixtures of liquid crystals and they have further stated that where two compoments are not isomorphous and completely soluble in each other, two phase regions may be obtained at the mesomorphic-mesomorphic and the mesomorphic-isotropic transitions.

Recently the formation of smectic mesophase in binary mixtures of nematic mesogenic compounds is reported(128). Cladis(129) has reported a new phase diagram for a binary systems where one component is nematogen and the other exhibiting both smectic and nematic mesophases. He reports that the nematic phase occurs at both higher and lower temperature than the smectic pahse.

Vora and Chhangawala(130) have recently reported the formation of a nematic mesophase in the binary system comprising a smectogen and non-mesogenic compounds.

## 10. Physical Properties :

In recent years a large amount of work is being done on the physical properties such as X-ray studies, spectroscopic studies, magnetic resonance studies, Mossbauer effect, viscosity, surface tension, dielectric constant, magnetic susceptibility, ultrasonic and calorimetric studies of liquid crystals.

### 10. a. X-ray Studies :

The first attempt to study the liquid crystals by X-ray structural analysis followed immediately after the discovery of X-ray diffraction(131). Huckel(132) and de Broglie and Friedel(133) studied X-ray diffraction patterns of the liquid crystals. They indicated that the X-ray diffraction patterns for mesomorphic phases and the corresponding ordinary liquids were similar.

Afterwards, more accurate experiments detected some differences between the X-ray patterns of amorphous isotropic liquids and mesophases(134,135). In particular, experiments with a nematic oriented by electric or magnetic fields gave X-ray patterns in which the main diffuse ring shifts into two cresents(136).

Detailed examinations of experiments made earlier than 1940 are available in Gray's book (58) and the review of Brown and Shaw(6), Chistyakov(137) and Chistyakov and Vainshtein(138) recently carried out a number of X-ray studies on liquid crystals.

de Vries(139) proposed more than one type of nematic phases with the help of X-ray diffraction studies supported by polarizing microscopy. Recently de Vries(28), on the basis of X-ray studies has proposed several modifications in the classification of liquid crystals.

Falgeuirettes and Delord(140) have recently reviewed the X-ray diffraction by liquid crystals obtained from non-amphiphilic systems. They conclude that X-ray diffraction remains very valuable and precise method for investigating mesophases, especially if one can use oriented specimens. In combination with other methods such as optical studies of the mesophases or differential thermal analysis, X-ray diffraction is an essential technique for the investigation of the polymorphism of mesophases(141).

## 10. b. Infrared, Raman, Visible and Ultraviolet Spectroscopic Studies :

One might ask what information is expected from a study of the molecular absorption spectra of liquid crystals.

The main definite feature of a mesophase is the existence of a degree of long-range translational or orientational order intermediate between that of the completely ordered solid and the disordered amorphous liquid. For spectrscopic studies, the crystalline solid and the amorphous isotropic liquid serve as points of reference for the comparision of the wave numbers, intensities, and shapes of absorption bands. Such comparisons can lead to more detailed information concerning the dynamics of molecular motion in a mesophase. In addition, the long-range order usually leads to anisotropies in the physical properties including absorption intensities measured in different directions with polarized radiation. These effects may be used to determine the degree of order. Finally some liquid crystals such as well oriented nematic , can be used as an orienting solvent for absorption polarization studies of dissolved molecules(142).

Maier and Englert(143) studied IR of number of mesogens. For all compounds studied the spectra of nematic and amorphous isotropic liquids were essentially equivalent except for some changes in relative intensity attributed to the orientation in the nematic. They also reported interesting results concerning the spectra of the crystalline solid phases of the mesogenic azoxyphenol ethers, having single conformation believed to contain the extended zig-zag chain. Other twisted rotational conformations appear to be accomodated in the crystal lattices of propyl and butyl compounds dependent on the growth rate of the crystals from solution.

L'vova and Sushchinski(144) studied IR spectra of nematogens and cholesterogens at different transition temperatures and observed marked changes at solid mesomorphic transition temperatures compared to at mesomorphic-isotropic transition temperature.

The first Raman study of the nematic phase was reported by Koller et. al.(145) for unoriented and oriented nematic mesophase of p-n-butoxybenzoic acid. Bulkin et.al.(146) and Zhadanova et. al. (147) have studied Raman spectra.

The determination of the degree of order in nematics by infrared measurements of dichroism is reported by number of workers(148-151).

Ultraviolet and visible spectroscopic investigations of liquid crystals have been confined mostly to polarization studies of certain π-electronic absorption bands of the liquid or of oriented solute molecules dissolved in the liquid.

The ultraviolet spectra of the π-electronics state of stilbene., azobenzene etc. have been discussed and assigned by Saupe(152).

Several investigations have been reported in which the nematic phase or cholesteric mixtures were used as orientating solvents for polarization studies of the ultraviolet spectra(153,154).

Ceaser and Gray(155) used nematogen as solvent for polarization study. Heilmeier and Zanoni(156) have used the orientation induced by an electric field to bring about switching in colour of a sample containing dissolved dye molecules. In all these investigations, the long molecular axes of the solute molecules align parallel to the optic axis of the nematic phase. Recently Bloom and Hung have reported their UV and visible spectral study of number of azo compounds oriented in a nematogen (157) and of liquid crystalline cholesteryl azo dyes(158).

### 10. c. Magnetic Resonance Study :

During the past few years a large number of papers are published on magnetic resonance studies of liquid crystals. Spencer and co-workers(159-162) have observed that the NMR spectrum of p-azoxyanisole in the nematic phase was different than that of seen in solid or in normal liquids which they attributed to parallel orientation of molecules in nematogenic phase. Saupe and Englert(163) were the first to recognize 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 a wealth of information could be obtained about the ordered solute molecule including relative bond length and angles to a precision unequalled by other techniques. Thus their work opened a new avenue for liquid crystal research.

### (i). Nuclear Magnetic Resonance :

There are several interactions which may contribute to the NMR spectrum, seen from a liquid crystal or from a compound dissolved and ordered in a liquid crystal, of these the magnetic dipole coupling between various nuclei within the molecule is of primary interest. In high resolution NMR spectroscopy, the phenomena which result from interactions of the nuclei with electrons such as chemical shifts and indirect coupling of nuclear spins may become important. The success of NMR in liquid crystal systems is due to the rapid translational diffusion of the molecules in many of these phases. Consequently 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 NMR spectrum exists at all is 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.

To reduce the complexity of the spectrum of liquid crystal and molecules; small liquid crystal molecule is selected. Rowell et. al. (164) selectively deuterated p-azoxyanisole to simplify the spectrum. Saupe(165) and later Nehring and Saupe(166) observed little variation in NMR spectra indicating that dipole forces are of minor importance. Khetrapal and co-workers(167,168) have studied NMR spectra of different compounds oriented in nematic mesophase, Diehl et. al.(169) have studied the effect of electric field on NMR spectrum of molecules oriented in the nematic phase.

Yanoni(170) has succeeded in ordering a solute molecule in a smectic A phase. Khetrapal et.al.(171) have studied the spectra of different molecules in lyotropic mesophase.

A number of review papers on NMR have appeared in the literature(172-175).

### (ii). Electron Paramagnetic Resonance :

A technique which has been gaining interest in liquid crystal studies is that of electron paramagnetic resonance (EPR). The compounds which show liquid crystallanity are not, in general, paramagnetic. Therefore, this technique is limited to solute studies where the solute molecules contain 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 properties of this state of matter are strongly dependent on dissolved foreign substances. The first reported study of EPR in liquid crystals was that of Carrington and Luckhurst(176). The vanadyl acetylacetonate(VAAC) containing $Vo^{2+}$ radical has been most popular probe in recent investigations. Chen and Luckhurst(177) have studied the effect of solute concentration on the order of nematic phase. They report that the presence of the solute does not seriously disturb the order of the nematic mesophase.

Sackmann and Krebs have reported ESR spectra of charge transfer complexes oriented in the liquid crystalline phase(178).

### (iii). Mössbauer Effect :

One of the most spectacular and significant of the recent investigations in liquid crystals is that of the observation of the Mossbauer effect in these phases. Uhrich et. al.(179) for the first time studied the spectrum 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. Sakamoto et.al. (182) and Kartha and Padmini(183) studied viscosity of cholesteric esters by using cone and plate viscometer.

### 10(e) SURFACE TENSION:

Ferguson and Kennedy(184) found that the surface tension of the mesophases increases with rising temperature. Naggior (185) 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 the observations of Ferguson and Kennedy, Schwartz and Moseley(186) confirmed Naggiar's results by studing p-azoxyphenetole and ethyl p-azoxybenzoate using the ring method on a du Nouy tensiometer Churchil and Bailey(187) recently determined the surface tension of liquid crystals in the nematic and isotropic phases using the pendant drop method.

### 10(f) Dielectric Constant

Kast(189) has given a critical summary of the work done in this field on liquid crystals upto 1931. Bhide and Bhide (190) measured dielectric constant and absorption of p-azoxyanisole and cholesteryl benzoate by the resonance method at different frequencies. Avadhanlu and Murty(191) studied the effect of electonic field on the molecular alignment in the liquid crystals using dielectric constant measurements.

10(g) Calorimetry:

Calorimetry is a valuable method for the detection of phase transitions. It yields quantitative results and therefore, conclusions may be drawn concerning the nature of the phases which participate in the transitions. Calorimetric measurements have been made, using adiabatic calorimetry, differential scanning calorimetry (DSC) and differential thermal analysis(DTA).

Significant thermodynamic studies have been reported in a series of papers by Arnold and co-workers(192-195). They use the adiabatic calorimetry for the determination of heat capacities and latent heats. Barrall et.al.(196) and Ennulat(197) have used DSC and DTA methods. Brown et.al.(43) have compared the results of Arnold and co-workers and Barrall et.al. They state that the large discrepancy in these values is an indication of the uncertainity of the DTA method and suggest that caution should be exercised in the interpertation of the results based on this method. The entropy changes of nematic-isotropic and cholesteric-isotropic transition are of the same order of magnitude. Marzotko and Demus(198) reviewed the previous calorimetric studies on liquid crystals and found that there are certain trends of transition enthalpies in homologous series.

Dewar and Griffin(102) recently report that the change in nematic-isotropic transition temperatures arise from changes in the entropy of transition and not in the heat of transition. Their results lead to some general conclusions concerning the relationship between the structure and the mesophase stability. Recently Barrall and Johnson have revied the thermal properties of liquid crystal(199).

## 10(h) Chromatography:

The use of liquid crystals as stationary phases in gas liquid - chromatogrphy(GLC) is very promising. Kelker(200), and Dewar et.al.(201,202) carried out the initial investigation in this field. Dewar et.al.mention(201) that the results of the mixed liquid crystal study of Dave and Dewar(120) which showed that linear solute molecules have been shown to have smaller disruptive effect on nematics than by bulky non-linear molecules, presumably because the former fit more readily into the nematic 'lattice' being oriented with their long axes parallel to those of the solvent molecules, prompted them to use liquid crystals as stationary phases. Such behaviour suggested that nematic solvents might display selectivity towards solute molecules on the basis of molecular shape.

Number of liquid crystals, smectogens, nematogens and cholesterogens are tried as stationary phases in GLC. Schroeder(203) has reviewed the use of liquid crystals in Gas-liquid chromatography.

## 11. Applications of Liquid Crystals:

### 11.a. Cholesteric Liquid Crystals:

The important contributing factor in the application of cholesteric liquid crystal is its optical property. When illuminated with white light the cholesteric liquid crystals scatter light to give irridescent colours with change in temperature or pressure new colours are produced.

#### (i) Thermographic measurements of human skin(204-206)

Skin temperature measurements is of great potential value in biological study. The skin over subcutaneous lesions and tumors is warmer than the normal surrounding skin. Thermotopographic measurement by liquid crystals forms an important test for measurement of size and response to the treatment, cholesteric liquid thermography permits immediate visualization of surface temperature.

#### (ii) Clinical thermometer:

A cholesteric liquid crystal can be used in the preparation of the clinical thermometer. A thin strip of black polyvinyl chloride is coated with cholesteric material which is then covered with the transparent acrylic polymer. These are used for the rapid detection of fever especially by oral temperature measurements.

(iii) Non-Destructive testing(99, 206,207)

Cholesteric liquid crystals can be used for the non-destructive testing of materials in many ways. They can be used to reveal blockages in heat conducting systems,local overheating in metal surfaces due to eddy curents in wind-tunnel experiments variation in heat transfer between well-bonded and poorly bonded areas in honeycomb structure and to locate hot spots in integrated circuits. They are also used in mapping out heating elements in moulded rubber pads, cholesteric liquid crystals have found use as temperature sensors in studies of heat flow and convection in weightless liquids and gases. These studies were made during the return flight from the moon of the space ship Apollo 14.

(iv) Publicity materials and toys:

Cholesteric liquid crystals react to pressure as well as temperature by colour changes. These can be used to make some very interesting temperature or pressure sensitive publicity materials and toys. The phenomenon is very impressive when the material is incroporated in plastic sheets against a black background.

(v) Other uses(99)

In addition to their uses for temperature measurements cholesteric liquid crystals may be used as an analytical tool to detect the presence of very small amount og gases or solvent vapours(acetone, chloroform,petrol,benzene etc.) by means of colour changes(208). The lower limit of detection is about 1 ppm. They are reported to have potential applications as detectors of small amount of contaminants in the atmosphere. They also provide a means for measuring microwave energy, ir. and visible light and laser output.

## 11.b Nematic liquid Crystals

Recently nematic and nematic - cholesteric mixtures of substances have been employed which have stimulated progress in electronic research and industry. In the liquid crystalline state compounds with nematic mesophase possess the ability to scatter light on the strength of an applied electric field. Thus the principle can be employed to convert information from an electrical form to an optical form.

## 11.(c) Liquid crystal display devices:(209-212)

(i) In recent years a large number of devices utilizing nematic and cholesteric liquid crystals are produced. A liquid crystal device differs fundamentally from an electronic display device such as cathode ray tube in that a liquid crystal device generates no light of its own but it scatters light. Such a device offers two advantages:(a) Since it reflects light instead of generating light, it can be viewed under a wide range of light conditions including direct sunlight or a flood light,

(ii) Since the liquid crystal device does not emit light, it should require relatively little power.

A liquid crystal device(cell) is made by sandwiching a liquid crystal mixed with some dopent between two glass plates which are coated by some electrically conducting transparent material such as tin oxide. By applying the electric ~~current~~ field (10-300 volts) to the plates the liquid crystalline molecules can be oriented in the desired manner and cell becomes opalescent. When the field is switched off the cell generally becomes transparent again within micro second. Some liquid crystal systems remain oplascent even after the electric field is switched off, for the latter to become transparent again, a high frequency voltage must be applied. This phenomenon is used to produce memory storage devices. Liquid crystals may be used to provide a thin screen television display.

New uses for liquid crystal displays are rapidly emerging in all areas of applications related technology.

A large volume of published materials is available on the application of liquid crystals(99,212,213-215).

## AIM AND SCOPE OF THE PRESENT WORK

A Large amount of work has been done on the synthesis of cholesterogenic nematogenic and smectogenic compounds. A Number of homologous series exhbiting the above mesophases are synthesized and studied to investigate and establish the relationship between molecular structure on liquid crystalline properties and phase transitions. Recent technological applications of liquid crystals created upheaval in the synthasis of new liquid crystals. Comperatively less work has been done on azo mesogens as they are coloured compounds. Recently the azodyes are being used in liquid crystal display devices for the guest-host int eractions. This has created an interest for the synthesis of new suitable azodyes.

Mesogenic azo dyes finding applicationsin technological fields prompted to synthesize such ~~more~~ dyes as other azo dyes were being synthesized and evaluated for the part of this thesis.

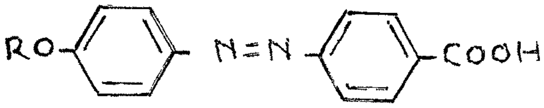
It was proposed to synthesize four new azo mesogenic homologous series, with a view to enhance our knowledge of the effect of chemical constitution on such mesogens,this inturn may help to bring out more suitable azodyes exhibiting mesophases.

The synthesized dyes are studied for their mesomorphic properties. The thermal stabilities of all the series are compared with those of related homologous series.

# EXPERIMENTAL

# EXPERIMENTAL

## 1., Preparation of 4(4'-n-Alkoxy-2'-Methylphenylazo) Benzoic Acids :



## 1.a. Preparation of 4(4'-Hydroxy-2'-Methylphenylazo) Benzoic Acid :

p-Aminobenzoic acid (13.7g) was dissolved in 1:1 hydrochloric acid (150 ml) and the solution was cooled to 0°C. This was diazotized by adding saturated sodium nitrite solution (6.9g) with constant stirring. After the completion of diazotization the cold solution of this diazotized p-aminobenzoic acid was coupled with m-cresol (10.8g) in alkaline solution at 0-5°C. After the addition of diazotized solution the material was left for about fifteen minutes and then acidified with concentrated hydrochloric acid. The precipitate obtained was filtered and washed with water. It was then dried and crystallized from ethyl alcohol. m.p. 247, yield 76%.

Analysis :

Found : N, 10.65%

Required : N, 10.94%

## 1.b. Preparation of 4(4'-n-Alkoxy-2'-Methylphenylazo)-Benzoic Acids :

The alkylation of p-hydroxybenzoic acid is described by B.Jones(216). Dave and Vora(217) have observed that this method gives poor yield for the higher members of the series. They have described the modified method of alkylation. In the present study the modified method of Dave and Vora(217) is used for the alkylation of all the hydroxy acids.

4(4'-Hydroxy-2'-methylphenylazo) benzoic acid (1 mole) was dissolved in (about 270 ml) solution of alcoholic potassium hydroxide (2 mole). To this respective alkyliodide or alkylbromide (1.1 mole) was added and the mixture was refluxed for 2 to 3 hours for the completion of the reaction. The clear reaction mixture was then added to water (350 ml) with stirring and acidified with concentrated hydrochloric acid. The light orange coloured solid obtained was filtered, dried and crystallized from acetic acid or alcohol till the constant transition temperatures are obtained. In the case of higher homologues, n-amyloxy to n-octadecyloxy derivatives, the heating was continued for four to six hours.(Yield : 70 to 80%).

The melting points and transition temperatures are recorded in Table ~~1~~ 5. The analytical data is given in Table ~~5~~ 1.

## 2. Preparation of Alkyl p-Aminobenzoates(218):

### 2.a. Preparation of Ethyl p-Aminobenzoate(218):

Absolute ethanol was prepared by the method described in the practical organic chemistry(218) by using quicklime as dehydrating agent.

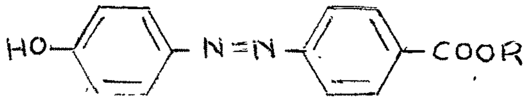
Dry hydrogen chloride gas was passed through the absolute ethanol (80 ml) until saturated in a 250 ml round bottom flask to increase in weight ~~up~~to 20 grams. p-Aminobenzoic acid (12 g) was then added to it and refluxed with double walled condenser for about two hours by using a guard tube. The content of the flask was then poured in water (1000 ml) and neutralized by adding saturated solution of sodium carbonate. Ethyl-p-aminobenzoate obtained was crystallized from dilute alcohol in rhombohedra form. m.p. 91°C (reported 91°C)(218). yield 75%.

### 2.b. Preparation of Methyl p-Aminobenzoate(219) and Propyl p-Aminobenzoate(220):

Methyl-p-aminobenzoate and propyl p-aminobenzoate were prepared by using absolute methanol and 1-propanol as described above respectively, passing dry hydrogen chloride gas till saturation and condensing them with p-aminobenzoic acid as described above. The products obtained were crystallized from alcohol. Methyl p-aminobenzoate m.p. 112° (reported 112°), n-propyl p-aminobenzoate m.p. 73° (reported 73-4°).

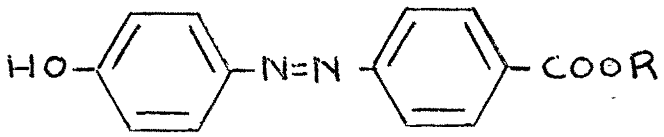
## 3. Preparation of Alkyl 4-(4'-n-Alkoxyphenylazo) Benzoates:

### 3.a. Preparation of Alkyl 4-(4'-Hydroxyphenylazo) Benzoates :



Alkyl p-aminobenzoates (1 mole) were dissolved in cold 1:1 hydrochloric acid (150 ml) and the solutions were cooled to 0°C. These were then diazotized by adding saturated sodium nitrite solution (6.9g) as described earlier with constant stirring. After the completion of diazotization, the cold solution of these diazotized alkyl-p-aminobenzoates were coupled with phenol (1 mole) in alkaline solution at 0-5°C. After the addition of diazotized solution the material was left for fifteen minutes. The solutions were acidified with concentrated hydrochloric acid. The precipitates obtained were filtered and washed with water, and crystallized from appropriate solvent.

The analytical data are given below :



| No. | Alkyl group R | Cryst-allized from | Shape and colour | M.Ps. °C | Analytical data | |
|---|---|---|---|---|---|---|
| | | | | | %Found N | %Required N |
| 1. | Methyl | Alcohol | Orange flackes | 212.0 | 10.80 | 10.94 |
| 2. | Ethyl | Alcohol | Orange needles | 163.0 | 10.80 | 10.37 |
| 3. | Propyl | Alcohol | Orange needles | 130.0 | 9.52 | 9.86 |

### 3.b. Alkylation of Alkyl 4-(4'-Hydroxyphenylazo) Benzoates:

The alkylation was carried out as per the method of Vyas and Shah(221).

### 3.c. Preparation of Methyl 4-(4'-n-Alkoxyphenylazo) Benzoates :

Methyl 4-(4'-Hydroxyphenylazo) benzoate (0.1 mole), anhydrous potassium carbonate (0.15 mole) and respective n-alkyliodide or bromide (0.15 mole) were added to dry acetone (60 ml). The mixture was refluxed using a double walled refluxed condenser and water bath for three to four hours. In the case of higher homologues the reflux period was extended upto six hours for completion of the reaction. The reaction mixture was filtered through cotton and acetone was evaporated and the solid separated was suspended in ice water and then it was filtered and washed with 2% sodium hydroxide solution followed by water. It was then dried and crystallized from alcohol till the constant transition temperatures are obtained. Yield: 70 to 80%.

The melting points and transition temperatures are recorded in Table 2. The analytical data are given in Table 6.

### 3.d. <u>Preparation of Ethyl 4-(4'-n-Alkoxyphenylazo) Benzoates</u> :

Ethyl 4-(4'-hydroxyphenylazo) benzoate (0.1 mole) anhydrous potassium carbonate (0.15 mole) and ~~respective~~ either alkyl iodide or bromide (0.15 mole) were added to dry acetone (60 ml). The mixture was refluxed using double walled reflux condenser and water bath for three to five hours. On working out the reaction mixtures as mentioned above the ethyl-4-(4'-n-alkoxyphenylazo) benzoates were obtained. Crystallization was carried out till the constant transition temperatures are obtained, yield 70-80%.

The melting points and transition temperatures are recorded in Table ~~3~~ 7, the analytical data are given in Table ~~7~~. 3

## 3.e. Preparation of n- Propyl 4-(4'-n-Alkoxyphenylazo) Benzoates :

n-Propyl 4-(4'-hydroxyphenylazo) benzoate (0.1 mole), anhydrous potassium carbonate (0.15 mole) and respective alkyl iodide or bromide (0.15 mole) were added to dry acetone (60 ml). The mixture was refluxed using double walled reflux condenser and water bath for three to five hours. On working out the the reaction mixture as mentioned above the propyl-4-(4'-n-alkoxyphenylazo) benzoates were obtained. Crystallization was carried out till the constant transition temperatures are obtained, yield 70-80%.

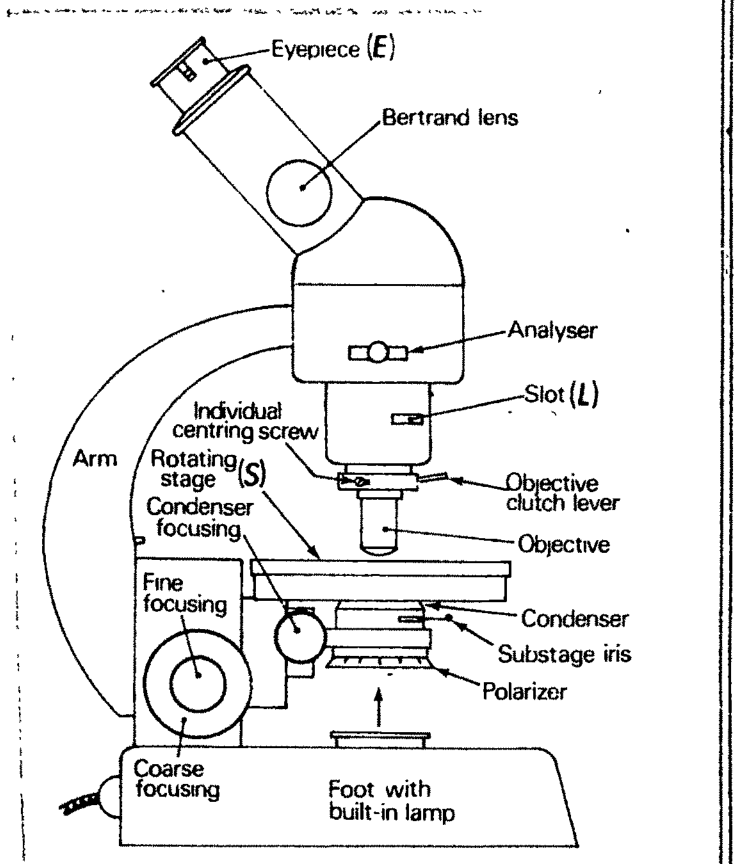
The melting points and transition temperatures are recorded in Table ~~4~~ 8. The analytical data are given in Table ~~8~~. 4

## 4. Study of Transition Temperatures :

### 4.a. Determination of Transition Temperatures With the Help of Microscope :

It is rather difficult to detect different textures of nematic and smectic mesophases accurately by the usual method. Hence, the use of a microscope becomes essential for the detection of such changes with great accuracy. The microscope used in this investigation for the mesomrophic transition temperature was a Thermopan Kofler polarising microscope having a binocular attachment~~s~~ for observing the specimen on the slide. It is fitted with an electrical heating block. This block is provided with a slide slot to insert the slide and a thermometer pocket to insert the thermometer. The temperature of the heating block can be electrically controlled by a regulator from room temperature to 360°C and can be conveniently read by the suitable thermometers graduated in 0.1°C. The specimen is illuminated by polarized light, the light source being ~~as~~ an electric lamp. By means of the eyepieces in the binocular tubes, the specimen can be seen.

The slides are prepared by three different methods. In the first case the substance is heated on the slide up to its isotropic temperature, a coverslip is placed over it and cooled. In the second method the substance is dissolved in a suitable solvent. A few drops of the solution of the compound are placed on the slide and the solvent allowed to evaporate. A coverslip is then placed over it. In the third case slides are prepared by heating the substances on the slide upto its mesomorphic temperature and putting the coverslip over it and cooling .



[illegible]. The polarizing microscope.

The accuracy of the heating device is checked by taking melting points and/or transition points of ~~the~~ known compounds, Such as benzoic acid, a-naphthol, succinic acid, anthracene, p-azoxyanisole, p-methoxycinnamic acid, p-acetoxybenzylidene-p-phenitidine, ethyl p-azoxybenzoate etc.

To determine the various, transitions, the prepared slide with a thin section of the material, is inserted in the specimen chamber and the temperature is raised fairly fast (5°C/minute) to find the approximate transition temperatures. The heating stage is then allowed to cool until the stable solid reappears. The measurements are then repeated with a rate of heating 1°C per minute from 5°C below the transition points to be observed. The transitions and the various phases are clearly observed and recorded by the appearance of the focal-conic, plane, homeotropic and the threaded structures of the smectic and nematic phases in the polarized light. The transition to the isotropic liquid is clealy marked when the field of vision becomes extinct in polarized light.

In the compounds exhibiting smectic mesomorphism, the focalconic pattern is frequently maintained in the solid when the thin section of the glass slide is prepared by cooling the slide slowly. This pseudomesomorphic condition often created a difficulty ~~to find~~ in finding the solid-smectic transition; however, the disappearance of cleavage lines in the solid is taken as the solid-smectic transition. To confirm the change the solid was disturbed with the help of a spatula; in the case of smectic phase the disturbed texture can be seen indicating that it is not solid and the transition has taken place. In the enantiotropic mesomorphism, all the transitions are clearly detected while cooling the isotropic liquid, the reverse transitions taking place at the same temperature or within ± 0.2°C to 1.5°C. Isotropic-nematic changes are observed by the separation of small bubbles from the isotropic liquid. These bubbles then coalesce and a threaded region which is characteristic of the nematic phase is formed. The isotropic-smectic transition is indicated by the separation of batonnets which coalesce to form fine mosaic of focal-conic pattern. The monotropic transition points are determined by carefully observing the isotropic liquid as it cools slowly until the batonnets of the smectic phase or bubbles of the nematic phase appear. In the case of monotropic mesomorphism, it was possible to raise the temperature before crystallization took place and the mesophase disappeared at the same temperature at which it had appeared, thus confirming the isotropic-mesomorphic transition temperature. All the compounds were observed contineuously under the microscope from their solid state to the isotropic state while heating and from isotropic state to the solid state while cooling so that no transition could escape unnoticed.

In the case of homologous series "4-(4'-n-alkoxy-2'-methylphenylazo) benzoic acids" some compounds decompose before they become isotropic. In such case the slide prepared by the second method gives accurate results. In the case of other homologous series slides prepared by third method gave quite satisfactory and reproducible results.

## Table 1

### 4-(4'-n-Alkoxy-2'-Methylphenylazo) Benzoic acids

| No. | n-Alkyl group | Crystallized from | Molecular formula | % Found | | | % Required | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | C | H | N | C | H | N |
| 1. | 2. | 3. | 4. | 5. | 6. | 7. | 8. | 9. | 10. |
| 1. | Methyl | Alcohol | $C_{15}H_{14}N_2O_3$ | 66.13 | 4.799 | 10.39 | 66.66 | 5.185 | 10.37 |
| 2. | Ethyl | Alcohol | $C_{16}H_{16}N_2O_3$ | 66.79 | 5.198 | 9.740 | 67.60 | 5.632 | 9.859 |
| 3. | Propyl | Alcohol | $C_{17}H_{18}N_2O_3$ | 68.08 | 5.906 | 9.441 | 68.46 | 6.040 | 9.395 |
| 4. | Butyl | Alcohol | $C_{18}H_{20}N_2O_3$ | 69.94 | 6.811 | 9.095 | 69.23 | 6.410 | 8.974 |
| 5. | Pentyl | Alcohol | $C_{19}H_{22}N_2O_3$ | 69.98 | 6.30 | 8.565 | 69.93 | 6.748 | 8.586 |
| 6. | Hexyl | Alcohol | $C_{20}H_{24}N_2O_3$ | 70.77 | 7.238 | 8.087 | 70.58 | 7.588 | 8.235 |

Table 1 (cont.)

| 1. | 2. | 3. | 4. | 5. | 6. | 7. | 8. | 9. | 10. |
|---|---|---|---|---|---|---|---|---|---|
| 7. | Heptyl | Alcohol | $C_{21}H_{26}N_2O_3$ | 70.69 | 6.902 | 7.650 | 71.18 | 7.344 | 7.907 |
| 8. | Octyl | Alcohol | $C_{22}H_{28}N_2O_3$ | 71.86 | 7.190 | 8.150 | 71.73 | 7.608 | 7.608 |
| 9. | Decyl | Alcohol | $C_{24}H_{32}N_2O_3$ | 72.25 | 7.650 | 7.545 | 72.72 | 8.080 | 7.070 |
| 10. | Dodecyl | Alcohol | $C_{26}H_{36}N_2O_3$ | 73.15 | 8.118 | 6.500 | 73.58 | 8.490 | 6.603 |
| 11. | Tetradecyl | Alcohol | $C_{28}H_{40}N_2O_3$ | 73.93 | 9.082 | 5.883 | 74.33 | 8.849 | 6.192 |
| 12. | Hexadecyl | Alcohol | $C_{30}H_{44}N_2O_3$ | 74.49 | 9.260 | 5.423 | 74.98 | 9.166 | 5.833 |
| 13. | Octadecyl | Alcohol | $C_{32}H_{48}N_2O_3$ | 75.14 | 9.886 | 5.374 | 75.59 | 9.448 | 5.511 |

### Table 2.

Methyl 4-(4'-n-Alkoxyphenylazo) Benzoates

| No. | n-Alkyl group | Crystallized from | Molecular formula | % Found | | | % Required | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | C | H | N | C | H | N |
| 1. | 2. | 3. | 4. | 5. | 6. | 7. | 8. | 9. | 10. |
| 1. | Methyl | Alcohol | $C_{15}H_{14}N_2O_3$ | 67.12 | 5.486 | 10.86 | 66.66 | 5.185 | 10.37 |
| 2. | Ethyl | Alcohol | $C_{16}H_{16}N_2O_3$ | 67.64 | 5.969 | 10.19 | 67.60 | 5.632 | 9.859 |
| 3. | Propyl | Alcohol | $C_{17}H_{18}N_2O_3$ | 68.71 | 6.502 | 9.814 | 68.46 | 6.040 | 9.395 |
| 4. | Butyl | Alcohol | $C_{18}H_{20}N_2O_3$ | 69.21 | 6.355 | 9.239 | 69.23 | 6.410 | 8.974 |
| 5. | Pentyl | Alcohol | $C_{19}H_{22}N_2O_3$ | 69.87 | 6.683 | 8.366 | 69.93 | 6.748 | 8.586 |
| 6. | Hexyl | Alcohol | $C_{20}H_{24}N_2O_3$ | 70.43 | 7.003 | 8.111 | 70.58 | 7.588 | 8.235 |

Table 2 (cont.)

| 1. | 2. | 3. | 4. | 5. | 6. | 7. | 8. | 9. | 10. |
|---|---|---|---|---|---|---|---|---|---|
| 7. | Heptyl | Alcohol | $C_{21}H_{26}N_2O_3$ | 71.11 | 7.298 | 7.706 | 71.18 | 7.344 | 7.907 |
| 8. | Octyl | Alcohol | $C_{22}H_{28}N_2O_3$ | 72.33 | 7.665 | 7.392 | 71.18 | 7.608 | 7.608 |
| 9. | Decyl | Alcohol | $C_{24}H_{32}N_2O_3$ | 72.98 | 8.112 | 7.008 | 72.72 | 8.080 | 7.070 |
| 10. | Dodecyl | Alcohol | $C_{26}H_{36}N_2O_3$ | 73.53 | 8.443 | 6.500 | 73.58 | 8.490 | 6.603 |
| 11. | Tetradecyl | Alcohol | $C_{28}H_{40}N_2O_3$ | 74.11 | 8.663 | 6.133 | 74.33 | 8.849 | 6.192 |
| 12. | Hexadecyl | Alcohol | $C_{30}H_{44}N_2O_3$ | 74.68 | 9.184 | 5.691 | 74.98 | 9.166 | 5.833 |
| 13. | Octadecyl | Alcohol | $C_{32}H_{48}N_2O_3$ | 75.52 | 9.384 | 5.462 | 75.59 | 9.448 | 5.511 |

## Table 3

### Ethyl 4-(4'-n-Alkoxyphenylazo) Benzoates

| No. | n-Alkyl group | Crystallized from | Molecular formula | % Found | | | % Required | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | C | H | N | C | H | N |
| 1. | 2. | 3. | 4. | 5. | 6. | 7. | 8. | 9. | 10. |
| 1. | Methyl | Alcohol | $C_{16}H_{16}N_2O_3$ | 67.41 | 6.109 | 10.11 | 67.60 | 5.633 | 9.859 |
| 2. | Ethyl | Alcohol | $C_{17}H_{18}N_2O_3$ | 68.11 | 5.555 | 9.493 | 68.45 | 6.040 | 9.395 |
| 3. | Propyl | Alcohol | $C_{18}H_{20}N_2O_3$ | 69.66 | 5.996 | 9.059 | 69.23 | 6.410 | 8.974 |
| 4. | Butyl | Alcohol | $C_{19}H_{22}N_2O_3$ | 69.76 | 6.900 | 8.851 | 69.94 | 6.748 | 8.589 |
| 5. | Pentyl | Alcohol | $C_{20}H_{24}N_2O_3$ | 70.58 | 7.243 | 8.941 | 70.59 | 7.058 | 8.235 |
| 6. | Hexyl | Alcohol | $C_{21}H_{26}N_2O_3$ | 71.58 | 7.688 | 8.399 | 71.19 | 7.345 | 7.909 |

Table 3 (cont.)

| 1. | 2. | 3. | 4. | 5. | 6. | 7. | 8. | 9. | 10. |
|---|---|---|---|---|---|---|---|---|---|
| 7. | Heptyl | Alcohol | $C_{22}H_{28}N_2O_3$ | 71.64 | 7.600 | 7.408 | 71.73 | 7.608 | 7.608 |
| 8. | Octyl | Alcohol | $C_{23}H_{30}N_2O_3$ | 72.12 | 7.596 | 7.183 | 72.25 | 7.853 | 7.329 |
| 9. | Decyl | Alcohol | $C_{25}H_{34}N_2O_3$ | 73.12 | 8.163 | 6.638 | 73.17 | 8.292 | 6.829 |
| 10. | Dodecyl | Alcohol | $C_{27}H_{38}N_2O_3$ | 73.83 | 8.610 | 6.333 | 73.97 | 8.676 | 6.392 |
| 11. | Tetradecyl | Alcohol | $C_{29}H_{42}N_2O_3$ | 73.99 | 8.938 | 6.083 | 74.67 | 9.012 | 6.008 |
| 12. | Hexadecyl | Alcohol | $C_{31}H_{46}N_2O_3$ | 75.13 | 9.011 | 5.588 | 75.30 | 9.311 | 5.702 |
| 13. | Octadecyl | Alcohol | $C_{33}H_{50}N_2O_3$ | 75.39 | 9.381 | 6.101 | 75.86 | 9.578 | 5.564 |

## Table 4

n-Propyl 4-(4'-n-Alkoxyphenylazo) Benzoates

| No. | n-Alkyl group | Crystallized from | Molecular formula | % Found |  |  | % Required |  |  |
|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  | C | H | N | C | H | N |
| 1. | 2. | 3. | 4. | 5. | 6. | 7. | 8. | 9. | 10. |
| 1. | Methyl | Alcohol | $C_{17}H_{18}N_2O_3$ | 68.90 | 6.331 | 9.809 | 68.45 | 6.040 | 9.397 |
| 2. | Ethyl | Alcohol | $C_{18}H_{20}N_2O_3$ | 69.34 | 6.753 | 9.425 | 69.23 | 6.409 | 8.974 |
| 3. | Propyl | Alcohol | $C_{19}H_{22}N_2O_3$ | 69.56 | 6.428 | 9.028 | 69.93 | 6.747 | 8.590 |
| 4. | Butyl | Alcohol | $C_{20}H_{24}N_2O_3$ | 70.86 | 7.480 | 8.701 | 70.60 | 7.058 | 8.235 |
| 5. | Pentyl | Alcohol | $C_{21}H_{26}N_2O_3$ | 70.76 | 7.236 | 8.407 | 71.19 | 7.345 | 7.911 |
| 6. | Hexyl | Alcohol | $C_{22}H_{28}N_2O_3$ | 71.44 | 7.432 | 8.065 | 71.74 | 7.610 | 7.610 |

Table 4 (cont.)

| 1. | 2. | 3. | 4. | 5. | 6. | 7. | 8. | 9. | 10. |
|---|---|---|---|---|---|---|---|---|---|
| 7. | Heptyl | Alcohol | $C_{23}H_{30}N_2O_3$ | 72.63 | 8.226 | 7.828 | 72.24 | 7.852 | 7.330 |
| 8. | Octyl | Alcohol | $C_{24}H_{32}N_2O_3$ | 72.79 | 8.114 | 7.517 | 72.73 | 8.079 | 7.071 |
| 9. | Decyl | Alcohol | $C_{26}H_{36}N_2O_3$ | 73.38 | 8.138 | 6.201 | 73.58 | 8.489 | 6.604 |
| 10. | Dodecyl | Alcohol | $C_{28}H_{40}N_2O_3$ | 74.23 | 8.436 | 6.100 | 74.56 | 8.851 | 6.195 |
| 11. | Tetradecyl | Alcohol | $C_{30}H_{44}N_2O_3$ | 74.53 | 9,232 | 6.300 | 75.01 | 9.168 | 5.834 |
| 12. | Hexadecyl | Alcohol | $C_{32}H_{48}N_2O_3$ | 75.15 | 9.133 | 5.163 | 75.58 | 9.449 | 5.512 |
| 13. | Octadecyl | Alcohol | $C_{34}H_{52}N_2O_3$ | 75.84 | 9.701 | 5.288 | 76.12 | 9.700 | 5.224 |

### Table 5

4-(4'-n-Alkoxy 2'-Methylphenylazo) Benzoic Acids :

| No. | n-Alkyl group | Transition temperatures °C | |
|---|---|---|---|
| | | Nematic | Isotropic |
| 1. | Methyl | 230 | 246 (d) |
| 2. | Ethyl | 211 | 257 |
| 3. | Propyl | 203 | 228 |
| 4. | Butyl | 192 | 235 |
| 5. | Pentyl | 182 | 227 |
| 6. | Hexyl | 172 | 223 |
| 7. | Heptyl | 170 | 220 |
| 8. | Octyl | 163 | 218 |
| 9. | Decyl | 158 | 211 |
| 10. | Dodecyl | 155 | 202 |
| 11. | Tetradecyl | 155 | 201 |
| 12. | Hexadecyl | 160 | 192 |
| 13. | Octadecyl | 155 | 176 |

## Table 6

### Methyl 4-(4'-n-Alkoxyphenylazo) Benzoates

| No. | n- Alkyl group | Transition temperature °C | |
|---|---|---|---|
| | | Smectic | Isotropic |
| 1. | Methyl | - | 169 |
| 2. | Ethyl | - | 158 |
| 3. | Propyl | - | 140 |
| 4. | Butyl | - | 130 |
| 5. | Pentyl | - | 121 |
| 6. | Hexyl | - | 120 |
| 7. | Heptyl | (118.0)* | 120 |
| 8. | Octyl | (120.5) | 121 |
| 9. | Decyl | (124.0) | 123 |
| 10. | Dodecyl | (121.5) | 120 |
| 11. | Tetradecyl | - | 112 |
| 12. | Hexadecyl | - | 116 |
| 13. | Octadecyl | - | 113 |

* Values in the parentheses indicate monotropy.

## Table 7

Ethyl 4-(4'-n-Alkoxyphenylazo) Benzoates

| No. | n-Alkyl group | Transition temperatures °C | |
|---|---|---|---|
| | | Smectic | Isotropic |
| 1. | Methyl | - | 103 |
| 2. | Ethyl | - | 111 |
| 3. | Propyl | - | 105 |
| 4. | Butyl | - | 82 |
| 5. | Pentyl | (85)* | 90 |
| 6. | Hexyl | 92 | 100 |
| 7. | Heptyl | 76 | 102 |
| 8. | Octyl | 85 | 105.5 |
| 9. | Decyl | 100 | 104 |
| 10. | Dodecyl | 92 | 102 |
| 11. | Tetradecyl | 88 | 99 |
| 12. | Hexadecyl | 85 | 98 |
| 13. | Octadecyl | 78 | 94 |

* Values in the parentheses indicate monotropy.

### Table 8

n-Propyl 4-(4'-n-Alkoxyphenylazo) Benzoates

| No. | n-Alkyl group | Transition temperature °C | |
|---|---|---|---|
| | | Smectic | Isotropic |
| 1. | Methyl | - | 86 |
| 2. | Ethyl | - | 96 |
| 3. | Propyl | - | 76 |
| 4. | Butyl | 74 | 91 |
| 5. | Pentyl | 72 | 85 |
| 6. | Hexyl | 64 | 95 |
| 7. | Heptyl | 68 | 96 |
| 8. | Octyl | 70 | 101 |
| 9. | Decyl | 78 | 99 |
| 10. | Dodecyl | 73 | 95 |
| 11. | Tetradecyl | 76 | 90 |
| 12. | Hexadecyl | 75 | 86 |
| 13. | Octadecyl | 70 | 77 |