CHAPTER 1

GENERAL INTRODUCTION.

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1.1. What is liquid Crystal

The term liquid crystal was not known to us before 1888. Reintzer[1,2] and O.Lehmann[2] observed unusual melting behaviour in certain organic compound and it was O.Lehmann who designated a state of matter that is intermediate between solid crystalline and the isotropic liquid phase in 1890 and used the term "Liquid Crystals". Because of their intermediate nature liquid crystals are also called mesophase or mesomorphic phase[4a,4b] that lies between the rigidly ordered solid phase where the mobility of the individual molecule is restricted and the isotropic phase where the molecular mobility and a general lack of molecular order exists. On reaching a certain temperature the solid undergoes transformation into a turbid condition, where there is no correlation between the directions or centres of mass of the molecules (as in isotropic liquid), but adopts a structure where although ~~3~~ 3-dimensional lattice structure is broken the molecules still retain some sort of order regarding direction of their long axes that is both birefringent and fluid. At a higher temperatures called the clearing temperature, the turbid condition disappears and the isotropic liquid state is formed. These changes take place in reverse order on cooling for most of the liquid crystalline substances.

Almost all liquid crystalline materials are organic compounds. Several thousands of organic compounds are now known

to form liquid crystals[4,5]. Kelker[6] has written a historical summary about liquid crystals. Numerous review articles have been appeared including those of Bragg[7] and Brown & Shaw[8]. Some other review articles and books on liquid crystals are also referred here[9-17] where details about various types of liquid crystals, their theory, experimental data and applications are given.

1.2. Classification of liquid crystals:

The two major categories of liquid crystals are identified as 'thermotropic' and 'lyotropic'. Thermotropic liquid-crystals are obtained by heating certain chemical compounds. Lyotropic liquid crystals occur in solution. The best known representative of this group are aqueous soap solutions. However, we will not discuss about lyotropic liquid crystals further as only thermotropic liquid crystals concern us in this thesis.

Thermotropic liquid crystals are obtained when some organic substances are melted. They are formed at the stage of melting when insufficient heat has been supplied to bring about the transition into normal isotropic liquid.

Thermotropic liquid can be classified into three types - Nematics, Smectics and cholesterics[18]. The classification system proposed by Sackman and Co-workers[19] was expanded by de Vries[20,21] to included three kinds of nematic, two cholesterics, eight distinguishable smectic phases ranging from A to H. A columnar phase has also been recently observed in certain disc like molecules.

Nematics

The word nematic comes from the Greek word thread and refers to certain thread like defects which commonly observed in these materials. Nematic liquid crystals differ from ordinary isotropic liquid by a long range orientational order of the long axes of the rod like molecules i.e. the molecules tend to align parallel to a preferred direction $\bar{n}$ usually ~~xix~~ called the director. The preferred direction usually varies from point to point in the medium. Nematic liquid crystal has no long range translational order, i.e. there is no long range correlation of the molecular centre of mass positions and thus the nematic phase is fluid. Fig. 1.1 shows the schematic representation of molecules in nematic and isotropic phase. The molecules are allowed to rotate freely about their long axis. In the state of thermal equilibrium the nematic phase has the axis of symmetry which is identical with the director direction. Nematic phase is optically uniaxial. The nematic phase is mobile and markedly affected by the external fields and forces; the molecules therefore possess a high degree of mobility and are capable of rotational movement. According to the molecular statistical theory of Maier and Saupe[22] the anisotropy of the molecular polarisability is responsible for the occurrence of the liquid crystalline phase. The relation between molecular structure has been discussed in details by Gray and Winsor[23] and Jen and Van der Veen[24].

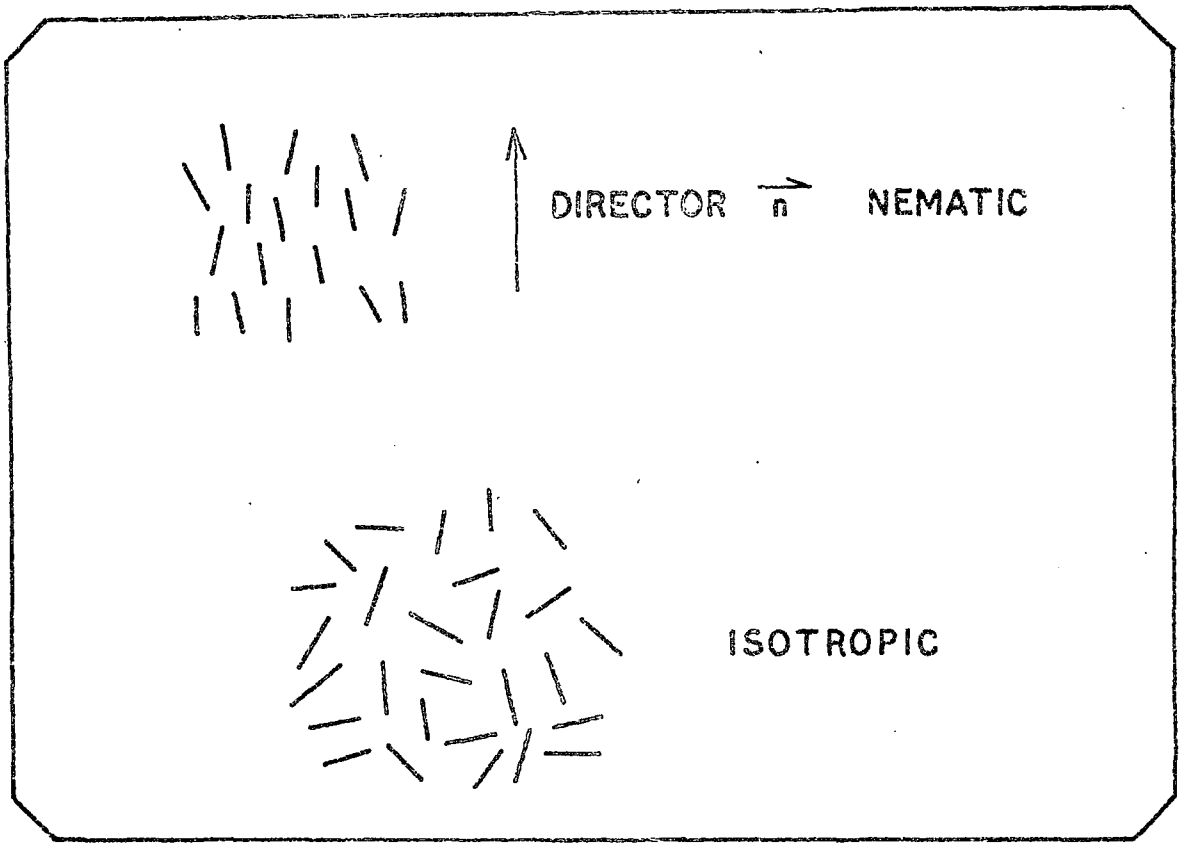


FIG. I.I. SCHEMATIC REPRESENTATION OF MOLECULES IN NEMATIC AND ISOTROPIC STATES.

Molecular ordering within a classic nematic phase is such that there is no regular arrangement between neighbouring molecules. de Vries[25,26] has proposed more than one type of nematic phase from his experimental observations namely -

(1) Normal Nematic phase,

(2) Cybotactic phase, and

(3) Skew cybotactic phase.

Smectics:

All smectic liquid crystals have a layered structure. The centre of gravity of the elongated molecules are arranged in equidistant layers. The long axes of the molecules are parallel to a preferred direction $\bar{n}$ which may be normal to the plane as in case smectic A (S_A) (Fig. 1.2 a) or tilted in case of smectic C (S_C)(Fig. 1.2 b). The arrangement of the centres of gravity within the planes may be regular or at random in the liquid like fashion. The thickness of the layer is of the order of the length of the free molecule. The interlayer attractions were weak as compared with the lateral forces between the molecules and in consequence the layers are able to slide over one another easily.

Information about the molecular ordering has been obtained from X-ray analysis. In case of S_A and S_C, the centres of mass of the molecules in each layer may be arranged randomly. S_B phase differs from the S_A phase by the fact that in S_B type the centres of mass of molecules in each layer form a two-dimensional hexagonal closed packed structure [Fig - 1.2 c].

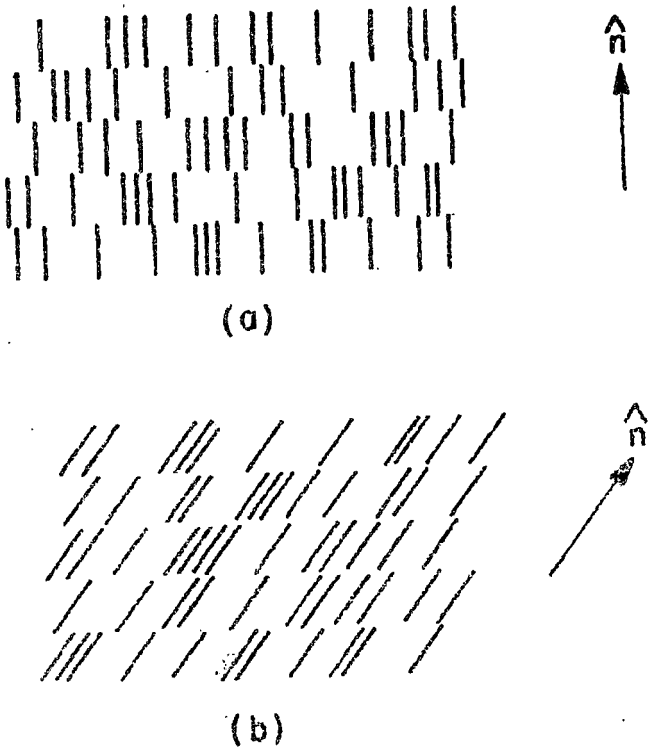
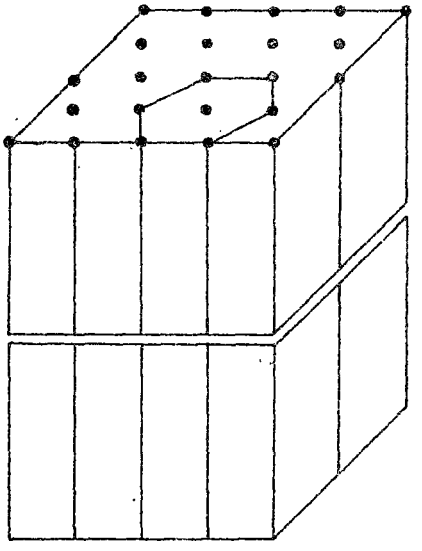
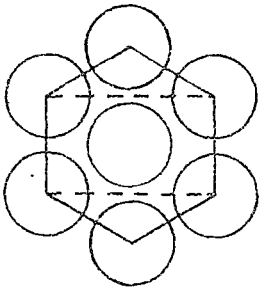


Fig. 1.2. Schematic representation of two types of smectic order: (a) smectic A order; (b) smectic C order.



(a)



(b)

(a) TWO LAYERS (b) SECTIONS IN THE BASIC PLANE, THE ROTATING MOLECULES HAVE CIRCULAR CROSS SECTIONS.

FIG.1.2(c).STRUCTURE OF HEXAGONAL SMECTIC B.

The various types of smectic phase have been identified by texture analysis in a polarising microscope. Polymorphism in smectic phase is obvious and the classification and characteristics of different phases have been investigated by Sackman and many workers[28,29,30]. At least five other distinct modifications have been identified. These are S_D S_E S_F S_G and S_H[31,32,33,34,20].

Smectic phases can be arranged in sequences as follows[35]

S_A

S_D

S_C

S_B

S_E

$S_{F,G,H.}$ ....

where the lower temperature phase stand further to the right.

From reports of recent workers[36-39] the existences of some other smectic phases as S_I, S_J and S_K are also found. Since in the present work we are concerned with only S_A and S_B phase, detailed discussion of other phases has been omitted.

Cholesterics

In 1888 Reintzer[1,2] reported the synthesis and thermal behaviour of a series of cholesteryl esters. Among these are the first recognised example of liquid crystals, specifically cholesteric liquid crystals. Cholesteric liquid crystals are denominated after cholesterol since many cholesterol esters form type of liquid crystals (cholesterol itself exhibits no mesomorphic phase).

The cholesteric mesophase is also a nematic type of liquid crystal except that it is composed of optically active molecules, which can be described[40-42], as a twisted nematic Fig. 1.3. The cholesteric structure has a screw axis super imposed normal to the preferred molecular direction. The structure of cholesteric liquid crystal is periodic with a spatial period given by $L = \frac{\pi}{|q_0|}$

The sign of q_0 (the sign of rotation of the helix) may be left handed (type "leavo") or right handed (type "dextro") and its magnitude determines the spatial period. With infinite pitch, i.e. $q_0 = 0$ a cholesteric liquid crystal is nothing, but a nematic liquid crystal. A necessary condition for the formation of the cholesteric mesophase is that the molecules are chiralic. Another type of liquid crystals was discovered by Chandrasekhar et al[43] the columnar phase, where the molecules are stacked in columns and so the plane of the molecules are perpendicular to the director, but in earlier cases we have

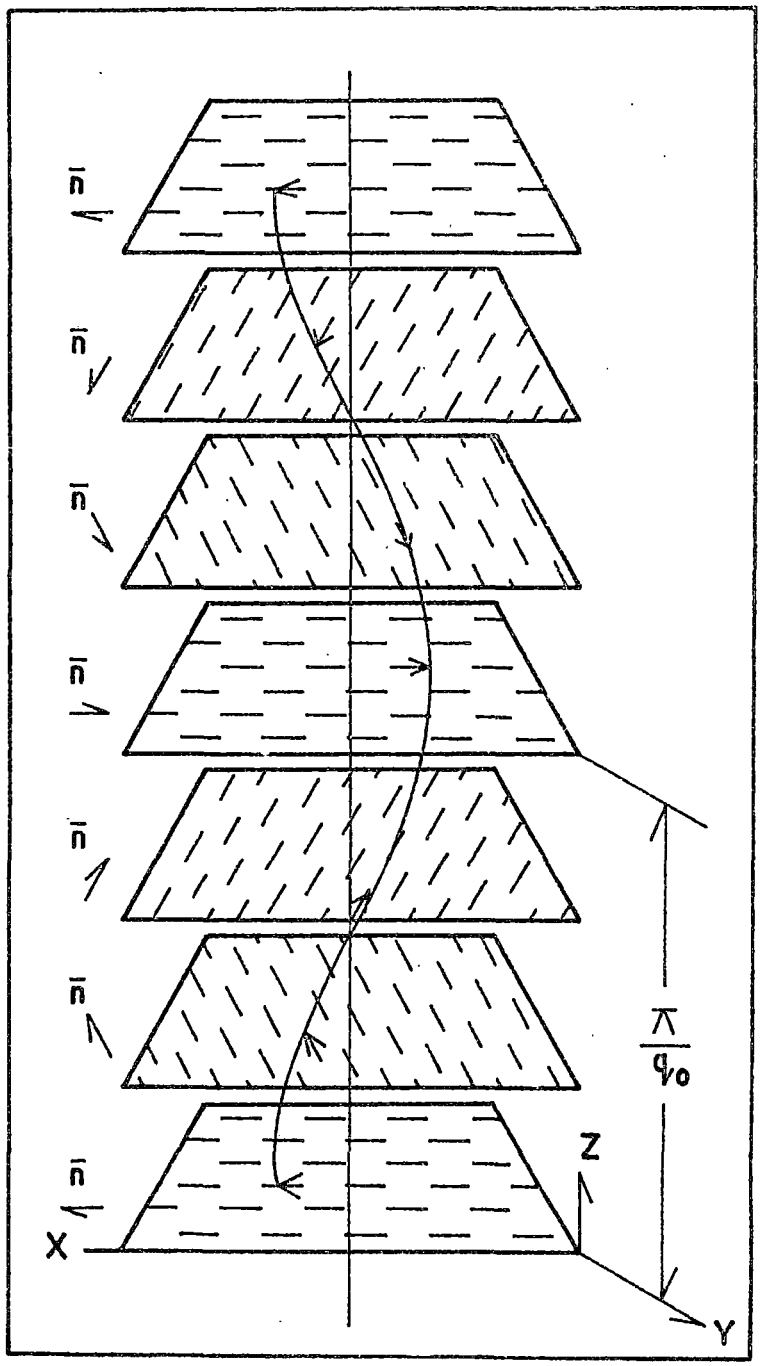


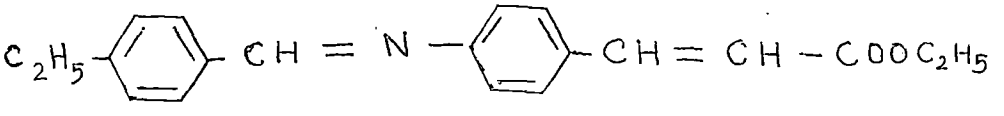
FIG. 1.3.

observed red or lath like molecules with their long axes parallel to the director[44]. However, we will not discuss any more about this columnar phase here.

A liquid crystalline sample may possess more than one mesomorphic phase i.e. smectic, nematic and cholesteric.

A typical example for a compound forming a smectic phase is

p-(p'-ethoxybenzylidene amino)-ethylcinnamate



which has the following transition path and temperatures (in °C)

$$C \underset{81}{\rightleftharpoons} S_B \underset{118.5}{\rightleftharpoons} S_A \underset{156.5}{\rightleftharpoons} N \underset{159}{\rightleftharpoons} I$$

The abbreviations used are defined as[45]

C - Crystal

S - Smectic liquid crystal

N - Nematic liquid crystal

Ch- Cholesteric liquid crystal

I - Amorphous isotropic liquid.

Any substance possessing smectic and cholesteric phases has the following transition path

$$C \rightleftharpoons S \rightleftharpoons Ch \rightleftharpoons I$$

Nematic and cholesteric phases do not occur in the same sample though cholesteric can undergo a transition to nematic phase under the action of electric or magnetic field.

Normally in phase transition the higher temperature phase is less ordered i.e. more symmetric than the lower temperature phase[46]. However, as a counter example, the re-entrant nematic phase[47] is one where the more symmetric phase reφoccuring at a lower temperature than the less symmetric smectic A phase[47a].

It was discovered by Cladis[47] that binary mixtures of certain mesogenic cyano compounds that exhibited the following transition path during cooling

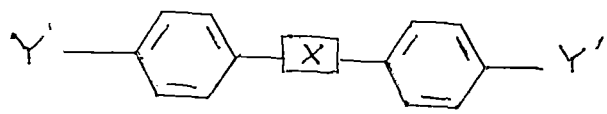
Isotropic - Nematic - Smectic A - Nematic

The low temperature nematic phase below the smectic phase is called re-entrant nematic phase[47]. At elevated pressure Cladis et al[48,49] have observed this phenomenon.

A mechanism which lead to the reentrant nematic at lower temperature has been explained by Cladis[50]. Recently the reentrant nematic phase has been observed in some pure compounds[51,52,53] and their mixtures at atmospheric pressure. Reentrant smectic phases have also been reported.[102]

1.3. Chemical Constitution of Mesomorphic Compounds:

The molecular architecture for thermotropic liquid crystalline compounds is generally two or more planar ring system e.g. aromatic nuclei (or more rarely heteroatomic and/or cycloaliphatic) joined by central linkage and having appropriate flexible terminal groups like -



structure 1.1.

where X represents the central linkage and Y & Y' the terminal groups (mostly alkyl or alkoxy chains) may be same or different usually on the long axis of the molecule. The terminal groups frequently determines which mesophase will be observed[55].

It is evident that intermolecular attractive forces play an important role in the mesophase stability from the fact that the various mesophases differ from each other and from isotropic liquid by the degree of freedom of molecular motion. The long range ordering of molecules would more clearly be encountered more often as the molecules become less spherical in shape. Thus it is more evident that the mesophases will be observed more easily for rod like molecules. Thermal stability (i.e. the maximum temperature of the mesomorphic substance at which the particular liquid crystalline behaviour is observed) of the mesophase is favoured by the molecular rigidity, permanent dipoles within the molecule and a high level of molecular polarizability along the long axis of the molecules in addition to the molecular shape (linear molecule i.e. considerable longer than it is wide). Generally most of the molecules contain multiple bonds along their long axis, aromatic nuclei and either polar or long chain terminal groups (as shown in structure 1.1). In addition to thatmelting point must not be too high, otherwise only supercooled metastable mesophases be found monotropically. Monotropic liquid crystals are those formed by cooling from the isotropic state, a mesomorphic state is formed below the melting temperature of the liquid crystal (i.e. supercooled region),

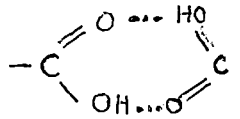
but when the crystal melts directly to isotropic state on heating. The other type of mesomorphic phase formed both by heating the crystal and cooling the isotropic liquid is called enantiotropic.

Thus an essential requirement for the mesomorphism to occur is that the molecules must be highly geometrically anisotropic (i.e. the intermolecular forces are also likely to be anisotropic), usually long and narrow.

In structure 1.1, the aromatic rings are joined by a central group X. The aromatic nuclei are rigid, polarizable and planar. Mesophase is formed if the central groups that joins the ring is itself rigid in nature, e.g. involves a multiple bond, a system of conjugate double bonds or a ring formed by dimerization of carboxyl groups and if the rings are parasubstituted. The more extended the rigid central part of the molecule the more thermally stable the liquid crystal will be. The two rings and the central group should constitute a lath or rod like core of the molecule.

Following the structural principle Vörlander first formulated the list of the known molecular building blocks in detail[56].

Common central linkage of mesogenic compounds of structure 1.1 are shown as follows[55]



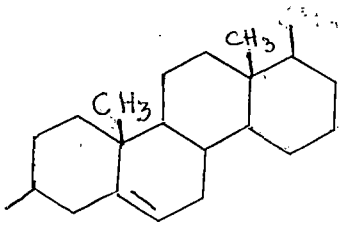
Acid dimers

$-CH=CH-$

Olefin

$-C\equiv C-$

Acetylene



Δ^5-Steroid

$-CH=N-$

Azomethine

$-CH=\overset{\downarrow}{N}(\rightarrow O)-$

Nitrone

$-N=N-$

Azo

$-\overset{\downarrow}{N}(\rightarrow O)=N-$

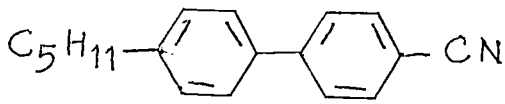
Azoxy

$-C(=O)-O-$

Esters

The aromatic rings are sometimes connected directly[57] as in

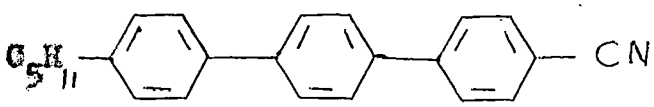
4-cyano-4'-n-pentylbiphenyl



Here C - N = 22.5°C and N - I = 35°C.

When an additional phenyl ring is added to the rigid core increasing its length forms the substance.

4-Cyano-4'-npentylterphenyl- the mesomorphic behaviour is greatly influenced.



C - N = 130°C, N - I = 239°C.

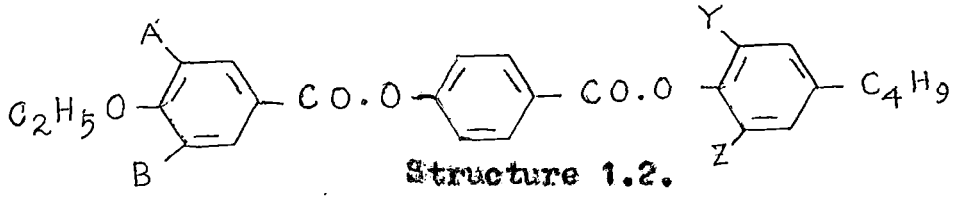
Gray has discussed[58] several other examples how the length of the molecule can be increased and in consequence the anisotropy and polarizability by an extending the rigid core structure. The thermal stability of the mesophase increases by this process.

Because of lateral attractions the possibility of formation of a layered arrangement increases due to the existence of dipoles acting transverse to the molecular axis[55]. Smectic phases are expected to occur from a layered crystal lattice[59].

The effect of broadening of a molecule by introducing one or more substituents in place of hydrogen along the side of the core structure is given in detail by Gray[59].

When hydrogen is replaced by substituents the molecule is broadened reducing anisotropic polarizability and consequently the intermolecular attraction.

Young et al[60] had studied the following structure:



Structure 1.2.

and found a systematic decrease in N-I temperature as the number of CH_3 groups introduced at positions A,B, or Y, Z was increased.

To obtain a mesophase it is generally (but not essentially) required that the terminal group of the molecule contain permanent dipoles. Other than ~~xxx~~ smectics if a terminal hydrogen is replaced by a substituent the thermal stability of the mesophase is increased generally. It was established by Gray[58,59] that the plots of transition temperature versus the number of carbon atoms in n-alkyl groups of a homologous series gives some smooth curves though the melting points do

not show any regularity.

(a) So called odd even[59] effect is obtained when we find that the N-I temperatures fit in two curves, one for even and the other for odd numbers of carbon atoms in n-alkyl chains. The N-I temperature alternates as we pass on serially to different members of the homologous series.

(b) With increasing chain length the mesophase to isotropic transition temperatures usually falls. There are exceptions to this rule, possibly because the aromatic nuclei in this cases do not adopt coplanar conformation, and so termini of one molecule may interact strongly with one of the rings of another molecule giving rise to additional attractions. The thermal stability of the molecule increases because of the increase in additional attack attraction when the length of the terminal group increases.

(c) The plot of the clearing points of smectics and their transition points to nematics usually reaches a maximum at a moderate chain length and decreases gradually with further elongation of the chain. Normally no distinct odd-even effect is observed in this point.

(d) In a homologous series, smectics are rarer with shorter chains. But becomes more common with longer chains increasing the nematic thermal stability. Longer molecules are prevented from sliding, favouring the formation of smectic phase, whereas the flexibility of longer chains generally hinders the parallel orientations. Chemical cons-

titution of different mesophases are listed by Kelker and Hatz[59(a)].

1.4. Theories of Nematic Liquid Crystals:-

Before starting the deduction of molecular mean field theory of mesophases the term "Order Parameter" must be explained.

It has been already stated that nematic liquid crystal differ from ordinary isotropic liquid by a long range orientational order of the long axes of the rod like molecules. In any system in which long range orientational order exists, for convenience, it is customary to introduce an order parameter, a quantity that vanishes in the disordered isotropic phase, but is different from zero in the ordered phase and will be unity when the molecules of the substance are perfectly ordered. Thus a suitable order parameter which describes the ordering in a nematic phase must be defined.

Order parameter -

In a homogeneously ordered nematic liquid crystal sample the long axes of the molecules are all almost parallel to the preferred direction which is represented by $\bar{n}$ the director. Assuming the molecules as rigid rods, the orientation of a particular molecule with respect to the director $\bar{n}$ (taken to be the z direction) be completely defined by three Eulerian angles θ , ϕ & ψ ,(Fig. 1.4 (a)). Due to the thermal energy the individual molecules or small

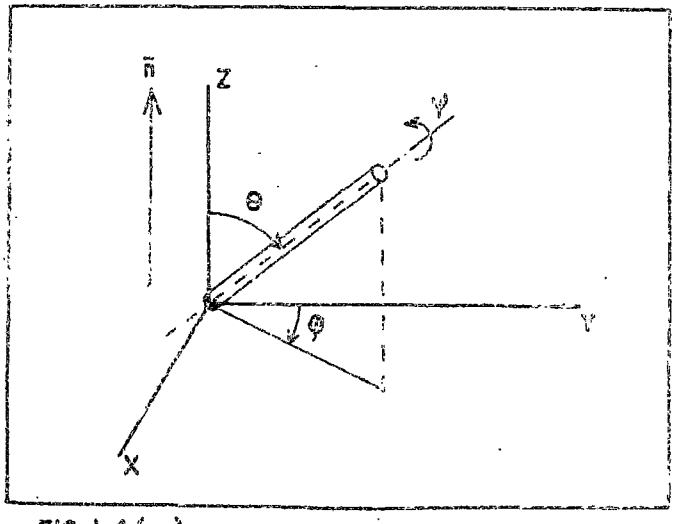


FIG. I.4(a).

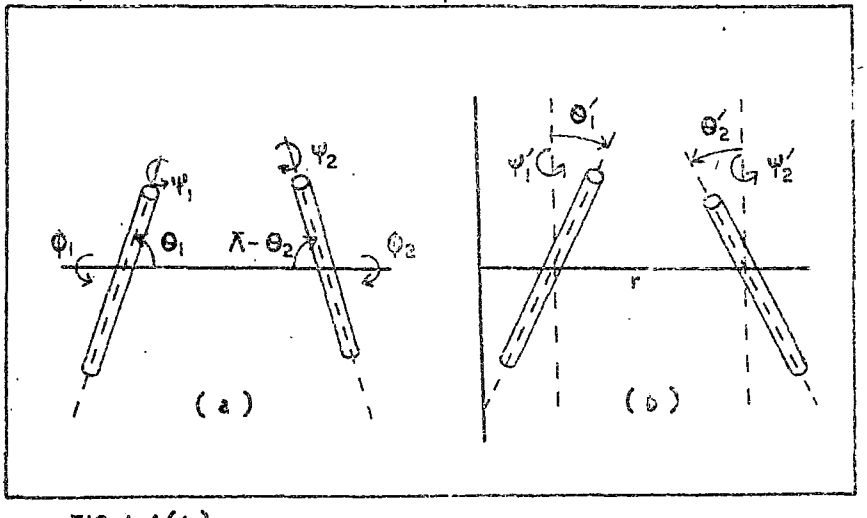


FIG. I.4(b).

groups of molecules tumble about the preferred direction. The efficiency of the molecular orientation in the nematic phase along $\bar{n}$ can be described by a single order parameter. It is also assumed that the director $\bar{n}$ and $-\bar{n}$ are equivalent and the molecules are cylindrically symmetric. But in practice none of the above assumption are strictly realisable, i.e. (i) molecules are not perfectly rigid some flexibility are also there (ii) $\bar{n}$ and $-\bar{n}$ are not equivalent i.e head and tails of a molecule can be distinguished in some cases. (iii) The molecules are more lath-like than cylindrical.

Considering that deviations from the idealised case are small the molecules are assumed to rotate freely around the long molecular axes. In order to maintain the cylindrical symmetry no order could exist for ϕ and ψ and under the most simplified consideration θ becomes the only quantity that characterises the orientational ordering about the director $\bar{n}$.

Simple scalar form of order parameter for nematic is defined as

$$\langle P_2 \rangle = \frac{1}{2}\left(3\langle \cos^2\theta \rangle - 1\right) = \langle P_2(\cos\theta) \rangle$$

The brakets indicate the ensemble average i.e. the average is carried over all the molecules. P_2 ($\cos\theta$) is the Legendre polynomial of the second order. $P_2 = 1$ for perfectly parallel alignment (i.e. $\theta = 0$) and $P_2 = 0$ for

random orientation of molecules (isotropic phase). In the nematic phase it has an intermediate value which decreases rapidly with temperatures and drops abruptly to zero at the nematic isotropic point T_{NI} in a weak first order transition.

Phase transitions -

The order of the phase transition is related to the degree of abruptness of change in physical properties which takes place during a phase transition. In a first order transition e.g. melting or condensation away from the critical point there is a finite jump in the enthalpy, the entropy and in the 1st.derivative of the free energy. In a higher order transition, however, the entropy changes is continuous across the transition. The nematic - isotropic phase transition is a 1st. order with a small latent heat. For this reason it is often called a weak 1st. order phase transition. Such transitions are generally accompanied by pre-transitional effect which are the characteristic of the 2nd. order phase transition and are not usually seen at 1st. order transitions. It is the weakness of the forces responsible for the long range orientational ordering as reflected in small change in enthalpy, that gives rise to the pre-transition effect. At nematic isotropic transitions the forces responsible for long range orientational ordering disappears. Because of this pre-transitional effects sometimes confusion arises to the 1st. order phase transition of nematic phase to isotropic phase.

Chandrasekhar could show that the N-I transition is always of the 1st. order, and there always remains a short range order in the isotropic phase in spite of sudden disappearance of any long range order at the clearing point[61].

Molecular field theories for nematic mesophases:-

As early as in 1916 M. Born[62] proposed the first mean field theory of nematic state in which the medium has been treated as an assembly of permanent electric dipoles. When the temperature is lowered a transition from an isotropic to an anisotropic phase is possible. This result is however, only qualitative importance because it is now established that the permanent dipole moments are not necessary for the existence of liquid crystals. According to this theory the aligned phase should be ferroelectric, which in fact does not appear even in polar molecule. Maier and Saupe[63] have developed a statistical theory for the phase transition in a nematic liquid crystal. The theory says that the occurrence of liquid crystalline phase is due to the anisotropy of the molecular polarizability. The theory is mainly based on these assumptions - (i) The molecules interact through an attractive orientation dependent Vander Waals interaction. (ii) The orientation dependent interaction does not effect the configuration of the centre of mass and (iii) The mean field approximation - each molecule is assumed to be in an average orientating field due to its environment, but other-

wise uncorrelated with its neighbours. As a result a given molecule feels an effective potential of the mean field or single molecule potential or pseudopotential .

The interaction potential between the molecule 1 & 2 is taken as the starting point for the derivation of pseudopotential for a rod like molecule. The intermolecular pair potential V_{12} is a function of five co-ordinates[64],

$$V_{12} = V_{12}(r, \theta_1, \phi_1, \theta_2, \phi_2) \ldots.$$

Fig. 1.4 (b) represents the different coordinates required to describe the interaction between a pair of assymetric molecules. Where r is the separation of the centre of gravity and θ_i , ϕ_i , ψ_i are three Eulerian angles. Since, in case of nematics the molecules have no ordering about their long axis the angles ψ_i are eliminated.

Pople[65] expanded the two body interaction potential as

$$V_{12} = V_{12}(r, \theta_1, \phi_1, \theta_2, \phi_2)$$

$$= 4\pi \sum_{L_1 L_2 m} U_{L_1 L_2 m}(r)\, Y_{L_1 m}(\theta_1, \phi_1)\, Y^{*}_{L_2 m}(\theta_2, \phi_2) \quad \ldots (1)$$

where $Y_{Lm}(\theta, \phi)$ are the usual spherical harmonics.

The expression is convenient because it not only separates the distance and angular part of the potential, but in addition to the expansion coefficient $U_{L_1 L_2 m}(r)$ are found to decrease rapidly with increasing L_1 and L_2.

In order to derive mean field approximation to the potential first we have to express V_{12} in terms of polar co-ordinate system based on the director $\bar{n}$ as the polar axis.

The rotation of the molecule 1 and 2 is required and mathematically rotation of the coordinate axes transforms the spherical harmonic into the form

$$Y_{Lm}(\theta,\phi) = \sum_{p} D^{L}_{pm} Y_{Lp}(\theta',\phi') \qquad \ldots (2)$$

where D^{L}_{pm} are the elements of Wigner rotation matrices. Therefore eqn. (1) can be transformed using Wigner rotation matrices[66] from the coordinate system containing the intermolecular vector to this spatial axis system we get

$$V_{12} = 4\pi \sum_{L_1,L_2,m} \sum_{pq} u_{L_1,L_2,m}(r)\, Y_{L_1 p}(\theta_1',\phi_1')\, Y^{*}_{L_2 q}(\theta_2',\phi_2') \left(D^{L_1}_{pm}\right)\left(D^{L_2}_{qm}\right)^{*} \qquad \ldots (3)$$

Primed angles represents the orientation of the molecule with respect to the new rotated coordinate system (space fixed coordinate system).

Pseudopotential from the pairwise intermolecular potential can be obtained by taking three averages[64]. First average is over all orientations of the intermolecular vector $\bar{r}$ in the spatial coordinate system, then we average over all orientations of the molecules 2 (which has influence only on the spherical harmonics in θ_2', ϕ_2') and finally we average V_{12} over all values of the intermolecular separation $|r|$.

The potential obtained after taking the above mentioned averages is given as

$$\langle\langle\langle V_{12}\rangle\rangle\rangle = \sum_{Lm} \langle U_{LLm}(r)\rangle P_L(\cos\theta_i')\langle P_L\rangle \quad \ldots (4)$$

where P_Ls are the Lth. order legendre polynomials. The desired single molecule potential in the mean field approximation, which can be written by dropping the pined as

$$V_1(\cos\theta) = \sum_L U_L \langle P_L\rangle P_L(\cos\theta)$$

$$U_L = \sum_m \langle U_{LLm}(r)\rangle \quad \ldots (5)$$

Since for most nematic liquid crystals director directions $\bar{n}$ and $-\bar{n}$ are indistinguishable, averages over all odd powers of Cos θ vanish, then only the even values of L are required in equation (5). L = 0 term being a mere additive constant can be neglected. The eqn. (5) can be written as

$$V_1(\cos\theta) = U_2\langle P_2\rangle P_2(\cos\theta) + U_4\langle P_4\rangle P_4(\cos\theta) + U_6\langle P_6\rangle P_6(\cos\theta) + \ldots\ldots \quad \ldots (6)$$

The equation for the pseudopotential is equivalent to that in the Maier-Saupe theory if the summations are restricted to terms with L = 2 i.e. the 1st. term only in equation (6)

$$V_1(\cos\theta) = U_2\langle P_2\rangle P_2(\cos\theta) \quad \ldots (6\,a)$$

Accordingly to Humphrie et al[67] if we consider the true cylindrical symmetry of the distribution function for the orientation of the intermolecular Vector the <u>single molecular potential</u> will contain the terms which are proportional to

$$\langle U_{L_1 L_2 m}(r)\rangle \left(P_{L_1}\langle P_{L_2}\rangle + P_{L_2}\langle P_{L_1}\rangle\right)$$

Thus the equation for pseudopotential is equivalent to that in the Maier Saupe theory[63] if the summation are restricted to term with $L = 2$.

<u>Orientational distribution function</u> $(f_1(\cos\theta))$

Orientational distribution function $(P_1(\cos\theta))$ gives the probability of finding a molecule whole axis makes an angle θ with the director $\bar{n}$.

Orientational distribution function corresponding to the single molecule potential has the form

$$f_1(\cos\theta) = Z_1^{-1} \exp\left[-\beta V_1(\cos\theta)\right], \qquad \ldots (7)$$

$$Z_1 = \int_0^1 \exp\left[-\beta V_1(\cos\theta)\right] d(\cos\theta), \qquad \ldots (8)$$

where Z_1 is the single molecule partition function and $\beta = \frac{1}{KT}$ (k is the Boltzmann's constant and T is the temperature in absolute unit).

Since both V_1 and f_1 are even functions of $\cos\theta$ as $\bar{n}$ and $-\bar{n}$ are indistinguishable over all possible orientations can be restricted to $0 \leqslant \cos\theta \leqslant 1$.

The orientational order parameter

The orientational order parameter has already been defined as

$$\langle P_2 \rangle = \frac{1}{2} \left(3 \langle \cos^2\theta \rangle - 1 \right) = \langle P_2 (\cos\theta) \rangle$$

This holds either in time or space average. This is one of the earliest definition of the orientational order parameter which was given by Zwetkoff[68] in proposing the semi empirical theory of nematogens.

In eqn. (7) and (8) the functions V_1 and hence φ_1 contains the order parameter $\langle P_L \rangle$ which is as yet undetermined functions of temperatures, so average values cannot be calculated from the eqns. (5) and (7). Its temperature dependence can be obtained as follows:

$\langle P_L \rangle$ is the average value of Lth. Legendre function for a given molecule. Therefore, from eqn. (7)

$$\langle P_L \rangle = \int_0^1 P_L (\cos\theta)\, \varphi_1 (\cos\theta)\, d(\cos\theta) \qquad \ldots (9)$$

combining this equation with eqn. (7) we get

$$\langle P_L \rangle = \frac{\int_0^1 P_L (\cos\theta) \exp\left[-\beta V_1 (\cos\theta)\right] d(\cos\theta)}{\int_0^1 \exp\left[-\beta V_1 (\cos\theta)\right] d(\cos\theta)} \qquad \ldots (10)$$

which is a self consistent equation for the determination of the temperature dependence of $\langle P_L \rangle$.

From a simultaneous solution of equations (6) and (10) we get the temperature dependence of all the P_L s originally included in the potential V_1. For L = 2 we get the solution

of $\langle P_2 \rangle$ and from the solution of $\langle P_2 \rangle$ we get the traditional order parameter in the nematic phase. $\langle P_2 \rangle = 0$ is at all temperatures which is disordered normal isotropic liquid phase; below certain temperatures determined by $KT/v = 0.22284$, two other solutions appear. Of the three solutions below the critical temperature the one which satisfies the thermodynamic condition of minimum free energy will give the stable phase.

The free energy is given by $F = E - TS$. Where E is the internal energy and S the entropy.

For a system of N molecules we have the following expressions for E, S and F[64].

$$E = \frac{1}{2} N \langle V_i \rangle = \frac{1}{2} N \sum_L U_L \langle P_L \rangle^2,$$

$$S = -Nk \langle \ln \rho_i \rangle = \frac{N}{T} \sum_L U_L \langle P_L \rangle^2 + Nk \ln Z_1$$

$$F = E - TS = -N k T \ln Z_1 - \frac{1}{2} N \sum_L U_L \langle P_L \rangle^2.$$

It is found that for $KT/v = 0$ to $KT/v = 0.22019$ from the condition of minimum free energy (64.a) (calculated by using the obtained $\langle P_2 \rangle$ values for each T) the positive values of $\langle P_2 \rangle$ (i.e. the molecules tend to align parallel to the director) gives the stable nematic phase. While for T corresponding to $KT/v > 0.22019$ the solution $\langle P_2 \rangle = 0$ gives the stable isotropic phase. $\langle P_2 \rangle$ decreases from unity to 0.43 from $T = 0$ to $T = 0.22019\ v/k$ and then suddenly it decreases to zero $[\langle P_2 \rangle = 0]$ at $T = 0.22019\ v/k$. Accompanied by latent heat of transition, discontinuous entropy and volume changes, a 1st. order transition from nematic to isotropic phase takes place at

this temperature (T_{NI}). As the temperature is lowered down in the nematic phase, however, the substance attains smectic phase or solid crystalline phase long before $\langle P_2 \rangle$ can attain the value of unity at absolute zero. This theory predicts that $\langle P_2 \rangle$ is same at T_{NI} for all substance[63].

It is observed that the mean field theory of Maier-Saupe is obtained by the retention of only the 1st. term in the equation (6). Maier and Saupe[63] first attempted to elucidate the nature of intermolecular forces in nematics. The character of which is contained in the parameter of the one molecule potential V_1 (orientation dependent part only). It was assumed by them that the nematic order is mainly due to dispersion forces (i.e. induced dipole-induced dipole). This restriction gives[64].

$$V_1 = -\frac{A}{v^2}\langle P_2 \rangle P_2(\cos\theta)$$

Where, A is a constant to be determined which is a character of the substance (related to the polarisability) can be calculated from the transition temperature if the molar volume of the nematic and isotropic liquid at clearing point is known. v is the mean molecular volume. This volume dependence comes from the fact that the potential of dispersion force is dependent on the intermolecular separation as r^{-6} (whether between symmetric or assymetric molecules). It is assumed from M.S. theory[63] that $V_1 \propto v^{-2}$.

In their development of the mean field theory Humphries et al[67] decided the volume dependence as $v^{-\gamma}$, γ being an adjustable parameter. Experimental data[69] on the pressure dependence of the order parameter of PAA indicates that $V_1 \propto v^{-4}$. On the other hand a recent argument due to Cotter[70] (referred by Chandrasekhar[70.a]) suggests that thermodynamic consistency of the mean field theory requires v^{-1} dependence. A force fitting experimental results with theory however yielded values of γ in some cases[71] which are neither thermodynamically self consistent nor the values are expected to come from the consideration of dispersion forces (v^{-2} dependence).

Chandrasekhar and Madhusudan[72] obtained an average of v^{-3} dependence after calculation considering to permanent dipole-permanent dipole forces, induced dipole-induced quadrupole part of the dispersion forces.

In order to avoid all these ambiguities regarding a knowledge of volume dependence, it is preferable to assume that the coefficients of V_1 in eqn. (6) are independent of volume and to restrict the fitting of the theory to experiment to a narrow range of temperature T_{NI}. Finally different forms of volume dependence may be included.

According to M.S. theory plot of $\langle P_2 \rangle$ versus T/T_{NI} is a universal curve for all substances. Experimentally these are small but systematic derivations from this curve[8a,73] and the need of higher order terms in the potential function has been emphasized by Chandrasekhar et al[72] and Humphries et al[67]. When theoretical values of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ obtained

from M.S. potential are compared with some experimental results.

The temperature dependence of the $\langle P_2 \rangle$ and $\langle P_4 \rangle$ of MBBA are determined by Jen et al[74] using Raman Scattering technique and found that $\langle P_4 \rangle$ values are much lower than that predicted by M.S. theory and even negative near the transition. Kabinata et al[75] in more recent work reported the results of measurement of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ by resonance Raman polarization measurements of all trans β -carotene dissolved in MBBA and 5CB (utilised as orientational probe). The value of $\langle P_4 \rangle$ obtained for MBBA is not negative in their case while for 5 CB becomes negative (within experimental uncertainity) just before the transition temperature.

These values of $\langle P_4 \rangle$ are also much lower than those predicted by MF theories. The negative values of $\langle P_4 \rangle$ are not predicted even if the higher term in the mean field potential is included although the inclusion improves the agreement to some extent.

Further the long wavelength orientational fluctuations in the medium which diminish the effective order parameter and this has to be taken into the theory according to Luckhurst[76]. The assumption that the molecule is a rigid rod is also an over simplification. A realistic calculation has been made by Marcelja[77] of the contribution of flexible end chain in the ordering process, which accounts for the alternation in the transition temperatures, the order parameter and other related properties of the successive members of a homologous series. Recent theoretical work by Luckhurst[78] shows that

the effect of the flexibility of molecules on order parameter is only marginal.

McMillan's theory for Smectic A (SA)

Contribution to the theory of S_A liquid crystals have been made by a number of Investigations[79-83]. All the treatments are extensions of the Maier-Saupe[63] theory of nematics. Here we will discuss the theory as given McMillan.

The McMillan form of the single molecule potential is deduced starting from the Kobayashi form of the potential[79,80] and using the formal development presented earlier[64.a, 64].

The McMillan model of the potential[84] is given in the form

$$V_m(\cos\theta, z) = -v\left[\delta\alpha\tau\cos(2\pi z/d) + \eta + \alpha\sigma\cos(2\pi z/d)\,P_2(\cos\theta)\right]$$

The smectic A liquid crystals possess both orientational and translational order. The centre of mass of the molecule tends to lie on a plane perpendicular to the Z direction (i.e. to the director). The molecular distribution function must therefore describe both the tendency of the molecule to orient along $\bar{n}$ Fig. 2(b) and form layers perpendicular to $\bar{n}$. The distribution function is thus a function of both $\cos\theta$ and z and can be expanded in a double series

$$f(\cos\theta, z) = \sum_{L=0\,(\text{even})}^{\infty}\sum_{n=0}^{\infty} A_{Ln}\,P_L(\cos\theta)\cos(2\pi nz/d)\,, \text{ and}$$

$$\int_{-1}^{+1}\int_{0}^{d} f(\cos\theta, z)\,\frac{dz}{d}\,(d\cos\theta) = 1\,.$$

The coefficients A_{Ln} are found after integrating and recognizing the definition of averages[84].

The results are

$$A_{00} = \frac{1}{2d},$$
$$A_{0n} = \frac{1}{d}\left\langle \cos\left(2\pi n z/d\right)\right\rangle, \quad (n \neq 0),$$
$$A_{L0} = \frac{2L+1}{2d}\left\langle P_L(\cos\theta)\right\rangle; \quad (L \neq 0), \qquad \ldots(11)$$
$$A_{Ln} = \frac{2L+1}{2d}\left\langle P_L(\cos\theta)\cdot\cos\left(2\pi n z/d\right)\right\rangle; \quad (L, n \neq 0)$$

In addition to the purely orientational and translational order parameter, the $\langle P_L(\cos\theta)\rangle$ and $\langle\cos(2\pi n z/d)\rangle$ we find a set of mixed order parameters, $\langle P_L(\cos\theta)\cos(2\pi n z/d)\rangle$

This describes the correlation coupling between the degree of orientational and translational order. The three order parameters of lowest degree in eqn. (11) of the S_A phase have been given symbols

$$\eta \equiv \langle P_2(\cos\theta)\rangle,$$
$$\tau \equiv \langle\cos(2\pi z/d)\rangle,$$
$$\sigma \equiv \langle P_2(\cos\theta)\cos(2\pi z/d)\rangle$$

In the isotropic phase, $\eta = \tau = \sigma = 0$

In the nematic phase $\eta \neq 0$, $\tau = \sigma = 0$

In the smectic A phase $\eta \neq 0$, $\tau \neq 0$, $\sigma \neq 0$

For perfect order all three tend to unity.

1.5. (a) Alignment of nematic mesophases-

In a large volume of a nematic liquid crystal the preferential direction $\bar{n}$ is in general not uniform but changes from place to place under the action of disturbing forces such as convention flow, wall effects etc. However, even large samples can be aligned by both magnetic and electric field. The field induced alignment of a liquid crystal is a strong effect. This is due to the particular intermolecular forces responsible for the mesomorphic state and lead to a co-operative behaviour of the molecules.

An anisotropic dielectric or diamagnetic component will tend to align such that the largest component of dielectric or diamagnetic constants lie in the direction of the applied field. Nematic molecules behave as dipolar species with $\epsilon_{\parallel} \neq \epsilon_{\perp}$ ($\chi_{\parallel} \neq \chi_{\perp}$) where ϵ and χ are dielectric and diamagnetic susceptibilities parallel and perpendicular to the long molecular axis. When $\epsilon_{\parallel} > \epsilon_{\perp} (\chi_{\parallel} > \chi_{\perp})$ the nematic liquid crystal along molecular axis will tend to align with the applied field.

For example, p-methoxy-p'-cyanobenzylideneaniline is a highly polarizable molecule with positive dielectric aniso-

trony, i.e. $\epsilon_{\parallel} > \epsilon_{\perp}$, that will align its long molecular axis with an applied field. On the other hand p-methoxy-p-n-butylbenzylideneaniline with $\epsilon_{\perp} > \epsilon_{\parallel}$, will tend to align its long molecular axis perpendicular to the applied field.

Thin films of liquid crystals upto 100 μm can be aligned by surface generated orienting forces which results from physico chemical processes, e.g. hydrogen bonding, Vander waals, interactions or dipolar interactions and from mechanical interactions as a result of the anisotropic elasticity of the liquid crystals[85].

Ordered layers of nematic phases upto about 0.1 mm thickness can be prepared by sandwiching the liquid crystal between flat glass plates. If the surface is rubbed with a piece of cotton, paper or leather a number of times in a particular direction the molecules are aligned in the direction of rubbing (i.e. homogeneous[85], alignment. By depositing suitable chemical at particular angle on the surface the alignment can be made more uniform. Homeotropic orientation (perpendicular to the surface) can also be obtained in the same way[85]. Homogeneous oriented nematic layers have been used for UV and infrared spectroscopic studies[85].

A variety of electro-optic effects of liquid crystals are based on the electric field molecular re-alignment. Using the surface treatment to produce a molecular alignment which is orthogonal to that produced by the applied field the molecular reorientations can readily be intereconverted within a

millisecond response time. The alignment of nematic liquid crystals by external electric field has been recently reviewed by Gray[86] and was first observed by Freedericksz[87]. Variation of the linear birefrengence or light absorption (linear dichroism) can be observed by reorientating nematic molecules with positive dielectric anisotropy $(\epsilon_{\parallel} > \epsilon_{\perp})$.

Nonliquid crystalline dye molecules may be aligned by the nematic molecules to produce display applications[88].

Nematic liquid crystals can easily be oriented by static magnetic fields. Two cases have to be distinguished depending on the sign of the diamagnetic anisotropy $(\chi_{\parallel} - \chi_{\perp})$ of the molecules forming the liquid crystals. The aromatic nematogens are examples of compounds with positive diamagnetic anisotropy i.e. $(\chi_{\parallel} - \chi_{\perp}) > 0$. The long axis of the molecule tend to align parallel to the direction of the magnetic field. The nematic liquid crystals orient in the magnetic field $\overline{H}$ in such a way that the directors of the spontaneously ordered domains are all aligned uniformly in one direction (parallel to $\overline{H}$). In general field strength of several hundred gauss are sufficient to produce uniform orientation i.e. monodomain sample.

1.5. (b) Alignment of smectic phases:-

Meiboom and Luz[89] have as shown that smectic liquid crystals of compounds which exhibit a nematic and a smectic phase may be oriented uniformly by the application of a magnetic field in the following way: First the nematic phase is oriented

in the magnetic field. Then the sample is slowly cooled below the nematic to smectic transition while it is kept in the magnetic field. In this way all the three smectic phases A,B,C, of ~~EM~~ TBBA can be ordered uniformly.

1.6. Texture analysis by polarising microscope:

When liquid crystals are studied with a polarising microscope, they are usually observed as thin films between glass plates.

Nematics:-

On cooling from the amorphous isotropic liquid circular birefringent areas appear at first in case of nematics. The appearance of the textures that form after the completed transitions often depend considerably on the layer thickness. Thicker nematic layers may show the typical threaded schelieren textures. The well defined thread like textures may move and float around in the ~~xxxxxxxx~~ nematic. The term nematic refers to these features, being derived from the Greak word "nema" a thread. The threads have elastic properties. In thinner layers the threaded texture changes to the schliern texture. By a suitable surface treatment it is possible to obtain films with ~~xxx~~ uniform molecular alignment. A film that has been aligned between the rubbed surface is shown by Saupe. With untreated surface, the surface effect may produce an irregular marble texture. It is also possible to obtain uniformly aligned films with the optic axis normal to the surface.

Pseudo isotropic textures are often obtained with compounds that form, in addition to the nematic phase, a smectic A phase at lower temperatures[90].

Cholesterics:-

Cholesteric liquid crystal -- can occur in three textures. On cooling, an isotropic texture or modification can be obtained first at the liquid to cholesteric liquid crystal transition, which at a lower temperature changes to a birefringent texture. Transition point is not easily observed in this case. Where in other cases when the birefringent texture is formed directly, transition can be easily observed. Elongated banana shaped forms may appear first (referred to as a batonnets).

The photograph of birefringent "focal-conic" texture of a cholesteric phase is given by Saupe[91]. When the cover glass is shifted focal conic texture is shifted to planner texture. Wedge Shaped samples, when the surfaces are prepared for a parallel alignment, show a particular feature called Grandjean steps or threads. The variation of pitch is directly observable by the colour change in the sample that show reflection colours.

Smectics:-

Typical texture obtained with smectic A liquid crystals are focal conic textures. The appearance of the focal conic texture is directly related to the focal conic layered structure of the smectic. In thinner layers the focal conic texture changes its appearance and gives the fan texture or more accurately the fan-shaped focal-conic textures. A shift of the cover glass often changes the fan texture suddenly to a pseudo-isotropic texture.

In contrast to nematics, a ~~sh~~ slight shift of the cover glass has no optical effects on a pseudo-isotropic smectic - A film. This type of texture can also form spontaneously at the phase transition during cooling from a pseudo-isotropic nematic. Disappearance of Brownian motion can only indicate the transition in such cases. Smectic A phases shows 'batonnates' when it is formed directly from amorphus isotropic liquid. They float in normal liquid and on cooling they merge resulting into a fan texture.

Typical textures of smectic are the 'broken fan' and 'broken focal - conic textures. They are less regular and disturbed by additional disclinations in comparison with S_A phase. Schlieren textures of smectic C are also observed which corresponds to pseudopotentic-isotropic texture of S_A. At the transition from a normal isotropic liquid to S_C batonnets appear first to those of S_A phase.

The characteristic of liquid crystals with structured layer is the "mosaic" texture. The most common smectic with structured layer is smectic B. The mosaic texture has been observed with S_B and slightly modified also with other smectics with structured layers. A modification of fan textures and of Schlieren textures can also be observed with smectic B films that are obtained on cooling from a S_A or a S_C. The pseudo-isotropic textures can also be observed with S_B the existence of the texture shows directly that the corresponding S_B phase is uniaxial and has upright layers.

Photographs of all the typical textures discussed above are given by Saupe[91].

Demus and Richter[92] have discussed details about texture analysis with several photographs of different mesomorphic phases with their typical textures.

Order parameters of different mesophases (specially for nematics) have been determined by many workers by employing various experimental techniques including diamagnetic anisotropy[93] optical anisotropy[93,94] magnetic resonance spectroscopy. Raman scattering[96,97], Infrared spectroscopy[97], UV and visible spectroscopy[96], Mössbauer spectroscopy[98], Neutron scattering[98], positron annihilation[98], dielectric anisotropy[98], Guest host interaction[99,100], X-ray diffraction etc. Comparison of these results with the Maier Saupe theory is briefly discussed in Brown's book[101].

The details about all the experimental techniques are reviewed by different workers[98]. In this thesis we are not going to discuss about all the techniques other than the use of X-ray diffraction in determination of order parameters of different mesophases and the orientation of different non-liquid crystalline azo dyes doped in different nematic mesophases by spectroscopic method (Guest Host effect). Details about the X-ray and spectroscopic works on liquid crystalline phase made by us will be presented in next few chapters.

1.7. MOTIVATION AND SCOPE OF THIS WORK

While enormous advances in the technical applications of liquid crystals have been made, the basic reason for the formation of various mesophases is not fully understood. There are several theories of liquid crystals based on Mean field approximation. My aim was to test these theories from my X-ray and spectroscopic data. I have been able to analyze my X-ray diffraction data from several aligned liquid crystal samples (nematic and smectic A) to give the orientational distribution function, $f(\beta)$, which in turn provides the angular part of the Mean field potential. This experimentally obtained distribution function has been compared with those obtained from different theories and large discrepancies have been found for cyano compounds having strong terminal dipole moment.

X-ray data have also been analyzed for apparent molecular length and intermolecular distances. The apparent molecular lengths for cyano compounds were found to be larger than molecular model lengths, showing formation of association in the mesophase. I have also calculated the orientational order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ for aligned nematic and smectic A phases and contrary to some earlier works my $\langle P_4 \rangle$ values are always positive.

The $\langle P_2 \rangle$ value can be obtained experimentally using various techniques, viz. refractive index, magnetic susceptibility anisotropy, NMR, Raman Spectra, etc., and the calculation of $\langle P_2 \rangle$ from the experimental data involve

certain assumptions in each case. By comparing $\langle P_2 \rangle$ values obtained from different methods, we can get an idea about the accuracy of these assumptions. With this motivation, I wanted to measure $\langle P_2 \rangle$ by a spectroscopic method using a guest dye in an aligned liquid crystalline host. However, the $\langle P_2 \rangle$ values obtained by this method did not agree at all with the values obtained from our X-ray studies. The ~~problem~~ probable reasons for this discrepancy have been discussed.

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