# Chapter - 1

# INTRODUCTION

## 1.1 LIQUID CRYSTALS

> *"I venture to ask you to investigate somewhat closer the physical isomerism of the two enclosed substances. Both substances show such striking and beautiful phenomena that I can hopefully expect that they will also interest you to a high degree...."*

This is from a letter of Friedrich Reinitzer, the Austrian botanist, written to Otto Lehmann, the German physicist in 1888[1] — while discovering **'Liquid Crystals'**, a term latter coined by Lehmann[2]. Not only to Lehmann but also it has grown interest to a large section of scientific community. Liquid Crystals, usually organic or organometalic compound[3-5], represent a different state of matter in which the degree of molecular order lie intermediate between the perfect long-range positional and orientational order found in solid crystals and the statistical long-range disorder found in ordinary isotropic liquids and gases. It can flow like a liquid and form droplets, yet it is anisotropic, which is reminiscent of crystals. Now-a-days, following Friedel's[6,7] suggestion the term 'mesomorphic phase' or 'mesophase' meaning intermediate phase, are also used along with the term liquid crystals.

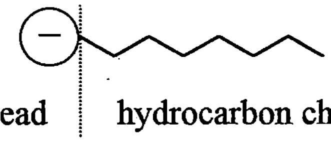
An important factor governing the formation of a mesophase is molecular shape[5,8]. The molecules are usually geometrically anisotropic. Mesogens which are formed by the molecules elongated in one dimension i.e., rod-like or reed-like are called calamitic and which are formed by the molecules extended in two dimensions i.e., disk-like or lath-like are called columnar or discotic. The molecular shape may even be bowl-shaped[9], sofa-shaped, banana-shaped[10-13], U[11],Y[14], H[15] and T[16] -shaped.

## 1.2 CLASSIFICATION OF LIQUID CRYSTALS

Liquid crystals are divided into two main subgroups:

### 1.2.1. Lyotropic Liquid Crystals

Lyotropic liquid crystals (LLC)[17-21] are mixtures of an anisotropic amphiphilic compound (surfactant) and one or more polar solvents such as water. Amphiphilic compound has two groups — a hydrophilic polar head and a



hydrophobic hydrocarbon chain. It is highly soluble in water. The temperature range of the mesophase of a LLC is determined by its concentration. At low concentration the solute molecules are distributed randomly throughout the solvent. Below certain concentration LLC will not form. This concentration is called critical concentration. In LLC solute-solvent interaction plays a major role to maintain long-range ordering. Here solute-solute interaction is secondary. The lyotropic liquid crystalline phases have relevance to biological systems. Biological membrane consists of lipids and water and usually also proteins which have liquid crystalline properties. Moreover, Lyotropic systems, are usually as sensitive to changes in temperature as thermotropic systems. There are different types of LLCs but as this dissertation is not concerned with LLC, it shall not be discussed any further.

### 1.2.2. Thermotropic Liquid Crystals

Depending on the molecular structure, a particular compound may pass through one or more mesophases before it is transformed from low temperature solid into the high temperature isotropic liquid or vice-versa. They are commonly designated as thermotropic. Thermotropic liquid crystals (TLC) can be classified into three main types: A) nematic, B) smectic and C) columnar phases[7,8,17,21-23].

A) <u>Nematics</u>

The word 'nematic' comes from a Greek word *νημα* means 'thread' and it indicates thread-like defects in this type of mesophase. The properties are as follows:

i) Nematic liquid crystals have no translational or positional order.

ii) They have long-range orientational order about the molecular long-axis.

iii) Molecules are aligned along time averaged preferred direction, labelled by a unit vector (called director) **n**.

iv) The direction of **n** may be determined by some minor forces such as surface force.

v) The states of the director **n** and - **n** are indistinguishable. If the individual molecules carry a permanent electric dipole there are just as many dipoles 'up' as there are dipoles 'down'.

vi) It is optically uniaxial.

vii)The molecules are either optically inactive or, if they are optically active, right and left handed molecules must be racemic (1:1).

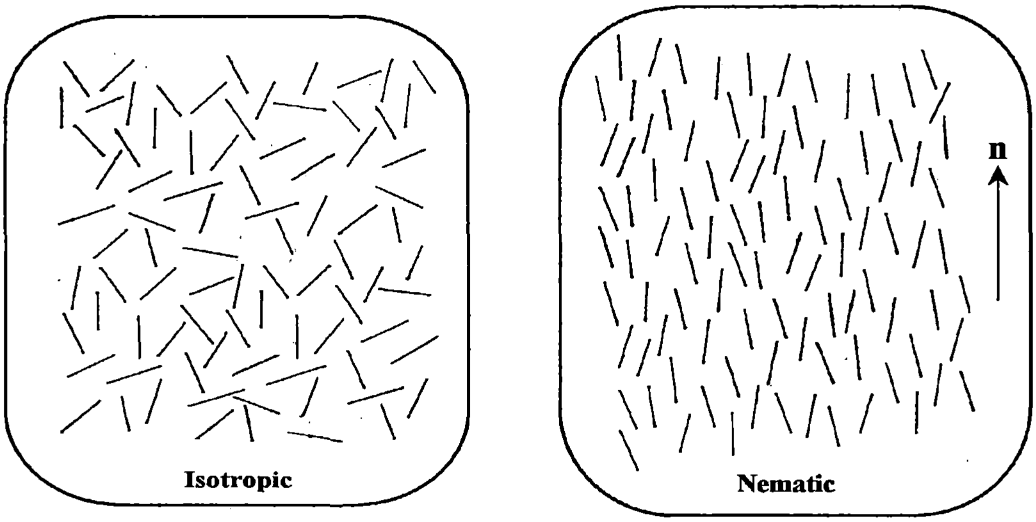


Fig.- 1.1 Schematic diagram of molecular order in the isotropic and nematic phase.

Apart from ordinary nematics two other nematic phases are common. These are a) cholesteric or chiral type nematic and b) cybotactic nematic.

a) Cholesteric or chiral-nematics

Cholesteric ($N^*$ or $N_{ch}$) are very similar to a nematic material[22]. The centre of gravity have no long-range order and the molecular orientation shows a preferred axis labelled by a director **n**. However, **n** is not constant in space. The preferred conformation, shown in Fig.-1.2, is helical. If we call the z-axis the helical axis, we have the following structure for **n**

$n_x = \cos(q_0 z + \varphi)$ ; $n_y = \sin(q_0 z + \varphi)$ ; $n_z = 0$.

Both the helical axis (z) and the value of $\varphi$ are arbitrary. The structure is periodic along z and (since the states **n** and **-n** are again equivalent) the spatial period L is equal to one-half of the pitch:

$L = \pi / |q_o|$.

Both the magnitude and sign of $q_o$ are meaningful. The sign distinguishes between right- and left-handed helices; a given sample at a given temperature always produces helices of the same sign. Magnitude of $q_o$ depends on temperature and concentration.

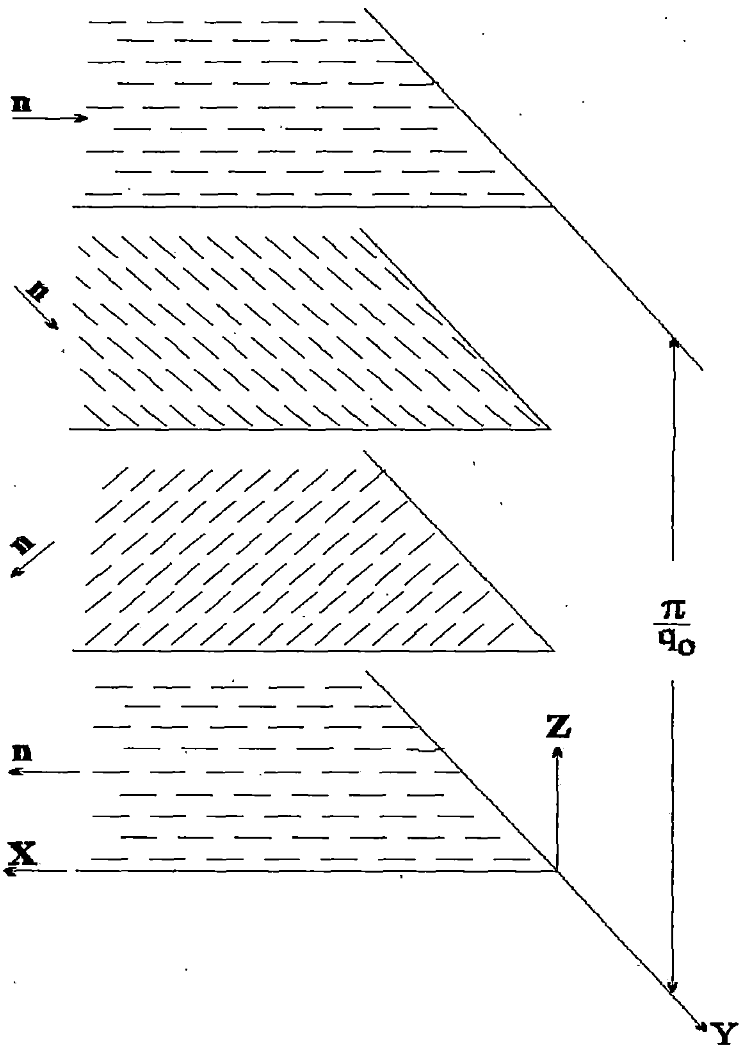
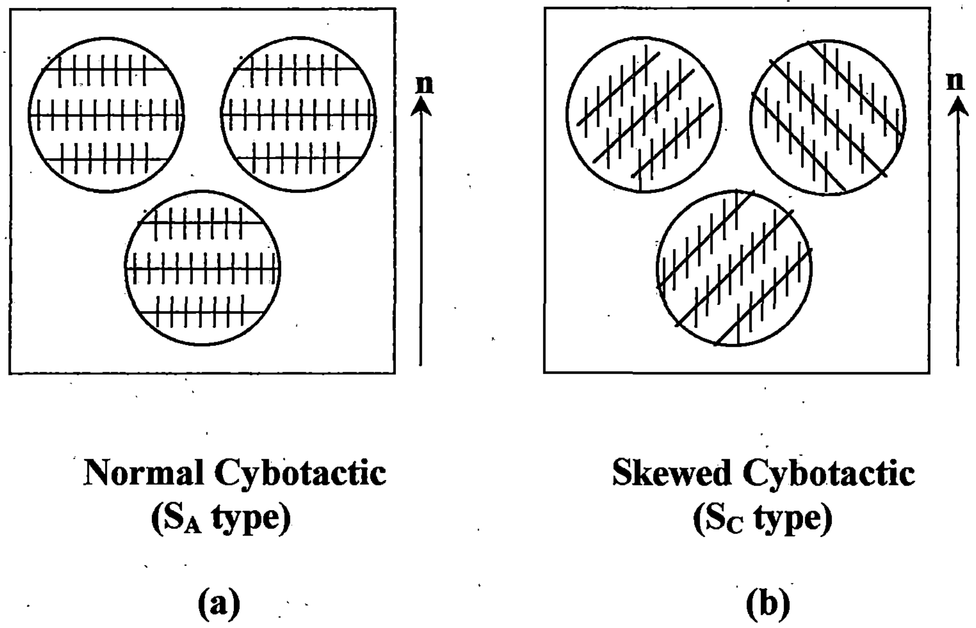


Fig.- 1.2 Schematic representation of the helical structure of the cholesteric liquid crystals.

b) Cybotactic nematic

This phase was first observed by de Vries[24,25] from x-ray studies. It contains a groups of molecules and the molecular centre in each group lie in a well defined plane. When molecular long-axis is arranged perpendicular to the plane or tilted with respect to the plane, the phases are called normal or skewed cybotactic nematic phase respectively. This phase looks like nematics with smectic fluctuation.



**Normal Cybotactic**
**($S_A$ type)**
**(a)**

**Skewed Cybotactic**
**($S_C$ type)**
**(b)**

Fig. - 1.3 Schematic representation showing molecular arrangements in cybotactic nematic phase

Although biaxial nematic was theoretically predicted by Freiser in 1971 it has been observed in mid 80's in polymeric as well as low molecular weight thermotropic systems[22,26-28].

B) Smectics

The properties of smectic mesophases (Sm) are as follows:

i) This type of mesophases have a lamellar structure

ii) Within each layer molecules are mobile in two directions and can rotate about one axis in some cases.

iii) Inter layer attraction forces are weaker than the lateral forces among molecules within a layer and thus the layers can easily slide over one another.

iv) Molecules may be normal to the plane of the layers or inclined.

v) This phase is more viscous than nematic.

vi) For a given material usually occur at temperatures below the nematic domain.

Though Friedel[23] recognised only one type of smectic, now called smectic A, over the years a large number of different smectic phases have been identified[8,22,29-38]. These have been tabulated in Tables - 1.1–1.2. Only those smectic phases which are relevant to the present work described below.

Smectic A (SmA)

i) Molecular long axes are normal to the plane of the layer.

ii) The centres of mass of the molecules possess short-range one-dimensional translational periodicity along the layer normal.

iii) Within each layer molecules have only orientational ordering.

iv) The phase is optically uniaxial.

**SmA$_1$:** This phase is a monolayer phase arranged in a liquid like fashion with the dipolar heads oriented up and down randomly within each layer. It produces the periodicity d equal to l, the molecular length.

**SmA$_2$:** It is a bi-layer phase. This is attributed to a preferential up-down ordering of the dipolar heads within each layer, which alternates from layer to layer producing a periodicity d equal to twice the molecular length, 2l.

**SmA$_d$:** This is an intermediate phase of SmA$_1$ and SmA$_2$ characterised by the layer thickness between one and two molecular lengths (i.e., $l < d < 2l$) due to head to tail association of molecules with some overlapping, contrast to no overlapping as in SmA$_2$ phase. Thus this is a partially bilayer phase, indistinguishable with SmA$_2$ phase in context of microscopic symmetries.

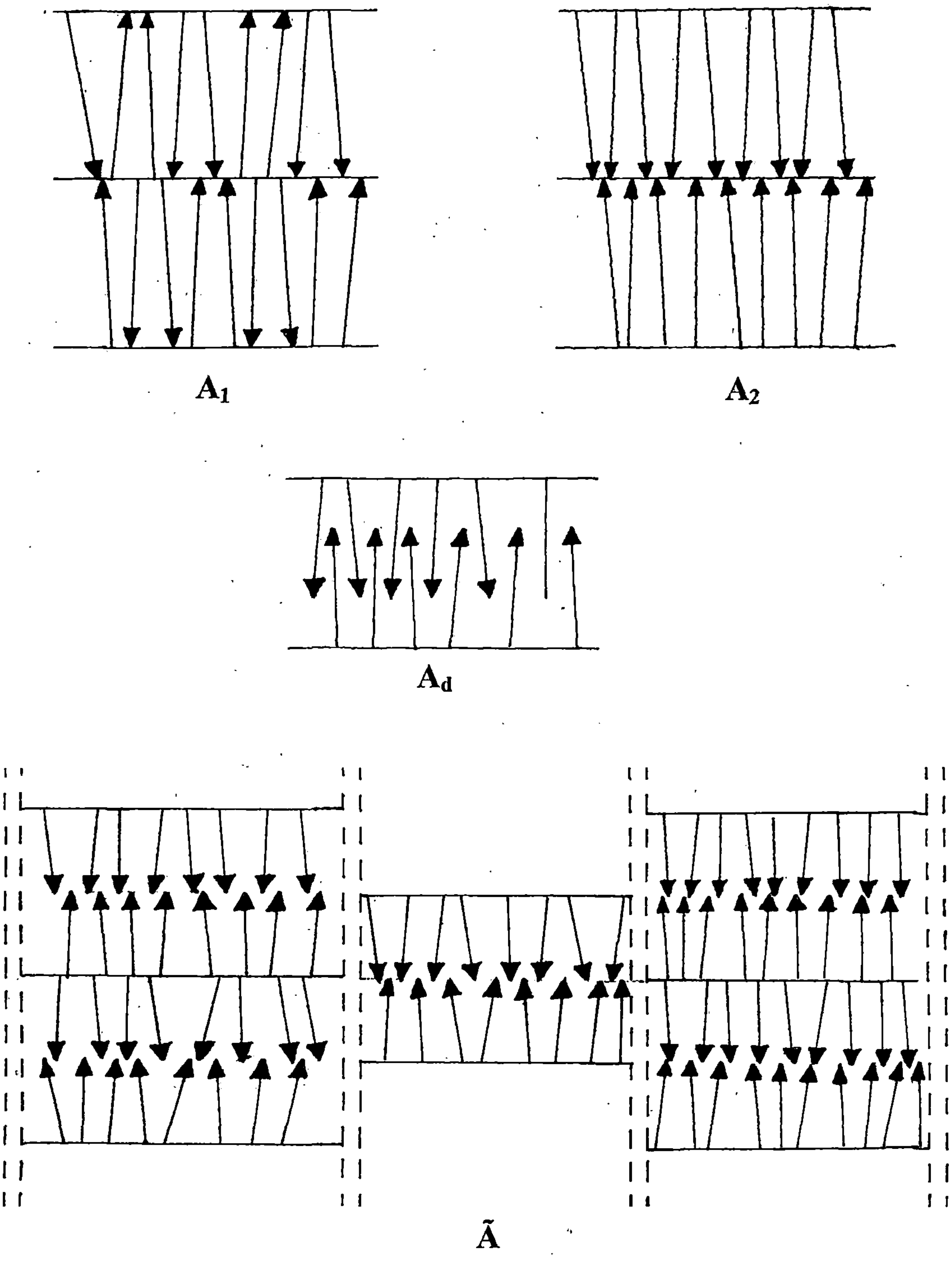


Fig. - 1.4 Schematic representation of the molecular arrangement in the different forms of smectic A phase composed of polar molecules; monolayer $A_1$, bilayer $A_2$, partially bilayer $A_d$ and antiphase $\tilde{A}$.

**$\mathrm{Sm}\tilde{\mathrm{A}}$:** This is actually a two dimensionally ordered bilayer smectic phase, called antiphase, with modulation in the direction perpendicular to the layer normal[39].

There is a new type of SmA phase denoted by $\mathrm{SmA_{ic}}$[40] which intervenes between the $\mathrm{SmA_d}$ and $\mathrm{SmA_2}$ phases. This phase has two collinear incommensurate density modulations.

Smectic C (SmC)

The properties of SmC phase are as follows:

i) Molecules in a strata are arranged in a tilted manner with respect to the layer normal. Each layer is a 2-D liquid.

ii) Tilt angle may be constant or temperature dependent [34].

iii) The phase is optically biaxial.

Further it is classified into three subgroups, viz., $C_1$, $C_2$ and $C_3$ depending on the nature of tilt angles.

Smectic B (SmB)

The properties of SmB phase are as follows:

i) Within a layer molecular long axes are parallel to the layer normal but the centres of mass of the molecules are arranged in hexagonal symmetry.

ii) It is optically uniaxial.

This mesogen is reclassified into CrB (or L phase) and hexatic B phases. Both the phases exhibit long range bond orientational order but CrB (or L) shows inter and intra layer long range translational order whereas hexatic B exhibits quasi long range inter layer and short range intra layer translational order.

## 1.3 FEW OTHER MESOPHASES

Discotic

In 1977 S. Chandrasekhar et al.[41] first reported discotic phase mesophase in a system of disc like molecule. Two distinct phases are observed in this case — columnar and nematic. There are several columnar mesophases exhibited by discotic materials; these arise because of the different symmetry claseses of the two - dimentional lattice of columns and order or disorder of the molecular stacking within the columns. In recent years, significant amount of research works have been performed in this section[ 42-45].

## Blue phase

Some cholesteric liquid crystal materials having cubic symmetry and short pitch (<7000 Å) show a specific bluish - violet colour at a very short temperature region (~ 0.1 – $0.5^0$C) below its clearing temperature. These mesophases are called 'blue phase' due to its colour[44-48]. From thermodynamic and optical studies it is confirmed that these phases are stable in a narrow temperature interval. Three principal types of blue phases (I, II and III) have been observed depending upon their helical pitch. In increasing the pitch, phase III is the first to lose the stability, then phase II and at last phase I. These mesophases do not exhibit optical birefringence[49] but show optical activity and selective reflection of circularly polarised light.

## Re-entrant phase

In liquid crystalline compounds different phases appear in a fixed sequences as a function of temperature. The sequence of the mesophases during cooling from isotropic phase is given below:

Iso→Blue→N→A→C→B(hex)→I→B(Cr.)→F→J→G→E→K→H→Solid Crystal.

However, there is no single compound which exhibits all the phases. When temperature is changed if any phase reappears after normal occurrence in the above sequence, then that phase is called re-entrant phase. Re-entrant nematic ($N_r$) phase sequence ($N – S – N_r$) was first observed by P. E. Cladis[50], in a binary mixture of two polar cyano compounds. Later this behaviour is observed in many systems either in mixtures, in pure state, under pressure or some combination of these three conditions[51]. Multiple re-entrant behaviour has also been observed[52]. Cladis explained the re-entrance phenomenon in system of polar molecules in terms of dipole-dipole interaction. de Gennes gave simple models based on mean-field arrangements to explain single and double re-entrance behaviour[22]. The re-entrant phenomenon in mixtures and in pure compounds, according to Brodzik and Dabrowski[47], is due to the change in an equilibrium between associated and non-associated forms of the molecules as a result of change in temperature and the competition between short and long range order.

## Induced and enhanced Smectic phases

Sometimes binary mixtures of two purely nematic compounds show smectic phase depending upon the charge distribution of individual compounds. This type of smectic phase is known as induced smectic phase. One of the components of the mixture be a strongly polar compound and other is non-polar or weakly polar[53-68].

Components of binary mixture, having smectic phase in their pure states may exhibit a smectic phase over wider temperature region for certain concentrations. This phase in binary mixture is known as enhanced smectic phase.

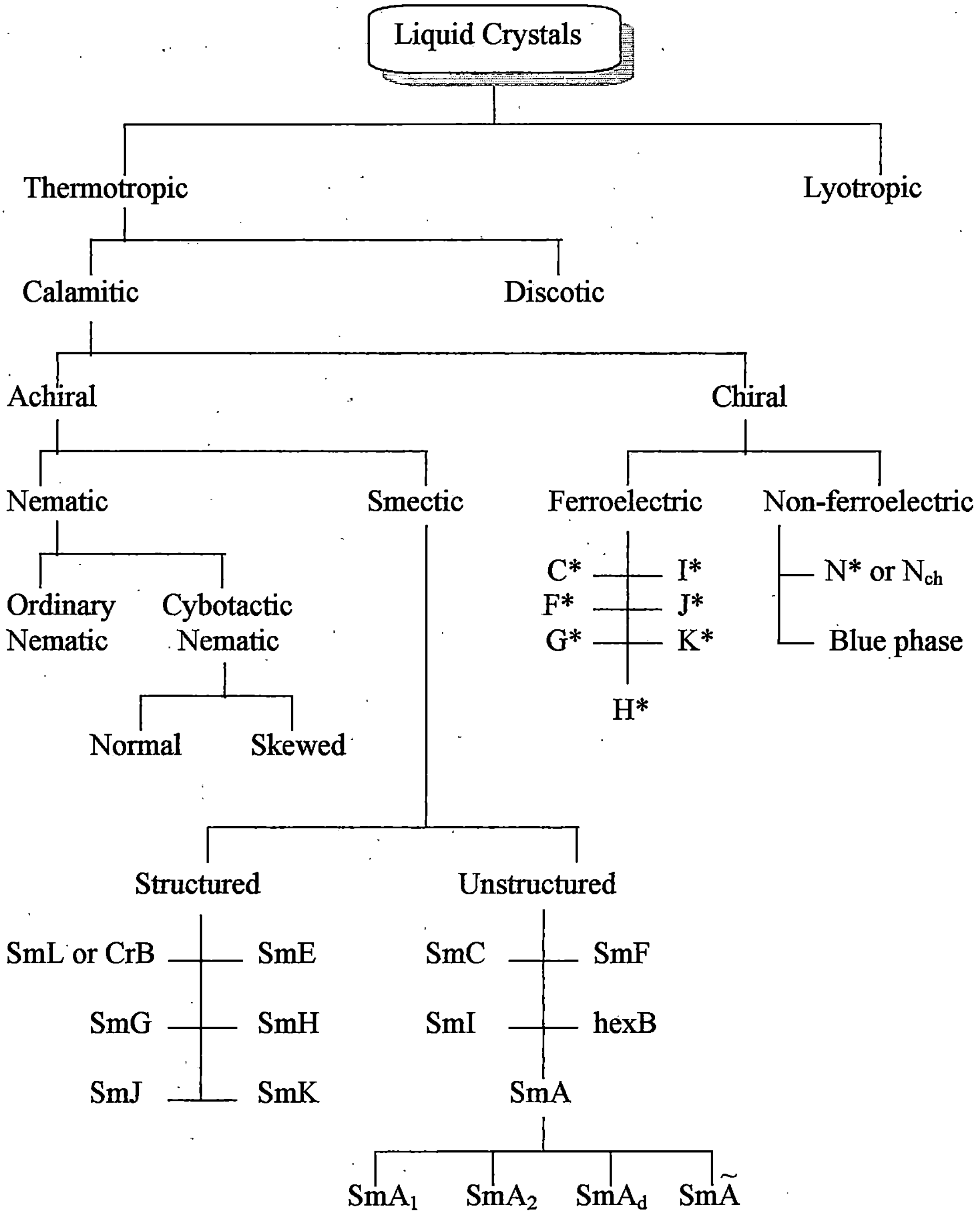
The formation of induced smectic $A_d$ phase may be explained by mean field approximation model of Longa and de Jeu[69] or Berker's frustrated spin glass model[70]. In both the models molecular association due to dipole-dipole interaction and role of alkyl chain length are important.

## Chiral tilted smectic phase

Within various types of smectic liquid crystals seven viz., C, I, F, J, G, K and H have tilted structure. Since the molecules are tilted with respect to the layer normal, the rotation of the molecules about the director is anisotropic, resulting in a non-compensated macroscopic component of the molecular dipole moment. In addition to this if a chirality is present in the molecules they can give rise to spontaneous polarisation. These are called ferro-electric liquid crystals and are denoted by C*, I*, F*, J*, G*, K* and H*[56].

## Table - 1.1

### Classification of Liquid Crystals



## Table - 1.2

**Phase type and ordering**

| Phase type | Molecular orientation | Molecular packing | Molecular orientational ordering | Bond orientational ordering | Positional ordering | |
|---|---|---|---|---|---|---|
| | | | | | Normal to the layer | within the layer |
| N | parallelism of long molecular axis | random | LRO | Nil | Nil | Nil |
| $S_A$ | orthogonal | random | LRO | SRO | QLRO | SRO |
| $S_C$ | tilted | random | LRO | SRO | QLRO | SRO |
| hex B | orthogonal | hexagonal | LRO | LRO | QLRO | SRO |
| $S_I$ | tilt to apex of hexagon | pseudo hexagonal | LRO | LRO | QLRO | SRO |
| $S_F$ | tilt to side of hexagon | pseudo hexagonal | LRO | LRO | QLRO | SRO |
| $S_L$ | orthogonal | hexagonal | LRO | LRO | LRO | LRO |
| $S_J$ | tilt to apex of hexagon | pseudo hexagonal | LRO | LRO | LRO | LRO |
| $S_G$ | tilt to side of hexagon | pseudo hexagonal | LRO | LRO | LRO | LRO |
| $S_E$ | orthogonal | ortho- rhombic | LRO | LRO | LRO | LRO |
| $S_K$ | tilted to side a | mono-clinic | LRO | LRO | LRO | LRO |
| $S_H$ | tilted to side b | mono-clinic | LRO | LRO | LRO | LRO |

SRO : short range order, LRO : long range order, QLRO : quasi-long range order