GENERAL INTRODUCTION

1.1 Introduction

In the Early 1960’s the pioneering research efforts at RCA and Xerox brought attention to possibility of using a relatively unknown class of organic materials, i.e., liquid crystals (LC’s), for modulating electro-optic properties of light for fabricating a revolutionary new flat panel display. Today the flat panel liquid crystal display devices, (LCD’s) have replaced the bulky and power-hungry cathode ray tubes (CRTs) and thus changed the face of the modern office.

Liquid-crystalline material research has contributed significantly both to the development of liquid-crystalline display (LCD) technology and also to the better understanding of the phase behavior of soft condensed matter systems. Quantitative knowledge of the physical properties is necessary, so that improved materials may be devised for applications. Thus, attempts are continuously being made to study the material properties of both pure compounds as well as their mixtures for a better insight into the basic understanding of liquid crystalline behavior so that a newer and more acceptable class of materials suitable for display devices emerges.

Any material, if the temperature is raised more and more, it generally changes its state from solid to liquid and to gaseous. An Austrian botanist, Friedrich Reinitzer first observed liquid crystals in 1888. He discovered a strange material that exhibited a mesophase between solid state and liquid state. At a temperature of 145 °C, it melted, becoming cloudy white and viscous. At a temperature of 179 °C, it became isotropic and clear. The material he discovered was cholesteryl benzoate. On March 14, 1889, he wrote a letter to Otto Lehmann, telling him about the two melting points. Lehmann studied the material and discovered that the liquid at the mesophase exhibited a double refraction effect, characteristic of a crystal. Because it shared characteristics of both liquid and crystal, he named it “fliessende krystalle” and the name “liquid crystal” was born.

Liquid crystal is a state of matter that is neither a solid crystal nor an isotropic liquid. The basic difference between crystals and liquids is that the molecules in a
crystal are ordered whereas in a liquid they are not. The existing order in a crystal is usually both positional and orientational, i.e., the molecules are constrained both to occupy specific sites in a lattice and to point their molecular axes in specific directions. Contrary to this, the molecules in liquids diffuse randomly throughout the sample container with the molecular axes tumbling wildly. The states of matter whose symmetric and mechanical properties are intermediate between those of a crystalline solid and an isotropic liquid are called `liquid crystals\(^3\)\(^-\)\(^6\) (LC). Liquid crystals exhibit anisotropy in their mechanical, electrical, and optical properties, behaving in this sense as solid crystal. Nevertheless, they have no ability to support shearing, and thus they flow like ordinary liquids\(^7\).

This is why liquid crystals attain their importance in technological applications, especially in electro optic switches and in liquid-crystal displays\(^8\). Therefore, thermal stability of liquid-crystalline mesophase and its molecular ordering are of great importance.

### 1.2 Chemical structure of liquid crystals

The role of molecular structure or geometry in liquid crystals is extensively studied by Gray\(^9\). In order to exhibit the mesomorphism, the molecules should possess highly geometrical anisotropy in shape, namely it should be either rod like or disc like. The mosomorphic molecule mainly consists of three units such as core, linking groups and terminal groups. The core should be highly rigid to form liquid crystalline phases because it makes the interaction with other molecules anisotropic. In addition to the core rigidity, there is a need to have certain flexibility for the molecule in order to ensure reasonable low melting points and stability. This flexibility can be obtained by attaching the terminal groups.
The general molecular structure is given as below

![Molecular Structure](image)

where R and R” are flexible terminal groups, while A and B are aromatic groups and Z is the linking group. This part including aromatic rings and linking group together is called as central rigid core. Z represents a linkage of the type \(-\text{A}=\text{B}\) between two benzene or hexane rings. The aromatic rings linked through a central group Z which often involves a double bond or a triple bond to preserve the rigidity and linearity of the molecules.

R and R” may be same or different and represent groups example, \(R = \text{n-alkyl}\) and \(R” = \text{n-alkoxy}\) or vice versa, \(R \text{ and } R” = \text{n-alkyl}\)

Generally the linking group used is as follows

- Saturated groups, such as ethylene (\(\text{C}_2\text{H}_4\)), ester (-COO-)
- Unsaturated groups containing double bonds, such as stilbene (-CH=N-), auzoxy (-N=N-) and schiff’s base (-CH=N-).
- Unsaturated groups containing triple bond such as acetylene (-C≡C-), and diacetylene (-C≡C-C≡C-)\(^{10-13}\).

### 1.3 Classification of liquid crystals

The Liquid crystal nature is exhibited by many number of different classes of materials which includes organic compounds, amphiphilic organic compounds, polymeric liquid crystals and colloidal dispersion of inorganic materials\(^{14,15}\).

The transitions to the mesophases may be obtained in two different ways either by the change of temperature or by the change of concentration of a solvent, usually water
1.3.1. Thermotropic liquid crystals

Thermotropic liquid crystal phases are observed due to the change in temperature. Thermotropic liquid crystals in which the transitions take place reversibly on both heating and cooling are the thermotropic liquid crystals which are stable above the melting point of the compound are called enantiotropic. In certain cases the phases are observed only on cooling, and the liquid crystalline state is stable at temperature below the melting point. The phases are called monotropic. Thermochochronic liquid crystals are thermotropic in origin and have chiral (twisted) structures\(^{16, 17}\).

1.3.2. Lyotropic liquid crystals

Lyotropic phases are formed in the presence of a suitable solvent and also concentration. The molecules that make up lyotropic liquid crystals are amphiphilic or surfactants consisting of two distinct parts: a polar (often ionic) head and a non-polar (often a hydrocarbon) tail. Following the rule of the like dissolve like, the head is attached to water (or hydrophilic) and the tail is repelled by water (hydrophobic). These amphiphilic molecules of material form liquid crystals on dissociation in solvent\(^{18-20}\). Deoxyribonucleic acid (DNA), certain viruses like tobacco mosaic virus (TMV) form lyotropic mesophases when dissolved in an appropriate solvent (usually water) in suitable concentration. Soaps and detergents when used with water form liquid crystals.

1.3.3. Polymeric liquid crystals

Liquid crystalline polymers combine the self organization of the mesogenic groups into the ordered structure of liquid crystalline phases with some typical polymer properties such as freezing of the disordered polymer chain at glass transition temperature. These can be prepared by incorporation of the anisotropic mesogenic groups into polymeric systems. These are classified either as main chain liquid crystalline polymers [MCLCP] or polymers with mesogenic side groups [SCLCP] or as liquid crystalline elastomers\(^{21-24}\).
Liquid crystalline materials in general may have various types of molecular structure. Basing on the geometrical structure, the thermotropic liquid crystals can be divided into rod like, disc like, sanidic or brick-like or lath-like and bowlic for bowl-like. The liquid crystals derived from the rod-like molecules are called calamitics. The liquid crystals formed from disc-shape molecules are known as discotics. Intermediate between rod-like and disc-like molecules are the lath-like species. The symmetry-based classification of liquid crystals was first made by Friedel.

**Liquid Crystals may be broadly classified as follows**

![Diagram of liquid crystals classification]

**Nematics:**

The first phase that condenses when isotropic liquid is cooled is called nematic and also is known as high temperature liquid crystal phase. This phase possesses long range orientational order. The phase is fluid and there is no long-range correlation of the molecular centre of mass position. The long axis of the molecules on an average are aligned about a specific direction, which is denoted by a unit vector, called the director, \( \hat{n} \). Nematic phase is apolar in nature i.e., \( \hat{n} \) and \(-\hat{n}\) are physically equivalent. Thus the material is still anisotropic. In thermal equilibrium it has...
∞/mm symmetry and is uniaxial. The important variable in nematic liquid crystal is the order parameter, which measures how the molecules are aligned with the director. The usual measure of this order is,

$$S = \frac{1}{2} <3 \cos^2 \theta - 1>$$

where S represents the thermal fluctuations of the individual molecular long axis and the brackets <> denote a thermal averaging and $\theta$ is the angle between the molecule (molecular long axis) and the director $\mathbf{n}$.

If the classical nematic has an additional short range smectic like ordering, then it is called cybotactic nematic. The short range smectic like layers are either orthogonal or tilted to the layer planes and they are denoted as normal cybotactic, $N_{nc}$ and skewed cybotactic, $N_{sc}$ phases respectively. Biaxial nematics are also reported$^{32,33}$. The nematics exhibit schlieren, threaded marble, pseudo isotropic textures when the sample is observed through crossed polarizers.

**Cholesteric or spontaneously twisted nematic**

Cholesteric LC’s are regarded as special kind of nematics. The nematic phase exhibited by an optically active compound is called spontaneously twisted nematic or cholesteric. The name cholesteric is given to these compounds as the first materials exhibiting this phase are from cholesterol derivatives. In this phase, the molecules prefer to lie next to each other in a slightly skewed orientation. This induces helical director configuration in which the director rotates through the material. These are composed of helical aggregation of the molecules. Such a structure is envisaged as being composed of sheets of molecules and within each sheet the molecules behave as in nematic phase and has an average direction defined by a director $\mathbf{n}$.

To quantify
the degree of twist, the pitch length, P of the helix is defined by convention as the longitudinal distance in which the director has made one complete $360^\circ$ revolution. The pitch length varies with time. Each molecule is skewed at some average angle with respect to its neighbors in a sheet above and below. Two such helical arrangements are possible one right-handed, other left-handed, but one will have a lower energy than the other $^{34-37}$. These are uniaxial (both positive and negative).

These exhibit focal conic with Grandjean, homogeneous and pseudo isotropic textures. The molecular arrangement is shown below.

Smectics

Smectic is the name coined by G.Friedel for certain mesophases with mechanical properties reminiscent of soaps. From a structural point of view, all the smectics are layered structures, with well defined inter-layer spacing which can be measured by X-ray diffraction technique$^{28}$. Smectic phases are characterized by both long range orientational order as well as short range positional order. With simple changes in mutual arrangement of the layers and with changes (in the state of order) inside the layers, a variety of smectic phases can be obtained$^{38-41}$. The smectics exhibit subtle polymorphism than nematics. No single compound is found to exhibit all the smectic phases (S$_A$ to S$_X$) so far.

There are various modifications of the smectic phases, each with different combination of in-plane order and tilt angle. These have been named as the smectic A, B, C, D, E, F, G, H, I, J and K phases designated as, Smectic-A$^{42-47}$, Smectic-B$^{48-49}$, Smectic-C$^{50-53}$, Smectic-D$^{54-55}$, Smectic-E$^{55-59}$, Smectic-F$^{60-64}$, Smectic-G, Smectic-
Smectic-I$^{44}$, Smectic-J$^{44}$ and Smectic-K$^{44}$ or S$_A$, S$_B$, S$_C$, S$_D$, S$_E$, S$_F$, S$_G$, S$_H$, S$_I$, S$_J$, and S$_K$, with the letters denoting the chronological order of their discovery. The thermal sequence of their occurrence is S$_A$, S$_D$, S$_C$, S$_B$, S$_E$, S$_I$, S$_F$, S$_G$, S$_G'$ (S$_J$), S$_H$ and S$_H'$ (S$_K$) with decreasing temperature. S$_B$, S$_G$, S$_J$, S$_E$, S$_H$ and S$_K$ are found to be more crystalline than remaining liquid crystalline phases.

The structural characteristics of smectic phases of classic liquid crystalline compounds is given in Table 1.1.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Phase type</th>
<th>Molecular Packing</th>
<th>Molecular Orientation</th>
<th>In-plane Correlation</th>
<th>Layer correlation</th>
<th>Bond-orientation order</th>
<th>Dimensionality</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>fluid</td>
<td>random</td>
<td>orthogonal</td>
<td>Short-range</td>
<td>None</td>
<td>Short-range</td>
<td>---------------</td>
</tr>
<tr>
<td>B</td>
<td>Hexatic</td>
<td>hexagonal</td>
<td>orthogonal</td>
<td>Short-range</td>
<td>None</td>
<td>Long-range</td>
<td>3D hexatic</td>
</tr>
<tr>
<td></td>
<td>Crystal B</td>
<td>crystal</td>
<td>Hexagonal</td>
<td>long-range</td>
<td>long-range</td>
<td>long-range</td>
<td>3D</td>
</tr>
<tr>
<td>C</td>
<td>fluid</td>
<td>random</td>
<td>tilted</td>
<td>Short-range</td>
<td>None</td>
<td>Long-range</td>
<td>---------------</td>
</tr>
<tr>
<td>D</td>
<td>Plastic</td>
<td>rods</td>
<td>ortgogonal</td>
<td>long-range</td>
<td>None</td>
<td>isotropic</td>
<td>3D</td>
</tr>
<tr>
<td>E</td>
<td>crystal</td>
<td>orthorhomobic</td>
<td>orthogonal</td>
<td>long-range</td>
<td>long-range</td>
<td>long-range</td>
<td>3D</td>
</tr>
<tr>
<td>F</td>
<td>hexatic</td>
<td>Pseudo hexagonal</td>
<td>Tilt to side</td>
<td>Short-range</td>
<td>None</td>
<td>long-range</td>
<td>3D hexatic</td>
</tr>
<tr>
<td>G</td>
<td>crystal</td>
<td>Pseudo hexagonal</td>
<td>Tilt to side</td>
<td>long-range</td>
<td>long-range</td>
<td>long-range</td>
<td>3D</td>
</tr>
<tr>
<td>H</td>
<td>crystal</td>
<td>Herringbone</td>
<td>Tilted’</td>
<td>long-range</td>
<td>long-range</td>
<td>long-range</td>
<td>3D</td>
</tr>
<tr>
<td>I</td>
<td>Pseudo hexagonal</td>
<td>Tilt to apex</td>
<td>Possibly long range</td>
<td>None</td>
<td>long-range</td>
<td>Stacked 2D crystal &amp; 3D hexatic</td>
<td></td>
</tr>
<tr>
<td>J(G’)</td>
<td>crystal Pseudo hexagonal</td>
<td>Tilt to apex</td>
<td>long-range</td>
<td>long-range</td>
<td>long-range</td>
<td>3D</td>
<td></td>
</tr>
<tr>
<td>K(H’)</td>
<td>crystal Herringbone Monoclinic</td>
<td>Tilted’</td>
<td>long-range</td>
<td>long-range</td>
<td>long-range</td>
<td>3D</td>
<td></td>
</tr>
</tbody>
</table>
Discotics

Mesogens with disc-like molecules are called discotics. The existence was theoretically predicted in 1970 and mesomorphism in discotic materials (hexa alkonoyl benzenes) was first reported in 1977 by Chandrasekhar et al\(^2\)\(^5\). The molecules of these classes are flat and disc-like in shape and able to be packed in different structures. The classification of columnar phase is given below.

The tilted variants are also possible. Similar to rod shaped molecules the disc-shaped molecules can also form a nematic phase characterized by a long range orientational order, but no positional order with the director parallel to the disc normal. In chiral compounds, the discotic nematic exhibits a twisted structure\(^6\)-\(^7\).\(^0\)

Sanidic

These are characterized by boards. Depending up on the relative size of the main axes, these molecules can be derived from either rod-like or disc-like molecules. Derived from Greek word for board, these phases are called sanidic. The rod-like and disc-like liquid materials are characterized by the rotational symmetry of the molecular models, which means the anisotropy of the models can be described by two main axes. The more general case would be the consideration of molecular models with three different main axes. The structure of sanidic phases can be characterized by three translational periods (in accordance with length, breadth and thickness) of scattering maxima, which cause three molecular units by investigation with X-rays\(^7\).\(^1\).
Bowlics

Mesogens with bowl-like molecules forms the bowlic liquid crystal. These contain molecules, which are three dimensional in a physical sense and can exhibit mesophases as the one-dimensional rod-like and two-dimensional disc-like bowlic compounds. Lin first proposed these bowl like molecules. Pyramidal shape and cone-shaped are later reported. X-ray diffraction studies performed to investigate the structure of these phases showed either classical columnar or a hexagonal or oblique lattice in a two dimensional array with a disordered array in three dimensions.
1.4. Statement of the problem

The research on materials is mainly directed towards the design, fabrication and synthesis of novel systems and the study of the physical properties of these for the usage in fundamental and applied research for their applications which are useful for the society. These include the fascinating and novel liquid crystal materials also. These systems function as both ordered crystalline solids and isotropic liquids. That is they have the flow as well as anisotropic nature. The research interest in these materials is two fold. On one hand new properties are expected and on the other hand the study of interaction of different systems (namely the effect of end chains, rigidity of the core, position of certain polar atoms like N, O, Cl etc, in the molecule) is fascinating and interesting. Now the research is mainly directed towards the design and fabrication of such materials for their use in chronological and scientific interest, which involve the characterization and study of their properties with different experimental techniques including density and optical measurements.

In recent years, liquid crystals have become lucrative and alternative candidates for the electro optic displays in the place of conventional inorganic materials, as they are easy to design and also for synthesis. However, these materials underline much importance to an experimental solid-state chemist and condensed matter physicist, as they are representative of low-dimensional systems, workable at ambient temperatures. On the other side, if the information of these phase transitions is systematically studied in the domain of fundamental molecular forces and the higher archive of fundamental scaling laws, it gives totality of understanding in exploitation of their application viabilities. Moreover, these materials exhibit polymorphism involving phase transitions of rare occurrence and far awaited theoretical expectations at the inter phase one, two, and three –dimensional melting.

The Schiff’s base N-(p-n-alkoxybenzyldiene)-p-n-alkoxy anlines popularly known as nO.Om’s where the chain number on both sides can be varied from 1 to 18 to realize a variety of phase sequences (variants). The quenching of oxygen atom in the molecular moiety on either side or on both sides will provide a variety of changes in phases or the clearing temperatures or both. That is, the electro negative oxygen atom plays an important role in deciding the clearing temperature as well as the phase variants. It is well established that the oxygen atom in the molecular moiety enhances the clearing temperatures as well as the nematic phase abundance in a homologous series.
The earlier systematic studies are carried out at CLCRE, Acharya Nagarjuna University and the literature survey on a number of nO.Om, nO.m, n.Om and n.m compounds regarding the phase transitions across different LC phases and the molecular polarizability studies which includes the estimation of molecular polarizability anisotropy of a liquid crystal material employing the modified Lippincott - $\delta$ function and molecular vibrational models, motivated the author to synthesize N-(p-n-heptyloxybenzylidene)-p-n-alkoxy anlines with alkoxy chain number, $m = 3, 5, 6, 7,$ and $9$ with the molecular formula.

$$\text{C}_7\text{H}_{15}\text{O}\begin{array}{c} \text{CH} = \text{N} \\ \end{array}\text{OC}_m\text{H}_{2m+1}$$

These liquid crystal materials show different phase variants namely N, N-C, N-C-I giving rise to different phase transformations, such as isotropic to nematic, nematic to smectic-C, and smecti-C to smectic-I phases.

The order of phase transitions can be studied by number of experimental techniques. The author used the density studies to arrive at the order of the phase transformation.

These experimental and semi empirical theoretical calculations enabled for the study of temperature variation of orientational nematic order parameter, $S$ in the nematic phase.

In the estimation of order parameter, $S$ the author used different methods and field models. The author used the birefringence data along with density results to understand the nature of phase transformations and for the determination of molecular polarizabilities of the molecule employing different local field models which the molecule experiences in the nematic phase. Further, the author studied the variation of order parameter, $S$ with temperature in all the compounds and able to discuss the results with the body of the data available. The comparative study of $S$ from different methods on these compounds and the compounds available in literature is studied.

Further, different thermodynamic parameters are estimated from the density data for these compounds and compared the results with the other compounds available in literature.
1.5. References


