Chapter 1

Liquid crystals are known for about hundred and twenty five years. The credit for the discovery of liquid crystalline phenomenon is given to an Austrian botanist Reinitzer. He observed that the compound cholesteryl benzoate appeared to have two melting points. At 145 °C the solid structure collapsed to form a turbid liquid (liquid crystal), which on further heating became transparent at 179 °C, giving a true isotropic liquid. The term Liquid Crystals suggests that a substance is in two quite different states of matter at the same time. A crystal can not possess the properties of a perfect liquid or vice versa. Conventionally, matter exists in one of the three well-defined states of aggregation, namely, solids, liquids and gases, each having properties characteristic of its own. The transition from one state to another normally occurs at a very precise temperature. When pure crystalline solid is heated beyond its melting temperature, it undergoes a single transition to isotropic liquid. There are, however, many organic compounds that do not immediately transform to liquid phase when heated beyond the melting temperature but exhibit more than a single transition from solid to liquid showing the existence of one or more intermediate phases, exhibiting the properties of both solids and liquids. Lehmann described this state as fluid crystals and established for the first time the terminology ‘liquid crystals’. Many other terms such as mesomorphic state, mesoform, mesophase, mesogen, anisotropic liquid, fluid crystals have been proposed and are used but the term ‘liquid crystals’ is still widely used.

Liquid crystals have been divided into two main categories, Thermotropic liquid crystals and Lyotropic liquid crystals in accordance with the manner in which these are obtained. Liquid crystals formed by heating solids are known as Thermotropic liquid crystals. The liquid crystalline systems formed when certain compounds are treated with a controlled amount of water or the polar solvent is known as Lyotropic liquid crystals.

With a large number of liquid crystalline substances available, Friedel carried out detailed optical studies of these compounds and classified them into three types as smectic, nematic and cholesteric. Smectic and nematic are the most common types of mesophases and the study of their optical properties made it possible to assign structures to them. These structures do not extend uniformly throughout the melt but
the whole melt is composed of the random orientations of groups or swarms of molecules as proposed by Bose’s swarm theory.

Many mesomorphic substances which have been studied are either of exclusively smectic structure or of exclusively nematic structure, but some can exist as both types of structures, smectic followed by nematic, and in these cases there are always definite transition temperatures defining the stability of different phases, which are completely reproducible. A few substances have been found to possess more than one phase and here also the temperature range of stability of the different phases are sharply defined. This is known as polymesomorphism.

Liquid crystalline materials are being exploited for their different applications. New developments have further encouraged chemists to explore structural variations in the liquid crystalline materials in search of new liquid crystals for different applications.

Chapter 2

This chapter deals with the syntheses and detailed characterization for the thirteen homologues of thiadiazole mesogens.

Heterocycles are of great important as core units in liquid crystals due to their ability to impart lateral and / or longitudinal dipoles combined with changes in the molecular shape. These materials hold great potential for use in spatial light modulation, all-optical signal processing, optical information storage, organic thin-film transistors, fast switching ferroelectric materials, fluorescent probes for the detection and analysis of biomolecules etc. Also, these materials have been patented in agricultural field as herbicides, fungicides and bactericides.

1,3,4-Thiadiazoles are relatively common in the liquid crystal literature although the variety of structural modifications that have been studied are actually very limited. The majority of systems have the 1,3,4-thiadiazole core substituted at the 2 and 5-positions by aryl units or a combination of aryl and alkyl / cyclo alkyl units. These materials are constructed through sulfurization and cyclization of appropriate diacylhydrazines. The 1,3,4-thiadiazole core imparts a large lateral dipole from S to the centre of the N-N bond.

In the present study it was proposed to synthesize low molecular weight materials with special structural features as well as to study the effect of rigidity on
the liquid crystalline properties of the mesogenic systems. With this in view, we have synthesized homologous series **I** as shown in figure 1 and studied their mesogenic properties. The purity of the compounds was checked by thin layer chromatography (TLC) and mesogenic properties of these compounds were observed under polarizing optical microscope provided with a Linkam heating stage. The transition temperatures were confirmed by Differential Scanning Calorimeter. Lower members exhibit nematic phases and higher members exhibit both smectic and nematic phases. Nematic phase shows its thread like texture and smectic phase shows broken fan shape texture (figure 2). Smectic phase commences from \( n \)-heptyl derivative and persist upto last members of the series. The average thermal stability of compounds of series is higher than reported series due to the introduction of rigid phenyl core.

The plot of transition temperatures versus number of carbon atoms in alkoxy chain exhibits falling tendency for Nematic-Isotropic transition temperatures. Smectic C-Nematic transition temperature curve rises to the maximum and then falls off at \( n \)-octadecyloxy derivative. The Smectic C-Nematic transition temperature curve rises but does not merge with the falling Nematic-Isotropic transition temperature curve even in the \( n \)-octadecyloxy derivative.

The calorimetric study has provided information of enthalpy changes involved in different phase transitions. It also helps in further confirmation of phases exhibited by the homologues.

![Series I](image)

**Series I**

Where, \( R = n-C_nH_{2n+1}, n = 1 \) to 8, 10, 12, 14, 16 and 18.

**Figure 1. Structure of the series I compounds**
1,3,4-Thiadiazoles have been investigated as a candidate for light-emitting materials due to their fluorescent properties. We were interested in studying some optical properties of our synthesized compounds. Hence, the ultraviolet-visible (UV-Vis) and fluorescence spectra were recorded. The UV-Vis absorption and fluorescence spectra of the homologue C\textsubscript{14} in CHCl\textsubscript{3} solution are shown in figure 3. In UV-Vis absorption spectra, the λ\textsubscript{max} occurred at 307 nm. The fluorescent emission peak is observed at 375 nm. All homologues of the series exhibit fluorescence property.
Chapter 3

This chapter consists of the syntheses and characterization of the thirteen homologues having a terminal cholesteryl moiety.

Over the last decade, cholesterol-based liquid crystals have attracted attention from more and more researchers, because cholesterol is abundant in nature and a commercially available chiral compound. Moreover, cholesterol-based compounds have many unique optical properties, such as selective reflection, circular dichroism, electro-optical and magneto-optical effects; they could be applied to optical storage, optical switching, nonlinear optics and liquid crystal display devices.

Many liquid crystalline compounds consisting of a cholesteryl ester unit as a chiral segment joined to different mesogenic moieties such as benzoate ester, Schiff’s base, azobenzene, biphenyl or tolane etc., through flexible spacers, have been synthesized and extensively studied. Their liquid crystalline properties are affected by spacer length and polarity, the length of the terminal group attached to the aromatic rings, as well as the type of linking group between the spacer and mesogenic units, such as ethers and esters. They have shown interesting mesomorphic phase behaviour including SmA phases, Twist Grain Boundary (TGB) phases, blue phases, and the chiral nematic (N*) mesophase. Highly viscous Cholesteric liquid crystalline materials show mechanical properties that make them very attractive for a new generation of mechanical sensors or materials able to visualize mechanical stress.

We have synthesized homologous series II possesses amide linkage and a terminus cholesteryl moiety as shown in figure 4 and studied their mesogenic properties. The cholesterol imparts chirality hence series is also chiral. Mesogenic properties of these compounds were checked by polarizing optical microscope provided with a Linkam heating stage. The transition temperatures were confirmed by Differential Scanning Calorimeter. All the compounds exhibit chiral nematic phase of broad range and high transition temperatures. Chiral nematic phase shows its oily streaks texture (figure 5). N* phase commences from methoxy derivative and persists upto last members of the series. Hence, it is purely nematogenic series. -CH=CH-spacer increases the flexibility and eliminates the Sm mesophase. The average thermal stability of compounds of series is lower than reported series due to the introduction of flexible spacer and lateral methoxy substituent.
The plot of transition temperatures versus number of carbon atoms in alkoxy chain exhibits odd-even effect and falling tendency for N*-Isotropic transition temperatures.

Series II

Where, \( R = n\text{-C}_n\text{H}_{2n+1} \), \( n = 1 \) to 8, 10, 12, 14, 16 and 18.

**Figure 4. Structure of the series II compounds**

**Figure 5. Polarized optical microphotograph of homologue C\textsubscript{5} on heating**

These cholesteric derivatives have been investigated for Specific Optical Rotation. The results for the homologues \( C_5 \) and \( C_6 \) are as follows:

<table>
<thead>
<tr>
<th>Homologue</th>
<th>( [\alpha] ) (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_5 )</td>
<td>+18.1</td>
</tr>
<tr>
<td>( C_6 )</td>
<td>+17.7</td>
</tr>
</tbody>
</table>
Chapter 4

This chapter includes the syntheses and detailed characterization of the thirteen compounds of biphenyl homologues.

Linearity, rigidity and polarizability are important factors for a molecule to display liquid crystalline properties. Different aromatic moieties have been used as rigid core in synthesizing liquid crystals. Biphenyl can be seen as rigid core of many mesogenic compounds and liquid crystalline or semi-crystalline aromatic polymers. Moreover, since biphenyl is a molecule interesting and fascinating itself, it has been the object, over many years, of many studies, both experimental and theoretical. Such interest is mainly due to its relatively simple structure and to the strong conformational dependence of the molecule on the phase of the material.

Biphenyl provides rich source of liquid crystals which are thermally more stable than those of benzene substituted analogues, which increase linearity and rigidity of the molecules. Biphenyl derivatives are also important in the formation of ferroelectric and anti-ferroelectric liquid crystals. Furthermore, biphenyl derivatives are able to undergo functionalization reactions, providing access to a variety of compounds. Mostly 4, 4’-substituted biphenyl derivatives exhibit one or more smectic phases and extraordinarily high clearing temperatures.

In present investigation, we have synthesized homologous series III as shown in figure 6 and carried out study of the effect of cinnamoyl linkage and nitrobiphenyl moiety on the mesomorphic properties. Mesogenic properties of these compounds were checked by polarizing optical microscope provided with a Linkam heating stage. The transition temperatures were confirmed by Differential Scanning Calorimeter.

![Structure of the series III compounds](image)

**Series III**

Where, \( R = n-C_nH_{2n+1}, \) \( n = 1 \) to 8, 10, 12, 14, 16 and 18.

*Figure 6. Structure of the series III compounds*
Lower members exhibit both smectic and nematic phases and higher members exhibit only smectic phase. Smectic phase shows focal conic texture and Nematic phase shows thread like texture as shown in figure 7. Smectogenic character should predominate at the expense of nematic mesophase. Smectic A phase commences from methoxy derivative and persist upto last member of the series. Nematic phase disappears from \textit{n}-hexyloxy derivative. Introduction of methoxy group increases acoplanarity, which results in decrease in the transition temperatures and also the thermal stability of compounds.

In the plot of transition temperatures versus number of carbon atoms in the alkoxy chain, Smectic A-Nematic and Nematic-Isotropic transition temperature curves exhibit Zig-Zag patterns upto \textit{n}-pentyloxy derivative of the series. The Nematic-Isotropic transition temperature curve raises steeply upto \textit{n}-decyloxy derivative then falls off upto last member of the series.

The members of the series (I to III) are characterized by standard spectroscopic methods.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure7.png}
\caption{Polarized optical microphotograph of homologue C$_5$ on heating}
\end{figure}
This chapter deals with the syntheses and evaluation of liquid crystalline properties of model compounds and binary mixtures.

Number of model compounds having ester and amide linkages as well as ester and azoic linkages are synthesized to understand the mesogenic properties of the homologues. Most of the compounds exhibit mesomorphism. Structural aspects and mesogenic properties are correlated which throws good light on the subject.

Liquid Crystals with low crystal - mesophase transition temperatures and with wide phase length have been primary goal of organic chemists in recent years. Since the occurrence of single component, room temperature Liquid Crystal with wide mesophase is rare, it is necessary to mix two or more low melting materials which may give room temperature mesomorphic mixture with wide mesophase length. Just as the melting points of the solids are depressed by the addition of other substances, so also are the transition temperatures of liquid crystals lowered by the addition of other substances.

In general, binary systems exhibiting mixed mesomorphism can be of three types:

- Where both the components are mesomorphic,
- Where only one component is mesomorphic and
- Where both the components are non-mesomorphic

We have taken following system A and studied their binary mixtures.

**System A:**

Component a: 4-nitro-4’-octyloxy biphenyl
Component b: 4-nitro-4’-dodecyloxy biphenyl

We have also focused on binary mixture study of system B and studied their mesomorphic properties.

**System B:**

Component a: 4’-nitro-biphenyl-4-n-tetradecanoate
Component b: 4’-nitro-biphenyl-4-n-hexadecanoate

Binary mixtures are helpful in lowering the transition temperatures of liquid crystalline compounds by the addition of other substances. Binary mixtures are driving force for the liquid crystalline applications. Binary mixtures are also useful for phase identification.
References