

Summary & Conclusions

Chapter I

Liquid crystals have been found approximately 125 years ago. Reinitzer, an Austrian botanist, is given credit for discovering the liquid crystalline phenomena.

Liquid crystals can be classified as either thermotropic or lyotropic, depending on their main characteristics. Thermotropic liquid crystals are liquid crystals formed by heating solid materials. Lyotropic liquid crystals are liquid crystalline systems formed when specific chemicals are treated with a specific volume of water or polar solvent. Friedel studied extensive optical analyses on a wide range of liquid crystalline substances and categorized them into three groups: smectic, nematic, and cholesteric. The two most prevalent types of mesophases are nematic and smectic, and structures for both have been determined by an analysis of their optical properties. According to Bose's swarm theory, the random orientations of groups of molecules make up the entire melt; these structures do not spread uniformly throughout. A considerable number of mesomorphic substances that have been examined possess solely smectic or nematic structures; nevertheless, certain compounds can exhibit both smectic and nematic features simultaneously.

However, some possess both types of phases smectic followed by nematic and in these situations, there are always precise, repeatable transition temperatures that define the stability of various phases.

Applications for liquid crystal materials are numerous and are being utilized. Chemists are now more motivated than ever to investigate structural differences in liquid crystalline materials to find novel liquid crystals with a variety of uses.

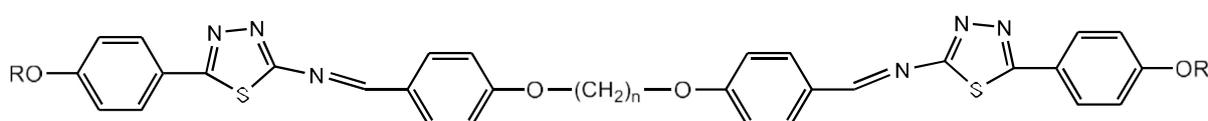
Chapter II

The section of this chapter includes the synthesis and study of the mesomorphic behaviour of thiadiazole derivatives possessing azomethine linkages.

In the literature on liquid crystals, 1,3,4-thiadiazoles are somewhat abundant, although the range of structural alterations that have been examined is quite small. Most systems possess aryl units or a mix of aryl and alkyl/cyclo alkyl units in place of the 1,3,4-thiadiazole core at positions 2 and 5. Appropriate diacylhydrazines undergo sulfurization and cyclization to create these materials. A substantial lateral dipole is imparted from S to the N-N bond's center by the 1,3,4-thiadiazole core.

In the present chapter, we have synthesized and investigated two homologous series (Series-I & II) of thiadiazole derivatives as depicted in Figure 1. Thin-layer chromatography is used to assess the purity of all the synthesized compounds. All the compounds were characterized using

elemental analysis, FT-IR, and $^1\text{H-NMR}$. Liquid crystalline properties were observed under a POM and confirmed by differential scanning calorimetry (DSC). The lower homologue up to n-propyl and n-butyl derivatives possess a nematic phase, and from n-butyl onwards smectic phase emerges till the hexadecyl derivative. A Fan-shaped, focal conical texture of Smectic A and a typical marble-like texture of the nematic phase (Figure 2) was observed in heating as well as cooling cycles. All the compounds exhibit enantiotropic behavior. The average thermal stabilities of both the synthesized series of compounds were compared with the reported series. The structure-mesomorphic properties were carefully studied.



where R = $-\text{C}_n\text{H}_{2n+1}$, where n = 1-8, 10, 12, 14 and 16

For n = 3 (Series II), n = 4 (Series I)

Figure 1: Structure of Series I & II compounds

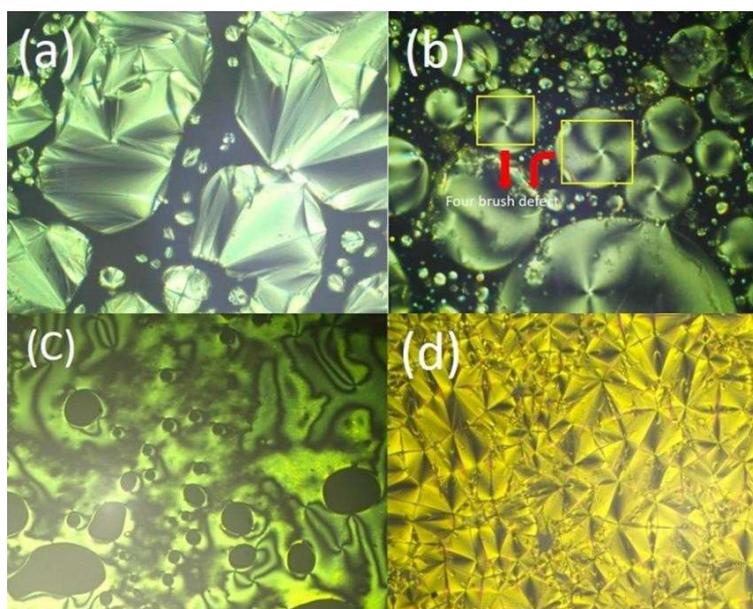


Figure 2: Microscopic textures were observed under POM for the different mesophases placed between two untreated glass slides.

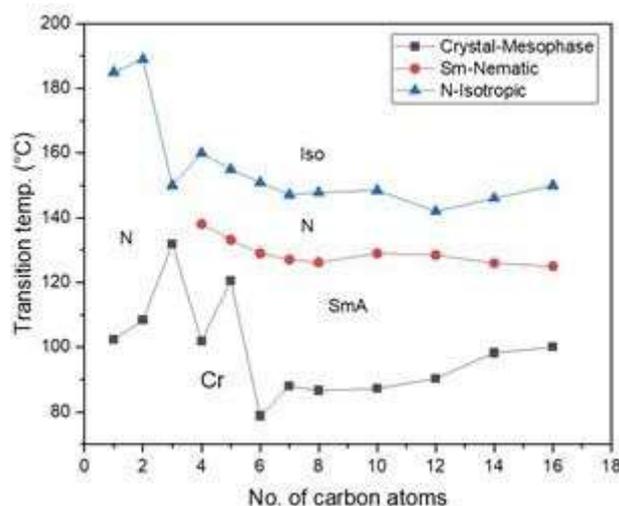


Figure 3: Variation of transition temperature with a number of carbon atoms in the alkoxy chain of the mesogenic compounds.

Chapter III

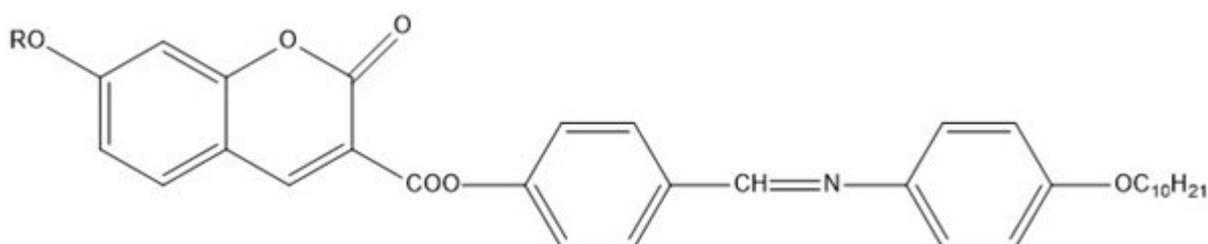
The section of this chapter includes the synthesis, characterization, and study of nematogenic homologous series of coumarin derivatives containing azomethine-ester linkages.

Organic chemistry and materials science research have led to the discovery and development of liquid crystalline coumarin derivatives. To obtain compounds with liquid crystal properties, researchers have been experimenting with the structures of coumarins. The different substituents or functional groups of the coumarin core can be changed by researchers to alter the molecules physical properties, such as its ability to behave like a liquid crystal. The synthesis and study of liquid crystalline coumarin derivatives involve a combination of structural alterations, organic synthesis techniques, and property assessment.

Currently, one of the most significant fields of antibacterial research is the design of novel chemicals to deal with resistant bacteria, as the resistance of pathogenic bacteria to current antibiotics is rapidly becoming a major global concern. Moreover, the growing number of immunocompromised individuals is contributing to the rapid rise in the most serious and opportunistic fungal infections. As is well known, the primary obstacle to creating safe and effective antifungals is not only the biochemical similarity between human cells and fungi, which hinders their ability to exhibit selective activity but also the ease with which resistance can be developed. Several novel 3-cinnamoyl-4-hydroxycoumarins were synthesized by Wan *et al.* and their microbial activity was assessed using the disc diffusion and dilution techniques.

Coumarin derivatives show very good fluorescence properties with large Stokes shift and narrow emission range. The type and position of the functional group have a significant impact on the emission properties of coumarin derivatives. Derivatives of coumarin have been employed as dopants in the production of liquid crystal materials based on fluorescent polymers. Small compounds based on coumarins have recently been investigated as a potential source of emissive liquid crystal materials.

In this chapter, we report the synthesis of a complete novel homologous series (Series III) (Figure 4) of compounds containing Schiff's Base and coumarin moiety incorporated in a molecule with an alkoxy group ($n = 1-10, 12, 14, 16$) attached at one of the terminal ends and n -decyloxy at another terminal end of the molecule. All the compounds were categorized using elemental analysis, FT-IR, $^1\text{H-NMR}$, and $^{13}\text{C-NMR}$. The microscopic textures (Figure 5) and the determination of phase transition temperatures were confirmed with the help of a polarizing optical microscope and differential scanning calorimetry. The thermal stability was assessed by TGA. The structure-mesomorphic relationship was carefully studied. The photophysical properties have been carefully studied. The DFT study implied that the length of the terminal alkoxy chains has an insignificant effect on the energy gap between FMOs of the compounds. The negative charge localized in the core region of the compounds **6d**, **6e**, **6g**, **6h**, and **6k** may permit a high degree of molecular packing; so these compounds possess mesomorphic properties. As the alkoxy chain length increases, it influences the breadth of the synthesized compounds resulting in the lower aspect ratio. All the synthesized compounds were screened for their in-vitro antibacterial activity against *Escherichia Coli* and *Staphylococcus aureus* showing good to moderate activity compared to the used standard. The structure-mesomorphic relationship was thoroughly studied (Figure 6).



Where $R = -\text{C}_n\text{H}_{2n+1}$, where $n = 1-10, 12, 14$ and 16

Series III

Figure 4: General chemical structure of mesogenic compounds possessing Coumarin moiety and an alkoxy group at terminal ends.

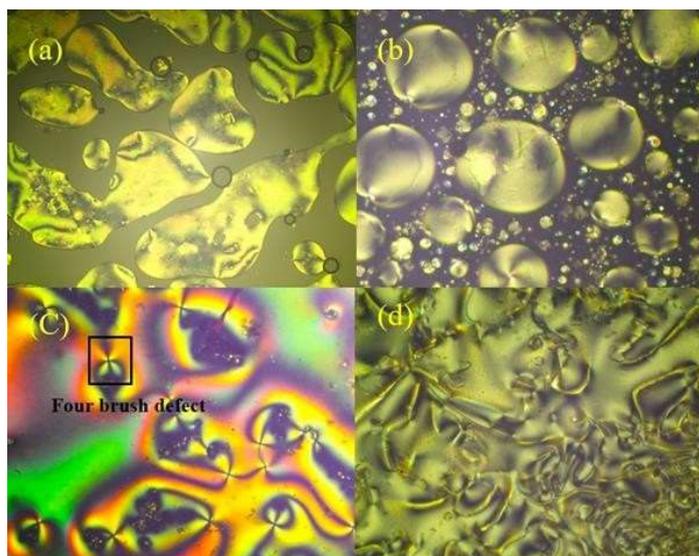


Figure 5: POM textures of coumarin based Schiff's-base derivatives upon heating and cooling cycles.

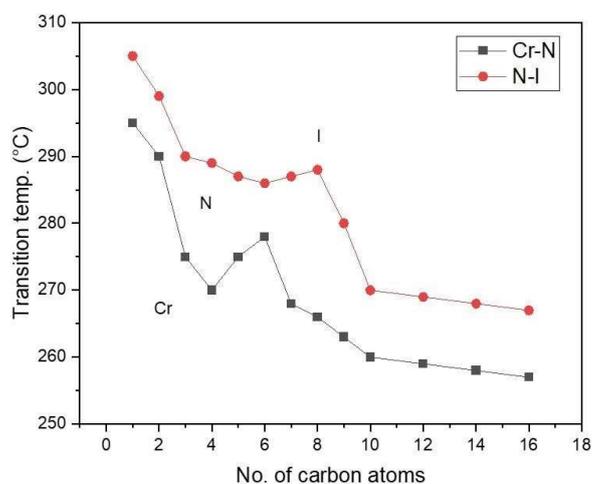


Figure 6: Variation of transition temperatures with a number of carbon atoms in the alkoxy chain of the mesogenic compounds.

Chapter IV

The unique property of liquid crystalline materials is the ability to give molecules more flexibility and a well-organized pattern. Liquid crystals have a fluid-like structure with the visual characteristics of solids. The liquid crystalline state has a more ordered molecular arrangement than the liquid state, although not being as ordered as the solid state. These days, optical storage systems, chemical sensors, solar cells, thermosensors, and bioimaging all use liquid crystalline materials. A larger lateral group on linear-shaped molecules provides greater

dipole-dipole interactions with polarity and polarizability towards the molecular system, as well as greater mesophase stability. On the other hand, due to the steric effect, the lateral substituent groups effectively broaden the molecular core and further enhance the intermolecular separation. Most liquid crystalline compounds have a rod- or disc-shaped structure to them. Usually, they exhibit a lamellar or columnar mesophase. Since the discovery of the unique feature of achiral bent-core molecules producing a polar-order mesophase, numerous attempts have been made to synthesize this type of material.

In liquid crystal materials, lateral groups affect the molecular packing and alignment. These groups, depending on their size, shape, and chemical composition, can either promote or hinder the formation of ordered structures inside the material. Accurate alignment is necessary for the development of liquid crystalline properties such as anisotropic flow and birefringence. Lateral groups can influence the phase behaviour of liquid crystalline materials.

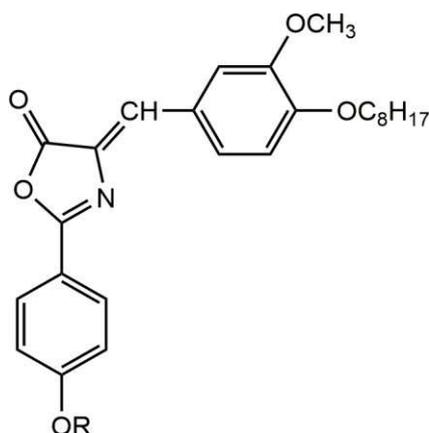
In the present chapter, a novel homologous series of compounds with imine linkage has been synthesized. The structure of every proposed compound was elucidated using FT-IR, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, and elemental analysis. The liquid crystalline behaviour was observed using POM. The transition temperatures and the phase transition enthalpy change data values were recorded using differential scanning calorimetry. By varying terminal alkoxy chain length ($n = 1-10, 12, 14, 16$) at one side, nematic phases were observed in heating and cooling cycles. The structure-property relationship was carefully studied. To assess the thermal stability of all prepared compounds, a thermogravimetry study was performed.

Chapter V

In the present chapter, the synthesis of oxazolone derivatives (Figure 7) was carried out using two different synthetic routes.

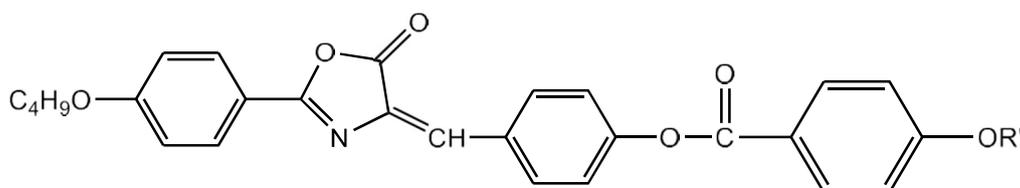
Based on the antibacterial activity data, it was determined that when compared to the reference standard streptomycin, all of the compounds (Scheme 5.14 & Scheme 5.15) exhibit antibacterial activity against *E. Coli* and *Micrococcus luteus*. In terms of antibacterial activity, **1**, **3**, **1'**, and **4'** exhibit the highest activity against *Micrococcus luteus*, and **2**, **3**, **1'**, and **4'** exhibit the highest activity against *E. Coli*. In the Seed Infusion technique, a compound possessing p-substituted alkoxy groups (Scheme 5.14 & 5.15) does not inhibit germination and the growth of radicle and plumule whereas the presence of electron-withdrawing group like $-\text{NO}_2$ (Scheme 5.14) completely inhibits the germination of seeds and hence it hinders the propagation and proliferation even after 5 days of incubation. In the novel synthesized compounds (Scheme 5.14), hydrogen bonding in the amide linkage and the presence of the $-\text{NO}_2$

OCH_3 group at the lateral position of the aromatic ring of the oxazolone derivatives are responsible for the molecule being non-mesogenic. Because of increased steric hindrance of the alkyl chain, it is noticed that the melting points (Scheme 5.15) drop with an increase in the number of carbon in the alkoxy group at the R position. The unique synthetic compound's non-mesogenic characteristics are also a result of its molecular makeup.



where R = $-\text{C}_6\text{H}_{13}$, $-\text{C}_8\text{H}_{17}$, $-\text{C}_{10}\text{H}_{21}$, $-\text{C}_{12}\text{H}_{25}$, $-\text{C}_{14}\text{H}_{29}$, $-\text{NO}_2$

(I)



where R = $-\text{CH}_3$, $-\text{C}_8\text{H}_{17}$, $-\text{C}_{14}\text{H}_{29}$, $-\text{C}_{16}\text{H}_{33}$.

(II)

Figure 7: Structure of oxazolone derivatives [(I) – Scheme 5.14 and (II) – Scheme 5.15]