

# **ABSTRACT**

*of the Thesis entitled*

## **“Synthesis and Characterization of New Liquid Crystalline Compounds”**

*Submitted to*

**The Maharaja Sayajirao University of Baroda**

*For the degree of*

**DOCTOR OF PHILOSOPHY  
IN  
CHEMISTRY**

*Submitted by*

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*Under the guidance of*

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## **Abstract of the Thesis**

To be submitted to The Maharaja Sayajirao University of Baroda for the award of the degree of *DOCTOR OF PHILOSOPHY* in Chemistry.

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**Title of the Thesis:** "Synthesis and Characterization of New Liquid Crystalline Compounds"

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**The Thesis will be presented in the form of the following chapters:**

## CHAPTER 1

INTRODUCTION OF THE LIQUID CRYSTALS

## CHAPTER 2

(A) SYMMETRICAL LIQUID CRYSTALLINE DIMERS OF  
AZO/AZOMETHINE NAPHTHALENE

(B) NAPHTHYL DERIVATIVES WITH BROMOALKOXY TAIL: SYNTHESIS,  
CHARACTERIZATION AND ITS MESOMORPHIC PROPERTIES

## CHAPTER 3

UNSYMMETRICAL MESOGENIC DIMERS OF CYANOAZOBENZENE AND  
AZO/ AZOMETHINE NAPHTHALENE: SYNTHESIS, CHARACTERIZATION  
AND MESOMORPHIC BEHAVIOUR

## CHAPTER 4

SYNTHESIS, CHARACTERIZATION, AND MESOMORPHIC BEHAVIOR OF  
UNSYMMETRICAL LIQUID CRYSTALLINE DIMERS WITH  
CYANOBIHENYL AND AZO/AZOMETHINE NAPHTHALENE

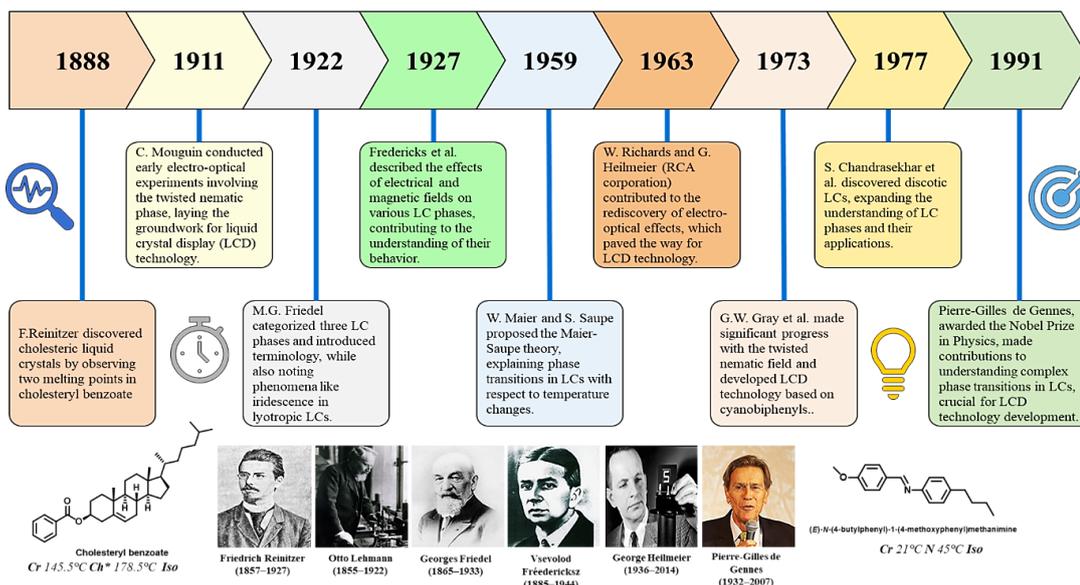
## CHAPTER 5

CHOLESTEROL AND NAPHTHALENE-BASED UNSYMMETRICAL LIQUID  
CRYSTALLINE DIMERS: SYNTHESIS, CHARACTERIZATION, AND  
INSIGHTS INTO ITS MESOMORPHIC BEHAVIOUR

## CHAPTER 1

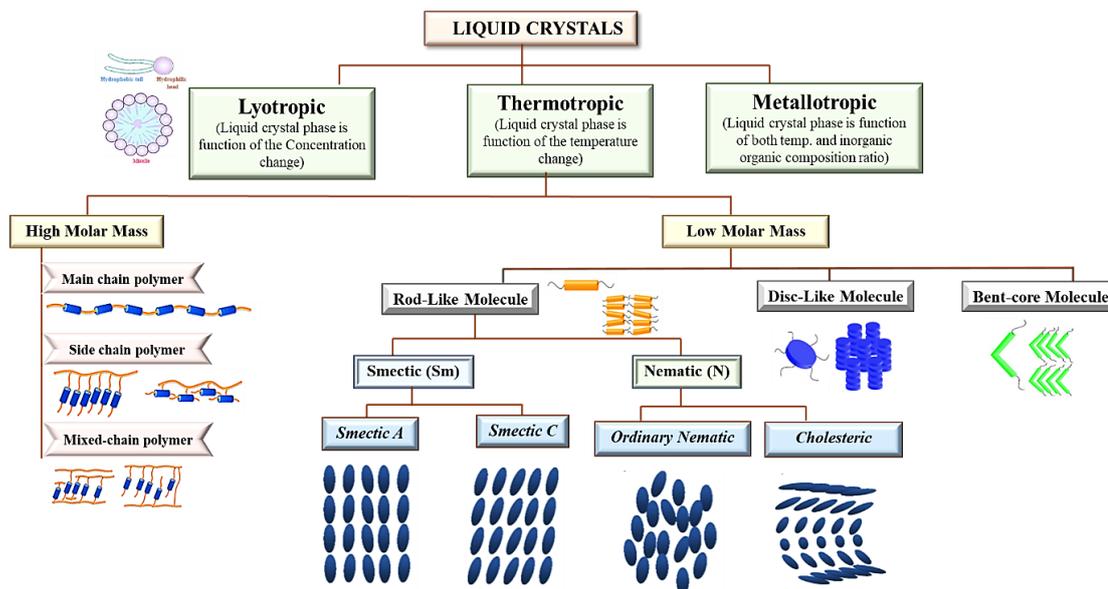
### INTRODUCTION OF THE LIQUID CRYSTALS

Liquid crystals (LCs) represent a unique state of matter, blending the properties of solids and liquids. Their ability to flow like a liquid while maintaining ordered structures makes them incredibly versatile and useful in various applications, from display technologies to advanced materials.



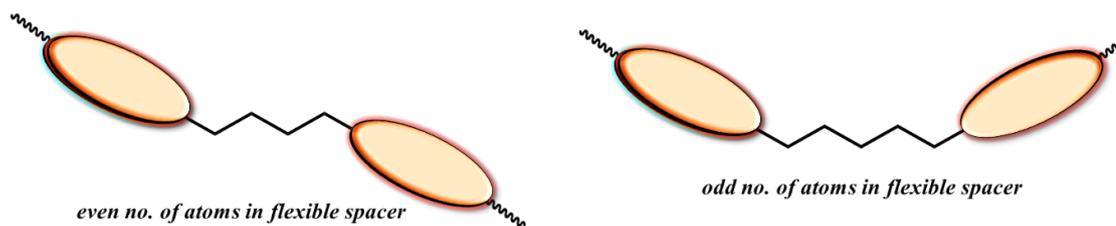
LCs are fascinating materials that exhibit properties of both solid and liquid states. Unlike most substances, which transition directly from solid to liquid as they are heated, liquid crystals exhibit intermediate phases that retain some level of molecular order. This unique behaviour results in materials that flow like liquids while maintaining an ordered structure similar to that of a crystal. Liquid crystals are optically birefringent due to their orientational order, allowing them to manipulate light in unique ways. Their behaviour can be classified based on the conditions that induce their liquid crystalline phases.

**Thermotropic Liquid Crystals:** Thermotropic liquid crystals are those that exhibit mesophases within certain temperature ranges. As the temperature increases, these materials transition from solid to liquid crystal and eventually to an isotropic liquid if the temperature becomes too high. The delicate balance of molecular ordering in these materials is highly temperature-dependent.



### Liquid Crystalline Dimers

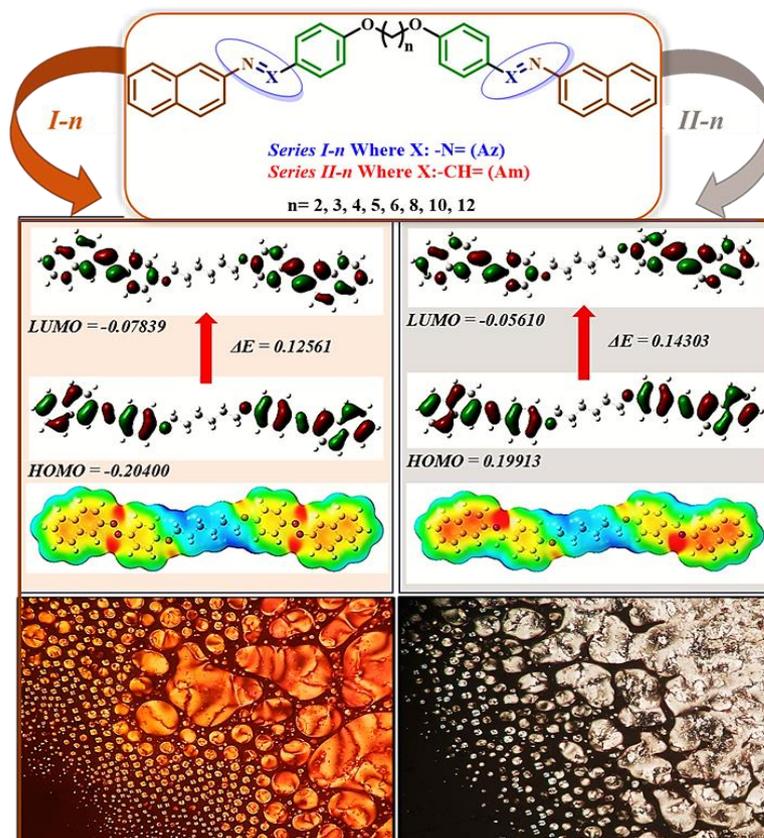
Liquid crystalline dimers are specialized materials where two mesogenic (liquid crystal-forming) units are connected by a flexible spacer. This molecular architecture results in unique liquid crystalline properties that differ from those of monomeric liquid crystals. The mesogenic units, typically composed of rigid aromatic rings, are linked by a flexible aliphatic chain, which allows the dimers to exhibit a combination of properties from both nematic and smectic phases.



These dimers can show a wide range of mesophases, depending on the length and flexibility of the spacer, as well as the specific nature of the mesogenic units. The spacer length plays a crucial role in determining the type of mesophase formed and the temperature range over which these phases are stable. Their ability to form diverse mesophases and their potential applications in advanced display technologies, sensors, and other optoelectronic devices make them a significant area of study in the field of liquid crystal research.

CHAPTER 2(A)  
SYMMETRICAL LIQUID CRYSTALLINE DIMERS OF AZO/AZOMETHINE  
NAPHTHALENE

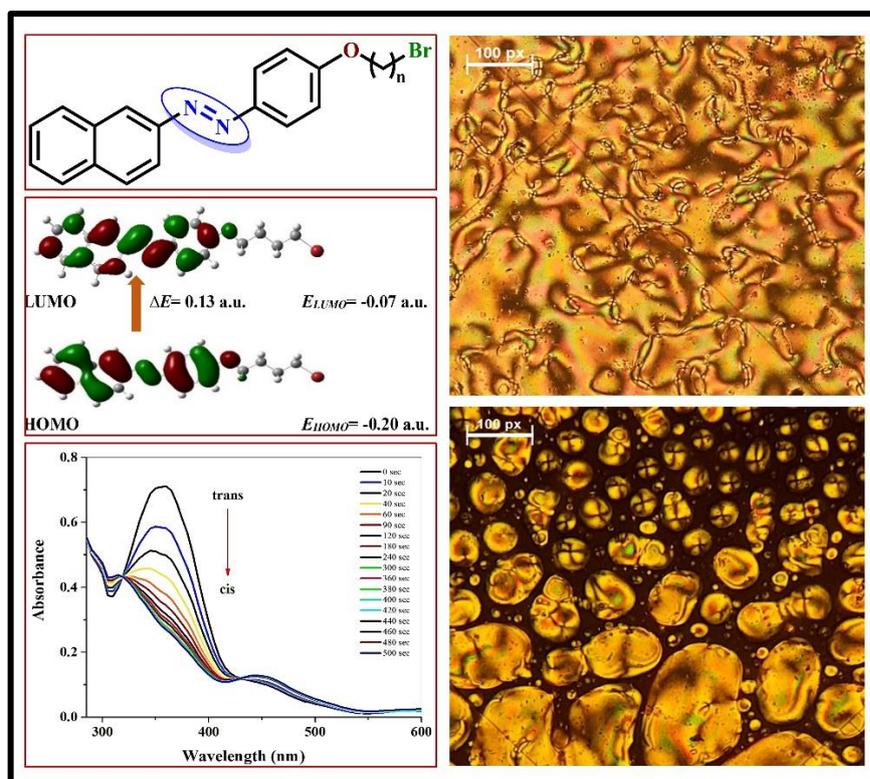
This chapter discusses the synthesis of two series of symmetric LC dimers, series **I-n**; 1,N-bis(4-((E)-naphthalen-2-yl diazenyl)phenoxy)alkane and series **II-n**; (N,N'E,N,N'E)-N,N'-(((butane-1,4-diylbis(oxy))bis(4,1-phenylene))bis(methanylylidene))bis(naphthalen-2-amine) containing naphthalene moiety at both ends possessing chains of varying central methylene spacer lengths ( $n = 2,3,4,5,6,8,10,12$ ). The dimers are characterized using FT-IR,  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ , and mass spectrometry, while their mesomorphic behaviour is studied via DSC and POM. The results reveal that symmetrical dimers with an even number of flexible spacers predominantly exhibit nematic phases. The odd-numbered dimers are non-mesogenic, primarily due to the bent molecular structure, which disrupts mesophase formation. Azo dimers show enantiotropic nematic mesophases, while azomethine dimers exhibit monotropic nematic phases, with the azomethine series showing a wider mesophase range.



## CHAPTER 2 (B)

## NAPHTHYL DERIVATIVES WITH BROMOALKOXY TAIL: SYNTHESIS, CHARACTERIZATION AND ITS MESOMORPHIC PROPERTIES

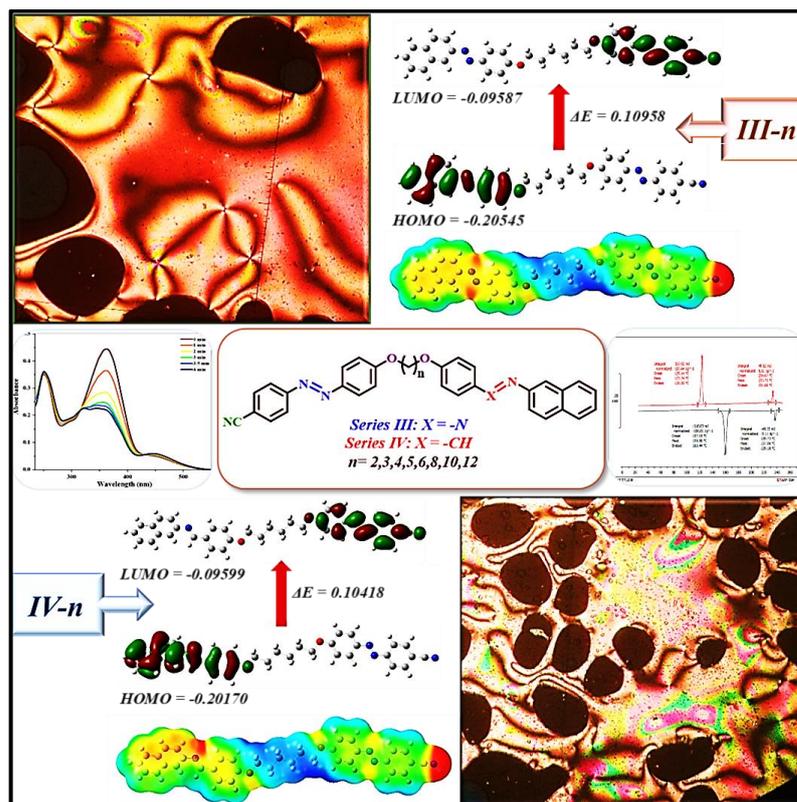
As naphthalene derivatives display rich mesomorphism, a significant number of mesogenic naphthalene derivatives with different linkages (i.e. azo, azoemthine, ester, cinnamoyl linkages) are documented. The rigid core of naphthalene is attached to linking unit azobenzene leads to stability of less ordered mesophases. The presence of terminal chain with polar bromine (Br) atom in the structure gives flexibility to the molecule. The objective of the current work is to synthesize bromine-terminated naphthyl azomesogens (NpAzOnBr) and examine their mesomorphism, as well as their optical properties and thermal properties. The effect of the number of flexible methylene spacers ( $n = 2,3,4,5,6,8,10,12$ ) on transition temperatures and their thermal stability were studied. Density functional theory (DFT) calculations were used to study various theoretical parameters. Only three compounds show nematogenic behaviour and the rest are non-mesogenic.



## CHAPTER 3

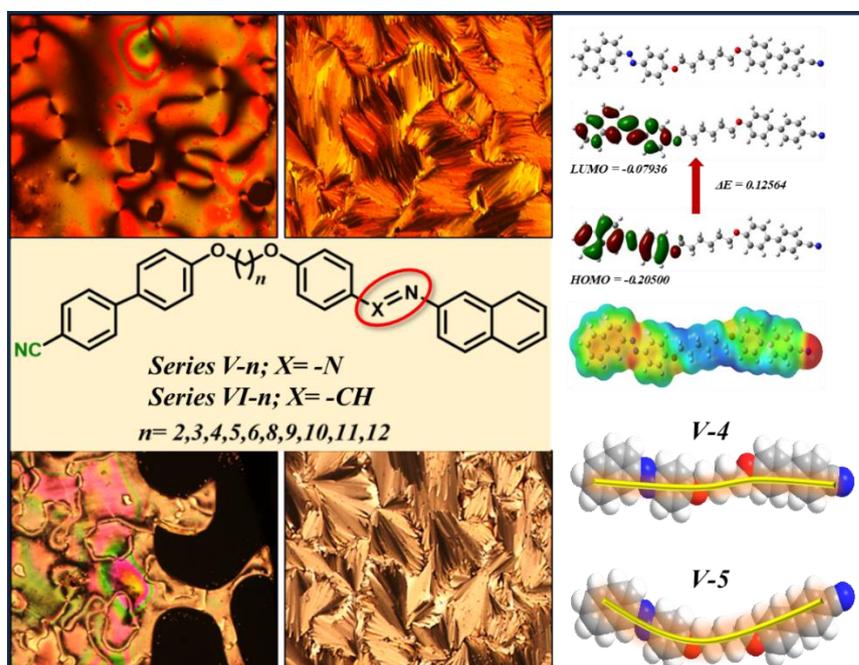
## UNSYMMETRICAL MESOGENIC DIMERS OF CYANOAZOBENZENE AND AZO/ AZOMETHINE NAPHTHALENE: SYNTHESIS, CHARACTERIZATION AND MESOMORPHIC BEHAVIOUR

The synthesis and characterization of two series of unsymmetrical LC dimers, consisting of cyanoazobenzene and azo/azomethine naphthyl moieties, are covered in this chapter. The influence of spacer length ( $n = 2-12$ ) on mesophase formation is investigated. Both series exhibit enantiotropic nematic phases, with thermal stability and mesophase range governed by the odd-even effect. The dimers with cyanoazobenzene (Series III) show higher thermal stability than their azomethine counterparts (Series IV). Azo linkages provide higher thermal stability, while azomethine linkages offer a broader mesophase range. The dimers exhibited enantiotropic nematic phases, with transition temperatures influenced by spacer length and odd-even effects. Photochromic behaviour was observed, with rapid photoisomerization. The spontaneous thermal back relaxation process revealed full restoration of the stable trans configuration. Computational studies added insights into the electronic structure, electrostatic potential, and optical characteristics of the dimers.



**CHAPTER 4**  
**SYNTHESIS, CHARACTERIZATION, AND MESOMORPHIC BEHAVIOR OF**  
**UNSYMMETRICAL LIQUID CRYSTALLINE DIMERS WITH**  
**CYANOBIPHENYL AND AZO/AZOMETHINE NAPHTHALENE**

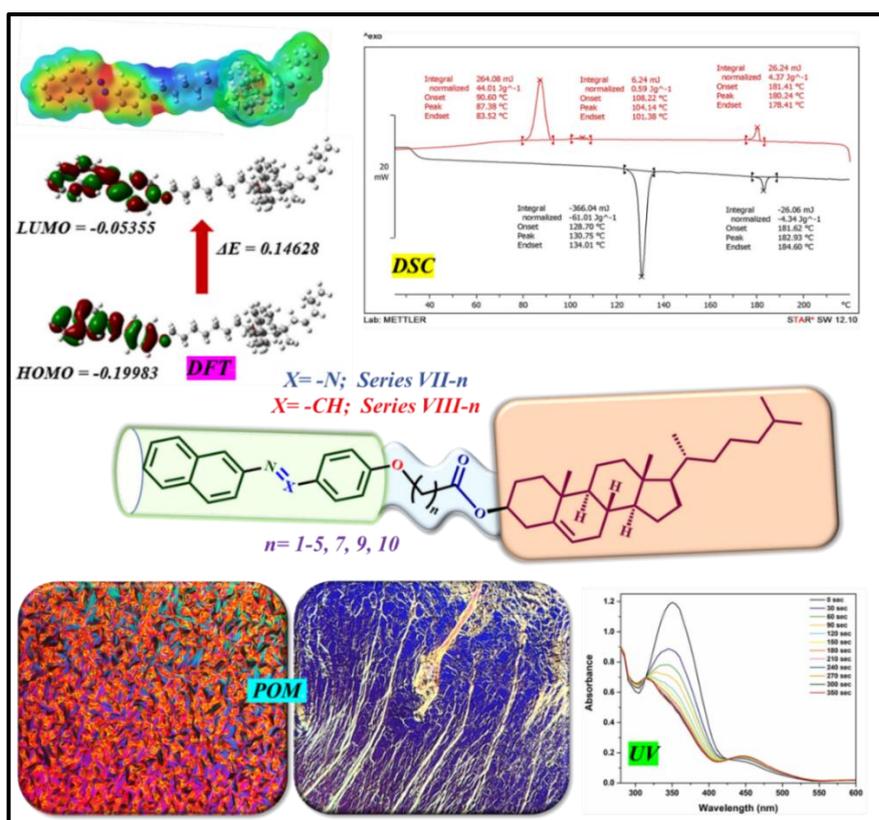
This chapter focuses on two series of unsymmetrical LC dimers, incorporating cyanobiphenyl and azo/azomethine naphthyl units. The dimers exhibit both nematic and smectic phases, with the transition temperatures significantly influenced by spacer length and the odd-even effect. Longer spacers ( $n = 8-12$ ) favour smectic phases, while shorter ones ( $n = 2-5$ ) exhibit nematic phases. The odd-even effect is evident, with odd-numbered dimers demonstrating lower clearing temperatures and monotropic behaviour. Photochromic behaviour is studied, and all dimers show high photoisomerization efficiency under UV irradiation. Thermogravimetric analysis (TGA) reveals that these dimers are thermally stable up to 300°C. An increase in chain length often leads to the emergence of smectogenic behaviour. Odd-membered dimers often exhibit comparatively lower clearing temperatures, a characteristic known as the odd-even effect. As the number of carbons in the flexible spacer increases, the clearing temperatures or melting points tend to decrease. It is observed that azomethine dimers exhibit comparatively higher nematic mesophase length in comparison to azo dimers, indicating a difference in the nematic mesophase length between these two types of dimers. Optical properties and physical properties were studied.



## CHAPTER 5

**CHOLESTEROL AND NAPHTHALENE-BASED UNSYMMETRICAL LIQUID CRYSTALLINE DIMERS: SYNTHESIS, CHARACTERIZATION, AND INSIGHTS INTO ITS MESOMORPHIC BEHAVIOUR**

The incorporation of cholesterol allows for the induction of chirality in liquid crystals, influencing the formation of various phases. The final chapter explores the synthesis and characterization of cholesterol-based unsymmetrical LC dimers, incorporating either naphthyl azo or naphthyl azomethine moieties. The mesogenic units in these compounds are connected via ester and ether bonds, with different flexible spacers ranging in length from 1-5, 7, 9, and 10 methylene groups. Mesophase behaviour is characterized using DSC and POM, revealing that short-spacer members ( $n = 1, 2$ ) do not exhibit mesogenic properties, while higher members ( $n = 3-10$ ) demonstrate enantiotropic chiral nematic phases. Odd-numbered dimers with longer spacers exhibit smectic C\* phases (SmC\*), suggesting enhanced molecular interactions required for chiral smectic phases. UV-Vis studies confirm trans-cis isomerization, with notable photo conversion efficiency. TGA indicates higher thermal stability for the cholesterol-based dimers compared to their naphthyl counterparts.



**Conclusion**

Eight Different series of new symmetrical and unsymmetrical liquid crystalline dimers have been successfully synthesized, featuring variations in the chain length of the flexible spacers and different mesogenic cores, while maintaining a constant naphthalene moiety at one end. The synthesized compounds were thoroughly characterized using various techniques, including IR, NMR, Mass spectrometry, etc. Their mesomorphic behaviour was investigated through Polarizing Optical Microscopy (POM) and further validated using Differential Scanning Calorimetry (DSC). The results revealed that the different series exhibited distinct types of mesophases, each with varying phase stability temperatures. Additionally, the optical properties of the prepared dimers were explored, and theoretical calculations were conducted to provide further insight into the behaviour of the reported series.

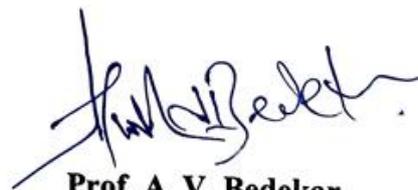


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