Executive Summary

of the Thesis entitled

"Synthesis and Characterization of New Liquid Crystalline Compounds"

Thesis Submitted to

The Maharaja Sayajirao University of Baroda

For the degree of

DOCTOR OF PHILOSOPHY
IN
CHEMISTRY

Submitted by

Rabari Mahimaben Kanubhai

(Reg. No.: FOS/2254; 29-01-2021)

Under the guidance of

Prof. A. K. Prajapati

Department of Chemistry,
Faculty of Science
The Maharaja Sayajirao University of Baroda
Vadodara - 390002, Gujarat, India

October 2024

Executive Summary 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.

Name of Student: Rabari Mahimaben Kanubhai

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

Name of the Supervisor: Prof. A. K. Prajapati

Faculty: Faculty of Science, The Maharaja Sayajirao University of Baroda

Department: Department of Chemistry

Registration No.: FOS/2254

Date of Registration: 29th January 2021

Rabari Mahimaben Kanubhai
Research Student

Prof. A. K. Prajapati
Research Guide

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 Cyanobiphenyl and Azo/Azomethine Naphthalene

Chapter 5

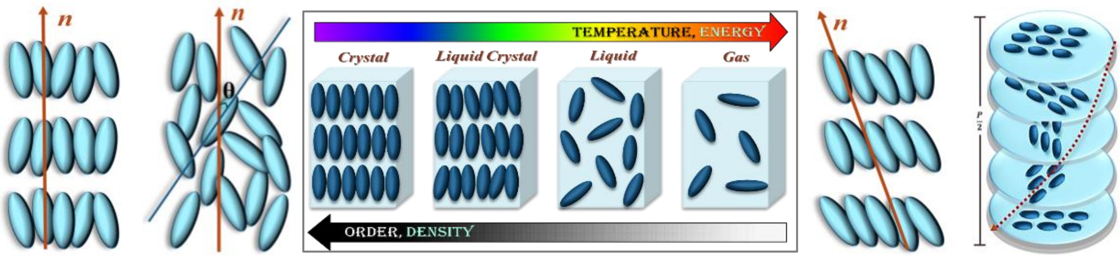
Cholesterol and Naphthalene-Based Unsymmetrical Liquid Crystalline Dimers: Synthesis, Characterization, and insights into its Mesomorphic Behaviour

Table of Contents

Chapter 1
Introduction of the Liquid Crystals

1.1 Introduction:

Liquid crystals (LCs) represent a unique state of matter, blending the properties of solids and liquids.[1] 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.[2,3] Understanding their classification, behaviour, and the criteria for their formation is essential for harnessing their full potential in scientific and technological advancements. LCs are fascinating materials that exhibit properties of both solid and liquid states.[4] 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.[5–7]



Different state of matter and orientation of the molecules in different mesophase

Classification of Liquid Crystals

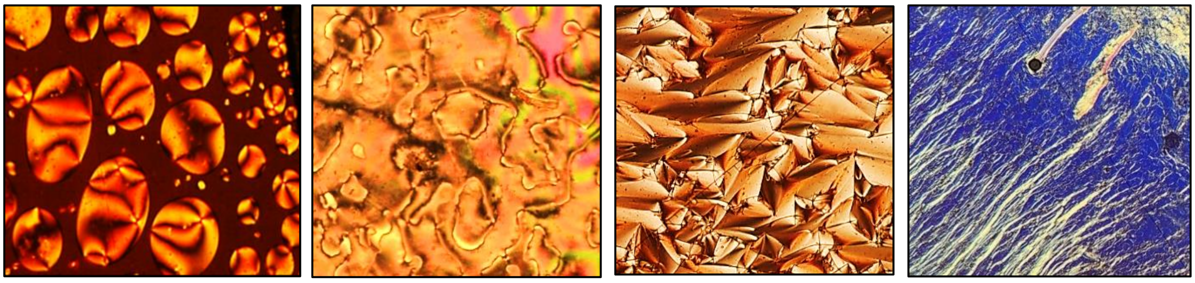
- ***Lyotropic Liquid Crystals:*** Lyotropic liquid crystals form mesophases based on the concentration of a solvent. These phases depend on the solvent and concentration conditions, differing fundamentally from thermotropic liquid crystals.
- ***Metallotropic Liquid Crystals:*** Metallomesogens, metal complexes with liquid-crystalline properties, exhibit diverse mesophases like nematic, smectic, and even cubic forms. They can be covalent or ionic, with various low molar mass thermotropic and some lyotropic examples.[8]
- ***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.[9]

Thermotropic liquid crystals are categorized into three primary groups based on the shape of the mesogenic molecules: Calamitic (rod-shaped), bent-core (including boomerang, and banana-like), and discotic (disk-like) liquid crystals.

Thermotropic mesogens exhibit three primary types of mesophases:

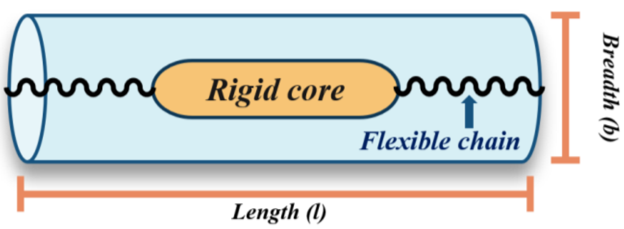
- *Smectic Mesophase*: Molecules are arranged in layers, providing both orientational and positional order. Smectic A (SmA) phases have molecules organized into distinct layers, while Smectic C (SmC) phases have molecules that are tilted within these layers.
- *Nematic Mesophase*: Nematic phases lack positional order but maintain orientational order. Molecules in this phase align along a common direction called the director.
- *Cholesteric Mesophase*: Also known as the chiral nematic phase, this phase occurs in systems with chiral molecules. Cholesteric phases can be induced by doping nematic liquid crystals with optically active molecules, resulting in a helical arrangement of the molecules.



Different optical textures of mesophases under POM

Criteria for Liquid Crystalline Phase

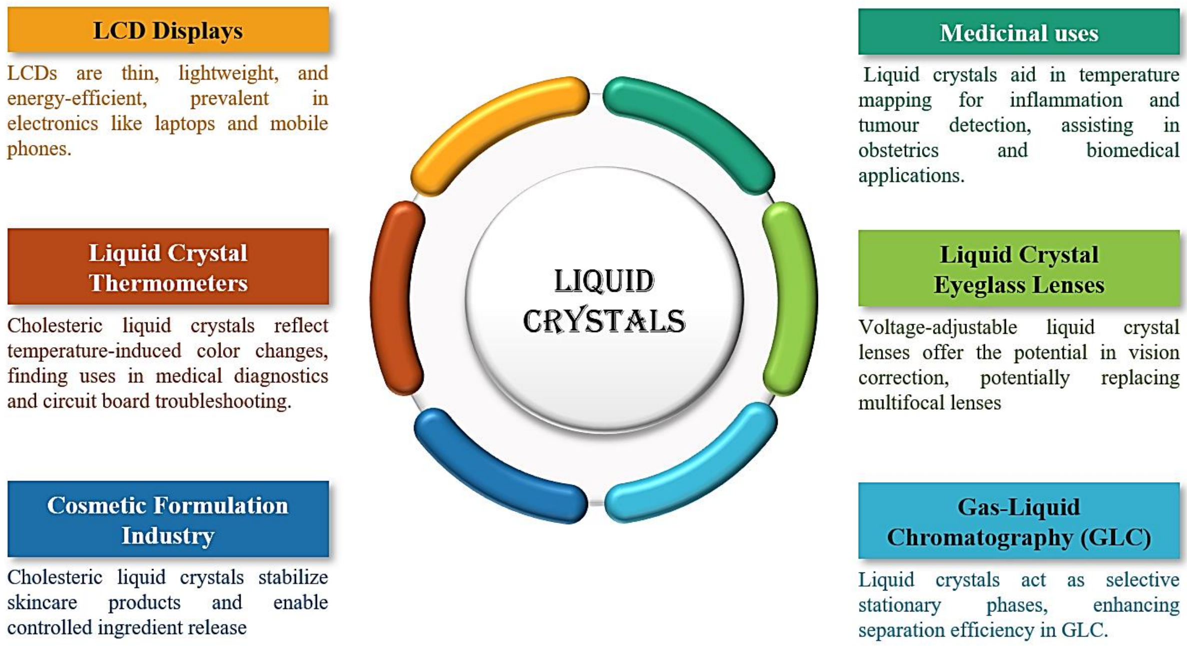
Liquid crystalline materials typically consist of aromatic rings attached to aliphatic tails. The aromatic rings provide rigidity, mimicking the solid-like properties, while the aliphatic tails offer the fluidity characteristic of liquids. This combination of rigidity and flexibility is crucial for achieving the liquid crystalline phase.



Representation of a calamitic liquid crystals

Applications of Liquid Crystals

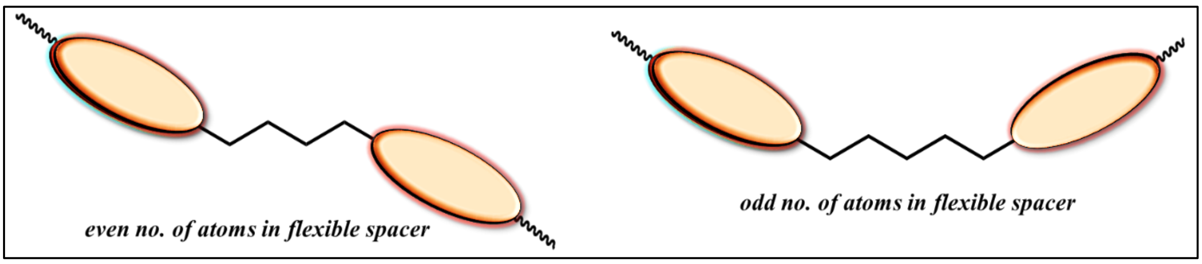
Sensitivity of LCs to minute changes in temperature, electromagnetic radiation, and mechanical stress renders them indispensable in numerous applications. [10,11]



Different Applications of Liquid Crystals

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.



Odd-even effect in the liquid crystal dimers

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.[12–14]

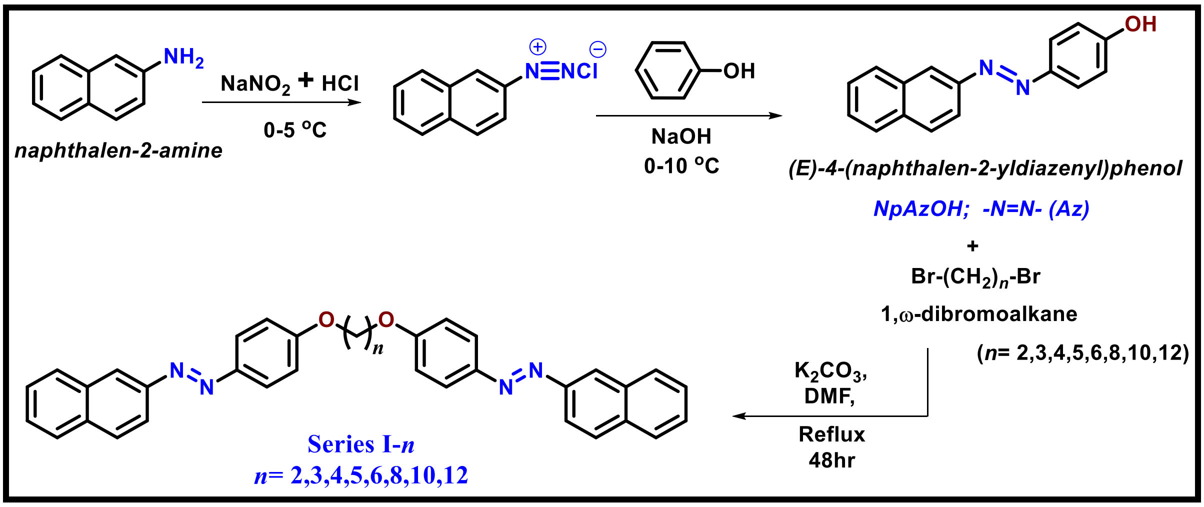
Chapter 2
(A) Symmetrical Liquid crystalline dimers of azo/azomethine naphthalene

2A.1 Introduction:

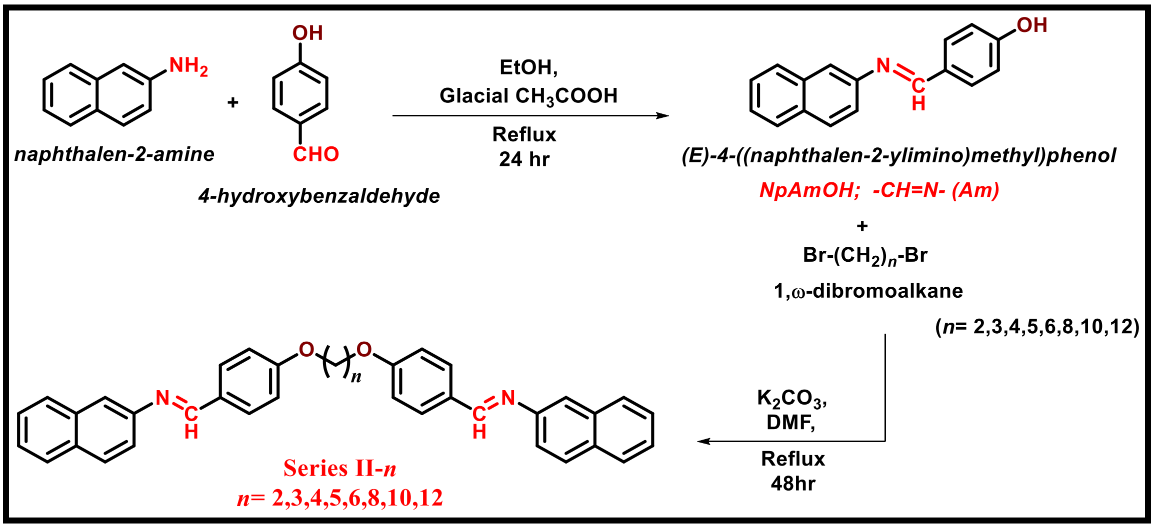
The introduction of a bulky naphthalene moiety in the molecule of liquid crystalline (LC) material can change its transition temperatures. Calamitic liquid crystal (LC) dimers, characterized by their rod-shaped structure. Symmetrical Liquid crystalline dimers are created by linking two identical mesogenic units with a flexible spacer. This spacer allows molecular motion, while the mesogenic units maintain the necessary rigidity for the ordered orientation crucial for liquid crystal phase formation. Azo (-N=N-) and azomethine (-CH=N-) groups are considered effective linking groups. These linkages, especially Schiff bases and azo groups, stabilize the mesomorphic properties by preserving the rigidity and linearity of the molecular geometry.[15,16] This chapter focuses on symmetrical liquid crystalline dimers created by linking two identical mesogenic units with flexible spacers. These dimers contain azo (-N=N-) and azomethine (-CH=N-) linkages, which provide rigidity and linearity, stabilizing mesomorphic properties. The chapter investigates the synthesis and characterization of two series of dimers, Series ***I-n*** and ***II-n***, which incorporate naphthalene moieties and vary in spacer lengths (n = 2, 3, 4, 5, 6, 8, 10, 12).

2A.2 Synthesis Scheme:

The synthetic route for the dimers ***I-n*** (Scheme 2A.1) and ***II-n*** (Scheme 2A.2) having methylene spacer length n = 2,3,4,5,6,8,10,12 is shown here in Scheme 2A.1 and 2A.2, respectively.



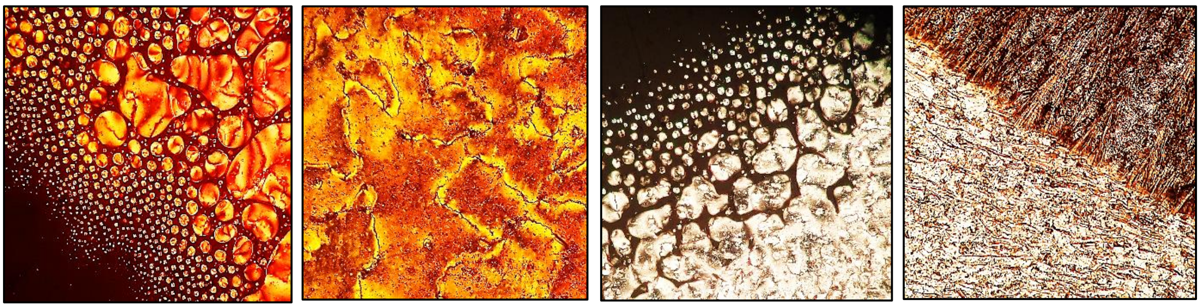
Scheme 2A.1: Synthetic route for the dimers of Series *I-n*



Scheme 2A.2: Synthetic route for the dimers of Series *II-n*

2A.3 Results and Discussion:

Techniques like polarizing optical microscopy (POM), differential scanning calorimetry (DSC), TGA and UV-Vis spectroscopy were used to analyze mesomorphism, photophysical, and thermal properties. All the naphthalene-based symmetrical dimers with an even number of flexible spacers (-methylene unit) are nematogenic.



All the naphthalene-based symmetrical dimers with an odd number of atoms in the linking group joining two azobenzene and azomethine moieties are non-mesogenic due to the bent shape of the molecular structure. The dimers with azo-central linkages exhibited enantiotropic nematic mesophase while the dimers with azomethine central linkage exhibited monotropic nematic mesophase. The symmetrical azomethine (***II*-n**) dimer having naphthalene moiety exhibits purely nematic mesophase with greater nematic mesophase length compared to azo dimers, whereas azo dimers (***I*-n**) have very high thermal stability as they have higher Nematic-Isotropic (N-Iso) transition temperatures.

2A.4 Conclusion:

Dimers with even spacers were nematogenic, while those with odd spacers were non-mesogenic due to their bent molecular structure. Azo dimers showed enantiotropic nematic mesophase with higher thermal stability, while azomethine dimers exhibited monotropic nematic mesophase with greater mesophase length. Transition temperatures increased with spacer length, indicating a strong influence of spacer length on mesophase behavior. Azo dimers displayed higher nematic-isotropic transition temperatures compared to azomethine dimers, which had wider nematic mesophase ranges. The effect of spacer length and odd-even patterns played a key role in determining mesomorphic properties.

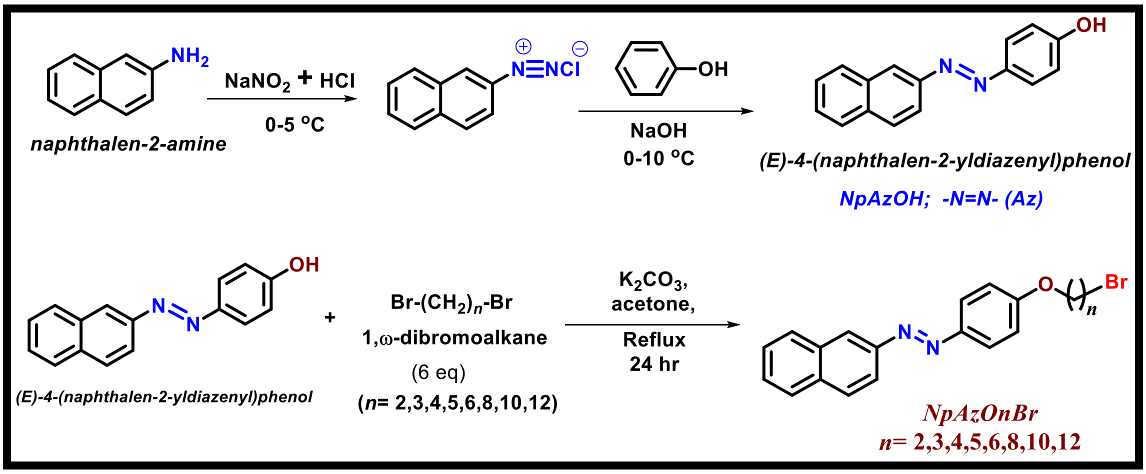
Chapter 2

(B) Naphthyl derivatives with bromoalkoxy tail: Synthesis, Characterization and its mesomorphic properties

2B.1 Introduction:

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. Azobenzene molecules are particularly appealing for storage devices and molecular switches because they can be switched back and forth between their two isomers with relatively small changes in the physical environment such as temperature, light, and electric fields. 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.

2B.2 Synthesis Scheme:



Scheme 2B.1: Synthesis scheme for the naphthyl derivatives

2B.3 Results and Discussion:

Through the use of various analytical methods, including FT-IR, ^{1}H NMR, ^{13}C NMR, mass spectrometry and ESI-Mass, the correct structures were verified. Techniques like polarizing optical microscopy (POM), differential scanning calorimetry (DSC), TGA and UV-Vis spectroscopy were used to analyze mesomorphism, photophysical, and thermal properties. Only three compounds show nematogenic behaviour and the rest are non-mesogenic.

Table: Transition temperatures (in °C) and associated enthalpy of transition (ΔH) in (kJ mol^{-1}) of NpAzOnBr

Compound	n	Transition Temperatures (°C) and ΔH (kJmol^{-1}) *Heating cycle*	Transition temperatures (°C) and ΔH (kJmol^{-1}) *Cooling cycle*
NpAzO2Br	2	Cr 134(24.81) Iso	Iso 75(-24.79) Cr
NpAzO3Br	3	Cr 108(76.53) Iso	Iso 57(-19.88) Cr
NpAzO4Br	4	Cr 113(40.9) Iso	Iso 110 (-0.94) N 98(-36.24) Cr
NpAzO5Br	5	Cr 109(141.7) Iso	Iso 54(-2.13) N 45(-8.81) Cr
NpAzO6Br	6	Cr 126(24.03) Iso	Iso 92(-0.82) N 82(-10.8) Cr
NpAzO8Br	8	Cr 112(178.7) Iso	Iso 92(-181.56) Cr
NpAzO10Br	10	Cr 106(71.8) Iso	Iso 91(-144.2) Cr
NpAzO12Br	12	Cr 111(46.8) Iso	Iso 101(-32.3) Cr

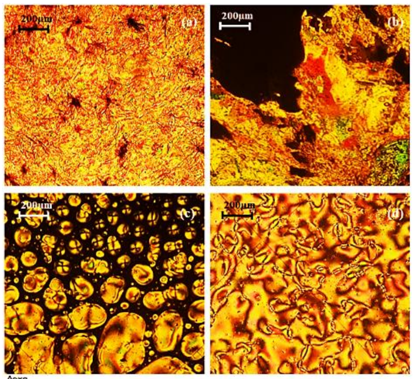


Figure: Optical photomicrograph of compound NpAzO4Br (a) Crystalline state (b) Cr-Iso transition at 113 °C (c) nematic droplets of Iso-N transition at 110 °C (d) Schlieren texture at 108 °C

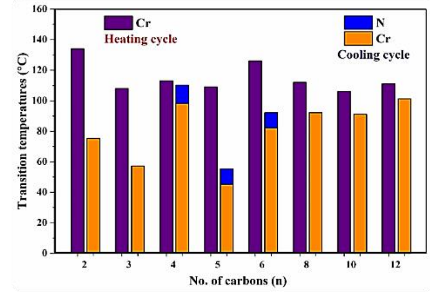


Figure: Bar graph of transition temperatures against no. of carbon of NpAzOnBr showing thermal stability of the mesophase in heating and cooling cycle

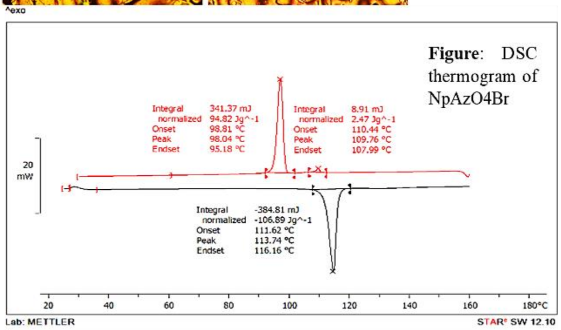


Figure: DSC thermogram of NpAzO4Br

2B.4 Conclusion:

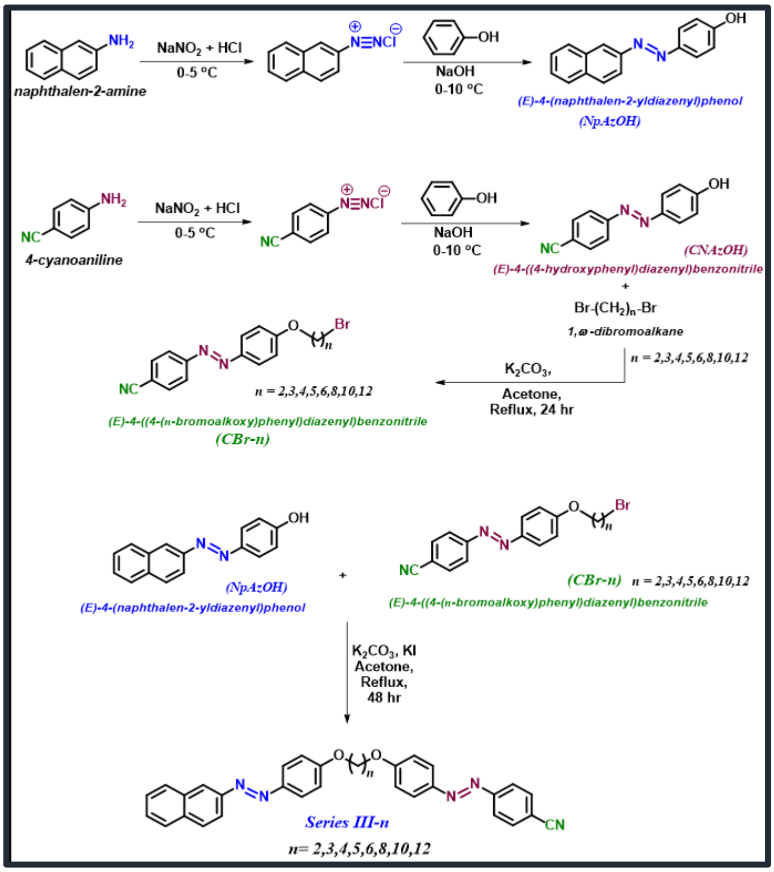
One new homologous series of liquid crystalline bromine terminate compounds having ether linkages containing naphthalene moiety as a rigid core was synthesized by the reaction of various dibromoalkanes and azodye of 2-amino naphthalene respectively. Their right structure was confirmed by FTIR, ^{1}H-NMR, ^{13}C-NMR spectroscopy. Their thermotropic properties were studied on a hot-stage of a polarising optical microscope (POM) and further it was investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). A view on their photophysical behaviour was gained by UV-Vis spectroscopy. Compounds are showing excellent photo switching properties. The compounds with flexible spacer (n=4, 5, 6) shows excellent liquid crystalline property, whereas lower (n=2, 3) and higher (n=8, 10, 12) members of the series are non-mesogenic. The compounds with odd number of carbon in chain shows comparatively lower temperatures than that of with even number. Their structure-property relationships, the influence of different flexible space and the mesophase ranges were described.

Chapter 3
Unsymmetrical mesogenic dimers of Cyanoazobenzene and azo/ azomethine naphthalene: synthesis, characterization and mesomorphic behaviour

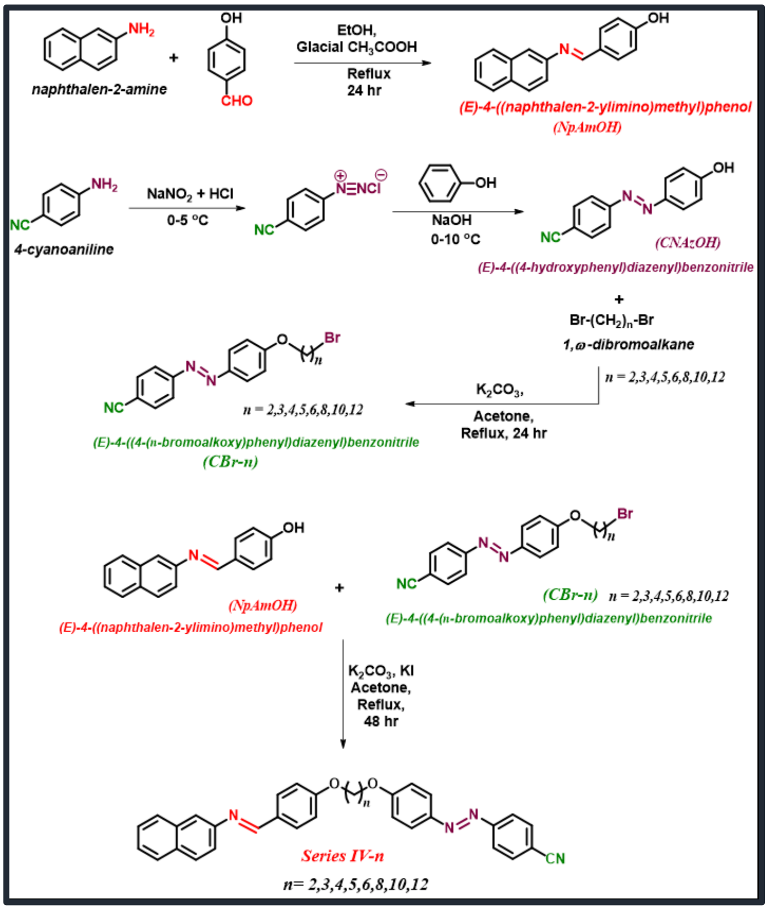
3.1 Introduction:

Non-symmetric dimers stand out for their intriguing polymorphic properties. The introduction of non-symmetry in dimers can be achieved by connecting different mesogenic units, adjusting the length of terminal chains, employing diverse terminal groups, or varying the length and evenness of the spacer group.[17] Cyanoazobenzene has gained attention as a promising component for LC dimers due to its unique photo-responsive properties. The development of new unsymmetrical calamitic dimeric molecules incorporating naphthalene units is a promising avenue for creating LC materials with tailored optical and electronic properties.[18] To address this, we have chosen to incorporate naphthalene moieties into our dimers and synthesized two series of compounds.

3.2 Synthesis Scheme:



Scheme 3.1: Synthesis scheme for the dimers of series *III-n*

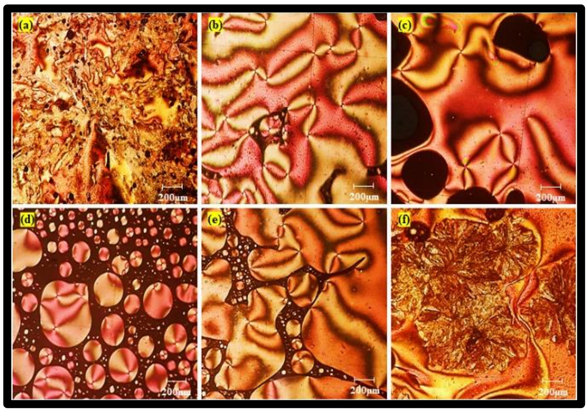


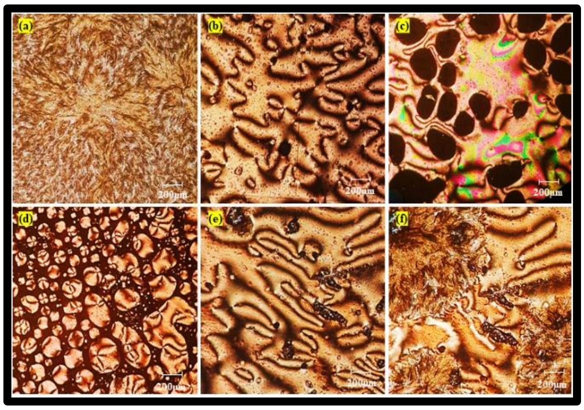
Scheme 3.2: Synthesis scheme for the dimers of series *IV-n*

In ***Series III-n***, one end contains cyanoazobenzene moiety while the other end contains azo naphthyl, whereas in ***Series IV-n***, the other end contains azomethine naphthyl. We have varied the length of the flexible spacer from n=2-6, 8, 10, and 12 to study its effect on the LC properties of the resulting dimers. By systematically varying the structure of the dimers and characterizing their liquid crystalline behavior, we aim to gain insights into the role of naphthalene moieties as mesogenic cores and understand how different spacer lengths impact the LC properties of the dimers.

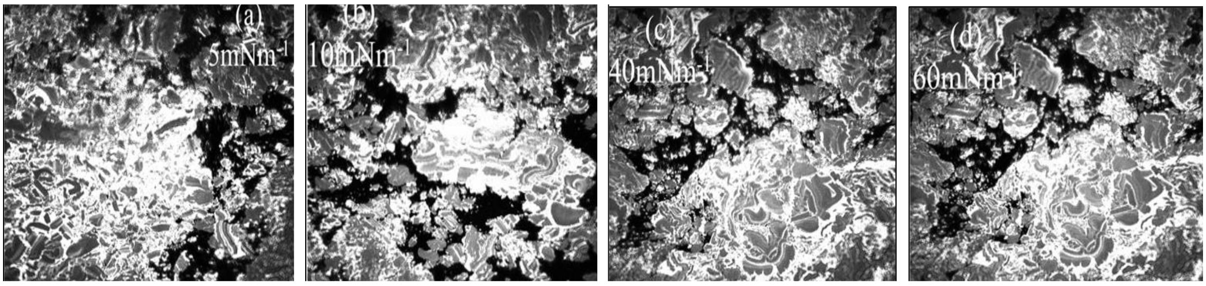
3.3 Results and Discussion:

The dimers exhibited enantiotropic nematic phases, with transition temperatures influenced by spacer length and odd-even effects. Dimers of ***Series III-n*** displayed higher thermal stability than azomethine naphthalene dimers (***Series IV-n***), with more pronounced mesophase stability during cooling. The azomethine linkages provided greater mesophase range, while the azo linkages offered higher thermal stability. 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.





We also studied thermo-photoisomerization of the molecule using the Langmuir monolayer technique. The surface pressure-area per molecule isotherm studies show that the cis-form of the ***III-6*** occupies a lower area and exhibits a co-existence region between liquid expanded and condensed phases.



BAM images of the trans-*III-6* monolayer

3.4 Conclusion:

Two new series of unsymmetrical liquid crystal dimers ***III-n*** and ***IV-n*** (n = 2–6,8,10,12) possessing cyanoazobenzene and azo/azomethine naphthyl have been synthesized and all the dimers were characterized with different spectroscopic techniques like FT-IR, ^{1}H-NMR, ^{13}C-NMR and mass spectrometry. Its mesomorphic behaviour was identified with the DSC and POM. The effect of the length and structure of the mesogenic units and the nature of the spacer have been studied in sixteen symmetrical dimers. The dimers exhibited enantiotropic nematic phases, with transition temperatures influenced by spacer length and odd-even effects. Dimers of series III displayed higher thermal stability than azomethine naphthalene dimers (Series IV), with more pronounced mesophase stability during cooling. The azomethine linkages provided greater mesophase range, while the azo linkages offered higher thermal stability. Photochromic behaviour was observed, with rapid photoisomerization. The spontaneous thermal back relaxation process revealed full restoration of the stable trans configuration.

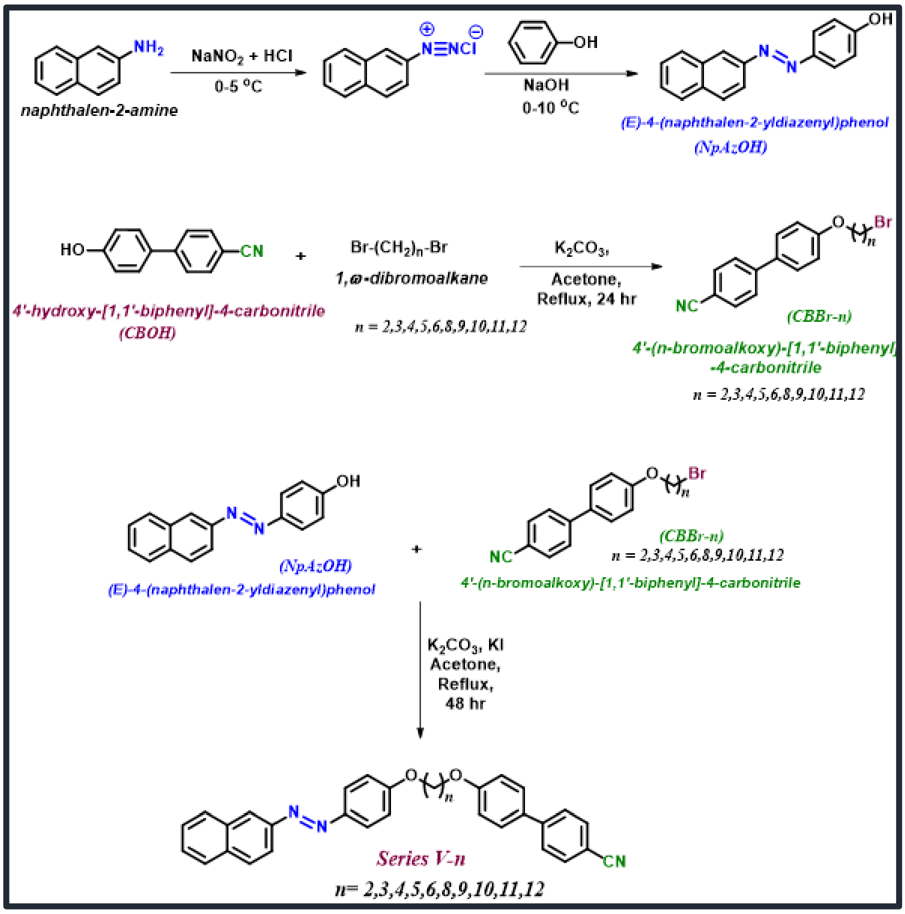
Chapter 4

Synthesis, Characterization, and Mesomorphic Behavior of Unsymmetrical Liquid Crystalline Dimers with Cyanobiphenyl and Azo/Azomethine Naphthalene

4.1 Introduction:

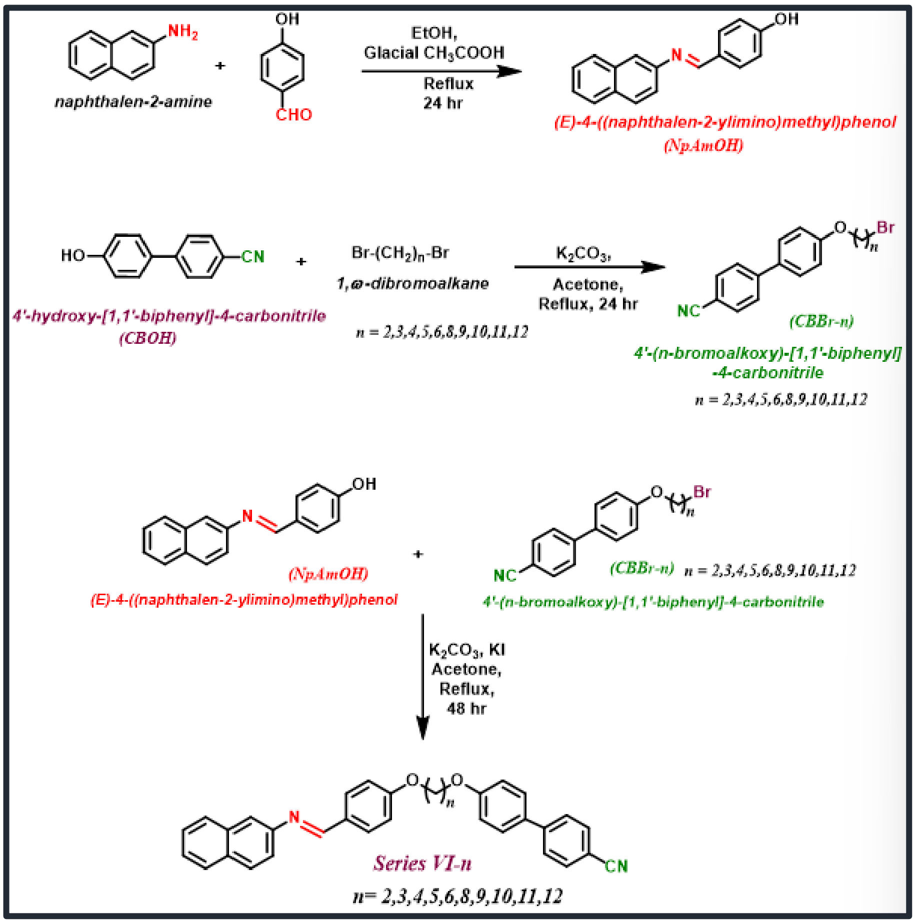
The adaptability of cyanobiphenyl groups allows for facile modifications with polar lateral or terminal groups, enabling the induction of dipole moments and the enhancement of bulk dielectric anisotropy. This capability facilitates the fine-tuning of mesomorphic properties.[19,20] To deepen our understanding of the relationships between structure and properties in dimers based on Cyanobiphenyl and incorporating naphthalene entities, and to evaluate how different flexible spacers influence their phase behaviour, we synthesized a new series of Calamitic-Calamitic dimers. These dimers contain cyanobiphenyl ether and naphthyl azo/ azomethine groups. The mesogenic units in these compounds are linked via ether bonds, with flexible spacers ranging from 2-6, 8-12 methylene groups in length.

4.2 Synthesis Scheme:



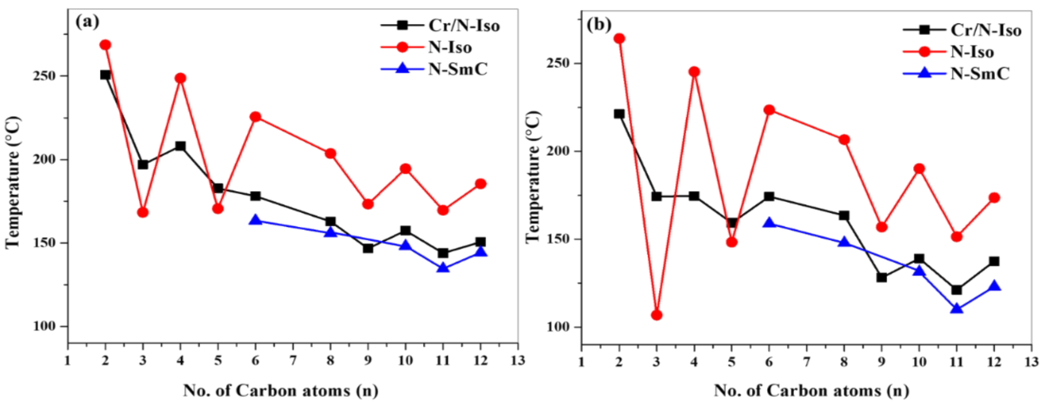
Scheme 4.1: Synthesis scheme for the dimers of *Series V-n*

The abbreviated name CBOH represents compounds where "CB" denotes the cyanobiphenyl group. In, NpAzOH, the word “NpAz” indicates the rodlike azonaphthyl. In NpAmOH, “NpAm” denotes naphthyl azomethine or Schiff base mesogenic group. ***Series V-n*** dimers are dimers in which one end bears cyanobiphenylgroup and the other end bears azonaphthyl moiety and ***VI-n*** have azomethine naphthyl moiety at the other end. n" signifies the length of the flexible spacer for these unsymmetrical dimers.



Scheme 4.2: Synthesis scheme for the dimers of series *VI-n*

4.3 Results and Discussion:



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.

Dimers with longer spacers exhibited smectic phases, while shorter spacers predominantly resulted in nematic phases. Odd-membered dimers displayed lower clearing temperatures due to the odd-even effect. Azomethine dimers had a longer nematic mesophase compared to azo dimers. The cyanobiphenyl groups enabled easy modifications and higher dipole moments, contributing to better mesomorphic behaviour.

4.4 Conclusion:

Two new series of unsymmetrical liquid crystal dimers incorporating cyanobiphenyl and azo/azomethine naphthyl moieties have been synthesized and characterized, providing valuable insights into their mesomorphic behaviour. The dimers exhibited both nematic and smectic phases, with their transition temperatures significantly influenced by the length of the flexible spacer and the odd-even effect. As the number of carbon atoms in the spacer increases, the clearing temperatures or melting points tend to decrease, which is attributed to the increased flexibility and decreased intermolecular forces of longer chains. Photochromic behaviour was studied by UV-Vis spectroscopy. All the dimers shows similar conversion efficiency rate of 88-95% indicting the high sensitivity for the molecules under UV irradiation. Dimers of both series are fairly stable up to 300 °C, confirmed with the TGA studies. Optical storage device was also fabricated showing excellent dark and bright contract depicting the feasibility of the materials for the further investigations. Physical properties like birefringence and dielectric constant were studied for VI-9 dimer.

Chapter 5

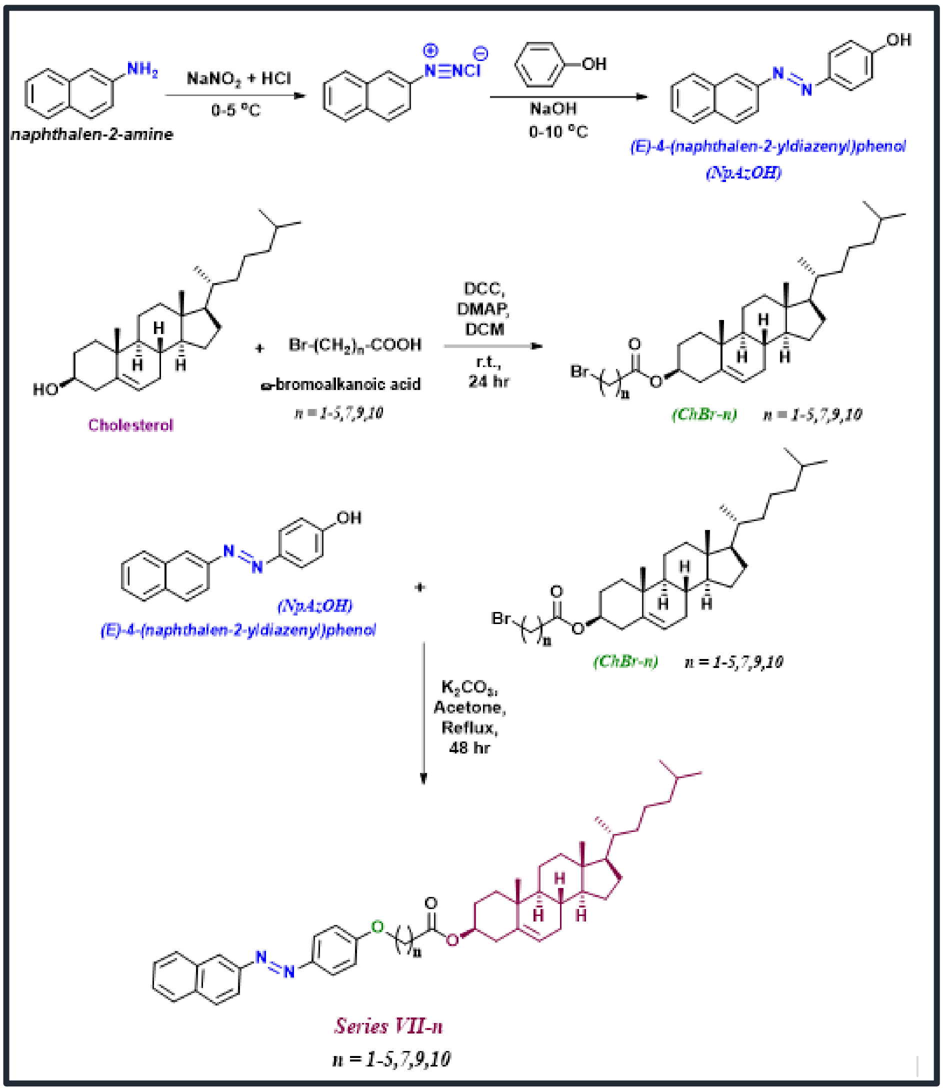
Cholesterol and Naphthalene-Based Unsymmetrical Liquid Crystalline Dimers: Synthesis, Characterization, and insights into its Mesomorphic Behaviour

5.1 Introduction:

Chiral liquid crystals (LCs) are notable for their unique physical properties. Cholesterol is a significant biologically active organic compound and is a key source of chiral mesophases due to their distinctive structural features. Cholesterol, due to its abundant natural presence and commercial availability, serves as a common component in these dimers, contributing to their chiral properties owing to its eight chiral centers. The incorporation of cholesterol allows for the induction of chirality in liquid crystals, influencing the formation of various phases.[21–23]

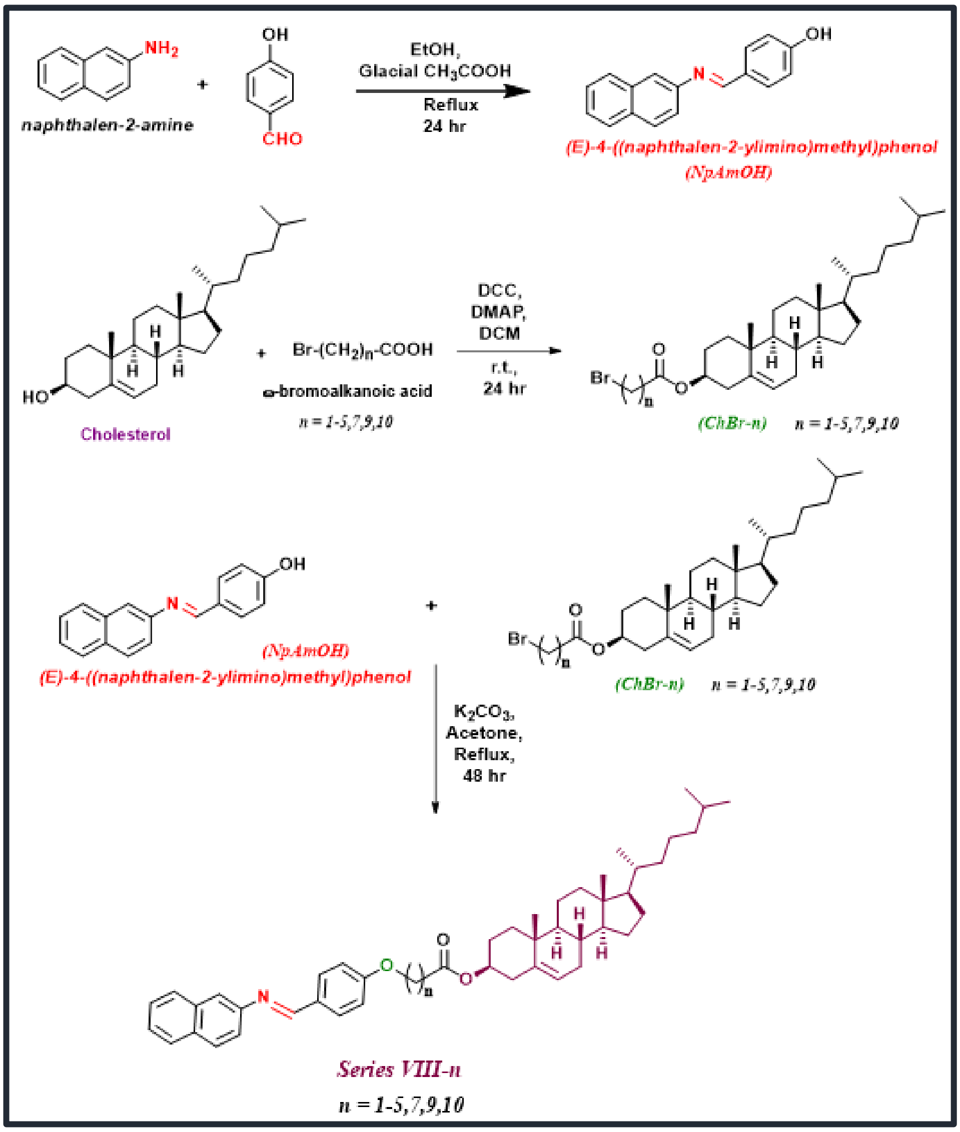
To enhance our comprehension of the structure-property relationships in cholesterol-based dimers incorporating azobenzene and Schiff base entities, and to assess the impact of various flexible spacers on their phase behaviour, we synthesized two novel series of Cholesteric-Calamitic dimers. These dimers feature cholesteryl ester along with 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.

5.2 Synthesis Scheme:



Scheme 5.1: Synthesis scheme for the dimers of series *VII-n*

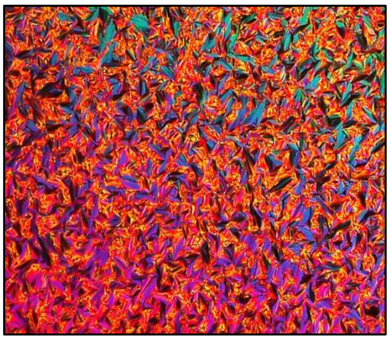
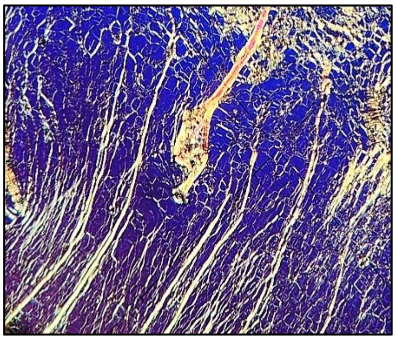
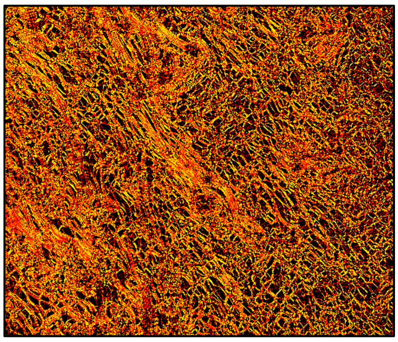
The abbreviated name NpAzOH, the word "Np' denotes naphthalene moiety and Az" indicates the azo linkage. In NpAmOH, "Am" denotes azomethine linkage. ***Series VII-n*** dimers are dimers in which one end bears cholesterol group and the other end bears azonaphthyl moiety and ***Series VIII-n*** have azomethine naphthyl moiety at the other end. Differential Scanning Calorimetry and Polarizing Optical Microscopy were used to investigate phase transition temperatures and mesomorphic behaviour.



Scheme 5.2: Synthesis scheme for the dimers of series *VIII-n*

The study revealed that spacer chain length significantly impacts these properties. Dimers with shorter spacers (n=1, 2) did not exhibit mesogenic properties, while those with longer spacers (n=3–5, 7, 9, 10) displayed enantiotropic chiral nematic phases and, in some cases, smectic phases.

5.3 Results and Discussion:

UV-Vis spectroscopy studies indicated efficient trans-cis isomerization, with a photo conversion efficiency (CE) of 56.7% for the ***VII-7*** dimer. Density Functional Theory (DFT) calculations provided insights into the optimized molecular structures and vibrational frequencies. Overall, the findings underscore the crucial role of spacer chain length and molecular rigidity in determining the liquid crystalline properties of these cholesterol-based dimers. Dimers with shorter spacers (n=1, 2) did not exhibit mesogenic behaviour, while those with longer spacers (n=3-10) displayed enantiotropic chiral nematic phases and, in some cases, smectic phases. Azomethine dimers showed a wider nematic range than azo dimers, while azo dimers had higher thermal stability. UV-Vis studies indicated efficient trans-cis isomerization.

5.4 Conclusion:

This chapter involves the synthesis and characterization of two series of cholesterol-based unsymmetrical liquid crystalline dimers, incorporating either naphthyl azo or naphthyl azomethine moieties. Differential Scanning Calorimetry and Polarizing Optical Microscopy were used to investigate phase transition temperatures and mesomorphic behaviour. The first two members (n=1,2) of each series do not exhibit mesogenic properties due to their short, flexible spacers. Members with n=3−5,7,9,10 demonstrate enantiotropic chiral nematic phases, indicative of their ability to form aligned liquid crystalline phases with thermal reversibility. Notably, higher members with odd spacers (n=5,7,9) show SmC* phases, suggesting that the increased length and odd number of spacers enhance the molecular interactions necessary for chiral smectic C phases. Dimers in series ***VII-n*** exhibit slightly higher thermal stability, indicated by higher clearing temperatures (TCr/N-Iso), compared to those in series ***VIII-n***. UV-Vis spectroscopy studies indicated trans-cis isomerization, with a photo conversion efficiency (CE) of 56.7% for the VII-7 dimer. Overall, the findings underscore the crucial role of spacer chain length and molecular rigidity in determining the liquid crystalline properties of these cholesterol-based dimers.

Conclusion of the Thesis

A 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.

References

1 E. B. Priestley, in *Introduction to Liquid Crystals*, eds. E. B. Priestley, P. J. Wojtowicz and P. Sheng, Springer US, Boston, MA, 1975, pp. 1–13.

2 G. A. DiLisi, *An Introduction to Liquid Crystals*, Morgan & Claypool Publishers, 2019.

3 S. Singh, in *Handbook of Liquid Crystals---Volume I: Foundations and Fundamental Aspects*, Springer International Publishing, Cham, 2024, pp. 1–52.

4 P. K. Choudhury and A.-B. M. A. Ibrahim, eds. P. K. Choudhury and A.-B. M. A. Ibrahim, IntechOpen, Rijeka, 2022, p. Ch. 1.

5 R. Bala, R. K. Sindhu, B. Kaundle, R. Madaan and S. Cavalu, *J. Mol. Struct.*, 2021, **1245**, 131117.

6 A. Momeni, C. M. Walters, Y.-T. Xu, W. Y. Hamad and M. J. MacLachlan, *Nanoscale Adv.*, 2021, **3**, 5111–5121.

7 R. J. Mandle and J. W. Goodby, *RSC Adv.*, 2016, **6**, 34885–34893.

8 J. D. Martin, C. L. Keary, T. A. Thornton, M. P. Novotnak, J. W. Knutson and J. C. W. Folmer, *Nat. Mater.*, 2006, **5**, 271–275.

9 A. Ramamoorthy, *Thermotropic Liquid Crystals: Recent Advances*, 2007.

10 J. Vallamkondu, E. B. Corgiat, G. Buchaiah, R. Kandimalla and P. H. Reddy, *Cancers,* 2011, **6,** 104-113

11 B. Gurboga, E. B. Tuncgovde and E. Kemiklioglu, *Biotechnol. Bioeng.*, 2022, **119**, 1047–1052.

12 C. Imrie and G. Luckhurst, *Liq. Cryst.*, 2002, **7,** 298-311.

13 S. Kumar and S. K. Pal, in *Liquid Crystal Dimers*, Cambridge University Press, 2017, pp. 1–9.

14 E. Do, K. Kim, Y. Kwon and J. Jin, *Liq. Cryst.*, 2006, **33**, 511–519.

15 C. Wu, *Mater. Lett.*, 2007, **61**, 1380–1383.

16 D. Zaton, A. Karamoula, G. J. Strachan, J. M. D. Storey, C. T. Imrie and A. Martinez-Felipe, *J. Mol. Liq.*, 2021, **344**, 117680.

17 M. Rabari, C. Koli and A. K. Prajapati, *Soft Mater.*, 2024, **22**, 1–12.

18 M. Rabari and A. K. Prajapati, *J. Mol. Struct.*, 2024, **1308**, 138101.

19 T. N. Chan, Z. Lu, G. Y. Yeap and C. T. Imrie, *Liq. Cryst.*, 2012, **39**, 393–402.

20 Y. Arakawa, Y. Ishida, K. Komatsu, Y. Arai and H. Tsuji, *Tetrahedron*, 2021, **95**, 132351.

21 U. S. Hiremath, *Tetrahedron*, 2014, **70**, 4745–4753.

22 A. Al-shargabi, G. Y. Yeap, W. A. K. Mahmood, C. C. Han, H. C. Lin and M. M. Ito, *Liq. Cryst.*, 2020, **47**, 219–230.

23 M. Mitov, *Soft Matter*, 2017, **13**, 4176–4209.

Conferences and Paper Presentations

1. 27th National Conference on Liquid Crystals-2020, **NCLC-2020**, 21st-23rd December 2020, organized by Amity Institute of Applied Sciences, Amity University, Noida (**Poster presentation**)
2. 28th National Conference on Liquid Crystals-2021, **NCLC-2021**, 21st-23rd December 2021, organized by Department of Chemistry, Assam University, Silchar, Assam (**Poster presentation**)
3. 29th National Conference on Liquid Crystals-2022, **NCLC-2022**, 8th-10th December 2022, organized by Christ University, Bengaluru, Karnataka **(Oral presentation)**
4. International Conference on Smart Nanotechnologies, **ICONST-2023**, 6th-8th July 2023, organized by Department of Chemistry, GITAM University, Visakhapatnam **(Oral presentation)**
5. 30th National Conference on Liquid Crystals-2023, **NCLC-2023**, 2nd-4th November 2023, organized by Andhra University, Visakhapatnam **(Oral presentation)**
6. National Conference on Scientific Innovation towards Developed India, 28th February 2024, Faculty of Science, The Maharaja Sayajirao University of Baroda, Vadodara, Gujarat **(Oral presentation)**
7. 8th All Gujarat Research Scholar's Meet, **AGRSM-VIII**, 26th February 2023, organized by Indian Chemical Society, Vadodara Chapter; In association with Department of Chemistry, Faculty of Science, The Maharaja Sayajirao University of Baroda, Vadodara, Gujarat **(Oral presentation)**
8. Gujarat Research Scholar's Connect, **GRSC-2023**, 7th-8th December 2023, organized by CSIR-Central Salt & Marine Chemicals Research Institute (CSMCRI), Bhavnagar, Gujarat **(Poster presentation)**
9. National Symposium on Recent Trends in Inorganic Chemistry, **RTIC-2023**, Department of Chemistry, Faculty of Science, The Maharaja Sayajirao University of Baroda, Vadodara, Gujarat **(Poster presentation)**

Publications

Thesis work

1. M. Rabari, R.S. Kumar CH, A. K. Prajapati, Liquid crystalline naphthyl derivatives with bromoalkoxy tail: Photophysical behavior and DFT studies, *J. Mol. Struct*. 1293 (2023) 136252. https://doi.org/https://doi.org/10.1016/j.molstruc.2023.136252.

2. M. Rabari, A. K. Prajapati, Unsymmetrical mesogenic dimers containing azo and azomethine naphthalenes : Synthesis , characterization , mesomorphic properties and DFT studies, *J. Mol. Struct.* 1308 (2024) 138101. https://doi.org/10.1016/j.molstruc.2024.138101.

3. M. Rabari, A. K. Prajapati, Naphthalene-based symmetrical liquid crystalline dimers: Synthesis, characterization, mesomorphic behaviour and DFT studies, *J. Mol. Struct.* 1307 (2024) 137971. https://doi.org/10.1016/j.molstruc.2024.137971.

4. M. Rabari, A. K. Prajapati, Mesogenic cholesterol-naphthalene dimers: Synthesis, characterization, mesogenic properties, photochromic behaviour and theoretical insights, *J. Mol. Liq*. 14 (2024) 126296. https://doi.org/https://doi.org/10.1016/j.molliq.2024.126296.

5. M. Rabari, A. K. Prajapati, S. Mahesha, M.K. Akshaya, B. Kumar, A study on the thermo-photoisomerization of a liquid crystalline dimer of cyanoazobenzene and naphthalene, *Soft Matter* 21 (2025) 1395. https://doi.org/10.1039/d4sm01172d.

Other Publications

6. M. Rabari, S. Solanki, A. K. Prajapati, "Novel Magneson-I derived λ-shaped tris azo liquid crystalline trimers," Dye. Pigment. 220 (2023) 111757. https://doi.org/10.1016/j.dyepig.2023.111757.

7. M. Rabari, Y. Parmar, A. K. Prajapati, Unsymmetrical liquid crystalline dimers containing biphenyl moiety: synthesis, characterisation, mesomorphic study and DFT studies, Liq. Cryst. 50 (2023) 2552–2570. https://doi.org/10.1080/02678292.2023.2264793.

8. M. Rabari, C. Koli, A. K. Prajapati, Synthesis, characterization, mesogenic properties, and DFT studies of unsymmetrical liquid crystalline dimers of biphenyl, Soft Materials, 22 (2023), 1–12. https://doi.org/10.1080/1539445X.2023.2282495.

9. M. Rabari, M. Bhatt, A. K. Prajapati, Symmetrical liquid crystalline dimers containing azo and azomethine linkages: synthesis, characterisation, mesomorphic study and DFT studies, Liq. Cryst., 1 (2024) 1–17. https://doi.org/10.1080/02678292.2024.2351105.

10. M. Rabari, V. Patel, A. K. Prajapati, "Liquid crystalline compounds containing lateral thiol group: synthesis, characterisation, its mesomorphic properties and DFT studies," Liq. Cryst. 12 (2023) 1–15. https://doi.org/10.1080/02678292.2023.2229784.