A SYNOPSIS

of the Thesis entitled

Synthesis and Characterization of New Liquid Crystalline Compounds

To be Submitted to
As a partial fulfilment for the award of the degree of

DOCTOR OF PHILOSOPHY
in
CHEMISTRY

Submitted by

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Synopsis 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
The Maharaja Sayajirao University of Baroda

Faculty: Faculty of Science

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

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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

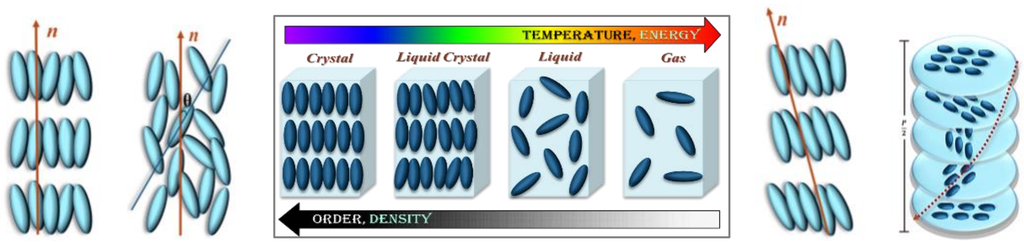
Chapter 5

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

Chapter 1
Introduction of the Liquid Crystals

Liquid Crystals: The Fourth State of Matter

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]



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 liquid crystals can further be categorized based on their stability:

Enantiotropic Liquid Crystals: These mesophases are thermodynamically stable and can be observed both upon heating and cooling.

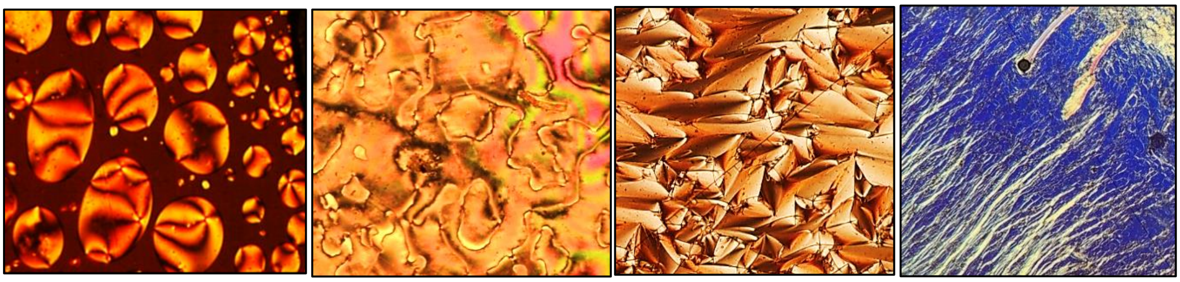
Monotropic Liquid Crystals: These mesophases are only observed upon cooling and are not stable when heated.

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.

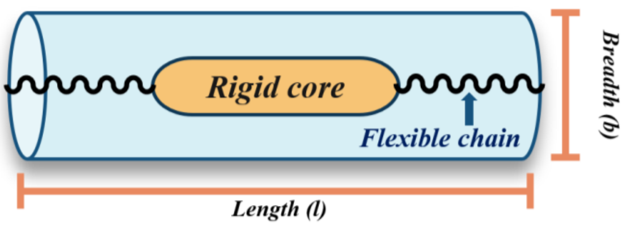
Nematic Mesophase: Nematic phases lack positional order but maintain orientational order. Molecules in this phase align along a common direction called the director.

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.



<u>Criteria for Liquid Crystalline Phase</u>

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.

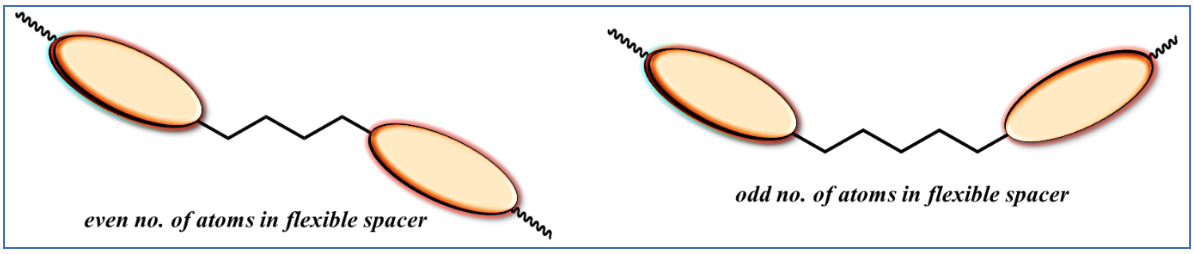


Applications of Liquid Crystals

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

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.[12–14]



Objectives

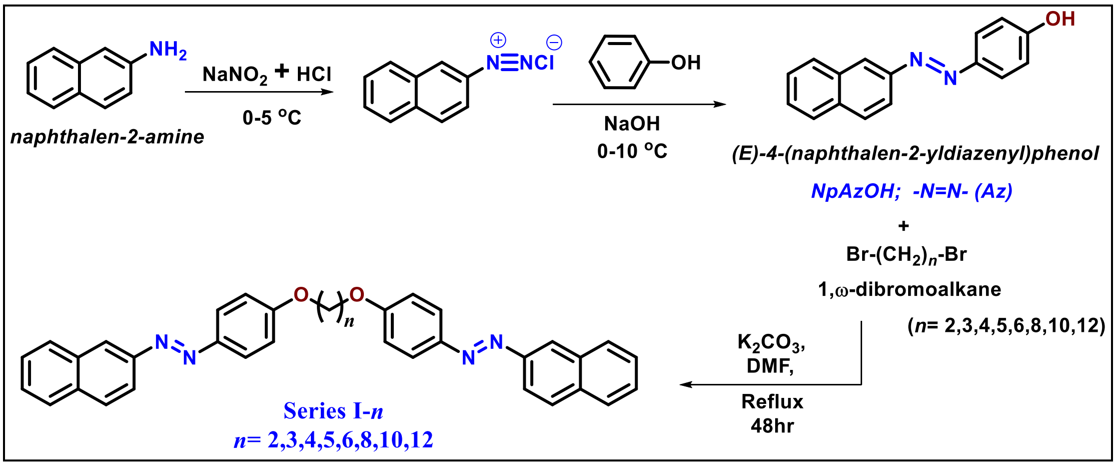
- ✓ To develop and synthesize new liquid crystalline dimers based on naphthalene structures, aiming to explore their unique mesomorphic properties.
- ✓ To conduct comprehensive physicochemical characterization of the synthesized dimers using various spectroscopic techniques such as Fourier-Transform Infrared (FT-IR) Spectroscopy, Nuclear Magnetic Resonance (NMR) Spectroscopy, and Mass Spectrometry (ESI-MS). This will help in confirming the molecular structure and composition of the compounds.
- ✓ To investigate the influence of varying the length of the flexible spacer chains on the mesomorphic behaviour of the synthesized dimers. This will involve analyzing how different chain lengths affect the formation and stability of liquid crystalline phases.
- ✓ To examine the optical properties of the synthesized dimers using UV-Visible Spectroscopy, determining their absorbance and transmittance characteristics. This study will provide insights into the potential applications of these materials in optoelectronic devices.
- ✓ To compare the mesomorphic and physicochemical properties of the synthesized dimers with those reported in the literature. This will involve a detailed discussion on the structure-property relationships, identifying how molecular design influences the liquid crystalline behaviour and other relevant properties of the compounds.

Chapter 2

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

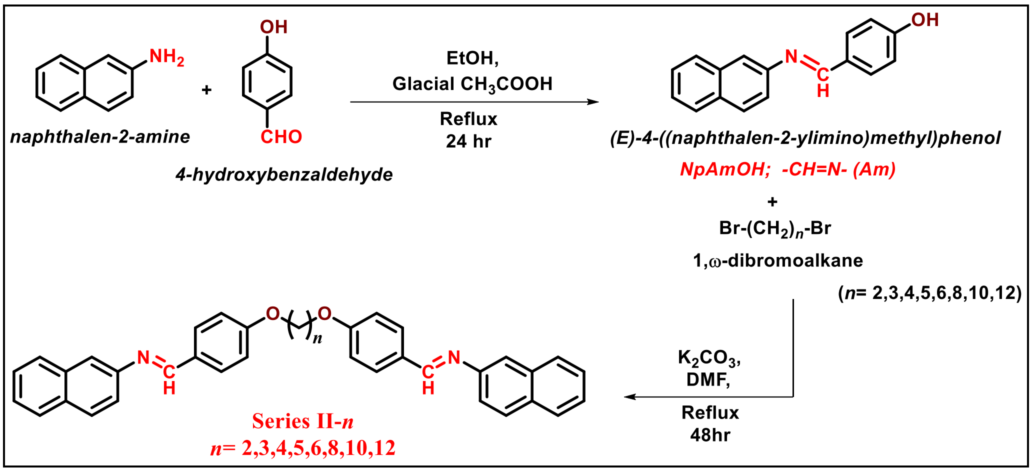
Symmetrical Liquid crystalline dimers are created by linking two identical mesogenic units with a flexible spacer. This spacer allows molecular motion, while the mesogenic units maintain the necessary rigidity for the ordered orientation crucial for liquid crystal phase formation. Azo (-N=N-) and azomethine (-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]

Synthesis, characterization and study of mesomorphic properties of 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 objective of the current work is to synthesize and examine their mesomorphism, as well as their photophysical 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 were studied.

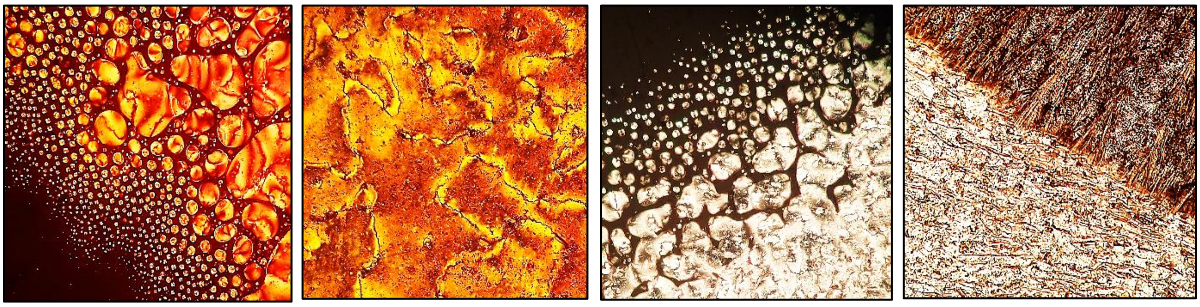


Scheme 1: Synthetic route for the dimers of Series *I-n*

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.

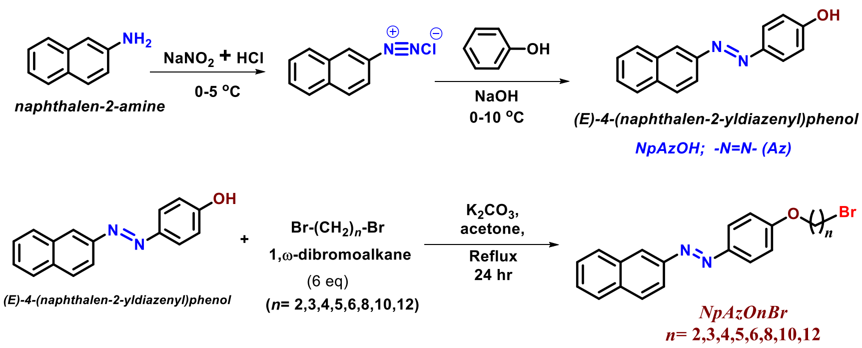


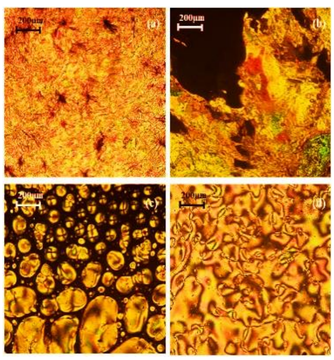
Scheme 2: Synthetic route for the dimers of Series *II-n*



(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. Our aim is to synthesize new naphthyl derivatives with azo linkages, characterize it and study of its mesomorphic properties.





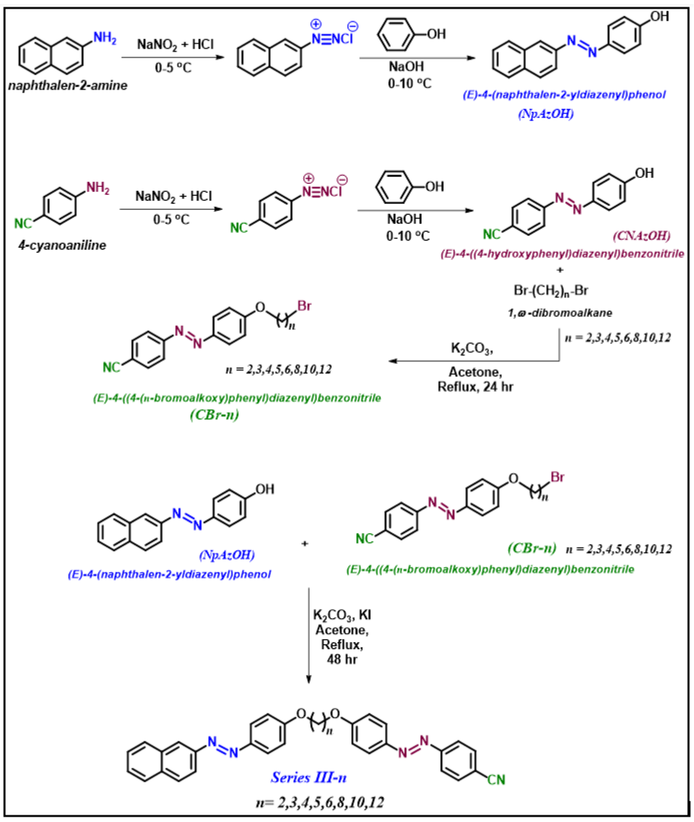
Only three compounds show nematogenic behaviour and the rest are non-mesogenic.

Chapter 3

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

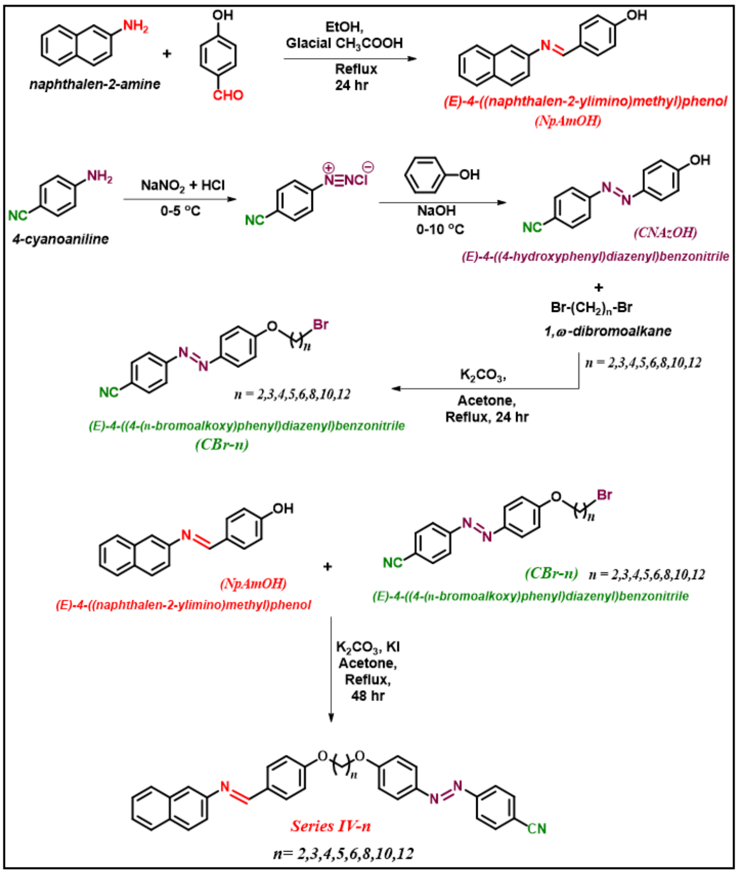
Non-symmetric dimers stand out for their intriguing polymorphic properties. The introduction of non-symmetry in dimers can be achieved by connecting different mesogenic units, adjusting the length of terminal chains, employing diverse terminal groups, or varying the length and evenness of the spacer 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]

The objective of our work is to synthesis of unsymmetrical liquid crystalline (LC) dimers to investigate the influence of naphthalene moieties on mesomorphism. While unsymmetrical dimers incorporating azobenzene and azomethine linkages with various mesogenic cores have been extensively reported, those utilizing simple aromatic units are relatively scarce. Given that naphthalene moieties tend to increase the breadth of molecules, there's a concern that they might diminish the likelihood of exhibiting LC properties.



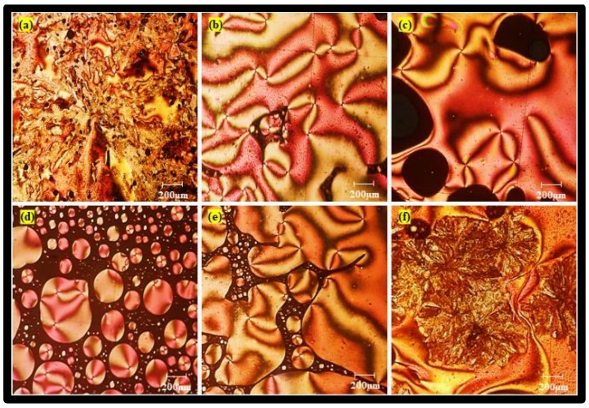
Scheme 1: Synthesis scheme for the dimers of series *III-n*

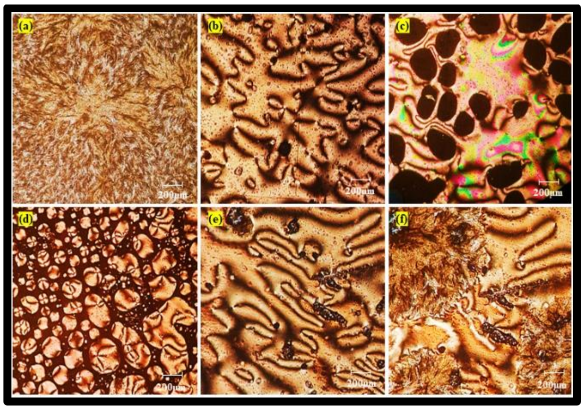
To address this, we have chosen to incorporate naphthalene moieties into our dimers and synthesized two series of compounds. In ***Series III-n***, one end contains cyanoazobenzene moiety while the other end contains azo naphthyl, whereas in ***Series IV-n***, the other end contains azomethine naphthyl. 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.



Scheme 2: Synthesis scheme for the dimers of series *IV—n*

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.

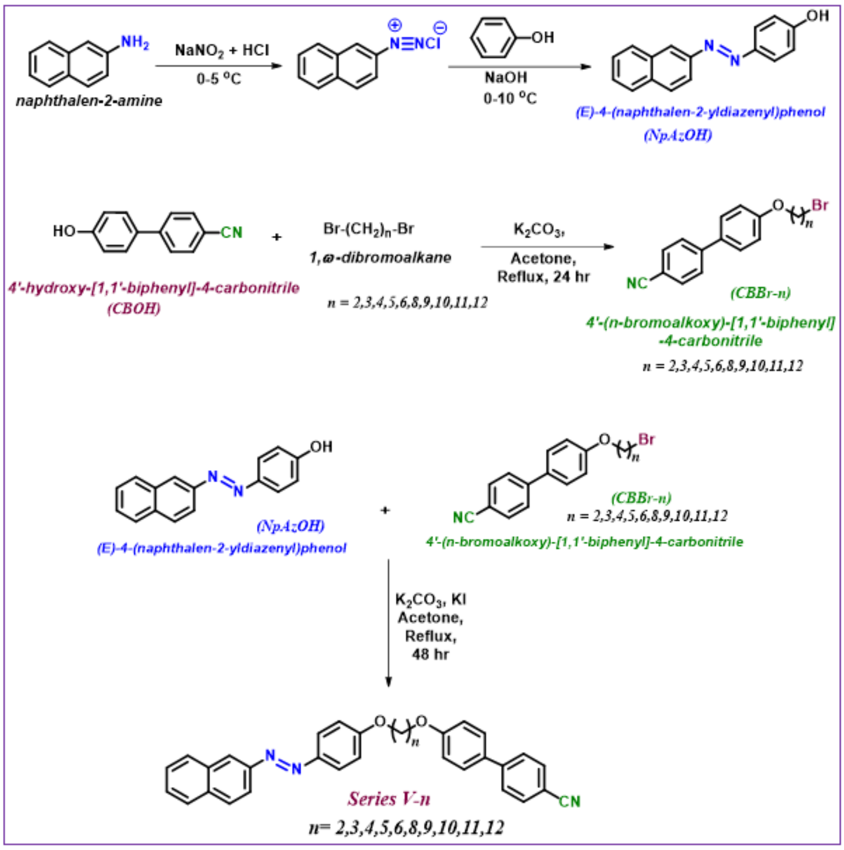




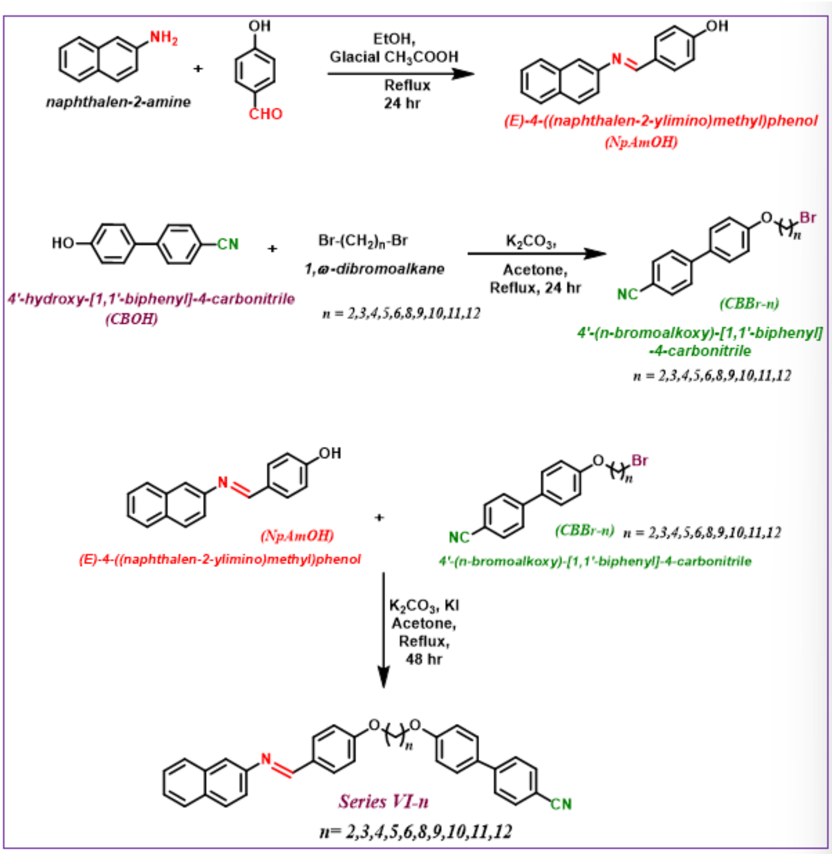
Chapter 4

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

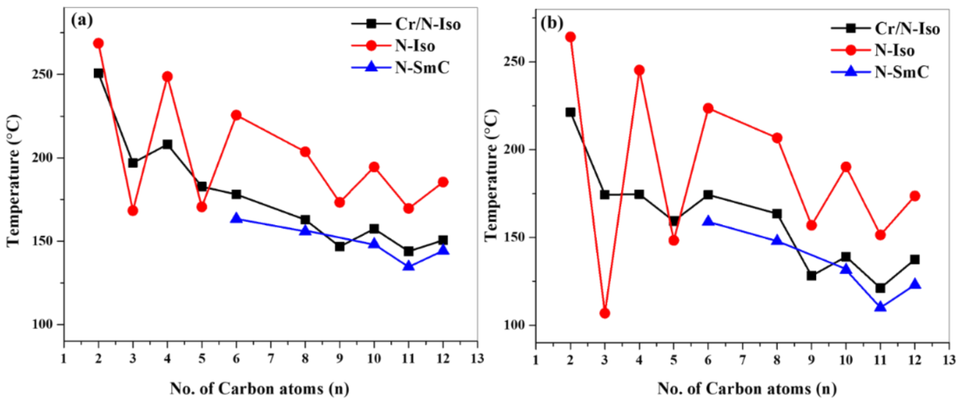
The adaptability of cyanobiphenyl groups allows for facile modifications with polar lateral or terminal groups, enabling the induction of dipole moments and the enhancement of bulk dielectric anisotropy. This capability facilitates the fine-tuning of mesomorphic properties.[19,20] To deepen our understanding 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. 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 1: Synthesis scheme for the dimers of *Series V-n*



Scheme 2: Synthesis scheme for the dimers of series *VI-n*



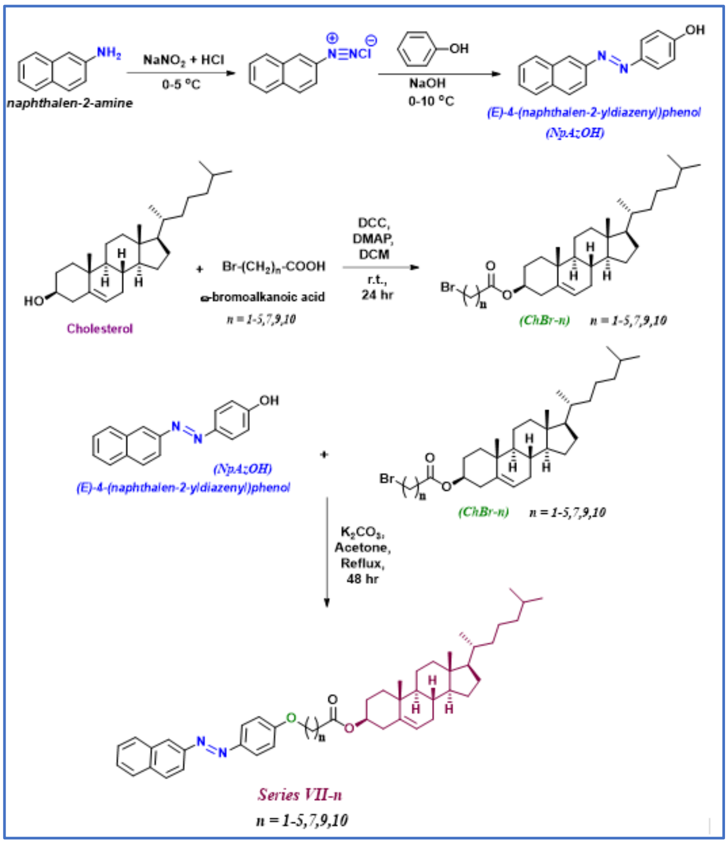
An increase in chain length often leads to the emergence of smectogenic behaviour. Odd-membered dimers often exhibit comparatively lower clearing temperatures, a characteristic known as the odd-even effect. As the number of carbons in the flexible spacer increases, the clearing temperatures or melting 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.

Chapter 5

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

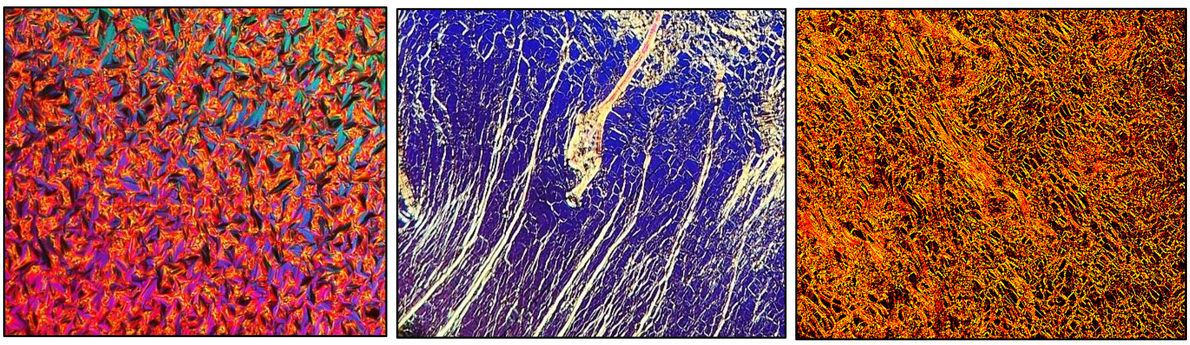
Chiral liquid crystals (LCs) are notable for their unique physical properties. Cholesterol is a significant biologically active organic compound and is a key source of chiral mesophases due to their distinctive structural features. Cholesterol, due to its abundant natural presence and commercial availability, 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. 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. 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.

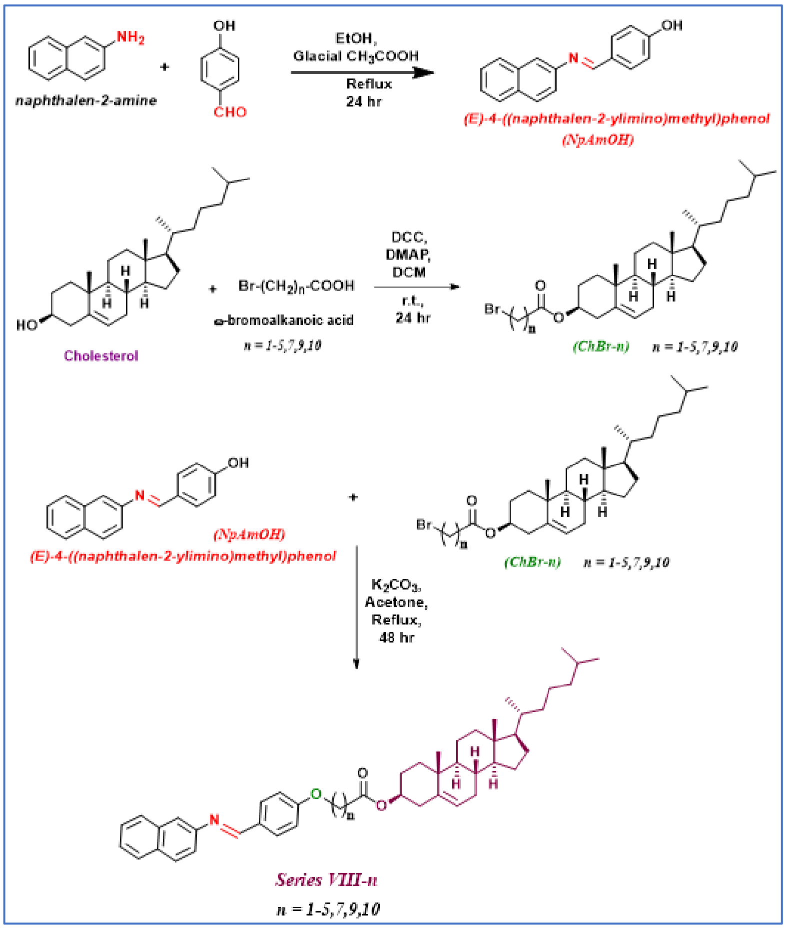


Scheme 1: Synthesis scheme for the dimers of series *VII-n*

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.



Scheme 2: Synthesis scheme for the dimers of series *VIII-n*

Conclusion:

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.

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