

A DISSERTATION ON  
**“A THEORETICAL STUDY ON OPTICAL PROPERTIES OF  
DIFFERENT DLCs USING DFT”.**

PROJECT REPORT SUBMITTED TO THE  
DEPARTMENT OF PHYSICS  
INTEGRAL UNIVERSITY, LUCKNOW  
IN PARTIAL FULLFILLMENT FOR THE DEGREE OF  
MASTER OF SCIENCE  
IN PHYSICS



SUBMITTED BY

ERAM FATIMA  
M.Sc. PHYSICS  
(IV SEMESTER)  
ROLL NO NO-2101080001

UNDER THE SUPERVISION OF

PROF. POONAM TANDON

DEAN STUDENT WELFARE  
DEPARTMENT OF PHYSICS



DEPARTMENT OF PHYSICS  
UNIVERSITY OF LUCKNOW  
LUCKNOW-226007



## CERTIFICATE OF ORIGINALITY

This is to certify, that the dissertation work submitted by me, entitled, “***A Theoretical Investigation on Optical Properties of Different DLCs Using DFT***” submitted to the Department of Physics, Integral University, Lucknow in partial fulfilment of requirement for the award of master of science in physics is an outcome of my independent and original work carried out in Macromolecular lab, Department of Physics, University of Lucknow. This project work has not been submitted elsewhere for any other degree or diploma.

Name of Author(s): ERAM FATIMA

Designation: STUDENT

Affiliated Institution: INTEGRAL UNIVERSITY, LUCKNOW

Title of the Dissertation: “**A THEORETICAL INVESTIGATION ON OPTICAL PROPERTIES OF DIFFERENT DLCS USING DFT**”

Email: [ermfatima@student.iul.ac.in](mailto:ermfatima@student.iul.ac.in)



### CERTIFICATE FROM SUPERVISOR

This is to certify that **Eram Fatima**, a student of **M.Sc. Physics (II Year/ IV Semester)** Integral University has completed her Dissertation work entitled "***A Theoretical Investigation on Optical Properties of Different DLCs Using DFT***" successfully. She has completed the work from University of Lucknow under Prof. Poonam Tandon, Head, Department of physics, University of Lucknow, for the partial fulfilment of the requirement for award of the degree of Master of Science. Further, this has not been submitted anywhere else for the award of any other degree or diploma.

I wish her good luck and bright future.

**Dr. Seema Srivastava**

(Supervisor)

Head,  
Department of Physics Integral University  
Lucknow

**Date**



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I wish her good luck and bright future.

**Prof. Poonam Tandon**  
(Internal Advisor)  
Department of Physics  
Lucknow University  
Lucknow

**Date:**

## **ACKNOWLEDGEMENT**

First and foremost, I would like to express my thanks towards Almighty on having successfully completed this project within the stipulated time period. It was an exciting experience that taught me many things and greatly improved my understanding in the field of physics.

I am sincerely thankful and express my gratitude to my **supervisor Prof. Poonam Tandon, Dean Student Welfare; University of Lucknow** for giving me an opportunity to avail the facility of this esteemed University and to join her prestigious lab and letting me explore this interesting and stimulating project. Without her guidance it would have been difficult, to reach the goal.

I am also very thankful and express my deepest gratitude to **Dr. Seema Srivastava, Head of Department (Physics); Integral University Lucknow** for her unconditional support encouragement and guidance that made this task interesting.

I have fallen short of words to describe how grateful I am to **Miss. Rajni Chaudhary, Research Scholar, Department of Physics; University of Lucknow** who not only happens to be my mentor, but also someone who supported me throughout this project in each step. It was his useful suggestion and guidance which helped me in completing the project work on time. His kind words and guidance will always be worthwhile.

I would like to extend my sincere thanks to all the members of **Department of Physics, Integral University, Lucknow**, who generously devoted their valuable time and guided me through their kind efforts. Special thanks to all the members of the **Macromolecular Lab, Department of Physics, University of Lucknow**, for their warmth support throughout my project work.

At last, a special token of appreciation goes to all my family and friends, who stood by me through thick and thin and encouraged me, whose blessings and support were always with me during my entire academic career.

**ERAM FATIMA**

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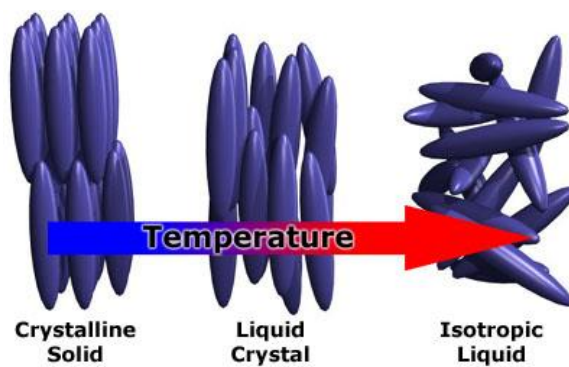


## LIST OF SYMBOLS AND ABBREVIATION

- LCs – Liquid Crystals
- DLCs – Discotic Liquid Crystals
- DFT – Density Functional Theory
- NLO – Non-Linear Optical property
- HAB - hexa-n-alkanoates of benzene
- LEDs - Light-emitting diodes
- OLEDs - organic light emitting diodes
- OPVs - Organic photovoltaic
- Col - columnar phase
- Col<sub>h</sub> - hexagonal columnar phase
- Col<sub>hd</sub> – hexagonal disordered columnar phase
- Col<sub>ho</sub> – hexagonal ordered columnar phase
- Col<sub>l</sub> – lamellar columnar phase
- Col<sub>ob</sub> – oblique columnar phase
- Col<sub>p</sub> - plastic columnar phase
- Col<sub>r</sub> - rectangular columnar phase
- GTOs- Gaussian-Type Basis Sets
- STOs - Slater- Type Basis Sets
- $\chi$  = Chi
- $\mu$  = Mu
- $\eta$  = Eta
- S = Softness
- $\omega$  = Omega

## 1. INTRODUCTION

Liquid crystals are a type of material that exhibit properties of both liquids and solids. They flow like a liquid, but their molecules are ordered like those in a crystal. Liquid crystals can align themselves in response to an electric field, which changes the polarization of light passing through them.[1] When liquid crystals are exposed to an electromagnetic field, they can exhibit both linear and non-linear optical properties..



*Fig. 1: Representation of States of matter along with molecular orientation in crystalline, liquid crystal and isotropic liquid phase.*

Linear optical properties of liquid crystals are often used to design optical devices such as polarizers, filters, and wave plates. Non-linear optical properties are used to design non-linear optical devices such as photonic crystals, optical switches and modulators, non-linear optical microscopy, optical frequency converters, optoelectronic devices such as LCDs, OLEDs. Liquid crystal exhibit different phases or states of matter depending on temperature such as nematic, smectic and cholesteric phase.[2] Discotic Liquid crystal is one of the types of liquid crystal which have unique electrical and optical properties, making them useful for various applications, such as OPVs, Optical storage devices and LEDs. [1]

The stability of these molecules is due to the strong  $\pi$ - $\pi$  stacking interactions between the aromatic cores of the disc-shaped molecules. [3]The side chains of DLCs typically have flexible aliphatic chains, which undergo rapid thermal motion and create a dynamic disorder. DLCs offer the potential for low-cost and easily processed solar cells due to their unique properties. [4]

The discovery of HAB by S. Chandrashekar in 1977 marked a significant milestone in the field of liquid crystals. HAB is a disk-shaped liquid crystal that exhibits a hexagonal columnar mesophase, which is characterized by the formation of cylindrical columns of molecules with long-range positional and orientational order.[3] In 1978, J. Billard and colleagues proposed the name "discotic" to refer to the mesophases exhibited by the disc-like mesogens, in contrast to the "calamitic" mesogens, which have a rod-like shape. DLCs have several remarkable properties that make them attractive for a wide range of applications.[5]

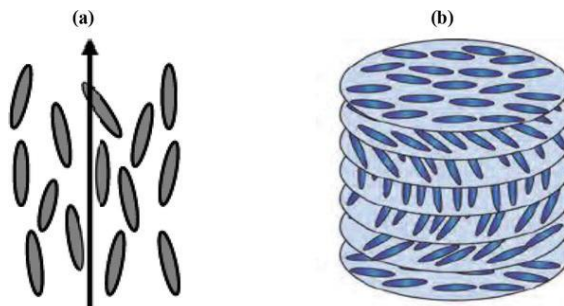
Another important property of DLCs is their anion-selective photoluminescence, which refers to their ability to selectively detect and respond to different anions in solution. This property has potential applications in sensing and environmental monitoring.[6]

DLCs also exhibit electrical conductivity, which is attributed to the delocalized  $\pi$ -electron system of the disc-like molecules. This property has led to the development of discotic liquid crystal-based organic semiconductors and electronic devices. Discotic liquid crystals (DLCs) typically consist of a rigid aromatic core with two, three, four, or six-fold rotational symmetry, which is surrounded by flexible side chains and linking groups. [2] The choice of core, linking group, and terminal functional group is critical in determining the properties and stability of the mesophases exhibited by DLCs, as well as their transition points.

Discotic liquid crystals (DLCs) feature a rigid aromatic core that drives self-assembly into columnar mesophases. Higher degrees of symmetry in the core lead to more stable and ordered mesophases.[7] The flexible side chains and linking groups provide flexibility, enabling the formation of the columnar structure. The length and shape of the side chains impact the properties and stability of the mesophases. DLCs typically consist of a rigid aromatic core with two, three, four, or six-fold rotational symmetry, surrounded by flexible side chains and linking groups. Azo-, ester-, and imine-based DLCs exhibit diverse mesophases. Azo-based DLCs are extensively studied for their photoluminescence properties and find applications in sensing, such as detecting explosives and pollutants.[4]

## 1.1 Fundamental of Liquid Crystal:

On a broad scale, liquid crystal classifications prepare the way for several fundamental meso-phases. Temperature, solution concentration, and other factors can change the chemical and physical characteristics of liquid crystals, which impacts the long-range orientational as well as positional order of molecules.[4] Due to temperature variations, thermotropic liquid crystals create a few meso-phases that can be controlled thermally. The mechanism further classifies thermotropic liquid crystals into two groups: enantiotropic liquid crystals, which can only be created by raising the temperature of solids or decreasing the temperature of liquids, and monotropic liquid crystals, which can be created by increasing the temperature of solids or decreasing the temperature of liquids to create an aligned and ordered liquid crystal arrangement.

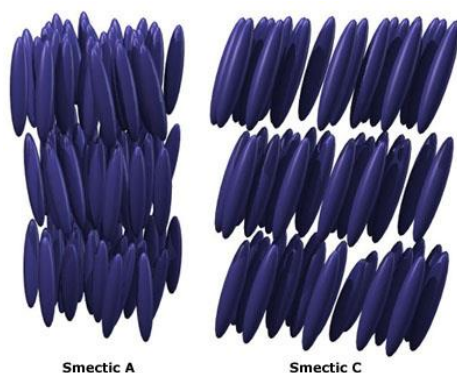


*Fig. 2: Schematic diagram of (a) Nematic, (b) Cholesterics Liquid Crystals)*

Thermotropic liquid crystals are divided into four main categories based on the molecular structure and symmetry: nematics, cholesterics, smectics, and columnar liquid crystals. Among the characteristics that describe liquid crystal types are the orientational order, positional order, and bond orientational order.[8] The basic liquid crystal phase, called nematic mesophase, includes an interaction among molecule orientation and local molecular-axis orientation that can be affected by external forces, such as an electric field, which causes the molecular axis to align appropriately. These anisotropic liquid crystal structures include a solid molecular backbone that encircles the long axis of molecules and a long-range orientational order, but they lack an order of molecular centre of mass positions. [9] These crystalline compounds may be easily polarised due to their large dipole moment and high refractive index, making them appropriate in display applications. Since their molecular structure into a long axis that is parallel to the molecular, and the molecular axis is defined as helical, these

compounds also display long-range orientational order. The pitch, or the length of the long axis on which the director revolves, is defines the cholesteric structure.

Cholesterics are finite pitch structures with a few hundred nanometers of pitch; however, if nematics are doped with an enantiomorphic chemical, they can also be of the finite pitch. Although this pitch can be sensitive to a number of factors, it is similar to visible light and causes white light scattering due to the Bragg's reflection phenomena, which can be used for various optical applications. Layer ordering distinguishes smectic liquid crystals apart from others, yet molecule orientation and layer alignment are similar to nematic structures, which also include positional and orientational orders.[10] The smectic liquid crystal phases are more ordered than the nematic liquid crystal phases in that they have molecules arranged perpendicular to layers, hexagonally structured, and tilt angle measurement.[6]



*Fig. 3: Schematic diagram of Smectic A and Smectic C phase of liquid crystals.*

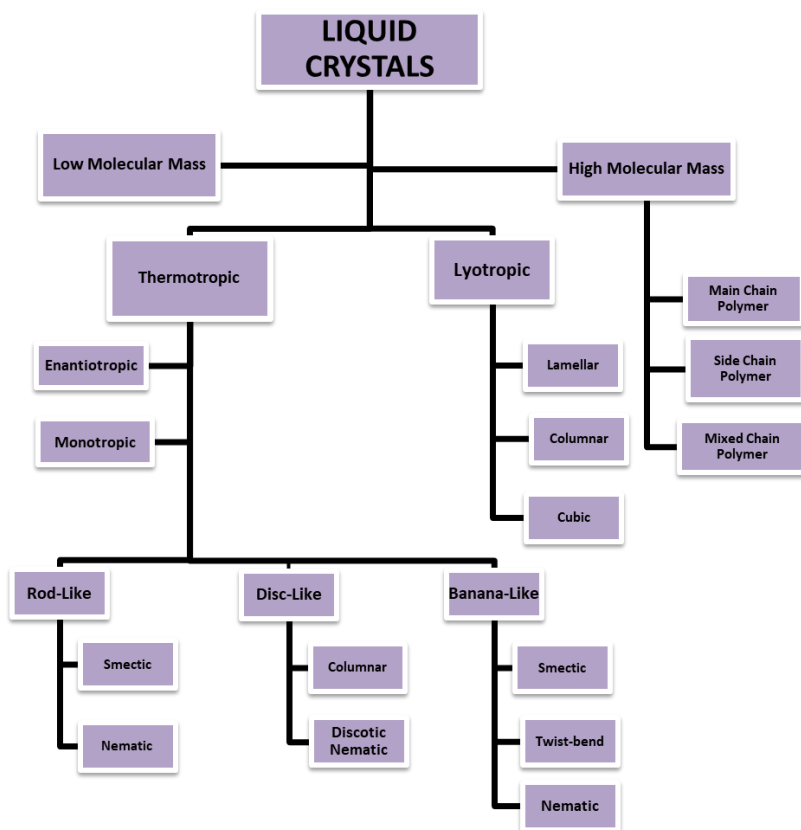
Smectic A and C are shown in Figure 3 with any molecular positional ordering within each individual layer. Smectic A molecules are oriented perpendicular to the layer, while Smectic C molecules are slanted away from the layer orientation, resulting in order in just one direction.[11] Due to the disc-shaped molecular structures that are stacked in column form and arranged in different shapes, columnar liquid crystals are also referred to as discotic liquid crystals.

The columnar phase molecules are categorised based on their packing reasons. They are built in their respective lattices and arranged in two-dimensional structures such as hexagonal, rectangular, oblique, and lamellar. Lyotropic liquid crystal transitions are a different category of liquid crystal changes that occur when the temperature and solvent

concentration are changed.[4] Different lyotropic liquid crystals were produced by amphiphilic molecules in a solution with hydrophobic and hydrophilic components, and different circular or rod-shaped micelles were produced by different concentrations.

While the circular micelles form a cubic pattern of lyotropic liquid crystal that does not include shear planes to make them more viscous than the hexagonal lyotropic phase, the rod-shaped micelles are arranged to form a very viscous hexagonal lyotropic liquid crystal. By adjusting the solution's micelle shape, it is possible to produce a wide variety of lyotropic liquid crystals that are shape-dependent.[12]

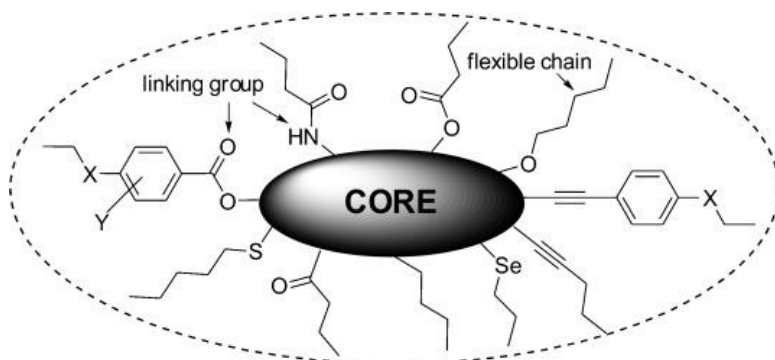
## 1.2 Classification of Liquid Crystals



*Fig. 4: General classification of the different kind of liquid crystals on the basis of shape and molecular orientation.*

### 1.3 Discotic Liquid Crystal

In 1977, the Raman Research Institute in India's Sivaramakrishna Chandrasekhar and colleagues were the first to describe disc-like compounds (discotic) as LCs. They created many benzene hexa-alkanoate derivatives and used optical, thermodynamic, and X-ray experiments to establish their LC properties



*Figure 5: Illustration of basic design of DLCs exhibiting core, linking group, and flexible side chains.*

Discotic liquid crystals are a type of liquid crystal in which the molecules have a disc-like shape. These molecules typically have a flat core made up of six or eight aromatic rings that are linked together by long, flexible chains. [7] The chains are often composed of ester or ether groups. A completely new class of LCs was created as a result of the spontaneous self-organization behaviour of disk-like (discotic) molecules. Nematic, smectic, cubic, and columnar phases are the other main categories of discotic mesophases. While very few smectic and cubic discotic phases have been observed, there are a few events of nematic discotic mesophases. They are composed of flat aromatic or heterocyclic molecules with peripheral substituents that promote the formation of columnar structures. However, DLCs that display more than one type of columnar mesophase are more common [13]. Due to their outstanding unidirectional charge migration feature and use in wide-viewing liquid crystal display (LCD) technologies, discotic liquid crystals (DLCs) are of immense scientific interest. [9] When disc-shaped molecules self-organize with either only orientational order or both orientational and positional order, DLCs are created. Nematic (ND) phase, the least ordered mesophase, is defined as having only orientational order of disc-shaped

molecules. More ordered columnar (Col) mesophases are generated by stacking discs on top of one another like a stack of coins. Then, these columns of discs can self-organize into various lattices, such as the hexagonal Col<sub>h</sub>, rectangular Col<sub>r</sub>, and oblique Collob lattices. A few specimens of DLCs are known to display smectic and cubic phases in addition to the often seen columnar and nematic phases.[14] About 95% of DLCs are in the columnar phase, which is followed by the nematic phase; the remaining phases are only occasionally seen. Although some materials have been found to demonstrate polymorphism, the majority of discotics only show one form of mesophase.

### **1.5 Structure of Discotic Mesophases**

A typical DLC comprises a central discotic core (often aromatic) that is peripherally substituted by at least three flexible chains. The total molecule frequently has rotational symmetry of two, three, four, and six folds. DLCs with non-aromatic cores and lesser symmetry have also been reported, but are not as common mainly because these compounds' synthesis methods are usually more involved. [15] Although connecting groups may be important if they are involved in dipole–dipole interactions (e.g., carbonyl groups) or H–bonding (e.g., amide groups), the weakly attractive stacking forces in columnar mesophases are frequently defined by the stacking interactions between discotic cores, or  $\pi$ - $\pi$  stacking interactions. Inducing microphase segregation between the cores and side chains and lowering melting temperatures and increasing fluidity are the two purposes of the surrounding side chains, which greatly aid columnar stacking.[11]

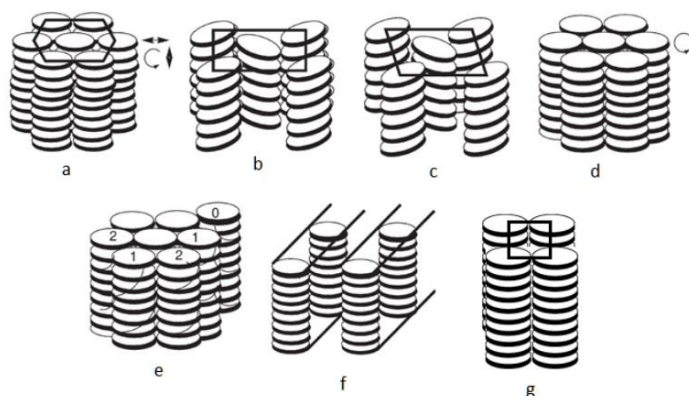
They determine the shape and flexibility of their attachment, linking groups affect the characteristics of side chains, yet they are typically seen of as a component of the core interactions. While many aliphatic (linear and branched) and polyether side chains have been described, a vast number of discotic cores and connecting groups have not. There have been some examples of side chains that included fluorine 22 and some side chains have been functionalized, usually terminally, with groups like OH, CN, and vinyl.

### **1.6 Structure of Discotic Columnar Mesophases**

The molecules self-organize into one-dimensional stacks on average in fluid columnar discotic mesophases, but their intra-columnar stacking distances oscillate and they



continue to interchange between columns, flip within columns, and rotate about the stacking axis quickly. Columnar mesophases have previously been referred to as "disordered" if an X-ray diffraction analysis fails to reveal a reflection for the intra-columnar stacking [16].



**Fig. 6:** Schematic representations of arrangement of molecules of DLCs in (a) hexagonal, (b) rectangular, (c) oblique, (d) hexagonal plastic, (e) helical, (f) lamellar, and (g) tetragonal, columnar mesophase.

## 2. REVIEW OF LITERATURE

### 2.1 History of Discotic Liquid Crystals:

In 1970s, Chandrasekhar and his team conducted ground breaking experiments that provided evidence for the existence of a new class of liquid crystals known as discotics. Unlike traditional liquid crystals composed of rod-like molecules (nematics) or flat molecules (smectics), discotic liquid crystals are composed of disc-shaped molecules. Discotic liquid crystals have attracted significant attention due to their unique molecular architecture and potential applications in optoelectronic devices. The optical properties of DLCs, including absorption, emission, luminescence, and non-linear optical behaviour, are crucial for their functionality. This review aims to provide a comprehensive analysis of the optical properties and structural characteristics of DLC A8, DLC B8, and DLC C8. The objectives of this review include investigating

**Commented [H1]:** Write about history of DLC, from S Chandrasekhar, or about first DLC. Something like that.

optimized structures, analysing HOMO-LUMO energy gaps, exploring non-linear optical properties, and calculating various molecular descriptors.

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Understanding the phase behaviour and mesophase transitions of DLCs is crucial for their practical applications in fields such as organic electronics and photovoltaics. This review focuses on the investigation of DLC A8, a discotic liquid crystal composed of 4-((2,3,4-tris(octyloxy)phenyl)diazenyl) benzoic acid, based on several research paper. DLCs A8 exhibited the presence of enantiotropic nematic and monotropic columnar mesophases, which are commonly observed in other DLCs and within the same series of compounds. The molecular structure of DLC A8, 4-((2,3,4- tris(octyloxy) phenyl) diazenyl)benzoic acid, likely influenced its phase behaviour, resulting in the observed mesophases. The enantiotropic nematic phases, while the monotropic columnar phase suggests a unidirectional transition from the nematic to columnar phase. The cooling cycle exhibited the following transitions: Isotropic (Iso) → Discotic nematic (ND) → Columnar (Col) → Crystalline (Cry). Conversely, during the heating cycle, the transitions were Cry → ND → Iso, consistent with previous studies [13]

## 2.2 Fundamentals of Discotic Liquid Crystals:

This section provides an overview of liquid crystals, their classification, and the unique features of discotic liquid crystals. It discusses the disk-like molecular shape,  $\pi$ - $\pi$  stacking interactions, anisotropic optical properties[17], and self-assembly [18] behaviour of DLCs.

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## 2.3 Methods and Techniques:

It covers computational methods for structure optimization, calculation of HOMO-LUMO energy gaps, assessment of non-linear optical properties, and determination of molecular descriptors. Density functional theory (DFT) and other computational approaches are commonly employed for studying the optical and structural properties of DLCs.

## 2.4 Structural Analysis:

The molecular structure of DLCs we have opted for our research work was already synthesized and reported by Veena et. al. [ref]. The molecular structures of monomers and dimers of A8, B8, and C8. The optimized structures are obtained through computational methods, and their key structural characteristics are discussed. A comparative analysis of the structures of A8, B8, and C8 molecules is also provided, highlighting any differences or similarities.

## **2.5 HOMO-LUMO Energy Gap Analysis:**

The homo-lumo energy gap is an important parameter for understanding the optical properties of DLCs. This section focuses on the calculation and analysis of HOMO-LUMO energy gaps for A8, B8, and C8 monomers and dimers. The significance of the homo-lumo energy gap in optical properties is discussed, and the calculated values are interpreted in relation to the molecular structures.

## **2.6 Non-Linear Optical Properties:**

Non-linear optical properties are crucial for applications in photonics and optoelectronics. This section explores the non-linear optical behaviour of A8, B8, and C8 monomers and dimers within DLCs.

## **2.7 Molecular Descriptors:**

Molecular descriptors provide valuable information about the chemical and electronic properties of DLCs. This section discusses the calculation of ionization potential, electron affinity, chemical potential, global hardness, electronegativity, global softness, and global electrophilicity index for A8, B8, and C8 monomers and dimers. The implications of these descriptors for understanding the optical properties and reactivity of DLCs are explored.

In summary, this review provides a comprehensive analysis of the optical properties and structural characteristics of A8, B8, and C8 monomers and dimers within DLCs. The study sheds light on the relationship between molecular structure and optical properties, emphasizing the importance of understanding these properties for the design and development of DLC materials with enhanced performance. The findings from this review contribute to the existing knowledge in the field and pave the way for future research on discotic liquid crystals.

# **3. METHODOLOGY**

## **3.1 Computational Details:**

In this work, DFT/B3LYP/6-311++G(d,p) method has been utilized for the structural optimization and polarizability calculation of all the Liquid crystals (LCs). Here, DFT stands for density functional theory, B3LYP is a hybrid functional and 6-311++G (d,p) is a basis set, which were discussed later. Gaussian 16 software is used for

computational calculations while the geometrical structures of the LCs were built in GaussView 6.0, graphical user interface of Gaussian 16. DFT is ab-initio method used for quantum mechanical simulations [12].

In the context of density functional theory (DFT), the merging of theoretical methods and basis sets is also essential to achieve a balance between accuracy and computational efficiency.

### **3.2 Density Functional Theory (DFT)**

The Hohenberg-Kohn theorem (HK), which claimed that the ground-state energy derived from Schrodinger's equation is a distinct functional of the electron density, was composed by Pierre Hohenberg and Hohenberg Kohn in the year 1964 and served as the theoretical foundation for the development of density functional theory.[17]

Ab initio methods, semi-empirical methods, the density-functional method, and the molecular mechanics method are the four basic methods for computing molecular properties. Semi-empirical molecular quantum-mechanical methods use parameters whose values are changed to fit experimental data or the outcomes of ab initio calculations, as well as a simpler Hamiltonian than the actual molecular Hamiltonian. DFT predicts a wide range of ground-state molecular characteristics, including hydrogen bonding, potential barriers and reaction pathways, vibrational frequencies, thermodynamic properties, and molecule structures and physicochemical characteristics [19]. It has been used in a variety of contexts, including the study of spin-polarized systems, multicomponent systems, free energy at finite temperatures, superconductors with electronic pairing mechanisms, relativistic electrons, time-dependent phenomena, excited states.

Density functional theory has three different ways to calculate as follows:

1. The Local Density Approximation (L.D.A.) method is the fastest, provides good band structures, and yields less precise geometry.
2. Gradient corrected functional have improved calculations of the total energies of atoms and molecules by
  - (i) Supplying more precise geometries and
  - (ii) Providing more accurate results.

3. Hybrid functional provide

(i) More precise geometries.

(ii) A D.F.T. approximation of the exchange-correlation energy functional.

### 3.3 Basis Set

A basis set is a mathematical representation of a molecule's chemical orbitals. Each electron can be thought of as being contained in a specific area of space by the basis set. Although there are several sorts of basis sets, the distinction between Slater-Type Basis Sets (STOs) and Gaussian-Type Basis Sets (GTOs) is not dependent on the three forms. Based on the mathematical formulas used to explain atomic orbitals, classification is made [19].

Functions that are theoretically defined by Slater orbitals are known as Slater-Type Basis Sets (STOs). These orbitals consider the nuclear charge and electron-electron repulsion since they are Schrödinger equation solutions for an atom that resembles hydrogen. STOs are less frequently utilized in quantum chemistry calculations than basis sets of the Gaussian type, although having some computing advantages being computationally costly [13].

Functions called Gaussian-Type Basis Sets (GTOs) use Gaussian functions to describe atomic orbitals. Gaussian functions can be more adaptable in describing various shapes and sizes of atomic orbitals and have appealing mathematical qualities that make them computationally efficient. Due to their precision and effectiveness, GTOs are frequently employed in quantum chemical calculations [20].

Some common classifications include:

*Minimal Basis Sets:* These are small basis sets that provide a simple and computationally efficient representation of atomic orbitals. They typically include a single Gaussian or Slater orbital for each atomic orbital. The "minimal" or "minimum" basis set is the smallest basis set used to model an atomic orbital. For each atomic orbital in the inner shell and valence shell of this basis set, one STO is employed. As an illustration, the 1s STO on each hydrogen atom and the 1s, 2s, 2px, 2py, and 2pz atomic orbitals on the carbon atom make up the minimal basic set for methane (CH<sub>4</sub>).

*Split-Valence Basis Sets:* Split-valence (SV) basis sets employ a combination of multiple Gaussian or Slater orbitals to describe each atomic orbital. They are designed to better represent the electronic structure of atoms and molecules, particularly the

electron correlation effects.[27] The valence atomic orbitals are divided into an inner compact orbital and an outer diffuse orbital to increase flexibility. A single example of a split-valence basis set is the double zeta (DZ) basis set, which is created by substituting two STOs for each STO in the minimal basis set, each of which has a different orbital exponent.

These basis sets, which are also known as Pople basis sets, allow for the size-adjustable determination of the number of GTOs to be used for the core and valence electrons individually. These are triple Zeta or double Zeta (two functions per AO). Following is the notation: K-LMG, where

- K = number of sp-type inner shell GTOs
- L = number of inner valence s- and p-type GTOs
- M = number of outer valence s- and p-type GTOs
- G = indicates that GTOs are used

POPLE basis sets are usually employed for organic molecules:

- 3-21G : 3 GTOs for inner shell, 2 GTOs for inner valence, 1 GTO for outer valence
- 6-31G
- 6-311G : 6 GTOs for core orbital, 3 GTOs for inner valence, 2 different GTOs for outer valence (triple zeta).

### **Polarized**

Pople basis sets can be modified to get an approximation that more accurately represents the system you're working with. This can be accomplished, for instance, by allowing the AOs to deviate from their initial form (becoming polarised as a result of their context). Polarisation may be expressed as a \* or (d) [29].

- (d) or \* type : f-type functions added to transition metals and d-type functions added to atoms other than hydrogens..
- (d,p) or \*\* type : Hydrogens have p-type functions, all other atoms are given d-type functions, and transition metals are given f-type values.

Ex: 6-31G(d) or 6-31G\*\*

### **Diffuse**

In order to create diffuse orbitals, one can also alter pople basis sets by allowing the electron to move far from the nucleus. When interacting with anions, excited states, and

molecules with lone pairs, this modification is useful. The G can have diffuse functions added such as + or ++[28].

- + : diffuse functions added on to atoms other than Hydrogens
- ++ : diffuse functions added on to all atoms

*Polarization Basis Sets:* After the DZ and SV basis sets, polarisation functions are the next step, including a polarisation function in a basis set of H, this effect is mitigated. Minimal basis sets generally produce imprecise, inadequate results. The minimal basis sets STO-2G, STO-3G, STO6G, and STO-3G\*(polarized) are frequently used. A Slater type orbital fitted with a linear combination of three Gaussian type orbitals is referred to as a STO-3G basis set.[11] Typical split-valence basis sets with or without polarisation and diffuse functions include, among others:

3-21G

3-21G\*- Polarisation function on heavy atoms,

3-21G\*\*- Functions of polarisation in heavy atoms and hydrogen.

3-21+G- Heavy atoms with diffuse functions

3-21++G- Diffuse functions on hydrogen and heavier atoms

3-21+G\*- On heavy atoms, diffuse and polarisation functions

3-21+G\*\*- Diffuse functions on heavy atoms as well as polarisation functions on hydrogens and heavy atoms.

### 3.4 Software Used

Gaussian16 provides a range of capabilities for modeling and simulating chemical systems, including molecular geometry optimization, vibrational frequency analysis, electronic structure calculations, reaction mechanisms, and more. It utilizes various theoretical methods, such as Hartree-Fock theory, density functional theory (DFT), and post-Hartree-Fock methods, to perform accurate calculations on molecular systems. GaussView is a graphical user interface (GUI) software for preparing, visualizing, and analyzing molecular structures and running electronic structure calculations using Gaussian or other computational chemistry programs. GaussView provides a user-friendly and intuitive interface that allows researchers to interact with molecular systems visually. It offers a range of features and tools to build, modify, and optimize molecular structures.

### 3.5 Theoretical Framework

The HOMO-LUMO energy gap is a crucial factor in determining a molecule's chemical and physical characteristics. The estimate HOMO-LUMO orbitals serve as electron donors and acceptors, respectively, in the same manner. The ionization potential and the magnitude of HOMO energy are both intimately correlated with the electron affinity[20]. The HOMO-LUMO energy gap and the molecule's chemical reactivity are related to one another. The energy gap, which measures electron conductivity and is primarily in charge of the chemical and spectroscopic properties of the molecules, is a crucial factor in defining the molecular electrical transport capabilities and chemical stability of the molecule. Less HOMO-LUMO gap means a molecule is more polarizable, which is typically indicative of low kinetic stability and high chemical reactivity.[22] The molecule's chemical stability and electrical transport characteristics are governed by the gap between the HOMO and LUMO.

According to Koopman's theorem, the ionization energy of a molecule is equal to the negative of the energy of removing an electron from the HOMO orbital. In other words, the ionization energy can be approximated as the negative of the energy difference between the ground state of the neutral molecule and the cationic state obtained by removing an electron from the HOMO [25]. Koopman's theorem states that the energies of frontier molecular orbitals  $\epsilon_{HOMO}$  and  $\epsilon_{LUMO}$  are used to calculate the various global reactivity descriptors, including electronegativity ( $\chi$ ), chemical potential ( $\mu$ ), global hardness ( $\eta$ ), global electrophilicity index ( $\omega$ ), and global softness ( $S$ ) [26].

Some of the commonly calculated global reactivity descriptors using Koopman's theorem are:

**Electronegativity ( $\chi$ ):** It represents the tendency of an atom or functional group to attract electrons towards itself. It can be approximated as the negative of the HOMO energy.

$$\text{Electronegativity } (\chi) = -\frac{1}{2}(\epsilon_{HOMO} + \epsilon_{LUMO})$$

**Chemical potential ( $\mu$ ):** It is related to the ionization potential and electron affinity and provides information about the availability of electrons in the system. It is given by the average of the HOMO and LUMO energies.

$$\text{Chemical Potential } (\mu) = -\chi = \frac{1}{2}(\epsilon_{HOMO} + \epsilon_{LUMO})$$

**Commented [H4]:** Define Koopman's theorem statement



**Global hardness ( $\eta$ ):** It quantifies the resistance of a molecule to electron transfer and is related to the energy difference between the HOMO and LUMO.

$$\text{Global Hardness } (\eta) = \frac{1}{2}(\epsilon_{HOMO} - \epsilon_{LUMO})$$

**Global electrophilicity index ( $\omega$ ):** It characterizes the nucleophilic or electrophilic behaviour of a molecule which is related to the chemical potential and global hardness.

$$\text{Electrophilicity } (\omega) = \frac{\mu^2}{2\eta}$$

$\omega$  is a global reactivity indicator similar to chemical potential and chemical hardness, according to Parr et al. It is a definite, positive quantity [27].

**Global softness ( $S$ ):** It represents the inverse of global hardness and indicates the ease of electron transfer.

$$\text{Softness } (S) = \frac{1}{2\eta}$$

These above mentioned formulae were used in our research work for the study of electro-optical properties.

### 3.6 Non Linear Optical Property in DFT

In order to study organic non-linear optical (NLO) materials, density functional theory has proven to be a successful approach. Recent research studies have demonstrated that organic non-linear optical materials exhibit higher optical non-linearity than inorganic materials [29]. The energy of a system in the presence of an applied electric field depends on the electric field. The reaction of a system to an applied electric field is defined by polarizabilities and hyperpolarizabilities [23]. They determine the cross sections of various scattering and collision processes, as well as the NLO properties of the system, in addition to the strength of molecular relations. Investigations were conducted on the present compound's electronic dipole moment, molecular polarizability, anisotropy of polarizability, and molecular first hyperpolarizability. The total static dipole moment ( $\mu$ ), mean dipole polarizability ( $\alpha$ ), polarizability ( $\Delta\alpha$ ) anisotropy, and total first order hyperpolarizability are all defined by using the x, y, and z components, respectively [29].

In the investigation of the optoelectronic properties of molecular materials, the dipole moment, electrical polarizability, and hyperpolarizability are important parameters (Veved et al. 2019). The dipole moment is a measure of the separation of positive and

negative charges within a molecule and is an important parameter in understanding molecular interactions and polarization [26]. It is common to analyze these parameters to understand and predict the behaviour of molecules under different external electric field conditions. The dipole moment is determined by the relation in the nonlinear domain:

$$\mu = \alpha E + \beta E^2 + \gamma E^3$$

Where the first and second hyperpolarizability are, respectively,  $\alpha$  and  $\beta$ . Data from the Gaussian output file were used to determine the first order hyperpolarizability using the formula:

$$\beta = [(\beta_{XXX} + \beta_{XYX} + \beta_{XZZ})^2 + (\beta_{YYX} + \beta_{YXX} + \beta_{YZZ})^2 + (\beta_{ZZX} + \beta_{ZXX} + \beta_{ZYY})^2]^{\frac{1}{2}}$$

Additionally, the following equation defines the mean polarizability:

$$\langle \alpha \rangle = \frac{1}{3} (\langle \alpha_{XX} \rangle + \langle \alpha_{YY} \rangle + \langle \alpha_{ZZ} \rangle)$$

The anisotropy ( $\Delta\alpha$ ) provides information about the degree of polarization anisotropy or the difference in polarizability along different directions. A higher value of  $\Delta\alpha$  indicates a greater difference in polarizability along different axes, indicating higher anisotropy in the molecule's response to external electric fields [30]. The following relation can be used to determine the anisotropy from the polarizability matrix:

$$\Delta\alpha = \frac{1}{2} [(\alpha_{XX} - \alpha_{YY})^2 + (\alpha_{YY} - \alpha_{ZZ})^2 + (\alpha_{ZZ} - \alpha_{XX})^2 + 6(\alpha_{XY}^2 + \alpha_{YZ}^2 + \alpha_{ZX}^2)]^{\frac{1}{2}}$$

In DFT, the energy gap (Eg) can be calculated as the energy difference between the LUMO and HUMO levels:

$$\text{Energy Gap } (E_g) = E_{LUMO} - E_{HUMO}$$

## 4. RESULTS AND DISCUSSION

### 4.1 Geometrical Optimization

Geometrical optimization is a very important step of almost all the quantum calculations that are related to the structure of the molecules[24]. The geometrical optimization has been done by energy minimization of monomeric and dimeric of different DLCs by using DFT/B3LYP/6-311++G (d,p) method. The geometry for the

different DLCs such as (i) Monomer of A8, B8 and C8 (ii) Dimer of A8,B8 and C8 was constructed based on the molecular structure. After optimization of all above mentioned structures there is a change in bond lengths.

Here discotic liquid crystal 4-(3-(heptyloxy)-2,4-bis(octyloxy)phenyl)diazenyl)benzoic acid is referred as Monomer A8. Dimer A8 is referred as 4-(2,3,4-tris(octyloxy)phenyl)diazenyl)benzoic acid.

Dimer B8 is 4-(3,4-bis(octyloxy)phenyl)diazenyl) benzoic acid. Monomer B8 is 4-(3-(4-(3-(heptyloxy)-2,4-bis(octyloxy)phenyl)diazenyl)benzoic acid). Here discotic liquid crystal 4-(3-(heptyloxy)-2,4-bis(octyloxy)phenyl)diazenyl)benzoic acid is referred as Monomer C8. Dimer C8 is referred as 4-(4-(octyloxy)phenyl)diazenyl) benzoic acid.

The ground state energy of the A8, B8, and C8 monomers and dimers.

(i) Monomers:

Monomer of A8 = -1931.022825 Hartree

Monomer of B8 = -1541.199828 Hartree

Monomer of C8 = -1151.379103 Hartree

(ii) Dimers:

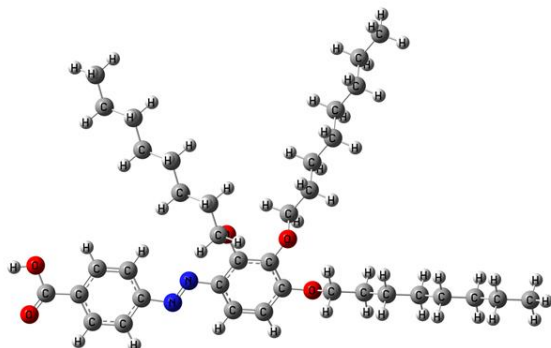
Dimer of A8 = -3862.072 Hartree

Dimer of B8 = -3082.425637 Hartree

Dimer of C8 = -2302.784199 Hartree

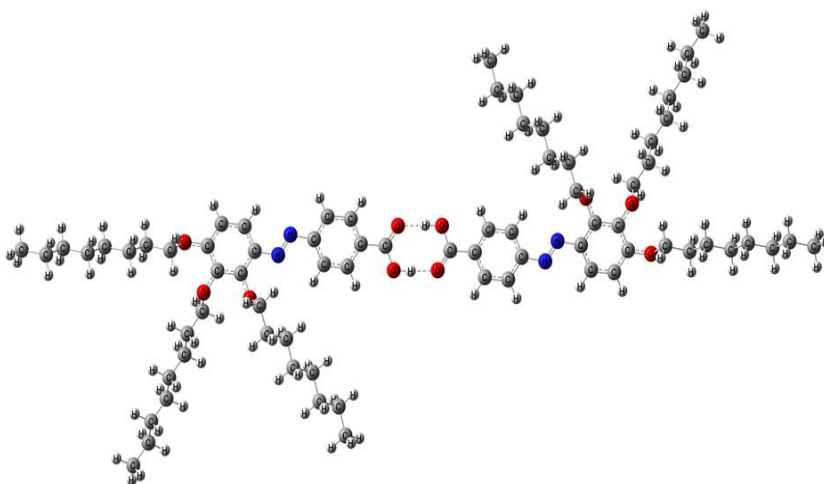
From the given information, we can observe that the energy of the monomers and dimers is provided in Hartree units. The energy values indicate the stability of each structure, with lower values indicating a more stable configuration.

Based on the energy values, it can be inferred that the optimized structures have lower energies compared to the initial structures. This suggests that the geometrical optimization has resulted in more stable configurations for both the monomers and dimers.

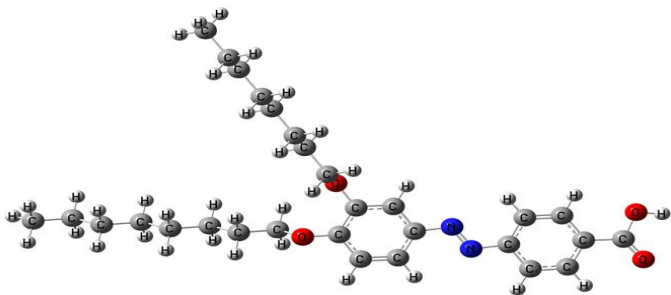


*Fig. 7: Optimized structure of monomer of A8 having two benzene ring connected with N=N group and three flexible side chain of  $-OC_8H_{17}$ . Ground state energy is -1931.022825 Hartree*

**Commented [H5]:** Write about the ground state energy of monomer and dimer of A8.

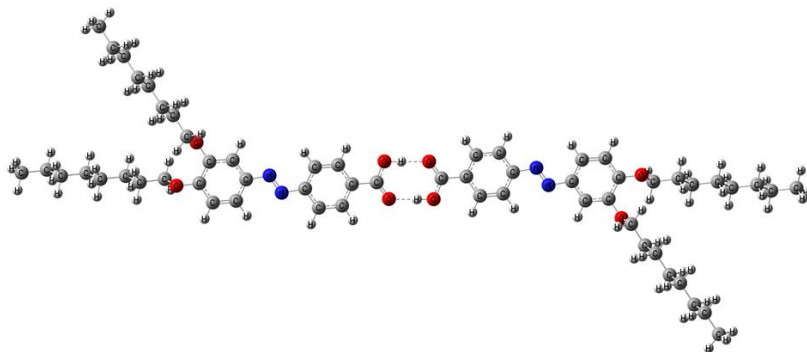


*Fig. 8: Optimized structure of dimer of A8 exhibiting two intermolecular hydrogen bonding which provides discotic shape to this LC. Ground state energy is -3862.072 Hartree.*

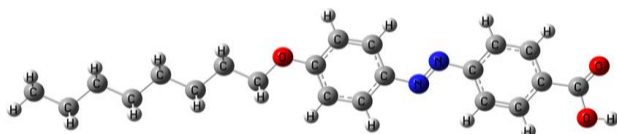


**Fig. 9:** Optimized structure of monomer of B8 having two benzene ring connected with N=N group and two flexible side chain of  $-OC_8H_{17}$ . Ground state energy is -1541.199828 Hartree

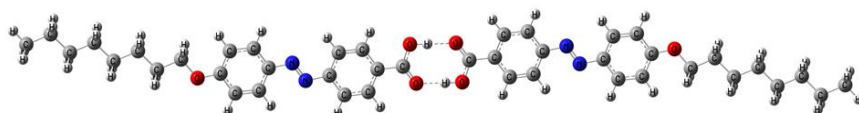
**Commented [H6]:** Write about the ground state energy of monomer and dimer of B8.



**Fig. 10:** Optimized structure of dimer of B8 exhibiting two intermolecular hydrogen bonding which provides discotic shape to this LC. Ground state energy is -3082.425637 Hartree



**Fig. 11:** Optimized structure of monomer of C8 having two benzene ring connected with N=N group and one flexible side chain of  $-OC_8H_{17}$ . Ground state energy is -1151.379103 Hartree.



**Fig. 12:** Optimized structure of dimer of C8 exhibiting two intermolecular hydrogen bonding between COOH groups attached with benzene ring. Ground state energy is -2302.784199 Hartree.

## 4.2 Frontier Molecular Orbital Analysis

Frontier Molecular Orbitals (FMO) analysis involves examining the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of DLCs. These orbitals represent the outermost electrons involved in chemical reactions and electronic transitions [32]. There are number of ways to calculate the excitation of energies. The HOMO is the simplest one. It involves the difference between the HOMO and the LUMO of a neutral system. As they lie at the outermost boundaries of the electrons of the molecules they are also called Frontier Orbitals [35].

The energy gap between the HOMO and LUMO is referred to as the HOMO-LUMO gap or the energy gap (Eg). The HOMO-LUMO gap is an important parameter that determines the electronic transitions and reactivity of the molecule [36]. A smaller energy gap indicates a higher likelihood of electronic transitions and higher reactivity.

**Table 1.** Comparison of HOMO-LUMO energies of monomer and dimer of DLC A8, B8 and C8.

Global parameters	Monomer			Dimer		
	A8	B8	C8	A8	B8	C8
HOMO	-6.35254	-6.45323	-6.24859	-6.31907	-6.41785	-6.20097
LUMO	-2.84742	-2.87844	-2.75735	-2.84143	-2.87109	-2.73585
ENERGY GAP (eV)	3.50512	3.574	3.491	3.47764	3.546	3.456

### Highest Occupied Molecular Orbital (HOMO)

The provided data includes the Highest Occupied Molecular Orbital (HOMO) energy levels for different molecules and their dimers. The HOMO energy level is an

important parameter in understanding the electronic structure and reactivity of molecules. From the data, it can be observed that dimerization has a minor influence on the HOMO energy of the studied molecules [37]. The dimers of A8, B8, and C8 exhibit slightly higher or lower HOMO energy levels compared to their respective monomers. Among the studied molecules, the monomer of C8 has the highest HOMO energy level at -6.24859 eV. A higher HOMO energy level indicates greater stability of the molecule and resistance to oxidation. This makes it more suitable for electron-donating applications.[26] One useful application of molecules with high HOMO energy levels is in organic photovoltaic devices, where they can serve as efficient electron donors. Additionally, these molecules can be utilized as hole transport materials in organic electronic devices, thanks to their ability to readily donate electrons. In summary, the dimerization of A8, B8, and C8 has a minor impact on their HOMO energy levels. The monomer of C8 exhibits the highest HOMO energy level among the studied molecules, making it valuable for electron-donating applications in organic photovoltaic and electronic devices [38].

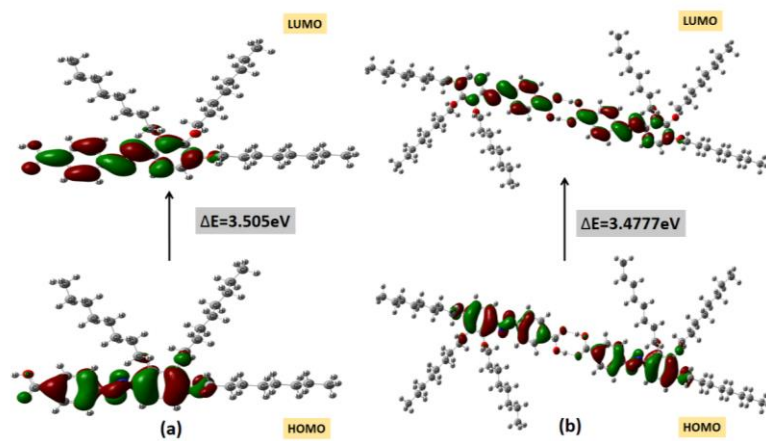
#### **Lowest Unoccupied Molecular Orbital (LUMO)**

Table 1, shows the LUMO energy levels of various monomers and dimers, specifically A8, B8, and C8. The dimerization of these molecules has a minor influence on the LUMO energy, with slight variations observed. The highest LUMO energy level is -2.73585 eV for the dimer of C8. A higher LUMO energy level indicates a lower electron affinity and a greater ability to accept electrons. Molecules with high LUMO energy levels are valuable in applications such as organic photovoltaic devices and organic electronic devices, where they can serve as electron acceptors or electron transport materials [39].

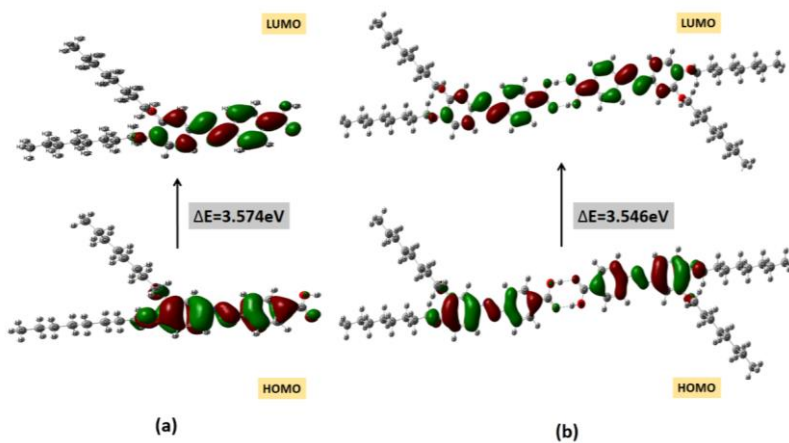
#### **4.2.1 Energy Gap (E<sub>g</sub>)**

The energy gaps of the monomer of A8 and the dimer of A8 from fig.13, were determined to be 3.50512 eV and 3.47764 eV, respectively. These energy gap values provide insights into the polarizability of the molecules and the benefits associated with the energy gap in these discotic liquid crystals. In this study, the dimer of A8 exhibited a slightly smaller energy gap (3.47764 eV) compared to the monomer (3.50512 eV) and it is obvious. This suggests that the dimer possesses a slightly higher polarizability than the monomer. In HOMO-LUMO diagram, the green colour shows positive charge

while red colour represents negative charge accumulation over the discussed molecule. The energy gap represents chemical stability of the molecule.



*Fig. 13: Representation of HOMO-LUMO energy diagram of (a) monomer A8, and (b) dimer of A8.*

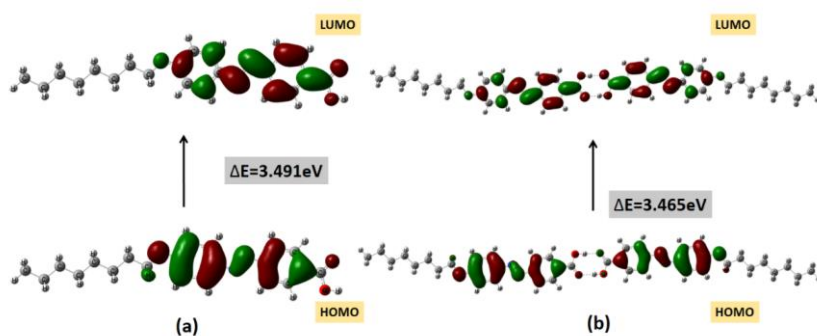


*Fig. 14: Representation of HOMO-LUMO energy diagram of (a) monomer B8, and (b) dimer of B8.*



In this study, the energy gaps of the monomer of B8 and the dimer of B8 from fig.14, were determined to be 3.491 eV and 3.456 eV, respectively. These energy gap values provide insights into the polarizability of the molecules and the benefits associated with the energy gap in these discotic liquid crystals. Polarizability is a measure of a molecule's ability to undergo deformation in response to an external electric field. A smaller energy gap indicates a higher polarizability, meaning that the molecule can more easily deform its electron cloud when subjected to an applied electric field [40].

The smaller energy gap observed in the dimer of B8 (3.456 eV) compared to the monomer (3.491 eV) suggests that the dimer exhibits slightly higher polarizability. This implies that the dimer can more readily respond to external electric fields and undergo deformation compared to the monomer. The benefits of a smaller energy gap (higher polarizability) in these discotic liquid crystals can be associated with several factors of enhanced optical properties and improved charges transport etc [40].



*Fig. 15: Representation of HOMO-LUMO energy diagram of (a) monomer C8, and (b) dimer of C8.*

The energy gaps of the monomer of C8 and the dimer of C8 were determined to be 3.491 eV and 3.456 eV, respectively. These energy gap values provide insights into the polarizability of the molecules and the benefits associated with the energy gap in these discotic liquid crystals. Polarizability refers to a molecule's ability to deform its electron cloud in response to an external electric field. A smaller energy gap indicates a higher polarizability, suggesting that the molecule can more easily undergo deformation when subjected to an applied electric field.

In this study, the dimer of C8 exhibited a slightly smaller energy gap (3.456 eV) compared to the monomer (3.491 eV). This suggests that the dimer possesses a slightly higher polarizability than the monomer as shown in fig.14.

On comparing the energy gaps of the above mentioned monomers and dimers, it can be concluded that the dimers generally exhibit slightly smaller energy gaps, suggesting higher polarizability compared to the corresponding monomers. The benefits of a smaller energy gap (higher polarizability) in these discotic liquid crystals can be summarized as follows:

**Enhanced Optical Properties:** Higher polarizability allows for improved absorption and emission of light, making these materials suitable for optoelectronic applications.

**Improved Charge Transport:** Higher polarizability enhances the charge transport properties within the discotic liquid crystals, enabling efficient charge mobility in organic semiconductors and field-effect transistors.

**Increased responsiveness to External Fields:** Higher polarizability enables discotic liquid crystals to more readily respond to external electric fields, making them suitable for sensors, actuators, and other responsive applications [28].

**Table 2.** Comparison of Global parameters of monomer and dimer of DLC A8, B8 and C8.

Global parameters	Monomer			Dimer		
	A8	B8	C8	A8	B8	C8
<b>Ionization Potential(eV)</b>	6.35254	6.45323	6.24859	6.31907	6.41785	6.20097
<b>Electron Affinity (eV)</b>	2.84742	2.87844	2.75735	2.84143	2.87109	2.73585
<b>Electronegativity <math>\chi</math> (eV)</b>	4.59998	4.665835	4.50297	4.58025	4.64447	4.46841
<b>Electronic Chemical Potential <math>\mu</math> (eV)</b>	-4.59998	-4.66584	-4.50297	-4.58025	-4.64447	-4.46841
<b>Global Hardness <math>\eta</math>(eV)</b>	1.75256	1.787395	1.74562	1.73882	1.77338	1.73256
<b>Softness(S)</b>	0.285297	0.279737	0.286431	0.287551	0.281947	0.28859
<b>Energy Gap(Eg)</b>	3.50512	3.57479	3.49124	3.47764	3.54676	3.46512
<b>Electrophilicity Index(<math>\omega</math>)</b>	6.036831	6.089873	5.80789	6.03245	6.081917	5.762192

#### 4.2.2. Ionisation Potential

The provided data includes the ionization potential (IP) values for different molecules and their dimers. The ionization potential represents the minimum energy required to remove an electron from a neutral molecule, indicating the ease of electron removal and the stability of the resulting cation. From the data, it can be observed that dimerization has a minor impact on the Ionization Potential of the studied molecules [23]. The dimers of A8, B8, and C8 exhibit slightly lower ionization potential values compared to their respective monomers. Among the studied molecules, the monomer of B8 has the highest ionization potential value at 6.45323 eV. This indicates that the monomer of B8 requires the highest energy to remove an electron and form a positive ion among the studied molecules. In summary, the dimerization of A8, B8, and C8 has a minor influence on their ionization potential values, and the monomer of B8 exhibits the highest ionization potential among the studied molecules.

#### 4.2.3 Electron Affinity

The monomers of A8, B8, and C8 exhibit higher electron affinity values compared to their respective dimers. Furthermore, among the studied molecules, the monomer of B8 has the highest Electron Affinity at 2.87844 eV, indicating its strongest tendency to accept an electron. In summary, the monomers of A8, B8, and C8 have higher electron affinity values compared to their dimers, and the monomer of B8 exhibits the highest electron affinity among the studied molecules. The high electron affinity of molecules is advantageous in electron acceptor applications, catalysis, and electron transport, enabling improved energy conversion, enhanced chemical reactions, and efficient electronic device performance. The high electron affinity of molecules is advantageous in electron acceptor applications, catalysis, and electron transport, enabling improved energy conversion, enhanced chemical reactions, and efficient electronic device performance. The low electron affinity of molecules is advantageous in electron donor applications, as reducing agents, and in providing stability against oxidation, ensuring efficient charge transfer, facilitating desired chemical reactions, and maintaining material integrity.

#### 4.2.4 Electronegativity ( $\chi$ )

From table 2, it can be observed that the monomers of A8, B8, and C8 have higher electronegativity values compared to their respective dimers. This suggests that

dimerization has a minor impact on the electronegativity of these molecules. Among the studied molecules, the monomer of B8 has the highest electronegativity value at 4.665835 eV. This indicates that the monomer of B8 has the strongest tendency to attract electrons towards itself in a chemical bond.

In summary, the electronegativity values provide insights into the relative electron-attracting capabilities of the molecules and their dimers. These values are important in understanding and predicting chemical bonding behaviours and reactivity.

#### **4.2.5 Electronic Chemical Potential ( $\mu$ )**

The electronic chemical potential is a measure of the average energy required to add or remove an electron from a molecule. It indicates the stability and reactivity of the molecule with respect to electron transfer processes. In this case, the data shows that the monomer of B8 (-4.66584 eV) has the lowest electronic chemical potential, indicating that it has a higher electron-accepting ability compared to the other molecules. On the other hand, the monomer of C8 (-4.50297 eV) has the highest electronic chemical potential, suggesting that it has a relatively higher electron-donating ability. In Table 2, the values of the electronic chemical potential ( $\mu$ ) for different molecules: monomer of A8, dimer of A8, monomer of B8, dimer of B8, monomer of C8, and dimer of C8.

The electronic chemical potential is a useful parameter in understanding the electronic structure and behaviour of molecules. It can provide insights into their reactivity, charge transfer processes, and electronic interactions with other molecules or materials

#### **4.2.6 Global Hardness (H)**

The given data represents the values of the global hardness ( $\eta$ ) for different molecules: monomer of A8, dimer of A8, monomer of B8, dimer of B8, monomer of C8, and dimer of C8. The global hardness is a measure of the resistance of a molecule to electron flow or polarization. It is calculated as half the difference between the ionization potential and the electron affinity of a molecule. In this case, the data shows that the monomer of B8 ( $\eta = 1.787395$  eV) has the highest global hardness, indicating that it has a relatively higher resistance to electron flow or polarization. On the other hand, the monomer of C8 ( $\eta = 1.73256$  eV) has the lowest global hardness, suggesting that it is more prone to electron flow or polarization.

The global hardness is a useful parameter in understanding the reactivity and stability of molecules. It provides insights into their ability to donate or accept electrons and

their response to external perturbations. Higher hardness values indicate greater stability and resistance to electron transfer, while lower hardness values suggest higher reactivity and susceptibility to electron transfer [42].

#### **4.2.7 Softness (S)**

The Softness (S) is a measure of the ease with which a molecule can be polarized or undergo electron transfer. It is the reciprocal of the global hardness ( $\eta$ ). In this case, from table 2, the data shows that the monomer of B8 ( $S = 0.279737$ ) has the lowest softness, indicating that it is less prone to polarization or electron transfer. On the other hand, the monomer of A8 ( $S = 0.285297$ ) has the highest softness, suggesting that it is more easily polarizable or capable of electron transfer. The softness parameter is useful in characterizing the reactivity and stability of molecules. A lower softness value indicates higher stability and resistance to polarization or electron transfer, while a higher softness value suggests higher reactivity and susceptibility to polarization or electron transfer.

The softness parameter is particularly relevant in the field of computational chemistry and chemical reactivity studies. It helps in predicting and understanding the response of molecules to external perturbations and their behaviour in chemical reactions [44]. Softness also plays a role in the design of materials with desired electronic properties, as it influences their ability to undergo charge transfer processes.

#### **4.2.8 Electrophilicity Index ( $\omega$ )**

In this case, the data shows from the table 2, that the monomer of B8 ( $\omega = 6.089873$ ) has the highest electrophilicity index, indicating its high tendency to act as an electrophile and accept electrons during chemical reactions. On the other hand, the dimer of C8 ( $\omega = 5.762192$ ) has the lowest electrophilicity index, suggesting it has a relatively lower reactivity as an electrophile.

### **4.3 Non-Linear Optical Properties**

#### **4.3.1 Dipole Moment ( $\mu$ )**

From table 3, we observe that A8 and B8 (both monomers) have relatively high dipole moments of 4.3104 Debye and 4.5288 Debye, respectively. This suggests that these molecules possess a significant charge separation and polarity. On the other hand, the dimer of A8 and the dimer of C8 exhibit lower dipole moments of 2.4457 Debye and

2.8453 Debye, respectively. The dimer of B8 shows an even lower dipole moment of 0.1377 Debye.

These variations in dipole moments indicate differences in the molecular structure and charge distribution among the molecules and their dimers. Additionally, dipole moments are relevant in applications such as solvent properties, chemical reactivity, and the design of materials with specific polar characteristics.

### **4.3.2 Mean Polarizability ( $\langle\alpha\rangle$ )**

From Table 3, we observe that the mean polarizability values can be both positive and negative. A positive value indicates that the electron cloud is easily deformable, while a negative value suggests resistance to deformation.

In this case, A8 (monomer) has a positive mean polarizability value of 279.853, indicating its susceptibility to deformation. However, the dimer of A8 has a negative mean polarizability value of -503.4663, indicating its resistance to deformation.

Similarly, B8 (monomer) has a positive mean polarizability value of 221.9344, while its dimer has a higher positive value of 374.5393, suggesting an increased ease of deformation upon dimerization.

C8 (monomer) has a relatively lower positive mean polarizability value of 159.5369, and its dimer shows a slightly higher positive value of 261.4030.

These values provide insights into the molecular polarizability and their response to external electric fields. The magnitude and sign of the mean polarizability can be important in various applications, such as understanding the optical properties, design of materials for electro-optical devices, and studying intermolecular interactions

### **4.3.3 Anisotropy in Polarizability ( $\Delta\alpha$ )**

From the Table 3, we observe that the anisotropy in polarizability values can vary for different molecules and their dimers.

For A8, both the monomer and dimer show positive values, with the dimer having a higher value than the monomer. This indicates that the electron distribution in the dimer is more anisotropic, suggesting a greater difference in polarizability along different directions compared to the monomer. Similarly, B8 and its dimer also exhibit positive values for anisotropy in polarizability, with the dimer again showing a higher value.

This suggests a higher degree of anisotropy in the dimer as compared to the monomer C8 and its dimer have relatively lower positive values for anisotropy in polarizability, indicating a lower degree of anisotropy in these molecules. The values of anisotropy in polarizability provide insights into the molecular symmetry and how the electron distribution is influenced by external electric fields. Understanding the anisotropy in polarizability is important in various applications, including the design of optoelectronic materials, understanding light-matter interactions, and studying the behaviour of molecules in electric fields.

#### 4.3.4 Hyperpolarizability ( $\beta$ )

For A8, the dimer has a higher hyperpolarizability value compared to the monomer, indicating that the dimer exhibits stronger nonlinear optical responses. Similarly, the dimer of B8 also has a higher hyperpolarizability value than the monomer, suggesting enhanced nonlinear optical properties in the dimer form.

In the case of C8, the dimer shows a significantly higher hyperpolarizability value compared to the monomer, indicating a substantial increase in the molecule's nonlinear optical response when it forms a dimer.

The values of hyperpolarizability provide insights into the nonlinear optical behaviour of molecules and their potential applications in various areas such as nonlinear optics, optical data storage, and optoelectronic devices. Molecules with high hyperpolarizability values are desirable for their ability to efficiently convert and manipulate light, making them valuable in fields related to nonlinear optics and photonics. Hence, electro-optical properties provide insights into the structural, electronic, and optical characteristics of the molecules and their dimers.

**Table 3.** Comparison of Electro optical properties of in investigated molecules.

#### Electro-Optical Properties

<i>Properties</i>	<i>Monomer</i>			<i>Dimer</i>		
	A8	B8	C8	A8	B8	C8
<b>Dipole Moment(<math>\mu</math>) (Debye)</b>	4.3104	4.5288	4.4696	2.4457	0.1377	2.8453
<b>Mean Polarizability (<math>\alpha</math>)</b>	279.853	221.9344	159.5369	503.4663	374.5393	261.4030
<b>Anisotropy in Polarizability (<math>\Delta\alpha</math>)</b>	41.5385	39.1666	27.6964	81.1119	104.957	117.6153
<b>Hyperpolarizability (<math>\beta</math>)</b>	229.3993	103.9506	113.3866	302.8689	310.837	589.1176

## 5. CONCLUSION

On conclusion, the provided data on various global parameters, including electronic, electro-optical, and optical properties, provides insights into the molecular characteristics and behaviour of different monomers and dimers. Comparing the values, we observe that the dimers generally exhibit slight variations in their properties compared to their respective monomers. The differences indicate the influence of dimerization on the electronic structure, stability, and optical properties of the molecules.

Specifically, the dipole moment, mean polarizability, and hyperpolarizability values show notable changes upon dimerization, indicating enhanced polarity and optical response. These properties make the dimers suitable for applications in fields such as nonlinear optics, photonics, and material science, where materials with strong dipole moments and high optical response are desirable.

Additionally, the data on HOMO, LUMO, ionization potential, electron affinity, electronegativity, and other electronic parameters provide insights into the stability, reactivity, and electron interaction of the molecules. However, no clear trends or significant differences can be observed in these parameters between the monomers and dimers.

Overall, the data highlights the impact of dimer formation on the electro-optical and electronic properties of the molecules. This knowledge is valuable for understanding the behaviour of molecules in various applications, including materials design, organic electronics, and computational chemistry, where the control and prediction of molecular properties are crucial for developing advanced materials and technologies.



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