Electro-optical properties of Liquid Crystal molecules by Quantum Mechanical methods

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Submitted for the Award of the Degree
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Submitted By
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Enrollment No. 058/14

Under the supervision of
Prof. Devesh Kumar

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2021

Dedicated

To

My Loving Parents

DECLARATION

I declare that the thesis entitled "**Electro-optical properties of Liquid Crystal molecules by Quantum Mechanical methods**" has been prepared by me under the supervision of **Prof. Devesh Kumar,** Department of Applied Physics, School for Physical Sciences, Babasaheb Bhimrao Ambedkar University, Lucknow. No part of this thesis has formed the basis for the award of any degree, diploma or fellowship previously. Further, I declare that the material embodied in the present work is based on original research work and the indebtedness to others has been duly acknowledged at relevant places. This is also declared that the thesis is essentially free from all kinds of plagiarism.

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This is to certify that the thesis titled "**Electro-optical properties of Liquid Crystal molecules by Quantum Mechanical methods**" submitted by **Ms. Shivani Chaudhary** is an original research work and has not been previously submitted in part or full for the award of any other degree or diploma to this or any other university. The thesis submitted to Babasaheb Bhimrao Ambedkar University, Lucknow satisfies all the requirements as stipulated in the *Doctor of Philosophy (Ph.D.) regulations- 1999 as amended in ~~2008/2010~~/2013* and it is fit for submission and evaluation for the award of the degree of Doctor of Philosophy of the University.

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ABSTRACT

The liquid crystal compounds are selected for the display technology following their optical properties. The liquid crystal molecule has a large optical anisotropy that is required in display technology; also it has a small cell thickness and small switching time. The orientation of the liquid crystal molecules can be changed by applying the external electric field. The external field affects the liquid crystal by changing the order of the molecule. The polarization of the molecule is going through the process of permanent dipole moments of the molecules and the molecular polarizability. At optical frequencies, there is no contribution to the polarization from the permanent dipole moments. Then the polarization is due to the dipole moment induced by the local field (E). The local field consists of the fields due to the dipole moments of the other molecules as well as the applied field. Electric fields have very strong effects on the rod shape of liquid crystal molecules. When the liquid crystal molecules are put into an electric field, then one end of a molecule has positive charge while the other end becomes negatively charged and forms an electric dipole. As a result, the director of the liquid crystal molecules will be reoriented along the direction of the applied external electric field. Therefore, the electric field is the most commonly used method to drive the liquid crystal molecule devices. Utilizing this characteristic of the liquid crystal, efforts have been made to combine liquid crystals to develop electronically controlled transmission and absorption of the molecular structures concerning their applications on switches.

PREFACE

The electro-optical properties of liquid crystal molecules are calculated by imposing an electric field to the molecules. Due to the anisotropic nature, liquid crystals are used in many display device applications. The present work reported about electro-optical properties of liquid crystals which are calculated by using computational methods.

Chapter 1

Chapter 1 gives a brief introduction and history of the liquid crystal molecules. Liquid crystal molecules are categorized into different types depending upon their orientation and positional order. The chapter includes different types and their phases due to which properties of the liquid crystal molecules are explained. Liquid crystals exhibit many properties in the physical, optical, electrical, mechanical field, etc., based on the molecular arrangement, orientational order, etc. The physical properties of the material involve dielectric anisotropy, optical anisotropy (birefringence), order parameter, refractive index, etc. This chapter also includes a brief introduction to the effect of electric fields on liquid crystal molecules. Various electro-optical applications by using liquid crystal molecules have also been introduced in the chapter.

Chapter 2

In chapter 2, the computational methodology has been revealed. It deals with the different computational Quantum mechanical methods such as ab initio method, Hartree-Fock method, Density functional theory method with some mathematical formulation. The chapter also includes the introduction of the basis set and its various types which depend on their molecular orbital. Liquid crystal molecules are designed

and optimized by Gaussian 09 software. The computational methodology and some derived mathematical formulae of the proposed work also have been discussed in the chapter.

Chapter 3

Chapter 3 introduces the odd-even effect of the APAPA liquid crystal molecule under the influence of an electric field in the THz frequency region. The molecular geometries of the APAPA liquid crystal series have been designed and optimized using Gaussian 09 software with density functional theory (DFT) method. After the simulation of the homologous series, the electric field is applied to the molecular series, after which the molecular polarizability is calculated along the molecular axis (x-axis) and perpendicular to the axis (y-axis). By evaluating the values of molecular polarizabilities, we have calculated the refractive index, order parameter, birefringence, and magic angle according to the equations given in the chapter.

Chapter 4

In chapter 4, the electro-optical properties of the 10CB liquid crystal molecule are studied under the influence of an electric field in the THz frequency region. The 10CB liquid crystal molecule has been designed and optimized using Gaussian 09 software with the DFT method using preferred basis sets. After the simulation, an electric field is applied to the liquid crystal molecule. The chapter includes the derived mathematical formulae of the different electro-optical parameters. From the chapter, it has been discovered that the 10CB liquid crystal compound exhibits the negative order parameter with the high electric field, according to which the compound has been used in ultrafast electro-optic applications.

Chapter 5

Chapter 5 gives the comparative DFT study of the different conformation of the 5CB and 6CB liquid crystal dimers. By using the NWChem software package, all the geometries of 5CB and 6CB liquid crystal molecules have been optimized using the density functional theory method with a proposed basis set. In this chapter, 360 conformations are generated out of which 4 conformations of 5CB and 6CB dimers of minimum energies are taken. All monomers of liquid crystals arbitrarily interact with each other and perform minimum energy calculations and generate the 5CB, 6CB, and 5CB-6CB liquid crystal dimers. The present chapter gives the enhancement or decrement in the thermochemistry, interaction energy, polarizability, and dipole moment, etc. depending on the functioning conformations.

Chapter 6

Chapter 6 gives the brief conclusion and future prospects of the thesis using preferred work. By introducing the external electric field to the liquid crystal molecules, different electro-optical properties were investigated. Birefringence plays an important role in optical display device applications. The electro-optical application by using various liquid crystal molecules with the help of computational methodology is discussed in the chapter.

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LIST OF ABBREVIATIONS AND SYMBOLS

ϕ	Azimuthal angle
n	Director
SmA	Smectic A liquid crystal
SmB	Smectic B liquid crystal
SmC	Smectic C liquid crystal
SmF	Smectic F liquid crystal
SmA*	Smectic A* liquid crystal
SmC*	Smectic C* liquid crystal
P	Pitch
λ	Wavelength of light
n	Refractive index
BP	Blue phase
n_e	Extraordinary refractive index
n_o	Ordinary ray refractive index
ε	Dielectric permittivity
$\varepsilon_{\parallel}$	Parallel component of Dielectric permittivity
$\varepsilon_{\perp}$	Perpendicular component of Dielectric permittivity
k_1, k_2, k_3	Elastic constants
η_1, η_2, η_3	Viscosity constants
Θ	Director Angle
LCD	Liquid crystal display
CRT	Cathode ray tube
LED	Light emitting diode
LC	Liquid crystal
DFT	Density functional theory
HF	Hartree-Fock
ρ	electron density
STO	Slater-type atomic orbitals

LCAO	Linear combination of atomic-orbital self-consistent field
α	Molecular Polarizabilities
α_e	Extraordinary molecular Polarizability
α_o	Ordinary molecular Polarizability
μ	Dipole moment
β	First-order hyperpolarizability
APAPA	Anisylidene Para Amino Phenyl Acetate
CB	Cyano Biphenyl
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Occupied Molecular Orbital

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Chapter-1

Introduction

Chapter 1

Introduction

1.1 Introduction of Liquid Crystal

In the physical world, substances include three phases; solid, liquid, and gas. Commonly, there exist some types of organic molecules which are not changing their phase from solid to liquid or liquid to solid, but the transition involves additional states [1-3]. Physical, mechanical and symmetry characteristics of such phases are the intermediary phase among crystalline solid together with isotropic liquid. The given phase is named as *"liquid crystal"*, also the more proper name is *mesogens*, and such phase is known as the *mesomorphic phase* [3-5]. Liquid crystals are known to be wonderful substances and the characteristics of liquid crystals lie between conventional liquid and solid crystals. The building block of matter is dependent on the intermolecular forces, due to which the molecules in solids exhibit positional, followed by orientational order which means that molecules within solids are forced to point only in specific position relatively [6-11]. Molecules in the liquid phase are closely packed together and lack order with respect to their position and orientation i.e. the direction of molecules point in a particular fashion and their position is random. The center of gravity in the liquid is not ordered as shown in Figure 1.1. Thus these two

states of matter differ most obviously. Liquid crystals lie in an intermediary state in which the molecules have a tendency to flow like a liquid but the crystals possess some physical characteristics where these molecules show orientational order [12-16]. The direction of preferred orientation during a liquid crystal is named as the *director*. As the molecules do not possess any positional order they are in constant motion and they spend more time pointing along with the director than in any other direction [17-20].

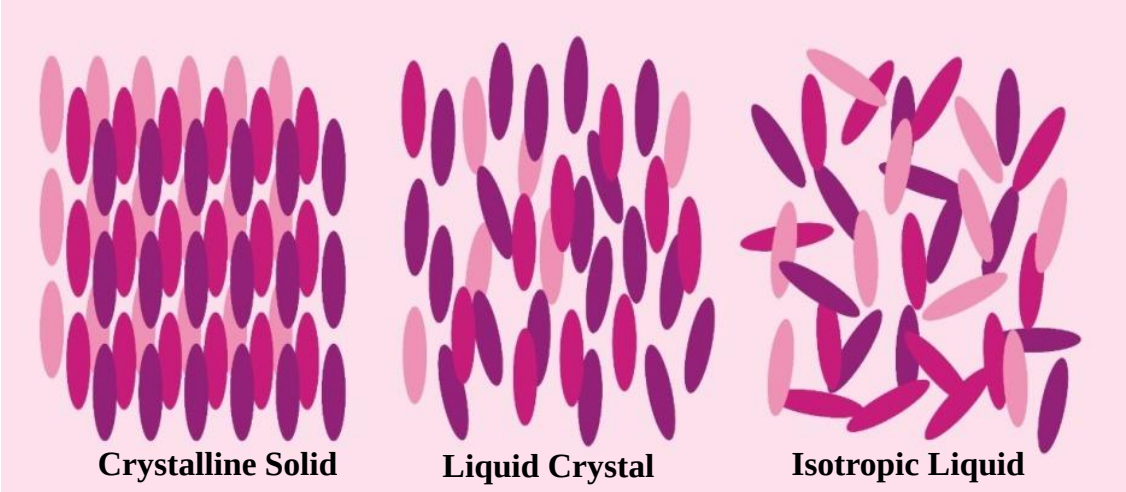


Figure 1.1 Arrangements of LC molecules.

In this way, LC's are the substance that are described to be "ordered liquids by their orientation" whereas "disordered crystals by their position" and are held together with the characteristics of crystalline solids as well as isotropic liquids [21-23].

1.2 History of Liquid Crystal

Austrian scientist F. Reinitzer [24-25], studied two substances extract that comes from carrot, hydrocarotin of light-colored, and carotin of dark-red color. From the other previous articles, it was known to him that the properties of hydrocarotin are identical to the properties of cholesterol due to it's composition and chemical properties. According to Reinitzer, hydrocarotin is a compound of cholesterol derivatives [26]. By

determining their melting temperature, Reinitzer saw that the compound became colored. The coloring of colorless compounds has a strange fact at that time. Reinitzer described the coloring of cholesterol acetate as below:

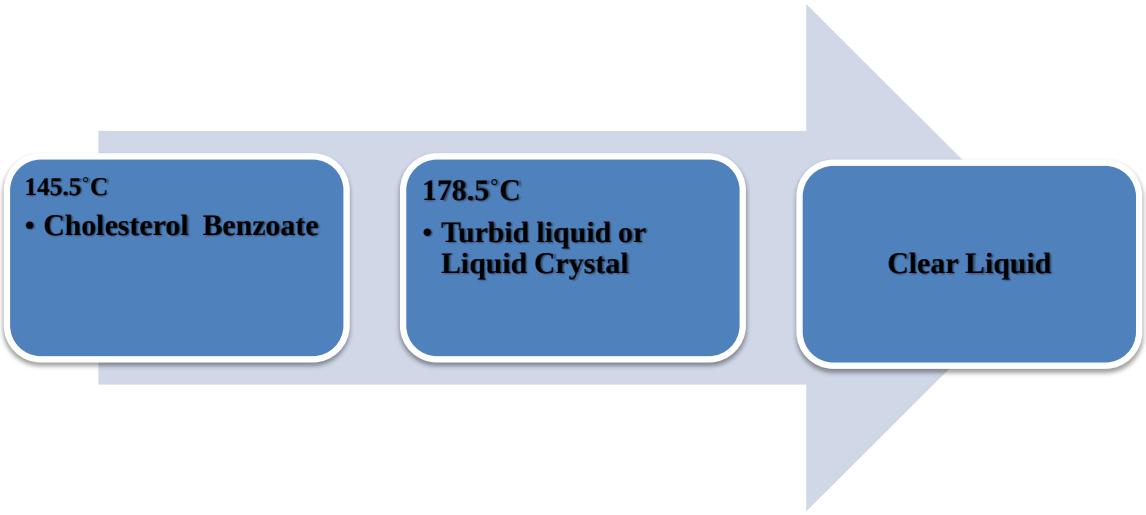


Figure 1.2 Block process of LC phenomena.

Reinitzer observed two melting points of cholesterol benzoate. The cholesterol benzoate powder transforms into dense clear liquid at 145.5°C temperature i.e., in a turbid liquid. On further heating at 178.5°C, the turbidity of cholesterol benzoate suddenly disappears. This color is temperature-dependent. According to Reinitzer, the cholesterol acetate and cholesterol benzoate compound experienced unique diversity of the physical isomerism. Reinitzer failed to separate these two isomers due to which, he sent the substance to professor O. Lehman [27]. On the evaluation, the properties of the compound show high ductility due to which they perform the crystal-like behavior and the crystals of high ductility are known as *liquid crystals* [9-11]. After a thorough investigation of cholesterol acetate and cholesterol benzoate, Lehman called the cholesterol compound a fluid crystal and nitro oxide compound as a drop-liquid crystal.

The physical properties of liquid crystals turn into an anisotropic fluid like other crystals. In these liquid crystals, cholesterol benzoate was one of them. In the characteristics of real crystals, anisotropy with homogeneity are the main aspects and hence material anisotropy is known as the dependency of properties to the crystal on the direction. The process is resulting in optical anisotropy which means the double-refraction phenomenon, whereas homogeneity defines the equal optical properties along with parallel directions. Such properties forced to align molecules in periodic arrangements in the crystal. The growth of the oversaturated solution is also an important parameter of crystal. Reinitzer and Lehman studied the liquid crystals for a long period [25-27]. Thus the liquid crystal state is described to be the fourth (4^{th}) state of substance and also it lies among the crystalline solids and liquid states as the intermediary [2].

1.3 Chemical Structure of the Liquid Crystal

Liquid crystals are organic molecules that show aromaticity when they contain benzene rings and become benzene derivatives.

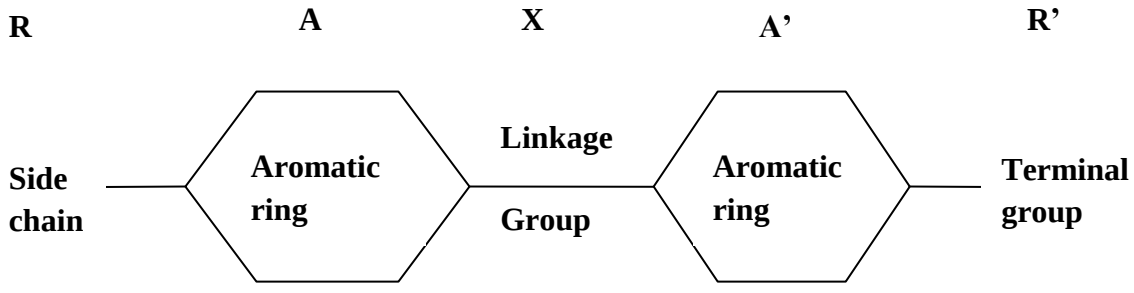


Figure 1.3 Composition of liquid crystal.

Figure 1.3 shows that liquid crystal constitutes R as a side-chain which interacts with A and A' as the aromatic rings, associated with X and Y as the linkage groups also other

end consists of R'as terminal group. The terminal groups and side chain are alkoxy ($C_nH_{2n+1}O$), alkyl (C_nH_{2n+1}), tolane (–C≡C–), Schiff base (–CH=N–), ester (–COO), azoxy (–N=N–), are the Xs of the linkage groups of the liquid crystal molecule [11, 28-30].

1.4 Orientational & Positional order of the Liquid Crystal

The study reveals that molecules in a crystal are ordered; which is positional as well as orientational in order, while in a liquid they are not ordered. The liquid crystal molecules possess both orientational as well as positional degree of order [31]. The extent of order in liquid crystals is relatively low [32].

As the molecules go through diffusion, the molecular axis is inclined along with a point through the desired direction. The directional orientation in an LC is defined through a unit vector (n) described as the director [8].

1.5 Types of the Liquid Crystals

A fully ordered crystal or crystalline solid is one in which the composition has long-range order of the molecular positions in three dimensions. The process of thermal vibrations takes place from the heating of the molecular crystal, due to which, the arrangement of molecules within the lattice increase. The arrangement of the structured molecules gets disordered in the absence of orientational and positional order owing to high intensities of the thermal vibrations and hence disordered isotropic LC's are generated [16-33]. As the temperature is being increased, the process is happening alongside in one or more intermediate phases. The phase is known as mesophase [1, 4-5]. The liquid crystalline mesophases have their material properties like refractive index, elasticity, viscosity, and permittivity. These properties are restricted to

anisotropic molecules consisting of partial ordering; however, the order of the molecules tends to get changed on moving from a certain direction to another direction [34-36].

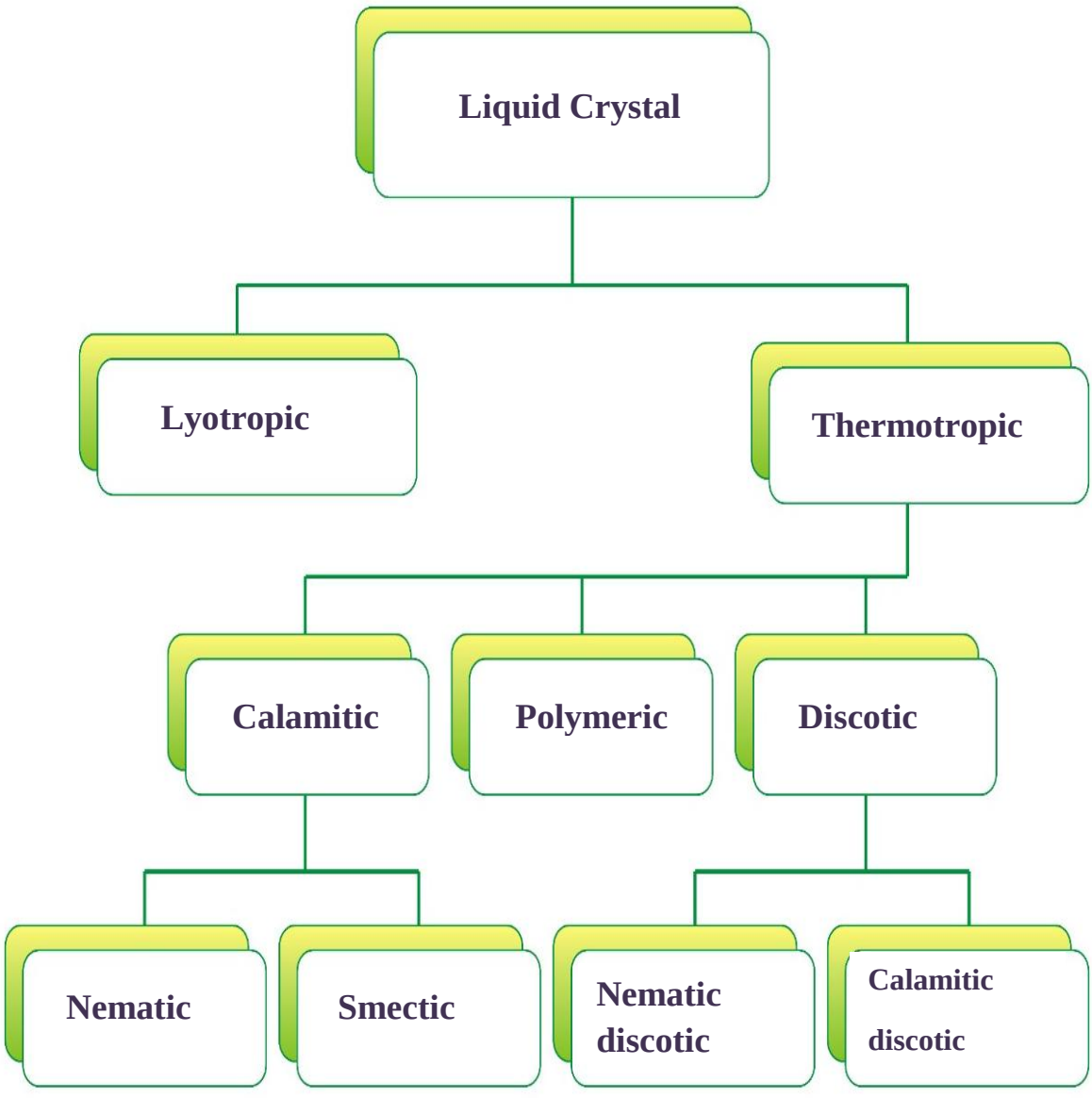


Figure 1.4 Types of liquid crystals.

The liquid crystal state is obtained by either the operation of heat on the mesogens also the operation of solvent on amphiphilic compounds.

Mesogenic compounds usually consist of lath-like, long, narrow, and fairly rigid molecules. The molecules of the crystal state are held together by their strong intermolecular forces of attraction due to which the rod-like structure is anisotropic [37-38].

LC may be categorized into various kinds depending on the geometrical structure of mesogenic molecules. These consist of distinct types of liquid crystals that show properties of liquid crystallinity as a function of various physical characters and their environments. French physicist Georges Fridel examined the thin layers of liquid crystals that are microscopic [26]. Fridel found that the chemical structure of the compound's liquid crystals found a minimum number of optical pictures. According to this, Fridel suggested that the classification of liquid crystals is depending on the optical pictures that are noticed with the ordering of molecules. Liquid crystals are categorized into two types; Lyotropic and Thermotropic liquid crystals. Thermotropic liquid crystals are further grouped into calamitic, discotic, and polymeric. Calamitic liquid crystals are further apart into two types i.e. nematic and smectic liquid crystals. Discotic liquid crystals are nematic discotic and columnar discotic [39-40].

1.5.1 Lyotropic Liquid Crystal

Lyotropic liquid crystals are concentration-dependent molecules that contain two or more compounds and show the properties of liquid-crystallinity in specific concentration order. These are attained when a suitable concentration of a substance is solvate in a solvent. Here, the space around the compounds by solvent molecules provides fluidity to the system [41]. Water and amphiphilic molecules are the most common systems like soap, detergents, and lipids [22, 42]. Since amphiphilic molecules have two non-miscible hydrophilic parts together with hydrophobic parts of

the same molecule. There exist a lot of amphiphilic substances that have properties of lyotropic liquid crystals depending upon the volume that balances hydrophilic and hydrophobic parts. In the lyotropic liquid crystal, a hydrophobic part is attached to one end while a hydrophilic part is attached to the other end. These kinds of amphiphilic molecules made ordered structures in both polar and non-polar solvents. The compounds having lyotropic mesophase generally contain a hydrocarbon group at the tail along with a polar at the head group.

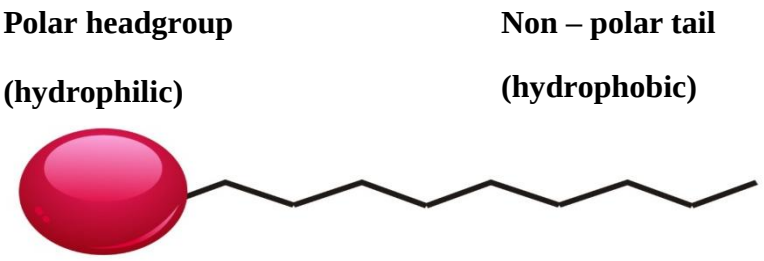


Figure 1.5 Structure of lyotropic liquid crystal.

When surfactants of the amphiphilic molecules are mixed within a polar solvent, a molecular mixture exists at a concentration of minimum surfactant. The small aggregates of the definite size, known as micelles are constructed when this concentration is reached at a critical point so that the polar groups involve the interface regarding the polar solvent. On further increasing the concentration, the solution is cooled, the micelles can then turn to supermolecular aggregates like cylindrical, disc-like, and plate-like those have the property of organization of their molecules into various cubic, nematic, hexagonal columnar, and lamellar lyotropic mesophases [7].

There are few samples of the lyotropic phase are found by the decomposition of soap in water, living organisms, biological membranes, DNA, etc.

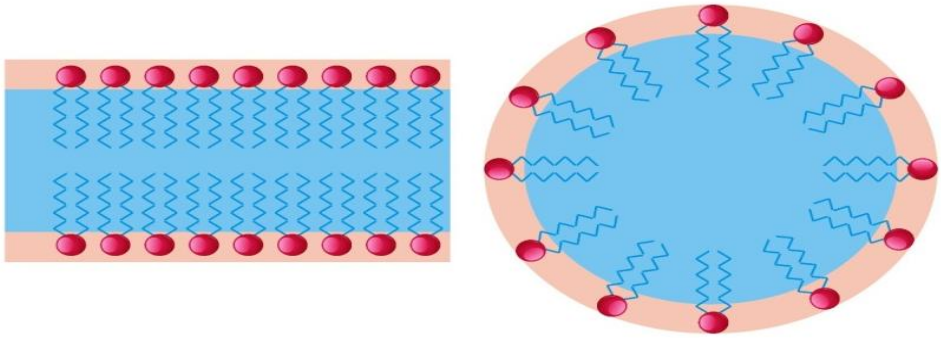


Figure 1.6 Lyotropic liquid crystals.

1.5.2 Thermotropic Liquid Crystal

Thermotropic liquid crystals are widely used for linear and nonlinear optical applications. These are obtained within a certain temperature range [1, 4] and exhibit various liquid crystalline phases. At the melting point, the thermal motion of the molecules increases as the material goes through the process of conversion of solid into LC state below room temperature. Thermotropic LC may form more than one liquid crystal state on increasing temperature and convert into a clear liquid at clearing point [43, 48, 49]. The ordering of the liquid crystal phases will be consumed by the effects of thermal motion of the molecule i.e. whether the temperature is very high then the conventional state turns to the isotropic liquid state. During the case of minimum temperature, many liquid crystal compounds will structure a regular crystal. The property of thermotropic liquid crystals discloses the variation of states in changing the temperature. When a liquid crystal molecule undergoes the process of heating, it shows different smectic phases that are proceeded by the nematic phase, then lastly in the isotropic state as long as the temperature is increased [14-17]. The molecular structure of thermotropic liquid crystals is quite complicated which is sometimes defined as

"rigid rods". In concluding the formation and various types of liquid crystalline phases, molecular shape anisotropy is significantly important [43]. According to Friedel, thermotropic liquid crystals are classified as calamitic, polymeric, discotic, and banana shape liquid crystals. Calamitic is divided into nematic, smectic, and cholesteric while discotic is divided into nematic discotic and columnar [22, 8].

1.6 Classification of Thermotropic Liquid Crystal

LC's are arranged in such a way owing to the unsymmetrical figure of the mesogens. Molecular shape and low molar mass is an important factor for determining the type of liquid crystal phases.

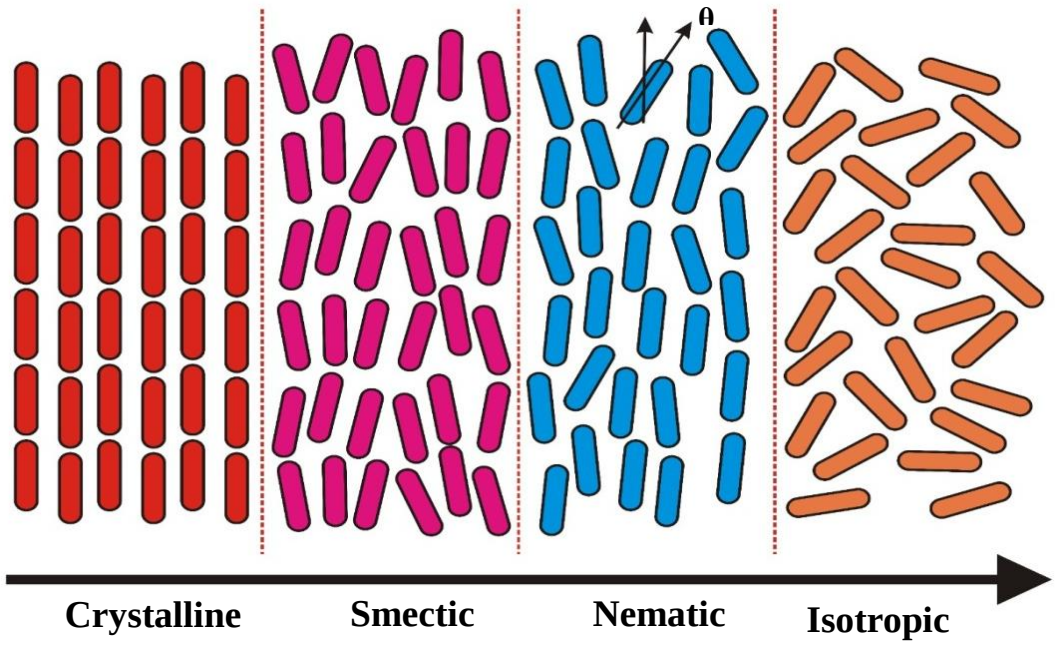


Figure 1.7 Classification of thermotropic liquid crystal.

The chemical design and shape of the mesogenic compounds along with external variables like pressure and temperature. There has been an extensive variety of liquid crystal phases have been observed. These conventional liquid crystals sometimes

represent rod-like structures i.e. calamitic or disk-like structures also known as discotic mesogenic molecules [33].

1.6.1 Calamitic Liquid Crystal

In calamitic mesogens, the molecules are rod-like structures having rigidness in its central field [14-17]. Terminal points can be flexible chains or polar groups attached to the central part of the molecule. There are three different types of mesophases in calamitic mesogens that are categorized as nematic, smectic, and cholesteric which are placed on the degree of positional order with orientational order. An increase in complexity is observed with the discovery of every new phase in liquid crystals [43].

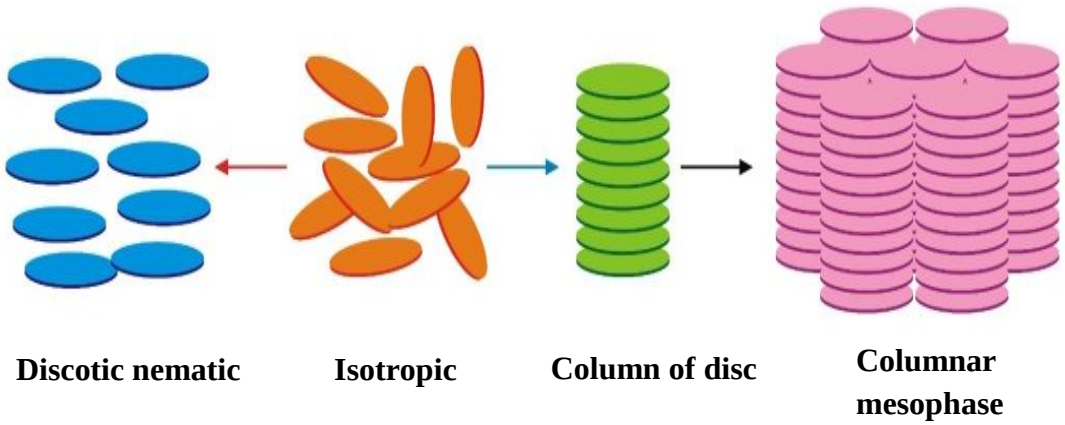


Figure 1.8 Arrangement of calamitic liquid crystal.

1.6.2 Nematic Liquid Crystal

The nematic liquid crystal state generally takes place near the isotropic state. Nematic phase is known as the simplest phase. N represents the direction of nematic LC about the mean direction along with the molecules. These N phase shows the properties of marble, pseudo-isotropic textures, and schlieren, building on the surface environment [43-47]. The rod-shaped organic molecules or calamitic in the nematic phase do not

show positional order while the molecules are generally [50-51], aligned along the distinct direction known as director (n) [10-12]. Thus, the molecules are free to flow in liquids with irregular arrangement of their center of mass position with long-range directional order [5, 24]. On application of external field, nematic LC molecules tend to align along a certain direction [14-17]. Nematic molecules also have fluidity similar to ordinary liquids (isotropic). Nematic liquid crystals show peculiar textures while observed under a microscope of a cross-polarized light [22].

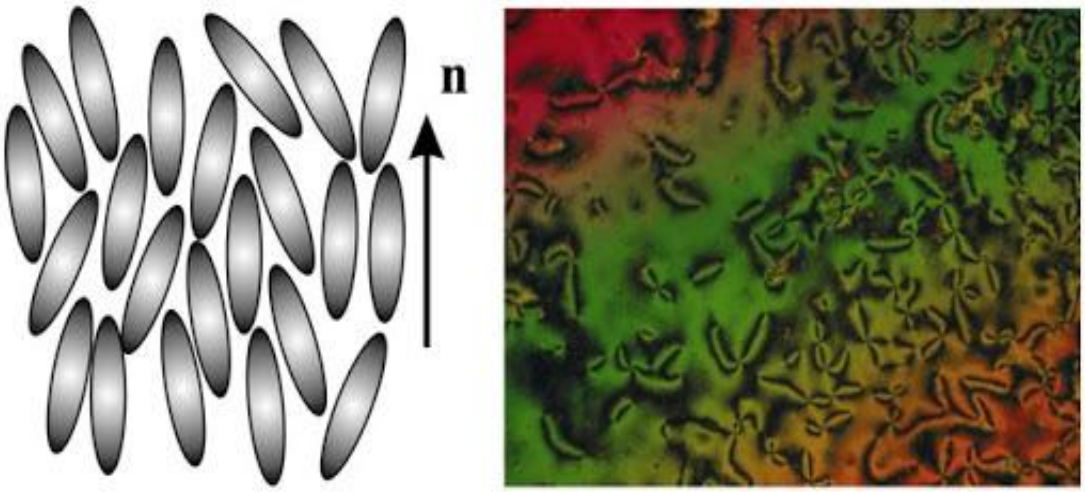


Figure 1.9 Nematic liquid crystal.

Such compounds looked like "thread". The nematic LC which is directed towards the direction has optical characteristics of uniaxial crystals i.e. Birefringent, allowing light with different polarizations to go through at different speeds. Cyanobiphenyl (CB) is one of the samples of the nematic liquid crystals [13]. To operate a liquid crystal, it is very important to control the temperature range because most liquid crystals are not made up of single molecules and when molecules are combined, they give the desired transition temperature on the low end and high end of operating temperatures [19-22].

1.6.3 Smectic Liquid Crystal

The smectic word is taken from the Latin word *"smectius"* according to which the molecule possesses soap-like properties [5, 9, 24] and also possesses a high degree of order relative to nematics. Smectic liquid crystals possess positional order together with directional order in their molecular ordering [44-47]. Smectic liquid crystals possess a layered structure due to orientational order and positional order which is the basis of their molecular center of gravity that is on average placed in equally separated planes. Smectic liquid crystals are classified according to their molecular arrangement of the layer and the range of interlayer correlations [6,7]. To represent the layering arrangement, different smectic liquid crystal phases are discovered that are known as smectic A, B, C, F, and I. Further, smectic phase is divide into two distinct sections [22]. The SmA, as well as SmB phases, are non-tilted in molecular structure while SmC, SmF, and SmI have tilted structures. On the molecule is being chiral, the smectic LC is named chiral smectic A, C, and F phases. Amongst all smectic phases, smectic A and smectic C are the two most regularly observed and extensively consider mesophases [43].

1.6.4 Smectic A (SmA) and Chiral Smectic A (SmA*) Liquid Crystal

The director in smectic A state is directed normally along with the layer. Molecular arrangement of layers seems to be liquid. It does not have long-range positional correlation [19-21] and also in successive layers, there is no connection between the sidewise location of the molecules. Thus the smectic A phase of LC may be expressed as a one-dimensional mass density wave due to disarrayed molecular layers [14-20,

22]. SmA_2 has a dual-layer phase in their molecules while SmA_d has moderately dual-layer properties in-phase and SmA is a modulated phase. SmA can also be termed as biaxial smectic A (SmA_b) because of biaxial symmetry where the molecules are supposed to be perpendicular about layer but have an additional director in the plane of the layers [44].

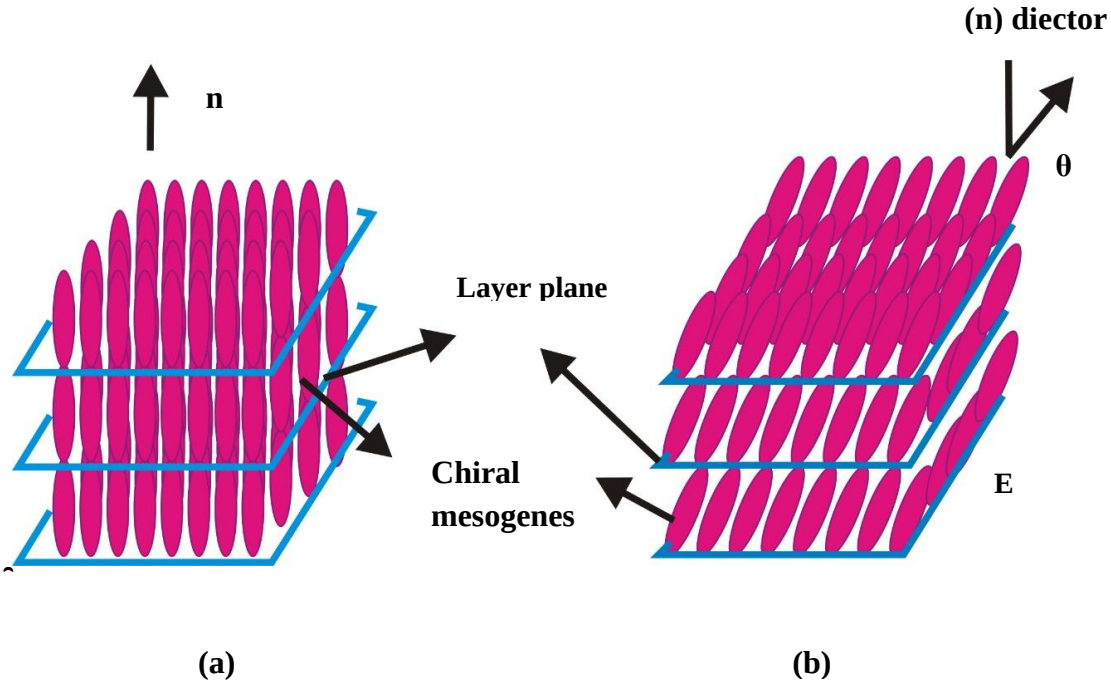


Figure 1.10 (a) Orthogonal layered geometry of SmA phase; (b) tilted layered geometry of SmA phase.

1.6.5 Smectic C (SmC) and Chiral Smectic C (SmC*) Liquid Crystal

The smectic A phase has uniaxial characteristics in its optic axis while smectic C liquid crystal has biaxial characteristics in its optical axis. During smectic C phase, director of every layer is tending along the angle that is normal to the layer, from which the smectic C phase has a change from smectic A phase, and also that angle is being

similar for all the layers [21-22, 46]. The tilt angle in smectic C state would be changed following temperature and sometimes this angle is increased monotonically with decreasing temperature. There exist macroscopic molecules in the state of chiral smectic C which is made of optically active molecules. This is shown in Figure 11(a) that the helical form of the molecules is established by the slight difference in tilt direction (n) of the molecule in every line through the axis that is perpendicular to the planes of the layer [52, 53].

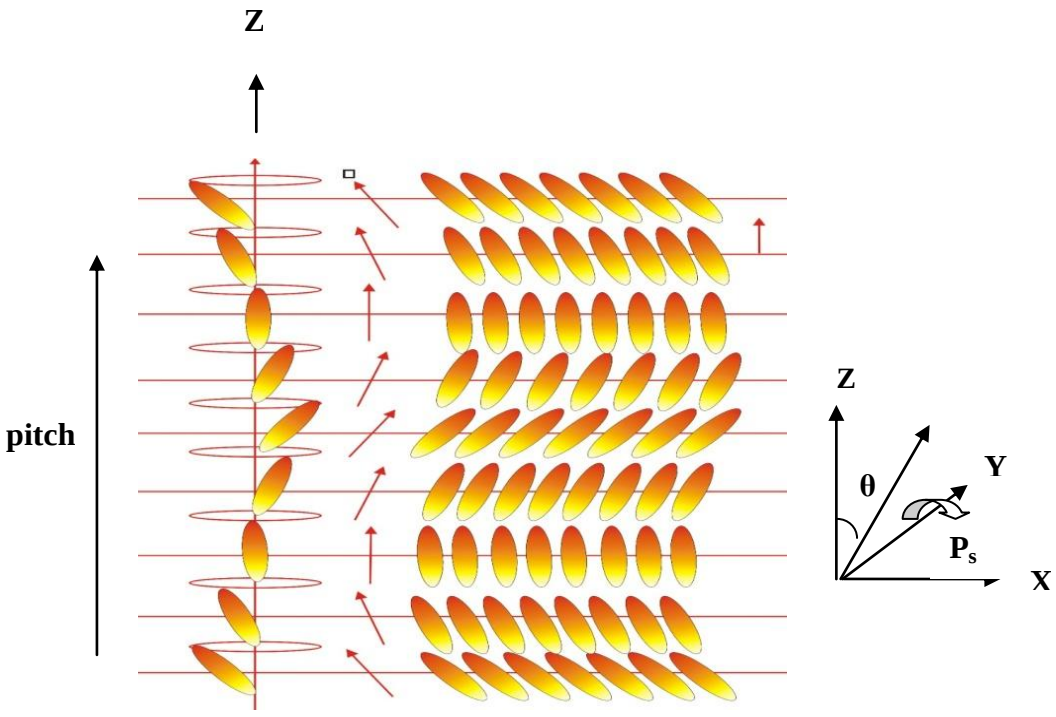


Figure 1.11 (a) LHS: Helical configuration of SmC* phase consisting successive layers about the normal layer (z); RHS: the precession of a chiral molecule in the successive layers; (b) representation of chiral molecule along xy direction with polarisation, Ps due to chirality in SmC* phase.

In the existence of chiral molecules, the SmC* phase lessens C_2 symmetry which results in equivalence of dipole moment across the C_2 axis normal to the tilt direction as Figure 11(b). The helix region results average out Ps to zero [46-47]. The macroscopic spontaneous polarization can be obtained by unwound of helix through the electric field.

The arrangement of molecules gets affected by several molecular layers above and below in smectic phases, therefore, a small range of three-dimensional order is observed as an example smectic G phase liquid crystals.

1.6.6 Cholesteric Liquid Crystal

Cholesteric mesophases are in the form of chiral nematic mesophases which contain a chiral center. Besides this, cholesteric LC's are obtained when the nematic LC is mixed with optically active molecules [21]. Within the Cholesteric LC, the molecular twist is normal in a direction along the optical axis of the molecules. The chirality of the molecules appears due to limited twisting adjacent molecules with asymmetric packing. The director of the cholesteric liquid crystal established a helical arrangement with the layer normal [1, 8, 33] which is shown in the given Figure 1.12.

In Figure 1.12, the molecules are represented so many chiral nematic mesogens that are situated in the slabs of very small thickness with the distribution of orientation of the molecules about the director. Cholesteric LC shows a property of diffraction that is they can diffract light. Dependency between the pitch of the LC molecules and diffracted light is observed according to the equation $\lambda=np$, where λ is known as the wavelength of light, n is known as the refractive index, p is known as the pitch. In

cholesteric mesophase, pitch "p" is an important parameter which is known as the distance from which the liquid crystal molecules sustain a full 360-degree twist.

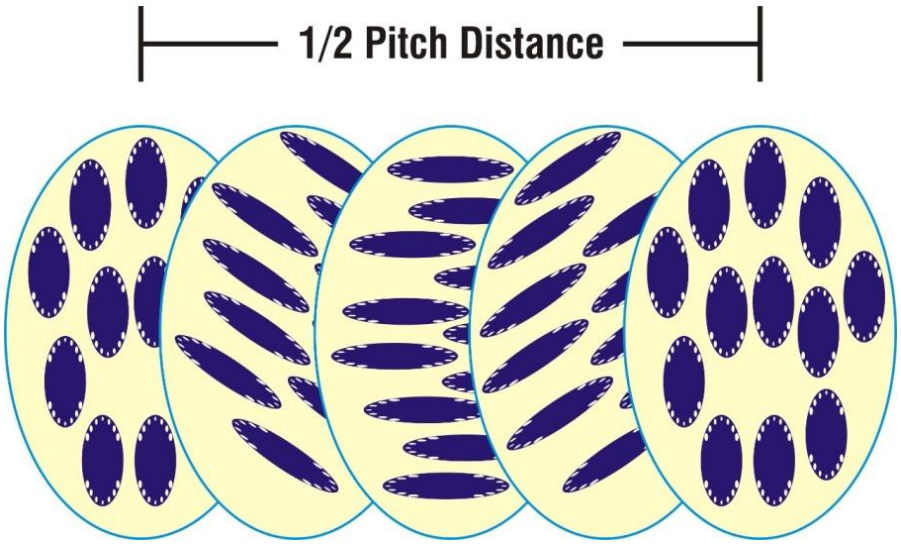
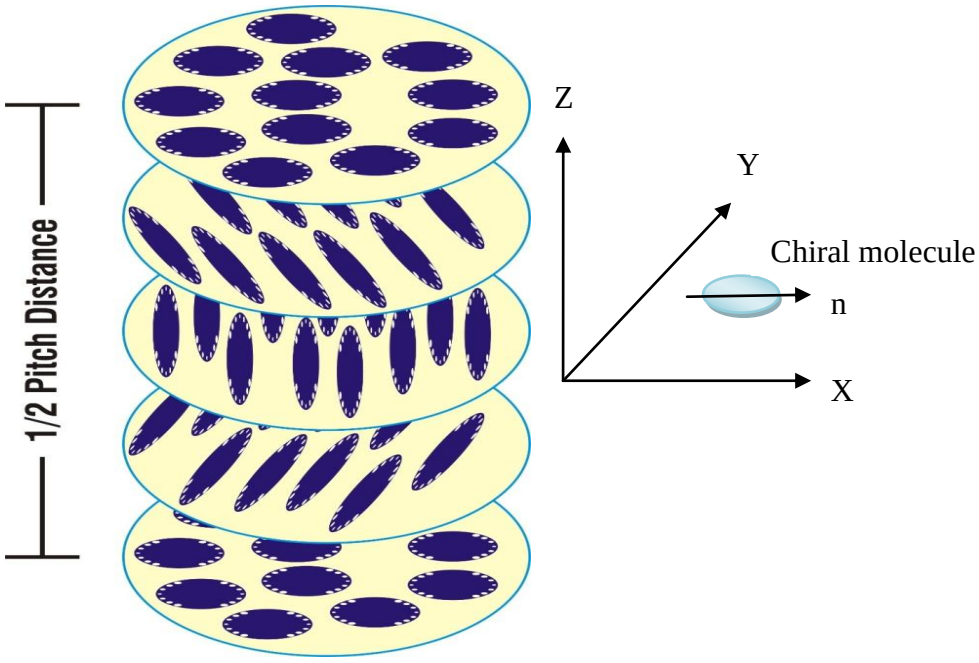


Figure 1.12 Cholesteric liquid crystal.

Chiral nematic liquid crystal governs the procedure of degradation and contamination in the production of the films directly on black surroundings. Such crystals are micro-encapsulated into low-dimensional particles [48]. Also, the obtained material is low temperature sensitive and can be used to fabricate various materials like clothing, dolls, inks, paints, and so on.

By controlling the chemical composition of the compound, the reflective wavelength can be regulated easily. The chiral behavior of cholesteric liquid crystals is dependent on the consisting chiral molecules or chiral dispersed nematic molecules. Using the concentration of the doping element, the chirality and pitch of liquid crystals can be tuned [47, 54].



(a) (b)

Figure 1.13 (a) Helical arrangement of molecules in the chiral nematic liquid crystal; (b) Molecular orientation into xy direction perpendicular to helix direction (z).

1.6.7 Blue Phase

In the highly chiral liquid crystals of the helical phase and isotropic phase, there is a intermediate phase which is known as the blue phase [48, 60]. These chiral liquid crystals have additional blue phases, as they are going through the process of heating including the helical phase to isotropic phase in the molecules [61, 62]. On increasing the temperature of the molecules, three blue phases are obtained which are BPI, BPII, and BPIII. BPI is called body-centered cubic whereas BPII is called simple cubic [60, 61]. The molecules of blue phases have no orientational order and positional order, the symmetries are not associated with their molecular geometries with lattice sites. The BPI and BPII blue phases presents a mixture of colors on display. In the blue phase, the

mixture of colors shows the various colored platelets which are randomly oriented [63, 64].

The blue phase has a non-zero elastic shear modulus because it is a liquid phase. Since the elastic shear modulus degree is relatively low; the liquid can resist static shears at all [21]. The blue phase encloses a high value of viscosity in the range of 10^6, corresponding to the helical and isotropic states [65]. Both in the phases of helical and isotropic phase, blue phases exhibits the liquid characteristics in the crystalline ordering of the molecules, which are generally connected with the properties of solids [55].

1.7 Polymeric Liquid Crystal

Polymeric liquid crystal exhibit properties of polymer with liquid crystals. In polymer molecules, they demonstrate the ordering properties and there must exhibit the anisotropically shaped rod-like or disk-likes elements which are also known as mesogenic units [16-17].

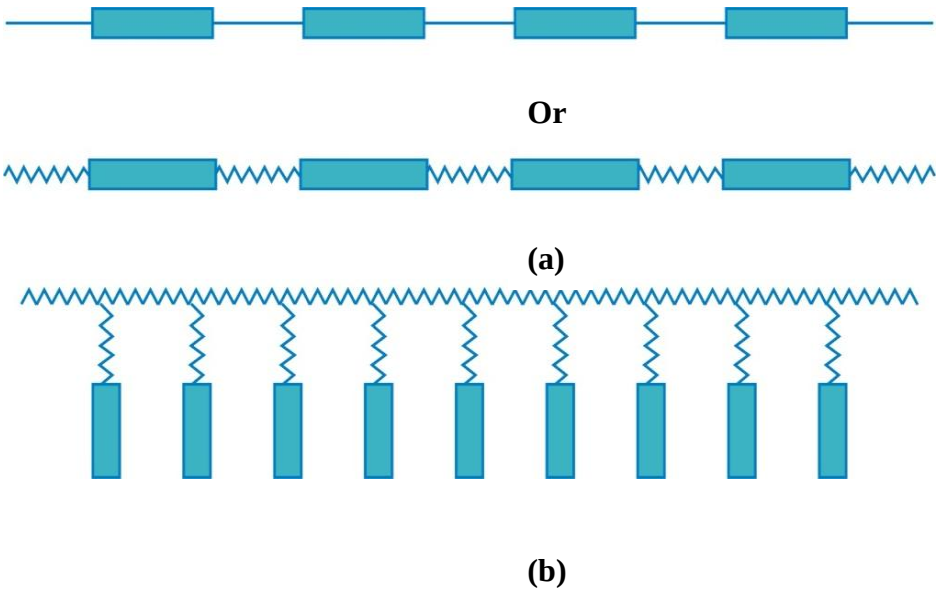


Figure 1.14 (a) Main chain polymeric LC (b) Side chain polymeric LC

Polymeric LC's are feasible to separate into two types. One is the main chain while the second is the side chain which depends on the location of mesophases moieties [66-67].

Mesogenic units in main chain polymers act in the main element backbone and remain separated by a flexible chain from other units [70-79] but in the case of side-chain polymers, backbone chain attached by several mesogenic units and connected by less flexible chains [55-57]. The degree of freedom of the polymeric liquid crystals is dependent on the limit of the flexibility of the chain. Generally, the nematic or smectic side-chain polymer has a naturally large degree of freedom [80-89] due to parallel arrangement of mesogenic units in obtaining phase [58-59]. The flexibility of the backbone or main unit in the polymeric chain which also responsible for liquid crystalline state [6].

1.8 Discotic Liquid Crystal

According to many scientists, only rod-like structures showed mesomorphism. Chandrasekhar *et al.* in 1977, described that disc-like molecules like Hexa-n-alkanoyloxybenzenes show mesomorphic behavior [90]. Such compounds are known as "discotic" compounds [91] and these molecules have the rigidity at the center of the molecules [94]. In discotic, the structure of molecules are organized in layered formation as in smectic crystals. The discotic molecules are present in the plane layer creating close hexagonal packing. Achiral discotic liquid crystals have different types of mesophases [91-93]. These are nematic, lamellar, and columnar phases. There is a difference between the director regarding the calamitic and nematic liquid crystals [95-97]. The director is defined in calamitic liquid crystals, as being along the axis towards the moment of inertia regarding the molecules while the director is normal about the average plane towards all the LC's in nematic liquid crystals.

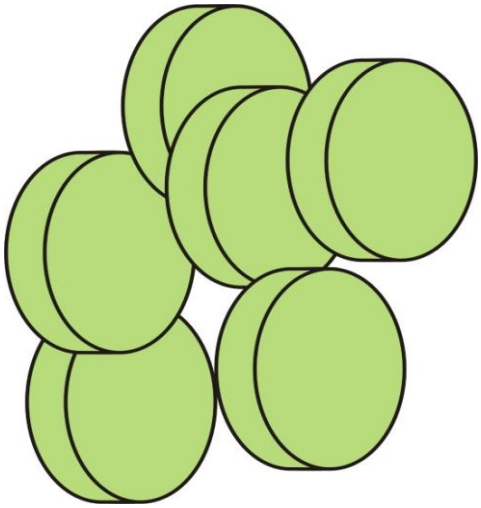


Figure 1.15 Discotic liquid crystal.

1.8.1 Nematic Discotic Liquid Crystal

The nematic discotic LC does not possess order in its position between molecules [98]. They possess only orientational order. The discotic nematics containing the disc-like molecules are formed on the cooling of the isotropic phase. This phase is a non-miscible phase with calamitic nematics despite the same symmetry: n= -n [1].

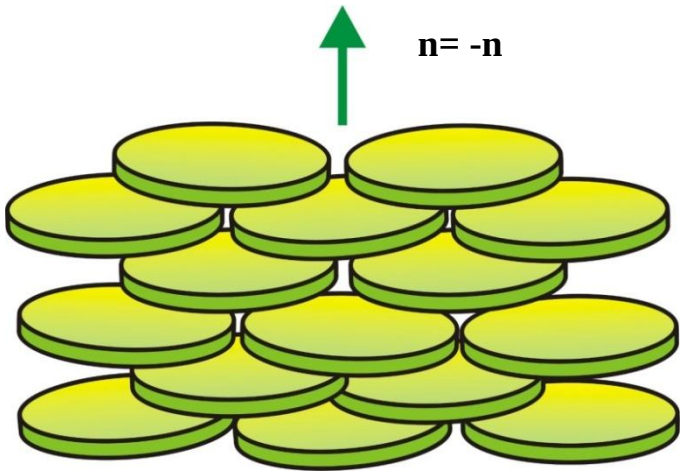
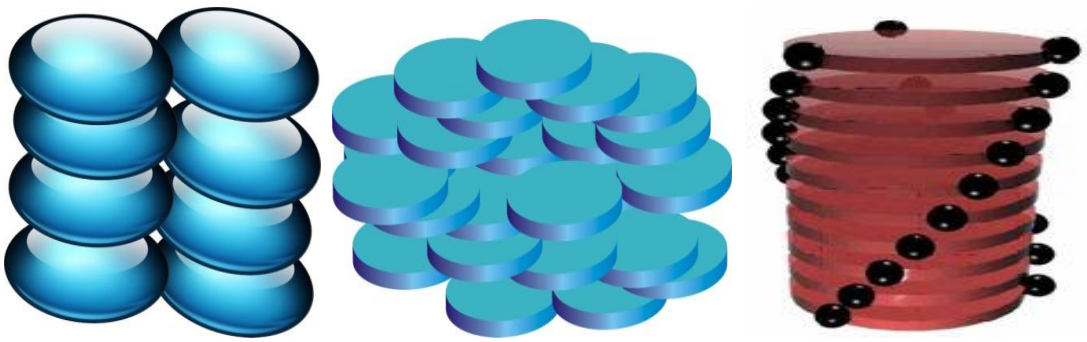


Figure 1.16 Nematic Discotic liquid crystal.

So the characteristics of discotic nematics in hydrodynamic region are changed to calamitic nematic liquid crystal [99-100].

1.8.2 Columnar Discotic Nematic Phase

Columnar phase is familiar with the atmost common phase which is expressed by the disc-like molecules in which disc stacks into columns. In the columnar discotic phase, the molecules lie roughly on top of each other having some degree of positional order. Columnar liquid crystals have the property of polymorphism which is classified in three levels depending upon the symmetry of the 2D array namely hexagonal and, rectangular as shown in Figure 1.17 [101-103].



(a) (b) (c)

Figure 1.17 (a) Columnar hexagonal (b) Columnar rectangular (c) Columnar oblique.

The molecules exhibit a periodic arrangement insides the column, in the hexagonal shape for the columnar LC. In rectangular and oblique states, arrangement of molecules is like liquid, and columns are organized as rectangular or oblique packing respectively. The stacking of the disc insides of the columns may be ordered otherwise disordered.

Columnar discotic plays an important role in optical devices like quasi-one-dimensional conductors, photo conducting devices, ferroelectric, light-emitting diodes, optical storage devices, photovoltaic solar cells, hybrid computer chips for molecular electronics, etc [104].

1.9 Properties of Liquid Crystals

Liquid crystals exhibit many properties in the physical, optical, electrical, mechanical field, etc., based on the molecular arrangement, orientational order, and anisotropy of material, etc.

1.9.1 Physical Characteristics of Liquid Crystal

The director of nematic LC "n", change under the action of disturbing forces like convection flow, wall effects, etc. The intermolecular force of molecules is responsible for the mesomorphic state [105, 106].

As the LC has anisotropic nature, the physical characteristics of those are not the same. The anisotropic substance gives a hike in the anisotropy regarding the many physical parameters for their parallel alignment due to which there exist several applications for liquid crystals.

1.9.1.1 Optical Anisotropy (Birefringence)

There exist many crystals which have the properties of optical anisotropy (birefringence). Birefringence is a double refraction phenomenon, when a light ray is passing through the birefringent material, it splits into more rays in different directions [8]. Birefringence is the maximum difference between refractive indices [107-111]. Birefringence is a uniaxial material phenomenon associated with control of optical

anisotropy along a single direction while all other directions are perpendicular to molecular geometry are equivalent. The optical behavior remains unchanged by any rotation around a certain direction and that direction is called as the optical axis of the material. Polarization perpendicular to this axis contributes to the refractive index n_o known as an *ordinary ray* while the polarization of light is governed by the optical axis n_e is known as an *extraordinary ray*. The difference between ordinary refractive index and extraordinary refractive index is defined as birefringence which is; $\Delta \mathbf{n = -n_o}$

In positive birefringence, i.e. $\Delta n>0$ of liquid crystals**,** the extraordinary ray is slow in phase rather than ordinary ray as transmitting through the liquid crystal phase. Generally, nematic, smectic, and columnar liquid crystals show uniaxial behavior although tilted smectic and columnar phases express biaxiality. The value of principal refractive indices lies under the range of 1.4 to 1.9 and for uniaxial liquid crystal, it can be found between 0.02 and 0.4. The discotic liquid crystal also shows negative birefringence under certain circumstances.

1.9.1.2 Dielectric Anisotropy

The anisotropic liquid crystal is responsible for the process of dielectric anisotropy shape, structure, and the types of atoms in the molecules. The applied electric field produces polarization which is contingent on the direction regarding an applied field. Dielectric permittivity (ε) is the main factor for measuring the interaction between electric field and LC compound, which would be determined in a parallel and perpendicular direction along with director. The difference between dielectric permittivity in the parallel and perpendicular direction is given as $\Delta\varepsilon=\varepsilon_{\parallel}-\varepsilon_{\perp}$. This can be both positive and negative [111].

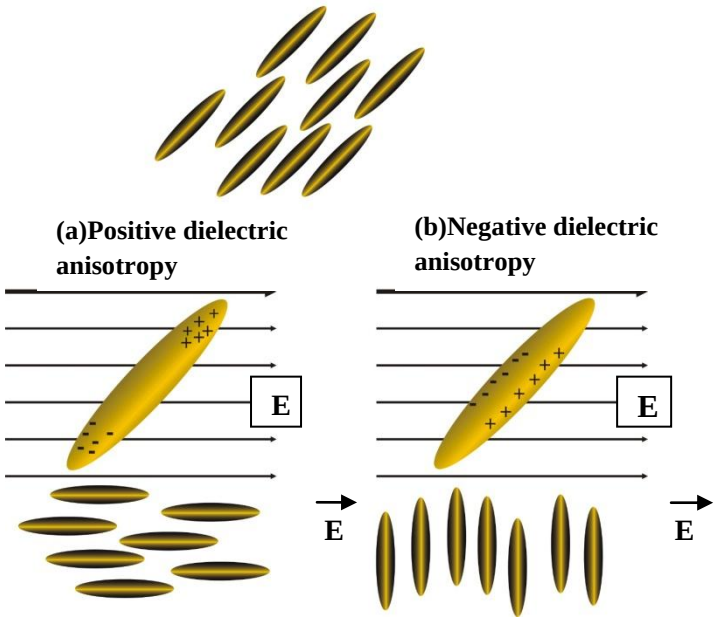


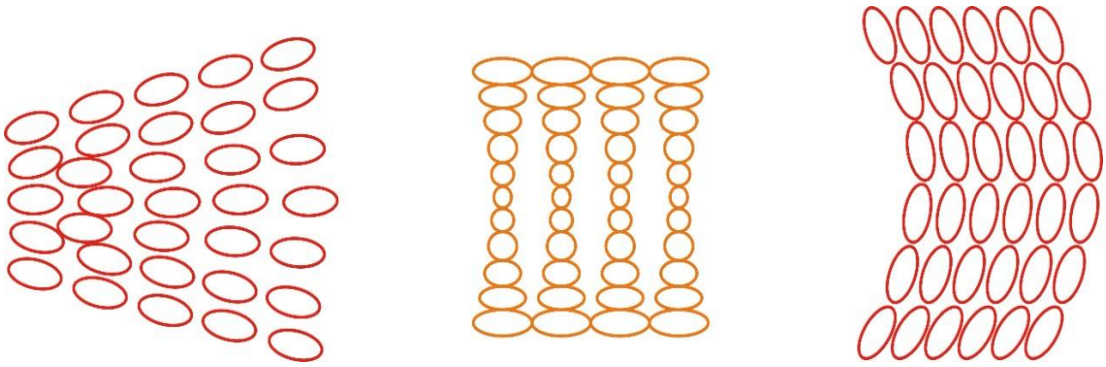
Figure 1.18 (a) Positive dielectric anisotropy (b) Negative dielectric anisotropy.

As compound aligns parallel along an electric field, dielectric anisotropy becomes positive ($\Delta\varepsilon>0$). Most compounds show positive anisotropy. The given Figure 1.18 shows the dielectric anisotropy in the form of induced dipole moment. With the interaction of electric field, the orientation of a longer molecular axis parallel to applied field leads to an induced dipole in the molecules with $\Delta\varepsilon>0$. The permanent dipole moment in the molecules shows an increase or decrease in $\Delta\varepsilon$, which is the reason for calamitic liquid crystals have the property of negative dielectric anisotropy. In the isotropic phase, this dielectric constant tends to become zero ($\Delta\varepsilon \rightarrow 0$) as it is a function of temperature.

1.9.1.3 Elastic Constant

Elastic constants represent restoring force for LC compounds, that is applying to the molecules. LC substances exhibits the property of elasticity in the form of curvature which is directed by a class of elastic constants. The elasticity in a liquid crystal state is obtained by the elastic constants namely k_1, k_2, and k_3 which are related to splay, twist,

and bend distortion [112-113]. Under the external fields, the spatial and temporal responses of the director also depend on the elastic constants [114].



SPLAY K11 **TWIST K22** **BEND K33**

Figure 1.19 Splay, twists, and bends deformation.

1.9.1.4 Viscosity

The viscosity of liquids is a very important parameter that plays a vital role in its properties, generally, the fraction of shearing stress with the shear rate is known as viscosity, and shear comes across the intermolecular forces acting within fluid [115-120]. The anisotropic property of viscosity relies on the flow direction of the individual molecule relative to a director or optic axis within the medium. In the nematic phase, normally three constant η_1, η_2, η_3 represents the viscosity and is strongly related to the shape of the molecules in the liquid. The first parameter η_1 is equidistant along the gradient of velocity but normal towards flow direction, the second parameter η_2 is equidistant along the flow direction but normal towards the velocity gradient direction, while η_3 is also perpendicular to the flow direction of flow and velocity gradient direction. Also, the bulk viscosity of the aligned molecules in the nematic phase can be studied by taking an average of these three viscosity coefficients of the liquid [121]. The viscosity coefficients of the liquid also regulate the optical responses of the

electro-optical due to boundary conditions in the anisotropic circumstances along with the unidirectional behavior of the material.

1.9.1.5 Order Parameter

The orientational order parameter gives information about the alignment of liquid crystal molecules. It's value is unity when molecules are perfectly aligned and have zero value on random orientation [1, 4, 16]. An order parameter can be constructed with the help of a mass moment tensor. The rate of orientational order varies during the presence of boundaries. The molecular order parameter is linked with temperature. Order parameter helps to calculate free energy density, photo-induced birefringence, and dichroism. Experimentally, chemical content and exposure time are the two key factors on which order parameter is dependent. Order parameter has both negative as well as positive values [122-125]. If any variation in the molecule exceeds the molecular size, then the order parameter remains unchanged [126].

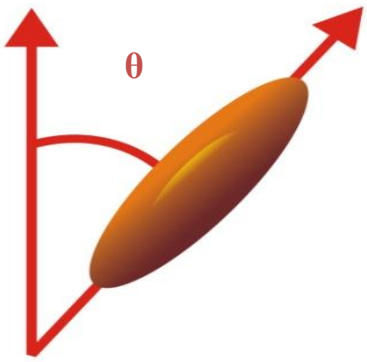


Figure 1.20 Molecular orientations of LC in the extraneous field.

1.10 Advances of Electric Field on Liquid Crystals

LC material shows remarkable changes at the macroscopic level because due to some external perturbations produced by the electric field [127]. These fields are applied in a

particular direction. Molecules have permanent electric dipoles due to positive charges at one end and negative charges at the other end. The liquid crystal molecules directed each other through the orientation of the applied electric field [128, 132].

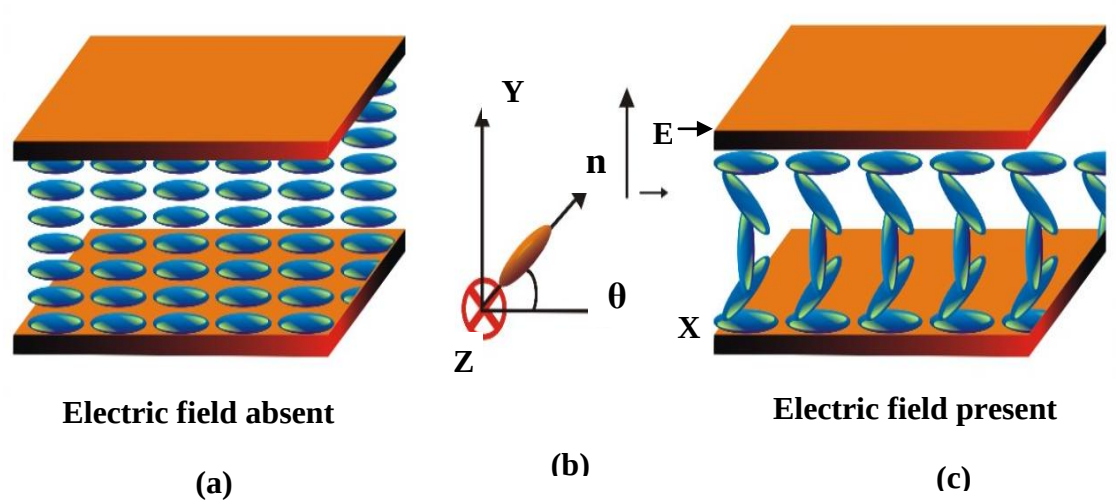


Figure 1.21 Direction of the molecules on the application of electric field.

1.11 Application of Liquid Crystals

LC compounds have various applications in the field of science, engineering, medical and also in technology. Liquid crystal molecules are widely used in display applications. Liquid crystals are utilized in the display devices, optical imaging, polymer dispersed liquid crystals, nanomaterial, visualization of radiofrequency waves, temperature sensors, liquid crystal thermometers, medical sciences, etc.

1.11.1 Liquid Crystal Display

In the applications of electro-optical display devices, LC compounds are widely used. Liquid crystal display is familiar with the flat panel device that implements the light-modulating characteristics of liquid crystals [133-135]. The optical properties of LCD's having liquid crystalline compounds are used under external fields. The fluid property

of the liquid crystals can be quickly prepared into slightly fine films. Due to the super-thin technology of LCD's, they are used as display screens of the laptop, computers, etc in comparison to the cathode ray tube (CRT). Liquid crystal does not produce light directly but using a reflector to emit colored images. LCD consumes less power or voltage than LED because it depends on the principle of blocking the light instead of emitting light. Each pixel in the liquid crystal layer (4μm thick) consists of two crossed polarizers (parallel or perpendicular) or transparent electrodes i.e. they are aligned at an angle of 90 degrees to each other [90, 104].

A liquid crystal substance is put between two glass sheets which are arranged in parallel and kept at a distance of few micrometers. There are transparent electrodes which are white or red, are deposited on the glass substrate to balance the director from the re-alignment process. When the liquid crystal is not filled between the polarizers, the first filter transmits the light and second filter obstruct the transmission. The orientation of molecules can be tuned by applying a field on the electrodes attached to the surfaces of the cell. So, with liquid crystals, the first filter transit the light, and second filter absorbed light without any orientation of light. Thus higher the voltage, the device failed in its transparency. The directions of surface alignment are perpendicular to one another at these two electrodes in a twisted nematics device. Hence the molecules orient themselves in a helix or twisted structure. From this, the rotation of the polarization of the interacting light is increasing, and the device converts into gray color. The functioning voltage on the LC layer in every pixel is controlled then light is allowing to pass through in changing amounts. This technique is also used for a color liquid crystal display system to caused red, green, and blue pixels [133-142].

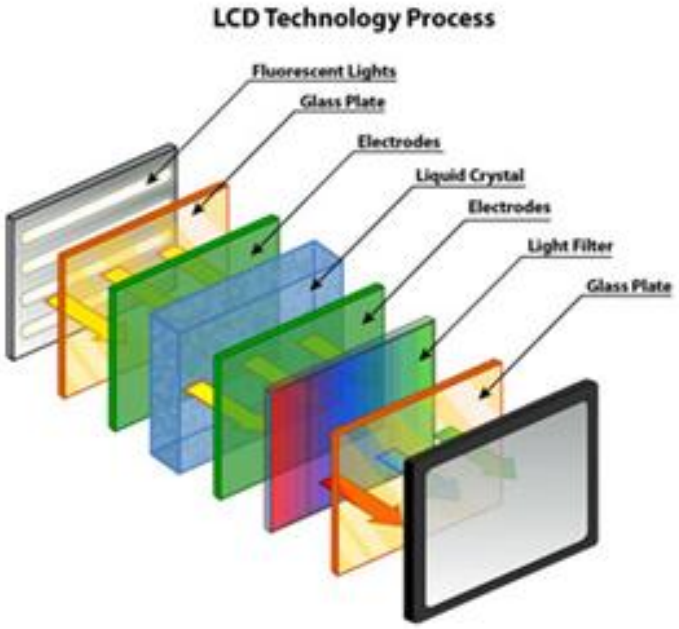


Figure 1.22 Liquid Crystal Display process.

Liquid crystals are broadly used in numerous applications including televisions, computer monitors, such devices consist of arrays of highly resolution matrix pixels to display random images or data by backlighting with a dark background. Liquid crystals are used as electronic products like DVD players, instrumental panels, video game devices, aircraft cockpit displays, indoor and outdoor signage [143,144]. Liquid crystals having small screens are used in watches, mobile, digital cameras, calculators, telephones, and also in smartphones [145-147].

Figure 1.23 Liquid Crystal Display in many forms.

1.11.2 Liquid Crystal Thermometer

Cholesteric liquid crystals have the property of reflection of light having a wavelength comparable to the extent of the pitch. This pitch is temperature-dependent. So the reflected color is also controlled by temperature. Hence with the help of cholesteric LC, it may be possible to determine the temperature just by looking at the color. This technique is used for many practical applications in daily ways in medicine, packing industry, and electronics. The liquid crystal thermometer shows various temperatures and consists of a liquid crystal in a plastic strip that is sensitive to heat [148].

Tumors also contain various temperatures than the nearby tissues, so it will be useful for detecting the higher temperature characteristics. The temperature sensor may also be operated on an electrical circuit board to detect the wrong connections [149].

Figure 1.24 Liquid Crystal Thermometer.

1.11.3 Other Applications

Liquid crystal is treated as an anisotropic solvent for the study of many physicochemical properties. Liquid crystal polymers made an important subclass and presented as a solution of few biopolymers. These biopolymers are crucial in the preparation of high-modulus materials as Kevlar [150-152]. The nematic phase of liquid crystal is deployed as the anisotropic solvents in NMR spectroscopy because the molecules in the nematic phase can be homogeneously oriented under external fields such as electric or magnetic fields and in this state the optic axis orients along parallel to the external field. Lyotropic liquid crystal is used in detergents and cosmetics. These are also used for the simulation of biomembrane [153-154]. Recently liquid crystals are used for controlled drug release.

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Chapter-2

Computational Methodology

Chapter 2

Computational Methodology

2.1 Computational Quantum Mechanics

The size of electrons is so small and their movement is so fast that we cannot measure their movement with an instrument [1]. This could not be done by Newton's laws, as being of size in nanometer. Hence, to predict the properties of nano-size systems, Quantum mechanics are used. Quantum mechanics deals with very small-sized things. When we solve quantum states of electronic motion of one electron problem like H atom, we may solve it easily by the Schrodinger equation. But when we solve the Schrodinger equation for the many-body problem, then several difficulties are faced. Hartree proposed an idea to solve many-body problems for the atoms which contain multiple electrons based on fundamental physical principles. It represents electrons in a calculation. So it is possible to calculate properties that depend upon the electronic distribution [2, 3]. By adding approximation to the Schrodinger equation, the solution is based on semiempirical calculations, and without approximation; the solution is based on a higher-level quantum mechanical calculation which is also known as the *"ab initio"* solution. The computations in ab initio are relative to the basis set of orbitals.

The accurate results are calculated using a higher number of orbitals, but with a slower calculation [4].

2.2 ab-initio Method

The ab initio method is based on the Schrodinger equation method. The word ab initio comes from the Latin word “from first principles”. The ab-initio method becomes useful for the modeling of atoms, molecules, the complex systems of biology, quantum chemistry, and also used in material sciences. In 1998, J. Pople and W. Kohn [5,6] have been awarded the Noble prize for obtaining the “good-enough” solutions to the Schrodinger equation for the small system and also for the higher systems of hundreds of atoms [2,3].

The molecular energy is evaluated using the ab-initio calculations with the help of the Schrodinger equation for the specified nuclear ordering, which is first used in the Born approximation method applied to the molecules (Here both the nuclear and electronic movements are managed independently) [7]. Although the Schrodinger equation is unable in the solution of larger structure totally, so there are electronic wave functions that are expressed in definite basis sets, according to which the Schrodinger equation is a change in an algebraic equation which are solved with the help of numerical methods [3,8].

2.3 Hartree-Fock Method

For solving the wave function and energy of many-body problems, the Hartree-Fock method is used. For the N-body wave function of a compound, an individual Slater determinant (the wave function towards the numerous-electron compounds is represented as a linear combination of anti-symmetrized products) is used.

The Hartree-Fock method was developed for the solutions of the time-independent Schrodinger equation. An electronic Schrodinger equation in which *r* represents the electronic besides *R* represents the nuclear degrees of freedom in atomic units is given as follows:

$$\left[\frac{1}{2}\sum_t \nabla_1^2 - \sum_{A,t}\frac{Z_A}{r_{At}} + \sum_{A>B}\frac{Z_A Z_B}{R_{AB}} + \sum_{t>j}\frac{1}{r_{ij}}\right]\psi(r;R) = E_{el}\psi(r;R) \qquad (2.1)$$

This equation is also written in the following type;

$$\left[\hat{T}_c(r) + \hat{V}_{CN}(r;R) + \hat{V}_{CC}(r)\right]\psi(r;R) = E_{el}\psi(r;R) \qquad (2.2)$$

According to Born-Oppenheimer approximation, E_{el} denotes the potential energy of the nucleus which is in the form of potential surface energy from which one can obtain the equilibrium geometry with vibrational frequencies [2,9].

ψ (r; R) shows the electronic wave function of compounds which has a lot of detail of molecular characteristics like dipole moments, polarizability, etc.

2.4 Density Functional Theory

The molecular energy, including the acquired uses, depends on the calculation of the wave function in ab-initio system. Density functional theory comes after ab initio theory. The basis of DFT is that if one can find the density of electrons in a molecule, other things can also find out about the molecule. DFT calculations give more accurate results than the ab initio method [10-14].

The fundamental of this theory depends on functional. A functional is known as the function of a function. A new factor "y" relies on several variables, in a function. In ab initio, we calculated wave function that is dependent on another variable as electron coordinates – x, y, and z [15-16].

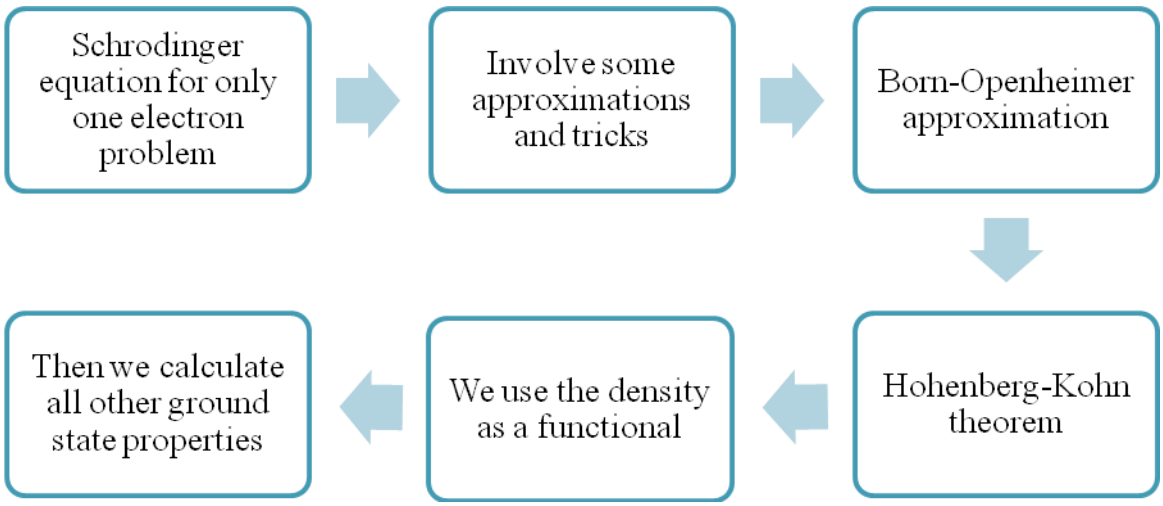

Figure 2.1 Block diagram of DFT method.

A function is indicated according to the given equation:

$$y = F [f (x)] \quad (2.3)$$

Here, the value of y is dependent on another function. F (x) which is the function of a function.

The molecular energy in DFT is described to be functional regarding the electron density. Electron density depends on three variables which are x-direction, y-direction, and z-direction of the electron. Here, the functional of the electron density provides energy to the compounds.

$$\text{Electron density} = \rho (x, y, z)$$

$$\text{Energy} = F [\rho (x, y, z)]$$

To calculate the value of functional F in the DFT method, in 1965, Kohn and Sham suggested using another form of density functional theory which is given as:

$$E_{DFT}[\rho] = T[\rho] + E_{ne}[\rho] + J[\rho] + E_{xc}[\rho] \quad (2.4)$$

Above equation contains E, T, E_{ne}, J, and E_{xc} which represent energy, an electron's kinetic energy, energy of nuclear-electron attraction, energy of electron-electron repulsive, also the energy of electron-electron exchange-correlation. The total terms that appeared in the density function are also a function of position coordinates, (x, y, z).

The first three terms of equation (2.4) can be calculated using the ab initio method and semi-empirical method. According to many scientists, it has been considered that DFT is an accurate method to study the molecular properties unlike other theories, molecular mechanics, semi-empirical, etc. [16-29]. The last term E_{xc} electron exchange-correlation energy is most important to determine the electron correlation which expresses the quantum mechanical characteristics of electrons connected to interchange among the fermions and boson [2].

2.5 Basis set

Basis sets are used to express the electronic wave function. These are composed of atomic functions and are mostly used in the calculations of quantum mechanics as Hartree-Fock or density functional theory method. They are applied for the change in partial differential equations into an algebraic equation of a system that is relevant for the appropriate execution on a computer [30-32].

2.5.1 STO-3G

This is a method of self-consistent molecular orbital that is used for Gaussian expansions in the atomic orbital of Slater-type [8]. A linear combination of LCAO SCF with slater-type atomic orbitals (STO's) is used to moderate large organic molecules. This use

one orbital to represent each atomic orbital for example (for C, use 1s, 2s, 2px, 2py, 2pz; for H use 1s). Each orbital is represented by the sum of 3 Gaussians [30-32].

2.5.2 3-21 G

The method of self-consistent molecular orbital is used for a small split-valence basis set regarding the first-row element. Two basis functions are utilized in this type of basis set, for every valence atomic orbital. One basis function (the sum of 3 Gaussians) represents each core, i.e. non-valence orbital and two basis functions (one is the sum of 2 Gaussians, while the other is single Gaussian) are used for each valence orbital. For example, for C, use one basis function for the 1s, two for 2s, and two for each 2p orbital. This is more flexible and slightly better than STO-3G. This basis set demonstrates a good description of the relative energies also the geometrical features of some molecules. This basis set is used for relatively small molecules [8].

2.5.3 6-31 G

This basis set is generally used to calculate the medium to the large molecule. This is similar to 3-21 G. One basis function (the sum of 6 Gaussian) to represent each core orbital; two basis functions (one is the sum of 3 Gaussian, the other is a single Gaussian) are used for each valence orbital [8, 33].

2.5.4 6-31G*

This basis set is used for third-row elements in the periodic table. 6-31G* basis set defined for 6 Cartesian d-type functions and recognized as 6-31G (d). 6-31G* is an addition with 6-31G with the polarization functions on atoms other than hydrogen. For example, C has now 6 d-type orbits to the addition of 1s, 2s, and 2p functions. This

basis set is very useful for accurately describing the bond angle. 6-31G* is a very popular basis set and also more expensive than 6-31G [8, 34-35].

2.5.5 6-31G**

This is a 6-31G* plus p polarization function for hydrogen. 6-31G** and makes a difference into the results of molecules with normal hydrogen atoms. Polarization functions are required to accurately treat molecules with bridging H-atom such as boranes or FHF and for hydrogen or proton transfer reactions [2, 34-35].

2.6 Methods

2.6.1 B3LYP

This is a hybrid method containing elements from DFT with the HF method. HF theory is used in the equation of Kohn-Sham for exchange-correlation potential, however, it experienced some difficulties in retrieving the kinetic electron-correlation, but in the case of DFT, an accurate form of dynamic electron correlation has been obtained. As DFT does not include the Quantum mechanical properties, it should approximate exchange-correlation.

B3 is defined by Becke's 3 parameter exchange-correlation functional that comprises the parameter to mix in the exact Hartree-Fock exchange-correlation. LYP is the Lee-Yang Parr correlation [36] functional that resumes the dynamic electron-correlation. The method B3LYP is close to the most post-Hartree–Fock technique and normally yields a similar result [37]. B3LYP is not strongly parameterized comparing to another hybrid functional [38-39]. It containing only 3 whereas some methods have up to 26 parameters.

2.6.2 M062X

This is known as Minnesota functional (Myz) which is a highly parametrized approximate exchange-correlation energy functional in DFT. These functionals are used for quantum chemistry and solid-state physics calculations. Besides B3LYP, M062X shows high nonlocality with double nonlocal exchange (2X), which is parameterized only for non-metals [40-41].

2.7 Electric field effect on Liquid Crystals

By using electric field on the LC compounds, they become a very important tool in the field of display applications [42-46]. By applying a little amount of volt across the liquid crystal compound, the orientation of the director could be easily changed. By changing the orientation of molecules, their optical properties change because of their large birefringence [47-48].

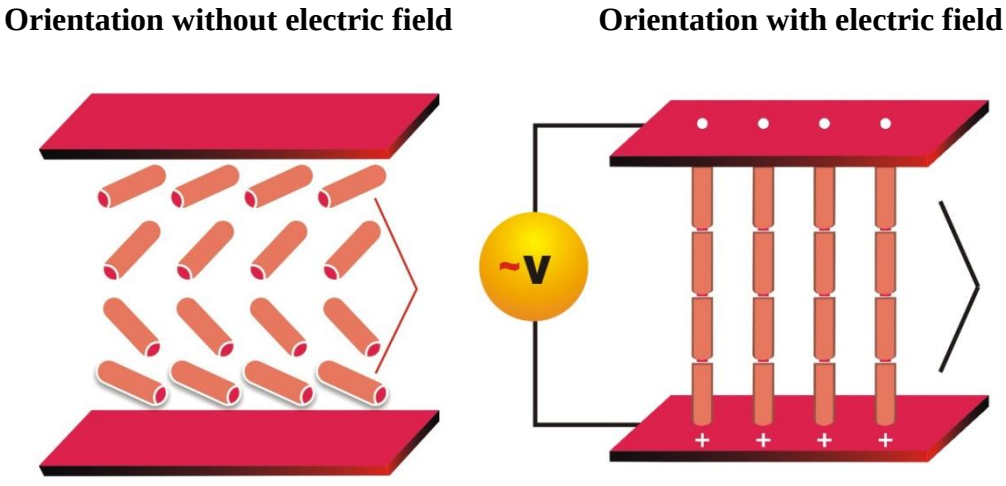

Figure 2.2 The effect of electric field.

Effect of an electric field can be categorized into two groups [49]. In the first group, the orientation state of the mesophase does not change under the action of the field.

The second group includes changes in the macroscopic structure under the direct action of the field. The large extent of birefringence and easy acceptance of external field perturbation is the main characteristics of the liquid crystal [44]. On applying a voltage up to a few volts to micron sized thin film, phase shift appears for optical application in the visible to the near-infrared regime.

2.8 Methodology

In the present thesis, Gaussian 09 software package [50, 2] is used to design and optimization of the molecules using the method of DFT. Here B3LYP [36-38] and M062X [40] methods are used. 6-31G* also 6-31G** basis sets are used [35, 51]. Electric field (a.u) is exerted after the simulation of LC compounds parallel along a molecular axis (x-axis) and perpendicular to the molecular axis (y-axis). The electric field is varied in the interval of 0.0020 (a.u), starts from 0.0000 (a.u) to 0.1000 (a.u). The value of 1 a.u is 5.14 x 10^{11} V/m [52] or 6.5 x 10^{15} Hz. Molecular polarizability is calculated after applying an electric field to the molecular series. Here ordinary (α_o) molecular polarizability is across the y-axis, whereas extraordinary (α_e) molecular polarizability is across the x-axis. Using α_e and α_o, the properties of molecular series are calculated according to the equations described below. Where α is the component of polarizability, μ is the component of dipole moment, and β is the component of first-order hyperpolarizability [53-54].

$$\alpha = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$

$$\beta = \left[(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{xxy} + \beta_{yzz})^2 + (\beta_{zzz} + \beta_{xxz} + \beta_{yyz})^2\right]^{1/2}$$

$$\mu = (\mu_x{}^2 + \mu_y{}^2 + \mu_z{}^2)^{1/2}$$

$$\Delta\alpha = 2^{-1/2}\left[(\alpha_{xx}-\alpha_{yy})^2+(\alpha_{yy}-\alpha_{zz})^2+(\alpha_{zz}-\alpha_{xx})^2\right]^{1/2}$$

$$\Delta\tilde{\alpha} = \alpha_e - \alpha_o$$

$$\Delta\tilde{\alpha} = S\Delta\alpha$$

Order Parameter (S):

$$S = \frac{\alpha_e - \alpha_o}{\alpha_e + \alpha_o} \qquad (2.5)$$

Birefringence (Δn):

$$\Delta n = \frac{(\alpha_e - \alpha_o)}{6.3631}\left[R^3 - \left(\frac{2\alpha_o + \alpha_e}{20.244}\right)\right]^{-1} \qquad (2.6)$$

Where R is known as the radius of the liquid crystal molecule.

Magic angle (θ):

$$\theta = \cos^{-1}\left[\frac{(2S+1)}{3}\right] \qquad (2.7)$$

Refractive index (n):

$$\alpha = \frac{2\alpha_o + \alpha_e}{3}, \quad \gamma_e = \alpha + \frac{2(\alpha_e - \alpha_o)}{3S}, \quad \gamma_o = \alpha - \frac{(\alpha_e - \alpha_o)}{3S}$$

$$n_e = \frac{7}{2\sqrt{10}} + \frac{(2\sqrt{10}/5)\pi N\alpha}{1-\frac{4\pi N\alpha}{3}} + \frac{(4\sqrt{10}/15)\pi NS(\gamma_e - \gamma_o)}{1-\frac{4\pi N\alpha}{3}}$$

$$n_o = \frac{7}{2\sqrt{10}} + \frac{(2\sqrt{10}/5)\pi N\alpha}{1-\frac{4\pi N\alpha}{3}} - \frac{(2\sqrt{10}/15)\pi NS(\gamma_e - \gamma_o)}{1-\frac{4\pi N\alpha}{3}}$$

$$n = \frac{7}{2\sqrt{10}} + \frac{\left(2\sqrt{10}/5\right)\pi N\alpha}{1 - \frac{4\pi N\alpha}{3}} \qquad (2.8)$$

Here N denotes the molecular number in the liquid crystal which is equal to 1. Other molecular parameters, γ_o, γ_e and $(\gamma_e-\gamma_o)$ are ordinary, extraordinary internal field constants, differential molecular polarizability of molecule. Also n_o and n_e are generally known as ordinary and extraordinary refractive indexes regarding the substance.

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Chapter-3

Electro-optical odd-even effect of the APAPA liquid crystal molecule studied under the influence of an extraneous electric field (THz): A theoretical approach

Chapter 3

Electro-optical odd-even effect of the APAPA liquid crystal molecule studied under the influence of an extraneous electric field (THz): A theoretical approach

3.1 Introduction

LC's are compounds with property of flow as a liquid; although, there is some degree of order to organize the molecule. The liquid crystal state is the intermediary state that occurs among the crystalline solid and liquid states. The nematic liquid crystal has the simplest phase and the lowest symmetry is mostly along the single axis. It doesn't express translational correlation regarding the molecular center. The rod-like nematic LC is easy to rotate along the long molecular axis under the effect of the electric field. Rod-like liquid crystal has strong electron conjugation, which is good for display and other applications. The dielectric characteristics of the LC molecules contribute for the dielectric anisotropy phenomenon. The reorientation of the LC plays an influential role in the applications of electro-optical objects. A union-based LC creates a double bond between N and C disclosed in the molecular structure which contributes to the

molecular polarizability and resulting in the intermolecular interaction in the nematic liquid crystal. Various terminal positions possess various dipole moments; so, the appropriate position of the polar group can enhance the molecular polarizability. In this way, molecular polarizability gives stability to the LC states. The APAPA LC holds two benzene rings which are linked to the linkage group of Schiff base whereas the terminal of the benzene ring is linked to the alkoxy and ester group [1-2].

According to Mandal et al. [3], APAPA liquid crystal shows influential scattering results that are used for the application regarding liquid crystal display devices. Nematic state of the APAPA liquid crystal is from 83°C-108°C temperature. Liquid crystal compounds having Schiff base are easily affected by atmospheric moisture; so, at the time of manufacturing of the optical units with these LC substances, there is a need for safety due to moisture. Order parameter of APAPA liquid crystal is 0.61 to 0.40. It is familiar to MBA liquid crystal that establishes the nematic state in the influence of temperature with pressure. Leenhouts et al. [4] have described the series of APAPA liquid crystals that may also be designated to APAPAm liquid crystal, here m means for the number of the carbon atom in the alkyl chain length of the ester group $OCOC_m\ H_{2m+1}$. The elastic constant of the homologous series of APAPA liquid crystal decreases with an increase of alkyl chain length due to short-range correlation in the plane that is perpendicular to the director (Y-axis). Somashekar et al. [5] described that the order parameter of 1MBA liquid crystal is ranging within 0.5 to 0.6, whereas the order parameter of 3MBA liquid crystal is ranging within 0.5 to 0.65.

Onnagawa et al. [6] disclosed that with electric and magnetic fields, APAPA molecule maintains alignment in nematic phase. Meulen et al. [7] have reported that with the help of dynamic light scattering, we can easily calculate the elastic properties of nematic liquid crystal. Moreover, according to Deutsch, et al. [8], scattering of laser

beam using the APAPA liquid crystal in the dynamic scattering mode be used as a scattering material. In the work presented here, an electric field is applied to the homologous series of the APAPA liquid crystal. The optical parameter exhibits an odd-even effect under the impact of an electric field. It shows the new orientation of the molecules which is mostly applied in the applications of electro-optics.

3.2 Computational Methodology

The molecular geometries are optimized by the Gaussian 09 software [9]. The Density functional theory is used with B3LYP [10-11] and M062X [12] by 6-31G** basis set [13-14]. We have applied an electric field (a.u) having range 0.0000 (a.u) to 0.1000 (a.u) at the interval of 0.0020 (a.u), to the homologous series, along the molecular axis (x-axis) and perpendicular to the axis (y-axis), after the simulation of the APAPA molecules. Where the value of 1 a.u=5.14 x 10^{11} V/m [15] or 6.5 x 10^{15} Hz. The molecular polarizability of the molecular series is calculated after applying an electric field. We considered the extraordinary molecular Polarizabilities (α_e) along the x-axis and ordinary molecular polarizabilities (α_o) along the y-axis. By evaluating the values of extraordinary molecular polarizabilities (α_e) and ordinary molecular polarizabilities (α_o), we have calculated the refractive index, order parameter, birefringence, and magic angle according to the equations given below. Here α denotes the component of the polarizability, μ denotes the component of dipole moment, while β denotes the component of first-order hyperpolarizability [16-18].

$$\alpha = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$

$$\beta = \left[(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{xxy} + \beta_{yzz})^2 + (\beta_{zzz} + \beta_{xxz} + \beta_{yyz})^2\right]^{1/2}$$

$$\mu = (\mu_x{}^2 + \mu_y{}^2 + \mu_z{}^2)^{1/2}$$

$$\Delta\alpha = 2^{-1/2}\left[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2\right]^{1/2}$$

$$\Delta\tilde{\alpha} = \alpha_e - \alpha_o$$

$$\Delta\tilde{\alpha} = S\Delta\alpha$$

Order Parameter (S):

$$S = \frac{\alpha_e - \alpha_o}{\alpha_e + \alpha_o} \tag{3.1}$$

Birefringence (Δn):

$$\Delta n = \frac{(\alpha_e - \alpha_o)}{6.3631}\left[R^3 - \left(\frac{2\alpha_o + \alpha_e}{20.244}\right)\right]^{-1} \tag{3.2}$$

Here R is known as the radius of the liquid crystal

Magic angle (θ):

$$\theta = \cos^{-1}\left[\frac{(2S+1)}{3}\right] \tag{3.3}$$

Refractive index (n):

$$\alpha = \frac{2\alpha_o + \alpha_e}{3}, \quad \gamma_e = \alpha + \frac{2(\alpha_e - \alpha_o)}{3S}, \quad \gamma_o = \alpha - \frac{(\alpha_e - \alpha_o)}{3S}$$

$$n_e = \frac{7}{2\sqrt{10}} + \frac{(2\sqrt{10}/5)\pi N\alpha}{1 - \frac{4\pi N\alpha}{3}} + \frac{(4\sqrt{10}/15)\pi NS(\gamma_e - \gamma_o)}{1 - \frac{4\pi N\alpha}{3}}$$

$$n_o = \frac{7}{2\sqrt{10}} + \frac{\left(2\sqrt{10}/5\right)\pi N\alpha}{1-\frac{4\pi N\alpha}{3}} - \frac{\left(2\sqrt{10}/15\right)\pi NS\left(\gamma_e - \gamma_o\right)}{1-\frac{4\pi N\alpha}{3}}$$

$$n = \frac{7}{2\sqrt{10}} + \frac{\left(2\sqrt{10}/5\right)\pi N\alpha}{1-\frac{4\pi N\alpha}{3}} \quad (3.4)$$

Where the value of N is known as the number of molecules in liquid crystal is equal to 1. γ_o is an ordinary internal field constant and γ_e is an extraordinary internal field constant. The difference of γ_o and γ_e (γ_e-γ_o) gives the value of differential molecular polarizability. Ordinary refractive index is denoted by n_o and extraordinary refractive index is denoted by n_e.

3.3 Results and discussion

The B3LYP method is prevalent in the atomic contribution of the molecule; whereas, the M062X method is prevalent in the molecular contribution of the molecules. In the adjacent work, the atomic contribution presents identical properties as the molecular contribution; therefore, the molecular contribution is mostly correlated with the experimental evidence. The B3LYP and M062X DFT methods are the most suitable methods for the optimization of an organic compound (liquid crystal) [19]. The homologous series of the APAPA liquid crystal shows a higher absorbance due to C-O atom stretching [20]. The effects of an electric field are prevalent in computational chemistry because of the analysis of the chemical reaction mechanism [21].

3.3.1 Temperature versus increased alkyl chain length of the APAPA liquid crystal

An odd-even effect has been- observed by the homologous series of the APAPA liquid crystal from the conversion of nematic to isotropic phase under the effect of temperature, which is presented in Figure 3.1. The transition temperature is increased for the odd member of the homologous series as the odd member makes a smaller angle with the molecular axis as presented in Figure 3.1; therefore, transition temperature decreases for the even members.

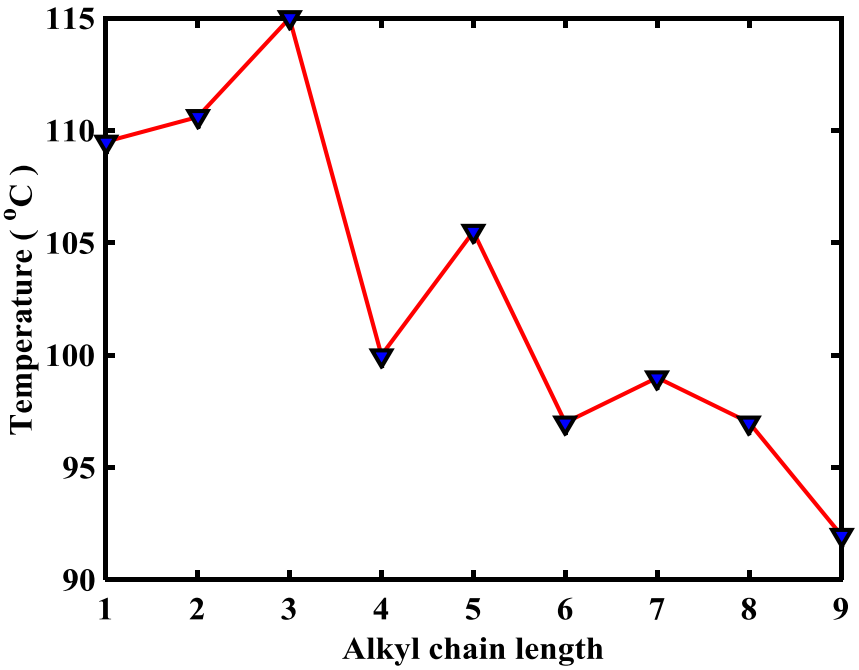

Figure 3.1. Odd-even effect of the homologous series calculated under the impact of temperature [22].

Although, a larger angle is made by the even member with the long molecular axis. The transition temperature is increased due to the small distance from the long molecular axis; consequently, the temperature is decreased due to the large distance

with the long molecular axis [22]. The carbon atom numbers (6, 7, and 8) of the alkyl chain are continuously decreased due to a large angle with the long molecular axis (x-axis).

3.3.2 Birefringence versus increased alkyl chain length of the APAPA liquid crystal

The birefringence of the homologous series expresses an odd-even effect under the impact of an electric field in the frequency of THz, according to Figure 3.2 (A). The birefringence has been determined using equation 3.2 under an electric field. Because of the smaller angle with the long molecular axis, the birefringence increases towards the even member of the alkyl chain; because of the decrement in the largest angle with the molecular axis.

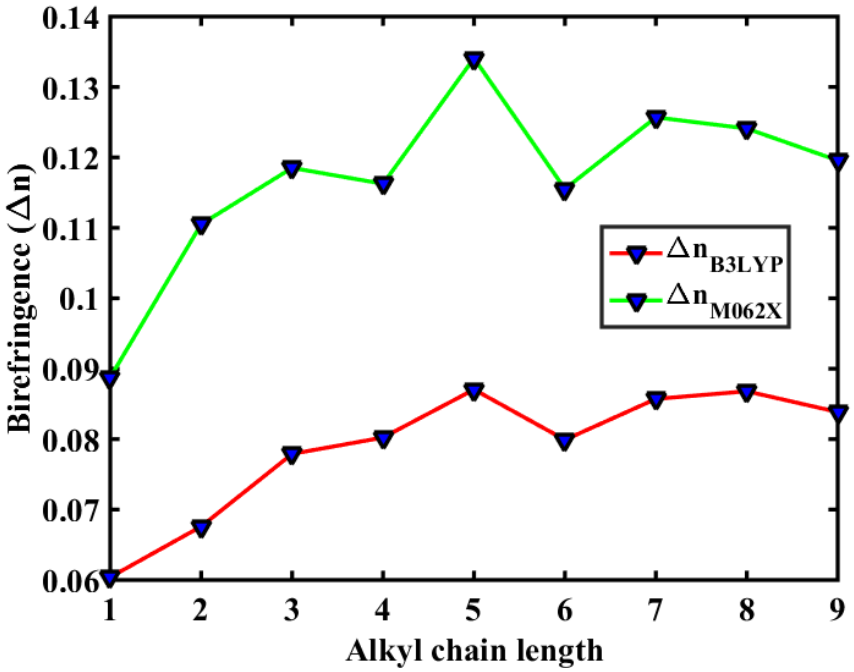

Figure 3.2 (A). Odd-even effect of birefringence calculated under the influence of an electric field.

The most valuable birefringence is for the APAPA5 LC, preferable for the applications in electro-optics in the frequency of THz. A similar odd-even effect has been expressed in the series by the effect of temperature and electric field. According to Ji et al. [23], the effect of an electric field with a controlled frequency of THz region, the birefringence can be used for applications in electro-optical field. Both positive and negative birefringence shows the realignment of the molecules, which is given in Figure 3.2 (B).

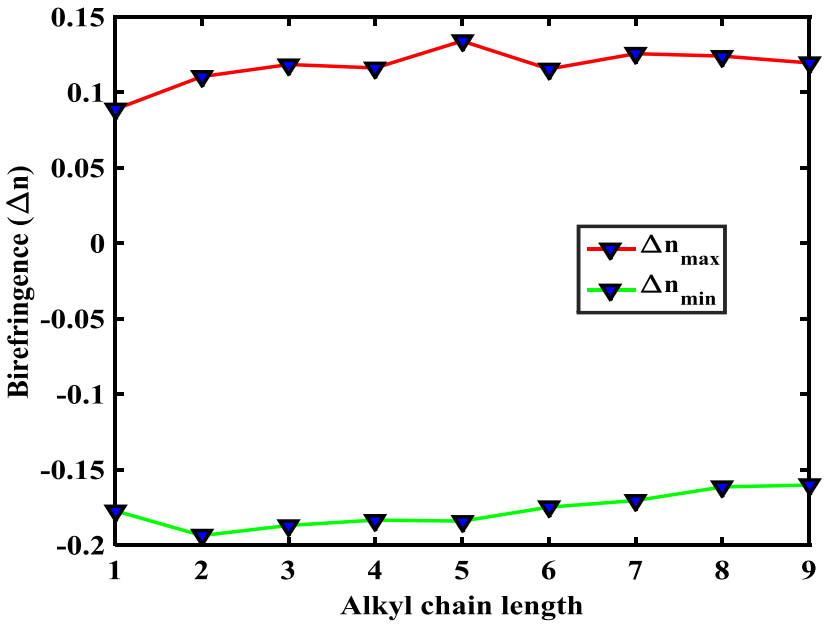

Figure 3.2 (B). Positive as well as negative birefringence under the influence of an extraneous electric field in THz frequency.

3.3.3 Order parameter versus increased alkyl chain length of the APAPA liquid crystal

The order parameter of the APAPA liquid crystal series is observed using equation 3.1 by applying the electric field in the frequency of THz. On increasing the length of alkyl chain, order parameter increases continuously. The molecular contribution expresses a

small amount of odd-even results; while, atomic contribution grows forward and doesn't express odd-even effects. The order parameter of the APAPA5 liquid crystal instantly increases due to the strong electron conjugation. The APAPA5 liquid crystal is probably useful in the applications of electro-optics as the order parameter with birefringence both increased. The ionization potential is decreased, and electron affinity rises only for the APAPA5 liquid crystal, which is one more purpose for the applications in optical field. Jampani et al. [24] have described that the liquid crystal has a negative order parameter due to the parallel orientation of molecules. The homologous series also has a negative as well as a positive order parameter, as shown in Figure 3.3 (B).

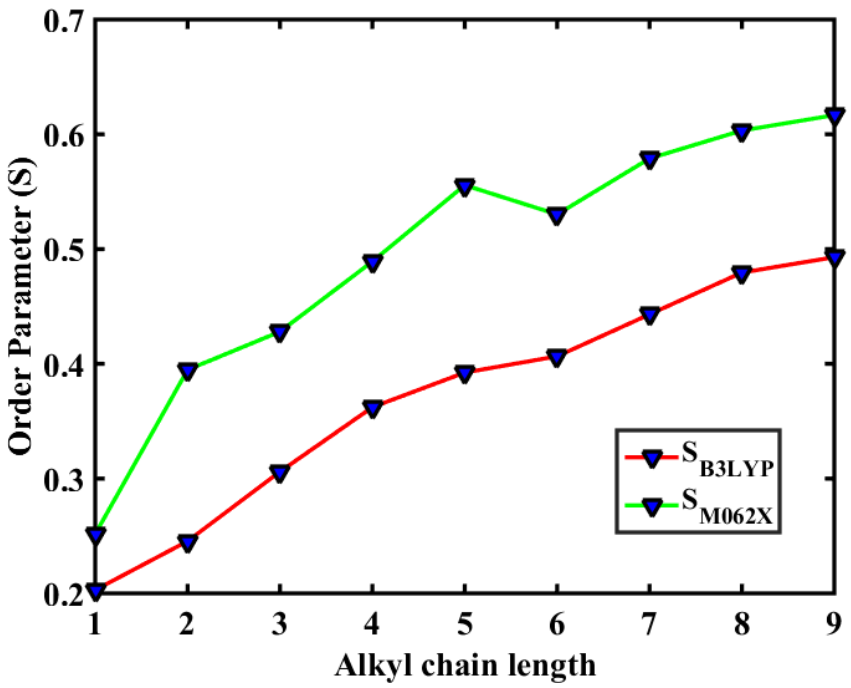

Figure 3.3 (A). The order parameter of the homologous series continually increases with an extension of the alkyl chain length.

Both positive and negative order parameter-dependent liquid crystals are highly preferable in electro-optical and other optical applications. Mandal et al. [3] have

described that the order parameter of the APAPA liquid crystal placed from 0.4 to 0.6 which is also described in the given work. The value of the order parameter of APAPA liquid crystal is -0.54, which is presented in Figure 3.3 (B). Somashekar et al. [5] have described that the value of order parameter placed from 0.5 to 0.6 of 1MBA also the order parameter of 3MBA liquid crystal placed from 0.5 to 0.65. In the present work, the order parameter of 1MBA and 3MBA is -0.54 & -0.68. The experimental evidence is correlated with the theoretical prediction. The negative order parameter is first time experimentally reported by Jampani et al. [24] is the reason for the inverted sign of the order parameter in the present work.

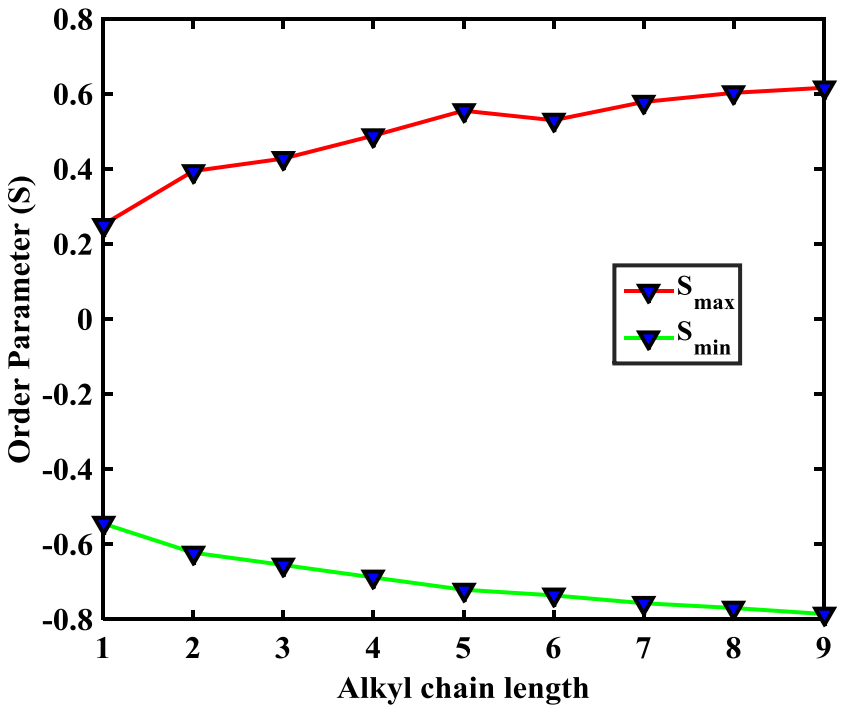

Figure 3.3 (B). Positive as well as negative order parameters were calculated under the influence of an extraneous electric field in THz frequency.

3.3.4 Refractive index versus increased alkyl chain length of the APAPA liquid crystal

The refractive index of the APAPA liquid crystal series is observed using equation number 3.4, according to Figure 3.4. The refractive index continuously increases with an extension of length of alkyl chain and doesn't show odd-even effect. Atomic and molecular contributions give identical properties with distinct values. The refractive index range of series placed from 1.57 to 1.58. Ji et al. [23] have suggested that the refractive index sustains stability under the impact of an electric field in the THz frequency.

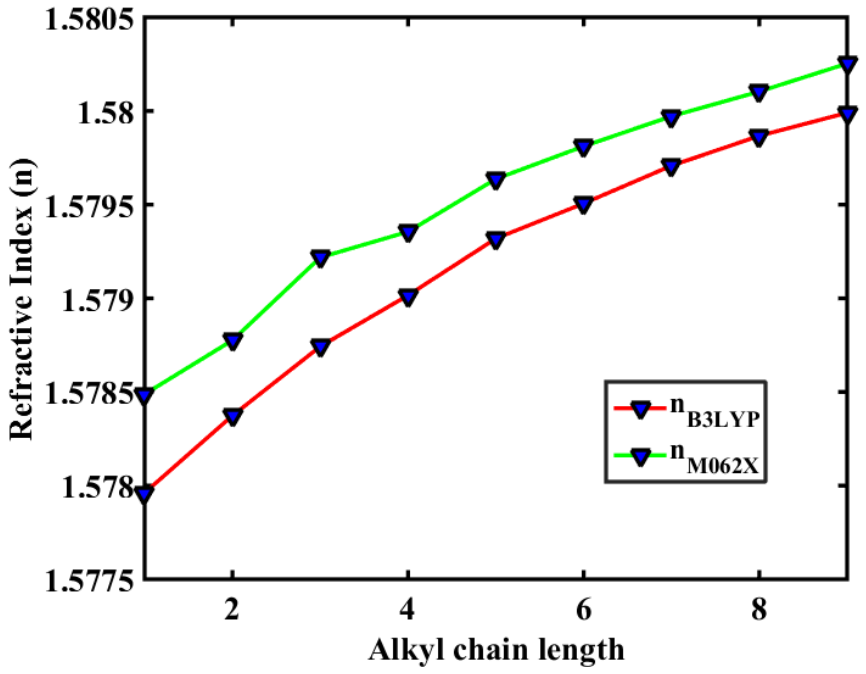

Figure 3.4. The Refractive index of homologous series continually increases with an extension of alkyl chain length.

3.3.5 Director angle versus increased alkyl chain length of the APAPA liquid crystal

The director angle of APAPA liquid crystal series is observed using equation 3.3 with the electric field in the THz frequency region, given in Figure 3.5. The director angle kept stable for the entire homologous series. The atomic and molecular contribution gives identical envision as the director angle (θ=90) kept stable. Meulen et al. [7] and Deutsch, et al. [8] have suggested that the APAPA liquid crystal is used for the dynamic scattering mode because the molecule maintains stability at the angle θ=90 degrees, therefore, incident light is scattered at θ=90 angles. In this way, we can say that it is appropriate for the applications of scattering in the THz frequency region.

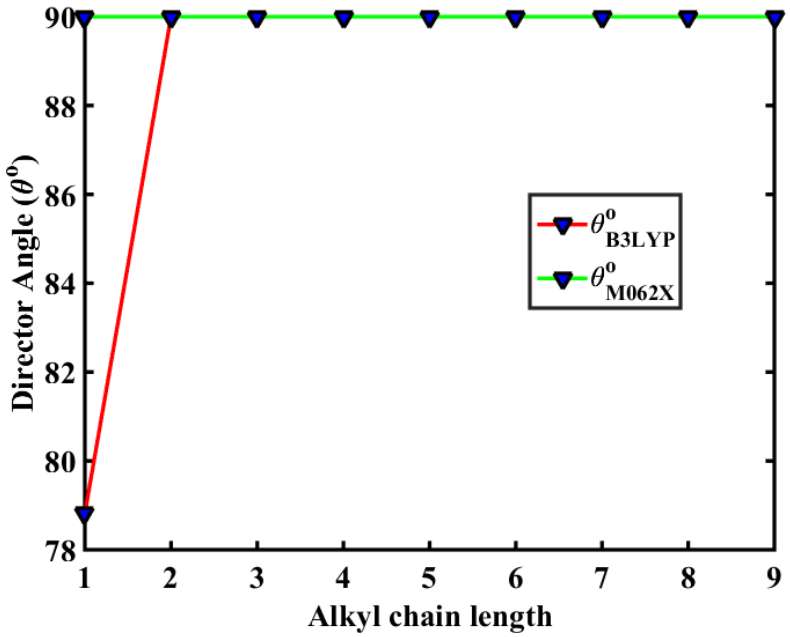

Figure 3.5. Director angle remains constant of the homologous series under the influence of the electric field.

3.3.6 Electron affinity and Ionization potential versus increased alkyl chain length of the APAPA liquid crystal

With an expansion of the length in alkyl chain series, electron affinity and the ionization potential shows the odd-even effect according to Figures 3.6 and 3.7. The APAPA5 liquid crystal increases the electron affinity and decreases the ionization potential; so, it is used for photoluminance objects. The value of the electron affinity is increased for the odd members and is decreased for the even members of the series.

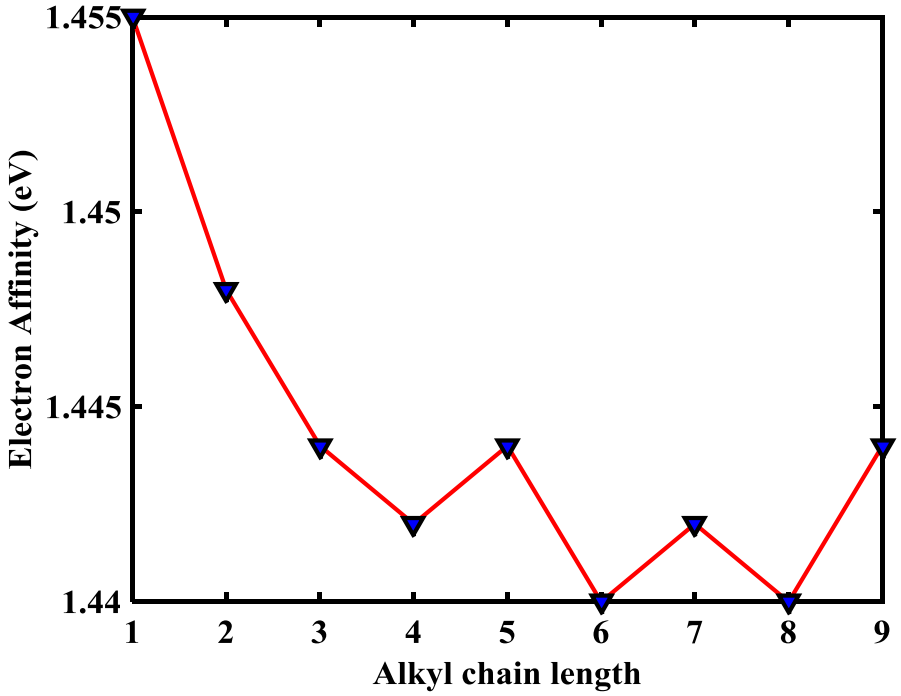

Figure 3.6. The odd-even effect of the homologous series indicates by electron affinity with an expansion of alkyl chain length.

While the value of ionization potential is reduced for the odd member of the series and it increases for the even member of the series. The electron affinity of the series correlates with the experimentally calculated temperature variation and theoretically calculated birefringence variation.

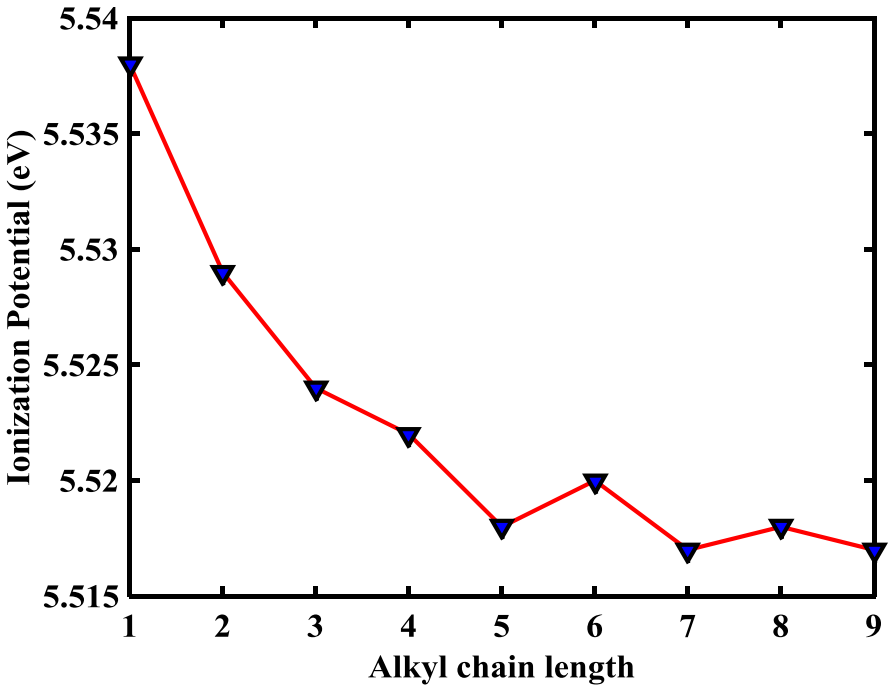

Figure 3.7. Odd-even effect of the homologous series is indicated by Ionization potential with an expansion of alkyl chain length.

3.3.7 Dipole moment of the homologous series and dipolar strength of the APAPA5 liquid crystal

The dipole moment of the homologous series continuously decreases with an extension of length in alkyl chain, which is given in Figure 3.8, and the dipolar strength of the APAPA5 liquid crystal is shown in Figure 3.9. The dipole moment of the homologous series continuously decreases, which is the reason due to which a higher range of homologous series is not useful for the liquid crystal properties. Dwivedi et al. [20] have suggested that the homologous series of the APAPA liquid crystal owes the higher absorbance due to stretching in the C-O atom. The adjacent work also describes that the dipolar strength contributes by the stretching in C-O atom, wagging in H atoms, and scissoring in C atoms in the alkyl chain.

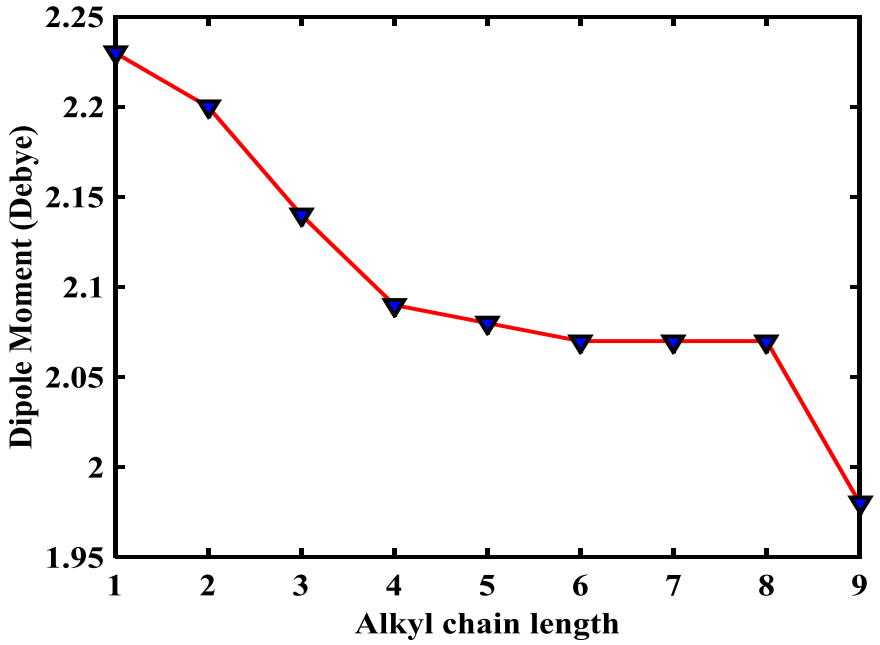

Figure 3.8. The dipole moment of the homologous series is calculated with an extension in alkyl chain length.

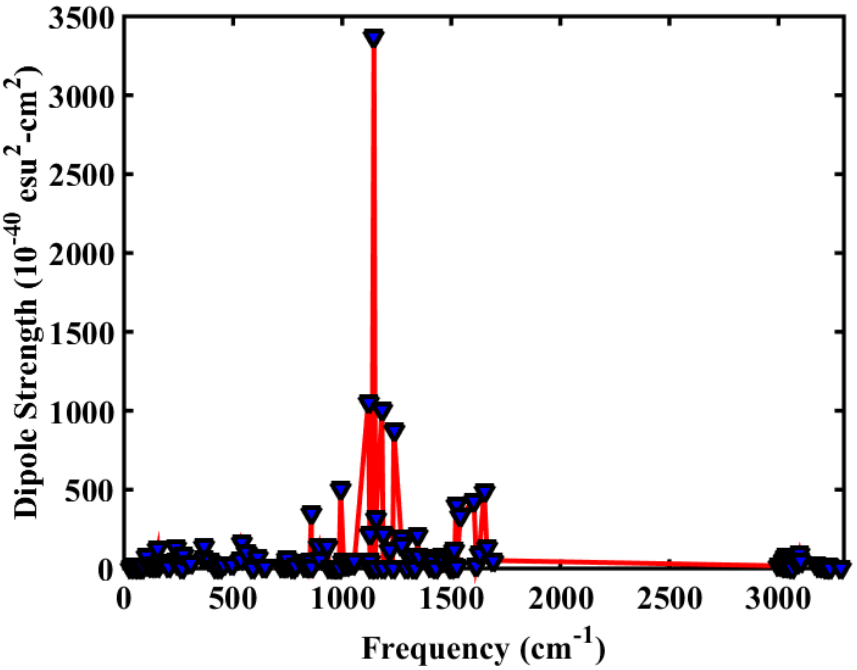

Figure 3.9. Dipolar strength of the APAPA5 liquid crystal with an increase in alkyl chain length.

The dipole moment is reduced due to the stretching in phenyl ring and the O atom which minimizes the frequency loop. Since APAPA5 liquid crystals consist of a wider area of transmission; so, this is used in the application of filtering and sensing.

3.3.8 HOMO-LUMO gap versus increased alkyl chain length of the APAPA liquid crystal

The homologous series of the APAPA liquid crystal shows a very high about 4 eV HOMO-LUMO gap, due to which it performs like an insulator. Few carbon atom numbers (1-3, 6) of the alkyl chain have marked 4.08 eV along with a low 4.07 eV HOMO-LUMO gap, represented in Figure 3.10. This gap is steeply increasing in APAPA6 liquid crystal due to the decrease in electron affinity, and therefore, the increase in ionization potential.

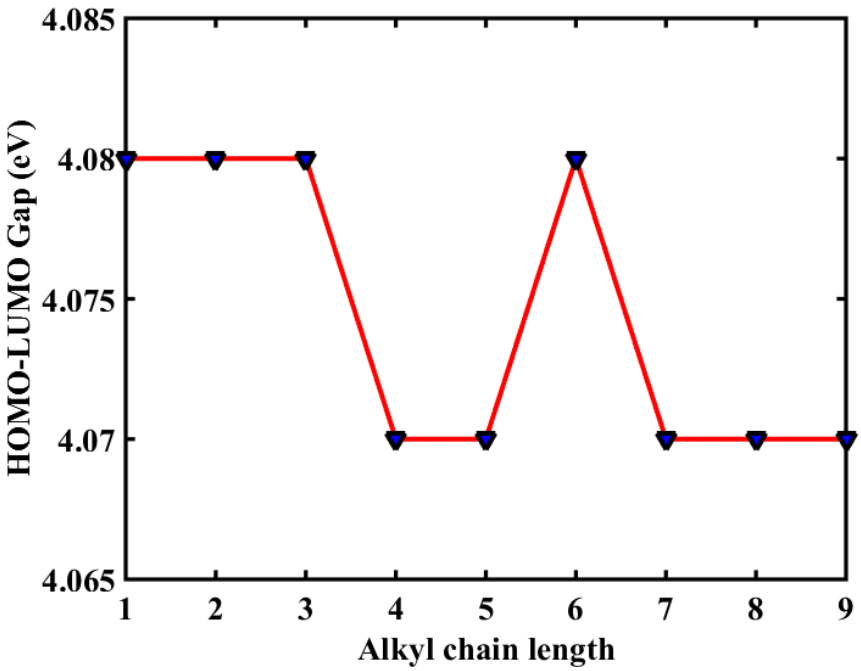

Figure 3.10. HOMO-LUMO gap of the homologous series calculated with an increased alkyl chain.

The order parameter, transition temperature, birefringence of the APAPA6 liquid crystal were also reduced because of the stretching in C-O atom, wagging in C atom of the alkyl chain which expresses a positive rotational strength.

3.4 Conclusion

The adjacent chapter, concludes that odd-even effect has been detected in homologous series of APAPA liquid crystals using the electric field of THz frequency region as well as under the impact of temperature too. The influence of electric field on the liquid crystal has also been associated with temperature variation. With the expansion of length of alkyl chain of the series, the electron affinity also with ionization potential show an odd-even effect. The birefringence also has the property of odd-even effect with electric field. The order parameter and refractive index do not show any odd-even effect with an increment of alkyl chain length. The director angle remains constant at $\theta=90°$ for the whole homologous series, which is best for the scattering applications. The homologous series expresses both positive and negative variations of birefringence, makes relevant application in electro-optics. The APAPA liquid crystal series is best for Photo luminance, insulating material, sensing, filtering, scattering, and THz application devices.

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Chapter-4

Electro-optical parameters with adverse order of 10CB liquid crystal molecule studied under the influence of an external high electric field: A theoretical approach

Chapter 4

Electro-optical parameters with adverse order of 10CB liquid crystal molecule studied under the influence of an external high electric field: A theoretical approach

4.1 Introduction

Liquid crystals are the intermediate phases that are considered mesomorphic phases. The molecular optical parameters of the nematic liquid crystals are studied by various scientific groups. The length and parity of flexible spacers are the main factors regarding this compound in case of determining its transitional properties. Because of the high value of molecular polarizability, it is also useful in optical communication. Molecular polarizability is essential in the fabrication of the display devices, as it reveals the action of light (EM wave) with liquid crystals [1-2]. The rod-like gold nanoparticles show the negative orientation order parameter and the large absorption anisotropy which enhances the optical birefringence with a reversal sign [3-4]. The rod-like (a negative ordered) nematic liquid crystal exists in parallel form with the 90° director angle [5-8]. The positive dipole liquids are investigating with the electric field

or and show the maximum torque in the impact of electric field [9-10]. Order parameter of the nematic LC comes from quenching of director orientation at a very high electric field of 10^8 V/m. The nanosecond switching under electrical remodeling of the order parameter influenced the optical applications in the electro-optical devices [11-12].

The structure of decyl cyano biphenyl holds a methyl group attached to the carbon chain, which gives rise to a stable smectic phase. It is used to calculate the surface temperature as various colours are observed over a surface of a liquid crystal. For detecting skin cancer in medical applications, this property is widely used. George William Gray discovered the pentyl cyano biphenyl, after that many attempts were made to synthesize similar homologous compounds. Cyano group is working as a substituent in the aromatic ring and used to changes the acidity in-ground as well as excited states. The homologous compound of cyano biphenyl is widely used in electro-optical devices because they are highly stable, give the colorless intermediate phase at room temperature, and have a positive value of dielectric anisotropy, and one particular effect shown by these compounds is known as the odd-even effect [13]. An alters the physical characteristics of a compound, depending upon the number of carbon atoms. Molecular dynamics is used to study this odd-even effect. Due to the peculiar nature of order and mobility at the microscopic and bulk level, they respond to stimuli very quickly [14-15].

The ground state energy of cyano biphenyl compounds depends on their particular configuration which is an important point to keep in mind while modeling these compounds since this ground state energy. It is quite easy to understand the interaction with various other compounds. These relative energies are also useful in the calculation

of thermodynamic properties such as entropy, free energies, etc. The alkyl chain can be easily broken down or displaced, which gives enhancement to multi conformational changes [16-18]. The higher homologous structure indicates planar structure which helps in stacking of the compound, which leads to rigidity, as compared to the lower homologous. 10CB liquid crystal has a higher value of the bandgap according to the HOMO-LUMO analysis, indicating it has a low amount of conductivity. Also, it is highly complex due to the substantial amount of dipole moment along the molecular axis. Cyano biphenyl is considered a suitable compound in the list of liquid crystals depending upon the various properties [19-21].

4.2 Computational Methodology

With the help of Gaussian 09 Software [22], 10CB liquid crystal molecule is optimized using DFT with method B3LYP [23-24], 6-31G** basis set [25]. An electric field having a scale of 0.000 a.u. to 0.200 a.u. with the gap of 0.0020 a.u, is applied to the 10CB liquid crystal molecule in parallel to the x-axis as well as normal to the y-axis of molecular geometry. Value of 1 a.u is 5.14 x 10^{11} V/m [26] or 1 a.u. = 6.5 x 10^{15} Hz. The molecular polarizability of 10CB compound is calculated after imposing an electric field. The molecular polarizabilities, extraordinary (α_e) towards the x-axis, and ordinary (α_o) phase towards the y-axis, is used for the calculation of the order parameter using equation no. 1, The total molecular energy following the effect of electric field find using finite-field energy equation which is given below:

$$E = E_o - \mu_i F_i - \frac{1}{2}\alpha_{ij}F_iF_j - \frac{1}{6}\beta_{ijk}F_iF_jF_k$$

In the above equation, E_o represents the total energy without using electric field. F_i denotes a component regarding an electric field, α_{ij} denotes the component of

polarizability, $\mu_{i,}$ is the component of the dipole moment, and β_{ijk} is the component of the first-order hyper-polarizability. The directions of the electric field are described using the subscripts i=x, j=y, and k=z. Using different polarization values under the electric field for x and y directions, we use mathematical formulation to study the optical parameters such as order parameter, birefringence, refractive index, and director angle. α, β, μ, and Δα are very important parameters in the numerical calculations applicable to the external electric field with the interval of 0.002 a.u. as below [27-28];

$$\alpha = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$

$$\beta = \left[(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{xxy} + \beta_{yzz})^2 + (\beta_{zzz} + \beta_{xxz} + \beta_{yyz})^2\right]^{1/2}$$

$$\mu = (\mu_x{}^2 + \mu_y{}^2 + \mu_z{}^2)^{1/2}$$

$$\Delta\alpha = 2^{-1/2}\left[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2\right]^{1/2}$$

$$\Delta\tilde{\alpha} = \alpha_e - \alpha_o$$

$$\Delta\tilde{\alpha} = S\Delta\alpha$$

Where $\tilde{\alpha}$ is known as mean isotropic polarizability.

Order Parameter (S):

$$S = \frac{\alpha_e - \alpha_o}{\alpha_e + \alpha_o} \qquad (4.1)$$

Director angle or Magic angle (θ):

$$\theta = \cos^{-1}\left[\frac{(2S+1)}{3}\right] \qquad (4.2)$$

Birefringence (Δn):

$$\alpha = \frac{2\alpha_o + \alpha_e}{3}, \quad \gamma_e = \alpha + \frac{2(\alpha_e - \alpha_o)}{3S}, \quad \gamma_o = \alpha - \frac{(\alpha_e - \alpha_o)}{3S}$$

$$n_e = \frac{7}{2\sqrt{10}} + \frac{\left(2\sqrt{10}/5\right)\pi N\alpha}{1 - \frac{4\pi N\alpha}{3}} + \frac{\left(4\sqrt{10}/15\right)\pi NS(\gamma_e - \gamma_o)}{1 - \frac{4\pi N\alpha}{3}}$$

$$n_o = \frac{7}{2\sqrt{10}} + \frac{\left(2\sqrt{10}/5\right)\pi N\alpha}{1 - \frac{4\pi N\alpha}{3}} - \frac{\left(2\sqrt{10}/15\right)\pi NS(\gamma_e - \gamma_o)}{1 - \frac{4\pi N\alpha}{3}}$$

$$\Delta n = \frac{7}{2\sqrt{10}} + \frac{\left(2\sqrt{10}/5\right)\pi N\alpha}{1 - \frac{4\pi N\alpha}{3}} \qquad (4.3)$$

4.3 Results & Discussion

The 10CB liquid crystal shows three phases with a functioning electric field which is given in Figure 4.1. The electric field from 0.010 a.u to 0.028 a.u shows the first state of liquid crystal and the molecule is more stable in this range, From 0.034 a.u to 0.052 a.u 10CB expresses the second state, the molecule is less stable in comparison with the previous stage and from 0.056 a.u to 0.072 a.u represents the third phase where molecule remains unstable for this range and finally, the molecule is converted into isotropic phase. The 0.008 a.u, 0.032 a.u and 0.054 a.u reveal phase transition field of 10CB. In the field of 0.074 a.u, the molecule finally gains the isotropic phase. The positive order parameter of 10CB is 0.63, where the negative order parameter comes out -0.40 shown in Figure 4.1. With the field of 0.098 a.u, the molecule reveals the negative order parameter. The highest and lowest range to order parameter for ordinary liquid crystal is +0.8 to -0.5.

The 10CB liquid crystal also has an order parameter that ranges between +0.8 to -0.5. At a higher electric field (0.098 a.u), the molecule maintains the stability of the isotropic phase. After the field of 0.078 a.u, the molecule gains 0.00 value of order parameter and exhibits the isotropic state.

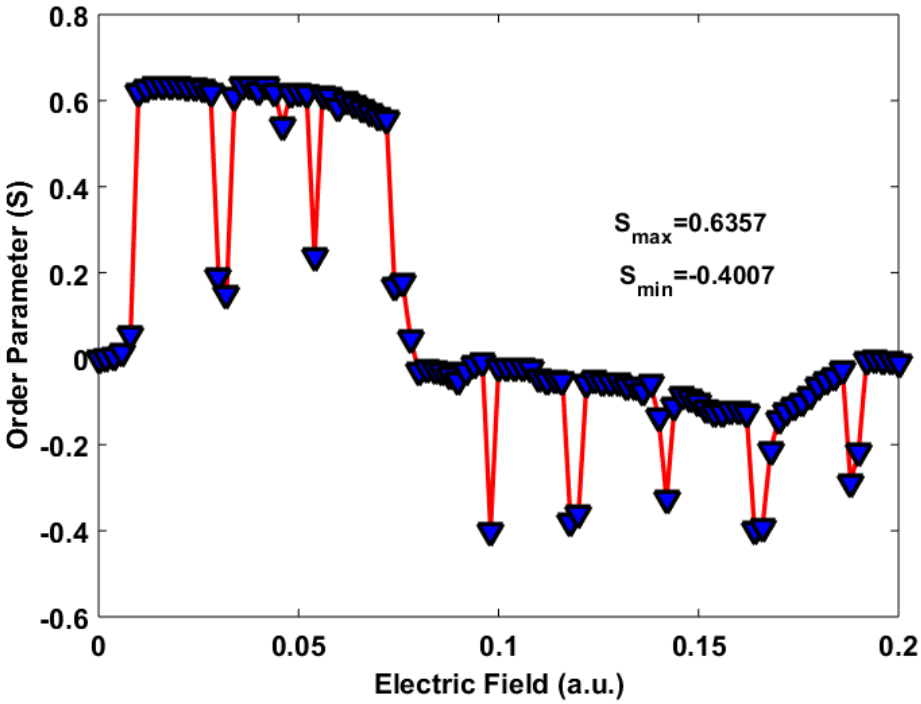

Figure 4.1 Order parameter of 10 CB liquid crystal under the electric field. (It is determined with the mathematical equation 1).

Liu et al. [29] reported that the bandgap of liquid crystals can be controlled under a functioning electric field, which may be used as tunable bandgap applications. The magic angle of the organic molecule is found at 54.74^{o} of LC. Highest value of the director angle is 75.09, and lowest value is coming out 29.52, which is shown in Figure 4.2. The director angle (θ) is stable for the smectic A phase, whereas θ is stable for the isotropic state, by the increment in an electric field. According to equation no. 2, the director angle is comparable with the order parameter. The bandgap is decreased for

the smectic A state whereas it increases for the isotropic state. For positive order parameter, band gap decreases while the order parameter increases for the negative order parameter.

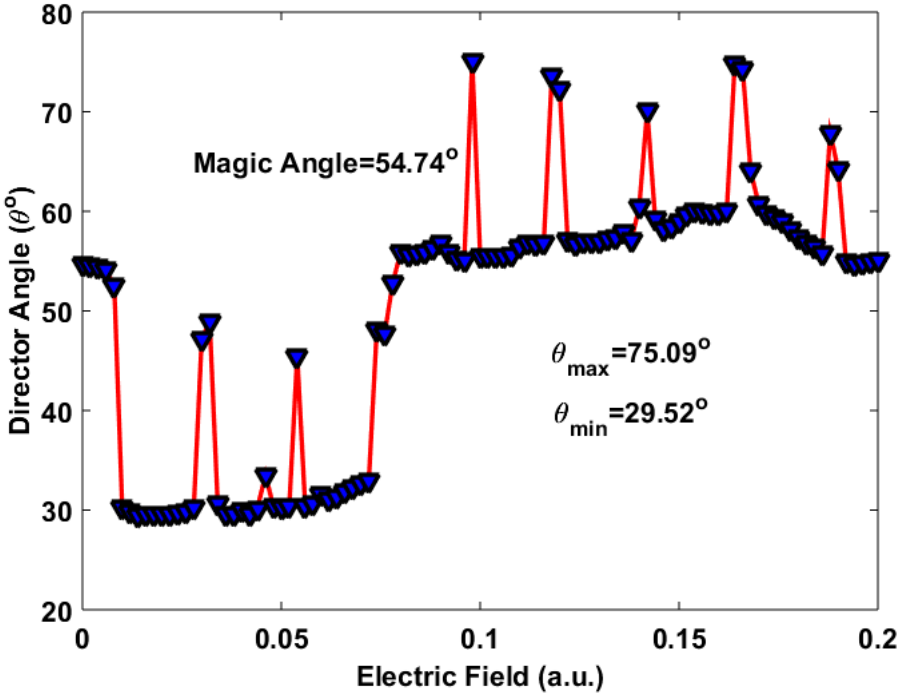

Figure 4.2 Director angle of 10CB liquid crystal. (The director angle remains in a stable position for the smectic along with the isotropic state. The lower value of the director angle is 29.52^o and the higher value of the director angle is 75.09^o; it means the molecule of 10CB is not perfectly along an electric field. At 90 degrees, 10CB molecules align along an electric field with negative order of liquid crystals).

Mitra et al. [30-31] described the molecular polarizability calculated by Vuks and Neugebauer's formula responsible for the calculation of birefringence, refractive index, and order parameter. In the present work, we are using the modified formula of the birefringence [28]. The order parameter related to the director angle remarkably the director angle is easily calculated by the order parameter given in equation no. 2. Liu et

al. [3-4] reported the negative orientation order parameter, and the large absorption anisotropy enhances the optical birefringence with a reversal of signs shown in Figure 4.3.

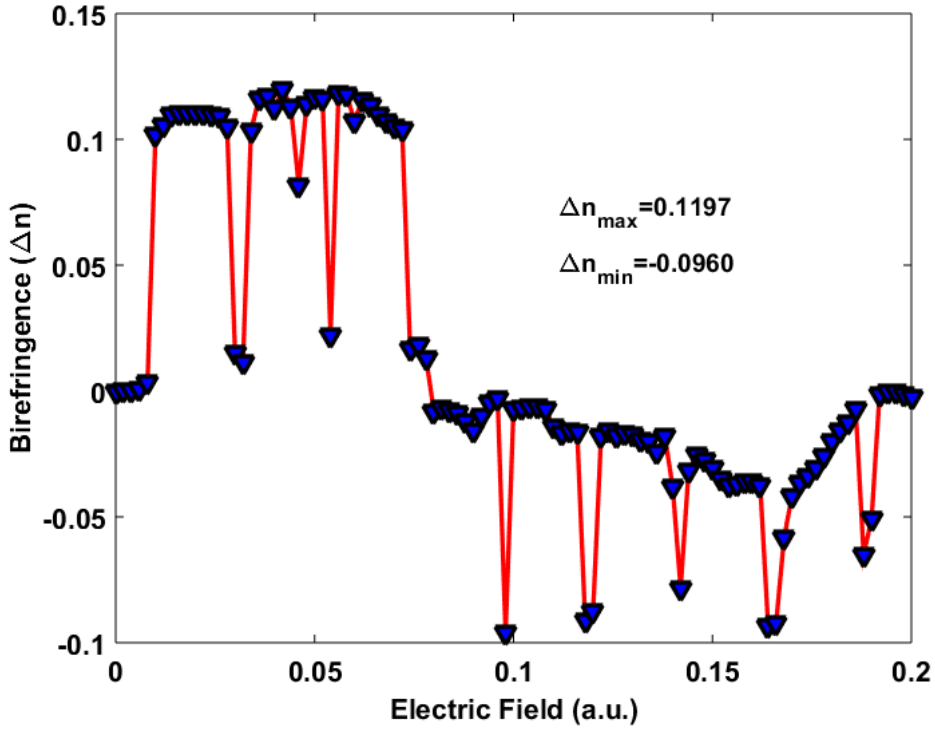

Figure 4.3 Birefringence of 10CB liquid crystal. (The maximum birefringence of 10CB LC is Δn=0.1197 and the minimum birefringence is Δn=-0.0960).

Wood et al. [32] described that the bandgap of nematic liquid crystal decreases under an applied electric field. Busch et al. [33] revealed the inverse birefringent nematic liquid crystal used for the photonic bandgap materials relative to an electric field. Dipole moment regarding the 10CB compound is found to be 6.09 Debye, and the existing band gap is 3.60 eV, which is presented in Figure 4.4. As the result of the large bandgap of 10CB, LC behaves as an insulator; therefore, insulating materials are used in the THz frequency range for better performance. The HOMO-LUMO gap gives molecular stability to the 10CB molecule. The dipolar strength of the 10CB liquid

crystal is maximum and contributes to the asymmetric stretching of the C-H atom of the alkyl chain, which is presented in Figure 4.5.

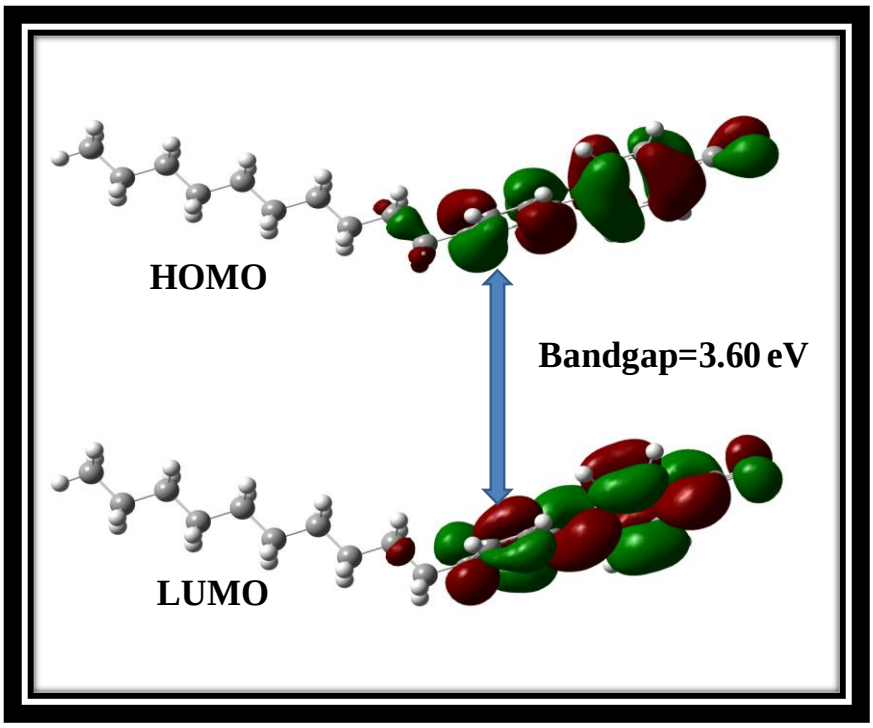

Figure 4.4 Bandgap of 10CB liquid crystal.

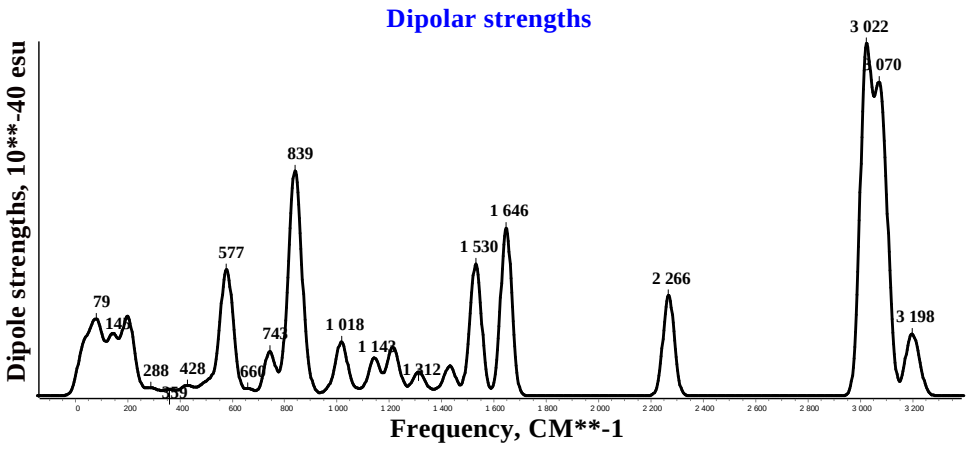

Figure 4.5 Dipolar strength of 10CB liquid crystal measured by DFT methodology.

4.4 Conclusion

From the chapter, it has been found that the 10CB liquid crystal expresses a negative order parameter with the high electric field, and the C≡N atom stretching is decreased in 10CB that shows the decrement of the order parameter. The HOMO and LUMO gap increases for the negative order parameter and the same decreases for the positive order parameter. The director angle of the molecule is linked by the order parameter; if the order parameter is affected, then director angle is also affected. The negative orientation of the order parameter with the large absorption anisotropy increases the optical birefringence with a negative sign. Hence 10CB liquid crystal is suitable for terahertz applications. In 10CB liquid crystal the IR absorbance increases which are responsible for the negative order parameter. The bandgap is affected by applying the electric field, so the liquid crystals are used as tunable bandgap applications. The 10CB liquid crystal is a member of the cyano biphenyl series; therefore, dipole strength, maximum contributed by the C-H atom asymmetric stretching of the alkyl chain length, and 10CB liquid crystal have a large bandgap (3.60 eV). The order parameter influenced the parameters of electro-optics in liquid crystals within the field from display devices to optical switches.

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Chapter-5

Comparative DFT study of parallel and antiparallel conformation of 5CB and 6CB liquid crystal dimers

Chapter 5

Comparative DFT study of parallel and antiparallel conformation of 5CB and 6CB liquid crystal dimers

5.1 Introduction

The liquid crystal dimers shows the broad range of mesomorphic states of the different optical applications [1-3]. Among the different organic liquid crystals, 5CB and 6CB molecules consist of conjugated rigid cores in long-range and cyano groups (polar) which are essential to exhibit higher birefringence in comparison to other liquid crystals [4-6]. The 5CB liquid crystal has linear conjugation of π-electron with the rigid core (biphenyl) and the cyano group, therefore, the dielectric and optical anisotropic properties are comparatively higher in 5CB liquid crystal [7-8]. The 6CB liquid crystal has a higher dipole moment in comparison to the 5CB liquid crystal [9-10] and the existing cyano (CN) groups in the molecular structure have extreme polarization and Huckel charges on the triple bonded carbon and hydrogen atoms. In the molecular structure, all the CB derivative dimers are building using the strong intermolecular

interactions between the nitrile group [11-18]. The dimer structure of two 5CB molecules (5CB-5CB) has interaction energy at 4.2Å distance [19].

In the nematic liquid crystals, the enthalpy decreases with the pressure applied to molecules. The dimer o 5CB show different types of conformations and electrostatic energies. In the antiparallel conformation of nematic phase liquid crystal, the electrostatic repulsion energies between the dipole of the cyano groups vanished [20]. In contrast to optical applications of liquid crystals, the polar cyano-biphenyl-derived liquid crystals play a prominent role in display applications. In the antiparallel conformations of liquid crystal, dimers have sufficiently reduced dipole moment. The distribution of liquid crystals expresses the formation of mesophases as well as regulates the optical properties especially display applications [21]. In the molecule, the molecular axis also dependent on the cyano group shows a high dipole moment. The textures of cyanobiphenyl organic compounds are generally colorless, have low melting points and are photochemically and chemically stable [22].

In the molecular structure of liquid crystals, different molecular forces exist depending on the polarity of the groups. The acting intermolecular forces in the molecular structure of 5CB and 6CB are strong due to the higher polarity of the terminal groups of the molecules [23]. Depending on the alkyl chain, the different liquid crystal expands their series with different optical properties. The even member of the cyano-biphenyl liquid crystal dimer series are aligned in antiparallel conformations, with strong interaction of CN group with phenyl in the dimer [24].

The negative values of intermolecular energy of the liquid crystal dimer are accountable for the antiparallel conformations having negative entropy [25]. The homogeneous phase of the liquid crystal has negative interaction energy and entropy of the dimers,

The entropy of the 6CB LC is higher between nematic to isotropic (N-I) phase transition corresponding to 5CB liquid crystal [26, 27]. Here only π-electrons appear in phenyl rings and σ-electrons are present on cyclohexyl rings. The presence of phenyl and cyclohexyl rings in the liquid crystal provides the short-range intermolecular force which is essential for the formation of the nematic state and modifies the optical properties including absorption, dielectric indices, birefringence, viscosity, elastic constant, etc.

The length and constitution of alkyl chain modify the dielectric property of liquid crystal. In the polar terminal group of liquid crystals, the cyano group adds significantly to the changes in the dielectric anisotropy of the molecules. Cyano group provides high anisotropy and birefringence to the molecules because of high polarity due to which the liquid crystals show instability, insufficient resistivity, high viscosity for UV explorations. These liquid crystal compounds are not suitable for high-temperature device applications like projection display devices. Besides, liquid crystals with the CN terminal groups are dissociated from UV illumination [28-33]. The length of the pair is higher for the antiparallel conformation of CB-based liquid crystal dimers. So it minimizes the dipolar energy of the molecular structure [34]. While the even member of dimers (6CB) frequently obtain antiparallel conformations and hence the dipole moment of the dimer decrease. Also, the odd member of liquid crystal dimers (5CB) generally grows where inclined or parallel mesogenic phase and increases the dipolar energy supported with the length of the dimer is minor [35].

The liquid crystals 1CB to 3CB molecules have a rod-like structure and forms crystalline arrangements. Due to enhanced intermolecular forces in the geometry, the polarity of CN group increases the property of anisotropy of liquid crystals. The

molecules have molecular rigidity due to the triple bond of cyano group and hence structure cannot capable of rotation of molecules [36-40].

5.2 Computational Methodology

Using the NWChem software package [41], all the geometries of 5CB and 6CB liquid crystal have been optimized using density functional theory with B3LYP [42-43] method and 6-31G basis set [44]. We have generated 360 conformations and out of 360 conformations, we have taken only 4 conformations of 5CB and 6CB dimers of minimum energies. All monomers of liquid crystals arbitrarily interact with each other and perform minimum energy calculations under free optimizations. Initially, we have generated 5CB, 6CB, and 5CB-6CB liquid crystal dimers, and the first monomer in the dimer is fixed while the second monomer is made to move in a forward or backward direction with a distance of 0.5Å leading to enhancement or decrement in the thermochemistry, interaction energy, polarizability, and dipole moment depending on the functioning conformations.

5.3 Results and discussion

Concerning molecular interactions, different molecular properties of different conformations of 5CB, 6CB, and their dimers have been calculated using DFT method LC-BLYP with the help of NWChem software in the following sections.

5.3.1 5CB-5CB Parallel conformation

In this part, we have studied the interaction properties of the 5CB-5CB dimer in the parallel conformation as represented in Figure 5.1. In the 5CB-5CB conformation, the polarizability decreases as the monomer moves forward or backward as shown in

Figure 5.1. The total energy of the system increases while overall energy drops. The cyano group of the first monomer interacts with the benzene of the second monomer at a distance of 2.43Å. Similarly, at 2.71Å distance, the terminal group of the first monomer interacts with the benzene ring of the second monomer. All the possible conformations were considered with free optimization and have the lowest energy with parallel conformation.

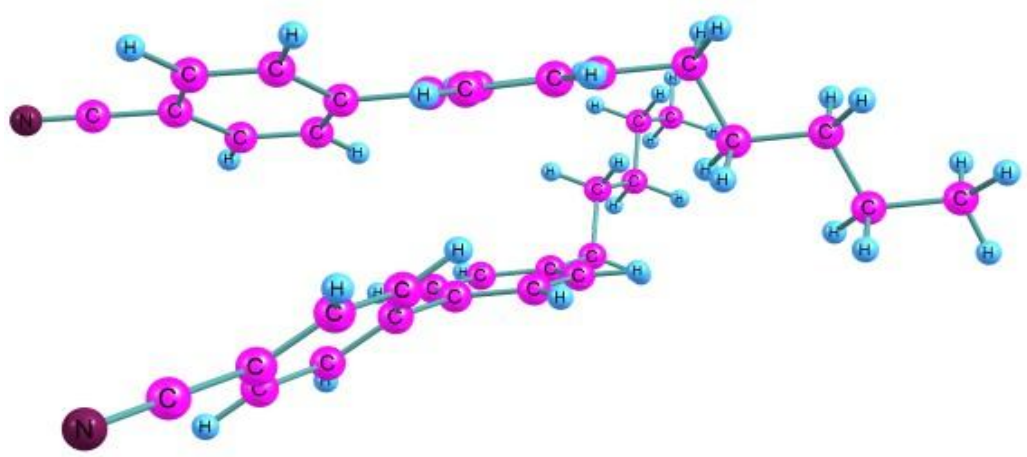

Figure 5.1 5CB liquid crystal dimer in the parallel conformation.

The monomers (5CB) arbitrarily interact with each other; the first monomer (5CB) remains stable and the other second monomer (5CB) moves onward, then the following interaction properties of the dimer in these conformations are tabulated as in Table 5.1, and hence we accomplish the succeeding remarks as:

1. The value of the HOMO-LUMO gap continuously increases.

2. The value of polarizability continuously decreases.

3. The total energy of the dimer continuously increases.

4. The dipole moment of the dimer continuously decreases

5. In the dimer, the internal thermal energy first decreases and then continuously increases.

6. The value of constant volume heat capacity first decreases and then increases in the dimer.

7. The entropy of the dimer first decreases and then increases.

8. The value of zero-point energy of the dimer first decreases and then increases.

9. The value of enthalpy of the dimer first decreases and then increases continuously.

10. Gibbs's energy of the dimer first decreases then increases and then again decreases

Table 5.1 The molecular properties of the 5CB-5CB dimer with parallel conformation at different positions in the forward direction.

5CB-5CB Parallel conformation	**0.5Å**	**1.0Å**	**1.5Å**	**2.0Å**	**2.5Å**
HOMO-LUMO*(eV)*	4.50	4.51	4.51	4.52	4.52
Dipole moment *(Debye)*	10.37	10.36	10.36	10.35	10.34
Thermal Energy*(kcal/mol)*	427.71	427.69	427.08	427.07	427.68
Polarizability*(kcal/mol)*	256867	256779	256691	256603	256522
Total Energy *(kcal/mol)*	-9440.86	-9440.91	-9440.95	-9440.99	-9441.02
Heat capacity (C_v) *(kcal/mol)*	0.14	0.14	0.13	0.13	0.14
Entropy *(kcal/mol)*	0.23	0.23	0.22	0.22	0.23
ZPE*(kcal/mol)*	404.53	404.50	404.44	404.43	404.46
Enthalpy *(kcal/mol)*	428.29	428.28	427.66	427.66	428.27
Gibbs Energy *(kcal/mol)*	358.39	357.92	360.19	360.06	358.19

When the first monomer (5CB) is stable and the second monomer (5CB) is proceeding backward in direction, then all possible properties of this conformation can be given as Table 5.2, and we can draw the following inferences:

1. The value of the HOMO-LUMO gap continuously decreases.

2. The value of polarizability of the dimer continuously decreases.

3. The value of the total energy of the dimer increases and then decreases continuously.

4. The dipole moment of the dimer first decreases and then increases continuously.

5. The value of internal thermal energy of the dimer continuously increases.

6. The value of the constant volume heat capacity of the dimer remains constant.

7. The value of entropy of the dimer first increases and then decreases.

8. The value of zero-point energy of the dimer first increases and then decreases

9. The value of Enthalpy of the dimer continuously increases.

10. The value of Gibbs's energy of the dimer first decreases and then increases and again decreases.

Table 5.2 The molecular properties of the 5CB-5CB dimer with parallel conformation at a different position in the backward direction.

5CB-5CB Parallel conformation	**0.5Å**	**1.0Å**	**1.5Å**	**2.0Å**	**2.5Å**
HOMO-LUMO*(eV)*	4.51	4.51	4.50	4.49	4.48
Dipole moment *(Debye)*	10.35	10.34	10.34	10.35	10.35
Thermal Energy*(kcal/mol)*	427.68	427.69	427.72	427.74	427.74
Polarizability*(kcal/mol)*	256377	256308	256239	256183	256120

Total Energy *(kcal/mol)*	-9440.06	-9440.07	-9440.07	-9440.07	-9440.06
Heat capacity (C_v)*(kcal/mol)*	0.14	0.14	0.14	0.14	0.14
Entropy *(kcal/mol)*	0.23	0.24	0.23	0.23	0.22
ZPE*(kcal/mol)*	404.46	404.46	404.50	404.54	404.53
Enthalpy *(kcal/mol)*	428.27	428.28	428.30	428.33	428.33
Gibbs Energy *(kcal/mol)*	358.11	357.89	358.25	358.43	358.16

5.3.2 5CB-5CB Antiparallel conformation

In this part, we investigate the interaction properties of the 5CB-5CB dimers in the antiparallel configuration (Figure 5.2).

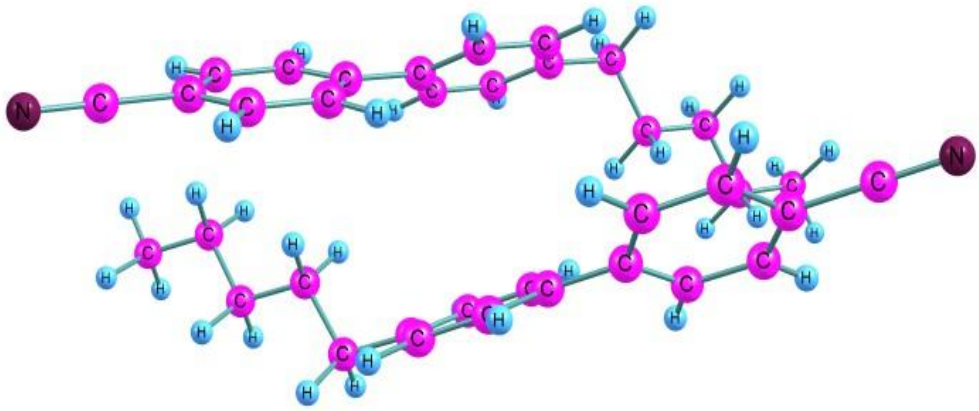

Figure 5.2 5CB liquid crystal dimer in antiparallel conformation.

According to Figure 5.2, the polarizability of antiparallel conformation of the 5CB-5CB dimer continuously decreases when the monomer 5CB moves forward or backward direction. The 5CB-5CB antiparallel conformation has the smallest dipole moment compared to the other 4 conformations of the 5CB dimer. The CN group of the 5CB interacts with the end of another monomer of 5CB at a 2.82Å distance. The benzene ring of the 5CB interacts with the benzene ring of another 5CB at a 2.60Å

distance. The benzene ring of the first monomer interacts with the benzene ring of the second monomer at a 2.39Å distance. The cyano group of the first monomer interacts with the end of the second monomer at a 2.80Å distance. The 5CB-5CB antiparallel conformation shows the least energy in comparison to all the conformations of the 5CB dimer. The interaction energy is higher in comparison to other conformations of the 5CB dimer. The molecular properties of this conformation are given in Table 5.3.

1. The value of the HOMO-LUMO gap of the dimer remains constant.

2. The value of polarizability of the dimer continuously decreases.

3. The value of the total energy of the dimer continuously increases.

4.The dipole moment of the dimer continuously increases.

5. The value of internal thermal energy of the dimer continuously decreases.

6. The value of the constant volume heat capacity of the dimer remains constant.

7. The value of entropy of the dimer remains constant.

8. The value of zero-point energy first decreases and then increases and again decreases

9. The value of enthalpy of the dimer continuously decreases.

10. The value of Gibbs's energy first decreases and then increases and again decreases.

Table 5.3 The molecular properties of the 5CB-5CB dimer with antiparallel conformation at a different position in the forward direction.

5CB-5CB Antiparallel conformation	**0.5Å**	**1.0Å**	**1.5Å**	**2.0Å**	**2.5Å**
HOMO-LUMO*(eV)*	4.53	4.53	4.53	4.53	4.53
Dipole moment *(Debye)*	4.69	4.70	4.72	4.73	4.74
Thermal Energy*(kcal/mol)*	427.66	427.66	427.65	427.64	427.63

Polarizability*(kcal/mol)*	256478	256346	256227	256107	255994
Total Energy *(kcal/mol)*	-9440.10	-9440.20	-9440.30	-9440.30	-9440.40
Heat capacity (C_v) *(kcal/mol)*	0.14	0.14	0.14	0.14	0.14
Entropy *(kcal/mol)*	0.23	0.23	0.23	0.23	0.23
ZPE*(kcal/mol)*	404.43	404.42	404.67	404.39	404.36
Enthalpy *(kcal/mol)*	428.25	428.24	428.24	428.23	428.21
Gibbs Energy *(kcal/mol)*	358.44	358.33	358.36	358.27	357.94

When the former monomer of 5CB is fixed and the further monomer transfers backward then all possible interaction characteristics of obtained conformations are tabulated as Table 5.4, and hence we conclude as:

1. The value of the HOMO-LUMO of the dimer gap increases continuously.

2. The value of polarizability of the dimer continuously decreases.

3. The value of the total energy of the dimer continuously increases.

4. The dipole moment of the dimer continuously increases.

5. The value of internal thermal energy of the dimer continuously increases.

6. The value of the constant volume heat capacity of the dimer remains constant.

7. The value of entropy of the dimer remains constant.

8. The value of zero-point energy of the dimer first decreases and then increases.

9. The value of enthalpy of the dimer first decreases and then increases.

10. The value of Gibbs's energy of the dimer first decreases and then increases.

Table 5.4 The molecular properties of the 5CB-5CB dimer with antiparallel conformation at a different position in the backward direction.

5CB-5CB Antiparallel conformation	**0.5Å**	**1.0Å**	**1.5Å**	**2.0Å**	**2.5Å**
HOMO-LUMO*(eV)*	4.53	4.53	4.53	4.53	4.54
Dipole moment *(Debye)*	4.76	4.76	4.77	4.78	4.78
Thermal Energy*(kcal/mol)*	427.59	427.59	427.59	427.60	427.61
Polarizability*(kcal/mol)*	255794	255699	255612	255536	255474
Total Energy *(kcal/mol)*	-9440.30	-9440.40	-9440.50	-9440.60	-9440.70
Heat capacity (C_v) *(kcal/mol)*	0.14	0.14	0.14	0.14	0.14
Entropy *(kcal/mol)*	0.23	0.23	0.23	0.23	0.23
ZPE*(kcal/mol)*	404.29	404.27	404.27	404.29	404.30
Enthalpy *(kcal/mol)*	428.18	428.17	428.18	428.19	428.19
Gibbs Energy *(kcal/mol)*	357.27	357.25	357.23	357.36	357.43

5.3.3 5CB-5CB Cross conformation

Here, we study the interaction properties of the same dimer (5CB-5CB) but in the cross to each other conformation, as shown in Figure 5.3. The polarizability, Gibbs energy, and total energy of the performed conformation decrease when the monomer (5CB) is moves in a forward or backward direction. The benzene ring of the first monomer of the 5CB interacts with the end of the second monomer of the 5CB at a distance of 2.96Å while the benzene ring of the second monomer interacts with the end of the first monomer of the 5CB at a distance of 2.87Å. The chosen cross conformation of 5CB-5CB shows better interaction energy in comparison to 5CB dimer parallel

conformation. This conformation does not provide the finest interaction in comparison to antiparallel conformation due to higher electronic energy.

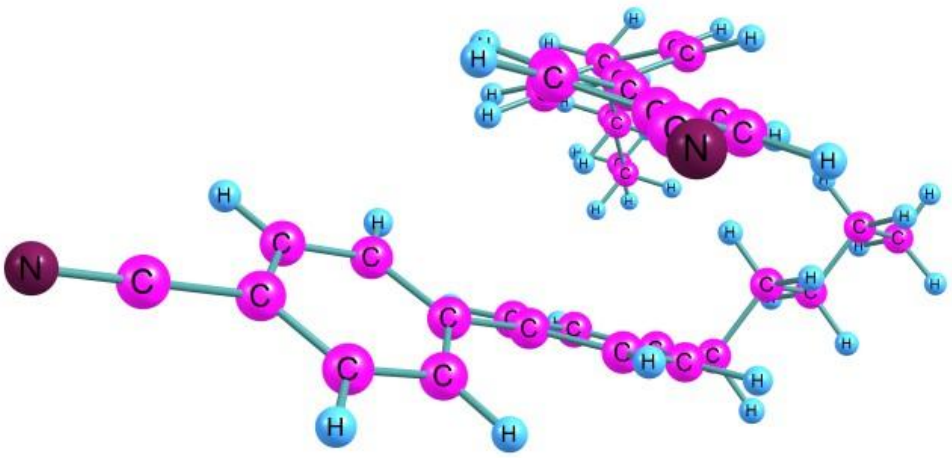

Figure 5.3 5CB liquid crystal dimer in cross conformation.

When the first monomer is being stable and the second monomer moves in a forward direction then all the possible properties of the dimer in this conformation is given in Table 5.5, and we conclude the important conclusions:

1. The value of the HOMO-LUMO gap of the dimer continuously increases.

2. The value of polarizability of the dimer continuously decreases.

3. The value of the total energy of the dimer continuously decreases.

4. The dipole moment of the dimer continuously increases.

5. The value of internal thermal energy of the dimer first decreases and then increases

6. The value of constant volume heat capacity of the dimer first decreases and then increases.

7. The value of entropyof the dimer decreases and then continuously increases.

8. The value of zero-point energy of the dimer continuously decreases.

9. The value of enthalpy first of the dimer decreases and then increases.

10. The value of Gibbs's energy of the dimer first increases and then decreases.

Table 5.5 The molecular properties of the 5CB-5CB dimer with cross conformation at a different position in the forward direction.

5CB-5CB Cross conformation	**0.5Å**	**1.0Å**	**1.5Å**	**2.0Å**	**2.5Å**
HOMO-LUMO*(eV)*	4.51	4.51	4.52	4.52	4.52
Dipole moment *(Debye)*	10.47	10.48	10.49	10.49	10.49
Thermal Energy*(kcal/mol)*	427.61	427.00	426.98	426.98	427.56
Polarizability*(kcal/mol)*	256089	255963	255844	255731	255630
Total Energy *(kcal/mol)*	-9440.40	-9440.30	-9440.20	-9440.10	-9440.00
Heat capacity (C_v) *(kcal/mol)*	0.14	0.13	0.13	0.13	0.14
Entropy *(kcal/mol)*	0.23	0.22	0.22	0.22	0.23
ZPE*(kcal/mol)*	404.38	404.34	404.33	404.32	404.31
Enthalpy *(kcal/mol)*	428.19	427.58	427.57	427.56	428.15
Gibbs Energy *(kcal/mol)*	358.09	360.02	359.93	359.87	357.49

When the first monomer of the dimer is stable and the second monomer of the dimer moves backward in direction, then interaction properties of such conformation is given as Table 5.6, and hence we can draw the following conclusions:

1. The value of the HOMO-LUMO gap of the dimer remains constant.

2. The value of polarizability of the dimer continuously decreases.

3. The value of the total energy of the dimer continuously decreases.

4. The dipole moment of the dimer increases constantly.

5. The value of internal thermal energy of the dimer continuously increases.

6. The value of the constant volume heat capacity of the dimer continuously increases.

7. The value of entropy of the dimer continuously increases.

8. The value of zero-point energy of the dimer first decreases and then increases.

9. The value of enthalpy of the dimer continuously increases.

10. The value of Gibbs's energy of the dimer continuously decreases.

Table 5.6 The molecular properties of the 5CB-5CB dimer in cross conformation at a different position in the backward direction.

5CB-5CB Cross conformation	**0.5Å**	**1.0Å**	**1.5Å**	**2.0Å**	**2.5Å**
HOMO-LUMO*(eV)*	4.51	4.51	4.51	4.51	4.51
Dipole moment *(Debye)*	10.50	10.50	10.51	10.51	10.52
Thermal Energy*(kcal/mol)*	423.97	426.96	426.96	427.56	427.56
Polarizability*(kcal/mol)*	255436	255348	255267	255197	255122
Total Energy *(kcal/mol)*	-9440.10	-9440.08	-9440.06	-9440.05	-9440.03
Heat capacity (C_v) *(kcal/mol)*	0.13	0.13	0.13	0.14	0.14
Entropy *(kcal/mol)*	0.22	0.22	0.22	0.23	0.23
ZPE*(kcal/mol)*	404.29	404.27	404.27	404.28	404.28
Enthalpy *(kcal/mol)*	427.55	427.55	427.55	428.14	428.14
Gibbs Energy *(kcal/mol)*	359.67	359.56	359.48	353.21	357.10

5.3.4 6CB-6CB Parallel conformation

Now, we investigate the interaction properties of the 6CB-6CB dimer in parallel conformation, (Figure 5.4).

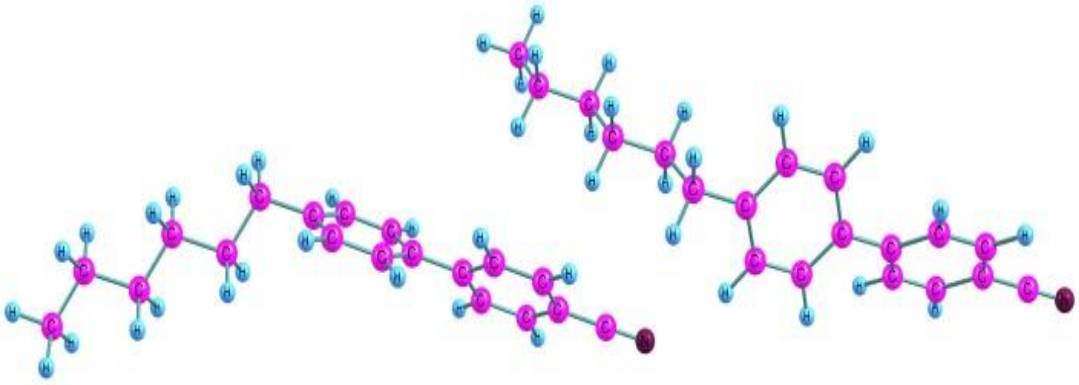

Figure 5.4 6CB liquid crystal dimer in parallel conformation.

The 6CB-6CB liquid crystal dimer in the parallel geometrical, the total energy, polarizability, and internal energy increases, when the monomer (6CB) moving in forward or backward in direction. The benzene ring of the former molecules (6CB) interacts with the benzene ring of the second molecules (6CB) at a distance of 2.43Å. The benzene-benzene interaction at 2.43Å is equal to benzene-benzene interaction of 6CB dimers under parallel conformations. The tail of the first molecule 6CB interacts with the benzene of the other monomer 6CB at a fixed 2.80Å distance. Also tail of the second molecule 6CB interacts with the benzene ring of the first 6CB at 2.63Å distance. When the first monomer is kept stable and the second monomer moving in a forward direction then all properties of the conformation are given in Table 5.7, and the following statements are described for this table which is as follows:

1. The value of the HOMO-LUMO gap of the dimer is constant.

2. The value of polarizability of the dimer continuously increases.

3. The value of the total energy of the dimer continuously increases.

4. The dipole moment of the dimer continuously decreases.

5. The value of internal thermal energy of the dimer continuously increases.

6. The value of the constant volume heat capacity of the dimer remains constant.

7. The value of entropy of the dimer remains constant.

8. The value of zero-point energy of the dimer first increases and then decreases and again increases.

9. The value of enthalpy of the dimer remains constant.

10. The value of Gibbs's energy of the dimer first increases and then decreases and again increases.

Table 5.7 The molecular properties of the 6CB-6CB dimer with parallel conformation at a different position in the forward direction.

6CB-6CB Parallel conformation	**0.5Å**	**1.0Å**	**1.5Å**	**2.0Å**	**2.5Å**
HOMO-LUMO*(eV)*	4.63	4.63	4.63	4.63	4.63
Dipole moment *(Debye)*	10.43	10.42	10.41	10.40	10.39
Thermal Energy*(kcal/mol)*	465.08	465.08	465.08	465.09	465.09
Polarizability*(kcal/mol)*	272065	272203	272341	272479	272623
Total Energy *(kcal/mol)*	-9933.32	-9933.38	-9933.43	-9933.48	-9933.54
Heat capacity (C_v) *(kcal/mol)*	0.15	0.15	0.15	0.15	0.15
Entropy *(kcal/mol)*	0.25	0.25	0.25	0.25	0.25
ZPE*(kcal/mol)*	440.16	440.16	440.17	440.16	440.17
Enthalpy *(kcal/mol)*	465.67	465.67	465.67	465.67	465.67

Gibbs Energy *(kcal/mol)*	390.70	390.76	390.76	390.43	390.55

When the first monomer (6CB) is kept stable and the second monomer (6CB) is moving in a backward direction then, then the interaction properties of the dimer in this conformation are given in Table 5.8, following statements are very important to describe the properties of the dimer:

1. The value of the HOMO-LUMO gap of the dimer remains constant.

2. The value of polarizability of the dimer continuously increases.

3. The value of the total energy of the dimer continuously increases.

4. The dipole moment of the dimer continuously decreases.

5. The value of internal thermal energy of the dimer first decreases and then increases.

6. The value of the constant volume heat capacity of the dimer remains constant.

7. The value of entropy of the dimer remains constant.

8. The value of zero-point energy of the dimer first decreases and then increases.

9. The value of enthalpy of the dimer continuously increases.

10. The value of Gibbs's energy of the dimer first decreases and then increases continuously.

Table 5.8 The molecular properties of the 6CB-6CB dimer with parallel conformation at a different position in the backward direction.

6CB-6CB Parallel conformation	0.5Å	1.0Å	1.5Å	2.0Å	2.5Å
HOMO-LUMO*(eV)*	4.64	4.64	4.64	4.64	4.64
Dipole moment *(Debye)*	10.38	10.37	10.37	10.36	10.35
Thermal Energy*(kcal/mol)*	464.49	464.48	464.48	464.49	464.49
Polarizability*(kcal/mol)*	272912	273056	273207	273351	273495
Total Energy *(kcal/mol)*	-9933.60	-9933.70	-9933.70	-9933.80	-9933.90
Heat capacity (C_v) *(kcal/mol)*	0.14	0.14	0.14	0.14	0.14
Entropy *(kcal/mol)*	0.24	0.24	0.24	0.24	0.24
ZPE*(kcal/mol)*	440.15	440.14	440.13	440.14	440.15
Enthalpy *(kcal/mol)*	465.07	465.07	465.07	465.07	465.08
Gibbs Energy *(kcal/mol)*	392.95	392.90	392.91	392.92	392.92

5.3.5 6CB-6CB Antiparallel conformation

In this part, the interaction belongings of antiparallel conformation of 6CB-6CB dimers (Figure 5.5) have been studied. The total energy, dipole moment, and entropy of the 6CB monomer under antiparallel conformation increase with the movement of the first monomer. The tail of the first molecule 6CB interacts with the benzene ring of the other 6CB monomer at 2.91Å distance. The tail end of the 6CB second monomer interacts with the benzene ring of the earlier molecule at a distance of 2.95Å.

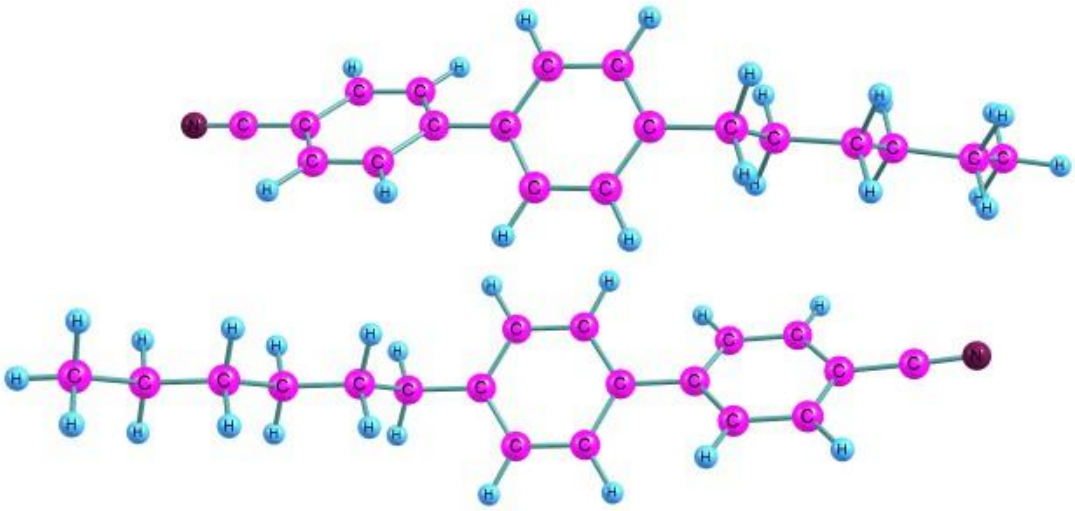

Figure 5.5 6CB liquid crystal dimer in antiparallel conformation.

When the first 6CB monomer remains unchanged while the second monomer (6CB) passes forward and the interaction properties are given in Table 5.9, and hence we can draw the following inferences:

1. The value of the HOMO-LUMO gap of the dimer continuously decreases.

2. The value of polarizability of the dimer continuously decreases.

3. The value of the total energy of the dimer first decreases and then increases.

4. The dipole moment of the dimer continuously increases.

5. The value of internal thermal energy of the dimer continuously increases.

6. The value of the constant volume of heat capacity of the dimer continuously increases.

7. The value of entropy of the dimer continuously increases.

8. The value of zero-point energy of the dimer continuously increases.

9. The value of enthalpy of the dimer continuously increases.

10. The value of Gibbs's energy of the dimer first decreases and then increases and again decreases.

Table 5.9 The molecular properties of 6CB-6CB with antiparallel conformation at a different position in the forward direction.

6CB-6CB Antiparallel conformation	**0.5Å**	**1.0Å**	**1.5Å**	**2.0Å**	**2.5Å**
HOMO-LUMO*(eV)*	4.51	4.51	4.51	4.51	4.50
Dipole moment *(Debye)*	2.40	2.41	2.41	2.42	2.43
Thermal Energy*(kcal/mol)*	464.47	465.07	465.07	465.07	465.08
Polarizability*(kcal/mol)*	271406	271343	271274	271211	271155
Total Energy *(kcal/mol)*	-9933.96	-9933.07	-9933.17	-9933.26	-9933.34
Heat capacity (C_v) *(kcal/mol)*	0.14	0.15	0.15	0.15	0.15
Entropy *(kcal/mol)*	0.23	0.24	0.24	0.25	0.25
ZPE*(kcal/mol)*	440.20	440.21	440.21	440.21	440.21
Enthalpy *(kcal/mol)*	465.06	465.65	465.66	465.66	465.66
Gibbs Energy *(kcal/mol)*	394.14	391.94	392.26	392.25	392.24

When the first monomer of 6CB is fixed and the second monomer of 6CB is moving in the backward direction, then in this conformation, properties of the dimer are given in Table 5.10, and hence we may conclude the following statements:

1. The value of the HOMO-LUMO gap of the dimer continuously decreases.

2. The value of polarizability of the dimer continuously decreases.

3. The value of the total energy of the dimer continuously increases.

4. The dipole moment of the dimer continuously increases.

5. The value of internal thermal energy of the dimer continuously decreases.

6. The value of the constant volume heat capacity of the dimer remains constant.

7. The value of entropy of the dimer continuously increases.

8. The value of zero-point energy of the dimer continuously decreases.

9. The value of enthalpy of the dimer continuously decreases.

10. The value of Gibbs's energy first decreases and then increases and again decreases.

Table 5.10 The molecular properties of 6CB-6CB in antiparallel conformation at a different position in the backward direction.

6CB-6CB Antiparallel conformation	**0.5Å**	**1.0Å**	**1.5Å**	**2.0Å**	**2.5Å**
HOMO-LUMO*(eV)*	4.50	4.49	4.49	4.49	4.48
Dipole moment *(Debye)*	2.44	2.45	2.46	2.46	2.47
Thermal Energy*(kcal/mol)*	465.07	465.06	465.05	465.04	465.04
Polarizability*(kcal/mol)*	271042	270992	270948	270910	270872
Total Energy *(kcal/mol)*	-9933.40	-9933.50	-9933.60	-9933.70	-9933.80
Heat capacity (C_v) *(kcal/mol)*	0.15	0.15	0.15	0.15	0.15
Entropy *(kcal/mol)*	0.24	0.24	0.25	0.25	0.26
ZPE*(kcal/mol)*	440.18	440.14	440.12	440.11	440.09
Enthalpy *(kcal/mol)*	465.65	465.64	465.63	465.63	465.62
Gibbs Energy *(kcal/mol)*	392.05	391.80	391.69	392.04	391.50

5.3.6 5CB-6CB Antiparallel conformation

Now, we study the interaction of 5CB with 6CB liquid crystal in antiparallel conformation, as shown in Figure 5.6.

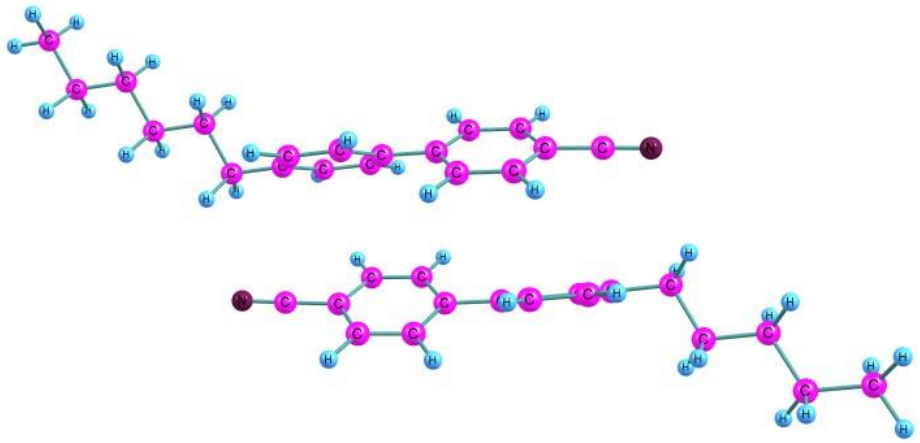

Figure 5.6 5CB-6CB liquid crystal dimer in antiparallel conformation

There has been π-π interaction in the antiparallel conformation of 5CB and 6CB monomers as shown in Figure 5.6. The CN group of the 6CB monomer interacts with the tail of the 5CB monomer at a distance of 2.71Å. The benzene ring of the first 5CB interacts with the benzene ring of the 6CB at a distance of 2.88Å. The CN group of 5CB interacts with the tail of the 6CB monomer at a distance of 2.84Å. The first 5CB is fixed and the 6CB monomer moves forward, all possible properties are shown in Table 5.11, and hence then we conclude the following statements:

1. The value of the HOMO-LUMO gap of the dimer first decreases and then increases.

2. The value of polarizability of the dimer first decreases and then increases.

3. The value of the total energy of the dimer continuously decreases.

4. The dipole moment of the dimer continuously increases.

5. The value of internal thermal energy of the dimer first decreases and then increases.

6. The value of the constant volume heat capacity of the dimer remains constant.

7. The value of entropy of the dimer first decreases and then increases.

8. The value of zero-point energy of the dimer increases then decreases and again increases.

9. The value of enthalpy of the dimer first decreases and then increases.

10. The value of Gibbs's energy of the dimer first increases then decreases and then again increases.

Table 5.11 The molecular properties of the 5CB-6CB dimer with antiparallel conformation at a different position in the forward direction.

5CB-6CB Antiparallel conformation	**0.5Å**	**1.0Å**	**1.5Å**	**2.0Å**	**2.5Å**
HOMO-LUMO *(eV)*	4.42	4.28	4.28	4.44	4.57
Dipole moment *(Debye)*	0.54	0.55	0.56	0.57	0.58
Thermal Energy *(kcal/mol)*	444.78	444.30	444.35	444.93	445.04
Polarizability *(kcal/mol)*	259408	258705	258486	258875	259345
Total Energy *(kcal/mol)*	-9686.40	-9686.35	-9686.30	-9686.25	-9686.20
Heat capacity (C_v) *(kcal/mol)*	0.13	0.13	0.13	0.13	0.13
Entropy *(kcal/mol)*	0.21	0.20	0.20	0.21	0.21
ZPE*(kcal/mol)*	423.16	423.38	423.47	423.45	423.61
Enthalpy *(kcal/mol)*	445.37	444.89	444.93	445.52	445.62
Gibbs Energy *(kcal/mol)*	380.11	383.12	383.27	381.54	381.88

When the first monomer of 5CB is fixed and the second monomer of 6CB is moving in the backward direction, then in this conformation, the properties are given in Table 5.12 and hence we can draw the following statements:

1. The value of the HOMO-LUMO gap of the dimer first decreases and then increases.

2. The value of the polarizability of the dimer first decreases and then increases.

3. The value of the total energy of the dimer first decreases and then increases.

4. The dipole moment of the dimer continuously decreases.

5. The value of internal thermal energy of the dimer first decreases then increases and then again decreases.

6. The value of the constant volume heat capacity of the dimer remains constant.

7. The value of entropy of the dimer first increases and then decreases.

8. The value of zero-point energy of the dimer continuously decreases.

9. The value of enthalpy of the dimer first decreases then increases and then again decreases.

10. The value of Gibbs's energy of the dimer first increases then decreases and then again increases.

Table 5.12 The molecular properties of the 5CB-6CB dimer with antiparallel conformation at a different position in the backward direction.

5CB-6CB Antiparallel conformation	**0.5 Å**	**1.0 Å**	**1.5 Å**	**2.0 Å**	**2.5 Å**
HOMO-LUMO *(eV)*	4.50	4.42	4.46	4.56	4.62
Dipole moment *(Debye)*	0.54	0.53	0.52	0.52	0.51

Thermal Energy *(kcal/mol)*	444.69	444.04	443.95	444.52	443.32
Polarizability *(kcal/mol)*	262834	260625	261209	262050	263079
Total Energy *(kcal/mol)*	-9686.80	-9686.30	-9686.40	-9686.40	-9686.43
Heat capacity (C_v) *(kcal/mol)*	0.13	0.13	0.13	0.13	0.13
Entropy *(kcal/mol)*	0.21	0.21	0.21	0.22	0.21
ZPE *(kcal/mol)*	422.91	422.75	422.57	422.53	422.45
Enthalpy *(kcal/mol)*	445.27	444.62	444.54	445.11	443.90
Gibbs Energy *(kcal/mol)*	379.75	380.77	379.83	377.20	381.01

5.3.7 5CB-6CB Parallel conformation

In this part, we investigate the interaction characteristics of the 5CB-6CB with parallel conformation (Figure 5.7).

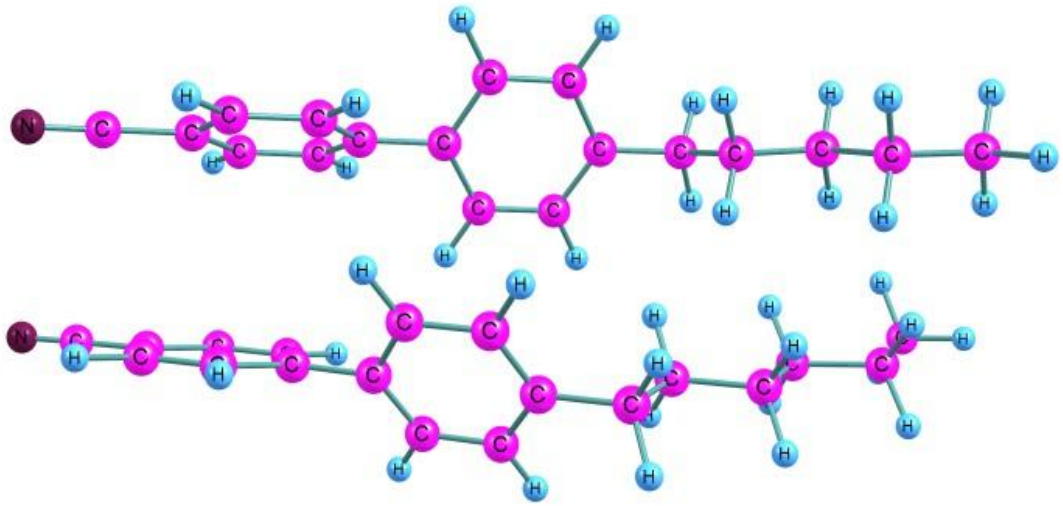

Figure 5.7 5CB-6CB liquid crystal dimer in parallel conformation.

The polarizability increases rapidly for this conformation as 5CB and 6CB moves forward or backward. Further, total energy decreases as 5CB and 6CB pass forward or backward consistent with their levels. The obtained conformation exhibits π-π

interaction between 5CB and 6CB as shown in Figure 5.7. The end tail of 6CB interacts with the end group of 5CB at a distance of 2.19Å. The benzene ring of 6CB interacts with the benzene ring of the 5CB at a 2.47Å distance. When the first 5CB monomer is fixed and the second 6CB travels forward and all possible properties of the conformation are given in Table 5.13, and we can draw the following remarks:

1. The value of the HOMO-LUMO gap of the dimer continuously decreases.

2. The value of polarizability of the dimer continuously increases.

3. The value of the total energy of the dimer continuously decreases.

4. The dipole moment of the dimer first decreases and then increases.

5. The value of internal thermal energy of the dimer first increases and then decreases.

6. The value of the constant volume of heat capacity of the dimer continuously decreases.

7. The value of entropy of the dimer continuously decreases.

8. The value of zero-point energy of the dimer first increases and then decreases.

9. The value of enthalpy of the dimer first increases and then decreases continuously.

10. The value of Gibbs's energy of the dimer first increases then decreases and then again increases.

Table 5.13 The molecular properties of the 5CB-6CB dimer with parallel conformation at a different position in the forward direction.

5CB-6CB Parallel conformation	**0.5 Å**	**1.0 Å**	**1.5 Å**	**2.0 Å**	**2.5 Å**
HOMO-LUMO *(eV)*	5.02	4.98	4.71	3.72	2.81
Dipole moment *(Debye)*	4.10	4.03	4.09	4.55	5.42
Thermal Energy*(kcal/mol)*	446.00	446.16	445.89	445.58	444.31
Polarizability*(kcal/mol)*	248301	249638	251834	254717	257940
Total Energy *(kcal/mol)*	-9686.55	-9686.40	-9685.40	-9685.35	-9683.30
Heat capacity (C_v) *(kcal/mol)*	0.13	0.13	0.12	0.12	0.12
Entropy *(kcal/mol)*	0.21	0.20	0.19	0.19	0.18
ZPE*(kcal/mol)*	424.19	425.10	426.04	426.17	426.05
Enthalpy *(kcal/mol)*	426.59	446.74	446.47	446.17	444.89
Gibbs Energy *(kcal/mol)*	382.06	384.79	387.66	386.86	388.94

When the first monomer of 5CB is fixed and the second monomer of 6CB is moving in the backward direction, then in this conformation, the properties are given in Table 5.14 and therefore we may conclude the following points:

1. The value of the HOMO-LUMO gap of the dimer first increases and then decreases.

2. The value of polarizability of the dimer continuously increases.

3. The value of the total energy of the dimer continuously decreases.

4. The dipole moment of the dimer first increases and then decreases.

5. The value of internal thermal energy of the dimer first decreases and then increases.

6. The value of the constant volume of heat capacity of the dimer continuously decreases.

7. The value of entropy of the dimer continuously decreases.

8. The value of zero-point energy of the dimer first decreases and then increases.

9. The value of enthalpy of the dimer first decreases then increases and then again decreases.

10. The value of Gibbs's energy of the dimer continuously increases.

Table 5.14 The molecular properties of the 5CB-6CB dimer with parallel conformation at different positions in the backward direction.

5CB- 6CB Parallel conformation	**0.5 Å**	**1.0 Å**	**1.5 Å**	**2.0 Å**	**2.5 Å**
HOMO-LUMO*(eV)*	5.05	5.06	5.03	4.98	4.92
Dipole moment *(Debye)*	4.26	4.33	4.36	4.32	4.25
Thermal Energy*(kcal/mol)*	445.03	444.46	443.93	443.56	443.76
Polarizability*(kcal/mol)*	247291	247373	247906	248910	250127
Total Energy *(kcal/mol)*	-9686.45	-9686.40	-9685.20	-9685.14	-9685.12
Heat capacity(C_v) *(kcal/mol)*	0.13	0.13	0.13	0.12	0.12
Entropy *(kcal/mol)*	0.21	0.20	0.20	0.19	0.19
ZPE*(kcal/mol)*	423.45	423.42	423.42	423.86	423.92
Enthalpy *(kcal/mol)*	445.61	444.45	444.52	444.15	444.34
Gibbs Energy *(kcal/mol)*	380.67	382.48	383.11	385.01	385.14

5.3.8 5CB-6CB Cross conformation

Lastly, we study the interaction of 5CB and 6CB liquid crystals in cross conformation, as shown in Figure 5.8.

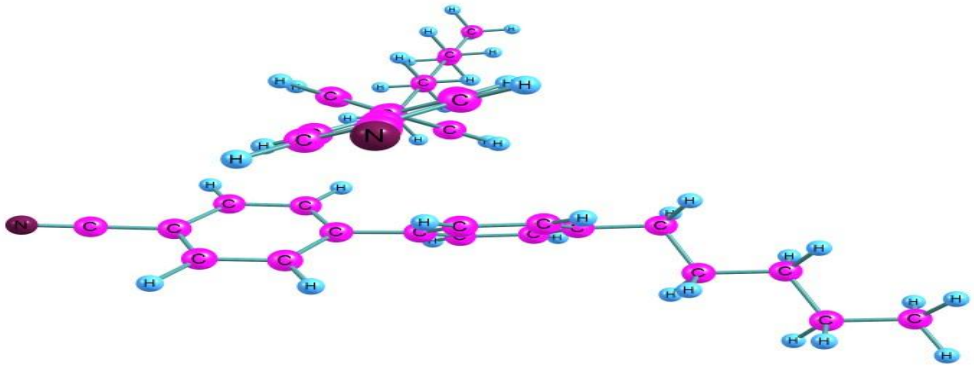

Figure 5.8 5CB-6CB liquid crystal dimer in cross conformation.

As 5CB and 6CB pass forward or backward then the total energy of the dimer falls rapidly shown in Figure 5.8. The benzene ring of 5CB interacts with the benzene ring of the 6CB monomer at a distance of 2.94. The former 5CB is fixed and 6CB passes forward, then the following conclusion can be described in Table 5.15.

1. The value of the HOMO-LUMO gap of the dimer continuously decreases.

2. The value of polarizability of the dimer continuously increases.

3. The value of the total energy of the dimer continuously decreases.

4. The dipole moment of the dimer first increases and then decreases.

5. The value of internal thermal energy of the dimer first increases then decreases and then again increases.

6. The value of constant volume heat capacity of the dimer first decreases and then increases.

7. The value of entropy of the dimer first decreases and then increases.

8. The value of zero-point energy of the dimer continuously increases.

9. The value of enthalpy of the dimer first decreases and then increases.

10. The value of Gibbs's energy of the dimer first increases and then decreases continuously.

Table 5.15 The molecular properties of the 5CB-6CB dimer with cross conformation at a different position in the forward direction.

5CB-6CB Cross conformation	**0.5 Å**	**1.0 Å**	**1.5 Å**	**2.0 Å**	**2.5 Å**
HOMO-LUMO*(eV)*	4.76	4.72	4.63	4.49	4.41
Dipole moment *(Debye)*	8.17	8.17	8.19	8.17	8.12
Thermal Energy*(kcal/mol)*	444.26	444.72	443.24	443.45	444.88
Polarizability*(kcal/mol)*	257369	257369	259904	261265	262351
Total Energy *(kcal/mol)*	-9686.89	-9686.84	-9686.77	-9686.70	-9686.65
Heat capacity (C_v) *(kcal/mol)*	0.13	0.13	0.12	0.12	0.13
Entropy *(kcal/mol)*	0.21	0.20	0.19	0.19	0.21
ZPE*(kcal/mol)*	423.10	423.15	423.34	423.64	424.00
Enthalpy *(kcal/mol)*	444.85	444.30	443.83	444.04	445.47
Gibbs Energy *(kcal/mol)*	381.03	382.50	384.67	385.13	381.26

As the first 5CB is located fixed and the 6CB approaches backward then all changes in electronic properties for such conformation are given as Table 5.16, and we find some important remarks as:

1. The value of the HOMO-LUMO gap of the dimer first increases and then decreases.

2. The value of polarizability of the dimer continuously increases.

3. The value of the total energy of the dimer continuously decreases.

4. The dipole moment of the dimer continuously decreases.

5. The value of internal thermal energy of the dimer first decreases and then increases

6. The value of constant volume heat capacity of the dimer first decreases and then increases.

7. The value of entropy of the dimer continuously decreases.

8. The value of zero-point energy of the dimer continuously increases.

9. The value of enthalpy of the dimer first decreases and then increases.

10. The value of Gibbs's energy of the dimer first increases and then decreases.

Table 5.16 The molecular properties of 5CB-6CB dimer having cross conformation at different positions in the backward direction.

5CB-6CB Cross conformation	**0.5 Å**	**1.0 Å**	**1.5 Å**	**2.0 Å**	**2.5 Å**
HOMO-LUMO*(eV)*	4.80	4.81	4.76	4.71	4.70
Dipole moment *(Debye)*	8.19	8.16	8.12	8.09	8.05
Thermal Energy*(kcal/mol)*	444.12	443.65	443.16	443.28	443.99
Polarizability*(kcal/mol)*	256980	257356	258046	259057	260111
Total Energy *(kcal/mol)*	-9686.90	-9686.88	-9686.85	-9686.81	-9686.79
Heat capacity (C_v) *(kcal/mol)*	0.13	0.13	0.12	0.12	0.13
Entropy *(kcal/mol)*	0.21	0.20	0.20	0.20	0.20
ZPE*(kcal/mol)*	422.98	422.98	423.12	423.24	423.43
Enthalpy *(kcal/mol)*	444.79	444.24	443.75	443.86	444.58
Gibbs Energy *(kcal/mol)*	380.60	381.76	383.94	383.86	382.44

Table 5.17 The interaction energy of all the dimers in parallel and antiparallel configurations.

Conformations	Dimer E_1 (kcal/mol)	Monomer x Monomer E_0 (kcal/mol)	Interaction energy ($E_1 - E_{0)}$ (kcal/mol)
5CB-5CB-Parallel	-943931.96	-943923.76	-8.20
5CB-5CB-Antiparallel	-943931.34	-943923.76	-7.58
5CB-5CB-Cross	-943929.54	-943923.76	-5.78
6CB-6CB-Parallel	-993269.59	-993264.40	-5.19
6CB-6CB-Antiparallel	-993269.41	-993264.40	-5.01
5CB-6CB-Antiparallel	-968591.63	-968594.08	2.44
5CB-6CB-Parallel	-968585.59	-968594.08	8.48
5CB-6CB-Cross	-968591.46	-968594.08	2.62

The interaction energies of the stable geometries of dimers have been tabulating as in Table 5.17, which reflects the interaction and dimers energies of 5CB and 6CB and their dimers in different configurations.

5.4 Conclusion

The present chapter describes the antiparallel conformation of 5CB and 6CB dimers which gives the minimum negative interaction energy and smallest dipole moment with the smallest negative entropy in comparison to other dimer conformations. The parallel conformations of 5CB molecules have high polarizability in comparing to other dimer conformations. The 5CB dimer shows the least polarizability and Gibb's energy in the crossed conformation. The 6CB dimer shows the minimum value of negative polarizability and higher Gibbs energy in the antiparallel conformations in comparison to other conformations. The 5CB and 6CB liquid crystal dimers feebly interact with each other. Hence all the conformations of 5CB-6CB dimer declared the positive interaction energy. The 5CB-6CB dimer has minimum negative polarizability and the

small value of the dipole moment in the antiparallel conformations with minimum negative interaction energy. The 6CB-6CB dimer has a low value of isotropic polarizability in antiparallel conformation, whereas, in the parallel conformation of the 6CB dimer, isotropic polarizability is maximum. The 5CB-5CB dimer shows the smallest isotropic polarizability in the cross conformation, but this dimer has the maximum isotropic polarizability in the parallel conformation.

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Chapter-6

Conclusion

and

future prospects

Chapter 6

Conclusion and future prospects

The computational methodology used in the following thesis is implementing to the Density Functional Theory (DFT) method. By exposing the electric field on the liquid crystal compounds or molecules, different electro-optical properties were investigated. Order parameter, birefringence, director angle, HOMO LUMO gap, isotropic polarizability, refractive index, etc. of the given liquid crystals is determined. Using the DFT methodology, these electro-optical properties are determined by various unknown liquid crystal compounds including molecules. By evaluating the molecular polarizabilities under the electric field, the odd-even effect is shown by the optical parameters using increment in alkyl chain length. Once the molecular polarizability is calculated, the transition states of the liquid crystal organic compound are determined. DFT study helps to reveal the anisotropic properties like birefringence and order parameter that can be changed with the help of electric field. Also one can understand molecular conformation, atomic orbital conformation, absolute energy, and relative HOMO LUMO gap of the liquid crystal.

Birefringence of the organic molecules is very crucial in optical display device applications. Director angle (magic angle) helps in the arrangement or orientation of a

liquid crystal so that we can get anisotropic properties. By changing the electric field, value of director angle also varies which leads to the electro-optical parameters of LC. Order parameter helps in calculating the birefringence of liquid crystal molecules. Here, polarizability plays an important role as it is changing with an electric field. We controlled the molecular orientation by tuning the electric field. This quality of liquid crystal differentiates it from isotropic liquid and it is the basic requirement for display devices.

In this study, order-disorder transition is observed when an LC changes to an isotropic liquid. Rod-like molecules studied here constitute the nematic parameters for the LC. During pneumatics, rotational symmetry would be governed by a particular axis known as a director. On reaching the value of transition temperature, many liquid crystal molecules move in a bulk manner and this diverges the magnitude of order parameter.

In chapter three, the odd-even effect of the APAPA molecule has been investigated. The APAPA molecular series (homologous) have studied the effect of electric field during THz frequency as well as temperature. The liquid crystal series gets affected by the electric field, which is associated with the effect of temperature fluctuation. The electron affinity as well as ionization potential, show the odd-even effect of alkyl chain with the increment in length of molecules. The odd-even effect is also found in birefringence under electric field of studied molecules. The series of APAPA molecules have positive and negative birefringence due to which it is used in electro-optical applications. The odd-even effect is not found in order parameter and refractive index of the studying molecules. The value of director angle $\theta=90°$ remains constant for the entire series, which may be utilized in the application of scattering. The series (homologous) experienced both positive and negative variations of the birefringence,

after which it is found worthy for the application in the electro-optical region. The APAPA liquid crystals series are best for use in Photo luminance, insulating material, sensing, filtering, scattering, and THz application devices.

In chapter four, the electro-optical properties like order parameter, birefringence, dipole moment, HOMO LUMO gap, director angle, etc. of 10CB liquid crystal molecules have been investigated. From this chapter, it has been found that the 10CB liquid crystal expresses a negative order parameter with a high electric field. The C≡N atom stretching has decreased only in 10CB that shows the decrement of the order parameter. The HOMO and LUMO gap increase for the negative order parameter while decreases for positive order parameter. The director angle is correlated to the order parameter in LC compounds. Negative orientation of order parameter together with the large absorption anisotropy increases the optical birefringence with a negative sign. Hence 10CB liquid crystal is suitable for terahertz applications. In 10CB liquid crystal, the IR absorbance has increased which is responsible for the negative order parameter. The bandgap is affected by applying the electric field, so the liquid crystals are used as tunable bandgap applications. The 10CB liquid crystal is a member of the cyano biphenyl series; therefore, dipole strength, maximum contributed by the C-H atom asymmetric stretching of the alkyl chain length, and 10CB liquid crystal have a large bandgap (3.60 eV). The order parameter influences the applications of ultrafast electro-optics, which is differ from displays to optical shutters, modulators, steerers, limiters, and switches as the switchable optical filter.

In chapter five, the interaction study of 5CB and 6CB liquid crystal molecules is studied in detail. It has been originating that the antiparallel conformation of 5CB and 6CB dimers reveals the minimum negative interaction energy and smallest dipole

moment in comparison to other dimer conformations. The antiparallel conformations of 5CB and 6CB have the smallest negative entropy. Also, the parallel conformations of 5CB molecules have high polarizability in comparison to other dimer conformations of the 5CB molecules. The crossed conformation of the 5CB shows the least polarizability and Gibbs energy. Besides, the antiparallel conformations of 6CB dimer exhibit minimum negative polarizability and higher Gibbs energy in comparison to other conformations. But all the conformations of 5CB-6CB dimer insist on the positive interaction energy; therefore, the 5CB and 6CB feebly interact with each other. The antiparallel conformations of the 5CB-6CB dimer have minimum negative polarizability and the least dipole moment. The obtained interaction energy is negative in the antiparallel conformation of 5CB and 6CB dimers with the least value, while the interaction energy is found positive for the same dimer of all the exhibiting possible conformations. The isotropic polarizability is found lowest for the antiparallel conformation of the 6CB-6CB, but the value of isotropic polarizability is higher in the 6CB dimer of the parallel conformation. The 5CB dimer shows the smallest isotropic polarizability in the cross conformation, but the parallel conformation of this dimer has the maximum isotropic polarizability.

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Electro-optical odd-even effect of APAPA liquid crystal molecules studied under the influence of an extraneous electric field (THz): A theoretical approach

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ABSTRACT

The homologous series of APAPA (*anisylidene-para-amino-phenyl-acetate*) liquid crystal (LC) express the odd-even effect under the influence of an electric field in THz frequency region. The homologous series revealed an odd-even effect under the impact of temperature. The electron affinity and ionization potential have exhibited an odd-even effect with the extension of the alkyl chain length. The birefringence has expressed an odd-even effect under the influence of an extraneous electric field. The homologous series has positive as well as the negative orientation of the birefringence, which is suitable for electro-optical application devices. The order parameter and refractive index have continually increased with an expansion of alkyl chain length. The director angle remains constant at $\theta = 90°$ for the whole series of LC. The extraneous influence of the electric field has correlated with the impact of temperature variation.

1. Introduction

The liquid crystal (LC) is organic substance that flows like a liquid; however, it has some degree of order to arrange the molecules. The LC phase is the intermediate phase exists between the crystalline and liquid phases. The lowest symmetry-based nematic LC is mostly uniaxial and does not show any translational correlation of the molecular center. Rod-like nematic LC is easy to rotate along the long molecular axis under the impact of the electric field. Rod-like LC has strong electron conjugation, which is better for the display and other applications. The dielectric behavior of LC contributes to the dielectric anisotropy, which is responsible for the reorientation of the LC molecules under the influence of an electric field. The reorientation of the LC plays a crucial role in the electro-optical device applications. An imine based liquid crystal does made from a double bond between N and C presented in the molecular structure which contributes to the molecular polarizability and resulting intermolecular interactions in the nematic liquid crystals. The different terminal location has different dipole moment; therefore, the suitable place of the polar group can enhances the molecular polarizability; thus, molecular polarizability contributes to the stability of LC phase. The APAPA LC contains two benzene rings connected with the Schiff base linkage group and the terminal of the benzene ring combined with the alkoxy and ester group [1,2]. Mandal et al. [3] have reported that APAPA LC expresses the dynamic scattering effect, which helps to liquid crystal display (LCD) application. The APAPA LC has a nematic phase between 83 °C to 108 °C temperature. The Schiff base LC compound is susceptible to the atmosphere moisture; therefore, during the fabrication of the optical devices using such liquid crystals, the protection from the moisture is necessary. The order parameter of APAPA LC has value between 0.61 and 0.40. APAPA LC is also known as MBA LC which maintains the nematic phase under the impact of temperature and pressure. Leenhouts et al. [4] have reported that the homologous series of APAPA LC can also be denoted as the APAPAm LC, where m stands for the number of the carbon atom in the alkyl chain length of the ester group $OCOC_m H_{2m+1}$. The elastic constant of the homologous series of APAPA LC decreases with an extension of alkyl chain length due to short-range correlation in the plane perpendicular to the director (Y-axis). Somashekar et al. [5] have reported that the order parameter of 1MBA LC exists between 0.5 and 0.6, while the order parameter of 3MBA LC exists between 0.5 and 0.65. Onnagawa et al. [6] have reported that APAPA LC maintain alignment in the nematic phase under the influence of electric and magnetic field. Meulen et al. [7] have investigated that the elastic properties of nematic LC easy to calculate by dynamic light scattering. Moreover, Deutsch et al. [8] have reported the laser light scattering by APAPA LC in the dynamic scattering mode; therefore, it may be used as a scattering material. In the present work, we have applied electric field to the homologous series of APAPA LC. Under the influence of an extraneous electric field,

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the optical parameter exhibits an odd-even effect. It expresses a reorientation of the molecules which is most suitable for the electro-optical applications.

2. Computational methodology

All the geomteries of the molecules are optimized by the Gaussian 09 software [9] with the help of density functional theory (DFT) method B3LYP [10,11] and M062X [12] by 6-31G** basis set [13,14]. After the simulation of APAPA molecules, we have applied electric field (a.u) to the homologous series along the molecular axis (x-axis) and perpendicular axis (y-axis). The range of applied electric field is 0.0000 (a.u) to 0.1000 (a.u) at the interval of 0.0020 (a.u), where 1 a. u = 5.14×10^{11} V/m [15] = 6.5×10^{15} Hz. After an applied electric field, we have calculated the molecular polarizability of the molecular series. We considered the extraordinary (α_e), and ordinary (α_o) molecular polarizabilities along the x-axis and y-axis, respectively. By calculating the values of α_e and α_o, we have calculated the birefringence, order parameter, refractive index, and magic angle as per the equations given below, where α, μ, and β equivalent to the components of the polarizability, dipole moment, and first-order hyperpolarizability [16–18].

$$\alpha = \frac{1}{3}\left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right)$$

$$\beta = \left[\left(\beta_{xxx} + \beta_{xyy} + \beta_{xzz}\right)^2 + \left(\beta_{yyy} + \beta_{xxy} + \beta_{yzz}\right)^2 + \left(\beta_{zzz} + \beta_{xxz} + \beta_{yyz}\right)^2\right]^{1/2}$$

$$\mu = \left(\mu_x^2 + \mu_y^2 + \mu_z^2\right)^{1/2}$$

$$\Delta\alpha = 2^{-1/2}\left[\left(\alpha_{xx} - \alpha_{yy}\right)^2 + \left(\alpha_{yy} - \alpha_{zz}\right)^2 + \left(\alpha_{zz} - \alpha_{xx}\right)^2\right]^{1/2}$$

$$\Delta\tilde{\alpha} = \alpha_e - \alpha_o$$

$$\Delta\tilde{\alpha} = S\Delta\alpha$$

Order parameter (S):

$$S = \frac{\alpha_e - \alpha_o}{\alpha_e + \alpha_o} \tag{1}$$

Birefringence (Δn):

$$\Delta n = \frac{(\alpha_e - \alpha_o)}{6.3631}\left[R^3 - \left(\frac{2\alpha_o + \alpha_e}{20.244}\right)\right]^{-1} \tag{2}$$

Where, R is the radius of the liquid crystal molecule.
Magic angle (θ):

$$\theta = \cos^{-1}\left[\frac{(2S+1)}{3}\right] \tag{3}$$

Refractive index (n):

$$\alpha = \frac{2\alpha_o + \alpha_e}{3}, \gamma_e = \alpha + \frac{2(\alpha_e - \alpha_o)}{3S}, \gamma_o = \alpha - \frac{(\alpha_e - \alpha_o)}{3S}$$

$$n_e = \frac{7}{2\sqrt{10}} + \frac{\left(2\sqrt{10}/5\right)\pi N\alpha}{1 - \frac{4\pi N\alpha}{3}} + \frac{\left(4\sqrt{10}/15\right)\pi NS(\gamma_e - \gamma_o)}{1 - \frac{4\pi N\alpha}{3}}$$

$$n_o = \frac{7}{2\sqrt{10}} + \frac{\left(2\sqrt{10}/5\right)\pi N\alpha}{1 - \frac{4\pi N\alpha}{3}} + \frac{\left(2\sqrt{10}/15\right)\pi NS(\gamma_e - \gamma_o)}{1 - \frac{4\pi N\alpha}{3}} \tag{4}$$

$$n = \frac{7}{2\sqrt{10}} + \frac{\left(2\sqrt{10}/5\right)\pi N\alpha}{1 - \frac{4\pi N\alpha}{3}}$$

where $N = 1$ is the number of liquid crystal molecules and γ_o, γ_e is representing the ordinary and extraordinary internal field constant. The difference of γ_e-γ_o is to given the differential molecular polarizability. The n_o and n_e is representing the ordinary and extraordinary refractive index.

3. Results and discussion

The B3LYP method is predominant in the atomic contribution of the molecule; however, the M062X method is predominant in the molecular contribution of the molecules. In the present work, the atomic contribution gives similar characteristics as a comparison with the molecular contribution; however, the molecular contribution maximum correlated with the experimental evidence. The B3LYP and M062X DFT methods are most suitable for the optimization of an organic compound (liquid crystal) [19]. The homologous series of APAPA LC is to express the higher absorbance due to C—O atom stretching [20]. Electric field effects are prevalent in computational chemistry because of analysis of the chemical reaction mechanism [21].

3.1. Temperature versus increased alkyl chain length of APAPA LC

The homologous series of APAPA LC shows an odd-even effect from nematic to isotropic phase transition under the impact of temperature, as shown in Fig. 1. The transition temperature is increased for the odd member of the homologous series because odd member makes a smaller angle with the molecular axis as shown in the abstract figure;

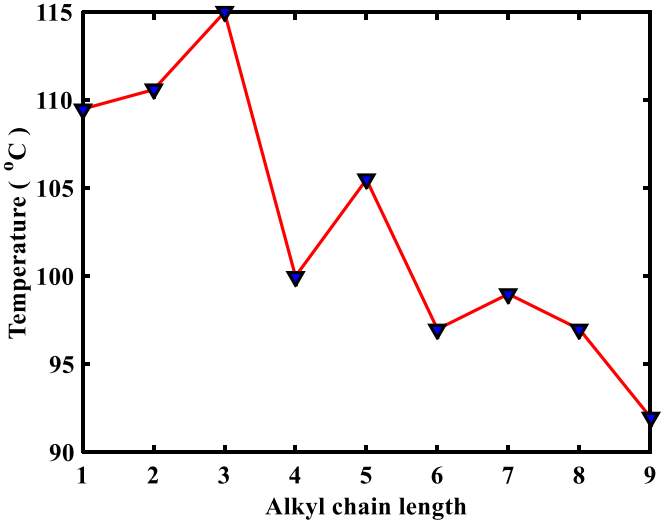


Fig. 1. Odd-even effect of the homologous series calculated under the impact of temperature [22].

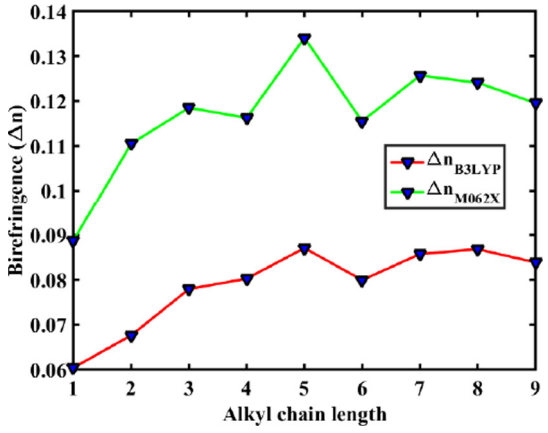
however, transition temperature decreases for the even members. After all, the even member makes a larger angle with the long molecular axis. The transition temperature is increased due to smaller distance from the long molecular axis, consequently temperature is decreased due to large distance with the long molecular axis [22]. The carbon atom numbers (6, 7, and 8) of the alkyl chain are continuously decreased due to a large angle with the long molecular axis (x-axis).

3.2. Birefringence versus increased alkyl chain length of APAPA LC

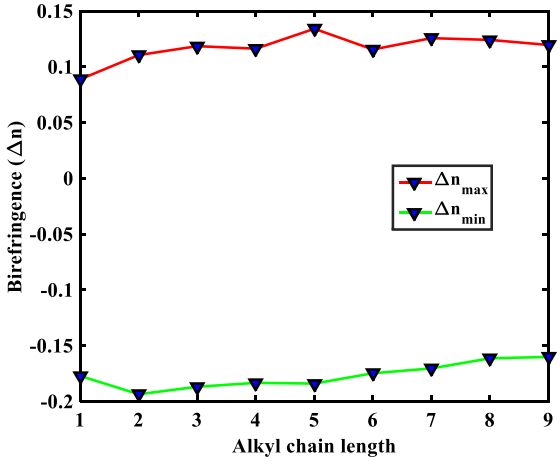
The birefringence of the homologous series expresses an odd-even effect under the influence of an electric field in THz frequency, as shown in Fig. 2. The birefringence has calculated with the help of Eq. (2) under the influence of an electric field. The birefringence increases for the even member of the alkyl chain length due to a smaller angle with the long molecular axis; however, the reason for decrement is the larger angle with the molecular axis. The APAPA5 LC has the most significant birefringence, which is suitable for the electro-optical applications in THz frequency. The impact of temperature and influence of an electric field on the homologous series indicate similar odd-even effect. Ji et al. [23] have reported under the influence of an extraneous electric field in THz frequency controlled the birefringence for electro-optical applications. The positive, as well as negative birefringence, express the reorientation of the molecules, as shown in Fig. 2(B) and also given in the supporting information figure SF10 to SF18.

3.3. Order parameter versus increased alkyl chain length of APAPA LC

The order parameter has calculated under the influence of an electric field in THz frequency with the help of Eq. (1). The order parameter continually increases with an expansion of alkyl chain length. The molecular contribution shows minor odd-even effects; however, atomic contribution nothing to show it would be grow forward. The order parameter of APAPA5 LC suddenly increases due to strong electron conjugation. The APAPA5 LC may be suitable for the electro-optical applications because the order parameter and birefringence both are increased. The ionization potential is decreased, and electron affinity rises only for the APAPA5 LC, which is another reason for the optical applications. Jampani et al. [24] have reported the LC has a negative order parameter due to the parallel alignment of all the molecules. The homologous series also have a negative as well as a positive order parameter, as shown in Fig. 3(B) and given in supporting information

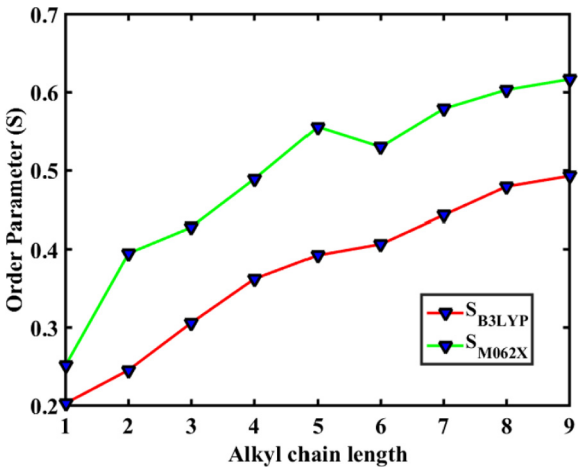


(A)

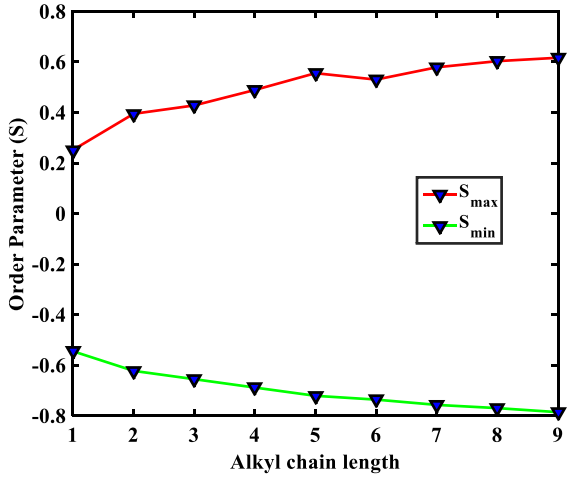


(B)

Fig. 2. (A). Odd-even effect of birefringence calculated under the influence of an electric field. (B). Positive as well as negative birefringence under the influence of an extraneous electric field in THz frequency.



(A)



(B).

Fig. 3. (A). Order parameter of the homologous series continually increases with an extension of the alkyl chain length. (B). Positive as well as negative order parameter calculated under the influence of an extraneous electric field in THz frequency.

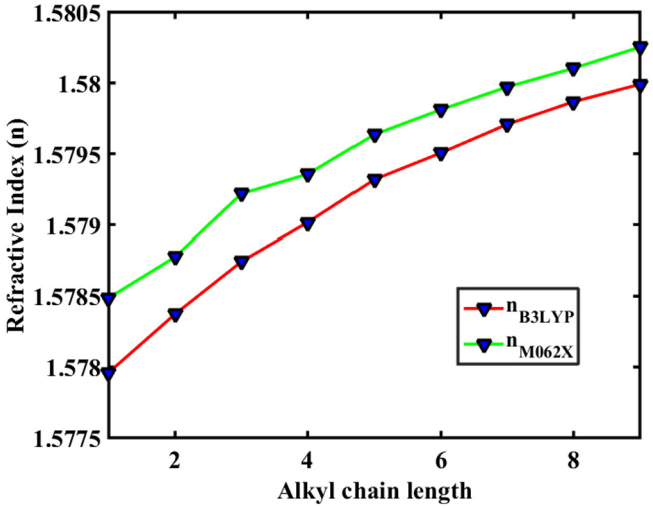


Fig. 4. Refractive index of homologous series continually increases with an extension of alkyl chain length.

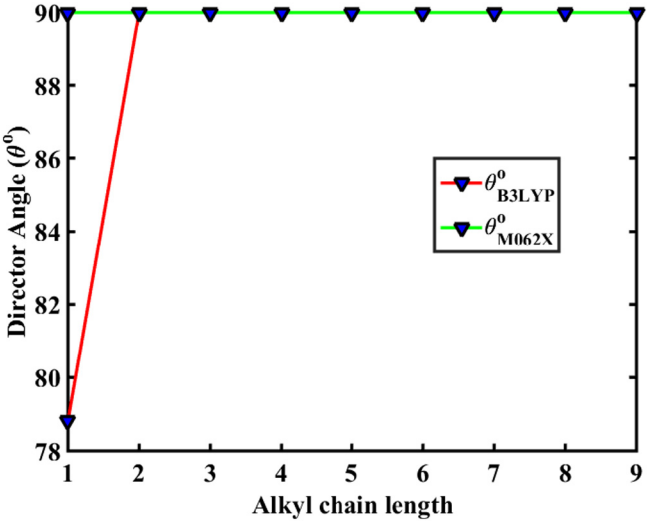


Fig. 5. Director angle remains constant of the homologous series under the influence of the electric field.

figure SF1 to SF9. The positive and negative order parameter based LC is most suitable for the electro-optical and other optical applications. Mandal et al. [3] have reported the order parameter of APAPA LC exists between 0.4 and 0.6 which is also reported in the present work; the order parameter of APAPA LC is −0.54, as shown in Fig. 3(B). Somashekar et al. [5] have reported the order parameter of 1MBA LC exists between 0.5 and 0.6, and the order parameter of 3MBA LC exists between 0.5 and 0.65 in the present work the order parameter of 1MBA and 3MBA is −0.54 & −0.68 experimental evidence correlated with the theoretical prediction. The negative order parameter, the first time experimentally reported by Jampani et al. [24] which is reason for the inverted sign of the order parameter in the present work.

3.4. Refractive index versus increased alkyl chain length of APAPA LC

The refractive index has calculated under the influence of an electric field by Eq. (4), as shown in Fig. 4. The refractive index continually increases with an expansion of alkyl chain length and does not express any odd-even effect. Atomic and molecular contribution gives similar characteristics with different values. The range of the refractive index of the homologous series lies between 1.57 and 1.58. Ji et al. [23] have reported the refractive index maintains stability under the influence of an extraneous electric field in THz frequency in the present work; also, the refractive index expresses the stability as given in the supporting information figure SF19 to SF27.

3.5. Director angle versus increased alkyl chain length of APAPA LC

The director angle has calculated under the influence of the electric field in THz frequency with the help of Eq. (3), as shown in Fig. 5. The director angle remains constant for the whole homologous series. The atomic and molecular contribution gives a similar prediction because the director angle ($\theta = 90$) maintains stability given in the supporting information figure SF28 to SF36. Meulen et al. [7] and Deutsch et al. [8] have reported that the APAPA LC suitable for the dynamic scattering mode because the molecule maintains stability at the angle $\theta = 90$, therefore, incident light scattering at $\theta = 90$ angle. Thus we can predict it is suitable for the scattering applications in the THz frequency range.

3.6. Electron affinity and ionization potential versus increased alkyl chain length of APAPA LC

The electron affinity and Ionization potential express the odd-even effect with an expansion of alkyl chain length, as shown in Figs. 6 and 7. The APAPA5 LC increases the electron affinity and decreases the ionization potential; therefore, it is suitable for the photoluminance application devices. The values of electron affinity enhanced for the odd members and decreases for the even members of the alkyl chain length. The ionization potential is decreased for the odd members and increases for the even members of the alkyl chain length. The electron affinity of the homologous series has correlated with the experimentally calculated temperature variation and theoretically calculated birefringence variation.

3.7. Dipole moment of the homologous series and dipolar strength of APAP A5 LC

The dipole moment of the homologous series continually decreases with an expansion of alkyl chain length, as shown in Fig. 8, and the dipolar strength of APAPA5 LC indicates in Fig. 9. The dipole moment of the homologous series continually decreases; therefore, a higher range of homologous series not suitable for the LC characteristics. Dwivedi et al. [20] have reported the homologous series of APAPA LC express the higher absorbance due to C—O atom stretching. In the present

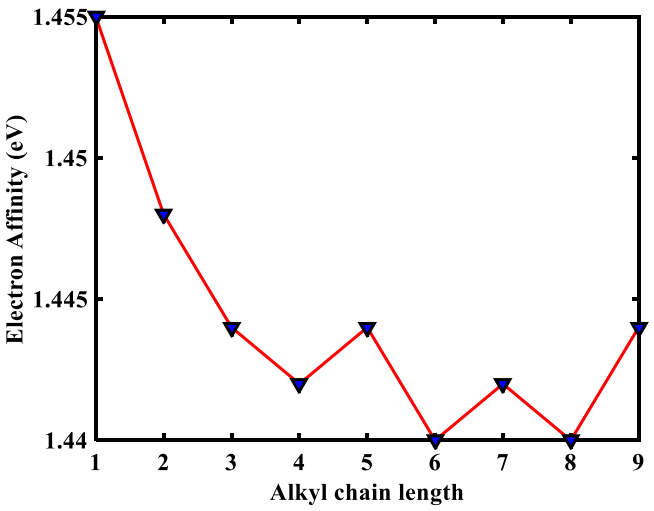


Fig. 6. Odd-even effect of the homologous series indicate by electron affinity with an expansion of alkyl chain length.

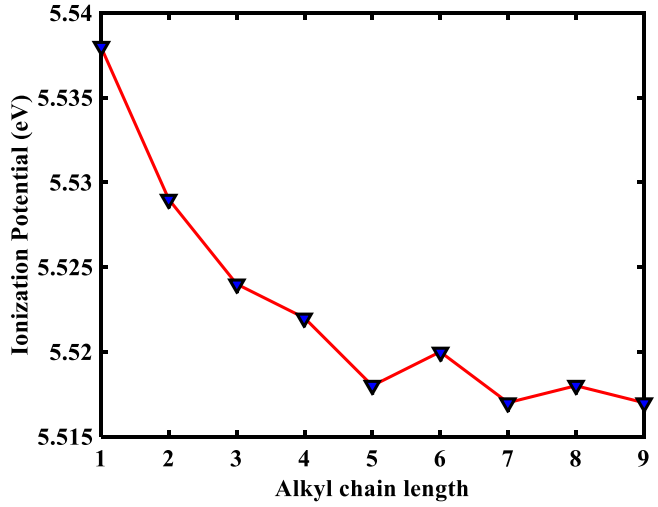


Fig. 7. Odd-even effect of the homologous series indicated by Ionization potential with an expansion of alkyl chain length.

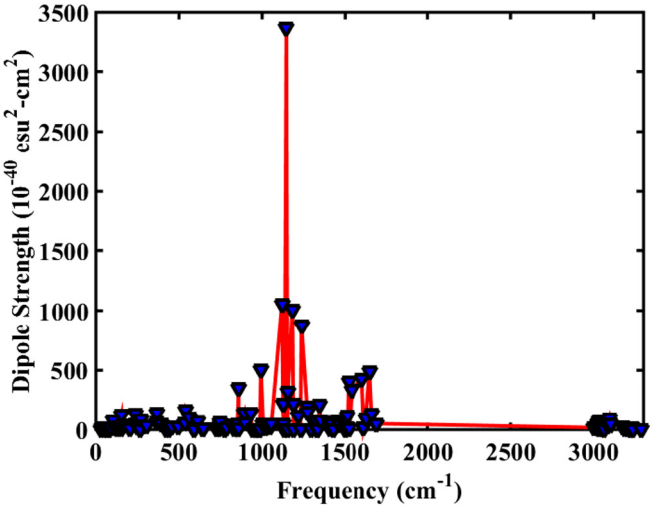


Fig. 9. Dipolar strength of the APAPA5 LC with an expansion of alkyl chain length.

work, we have also discussed the dipolar strength contribute by the C—O atom stretching, Wagging of H atoms and Scissoring of C atoms in the alkyl chain. The phenyl ring and oxygen atom stretching reduce the frequency band, which is the reason for the reduction of dipole moment. The APAPA5 LC has a broad range of transmission; therefore, it is suitable for filtering and sensing applications.

3.8. HOMO-LUMO gap versus increased alkyl chain length of APAPA LC

The homologous series of APAPA LC reveals approximately 4 eV HOMO-LUMO gap, which is very high, and therefore it behaves as an insulator. Few carbon atom numbers (1–3, 6) of the alkyl chain have an indicated 4.08 eV as well as low 4.07 eV HOMO-LUMO gaps, as shown in Fig. 10. The HOMO-LUMO gap sharply increased in APAPA6 because electron affinity has decreased as well as ionization potential increased. The transition temperature, birefringence, and order parameter also reduced for the APAPA6 LC because C—O atom stretching, and the wagging of the carbon atom of the alkyl chain express positive rotational strength.

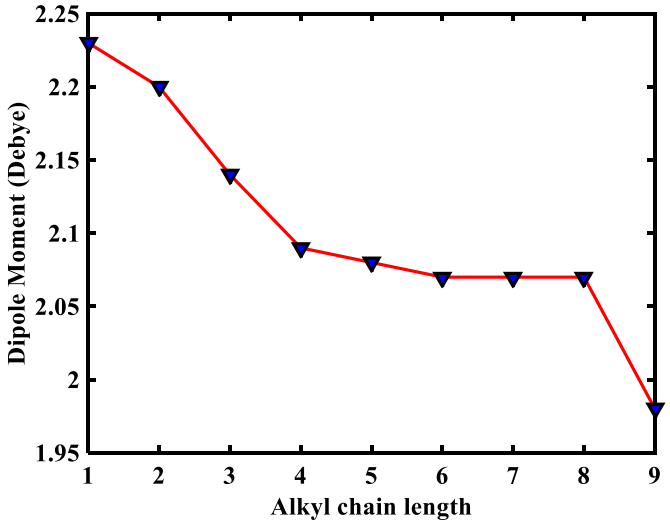


Fig. 8. Dipole moment of the homologous series has calculated with an expansion of alkyl chain length.

4. Conclusion

In the present work, we conclude that the homologous series of APAPA LC express the odd-even effect under the influence of an electric field in THz frequency region. The homologous series reveals the odd-even effect under the impact of temperature. The effect of the electric field on the LC series has correlated with the external impact of temperature variation. The electron affinity and ionization potential express an odd-even effect with the extension of the alkyl chain length. The birefringence also reveals an odd-even effect under the influence of an external electric field. The order parameter and refractive index do not show any odd-even effect with an expansion of alkyl chain length. The director angle remains constant at $\theta = 90°$ for the whole homologous series, which is best for the scattering applications. The homologous series has positive as well as the negative variation of the birefringence, which is suitable for electro-optical application devices. The Homologous series of APAPA LC is ideal for scattering, Photo luminance, insulating material, sensing, filtering, and THz application devices.

Declaration of competing interest

The authors declare that there are no conflicts of interest regarding the publication of this article.

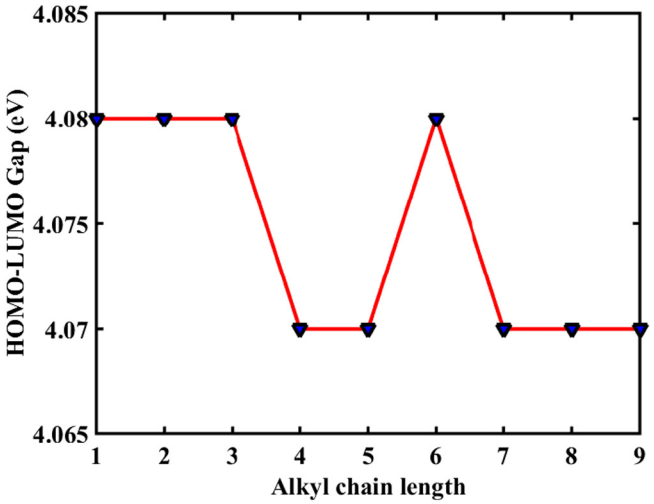


Fig. 10. HOMO-LUMO gap of the homologous series calculated with an expansion of alkyl chain length.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molliq.2020.114254.

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ARTICLE

Electro-Optical Parameters with Adverse Order of 10CB Liquid Crystal Molecules Studied under the Influence of an External High Electric Field: A Theoretical Approach

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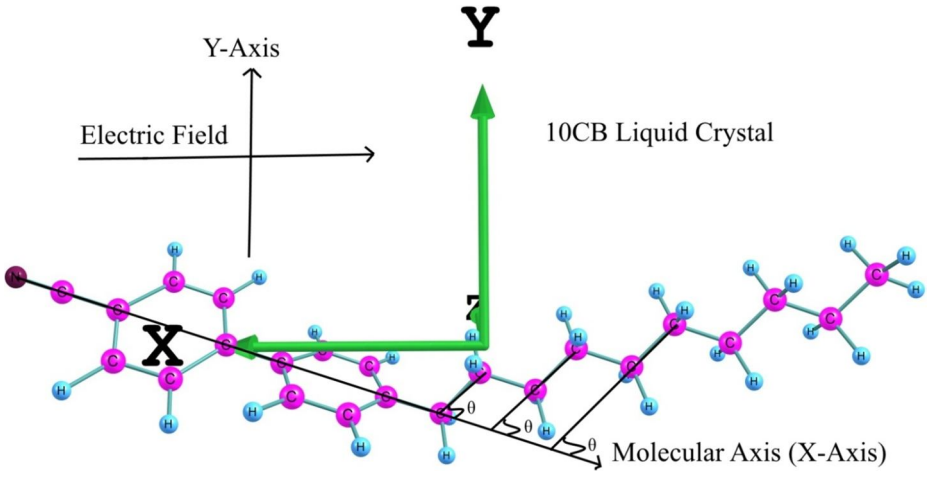
Abstract: The 10CB liquid crystal (LC) at the higher electric field has a negative-order parameter. The 10CB LC has a definite order that maintains smectic phase stability. 10CB LC has supported the isotropic phase stability at an elevated external electric field and exhibited an unfavorable orientation of the order parameter. At the more upper electric field, the director angle (θ) fluctuated and contained θ less than 90°. The negative orientation of the order parameter and the large absorption anisotropy enhanced the optical birefringence with a reversal of sign. The negative-order parameter responsible for the IR absorbance has increased instead of reduction. The 10CB liquid crystal is a member of the cyano biphenyl series; therefore, the dipolar strength is maximum contributed to by the C-H atom asymmetric stretching of the alkyl chain length. The 10CB LC has a large bandgap (3.60 eV).

Keywords: 10CB, Electric field, Electro-optical effect, Spectroscopy, Density functional theory (DFT).



Introduction

Liquid crystals are considered to lie in the mesomorphic phase. The properties of nematic liquid crystals have been widely studied by different research groups. The transitional properties of this compound depend on the length and parity of flexible spacers. It is also useful in optical communication, as it has a high value of molecular polarizability. In the fabrication of display devices, molecular polarizability plays a vital role as it reveals the

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action of light (EM wave) with liquid crystals [1-2]. The rod-like gold nanoparticles exhibit a negative orientation order parameter and the large absorption anisotropy enhanced the optical birefringence with a reversal of sign [3-4]. The rod-like negative ordered nematic liquid crystal exists in the parallel form with the 90° director angle [5-8]. Under the effect of the external electric field, the positive dipole liquids are perpendicular to the electric field and exhibit the maximum torque [9-10]. The order parameter of the nematic phase comes from the quenching of the director orientation at a very high electric field in the order of 10^8 V/m. The nanosecond switching under electrical modification of the order parameter affect the ultrafast electro-optic applications ranging from displays to modulators, optical shutters, limiters, beam steerers and switches as the switchable optical retardance [11-12].

The structure of decyl cyano biphenyl contains a methyl group attached to the carbon chain, which gives rise to a stable smectic phase. It is used to calculate the surface temperature as different colors which are observed over a surface. This property is utilized in medical applications to detect skin cancer. After the discovery of pentyl cyano biphenyl by George William Gray, many attempts were made to synthesize similar homologous versions of this compound. Cyano group acts as a substituent in the aromatic ring and changes acidity in ground as well as excited states. Since the cyano group is an electron acceptor, the need for an aqueous solvent has also been eliminated. The homologous compound of cyano biphenyl is extensively used in electro-optical devices, as it is stable, gives the colorless intermediate phase at room temperature and has a positive value of dielectric anisotropy; one particular effect shown by these compounds is known as the odd-even effect [13]. It alters the physical properties of the compound, depending upon the number of carbon atoms. This odd-even effect is also studied with the help of molecular dynamics. Due to the peculiar nature in order and mobility at the microscopic and bulk levels, such compounds respond to stimuli very quickly [14-15].

The main keynote kept in mind while modeling these compounds is their configuration and corresponding to that particular configuration their ground-state energy. This ground-state energy helps in the interaction of these compounds with various other compounds. The relative energies are also useful in the calculation of thermodynamic properties, such as entropy, free energies, … etc. The alkyl chain can be easily broken down or displaced, which gives rise to multi conformational changes [16-18]. The higher homologous compound shows a more planar structure as compared to the lower homologous one. This planar structure helps in the stacking of the compound, which leads to rigidity. Based on Homo Lumo analysis, 10CB liquid crystal has a higher value of bandgap, indicating that it has a low amount of conductivity. Also, it is highly complex due to the significant amount of dipole moment along the molecular axis. Based on these properties, cyano biphenyl is considered a suitable compound in the list of liquid crystals [19-21].

Computational Methodology

The 10CB molecules are optimized by the Gaussian 09 Software [22] with the help of the density functional theory (DFT) method B3LYP [23-24] by 6-31G** basis set [25]. After optimization, the electric field is applied to the 10CB liquid crystal compound along with the molecular axis (x-axis) and perpendicularth (y-axis). The range of the applied electric field is 0.000 a.u to 0.200 a.u at the interval of 0.0020 a.u., where 1 a.u=5.14 x 10^{11} V/m [26] or 1 a.u.= 6.5 x 10^{15} Hz. After electric field application, the molecular polarizability of the 10CB liquid crystal is calculated. The molecular polarizability along the x-axis is considered as extraordinary molecular polarizability (α_e) and along the y-axis, it is considered as ordinary molecular polarizability (α_o). The extraordinary molecular polarizability (α_e) and ordinary molecular polarizability (α_o) calculate the order parameter with the help of Equation 1. The finite-field approach framework predicts the total molecular energy under the impact of the electric field as given below:

$$E = E_o - \mu_i F_i - \frac{1}{2}\alpha_{ij}F_iF_j - \frac{1}{6}\beta_{ijk}F_iF_jF_k$$

where E_o is the total energy in the absence of the electric field and F_i, α_{ij}, μ_i and β_{ijk} are equivalent to the components of the electric field, polarizability, dipole moment, and first-order hyperpolarizability, where the respective directions are specified along with the subscripts i, j and k=x, y and z. The α, β, μ and molecular

anisotropy in polarizability (Δα) can be expressed as numerical differentiation with an electric field of magnitude 0.002 a.u. The respective equations are given below [27-28]:

$$\alpha = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$

$$\beta = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{xxy} + \beta_{yzz})^2 + (\beta_{zzz} + \beta_{xxz} + \beta_{yyz})^2]^{1/2}$$

$$\mu = (\mu_x^{\ 2} + \mu_y^{\ 2} + \mu_z^{\ 2})^{1/2}$$

$$\Delta\alpha = 2^{-1/2}[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2]^{1/2}$$

$$\Delta\tilde{\alpha} = \alpha_e - \alpha_o$$

$$\Delta\tilde{\alpha} = S\Delta\alpha$$

where α̃ is the mean isotropic polarizability.

Order parameter (S) is given as:

$$S = \frac{\alpha_e - \alpha_o}{\alpha_e + \alpha_o}. \quad (1)$$

Director angle or magic angle (θ) is calculated as:

$$\theta = \cos^{-1}\left[\frac{(2S+1)}{3}\right] \quad (2)$$

Birefringence (Δn) is obtained as follows:

$$\alpha = \frac{2\alpha_o + \alpha_e}{3}, \quad \gamma_e = \alpha + \frac{2(\alpha_e - \alpha_o)}{3S},$$

$$\gamma_o = \alpha - \frac{(\alpha_e - \alpha_o)}{3S}$$

$$n_e = \frac{7}{2\sqrt{10}} + \frac{(2\sqrt{10}/5)\pi N\alpha}{1-\frac{4\pi N\alpha}{3}} + \frac{(4\sqrt{10}/15)\pi NS(\gamma_e - \gamma_o)}{1-\frac{4\pi N\alpha}{3}}$$

$$n_o = \frac{7}{2\sqrt{10}} + \frac{(2\sqrt{10}/5)\pi N\alpha}{1-\frac{4\pi N\alpha}{3}} - \frac{(2\sqrt{10}/15)\pi NS(\gamma_e - \gamma_o)}{1-\frac{4\pi N\alpha}{3}}$$

$$\Delta n = \frac{7}{2\sqrt{10}} + \frac{(2\sqrt{10}/5)\pi N\alpha}{1-\frac{4\pi N\alpha}{3}} \quad (3)$$

Results and Discussion

The 10CB LC expresses three phases under the influence of an electric field, as shown in Fig. 1: from 0.010 a.u. to 0.028 a.u. having the first phase of LC and the molecule is more stable in this range, from 0.034 a.u. to 0.052 a.u. 10CB LC expresses the second phase, where the molecule is less stable in comparison with the previous phase and from 0.056 a.u. to 0.072 a.u. represents the third phase, where the molecule is not stable for this range. Finally, the molecule is converted into the isotropic phase. The values 0.008 a.u., 0.032 a.u. and 0.054 a.u. reveal the phase transition field of 10CB. In the field of 0.074 a.u., the molecule finally gains the isotropic phase. The positive-order parameter of 10CB is 0.63 and the negative-order parameter is -0.40, as given in Fig. 1. In the field of 0.098 a.u. the molecule reveals a negative-order parameter. The maximum and minimum range of the order parameter for ordinary liquid crystal is from +0.8 to -0.5.

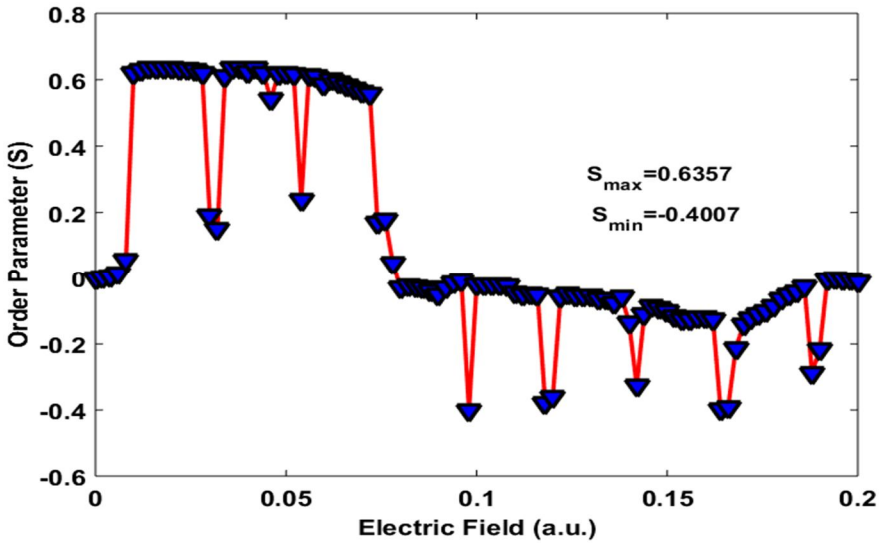

FIG. 1. Order parameter of 10 CB LC under the influence of the electric field (The order parameter is calculated by the mathematical Equation 1. Molecular polarizabilities of 10CB LC are optimized with the help of DFT (B3LYP) methodology by Gaussian 09 software package).

The 10CB liquid crystal has an order parameter in the range between +0.8 and -0.5. At a higher electric field (0.098 a.u.), the molecule maintains the stability of the isotropic phase. After the field of 0.078 a.u., the molecule gains 0.00 order parameter and exhibits the isotropic phase. The C-H asymmetric stretching corresponds to IR absorbance in the benzene ring, an improvement for the odd member, and falls for the even member of the alkyl chain. The 10CB liquid crystal shows an even member of the cyano biphenyl series, where the IR absorbance has increased instead of a decrease; that is the reason for the negative-order parameter.

Liu *et al*. [29] reported that under the influence of an electric field, the bandgap of liquid crystals is controlled, which is used in tunable bandgap applications. The magic angle of liquid crystals is 54.74. The maximum value of the director angle is 75.09 and the minimum value of the director angle is 29.52, as shown in Fig. 2. The director angle (θ) is stable for the smectic A phase and with an expension of the electric field, θ is finally stable for the isotropic phase. The director angle is related to the order parameter according to Eq. (2). Under the influence of the electric field, the bandgap decreases for the smectic A phase and the bandgap increases for the isotropic phase. For a positive-order parameter, the bandgap decreases, while the bandgap increases for a negative-order parameter.

Mitra et al. [30-31] utilized the molecular polarizability calculated by Vuks and Neugebauer's formula responsible for the order parameter, birefringence and refractive index. In the present work, we are using the modified formula of birefringence [28]. The order parameter is remarkably related to the director angle, where the director angle is easily calculated by the order parameter as given in Eq. (2). Liu *et al*. [3-4] reported a negative orientation order parameter and the large absorption anisotropy enhanced the optical birefringence with a reversal of sign, as shown in Fig. 3.

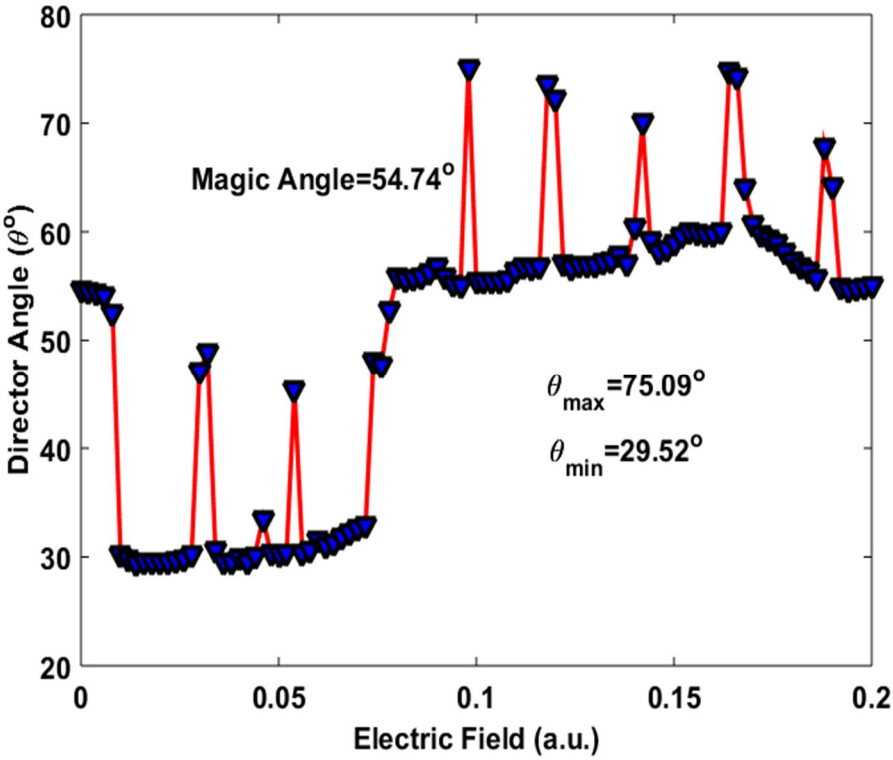

FIG. 2. Director angle of 10CB LC under the influence of an electric field. (The director angle is stable for the smectic and isotropic phases. The minimum director angle is 29.52 and the maximum director angle is 75.09. This means that the molecule of 10CB is not perfectly parallel to the electric field. At the angle of 90°, all the molecules are parallel to the electric field with negative order of the liquid crystal).

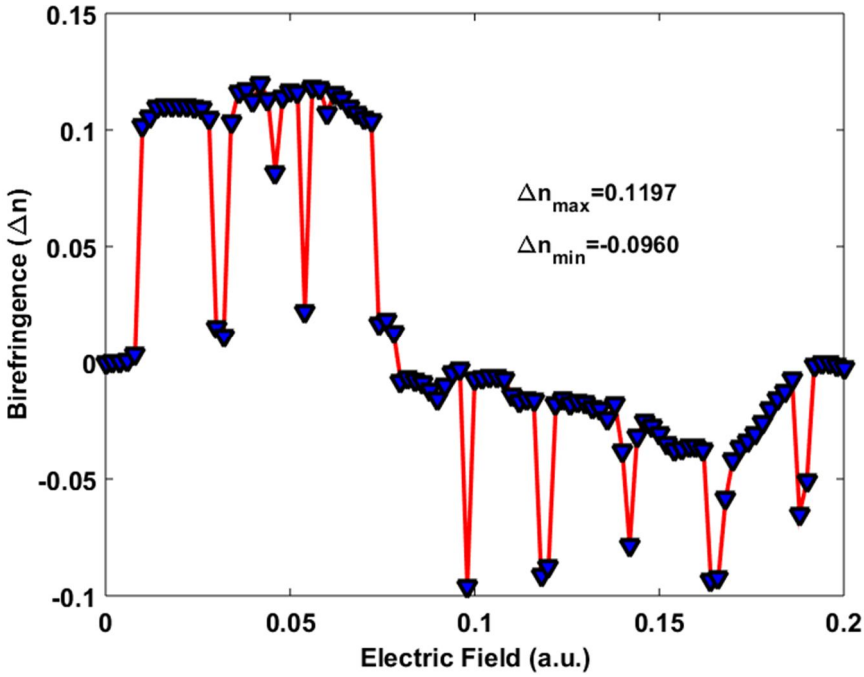

FIG. 3. Birefringence of 10CB LC under the effect of an electric field. (The maximum birefringence of 10CB LC is Δn = 0.1197 and the minimum birefringence is Δn = -0.0960. The birefringence is calculated with the help of Eq. (3), under the influence of an electric field).

Wood et al. [32] reported that the bandgap of nematic LC decreases under an applied electric field. Busch et al. [33] reported on inverse birefringent nematic LC used for photonic bandgap materials under the influence of an electric field. The dipole moment of 10CB liquid crystal is 6.09 Debye and the existing bandgap is 3.60eV, as shown in Fig 4. Due to the large bandgap of 10CB, the liquid crystal behaves as an insulator; therefore, insulating materials are used in the THz frequency range for better performance. The HOMO-LUMO bandgap is indicating the molecular stability of 10CB. The dipolar strength of 10CB LC is maximum contributed to by the asymmetric stretching of C-H atom of the alkyl chain length, as shown in Fig. 5.

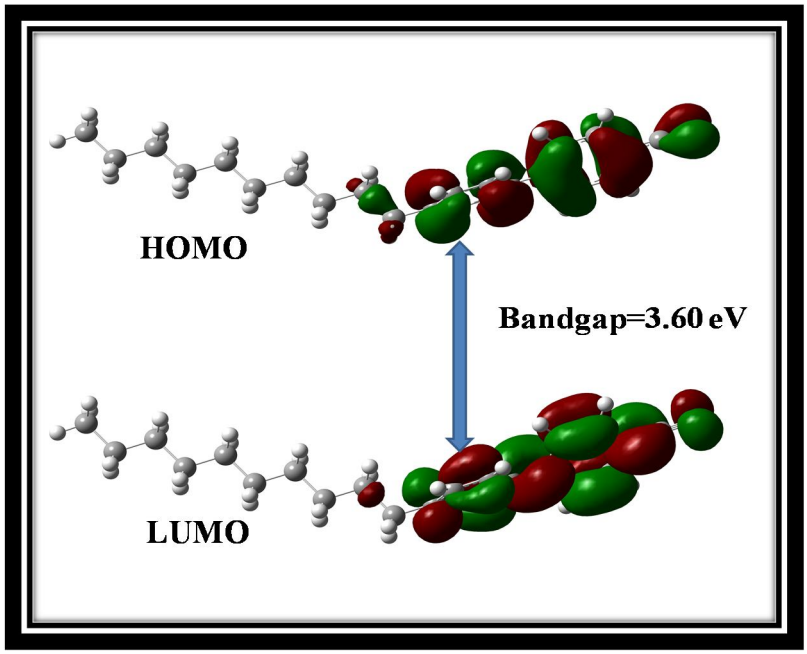

FIG. 4. Bandgap of 10CB liquid crystal molecule calculated by DFT methodology (Red color indicates a negative charge and green color indicates a positive charge).

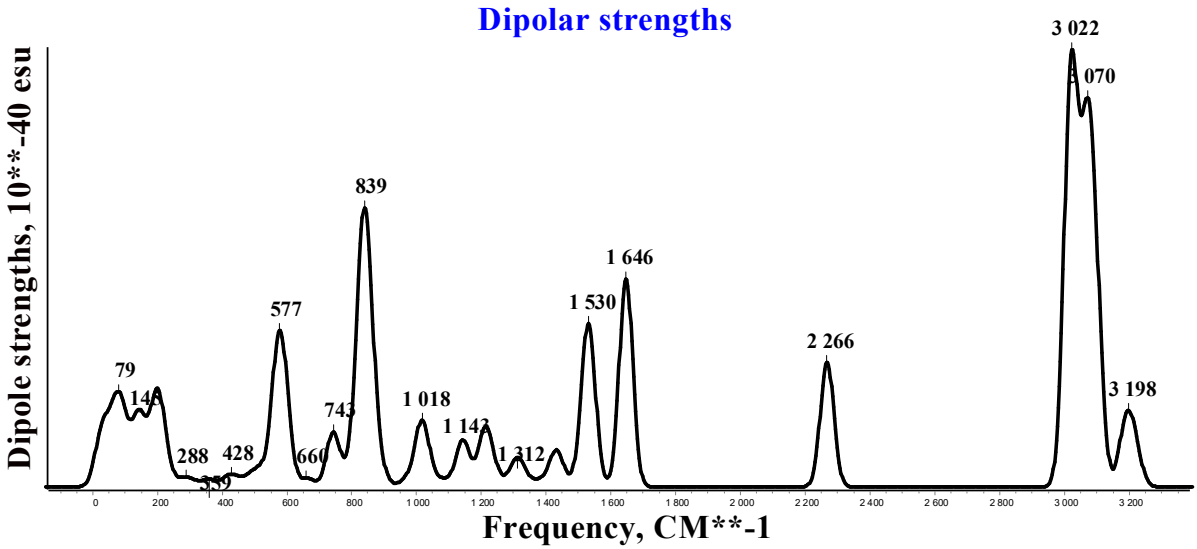

FIG. 5. Dipolar strength of 10CB liquid crystal measured by DFT methodology.

Conclusions

It has been found that the 10CB LC expresses a negative-order parameter with higher electric field. The C≡N atom stretching has decreased only in 10CB, which indicates the decrement of the order parameter. The **HOMO 'Highest Occupied Molecular Orbital'** and **LUMO 'Lowest Unoccupied Molecular Orbital'** gap increases for the negative-order parameter and decreases for the positive-order parameter. The director angle is related to the order parameter; if the order parameter is affected, then the director angle is also affected. The negative orientation of the order parameter with the large absorption anisotropy enhanced the optical birefringence with a reversal of sign. In 10CB LC, the IR absorbance has increased instead of a decrease, which is responsible for the negative-order parameter. The bandgap is affected under the influence of an electric field; so, liquid crystals are used in tunable bandgap applications. The 10CB liquid crystal is a member of the cyano biphenyl series; therefore, dipolar strength is maximum contributed to by the C-H atom asymmetric stretching of the alkyl chain length and 10CB LC has a large bandgap (3.60 eV). The order parameter affects the ultrafast electro-optic applications ranging from displays to modulators, optical shutters, limiters, beam steerers and switches as the switchable optical filter. The 10 CB liquid crystal is also suitable for terahertz applications, because it has negative birefringence at higher electric fields.

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Supportive Information

TABLE ST1. Molecular spectroscopy of 4CB

S. No.	Frequency (cm^{-1})	Vibrations of 4CB	Infrared absorbance
1.	567	C-H atom wagging	14.4115
2.	841	C-H atom wagging	32.7990
3.	1017	C-C symmetric scissoring in the benzene ring	10.6536
4.	1431	Stretching in C-H atom	10.6063
5.	1531	H atom rocking in both benzene rings	47.1805
6.	1646	H atom rocking in both benzene rings	75.5904
7.	2266	C≡N atom stretching	66.0374
8.	3029	C-H symmetric stretching in the alkyl chain	49.9012
9.	3098	C-H asymmetric stretching in the alkyl chain	56.5727
10.	3184	C-H asymmetric stretching in the benzene ring	18.9294

TABLE ST2. Molecular spectroscopy of 5CB

S. No.	Frequency (cm^{-1})	Vibrations of 5CB	Infrared absorbance
1.	569	C-H atom wagging	14.2067
2.	843	C-H atom wagging	38.8640
3.	1017	C-C symmetric scissoring in the benzene ring	11.3704
4.	1531	H atom rocking in both benzene rings	47.7280
5.	1646	H atom rocking in both benzene rings	77.6846
6.	2266	C≡N atom stretching	66.6334
7.	3026	C-H symmetric stretching in the alkyl chain	51.4412
8.	3096	C-H asymmetric stretching in the alkyl chain	60.4378
9.	3184	C-H asymmetric stretching in the benzene ring	19.0613

TABLE ST3. Molecular spectroscopy of 6CB

S. No.	Frequency (cm^{-1})	Vibrations of 6CB	Infrared absorbance
1.	569	C-H atom wagging	14.3463
2.	845	C-H atom wagging	32.6777
3.	1017	C-C symmetric scissoring in the benzene ring	11.5199
4.	1531	H atom rocking in both benzene rings	48.4753
5.	1646	H atom rocking in both benzene rings	78.8627
6.	2266	C≡N atom stretching	66.9738
7.	3027	C-H symmetric stretching in the alkyl chain	69.0056
8.	3096	C-H asymmetric stretching in the alkyl chain	60.9689
9.	3184	C-H asymmetric stretching in the benzene ring	18.6464

TABLE ST4. Molecular spectroscopy of 7CB

S. No.	Frequency (cm^{-1})	Vibrations of 7CB	Infrared absorbance
1.	569	C-H atom wagging	14.4318
2.	844	C-H atom wagging	30.2113
3.	1017	C-C symmetric scissoring in the benzene ring	11.9051
4.	1531	H atom rocking in both benzene rings	48.7830
5.	1646	H atom rocking in both benzene rings	79.8968
6.	2266	C≡N atom stretching	67.2729
7.	3027	C-H symmetric stretching in the alkyl chain	52.4092
8.	3076	C-H asymmetric stretching in the alkyl chain	78.0385
9.	3184	C-H asymmetric stretching in the benzene ring	18.7277

TABLE ST5. Molecular spectroscopy of 8CB

S. No.	Frequency (cm^{-1})	Vibrations of 8CB	Infrared absorbance
1.	570	C-H atom wagging	14.0818
2.	844	C-H atom wagging	32.6066
3.	1017	C-C symmetric scissoring in the benzene ring	11.3718
4.	1531	H atom rocking in both benzene rings	49.1511
5.	1646	H atom rocking in both benzene rings	80.3690
6.	2266	C≡N atom stretching	67.4233
7.	3027	C-H symmetric stretching in the alkyl chain	68.0403
8.	3076	C-H asymmetric stretching in the alkyl chain	84.3813
9.	3184	C-H asymmetric stretching in the benzene ring	18.7214

TABLE ST6. Molecular spectroscopy of 9CB

S. No.	Frequency (cm^{-1})	Vibrations of 9CB	Infrared absorbance
1.	570	C-H atom wagging	14.1481
2.	844	C-H atom wagging	32.2473
3.	1017	C-C symmetric scissoring in the benzene ring	12.0875
4.	1531	H atom rocking in both benzene rings	49.3004
5.	1647	H atom rocking in both benzene rings	80.8472
6.	2266	C≡N atom stretching	67.5816
7.	3027	C-H symmetric stretching in the alkyl chain	103.2722
8.	3064	C-H asymmetric stretching in the alkyl chain	107.3792
9.	3184	C-H asymmetric stretching in the benzene ring	18.9479

TABLE ST7. Molecular spectroscopy of 10CB

S. No.	Frequency (cm^{-1})	Vibrations of 10CB	Infrared absorbance
1.	570	C-H atom wagging	14.1221
2.	844	C-H atom wagging	32.1331
3.	1017	C-C symmetric scissoring in the benzene ring	11.3436
4.	1532	H atom rocking in both benzene rings	49.3276
5.	1646	H atom rocking in both benzene rings	80.9406
6.	2265	C-N atom stretching	67.6449
7.	3026	C-H symmetric stretching in the alkyl chain	72.6780
8.	3064	C-H asymmetric stretching in the alkyl chain	135.1362
9.	3184	C-H asymmetric stretching in the benzene ring	19.6324

TABLE ST8. Molecular spectroscopy of 11CB

S. No.	Frequency (cm^{-1})	Vibrations of 11CB	Infrared absorbance
1.	570	C-H atom wagging	14.2334
2.	844	C-H atom wagging	31.6043
3.	1017	C-C symmetric scissoring in the benzene ring	9.3491
4.	1531	H atom rocking in both benzene rings	49.5608
5.	1646	H atom rocking in both benzene rings	81.3196
6.	2266	C≡N atom stretching	67.7372
7.	3027	C-H symmetric stretching in the alkyl chain	109.3245
8.	3065	C-H asymmetric stretching in the alkyl chain	163.9189
9.	3184	C-H asymmetric stretching in the benzene ring	19.8023

TABLE ST9. Molecular spectroscopy of 12CB

S. No.	Frequency (cm^{-1})	Vibrations of 12CB	Infrared absorbance
1.	570	C-H atom wagging	14.2432
2.	844	C-H atom wagging	31.5740
3.	1017	C-C symmetric scissoring in the benzene ring	11.6812
4.	1531	H atom rocking in both benzene rings	49.64089
5.	1646	H atom rocking in both benzene rings	81.4398
6.	2266	C≡N atom stretching	67.7678
7.	3027	C-H symmetric stretching in the alkyl chain	96.2863
8.	3065	C-H asymmetric stretching in the alkyl chain	193.9285
9.	3184	C-H asymmetric stretching in the benzene ring	20.5369

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Comparative DFT Study of Parallel and Antiparallel Conformation of 5CB and 6CB Liquid Crystal Dimers

Research Article

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Abstract. An investigation of the interaction of 5CB and 6CB liquid crystals along with their dimer configurations in different conformations. The total energy, thermal energy, HOMO-LUMO Gap, dipole moment, polarizability, constant volume heat capacity, entropy, zero-point energy (ZPE), and enthalpy of the different configurations of 5CB and 6CB liquid crystal dimers are affected during the molecular interaction. The different interaction properties of 5CB, 6CB, and 5CB-6CB dimers studied in parallel and antiparallel conformation with the help of density functional theory method lc-blyp by NWChem software package. The 5CB and 6CB liquid crystal dimers have the least dipole moment and negative entropy in the antiparallel conformation. The cross conformation of 5CB liquid crystal dimer (5CB-5CB) has the least isotropic polarizability; however, the parallel conformation of 5CB liquid crystal dimer has the highest isotropic polarizability. The isotropic polarizability is minimum in the antiparallel conformation of 6CB liquid crystal dimer (6CB-6CB), while isotropic polarizability is maximum in the parallel conformation of 6CB liquid crystal dimer. The 5CB liquid crystal dimer and 6CB liquid crystal dimer have minimum negative interaction energy in the antiparallel conformation, but 5CB-6CB liquid crystal dimer has positive interaction energy for all the possible conformations.

Keywords. 5CB-6CB; DFT (LC-BLYP); Molecular properties; Interaction energy

PACS. 78.20.Ci; 73.50.Rb; 78.67.-n; 68.55.-a; 78.66.Bz; 78.20.-e

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1. Introduction

The liquid crystal [22, 32] dimer exhibits the broadest range of mesomorphic phase for the desired applications [4]. The 5CB and 6CB liquid crystal molecules have long-range conjugated rigid cores and active polar groups (cyano) that required for exhibits high-birefringence liquid crystals [9, 11, 12]. The 5CB liquid crystal has linear π-electron conjugation continual with the biphenyl rigid core and the polar terminal cyano group, so the optical and dielectric anisotropy is comparatively high in the 5CB liquid crystal [10, 38]. The 6CB liquid crystal has a more top dipole moment comparison of the 5CB liquid crystal molecule [17, 25]. The Cyano (CN) groups have an extreme polarization with the carbon-hydrogen triple bond, and the Huckel charges of the carbon and nitrogen atoms are very high. All cyanobiphenyl derivative dimers would be established by strong intermolecular interactions between the nitrile groups [5, 7, 8, 14, 27, 28, 30, 35]. The 5CB liquid crystal dimers (5CB-5CB) have excellent interaction energy at a distance of 4.2Å [2]. In the nematic phase, the enthalpy decreases as the pressure on molecules increases. The electrostatic repulsion between the dipole of the cyano groups diminishes in the anti-parallel conformation and also have a nematic phase of cyanobiphenyl dimer [36]. The potent polar cyanobiphenyl derivatives are the most important molecules for the applications of nematic liquid crystal in display applications. The antiparallel conformations of cyanobiphenyl liquid crystal dimers have reduced sufficient dipole moment. The liquid crystal packing plays a vital role in the creation of their mesophase and defines their optical properties for the display applications [26]. The cyano group terminal possesses a massive dipole moment along the long molecular axis. The cyanobiphenyl compounds are colorless, have a low melting point, chemically and photochemically stable [31]. The intermolecular forces are durable due to the polarity of the terminal groups of the 5CB and 6CB liquid crystal molecules [33]. The entire even member dimer of cyanobiphenyl liquid crystal has antiparallel conformation, and they also have CN-Phenyl strong interaction between the dimer [18]. The negative intermolecular energy of the dimer is responsible for the antiparallel structure which has negative entropy [13]. If the interaction energy is negative, then the entropy of the dimer is too negative that is responsible for the homogeneous phase [39]. The entropy is higher in 6CB liquid crystal as comparison of the 5CB liquid crystal during nematic to isotropic (N-I) phase transition [1]. It is important to note that only σ-electrons exist on cyclohexyl rings, whereas π-electrons live in phenyl rings. The presence of the rings in liquid crystal provides the short-range intermolecular forces needed to form the nematic phase, and they also affect the absorption, dielectric anisotropy, birefringence, elastic constant, and viscosity. Alkyl is the non-polar group that has a small effect on the dielectric anisotropy of liquid crystals. On the other hand, a polar terminal group such as a cyano group can contribute significantly to the dielectric anisotropy. The cyano group has the highest polarity leads to a high dielectric anisotropy and optical birefringence property. The liquid crystal compounds containing cyano group as terminal exhibit high viscosity, insufficient resistivity, and stability problems under UV illumination. Such liquid crystal compounds are not suitable for high-temperature operation as those used in a projection display application. Besides, liquid crystal molecules with the CN terminal group could be dissociated from the illumination of UV [6, 20, 23, 41–43]. In the antiparallel conformation of cyanobiphenyl liquid crystal dimer, the length of the pair is higher, so it minimizes the dipolar energy [40]. The even member dimer (6CB) mostly acquires antiparallel conformation because the length of the pair is higher, so it reduces the dipole moment of the dimer. In contrast, the odd member dimer (5CB)

mostly gets inclined or parallel mesogenic, so it increases the dipolar energy because the length of the dimer is small [24]. The 1CB to 3CB molecules have the rod-like structure that is useful to the formation of a crystalline structure. The active polarity of the cyano group increased the anisotropy of the molecule due to the reason the intermolecular forces increased. The triple bond of cyano group $-C\equiv N$ cannot rotate freely; that is the reason the molecular rigidity and melting temperature increased [16, 19, 29, 34, 44].

2. Computational Methodology

The 5CB and 6CB liquid crystal molecules optimized with the NWChem software package [37] with the help of DFT method LC-BLYP [3, 21] and 6-31G basis set [15]. After the optimization of liquid crystal molecules, we generated 360 conformations by python aggregation. Out of 360 conformations; we have considered four minimum energy conformations of the 5CB and 6CB dimers. Out of 360 conformations, we have found only four minimum energy conformations. All conformations are generated under free optimization (co-ordinates not fixed). Under free optimization, all monomers randomly interact with each other and generate minimum energy conformations. Firstly, we create 5CB, 6CB, and 5CB-6CB liquid crystal dimer molecules. All the liquid crystal dimers have the first monomer fixed, and the second monomer moves forward or backward at a distance of 0.5Å. When the first monomer set and the other monomer moved forward or backward, then the interaction energy, polarizability, thermochemistry, and dipole moment will increase or decrease depending on the conformation of the liquid crystal dimer molecules.

3. Results and Discussion

Based on molecular interactions, we have studied different molecular properties of different conformations of 5CB, 6CB, and their dimers using the density functional theory method LC-BLYP with the help of NWChem software package in different sections.

3.1 5CB-5CB Parallel Conformation

In this section, we study the interaction properties of 5CB-5CB liquid crystal dimers in parallel conformation, as shown in Figure 1.

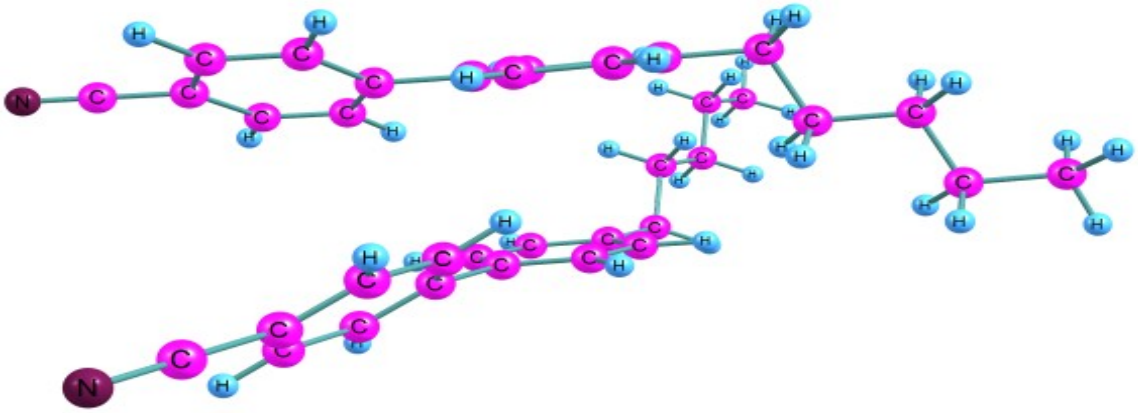

Figure 1. Parallel conformation of 5CB liquid crystal dimer

The polarizability of 5CB-5CB conformation decreases continually when the 5CB monomer moves in forwarding or backward direction (Figure 1). In this conformation, total energy increases continuously, and overall energy decreases. The cyano (CN) group of the first monomer interacts towards the benzene of the second monomer at a distance of 2.43Å. The tail of the first monomer interacts with the benzene of the second monomer at a range of 2.71Å. These conformations are generated under free optimization (co-ordinates not fixed) and have the minimum energy of the parallel conformation. Under free optimization, monomers (5CB) randomly interact with each other. When the first monomer (5CB) has fixed and the second monomer (5CB) moves forward then all possible interaction properties of the dimer in this conformation can be tabulated as Table 1, and hence we conclude the following statements:

(i) The HOMO-LUMO gap increases continually.
(ii) Polarizability decreases continually.
(iii) Total energy increases continually.
(iv) Dipole moment decreases continually.
(v) Internal thermal energy first decreases and then increases continually.
(vi) Constant volume heat capacity first decreases and then increases continually.
(vii) Entropyfirst decrease and then increases continually.
(viii) Zero-point energy first decreases and then increases continually.
(ix) Enthalpy first decreases and then increases continually.
(x) Gibbs's energy first decreases and then increases and again decreases continually.

Table 1. The Highest occupied molecular orbital(HOMO) and lowest unoccupied molecular orbital (LUMO) gap, dipole moment, thermal energy, polarizability, total energy, constant volume heat capacity, entropy, zero-point energy (ZPE), enthalpy, Gibbs energy of 5CB-5CB dimer in parallel conformation at different interacting position (translation along the long molecular axis) in the forward direction

5CB-5CB Parallel Conformation	0.5Å	1.0Å	1.5Å	2.0Å	2.5Å
HOMO-LUMO (eV)	4.50	4.51	4.51	4.52	4.52
Dipole moment (Debye)	10.37	10.36	10.36	10.35	10.34
Thermal Energy (kcal/mol)	427.71	427.69	427.08	427.07	427.68
Polarizability (kcal/mol)	256867	256779	256691	256603	256522
Total Energy (kcal/mol)	−9440.86	−9440.91	−9440.95	−9440.99	−9441.02
Heat capacity (C_v) (kcal/mol)	0.14	0.14	0.13	0.13	0.14
Entropy (kcal/mol)	0.23	0.23	0.22	0.22	0.23
ZPE (kcal/mol)	404.53	404.50	404.44	404.43	404.46
Enthalpy (kcal/mol)	428.29	428.28	427.66	427.66	428.27
Gibbs Energy (kcal/mol)	358.39	357.92	360.19	360.06	358.19

When the first monomer (5CB) has fixed and the second monomer (5CB) moves backward then all possible interaction properties of the dimer in this conformation can be tabulated as Table 2, and we conclude the following statements:

(i) The HOMO-LUMO gap decreases continually.
(ii) Polarizability decreases continually.

(iii) Total energy increases and then decreases continually.
(iv) Dipole moment first decreases and then increases continually.
(v) Internal thermal energy increases continually.
(vi) Constant volume heat capacity remains constant.
(vii) Entropy first increases and then decreases continually.
(viii) Zero-point energy first increases and then decreases continually.
(ix) Enthalpy increases continually.
(x) Gibbs's energy first decreases and then increases and again decreases continually.

Table 2. The Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) gap, dipole moment, thermal energy, polarizability, total energy, constant volume heat capacity, entropy, zero-point energy (ZPE), enthalpy, Gibbs energy of 5CB-5CB dimer in parallel conformation at different interacting position (translation along the long molecular axis) in the backward direction

5CB-5CB Parallel conformation	0.5Å	1.0Å	1.5Å	2.0Å	2.5Å
HOMO-LUMO (eV)	4.51	4.51	4.50	4.49	4.48
Dipole moment (Debye)	10.35	10.34	10.34	10.35	10.35
Thermal Energy (kcal/mol)	427.68	427.69	427.72	427.74	427.74
Polarizability (kcal/mol)	256377	256308	256239	256183	256120
Total Energy (kcal/mol)	−9440.06	−9440.07	−9440.07	−9440.07	−9440.06
Heat capacity (C_v) (kcal/mol)	0.14	0.14	0.14	0.14	0.14
Entropy (kcal/mol)	0.23	0.24	0.23	0.23	0.22
ZPE (kcal/mol)	404.46	404.46	404.50	404.54	404.53
Enthalpy (kcal/mol)	428.27	428.28	428.30	428.33	428.33
Gibbs Energy (kcal/mol)	358.11	357.89	358.25	358.43	358.16

3.2 5CB-5CB Antiparallel Conformation

In this section, we study the interaction of 5CB-5CB liquid crystal dimers in the antiparallel configuration, as shown in Figure 2.

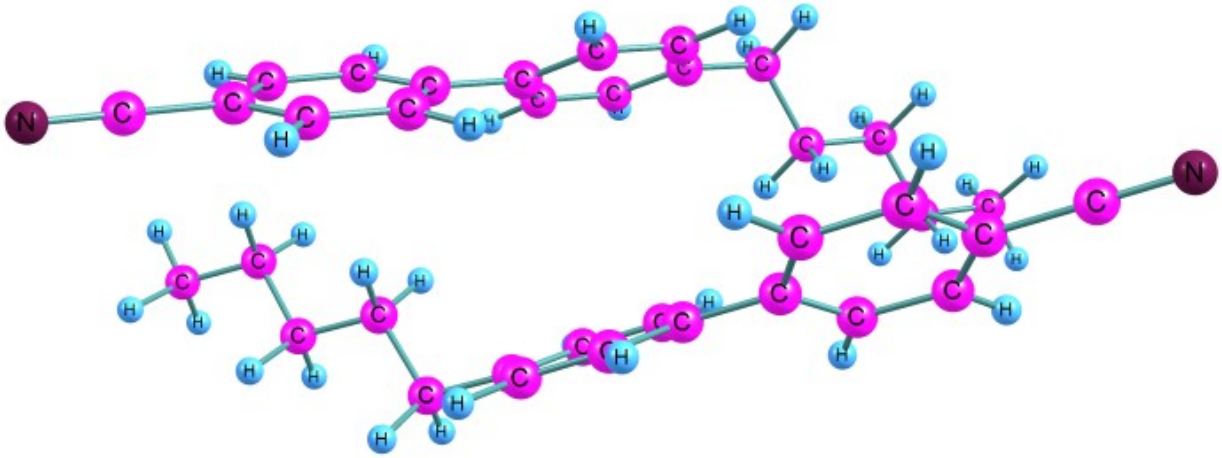

Figure 2. Antiparallel conformation of 5CB liquid crystal dimer

The polarizability of the 5CB-5CB dimer in antiparallel conformation decreases continually when the 5CB monomer moves in forwarding or backward direction in contrast to Figure 2. The dipole moment of this dimer in antiparallel conformation increases continuously when the monomer (5CB) moves in forward or backward direction. This conformation has the least dipole moment as a comparison to the four conformations of 5CB liquid crystal dimer. The cyano group of the first monomer (5CB) interacts with the tail of another monomer at a distance of 2.82Å. The benzene of the first monomer (5CB) interacts with the benzene another monomer (5CB) at a range of 2.60Å. The benzene of the first monomer interacts with the benzene of another monomer; they interact mutually at a distance of 2.39Å. The cyano group of the first monomer interacts with the tail of another monomer at a range of 2.80Å. This conformation has the least energy as a comparison to all the conformation of 5CB dimer the interaction energy of this conformation (antiparallel Figure 2) is higher as a comparison with all the conformations of the 5CB dimer. When the first monomer (5CB) has fixed and the second monomer (5CB) moves forward then all possible interaction properties of the dimer in this conformation have been tabulated as Table 3, and hence we conclude the following statements:

(i) The HOMO-LUMO gap remains constant.

(ii) Polarizability decreases continually.

(iii) Total energy increases continually.

(iv) Dipole moment increases continually.

(v) Internal thermal energy decreases continually.

(vi) Constant volume heat capacity remains constant.

(vii) Entropy remains constant.

(viii) Zero-point energy first decreases and then increases and again decreases continually.

(ix) Enthalpy decreases continually.

(x) Gibbs's energy first decreases and then increases and again decreases continually.

Table 3. The Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) gap, dipole moment, thermal energy, polarizability, total energy, constant volume heat capacity, entropy, zero-point energy (ZPE), enthalpy, Gibbs energy of 5CB-5CB dimer in antiparallel conformation at different interacting position (translation along the long molecular axis) in the forward direction

5CB-5CB Antiparallel conformation	0.5Å	1.0Å	1.5Å	2.0Å	2.5Å
HOMO-LUMO (eV)	4.53	4.53	4.53	4.53	4.53
Dipole moment (Debye)	4.69	4.70	4.72	4.73	4.74
Thermal Energy (kcal/mol)	427.66	427.66	427.65	427.64	427.63
Polarizability (kcal/mol)	256478	256346	256227	256107	255994
Total Energy (kcal/mol)	−9440.10	−9440.20	−9440.30	−9440.30	−9440.40
Heat capacity (C_v) (kcal/mol)	0.14	0.14	0.14	0.14	0.14
Entropy (kcal/mol)	0.23	0.23	0.23	0.23	0.23
ZPE (kcal/mol)	404.43	404.42	404.67	404.39	404.36
Enthalpy (kcal/mol)	428.25	428.24	428.24	428.23	428.21
Gibbs Energy (kcal/mol)	358.44	358.33	358.36	358.27	357.94

When the first monomer (5CB) has fixed and the second monomer (5CB)moves backward then all possible interaction properties of the dimer in this conformation have been tabulated as Table 4, and hence we conclude the following statements:

(i) The HOMO-LUMO gap increases continually.

(ii) Polarizability decreases continually.

(iii) Total energy increases continually.

(iv) Dipole moment increases continually.

(v) Internal thermal energy increases continually.

(vi) Constant volume heat capacity remains constant.

(vii) Entropy first remains constant.

(viii) Zero-point energy first decreases and then increases continually.

(ix) Enthalpy first decreases and then increases continually.

(x) Gibbs's energy first decreases and then increases continually.

Table 4. The Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) gap, dipole moment, thermal energy, polarizability, total energy, constant volume heat capacity, entropy, zero-point energy (ZPE), enthalpy, Gibbs energy of 5CB-5CB dimer in antiparallel conformation at different interacting position (translation along the long molecular axis) in the backward direction

5CB-5CB Antiparallel conformation	0.5Å	1.0Å	1.5Å	2.0Å	2.5Å
HOMO-LUMO (eV)	4.53	4.53	4.53	4.53	4.54
Dipole moment (Debye)	4.76	4.76	4.77	4.78	4.78
Thermal Energy (kcal/mol)	427.59	427.59	427.59	427.60	427.61
Polarizability (kcal/mol)	255794	255699	255612	255536	255474
Total Energy (kcal/mol)	−9440.30	−9440.40	−9440.50	−9440.60	−9440.70
Heat capacity (C_v) (kcal/mol)	0.14	0.14	0.14	0.14	0.14
Entropy (kcal/mol)	0.23	0.23	0.23	0.23	0.23
ZPE (kcal/mol)	404.29	404.27	404.27	404.29	404.30
Enthalpy (kcal/mol)	428.18	428.17	428.18	428.19	428.19
Gibbs Energy (kcal/mol)	357.27	357.25	357.23	357.36	357.43

3.3 5CB-5CB Cross to Each other Conformation

Here, we study the interaction properties of the same dimer (5CB-5CB) but in the cross to each other conformation, as shown in Figure 3.

The polarizability, total energy, and Gibbs energy of this dimer conformation decrease continually when the monomer (5CB) moves in forward or backward direction. The dipole moment and entropy of this dimer increases continuously when the monomer (5CB) moves in forward or backward direction. The benzene of the first monomer (5CB) interacts with the tail of another monomer (5CB) at a distance of 2.96Å. The benzene of the second monomer interacts with the tail of the first monomer at a distance of 2.87Å. This cross conformation of 5CB-5CB represents better interaction energy as a comparison with the parallel conformation of 5CB dimer. Still, this conformation does not give the best interaction energy as a comparison with

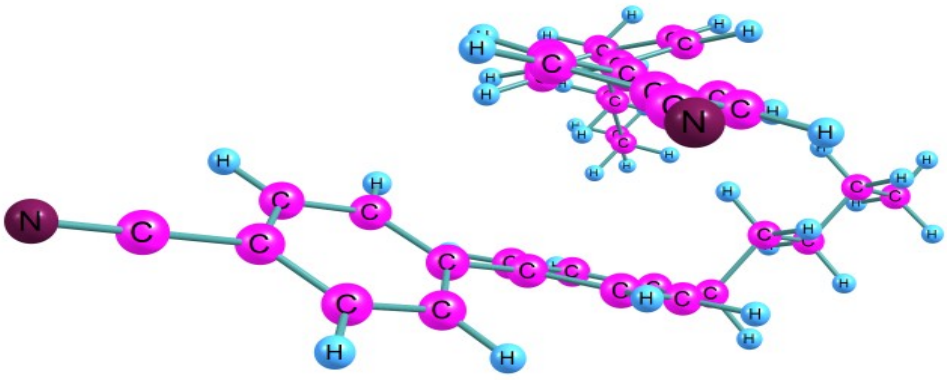

Figure 3. Cross conformation of 5CB liquid crystal dimer

antiparallel conformation because this conformation represents higher electronic energy. When the first monomer (5CB) has fixed and the second monomer (5CB)moves forward then all possible interaction properties of the dimer in this conformation have been tabulated as Table 5, and hence we conclude the following statements:

(i) The HOMO-LUMO gap increases continually.
(ii) Polarizability decreases continually.
(iii) Total energy decreases continually.
(iv) Dipole moment increases continually.
(v) Internal thermal energy first decreases and then increases continually.
(vi) Constant volume heat capacity first decreases and then increases continually.
(vii) Entropy first decreases and then increases continually.
(viii) Zero-point energy decreases continually.
(ix) Enthalpy first decreases and then increases continually.
(x) Gibbs's energy first increases and then decreases continually.

Table 5. The Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) gap, dipole moment, thermal energy, polarizability, total energy, constant volume heat capacity, entropy, zero-point energy (ZPE), enthalpy, Gibbs energy of 5CB-5CB dimer in cross conformation at different interacting position (translation along the long molecular axis) in the forward direction

5CB-5CB Cross conformation	0.5Å	1.0Å	1.5Å	2.0Å	2.5Å
HOMO-LUMO(eV)	4.51	4.51	4.52	4.52	4.52
Dipole moment (Debye)	10.47	10.48	10.49	10.49	10.49
Thermal Energy (kcal/mol)	427.61	427.00	426.98	426.98	427.56
Polarizability (kcal/mol)	256089	255963	255844	255731	255630
Total Energy (kcal/mol)	−9440.40	−9440.30	−9440.20	−9440.10	−9440.00
Heat capacity (C_v) (kcal/mol)	0.14	0.13	0.13	0.13	0.14
Entropy (kcal/mol)	0.23	0.22	0.22	0.22	0.23
ZPE(kcal/mol)	404.38	404.34	404.33	404.32	404.31
Enthalpy (kcal/mol)	428.19	427.58	427.57	427.56	428.15
Gibbs Energy (kcal/mol)	358.09	360.02	359.93	359.87	357.49

When the first monomer (5CB) has fixed and the second monomer (5CB) moves backward then all possible interaction properties of the dimer in this conformation have been tabulated as Table 6, and hence we conclude the following statements:

(i) The HOMO-LUMO gap remains constant.
(ii) Polarizability decreases continually.
(iii) Total energy decreases continually.
(iv) Dipole moment increases constantly.
(v) Internal thermal energy increases continually.
(vi) Constant volume heat capacity increases continually.
(vii) Entropy increases continually.
(viii) Zero-point energy first decreases and then increases continually.
(ix) Enthalpy increases continually.
(x) Gibbs's energy decreases continually.

Table 6. The Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) gap, dipole moment, thermal energy, polarizability, total energy, constant volume heat capacity, entropy, zero-point energy (ZPE), enthalpy, Gibbs energy of 5CB-5CB dimer in cross conformation at different interacting position (translation along the long molecular axis) in backward direction

5CB-5CB Cross conformation	0.5Å	1.0Å	1.5Å	2.0Å	2.5Å
HOMO-LUMO (eV)	4.51	4.51	4.51	4.51	4.51
Dipole moment (Debye)	10.50	10.50	10.51	10.51	10.52
Thermal Energy (kcal/mol)	423.97	426.96	426.96	427.56	427.56
Polarizability (kcal/mol)	255436	255348	255267	255197	255122
Total Energy (kcal/mol)	−9440.10	−9440.08	−9440.06	−9440.05	−9440.03
Heat capacity (C_v) (kcal/mol)	0.13	0.13	0.13	0.14	0.14
Entropy (kcal/mol)	0.22	0.22	0.22	0.23	0.23
ZPE (kcal/mol)	404.29	404.27	404.27	404.28	404.28
Enthalpy (kcal/mol)	427.55	427.55	427.55	428.14	428.14
Gibbs Energy (kcal/mol)	359.67	359.56	359.48	353.21	357.10

3.4 6CB-6CB Parallel Conformation

Now, we study the interaction properties of another dimer 6CB-6CB in parallel conformation, as shown in Figure 4.

Figure 4. Parallel conformation of 6CB liquid crystal dimer

The polarizability, total energy, and internal thermal energy of this dimer increase continually when the monomer (6CB) moves in forward or backward direction. The dipole moment of this dimer decreases continuously when the monomer (6CB) moves in forwarding or backward direction. The benzene of the first monomer (6CB) interacts with the benzene of the second monomer (6CB) at a distance of 2.43Å. The benzene-benzene interaction (2.43Å) of the 5CB dimer is equivalent to the benzene-benzene interaction (2.43Å) of the 6CB dimer in parallel conformations. The tail of the first monomer (6CB) interacts with the benzene of the second monomer (6CB) at a distance of 2.80Å. The tail of the second monomer (6CB) interacts with the benzene of the first monomer (6CB) at a distance of 2.63Å. When the first monomer (6CB) has fixed and the second monomer (6CB) moves forward all possible interaction properties of the dimer in this conformation have been tabulated as Table 7, and hence we conclude the following statements:

(i) The HOMO-LUMO gap remains constant.

(ii) Polarizability increases continually.

(iii) Total energy increases continually.

(iv) Dipole moment decreases continually.

(v) Internal thermal energy increases continually.

(vi) Constant volume heat capacity remains constant.

(vii) Entropy remains constant.

(viii) Zero-point energy first increases and then decreases and again increases continually.

(ix) Enthalpy remains constant.

(x) Gibbs's energy first increases and then suddenly it falls and again increases continually.

Table 7. The Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) gap, dipole moment, thermal energy, polarizability, total energy, constant volume heat capacity, entropy, zero-point energy (ZPE), enthalpy, Gibbs energy of 6CB-6CB dimer in parallel conformation at different interacting position (translation along the long molecular axis) in the forward direction

6CB-6CBParallel conformation	0.5Å	1.0Å	1.5Å	2.0Å	2.5Å
HOMO-LUMO (eV)	4.63	4.63	4.63	4.63	4.63
Dipole moment (Debye)	10.43	10.42	10.41	10.40	10.39
Thermal Energy (kcal/mol)	465.08	465.08	465.08	465.09	465.09
Polarizability (kcal/mol)	272065	272203	272341	272479	272623
Total Energy (kcal/mol)	−9933.32	−9933.38	−9933.43	−9933.48	−9933.54
Heat capacity (C_v) (kcal/mol)	0.15	0.15	0.15	0.15	0.15
Entropy (kcal/mol)	0.25	0.25	0.25	0.25	0.25
ZPE (kcal/mol)	440.16	440.16	440.17	440.16	440.17
Enthalpy (kcal/mol)	465.67	465.67	465.67	465.67	465.67
Gibbs Energy (kcal/mol)	390.70	390.76	390.76	390.43	390.55

When the first monomer (6CB) has fixed and the second monomer (6CB) moves backward then the all possible interaction properties of the dimer in this conformation can be tabulated as Table 8, and hence then we conclude the following statements:

(i) The HOMO-LUMO gap remains constant.
(ii) Polarizability increases continually.
(iii) Total energy increases continually.
(iv) Dipole moment decreases continually.
(v) Internal thermal energy first decreases and then increases continually.
(vi) Constant volume heat capacity remains constant.
(vii) Entropy remains constant.
(viii) Zero-point energy first decreases and then increases continually.
(ix) Enthalpyincreases continually.
(x) Gibbs's energy first decreases and then increases continually.

Table 8. The Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) gap, dipole moment, thermal energy, polarizability, total energy, constant volume heat capacity, entropy, zero-point energy (ZPE), enthalpy, Gibbs energy of 6CB-6CB dimer in parallel conformation at different interacting position (translation along the long molecular axis) in backward direction

6CB-6CB Parallel conformation	0.5Å	1.0Å	1.5Å	2.0Å	2.5Å
HOMO-LUMO (eV)	4.64	4.64	4.64	4.64	4.64
Dipole moment (Debye)	10.38	10.37	10.37	10.36	10.35
Thermal Energy (kcal/mol)	464.49	464.48	464.48	464.49	464.49
Polarizability (kcal/mol)	272912	273056	273207	273351	273495
Total Energy (kcal/mol)	−9933.60	−9933.70	−9933.70	−9933.80	−9933.90
Heat capacity (C_v) (kcal/mol)	0.14	0.14	0.14	0.14	0.14
Entropy (kcal/mol)	0.24	0.24	0.24	0.24	0.24
ZPE (kcal/mol)	440.15	440.14	440.13	440.14	440.15
Enthalpy (kcal/mol)	465.07	465.07	465.07	465.07	465.08
Gibbs Energy (kcal/mol)	392.95	392.90	392.91	392.92	392.92

3.5 6CB-6CB Antiparallel Conformation

In this section, the interaction properties of antiparallel conformation of 6CB-6CB liquid crystal dimers (Figure 5) have studied.

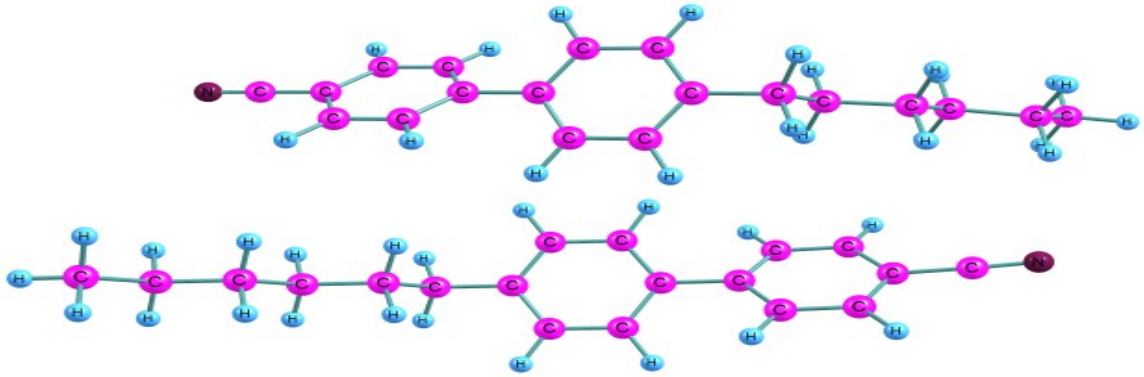

Figure 5. Antiparallel conformation of 6CB liquid crystal dimer

The dipole moment, total energy, and entropy of this dimer in antiparallel conformation increase continually when the monomer (6CB) moves in forward or backward direction. The polarizability of this dimer decreases continuously when the monomer (6CB) moves in forwarding or backward direction. The tail of the first monomer (6CB) interacts with the benzene of the second monomer (6CB) at a distance of 2.91Å. The tail of the second monomer (6CB) interacts with the benzene of the first monomer (6CB) at a distance of 2.95Å. When the first monomer (6CB) has fixed, and the other monomer (6CB) moves forward all possible interaction properties of the dimer in this conformation can be tabulated as Table 9, and hence then we conclude the following statements:

(i) The HOMO-LUMO gap decreases continually.
(ii) Polarizability decreases continually.
(iii) Total energy first decreases and then increases continually.
(iv) Dipole moment increases continually.
(v) Internal thermal energy increases continually.
(vi) Constant volume of heat capacity increases continually.
(vii) Entropy increases continually.
(viii) Zero-point energy increases continually.
(ix) Enthalpy increases continually.
(x) Gibbs's energy first decreases and then increases and again decreases continually.

Table 9. The Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) gap, dipole moment, thermal energy, polarizability, total energy, constant volume heat capacity, entropy, zero-point energy (ZPE), enthalpy, Gibbs energy of 6CB-6CB dimer in antiparallel conformation at different interacting position (translation along the long molecular axis) in the forward direction

6CB-6CB Antiparallel conformation	0.5Å	1.0Å	1.5Å	2.0Å	2.5Å
HOMO-LUMO (eV)	4.51	4.51	4.51	4.51	4.50
Dipole moment (Debye)	2.40	2.41	2.41	2.42	2.43
Thermal Energy (kcal/mol)	464.47	465.07	465.07	465.07	465.08
Polarizability (kcal/mol)	271406	271343	271274	271211	271155
Total Energy (kcal/mol)	−9933.96	−9933.07	−9933.17	−9933.26	−9933.34
Heat capacity (C_v) (kcal/mol)	0.14	0.15	0.15	0.15	0.15
Entropy (kcal/mol)	0.23	0.24	0.24	0.25	0.25
ZPE (kcal/mol)	440.20	440.21	440.21	440.21	440.21
Enthalpy (kcal/mol)	465.06	465.65	465.66	465.66	465.66
Gibbs Energy (kcal/mol)	394.14	391.94	392.26	392.25	392.24

When the first monomer (6CB) has fixed and the second monomer (6CB) moves backward then all possible interaction properties of the dimer in this conformation can be tabulated as Table 10, and hence we concluded the following statements:

(i) The HOMO-LUMO gap decreases continually.
(ii) Polarizability decreases continually.
(iii) Total energy increases continually.

(iv) Dipole moment increases continually.

(v) Internal thermal energy decreases continually.

(vi) Constant volume heat capacity remains constant.

(vii) Entropy increases continually.

(viii) Zero-point energy decreases continually.

(ix) Enthalpy decreases continually.

(x) Gibbs's energy first decreases and then increases and again decreases continually.

Table 10. The Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) gap, dipole moment, thermal energy, polarizability, total energy, constant volume heat capacity, entropy, zero-point energy (ZPE), enthalpy, Gibbs energy of 6CB-6CB dimer in antiparallel conformation at different interacting position (translation along the long molecular axis) in the backward direction

6CB-6CB Antiparallel conformation	0.5Å	1.0Å	1.5Å	2.0Å	2.5Å
HOMO-LUMO (eV)	4.50	4.49	4.49	4.49	4.48
Dipole moment (Debye)	2.44	2.45	2.46	2.46	2.47
Thermal Energy (kcal/mol)	465.07	465.06	465.05	465.04	465.04
Polarizability (kcal/mol)	271042	270992	270948	270910	270872
Total Energy (kcal/mol)	-9933.40	-9933.50	-9933.60	-9933.70	-9933.80
Heat capacity (C_v) (kcal/mol)	0.15	0.15	0.15	0.15	0.15
Entropy (kcal/mol)	0.24	0.24	0.25	0.25	0.26
ZPE (kcal/mol)	440.18	440.14	440.12	440.11	440.09
Enthalpy (kcal/mol)	465.65	465.64	465.63	465.63	465.62
Gibbs Energy (kcal/mol)	392.05	391.80	391.69	392.04	391.50

3.6 5CB-6CB Antiparallel Conformation

Now, we study the interaction of 5CB with 6CB liquid crystal in antiparallel conformation, as shown in Figure 6.

The 5CB and 6CB monomer have π-π interactions in the antiparallel conformation that has shown in Figure 6. This antiparallel conformation has the least dipole moment as a comparison to the four conformations of 5CB-6CB liquid crystal dimer. The cyano group of 6CB monomer interacts with the tail 5CB monomer at a distance of 2.71Å. The benzene of 5CB monomer interacts with the benzene of 6CB monomer at a distance of 2.88Å. The cyano group of 5CB monomer interacts with the tail of 6CB monomer at a distance of 2.84Å. When the first 5CB monomer has fixed and the second 6CB monomer moves forward and all possible interaction properties of dimer shown in Table 11, and hence then we conclude the following statements:

(i) The HOMO-LUMO gap first decreases and then increases continually.

(ii) The polarizability first decreases and then increases continually.

(iii) Total energy decreases continually.

(iv) Dipole moment increases continually.

(v) Internal thermal energy first decreases and then increases continually.

(vi) Constant volume heat capacity remains constant.

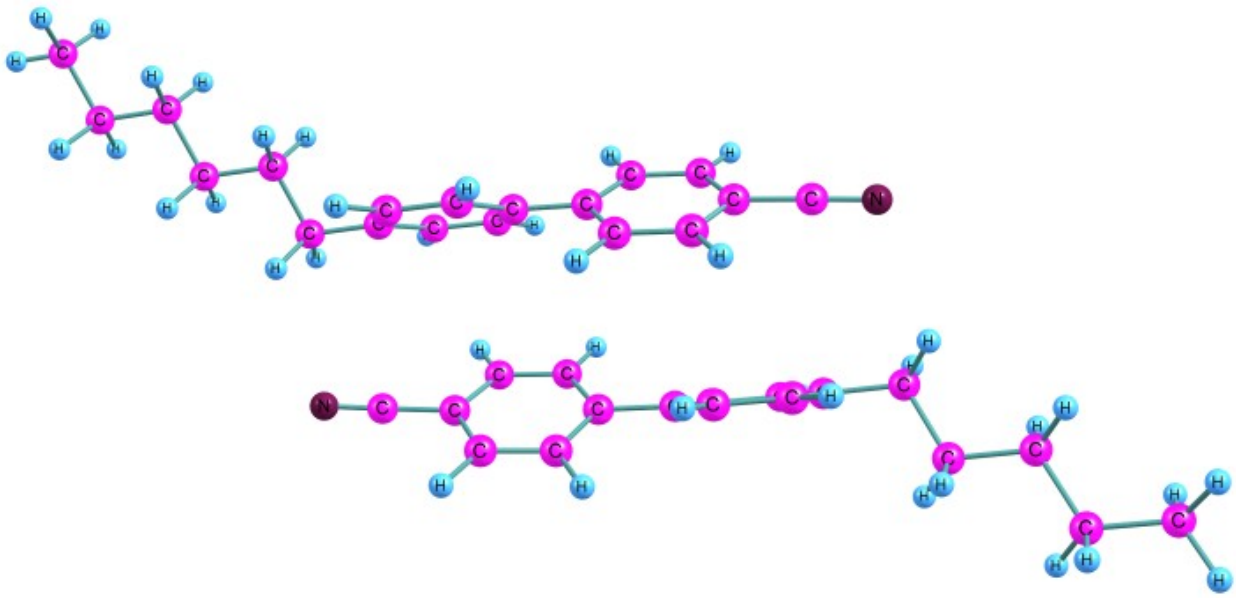

Figure 6. Antiparallel conformation of 5CB and 6CB liquid crystal dimer

(vii) Entropy first decreases and then increases continually.

(viii) Zero-point energy increases and then decreases and again increases continually.

(ix) Enthalpy first decreases and then increases continually.

(x) Gibbs's energy first increases then decreases and then again increases continually.

Table 11. The Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) gap, dipole moment, thermal energy, polarizability, total energy, constant volume heat capacity, entropy, zero-point energy (ZPE), enthalpy, Gibbs energy of 5CB-6CB dimer in antiparallel conformation at different interacting position (translation along the long molecular axis) in the forward direction

5CB-6CB Antiparallel conformation	0.5Å	1.0Å	1.5Å	2.0Å	2.5Å
HOMO-LUMO (eV)	4.42	4.28	4.28	4.44	4.57
Dipole moment (Debye)	0.54	0.55	0.56	0.57	0.58
Thermal Energy (kcal/mol)	444.78	444.30	444.35	444.93	445.04
Polarizability (kcal/mol)	259408	258705	258486	258875	259345
Total Energy (kcal/mol)	−9686.40	−9686.35	−9686.30	−9686.25	−9686.20
Heat capacity (C_v) (kcal/mol)	0.13	0.13	0.13	0.13	0.13
Entropy (kcal/mol)	0.21	0.20	0.20	0.21	0.21
ZPE (kcal/mol)	423.16	423.38	423.47	423.45	423.61
Enthalpy (kcal/mol)	445.37	444.89	444.93	445.52	445.62
Gibbs Energy (kcal/mol)	380.11	383.12	383.27	381.54	381.88

When the first 5CB monomer has fixed and the second 6CB monomer moves backward then all possible interaction properties of the dimer in this conformation can be tabulated as Table 12 and hence we conclude the following statements:

(i) The HOMO-LUMO gap first decreases and then increases continually.

(ii) The polarizability first decreases and then increases continually.

(iii) Total energy first decreases and then increases continually.

(iv) Dipole moment decreases continually.

(v) Internal thermal energy first decreases and then increases and again decreases continually.

(vi) Constant volume heat capacity remains constant.

(vii) Entropy first increases and then decreases continually.

(viii) Zero-point energy decreases continually.

(ix) Enthalpyfirst decreases and then increases and then again decreases continually.

(x) Gibbs's energy first increases and then decreases and again increases continually.

Table 12. The Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) gap, dipole moment, thermal energy, polarizability, total energy, constant volume heat capacity, entropy, zero-point energy (ZPE), enthalpy, Gibbs energy of 5CB-6CB dimer in antiparallel conformation at different interacting position (translation along the long molecular axis) in the backward direction

5CB-6CB Antiparallel conformation	0.5Å	1.0Å	1.5Å	2.0Å	2.5Å
HOMO-LUMO (eV)	4.50	4.42	4.46	4.56	4.62
Dipole moment (Debye)	0.54	0.53	0.52	0.52	0.51
Thermal Energy (kcal/mol)	444.69	444.04	443.95	444.52	443.32
Polarizability (kcal/mol)	262834	260625	261209	262050	263079
Total Energy (kcal/mol)	−9686.80	−9686.30	−9686.40	−9686.40	−9686.43
Heat capacity (C_v) (kcal/mol)	0.13	0.13	0.13	0.13	0.13
Entropy (kcal/mol)	0.21	0.21	0.21	0.22	0.21
ZPE (kcal/mol)	422.91	422.75	422.57	422.53	422.45
Enthalpy (kcal/mol)	445.27	444.62	444.54	445.11	443.90
Gibbs Energy (kcal/mol)	379.75	380.77	379.83	377.20	381.01

3.7 5CB-6CB Parallel Conformation

In this section, we study the interaction properties of the 5CB-6CB in parallel conformation, as shown in Figure 7.

The polarizability of this dimer in parallel conformation increases continually when the 5CB and 6CB monomer moves in forward or backward direction. The total energy of this dimer decreases continuously when the 5CB and 6CB monomer moves in forward or backward direction. This conformation has π-π interaction between 5CB and 6CB liquid crystal dimer, as shown in Figure 7. The tail of the 6CB monomer interacts with the tail of 5CB monomer at a distance of 2.19Å. The benzene of 6CB monomer interacts with the benzene of 5CB monomer at a distance of 2.47Å. When the first 5CB monomer has fixed and the second 6CB monomer moves forward then all possible interaction properties of the dimer in this conformation can be tabulated as Table 13, and hence we conclude the following statements:

(i) The HOMO-LUMO gap decreases continually.

(ii) Polarizability increases continually.

(iii) Total energy decreases continually.

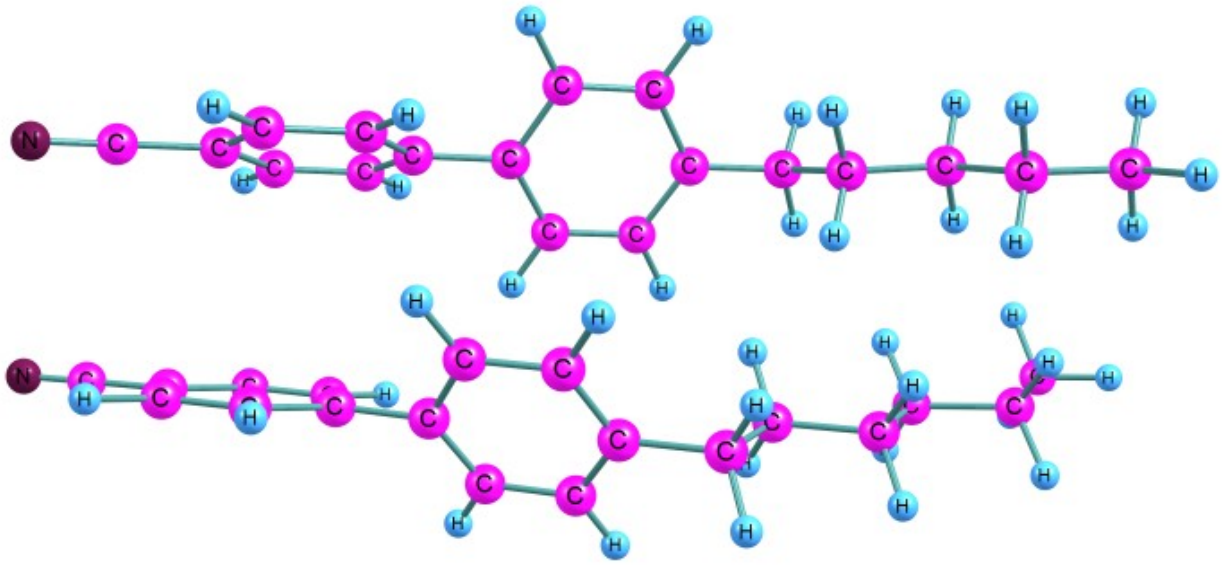

Figure 7. Parallel conformation of 5CB and 6CB liquid crystal dimer

(iv) Dipole moment first decreases and then increases continually.
(v) Internal thermal energy first increases and then decreases continually.
(vi) Constant volume of heat capacity decreases continually.
(vii) Entropy decreases continually.
(viii) Zero-point energy first increases and then decreases continually.
(ix) Enthalpy first increases and then decreases continually.
(x) Gibbs's energy first increases and then decreases and again increases continually.

Table 13. The Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) gap, dipole moment, thermal energy, polarizability, total energy, constant volume heat capacity, entropy, zero-point energy (ZPE), enthalpy, Gibbs energy of 5CB-6CB dimer in parallel conformation at different interacting position (translation along the long molecular axis) in the forward direction

5CB-6CB Parallel conformation	0.5Å	1.0Å	1.5Å	2.0Å	2.5Å
HOMO-LUMO (eV)	5.02	4.98	4.71	3.72	2.81
Dipole moment (Debye)	4.10	4.03	4.09	4.55	5.42
Thermal Energy (kcal/mol)	446.00	446.16	445.89	445.58	444.31
Polarizability (kcal/mol)	248301	249638	251834	254714	257940
Total Energy (kcal/mol)	−9686.55	−9686.40	−9685.40	−9685.35	−9683.30
Heat capacity (C_v) (kcal/mol)	0.13	0.13	0.12	0.12	0.12
Entropy (kcal/mol)	0.21	0.20	0.19	0.19	0.18
ZPE (kcal/mol)	424.19	425.10	426.04	426.17	426.05
Enthalpy (kcal/mol)	446.59	446.74	446.47	446.17	444.89
Gibbs Energy (kcal/mol)	382.06	384.79	387.66	386.86	388.94

When the first 5CB monomer has fixed and the second 6CB monomer moves backward then all possible interaction properties of the dimer in this conformation can be tabulated as Table 14 and hence we conclude the following statements:

(i) The HOMO-LUMO gap first increases and then decreases continually.

(ii) Polarizability increases continually.

(iii) Total energy decreases continually.

(iv) Dipole moment first increases and then decreases continually.

(v) Internal thermal energy first decreases and then increases continually.

(vi) Constant volume of heat capacity decreases continually.

(vii) Entropy decreases continually.

(viii) Zero-point energy first decreases and then increases continually.

(ix) Enthalpy first decreases and then increases and again decreases continually.

(x) Gibbs's energy increases continually.

Table 14. The Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) gap, dipole moment, thermal energy, polarizability, total energy, constant volume heat capacity, entropy, zero-point energy (ZPE), enthalpy, Gibbs energy of 5CB-6CB dimer in parallel conformation at different interacting position (translation along the long molecular axis) in the backward direction

5CB-6CB Parallel conformation	0.5Å	1.0Å	1.5Å	2.0Å	2.5Å
HOMO-LUMO (eV)	5.05	5.06	5.03	4.98	4.92
Dipole moment (Debye)	4.26	4.33	4.36	4.32	4.25
Thermal Energy (kcal/mol)	445.03	444.46	443.93	443.56	443.76
Polarizability (kcal/mol)	247291	247373	247906	248910	250127
Total Energy (kcal/mol)	−9686.45	−9686.40	−9685.20	−9685.14	−9685.12
Heat capacity (C_v) (kcal/mol)	0.13	0.13	0.13	0.12	0.12
Entropy (kcal/mol)	0.21	0.20	0.20	0.19	0.19
ZPE (kcal/mol)	423.45	423.42	423.42	423.86	423.92
Enthalpy (kcal/mol)	445.61	444.45	444.52	444.15	444.34
Gibbs Energy (kcal/mol)	380.67	382.48	383.11	385.01	385.14

3.8 5CB-6CB Cross Conformation

Lastly, we study the interaction of 5CB and 6CB liquid crystal in cross conformation, as shown in Figure 8.

The total energy of this dimer decreases continually when the 5CB and 6CB monomer moves in forwarding or backward direction, as shown in Figure 8. The zero-point energy of this conformation increases continuously when the 5CB and 6CB monomer moves in forward or backward direction. The benzene of 5CB monomer interacts with the benzene of 6CB monomer at a distance of 2.94Å. When the first 5CB monomer has fixed and the second 6CB monomer moves forward then all possible interaction properties of the dimer in this conformation can be tabulated as Table 15, and hence we conclude the following statements:

(i) The HOMO-LUMO gap decreases continually.

(ii) Polarizability increases continually.

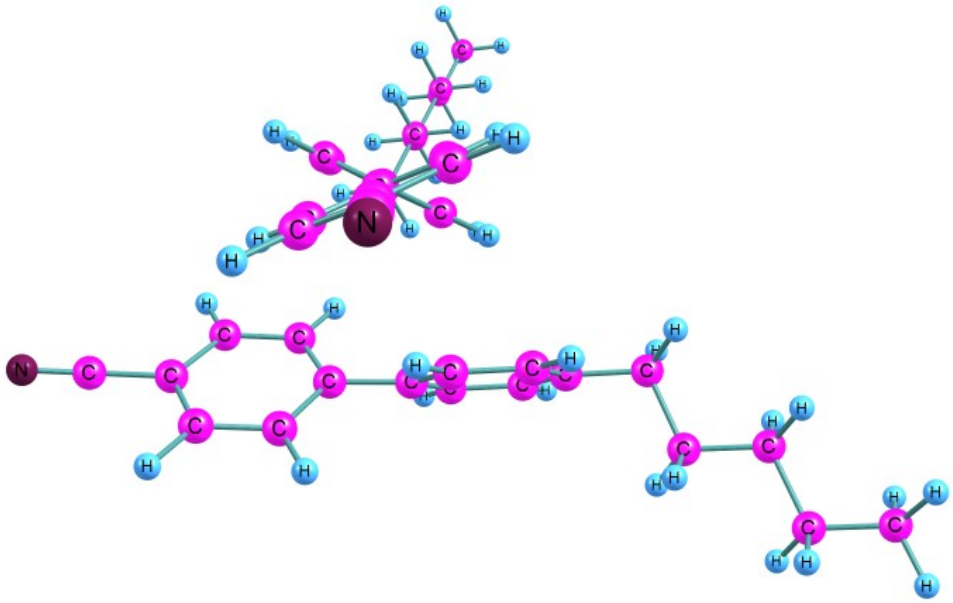

Figure 8. Cross conformation of 5CB and 6CB liquid crystal dimer

(iii) Total energy decreases continually.

(iv) Dipole moment first increases and then decreases continually.

(v) Internal thermal energy first increases and then decreases and increases continually.

(vi) Constant volume heat capacity first decreases and then increases continually.

(vii) Entropy first decreases and then increases continually.

(viii) Zero-point energy increases continually.

(ix) Enthalpy first decreases and then increases continually.

(x) Gibbs's energy first increases and then decreases continually.

Table 15. The Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) gap, dipole moment, thermal energy, polarizability, total energy, constant volume heat capacity, entropy, zero-point energy (ZPE), enthalpy, Gibbs energy of 5CB-6CB dimer in cross conformation at different interacting position (translation along the long molecular axis) in the forward direction

5CB-6CB Cross conformation	0.5Å	1.0Å	1.5Å	2.0Å	2.5Å
HOMO-LUMO (eV)	4.76	4.72	4.63	4.49	4.41
Dipole moment (Debye)	8.17	8.17	8.19	8.17	8.12
Thermal Energy (kcal/mol)	444.26	444.72	443.24	443.45	444.88
Polarizability (kcal/mol)	257369	258404	259904	261265	262351
Total Energy (kcal/mol)	−9686.89	−9686.84	−9686.77	−9686.70	−9686.65
Heat capacity (C_v) (kcal/mol)	0.13	0.13	0.12	0.12	0.13
Entropy (kcal/mol)	0.21	0.20	0.19	0.19	0.21
ZPE (kcal/mol)	423.10	423.15	423.34	423.64	424.00
Enthalpy (kcal/mol)	444.85	444.30	443.83	444.04	445.47
Gibbs Energy (kcal/mol)	381.03	382.50	384.67	385.13	381.26

When the first 5CB monomer cab be fix and the second 6CB monomer moves backward then all possible interaction properties of the dimer in this conformation can be tabulated as Table 16, and hence we conclude the following statements:

(i) The HOMO-LUMO gap first increases and then decreases continually.
(ii) Polarizability increases continually.
(iii) Total energy decreases continually.
(iv) Dipole moment decreases continually.
(v) Internal thermal energy first decreases and then increases continually.
(vi) Constant volume heat capacity first decreases and then increases continually.
(vii) Entropy decreases continually.
(viii) Zero-point energy increases continually.
(ix) Enthalpy first decreases and then increases continually.
(x) Gibbs's energy first increases and then decreases continually.

Table 16. The Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) gap, dipole moment, thermal energy, polarizability, total energy, constant volume heat capacity, entropy, zero-point energy (ZPE), enthalpy, Gibbs energy of 5CB-6CB dimer in cross conformation at different interacting position(translation along the long molecular axis) in the backward direction

5CB-6CB Cross conformation	0.5Å	1.0Å	1.5Å	2.0Å	2.5Å
HOMO-LUMO (eV)	4.80	4.81	4.76	4.71	4.70
Dipole moment (Debye)	8.19	8.16	8.12	8.09	8.05
Thermal Energy (kcal/mol)	444.21	443.65	443.16	443.28	443.99
Polarizability (kcal/mol)	256980	257356	258046	259057	260111
Total Energy (kcal/mol)	−9686.90	−9686.88	−9686.85	−9686.81	−9686.79
Heat capacity (C_v) (kcal/mol)	0.13	0.13	0.12	0.12	0.13
Entropy (kcal/mol)	0.21	0.20	0.20	0.20	0.20
ZPE (kcal/mol)	422.98	422.98	423.12	423.24	423.43
Enthalpy (kcal/mol)	444.79	444.24	443.75	443.86	444.58
Gibbs Energy (kcal/mol)	380.60	381.76	383.94	383.86	382.44

Table 17. The Interaction energy of all the Dimers in parallel and antiparallel configurations

Conformations	Dimer E_1 (kcal/mol)	Monomer × Monomer E_0 (kcal/mol)	Interaction energy (E_1-E_0) (kcal/mol)
5CB-5CB-Parallel	−943931.96	−943923.76	−8.20
5CB-5CB-Antiparallel	−943931.34	−943923.76	−7.58
5CB-5CB-Cross	−943929.54	−943923.76	−5.78
6CB-6CB-Parallel	−993269.59	−993264.40	−5.19
6CB-6CB-Antiparallel	−993269.41	−993264.40	−5.01
5CB-6CB-Antiparallel	−968591.63	−968594.08	2.44
5CB-6CB-Parallel	−968585.59	−968594.08	8.48
5CB-6CB-Cross	−968591.46	−968594.08	2.62

The interaction energies of the stable geometries of dimers have been tabulating as in Table 17, which reflects the interaction and dimers energies of 5CB and 6CB and their dimers in different configurations.

4. Conclusions

In this work, it has found that the antiparallel conformation of 5CB and 6CB liquid crystal dimers have minimum negative interaction energy and also have the least dipole moment as a comparison to all conformations of the dimers. The antiparallel conformations of 5CB and 6CB liquid crystal dimer have the least negative entropy. The parallel conformations of 5CB liquid crystal dimer have higher polarizability as a comparison to all the conformations of the 5CB dimer. The cross conformation of the 5CB dimer has the least polarizability and Gibbs energy. The antiparallel conformations of 6CB dimer have minimum negative polarizability and also have higher Gibbs energy as comparison to all the conformations of the 6CB dimer. But all the conformations of 5CB-6CB dimer have positive interaction energy, so we can conclude that the 5CB and 6CB liquid crystals weakly interact with each other. The antiparallel conformations of the 5CB-6CB dimer have minimum negative polarizability and also have the least dipole moment. On the basis of molecular interaction of 5CB and 6CB, we study the 5CB, and 6CB liquid crystal dimers have minimum negative interaction energy in the antiparallel conformation, but 5CB-6CB liquid crystal dimer has positive interaction energy for all the possible conformations. The isotropic polarizability is minimum in the antiparallel conformation of 6CB liquid crystal dimer (6CB-6CB), but isotropic polarizability is maximum in the parallel conformation of 6CB liquid crystal dimer. The cross conformation of 5CB liquid crystal dimer (5CB-5CB) has the least isotropic polarizability, but the parallel conformation of 5CB liquid crystal dimer has the highest isotropic polarizability.

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Competing Interests

The authors declare that they have no competing interests.

Authors' Contributions

All the authors contributed significantly in writing this article. The authors read and approved the final manuscript.

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