Quantum mechanical study of liquid crystals

DISSERTATION SUBMITTED FOR THE AWARD OF THE DEGREE OF

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in
Physics

By

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***Enrolment No.:**1134/16*

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2021

Dedicated
to my
Mother and
my loving
family

DECLARATION

I declare that the dissertation entitled "**Quantum mechanical study of liquid crystals**" has been prepared by me under the supervision of Dr. Devendra Singh, Assistant Professor, Department of Physics, School of Physical and Decision Sciences, Babasaheb Bhimrao Ambedkar University, Lucknow. No part of this dissertation 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 dissertation is essentially free from all kinds of plagiarism.

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CERTIFICATE

This is to certify that the M. Phil. dissertation titled “**Quantum mechanical study of liquid crystals**” submitted by Mr. Sumit Tiwari 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 M. Phil. dissertation submitted to Babasaheb Bhimrao Ambedkar University, Lucknow satisfies all the requirements as stipulated in the Master of Philosophy (M.Phil.)/Doctor of Philosophy (Ph.D.) regulations as amended in 2019 and it is fit for submission and evaluation for the award of the degree of Master of Philosophy of the University.

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Date: 5·3·2021 Supervisor

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(Sumit Tiwari)

ABSTRACT

Liquid crystals (LCs) are the materials with properties lying between crystalline solids and liquids, sometimes they are considered as fourth state of matter. Liquid crystals are optically anisotropic materials. There are different types of liquid crystal phases (smectic, nematic etc), these may be distinguished by their unique optical properties (such as birefringence) and the properties obtained under the applied electric field. Cynobiphenyls and nitrosobenzonitriles have shown promising applications in liquid crystal devices (LCDs). Both are rod like LCs and serve as models for study of various properties of liquid crystals at molecular level. In this computational work, 4NB and nCB (n=1-5) liquid crystals have been chosen for studying molecular orbitals, HOMO LUMO gap and infra-red spectra. Dielectric constant and polarizability constants have been calculated. Geometry optimizations have been followed by SCF calculations, phonon calculations and spectral analysis.

Density functional theory has emerged as a popular technique for studying complex systems at molecular level. With efforts of Hohenburg, Kohn and Sham, an efficient computational quantum mechanical modelling method evolved and which eventually became quite popular amongst physicists, chemists and material scientists quickly for investigating electronic/nuclear structure with low computational cost. Plane wave self-consistent field method calculates the electronic structure and other related properties using plane wave basis set and pseudopotentials.

PREFACE

Liquid crystals have become increasingly popular due to their immense applications in flat panel displays, bio-sensors, solar cells etc. This dissertation, entitled **"Quantum mechanical study of liquid crystals"**, sums up the results obtained on theoretical research carried out in the Department of Physics, Babasaheb Bhimrao Ambedkar University, Lucknow in between 2019-2021 under the supervision of Dr. Devendra Singh, Assistant Professor, Department of Physics of the University. Structure of liquid crystals has been verified by geometry optimizations. Molecular orbitals have been studied for distribution of electrons and bonding character. To get a glimpse of optical properties of LCs or their response to electric field, polarizability, dielectric constant and band gap have been studied.

The work carried out in the present M. Phil. dissertation is divided into 4 chapters:

Chapter 1

It contains a brief review on liquid crystals, its history, classification, types of liquid crystals and also discusses the properties of liquid crystals and subsequently their applications. This chapter serves as background and motivation for the research work done.

Chapter 2

The chapter 2 describes the computational methods used in molecular modelling arena (ab-initio, DFT, basis set, pseudopotential etc.). The method used in current research work have been summarised in this chapter.

Chapter 3

In this chapter we have studied the molecular properties of 1CB-5CB and 4NB liquid crystals. The molecules were optimized using Projector augmented wave (PAW) and norm conserving (NC) pseudopotentials. Properties like bond length, molecular orbital, IR spectra, polarizability and dielectric constant of the system were calculated.

Chapter 4

It deals with the conclusions and discussions of the current research work. Future scope has also been discussed.

Theoretical methods act as an aid to experimentalists by providing important data of the given material, thus saving chemicals or other equipment cost. This may help in saving environment and act as tool for achieving efficiency of experimental procedures enabling to achieving the objects of green chemistry.

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CHAPTER 1

INTRODUCTION

CHAPTER 1

INTRODUCTION

Matter exists in three states, namely solid liquid and gas. It is only a common perception and is not wholly correct. Many organic substances show multiple melting points when heated. Before reaching the phase of an isotropic liquid, they form intermediate phases where they flow like liquids, still possessing some physical properties or characteristics of a crystal. Materials that exhibit such unusual intermediate phases are known as mesogens. They are termed as mesogenic and various phases in which they show their existence are termed as mesophases [1]. Molecules possessing such phases are popularly known as liquid crystals (LC). Another popular name for it is mesomorphic phase (mesomorphic means ‘of intermediate form’).

The solids have both positional and orientational order in crystalline state i.e. the molecules in solids are constrained to a certain direction and position. The molecules in a liquid are also packed together but they do not have a certain positional or orientational order. The liquid crystals on the other hand can flow like the liquids, but the molecules in the liquid crystals are organized and/or in favour of a crystal-like manner.

Thus liquid crystals can be termed as “orientationally ordered liquids” or positionally disordered crystals as they consist of the properties of both crystalline solids as well as liquid states.

Two generic classes of liquid crystals exist: (a) one in which the changes are driven by thermal processes are known as thermotropic liquid crystals, (b) other is called lyotropic liquid crystal which is strongly influenced by solvents. Many thermotropic liquid crystals exhibit a diversity of stages as the temperature of the system is altered. For example, an LC molecule may exhibit numerous smectic and nematic phases as the temperature is increased.

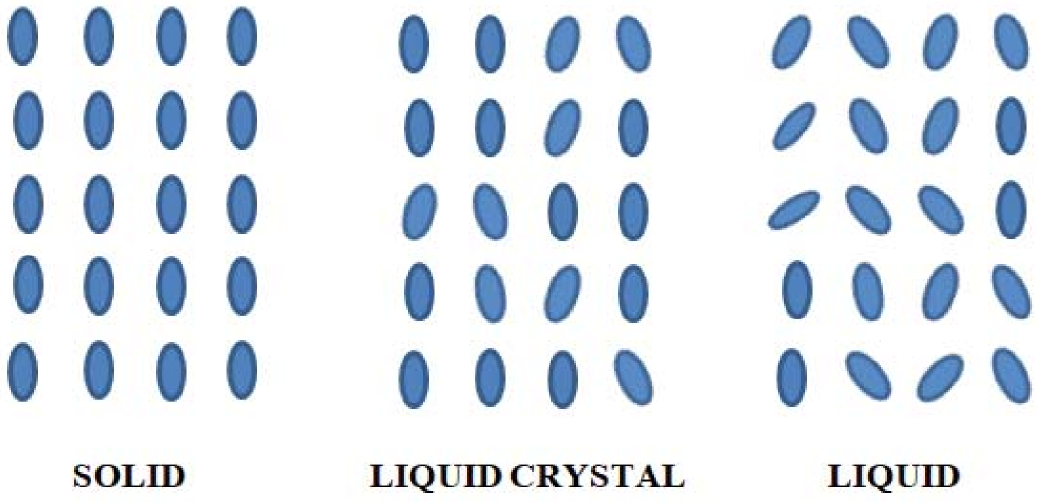

Fig. 1.1 Liquid crystal molecules

Typical arrangement of molecules in solid, liquid crystalline and liquid state is depicted in figure 1.1. The orientation or position in liquid crystal may be ordered depending on type of LC molecule or temperature conditions.

1.1 HISTORY

In the middle of the nineteenth century there was a huge scientific interest in liquid crystals which was centred more on organic materials or products produced from them, e.g., soap. The first report about anisotropic liquids I could find comes from an author, Edgar Allan Poe, who liked to embellish his stories with excursions into natural and technical science. In 1837 he described an anisotropic phase in his narrative of Arthur Gordon Pym [2].

In the late nineteenth century, an Austrian botanist by the name Friedrich Reinitzer, who was studying the cholesteryl benzoate in carrots observed that it showed two melting points. When he heated cholesteryl benzoate, initially at 419 K (145°C), it melted and turned into a cloudy fluid. When it reached 451.65 K (178.5°C), it changed again, but this time into a clear liquid. He also observed two other characteristics of the substance; it reflected polarized light and could also rotate the polarization direction of light.

Surprised by his findings, he approached for help from German physicist Otto Lehmann. When Lehmann studied the cloudy fluid under a microscope, he saw crystallites. He noted that the cloudy phase flowed like a liquid, but that there were other characteristics, such as a rod-like molecular structure that was ordered. This convinced Lehmann that the substance he's studying is a solid. Lehmann continued to study cholesteryl benzoate and other related materials. He concluded that the cloudy fluid represented a newly discovered phase of matter and called it 'liquid crystal'.

In early 1960s chemist Richard Williams began to research the use of liquid crystals while he worked for RCA Laboratories. He discovered that when an electric field was applied to a thin layer of liquid crystals, the crystals would form stripe patterns and enter into a nematic state. His discovery would come to be known as "William's domain" and led to the possiblity of use of liquid crystal in display devices.

A nematic liquid crystal causes the polarization of light waves to change as the waves pass through it, the extent of which depends upon the intensity of the electrical field. One problem Williams encountered, while he attempted to use liquid crystals for displays, was that in order for liquid crystals to enter a nematic state, they needed to be heated to a temperature impractical for consumer use.

1.2 CHEMICAL STRUCTURE OF LIQUID CRYSTALS

Liquids crystals are organic molecules. They are aromatic. When they contain benzene ring, they are referred as benzene derivatives. Typical aromatic liquid crystal comprises of a side chain R, two or more aromatic rings A and A', connected by linkage group X and a terminal group R' connected to other end (fig 1.2a). Side chain and terminal group are alkyl (C_nH_{2n+1}) or alkoxy ($C_nH_{2n+1}O$) group, such as acyloxyl, alkyl carbonate, alkoxy carbonyl, nitro and cyno groups. The Xs of the lineage group are (-CH=CH-) stilbane, (-COO) ester, (-C≡C-) tolane, (-C≡C-C≡C-) di acetylene, (-N=N-) azoxy, (-CH=N-) Schiff base etc [3]. The list is detailed in table 1.1.

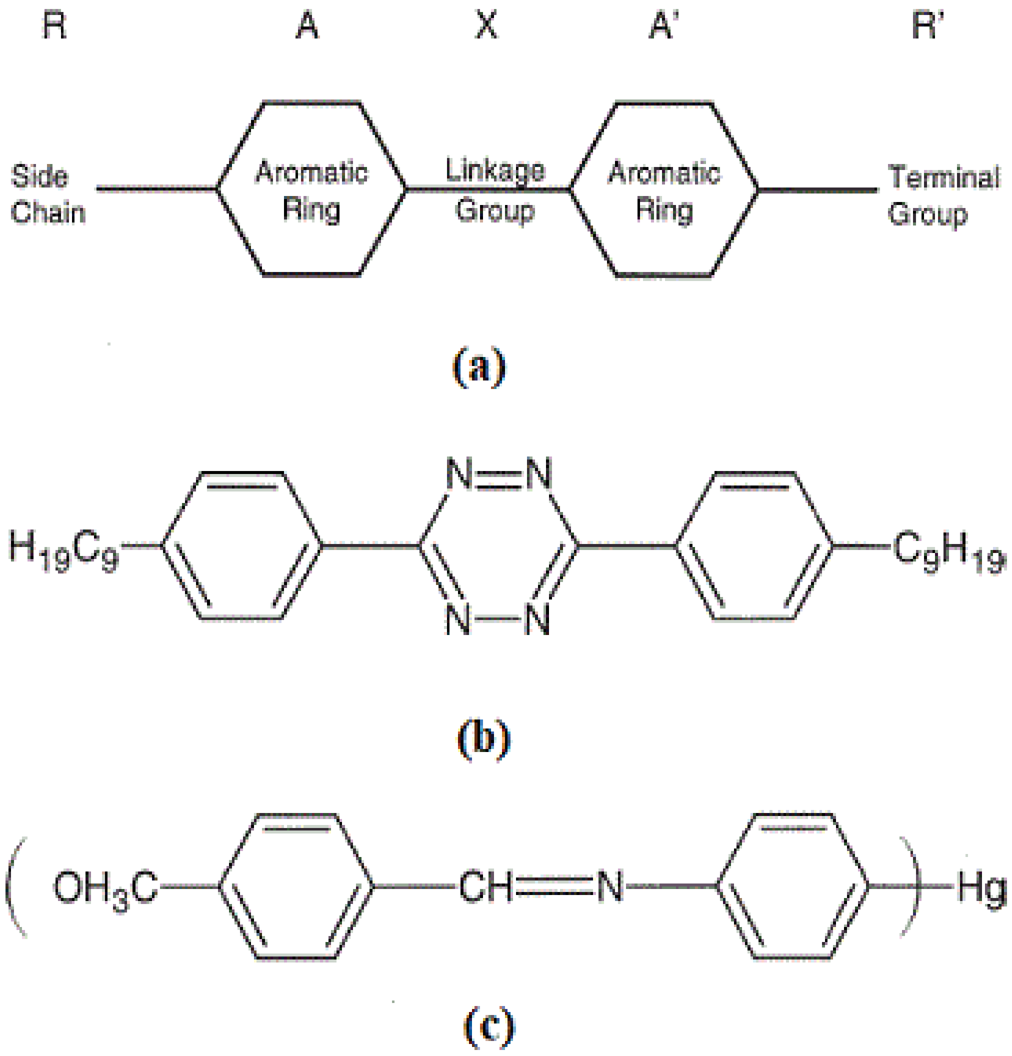

Fig 1.2(a) Molecular structure of a typical liquid crystal **(b)** Molecular structure of a heterocyclic liquid crystal **(c)** Molecular structure of an organometallic liquid crystal

Table 1.1 Description of rigid core, linking group flexible chain and lateral substituents in liquid crystal

Ring or Rigid Core	**Linkage Group**	**Flexible chain**	**Lateral Substituents**
1,4-Phenyl	$-CH_2-CH_2-$	Alkoxy chain	Cl/F/I/Br
1,4-Cyclopentyl	$-(CH=CH)_n-$	CN	NO_2
2,6-Naphthyl	-COO-	NCS	CH_3
2,5-Pyrimidinyl	$-C\equiv C-$	Alkyl chain	CN
1,4-Biphenyl	-CH=CH-	Cl/F/I/Br	CN
1,4-Cyclohexyl	-COS-	CF_3	
	-N=N-	CH_3	
	-CH=N-	NO_2	
	$-O-CH_2-CH_2-O-$		
	-CH=CH-COO-		

1.3 ORIENTATIONAL AND POSITIONAL ORDER

It is evident that the molecules in a crystalline solid are ordered while those in a liquid are disordered. The order in a crystalline solid is positional and orientational whereas both positional and orientational orders do not exist in a liquid. The liquid crystal possesses both positional as well as orientational order. Obviously, the order in a liquid crystal is small as compared to a crystal while it is more than that of a liquid. The order of a crystal is lost when it transforms into a liquid crystal which is found by the amount of value of latent heat. The value is around 250J/g typically for a crystal to a liquid transition. However, the value of latent heat is much smaller around 5J/g when a liquid crystal transforms to a liquid. The molecular axis tends to point along a preferred direction as the molecule under study undergoes diffusion. Such direction is called the director and is denoted by the unit vector $\hat{n}$. The lines perpendicular to the director are equivalent in the most simple liquid crystal phases; the orientational distribution function does not depend on the azimuthal angle ϕ. The order parameter is used to determine the order in a liquid crystal. This can be done using the second Legendre polynomial, $P_2(\cos\theta)$.

Solid crystalline substances have near-perfect orientational order. In mesophases, degree of order is partially lost but the molecules still prefer to lie along a common orientation axis/direction (director). The degree of order is denoted by order parameter (S) defined as a measure of angle between director and long axis of LC molecule. For isotropic substances S=0, for perfect crystals S=1 and for typical LC's 0.3<S<0.8. At higher temperature, the disorder increases in mesogens, hence S gradually decreases (figure 1.3).

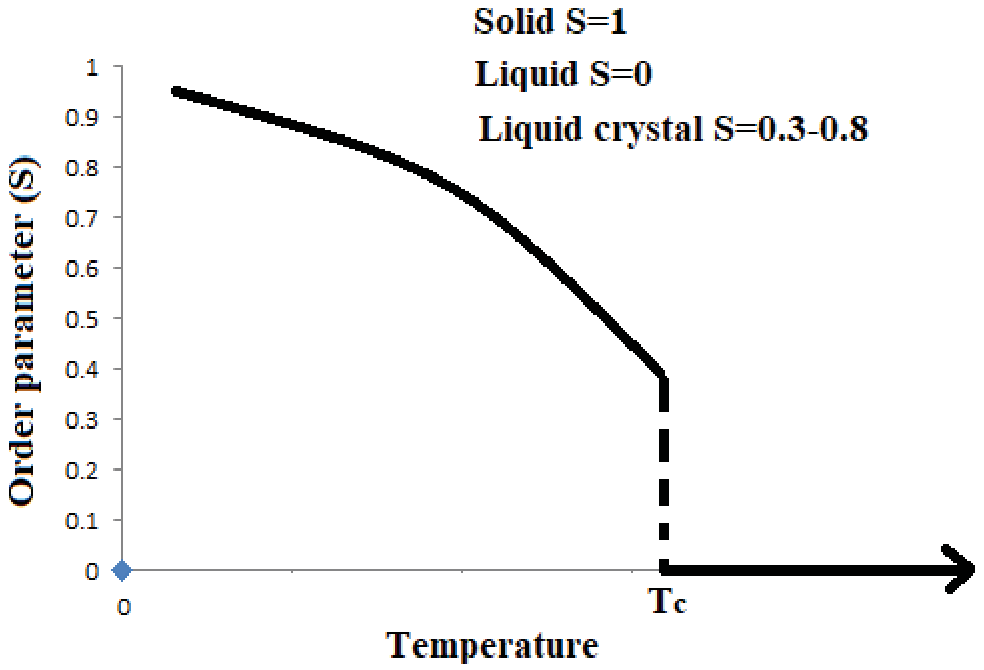

Fig 1.3 Order parameter

1.4 CLASSIFICATION OF LIQUID CRYSTALS

The liquid crystals can be categorized in two main categories i.e. Thermotropic and Lyotropic. These categories are further distinguished into various phases depending on the variations in their orientational or positional order under effect of external factors such as temperature [4]. In suitable conditions, the molecules of LCs show orientational direction such that all the axes line up and form a supposed nematic liquid crystal. The molecules are still capable of transferring the world over in the fluid, but their orientation remains the same. It is the least well-arranged LC phase. On the contrary, smectic (S_m) phase displays the orientational order but also positional order. In a smectic phase, the molecular cores of mass are organized in layers and the drive is mainly limited inside the layers. In cholesteric LC phase, molecules express intermolecular forces that rearrange arrangement between molecules at a minor angle to one another.

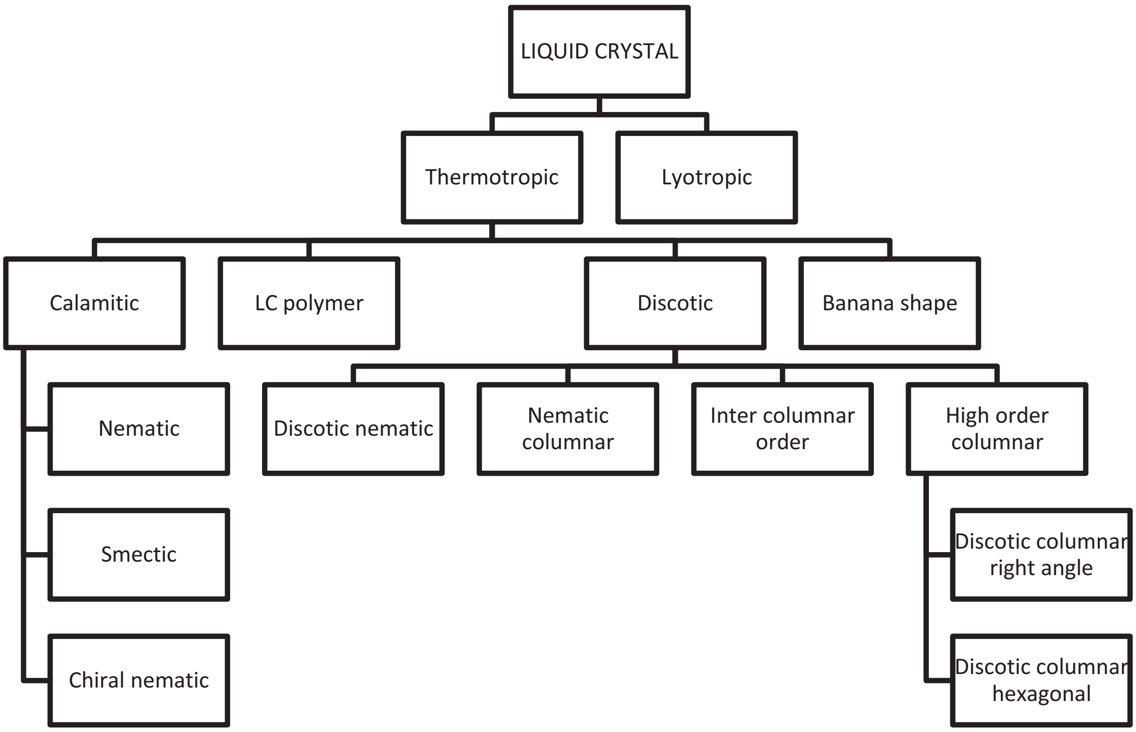

Fig.1.4 Types of liquid crystals

1.4.1 Lyotropic Liquid Crystals

Lyotropic liquid crystal consists of the components that entertain liquid crystalline properties in certain concentration ranges. Lyotropic liquid crystals instead are detected when the concentration of a shape or property anisotropic dispersant in an isotropic solvent is altered. These phases are observed as a function of the amount of amphiphilic molecules in aqua or other solvents. These mesophases are usually comprised of a flexible lypophilic chain (the tail) and a polar (non-ionic or ionic) head group (figure 1.5).

Fig.1.5 Structure of lyotropic liquid crystals

Below the critical micelle concentration (cmc), the amphiphiles are molecularly isolated in the solvent, at superior concentrations form micelles, which can be spherical, rod or disk -like type, depending on the molecular shape. At even greater concentrations, these micelles aggregate to well-ordered structures and can procedure hexagonal, cubic or lamellar phases, also of the inverse Nanomaterials type [5], as shown in figure 1.6.

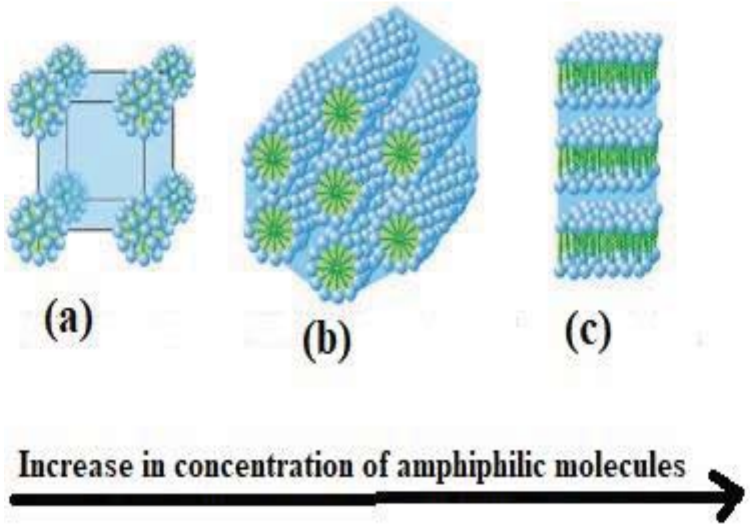

Fig 1.6. (a) Cubic mesophases, **(b)** Hexagonal mesophases, **(c)** Lamellar mesophases of liquid crystal

1.4.2Thermotropic Liquid Crystals

Thermotropic LCs are the ones which are extensively recognized due to their influential applications in laptop, flat screen televisions and tablet displays or mobile phones. All these applications depend on the point that LCs reveal elastic behavior and can be addressed via electric or magnetic fields, which alter the orientation of the optic axis and therefore the birefringence.

Thermotropic LCs are additionally distinguished by their degree of order and show more stages of transitions inside the temperature regime of the liquid crystalline state [6]. They tend to show various crystalline phases as a function of temperature. The thermal motion of molecules at the melting point gets increased to such an extent that the material transitions from solid phase to liquid crystal phase. This process takes place below room temperature, on further heating, the liquid crystal gets transformed into other liquid crystal phases and then eventually transforms to an isotropic clear liquid [7].

1.5 CLASSIFICATION OF THERMOTROPIC LIQUID CRYSTAL AND THEIR RESPECTIVE MESOPHASES

For the determination of the type of liquid crystal phases, the molecular shape and low molar mass of the molecule plays a very crucial role. On the basis of geometric shape of the respective mesogenic molecule the classification is done. The liquid crystal phases are observed on the basis of some internal parameters which include the chemical structure of the mesogenic molecule and also some external parameters such as pressure and temperature. The most commonly found variety of the liquid crystal is either calamitic or rod like shaped or either discotic or disk kind shaped. Both discotic and calamitic liquid crystal shows a very high degree of dielectric anisotropy. The mean or effective shape mesogens are represented by these cylinders and these mesogens are free to rotate around their molecular axis.

1.5.1 Calamitic Liquid Crystal

In the case of calamitic mesogens, the molecules are essentially rod like structured but these mesogens possess some kind of stiffness or rigidity in the central region. The terminal group of these mesogens are attached to the central part. These terminal groups can be either flexible chains or polar groups. A permanent dipole is possessed by these molecules and these mesogens undergo anisotropic polarization. On the basis of their positional and orientational order these liquid crystals can be classified as nematic, smectic and cholesteric mesophases. With the addition of more complexity, new liquid crystal phases are observed. The typical structure of a calamitic liquid crystal is shown in the figure 1.7.

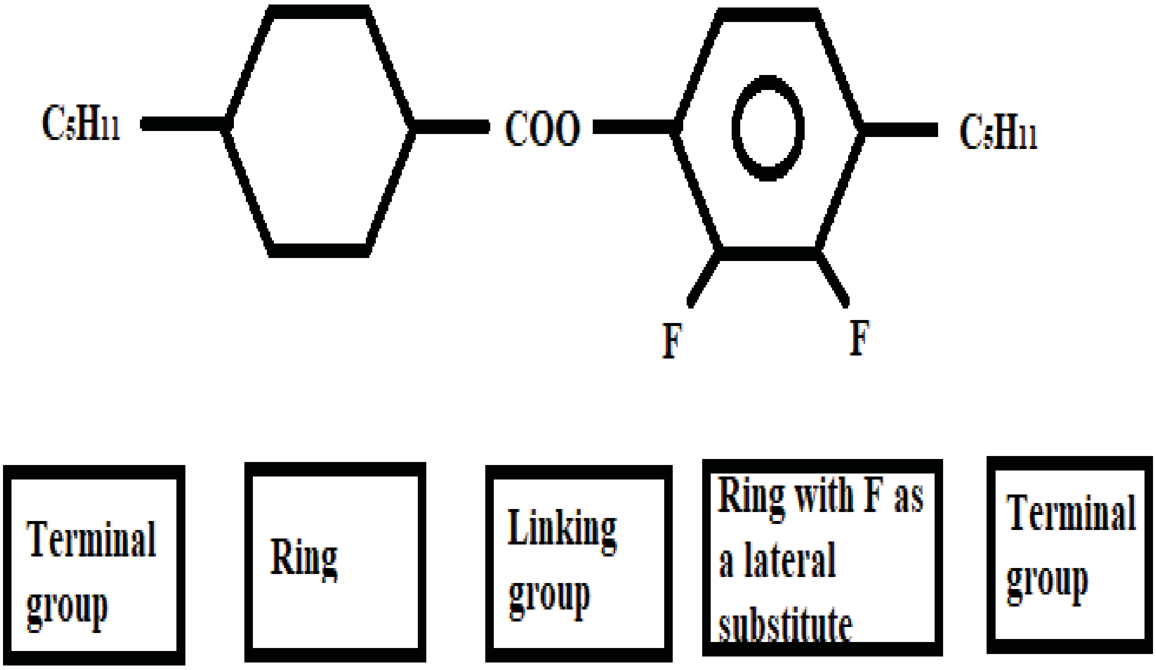

Fig 1.7 Structure of calamitic liquid crystal

1.5.2 Nematic Phase

The most common phase of the liquid crystal is the nematic phase of the liquid crystal. It occurs just before the isotropic phase and it is of no surprise that the viscosity of the nematic liquid crystal is of the order of isotropic liquids. The origin of the word nematic comes from the Greek word “nema”, which literally translates to “thread”. The mean direction of the major axes is defined by the direction **n** in a nematic liquid crystal. On the basis of the topographical conditions, the N phase exhibits marble, schlieren and pseudo type textures.

There is no positional order present in these organic rod shaped molecules but the orientation of these molecules is present along the director, **n**. As it is evident that the molecules in a liquid are moving freely and the center of mass of these liquids is not evenly distributed, but still the molecules of liquid exhibit a long range directional order. Usually the nematic materials are uniaxial and possess a centre of symmetry. The nematic crystals have one major axis which is preferred and the other two are equivalent. In some cases, the nematic liquid crystal can be biaxial i.e. they can orient themselves in their primary as well as their secondary axis. Upon applying an external field, be it electric or magnetic field, the molecules of the crystal align themselves in the preferred direction. Nematic LCs consist of fluidity on the same level as that of the isotropic liquids. Under the observation of a cross polarized microscope these crystals show some characteristic texture. The nematic LCs that are aligned show the optical properties as that of a uniaxial crystal i.e. birefringence which allows light with different polarization to pass at various speed along different directions. The orientational parameter of the phase is decided by the order parameter whose value varies from 0.3 near the clearing temperature to 0.6-0.7 at the temperature below the clearing temperature. The most common use of the nematic liquid crystal is in the liquid crystal displays (LCDs) which is implemented using twisted nematic geometry. One of the most commonly and frequently used material in LCD's is the cyno biphenyl. A very important point to note is that it is really necessary to control temperature range in order to operate the liquid crystal and often when molecules we get the desired low transition temperature and high operating temperature.

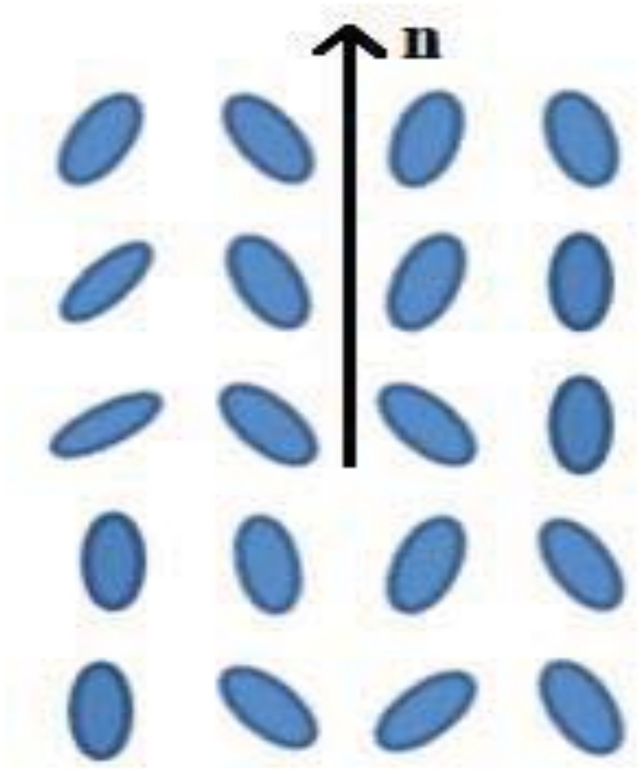

Fig 1.8 Nematic liquid crystal

1.5.3 Smectic Phases

The origin of the word Smectic comes from the Latin word “smecticus” which literally translates to “soap-like”, so the molecules possessing soap like properties are called smectic liquid crystals. The order in a smectic LC is more than that of a nematic liquid crystal. Unlike in the case of a nematic liquid crystal which only contains orientational ordering, the smectic liquid crystal possesses positional ordering which leads to a layered structure of the smectic liquid crystal.

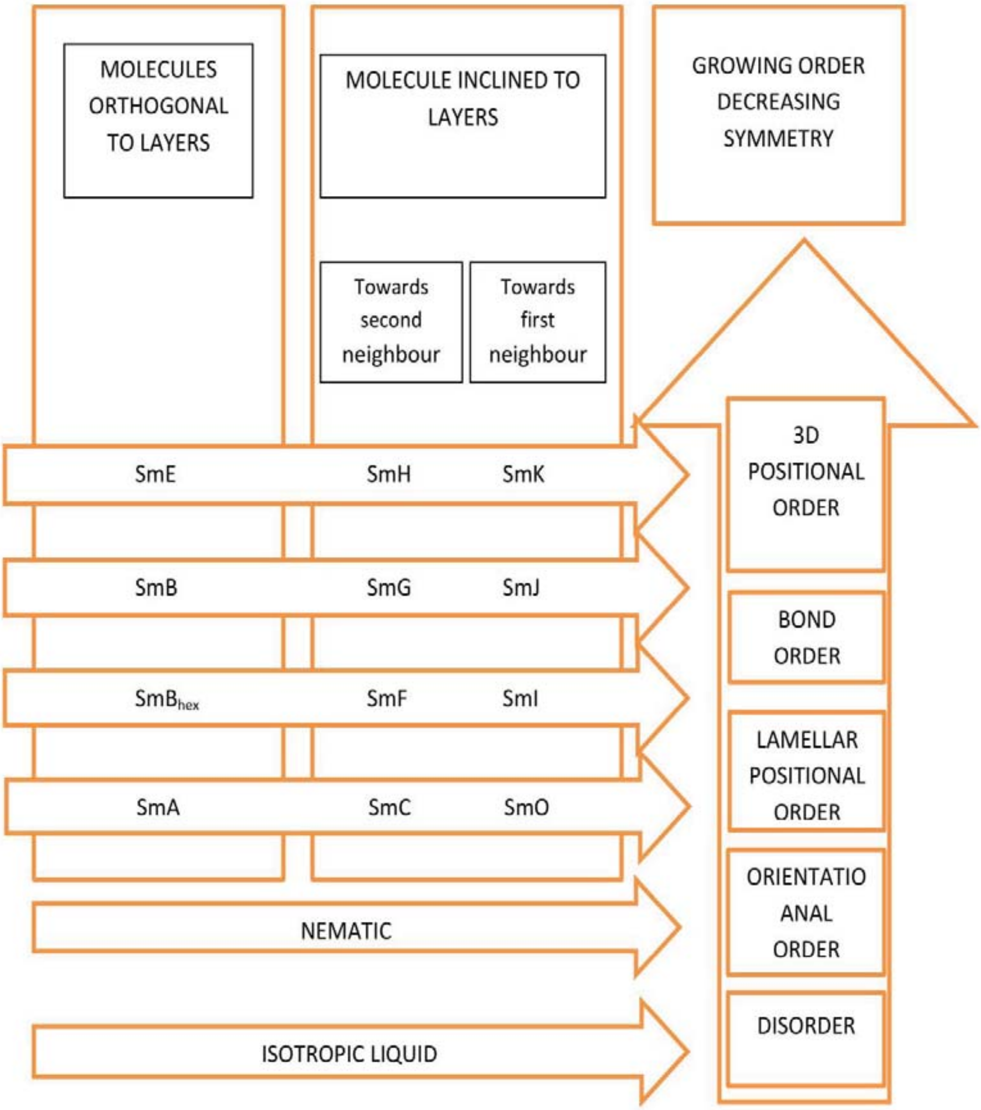

Fig 1.9 Classification of smectic phases of LC's

Further classification can be done for a smectic liquid crystal based on the molecular arrangement amongst the layers and the extent of correlation between the layers. The angle between the director **n** and the centre of mass and molecule length decide the thickness of the layer. On the basis of the chronological order the smectic phases have been assigned code letters for example A, B, C etc. The fluidity between the layers is the most important feature of the smectic liquid crystal. In order to represent the arrangement of the layers, we have to consider a one dimensional mass density wave. Various types of discovered smectic LC phases are smectic A(SmA), smectic B (SmB), smectic C(SmC), smectic F (SmF) and smectic I (SmI). Further classification can also be done on the basis of the fact whether the respective molecules can be tilted with respect to the normal layer. The first two mentioned phases i.e. smectic A and smectic B are orthogonal and non-tilted with the layers on the other hand smectic C, smectic F and smectic I are the tilted phases. If the constituent molecule is chiral further mesophases are formed which are chiral smectic A (SmA*), chiral smectic B (SmB*) and chiral smectic C(SmC*) respective phases. The most widely studied and observed phases among these phases are the SmA and SmC phases.

1.5.4 Smectic A (SmA) and Chiral SmA Phases

The direction of the director is directed normal to the layer in a smectic A liquid crystal. There does not seem to be a long range positional correlation between the layers and the arrangement seems to be that of a liquid. The correlation between the successive layers is absent. Thus the SmA phase can be mentioned as the 1-d mass density wave because the molecules are not ordered. The subsequent sub-phases of smectic A such as SmA_2 is a bilayer phase and SmA_d is a minutely biphase. Because of the presence of biaxial symmetry the smectic A phase can also be coined as biaxial smectic, here the molecules are perpendicular to the layer but in the plane of the layer there’s an additional director.

The long molecular axis of the molecule will tilt and there will be coupling of the electro-clinical susceptibility on the application of electric field; the tilt angle varies linearly when the applied field is of low intensity, this phenomenon is coined as electro-clinic effect. For smectic A and chiral smectic A the focal-conic texture is observed and homeotropic orientation is treated under dark field of view.

1.5.5 SmC and SmC* Phases

Smectic A phase is optically uniaxial while that of smectic C phase is optically biaxial. The SmC phase differs from the SmA phase because the director of each layer is inclined and making an angle with the layer. The tilt angle with the layers varies with the temperature and increases with the tilt angle increases with the decrease in temperature. The point group C_{2h}corresponds to the symmetry element of the phase. In the chiral phase, a macroscopic molecule exists. It is formed by the optically active molecules.

There is a reduced C_2 symmetry in the presence of chiral molecules which leads to a dipole moment along the C_2 axis perpendicular to the tilt direction which leads to spontaneous polarization.

Due to the presence of the upper and lower layers the molecules are affected in some mesophases of smectic liquid crystal. Hence a small order of 3-d order is observed, smectic G (SmG) is one of the relevant example of this kind of arrangement.

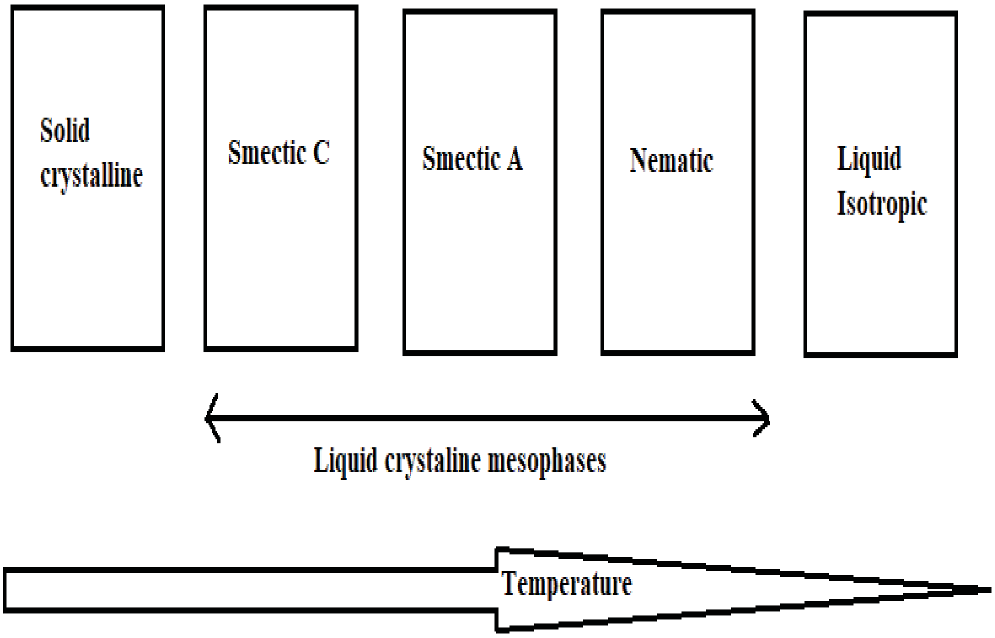

Fig 1.10 Effect of temperature on molecules

1.5.6 Cholesteric Phases

The chiral form of the nematic phases of liquid crystal is termed as cholesteric mesophases. It contains a chiral centre which leads to the intermolecular forces that causes alignment between molecules at a slight angle to one another. Hence it is also commonly termed as chiral nematic phase. The chiral nematic molecules can be obtained by doping nematic LC's to optically active molecules. The cholesteric phase has a historical importance because these types of molecules were first obtained in cholesterol derivatives. In the cholesteric mesophase, the twisting of the respective molecules is normal to the director **n** with the molecular axis parallel to **n**. The chiral order (long range) is a result of a finite magnitude of twist in the twist angle between the adjacent molecules the respective packing arrangement (asymmetry). A continuous helical pattern is formed about the normal to the layer in the structure of a cholesteric LC.

In the slabs of infinitesimal thickness the chiral nematic mesogens are lying with the distribution of orientation about the director. There is a positional ordering in the SmC* phase layered structure and there is a finite tilt in the molecules which is perpendicular to the layer. It results in an azimuthal twist from one layer to the other. Upon doping it with a chiral dopant with a nematic LC will generate a helical twist in order to create a chiral nematic phase. Diffraction of light can be caused by a cholesteric LC depending upon the pitch of the liquid crystal which can be shown with the equation:

$$\lambda=np$$

where, λ is the wavelength of light

n is the refractive index

p is the pitch

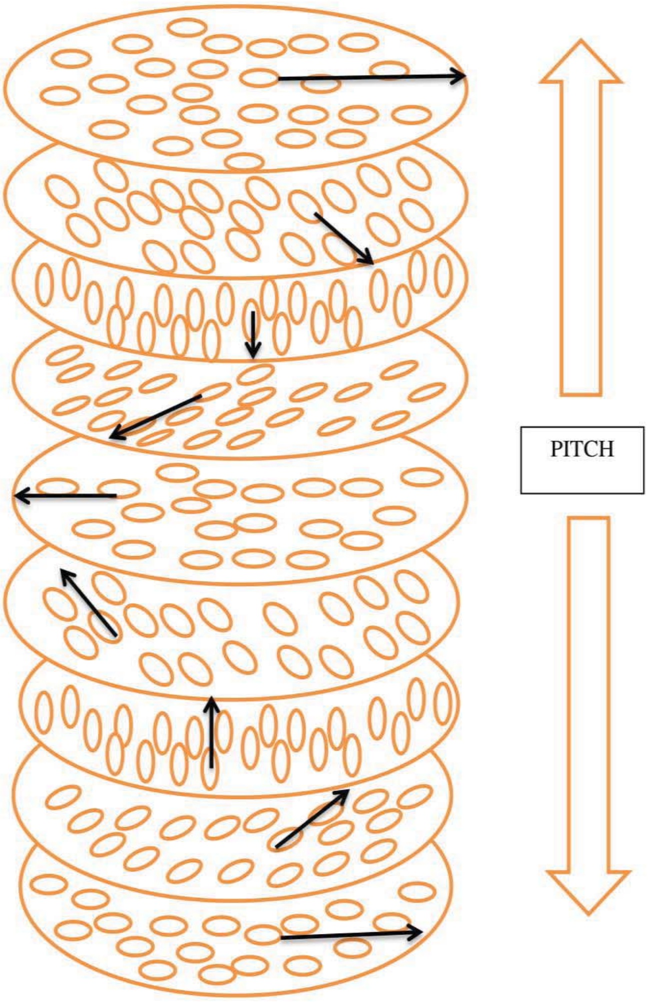

Fig 1.11 Periodic helical phase of a chiral nematic phase of a liquid crystal, the pitch of these cholesteric liquid crystals corresponds to the rotation of molecular orientation by 360 degrees.

One of the most important characteristics of the liquid crystal is the pitch of the liquid crystal which can be described as the distance up to which an LC molecule can undergo a full 360 degree twist. This distance is the one which takes the director to take a full turn. Due to this helical structure of the cholesteric liquid crystal, it holds the ability to selectively reflect light of the order of pitch of the liquid crystal and this is a very crucial characteristic. The respective mesophase (chiral) is coloured when the pitch of helical structure of the liquid crystal corresponds to the light of visible spectrum which lies typically in the range of 400-800nm. Another thing to note is that the helical structure is sensitive to temperature, so any change in the temperature will cause the pitch of the helical structure to change and hence the wavelength corresponding to the pitch of the mesophase will also undergo a change. With the increase of the temperature the director angle will tighten the pitch, hence the pitch length decreases with an increase in temperature. This property comes handy in the application of the liquid crystal thermometers which can display the temperature of the surrounding on the basis of reflected colour. This causes unique optical properties such as Bragg's reflection and low-threshold laser emission. In the case of Bragg's reflection only lowest order wavelengths are allowed while higher order wavelengths are only allowed for oblique incidence. The temperature sensitivity of the pitch length leads to its use in thermometers. The temperature sensitivity leads to its use in the sensors for various purposes.

On putting these LC's in the black background prevent the degradation of the films as it only allows a certain wavelength of light and prevents the unnecessary wavelength. It is also used to create dyes and paints.

Further the pitch length can be changed by changing the chemical composition, by doping it with other chiral molecules. The dopant concentration is used to control the chirality and hence the pitch.

1.5.7 Blue phase

In the case of highly chiral LC's a set of thermodynamically distinct phases occur between helical phase and the isotropic phase of the liquid crystal, this is coined as Blue phase. In the case of highly chiral molecules, upon heating them from helical phase to the isotropic phase they exhibit one or more blue phases(BP). When the temperature is increased the blue phases are referred as BPI, BPII and BPIII, where BPI is the BCC structure and BPII is a simple cubic structure. The point here to note is that these blue phases don’t consist of any orientational order. The symmetries are not associated with positionally ordered LC’s at the crystal sites. The pitch and the lattice constant are of the same order which is in the range of light of the visible spectra. Different coloured platelets display a variety of colours which correspond to the crystal ordering.

There are some interesting properties which include the non-zero elastic shear modulus which corresponds to the liquid phase of the molecule. The viscosity of the helical phase is substantially higher than that of the helical phase.

1.6 POLYMERIC LIQUID CRYSTAL

The liquid crystal exhibiting properties of a polymer are polymeric liquid crystal, Anisotropic characteristics are shown by these macromolecular compounds. And they also possess properties of polymer which are really useful and versatile. The properties of a polymer liquid crystal can vary with that of its counterpart low molecular liquid crystal. In the polymeric molecules the molecular ordering is used to denote anisotropically shaped disk or rod like elements which are termed as mesogenic units.

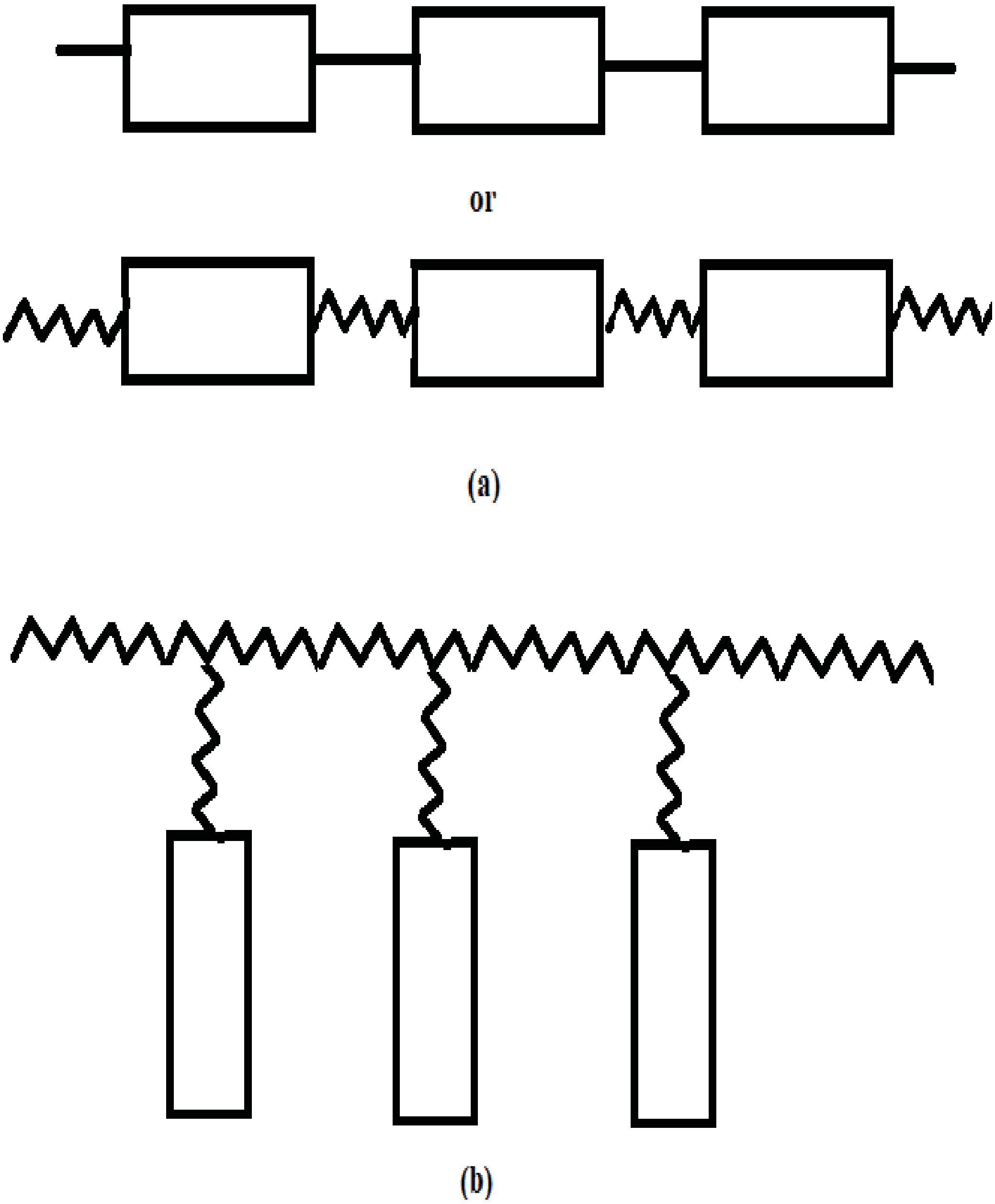

Fig 1.12 Polymeric liquid crystals (a) main chain (b) side chain

The location of the of the mesogenic units decides whether the polymeric liquid crystal will be main chain or a side chain PLC. In the case of main chain liquid crystal the mesogenic units are embedded in the skeleton of the systems separated by a flexible chain while in the case of a side chain liquid crystal the liquid crystals are linked by the flexible chain.

In summary, the mesophases of the liquid-crystalline materials exist in the melting process of the mesogenic phase between the solid and liquid state, which encompasses long-range positional ordering of its molecules in three-dimensions, and the completely disorganized liquid state. Similarly the physical properties and the structures of these thermodynamically stable modifications are also intermediary between those of a liquid and those of a solid.

Liquid-crystalline mesophases of rod -shaped molecules can be divided into three general categories:

- The molecules in the case of the nematic crystals are only orientationally ordered such that their long axes are nearly parallel.
- In smectic liquid crystals, the molecules exhibit a short-range positional ordering and long-range orientational ordering combined with a diffuse layer structuring.
- Finally in the smectic liquid crystals, the molecules that have a long-range positional and orientational ordering and are packed in less diffuse layers, but yet they still retain a rapid re-orientational motion about their long axes (i.e., these phases can be termed anisotropic plastic crystals).

1.7 PROPERTIES OF LIQUID CRYSTAL

On the basis of molecular arrangement, anisotropy of material and orientational order liquid crystal shows many physical, electrical, optical and mechanical properties.

1.7.1 Physical properties of nematic liquid crystal

The director of nematic liquid crystal **n** in a macroscopic volume is not uniform at all but changes from place to place under the action of disturbing forces such as convection flow, wall effects etc. Even both magnetic and electric fields are aligned for a large number of molecules. The intermolecular force is responsible for the mesomorphic state and they lead to a cooperative behaviour of molecules.

1.7.1.1 OPTICAL ANISOTROPY (Birefringence)

There exist many crystals which show the property of optical anisotropy i.e. birefringence. The rotation of molecules in liquid is rotation free which averages out any symmetry of molecular shape and the medium of molecules becomes optically anisotropic. The refractive index of the birefringent material depends on the polarization and propagation in the direction of light. The birefringence is sometimes quantified as the maximum difference between the refractive indices exhibited by the material. Birefringence is responsible for the double refraction phenomena where a ray of light is incident upon a birefringent material and is split by the polarization into rays with slightly different paths as shown in fig 1.13.

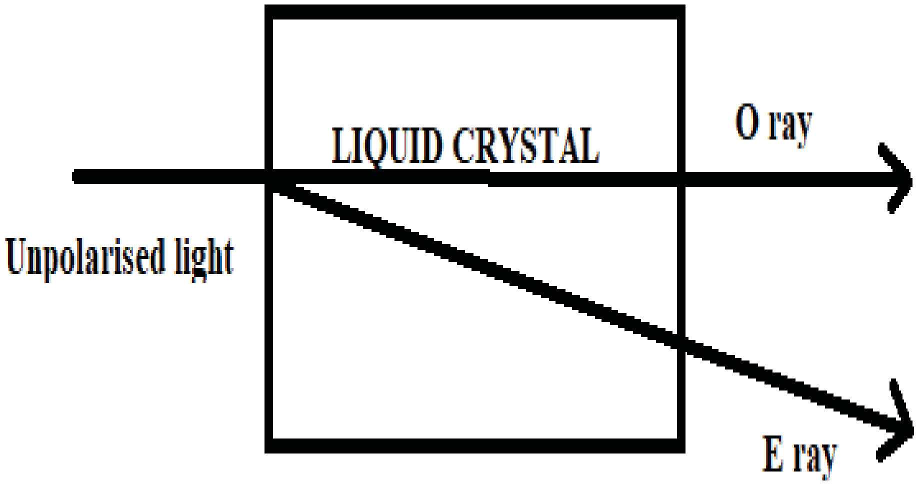

Fig.1.13 Birefringence of a liquid crystal

Birefringence is described as uniaxial [9,10] i.e. a single direction is governing the optical anisotropy whereas all directions perpendicular to it are optically equivalent. Thus the optical behaviour is not changed by rotating the material around the axis. The direction is known as the optic axis of the material. The polarization of light which is perpendicular to the optic axis is defined by $n_0$and this ray is known as ordinary ray. The polarization of light which is in the direction of the optic axis is governed by n_e and the corresponding ray is known as extraordinary ray. The magnitude of the difference is birefringence:

$$\Delta n = n_o - n_e$$

Most nematic liquid crystals have positive birefringence ($\Delta n > 0$) i.e. the extraordinary ray is delayed according to the ordinary ray which passes through the liquid crystal phase. Interference between the extraordinary ray and ordinary ray that travel through the medium with different velocities gives rise to the coloured appearance of these thin films. Most nematic, orthogonal sematic and columnar phases are uniaxial while the titled smectic and columnar phases are biaxial in nature. Principle refractive indices of liquid crystal are in the range of 1.4 to 1.9 and uniaxial birefringence can be between 0.02 and 0.4. Negative birefringence is the discotic phase of the liquid crystal.

$$\Delta n = \frac{(\alpha_e - \alpha_o)}{6.3621}\left(R^3 - \frac{(\alpha_e - \alpha_o)}{20.244}\right)^{-1}$$

Where, α_e is the polarizability along the major axis

α_o is the polarizability along the minor axis

R is the radius of the liquid crystal

1.7.1.2 Dielectric Anisotropy

Dielectric properties of a material are a product of the interaction of electric field with the matter. The measure of these phenomena is dielectric permittivity. For a material containing non-polar molecules, induced polarization can be classified two types:

(a). Electronic polarization: Electronic polarization occurs when the negative cloud around a positive nuclei gets displaced in the opposite direction of the field applied.

(b). Ionic polarization: Ionic polarisation occurs in the ionic materials where the anions gets separated moving in the opposite direction of the applied field giving rise to a net dipole moment.

Materials consisting of polar molecules also have orientational polarization in addition to the above polarization [11]. A theoretical study of liquid crystal having anisotropic behaviour reveals that the anisotropy arises due to individual molecular entities. A dipole-dipole correlation in smectic phase is different from the nematic phase. It arises due to the different types of interaction with the surrounding dipoles of molecules. This leads to a change in the value of dielectric anisotropy [12].

The anisotropy is shown by the dielectric permittivity tensor i.e. D=εE

$$\begin{pmatrix} Dx \\ Dy \\ Dz \end{pmatrix} = \begin{pmatrix} \varepsilon_{xx} & \varepsilon_{xy} & \varepsilon_{xz} \\ \varepsilon_{yx} & \varepsilon_{yy} & \varepsilon_{yz} \\ \varepsilon_{zx} & \varepsilon_{zy} & \varepsilon_{zz} \end{pmatrix} \begin{pmatrix} Ex \\ Ey \\ Ez \end{pmatrix}$$

For symmetry, the permittivity tensor must be symmetric i.e. $\varepsilon_{ij}=\varepsilon_{ji}$. Another thing to note is that the off diagonal terms are zero when the axes of the crystal systems and the eigenvectors of the liquid crystal systems are aligned.

1.7.1.3 Diamagnetic Anisotropy

A property most widely used in the study of liquid crystals is magnetic susceptibility as liquid crystals gave a quick response to change in the magnetic field. Like, many of the organic substances, liquid crystals are diamagnetic in nature [13]. The magnetic properties of individual molecular components result in diamagnetic behaviour. Magnetic susceptibility is a measure of response occurred when external magnetic field changes in a liquid crystal. The nature of the response is linear when the value of the magnetic field is small [14]. Magnetic susceptibility has a negative value for diamagnetic material and does not depend on field strength and temperature. Liquid crystals containing aromatic ring have positive dielectric anisotropy; with the substitution of every cyclohexane ring with a benzene ring, the value decreases. A negative value is observed in cycloaliphatic LCs [15].

1.7.1.4 Elastic Constants

One more important property of the liquid crystal is its elastic properties. When the uniform alignment between the director and the layers are tried to be deformed the liquid crystal show elastic behaviour and it causes it to form a uniform strain that can cause a change in the distance between adjacent layers, and thus this change is opposed by restoring forces. But in the case of nematic liquid crystals, permanent opposing forces are absent [16,17].

1.8 nCB and 4NB Liquid crystal

The nCB molecules are rigid rod like molecules having cylindrical symmetry about axis of maximum polarizability. Hence they can be used to test molecular theories. The general structure of nCB liquid crystal is given in fig 1.14.

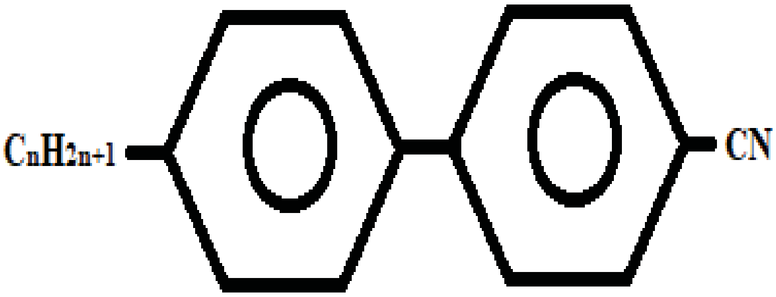

Fig 1.14 General structure of nCB

Table 1.2 Common name and chemical name for the nCB liquid crystal

COMMON NAME	CHEMICAL NAME
1CB	4’-methyl-(1,1’- biphenyl)- 4-carbonitrile
2CB	4’-ethyl-(1,1’- biphenyl)- 4-carbonitrile
3CB	4’-propyl-(1,1’- biphenyl)- 4-carbonitrile
4CB	4’-butyl-(1,1’- biphenyl)- 4-carbonitrile
5CB	4’-pentyl-(1,1’- biphenyl)- 4-carbonitrile
6CB	4’-Hexyl-(1,1’- biphenyl)- 4-carbonitrile
7CB	4’-heptyl-(1,1’- biphenyl)- 4-carbonitrile
8CB	4’-octyl-(1,1’- biphenyl)- 4-carbonitrile
9CB	4’-nonyl-(1,1’- biphenyl)- 4-carbonitrile
10CB	4’-decyl-(1,1’- biphenyl)- 4-carbonitrile
4NB	4 Nitrosobenzonitrile

The common name and chemical formulae of smaller nCB LCs are shown in table 1.2. nCB LCs till n=12 have been reported. These type of LCs have profound applications in passive matrix LCD’s and variety of photonic applications. The chemical structures of the molecules from 1-5CB is given in fig 1.15.

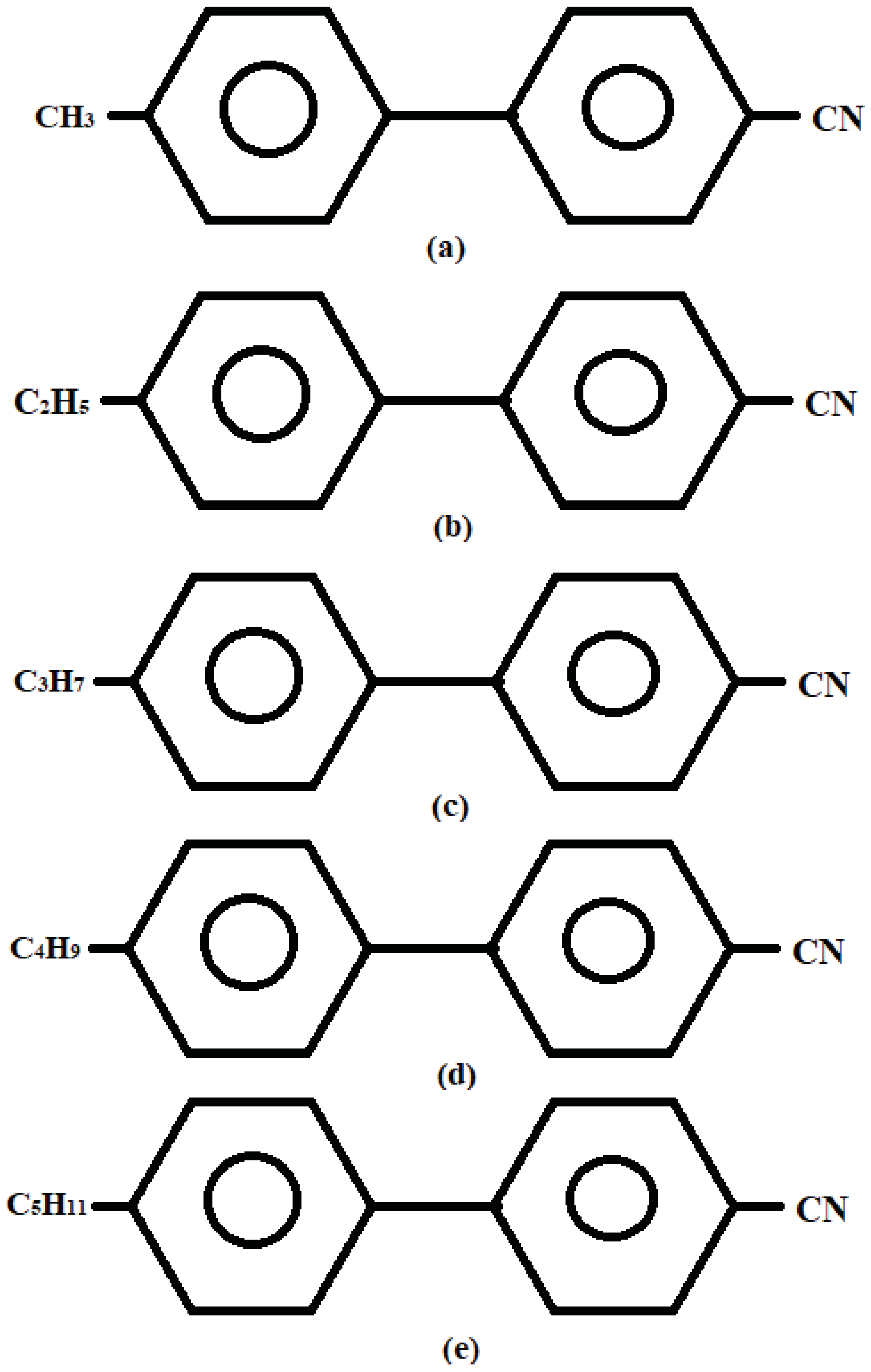

Fig 1.15 Chemical structure: (a) 1CB (b) 2CB (c) 3CB (d) 4CB (e) 5CB

Due to the presence of cyano group, the nCB molecules are a popular choice for use in most passive matrix LCD’s due to large dipole and contribution to the enhancement of the birefringence. The group is immensely useful for display and photonic applications.

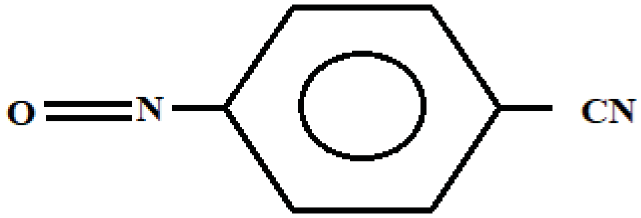

Fig 1.16 Chemical structure of 4NB

4- nitroso benzonitrile is a very widely used liquid crystal in liquid crystal display devices as it has substituent in the ortho and para positions of the benzene ring as shown in fig 1.13. The organic molecules have lower value of refractive indices as compared to inorganic molecules. The presence of weak bonds in 4-nitrosobenzonitrile makes it more reliable for telecommunication purposes. The extent of charge delocalization helps in getting high value of conversion efficiency.

1.9 APPLICATIONS OF LIQUID CRYSTAL

There are various applications of liquid crystals ranging from various kinds of sensors to switches. They also find applications in the medical treatment as a medicine. The liquid crystals find a variety of applications in various sectors due to the fact that the liquid crystal molecules reorient themselves with the applied electric field. Here are a few applications:

1.9.1 Medical uses

In recent development of science, the liquid crystals have started finding applications in the pharmaceutical sector, the liquid crystal molecules are in particular used as a drug vehicle which is useful in carrying the drug to the required biological target[21-23]. Molecules in a crystal are highly ordered while the molecules in a liquid are free to roam around; liquid crystals carry some degree of order in them. The cubic and hexagonal mesophases are in particularly investigated due to their ability to sustain both hydrophilic and hydrophobic molecules. The drug molecules can be incorporated in these gel like phases. Further the liquid crystals are non-toxic and biodegradable adding to the further importance.

1.9.2 Temperature Sensors

Cholesteric device has the ability to reflect light proportional to that of the pitch of the liquid crystal.

The helical structure is sensitive to temperature, so any change in the temperature will cause the pitch of the helical structure to change and hence the wavelength corresponding to the pitch of the mesophase will also undergo a change. With the increase in temperature, the director angle will tighten the pitch; hence the pitch length decreases with an increase in temperature. This property comes handy in the application of the temperature sensors which be used in various experimental purposes.

1.9.3. Liquid Crystal Display (LCDs)

One of the most widely used applications of liquid crystal is in the field of display devices. It utilizes the opto-electronic applications of the liquid crystal. Liquid crystals form constituent of a flat panel display that manipulates the light modulating properties of liquid crystal. LCD’s are used in manipulating the optical properties in either the presence or absence of electric field. These LCs can be easily processed as thin films because of the fluid nature of the liquid crystals. It does not emit light but instead uses a backlight or reflector to produce images[25]. Each pixel in LCD’s consists of two cross polarisers or transparent electrodes which orient at 90 degree to each other.

The liquid crystal material is inserted between two sheets of glass which are held parallel and separated by a range of few micrometres distance. In order to control the orientation of the director the transparent electrodes are substituted on the glass substrate which is white or red. When the liquid crystal is absent between the glass the light passing through the first glass is blocked by the second polariser.On applying the electric field the liquid crystal molecule reorients itself with the field, thus allowing for image display.

The pixel is controlled by the amount of light that is allowed to pass though the liquid crystal in various amounts. This technique is used with the use of coloured filters to generate red green and blue pixels which are the universal basis for all colours.

Liquid crystals are quite widely used in the manufacturing of televisions, computer monitors and many other display devices.

1.9.4 Solar Cells

Due to the limited availability of fossil fuel and the burning of hydrocarbons and due to its growing effect on the environment surrounding us has led to an increase in demand for solar cells and that has led to the development of organic photovoltaic’s or OPV’s. For the manufacturing of bilayer and BHJ’s solar cell the organic monomeric, oligometric and polymeric materials are in use.

In order to impart order to the solar cell, these organic photovoltaics are used which are fascinating state of combination involving mobility both at the microscopic and macroscoscopic level. The discotic derivatives of HBC, porphyrines etc. are used both as a donar, acceptor and a processing additives in the solar cells. The addition of discotic liquid crystal in the active layers of the commonly prevalent solar cell leads to a significant improvement in the efficiency of the solar cell.

1.9.5. Liquid crystal thermometers

Cholesteric device has the ability to reflect light proportional to that of the pitch of the liquid crystal.

The helical structure is sensitive to temperature, so any change in the temperature will cause the pitch of the helical structure to change and hence the wavelength corresponding to the pitch of the mesophase will also undergo a change. With the increase in temperature, the director angle will tighten the pitch; hence the pitch length decreases with an increase in temperature. This property comes handy in the application of the liquid crystal thermometers which can display the temperature of the surrounding on the basis of reflected colour.

There are various other kind of applications in which the liquid crystals can be used and it involves a huge scope of its use in various technologies as the liquid crystals technologies are advancing, some other applications involving liquid crystal are shown below.

(a) Electrical devices

(b) Optical Imaging

(c) Chromatographic separations

1.10 LITERATURE SURVEY

In the previous years, many new structural and synthesis analysis techniques have come up which have profound impact in the field of liquid crystals. A brief compilation of the literature survey regarding the development in the field of liquid crystal in given in Table 1.3.

Table 1.3 Literature survey of the previous work reported in past decades regarding the structural and synthesis analysis techniques in liquid crystal

Author/Research group	**Work done**
J. K. Lim et al. [25]	Calculation of 5CB liquid crystal in the presence of electric field.
I. Chashechnikova [26]	Electro-optic memory effect in composite made of 5CB and mineral clay
J. F. Blach et. al. [27]	Raman mapping of PMMA dispered nematic LC in droplets form
C. Zannoni et. al. [28]	Modelling and MD stimulations of n-cynobiphenyl series where n=4-8
J. Han et. al. [29]	Synthesis of non- symmetric liquid crystal compounds
R. Dabrowski et. al. [30].	Mesogenic properties of 3 or 4 ring compounds
A Murauski et. al. [31]	Provided new technique for measuring polar anchoring energy of nematic liquid crystal
G. De. Luca et. al. [32]	Analysed the structure conformations and structure of isotropic phasesusing NMR technique

T. Yatabe et. al. [33]	Did synthesis and studied the geometric property of liquid crystalline alkyl-substituted oligo-compounds
D V Sai et. al. [34]	Reporting of optical properties of homologous series of bi-cyclohexane liquid crystal
G. Y Yeap et. al. [35]	Preparation of new di-symmetric dimers
D. Tagayuchi et. al. [36]	Determination of orientational order of 4V-n-penyl-4-cynobiphenyl molecules depositing 5CB molecules onto silica substrate
S. T. Ha et. al. [37]	Synthesis of thermotropic Schiff base liquid crystal
J S Dave et. al. [38]	Effect of lateral substituent on mesogenic physical properties
A Ivan et. al. [39]	Synthesis by the use of one-step route and characterised azomethines
M Roychaoudhary et. al. [40].	Stacking, in-plane and terminal interaction for a pair of molecule in agreement to crystal packing
D P Ojha et. al. [41-47]	Study of Odd-even effect in transition liquid crystal using interaction studies
J Hemine et. al. [48]	Calculated Helical pitch and electro-optical properties of ferroelectric LC
Vladimira Novotna et. al. [49].	Preparation of rod-like mesogen
V F Petrov et. al. [50]	Studied pysio-chemical studies of pyridine derivatives

K. Hori et. al. [51]	Crystal structure analysis of Bi-phenyl ester LC
C. Yu Ksektepe et. al. [52]	Using DFT, studied crystal structure anf spectroscopic properties of N-[4-(3-Methyl-3-phenyl-cyclobutyl)-Thaizol-2-yl]-N0-(1HPyrol-2-Ylmethylene)-hydazine
Z Li et al. [53]	Discussion of the relationship between phase transition and the phase transition of cholesteric liquid crystal

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CHAPTER-2

METHODOLOGY

CHAPTER 2

METHODOLOGY

2.1 QUANTUM MECHANICS

Quantum mechanics is termed as a fundamental theory that provides information about the nature at the level of atoms and subatomic particles. It is capable of calculating the physical properties of atoms, molecule or cluster of molecules by describing the positions of electrons around nucleus. Quantum mechanics is capable of calculating the ground state energy of the molecules with different distances between the atoms. As the number of atoms increases in a molecule the calculations become tedious in calculating the various properties of the molecules. Quantum Mechanics is a useful tool in describing a single particle. As we know that a molecule is made up of atoms that are composed of protons neutron and electrons, and many subatomic particles if taken into consideration, if necessary. Quantum mechanics deals with the problem of describing the system in terms of a Schrodinger equation for non-relativistic systems or quite possibly a Dirac or even the Klein-Gordon equations for a relativistic system, while Quantum Field theory is a unified theory that generalises all the above equations. An electron is represented by the Dirac equation while a photon by the Klein-Gordon equation. To explain the interaction between electron and phonons the theory of Quantum Electrodynamics is used. To determine the molecular, electronic structures and optical properties of the molecules the QM methods are used. The Schrödinger equation solution is compatible with the QM theory because QM theory contributes to the biological system's QM calculations. The primary aim is to calculate the molecular properties of the molecule without considering any experimental parameters. The molecular system can be described at the atomic level (molecular mechanics) and the electronic level (QM) by molecular modelling. In theoretical chemistry the QM calculation is one of the oldest methods used for mathematical formalism.

As described by quantum mechanics, all possible important information about the molecular system is encoded in the wavefunction of the system Ψ, which is calculated by solving the Schrödinger wave equation.

The Schrodinger equation is described by

$$\frac{-\hbar^{2}}{2m}\nabla^{2}\Psi + V\Psi = \mathrm{E}\Psi$$

Where,

Ψ denotes the wave function of the system of system

V denotes the potential associated with the system

E denotes the total energy of the system

The Schrödinger equation is one of the basic and important equationS in QM and provides the basis for obtaining a complete electronic description of the molecule [1, 2]. The Quantum mechanical methods have been classified into two main classes

- Semi-empirical methods (such as PM7, AM1, MNDO etc.)
- Non-empirical (ab initio, DFT etc.) methods.

To describe briefly, in semi-empirical methods, some parameters of the calculation are described from the experimental data in order to simplify the procedure and it is less demanding in terms of computation as compared to ab initio methods. In contrast, ab initio calculation uses the correct Hamiltonian. No experimental data is used other than values of some physical constants such as the speed of light, the masses/charges of the electrons and nuclei, Plank's constant etc. [3-5].

2.2 MOLECULAR MODELLING

A method (computer based) used for manipulating, representing and derive the structure and reactions of molecules and the collection of all those properties that are dependent on the three dimensional structure of the molecule is called molecular modelling. These tools help the people intending to study and rationalize structure and reactivity of organic, bio-organic and organometallic molecules. Molecular modelling is an efficient technique that helps to ease the calculations in the computational field. It helps to solve any reasonably sized complex system that is too tedious to be solved by hand. It helps to analyse the molecular geometry of the molecules and to find out the parameters like bond length, bond angles, energy of molecules and their transition states. In the chemical reactivity it can be used to find out the information as to which reagent would attack a molecule knowing where the electrons are concentrated and where they want to go. The spectroscopic properties of the molecule can also be calculated. This technique can also be implemented in the biological systems which would help to investigate the interaction of substrate with the enzyme also it could help in the drug design as to see how a molecule dock in to an active site of an enzyme.

2.3 MOLECULAR MODELLING METHODS

2.3.1 Molecular mechanics

It is one of the methods for molecular modelling. It assumes atoms to be composed of nucleus and electrons. In molecular mechanics we work on the assumption that the whole molecule is a collection of atoms held together by springs. The force of interaction between the atoms can be described by spring like interactions and van der Waals forces. The other common name used for molecular mechanics is force field method which ignores the electronic motion of molecules. This helps in the computation of the structure and energy of the system which depend only on the nuclear motion of the molecules. The calculations are carried out on computers as there is a significant number of atoms associated. This force field theory can provide calculation with a very high degree of accuracy so much as to match the level of highest quantum mechanical calculations.

There are certain assumptions that the molecular mechanics works on, the first one is the Born-Oppenheimer approximations in which the nuclei is assumed infinitely heavier than the electrons and the movement of the nuclei is very negligible as compared to the electrons. The motion of the electron is decoupled from the motion of the nuclei. When the above approximation is used we only concentrate on the motions of electrons. Applying the above approximation the Schrodinger equation is solved for the electrons alone in the force field of the nucleus. Function of nuclear coordinates determine the energy of the system[4].

Molecular mechanics works on the following mentioned assumptions:

- Both the electrons and the nuclei are held together and treated as a uniform atom like particle.
- These atom like particles are also treated as spherical balls.
- The interactions between the particles are treated as using a potential function which can be derived from classical mechanics.
- The bonds between the particles can be assumed as a spring.
- To derive the different type of interactions, individual potential functions are used.
- The potential functions and its parameters are used for evaluating the interactions termed as a force field.

2.3.2 Ab initio Method

The Ab inito is a Latin word that translates to “from the start”. In our context, it is based on the Schrodinger wave equation. It has come out to be a very essential tool in solving the biological, quantum chemistry and also reasonable problems of material science. Ab initio method tends to a reasonable approximate solution of the Schrodinger equations. The noble prize in 1998 was awarded to John Pople and Walter Kohn for obtaining the solution of the Schrodinger wave equation to a high degree of accuracy for tens or even hundreds of atoms. Basis set that are used to solve the Schrodinger equations are incomplete and not span the Hilbert space which is associated with the scattering and ionizing potential processes [2].

Born approximation is applied to the molecule so the nuclear and electronic motions are both treated separately. The Ab initio method is used to solve the Schrodinger equation for a fixed nuclear configuration. These potential energy surfaces are defined by the electronic energy. The electronic Schrodinger equation cannot be solved except for a hydrogen atom which is a two body problem, reducible to single particle problem [3]. We define the electronic wave functions in the form of basis sets which leads to the Schrodinger equation being transformed into a set of algebraic equations which can be solved by appropriate numerical techniques. We can classify this method into two classes of approximations. In the first one, we assume basis sets representing the one-electron functional which is termed as molecular orbital and the second approximation deals with the many-electron wave functional with N-electron functions.

In order to compute the molecular orbitals, one needs to compute the required integrals. For this, a Gaussian basis function is used to make it quicker.

To describe the wave function for this many electron problem, it is represented as a linear combination of Slater determinants or the anti-symmetrised products of the molecular orbitals. Slater determinants for all possible configurations of the orbital basis are used which calculates the best possible results for one-electron basis that is chosen which is called full configuration calculation. The constructed Slater determinant can be enormous and very quickly increase the number of electron and orbital. So there’s a need of approximation in determining all subset of wave function for the Slater determinant.

One of the common approximations used is the Hartree-Fock approximation which is used to optimise the orbital. This is the first step to ab initio calculations. The mentioned approximation is the equivalent of the mean-field approximation in which every electron is described as moving in the average field exerted due to the presence of all the other electrons present in its vicinity. Thus it is to be noted that the Coulomb interaction of the electrons are treated in an average way. Also the electrons are overestimated in the HF approximation.

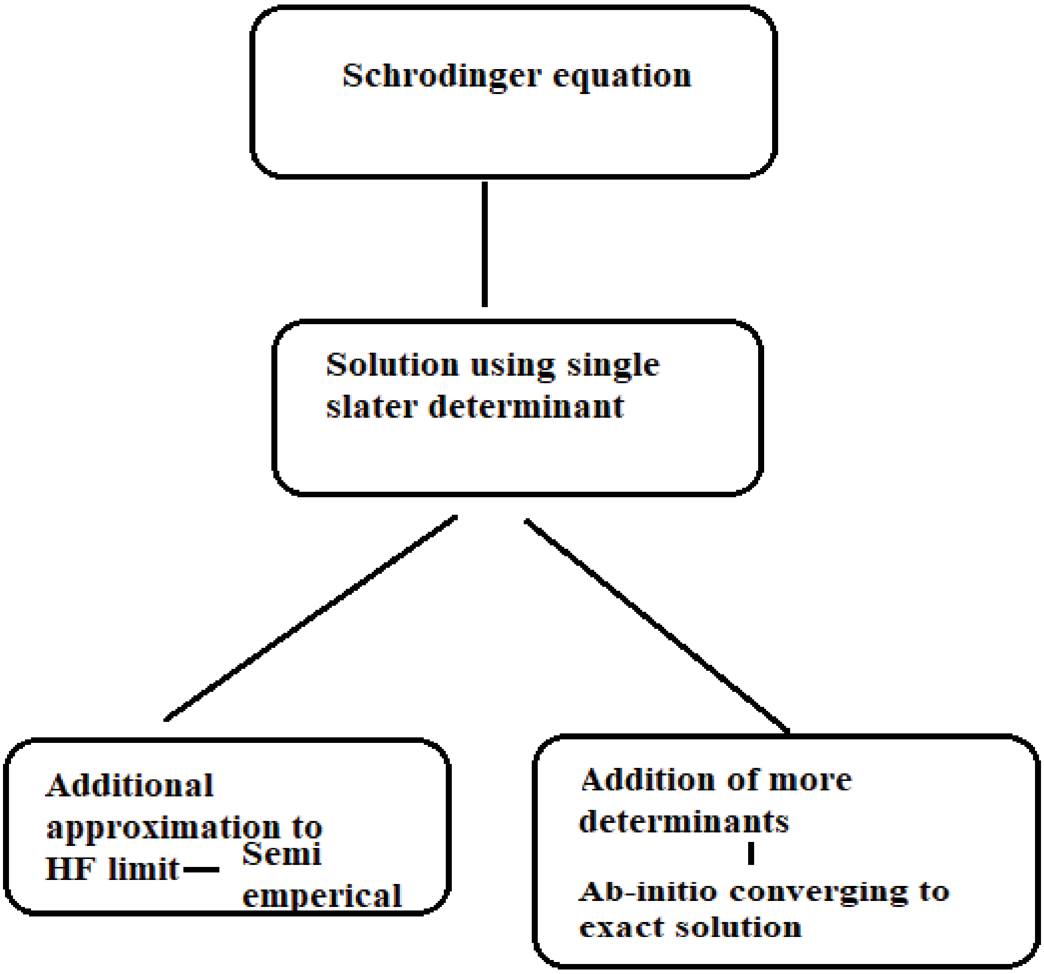

Fig 2.1 Scheme for ab initio calculation

2.3.3 Hartree Fock Method

The wave function is measured at the stationary state in the Hartree-Fock (H-F) approximation. A more common term coined for the H-F method is also known as the self-consistent field method (SCF). It can be described as an approximate method of solving the Schrodinger equation. The electron correlation is neglected in the H-F approximation by considering a single determinant. There's no adequate description of the electronic structure in the approximation. To do a quantitatively accurate prediction, the H-F approximation is insufficiently accurate enough.

The energy form in the Hartree Fock approximation is

$E_{HF} = V + \langle hP\rangle + 1/2\langle PJ(P)\rangle - 1/2\langle PK(P)\rangle$

Where, V is nuclear repulsion energy

<hP> is the one-electron energy

P is the density matrix

$1/2\langle PJ(P)\rangle$ is the coulomb repulsion energy

$- 1/2\langle PK(P)\rangle$ is the exchange energy arising from the quantum nature of electrons

Thus H-F theory is used to solve the Schrodinger equation for a multi electron system with the application of Born Oppenheimer approximation. These equations are solved numerically using multiple iterations as non-linearity is introduced in the equations due to Hartree Fock approximation.

Four major simplifications provided by H-F approximation are:

- The wave function of the molecule is described by the position of nuclei and the respective electrons in its vicinity and the Born Oppenheimer approximation is apparent in the calculations.
- Relativistic effects are completely neglected in the HartreeFock approximation.
- A single slater determinant describes the energy eigen function of the system.
- The mean field approximation is completely implemented for electrons with opposite spins which is ignored for electrons with the same spin.

One of the major drawbacks of H-F theory is that it fails to acknowledge the electron correlation. In this approximation, all the electrons are assumed to be moving in a combined average potential. The single position of a single electron is not influenced by the presence of other electrons. The electron correlation can be defined as the difference between the Hartree Fock energy and the total energy of the system. By neglecting the correlation energy, one gets a significant difference with experimental results.

As per the Kohn-Sham formulation of DFT, single determinant is described for the exchange energy. The functional (exchange-correlation), which can include terms calculating for both the exchange and the electron correlation energies, the exchange-correlation functional not present in H-F theory.

$E_{KS} = V + \langle hP \rangle + 1/2\langle PJ(P) \rangle + E_X[P] + E_C[P]$

where $E_x[P]$ is the exchange of functional energy, and $E_c[P]$ is the correlation functional energy.

2.3.4 Density Functional Theory

Density functional theory is one of the most accurate approaches to calculate the electronic properties of solid, liquid and gas. Application of DFT varies to different ranges, from molecules to atoms, and nuclei to solids and quantum to classical fluids. The density functional theory's original formulation gives us the information about the ground state properties of a system, and the electron density of the system plays a vital role. Various molecular features are described by DFT: vibrational frequencies, molecular structures, ionization energies, atomization energies, magnetic and electric properties, reaction paths, etc. It is generalized to deal with many different situations: electron-hole droplets, time-dependent phenomena, multi-component systems such as nuclei, excited states, spin-polarized systems, free energy at finite temperatures, superconductors with electronic pairing mechanisms, relativistic bosons, electrons, molecular dynamics, etc. [4] The time-independent Schrödinger equation is

$$\hat{H}\Psi_i(x_1, x_2, x_3 \dots x_N, R_1, R_2, \dots R_N) = E\Psi_i(x_1, x_2, x_3 \dots x_N, R_1, R_2, \dots R_N)$$

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \frac{1}{2}\sum_{A=1}^{M}\frac{1}{M_A}\nabla_A^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}} + \sum_{i=1}^{N}\sum_{j>1}^{N}\frac{Z_A}{r_{ij}} + \sum_{A=1}^{M}\sum_{B>A}^{M}\frac{Z_A Z_B}{r_{AB}}$$

A and B are computed over the M nuclei while *i* and *j* are usedindicate the N electrons in the system.

1st and 2nd term of the equation represents the kinetic energy of the electrons and nuclei. The last three terms indicate the attractive electrostatic interaction between the electrons and nuclei and, respectively, potential due to the electron-electron and nucleus-nucleus interactions.

2.4 BASIS SET

Basis sets were first demonstrated by J. C. Slater. Expression for a basis function is expressed as:

Basis Function = $N^{*}e^{(-alpha * r)}$

N is Normalization constant

alpha is orbital exponent

r is radius in angstrom

Basis sets can be expressed as the set of functions that are used in density function theory and HartreeFock calculations

2.5 PERIODIC POTENTIALS

When talking about lattice structure of a molecule we have to make an approximation in the kind of potential we are using. Until now we have discussed all our assumptions for an isolated molecule. As we know that matter exists in various forms of matter primarily, solid, liquid and gas. Depending on the type of matter the order of the system is decided. For a solid has periodicity in the lattice and the arrangement of atoms is ordered, in liquids there is very limited or no periodicity and; for gases there's no periodicity at all. The atoms of solids are bound and there exists a potential due to this periodicity. Until now we have only made approximation to the Hamiltonian operator. In the next step is the approximation to be made in order to deal with the geometry and arrangement of atoms in the space. To discuss the periodic systems a whole new set of periodic approximations is needed. The point to be noted is that this is true for a perfect lattice, devoid of any defects but the crystals can be approximated so as to achieve minimal error [6].

The crystal nature of a system is described using the Bravais lattice which implies that the unit cell of the crystals repeats itself in different direction in a regular array. This brings us to infer that same environment is experienced by the neighbouring cell as its image.

Assuming V($\mathbf{q}$) is the potential, this can be described as

$$V(\boldsymbol{q}+\boldsymbol{R})=V(\boldsymbol{q})$$

With **R** is described as being a linear combination of the primitive lattice vectors. Since the potential describes the force acted upon by the electrons, this also implies that the ground state wave functions inside each crystal are identical in each cell and respect the translational periodicity of the crystal [7]. It then follows by further conclusions and leads to Bloch's theorem.

2.5.1 Periodic boundary conditions (PBC) calculations

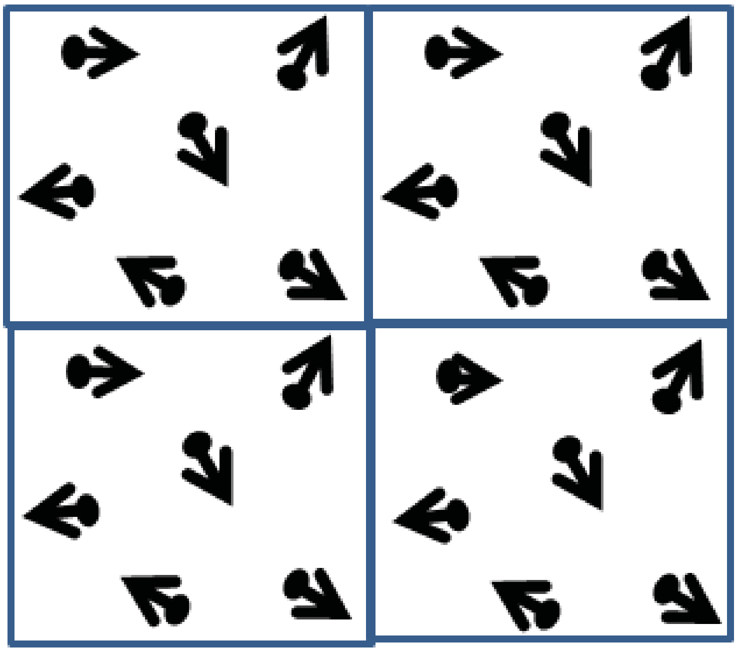

Fig 2.2 Periodic boundary conditions

The computer stimulations are usually carried out using atomised potentials to a small system of molecules. Now suppose a lattice contains a large number of molecules. Each system would contain a large set of molecules and these systems are surrounded by other identical behaving systems and the systems are connected by boundaries as shown in fig 2.1. Hence if a molecule leaves from one box, an identical molecule from another box with identical surroundings enters the previous box.

2.6 BLOCH'S THEOREM

Bloch theorem connects the properties of an electron in a lattice to that of the Unit cell. Thus, as we know that the potential of the system can vary periodically from cell to cell, we can write the wave function for the system applying the boundary conditions. The one-electron wave function can be given as

$$\Psi_k(q) = e^{-ik.q} V_k(q)$$

where k is the positional momentum vector.

Displacing the wave function by position vector R

$$\mathit{\Psi}_k(q+R) = e^{-ik.q} \mathit{\Psi}_k(q)$$

2.7 PLANE -WAVE BASIS SETS

To match the atomic orbitals, we need a finite set of basis functions which replicate the behaviour of the actual atomic orbitals. [8]. In order to deal with the periodic systems as we discussed above, we make use of the periodic wavefunction. So we need an appropriate number of basis composed of plane wave as they offer many useful explanation for describing these systems. One of the major requirements is that they should not violate the Bloch theorem. In other words the periodicity in these basis set should be maintained to offer an accurate solution. For a given wave function to offer an accurate solution it should contains a periodic as well a phase part with a relative frequency attached to it [7]. In Plane-wave, this property comes naturally. It is inherent in it and it provides the solution to the Schrodinger equation in a constant external potential [7]. It is to be noted that as one moves closer and closer to the nuclei the potential tend to deviate from its periodic nature hence it is required to do an increasing number of linear combination of plane wave. One of the more useful feature of a plane wave basis set is that they tend to be mutually orthogonal, and they are fairly easy to calculate using a fast Fourier transform.As more basis functions are added they show a better result [9].

2.8 PSEUDOPOTENTIALS

The work of Hans Hellman gave the concept of Pseudopotentials around 1935, for valence electron being scattered from the atomic ion core he proposed an effective potential. However, in the potential, he ended up being slight less effective and the perturbation methods of the time did not allow for a reasonable result [9]. Only after Slater in 1937 and Herring 1940 proposed expansions to the problem by the use of augmented plane wave (PW) expansions combined with the spherical solution to the atomic problem i.e. augmented plane-wave method (APW) and also the linear combinations of core wave functions and the plane-wave for valence wave functions (orthogonalized plane-wave method,OPW), respectively [7].

As in the mentioned OPW method, the wave functions became orthogonal to the core states, and the number of plane wave-component for valence state reproduction is significantly reduced by the use of core orbitals. This led to the development of modern Pseudopotential method as mentioned in the work of Philips and Kleinmann in 1959 [11]. They further contributed to the development of the OPW method by creating equations for the valence electrons depending on a weaker or softer effective potential [9]. The problem of OCW has been based of the PW basis sets. To solve the problem of giant basis sets the strong Coulomb potential pertaining to the nucleus and also the core electrons are replaced by an effective ionic potential which acts on the valence electrons [9]. Thus, the core states of the system are fixed effectively in an atomic reference configuration (frozen core approximation) and the ground state pseudo-wavefunction identically mimics the all-electron wavefunction outside of the core cut-off radius [12]. Fitting of the pseudopotentials is generally accomplished by comparison to all-electron wavefunctions, with the advantage of reducing the number of electrons, electronic states, and basis sets to be considered, and at the expense of calculation [7].

The Pseudopotentials are generally classified into three types: norm conserving, ultrasoft and projector augmented wave pseudopotentials.

2.8.1 Norm-Conserving Pseudopotential

The first type of pseudopotential has some base in its physical considerations. The norm-conserving pseudopotentials is based on following assumptions[9]:

- Atomic reference states are agreed for pseudo-valence and all electron eigenvalue.
- The radius core R_c is agreed beyond a certain core for both.
- Pseudo wavefunction and all-electron wavefunction logarithmic derivatives agree at the point Rc.
- An important norm conserving condition is that the integrated charge for each wave function agrees inside the core radius.
- The first energy derivative of the log derivatives of both wavefunctions agree at Rc.

This produces transferable wave functions with an reasonably accurate and is popular in the research community [11].

A low cut-off radius is needed in order to attain high transferability and a considerable degree of accuracy which makes it a hard potential. This is one of the major drawback of norm conserving potentials.

2.8.2. Ultrasoft Pseudopotentials

In order to tackle the problem of hardness and high cut-off energy values of the norm conserving potentials, Vanderbilt in 1990 suggested an alternative. He allowed a softer potential with a significant reduction in the cut-off values of energy. [11]. This turned out to be one of the founding stones for the ultrasoft pseudopotentials. With the use of fewer basis sets the softness in the pseudopotentials is inherent and the issue is re-addressed as an auxiliary function and a smooth function which is localized around the core to study the rapid variation in the density which allows for the larger cut-off radii[9]. The difference in charge density is compensated by adding an additional term in order to produce accurate results from the all-electron wave function[7]. As shown in the works of Koval et. al. in simulating oxygen a significant reduction in energy cut-off values for plane wave calculations has been achieved from 150 Ry to 40 Ry [12].

2.8.3 Projected Augmented Wave Pseudopotentials

Projector augmented waves (PAW) is a more generalised version of linear augmented plane wave method. is a technique that helps in restoring the pseudo- to the all-electron wavefunctions and uses pseudopotentials which are linked closely to ultrasoft pseudopotentials. It expands all-electron wavefunction withinan atomic siteinto a basis set of atomic wavefunctions called partial waves. The pseudo-wavefunctions are also expanded into a basis set of pseudo-partial waves which correspond to pseudised versions of the all-electron partial waves. Usually PAW pseudopotentials are considered more accurate as compared to the Ultrasoft or norm conserving pseudopotentials.

2.9 GEOMETRY OPTIMIZATION

In the mathematical terms the optimization refers to as finding the points where the first derivative is zero or the stationary point of the given function. In most of the cases, the desired stationary point comes out to be a minimum i.e. when the second derivative comes out to be positive, but there are few times when the stationary point comes out to be a maximum which is the case when the second derivatives is negative, in some cases the desired point is a saddle point i.e. second derivative is positive in one direction and turns out to be negative in the other.

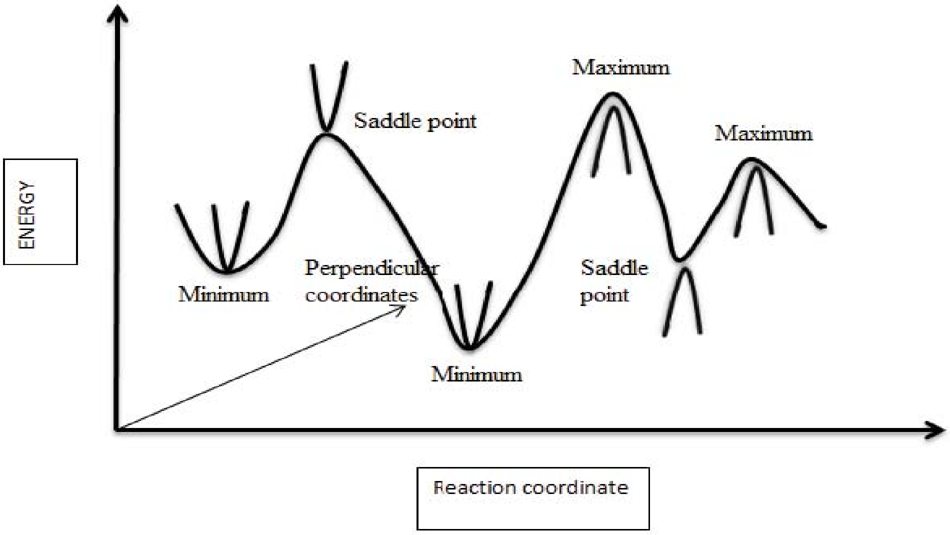

Fig 2.3 Illustration of various points on energy surface

2.9.1 Optimizing general functions

For the optimization of functions and using the construction of an irregular polyhedron in parameter the approach of simplex method is used. As it is evident that the polyhedron is approaching the minimum while the size of the polyhedron is allowed to expand and contract to improve the possibility of convergence. However, it is noticed that the simplex method approach is very slow for the many-dimensional functions.

Another approach used is to utilise the property of gradient vector **g** which points in the direction where there is a substantial increase in the value of the function. The function value is decreased by performing a set of function evaluations in the negative gradient direction, i.e. along the direction defined as

d= -g

The interpolation between the calculated points determines the approximate minimum. On the point that is interpolated, a new gradient is evaluated and is used for the next line search. Because of the nature of this approach, it can only spot local minima. However the plus point involves its simplicity and requires only the storage of gradient vector only.

The drawbacks involving steepest gradient method is that upon reaching towards the minima, the rate at which the function convergences slows down and never really reach the exact minimum, it just keep crawling with a decreased speed. To drawback is resolved using another approach is used which is known as the conjugate gradient method in which each line search along the line is carried out such that it is conjugate to the previously searched directions.

2.10 COMPUTATIONAL METHODOLOGY

The system of interest chosen for study is nCB liquid crystal.

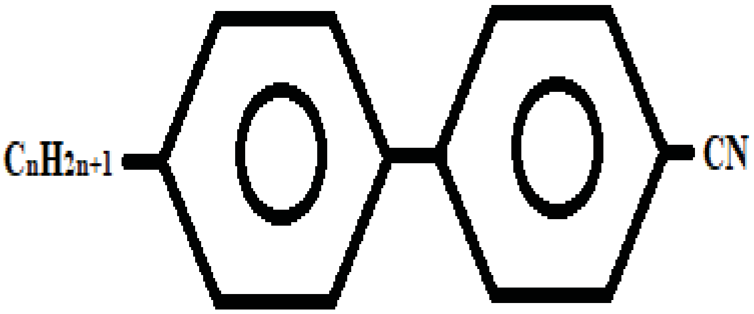

Fig 2.4 Structure of nCB

All the atoms are optimised by PWscf method using PAW and norm conserving pseudo potentials and the optimised co-ordinates are recorded. Then, scf calculations of the system are performed on this optimised molecule. The molecules are chosen to be a monoclinic unit cell as stated in Hanemann et al [13].

For optimising the coordinates the relax calculations are done quantum espresso software[14-16], and then the scf calculation calculations are performed. Later, phonon calculations are performed for calculating the dielectric constant and polarizability of the system.

The calculations are performed using the plane wave pseudopotential method. The energy cut-off value properly chosen as a balance between accuracy and time consumed in calculations. The energy cut-off is chosen in such a way that the value of total energy settles to a stable value as given in Fig 2.5.

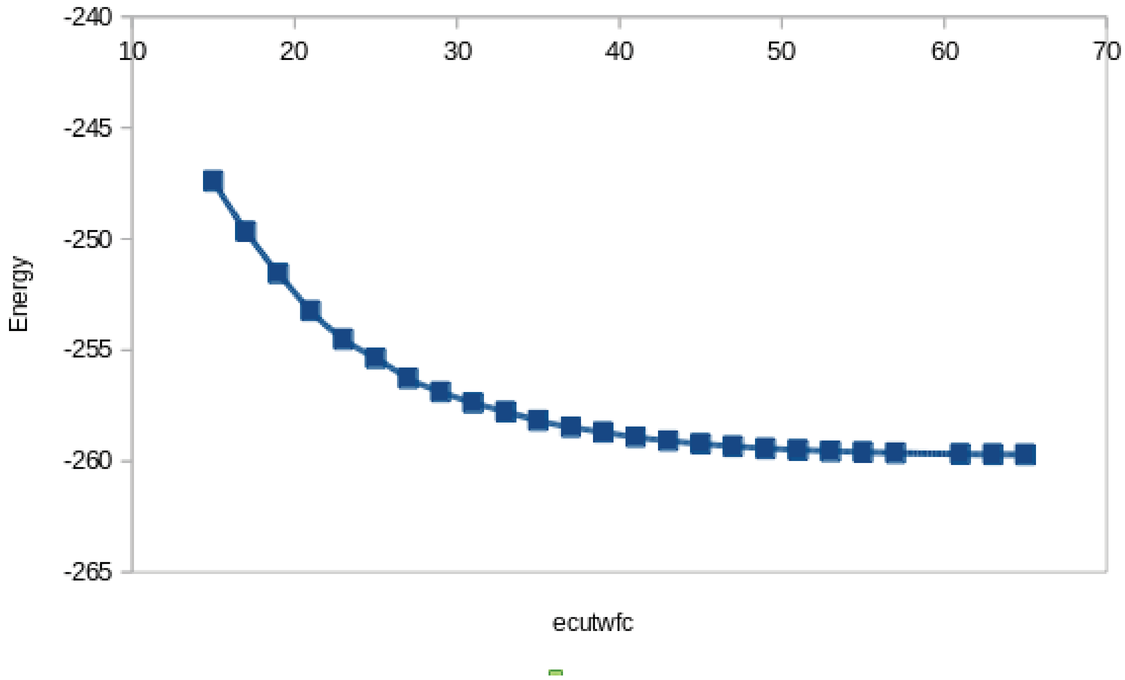

Fig 2.5 Plot of energy cut-off to total energy of the system

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CHAPTER-3

RESULTS AND DISCUSSIONS

CHAPTER 3

RESULTS AND DISCUSSIONS

nCB liquid crystals have been chosen for studying optimized structure, molecular orbitals, HOMO LUMO gap and infra-red spectra. Dielectric constant and polarizability constants have been calculated.

Quantum espresso is an OPEN software for DFT calculations employing Plane wave self-consistent field methodology. Geometry optimizations have been followed by SCF calculations, phonon calculations and spectral analysis.

3.1 4’-methyl-(1, 1’- biphenyl)- 4-carbonitrile (1CB)

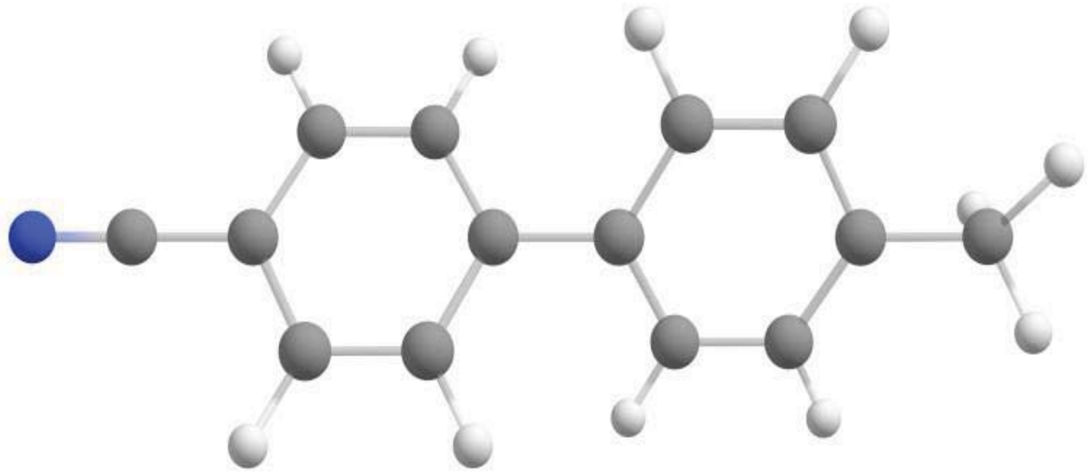

Fig 3.1 Optimised structure of 1CB molecule

The common name of 4’-methyl-(1,1’- biphenyl)- 4-carbonitrile is 1CB. It is a nematogenic liquid crystal and is commonly used as a liquid crystal device.

The calculations are performed using the PAW and norm conserving pseudopotentials. The energy cut-off (ecutwfc) chosen to be 30 Ry. The energy cut-off is chosen in such a way that the value of total energy settles to a stable value as given in fig 3.2 and saving computational time also.

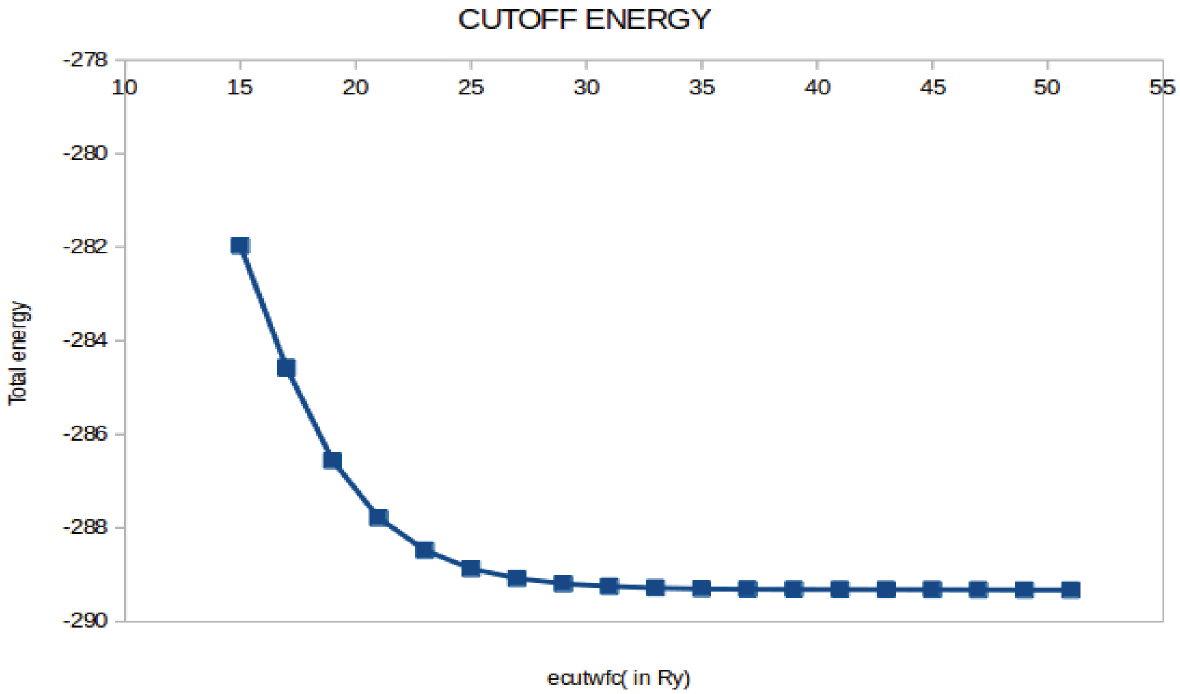

Fig 3.2 Plot of energy cut-off to total energy of the system

The HOMO-LUMO of the molecule is shown in fig 3.4. The energy gap (E_g) of HOMO-LUMO is 2.94 eV (NC) & 3.02 eV (PAW). The HOMO of the molecule is largely centered around the phenyl rings involving the carbon atoms, and the nitrogen that exist at the end is occupied. In LUMO the delocalization of valence orbital is there throughout the molecule.

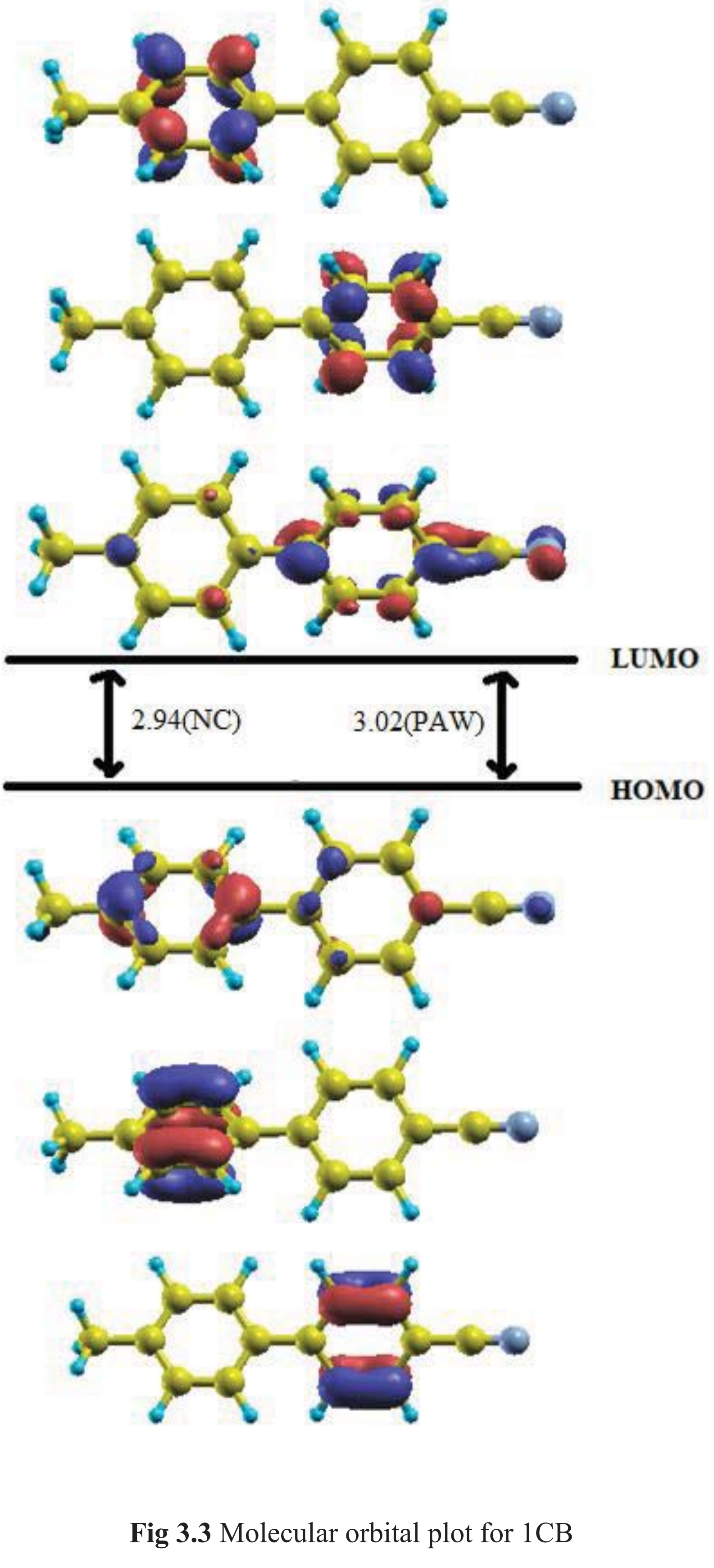

Fig 3.3 Molecular orbital plot for 1CB

Bond lengths have been calculated (in Angstrom) and optimised for 1CB molecules for both PAW and norm conserving pseudopotentials given in table 3.1 and positioning of atoms is given in fig 3.4.

Table 3.1 Bond length of optimised geometry of 1CB molecule

POSITION OF ATOMS	TYPE OF BOND	BOND LENGTH (PAW)	POSITION OF ATOMS	TYPE OF BOND	BOND LENGTH (NC)
16 20	C-H	1.13225	14 19	C-H	1.15266
14 19	C-H	1.13227	16 20	C-H	1.15269
12 15	C-H	1.13424	2 8	C-H	1.15466
13 17	C-H	1.13425	12 15	C-H	1.15466
4 9	C-H	1.13458	4 9	C-H	1.15468
2 8	C-H	1.1346	13 17	C-H	1.15473
1 7	C-H	1.13478	1 7	C-H	1.15509
5 10	C-H	1.13485	5 10	C-H	1.15509
23 26	C-H	1.14093	23 26	C-H	1.16132
23 24	C-H	1.14166	23 24	C-H	1.16223
23 25	C-H	1.14619	23 25	C-H	1.16622
21 22	C-N	1.21595	21 22	C-N	1.27415
13 16	C-C	1.42216	13 16	C-C	1.45494
12 14	C-C	1.42222	12 14	C-C	1.45499
4 5	C-C	1.42441	4 5	C-C	1.45776
1 2	C-C	1.42456	1 2	C-C	1.4578
1 6	C-C	1.43371	1 6	C-C	1.46722
5 6	C-C	1.43373	5 6	C-C	1.46733
2 3	C-C	1.43515	2 3	C-C	1.46875
3 4	C-C	1.43536	3 4	C-C	1.4689
14 18	C-C	1.43556	14 18	C-C	1.47059
16 18	C-C	1.43568	16 18	C-C	1.47072
11 13	C-C	1.43825	11 13	C-C	1.47133
11 12	C-C	1.4383	11 12	C-C	1.47134
18 21	C-C	1.45024	18 21	C-C	1.48483
3 11	C-C	1.48465	3 11	C-C	1.5191
6 23	C-C	1.50453	6 23	C-C	1.54175
25 26	H-H	1.83471	24 25	H-H	1.86904
24 25	H-H	1.83503	25 26	H-H	1.86924
24 26	H-H	1.84852	24 26	H-H	1.88322
6 25	C-H	2.19706	6 25	C-H	2.24293
6 26	C-H	2.20054	6 26	C-H	2.24727
6 24	C-H	2.20278	6 24	C-H	2.24996
14 15	C-H	2.21598	16 17	C-H	2.2634
16 17	C-H	2.21602	14 15	C-H	2.26349
6 7	C-H	2.21795	6 7	C-H	2.26461

6 10	C-H	2.21805	6 10	C-H	2.26491
4 10	C-H	2.21903	4 10	C-H	2.26665
2 7	C-H	2.2192	2 7	C-H	2.2668
1 8	C-H	2.21981	3 8	C-H	2.26836
5 9	C-H	2.22002	3 9	C-H	2.26869
18 19	C-H	2.22183	18 20	C-H	2.26906
18 20	C-H	2.22188	18 19	C-H	2.26914
3 8	C-H	2.22286	1 8	C-H	2.26918
3 9	C-H	2.22305	5 9	C-H	2.26926
11 17	C-H	2.2238	11 15	C-H	2.27075
11 15	C-H	2.22406	11 17	C-H	2.27093
12 19	C-H	2.22839	12 19	C-H	2.27631
13 20	C-H	2.22846	13 20	C-H	2.27641
9 15	H-H	2.30409	9 15	H-H	2.3441
8 17	H-H	2.30735	8 17	H-H	2.34847
1 5	C-C	2.4562	1 5	C-C	2.51642
2 4	C-C	2.46342	2 4	C-C	2.52463
13 18	C-C	2.46977	12 18	C-C	2.52789
12 18	C-C	2.46984	13 18	C-C	2.52803
12 13	C-C	2.47315	12 13	C-C	2.53387
3 5	C-C	2.48579	1 3	C-C	2.54195
1 3	C-C	2.48582	3 5	C-C	2.54205
14 16	C-C	2.48891	11 16	C-C	2.54545
11 14	C-C	2.48995	11 14	C-C	2.54558
11 16	C-C	2.48999	2 6	C-C	2.54737
2 6	C-C	2.49021	4 6	C-C	2.54738
4 6	C-C	2.49023	14 16	C-C	2.55035
16 21	C-C	2.49791	16 21	C-C	2.55762
14 21	C-C	2.49822	14 21	C-C	2.55831
7 26	H-H	2.50635	7 26	H-H	2.5592
10 24	H-H	2.53068	10 24	H-H	2.58849
2 11	C-C	2.5397	2 11	C-C	2.59694
3 13	C-C	2.54006	3 13	C-C	2.59712
4 11	C-C	2.54039	3 12	C-C	2.59729
3 12	C-C	2.54082	4 11	C-C	2.59797
7 8	H-H	2.55434	9 10	H-H	2.61361
9 10	H-H	2.55461	7 8	H-H	2.61364
1 23	C-C	2.55821	1 23	C-C	2.61822
5 23	C-C	2.55842	5 23	C-C	2.61894
15 19	H-H	2.56924	15 19	H-H	2.62663
17 20	H-H	2.56952	17 20	H-H	2.62666
18 22	C-N	2.66619	18 22	C-N	2.75898
20 21	H-C	2.72687	20 21	H-C	2.78739
19 21	H-C	2.72752	19 21	H-C	2.78896
1 26	C-H	2.73361	1 26	C-H	2.79229
5 24	C-H	2.74445	5 24	C-H	2.80593
3 17	C-H	2.76377	3 17	C-H	2.82373
3 15	C-H	2.7654	3 15	C-H	2.82375

8 11	H-C	2.76725	8 11	H-C	2.82419
9 11	H-C	2.76834	9 11	H-C	2.82614
10 23	H-C	2.77569	4 15	C-H	2.83223
7 23	H-C	2.77578	9 12	H-C	2.83426
4 15	C-H	2.779	2 17	C-H	2.83434
2 17	C-H	2.77907	8 13	H-C	2.83442
9 12	H-C	2.78235	7 23	H-C	2.83691
8 13	H-C	2.78309	10 23	H-C	2.83777
2 5	C-C	2.84242	1 4	C-C	2.91169
1 4	C-C	2.84255	2 5	C-C	2.91175
13 14	C-C	2.85964	12 16	C-C	2.92895
12 16	C-C	2.85983	13 14	C-C	2.92911
11 18	C-C	2.87246	11 18	C-C	2.93571
3 6	C-C	2.90105	3 6	C-C	2.96362

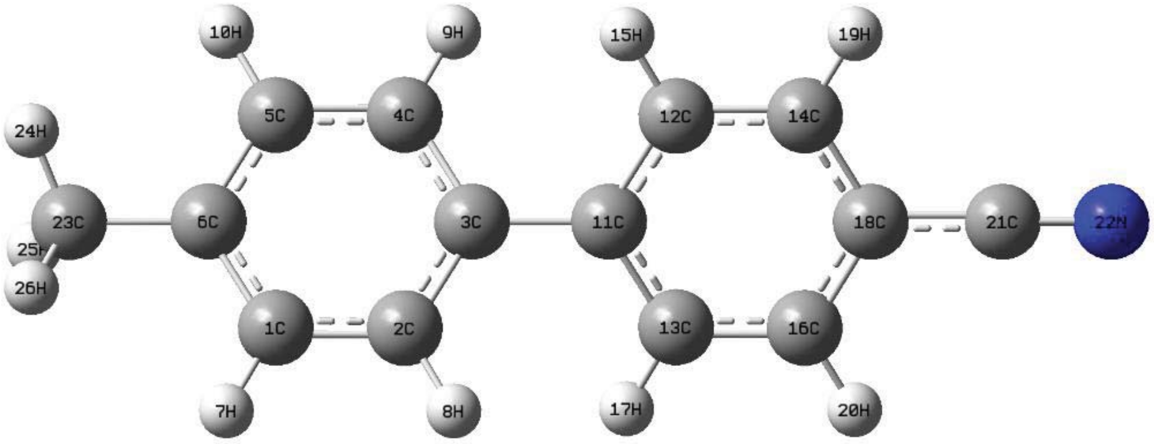

Fig 3.4 Structure of 1CB with positioning of atoms

The IR peak intensities are given in table 3.2 and the spectra plot of the given molecule is given in fig 3.5.

Table 3.2 IR spectra of 1CB

Experimental frequencies(cm^{-1})[1]	**Calculated frequency**	**IR intensity**
411	406.5	0.0827
474	461.25	0.0451
527	520.05	0.144
551	545.68	0.0342
637	624.59	0.0001
650	629.62	0.0073
776	759.97	0.3673
807	815.94	0.013
824	849.57	0.0534

885	889.6	0.1928
1003	1005.61	0.0312
1019	1040.45	0.0115
1061	1066.1	0.0022
1121	1176.41	0.0964
1179	1188.41	0.1028
1287	1285.4	0.1699
1374	1386.08	0.022
1456	1428.56	0.0119
1522	1533.71	1.3696
1605	1601.67	0.0217
2220	2253.33	0.9049
3032	3055.07	0.6212
3070	3138.51	0.2175

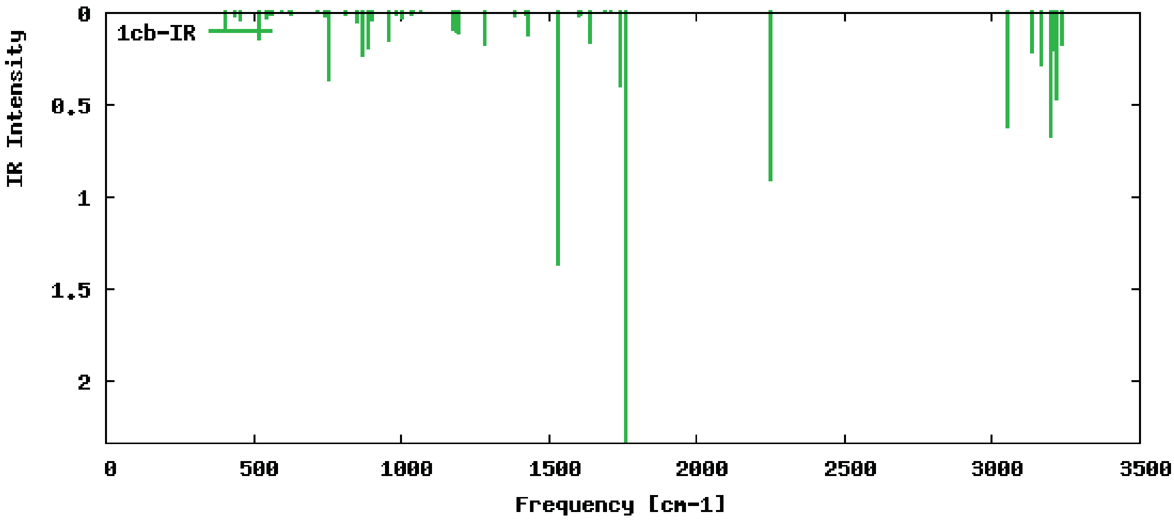

Fig 3.5IR spectra of 1CB

The dielectric tensor of the molecule is calculated. The diagonalized elements are:

$$\varepsilon_{r(NC)} = \begin{pmatrix} 1.407945032 \\ 1.159207466 \\ 1.107939205 \end{pmatrix},\ \varepsilon_{r(PAW)} = \begin{pmatrix} 1.357350218 \\ 1.146417435 \\ 1.098832143 \end{pmatrix},$$

Average value of dielectric constant comes out to be 1.225 (NC) and 1.201 (PAW).

The value of polarizability comes out to be $\propto = \begin{pmatrix} 420.42 \\ 176.99 \\ 121.98 \end{pmatrix}, \propto = \begin{pmatrix} 373.82 \\ 163.44 \\ 112.98 \end{pmatrix}$ and the average value of polarizability is 239.80 au^3 (NC) and 216.423 au^3 (PAW).

3.2 4’-ethyl-(1, 1’- biphenyl) - 4-carbonitrile (2CB)

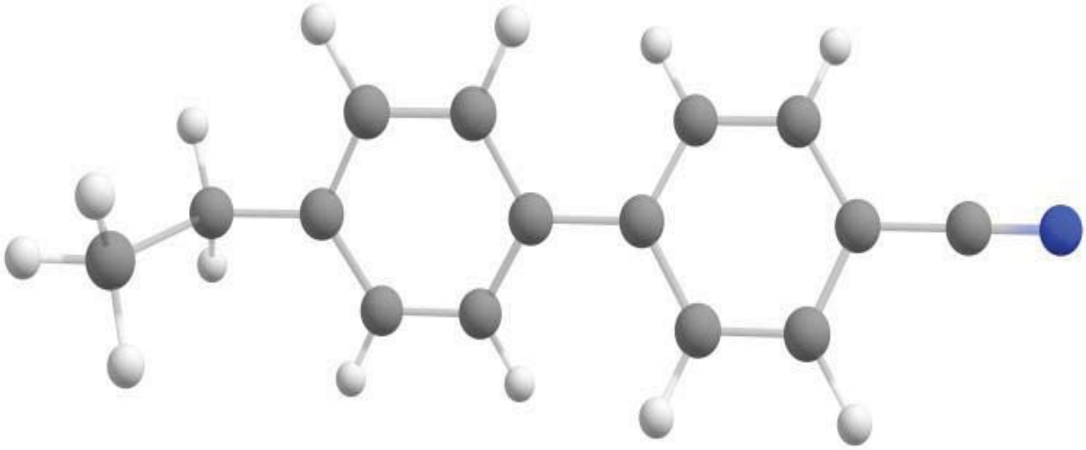

Fig 3.6 Optimised structure of 2CB molecule

The nematic phase of the given molecule is 4’-ethyl-(1,1’- biphenyl)- 4-carbonitrile and it’s a nematogenic liquid crystal and is commonly used as a liquid crystal device.

The calculations are performed using the PAW and norm conserving pseudopotentials. The energy cut-off chosen to be 30 Ry. The energy cut-off is chosen in such a way that the value of total energy settles to a stable value as given in Fig 3.7.

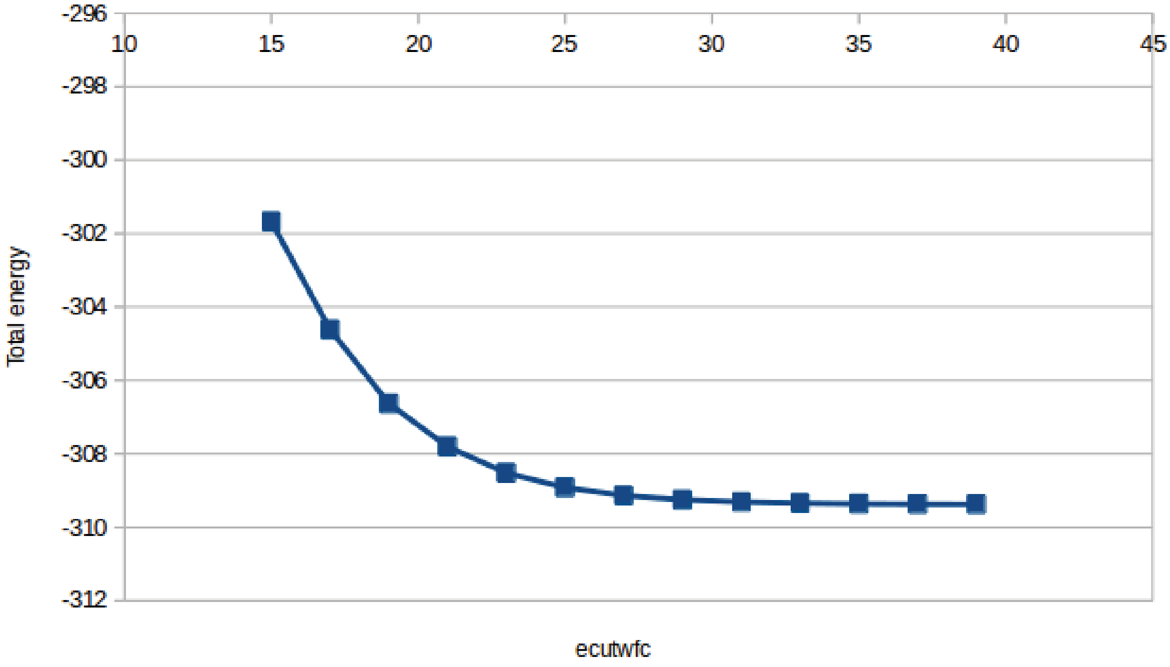

Fig 3.7 Plot of energy cut-off to total energy of the system

The HOMO-LUMO of the molecule is shown in fig 3.8. The energy gap (E_g) 0f HOMO-LUMO is 3.40 eV (NC) & 3.55 eV (PAW). It can be deduced that that the molecule is dominated by its functional groups. The HOMO of the molecule is largely centred on the phenyl rings involving the carbon atoms, and the nitrogen that exists at the end is occupied. In LUMO the delocalization of valence orbitals is there throughout the molecule.

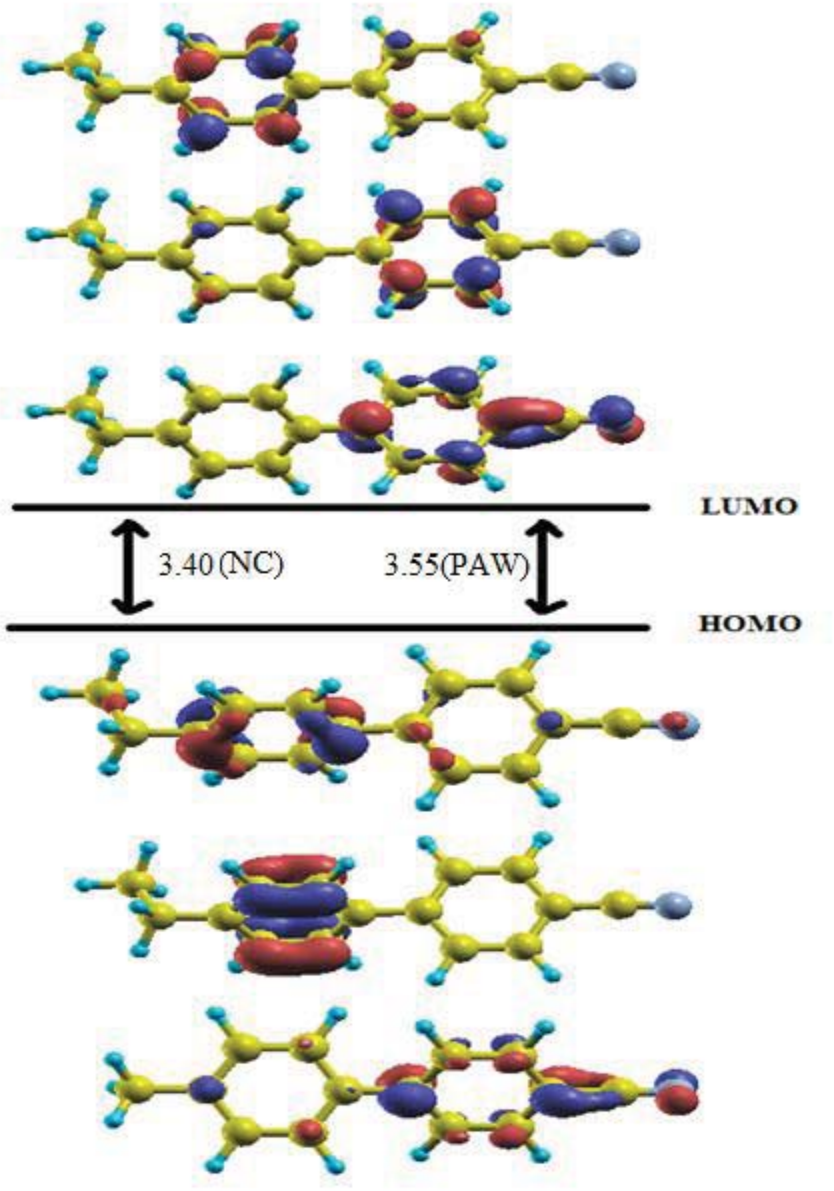

Fig 3.8 Molecular orbital plot for 2CB

Bond lengths have been calculated (in Angstrom) and optimised for 2CB molecules for both PAW and norm conserving pseudopotentials, as given in table 3.3, and positioning of atoms is given in fig 3.9.

Table 3.3 Bond length of optimised geometry of 2CB molecule

POSITION OF ATOMS	TYPE OF BOND	BOND LENGTH (PAW)	POSITION OF ATOMS	TYPE OF BOND	BOND LENGTH (NC)
16 20	C-H	1.13291	16 20	C-H	1.15113
14 19	C-H	1.13309	14 19	C-H	1.15185
13 17	C-H	1.13408	1 7	C-H	1.15483
2 8	C-H	1.13439	12 15	C-H	1.15558
12 15	C-H	1.13501	4 9	C-H	1.15565
4 9	C-H	1.13609	13 17	C-H	1.15605
1 7	C-H	1.13702	2 8	C-H	1.1568
5 10	C-H	1.13855	5 10	C-H	1.15718
26 27	C-H	1.1441	26 28	C-H	1.16367
26 28	C-H	1.14571	26 27	C-H	1.16496
23 25	C-H	1.14761	23 25	C-H	1.16801
23 24	C-H	1.16245	26 29	C-H	1.18792
26 29	C-H	1.1635	23 24	C-H	1.18807
21 22	C-N	1.21658	21 22	C-N	1.27465
13 16	C-C	1.42485	13 16	C-C	1.45812
1 2	C-C	1.4273	1 2	C-C	1.46405
12 14	C-C	1.42771	4 5	C-C	1.46408
4 5	C-C	1.43041	12 14	C-C	1.46459
2 3	C-C	1.43196	5 6	C-C	1.46611
3 4	C-C	1.43233	1 6	C-C	1.46671
1 6	C-C	1.43235	11 13	C-C	1.46708
5 6	C-C	1.43239	2 3	C-C	1.46791
11 13	C-C	1.43341	14 18	C-C	1.47035
11 12	C-C	1.43462	11 12	C-C	1.47129
14 18	C-C	1.43575	3 4	C-C	1.47179
16 18	C-C	1.43636	16 18	C-C	1.47581
18 21	C-C	1.45384	18 21	C-C	1.48893
3 11	C-C	1.48955	3 11	C-C	1.52876
6 23	C-C	1.51116	6 23	C-C	1.55105
23 26	C-C	1.53632	23 26	C-C	1.56374
24 25	H-H	1.8469	24 25	H-H	1.87093
28 29	H-H	1.84808	27 29	H-H	1.88698
27 28	H-H	1.85712	28 29	H-H	1.88726
27 29	H-H	1.85764	27 28	H-H	1.89857
6 24	C-H	2.17971	6 24	C-H	2.2102
6 25	C-H	2.188	23 28	C-H	2.25016
25 26	H-C	2.21239	6 25	C-H	2.25271
3 8	C-H	2.21815	25 26	H-C	2.2547

11 17	C-H	2.21882	16 17	C-H	2.25859
11 15	C-H	2.219	6 10	C-H	2.26305
2 7	C-H	2.22118	24 26	H-C	2.26468
6 10	C-H	2.22187	6 7	C-H	2.2669
18 20	C-H	2.22335	1 8	C-H	2.26853
23 28	C-H	2.22372	12 19	C-H	2.26887
16 17	C-H	2.2241	2 7	C-H	2.26909
14 15	C-H	2.226	14 15	C-H	2.2696
6 7	C-H	2.2264	13 20	C-H	2.27251
1 8	C-H	2.2269	23 27	C-H	2.27343
3 9	C-H	2.22712	5 9	C-H	2.27394
4 10	C-H	2.22794	11 17	C-H	2.27429
5 9	C-H	2.22859	11 15	C-H	2.27741
12 19	C-H	2.22959	18 19	C-H	2.27857
13 20	C-H	2.22973	18 20	C-H	2.27881
18 19	C-H	2.23052	3 9	C-H	2.27898
24 26	H-C	2.23297	4 10	C-H	2.27925
23 27	C-H	2.23651	3 8	C-H	2.28521
23 29	C-H	2.23732	23 29	C-H	2.28658
10 24	H-H	2.44758	10 24	H-H	2.34066
1 5	C-C	2.46268	1 5	C-C	2.51866
16 21	C-C	2.4659	12 13	C-C	2.53274
2 4	C-C	2.46949	16 21	C-C	2.53351
12 18	C-C	2.47093	13 18	C-C	2.53432
12 13	C-C	2.474	2 4	C-C	2.53471
13 18	C-C	2.4743	1 3	C-C	2.53859
3 5	C-C	2.48027	12 18	C-C	2.54163
11 16	C-C	2.48247	3 5	C-C	2.54432
1 3	C-C	2.48252	11 14	C-C	2.5474
2 6	C-C	2.48545	11 16	C-C	2.54768
11 14	C-C	2.48944	4 6	C-C	2.54872
14 16	C-C	2.49095	14 16	C-C	2.54891
4 6	C-C	2.49157	2 6	C-C	2.55265
6 26	C-C	2.51033	4 11	C-C	2.57993
2 11	C-C	2.52369	8 17	H-H	2.5804
14 21	C-C	2.5318	24 29	H-H	2.58956
3 13	C-C	2.53297	3 13	C-C	2.59501
3 12	C-C	2.54066	6 26	C-C	2.59693
25 27	H-H	2.54786	14 21	C-C	2.59789
4 11	C-C	2.54806	7 29	H-H	2.60145
1 23	C-C	2.5569	7 8	H-H	2.60345
7 25	H-H	2.55708	3 12	C-C	2.60524
5 23	C-C	2.55895	15 19	H-H	2.60761
7 8	H-H	2.56188	17 20	H-H	2.60863
9 10	H-H	2.567	5 23	C-C	2.61095
15 19	H-H	2.57571	24 27	H-H	2.62148
24 28	H-H	2.57799	2 11	C-C	2.62315
17 20	H-H	2.57877	9 10	H-H	2.62663

25 29	H-H	2.64264	1 23	C-C	2.63583
24 27	H-H	2.64717	25 27	H-H	2.63686
18 22	C-N	2.66326	5 24	C-H	2.63863
20 21	H-C	2.67541	25 29	H-H	2.65093
5 24	C-H	2.68376	24 28	H-H	2.65835
8 11	H-C	2.73515	20 21	H-C	2.75469
1 25	C-H	2.74437	18 22	C-N	2.76058
3 17	C-H	2.74893	9 11	H-C	2.79896
24 29	H-H	2.75036	10 23	H-C	2.81464
3 15	C-H	2.75881	3 17	C-H	2.82674
6 29	C-H	2.76035	6 28	C-H	2.82987
10 23	H-C	2.77725	3 15	C-H	2.83924
7 23	H-C	2.78287	7 23	H-C	2.86265
9 11	H-C	2.78804	19 21	H-C	2.86701
19 21	H-C	2.79535	8 11	H-C	2.88619
6 28	C-H	2.82877	10 29	H-H	2.89717
2 5	C-C	2.84632	1 4	C-C	2.91752
1 4	C-C	2.85387	7 25	H-H	2.91775
12 16	C-C	2.859	2 5	C-C	2.92278
11 18	C-C	2.86596	13 14	C-C	2.92559
13 14	C-C	2.86703	12 16	C-C	2.93632
3 6	C-C	2.88606	9 15	H-H	2.94046
7 29	H-H	2.91465	11 18	C-C	2.94378
8 17	H-H	2.99385	6 29	C-H	2.95215

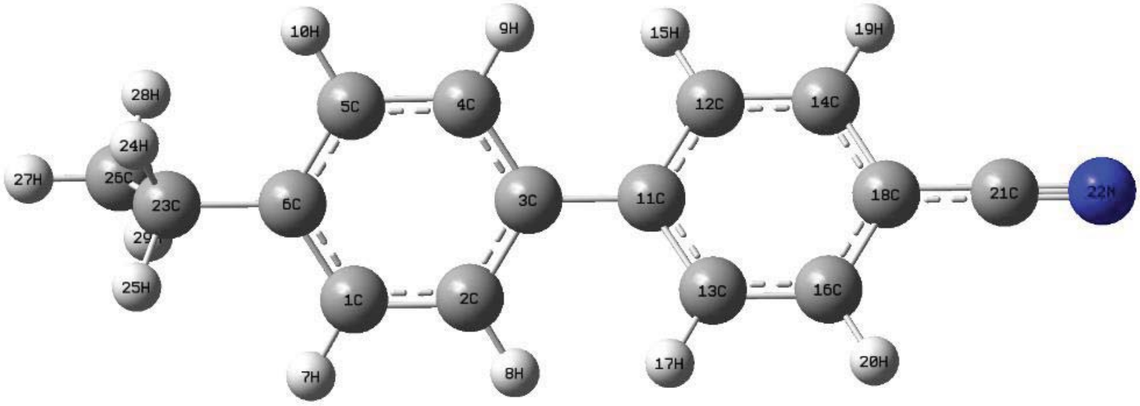

Fig 3.9 Structure of 2CB with positioning of atoms

The IR peak intensities are given in table 3.4 and the spectra plot of the given molecule is given in fig 3.10.

Table 3.4 IR spectra of 2CB

Experimental frequencies(cm^{-1})[2]	Calculated frequency	IR intensity
411	410.34	0.1657
474	443.62	0.2351
527	560.64	0.0115
551	574.6	0.0732
637	630.27	0.0865
650	669.31	0.2667
776	773.82	0.0026
807	806.71	0.056
885	891.13	0.4288
1003	1014.9	0.0706
1019	1039.62	0.0076
1061	1069.31	0.016
1121	1119.04	0.0146
1179	1185.53	0.0077
1287	1267.54	0.1462
1314	1325.44	0.0545
1348	1345.19	0.0941
1374	1368.34	0.0778
1456	1410.74	0.094
1522	1517.55	0.3368
1605	1608.04	0.1508
2866	2859.52	1.0471
2964	2926.58	0.0055

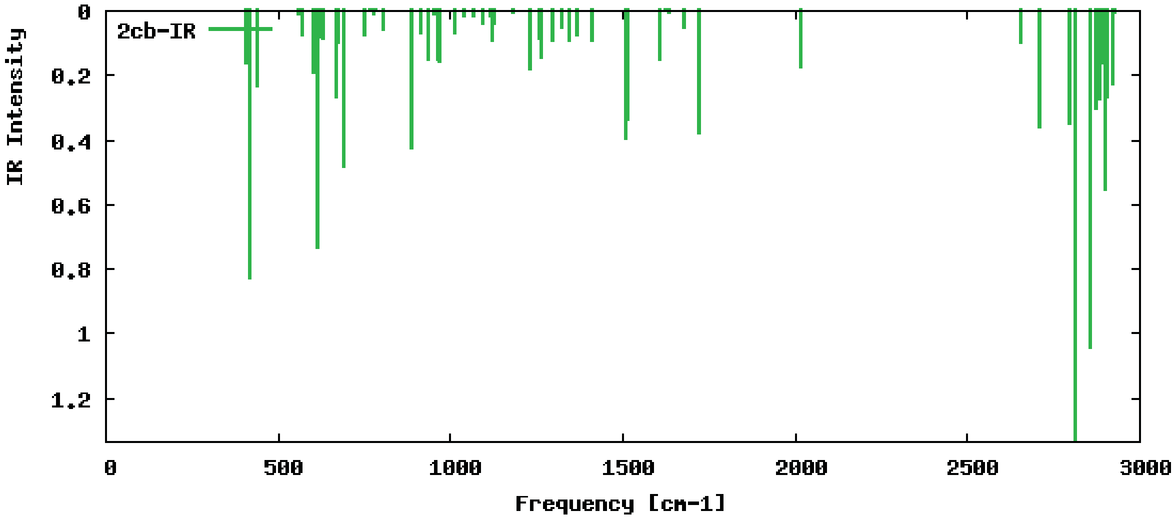

Fig 3.10 IR spectra plot of 2CB

The dielectric tensor of the molecule is calculated. The diagonalized elements are:

$$\varepsilon_{r(NC)} = \begin{pmatrix} 1.774645132 \\ 1.322363457 \\ 1.541202401 \end{pmatrix}, \ \varepsilon_{r(PAW)} = \begin{pmatrix} 1.659667675 \\ 1.358449148 \\ 1.390910634 \end{pmatrix}$$

Average value of dielectric constant comes out to be 1.55(NC) and 1.47(PAW).

And the value of polarizability comes out to be $\propto = \begin{pmatrix} 299.74 \\ 141.72 \\ 223.22 \end{pmatrix}$, $\propto = \begin{pmatrix} 263.27 \\ 155.89 \\ 168.38 \end{pmatrix}$ and the average value of polarizability is 221.56 au^3 (NC) and 195.85 au^3 (PAW).

3.3 4’-propyl-(1, 1’- biphenyl) - 4-carbonitrile (3CB)

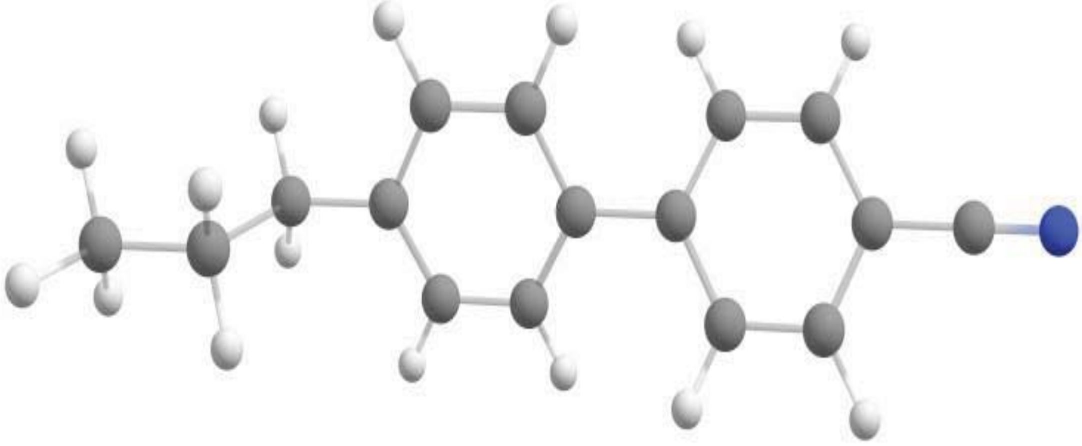

Fig 3.11 (a) Optimised structure of molecule (b) Chemical structure of molecule

The nematic phase of the given molecule is 4’-propyl-(1, 1’- biphenyl) - 4-carbonitrile and it’s a nematogenic liquid crystal and is commonly used as a liquid crystal device.

The calculations are performed using the PAW and norm conserving pseudopotentials. The energy cut-off or ecutwfc is chosen to be 30 Ry. The energy cut-off is chosen in such a way that the value of total energy settles to a stable value as given in Fig 3.12.

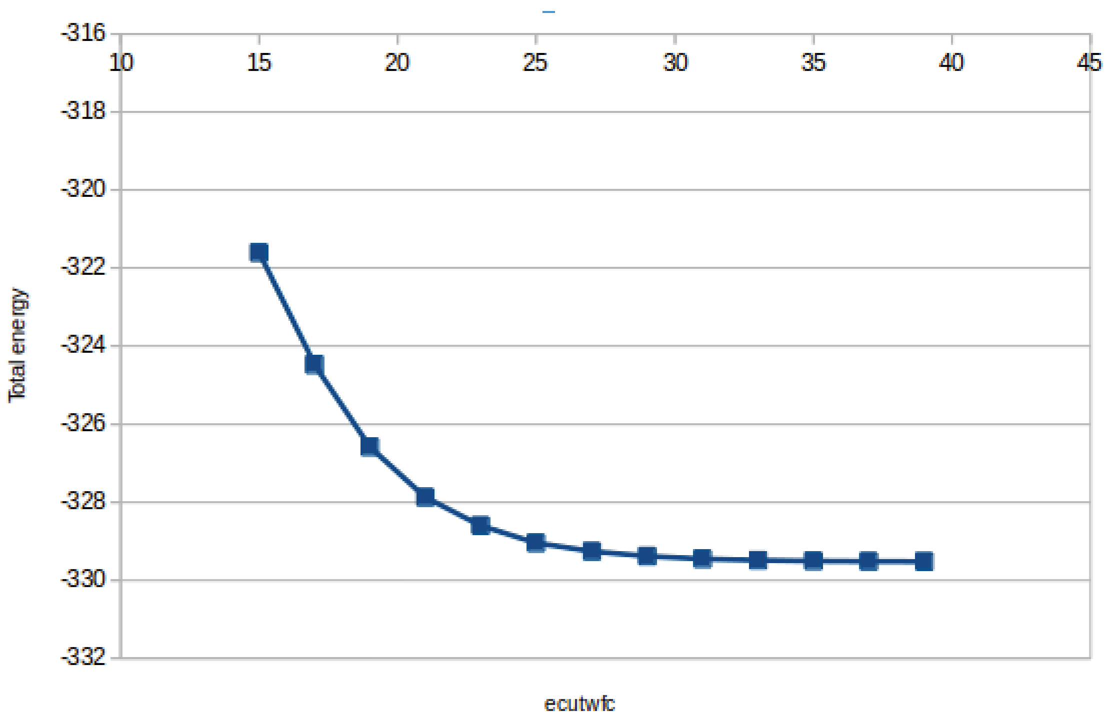

Fig 3.12 Plot of energy cut-off to total energy of the system

The HOMO-LUMO of the molecule is shown in fig 3.13. The energy gap (E_g) 0f HOMO-LUMO is 3.10 eV (NC) & 3.55 eV (PAW). The HOMO of the molecule is largely centred around the phenyl rings involving the carbon atoms, and the nitrogen that exist at the end is occupied. For LUMO, the delocalization of valence orbitals is there throughout the molecule.

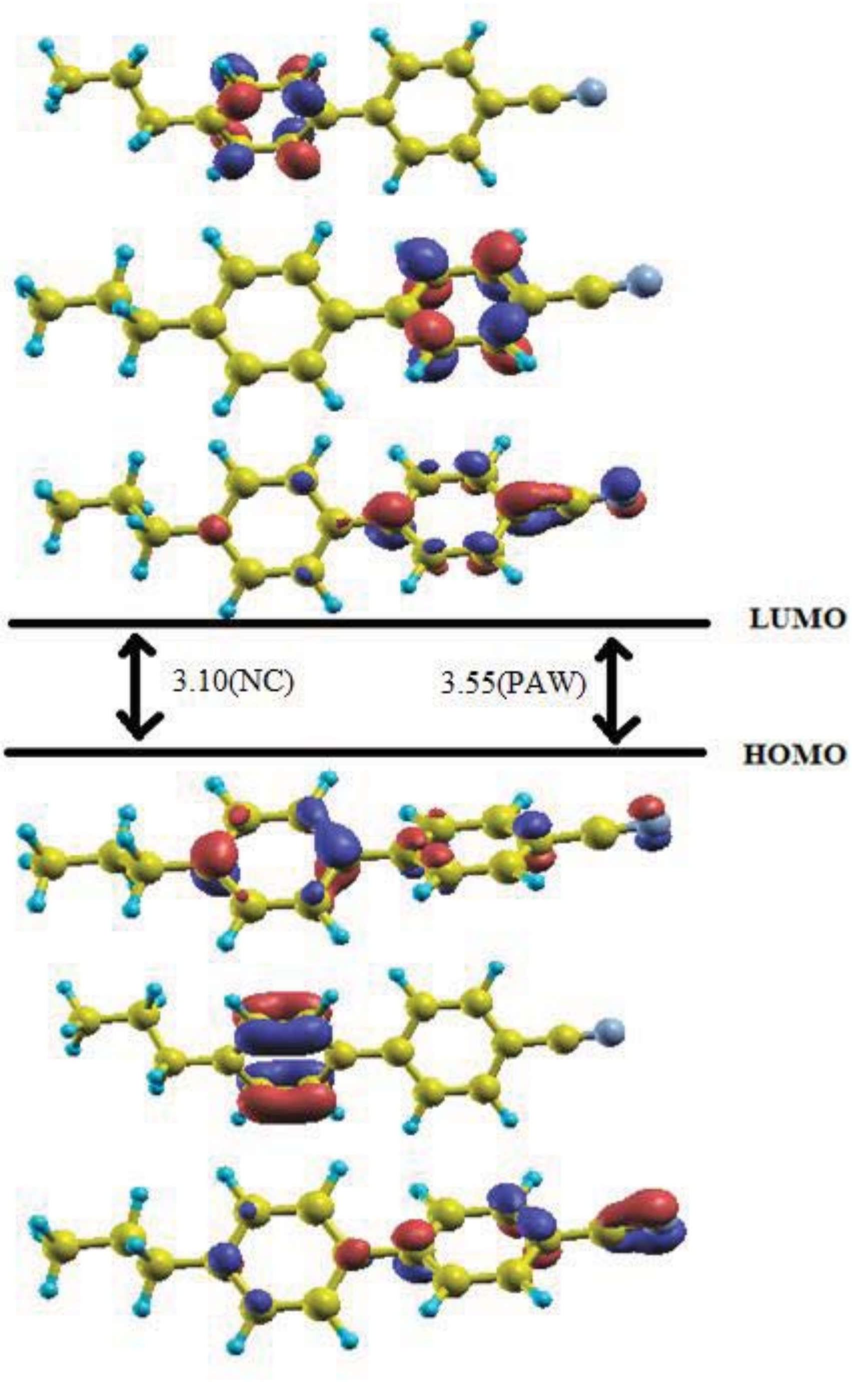

Fig 3.13 Molecular orbital plot for 3CB

Bond length have been calculated (in Angstrom) and optimised for 3CB molecules for both PAW and norm conserving pseudopotentials given in table 3.5 and positioning of atoms is given in fig 3.14.

Table 3.5 Bond length of optimised geometry of 3CB molecule

POSITION OF ATOMS	TYPE OF BOND	BOND LENGTH (PAW)	POSITION OF ATOMS	TYPE OF BOND	BOND LENGTH (NC)
16 20	C-H	1.13133	14 19	C-H	1.15316
14 19	C-H	1.13196	16 20	C-H	1.15322
13 17	C-H	1.13347	12 15	C-H	1.15427
4 9	C-H	1.13376	2 8	C-H	1.15446
5 10	C-H	1.13433	5 10	C-H	1.15454
12 15	C-H	1.13518	13 17	C-H	1.15456
2 8	C-H	1.13571	1 7	C-H	1.15496
1 7	C-H	1.13709	4 9	C-H	1.15516
29 31	C-H	1.14194	29 31	C-H	1.16128
29 30	C-H	1.14538	29 30	C-H	1.16289
29 32	C-H	1.14719	29 32	C-H	1.16476
23 25	C-H	1.14935	23 25	C-H	1.16928
26 27	C-H	1.15107	26 27	C-H	1.16968
26 28	C-H	1.15632	26 28	C-H	1.17937
23 24	C-H	1.15923	23 24	C-H	1.18267
21 22	C-N	1.21584	21 22	C-N	1.27391
12 14	C-C	1.42116	4 5	C-C	1.45422
4 5	C-C	1.42359	12 14	C-C	1.45498
13 16	C-C	1.42364	13 16	C-C	1.45729
1 2	C-C	1.42458	1 2	C-C	1.45748
2 3	C-C	1.43313	1 6	C-C	1.46331
5 6	C-C	1.43359	2 3	C-C	1.46611
1 6	C-C	1.43426	5 6	C-C	1.46634
16 18	C-C	1.43438	3 4	C-C	1.46866
3 4	C-C	1.43478	11 13	C-C	1.4694
14 18	C-C	1.43683	11 12	C-C	1.47019
11 13	C-C	1.43778	16 18	C-C	1.47024
11 12	C-C	1.43855	14 18	C-C	1.47077
18 21	C-C	1.45001	18 21	C-C	1.48599
3 11	C-C	1.4842	3 11	C-C	1.51888
6 23	C-C	1.51014	6 23	C-C	1.54393
26 29	C-C	1.52336	26 29	C-C	1.55929
23 26	C-C	1.52918	23 26	C-C	1.56492
24 25	H-H	1.84035	27 28	H-H	1.8698
27 28	H-H	1.84071	24 25	H-H	1.87226
31 32	H-H	1.84119	31 32	H-H	1.87362
30 31	H-H	1.84456	30 32	H-H	1.87495
30 32	H-H	1.84685	30 31	H-H	1.87962
6 25	C-H	2.17568	6 25	C-H	2.22185
25 26	H-C	2.18366	6 24	C-H	2.23449
24 26	H-C	2.18555	23 27	C-H	2.23994
6 24	C-H	2.19447	24 26	H-C	2.2411
23 28	C-H	2.19656	23 28	C-H	2.24823

27 29	H-C	2.1968	27 29	H-C	2.25063
26 32	C-H	2.20832	25 26	H-C	2.25425
23 27	C-H	2.21013	26 30	C-H	2.25582
28 29	H-C	2.21086	6 7	C-H	2.25611
4 10	C-H	2.21235	26 32	C-H	2.2592
10 27	H-H	2.21385	28 29	H-C	2.25987
3 9	C-H	2.21432	4 10	C-H	2.26045
16 17	C-H	2.21601	26 31	C-H	2.26283
18 20	C-H	2.21682	11 15	C-H	2.26495
3 8	C-H	2.21699	14 15	C-H	2.26556
6 7	C-H	2.21845	3 9	C-H	2.26732
26 31	C-H	2.22011	16 17	C-H	2.26774
14 15	C-H	2.22052	5 9	C-H	2.26805
18 19	C-H	2.22073	6 10	C-H	2.26809
26 30	C-H	2.22093	1 8	C-H	2.26907
11 15	C-H	2.22186	2 7	C-H	2.26946
2 7	C-H	2.22272	18 20	C-H	2.26962
6 10	C-H	2.22376	11 17	C-H	2.26974
1 8	C-H	2.22492	3 8	C-H	2.26985
5 9	C-H	2.22513	18 19	C-H	2.27144
11 17	C-H	2.22659	13 20	C-H	2.2765
12 19	C-H	2.23118	12 19	C-H	2.27803
13 20	C-H	2.23306	10 27	H-H	2.34458
9 15	H-H	2.23616	7 25	H-H	2.3967
8 17	H-H	2.33625	9 15	H-H	2.4604
7 25	H-H	2.3704	1 5	C-C	2.51392
25 32	H-H	2.43816	12 18	C-C	2.52461
1 5	C-C	2.45585	2 4	C-C	2.5253
2 4	C-C	2.46095	8 17	H-H	2.52674
12 18	C-C	2.46742	13 18	C-C	2.5318
13 18	C-C	2.4688	12 13	C-C	2.53299
12 13	C-C	2.4774	1 3	C-C	2.53485
1 3	C-C	2.48396	3 5	C-C	2.53863
3 5	C-C	2.4859	4 6	C-C	2.54136
14 21	C-C	2.48634	11 16	C-C	2.54181
11 16	C-C	2.4875	2 6	C-C	2.54566
11 14	C-C	2.48785	11 14	C-C	2.54704
4 6	C-C	2.48863	14 21	C-C	2.54871
2 6	C-C	2.49107	14 16	C-C	2.55066
14 16	C-C	2.49274	24 30	H-H	2.55589
16 21	C-C	2.50503	16 21	C-C	2.56765
23 29	C-C	2.52296	3 12	C-C	2.58483
28 31	H-H	2.5248	4 11	C-C	2.58848
3 12	C-C	2.5308	27 31	H-H	2.58897
4 11	C-C	2.53279	23 29	C-C	2.59052
27 30	H-H	2.53757	2 11	C-C	2.60037
2 11	C-C	2.54438	6 26	C-C	2.60347
3 13	C-C	2.54454	3 13	C-C	2.60465

9 10	H-H	2.55472	9 10	H-H	2.60843
5 23	C-C	2.5559	28 32	H-H	2.61431
24 27	H-H	2.5563	5 23	C-C	2.6148
7 8	H-H	2.56523	7 8	H-H	2.61836
25 28	H-H	2.56788	24 27	H-H	2.61985
6 26	C-C	2.56874	1 23	C-C	2.62046
1 23	C-C	2.5714	17 20	H-H	2.62898
17 20	H-H	2.57544	15 19	H-H	2.63245
15 19	H-H	2.58222	25 28	H-H	2.63422
27 31	H-H	2.61395	28 31	H-H	2.65507
24 30	H-H	2.62586	27 30	H-H	2.66978
28 32	H-H	2.63619	1 25	C-H	2.69061
1 25	C-H	2.64547	25 32	H-H	2.69582
18 22	C-N	2.66335	18 22	C-N	2.75873
19 21	H-C	2.70449	19 21	H-C	2.77647
25 29	H-C	2.72663	3 15	C-H	2.79707
9 12	H-C	2.72744	20 21	H-C	2.8043
20 21	H-C	2.73411	9 11	H-C	2.80859
4 15	C-H	2.73708	24 29	H-C	2.81785
23 32	C-H	2.73853	7 23	H-C	2.83188
9 11	H-C	2.74358	10 23	H-C	2.83673
3 15	C-H	2.74445	23 30	C-H	2.83718
24 29	H-C	2.75471	8 11	H-C	2.83734
8 11	H-C	2.76863	3 17	C-H	2.83789
10 23	H-C	2.77709	6 27	C-H	2.84289
3 17	C-H	2.77756	25 29	H-C	2.85592
7 23	H-C	2.78997	4 15	C-H	2.8593
6 28	C-H	2.80803	5 27	C-H	2.86171
2 17	C-H	2.80994	9 12	H-C	2.86344
8 13	H-C	2.81405	6 28	C-H	2.86924
5 27	C-H	2.82697	1 4	C-C	2.90627
1 4	C-C	2.83974	10 24	H-H	2.91201
2 5	C-C	2.84237	2 5	C-C	2.91358
12 16	C-C	2.86215	23 32	C-H	2.92004
6 27	C-H	2.86294	12 16	C-C	2.92407
13 14	C-C	2.86454	11 18	C-C	2.93363
11 18	C-C	2.86523	13 14	C-C	2.93462
10 26	H-C	2.87518	2 17	C-H	2.93687
23 30	C-H	2.88209	8 13	H-C	2.93931
3 6	C-C	2.90084	3 6	C-C	2.9556
5 24	C-H	2.98015	5 24	C-H	2.96087
10 24	H-H	2.99041	14 19	C-H	1.15316

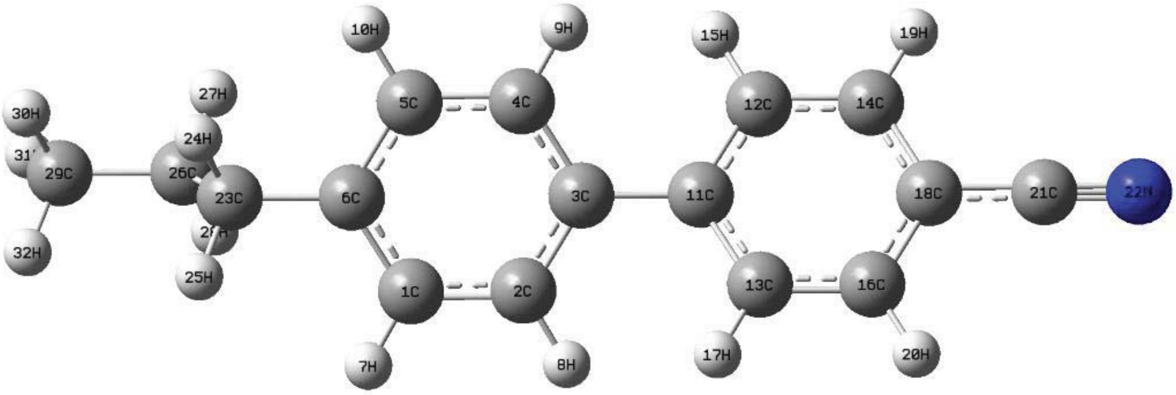

Fig 3.14 Structure of 3CB with positioning of atoms

The IR peak intensities are given in table 3.6 and the spectra plot of the given molecule is given in fig 3.15.

Table 3.6 IR spectra of 3CB

Experimental frequencies(cm^{-1})[3]	Calculated frequency	IR intensity
411	424.94	0.0436
474	473.22	0.1344
527	558.23	0.065
551	576.68	0.0555
637	630.64	0.5187
650	647.5	0.6549
776	776.88	0.0319
807	809.26	0.0271
885	865.02	0.0737
1003	986.45	0.2308
1019	1015.33	0.0566
1061	1051.17	0.05
1121	1121.14	0.024
1179	1155.44	0.0204
1187	1190.58	0.0034
1314	1324.31	0.137
1348	1349.75	0.097
1374	1390.53	0.0277
1456	1460.47	0.1144
1522	1529.69	0.4214
1605	1613.82	0.2562
2866	2878.77	1.1478
2964	2915.71	0.2617

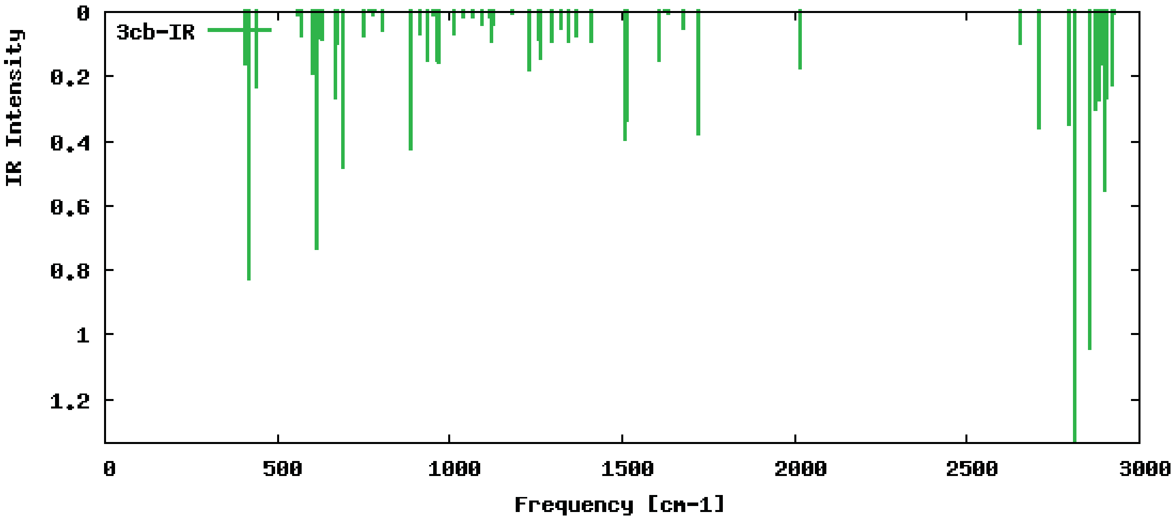

Fig 3.15IR spectra of 3CB

The dielectric tensor of the molecule is also calculated and is given as

$$\varepsilon_{r(NC)} = \begin{pmatrix} 1.631541829 \\ 1.287090128 \\ 1.272987638 \end{pmatrix}, \varepsilon_{r(PAW)} = \begin{pmatrix} 1.561010322 \\ 1.261360929 \\ 1.272987638 \end{pmatrix}$$

Average value of dielectric constant comes out to be 1.4(NC) and 1.36(PAW).

And the value of polarizability comes out to be $\propto = \begin{pmatrix} 370.43 \\ 186.04 \\ 177.66 \end{pmatrix}$, $\propto = \begin{pmatrix} 335.58 \\ 170.70 \\ 164.55 \end{pmatrix}$ and the average value of polarizability is 244.71 au^3 (NC) and 223.61 au^3 (PAW).

3.4 4’-butyl-(1,1’- biphenyl)- 4-carbonitrile (4CB)

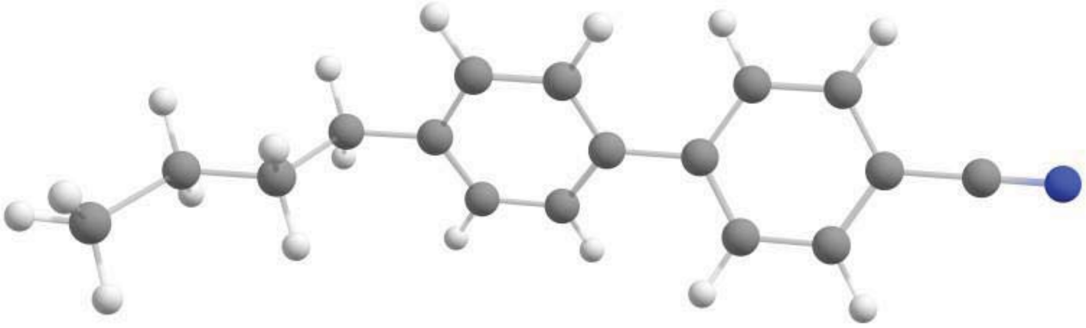

Fig 3.16 Optimised structure of 4CB molecule

The nematic phase of the given molecule is 4'-Butyl-(1,1'- biphenyl)- 4-carbonitrile and it's a nematogenic liquid crystal and is commonly used as a liquid crystal device.

The calculations are performed using the PAW pseudopotentials. The energy cut-off or ecutwfc is chosen to be 30 Ry. The energy cut-off is chosen in such a way that the value of total energy settles to a stable value as given in Fig 3.17.

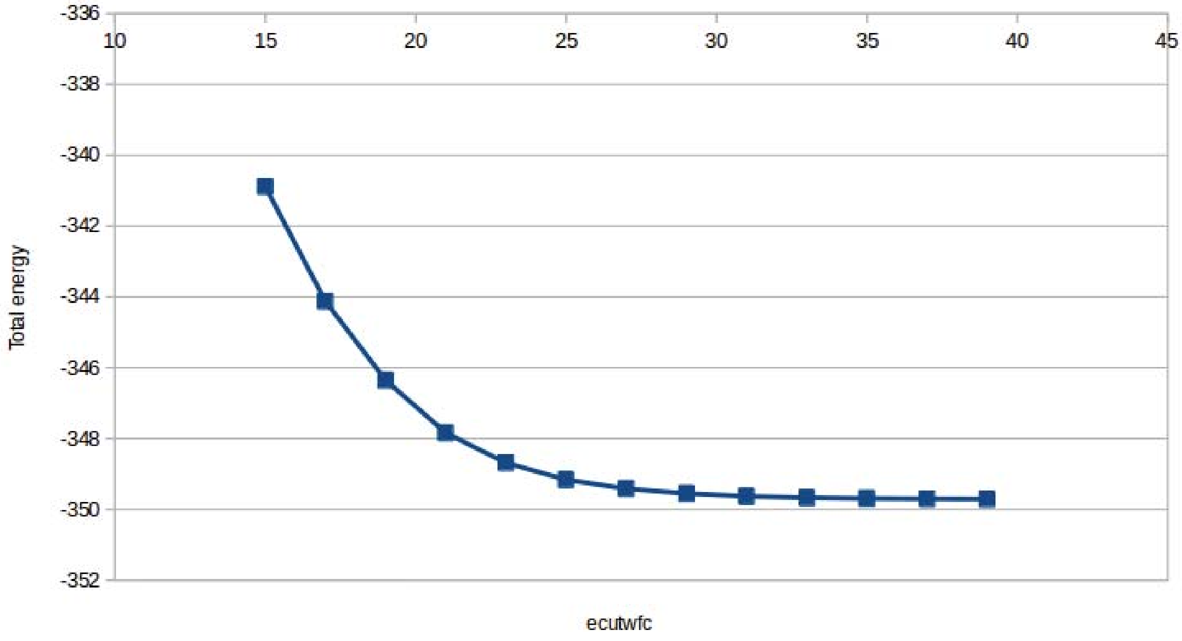

Fig 3.17 Plot of energy cut-off to total energy of the system

The HOMO-LUMO of the molecule is shown in fig 3.24. The energy gap (E_g) 0f HOMO-LUMO is 3.20 eV (NC) & 3.24 eV (PAW).The HOMO of the molecule is largely centred around the phenyl rings involving the carbon atoms, and the nitrogen that exist at the end is occupied. For LUMO, the delocalization of valence orbitals is there throughout the molecule.

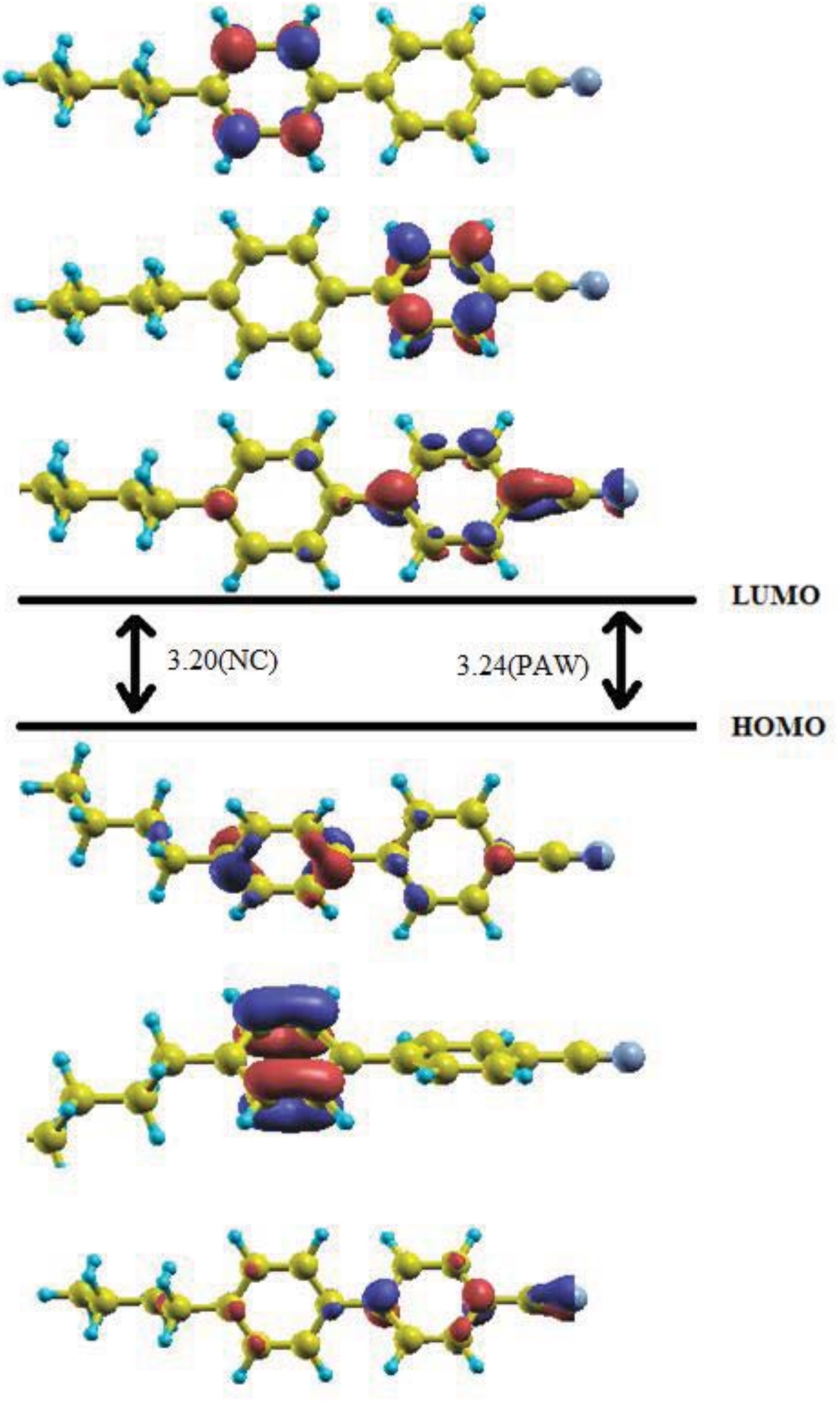

Fig 3.18 Molecular orbital plot for 4CB

Bond length have been calculated (in Angstrom) and optimised for 4CB molecules for both PAW and norm conserving pseudopotentials given in table 3.7 and positioning of atoms is given in fig 3.19.

Table 3.7 Bond length of optimised geometry of 4CB molecule

POSITION OF ATOMS	**TYPE OF BOND**	**BOND LENGTH (PAW)**	**POSITION OF ATOMS**	**TYPE OF BOND**	**BOND LENGTH (NC)**
14 19	C-H	1.13244	14 19	C-H	1.1516
16 20	C-H	1.13322	16 20	C-H	1.15268
13 17	C-H	1.13387	13 17	C-H	1.1543
12 15	C-H	1.13473	1 7	C-H	1.1551
1 7	C-H	1.13521	4 9	C-H	1.15534
4 9	C-H	1.13523	12 15	C-H	1.15579
5 10	C-H	1.1354	5 10	C-H	1.15618
2 8	C-H	1.13651	2 8	C-H	1.15653
32 34	C-H	1.14312	32 34	C-H	1.16443
32 35	C-H	1.14542	32 33	C-H	1.16621
32 33	C-H	1.14549	23 24	C-H	1.16845
23 24	C-H	1.14702	32 35	C-H	1.17058
29 30	C-H	1.14983	29 30	C-H	1.17129
23 25	C-H	1.1503	26 28	C-H	1.17319
26 28	C-H	1.15158	23 25	C-H	1.1769
29 31	C-H	1.15225	29 31	C-H	1.18308
26 27	C-H	1.15285	26 27	C-H	1.18327
21 22	C-N	1.21669	21 22	C-N	1.27424
12 14	C-C	1.42471	1 2	C-C	1.4567
1 2	C-C	1.42749	12 14	C-C	1.45761
13 16	C-C	1.42798	13 16	C-C	1.45765
4 5	C-C	1.42945	4 5	C-C	1.46587
5 6	C-C	1.43315	5 6	C-C	1.46763
3 4	C-C	1.43459	2 3	C-C	1.46792
2 3	C-C	1.43544	1 6	C-C	1.46952
1 6	C-C	1.43593	3 4	C-C	1.47002
11 12	C-C	1.43713	11 12	C-C	1.47039
16 18	C-C	1.43768	11 13	C-C	1.47144
14 18	C-C	1.43807	16 18	C-C	1.47259
11 13	C-C	1.43881	14 18	C-C	1.47338
18 21	C-C	1.45216	18 21	C-C	1.48461
3 11	C-C	1.49004	3 11	C-C	1.52405
6 23	C-C	1.51003	6 23	C-C	1.54363
29 32	C-C	1.52014	29 32	C-C	1.55464
26 29	C-C	1.52473	26 29	C-C	1.55772
23 26	C-C	1.5284	23 26	C-C	1.56517
30 31	H-H	1.83492	30 31	H-H	1.87605
24 25	H-H	1.83806	33 35	H-H	1.88162

27 28	H-H	1.84222	27 28	H-H	1.88209
34 35	H-H	1.8496	34 35	H-H	1.8847
33 35	H-H	1.85288	24 25	H-H	1.88682
33 34	H-H	1.85574	33 34	H-H	1.8909
25 26	H-C	2.16969	6 25	C-H	2.20736
6 25	C-H	2.17597	25 26	H-C	2.21737
6 24	C-H	2.18829	26 31	C-H	2.23379
24 26	H-C	2.18853	30 32	H-C	2.23382
26 31	C-H	2.18879	26 30	C-H	2.23809
30 32	H-C	2.19055	29 35	C-H	2.24202
28 29	H-C	2.19505	23 28	C-H	2.24261
27 29	H-C	2.19557	28 29	H-C	2.25089
31 32	H-C	2.19586	6 24	C-H	2.25236
23 28	C-H	2.19875	27 29	H-C	2.25585
29 34	C-H	2.20247	29 34	C-H	2.25707
29 35	C-H	2.2044	24 26	H-C	2.25776
23 27	C-H	2.20617	31 32	H-C	2.25783
29 33	C-H	2.20681	2 7	C-H	2.26092
26 30	C-H	2.207	4 10	C-H	2.26361
16 17	C-H	2.21519	23 27	C-H	2.26418
2 7	C-H	2.21754	16 17	C-H	2.26459
14 15	C-H	2.21765	29 33	C-H	2.26597
4 10	C-H	2.21881	14 15	C-H	2.26652
6 7	C-H	2.22265	1 8	C-H	2.26975
3 9	C-H	2.22369	3 8	C-H	2.27183
1 8	C-H	2.22409	5 9	C-H	2.27223
11 15	C-H	2.22422	12 19	C-H	2.27298
5 9	C-H	2.22512	11 17	C-H	2.27328
6 10	C-H	2.22661	18 19	C-H	2.27528
18 19	C-H	2.22786	6 7	C-H	2.27546
18 20	C-H	2.22912	13 20	C-H	2.27577
12 19	C-H	2.22923	11 15	C-H	2.27586
3 8	C-H	2.23105	18 20	C-H	2.27822
13 20	C-H	2.23209	6 10	C-H	2.28089
11 17	C-H	2.23252	3 9	C-H	2.28315
25 31	H-H	2.38815	25 31	H-H	2.40187
1 5	C-C	2.45974	7 25	H-H	2.418
2 4	C-C	2.46992	8 15	H-H	2.52477
12 18	C-C	2.47165	13 18	C-C	2.52717
13 18	C-C	2.47413	1 5	C-C	2.52767
12 13	C-C	2.47661	12 18	C-C	2.53275
10 24	H-H	2.47793	24 27	H-H	2.53553
1 3	C-C	2.48107	2 4	C-C	2.53677
30 34	H-H	2.48394	1 3	C-C	2.53701
14 21	C-C	2.4861	30 34	H-H	2.53983
3 5	C-C	2.48864	11 14	C-C	2.54069
4 6	C-C	2.49017	3 5	C-C	2.54112
11 14	C-C	2.49074	12 13	C-C	2.54112

11 16	C-C	2.49283	2 6	C-C	2.54403
14 16	C-C	2.49547	11 16	C-C	2.54646
2 6	C-C	2.49733	4 6	C-C	2.55069
16 21	C-C	2.51302	27 35	H-H	2.55118
24 27	H-H	2.519	14 21	C-C	2.55502
31 33	H-H	2.52479	14 16	C-C	2.55839
3 12	C-C	2.52683	2 11	C-C	2.55927
26 32	C-C	2.52979	22 30	N-H	2.56021
23 29	C-C	2.53573	16 21	C-C	2.56044
4 11	C-C	2.53891	23 29	C-C	2.57619
2 11	C-C	2.54229	1 23	C-C	2.58243
27 35	H-H	2.5441	6 26	C-C	2.58597
22 34	N-H	2.5479	3 13	C-C	2.58865
1 23	C-C	2.55127	28 31	H-H	2.58995
7 8	H-H	2.55132	9 10	H-H	2.59762
9 10	H-H	2.55217	26 32	C-C	2.60229
3 13	C-C	2.55837	3 12	C-C	2.6027
6 26	C-C	2.55917	7 8	H-H	2.6058
27 30	H-H	2.56009	31 33	H-H	2.61266
17 20	H-H	2.56299	15 19	H-H	2.62132
15 19	H-H	2.56808	17 20	H-H	2.62293
5 23	C-C	2.57415	4 11	C-C	2.63061
28 31	H-H	2.57775	25 29	H-C	2.64658
31 34	H-H	2.58997	5 23	C-C	2.648
25 28	H-H	2.59256	22 34	N-H	2.65368
7 25	H-H	2.59676	30 35	H-H	2.65502
28 33	H-H	2.60559	27 30	H-H	2.66127
30 35	H-H	2.61528	1 25	C-H	2.66818
24 30	H-H	2.62892	31 34	H-H	2.67277
18 22	C-N	2.6675	6 28	C-H	2.6819
8 15	H-H	2.66828	25 28	H-H	2.7179
25 29	H-C	2.68468	10 24	H-H	2.72395
9 15	H-H	2.68473	24 30	H-H	2.73817
7 28	H-H	2.69346	18 22	C-N	2.75871
5 24	C-H	2.70151	8 17	H-H	2.76115
19 21	H-C	2.71232	8 11	H-C	2.76369
3 15	C-H	2.73991	23 30	C-H	2.78529
1 25	C-H	2.74488	19 21	H-C	2.78946
23 31	C-H	2.74771	7 23	H-C	2.78982
28 32	H-C	2.75247	28 33	H-H	2.78994
6 28	C-H	2.75731	20 21	H-C	2.80407
20 21	H-C	2.76041	3 17	C-H	2.81297
7 23	H-C	2.76259	26 35	C-H	2.82533
26 35	C-H	2.76313	23 31	C-H	2.83299
9 11	H-C	2.76367	3 15	C-H	2.83828
8 11	H-C	2.77771	27 32	H-C	2.83996
22 30	N-H	2.77784	25 30	H-H	2.84287
27 32	H-C	2.80356	5 24	C-H	2.87818

3 17	C-H	2.80393	9 11	H-C	2.89753
10 23	H-C	2.81176	10 23	H-C	2.91064
23 30	C-H	2.82122	28 32	H-C	2.91108
24 29	H-C	2.82935	2 5	C-C	2.9214
1 4	C-C	2.8426	1 4	C-C	2.9256
8 17	H-H	2.84471	11 18	C-C	2.92859
2 5	C-C	2.85492	9 15	H-H	2.92992
12 16	C-C	2.86516	13 14	C-C	2.93262
26 33	C-H	2.86648	12 16	C-C	2.94127
13 14	C-C	2.86702	8 13	H-C	2.94309
11 18	C-C	2.87077	3 6	C-C	2.95012
3 6	C-C	2.89706	26 33	C-H	2.96327
6 27	C-H	2.89816	8 9	H-H	2.99031
4 15	C-H	2.92861	24 29	H-C	2.99536
15 17	H-H	2.9585	14 19	C-H	1.1516
9 12	H-C	2.97516	16 20	C-H	1.15268
1 28	C-H	2.98765	13 17	C-H	1.1543

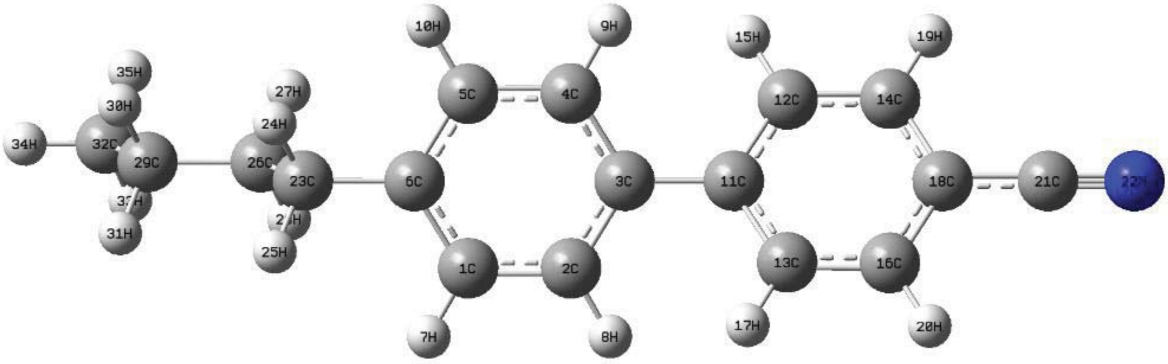

Fig 3.19 Structure of 4CB with positioning of atoms

The IR peak intensities are given in table 3.8 and the spectra plot of the given molecule is given in fig 3.20.

Table 3.8 IR spectra of 4CB

Experimental frequencies(cm^{-1})[4]	**Calculated frequency**	**IR intensity**
402	407.73	0.0154
429	432.2	0.0044
455	460.88	0.0896
519	506.68	0.3045

528	528.01	0.033
541	542.28	0.0261
553	562.56	0.1723
567	580.01	0.0136
636	636.29	0.038
657	652.48	0.1054
749	754.8	0.1903
827	828.46	0.0383
841	847.63	0.097
856	861.57	1.1702
882	894.89	0.2343
928	923.32	0.3368
970	973.31	0.0254
998	996.61	0.0931
1005	1000.53	0.0976
1027	1029.74	0.0479
1067	1064.79	0.0072
1182	1162.04	0.2873
1186	1190.32	0.0357
1207	1207.31	0.2061
1246	1224.45	0.439
1270	1265.64	0.1113
1342	1325.79	0.0164
1381	1389.92	0.1201
1427	1421.87	0.1388
1446	1443.88	0.0152
1521	1532.55	1.0343
1608	1600.23	0.4873
2224	2255	0.5528
3037	3054.05	0.0214
3051	3055.37	0.6455
3066	3062.81	0.7177
3085	3071.29	1.6188

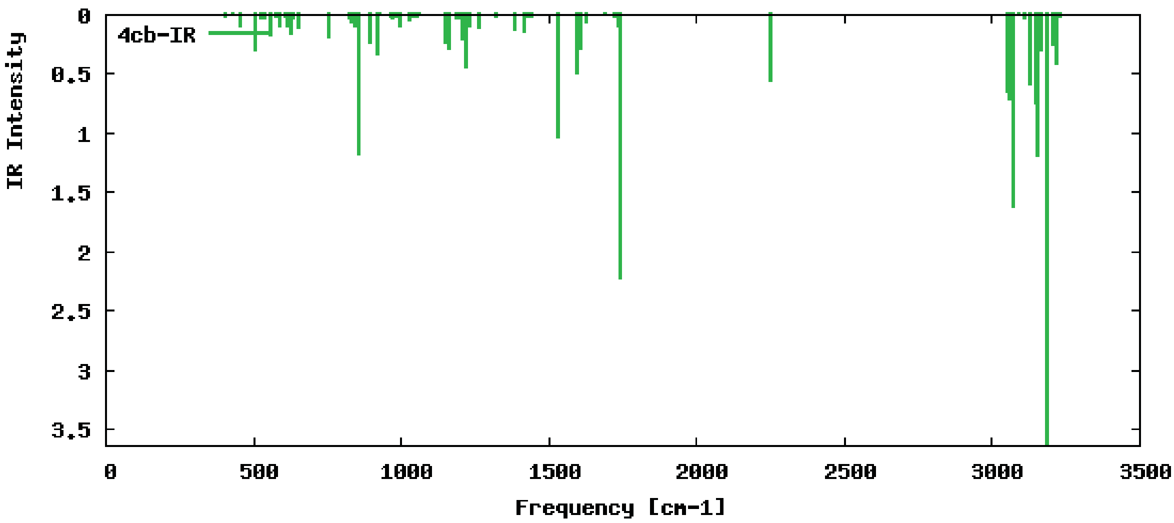

Fig 3.20 IR spectra of 4CB liquid crystal

The dielectric tensor of the molecule is calculated. The diagonalized elements are:

$$\varepsilon_{r(NC)} = \begin{pmatrix} 2.184657918 \\ 1.688872132 \\ 1.435866804 \end{pmatrix}, \varepsilon_{r(PAW)} = \begin{pmatrix} 2.041920365 \\ 1.611658858 \\ 1.395207403 \end{pmatrix}$$

Average value of dielectric constant comes out to be 1.77(NC) and 1.68(PAW).

And the value of polarizability comes out to be $\propto = \begin{pmatrix} 337.65 \\ 249.12 \\ 169.23 \end{pmatrix}$, $\propto = \begin{pmatrix} 343.88 \\ 225.92 \\ 155.28 \end{pmatrix}$ and the average value of polarizability is 252 au^3 (NC) and 241.69 au^3 (PAW).

3.5 4’-pentyl-(1, 1’- biphenyl) - 4-carbonitrile (5CB)

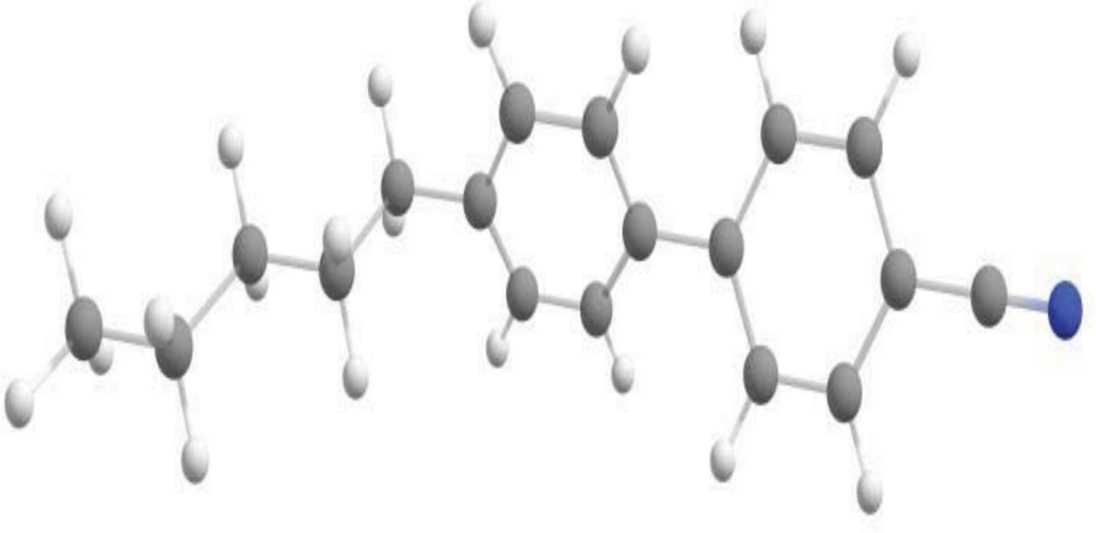

Fig 3.21 Optimised structure of 5CB molecule

The nematic phase of the given molecule is 4’-pentyl-(1, 1’- biphenyl) - 4-carbonitrile. It is a nematogenic liquid crystal and is commonly used as a liquid crystal device.

The calculations are performed using the PAW and norm conserving pseudopotentials. The energy cut-off or ecutwfc is chosen to be 30 Ry. The energy cut-off is chosen in such a way that the value of total energy settles to a stable value as given in Fig 3.22.

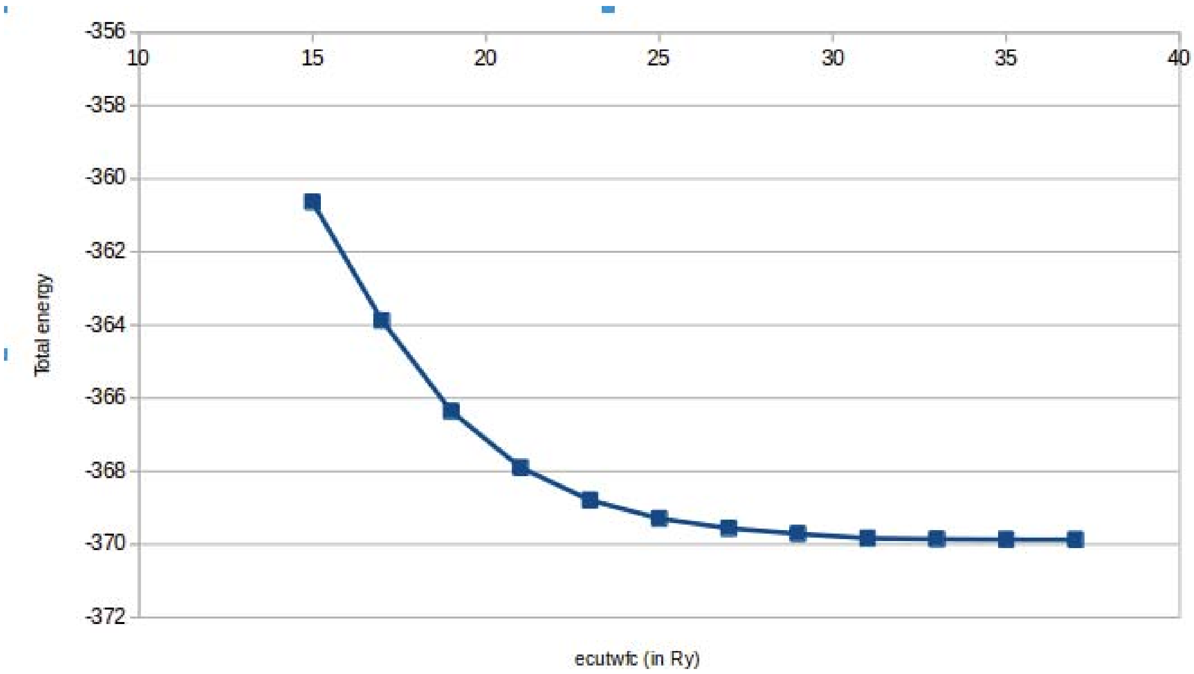

Fig 3.22 Plot of energy cut-off to total energy of the system

The HOMO-LUMO of the molecule is shown in fig 3.23. The energy gap (E_g) 0f HOMO-LUMO is 2.98 eV (NC) & 3.05 eV (PAW).The HOMO of the molecule is largely centered around the phenyl rings involving the carbon atoms, and the nitrogen that exist at the end is occupied. For LUMO the delocalization of valence orbitals is there throughout the molecule.

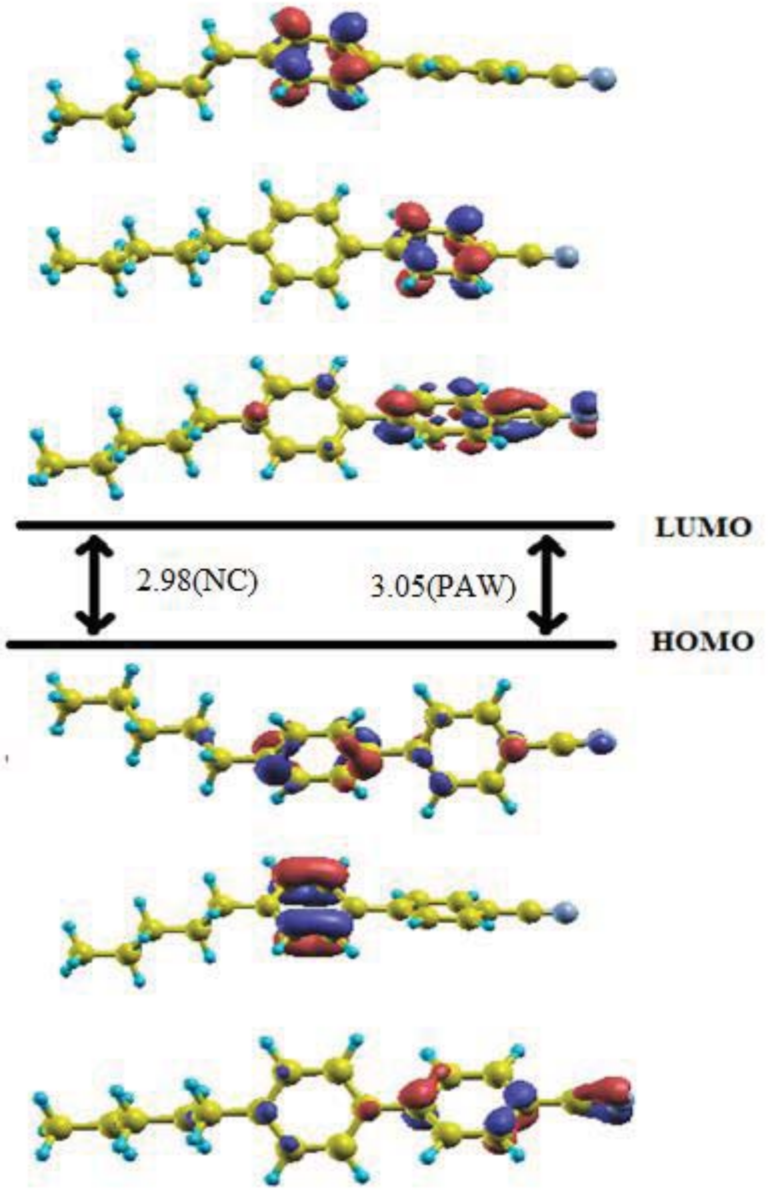

Fig 3.23 Molecular orbital plot for 5CB

Bond length have been calculated (in Angstrom) and optimised for 5CB molecules for both PAW and norm conserving pseudopotentials given in table 3.9 and positioning of atoms is given in fig 3.23.

Table 3.9 Bond length of optimised geometry of 5CB molecule

POSITION OF ATOMS	TYPE OF BOND	BOND LENGTH (PAW)	POSITION OF ATOMS	TYPE OF BOND	BOND LENGTH (NC)
16 20	C-H	1.13206	16 20	C-H	1.15251
14 19	C-H	1.13213	14 19	C-H	1.15257
12 15	C-H	1.13414	12 15	C-H	1.15383
13 17	C-H	1.13421	13 17	C-H	1.15387
4 9	C-H	1.13494	4 9	C-H	1.15565
2 8	C-H	1.135	2 8	C-H	1.15567
5 10	C-H	1.13546	1 7	C-H	1.15593
1 7	C-H	1.1355	5 10	C-H	1.15606
35 37	C-H	1.14314	35 37	C-H	1.1635
35 36	C-H	1.145	35 36	C-H	1.16555
35 38	C-H	1.14524	35 38	C-H	1.1657
23 24	C-H	1.14847	23 24	C-H	1.16932
23 25	C-H	1.14887	23 25	C-H	1.16968
32 33	C-H	1.14986	32 33	C-H	1.17074
32 34	C-H	1.1502	32 34	C-H	1.17111
26 28	C-H	1.15076	26 28	C-H	1.17185
26 27	C-H	1.15081	26 27	C-H	1.17195
29 30	C-H	1.15104	29 30	C-H	1.17249
29 31	C-H	1.15145	29 31	C-H	1.17288
21 22	C-N	1.21712	21 22	C-N	1.27655
13 16	C-C	1.42309	13 16	C-C	1.4545
12 14	C-C	1.42311	12 14	C-C	1.45557
4 5	C-C	1.42531	4 5	C-C	1.45847
1 2	C-C	1.4254	1 2	C-C	1.45863
5 6	C-C	1.43278	5 6	C-C	1.46715
1 6	C-C	1.43325	1 6	C-C	1.46755
3 4	C-C	1.43574	3 4	C-C	1.46908
2 3	C-C	1.43584	2 3	C-C	1.46956
14 18	C-C	1.43606	11 13	C-C	1.47095
16 18	C-C	1.43612	14 18	C-C	1.4711
11 13	C-C	1.43805	16 18	C-C	1.47112
11 12	C-C	1.43829	11 12	C-C	1.4715
18 21	C-C	1.45103	18 21	C-C	1.48481
3 11	C-C	1.48448	3 11	C-C	1.51854
6 23	C-C	1.5054	6 23	C-C	1.5432
26 29	C-C	1.52013	26 29	C-C	1.55891
32 35	C-C	1.52189	32 35	C-C	1.5601
29 32	C-C	1.52376	29 32	C-C	1.56334
23 26	C-C	1.52975	23 26	C-C	1.56965
30 31	H-H	1.8268	36 38	H-H	1.86128
33 34	H-H	1.82949	33 34	H-H	1.86459
36 38	H-H	1.82966	30 31	H-H	1.86467
27 28	H-H	1.83062	27 28	H-H	1.86685

24 25	H-H	1.8399	24 25	H-H	1.87547
37 38	H-H	1.84821	37 38	H-H	1.88151
36 37	H-H	1.85143	36 37	H-H	1.8852
6 24	C-H	2.17958	6 24	C-H	2.22484
6 25	C-H	2.18136	6 25	C-H	2.22787
29 34	C-H	2.18664	29 34	C-H	2.24027
29 33	C-H	2.18675	31 32	H-C	2.24031
25 26	H-C	2.19212	30 32	H-C	2.24068
24 26	H-C	2.19306	29 33	C-H	2.24111
26 31	C-H	2.19389	23 28	C-H	2.24219
30 32	H-C	2.19433	23 27	C-H	2.24225
31 32	H-C	2.19441	26 31	C-H	2.2463
26 30	C-H	2.19604	26 30	C-H	2.2475
23 28	C-H	2.19625	25 26	H-C	2.24794
23 27	C-H	2.19748	24 26	H-C	2.24876
28 29	H-C	2.20037	28 29	H-C	2.25027
27 29	H-C	2.20098	27 29	H-C	2.25125
33 35	H-C	2.20301	33 35	H-C	2.25385
34 35	H-C	2.20352	34 35	H-C	2.25438
32 38	C-H	2.21172	32 38	C-H	2.25761
32 36	C-H	2.21544	32 36	C-H	2.26028
16 17	C-H	2.2157	16 17	C-H	2.26331
14 15	C-H	2.21625	14 15	C-H	2.26368
6 10	C-H	2.21632	6 10	C-H	2.26473
6 7	C-H	2.21705	6 7	C-H	2.26579
32 37	C-H	2.21873	11 17	C-H	2.26714
5 9	C-H	2.21994	2 7	C-H	2.26781
1 8	C-H	2.22008	4 10	C-H	2.2681
2 7	C-H	2.22117	3 9	C-H	2.26898
4 10	C-H	2.2215	11 15	C-H	2.2691
18 20	C-H	2.22173	18 19	C-H	2.2692
18 19	C-H	2.22178	18 20	C-H	2.2697
3 9	C-H	2.22377	3 8	C-H	2.27027
11 15	C-H	2.22393	1 8	C-H	2.2713
11 17	C-H	2.22414	5 9	C-H	2.27144
3 8	C-H	2.22495	13 20	C-H	2.27493
12 19	C-H	2.22862	32 37	C-H	2.27551
13 20	C-H	2.2289	12 19	C-H	2.27625
8 17	H-H	2.30469	8 17	H-H	2.3281
9 15	H-H	2.31244	9 15	H-H	2.36432
1 5	C-C	2.4549	1 5	C-C	2.51643
2 4	C-C	2.46307	2 4	C-C	2.52602
12 13	C-C	2.47168	13 18	C-C	2.52864
13 18	C-C	2.47171	12 18	C-C	2.52984
12 18	C-C	2.47204	12 13	C-C	2.53119
10 24	H-H	2.48579	10 24	H-H	2.53855
1 3	C-C	2.48718	3 5	C-C	2.54238
3 5	C-C	2.48764	1 3	C-C	2.54259

14 16	C-C	2.4878	11 16	C-C	2.54679
4 6	C-C	2.4902	11 14	C-C	2.54715
2 6	C-C	2.49109	4 6	C-C	2.54827
11 14	C-C	2.49127	2 6	C-C	2.54874
11 16	C-C	2.49147	14 16	C-C	2.54889
16 21	C-C	2.50002	16 21	C-C	2.55674
14 21	C-C	2.50021	14 21	C-C	2.56221
7 25	H-H	2.51442	7 25	H-H	2.57004
25 31	H-H	2.51776	6 26	C-C	2.58158
24 30	H-H	2.52483	29 35	C-C	2.58586
6 26	C-C	2.52495	3 13	C-C	2.59384
23 29	C-C	2.53286	30 36	H-H	2.59559
29 35	C-C	2.53489	2 11	C-C	2.59622
4 11	C-C	2.54047	4 11	C-C	2.598
26 32	C-C	2.54052	3 12	C-C	2.60184
3 13	C-C	2.54068	31 38	H-H	2.60491
3 12	C-C	2.54097	23 29	C-C	2.6058
2 11	C-C	2.5415	26 32	C-C	2.60709
27 34	H-H	2.54332	25 31	H-H	2.61303
28 33	H-H	2.54374	7 8	H-H	2.61563
7 8	H-H	2.55541	9 10	H-H	2.61635
9 10	H-H	2.55597	24 30	H-H	2.61809
5 23	C-C	2.55721	25 28	H-H	2.61815
1 23	C-C	2.55946	5 23	C-C	2.61818
25 28	H-H	2.56262	28 33	H-H	2.61847
24 27	H-H	2.56339	24 27	H-H	2.61949
31 33	H-H	2.56468	30 34	H-H	2.61998
30 34	H-H	2.56592	31 33	H-H	2.62059
34 37	H-H	2.56681	1 23	C-C	2.62112
33 37	H-H	2.56763	27 34	H-H	2.62184
17 20	H-H	2.5682	17 20	H-H	2.62577
15 19	H-H	2.56863	15 19	H-H	2.6265
30 36	H-H	2.57165	34 37	H-H	2.63298
31 38	H-H	2.57487	28 31	H-H	2.63555
28 31	H-H	2.57707	27 30	H-H	2.63767
27 30	H-H	2.58255	33 37	H-H	2.63809
33 38	H-H	2.58782	33 38	H-H	2.64063
34 36	H-H	2.59822	34 36	H-H	2.65421
18 22	C-N	2.66814	18 22	C-N	2.76132
5 24	C-H	2.70993	5 24	C-H	2.76897
1 25	C-H	2.72215	22 36	N-H	2.78125
20 21	H-C	2.72879	1 25	C-H	2.78301
19 21	H-C	2.72916	20 21	H-C	2.78651
3 15	C-H	2.76558	19 21	H-C	2.79446
3 17	C-H	2.76589	3 17	C-H	2.81412
6 28	C-H	2.76874	2 17	C-H	2.81711
9 11	H-C	2.76887	6 27	C-H	2.81961
25 29	H-C	2.77153	6 28	C-H	2.82154

6 27	C-H	2.77169	31 35	H-C	2.8232
8 11	H-C	2.77206	30 35	H-C	2.82365
10 23	H-C	2.77228	8 11	H-C	2.82411
7 23	H-C	2.77544	8 13	H-C	2.82558
24 29	H-C	2.77597	9 11	H-C	2.82599
26 33	C-H	2.77742	3 15	C-H	2.82935
26 34	C-H	2.77759	10 23	H-C	2.83637
30 35	H-C	2.77796	7 23	H-C	2.84077
23 31	C-H	2.77822	4 15	C-H	2.84644
31 35	H-C	2.77938	9 12	H-C	2.84972
23 30	C-H	2.77985	26 33	C-H	2.8538
2 17	C-H	2.78017	26 34	C-H	2.85412
4 15	C-H	2.78047	25 29	H-C	2.86015
8 13	H-C	2.78625	23 31	C-H	2.86028
9 12	H-C	2.78883	29 36	C-H	2.86074
27 32	H-C	2.80268	24 29	H-C	2.86178
28 32	H-C	2.80308	23 30	C-H	2.86295
29 36	C-H	2.82073	29 38	C-H	2.86975
29 38	C-H	2.82243	28 32	H-C	2.87278
1 4	C-C	2.84171	27 32	H-C	2.87571
2 5	C-C	2.84273	1 4	C-C	2.91259
13 14	C-C	2.85877	2 5	C-C	2.91284
12 16	C-C	2.85937	13 14	C-C	2.92675
11 18	C-C	2.8763	12 16	C-C	2.92777
3 6	C-C	2.90298	11 18	C-C	2.93999
22 36	N-H	2.95034	3 6	C-C	2.96431
7 28	H-H	2.98729	16 20	C-H	1.15251

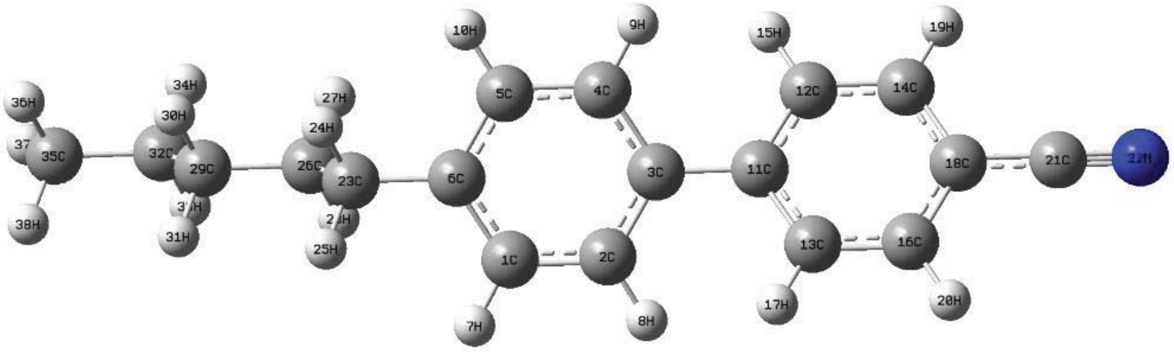

Fig 3.24 Structure of 5CB with positioning of atoms

The IR peak intensities are given in table 3.10 and the spectra plot of the given molecule is given in fig 3.25.

Table 3.10 IR spectra of 5CB

Calculated Frequency (cm^{-1})	IR Intensity
404.05	0.2179
423.47	0.1878
426.63	0.034
471.78	0.0698
550.84	0.0173
567.49	0.0024
580.58	0.0183
582.73	0.0434
611.83	0.0242
619.22	0.0393
637.92	0.3823
652.98	0.177
659.02	0.2626
660.04	0.1985
661.87	0.1487
692.87	0.1588
757.71	0.002
768.28	0.0049
774.00	0.0243

774.93	0.1687
783.66	0.0109
783.81	0.0031
811.41	0.0172
851.77	0.1037
935.98	0.0037
947.15	0.1521
959.51	0.0011
973.93	0.0325
985.4	0.3108
1015.9	0.0709
1031.1	0.0932
1043.29	0.0313
1050.81	0.0923
1053.52	0.0027
1060.03	0.0117
1079.95	0.2388
1095.76	0.036
1111.54	0.0014
1128.19	0.0235
1132.43	0.014
1133.8	0.0012
1146.48	0.0054
1155.7	0.0224
1183.73	0.0699
1197.46	0.2252
1220.92	0.0457
1256.49	0.0104
1271.78	0.1944
1279.62	0.1746
1283.7	0.1889
1283.85	0.0962
1305.64	0.1093
1331.93	0.1485
1351.54	0.068
1393.97	0.0138
1403.54	0.001
1448.6	0.2907
1519.61	0.47
1530.82	0.0156
1539.32	0.0193
1542.23	0.3851

1618.95	0.3895
1634.77	0.0033
1652.47	0.0001
1693.38	0.3859
1718.13	2.2514
2020.24	1.0644
2759.45	0.0331
2762.93	0.0152
2768.31	2.8172
2777.25	2.2645
2779.94	1.2177
2785.01	0.0074
2798.62	0.0156
2815.2	0.7469
2830.21	1.4976
2855.33	1.1468
2864.89	1.0171
2893.64	0.7988
2895.28	0.0464
2909.5	0.181
2911.08	0.0421
2914.1	0.4756
2915.75	0.027
2934.82	0.0964
2935.31	0.02

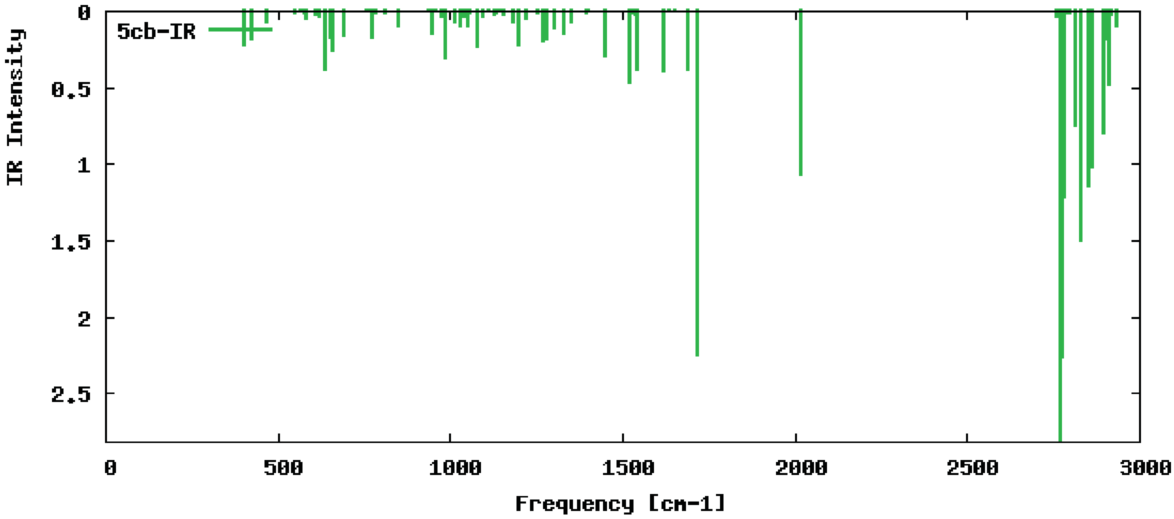

Fig 3.25 IR spectra plot of 5CB

The dielectric tensor of the molecule is calculated. The diagonalized elements are:

$$\varepsilon_{r(NC)} = \begin{pmatrix} 1.682415153 \\ 1.278595991 \\ 1.240497075 \end{pmatrix}, \varepsilon_{r(PAW)} = \begin{pmatrix} 1.601823295 \\ 1.256839434 \\ 1.217472032 \end{pmatrix}$$

Average value of dielectric constant comes out to be 1.4(NC) and 1.36(PAW).

The value of polarizability comes out to be $\propto = \begin{pmatrix} 479.36 \\ 219.80 \\ 191.98 \end{pmatrix}$, $\propto = \begin{pmatrix} 432.21 \\ 203.99 \\ 174.84 \end{pmatrix}$ and the average value of polarizability is 297.05 au^3 (NC) and 270.34 au^3 (PAW).

3.6 4-Nitrosobenzonitrile (4NB)

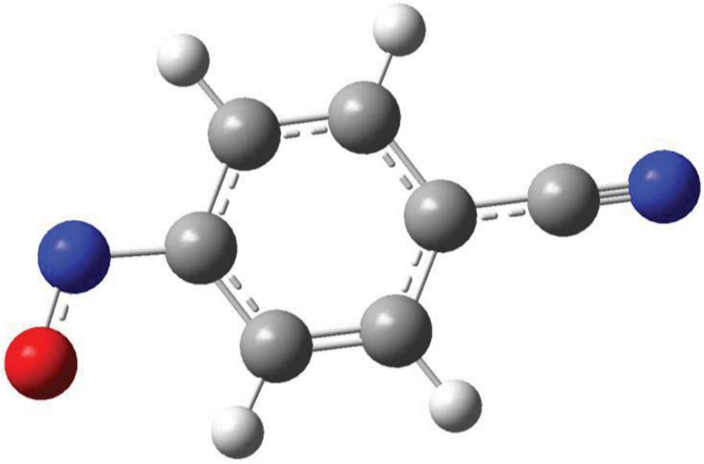

Fig 3.26 Optimised structure of 4NB

The given liquid molecule is 4-Nitrosobenzonitrile is a commonly used liquid crystal device used in LCD's.

The calculations are performed using the PAW and norm conserving pseudopotentials. The energy cut-off or ecutwfc is chosen to be 30 Ry. The energy cut-off is chosen in such a way that the value of total energy settles to a stable value as given in Fig 3.27.

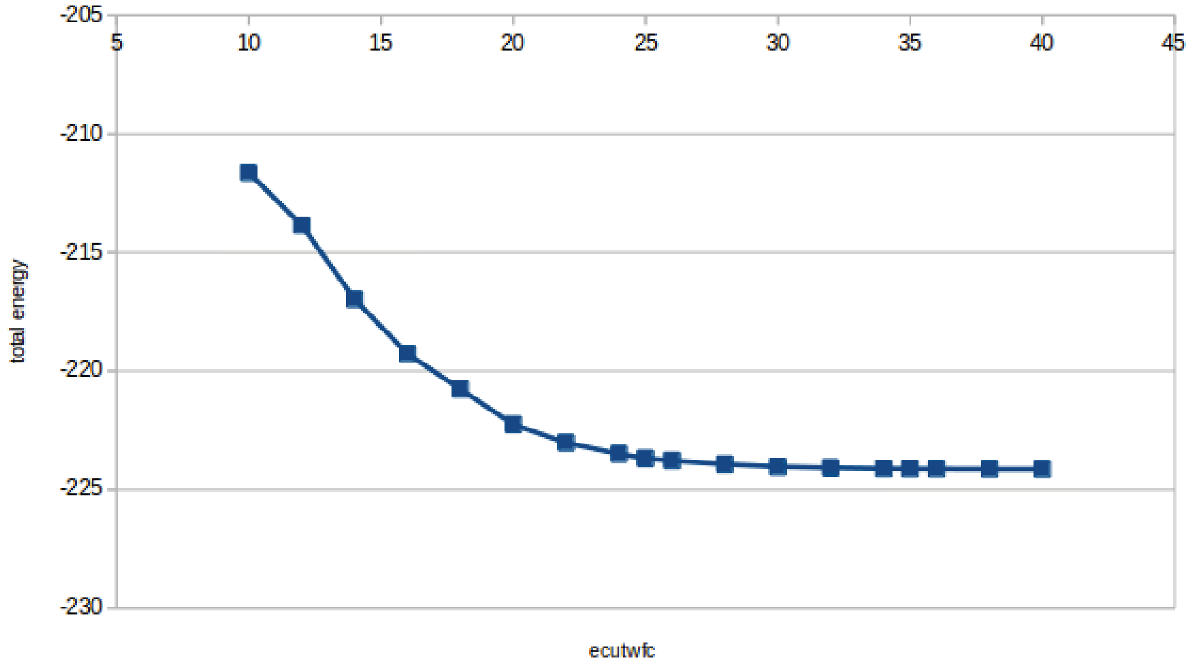

Fig 3.27 Plot of total energy vs cutoff wave function

The HOMO-LUMO of the molecule is shown in fig 3.28. The energy gap (E_g) 0f HOMO-LUMO is 1.4 eV (NC) & 0.90 eV (PAW).

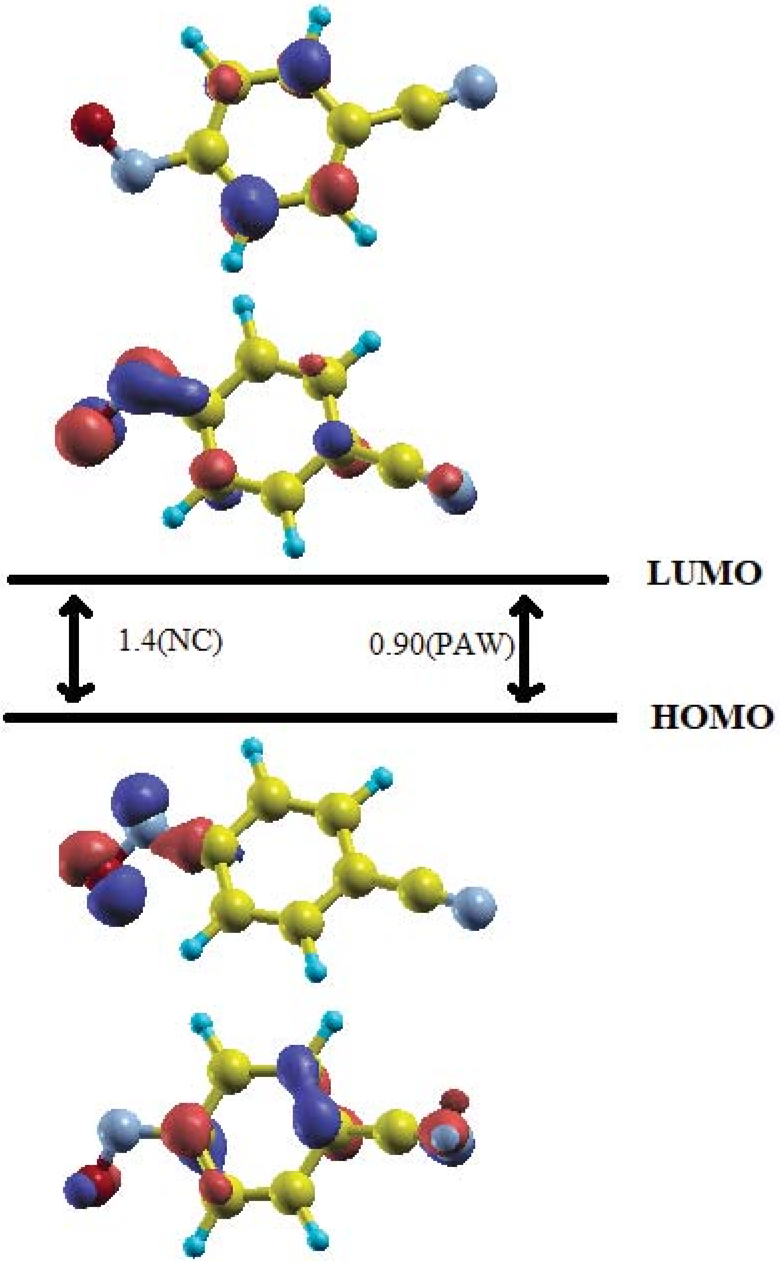

Fig 3.28 Molecular orbital plot of 4NB

Bond length have been calculated (in Angstrom) and optimised for 4nB molecules for both PAW and norm conserving pseudopotentials given in table 3.11 and positioning of atoms is given in fig 3.29.

Table 3.11 Bond length of optimised geometry of 4NB molecule

POSITION OF ATOMS	TYPE OF BOND	BOND LENGTH (PAW)	POSITION OF ATOMS	TYPE OF BOND	BOND LENGTH (NC)
3 8	C-H	1.10358	3 8	C-H	1.10358
6 10	C-H	1.10749	6 10	C-H	1.10749
4 9	C-H	1.11251	4 9	C-H	1.11251
1 7	C-H	1.11923	1 7	C-H	1.11923
13 14	C-N	1.15254	13 14	C-N	1.15254
11 12	N-O	1.21415	11 12	N-O	1.21415
3 4	C-C	1.37152	3 4	C-C	1.37152
1 6	C-C	1.37797	1 6	C-C	1.37797
2 3	C-C	1.38985	2 3	C-C	1.38985
5 6	C-C	1.39152	5 6	C-C	1.39152
1 2	C-C	1.39473	1 2	C-C	1.39473
4 5	C-C	1.3963	4 5	C-C	1.3963
5 13	C-C	1.40911	5 13	C-C	1.40911
2 11	C-N	1.42903	2 11	C-N	1.42903
4 8	C-H	2.13995	4 8	C-H	2.13995
5 10	C-H	2.14435	5 10	C-H	2.14435
5 9	C-H	2.15955	5 9	C-H	2.15955
3 9	C-H	2.16151	3 9	C-H	2.16151
2 7	C-H	2.16302	2 7	C-H	2.16302
1 10	C-H	2.17683	1 10	C-H	2.17683
2 8	C-H	2.18656	2 8	C-H	2.18656
6 7	C-H	2.19531	6 7	C-H	2.19531
2 12	C-O	2.24146	2 12	C-O	2.24146
4 13	C-C	2.35101	4 13	C-C	2.35101
2 4	C-C	2.37293	2 4	C-C	2.37293
1 11	C-N	2.37935	1 11	C-N	2.37935
2 6	C-C	2.38773	2 6	C-C	2.38773
7 9	H-H	2.3931	7 9	H-H	2.3931
1 5	C-C	2.40213	1 5	C-C	2.40213
4 6	C-C	2.40826	4 6	C-C	2.40826
3 5	C-C	2.40936	3 5	C-C	2.40936
1 3	C-C	2.4307	1 3	C-C	2.4307
8 9	H-H	2.47757	8 9	H-H	2.47757
3 11	C-N	2.48395	3 11	C-N	2.48395
6 13	C-C	2.4959	6 13	C-C	2.4959
9 13	H-C	2.52071	9 13	H-C	2.52071
7 11	H-N	2.54487	7 11	H-N	2.54487
5 14	C-N	2.55856	5 14	C-N	2.55856
7 10	H-H	2.56941	7 10	H-H	2.56941
8 12	H-O	2.59883	8 12	H-O	2.59883
10 13	H-C	2.74887	10 13	H-C	2.74887
2 5	C-C	2.75492	2 5	C-C	2.75492
3 12	C-O	2.77122	3 12	C-O	2.77122

1 4	C-C	2.77584	1 4	C-C	2.77584
8 11	H-N	2.77876	8 11	H-N	2.77876
3 6	C-C	2.78885	3 6	C-C	2.78885
7 8	H-H	2.90634	7 8	H-H	2.90634

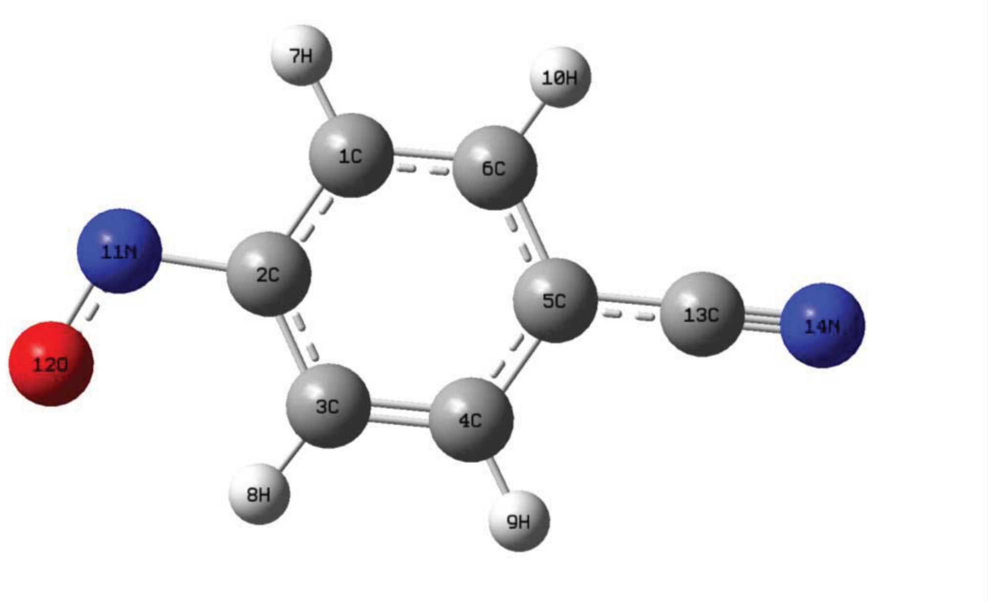

Fig 3.29 Position of atoms for 4NB

The IR peak intensities are given in table 3.12 and the spectra plot of the given molecule is given in fig 3.30.

Table 3.12 IR spectra of 4NB

Calculated frequency	**IR Intensity**
420.22	0.349
425.07	0.0153
457.43	0.0115
495.3	0.7739
497.74	0.0118
543.67	0.5312
572.38	0.0979
612.49	0.025
760.56	0.247

760.68	0.1851
784.36	3.6665
874.22	0.8469
908.68	0.0091
936.61	2.2536
1080.06	0.0144
1094.17	0.2092
1177.01	0.1312
1207.35	1.0698
1225.25	20.5513
1380.02	2.8913
1524.33	1.3306
1568.17	2.346
1661.73	4.8656
1799.71	2.3757
1830.45	0.0678
2218.48	2.2128
3205.06	0.2994
3213.5	0.5767
3333.61	0.2331

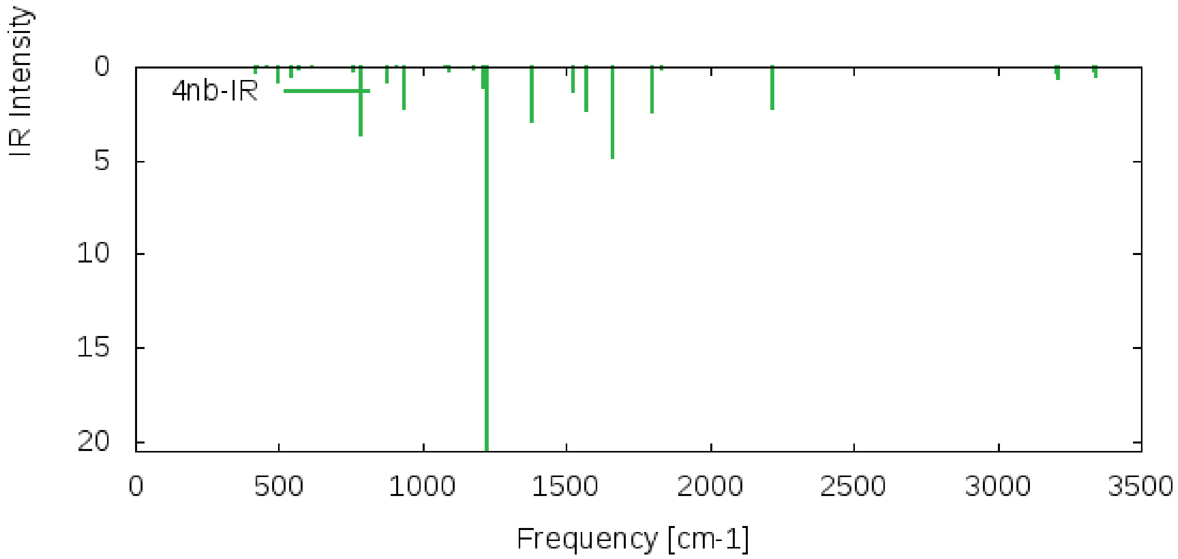

Fig 3.30 IR spectra plot of 4NB

The dielectric tensor of the molecule is also calculated and is given as

$$\varepsilon_{r(NC)} = \begin{pmatrix} 2.758437298 \\ 1.946325168 \\ 2.952548820 \end{pmatrix}, \varepsilon_{r(PAW)} = \begin{pmatrix} 2.656605588 \\ 2.982627225 \\ 2.696076669 \end{pmatrix}$$

Average value of dielectric constant comes out to be 2.55(NC) and 2.45(PAW)

And the value of polarizability comes out to be $\propto = \begin{pmatrix} 124.36 \\ 80.7 \\ 132.68 \end{pmatrix}$, $\propto = \begin{pmatrix} 119.72 \\ 83.03 \\ 121.54 \end{pmatrix}$ and the average value of polarizability is 112.58(NC) and 108.1(PAW).

Discussion

The band gap and dielectric constant show odd-even effect in the n-cynobiphenyl series where n is the number of carbon atoms in the alkyl chain of nCB as reported by Kumar et al. [5]. The value of band gap for 1CB is 3.02 eV and for 2CB it increases to 3.55 eV and then decreases for 3CB to 3.17 eV for and then increases for 4CB to 3.24 eV as shown in Fig 3.31. The dielectric constant for 1CB is 1.2 and for 2CB it increases to 1.469 and subsequently for 3CB it decreases to 1.36, subsequently increases for 4CB to 1.68 and later decreases to 1.36 for 5CB. The seemingly erroneous pattern may be due to smaller energy cut-off values (ecutwfc).

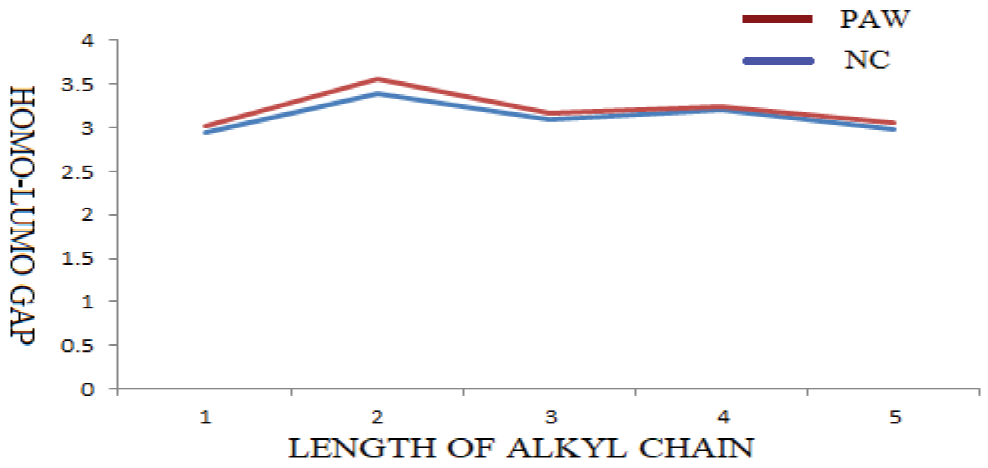

Fig 3.31 ODD-EVEN effect in HOMO-LUMO gap

The structure of molecule is nearly same for both PAW and Norm Conserving pseudopotentials. The bond lengths vary within nearly 2.3% of each other.

The infra-red spectra wave numbers also lie within nearly 2.25% (for 3CB) to 6.4% (for 2CB) of the experimental values. Higher cut-off wave functions or bigger k-point grid may be used to reduce error. However, it becomes computationally costly.

The Molecular orbital studies are in consonance with the previous theoretical calculated parameters [1-4].

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CHAPTER 4

CONCLUSIONS

CHAPTER 4

CONCLUSIONS AND FUTURE SCOPE

The structure of nCB (n=1-5) has been optimised using PWscf method implemented using Quantum Espresso. The given structures are optimised using PAW and NC Pseudopotentials and the bond length of the given molecules are compared. With the use of optimised co-ordinates, the value of band gap, polarizability and dielectric constant is calculated.

Table 4.1 Calculated parameters of 1-5CB and 4NB

Molecule	HOMO LUMO gap(eV)		Polarizability (a.u^3)		Dielectric constant	
	NC	PAW	NC	PAW	NC	PAW
1CB	2.94	3.02	239.80	216.42	1.225	1.201
2CB	3.40	3.55	221.56	195.85	1.546	1.47
3CB	3.10	3.17	244.71	223.61	1.397	1.358
4CB	3.20	3.24	252.00	241.69	1.77	1.683
5CB	2.98	3.05	297.05	270.35	1.401	1.359
4NB	1.40	0.90	112.58	108.10	2.552	2.445

It can be deduced that the molecule is dominated by its functional groups. In nCB, the HOMO of the molecule is largely centered on the phenyl rings involving the carbon atoms and the nitrogen that exists at the end is occupied. For LUMO the delocalization of valence orbitals is there throughout the molecule.

Also the HOMO LUMO of 4NB is dominated by the presence of its functional groups.

There could be seen an odd even effect in the nCB series of liquid crystals where n is the number of carbon atoms in the alkyl chain attached to the benzene ring, it increases for the value of even number of carbon atoms and then decreases for the odd number of carbon atoms. The subsequent pattern is visible for the HOMO-LUMO and polarizability of the molecule. The value of HOMO-LUMO gap for 1CB is 2.94 eV

(NC) and for 2CB it increases to 3.40 eV (NC) and then decreases for 3CB to 3.10 (NC) and then increases for 4CB to 3.20 eV (NC) and then again decreases for 5CB to 2.98eV (NC). The same pattern is observed for the dielectric constant of the molecules. The given pattern follows for PAW pseudopotentials also.

Future scope

Quantum Espresso does calculations on period structures. The studies presented here assume perfectly crystalline state of liquid crystal. However, the liquid crystals do not show exact periodicity at room temperature. Hence, there is scope of further study of properties at NTP. Since LCs have promising applications in display devices which in turn are governed by birefringence on account of applied electric field applied, therefore, electric field calculations have good scope. Regarding periodicity, a supercell may be constructed with a few LC molecules populated inside it having minimum energy configuration. A cluster formation approach within this supercell of appropriate size must be designed. For this, molecular dynamic stimulations of the molecules may be performed. It is of significance to study the effect of electric field and calculate the electro-optical properties of the molecules which include birefringence, order parameter and refractive index of the molecule. Later, non-linear properties may also be investigated.

In the near future I would like to increase the length of alkyl chain in the nCB series of molecule and wish to calculate the properties of higher order molecules of the biphenyl series. Study of effect of applied electric field to LC molecule is expected to help understand the nature of performance of LC devices at molecular level.

Published Paper

“Molecular Spectroscopy of 4 Nitroso Benzonitrile Liquid Crystal Molecule Studied by DFT Methodology” Mohiuddin Ansari , Rajesh Kumar Singh , Arvind Kumar Dwivedi , **Sumit Tiwari** , Devendra Singh , Bhavna Pal, Journal of Information and Computational Science, 10,10, 489-493 (2020).

Conference attended

Presented a Flash Talk contribution entitled “Ab-initio study of liquid crystals” at the 27th National Conference on Liquid Crystals December, 21-23, 2020 Amity Institute of Applied Sciences, Amity University Uttar Pradesh, Noida.

Journal of Information and Computational Science **ISSN: 1548-7741**

Molecular Spectroscopy of 4 Nitroso Benzonitrile Liquid Crystal Molecule Studied by DFT Methodology

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Abstract

In the present work, the spectroscopic properties of 4-nitroso benzonitrile are studied. The different modes of vibration in this molecule are studied from the IR spectrum. Here, due to the C-N group, the molecule shows different types of vibration at different frequencies. In the IR spectra of the molecule, the frequencies are found at 2338 cm^{-1} (stretching in C-N atom), 1630 cm^{-1} (scissoring in C-H atom), 1536 cm^{-1} (rocking in C-H atom), 3241 cm^{-1} (stretching in C-H atom) associated with different type of vibration of the molecule. The dipole moment of 4-nitroso benzonitrile is found to be 0.6197 debye and HOMO-LUMO gap is 0.11049. This molecule is useful in biological and medicinal purposes.

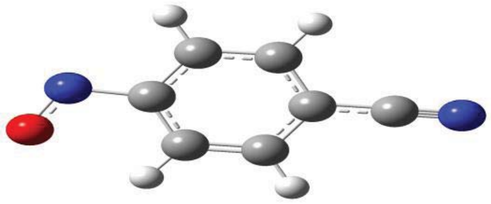

Fig 1. Molecular structure of 4-nitroso benzonitrile

27th National Conference on Liquid Crystals

(Under the auspices of Indian Liquid Crystal Society)

DECEMBER 21–23, 2020

Department of Physics

Amity Institute of Applied Sciences, Amity University Uttar Pradesh, Noida

CERTIFICATE

This is to certify that **Mr. Sumit Tiwari** of **Babasaheb Bhimrao Ambedkar University, Lucknow** has attended the 27th National Conference on Liquid Crystals organized by Amity Institute of Applied Sciences, Amity University Uttar Pradesh, Noida during December 21-23, 2020. He has presented a Flash Talk contribution entitled **Ab-initio study of liquid crystals** at the conference.

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