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**INVESTIGATION OF SPECTROSCOPIC AND SOME
ELECTRONIC PROPERTIES OF (E)-4-((P-
TOLYLIMINO)METHYL)PHENOL SCHIFF BASE BY DFT
METHOD**

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PROPERTIES OF (E)-4-((P-TOLYLIMINO)METHYL)PHENOL SCHIFF BASE BY
DFT METHOD

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August 2023

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ABSTRACT

INVESTIGATION OF SPECTROSCOPIC AND SOME ELECTRONIC PROPERTIES OF (E)-4-((P-TOLYLIMINO)METHYL)PHENOL SCHIFF BASE BY DFT METHOD

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Master of Science in Physics

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Schiff' base is an organic compound consisting of the union of nitrogen atom in the primary amines with the carbonyl group in various aldehydes or ketones to form the group of azomethine. The usage area of Schiff bases and metal complexes is quite wide. Schiff bases; They are compounds that are important in various branches such as pharmacy, medicine, biological systems, cosmetics, agriculture, dyestuff production, plastic industry, aircraft industry, liquid crystal technology, electronics industry and analytical chemistry. In addition to the properties of these compounds such as synthetic oxygen carriers, intermediate product creators in enzymatic reactions, and antitumor effects, their use in analytical chemistry as spectrophotometric reagents by giving selective and specific reactions to some metal ions is also important. Schiff Bases are generally colored solids. By taking advantage of these features, it can also be used widely in the paint industry. Apart from these, it can also be used as a liquid crystal in electronic display systems and as a polymer formation accelerator. This study aims to theoretically investigate the spectroscopic and electronic properties of (E)-4-((p-tolylimino)methyl)phenol Schiff base using density functional theory (DFT) and the 6-311++G(d,p) basis set. . The structure of the Schiff base compound was theoretically elucidated by FT-IR, ^1H -NMR and ^{13}C -NMR spectroscopy. The structure of the compound was optimized at the B3LYP/6-311++G(d,p) theory level. After the optimization calculation, the harmonic frequency calculation was made and it was understood that the molecule was in a stable structure since no negative frequency was observed as a result of the calculation. Since the (E)-4-((p-tolylimino)methyl)phenol

Schiff base does not have crystal data in the literature, it was compared with the structural parameters of similar molecules and it was seen that the results were compatible with the experimental data. The vibration frequencies were assigned and it was seen that the calculated theoretical frequency values were in good agreement with the experimental spectra. The calculated NMR chemical shifts were also found to be in good agreement with the experimental values. Also, nonlinear optical (NLO) properties of Schiff base with HOMO-LUMO molecular orbital energies were calculated and found to have significant NLO activity. Finally, the molecular electrostatic potential (MEP) analysis was performed to study the reactivity and potential sites of electrophilic and nucleophilic attacks. The results of this study provide valuable insights into the spectroscopic and electronic properties of the (E)-4-((p-tolylimino)methyl)phenol Schiff base and could be useful in designing novel organic materials with promising optical and electronic properties.

2023, 50 pages

Keywords: FT-IR, NMR, NLO, MEP, HOMO, LUMO

ÖZET

(E)-4-((P-TOLİLİMİNO)METİL)FENOL SCHIFF BAZININ SPEKTROSKOPİK VE BAZI ELEKTRONİK ÖZELLİKLERİNİN DFT METODUYLA İNCELENMESİ

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Schiff bazı primer aminlerdeki nitrojen atomunun çeşitli aldehit veya ketonlardaki karbonil grubu ile birleşerek azometin grubunu oluşturmasından oluşan organik bir bileşiktir. Schiff bazlarının ve metal komplekslerinin kullanım sahası oldukça geniştir. Schiff bazları; eczacılıkta, tıpta, biyolojik sistemlerde, kozmetikte, tarım alanında, boyar maddelerin üretiminde, plastik sanayisinde, uçak sanayisinde, sıvı kristal teknolojisinde, elektronik endüstrisinde ve analitik kimya gibi çeşitli dallarda öneme sahip bileşiklerdir. Bu bileşiklerin sentetik oksijen taşıyıcı, enzimatik reaksiyonlarda ara ürün oluşturucu, antitümör etkisi gibi özelliklerinin yanında bazı metal iyonlarına karşı seçici ve spesifik reaksiyon vererek spektrofotometrik reaktif olarak analitik kimyada kullanımları da önem taşımaktadır. Schiff Bazları genelde renkli katılardır. Bu özelliklerinden yararlanılarak boya endüstrisinde de oldukça fazla kullanılabilir. Bunların dışında elektronik gösteri sistemleri içinde sıvı kristal olarak ve polimer oluşumunu hızlandırıcı olarak da kullanılabilir. Bu çalışma, (E)- 4 - ((p-tolilimino)metil)fenol Schiff bazının spektroskopik ve elektronik özelliklerini yoğunluk fonksiyonel teorisi (DFT) ve 6-311++G(d,p) temel seti kullanarak teorik olarak incelemeyi amaçlamaktadır. Schiff bazı bileşiğinin yapısı FT-IR,¹H-NMR ve ¹³C- NMR spektroskopisi ile teorik olarak aydınlatıldı. Bileşiğin yapısı B3LYP/6-311++G(d,p) teori düzeyinde optimize edildi. Optimizasyon hesabından sonra harmonik frekans hesabı yapıldı ve hesaplama sonucunda negatif frekans görülmediği için molekülün kararlı yapıda olduğu anlaşıldı. (E)- 4 - ((p-tolilimino)metil)fenol Schiff bazının literatürde kristal verileri olmadığı için benzer moleküllerin yapısal parametreleri ile

karşılaştırılması yapıldı ve deneysel verilerle uyumlu sonuçlar elde edildiği görüldü. Titreşim frekanslarının işaretlemeleri yapıldı ve hesaplanan teorik frekans değerlerinin deneysel spektrumla iyi bir uyum içinde olduğu görüldü. Hesaplanan NMR kimyasal kaymalarının da deneysel değerlerle iyi bir uyum içinde olduğu bulundu. Ayrıca, Schiff bazının HOMO-LUMO moleküler orbital enerjileri ile doğrusal olmayan optik (NLO) özellikleri hesaplandı ve önemli ölçüde NLO aktivitesine sahip olduğu bulundu. Son olarak, elektrofilik ve nükleofilik saldırıların reaktivitesini ve potansiyel bölgelerini incelemek için moleküler elektrostatik potansiyel (MEP) analizi yapıldı. Bu çalışmanın sonuçları, (E)- 4 - ((p-tolilimino)metil)fenol Schiff bazının spektroskopik ve elektronik özelliklerine ilişkin değerli bilgiler sağlar ve gelecek vaat eden optik ve elektronik özelliklere sahip yeni organik materyallerin tasarlanmasında faydalı olabilir.

2023, 50 sayfa

Anahtar Kelimeler: FT-IR, NMR, NLO, MEP, HOMO- LUMO

PREFACE AND ACKNOWLEDGEMENTS

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LIST OF SYMBOLS

α_{ave}	Avarage polarizability
β	In-plane angle bending
γ	Out -of-plane angle bending
Ψ	Wave function
δ	Bending vibrations
ν	Stretching vibration
τ	Torsion vibration
β_{tot}	Total hyper polarizability



LIST OF ABBREVIATIONS

AAS	Atomic absorption spectroscopy
BO	Born-oppenheimer
DFT	Density function theory
FT-IR	Fourier-transform infrared spectroscopy
GTOs	Gaussian type orbitals
HOMO	Highest energy occupied molecular orbital
IR	Infrared
LUMO	Lowest energy vacant molecular orbital
MESP	Molecular electrostatic potential
MS	Mass spectrometry
NLO	Nonlinear optic
NMR	Nuclear magnetic resonance
PES	Potential energy surface
RW	Radio waves
SCF	Self-consistent field
STO	Slater type orbitals
UV	Ultraviolet

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1. INTRODUCTION

Hugo Schiff is a German chemist who is naturalised with Italian citizenship. He discovered Schiff's base and other righties, and conducted research into aldehydes that led to his discovery of the Schiff test. In addition, he studied amino acids and a chemical reagent he called pyurate. Hugo Schiff, a German scientist, is credited with being the first to identify the products formed when primary amines react with carbonyl compounds in 1864. The dye industry, catalysis, fungicides, and agricultural chemicals all benefit from Schiff bases (Gaur 2003, Genin *et al.* 2000).

Remarkable antibacterial, antifungal, and anticancer properties in a variety of Schiff bases have been identified (Supuran *et al.* 1996). The biological activity of this group of chemicals depends on the presence of the C=N moiety. Forming a Schiff's base from aromatic amines often takes place under simple circumstances.

The bond formed between a ketone and an aldehyde is called an imine or ketamine, whereas the link formed between two ketones is called an azomethine or aldimine. Schiff bases (imines) have been of particular interest as a kind of chemical due to their stability and ease of production. The versatility of imines, which ranges from utilization in biological systems to other fields, is remarkable (Sharaby *et al.* 2017) to chemical catalysis (Redshaw 2017) to medicine and pharmacy (Roberts *et al.* 2017) to chemical analyses and cutting-edge technology (Dirisio *et al.* 2017, Upadhyay *et al.* 2008). Additionally, Schiff bases are used in many other industries, such as the manufacturing of cation carriers and ion selective electrodes (Aydnalı 2006), corrosion inhibitors (Emregul *et al.* 2006), and paint (Serin and Gök 1988).

Both biological systems and the industry are relying more and more on coordination chemicals. A common ligand in coordination chemistry, schiff bases are useful because of their structural and biological properties.

The theoretical level of the molecule, DFT/B3LYP/6-311++G (d, p), has been improved in this thesis to determine its stable low-energy configurations. First, the vibration frequencies of the stable structure of the molecule were measured, and ^1H -NMR and ^{13}C -NMR calculations were performed. In the DFT/B3LYP/6-311++ G (d, p) theoretical plane, we have looked at nonlinear optical properties (NLO), molecular electrostatic potential (MESP) maps, HOMO, and LUMO molecular orbital energies. These calculations were performed using Gaussian 09 (Linux) and Gauss View 5.0.



2. LITERATURE REVIEW

2.1 Electromagnetic Waves

The electromagnetic spectrum is the distribution of electromagnetic waves organized according to their frequency and wavelength. Depending on the subject of study, the electromagnetic spectrum might range from radio waves to gamma rays in terms of energy (Britannica 2023).

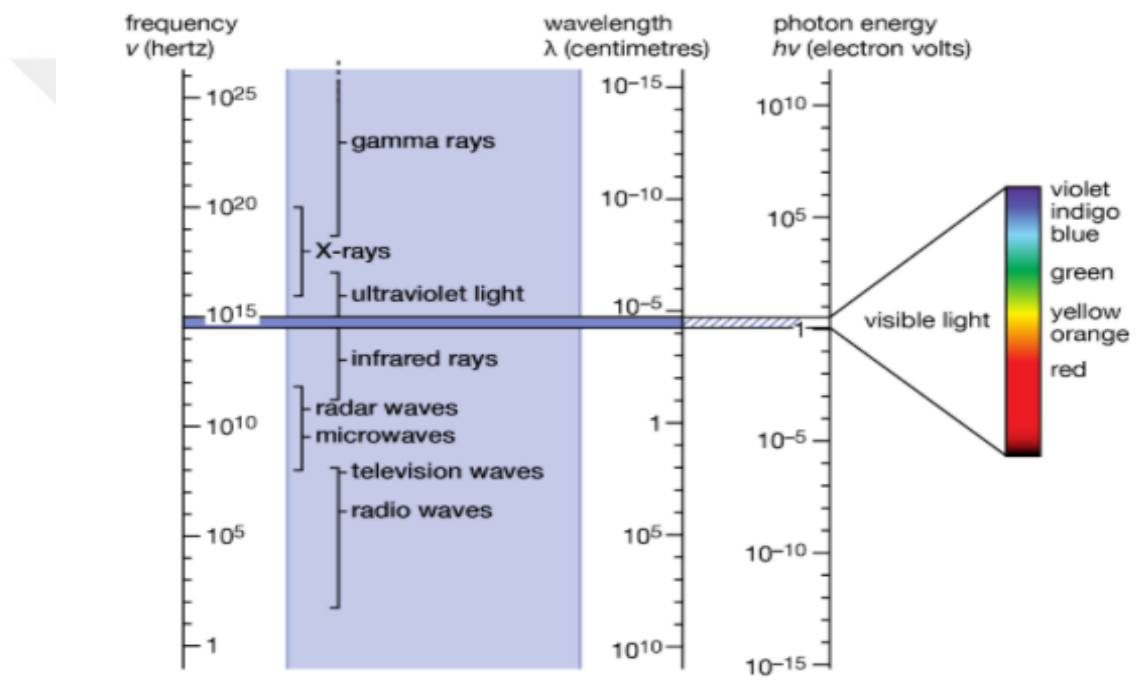


Figure 2.1 Electromagnetic spectra (Britannica 2023)

2.1.1 Radio waves

German bomber Horten Ho 229 is (also known as Gotha Go 229) wings were constructed in 1944 from CB-impregnated plywood and joined with an adhesive comprised of charcoal and sawdust. Likewise, Germans employed in a three-layer structure, graphite particles are distributed in a rubber matrix next to regular paper. Sumpf (German for "swamp") and Schornsteinfeger (German for "chimney-sweeper")

materials. Utilizing this composite has made it possible to decrease radio waves' reflectance in the periscopes for submarines (Johnson 2004). American citizens independently devised a similar technique, but they used CB instead of graphite to create Halpern Anti-Radiation Paint (HARP), which is used in aircraft (Halpern 1960). Unfortunately, a signal can't get to places that are too far away. The wave that transmits a signal across vast distances is known as a carrier wave. Consequently, a radio wave is composed of a carrier wave and a signal. The electromagnetic properties of radio waves are what make them so valuable. It travels at the same speed as light, or 3×10^8 m/s. The carrier wave has a higher frequency than the signal. Carriers are created by oscillators. On the other hand, a radio wave can be thought of as a disturbance that moves through space. Electrons move quickly back and forth on a radio wave. Heat and light are also carried through space by waves (In 2019).

2.1.2 Microwaves

Microwaves (0.3-300 GHz) are electromagnetic radiations that fall between infrared and radiofrequency radiations. The majority of people concur that microwave radiation accelerates The impact's warmth generates chemical reactions. When subjected to microwaves, a medium molecule constantly realigns with the changing field. As a result, electromagnetic energy is transformed into heat energy. The dielectric constant, which gauges a molecule's ability to be polarized by an electric field, determines the medium's capacity to be heated by microwave irradiation. As a result, while hexane, toluene, and diethyl ether are unaffected by microwaves, solvents including water, methanol, and dimethyl form amide quickly warm up Some workers, though, believe that there are non-thermal effects as well. In a recent article (Caddick 1995). The two conflicting points of view are succinctly summarized. In many syntheses, according to Whittaker and Mingos, the rate of a reaction (Adam 2003).

2.1.3 Infrared (IR)

The hybrid technique known as AFM-based infrared spectroscopy (AFM-IR) combines atomic force microscopy's (AFM's) spatial resolution with the ability to study chemical compounds using infrared (IR) spectroscopy (Dazzi *et al.* 2005). By itself, atomic force microscopy (AFM) and infrared spectroscopy (IR) are both powerful and widely used methods. Topographic imaging using an AFM is widely employed in many fields, including industry, materials science, and biology. One of the most used methods for chemical analysis is infrared spectroscopy. Infrared spectroscopy measures infrared absorption spectra, or the quantity of infrared light absorbed, to conduct chemical analysis. Absorption peaks in IR spectra may be utilized as a fingerprint to characterize and/or identify different chemical species. Spatially resolved infrared micro spectroscopy was achieved in the mid-1990s by combining infrared spectroscopy with microscope and array detectors. By using this technique, it has become possible to give imaging based on chemical contrast and chemically evaluate small parts of a sample with outstanding efficiency. Two reviews on the subject have previously been published, one of which focuses on the AFM-IR technique⁴ and the other of which places it in the context of scattering-based scanning near-field optical microscopy (Centrone *et al.* 2015).

2.1.4 Visible light

The human eye is sensitive to electromagnetic radiation between 400 and 700 nm, with some people also being able to detect radiation between 380 and 780 nm; this range is known as the visible spectrum. In the green part of the optical spectrum, at 555 nm, a photopic eye has its greatest sensitivity. A photopic eye is one that has been exposed to light that was quite high in intensity, allowing the retina to undergo photochemical changes and the pupil to constrict. Technically, it is incorrect to refer to UV light. It is preferable to refer to the radiation wavelengths that give rise to visual awareness as "light." UV radiation is the recommended term (Diffey and Kochevar 2007).

2.1.5 Ultraviolet (UV)

Before continuing, we must first determine which portion of the electromagnetic spectrum corresponds to the UV. Originally, light with wavelengths shorter than those that humans could sense was referred to as "ultraviolet," which is a term that refers to light that is "beyond violet." (The human spectral range is here referred to as "visible light," which is less challenging.) For reasons that will become clear below, the exact cutoff wavelength between violet and ultraviolet varies from person to person, hence the term has been narrowed to describe light with a wavelength of 100 to 400 nm. Because of atmospheric absorption, this spectrum is mostly absent from Earth's surface. The ultraviolet (UV) spectrum is often divided into three classes: Ultraviolet-A (UVA), Ultraviolet-B (UVB), and Ultraviolet-C (UVC). While UVC is effectively blocked by the atmosphere, some UVB and even more UVA are able to reach Earth's surface (Figure 2.2). Animal eyesight is almost entirely limited to the UVA spectrum, despite UVB radiation having significant biological implications due to its absorption by proteins and nucleic acids. While most visual pigments, including those in the retina, are very UV-photosensitive, we and many other animals have UV-absorbing pigments in the lens that entirely prohibit the transmission of this spectral range to the retina (Douglas and Cronin 2016). Age-related changes in the density of these lens pigments increase sensitivity to wavelengths such as

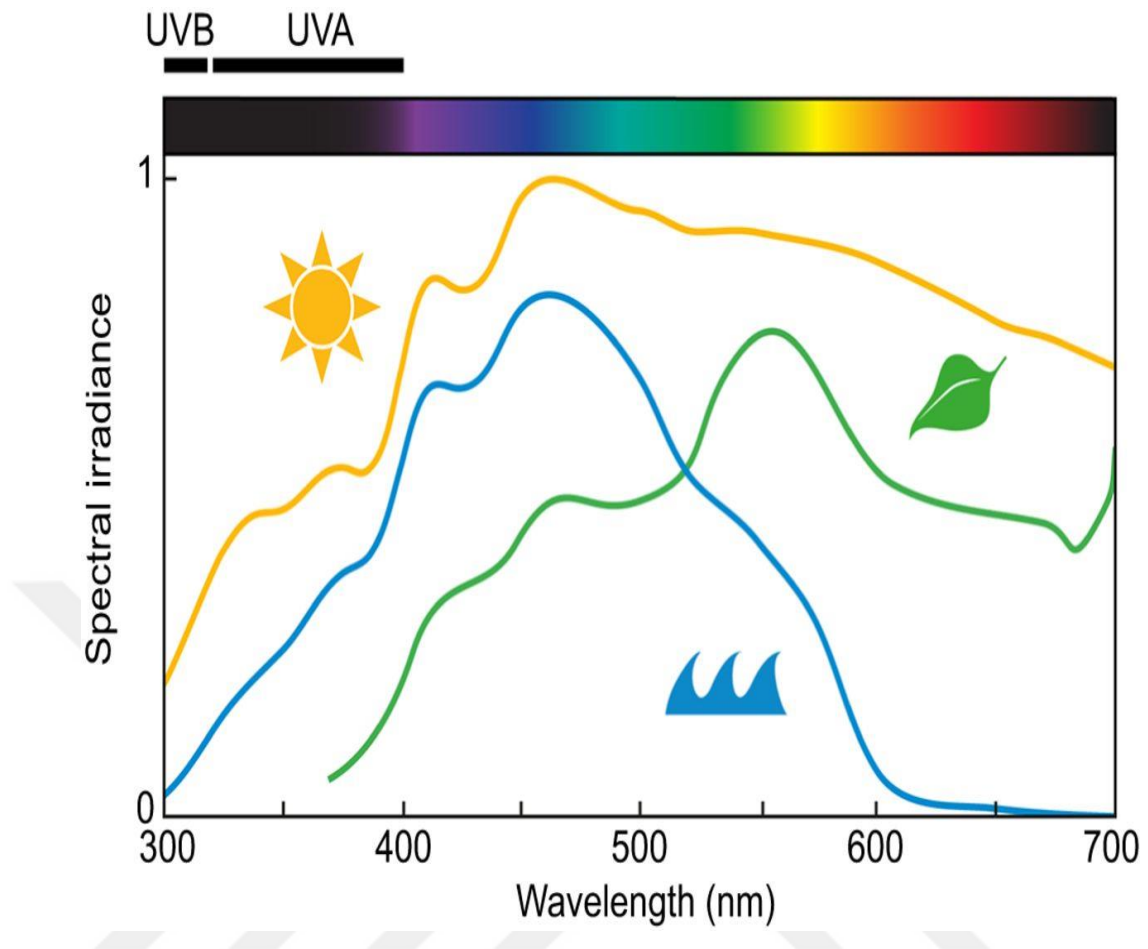


Figure 2.2 Natural ultraviolet radiation. Spectral irradiance of the sun at three different locations: at ground level (yellow trace, represented by a sun sign), at 5 meters deep (blue trace, represented by a waves symbol), and beneath a forest canopy (green trace, represented by a leaf symbol). Radiation from ultraviolet A and B are shown. Solar irradiation standard ASTM G173 (A1.5), aquatic attenuation coefficients Smith and Baker (1981), and the work of (Chiao *et al.* 2000)

2.1.6 X-ray

Atoms in solids scatter x-rays when they come into contact with them thanks to their electrons. Atoms emit scattered waves (diffraction pattern) at multiple locations, and this interference between the waves can either be beneficial or harmful. However, when the solid's atomic structure is organized in an ordered way, positive interference takes place. The periodic atomic structure of crystals in materials and diffraction patterns are closely related. In contrast to diffraction at high angles, which is generated by short repeated distances, diffraction at small angles is induced by atomic arrangement

(periodicity) with long repeated distances (Fultz and Howe 2013). The location of diffraction peaks is used to estimate the shape and size of the unit cell, while the strength of the peaks is used to identify the location of the atoms inside the cell and the atomic number (Zhang *et al.* 2002). To characterize and examine the organization of atoms in each unit cell, position of atoms due to comparative advantages, and atomic spacing angles x-ray wavelength to atomic size, X-ray diffraction techniques use diffraction patterns or intensities (Pappas 2006). The diffraction of x-rays is a non-destructive technology that offers a wide diversity of material. Solar cells and semiconductors are analyzed using mineral, metal, polymer, ceramic, and plastic data (Guma *et al.* 2012).

2.1.7 Gamma ray

In particular, we had to identify shielding effects in the low-energy photopeaks by isolating them from the source photopeaks, adjusting the calibration depending on the background photopeaks, and so on. In order to match isotopes to a spectrum after photopeaks have been identified, spectroscopists may use their knowledge of isotope emissions (or a library of such emissions). In addition to relying on textbook knowledge, the research authors noted that spectroscopists also depend on the intuition they get through studying dozens or hundreds of gamma-ray spectra. The researchers also understood how challenging it would be to incorporate ad hoc studies like this into a robotic process. Neural networks (NNs) may imitate the intuitive process employed by human spectroscopists to discern spectra. The ability to train NNs to recognize and measure isotopes in gamma-ray spectra has been shown in previous research.

2.2 Spectroscopy

Though imaging spectrometry was created much later than field spectroscopy, the two approaches have many similarities in their pursuit of accurate data on the spectral reflectance of minerals making up the Earth's surface from afar. Field spectroscopy is technically easier since the sensing device may remain stationary over the item of interest for longer and the distance between the instrument and the thing being

measured is shorter. However, How to sample the surface of interest becomes an additional factor because field spectroradiometers typically measure a considerably smaller area. In order to better understand how humans see color, field spectroradiometers were initially used to examine the color of the Earth's surface as seen from the air (Penndorf 1956). Even when there is no change in energy level, can occur. Even if the incident light is not strong enough to activate molecules, it may nevertheless scatter at the frequency of the incoming light. One of the most prevalent types of scattering, elastic scattering, may be explained by either the Rayleigh or Mie theories. Inelastically scattered light occurs when incoming radiation is absorbed by a molecule and re-emitted at a different frequency. In inelastic scattering, the energy of the incident photons is transferred to the material rather than being absorbed (Gauthier 2014).

2.3 Spectroscopic Methods

Rays form the core of spectroscopy. The photons in an electromagnetic light beam that passes a sample come into contact with it. A sample's electrons and chemical bonds are affected by absorbed radiation.

In some instances, the radiation that is absorbed results in the release of low-energy photons. In spectroscopy, the sample's response to radiation is examined. Information about the substance can be gleaned from the emitted and absorbed spectra. As the interaction relies on the wavelength of the light, there are numerous varieties of spectroscopy.

2.3.1 Ultraviolet–visible spectroscopy

Since light causes electrons to hop from lower-energy to higher-energy atomic or molecular orbitals, electronic spectroscopy refers to measurements done in the UV, Vis, and NIR parts of the electromagnetic spectrum (Weckhuysen *et al.* 2000). The n-r* and Tr-a* transitions are the most common types of electron transfer in inorganic and

organic molecules, while the d-d transition and ligand-to-metal or metal-to-ligand charge transfer transitions are also common in transition metal ions. Those are accountable for what gives matter its color. Research using spectroscopy of solutions, gas phase, and Transmission typically involves individual crystals, however it is extremely challenging to obtain clear powder films and materials that facilitate transmission, such as heterogeneous catalysts experiments are really challenging. It is also possible to capture diffusely reflected light, and this method has been DRS stands for diffuse reflectance spectroscopy (Weckhuysen *et al.* 1999).

2.3.2 Atomic absorption spectroscopy

Two forms of spectroscopy that employ the emission and absorption of light by free atoms in a gaseous state to determine elemental concentrations are known as atomic absorption spectroscopy (AAS) and atomic emission spectroscopy (AES), respectively. In atomic absorption spectroscopy, light is absorbed by free metallic ions. The method is used by analytical chemists to quantify the amount of analyte in a sample. In pharmacology, biophysics, archaeology, and toxicology, electrothermal vaporization is utilized to identify over 70 different elements in solution and directly in solid objects. The foundations of atomic theory were laid by Robert Wilhelm Bunsen and Gustav Robert Kirchhoff of Germany's University of Heidelberg in the middle of the nineteenth century (Abragam *et al.* 1961).

2.3.3 Nuclear magnetic resonance spectroscopy

Nuclear magnetic resonance spectroscopy, often known as NMR spectroscopy, makes use of radiofrequency waves in order to get information about magnetic nuclei. NMR spectroscopy is just one of several spectroscopic techniques used regularly in biological applications since the term "spectroscopy" refers to any approach that uses electromagnetic (EM) radiation to examine atoms. However, NMR varies from other types of spectroscopies in three key areas for reasons that we shall discuss in this article. NMR has a wider variety of potential uses than other spectroscopic techniques since it examines the distribution of nuclei of a user-selected chemical element inside the

molecules of a sample. Second, NMR signals provide a method for investigating the chemical and physical surroundings of the nuclei under study. To this magnetic compass analogy, there are two elements that we must add in order to comprehend NMR sufficiently for the majority of biological applications. A magnetic compass first any direction by deflection, but quantum mechanics Magnetic nuclei are limited by mechanical principles to pointing in substantially more constrained instructions. These are the "directions." Interestingly, there are levels of nuclear energy dubbed "spin states," where "spin" refers to the possibility that a specific nucleus' magnetism ((Rabi 1937, Rabi *et al.* 1938).

2.3.4 Mass spectrometry

It is hypothesized that hexylundecylacetic ester (XXII) (Type H) forms when a 'Y-hydrogen is rearranged and one of the ester's side chains is removed. Degradation of fungichromine into 7,21-tritriacontane allowed mass spectrometry to reveal that it shares a carbon skeleton with XXI and contains 33 carbon atoms with I-carbon substituents at positions C-7 and C-21 (Cope *et al.* 1962). Using mass spectra, the saturated hydrogenation product corresponding to the antibiotic marasin from *Marasmius ramaelis*, which was identified as (-)-nona-3, 4-diene-6, 8-diyne-1-ol, was identified as n-nonanol (Bendz *et al.* 1959). According to the mass spectrum, isomarasin produced 2-pentyltetrahydrofuran as an isomerization byproduct during hydrogenation (Bendz *et al.* 1959). This demonstrated, when combined with additional spectroscopic data Tetrahydro-2-(penta-2,4-diynylidene)-furan is what isomarasin is made of Using mass spectrometric data.

Anhydro-aspergillomarasmine B, a metabolite produced by mold, has its molecular weight and number of free carboxyl groups determined by mass spectrometry (Robert *et al.* 1962). By esterifying with methanol, a mol wt 302 ester was created, while esterifying with ethanol, which required a mol wt. of 260 and three carboxyl groups for the parent molecule, produced a mol wt 344 ester. The mass spectra provided more evidence in favor of aspergillomarasmine B, which is composed of non-peptidic aspartic acid, diamino propionic acid, and glycine (Robert *et al.* 1962).

2.3.5 X-ray spectroscopy

Stargazing has been the primary use of modern X-ray telescopes. Except for A-type stars and the coldest giants of spectral type M, X-ray sources have been discovered in practically every region of the Hertzsprung-Russell diagram. However, even those categories include some outliers. The most massive and energetic stars known, O-type and Wolf-Rayet stars, have been demonstrated to produce X-rays. It is believed that the million-degree plasma and accompanying X-ray emission is generated by shocks in the star's chaotic winds. This means that X-rays may be employed as reliable tracers of mass loss in stars and as diagnostic tools for understanding the fundamental mechanisms at action in stellar winds. A area of very hot plasma is created when the winds of two stars clash. Insights on the wind characteristics of each star may be gleaned from the X-ray emission and its variability with orbital phase. Cooler stars in the F to M spectral range generate X-rays that are sensitive enough to detect a magnetic corona akin to the solar corona. These coronae are amplified due to flares, which occur when the Sun's inherently unstable magnetic fields reunite and release vast quantities of energy in a short period of time. It is possible that an internal dynamo is responsible for the magnetic fields seen in the coronae of these stars. X-rays may be used to identify these fields in the corona, although the phenomena is best understood as a collection of closed magnetic fields (Bowyer *et al.* 2000).

2.3.6 Raman spectroscopy

The spectroscopic method known as Raman spectroscopy relies on the inelastic scattering of monochromatic light from a laser source. The sample both absorbs and re-emits laser light. The energy of the photons emitted by the Raman effect varies according to the vibrational state of the molecule being studied. Although it is far more energetic than anti-Stokes radiation, Rayleigh radiation is less energetic than Stokes radiation. Since the vibrational and rotational energies contained in the scattered radiation of the Raman effect depend on the atoms or ions that make up the molecule, the chemical bonds between them, and other factors, the observed Raman shift of the Stokes and anti-Stokes features is a direct measure of these details (John *et al.* 2010).

2.3.7 Infrared spectroscopy

The term "near-infrared" (NIR; 1000-2500 nm; 10,000-4000 cm⁻¹) spectroscopy can be used to describe a vibrational spectroscopy technique (Huck *et al.* 2019, Czarnecki *et al.* 2015) that fills a distinctive niche in the bioscience community. When it comes to the study of medicinal plants or issues relating to the quality control of natural goods, for example, it has become the instrument of choice for many applications requiring both qualitative and quantitative assessment of bio-related materials. Raman spectroscopy and infrared (IR, i.e. mid-infrared, MIR; 4000-400 cm⁻¹; 2500-25,000 nm) spectroscopy are two examples of more established technologies with which it competes. The typical critical domains include, for example, bioanalytical research and biomedical diagnosis, where IR and Raman techniques have traditionally cast a shadow over NIR spectroscopy (Be'c *et al.* 2020).

2.4 Molecular Vibration Types

Numerous microscopy techniques are built on molecular vibration, which makes it possible to find particular molecules inside of cells and tissues. Raman scattering, infrared absorption, and near-infrared (NIR) absorption are some of these techniques that have been extensively exploited for chemical imaging in biomedicine (Fernandez *et al.* 2005) Similar to nonlinear vibrational approaches, 3D spatial resolution and great sensitivity of coherent antismoke Raman scattering (Duncan *et al.* 1982, Andreas Zumbusch *et al.* 1999) and stimulated Raman scattering (Freudiger *et al.* 2008) microscopies have permitted novel biological findings (Yue *et al.* 2014). However, the imaging depth for all of these methods is just a few hundred micrometers or less because of strong optical in biological tissue, scattering Consequently, their potential use at the organ level is constrained in vivo and in therapeutic settings. A deep-tissue imaging technique that can keep both high (Sehgal *et al.* 1984).

2.4.1 Stretching vibrations

It is caused by the atoms in the molecule moving periodically along the bond axis. The link between two atoms may either extend or shorten during the stretching process, with the outcome depending on the equilibrium position. The bond angle remains the same because the stretching motion occurs along the axis of the link between the atoms. Vibrational tension is represented by a ν . It is possible to classify it as either symmetric (ν_s) or asymmetric (ν_{as}). When all of the bonds in a molecule are stretched at the same time, the outcome is a symmetric vibration; when some bonds are extended while others are shortened, an asymmetric vibration occurs.

2.4.2 Bending vibrations (δ)

With this form of vibration, atomic bonds maintain their length while bond angles oscillate. The vibrational motion vectors during bending are orthogonal to the bond axis. The symbol δ denotes a bending movement. It's possible for it to take place either in or out of the molecule's plane. Scissor (s) and rocking (r) vibrations are examples of in-plane bending vibrations, whereas wagging (w), twisting (t), and torsion (δ_s) vibrations are examples of out-of-plane bending vibrations. Ammonia adsorption on Lewis acidic metal oxides (Al_2O_3 , ZrO_2 , and TiO_2) and zeolite was analyzed by analyzing the bending vibrations in their respective infrared spectra using density functional theory (DFT) simulations. Calculations using density functional theory demonstrate the vibrational wavenumbers (m_4 and m_2) of NH_4 coupled to a Brnsted acid site and the (ds and dd) of NH_3 species coordinated to a Lewis acidic metal center ($M = \text{Al, Zr, or Ti}$). Experimental findings were found to be in fair agreement with DFT wavenumber calculations. The wavenumber estimation demonstrates that the skeletal vibration effectively absorbs the ds vibration of NH_3 hydrogen-bonded to a zeolite. In contrast, several bands of asymmetric bending modes (dd and m_2) were ascribed to a zeolite. Based on the peak assignment, a technique is given for quantifying Bronzed and Lewis acid sites, as well as hydrogen-bonded NH_3 . Deformation vibrations, which include bending vibrations, have another name. Two distinct classes of deformation vibrations may be identified.

A. Vibrations in which the bond angle shifts produce plane bending motions. Such a bending takes place in the same plane. There are two distinct types of plane bending.

- Bond-angle scissor cutting.

- When both bonds are relocating in the same plane while maintaining the same angle, the system is rocking.

B. Bending out of round (γ)

Such a twist displaces the molecular plane beyond the molecule.

- Both atoms travel in the same direction, to one side of the plane, during a wagging motion.

- Turning that places one atom slightly above and the other slightly below the plane (Mendes and Duarte 2021).

2.4.3 Torsion vibration (τ)

Torsional vibration is caused by the reciprocating combustion engine's pulse torque (Geveci *et al.* 2005) fluctuating propeller power output, and the power transmission system's torsional elasticity. The system's crankshaft, intermediate shaft, propeller shaft, and any additional optional parts. Couplings and gears are needed to transmit the static torque as well as the additional dynamic torque. Researching methods for (Wilson 1963, Nestorides 1958).

2.5 Molecular Modeling with Quantum Mechanical Methods

The most powerful and efficient graphics software in contemporary molecular modeling technologies is connected to a broad variety of computer systems ranging from desktop

PCs (and even portable devices) to massively parallel supercomputers. The previous decade has seen significant advancements in our ability to visualize molecular and periodic system structure representations. Not more than a decade ago, almost all students in chemistry and mineralogy were required to physically handle authentic ball-and-stick models of molecules and crystals in order to better grasp the structure and arrangement of atoms (Rouvray 1995).

Simulations using molecular dynamics (MD). Protein Data Bank entry 2W3M, which has a resolution of 1.60, contains the starting enzyme structure of human DHFR. Brookhaven National Laboratory's bank. The MKTOP program was used to create the ligand topologies (Ribeiro *et al.* 2008). The receptor-ligand complexes' MD simulations were utilizing the GROMACS 4.0 simulation tool (Berendsen *et al.* 1995) using the rigid SPC water and the OPLS-AA force field (van Buuren *et al.* 1993). a cubic box with cyclical boundary conditions and model (Berendsen *et al.* 1981). There were roughly 14 500 water molecules in all.

2.5.1 Quantum mechanics equation of motion: Schrödinger equation

To solve the time-independent many-particle Schrödinger equation, for (absolute) molecular energies beyond spectroscopic accuracy, corresponding to different nonrelativistic quantum numbers N , N_z , p , S_a , MS_a , S_b , MS_b ,..., a general $(np + 1)$ -particle variation approach was developed in Refs. Since we didn't want to artificially divide particles into categories, our computational approach works for all values of the $3(np + 1)$ physical parameters (i.e., particle mass, electric charge, and spin, which can be either bosonic or fermionic) within the allowed physical range (i.e., $i = 1, \dots, np + 1$). In the following sections, we'll go through the specifics of the variational approach in light of the following criteria:

(1) Cartesian coordinates that are either "translationally invariant" (TI) or "laboratory-fixed" (LF).

(2) Hamiltonian, both the TI and LF varieties.

(3) ECGs modified with a polynomial prefactor in order to account for spatial symmetries are the basis functions.

(4) Elements of a matrix may be expressed using infinite-precision arithmetic or analytic expressions with quasi-normalization.

(5) Eigensolver with non-orthogonal basis sets, numerical handling of near-linear relationships, and direct diagonalization using LAPACK library methods.

(5 + 1) Expanding and refining the basis set function by function, the rapid eigenvalue estimator, sampling-importance resampling, a random walk, or Powell's approach are all examples of ways to parameterize the basis functions.

2.5.2 Born - Oppenheimer approach

Since the molecule is seen as a quantum system in pre-Born-Oppenheimer (pre-BO) theory, electrons and atomic nuclei are given equal weight. This method differs significantly from the conventional quantum chemistry technique, which emphasizes treating electron and nucleon motion independently. Future advancements and applications might benefit greatly from a completely quantum mechanical explanation of molecules. More generally, it could be used to avoid the time-consuming computation and fitting of potential energy surfaces and non-adiabatic coupling vectors while still accounting for the quantum nuclear motion, also known as "molecular quantum dynamics." This would be especially useful for defining new schemes for metrology and testing fundamental physical theories. The assessment identifies crucial technical and fundamental outstanding problems that need to be answered to realize these objectives. What's most intriguing is that the difficulties inherent in reconciling pre-BO theory with classical chemistry knowledge are comparable to the measurement issue in quantum physics.

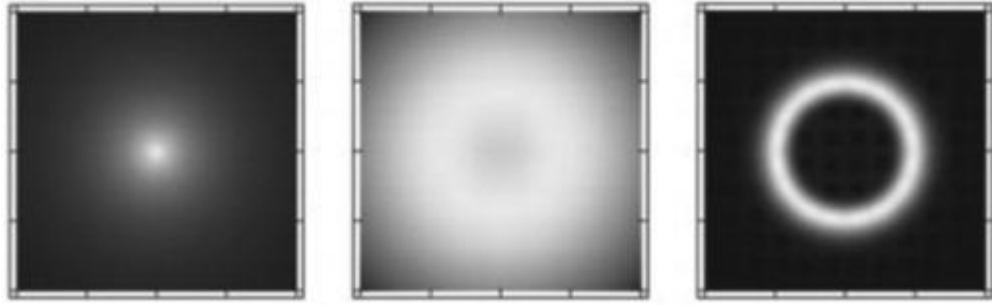


Figure 2.3 Per-Born-Oppenheimer theory (Mátyus 2019)

2.5.3 Variation method

Kikuchi pioneered the cluster variation approach (CVM) (Kikuchi 1951). The Bethe-Peierls approximation (Bethe 1935, Peierls 1936) for equilibrium statistical mechanics of lattice (Ising-like) models was proposed in 1951, and its extension has been analyzed in many textbooks (Plischke and Bergersen 1994, Lavis and Bell 1999). The cubic (or triangular, or face-centered cubic) lattice approximation of the CVM for the Ising model is the current gold standard, and Kikuchi presented a combinatorial derivation of this approximation. Since its origin, the idea has been used and recast in many fields, but statistical physics and materials science have benefited the most (Morita *et al.* 1994).

2.5.4 Hartree - Fock method

One of the simplest approximating theories for the many-body Hamiltonian is Hartree Fock theory. The genuine many-body wavefunction is approximated by the assumption that it may be expressed in terms of a single Slater determinant.

By describing the particle's connection with the outside environment as an interaction with some average (mean) field, Hartree-Fock reduces the multi-particle issue to a one-particle problem.

When characterizing the electronic structure of atoms, the Hartree Fock technique is the practical solution to solve quantum mechanics difficulties.

For a system with a single determinant wavefunction, this is the lowest achievable energy. The energy is the Hartree-Fock energy; the molecular orbitals responsible for this limit are termed Hartree-Fock orbitals; and the wavefunction that determines this limit is called the Hartree-Fock wavefunction.

The electric potential energy of a hydrogen atom in its ground state is equal to the hartree energy, in absolute value. An H-atom's ground-state electron has an energy of , where $E_H = 2 R_\infty \cdot h c$. The 2006 CODATA recommended value was $E_H = 4.35974394 (22) \times 10^{-18} \text{ J} = 27.21138386 (68) \text{ eV}$.

2.5.5 Density functional method (DFT)

The density function theory is widely used in quantum calculations due to its versatility (it can be applied to different systems quickly and cheaply) and importance (it is one of the most important methods used in theoretical physics and chemistry for determining the properties of a multi-particle system). Many-body systems, such as atoms, molecules, and the condensed phases, are studied in physics, chemistry, and materials science using computational quantum mechanical models to examine their electronic structure (or nuclear structure; essentially the ground state). In this theory, the features of a system with many electrons are calculated using functionals, or functions of functions. At density functional theory, these are functionals of the electron density at different locations. Computational chemistry, physics, and the study of condensed-matter physics all make extensive use of density-functional theory.

Since the 1970s, DFT calculations have been widely used in the field of solid-state physics. DFT was not considered accurate enough for quantum chemistry calculations until the approximations used in DFT were significantly updated in the 1990s to better capture the exchange and correlation interactions. When compared to the likes of exchange only Hartree-Fock theory and its progeny like electron correlation, the computational costs of this technique are negligible. DFT has become an essential tool for nuclear spectroscopy methods like Mössbauer spectroscopy and perturbed angular correlation that aim to identify the origin of localized electric field gradients in crystals.

Despite recent advancements, density functional theory still struggles to describe intermolecular interactions (essential to understanding chemical reactions), in particular van der Waals forces (dispersion); charge transfer excitations; transition states; global potential energy surfaces; dopant interactions; some strongly correlated systems; and calculations of the band gap and ferromagnetism in semiconductors.

2.6 Properties Calculated From Energy

2.6.1 Potential energy surface

By stating where each atom is located within the molecule, the structure of the molecule can be determined. A molecule has a specified amount of energy for a particular structure and electronic state. The term "potential energy surface" how a molecule's energy changes depending on its condition vary depending on the molecule's structure. A straightforward depiction of a potential energy surface Figure 2.4 displays the vertical energy as a function of two spatial (geometric) axes. These two lines represent the horizontal axis. The Born-Oppenheimer approximation allows us to calculate potential energy surfaces and conceptualize molecular structure.

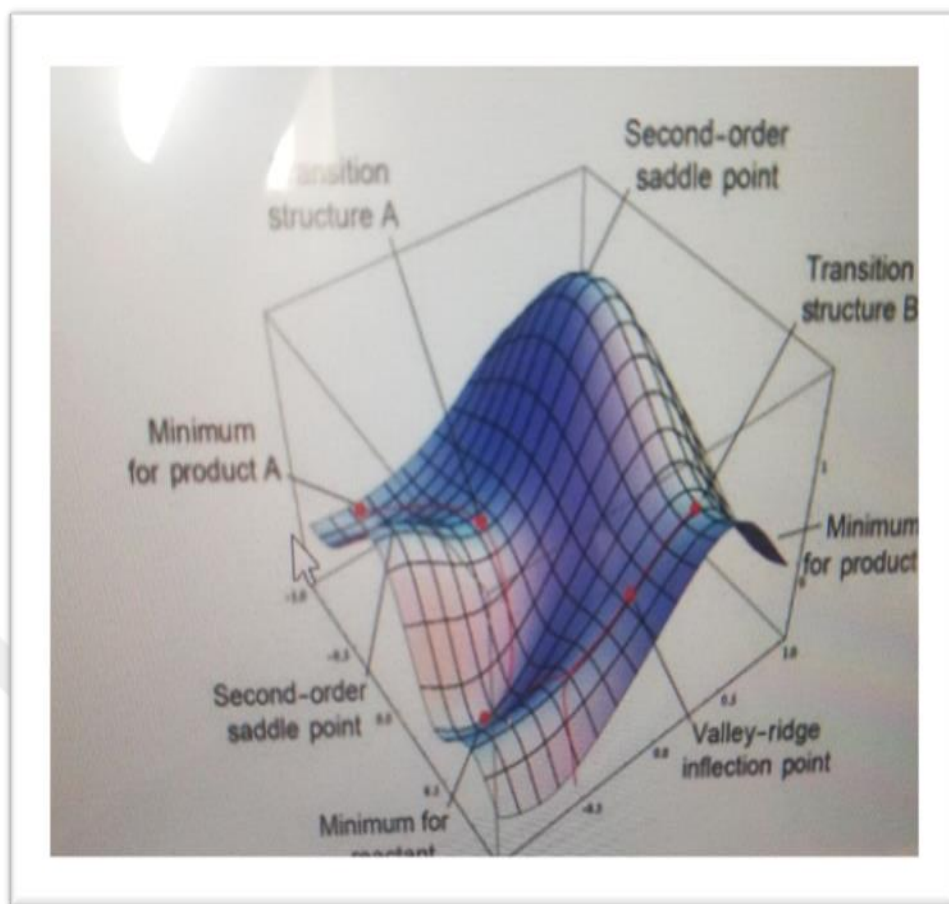


Figure 2.4 Minima, transition structures, second-order saddle points, reaction routes, and an inflection point at a valley ridge are all shown on the model's potential energy surface

In order to separate nuclear motion from electron mobility. By solving the electronic structure problem for a certain set of nuclear positions, the energy of a molecule may be calculated within the Born-Oppenheimer approximation. The difference in size and speed between nuclei and electrons causes this. The energy of a molecule may be expressed as a parametric function of the nuclear locations by repeating this process for each possible configuration of the nuclei. Figure 2.4 shows a potential energy surface that has valleys, peaks, and passes and may be interpreted as a topographical map. Even though most molecular characteristics may be defined by a maximum of two geometric components, the majority of molecules include more than two such components. Potential energy surfaces may be thought of as a three-dimensional space, with the reactants, intermediates, and products of a process occupying the valleys. The valley's

equilibrium structure is located at its lowest point. Roughly speaking, the energy liberated in a reaction is equal to the difference in potential energy between the valleys of the product and reactant. It is possible to do calculations based on the molecule's vibrational motion around the equilibrium geometries of the reactant and the product. Adjustments to the enthalpy-free-energy gap are required to include thermal and zero-point energy (McQuarrie 1973). A wide variety of physical processes, including crystallization, phase transition of materials (with the change of coordination), and heterogeneous catalytic reactions, require molecules/materials establishing and breaking chemical bonds at the minority/defective sites in nanostructures. The lack of theoretical methodologies and effective computational tools makes direct modeling of these processes difficult even with advanced supercomputing capabilities. The conventional atomistic modeling approaches have two major flaws when applied to nanomaterial systems with hundreds of atoms: inaccurate potential energy surface descriptions and wasteful calculations (PES). For instance, $O(N^2)$ scales normally for the cost of computing the electrical structure. Typically, the number of atoms in the simulation does not exceed a few hundred. In 2018, work on the LASP initiative will start up in the first quarter. Two sophisticated simulation tools have been created by the Liu group over the last decade, and the major goal is to merge them into a single package for easier usage. Stochastic surface walking (SSW) is the basis for these technologies, which I use to explore PES networks worldwide (Shang *et al.* 2013, Shang *et al.* 2014).

2.6.2 Geometry optimization

That we are aware of thanks to the Lagrangian interpretation of classical mechanics. Using this fundamental tenet of physics, we may explain a variety of phenomena, such as why light rays pick the path that requires the least amount of time to travel. Because of the exponentially growing number, these optimization tasks are regarded as challenging. Many potential solutions as the subject system gets bigger. Classification of optimization issues in the non-deterministic polynomial complexity class (NP) (Jong *et al.* 1989) It is impossible to reduce their solution time to a polynomial without using an approximation because their solution time scales exponentially with system size. Because these exponentially growing solution candidates in the configuration space

correspond to local extrema that are topologically similar to the desired global extremum, the only way to tell if an extremum is local or global is to keep searching for better solutions. A well-known example of an NP-hard task is the combinatorial problem known as the "traveling salesman problem" (TSP) (Bryant *et al.* 2000). For a salesperson whose objective is to visit a certain number of places before eventually returning to the originating city, it looks for the shortest path. As cities expand in number linearly, the number of other routes grows exponentially, therefore Our disgruntled salesman starts to have trouble figuring out the shortest path for his journey. Another Finding the best stable answer to the well-known NP difficulty class problem in chemical physics A precise number and diversity of atoms or molecules make up the structure of nanoparticles (wales *et al.* 1999).

2.6.3 Slater type orbitals

O-ohata, Taketa, and Huzina a reported on the use of the least squares method to generate Gaussian expansions for a number of Slatertype orbitals (ohata *et al.* 1966). Includes findings for a few of the first-row atoms' mild Hartree-Fock atomic orbital Gaussian expansions. specified least squares expansions of Gaussian Slater-type orbitals The LCAO SCF approximation is used for minimum basis sets in ab initio enquiries (Hehre *et al.* 1968). Molecular orbitals constructed with small expansions (three or four Gaussians) are remarkably similar to those constructed using a collection of Slater-type orbitals (STOs). Small Gaussian expansions of STOs allow for the molecular and atomic investigation of rather massive organic molecules (Hehre *et al.* 1969). In molecular structure simulations, Slater-type orbitals (STO) serve as the atomic basis set and carry out the most basic analytical procedures (Fernández *et al.* 2001).

2.6.4 Gaussian type orbitalis

In molecular quantum-mechanical calculations, selecting reliable foundation atomic orbitals is crucial since the structure of these orbitals affects the caliber of molecular properties. Recently, basis functions of the Gaussian type orbitals have gained popularity due to their practicality (GTOs). The need for a straightforward method of

calculating integrals involving several centers drove us to design this. The GTO's basis functions blatantly flout two mathematical restrictions for atomic electronic distributions: the cusp condition at the origin and the cusp condition at the origin (Kato 1957). For Gaussians, a similar issue arises (Slater 1928).

2.6.5 Basis sets

Multicenter integrals can be computed using Gaussian basis sets, but much care must be taken while creating these bases sets to achieve the perfect balance between accuracy and efficiency. While other Hartree-Fock optimized basis sets like the well-known Pople's 6-31G** basis set (Hehre et al. 1968, Hariharan *et al.* 1972). Give logical geometries for the molecules for molecular OFT calculations, Hartree-Fock optimized basis sets are insufficient since reaction energies are more delicate. For the newall-electron LSD, optimized basis sets have been designed with this goal in mind (Godbout et al.in press) are used for all elements in the current investigation, from H to Xe. The optimization procedure is built on the work of Tatewaki and Huzinaga (Tatewaki *et al.* 1979). This double-zeta basis set with polarization functions (DZVP) is built from nine s-type, five p-type, and one d-type polarization function for the elements B to Ne, respectively. Three s-type functions and two p-type functions are all that is needed to condense the (621/41/1) primitives. The polarization functions and this result in a reduced set that is [3/2/1]. In this DZVP set, hydrogen is represented by the (41) set. Excellent quality for the valence orbitals and minimum basis set superposition errors (BSSE) are found when comparing these LSD-optimized Gaussian basis sets to energies and orbitals created by a computerized technique (Andzelm *et al.* 1985).

3. MATERIALS AND METHODS

We will do optimization at the DFT/B3LYP/6-311++G (d, p) theoretical level for the first time to discover the most stable structures with the lowest amount of energy. The same framework established in the DMSO phase will then be used to calculate the vibrational frequencies of these compounds and analyze the corresponding ^1H and ^{13}C NMR data. The HOMO and LUMO orbital energies, nonlinear optical properties (NLO), and molecular electrostatic potential (MESP) maps will next be studied using a theoretical level of DFT/B3LYP/6-311++G (d, p). To make sense of the results, it is necessary to compare and contrast them with the theoretically predicted outcomes and the actual experimental data. All calculations will be done using the aforementioned package's Gaussian 09 and Gauss View 5 programs.

4. RESULTS AND DISCUSSION

4.1 Structural Parameters

The three-dimensional approximate geometry of the (E)-4-((p-tolylimino)methyl)phenol schiff base was drawn in the GaussView 5.0 program. First of all, in order to find the most stable structure of the molecule, gas phase geometry optimization was carried out using the semi-empirical PM3 self-consistent molecular orbital method using the Gaussian 09 program. Then, the geometry of the molecule was optimized with DFT method, 6-311G++(d,p) basis set including diffuse and polarize functions, and the most stable positions and spatial structure of each atom in the compound were determined with minimum energy.

Bond lengths and bond angles of the molecule were theoretically determined using the optimal structure. When the B3LYP technique is used to optimize molecules with a 6-311++G (d,p) basis set, the resulting bond lengths and bond angles are in agreement with the atomic numbers presented in Figure 4.1. Also included is Table 4.1. Comparisons were made between the theoretically estimated C-H bond lengths in the phenyl ring of (E)-4-((p-tolylimino)methyl)phenol schiff base and the C-C bond lengths reported in the literature to determine the extent to which the former agree with the latter. In the literature, all C-H bond lengths in the benzene ring have been measured as 1.084 Å, and C-C bond lengths as 1.397 Å (Fesenden and Fesenden 1986, İközler 1996). The averages of C-H bond lengths in the phenyl group in the structure of the related compound were found as B3LYP/6-311G++(d, p) 1.074 Å.

The averages of phenyl C-C bond lengths were obtained as 1.403 Å. In the literature, this value was measured as 1.392 Å experimentally and 1.402 Å was calculated theoretically by DFT/B3LYP method. The average C-C bond length found according to the B3LYP basis set was found to be close to the value in the literature (Fesenden and Fesenden 1986, Alyar *et al.* 2012).

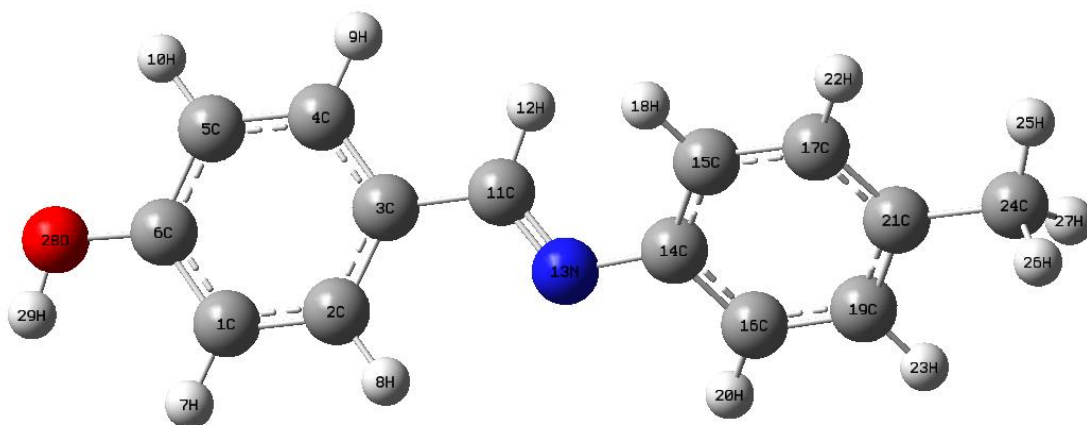


Figure 4.1 Using the B3LYP/6-311++G(d, p) density functional, the optimal molecular structure of (E)-4-((p-tolylimino)methyl)phenol was determined

Table 4.1 The (E)-4-((p-tolylimino)methyl)phenol bond characteristics were computed using the B3LYP/6-311++G(d,p) basis set

Bond Length	B3LYP-6311++G(d,p)	Bond Angles	B3LYP-6311++G(d,p)	Torsion Angle	B3LYP-6311++G(d,p)
C1-C2	1.389	C2-C1-C6	119.79	C6-C1-C2-C3	0.120
C1-C6	1.408	C2-C1-H7	121.38	C6-C1-C2-C8	-179.967
C1-H7	1.019	C6-C1-H7	118.82	H7-C1-C2-C3	-179.963
C2-C3	1.414	C1-C2-C3	120.98	C2-C1-C6-C5	-0.063
C2-H8	1.091	C1-C2-H8	120.70	C2-C1-C6-O28	179.938
C3-C4	1.408	C3-C2-H8	118.31	H-C1-C6-C5	-179.983
C3-C11	1.462	C2-C3-C4	118.41	H7-C1-C6-O28	0.018
C4-C5	1.396	C2-C3-C11	121.89	C1-C2-C3-C4	-0.097
C4-H9	1.093	C4-C3-C11	119.68	C1-C2-C3-C11	179.871
C5-C6	1.404	C3-C4-C5	121.10	H8-C2-C3-C4	179.987
C5-G10	1.094	C3-C4-H9	119.45	H8-C2-C3-C11	-0.044
C6-O28	1.371	C5-C4-H9	119.44	C2-C3-C4-C5	0.018
C11-H12	1.109	C4-C5-C6	119.56	C2-C3-C4-H9	179.964
C11-N13	1.290	C4-C5-H10	120.31	C11-C3-C4-C5	-179.951
N13-C14	1.405	C6-C5-H10	120.12	C11-C3-C4-C9	-0.006
C14-C15	1.411	C1-C6-C5	120.13	C2-C3-C11-C12	179.472
C14-C16	1.411	C1-C6-O28	117.13	C2-C3-C11-N13	-1.554
C15-C17	1.398	C5-C6-O28	122.72	C4-C3-C11-H12	-0.560C
C15-H18	1.092	C3-C11-H12	115.61	C4-C3-C11-N13	178.414
C16-C19	1.394	C3-C11-N13	122.90	C3-C4-C5-C6	0.037
C16-H20	1.092	H12-C11-N13	121.47	C3-C4-C5-H10	-179.983
C17-C21	1.405	C11-N13-C14	119.96	H9-C4-C5-C6	-179.908
C17-H22	1.094	N13-C14-C15	123.55	H9-C4-C5-H10	0.072
C19-C21	1.408	N13-C14-C16	118.13	C4-C5-C6-C1	-0.015
C19-H23	1.094	C15-C14-C16	118.25	C4-C5-C6-O28	179.984

Table 4.1 The (E)-4-((p-tolylimino)methyl)phenol bond characteristics were computed using the B3LYP/6-311++G(d,p) basis set (Continued)

C21-C24	1.511	C14-C15-C17	120.46	H10-C5-C6-C1	-179.995
C24-H25	1.103	C14-C15-H18	119.64	H10-C5-C6-O28	0.004
C24-H26	1.099	C17-C15-H18	119.85	C1-C6-O28-H29	179.818
C24-H27	1.101	C14-C16-C19	120.66	C5-C6-O28-H29	-0.181
O28-H29	0.972	C14-C16-H20	118.37	C3-C11-N13-C14	176.314
		C19-C16-H20	120.95	H12-C11-N13-C14	-4.771
		C15-C17-C21	121.94	C11-N13-C14-C16	144.157
		C15-C17-H22	119.27	N13-C14-C15-C17	-178.597
		C21-C17-H22	119.28	N13-C14-C15-H18	-0.867
		C16-C19-C21	121.38	C16-C14-C15-C17	-1.432
		C16-C19-H23	119.25	C16-C14-C15-H18	176.298
		C21-C19-H23	119.36	N13-C14-C16-C19	179.751
		C17-C21-C19	117.69	N13-C14-C16-H20	-1.322
		C17-C21-C24	121.29	C15-C14-C16-C19	2.430
		C19-C21-C24	120.97	C15-C14-C16-H20	-178.643
		C21-C24-H25	111.26	C14-C15-C17-C21	-0.122
		C21-C24-H26	111.41	C14-C15-C17-H22	179.172
		C21-C24-H27	111.47	H18-C15-C17-C21	-177.847
		H25-C24-H26	107.43	H18-C15-C17-H22	1.447
		H25-C24-H27	107.07	C14-C16-C19-C21	-1.906
		H26-C24-H27	107.96	C14-C16-C19-H23	178.798
		C6-O28-H9	109.01	H20-C16-C19-C21	179.196
				H20-C16-C19-H23	-0.100
				C15-C17-C21-C19	0.696
				C15-C17-C21-C24	178.801
				H22-C17-C21-C19	-178.597
				H22-C17-C21-C24	-0.493
				C16-C19-C21-C17	0.313
				C16-C19-C21-C24	-177.798
				H23-C19-C21-C17	179.608
				H23-C19-C21-C24	1.497
				C17-C21-C24-H25	-102.546
				C17-C21-C24-H26	17.323
				C17-C21-C24-H27	138.004
				C19-C21-C24-C25	75.496
				C19-C21-C24-H26	-164.634
				C19-C21-C24-H27	-43.954

4.2 Vibrational Assignment

Using the B3LYP/6-311++G(d,p) basis set, we calculated the vibrational frequencies of the molecule and compared our findings to those found in the published experimental literature. The primary vibrations studied were those of OH stretching, symmetric and antisymmetric CH₃ stretching, in-plane and out-of-plane CH bending, and aromatic CH stretching. Figure 4 shows the FT-IR spectrum of the experimentally produced (E)-4-((p-tolylimino)methyl)phenol molecule.² Frequencies of vibration, both theoretical and experimental, are listed in Table 4.2.

In the literature, aromatic CH vibrational stretching are in the frequency range of 3100-3000 cm⁻¹ (in the form of multiple bands), CH₃ vibrations are in the range of 3000-2850 cm⁻¹, in-plane CH bending vibrations are in the range of 1100-1500 cm⁻¹ as sharp peaks, out-of-plane bending vibrations it is seen that it is given in the range of 800-1000 cm⁻¹ (Versanyi 1973, Jag 2001, Du *et al.* 2002).

When the IR spectrum of the compound is examined, the stress peak of the OH group is observed at 3291-2388 cm⁻¹. These peak calculated at 3291 cm⁻¹. The peaks of aliphatic C-H stretching were detected at 2919 cm⁻¹ and 2861 cm⁻¹. These peak calculated at 2909 cm⁻¹. Aromatic C=C peaks were detected at 1605 cm⁻¹ and 1574 cm⁻¹, -CH=N stretching at 1605 cm⁻¹ and Ar-O stretching peaks at 1284 cm⁻¹, 1241 cm⁻¹ and 1162 cm⁻¹. Aromatic C=C peaks were calculated at between 1603-1199 cm⁻¹, -CH=N stretching at 1585 cm⁻¹ and Ar-O stretching peaks at 1496 and 1255 cm⁻¹.

The aromatic C-H peak of the -CH₃ group is observed at 3027 cm⁻¹ (Erdik, 2008). These peaks calculated at 3037, 3008 and 2952 cm⁻¹. Aromatic CH symmetric stretching vibrations calculated at 3127, 3114 and 3103 cm⁻¹. Also aromatic CH asymmetric vibrations calculated at 3114, 3096, 3083, 3079 and 3037 cm⁻¹.

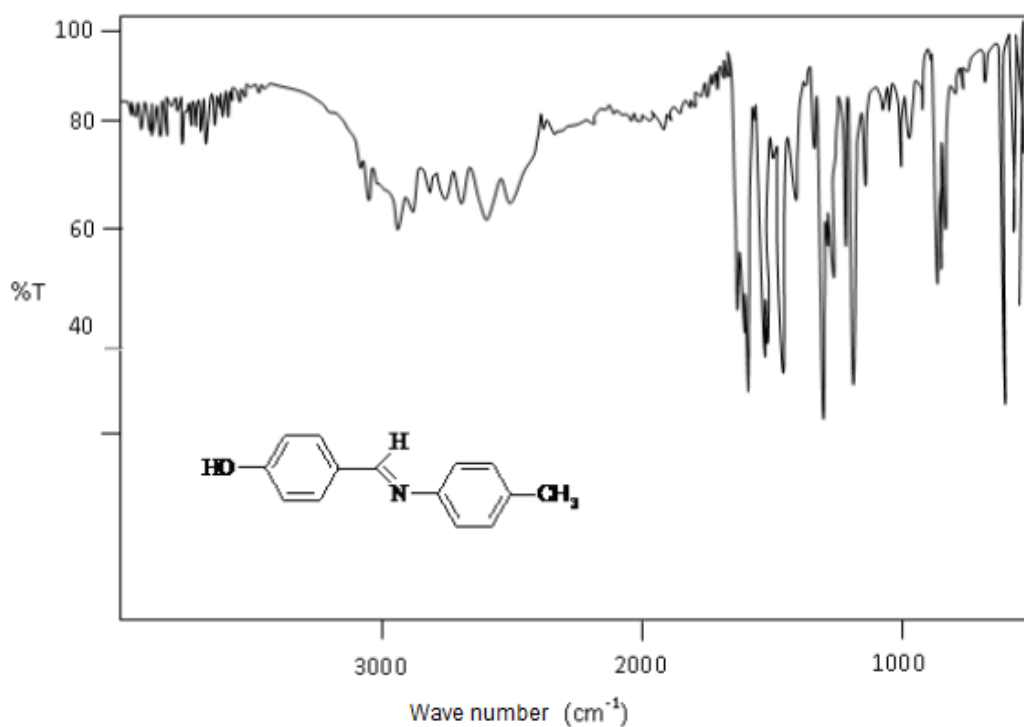


Figure 4.2 FT-IR spectrum of (E)-4-((p-tolylimino)methyl)phenol compound (Silku 2014)

Table 4.2 Vibration frequencies of (E)-4-((p-tolylimino)methyl)phenol compound, both theoretically and experimentally determined via Fourier transform infrared spectroscopy

Mode	Exp. (Silku 2014)	Calculated	Intensity	Descriptions
81	3291	3706	98.8	$\nu(\text{OH})$
80		3127	6.16	$\nu_s(\text{CH})_{\text{ring1}}$
79		3114	1.78	$\nu_{\text{as}}(\text{CH})_{\text{ring1}}$
78		3114	8.03	$\nu_s(\text{CH})_{\text{ring2}}$
77		3103	10.76	$\nu_s(\text{CH})_{\text{ring2}}$
76		3096	13.19	$\nu_{\text{as}}(\text{CH})_{\text{ring1}}$
75		3083	22.28	$\nu_{\text{as}}(\text{CH})_{\text{ring2}}$
74		3079	18.44	$\nu_{\text{as}}(\text{CH})_{\text{ring2}}$
73		3078	22.89	$\nu_{\text{as}}(\text{CH})_{\text{ring1}}$
72	3027	3037	16.08	$\nu_{\text{as}}(\text{CH}_3)$
71		3008	18.76	$\nu_{\text{as}}(\text{CH}_3)$
70		2952	51.18	$\nu_s(\text{CH}_3)$
69	2919	2909	49.46	$\nu(\text{C1H}) + \beta(\text{CCH})_{\text{ring1,2}}$
68		1623	35.74	$\nu(\text{C=N}) + \nu(\text{CC})_{\text{ring1,2}}$
67		1603	139.8	$\nu(\text{CC})_{\text{ring1,2}} + \beta(\text{CCH})_{\text{ring1,2}} + \beta(\text{COH})$
66	1605	1585	45.4	$\nu(\text{C=N}) + \nu(\text{CC})_{\text{ring1,2}} + \beta(\text{CCH})_{\text{ring1}} + \beta(\text{COH})$
65	1574	1566	179.5	$\nu(\text{C=N}) + \nu(\text{CC})_{\text{ring1}} + \beta(\text{CCH})_{\text{ring1}} + \beta(\text{COH})$

Table 4.2 Vibration frequencies of (E)-4-((p-tolylimino)methyl)phenol compound, both theoretically and experimentally determined via Fourier transform infrared spectroscopy (Continued)

64		1550	2.97	$\nu(\text{CC})_{\text{ring2}} + \beta(\text{CCH})_{\text{ring2}} + \beta(\text{C-CH}_3)$
63		1496	156.1	$\nu(\text{CO}) + \nu(\text{CC11}) + \nu(\text{CC})_{\text{ring1}} + \beta(\text{CCH})_{\text{ring1}}$
62		1481	14.36	$\nu(\text{C21C24}) + \nu(\text{C14N}) + \nu(\text{CC})_{\text{ring2}} + \beta(\text{CCH})_{\text{ring2}}$
61		1446	8.5	$\beta(\text{CH}_3) + \beta(\text{CCH})_{\text{ring2}}$
60		1438	7.02	$\nu(\text{CC})_{\text{ring}} + \beta(\text{CN}_{21}\text{H}) + \beta(\text{CCH})_{\text{ring}}$
59		1426	1.08	$\nu(\text{CC})_{\text{ring1}} + \beta(\text{CN}_{12}\text{H}) + \beta(\text{CCH})_{\text{ring1}} + \beta(\text{COH})$
58		1397	1.26	$\nu(\text{CC})_{\text{ring}} + \beta(\text{CN}_{12}\text{H}) + \beta(\text{CCH})_{\text{ring2}}$
57		1370	17.71	$\nu(\text{CC})_{\text{ring1}} + \beta(\text{CN}_{12}\text{H}) + \beta(\text{CCH})_{\text{ring1}} + \beta(\text{COH})$
56		1362	0.02	$\beta(\text{CH}_3)$
55		1345	5.68	$\nu(\text{CC})_{\text{ring1}} + \beta(\text{CN}_{12}\text{H}) + \beta(\text{COH})$
54		1316	0.07	$\nu(\text{CC})_{\text{ring2}} + \beta(\text{CCH})_{\text{ring2}} + \beta(\text{C-CH}_3) + \beta(\text{CN}_{12}\text{H}) + \beta(\text{COH})$
53		1286	65.1	$\beta(\text{CCH})_{\text{ring1+2}} + \beta(\text{COH})$
52		1277	12.33	$\beta(\text{CCH})_{\text{ring1,2}}$
51	1241	1255	135.2	$\nu(\text{CO}) + \beta(\text{CN}_{12}\text{H}) + \beta(\text{CCH})_{\text{ring1}}$
50		1231	21.44	$\nu(\text{C14N}) + \nu(\text{CC})_{\text{ring2}} + \beta(\text{CCH})_{\text{ring1}}$
49		1199	5.20	$\nu(\text{CC})_{\text{ring2}} + \beta(\text{CCH})_{\text{ring2}} + \beta(\text{C-CH}_3)$
48		1187	28.7	$\nu(\text{C14N}) + \beta(\text{CN}_{12}\text{H}) + \beta(\text{CCH})_{\text{ring1,2}}$
47		1157	154.4	$\beta(\text{CCH})_{\text{ring1}} + \beta(\text{COH})$
46		1153	5.09	$\nu(\text{C14N}) + \beta(\text{CCH})_{\text{ring1,2}}$
45		1145	188.3	$\beta(\text{CCH})_{\text{ring1,2}} + \beta(\text{COH})$
44		1100	9.88	$\beta(\text{CCH})_{\text{ring2}} + \beta(\text{C-CH}_3)$
43		1088	12.29	$\beta(\text{CCH})_{\text{ring1}} + \beta(\text{COH})$
42		1017	13.44	$\beta(\text{C-CH}_3)$
41		998.9	1.79	$\beta(\text{CCH})_{\text{ring2}} + \beta(\text{C-CH}_3)$
40		992.8	0.26	$\beta(\text{CCH})_{\text{ring1}}$
39		971.7	0.88	$\beta(\text{CCH})_{\text{ring2}} + \beta(\text{C-CH}_3)$
38		956.3	10.84	$\nu_{\text{as}}(\text{CH})_{\text{ring1}} + \beta(\text{C-CH}_3)$
37		945.5	2.18	$\nu_{\text{as}}(\text{CH})_{\text{ring1,2}}$
36		930.9	0.54	$\nu_{\text{as}}(\text{CH})_{\text{ring2}}$
35		908.2	0.98	$\nu_{\text{as}}(\text{CH})_{\text{ring2}} + \beta(\text{CN}_{12}\text{H})$
34		894.6	0.41	$\nu_{\text{as}}(\text{CH})_{\text{ring1}}$
33		871.0	18.1	$\nu(\text{C=N}) + \nu(\text{CC})_{\text{ring1,2}} + \beta(\text{CCH})_{\text{ring1}} + \beta(\text{COH})$
32		838.0	1.95	$\nu(\text{C-N}) + \beta(\text{CCC})_{\text{ring1,2}}$
31		818.7	43.9	$\gamma(\text{CCH})_{\text{ring1,2}}$
30		807.5	14.2	$\gamma(\text{CCH})_{\text{ring2}} + \beta(\text{CCH})_{\text{ring2}}$
29		799.1	14.1	$\beta(\text{CCC})_{\text{ring1}} + \gamma(\text{CCH})_{\text{ring2}}$
28		783.0	12.1	$\gamma(\text{CCH})_{\text{ring2}} + \beta(\text{C-CH}_3) + \beta(\text{CCH})_{\text{ring1}}$
27		774.3	14.5	$\gamma(\text{CCH})_{\text{ring1}}$
26		744.0	5.52	$\nu(\text{C--N}) + \nu(\text{CC})_{\text{ring2}} + \beta(\text{CCC})_{\text{ring1,2}} + \beta(\text{CCH})_{\text{ring1}}$
25		704.0	3.43	$\gamma(\text{CCH})_{\text{ring1,2}} + \gamma(\text{CH}_2)$
24		692.5	1.25	$\gamma(\text{C=NH}) + \gamma(\text{CCH})_{\text{ring1,2}} + \gamma(\text{CH}_2)$
23		636.1	0.32	$\beta(\text{CCC})_{\text{ring1,2}} + \beta(\text{CCH})_{\text{ring1,2}}$
22		629.2	0.60	$\gamma(\text{CCH})_{\text{ring1,2}} + \beta(\text{CCC})_{\text{ring1,2}} + \beta(\text{CCH})_{\text{ring1,2}}$
21		577.8	10.9	$\beta(\text{CCH})_{\text{ring1+2}} + \beta(\text{COH}) + \gamma(\text{CCH})_{\text{ring1,2}}$
20		525.8	29.8	$\gamma(\text{CCH})_{\text{ring1,2}} + \beta(\text{CCH})_{\text{ring2}} + \beta(\text{C-CH}_3)$
19		510.0	4.06	$\beta(\text{CCH})_{\text{ring1+2}} + \beta(\text{C=NH}) + \gamma(\text{CCH})_{\text{ring1}}$

4.3 NMR Results

Recently, there have been many studies in the literature on NMR chemical shift calculations made by quantum chemical methods (Alyar *et al.* 2012). These studies show that molecular geometric optimization is an important factor for NMR chemical shift values. In fact, NMR spectroscopy has proven to be an outstanding tool for elucidating the structure of large biomolecules. Considering these situations, stable molecular geometric structures are obtained for these theoretical NMR chemical shift calculations.

The chemical shift values obtained as a result of our calculations and the experimental data given in the literature for the (E)-4-((p-tolylimino)methyl)phenol compound are given comparatively in Table 4.3.

Aromatic protons produce signals at 7.4 and 7.9 ppm (Chandramohan *et al.* 2008). As seen in Table 4.3, in our study, these peaks were calculated at range 6.81-8.35ppm with the B3LYP method, and were observed experimentally at range 6.92-7.74 ppm.

When the ¹H-NMR spectrum of the (E)-4-((p-tolylimino)methyl)phenol compound is examined in Figure 4.3, the singlet peak belonging to the OH group at 10.18 ppm and the singlet peak belonging to the imine group at 8.46 ppm show the formation of Schiff base. H2 with aromatic protons belonging to the benzaldehyde phenyl ring (6.92 ppm, d, 2H); H3(7.74 ppm, d, 2H); values, while the aromatic protons of the aniline phenyl ring are H5 (7.17 ppm, d, 2H); H6 (7.12 ppm, d, 2H); values were determined in accordance with the literature. The peak belonging to the methyl group in the structure was determined as a singlet peak at 2.37 ppm.

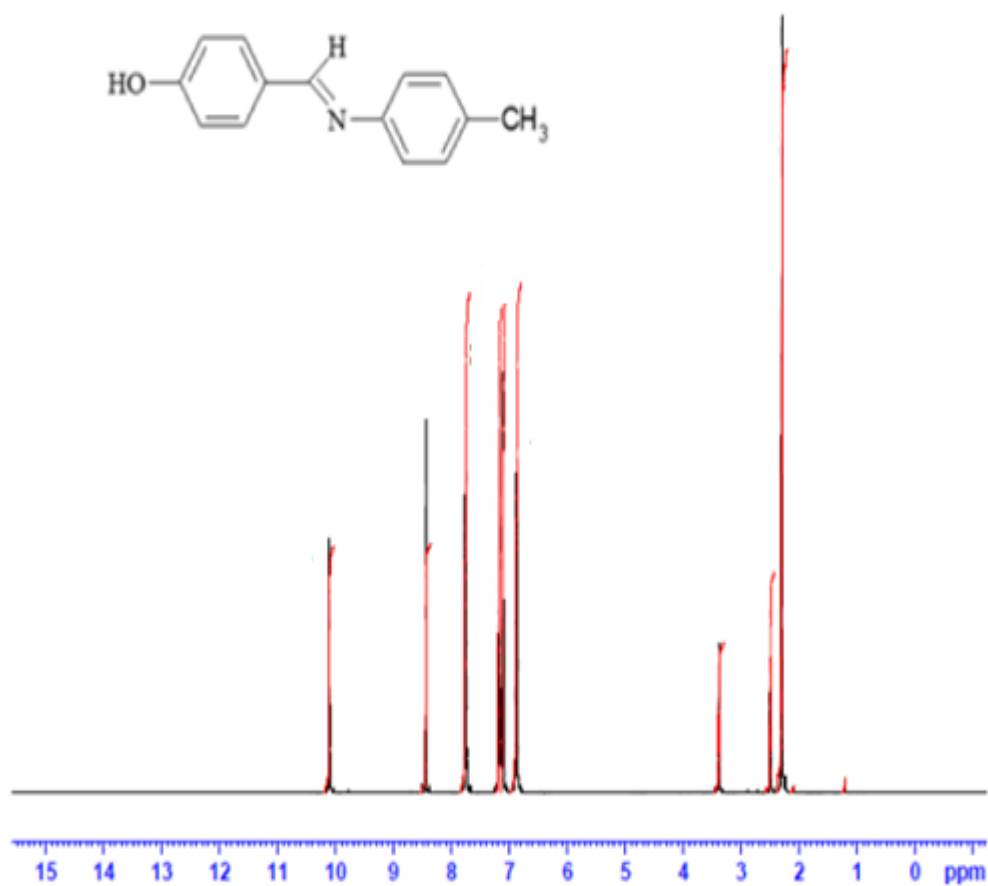


Figure 4.3 ¹H-NMR spectrum of (E)-4-((p-tolylimino)methyl)phenol compound (Silku 2014)

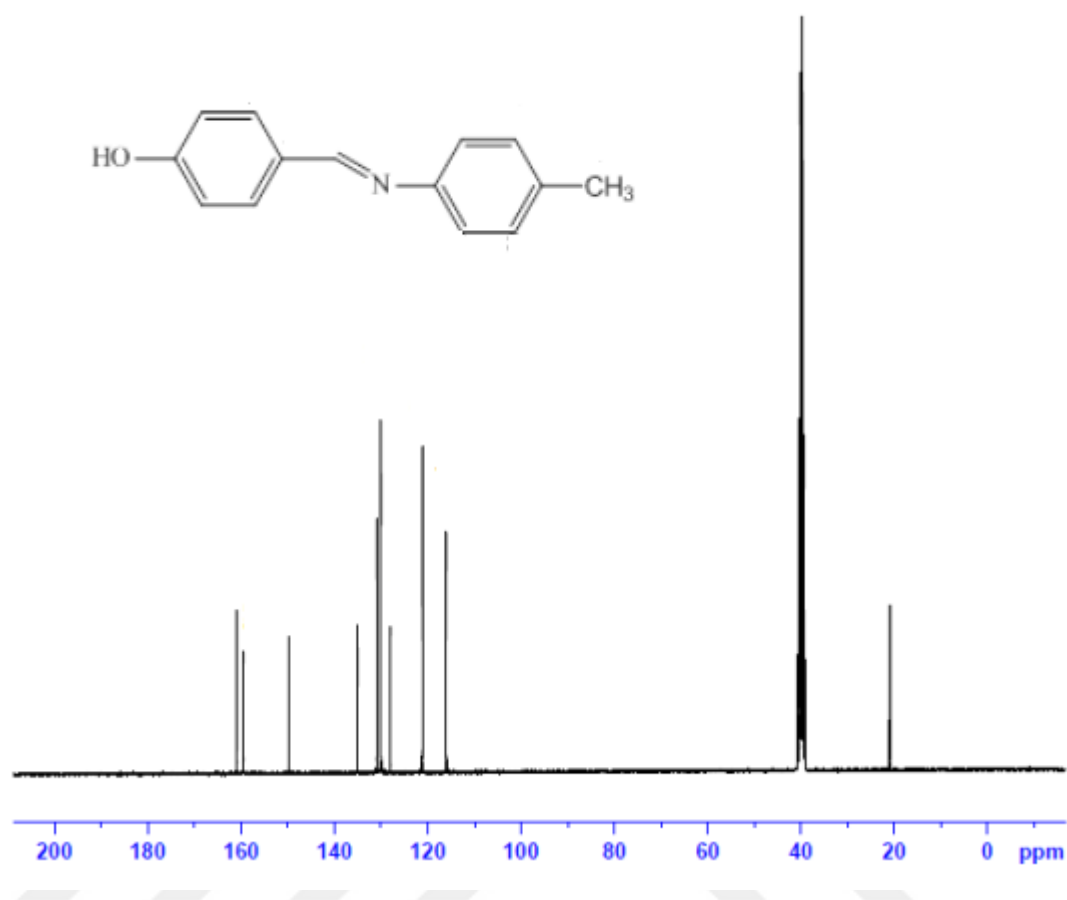


Figure 4.4 ^{13}C -NMR spectrum of (E)-4-((p-tolylimino)methyl)phenol compound (Silku 2014)

When the ^{13}C -NMR spectrum of compound in Figure 4.4 is examined, the peak of the C11 carbon atom belonging to the $-\text{CH}=\text{N}$ group at 159.57 ppm was detected in accordance with the sources. Also, this peak calculated as 157.50 ppm. While the C24 peak belonging to the $-\text{CH}_3$ group in the structure is seen at 21.02 ppm and calculated as 20.36, the peaks belonging to the aromatic ring are respectively, 160.93 ppm C6; 116.07 ppm C1 and C5; 130.99 ppm C2 and C4; 128.08 ppm C3; 149.79 ppm C14; 121.26 ppm C15 and C16; 130.09 ppm C17 and 19; 135.03 ppm C21 peaks are suitable for the sources. These peaks calculated as 160.27 ppm C6; 114.56 and 114.28 ppm for C1 and C5; 129.9 and 135.41 ppm for C2 and C4; 130.13 ppm C3; 150.97 ppm C14. The calculated other peaks can be seen on the Table 4.3.

Table 4.3 ^1H -NMR and ^{13}C -NMR results of (E)-4-((p-tolylimino)methyl)phenol compound

Assignment	$\delta_{\text{exp.}}$	$\delta_{\text{calc.}}$
C6	160.93	160.27
C11	159.57	157.50
C14	149.79	150.97
C21	135.03	137.58
C4	130.99	135.41
C3	128.08	130.13
C17	130.09	129.72
C19	130.09	129.32
C2	130.99	129.9
C16	121.26	125.14
C15	121.26	115.84
C1	116.07	114.56
C5	116.07	114.28
C24	21.02	20.36
H12	8.46	8.355
H8	7.74	8.347
H9	7.74	7.90
H23	7.12	7.354
H22	7.12	7.58
H20	7.17	7.254
H18	7.17	7.066
H10	6.92	7.037
H7	6.92	6.809
H26	2.37	2.579
H27	2.37	2.414
H25	2.37	2.143
$\delta^{13}\text{C} = 175.7-0.963 \delta^{13}\text{C}$ and $\delta^1\text{H} = 31.0-0.970 \delta^1\text{H}$		

4.4 HOMO-LUMO Analyze

Well-known quantum mechanical descriptors, the HOMO and LUMO energies (Zhou and Parr 1990) play a crucial role in regulating a broad variety of chemical interactions. Frontier orbital distribution may be utilized to learn about the molecule's reactivity and locate its active site. Electron density distributions may be utilized to determine molecular orbital geometries, electrostatic potentials, chemical hardness and softness characteristics, and ionization potentials of structures. Molecular orbitals, or HOMOs and LUMOs, go by these names. Here, the highest energy orbital is the one that is occupied, while HOMO refers to the molecule's propensity to give up electrons. The molecule's net gain of electrons is its LUMO. Typically, the orbital with the lowest energy will be free (Gümüş and Atalay 2017). When the molecule's energy difference

(E) is high, there is less fluctuation in the distribution of its electrons, and hence less polarization.

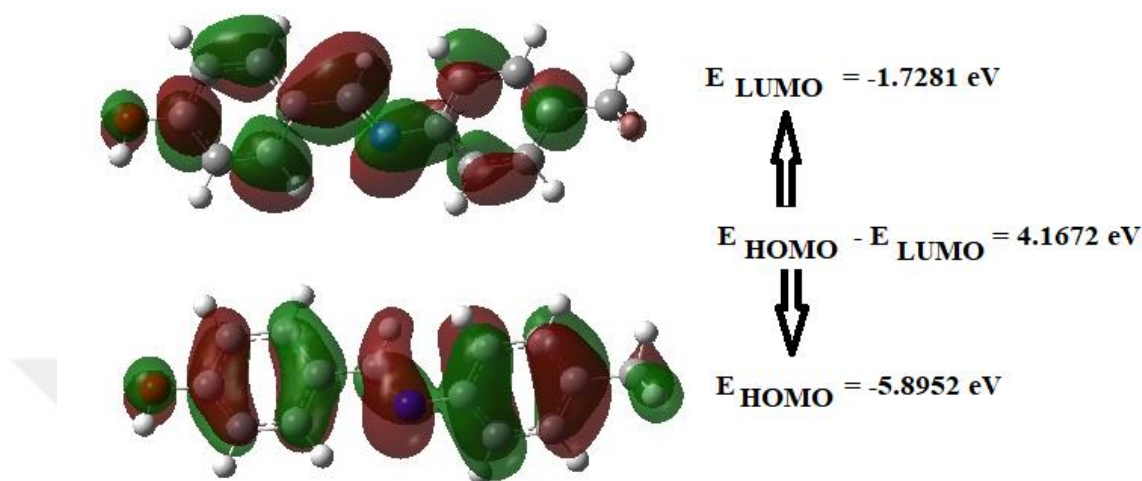


Figure 4.5 The (E)-4-((p-tolylimino)methyl)phenol energy levels and 3D graphs of the HOMO and LUMO states

The structure showing the energy difference between HOMO and LUMO for (E)-4-((p-tolylimino)methyl)phenol compound are given in Figure 4.5. The HOMO and LUMO energies were calculated as -5.8952 eV and -1.7281 eV, respectively. In this case, the energy difference ΔE was calculated as 4.1672 eV.

4.5 Nonlinear Optical (NLO) Properties

Nonlinear optical characteristics (NLO) may be predicted computationally based on polarizability (α) and hyperpolarizability (β) values (Govindarajan *et al.* 2012). Polarizability is the defining characteristic of optical characteristics in organic materials. The material's nonlinear optical characteristics are affected by a property called hyperpolarizability (Leszczynski 2006). A molecule with NLO characteristics has strong polarizability, hyperpolarizability, and dipole moment with a low HOMO-LUMO energy gap.

Maximum hyperpolarizability occurs at the lowest HOMO-LUMO energy gap. highest hyperpolarizability should correspond to highest dipole moment. The average linear polarizability is used in the calculation of nonlinear optical characteristics Equation (4.1).

$$\alpha = 1/3(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (4.1)$$

And for total static hyperpolarizability Equation (4.2)

$$\beta = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{xxy} + \beta_{yzz})^2 + (\beta_{zzz} + \beta_{xxz} + \beta_{yyz})^2]^{1/2} \quad (4.2)$$

Equations are used. In Table 4.4, the polarizability (α_{ave}) and hyperpolarization (β_{tot}) values calculated using the molecule in the gas phase are given.

Table 4.4 Using density functional theory (DFT) with the B3LYP/6-311++G (d,p) basis set, we calculate the electric dipole moment μ (D), the mean polarizability $\langle\alpha\rangle$, and the initial hyperpolarizability (tot)

Parameter	(E)-4-((p-tolylimino)methyl)phenol	Parameter	(E)-4-((p-tolylimino)methyl)phenol
μ_x	-0.6244	β_{xxx}	511.63
μ_y	0.3046	β_{xxy}	176.81
μ_z	0.4111	β_{xyy}	-22.35
μ_{tot}	0.8073	β_{yyy}	38.32
α_{xx}	345.91	β_{xxz}	-124.62
α_{xy}	-1.96	β_{xyz}	32.98
α_{yy}	162.59	β_{yyz}	-17.39
α_{xz}	-1.28	β_{xzz}	38.44
α_{yz}	-0.62	β_{yzz}	-0.37
α_{zz}	105.39	β_{zzz}	-20.67
$\langle\alpha\rangle$ (a.u)	204.63	β_{tot} (a.u)	595.50
$\langle\alpha\rangle$ (esu)	30.32×10^{-24} esu	β_{tot} (esu)	5144.7×10^{-33} esu

α : 1a.u = 0.1482×10^{-24} esu , β : 1a.u = 8.6393×10^{-33} esu

4.6 Molecular Electrostatic Potential Energy (MESP) Map

The molecule-electron-system potential (MESP) is the energy dissipated during the interaction of a unit positive charge with the charge distribution of a molecule. The

MESP map colors the areas with the highest negative potential red and the highest positive potential blue (Cramer 2004). The chemical interactions between two molecules affect the MESP of both molecules when they are close together.

Since it plays such a crucial function, molecular electrostatic potential (MESP) is often negative in regions that are more susceptible to electrophilic attack and positive in regions that are more susceptible to nucleophilic attack (Levine 2000). The compound's MESP map is shown in Figure 4.6.

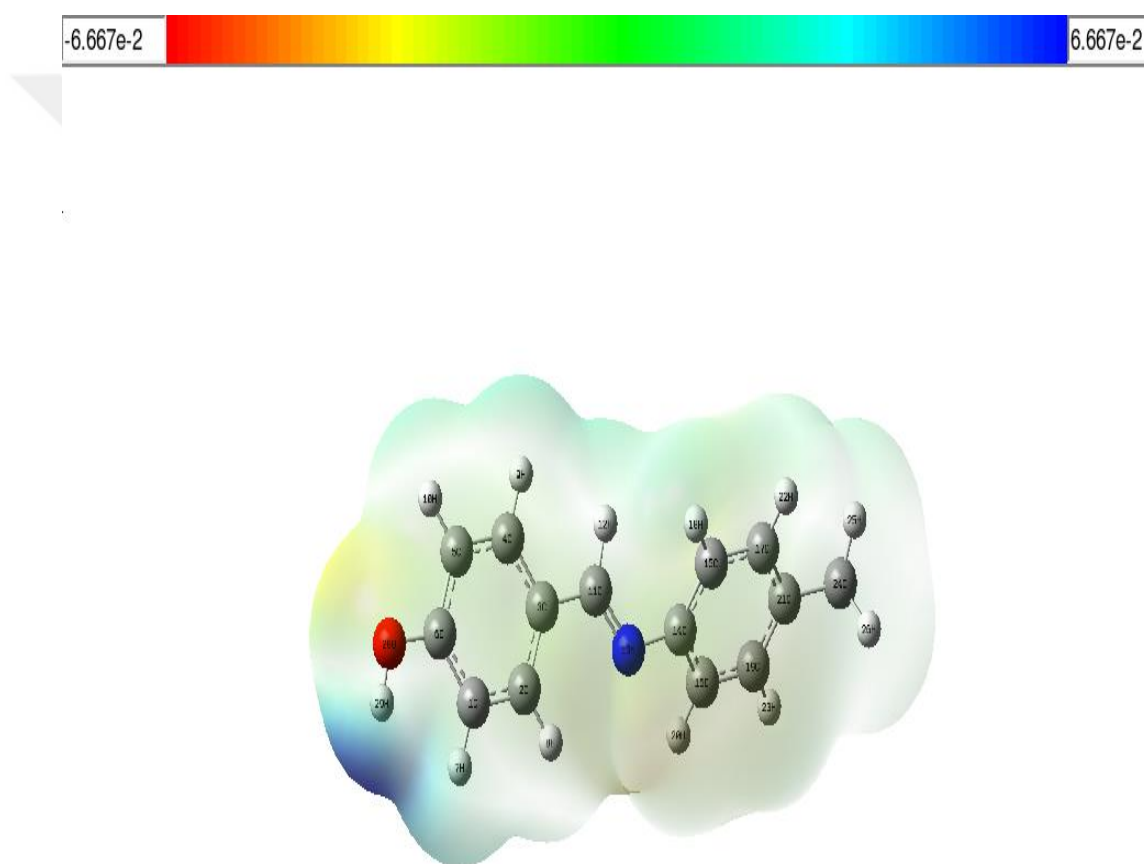


Figure 4.6 The calculated MESP map of (E)-4-((p-tolylimino)methyl)phenol Schiff base by using the B3LYP/6-311G(d, p) in gas media

5. CONCLUSIONS AND RECOMMENDATION

5.1 Conclusions

Using the DFT/6-311++G(d,p) technique implemented in the Gaussian 09 software, the theoretical geometric optimization computation of the (E)-4-((p-tolylimino)methyl)phenol molecule was performed in the present investigation. The calculated bond lengths, bond angles, and dihedral angles of the compound were then compared to those of other compounds with comparable structures found in the literature. The results of the analyses showed that the computed values agreed with those of other, similar structures in the literature. The vibration frequencies of the compound were calculated and no negative frequency values were found among the frequency values. It showed that this compound has a stable structure. In addition, it was concluded that the vibration frequency values obtained from IR calculations made with the DFT (B3LYP) method are close to the experimental data. HOMO-LUMO energy values were calculated and the energy difference was obtained as 4.1672 eV.

^1H -NMR and ^{13}C -NMR chemical shift values were found to be in agreement between the calculated and experimentally obtained values for the compound investigated according to the B3LYP/6-311G++(d,p) (DMSO) method.

In this study, the nonlinear optical properties of the (E)-4-((p-tolylimino)methyl)phenol Schiff base compound were calculated theoretically. Urea is used as a reference in compounds with non-linear optical properties. The hyperpolarizability value of urea is known as 0.77×10^{-30} esu. It has been observed that the related molecule has a higher hyperpolarizability value than urea and can be used in nonlinear optics (NLO) applications.

5.2 Recommendations

- Using the most stable molecular structure of (E)-4-((p-tolylimino)methyl)phenol Schiff base the molecular structure obtained from this thesis study, its interaction with protein structures can be investigated by molecular docking study.
- The physical and chemical properties of (E)-4-((p-tolylimino)methyl)phenol Schiff base molecule the molecular structure from different solvent environments can be investigated and compared.



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