Combined Spectroscopic and DFT Studies of Pyridoxine

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Abstract: The Fourier transform Infrared (FTIR) and FT-Raman (FTR) spectra of 4, 5-bis (hydroxy methyl)-2-methylpyridin-3-ol have been recorded in the regions 4000-450 cm\(^{-1}\) and 4000-500 cm\(^{-1}\) respectively. Utilizing the observed FTIR and FT-Raman data, a complete vibrational assignment and analysis of the fundamental modes of pyridoxine have been carried out. The optimum molecular geometry, infrared intensities have been calculated by density functional theory (DFT/B3LYP) method with 6-311G (d, p), 6-311++G(d, p) and RHF/6-31G(d, p) basis sets. The complete vibrational assignments were performed on the basis of the potential energy distribution (PED) of the Vibrational modes calculated using Vibrational Energy Distribution Analysis (VEDA 4) program. The calculated HOMO-LUMO energy gap revealed that charge transfer occurs within the molecule. The thermodynamic properties like Entropy, Enthalpy, Specific Heat Capacity and Zero vibrational energy have been calculated. Besides, molecular Electrostatic potential (MEP) was investigated using theoretical calculations. Stability of the molecule arising from hyper conjugative interactions, charge delocalization have been analyzed using NBO (Natural Bond Orbital analysis)

Keywords: FTIR, FT-Raman, HOMO-LUMO, Mulliken atomic charges, MEP, UV, NBO

1. Introduction

Vitamin B6 is called pyridoxine and it’s a white crystalline powder. Its IUPAC name is 4, 5-bis (hydroxy methyl)-2-methylpyridin-3-ol; Pyridoxine chemical formula is \(\text{C}_9\text{H}_7\text{NO}_3\), Its molecular weight169.18 g/mol. It dissolves in about 4.5 ml water, 90 ml alcohol; soluble in propylene glycol; sparingly soluble in acetone; insoluble in ether, chloroform. Its photosensitive will degrade slowly when exposed to light and preparations should be protected from light and stored in well-closed containers at a temperature less than 40°C, preferably between 15-30°C. Pyridoxine is essential to red blood cell, nervous system, and immune system functions and helps to maintain normal blood glucose levels. B6 is found in bananas, legumes, peanuts, potatoes, wheat cream, brewer’s yeast and organ meats (especially liver). Pyridoxine is usually nontoxic. Treating a type of anemia called sideroblastic anemia and seizures in infants. Vitamin B6 plays a vital role in several enzymatic reactions. It acts as a coenzyme for numerous enzyme-catalyzed reactions such as transamination, \(\alpha\)- and \(\beta\)-decarboxylation’s, \(\beta\)- and \(\gamma\)- eliminations, and racemization’s and aldol reactions [1]. Cinta et al. [2] investigated the pH dependence of the Raman and SERS spectra of pyridoxine hydrochloride and assigned the vibrational modes by the aid of ab initio (3-STO) and semi empirical (PM3) calculations. Srivastava et al. [3] calculated the harmonic vibrational wavenumbers for the optimized geometry pyridoxine, using density functional theory method B3LYP/ 6-311++G** level of theory. But the geometry optimization was not performed by torsion potential energy surfaces scan studies through the dihedral angles. It is well known that vibrational wavenumbers are strongly dependent on the conformational changes, for this reason, vibrational behavior of the lowest energy conformer of pyridoxine monomer was investigated. B. Atak-Bulbul et al.[4] investigate the possible stable conformers of free pyridoxine molecule and searched by means of torsion potential energy surfaces scan studies through the dihedral angles, D1 (9H-8O-4C-3C), D2 (12H-10C-5C-6N), D3 (15O-14C-2C-1C) and D4 (O22-19H-3C-2C). The final Geometrical parameters for the obtained stable conformers were determined by means of geometry optimization, carried out at DFT/B3LYP/6-311G++ (d, p) theory level. [5] G. A. Gamov et al. investigate on geometric optimization for the neutral, zwitterionic, and protonated forms of pyridoxine in vacuum and in water with a solvent within the polarizable continuum model (PCM). The structural parameters are optimized for pyridoxine complexes in the neutral and zwitterionic forms with 4-10 water molecules. An analysis was also performed to find the number of molecules of the solvent set by the model affects the agreement between the calculated and experimental NMR spectra. Quassila Attou-Yahia [6] investigate the occurrence of hydrogen bonding (HB) interactions, including intra and intermolecular HB, in the stability of the inclusion complex Pyridoxine/\(\beta\)-cyclodextrin, conformational research achieved with PM3MM, ONIOM-2 and DFT (B3LYP/6-31Gd) calculations gave a geometrical structure for the lowest energy complex in which the pyridine ring of the guest is self-imbedded inside the hydrophobic cavity of \(\beta\)-CD [7]. Electronic and spectroscopic properties of vitamin B6 (pyridoxine) and some of its main charged and protonated/deprotonated species are explored using hybrid density functional theory (DFT) methods including polarized solvation models found that the dominant species at low pH is
the N1-protonated form and, at high pH, the O3’-deprotonated compound. Literature survey reveals that to the best of our knowledge no DFT/B3LYP with 6-311++G (d,p), 6-311G (d, p) and RHF/6-31G(d, p) basis sets calculations of pyridoxine have been reported so far. Therefore an attempt has been made in the present study the detailed theoretical DFT and Experimental (FTIR, FT-Raman, UV) spectral investigation of pyridoxine. The FT-IR and FT Raman spectra of this compound have been stimulated with the use of the standard 6-311++G (d,p), 6-311G (d, p) and RHF/6-31G(d, p) basis sets. The results of the theoretical and spectroscopic studies are reported here in. Detailed interpretations of the vibrational spectra of pyridoxine have been made on the basis of the calculated potential energy distribution (PED). By using DFT (B3LYP) method, we have calculated the geometric parameters in the ground state, thermodynamic properties, vibrational energies, rotational constant, entropy, molar capacity and thermal energies by using Gaussian 03 programs. In addition, the energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of pyridoxine in the ground state are calculated by using B3LYP method with 6-311++G (d, p) basis set. UV-visible spectrum, Mulliken atomic charges and Natural Bond Orbital (NBO) analysis were also calculated.

2. Experimental Details

The Spectroscopic pure samples of pyridoxine was procured from a pharmaceutical company with more than 99% purity and used as such for the spectral recordings. FTIR ATR spectrum was recorded using Perkin-Elmer spectrum two FTIR spectrometer with ATR accessory, in the range of 4000-450 cm\(^{-1}\) and UV – visible spectral analysis was made using Perkin Elmer –Lambda 35 UV WINLAB V 6.0 spectrometer in the region 200-800 nm. These spectral recordings were carried out at Sophisticated Analytical Instrumentation Facility (SAIF), St. Peter’s University, Avadi, and Chennai, India. FT-Raman spectrum was recorded using 1064 nm line Nd: YAG laser operating at 200mw on Bruker RFS 27 spectrometer with 8 scans at a resolution of 2cm\(^{-1}\) in the range of 4000-50 cm\(^{-1}\) at Sophisticated Analytical Instrumentation Facility (SAIF), IIT Madras, India.

3. Computation details

The quantum chemical theoretical calculations were performed by using DFT-B3LYP levels on MSRC3 Intel ® core (TM) i5-3470 CPU @ 3.20GHz personal computer. The primary task for the computational work was to determine the optimized geometry of the compound using Gaussian 03 software [8] programs, invoking gradient geometry optimization [9]. DFT calculations were performed using Becke’s three-parameter [10, 11] hybrid model using Lee-yang-Parr (B3LYP) [12] correlation functional method. The computations were performed at RHF/6-31G (d, p), B3LYP/6-31++G(d,p), B3LYP/6-311G(d,p) basis sets [13, 14] have been utilized for the computation of molecular structure optimization, geometrical parameters, vibrational scaled wave numbers of the normal modes, IR intensities, atomic charges and thermodynamic parameters of the title compound. The complete assignments were performed on the basis of the potential Energy distribution Analysis (VEDA) 4 program.

4. Results and Discussion

4.1 Molecular geometry

The molecular structure of Pyridoxine belongs to C\(_1\) point group symmetry. All vibrations are active in both IR and Raman. The optimized molecular structure of pyridoxine is shown in the Fig 1. The optimized geometrical parameters such as bond lengths and bond angles obtained by the DFT/B3LYP methods with the 6-311G (d, p), 6-311++G(d, p) and RHF/ 6-31G(d, p) respectively are shown in table 1. The various bond lengths and bond angles are found to be almost same at B3LYP/6-311G (d, p), 6-311++G(d, p) methods. The bond length between atoms C2-C11 was calculated as in the range of 1.337\(^{\circ}\) and 1.42\(^{\circ}\) by using the DFT/B3LYP with two different basis sets and 1.394\(^{\circ}\) by RHF method. Both methods are in good agreement with experimental data 1.394\(^{\circ}\). The distance between C4-C5 was calculated as in the range of 1.337\(^{\circ}\) and 1.42\(^{\circ}\) by using DFT/B3LYP with two different basis sets and corresponding RHF value is 1.3834\(^{\circ}\) and both the methods are in good agreement with experimental values 1.394\(^{\circ}\). The bond angle between C3-C4-C5 in RHF and B3LYP methods are 120.0004\(^{\circ}\), 123.5\(^{\circ}\), and 123.0049\(^{\circ}\) which match exactly with the experimental value of 123.3. The bond angle between C5-C4-C16 in RHF is 120.8365\(^{\circ}\) and in B3LYP methods are 119.9941\(^{\circ}\), 118.2489\(^{\circ}\) which match exactly with the experimental value 120.3. The dihedral angle between C6-C5-C8-C11 by B3LYP/6-311G (d, p) is 180 and B3LYP/6-31++G(d,p) value 179.447 and RHF/6-31G(d, p) value is 179.5449 respectively. The calculated geometric parameters can be used to determine the other parameters of PYR. The optimized bond lengths are larger than the experimental values as the theoretical calculations result from isolated molecules in gaseous state. Bond angles and dihedral angles were referred from [15].

![Figure 1: Molecular Structure of 4, 5-bis (hydroxymethyl)-2-methylpyridin-3-ol](image-url)
4.2 Vibrational spectral analysis

The FTIR-ATR spectrum of a compound is the superposition of the absorption bands of specific functional groups. By observing the position, shape and relative intensities of the vibrational bands in FTIR spectra of the powder molecules of Pyridoxine vibrational band assignment has been made and summarized in Table 1. The FTIR-ATR and FT-Raman spectra of Pyridoxine by experimental and theoretical spectrum are shown in Fig.2 and the description of various band assignments are as follows.

4.2.1 O-H Vibrations

The O-H group vibrations are likely be the most sensitive to the environment, so they show pronounced shifts in the spectra of the hydrogen bonded species. The O-H stretching vibrations are usually observed in the region 3500 cm⁻¹[16]. In the present work O-H stretching vibrations are occur at 3322, 3232 cm⁻¹ in FTIR and 3233 occur in FT- Raman spectrum. Theoretically the scaled B3LYP/6-311++G (d, p) values are 3340, 3335, 3323 cm⁻¹ and corresponding B3LYP/6-311G(d, p) Values are 3343, 3330, 3329 cm⁻¹ respectively. Kanagathara et al. [17] have also observed O-H stretching at 3882 cm⁻¹ in FTIR spectrum. Santhana Krishnan et.al [18] too have observed O-H vibration at 3660 cm⁻¹ in FTIR.

4.2.2 C-H Vibrations

The hetero aromatic structure shows the presence of C-H stretching vibrations in the region 3100-3000 cm⁻¹ which is the characteristic region for the ready identification of C-H stretching vibration [19]. The C-H stretching is typically exhibited as a multiplicity of weak to moderate bands, compared with the aliphatic C-H stretching. In our present investigation 3086, 2815, 1827, 1731 cm⁻¹ occur at FTIR and 3099, 2975, 2934, 2901, 2865, 2828 cm⁻¹ occur at FT-Raman are assigned to C-H stretching vibrations. The B3LYP/6-311++G (d, p) value are 2767, 2726, 2690, 2687, 2648, 2622, 2610, 2590 cm⁻¹ are assigned to C-H stretching and B3LYP/6-311G(d, p) value are 2735, 2728, 2683, 2657, 2647, 2637, 2610, 2609 cm⁻¹ respectively. As indicated by PED these modes involve maximum contribution of about 96% suggesting that they are due to pure stretching modes. Arivazhagan et.al [20] have also observed C-H stretching at 3000, 2983 cm⁻¹ in FT-Raman spectra. Ramkumar et. al. [21] have reported C-H stretching at 3167, 2933 cm⁻¹ in FTIR and at 2941 cm⁻¹ in FT-Raman spectra respectively.

4.2.3 C-C Vibrations

The C-C aromatic stretching vibrations give rise to characteristic bands in the spectral range from 1600-1400 cm⁻¹[22]. C-C Stretching vibrations for title compound is observed at 1542 cm⁻¹ FTIR and at 1499, 1232 cm⁻¹ in FT- Raman spectra. Theoretically C-C stretching vibration are observed at 1429, 1223, 1135, 1067 cm⁻¹ in B3LYP/6-311++G (d,p) and B3LYP/6-311G(d, p) values are 1433, 1246, 1117, 1081 cm⁻¹ respectively.

4.2.4 N-C Vibrations

N-C stretching vibrations are occur in the region of 1000-1350 cm⁻¹. In the present work N-C stretching vibrations are occurred at 1542, 1462 in FTIR and 1449, 1392 are observed at FT-Raman respectively. Theoretically N-C stretching vibrations occur at 1429, 1323, 1135, 1112, 1067 in B3LYP/6-311++G (d, p) and 1433, 1332, 1117, 1114, 1081 in B3LYP/6-311G(d, p) respectively.

4.2.5 C-O vibration

The C-O stretching vibration is normally at 1320–1210 cm⁻¹ due to C-O stretching vibrations [23]. Accordingly in the present study the C-O stretching vibration of PYR are observed at 1214 cm⁻¹ in FTIR spectrum, and medium band observed at 1323, 1217 cm⁻¹ in Raman spectrum. The theoretically computed frequencies at 1223, 1218, 1607 cm⁻¹ and at B3LYP/6-311G (d, p) and 1246, 1220 cm⁻¹ in 6-311++G(d, p) basis sets respectively.

4.3 Thermodynamic Properties

The statistical thermo chemical analysis of pyridoxine was performed considering the molecule to be at room temperature 298.15 K and one atmospheric pressure. All the thermodynamic data supply helpful information for further study of the title molecule. Using B3LYP/6-311++G (d, p) and RHF/6-31G(d, p) several thermodynamic properties such as heat capacity at constant pressure (Cp), entropy (S) and enthalpy (ΔH) for the title compound were evaluate from the theoretical harmonic frequencies obtained from the temperature 100-1000K and are listed in Table 3.

![Figure 2: FTIR experimental Spectrum of pyridoxine](image-url)
From this table it is evident that the properties increase with increase in temperature due to the fact that the vibrational intensities of the molecules increase with temperature. The correlation between these thermodynamic properties and temperature are fitted by quadratic formula as follows and corresponding fitting factors ($R^2$) for these thermodynamic properties were found to be 0.99978, 0.99986 and 0.99962. The temperature dependent correlation graphs are shown in Fig 8. The ZPVE’S energy is much lower in the DFT/B3LYP level at 6-311++G (d, p) basis set than the other basis sets [24]. The bigger value of ZPVE’s of Pyridoxine is 125.83731(Kcal/Mol) obtained by RHF/6-31G(d, p) method. The minimum value of entropy are calculated in 107.581 at RHF/6-31G (d, p) and maximum one was calculated at 109.551 at B3LYP/6-311++G(d, p) in pyridoxine molecule. The transitional and rotational thermal energies, molar capacity are also same for B3LYP level with all basis sets are shown in table 5. The Homo-Lumo energies, energy gap, chemical hardness, electronegativity, electrophilicity, chemical potential are also calculated and shown in table 4.
The Mulliken charge is directly related to the vibrational properties of the molecule and quantifies how the electronic structure charges under atomic displacement. It is therefore related directly to the chemical bonds present in the molecule. It affects dipole momentum polarizability electronic structure and more properties of molecular system [25]. The Mulliken analysis was performed on the title molecule by B3LYP and RHF methods using 6-311++G (d, p), 6-311G(d, p) and 6-31G (d, p) as the basis set and presented in the table [6]. The illustration of Mulliken atomic charge plotted is shown in Fig.9. The oxygen atoms O7, O10, O12 have charges _0.270178, _0.25063 and _0.236904 respectively in the B3LYP method, of which O7 has the highest negative value. N3 as the least negative value of _0.001575 by B3LYP method and all the hydrogen atoms have positive values and the H23 has the highest positive values. The net charge of hydrogen atoms is 2.187436 in B3LYP method. The presence of negative charge on nitrogen and oxygen atoms and the net +ve charge on hydrogen atoms may suggest the formation of intramolecular interaction in solid forms. The advantage of population analysis is that it is useful for comparing changes in partial charge assignment between two different geometries with the same size basis sets.

4.5 UV-Visible Spectral analysis

UV-Visible spectral analysis of PYR has been done experimentally and theoretically . Time dependent density functional theory (TD-DFT) is a powerful tool for investigating the static and dynamic properties of the molecules in their excited states [26]. UV spectral studies are very useful in determining the transmittance and absorption on an optically active material [27]. Fig. 10 Shows the UV spectrum of pyridoxine and Table 7 shows the experimental and calculated absorption wavelength (λ), excitation state, Oscillator strength (f), electronic absorption value and transition of pyridoxine. According to Franck-Condon principle, the maximum absorption peak (λ_{max}) corresponds to vertical excitation. Theoretical calculations predicts one intense electronic transition at 204nm with an oscillator strength f=0.2853 and electronic absorption value 6.0675E+00 which is in good agreement with the experimental value 477 nm corresponding to HOMO–LUMO+1, HOMO-LUMO+2, HOMO-LUMO+3, HOMO -LUMO+4 transition. Another peak at 201 nm with oscillator strength 0.0030 and electronic absorption value 6.1390E+00 corresponds to the second excited state with transitions HOMO-LUMO+1 to HUMO-LUMO+6, which is in good agreement with the experimental value 268 nm. The third peak 184nm at 6.7124E+00 with oscillator strength 0.0204 corresponds the third excited state and the corresponding transition occurs between HOMO-LUMO +1 TO HOMO-LUMO+8.
Energy difference between HOMO and LUMO orbital is called as energy gap that is an important stability for structure [29] and reveals the chemical activity of the molecule. The HOMO–LUMO orbitals computed at B3LYP level with 6-311G(d, p) is shown in fig 8. The lower HOMO-LUMO energy gap explains the eventual charge transfer interactions taking place within the molecule. It is an established fact that a large frontier orbital energy gap implies high kinetic stability and low chemical reactivity. Because it is energetically unfavorable to add electrons to a high-lying LUMO to extract electrons from low–lying HOMO [30] for PYR. The HOMO-LUMO energy gap reflects the chemical activity of the molecule. The LUMO as an electron acceptor represent the ability to obtain an electron. The HOMO represents the ability to donate an electron.

4.7 Molecular Electrostatic Potential

Molecular electrostatic potential (MESP) at a point in the space around a molecule gives an indication of the net electrostatic effect produced at that point by the total charge distribution (electron+ nuclei) of the molecule and correlates with the dipole moments, electronegativity, partial charges chemical reactivity of the molecules. It provides a visual method to understand the relative polarity of the molecule. Thus, MESP serves as a useful quantity to explain hydrogen bonding, reactivity and structure–activity relationship of molecule including biomolecules and drugs [31-33]. The different values of the electrostatic potential, at the surface are represented by different colour’s; red represents regions of most negative electrostatic

**Excited state = -0.04197 a. u**

**Energy gap = 0.19824 a.u**

**Ground state -0.24021a.u**

Figure 11: The atomic orbital composition of the frontier molecular orbital for pyridoxine potential, which corresponds to an attraction of the proton by the concentrated electron density in the molecule; blue represents regions most positive electrostatic potential and green represents regions atoms of zero potential. Potential increases in the order red<orange<yellow<green<blue. The atoms O12, O10, O7 were electrophilic sites. Nitrogen atom N3 was a nucleophilic site from these results; one can say that the nitrogen atom and hydrogen atoms indicate strongest attraction, while oxygen atoms indicate strongest repulsion. These sites give information about the region from where the compound can have intermolecular interactions.
larger $E(2)$ value of the second order orbital and the interacting stabilization energy resulted from molecular systems. Some electron donor orbital investigating charge transfer or conjugative interaction studying intra and inter molecular bonding and elements and $F(i,j)$ is the off diagonal NBO Fock matrix was carried out to evaluate donor filled and virtual orbital spaces that could enhance the percentage of the electron density. A useful aspect of NBO Lewis structure into an empty non-Lewis orbital. For each donor (i) and acceptor (j), the stabilization energy $E^2$ associated with the delocalization $i \rightarrow j$ is estimated as

$$F(i, j)^2 \left( \varepsilon_j - \varepsilon_i \right)$$

$E^{(2)} = \Delta E_{ij} = q_i$

Where $q_i$ is the donor orbital frequency, $\varepsilon_i$ and $\varepsilon_j$ are diagonal elements and $F(i, j)$ is the off diagonal NBO Fock matrix element. NBO analyses provide an efficient method for studying intra and inter molecular bonding and interaction among bonds and also provide a convenient basis for investigating charge transfer or conjugative interaction molecular systems. Some electron donor orbital, acceptor orbital and the interacting stabilization energy resulted from the second order micro-disturbance theory are reported. The larger $E(2)$ value, the more intensive is the interaction between the electron donor and acceptors, i.e. the more donating tendency from the form the electron donors to electron acceptors and the greater extent of conjugation of the whole system. Delocalization of electron density between occupied Lewis type (bond or lone pair) NBO orbitals and formally unoccupied (anti-bond or Rydberg) non Lewis NBO orbitals correspond to a stabilizing donor-acceptor interaction. NBO analysis has been performed on the molecule at the B3LYP/6-311++G (d, p) level in order to elucidate the intra molecular, rehybridization and delocalization of electron density with in the molecule. The interaction between lone pair LP (3) of type O12 of type O11 with $\sigma^*(C2-C11)$ results in a stabilization energy of 28.67KJ/mol and lone pair LP (2) of type O10 with $\sigma^*(C6-O7)$ results in stabilization energy of 10.02KJ/mol. These indicate larger delocalization. The intramolecular hyperconjugative interaction of $\sigma(C4-C5)$ to $\sigma^*(C6-O7)$ leading to strong stabilization of 10.81KJ/mol. The intramolecular hyperconjugative interaction of $\sigma(C5-C6)$ to $\sigma^*(C5-C8)$ and $\sigma(C5-C8)$ to $\sigma^*(C8-C11)$ leads to stabilization of 8.08 and 8.06KJ/mol respectively. These interactions are observed as increase in electron density in antibonding orbital that weakens the respective bonds. These charge transfer interactions in pyridoxine are responsible for biological properties. Hence pyridoxine structure is stabilized by these orbital Interactions. In pyridoxine, the oxygen has larger polarization co-efficient because it has the higher electronegativity. The calculated values of $E(2)$ are given in Table [8].

Figure 12: Electrostatic potential surfaces of PYR by B3LYP/6-311++G (d, p)

The site corresponding to the benzene ring is highly active and it can play an important role in the activity of PYR. The figures confirm the different positive and negative sites of the molecule in accordance with the total electron density surface. Such electrostatic potential surfaces have been for PYR in B3LYP/6-311++G (d, p) shown in fig [11].

4.8 NBO analysis

NBO analysis provides the most accurate possible ‘natural Lewis structure’ picture of $\varphi_i$, because all orbital details are mathematically chosen to include the highest possible percentage of the electron density. A useful aspect of NBO method is that it gives information’s about interactions in both filled and virtual orbital spaces that could enhance the analysis of intra and inter molecular interactions. The second Fock matrix was carried out to evaluate donor-acceptor interactions in the NBO analysis. The interactions result is a loss of occupancy from the localized NBO of the idealized Lewis structure into an empty non-Lewis orbital. For each donor (i) and acceptor (j), the stabilization energy $E^2$ associated with the delocalization $i \rightarrow j$ is estimated as

$$F(i, j)^2 \left( \varepsilon_j - \varepsilon_i \right)$$

$E^{(2)} = \Delta E_{ij} = q_i$

Where $q_i$ is the donor orbital frequency, $\varepsilon_i$ and $\varepsilon_j$ are diagonal elements and $F(i, j)$ is the off diagonal NBO Fock matrix element. NBO analyses provide an efficient method for studying intra and inter molecular bonding and interaction among bonds and also provide a convenient basis for investigating charge transfer or conjugative interaction molecular systems. Some electron donor orbital, acceptor orbital and the interacting stabilization energy resulted from the second order micro-disturbance theory are reported. The larger $E(2)$ value, the more intensive is the interaction between the electron donor and acceptors, i.e. the more donating tendency from the form the electron donors to electron acceptors and the greater extent of conjugation of the whole system. Delocalization of electron density between occupied Lewis type (bond or lone pair) NBO orbitals and formally unoccupied (anti-bond or Rydberg) non Lewis NBO orbitals correspond to a stabilizing donor-acceptor interaction. NBO analysis has been performed on the molecule at the B3LYP/6-311++G (d, p) level in order to elucidate the intra molecular, rehybridization and delocalization of electron density with in the molecule. The interaction between lone pair LP (3) of type O12 of type O11 with $\sigma^*(C2-C11)$ results in a stabilization energy of 28.67KJ/mol and lone pair LP (2) of type O10 with $\sigma^*(C6-O7)$ results in stabilization energy of 10.02KJ/mol. These indicate larger delocalization. The intramolecular hyperconjugative interaction of $\sigma(C4-C5)$ to $\sigma^*(C6-O7)$ leading to strong stabilization of 10.81KJ/mol. The intramolecular hyperconjugative interaction of $\sigma(C5-C6)$ to $\sigma^*(C5-C8)$ and $\sigma(C5-C8)$ to $\sigma^*(C8-C11)$ leads to stabilization of 8.08 and 8.06KJ/mol respectively. These interactions are observed as increase in electron density in antibonding orbital that weakens the respective bonds. These charge transfer interactions in pyridoxine are responsible for biological properties. Hence pyridoxine structure is stabilized by these orbital Interactions. In pyridoxine, the oxygen has larger polarization co-efficient because it has the higher electronegativity. The calculated values of $E(2)$ are given in Table [8].

5. Conclusion

A complete vibrational analysis of 4, 5-bis (hydroxymethyl)-2-methylpyridin-3-ol is performed by DFT/B3LYP level with 6-311++G (d,p), 6-311G(d, p) and RHF/6-31G(d, p) basis sets. On the basis of calculated potential energy distribution results assignments of the fundamental vibrational frequencies have been made unambiguously. The calculated geometrical parameters were found to be in good agreement with the experimental data. Thermodynamic properties zero point Vibrational energies rotational constant, thermal energy, molar capacity are discussed elaborately. The stability and intermolecular interactions have been interpreted by NBO analysis and the transitions give stabilization to the structure have been identified by second perturbation energy calculations. The lowering of HOMO-LUMO energy gap, a quantum chemical descriptor, explains the charge transfer interactions taking place within the molecule. The Mulliken atomic charges gives the proper understanding of the atomic theory and the energies of important MOs and the $\lambda_{max}$ of the compounds were also evaluated from TD-DFT method.

6. Acknowledgement

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References

Table 1: Geometrical parameter optimized in Pyridoxine by B3LYP with B3LYP/6-311 G(d, p), B3LYP/6-311G(d, p), RHF/6-31G(d, p)

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Table 2: Observed and theoretical vibrational assignments of Pyridoxine at DFT-B3LYP methods

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Vibrational assignments

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<td>116</td>
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<td>87</td>
<td>2.7786</td>
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<td>66</td>
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<td>71</td>
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<tr>
<td>63</td>
<td>52</td>
<td>2.5387</td>
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ν = stretching, β = bending, γ = out of plane bending, t = torsion
Table 3: Temperature dependent of thermodynamic properties Pyridoxine

<table>
<thead>
<tr>
<th>S No</th>
<th>parameters</th>
<th>B3LYP/6-311++G(d, p)</th>
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<tr>
<td>1</td>
<td>$E_{HOMO}$ (eV)</td>
<td>-0.24021</td>
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<tr>
<td>2</td>
<td>$E_{LUMO}$ (eV)</td>
<td>-0.04197</td>
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<tr>
<td>3</td>
<td>$E_{HOMO-LUMO}$ energy gap (eV)</td>
<td>0.19824</td>
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<tr>
<td>4</td>
<td>Chemical hardness</td>
<td>0.14109</td>
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<tr>
<td>5</td>
<td>Softness (s)</td>
<td>3.543837</td>
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<tr>
<td>6</td>
<td>Electronegativity</td>
<td>0.09912</td>
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<tr>
<td>7</td>
<td>Electrophilicity($\omega$)</td>
<td>0.034814</td>
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<tr>
<td>8</td>
<td>Chemical potential</td>
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Table 4: Calculated energy values of Pyridoxine By B3LYP/6-31++G (d, p)

<table>
<thead>
<tr>
<th>T (K)</th>
<th>S (J/mol.K)</th>
<th>Cp (J/mol.K)</th>
<th>ddH (kJ/mol)</th>
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<tr>
<td>100</td>
<td>306.52</td>
<td>93.56</td>
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<tr>
<td>200</td>
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<td>298.15</td>
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<tr>
<td>300</td>
<td>460.75</td>
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<td>251.55</td>
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<td>696.86</td>
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<td>800</td>
<td>746.51</td>
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<td>792.91</td>
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<td>1000</td>
<td>836.39</td>
<td>421.25</td>
<td>269.79</td>
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Table 5: The calculated Thermodynamic parameters of Pyridoxine

<table>
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<tr>
<th>Parameters</th>
<th>B3LYP/6-31(G(d, p))</th>
<th>RHF/6-31G(d, p)</th>
<th>B3LYP/6-311++G(d, p)</th>
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<tbody>
<tr>
<td>Zero-point vibrational energy (Kcal/Mol)</td>
<td>116.64819</td>
<td>125.83731</td>
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<td>Rotational constants (GHZ)</td>
<td>1.39516</td>
<td>0.06749</td>
<td>1.2672</td>
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<td>Rotational temperatures (Kelvin)</td>
<td>0.06696</td>
<td>1.4062</td>
<td>0.06082</td>
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<tr>
<td>Molar capacity at constant volume (cal/Mol-kelvin)</td>
<td>45.856</td>
<td>42.957</td>
<td>46.114</td>
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<tr>
<td>Entropy (Cal/Mol-Kelvin)</td>
<td>109.551</td>
<td>107.581</td>
<td>109.797</td>
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<tr>
<td>Energy(kcal/Mol)</td>
<td>124.509</td>
<td>133.314</td>
<td>124.165</td>
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### Table 7: Experimental and calculated absorption wavelength (λ), excitation state, oscillator strength (f), electronic absorption value (ev) and transition of P pyridoxine by TD-DFT method (B3LYP/6-311++G (d, p))

<table>
<thead>
<tr>
<th>Excitation Singlet</th>
<th>Acal. Wavelength (nm)</th>
<th>Excitation Wavelength (nm)</th>
<th>Oscillator strength (f)</th>
<th>Electronic absorption value (ev)</th>
<th>Transition</th>
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<tr>
<td>Excited State 1</td>
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<tr>
<td>45 - 49 0.10642</td>
<td>204.34 6.0.0675 0.2853</td>
<td>HOMO - LUMO</td>
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<td></td>
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<tr>
<td>45 - 55 -0.24527</td>
<td>HOMO - LUMO+1</td>
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<td>45 - 58 -0.31263</td>
<td>HOMO - LUMO+2</td>
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<tr>
<td>45 - 59 0.51592</td>
<td>HOMO - LUMO+3</td>
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<td>Excited State 2</td>
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<td>45 - 46 0.49061</td>
<td>201.96 6.1.390 0.0230</td>
<td>HOMO - LUMO</td>
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<td></td>
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<tr>
<td>45 - 47 0.20346</td>
<td>HOMO - LUMO+1</td>
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<tr>
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<tr>
<td>45 - 64 -0.15118</td>
<td>HOMO - LUMO+5</td>
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<td>Excited State 3</td>
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<td>44 - 59 0.13237</td>
<td>184.71 6.7124 0.0204</td>
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<tr>
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<td>HOMO - LUMO+2</td>
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<tr>
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### Table 8: Second order perturbation theory analysis of FOCK matrix in NBO analysis for Pyridoxine

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<thead>
<tr>
<th>Donor (i)</th>
<th>TYPE</th>
<th>Acceptor (j)</th>
<th>Type</th>
<th>E(^{\text{occ}})</th>
<th>E(^{\text{exc}}) (\mu\text{H})</th>
<th>F(L, J) (a.u.)</th>
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</thead>
<tbody>
<tr>
<td>(\Sigma)</td>
<td>C1-C2</td>
<td>(\sigma^*)</td>
<td>C2-N3</td>
<td>1.27</td>
<td>1.16</td>
<td>0.034</td>
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<tr>
<td>(\Sigma)</td>
<td>C1-C2</td>
<td>(\sigma^*)</td>
<td>C2-C11</td>
<td>1.52</td>
<td>1.17</td>
<td>0.038</td>
</tr>
<tr>
<td>(\Sigma)</td>
<td>C1-C2</td>
<td>(\sigma^*)</td>
<td>C3-C4</td>
<td>3.18</td>
<td>1.16</td>
<td>0.054</td>
</tr>
<tr>
<td>(\Sigma)</td>
<td>C1-C2</td>
<td>(\sigma^*)</td>
<td>C8-C11</td>
<td>2.49</td>
<td>1.17</td>
<td>0.049</td>
</tr>
<tr>
<td>(\Sigma)</td>
<td>C1-H13</td>
<td>(\sigma^*)</td>
<td>C2-N3</td>
<td>1.85</td>
<td>1.02</td>
<td>0.039</td>
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<tr>
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<td>C1-H13</td>
<td>(\pi^*)</td>
<td>C2-C11</td>
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<td>1.03</td>
<td>0.056</td>
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<td>π*</td>
<td>C2-C11</td>
<td>2.3</td>
<td>0.52</td>
<td>0.034</td>
</tr>
<tr>
<td>Σ</td>
<td>C2-N3</td>
<td>σ*</td>
<td>C2-C11</td>
<td>1.54</td>
<td>1.33</td>
<td>0.041</td>
</tr>
<tr>
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<td>C2-N3</td>
<td>σ*</td>
<td>C4-H16</td>
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<td>1.22</td>
<td>0.049</td>
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<td>σ*</td>
<td>C11-O12</td>
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<td>C1-H13</td>
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<td>σ*</td>
<td>C1-H15</td>
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<td>σ*</td>
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<td>σ*</td>
<td>C5-C6</td>
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<td>1.12</td>
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<td>C11-O12</td>
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