

Spectroscopic (FT-IR and FT-RAMAN) Investigation, NLO, NBO, HOMO-LUMO Analyses of 2-Chloro-5-Hydroxypyridine

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Abstract

In the present work, the FT-IR and FT-Raman spectra of 2-chloro-5-hydroxypyridine (CHP) have been recorded in the region 4000-400 cm^{-1} and 3500-50 cm^{-1} , respectively. The fundamental modes of vibrational frequencies of (CHP) are assigned. Theoretical information on the optimized geometry, harmonic vibrational frequencies, infrared and Raman intensities were obtained by means of density functional theory (DFT) gradient calculations with complete relaxation in the potential energy surface using 6-311++G(d,p) and 3-21G basis sets. The vibrational frequencies which were determined experimentally from the spectral data are compared with those obtained theoretically DFT calculations. A close agreement was achieved between the observed and calculated frequencies by refinement of the scale factors. The infrared and Raman spectra were also predicted from the calculated intensities. Thermodynamic properties like entropy, heat capacity, zero point energy, have been calculated for the molecule. The predicted first hyperpolarizability also shows that the molecule might have a reasonably good non-linear optical (NLO) behaviour. The calculated HOMO-LUMO energy gap reveals that charge transfer occurs within the molecule. Stability of the molecule arising from hyper conjugative interactions, charge delocalization have been analyzed using natural bond orbitals (NBO) analysis. Unambiguous vibrational assignment of all the fundamentals was made using the total energy distribution (TED).

Key Words: DFT, NBO, HOMO, LUMO and NLO

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INTRODUCTION

It is well known that the n-heterocyclic compounds like pyridine, pyrimidine, adenine, uracil, anisoles, purine, pyradizine are very important because of bactericidal, fungicidal, germicidal and pharmacological activities [1-5]. The pyridine derivatives have an important

position among the heterocyclic compounds because they can be used as nonlinear materials and photochemicals [6,7]. The study of the vibrational spectra of substituted pyridine attracts the attention of many spectroscopists due to their wide application in pharmacology and agro-chemistry. Pyridine heterocycles are a repeated moiety in many large molecules with interesting photo physical, electrochemical and catalytic applications [8-15]. They serve as good anesthetic agent and hence they are used in the preparation of drugs for certain brain disease. These pharmaceutically acceptable salts and the pre-drugs are used for the treatment (or) prevention of diabetic neuropathy [16,17]. The vibrational spectra of substituted pyridine have been the subject of several investigations [18,20]. More recently [21,22], FT-IR and FT-Raman spectra of nitro pyridine have been reported together with the vibrational assignments of the normal modes. However, the detailed comparative studies on the complete FT-IR and FT-Raman spectra of 2-chloro-5-hydroxypyridine (CHP) have not been reported so far. In this study, molecular geometry, optimized parameters and vibrational frequencies are computed and the performance of the computational methods for density functional theory (B3LYP) at 6-311++G(d,p) and 3-21G basis sets are compared. These methods predict relatively accurate molecular structure and vibrational spectra with moderate computational effort. In particular, for polyatomic molecules the DFT methods lead to the prediction of more accurate molecular structure and vibrational frequencies. In DFT methods, Becke's three parameter exact exchange-functional (B3) [23] combined with gradient-corrected correlational functional of Lee, Yang and Parr (LYP) [24,25] are the best predicting results for molecular geometry and vibrational wavenumbers for moderately larger molecule [26,27]. The optimized geometrical parameters, fundamental vibrational frequencies, IR intensity, Raman activity, atomic charges, dipole moment, force constants and other thermodynamic parameters and energy gap through HOMO and LUMO energy, are calculated using the GAUSSIAN 09W packages.

EXPERIMENTAL DETAILS

The compound under investigation namely 2-chloro-5-hydroxypyridine (CHP) was purchased from Lancaster Chemical Company (U.K.) and used as such for recording the spectra without any further purification. The FT-IR spectrum of CHP in the region 4000-450 cm^{-1} has been recorded with a BRUKER IFS 66V spectrophotometer using KBr pellet. The FT-Raman spectrum of the title compound was recorded in the region 5000-50 cm^{-1} with a BRUKER RFS 100/s 66V spectrophotometer using KBr pellet technique. Raman module equipped with Nd:YAG laser source operating at 1064 nm line width 150 mw power. The spectra were recorded with a scanning speed of 50 $\text{cm}^{-1} \text{min}^{-1}$ of spectral width 4 cm^{-1} . The reported wave numbers are believed to be accurate within $\pm 1 \text{ cm}^{-1}$.

COMPUTATIONAL DETAILS

Quantum chemical density functional theory calculations were carried out using the 2009 version of the GAUSSIAN program package [28] with B3LYP methods combined with the standard 6-311++G(d,p) and 3-21G basis sets. The Cartesian representation of the theoretical force constants has been computed at the optimized geometry by assuming C_1 point group symmetry.

Scaling of the force field was performed according to the SQM procedure using selective scaling in the natural internal coordinate representation. Transformation of the force field and the subsequent normal coordinate analysis (NCA) including the least squares refinement of the scaling factors, and calculation of total energy distribution (TED) were done on a PC with the MOLVIB program (version 7.0 – G77) written by Sundius [29,30,31].

The Raman activities (S_i) calculated with the GAUSSIAN 09W program are subsequently converted to relative Raman intensities (I_i) using the following relationship derived from the basic theory of Raman scattering [32-34].

$$I_i = f(v_0 - \nu_i)^4 S_i \dots (1) \nu_i \left[\frac{1}{1 - \frac{h\nu_i}{kT}} - \frac{1}{1 + \frac{h\nu_i}{kT}} \right]$$

where ν_0 is the exciting frequency in cm^{-1} , ν_i the vibrational wave number of the i^{th} normal mode, h , c , k are the fundamental constants and f is a suitably chosen common normalization factor for all the peak intensities.

RESULTS AND DISCUSSION Geometry optimization

The molecular structure with the numbering scheme of 2-chloro-5-hydroxypyridine is shown in Fig.1. The calculated optimized geometrical parameters of CHP obtained by B3LYP with 6-311++G(d,p) and 3-21G basis set are presented in Table 1. A detailed description of vibrational modes can be given by means of normal coordinate analysis. The internal coordinates describe the position of the atoms in terms of distances, angles and dihedral angles with respect to an origin atom. For this purpose, a full set of standard internal co-ordinates containing 11 redundancies and non-redundant set of local symmetry coordinates were constructed, [35] and are listed in Tables 2 and 3, respectively.

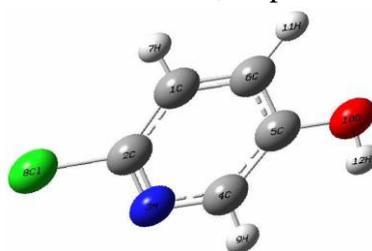
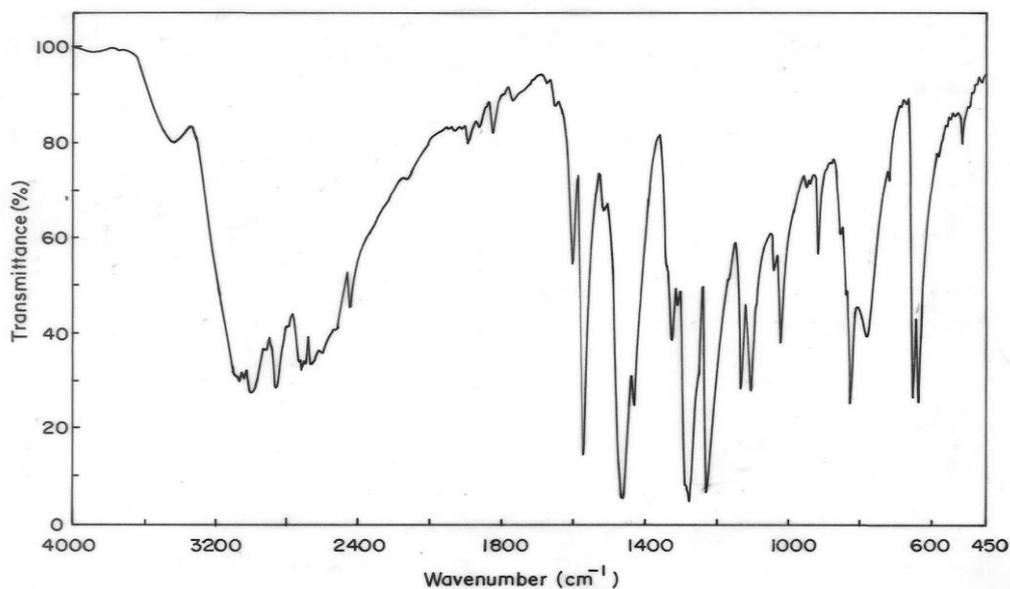
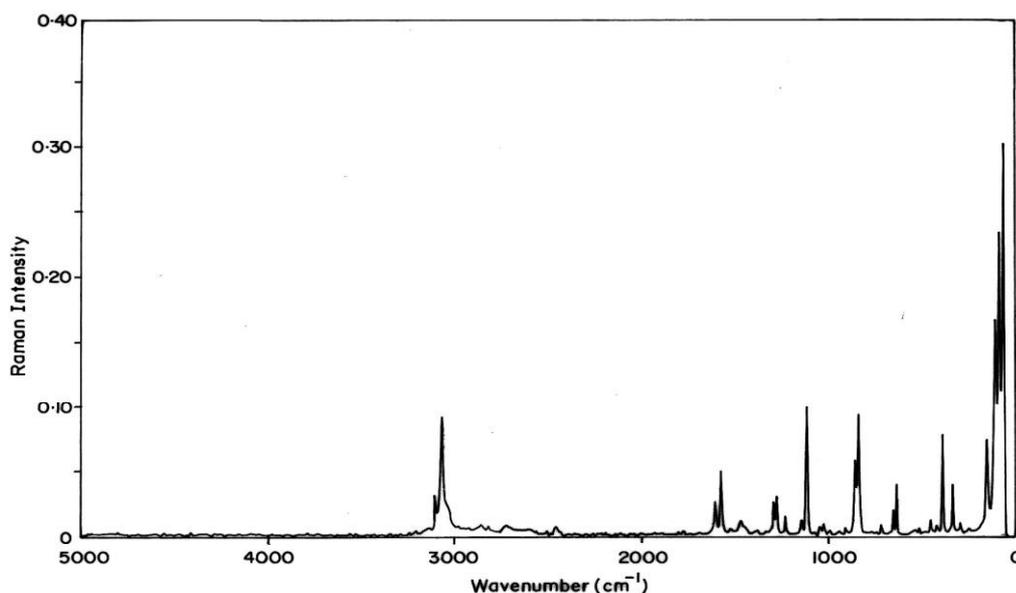


FIGURE 1. Molecular structure of 2-chloro-5-hydroxypyridine

Vibrational spectra

The vibrational frequencies IR intensities and Raman activities are calculated for CHP at B3LYP level using 6-311++G(d,p) and 3-21G method and basis sets have been collected in Table 4 along with the observed FT-IR and FT-Raman Spectral data. The observed FT-IR and FT-Raman spectra of CHP are shown in Figs. 2 and 3, respectively.

**FIGURE 2.** FT-IR spectrum of 2-chloro-5-hydroxypyridine**FIGURE 3.** FT-Raman spectrum of 2-chloro-5-hydroxypyridine

C–C vibrations

The benzene possesses six stretching vibrations of which the four with highest wave numbers occurring near 1650–1400 cm^{-1} are good group vibrations [36]. With heavy substituents, the bonds tend to shift to somewhat lower wave numbers and greater the number of substituents on the ring, broader the absorption regions. In the title molecule, the FT-IR bands observed at 1605, 1574, 1464, 1432 cm^{-1} and FT-Raman bands at 1605, 1574, cm^{-1} have been assigned to C–C stretching vibrations are due to the substituents in benzene ring. The higher percentage of total energy distribution (TED) obtained for this group encouraging and

confirms the assignments proposed in this study for C–C stretching vibrations. The in-plane and out-of-plane bending vibrations of C–C group are also listed in Table 4.

C–H vibrations

The hetero aromatic structure shows the presence of C–H stretching vibrations in the region 3100–3000 cm^{-1} [37,38,39]. This is the characteristic region for the ready identification of C–H stretching vibrations. In this region, the bands are not affected appreciably by the nature of the substitutions. In the present investigation, the C–H vibrations are observed at 3070 and 3003 cm^{-1} in the FT-IR spectrum and at 3103 and 3070 cm^{-1} in the Raman for CHP. The C–H in-plane and out-of-plane bending vibrations of the CHP have also been identified and listed in Table 4.

O–H Vibrations

The precise positions of O–H band are dependent on the strength of hydrogen bond. The O–H stretching vibration is normally observed at about 3350 cm^{-1} . The O–H in-plane bending vibration is observed in the region 1440–1260 cm^{-1} [40]. In CHP, the bands appeared at 3435 cm^{-1} in FT-IR spectrum were assigned to O–H stretching modes of vibrations. The in-plane bending vibrations of hydroxy groups have been identified at 1134 cm^{-1} , in IR spectrum. The O–H out-of-plane vibrations of the title compound have also been identified and listed in Table 4.

C–N vibrations

In aromatic compounds, the C–N stretching vibrations usually lie in the region 1400–1200 cm^{-1} [41]. In the present work, the FT-IR band appeared at 1327 cm^{-1} and 1310 cm^{-1} have been designated to C–N stretching vibrations. The in-plane and out-of-plane bending vibrations assigned in this study are also supported by the literature [42]. The identification of C–N vibration is a difficult task, since it falls in a complicated region of the vibrational spectrum. However, with the help of force field calculations, the C–N vibrations are identified and assigned in this work.

Calculations are made for a free molecule in vacuum, while experiments are performed for solid sample, so there are disagreements between the calculated and observed vibrational wave numbers. Comparison of the frequencies calculated at DFT (B3LYP) level using 6-311++G(d,p) and 3-21G basis sets with experimental values reveals the overestimation of the calculated vibrational modes due to neglect of unharmonicity in real system.

C–Cl vibrations

The C–Cl stretching vibrations generally give strong bands in the region 760–505 cm^{-1} [43]. The FT-IR band observed at 828 cm^{-1} has been assigned to C–Cl stretching; this was also confirmed by TED output. Most of the aromatic chloro compounds have a band of strong-to-medium intensity in the region 385–265 cm^{-1} due to C–Cl in-plane bending vibrations [44]. Accordingly the FT-IR band identified at 518 cm^{-1} has been assigned to the C–Cl in-plane

bending mode. The C–Cl out of plane deformation vibration has been established at 338 cm^{-1} in FT-Raman spectrum.

Carbon Oxygen vibrations

The interaction of carbonyl groups present in the system did not produce such a drastic and characteristic change in the frequency of C–O stretch as did by interaction of N–H stretch. The absorption caused by C–O stretching occurs in the region $1260\text{--}1000\text{ cm}^{-1}$. In the present investigation the FT-Raman band at 1294 cm^{-1} is assigned to C–O stretching vibration of CHP. The in-plane and out-of-plane vibrations of C–O group are presented in Table 4.

HOMO–LUMO BAND GAP

This electronic absorption corresponds to the transition from the ground to the first excited state and is mainly described by one electron excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) [45,46]. Many organic molecule, containing conjugated π electrons are characterized by large values of molecular first hyper polarizabilities, are analyzed by means of vibrational spectroscopy. In most of the cases, even in the absence of inversion symmetry, the strongest band in the Raman spectrum is weak in the IR spectrum and vice-versa. But the intramolecular charge from the donor to acceptor group through a single-double bond conjugated path can induce large variations of both the molecular dipole moment and the molecular polarizability, making IR and Raman activity strong at the same time. The experimental spectroscopic behavior described above is well accounted for DFT calculations in π conjugated system that predict exceptionally infrared intensities for the same normal modes. The analysis of the wave function indicates that the electron absorption corresponds to the transition from the ground to the first excited state and is mainly described by one-electron excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied orbital (LUMO). The LUMO; of π nature, (i.e. pyridine ring) is delocalized over the whole C–C bond. The HOMO is located over chlorine and hydroxyl group and the HOMO–LUMO transition implies an electron density transfer to the pyridine ring from hydroxyl group and chlorine atom. Moreover, the compositions of the frontier molecular orbital for CHP are shown in Figs. 4 and 5.

The HOMO–LUMO energy gap of CHP is calculated at B3LYP/3-21G and B3LYP/6-311++G(d,p) level, which reveals that the energy gap reflects the chemical activity of the molecule. The LUMO as an electron acceptor (EA) represents the ability to obtain an electron and HOMO represents ability to donate an electron (ED). The ED groups to the efficient EA groups through π -conjugated path.

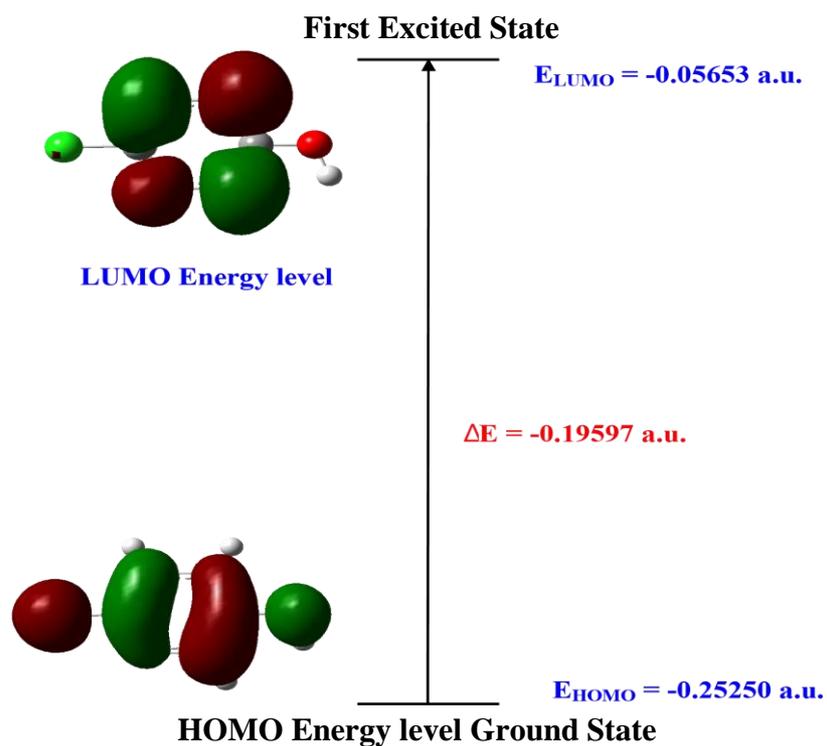


FIGURE 4. HOMO-LUMO energy gap of 2-chloro-5-hydroxypyridine by B3LYP/6-311++G(d,p)

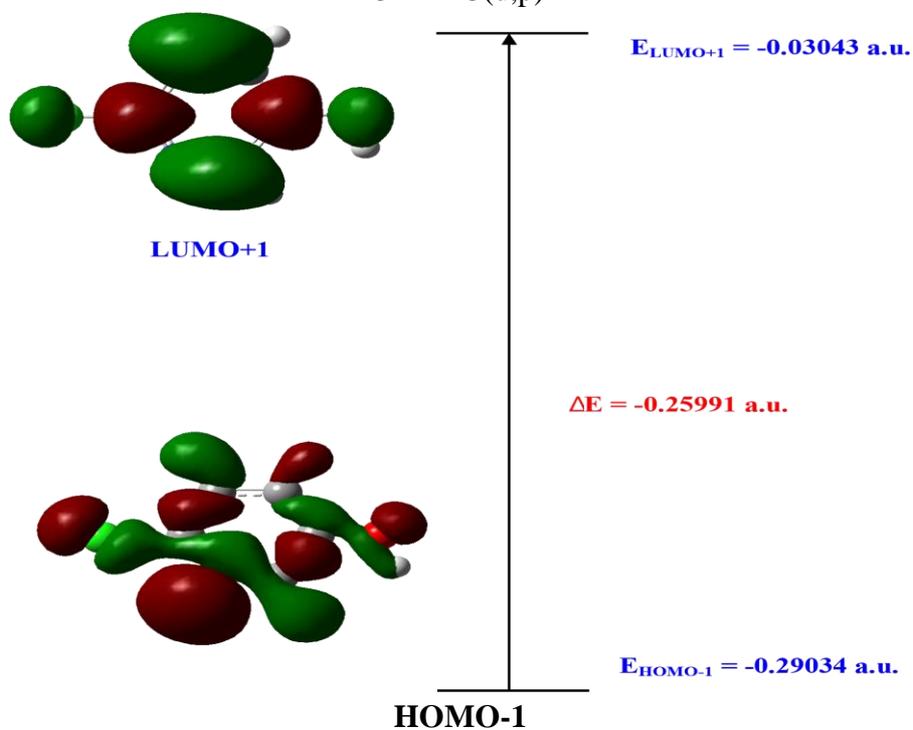


FIGURE 5. HOMO-1-LUMO+1 energy gap of 2-chloro-5-hydroxypyridine by B3LYP/6-311++G(d,p)

The strong charge transfer interaction through π -conjugated bridge results in substantial ground state Donor-Acceptor (DA) mixing and the appearance of a charge transfer band in the electron absorption spectrum. By B3LYP/6-311++G(d,p) level, HOMO energy = -0.25250 a.u. LUMO energy = -0.05653 a.u.

HOMO-LUMO energy gap = -0.19597 a.u.

The calculated self-consistent field (SCF) energy or optimized global minimum energy of CHP is -783.222 Hartrees at B3LYP/6-311++G(d,p) and -779.10677992 Hartrees at B3LYP/3-21G methods. The calculated HOMO, LUMO and other related properties at B3LYP/6-311++G(d,p) and B3LYP/3-21G levels are listed in Table 5. The HOMO and LUMO energy gap explains the fact that eventual charge transfer interaction is taking place within the molecule.

NBO ANALYSIS

The natural bond orbital (NBO) calculation was performed using NBO 3.3 program implemented in the GAUSSIAN 09W package at the B3LYP/6-311++G(d,p) level in order to understand various second-order interactions between the filled orbitals of one subsystem and vacant orbitals of another subsystem which is a measure of the delocalization or hyperconjugation. A useful aspect of the NBO method is that it gives information about interactions in both filled and virtual orbital spaces that could enhance the analysis of intra and intermolecular interactions. The second order Fock matrix was carried out to evaluate the donor-acceptor interactions in the NBO analysis [46]. 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,j) is estimated as $F_{ij}^2 / (\epsilon_j - \epsilon_i)$

(2)

$$E^{(2)} = \frac{F_{ij}^2}{\epsilon_j - \epsilon_i} \quad q_i \quad \dots \quad (2)$$

where q_i is the donor orbital occupancy and are ϵ_i and ϵ_j diagonal elements and F_{ij} is the off diagonal NBO Fock matrix element. Natural bond orbital analysis provides an efficient method for studying intra and intermolecular bonding and interaction among bonds, and also provides a convenient basis for investigating charge transfer or conjugative interaction in molecular systems. Some electron donor orbital, acceptor orbital and the interacting stabilization energy resulted from the second order micro-disturbance theory are reported [47,48]. The larger the $E^{(2)}$ value, the more intensive is the interaction between electron donors and electron acceptors, i.e. the more donating tendency from electron donors to electron acceptors and the greater the extent of conjugation of the whole system. Delocalization of electron density between occupied Lewis-type (bond or lone pair) NBO orbitals and formally unoccupied (antibond or Rydberg) non-Lewis NBO orbitals correspond to a stabilizing donor-acceptor interaction. The intramolecular interactions are formed by the orbital overlap between bonding C-C, C-N, and antibonding C-N orbital which results intramolecular charge transfer (ICT) causing stabilization of the system for CHP as shown in Table 6. The strong intramolecular hyperconjugative interaction of π (C-C) to the anti π^* (C-C) bond of the ring leads to

stabilization of some part of the ring as evident from Table 6. For example the intramolecular hyper conjugative interaction of $\pi^*(C2-N3)$, distribute to $\pi^*(C4-C5)$ and $\pi^*(C1-C6)$ leading to stabilization of 194.47 and 137.97 kJ/mol, respectively. This enhanced further conjugate with antibonding.

This strong stabilization denotes the larger delocalization. The interesting interactions in CHP compound is LP_2O_{10} with that of anti-bonding C4-C5. This interaction result the stabilization energy of 27.87KJ/mol. This highest interaction around the ring can induce the large bioactivity in the compound.

PREDICTION OF FIRST HYPERPOLARIZABILITY – A NLO PROPERTY

There is an intense current research activity in the area of molecular linear and non-linear optics, devoted to the search for efficient, stable, simple organic compounds exhibiting large hyper polarizabilities [49-52]. Aromatic backbone compounds are still common and show large non-linear optical properties. Organic non-linear materials have attracted a keen interest in recent year owing to their potential applications in various photonic technologies. Significant effects have focused on studying the electronic and structural properties of donor-acceptor substituted π -conjugated organic compounds with large molecular non-linear optical (NLO) response (β -first-order hyperpolarizability) [53]. Two factors are attributed to NLO properties of such compounds in an electric field: the altered ground state charge distribution by the donor and acceptor moieties and the enhanced- π -electronic charge redistribution through the π -conjugation. The first hyperpolarizability β is associated with the intramolecular charge transfer (ICT), resulting from the electron cloud movement through the π -conjugated framework from electron donor to acceptor groups. The electron cloud is capable of interacting with an external electric field and thereby altering the dipole moment and the first hyperpolarizability.

A reliable prediction of molecular hyperpolarizability requires adequate basis sets and therefore must involve both diffuse and polarization functions. As the basis becomes larger, one expects a better description of the compound and accordingly, more accurate results. In the view of these points, B3LYP/6-311++G(d,p) and B3LYP/3-21G method has been used for present study in order to see the effect of the level of theory and basis set. The title compound fully optimized at B3LYP/6-311++G(d,p) method in the GAUSSIAN 09W program. The tensor component of the static first hyperpolarizabilities, β , was analytically calculated by using the same method as mentioned above. From the computed tensorial component β , β_{vec} is calculated for the title compound by taking into account the Kleinman symmetry relations and the squared norm of the Cartesian expression for the β tensor [54]. The relevant expressions used for the calculation are shown below:

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \quad \beta = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \quad \text{where } \beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$$

$$\beta_y = \beta_{yyy} + \beta_{xxy} + \beta_{yzz} \quad \beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yyz}$$

The calculated first hyperpolarizability for CHP is 0.46599×10^{-30} esu, and 0.679178×10^{-30} esu by B3LYP with 6311++G(d,p) and 3-21G methods, respectively and is reported in Table 7. The large value of hyperpolarizability, β which is a measure of the non-linear optical activity of the molecular system, is associated with the intramolecular charge transfer, resulting from

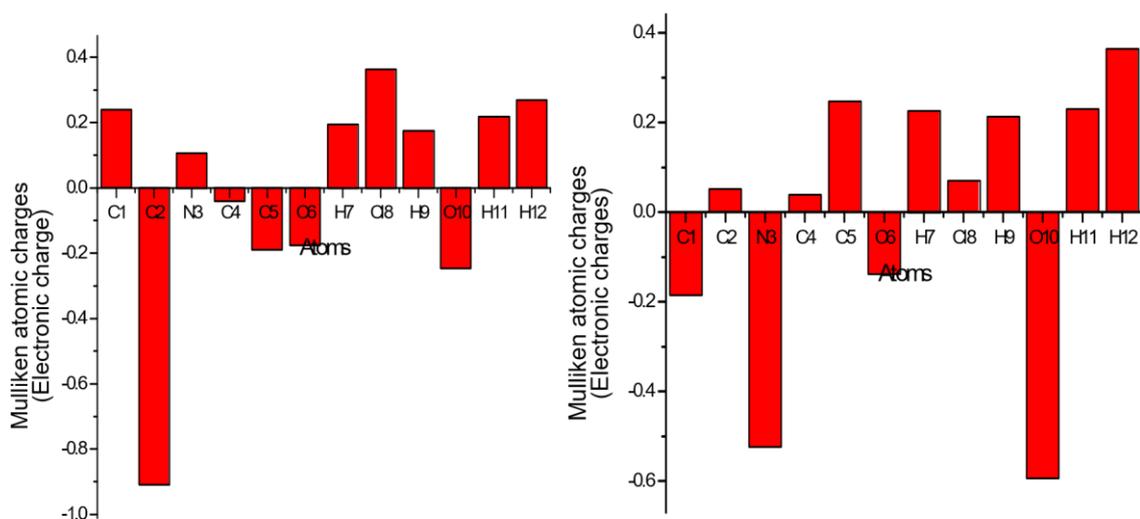
the electron cloud movement through π conjugated frame work from electron donor to electron acceptor groups. So, the title compound is an attractive object for future studies of nonlinear optical properties.

THERMODYNAMIC PROPERTIES

The thermodynamic parameters namely heat capacity, entropy, rotational constants, dipole moments, zero point vibrational energies (ZPVE) of the compound CHP have also been computed at B3LYP levels using 6-311+G(d,p) and 3-21G basis set are presented in Table 8. The variation in the ZPVE seems to be insignificant.

MULLIKEN'S POPULATION ANALYSIS

Mulliken atomic charge calculation has a significant role in the application of quantum chemical calculation to molecular system, because of atomic charges affect electronic structure, dipole moment, molecular polarizability and other properties of molecular systems. The total atomic charges of CHP obtained by Mulliken population analysis with 6-311++G(d,p) and 3-21G basis sets are listed in Table 9. From the result it is clear that the substitution of aromatic ring by hydroxyl leads to a redistribution of electron density. The charge distribution on the molecule has an important influence on the vibrational spectra [55]. The corresponding plot of Mulliken's charges are shown in Figs. 6 and 7, respectively.



FIGURES 6,7. Mulliken atomic charges of 2-chloro-5-hydroxypyridine by B3LYP/6-311G(d,p) and 3-21G methods

POTENTIAL ENERGY SURFACE SCAN ANALYSIS

Conformation analysis is carried for CHP by potential energy surface scan to find all possible conformers with B3LYP method using 6-311++G(d,p) basis set. The results obtained in PES scan studies by varying the torsional perturbation of τ C4–C5–O10–H12 with step angle of 10° are plotted in Fig.8. The calculated molecular energy at 0° torsion angle, (τ C4–C5–O10–H12) is about -779.1067799230 Hartrees. The energy profile obtained from DFT method is shown in Fig. 8 has shown the minimum at 0° and the maximum at 90° .

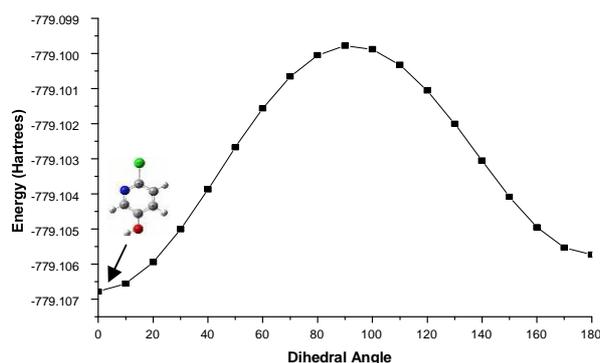


FIGURE 8. Potential energy surface scan of 2-chloro-5-hydroxypyridine

CONCLUSION

The optimized geometrical parameters and vibrational frequencies of the fundamental modes of 2-chloro-5hydroxypyridine have been obtained from B3LYP method with 6-311++G(d,p) and 3-21G calculations. The theoretical results have been compared with the experimental vibrations. Although both the types of calculations are useful to explain vibrational spectra of CHP, DFT calculations at B3LYP/3-21G level is found little poorer than B3LYP/6311+G(d,p) level calculations. The closer agreement obtained between the observed and scaled frequencies and the TED calculations are also supporting the assignments made for various functional groups present in the compound.

The results confirm the ability of methodology applied for interpretation of the vibrational spectra of the title compound in the solid phase. Furthermore, non-linear optical, first-order hyperpolarizability and NBO properties of the compound have been calculated in order to get insight into the compound. The calculated HOMO–LUMO energy gap also shows that eventual charge transfer takes place within the compound. Calculations show that the title compound is an attractive object for future studies of nonlinear optical properties. The results are of assistance in the quest of the experimental and theoretical evidence for 2-chloro-5-hydroxypyridine in reaction intermediates, non linear optical and photoelectric materials.

TABLE 1. Optimized geometrical parameters of 2-chloro-5-hydroxypyridine obtained by B3LYP/6-311++G(d,p) and B3LYP/3-21G level calculations.

| | Value (Å) | | Value (°) | | | Value (°) | | |
|--------|------------------------------|-----------------------|---------------------------------|---------------|---------------------|---------------------------------|------------------|-------|
| | B3LYP/ 311++G(d,p) 21G | Bond 6-angle 3- | B3LYP/ 6- 311++G(d, p) | 33LYP/ 21G | 3-Dihedral Angle | B3LYP/ 6- 311++G(d, p) | 33LY P/ 3- | |
| Length | | | | | | | | |
| C1-C2 | 1.3972 | 1.3931 | C2-C1-C6 | 117.8274 | 117.2359 | C6-C1-C2-N3 | 0.0018 | 0.0 |
| C1-C6 | 1.3858 | 1.3881 | C2-C1- H7 | 120.7923 | 120.8111 | C6-C1-C2-C18 | 180.0021 | 180.0 |

| | | | | | | | | |
|---------|--------|--------|------------|----------|----------|---------------|-----------|-------|
| C1-H7 | 1.0816 | 1.08 | C6-C1-H7 | 121.8803 | 121.953 | H7-C1-C2-N3 | 180.0048 | 180.0 |
| C2-N3 | 1.3139 | 1.3123 | C1-C2-N3 | 124.0959 | 124.6322 | N7-C1-C2-C1 | 180.0051 | 0.0 |
| C2-C18 | 1.7633 | 1.846 | C1-C2-C18 | 118.8766 | 117.344 | C2-C1-C6-C5 | 0.0007 | 0.0 |
| N3-C4 | 1.3366 | 1.3504 | N3-C2-C18 | 117.0275 | 118.0238 | C2-C1-C6-H11 | -179.9958 | 180.0 |
| C4-C5 | 1.3939 | 1.3964 | C2-N3-C4 | 118.0588 | 118.4101 | H7-C1-C6-C5 | -180.0023 | 180.0 |
| C4-H9 | 1.0882 | 1.0852 | N3-C4-C5 | 122.8778 | 122.0741 | H7-C1-C6-H11 | 0.0012 | 0.0 |
| C5-C6 | 1.3966 | 1.4044 | N3-C4-H9 | 116.4263 | 116.9469 | C1-C2-N3-C4 | -0.0057 | 0.0 |
| C5-O10 | 1.3636 | 1.378 | C5-C4-H9 | 120.696 | 120.979 | C18-C2-N3-C4 | 180.0059 | 180.0 |
| C6-H11 | 1.0833 | 1.0814 | C4-C5-C6 | 118.316 | 118.1888 | C2-N3-C4-C5 | 0.0072 | 0.0 |
| O10-H12 | 0.9636 | 0.9927 | C4-C5-O10 | 123.3917 | 124.1618 | C2-N3-C4-H9 | 180.001 | 180.0 |
| | | | C6-C5-O10 | 118.2923 | 117.1618 | N3-C4-C5-C6 | -0.0048 | 0.0 |
| | | | C1-C6-C5 | 118.8242 | 119.459 | N3-C4-C5-O10 | -179.9893 | 180.0 |
| | | | C1-C6-H11 | 121.4429 | 121.6449 | H9-C4-C5-C6 | -179.9984 | 180.0 |
| | | | C5-C6-H11 | 119.7329 | 118.8961 | H9-C4-C5-O10 | 0.0172 | 0.0 |
| | | | C5-O10-H12 | 110.1639 | 110.6422 | C4-C5-C6-C1 | 0.0008 | 0.0 |
| | | | | | | C4-C5-C6-H11 | 179.9973 | 180.0 |
| | | | | | | O10-C5-C6-C1 | 179.986 | 180.0 |
| | | | | | | O4-C5-C10-H12 | -0.0941 | 0.0 |

Bond

TABLE 2. Definition of internal coordinates of 2-chloro-5-hydroxypyridine

| No. (i) | Symbo l | Type | Definition ^a |
|-----------------------------|-------------|-------------|--|
| Stretching | | | |
| 1-3 | r_i | C-H | C1-H7, C4-H9, C6-H11 |
| 4 | P_i | C-Cl | C2-Cl8 |
| 5 | q_i | C-O | C5-O10 |
| 6 | S_i | O-H | O10-H12 |
| 7-10 | r_i | C-C | C1-C2, C1-C6, C4-C5, C5-C6 |
| 11,12 | Q_i | C-N | C2-N3, C4-N3 |
| In-plane bending | | | |
| 13-18 | α_i | Ring | C1-C2-N3, C2-N3-C4, N3-C4-C5, C4-C5-C6, C5-C6-C1, C6-C1-C2 |
| 19-23 | γ_i | C-C-H | C2-C1-H7, C6-C1-H7, C1-C6-H11, C5-C6-H11, C5-C4-H9 |
| 24 | γ_i | N-C-H | N3-C4-H9 |
| 25 | π_i | C-C-Cl | C1-C2-Cl8 |
| 26 | π_i | N-C-Cl | N3-C2-Cl8 |
| 27,28 | ϕ_i | C-C-O | C6-C5-O10, C4-C5-O10 |
| 29 | μ_i | C-O-H | C5-O10-H12 |
| Out-of-plane bending | | | |
| 30 | ω_i | C-Cl | Cl8-C2-C1-N3 |
| 31 | ψ_i | C-O | O10-C5-C4-C6 |
| 32-34 | λ_i | C-H | H7-C1-C2-C6, H9-C4-N3-C5, H11-C6-C5-C1 |
| Torsion | | | |
| 35-40 | τ_i | t Ring | C1-C2-N3-C4, C2-N3-C4-C5, N3-C4-C5-C6, C4-C5-C6-C1, C5-C6-C1-C2, C6-C1-C2-N3 |
| 41 | t_i | τ C-OH | (C4,C6)-C5-O10-H12 |

a

For numbering of atoms refer Fig. 1.

TABLE 3. Definition of Local Symmetry Coordinates of 2-Chloro-5-Hydroxypyridine

| No. (i) | a | | | b | | | Definition |
|---------|---------|-------|----|-------|----|-------|--|
| | Type | | | | | | |
| 1-3 | CH | | | | | | r_1, r_2, r_3 |
| 4 | CCl | P_4 | CO | q_5 | OH | S_6 | |
| 7-10 | CC | | | | | | r_7, r_8, r_9, r_{10} |
| 11,12 | CN | | | | | | Q_{11}, Q_{12} |
| 13 | R trigd | | | | | | $(\alpha_{13} - \alpha_{14} + \alpha_{15} - \alpha_{16} + \alpha_{17} - \alpha_{18})/\sqrt{6}$ |
| 14 | R symd | | | | | | $(-\alpha_{13} - \alpha_{14} + 2\alpha_{15} - \alpha_{16} - \alpha_{17} + 2\alpha_{18})/12$ |
| 15 | R asymd | | | | | | $(\alpha_{13} - \alpha_{14} + \alpha_{16} - \alpha_{17})/2$ |

| | | |
|-------|--------------|---|
| 16-18 | b CH | $(\gamma_{19} - \gamma_{20})/\sqrt{2}, (\gamma_{21} - \gamma_{22})/\sqrt{2}, (\gamma_{23} - \gamma_{24})/2$ |
| 19 | b CCl | $(\pi_{25} - \pi_{26})/2$ |
| 20 | b CO | $(\theta_{27} - \theta_{28})/\sqrt{2}$ |
| 21 | b OH | μ_{29} |
| 22 | ω CCl | ω_{30} |
| 23 | ψ CO | ψ_{31} |
| | λ CH | |
| 27 | t R trigd | $(\tau_{35} - \tau_{36} + \tau_{37} - \tau_{38} + \tau_{39} - \tau_{40})/\sqrt{6}$ |
| 28 | t R symd | $(\tau_{35} - \tau_{37} + \tau_{38} - \tau_{40})/\sqrt{2}$ |
| 29 | t R asymd | $(-\tau_{35} + 2\tau_{36} - \tau_{37} - \tau_{38} + 2\tau_{39} - \tau_{40})/\sqrt{12}$ |
| 30 | COH | τ_{41} |
| <hr/> | | |
| 24-26 | | $\lambda_{32}, \lambda_{33}, \lambda_{34}$ |

These symbols are used for description of normal modes by TED in Table 5.

b

The internal coordinates used here are defined in Table 2.

TABLE 4. The observed (FT-IR and FT-Raman) and calculated (Unscaled and Scaled) frequencies (cm^{-1}), IR intensity (Km mol^{-1}), Raman activity ($\text{A}^4 \text{amu}^{-1}$) and probable assignments (characterized by TED) of 2-chloro-5-hydroxypyridine using B3LYP/6-311++G(d,p) and B3LYP/3-21G calculations.

| S. No. | Observed | | B3LYP/6-311++G(d,p) | | | | B3LYP/3-21G | | | | Assign | | | |
|--------|----------------------|----------------------|----------------------|--------|--------|------------|----------------------|-----------|--------|--------|------------|-----------|-------|-----------|
| | freq-1 | uen | Calculate | Reduce | Force | IR | Rama d | Calculate | Reduce | Force | IR | Rama n | % of | |
| | FT- an | FT- IR | Unscaled | Mass | nts | Intensi ty | Activi ty | Unscaled | Mass | nts | Intensi ty | Activi ty | TED | |
| | (cm^{-1}) | (cm^{-1}) | (cm^{-1}) | | | | (cm^{-1}) | | | | | | | |
| | | | scaled | | | | Scaled | | | | | | | |
| 1 | 343 - 5 | 3826 | 3486 | 1.0678 | 7.7660 | 35.168 | 168.4 | 3519 | 3432 | 1.0658 | 7.7760 | 35.158 | 169.4 | v OH (99) |
| 2 | - 3103 | 3214 | 3178 | 1.0956 | 6.6643 | 0.4127 | 124.1 | 3254 | 3167 | 1.0949 | 6.8510 | 0.0708 | 101.7 | vCH (98) |
| 3 | 307 3070 | 3194 | 3128 | 1.0902 | 6.5509 | 1.8216 | 84.89 | 3238 | 3148 | 1.0890 | 6.7289 | 0.4764 | 73.77 | vCH (96) |
| 4 | 300 - 3 | 3134 | 3078 | 1.0904 | 6.2983 | 27.544 | 126.7 | 3180 | 3112 | 1.0906 | 6.4970 | 21.406 | 107.3 | vCH (97) |
| 5 | 160 1605 | 1631 | 1615 | 6.3363 | 9.9293 | 3.2556 | 17.21 | 1621 | 1613 | 4.8621 | 7.5328 | 1.5664 | 8.426 | vCC (92) |
| 6 | 154 1574 | 1614 | 1598 | 5.9908 | 9.1955 | 16.836 | 12.36 | 1585 | 1578 | 5.1493 | 7.6191 | 14.754 | 11.05 | vCC (90) |
| 7 | 146 - 4 | 1497 | 1474 | 2.6253 | 3.4675 | 186.66 | 186.8 | 1512 | 1474 | 2.6130 | 3.5191 | 165.49 | 3.837 | vCC (89) |

| | | | | | | | | | | | | | | |
|----|---------|------|------|--------|--------|--------|-------|------|------|--------|--------|--------|-------|---------------|
| 8 | 143 - 2 | 1429 | 1431 | 2.5875 | 3.1146 | 139.43 | 139.4 | 1439 | 1437 | 1.8624 | 2.2732 | 101.84 | 0.546 | vCC |
| | | | | | | 9 | 3 | | | | | 9 | | (87) |
| 9 | 132 - 7 | 1317 | 1321 | 2.5874 | 2.6477 | 6.4969 | 6.496 | 1335 | 1325 | 1.4752 | 1.5502 | 15.618 | 5.039 | vCN |
| | | | | | | | 9 | | | | | 4 | 6 | (86) |
| 10 | 131 - 0 | 1309 | 1309 | 1.7280 | 1.7430 | 11.243 | 2.622 | 1319 | 1312 | 2.5785 | 2.6420 | 11.688 | 2.417 | vCN |
| | | | | | | 0 | 9 | | | | | 8 | 0 | (84) |
| 11 | - 1294 | 1289 | 1288 | 4.1818 | 4.0942 | 113.88 | 10.81 | 1293 | 1293 | 7.1181 | 7.0119 | 30.245 | 7.124 | vCO |
| | | | | | | | 60 | | | | | 4 | 2 | (85) |
| 12 | 127 9 | 1276 | 1189 | 1.5128 | 1.2602 | 129.81 | 4.738 | 1180 | 1180 | 1.5245 | 1.2504 | 203.38 | 1.471 | bCH |
| | | | | | | | 22 | | | | | 91 | 9 | (81) |
| 13 | 122 8 | 1228 | 1143 | 1.4182 | 1.0934 | 18.898 | 2.024 | 1161 | 1161 | 1.5508 | 1.2318 | 62.443 | 5.456 | bCH |
| | | | | | | 0 | 7 | | | | | 0 | 4 | (78) |
| 14 | - 1146 | 1123 | 1127 | 2.9693 | 2.2072 | 92.568 | 17.67 | 1137 | 1142 | 5.1184 | 3.899 | 77.833 | 7.473 | bCH |
| | | | | | | 9 | 19 | | | | | 5 | 9 | (79) |
| 15 | 113 - 4 | 1115 | 1114 | 3.0971 | 1.9385 | 9.7819 | 2.628 | 1038 | 1078 | 1.4243 | 0.9052 | 0.7291 | 0.517 | bOH |
| | | | | | | | 5 | | | | | 5 | | (78) |
| 16 | - 1117 | 1101 | 1100 | 1.3120 | 0.7273 | 0.2093 | 0.027 | 1034 | 1042 | 3.2138 | 2.0245 | 13.372 | 1.417 | Rasymd |
| | | | | | | | 3 | | | | | 5 | 0 | (75) |
| 17 | 110 - 6 | 1098 | 1097 | 1.4062 | 0.6689 | 7.6334 | 0.250 | 1096 | 1095 | 1.6218 | 0.8784 | 19.005 | 3.087 | Rtrid(7 |
| | | | | | | | 7 | | | | | 8 | 1 | 4) |
| 18 | 102 - 4 | 1014 | 1012 | 7.4839 | 3.1819 | 1.0690 | 27.06 | 1010 | 1010 | 1.4601 | 0.6874 | 41.619 | 2.759 | Rsy |
| | | | | | | | 23 | | | | | 8 | 2 | (72) |
| 19 | 918 - | 925 | 918 | 1.4705 | 0.6143 | 32.452 | 0.443 | 928 | 918 | 7.6418 | 3.1986 | 2.4370 | 24.46 | ω CH(7 |
| | | | | | | 1 | 5 | | | | | 19 | 0) | |
| 20 | 857 858 | 900 | 863 | 5.5358 | 1.7706 | 2.5884 | 0.193 | 891 | 860 | 3.3491 | 1.2465 | 4.2615 | 0.688 | ω CH(6 |
| | | | | | | | 6 | | | | | 2 | 8) | |
| 21 | 828 - | 837 | 830 | 8.5716 | 2.1416 | 37.906 | 2.930 | 847 | 843 | 8.7080 | 2.1859 | 4.4552 | 7.689 | vCCl(7 |
| | | | | | | 6 | 1 | | | | | 6 | 5) | |
| 22 | - 841 | 851 | 845 | 7.9560 | 1.9221 | 21.742 | 3.660 | 849 | 843 | 8.3090 | 1.1982 | 59.212 | 0.400 | ω CH(6 |
| | | | | | | 5 | 9 | | | | | 3 | 4 | 6) |
| 23 | 783 - | 793 | 773 | 3.0975 | 0.4341 | 3.6342 | 0.336 | 791 | 788 | 3.1675 | 0.5815 | 1.0495 | 0.633 | bCO |
| | | | | | | | 2 | | | | | 9 | | (71) |
| 24 | 722 - | 756 | 737 | 3.5140 | 0.3844 | 10.164 | 0.235 | 752 | 735 | 3.1339 | 0.3819 | 2.9186 | 0.579 | ttrigd |
| | | | | | | 0 | 5 | | | | | 6 | | (69 |
| 25 | 652 657 | 669 | 648 | 4.4480 | 0.4719 | 11.354 | 0.825 | 667 | 661 | 4.1208 | 0.4131 | 14.417 | 1.151 | tRsy |
| | | | | | | 8 | 5 | | | | | 9 | 5 | (66) |
| 26 | 639 638 | 651 | 639 | 12.550 | 1.0990 | 7.6609 | 10.32 | 648 | 639 | 1.1847 | 0.1060 | 167.68 | 5.702 | tRasd |
| | | | | | | | 20 | | | | | 2 | | (65) |
| 27 | 518 - | 529 | 521 | 4.5417 | 0.3151 | 25.020 | 1.771 | 527 | 523 | 16.505 | 1.2821 | 12.936 | 16.01 | bCCl(6 |
| | | | | | | 9 | 3 | | | 7 | | 1 | 79 | 9) |
| 28 | - 392 | 413 | 387 | 1.1632 | 0.0711 | 95.848 | 0.555 | 411 | 397 | 4.1026 | 0.2953 | 3.4958 | 0.102 | ω CO(6 |
| | | | | | | 9 | 3 | | | | | 9 | 5) | |

| | | | | | | | | | | | | | | | |
|----|---|-----|-----|-----|--------|--------|--------|-------|------|-----|--------|--------|--------|-------|-----------------|
| 29 | - | 338 | 356 | 341 | 8.6405 | 0.3680 | 1.2725 | 0.479 | 5173 | 339 | 8.6693 | 0.3087 | 2.1095 | 1.471 | ω CCl(6 |
| | | | | | | | | | | | | | | 3 | 4) |
| 30 | - | 156 | 171 | 159 | 8.8908 | 0.0734 | 0.0016 | 0.014 | 169 | 158 | 9.0372 | 0.0798 | 0.0298 | 0.001 | ω O (63) |
| | | | | | | | | | | | | | | 5 | |

Abbreviations: ν -stretching; α s-asymmetric stretching; α ss-symmetric stretching; α b-in-plane-bending; α ω -out-of-plane bending; α t-torsion.

TABLE 5. HOMO-LUMO energy and other related properties of 2-chloro-5-hydroxy pyridine in a.u. based on B3LYP/6-311++G(d,p) and B3LYP-3-21G methods

| Parameters | B3LYP/6-311++G(d,p) | B3LYP/3-21G |
|---|---------------------|-------------|
| HOMO | -0.25250 | -0.24744 |
| LUMO | -0.05653 | -0.04101 |
| Global hardness (η) | 0.09798 | 0.103215 |
| Electronic chemical potential (μ) | -0.15451 | -0.14423 |
| Electrophilicity index (ω) | 0.12183 | 0.100765 |
| Ionization energy (I) | 0.25250 | 0.24744 |
| Electron affinity (A) | 0.05653 | 0.04101 |

TABLE 6. Second order perturbation theory of fock matrix in NBO basis using B3LYP/6-311++G(d,p) basis set for 2-chloro-5-hydroxypyridine

| Donor NBO (i) | Acceptor NBO (j) | Occupancy | E(2) jK/mol | E(j) – E(i) a.u. | F(i, j) a.u. |
|-----------------|-------------------|-----------|-------------|------------------|--------------|
| $\pi^*(C2-N3)$ | $\pi^*(C4-C5)$ | 0.43870 | 194.47 | 0.02 | 0.080 |
| $\pi^*(C2-N3)$ | $\pi^*(C1-C6)$ | 0.43870 | 137.97 | 0.02 | 0.084 |
| n2(O10) | $\pi^*(C4-C5)$ | 1.87796 | 27.87 | 0.35 | 0.093 |
| $\pi(C1-C6)$ | $\pi^*(C2-N3)$ | 1.68943 | 24.32 | 0.26 | 0.074 |
| $\pi(C2-N3)$ | $\pi^*(C4-C5)$ | 1.75795 | 20.27 | 0.33 | 0.075 |
| $\pi(C1-C6)$ | $\pi^*(C4-C5)$ | 1.68943 | 19.69 | 0.28 | 0.067 |
| $\pi(C4-C5)$ | $\pi^*(C2-N3)$ | 1.63925 | 19.61 | 0.27 | 0.066 |
| $\pi(C4-C5)$ | $\pi^*(C1-C6)$ | 1.63925 | 18.88 | 0.29 | 0.068 |
| n3(Cl8) | $\pi^*(C2-N3)$ | 1.92542 | 14.48 | 0.30 | 0.065 |
| $\pi(C2-N3)$ | $\pi^*(C1-C6)$ | 1.75795 | 13.15 | 0.34 | 0.060 |
| n1(N3) | $\sigma^*(C1-C2)$ | 1.89382 | 10.22 | 0.89 | 0.087 |
| n1(N3) | $\sigma^*(C4-C5)$ | 1.89382 | 8.53 | 0.88 | 0.079 |
| n2(Cl8) | $\sigma^*(C2-N3)$ | 1.96893 | 5.99 | 0.86 | 0.064 |
| $\sigma(N3-C4)$ | $\sigma^*(C2Cl8)$ | 1.97396 | 5.31 | 0.97 | 0.065 |
| n1(N3) | $\sigma^*(C2-18)$ | 1.89382 | 5.21 | 0.49 | 0.045 |

| | | | | | |
|-------------------------|--------------------------|---------|------|------|-------|
| $\sigma(\text{C1-H7})$ | $\sigma^*(\text{C2-N3})$ | 1.97889 | 5.01 | 1.09 | 0.066 |
| $\sigma(\text{C1-C6})$ | $\sigma^*(\text{C2-I8})$ | 1.97005 | 4.73 | 0.86 | 0.058 |
| $\sigma(\text{O10-12})$ | $\sigma^*(\text{C5-C6})$ | 1.98687 | 4.38 | 1.30 | 0.067 |
| $\sigma(\text{C4-H9})$ | $\sigma^*(\text{C2-N3})$ | 1.98085 | 4.15 | 1.09 | 0.060 |
| $n_1(\text{N3})$ | $\sigma^*(\text{C4-H9})$ | 1.89382 | 4.11 | 0.75 | 0.050 |
| $\sigma(\text{C1-C6})$ | $\sigma^*(\text{C5-10})$ | 1.97005 | 3.85 | 1.06 | 0.057 |
| $\sigma(\text{C4-C5})$ | $\sigma^*(\text{C5-C6})$ | 1.98390 | 3.77 | 1.28 | 0.062 |
| $\sigma(\text{C2-Cl8})$ | $\sigma^*(\text{N3-C4})$ | 1.98661 | 3.31 | 1.23 | 0.057 |
| $\sigma(\text{C1-C6})$ | $\sigma^*(\text{C1-C2})$ | 1.97005 | 3.14 | 1.27 | 0.056 |

TABLE 7. Nonlinear optical properties of based on 2-chloro-5-hydroxypyridine based on B3LYP/6-311++G(d,p) and B3LYP/3-21G methods

| NLO Behaviour | B3LYP/6-311++G(d,p) | B3LYP/3-21G |
|---|-------------------------------|--------------------------------|
| Dipole moment (μ) | 3.0104 Debye | 3.9381 Debye |
| Mean polarizability(α) | $.69318 \times 10^{-30}$ esu | $.53699 \times 10^{-30}$ esu |
| Anisotropy of the polarizability ($\Delta\alpha$) | $.856140 \times 10^{-30}$ esu | 1.15427×10^{-30} esu. |
| First hyperpolarizability(β) | $.46599 \times 10^{-30}$ esu | $.679178 \times 10^{-30}$ esu |
| Energy | -783.222 a.u. | -779.107 a.u |

TABLE 8. Theoretically computed zero point vibrational energy (kcal mol^{-1}), rotational constant (GHz), rotational temperature (kelvin), thermal energy (kcal mol^{-1}), molar capacity at constant volume ($\text{cal mol}^{-1} \text{kelvin}^{-1}$), entropy ($\text{cal mol}^{-1} \text{kelvin}^{-1}$), dipole moment (Debyes) and vibrational temperature (kelvin) of 2-chloro-5-hydroxypyridine by B3LYP/6-311++G(d,p) and B3LYP/3-21G methods

| Parameter | B3LYP/6-311++G(d,p) | B3LYP/3-21G |
|-------------------------------|----------------------------|-------------------------------|
| Zero point vibrational energy | 51.94958 | 52.21331 |
| Rotational constant | 5.85205 0.99639 0.85142 | 5.83821 0.96207 0.82596 |
| Rotational temperatures | 0.28085 0.04782 0.04086 | 0.28019 0.04617 0.03964 |
| Energy | 56.091 | 56.280 |

| | | |
|--|--------|-----------------------|
| Total | | |
| Translation | 0.889 | 0.889 |
| Rotational | 0.889 | 0.889 |
| Vibrational | 54.313 | 54.502 |
| Molar capacity at constant volume | | |
| Total | 24.844 | 24.321 |
| Translational | 2.981 | 2.981 |
| Rotational | 2.981 | 2.981 |
| Vibrational | 18.882 | Entropy 18.359 |
| Total | 81.595 | 81.263 |
| Translational | 40.477 | 40.477 |
| Rotational | 28.561 | 28.629 |
| Vibrational | 12.557 | 12.157 |

TABLE 9. The Mulliken charge distribution of 2-chloro-5-hydroxypyridine based on B3LYP/6-311++G(d,p) and B3LYP/321G methods

Atomic Charges (Mulliken)

| | B3LYP/6-311G(d,p) | B3LYP/3-21G |
|-----------------|-------------------|-------------|
| C1 | 0.238199 | -0.183977 |
| C2 | -0.910014 | 0.052003 |
| N3 | 0.105987 | -0.523698 |
| C4 | -0.039883 | 0.038112 |
| C5 | -0.190118 | 0.246693 |
| C6 | -0.176760 | -0.138101 |
| H7 | 0.194827 | 0.225987 |
| Cl ₈ | 0.363729 | 0.070297 |
| H9 | 0.174068 | 0.211729 |
| O ₁₀ | -0.245673 | -0.593801 |
| H ₁₁ | 0.218087 | 0.229848 |
| H ₁₂ | 0.267550 | 0.364907 |

Atoms

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