Structural and vibrational analysis of (E)-N’-(Pyridin-2-yl) methylene) nicotinohydrazide using Quantum chemical calculation

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ABSTRACT. FT-IR, FT-Raman and UV-Vis spectra of the Schiff base compound (E)-N’-(Pyridin-2-yl) methylene) nicotinohydrazide (P2CNH) have been recorded and analyzed. The optimized molecular structures, vibrational assignment of P2CNH have been investigated by using DFT/B3LYP/6-311++G(d,p) level of theory. The Non-linear optical behavior of the title compound was measured using first order hyperpolarizability calculation. Hyperconjugative interaction and electron densities of donor (i) and acceptor (j) bonds were calculated using NBO analysis. The energy gap of the molecule was found using HOMO and LUMO calculation. The electronic transition was studied using TD-DFT method. In addition of Mulliken atomic charges and MEP surface have been also analyzed.

1. INTRODUCTION

The chemical properties of hydrazones having N, O-donor atoms have been intensively investigated in several research areas. The hydrazones having a variety of applications in medicine, analytical, industrial, and organic synthesis [1-6]. Hydrazones are a versatile class of ligands having great physiological and biological activities and have been used as injecticide, anticoagulants, antitumor agents, antioxidants, plant growth regulators and metal complexes have found applications in various chemical processes like nonlinear optics, sensors, medicine, etc [7, 8]. The aim of the present work is to synthesize and characterized by (E)-N’-(Pyridin-2-yl)methylene)nicotinohydrazide. DFT method has a great accuracy in reproducing the experimental values in terms of geometry, dipole moment and vibrational frequency. The NBO analysis has also been carried out to elucidate information regarding the intra-molecular charge transfer within the molecule. The FT-IR, FT-Raman and UV-Visible spectra of the title molecule were carried out by using B3LYP/6-311++G(d,p) level of calculation.

2. COMPUTATIONAL DETAILS

The entire calculation was performed at DFT level of theory using 6-311++G(d,p) basis set on personal computer using Gaussian 03W [9] program package, invoking gradient geometry optimization [10] on Pentium IV personal computer. Initial geometry generated from standard geometrical parameters was minimized without any constraint in the potential energy surface at DFT level, adopting the standard 6-311++G(d,p) basis set. We have utilized the gradient corrected density functional theory [11]. The computation of molecular structure, vibrational frequencies and energies of optimized structures. By combining the results of the Gauss view program [12]. Vibrational frequencies are than scaled using suitable scale factors [13]. To investigate the reactive sites of the structure the molecular electrostatic potential was evaluated using the B3LYP/6-311++G(d,p) method. In addition, the distributions and energy levels of HOMO-LUMO, NBO, UV,
NLO and Mulliken population analysis were computed at the B3LYP/6-311++G(d,p) level of theory.

**Experimental details**

**Synthesis**

10 mL of ethanolic solution of Pyridine-2-carboxaldehyde (1 ml, 0.01 mol) were added to 5 mL of aqueous solution of nicotinic acid hydrazide (1.37 g, 0.01 mol) and stirred for an hour in the presence of hydrochloric acid to form a white precipitate. The precipitate was washed with water and filtered and again washed with petroleum ether (40–60%) and dried over in a vacuum desicator. The compound was recrystallized from ethanol.

![Chemical reaction](image)

**3. RESULT AND DISCUSSION:**

**Molecular geometry:**

The molecular geometry can be used to predict many molecular properties, such as its dipole moment and its allowed spectroscopic transitions. The atom numerical labels in the following discussion refer to Fig. 1. The calculations converge to optimized geometries, which correspond to true energy minima, as exposed by the lack of imaginary frequencies in the vibrational mode calculation. The structural parameter of bond lengths, bond angles, and dihedral angles are shown in Table 1. The bond length is all the C-C bond length except in C16-C18, C2-C11, C2-C3, C5-C6 values are 1.5022, 1.4681, 1.4025, 1.299, and 1.3548 Å. The increase in C16-C18 bond length value is 1.5022 Å reasons is the attached with Pyridine ring in single bond character of the carbon atom. All the double bond has shortening of bond length and also this will be stronger than the longer bond length [14] i.e. single bond character. In substituted N-H, the N atom exert a large attraction on the valence electron cloud of the H atom resulting in an increase in the N-H force constant and a decrease in the corresponding bond length. The N-H bond length is 1.0159 the bond length C11-N13 (1.2791 Å) and C16=O17 (1.2125 Å) are typical of double bonds, so that the chain likely corresponds to C11-N13-N14-C16=O17. The P2CNH has planar conformation of part of the molecule the angle O17-C16-N14 (123.48 °) is significantly greater than O17-C16-C18 (122.22 °) possibly in order of electrons on atoms N13 and O17. The central part of the molecule C11-N13-N14-C16-C18 adopts a completely extended conformation.

The Pyridine ring bond angle is 123 0 reason is the substitute in within the Pyridine ring. Moreover, the largest discrepancies of bond angles were observed for the angles 124.23 0 that corresponded to the oxygen atoms in the Pyridine ring. This clearly shows that strong delocalization and conjugation of the electrons with in the ring which erased the distinction between the double bond and single bond. The dihedral angles values are also calculated.
Vibrational assignments:

The P2CNH molecule belongs to C$_1$ point group symmetry. It consists of 27 atoms which undergoes 75 normal modes of vibrations. In this 51 modes of vibrations are in-plane and remaining 24 are out-of-plane vibrations. The title molecule was characterized by FT-IR and FT-Raman vibrational spectra. The vibrational study of the title molecule was carried out by using DFT/B3LYP/6-311++G(d,p) level of basis set. The observed and calculated spectral results were compared and assigned to the corresponding modes of vibrations. The total energy distribution analysis was performed by VEDA4 Program [15]. The recorded and calculated spectral results were given in Table 2. The combined FT-IR and FT-Raman spectra of P2CNH were shown in Figs. 2 and 3.

N-H Vibrations

In generally, the N-H stretching vibration occurs in the region of 3300–3500 cm$^{-1}$ [16]. The hetero aromatic molecule containing the N-H stretching vibration appears in the region of 3500–3220 cm$^{-1}$ [17]. In this study, the stretching vibration of P2CNH mode is recorded at 3373 cm$^{-1}$ as a medium intensity band in FT-IR spectrum, whereas the calculated wavenumber assigned at 3368 cm$^{-1}$ (mode no: 75) and its TED value is 100%. It is found that a small deviation between experimental and theoretical value is only because of the intra-molecular charge transfer between amino and carbonyl group in the hydrazone linkage.

The in-plane bending of P2CNH was recorded as a mixed vibration of $\beta$H$_{13}$N$_{14}$N$_{13}$(60%) which shows as medium band at 1476 cm$^{-1}$ in FT-Raman, whereas the calculated wavenumber lies at 1496 cm$^{-1}$ (mode no: 59). The experimental FT-Raman value shows a negative deviation with the theoretical value. The out-of-plane bending of N-H was recorded at 925 cm$^{-1}$ (FT-IR: weak) and 923 cm$^{-1}$ (FT-Raman: weak). These observed bands are coinciding with the calculated value of 925 cm$^{-1}$ (mode no: 33) for GC$_{20}$C$_{18}$N$_{23}$H$_{24}$ (78%). The above recorded and calculated values were coinciding well with literature [18].

C-H vibrations

The heteroaromatic structure, the C-H stretching vibrations normally occur in the region of 3100–3000 cm$^{-1}$ [19]. In the present study, Pyridine ring observed the stretching vibrations occur at 3040 (w) cm$^{-1}$ in FT-IR (mode no: 69) and 3063 cm$^{-1}$ (w)/FT-Raman (mode no: 72), where as the calculated wavenumber appeared in the region of 3080, 3076, 3062, 3050, 3032, 3029, 3017 and 2931 cm$^{-1}$ (mode nos: 74-66). These assignments are in good agreement with literature values [19] and also well supported by the TED values.
The Pyridine ring, the C-H in-plane bending vibrations appeared at 1459(m), 1419 (m), 1348 (m) in FT-IR and 1297 (s), 1262 (w), 1155 (m) in FT-Raman, where as the calculated values lies at 1448, 1406, 1314, 1308, 1252, and 1173 (mode nos: 58, 56, 54, 53, 51, and 47). The C-H out-of-plane bending vibration of P2CNH molecule, Likewise for the Pyridine ring, the ГC19C14C21H22 (10%) appears at 925 (w) cm\(^{-1}\) in FT-IR and the corresponding Raman counterpart shown at 923 (w) cm\(^{-1}\), whereas the calculated value lies in the range of 925 cm\(^{-1}\) (mode no: 33). These assignments are well supported by literature value [18, 20] and also find support from TED values. Further, the mode number 27 assigned to ГC3C4C6H9 (12%) and the experimental value of FT-IR assigned at 784 (m) cm\(^{-1}\).

**C=O vibrations**

The carbon=oxygen double bond is formed by Pπ–Pπ bonding between carbon and oxygen. The lone pair of electron in oxygen also determines the nature of the carbonyl group [21]. The carbonyl C=O stretching vibration is expected to occur in the region 1680–1715 cm\(^{-1}\) [22,23]. In our present study the carbonyl group stretching vibration occurs at 1661 cm\(^{-1}\) as medium band in FT-IR spectrum and weak FT-Raman band at 1663 cm\(^{-1}\). For the same mode the harmonic frequency 1691 cm\(^{-1}\) (mode no: 65) is having 90% of TED value. The carbonyl group (ВC16=O17) assigned in the present study is in line with calculated and also with literature values [23, 24].

The βC16=O17 in-plane bending vibration observed at 714 (m) cm\(^{-1}\) in FT-IR (mode no: 25) with low percentage value (10%) of TED and the corresponding calculated value is 712 cm\(^{-1}\). The out-of-plane bending of ГC=O was calculated at 824 cm\(^{-1}\) and 727 cm\(^{-1}\) (mode nos: 29 and 26). The above in-plane vibrations of C=O group is well supported by the literature value [24].

**C-C vibrations**

Krishnakumar et al. [25] assigned C-C stretching absorption in the region of 1668–1218 cm\(^{-1}\) for some substituted Pyridines. The C-C stretching vibrations observed at 1288 cm\(^{-1}\) (strong) in FT-IR spectrum and the corresponding calculated value is 1267 cm\(^{-1}\) (mode no: 52). The Raman band observed at 1587, 1233 cm\(^{-1}\) and the harmonic value is 1564, 1240 cm\(^{-1}\) (mode nos: 63, 53) in pyridine rings. These assignments coinciding well with the literature value [26].

In Pyridine ring, the in-plane bending vibrations of ГC21C25N23 (20%) and ГC25C21C19 (26%) appeared at 714 and 623 cm\(^{-1}\) in FT-IR spectrum and FT-Raman observed at 625 cm\(^{-1}\) (mode nos: 25 and 21) as mixed vibrations of the in-plane bending mode and their harmonic values occur at 712 and 608 cm\(^{-1}\). The out-of-plane modes of ГC3C4C6H9 (38%), ГC14C18C21H22 (10%) and ГC3C4C6H9 (12%) observed at 925, 784 cm\(^{-1}\) in FT-IR (mode nos: 33, 27) and 997 (m), 923 (w) cm\(^{-1}\) in FT-Raman (mode nos: 39, 33). These assignments find support from literatures for Pyridine rings [25].

**C=N, C-N and N-N vibrations**

The hydrazone linkage at two Pyridine rings, which leads the vibrations such as C=N, C-N and N-N stretching as well as bending modes. The C=N stretching vibration appears in the region of 1670–1600 cm\(^{-1}\) [27]. The literature survey [28] assigned the C=N stretching vibration at 1639 cm\(^{-1}\). In the present study the ВC11=N13 stretching vibration in hydrazone linkage appeared at 1606 cm\(^{-1}\) as a medium band in FT-Raman spectrum. The corresponding theoretical wavenumber was calculated at 1608 cm\(^{-1}\) (mode no: 64).

The C-N stretching absorption appeared in the region 1382–1266 cm\(^{-1}\) for aromatic amines [29]. In Pyridine ring, the VN1-C6 (50%), VN23-C20(52) mode assigned to 1262 cm\(^{-1}\) (w) (FT-Raman) and 1233(m) cm\(^{-1}\) in FT-Raman and its corresponding computed wavenumber is 1252, 1240 cm\(^{-1}\) (mode nos: 51, 50). These observed and calculated frequencies of VC-N coincide well with the literature.

In hydrazone linkage, the in-plane bending vibration of βH12C11N13 (40%), βH12C11N13 (36%) assigned to 1314 cm\(^{-1}\) in harmonic value and 1348 cm\(^{-1}\) in FT-Raman (mode no: 54) and 1308 cm\(^{-1}\) in calculated value and 1297 cm\(^{-1}\) in FT-Raman (mode no: 53). The in-plane bending
mode observed at (1459 cm\(^{-1}\)/FT-IR, 1437 cm\(^{-1}\)/FT-Raman) and its corresponding harmonic value is 1448 cm\(^{-1}\) (mode no: 58) in Pyridine ring. This ring belongs to the out-of-plane bending mode observed at 925 cm\(^{-1}\) in FT-IR/923 cm\(^{-1}\) in FT-Raman and its corresponding calculated value is 925 cm\(^{-1}\) (mode no:33).

The bond N\(_{13}-N_{14}\) in hydrazone linkage fuses the two Pyridine rings. The \(\nu_{N_{13}-N_{14}}\) vibrations observed at 1137 cm\(^{-1}\) in FT-IR/1130 cm\(^{-1}\) in FT-Raman and its calculated value occur at 1128 cm\(^{-1}\) (mode no: 46), the in-plane bending vibrations of (βN-N) were calculated at 910 and 235 cm\(^{-1}\) (mode nos: 32 and 9).

![Fig. 2. The calculated and experimental FT-IR spectra of P2CNH](image)

![Fig. 3. The calculated and experimental FT-Raman spectra of P2CNH](image)
Table 2. The experimental and calculated frequencies assignments of P2CNH using B3LYP/6-311++G(d,p) level of basis set

| Mode No | Calculated Frequencies (cm⁻¹) | Observed Frequencies (cm⁻¹) | IR Intensity | Raman Intensity | Reduced Masses | Force Constants | Vibrational Assignments TED≥10% |
|---------|-------------------------------|----------------------------|--------------|---------------|---------------|----------------|---------------------------|
| 1       | 29                            | 0.24                       | 19.01        | 4.43          | 0.00          | tC₆H₅C₁₉N₁₄(24)+tC₂O₄C₁₈N₁₄(40)+tC₁₆N₁₄C₁₈(35) |
| 2       | 31                            | 0.48                       | 5.83         | 5.76          | 0.00          | tC₆H₅C₁₉N₁₄(80) |
| 3       | 45                            | 0.46                       | 4.08         | 6.00          | 0.01          | βC₆H₅C₁₉N₁₄(32)+βC₁₆N₁₄C₁₈(42) |
| 4       | 61                            | 79m                        | 1.60         | 8.89          | 5.70          | tN₁₃C₁₈N₁₄(25)+tC₂O₄C₁₈N₁₄(48) |
| 5       | 115                           | 2.69                       | 1.18         | 5.90          | 0.05          | βC₁₆C₁₈C₁₄N₁₄(50)+βC₆H₅C₁₉C₁₈(12) |
| 6       | 120                           | 1.15                       | 2.62         | 6.01          | 0.05          | tC₆H₅C₁₉N₁₄(28)+tC₁₆N₁₄C₁₈(10)+tC₂O₄C₁₈C₁₈(25) |
| 7       | 170                           | 186w                       | 2.48         | 2.48          | 5.07          | 0.09          | βC₂O₄C₁₈C₁₈(10)+tN₁₃C₁₈N₁₄(12)+tC₁₆N₁₄C₁₈(15)+tC₂O₄C₁₈C₁₈(20) |
| 8       | 220                           | 4.66                       | 1.79         | 3.11          | 0.10          | tN₁₃C₁₈N₁₄(16)+tC₁₆N₁₄C₁₈(15)+tC₂O₄C₁₈C₁₈(20) |
| 9       | 235                           | 0.89                       | 1.33         | 6.82          | 0.24          | 0.24          | V₃N₁₃C₁₈(10)+V₃C₁₈C₁₈(12)+βC₆H₅C₁₉C₁₈(15)+βC₁₆N₁₄C₁₈(18) |
| 10      | 251                           | 1.92                       | 1.11         | 5.01          | 0.20          | βC₂O₄C₁₈C₁₈(26)+tC₂O₄N₁₄(15)+tC₁₆C₁₈N₁₄(12) |
| 11      | 308                           | 1.17                       | 0.60         | 5.34          | 0.32          | tC₆H₅C₁₉C₁₈(75) |
| 12      | 364                           | 0.05                       | 0.13         | 7.70          | 0.65          | 0.65          | VC₆H₅C₁₉(20)+βC₂O₄C₁₈C₁₈(22)+T₄N₁₃C₁₈(26) |
| 13      | 381                           | 0.86                       | 0.09         | 3.31          | 0.31          | 0.31          | tC₂O₄C₁₈C₁₈(50) |
| 14      | 401                           | 0.91                       | 0.14         | 3.71          | 0.38          | 0.38          | tC₆H₅C₁₉C₁₈(60)+tC₂O₄C₁₈N₁₄(15) |
| 15      | 404                           | 2.32                       | 0.14         | 4.59          | 0.48          | 0.48          | tC₂O₄C₁₈C₁₈(20)+tC₂O₄N₁₄C₁₈(35) |
| 16      | 468                           | 0.23                       | 0.69         | 6.31          | 0.88          | 0.88          | βC₁₆N₁₄C₁₈(12)+βC₆H₅C₁₉C₁₈(35) |
| 17      | 499                           | 2.57                       | 0.64         | 2.49          | 0.40          | 0.40          | βC₁₆N₁₄C₁₈(12)+tH₃N₁₃C₁₈(32) |
| 18      | 511                           | 1.61                       | 0.46         | 3.52          | 0.59          | 0.59          | tC₆H₅C₁₉C₁₈N₁₄(18)+tC₁₆N₁₄C₁₈(12)+tC₆H₅C₁₉C₁₈(20) |
| 19      | 519                           | 15.10                      | 2.89         | 1.57          | 0.27          | 0.27          | tH₃N₁₃C₁₈(65) |
| 20      | 608                           | 2.31                       | 1.42         | 7.37          | 1.74          | 1.74          | βC₂O₄C₁₈(28)+βC₆H₅C₁₉C₁₈(45) |
| 21      | 608                           | 623m                       | 0.77         | 0.90          | 7.64          | 1.80          | tC₂O₄C₁₈(20)+tC₂O₄N₁₄C₁₈(32)+βC₂O₄C₁₈(26) |
| 22      | 655                           | 1.93                       | 1.33         | 6.15          | 1.68          | 1.68          | βC₁₆N₁₄C₁₈(14)+βC₂O₄C₁₈(50) |
| 23      | 691                           | 5.56                       | 0.17         | 3.45          | 1.05          | 1.05          | tC₂O₄C₁₈C₁₈(52)+tC₂O₄N₁₄C₁₈(12) |
| 24      | 696                           | 6.31                       | 0.71         | 4.66          | 1.44          | 1.44          | tC₂O₄C₁₈C₁₈(52)+tC₂O₄N₁₄C₁₈(12) |
| 25      | 712                           | 714m                       | 7.75         | 0.86          | 2.83          | 0.92          | tN₁₃C₁₈O₄(10)+tC₂O₄C₁₈(20)+tC₁₆N₁₄C₁₈(15)+tC₂O₄C₁₈(12) |
| 26      | 727                           | 5.42                       | 0.02         | 2.06          | 0.70          | 0.70          | tC₂O₄C₁₈(15)+tC₂O₄C₁₈(20)+tC₂O₄N₁₄C₁₈(60) |
| 27      | 763                           | 784m                       | 9.44         | 0.11          | 1.84          | 0.68          | tC₂O₄C₁₈(25)+tC₂O₄C₁₈(25)+tC₂O₄N₁₄C₁₈(50) |
| 28      | 807                           | 3.68                       | 1.09         | 1.88          | 0.78          | 0.78          | tC₂O₄C₁₈(42)+tC₂O₄C₁₈(30) |
| 29      | 824                           | 2.35                       | 2.55         | 5.10          | 2.21          | 2.21          | tC₂O₄C₁₈(30)+tC₂O₄C₁₈(30)+tC₁₆N₁₄C₁₈(12) |
| 30 | 881 | 0.02 | 0.05 | 1.31 | 0.65 | \( \text{VN}_2C_6(30)+\beta C_6C_5C_4(15) \) |
| 31 | 901 | 9.83 | 2.03 | 5.48 | 2.84 | \( \Gamma C_6C_5C_4(65)+\text{thH}_2C_2C_1H_4(30) \) |
| 32 | 910 | 0.26 | 0.12 | 1.38 | 0.73 | \( \beta N_13C_6O_3(20)+\beta C_6N_6N_4(12) \) |
| 33 | 925 | 4.25 | 1.00 | 1.52 | 0.83 | \( \Gamma C_6C_1C_2H_2(10)+\Gamma C_2C_6N_2C_5H_4(78) \) |
| 34 | 947 | 0.93 | 0.01 | 1.44 | 0.82 | \( \text{thH}_2C_13N_3N_4(85) \) |
| 35 | 949 | 0.23 | 0.14 | 1.43 | 0.82 | \( \text{thH}_2C_13C_5(75) \) |
| 36 | 970 | 2.08 | 16.07 | 7.25 | 4.35 | \( \Gamma C_1C_6C_1H_2(32)+\Gamma C_2C_6N_2C_5H_4(40)+\text{thH}_2C_5C_2C_6(48) \) |
| 37 | 974 | 0.66 | 0.13 | 1.38 | 0.84 | \( \text{VN}_2C_6(25)+\beta C_6C_5C_4(36)+\beta C_6N_6C_5(18) \) |
| 38 | 977 | 0.07 | 0.07 | 1.32 | 0.80 | \( \text{thH}_2C_13C_5(75)+\text{thH}_2C_5C_2C_6(18) \) |
| 39 | 999 | 4.12 | 4.92 | 4.31 | 2.74 | \( \Gamma C_6C_5C_4(38)+\text{thH}_2C_2C_1H_4(55) \) |
| 40 | 1016 | 0.48 | 5.70 | 3.38 | 2.22 | \( \beta C_6N_6C_6(25)+\beta C_6C_5C_4(22)+\beta C_5C_2C_6C_4(40) \) |
| 41 | 1022 | 1.31 | 2.76 | 2.20 | 1.47 | \( \text{VN}_2C_6(15)+\text{VC}_5C_2(40) \) |
| 42 | 1044 | 1.11 | 1.34 | 3.32 | 2.31 | \( \text{VC}_5C_2(60) \) |
| 43 | 1072 | 2.05 | 2.91 | 1.63 | 1.19 | \( \text{VN}_2C_6(20)+\text{VN}_6N_3(25) \) |
| 44 | 1090 | 12.35 | 2.82 | 1.44 | 1.09 | \( \text{VC}_5C_2(25)+\text{thH}_2C_6C_4(40) \) |
| 45 | 1125 | 86.61 | 37.17 | 3.54 | 2.86 | \( \text{VC}_5C_2(15)+\text{thH}_2C_5C_2(55) \) |
| 46 | 1128 | 1130w | 7.75 | 8.04 | 1.16 | 0.94 | \( \text{VN}_2C_6(18)+\text{VN}_6N_3(45) \) |
| 47 | 1173 | 1155m | 11.14 | 12.84 | 1.61 | 1.41 | \( \text{VC}_5C_2(10)+\text{thH}_2C_6C_4(75) \) |
| 48 | 1206 | 4.87 | 45.45 | 2.19 | 2.03 | \( \text{V}_2C_6C_2(15)+\beta C_5C_2C_1(20)+\beta C_3C_2N_2(26) \) |
| 49 | 1217 | 95.89 | 16.25 | 2.60 | 2.46 | \( \text{VC}_5C_2(20)+\beta C_5C_2C_1(15) \) |
| 50 | 1240 | 1233m | 6.39 | 2.09 | 7.36 | 7.23 | \( \text{VC}_5C_2(18)+\text{VN}_6C_5(52) \) |
| 51 | 1252 | 1262w | 0.05 | 4.99 | 2.76 | 2.76 | \( \text{VN}_2C_6(30)+\beta H_2C_6C_4(20) \) |
| 52 | 1267 | 1288s | 1.06 | 13.89 | 2.12 | 2.17 | \( \text{VC}_5C_2(30)+\beta H_2C_6C_4(45) \) |
| 53 | 1308 | 1297s | 1.29 | 0.44 | 1.35 | 1.48 | \( \beta H_2C_6C_4(20)+\beta H_2C_1N_4(36) \) |
| 54 | 1314 | 1348m | 5.69 | 0.90 | 1.53 | 1.69 | \( \beta H_2C_1N_4(18) \) |
| 55 | 1391 | 8.51 | 1.08 | 2.18 | 2.70 | \( \beta C_6C_2N_2(21)+\beta H_2C_5C_2(40) \) |
| 56 | 1406 | 1419m | 10.91 | 19.47 | 2.18 | 2.75 | \( \text{VN}_2C_6(12)+\text{VC}_5C_2(10)+\beta H_2C_6C_4(50) \) |
| 57 | 1437 | 35.68 | 5.10 | 2.11 | 2.78 | \( \text{VN}_2C_6(15)+\beta H_2C_6C_4(40) \) |
| 58 | 1448 | 1459m | 0.76 | 2.93 | 2.20 | 2.95 | \( \beta H_2C_6C_4(25)+\beta H_2C_5N_2(26) \) |
| 59 | 1496 | 1476w | 100.00 | 17.55 | 1.84 | 2.63 | \( \text{VN}_2C_6(15)+\beta H_2C_5N_4(36) \) |
| 60 | 1542 | 2.19 | 0.41 | 5.23 | 7.93 | \( \text{VN}_2C_6(25)+\text{VC}_5C_2(25)+\beta C_6C_2N_2(18)+\beta C_6N_3C_5C_2(15) \) |
| 61 | 1543 | 3.80 | 0.19 | 5.71 | 8.68 | \( \text{VC}_5C_2(15)+\text{VC}_5C_2(30) \) |
| 62 | 1559 | 10.82 | 88.24 | 5.29 | 8.21 | \( \text{VC}_5C_2(55) \) |
| 63 | 1564 | 1587s | 8.69 | 5.66 | 5.71 | 8.92 | \( \text{VC}_5C_2(25)+\beta C_6C_1C_6(15) \) |
| 64 | 1608 | 1606m | 0.67 | 100.00 | 8.35 | 13.77 | \( \text{VN}_2C_6(75) \) |
| 65 | 1691 | 1661m | 95.72 | 9.33 | 11.14 | 20.33 | \( \text{VO}_2C_6(40) \) |
| 66 | 2931 | 2930w | 10.69 | 0.74 | 1.09 | 5.97 | \( \text{VC}_5H_2(100) \) |
| Parameters | B3LYP/6-311++G(d,p) | Debye |
|------------|---------------------|-------|
| Dipole moment (μ) |                      |       |
| μ_x        | 0.2705581           |       |
| μ_y        | -0.1743668          |       |
| μ_z        | -0.4053984          |       |
| μ          | 0.517642 Debye       |       |
| Hyperpolarizability (β₀) | x10⁻³⁰ esu |       |
| β_xxx      | -40.8058383         |       |
| β_xxy      | 237.7477272         |       |
| β_xyy      | -77.8982342         |       |
| β_yyy      | -131.1196262        |       |
| β_xxz      | -25.3858546         |       |
| β_xyz      | -24.1529611         |       |
| β_yxz      | -18.3148965         |       |
| β_xzz      | 27.2342323          |       |
| β_yzz      | -4.0280518          |       |
| β_zzz      | -21.0494327         |       |
| β₀         | 1.312664x10⁻³⁰ esu   |       |

Table 3. The non-linear measurements of P2CNH.
NLO property:
Non linear effect arise from the interactions of electromagnetic fields in various media to produce new fields altered in phase, frequency, amplitude or other propagation characteristics from incident field [30]. The hyperpolarizability β, dipole moment μ and Polarizability α is calculated using B3LYP/6-311+G(d,p) basis set on the basis of the finite-field approach. The complete equations for calculating the magnitude of total static dipole moment μ, the mean polarizability α, the anisotropy of the polarizability α and the mean first polarizability β0, using the x, y, z components,

\[ \mu = \mu_x^2 + \mu_y^2 + \mu_z^2 \]

\[ \alpha_0 = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3} \]

\[ \Delta \alpha = 2^{1/2} \left[ (\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + 6 \alpha_{zz}^2 \right]^{-1/2} \]

\[ \beta_0 = \left( \beta_x^2 + \beta_y^2 + \beta_z^2 \right)^{1/2} \]

Table. 3 show that the total first order hyperpolarizability of the title molecule is 1.312664x10⁻³⁰esu and the total dipole moment value is 0.517642 Debye, respectively. The β₀ of P2CNH is 4 times greater than that of urea; hence the first order hyperpolarizability value plays an important role in determining the NLO activity of the title molecule. The P2CNH molecule value is high which confirms its NLO activity.

NBO analysis:
The larger E_(2) value the more intensive is the interaction between electron donors and acceptor, i.e. The more donation tendency from electron donors to electron acceptors and the greater the extent of conjugation of the whole system [31]. In this present work the π electron delocalization is maximum around N1-C2, C3-C4, C5-C6 distributed to π* anti-bonding of C3-C4, N1-C2, with a stabilization energy of about 109.96, 112.63, 71.92 KJ/Mol as shown in Table 3. The other interaction energy in this molecule is π electron donation from C11-N13→π*(N1-C2), π(C16-O17)→π*(C18-C20), π(C18-C20)→π*(C19-C21), π(C19-C21)→π*(N23-C25), π(N23-C25)→π*(C18-C20) resulting a stabilization energy of about 42.30, 15.15, 89.70, 122.17, 113.64 KJ/Mol. The another most important interaction energy is Lp (N14)→π*(C16-O17), LP(2) (O17)→σ*(N14-C16) of about 189.24 and 118.74 KJ/Mol shows higher values than those of the other delocalization around the ring. The π*(N23-C25)→π*(C18-C20) and π*(N1-C2)→π*(C3-C4) resulting to stabilization of 861.15 and 639.94 KJ/mol, respectively shown in Table 4.3.

Table 4. The Second order perturbation theory analysis of Fock Matrix in NBO basis for P2CNH

| Type | Donor NBO (i) | ED/e | Acceptor NBO (j) | ED/e | E{(2)} KJ/mol | E(j)-E(i) a.u. | F(i,j) a.u. |
|------|--------------|------|-----------------|------|---------------|---------------|-------------|
| π-π* | BD ( 2) N 1 - C 2 | 1.69862 | BD*( 2) C 3 - C 4 | 0.2768 | 52.97 | 0.33 | 0.06 |
|      |              |      | BD*( 2) C 5 - C 6 | 0.30054 | 109.96 | 0.32 | 0.08 |
|      |              |      | BD*( 2) C 11 - N 13 | 0.17076 | 54.43 | 0.31 | 0.06 |
| π-π* | BD ( 2) C 3 - C 4 | 1.64773 | BD*( 2) N 1 - C 2 | 0.43344 | 112.63 | 0.27 | 0.08 |
|      |              |      | BD*( 2) C 5 - C 6 | 0.30054 | 75.27 | 0.28 | 0.06 |
| π-π* | BD ( 2) C 5 - C 6 | 1.63234 | BD*( 2) N 1 - C 2 | 0.43344 | 71.92 | 0.27 | 0.06 |
|      |              |      | BD*( 2) C 3 - C 4 | 0.2768 | 87.03 | 0.29 | 0.07 |
| π-π* | BD ( 2) C 11 - N 13 | 1.92281 | BD*( 2) N 1 - C 2 | 0.43344 | 42.3 | 0.35 | 0.06 |
| π-π* | BD ( 2) C 16 - O 17 | 1.98051 | BD*( 2) C 18 - C 20 | 0.33618 | 15.15 | 0.4 | 0.04 |
| π-π* | BD ( 2) C 18 - C 20 | 1.63337 | BD*( 2) C 16 - O 17 | 0.2718 | 66.94 | 0.3 | 0.06 |
|      |              |      | BD*( 2) C 19 - C 21 | 0.27659 | 89.7 | 0.29 | 0.07 |
|      |              |      | BD*( 2) N 23 - C 25 | 0.36485 | 69.16 | 0.27 | 0.06 |
| π-π* | BD ( 2) C 19 - C 21 | 1.63693 | BD*( 2) C 18 - C 20 | 0.33618 | 74.64 | 0.28 | 0.06 |
|      |              |      | BD*( 2) N 23 - C 25 | 0.36485 | 122.17 | 0.27 | 0.08 |
### Homo Lumo analysis:

The Homo is the orbital that primarily acts as an electron donor and the Lumo is the orbital that largely acts as the electron acceptor, and the gap between Homo and Lumo characterizes the molecular chemical stability [32]. The frontier orbital gap helps the chemical reactivity and kinetic stability of the molecule. A molecule with a small frontier orbital gap is more polarizability and is generally associated with a high chemical reactivity, low kinetic stability and is also termed as soft molecule [33,34]. The positive phase is green and the negative is red. From Fig 4. Shows the homo of P2CNH presents a charge density localized on the ring and expect of OH group, but Lumo is characterized by a charge distribution on whole molecule expect of hydrogen atoms in OH group. The Homo and Lumo energy values are -6.7282 eV and -2.3025 eV. The energy gap value is 4.4257 eV. The physico-chemical properties of P2CNH molecule are presented in Table. 5.

**Table. 5. The physico-chemical properties of P2CNH**

| Parameters                  | Values            |
|-----------------------------|-------------------|
| HOMO                        | -5.919836 eV      |
| LUMO                        | -2.461813 eV      |
| Energy gap                  | 3.458023 eV       |
| Ionization potential (IP)   | -5.919836 eV      |
| Electron affinity (EA)      | -2.461813 eV      |
| Electrophilicity Index (ω)  | 2.5394            |
| Chemical Potential (μ)      | 4.1908            |
| Electronegativity (χ)       | -4.1908 eV        |
| Hardness (η)                | -3.458023         |

### UV-Visible analysis:

In the UV-Vis region with high extinction coefficients, all molecules allow strong π-π* and σ-σ* transition [35]. In order to understand electronic transitions of compound, DFT calculation on
electronic absorption spectra in gas phase and solvent phase (Ethanol) was performed. The computed electronic values, such as absorption wavelength (λ), excitation energies (E), frontier orbital energies and oscillator strength (f) are tabulated in Table 6 and Fig 5. The experimental wavelengths (λmax) observed at 301, 254 nm and the corresponding theoretical absorption bands occur at 305, 302 and 291 from gas phase. Due to the Frank-Condon principle, the maximum absorption peak (λmax) in an UV-Visible spectrum corresponds to vertical excitation. In view of calculated absorption spectra, the maximum absorption wavelength corresponds to the electronic transition from Homo to Lumo. The π-π* transitions leads to more polar excited state that is more easily stabilized by polar solvent associations H-bonds. The π* state is more polar and stabilized more in polar solvent relative to non polar one, thus in going from non polar to polar solvent there is a red shift or bathochromic shift. Increase in λmax decrease in ΔE.

| Calculated at B3LYP/6-311++G(d,p) | Oscillator strength | Calculated Band gap(ev/nm) | Experimental Band gap(ev/nm) |
|----------------------------------|---------------------|-----------------------------|----------------------------|
| Excited State 1                  | Singlet-A(f=0.6623) | 4.0602 eV/305.36 nm         | 301                        |
| 58 -> 60                         | -0.18909            | 5.096433                    |                            |
| 59 -> 60                         | 0.61995             | 4.4257065                   |                            |
| Excited State 2                  | Singlet-A(f=0.0919) | 4.0967 eV/302.65 nm         | 254                        |
| 58 -> 60                         | 0.61846             | 5.096433                    |                            |
| 58 -> 61                         | 0.16940             | 5.846884                    |                            |
| 59 -> 60                         | 0.18999             | 4.4257065                   |                            |
| Excited State 3                  | Singlet-A(f=0.0006) | 4.2549 eV/291.39 nm         |                            |
| 57 -> 60                         | 0.62506             | 5.248809                    |                            |
| 57 -> 61                         | -0.20084            | 5.9992608                   |                            |

Molecular electrostatic potential:

The compound 3D plot of molecule electrostatic potential MEP for P2CNH is shown in Fig. 6, which is based on the electron density at different point on the molecule. The red color in the map indicates the negatively charged portion and the blue color indicate the positive region, while the green color indicates the neutral region. From the Fig. 6 the color code of the maps lies in the range -8.785 e^-2 a.u, deepest red to 8.785 e^-2 a.u deepest blue in compound, As can be from the map of the title molecule, the ring having neutral potential site than the substituent. The strong negative region was observed around the carbonyl group C=O and more positive around the hydrozone linkage in NH atom. These sites are prone to electrophilic and nucleophilic attack.

Mulliken population Analysis:

The calculation of effective atomic charges plays a dominant role in the application of quantum mechanical calculations to molecular systems. The Mulliken analysis is the most common population analysis method. This calculations which depicts the charges of the every atom in the molecule distribution of positive and negative charges are vital to increase or decrease of bond length between the atoms. The survey of literature reveals that effective atomic calculations gave an important role in the application of chemical calculation to molecular system because of atomic charges effect dipole moment, molecular polarizability, electronic structure, acidity-basicity behavior and a lot of properties of molecular system [36]. The Mulliken charges calculated at B3LYP/6-311++G(d,p) level for the molecule under study are given in Table 7 and Fig. 7. The carbon atoms (C18) have most positive charge. The reason is C18 atom attached with carboxyl group. The most negative charge occurs at C4 atom, which is attached within the Pyridine ring. All the hydrogen atoms have positive chargers.

The electronegative atoms pull out the partial charges from the carbon atom and hence they become positive charges hydrogen atom the donor and acceptor atoms may suggest the presence of both inter-molecular hydrogen bonding in crystalline phase.
Table 7. The Mulliken atomic charges of P2CNH

| Atoms  | Charges  | Atoms  | Charges  |
|--------|----------|--------|----------|
| N1     | 0.004400 | H15    | 0.270247 |
| C2     | -0.615851| C16    | -0.848144|
| C3     | 0.781355 | O17    | -0.288104|
| C4     | -0.981882| C18    | 1.054397 |
| C5     | 0.133863 | C19    | 0.076538 |
| C6     | -0.245836| C20    | -0.583509|
| H7     | 0.185369 | C21    | -0.085996|
| H8     | 0.258749 | H22    | 0.225932 |
| H9     | 0.186801 | N23    | -0.012851|
| H10    | 0.197946 | H24    | 0.176862 |
| C11    | -0.164065| C25    | -0.349724|
| H12    | 0.111848 | H26    | 0.190669 |
| N13    | 0.223186 | H27    | 0.192018 |
| N14    | -0.094219|        |          |

Homo = -6.728216 eV    Energy Gap = 4.425706 eV    Lumo = -2.302510 eV

Fig. 4. The Homo-Lumo diagram of P2CNH.
Figure. 5. The calculated and experimental UV-Visible spectra of P2CNH.

Figure. 6. The MEP surfaces of P2CNH

Figure. 7. The Mulliken atomic charges of P2CNH
Figure. 8. The correlation graph between different temperatures and functions of P2CNH

Thermodynamic properties

The standard statistical thermodynamic functions: standard heat capacities (C_p,m) standard entropies (S_m) and standard enthalpy changes (ΔH_m) for the title compounds were obtained from the theoretical harmonic frequencies. It can be observed that these thermodynamic functions are increasing with temperature ranging from 100 to 1000 k due to the fact that the molecular vibrational intensities increase with temperature [37]. The correlation equations between heat capacities, entropies, enthalpy changes and temperature were fitting factor (R^2) of the thermodynamic functions such as heat capacity, entropy, and enthalpy changes are 0.99492, 0.99947, 0.9999 and 0.9999 respectively. The correlation graphs between different temperatures and thermodynamic functions for P2CNH molecule is shown in Fig. 8.

All the thermodynamic data will be helpful information for further study on the P2CNH. They can be used to compute the other thermodynamic energies from thermodynamic functions and can estimate directions of chemical reactions according to the second law of thermodynamics is thermochemical field [38,39]. All thermodynamic calculations were done in gas phase and they could not be used in solution.

4. CONCLUSION

The spectroscopic properties and vibrational analysis is made for P2CNH in the present work. Complete vibrational assignments on the observed spectra are made with vibrational frequencies obtained by DFT/6-311++G(d,p) basis set. The electrical and optical and bio molecular properties are profoundly investigated using frontier molecular orbital. The NBO analysis shows strong inter-molecular hyperconjugative interactions of π-electrons, the strong delocalization of π*-electrons in the molecule leading to stabilization of the molecule. The experimental techniques (FT-IR, FT-Raman and UV-Visible spectra) and density functional theory DFT employing B3LYP exchange correlation with the 6-311++G(d,p) basis set. The MEP shows that the negative potential sites are around oxygen atoms as well as the positive potential sites are around the NH atoms. The Mulliken atomic charges of the compound were computed and the redistribution of electron density was studied. The electronic absorption spectrum was calculated by TD-DFT method. The thermodynamic properties (heat capacity, entropy and enthalpy) in the temperature range from 100 to 1000 k also calculated. The calculated first hyperpolarizability is found to be 1.312664x10^-30 esu, which is 4 times greater than that of urea which imply that the title compound might become a kind of good NLO material.
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