



ISSN 0975-413X
CODEN (USA): PCHHAX

Der Pharma Chemica, 2016, 8(6):189-198
(<http://derpharmachemica.com/archive.html>)

Analysis of Molecular Structure, Vibrational spectra and Electronic Properties of 2- amino-3-nitro-6-picoline by Density Functional Methods

David Pegu

Department of Physics, Haflong Govt. College, Haflong, Assam, India

ABSTRACT

In the present study the geometrical parameters and vibrational spectroscopic properties of the compound 2-amino-3-nitro-6-picoline (2A3N6P) have been calculated by using Hartree-Fock and Density functional method (B3LYP) with 6-311++G(d,p) basis set. The calculated optimized structural parameters and the scaled frequencies are investigated and compared with earlier reported data. The complete vibrational assignment and analysis of the fundamental modes of the molecule were carried out. In addition, molecular electrostatic potential and total electron density has been analyzed to investigate size, shape, charge density distribution and site on chemical reactivity of the molecule. Finally the Mulliken atomic charges of the compound have been studied.

Key words: FT-IR, FT-Raman, MESP, DFT.

INTRODUCTION

Pyridines and its derivatives are heterocyclic compounds occurring naturally a large number that are building blocks of biologically important molecules and important industrial, pharmaceutical and agricultural products [1,2]. The chemistry and applications of pyridine compounds have recently received much attention due to their efficacy as synthetic intermediates and biological importance. Pyridine derivatives exhibited various types of biological activities antimicrobial [3], antimalarial [4], antitumoral [5,6] and anti-diabetics [7]. Pyridine derivatives act as anesthetic agents, drugs for certain brain diseases, and prodrugs for treating neuronal damage caused by stroke [9-10]. They also underpin analgesics for acute and chronic pain, treatment for tinnitus, depression, and even diabetic neuropathy. The literature survey reveals that vibrational and electronic spectra of pyridine and its derivatives have been investigated by many authors [11-14]. A A Dahy et al. evaluated structure and vibrational assignments of 2-amino-3-nitro pyridine based on *ab initio* (MP₂) and DFT calculations [15]. The harmonic frequencies of amino and methyl substituted pyridine were calculated by many authors and the anharmonicity was estimated by N. Sundaraganesan et al [16].

It appears that structural and vibrational assignments of alkyl amino, nitro and methyl substituted pyridines have not been subjected to a systematic study using *ab-initio* and DFT calculations. The theoretical *ab-initio* and DFT calculations give information regarding the nature of the electronic structure, the functional groups, orbital interactions and mixing of skeletal frequencies. A comprehensive investigation of geometrical structure, spectral analysis and along with molecular electrostatic potential surfaces of may lead to the better understanding of structural and spectral characteristics. Therefore, in the present study theoretical analysis of the title compound 2A3N6P have been carried out using *ab-initio* and DFT calculations. The main objective of the present study is to

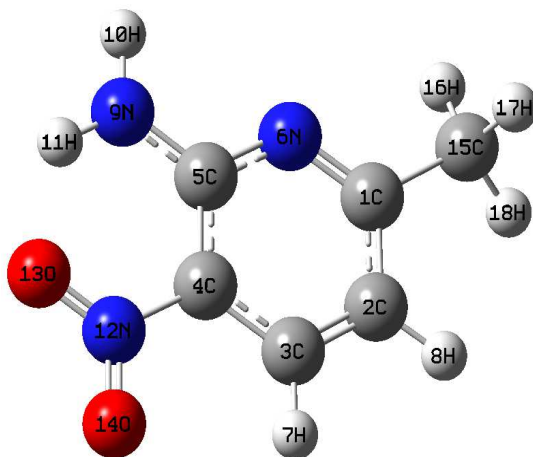
investigate structure and vibrational frequencies in order to obtain a complete description of vibrational assignments along with normal mode analysis of the title compound.

COMPUTATIONAL DETAILS

All calculations were performed at HF and B3LYP levels on a Pentium IV personal computer using Gaussian 03W program Package [17] and Gauss-View molecular visualization program package. Initial geometry generated from standard geometrical parameters was minimized without any constraint in the potential energy surface at the Hartree-Fock level, adopting the standard 6-311G++ (d, p) basis set. This geometry was then reoptimized again at Becke-Lee-Parr (B3LYP) [18-20] hybrid exchange-correlation three-parameter functional level, using basis set 6-311++G (d, p). The optimized structural parameters were used to calculate the vibrational frequencies of the compound at HF and DFT levels with same basis set to characterize all stationary points as minima. As a result, the unscaled frequencies, force constants, infrared intensities and Raman activities are obtained. To overcome the negligence of electron correlation we have used uniform scaling factor values 0.96 for B3LYP / 6-311++G (d,p) and 0.89 for the HF / 6-311++G(d,p) basis set.

GEOMETRICAL PARAMETERS

The optimized molecular structure of the title molecule calculated by ab-initio HF and DFT-B3LYP with 6-311++G(d,p) basis set are listed in Table (i) in accordance with the atom numbering scheme shown in the fig. (i). The comparisons among the HF and DFT (B3LYP) are given in order and the results shows that both levels predict consistent results.



Figure(i): Optimized molecular structure of 2A3N6P

Table (i): Optimized geometrical parameters of 2-amino-3-nitro-6-picoline

| Bond length in (angstroms) | | | Bond angles in (degrees) | | | | Dihedral angles in (degrees) | | |
|----------------------------|-------|-------|--------------------------|--------|--------|---------------|------------------------------|---------|--|
| | HF | B3LYP | | HF | B3LYP | | HF | B3LYP | |
| C1-C2 | 1.398 | 1.399 | C2-C1-N6 | 122.79 | 122.8 | N6-C1-C2-C3 | 0.0104 | 0.0223 | |
| C1-N6 | 1.313 | 1.313 | C2-C1-C15 | 121.19 | 121.18 | N6-N1-N2-H8 | 179.994 | 179.983 | |
| C1-C15 | 1.504 | 1.504 | N6-C1-C15 | 116.02 | 116.02 | C15-C1-C2-C3 | 179.971 | 179.932 | |
| C2-C3 | 1.373 | 1.373 | C1-C2-C3 | 117.62 | 117.62 | CC2-C1-N6-C5 | 0.0029 | 0.0139 | |
| C2-H8 | 1.072 | 1.072 | C2-C3-C4 | 119.92 | 119.89 | C15-C1-N6-C5 | 179.979 | 179.929 | |
| C3-C4 | 1.388 | 1.388 | C3-C4-C5 | 119.00 | 119.05 | N6-C1-C15-H16 | 58.6678 | 58.6848 | |
| C3-H7 | 1.072 | 1.072 | C3-C4-N12 | 118.01 | 117.97 | C1-C2-C3-C4 | 0.0044 | 0.0144 | |
| C4-C5 | 1.414 | 1.413 | C5-C4-N12 | 123.02 | 122.98 | C2-C3-C4-N12 | 179.989 | 180.00 | |
| C4-N12 | 1.44 | 1.441 | C4-C5-N6 | 119.65 | 119.63 | C7-C3-C4-N12 | 0.0098 | 0.0032 | |
| C5-N6 | 1.333 | 1.333 | C4-C5-N9 | 125.18 | 125.2 | C3-C4-C5-N6 | 0.0158 | 0.0086 | |
| C5-N9 | 1.339 | 1.339 | N6-C5-N9 | 115.18 | 115.16 | C3-C4-C5-C9 | 179.953 | 179.914 | |
| C9-H10 | 0.992 | 0.992 | C1-N6-C5 | 121.03 | 121.01 | N12-C4-C5-N6 | 179.981 | 179.991 | |
| C9-C11 | 0.991 | 0.993 | C5-N9-H10 | 116.93 | 116.93 | C12-C4-C5-N9 | 0.0504 | 0.0858 | |
| C12-O13 | 1.197 | 1.197 | C10-N9-H11 | 121.52 | 121.52 | C3-C4-N12-O13 | 179.911 | 179.876 | |
| C12-O14 | 1.189 | 1.189 | C4-N12-O13 | 118.48 | 118.48 | C5-C4-N12-O13 | 0.0861 | 0.1238 | |
| C15-H16 | 1.085 | 1.085 | O13-N12-O14 | 123.42 | 123.42 | C4-C5-N6-C1 | 0.0103 | 0.0018 | |
| C15-H17 | 1.085 | 1.085 | C1-C15-H16 | 109.56 | 109.56 | C9-C5-N6-C1 | 179.961 | 179.917 | |
| C15-H18 | 1.083 | 1.083 | C16-C15-H17 | 107.65 | 107.65 | C4-C5-N6-C1 | 179.961 | 179.865 | |

MULLIKEN ATOMIC CHARGES

The computed of Mulliken atomic charges play an important role in the application of quantum mechanical calculations of the molecular system. The Mulliken atomic charges of title molecule obtained by HF and B3LYP method with 6-311++G(d,p) basis set are presented in Table (ii) and the graphical representation of the results are shown in Fig. (ii).

Table (ii): Mulliken atomic charges of 2-amino-3-nitro-6-picoline

| Atoms | HF/6-311++ G(d,p) | B3LYP/6-311++G(d,p) |
|-------|-------------------|---------------------|
| C1 | -0.22583 | -0.316886 |
| C2 | -0.460668 | -0.175212 |
| C3 | 0.187974 | 0.171964 |
| C4 | -0.277859 | -0.088511 |
| C5 | 0.448166 | -0.084269 |
| N6 | -0.291657 | -0.143565 |
| H7 | 0.320555 | 0.268773 |
| H8 | 0.215794 | 0.185451 |
| N9 | -0.509241 | -0.323927 |
| H10 | 0.343353 | 0.302033 |
| H11 | 0.353519 | 0.316505 |
| N12 | -0.16949 | -0.229709 |
| O13 | -0.094638 | -0.058151 |
| O14 | -0.070329 | -0.021695 |
| H15 | 0.230353 | 0.197199 |

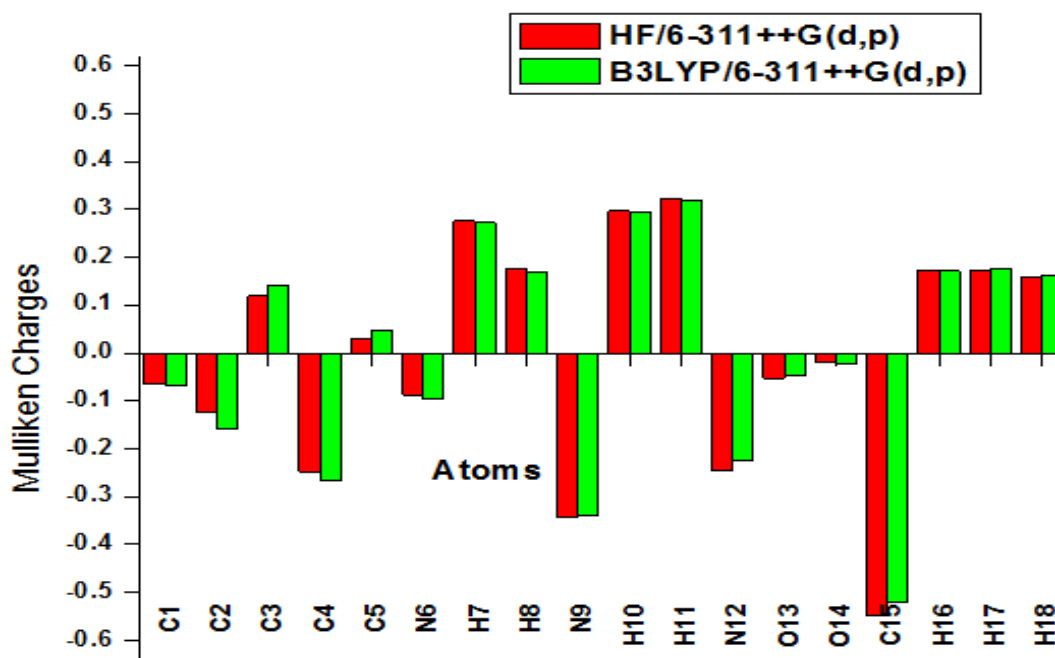


Figure (ii): Mulliken atomic charge distributributions of 2-amino-3-nitro-6-picoline

As can be seen in Table (ii) and Figure (ii), all hydrogen atoms and two carbon atoms in the ring C3, C5 have a net positive charge. It is interesting to see all the nitrogen atoms (N6, N9 and N12) and two oxygen atoms (O13 and O14) have a net negative charge. The maximum negative charges attained by C4, C15, N9 which are more donor atoms. Tendency to behave more acceptor atoms are C3, C5 and all hydrogen atoms which are positively charged. The donor and acceptor atoms may suggest the population of electron distribution of each atom in the compound.

VIBRATIONAL ANALYSIS

The maximum number of potentially active observable fundamentals of a non-linear molecule, which contains N atoms, is equal to $3N-6$ apart from three rotational degrees of freedom. The molecule 2A3N6MP has 18 atoms

which are distributed as $\Gamma = 3N-6 = 48$ fundamental modes of vibrations. The molecule belongs to C_1 point group symmetry and 48 normal modes of vibrations are distributed as 35 in- plane and 13 out of plane vibrations. The detailed vibrational assignment of the fundamental modes of 2A3N6MP along with the calculated IR intensity and Raman activity and normal descriptions are reported in the Table (iii). The comparative graph of the calculated IR intensities and Raman activities for the title molecule are presented in Figure (iii) and (iv). Some important modes of vibrations along with scaled wave nos. and observation nos. have been discussed as follows.

Table(iii): Vibrational wavenumbers obtained for 2-amino-3-nitro-6—picoline at HF and B3LYP using 6311++ G(d,p) basis set [harmonic frequency (cm^{-1}), IR intensities (km mol^{-1}), Raman scattering activities ($\text{A}^0 \text{amu}^{-1}$)]

| Obs. nos. | Sym. Species | HF/6-311++G(d,p) | | IR intensity | Raman activity | B3LYP/6-311++G(d,p) | | IR intensity | Raman activity | Assignments |
|-----------|--------------|------------------------------|-----------------------------|--------------|----------------|------------------------------|-----------------------------|--------------|----------------|--|
| | | Unsltd. (cm^{-1}) | Scaled (cm^{-1}) | | | Unsltd. (cm^{-1}) | Scaled (cm^{-1}) | | | |
| 1 | A'' | 52 | 46 | 0.013 | 0.2981 | 23 | 22 | 0.1108 | 0.6126 | τ (CH3) |
| 2 | A'' | 58 | 52 | 3.817 | 0.2185 | 67 | 64 | 1.8447 | 0.0348 | τ (NO2)+ ϕ (ring) |
| 3 | A'' | 97 | 86 | 0.006 | 0.1133 | 85 | 82 | 0.0027 | 0.1145 | ϕ (ring)+ ϕ CH3 |
| 4 | A'' | 218 | 194 | 3.884 | 0.0012 | 203 | 195 | 0.0437 | 0.0041 | ϕ C-NH2+ ϕ (ring) |
| 5 | A' | 266 | 236 | 1.962 | 0.5765 | 249 | 239 | 1.7418 | 0.4881 | β CH3+ β NO2 |
| 6 | A'' | 273 | 243 | 106.2 | 0.7236 | 259 | 249 | 23.0725 | 0.6897 | τ NH2 |
| 7 | A'' | 312 | 278 | 149.8 | 1.1919 | 319 | 306 | 187.225 | 0.4325 | τ NH2 |
| 8 | A' | 362 | 322 | 6.379 | 0.9489 | 339 | 325 | 6.0993 | 2.4175 | β NH2+ β CH3 |
| 9 | A' | 397 | 353 | 0.643 | 4.1851 | 369 | 354 | 0.1505 | 8.1468 | β CCC+ β CH3 |
| 10 | A' | 458 | 408 | 2.888 | 1.9387 | 421 | 404 | 2.549 | 2.8391 | β NH2 |
| 11 | A'' | 468 | 417 | 0.169 | 0.6415 | 435 | 418 | 3.2491 | 0.7937 | ϕ CH |
| 12 | A' | 605 | 538 | 8.272 | 3.0274 | 561 | 539 | 7.4607 | 2.6154 | β NH2+s(ring) |
| 13 | A' | 634 | 564 | 9.372 | 5.1506 | 587 | 564 | 2.2022 | 11.364 | S(ring) |
| 14 | A' | 642 | 571 | 0.556 | 0.2524 | 619 | 594 | 1.4272 | 0.4552 | tNH2 |
| 15 | A' | 682 | 607 | 1.611 | 4.1825 | 634 | 609 | 1.0494 | 3.3769 | ω NO2+ γ C-CH3+s(ring) |
| 16 | A' | 696 | 619 | 0.181 | 0.4568 | 653 | 627 | 1.9984 | 0.0495 | tNH2 |
| 17 | A' | 792 | 705 | 11.04 | 22.7421 | 715 | 686 | 11.4399 | 0.3273 | ω NO2+ ϕ CH |
| 18 | A' | 812 | 723 | 47.65 | 1.4033 | 744 | 714 | 3.1574 | 16.282 | γ C-CH3+ ring deformation |
| 19 | A'' | 826 | 735 | 1.161 | 0.026 | 745 | 715 | 4.581 | 1.3203 | ϕ CNC(ring)+ ϕ (ring) |
| 20 | A'' | 881 | 784 | 26.94 | 1.3124 | 810 | 778 | 25.2489 | 0.6672 | ϕ CH |
| 21 | A' | 956 | 851 | 54.42 | 11.7825 | 853 | 819 | 23.8985 | 27.896 | sNO2+ β CH |
| 22 | A' | 1038 | 924 | 15.81 | 5.4176 | 967 | 928 | 11.9151 | 1.7443 | sNH2+ β (ring) |
| 23 | A'' | 1097 | 976 | 2.53 | 2.1176 | 990 | 950 | 1.0293 | 0.1955 | ϕ CH |
| 24 | A'' | 1113 | 991 | 0.051 | 0.2808 | 1004 | 964 | 0.5779 | 4.4878 | rCH3+ β NH2 |
| 25 | A'' | 1154 | 1027 | 6.953 | 0.078 | 1054 | 1012 | 6.1638 | 0.2245 | ϕ C-CH3 |
| 26 | A' | 1174 | 1045 | 72.01 | 6.9189 | 1097 | 1054 | 16.7751 | 3.5069 | β CH+ γ CN |
| 27 | A' | 1214 | 1080 | 64.29 | 42.1996 | 1113 | 1068 | 44.2496 | 35.758 | β NH2+ γ CN+rNH2 |
| 28 | A' | 1268 | 1129 | 23.03 | 20.9569 | 1184 | 1137 | 13.3704 | 5.9776 | β CH+ γ NO |
| 29 | A' | 1310 | 1166 | 160 | 9.3067 | 1254 | 1204 | 4.6941 | 11.41 | β CH+ γ CCH3 |
| 30 | A' | 1359 | 1210 | 17.16 | 3.8054 | 1290 | 1238 | 463.209 | 140.65 | γ (ring)+ γ CN+ γ NO2+ ω NH2 |
| 31 | A' | 1442 | 1283 | 40.22 | 23.3219 | 1343 | 1289 | 0.9824 | 1.145 | β CH+ γ (ring) |
| 32 | A' | 1530 | 1362 | 1.356 | 8.5169 | 1357 | 1303 | 158.133 | 183.53 | γ ring+sNO2+ γ CN |
| 33 | A' | 1545 | 1375 | 64.4 | 129.5 | 1407 | 1351 | 36.5011 | 36.677 | ω CH3 |
| 34 | A' | 1593 | 1418 | 273.1 | 103.347 | 1447 | 1389 | 128.429 | 11.241 | γ NO2+ ω CH3+ ω NH2 |
| 35 | A'' | 1595 | 1420 | 7.698 | 9.1498 | 1476 | 1417 | 8.3251 | 9.0618 | δ CH3 |
| 36 | A' | 1610 | 1433 | 305.8 | 53.0619 | 1486 | 1427 | 19.3092 | 4.9251 | γ NO2+ δ CH3 |
| 37 | A' | 1622 | 1444 | 96.41 | 1.8832 | 1489 | 1429 | 44.1458 | 1.844 | β CH + γ CCC |
| 38 | A' | 1710 | 1522 | 62.05 | 7.2204 | 1540 | 1478 | 167.431 | 17.075 | γ NO2+ δ CH3 |
| 39 | A' | 1766 | 1572 | 347.1 | 47.3054 | 1595 | 1531 | 57.7084 | 21.547 | sNH2 |
| 40 | A' | 1776 | 1581 | 188 | 21.2667 | 1617 | 1552 | 182.682 | 41.372 | Γ (ring)+sNH2 |
| 41 | A' | 1813 | 1614 | 981.4 | 8.4603 | 1648 | 1582 | 572.215 | 9.9589 | γ CCC+sNH2 |
| 42 | A' | 3183 | 2833 | 14.22 | 209.65 | 3038 | 2916 | 9.3231 | 304.8 | γ_{sy} CH3 |
| 43 | A' | 3246 | 2889 | 11.54 | 78.9536 | 3094 | 2970 | 6.7905 | 95.598 | γ_{as} CH3 |
| 44 | A' | 3263 | 2904 | 21.19 | 58.6393 | 3122 | 2996 | 15.2349 | 63.842 | γ_{as} CH3 |
| 45 | A' | 3366 | 2996 | 2.446 | 70.6242 | 3199 | 3071 | 3.3629 | 86.472 | γ_{as} CH |
| 46 | A' | 3393 | 3019 | 2.517 | 71.0105 | 3220 | 3091 | 3.1957 | 83.568 | γ_{sy} CH |
| 47 | A' | 3841 | 3418 | 112.7 | 127.19 | 3575 | 3432 | 85.8479 | 181.9 | γ_{sy} NH2 |
| 48 | A' | 3985 | 3547 | 123.7 | 23.789 | 3718 | 3570 | 101.254 | 35.976 | γ_{as} NH2 |

Notes : A' - in plne, A'' - out of plne, τ - twisting, ϕ - out-of-plane bending, β - in-plane-bending, ω - wagging, r - rocking, γ - stretching, s - scissoring, γ_{as} - asymmetric stretching, γ_{sy} - symmetric stretching, Γ - torsion, sym. - Symmetry, unsltd. - unscaled

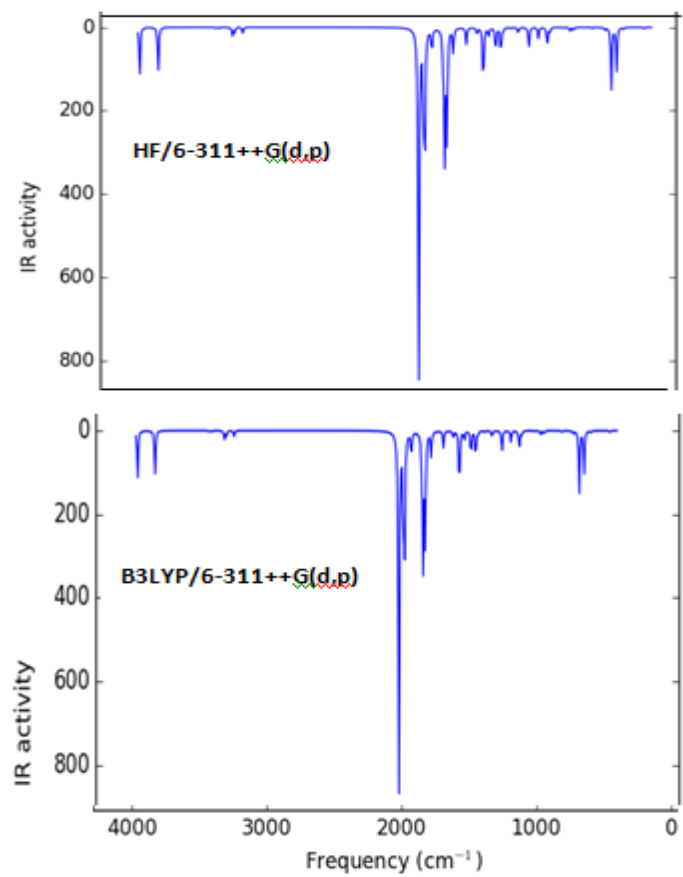


Figure (iii): Calculated FT-IR spectrum of 2A3N6P

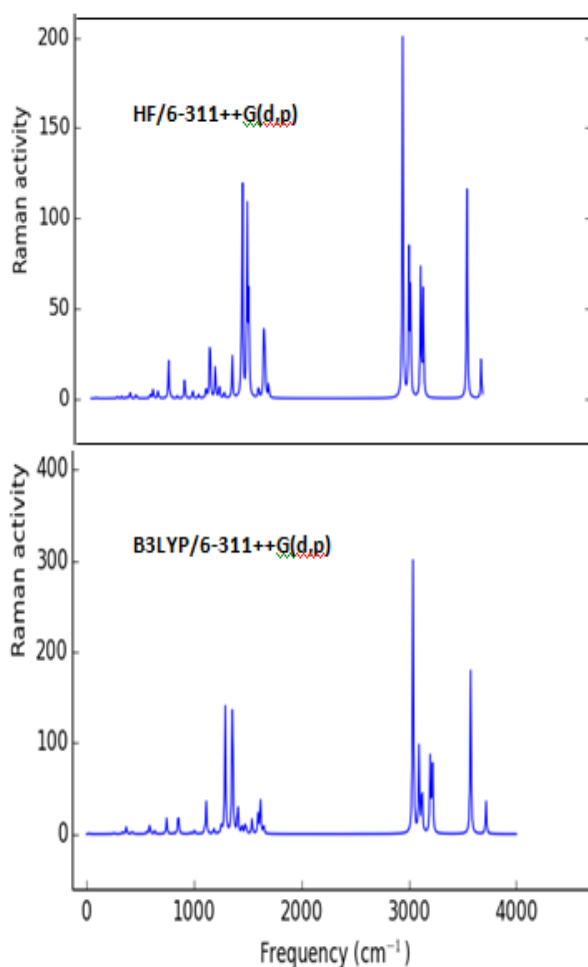


Figure (iv): Calculated FT-Raman spectrum of 2A3N6P

Methyl group vibrations: The title compound possesses only one methyl group at the 6th position with respect to the nitrogen in the pyridine ring. For methyl substituted benzene derivative the CH₃ asymmetric stretching vibration normally expected in the region 2900-3000 cm⁻¹ and symmetric stretching appear between 2800-2900 cm⁻¹ [28-30]. The symmetric CH₃ vibrations observed around 2980 cm⁻¹ and asymmetric CH₃ vibration in the region 2870 cm⁻¹ for similar molecules.[31-34].

The asymmetric C-H stretching vibration in methyl group appears higher than the symmetric stretching. The asymmetric CH₃ vibrations are observed at 2890(43), 2905(44) for HF/6-311++G (d,p) and 2970(43), 2997(44) for B3LYP / 6-311++G (d,p). One CH₃ symmetric stretching vibration observed at 2916(42) by B3LYP/6-311++G (d,p) and for HF/6-311++G(d,p) this stretching vibration observed at 2833(42). Bellamy suggested that each CH₃ group gives rise to three C-H oscillations (2800-3000 cm⁻¹) and three C-H deformations. The CH₃ torsional modes observed at 22 (1) by B3LYP / 6-311++G(d,P) and 46 (1) by HF /6-311++G(d,P) are below 400 cm⁻¹ as expected .

The rocking CH₃ vibrations at 965(24) and 1028(25) by B3LYP and HF are well agree with the Long et al [35-36] within the region (974-1041 cm⁻¹). Two CH₃ wagging at 1375 (33), 1418(34) at HF and 1352 (33), 1389 (34) at B3LYP vibrations are observed which are also similar with earlier results. In our present investigations some in plane C-H vibrations are also observed with ring stretching vibration. Two in-plane bending C-CH₃ at 326(8), 239(5) and 237(5), 323(8) are within the range (390-260 cm⁻¹) in both B3LYP and HF and out- of- plane C-CH₃ bending appears at 249 and 243 cm⁻¹ in both level in mode no.6. The assignments are in good agreement obtained for methyl substituted pyridine derivatives [37].

C-N and C-C (ring vibrations) :

The description of the C-N stretching pyridine ring and C-C stretching bands of aromatic ring usually observed in the same frequency range $1450\text{-}1600\text{ cm}^{-1}$ and $950\text{-}1450\text{ cm}^{-1}$ [38-39]. The C-N stretching vibrations for aromatic amine observed in the region $1266\text{-}1382\text{ cm}^{-1}$. In our present study C-N and C-C stretching vibrations are varied together which occur in the frequency region $1238\text{-}1362\text{ cm}^{-1}$. The stretching ring vibrations both CCC and CNC appears at 1239(30), 1290(31), 1303(32) and 1210(30), 1284(31), 1362(32) in B3LYP and HF respectively. Some out of plane ring vibrations are observed at 715 (19), 196(4), 81(3) and one in-plane vibration at 408(10) in B3LYP and similar vibrations are observed at 736(19), 194(4), 87(3) and 408(10) in HF method.

NO₂ Vibrations:

The vibrations of nitro groups are vibrate with strong intensity and relatively independent with rest of the molecules [40]. The various vibration associated with nitro groups are symmetric and asymmetric stretching, in plane vibrations (scissoring and rocking), out of plane vibration (wagging and twisting). The asymmetric and symmetric NO₂ stretching vibrations of the aromatic nitro compounds gives a band in the range $1570\text{-}1485\text{ cm}^{-1}$ and $1370\text{-}1320\text{ cm}^{-1}$ [41] respectively. The NO₂ stretching vibrations are observed at 1647 and 1595 cm^{-1} for 2-amino-3-nitro pyridine by A A Dahy et. al. and our computed results symmetric and asymmetric NO₂ stretching vibrations are occurs at 1418, 1433, 1523 (mode nos. 34, 36, 38) and 1389, 1427, 1479 (mode nos. 34, 36, 38) by HF and B3LYP method. A very strong NO₂ stretching vibrations are occurs at mode nos. 36 in both HF and B3LYP may be due to the electronic effects of the substituted methyl group. The deformation vibration of NO₂ group (scissoring, wagging, rocking and twisting) contributes to several modes in the low frequency region [42]. In our present calculation NO₂ twisting vibration occurs at 64 (2) cm^{-1} by B3LYP and at 52 (2) by HF and NO₂ scissoring at 851, 925 at mode nos. 21 and 22 in HF and frequencies 820, 929 cm^{-1} for B3LYP are nearly within the region 890- 835 cm^{-1} reported by C Brian Smith et al. [43]. In the present investigation NO₂ wagging vibrations are appears at 634 and 608 at mode nos. 15 for both B3LYP and HF in which γ C-H₃ are also active. The NO₂ rocking vibrations are active in the region 515- 590 cm^{-1} [44] and in 2A3N6MP it appears at 564 cm^{-1} and 563 cm^{-1} for HF and B3LYP respectively. Besides stretching and deformation of nitro group C-NO₂ in-plane-and out-of-plane vibrations are also observed in both HF and B3LYP within the expected region [45] which is presented in the Table (iii).

C-H Vibrations:

The heteroaromatic substituted pyridine compound shows the presence of C-H stretching, in-plane and out-of-plane bending vibrations. The titled molecules has only two C-H moieties give rise to two C-H stretching vibrations and these stretching vibrations are observed around $3100\text{-}3000\text{ cm}^{-1}$ which is their characteristics region [46]. The C-H in-plane vibration usually occur in the region ($1000\text{-}1300\text{ cm}^{-1}$) [47] and out-of-plane bending modes in the region ($950\text{-}600\text{ cm}^{-1}$) [48]. The title molecule 2A3N6MP the C-H symmetric and asymmetric stretching found to be present at scaled frequencies 3092(46) and 3072 (45) cm^{-1} in case of B3LYP. At the HF level these two stretching vibrations are observed at 3020 (46) and 2996 (45). The stretching vibration corresponds to the C₃-H₇ and C₂-H₈ in both the level of theory are in agreement with the theoretical and experimental value in the literature [49]. At HF level of theory C-H in plane vibrations contaminated with other modes of vibration are observed at 1444(37), 1284(31), 1167 (29), 1129(28) and 1045(26) and at B3LYP level these vibrations are observed at 1430(37), 1290(31), 1204(29), 1054(26). The C-H in plane vibrations assigned in the title molecule is found to be in the region in the literature [50]. In the present investigation, in HF method the bands at 784(20), 991(24) and at B3LYP the bands at 951(23), 778(20) are appear as out-of-plane bending C-H vibrations occur in the region ($978\text{-}990\text{ cm}^{-1}$) which are within the range found in literature [51].

NH₂ vibrations:

In our present observation two NH₂ stretching vibrations in each B3LYP and HF methods are observed. Asymmetric and symmetric stretching modes are observed at 3418 and 3547 at HF level and at B3LYP level these vibrations are observed at 3432 and 3569 cm^{-1} . Thus the asymmetric vibrations are higher than the symmetric and the above NH₂ stretching vibrations are in agree with the literature data [52]. In addition to the stretching vibration NH₂ group has occurred scissoring at frequencies 1553(40), 1583(41) in B3LYP and 1572(39), 1581(40) in HF. It is found that the NH₂ scissoring vibrations are within the range (1590- 1650) reported by Thompson [53]. The NH₂ rocking vibrations has been identified in the mode nos. 27 with frequency 1069 for B3LYP and at frequency 1080 in HF at mode no 27 are excellent agreement with predicted results within the region 1077-1057 reported by N. Sundaraganesan et al for 2-amino-6-methyl pyridine. The NH₂ wagging computed at 408, 539 cm^{-1} (mode nos. 10 and 12) in HF and for B3LYP 404, 539 cm^{-1} (mode nos. 10 and 12) which are nearly expected value [54]. Two

torsional modes are observed at 249, 307 cm^{-1} in B3LYP and at 243, 279 in HF with same mode nos. 6 and 7 respectively.

OTHER MOLECULAR PROPERTIES

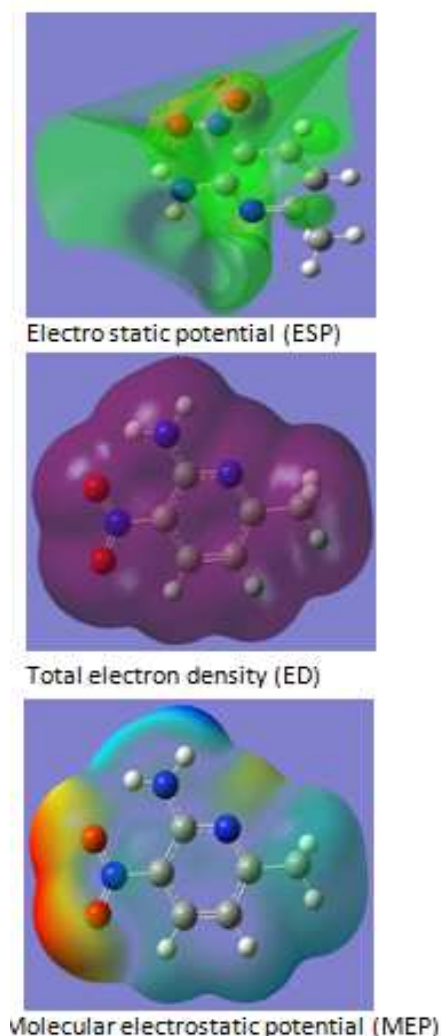


Figure (v): Electrostatic potential (ESP), electron density (ED) and the molecular electrostatic potential (MEP) map of 4F4HBP molecule

Electrostatic potential, electron density and molecular electrostatic potential and electrostatic potential are useful quantities to illustrate the charge distributions of molecules are used to visualize variably charged regions of a molecule. Therefore, the charge distributions can give the information about how the molecules interact with another molecule. In the present study, electrostatic potential, electron density (ED) and the molecular electrostatic potential (MESP) of the molecule under investigation are constructed to predict reactive sides for electrophilic and nucleophilic attack at B3LYP/6-311++ G(d,p) method. The electrostatic potential, total electron density surface and the molecular electrostatic potential mapped into the constant electron density surface are shown in the Fig. v and Fig. v (b). The ED plots for the title molecule show a uniform distribution. MESP helps to predict molecular shape, size as well as reactive sites for electrophonic and nucleophilic attack in terms of color grading of a molecule. The different values of the electrostatic potential at the surface are represented by different colors. Red and blue areas in the MESP refer to the regions of positive and negative potentials and correspond to the electron rich and electron-poor regions, respectively, whereas the green color signifies the neutral electrostatic potential. The electrostatic potential increases in order red<orange<yellow<green<blue. The intensity of the color scheme for the MESP surface is red, electron rich, partially negative charge; blue, electron deficient, partially positive charge; light blue, slightly

electron deficient region; yellow, slightly electron rich region; green, neutral; respectively [55]. It can be seen from the MESP figures v(b), that the yellowish blob localized more over the oxygen in the nitro group indicates negative ESP, while the positive ESP is localized on the rest of the molecules. From the figure it is found that the region around the nitro group represents the most negative potential region (red), while regions around hydrogen atoms represent positive potential (blue). However, the hydrogen atoms at the CH₃ group and in the ring have smaller value than the hydrogen in the NH₂ group.

CONCLUSION

In the present work, the molecular structure parameters of the compound 2-amino-3-nitro-6-picoline have been obtained using HF and density functional theory computed optimized geometric parameters of the molecule were compared and analyzed with available experimental data. The vibrational frequencies of the fundamental modes of the compound have been precisely assigned and analyzed, and the theoretical results were compared with earlier reported literature results. The calculated MESP, total electron density provides the information of size, shape and charge distribution which further lead to the understanding of properties reactive side of the title molecule. Mulliken's net charges have been calculated and interpreted.

Acknowledgements

I would like to thank Dr. Utpal Sarkar, Department of Physics, Assam University, Silchar, Assam, for his help in various ways to carry out this research work.

REFERENCES

- [1] T. Anderson, J. Liebig's *Ann. Chem.*, **1846**, 60, 86-103.,
- [2] Pyridine And Pyridine Derivatives Vol 20; Kirk-Othmer Kirk-Othmer Encyclopedia of Chemical Technology (4th Edition).
- [3] S. Tomaru, S. Matsumoto, T. Kurihara, H. Suzuki, N. Oobara, T. Kaino, *Appl. Phys. Lett.* 58 **1991**, 2583–2585.
- [4] C. Kaneko, S. Yamada, I. Yokoe, N. Hata, Y. Ubata, *Tetrahedron Lett.* 7 **1966**, 4729–4733.
- [5] C. Kaneko, I. Yokoe, S. Yamada, *Tetrahedron Lett.* 8 **1967**, 775–778.
- [6] N. Hata, E. Okutsu, I. Tanaka, *Bull. Chem. Soc. Jpn* 41, **1968**, 1769–1775.
- [7] N. Hata, I. Ono, T. Tuchiya, *Bull. Chem. Soc. Jpn* 45, **1972**, 2386–2391.
- [8] I. Ono, N. Hata, *Bull. Chem. Soc. Jpn* 45, **1972**, 2951–2953.
- [9] D. Doppl, Davidson (Ed.) 55, Springer, Berlin, **1975**, p. 49.
- [10] K. C. Medhi, R.N. Medhi, *Spectrochim. Acta* 49A **1993**, 1024–1029.
- [11] S. P. Jose, S. Mohan, *Spectrochim. Acta* 64A, **2006**, 240–245.
- [12] D. Gandolfo, J. Zarembowitch, *Spectrochim. Acta* 33A, **1977**, 158-164
- [13] J.H.S. Green, W. Kynaston, H.M. Paisley, *Spectrochim. Acta* 19, **1963**, 549
- [14] D.A. Long, W.O. George, *Spectrochim Acta* 19, **1963**, 1777
- [15] A. A. Dahy, S. T. Akriche, M. Rzaigui, N. S. Al-Hokbany, N. M. Abd El-Salam, U. Karama, *Journal of Chemistry* **2012**, 9(4), 2191-2204
- [16] N. Sundaraganesan, C. Meganathan, M. Kurt; *Journal of Molecular Structure* 891, **2008**, 284-291
- [17] M. J. Frisch, et al., Gaussian 03 Program, Gaussian, Inc., Wallingford, CT, **2004**.
- [18] A. D. Becke, *J. Chem. Phys.* 98 (**1999**) 5648.
- [19] J. B. Foresman, A. Frisch, Exploring Chemistry with Electronic Structure Methods, second ed., Gaussian Inc., Pittsburgh, USA, **1996**.
- [20] C. Lee, W. Yang, R.G. Parr, *Phys. Rev. B* 37, **1988**, 785-789.
- [21] D. Buckingham, *Adv. Chem. Phys.*, 1967, 12, 107-142. B. Miehlich, A. Savin, H. Stoll, H. Preuss, *Chem. Phys. Lett.* 157, **1989**, 200–206.
- [22] A. Domenicano, A. Vaciago, *Acta Crystallogr. B* 35, **1979**, 1382.
- [23] A. Domenicano, P. Murray–Rust, C.A. Vaciago, *Acta Crystallogr. B* 39, **1983**.
- [24] A. Domenicano, P. Murray–Rust, *Tetrahedron Lett.*, **1979**, 2283.
- [25] R. I. Dennington, T. Keith, J. Milliam, K. Eppinnett, W. Hovell, Gauss View Version, **2003**.
- [26] I. Nahrungbauer, Ake Kvick, *Acta Cryst.* B33, **1977**, 2902.
- [27] C. B. Aakeroe, A M Beatty, M Nievwenhuyzen, M. Zou, *J. Mat. Chem.*, 1988, 8, 1385
- [28] D. A. Kleinman, *Phys. Rev.* 126, **1962**, 1977.
- [29] B. Smith, Infrared spectral interpretation, A Systematic Approach, CRC Press, Washington, DC, **1999**.

- [30] N. B. Colthup, L.H. Daly, S.E. Wiberly, Introduction to Infrared and Raman Spectroscopy, Academic Press, New York, **1990**.
- [31] G. Socrates, Infrared Characteristic Frequencies, Wiley-Interscience Publication, New York, **1990**.
- [32] D. A. Long, W.O. George, *Spectrochim. Acta* 19, **1963**, 1777
- [33] J. F. Arenas, I. Tocon, J.C. Otero, J.I. Marcos, *J. Mol. Struct.*, **1997**, 443, 410–411
- [34] H. F. Hameka, J.O. Jensen, *J. Mol. Struct. (Theochem.)*, 362, **1996**, 325.
- [35] F. P. Urena, M.F. Gomez, J.J.L. Gonzalez, E.M. Torres, *Spectrochim. Acta A* 59, **2003**, 2815.
- [36] G. Varsanyi, S. Szoke, Vibrational Spectra of Benzene Derivatives, Academic Press, Budapest, New York, London, **1969**.
- [37] H. Ji Singh & P. Srivastava, Indian Journal of Pure & Applied Physics, Vol.47, August **2009**, 557-562.
- [38] G. Socrates, Infrared and Raman Characteristic group Frequencies, Tables and Charts, Wiley, Chichester, **2001**.
- [39] S. Kalaiselvan, N. Sundaraganesan and B. Dominic Joshua, *Indian. J. Chem.* 47A, 1632- 1641.
- [40] C. Brian Smith, Infrared Spectral Interpretation A Systematic Approach, CRC press, USA, **1999**.
- [41] B. S. Yadav, Israt Ali, Pradeep Kumar & Preeti Yadav, *Indian Journal of Pure & Applied Physics*, Vol. 45, December **2007**, pp. 979-983.
- [42] V. Krishnakumar, N. Jayamani, R. Mathammal, K. Parasuraman, *J. Raman Spectrosc.* 40, **2009**, 1551–1556.
- [43] N.B. Colthup, L.H. Daly, S.E. Wiberly, Introduction to Infrared and Raman Spectroscopy, Academic Press, New York, **1964**, 226.
- [44] G. Socrates, Infrared and Raman Characteristic Group Frequencies – Tables and Charts, 3rd ed., Wiley, New York, **2001**.
- [45] I. F. Shishkov, N. I. Sadova, V. P. Novikov, L.V. Vilkov, *Zh. Strukt. Khim.* 25, **1984**, 98.
- [46] K. Raslogi, M. A. Plalfox, R. P. Tanwar, L. Mithal, *Spectrochim. Acta A* 58, **2002**, 1989.
- [47] M. Pagannone, B. Formari, G. Mattel, *Spectrochim. Acta* 43A, **1986**, 621.
- [48] M. Jag, Organic Spectroscopy – Principles and Applications, second edn., Narosa Publishing House, New Delhi, **2001**.
- [49] H. Rostkowska, M. J. Nowak, L. Lapinski, M. Bertner, T. Kulikowski, A. Les, L.Adamowicz, *Spectrochim. Acta* 49A, **1993**, 551.
- [50] L. J. Bellamy, R. L. Williams, *Spectrochim. Acta* 9, **1957**, 311.
- [51] J. C. Evans *Spectromica Acta*, 16, **1960**, 428.
- [52] J. M. Seminario, Recent Developments and Applications of Modern Density Functional Theory, vol. 4, Elsevier, **1996**, 800–806.
- [53] B. Kosar, C. Albayrak, *Spectrochim. Acta A* 78, **2011**, 160–167.
- [54] P. Thul, V.P. Gupta, V.J. Ram, P. Tandon, *Spectrochim. Acta* 75, **2010**, 251–260.
- [55] P. Politzer, J.S. Murray, *Theor. Chem. Accts.* 108, **2002**, 134–142.