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Quantum chemical study on 2-bromo-3-hydroxy-6-methyl pyridine-A D. F. T. study

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ABSTRACT

We have done a study of 2-Bromo-3-hydroxy-6-Methyl Pyridine with B3LYP with 6-311 G (d, p) as the basis set. Here we have studied their structure, vibrational assignments, thermal, electronic and optical properties of 2-Bromo-3-hydroxy-6-Methyl Pyridine. We have plotted frontier orbital HOMO- LUMO surfaces, Molecular electrostatic potential surfaces to explain the reactive nature of 2-Bromo-3-hydroxy-6-Methyl Pyridine.

Keywords: 2-Bromo-3-hydroxy-6-Methyl Pyridine, vibrational analysis, DFT, HOMO-LUMO, MESP

INTRODUCTION

Pyridine is a basic heterocyclic organic compound with the chemical formula C5H5N. It is structurally related to benzene, with one methane group (=CH) replaced by a nitrogen atom. The pyridine ring occurs in many important compounds, including amines and the vitamins niacin and pyridoxal. Pyridine was discovered in 1849 by the Scottish Chemist Thomas Andersons one of the constituents of bone oil. Two years later, Anderson isolated pure pyridine through fractional distillation of the oil. It is a colorless, highly flammable, weakly alkaline, water-soluble liquid with a distinctive, unpleasant fish-like odor. Pyridine is also an important solvent and reagent. Pyridine is added to ethanol to make it unsuitable for drinking (see denatured alcohol). It is used in the in vitro synthesis of DNA [1]. In the synthesis of sulfa pyridine(a drug against bacterial and viral infections), antihistaminic Drugs tripe lennamine and mepyramine, as well as water repellents, bactericides, and herbicides. Some chemical compounds, although not synthesized from pyridine, contain its ring structure. They include B vitamins niacin and pyridoxal, the anti-tuberculosis drug ionized, nicotine and other nitrogen-containing plant products [2]. Pyridine was produced from coal tar and as a by-product of the coal gasification. However, increased demand for pyridine resulted in the development of more economical methods of synthesis from acetaldehyde and ammonia, and more than 20,000 tons per year are manufactured worldwide. 2-Methylpyridine, or 2-picoline, is the compound described With formula C6H7N. 2-Picoline is a colorless liquid that has an unpleasant odor similar to pyridine. Pyridines including 2-picoline are most crudely prepared by the reaction of acetylene and hydrogen cyanide. 3-Methylpyridine, or 3-picoline, is the organic compound with formula 3-CH3C5H4N. It is one of the three isomers of Methyl pyridine. This colorless liquid is a precursor to pyridine. Derivatives that have applications in the pharmaceutical and agricultural industries. Like pyridine, 3-methylpyridine is a colorless liquid with a strong odor. It is classified as a weak base. 4-Methylpyridine is the organic compound with the formula CH3C5H4N. It is one of the three isomers

of methyl pyridine. This colourless pungent liquid is a building block for the synthesis of other heterocyclic compounds [3, 4].

As a part of our ongoing research work [5-9], we report the study of 2-Bromo-3-hydroxy-6-Methyl Pyridine by DFT study. To the best of our knowledge no comparative quantum chemical calculations of this molecule has been reported so far in the literature.

2. Computational methods

All the calculations were performed by the B3LYP [10, 11] method using the 6-311 G (d, p) basis set of Density functional theory [12]. All computations were carried out with the GAUSSIAN 09 package [13]. By combining the results of the GAUSSVIEW'S program [14] with symmetry considerations, vibrational frequency assignments were made with a high degree of accuracy. Vibrational frequencies for these molecules were calculated with these methods and then scaled [15] by 0.9613.

RESULTS AND DISCUSSION

3.1 Geometry Optimization

The optimized structure parameters of 2-bromo-3-hydroxy-6-methylpyridine calculated by B3LYP, method with the 6-311G (d, p) basis set are listed in table 1 and are in accordance with the atom numbering scheme as shown in fig. (1). After geometry optimization local minimum energy obtained for structure optimization of 2-bromo-3-hydroxy-6-methylpyridine with 6-311G (d, p) basis set is approximately (-2936.4687) atomic unite for B3LYP method.

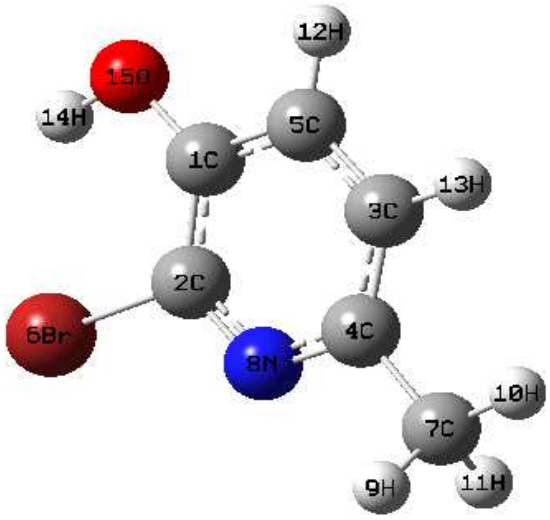

Figure 1:- Model molecular structure of 2-bromo-3-hydroxy-6-methylpridine

The (C-C) bond length varies between the value 1.390 Å-1.504 Å, while (C-O) and (C-Br) bond length is of 1.350 Å and 1.948Å respectively. For (C-N), Bond length varies between the value 1.303 Å - 1.343 Å while, (C-H) bond length Varies between the 1.083 Å -1.093 Å. Here (O-H) bond length is 0.963 Å. All the Calculated bond lengths are in good agreement with experimental data as given In Table 1.

The (C-C-C) bond angle varies from 112.9 - 119.9 degree while, (C-C-O) bond Angle is of 124.6 degree. The (C-C-Br) bond angles is of 119.9 degree while, the (C-C-N) bond Angle varies from 116.8-125.3 degree. (Br-C-N) bond angle is of 117.7 degree while, (C-C-H) Bond angle varies from 110.4-120.1 degree. The (H-C-H) bond angle varies from 107.1-108.6 degree, while the (C-N-C) bond angle is of 119.3 degree. Here (C-O-H) bond angle is of 108.4 degree. All The calculated bond angles are in good agreement with experimental data as Given in Table 1.

Table -1 Bond length (A^0) and bond angle of 2-bromo-3-hydroxy-6-methyl pyridine

S. No.	Parameters	Experimental	Calculated
1	C_1-C_2	1.385	1.403
2	C_1-C_5	1.386	1.393
3	C_1-O_{15}	1.338	1.350
4	C_2-Br_6	1.894	1.948
5	C_2-N_8	1.313	1.303
6	C_3-C_4	1.378	1.396
7	C_3-C_5	1.370	1.390
8	C_3-H_{13}	0.930	1.083
9	C_4-C_7	1.493	1.504
10	C_4-N_8	1.347	1.343
11	C_5-H_{12}	0.930	1.083
12	C_7-H_9	0.960	1.093
13	C_7-H_{10}	0.960	1.091
14	C_7-H_{11}	0.960	1.093
15	H_{14}-O_{15}	0.800	0.969
16	C_2-C_1-C_5	115.5	115.6
17	C_2-C_1-O_{15}	119.2	124.6
18	C_5-C_1-C_{15}	125.3	119.7
19	C_1-C_2-Br_6	118.5	116.9
20	C_1-C_2-N_8	125.0	125.3
21	Br_6-C_2-N_8	116.4	117.7
22	C_4-C_3-C_5	120.3	119.9
23	C_4-C_3-H_{13}	120.0	120.1
24	C_5-C_3-H_{13}	120.0	119.9
25	C_3-C_4-C_7	123.4	112.9
26	C_3-C_4-N_8	119.9	120.1
25	C_7-C_4-N_8	116.7	116.8
26	C_1-C_5-C_3	120.2	119.5
27	C_1-C_5-H_{12}	120.0	118.6
28	C_3-C_5-H_{12}	120.0	112.7
29	C_4-C_7-H_9	109.0	110.4
30	C_4-C_7-H_{10}	109.0	111.4
31	C_4-C_7-H_{11}	110.0	110.4
32	H_9-C_7-H_{10}	109.0	108.5
33	H_9-C_7-H_{11}	109.0	107.1
33	H_{10}-C_7-H_{11}	109.0	108.6
34	C_2-N_8-C_4	119.0	119.3
35	C_1-O_{15}-H_{14}	113.0	108.4

3.2 Electronic and Thermodynamic properties

The interaction with other species in a chemical system is also determined by frontier orbital's, HOMO and LUMO. It can also be determined by experimental data. The frontier orbital gap helps to distinguish the chemical reactivity and kinetic stability of the molecule.

A molecule which has a larger orbital gap is more polarized having reactive part as far as reaction is concerted. The frontier orbital gap in case of the given molecule is -5.39512 eV for 2- bromo -3-hydroxy- 6-methylpyridine given in Table 2. The contour plots of the HOMO, LUMO MESP structure of the molecule are shown in Figure 2. The importance of MESP lies in the fact that it simultaneously displays molecular size, shape as well as positive, negative, and neutral electrostatic potential region in terms of grading and is very useful in the investigation of molecular structure with its physiochemical property relationship Several calculated thermodynamic properties based on the Vibrational analysis at B3LYP and 6-311G (d, p) level, like internal thermal energy (E), constant volume heat capacity (C_v), and entropy (S), have been calculated and listed in Table 3. At the room temperature, conduction band is almost empty so electronic contribution in total energy negligible. Thermodynamic parameters clearly indicate that vibration motion plays a crucial role in assessing thermo dynamical behavior of title compounds.

Table -2 Total Energy, Homo, Lumo, Energy Gap and Dipole Moment of 2- bromo -3-hydroxy- 6- methylpyridine

S.No.	Parameters	Value
1.	Total Energy E (a.u.)	-2936.4687
2.	Homo	-0.24189
3.	Lumo	-0.04354
4.	Frontier Orbital Energy Gap (eV)	5.39512
5.	Dipole Moment (Debye)	1.9384

Table -3 Thermodynamic properties of 2- bromo -3-hydroxy- 6-methylpyridine

Parameters	E(Thermal) KCal/Mol	CV (Cal/Mol-elvin)	S (Cal/Mol-elvin)
Total	74.240	31.001	93.213
Translational	0.889	2.981	41.583
Vibrational	72.463	25.039	21.339

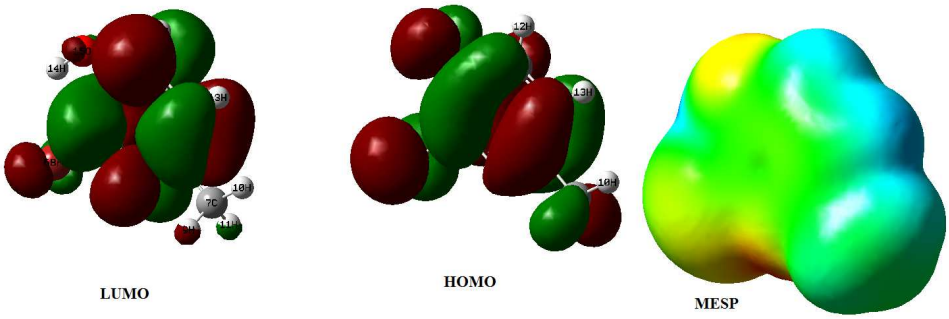

Figure 2. LUMO-HOMO and MESP pictures of 2- bromo -3-hydroxy- 6-methylpyridine

3.3 Atomic Charge, Polarizability and Hyper Polarizability

In Gas Phase, the Mulliken atomic charges for all atoms of the 2-bromo-3-hydroxy-6- methyl pyridine compound are calculated by B3LYP, methods with 6-311G(d, p) as basis set in gas phase and are presented in Table 4. Dipole moment (μ), polarizability <α> and total first static hyper polarizability β [16-17] are also calculated (Table 5) by using density functional theory. They can be expressed in terms of *x*, *y*, *z* components and are given by following equations 1, 2 and 3-

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1\backslash 2} \quad (1)$$

$$<\alpha> = 1\backslash 3\ [\alpha_{xx} + \alpha_{yy} + \alpha_{zz}] \quad (2)$$

$$\beta_{Total} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1\backslash 2} = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yxx} + \beta_{yzz})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2]^{1\backslash 2} \quad (3)$$

The β components of Gaussian output are reported in atomic units. Where (1 a.u. = $8.3693X10^{-33}$ e.s.u.). For 2-bromo-3-hydroxy-6- methyl pyridine, the calculated dipole moment value is 1.9384 Debye. Having higher dipole moment than water (2.16 Debye), 2-bromo-3-hydroxy-6- methyl pyridine can be used as better solvent. As we see a greater contribution of α_{yz} in molecule which shows that molecule is elongated more towards X direction and more contracted to X direction. Perpendicular part Z contributes less part of polarizability of molecule. β_{xxx}, β_{zzz} contribute larger part of hyper polarizability in the molecule. This shows that XZ plane and X-axis more optical active in these direction.

3.4 Assignment of Fundamentals

2- bromo -3-hydroxy- 6-methylpyridine has 15 atoms with 39 normal modes of vibration. We made a reliable one-to-one correspondence between the fundamentals and the frequencies calculated by DFT (B3LYP) methods. All modes are discussed hereafter in table 6 with vibrational assignments.

3.4.1 Vibrational modes Description

3.4.1.1 Spectral region above 2800 cm^{-1}

The C-H stretching vibrations are generally observed in the region 2800-3500cm^{-1}. Accordingly, in the present study for 2- bromo -3-hydroxy- 6-methylpyridine, the C-H stretching vibrations are calculated at 2923, 2976, 2999, 3063, 3079, 3578, cm^{-1} respectively**.**

Table 4Atomic charges of 2-bromo-3-hydroxy-6- methyl pyridine

S. No.	Atom	Atomic Charge
1	C_1	0.160466
2	C_2	0.013277
3	C_3	-0.123214
4	C_4	0.049873
5	C_5	-0.007522
6	Br_1	-0.046432
7	C_6	-0.230649
8	N	-0.310328
9	H_1	0.128423
10	H_2	0.102629
11	H_3	0.128424
12	H_4	0.117861
13	H_5	0.101464
14	H	0.248362
15	O	-0.332633

Table 5Polarizability and Hyper Polarizability of 2-bromo-3-hydroxy-6- methyl pyridine

Polarizability	**Value**
α_{xx}	-54.7264
α_{xy}	-0.0771
α_{yy}	-66.5090
α_{yz}	0.0004
α_{zz}	-66.7250
α_{zx}	0.0000
α	62.6535
Hyper Polarizability	**Value**
β_{xxx}	-52.2575
β_{xxy}	-0.5520
β_{xyy}	-13.0059
β_{yyy}	-15.8613
β^{zzz}	0.0010
β_{xxz}	0.0009
β_{xzz}	-23.5231
β_{yzz}	-7.0340
β_{yyz}	0.0007
β_{xyz}	-0.0013
β	91.9578

3.4.1.2 Spectral region between 1000cm^{-1} to 2300cm^{-1}

C-H, and C-O-H and C-C-H in plane bending (β) vibrations are observed at 1100 cm^{-1} and 1375 cm^{-1}. Ring deformation is seen at 1549 and 1574 cm^{-1} while Scissoring H-C-H at 1442 cm^{-1}. Twist in C-H are also observed at 1021, 1423, 1433cm^{-1} in middle region.

3.4.1.3 Spectral region below 1000cm^{-1}

Twisting in whole ring is at 55 cm^{-1} and torsion τ is at 181, 469, 478, 570, 652 and 714, cm^{-1} in calculated spectrum. Out of plane bending (C-C-H) is observed at 120, 168, 343, 435, 456, 814, 929 cm^{-1} while butterfly motion is presented at 975cm^{-1} in theoretical spectrum.

Table -6 Calculated wave numbers and IR intensity of 2-bromo-3-hydroxy-6- methyl pyridine

S. No.	Frequency	IR intensity	Vibrational Assignments
1	55	0.963	Twist CH_2
2	120	1.926	Out of plane bending in C-C-H
3	168	2.889	Out of plane bending in C-C-H
4	181	3.852	τ (torsion) (C-C-C-H)
5	244	4.815	ν (Br_6-C_2)
6	331	5.778	β(C_3-C_4-C_7)
7	343	6.741	Out of plane bending in C-C-H
8	432	7.704	Out of plane bending in C-C-H
9	456	8.667	Out of plane bending in C-C-H
10	469	9.630	τ(torsion) (C-C-C-C)
11	478	10.59	τ(torsion) (C-C-C-H)
12	570	11.55	τ(torsion) (C-C-C-C)
13	652	12.51	τ(torsion) (C-C-C-H)
14	714	13.48	τ(torsion) (C-C-C-C)
15	744	14.44	τ(torsion) (C-C-C-C)
16	814	15.40	Out of plane bending in C-C-H
17	840	16.37	Ring deformation
18	929	17.33	Out of plane bending in C-C-H
19	975	18.29	Butterfly motion in (C-H_3)
20	1021	19.26	Twist in (C_7-H_9)+(C_7-H_{11})
21	1033	20.22	Ring deformation
22	1100	21.18	β (H_{12}-C_5-C_3)+ β(H_{13}-C_3-H_5)
23	1173	22.14	Ring deformation
24	1224	23.11	ν (C_4-H_7)
25	1247	24.07	ν (C_4-N_8)
26	1311	25.03	ν (C_2-N_8)
27	1360	26.00	Butterfly motion in(C-H_3)
28	1375	26.96	β(C_1-O_{15}-H_{14})+ β(C_3-C_5-H_{12})
29	1423	27.92	Twist in (C-H_3)
30	1433	28.89	ν (C-H)
31	1442	29.85	S(H-C-H) (Scissoring)
32	1549	30.81	Ring deformation
33	1574	31.77	Ring deformation
34	2923	32.74	ν (C_7-H_9)+ ν(C_7-H_{11})+ ν(C_7-H_{10})
35	2976	33.70	ν(C_7-H_{11})+ ν(C_7-H_9)
36	2999	34.66	ν (C_7-H_{10})
37	3063	35.63	ν(C_3-H_{13})+ ν(C_5-H_{12})
38	3079	36.59	ν(C_3-H_{13})+ ν(C_5-H_{12})
39	3578	37.55	ν(O_{15}-H_{14})

CONCLUSION

In this work a detailed vibrational analysis has been carried out using Density Functional B3LYP method with suitable basis set combination. This study is very useful in assigning the correct frequencies for several modes of vibrations. The total energy, entropy and full geometry optimization has been also performed using same method, which is very useful for the study of structure and thermodynamics of the molecule. Normal modes are discussed in detail with the help of gauss view program. Dipole moment shows the solvency properties of these molecules while Thermodynamic properties show that vibrational motion plays an important role in the field of this research . No experimental FTIR spectrum is available for comparison of e2- bromo -3-hydroxy- 6-methylpyridine so it will provide a suitable path for experimental researchers.

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