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Quantum chemical study on 2,6-bis(bromo-methyl)pyridine-A D.F.T. study

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ABSTRACT

Pyridine is miscible with water and virtually all organic solvents. It is weakly basic, and with hydrochloric acid it forms a crystalline hydrochloride salt that melts at 145–147 °C. Most chemical properties of pyridine are typical of a heteroaromatic compound. In organic reactions, pyridine behaves both as a tertiary amine, undergoing protonation, alkylation, acylation, and N-oxidation at the nitrogen atom, and as an aromatic compound, undergoing nucleophilic substitutions. So we have done a vibrational spectroscopic investigation on 2, 6 Bis (Bromo-methyl) Pyridine which is a derivative of benzonitrile. The optimized geometry of the 2, 6 Bis (Bromo-methyl) Pyridine molecule has been determined by the method of density functional theory (DFT). For both geometry and total energy, it has been combined with B3LYP functional having 6-311 g (d, p) as the basis set. Using this optimized structure, we have calculated the infrared wave numbers, which are very useful in absence of experimental data. On Based on these results, we have discussed the correlation between the vibrational modes and the crystalline structure of 2, 6 Bis (Bromo-methyl) Pyridine. A complete assignment has been done with theoretical IR spectra. .

Keywords: DFT, 2, 6 Bis (Bromo-methyl) Pyridine, Vibrational analysis HOMO-LUMO Gap

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INTRODUCTION

Pyridine is a basic heterocyclic organic compound with the chemical formula C5H5N. It is structurally related to benzene, with one methine group (=CH-) replaced by a nitrogen atom. The pyridine ring occurs in many important compounds, including azines and the vitamins niacin and pyridoxal. Pyridine was discovered in 1849 by the Scottish chemist Thomas Anderson as 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 used as a precursor to agrochemicals and pharmaceuticals and 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 sulfapyridine (a drug against bacterial and viral infections), antihistaminic drugs tripelennamine 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 isoniazid, nicotine and other nitrogen-containing plant products.[2] Historically, 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 tonnes per year are manufactured worldwide.

MATERIALS AND METHODS

Computational details

Initial geometry was generated from standard geometrical parameters and was minimized without any constraint in the potential energy surface. The gradient corrected density functional theory (DFT) with the three-parameter hybrid functional (B3) [3] for the exchange part and the Lee-Yang-Parr (LYP) correlation function [4] has been employed for the computation of molecular structure, vibrational frequencies, HOMO-LUMO, and energies of the optimized structures, using GAUSSIAN 09 [5]. The calculated vibrational frequencies have also been scaled by a factor of 0.963 [6]. By combining the results of GaussView's program [7] with symmetry considerations, vibrational frequency assignments were made with a high degree of accuracy. We used this approach for the prediction of IR frequencies of title compound and found it to be very straightforward. Density functional theory calculations are reported to provide excellent vibrational frequencies of organic compound if the calculated frequencies are scaled to compensate for the approximate treatment of electron correlation, for basis set deficiencies and for anharmonicity. A number of studies have been carried out regarding calculations of vibrational spectra by using B3LYP methods with LANL2DZ and 6-311 G (d, p) basis sets. The scaling factor was applied successfully for B3LYP method and was found to be easily transferable in a number of molecules.

RESULTS AND DISCUSSION

The optimized Structure parameters of 2, 6 Bis (Bromo-methyl) Pyridine 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 Figure 1, respectively. After geometry optimization local minimum energy obtained for structured optimization of 2, 6 Bis (Bromo-methyl) Pyridine with 6-311G (d, p) basis set is approximately -5474.0925 (a.u.). For B3LYP method, the optimized bond parameters of molecule calculated by various methods are listed in Table 1.

The (C-C) bond length varies between the values 1.382 Å- 1.496 Å, while (C-Br) bond length varies between 1.950 Å- 1.956 Å. (C-H) bond length varies between 0.93 Å- 0.97 Å while (C-N) bond length is 1.334 Å.-1.343 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 118.4- 121.1 while (C-C-Br) varies between 110.4- 110.6. The (C-C-H) bond angle varies between 109.0- 120.8. All the calculated bond angles are in good agreement with experimental data as given in Table 1.

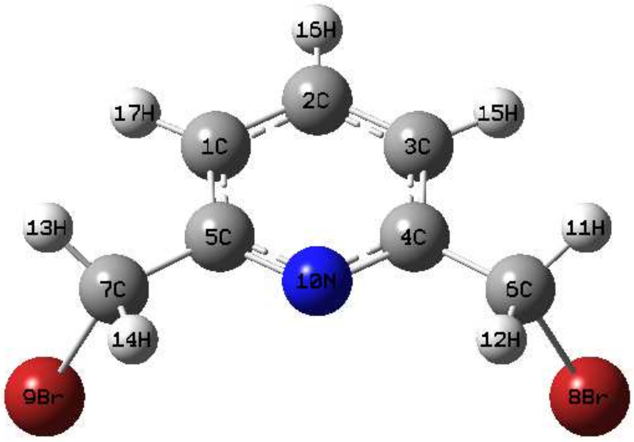

Figure 1. Model molecular structure of 2,6-Bis(Bromomethyl)Pyridine

TABLE-1 Bond Lengths (Å) & Bond Angle of 2, 6 –Bis(bromomethyl)Pyridine

S.No.	Parameters	Experimental Value	Calculated Value
"Bond lengths"			
1.	C_1-C_2	1.382	1.389
2.	C_1-C_5	1.387	1.397
3.	C_1-H_{17}	0.930	1.083
4.	C_2-C_3	1.383	1.389

5.	C_2-H_{16}	0.930	1.083
6.	C_3-C_4	1.382	1.397
7.	C_3-H_{15}	0.930	1.083
8.	C_4-C_6	1.496	1.497
9.	C_4-N_{10}	1.334	1.337
10.	C_5-C_7	1.491	1.497
11.	C_5-N_{10}	1.343	1.337
12.	C_6-Br_8	1.950	1.995
13.	C_6-H_{11}	0.970	1.086
14.	C_6-H_{12}	0.970	1.084
15.	C_7-Br_9	1.956	1.995
16.	C_7-H_{13}	0.970	1.086
17.	C_7-H_{14}	0.970	1.084
“Bond Angles”			
18.	C_2-C_1-C_5	119.2	118.6
19.	C_2-C_1-H_{17}	120.4	121.0
20.	C_5-C_1-H_{17}	120.4	120.2
21.	C_1-C_2-C_3	118.4	118.9
22 .	C_1-C_2-H_{16}	120.8	120.5
23.	C_3-C_2-H_{16}	120.8	120.5
24.	C_2-C_3-C_4	118.8	118.6
25.	C_2-C_3-H_{15}	120.6	121.0
26.	C_4-C_3-H_{15}	120.6	120.2
27.	C_3-C_4-C_6	120.3	121.4
28.	C_3-C_4-N_{10}	123.4	122.5
29.	C_6-C_4-N_{10}	116.3	116.0
30.	C_1-C_5-C_7	121.1	121.4
31.	C_1-C_5-N_{10}	122.6	122.5
32.	C_7-C_5-N_{10}	116.3	116.0
33.	C_4-C_6-Br_8	110.4	111.7
34.	C_4-C_6-H_{11}	109.6	112.9
35.	C_4-C_6-H_{12}	109.6	110.5
36.	Br_8-C_6-H_{11}	109.6	104.4
37.	Br_8-C_6-H_{12}	109.6	105.3
38.	H_{11}-H_{12}-C_6	108.1	111.4
39.	C_5-C_7-Br_9	110.6	111.7
40.	C_5-C_7-H_{13}	109.5	112.9
41.	C_5-C_7-H_{14}	109.5	110.5
42.	Br_9-C_7-H_{13}	109.5	104.4
43.	Br_9-C_7-H_{14}	109.5	105.3
44.	H_{13}-C_7-H_{14}	108.1	111.4
45.	C_4-N_{10}-C_5	117.5	118.7

Atomic charge, Polarizibility, Hyper Polarizibility and Thermodynamic Properties:
The Mulliken atomic charges for all the atoms of the 2, 6 Bis (Bromo-methyl) Pyridine is calculated by B3LYP method with 6-311G (d, p) as basis set in gas phase and are presented in Table 2.

Dipole moment (μ), polarizibility <α> and total first static hyperpolarizlbility β [8, 9] are also calculated (In Table 3) 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-

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

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

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

The β components of Gaussian output are reported in atomic units.
Where (1 a.u. = $8.3693\text{X}10^{-33}$ e.s.u.). For 2, 6 Bis (Bromo-methyl) Pyridine, the calculated dipole moment value is 4.2863 Debye. Having higher dipole moment than water (2.16 Debye), 2, 6 Bis (Bromo-methyl) Pyridine can be used as better solvent. As we see a greater contribution of α_{xx} in molecule which shows that molecule is elongated

more towards X direction and more contracted to Y direction. $\beta_{yyy,}$ β_{yzz} contribute larger part of hyperpolarizibity in the molecule. This shows that Y axis and YZ plane more optical active in these direction.

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 4. 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 thermodynamical behavior of title compounds. The calculated dipole moments at B3LYP/6-311G (d, p) level are 6.6832 for 2, 6 Bis (Bromo-methyl) Pyridine.

TABLE-2 Mulliken atomic charges (e) of the 2, 6 –Bis (bromomethyl) pyridine

s.no.	Atom	Atomic charge
1.	C_1	-0.106031
2.	C_2	0.000552
3.	C_3	-0.106030
4.	C_4	0.117055
5.	C_5	0.117060
6.	C_6	-0.294362
7.	C_7	-0.294369
8.	Br_1	-0.071421
9.	Br_2	-0.071415
10.	N	-0.318863
11.	H_1	0.169284
12.	H_2	0.181275
13.	H_3	0.169285
14.	H_4	0.181274
15.	H_5	0.108153
16.	H_6	0.110398
17.	H_7	0.108155

TABLE-3 Polarizability & Hyper Polarizability 2, 6-Bis (Bromomethyl) Pyridine

Polarizability	
α_{xx}	--86.7767
α_{xy}	0.0005
α_{yy}	-79.0187
α_{yz}	-1.8704
α_{zz}	-81.3624
α_{zx}	0.0001
α	82.3858333
Hyper Polarizability	
β_{xxx}	0.0001
β_{xxy}	5.8570
β_{xyy}	5.8570
β_{yyy}	-46.7375
β_{zzz}	-11.8800
β_{xxz}	7.0034
β_{xzz}	-0.0011
β_{yzz}	-19.9482
β_{yyz}	-19.6815
β_{xyz}	0.0001
βtotal	60.9071316

TABLE-4 Thermodynamic properties of 2, 6 – Bis (Bromomethyl) Pyridine

Parameter	E (Thermal) Kcal/mol	CV (cal/mol-kelvin)	S (cal/mol-kelvin)
Total	84.729	34.287	107.052
Translational	0.889	2.981	42.599
Rotational	0.889	2.981	32.868
Vibrational	82.951	28.326	31.584

Electronic Properties:

The interaction with other species in a chemical system is also determined by frontier orbitals, HOMO and LUMO. It can also be determined by experimental data. The frontier orbital gape helps to distinguish the chemical reactivity and kinetic stability of the molecule. A molecule which has a larger orbital gape is more polarized having reactive part as far as reaction is concerted [10]. The frontier orbital gape in case of the given molecule is 4.65 eV for 2, 6 Bis (Bromo-methyl) Pyridine given in Table 5.

The contour plots of the HOMO, LUMO structure of the molecules are shown in Figure 4, 5. 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 [11,12]. The MESP diagram is shown in Figure 6.

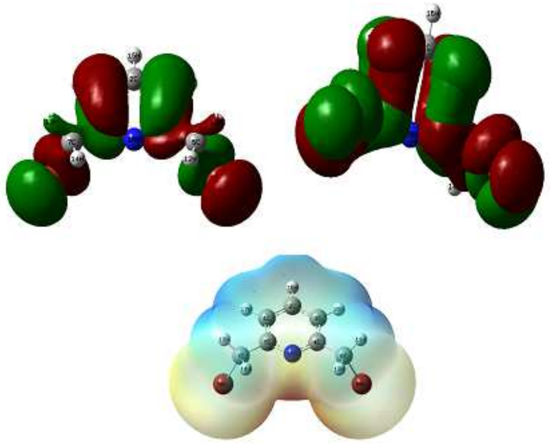

Figure 2 HOMO (Left)- LUMO (Right) and MESP (Down Center) pictures of 2, 6-Bis (Bromomethyl) Pyridine

TABLE-5 HOMO-LUMO Gap (Frontier Orbital Energy Gap) and Dipole moment of 2, 6-Bis(Bromomethyl) Pyridine

Parameters	**Value**
Total energy E(a.u.)	-5474.0925
Dipole moment (Debye)	4.2863
LUMO	-0.26789
HOMO	-0.06572
Frontier Orbital Energy Gap (ev)	5.499024

Assignment of fundamentals

2, 6 Bis (Bromo-methyl) Pyridine has 17 atoms 45 normal modes of vibration. We made a reliable one-to-one correspondence between the fundamentals and the frequencies calculated by DFT (B3LYP). The relative band intensities are also very satisfactory along with their positions. Some important modes are discussed hereafter.

Vibrational Modes Discription:

C-H stretching vibrations are generally observed in the region 2800-3200 cm^{-1}. Accordingly, in the present study for 2, 6 Bis (Bromo-methyl) Pyridine, the C-H stretching vibrations are calculated at 2998, 2998, 3057, 3069, 3072, 3072 and 3078 cm^{-1}, respectively.

A strong scissoring vibrations (H-C-H) are observed in the region 1406 and 1415 cm^{-1}. In plane bending vibrations are found in the region 1064 cm^{-1} and 1042 cm^{-1}. Between the region 1000- 2300 cm^{-1} we have observed that in two region 1557 cm^{-1} and 1567 cm^{-1} the whole ring deformed. Also strong CH2 rocking mode vibration is calculated at 1195 cm^{-1} in spectral region.

Torsion, wagging and out of plane bending modes are generally present in lower region. Ring Torsion is shown at 554 and 578 cm^{-1}, while Twisting in (C-CH$_2$-Br) bond is shown in 298 cm^{-1}. Ring Breathing vibration is observed at 218 cm^{-1} and also out of plane banding in C-C-H observed in 423 cm^{-1}.

TABLE-6 Calculated Wave Numbers, it's Respective IR Intensity and vibrational assignments of 2 ,6 –Bis(Bromomethyl) Pyridine

S.no.	Frequency	IR intensity	Vibrational Assignment
1	16	0.358	ω(C-Br)
2	28	0.002	Twist in whole ring
3	86	2.731	Banding of ring
4	91	1.931	Twisting in whole ring
5	207	4.221	Twisting in whole ring
6	218	2.033	Breathing
7	258	2.447	Twist (C-CH$_2$-Br) in both places
8	385	1.637	Twist (C-CH$_2$-Br) in both places
9	423	3.322	γ(C-C-H) out of plane banding in whole ring
10	470	3.437	Out of plane banding in whole ring
11	552	44.81	Ring deformation
12	554	20.26	τ(C-C-C-N)in whole ring
13	578	37.67	τ(C-C-C-C) in whole ring
14	683	1.582	Out of plane banding in whole ring
15	712	5.291	Ring breathing
16	737	15.45	γ(C-C-H)
17	810	15.20	γ(C-C-C)
18	844	1.155	Twist in both C-H$_2$
19	846	3.539	Twist in both C-H$_2$-Br
20	894	0.095	γ Out of plane banding(C-C-H)
21	938	3.764	β(C-C-C) whole ring
22	972	3.290	Ring breathing
23	974	3.305	Ring breathing
24	1064	12.93	β(C-C-H)
25	1093	0.450	β(C-C-H)
26	1101	1.958	β(C-C-H)
27	1142	2.537	β(C-C-H)
28	1195	44.90	Rocking CH2
29	1199	29.34	Rocking CH2
30	1207	0.024	β(C-C-H) whole molecule
31	1244	3.629	Ring breathing
32	1269	0.754	Stretching ν(C-C) whole ring
33	1406	1.159	Scissoring $S(H_{13}\text{-}C_7\text{-}H_{14}) + (H_{11}\text{-}C_6\text{-}H_{12})$
34	1415	0.386	Scissoring $S(H_{13}\text{-}C_7\text{-}H_{14}) + (H_{11}\text{-}C_6\text{-}H_{12})$
35	1426	6.882	$\beta(H_{14}\text{-}C_7\text{-}H_{13}) + \beta(H_{11}\text{-}C_6\text{-}H_{12})$
36	1432	48.75	$\omega(C_1\text{-}H_{17}) + \omega(C_2\text{-}H_{16}) + \omega(C_3\text{-}H_{15})$
37	1557	33.32	Ring deformation
38	1567	28.29	Ring deformation
39	2998	1.833	$\nu(C_7\text{-}H_{13}) + \nu(C_7\text{-}H_{14}) + \nu(C_6\text{-}H_{12}) + \nu(C_6\text{-}H_{11})$
40	2998	12.80	$\nu(C_7\text{-}H_{13}) + \nu(C_7\text{-}H_{14}) + \nu(C_6\text{-}H_{12}) + \nu(C_6\text{-}H_{11})$
41	3057	3.303	$\nu(C_1\text{-}H_{17}) + \nu(C_2\text{-}H_{16}) + \nu(C_3\text{-}H_{15})$
42	3069	6.849	$\nu(C_1\text{-}H_{17}) + \nu(C_3\text{-}H_{15})$
43	3072	0.123	$\nu(C_7\text{-}H_{13}) + \nu(C_7\text{-}H_{14}) + \nu(C_6\text{-}H_{12}) + \nu(C_6\text{-}H_{11})$
44	3072	0.637	$\nu(H_{13}\text{-}C_7) + \nu(C_7\text{-}H_{14}) + \nu(C_1\text{-}H_{17}) + \nu(C_3\text{-}H_{15}) + \nu(C_6\text{-}H_{11}) + \nu(C_6\text{-}H_{12})$
45	3078	7.339	$\nu(C_1\text{-}H_{17}) + \nu(C_2\text{-}H_{16}) + \nu(C_3\text{-}H_{15})$

CONCLUSION

We have done a Structural, electronic, optical and vibrational properties of 2, 6 Bis (Bromo-methyl) Pyridine Using Density Functional Theory. All frequencies are real in the molecule. Hence the compound is stable. The method B3LYP /6-311G (d, p) gives us most successfully described the vibrational spectra of 2, 6 Bis (Bromo-methyl) Pyridine. Reactivity reflects the susceptibility of a substance towards a specific chemical reaction and plays a key role in, for example, the design of new molecules and understanding biological systems and material science. Hyper polarizability is mainly controlled by the planarity of the molecules, the donor and accepter strength, and bond length alteration. The values of hyper polarizability indicate a possible use of these compounds in electro-optical applications. The present work might encourage the need for an extensive study by the experimentalists interested in the vibrational spectra and the structure of these compounds.

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REFERENCES

[1] Pyridine, Encyclopædia Britannica on-line, **2014**.
[2] Lide, D. R., ed. (**2009**). Handbook of Chemistry and Physics (90th ed.). Boca Raton: CRC Press. ISBN 978-1-4200-9084-0
[3] A.D. Becke, "Density-functional thermochemistry. III.The role of exact exchange," *The Journal of Chemical Physics*, vol. 98, no. 7, pp. 5648–5652, **1993**.
[4] C. Lee, W. Yang, and R. G. Parr, *Physical Review B*, vol. 37, no. 2, pp. 785–789, **1988**.
[5] M. J. Frisch, G. W. Trucks, H. B. Schlegel et al., *Gaussian 09*, Gaussian, Pittsburgh, Pa, USA, **2009**.
[6] P. L. Fast, J. C. Corchado, M. L. S´anchez, and D. G. Truhlar, *Journal of Physical Chemistry A*, vol. 103, no. 17, pp. 3139–3143, **1999**.
[7] A. Frisch, A. B. Nelson, and A. J. Holder, *Gauss View*, Gauss, Pittsburgh, Pa, USA, **2000**.
[8] P. K. Chattaraj and S. Giri, *Journal of Physical Chemistry A*, vol. 111, no. 43, pp. 11116–11121, **2007**.
[9] J. Padmanabhan, R. Parthasarathi, V. Subramanian, and P. K. Chattaraj, *Journal of Physical Chemistry A*, vol. 111, no. 7, pp. 1358–1361, **2007**.
[10] I. Fleming, frontier Orbitals and Organic Chemical Reactions, John Wiley & Sons, New York, NY, USA, 1976.
[11] J. S. Murray and K. Sen, Molecular Electrostatic Potential, Concepts and Applications, Elsevier, Amsterdam, The Netherlands, **1996**.
[12] J. Sponer and P. Hobza, *International Journal of Quantum Chemistry*, vol. 57, no. 5, pp. 959-970, **1996**.