VIBRATIONAL SPECTRAL STUDIES AND NLO PROPERTIES OF 5-BROMO-2-HYDROXY-3-METHOXY BENZALDEHYDE BY DFT.

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Abstract—*In the present study 5-BROMO-2-HYDROXY-3-METHOXY BENZALDEHYDE was taken for the vibrational, spectral and NLO studies as among aromatic aldehydes, benzaldehydes and its derivatives are the simplest, they have a large usage in different industries as perfumes, flavouring compounds, soaps, foods, preparations of some aniline dyes, solvent for oils etc. They have also shown anti tumor activity in mice. The spectral studies were performed for FT IR (KBr and Nuzol), Raman and UV. The laser Raman spectra of the molecule was also recorded. Quantum mechanical calculations of geometries, energies, vibrational wave numbers and thermodynamic constants have been performed with Gaussian 09W program package using the Becke-3Lee-Yang-Parr (B3LYP) functional supplemented with the standard 6-31G (DP). The optimised geometrical parameters obtained by computational method used shows good agreement with the experimental data. The thermodynamic properties as heat capacity, entropy, enthalpy and gibbs free energy of the titled compounds at different temperatures were also calculated along with dipole moment, polarisability and hyper polarisability.*

Keywords: *5-BROMO-2-HYDROXY-3-METHOXY BENZALDEHYDE, vibrational, NLO, Gaussian 09W, DFT/ B3LYP , thermodynamic parameters, FTIR, dipole moment, polarisability, hyperpolarisability.*

1. INTRODUCTION

In aromatic aldehydes, benzaldehydes and its derivatives are the simplest, they have a large usage in different industries as perfumes, flavouring compounds, soaps, foods, preparations of some aniline dyes, solvent for oils etc. They have also shown anti tumor activity in mice [1, 2]. They are used in different compositions in manufacturing and processing of perfumes, soaps, foods flavourings, solvent for oils resins etc.. In this light lots of aspects of substituted benzaldehydes and its derivatives are unexplored inspite of the fact that much work has been done on these compounds.[3-7].

2. EXPERIMENTAL

Spec-pure grade sample of 5-bromo-2hydroxy-3methoxy benzaldehyde (abbreviated as 5B2H3MB) were obtained from M/S Aldrich Chemie, West Germany. The Purity of sample was confirmed by elemental analysis and melting point determination. The laser Raman spectra of both the molecules were recorded on Spex Rama Lab spectrophotometer using 52 MW Argon-Krypton laser beam of wavelength 488 nm. The infrared spectra of these two compounds were recorded on Perkin Elmer spectrophotometer model -52 in the region 400-4000 cm⁻¹ using KBr and nuzol technique.

3. COMPUTATIONAL

All the calculations were were carried out for DMBA and MMBA with Gaussian 03W program package [8]using the Becke-3Lee-Yang-Parr (B3LYP) functional supplemented with the standard 6-31G_ basis set further referred as DFT calculations. All the parameters were allowed to relax and all the calculations converged to an optimized geometry which corresponds to a true energy minimum, as revealed by the absence of imaginary values in the wave number calculations.

4. RESULTS AND DISCUSSION

4.1 MOLECULAR STRUCTURE

The molecular structure of 5B2H3MB is shown with labelled atoms in fig 1.. The optimized bond lengths, bond angles and dihedral angles calculated by DFT-B3LYP level with 6-31++G(d, p), basis sets are compared with the experimental data and are presented in Table 1.In the substitution of the aldehyde , hydroxyl, methoxy and bromo group the bond lengths, bond angle and dihedral angles are in good agreement with the reported values for the compound 5B2H3MB.

Figure1

TABLE 1: Calculated Optimized Geometrical Parameters of 5-bromo-2-hydroxy-3-methoxy benzaldehyde, at B3LYP/6-31G(d, p): bond length (Å), bond angle(°), dihedral angles(°)

Atoms Of molecule	Bond length (A0)	Angle between atoms	Bond Angle(o)	Dihedral angle between atoms	Dihedral angle(0)
R(1, 2)	1.4014	A(2, 1, 6)	119.9858	D(6, 1, 2, 3)	1.5833
R(1, 6)	1.4016	A(2, 1, 9)	120.0	D(6, 1, 2, 12)	-178.4167
R(1, 9)	1.54	A(6, 1, 9)	119.9953	D(9, 1, 2, 3)	179.9999
R(2, 3)	1.4014	A(1, 2, 3)	120.0	D(9, 1, 2, 12)	-0.0001
R(2, 12)	1.43	A(1, 2, 12)	120.0	D(2, 1, 6, 5)	-1.5833
R(3, 4)	1.4014	A(3, 2, 12)	120.0	D(2, 1, 6, 8)	179.2083
R(3, 14）	1.43	A(2, 3, 4)	120.0	D(9, 1, 6, 5)	180.0000
R(4, 5)	1.4016	A(2, 3, 14)	120.0	D(9, 1, 6, 8)	0.7916
R(4, 7)	1.07	A(4, 3, 14)	120	D(2, 1, 9, 10)	179.9998
R(5, 6)	1.4014	A(3, 4, 5)	119.9858	D(2, 1, 9, 11)	0.0000
R(5, 19)	1.91	A(3, 4, 7)	120.0	D(6, 1, 9, 10)	-1.5837
R(6, 8)	1.07	A(5, 4, 7)	119.9953	D(6, 1, 9, 11)	178.4165
R(9, 10)	1.07	A(4, 5, 6)	119.9953	D(1, 2, 3, 4)	-1.5836
R(9, 11)	1.2584	A(4, 5, 19)	120.0	D(1, 2, 3, 14)	178.4164
R(12, 13)	0.96	A(6, 5, 19)	120.0	D(12, 2, 3, 4)	178.4164
R(14, 15)	1.43	A(1, 6, 5)	119.9953	D(12, 2, 3, 14)	-1.5836
R(15, 16)	1.07	A(1, 6, 8)	120.0	D(1, 2, 12, 13)	150.0000
R(1, 17)	1.07	A(5, 6, 8)	120.0	D(3, 2, 12, 13)	-30.0000
R(15, 18)	1.07	A(1, 9, 10)	120.0	D(2, 3, 4, 5)	1.5834
		A(1, 9, 11)	120.0	D(2, 3, 4, 7)	-180.0000
		A(10, 9, 11)	120.0	D(14, 3, 4, 5)	-178.4165
		A(2, 12, 13)	109.4712	D(14, 3, 4, 7)	0.0001
		A(3, 14, 15)	109.4712	D(2, 3, 14, 15)	150.0000
		A(14, 15, 16)	109.4713	D(4, 3, 14, 15)	-30.0000
		A(14, 15, 17)	109.4713	D(3, 4, 5, 6)	-1.5835
		A(14, 15, 18)	109.4713	D(3, 4, 5, 19)	179.2084
		A(16, 15, 17)	109.4712	D(7, 4, 5, 6)	179.9998
		A(16, 15, 18)	109.4712	D(7, 4, 5, 19)	0.7917
		A(17, 15, 18)	109.4712	D(4, 5, 6, 1)	1.5836
				D(4, 5, 6, 8)	-179.2081
				D(19, 5, 6, 1)	-179.2083
				D(19, 5, 6, 8)	0.0001
				D(3, 14, 15, 16)	60.0000
				D(3, 14, 15, 17)	-180.0000
				D(3, 14, 15, 18)	-60.0000

4.2 VIBRATIONAL SPECTROSCOPY

A detailed vibrational description has been carried out of the reported compound and its vibrational frequencies have been calculated using DFT-B3LYP level with 6-31++G(d, p), there is a good agreement between the observed frequencies and those calculated by the DFT.

The observed FTIR, FT-Raman and calculated frequencies (cm^{-1}), IR intensity (km/mol), Raman activity (A^0 amu^{-1}) and probable assignments of 5-bromo-2-hydroxy-3-methoxy benzaldehyde using DFT-B3LYP method with 6-311G(DP) basis set.

Table 2

S.No.	Experimental Frequencies				Calculated Frequencies		Assignments
	FTIR	Raman	IR(kbr)	IR(nuzol)	IR intensities	Raman activity	
1	-	50	-	-	143.8102	5.1791	
2	-	-	415	-	0.3303	0.1791	
3	-	-	437	-	7.8291	1.2256	
4	-	-	505	-	12.6698	4.0634	
5	-	-	531	-	2.1915	0.9934	
6	573.1	-	570	-	0.5901	2.7976	-Br, bending
7	690.2	-	690	-	2.1967	0.6386	-Br, stetching
8	-	-	707	722	1.9326	0.6319	
9	-	-	759	-	3.3585	1.4920	
10	-	-	803	801	6.8625	9.8059	
11	848.1	-	846	845	14.2223	0.3502	
12	-	-	865	864	8.4060	2.2569	
13	939.7	-	933	931	1.3315	1.5717	-OH group
14	1082.3	-	1077	1076	5.7545	0.5508	
15	1103	-	-	-	15.1727	3.0793	-OCH3, bending
16	1184.2	-	1186	1184	12.5032	6.8241	-OCH3 stretching
17	1250.4	-	1247	-	3.5017	0.6538	-C=O bending
18	-	-	1269	1244	17.1538	0.1966	
19	-	-	1353	1377	59.5358	6.2672	
20	-	-	1403	1402	63.0128	1.1898	
21	-	-	1419	-	26.6617	1.4901	
22	-	-	1438	-	43.4972	6.0086	
23	-	-	1455	-	77.3776	4.0949	
24	-	-	1468	1461	8.7013	0.8324	
25	1505	-	1489	-	8.8493	3.1753	
26	-	-	1588	1585	13.1284	4.3653	
27	1662	-	1667	1664	90.9398	30.5536	
28	-	1700	1719	-	79.4273	3.2987	-C=O stretching
29	-	-	1742	1742	8.9550	4.3275	
30	-	-	1775	-	0.8331	5.0681	
31	-	-	2346	2346	18.1069	4.0431	
32	-	-	-	2855	116.2318	7.1258	
33	-	-	2907	2927	112.4254	9.6702	
34	-	-	2945	-	7.7670	1.0263	
35	-	-	2979	-	20.2307	2.6065	
36	-	-	3079	-	28.0725	7.8126	
37	-	3180	3171	-	3.1458	0.1895	-C=C stretching
38	-	3439.9	-	-	77.4138	30.2132	C-C bending
39	-	-	3569	3588	15.2868	21.2183	
40	-	-	3631	3631	13.4572	14.3881	
41	-	-	3651	-	152.1011	37.4955	
42	-	-	3678	-	14.4977	45.2344	
43	-	-	3691	-	18.8965	8.4008	
44					13.1008	8.8562	
45					35.5681	95.0689	
46					94.7215	140.2953	
47					22.9092	35.1558	
48					0.2555	55.1727	
49					14.9976	109.5112	
50					10.6405	57.0187	

4.2.1 C-C VIBRATIONS

In all substituted benzenes, a group of four bands is usually observed in the region 1400-1650 cm^{-1} which represents the characteristic skeletal stretching modes of the semi-unsaturated carbon-carbon bands [9, 10]. Two degenerate vibrations, (1595cm^{-1}) and (1485cm^{-1}) of benzene are responsible for the appearance of these four bands [9, 10]. The

carbon variation (1310 cm^{-1}) mode of benzene which is known as Kekule mode occurs in the region 1240-1290 cm^{-1} (11). Hence the very strong bands at 1269 (KBr) / 1244 cm^{-1} (nujol) with Raman band at 1280 cm^{-1} have been identified as the component of mode.

4.2.2 C-X Vibrations

Some worker have assigned C-OH stretching modes around 1300 cm^{-1} in substituted benzene. Gupta et al [12] have assigned these mode at 1262 and 1265 cm^{-1} and 1270 cm^{-1} in hydroxyl methoxy benzeldehyde while Yadav et al [13] have assigned these mode at 1270 cm^{-1} in the identical compound. In the view of these assignments the band observed at 1295 cm^{-1} has been assigned to this mode. The (C-OH) in-plane bending modes have been assigned at 590 cm^{-1} in the compound 5B2H3MB.

4.2.3 C-H VIBRATIONS

Since the molecule under present study is a tetrasubstituted benzene, therefore only twohydrogen atoms are left around the ring. As such two C-H valence oscillations are expected in the region 3000–3100 cm^{-1} [12]. In this study, the bands observed at 3079 cm^{-1} (KBr), 3171 (KBr) have been taken to represent C-H stretching mode.

4.2.4 Group Vibrations

The aldehyde group gives rise to six vibrations, namely C=0 stretching, C=0 in plane bending, C=0 out-of-plane bending, C-H stretching, C-H in-plane bending and C-H out-of-plane bending vibrations. The C=0 stretching vibrations gives rise to a prominent absorption in the region 1680-1815 cm^{-1}. In the molecule presently studied, the strong band observed at 1667 cm^{-}1(KBr), 1664 cm^{-1} (nuzol) with the counter part of Raman band at 1700 cm^{-1} may be assigned to C=O stretching mode. The C-H planar bending mode of the CHO group is observed near 1250 cm^{-1} for benzaldehyde and its derivatives.[13, 14, 15]

4.3 THERMODYNAMIC PROPERTIES

Theoretical geometrical parameters represent a good approximation and they are the basis for calculating vibrational frequencies and thermodynamic parameters. The frequency calculations compute the zero point energies, thermal correction to internal energy and entropy as well as the heat capacity for a molecular system. These functions describe the thermodynamic stability of the system at the given conditions of pressure and temperature.

Zero-point correction = 0.136706

Thermal correction to Energy = 0.146547

Thermal correction to Enthalpy = 0.147491

Thermal correction to Gibbs Free Energy =0.099836

Sum of electronic and zero-point Energies = -3093.400966

Sum of electronic and thermal Energies = -3093.391125

Sum of electronic and thermal Enthalpies = -3093.390181

Sum of electronic and thermal Free Energies=-3093.437836

Thermo dynamical Constants

	E (Thermal)	CV	S
KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin	
Total	91.959	36.676	100.298
Electronic	0.000	0.000	0.000
Translational	0.889	2.981	42.200
Rotational	0.889	2.981	32.355
Vibrational	90.182	30.715	25.743
Vibration 1	0.599	1.966	4.039
Vibration 2	0.610	1.931	3.067
Vibration 3	0.616	1.911	2.768
Vibration 4	0.631	1.861	2.284
Vibration 5	0.635	1.850	2.198
Vibration 6	0.672	1.736	1.622
Vibration 7	0.686	1.694	1.480
Vibration 8	0.701	1.648	1.343
Vibration 9	0.735	1.554	1.121
Vibration 10	0.770	1.459	0.944
Vibration 11	0.814	1.347	0.777
Vibration 12	0.856	1.249	0.657
Vibration 13	0.872	1.213	0.618
Vibration 14	0.932	1.084	0.494

4.3.1 ELECTRIC MOMENTS

The dipole moment in a molecule is an important property that is mainly used to study the intermolecular interactions involving the non-bonded type dipole–dipole interactions, because higher the dipole moment, stronger will be the intermolecular interactions. In the absence of experimental data, the values of polarizability and hyperpolarizability calculated at the same level of theory and the same basis set for the compound 5B2H3MB, can provide a satisfactory comparison of these quantities.

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DIPOLE MOMENT POLARISABILITY AND HYPERPOLARISABILITY

TABLE-Calculated dipole moment (μ, in Debye), mean polarizabilit ($\bar{\alpha}$, in a.u.), anisotropy of polarizability ($\Delta\alpha$, in a.u.) and first hyperpolarizability (β, in a.u.) of 5B2H3MB by DFT by B3LYP/6-31G(d, p).

Table3

Dipole moment		Polarizability		Hyperpolarizability	
μx	2.5284	αxx	-94.4943	βxxx	115.7391
μy	2.8826	αyy	-67.3641	βyyy	18.9874
μz	1.5548	αzz	-83.0564	βzzz	1.1036
		αxy	-7.7200	βxxy	37.6428
		αxz	-3.6902	βxxz	10.0769
		αyz	2.8959	βxyy	28.4211
		α		βxyz	-6.9449
		α		βxzz	18.0309
				βyyz	9.0160
				βyzz	-2.0021

The component of dipole moment μ, polarizability α and the first hyperpolarizability β can be calculated by using the following equations

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

$\bar{\alpha} = 1/3(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$

$\Delta\alpha = 1/\sqrt{2}\{[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6\alpha^2_{xz}]\}^{1/2}$

First order polarizability $\beta = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{xxy} + \beta_{yzz})^2 + (\beta_{zzz} + \beta_{xxz} + \beta_{yyz})^2]^{1/2}$

Using these equations values comes out to be as follows....

$\mu = 4.1375$

$\bar{\alpha} = -81.6382$

$\Delta\alpha = 28.3141$

$\beta = 171.2027$

5. CONCLUSION

In the present work we have calculated the geometric parameters, the vibrational frequencies and NLO properties of 5-bromo-2-hydroxy-3-methoxy benzaldehyde by using Becke-3Lee-Yang-Parr (B3LYP) functional supplemented with the standard 6-31G (DP) basis and compared these values with the experimentally recorded FTIR, IR (KBr and nuzol) and Raman spectra. In general, a good agreement between experimental and calculated normal modes of vibrations have been observed. We also calculated thermodynamic properties as heat capacity, entropy, enthalpy and gibbs free energy of the titled compounds at different temperatures along with dipole moment, polarisability and hyper polarisability.

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