

Molecular Structure, Vibrational Spectral Studies and Nlo Properties of 5-Bromo-2, 4-Dimethoxy-Benzaldehyde by Dft

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Abstract: Benzaldehydes and its derivatives are the simplest in aromatic aldehydes and have wide range of use in different industries, they also exhibits different biological activities. Due to this reason there exist a vast field of study of substituted benzaldehydes. In the present study 5-bromo-2,4-dimethoxy benzaldehyde is taken for study. The spectral studies were performed for FTIR, IR (KBr and Nuzol) and Raman. 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 Gibb's free energy of the titled compounds at different temperatures were also calculated along with dipole moment, polarisability and hyperpolarisability.

KEYWORDS: 5-bromo-2,4-dimethoxy-benzaldehyde, vibrational, NLO, Gaussian 09 W, DFT/ B3LYP, thermodynamic parameters, FTIR, dipole moment, polarisability, hyper polarisability.

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I. Introduction

Spectroscopic studies of the benzaldehyde and their derivatives have been carried out as the vibrational spectra are very useful for understanding of specific biological activities and for the analysis of relatively complex system. Benzaldehydes have a large usage in different industries as perfumes, flavouring compounds, soaps, foods, preparations of some aniline dyes, solvent for oils etc.[1]. They have also shown anti tumour activity in mice [1,2]. In this light lots of aspects of substituted benzaldehydes and its derivatives are unexplored in spite of the fact that much work has been done on these compounds.[3-6].

II. Experimental

Spec-pure grade sample of 5-bromo-2,4-dimethoxy benzaldehyde (abbreviated and further mentioned as 5B2,4DMB) was 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.

III. Computational

All the calculations were carried out for 5B2,4DMB with Gaussian 03W program package [7] 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.

IV. Results And Discussion

4.1 Molecular Structure

The molecular structure of the mentioned compound 5B2,4DMB is shown in Figure 1. The optimized bond lengths, bond angles and dihedral angles of the compound is calculated by B3LYP method using B3LYP 6-311++G (d) and 6-311++G (D,P) basis sets are listed in Table 1 is in accordance with atom numbering scheme as shown in Fig. 1. Since the exact crystal structure of the compound 5B2,4DMB is not available till

now, the optimized structure can only be compared with other similar system [8] for which the crystal structures have been solved.



FIGURE 1

Calculated Optimized Geometrical Parameters of 5B2,4DMB, at B3LYP/6-31G(d,p): bond length (Å), bond angle(°), dihedral angles(°)

S. No	Atoms of molecule	Bond length (Å)	Angle between atoms (°)	Bond angle (°)	Dihedral angle between atoms (°)	Dihedral angle (°)
1.	R(1,2)	1.3952	A(2,1,6)	119.9985	D(6,1,2,3)	0.0323
2.	R(1,6)	1.3948	A(2,1,9)	119.9972	D(6,1,2,13)	179.9532
3.	R(1,9)	1.54	A(6,1,9)	120.0043	D(9,1,2,3)	-179.9729
4.	R(2,3)	1.3947	A(1,2,3)	120.0086	D(9,1,2,13)	-0.052
5.	R(2,13)	1.43	A(1,2,13)	119.9808	D(2,1,6,5)	0.0149
6.	R(3,4)	1.3954	A(3,2,13)	120.0106	D(2,1,6,8)	179.9892
7.	R(3,7)	1.0097	A(2,3,4)	119.9942	D(9,1,6,5)	-179.9798
8.	R(4,5)	1.3948	A(2,3,7)	120.0128	D(9,1,6,8)	-0.0056
9.	R(4,14)	1.43	A(4,3,7)	119.993	D(2,1,9,10)	-89.9606
10.	R(5,6)	1.3951	A(3,4,5)	119.994	D(2,1,9,11)	90.0394
11.	R(5,12)	1.91	A(3,4,14)	119.081	D(6,1,9,10)	90.0341
12.	R(6,8)	1.0096	A(5,4,14)	120.0249	D(6,1,9,11)	-89.9695
13.	R(9,10)	1.07	A(4,5,6)	120.0047	D(1,2,3,4)	-0.0568
14.	R(9,11)	1.2584	A(4,5,12)	120.0113	D(1,2,3,7)	179.9619
15.	R(13,15)	1.43	A(6,5,12)	119.984	D(13,2,3,4)	-179.9777
16.	R(14,19)	1.43	A(1,6,5)	120.0	D(13,2,3,7)	0.041
17.	R(15,16)	1.07	A(1,6,8)	120.008	D(1,2,13,15)	153.3156
18.	R(15,17)	1.07	A(5,6,8)	119.992	D(3,2,13,15)	-26.7635
19.	R(15,18)	1.07	A(1,9,10)	119.8865	D(2,3,4,5)	0.0341
20.	R(19,20)	1.07	A(1,9,11)	120.2269	D(2,3,4,14)	-179.9846
21.	R(19,21)	1.07	A(10,9,11)	119.8865	D(7,3,4,5)	-179.9846

22.	R(19,22)	1.07	A(2,13,15)	109.5	D(7,3,4,14)	-0.0151
23.			A(4,14,19)	109.5	D(3,4,5,6)	0.0131
24.			A(13,15,16)	109.4712	D(3,4,5,12)	-179.9995
25.			A(13,15,17)	109.4712	D(14,4,5,6)	-179.9563
26.			A(13,15,18)	109.4712	D(14,4,5,12)	0.0311
27.			A(16,15,17)	109.4713	D(3,4,14,19)	1.4301
28.			A(16,15,18)	109.4712	D(5,4,14,19)	-178.6004
29.			A(17,15,18)	109.4712	D(4,5,6,1)	-0.0376
30.			A(14,19,20)	109.4712	D(4,5,6,8)	179.9881
31.			A(14,19,21)	109.4712	D(12,5,6,1)	179.975
32.			A(14,19,22)	109.4712	D(12,5,6,8)	0.0007
33.			A(20,19,21)	109.4712	D(2,13,15,16)	71.9089
34.			A(20,19,22)	109.4712	D(2,13,15,17)	-168.0911
35.			A(21,19,22)	109.4712	D(2,13,15,18)	-48.0911
36.					D(4,14,19,20)	-59.765
37.					D(4,14,19,21)	60.2351
38.					D(4,14,19,22)	-179.765

Table 1

4.2 Vibrational Spectra

A detailed vibrational description has been carried out of the reported compound 5B2,4DMB 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 comparative chart is shown in Table 2 in which experimental values of IR (KBr and nuzol), FTIR and laser Raman are displayed and simultaneously compared with the calculated values , respective assignments are shown corresponding to the results.

S.No	EXPERIMENTAL FREQUENCIES				CALCULATED FREQUENCIES		ASSIGNMENTS
	FTIR	IR(KBr)	IR(nuzol)	RAMAN	IR	RAMAN ACTIVITY	
1.				100	0.1076	0.75	
2.				162	0.3101	0.75	
3.				219	0.0311	0.75	
4.				276	2.5693	0.7447	
5.				326	0.803	0.5641	
6.				380	0.3841	0.7499	
7.				405	0.7586	0.5131	
8.		466		478	0.8335	0.75	C-C out of plane bending
9.	512	506		519	2.3907	0.75	
10.		572		583	0.7331	0.75	C-Br bending
11.		620			5.1072	0.5712	
12.		670	669		0.4129	0.75	
13.	695.3	690	690	684	9.2782	0.1305	C-C in plane bending
14.		715	715	701	6.8724	0.175	
15.	837.9	841	841	862	0.2297	0.75	
16.		917	917	938	1.8089	0.7494	C-H in plane deformation mode
17.		961	960	970	2.9243	0.5958	
18.	1021.2	1021	1021	1024	0.2064	0.75	
19.		1052	1051		0.7031	0.5151	
20.	1153.6	1154	1154		4.5155	0.3612	C-H out of plane bending
21.		1177	1177	1189	23.2206	0.1734	
22.	1214.7	1215	1214	1231	0.8645	0.75	C-H out of plane bending
23.		1251	1251	1261	0.6858	0.75	
24.	1270.7	1274	1274		2.9957	0.5372	

25.		1322	1322		4.3634	0.544	
26.			1378		1.7045	0.75	
27.		1397	1396		2.815	0.75	
28.		1428	1428	1409	1.6846	0.5892	C-H in plane bending
29.		1445		1440	0.7973	0.1573	C-H in plane bending
30.		1470	1467	1453	5.2033	0.75	C-H in plane bending
31.		1488	1487	1550	3.9512	0.75	
32.		1593	1593	1600	10.2749	0.75	
33.				1604	1.7486	0.75	
34.				1615	4.704	0.1037	
35.	1667.9	1666	1665	1673	17.5956	0.6052	C-C stretching, C=O stretching
36.				1775	3.6417	0.384	
37.		2597			7.0372	0.5089	
38.		2878	2855	2891	18.6136	0.2003	C-H stretching
39.		2949	2923	2962	15.4555	0.2961	
40.		2981		2998	9.9079	0.3321	C-H stretching
41.		3005		3018	12.4998	0.4228	C-H stretching
42.		3042		3035	0.4359	0.6507	
43.		3103	3101		19.8222	0.5525	
44.	3445	3413			1.7862	0.241	C-H stretching
45.			3584		33.6653	0.75	
46.				4025	34.5508	0.75	
47.					18.2149	0.5365	
48.					32.6717	0.7495	
49.					9.3007	0.2513	
50.					169.4777	0.5595	
51.					77.4981	0.2659	
52.					118.9312	0.3242	
53.					29.2611	0.091	
54.					202.7541	0.0212	
55.					36.8128	0.75	
56.					62.6705	0.75	
57.					110.1906	0.5065	
58.					117.8208	0.4838	
59.					42.3009	0.2514	
60.					61.6808	0.2083	

Table 2

4.3 Vibrational Analysis

4.3.1 C-Br vibrations

Most aromatic bromo compounds absorb strongly in the region 650–395 cm^{-1} due to C-Br stretching vibrations. The C-Br stretching vibration is assigned to the weak mode 620 cm^{-1} in the infrared spectra. The in-plane C-Br bending mode is observed at 572 cm^{-1} , while the out-of-plane bending mode is at 162 cm^{-1} in Raman spectrum.

4.3.2 C-C vibrations

The ring C=C and C-C stretching vibrations, known as semicircle stretching usually occur in the region 1400–1625 cm^{-1} [9,10]. Hence in the present investigation, the FTIR bands identified at 1667.9 cm^{-1} and the Raman bands at 1673, 1615, 1604 and 1600 cm^{-1} are assigned to C-C stretching vibrations of 5B2,4DMB. The band ascribed at 695.3 cm^{-1} in FTIR and 478 cm^{-1} in Raman spectra has been designated to C-C in-plane and out-of-plane bending mode respectively. These values are in agreement with the literature values.

4.3.3 Aldehyde group vibrations

The C-H stretching vibrations of the aldehyde group usually appear in the region 2871–2806 cm^{-1} [11]. These are observed 2891 cm^{-1} in Raman and 2878 cm^{-1} in IR (KBr) 2855 cm^{-1} in IR (nuzol) is in agreement with the literature values. The in-plane C-H deformation mode of aldehyde group is observed at 938 cm^{-1} with strong intensity in FTIR spectrum. The carbonyl C=O stretching vibrations in the substituted benzaldehydes are reported near 1700 cm^{-1} [11]. The very strong band centered 1667.9 cm^{-1} in FTIR, 1666 cm^{-1} in IR (KBr) and 1665 (nuzol) and 1673 cm^{-1} in Raman for 5B2H3MB is attributed to C=O stretching vibration of the aldehyde group. A weak-to-medium intensity band due to the aldehyde group CHO deformation vibration is found in the region 975–780 cm^{-1} [12]. In agreement with this, the bands at 938 cm^{-1} in Raman and 917 cm^{-1} could be assigned to CHO out-of-plane deformation for 5B2,4DMB.

4.3.4 C-H Vibrations

The modes of vibrations of aromatic compounds are considered as separate C-H or ring C-C vibrations. According to the literature in infrared spectra, most mononuclear and polynuclear aromatic compounds have three or four peaks in the region 3000–3100 cm^{-1} , these are due to the stretching vibrations of the ring CH bands. [11,13] In the present case of 5B2,4DMB, the FTIR bands identified at 3445 cm^{-1} and Raman bands at 3035, 3018 and 2998 cm^{-1} are assigned to C–H stretching vibrations of 5B2,4DMB. The IR bands at 1470 cm^{-1} in (KBr), and 1467 cm^{-1} in (nuzol) and the Raman bands at 1440 and 1409 cm^{-1} are assigned to C-H in-plane bending vibration of the mentioned compound. The C-H out-of-plane bending vibrations of the 5B2,4DMB are well identified at 1214.7, and 1153.6 cm^{-1} in the FTIR and 1231 cm^{-1} in the Raman which are in fair agreement with the characteristic values. These values shows fair agreement with the computed values shown in figure 2.

IR spectrum and Raman activity plots as obtained by Gaussian 09W program package using the Becke-3Lee-Yang-Parr (B3LYP) functional supplemented with the standard 6-31G (DP)

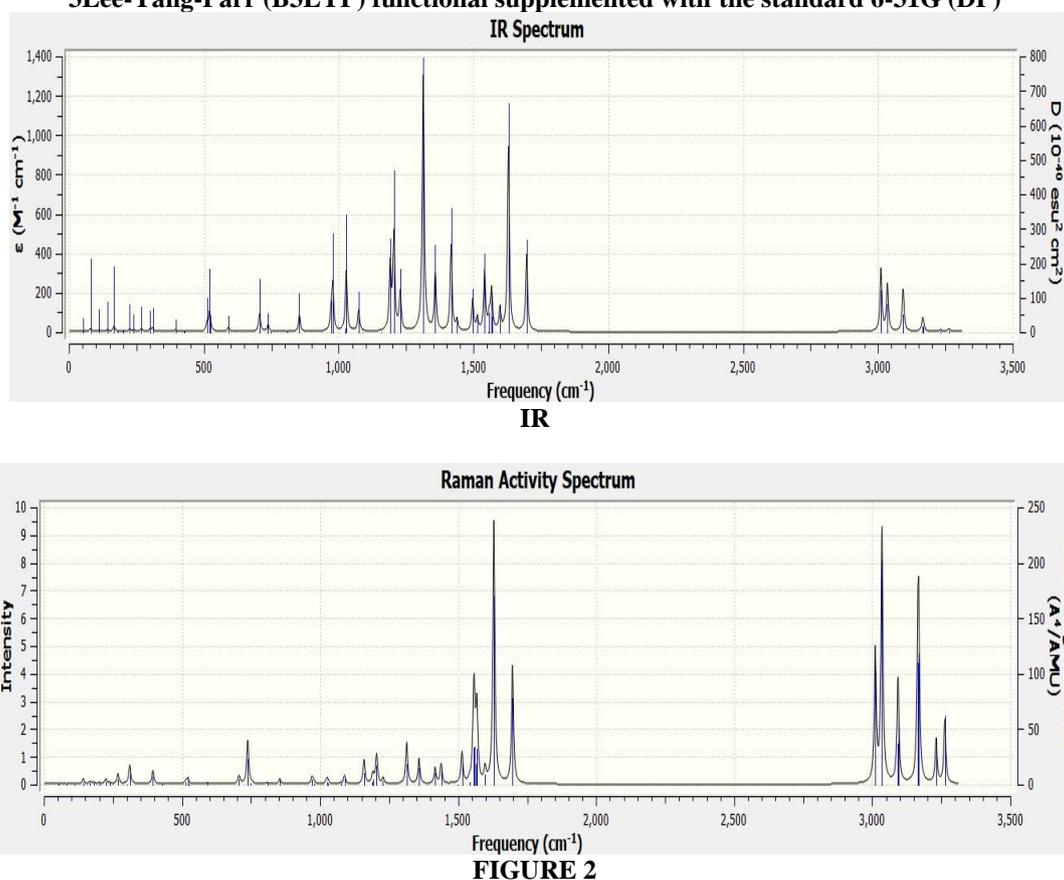


FIGURE 2

4.4 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	=	0.166752 (Hartree/Particle)
Thermal correction to Energy	=	0.176255
Thermal correction to Enthalpy	=	0.177199
Thermal correction to Gibbs Free Energy	=	0.130323
Sum of electronic and zero-point Energies	=	-3132.450803
Sum of electronic and thermal Energies	=	-3132.441300
Sum of electronic and thermal Enthalpies	=	-3132.440356

Sum of electronic and thermal Free Energies= -3132.48723

Thermo dynamical Constants

	E (Thermal) Kcal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	110.602	36.393	98.66
Electronic	0	0	0
Translational	0.889	2.981	42.377
Rotational	0.889	2.981	32.632
Vibrational	108.824	30.432	23.651
Vibration 1	0.612	1.924	2.96
Vibration 2	0.614	1.915	2.833
Vibration 3	0.619	1.899	2.63
Vibration 4	0.623	1.888	2.512
Vibration 5	0.636	1.846	2.176
Vibration 6	0.682	1.703	1.509
Vibration 7	0.7	1.651	1.353
Vibration 8	0.713	1.614	1.255
Vibration 9	0.768	1.465	0.954
Vibration 10	0.777	1.441	0.914
Vibration 11	0.856	1.248	0.656
Vibration 12	0.88	1.193	0.597
Vibration 13	0.911	1.127	0.532
Vibration	0.94	1.068	0.48

Table 3

4.5 Electric Moment

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 5B2,4DMB, can provide a satisfactory comparison of these quantities.

Calculated dipole moment (μ , in Debye), mean polarizability ($\bar{\alpha}$, in a.u.), anisotropy of polarizability ($\Delta\alpha$, in a.u.) and first hyperpolarizability (β , in a.u.) of 5B2,4DMB by DFT by B3LYP/6-31G(d,p).

Dipole moment	Polarizability		Hyperpolarizability		
μ_x	0.8768	α_{xx}	-92.6864	β_{xxx}	-78.9399
μ_y	4.2349	α_{yy}	-76.0750	β_{yyy}	35.3548
μ_z	-2.2494	α_{zz}	-90.2719	β_{zzz}	-0.2383
		α_{xy}	11.8995	β_{xyy}	-30.8455
		α_{xz}	-7.3200	β_{xxy}	26.7940
		α_{yz}	5.4524	β_{xxz}	-23.2411
				β_{xzz}	-24.5166
				β_{yzz}	-2.9695
				β_{yyz}	-12.2392
				β_{xyz}	10.6031

Table 4

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

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

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

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

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

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

$$\mu = 4.8747$$

$$\bar{\alpha} = -86.3444$$

$$\Delta\alpha = 17.9389$$

$$\beta = 151.0464$$

V. Conclusion

In the present work we have calculated the geometric parameters, the vibrational frequencies and NLO properties of 5-bromo-2,4-dimethoxy 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 Gibb's free energy of the titled compounds at different temperatures along with dipole moment, polarisability and hyperpolarisability .

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