

Comparative Analysis of Molecular Structure, Vibrational Spectral Studies and Nlo Properties of 3-Hydroxy-4-methoxy-Benzaldehyde and 4-Hydroxy-3-Methoxy-Benzaldehyde by DFT

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ABSTRACT

Benzaldehyde is best known as being artificial essential oil of almond and it has many other uses such as; the manufacturing of dyes, perfumes, flavourings, cinnamic and mandelic acids, and it is also used as a solvent. Some more recent developments in the use of benzaldehyde are for the health and agriculture industries. Due to these basic reasons there exist a vast field of study of substituted benzaldehydes. In the present study a comparative analysis is done between 3-hydroxy-4-methoxy-benzaldehyde and 4-hydroxy-3-methoxy-benzaldehyde. 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 : 3-hydroxy-4-methoxy-benzaldehyde , 4-hydroxy-3-methoxy-benzaldehyde, vibrational spectral , NLO, Gaussian 09W, DFT/ B3LYP ,thermodynamic parameters, FTIR, dipole moment, polarisability, hyperpolarisability.

I. INTRODUCTION

Benzaldehydes and its derivatives are one of the the simplest in aromatic aldehydes and is known as artificial essential oil of almond it has many other uses such as in manufacturing of dyes, perfumes, flavorings, cinnamic and mandelic acids, and it is also used as a solvent[1]. It is synthesized in laboratories from toluene being chlorinated to benzyl chloride or by direct oxidation of toluene with manganese dioxide. Some more recent developments in the use of benzaldehyde are for the health and agriculture industries. Benzaldehyde is being used as a pesticide

and also as an anticancer agent and have shown anti tumour activity in mice.[1,2] It is used as a bee repellent in the harvesting of honey. These uses are still in development but would be very helpful in solving some of these problems of today. The benzaldehyde and its derivatives have received attention because of their chemical and biological importance. The benzaldehyde and substituted benzaldehydes have been subjected to various spectroscopic studies [3-7]. In this light a comparative study is carries out on different aspects of 3-hydroxy-4-methoxy-benzaldehyde (abbreviated and further mentioned as 3,4HMB) and 4-hydroxy-3-methoxy-

benzaldehyde (abbreviated and further mentioned as 4,3HMB).

II. EXPERIMENTAL

Spec-pure grade sample of 3,4HMB and 4,3HMB 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 BMB with Gaussian 03W program package [8] using the Becke-3Lee-Yang-Parr (B3LYP) functional supplemented with the standard 6-31G(DP) 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

A. MOLECULAR STRUCTURE

The molecular structures of the mentioned compounds 3,4HMB and 4,3HMB are shown in

Figure 1 and 2 respectively. The optimized bond lengths, bond angles and dihedral angles of the compounds are calculated by B3LYP method using B3LYP 6-311++G (d) and 6-311++G (D,P) basis sets are listed in Table 1 and 2 respectively and are in accordance with atom numbering scheme as shown in Fig. 1 and 2. Since the exact crystal structures of the reported compounds are not available, the optimized structure can only be compared with other similar system for which the crystal structures have been solved. [9]

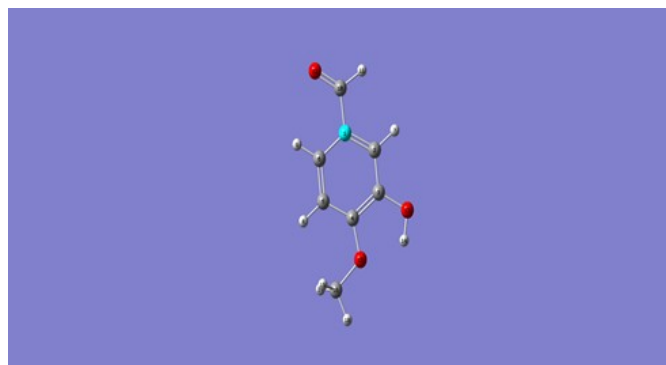


Figure 1. Molecular structure of 3,4HMB

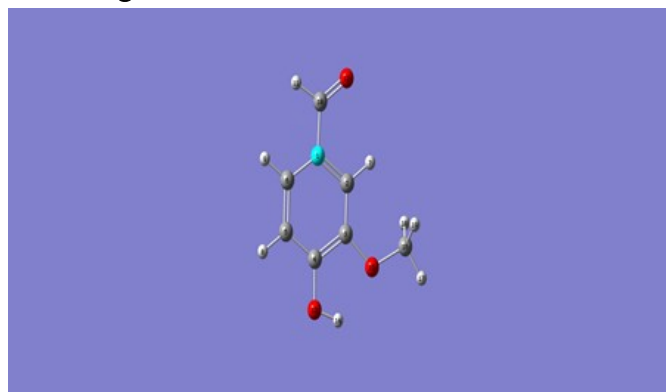


Figure 2. Molecular structure of 4,3HMB

TABLE 1
CALCULATED OPTIMIZED GEOMETRICAL
PARAMETERS OF 3,4HMB, AT B3LYP/6-31G(D,P):
BOND LENGTH (\AA), BOND ANGLE($^\circ$), DIHEDRAL
ANGLES($^\circ$)

S. No	Atoms of molecule	Bond length (\AA)	Angle between atoms ($^\circ$)	Bond angle ($^\circ$)	Dihedral angle between atoms ($^\circ$)	Dihedral angle ($^\circ$)
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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(2,1,10)	119.9972	D(6,1,2,7)	179.9532
3.	R(1,10)	1.54	A(6,1,10)	120.0043	D(10,1,2,3)	-179.9729
4.	R(2,3)	1.3947	A(1,2,3)	120.0086	D(10,1,2,7)	-0.052
5.	R(2,7)	0.0097	A(1,2,7)	119.9808	D(2,1,6,5)	0.0149
6.	R(3,4)	1.39	A(3,2,7)	120.01	D(2,1,6,9)	179.98

		54		06		92
7.	R(3,13)	1.43	A(2,3,4)	119.9942	D(10,1,6,5)	-179.9798
8.	R(4,5)	1.3948	A(2,3,13)	120.0128	D(10,1,6,9)	-0.0056
9.	R(4,15)	1.43	A(4,3,13)	119.993	D(2,1,10,1)	-89.9606
10.	R(5,6)	1.3951	A(3,4,5)	119.994	D(2,1,10,1)	90.0394
11.	R(5,8)	1.0998	A(3,4,15)	119.9811	D(6,1,10,1)	90.0341
12.	R(6,9)	1.0996	A(5,4,15)	120.0249	D(6,1,10,1)	-89.9659
13.	R(10,1)	1.07	A(4,5,6)	120.0047	D(1,2,3,4)	-0.0568
14.	R(10,1)	1.2584	A(4,5,8)	120.0113	D(1,2,3,13)	179.9619
15.	R(13,1)	0.96	A(6,5,8)	119.984	D(7,2,3,4)	-179.9777
16.	R(15,1)	1.43	A(1,6,5)	120.00	D(7,2,3,13)	0.041
17.	R(16,1)	1.07	A(1,6,9)	120.008	D(2,3,4,5)	0.0341
18.	R(16,1)	1.07	A(5,6,9)	119.992	D(2,3,4,15)	-179.9964
19.	R(16,1)	1.07	A(1,10,1)	119.8865	D(13,3,4,5)	-179.9846
20.			A(1,10,1)	120.2269	D(13,3,4,1)	-0.0151
21.			A(11,10,12)	119.8865	D(2,3,13,1)	115.343
22.			A(3,13,14)	109.5	D(4,3,13,1)	-64.6385
23.			A(4,15,16)	109.5	D(3,4,5,6)	0.0131
24.			A(15,16,17)	109.4712	D(3,4,5,8)	-179.9995
25.			A(15,16,18)	109.4712	D(15,4,5,6)	-179.9563
26.			A(15,16,19)	109.4712	D(15,4,5,8)	0.0311

27.			A(17,16,18)	109.4713	D(3,4,15,1)	151.2896
28.			A(17,16,19)	109.4712	D(5,4,15,1)	-28.7409
29.			A(18,16,19)	109.4712	D(4,5,6,1)	-0.0376
30.					D(4,5,6,9)	179.9881
31.					D(8,5,6,1)	-0.0376
32.					D(8,5,6,9)	.0007
33.					D(4,15,16,17)	73.033
34.					D(4,15,16,18)	-166.967
35.					D(4,15,16,19)	-46.967

TABLE 2
CALCULATED OPTIMIZED GEOMETRICAL
PARAMETERS OF 4,3HMB, 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)	1.3958	A(2,1,6)	119.9985	D(6,1,2,3)	0.0323
2.	R(1,6)	1.3948	A(2,1,10)	119.9972	D(6,1,2,7)	179.9532
3.	R(1,10)	1.54	A(6,1,10)	120.0043	D(10,1,2,3)	-179.9729
4.	R(2,3)	1.3947	A(1,2,3)	120.0086	D(10,1,2,7)	-0.052
5.	R(2,7)	1.0997	A(1,2,7)	119.9808	D(2,1,6,5)	0.0149
6.	R(3,4)	1.3	A(3,2,7)	120.0	D(2,1,6,5)	179.9

)	954)	106	9)	892
7.	R(3,1 5)	1.4 3	A(2,3,4)	119.9 942	D(10,1, 6,5)	- 179.9 798
8.	R(4,5)	1.3 948	A(2,3,1 5)	120.0 128	D(10,1, 6,9)	- 0.005 6
9.	R(4,1 3)	1.4 3	A(4,3,1 5)	119.9 93	D(2,1,1 0,11)	- 89.96 06
10.	R(5,6)	1.3 951	A(3,4,5)	119.9 94	D(2,1,1 0,12)	90.03 94
11.	R(5,8)	1.0 998	A(3,4,1 3)	119.9 811	D(6,1,1 0,11)	90.03 41
12.	R(6,9)	1.0 996	A(5,4,1 3)	120.0 249	D(6,1,1 0,12)	- 89.96 54
13.	R(10, 11)	1.0 7	A(4,5,6)	120.0 047	D(1,2,3, 4)	- 0.056 8
14.	R(10, 12)	1.2 584	A(4,5,8)	120.0 113	D(1,2,3, 15)	179.9 619
15.	R(13, 14)	0.9 6	A(6,5,8)	119.9 84	D(7,2,3, 4)	- 179.9 777
16.	R(15, 16)	1.4 3	A(1,6,5)	120.0 0	D(7,2,3, 15)	0.041
17.	R(16, 17)	1.0 7	A(1,6,9)	120.0 08	D(2,3,4, 5)	0.034 1
18.	R(16, 18)	1.0 7	A(5,6,9)	119.9 92	D(2,3,4, 13)	- 179.9 964
19.	R(16, 19)	1.0 7	A(1,10, 11)	119.8 865	D(15,3, 4,5)	- 179.9 846
20.			A(1,10, 12)	120.2 269	D(15,3, 4,13)	- 0.015 1
21.			A(11,1 0,12)	119.8 865	D(2,3,1 5,16)	57.69 45
22.			A(4,13,)	109.5	D(4,3,1)	-

2.			14)		5,16)	122.2 868
2.			A(3,15, 16)	109.5	D(3,4,5, 6)	0.013 1
2.			A(15,1 6,17)	109.4 712	D(3,4,5, 8)	- 179.9 95
2.			A(15,1 6,18)	109.4 712	D(13,4, 5,6)	- 179.9 563
2.			A(15,1 6,19)	109.4 712	D(13,4, 5,8)	0.031 1
2.			A(17,1 6,18)	109.4 713	D(3,4,1 3,14)	90.11 78
2.			A(17,1 6,19)	109.4 712	D(5,4,1 3,14)	90.11 78
2.			A(18,1 6,19)	109.4 712	D(4,5,6, 1)	- 0.037 6
3.					D(4,5,6, 9)	179.9 881
3.					D(8,5,6, 1)	179.9 75
3.					D(8,5,6, 9)	.0007
3.					D(3,15, 16,17)	158.2 443
3.					D(3,15, 16,18)	- 81.75 59
3.					D(3,15, 16,19)	38.24 43

The calculated optimised geometrical parameters i.e bond length, bond angle and dihedral angles of both the reported compounds are similar to a greater extent with slight variations thus we can conclude that mere exchanging the positions of the functional groups does not affect the geometries of the compounds very significantly.

B. VIBRATIONAL SPECTRA

A detailed study of vibrational spectra has been carried out of the reported compounds and the 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 3 in which experimental values of IR (KBr and nuzol), FTIR and laser Raman are displayed and simultaneously compared with the calculated values (scaled and unscaled)

TABLE 3. EXPERIMENTAL AND CALCULATED VALUES OF FREQUENCIES FOR 3,4HMB

S.No.	Experimental Frequencies				Calculated Frequencies			
	FTIR	Raman	IR(kbr)	IR(nuzol)	unscaled	scaled	IR intensities	Raman activity
1		50						
2		72			74.62	70.14	2.9333	1.4341
3					119.63	112.63	6.8262	0.6420
4					166.25	156.25	7.6612	0.5780
5					174.38	163.91	0.4465	3.0202
6					224.59	211.11	0.0189	0.4937
7					229.68	215.68	0.7669	0.0747
8					339.70	319.31	5.8455	6.0849
9		362			378.17	355.47	2.4019	0.9649
10					386.49	363.30	3.8944	6.881
11		431						
12		484			479.04	450.29	22.0886	0.0844
13		515	504		508.39	477.88	12.2997	3.7435
14					554.93	521.63	121.7148	4.1262

15		603	589		597.02	561.19	6.9926	5.7959
16	634.2	649	636	636	632.35	594.40	6.8335	0.3562
17			682	678	647.69	608.82	31.4670	0.7632
18		746	731	730				
19		774	759	759	758.33	712.83	11.0268	15.5836
20					789.70	742.31	0.0984	0.9191
21		809	793	792	806.79	758.39	53.8394	11.4865
22	837.9		831	831				
23		881	867	867	874	821.56	56.3066	2.5884
24					936	879.84	19.7455	1.2968
25		976	966	966	968.35	910.24	19.9125	3.9391
26	1021.2		1023	1023	1016	955.04	1.6738	0.5428
27					1033.5	971.49	74.9363	3.2715
28					1074	1009.56	1.2251	8.4373
29	1123.1	1129.0	1121	1121	1140	1071.6	132.5518	15.5920
30					1165.62	1095.68	0.0004	7.2083
31		1192	1169	1168	1185.91	1114.75	0.0834	2.0079
32					1199.	1127.	28.098	4.2784

					27	31	2	
33		12 31	12 19	121 7	1243	1168. 42	79.674 3	2.6684
34		12 50	12 47	124 6				
35	1 2 7 5 .8				1270. 95	1194. 69	115.07 06	3.9886
36								
37		12 92	13 02	130 2	1298	1220. 12	328.42 14	30.8505
38		13 58	13 44	134 3	1345	1264. 3	19.903 9	4.5991
39		14 07		137 7	1378. 63	1295. 91	77.827 5	26.5776
40			14 46	144 6	1447. 59	1360. 73	11.994 1	14.1129
41		14 57	14 49	146 0				
42					1501. 46	1411. 37	31.180 6	5.0581
43	1 5 2 0 .2	15 27	15 13	151 1	1517. 41	1426. 36	9.5105	18.0896
44					1555. 01	1461. 70	10.265 5	35.0992
45		15 92	15 79	157 8	1571. 8	1477. 49	12.407 4	17.9563
46		16 21	16 08	160 7	1608. 39	1511. 88	66.303 8	175.906 4
47	1 6 7 8 .1	16 85	16 73	167 3	1649. 74	1550. 75	66.303 8	175.956 3
48			17 59	175 3	1715. 70	1612. 75	125.51 59	66.7046
49			19 12	191 2				
50		18 25						
51		20	20					

		50	39					
52			23 46					
53		25 00						
54	2 8 4 4 .1		28 47	285 5				
55		29 00	28 67		2915. 82	2740. 87	150.92 06	135.457 3
56	2 9 4 0 .9		29 37	292 6				
57			29 76					
58		30 31	30 03		3040. 44	2858. 01	36.459 1	116.454 8
59					3099. 72	2913. 73	29.512 8	53.6200
60					3163. 66	2973. 84	13.585 5	110.996 2
61	3 2 4 6 .4		32 21	321 4	3219. 23	3026. 07	1.6428	41.0935
62					3233. 28	3039. 28	6.4016	101.907 7
63		35 00	35 50	355 4	3448. 00	3241. 12	71.012 2	72.1404

TABLE 4. EXPERIMENTAL AND CALCULATED VALUES OF FREQUENCIES FOR 4,3 HMB

S.No.	Experimental Frequencies				Calculated Frequencies			
	FT IR	Raman	IR(kbr)	IR(nuzol)	unscaled	scaled	IR intensities	Raman activity
1.		40						
2.		54						
3.		84			76.0	71.	10.0	1.93

					9	52	920	91
4.		11			114.	107	0.08	0.64
		0			23	.37	99	81
5.					149.	140	9.19	1.42
					03	.08	20	51
6.		19			188.	176	0.03	2.03
		5			00	.72	40	80
7.		22			227.	214	5.25	0.76
		4			74	.07	75	34
8.					236.	221	4.17	0.46
					07	.90	10	84
9.					258.	242	0.12	2.04
					46	.95	95	76
10.		37			331.	311	3.59	2.21
		3			12	.25	35	86
11.		44			422.	397	0.39	8.63
		2			81	.44	84	41
12.					495.	465	11.1	0.37
					66	.92	824	43
13.		52	517					
		9						
14.			536		543.	510	6.33	3.06
					38	.77	11	17
15.					555.	522	4.44	4.04
					62	.27	24	49
16.					600.	564	136.	3.72
					62	.58	9021	60
17.					628.	590	11.6	0.83
					46	.75	012	79
18.			642	641	638.	599	43.6	6.59
					24	.94	194	96
19.	72	73	720	720				
	5.9	2						
20.			738	737	745.	700	41.0	11.8
					71	.96	098	377
21.			764	763				
22.			782	782	797.	749	0.15	0.66
					10	.27	73	33
23.					831.	781	1.07	12.3
					15	.28	24	040
24.		85	839	839	867.	815	46.9	1.42
		2			52	.46	106	63
25.			896	896				
26.	96		949	948	961.	904	6.13	2.03
	0.1				87	.15	50	29
27.					967.	909	18.7	3.63
					87	.79	571	03
28.					100	941	8.89	1.01
					1.73	.62	24	63

29.						104	983	60.1	7.18
						6.53	.73	196	48
30.	10	11	107	1071	107	100	1.65	6.87	
	82.	06	1		2.23	7.8	84	41	
	3					9			
31.					115	108	51.3	1.15	
					6.18	6.8	916	58	
						0			
32.			116	1165	116	109	0.00	6.56	
			5		6.08	6.1	07	48	
						1			
33.			118	1183	117	110	69.7	2.14	
			3		3.21	2.8	627	88	
						1			
34.		11			119	112	51.3	7.06	
		99			7.21	5.3	097	60	
						7			
35.			121	1218					
			9						
36.	12	12	126	1258	124	116	220.	20.3	
	65.	32	1		3.00	8.4	9489	670	
	6					2			
37.					127	119	58.0	6.89	
					3.71	7.2	048	77	
						8			
38.					129	121	216.	10.2	
					6.95	9.1	2342	144	
						3			
39.		13	132	1326	134	125	6.52	5.67	
		38	7		0.01	9.6	74	30	
						0			
40.		13	139	1378					
		86	0						
41.			143		142	134	6.89	5.71	
			5		7.72	2.0	19	03	
						5			
42.			145	1456	145	136	60.1	15.3	
			6		3.90	6.6	646	699	
						6			
43.	14	14	147		148	139	112.	16.6	
	64.	71	1		4.23	5.1	4672	781	
	2					7			
44.		14	151		151	141	4.81	9.35	
		81	0		0.26	9.6	32	39	
						4			
45.			154		154	145	135.	2.79	
			4		4.73	2.0	8861	37	
						4			
46.			156		155	145	10.1	31.6	
			2		2.26	9.1	285	183	

						2		
47.			1590	1589	1571.70	1477.39	8.8578	12.7912
48.					1632.74	1534.77	41.0711	41.7298
49.	1662.8	1655	1640	1640	1638.31	1540.01	107.4711	126.5533
50.			1719		1705.89	1603.53	125.0929	71.9202
51.			1736	1736				
52.			1784	1784				
53.			1857	1846				
54.			1911	1910				
55.			2018					
56.	2200							
57.			2346					
58.	2700			2726				
59.			2840	2857				
60.			2885		2918.31	2743.21	150.4067	144.4872
61.				2927				
62.			2941					
63.			2974					
64.			3016		3040.66	2858.22	29.4820	101.7137
65.			3070		3099.70	2913.71	28.5136	41.9535
66.					3163.26	2973.46	14.2012	102.5977
67.					319	300	5.03	65.2

					4.45	2.78	44	424
68.					3228.82	3035.09	4.6281	23.6939
69.					3278.41	3081.70	3.1893	140.3698
70.	3429.7		3413	3435	3423.02	3217.63	104.1555	115.8013
71.		4000						

B.I C – C vibrations

The bands in the range 1400-1650 cm-1 are generally assigned to C-C stretching mode .[10] The bands of variable intensity are generally observed at 1625-1590 cm-1, 1590- 1575cm-1, 1540-1470cm-1, 1465- 1430cm-1 and 1380-1280cm-1 from the frequency ranges given by Varsanyi.[11] The bands at 1579 (KBr) /1578(nuzol)/1592 cm-1 Raman for 3,4-HMB and 1590(KBr)/1589(nuzol)/1481 cm-1 Raman for 4,3-HMB have been clearly identified as the components of e1u(1595 cm-1)mode of benzene. The components of e2g(1485 cm-1) mode of benzene have been assigned at 1460 cm-1 for 3,4-HMB and 1464 cm-1 for 4,3-HMB. These values are in fair agreement with the calculated values.

B.II C-H VIBRATIONS

In the high frequency region the bands observed at 2926cm-1 (nujol) for 3,4-HMB and 2927 cm-1 (nujol) for 4,3-HMB with the counterpart of Raman band at 3031 cm-1 and 2700 cm-1 respectively and 3003cm-1 (KBr) and 2845 cm-1 (KBr) have been identified as ring stretching modes and well lie in the region predicted by Bellamy[12] for this mode. The C-H in-plane bending frequency and out-of-plane bending modes lie in the region 1225-950 cm-1 and 950-650 cm-1 respectively[12]. In view of the above, the bands observed at 1023 cm-1 (nujol)/ 1023 cm-1 (KBr) for 3,4-HMB and 1071 cm-1(nujol)/

1071 cm⁻¹ (KBr) for 4,3-HMB and very strong Raman band observed at 1129 cm⁻¹ for 3,4-HMB and 1106 cm⁻¹ for 4,3-HMB respectively have been assigned as C-H i.p.b. mode while the bands observed at 831 cm⁻¹ (KBr)/ 831 cm⁻¹ (nuzol) for 3,4-HMB and 839 cm⁻¹ (KBr)/839 cm⁻¹ (nuzol) for 4,3-HMB respectively and strong band at 809 cm⁻¹ for 3,4-HMB and 852 cm⁻¹ for 4,3-HMB respectively in Raman have been identified as C-H o.p.b. mode.

B.III Aldehyde group vibrations

The C-H stretching vibrations of the aldehyde group usually appear in the region 2871–2806 cm⁻¹ [13]. The bands at 2900 cm⁻¹ for Raman and 2937 cm⁻¹(KBr)/ 2926 cm⁻¹(nuzol) for IR are assigned to aldehyde group vibrations and shows close proximity with the calculated value which is 2915.82 cm⁻¹ for 3,4HMB whereas the bands at 2700 cm⁻¹ at Raman and 2840 cm⁻¹(KBr)/ 2857 cm⁻¹ (nuzol) for IR are assigned for this group vibration which corresponds to 2918.31 cm⁻¹ for the calculated value for 4,3HMB.

C. 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. The first set and table 4 represents the thermal functions for 3,4HMB and second set and table 5 for 4,3HMB respectively.

Zero-point correction = 0.147490 (Hartree/Particle)

Thermal correction to Energy = 0.157263

Thermal correction to Enthalpy = 0.158207

Thermal correction to Gibbs Free Energy = 0.112288

Sum of electronic and zero-point Energies = -532.220615

Sum of electronic and thermal Energies = -532.210842

Sum of electronic and thermal Enthalpies = -532.209898

Sum of electronic and thermal Free Energies = -532.255817

TABLE 4

	E (Thermal) KCal/Mol	CV Cal/Mol- Kelvin	S Cal/Mol- Kelvin
Total	98.684	36.723	96.644
Electronic	0.000	0.000	0.000
Translational	0.889	2.981	40.967
Rotational	0.889	2.981	30.327
Vibrational	96.907	30.762	25.350
Vibration 1	0.599	1.966	4.028
Vibration 2	0.609	1.933	3.106
Vibration 3	0.624	1.884	2.477
Vibration 4	0.627	1.874	2.388
Vibration 5	0.649	1.804	1.922
Vibration 6	0.652	1.796	1.881
Vibration 7	0.686	1.693	1.477
Vibration 8	0.720	1.596	1.214
Vibration 9	0.748	1.517	1.046
Vibration 10	0.755	1.499	1.014
Vibration 11	0.835	1.297	0.713
Vibration 12	0.864	1.231	0.637
Vibration 13	0.910	1.129	0.534
Vibration 14	0.955	1.038	0.455

Zero-point correction = 0.147724 (Hartree/Particle)

Thermal correction to Energy = 0.157447

Thermal correction to Enthalpy = 0.158391

Thermal correction to Gibbs Free Energy = 0.112495

Sum of electronic and zero-point Energies = -
532.223477

Sum of electronic and thermal Energies = -
532.213754

Sum of electronic and thermal Enthalpies = -
532.212810

Sum of electronic and thermal Free Energies = -
532.258706

TABLE 5

	E (Thermal) KCal/Mol	CV Cal/Mol- Kelvin	S Cal/Mol- Kelvin
Total	98.799	36.492	96.597
Electronic	0.000	0.000	0.000
Translational	0.889	2.981	40.967
Rotational	0.889	2.981	30.361
Vibrational	97.022	30.531	25.268
Vibration 1	0.599	1.965	3.989
Vibration 2	0.607	1.938	3.196
Vibration 3	0.618	1.904	2.684
Vibration 4	0.633	1.856	2.247
Vibration 5	0.651	1.799	1.897
Vibration 6	0.655	1.786	1.832
Vibration 7	0.667	1.748	1.672
Vibration 8	0.713	1.613	1.255
Vibration 9	0.768	1.464	0.952
Vibration 10	0.785	1.421	0.882
Vibration 11	0.851	1.260	0.669
Vibration 12	0.899	1.154	0.558
Vibration 13	0.911	1.127	0.533
Vibration 14	0.959	1.030	0.449

D. 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, as we know that 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 compounds 3,4BMB and 4,3HMB can provide a satisfactory comparison of these quantities.

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

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

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

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

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

So the table 6 represents the values of dipole moment, polarizability and hyperpolarizability for 3,4HMB and table 7 for 4,3HMB respectively.

TABLE 6

Dipole moment		Polarizability		Hyperpolarizability	
μ_x	5.0370	α_{xx}	-63.0787	β_{xxx}	111.2712
μ_y	-1.2685	α_{yy}	-61.2540	β_{yyy}	-14.3230
μ_z	-0.0008	α_{zz}	-65.6852	β_{zzz}	-0.0015
		α_{xy}	-11.4386	β_{xyy}	9.2691
		α_{xz}	-0.0038	β_{xxy}	15.2291
		α_{yz}	0.0002	β_{xxx}	-0.0099
				β_{xzz}	2.7672
				β_{yzz}	1.0604

				β_{yyz}	0.0018
				β_{xyz}	0.0038

$$\Delta\alpha = 3.8573$$

$$\Delta\alpha = 9.4161$$

$$\beta = 133.3220$$

$$\beta = 66.5344$$

TABLE 7

Dipole moment		Polarizability		Hyperpolarizability	
μ_x	- 2.3742	α_{xx}	- 67.0736	β_{xxx}	-46.9792
μ_y	- 0.7684	α_{yy}	- 57.0400	β_{yyy}	-17.8053
μ_z	0.0008	α_{zz}	- 65.6841	β_{zzz}	0.0013
		α_{xy}	14.5315	β_{xyy}	-14.1540
		α_{xz}	-0.0008	β_{xxy}	9.3349
		α_{yz}	-0.0013	β_{xxz}	0.0027
				β_{xzz}	-3.6143
				β_{yzz}	-6.8465
				β_{yyz}	0.0002
				β_{xyz}	0.0016

Using the values of dipole moment, polarizability and hyperpolarizability from table 6 and 7 for reported compounds 3,4HMB and 4,3HMB respectively we get the values of μ , $\bar{\alpha}$, $\Delta\alpha$ and β as follows :-

For 3,4HMB

For 4,3HMB

$$\mu = 5.1943$$

$$\mu = 2.4954$$

$$\bar{\alpha} = 63.2659$$

$$\bar{\alpha} = 63.2659$$

V. CONCLUSION

In the present work we have calculated and compared the geometric parameters, the vibrational frequencies and NLO properties of 3-hydroxy-4-methoxy-benzaldehyde and 4-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 Gibb's free energy of the titled compounds at different temperatures along with dipole moment, polarisability and hyperpolarisability.

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