

Molecular Structure, Vibrational Spectral Studies, NLO Properties and Frontier Molecular Investigations of 4-Ethoxy-3-Methoxybenzaldehyde by DFT

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Abstract: Benzaldehyde and its derivatives are the simplest in aromatic aldehydes and are widely used in different industries, so there exist a vast field of study of substituted benzaldehydes. We have taken 4-ethoxy-3-methoxybenzaldehyde for study. Quantum calculations plays a pivotal role in further detailed studies of the compounds, these calculations were carried out by Gaussian 09 software. DFT/B3LYP/6-311G (d, p) basis was used to perform geometric optimization and vibrational frequency determination of the molecule. The statistical thermochemical calculations of the molecule were done at DFT/B3LYP/6-311G (d, p) basis set to calculate the standard thermodynamic functions: heat capacity (C_v), entropy (S) and Enthalpy (E). DFT/B3LYP/6-311G (d, p) basis set was used to calculate the various NLO properties like dipole moment (μ), mean linear polarizability (α), anisotropic polarizability ($\Delta\alpha$), first order hyperpolarizability (β) also frontier molecular orbital studies were performed and HOMO-LUMO investigations were performed.

Key-Words: 4-ethoxy-3-methoxybenzaldehyde, DFT/B3LYP/6-311G (d, p) basis, frontier molecular orbital, HOMO-LUMO, Gaussian 09, NLO properties.

I. INTRODUCTION

Benzaldehydes and its derivatives are one of the simplest aromatic aldehydes and known as artificial essential oil of almond. 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-tumor activity in mice. [1,2] It is used as a bee repellent in the harvesting of honey. Because of their biological and chemical importance lot of studies have been done on substituted benzaldehydes. Spectroscopic investigations plays a major role in detailed studies of any compound, a lot of spectroscopic studies have been done by the researchers on these compounds. [3-7] In this light we have taken 4-ethoxy-3-methoxybenzaldehyde (abbreviated and further mentioned as 4,3EMB)

II. COMPUTATIONAL

All the calculations were carried out for 4,3EMB with Gaussian 03W program package [8] using the Becke3Lee-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.

1. RESULTS & DISCUSSION

(A). MOLECULAR STRUCTURE: The molecular structure of 4,3EMB is shown in Figure1

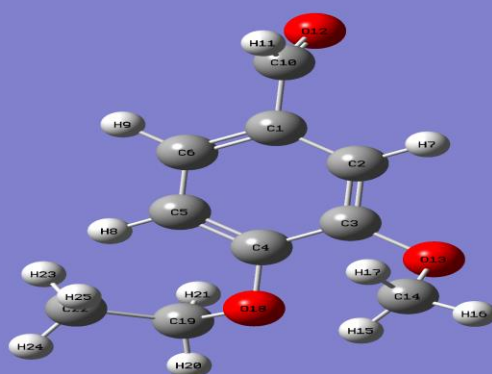


Figure 1

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.

Table 1

Atoms Of molecule	Bond length(A ⁰)	Angle between atoms	Bond Angle(°)	Dihedral angle between atoms	Dihedral angle(°)
R (1,2)	1.3952	A (2,1,6)	119.9985	D (6,1,2,3)	0.0323
R (1,6)	1.3948	A (2,1,10)	119.9972	D (6,1,2,7)	179.9532
R (1,10)	1.54	A (6,1,10)	120.0043	D (10,1,2,3)	-179.9729
R (2,3)	1.3947	A (1,2,3)	120.0086	D (10,1,2,7)	-0.052
R (2,7)	1.0997	A (1,2,7)	119.9808	D (2,1,6,5)	0.0149
R (3,4)	1.3954	A (3,2,7)	120.0106	D (2,1,6,9)	179.9892
R (3,13)	1.43	A (2,3,4)	119.9942	D (10,1,6,5)	-179.9798
R (4,5)	1.3948	A (2,3,13)	120.0128	D (10,1,6,9)	-0.0056
R (4,18)	1.43	A (4,3,13)	119.993	D (2,1,10,11)	-89.9606
R (5,6)	1.3951	A (3,4,5)	119.994	D (2,1,10,12)	90.0394
R (5,8)	1.0998	A (3,4,18)	119.9811	D (6,1,10,11)	90.0341
R (6,9)	1.0996	A (5,4,18)	120.0249	D (6,1,10,12)	-89.9659
R (10,11)	1.07	A (4,5,6)	120.0047	D (1,2,3,4)	-0.0568
R (10,12)	1.2584	A (4,5,8)	120.0113	D (1,2,3,13)	179.9619
R (13,14)	1.43	A (6,5,8)	119.984	D (7,2,3,4)	-179.9777
R (14,15)	1.07	A (1,6,5)	120.0	D (7,2,3,13)	0.041
R (14,16)	1.07	A (1,6,9)	120.008	D (2,3,4,5)	0.0341
R (14,17)	1.07	A (5,6,9)	119.992	D (2,3,4,18)	-179.9964

R (18,19)	1.43	A (1,10,11)	119.8865	D (13,3,4,5)	-179.9777
R (19,20)	1.07	A (1,10,12)	120.2269	D (13,3,4,18)	-0.0151
R (19,21)	1.07	A (11,10,12)	119.8865	D (2,3,13,14)	115.343
R (19,22)	1.54	A (3,13,14)	109.5	D (4,3,13,14)	-64.6383
R (22,23)	1.07	A (13,14,15)	109.4712	D (3,4,5,6)	0.0131
R (22,24)	1.07	A (13,14,16)	109.4712	D (3,4,5,8)	-179.9995
R (22,2)	1.07	A (13,14,17)	109.4712	D (18,4,5,6)	-179.9563
		A (15,14,16)	109.4713	D (18,4,5,8)	0.0311
		A (15,14,17)	109.4712	D (3,4,18,19)	-152.3808
		A (16,14,17)	109.4712	D (5,4,18,19)	27.5887
		A (4,18,19)	109.5	D (4,5,6,1)	-0.0376
		A (18,19,20)	109.4712	D (4,5,6,9)	179.9881
		A (18,19,21)	109.4712	D (8,5,6,1)	179.975
		A (18,19,22)	109.4712	D (8,5,6,9)	0.0007
		A (20,19,21)	109.4712	D (3,13,14,15)	76.9338
		A (20,19,22)	109.4713	D (3,13,14,16)	-163.0662
		A (21,19,22)	109.4712	D (3,13,14,17)	-43.0662
		A (19,22,23)	109.4712	D (4,18,19,20)	167.6841
		A (19,22,24)	109.4712	D (4,18,19,21)	47.6841
		A (19,22,25)	109.4712	D (4,18,19,22)	-72.3159
		A (23,22,24)	109.4713	D (18,19,22,23)	115.8229
		A (23,22,25)	109.4712	D (18,19,22,24)	-124.1771
		A (24,22,25)	109.4712	D (18,19,22,25)	-4.1771
				D (20,19,22,23)	-124.1771
				D (20,19,22,24)	-4.1771
				D (20,19,22,25)	115.8229
				D (21,19,22,23)	-4.1771
				D (21,19,22,24)	11.8229
				D (21,19,22,25)	-124.1771

(C). 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) for 4,3EMB and the results so obtained are displayed in table 2.

Table 2

Mode	Frequency	Infrared	Raman Activity
1.	50.2	0.7771	2.0212
2.	75.82	2.6843	1.1572
3.	84.26	0.7684	0.6683
4.	124.22	4.6795	2.1110
5.	139.66	3.0192	3.5111
6.	162.68	2.5849	0.6536
7.	184.21	5.4229	1.5867
8.	199.33	2.4373	0.4273
9.	233.09	0.4449	0.6099
10.	261.17	8.8900	0.3883
11.	305.62	0.4918	2.0797
12.	336.13	9.8863	1.7990
13.	373.94	1.4677	10.4054
14.	388.62	3.3867	1.4152
15.	419.78	7.7466	1.0969
16.	494.40	7.2825	3.8927
17.	520.11	3.3361	1.0749
18.	604.52	9.3806	2.9477
19.	646.71	25.1691	0.6077
20.	654.91	5.3925	0.6480
21.	734.78	8.1835	21.1056
22.	794.78	29.9506	4.9050
23.	806.17	2.0852	0.7058
24.	843.57	2.1680	0.8152
25.	880.90	47.9534	2.3832
26.	897.76	6.2180	9.1180
27.	923.70	49.3499	5.5361
28.	959.20	13.5229	1.6548
29.	1019.62	40.9885	6.2842
30.	1027.25	12.4571	1.5709
31.	1031.26	68.2260	9.5307
32.	1076.14	1.0040	8.4386
33.	1129.90	3.3079	4.6920
34.	1136.54	170.5492	6.3737
35.	1150.39	12.0603	10.3864
36.	1189.27	9.3237	5.9377
37.	1192.87	6.6261	8.1734
38.	1215.94	7.4914	8.7526
39.	1244.95	42.6746	9.7526
40.	1291.97	500.2067	53.1629
41.	1326.46	6.6505	2.5156
42.	1330.71	10.1233	7.3263
43.	1344.84	64.6854	33.9260
44.	1413.24	16.2756	5.8469
45.	1417.33	5.6773	5.5725
46.	1454.13	8.8437	11.9980
47.	1464.95	17.5574	3.9230
48.	1495.90	3.1141	13.0481
49.	1542.08	93.4182	10.0554
50.	1551.59	19.7771	25.2902
51.	1554.82	9.3582	31.2540
52.	1561.29	2.2622	39.4035
53.	1572.76	4.7458	4.0167
54.	1587.42	11.9346	14.4177
55.	1590.75	66.0150	61.6977
56.	1632.48	92.9518	166.6655
57.	1711.97	153.8473	97.3483
58.	2912.79	155.8850	141.4890
59.	3045.13	55.1963	93.0990
60.	3067.16	12.6197	87.9361
61.	3068.55	23.4695	111.4930
62.	3124.88	1.1181	112.9246
63.	3133.00	22.6647	88.9464
64.	3136.72	33.0846	102.4049

65.	3151.21	29.0128	18.6451
66.	3180.30	7.8037	47.8762
67.	3209.10	2.4368	63.7808
68.	3217.97	0.3900	38.0113
69.	3238.04	10.6532	96.7158

The corresponding curves of infrared and Raman activities are shown in Figure 2 and 3 respectively .

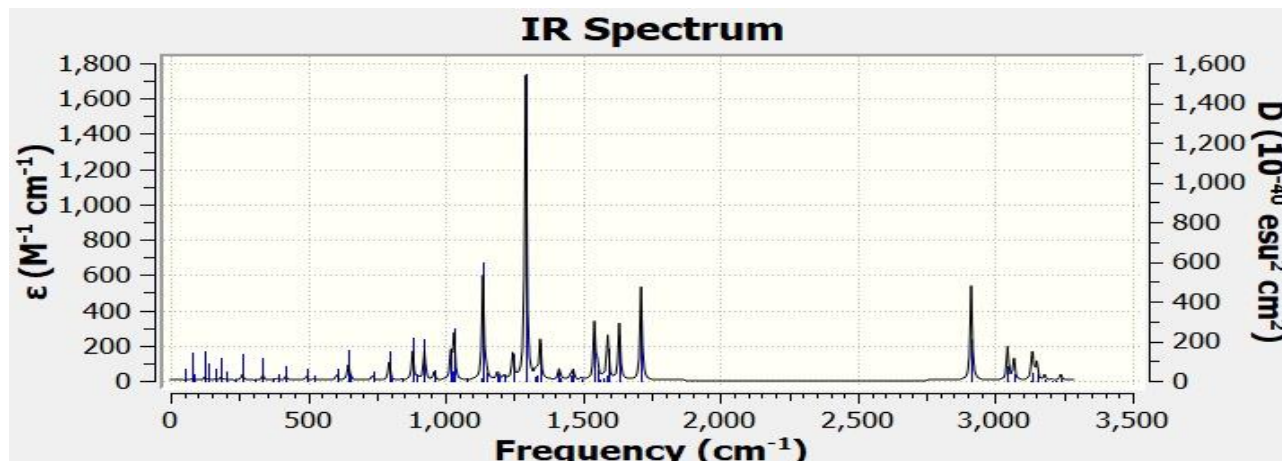


Figure 2

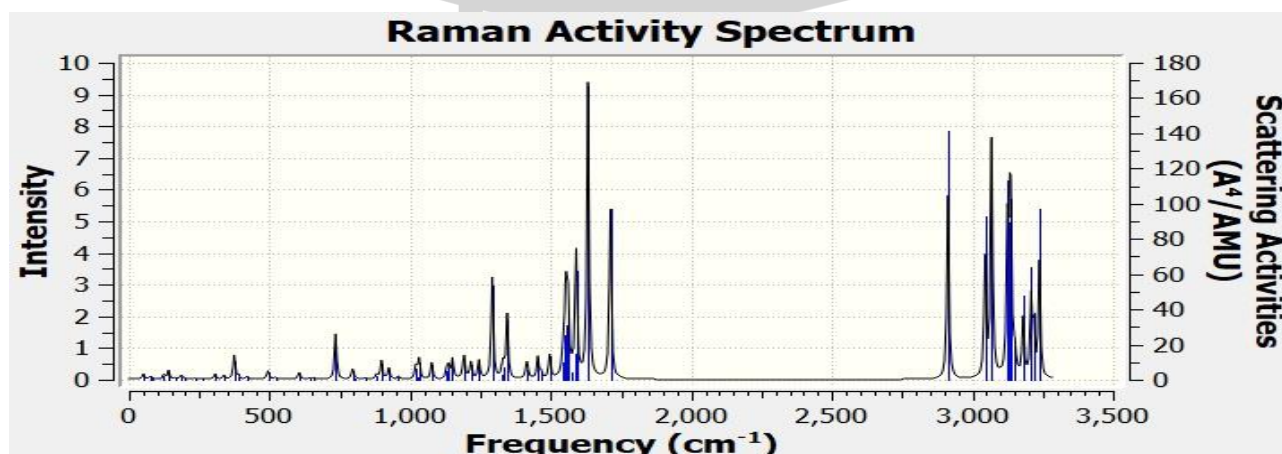


Figure 3

These calculated values shows fair agreement with the experimental values for different assignments of vibrations. [9]

(D). UV-VISIBLE SPECTRA: Time dependent DFT calculations are a powerful tool to study electronic absorption spectrum in terms of Excitation energies (E), absorption wavelength (λ), oscillator strengths (f), molecular orbitals undergoing transitions, transition energy, electronic transitions. These values calculated by DFT are shown in table 3, and the corresponding UV-Visible curve is shown in Figure 4.

Table 3

Excited state	Excitation Energy (E)	Absorption Wavelength (λ)	Oscillator Strength (f)	Excitation Transition (MO)	Transition Energy (MO) Singlet A
1.	3.7267 eV	332.69 nm	f=0.0002	46 -> 49 48 -> 49	0.61954 0.31126
2.	4.3739 eV	283.47 nm	f=0.0002	46 -> 49 47 -> 49 48 -> 49	0.29609 0.10849 0.62598
3.	4.9423 eV	250.86 nm	f=0.0004	46 -> 49 47 -> 49	0.14836 0.68045

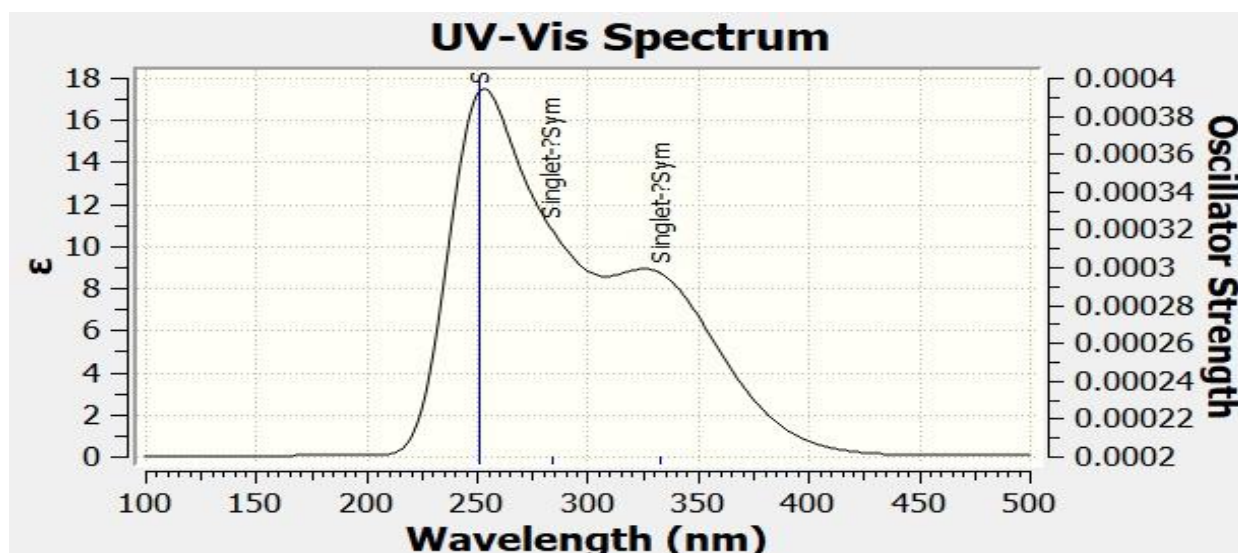


Figure 4

(E). THERMODYNAMICAL 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 calculated values of thermodynamic functions of 4,3EMB by frequency calculations are given in table 4 and thermodynamic properties of 4,3EMB computed BY DFT/B3LYP/6-311 G (d, p) level basis set is given in table 5.

Table 4

Thermodynamic Functions	Value
Zero-point correction	0.204680 (Hartree/Particle)
Thermal correction to Energy	0.217482
Thermal correction to Enthalpy	0.218426
Thermal correction to Gibbs Free Energy	0.165082
Sum of electronic and zero-point Energies	-610.357030
Sum of electronic and thermal Energies	-610.344229
Sum of electronic and thermal Enthalpies	-610.343284
Sum of electronic and thermal Free Energies	-610.396629

Table 5

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	136.472	46.842	112.272
Electronic	0.000	0.000	0.000
Translational	0.889	2.981	41.471
Rotational	0.889	2.981	31.611
Vibrational	134.695	40.881	39.190
Vibration 1	0.595	1.977	4.797
Vibration 2	0.599	1.965	3.996
Vibration 3	0.601	1.960	3.789
Vibration 4	0.610	1.929	3.034
Vibration 5	0.615	1.914	2.809
Vibration 6	0.623	1.888	2.518
Vibration 7	0.631	1.861	2.285
Vibration 8	0.637	1.841	2.139

Vibration 9	0.654	1.790	1.855
Vibration 10	0.669	1.744	1.654
Vibration 11	0.696	1.663	1.386
Vibration 12	0.717	1.603	1.230
Vibration 13	0.745	1.526	1.064
Vibration 14	0.757	1.495	1.005
Vibration 15	0.782	1.427	0.893
Vibration 16	0.850	1.262	0.672
Vibration 17	0.875	1.205	0.610
Vibration 18	0.963	1.022	0.442

(F). ELECTRIC MOMENTS: The dipole moment in a molecule is a important property that is mainly used to study the intermolecular interactions involving the nonbonded 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 compound 2,6-CFB can provide a satisfactory comparison of these quantities.

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

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

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

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

Table 6 represents the value of dipole moment polarizability and hyperpolarizability for the mentioned compound

Table 6

Dipole moment		Polarizability		Hyperpolarizability	
μ_x	4.9668	α_{xx}	-81.3442	β_{xxx}	106.0155
μ_y	-0.5333	α_{yy}	-71.2037	β_{yyy}	-0.0357
μ_z	0.9524	α_{zz}	-78.3753	β_{zzz}	0.1583
		α_{xy}	-10.4239	β_{xxy}	29.4568
		α_{xz}	1.8665	β_{xxz}	-5.6656
		α_{yz}	4.5348	β_{xyy}	19.6521
				β_{xyz}	4.7139
				β_{xzz}	4.3046
				β_{yyz}	6.0479
				β_{yzz}	1.2378

Using the values of dipole moment, polarizability and hyperpolarizability from table 6, we get the values μ , α , $\Delta\alpha$ and β as following.

$$\mu = 4.2363$$

$$\alpha = 76.3153$$

$$\Delta\alpha = 15.6184$$

$$\beta = 90.6145$$

(G). HOMO-LUMO BAND GAP: The molecules which are conjugated can be distinguished on the basis of frontier molecular orbits and can be well explained by the separation between these orbits, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), the separation between these orbitals provide the stability of the molecule which in turn provides significant degree of intramolecular charge transfer from the end-capping electron-donor groups through P-conjugated path. Through P-conjugated bridge the strong charge transfer interaction results in substantial ground state donor–acceptor mixing and the emergence of a charge transfer band in the electronic absorption spectrum of a charge transfer band in the electronic absorption spectrum. The wave function analysis shows that the electron absorption corresponds to the transition from the ground state to the first excited state and is mainly described by one-electron excitation from the HOMO to LUMO. The HOMO and LUMO energies of the reported compound 2,6 CFB have been calculated at B3LYP/6-31G (d,p) level. Figures 5 and 6 shows HOMO and LUMO respectively. The HOMO and LUMO energies thus obtained from DFT calculations are -0.23188 a.u. and -0.04393 a.u. respectively and the energy difference between HOMO and LUMO is 0.18795 a.u. which indicates fairly high stability of molecule.

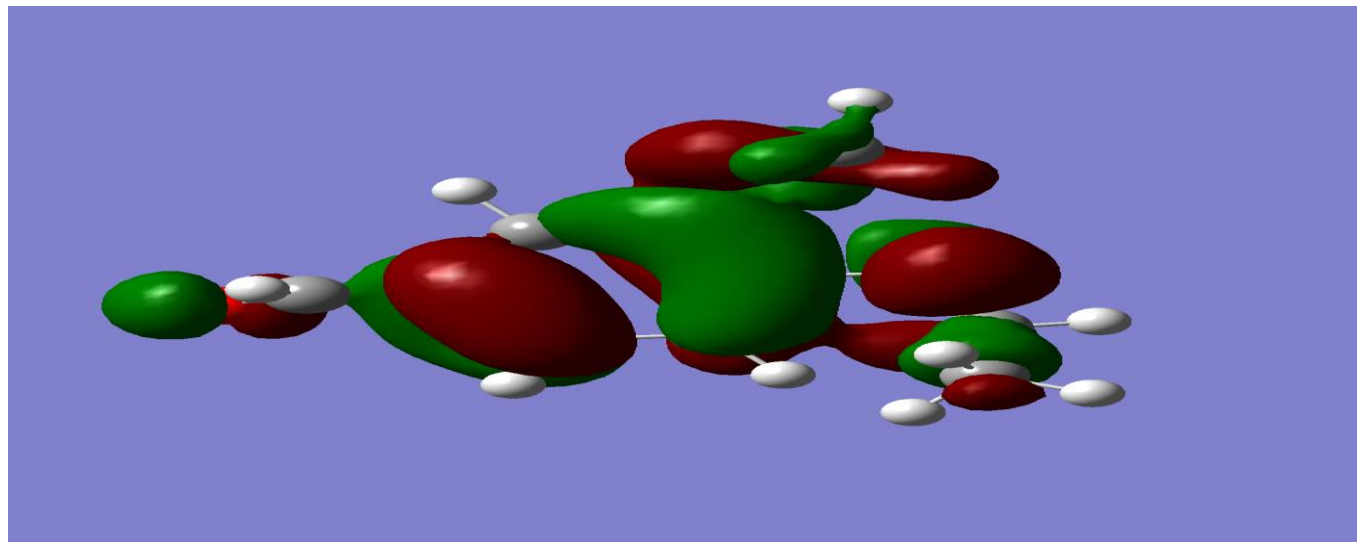


Figure 5

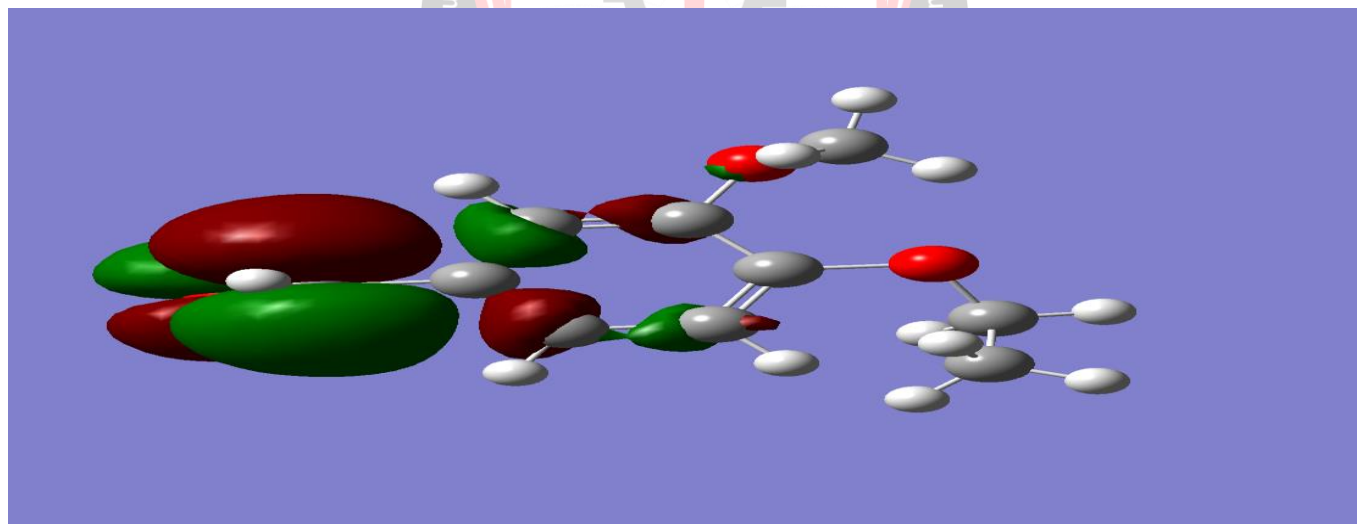


Figure 6

CONCLUSION

In this study an attempt is made to determine the structural parameters, vibrational frequencies, thermodynamic and NLO properties, frontier orbitals by DFT calculations performed by Gaussian 09 using B3LYP/6-311 G (d, p) basis set. The derived values are in good agreement with the experimental work performed by other researchers on similar compounds infact these values at some places gives more accurate values. These results can be further used for further research purposes.

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