

Molecular Structure, Vibrational Spectral Studies, NLO Properties and frontier molecular investigations of 2-Chloro-6-Fluoro Benzaldehyde by DFT

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ABSTRACT

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Benzaldehyde and its derivatives are the simplest in aromatic aldehydes and have wide range of use in different industries. Due to this reason, there exist a vast field of study of substituted benzaldehydes. Quantum mechanical calculations of geometries, energies, vibrational wave numbers and thermodynamic constants have been performed with Gaussian 09 program package using the beece-3-Lee-Yang-Parr- (B3LYP) functional supplemented with the standard 6-31G (DP). The optimized 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 temperature were also calculated along with the dipole moment, Polarizability and hyperpolarizability.

Keywords :- 2-Chloro-6-fluoro benzaldehyde, NLO, Gaussian 09w DFT/B3LYP, thermodynamic parameters, dipole moment, polarizability, hyperpolarizability.

I. INTRODUCTION

Benzaldehyde is the simplest aromatic aldehyde and substitution of a functional group in benzaldehyde changes the spectra remarkably. Raman spectra of some substituted benzaldehydes have been recorded . Benzaldehyde is being used as a pesticide and also as an anti-cancerous and have shown anti-tumor activity in mice. [1,2]

The vibrational spectra of benzaldehyde and its derivatives have been extensively investigated by many early researchers. [3-6] In the present study

quantum mechanical calculation of geometries, energies ware numbers and thermodynamic function of the compound have been performed. In this study we will investigate vibrational spectroscopic properties and other parameters of 2-Chloro-6-fluoro benzaldehyde, (hereafter referred as 2,6-CFB).

II. COMPUTATIONAL

All the calculation were carried out with Gaussian 09W program package [7] using the Beckle-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.

III. RESULTS AND DISCUSSION

Various physical and chemical properties of 2,6-CFB are as follows

1.	Molecular Formula	C ₇ H ₄ ClFO
2.	Molecular Weight	158.56
3.	Exact Mass	157.9934706
4.	Monoisotopic Mass	157.9934706
5.	Topological Polar Surface Area	17.1 Å
6.	Melting Point	32-35 °C
7.	Boiling Point	92 °C
8.	Density	1.352 g/cm ³
9.	Flash Point	101 °C
10.	Refractive Index	1.559

A- *Molecular Structure:* -

The molecular structure of the mentioned compound 2,6-CFB is shown in Figure-1. The optimized bond lengths bond angles dihedral angles of the compound is calculated by B3LYP method using B3LYP 6-311+ + G(d) and 6-311+ + G(d,p) bases are listed in Table-1 and is in accordance with atom numbering scheme as shown in Fig-1. Since the exact crystal structure of the compound is not available, the optimized structure can only be compared with other similar system for which the crystal structures have been solved.

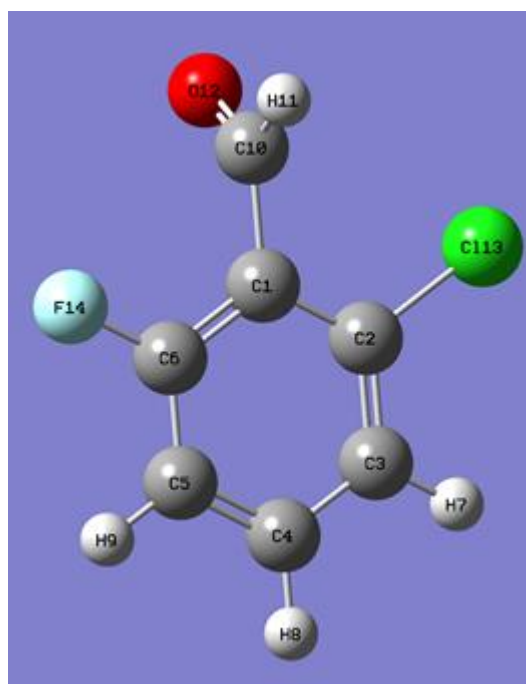


Fig-1 Molecular structure of 2,6-CFB

Table -1

Calculated Optimized Geometrical Parameters of 2,6-CFB at B3LYP/6-31G(d,p)
Bond length (Å), Bond Angle (°), Dihedral Angle (°)

Atoms Of molecule	Bond length(Å)	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(6,1,2,13)	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(10,1,2,13)	-0.052
R(2,13)	1.76	A(1,2,13)	119.9808	D(2,1,6,5)	0.0149
R(3,4)	1.3954	A(3,2,13)	120.00106	D(2,1,6,14)	179.9892
R(3,7)	1.0997	A(2,3,4)	119.9942	D(10,1,6,5)	-179.9798
R(4,5)	1.3948	A(2,3,7)	120.0128	D(10,1,6,14)	-0.056
R(4,8)	1.0997	A(4,3,7)	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(5,9)	1.0998	A(3,4,8)	119.9811	D(6,1,10,11)	90.0341
R(6,14)	1.35	A(5,4,8)	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(4,5,9)	120.0113	D(1,2,3,7)	179.9619
		A(6,5,9)	119.984	D(13,2,3,4)	-179.9777
		A(1,6,5)	120.0	D(13,2,3,7)	0.041
		A(1,6,14)	120.008	D(2,3,4,5)	0.0341
		A(5,6,14)	119.992	D(2,3,4,8)	-179.9964
		A(1,10,11)	119.8865	D(7,3,4,5)	-179.9846
		A(1,10,12)	120.2269	D(7,3,4,8)	-0.0151
		A(11,10,12)	119.8865	D(3,4,5,6)	0.0131
				D(3,4,5,9)	-179.9995
				D(8,4,5,6)	-179.9563
				D(8,4,5,9)	0.0311
				D(4,5,6,1)	-0.0376
				D(4,5,6,14)	179.9881
				D(9,5,6,1)	179.975
				D(9,5,6,14)	0.0007

B. Vibrational Spectra

A detailed study of Vibrational spectra has been carried out of the reported compound and its vibrational frequencies have been calculated using DFT-B3LYP level with 6-311+ + G(d,p), there is a good agreement between the observed frequencies [10] and those calculated by the DFT. A 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.

Table 2
Calculated Frequencies

Mode	Frequency	Infrared	Raman Activity
1.	89.29	0.0932	1.7407
2.	147.27	10.605	3.5035
3.	216.94	3.5404	4.1456
4.	227.12	4.0467	2.9963
5.	254.10	0.1540	1.8647
6.	288.30	6.0682	5.9608
7.	370.01	4.9874	13.9323
8.	423.92	33.1624	11.7099
9.	461.98	5.5853	8.1317
10.	531.37	0.0606	0.6337
11.	589.49	2.0756	21.0182
12.	613.75	2.3159	0.7831
13.	705.97	25.6381	5.1524
14.	781.36	42.3826	3.9844
15.	813.24	64.1729	8.8284
16.	860.71	56.7730	0.6167
17.	923.72	107.9414	8.2932
18.	968.90	2.3087	1.9129
19.	1056.37	4.8798	0.1656
20.	1090.56	0.1079	10.0093
21.	1096.07	0.5208	55.3954
22.	1191.18	13.4978	5.2519
23.	1225.10	150.8762	56.4407
24.	1243.49	20.4022	15.3639
25.	1320.79	11.8695	19.7427
26.	1338.04	10.9679	30.1950
27.	1462.33	63.1909	20.7026
28.	1473.89	21.1824	17.2158
29.	1514.20	111.6727	38.1445
30.	1585.65	147.4089	90.6789
31.	1637.24	153.8389	97.9203
32.	1707.41	273.3723	104.0877

33.	3021.00	87.2039	155.9042
34.	3229.41	1.7549	139.9645
35.	3248.08	0.0788	129.0763
36.	3253.63	0.5832	361.2170

The corresponding curves of Infrared and Raman activities are shown in Fig. 2 and 3.

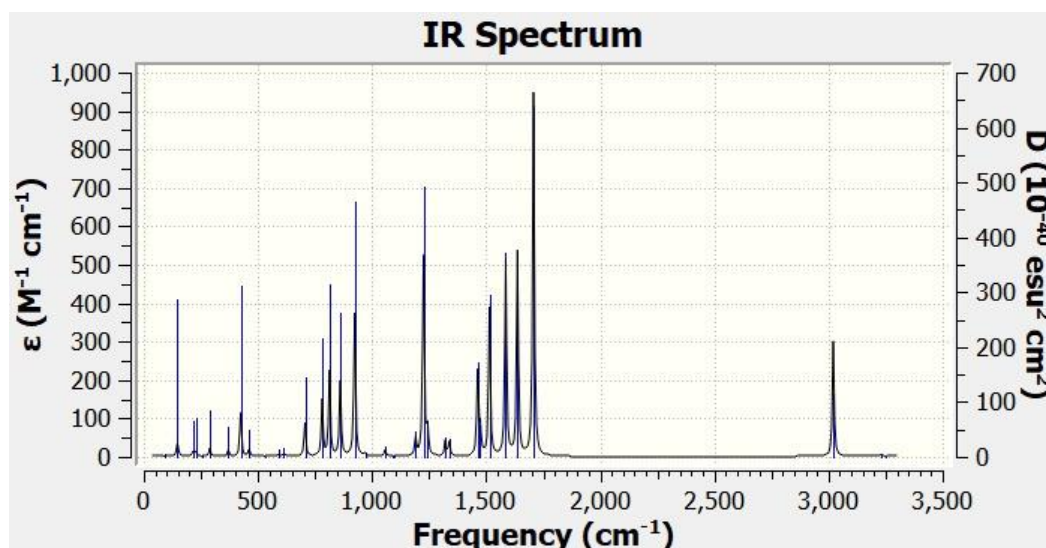


Figure 2

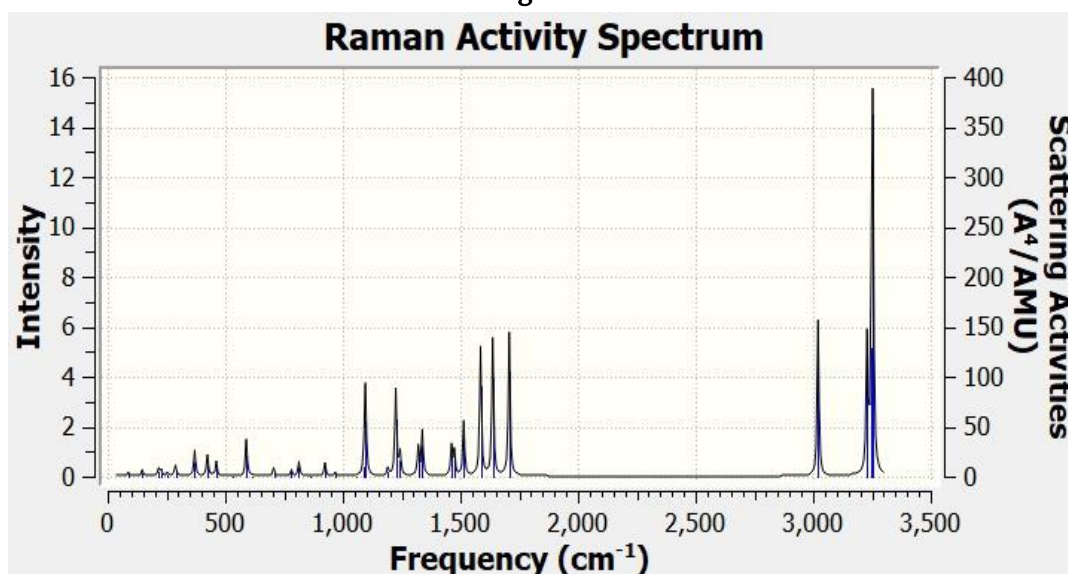


Figure 3

The results obtained by the DFT calculations are in accordance with the experimental results obtained for substituted benzaldehydes as shown by several researchers time to time.[8-11]

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.

Table 3: Calculated values of 2,6CFB thermodynamic functions by frequency calculations

Thermodynamic Functions	Value
Zero-point correction	0.093314 (Hartree/Particle)
Thermal correction to Energy	0.101516
Thermal correction to Enthalpy	0.102460
Thermal correction to Gibbs Free Energy	0.059498
Sum of electronic and zero-point Energies	-899.666315
Sum of electronic and thermal Energies	-899.658113
Sum of electronic and thermal Enthalpies	-899.657169
Sum of electronic and thermal Free Energies	-899.700131

Table 4: Thermodynamic properties of 2,6CFB as calculated BY DFT/B3LYP/6-311 G (d, p) level basis set

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	63.702	30.096	90.421
Electronic	0.000	0.000	0.000
Translational	0.889	2.981	41.081
Rotational	0.889	2.981	30.141
Vibrational	61.925	24.134	19.198
Vibration 1	0.602	1.957	3.681
Vibration 2	0.617	1.906	2.707
Vibration 3	0.646	1.815	1.985
Vibration 4	0.651	1.800	1.902
Vibration 5	0.665	1.756	1.702
Vibration 6	0.685	1.696	1.484
Vibration 7	0.742	1.534	1.080
Vibration 8	0.786	1.418	0.879
Vibration 9	0.820	1.334	0.760
Vibration 10	0.886	1.181	0.584
Vibration 11	0.947	1.054	0.468
Vibration 12	0.973	1.003	0.427

D. Electric Moments

The dipole moment in a molecule is an 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.

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

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

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

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 4 Represents the value of dipole moment polarizability and hyperpolarizability for the mentioned compound

Table 4

Dipole moment		Polarizability		Hyperpolarizability	
μ_x	-1.2201	α_{xx}	-67.3700	β_{xxx}	11.6927
μ_y	-5.1620	α_{yy}	-58.2306	β_{yyy}	-36.4569
μ_z	-0.0008	α_{zz}	-64.6266	β_{zzz}	-0.0021
		α_{xy}	-6.2761	β_{xxy}	-16.7592
		α_{xz}	-0.0041	β_{xxz}	-0.0018
		α_{yz}	-0.0084	β_{xyy}	-9.1817
				β_{xyz}	-0.0051
				β_{xzz}	7.3464
				β_{yyz}	-0.0006
				β_{yzz}	9.8675

Using the values of dipole moment, polarizability and hyperpolarizability from table 4, we get the values μ , α , $\Delta\alpha$ and β as following.

$$\mu = 5.3042$$

$$\alpha = -63.4090$$

$$\Delta\alpha = 8.12414$$

$$\beta = 44.4552$$

E. HOMO-LUMO Band Gap

The molecules which are conjugated can be distinguished on the basis of frontier molecular orbitals and can be well explained by the separation between these orbitals, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), the separation between these orbitals provides 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 2,6CFB have been calculated at B3LYP/6-31G (d,p) level. Figures 4 and 5 shows HOMO and LUMO respectively. The HOMO and LUMO energies thus obtained from DFT calculations are -0.26095 a.u. and -0.08002 a.u. respectively and the energy difference between HOMO and LUMO is 0.18093 a.u. which indicates fairly high stability of molecule.

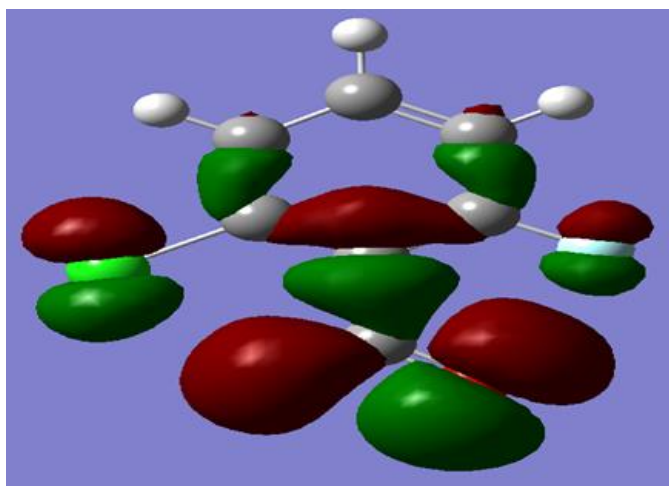


Figure 4

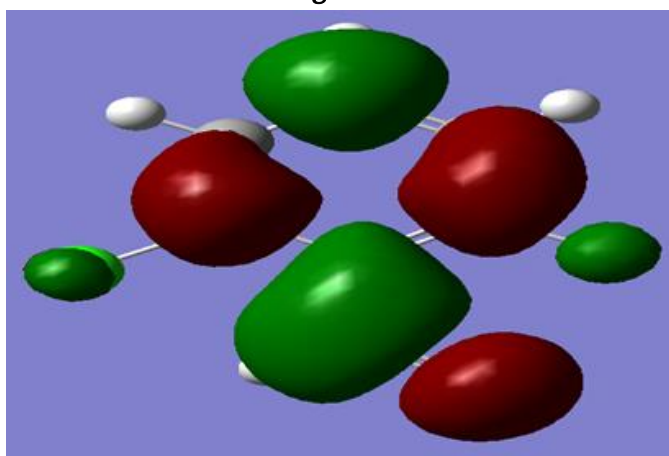


Figure 5

IV. CONCLUSION

In the present work we have calculated the geometrical parameters, vibrational frequencies, frontier molecular orbitals and NLO properties of 2,6-CFB by using Becke-3Lee-Yang-Parr(B3LYP) functional supplemented with the standard 6-31G(d,p) . We have also calculated thermodynamic properties of the mentioned compound at different temperatures along with dipolemoment, polarizability and hyperpolarizability. The HOMO-LUMO energy gap predicts the greater stability of the compound.

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