

## Vibrational Spectral Studies, Thermodynamic **Properties And Molecular Orbital Analysis Of 2-**Chloro-6-Florobenzldehydea By D.F.T.

Seema, Associate Prof. Deptt. of Chemistry, Meerut College, Meerut, India.

B.S.Yadav, Principal, D.N. (P.G.) college, Meerut, India.

Sachin Kumar, Associate Prof. and Head Department of Physics A.S. (P.G.) College, Mawana,

#### Meerut, India. sachin\_sks1@yahoo.com

ABSTRACT: Benzaldehydes are the simple aromatic aldehydes and its derivatives are widely used in different industries such as dyes, flavouring, artificial flavours, solvents etc. they also exhibits different biological activities. Due to these reasons there exist a vast scope of study of substituted benzaldehydes, in this light 2-Chloro-6-Florobenzaldehyde is reported for study. The experimental values of IR and Raman spectra are compared with those obtained by Gaussian 09W program package using the Becke-3Lee-Yang-Parr (B3LYP) functional supplemented with the standard 6-31G (DP). The thermodynamic properties are discusses with the different thermodynamic constants obtained in the temperature range 200K-1500K. Frontier molecular orbits (HOMO-LUMO) and molecular electrostatic potentials (MESP) are also studied.

KEY-WORDS: 2-Chloro-6-florobenzaldehydes, Gaussian 09W, Becke-3Lee-Yang-Parr (B3LYP), Thermodynamic constants, Frontier molecular orbits, MESP.

### I. INTRODUCTION

Spectroscopic studies of the benzaldehyde and their derivatives have been carried out on the experimental and calculation grounds as the vibrational spectra are very useful for understanding of specific biological activities and for the analysis of relatively complex system. Benzaldehydes have a wide range of 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]. So the IR and Raman spectra obtained experimentally is compared along with assignments with the one obtained from Gaussian 09 W program [7] Molecular structure with bond lengths, bond angles and dihaderal angles is obtained by the software and frontier molecular orbitals and molecular electrostatic potentials are displayed pictorially.

#### **II. EXPERIMENTAL**

Spec. pure grade sample of 2-chloro-6-fluorobenzaldehyde (here after referred as 2,6-CFB, M.P 32°C) was purchased from M/s Aldrich Chemical Co., U.S.A. and was used as such. Its purity was confirmed by melting point determination. The infrared spectra of the compound 2,6CFB were recorded on Perkin-Elmer M-683 spectrophotometer in the region 400-4000 cm-1 using KBr pellets and nujolmull solvent. The laser Raman spectrum in the region 40-4300 cm-1 was recorded on "Spex Rama Lab" spectrophotometer using 52 mg argon-krypton laser beam of wavelength 488 nm.[8]

### **III. COMPUTATIONAL**

n Engineering A Experimental and theoretical investigations have been focused on elucidating the structure and normal vibrations of benzaldehyde and its derivatives. Ab initio Density functional theory calculations are reported to provide excellent vibrational frequencies of aromatic organic compounds. The molecular structures of benzaldehyde derivatives in the ground state will be computed by density functional theory (DFT) methods with Gaussview molecular visualisation program and Gaussian09 program [7]. DFT method employs Becke's three-parameter hybrid functional of Lee, Yang, and Parr (LYP). The following basis sets B3LYP/6-31G(d, p) and B3LYP/6-311G(d, p) and B3LYP/6-311++G(2d, 2p) were used. 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**

MOLECULAR STRUCTURE: The molecular structure of the mentioned compound 2,6 CFB 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 BMB is not available till now, the optimized structure can only be compared with other similar system for which the crystal structures have been solved. [9]



# FIGURE 1 TABLE1

#### Calculated Optimized Geometrical Parameters of BMB, at B3LYP/6-31G(d,p): bond length (Å),

#### bond angle(<sup>o</sup>), dihedral angles(<sup>o</sup>)

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S. No	Atoms of molecule	Bond length (Å)	Angle between atoms (°) Research in Engineerit	Bond angle (°)	Dihedral angle between atoms (°)	Dihedral angle (°)
1.	R(1,2)	1.3839	A(2,1,6)	116.5839	D(6,1,2,3)	-0.0399
2.	R(1,6)	1.385	A(2,1,10)	122.3489	D(6,1,2,13)	179.9971
3.	R(1,10)	1.4844	A(6,1,10)	121.0671	D(10,1,2,3)	-179.9848
4.	R(2,3)	1.371	A(1,2,3)	122.8852	D(10,1,2,13)	0.0522
5.	R(2,13)	1.8182	A(1,2,13)	120.5933	D(2,1,6,5)	0.0123
6.	R(3,4)	1.3844	A(3,2,13)	116.5215	D(2,1,6,14)	-179.9822
7.	R(3,7)	1.0685	A(2,3,4)	118.7625	D(10,1,6,5)	179.958
8.	R(4,5)	1.3781	A(2,3,7)	120.0465	D(10,1,6,14)	-0.0365
9.	<b>R</b> (4,8)	1.0706	A(4,3,7)	121.1911	D(2,1,10,11)	-0.0776
10.	R(5,6)	1.3743	A(3,4,5)	120.1618	D(2,1,10,12)	179.9551
11.	R(5,9)	1.0687	A(3,4,8)	119.7406	D(6,1,10,11)	179.98
12.	R(6,14)	1.3461	A(5,4,8)	120.0977	D(6,1,10,12)	0.0126
13.	R(10,11)	1.0781	A(4,5,6)	119.4542	D(1,2,3,4)	0.0379
14.	R(10,12)	1.2078	A(4,5,9)	121.7654	D(1,2,3,7)	-179.9822



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15.	A(6,5,9)	118.7804	D(13,2,3,4)	-179.9977
16.	A(1,6,5)	122.1524	D(13,2,3,7)	-0.0178
17.	A(1,6,14)	120.1829	D(2,3,4,5)	-0.0073
18.	A(5,6,14)	117.6647	D(2,3,4,8)	179.9882
19.	A(1,10,11)	113.73	D(7,3,4,5)	-179.9869
20.	A(1,10,12)	125.0603	D(7,3,4,8)	0.0085
21.	A(11,10,12)	121.2096	D(3,4,5,6)	-0.0188
22.			D(3,4,5,9)	-179.9975
23.			D(8,4,5,6)	179.9858
24.			D(8,4,5,9)	0.0071

*VIBRATIONAL SPECTRA:* A detailed study of vibrational spectra has been carried out of the reported compound 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 2 in which experimental values of IR (KBr and nuzol), FTIR and laser Raman are displayed and simultaneously compared with the calculated values.

TABLE2

S.No.	Experimental			Calculated	Assignments	
	Raman	IR(KBr)	IR(nuzol)			
1.	40					
2.	66					
3.	200			218.44	α (C-F)	
4.	239	Inter		227.92	α (C-Cl)	
5.	285	natio		288.70	β (C-Cl)	
6.	396	1121	TIREAN	371.61	β (C-CHO)	
7.		406	IJINEAN	, silon	α (C-C)	
8.	446	433	423 Search in a site	425.31		
9.		560	560 The Engineer	534.44	β(C-F)	
10.	578		583	590.69	β (C-C)	
11.		692			β (C-C)	
12.	703	708	710	709.31	a (C-C)	
13.		810	817	816.01	v (C-C)	
14.		840	826	860.75	α (C-H)	
15.		913	919	930.41	α (C-H)	
16.		967		964.69	β (C-C)	
17.			989		v(C-H)	
18.	1074	1062	1066	1087.83	β (C-H),v(C-Cl)	
19.	1156		1160	1194.23	β (C-H)	
20.	1194	1194	1200	1221.91	v(C-CHO)	
21.	1256	1250	1260	1245.91		



22.	1298	1293	1282		β (C-H)
23.			1311	1322.90	
24.		1485		1476.99	v(C-C)
25.		1493			
26.		1560		1593.10	v(C-C)
27.	1600	1602	1606	1642.44	v(C-C)
28.		3016		3012.03	v(C-F)
29.		3054	3050		v(C-F)
30.		3093	3090		v(C-F)

Where  $\alpha$  is out of plane bending,  $\beta$  is in-plane bending and v is stretching.

All the experimental[8] vibrations and calculated vibrations obtained from DFT calculations along with the assignments are simultaneously displayed in table 2. The brief discussion of the different vibrations is as follows:

*C-H Vibrations:* Since the molecule under present study is a trisubstituted benzene, therefore only three hydrogen atoms are left around the ring. As such three C-H valence oscillations are expected in the region 3000-3100 cm-1 [10]. In this study, the bands observed at 3016 cm-1 (KBr), 3054 (nujol)/3050 cm-1 (Raman) and 3093 (nujol) / 3090 cm-1 (Raman) corresponding to 3012.03 cm-1 for the calculated value have been taken to represent C-H stretching mode.

*C-C VIBRATIONS*: The group of four bands, appearing between 1400-1650 cm-1 in the spectra of substituted benzenes represents the characteristics skeletal stretching modes, these correspond to doubly degenerate C-C stretching vibrations of benzene at 1560cm-1 and 1485cm-1 modes with the calculated value of 1593.10cm-1. There are two more C-C stretching modes as 1310cm-1 and 989cm-1 of benzene. Except for the ring breathing mode, all these are known to remain practically unaffected by the substitution. In view of these, the bands assigned to the above modes are clearly indicated in the table.

*C-X Vibratoions* The C-Cl stretching mode has been assigned at 1055 cm-1 in 5-chloro-2,4-dimethoxy aniline [11] and 2,4,5,6-tetrachloro pyrimidine [12]. Hence, in the present study this mode has been identified at 1062 cm-1 (KBr)/1066 cm-1 (nujol) which find support from Raman value (1074 cm-1). Gupta et al [13] and Singh and Singh [14] have assigned C-Cl in-plane-bending at 295 cm-1 and 320 cm-1 for 2,6-di-chloro-4-nitro aniline and 2,5-dichloro nitrobenzene respectively. In the present study this mode has been identified at 285 cm-1 coressponding to 288.70cm-1 for the calculated value. R.K. Goel [15] and

R.P. Singh and R. N. Singh [16] have assigned C-F stretching mode at 1240, 1228, 1195 and 1204 cm-1 for 2-fluoro-5-iodotoluene,4-fluoro-2-iodotoluene,2,4-difluoro-tuolene and 2,5-difluorotuluene respectively. In view of these assignments, this mode has been identified at 1250 cm-1 for IR (KBr) and1260 cm-1 IR(nujol) which finds support from Raman value 1256 cm-1 and calculated value of 1245.91 cm-1.

Aldehyde 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 1600-1815 cm-1. In the molecule presently studied, the strong band observed at 1602/1606 cm-1 for IR (KBr/nuzol) with the counter part of Raman band at 1600 cm-1 with calculated value of 1642.044 may be assigned to C=O stretching mode.

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 = 0.093381 (Hartree/Particle)

Thermal correction to Energy = 0.101567

Thermal correction to Enthalpy = 0.102511

Thermal correction to Gibbs Free Energy = 0.059577

Sum of electronic and zero-point Energies= -899.659258

Sum of electronic and thermal Energies= -899.651072

Sum of electronic and thermal Enthalpies = -899.650128

Sum of electronic and thermal Free Energies =-899.693062



#### Table 3

	E (Thermal)	CV Cal/Mal Kalvin	S Col/Mol Kolvin
Total	63.734	30.050	90.364
Electronic	0.000	0.000	0.000
Translational	0.889	2.981	41.081
Rotational	0.889	2.981	30.139
Vibrational	61.957	24.089	19.143
Vibration 1	0.602	1.957	3.679
Vibration 2	0.617	1.907	2.721
Vibration 3	0.646	1.813	1.972
Vibration 4	0.651	1.798	1.895
Vibration 5	0.666	1.753	1.690
Vibration 6	0.685	1.695	1.482
Vibration 7	0.743	1.530	1.073
Vibration 8	0.787	1.415	0.874
Vibration 9	0.820	= 1.333	0.759
Vibration 10	0.889	1.174	0.577
Vibration 11	<b>IIRE 0.948</b>	1.052	0.466
Vibration 12	0.976	0.997	0.422

 $\left(\frac{H^0-E_0^0}{T}\right)$ 

THERMODYNAMIC FUNCTIONS Thermodynamic functions viz. enthalpy function

heat capacity

function  $C_p^0$ , free energy function

 $\left(\frac{F^0-E_0^0}{T}\right)$ ) and entropy function S0 of 2,6-CFB have been computed using the standard

expressions.

Temperature (K)	$ \begin{pmatrix} \mathbf{Enthalpy} \\ \left( \frac{\boldsymbol{H}_0 - \boldsymbol{E}_0^0}{T} \right) \\ \end{cases} $	Heat Capacity $(C_p^{(0)})$	Free Energy - $\left(\frac{F_0 - E_0^0}{T}\right)$	Entropy (S°)
200	15.340	21.868	110.0416	126.3821
300	18.697	29.045	117.890	136.5874
400	22.207	36.387	128.747	145.9552

Table 4



the proposition				
500	25.731	43.119	129.082	154.8143
600	29.123	48.873	134.076	163.2001
700	32.296	53.633	138.807	171.1035
800	35.214	57.521	143.313	178.5280
900	37.875	60.692	147.617	185.4923
1000	40.290	63.285	151.734	192.0257
1100	42.481	65.418	155.679	198.1607
1200	44.468	67.184	159.462	203.9310
1300	46.274	68.656	163.0942	209.3685
1400	47.918	69.893	166.5846	214.5051
1500	49.419	70.938	169.9426	219.369

*HOMO–LUMO BAND GAP:* The conjugated molecules are characterized by the separation between highest occupied molecular orbital and lowest unoccupied molecular orbital (HOMO–LUMO), which is the result of a significant degree of intramolecular charge transfer (ICT) from the end-capping electron-donor groups through Pconjugated path. The strong charge transfer interaction through P-conjugated bridge results in substantial ground state donor-acceptor mixing and the appearance of a charge transfer band in the electronic absorption spectrum of a charge transfer band in the electronic absorption spectrum.[17] Figure 2 shows the HOMO-LUMO band gap. The HOMO energy is -0.25554 a.u. and LUMO energy -0.07950 a.u. and the energy gap is 0.17604 which indicates good stability of the molecule.







*Molecular electrostatic potential:* The MESP is a pictorial representation of electrostatic potential shown on the constant electron density surface and it simultaneously exhibits the molecular size, shape and electrostatic potential value in terms of colour coding. The different values of the electrostatic potential on the surface are represented by different colours as red represents the

region of the most electronegative electrostatic potential, blue represents the region of the most positive electrostatic potential, green represents the region of zero potential and yellow represents slightly electron rich region. The molecular electrostatic potential obtained by B3LYP/6-311 is shown in figure 3.



#### Figure 3

#### V. CONCLUSIONS

In the present paper attempt has been made to predict proper frequency assignments to the compound 2,6CFB by the help of the Raman and IR spectra recorded experimentally. The equilibrium geometries and harmonic frequencies of the mentioned compound are calculated by DFT calculations using Gaussian 09W software and further these results are analysed and compared with the experimental results. The vibrational spectral results, the discussed thermodynamical functions and frontier molecular orbital studies provide sufficient results for the further detailed study of the compound on different parameters.

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