A DFT Study of the Conformational Behavior of N''-[1-(5-chloro-2hydroxyphenyl) ethylidene]- N'''-[(1-(2-hydroxy-5-methylphenyl) ethylidene] carbohydrazide

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Abstract- Conformational behavior of N''-[1-(5-chloro-2hydroxyphenyl) ethylidene]-N'''-[(1-(2-hydroxy-5-methyl phenyl) ethylidene] carbohydrazide molecule is reported. Molecule has been studied employing the technique of density function theory. Three main conformers arising due to rotation of one of the benzene ring about C-C single bond has been predicted. The s-trans conformer with –OH groups trans to each other was found to be of lowest energy while s-cis conformer was found to be of highest energy. The gauche conformer with one benzene ring almost perpendicular to the plane of the molecule was found to be of intermediate energy. Complete geometry of the s-trans conformer its vibrational frequencies along with their assignments is reported. The IR spectrum of the ligand L is also reported and it was found that theoretical calculations matches well with experimental values within the acceptable range. The structural parameter table is also given in which our theoretical calculations matches well with reported bond length. Nature of frontier molecular orbitals has been discussed and band gap has been calculated.

Index Terms- DFT, Conformational analysis, Schiff base, Vibrational analysis, Band Gap, FMO, Ligand.

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1 INTRODUCTION

Azomethines (known as Schiff-bases), having imine group (HC=N) are important class of ligand in coordination and catalytic chemistry due to their synthetic flexibility, selectivity and sensitivity toward a variety of metal atoms [1]. They are found useful in catalysis, in medicine as antibiotic and anti-inflammatory agents [2-3]. The metal complexes of Schiff bases derived from heterocyclic compounds have been the center of attraction for many workers in recent years. Tetra-dentate Schiff bases synthesized by reacting hydroxyl aromatic aldehydes and ketones with ethylene diamine and carbohydrazide are important since their metal complexes are commercial catalysts for epoxidation of alkenes and styrene [4-7]. Epoxides are valuable commercial commodity for production of polymers and perfumes. A very important advantage attached with these catalysts is that by using chiral amine, one can prepare chiral Schiff base and thus chiral metal Schiff base complex which can be used as chiral catalyst for production of chiral epoxides and their derivatives [8].

In recent years, density functional theory (DFT) has been a shooting star in theoretical modeling. The development of better and better exchange –correlation functional made it possible to calculate many molecular properties with comparable accuracy to traditional correlated *ab initio* methods, with more favorable computational cost. Literature survey revealed that the DFT has a great accuracy in reproducing the experimental values in geometry, dipole moment vibra-

tional frequencies and so on. [9-26]

Although, Schiff bases are playing important role in the field of coordination chemistry, catalysis and medicines and there are reports on the theoretical study of many Schiff bases, to the best of our knowledge there is no report on the conformational behavior of N''-[1-(5-chloro-2hydroxyphenyl)ethylidene]-N'''-[(1-(2-hydroxy-5-methylphenyl) ethylidene] carbohydrazide (L) molecule employing the technique of density function theory. The present problem was therefore undertaken with the objectives of (1) predicting the possible conformers of the molecule, by performing quantum mechanical computations of the molecule at DFT level (2) to report the optimized geometry of the most stable conformer along with its dipole moment (3) to assign the vibrational spectra of the molecule and to discus the nature of few important frontier molecular orbitals and to report the band gap. It is worth mentioning that geometry calculations at DFT level are superior to that obtained by single crystal method in the sense that position of hydrogen atoms, which posses poor sensitivity to x-rays, can be calculated accurately by DFT method.

2. Computational Details-

The DFT calculation with a hybrid functionals B3LYP (Becke's three parameter hybrid functional using the LYP correlation functional) at 6-311G d,p basis set by the berny method were performed with the Gaussian 09W software package [27-28]. The calculated vibrational frequencies as-

certained that the structure is stable (no imaginary frequencies). All calculations were performed on a Pentium IV processor personal computer without any constrain on the geometry.

3. RESULTS AND DISCUSSION

3.1. Conformational properties. The conformational properties of the molecule are listed in Table-1.

Table-1 Conformational properties of the N"-[1-(5-chloro-2hydroxyphenyl) ethylidene]- N"'-[(1-(2-hydroxy-5-methylphenyl) ethylidene] carbohydrazide molecule

Conformer	Energy (a.u.)	Band Gap (ev)	Dipole Moment (Debye)
s-Cis	-1601.43	2.37	8.31
s-Trans	-1601.84	4.16	8.84
Gauche	-1601.83	4.49	6.78

Three conformations namely s-cis, s-trans and gauche are identified possessing energies of - 1601.43 a.u., -1601.84 a.u. and -1601.83 a.u. are shown in Figure 1. In the s- cis conformer both OH bonds are cis to each other while in s-trans conformer both OH bonds are trans to each other. In the gauche conformer the 2H5CA group is almost at a dihedral angle of 113.48° with respect to plane of the molecule and the gauche-trans conformational energy difference is 6.27 kcal mol^{-1}. S-Trans conformers with a dipole moment of 8.84 D are found to more polar than s-cis (8.31 D) and gauche conformer with dipole moment of (6.78 D) is found to be least polar. The band gap was calculated as difference of LUMO-HOMO for the three conformers, s-cis, s-trans, gauche and was found to be 2.37 eV, 4.16 eV and 4.49 eV respectively.
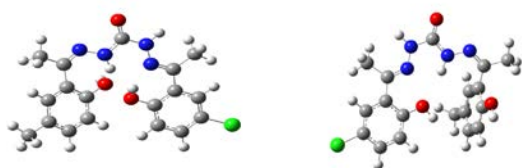
(A) s-Cis   **(B) Gauche**
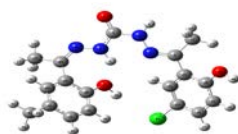
(C) s-Trans

Figure-1 Optimizes Geometry of Different Conformers of N"-[1-(5-chloro-2hydroxyphenyl) ethylidene]-N"'-[(1-(2-hydroxy-5-methylphenyl) ethylidene] carbohydrazide.

3.2. Geometrical parameters.

Selected bond lengths (Å) and bond angles (°) obtained from the geometry optimizations are listed in Table 2. Although in the initial geometry the two hydroxyl groups were cis to each other, in the optimized geometry, they posses trans positions. This has resulted due to rotation of one of the aromatic ring about C-C single bond.

Bond length/ Å	Cis	Gauche	Trans	Bond Angle / °	Cis	Gauche	Trans
C_1-N_3	1.41	1.41	1.41	C_1-N_3-H_4	113.8	115.6	114.9
C_1-O_2	1.24	1.24	1.24	C_1-N_5-H_6	119.8	116.79	119.2
C_1-N_5	1.36	1.37	1.37	H_4-N_3-N_7	123	124.4	127.5
N_3-H_4	1.01	1.01	1.01	H_6-N_5-N_8	117.6	124.8	120.9
N_3-N_7	1.36	1.36	1.35	C_9-C_{11}-H_{12}	110.2	110.6	111.2
N_5-H_6	1.02	1.02	1.01	C_9-C_{11}-H_{13}	111.7	114.7	111.7
N_5-N_8	1.38	1.36	1.38	C_9-C_{11}-H_{14}	112.2	112.2	110.1
N_7=C_9	1.3	1.3	1.3	C_{10}-C_{15}-H_{16}	111	110.8	110.6
N_8=C_{10}	1.3	1.29	1.29	C_{10}-C_{15}-H_{17}	112.4	111.5	112
C_9-C_{19}	1.48	1.48	1.48	C_{10}-C_{15}-H_{18}	108.5	109.3	109
C_{10}-C_{28}	1.49	1.49	1.49	C_{28}-C_{29}-C_{32}	118.4	118.4	118.3
C_9-C_{11}	1.51	1.51	1.5	C_{19}-C_{21}-H_{24}	119.5	120.2	117.6
C_{10}-C_{15}	1.51	1.51	1.51	C_{21}-C_{19}-C_{20}	116.4	116.2	117.1
C_{11}-H_{13}	1.09	1.08	1.08	C_{19}-C_{20}-C_{22}	121.6	120.8	121
C_{11}-H_{12}	1.09	1.09	1.09	C_{20}-C_{22}-C_{25}	120.9	121.6	121
C_{11}-H_{14}	1.09	1.09	1.09	C_{20}-C_{22}-H_{26}	119.3	118.9	119.5
C_{15}-H_{16}	1.09	1.09	1.09	C_{22}-C_{25}-H_{27}	121	121	120.9
C_{15}-H_{17}	1.09	1.09	1.09	C_{22}-C_{25}-C_{23}	117.8	117.8	117.6
C_{15}-H_{18}	1.09	1.09	1.09	C_{25}-C_{23}-Cl_{41}	119.1	119.3	119.4
C_{19}-C_{20}	1.41	1.42	1.4	C_{25}-C_{23}-C_{21}	121.8	121.8	122.2
C_{19}-C_{21}	1.41	1.41	1.4	C_{23}-C_{21}-H_{24}	119.1	117.9	121.4
C_{20}-O_{39}	1.41	1.38	1.39	C_{20}-O_{39}-H_{40}	111.4	111.9	111.6
C_{20}=C_{22}	1.39	1.4	1.4	C_{19}-C_{20}-O_{39}	119.9	119.6	118.4
C_{21}-H_{24}	1.08	1.08	1.08	C_{28}-C_{30}-O_{37}	119.1	116.9	117.5
C_{21}=C_{23}	1.38	1.38	1.38	C_{30}-O_{37}-H_{38}	113.3	112.2	111.8
C_{22}-H_{26}	1.08	1.08	1.08	C_{28}-C_{30}-C_{33}	120.8	120.54	121
C_{22}=C_{25}	1.39	1.39	1.39	C_{30}-C_{33}-H_{35}	118.9	119.7	119.6
C_{23}-C_{25}	1.39	1.38	1.39	C_{30}-C_{33}-C_{34}	120.7	120.1	120
C_{23}-Cl_{41}	1.82	1.82	1.83	C_{33}-C_{34}-H_{36}	119.7	119.3	119.3
C_{25}-H_{27}	1.08	1.08	1.08	C_{33}-C_{34}-C_{31}	120.3	120.8	120.7
C_{28}=C_{30}	1.41	1.4	1.4	C_{34}-C_{31}-C_{42}	120.9	120.9	120

$C_{28}=C_{29}$	1.41	1.4	1.4	$C_{31}-C_{42}-H_{45}$	111.4	111.4	111.4
$C_{29}=C_{31}$	1.39	1.4	1.4	$C_{31}-C_{42}-H_{43}$	111.3	111.3	111.4
$C_{29}-H_{32}$	1.08	1.08	1.08	$C_{31}-C_{42}-H_{44}$	111.4	111.4	111.3
$C_{30}-O_{37}$	1.39	1.38	1.4	$C_{31}-C_{29}-H_{32}$	118	118.9	118.7
Continued...							
$C_{30}=C_{33}$	1.4	1.4	1.39				
$C_{31}=C_{34}$	1.4	1.4	1.4				
$C_{31}-C_{42}$	1.51	1.51	1.51				
$C_{33}-H_{35}$	1.08	1.08	1.08				
$C_{33}=C_{34}$	1.39	1.39	1.39	Dihedral angle/^{0}	Cis	Gauche	Trans
$C_{34}-H_{36}$	1.08	1.08	1.08	$N8-C10-C28-C30$	-56.99	-113.48	-57.12
$O_{37}-H_{38}$	0.99	0.97	0.97	$N7-C9-C19-C20$	-0.49	-21.1	-155.02
$O_{39}-H_{40}$	0.97	0.98	0.97	$O_2-C_1-N_5-N_8$	11.21	7.93	11.23
$C_{42}-H_{43}$	1.09	1.09	1.09	$O_2-C_1-N_3-N_7$	-176.8	-174.8	-177.01
$C_{42}-H_{44}$	1.09	1.09	1.09	$O_2-C_1-N_3-H_4$	1.08	1.32	1.15
$C_{42}-H_{45}$	1.09	1.09	1.09	$O_2-C_1-N_5-H_6$	176.6	-178.5	176.6

The C_1-N_3 and C_1-N_5 bond lengths are 1.41 Å and 1.37 Å respectively suggesting C_1-N_3 bond to have slightly more double bond character. As expected $C_1=O_2$ is found to have its characteristic double bond character with the bond length of 1.24 Å and N_7-C_9 and N_8-C_{10} bonds are almost equal value of 1.30 Å . While all methyl C-H bonds are of almost equal value of (1.09 Å) the aromatic CH bonds are slightly lower (1.08 Å). Theoretical calculations with Gaussian 09 is expected to be superior to XRD method of computing location of hydrogen, because the scattered intensity which is proportional to the atomic number, is expected to be least for these atoms.

The most notable change exists in the orientation of the 2-hydroxy-5-chloroacetophenone (2H5CA) and 2-hydroxy-5-methyl acetophenone (2H5MA) ring in the L. The orientation of the ring is defined by torsional angle $N_8-C_{10}-C_{28}-C_{29}$ (-57.1°) and $N_7-C_9-C_{19}-C_2$ (-155.0°) in s-trans conformer.

3.3. Frontier Molecular Orbital study:

Frontier molecular orbitals play an important role in the electric and optical properties, as well as in UV-VIS spectra and chemical reactions [29]. Figure 2. shows the distribution and energy levels of HOMO-1, HOMO, LUMO, and LUMO +1 orbitals computed at B3LYP/6-31G level for L. As seen from Figure 2. HOMO is mainly localized on all the heavy atom of the molecule except methyl group and few atom of the 2H5CA and HOMO -1 is delocalized on the all the heavy atom except carbon of methyl group of 2H5MA. LUMO is mainly localized on all heavy atoms of carbohydrazide moiety as well as 2H5CA moiety while LUMO +1 is mainly localized on all the heavy atom of 2H5MA except methyl groups. The band gap for the molecule is found to be 4.16 eV. This large HOMO-LUMO gap suggests high excitation energies for many of excit-
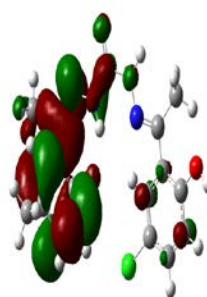
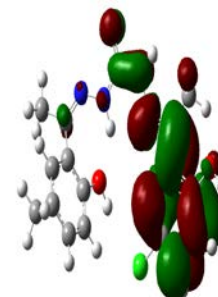ed states, a good stability and a high chemical hardness for ligand.
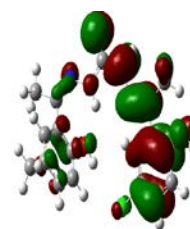
(A) HOMO-1(-6.03eV)   **(B) HOMO (-5.71eV)**

(C) LUMO (-1.55eV)   **(D) LUMO+1(-0.65eV)**

Figure-2 MO Diagram of s-Trans conformer of N''-[1-(5-chloro-2hydroxyphenyl) ethylidene]-N'''-[(1-(2-hydroxy-5-methylphenyl) ethylidene] carbonohydrazide

In the case of s-Cis isomer the situation is little different. HOMO-1 is mainly localized on benzene ring of both 2H5CA and 2H5MA moieties and few heavy atoms except Chlorine atom while, HOMO is mainly localized on 2H5MA moiety and few heavy atoms except methyl group as shown in Figure 3.

LUMO is mainly localized on 2H5CA moiety and N_3, N_7, O_2 atoms while, LUMO+1 is mainly localized on 2H5CA moiety and Cl_{41}, N_7 atoms.

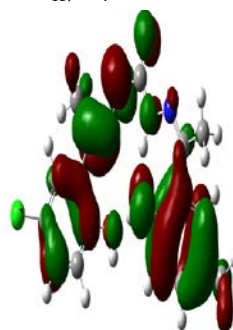(A) HOMO -1 (-6.21 eV)   (B) HOMO (-5.57 eV)

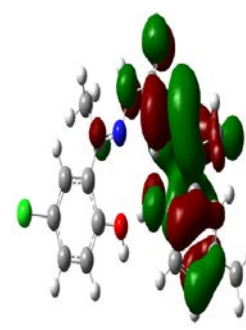(C) LUMO (-1.62 eV)   (D) LUMO+1(-0.94 eV)

Figure- 3 MO Diagram of s-Cis conformer of N"-[1-(5-chloro-2hydroxyphenyl) ethylidene]-N'''-[(1-(2-hydroxy-5-methylphenyl) ethylidene] carbonohydrazide molecule.
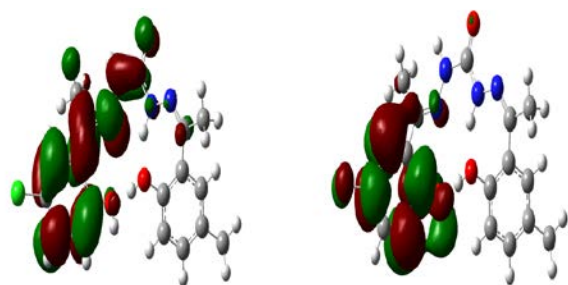
3.4. Vibration spectrum.
3.4.1 Light atom stretching modes.

The calculated IR spectrum is reproduced in Figure 4. and the assignment shown in Table 3. The assignments are made on the basis of pictorial movements of atoms during particular vibration and cartesian displacement. An inspection of Table 3 shows that -OH stretching (3669.8, 3632.6 cm^{-1}) and –NH stretching (3572.4, 3531.9 cm^{-1}) frequencies mostly depend up-on the movement of hydrogen atoms. The frequencies ap-peared at 3271.8 , 3248.7, 3209.5, 3206.1 , 3192.1 , 3189cm^{-1} are assigned to aromatic hydrogen stretching modes while those appeared at 3214.5 , 3167.9 , 3128.7 , 3098.9 , 3096.7 , 3076.5 , 3043.1 , 3035.3 , 3024.1 cm^{-1} are assigned to CH stretching modes of methyl groups.
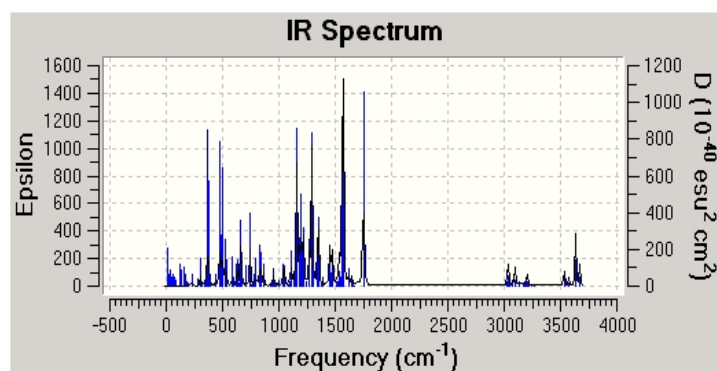
3.4.2 Heavy atoms stretching modes.

The frequencies appeared at 1750.5 cm^{-1} can be assigned to C=O stretching mode f carbonyl group while those frequen-cies appeared at 1671.4 and 1644 cm^{-1} can be assigned to C=N stretching mode. The last mode is highly interactive with benzene ring stretching mode.

S.No	Frequency	Force Constant (mdyn Å^{-1})	Assignment	S.No	Frequency	Force Constant (mdyn Å^{-1})	Assignments
1	3669.8	8.5	ν_{OH}	66	1033.3	1.6	β C-H
2	3632.6	8.3	ν_{OH}	67	999.4	2.8	ν_{N-N}
3	3572.4	8.1	ν_{NH}	68	978.9	0.7	β Cb-H
4	3531.9	7.9	ν_{NH}	69	964.7	0.7	β Cb-H
5	3271.8	6.9	$\nu_{CH(B)}$	70	949.5	0.7	β Cb-H
6	3248.7	6.8	$\nu_{CH(B)}$	71	934.46	0.7	β Cb-H
7	3214.5	6.6	$\nu_{asCH(M)}$	72	926.86	2.4	β Cb=Cb
8	3209.46	6.6	$\nu_{sCH(B)}$	73	865.16	2.8	β Cb=Cb
9	3206.1	6.6	$\nu_{asCH(B)}$	74	843.32	0.6	β Cb-H
10	3192.1	6.5	$\nu_{asCH(B)}$	75	826.3	0.6	β Cb-H
11	3189	6.5	$\nu_{asCH(B)}$	76	798.4	1.6137	Π Cb-H + Π N-H
12	3167.9	6.5	$\nu_{asCH(M)}$	77	782.1	1.7723	Π C-H
13	3128.7	6.3	$\nu_{asCH(B)}$	78	772	1.4	β Cb=Cb
14	3098.9	6.2	νC-H	79	753.7	1.1	β Cb=Cb
15	3096.7	6.2	νC-H	80	743.7	2.2	β C-O
16	3076.5	6.1	νC-H	81	738	1.8	β Cb=Cb
17	3043.1	5.7	νC-H	82	710.7	1.8	β Cb=Cb
18	3038.3	5.6	νC-H	83	674.64	0.4	Π N-H
19	3024.1	5.6	νC-H	84	659.5	1.1612	β Cb=Cb
20	1750.5	12	νC=O	85	656.8	1.7	ν C-Cl
21	1671.4	13	νC=N	86	640.6	0.8974	β Cb=Cb
22	1664.4	9.4	νCb=Cb	87	633.8	0.6532	β N-H
23	1662.6	12	νCb=Cb	88	624	0.78	β Cb=Cb
24	1649	9.6	νCb=Cb	89	597.6	0.7414	β Cb=Cb
25	1644	11	νC=N	90	580.6	0.4	β N-H
26	1618.1	9.4	νCb=Cb	91	540.4	0.5	β Cb=Cb
27	1572.1	2.4	β N-H	92	532.4	0.5436	β Heavy atom
28	1559.8	3	β N-H	93	521.4	0.4739	β Heavy atom
29	1552.2	2.4	β C-H	94	503.8	0.4169	Π Heavy atom
30	1540.1	1.7	β C-H	95	489.5	0.2589	Π O-H
31	1539.4	1.6	β C-H	96	479.3	0.518	β Heavy atom
32	1533.9	1.7	β C-H	97	474.5	0.7036	β Heavy atom

33	1533.5	1.4	β C-H	98	472.3	0.2541	Π Heavy atom
34	1529.6	1.4	β C-H	99	437.2	0.4075	β Heavy atom
35	1517.9	1.4	β C-H	100	389.3	0.5	β Heavy atom
36	1476.8	1.8	β N-H	101	374.9	0.22	ω O-H
37	1465.2	1.5	β C-H	102	371.4	0.34	β Heavy atom
38	1460.8	1.6	β C-H	103	362.7	0.12	ω O-H
39	1455.7	3.4	β CH	104	356.6	0.5	β Heavy atom
40	1454.5	1.8	β C-H	105	352.4	0.23	Π Heavy atom
41	1450.7	3.3	νCb=Cb	106	344.3	0.27	Π Heavy atom
42	1386.5	4.0	β C-H	107	321.8	0.22	Π CH3
43	1383.6	3.0	νCb=Cb	108	304.9	0.27	π Heavy atom
44	1351.9	3	νC-Cb	109	304.4	0.3	β Heavy atom
45	1349.6	2.1	β Cb-H	110	283.2	0.2	β Heavy atom
46	1341.9	1.7	β Cb-H	111	236.3	0.22	β Heavy atom
47	1310.2	4.4	νC-Cb	112	231.3	0.17	β Heavy atoms
48	1292.3	2.9	νCb-O	113	195.8	0.10	Π Heavy atoms
49	1287	2.9	νCb-O	114	178.6	0.02	τ me
50	1270.7	3.0	Mixed Vibration	115	165.7	0.04	τ me

51	1243	2.1	νCb-C	116	156.3	0.04	Π Heavy atom
52	1219	1.2	β Cb-H	117	153.5	0.06	Π Heavy atom
53	1208.3	1.0	β Cb-H	118	133.4	0.03	τ me
54	1190.4	2.0	β N-H	119	124.6	0.02	τ me
55	1179.3	1.6	β O-H	120	118.3	0.01	τ me
56	1159.3	1.4	β O-H	121	115.3	0.04	r me
57	1151.6	1.9	β N-H	122	83.4	0.02	N-C-N bending
58	1128.4	2	β C=C	123	69.6	0.01	π ring
59	1114.7	1.7	β C=C	124	56.2	0.008	τ me
60	1105.6	1.7	β C=C	125	50.1	0.01	τ phenyl
61	1100.9	1.0	β C-H	126	34.5	0.004	τ phenyl
62	1089	1.0	β C-H	127	28.4	0.0007	τ me
63	1088.3	1.0	β C-H	128	23.6	0.0006	τ me
64	1049.4	0.9	β C-H	129	17.3	0.001	τ phenyl
65	1045.4	1.7	β C-H				

3.4.3 Benzene ring vibrations.

The C-C ring stretching modes which can be correlated to 8a, 8b, 19a, 10b, 14 and 1 modes of benzene in Wilson's notation are assigned in case of most of the vibrational analysis of benzene derivatives to frequencies at 1600, 1585, 1485, 1430, 1375 and 1000 cm⁻¹. In the present case frequencies calculated at. 1664.4, 1662.6, 1649, 1618, 1450.7, 1386.5, 1351.9, 1349.6, 1341.9, 1310.2, 926.8, 865.1 cm⁻¹ are assigned to C-C ring stretching vibrations.

3.4.4 Methyl group bending frequencies.

Most of the vibrations calculated in the range of 1533-1000 cm⁻¹ are assigned to different C-H bending modes and whose below 1000 cm⁻¹ are assigned to out of plane C-H bending modes and heavy atom bends. Torsional modes are computed to be below 200 cm⁻¹. Most of the heavy atom vibrations are mixed. Complete assignments are shown in Table 3. Complete Table showing Cartesian displacement can be supplied on demand.

4 CONCLUSION

A structural and spectral study of the present molecule is performed. Conformational behavior of molecule is also studied using Gaussian 09 suite and DFT formalism. The all theoretical calculations are in close agreement with reported or experimental values. The s-trans conformer is found to be of lowest energy with a band gap of 4.16 eV. Complete geometrical parameters, vibrational frequencies along with their assignments are reported for the s-trans conformer.

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