



Structural and Vibrational studies on (E)-1-(4-methoxybenzylidene) Semicarbazide (MBSC) using experimental and DFT methods

KEYWORDS

FT-IR, FT-Raman, TED, MBSC, anharmonicity

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ABSTRACT FT-IR, FT-Raman spectra were recorded for the MBSC compound in the solid state. The equilibrium geometries, harmonic vibrational frequencies, FT-IR and FT-Raman scattering intensities were computed using the Gaussian 03 package. Computations were made using density functional theory (DFT) with B3LYP/6-311++G (d, p) basis set level. The optimized geometrical parameters obtained from DFT calculations are in good agreement with the reported single crystal XRD data of the same molecule. Results obtained were used for a detailed interpretation of the Infrared, Raman based on the total energy distribution (TED) of the normal modes.

Introduction

The benzylidene derivatives are intermediates in various pharmaceuticals, agro chemicals and perfumes. Semicarbazones known to have antiviral, antibacterial and antifungal effects in the field of medicine, pest control and used as drugs to cure diseases.

Experimental details

Synthesis

The 2.1 mL (0.025mol) ethanolic solution of anisaldehyde was added to (0.025mol) 2.8 g of Semicarbazide hydrochloride. The reaction mixture was taken in a round bottom flask and kept over a magnetic stirrer and stirred well in ice cold condition for two hours. The white precipitate obtained was filtered and dried over vacuum. The product was recrystallized from absolute alcohol.

Spectroscopic studies

The FT-IR spectrum of MBSC was recorded in the region 400-4000 cm^{-1} on Shimadzu spectrometer using a KBr pellet technique, which was carried out from the Instrumentation laboratory, Jamal Mohamed College, Tiruchirapalli, Tamilnadu. The FT-Raman spectrum of MBSC has been recorded using 1064nm line of Nd: YAG laser as excitation wavelength in the region 50-4000 cm^{-1} on Bruker RFS27 model spectrometer at the spectral resolution of 2 cm^{-1} carried out from SAIF laboratory, IIT(M), Tamilnadu, India. The ultraviolet absorption spectrum of MBSC is examined in the range of 200-500nm using Perkin Elmer Lambda 35 spectrometer. The UV pattern is taken from a 10^{-5} molar solution of MBSC dissolved in methanol and the report was taken from ACIC, St. Joseph's College, Tiruchirapalli, Tamilnadu.

Molecular geometry

The molecular geometry of (E)-1-(4-methoxybenzylidene) semicarbazide (MBSC) was studied by the B3LYP/6-311++G (d, p) level of calculation. The geometrical parameters such as bond length, bond angles and dihedral angle are plays a vital role in the formation of molecular structure and its properties. In order to understand the molecular geometry of MBSC, the title molecule was compared with the literature [1]. The bond length of C1-C₂, C₂-C₃, C₃-C₄, C₄-C₅, C₅-C₆, and C₁-C₆ are calculated as 1.406, 1.401, 1.390, 1.401, 1.400 and 1.385Å respectively and the respective corresponding recorded values (XRD) are about 1.395, 1.396, 1.383, 1.382, 1.392 and 1.372 Å [1]. The bond length of ring carbon-

carbon C-C bond coincides well with literature values. The bond length of methoxy group oxygen with carbon ring lies about 1.361 Å and the recorded value appeared at 1.372 Å [a]. Similarly the bond length between oxygen and methyl group lies about 1.423Å^o and the XRD value appeared at 1.437 Å. The bond-length recorded for C=N and C-N were about 1.280 and 1.371 Å, its calculated bond length were lies in the ranges of 1.283 and 1.392Å^o respectively. The bond N-N being as fuse between C=N and C-N was calculated and recorded about 1.392 and 1.371 Å, which is coincided well with each other. Due to the electron density in C-NH₃ and C=O the bond length of the same decreases when compare with bond group. In evident with this the C₂₁=O₂₂ and C₂₁-N₂₃ bond length lies about 1.220 and 1.364 Å which were recorded about 1.241 and 1.336 Å respectively.

The bond angle of methoxy group with the benzene ring (C-O-C) is calculated as 118.87° and the recorded value of the same was about 117.38°, it shows a good consent with gas phase molecule.

Similarly the calculated and recorded bond angles of N₁₉-C₂₁-O₂₂ and O₂₂-C₂₁-N₂₃ are shown very good agreement with each other. The optimized molecular structure of MBSC is shown in fig. 1 and the calculated bond parameters are presented in Table.

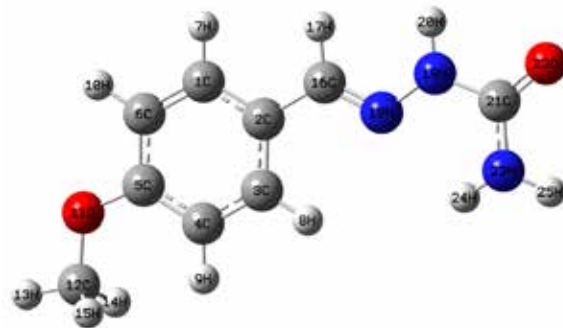


Fig.1 Optimized molecular structure of MBSC

Table 1. The bond parameters of MBSC using B3LYP/6-311++ G(d,p) level.

Parameters	Bond length Å	x-ray diffraction
C1-C2	1.406	1.395
C1-C6	1.385	1.372
C1-H7	1.085	0.93
C2-C3	1.401	1.396
C2-C16	1.461	1.372
C3-C4	1.390	1.383
C3-H8	1.083	0.93
C4-C5	1.401	1.382
C4-H9	1.082	0.93
C5-C6	1.400	1.392
C5-O11	1.361	1.372
C6-H10	1.083	0.93
O11-C12	1.423	1.437
C12-H13	1.089	0.96(A)
C12-H14	1.095	0.96(B)
C12-H15	1.095	0.96(C)
C16-H17	1.097	0.93
C16-N18	1.283	1.280
N18-N19	1.356	1.382
N19-H20	1.016	0.893
N19-C21	1.392	1.371
C21-O22	1.220	1.241
C21-N23	1.364	1.386
N23-H24	1.007	0.899
N23-H25	1.005	0.899
Parameters	Bond angle (°)	
C2-C1-C6	121.34	120.7
C2-C1-H7	119.50	119.7
C6-C1-H7	119.16	119.7
C1-C2-C3	117.96	117.78
C1-C2-C16	119.22	120.7
C3-C2-C16	122.83	
C2-C3-C4	121.31	121.8
C2-C3-H8	119.19	119.1
C4-C3-H8	119.51	119.1
C3-C4-C5	119.88	
C3-C4-H9	119.22	120.3
C5-C4-H9	120.90	
C4-C5-C6	119.50	
C4-C5-O11	124.56	
C6-C5-O11	115.93	
C1-C6-C5	120.01	120.8

C1-C6-H10	121.29	119.6
C5-C6-H10	118.70	
C5-O11-C12	118.87	117.38
O11-C12-H13	105.76	
O11-C12-H14	111.36	
O11-C12-H15	111.37	
H13-C12-H14	109.34	
H13-C12-H15	109.34	
H14-C12-H15	109.58	
C2-C16-H17	116.36	119.29
C2-C16-N18	123.13	122.91
H17-C16-N18	120.51	
C16-N18-N19	118.04	115.36
N18-N19-H20	121.76	118.7
N18-N19-C21	122.68	120.35
H20-N19-C21	115.55	119.9
N19-C21-O22	120.25	119.26
N19-C21-N23	114.78	
O22-C21-N23	124.97	124.21
C21-N23-H24	119.96	121.1
C21-N23-H25	116.87	120.9
H24-N23-H25	120.42	116.4
Parameters	Dihedral angle (°)	
C6-C1-C2-C3	-0.06	
C6-C1-C2-C16	179.98	
H7-C1-C2-C3	179.95	
H7-C1-C2-C16	-0.01	
C2-C1-C6-C5	0.01	
C2-C1-C6-H10	-180.00	
H7-C1-C6-C5	-180.00	
H7-C1-C6-H10	0.00	
C1-C2-C3-C4	0.06	
C1-C2-C3-H8	-179.86	
C16-C2-C3-C4	-179.98	
C16-C2-C3-H8	0.10	
C1-C2-C16-H17	0.67	
C1-C2-C16-N18	-179.30	
C3-C2-C16-H17	-179.29	
C3-C2-C16-N18	0.74	
C2-C3-C4-C5	-0.02	
C2-C3-C4-H9	-179.98	
H8-C3-C4-C5	179.90	
H8-C3-C4-H9	-0.06	
C3-C4-C5-C6	-0.03	
C3-C4-C5-O11	180.00	

H9-C4-C5-C6	179.93	
H9-C4-C5-O11	-0.04	
C4-C5-C6- C1	0.04	
C4-C5-C6-H10	-179.96	
O11-C5-C6- C1	-179.99	
O11-C5-C6-H10	0.01	
C4-C5-O11-C12	-0.02	
C6-C5-O11-C12	-179.99	
C5-O11-C12-H13	-179.97	
C5-O11-C12-H14	-61.29	
C5-O11-C12-H15	61.35	
C2-C16-N18-N19	179.95	
H17-C16-N18-N19	-0.02	
C16-N18-N19-H20	-1.10	
C16-N18-N19-C21	-179.57	
N18-N19-C21-O22	178.07	
N18-N19-C21-N23	-3.07	
H20-N19-C21-O22	-0.49	
H20-N19-C21-N23	178.38	
N19-C21-N23-H24	9.65	
N19-C21-N23-H25	170.93	
O22-C21-N23-H24	-171.55	
O22-C21-N23-H25	-10.27	

Vibrational analysis

The recorded FT-IR, FT-Raman and calculated wavenumbers along with their relative intensities and probable assignments with TED of the title molecule are given in Table 2. The calculated spectra are found to be close to the experimental values with reasonable accuracy. Comparison of the frequencies calculated at B3LYP with experimental values reveals the overestimation of the calculated vibrational modes due to neglect of anharmonicity in real system. Inclusion of electron correlation in density functional theory (DFT) to a certain extent makes the frequency values smaller in comparison with the 6-311++G (d, p) data.

C-C vibrations

The ring carbon-carbon stretching vibrations in benzene ring occur in the region 1625-1430 cm^{-1} . In general, the bonds are of variable intensity and are occur in the region 1625-1590, 1590-1575, 1540-1470, 1465-1430 and 1380 – 1280 cm^{-1} [2]. Krishnakumar [3] and Furic [4], reported the C-C stretching vibrations in the region 1625-1400 cm^{-1} . In the present investigation the frequencies computed by B3LYP method for the title molecule (MBSC) reported at 1580, 1542, 1486, 1392, 1286, 1231, 1202, 1088, 983, 837, 756 (mode nos: 14, 15, 17, 22, 25, 27, 28, 33, 36, 41, 44) have been assigned to C-C stretching vibrations.

The corresponding experimental observation appears in the FT-IR at 1604(vs), 833(ms), 766(ms) and the FT-Raman appears at 1580(ms), 1550(s), 1361(w), 1225(w), 869(w). This results exactly correlates with the theoretical data.

The in-plane bending vibrations are at higher wave numbers than the out-of-plane vibrations. Shimanouchi [5], assigned the wavenumber data for these vibrations for five different benzene derivatives as a result of normal coordinate analysis. In the present study, the theoretical calculation by B3LYP

method predicts the in-plane bending vibration at 983 cm^{-1} (mode no. 36). The C-C out-of-plane vibration assigned at 635 cm^{-1} (mode no.47) and 403 cm^{-1} (mode no.56) in B3LYP method and the corresponding experimental value shows at 628 (w), 405 cm^{-1} (w) / FT-Raman respectively. The shows the good agreement with literature [5].

C-H Vibrations

Substituted benzenes have large number of sensitive bands, i.e., bands whose position is significantly affected by the mass and electronic properties, mesomeric or inductive of the substituent. According to the literature [6,7], in infrared spectra, most mononuclear and polynuclear aromatic compounds have three or four peaks in the region 2900-3100 cm^{-1} , these are due to the stretching vibrations of the ring CH bands.

The aromatic C-H stretching vibrations are expected to appear in the range of 3100-3000 cm^{-1} with some weak bands. The vibrational bands in this region can not affect due to the substituent's [8, 9]. In the present study, FT-IR bands identified at 3184 (s), 3067 (ms) and FT-Raman bands at 3053 (w) assigned to C-H stretching vibrations of MBSC. In B3LYP/6-311++ G (d, p) method, the values calculated at 3082, 3071, 3065, 3037 and 2912 cm^{-1} . This shows the good agreement between the experimental and calculated values. In aromatic compounds, the presence of C-H in-plane bending vibration appears in the range of 1000-1300 cm^{-1} whereas the out-of-plane bending vibration lies at the range of 750-1000 cm^{-1} [2,10]. The FT-IR bands at 1252 (vs), 1133 cm^{-1} (ms) and the FT-Raman bands at 1361 (w), 1311(w), 1252(w), 1134 cm^{-1} (w) were assigned to C-H in-plane bending vibration of MBSC and the calculated frequency lies at 1392, 1320, 1279, 1144, 983 cm^{-1} (mode nos. 22, 24, 26, 30, 36). This shows the good agreement between experimental and calculated values. The shows the exact correlation between the experimentally accepted values (FT-IR /FT-Raman) and also good agreement with the calculated theoretical values.

The C-H out-of-plane bending vibrations of MBSC are identified at 539 cm^{-1} (vs) in the FT-IR and 775 (w) cm^{-1} , in the FT-Raman spectra whereas, the theoretically calculated frequencies observed at 933, 962, 810, 789, 702, 264 cm^{-1} from respective mode nos. 38, 39, 42, 43, 46, 59 and found to be well within the characteristic region as well as good agreement with the literature value [2,10].

C=O, C-O Vibrations

The characteristic infrared absorption frequency of C=O are normally strong in intensity and recorded in the region 1800-1690 cm^{-1} [11]. The position of C=O stretching is more effective to analyze the various factors in ring aromatic compounds. The C=O bond formed by π - π bond between C and O intermolecular hydrogen bonding, reduces the frequencies of the C=O stretching absorption to a great degree than intermolecular H bonding because of the different electro-negatives of C and O the bonding are not equally distributed between the two atoms. The lone pair of electrons on oxygen also determines the nature of the carbonyl groups. In evidence with this, carbonyl peak appeared at 1689 cm^{-1} as a strong band in FT-IR and DFT result assigned at 1706 cm^{-1} (mode no.12) with 69% of TED contribution.

The in-plane bending vibration of $\delta_{\text{C=O}}$ appeared at 595 (w) cm^{-1} / FT-Raman as a experimental value and the calculated value lies at 573 cm^{-1} (mode no. 49) and 507 cm^{-1} (mode no.52)

The calculated frequencies at 1231 cm^{-1} , 1015 cm^{-1} and the corresponding observed Raman values at 1225 (w), 1003 (ms) for $\nu_{\text{(C-O)}}$ coincide well with the assignment proposed by the literature [12]. The in-plane bending of $\delta_{\text{C-O}}$ contributes in the range between 507 and 178 (mode nos. 52, 55, 58, 61, 64) and the calculated out-of-plane values lies at 188, 105, 70 cm^{-1} (mode nos. 63, 65, 66).

C=N, C-N vibrations

The identification of C=N and C-N vibrations are very difficult task since the mixing of several bands are possible in this region [11]. The C=N stretching appears in the region 1600-1670 cm^{-1} [13], assigned at 1633 cm^{-1} (FT-IR) and 1625 cm^{-1} (FT-Raman) to aforementioned band. The C=N (aromatic) stretching mode appeared in the region 1490-1570 cm^{-1} [14].

In the present study, C=N bond stretching vibration is observed at 1647 cm^{-1} (as medium strong) in FT-IR spectrum and 1610 cm^{-1} (as very strong), 1311 (w) in the FT-Raman counterpart. The calculated C=N group frequency lies at 1606 cm^{-1} (mode no: 13) and 1320 (mode no: 24) using B3LYP/6-311++G (d, p) basis set, coincide well with the experimental data.

The in-plane bending vibration of $\delta_{\text{C=N}}$ observed as a mixed vibration of $\delta_{\text{H}^{17}\text{C}^{16}\text{N}^{18}}$ at 1311 cm^{-1} (w) in FT-Raman whereas the corresponding calculated frequency at 1320 cm^{-1} (mode no.24) with 25% of TED contribution.

The out-of-plane bending $\Gamma_{\text{C=N}}$ also contributes a mixed vibration of $\Gamma_{\text{N}^{19}\text{N}^{18}\text{C}^{16}\text{H}^{17}}$ (mode no: 39) is recorded as 925 as a calculated frequency with 30% of TED contribution.

C-N vibrations

Silverstein [11], assigned C-N stretching absorption in the region 1382-1266 cm^{-1} for aromatic amines. For the title compound MBSC, it is interesting to note that both the stretching vibration ($\nu_{\text{C-N}}$) and the in-plane bending vibration ($\delta_{\text{C-N}}$) occur in the same mode (mode no: 19), and the calculated frequency by B3LYP/6-311++G (d,p) is lies at 1438 cm^{-1} .

The out-of-plane bending lies in the mode numbers: 40, 45 and the respective calculated frequencies lies at 903, 722 cm^{-1} .

NH₂ vibrations

The NH₂ group gives rise to six internal modes of vibrations such as the asymmetric stretching (ν_{asy}), symmetric stretching (ν_{sy}), scissoring (δ_{s}), rocking (δ_{asy}), the symmetric non-planar

deformation (wagging) and the anti-symmetric non-planar deformation (torsion). The amino group (NH₂) stretching vibration usually appear in the range of 3500-3300 cm^{-1} (Dereli). The NH₂ group in PMSC molecule appears at 3413 cm^{-1} using FT-IR spectrum, whereas the same group was recorded for MBSC at 3454 cm^{-1} as a strong band by FT-IR spectrum. The computed frequencies for NH₂ group are about 3592 and 3460 cm^{-1} (mode no.1and2). The band at 3283 cm^{-1} was assigned to N-H stretching of hydrozone group, which is negatively deviated for the computed value of 3387 cm^{-1} at mode number 3.

The scissoring vibration of NH₂ group is appeared at 1510 cm^{-1} as strong and weak band using FT-IR and FT-Raman spectra respectively. The calculated wavenumber for this mode is about 1530 cm^{-1} (mode no.16).

Methyl group vibration

The methyl group produces nine vibrations, in which five in-plane and four out-of-plane vibrations. When the CH₃ group is directly attached to an oxygen atom, the C-H stretching and bending bands can shift the position due to electronic effects [15]. For aryl methoxy group, the methyl stretching bands occur in the region 3000-2815 cm^{-1} . The methyl group in MBSC molecule shows the symmetric stretching vibration at 2999 cm^{-1} as a medium band in FT-IR and 3003 cm^{-1} as weak band in FT-Raman spectrum. The asymmetric band for -OCH₃ in MBSC was recorded at 2929 cm^{-1} (FT-IR/medium). Their corresponding computed values are about 3015 and 2948 cm^{-1} (mode no: 8 and 9) for symmetric and asymmetric vibration respectively. The TED for methyl group is about 92% symmetric and 100% asymmetric [$\nu_{\text{C}^{12}\text{H}^{14}(50)}$, $\nu_{\text{C}^{12}\text{H}^{15}(50)}$].

The scissoring vibration of CH₃ was recorded at 1436 cm^{-1} using FT-IR spectrum. Its computed value lies at 1446 cm^{-1} (mode no.18). In mode 21, the wavenumber 1417 cm^{-1} for methyl scissoring appears as coupled vibration of δ_{HCO} , their recorded is about 1419 cm^{-1} . The above recorded and calculated values are moderately coincide with literature [15].

Table 2. Vibrational wavenumbers obtained for MBSC at B3LYP/6-311++G(d,p) [harmonic frequency (cm⁻¹), IR, Raman intensities (km/mol)].

Mode No.	Frequencies (cm ⁻¹)		Observed (cm ⁻¹)		Intensity		Red. Masses	Force Const.	Vibrational assignments TED \geq 10%
	Un scaled	scaled	FT-IR	FT-Raman	IR Rel.	Raman Rel.			
1	3738	3592			13.17	0.31	1.11	9.10	$\nu_{\text{N}^{23}\text{H}^{24}(62)}$, $\nu_{\text{N}^{23}\text{H}^{25}(39)}$,
2	3602	3460	3454s		3.58	1.07	1.04	7.99	$\nu_{\text{N}^{23}\text{H}^{24}(38)}$, $\nu_{\text{N}^{23}\text{H}^{25}(61)}$,
3	3526	3387	3283s		1.74	2.25	1.08	7.88	$\nu_{\text{N}^{19}\text{H}^{20}(100)}$,
4	3207	3082	3184s		1.00	1.08	1.09	6.63	$\nu_{\text{C}^{4}\text{H}^{9}(97)}$,
5	3196	3071			0.64	1.87	1.09	6.58	$\nu_{\text{C}^{1}\text{H}^{7}(69)}$, $\nu_{\text{C}^{6}\text{H}^{10}(30)}$,
6	3190	3065	3067ms	3053w	0.56	0.23	1.09	6.52	$\nu_{\text{C}^{1}\text{H}^{7}(30)}$, $\nu_{\text{C}^{6}\text{H}^{10}(70)}$,
7	3161	3037			1.38	0.75	1.09	6.41	$\nu_{\text{C}^{3}\text{H}^{8}(97)}$,
8	3138	3015	2999m	3003w	2.70	1.87	1.10	6.38	$\nu_{\text{C}^{12}\text{H}^{13}(92)}$,
9	3068	2948	2929m		4.47	0.75	1.11	6.14	$\nu_{\text{C}^{12}\text{H}^{14}(50)}$, $\nu_{\text{C}^{12}\text{H}^{15}(50)}$,
10	3031	2912			6.45	1.02	1.09	5.88	$\nu_{\text{C}^{16}\text{H}^{17}(100)}$,
11	3008	2890	2822m	2833w	7.87	2.44	1.03	5.51	$\nu_{\text{C}^{12}\text{H}^{14}(46)}$, $\nu_{\text{C}^{12}\text{H}^{15}(46)}$,
12	1775	1706	1689s		100	5.55	6.87	12.76	$\nu_{\text{C}^{21}=\text{O}^{22}(69)}$,
13	1671	1606	1647ms	1610vs	7.95	56.63	7.57	12.46	$\nu_{\text{C}^{16}=\text{N}^{18}(69)}$,
14	1645	1580	1604vs	1580ms	13.58	100	5.68	9.06	$\nu_{\text{C}^{3}\text{C}^{2}(11)}$, $\nu_{\text{C}^{4}\text{C}^{3}(17)}$, $\nu_{\text{C}^{6}\text{C}^{1}(23)}$,
15	1605	1542		1550s	1.85	5.67	6.75	10.25	$\nu_{\text{C}^{2}\text{C}^{1}(15)}$, $\nu_{\text{C}^{3}\text{C}^{2}(15)}$, $\nu_{\text{C}^{5}\text{C}^{4}(23)}$, $\nu_{\text{C}^{6}\text{C}^{5}(12)}$,
16	1592	1530	1510s	1510w	40.12	4.36	1.31	1.95	$\delta_{\text{H}^{25}\text{N}^{23}\text{C}^{21}(21)}$, $\delta_{\text{H}^{24}\text{N}^{23}\text{H}^{25}(55)}$,

17	1547	1486			10.83	2.94	2.63	3.70	$V_{C6C5(10)}$,
18	1505	1446	1436m		1.99	1.79	1.10	1.47	$\delta_{H14C12H15(47)}$,
19	1497	1438			27.06	3.34	1.81	2.39	$V_{C21N19(10)}$, $\delta_{H20N19N18(25)}$, $\delta_{H20N19C21(14)}$,
20	1493	1434			1.22	0.99	1.05	1.37	$\delta_{H13C12H14(35)}$, $\delta_{H13C12H15(35)}$, $\Gamma_{H13C12O11C5(14)}$,
21	1475	1417		1419w	1.52	0.32	1.20	1.54	$\delta_{HCO(45)}$, $\delta_{H13C12H14(16)}$, $\delta_{H13C12H15(16)}$, $\delta_{H14C12H15(14)}$,
22	1448	1392		1361w	1.72	1.52	3.03	3.74	$V_{C4C3(18)}$, $V_{C6C1(23)}$, $\delta_{C5C4H9(10)}$,
23	1401	1346	1358w		50.01	0.33	2.41	2.79	$V_{C21N19(18)}$, $V_{N23C21(22)}$, $\delta_{H20N19C21(12)}$, $\delta_{H24N23C21(13)}$,
24	1374	1320		1311w	5.19	1.94	1.49	1.66	$V_{N18C16(10)}$, $\delta_{H17C16C2(21)}$, $\delta_{H17C16N18(25)}$,
25	1338	1286			10.23	12.48	5.54	5.85	$V_{C3C2(13)}$, $V_{C5C4(18)}$, $V_{C6C5(13)}$,
26	1331	1279	1252vs	1252w	1.19	0.63	1.48	1.54	$\delta_{C2C1H7(12)}$, $\delta_{C6C1H7(13)}$, $\delta_{H10C6C1(11)}$,
27	1281	1231		1225w	48.12	0.62	4.09	3.95	$V_{C4C3(16)}$, $V_{O11C5(41)}$,
28	1251	1202			4.88	20.83	2.28	2.11	$V_{C16C2(30)}$,
29	1201	1154	1176ms	1171w	1.13	0.82	1.41	1.20	$\delta_{H13C12O11(47)}$,
30	1191	1144	1133ms	1134w	11.10	18.66	1.18	0.98	$\delta_{H8C3C2(13)}$, $\delta_{C4C3H8(14)}$, $\delta_{H9C4C3(12)}$,
31	1166	1121			0.09	0.25	1.27	1.02	$\delta_{H14C12O11(42)}$, $\delta_{H15C12O11(43)}$,
32	1164	1119	1103w	1105w	21.36	11.17	3.13	2.50	$V_{N19N18(55)}$,
33	1132	1088			4.23	2.03	1.43	1.08	$V_{C4C3(13)}$, $\delta_{C6C1H7(13)}$, $\delta_{H10C6C1(14)}$,
34	1093	1050	1027s		10.21	0.06	1.78	1.26	$\delta_{H24N23C21(28)}$, $\delta_{H25N23C21(33)}$,
35	1056	1015		1003ms	9.36	0.92	6.55	4.31	$V_{C12O11(77)}$,
36	1023	983			0.07	0.21	2.63	1.62	$V_{CC(33)}$, $\delta_{CCC(33)}$, $\delta_{HCC(32)}$
37	992	953			1.10	1.36	4.01	2.33	$V_{C21N19(22)}$, $V_{N23C21(42)}$, $\delta_{N19N18C16(11)}$,
38	971	933			0.07	0.08	1.35	0.75	$\Gamma_{C3C2C1H7(10)}$, $\Gamma_{H10C6C1H7(41)}$, $\Gamma_{C16C2C1H7(13)}$,
39	962	925			0.97	0.53	1.43	0.78	$\Gamma_{H9C4C3H8(13)}$, $\Gamma_{H17C16C2C3(17)}$, $\Gamma_{N19N18C16H17(30)}$,
40	940	903			1.11	0.40	1.38	0.72	$\Gamma_{H9C4C3H8(27)}$, $\Gamma_{N19N18C16H17(17)}$,
41	871	837	833ms	869w	0.27	2.01	4.98	2.23	$V_{C2C1(22)}$, $V_{C16C2(12)}$,
42	843	810			6.48	0.05	1.65	0.69	$\Gamma_{C5C6C1H7(14)}$, $\Gamma_{H10C6C1C2(17)}$, $\Gamma_{H10C6C5O11(21)}$, $\Gamma_{C16C2C1H7(12)}$,
43	821	789		775w	0.27	0.02	1.27	0.50	$\Gamma_{C5C4C3H8(12)}$, $\Gamma_{HCCC(28)}$, $\Gamma_{C6C5C4H9(13)}$, $\Gamma_{O11C5C4H9(21)}$,
44	787	756	766ms		1.70	4.25	4.83	1.76	$V_{C5C4(11)}$, $V_{O11C5(21)}$, $\delta_{C3C2C1(13)}$,
45	751	722			1.73	0.04	9.68	3.22	$\Gamma_{O22C21N19H20(17)}$, $\Gamma_{N23C21N19N18(13)}$, $\Gamma_{HNCO(40)}$,
46	730	702			0.04	0.32	3.95	1.24	$\Gamma_{CCCC(50)}$, $\Gamma_{HCCC(19)}$
47	661	635		628w	0.60	0.38	6.20	1.59	$\Gamma_{CCCC(17)}$
48	641	616	607ms		0.40	1.87	6.75	1.63	$\delta_{C4C3C2(11)}$, $\delta_{C2C1C6(11)}$, $\delta_{C1C6C5(13)}$,
49	596	573		595w	1.10	1.17	2.79	0.58	$\delta_{O22C21N23(20)}$,
50	560	538	539vs		2.05	0.34	1.27	0.23	$\Gamma_{H24N23C21N19(19)}$, $\Gamma_{HNCO(23)}$, $\Gamma_{H25N23C21N19(20)}$,
51	536	515			3.13	0.02	2.34	0.40	$\Gamma_{H10C6C5C4(10)}$,
52	527	507			4.27	0.10	3.30	0.54	$\delta_{C12O11C5(13)}$, $\delta_{O22C21N19(17)}$, $\delta_{O22C21N23(18)}$,
53	477	459		465w	4.13	0.44	5.18	0.69	$\Gamma_{H20N19N18C16(16)}$, $\Gamma_{O22C21N19H20(13)}$,
54	456	438		425w	11.89	0.39	1.09	0.13	$\Gamma_{H20N19N18C16(19)}$, $\Gamma_{O22C21N19H20(16)}$, $\Gamma_{N23C21N19H20(11)}$,
55	426	410			0.38	0.09	3.07	0.33	$\delta_{C12O11C5(12)}$, $\delta_{N23C21N19(16)}$,
56	419	403		405w	4.21	2.50	4.16	0.43	$\Gamma_{C5C4C3C2(16)}$,
57	398	383			0.34	0.94	5.32	0.50	$\Gamma_{C1C6C5O11(13)}$, $\Gamma_{C16C2C1C6(14)}$, $\Gamma_{N19N18C16C2(15)}$,
58	287	276			12.98	1.41	2.41	0.12	$\delta_{C6C5O11(14)}$, $\delta_{C12O11C5(16)}$,

59	275	264			0.27	0.14	4.23	0.19	$\Gamma_{H17C16C2C1(12)}$, $\Gamma_{H20N19N18C16(19)}$, $\Gamma_{N23C21N19N18(10)}$,
60	257	247			0.28	2.98	5.67	0.22	$\Gamma_{H13C12O11C5(25)}$, $\Gamma_{H14C12O11C5(23)}$, $\Gamma_{H15C12O11C5(22)}$,
61	247	238			3.31	0.66	1.47	0.05	$\nu_{C16C2(11)}$, $\delta_{C12O11C5(15)}$, $\delta_{N19N18C16(11)}$,
62	211	203			7.93	3.12	1.54	0.04	$\Gamma_{H24N23C21N19(14)}$, $\Gamma_{H24N23C21O22(11)}$, $\Gamma_{H25N23C21O22(11)}$,
63	196	188		198w	3.35	1.82	2.12	0.05	$\Gamma_{OCCC(11)}$, $\Gamma_{NCCC(12)}$
64	185	178			1.09	1.79	4.48	0.09	$\delta_{C12O11C5(10)}$, $\delta_{C3C2C16(11)}$, $\delta_{C21N19N18(17)}$,
65	109	105		130w	0.83	0.75	5.15	0.04	$\Gamma_{C12O11C5C4(26)}$, $\Gamma_{C12O11C5C6(31)}$,
66	73	70		96m	0.09	0.87	4.30	0.01	$\Gamma_{C12O11C5C4(13)}$, $\Gamma_{C12O11C5C6(21)}$, $\Gamma_{C21N19N18C16(22)}$,
67	63	60			0.20	6.71	5.50	0.01	$\delta_{C16C2C1(12)}$, $\delta_{C3C2C16(11)}$, $\delta_{N18C16C2(23)}$, $\delta_{N19N18C16(23)}$,
68	43	42			0.03	3.05	5.68	0.01	$\Gamma_{H17C16C2C1(14)}$, $\Gamma_{N19N18C16C2(11)}$, $\Gamma_{H20N19N18C16(18)}$, $\Gamma_{O22C21N19N18(21)}$, $\Gamma_{N23C21N19N18(24)}$,
69	34	33			0.01	3.62	4.34	0.00	$\Gamma_{N18C16C2C1(16)}$, $\Gamma_{N18C16C2C3(26)}$, $\Gamma_{C21N19N18C16(27)}$,

CONCLUSION

The molecular conformation, vibrational transitions of (E)-1-(4-methoxybenzylidene) Semicarbazide (MSPC) molecule was determined by DFT (B3LYP) method and 6-311++G(d,p) basis set. Optimized geometric structure was found to be good agreement with experimental results. The vibrational wavenumbers were calculated and the complete assignments were performed on the basis of the total energy distribution (TED) of the vibrational modes. The slight difference observed between the experimental and the calculated wavenumbers could be due to the fact that the calculations have been performed for single molecule in the gaseous state. Thus the assignments made at (B3LYP/6-311++G (d,p) level of theory with only reasonable deviations from the experimental values seem feasible.

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