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

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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 400-4000cm⁻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 2cm⁻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-methonybenzylidene) 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 angle of methoxy group with the benzene ring (C-O-C) is calculated as 118.87 o and the recorded value of the same was about 117.38 o, 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.

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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               |
| C12-C1     | 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 | 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            |
method predicts the in-plane bending vibration at 983 cm⁻¹ (mode no. 36). The C–O 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), 3061 (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=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 electron-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 δ(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 ν(C=O), coincide well with the assignment proposed by the literature [12]. The in-plane bending of δ(C=O) contributes in the range between 507 and 178 (mode nos. 52, 55, 58, 61, 64) and the calculated out-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 δC=N observed as a mixed vibration of δC=N 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 ΠC-N also contributes a mixed vibration of ΠN19N18C16H17 (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 (νC-N) and the in-plane bending vibration (δC-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 (νas), symmetric stretching (νs), scissoring (δs), rocking (δ), 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 3500-3300cm⁻¹ (Derei). The NH₂ group in PMSC molecule appears at 3413 cm⁻¹ using FT-IR counter, whereas the same group was recorded for MBSC at 3454 cm⁻¹ as a strong band by FT-Raman 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 any methoxy group, the methyl stretching bands occur in the region 3000-2815cm⁻¹. The methyl group in MBSC molecule shows the symmetric stretching vibration at 2999cm⁻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 [νC1H7(46), νC1H7(50)].

The scissoring vibration of CH₃ was recorded at 1436cm⁻¹ using FT-IR spectrum. Its computed value lies at 1446cm⁻¹ (mode no.18). In mode 21, the wavenumber 1417cm⁻¹ for methyl scissoring appears as coupled vibration of δC1H7, their computed value is about 1419 cm⁻¹. The above recorded and calculated values are moderately coincide with literature [15].

| Mode No. | Frequencies (cm⁻¹) | Observed (cm⁻¹) | Intensity | Red. Masses | Force Const. | Vibrational assignments |
|---------|-------------------|----------------|-----------|-------------|--------------|-----------------------|
|         | Un. scaled | scaled | FT-IR | FT-Raman | IR Rel. | Raman Rel. | TED≥10% |                 |
| 1       | 3738   | 3592  | 13.17 | 0.31   | 1.11   | 9.10 | νC2H4(42), νC2H4(39) |                 |
| 2       | 3602   | 3460  | 3.58  | 1.07   | 1.04   | 7.99 | νC2H4(31), νC2H4(31) |                 |
| 3       | 3526   | 3387  | 1.74  | 2.25   | 1.08   | 7.88 | νC1H6H25(100) |                 |
| 4       | 3207   | 3082  | 1.00  | 1.08   | 1.09   | 6.63 | νC4H9(12) |                 |
| 5       | 3196   | 3071  | 0.64  | 1.87   | 1.09   | 6.58 | νC1H7(18), νC1H7(33) |                 |
| 6       | 3190   | 3065  | 0.56  | 0.23   | 1.09   | 6.52 | νC1H7(13), νC1H7(17) |                 |
| 7       | 3161   | 3037  | 1.38  | 0.75   | 1.09   | 6.41 | νC4H8(12) |                 |
| 8       | 3138   | 3015  | 2.70  | 1.87   | 1.10   | 6.38 | νC1H7(32) |                 |
| 9       | 3068   | 2948  | 4.47  | 0.75   | 1.11   | 6.14 | νC1H7(31), νC1H7(31) |                 |
| 10      | 3031   | 2912  | 6.45  | 1.02   | 1.09   | 5.88 | νC1H7(10) |                 |
| 11      | 3008   | 2890  | 7.87  | 2.44   | 1.03   | 5.51 | νC2H4(34), νC2H4(34) |                 |
| 12      | 1775   | 1706  | 100   | 5.55   | 6.87   | 12.76 | νC2H(122) |                 |
| 13      | 1671   | 1606  | 7.95  | 56.63  | 7.57   | 12.46 | νC1H7(169), νC1H7(169) |                 |
| 14      | 1645   | 1580  | 15.58 | 100    | 5.68   | 9.06 | νC4H9(31), νC4H9(31), νC4H9(31) |                 |
| 15      | 1605   | 1542  | 1.85  | 5.67   | 6.75   | 10.25 | νC4H9(31), νC4H9(31), νC4H9(31) |                 |
| 16      | 1592   | 1530  | 40.12 | 4.36   | 1.31   | 1.95 | δC2H4(12), δC2H4(12), δC2H4(12) |                 |

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


|   |   |   |   |   |   |
|---|---|---|---|---|---|
| 17| 1547| 1486| 10.83| 2.94| 2.63|
| 18| 1505| 1446| 1.99| 1.79| 1.10|
| 19| 1497| 1438| 27.06| 3.34| 1.81|
| 20| 1493| 1434| 1.22| 0.99| 1.05|
| 21| 1475| 1417| 1.52| 0.32| 1.20|
| 22| 1448| 1392| 1.72| 1.52| 3.03|
| 23| 1401| 1346| 50.01| 0.33| 2.41|
| 24| 1374| 1320| 5.19| 1.94| 1.49|
| 25| 1338| 1286| 10.23| 12.48| 5.54|
| 26| 1331| 1279| 1.19| 0.63| 1.48|
| 27| 1281| 1231| 48.12| 0.62| 4.09|
| 28| 1251| 1202| 4.88| 20.83| 2.28|
| 29| 1201| 1154| 1171w| 1.13| 0.82| 1.41|
| 30| 1191| 1144| 1133ms| 11.10| 18.66| 1.18|
| 31| 1166| 1121| 0.09| 0.25| 1.27|
| 32| 1164| 1119| 21.36| 11.17| 3.13|
| 33| 1132| 1088| 4.23| 2.03| 1.43|
| 34| 1093| 1050| 10.21| 0.06| 1.78|
| 35| 1056| 1015| 9.36| 0.92| 6.55|
| 36| 1023| 983| 0.07| 0.21| 2.63|
| 37| 992| 953| 1.10| 1.36| 4.01|
| 38| 971| 933| 0.07| 0.08| 1.35|
| 39| 962| 925| 0.97| 0.53| 1.43|
| 40| 940| 903| 1.11| 0.40| 1.38|
| 41| 871| 837| 833ms| 0.27| 2.01| 4.98|
| 42| 843| 810| 6.48| 0.05| 1.65|
| 43| 821| 789| 775w| 0.27| 0.02| 1.27|
| 44| 787| 756| 766ms| 1.70| 4.25| 4.83|
| 45| 751| 722| 1.73| 0.04| 9.68|
| 46| 730| 702| 0.04| 0.32| 3.95|
| 47| 661| 635| 628w| 0.60| 0.38| 6.20|
| 48| 641| 616| 607ms| 0.40| 1.87| 6.75|
| 49| 596| 573| 595w| 1.10| 1.17| 2.79|
| 50| 560| 538| 539vs| 2.05| 0.34| 1.27|
| 51| 536| 515| 3.13| 0.02| 2.34|
| 52| 527| 507| 4.27| 0.10| 3.30|
| 53| 477| 459| 465w| 4.13| 0.44| 5.18|
| 54| 456| 438| 425w| 11.89| 0.39| 1.09|
| 55| 426| 410| 0.38| 0.09| 3.07|
| 56| 419| 403| 405w| 4.21| 2.50| 4.16|
| 57| 398| 383| 0.34| 0.94| 5.32|
| 58| 287| 276| 12.98| 1.41| 2.41|

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**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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