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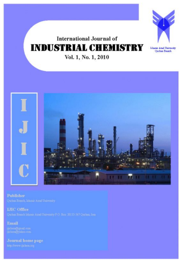

FT-IR, FT-Raman and Computational Study of Ethyl Methyl Ketone Semicarbazone

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ABSTRACT

FT-IR and FT-Raman spectra of ethyl methyl ketone semicarbazone were recorded and analyzed. The vibrational wavenumbers were computed using HF/6-31G*, B3PW91/6-31G* and B3LYP/6-31G* basis and compared with experimental data. The first hyperpolarizability, infrared intensities and Raman activities are reported. The calculated first hyperpolarizability is comparable with the reported values of similar derivatives and is an attractive object for future studies of non-linear optics. The extended π-electron delocalization over the carbazone moiety is responsible for the nonlinearity of the molecule. The geometrical parameters of the title compound are in agreement with that of similar derivatives. The red shift of the NH stretching wavenumber in the infrared spectrum from the computed wavenumber indicates the weakening of the NH bond resulting in proton transfer to the neighboring oxygen atom.

Keywords: DFT; FT-IR; FT-Raman; Hyperpolarizability; Semicarbazone

1. Introduction

Semicarbazones and thiosemicarbazones have been investigated due to interest in their coordination behaviour, analytical applications [1], and biological properties such as antibacterial [2], antimalarial [3], antifungal [4], and antitumor [5]. Because of their ease of preparation and rich and varies complexing abilities, semicarbazones represent a very interesting group of ligands to several main group metals of d and f-block elements [1,6-8]. Semicarbazones of aromatic and unsaturated carbonyl compounds have anticonvulsant properties and their advantage over the analogous thiosemicarbazones is their lower neurotoxicity [9]. Vanadium(V) complexes with salisilaldehyde semicarbazones derivatives show in vitro anti-tumor activity towards kidney tumor cells (TK-10) [10]. Leovac et al.[11] reported the physicochemical and structural characteristics of Ni(II) complexes with pyridoxal semicarbazones. Dimmock and Baker [12] reported the anticonvulsant activities of 4-bromo benzaldehyde semicarbazone. Jagst et al.[13]

studied the synthesis and structural characterization of lanthanide complexes with pentadentate asymmetric ligands system derived from 2,6-di-acetylpyridine or 2,6-diformyl pyridine with mixed semicarbazone /benzoyl hydrazone and semicarbazone/ thiosemicarbazone coordination sites. Semicarbazones [14, 15] and thiosemicarbazones [16,17] are biologically important nitrogen and oxygen/sulphur donor ligands. Computational method is at present widely used for simulating IR spectrum. Such simulations are indispensable tools to perform normal coordinate analysis so that modern vibrational spectroscopy is unimaginable without involving them. In the present study, the IR, Raman and theoretical calculations of the wavenumbers of the title compound are reported. Nonlinear optics deals with the interaction of applied electromagnetic fields in various materials to generate new electromagnetic fields, altered in wavenumber, phase, or other physical properties [18]. Organic molecules able to manipulate photonic signals efficiently are of importance in technologies such as optical communication, optical computing, and dynamic image processing [19, 20]. In this context, the hyperpolarizability of the title compound is also calculated in the present study.

2. Experimental

Semicarbazone of ethyl methyl ketone was synthesized from the starting materials of semicarbazide hydrochloride and ethyl methyl ketone using sodium acetate as catalyst. Semicarbazide hydrochloride and sodium acetate were dissolved in deionized water in the molar ratio 1:1.5 and then 0.5 M of ethyl methyl ketone was added to the solution. The mixture was stirred at room temperature for 1 hour, and the resultant precipitate was collected, dried and recrystalized from absolute ethanol (Yield-79%, M.P.138^{0}C).The CHN result agrees with the formula $C_5H_{11}N_3O$. Elemental analysis: calculated %:C, 46.50; H, 8.58; N, 32.53; found %: C, 46.48 ; H, 8.51 ; N, 32.03. The FT-IR spectrum (Fig. 1) was recorded on a DR/Jasco FT-IR-6300 spectrometer in KBr pellets. The spectral resolution was 4 cm^{-1}. The FT-Raman spectrum (Fig. 2) was obtained on a Bruker IFS 100/S, Germany. For excitation of the spectrum the emission of Nd:YAG laser was used, excitation wavelength 1064 nm, maximal power 150 mW, measurement on solid sample. The spectral resolution after apodization was 4 cm^{-1}.

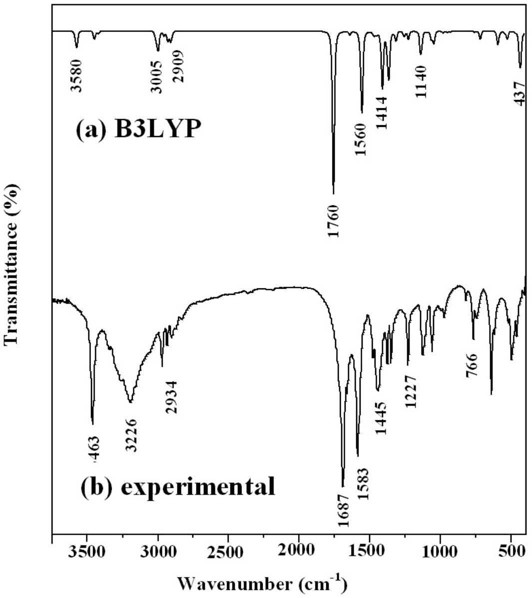

Fig. 1. FT-IR spectrum of ethyl methyl ketone semicarbazone (a) theoretical (b) experimental

3. Computational details

The vibrational wavenumbers were calculated using the Gaussian03 software package on a personal computer [21]. The computations were performed at HF/6-31G*, B3PW91/6-31G* and B3LYP/6-31G* levels of theory to get the optimized geometry (Fig. 3) and vibrational wavenumbers of the normal modes of the title compound. DFT calculations were carried out with Becke's three-parameter hybrid model using the Lee-Yang-Parr correlation functional (B3LYP) method. The wavenumber values computed contain known systematic errors and we therefore, have used the scaling factor values of 0.8929 and 0.9613 for HF and DFT basis sets [22]. Parameters corresponding to optimized geometry of the title compound (Fig. 3) are given in Tables 1-3.

The absence of imaginary values of wavenumbers in the calculated vibrational spectrum confirms that the structure deduced corresponds to minimum energy. The assignment of the calculated wavenumbers is aided by the animation option of MOLEKEL program, which gives a visual presentation of the vibrational modes [23, 24].

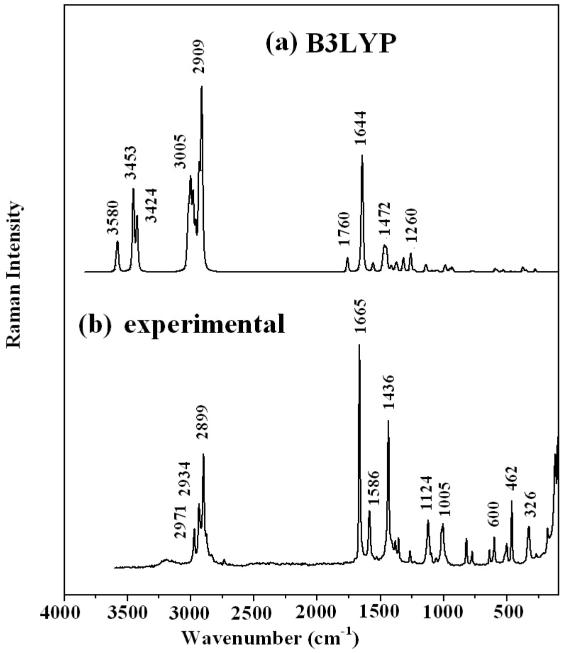

Fig. 2. FT-Raman spectrum of ethyl methyl ketone semicarbazone (a) theoretical (b) experimental

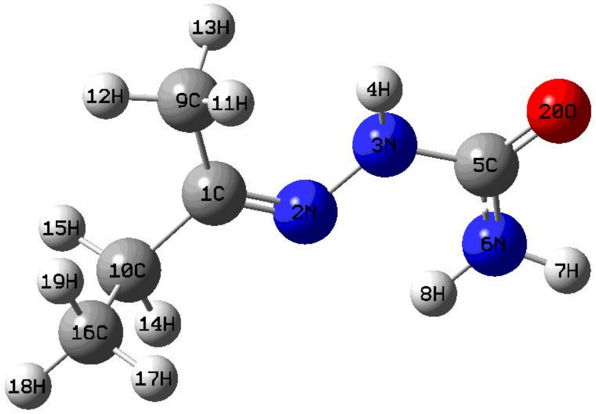

Fig. 3. Optimized geometry (B3LYP) of ethyl methyl ketone semicarbazone

4. Results and discussion

4. 1. IR and Raman spectra

The observed IR and Raman bands with their relative intensities and calculated (scaled) wavenumbers and assignments are given in Table 4. The carbonyl stretching C=O vibration [25,26] is expected in the region 1715-1680 cm^{-1} and in the present study this mode appears at 1687 cm^{-1} in the IR spectrum. The DFT calculations give this mode at 1760 cm^{-1}. The deviation of the calculated wave number for this mode can be attributed to the under estimation of the large degree of their π-electron delocalization due to conjugation of the molecule [27]. The intensity of the carbonyl group vibration can increase because of conjugation or formation of hydrogen bonds. The increase in conjugation, therefore, leads to the increase in the intensity of infrared bands. The conjugation and influence of inter molecular hydrogen bonds result in the lowering of the stretching wave numbers. The δ C=O in-plane deformation and the out-of-plane deformation γC=O are expected in the regions 625 ± 70 and 540 ± 80 cm^{-1} respectively [25]. The band observed at 617 cm^{-1} in the IR and 600 and 521 cm^{-1} in Raman spectrum are assigned as C=O deformation modes. The theoretically calculated values are 596 and 548 cm^{-1}.

Table 1. Bond lengths of the title compound, atom labeling according to fig. 3.

Bond lengths (Å)	HF/631G*	B3PW91/6-31G*	B3LYP/6-31G*
C_1-N_2	1.2583	1.2858	1.2868
C_1-C_9	1.5125	1.5068	1.5120
C_1-C_{10}	1.5089	1.5047	1.5094
N_2-N_3	1.3619	1.3544	1.3642
N_3-H_4	0.9963	1.014	1.0147
N_3-C_5	1.3765	1.3929	1.3971
C_5-N_6	1.3509	1.3628	1.3678
C_5-O_{20}	1.2019	1.2215	1.2230
N_6-H_7	0.9932	1.0069	1.0082
N_6-H_8	0.9930	1.0098	1.0106
C_9-H_{11}	1.0874	1.0993	1.0994
C_9-H_{12}	1.0819	1.0928	1.0927
C_9-H_{13}	1.0857	1.0988	1.0985
C_{10}-H_{14}	1.0826	1.0948	1.0945
C_{10}-H_{15}	1.0879	1.1002	1.1001
C_{10}-C_{16}	1.5333	1.5336	1.5392
C_{16}-H_{17}	1.0850	1.0954	1.0955
C_{16}-H_{18}	1.0848	1.0955	1.0955
C_{16}-H_{19}	1.0856	1.0962	1.0963

Table 2. Bond angles of the title compound, atom labeling according to fig. 3.

Bond angles (°)	HF/631G*	B3PW91/6-31G*	B3LYP/6-31G*
A(2,1,9)	124.1	123.7	123.7
A(2,1,10)	117.4	117.1	117.1
A(9,1,10)	118.5	119.2	119.1
A(1,2,3)	119.3	119.1	119.0
A(2,3,4)	121.1	122.8	122.5
A(2,3,5)	120.6	121.6	121.3
A(4,3,5)	113.9	114.7	114.4
A(3,5,6)	115.6	114.3	114.4
A(3,5,20)	120.2	120.3	120.3
A(6,5,20)	124.2	125.4	125.3
A(5,6,7)	116.2	116.1	115.7
A(5,6,8)	120.3	118.6	118.2
A(7,6,8)	119.5	119.6	119.2
A(1,9,11)	111.5	111.9	111.9
A(1,9,12)	111.0	111.3	111.3
A(1,9,13)	110.7	111.0	111.0
A(11,9,12)	107.6	107.4	107.4
A(11,9,13)	107.9	107.3	107.3
A(12,9,13)	108.1	107.7	107.8
A(1,10,14)	108.2	108.1	108.1
A(1,10,15)	108.9	109.0	109.0
A(1,10,16)	112.9	113.3	113.4
A(14,10,15)	107.5	107.2	107.3
A(14,10,16)	109.9	110.0	109.9
A(15,10,16)	109.4	109.1	109.0
A(10,16,17)	110.7	110.8	110.8
A(10,16,18)	110.4	110.6	110.6
A(10,16,19)	111.9	111.9	111.8
A(17,16,18)	108.1	108.1	108.1
A(17,16,19)	109.0	107.8	107.9
A(18,16,19)	107.6	107.5	107.6

Table 3. Dihedral angles of the title compound, atom labeling according to fig. 3.

Dihedral angles (°)	HF/631G*	B3PW91 /6-31G*	B3LYP/ 6-31G*
D(9,1,2,3)	0.2	0.5	0.4
D(10,1,2,3)	-179.6	-179.3	-179.4
D(2,1,9,11)	-68.2	-64.6	-65.3
D(2,1,9,12)	171.9	175.2	174.5
D(2,1,9,13)	51.9	55.3	54.4
D(10,1,9,11)	111.6	115.2	114.5
D(10,1,9,12)	-8.3	-5.0	-5.7
D(10,1,9,13)	-128.3	-124.9	-125.8
D(2,1,10,14)	-10.1	-9.6	-9.7
D(2,1,10,15)	-126.6	-125.8	-126.0
D(2,1,10,16)	111.7	112.5	112.4
D(9,1,10,14)	170.1	170.6	170.5
D(9,1,10,15)	53.5	54.4	54.2
D(9,1,10,16)	-68.1	-67.3	-67.4
D(1,2,3,4)	20.0	8.8	12.1
D(1,2,3,5)	174.8	177.6	175.9
D(2,3,5,6)	14.6	8.9	11.6
D(2,3,5,20)	-167.6	-173.2	-170.9
D(4,3,5,6)	171.1	178.5	176.6
D(4,3,5,20)	-11.1	-3.5	-5.8
D(3,5,6,7)	-171.8	-167.7	-166.9
D(3,5,6,8)	-14.2	-14.3	-16.3
D(20,5,6,7)	10.5	14.5	15.7
D(20,5,6,8)	168.1	167.9	166.3
D(1,10,16,17)	-60.6	-61.1	-61.0
D(1,10,16,18)	179.7	179.1	179.1
D(1,10,16,19)	59.9	59.3	59.3
D(14,10,16,17)	60.2	59.9	60.0
D(14,10,16,18)	-59.4	-59.9	-59.8
D(14,10,16,19)	-179.2	-179.7	-179.6
D(15,10,16,17)	178.0	177.2	177.3
D(15,10,16,18)	58.4	57.4	57.5
D(15,10,16,19)	-61.4	-62.4	-62.3

The C=N stretching skeletal bands [28-30] are observed in the range 1650-1550 cm^{-1}. For conjugated azines the υC=N mode is reported [31] at 1553 cm^{-1}. According to Socrates [32], the υC=N for semicarbazones is expected in the region 1655-1640 cm^{-1} in IR spectrum. For the title compound the band observed at 1647 cm^{-1} in the IR spectrum and at 1665 cm^{-1} in Raman spectrum is assigned as υC=N mode. The DFT calculations give this mode at 1644 cm^{-1}. Ferraz et al.[33] reported υC=N at 1643 cm^{-1} for thiosemicarbazone derivatives. Mangalam and Kurup [34] reported υC=N in the range 1571-1602 cm^{-1}, for thiosemicarbazone ligands. El-Asmy and Al-Hazmi [35] reported υC=N in the range 1606-1627 cm^{-1} for benzophenone-substituted thiosemicarbazones. The IR spectra of the reported thiosemicarbazones show bands in the region 1538-1647 cm^{-1} as stretching C=N [36-38]. A perusal through literature shows that C=O and C=N stretching modes are reported at 1668, 1671 and 1613, 1602 [10], 1719, 1600 [39,40], 1669, 1618 [41], 1680, 1586 [42], and at 1682, 1574 cm^{-1} for semicarbazone derivatives [43].

The NH stretching vibration [25] appears as a strong and broad band in the region 3390 ± 60 cm^{-1}. In the present study, the NH stretching band appeared as a doublet at 3346 and 3226 cm^{-1} in the IR spectrum owing to the Davydov coupling between the neighboring units. The splitting of about 120 cm^{-1} in the IR spectrum is due to strong intermolecular hydrogen bonding. Further more, the NH stretching wave number is red shifted by 78 cm^{-1} from the computational wave number which indicates the weakening of the N-H bond resulting in proton transfer to the neighbouring oxygen [26]. A similar type of splitting observed in acetanilide [44,45] and N-methylacetamide

[46] in the stretching band is attributed to the Davidov splitting. El-Asmy and Al-Hazmi [35] reported υNH in the region 3138-3323 cm^{-1} for benzophenone-substituted thiosemicarbazones and their Ni(II) and Cu(II) complexes. El-Asmy et al.[36] reported NH stretching in the range 3146 - 3223 cm^{-1} in the IR spectrum for thiosemicarbazone complexes. The CNH vibration in which N and H atoms move in opposite direction of carbon atom in the amide moiety appears at 1482 cm^{-1} in IR, 1500 cm^{-1} in Raman and 1480 cm^{-1} theoretically, and the CNH vibration in which N and H atoms move in the same direction of carbon atom in the amide group appears at 1349 (IR), 1356 (Raman) and 1368 cm^{-1} (DFT) [47-49]. The NH rock in the plane is observed at 1093 cm^{-1} in the Raman spectrum and at 1091 cm^{-1} theoretically [49]. The out-of-plane wagging [25] of NH is moderately active with a broad band in the region 790 ± 70 cm^{-1} and the band at 720 cm^{-1} (DFT) is assigned as this mode. El-Shahawy et al. [49] reported a value 710 cm^{-1} for this mode.

The C-N stretching vibration [25] coupled with the δNH, is active in the region 1275 ± 55 cm^{-1}. El-Shahawy et al.[49] observed a band at 1320 cm^{-1} in the IR spectrum as this υC-N mode. In the present case, the band at 1265 cm^{-1} in Raman spectrum is assigned as this mode. The DFT calculations give the corresponding bands at 1319 and 1260 cm^{-1}. υN-N has been reported at 1151 cm^{-1} by Crane et al.[50], 1121 cm^{-1} by Bezerra et al.[51] and 1130 cm^{-1} by El-Behery and El-Twigry [52]. In the present case, the band observed at 1124 cm^{-1} in both spectra and 1140 cm^{-1} (DFT) is assigned to the υN-N mode, which is not pure but contains contributions from other modes. υN-N is reported in the range 1037-1083 cm^{-1} for copper (II) complexes of thiosemicarbazones [53].

The vibrations of the CH_2 group, the asymmetric stretch, $\upsilon_{as}CH_2$, symmetric stretch $\upsilon_{s}CH_2$, scissoring vibration δCH_2 and wagging vibration ωCH_2 appear in the regions 3000 ± 50, 2965 ± 30, 1455 ± 55 and 1350 ± 85 cm^{-1}, respectively [25,47]. The DFT calculations give $\upsilon_{as}CH_2$ at 3020 cm^{-1} and $\upsilon_{s}CH_2$ at 2912 cm^{-1}. The CH_2 deformation band which comes near 1463 cm^{-1} in alkenes [54] is lowered to about 1440 cm^{-1} when the CH_2 group is next to a double or triple bond. A carbonyl, nitrile or nitro group each lowers the wavenumber of the adjacent CH_2 group [47] to about 1425 cm^{-1}. For the title compound the DFT calculations give band at 1414 cm^{-1} as the scissoring mode δCH_2. The CH_2 modes are observed at 3044 cm^{-1} in the IR spectrum and at 1407 cm^{-1} in the Raman spectrum. The CH_2 wagging modes are observed at 1376 cm^{-1} in IR spectrum and at 1376 cm^{-1} theoretically. The band at 1227 cm^{-1} in IR and 1233 cm^{-1} in Raman and 1229 cm^{-1} (DFT) is assigned as the twisting mode τCH_2. The rocking mode [25] is expected in the range 895 ± 85 cm^{-1}. The bands observed at 776 cm^{-1} in the Raman spectrum, 742 cm^{-1} in the IR spectrum and 763 cm^{-1}, (DFT) is assigned as ρCH_2 mode for the title compound. The torsional modes of CH_2 are seen in the low wavenumber range [25].

The NH_2 asymmetric stretching vibrations [25] give rise to a strong band in the region 3390 ± 60 cm^{-1} and the symmetric NH_2 stretching in the region 3210 ± 60 cm^{-1} with a some what weaker intensity. The DFT calculations give these modes at 3580 and 3453 cm^{-1} as $\upsilon_{as}NH_2$ and $\upsilon_{s}NH_2$ respectevely. Baran et al.[55] reported $\upsilon_{as}NH_2$ at 3381, 3186 and 3398, 3203 cm^{-1} respectively for copper complexes of L-asparagine and L-glutamine. The NH_2 deformation band [25] δNH_2 is expected in the region 1610 ± 30 cm^{-1}. Most primary amides [25] display this δNH_2 band at 1610 ± 20 cm^{-1}. For the title compound, the δNH_2 band is observed at 1583 cm^{-1} in IR, 1586 cm^{-1} in Raman and at 1560 cm^{-1} theoretically. δNH_2 is reported at 1680 (IR), 1694 (Raman) and 1664 (IR), 1695 cm^{-1} (Raman) for metal complexes of L-asparagine and L-glutamine [55]. The in-plane NH_2 rock absorbs weakly to moderately in the region [25] 1125 ± 45 cm^{-1}. For L-glutamic acid 5-

Table 4. Calculated vibrational wavenumbers (scaled), measured infrared and Raman bands positions and assignments

HF/631G*			B3PW91/6-31G*			B3LYP/6-31G*			$\upsilon_{(IR)}$ (cm^{-1})	$\upsilon_{(Raman)}$ (cm^{-1})	Assignments
υ (cm^{-1})	IR Intensity	Raman Activity	υ (cm^{-1})	IR Intensity	Raman Activity	υ (cm^{-1})	IR Intensity	Raman Activity			
3558	95.75	38.30	3608	80.51	55.87	3580	68.67	55.91			$\upsilon_{as}NH_2$
3446	13.60	69.86	3475	30.56	109.63	3453	27.28	115.19	3463 s		$\upsilon_{s}NH_2$
3441	65.85	63.91	3443	11.45	76.95	3424	9.69	76.20	3346 s, 3226 s		υNH
2949	24.57	62.20	3035	12.05	59.18	3020	15.17	61.08	3044 sh		$\upsilon_{as}CH_2$
2934	43.29	15.29	3022	28.82	55.31	3005	32.41	47.13			$\upsilon_{as}Me$
2925	48.35	106.21	3016	38.55	78.84	3001	43.31	84.53			$\upsilon_{as}Me$
2913	10.66	97.30	2995	1.41	89.07	2981	1.30	88.83	2970 sh	2971 s	$\upsilon_{as}Me$
2909	16.88	49.78	2975	12.05	50.77	2959	14.25	51.29			$\upsilon_{as}Me$
2864	31.74	183.12	2941	30.07	122.19	2933	30.03	120.17	2934 s	2934 s	$\upsilon_{s}Me$
2858	17.50	110.07	2922	26.00	209.40	2912	12.38	171.33			$\upsilon_{s}CH_2$
2857	26.11	31.08	2919	11.94	49.56	2909	27.24	77.57	2902 m	2899 s	$\upsilon_{s}Me$
1763	728.74	4.01	1777	492.52	18.45	1760	476.60	18.31	1687 s		$\upsilon C=O$
1735	5.54	137.53	1660	12.86	159.51	1644	11.41	150.92	1647 m	1665 vs	$\upsilon C=N$
1588	310.77	7.84	1558	332.46	14.09	1560	286.66	14.04	1583 s	1586 s	δNH_2
1483	14.23	3.52	1477	11.49	7.97	1480	4.93	8.48	1482 sh	1500 w	δNH
1472	5.89	6.31	1467	7.37	21.17	1472	6.83	21.20	1474 m		$\delta_{as}Me$
1469	14.92	10.85	1464	13.90	5.25	1467	4.65	4.43		1465 w	$\delta_{as}Me$
1461	3.72	22.70	1453	5.78	20.37	1458	5.26	20.77			$\delta_{as}Me$
1456	13.33	19.35	1444	14.32	18.22	1449	5.25	21.04	1445 s	1436 s	$\delta_{as}Me$
1441	84.05	14.55	1419	213.19	8.64	1414	173.93	8.24		1407 sh	δCH_2
1398	234.08	1.04	1378	52.60	2.62	1383	8.82	2.78		1382 w	$\delta_{s}Me$
1395	68.83	3.78	1374	85.93	8.08	1376	33.97	9.23	1376 s		$\delta_{s}Me$, ωCH_2
1393	8.91	4.00	1370	12.80	7.81	1368	161.98	5.46	1349 s	1356 m	δNH
1339	36.32	5.91	1318	27.89	22.54	1319	31.21	20.54			υCN
1266	17.76	14.66	1259	18.14	21.30	1260	16.38	24.78		1265 w	υCN
1229	36.38	2.08	1231	18.11	3.49	1229	26.47	2.45	1227 s	1233 w	τCH_2
1155	89.64	10.60	1158	112.76	12.98	1140	101.12	14.45	1124 s	1124 s	υNN, ρMe
1104	0.74	2.00	1088	3.08	2.34	1091	3.36	2.74		1093 w	ρNH
1079	30.06	1.90	1063	23.62	3.18	1064	30.12	2.21	1061 m	1058 w	ρMe, ρNH_2
1062	33.99	2.03	1060	15.60	2.29	1048	33.39	1.89			ρMe
995	0.57	5.17	993	4.90	8.36	990	2.17	6.94	994 w	1005 s	ρMe
985	5.23	5.96	980	3.77	3.15	982	6.01	4.50	973 w		υCC
959	9.74	4.19	960	3.16	3.73	953	4.94	4.42	941 w	965 w	υCC
923	2.68	8.29	939	5.73	5.73	931	4.38	7.00		930 w	τNH_2
781	2.74	3.14	787	0.79	2.32	785	0.47	1.66	766 m		ωNH_2
763	53.13	0.93	764	5.77	1.24	763	6.04	2.00	742 w	776 m	ρCH_2
756	17.50	2.90	725	23.49	0.33	720	26.04	0.33			ωNH
601	44.59	3.28	596	38.68	3.97	596	39.38	4.22	617 w	600 m	$\delta C=O$
580	2.80	2.30	582	4.23	3.07	580	4.73	3.26			δCC
554	8.69	1.99	549	3.45	0.74	548	4.44	0.84		521 w	$\gamma C=O$
537	21.19	3.17	532	22.70	3.63	531	26.03	3.31	515 w	501 m	$\delta C=N$
475	2.50	2.39	472	2.13	1.14	471	2.54	1.31	479 m	462 s	γCCH_2
432	124.26	2.32	434	153.99	1.26	437	162.81	1.20			γCNH
375	6.91	4.87	374	4.56	4.78	374	24.38	6.86		407 w	δCC
357	31.29	0.28	359	35.21	0.54	362	84.55	0.83			δCNN
284	151.91	1.09	318	189.57	3.01	344	99.66	2.82		326 s	tCH_2Me
265	122.37	4.83	276	5.10	4.88	276	4.13	5.16		256 w	tMe
225	3.45	0.29	227	1.75	0.244	228	1.68	0.25			tNH_2
204	1.37	0.11	200	2.16	0.24	201	1.56	0.22		198 w	tMe
153	0.59	0.27	146	1.77	0.28	143	1.92	0.33		178 m	tMe
132	2.22	0.05	131	2.85	0.07	132	2.71	0.09		118 s	γCNN
99	1.50	0.35	96	2.47	0.21	97	2.21	0.26		96 s	tCH_2
59	0.69	1.37	65	0.348	1.17	65	0.63	1.26			tC=O

υ-stretching, δ-in-plane bending, γ-out-of-plane bending, τ-twist, t- torsion; Me-methyl, s-strong, m-medium, w-weak, v-very, br-broad; sh- shoulder; subscripts; as, asymmetric; s, symmetric amide, ρNH_2 is reported at 1136 (IR), 1133 (Raman) and 1134 cm^{-1} theoretically [56].The band at 1058 cm^{-1} in Raman, 1061 cm^{-1} in IR and 1064 cm^{-1} (DFT) are assigned to ρNH_2 for the title compound. The amide band, absorbing in the region 775 ± 45 cm^{-1}, is assigned to NH_2 out-of-plane twist and wagging mode ωNH_2 is expected in the region [25] 670 ± 60 cm^{-1}. The NH_2 wag is usually clearly separated from the twist and is easy to recognize by its broad band structure. The out-of-plane twist τNH_2 is observed at 930 cm^{-1} in the Raman spectrum and at 931 cm^{-1} theoretically. The wagging mode ωNH_2 is observed at 766 cm^{-1} in IR spectrum and at 785 cm^{-1} (DFT) for the title compound. The wagging mode ωNH_2 is reported at 669, 675 (IR) and 663, 645 cm^{-1} (Raman) [56, 57]. For Cd(II) and Hg(II) thiosemicarbazone complexes [35] bands in the region 3254-3409 cm^{-1} and 3231-3367 cm^{-1}, are attributed to asymmetric and symmetric NH_2 stretching vibrations. For para-dimethylaminobenzaldehyde semicarbazone [58] NH_2 stretching vibration appears at 3466 cm^{-1} and 3415 cm^{-1} and NH stretching vibration appears at 3230 cm^{-1}.

In the spectra of methyl esters the overlap of the region in which both asymmetric stretching [25] $\upsilon_{as}CH_3$ absorb with a weak to medium intensity (2985 ± 25 and 2970 ± 30 cm^{-1}) is not large and regularly seen above 3000 cm^{-1}. The computed wavenumbers of modes corresponding to $\upsilon_{as}CH_3$ groups are 3005, 3001, 2981 and 2959 cm^{-1}. In this mode two C-H bonds of the methyl group are extending while the third one is contracting. For the title compound, band at 2970 cm^{-1} in the IR spectrum and 2971 cm^{-1} in the Raman spectrum is assigned as asymmetrical methyl stretching modes. The symmetrical stretching mode $\upsilon_s CH_3$ is expected in the range 2920 ± 80 cm^{-1} in which all the three C-H bonds extend and contract in phase [25]. The bands seen at 2933, 2909 (DFT), 2934, 2902 (IR) cm^{-1} and 2934, 2899 cm^{-1} (Raman) are assigned as these modes. Two bending vibrations can occur within a methyl group. The first of these, the symmetrical bending vibration $\delta_s CH_3$ involves the in-phase bending of the C-H bonds. The second, the asymmetrical bending mode $\delta_{as}CH_3$ involves out-of-phase bending of the C-H bonds [28]. With methyl esters the overlap of the regions in which methyl asymmetric deformations are active (1460 ± 25 and 1450 ± 15 cm^{-1}) is quite strong, which leads to many coinciding wavenumbers [25]. This is obvious, not only for the asymmetric deformations, but also for the symmetric deformations [25] mostly displayed in the range 1380 ± 15 cm^{-1}. The B3LYP calculations give 1472, 1467, 1458, 1449 cm^{-1} and 1383, 1376 cm^{-1} as asymmetric and symmetric CH_3 deformations, respectively, for the title compound. Experimentally $\delta_{as}CH_3$ vibration is observed in the Raman spectrum at 1465, 1436 cm^{-1} and at 1474, 1445 cm^{-1} in the IR spectrum while $\delta_s CH_3$ vibrations are observed at 1376 cm^{-1} in the IR spectrum and at 1382 cm^{-1} in the Raman spectrum. The methyl rocking wavenumbers are expected in the regions [25] 1100 ± 95 and 1080 ± 80 cm^{-1}. The bands calculated at 1140, 1091, 1048, 990 cm^{-1} are assigned as rocking modes of the methyl groups. The rocking modes are observed at 1124, 1061, 994 cm^{-1} in the IR spectrum and at 1124, 1058, 1005 cm^{-1} in the Raman spectrum.

4. 2. Geometrical parameters and first hyperpolarizability

To the best of our knowledge, no X-ray crystallographic data of this molecule has yet been established. However, the theoretical results obtained are almost comparable with the reported structural parameters of similar molecules. The B3LYP results give better agreement with that of similar reported molecules. The experimental N-N bond length of hydrazine [59] is reported at 1.449 Å and the electron diffraction N-N bond length of tetramethylhydrazine [60] is reported as 1.401 Å. Kostava et al.[61] calculated the N-N bond length in the range 1.318-1.357 Å for different molecules. In the present case, the N-N bond length is 1.3642 Å (B3LYP), which is somewhere between the length of an N-N single bond (1.45 Å) and an N=N double bond (1.25 Å). For semicarbazone derivatives, the N-N bond lengths are reported as 1.3782 – 1.389 [62], 1.3866 [63], 1.3894 [64], 1.3966 [65], 1.3796 [58], 1.3675 [11], 1.367 [66], 1.36 [67], and 1.369 Å [68].

For the title compound the bond length $C_1=N_2$ = 1.2868 Å (B3LYP), shows typical double bond characteristics. However, C_5-N_3 = 1.3971 Å (B3LYP) and C_5-N_6 = 1.3678 Å (B3LYP), bond lengths are shorter than the normal C-N single bond length which is about 1.48 Å. The shortening of the C-N bonds reveal the effect of resonance in this part of the molecule [69]. Ferraz et al.[33] reported the bond lengths N_2-N_3 =1.3815 Å, $C_1=N_2$ = 1.3005Å, N_3-C_5 =1.3105 Å for thiosemicarbazones metal complexes. Latheef et al.[53] reported the bond lengths N-N 1.3964, C-N 1.3485 and C-N 1.3175, 1.2965 Å which are comparable to that for C=N bond length for copper (II) complexes of thiosemicarbazones [70]. For semicarbazone derivatives, the reported values of $C_1=N_2$ = 1.2754Å [58], 1.2886Å [11], 1.296Å [66], 1.303Å [68]. C_5-N_3 = 1.3621Å [58], 1.3706Å [11], 1.336Å [66], 1.365Å [68] and C_5-N_6 = 1.3250Å [58], 1.3281Å [11], 1.331Å [66], 1.314 Å [68].

Seena and Kurup [71] reported the geometrical parameters as N-N 1.3967, C-N=1.2767, 1.3087, 1.3939, N-H 0.818Å, bond angles, C-N-N 115.6º, C-N-N 111.0º, for zinc(II) complexes of salicyladehyde N(4)-phenyl thiozemicabazone. For thiosemicarabazone derivatives, Hernandez et al.[62] reported the bond lengths as (XRD) as C_1-N_2 = 1.2844, N_3-C_5 = 1.3544, C_5-N_7 = 1.3424-1.3541Å and the bond angles N_3-N_2-C_1 = 115.0 – 118.6, N_2-N_3-C_5 = 119.8-113.5º and N_3-C_5-N_6 = 120.8º. Dilovic et al.[63] reported C_5-N_7 = 1.3462, C_5-N_3 = 1.3422 and N_2-C_1 = 1.2862Å. For the title compound, the $C_5=O_{20}$ bond length is 1.2230Å and the DFT calculations give the bond angles C_1-N_2-N_3 = 119º, N_2-N_3-C_5 = 121.3º, O_{20}-C_5-N_3 = 120.3, O_{20}-C_5-N_6 = 125.3º. The reported values of $C_5=O_{20}$ are, 1.2397[58], 1.2431 [11], 1.25 [67], 1.252 [68] and 1.266Å [41]. For the title compound, the B3LYP calculations give the bond angles C_1-N_2-N_3=119.0, N_2-N_3-C_5 =121.3, N_3-C_5-O_{20}=120.3, N_3-C_5-N_6=114.4 and O_{20}-C_5-N_6=125.3º. For similar derivatives, the reported values are C_1-N_2-N_3=115.4 [58], 118.5 [11], N_2-N_3-C_5 =120.3 [58], N_3-C_5-O_{20}=120.4 [11], N_3-C_5-N_6=116.0 [11], O_{20}-C_5-N_6=124.0 [58] and 123.6º [11].

The first hyperpolarizability (β_0) of this novel molecular system is calculated using B3LYP/6-31G* method, based on the finite field approach. In the presence of an applied electric field, the energy of a system is a function of the electric field. First hyperpolarizability is a third rank tensor that can be described by a 3 ×3 × 3 matrix. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry [72]. The components of β are defined as the coefficients in the Taylor series expansion of the energy in the external electric field. When the electric field is weak and homogeneous, this expansion becomes

$$E = E_0 - \sum_i \mu_i F^i - \frac{1}{2}\sum_{ij} \alpha_{ij} F^i F^j - \frac{1}{6}\sum_{ijk} \beta_{ijk} F^i F^j F^k - \frac{1}{24}\sum_{ijkl} \gamma_{ijkl} F^i F^j F^k F^l + ...$$

where E_0 is the energy of the unperturbed molecule, F^i is the field at the origin, μ_i, α_{ij}, β_{ijk} and γ_{ijkl} are the components of dipole moment, polarizability, the first hyper polarizabilities, and second hyperpolarizibilites, respectively. The calculated first hyperpolarizability of the title compound is 1.9 × 10^{-30} esu. The C-N distances in the calculated molecular structure vary from 1.2868-1.3971 which are intermediate between those of a C-N single bond (1.48) and a C=N double bond (1.28). Therefore, the calculated data suggest an extended π-electron delocalization over the carbazone moiety [73] which is responsible for the nonlinearity of the molecule. For thiosemicarbazone complexes, the calculated hyperpolarizabilities are reported in the range 2.6× 10^{-30} – 10.1× 10^{-30} esu [73]. We conclude that the title compound is an attractive object for future studies of non linear optical properties.

In order to investigate the performance and vibrational wavenumbers of the title compound root mean square value (RMS) and correlation coefficient between calculated and observed wavenumbers were calculated (Fig. 4**)**. RMS values of wavenumbers were evaluated using the following expression [74].

$$RMS = \sqrt{\frac{1}{n-1}\sum_{i}^{n}\left(\upsilon_i^{calc} - \upsilon_i^{\exp}\right)^2}$$

The RMS error of the observed Raman bands and IR bands are found to be 29.78, 44.56 for HF, 17.35, 31.16 for B3PW91 and 16.26, 25.21 for B3LYP methods. The small differences between experimental and calculated vibrational modes are observed. It must be due to the fact that hydrogen bond vibrations present in the crystal lead to strong perturbation of the infrared wavenumbers and intensities of many other modes. Also, we state that experimental results belong to solid phase and theoretical calculations belong to gaseous phase.

5. Conclusion

The FT-IR and FT-Raman spectra of ethyl methyl ketone semicarbazone were studied. The molecular geometry and wavenumbers were calculated using different levels of theory and compared with experimental values. Optimized geometrical parameters of the title compound are in agreement with the values of similar derivatives. The extended π-electron delocalization over the carbazone moiety is responsible for the nonlinearity of the molecule. The calculated first hyperpolarizability is comparable with the reported values of similar structures, which makes this compound an attractive object for future studies of nonlinear optics. The red shift of the NH stretching wavenumber in the infrared spectrum from the computed wavenumber indicates the weakening of the NH bond resulting in proton transfer to the neighboring oxygen atom.

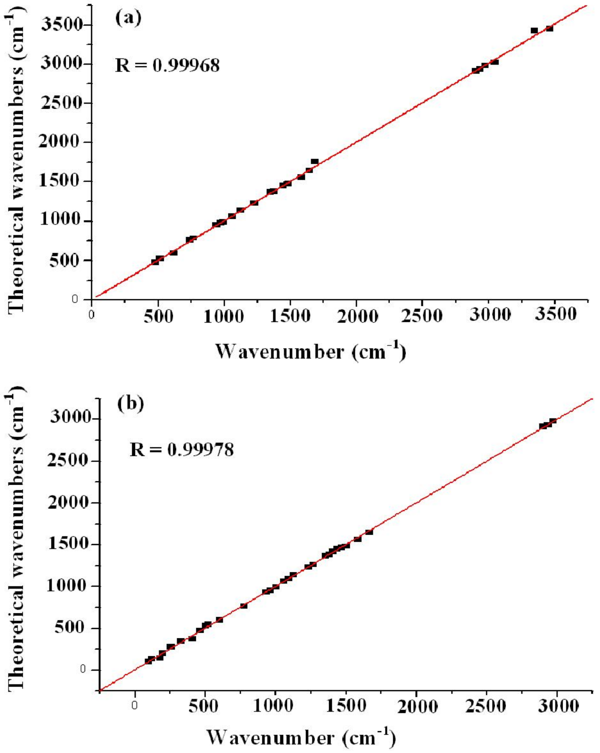

Fig. 4. Correlation graph (a) IR and theoretical (B3LYP) wavenumbers (b) Raman and theoretical (B3LYP) wavenumbers.

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