FT-IR and FT-Raman spectral studies and DFT calculations of tautomeric forms of benzaldehyde-*N*(4)-phenylsemicarbazone

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The vibrational wave numbers of the keto and enol forms of benzaldehyde-*N*(4)-phenylsemicarbazone have been computed using B3LYP/6-311++G** level of theory and compared with experimental FT-IR and FT-Raman data. Optimized geometrical parameters of the title compound are in agreement with the reported structures. The calculated first hyperpolarizability is comparable with the reported values of similar derivatives and is an attractive object for future studies on non-linear optics. The extended π-electron delocalization over the semicarbazone moiety is responsible for the nonlinearity of the molecule.

Semicarbazones are compounds with versatile structural features and can coordinate to the metal either as a neutral ligand or as a deprotonated anion. Semicarbazones exist in two tautomeric forms, (Scheme 1) keto and enol. We have earlier reported that the title compound exists in the keto form in the solid state[1]. The coordination possibilities in

Keto (A)   Enol (B)
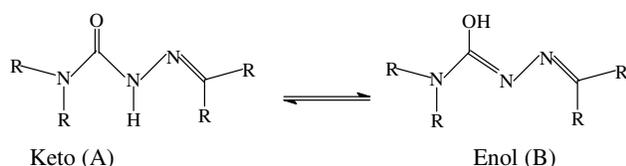
Scheme 1

semicarbazones are increased if the substituents of the aldehyde or ketone include additional donor atoms. The π-delocalization and the configurational flexibility of their molecular chain can give rise to a variety of coordination modes[2]. In some metal complexes, semicarbazone can act as a tridentate ligand[3] with a donor atom, apart from ketone/enol oxygen atom and azomethine nitrogen.

Literature survey reveals that neither the complete Raman and IR spectra nor the force fields for keto and enol forms of benzaldehyde-*N*(4)-phenylsemicarbazone (BPSC) have been reported so far. The aim of the present study is to give a complete description of the molecular geometry and molecular vibrations of the title compound. For this purpose, quantum chemical computations were carried out on keto and enol forms of BPSC using density functional theory. Density functional theory calculations are reported to provide excellent vibrational frequencies of organic compounds if the calculated frequencies are scaled to compensate for the approximate treatment of electron correlation for basis set deficiencies and for the anharmonicity[4-6]. We report herein the DFT theoretical calculations for the keto and enol forms of the title compound using the B3LYP method with 6-311++G** basis set. The obtained data are compared with experimental data. The hyperpolarizability of the title compound has also been calculated.

Methodology

N(4)-Phenylsemicarbazide (Sigma-Aldrich) and benzaldehyde (Merck) were of reagent grade and were used as received. Methanol (Merck) was used as the solvent without further purification.

The FT-IR spectrum was recorded on a Perkin Elmer infrared spectrometer with KBr pellets. The FT-Raman spectrum was obtained on a Bruker RFS 100/s instrument. For excitation of the spectrum, the emission of Nd:YAG laser was used (excitation wavelength 1064 nm, laser power 150 mW, resolution 4 cm⁻¹, number of scans 50 and measurement on solid sample).

Calculations for the keto and enol forms of the title compound were carried out with the Gaussion 03 program[7] at the B3LYP/6-311++G** level of theory

to get the optimized geometry and vibrational wave numbers. DFT calculations were carried out with Becke's three-parameter hybrid model using the Lee-Yang-Parr correlation functional (B3LYP) method. The wave number values computed at the DFT contain known systematic error[8]. We, therefore, have used the scaling factor[9] value of 0.9613 for DFT basis set. The absence of imaginary wave numbers on the calculated vibrational spectrum confirms that the structure deduced corresponds to minimum energy.

Results and discussion

The relative intensities, comparison of calculated (scaled) and observed IR and Raman bands of tautomeric forms of BPSC were studied. Comparison of the theoretical frequencies calculated at B3LYP/6-311++G** with the experimental values (Figs 1–3) reveals the overestimation of the calculated vibrational modes due to neglect of anharmonicity in the real system. Inclusion of electron correlation in density functional theory to a certain extent makes the frequency values smaller in comparison with the HF frequency data. Reduction in the computed harmonic vibrations, though basis set-sensitive, are only marginal as observed in the DFT values using B3LYP/6-311++G**. Not withstanding the level of calculations, it is customary to scale down the calculated harmonic frequencies in order to improve the agreement with the experimental data. Vibrational frequencies calculated at B3LYP/6-311++G** were scaled by 0.9613 (ref. 9). This value minimizes the root-mean square difference between calculated and experimental frequencies for bands with definite identification.
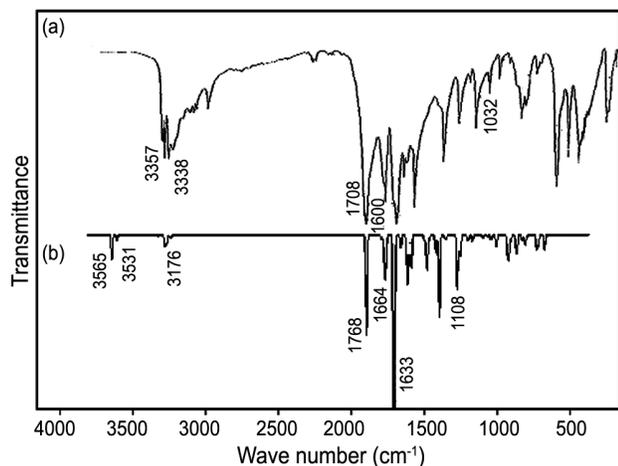
A band at 3338 cm^{-1} in the free ligand due to the $\nu_{s(N_3H_7)}$ vibration indicates that the ligand remains in the keto form in the solid state. E1-Asmy and A1-Hazmi[10] reported ν_{N-H} stretching in the range 3138-3323 cm^{-1}. $\nu_{s(N_4H_6)}$ stretching vibration increases from keto to enol form. A strong FT-IR band observed at 1708 cm^{-1} is assigned to C=O stretching vibration while that at 1669 cm^{-1} in BPSC corresponds to FT-Raman. The theoretically computed value of 1700 cm^{-1} for BPSC by B3LYP/6-311++G** method is in good agreement with experimental observation[11,12]. A sharp band at 1603 cm^{-1} in the semicarbazone can be attributed to the characteristic >C=N– group. The theoretical wave number of this band at 1600 cm^{-1} coincides well with the experimental as well as characteristic value[13,14] reported in literature. In the
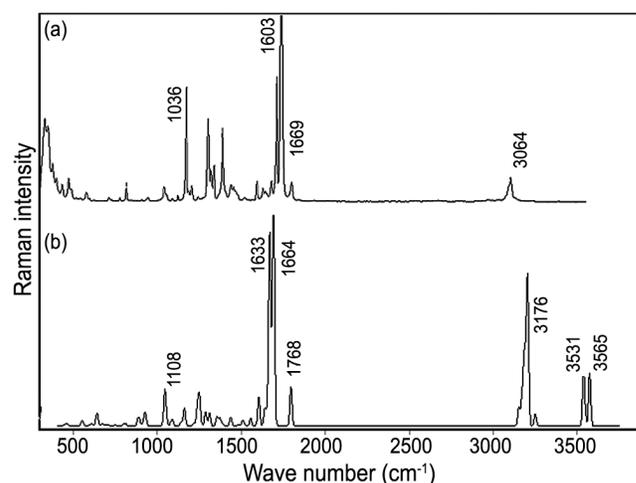

Fig. 2 – FT-Raman spectrum of keto form of benzaldehyde-*N*(4)-phenylsemicarbazone. [(a) experimental (b) calculated].

Fig. 1 – FT-IR spectrum of keto form of benzaldehyde-*N*(4)-phenylsemicarbazone. [(a) experimental, (b) calculated].
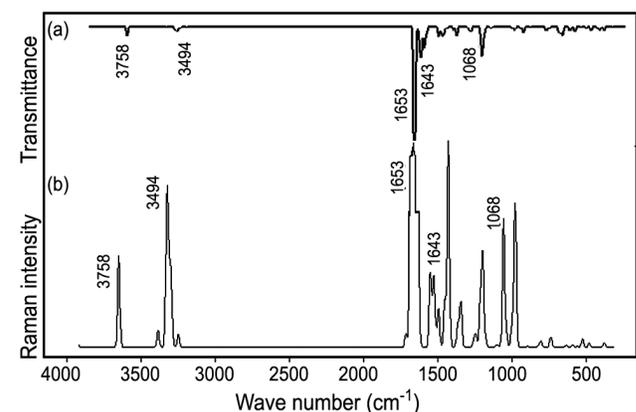

Fig. 3 – (a) Theoretically calculated FT-IR, and, (b) FT-Raman spectra of enol form of benzaldehyde-*N*(4)-phenylsemicarbazone.

enol form, the vibrations are found at 1589 cm^{-1}. Sreekanth *et al.*[15] reported $\nu_{C=N}$ in the range 1592–1621 cm^{-1} for Co(III) complexes of *N*(4)-phenyl semicarbazone. The theoretically scaled values at 1065 cm^{-1} by B3LYP/6-311++G** method due to ν_{N-N} exactly correlates with experimental observations. ν_{N-N} has been reported at 1053 cm^{-1} by Sreekanth *et al.*[15], at 1022 cm^{-1} by Alphonsa and Kurup[16] and at 1115 cm^{-1} by Crane *et al.*[17] In general, the aromatic C–H vibrations calculated theoretically are in agreement with the experimentally reported values[18]. The scaled vibrations in the range 3071-3067 cm^{-1} and 3065-3032 cm^{-1} correspond to symmetric and asymmetric stretching modes of C–H unit.

In order to investigate the performance and vibrational wave numbers of the title compound, the correlation coefficient between calculated and observed wave numbers were calculated. Small differences between experimental and calculated vibrational modes were observed, probably due to the fact that hydrogen bond vibrations present in the crystal lead to strong perturbation of the infrared wave numbers and intensities of many other modes. The experimental results reported here are for the solid phase while theoretical calculations pertain to the isolated molecule in gas-phase.

To the best of our knowledge, no X-ray crystallographic data of this molecule have yet been established. However, the theoretical results obtained are almost comparable with the reported structural parameters. The experimental N–N bond length is reported at 1.380 Å for acetone-*N*(4)-phenyl-semicarbazone[19] and at 1.390 Å for a Co(II)-*N*(4)-phenyl-semicarbazone complex[20]. Kostava *et al.*[21] calculated the N–N bond length in the range 1.318–1.357 Å for different molecules. In the present case, the keto form of the N_3–N_9 bond length is 1.355 Å and in the enol form at 1.379 Å, which is somewhere between the length of N–N single bond (1.45 Å) and N=N double bond (1.25 Å).

For the keto form of the title compound, the bonds C_{10}=N_9 (1.286 Å) and C_2=O_1 (1.219 Å) show typical double bond characteristics. However, the C_2–N_4, C_2–N_3 and C_{22}–N_4 bond lengths are shorter than the normal C–N single bond length of about 1.47 Å. The shortening of the C–N bonds reveals the effect of resonance in this part of the molecule[22]. For the enol form of the title compound, the bonds C_{10}=N_9 = 1.084 Å and C_2=N_3 = 1.306 Å show double bond characteristics. The geometrical parameters for

copper(II) *N*(4)-phenylsemicarbazone complex have been reported. Kala *et al.*[23] reported the bond lengths (XRD) as N_3–C_{10} = 1.409 Å, N_3–C_9 = 1.373 Å and N_1–N_2 = 1.393 Å. Reena *et al.*[12] reported the geometrical parameters O_1–C_7 = 1.350 Å, N_1–C_1 = 1.349 Å, N_1–C_5 = 1.479 Å, N_2–N_3 = 1.338 Å, N_3–C_7 = 1.368 Å, N_4–C_8 = 1.326 Å, N_4–C_7 = 1.354 Å, C_1–N_1–C_5 = 125.7, C_6–N_2–N_3 = 113.1, N_2–N_3–C_7 = 100.2 and O_1–C_7–N_3 = 130.7 °. Sreekanth *et al.*[15] reported the bond lengths O_2–C_{21} = 1.290 Å, N_1–N_2 = 1.214 Å, N_2–N_3 = 1.147 Å and bond angles C_{19}–N_6–N_7 = 117.9°, N_3–N_2–N_1 = 174.7°, C_{10}–N_5–C_6 = 118.0°. Some parameters corresponding to optimized geometry of the keto and enol forms of the title compound (Fig. 4) are given in Table 1. In the keto form of the title compound, the three bond angles around C_2 atom are not equal to 120° each. It is seen that the N_3–C_2–O_1 bond angle is considerably greater than the N_3–C_2–N_4 bond angle. This is explained as due to a decrease in repulsion between the lone pairs present in N_3 and O_1 atoms. The central part of the molecule adopts a completely extended double bonded conformation. This can be confirmed by the C_2–O_1 bond length, which is considerably longer than the standard C=O bond length of 1.21 Å, and, N_3–C_2 bond length, which is shorter than the standard single bond length of 1.47 Å.

The first hyperpolarizability (β_0) of this novel molecular system was calculated using DFT, based on the finite field approach. In the presence of an applied electric field, the energy of the system is a function of the electric field. The calculated first hyperpolarizability of the title compound is 2.01×10^{-30} esu, and is comparable
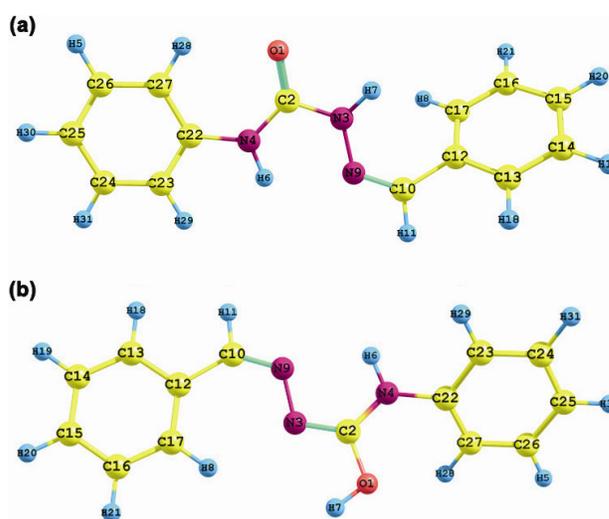

Fig. 4 – Optimized geometry of (a) keto, and, (b) enol forms of benzaldehyde-*N*(4)-phenylsemicarbazone.

Table 1 – Optimized geometrical parameters of keto and enol form of benzaldehyde-*N*(4)-phenylsemicarbazone[a] calculated at the B3LYP/6-311++G** level

Keto form

Bond lengths (Å)		Bond angles (°)		Dihedral angles (°)	
O_1–C_2	1.219	O_1–C_2–N_3	119.3	O_1–C_2–N_3–H_7	11.1
C_2–N_3	1.405	O_1–C_2–N_4	127.3	O_1–C_2–N_3–N_9	171.6
C_2–N_4	1.366	N_3–C_2–N_4	113.4	N_4–C_2–N_3–H_7	-170.0
N_3–N_9	1.355	C_2–N_3–N_9	121.1	N_4–C_2–N_3–N_9	-9.5
N_4–C_{22}	1.408	C_2–N_4–H_6	114.3	O_1–C_2–N_4–H_6	-177.9
N_9–C_{10}	1.286	C_2–N_4–C_{22}	128.4	O_1–C_2–N_4–C_{22}	0.1
C_{10}–C_{12}	1.476	N_3–N_9–C_{10}	121.3	N_3–C_2–N_4–C_{22}	-178.6
		N_9–C_{10}–H_{11}	113.5	C_2–N_4–C_{22}–C_{23}	-178.8
		C_{22}–N_4–H_6	117.3	C_2–N_4–C_{22}–C_{27}	1.3
		N_9–C_{10}–C_{12}	130.3	C_{23}–C_{22}–N_4–H_6	-0.8
		C_{12}–C_{10}–H_{11}	116.1	C_{27}–C_{22}–N_4–H_6	179.4
				N_9–C_{10}–C_{12}–C_{13}	146.0
				N_9–C_{10}–C_{12}–C_{17}	-36.6
				C_{13}–C_{12}–C_{10}–H_{11}	-31.8

Enol form

Bond lengths (Å)		Bond angles (°)		Dihedral angles (°)	
O_1–C_2	1.342	O_1–C_2–N_3	117.7	N_3–C_2–O_1–H_7	0.1
O_1–H_7	0.969	C_2–O_1–H_7	105.7	N_4–C_2–O_1–H_7	-179.9
C_2–N_3	1.306	O_1–C_2–N_4	117.4	O_1–C_2–N_3–N_9	-179.9
C_2–N_4	1.351	N_3–C_2–N_4	124.9	N_4–C_2–N_3–N_9	0.1
N_3–N_9	1.379	C_2–N_3–N_9	111.6	O_1–C_2–N_4–H_6	179.9
N_4–C_{22}	1.408	C_2–N_4–H_6	109.5	O_1–C_2–N_4–C_{22}	0.0002
N_9–C_{10}	1.084	C_2–N_4–C_{22}	133.2	N_3–C_2–N_4–H_6	-0.0013
C_{10}–C_{12}	1.469	C_{22}–N_4–H_6	117.4	N_3–C_2–N_4–C_{22}	-179.9
		N_3–N_9–C_{10}	119.1	C_2–N_3–N_9–C_{10}	-179.9
		N_9–C_{10}–H_{11}	112.6	C_2–N_4–C_{22}–C_{23}	179.9
		N_9–C_{10}–C_{12}	133.4	C_2–N_4–C_{22}–C_{27}	-0.1
		C_{12}–C_{10}–H_{11}	114.0	C_{23}–C_{22}–N_4–H_6	-0.004
				C_{27}–C_{22}–N_4–H_6	179.9
				N_3–N_9–C_{10}–H_{11}	-179.9
				N_3–N_9–C_{10}–C_{12}	0.0001
				N_9–C_{10}–C_{12}–C_{13}	-179.9
				N_9–C_{10}–C_{12}–C_{17}	0.002
				C_{13}–C_{12}–C_{10}–H_{11}	-179.9

[a] Labelling as in Fig. 4.

Table 2 – Theoretically computed thermodynamic parameters of keto and enol forms of benzaldehyde-*N*(4)-phenylsemicarbazone

	Keto	Enol
Total energy (au)	-781.0032669	-780.9820789
Zero-point energy (kcal mol^{-1})	154.81	154.63
Rotational constants (GHz)	1.6685	1.7013
	0.1423	0.1419
	0.1333	0.1309
Entropy (cal mol^{-1}K^{-1})		
Total	128.047	129.940
Translational	42.317	42.317
Rotational	33.584	33.586
Vibrational	52.146	54.037
Dipole moment (D)	4.4793	0.2150

with the reported value (1.9×10^{-30} esu) (ref. 24). This indicates that the title compound is an attractive object for future studies of nonlinear optical properties.

Several calculated thermodynamic parameters are presented in Table 2. Scale factors have been recommended[25] for an accurate prediction in determining the zero-point vibration energies (ZPVE), and the entropy $S_{vib}(T)$.

SAIF, CUSAT, Kochi, for elemental analyses, NIIST, Thiruvananthapuram for IR, electronic and NMR spectra and Sree Chitra Institute of Medical Sciences, Thiruvananthapuram for Raman spectrum.

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