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Structural and nonlinear optical properties of cross-conjugated system benzophenone thiosemicarbazone: a vibrational spectroscopic study

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The nonlinear optical (NLO) compound of interest benzophenone thiosemicarbazone (BTSC) was grown and the molecular structure generated with the aid of density functional theory (DFT). FT-Raman and IR spectra were recorded and analyzed. The harmonic wavenumbers and IR and Raman intensities were computed with the B3LYP method. The observed vibrational wavenumbers were compared with the calculated results. The assignments of the experimental spectra were made with the help of normal coordinate analysis (NCA) following the scaled quantum mechanical force field (SQMFF) methodology. The electronic structure of the most important molecular fragments is described in terms of natural bond orbital (NBO) analysis. Copyright © 2010 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this article.

Keywords: conjugation; natural bond orbital (NBO) analysis; ICT; FT-IR; FT-Raman

Introduction

Benzophenone derivatives show very interesting nonlinear optical (NLO) activity as well as transparency, and the crossconjugated path in these molecular systems appear as a powerful electronic system for the molecular engineering of efficient second-harmonic generation (SHG) materials. A number of benzophenone derivatives show significantly high SHG conversion efficiency.^[1-3] The structure of the benzophenone molecule has been established on the basis of quantum chemical calculations,^[4] and vibrational wavenumbers of benzophenone have been calculated.^[5] The crystal structures of benzophenone^[6] and benzophenone thiosemicarbazone (BTSC)^[7] have been reported. Thiosemicarbazones are photochromic materials and have attracted much attention because of their potential commercial value in applications such as high-density information storage systems, photoswitching, electro- or light-driven information display devices, and optical calculation.^[8,9] Vijayan and co-workers^[10-13] have reported the growth and characterization of some organic NLO semicarbazone derivatives.

Vibrational spectroscopy is an efficient tool for the characterization of crystalline materials. It is effectively used to identify functional groups and determining the molecular structure of synthesized crystals. The present work deals with growth and detailed vibrational spectral investigation of the crystal BTSC to elucidate the correlation between the molecular structure and NLO property, charge transfer interactions, and first hyperpolarizability, aided by using the scaled quantum mechanical force field (SQMFF) technique based on density functional theory (DFT) computation.

Experimental

Synthesis

Benzophenone (99% Aldrich) and thiosemicarbazide (99% Aldrich) were taken in 1:1 stoichiometric ratio and were dissolved in ethanol. A few drops of H_2SO_4 were added as catalyst. The prepared solution was slowly warmed till a clear solution was obtained. The solution was kept in a covered container for controlled evaporation. Good quality transparent crystals of BTSC were obtained within a week.

Spectroscopic measurements

The UV-vis absorption spectrum of the sample was recorded in acetone solution using a Varian-Cary 100 B10 UV-vis spectrophotometer. The Fourier transform infrared (FT-IR) spectrum of BTSC was recorded in the region 4000-400 cm⁻¹, with samples in KBr pellets, using a Perkin Elmer RXI spectrometer. The resolution of the spectrum is 4 cm⁻¹. The NIR-FT Raman spectrum of BTSC in the solid phase was recorded in the range 3500-50 cm⁻¹ using a Bruker RFS 100/S FT-Raman spectrophotometer with a 1064 nm Nd : YAG laser source of 100 mW power. A liquid-nitrogen-cooled Ge diode was used as the detector. The spectral resolution after apodization was 2 cm⁻¹.

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Figure 1. Second-harmonic generation variation in BTSC for different particle sizes as compared to urea: (a) 90 $< r < 150 \,\mu m$ and (b) 150 $< r < 180 \,\mu m$.

SHG analysis

The SHG efficiency of the microcrystalline powders of BTSC was examined by the powder reflection technique of Kurtz and Perry.^[14] Particle sizes (r), $150 < r < 180 \,\mu m$ and $90 < r < 150 \,\mu m$, graded using standard sieves were used for the measurement. A Nd: YAG pulsed laser (1064 nm, 15 ns) beam was used. Ninety-five percent of the beam was focused on the polycrystalline sample, while the remaining 5% was used as a reference beam to normalize the fluctuations of the incident laser. The second harmonic (SH) radiation at 532 nm obtained at the output was filtered using an SH separator to remove the fundamental input radiation. The SH generated was detected by an RCA-931A photomultiplier tube (PMT), which was connected to 100 MHz digital storage oscilloscope (DSO). The change in the intensity of the SH as a function of the fundamental was experimentally measured, and is shown in Fig. 1. The SHG efficiency of BTSC was evaluated to be on average 0.52 times that of urea.

Computational methods

The molecular geometry optimization and vibrational wavenumber calculations of BTSC were performed by DFT method using the Gaussian '98 package.^[15] The Becke three-parameter hybrid exchange functional and the Lee-Yang-Parr correlation functional (B3LYP) were utilized in the calculation with the 6-31G* basis set. Nowadays, DFT calculations have been proved to be useful for gaining insight into the structural properties of molecules.^[16-19] Normal coordinate analysis (NCA) was performed including the calculation of vibrational modes and potential energy distribution (PED) in local symmetry coordinates, as well as IR intensities and Raman activities corresponding to the scaled quantum mechanical (SQM) force field. These calculations were done with the MOLVIB program version 7.0 written by Sundius.^[20,21] Following the procedure of SQMFF, the harmonic force field for this compound was evaluated and scaled at the B3LYP/6-31G* level of theory transferring the recommended scale factors of Rauhut and Pulay.^[22,23] Natural bond orbital (NBO) calculations of BTSC were performed at the B3LYP/6-31G* level using the program NBO 3.1^[24] included in the Gaussian '98 program.^[15] The Raman activities (S_i) calculated by Gaussian 98 program were suitably adjusted by the scaling

procedure with MOLVIB and subsequently converted to relative Raman intensities (I_i) using the following relationship derived from the basic theory of Raman scattering^[25,26]:

$$I_{i} = \frac{f(v_{0} - v_{i})^{4}S_{i}}{v_{i}\left[1 - \exp\left(\frac{-hcv_{i}}{kT}\right)\right]}$$
(1)

where v_0 is the exciting wavenumber, v_i is the vibrational wavenumber of the *i*th normal mode, *h*, *c*, and *k* are universal constants, and 'f' is a suitably chosen common scaling factor for all the peak intensities. The simulated IR and Raman spectra were plotted using pure Lorentzian band shapes with a full width at half-maximum (FWHM) of 10 cm⁻¹.

The second-order polarizability or first hyperpolarizability β was calculated using HF/6-31G^{*} basis set on the basis of the finite-field approach. The components of the first hyperpolarizability can be calculated using the following equation:

$$\beta_i = \beta_{iii} + 1/3 \Sigma (\beta_{ijj} + \beta_{jij} + \beta_{jji}), (i \neq j)$$
(2)

Using the x, y, and z components, the magnitude of the first hyperpolarizability tensor can be calculated by

$$\beta = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$$
(3)

The complete equation for calculating the magnitude of first hyperpolarizability from Gaussian '98 W output is given as follows^[27]:

$$\beta = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2]^{1/2}$$
(4)

To calculate the hyperpolarizability, the origin of the Cartesian coordinate system was chosen as the center of mass of the compound.^[28] The components of the hyperpolarizability tensor are shown in Table S1 (Supporting Information). The calculated first hyperpolarizability of BTSC is 4.5×10^{-30} esu, which is 23 times that of urea. The time-dependent density functional theory (TD-DFT) method was used to calculate energies, oscillator strengths of electronic singlet-singlet transitions, and the absorption wavelengths. Solvent effects were considered using the polarizable continuum model (PCM) developed by Tomasi and co-workers.^[29–31]

Results and Discussion

Optimized geometry

The optimized molecular structure of BTSC (Fig. 2) was calculated using Gaussian '98 W program. The selected optimized geometrical parameters are shown in Table 1. The thiosemicarbazone moiety is nearly planar with the dihedral angle $N_{24} - N_{25} - C_{26} - N_{27}$ (2.07°) and adopts an *E* configuration with respect to the $C_7 = N_{24}$ bond. In the benzophenone fragment, two phenyl rings are nonplanar with $C_1 - C_6 - C_7 - C_8$ (-157.66°) and $C_6 - C_7 - C_8 - C_{13}$ (-121.16°) dihedral angles. The benzophenone and the thiosemicarbazone moieties are twisted, making the $C_1 - C_6 - C_7 - N_{24}$ and $C_{13} - C_8 - C_7 - N_{24}$ dihedral angles of 21.83° and 59.40°, respectively. The more deviation in Ph2 region ($C_{13} - C_8 - C_7 - N_{24}$) is due to the steric repulsion between the H₂₃ and H₂₉ atoms. The $C_6 - C_7$ and



Figure 2. Optimized structure of BTSC calculated at B3LYP/6-31G*.

C₇-C₈ bond lengths are slightly larger than other C-C bonds, indicating negligible conjugation interaction between the two phenyl ring systems. The deviations of C₆-C₇-N₂₄ (116.84°), C₈-C₇-N₂₄ (123.64°), C₇-N₂₄-N₂₅ (119.89°), N₂₄-N₂₅-C₂₆ (121.17°), and N₂₅-C₂₆-N₂₇ (115.09°) bond angles are due to the electronic coupling between the amino nitrogen lone pair electrons and the phenyl ring π system. The shortening of N₂₄-N₂₅ (1.356 Å) bond length indicates conjugation in the semicarbazone part. The elongation of the predicted C-N bond lengths from the X-ray data^[7] suggests intense delocalization in the whole molecule. The shortening of C-S bond length from the experimental results^[7] is due to its double bond character. Moreover, the C₂₆-N₂₇ bond

distance (1.347 Å) is indicative of a slight double bond character, suggesting extensive electron delocalization in the entire molecule. The short inter atomic distances $H_{23} \cdots H_{29}$ (2.551 Å) and $H_{29} \cdots S_{30}$ (2.729 Å) reveal the possibility of intramolecular hydrogen bonding.

NBO analysis

NBOs provide the most accurate possible 'natural Lewis structure' picture of ψ , because all orbital details are mathematically chosen to include the highest possible percentage of the electron density (ED). A useful aspect of the NBO method is that it provides information about interactions in both filled and virtual orbital spaces that could enhance the analysis of intra- and intermolecular interactions. These delocalization effects can thus be depicted as a charge transfer from the highest occupied bonding orbitals into unoccupied antibonding orbitals and their importance can be more quantitatively characterized through a second-order perturbative treatment that gives the energy lowering associated with such interactions. The strength of the delocalization interaction can be estimated by the second-order energy lowering $E^{(2)}$:

$$E^{(2)} = \Delta E_{ij} = q_i \frac{F(i,j)^2}{\varepsilon_i - \varepsilon_i}$$
(5)

where $E^{(2)}$ is the stabilization energy, q_i is the donor orbital occupancy, ε_i and ε_j are the diagonal elements (orbital energies), and F(i, j) is the off-diagonal NBO Fock or Kohn–Sham matrix element.^[32]

The intramolecular interactions are formed by the orbital overlap from $\pi \to \pi^*$ bond orbitals, which results in intramolecular charge transfer (ICT) causing stabilization of the system. These interactions are observed as an increase in ED in C–C antibonding orbital which weakens the respective bonds. The ED at the six conjugated π bonds (~1.65 e) and π^* bonds (~0.35 e) of the phenyl rings clearly

Table 1. Optimized geometrical parameters of BTSC based on B3LYP/6-31G* basis set									
Bond length (Å)				Bond angle (°)			Dihedral angle (°)		
Parameter	Cal.	Exp. ^a	Exp. ^b	Parameter	Cal.	Exp. ^a	Parameter	Cal.	Exp. ^a
C ₅ -C ₆	1.405	1.399	1.40	$C_1 - C_2 - C_3$	120.32	120.42	$C_1 - C_2 - C_3 - C_4$	-0.05	0.55
C ₆ -C ₇	1.483	1.480	1.48	$C_2 - C_3 - C_4$	119.54	119.70	$C_2 - C_3 - C_4 - C_5$	-0.01	-1.77
C7-C8	1.497	1.496	1.50	$C_5 - C_6 - C_7$	120.79	120.44	$C_2 - C_1 - C_6 - C_7$	-178.89	179.48
C ₁₂ -C ₁₃	1.396	1.389	1.41	$C_6 - C_7 - C_8$	119.52	118.97	$C_4 - C_5 - C_6 - C_7$	178.83	179.32
C ₈ -C ₁₃	1.405	1.394	1.40	$C_{10} - C_{11} - C_{12}$	119.80	119.82	$C_1 - C_6 - C_7 - C_8$	-157.66	-148.16
$C_1 - H_{14}$	1.085	0.950	-	$C_{11} - C_{12} - C_{13}$	120.13	120.39	$C_6 - C_7 - C_8 - C_{13}$	-121.16	-116.88
C7-N24	1.298	1.289	-	$C_8 - C_{13} - H_{23}$	119.64	119.96	$C_9 - C_8 - C_7 - N_{24}$	-120.37	-115.68
$N_{24} - N_{25}$	1.356	1.376	-	$C_6 - C_7 - N_{24}$	116.84	116.70	$C_5 - C_6 - C_7 - N_{24}$	-157.47	-149.59
$N_{25} - C_{26}$	1.374	1.358	-	$C_8 - C_7 - N_{24}$	123.64	124.31	$C_1 - C_6 - C_7 - N_{24}$	21.83	30.30
$C_{26} - N_{27}$	1.347	1.321	-	$C_7 - N_{24} - N_{25}$	119.89	117.43	$C_{13} - C_8 - C_7 - N_{24}$	59.40	64.78
$N_{27} - H_{28}$	1.011	0.880	-	$N_{24} - N_{25} - C_{26}$	121.17	119.70	$C_6 - C_7 - N_{24} - N_{25}$	-176.34	-177.67
$N_{25} - H_{29}$	1.017	0.881	-	$N_{25} - C_{26} - N_{27}$	115.09	116.70	$C_8 - C_7 - N_{24} - N_{25}$	3.12	0.71
$C_{26} - S_{30}$	1.679	1.687	-	$C_{26} - N_{27} - H_{28}$	120.08	120.01	$C_7 - N_{24} - N_{25} - C_{26}$	-178.51	-172.27
$N_{27} - H_{31}$	1.007	0.880	-	$N_{24} - N_{25} - H_{29}$	122.11	120.14	$N_{24} - N_{25} - C_{26} - N_{27}$	2.07	-5.45
$H_{23}\!\cdots\!H_{29}$	2.551	2.610	-	$N_{25} - C_{26} - S_{30}$	120.19	118.58	$N_{24} - N_{25} - C_{26} - S_{30}$	-178.25	173.91
$H_{29}{\cdots}S_{30}$	2.729	2.707	_	$C_{26} - N_{27} - H_{31}$	120.32	119.99	$N_{25}\!-\!C_{26}\!-\!N_{27}\!-\!H_{31}$	179.24	-179.95
a T. I f									

^a Taken from Ref. [7]. ^b Taken from Ref. [6].

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Table 2. Seco	ond-order perturb	ation theory analysis o	f Fock matrix in N	IBO basis		
Donor (i)	ED(<i>i</i>) (e)	Acceptor (i)	ED(<i>i</i>) (e)	E ^{(2)a} (kJ mol ⁻¹)	$E(i) - E(i)^{b}$ (arb. units)	<i>F(i, i</i>) ^c (arb. units)
	- () (-)	, v	- 97 (-7		y, (, (, , , , , , , , , , , , , , , , ,	
$\pi (C_1 - C_2)$	1.670	$\pi^* (C_3 - C_4)$	0.332	84.52	0.28	0.067
		$\pi^* (C_5 - C_6)$	0.419	85.14	0.28	0.069
π (C ₃ -C ₄)	1.657	$\pi^* (C_1 - C_2)$	0.301	81.17	0.28	0.067
		π^* (C ₅ -C ₆)	0.419	80.21	0.28	0.067
π (C ₅ -C ₆)	1.626	$\pi^* (C_1 - C_2)$	0.301	76.07	0.28	0.065
		π^* (C ₃ -C ₄)	0.332	84.39	0.28	0.068
		$\pi^* (C_7 - N_{24})$	0.417	111.88	0.20	0.067
π (C ₈ -C ₁₃)	1.630	$\pi^* (C_7 - N_{24})$	0.417	113.34	0.22	0.069
		$\pi^* (C_9 - C_{10})$	0.31	72.68	0.29	0.064
		π* (C ₁₁ -C ₁₂)	0.327	84.1	0.29	0.068
π (C ₉ -C ₁₀)	1.674	$\pi^* (C_8 - C_{13})$	0.431	90.88	0.27	0.071
		π* (C ₁₁ -C ₁₂)	0.327	80.58	0.28	0.065
π (C ₁₁ -C ₁₂)	1.650	$\pi^* (C_8 - C_{13})$	0.431	76.48	0.27	0.065
		$\pi^* (C_9 - C_{10})$	0.31	85.06	0.28	0.068
$n_1(N_{24})$	1.941	$\sigma^{*} (C_{1} - H_{14})$	0.013	2.09	0.90	0.019
		σ* (C ₇ -C ₈)	0.03	22.76	0.98	0.066
$n_1(S_{30})$	1.980	σ* (N ₂₅ – C ₂₆)	0.108	15.48	0.98	0.055
		σ* (C ₂₆ -N ₂₇)	0.084	14.94	0.99	0.054
$n_2(S_{30})$	1.817	$\sigma^* (N_{24} - N_{25})$	0.015	2.3	0.67	0.018
		σ* (N ₂₅ – C ₂₆)	0.108	92.34	0.47	0.092
		$\sigma^* (C_{26} - N_{27})$	0.084	85.52	0.48	0.091

ED, electron density.

^a $E^{(2)}$ means energy of hyperconjugative interactions; cf Eqn (5).

^b Energy difference between donor and acceptor *i* and *j* NBO orbitals.

^c F(i, j) is the Fock matrix element between *i* and *j* NBO orbitals.

Table 3. NBO results showing the formation of Lewis and non-Lewis orbitals by the valence hybrids corresponding to the intramolecular C-H···N hydrogen bonds of BTSC

Bond (A–B)	ED (e)	Energy (kJ mol ⁻¹)	ED _A (%)	ED _B (%)	NBO	S (%)	P (%)
σ (C ₇ -N ₂₄)	1.977	-1856.12	40.62	59.38	0.6373 (sp ^{2.92}) _C	25.48	74.44
					+0.7706 (sp ^{2.15}) _N	31.69	68.20
σ (N ₂₅ -C ₂₆)	1.984	-1981.57	60.78	39.22	0.7796 (sp ^{2.15}) _N	31.71	68.25
					+0.6263 (sp ^{2.48}) _C	28.69	71.21
σ (C ₂₆ -N ₂₇)	1.995	-1929.8	41.38	58.62	0.6433 (sp ^{2.40}) _C	29.40	70.52
					+0.7656 (sp ^{2.09}) _N	32.37	67.58
$\sigma (C_1 - H_{14})$	1.981	-1353.92	62.51	37.49	0.7906 (sp ^{2.28}) _C	30.45	69.47
					+0.6123 (s) _H	100.0	-
$\sigma (C_{26} - S_{30})$	1.990	-2304.14	57.81	42.19	0.7603 (sp ^{1.39}) _C	41.78	58.02
					+0.6495 (sp ^{2.69}) _S	26.82	72.18
$LP_1(N_{24})$	1.941	-1062.28	-	-	sp ^{1.53}	39.43	60.50

demonstrates strong delocalization leading to a stabilization of energy ~83.06 kJ mol⁻¹. The π electron cloud movement from donor to acceptor can make the molecule highly polarized and the ICT must be responsible for the NLO properties of BTSC. The orbital interaction energy between $\pi(C_8-C_{13}) \rightarrow \pi^*(C_7=N_{24})$ and $\pi(C_5-C_6) \rightarrow \pi^*(C_7=N_{24})$ are 113.34 and 111.88 kJ mol⁻¹, respectively (Table 2). These increases in the interaction energies are due to the strong ICT interactions leading to the stabilization of the molecule. According to NBO analysis (Table 3), all the CN bond orbitals are polarized toward the nitrogen atom (68% at N), whereas the $C_{26}-S_{30}$ bond orbitals are polarized toward the sulfur atom (72% at S). It is consistent with the charges on the nitrogen

and sulfur atoms. The ED distribution around the imino group mainly influences the polarity of the compound.

Mulliken charge analysis

The charge distribution on a molecule has a significant influence of the vibrational spectra. The Mulliken atomic charges were calculated at the B3LYP level using Gaussian '98, with the 6-31G* atomic basis set. The chart in Fig. 3 shows the Mulliken atomic net charges in BTSC. The atom N₂₇ shows more negative (-0.725 e) charge and C₂₆ more positive (0.386 e) charge, which suggests extensive charge delocalization in the entire molecule.



Figure 3. Mulliken charge distribution of BTSC.

The shortening of the C₂₆–N₂₇ bond (Table 1) also supports this conclusion. The positive charges are localized on the hydrogen atoms. Very similar values of positive charges are observed for the hydrogen atoms bonded to the nitrogen atoms (H_{28,29,31} ~0.361 e). In the two phenyl rings, all the C atoms have negative charges except C₆ (0.12 e) and C₈ (0.033 e), which suggests that the electronic delocalization is more intense between the carbon atoms responsible for charge transfer between the substituents. The charge noticed on the N₂₄ is smaller (compared to other N's) and equal to -0.312 e. This can be explained by high degree of conjugation, with a strong push–pull effect between the imino group and phenyl rings.^[33]

Absorption spectra and solvent effects

The electronic spectrum of BTSC was computed in the gas phase as well as in an ethanol environment and is listed in Table 4. The solvent effect was calculated using PCM-TD-DFT method. The observed and simulated (in gas phase and ethanol) UV–vis spectra are shown in Fig. 4.

The n $\rightarrow \pi^*$ transition energy is calculated at 406 cm⁻¹, above the experimental maximum in ethanol at 343 nm with strong intensity. There are also two $\pi \rightarrow \pi^*$ transitions. They are weak and observed at 297 and 233 cm⁻¹. The calculated absorption wavelengths in ethanol at 363 and 320 nm are identified as $\pi \rightarrow \pi^*$ transitions. The red shift of the computed transition energies is due to the charge transfer interaction. NBO analysis also shows the charge transfer interaction (explained earlier).

Vibrational spectral analysis

The vibrational spectral analysis of BTSC was made on the basis of NCA. A non-redundant set of internal coordinates for BTSC was defined (Tables S2 and S3), which was similar to the 'natural coordinates' recommended by Pulay *et al.*^[34] The calculated wavenumbers were selectively scaled according to the SQM procedure incorporating a set of eight transferable scale factors (shown in the last column of Table S3) recommended by Rauhut and Pulay.^[22] The SQM wavenumbers related to the observed bands are presented in Table 5 along with detailed assignments. The observed FT-IR and Raman spectra as well as the simulated theoretical spectra computed at B3LYP/6-31G^{*} level are given in Figs 5 and 6 for visual comparison.

Phenyl ring vibrations

The different normal vibrations of the monosubstituted phenyl rings are assigned according to Wilson's numbering convention.^[35] There are five C-H stretching vibrations in monosubstituted benzenes whose wavenumbers fall in the region 3120–3010 cm⁻¹.^[35] The C-H stretching vibrations in the phenyl rings arises from two nondegenerate modes a_{1g} and b_{1u} and two degenerate modes e_{2q} and e_{1u}, i.e. vibrations 2, 13, 7, and 20 respectively. In monosubstituted phenyl rings, 2, 7a, 7b, 20a, and 20b are active. The medium intensity band in IR at 3147 cm⁻¹ and the weak Raman band at 3142 cm⁻¹ are assigned to the 20a mode. The mode 20b is observed as strong Raman band at 3056 cm⁻¹ and a weak IR band at 3052 cm⁻¹. From NCA, the mode 20b is predicted at 3054 cm^{-1} with strong Raman intensity (92.97). Normal mode 2 is observed as a weak band in IR at 3026 cm^{-1} and the mode 7a is observed as weak bands at 2991 (IR) and 2992 $\rm cm^{-1}$ (Raman). Several C-H stretching modes are found to be weak, which is due to the charge transfer between the hydrogen atoms and carbon atoms.^[36] There are two doubly degenerate ring C-C stretching modes e_{2a} (8a, 8b) and e_{1u} (19a, 19b) which are not perturbed upon substitution.^[37] Normal vibrations 8a, 8b, 19a, 19b, and 14 are categorized as C-C stretching vibrations. The mode 8a of the monosubstituted ring is expected in the range 1614-1575 cm⁻¹, and 8b extends from 1597 to 1562 cm^{-1} . The normal mode 8a is found at higher wavenumbers than 8b and appears simultaneously as strong IR and Raman bands at 1598 and 1589 cm⁻¹, respectively. The enhanced intensity clearly exhibits the higher

Table 4. Calculated absorptions, energy, and oscillator strength of BTSC using TD-DFT method at B3LYP/6-31G* level								
	Ethanol							
					Wavelength (nm)			
Excitation	Wavelength (nm)	Energy (eV)	Oscillator strength	Excitation	Cal.	Exp.	Energy (eV)	Oscillator strength
67 ightarrow 68	406.41	3.0507	0.4934	67 ightarrow 68	406.46	343	3.0503	0.5020
66 ightarrow 68	366.28	3.3849	0.0005	66 ightarrow 68	362.64	297	3.4189	0.0004
66 ightarrow 70								
62 ightarrow 68	319.76	3.8774	0.0051	65 ightarrow 68	320.21	233	3.8720	0.0033
63 ightarrow 68				67 ightarrow 70				
65 ightarrow 68				67 ightarrow 72				
67 ightarrow 69								
67 ightarrow 70								



Figure 4. (a) Experimental UV-vis spectrum of the BTSC molecule in ethanol solvent. (b) Simulated UV-vis spectrum of the BTSC molecule in the gas phase. (c) Simulated UV-vis spectrum in ethanol for BTSC molecule calculated with the TD-DFT/PCM method.



Figure 5. (a) FT-IR spectrum of the BTSC molecule in the wavenumber range $4000-400 \text{ cm}^{-1}$. (b) Simulated IR spectra of the BTSC molecule computed at B3LYP/6-31G* basis set.

degree of the conjugation between the two rings.^[38] The ring mode 8b for Ph2 is observed only in Raman as a strong band at 1570 cm⁻¹. The 19a mode in monosubstituted benzene can be expected near 1500 cm⁻¹ with higher intensity, and 19b appears as weak band around 1470 cm⁻¹.^[35] This vibration 19 has a faint C-H in-plane bending nature with hydrogen and its carbon moving in opposite directions. The mode 19a appears as a strong band in IR at 1473 cm⁻¹. According to PED calculation, vibrational mode 19a has only 25% C-C stretching contribution and 39% C-H in-plane bending character. The weak band that appears at 1464 cm⁻¹ in Raman is assigned to the 19b mode of Ph1 and the weak band in IR at 1400 cm⁻¹ is assigned to 19b of Ph2. In Ph1, the ring mode 14 is observed as a medium intensity band in IR at 1323 cm⁻¹ and its counterpart in Raman occurs as a strong band at 1328 cm⁻¹. The bands observed at 1305 and 1308 cm⁻¹ in IR and Raman, respectively, are assigned to the mode 14 of Ph2. The simultaneous appearance of the ring C-C stretching bands



Figure 6. (a) FT-Raman spectrum of the BTSC molecule in the wavenumber range $3500-50 \text{ cm}^{-1}$. (b) Simulated Raman spectra of the BTSC molecule computed at B3LYP/6-31G* basis set.

in both IR and Raman of modes 8a and 14 evidences the charge transfer interactions.^[36,38,39] The normal modes 3, 9a, 15, 18a, and 18b are classified as C-H in-plane bending vibrations. The bands observed at 1283 cm⁻¹ in IR is assigned to the mode 3 of Ph1, and those at 1274 $\rm cm^{-1}$ (IR) and 1276 $\rm cm^{-1}$ (Raman) are assigned to the mode 3 of Ph2. The vibrational mode 9a is observed as a weak band in IR at 1161 cm⁻¹. The mode 15 is coupled with the ring C-C stretching coordinate and found to be active in IR at 1152 cm⁻¹ as a strong band. The very strong predicted intensities (126.64 (IR) and 161.83 (Raman)) of mode 15 is correlated with the experimental intensities. The mode 18b is observed as strong band in IR at 1067 cm⁻¹, and the mode 18a occurs as a strong band in IR at 1026 cm⁻¹ and in Raman at 1027 cm⁻¹ as weak band. The C-H out-of-plane bending (5, 10a, 10b, 11, and 17a), radial skeletal (1, 12, 6a, and 6b), and the out-of-plane skeletal (4,16a, and 16b) vibrations are listed in Table 5.



Table 5.	Vibrational assignmer	nt of BTSC by norm	al mode analysis	based on SQM for	ce field calculations
O fundam	bserved ientals (cm ⁻¹)			Selective scaled	B3LYP/6-31G* force field
ν _{IR}	ν_{Raman}	v_i (cm ⁻¹)	$A_i \mathrm{IR}^{\mathrm{a}}$	I _i R ^b	Assignment with PED (%) ^c
3410 m	_	3480	101.06	67.49	NH ₂ as (94)
3345 m	3347 w	3378	29.53	268.11	ν NH (99)
3238 m	3241 vw	3340	52.25	75.18	νNH ₂ ss (93)
3147 m	3142 w	3082	7.07	113.71	^{20a} vCHph1 (99)
-	-	3076	17.72	150.22	vCHph1 (98)
-	_	3076	13.48	288.24	vCHph2 (98)
-	-	3068	20.98	21.24	νCHph2 (99)
-	-	3067	34.13	189.8	vCHph1 (99)
-	-	3061	11.86	85.62	νCHph2 (99)
-	-	3054	11.16	164.84	νCHph1 (97)
3052 w	3056 s	3054	0.85	92.97	^{20b} <i>v</i> CHph2 (98)
3026 w	-	3048	1.13	16.97	² vCHph2 (99)
2991 vw	2992 w	3046	1.36	42.13	^{7a} vCHph1 (99)
1598 s	1589 vvs	1589	83.97	55.7	^{8a} νCCar1 (29), NH ₂ sci (23), νCN (20)
-	-	1584	153.98	74.55	NH ₂ sci (46), vCCar1 (24), vCN (14)
-	-	1580	1.67	94.83	νCCar2 (66), δR2CH (19), R2symd (10)
-	-	1567	24.51	1327.07	vCCar1 (33), vCN (18), CCCrock (14)
-	1570 vs	1556	1.8	6.94	^{8b} νCCar2 (58), δR2CH (15), νCCar1 (11)
-	-	1547	27.41	1300.29	νCN (35), νCCar1 (31), δR1CH (10)
1497 w	1498 m	1462	383.65	259.54	NHrock (31), νCN (19), δR1CH (15), νCCar1 (11)
1473 vs	-	1452	109.04	45.93	δ R2CH (39), ^{19a} ν CCar2 (25)
-	1464 w	1448	176.83	20.22	δR1CH (31), ^{19b} νCCar1 (19), δR2CH (16), NHrock (12)
1438 s	1446 m	1409	34.51	81.3	νCN (30), δR1CH (22), νCCar1 (18)
-	-	1404	45.06	5.73	δR1CH (25), νCCar1 (20), νCN (19), δR2CH (11)
1400 w	-	1401	63.2	18.57	δR2CH (37), ^{19b} νCCar2 (28), νCN (20)
1323 m	1328 s	1297	1.49	14.53	¹⁴ νCCar1 (76), δR1CH (13)
1305 w	1308 m	1289	2.32	6.69	¹⁴ νCCar2 (72), δR2CH (24)
-	-	1280	70.73	291.85	νCC (28), δCCN (21), δR2CH (12), δR1CH (10)
1283 sh	-	1268	9	7.01	³ δR1CH (48), δR2CH (15)
1274 m	1276 w	1254	81.09	56.04	$^{3}\delta$ R2CH (27), vCCar2 (25), NH ₂ rock (10)
1200 sh	-	1249	214.01	127.71	NHrock (17), ν CC (15), NH ₂ rock (14)
1170 s	1174 m	1157	38.48	26.2	vCC (21), vNN (19)
-	-	1139	4.12	6.84	δR2CH (78), νCCar2 (17)
-	1161 W	1137	12.36	45.24	$5^{43}\delta$ R1CH (74), vCCar1 (15)
1152 s	-	1119	0.02	5.51	$^{13}\delta$ R2CH (87), vCCar2 (13)
-	-	1117	0.3	12.82	$\delta R I C H (87), \nu C C ar I (12)$
1085 s	1091 s	1083	126.64	161.83	νNN (36), δCCN (14)
-	-	1053	14.93	6.89	ν CCarl (38), δ RICH (37)
1067 S	-	1052	9.77	0.85	ν CCar2 (39), $\frac{100}{3}$ R2CH (37)
1049 S	- 1027 w	1042	20.20	3.74	$V CN (32), NH_2 FOCK (10), \delta CNN (11)$
1020 VS	1027 W	1006	6.02 5.06	4.41	VCCall (40), ~ 0 RTCH (19), VCCall (17)
1000 511	1001 5	080	5.00	21.75	$PCCd12 (45), PCCd11 (16), \delta R2CH (10), R2tHgu (12)$
070 m	-	960	2.30	27.40	12 P1triad (48), vCCar2 (27), RT(1)g0(16)
970 111	-	960	0.33	0.73	Car2Hwag (84), PCCar1 (25), R2trigu (14), PCCar2 (12)
011 m	945 w	908	0.23	1.80	$\frac{5}{2}$
-		9 <u>/</u> 1	0.09	1.09	Car2Hwag (90)
930 m	_	928	0.40 0.81	1.70	17a Car2H wag (90)
922 \	_	930	12 72	73.66	$17a$ Car2Hwag (32) δ CCN (13) μ Car1 (12)
- vv	_	901	1 73	25.00	Car1Hwag (66) Car2Hwag (14)
888 w	_	897	5 77	3 38	10b Car2Hwag (45), 10b Car1Hwag (17)
_	_	833	0.94	7.07	Car2Hwag (98)
845 vs	848 vs	826	20.71	5.99	10a Car1Hwag (60), ν C=S (10)

Table 5. (Continued)

Observed fundamentals (cm^{-1})				Selective	scaled B3LYP/6-31G* force field	
ν _{IR}	v_{Raman}	v_i (cm ⁻¹)	$A_i \mathrm{IR}^{\mathrm{a}}$	<i>I</i> _i R ^b	Assignment with PED (%) ^c	
-	-	825	47.11	35.46	Car1Hwag (32), vC=S (16)	
775 vs	779 w	760	18.27	3.27	^{10a} Car2Hwag (28), R2puck (18), Car2Cwag (15), Car1Hwag (13)	
-	-	753	18.7	3.47	Car1Hwag (31), R1puck (17), Car1Cwag (13)	
724 m	729 w	713	3.79	3.92	¹¹ Car2Hwag (19), R2symd (18), νCC (14)	
698 vs	-	682	32.54	3.23	⁴ R2puck (46), Car2Hwag (33), Car2Cwag (10)	
671 s	675 vw	672	20.63	3.54	⁴ R1puck (49), Car1Hwag (30), Car1Cwag (11)	
-	650 vw	644	3.18	3.78	R1puck (22),-Ph1-C-Ph2-t (18)	
-	-	634	13.93	5.63	R2puck (23), R1asymd (12), N–C=Swag (11)	
-	619 w	627	13.27	1.57	R2puck (18), N–C=Swag (16), CNH ₂ t (12)	
-	-	613	0.04	7.96	R1symd (59), R1asymd (16)	
-	599 vw	607	0.3	3.48	^{6b} R2asymd (64)	
-	-	590	2.41	1.52	CCCrock (36), δCCN (24), R2symd (11)	
-	-	578	10.46	2.52	$N-C=Swag$ (53), CNH_2t (36)	
-	535 vw	537	66.81	5.77	CNH ₂ t (25), N ₂₅ Ct (23), NHwag (22), N ₂₄ Nt (17)	
-	499 m	482	1.71	12.15	^{16b} R2symt (20), Car2Cwag (11), Car1Cwag (10), R1asymt (10)	
-	481 vw	470	5.54	4.54	^{16a} R1asymt (16),-Ph1-C-Ph2-t (15), Car1Cwag (12)	
-	433 w	447	25.87	0.75	R2symt (20),-Ph1-C-Ph2-t (16), Car2Cwag (13), δCNN (10)	
-	412 w	408	5.72	3.38	N-C=Srock (36)	
-	-	393	0.05	2.17	R1symt (49), R1asymt (18), bCar1H (15), R2asymt (12)	
-	364 w	387	0.8	3.92	^{16a} R2asymt (64), Car2Hwag (13)	
-	-	342	10.82	2.1	C ₇ Nt (34), R1asymt (13)	
-	268 m	285	5.32	1.36	CCCrock (24), δCar1C (14), δCCN (10)	
-	-	257	8.24	1.52	R2symt (29), δCCN (21)	
-	225 w	241	5	4.1	δΝΝC (21), νCC (20)	
-	-	214	54.14	6.36	CNH ₂ wag (17), δCar2C (16), R1asymt (13)	
-	197 w	190	47.69	1.51	CNH_2 wag (24), δ Car2C (13), δ CCN (12)	
-	-	178	95.87	2.29	CNH ₂ wag (40)	
-	100 vs	133	2.24	4.45	-Ph1-C-Ph2-t (53), NHwag (10)	
-	-	72	0.36	7.86	CCCrock (47), δCCN (25)	
-	-	61	0.37	6.06	C ₈ C ₇ t (31), Car2Cwag (21), N ₂₅ Ct (10)	
-	-	57	0.53	4.67	N ₂₄ Nt (23)	
-	-	53	0.27	14.91	C ₆ C ₇ t (46), C ₈ C ₇ t (22)	
-	-	43	0.1	2.39	N ₂₅ Ct (24), C ₈ C ₇ t (24), NHwag (15), CNH ₂ wag (12), C ₇ Nt (10)	
-	-	29	0.31	2.29	-Ph1-C-Ph2-t (57), C ₈ C ₇ t (19), C ₆ C ₇ t (18)	

The notations in superscripts are as depicted in the study by Varsanyi.^[35]

vs, very strong; vvs, very very strong; s, strong; m, medium; sh, shoulder; w, weak; vw, very weak; R/ph/ar, phenyl ring; ν , stretching; ss, symmetric stretching; as, asymmetric stretching; b, δ , bending; t, torsion; sci, scissoring; wag, wagging; rock, rocking; trigd, trigonal deformation; symd, symmetric deformation; asymd, asymmetric deformation; symt, symmetric torsion; asymt, asymmetric torsion; puck, puckering. ^a Calculated IR intensities.

^b Relative Raman intensities normalized to 100 *cf* Eqn (1).

^c Only PED values greater than 10% are given.

NH₂ and NH vibrations

The NH₂ stretching vibrations of thioamides occur near 3380 and 3180 cm⁻¹ for asymmetric and symmetric stretching vibrations.^[40] The asymmetric NH₂ stretching is observed as a medium band in IR at 3410 cm⁻¹. The bands at 3238 cm⁻¹ (IR) and 3241 cm⁻¹ (Raman) are assigned to symmetrical NH₂ stretching mode. The blue shift of the NH₂ stretching wavenumbers is due to the formation of interand intramolecular N-H···N hydrogen bonds. The NH₂ scissoring that appears as strong bands at 1598 cm⁻¹ in the IR spectrum and 1589 cm⁻¹ in Raman has 23% of NH₂ bending character because of its association with 8a and CN stretching modes. The NH₂ rocking mode is coupled with ring C-C stretching and C-H

in-plane bending mode 3 to give a medium intensity band at 1274 cm⁻¹ in IR and a weak band at 1276 cm⁻¹ in Raman. The NH₂ out-of-plane vibrations are shown in Table 5. The bands appearing at 3345 cm⁻¹ (IR) and 3347 cm⁻¹ (Raman) are assigned to the N–H stretching mode. The N–H in-plane bending mode is observed as a medium intensity band in Raman at 1498 cm⁻¹ and as a weak band in IR at 1497 cm⁻¹. The NH stretching wavenumber is in good agreement with the PED (99%) results.

$\succ C = N - N - C \prec vibrations$

In phenyl-substituted hydrazones, the possibility of obtaining a charge transfer interaction is related to the absence of even a





Figure 7. (a) HOMO plot of BTSC at B3LYP/6-31G*. (b) LUMO plot of BTSC at B3LYP/6-31G*.

slight amount of strain in the hydrazono group, which must be perfectly planar to allow conjugation of the group.^[38] The C=N stretching modes of thiosemicarbazones occur in the region 1655–1642 cm⁻¹.^[40] The C=N stretching vibrations are coupled with the ring C-C stretching modes. The strong bands observed at 1598 and 1589 cm⁻¹ in IR and Raman, respectively, are assigned to the C=N stretching mode. The downshifting of C=N stretching wavenumber and the enhanced intensity are due to the charge transfer interaction between the phenyl rings through the $\prec N = C \overbrace{Ph1}^{Ph1} \succ$ skeleton.^[38] The N-N stretching mode

is observed as a medium intensity band at 1085 cm^{-1} (IR) and at 1091 cm^{-1} (Raman). The CNN bending vibration is prominent along with the ring C–H out-of-plane bending 17a and ring C–C stretching modes and seen as a weak band in IR at 922 cm⁻¹.

C = S vibrations

The C=S stretching mode of thioamides appears about 900 cm^{-1} .^[40] The C=S stretching vibration is found as an intense band in IR at 845 cm⁻¹ and its Raman counterpart appears at 848 cm⁻¹ and has only 10% of this stretching character because of its association with the phenyl 10a mode. The downshifting of C=S stretching wavenumbers can be attributed to the greater contribution of resonance form $>N^+=C-S^-$. The red shift of the C=S stretching wavenumber is also due to the hyperconjugation interaction between the lone pair sulfur atom and the σ^* (C–N) bonds. The NBO analysis (Table 2) clearly shows that there are \sim 15.21 and \sim 88.93 kJ mol⁻¹ involved in LP₁(S) $\rightarrow \sigma^*$ $(C_{26}-N_{25})/(C_{26}-N_{27})$ and $LP_2(S) \rightarrow \sigma^* (C_{26}-N_{25})/(C_{26}-N_{27})$ hyperconjugative interactions. The out-of-plane and in-plane bending vibrations of N-C=S are mixed with other internal coordinates in the PED (Table 5) and are observed as weak bands in Raman at 619 and 412 cm⁻¹, respectively.

HOMO-LUMO gap

The HOMO-LUMO gap of a molecule will play an important role in determining its NLO properties.^[36,38,39] Both HOMO and the LUMO are the main orbitals taking part in a chemical reaction. The HOMO energy characterizes the ability of electron giving, whereas the LUMO characterizes the ability of electron accepting, and the gap between HOMO and LUMO characterizes the molecular chemical stability. The effect on the LUMO levels is stronger when an electron accepting group is present. The results for the HOMO (-7.94 eV) and LUMO (-5.46 eV) energies indicate a charge delocalization taking place within the crystal. The HUMO-LUMO orbitals are

shown in Fig. 7. The HOMO-LUMO difference is 2.48 eV. The above results show that BTSC crystal is the best material for NLO applications.

Conclusion

The BTSC crystals were grown by the slow evaporation technique. The calculated first hyperpolarizability of BTSC is found to be 4.5×10^{-30} esu, which is 23 times that of urea. Kurtz and Perry powder reflection studies confirm the second-order NLO properties of the molecule. The optimized geometry shows that the two phenyl rings are nonplanar. The simultaneous occurrence of modes 8a and 14 provide evidence for the charge transfer interactions. The enhanced intensity of mode 8a clearly shows the higher degree of conjugation, which is responsible for the optical nonlinearity of the crystal. The red shift of the C=S stretching wavenumber confirms the greater contribution of resonance form $>N^+=C-S^-$. The elongation of the C-N bond length and the downshifting of C=N stretching wavenumber clearly bear out the charge transfer interaction between the phenyl rings through the $>-N=C-\prec$ skeleton. The shortening of the N-N bond observed in semicarbazone, which has an extensively delocalized group on N₂₅, confirms that the compound is a delocalized and conjugated one.

Supporting information

Supporting information may be found in the online version of this article.

References

- G. Anandha babu, K. Thirupugalmani, M. Jayaprakasan, P. Ramasamy, J. Cryst. Growth 2009, 311, 1607.
- [2] G. Anandha Babu, P. Ramasamy, Mater. Chem. Phys. 2010, 119, 533.
- [3] S. Genbo, G. Shouwu, P. Feng, H. Youping, L. Zhengdong, J. Phys. D: Appl. Phys. B 1993, 26, 236.
- [4] K. M. Weitzel, H. Bassler, J. Chem. Phys. **1986**, 84, 1590.
- [5] L. M. Babkov, M. A. Kovner, V. I. Mel'nik, G. A. Puchkovskaya, N. P. Chkarchenko, M. T. Shpak, *Opt. Spectrosc.* **1973**, *35*, 58. in Russian.
- [6] T. S. Lobana, S. Khanna, R. J. Butcher, A. D. Hunter, M. Zeller,
- Polyhedron 2006, 25, 2755.
 [7] E. B. Fleischer, N. Sung, S. Hawkinson, J. Phys. Chem. 1968, 72, 4311.
- [7] E. B. FIEISCHEF, N. SUNG, S. HAWKINSON, J. Phys. Chem. **1968**, 72, 4311
 [8] K. Nakatani, J. Delaire, Chem. Mater. **1997**, 9, 2682.
- [9] H. Kunkely, A. Vogler, J. Photochem. Photobiol. A: Chem. 2001, 138,
- [9] 11. Kulikely, A. Vogiel, *S. Photochem. Photoboli. A. chem.* **2001**, *136*, 51.
- [10] N. Vijayan, R. Ramesh Babu, R. Gopalakrishnana, S. Dhanuskodi, P. Ramasamy, J. Cryst. Growth 2001, 233, 863.
- [11] K. Sethuraman, R. Ramesh Babua, N. Vijayan, R. Gopalakrishnana, P. Ramasamy, J. Cryst. Growth 2006, 290, 539.
- [12] R. Ramesh Babu, N. Vijayan, M. Gunasekaran, R. Gopalakrishnan, P. Ramasamy, J. Cryst. Growth 2004, 265, 290.
- [13] R. Ramesh Babu, N. Vijayan, R. Gopalakrishnan, P. Ramasamy, J. Cryst. Growth 2002, 240, 545.
- [14] S. K. Kurtz, T. T. Perry, J. Appl. Phys. 1968, 39, 3798.
- [15] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery Jr. R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, B. Mennucci, C. Pomelli, C. Adamo, R. Cammi, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, B. Foresman, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, J. Cioslowski, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, GAUSSIAN 98, Revision A9, Gaussian, Inc., Pittsburgh, PA, 1998.

- [16] J. M. Ramos, O. Versiane, J. Felcman, C. A. Téllez S, Spectrochim. Acta A 2009, 72, 182.
- [17] C. A. Téllez S, E. Hollauer, T. Giannerini, M. I. Pais da Silva, M. A. Mondragón, J. R. Rodríguez T, V. M. Castaño, *Spectrochim. Acta A* 2004, 60, 2171.
- [18] T. A. Mohamed, R. S. Farag, Spectrochim. Acta A 2005, 62, 800.
- [19] C. Ravikumar, L. Padmaja, I. Hubert Joe, *Spectrochim. Acta A* **2010**, *75*, 859.
- [20] T. Sundius, J. Mol. Struct. **1990**, 218, 321.
- [21] T. Sundius, Vib. Spectrosc. 2002, 29, 89.
- [22] G. Rauhut, P. Pulay, J. Phys. Chem. 1995, 99, 3093.
- [23] G. Rauhut, P. Pulay, J. Phys. Chem. 1995, 99, 14572.
- [24] E. D. Glendening, A. E. Reed, J. E. Carpenter, F. Weinhold, NBO Version 3.1, TCI, University of Wisconsin: Madison, 1998.
- [25] G. Keresztury, S. Holly, J. Varga, G. Besenyei, A. Y. Wang, J. R. Durig, Spectrochim. Acta A **1993**, 49, 2007.
- [26] G. Keresztury, in Raman Spectroscopy: Theory in Handbook of Vibrational Spectroscopy, vol. 1 (Eds.:J. M. Chalmers, P. R. Griffith), John Wiley & Sons Ltd.: New York, 2002.
- [27] K. S. Thanthiriwatte, K. M. Nalin de Silva, J. Mol. Struct. (Theochem) 2002, 617, 169.
- [28] M. Adant, M. Dupuis, J. L. Bredas, Int. J. Quantum Chem. 1995, 56, 497.

- [29] S. Miertus, E. Scrocc, J. Tomasi Chem. Phys. 1981, 55, 117.
- [30] S. Miertus, J. Tomasi, Chem. Phys. 1982, 65, 239.
- [31] M. Cossi, V. Barone, R. Cammi, J. Tomasi, Chem. Phys. Lett. 1996, 255, 327.
- [32] A. E. Reed, L. A. Curtiss, F. Weinhold, Chem. Rev. 1988, 88, 899.
- [33] A. Trzesowska, J. Mol. Struct. 2009, 917, 125.
- [34] P. Pulay, G. Fogarasi, F. Pang, J. E. Boggs, J. Am. Chem. Soc. 1979, 101, 2550.
- [35] G. Varsanyi, Vibrational Spectra of Benzene Derivatives, Academic Press: New York, 1969.
- [36] C. Ravikumar, I. Hubert Joe, D. Sajan, Chem. Phys. 2010, 369, 1.
- [37] F. R. Dollish, W. G. Fateley, F. F. Bentley, Characteristic Raman Frequencies of Organic Compounds, John Wiley & Sons: New York, 1974.
- [38] C. Ravikumar, I. Hubert Joe, V. S. Jayakumar, Chem. Phys. Lett. 2008, 460, 552.
- [39] C. Ravikumar, I. Hubert Joe, Phys. Chem. Chem. Phys. 2010, 12, 9452.
- [40] D. L. Vein, N. B. Colthup, W. G. Fateley, J. G. Grasselli, The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules, Academic Press: New York, 1991.