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FT-IR, FT-Raman and ab-initio studies of 1,3-diphenyl thiourea

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ABSTRACT

The FT-IR and FT-Raman spectra of 1,3-diphenyl thiourea were recorded and analyzed. The vibrational wavenumbers were examined theoretically with the aid of the Gaussian03 package of programs using the HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) levels of theory. The data obtained from vibrational wavenumber calculations are used to assign vibrational bands obtained in IR and Raman spectroscopy of the studied molecule. The first hyperpolarizabililty, 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 geometrical parameters of the title compound are in agreement with the values of similar structures. The changes in the C-N bond lengths suggest an extended π-electron delocalization over the thiourea moiety which is responsible for the non-linearity of the molecule.

1. Introduction

Thiourea and substituted thioureas are versatile precursor units in the synthesis of many useful heterocyclic compounds [1]. Theoretical study of the Hg^{2+} recognition by 1,3-diphenylthiourea has been reported [2]. The mechanism of enantioselective Michael addition of acetylacetone to a nitroolefin catalyzed by a thiourea based chiral bifunctional organocatalyst is investigated using density functional theory calculations [3]. Yang *et al.* [4] reported the structural and spectroscopic study of *N*-2-fluorobenzoyl-*N'*-4-methoxyphenyl thiourea. Badawi reported the structural stability, C-N internal rotations and vibrational spectral analysis of non-planar phenylurea and phenylthiourea [5]. Metal organic coordination compounds as non linear optical (NLO) materials have attracted much more attention for their high NLO coefficients, stable physico-chemical properties and better mechanical intension. Many metal organic coordination complexes of thiourea materials with good NLO effects have been designed and synthesized [6-11]. Pfeffer *et al.* [12] reported the anion recognition using pre-orgranized thiourea functionalized polynorbornance receptors. There is currently great interest in the development of supramolecular systems that have the ability to bind and signal the presence of anions, as well as transporting such species across vesicle and cell membranes [13,14]. Molecules that possess functional groups such as amides, ureas and thioureas [15-17] have proven to be particularly effective in this regard as they are able to bind anions using directional hydrogen bonding interactions. Thiourea and substituted thioureas are especially important for their non linear optical properties. Hence the theoretical study of a symmetrically substituted aryl thiourea, 1,3-diphenyl thiourea, has been attempted.

2. Experimental

1,3-Diphenyl thiourea were prepared by reported method [18]. Briefly, 20 g sodium hydroxide (0.5 mol), 30 mL carbon disulphide (0.5 mol), 94 mL aniline (1 mol) and 5 mL ethyl alcohol were refluxed for 30 minutes in an RB flask. The solid thiourea separated is filtered at the pump, washed with water and ether and dried. White flake with a melting point of 153 °C was obtained. The purity was ascertained by TLC. The FT-IR (Figure 1) was recorded using a Perkin Elmer FTIR Spectrometer Spectrum RX1 with KBr pellets, number of scans 16, resolution 2 cm^{-1}. The FT-Raman spectrum (Figure 2) was obtained on a Bruker Equinox 55/s spectrometer with FRA Raman socket, 106/s. For excitation of the spectrum the emission of Nd:YAG laser was used, excitation wavelength 1064 nm, laser power 250 mW, resolution 2 cm^{-1}, number of scans 128, measurement on solid sample.

3. Computational details

Calculations of the title compound were carried out with Gaussian03 software program [19] using the HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) basis sets to predict the molecular structure and vibrational wavenumbers and also with Becke's three parameter hybrid model using the Lee-Yang-Parr correlation functional (B3LYP) method. Molecular geometries were fully optimized by Berny's optimization algorithm using redundant internal coordinates. Harmonic vibrational wavenumbers were calculated using analytic second derivatives to confirm the convergence to minima on the potential surface. At the optimized structure (Figure 3) of the examined species, no imaginary wavenumber modes were obtained, proving that a true minimum on the potential surface

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was found. The DFT hybrid B3LYP functional tends to overestimate the fundamental modes; therefore scaling factors have to be used for obtaining a considerably better agreement with experimental data. Therefore, a scaling factor of 0.9613 and 0.8929 were uniformly applied to the DFT and HF calculated wavenumbers [20]. The observed disagreement between theory and experiment could be a consequence of the anharmonicity and of the general tendency of the quantum chemical methods to overestimate the force constants at the exact equilibrium geometry. Table 1 gives the calculated (DFT) geometrical parameters of the title compound.

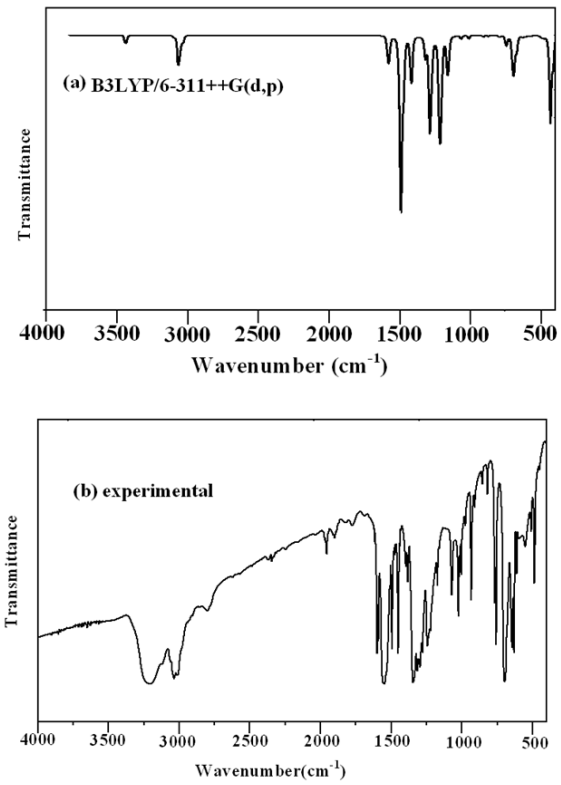

Figure 1. FT-IR spectrum of 1,3-diphenyl thiourea (a) theoretical (b) experimental.

4. Results and Discussion

4.1. IR and Raman spectra

The observed IR, Raman bands with the relative intensities, scaled wavenumbers and assignments are given in Table 2. The assignments of the benzene ring vibrations of the title compound in Wilson notation [21] is made by referring the case of benzene derivatives with mono substitution as summarized by Roeges [22]. The NH stretching vibration [22] appears as a strong broad band in the region 3390 ± 60 cm^{-1}. In the present study, the NH stretching band is observed at 3217 cm^{-1} in the IR spectrum and at 3207 cm^{-1} in the Raman spectrum. The corresponding calculated values (DFT) are 3438 and 3432 cm^{-1}. The NH stretching wavenumber is redshifted in the IR spectrum with a strong intensity from the computational wavenumber which indicates the weakening of the N-H bond resulting in proton transfer to the neighbouring sulfur [23]. El-Asmy and Al-Hazmi [24] reported νNH in the region 3138-3323 cm^{-1}. The CNH vibrations in which N and H atoms move in opposite directions of the carbon atom in the amide moiety appear at 1507, 1494 cm^{-1} in the IR spectrum, 1517, 1490 cm^{-1} in the Raman spectrum and at 1507, 1491 cm^{-1} theoretically (DFT) and the CNH vibrations in which N and H atoms move in the same direction of the carbon atom in the amide group appear at 1298, 1278 (IR), 1249 (Raman) and 1292, 1285 cm^{-1} (DFT) [25-27]. The NH rock in the plane is not seen in the IR spectrum but the DFT calculations give this mode at 1139 cm^{-1} [27]. The out-of-plane wagging [22] of NH is moderately active with a broad band in the region 790 ± 70 cm^{-1} and the band at 858 cm^{-1} in the IR spectrum, 858 cm^{-1} in the Raman spectrum and 872, 868 cm^{-1} (DFT) are assigned as this mode. El-Shahawy *et al.* [27] reported a value 710 cm^{-1} for this mode. Badawi reported [5] the NH vibrational modes at 3315, 1498, 1268 cm^{-1} in the IR spectrum, 3320, 1508, 1264 cm^{-1} in the Raman spectrum and at 3617, 1502, 1256 cm^{-1} theoretically. Panicker *et al.* [28] reported the NH bending modes at 1538, 1220 cm^{-1} in the IR spectrum and at 1558, 1223 cm^{-1} theoretically (DFT).The C-N stretching vibration [22] coupled with δNH, is moderately to strongly active in the region 1275 ± 55 cm^{-1}. El-Shahawy *et al.* [27] observed a band at 1320 cm^{-1} in the IR spectrum as the νCN mode. Yang *et al.* [4] reported aromatic C-N stretching band at 1359 cm^{-1}. In the present case, the bands at 1326, 1312 cm^{-1} in the IR spectrum and at 1345, 1316 cm^{-1} in the Raman spectrum are assigned as this mode. The DFT calculations give the corresponding bands at 1318 and 1307 cm^{-1} which are not pure but contain significant contributions from other modes also.

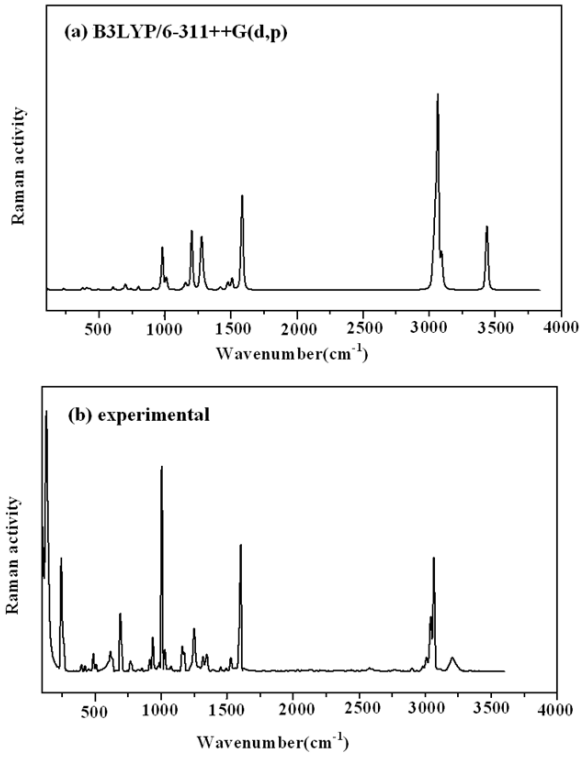

Figure 2. FT-Raman Spectrum of 1,3-diphenyl thiourea (a) theoretical (b) experimental.

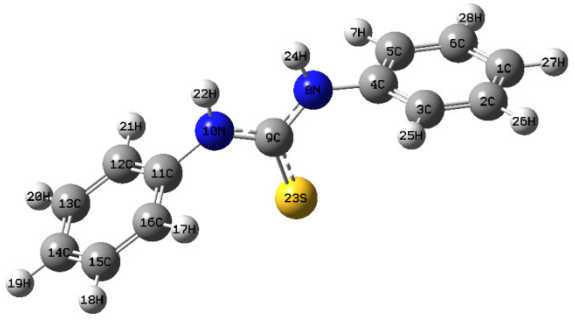

Figure 3. Optimized geometry of 1,3-diphenyl thiourea.

Table 1. Geometrical parameters (DFT) of 1,3-diphenyl thiourea, atom labeling according to Figure 3.

Bond lengths(Å)		Bond angles(°)		Dihedral angles(°)	
C_1-C_2	1.3949	C_2-C_1-C_6	119.4	C_6-C_1-C_2-C_3	-0.1
C_1-C_6	1.3928	C_1-C_2-C_3	120.8	C_2-C_1-C_6-C_5	-0.6
C_2-C_3	1.3915	C_2-C_3-C_4	119.7	C_1-C_2-C_3-C_4	0.8
C_3-C_4	1.3976	C_3-C_4-C_5	119.6	C_2-C_3-C_4-C_5	-0.8
C_4-C_5	1.3981	C_3-C_4-N_8	122.1	C_2-C_3-C_4-N_8	-177.0
C_4-N_8	1.4188	C_5-C_4-N_8	118.2	C_3-C_4-C_5-C_6	0.0
C_5-C_6	1.3928	C_4-C_5-C_6	120.3	N_8-C_4-C_5-C_6	176.4
C_9-N_8	1.3814	C_1-C_6-C_5	120.1	C_3-C_4-N_8-C_9	-47.3
C_9-N_{10}	1.3814	C_4-N_8-C_9	128.6	C_5-C_4-N_8-C_9	136.4
C_9-S_{23}	1.6636	N_8-C_9-N_{10}	110.1	C_4-C_5-C_6-C_1	0.7
C_{11}-N_{10}	1.4188	N_8-C_9-S_{23}	124.9	C_4-N_8-C_9-N_{10}	173.0
C_{11}-C_{12}	1.3975	N_{10}-C_9-S_{23}	124.9	C_4-N_8-C_9-S_{23}	-7.0
C_{11}-C_{16}	1.3981	C_9-N_{10}-C_{11}	128.6	N_8-C_9-N_{10}-C_{11}	173.1
C_{12}-C_{13}	1.3915	N_{10}-C_{11}-C_{12}	122.1	S_{23}-C_9-N_{10}-C_{11}	-6.9
C_{13}-C_{14}	1.3949	N_{10}-C_{11}-C_{16}	118.2	C_9-N_{10}-C_{11}-C_{12}	-47.4
C_{14}-C_{15}	1.3928	C_{12}-C_{11}-C_{16}	119.6	C_9-N_{10}-C_{11}-C_{16}	136.3
C_{15}-C_{16}	1.3928	C_{11}-C_{12}-C_{13}	119.7	N_{10}-C_{11}-C_{12}-C_{13}	-177.0
		C_{12}-C_{13}-C_{14}	120.8	C_{16}-C_{11}-C_{12}-C_{13}	-0.8
		C_{13}-C_{14}-C_{15}	119.4	N_{10}-C_{11}-C_{16}-C_{15}	176.4
		C_{14}-C_{15}-C_{16}	120.1	C_{12}-C_{11}-C_{16}-C_{15}	0.0
		C_{11}-C_{16}-C_{15}	120.3	C_{11}-C_{12}-C_{13}-C_{14}	0.8
				C_{12}-C_{13}-C_{14}-C_{15}	-0.2
				C_{13}-C_{14}-C_{15}-C_{16}	-0.6
				C_{14}-C_{15}-C_{16}-C_{11}	0.7

The C=S stretching bands [22,25,29] are observed in the range 800 ± 130 cm^{-1}, usually with a moderate intensity. Since the S atom is less electronegative than the O atom, the C=S group is not as polar as the C=O group and less prone to form bridges. The C=S deformation bands are expected in the regions [22] 510 ± 90 and 420 ± 100 cm^{-1}. Nigam *et al*. [30] reported the C=S stretching mode at 847 and 835 cm^{-1}. For the title compound, the C=S stretching mode is observed at 908 cm^{-1} in IR, 911 cm^{-1} in Raman and at 908 cm^{-1} theoretically (DFT).

The existence of one or more aromatic ring in a structure is normally readily determined from the C-H and C=C-C related vibrations. The C-H stretching occurs above 3000 cm^{-1} and is typically exhibited as a multiplicity of weak to moderate bands, compared with the aliphatic C-H stretch [31]. For mono substituted benzenes, the CH stretching modes are expected in the region 3105-3000 cm^{-1} [22]. There are five CH stretching modes 20a, 20b, 2, 13, 7b for mono substituted benzenes. According to selection rules all five bands are allowed in the IR spectrum [26]. The calculated values are in the range 3097-3032 cm^{-1}. The bands observed at 3113, 3062, 3042, 3020 cm^{-1} in the IR spectrum and at 3113, 3068, 3040, 3010 cm^{-1} in the Raman spectrum were assigned as υCH modes of the benzene rings.

The benzene ring possesses six ring stretching vibrations, of which the four with the highest wavenumbers (8a, 8b, 19a and 19b, occurring respectively near 1600, 1580, 1490 and 1440 cm^{-1}) are good group vibrations. In the absence of ring conjugation, the band near 1580 cm^{-1} is usually weaker than that at 1600 cm^{-1}. The fifth ring stretching vibration υPh 14 is active near 1335 ± 35 cm^{-1}, a region which overlaps strongly with that of the CH in-plane deformation and the intensity is in general, low or medium high [22,26]. The sixth ring stretching vibration or ring breathing mode υPh 1 appears as a weak band near 1000 cm^{-1} in mono substituted benzenes [22]. The bands observed at 1600, 1589, 1562, 1475, 1460, 1434, 1326, 1312 cm^{-1} in the IR spectrum and at 1602, 1465, 1345, 1316 cm^{-1} in the Raman spectrum are assigned as υPh ring stretching modes. As seen from the Table 2, the DFT calculations give these modes in the range 1584- 1307 cm^{-1}. These vibrations are expected in the region 1620-1300 cm^{-1} [22]. The frequency of the vibrational pair 8, 19a in mono substituted benzenes is rather insensitive of substitution [26]. The frequency interval for vibration 19a is 1470-1515 cm^{-1} [26,32] and for all mono substituted benzene derivatives 19a have a band between 1477 and 1511 cm^{-1} in the IR spectrum. When derivatives have substituents of donor character, the frequency is found between 1493 and 1511 cm^{-1} and in this group of derivatives the band has higher intensity when a carbon atom is attached directly to the ring. For the title compound the ring breathing modes are assigned at 979, 978 cm^{-1} theoretically. The strong band at 1004 cm^{-1} in the Raman spectrum is assigned with confidence to the characteristic ring breathing mode of the title compound. The ring breathing mode for mono substituted benzene is reported at 983 cm^{-1} by Panicker *et al*. [33] and at 1010 cm^{-1} in the Raman spectrum by Badawi *et al*. [5] for phenyl urea.

In mono substituted benzenes, there should be five CH in-plane bending vibrations 3, 9a, 9b, 15 and 18a. The mode 9a appears between 1170 and 1181 cm^{-1} in the spectra of all mono substituted benzene derivatives, mode 15 is found between 1060 and 1080 cm^{-1} and the intensity of 9a and 18a are the most intense in the IR spectrum [26,32]. The mode 3 is weak in general for both IR and Raman in the range 1253-1331 cm^{-1} [26]. In the present case the bands observed in the range 1003-1266 cm^{-1} in the IR spectrum, 1165 – 1024 cm^{-1} in the Raman spectrum and in the range 1009-1275 cm^{-1} (DFT) are assigned as δCH modes of the phenyl rings. Some modes are not pure, but contain significant contributions from other modes also. The in-plane CH vibrations are expected in the range 1015-1300 cm^{-1} for mono substituted benzenes [22].

The out-of-plane CH deformations γCH of mono substituted benzene derivatives have the modes 5, 10a, 11, 17a and 17b [22,26]. These modes are expected in the range 1000-700 cm^{-1} [22]. Generally, the CH out-of-plane deformations with the highest wavenumbers have a weaker intensity than those absorbing at lower wavenumbers. The stronger γCH band occurring in the region 775 ± 45 cm^{-1} (γCH 11 or umbrella mode) tends to shift to lower (higher) wavenumbers with increasing electron donating (attracting) power of the substituent, but seems to be more sensitive to mechanical interaction effects. The lowest wavenumbers for this umbrella mode are found in the spectra of benzenes substituted with a saturated carbon or heavy atoms such as halogen, sulfur or phosphorus [26,34-36]. The bands at 938, 809, 789, 752, 698 cm^{-1} in the IR spectrum, 936, 765, 690 cm^{-1} in the Raman spectrum and the calculated values (DFT) in the range 945-699 cm^{-1} are assigned as the out-of-plane CH modes of the phenyl rings. The out-of-plane CH deformation γCH 11 at 698 cm^{-1} and the out-of-plane ring deformation γPh 4 at 655, 632 cm^{-1} in the IR spectrum form a pair of strong bands characteristic of mono substituted benzene derivatives, which find support from computational results [22,36].

Table 2. Calculated (scaled) vibrational wavenumbers, measured infrared and Raman band positions and assignments for 1,3-diphenyl thiourea*.

HF/6-311++G(d,p)			B3LYP/6-311++G(d,p)			IR	Raman	Assignments
ν (cm^{-1})	IR intensity	Raman activity	ν (cm^{-1})	IR intensity	Raman activity	ν (cm^{-1})	ν (cm^{-1})	
3437	54.13	207.48	3438	18.55	273.43	3217 sbr	3207 sbr	νNH
3429	8.21	0.22	3432	10.57	28.07			νNH
3009	0.21	521.89	3097	0.26	90.23	3113 sh	3113 w	νCH 20a
3009	7.66	27.09	3097	4.36	21.65			νCH 20a
3005	54.10	0.71	3066	0.07	516.99		3068 s	νCH 20b
3005	0.00	0.04	3066	56.25	63.04	3062 sh		νCH 20b
2997	5.70	103.11	3054	25.16	104.16			νCH 2
2996	70.71	13.68	3054	28.19	87.46			νCH 2
2987	14.18	26.86	3044	0.27	118.88		3040 s	νCH 13
2987	0.79	198.91	3044	1.17	72.08	3042 m		νCH 13
2976	0.02	70.85	3032	8.47	42.84			νCH 7b
2976	0.32	6.60	3032	12.46	41.17	3020 w	3010 w	νCH 7b
1605	0.01	69.97	1584	0.68	378.46	1600 s	1602 vs	νPh 8a
1601	37.17	3.50	1583	27.14	4.37	1589 s		νPh 8a
1584	4.32	3.81	1578	1.36	7.12			νPh 8b
1583	0.00	19.94	1574	69.67	6.01	1562 sbr		νPh 8b
1529	0.75	5.15	1507	427.45	44.96	1507 m	1517 m	δNH
1514	694.37	14.95	1491	427.45	0.74	1494 s	1490 w	δNH
1478	0.08	1.81	1475	0.41	38.50	1475 w		νPh 19a
1478	3.31	2.65	1474	172.86	1.01	1460 s	1465 w	νPh 19a
1431	10.43	0.19	1426	2.85	8.28	1434 sh		νPh 19b
1431	0.00	2.05	1416	152.88	7.10			νPh 19b
1300	0.41	0.01	1318	48.36	2.73	1326 s	1345 m	νCN, νPh 14
1299	0.00	1.29	1307	2.35	4.15	1312 m	1316 w	νCN, νPh 14
1283	286.93	5.00	1292	26.02	47.13	1298 m		δNH
1234	405.06	2.81	1285	243.79	0.76	1278 m	1249 s	δNH
1224	97.96	32.87	1275	106.34	240.58	1266 m		δCH 3
1181	3.91	0.55	1216	368.10	0.35	1218 w		δCH 3
1181	0.00	0.77	1202	75.85	198.71			δCH 9a
1169	28.65	0.05	1161	75.94	0.28	1168 w	1165 m	ρCH 9a
1145	1.62	5.29	1159	0.52	20.29		1159 m	ρCH 9b
1144	6.15	0.83	1156	51.81	9.34	1156 w		δCH 9b
1071	14.49	0.00	1139	0.34	6.78			ρNH
1071	0.00	4.42	1139	1.01	4.21			ρNH
1039	1.96	0.46	1065	10.56	0.38	1070 s	1070 w	νCX(X) 7a, δCH 15
1039	0.00	0.36	1063	0.70	1.60			νCX(X) 7a, δCH 15
1001	0.73	11.18	1011	0.46	41.57	1018 m	1024 w	δCH 18a
998	13.77	0.27	1009	10.19	1.01	1003 w		δCH 18a
992	0.00	0.43	979	0.26	156.74		1004 vs	νPh 1
992	0.01	0.43	978	0.06	2.62	975 w		νPh 1
975	0.55	0.00	945	0.01	0.12			γCH 5
975	0.00	0.00	945	0.19	0.14	938 s		γCH 5
972.	0.62	76.75	920	0.53	1.78		936 w	γCH 17a
970	4.41	0.20	920	0.16	0.34			γCH 17a
931	4.33	0.06	908	6.07	9.76	908 w	911 w	νCS
930	1.64	34.93	872	4.01	0.41			ωNH
898	10.46	24.68	868	0.22	0.40	858 w	858 w	ωNH
839	2.26	0.71	800	0.73	0.56	809 w		γCH 17b
838	0.00	0.12	798	1.19	12.03			γCH 17b
807	10.40	1.43	792	3.90	1.21	789 s		γCH 10a
759	26.25	13.32	747	20.68	1.21	752 s	765 w	γCH 10a
756	12.66	2.89	742	13.22	4.86			γCH 11
684	7.79	0.20	699	64.56	27.49	698 s	690 s	γCH 11
683	145.77	6.87	691	70.30	0.66	690 s		δPh(X) 12
669	10.40	14.71	673	29.56	3.08			δPh(X) 12
637	0.51	0.00	667	10.06	0.12	655 s		γPh 4
635	14.26	0.37	629	6.45	2.33	632 s	628 w	γPh 4
619	16.00	3.96	608	2.50	4.14	611 m	615 m	δCS
604	0.00	8.57	607	0.74	8.56	599 w		δPh 6b
602	1.27	1.10	571	2.86	1.60	563 w		δPh 6b
490	9.63	2.85	497	5.95	3.54	505 w	506 w	γCS
476	13.50	2.01	488	0.75	1.74	486 s	485 w	γPh(X) 16b
436	0.01	0.23	478	4.96	0.02			γPh(X) 16b
425	102.84	0.30	433	216.39	5.80	439 w	440 w	ρCSN
410	0.00	0.02	415	74.15	6.74		419 w	γPh(X)
403	39.72	0.16	402	0.07	5.98			γPh(X)
400	0.00	0.17	401	0.15	0.42		398 w	δPh(X) 6a
380	1.73	0.29	375	2.79	8.72			δPh(X) 6a
238	0.83	3.53	321	0.32	0.21			δCX(X) 18b
222	4.407	2.09	235	0.75	7.78		242 s	δCX(X) 18b
218	0.35	4.50	228	2.54	0.77			ρC(=S)NH
175	0.00	0.02	204	1.03	0.79			ρCSN
103	4.98	4.25	130	8.04	1.88		129 s	γCX(X) 10b
71	0.00	0.75	106	0.03	8.58			γCX(X) 10b
52	0.84	1.94	54	0.31	4.35			tPh
27	2.95	0.15	40	1.80	4.71			tPh
20	3.68	8.51	32	0.05	12.78			tCSN
7	0.00	1.26	28	0.13	2.00			tCSN

* ν-stretching; δ-in-plane deformation; γ-out-of-plane deformation; ρ-rocking; ω-wagging; t-torsion; X-substituent sensitive; Ph-phenyl ring.

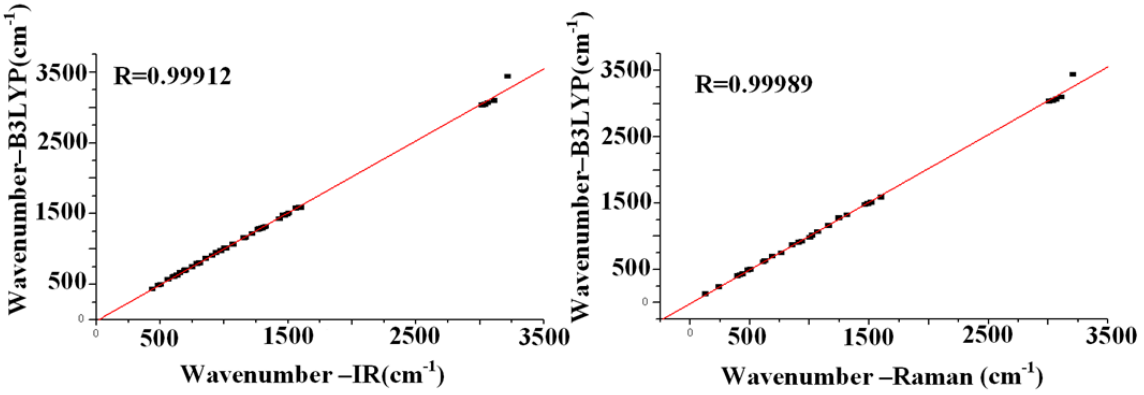

Figure 4. Correlation graph between experimental and calculated wavenumbers.

In mono substituted benzenes, six modes of vibrations are substituent sensitive, which means that their wavenumbers shift systematically with mass or inductive or mesomeric effects of the substituent. The highest substituent sensitive mode υCX(X) mode 7a appears in the region 1195 ± 90 cm^{-1} for mono substituted benzenes [22,37]. The band corresponding to mode 7a is generally strong both in IR and Raman spectra. For the title compound the υCX(X) modes are observed in the IR spectrum at 1070 cm^{-1}, and at 1070 cm^{-1} in Raman spectrum. The DFT calculations give values at 1065, 1063 cm^{-1}. Moreover, the other substituent sensitive modes are identified (Table 2). The correlation graph between experimental and calculated wavenumbers is shown in Figure 4. The IR bands in the 1729-2770 cm^{-1} region and their large broadening support the intra-molecular hydrogen bonding [33].

4.2. Geometrical parameters and first hyperpolarizability

The C-C bond length in the phenyl rings lie between 1.3915 and 1.3981 Å. Here for the title compound, benzene is a regular hexagon with bond lengths somewhere between the normal values for a single (1.54 Å) and a double (1.33 Å) bond [38]. The C_{11}-C_{12}, C_{11}-C_{16}, C_4-C_3 and C_4-C_5 bond lengths are longer than all the other C-C bonds. This is due to the presence of the electronegative nitrogen atom, which can pull electrons from the ring elongating the bond. Since the molecule is symmetric, all the structural parameters also exhibit the symmetry on both sides. Both the N-H bonds are oriented away from the C-S bond so as to reduce the repulsive forces. Another interesting feature of the molecule is that, the planes of both the benzene rings are perpendicular to each other. Yang *et al.* [4] reported bond lengths N_{10}-C_9=1.38, N_8-C_9=1.404 Å, whereas in the present case, the corresponding value is 1.3814 Å and shorter than C-N single bond of 1.4725 Å. The partial double bond character of the structure is presumed as a result of the intra-molecular H-bond "locking" the molecule into a planar six-numbered ring structure.

The C-S bond length in the present study 1.6636 Å lies between the values of C-S single and double bonds. The C_4-N_8 bond length for the title compound is 1.4188 Å, formally a single bond, which is remarkably shortened. The reported values of the bond lengths are, C_9-S_{23}=1.663 [4] and C_4-N_8 =1.421 Å [4]. Dilovic *et al.* [39] reported the bond lengths, C_9-S_{23}=1.6792, C_9-N_8=1.3422, C_9-N_{10}=1.3462. C_4-N_8=1.4122 Å, bond angles C_{11}-N_{10}-C_9=129.7, N_{10}-C_9-N_8=114.3, N_{10}-C_9-S_{23}= 116.8, S_{23}-C_9-N_8=128.8, C_9-N_8-C_4=130.7, N_8-C_4-C_5=124.7 ° and the dihedral angles C_{11}-N_{10}-C_9-S_{23}=-173.4, C_4-N_8-C_9-S_{23}=-1.8, C_4-N_8-C_9-N_{10}=179.1°, which are in agreement with the corresponding values for the title compound. Ramnathan *et al.* [40] reported C_9-S_{23}=1.7073, C4-N8=1.445, C_{11}-N_{10}=1.4375 Å, C_9-N_8-C_4=127.8 °, C_9-N_{10}-C_{11}=125.5 °, N_8-C_9-N_{10}=117.3°, N_8-C_9-S_{23}= 120.4°, N_{10}-C_9-S_{23}=122.2°, whereas the corresponding values in the present case are, 1.6636, 1.4188, 1.4188 Å, 128.6, 128.6, 110.1, 124.9, and 124.9 °.

The first hyperpolarizability (β_0) of this novel molecular system is calculated using B3LYP/6-311++G(d,p) 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 3x3x3 matrix. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry [41]. 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

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

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 hyperpolarizabilities, respectively. The calculated first hyperpolarizability of the title compound is 1.86x10^{-30} esu, which is 14.36 times that of urea (0.13x10^{-30} esu) [42]. The C-N distances in the calculated molecular structure vary from 1.3814 to 1.4188 Å which are intermediate between those of a C-N single bond (1.48 Å) and a C=N double bond (1.28 Å). Therefore, the calculated data suggest an extended π-electron delocalization over the thiourea moiety [42,43] which is responsible for the nonlinearity of the molecule. We conclude that the title compound is an attractive molecule in future for non linear optical applications.

5. Conclusion

The FT-IR and FT-Raman spectra of 1,3-diphenyl thiourea were recorded and analyzed. The wavenumbers are calculated theoretically using Gaussian03 software package. The normal modes of the phenyl ring are assigned by comparing experimental wavenumbers and theoretically calculated wavenumbers. The NH stretching wavenumber is redshifted in the IR spectrum with a strong intensity from the computational wavenumber which indicates the weakening of the N-H bond resulting in proton transfer to the neighboring sulfur atom. 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. Furthermore, we state that experimental results belong to solid phase and theoretical calculations belong to gaseous phase. The first hyperpolarizabililty, 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.

References

[1]. Katrizky, A.R, Advances in Heterocyclic Chemistry, Academic Press, New York, 1983.
[2]. Castro, M.; Cruz, J.; Otazo-Sanchez, E.; Perez-Marın, L. *J. Phys. Chem. A* **2003**, *107*, 9000-9007.
[3]. Hamza, A.; Schubert, G.; Soos, T.; Papai, I. *J. Am. Chem. Soc.* **2006**, *128*, 13151-13160
[4]. Yang, W.; Zhou, W.; Zhang, Z. *J. Mol. Struct*. **2007**, *828*, 46-53.
[5]. Badawi, H. M. *Spectrochim. Acta* **2009**, *72A*, 523-527.
[6]. Zhang, N.; Jiang, M. H.; Yuan, D. R.; Xu, D.; Tao, X. T.; Shao, Z. S. *J. Cryst. Growth* **1990**, *102*, 580-584.
[7]. Ushasree, P. M.; Muralidharan, R.; Jayavel, R.; Ramasamy, P. *J. Cryst. Growth* **2000**, *218*, 365-371.
[8]. Qussaid, M.; Becker, P.; Nedelec, C. C. *Phys. Stat. Sol.(b)* **1998**, *207*, 499-507.
[9]. Marcy, H.O.; Warren, L. F.; Webb, M. S.; Ebbers, C. A.; Velsko, S. P.; Kennedy, G. C.; Catella, G. C. *Appl. Opt.* **1992**, *31*, 5051-5060.
[10]. Selvaraju, K.; Valluvan, R.; Kumararaman, S. *Mater. Lett*. **2006**, *60*, 3130-3132.
[11]. Selvaraju, K.; Valluvan, R.; Kumararaman, S. *Mater. Lett*. **2007**, *61*, 751-753.
[12]. Pfeffer, F. M.; Gunnlaugsson, T.; Jensen, P.; Kruger, P. E. *Org. Lett*. **2005**, *7*, 5357-5360.
[13]. Beer, P.D.; Gale, P. A. *Angew. Chem. Int. Ed*. **2001**, *40*, 486-516.
[14]. Koulov, A. V.; Mahoney, J. M.; Smith, B. D. *Org. Biomol. Chem*. **2003**, *1*, 27-29.
[15]. Gunnlaugsson, T.; Ali, H. D. P.; Glynn, M.; Kruger, P. E.; Hussey, G. M.; Pfeffer, F. M.; dos Santos, C. M. G.; Tierney, J. *J. Fluoresc*. **2005**, *15*, 287-299.
[16]. Kim, S. K.; Singh, N. J.; Kim, S. J.; Swamy, K. M. K.; Kim, S. H.; Lee, K. H.; Kim, K. S.;. Yoon, J. *Tetrahedron* **2005**, *61*, 4545-4550.
[17]. Hay, B. P.; Firman, T. K.; Moyer, B. A. *J. Am. Chem. Soc*. **2005**, *127*, 1810-1819.
[18]. Vogel, A.I. *A Text Book of Practical Organic Chemistry*; Longmans: London, 1954, p 614.
[19]. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, M.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian 03, Revision C.02 Gaussian, Inc., Wallingford CT, 2004.
[20]. Foresman, J. B. in: Frisch, E. (Ed.), Exploring Chemistry with Electronic Structure Methods: A Guide to Using Gaussian, Pittsburg, PA 1996.
[21]. Wilson, E. B. *Phys. Rev*. **1934**, *45*, 706-714.
[22]. Roeges, N. P. G. A Guide to the Complete Interpretation of Infrared Spectra of Organic Structures, Wiley, New York, 1994.
[23]. Barthes, M.; De Nunzio, G.; Ribet, G. *Synth. Met*. **1996,** *76*, 337-340.
[24]. El-Asmy, A. A.; Al-Hazmi, G. A. A. *Spectrochim. Acta* **2009**, *71A*, 1885-1890.
[25]. Colthup, N. B.; Daly, L. H.; Wiberly, S. E. Introduction to Infrared and Raman Spectroscopy, third ed. Academic Press, Boston, MA, 1990.
[26]. Varsanyi, G. Assignments of Vibrational Spectra of Seven Hundred Benzene Derivatives, Wiley, New York, 1974.
[27]. El-Shahawy, A. S.; Ahmed, S. M.; Sayed, N. K. *Spectrochim. Acta* **2007**, *66A*, 143-152.
[28]. Panicker, C. Y.; Varghese, H. T.; Thansani, T. *Turk. J. Chem*. **2009**, *33*, 1-14.
[29]. Socrates, G. Infrared Characteristic Group Frequenceis, John Wiley and Sons, New York, 1980.
[30]. Nigam, S.; Patel, M. M.; Ray, A. *J. Phys. Chem. Solids* **2000**, *61*, 1389-1398.
[31]. Coates, J.; Meyers, R. A. Interpretation of Infrared Spectra, A Practical Approach, Chichester, John Wiley and Sons Ltd. 2000.
[32]. Harikumar, B; Varghese, H. T.; Panicker, C. Y.; Jayakumar, G. *Spectrochim. Acta* **2008**, *71A*, 731-738.
[33]. Panicker, C. Y.; Varghese, H. T.; Ambujakshan, K. R.; Mathew, S.; Ganguli, S.; Nanda, A. K.; Van Alsenoy, C.; Mary, Y. S. *J. Mol. Struct*. **2010**, *963*, 137-144.
[34]. Colthup, N. B. *Appl. Spectrosc*. **1976**, *30*, 589-593.
[35]. Kuwae, A.; Machida, K. *Spectrochim. Acta* **1978**, *34A*, 785-791.
[36]. Higuchi, S.; Tsuyama, H.; Tanaka, S.; Kamada, H. *Spectrochim. Acta* **1974**, *30A*, 463-472.
[37]. Varsanyi, G.; Szoke, S. Vibrational Spectra of Benzene Derivatives, Academic Press, New York, London, 1969.
[38]. Sykes, P. K. Guide book to mechanism in organic chemistry, (6th edn), Pearson Education, New Delhi, India, 2004.
[39]. Dilovic, I.; Rubcic, M.; Vrdoljak, V.; Pavelic, S. K.; Kralj, M.; Piantanida, I.; Cindric, M. *Bioorg. Med. Chem*. **2008,** *16*, 5189-5198
[40]. Ramnathan, A.; Sivkumar, K.; Subramanian, K.; Janardhana, N.; Ramadas, K.; Fun, H. K. *Acta Cryst*. **1995**, *C51*, 2446-2450.
[41]. Kleinman, D. A. *Phys. Rev*. **1962**, *126*, 1977-1979.
[42]. Adant, M.; Dupuis, I.; Bredas, L. *Int. J. Quantum. Chem*. **2004**, *56*, 497-507.
[43]. Koscien, E.; Sanetra, J.; Gondek, E.; Jarosz, B.; Kityk, I. V.; Ebothe, J.; Kityk, A. V. *Spectrochim. Acta* **2005**, *61A*, 1933-1938.