Crystal structure and spectroscopic characterization of bis(*N*-phenylthiourea)

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Bis(*N*-phenylthiourea) (BPTU) has been synthesized and characterized by means of X-ray, IR, Raman, UV-Vis, ¹H NMR, and FAB mass spectra. The BPTU crystal belongs to the monoclinic *C*2/*c* space group with the cell constants a = 26.992(8) Å, b = 6.336(3) Å, c = 9.463(3) Å, $\alpha = \gamma = 90^{\circ}$, $\beta = 105.97(7)^{\circ}$, Z = 4. The compound has been found to exist in the thione form, with cis configuration of the thiosemicarbazone moiety and skew conformation of the molecule.

KEY WORDS: Bis(*N*-phenylthiourea); crystal structure; IR; Raman; UV-Vis; ¹H NMR; FAB.

Introduction

The 1,2-hydrazinedicarbothioamide, N,N'diphenyl or hydrazine-N,N'-dicarbothioic acid diamide which is popularly known as bis(Nphenylthiourea) (BPTU) is an interesting compound with many different applications. This compound was reported as an antiviral agent active against potato virus (PVX) and this activity increases on coordination with nickel(II), copper(II), and cobalt(II) ions.¹ It was also used as an effective collector for recovery of platinum(II), gold(III), and silver(I) ions from sulfide ores² and for the preparation of several heterocyclic compounds.^{3,4} Being 1,4-disubstituted thiosemicarbazide, the BPTU may interact with transition metal ions coordinating through sulfur and hydrazinic nitrogen atoms.⁵ To our knowledge, based on surveys of the Cambridge and IUCr structural databases, the structure of BPTU has not been reported. Therefore, this paper describes the molecular structure of bis(N-phenylthiourea) and its spectroscopic characterization which may be useful in further research on BPTU interactions with other compounds or transition metal ions.

Experimental

Furlani and Tarantelli⁶ prepared BPTU by reaction of phenyl thiosemicarbazide and phenyl isothiocyanate. In our experiment, 100 mmol of phenyl isothiocyanate was dissolved in 50 cm³ of ethanol, then 50 mmol of hydrazine dissolved in 25 cm³ of ethanol was added dropwise to it. The resulting solution was refluxed on water bath for 2 h. On cooling to room temperature, colorless crystalline product was separated by filtration, washed with ethanol, followed by diethyl ether, and dried over fused CaCl₂. After slow

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evaporation of an ethanol–methanol (1:1) solution, crystals suitable for X-ray investigation were obtained (m.p. 178–179°C). Found: C, 55.68; N, 18.62; H, 4.69; $C_{14}H_{14}N_4S_2$ requires: C, 55.60; N, 18.53; H, 4.67.

Carbon, hydrogen, and nitrogen were analyzed using a Coleman ANALYZER at CDRI, Lucknow, India. FTIR spectra were recorded on Perkin Elmer 1600 and 2000 spectrometers using standard KBr pellet and nujol mull techniques. Raman transitions were measured on a Bruker RFS100 spectrometer equipped with Nd laser excitation. The reflectance spectrum was recorded on a CARY 500 Scan UV-Vis spectrometer. Positive ion fast atom bombardment (FAB) mass spectrum was obtained with m-nitrobenzyl alcohol as the matrix. The ¹H NMR spectrum was recorded as reported earlier.⁷

For the X-ray analysis, the crystal was mounted in a random orientation on Phillips PW 1100 four circle diffractometer. The structure was solved by Patterson, direct, and Fourier methods and refined by full-matrix least-squares and anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were refined isotropically. Sixty-nine reflections were suppressed from the final refinement as affected by counting errors or extinction. The atomic scattering factors used, corrected for anomalous dispersion, were from International Tables; the calculations were performed using the SHELX76,8 and PARST9 programs. A summary of data collection and structure refinement is given in Table 1. The final atomic positional parameters are quoted in Table 2.

Results and discussion

Structure of BPTU

BPTU crystallizes in C2/c space group, but discrete molecules are located on the twofold axes, out of the symmetry centers. Therefore, the BPTU molecule has lower C₂ symmetry as has been shown in Fig. 1. All bond distances and

Table 1. Crystal and Experimental Data

Empirical formula	C14H14N4S2
CCDC deposit no	CCDC-1003/6094
Formula weight	302.4
Crystal system	Monoclinic
Space group	$C_{2/c}$
Unit cell dimensions	a = 26.992(8) Å
	b = 6.336(3) Å
	c = 9.463(3) Å
	$\alpha = y = 90^{\circ}$
	$\beta = 105.97(7)^{\circ}$
Volume, Å ³	1555.9(1.1)
Ζ	4
Crystal color, habit	Colorless, rod
$D_{\rm c}, {\rm g/cm^{-3}}$	1.29
F(000)	632
Temperature, K	294
Diffractometer	Phillips PW 1100
μ , cm ⁻¹	29.27
Index ranges	$-31 \le h \le 31$
	$0 \le k \le 7$
	$0 \le l \le 9$
No. of reflections measured	1071
No. of reflections used	1002
No. of refined parameters	119
Residuals: R; Rw	0.0425; 0.0475

selected angles are quoted in Table 3. In the phenyl thiosemicarbazide moiety Ph—N2—C1(S)—N1—N1ⁱ, the N2 and N1ⁱ atoms are in cis configuration (Table 3) similar to that found previously

 Table 2. Atomic Coordinates (10⁴)

Atom	x/a	y/b	z/c
S	523(0)	2431(1)	1030(1)
N1	18(1)	1948(4)	-1742(3)
N2	730(1)	4070(5)	-1330(3)
C1	429(1)	2850(5)	-780(3)
C2	1172(2)	5163(6)	-464(4)
C3	1113(2)	7139(7)	99(5)
C4	1554(3)	8170(10)	914(6)
C5	2025(3)	7320(13)	1145(6)
C6	2078(2)	5354(12)	561(6)
C7	1654(2)	4300(8)	-231(5)
H1	-117(13)	915(57)	-1378(39)
H2	618(12)	4393(55)	-2289(41)
H3	793(18)	7626(67)	-64(49)
H4	1475(17)	9589(78)	1256(50)
H5	2365(19)	7884(68)	1677(50)
H6	2432(18)	4776(72)	848(49)
H7	1656(17)	2970(68)	-634(49)

Note. Esds are given in parentheses.



Fig. 1. ORTEP¹⁰ plot (20% ellipsoids) of the bis(N-phenylthiourea) molecule.

for phenyl thiosemicarbazide 11 as shown in Scheme 1.



Scheme. 1. Examples of cis¹¹ and trans¹² configuration of thiosemicarbazide moiety.

Thus, the configuration of BPTU differs from S-methyl thiosemicarbazide¹² hydronitrate, which has a trans configuration. The C1—S—N1—N2 group is nearly planar (maximum deviation is -0.011(3) Å for C1 atom) and forms with the phenyl ring a dihedral angle of 84.6(1)°. This angle and the torsion C1—N1—N1ⁱ—C1ⁱ angle of $-121.8(3)^{\circ}$ indicate the skew conformation of the molecule. The dihedral angle between the two phenyl rings is $51.5(2)^{\circ}$. The C1—S bond is shorter [1.681(3) Å] in BPTU molecule than observed in S-methyl thiosemicarbazide¹² [1.753(5) Å], but similar to that in phenyl thiosemicarbazide¹¹ [1.685(5) Å] (Table 3). Thus, the C1—S bond has a double bond character.⁷ The C1—N1 and C1—N2 bond

Table 3. Selected Bond Distances (Å) and Angles (deg)

Bond distances			
N1-N1 ⁱ	1.412(4)	C6-C7	1.359(6)
N1-C1	1.353(4)	C2-C7	1.371(5)
C1-N2	1.327(4)	N1-H1	0.86(3)
C1-S	1.681(3)	N2-H2	0.90(3)
N2-C2	1.428(4)	С3—Н3	0.89(4)
C2-C3	1.387(5)	C4-H4	1.00(4)
C3-C4	1.391(6)	C5-H5	0.98(4)
C4-C5	1.341(7)	C6-H6	0.99(4)
C5-C6	1.386(7)	С7—Н7	0.93(3)
Bond angles			
C1-N1-N1 ⁱ	119.8(3)	N2-C1-S	123.7(2)
N1-C1-S	119.0(2)	C1-N2-C2	124.2(3)
N1-C1-N2	117.3(2)	N2-C2-C3	119.4(4)
Torsion angles			
C1-N1-N1 ⁱ -C1 ⁱ	-121.8(3)	N1 ⁱ -N1-C1-S	-168.3(2)
N1 ⁱ -N1-C1-N2	13.4(9)	C2-N2-C1-S	1(2)
H1-N1-N1 ⁱ -H1 ⁱ	-59.8(39)	H2-N2-C1-N1	9(3)

Note. i = x, -y, z + 1/2.



Fig. 2. Packing diagram of the BPTU crystal structure. Only hydrogen atoms bonded to nitrogen ones have been shown for clarity and to present the examples of the H-bonds (middle–top molecules only).

lengths in the thiourea moiety are 1.353(4) Å and 1.327(4) Å, respectively, and they differ from thiosemicarbazide¹³ 1.326(2), 1.316(3) but are somewhat similar to phenyl thiosemicarbazide¹¹ 1.357(7), 1.349(7). For the BPTU molecule, the difference in C1-N1 and C1-N2 bond distances suggests greater bond order for the latter linkage which may be explained by some π -electron density delocalization in the region of the N2-C1-S bonding system. The conformation of the BPTU molecule as well as the crystal packing is stabilized by intra- and intermolecular hydrogen bonds. The inspection of interatomic contacts reveals that all hydrogen atoms bonded to nitrogen atoms are engaged in such linkage. The H2 atom forms a hydrogen intramolecular bond with the N1 atom (H2 \cdots N1 2.306(33) Å), indicating that the H2-N2-C1-N1 unit is almost flat. The intermolecular hydrogen bonds are formed with sulfur atoms: $N1 \cdots S^i$ 3.290(3) Å, $H1 \cdots S^{i}$ 2.450(37) Å, $N1 - H1 \cdots S^{i}$ 164(3)° $(i = -x, -y, -z); N2 \cdots S^{ii} 3.271(3) Å,$ $H2 \cdots S^{ii}$ 2.534(36) Å, N2- $H2 \cdots S^{ii}$ 140(3)° (ii = x, -y + 1, z - 1/2) and nitrogen atoms:

N2 · · · N1ⁱⁱⁱ 2.680(4) Å, H2 · · · N1ⁱⁱⁱ 2.306(33) Å, N2-H2 · · · N1ⁱⁱⁱ 105(3)° (iii = -x, y, -z - 1/2). The examples of the above hydrogen bonding have been shown in Fig. 2 presenting the crystal packing of BPTU.

¹H NMR spectroscopy

Results from the X-ray structure show that BPTU exists in thione tautomeric form. Further support comes from the ¹H NMR spectrum, which does not show a proton signal attributable to the SH group,¹⁴ but shows two proton signals in the low field region at 9.93 and 9.73 ppm. These signals are exchangeable and disappear on deuteration. The results of NOE experiments indicate an enhancement of signal at 7.55 ppm to a greater extent on the irradiation of the proton signal at 9.93 ppm. Thus the signal at 9.93 ppm could be assigned to the proton of NH group attached to a phenyl ring¹⁵ and consequently the signal at 7.55 ppm to the phenyl C(2)H/C(6)H protons (H3/H7 in the present X-ray structure). The second low field signal at 9.73 ppm could be



Fig. 3. Infrared (top) and Raman (bottom) spectra of solid BPTU. Second Raman spectrum is of ten times lower intensity.

assigned to NH—NH protons. The two remaining signals at 7.35 and 7.18 ppm belong to aromatic C(3)H/C(5)H (H4/H6) and C(4)H (H5) protons, respectively.

Vibrational spectroscopy

Infrared and Raman spectra of BPTU are compared in Fig. 3. In order to detect the hydrogen bonding effects and distinguish the N-H vibrations, the spectra of N-deuterated compound have also been recorded. The deuteration experiment unambiguously shows that two highest frequency IR bands at 3212, 3113 cm⁻¹ and their Raman counterparts at 3212, 3105 cm⁻¹ are generated by stretching ν (N–H) vibrations. These bands are shifted upon deuteration to 2390, 2276 (IR) and 2390, 2270 cm^{-1} (Raman), respectively. Since for lower energy transitions, the IR and Raman band positions are slightly different, these modes were attributed to vibrations of the N1-H groups which are joined by the N1-N1ⁱ bond, and vibrational coupling may occur between them. Similar coupling is negligible for the much more separated N2-H groups and therefore the IR and Raman bands showing exactly the same 3212 cm^{-1} position were assigned to the ν (N2—H) vibrations. Infrared absorptions with maxima at 3010, 2938, and 2800 cm⁻¹ are also sensitive to deuteration which suggests their origin from H-bonding vibrations. The N—H deformation modes may contribute to IR bands at 1547, 1189, 932–900, and 549 cm⁻¹ which show the largest deuteration shifts in the region below 1700 cm⁻¹. These modes are usually coupled with stretching vibrations related to neighboring bonds. In the case of BPTU such coupling is possible with ν (C—N) and ν (N—N) modes.

The thiosemicarbazone moiety also generates several coupled vibrations. According to the literature¹⁶, the ν (C1–N) and ν (C1–S) modes contribute in transitions at about 1450 and 780 cm⁻¹. Taking into account the high intensity of the 789 cm⁻¹ Raman band, this mode is predominantly due to the ν (C=S) vibrations which were found in a similar region of the *N*,*N'*dimethylthiourea¹⁷ IR spectrum. The stretching vibrations of the C_{ph}–N bonds have been assigned to transitions between 1300–1240 cm⁻¹. The central N–N bond vibrations coupled with neighboring ν (C–N) modes have been located⁷ at about 1330 cm⁻¹ and between 1100 and 1200 cm⁻¹. The ν (N—N) vibrations should be slightly sensitive to deuteration but transitions observed in the above regions of BPTU spectra do not satisfy such a condition. Probably the ν (N—N) mode is strongly coupled with other vibrations and cannot be considered as a characteristic transition.

The phenyl ring fundamentals are clearly seen in the Raman spectrum. The ν (C–H) "aromatic triplet" typical for monosubstituted benzene derivatives is observed at 3067, 3056, and 3049 cm^{-1} . Respective IR bands are overlapped by H-bonding vibrations. The C-H "in plane" bending vibrations are attributed to the 1167, 1160 cm^{-1} Raman doublet appearing at the same position after deuteration. The same criterion can be applied to the 615 cm^{-1} band resulting from the phenyl skeletal "out-of-plane" deformations. The most intense transition, characteristic for Raman spectra of substituted benzene compounds, is located slightly above 1000 cm^{-1} and results from a ν (C–C) "breathing" vibration. In the BPTU spectrum this mode is positioned at 1002 cm^{-1} and the satellite, bending C-H band at 1026 cm^{-1} . Intense Raman bands in the lowest wavenumber



Scheme. 2. Primary fragmentation of BPTU molecular ion.

region result from lattice modes and torsional deformations of the thiosemicarbazide moiety.¹⁷

Reflectance spectrum

The reflectance spectrum of BPTU has been recorded in the 10000–50000 cm⁻¹ region and shows two intense bands with maxima at 42000, 34700 cm⁻¹ and a shoulder located by digital filtration at 29500 cm⁻¹. The bands above 30000 cm⁻¹ are assignable to $\pi \to \pi^*$ transitions of the aromatic system. The absorption observed at 29500 cm⁻¹ results from a $\pi \to \pi^*$ transition of thiosemicarbazone group.¹⁶.



Scheme. 3. Secondary fragmentation of BPTU and cyclization reactions involving processes (b) and (e) in Scheme 1.

Mass spectral fragmentation

In the fast atom bombardment (FAB) mass spectrum of BPTU, the molecular ion peak was absent, but a peak due to $[M + H]^+$ has been observed at m/z, 303. Other most abundant ion peaks were found at m/z equal to 269, 268, 226, 210, 192, 166, 152, and 77. Scheme 2 shows different fragmentation patterns for the molecular and pseudomolecular ions. The base peak, observed at m/z 269, results from cyclization processes producing heterocyclic derivatives as has been presented in Scheme 3. Such reactions are very probable since, for example, the selenium analogue of BPTU is not stabile due to cyclization leading to a heterocyclic compound.¹⁸

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