Turk J Chem
34 (2010) , 761 – 770.

doi:10.3906/kim-0912-415

Synthesis, spectroscopic characterization, mass spectrometry, and crystal structure of N-{[(4-bromophenyl)amino]carbonothioyl}benzamide

Sohail SAEED[1,*], **Naghmana RASHID**[1], **Moazzam Hussain BHATTI**[1], **Peter G. JONES**[2]

[1] *Department of Chemistry, Research Complex, Allama Iqbal Open University, Islamabad PAKISTAN*

e-mail: sohail262001@yahoo.com, nrk_chem@yahoo.com, moazzamhussain_b@yahoo.com

[2] *Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, GERMANY*

e-mail: p.jones@tu-bs.de

Received 28.12.2009

N-{[(4-bromophenyl)amino]carbonothioyl}benzamide was synthesized and characterized by IR, ^{1}H- and ^{13}C-NMR, mass spectrometry, and elemental analysis. The crystal structure was determined from single crystal X-ray diffraction data. It crystallizes in monoclinic space group $P2_1/n$ with unit cell dimensions a = 13.822(3) Å, b = 5.927(2) Å, c = 16.642(3) Å, and β = 103.963(3)°. There is a strong intramolecular hydrogen bond of the type N--HΛO, with an HΛO distance of 2.6129 (11) Å. The mass fragmentation pattern is also discussed.

Key Words: Thiourea derivative, X-ray structure determination, mass fragmentation

Introduction

Sulfur is an interesting element, in particular because of the variety of its compounds and the variety of bonding types it is involved in.[1] It has a prominent bioorganic chemistry and a large number of enzymes and other proteins such as iron sulfur proteins exhibit fantastic properties involving the sulfur atoms in them.[2,3] It is an

*Corresponding author

important element forming chains[4] and, more interestingly, bridges in polymers and in a variety of composite materials, giving rise to strength and resistance to aging.

Thiourea and its derivatives are an important class of organic compounds in which sulfur is the major ligand atom, playing an important role in coordination chemistry with transition metals. Thiourea and its derivatives have found extensive applications in the fields of medicine, agriculture, and analytical chemistry. Substituted thioureas are an important class of compounds, precursors, or intermediates towards the synthesis of a variety of heterocyclic systems such as imidazole-2-thiones,[4] 2-imino-1,3-thiazolines,[5] pyrimidine-2-thiones, and (benzothiazolyl)-4-quinazolinones. Thioureas are also known to exhibit a wide range of biological activities including antiviral, antibacterial, antifungal, antitubercular, antithyroidal, herbicidal, and insecticidal activities[6] and as agrochemicals.[7–12] Thioureas are also well known chelating agents for transition metals.[8] N, N-Dialkyl-N'-benzoyl thioureas act as selective complexing agents for the enrichment of platinum metals even from strongly interfacing matrixes. The complexes of thiourea derivatives also show various biological activities.[9]

The thiourea derivatives containing amino functional groups are also known as epoxy resin curing agent.[13] As a part of our continuing interest in biologically active thiourea derivatives and their transition metal complexes, we report a route for synthesis of these compounds by using tetrabutylammonium bromide as phase transfer catalyst to augment the yield of products. Saeed and coworkers[14–16] have reported a number of N-aroyl-N'-arylthioureas based publications that are related to our article.

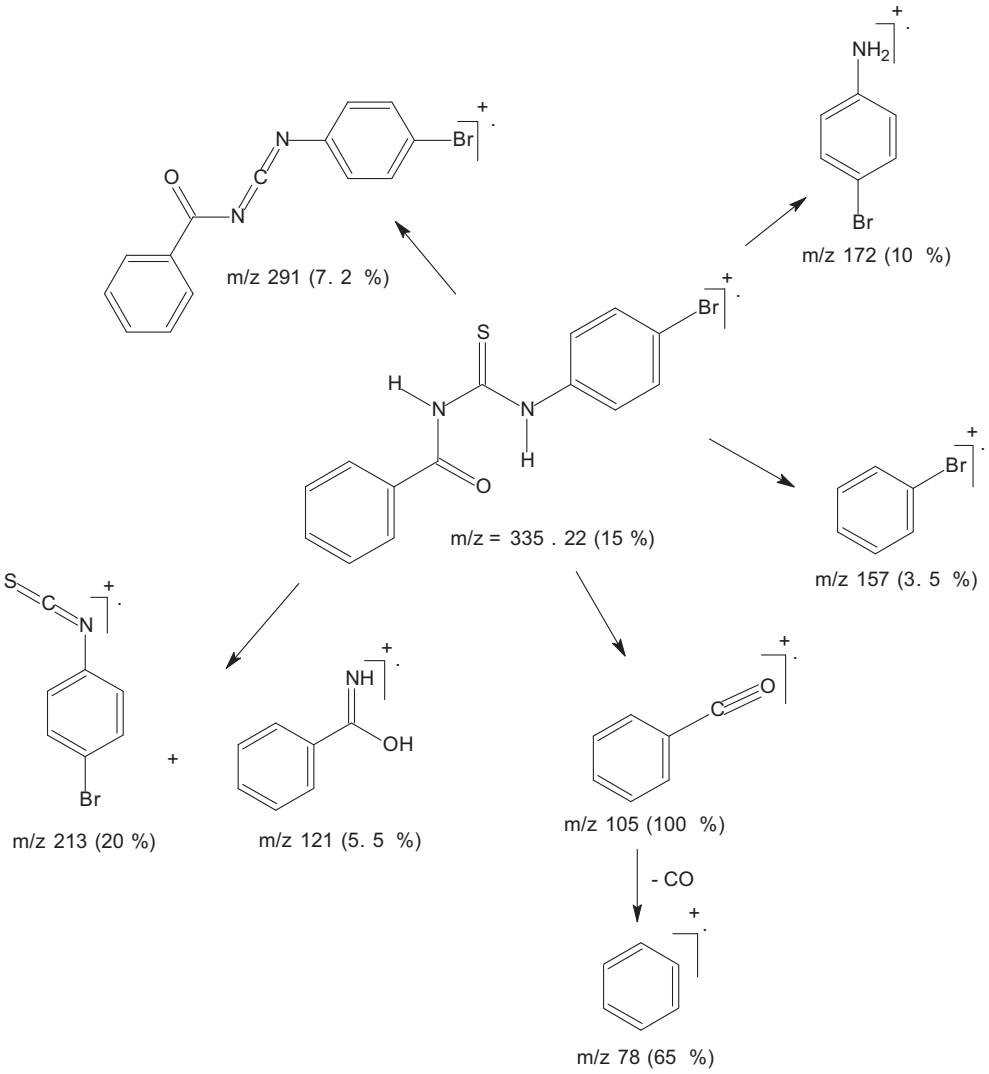
We became interested in the synthesis of N-aroyl-N'-arylthioureas as intermediates towards some heterocycles and for the systematic study of their bioactive complexes and epoxy resin curing agents. In this article, we describe the crystal structure of N-{[(4-bromophenyl)amino]carbonothioyl}benzamide as a typical representative of N-aroyl-N'-arylthioureas.

Results and discussion

The target compound was synthesized by a slight modification of our published procedures.[14–16] The use of phase transfer catalysts to agitate a heterogeneous reaction system is gaining recognition.[17,18] In an attempt to improve syntheses of the target substituted thiourea derivative by reacting isothiocyanates with nucleophiles, we found that the use of tetrabutylammonium bromide (TBAB) as phase transfer catalyst (PTC) can afford aroyl isothiocyanate in good yield. In this study, we conducted our reaction using tetrabutylammonium bromide (TBAB) as phase transfer catalyst to synthesize the intermediate aroyl thiourea derivative.

The chemical structure and purity of the compound were proved using elemental analysis, and ^{1}H-NMR, ^{13}C-NMR, and FTIR spectroscopy. The ^{1}H-NMR data of the compound obtained in DMSO solution are given in the Experimental section and are consistent with the structural results. The elemental analyses closely corresponded to calculated values. The analytical and spectroscopic data are consistent with the proposed structure.[19] IR (KBr) spectra of the compound had strong absorptions at 3352 cm^{-1} for free N-H and 3212 cm^{-1} for assoc N-H, and displayed absorptions at 1685 cm^{-1} and 1142 cm^{-1} that were assigned to C=O and C=S functions, respectively. The medium-strong $\upsilon_{C=O}$ band in the IR spectrum of the compound appeared at 1685 cm^{-1}, which is lower than that of the ordinary carbonyl absorption (1730 cm^{-1}); this may be attributed to the formation of hydrogen bonds. These results agree with the data in the literature.[20]

In ^{1}H-NMR, the compound exhibited broad signals at 12.95 and 12.03 ppm, which were assigned to the N-H protons. ^{13}C-NMR showed peaks at about δ 168.2 and 181.0 for C=O (amide) and C=S (thioamide), respectively. The mass spectrum showed the molecular ion peak at m/z 335. The fragment at m/z 121(5.5%) was derived from the N-McLafferty rearrangement and the base peak at m/z 105 (100%) originated from the aroyl cation (Scheme).



Scheme. Mass fragmentation pattern of N-{[(4-bromophenyl)amino]carbonothioyl} benzamide.

The molecular structure of the title compound is shown in Figure 1. Crystallographic data and refinements are presented in Table 1 and final atomic coordinates and equivalent isotropic displacement parameters appear in Table 2; bond lengths, angles, and torsion angles are presented in Tables 3 and 4, respectively. The C1-S and C2-O bonds show a typical double bond character with bond lengths of 1.6684(10) and 1.2324(12) Å, respectively. All of the C-N bonds, C1-N1 = 1.3415(13) Å, C11-N1 = 1.4137 (13) Å, C2-N2 = 1.3769 (13) Å, and C1-N2= 1.3992 (13) Å, also indicate a partial double bond character. The C1-N2 bond, due to its vicinity to

the carbonyl group, is slightly larger than the C1-N1 bond.[21] These bond distances are in good agreement with those observed in structures containing the N-benzoyl-N'-phenylthiourea moiety, as reported in the Cambridge Structural Database.[22] The packing is 3-dimensional, but a representative 2-dimensional view along the short axis is given in Figure 2. One classical H bond N1-H01ΛO and 4 "weak" H bonds of the form C-HΛX (X = O, S, Br) are observed. Numerical details are given in Table 5.

Table 1. Crystal data and structure refinement for N-{[(4-bromophenyl) amino]carbonothioyl}benzamide.

CCDC	724599
Empirical formula	$C_{14}H_{11}BrN_2OS$
Formula weight	335.22
Crystal size	0.25 X 0.20 X 0.15 mm^3
Temperature	100 (2) K
Wavelength	0.71073 Å
Crystal System	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a= 13.8228 (3) Å $\alpha = 90^o$
	b=5.9272 (2) Å $\beta = 103.963\ (3)^o$
	c= 16.6425(3) Å $\gamma = 90^o$
Volume	1323.24(6) $Å^3$
Density (calculated)	1.683 g/cm^3
Theta range of data collection	2.52 to 31.51^o
Max and min transmission	1.00000 and 0.71403
No of reflections measured	81955
No of independent reflections	4397
F (0 0 0)	672
Refinement method	Full-matrix least square on F^2
Final R indices [I > 2α(I)]	R1= 0.0168, wR2= 0.0437
R indices (all data)	R1= 0.0216, wR2= 0.0441
Goodness-of-fit on F^2	1.028
Maximum, Δ/σ	0.000
$(\Delta/\rho)_{max}$	0.430 e/$Å^3$
$(\Delta/\rho)_{min}$	-0.260 e/$Å^3$
Data collection program	Oxford Diffraction, 2008
Cell refinement program	CrysAlis CCD
Data reduction program	CrysAlis RED
Structure solving program	Sheldrick, 2008
Structure refinement program	Sheldrick, 2008

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for N-{[(4-bromophenyl) amino] carbonothioyl}benzamide.

	x	y	z	U(eq)
Br	4845.9(1)	-3040.6(2)	3191.3(1)	15.3(1)
S	739.1(2)	2065.6(5)	4673.5(2)	15.9(1)
N (1)	2676.8(6)	3345.6(15)	5018.8(5)	12.7(2)
N (2)	1619.6(6)	5431.2(15)	5600.6(5)	12.6(2)
O	3219.9(5)	6730.9(13)	6032.9(5)	17.1(2)
C (1)	1739.6(7)	3618.4(17)	5094.9(6)	11.7(2)
C (2)	2341.6(7)	6803.3(17)	6072.4(6)	12.6(2)
C (11)	3104.0(7)	1769.1(16)	4568.0(6)	10.9(2)
C (12)	2704.8(7)	-330.6(17)	4287.6(6)	12.7(2)
C (13)	3221.0(7)	-1736.5(17)	3865.8(6)	12.9(2)
C (14)	4129.4(7)	-1060.1(18)	3735.6(6)	11.9(2)
C (15)	4539.5(7)	1023.7(18)	4007.8(6)	12.7(2)
C (16)	4020.7(8)	2427.4(17)	4423.4(6)	12.4(2)
C (21)	2005.5(7)	8384.4(17)	6643.3(6)	12.2(2)
C (22)	1226.8(8)	7864.2(19)	7009.9(6)	15.2(2)
C (23)	971.7(8)	9372(2)	7563.9(7)	19.5(2)
C (24)	1479.5(8)	11400(2)	7742.3(7)	19.9(2)
C (25)	2263.0(9)	11906.7(18)	7383.7(7)	18.4(2)
C (26)	2532.7(8)	10394.4(18)	6840.3(6)	15.1(2)

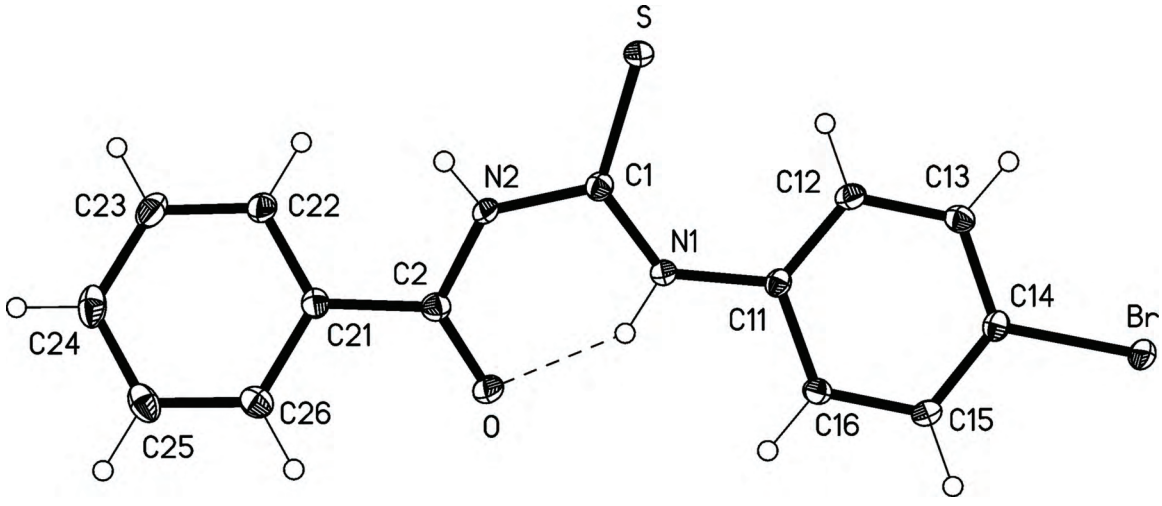


Figure 1. An ORTEP drawing of N-{[(4-bromophenyl)amino]carbonothioyl}benzamide with displacement ellipsoids plotted at 50% probability level. The dotted line shows the intramolecular H-bonding interaction.

Table 3. Bond lengths [Å] and angles [°] for N-{[(4-bromophenyl) amino] carbonothioyl} benzamide.

Bond Lengths	
Br-C (14)	1.9006(10)
S-C (1)	1.6684(10)
N(1)-C(1)	1.3415(13)
N(1)-C(11)	1.4137(13)
N(2)-C(2)	1.3769(13)
N(2)-C(1)	1.3992(13)
O-C(2)	1.2324(12)
C(2)-C(21)	1.4865(14)
C(11)-C(12)	1.3952(13)
C(11)-C(16)	1.4011(14)
C(12)-C(13)	1.3921(14)
C(13)-C(14)	1.3841(14)
C(14)-C(15)	1.3886(14)
C(15)-C(16)	1.3871(14)
C(21)-C(26)	1.3938(14)
C(21)-C(22)	1.3938(14)
C(22)-C(23)	1.3893(15)
C(23)-C(24)	1.3877(16)
C(24)-C(25)	1.3895(17)
C(25)-C(26)	1.3868(15)

Bond Angles	
C(1)-N(1)-C(11)	131.79(9)
C(2)-N(2)-C(1)	128.45(9)
N(1)-C(1)-N(2)	114.00(9)
N (1)-C (1)-S	127.97(8)
N (2)-C (1)-S	118.03(7)
O-C (2)-N (2)	122.47(9)
O-C (2)-C (21)	121.32(9)
N (2)-C (2)-C (21)	116.20(9)
C (12)-C (11)-C (16)	119.47(9)
C (12)-C (11)-N (1)	125.80(9)
C (16)-C (11)-N (1)	114.71(9)
C (13)-C (12)-C (11)	119.55(9)
C (14)-C (13)-C (12)	120.02(9)
C (13)-C (14)-C (15)	121.39(9)
C(13)-C(14)-Br	119.50(8)
C(15)-C(14)-Br	119.10(7)
C(16)-C(15)-C(14)	118.47(9)
C(15)-C(16)-C(11)	121.09(9)
C(26)-C(21)-C(22)	120.09(9)
C(26)-C(21)-C(2)	117.58(9)
C(22)-C(21)-C(2)	122.26(9)
C(23)-C(22)-C(21)	119.64(10)
C(24)-C(23)-C(22)	120.20(11)
C(23)-C(24)-C(25)	120.11(10)
C(26)-C(25)-C(24)	120.03(10)
C(25)-C(26)-C(21)	119.89(10)

Experimental protocols

Instrumentation

Melting point was recorded on Electrothermal IA9000 series digital melting point apparatus. The proton NMR and ^{13}C spectra were recorded in DMSO-d_6 solvent on a Jeol ECS-400 and 300 MHz spectrophotometer using tetramethylsilane as an internal reference, respectively. The apparent resonance multiplicity is described as s (singlet), br s (broad singlet), d (doublet), dd (doublet of doublets), t (triplet), q (quartet), and m (multiplet). Infrared measurement was recorded in the range 400-4000 cm^{-1} on a Spectrum 2000 (Perkin Elmer). Elemental analysis was carried out using a Perkin Elmer CHNS/O 2400. The mass spectrum was run on a Finnigan TSQ-70 spectrometer (Finnigan, USA) at 70 eV). X-ray diffraction data were collected on an Oxford Diffraction

Xcalibur Nova diffractometer. Thin layer chromatography (TLC) analysis was carried out on 5 × 20 cm plates coated with silica gel GF_{254} type 60 (25-250 mesh) using an ethyl acetate-petroleum ether mixture (1:2) as solvent.

Table 4. Torsion angles [°] for N-{[(4-bromophenyl)amino]carbonothioyl}benzamide.

C (11)-N (1)-C (1)-N (2)	-179.23(9)
C (11)-N (1)-C (1)-S	1.41(17)
C (2)-N (2)-C (1)-N (1)	-6.10(15)
C (2)-N (2)-C (1)-S	173.32(8)
C (1)-N (2)-C (2)-O	8.22(16)
C (1)-N (2)-C (2)-C (21)	-171.35(9)
C (1)-N (1)-C (11)-C (12)	-21.25(17)
C (1)-N (1)-C (11)-C (16)	160.41(10)
C (16)-C (11)-C (12)-C (13)	-0.25(14)
N(1)-C(11)-C(12)-C(13)	-178.51(10)
C(11)-C(12)-C(13)-C(14)	0.77(14)
C(12)-C(13)-C(14)-C(15)	-0.90(15)
C(12)-C(13)-C(14)-Br	177.91(7)
C(13)-C(14)-C(15)-C(16)	0.50(15)
Br-C(14)-C(15)-C(16)	-178.32(7)
C(14)-C(15)-C(16)-C(11)	0.04(15)
C(12)-C(11)-C(16)-C(15)	-0.16(15)
N(1)-C(11)-C(16)-C(15)	178.30(9)
O-C(2)-C(21)-C(26)	28.69(14)
N(2)-C(2)-C(21)-C(26)	-151.74(9)
O-C(2)-C(21)-C(22)	-148.06(10)
N(2)-C(2)-C(21)-C(22)	31.52(14)
C(26)-C(21)-C(22)-C(23)	0.79(15)
C(2)-C(21)-C(22)-C(23)	177.46(10)
C(21)-C(22)-C(23)-C(24)	0.96(16)
C(22)-C(23)-C(24)-C(25)	-1.68(17)
C(23)-C(24)-C(25)-C(26)	0.64(16)
C(24)-C(25)-C(26)-C(21)	1.12(15)
C(22)-C(21)-C(26)-C(25)	-1.83(15)
C(2)-C(21)-C(26)-C(25)	-178.65(9)

Table 5. Hydrogen bonds [Å and °] for N-{[(4-bromophenyl)amino]carbonothioyl} benzamide.

D-H...A	d (D-H)	d (H...A)	d (D...A)	< (DHA)
N (1)-H (01)...O	0.879(14)	1.843(15)	2.6129(11)	145.1(12)
N (2)-H (02)...S#1	0.806(13)	2.747(13)	3.5102(9)	158.6(12)
C (15)-H (15)...O#2	0.95	2.46	3.3866(12)	165.5
C (26)-H (26)...Br#2	0.95	3.13	3.9604(11)	147.5
C (24)-H (24)...S#3	0.95	2.90	3.7137(12)	144.7

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z+1

#2 -x+1,-y+1,-z+1

#3 x,-y+3/2,z+1/2

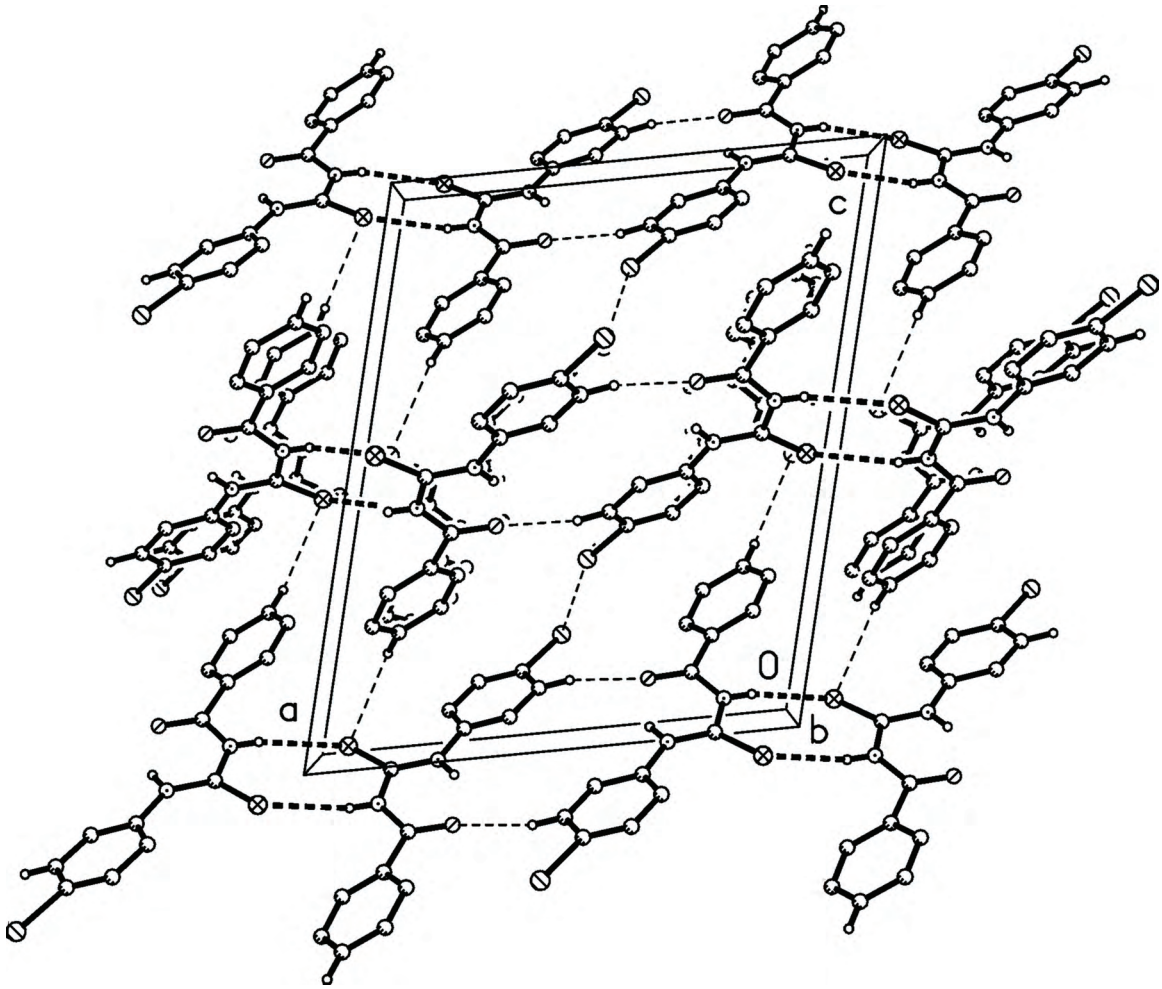


Figure 2. Packing diagram of N-{[(4-bromophenyl) amino]carbonothioyl}benzamide. The dashed lines denoted the C—H . . . O and N—H . . . O hydrogen bonds. Non-hydrogen bonded H atoms have been omitted for clarity.

Synthesis

The synthetic starting material, reagents, and solvents were of analytical reagent grade or of the highest quality commercially available and were purchased from Aldrich Chemical Co. and Merck Chemical Co. and were dried when necessary. A solution of benzoyl chloride (1.40 g, 0.01 mol) in anhydrous acetone (80 mL) and 3% tetrabutylammonium bromide (TBAB) in acetone was added dropwise to a suspension of ammonium thiocyanate (0.76 g, 0.01 mol) in acetone (50 mL) and the reaction mixture was refluxed for 45 min. After cooling to room temperature, a solution of the corresponding 2-bromoaniline (1.71 g, 0.01 mol) in acetone (25 mL) was added and the resulting mixture refluxed for 1.5 h. The reaction mixture was poured into 5 times its volume of cold water, whereupon the thiourea precipitated. The solid product was washed with water and purified by re-crystallization from an ethanol-dichloromethane mixture (1:2). Elemental analysis for $C_{14}H_{11}BrN_2OS$ (MW=335.22) in wt % calc. C=62.1, H=3.28, N=8.36, S=9.55 and found to be C=62.12, H=3.34, N=8.18, S= 9.43. mp. 141-142 °C, yield 93%. IR (KBr pellet) in cm $^{-1}$: 3352 (free NH), 3212 (assoc. NH), 1685 (C=O), 1509 (benzene ring), 1142 (C=S), 1402 (C-N stretching); ^{1}H-NMR (400 MHz, DMSO-d_6) in δ (ppm) and J (Hz): 12.95 (1H, br s, NH), 12.03 (1H, br s, NH), 7.74 (2H, d, J = 8.1 Hz), 7.66 (2H, d, J= 6.7 Hz) and 7.36 (2H, d, J = 8.4 Hz), 7.30 (2H, d, J= 8.0; ^{13}C-NMR (300 MHz, DMSO-d_6) in δ (ppm): 181.0 (C=S), 168.2 (C=O), 145.1(C), 143.3(C), 133.0 (C), 132.2 (C), 129.5 (2 CH), 128.6 (2 CH), 127.5 (4 CH); EI MS, m/z (%): 335 (15), 291 (7.2), 213 (20), 172 (10), 157 (3.5), 121 (5.5), 105 (100), 78 (65).

Single Crystal X-ray Crystallography

Crystal data: $C_{14}H_{11}BrN_2OS$, monoclinic, space group $P2_1/n$, a=13.8228(3), b =5.9272(2), c = 16.6425(3) Å, β = 103.963(3)°, V = 1323.24 Å^3, T = 100 K, Z = 4, F (000) = 672, D_x = 1.683 g cm^{-3}, μ = 4.0 mm^{-1}. Single crystals suitable for X-ray diffraction studies were obtained by evaporation from a dichloromethane/ethanol mixture. A colorless plate 0.25 × 0.20 × 0.15 mm^3 was mounted on a glass fiber in inert oil. Measurements were performed at 100 K on an Oxford Diffraction Xcalibur Nova diffractometer with mirror-focused Cu-Kα radiation to $2\theta_{max}$ 152° (99.8% complete to 31.51°). The data were corrected for absorption using the multi-scan method. Of 81,955 intensities, 4397 were independent (R_{int} 0.0273). The structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2 using the program SHELXL-97.[23] The non-hydrogen atoms were refined anisotropically. NH hydrogens were refined freely, other H atoms using a riding model. The final $wR2$ was 0.0437, with a conventional $R1$ of 0.0168, for 180 parameters; S = 1.028; max. $\Delta\rho$ 0.260 e Å^{-3}.

Supplementary crystallographic data

Crystallographic data for the structure reported in this article have been deposited with Cambridge Crystallographic Data Centre, CCDC 724599. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CBZ IEZ, UK. Facsimile (44) 01223 336 033, E-mail: deposit@ccdc.cam.ac.uk or http//www.ccdc.com.ac.uk/deposit.

Acknowledgements

The authors are grateful to the National Engineering & Scientific Commission and Allama Iqbal Open University, Islamabad, for providing the necessary lab and analytical facilities.

References

1. Verma, R. K.; Verma, L.; Ranjan, M.; Verma, B. P.; Mojumdar, S. C. *J. Therm. Anal. Cal.*, **2008**, *94*, 27-31.
2. Stiffel, E. I.; George, G. N. *Bioinorganic Chemistry*, Bertini, I.; Gray, H. B.; Lippard, S. J.; Valentine, J. S. University Science Books, **1998**.
3. Cotton, F. A.; Wilkinson, G.; Murillo, A.; Bochman, M. *Advanced Inorganic Chemistry*, John Wiley **1999**.
4. D'hooghe, M.; Waterinckx, A.; De Kimpe, N. *J. Org. Chem.* **2005**, *70*, 227-232.
5. Jain, V. K.; Rao, J. T. *J. Institute Chem. (India),* **2003,** *75*, 24-26.
6. Saeed, S.; Bhatti, M. H.; Yunus, U.; Jones, P. G. *Acta Crystallogr.* **2008**, *E64*, o1566.
7. Zhang, Y. M.; Wei, T. B.; Xian, L.; Gao, L. M. *Phosphorus, Sulfur Silicon Relat. Elem.* **2004**, *179*, 2007.
8. **8.** Arslan, H.; Duran, N.; Borekci, G.; Ozer, C. K.; Akbay, C. *Molecules*, **2009**, *14*, 519-527.
9. Gu, C.-L.; Liu, L.; Zhao, J.-L.; Wang, D.; Chen, Y.-J. *Tetrahedron*, **2007**, *18*, 455-463.
10. Saeed, S.; Rashid, N.; Hussain, R.; Jones, P. G. *Acta Crystallogr.* **2009**, *E65*, o2106.
11. Saeed, S.; Rahid, N.; Tahir, A.; Jones, P. G. *Acta Crystallogr.* **2009**, *E65*, o1870-o1871.
12. Saeed, S.; Rashid, N.; Hussain, R.; Jones, P. G. *Acta Crystallogr.* **2009**, *E65*, o2568-o2569.
13. Binzet, G.; Arslan, H.; Florke, U.; Kulcu, N.; Duran, N. *J. Coord. Chem.* **2006**, *59*, 1395-1406.
14. Saeed, S.; Bhatti, M. H.; Youns, U.; Jones, P. G. *Acta Crystallogr.* **2008**, *E64*, o1485.
15. Saeed, S.; Bhatti, M. H.; Tahir, M. K.; Jones, P. G. *Acta Crystallogr.* **2008**, *E64*, o1369.
16. Arslan, H.; Florke, U.; Kulcu, N. *J. Chem. Crystallogr.* **2003**, *33*, 919-924.
17. Wei, T. B.; Chen, J. C.; Wang, X. C. *Synth. Commun.* **1996**, *26*, 1147-1151.
18. Illi, V. O. *Tetrahedron Lett.* **1979**, *20*, 2431-2435.
19. Sacht, C.; Datt, M. S. *Polyhedron*, **2000**, *19*, 1347-1351.
20. Su, B. Q.; Liu, G. L.; Sheng, L.; Wang, X. Q.; Xian, L. *Phosphorus, Sulfur, and Silicon*, **2006**, *181*, 745-749.
21. Allen, F. H. *Acta Crystallogr.*, **2002**, *B.58,* 380-388.
22. Zhang, D. C.; Zhang, Y. Q.; Cao, Y.; Zao, B. *Acta Crystallogr.*, **1996**, *C52*, 11716-1718.
23. Sheldrick, G. M. *Acta Crystallogr.*, **2008**, *A64*, 112-122.