

THE CRYSTAL AND MOLECULAR STRUCTURE OF 1-(BIPHENYL-4-CARBONYL)-3-*p*-TOLYL-THIOUREA

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Abstract

1-(Biphenyl-4-carbonyl)-3-*p*-tolyl-thiourea (1) has been synthesized and characterized by elemental analysis and IR spectroscopy. The crystal and molecular structure of the title compound has been determined from single crystal X-ray diffraction data. It crystallizes in the triclinic space group P-1, $Z = 4$ with $a = 9.6482(17)$ Å, $b = 13.271(2)$ Å, $c = 14.109(3)$ Å, $\alpha = 92.793(4)^\circ$, $\beta = 96.140(4)^\circ$, $\gamma = 107.999(4)^\circ$, $V = 1701.9(5)$ Å³ and $D_{\text{calc}} = 1.352$ Mg/m³.

Key words: Thioureas, benzoylthioureas, syntheses, X-ray structures, single crystal, X-ray crystallography.

Introduction

Most of the thiourea derivatives have been successfully used in the extraction of Cu(II), Ni(II), Co(II), Pd(II), Pt(II), Co(III), Au(III), Rh(III) and Ru(III) from acidic media. These reagents have also been implemented in a solid supported liquid membrane system for the selective transport of relevant metals. Also thioureas have been shown to possess antibacterial, antifungal, antitubercular, antithroid and insecticidal properties.^{1,2}

The structures of several type thiourea derivatives and its several metal complexes have been determined during the past decades.³⁻⁸ The title compound derivative acts as a bidentate ligand coordinating through the sulfur atom and the benzoyl oxygen atom. The similar structures of these derivative palladium, nickel and copper complexes and ligands have been determined in previous studies.⁹⁻¹¹

We have recently begun to examine the coordination behaviour of a series of substituted benzoylthiourea derivatives that possess a number of interesting properties.^{5-8,11,12} Based upon the literature search, we could find no synthesis or characterization of title compound. In this paper, we discuss here the synthesis method and the structure of 1-(biphenyl-4-carbonyl)-3-*p*-tolyl-thiourea (**1**).

Results and discussion

The molecular structure of 1-(biphenyl-4-carbonyl)-3-*p*-tolyl-thiourea (**1**), showing the atom numbering scheme and selected bond lengths and angles is given in Fig. 1 and Table 1, respectively. There are two independent molecules A and B per asymmetric unit with almost identical geometries, so the following discussion focuses on A only.

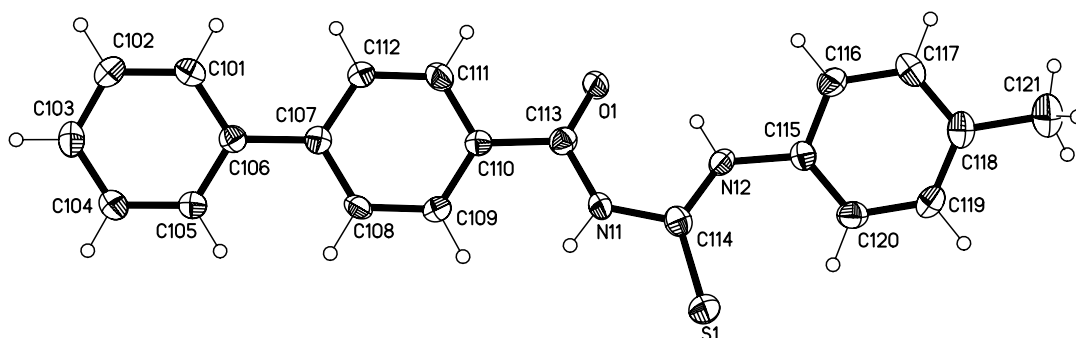


Figure 1. The molecular structure A of the title compound (**1**). The second independent molecule B (with atom numbering scheme 2xx) shows almost identical geometry. Displacement ellipsoids are drawn at the 50% probability level.

Table 1. Selected bond lengths (Å) and angles (°) for title compound, molecules A (numbering $x = 1$) and B ($x = 2$).

Bond lengths	$x=1$	$x=2$	Bond angles	$x=1$	$x=2$
Cx13-Ox	1.217(3)	1.224(3)	Nx1-Cx14-Nx2	113.7(3)	113.5(3)
Cx14-Sx	1.647(3)	1.647(3)	Cx10-Cx13-Nx1	115.7(3)	115.4(3)
Cx13-Nx1	1.367(4)	1.362(4)	Cx14-Nx1-Cx13	130.6(3)	130.4(3)
Cx14-Nx2	1.330(3)	1.330(3)	Cx14-Nx2-Cx15	129.5(3)	129.3(3)
Cx14-Nx1	1.387(4)	1.394(4)	Ox-Cx13-Nx1	122.9(3)	122.5(3)

The bond lengths and angles in the thiourea moiety are typical for thiourea derivatives; the Cx14-S and Cx13-O bonds both show typical double-bond character ($x = 1$ for molecule A, $x = 2$ for B). The C-N bonds Cx13-Nx1 (1.365 Å), Cx14-Nx1 (1.391 Å), Cx14-Nx2 (1.330 Å), and Cx15-Nx2 (1.424 Å) are shorter than the normal single C-N bond length (1.469 Å), indicating double bond character. LP electron on nitrogen atoms are shifted towards neighbouring atoms. As a result of this effect, hybridisation on nitrogen atoms changes from sp^3 to sp^2 . These results confirmed by bond angles and lengths (Table 1). This approach is agreement with that of Arslan et al.¹²

Intramolecular hydrogen bonds $Nx2-Hx2..O$ for molecule A and B each form six-membered rings, well known from related structures. The conformation of the molecule with respect to the thiocarbonyl and carbonyl moieties is twisted as reflected by the torsional angles $Cx14-Nx1-Cx13-Ox$ and $Cx13-Nx1-Cx14-Nx2$ of av. $7.1(5)^\circ$ and $-1.3(5)^\circ$, respectively. In the crystal structure (Fig. 2), molecules A and B form dimers each through strong intermolecular hydrogen bonds $C111-H11A..O1$ ($-x +1, -y+1, -z$) with $H..O$ 2.384 Å, $C-H..O$ 132.2° , $C..H$ 3.211(4) Å and $C209-H20G..O2$ ($-x +1, -y+1, -z$) with $H..O$ 2.427 Å, $C-H..O$ 121.7° , $C..O$ 3.133(4) Å. These values are normalized for N-H 1.030 and C-H 1.080 Å.

There are no significant differences in the bond distance and bond angles comparing with other phenyl thiourea.^{11-13,16} All the other bond lengths fall within the expected range.

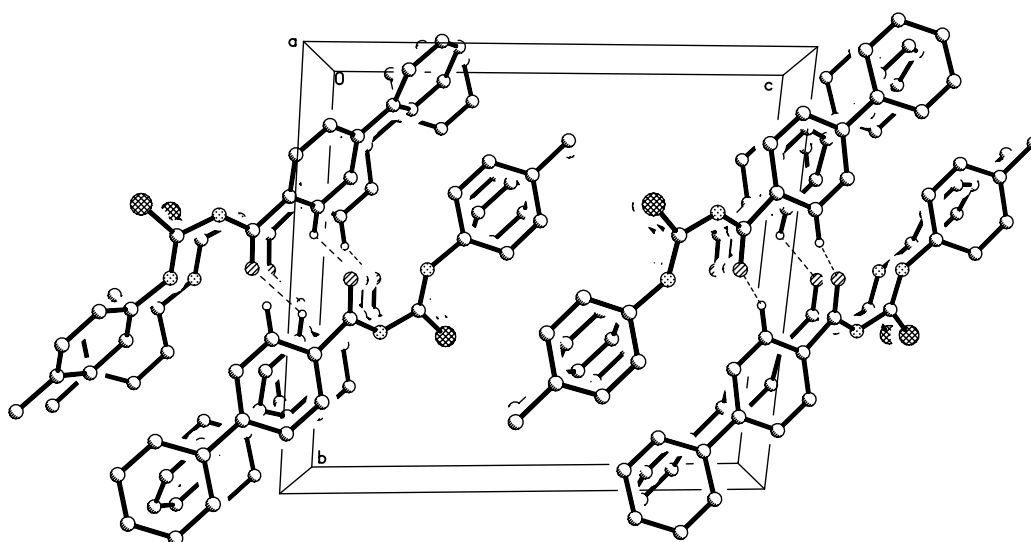


Figure 2. Packing diagram for (1) viewed along [100], H-atoms not involved omitted.

Experimental

Synthesis

All chemicals used for the preparation of the title compound were of reagent grade quality. Some of the solvent was distilled before use. The compound was prepared by a procedure similar to that reported in the literature.¹² A solution of an appropriately 4-phenyl benzoyl chloride (0.01 mol) in acetone (50 cm³) was added dropwise to a suspension of potassiumthiocyanate (0.01 mol) in acetone (30 cm³). The reaction

mixture was heated under reflux for 30 min, and then cooled to room temperature. A solution of *p*-tolylamine (0.01 mol) in acetone (10 cm³) was added and the resulting mixture was stirred for 2 h. Hydrochloric acid (0.1 N, 300 cm³) was added and then the solution filtered. The solid product was washed with water and purified by recrystallisation from ethanol/dichloromethane mixture (1:1). 1-(biphenyl-4-carbonyl)-3-*p*-tolyl-thiourea: White. Yield: 84%, m.p. 162-164 °C, Anal. Calcd For C₂₁H₁₈N₂OS: C 72.8, H 5.2, N 8.1. Found: C 72.1, H 5.1, N 7.9. IR (KBr): $\nu(\text{N-H})$ 3197 (br), $\nu(\text{C=O})$ 1674 (s) cm⁻¹.

Table 2. Crystal data and structure refinement for title compound.

Empirical formula	C ₂₁ H ₁₈ N ₂ OS
Formula weight / g	346.43
Temperature / K	153(2)
Wavelength (Mo K α) / Å	0.71073
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	
<i>a</i> / Å	9.6482(17)
<i>b</i> / Å	13.271(2)
<i>c</i> / Å	14.109(3)
α / °	92.793(4)
β / °	96.140(4)
γ / °	107.999(4)
Volume / Å ³	1701.9(5)
Z	4
Density (calculated) / Mg/m ³	1.352
Absorption coefficient / mm ⁻¹	0.201
F(000)	728
Crystal size / mm ³	0.35 x 0.10 x 0.08
Theta range for data collection / °	1.46 to 26.19
Index ranges	-11 ≤ <i>h</i> ≤ 10, -16 ≤ <i>k</i> ≤ 16, -16 ≤ <i>l</i> ≤ 17
Reflections collected	9993
Independent reflections	6711 [R(int) = 0.0406]
Completeness to theta = 26.19°	98.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.984 and 0.933
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	6711 / 0 / 453
Goodness-of-fit on F ²	0.972
Final R indices [I > 2σ(I)]	R1 = 0.0479
R indices (all data)	wR2 = 0.0800
Largest diff. peak and hole / e.Å ⁻³	0.23 and -0.25

Analysis and physical measurements

Fourier transformed infrared (FT-IR) spectra were recorded as KBr pellets on a Shimadzu 435 spectrophotometer, between 4000 - 400 cm^{-1} . C, H and N analyses were carried out on a Carlo Erba MOD 1106 elemental analyzer. Melting points were determined on a digital melting point instrument (Electrothermal model 9200).

Single crystal X-ray data were collected on a Bruker SMART APEX System including SAINT data reduction and SADABS corrections. The structures were solved by direct and conventional Fourier methods. Full-matrix least-squares refinement based on F^2 . Anisotropic atomic displacement parameters were refined for all non-hydrogen atoms, hydrogen atoms derived from Fourier maps were refined at idealized positions using a 'riding model' with $U_{\text{eq}}(\text{H}) = 1.2 U_{\text{eq}}(\text{N}, \text{C}_{\text{iso}})$ and $1.5 U_{\text{eq}}(\text{C}_{\text{iso}})$ for methyl groups, respectively. Two independent but geometrically identical molecules A and B per asymmetric unit. Programs used for calculations: SHELXTL.¹⁴ Further details concerning data collection and refinement are given in Table 2. Additional crystallographic data for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Centre (CCDC) with quotation number CCDC-244044 and can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44(1223)336-033, E-mail: deposit@ccdc.cam.ac.uk].

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References

1. O. F. Huebhr, J. L. Marsh, R. H. Mizzoni, R. P. Mull, D.C. Schroeder, H. A. Troxell, C. R. Scholz, *J. Am. Chem. Soc.* **1953**, *75*, 2274–2275.
2. V. K. Madan, A. D. Taneja, *Indian Chem. Soc.* **1991**, *68*, 471–472.
3. L. P. Battaglia, A. C. Bonamartini, G. Pelizzi, T. M. E. Vidoni, *J. Chem. Soc., Dalton Trans.* **1977**, 1141–1144.
4. E. A. H. Griffith, W. A. Spofford, E. L. Amma, *Inorg. Chem.* **1978**, *17*, 1913–1971.
5. H. Arslan, U. Flörke, N. Külcü, *Acta Crystallographica* **2003**, *E59*, o641–o642.
6. H. Arslan, U. Flörke, N. Külcü, *J. Chem. Crystallography* **2003**, *33*, 919–924.
7. H. Arslan, D. Vanderveer, F. Emen, N. Külcü, *Z. Kristallogr. NCS* **2003**, *218*, 479–480.
8. D. Ugur, U. Flörke, N. Külcü, H. Arslan, *Acta Crystallographica* **2003**, *E59*, o1345–o1346.

9. G. Firzl, L. Beyer, J. Sieler, R. Richter, J. Kaiser, E. Hoyer, *Z. Anorg. Allg. Chem.* **1977**, 433, 237–241.
10. R. Richter, L. Beyer, J. Kaiser, *Z. Anorg. Allg. Chem.* **1980**, 461, 67–73.
11. G. Avşar, H. Arslan, H.-J. Haupt, N. Külcü, *Turk. J. Chem.* **2003**, 27, 281–285.
12. H. Arslan, U. Flörke, N. Külcü, *Transition Metal Chemistry* **2003**, 28, 816–819.
13. A. Dago, M. A. Simonov, E. A. Pobedinskaya, A. Macias, A. Martin, *Kristallografiya* **1987**, 32, 1024–1026.
14. G. M. Sheldrick, SHELXTL v. 5.1, Structure Determination Software Suite, Bruker AXS, Madison, Wisconsin, USA, 1998.

Povzetek

Pripravili smo 1-(bifenil-4-karbonil)-3-(*p*-tolil)tiosečnino (**1**) in jo karakterizirali z elementno analizo in IR spektroskopijo. Kristalno in molekulsko strukturo **1** smo določili z rentgensko difrakcijsko analizo. Spojina kristalizira v triklinski prostorski skupini P-1, $Z = 4$, $a = 9.6482(17) \text{ \AA}$, $b = 13.271(2) \text{ \AA}$, $c = 14.109(3) \text{ \AA}$, $\alpha = 92.793(4)^\circ$, $\beta = 96.140(4)^\circ$, $\gamma = 107.999(4)^\circ$, $V = 1701.9(5) \text{ \AA}^3$ in $D_{\text{calc}} = 1.352 \text{ Mg/m}^3$.