

The Crystal and Molecular Structure of 1-(2-chloro-benzoyl)-3-*p*-tolyl-thiourea

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We would like to dedicate this article in honor of the 70th birthday of Professor Martin Trömel

1-(2-Chloro-benzoyl)-3-*p*-tolyl-thiourea was synthesized and characterized by elemental analysis and IR spectroscopy. The crystal and molecular structure of the title compound was determined from single-crystal X-ray diffraction data. It crystallizes in the triclinic space group P-1, with $a = 7.9942(9)$ Å, $b = 9.531(1)$ Å, $c = 11.075(1)$ Å, $\alpha = 97.235(2)^\circ$, $\beta = 111.099(2)^\circ$, and $\gamma = 106.105(2)^\circ$.

Key Words: Thioureas, X-ray structures, benzoylthiourea.

Introduction

N,N-Disubstituted thiourea possesses a remarkable capacity for coordination with transition metals giving rise to highly colored chelate compounds. The complexation capacity of thiourea derivatives has been reported in several studies^{1,2}. The metal complexes of thiourea are neutral and their colors vary with the nature of the metal ions. These chelating agents have been remarkable ones for analytical chemistry, especially for the trace analysis of platinum metals in complex matrices. Many transition metal complexes with such thiourea derivatives have been reported, and structures with O and S-binding to the metal ions in alkaline media were well proposed based on a series of physicochemical methods³⁻⁹. In addition, thioureas have been shown to possess antibacterial, antifungal, antitubercular, antithyroid and insecticidal properties^{10,11}. The biological activities of complexes with thiourea derivatives have been successfully screened for various biological actions¹²⁻¹⁵.

We have recently begun to examine the coordination behaviour of a series of substituted benzoylthiourea derivatives that possess a number of interesting properties¹⁶⁻²¹. Based upon a literature scan, we were able to find no reports of synthesis or characterization of the title compound. In this study, 1-(2-chloro-benzoyl)-3-*p*-tolyl-thiourea was synthesized and its crystal structure was determined by single-crystal X-ray diffraction.

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Experimental

Instrumentation

Fourier transformed infrared (FT-IR) spectra were recorded as KBr pellets on a Shimadzu 435 spectrophotometer, between 4000 and 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 AXS SMART APEX single crystal diffractometer using monochromated $\text{MoK}\alpha$ radiation at 153(2) K. Semi-empirical absorption corrections were made from equivalents. The structure was solved by the direct and conventional Fourier methods. Full-matrix least-squares refinement was based on F^2 and 182 parameters. All non-hydrogen atoms were refined anisotropically and geometrically placed hydrogen atoms were refined with a 'riding model' and $U_{iso}(\text{H}) = 1.2 U_{iso}(\text{N}, \text{C})$ and $1.5 U_{iso}(\text{C})$ for the methyl group, respectively. The program used for calculations was SHELXTL²². Further details concerning data collection and refinement are given in Table 1.

Table 1. Crystal data and structure refinement for the title compound.

| | |
|--------------------------------------|---|
| Empirical formula | $\text{C}_{15}\text{H}_{13}\text{ClN}_2\text{OS}$ |
| Formula weight | 304.78 |
| Temperature | 153(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Triclinic |
| Space group | P-1 |
| Unit cell dimensions | $a = 7.9942(9)$ Å $b = 9.531(1)$ Å $c = 11.075(1)$ Å $\alpha = 97.235(2)^\circ$ $\beta = 111.099(2)^\circ$ $\gamma = 106.105(2)^\circ$ |
| Volume | 731.93(15) Å ³ |
| <i>Z</i> | 2 |
| Density (calculated) | 1.383 Mg/m ³ |
| Absorption coefficient | 0.400 mm ⁻¹ |
| <i>F</i> (000) | 316 |
| Crystal size | 0.32 x 0.22 x 0.20 mm ³ |
| Theta range for data collection | 2.04 to 25.51 ° |
| Index ranges | $-8 \leq h \leq 9, -11 \leq k \leq 7, -13 \leq l \leq 12$ |
| Reflections collected | 4015 |
| Independent reflections | 2687 [R(int) = 0.023] |
| Completeness to theta = 25.51 ° | 98.0% |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.9244 and 0.8828 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data/parameters | 2687/182 |
| Goodness-of-fit on F^2 | 0.917 |
| Final R indices [$I > 2\sigma(I)$] | R1 = 0.037, wR2 = 0.074 |
| R indices (all data) | R1 = 0.052, wR2 = 0.078 |
| Largest diff. peak and hole | 0.263 and -0.199 e.Å ⁻³ |

Synthesis of the compound

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 with a procedure similar to that reported in the literature²¹. A solution of 2-chloro-benzoyl chloride (0.01 mol) in acetone (50 cm³) was added dropwise to a suspension of potassium thiocyanate (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 to the solution, which was then filtered. The solid product was washed with water and purified by recrystallization from an ethanol/dichloromethane mixture (1:1).

1-(2-Chloro-benzoyl)-3-p-tolyl-thiourea: White. Yield: 88% , m.p. 170-172 °C, anal. calcd for C₁₅H₁₃ClN₂OS: C 59.1, H 4.3, N 9.2. Found: C 58.6, H 4.3, N 9.1. IR (KBr, cm⁻¹): $\nu(\text{N-H})$ 3242 (br), $\nu(\text{C=O})$ 1687 (s).

Results and Discussion

The molecular structure of 1-(2-chloro-benzoyl)-3-*p*-tolyl-thiourea is depicted in Figure 1. Selected bond lengths and angles are presented in Table 2. Final atomic coordinates and equivalent isotropic displacement parameters are given in Table 3.

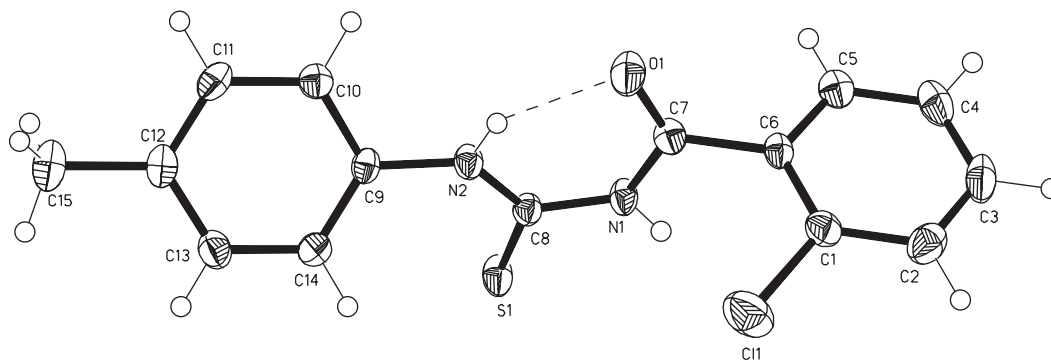


Figure 1. Molecular structure of 1-(2-chloro-benzoyl)-3-*p*-tolyl-thiourea in the crystal showing the atom numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.

Table 2. Selected bond lengths (Å) and angles (°).

| Bond lengths | | Bond angles | |
|--------------|----------|-------------|----------|
| C7-O1 | 1.216(2) | N1-C8-N2 | 115.2(2) |
| C8-S1 | 1.666(2) | C6-C7-N1 | 113.5(2) |
| C7-N1 | 1.366(2) | C8-N1-C7 | 128.7(2) |
| C8-N1 | 1.397(2) | C8-N2-C9 | 128.5(2) |
| C8-N2 | 1.330(2) | | |

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for the title compound.

| Atom | <i>x</i> | <i>y</i> | <i>z</i> | <i>U</i> (eq)* |
|------|----------|----------|----------|----------------|
| Cl1 | 4593(1) | 8749(1) | 8572(1) | 56(1) |
| S1 | 2172(1) | 3477(1) | 9521(1) | 38(1) |
| O1 | 2153(2) | 5251(2) | 5890(1) | 43(1) |
| N1 | 3427(2) | 5033(2) | 8026(2) | 29(1) |
| N2 | 156(2) | 3873(2) | 7149(2) | 27(1) |
| C1 | 6084(3) | 8151(2) | 7982(2) | 32(1) |
| C2 | 7869(3) | 9164(2) | 8252(2) | 41(1) |
| C3 | 9050(3) | 8673(3) | 7791(2) | 44(1) |
| C4 | 8455(3) | 7223(3) | 7058(2) | 42(1) |
| C5 | 6654(3) | 6218(2) | 6778(2) | 33(1) |
| C6 | 5458(3) | 6679(2) | 7251(2) | 26(1) |
| C7 | 3512(3) | 5595(2) | 6966(2) | 28(1) |
| C8 | 1827(3) | 4133(2) | 8159(2) | 26(1) |
| C9 | -1719(3) | 3111(2) | 7036(2) | 25(1) |
| C10 | -3102(3) | 2328(2) | 5769(2) | 29(1) |
| C11 | -4981(3) | 1679(2) | 5564(2) | 32(1) |
| C12 | -5530(3) | 1783(2) | 6614(2) | 32(1) |
| C13 | -4124(3) | 2563(2) | 7882(2) | 35(1) |
| C14 | -2241(3) | 3235(2) | 8095(2) | 32(1) |
| C15 | -7598(3) | 1073(2) | 6375(2) | 49(1) |

* $U_{(eq)}$ is defined as 1/3 of the trace of the orthogonalized U^{ij} tensor.

The bond lengths and angles in the thiourea moiety are typical for thiourea derivatives; the C8-S1 and C7-O1 bonds both show a typical double-bond character with 1.666(2) and 1.216(2) Å, respectively. Similar shortening for the C-N bonds C7-N1 1.366(2) Å, C8-N1 1.397(2) Å, C8-N2 1.330(2) Å, and C9-N2 1.424(2) Å also indicates a partial double-bond character. The elongation of C8-N1 relative to C8-N2 is known from other thioureas, which is probably due to the electron withdrawing effect of the carbonyl group^{16,19}. This approach is in agreement with that of Arslan et al.²¹.

The intramolecular hydrogen bond N2-H2 \cdots O1 (2.669(3) Å) forms a 6-membered ring with C7, N1 and C8. The dihedral angle between the best planes of the 2 aryl rings is 48.14(8)°. The conformation of the molecule with respect to the thiocarbonyl and carbonyl moieties is slightly twisted as reflected by the torsional angles O1-C7-N1-C8 and C7-N1-C8-N2 of -7.5(3)° and -4.8(3)°, respectively. There are no significant differences in the bond distances and angles compared with those of other phenyl thioureas^{16–21,23}. All other bond lengths fall within the expected range.

The crystal packing (Figure 2) shows intermolecular hydrogen bonds N1-H1 \cdots S1^{*i*} [*i*): -x +1, -y+1, -z+2] with H1 \cdots S1 2.33, N1 \cdots S1 3.338(1) Å, and N1-H1 \cdots S1 164.7° forming dimers stacked along [100]. These values are normalized for N1-H1 1.030 Å.

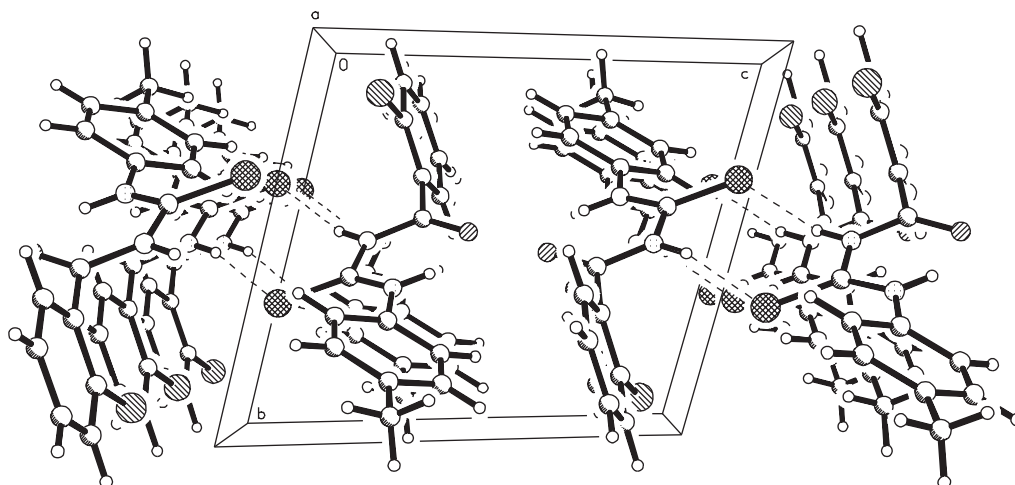


Figure 2. Packing diagram for 1-(2-chloro-benzoyl)-3-*p*-tolyl-thiourea along [100]. The dashed lines show the N-H...S intermolecular hydrogen bonds [Symmetry code: (*i*): $-x+1, -y+1, -z+2$].

Supplementary Material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data [CCDC-243001] can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [e-mail: deposit@ccdc.cam.ac.uk].

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