

Bin Zhang,<sup>a</sup> Bi-Quan Su<sup>b\*</sup> and  
Liang Xian<sup>c</sup><sup>a</sup>Chemical Engineering Institute, Northwest University for Nationalities, Lanzhou 730030, People's Republic of China, <sup>b</sup>School of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou 730070, People's Republic of China, and <sup>c</sup>State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Lanzhou 730000, People's Republic of China

Correspondence e-mail: subq@mail.lzjtu.cn

## Key indicators

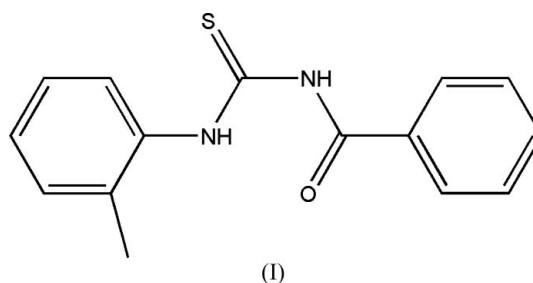
Single-crystal X-ray study  
 $T = 294$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å  
 $R$  factor = 0.039  
 $wR$  factor = 0.109  
Data-to-parameter ratio = 15.4For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.*N*-Benzoyl-*N'*-(2-methylphenyl)thiourea

In the title compound,  $\text{C}_{15}\text{H}_{14}\text{N}_2\text{OS}$ , intermolecular  $\text{N}-\text{H}\cdots\text{S}$  hydrogen bonds link pairs of molecules. The steric hindrance of the *o*-methyl group restricts the formation of a molecular conjugated plane and  $\pi-\pi$  stacking. The presence of a hydrogen-bond acceptor atom is more helpful for the thiourea ligand to promote its stability.

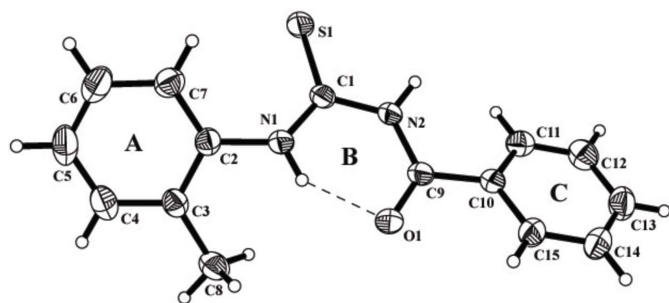
Received 15 June 2006  
Accepted 16 August 2006

## Comment

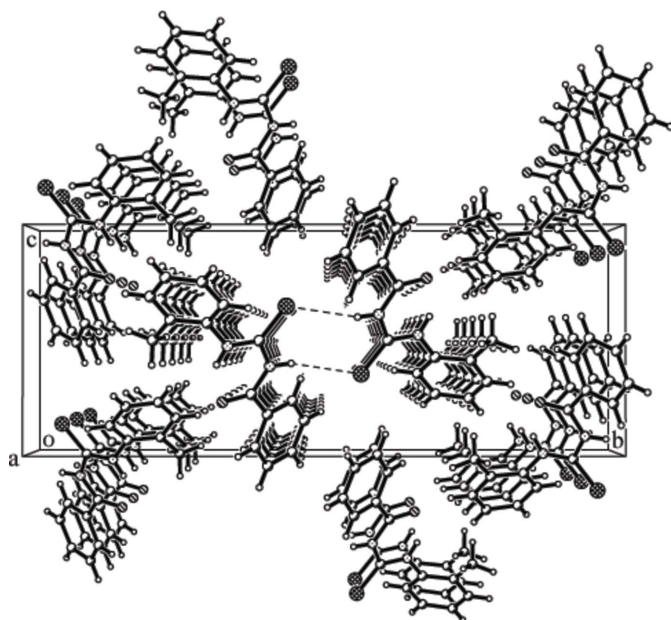
Carbonylthiourea and its derivatives are of very great interest to chemists because the presence of the carbonyl group and thiocarbonyl group promotes the coordination ability of thiourea ligands and the probability of forming supramolecular structures *via* intermolecular hydrogen-bonding interactions (Koch, 2001; Foss *et al.*, 2004; Bombicz *et al.*, 2004). In recent years, it was found that the coordination reaction of carbonylthiourea with copper can form some unexpected compounds. In previous research work on *N*-benzoyl-*N'*-(2-hydroxyethyl)thiourea (Zhang *et al.*, 2003), the desulfurization and cyclization of thiourea results in an oxazoline ring structure. In another experiment (Su *et al.*, 2005), it was also reported that a hexanuclear copper(I) cluster coordination compound was synthesized by the reaction of *N*-ethoxycarbonyl-*N'*-*o*-chlorophenylthiourea with cupric chloride in ethanol solution. In order to understand the hydrogen-bonding interactions in the coordination reactions of carbonylthiourea derivatives with transition metals, based on our previous research work (Su *et al.*, 2004, 2005, 2006), the synthesis, characterization and single-crystal structure determination of the title compound, (I), has been undertaken.



The molecular structure (Fig. 1) and the formation of pairs of molecules linked by intermolecular  $\text{N}-\text{H}\cdots\text{S}$  hydrogen bonds (Fig. 2) are similar to that observed in *N*-ethoxycarbonyl-*N'*-*o*-methoxyphenylthiourea, (*L*) (Su *et al.*, 2006). One important difference is that the conjugation in (*L*) is better than that in compound (I). In (I), the dihedral angle between ring *B* formed by hydrogen bonding and substituted benzene ring *A* is  $141.7(4)^\circ$ , and the dihedral angle between



**Figure 1**  
The molecular structure of compound (I). Displacement ellipsoids are drawn at the 50% probability level. The intramolecular hydrogen bond is indicated by a dashed line.



**Figure 2**  
View of the crystal packing along the *a* axis. Hydrogen bonds are indicated by dashed lines.

benzene ring C and substituted benzene ring A is  $120.8(3)^\circ$  (Fig. 1). The dihedral angles are similar to those of  $44.1$  and  $39.1^\circ$  between the six-membered hydrogen-bonded ring and the two benzene rings in *N-p*-nitrobenzoyl-*N'*-*p*-chlorophenylthiourea (Cambridge Crystallographic Data Centre No. 273455). However, in compound (L), the mean deviation from the molecular plane of non-H atoms is  $0.0855 \text{ \AA}$  – it is almost a planar molecule. From these differences it can be considered that the existence of the *o*-methyl group in compound (I) increases the steric restriction and leads to the non-planarity, and in compound (L), the formation of hydrogen bonds between the *o*-methoxyl group and N–H is helpful in increasing the degree of conjugation.

Commonly, benzoylthiourea prefers constructing a planar  $\pi$ - $\pi$  conjugated structure in order to promote molecular stability. However, in (I), the distances between the neighbouring parallel A rings are  $5.644(3)$  [at  $(x-1, y, z)$ ],  $5.646(2)$  [at  $(x+1, y, z)$ ] and  $5.454(3)$   $\text{\AA}$  [at  $(x, -y + \frac{1}{2}, z + \frac{1}{2})$ ],

respectively, which are a little longer than the common distance  $3.5$ – $4.5 \text{ \AA}$  for  $\pi$ - $\pi$  stacking. It could be also considered that the weak  $\pi$ - $\pi$  stacking results from the steric restriction of the *o*-methyl group in (I) and the absence of hydrogen-bond acceptor atoms.

From the above comparison it can be concluded that the existence of hydrogen-bond acceptor atoms, *e.g.* O and N atoms, is more helpful for promoting the stability of the thiourea ligands than the influence of  $\pi$ - $\pi$  stacking. Although compound (I) has two benzene rings, its structure shows a more non-planar character and weaker  $\pi$ - $\pi$  stacking than that of (L).

## Experimental

Compound (I) was synthesized under the conditions of phase transfer catalysis and characterized by elemental analysis, IR and  $^1\text{H}$  NMR. All chemicals used for the preparation of (I) were of reagent grade quality. Colourless single-crystals were obtained after one week by slow evaporation of a chloroform solution of (I). Yield 87%. M.p.  $389$ – $391 \text{ K}$ . Elemental analysis found (calculated): C  $65.45(66.67)$ , H  $4.98(5.19)$ , N  $10.76(10.37)\%$ . IR (KBr,  $\text{cm}^{-1}$ ):  $3268$  (N–H),  $1670$  (C=O),  $1586$ ,  $1527$  (C=C),  $1262$  (C=S),  $1154$ .  $^1\text{H}$  NMR (p.p.m.):  $\delta$   $2.26$  (s, 3H, CH<sub>3</sub>),  $7.20$ – $8.00$  (m, 9H, C<sub>6</sub>H<sub>5</sub>, C<sub>6</sub>H<sub>4</sub>),  $11.61$  (s, 1H, NH),  $12.29$  (s, 1H, NH).

### Crystal data

$\text{C}_{15}\text{H}_{14}\text{N}_2\text{OS}$	$Z = 4$
$M_r = 270.34$	$D_x = 1.305 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 5.6441(10) \text{ \AA}$	$\mu = 0.23 \text{ mm}^{-1}$
$b = 25.165(4) \text{ \AA}$	$T = 294(2) \text{ K}$
$c = 9.6851(17) \text{ \AA}$	Block, colourless
$\beta = 90.216(3)^\circ$	$0.36 \times 0.32 \times 0.26 \text{ mm}$
$V = 1375.6(4) \text{ \AA}^3$	

### Data collection

Bruker SMART CCD area-detector diffractometer	7656 measured reflections
$\varphi$ and $\omega$ scans	2792 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	1816 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.910$ , $T_{\max} = 0.942$	$R_{\text{int}} = 0.029$
	$\theta_{\max} = 26.4^\circ$

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0498P)^2 + 0.1902P]$
$R[F^2 > 2\sigma(F^2)] = 0.039$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.109$	$(\Delta/\sigma)_{\max} = 0.001$
$S = 1.03$	$\Delta\rho_{\max} = 0.18 \text{ e \AA}^{-3}$
2792 reflections	$\Delta\rho_{\min} = -0.17 \text{ e \AA}^{-3}$
181 parameters	
H atoms treated by a mixture of independent and constrained refinement	

**Table 1**  
Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
$\text{N2---H2}\cdots\text{S1}^i$	$0.86(2)$	$2.72(2)$	$3.5326(18)$	$157.9(17)$
$\text{N1---H1}\cdots\text{O1}$	$0.87(2)$	$1.87(2)$	$2.614(2)$	$142.4(19)$

Symmetry code: (i)  $-x + 1, -y + 1, -z + 1$ .

N-bound H atoms were refined freely. All other H atoms were positioned geometrically and refined as riding, with C–H = 0.93 and 0.96 Å, and with  $U_{\text{iso}}(\text{H})$  values of 1.2 (aromatic) or 1.5 (methyl) times  $U_{\text{eq}}(\text{C})$ .

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINTE* (Bruker, 1997); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a); molecular graphics: *SHELXTL* (Sheldrick, 1997b); software used to prepare material for publication: *SHELXTL*.

Financial support of this work by the Science-Technology Foundation for Middle-Aged and Young Scientists of Gansu Province (No. 3YS051-A25-011) and the Foundation of Lanzhou Jiaotong University is acknowledged.

## References

- Bombicz, P., Mutikainen, I., Krunk, M., Leskelä, T., Madarosz, J. & Niinistö, L. (2004). *Inorg. Chim. Acta*, **357**, 513–525.
- Bruker (1997). *SMART* and *SAINTE*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Foss, O., Husebye, S., Törnroos, K. W. & Fanwick, P. E. (2004). *Polyhedron*, **23**, 3021–3032.
- Koch, K. R. (2001). *Coord. Chem. Rev.* **216–217**, 473–488.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997a). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997b). *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Su, B. Q., Liu, G. L., Sheng, L., Wang, X. Q. & Xian, L. (2006). *Phosphorus Sulfur Silicon Relat. Elem.* **181**, 745–750.
- Su, B.-Q., Xian, L., Song, H.-B. & Sheng, L. (2004). *Acta Cryst.* **C60**, m661–m662.
- Su, B. Q., Xian, L., Zhang, B. & Song, H. B. (2005). *J. Chem. Res. (S)*, pp. 101–102.
- Zhang, Y. M., Xian, L., Wei, T. B. & Yu, K. B. (2003). *J. Chem. Res. (S)*, pp. 798–799.