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1-(2-Chlorophenyl)-3-(4-methylbenzoyl)thiourea

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Key indicators

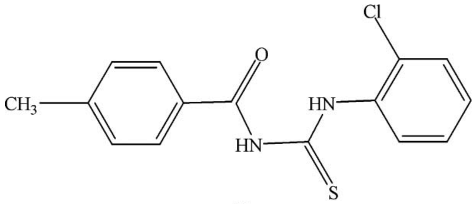
Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.002 Å
R factor = 0.042
wR factor = 0.103
Data-to-parameter ratio = 18.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The structure of the title compound, $C_{15}H_{13}ClN_2OS$, shows two independent molecules per asymmetric unit with notably different conformations. Intermolecular N—H···O and N—H···S hydrogen bonds link these molecules into infinite rows along [100].

Comment

Thiourea derivatives are extremely versatile building blocks for the manufacture of a wide variety of heterocyclic compounds. Thus, benzothiazoles have been prepared from arylthioureas in the presence of bromine (Patil & Chedekel, 1984), and condensations of thioureas with α-halocarbonyl compounds afford 2-aminothiazoles (Bailey *et al.*, 1996). Solid-phase Biginelli pyrimidine synthesis (Eynde & Watte, 2003) and syntheses of imidazoline derivatives (Fu *et al.*, 1999) have been carried out using resin-bound thioureas. 2-Methylaminothiazolines have been synthesized by cyclization of *N*-(2-hydroxyethyl)-*N*′-methylthioureas (Namgun *et al.*, 2001). A series of *N*-(*o*-fluorophenoxyacetyl)thiourea derivatives were converted into fluorophenoxyacetylimino-2*H*-1,2,4-thiadiazolo[2,3-*a*]pyrimidines possessing herbicidal activity by oxidative cyclization (Kea & Xueb, 2006). In addition, thioureas have been used in the synthesis of 1,3-thiazines (Jahn *et al.*, 1997), 1,3-diazines (Winckelmann & Larsen, 1986), 1,3-quinazolines (Gopalsamy & Yang, 2000) and 1,2,4-triazines (Yang & Kapalan, 2001). Thioureas are efficient guanylating agents (Maryanoff *et al.*, 1986). *N*,*N*-dialkyl-*N*-aroylthioureas are efficient ligands for the separation of platinum-group metals (Koch, 2001) and acylthioureas are well known for their superior pesticidal, fungicidal, antiviral and plant-growth regulating activities (Upadlgaya & Srivastava, 1982; Wegner *et al.*, 1986). They are also important intermediates in organic synthesis (Sarkis & Faisal, 1985). Symmetrical and unsymmetrical 1,3-dialkyl- or diarylthioureas have shown antifungal activity against the plant pathogens *Pyricularia oryzae* and *Drechslera oryzae* (Krishnamurthy *et al.*, 1999). 1-Aroyl-3-arylthioureas are an important class of thioureas which have recently been used in the synthesis of 1-aroyl-3-aryl-4-substituted imidazole-2-thiones (Zeng *et al.*, 2003; Wang *et al.*, 2005). We became interested in the synthesis of these thioureas as



(I)

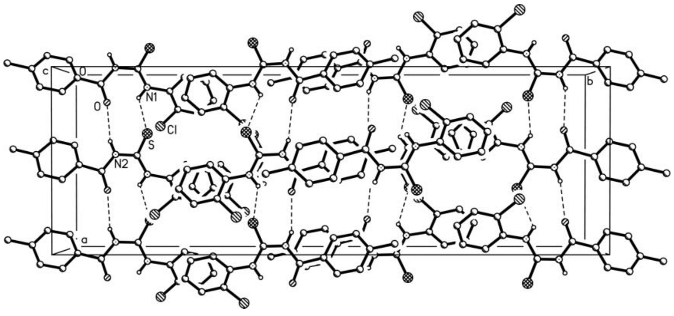


Figure 2
The crystal packing of (I), viewed along [001], with intermolecular hydrogen bonds indicated as dashed lines. H atoms not involved in hydrogen bonding have been omitted.

intermediates in the synthesis of novel heterocycles and for the systematic study of their bioactivity and complexation behaviour and we present here the crystal structure of the title compound, (I).

There are two independent molecules per asymmetric unit of (I), with essentially equal bond lengths and angles, showing the C═S and C═O double bonds and the shortened C—N bond lengths typical for thiourea systems (Table 1, Fig. 1). The conformation of the molecules with respect to the thiocarbonyl and carbonyl groups is slightly twisted, as reflected by the torsion angles C17—N12—C18—O11 = −7.2 (3)° and C18—N12—C17—N11 = 13.3 (3)° for molecule 1, and C27—N22—C28—O21 = −4.4 (3)° and C28—N22—C27—N21 = 19.1 (3)° for molecule 2.

The two molecules differ strongly in the orientation of their aromatic rings. The dihedral angle formed by the chlorophenyl and *p*-tolyl ring planes is 64.09 (4)° for molecule 1 but only 7.21 (8)° for molecule 2. The associated torsion angles are N12—C18—C19—C110 = 160.7 (2)° and N22—C28—C29—C210 = −151.1 (2)°. A related compound is 1-(2-chlorobenzoyl)-3-*p*-tolylthiourea (Arslan *et al.*, 2004). In this molecule, the chlorophenyl and tolyl groups are interchanged compared with (I) and the dihedral angle between the two aromatic ring planes is 48.17 (7)°.

In the crystal structure of (I), the typical thiourea intramolecular N—H⋯O hydrogen bond is noted (Table 2). The crystal packing shows intermolecular N—H⋯S and N—H⋯O hydrogen bonds (Table 2), which link alternating molecules 1 and 2 (Fig. 2) into infinite 'head-to-tail' rows along [100].

Experimental

A solution of 4-methylbenzoyl chloride (1.75 g, 10 mmol) in acetone (50 ml) was added dropwise to a suspension of potassium thiocyanate (0.97 g, 10 mmol) in acetone (30 ml) and the reaction mixture was refluxed for 30 min. After cooling to room temperature, a solution of 2-chloroaniline (1.28 g, 10 mmol) in acetone (10 ml) was added and the resulting mixture was refluxed for 2.5 h. The reaction mixture was poured into cold water, whereupon the title thiourea precipitated as a solid. Compound (I) was recrystallized from ethanol as colourless crystals (2.49 g, 8.2 mmol, 82%; m.p. 429 K). Spectroscopic analysis:

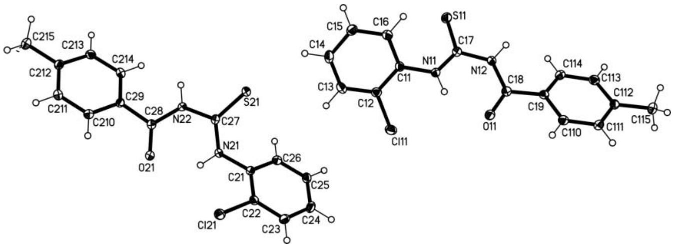


Figure 1
The structure of the asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

IR (KBr, ν, cm^{-1}): 3351 (free NH), 3200 (assoc. NH), 1667 (CO), 1610 (aromatic), 1529 (thioureido I) 1325 II, 1160 III, 744, 762. Analysis, calculated for $C_{15}H_{13}ClN_2OS$: C 59.11, H 4.30, N 9.19, S 10.52%; found: C 59.32, H 4.29, N 9.15, S 10.56%.

Crystal data

$C_{15}H_{13}ClN_2OS$
$M_r = 304.78$
Monoclinic, $P2_1/c$
$a = 10.8968\ (6)$ Å
$b = 32.2055\ (19)$ Å
$c = 7.8404\ (5)$ Å
$\beta = 90.819\ (1)°$
$V = 2751.2\ (3)$ Å^3

$Z = 8$
$D_x = 1.472$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.43$ mm^{-1}
$T = 120\ (2)$ K
Plate, colourless
0.48 × 0.41 × 0.09 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
$T_{\min} = 0.822$, $T_{\max} = 0.963$

27617 measured reflections
6699 independent reflections
5819 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.033$
$\theta_{\max} = 28.1°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.103$
$S = 1.08$
6699 reflections
361 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0492P)^2 + 1.2928P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.55$ e Å^{-3}
$\Delta\rho_{\min} = -0.26$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S11—C17	1.6582 (18)	S21—C27	1.6627 (17)
O11—C18	1.225 (2)	O21—C28	1.224 (2)
N11—C17	1.332 (2)	N21—C27	1.333 (2)
N11—C11	1.422 (2)	N21—C21	1.420 (2)
N12—C18	1.377 (2)	N22—C28	1.380 (2)
N12—C17	1.400 (2)	N22—C27	1.398 (2)
C17—N11—C11	124.76 (14)	C27—N21—C21	124.63 (14)
C18—N12—C17	128.84 (15)	C28—N22—C27	128.15 (15)

Table 2
Hydrogen-bond geometry (Å, °).

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
N11—H11*H*···O11	0.88	1.97	2.6695 (19)	136
N21—H21*H*···O21	0.88	2.01	2.6864 (19)	132
N11—H11*H*···S21^{i}	0.88	2.93	3.5545 (16)	130
N12—H12*A*···O21^{ii}	0.88	2.57	3.375 (2)	153
N21—H21*H*···S11^{iii}	0.88	2.92	3.6039 (16)	135
N22—H22*A*···O11^{iv}	0.88	2.46	3.3067 (19)	163

Symmetry codes: (i) $x, -y+\frac{1}{2}, z+\frac{1}{2}$; (ii) $x-1, -y+\frac{1}{2}, z+\frac{1}{2}$; (iii) $x+1, -y+\frac{1}{2}, z-\frac{1}{2}$; (iv) $x, -y+\frac{1}{2}, z-\frac{1}{2}$.

H atoms were located in a difference synthesis and were refined in idealized positions riding on their parent C or N atoms, with C—H = 0.95–0.98 Å and N—H = 0.88 Å, and with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C,N) or 1.5$U_{\rm eq}$(methyl C).

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2002); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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