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1-(2-Chlorophenyl)-3-pivaloylthiourea

Noreen Shoukat,[a] M. Khawar Rauf,[a] Michael Bolte[b] and Amin Badshah[a]*

[a]Department of Chemistry, Quaid-i-Azam University, Islamabad 45320, Pakistan, and [b]Institut für Anorganische Chemie, J. W. Goethe-Universität Frankfurt, Max-von-Laue-Strasse 7, 60438 Frankfurt/Main, Germany

Correspondence e-mail: aminbadshah@yahoo.com

Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.003 Å
R factor = 0.039
wR factor = 0.105
Data-to-parameter ratio = 15.9

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

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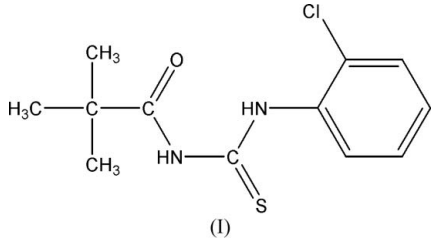
The title molecule, $C_{12}H_{15}ClN_2OS$, shows the typical geometric parameters of a substituted thiourea derivative. There is an intramolecular N—H···O hydrogen bond and the crystal packing is characterized by intermolecular N—H···S hydrogen bonds.

Comment

N,*N*′-Disubstituted thiourea derivatives are very useful building blocks for the synthesis of a wide range of aliphatic macromolecular and heterocyclic compounds. Thus, benzothiazoles have been prepared from arylthioureas in the presence of bromine (Patil & Chedekel, 1984), and condensation of thiourea with halocarbonyl compounds forms 2-aminothiazoles (Baily *et al.*, 1996). 2-Methylaminothiazolines have been synthesized by cyclization of *N*-(2-hydroxyethyl)-*N*′-methylthioureas (Namgun *et al.*, 2001). Thioureas are efficient guanylating agents (Maryanoff *et al.*, 1986). *N*,*N*-dialkyl-*N*-aroylthioureas have been efficiently used for the extraction of Ni, Pd and Pt metals (Koch, 2001). Aliphatic and acylthioureas are well known for their fungicidal, antiviral, pesticidal and plant-growth regulating activities (Upadlgaya & Srivastava, 1982; Wegner *et al.*, 1986). Symmetrical and unsymmetrical thioureas have shown antifungal activity against the plant pathogens *Pyricularia oryzae* and *Drechslera oryzae* (Krishnamurthy *et al.*, 1999). We became interested in the synthesis of these thioureas as intermediates in the synthesis of novel guanidines and heterocyclic compounds for the systematic study of bioactivity and complexation behaviour and we present here the crystal structure of the title compound, (I).



(I)

The molecular structure of (I) is shown in Fig. 1. The typical thiourea C=S and C=O double bonds as well as shortened C—N bond lengths are listed in Table 1. The plane containing the thiourea and carbonyl groups (N1/C2/S1/N2/O1/C1) forms a dihedral angle of 75.24 (5)° with the chlorophenyl ring. The expected typical thiourea intramolecular N—H···O hydrogen bond is present (Table 2). Other geometric parameters are comparable to those of previous structures (Khawar Rauf *et*

al., 2006*a*,*b*). In the crystal structure, intermolecular N—H···S hydrogen bonds (Table 2, Fig. 2), link the molecules into centrosymmetric dimers. Cl atoms are not involved in any type of hydrogen bonds.

Experimental

Freshly prepared pivaloyl chloride (1.20 g, 10 mmol) was added to a suspension of KSCN ((1.00 g, 10 mmol) in acetone (30 ml). The reaction mixture was stirred for 15 min. Neat 2-chloroaniline (1.29 g, 10 mmol) was then added and the resulting mixture was stirred for 1 h. The reaction mixture was then poured into acidified water (400 ml) and stirred well. The solid product was separated, washed with deionized water and purified by recrystallization from methanol/dichloromethane (1:1 *v*/*v*) to give fine crystals of (I) with an overall yield of 80%. Full spectroscopic and physical characterization will be reported elsewhere.

Crystal data

$C_{12}H_{15}ClN_2OS$
M_r = 270.77
Monoclinic, $P2_1/c$
a = 10.7622 (10) Å
b = 12.0925 (15) Å
c = 10.9239 (11) Å
β = 101.840 (8)°
V = 1391.4 (3) Å^3
Z = 4
D_x = 1.293 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.41 mm^{-1}
T = 173 (2) K
Block, colourless
0.37 × 0.33 × 0.31 mm

Data collection

Stoe IPDS-II two-circle diffractometer
ω scans
Absorption correction: multi-scan (*MULABS*; Spek, 2003; Blessing, 1995)
T_{min} = 0.863, T_{max} = 0.883
8633 measured reflections
2598 independent reflections
2085 reflections with $I > 2\sigma(I)$
R_{int} = 0.054
θ_{max} = 25.6°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.105
S = 1.05
2598 reflections
163 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0575P)^2 + 0.1984P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.019 (2)

Table 1
Selected bond lengths (Å).

S1—C2	1.676 (2)	N1—C2	1.388 (2)
C1—O1	1.228 (2)	C2—N2	1.337 (3)
C1—N1	1.395 (2)	N2—C21	1.432 (3)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···S1^{i}	0.97 (3)	2.53 (3)	3.4876 (18)	172.3 (19)
N2—H2···O1	0.86 (3)	1.88 (3)	2.616 (2)	142 (3)

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

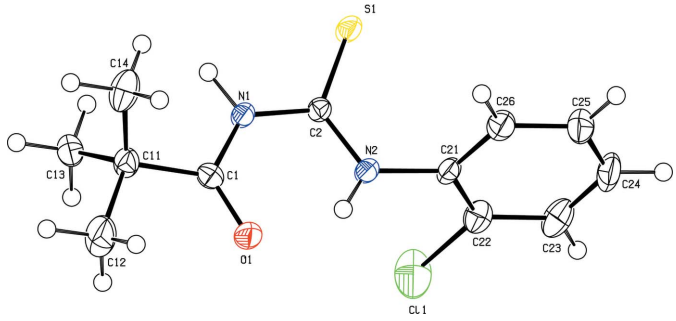


Figure 1
Molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level.

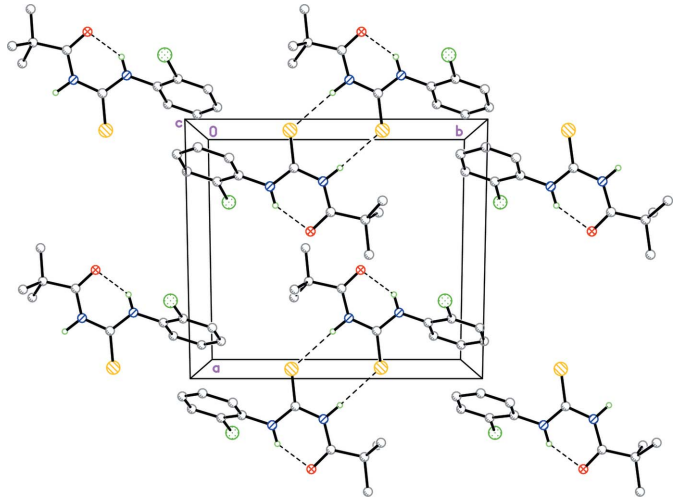


Figure 2
Part of the crystal structure of (I). H atoms not involved in hydrogen bonds have been omitted for clarity. Hydrogen bonds are shown as dashed lines.

H atoms were located in a difference map, but those bonded to C were placed in calculated positions with C—H = 0.95 or 0.98 Å for $C_{aromatic}$ and C_{methyl}, respectively, and included in a riding-model approximation with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(C_{methyl})$. H atoms bonded to N were refined freely.

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003) and *XP* in *SHELXTL-Plus* (Sheldrick, 1991); software used to prepare material for publication: *PLATON* and *SHELXL97*.

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