

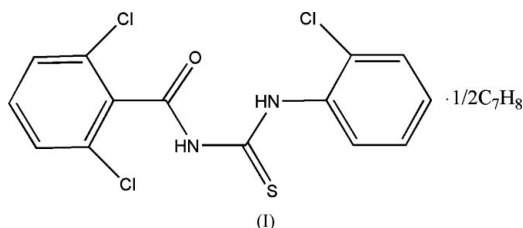
1-(2-Chlorophenyl)-3-(2,6-dichlorobenzoyl)-
thiourea toluene hemisolvateM. Khawar Rauf,^{a*} Amin
Badshah,^a Michael Bolte^b and
Imtiaz-ud-Din^a^aDepartment of Chemistry, Quaid-i-Azam
University, Islamabad 45320, Pakistan, and
^bInstitut für Anorganische Chemie, J. W.
Goethe-Universität Frankfurt, Max-von-Laue-
Strasse 7, 60438 Frankfurt/Main, GermanyCorrespondence e-mail:
khawar_rauf@hotmail.com

Key indicators

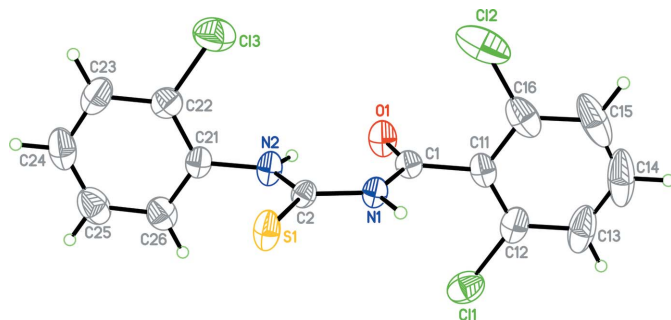
Single-crystal X-ray study
 $T = 173$ K
Mean $\sigma(\text{C}-\text{C}) = 0.005$ Å
Disorder in solvent or counterion
 R factor = 0.048
 wR factor = 0.123
Data-to-parameter ratio = 14.6For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.In the title compound, $\text{C}_{14}\text{H}_9\text{Cl}_3\text{N}_2\text{OS}\cdot 0.5\text{C}_7\text{H}_8$, the toluene
molecule is disordered over a centre of inversion. The dihedral
angle formed by the two benzene ring planes is $2.26(8)^\circ$.Received 21 July 2006
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Comment

1,3-Disubstituted thiourea derivatives are extremely versatile building blocks for the synthesis of a wide range of aliphatic macromolecular and heterocyclic compounds. Benzothiazoles have been prepared from arylthioureas in the presence of bromine (Patil & Chedekel, 1984), and condensation of thiourea with α -halocarbonyl compounds results in the formation of 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 guanylation agents (Maryanoff *et al.*, 1986). *N,N*-Dialkyl-*N*-aroylthioureas have been efficiently used for the extraction of nickel, palladium and platinum 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).



Compound (I) (Fig. 1) shows the typical thiourea $\text{C}=\text{O}$ and $\text{C}=\text{S}$ double bonds, as well as shortened $\text{C}-\text{N}$ bond lengths (Table 1). The thiocarbonyl and carbonyl groups are almost coplanar, as reflected by the torsion angles $\text{C}2-\text{N}1-\text{C}1-\text{O}1$ [$-1.4(4)^\circ$] and $\text{N}2-\text{C}2-\text{N}1-\text{C}1$ [$4.3(4)^\circ$]. The dichlorophenyl and chlorophenyl rings are twisted at right angles through the $\text{C}11-\text{C}1$ and $\text{C}21-\text{N}2$ single bonds, respectively, with the plane constituted by the thiocarbonyl and carbonyl groups. This is associated with the expected typical thiourea intramolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bond (Table 2). The


Figure 1

The molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level. The disordered toluene molecule has been omitted.

dihedral angle formed by the two benzene ring planes is 2.26 (8). Other geometric parameters present no unusual features (Khawar Rauf et al., 2006a,b).

Experimental

Freshly prepared 2,6-dichlorobenzoyl chloride (2.1 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. Afterwards neat 2-chloroaniline (1.27 g, 10 mmol) was added and the resulting mixture was stirred for 1 h. The reaction mixture was then poured into acidified water and stirred well. The solid product was separated and washed with deionized water and purified by recrystallization from methanol/dichloromethane (1:1) to give fine crystals of the title compound, (I), in an overall yield of 85%. Full spectroscopic and physical characterization will be reported elsewhere.

Crystal data

$C_{14}H_9Cl_3N_2OS \cdot 0.5C_7H_8$	$V = 941.1 (2) \text{ \AA}^3$
$M_r = 405.71$	$Z = 2$
Triclinic, $P\bar{1}$	$D_x = 1.432 \text{ Mg m}^{-3}$
$a = 9.9672 (16) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 10.6954 (16) \text{ \AA}$	$\mu = 0.61 \text{ mm}^{-1}$
$c = 10.7104 (16) \text{ \AA}$	$T = 173 (2) \text{ K}$
$\alpha = 64.032 (11)^\circ$	Block, colourless
$\beta = 67.438 (11)^\circ$	$0.47 \times 0.45 \times 0.39 \text{ mm}$
$\gamma = 86.053 (12)^\circ$	

Data collection

Stoe IPDS-II two-circle diffractometer	6951 measured reflections
ω scans	3438 independent reflections
Absorption correction: multi-scan (MULABS; Spek, 2003; Blessing, 1995)	2938 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.764$, $T_{\max} = 0.798$	$R_{\text{int}} = 0.028$
	$\theta_{\text{max}} = 25.5^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0517P)^2 + 1.0113P]$
$R[F^2 > 2\sigma(F^2)] = 0.048$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.123$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.03$	$\Delta\rho_{\text{max}} = 0.64 \text{ e \AA}^{-3}$
3438 reflections	$\Delta\rho_{\text{min}} = -0.61 \text{ e \AA}^{-3}$
236 parameters	Extinction correction: SHELXL97
H-atom parameters constrained	Extinction coefficient: 0.022 (3)

Table 1

Selected bond lengths (\AA).

O1—C1	1.223 (3)	N2—C21	1.430 (3)
C1—N1	1.379 (3)	Cl1—C12	1.749 (3)
N1—C2	1.399 (3)	Cl2—C16	1.744 (4)
C2—N2	1.334 (3)	Cl3—C22	1.727 (3)
C2—S1	1.676 (2)		

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1—H1 \cdots S1 ⁱ	0.88	2.48	3.340 (2)	167
N2—H2 \cdots O1	0.88	1.97	2.665 (3)	135

Symmetry code: (i) $-x + 2, -y + 1, -z + 2$.

The toluene molecule is disordered over a centre of inversion. It was refined with restraints for the C—C bonds of 1.4 (1) \AA . Furthermore, the C atoms of the toluene molecule were restrained to lie in a common plane. H atoms, except those of the disordered toluene molecule, were found in a difference map. All H atoms were positioned geometrically and allowed to ride on their parent atoms at distances of 0.88 and 0.95 \AA for NH and CH, respectively, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N})$ or $1.5U_{\text{eq}}(\text{methyl C})$.

Data collection: X-Area (Stoe & Cie, 2001); cell refinement: X-Area; data reduction: X-Area; program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: XP in SHELXTL-Plus (Sheldrick, 1991); software used to prepare material for publication: SHELXL97.

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