

1-(2,4-Dichlorobenzoyl)-3-(3,4-dichlorophenyl)thiourea

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Key indicators

Single-crystal X-ray study
 $T = 173$ K
Mean $\sigma(\text{C}-\text{C}) = 0.002$ Å
 R factor = 0.028
 wR factor = 0.071
Data-to-parameter ratio = 14.3For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

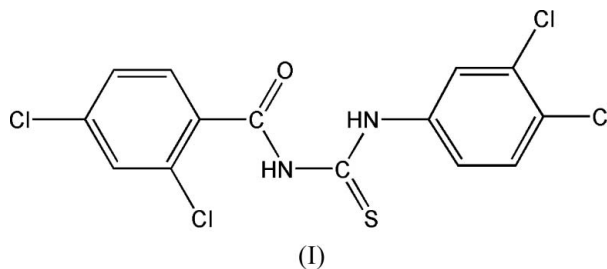
The title compound, $\text{C}_{14}\text{H}_8\text{Cl}_4\text{N}_2\text{OS}$, shows the typical geometric parameters of substituted thiourea derivatives. The dihedral angle formed by the two benzene ring planes is $38.39(7)^\circ$. The crystal packing is characterized by $\text{N}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{S}$ hydrogen bonds.

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Comment

N -substituted and 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), while the condensation of thiourea with α -halocarbonyl compounds forms 2-aminothiazoles (Baily *et al.*, 1996). 2-Methylaminothiazolines have been synthesized by the 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 (Upadgaya & 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 with the dichlorophenyl ring, as reflected by the torsion angles $\text{C}2-\text{N}1-\text{C}1-\text{O}1$ [$-4.0(3)^\circ$] and $\text{N}2-\text{C}2-\text{N}1-\text{C}1$ [$6.1(2)^\circ$]. This is associated with the expected typical

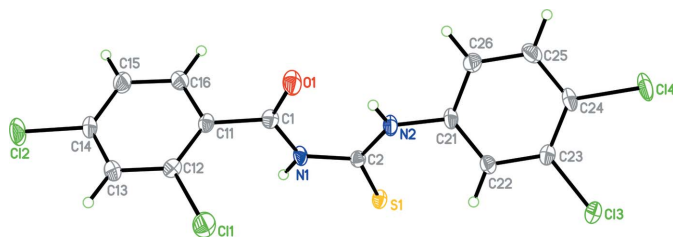


Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

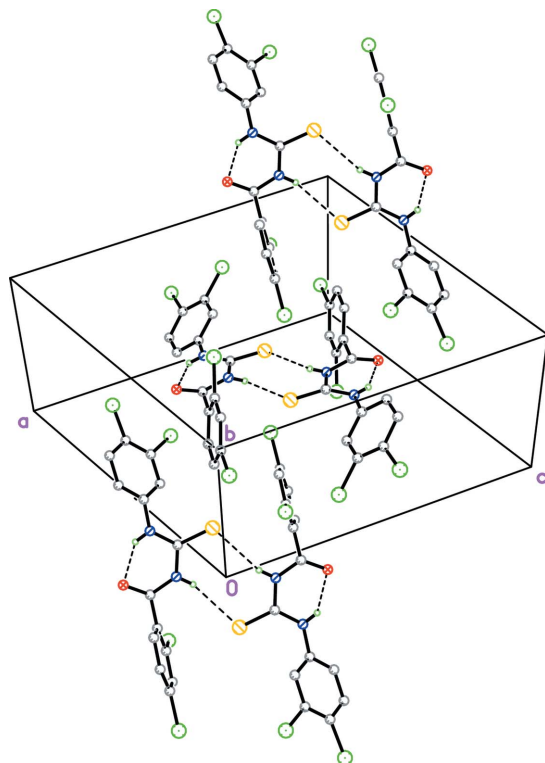


Figure 2
A packing diagram of (I). Hydrogen bonds are shown as dashed lines.

thiourea intramolecular N—H...O hydrogen bond (Table 2). The dihedral angle formed by the two benzene ring planes is 38.39 (7)°. Other geometric parameters present no unusual features (Khawar Rauf, Badshah & Bolte, 2006; Khawar Rauf, Badshah, Bolte & Imtiaz-ud-Din, 2006).

Intermolecular N—H...S hydrogen bonds (Table 2, Fig. 2) link the molecules into dimers. The Cl atoms are not involved in any type of hydrogen bonds.

Experimental

Freshly prepared 2,4-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. Neat 3,4-dichloroaniline (1.63 g, 10 mmol) was then added and the resulting mixture was stirred for 1 h. The reaction mixture was then poured into acidified water (300 ml) and stirred well. The solid product was separated off, washed with deionized water and purified by recrystallization from methanol-dichloromethane (1:1 v/v) to give fine crystals of (I), in an

overall yield of 80%. Full spectroscopic and physical characterization will be reported elsewhere.

Crystal data

$C_{14}H_8Cl_4N_2OS$	$Z = 4$
$M_r = 394.08$	$D_x = 1.628 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 12.7287 (11) \text{ \AA}$	$\mu = 0.87 \text{ mm}^{-1}$
$b = 9.2935 (6) \text{ \AA}$	$T = 173 (2) \text{ K}$
$c = 14.6300 (15) \text{ \AA}$	Block, colourless
$\beta = 111.697 (7)^\circ$	$0.43 \times 0.30 \times 0.28 \text{ mm}$
$V = 1608.0 (2) \text{ \AA}^3$	

Data collection

Stoe IPDSII two-circle diffractometer	10362 measured reflections
ω scans	2984 independent reflections
Absorption correction: multi-scan (MULABS; Spek, 2003; Blessing, 1995)	2703 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.707$, $T_{\max} = 0.794$	$R_{\text{int}} = 0.038$
	$\theta_{\max} = 25.6^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0379P)^2 + 0.8376P]$
$R[F^2 > 2\sigma(F^2)] = 0.028$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.071$	$(\Delta/\sigma)_{\max} = 0.001$
$S = 1.04$	$\Delta\rho_{\max} = 0.32 \text{ e \AA}^{-3}$
2984 reflections	$\Delta\rho_{\min} = -0.37 \text{ e \AA}^{-3}$
208 parameters	Extinction correction: SHELXL97 (Sheldrick, 1997)
H atoms treated by a mixture of independent and constrained refinement	Extinction coefficient: 0.0082 (8)

Table 1

Selected geometric parameters (\AA , $^\circ$).

S1—C2	1.6815 (16)	N1—C2	1.398 (2)
C1—O1	1.225 (2)	C2—N2	1.345 (2)
C1—N1	1.379 (2)		
C1—N1—C2	128.35 (14)	N2—C2—N1	114.97 (14)

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...S1 ⁱ	0.80 (2)	2.72 (2)	3.4910 (14)	162 (2)
N2—H2...O1	0.79 (2)	1.99 (2)	2.6681 (19)	143 (2)

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

H atoms were located in a difference map, but those bonded to C atoms were refined with fixed individual displacement parameters [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$] using a riding model, with C—H = 0.95 \AA . 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: XP in SHELXTL-Plus (Sheldrick, 1991); software used to prepare material for publication: SHELXL97.

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