

1-(2,6-Dichlorobenzoyl)-3-[(3-trifluoromethyl)-phenyl]thiourea

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Key indicators

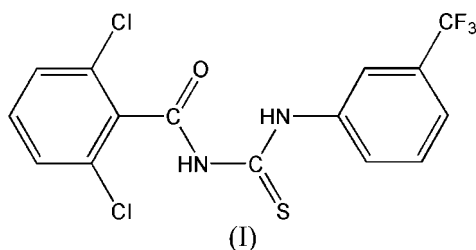
Single-crystal X-ray study
 $T = 173$ K
Mean $\sigma(\text{C}-\text{C}) = 0.008$ Å
 R factor = 0.067
 wR factor = 0.155
Data-to-parameter ratio = 13.8For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title structure, $\text{C}_{15}\text{H}_9\text{Cl}_2\text{F}_3\text{N}_2\text{OS}$, there are two independent molecules in the asymmetric unit, both of which show typical geometric parameters for substituted thiourea derivatives. The dihedral angles formed by the two benzene ring planes are $52.7(2)$ and $57.6(2)^\circ$ for the two molecules. The crystal structure is stabilized by $\text{N}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{S}$ hydrogen bonds.

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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 the condensation of thiourea with α -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 guanylation agents (Maryanoff *et al.*, 1986). N,N -dialkyl- N -arylothioureas 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 are interested in the synthesis of these thioureas as intermediates in the preparation 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).



The asymmetric unit of (I) is shown in Fig. 1 (each independent molecule has a similar atom-labelling scheme, except the labels for one molecule have the suffix *A*) and both independent molecules show the typical thiourea $\text{C}=\text{O}$ and $\text{C}=\text{S}$ double bonds, as well as shortened $\text{C}-\text{N}$ bonds (Table 1). The thiocarbonyl and carbonyl groups are almost coplanar, as reflected by the torsion angles of $-1.5(8)^\circ$ for

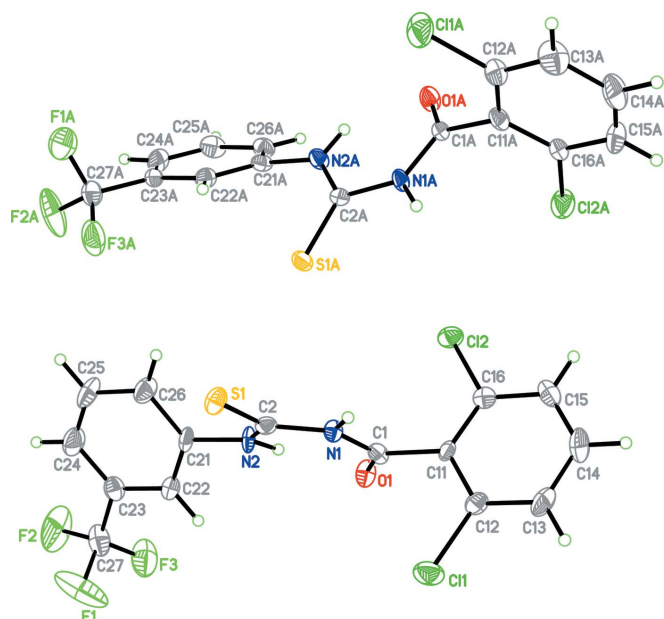


Figure 1
The asymmetric unit of (I). Displacement ellipsoids are drawn at the 50% probability level.

C2—N1—C1—O1, -6.0 (7) $^\circ$ for N2—C2—N1—C1, -10.1 (9) $^\circ$ for C2A—N1A—C1A—O1A and 0.4 (8) $^\circ$ for N2A—C2A—N1A—C1A. This is associated with the expected intramolecular N—H \cdots O hydrogen bonds (Table 2).

The dihedral angles formed by the two benzene ring planes are 52.7 (2) and 57.6 (2) $^\circ$, respectively, for the molecules with and without the suffix *A* in the atom labels. Other geometric parameters present no unusual features compared with previously determined related structures (Khawar Rauf *et al.*, 2006*a,b*).

The crystal structure of (I) is stabilized by intermolecular N—H \cdots S and N—H \cdots O hydrogen bonds (Table 2).

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) and the reaction mixture was stirred for 15 min. Neat 3-(trifluoromethyl)aniline (1.61 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; pH 4.0) 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 the title compound, (I), in an overall yield of 80%. Full spectroscopic and physical characterization will be reported elsewhere.

Crystal data

C₁₅H₉Cl₂F₃N₂OS
M_r = 393.20
 Monoclinic, *P*2₁/*c*
a = 16.1754 (12) Å
b = 13.6250 (13) Å
c = 16.2839 (12) Å
 β = 114.358 (5) $^\circ$
V = 3269.4 (5) Å³

Z = 8
D_x = 1.598 Mg m⁻³
 Mo *K* α radiation
 μ = 0.56 mm⁻¹
T = 173 (2) K
 Plate, colourless
 0.23 × 0.20 × 0.08 mm

Data collection

Stoe IPDSII two-circle diffractometer
 ω scans
 Absorption correction: multi-scan (MULABS; Spek, 2003; Blessing, 1995)
T_{min} = 0.882, *T_{max}* = 0.957

15119 measured reflections
 5993 independent reflections
 4655 reflections with *I* > 2 σ (*I*)
R_{int} = 0.062
 θ_{\max} = 25.4 $^\circ$

Refinement

Refinement on *F*²
R [*F*² > 2 σ (*F*²)] = 0.067
wR(*F*²) = 0.155
S = 1.19
 5993 reflections
 434 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0048P)^2 + 19.2275P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.54 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.39 \text{ e \AA}^{-3}$
 Extinction correction: SHELXL97 (Sheldrick, 1997)
 Extinction coefficient: 0.0029 (3)

Table 1

Selected bond lengths (Å).

C1—O1	1.227 (6)	C1A—O1A	1.230 (6)
C1—N1	1.363 (7)	C1A—N1A	1.374 (6)
C1—C11	1.518 (7)	C1A—C11A	1.515 (7)
N1—C2	1.416 (6)	C2A—N2A	1.357 (6)
C2—N2	1.334 (7)	C2A—N1A	1.412 (6)
C2—S1	1.675 (5)	C2A—S1A	1.666 (5)
N2—C21	1.443 (6)	N2A—C21A	1.428 (6)

Table 2

Hydrogen-bond geometry (Å, $^\circ$).

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1 \cdots S1A ⁱ	0.88	2.60	3.434 (4)	159
N2—H2 \cdots O1	0.88	1.96	2.670 (5)	137
N2—H2 \cdots O1A ⁱⁱ	0.88	2.38	3.115 (6)	141
N1A—H1A \cdots S1 ⁱ	0.88	2.43	3.305 (4)	172
N2A—H2A \cdots O1A	0.88	1.99	2.709 (6)	138
N2A—H2A \cdots O1 ⁱⁱⁱ	0.88	2.38	3.070 (6)	136

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

H atoms were located in a difference map, but were then refined with fixed individual displacement parameters [*U*_{iso}(H)] = 1.2*U*_{eq}(C,N)] using the riding-model approximation, with N—H = 0.88 Å and C—H = 0.95 Å.

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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