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1-(2,6-Dichlorobenzoyl)-3-(3,5-dichlorophenyl)thiourea

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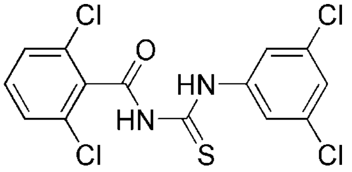
Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.002 Å; R factor = 0.032; wR factor = 0.087; data-to-parameter ratio = 17.9.

The crystal structure of the title compound, $C_{14}H_8Cl_4N_2OS$, is composed of discrete molecules with bond lengths and angles quite typical for thiourea compounds of this class. The plane containing the central SONNCC atom set subtends a dihedral angle of 31.47 (3)° with the benzene ring. An intramolecular N—H⋯O hydrogen bond stabilizes the molecular conformation and the molecules form centrosymmetric dimers *via* intermolecular N—H⋯S hydrogen bonds.

Related literature

For general background, see: Upadlgaya & Srivastava (1982); Wegner *et al.* (1986); Krishnamurthy *et al.* (1999). For related structures, see: Khawar Rauf *et al.* (2006*a*, 2007). For a description of the Cambridge Structural Database, see: Allen (2002). For bond lengths and angles in *N*,*N*′-disubstituted thiourea compounds, see: Arslan *et al.* (2004); Khawar Rauf *et al.* (2006*b*); Yamin & Yusof, (2003).



Experimental

Crystal data

$C_{14}H_8Cl_4N_2OS$
M_r = 394.08
Monoclinic, $P2_1/c$
a = 14.7737 (13) Å
b = 10.3744 (6) Å
c = 10.6935 (11) Å
β = 97.250 (7)°
V = 1625.9 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.86 mm^{-1}
T = 173 (2) K
0.42 × 0.38 × 0.21 mm

Data collection

Stoe IPDSII two-circle diffractometer
Absorption correction: multi-scan (*MULABS*; Spek, 2003; Blessing, 1995)
$T_{\min}$ = 0.715, $T_{\max}$ = 0.841
12823 measured reflections
3724 independent reflections
3306 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.046

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.087
S = 1.05
3724 reflections
208 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$ = 0.44 e Å^{-3}
$\Delta\rho_{\min}$ = −0.36 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N2—H2⋯O1	0.91 (2)	1.89 (2)	2.6581 (17)	141 (2)
N1—H1⋯S1$^{\rm i}$	0.82 (2)	2.57 (2)	3.3653 (14)	163 (2)

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

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FL2225).

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supplementary materials

Acta Cryst. (2009). E**65**, o177 [**doi:10.1107/S1600536808042736**]

1-(2,6-Dichlorobenzoyl)-3-(3,5-dichlorophenyl)thiourea

M. Khawar Rauf, **M. Bolte** and **A. Badshah**

Comment

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). The background to this study has been set out in our previous work on the structural and biological chemistry of chloro substituted *N*,*N'*-disubstituted thioureas (Khawar Rauf *et al.*, 2006*a*; 2007).The biological studies of these thiourea derivatives are under investigation. Herein, as a continuation of these studies, the structure of the title compound (I) is described (Fig. 1). Bond lengths and angles, can be regarded as typical for *N*,*N'*-disubstituted thiourea compounds as found in the Cambridge Structural Database v5.28 (Allen, 2002; Khawar Rauf *et al.*, 2006*b*; Arslan *et al.*, 2004; Yamin & Yusof, 2003).The molecule exists in the thione form with typical thiourea C—S and C—O bonds, as well as shortened C—N bond lengths. The thiocarbonyl and carbonyl groups are almost coplanar. The molecule features an intramolecular N—H···O hydrogen bond and in the crystal structure, molecules associate *via* N—H···S intermolecular hydrogen bonds to form centrosymmetric dimers (Table 1; Fig 2).In addition to the intramolecular hydrogen bond, O1 is involved in a short O···Cl contact [O1···Cl2^{i}: 3.0936 (14) Å, symmetry operator i: 1 - *x*, 1 - *y*, 1 - *z*].

Experimental

Freshly prepared 2,6-dichlorobenzoyl isothiocyanate (2.32 g, 10 mmol) was stirred in acetone (40 ml) for 20 minutes. Neat 3,5-dichloroaniline (1.62 g, 10 mmol) was then added and the resulting mixture was stirred for 1 h. The reaction mixture was then poured into acidified (pH 4) water and stirred well. The solid product was separated and washed with deionized water and purified by recrystallization from methanol/ 1,1-dichloromethane (1:10 *v/v*) to give fine crystals of (I), with an overall yield of 80%.

Refinement

Hydrogen atoms bonded to C were included in calculated positions and refined as riding on their parent C atom with C—H = 0.95 Å U_{iso}(H) = 1.2U_{eq}(C). The H atoms bonded to N were freely refined.

Figures

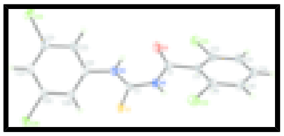

Fig. 1. Molecular structure of (I) showing atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

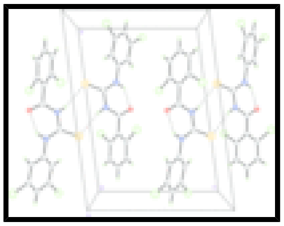

Fig. 2. Partial packing diagram of (I) with view onto the *ac* plane. Hydrogen bonds shown as dashed lines.

1-(2,6-Dichlorobenzoyl)-3-(3,5-dichlorophenyl)thiourea

Crystal data

$C_{14}H_8Cl_4N_2OS$

$M_r = 394.08$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 14.7737$ (13) Å

$b = 10.3744$ (6) Å

$c = 10.6935$ (11) Å

$\beta = 97.250$ (7)°

$V = 1625.9$ (2) Å^3

$Z = 4$

$F_{000} = 792$

$D_x = 1.610$ Mg m^{-3}

Mo *K*α radiation
$\lambda = 0.71073$ Å

Cell parameters from 13230 reflections

$\theta = 3.8$–27.8°

$\mu = 0.86$ mm^{-1}

$T = 173$ (2) K

Plate, colourless

0.42 × 0.38 × 0.21 mm

Data collection

Stoe IPDSII two-circle diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 173(2)$ K

ω scans

Absorption correction: multi-scan (MULABS; Spek, 2003; Blessing, 1995)

$T_{min} = 0.715$, $T_{max} = 0.841$

12823 measured reflections

3724 independent reflections

3306 reflections with $I > 2\sigma(I)$

$R_{int} = 0.046$

$\theta_{max} = 27.5$°

$\theta_{min} = 3.7$°

$h = -19 \rightarrow 19$

$k = -13 \rightarrow 13$

$l = -10 \rightarrow 13$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.032$

$wR(F^2) = 0.087$

$S = 1.05$

3724 reflections

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0525P)^2 + 0.486P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.44$ e Å^{-3}

$\Delta\rho_{min} = -0.36$ e Å^{-3}

208 parameters	Extinction correction: SHELXL97 (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0246 (15)
Secondary atom site location: difference Fourier map	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.35875 (3)	0.16745 (4)	0.09234 (4)	0.02939 (13)
Cl2	0.39163 (3)	0.58457 (4)	0.39696 (4)	0.02796 (12)
Cl3	0.93189 (3)	0.14605 (4)	0.52460 (4)	0.03065 (13)
Cl4	0.97033 (3)	0.59117 (4)	0.27286 (4)	0.02639 (12)
C1	0.46669 (10)	0.35599 (15)	0.26849 (14)	0.0171 (3)
O1	0.50255 (7)	0.29825 (13)	0.36158 (11)	0.0257 (3)
N1	0.51344 (8)	0.40910 (14)	0.17722 (13)	0.0185 (3)
H1	0.4844 (15)	0.443 (2)	0.115 (2)	0.028 (5)*
S1	0.64669 (2)	0.48065 (5)	0.04928 (4)	0.02559 (13)
C2	0.60770 (10)	0.41647 (15)	0.17586 (15)	0.0168 (3)
N2	0.65773 (8)	0.36848 (14)	0.27949 (13)	0.0178 (3)
H2	0.6248 (15)	0.327 (2)	0.333 (2)	0.033 (6)*
C11	0.36443 (10)	0.37608 (15)	0.24447 (14)	0.0170 (3)
C12	0.30851 (10)	0.29239 (16)	0.16745 (15)	0.0196 (3)
C13	0.21408 (11)	0.30756 (19)	0.14814 (18)	0.0265 (4)
H13	0.1771	0.2506	0.0941	0.032*
C14	0.17491 (11)	0.40754 (19)	0.2093 (2)	0.0300 (4)
H14	0.1105	0.4177	0.1978	0.036*
C15	0.22860 (12)	0.49305 (18)	0.28705 (18)	0.0270 (4)
H15	0.2014	0.5610	0.3288	0.032*
C16	0.32308 (10)	0.47701 (16)	0.30247 (15)	0.0195 (3)
C21	0.75373 (10)	0.37152 (16)	0.31296 (14)	0.0170 (3)
C22	0.79148 (10)	0.27196 (16)	0.39134 (15)	0.0196 (3)
H22	0.7539	0.2054	0.4175	0.024*
C23	0.88510 (10)	0.27226 (16)	0.43034 (15)	0.0208 (3)
C24	0.94227 (10)	0.36829 (17)	0.39447 (15)	0.0217 (3)
H24	1.0062	0.3666	0.4205	0.026*
C25	0.90178 (10)	0.46720 (16)	0.31857 (15)	0.0189 (3)

C26	0.80870 (10)	0.47105 (16)	0.27637 (15)	0.0184 (3)
H26	0.7832	0.5394	0.2242	0.022*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0285 (2)	0.0291 (2)	0.0314 (2)	−0.00172 (16)	0.00678 (17)	−0.00990 (17)
Cl2	0.0319 (2)	0.0247 (2)	0.0269 (2)	−0.00439 (15)	0.00228 (17)	−0.00444 (16)
Cl3	0.0275 (2)	0.0330 (2)	0.0291 (2)	0.00629 (16)	−0.00562 (16)	0.01025 (18)
Cl4	0.01753 (19)	0.0297 (2)	0.0324 (2)	−0.00597 (14)	0.00488 (15)	0.00171 (16)
C1	0.0145 (6)	0.0204 (8)	0.0165 (7)	−0.0021 (5)	0.0017 (5)	0.0004 (6)
O1	0.0169 (5)	0.0394 (7)	0.0207 (6)	−0.0008 (5)	0.0015 (4)	0.0116 (5)
N1	0.0121 (6)	0.0269 (7)	0.0160 (6)	0.0004 (5)	0.0005 (5)	0.0066 (5)
S1	0.01402 (18)	0.0436 (3)	0.0194 (2)	0.00106 (16)	0.00325 (14)	0.01158 (17)
C2	0.0135 (6)	0.0201 (8)	0.0168 (7)	0.0008 (5)	0.0018 (5)	0.0010 (6)
N2	0.0120 (6)	0.0237 (7)	0.0177 (6)	−0.0012 (5)	0.0014 (5)	0.0037 (5)
C11	0.0138 (6)	0.0216 (8)	0.0158 (7)	−0.0009 (5)	0.0032 (5)	0.0048 (6)
C12	0.0172 (7)	0.0226 (8)	0.0192 (8)	−0.0013 (6)	0.0035 (5)	0.0014 (6)
C13	0.0169 (7)	0.0316 (9)	0.0298 (9)	−0.0065 (6)	−0.0021 (6)	0.0016 (7)
C14	0.0135 (7)	0.0371 (10)	0.0391 (10)	0.0025 (7)	0.0016 (7)	0.0051 (8)
C15	0.0222 (8)	0.0267 (9)	0.0330 (10)	0.0065 (6)	0.0065 (7)	0.0029 (7)
C16	0.0191 (7)	0.0205 (8)	0.0186 (7)	−0.0009 (6)	0.0015 (6)	0.0028 (6)
C21	0.0126 (6)	0.0226 (8)	0.0157 (7)	0.0014 (5)	0.0009 (5)	−0.0016 (6)
C22	0.0178 (7)	0.0232 (8)	0.0178 (7)	−0.0002 (6)	0.0016 (5)	0.0013 (6)
C23	0.0213 (7)	0.0244 (8)	0.0157 (7)	0.0050 (6)	−0.0010 (6)	0.0017 (6)
C24	0.0142 (6)	0.0298 (9)	0.0204 (8)	0.0020 (6)	−0.0009 (5)	−0.0026 (7)
C25	0.0150 (7)	0.0242 (8)	0.0178 (7)	−0.0024 (6)	0.0027 (5)	−0.0019 (6)
C26	0.0147 (6)	0.0213 (8)	0.0188 (7)	0.0007 (5)	0.0011 (5)	0.0005 (6)

Geometric parameters (Å, °)

Cl1—C12	1.7397 (17)	C13—C14	1.390 (3)
Cl2—C16	1.7417 (17)	C13—H13	0.9500
Cl3—C23	1.7414 (17)	C14—C15	1.393 (3)
Cl4—C25	1.7445 (16)	C14—H14	0.9500
C1—O1	1.224 (2)	C15—C16	1.395 (2)
C1—N1	1.3796 (19)	C15—H15	0.9500
C1—C11	1.5146 (19)	C21—C26	1.400 (2)
N1—C2	1.3967 (18)	C21—C22	1.401 (2)
N1—H1	0.82 (2)	C22—C23	1.393 (2)
S1—C2	1.6745 (16)	C22—H22	0.9500
C2—N2	1.347 (2)	C23—C24	1.391 (2)
N2—C21	1.4186 (18)	C24—C25	1.395 (2)
N2—H2	0.91 (2)	C24—H24	0.9500
C11—C12	1.394 (2)	C25—C26	1.393 (2)
C11—C16	1.396 (2)	C26—H26	0.9500
C12—C13	1.393 (2)		
O1—C1—N1	124.54 (14)	C14—C15—C16	118.71 (16)

O1—C1—C11	121.70 (13)	C14—C15—H15	120.6
N1—C1—C11	113.75 (13)	C16—C15—H15	120.6
C1—N1—C2	128.18 (14)	C15—C16—C11	121.63 (15)
C1—N1—H1	118.9 (15)	C15—C16—Cl2	119.48 (13)
C2—N1—H1	112.9 (15)	C11—C16—Cl2	118.89 (12)
N2—C2—N1	114.54 (13)	C26—C21—C22	120.66 (14)
N2—C2—S1	127.07 (11)	C26—C21—N2	122.87 (14)
N1—C2—S1	118.38 (11)	C22—C21—N2	116.38 (14)
C2—N2—C21	128.79 (13)	C23—C22—C21	118.86 (15)
C2—N2—H2	114.5 (15)	C23—C22—H22	120.6
C21—N2—H2	116.7 (15)	C21—C22—H22	120.6
C12—C11—C16	118.01 (13)	C24—C23—C22	122.24 (15)
C12—C11—C1	121.24 (14)	C24—C23—Cl3	119.19 (12)
C16—C11—C1	120.72 (14)	C22—C23—Cl3	118.57 (13)
C13—C12—C11	121.66 (15)	C23—C24—C25	117.16 (14)
C13—C12—Cl1	119.56 (13)	C23—C24—H24	121.4
C11—C12—Cl1	118.78 (11)	C25—C24—H24	121.4
C14—C13—C12	118.88 (16)	C26—C25—C24	122.87 (15)
C14—C13—H13	120.6	C26—C25—Cl4	118.19 (13)
C12—C13—H13	120.6	C24—C25—Cl4	118.93 (12)
C13—C14—C15	121.08 (15)	C25—C26—C21	118.19 (14)
C13—C14—H14	119.5	C25—C26—H26	120.9
C15—C14—H14	119.5	C21—C26—H26	120.9

O1—C1—N1—C2	−4.9 (3)	C14—C15—C16—Cl2	178.83 (14)
C11—C1—N1—C2	174.63 (15)	C12—C11—C16—C15	1.5 (2)
C1—N1—C2—N2	−2.2 (2)	C1—C11—C16—C15	−176.47 (15)
C1—N1—C2—S1	177.27 (14)	C12—C11—C16—Cl2	−178.89 (12)
N1—C2—N2—C21	−173.75 (15)	C1—C11—C16—Cl2	3.2 (2)
S1—C2—N2—C21	6.9 (3)	C2—N2—C21—C26	30.3 (3)
O1—C1—C11—C12	−95.3 (2)	C2—N2—C21—C22	−152.93 (16)
N1—C1—C11—C12	85.17 (19)	C26—C21—C22—C23	−1.2 (2)
O1—C1—C11—C16	82.6 (2)	N2—C21—C22—C23	−178.08 (14)
N1—C1—C11—C16	−96.94 (18)	C21—C22—C23—C24	0.2 (2)
C16—C11—C12—C13	−0.1 (2)	C21—C22—C23—Cl3	−178.45 (12)
C1—C11—C12—C13	177.83 (15)	C22—C23—C24—C25	1.1 (2)
C16—C11—C12—Cl1	179.03 (12)	Cl3—C23—C24—C25	179.77 (12)
C1—C11—C12—Cl1	−3.0 (2)	C23—C24—C25—C26	−1.5 (2)
C11—C12—C13—C14	−1.1 (3)	C23—C24—C25—Cl4	179.11 (12)
Cl1—C12—C13—C14	179.72 (14)	C24—C25—C26—C21	0.5 (2)
C12—C13—C14—C15	1.1 (3)	Cl4—C25—C26—C21	179.94 (12)
C13—C14—C15—C16	0.2 (3)	C22—C21—C26—C25	0.9 (2)
C14—C15—C16—C11	−1.5 (3)	N2—C21—C26—C25	177.49 (14)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O1	0.91 (2)	1.89 (2)	2.6581 (17)	141 (2)
N1—H1···S1^{i}	0.82 (2)	2.57 (2)	3.3653 (14)	163 (2)

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*.

Fig. 1

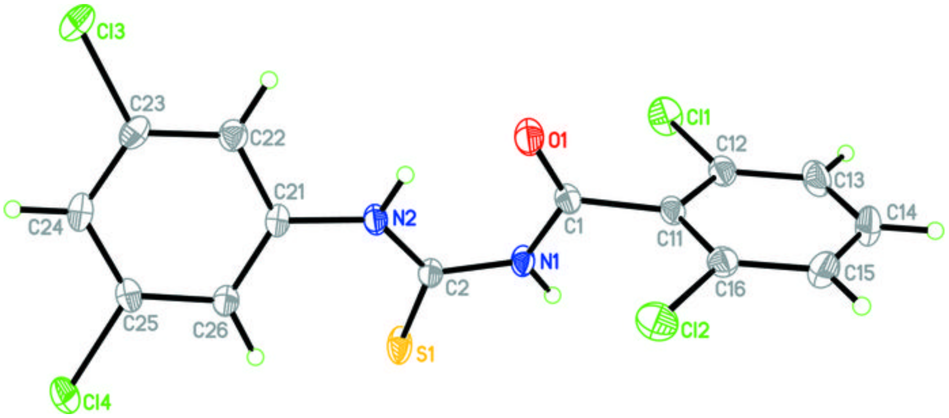
Cl3
C23
C22
C21
N2
C24
C25
C26
Cl4
C2
S1
O1
C1
N1
Cl1
C12
C13
C14
C11
C16
C15
Cl2

Fig. 2