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N-(3,4-Dichlorophenyl)thiourea

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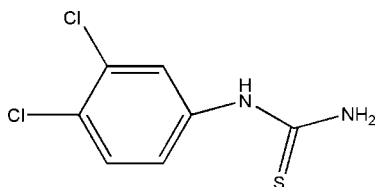
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 Key indicators: single-crystal X-ray study; $T = 291$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.084; wR factor = 0.236; data-to-parameter ratio = 12.8.

In the title compound, $\text{C}_7\text{H}_6\text{Cl}_2\text{N}_2\text{S}$, the benzene ring and the mean plane of the thiourea fragment [$-\text{N}-\text{C}(=\text{S})-\text{N}$] make a dihedral angle of $66.77(3)^\circ$. Intermolecular $\text{N}-\text{H}\cdots\text{S}$ and $\text{N}-\text{H}\cdots\text{Cl}$ hydrogen bonds link the molecules into a three-dimensional network.

Related literature

For the synthesis of the title compound, see: Liu *et al.* (1994). For details of the biological activity of thiazole and its derivatives, see: Holla *et al.* (2003).



Experimental

Crystal data

$\text{C}_7\text{H}_6\text{Cl}_2\text{N}_2\text{S}$
 $M_r = 221.10$
 Triclinic, $P\bar{1}$
 $a = 5.8168(19)$ Å
 $b = 8.489(3)$ Å
 $c = 9.771(3)$ Å

$\alpha = 107.042(4)^\circ$
 $\beta = 94.468(4)^\circ$
 $\gamma = 94.778(4)^\circ$
 $V = 457.0(3)$ Å³
 $Z = 2$
 Mo $K\alpha$ radiation

$\mu = 0.88$ mm⁻¹
 $T = 291$ K

$0.15 \times 0.10 \times 0.08$ mm

Data collection

Bruker SMART APEX CCD
 area-detector diffractometer
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.879$, $T_{\max} = 0.933$

1882 measured reflections
 1562 independent reflections
 1410 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.062$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.084$
 $wR(F^2) = 0.236$
 $S = 1.10$
 1562 reflections
 122 parameters
 3 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.75$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.76$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N7}-\text{H7X}\cdots\text{S9}^{\text{i}}$	0.86 (3)	2.51 (2)	3.342 (3)	161 (4)
$\text{N10}-\text{H10Y}\cdots\text{Cl11}^{\text{ii}}$	0.87 (3)	2.80 (2)	3.646 (3)	163 (4)

Symmetry codes: (i) $-x + 1, -y, -z$; (ii) $-x, -y + 1, -z + 1$.

Data collection: SMART (Bruker, 2005); cell refinement: SAINT (Bruker, 2005); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BG2297).

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supplementary materials

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N-(3,4-Dichlorophenyl)thiourea

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Comment

Thiazoles and their derivatives are found to be associated with various biological activities such as antibacterial, antifungal, anti-inflammatory activities (Holla *et al.*, 2003). The title compound, *N*-(3,4-dichlorophenyl)thiourea (I), is an important intermediate in the synthesis of thiazole and their derivatives. In our work, we present its crystal structure. In Fig. 1, the benzene ring of (I) is twisted out of the mean plane through the —N7—C8(=S9)—N10 group by a dihedral angle of $66.77(3)^\circ$. Weak intermolecular $\text{N—H}\cdots\text{S}$ and $\text{N—H}\cdots\text{Cl}$ hydrogen bonds (Table 1) link the molecules into a three-dimensional network.

Experimental

The title compound was obtained by refluxing 3,4-dichloroaniline (48.6 g, 0.3 mol), 36% aqueous HCl (30.4 g, 0.3 mol) and ammonium thiocyanate (22.8 g, 0.3 mol) in water for 7 hr, then a white precipitate was observed and filtered. The solid was recrystallized from alcohol to give the pure product. This was dissolved in THF, and the solution evaporated gradually at room temperature to afford single crystals of (I). (m.p. 489–490 K). MS(m/z , %): 220 (M^+ , 90), 187 (15), 178 (16), 161 (98), 126 (7), 99 (10), 74 (8), 60 (55).

Refinement

Atoms H7X, H10X and H10Y were located in difference Fourier maps and refined isotropically with the N—H bond restraint of $0.87(2)$ Å. Other H atoms were placed in calculated positions with $\text{C—H} = 0.93$ Å, and refined in riding mode, with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$.

Figures

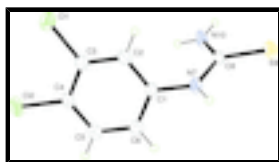


Fig. 1. The structure of (I), shown with 30% probability displacement ellipsoids.

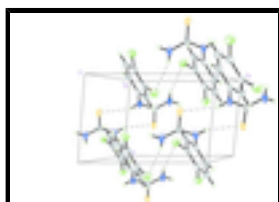


Fig. 2. $\text{N—H}\cdots\text{S}$ and $\text{N—H}\cdots\text{Cl}$ interactions (dotted line) in the title compound.

N-(3,4-Dichlorophenyl)thiourea

Crystal data

$C_7H_6Cl_2N_2S$	$Z = 2$
$M_r = 221.10$	$F_{000} = 224$
Triclinic, $P\bar{1}$	$D_x = 1.607 \text{ Mg m}^{-3}$
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$a = 5.8168 (19) \text{ \AA}$	Cell parameters from 843 reflections
$b = 8.489 (3) \text{ \AA}$	$\theta = 2.5\text{--}27.0^\circ$
$c = 9.771 (3) \text{ \AA}$	$\mu = 0.88 \text{ mm}^{-1}$
$\alpha = 107.042 (4)^\circ$	$T = 291 \text{ K}$
$\beta = 94.468 (4)^\circ$	Prism, orange
$\gamma = 94.778 (4)^\circ$	$0.15 \times 0.10 \times 0.08 \text{ mm}$
$V = 457.0 (3) \text{ \AA}^3$	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	1562 independent reflections
Radiation source: fine-focus sealed tube	1410 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.062$
$T = 291 \text{ K}$	$\theta_{\text{max}} = 25.0^\circ$
φ and ω scans	$\theta_{\text{min}} = 2.2^\circ$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -6 \rightarrow 3$
$T_{\text{min}} = 0.879$, $T_{\text{max}} = 0.933$	$k = -9 \rightarrow 10$
1882 measured reflections	$l = -11 \rightarrow 11$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.084$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.236$	$w = 1/[\sigma^2(F_o^2) + (0.1955P)^2]$
$S = 1.10$	where $P = (F_o^2 + 2F_c^2)/3$
1562 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
122 parameters	$\Delta\rho_{\text{max}} = 0.75 \text{ e \AA}^{-3}$
3 restraints	$\Delta\rho_{\text{min}} = -0.76 \text{ e \AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: SHELXL97 (Sheldrick, 2008), $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
	Extinction coefficient: 0.13 (4)

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.19736 (17)	0.43998 (14)	0.66939 (11)	0.0560 (6)
Cl2	-0.27770 (17)	0.21189 (14)	0.62155 (11)	0.0565 (6)
C1	0.1662 (6)	0.1685 (4)	0.2584 (4)	0.0365 (9)
C2	0.2383 (6)	0.2836 (4)	0.3921 (4)	0.0398 (9)
H2	0.3777	0.3512	0.4062	0.048*
C3	0.1023 (6)	0.2971 (4)	0.5034 (4)	0.0374 (9)
C4	-0.1046 (6)	0.1948 (4)	0.4830 (4)	0.0388 (9)
C5	-0.1748 (6)	0.0795 (5)	0.3507 (4)	0.0480 (11)
H5	-0.3127	0.0103	0.3372	0.058*
C6	-0.0398 (7)	0.0669 (4)	0.2380 (4)	0.0446 (9)
H6	-0.0879	-0.0101	0.1485	0.054*
N7	0.3073 (6)	0.1521 (3)	0.1444 (3)	0.0424 (9)
H7X	0.371 (7)	0.061 (4)	0.113 (5)	0.071 (15)*
C8	0.3732 (6)	0.2709 (4)	0.0853 (4)	0.0353 (8)
S9	0.58001 (18)	0.24215 (10)	-0.03037 (11)	0.0493 (6)
N10	0.2718 (6)	0.4075 (4)	0.1191 (4)	0.0508 (10)
H10X	0.308 (7)	0.486 (5)	0.083 (5)	0.055 (12)*
H10Y	0.159 (5)	0.422 (6)	0.173 (4)	0.054 (12)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0546 (8)	0.0620 (8)	0.0427 (7)	0.0057 (5)	0.0146 (5)	0.0001 (5)
Cl2	0.0577 (8)	0.0636 (9)	0.0549 (8)	0.0087 (5)	0.0328 (5)	0.0209 (6)
C1	0.0534 (19)	0.0253 (16)	0.0377 (19)	0.0123 (14)	0.0214 (15)	0.0137 (14)
C2	0.0404 (18)	0.0334 (18)	0.050 (2)	0.0026 (14)	0.0167 (15)	0.0160 (16)
C3	0.0453 (19)	0.0341 (18)	0.0375 (19)	0.0122 (14)	0.0132 (14)	0.0139 (15)
C4	0.0433 (19)	0.0396 (19)	0.042 (2)	0.0106 (15)	0.0200 (15)	0.0195 (16)
C5	0.048 (2)	0.043 (2)	0.051 (2)	-0.0046 (16)	0.0107 (18)	0.0127 (18)
C6	0.060 (2)	0.0344 (19)	0.039 (2)	0.0023 (15)	0.0123 (16)	0.0087 (15)
N7	0.064 (2)	0.0251 (15)	0.0460 (18)	0.0146 (13)	0.0319 (14)	0.0136 (13)
C8	0.0489 (19)	0.0257 (16)	0.0338 (18)	0.0059 (13)	0.0167 (14)	0.0091 (13)

supplementary materials

S9	0.0722 (9)	0.0288 (7)	0.0572 (8)	0.0151 (5)	0.0417 (6)	0.0175 (5)
N10	0.072 (2)	0.0312 (17)	0.064 (2)	0.0175 (15)	0.0434 (17)	0.0239 (15)

Geometric parameters (Å, °)

C11—C3	1.733 (4)	C5—C6	1.386 (5)
C12—C4	1.729 (4)	C5—H5	0.9300
C1—C6	1.382 (5)	C6—H6	0.9300
C1—C2	1.391 (5)	N7—C8	1.345 (4)
C1—N7	1.416 (5)	N7—H7X	0.87 (2)
C2—C3	1.378 (6)	C8—N10	1.312 (5)
C2—H2	0.9300	C8—S9	1.698 (4)
C3—C4	1.389 (5)	N10—H10X	0.86 (3)
C4—C5	1.380 (6)	N10—H10Y	0.87 (3)
C6—C1—C2	120.1 (3)	C6—C5—H5	120.0
C6—C1—N7	120.0 (3)	C1—C6—C5	120.0 (3)
C2—C1—N7	120.0 (3)	C1—C6—H6	120.0
C3—C2—C1	119.7 (3)	C5—C6—H6	120.0
C3—C2—H2	120.1	C8—N7—C1	126.3 (3)
C1—C2—H2	120.1	C8—N7—H7X	114 (3)
C2—C3—C4	120.2 (3)	C1—N7—H7X	119 (3)
C2—C3—C11	118.9 (3)	N10—C8—N7	118.0 (3)
C4—C3—C11	120.9 (3)	N10—C8—S9	121.7 (3)
C5—C4—C3	119.9 (3)	N7—C8—S9	120.4 (3)
C5—C4—C12	119.5 (3)	C8—N10—H10X	121 (3)
C3—C4—C12	120.6 (3)	C8—N10—H10Y	123 (3)
C4—C5—C6	120.0 (3)	H10X—N10—H10Y	116 (4)
C4—C5—H5	120.0		
C6—C1—C2—C3	-0.7 (5)	C12—C4—C5—C6	178.7 (3)
N7—C1—C2—C3	-178.9 (3)	C2—C1—C6—C5	0.0 (5)
C1—C2—C3—C4	0.9 (5)	N7—C1—C6—C5	178.1 (3)
C1—C2—C3—C11	179.3 (3)	C4—C5—C6—C1	0.6 (5)
C2—C3—C4—C5	-0.2 (5)	C6—C1—N7—C8	121.2 (4)
C11—C3—C4—C5	-178.7 (3)	C2—C1—N7—C8	-60.7 (5)
C2—C3—C4—C12	-179.5 (2)	C1—N7—C8—N10	-11.2 (5)
C11—C3—C4—C12	2.1 (4)	C1—N7—C8—S9	169.3 (3)
C3—C4—C5—C6	-0.5 (5)		

Hydrogen-bond geometry (Å, °)

<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>
N7—H7X \cdots S9 ⁱ	0.86 (3)	2.51 (2)	3.342 (3)	161 (4)
N10—H10Y \cdots C11 ⁱⁱ	0.87 (3)	2.80 (2)	3.646 (3)	163 (4)

Symmetry codes: (i) $-x+1, -y, -z$; (ii) $-x, -y+1, -z+1$.

Fig. 1

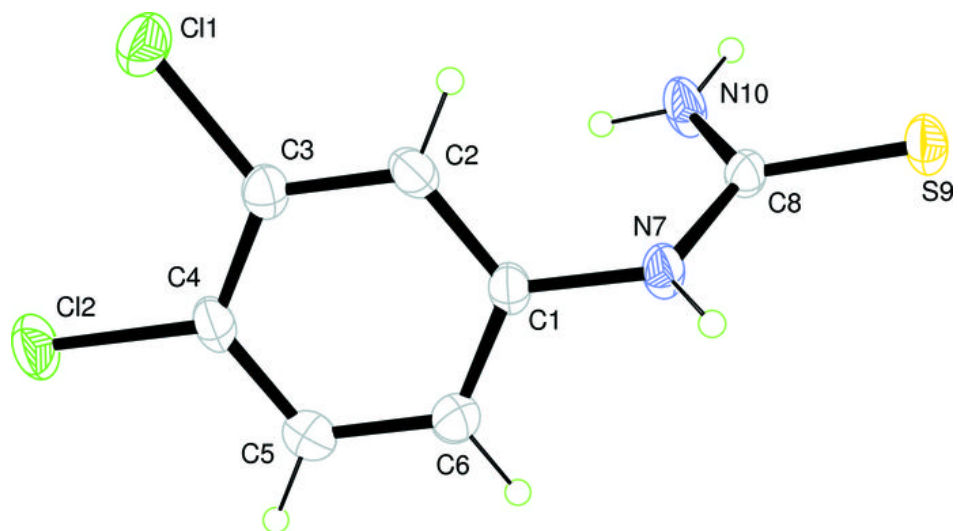


Fig. 2

