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## Structure Reports

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# N-(3,4-Dichlorophenyl)thiourea

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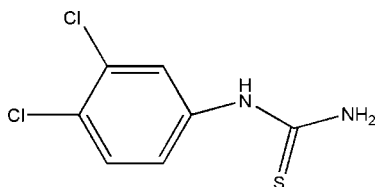
Received 26 August 2009; accepted 3 September 2009

 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

$\alpha = 107.042(4)^\circ$   
 $\beta = 94.468(4)^\circ$   
 $\gamma = 94.778(4)^\circ$   
 $V = 457.0(3)$  Å<sup>3</sup>  
 $Z = 2$   
 Mo  $K\alpha$  radiation

$\mu = 0.88$  mm<sup>-1</sup>  
 $T = 291$  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)  
 $T_{\text{min}} = 0.879$ ,  $T_{\text{max}} = 0.933$

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<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.76$  e Å<sup>-3</sup>

**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).

## References

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 Liu, B., Gao, H. Q. & Zhou, X. J. (1994). *Hua Xue Tong Bao*, **5**, 42–43.  
 Sheldrick, G. M. (1996). SADABS. University of Göttingen, Germany.  
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

## supporting information

*Acta Cryst.* (2009). E65, o2401 [doi:10.1107/S1600536809035569]

***N*-(3,4-Dichlorophenyl)thiourea****Hai-Bo Shi, Wei-Xiao Hu and Yan-Fang Lin****S1. Comment**

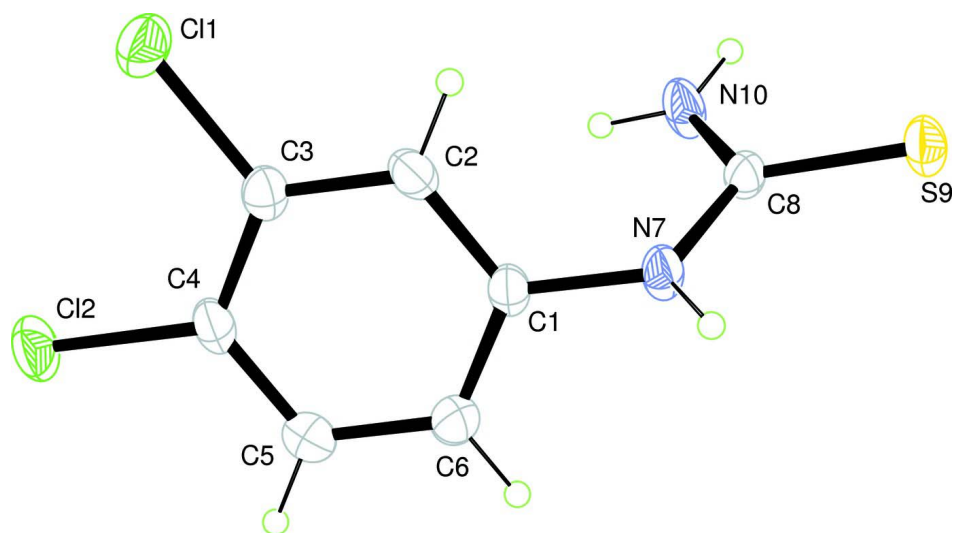
Thiazoles and their derivatives are found to be associated with various biological activities such as antibacterial, antifungal, anti-inflammatory activities (Holla *et al.*, 2003). The title compound, *N*-(3,4-dichlorophenyl)thiourea (I), is an important intermediate in the synthesis of thiazole and 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)°. Weak intermolecular N—H···S and N—H···Cl hydrogen bonds (Table 1) link the molecules into a three-dimensional network.

**S2. Experimental**

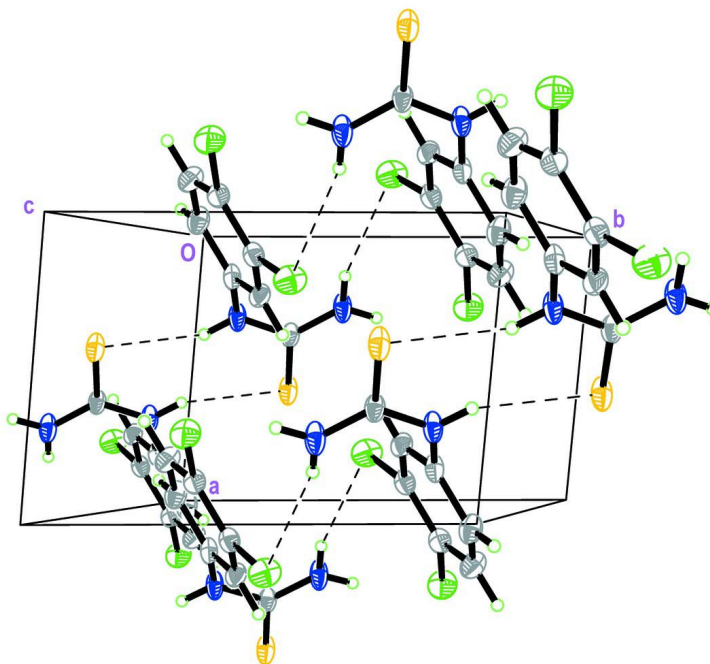
The title compound was obtained by refluxing 3,4-dichloroaniline (48.6 g, 0.3 mol), 36% aqueous HCl (30.4 g, 0.3 mol) and ammonium thiocyanate (22.8 g, 0.3 mol) in water for 7 hr, then a white precipitate was observed and filtered. The solid was recrystallized from alcohol to give the pure product. This 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*<sup>+</sup>, 90), 187 (15), 178 (16), 161 (98), 126 (7), 99 (10), 74 (8), 60 (55).

**S3. 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 C—H = 0.93 Å, and refined in riding mode, with  $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ .

**Figure 1**

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

**Figure 2**

N—H...S and N—H...Cl interactions (dotted line) in the title compound.

### *N*-(3,4-Dichlorophenyl)thiourea

#### Crystal data

$C_7H_6Cl_2N_2S$

$M_r = 221.10$

Triclinic,  $P\bar{1}$

Hall symbol:  $-P\ 1$

$a = 5.8168(19)\ \text{\AA}$

$b = 8.489(3)\ \text{\AA}$

$c = 9.771(3)\ \text{\AA}$

$\alpha = 107.042(4)^\circ$

$\beta = 94.468(4)^\circ$

$\gamma = 94.778(4)^\circ$

$V = 457.0(3)\ \text{\AA}^3$

$Z = 2$

$F(000) = 224$   
 $D_x = 1.607 \text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$   
 Cell parameters from 843 reflections  
 $\theta = 2.5\text{--}27.0^\circ$

$\mu = 0.88 \text{ mm}^{-1}$   
 $T = 291 \text{ K}$   
 Prism, orange  
 $0.15 \times 0.10 \times 0.08 \text{ mm}$

*Data collection*

Bruker SMART APEX CCD area-detector  
 diffractometer  
 Radiation source: fine-focus sealed tube  
 Graphite monochromator  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan  
 (SADABS; Sheldrick, 1996)  
 $T_{\min} = 0.879$ ,  $T_{\max} = 0.933$

1882 measured reflections  
 1562 independent reflections  
 1410 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.062$   
 $\theta_{\max} = 25.0^\circ$ ,  $\theta_{\min} = 2.2^\circ$   
 $h = -6 \rightarrow 3$   
 $k = -9 \rightarrow 10$   
 $l = -11 \rightarrow 11$

*Refinement*

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.084$   
 $wR(F^2) = 0.236$   
 $S = 1.10$   
 1562 reflections  
 122 parameters  
 3 restraints  
 Primary atom site location: structure-invariant  
 direct methods  
 Secondary atom site location: difference Fourier  
 map

Hydrogen site location: inferred from  
 neighbouring sites  
 H atoms treated by a mixture of independent  
 and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.1955P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.75 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.76 \text{ e \AA}^{-3}$   
 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 ( $\text{\AA}^2$ )*

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
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 (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
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)
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, °)*

Cl1—C3	1.733 (4)	C5—C6	1.386 (5)
Cl2—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—Cl1	118.9 (3)	N10—C8—N7	118.0 (3)
C4—C3—Cl1	120.9 (3)	N10—C8—S9	121.7 (3)
C5—C4—C3	119.9 (3)	N7—C8—S9	120.4 (3)
C5—C4—Cl2	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... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N7—H7X...S9 <sup>i</sup>	0.86 (3)	2.51 (2)	3.342 (3)	161 (4)
N10—H10Y...C11 <sup>ii</sup>	0.87 (3)	2.80 (2)	3.646 (3)	163 (4)

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