

Acta Crystallographica Section E

## Structure Reports

Online

ISSN 1600-5368

## N-(2,4-Dichlorophenyl)-1,3-thiazol-2-amine

Ayesha Babar,<sup>a</sup> Munawar Ali Munawar,<sup>a</sup> M. Nawaz Tahir,<sup>b\*</sup> Fateh Ullah<sup>c</sup> and Muhammad Ilyas Tariq<sup>d</sup>

<sup>a</sup>Institute of Chemistry, University of the Punjab, Lahore 54590, Pakistan, <sup>b</sup>University of Sargodha, Department of Physics, Sargodha, Pakistan, <sup>c</sup>Interdisciplinary Research Centre in Biomedical Materials, COMSATS Institute of Information Technology, Defence Road, Off Raiwind Road, Lahore, Pakistan, and <sup>d</sup>University of Sargodha, Department of Chemistry, Sargodha, Pakistan  
Correspondence e-mail: dmntahir\_uos@yahoo.com

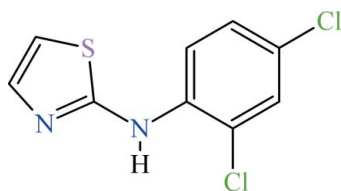
Received 1 August 2012; accepted 9 August 2012

Key indicators: single-crystal X-ray study;  $T = 296$  K; mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å;  $R$  factor = 0.029;  $wR$  factor = 0.080; data-to-parameter ratio = 17.7.

In the title molecule,  $\text{C}_9\text{H}_6\text{Cl}_2\text{N}_2\text{S}$ , the mean planes of the benzene and thiazole rings make a dihedral angle of  $54.18(8)^\circ$ . In the crystal, molecules are joined into dimers with an  $R_2^2(8)$  ring motif by pairs of  $\text{N}-\text{H}\cdots\text{N}$  hydrogen bonds. These dimers are linked by  $\text{C}-\text{H}\cdots\text{Cl}$  interactions into layers parallel to (011). The thiazole rings form columns along the  $c$ -axis direction, with a centroid-centroid separation of  $3.8581(9)$  Å, indicating  $\pi-\pi$  interactions. An intramolecular  $\text{C}-\text{H}\cdots\text{S}$  contact also occurs.

### Related literature

For the synthesis and crystal structure of a related compound, see: Babar *et al.* (2012). For graph-set notation, see: Bernstein *et al.* (1995).



### Experimental

#### Crystal data

$\text{C}_9\text{H}_6\text{Cl}_2\text{N}_2\text{S}$   
 $M_r = 245.12$   
Monoclinic,  $P2_1/c$

$a = 13.0270(9)$  Å  
 $b = 10.1183(6)$  Å  
 $c = 7.7159(5)$  Å

$\beta = 91.974(3)^\circ$   
 $V = 1016.44(11)$  Å<sup>3</sup>  
 $Z = 4$   
Mo  $K\alpha$  radiation

$\mu = 0.80$  mm<sup>-1</sup>  
 $T = 296$  K  
 $0.33 \times 0.28 \times 0.22$  mm

#### Data collection

Bruker Kappa APEXII CCD area-detector diffractometer  
Absorption correction: multi-scan (SADABS; Bruker, 2009)  
 $T_{\min} = 0.778$ ,  $T_{\max} = 0.844$   
8039 measured reflections  
2245 independent reflections  
1957 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.020$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$   
 $wR(F^2) = 0.080$   
 $S = 1.04$   
2245 reflections  
127 parameters  
H-atom parameters constrained  
 $\Delta\rho_{\max} = 0.24$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.30$  e Å<sup>-3</sup>

**Table 1**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1}\cdots\text{N2}^i$	0.86	2.07	2.9302 (19)	174
$\text{C3}-\text{H3}\cdots\text{Cl2}^{ii}$	0.93	2.82	3.7483 (17)	173
$\text{C6}-\text{H6}\cdots\text{S1}$	0.93	2.87	3.2056 (19)	103

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

Data collection: APEX2 (Bruker, 2009); cell refinement: SAINT (Bruker, 2009); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997) and PLATON (Spek, 2009); software used to prepare material for publication: WinGX (Farrugia, 1999) and PLATON.

The authors acknowledge the provision of funds for the purchase of a diffractometer and encouragement by Dr Muhammad Akram Chaudhary, Vice Chancellor, University of Sargodha, Pakistan. They are also thankful to the Higher Education Commission (HEC), Pakistan, for financial assistance.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: YK2069).

### References

- Babar, A., Munawar, M. A., Tahir, M. N., Khan, A. F. & Tariq, M. I. (2012). *Acta Cryst.* **E68**, o2441.  
Bernstein, J., Davis, R. E., Shimon, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.  
Bruker (2009). APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.  
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.  
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.  
Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.  
Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.

## supporting information

*Acta Cryst.* (2012). E68, o2704 [doi:10.1107/S1600536812035301]

***N*-(2,4-Dichlorophenyl)-1,3-thiazol-2-amine**

Ayesha Babar, Munawar Ali Munawar, M. Nawaz Tahir, Fateh Ullah and Muhammad Ilyas Tariq

**S1. Comment**

The title compound has been prepared in continuation to our ongoing project of synthesizing various derivatives of *N*-phenyl-1,3-thiazol-2-amine. We have recently published the synthesis and crystal structure of *N*-(2,4,6-trimethylphenyl)-1,3-thiazol-2-amine (Babar *et al.*, 2012) which is related to the title compound.

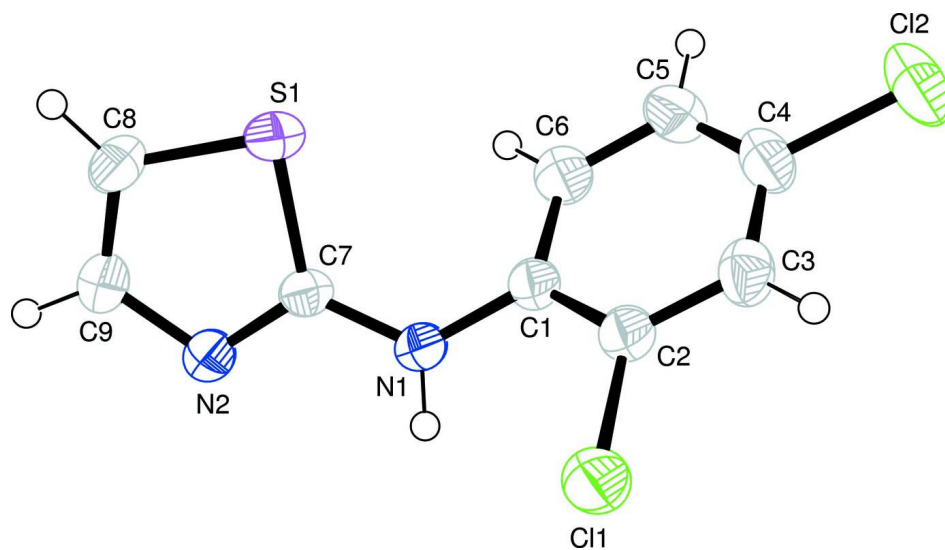
In the title compound (Fig. 1), the 1,3-dichlorobenzene group A (C1–C6/CL1/CL2) and 1,3-thiazol-2-amine group B (N1/C7/S1/C8/C9/N2) are planar with r.m.s. deviations of 0.009 Å and 0.030 Å, respectively. The dihedral angle between the planes of A and B is 53.28 (4)°. The molecules are joined into dimers by pairs of N—H···N hydrogen bonds (Table 1, Fig. 2), forming  $R_2^2(8)$  ring motif (Bernstein *et al.*, 1995). The dimers are further linked by C—H···Cl hydrogen bonds into layers parallel to (0 1 1). Thiazole rings form stacks along the *c* axis direction with intercentroid separation  $Cg^i \cdots Cg^j$  [ $i = x, 3/2 - y, \pm 1/2 + z$ ] of 3.8581 (9) Å, indicating  $\pi$ – $\pi$  interactions.

**S2. Experimental**

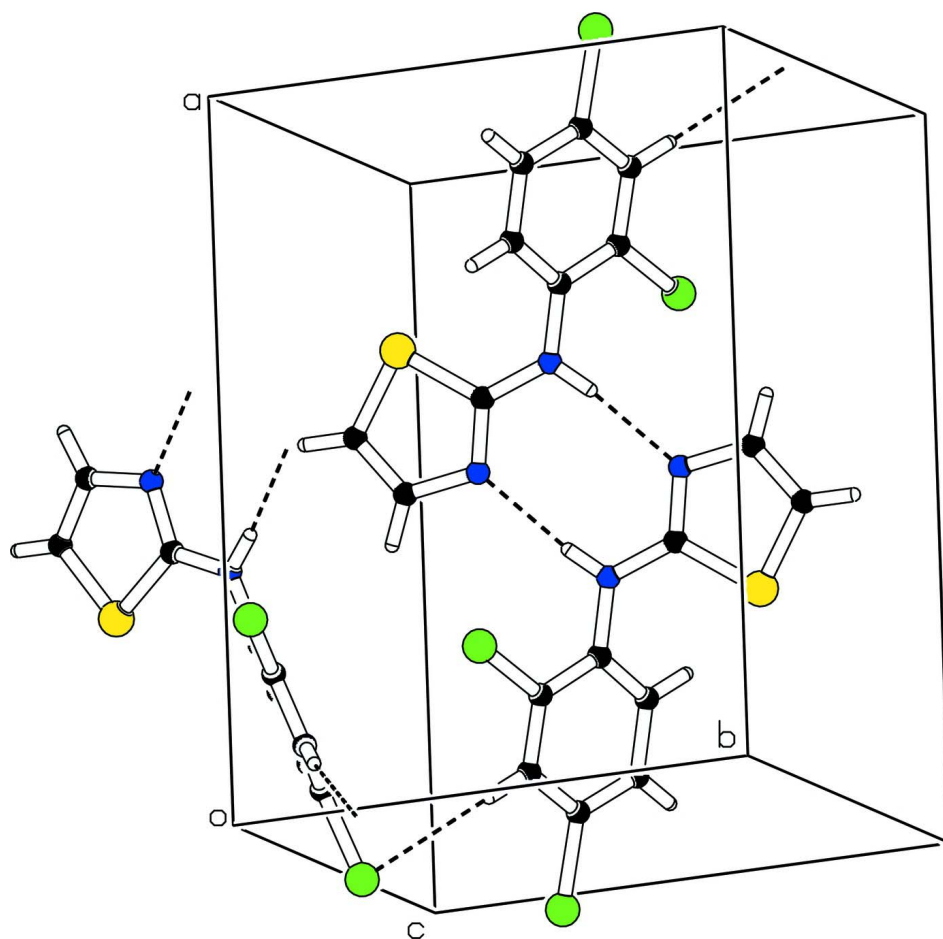
A mixture of *N*-(2,4-dichlorophenyl)thiourea (1.00 g, 4.52 mmol) and 2-chloro-1,1-dimethoxyethane (0.93 g, 6.12 mmol) was dissolved in water-methanol mixture (1:2) (100 mL). A few drops of concentrated HCl were added and the reaction mixture was refluxed for 4 h. Water (100 ml) was added, and the mixture was neutralized with aqueous NaOH to pH=8. The resulting precipitate was filtered and washed with ice cold water. The crude product was recrystallized from chloroform-hexane mixture (1:2) to obtain white prisms.

**S3. Refinement**

The hydrogen atoms were positioned geometrically (C—H = 0.93 Å, N—H = 0.86 Å) and refined as riding with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$ .

**Figure 1**

Molecular structure of the title compound showing the atom labelling scheme and displacement ellipsoids drawn at the 50% probability level.



**Figure 2**

The partial packing showing molecular dimer linked to the others by C—H···Cl interactions.

***N*-(2,4-Dichlorophenyl)-1,3-thiazol-2-amine***Crystal data*C<sub>9</sub>H<sub>6</sub>Cl<sub>2</sub>N<sub>2</sub>S $M_r = 245.12$ Monoclinic,  $P2_1/c$ 

Hall symbol: -P 2ybc

 $a = 13.0270$  (9) Å $b = 10.1183$  (6) Å $c = 7.7159$  (5) Å $\beta = 91.974$  (3)° $V = 1016.44$  (11) Å<sup>3</sup> $Z = 4$  $F(000) = 496$  $D_x = 1.602$  Mg m<sup>-3</sup>Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 912 reflections

 $\theta = 1.6$ – $27.2$ ° $\mu = 0.80$  mm<sup>-1</sup> $T = 296$  K

Prism, yellow

 $0.33 \times 0.28 \times 0.22$  mm*Data collection*

Bruker Kappa APEXII CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 7.80 pixels mm<sup>-1</sup> $\omega$  scans

Absorption correction: multi-scan

(SADABS; Bruker, 2009)

 $T_{\min} = 0.778$ ,  $T_{\max} = 0.844$ 

8039 measured reflections

2245 independent reflections

1957 reflections with  $I > 2\sigma(I)$  $R_{\text{int}} = 0.020$  $\theta_{\max} = 27.2$ °,  $\theta_{\min} = 1.6$ ° $h = -16$ → $16$  $k = -12$ → $12$  $l = -9$ → $9$ *Refinement*Refinement on  $F^2$ 

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.029$  $wR(F^2) = 0.080$  $S = 1.04$ 

2245 reflections

127 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0406P)^2 + 0.2925P]$ where  $P = (F_o^2 + 2F_c^2)/3$  $(\Delta/\sigma)_{\max} < 0.001$  $\Delta\rho_{\max} = 0.24$  e Å<sup>-3</sup> $\Delta\rho_{\min} = -0.30$  e Å<sup>-3</sup>*Special details*

**Geometry.** Bond distances, angles *etc.* have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

**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<sup>2</sup>)*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.24571 (4)	0.37457 (5)	0.29544 (6)	0.0545 (2)

Cl2	-0.05984 (3)	0.34681 (6)	0.74042 (8)	0.0662 (2)
S1	0.33053 (3)	0.77775 (4)	0.66934 (5)	0.0405 (1)
N1	0.35990 (10)	0.51946 (12)	0.57795 (18)	0.0403 (4)
N2	0.49723 (10)	0.66580 (13)	0.57830 (18)	0.0400 (4)
C1	0.26014 (11)	0.48156 (14)	0.6171 (2)	0.0353 (4)
C2	0.19932 (12)	0.41107 (15)	0.4977 (2)	0.0369 (4)
C3	0.10147 (12)	0.36979 (16)	0.5348 (2)	0.0434 (5)
C4	0.06296 (12)	0.40070 (17)	0.6935 (2)	0.0451 (5)
C5	0.12029 (14)	0.47052 (18)	0.8147 (2)	0.0505 (6)
C6	0.21843 (14)	0.50928 (18)	0.7763 (2)	0.0463 (5)
C7	0.40145 (11)	0.64084 (14)	0.60680 (18)	0.0326 (4)
C8	0.43848 (14)	0.87355 (15)	0.6496 (2)	0.0455 (5)
C9	0.51714 (14)	0.79861 (16)	0.6017 (2)	0.0462 (5)
H1	0.39818	0.46092	0.53165	0.0483*
H3	0.06225	0.32185	0.45384	0.0520*
H5	0.09331	0.49142	0.92130	0.0606*
H6	0.25772	0.55521	0.85926	0.0556*
H8	0.44170	0.96415	0.66933	0.0545*
H9	0.58188	0.83417	0.58503	0.0554*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cl1	0.0514 (3)	0.0636 (3)	0.0487 (3)	-0.0090 (2)	0.0058 (2)	-0.0158 (2)
Cl2	0.0351 (2)	0.0737 (3)	0.0905 (4)	-0.0031 (2)	0.0114 (2)	0.0243 (3)
S1	0.0421 (2)	0.0346 (2)	0.0453 (2)	0.0064 (2)	0.0081 (2)	-0.0047 (2)
N1	0.0325 (7)	0.0334 (6)	0.0554 (8)	-0.0019 (5)	0.0082 (6)	-0.0134 (6)
N2	0.0350 (7)	0.0333 (6)	0.0519 (8)	-0.0022 (5)	0.0059 (6)	-0.0070 (6)
C1	0.0319 (7)	0.0302 (7)	0.0438 (8)	0.0008 (6)	0.0034 (6)	-0.0011 (6)
C2	0.0365 (8)	0.0338 (7)	0.0405 (8)	0.0009 (6)	0.0019 (6)	-0.0005 (6)
C3	0.0351 (8)	0.0396 (8)	0.0550 (10)	-0.0030 (6)	-0.0047 (7)	0.0039 (7)
C4	0.0319 (8)	0.0420 (9)	0.0619 (11)	0.0019 (7)	0.0075 (7)	0.0141 (8)
C5	0.0470 (10)	0.0526 (10)	0.0530 (10)	0.0006 (8)	0.0170 (8)	-0.0013 (8)
C6	0.0454 (9)	0.0480 (9)	0.0458 (9)	-0.0049 (7)	0.0059 (7)	-0.0078 (7)
C7	0.0342 (8)	0.0313 (7)	0.0325 (7)	0.0025 (6)	0.0021 (6)	-0.0045 (5)
C8	0.0567 (10)	0.0289 (7)	0.0511 (9)	-0.0023 (7)	0.0071 (8)	-0.0040 (7)
C9	0.0449 (9)	0.0357 (8)	0.0583 (10)	-0.0084 (7)	0.0080 (8)	-0.0052 (7)

*Geometric parameters (Å, °)*

Cl1—C2	1.7327 (16)	C2—C3	1.381 (2)
Cl2—C4	1.7399 (16)	C3—C4	1.375 (2)
S1—C7	1.7425 (15)	C4—C5	1.372 (2)
S1—C8	1.7191 (18)	C5—C6	1.379 (3)
N1—C1	1.3979 (19)	C8—C9	1.337 (2)
N1—C7	1.3574 (19)	C3—H3	0.9300
N2—C7	1.2992 (19)	C5—H5	0.9300
N2—C9	1.379 (2)	C6—H6	0.9300

N1—H1	0.8600	C8—H8	0.9300
C1—C6	1.389 (2)	C9—H9	0.9300
C1—C2	1.391 (2)		
C7—S1—C8	88.89 (7)	C1—C6—C5	121.76 (15)
C1—N1—C7	125.53 (13)	S1—C7—N2	114.44 (11)
C7—N2—C9	110.16 (13)	S1—C7—N1	123.54 (11)
C7—N1—H1	117.00	N1—C7—N2	121.87 (13)
C1—N1—H1	117.00	S1—C8—C9	109.99 (12)
N1—C1—C6	122.05 (14)	N2—C9—C8	116.50 (16)
N1—C1—C2	120.67 (14)	C2—C3—H3	121.00
C2—C1—C6	117.26 (14)	C4—C3—H3	121.00
C1—C2—C3	121.78 (14)	C4—C5—H5	120.00
Cl1—C2—C3	118.39 (12)	C6—C5—H5	120.00
Cl1—C2—C1	119.83 (12)	C1—C6—H6	119.00
C2—C3—C4	118.92 (15)	C5—C6—H6	119.00
C3—C4—C5	121.14 (15)	S1—C8—H8	125.00
Cl2—C4—C3	118.70 (12)	C9—C8—H8	125.00
Cl2—C4—C5	120.15 (13)	N2—C9—H9	122.00
C4—C5—C6	119.13 (15)	C8—C9—H9	122.00
C8—S1—C7—N1	-174.25 (13)	C6—C1—C2—Cl1	179.25 (12)
C8—S1—C7—N2	1.39 (12)	C6—C1—C2—C3	-0.1 (2)
C7—S1—C8—C9	-0.80 (12)	N1—C1—C6—C5	-179.38 (15)
C7—N1—C1—C2	134.53 (16)	C2—C1—C6—C5	-0.9 (2)
C7—N1—C1—C6	-47.0 (2)	Cl1—C2—C3—C4	-178.59 (13)
C1—N1—C7—S1	-9.7 (2)	C1—C2—C3—C4	0.8 (2)
C1—N1—C7—N2	174.96 (14)	C2—C3—C4—Cl2	-179.29 (12)
C9—N2—C7—S1	-1.53 (17)	C2—C3—C4—C5	-0.5 (3)
C9—N2—C7—N1	174.19 (14)	Cl2—C4—C5—C6	178.34 (14)
C7—N2—C9—C8	0.9 (2)	C3—C4—C5—C6	-0.5 (3)
N1—C1—C2—Cl1	-2.2 (2)	C4—C5—C6—C1	1.2 (3)
N1—C1—C2—C3	178.44 (14)	S1—C8—C9—N2	0.13 (18)

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 $\cdots$ N2 <sup>i</sup>	0.86	2.07	2.9302 (19)	174
C3—H3 $\cdots$ Cl2 <sup>ii</sup>	0.93	2.82	3.7483 (17)	173
C6—H6 $\cdots$ S1	0.93	2.87	3.2056 (19)	103

Symmetry codes: (i)  $-x+1, -y+1, -z+1$ ; (ii)  $x, -y+1/2, z-1/2$ .