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## Structure Reports

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## 5-(4-Methylphenyl)-1,3,4-thiadiazol-2-amine

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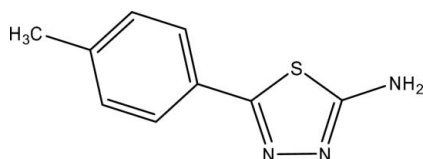
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Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{C}-\text{C}) = 0.006$  Å;  $R$  factor = 0.059;  $wR$  factor = 0.181; data-to-parameter ratio = 15.9.

The title compound,  $\text{C}_9\text{H}_9\text{N}_3\text{S}$ , was synthesized by the reaction of 4-methyl-benzoic acid and thiosemicarbazide. The thiadiazol ring adopts a planar conformation and makes a dihedral angle of  $31.19(18)^\circ$  with the phenyl ring. In the crystal, molecules are linked by  $\text{N}-\text{H}\cdots\text{N}$  hydrogen bonds.

## Related literature

For applications of thiadiazole ligands, see: Nakagawa *et al.* (1996); Wang *et al.* (1999); Han *et al.* (2007). For bond-length data, see: Allen *et al.* (1987).



## Experimental

## Crystal data

$\text{C}_9\text{H}_9\text{N}_3\text{S}$   
 $M_r = 191.25$   
 Monoclinic,  $P2_1/c$   
 $a = 12.284(3)$  Å  
 $b = 7.3730(15)$  Å

$c = 11.263(2)$  Å  
 $\beta = 109.09(3)^\circ$   
 $V = 964.0(3)$  Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation

$\mu = 0.29$  mm<sup>-1</sup>  
 $T = 293$  K

0.30 × 0.10 × 0.10 mm

## Data collection

Nonius CAD4 diffractometer  
 Absorption correction:  $\psi$  scan  
 (North *et al.*, 1968)  
 $T_{\min} = 0.918$ ,  $T_{\max} = 0.972$   
 1963 measured reflections  
 1875 independent reflections

1351 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.067$   
 3 standard reflections  
 every 200 reflections  
 intensity decay: 1%

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.059$   
 $wR(F^2) = 0.181$   
 $S = 1.01$   
 1875 reflections

118 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.26$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.43$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N3}-\text{H3A}\cdots\text{N2}^{\text{i}}$	0.86	2.13	2.970 (5)	166
$\text{N3}-\text{H3B}\cdots\text{N1}^{\text{ii}}$	0.86	2.18	3.025 (4)	166

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

Data collection: *CAD-4 EXPRESS* (Enraf-Nonius, 1989); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); 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: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: AT2758).

## References

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**supplementary materials**

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## 5-(4-Methylphenyl)-1,3,4-thiadiazol-2-amine

J.-N. Guan, R. Wan, Y. Wang, F. Han and C.-Z. Xu

### Comment

1,3,4-Thiadiazole derivatives represent an interesting class of compounds possessing broad spectrum biological activities (Nakagawa *et al.*, 1996; Wang *et al.*, 1999). These compounds are known to exhibit diverse biological effects, such as insecticidal, fungicidal activities (Wang *et al.*, 1999). We are focusing our synthetic and structural studies on thiadiazole derivatives and we have recently published the structure of 5-*m*-tolyl-[1,3,4]thiadiazol-2-ylamine (Han *et al.*, 2007). We report here the crystal structure of the title compound, (I).

In (I) (Fig. 1), the bond lengths and angles are within normal ranges (Allen *et al.*, 1987). The thiadiazole and the phenyl ring make a dihedral angle of 31.19 (18)°. The molecules link by N—H···N hydrogen bonds to stabilize the crystal structure (Fig. 2).

### Experimental

4-Methyl-benzoic acid (5 mmol) and thiosemicarbazide (5 mmol) were added in toluene (50 ml), which is heated under reflux for 4 h. The reaction mixture was left to cool to room temperature, poured into ice water, filtered, and the filter cake was crystallized from acetone to give pure compound (I). Crystals of (I) suitable for X-ray diffraction were obtained by slow evaporation of an acetone solution.

### Refinement

All H atoms were placed geometrically with C—H = 0.93–0.96 Å and N—H = 0.86 Å, and included in the refinement in riding motion approximation with  $U_{\text{iso}}(\text{H}) = 1.2$  or  $1.5U_{\text{eq}}$  of the carrier atom.

### Figures

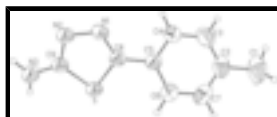


Fig. 1. A view of the molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level.

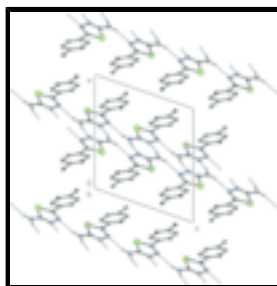


Fig. 2. View of the N—H···N hydrogen bonds (dashed lines) in the unit cell. Dashed lines indicate hydrogen bonds.

## 5-(4-methylphenyl)-1,3,4-thiadiazol-2-amine

### Crystal data

$C_9H_9N_3S$	$F_{000} = 400$
$M_r = 191.25$	$D_x = 1.318 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Melting point = 476–478 K
Hall symbol: -P 2ybc	Mo $K\alpha$ radiation
$a = 12.284 (3) \text{ \AA}$	$\lambda = 0.71073 \text{ \AA}$
$b = 7.3730 (15) \text{ \AA}$	Cell parameters from 25 reflections
$c = 11.263 (2) \text{ \AA}$	$\theta = 9\text{--}13^\circ$
$\beta = 109.09 (3)^\circ$	$\mu = 0.29 \text{ mm}^{-1}$
$V = 964.0 (3) \text{ \AA}^3$	$T = 293 \text{ K}$
$Z = 4$	Block, colourless
	$0.30 \times 0.10 \times 0.10 \text{ mm}$

### Data collection

Nonius CAD4 diffractometer	$R_{\text{int}} = 0.067$
Radiation source: fine-focus sealed tube	$\theta_{\text{max}} = 26.0^\circ$
Monochromator: graphite	$\theta_{\text{min}} = 1.8^\circ$
$T = 293 \text{ K}$	$h = -15 \rightarrow 0$
$\omega/2\theta$ scans	$k = 0 \rightarrow 9$
Absorption correction: $\psi$ scan (North <i>et al.</i> , 1968)	$l = -13 \rightarrow 13$
$T_{\text{min}} = 0.918$ , $T_{\text{max}} = 0.972$	3 standard reflections
1963 measured reflections	every 200 reflections
1875 independent reflections	intensity decay: 1%
1351 reflections with $I > 2\sigma(I)$	

### Refinement

Refinement on $F^2$	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.059$	H-atom parameters constrained
$wR(F^2) = 0.181$	$w = 1/[\sigma^2(F_o^2) + (0.1P)^2 + 0.5P]$
$S = 1.01$	where $P = (F_o^2 + 2F_c^2)/3$
1875 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
118 parameters	$\Delta\rho_{\text{max}} = 0.26 \text{ e \AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\text{min}} = -0.42 \text{ e \AA}^{-3}$
	Extinction correction: none

*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 ( $\text{\AA}^2$ )*

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
S	0.34151 (8)	0.08993 (12)	0.57346 (7)	0.0494 (3)
N1	0.3802 (2)	0.1397 (4)	0.3670 (2)	0.0477 (7)
N2	0.4336 (3)	0.2834 (4)	0.4424 (2)	0.0504 (8)
N3	0.4638 (3)	0.3988 (5)	0.6437 (3)	0.0662 (10)
H3A	0.5027	0.4894	0.6309	0.079*
H3B	0.4527	0.3872	0.7149	0.079*
C1	0.0739 (4)	-0.6083 (7)	0.1831 (5)	0.0932 (17)
H1B	0.0401	-0.5868	0.0945	0.140*
H1C	0.0143	-0.6328	0.2186	0.140*
H1D	0.1250	-0.7105	0.1966	0.140*
C2	0.1409 (3)	-0.4424 (6)	0.2453 (4)	0.0623 (11)
C3	0.1475 (3)	-0.2912 (6)	0.1764 (4)	0.0673 (11)
H3C	0.1101	-0.2917	0.0900	0.081*
C4	0.2085 (3)	-0.1380 (6)	0.2323 (3)	0.0583 (10)
H4A	0.2112	-0.0376	0.1834	0.070*
C5	0.2653 (3)	-0.1341 (5)	0.3606 (3)	0.0449 (8)
C6	0.2590 (3)	-0.2873 (5)	0.4300 (4)	0.0568 (9)
H6A	0.2967	-0.2886	0.5164	0.068*
C7	0.1975 (4)	-0.4375 (5)	0.3720 (4)	0.0640 (11)
H7A	0.1943	-0.5384	0.4203	0.077*
C8	0.3296 (3)	0.0279 (4)	0.4202 (3)	0.0414 (7)
C9	0.4208 (3)	0.2763 (5)	0.5533 (3)	0.0451 (8)

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
S	0.0640 (6)	0.0540 (6)	0.0378 (5)	-0.0091 (4)	0.0267 (4)	0.0006 (4)
N1	0.0611 (17)	0.0532 (17)	0.0353 (14)	-0.0070 (14)	0.0249 (13)	-0.0057 (12)
N2	0.0683 (18)	0.0538 (18)	0.0387 (15)	-0.0117 (15)	0.0305 (14)	-0.0064 (13)
N3	0.097 (3)	0.070 (2)	0.0441 (17)	-0.0336 (19)	0.0401 (17)	-0.0159 (15)
C1	0.095 (3)	0.086 (4)	0.108 (4)	-0.041 (3)	0.046 (3)	-0.035 (3)
C2	0.063 (2)	0.058 (2)	0.076 (3)	-0.0128 (19)	0.037 (2)	-0.019 (2)

## supplementary materials

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C3	0.072 (3)	0.080 (3)	0.053 (2)	-0.016 (2)	0.024 (2)	-0.015 (2)
C4	0.072 (2)	0.059 (2)	0.046 (2)	-0.011 (2)	0.0240 (18)	-0.0032 (17)
C5	0.0524 (19)	0.0435 (18)	0.0451 (18)	0.0001 (15)	0.0247 (16)	-0.0016 (14)
C6	0.064 (2)	0.051 (2)	0.055 (2)	-0.0024 (18)	0.0193 (18)	0.0026 (18)
C7	0.070 (2)	0.045 (2)	0.084 (3)	-0.0041 (19)	0.034 (2)	0.005 (2)
C8	0.0544 (19)	0.0384 (17)	0.0370 (16)	0.0016 (15)	0.0224 (15)	-0.0011 (13)
C9	0.0540 (19)	0.0482 (19)	0.0380 (17)	-0.0039 (16)	0.0218 (15)	0.0008 (14)

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

S—C9	1.742 (3)	C2—C7	1.368 (6)
S—C8	1.745 (3)	C2—C3	1.376 (6)
N1—C8	1.292 (4)	C3—C4	1.387 (6)
N1—N2	1.382 (4)	C3—H3C	0.9300
N2—C9	1.309 (4)	C4—C5	1.385 (5)
N3—C9	1.335 (4)	C4—H4A	0.9300
N3—H3A	0.8600	C5—C6	1.390 (5)
N3—H3B	0.8600	C5—C8	1.468 (5)
C1—C2	1.512 (6)	C6—C7	1.380 (5)
C1—H1B	0.9600	C6—H6A	0.9300
C1—H1C	0.9600	C7—H7A	0.9300
C1—H1D	0.9600		
C9—S—C8	86.96 (15)	C5—C4—C3	120.3 (4)
C8—N1—N2	114.0 (3)	C5—C4—H4A	119.9
C9—N2—N1	112.0 (3)	C3—C4—H4A	119.9
C9—N3—H3A	120.0	C4—C5—C6	117.9 (3)
C9—N3—H3B	120.0	C4—C5—C8	120.4 (3)
H3A—N3—H3B	120.0	C6—C5—C8	121.6 (3)
C2—C1—H1B	109.5	C7—C6—C5	120.6 (4)
C2—C1—H1C	109.5	C7—C6—H6A	119.7
H1B—C1—H1C	109.5	C5—C6—H6A	119.7
C2—C1—H1D	109.5	C2—C7—C6	121.9 (4)
H1B—C1—H1D	109.5	C2—C7—H7A	119.1
H1C—C1—H1D	109.5	C6—C7—H7A	119.1
C7—C2—C3	117.6 (4)	N1—C8—C5	125.2 (3)
C7—C2—C1	121.2 (4)	N1—C8—S	113.2 (2)
C3—C2—C1	121.2 (4)	C5—C8—S	121.6 (2)
C2—C3—C4	121.8 (4)	N2—C9—N3	124.1 (3)
C2—C3—H3C	119.1	N2—C9—S	113.8 (3)
C4—C3—H3C	119.1	N3—C9—S	122.2 (2)
C8—N1—N2—C9	-0.4 (4)	N2—N1—C8—S	0.5 (4)
C7—C2—C3—C4	-0.4 (6)	C4—C5—C8—N1	-30.4 (5)
C1—C2—C3—C4	179.9 (4)	C6—C5—C8—N1	149.7 (4)
C2—C3—C4—C5	0.3 (6)	C4—C5—C8—S	148.1 (3)
C3—C4—C5—C6	0.1 (6)	C6—C5—C8—S	-31.8 (4)
C3—C4—C5—C8	-179.8 (3)	C9—S—C8—N1	-0.3 (3)
C4—C5—C6—C7	-0.3 (5)	C9—S—C8—C5	-179.0 (3)
C8—C5—C6—C7	179.6 (3)	N1—N2—C9—N3	-179.9 (3)
C3—C2—C7—C6	0.2 (6)	N1—N2—C9—S	0.1 (4)

C1—C2—C7—C6	179.9 (4)	C8—S—C9—N2	0.1 (3)
C5—C6—C7—C2	0.2 (6)	C8—S—C9—N3	-179.9 (3)
N2—N1—C8—C5	179.1 (3)		

*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>
N3—H3A $\cdots$ N2 <sup>i</sup>	0.86	2.13	2.970 (5)	166
N3—H3B $\cdots$ N1 <sup>ii</sup>	0.86	2.18	3.025 (4)	166

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

Fig. 1

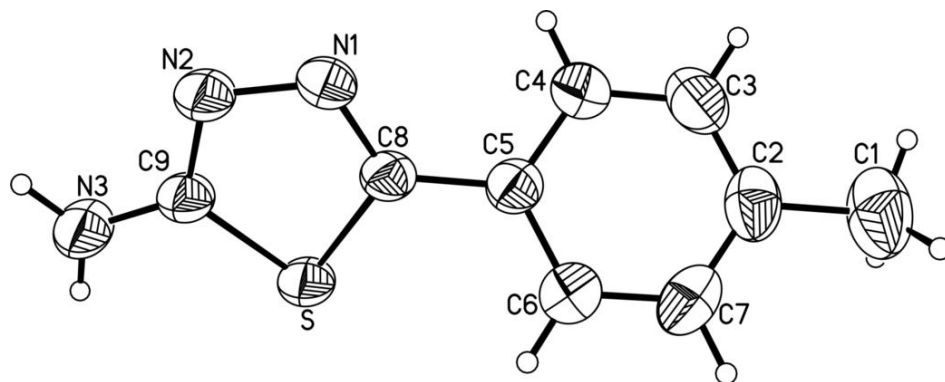


Fig. 2

