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

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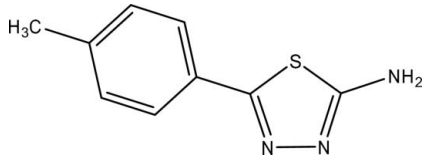
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.006 Å; R factor = 0.059; wR factor = 0.181; data-to-parameter ratio = 15.9.

The title compound, $C_9H_9N_3S$, 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)° with the phenyl ring. In the crystal, molecules are linked by N—H···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

$C_9H_9N_3S$
M_r = 191.25
Monoclinic, $P2_1/c$
a = 12.284 (3) Å
b = 7.3730 (15) Å
c = 11.263 (2) Å
β = 109.09 (3)°
V = 964.0 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.29 mm^{-1}
T = 293 K
0.30 × 0.10 × 0.10 mm

Data collection

Nonius CAD4 diffractometer
Absorption correction: ψ 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_{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
$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.43 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3A···N2^{i}	0.86	2.13	2.970 (5)	166
N3—H3B···N1^{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*.

The authors thank Professor Hua-Qin Wang of the Analysis Centre, Nanjing University, for collecting the crystallographic data.

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

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Enraf–Nonius (1989). *CAD-4 Software*. Enraf–Nonius, Delft, The Netherlands.
Han, F., Wan, R., Wu, W.-Y., Zhang, J.-J. & Wang, J.-T. (2007). *Acta Cryst.* E**63**, o717–o718.
Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg, Germany.
Nakagawa, Y., Nishimura, K., Izumi, K., Kinoshita, K., Kimura, T. & Kurihara, N. (1996). *J. Pestic. Sci.* **21**, 195-201.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Wang, Y. G., Cao, L., Yan, J., Ye, W. F., Zhou, Q. C. & Lu, B. X. (1999). *Chem. J. Chin. Univ.* **20**, 1903–1905.

supporting information

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

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S1. 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).

S2. 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.

S3. 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_{iso}(H) = 1.2 or 1.5U_{eq} of the carrier atom.

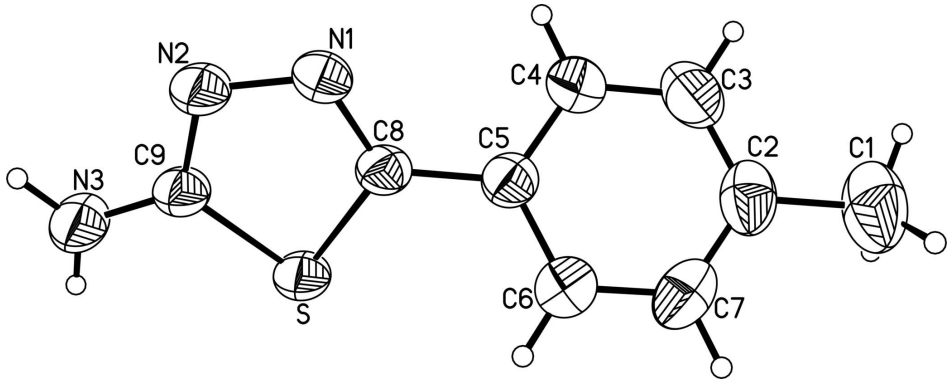

Figure 1

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

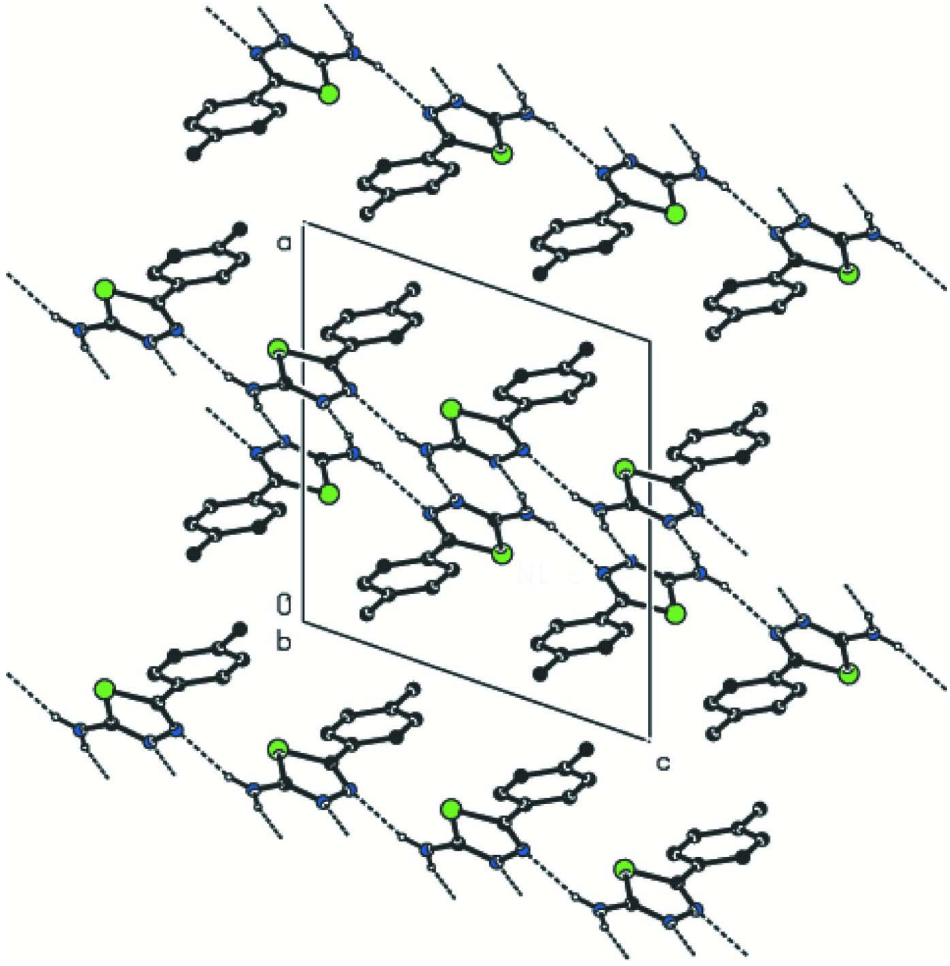

Figure 2

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

$C_9H_9N_3S$
$M_r = 191.25$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 12.284$ (3) Å
$b = 7.3730$ (15) Å
$c = 11.263$ (2) Å
$\beta = 109.09$ (3)°
$V = 964.0$ (3) Å^3
$Z = 4$

$F(000) = 400$
$D_x = 1.318$ Mg m^{-3}
Melting point = 476–478 K
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 9$–13°
$\mu = 0.29$ mm^{-1}
$T = 293$ K
Block, colourless
0.30 × 0.10 × 0.10 mm

Data collection

Nonius CAD4 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator

$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.918$, $T_{max} = 0.972$

1963 measured reflections
1875 independent reflections
1351 reflections with $I > 2\sigma(I)$
$R_{int} = 0.067$
$\theta_{max} = 26.0°$, $\theta_{min} = 1.8°$
$h = -15 \rightarrow 0$
$k = 0 \rightarrow 9$
$l = -13 \rightarrow 13$
3 standard reflections every 200 reflections
intensity decay: 1%

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.181$
$S = 1.01$
1875 reflections
118 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
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2 + 0.5P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.26$ e Å^{-3}
$\Delta\rho_{min} = -0.43$ e Å^{-3}

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}
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 (Å²)

	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)
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 (Å, º)

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, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3*A*···N2^{i}	0.86	2.13	2.970 (5)	166
N3—H3*B*···N1^{ii}	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.