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

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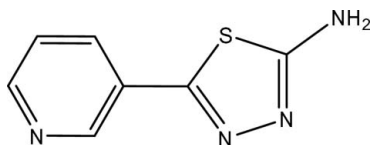
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Key indicators: single-crystal X-ray study; $T = 294$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.043; wR factor = 0.132; data-to-parameter ratio = 13.4.

The title compound, $\text{C}_7\text{H}_6\text{N}_4\text{S}$, was synthesized by reacting pyridine-3-carboxylic acid and thiosemicarbazide. The dihedral angle between the planes of the thiadiazole and pyridine rings is $32.42(14)^\circ$. In the crystal structure, intermolecular $\text{N}-\text{H}\cdots\text{N}$ interactions link the molecules into a three-dimensional network, forming $R_2^2(8)$ ring motifs. $\pi-\pi$ contacts between thiadiazole rings [centroid-centroid distance = $3.666(1)$ Å] may further stabilize the structure.

Related literature

For general background, see: Nakagawa *et al.* (1996); Wang *et al.* (1999). For a related structure, see: Wang *et al.* (2009). For bond-length data, see: Allen *et al.* (1987). For ring-motifs, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$\text{C}_7\text{H}_6\text{N}_4\text{S}$
 $M_r = 178.22$
Monoclinic, $P2_1/c$
 $a = 11.066(2)$ Å
 $b = 7.2380(14)$ Å
 $c = 11.271(2)$ Å
 $\beta = 116.79(3)^\circ$

$V = 805.9(3)$ Å³
 $Z = 4$
Mo $K\alpha$ radiation
 $\mu = 0.35$ mm⁻¹
 $T = 294$ K
 $0.10 \times 0.05 \times 0.05$ mm

Data collection

Enraf-Nonius CAD-4 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.966$, $T_{\max} = 0.983$
1542 measured reflections

1464 independent reflections
1220 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.026$
3 standard reflections
frequency: 120 min
intensity decay: 1%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.132$
 $S = 1.01$
1464 reflections

109 parameters
H-atom parameters constrained
 $\Delta\rho_{\max} = 0.29$ e Å⁻³
 $\Delta\rho_{\min} = -0.34$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N4}-\text{H4A}\cdots\text{N3}^i$	0.86	2.13	2.959(3)	163
$\text{N4}-\text{H4B}\cdots\text{N2}^{ii}$	0.86	2.16	3.006(3)	168

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

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989); cell refinement: *CAD-4 Software*; 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: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97*.

The authors gratefully acknowledge Professor Hua-Qin Wang of the Analysis Center, Nanjing University, for providing the Enraf-Nonius CAD-4 diffractometer for this research project.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HK2699).

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supplementary materials

Acta Cryst. (2009). E65, o1447 [doi:10.1107/S1600536809019564]

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

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Comment

1,3,4-Thiadiazole derivatives represent an interesting class of compounds possessing broad spectrum biological activities (Nakagawa *et al.*, 1996). These compounds are known to exhibit diverse biological effects, such as insecticidal and fungicidal activities (Wang *et al.*, 1999). We report herein the crystal structure of the title compound.

In the molecule of the title compound (Fig 1), the bond lengths (Allen *et al.*, 1987) and angles are within normal ranges, and are in accordance with the corresponding values in 5-(4-pyridyl)-1,3,4-thiadiazol-2-amine (Wang *et al.*, 2009). Rings A (N1/C1–C5) and B (S/N2/N3/C6/C7) are, of course, planar, and they are oriented at a dihedral angle of 32.42 (14)°.

In the crystal structure, intermolecular N—H···N interactions (Table 1) link the molecules into a three-dimensional network forming $R_2^2(8)$ ring motifs (Bernstein *et al.*, 1995) (Fig. 2), in which they may be effective in the stabilization of the structure. The π – π contact between the thiadiazole rings, Cg2—Cg2ⁱ, [symmetry code: (i) 1 - x, -y, 1 - z, where Cg2 is centroid of the ring B (S/N2/N3/C6/C7)] may further stabilize the structure, with centroid–centroid distance of 3.666 (1) Å.

Experimental

For the preparation of the title compound, 3-pyridine carboxylic acid (2 mmol) and thiosemicarbazide (5 mmol) were mixed in a 25 ml flask, and kept in the oil bath at 363 K for 6 h. After cooling, the crude product precipitated and was filtered. Crystals of suitable for X-ray analysis were obtained by slow evaporation of an acetone solution.

Refinement

H atoms were positioned geometrically, with N—H = 0.86 Å (for NH₂) and C—H = 0.93 Å for aromatic H and constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N})$.

Figures

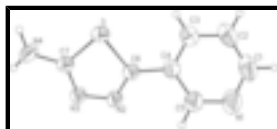


Fig. 1. The molecular structure of the title molecule, with the atom-numbering scheme. Displacement ellipsoids at the 50% probability level.

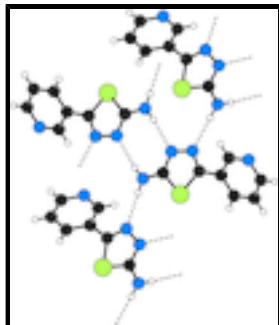


Fig. 2. A partial packing diagram of the title compound. Hydrogen bonds are shown as dashed lines.

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

Crystal data

$C_7H_6N_4S$

$M_r = 178.22$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2ybc$

$a = 11.066\ (2)\ \text{\AA}$

$b = 7.2380\ (14)\ \text{\AA}$

$c = 11.271\ (2)\ \text{\AA}$

$\beta = 116.79\ (3)^\circ$

$V = 805.9\ (3)\ \text{\AA}^3$

$Z = 4$

$F_{000} = 368$

$D_x = 1.469\ \text{Mg m}^{-3}$

Melting point: 550 K

Mo $K\alpha$ radiation

$\lambda = 0.71073\ \text{\AA}$

Cell parameters from 25 reflections

$\theta = 9\text{--}12^\circ$

$\mu = 0.35\ \text{mm}^{-1}$

$T = 294\ \text{K}$

Block, colourless

$0.10 \times 0.05 \times 0.05\ \text{mm}$

Data collection

Enraf–Nonius CAD-4
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 294\ \text{K}$

$\omega/2\theta$ scans

Absorption correction: ψ scan
(North *et al.*, 1968)

$T_{\min} = 0.966$, $T_{\max} = 0.983$

1542 measured reflections

1464 independent reflections

1220 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.026$

$\theta_{\max} = 25.3^\circ$

$\theta_{\min} = 2.1^\circ$

$h = 0 \rightarrow 13$

$k = 0 \rightarrow 8$

$l = -13 \rightarrow 12$

3 standard reflections

every 120 min

intensity decay: 1%

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.043$

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$wR(F^2) = 0.132$	$w = 1/[\sigma^2(F_o^2) + (0.098P)^2]$
$S = 1.01$	where $P = (F_o^2 + 2F_c^2)/3$
1464 reflections	$(\Delta/\sigma)_{\max} < 0.001$
109 parameters	$\Delta\rho_{\max} = 0.29 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\min} = -0.34 \text{ e } \text{\AA}^{-3}$
	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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
S	0.69244 (6)	0.09005 (8)	0.45516 (5)	0.0434 (3)
N1	0.9145 (3)	-0.2801 (4)	0.8931 (2)	0.0717 (7)
N2	0.63999 (19)	0.1376 (3)	0.65128 (17)	0.0421 (5)
N3	0.57605 (19)	0.2824 (3)	0.56552 (18)	0.0441 (5)
N4	0.5428 (3)	0.3989 (3)	0.3599 (2)	0.0595 (7)
H4A	0.4944	0.4890	0.3645	0.071*
H4B	0.5580	0.3880	0.2918	0.071*
C1	0.9215 (3)	-0.4300 (4)	0.8284 (3)	0.0634 (8)
H1B	0.9692	-0.5315	0.8782	0.076*
C2	0.8626 (3)	-0.4435 (4)	0.6931 (3)	0.0628 (8)
H2B	0.8714	-0.5509	0.6523	0.075*
C3	0.7896 (3)	-0.2946 (3)	0.6177 (3)	0.0547 (7)
H3B	0.7483	-0.3004	0.5253	0.066*
C4	0.7792 (2)	-0.1374 (3)	0.6817 (2)	0.0407 (5)
C5	0.8440 (3)	-0.1375 (4)	0.8191 (3)	0.0578 (7)
H5A	0.8380	-0.0315	0.8628	0.069*
C6	0.7037 (2)	0.0273 (3)	0.6091 (2)	0.0378 (5)
C7	0.5946 (2)	0.2753 (3)	0.4591 (2)	0.0407 (5)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S	0.0559 (4)	0.0461 (4)	0.0383 (4)	0.0125 (2)	0.0303 (3)	0.0041 (2)
N1	0.0875 (17)	0.0765 (17)	0.0569 (14)	0.0339 (14)	0.0375 (13)	0.0256 (13)
N2	0.0544 (11)	0.0423 (11)	0.0395 (10)	0.0099 (9)	0.0298 (9)	0.0079 (8)

supplementary materials

N3	0.0609 (12)	0.0421 (11)	0.0427 (11)	0.0143 (9)	0.0353 (9)	0.0107 (8)
N4	0.0877 (16)	0.0626 (15)	0.0468 (12)	0.0360 (12)	0.0467 (12)	0.0221 (10)
C1	0.0656 (17)	0.0579 (18)	0.078 (2)	0.0224 (13)	0.0426 (16)	0.0289 (14)
C2	0.0675 (17)	0.0420 (15)	0.088 (2)	0.0143 (12)	0.0426 (16)	0.0072 (13)
C3	0.0616 (16)	0.0471 (15)	0.0563 (15)	0.0085 (12)	0.0273 (13)	0.0009 (12)
C4	0.0430 (12)	0.0419 (13)	0.0456 (13)	0.0048 (10)	0.0275 (10)	0.0068 (10)
C5	0.0728 (17)	0.0574 (16)	0.0491 (14)	0.0208 (13)	0.0327 (13)	0.0100 (12)
C6	0.0428 (12)	0.0396 (12)	0.0367 (11)	0.0026 (9)	0.0229 (10)	0.0034 (9)
C7	0.0505 (12)	0.0425 (12)	0.0359 (11)	0.0087 (10)	0.0256 (10)	0.0030 (9)

Geometric parameters (\AA , $^\circ$)

S—C6	1.743 (2)	C1—C2	1.366 (4)
S—C7	1.736 (2)	C1—H1B	0.9300
N1—C1	1.329 (4)	C2—C3	1.385 (4)
N1—C5	1.335 (3)	C2—H2B	0.9300
N2—N3	1.384 (2)	C3—C4	1.379 (3)
N2—C6	1.289 (3)	C3—H3B	0.9300
N3—C7	1.306 (3)	C4—C5	1.383 (3)
N4—C7	1.342 (3)	C4—C6	1.474 (3)
N4—H4A	0.8600	C5—H5A	0.9300
N4—H4B	0.8600		
C7—S—C6	86.65 (10)	C4—C3—H3B	120.5
C1—N1—C5	116.8 (3)	C2—C3—H3B	120.5
C6—N2—N3	113.79 (18)	C3—C4—C5	117.5 (2)
C7—N3—N2	111.67 (17)	C3—C4—C6	122.5 (2)
C7—N4—H4A	120.0	C5—C4—C6	120.0 (2)
C7—N4—H4B	120.0	N1—C5—C4	124.1 (3)
H4A—N4—H4B	120.0	N1—C5—H5A	117.9
N1—C1—C2	123.7 (2)	C4—C5—H5A	117.9
N1—C1—H1B	118.2	N2—C6—C4	124.3 (2)
C2—C1—H1B	118.2	N2—C6—S	113.59 (17)
C1—C2—C3	118.8 (3)	C4—C6—S	122.13 (16)
C1—C2—H2B	120.6	N3—C7—N4	123.6 (2)
C3—C2—H2B	120.6	N3—C7—S	114.30 (16)
C4—C3—C2	119.0 (3)	N4—C7—S	122.07 (16)
C5—N1—C1—C2	0.9 (5)	C3—C4—C6—N2	147.8 (2)
N1—C1—C2—C3	-0.9 (5)	C5—C4—C6—N2	-32.8 (3)
C6—N2—N3—C7	0.0 (3)	C3—C4—C6—S	-32.0 (3)
C1—C2—C3—C4	0.2 (4)	C5—C4—C6—S	147.4 (2)
C2—C3—C4—C5	0.5 (4)	C7—S—C6—N2	-0.09 (18)
C2—C3—C4—C6	179.9 (2)	C7—S—C6—C4	179.73 (19)
C1—N1—C5—C4	-0.1 (5)	N2—N3—C7—N4	179.7 (2)
C3—C4—C5—N1	-0.6 (4)	N2—N3—C7—S	-0.1 (3)
C6—C4—C5—N1	180.0 (3)	C6—S—C7—N3	0.10 (19)
N3—N2—C6—C4	-179.8 (2)	C6—S—C7—N4	-179.7 (2)
N3—N2—C6—S	0.1 (3)		

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>
N4—H4A···N3 ⁱ	0.86	2.13	2.959 (3)	163
N4—H4B···N2 ⁱⁱ	0.86	2.16	3.006 (3)	168

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

Fig. 1

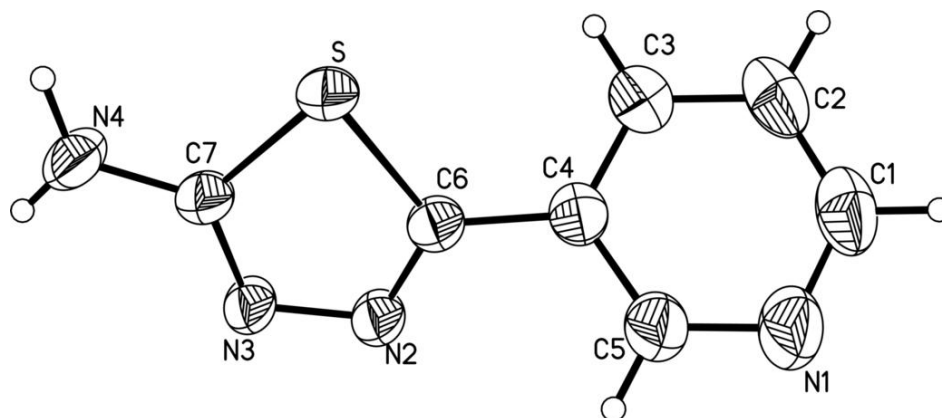


Fig. 2

