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N-(3-Pyridylmethylene)-*N*′-[5-(3-pyridylmethylsulfanyl)-1,3,4-thiadiazol-2-yl]hydrazine

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Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.004 Å
R factor = 0.043
wR factor = 0.049
Data-to-parameter ratio = 10.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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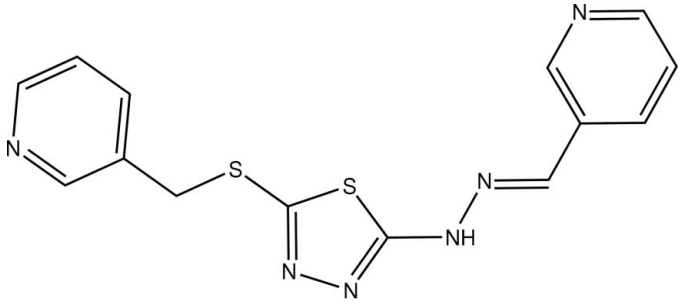
In the crystal structure of the title compound, $C_{14}H_{12}N_6S_2$, the molecules are linked into centrosymmetric dimers through N—H···N hydrogen interactions, forming two-dimensional layers parallel to (010).

Comment

1,3,4-Thiadiazole derivatives have been synthesized for their potential bioactivity. They have been used as herbicides and insecticides, and some of them are known to possess antimycobacterial, anesthetic and antidepressant activity (Demirbas *et al.*, 2004; Mamolo *et al.*, 2001; Orú *et al.*, 2004). The structure can be varied to explore the structure–activity relationship by substituting the alkyl or aryl groups at either end of the molecule. In the course of our research, we have managed to grow crystals of the title compound, (I), from ethanol.



(I)

In the crystal structure, the molecule is L-shaped, with the pyridine ring containing N1 bent at C6 with an angle of 112.42 (16)° for C4—C6—S1, while the rest of the molecule is nearly coplanar with the thiadiazole plane. The pyridine rings are *trans* to each other, as shown in Fig. 1. The C7—S2—C8 bond angle of 85.84 (11)° is at the lower end of the range reported in the literature (Vinkovic *et al.*, 1994), possibly due to the presence of two strong electron-donating atoms (S1 and N4) at either side of the ring. In the crystal structure, the molecules are linked through N—H···N hydrogen interactions (Table 2) into centrosymmetric dimers, forming two-dimensional layers parallel to (010).

Experimental

The title compound was synthesized according to the procedure described by Crouse *et al.* (2004). Brown–orange block-shaped crystals suitable for X-ray analysis were isolated after two weeks by slow evaporation of an ethanol solution of the crude product at room temperature.

Crystal data

$C_{14}H_{12}N_6S_2$
M_r = 328.42
Triclinic, $P\overline{1}$
a = 4.5955 (2) Å
b = 11.4301 (4) Å
c = 14.8292 (6) Å
α = 74.1696 (12)°
β = 83.0827 (14)°
γ = 80.8197 (13)°
V = 737.36 (5) Å^3
Z = 2
D_x = 1.479 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2920 reflections
θ = 1–27°
μ = 0.37 mm^{-1}
T = 150 K
Block, brown–orange
0.01 × 0.01 × 0.01 mm

Data collection

Nonius KappaCCD diffractometer
ω scans
Absorption correction: multi-scan *DENZO/SCALEPACK* (Otwinowski & Minor, 1997)
T_{min} = 1.00, T_{max} = 1.00
5604 measured reflections
3327 independent reflections
2154 reflections with $I > 3\sigma(I)$
R_{int} = 0.026
θ_{max} = 27.6°
$h = -5 \rightarrow 5$
$k = -14 \rightarrow 14$
$l = -18 \rightarrow 19$

Refinement

Refinement on F
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.049
S = 1.07
2154 reflections
203 parameters
H atoms treated by a mixture of independent and constrained refinement
Method, part 1, Chebychev polynomial (Watkin, 1994; Prince, 1982), [weight] = 1.0/[A_0*$T_0(x)$ + A_1*$T_1(x)$ ··· + A_{n-1}]*$T_{n-1}(x)$], where A_i are the Chebychev coefficients listed below and x = F/F_{max}. Method = robust weighting (Prince, 1982), W = [weight] * [1−(δF/6*σF)^2]^2, A_i are: 1.61, 0.745 and 1.30
$(\Delta/\sigma)_{max}$ < 0.001
$\Delta\rho_{max}$ = 0.39 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C6	1.831 (3)	N2—C7	1.298 (3)
S1—C7	1.746 (3)	N3—C8	1.310 (3)
S2—C7	1.750 (3)	N4—N5	1.372 (3)
S2—C8	1.727 (2)	N4—C8	1.357 (3)
N1—C1	1.336 (5)	N5—C9	1.281 (3)
N1—C2	1.344 (4)	N6—C13	1.344 (4)
N2—N3	1.392 (3)	N6—C14	1.344 (4)
C6—S1—C7	100.67 (12)	C4—C6—S1	112.42 (18)
C7—S2—C8	85.84 (11)	S2—C7—S1	119.78 (14)
C1—N1—C2	116.9 (3)	S2—C7—N2	114.84 (19)
N3—N2—C7	112.2 (2)	S1—C7—N2	125.4 (2)
N2—N3—C8	111.8 (2)	S2—C8—N4	122.56 (19)
N5—N4—C8	117.9 (2)	S2—C8—N3	115.38 (18)
N4—N5—C9	115.5 (2)	N4—C8—N3	122.1 (2)
C13—N6—C14	117.3 (3)	N5—C9—C10	120.9 (2)
N1—C1—C3	123.3 (3)	C12—C13—N6	123.2 (3)
N1—C2—C4	124.3 (3)	C10—C14—N6	123.7 (3)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N4—H7···N3^{i}	0.90 (4)	1.98 (4)	2.849 (3)	164 (3)

Symmetry code: (i) $-x, -y+1, -z$.

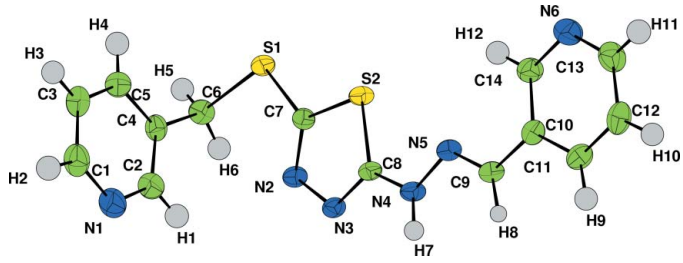


Figure 1
The molecular structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

The N-bound H atom was located in a difference map and refined freely. All C-bound H atoms were located in a difference map and initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C–H 0.93–98 Å) and isotropic atomic displacement parameters [U_{iso}(H) = 1.2 or 1.5U_{eq}(parent atom)], after which they were refined with riding constraints.

Data collection: *COLLECT* (Nonius, 2001); cell refinement: *DENZO/SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO/SCALEPACK*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *CRYSTALS*.

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The crystal structure forms an *L*-shaped molecule, with the pyridine ring containing N1 bent at C6 with an angle of 112.4 (3)°, while the rest of the molecule is nearly coplanar with the thiadiazole plane. The pyridine rings are *trans* to each other at both ends of the molecule, as shown in Fig. 1. The C7—S2—C8 bond angle of 85.9 (2)° is at the lower end of the range reported in the literature (reference?), possibly due to the presence of two strong electron-donating atoms (S1 and N4) at either side of the ring. In the crystal structure, the molecules are linked through N—H···N hydrogen interactions (Table 2) into centrosymmetric dimers, forming two-dimensional layers parallel to the *b* axis.

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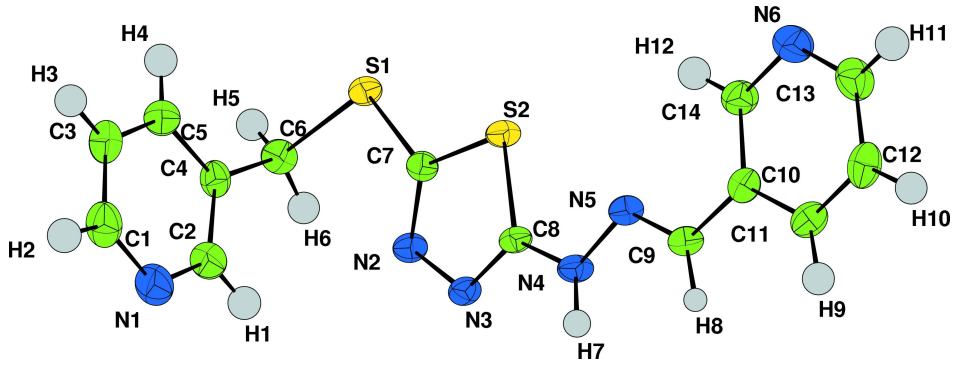
The N-bound H atom was located in a difference map and refined freely. All C-bound H atoms were located in a difference map and initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C–H 0.93–98 Å) and isotropic atomic displacement parameters [U_{iso}(H) = 1.2 or 1.5U_{eq}(parent atom)], after which they were refined with riding constraints.



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$h = -5\rightarrow5$
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$l = -18\rightarrow19$

Refinement

Refinement on F
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.049$
$S = 1.07$
2154 reflections
203 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
Method, part 1, Chebychev polynomial, (Watkin, 1994, *P*rince, 1982) [*w*eight] = $1.0/[A_0*T_0(x) + A_1*T_1(x) \cdots + A_{n-1}]*T_{n-1}(x)]$ where A_i are the Chebychev coefficients listed below and x = F /Fmax Method = Robust Weighting (*P*rince, 1982) W = [*w*eight] * $[1-(\delta F/6*\sigma F)^2]^2$ A_i are: 1.61 0.745 1.30
$(\Delta/\sigma)_{max} = 0.000202$
$\Delta\rho_{max} = 0.39$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
H1	−0.5252	0.6025	0.2993	0.0689*
H2	−0.0376	0.6182	0.5004	0.0730*
H3	−0.1511	0.8256	0.4622	0.0640*
H4	−0.4378	0.9288	0.3448	0.0680*
H5	−0.8580	0.8962	0.2436	0.0629*
H6	−0.7873	0.7770	0.2057	0.0630*
H7	0.257 (8)	0.543 (3)	−0.056 (2)	0.040 (8)*
H8	0.6066	0.5559	−0.1666	0.0340*
H9	1.0196	0.5613	−0.2946	0.0650*
H10	1.3262	0.6734	−0.4067	0.0640*
H11	1.3413	0.8767	−0.4148	0.0719*
H12	0.7091	0.8710	−0.2088	0.0669*
S1	−0.48631 (14)	0.92252 (5)	0.12260 (5)	0.0289
S2	0.00314 (14)	0.82978 (5)	−0.00637 (5)	0.0271
N1	−0.2752 (7)	0.5872 (2)	0.40325 (18)	0.0483
N2	−0.3359 (5)	0.68790 (18)	0.10971 (16)	0.0282
N3	−0.1392 (5)	0.61232 (18)	0.06430 (15)	0.0279
N4	0.2561 (5)	0.6195 (2)	−0.05079 (16)	0.0285
N5	0.4411 (5)	0.69178 (19)	−0.11336 (15)	0.0275
N6	1.0191 (6)	0.8947 (3)	−0.3149 (2)	0.0465
C1	−0.1688 (7)	0.6541 (3)	0.4497 (2)	0.0451
C2	−0.4437 (7)	0.6487 (3)	0.3328 (2)	0.0409
C3	−0.2263 (7)	0.7802 (3)	0.4293 (2)	0.0418
C4	−0.5131 (6)	0.7752 (2)	0.30629 (18)	0.0309
C5	−0.4004 (7)	0.8419 (3)	0.3564 (2)	0.0373
C6	−0.7004 (6)	0.8379 (2)	0.22499 (19)	0.0322
C7	−0.2880 (5)	0.8016 (2)	0.08095 (17)	0.0260
C8	0.0471 (5)	0.6741 (2)	0.00293 (17)	0.0242
C9	0.6176 (6)	0.6381 (2)	−0.16785 (19)	0.0292
C10	0.8247 (5)	0.7047 (2)	−0.23758 (18)	0.0292
C11	1.0169 (6)	0.6457 (3)	−0.2966 (2)	0.0349
C12	1.2071 (7)	0.7114 (3)	−0.3634 (2)	0.0423
C13	1.2005 (7)	0.8349 (3)	−0.3706 (2)	0.0445
C14	0.8345 (6)	0.8298 (3)	−0.2502 (2)	0.0355

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0334 (3)	0.0211 (3)	0.0310 (3)	0.0010 (2)	−0.0009 (3)	−0.0080 (2)
S2	0.0270 (3)	0.0201 (3)	0.0343 (4)	−0.0028 (2)	−0.0002 (2)	−0.0083 (2)
N1	0.0661 (18)	0.0356 (13)	0.0370 (14)	0.0067 (12)	−0.0094 (13)	−0.0042 (11)
N2	0.0291 (11)	0.0212 (10)	0.0335 (11)	0.0002 (8)	−0.0021 (9)	−0.0080 (8)
N3	0.0284 (11)	0.0221 (10)	0.0327 (11)	−0.0009 (8)	0.0026 (9)	−0.0097 (8)
N4	0.0285 (10)	0.0211 (10)	0.0364 (12)	−0.0037 (8)	0.0020 (8)	−0.0098 (8)
N5	0.0228 (10)	0.0259 (10)	0.0342 (11)	−0.0016 (8)	−0.0018 (8)	−0.0095 (8)

N6	0.0522 (16)	0.0396 (14)	0.0468 (15)	−0.0141 (12)	0.0065 (12)	−0.0096 (11)
C1	0.0476 (17)	0.0492 (17)	0.0327 (15)	0.0081 (14)	−0.0076 (13)	−0.0074 (13)
C2	0.0511 (18)	0.0330 (14)	0.0363 (14)	−0.0028 (12)	−0.0012 (13)	−0.0076 (12)
C3	0.0427 (16)	0.0501 (17)	0.0335 (15)	−0.0046 (13)	−0.0028 (12)	−0.0135 (13)
C4	0.0262 (12)	0.0354 (13)	0.0287 (12)	−0.0006 (10)	0.0016 (10)	−0.0082 (10)
C5	0.0414 (15)	0.0333 (14)	0.0366 (14)	−0.0036 (11)	−0.0028 (12)	−0.0092 (11)
C6	0.0282 (13)	0.0320 (13)	0.0351 (14)	−0.0019 (10)	−0.0011 (10)	−0.0080 (11)
C7	0.0243 (11)	0.0247 (11)	0.0280 (12)	−0.0019 (9)	−0.0039 (9)	−0.0051 (9)
C8	0.0233 (11)	0.0202 (10)	0.0297 (12)	−0.0014 (9)	−0.0053 (9)	−0.0069 (9)
C9	0.0292 (13)	0.0236 (11)	0.0354 (13)	−0.0039 (9)	−0.0021 (10)	−0.0087 (10)
C10	0.0236 (12)	0.0342 (13)	0.0311 (13)	−0.0028 (10)	−0.0052 (10)	−0.0100 (10)
C11	0.0309 (13)	0.0361 (14)	0.0398 (14)	−0.0018 (11)	−0.0018 (11)	−0.0151 (12)
C12	0.0325 (14)	0.0594 (19)	0.0382 (15)	−0.0037 (13)	0.0006 (12)	−0.0207 (14)
C13	0.0404 (16)	0.0528 (19)	0.0403 (16)	−0.0153 (14)	0.0021 (13)	−0.0089 (14)
C14	0.0352 (14)	0.0321 (13)	0.0404 (15)	−0.0064 (11)	0.0011 (11)	−0.0120 (11)

Geometric parameters (Å, º)

H1—C2	0.958	N2—N3	1.392 (3)
H2—C1	0.980	N2—C7	1.298 (3)
H3—C3	0.929	N3—C8	1.310 (3)
H4—C5	0.952	N4—N5	1.372 (3)
H5—C6	0.971	N4—C8	1.357 (3)
H6—C6	0.976	N5—C9	1.281 (3)
H7—N4	0.90 (4)	N6—C13	1.344 (4)
H8—C9	0.944	N6—C14	1.344 (4)
H9—C11	0.956	C1—C3	1.377 (5)
H10—C12	0.945	C2—C4	1.385 (4)
H11—C13	0.950	C3—C5	1.385 (4)
H12—C14	0.958	C4—C5	1.389 (4)
S1—C6	1.831 (3)	C4—C6	1.513 (4)
S1—C7	1.746 (3)	C9—C10	1.456 (4)
S2—C7	1.750 (3)	C10—C11	1.395 (4)
S2—C8	1.727 (2)	C10—C14	1.398 (4)
N1—C1	1.336 (5)	C11—C12	1.380 (4)
N1—C2	1.344 (4)	C12—C13	1.382 (5)
C6—S1—C7	100.67 (12)	C4—C6—H5	110.1
C7—S2—C8	85.84 (11)	S1—C6—H5	107.4
C1—N1—C2	116.9 (3)	H6—C6—H5	109.0
N3—N2—C7	112.2 (2)	S2—C7—S1	119.78 (14)
N2—N3—C8	111.8 (2)	S2—C7—N2	114.84 (19)
H7—N4—N5	118 (2)	S1—C7—N2	125.4 (2)
H7—N4—C8	123 (2)	S2—C8—N4	122.56 (19)
N5—N4—C8	117.9 (2)	S2—C8—N3	115.38 (18)
N4—N5—C9	115.5 (2)	N4—C8—N3	122.1 (2)
C13—N6—C14	117.3 (3)	H8—C9—N5	120.6
H2—C1—N1	123.1	H8—C9—C10	118.4

H2—C1—C3	113.5	N5—C9—C10	120.9 (2)
N1—C1—C3	123.3 (3)	C9—C10—C11	120.6 (2)
H1—C2—N1	118.3	C9—C10—C14	122.0 (2)
H1—C2—C4	117.4	C11—C10—C14	117.3 (3)
N1—C2—C4	124.3 (3)	H9—C11—C10	122.9
H3—C3—C1	122.5	H9—C11—C12	117.5
H3—C3—C5	118.6	C10—C11—C12	119.6 (3)
C1—C3—C5	118.9 (3)	H10—C12—C11	119.7
C2—C4—C5	117.3 (3)	H10—C12—C13	121.2
C2—C4—C6	121.2 (3)	C11—C12—C13	118.9 (3)
C5—C4—C6	121.5 (2)	H11—C13—C12	117.0
H4—C5—C4	124.1	H11—C13—N6	119.7
H4—C5—C3	116.6	C12—C13—N6	123.2 (3)
C4—C5—C3	119.2 (3)	H12—C14—C10	118.4
C4—C6—S1	112.42 (18)	H12—C14—N6	117.9
C4—C6—H6	109.8	C10—C14—N6	123.7 (3)
S1—C6—H6	108.0		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H7···N3^{i}	0.90 (4)	1.98 (4)	2.849 (3)	164 (3)

Symmetry code: (i) −*x*, −*y*+1, −*z*.