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Bis(1,3,4-thiadiazol-2-yl) disulfide

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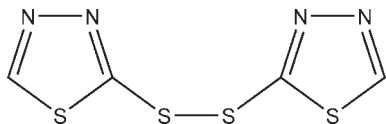
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Key indicators: single-crystal X-ray study; $T = 291$ K; mean $\sigma(\text{N-N}) = 0.002$ Å; R factor = 0.021; wR factor = 0.055; data-to-parameter ratio = 14.2.

The title compound, $\text{C}_4\text{H}_2\text{N}_4\text{S}_4$, lies about a twofold rotation axis situated at the mid-point of the central S—S bond. Each of two thiadiazole rings is essentially planar, with an rms deviation for the unique thiadiazole ring plane of 0.0019 (7) Å. C—H...N hydrogen bonds link adjacent molecules, forming zigzag chains along the c axis. In addition, these chains are connected by intermolecular S...S interactions [$\text{S}\cdots\text{S} = 3.5153$ (11) Å], forming corrugated sheets, and further fabricate a three-dimensional supramolecular structure by intermolecular N...S contacts [$\text{S}\cdots\text{N} = 3.1941$ (17) Å].

Related literature

For potential applications of thiadiazoles, see: Coyanis *et al.* (2002); Wang & Cao (2005). For their use as ligands in transition-metal coordination chemistry, see: Huang *et al.* (2004); Zheng *et al.* (2005). For the structure of bis(2-methyl-1,3,4-thiadiazolyl)-5,5'-disulfide, see: Hipler *et al.* (2003).



Experimental

Crystal data

 $\text{C}_4\text{H}_2\text{N}_4\text{S}_4$ $M_r = 234.34$

Monoclinic, $C2/c$
 $a = 9.706$ (2) Å
 $b = 4.8980$ (12) Å
 $c = 18.008$ (5) Å
 $\beta = 100.074$ (3)°
 $V = 842.9$ (4) Å³

$Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 1.07$ mm⁻¹
 $T = 291$ K
 $0.29 \times 0.20 \times 0.11$ mm

Data collection

Bruker SMART CCD area detector diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 1997)
 $T_{\min} = 0.746$, $T_{\max} = 0.889$

2915 measured reflections
 783 independent reflections
 727 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.017$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.021$
 $wR(F^2) = 0.055$
 $S = 1.11$
 783 reflections

55 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.17$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.26$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C2-H2\cdots N2^i$	0.93	2.52	3.249 (2)	136

Symmetry code: (i) $-x + 1, -y + 2, -z + 1$.

Data collection: SMART (Bruker, 1997); cell refinement: SAINT (Bruker, 1997); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2643).

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supplementary materials

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Bis(1,3,4-thiadiazol-2-yl) disulfide

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Comment

Thiadiazoles have attracted increasing attention because of their potential applications in pharmaceutical, agricultural, industrial, coordination and polymer chemistry (Coyanis *et al.*, 2002, Wang & Cao, 2005). Ligands involving thiadiazole group have also shown interesting coordination chemistry with transition metal ions (Huang *et al.*, 2004; Zheng *et al.*, 2005). Exploring the applications of thiadiazole derivatives as ligands for metal complexation, we report here the synthesis and structure of bis(1,3,4-thiadiazolyl)5,5'-disulfide (I), a new and potentially multi-functional ligand (Fig. 1).

The title compound, $C_4H_2N_4S_4$, lies about a twofold rotation axis situated at the mid-point of the central S–S bond. Each of the thiadiazole rings is essentially planar, with an rms deviation for the unique thiadiazole ring plane of 0.0019 (7) Å. The dihedral angle and centroid-centroid distance between the two thiadiazole rings are 86.64 (44)° and 5.25 (14) Å, respectively. The N1–C1 and N2–C2 bond lengths, 1.298 (2) Å and 1.290 (2) Å, respectively, indicate significant double bond character, which is very similar to the structure of bis(2-methyl-1,3,4-thiadiazolyl)-5,5'-disulfide (Hipler, *et al.*, 2003).

In the crystal structure, molecules of (I) form 1-dimensional zigzag chains by way of weak intermolecular C–H⋯N hydrogen bonds along the *c* axis (Fig. 3). In addition, these chains are linked by intermolecular S⋯S interactions [S2⋯S1 = 3.5153 (11) Å] to form corrugated sheets (Fig. 3). Further intermolecular N⋯S interactions (S2⋯N1 = 3.1941 (17) Å) generate a 3-dimensional supramolecular network structure (Fig. 4).

Experimental

The title compound was prepared by adding hydrogen peroxide (30%, 10.4 mL) drop-wise to a solution of 2-mercapto-1,3,4-thiadiazole (0.2 mol) in ethanol (30 mL) and water (20 mL) at room temperature. The mixture was then refluxed for 6 h. The reaction mixture was taken up in hexane (100 mL), washed with water and brine, and dried with Na_2SO_4 . The solvent was removed under reduced pressure, and the crude product was recrystallised from ethanol to give the title compound as colourless solid in 85% yield. Colorless block-like single crystals were obtained by slow evaporation from ethanol at room temperature.

Refinement

The H atoms were positioned geometrically and treated as riding with $d(C-H) = 0.93$ Å, $U_{iso} = 1.2U_{eq}(C)$

Figures

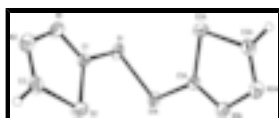


Fig. 1. View of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.



Fig. 2. The 1-dimensional zigzag chain formed by intermolecular C-H...N interactions, shown as dashed lines.

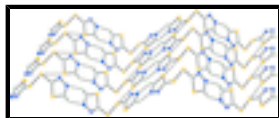


Fig. 3. Corrugated sheets formed by intermolecular C-H...N and S...S interactions, shown as dashed lines.

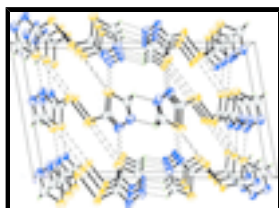


Fig. 4. The 3-dimensional network structure formed by intermolecular C-H...N, S...S and N...S interactions, shown as dashed lines.

Bis(1,3,4-thiadiazol-2-yl) disulfide

Crystal data

$C_4H_2N_4S_4$

$M_r = 234.34$

Monoclinic, $C2/c$

Hall symbol: $-C 2yc$

$a = 9.706 (2) \text{ \AA}$

$b = 4.8980 (12) \text{ \AA}$

$c = 18.008 (5) \text{ \AA}$

$\beta = 100.074 (3)^\circ$

$V = 842.9 (4) \text{ \AA}^3$

$Z = 4$

$F_{000} = 472$

$D_x = 1.847 \text{ Mg m}^{-3}$

Melting point: 384 K

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 1881 reflections

$\theta = 2.3\text{--}28.3^\circ$

$\mu = 1.07 \text{ mm}^{-1}$

$T = 291 \text{ K}$

Block, colorless

$0.29 \times 0.20 \times 0.11 \text{ mm}$

Data collection

Bruker SMART CCD area detector
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 291 \text{ K}$

φ and ω scans

Absorption correction: multi-scan
(SADABS; Bruker, 1997)

$T_{\min} = 0.746$, $T_{\max} = 0.889$

2915 measured reflections

783 independent reflections

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

$R_{\text{int}} = 0.017$

$\theta_{\max} = 25.5^\circ$

$\theta_{\min} = 2.3^\circ$

$h = -11 \rightarrow 11$

$k = -5 \rightarrow 5$

$l = -21 \rightarrow 21$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.021$

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$wR(F^2) = 0.055$	$w = 1/[\sigma^2(F_o^2) + (0.0269P)^2 + 0.5364P]$
$S = 1.11$	where $P = (F_o^2 + 2F_c^2)/3$
783 reflections	$(\Delta/\sigma)_{\max} = 0.001$
55 parameters	$\Delta\rho_{\max} = 0.17 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\min} = -0.26 \text{ e } \text{\AA}^{-3}$
	Extinction correction: none

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes)

are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 $F^2 > 2\sigma(F^2)$ 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	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.58334 (4)	0.20034 (8)	0.72250 (2)	0.03599 (15)
S2	0.37175 (4)	0.60103 (10)	0.63157 (3)	0.04226 (16)
C1	0.53518 (15)	0.4548 (3)	0.65306 (8)	0.0291 (3)
C2	0.43894 (19)	0.7877 (4)	0.56554 (9)	0.0393 (4)
H2	0.3858	0.9153	0.5347	0.047*
N1	0.62594 (14)	0.5425 (3)	0.61357 (8)	0.0388 (3)
N2	0.56803 (16)	0.7391 (3)	0.56152 (8)	0.0414 (4)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0434 (3)	0.0342 (3)	0.0334 (2)	0.00958 (17)	0.01497 (18)	0.00365 (16)

supplementary materials

S2	0.0290 (2)	0.0495 (3)	0.0495 (3)	0.00302 (18)	0.01012 (19)	0.0138 (2)
C1	0.0310 (8)	0.0296 (8)	0.0274 (7)	0.0002 (6)	0.0072 (6)	-0.0023 (6)
C2	0.0433 (10)	0.0400 (10)	0.0333 (9)	-0.0019 (7)	0.0034 (7)	0.0067 (7)
N1	0.0358 (8)	0.0441 (8)	0.0390 (8)	0.0026 (6)	0.0137 (6)	0.0069 (6)
N2	0.0463 (9)	0.0443 (8)	0.0354 (7)	-0.0022 (7)	0.0118 (6)	0.0079 (6)

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

S1—C1	1.7695 (16)	C1—N1	1.298 (2)
S1—S1 ⁱ	2.0393 (9)	C2—N2	1.290 (2)
S2—C2	1.7164 (17)	C2—H2	0.9300
S2—C1	1.7217 (16)	N1—N2	1.392 (2)
C1—S1—S1 ⁱ	102.08 (5)	N2—C2—S2	115.54 (13)
C2—S2—C1	86.01 (8)	N2—C2—H2	122.2
N1—C1—S2	115.22 (12)	S2—C2—H2	122.2
N1—C1—S1	119.96 (12)	C1—N1—N2	111.40 (13)
S2—C1—S1	124.81 (9)	C2—N2—N1	111.82 (14)
C2—S2—C1—N1	-0.11 (13)	S2—C1—N1—N2	-0.16 (18)
C2—S2—C1—S1	-179.53 (11)	S1—C1—N1—N2	179.30 (11)
S1 ⁱ —S1—C1—N1	169.70 (12)	S2—C2—N2—N1	-0.5 (2)
S1 ⁱ —S1—C1—S2	-10.90 (11)	C1—N1—N2—C2	0.4 (2)
C1—S2—C2—N2	0.38 (15)		

Symmetry codes: (i) $-x+1, y, -z+3/2$.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C2—H2 \cdots N2 ⁱⁱ	0.93	2.52	3.249 (2)	136

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

Fig. 1

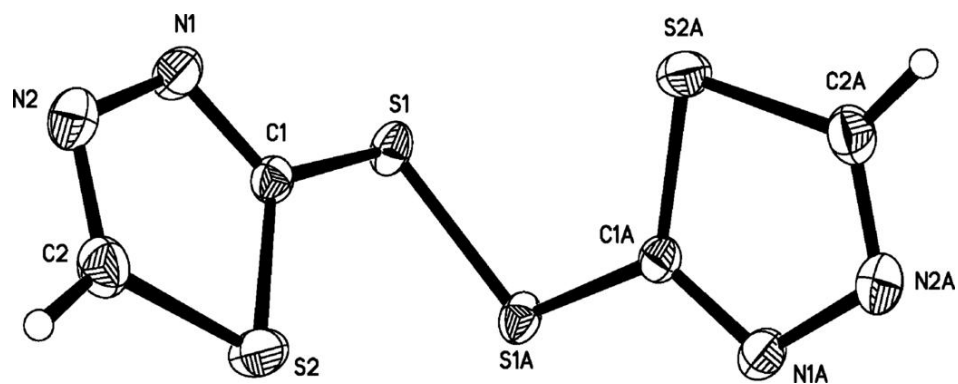


Fig. 2

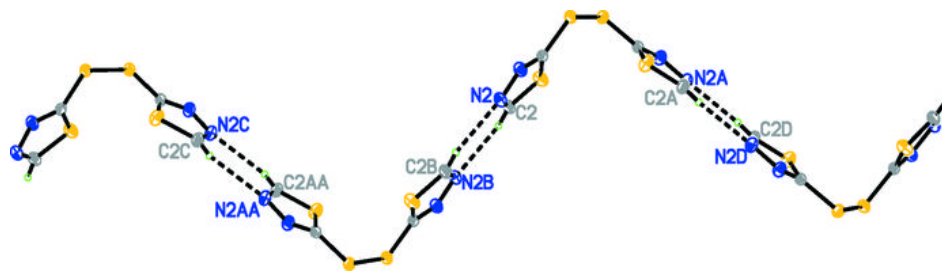


Fig. 3

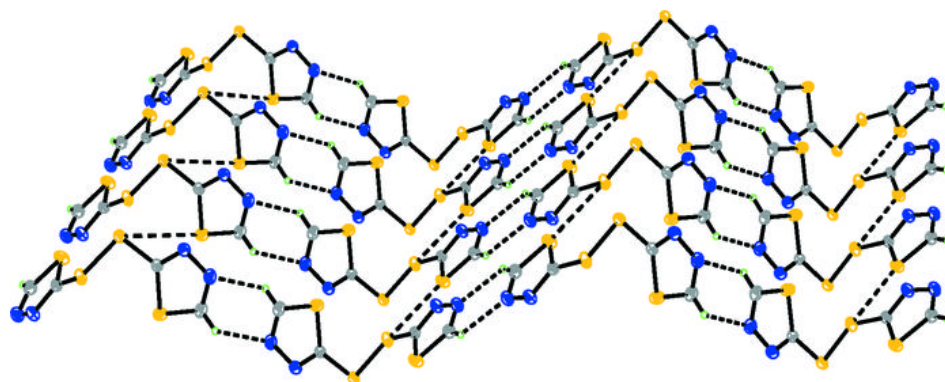


Fig. 4

