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Bis[(1-methyl-1H-tetrazol-5-yl)sulfanyl]ethane

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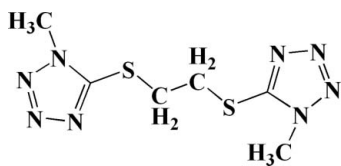
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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.047; wR factor = 0.135; data-to-parameter ratio = 13.4.

The title compound, $\text{C}_6\text{H}_{10}\text{N}_8\text{S}_2$, was prepared by the nucleophilic substitution reaction of 5-mercapto-1-methyl-tetrazole and dichloroethane. In the crystal, the molecule possesses an approximate non-crystallographic twofold symmetry axis. The crystal packing is stabilized by weak intermolecular $\text{C}-\text{H}\cdots\text{N}$ and $\pi-\pi$ interactions [centroid-centroid distances = 3.448 (6), 3.5085 (5) and 3.4591 (2) Å]. The two five-membered rings form a dihedral angle of 1.9 (2)°.

Related literature

For the synthesis and structures of closely related compounds, see: She *et al.* (2006); Wei *et al.* (2011). For the pharmacological activity of tetrazole-containing compounds, see: Gilchrist (1992); Armour *et al.* (1996); Upadhayaya *et al.* (2004). For applications of tetrazole derivatives in coordination chemistry and as energetic materials, see: Zhao *et al.* (2008); Wang *et al.* (2009).



Experimental

Crystal data

$\text{C}_6\text{H}_{10}\text{N}_8\text{S}_2$
 $M_r = 258.34$
 Triclinic, $P\bar{1}$
 $a = 7.5905$ (17) Å

$b = 7.9958$ (17) Å
 $c = 10.398$ (2) Å
 $\alpha = 95.206$ (3)°
 $\beta = 92.922$ (3)°

$\gamma = 115.109$ (2)°
 $V = 566.3$ (2) Å³
 $Z = 2$
 Mo $K\alpha$ radiation

$\mu = 0.46$ mm⁻¹
 $T = 296$ K
 $0.31 \times 0.27 \times 0.04$ mm

Data collection

Bruker APEXII CCD diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2002)
 $T_{\min} = 0.868$, $T_{\max} = 0.982$

2874 measured reflections
 1972 independent reflections
 1454 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.017$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.047$
 $wR(F^2) = 0.135$
 $S = 1.39$
 1972 reflections

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

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{C1}-\text{H1A}\cdots\text{N4}^{\text{i}}$	0.96	2.49	3.413 (5)	161
$\text{C6}-\text{H6B}\cdots\text{N5}^{\text{ii}}$	0.96	2.43	3.355 (5)	161

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

Data collection: SMART (Bruker, 2002); cell refinement: SAINT (Bruker, 2002); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 (Farrugia, 1997); 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: YK2010).

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supplementary materials

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Bis[(1-methyl-1*H*-tetrazol-5-yl)sulfanyl]ethane

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Comment

As is well known, tetrazole-containing compounds are used in pharmaceuticals, where they play a stimulative or sedative role for the central nervous system (Gilchrist, 1992; Armour *et al.*, 1996). Due to the various coordination modes of tetrazole group and high content of nitrogen, tetrazole derivatives have been widely applied in coordination chemistry (Zhao *et al.*, 2008) and the chemistry of energetic materials (Wang *et al.*, 2009). The title compound is a derivative of tetrazole. Nevertheless, reports on its use in pharmaceutical, coordination chemistry or energetic materials are very scarce. Here we report its crystal structure as a prerequisite of further investigation of possibilities for its use in the above fields.

In the crystal structure of the title, the molecule possesses approximate non-crystallographic twofold symmetry axis. Two 1-methyltetrazole groups are linked by —S—C₂H₄—S— bridge, and the two five-membered rings form a dihedral angle of 1.92° (Fig. 1). The values for the S1—C4 and S2—C3 bonds in the bridge [1.812 (4) Å and 1.814 (4) Å] are longer than the distances of S1—C5 and S2—C2 bonds [1.738 (3) Å and 1.725 (4) Å]. This difference can be attributed by electron attracting effect of 1-methyltetrazole groups. As shown in Fig. 2, tetrazole rings form stacks [intercentroid distances Cg1—Cg1(i) = 3.448 (6) Å, Cg2—Cg2(iii) = 3.5085 (5) Å, Cg1(ii)—Cg2 = 3.4591 (2) Å, (i) 1 - *x*, 1 - *y*, 1 - *z*; (ii) *x*, 1 + *y*, *z*; (iii) 1 - *x*, 2 - *y*, *x* - *z*].

Experimental

Sodium hydroxide (1.7 g, 0.043 mol) was added to 5-mercapto-1-methyltetrazole (5 g, 0.043 mol) in dry dimethylsulfoxide (35 ml). The reaction mixture was stirred at 363 K for 1 h. Dichloroethane (3.1 ml, 0.0215 mol) was then added to the solution dropwise with the formation of a grey suspension. The suspension was stirred for 4 h, cooled to room temperature and filtered. The solvent was removed completely under reduced pressure, and the obtained residue was recrystallized from ethanol to give a colorless flaky crystalline product (2.94 g; m.p. 411 - 414 K).

Refinement

All H atoms were positioned geometrically (C—H = 0.96 Å for CH₃ and 0.97 Å for CH₂ groups, respectively) and constrained to ride on their parent atoms with $U_{\text{iso}}(\text{H})$ values set to 1.5 times U_{eq} of the parent atoms.

Figures

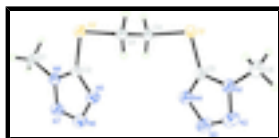


Fig. 1. Molecular structure of the title compound, showing the atom labeling scheme and displacement ellipsoids drawn at the 30% probability level.

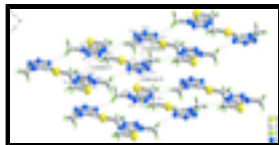


Fig. 2. A view of the crystal packing of the title compound, showing the C–H···N and π – π interactions. Symmetry operators: ⁱ $1 - x, 1 - y, 1 - z$; ⁱⁱ $x, 1 + y, z$; ⁱⁱⁱ $1 - x, 2 - y, x - z$.

Bis[(1-methyl-1H-tetrazol-5-yl)sulfanyl]ethane

Crystal data

$C_6H_{10}N_8S_2$
 $M_r = 258.34$

Triclinic, $P\bar{1}$

Hall symbol: $-P\ 1$
 $a = 7.5905\ (17)\ \text{\AA}$
 $b = 7.9958\ (17)\ \text{\AA}$
 $c = 10.398\ (2)\ \text{\AA}$
 $\alpha = 95.206\ (3)^\circ$
 $\beta = 92.922\ (3)^\circ$
 $\gamma = 115.109\ (2)^\circ$
 $V = 566.3\ (2)\ \text{\AA}^3$

$Z = 2$
 $F(000) = 268$
 $D_x = 1.515\ \text{Mg m}^{-3}$
 $D_m = 1.515\ \text{Mg m}^{-3}$
 D_m measured by not measured
 Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$
 Cell parameters from 816 reflections
 $\theta = 3.0\text{--}24.3^\circ$
 $\mu = 0.46\ \text{mm}^{-1}$
 $T = 296\ \text{K}$
 Flake-like, colourless
 $0.31 \times 0.27 \times 0.04\ \text{mm}$

Data collection

Bruker APEXII CCD
 diffractometer
 Radiation source: fine-focus sealed tube
 graphite
 φ and ω scans
 Absorption correction: multi-scan
 (*SADABS*; Bruker, 2002)
 $T_{\min} = 0.868, T_{\max} = 0.982$
 2874 measured reflections

1972 independent reflections
 1454 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.017$
 $\theta_{\max} = 25.1^\circ, \theta_{\min} = 2.0^\circ$
 $h = -8 \rightarrow 9$
 $k = -9 \rightarrow 9$
 $l = -12 \rightarrow 12$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.047$
 $wR(F^2) = 0.135$
 $S = 1.39$
 1972 reflections
 147 parameters

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
 $w = 1/[\sigma^2(F_o^2) + (0.050P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.26\ \text{e \AA}^{-3}$

0 restraints

$$\Delta\rho_{\min} = -0.26 \text{ e } \text{\AA}^{-3}$$

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.09578 (12)	0.84390 (12)	0.77838 (9)	0.0521 (3)
S2	0.09347 (12)	0.29485 (12)	0.68329 (10)	0.0556 (3)
C3	0.1006 (5)	0.5022 (4)	0.7748 (3)	0.0475 (8)
H3A	-0.0186	0.4695	0.8171	0.071*
H3B	0.2096	0.5507	0.8418	0.071*
C4	0.1213 (5)	0.6503 (4)	0.6906 (3)	0.0462 (8)
H4A	0.0224	0.5975	0.6169	0.069*
H4B	0.2485	0.6952	0.6576	0.069*
N8	0.4054 (4)	0.2801 (4)	0.5763 (3)	0.0453 (7)
N1	0.3945 (4)	1.1385 (4)	0.9194 (3)	0.0508 (7)
N7	0.6021 (4)	0.3722 (4)	0.5857 (3)	0.0553 (8)
C2	0.3378 (5)	0.3691 (4)	0.6618 (3)	0.0416 (8)
N4	0.4956 (4)	0.9965 (4)	0.7756 (3)	0.0593 (8)
N5	0.4887 (4)	0.5150 (4)	0.7245 (3)	0.0560 (8)
N3	0.6501 (4)	1.1452 (5)	0.8422 (3)	0.0673 (9)
C5	0.3392 (5)	0.9955 (5)	0.8249 (3)	0.0463 (8)
N6	0.6500 (4)	0.5133 (4)	0.6750 (3)	0.0611 (8)
C1	0.2987 (5)	0.1146 (5)	0.4834 (4)	0.0571 (10)
H1A	0.3772	0.1141	0.4140	0.086*
H1B	0.1791	0.1151	0.4489	0.086*
H1C	0.2693	0.0055	0.5260	0.086*
N2	0.5909 (5)	1.2321 (4)	0.9288 (3)	0.0664 (9)
C6	0.2779 (6)	1.1957 (6)	1.0046 (4)	0.0694 (12)
H6A	0.1958	1.2344	0.9540	0.104*
H6B	0.3631	1.2973	1.0675	0.104*
H6C	0.1981	1.0929	1.0482	0.104*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0445 (5)	0.0435 (5)	0.0671 (6)	0.0217 (4)	0.0033 (4)	-0.0113 (4)

supplementary materials

S2	0.0421 (5)	0.0364 (5)	0.0800 (7)	0.0130 (4)	0.0051 (4)	-0.0121 (5)
C3	0.046 (2)	0.0407 (19)	0.054 (2)	0.0201 (16)	0.0055 (15)	-0.0083 (16)
C4	0.046 (2)	0.0393 (19)	0.0510 (19)	0.0189 (16)	0.0026 (15)	-0.0081 (16)
N8	0.0426 (16)	0.0439 (16)	0.0483 (16)	0.0188 (13)	0.0039 (13)	-0.0006 (13)
N1	0.0494 (18)	0.0460 (17)	0.0492 (16)	0.0150 (15)	0.0033 (13)	-0.0037 (14)
N7	0.0469 (18)	0.059 (2)	0.0606 (18)	0.0229 (16)	0.0091 (14)	0.0061 (16)
C2	0.0393 (18)	0.0323 (17)	0.0483 (18)	0.0128 (15)	-0.0012 (15)	-0.0021 (15)
N4	0.0489 (19)	0.057 (2)	0.067 (2)	0.0194 (16)	0.0076 (15)	-0.0027 (16)
N5	0.0457 (18)	0.0510 (18)	0.0647 (19)	0.0192 (15)	-0.0068 (15)	-0.0098 (15)
N3	0.0475 (19)	0.063 (2)	0.075 (2)	0.0088 (17)	0.0081 (17)	0.0056 (18)
C5	0.051 (2)	0.0419 (19)	0.0460 (19)	0.0220 (17)	-0.0010 (16)	-0.0004 (16)
N6	0.0456 (18)	0.055 (2)	0.074 (2)	0.0171 (15)	-0.0039 (16)	-0.0024 (17)
C1	0.064 (2)	0.0388 (19)	0.059 (2)	0.0167 (18)	0.0033 (18)	-0.0145 (17)
N2	0.057 (2)	0.057 (2)	0.069 (2)	0.0104 (17)	-0.0027 (17)	0.0026 (17)
C6	0.070 (3)	0.074 (3)	0.060 (2)	0.034 (2)	0.005 (2)	-0.023 (2)

Geometric parameters (Å, °)

S1—C5	1.738 (4)	N1—C6	1.457 (4)
S1—C4	1.812 (3)	N7—N6	1.302 (4)
S2—C2	1.724 (3)	C2—N5	1.323 (4)
S2—C3	1.814 (3)	N4—C5	1.314 (4)
C3—C4	1.496 (5)	N4—N3	1.362 (4)
C3—H3A	0.9700	N5—N6	1.357 (4)
C3—H3B	0.9700	N3—N2	1.299 (4)
C4—H4A	0.9700	C1—H1A	0.9600
C4—H4B	0.9700	C1—H1B	0.9600
N8—C2	1.342 (4)	C1—H1C	0.9600
N8—N7	1.349 (4)	C6—H6A	0.9600
N8—C1	1.456 (4)	C6—H6B	0.9600
N1—C5	1.340 (4)	C6—H6C	0.9600
N1—N2	1.348 (4)		
C5—S1—C4	100.94 (15)	N5—C2—S2	128.0 (3)
C2—S2—C3	100.20 (15)	N8—C2—S2	123.6 (2)
C4—C3—S2	112.2 (2)	C5—N4—N3	105.8 (3)
C4—C3—H3A	109.2	C2—N5—N6	106.0 (3)
S2—C3—H3A	109.2	N2—N3—N4	110.7 (3)
C4—C3—H3B	109.2	N4—C5—N1	108.9 (3)
S2—C3—H3B	109.2	N4—C5—S1	128.2 (3)
H3A—C3—H3B	107.9	N1—C5—S1	122.9 (3)
C3—C4—S1	111.8 (2)	N7—N6—N5	110.8 (3)
C3—C4—H4A	109.3	N8—C1—H1A	109.5
S1—C4—H4A	109.3	N8—C1—H1B	109.5
C3—C4—H4B	109.3	H1A—C1—H1B	109.5
S1—C4—H4B	109.3	N8—C1—H1C	109.5
H4A—C4—H4B	107.9	H1A—C1—H1C	109.5
C2—N8—N7	108.6 (3)	H1B—C1—H1C	109.5
C2—N8—C1	129.7 (3)	N3—N2—N1	106.3 (3)
N7—N8—C1	121.7 (3)	N1—C6—H6A	109.5

C5—N1—N2	108.3 (3)	N1—C6—H6B	109.5
C5—N1—C6	130.2 (3)	H6A—C6—H6B	109.5
N2—N1—C6	121.5 (3)	N1—C6—H6C	109.5
N6—N7—N8	106.2 (2)	H6A—C6—H6C	109.5
N5—C2—N8	108.4 (3)	H6B—C6—H6C	109.5

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C1—H1A \cdots N4 ⁱ	0.96	2.49	3.413 (5)	161
C6—H6B \cdots N5 ⁱⁱ	0.96	2.43	3.355 (5)	161

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Fig. 1

