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[(Methylcarbamothioyl)disulfanyl]methyl N-methylcarbamodithioate

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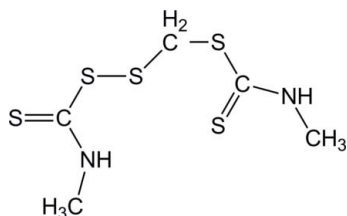
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{N}-\text{C}) = 0.003$ Å; R factor = 0.040; wR factor = 0.103; data-to-parameter ratio = 18.7.

The title compound, $\text{C}_5\text{H}_{10}\text{N}_2\text{S}_5$, was unintentionally obtained as the product of an attempted synthesis of a methylcarbamodithioic acid using methylamine and carbon disulfide. In the molecule, two dithiocarbamate groups are bridged by a $-\text{CH}_2\text{S}-$ unit. The $\text{C}-\text{S}-\text{S}-\text{C}$ torsion angle is -90.13 (11)°. The crystal structure is stabilized by $\text{N}-\text{H}\cdots\text{S}$ interactions between neighbouring molecules. An intramolecular $\text{N}-\text{H}\cdots\text{S}$ hydrogen bond also occurs.

Related literature

For dithiocarbamate ligands, see: Cox *et al.* (1999); Liu & Bao (2007); Nair *et al.* (2002).



Experimental

Crystal data

 $\text{C}_5\text{H}_{10}\text{N}_2\text{S}_5$ $M_r = 258.45$

Triclinic, $P\bar{1}$
 $a = 7.188$ (1) Å
 $b = 7.884$ (2) Å
 $c = 10.219$ (2) Å
 $\alpha = 101.23$ (3)°
 $\beta = 96.85$ (3)°
 $\gamma = 102.74$ (3)°

$V = 546.0$ (2) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 1.01$ mm⁻¹
 $T = 293$ K
 $0.30 \times 0.11 \times 0.10$ mm

Data collection

Stoe IPDS diffractometer
 4080 measured reflections
 2077 independent reflections

1924 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.101$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.103$
 $S = 1.15$
 2077 reflections

111 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.53$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.37$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1}\cdots\text{S3}$	0.86	2.50	3.073 (2)	125
$\text{N1}-\text{H1}\cdots\text{S3}^i$	0.86	3.02	3.595 (2)	127
$\text{N2}-\text{H2}\cdots\text{S1}^{ii}$	0.86	2.67	3.515 (2)	168

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

Data collection: *X-Area* (Stoe & Cie, 2002); cell refinement: *X-RED32* (Stoe & Cie, 2002); data reduction: *X-RED32*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2007); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: OM2358).

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supplementary materials

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[(Methylcarbamothioyl)disulfanyl]methyl *N*-methylcarbamdithioate

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Comment

Sulfur-containing organic compounds like dithiocarbamates and xanthates have been used as excellent metal complexing agents. They have applications as fungicides, pesticides, chelating agents for removal of heavy metal ions from toxic waste, precursors for metal-organic chemical vapour deposition (MOCVD) and synthesis of semi-conductor nanoparticles (Cox & Tiekink, *et al.*, 1999; Nair *et al.*, 2002.) Dithiocarbamates have also been used as protection groups in peptide synthesis, as linkers in solid phase organic synthesis and recently in the synthesis of ionic ligands (Liu *et al.*, 2007.) In the title compound (Fig. 1), the disulfide portion is substantially twisted, with C–S–S–C torsion angle of $-90.13(11)^\circ$. The molecular packing also features intra- and intermolecular N—H \cdots S interactions (Table 1).

Experimental

Distilled methylamine (3.00 g, 96.8 mmol) was added in purified methanol (30 ml) in a two neck flask (250 ml) and stirred for ten minutes at 273 K. Carbon disulfide 7.4 ml (117 mmol) was added drop by drop into the two neck flask containing methylamine and a colorless precipitate was formed at once. The stirring was continued for three hours to complete the reaction. The solvent was removed by vacuum distillation. The solid product was washed several times with methanol. The colorless product was purified by recrystallization from 1,1-dichloromethane/pet ether (8:2) V/V, to give fine crystals of the title compound with an overall yield of 85%.

Refinement

All hydrogen atoms were initially located in a difference Fourier map. H atoms on C and N were refined with a riding model, C–H = 0.96 Å with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl groups, C–H = 0.97 Å with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for methylene groups, and N–H = 0.86 Å with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Figures

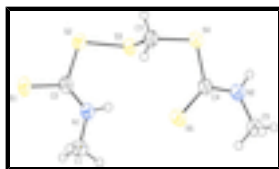


Fig. 1. The molecular structure with atom labels and 50% probability displacement ellipsoids for non-H atoms.

[(Methylcarbamothioyl)disulfanyl]methyl *N*-methylcarbamdithioate

Crystal data

C₅H₁₀N₂S₅

$V = 546.0(2) \text{ \AA}^3$

supplementary materials

$M_r = 258.45$	$Z = 2$
Triclinic, $P\bar{1}$	$F(000) = 268$
$a = 7.188$ (1) Å	$D_x = 1.572$ Mg m ⁻³
$b = 7.884$ (2) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$c = 10.219$ (2) Å	$\mu = 1.01$ mm ⁻¹
$\alpha = 101.23$ (3)°	$T = 293$ K
$\beta = 96.85$ (3)°	Needle, yellow
$\gamma = 102.74$ (3)°	$0.30 \times 0.11 \times 0.10$ mm

Data collection

Stoe IPDS diffractometer	1924 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube graphite	$R_{\text{int}} = 0.101$
ω scans	$\theta_{\text{max}} = 26.4^\circ$, $\theta_{\text{min}} = 4.1^\circ$
4080 measured reflections	$h = -8 \rightarrow 8$
2077 independent reflections	$k = -9 \rightarrow 9$
	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.040$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.103$	H-atom parameters constrained
$S = 1.15$	$w = 1/[\sigma^2(F_o^2) + (0.0496P)^2 + 0.0335P]$
2077 reflections	where $P = (F_o^2 + 2F_c^2)/3$
111 parameters	$(\Delta/\sigma)_{\text{max}} = 0.001$
0 restraints	$\Delta\rho_{\text{max}} = 0.53$ e Å ⁻³
	$\Delta\rho_{\text{min}} = -0.37$ 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 (Å²)

x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
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S1	0.24777 (9)	0.73176 (9)	0.11879 (5)	0.04736 (19)
S2	0.39011 (7)	0.69015 (8)	0.38202 (5)	0.03952 (18)
S3	0.28393 (7)	0.64232 (7)	0.55098 (5)	0.03611 (17)
S4	0.22813 (8)	0.85040 (8)	0.80525 (5)	0.04221 (18)
S5	-0.14480 (9)	0.82971 (9)	0.62019 (6)	0.04559 (19)
N1	0.0187 (3)	0.6694 (2)	0.30088 (18)	0.0370 (4)
H1	0.0090	0.6510	0.3803	0.044*
N2	-0.1092 (3)	0.7742 (3)	0.86906 (19)	0.0440 (5)
H2	-0.0358	0.7639	0.9384	0.053*
C1	-0.1562 (3)	0.6703 (4)	0.2139 (3)	0.0485 (6)
H1A	-0.1370	0.7799	0.1837	0.073*
H1B	-0.2619	0.6604	0.2634	0.073*
H1C	-0.1851	0.5713	0.1369	0.073*
C2	0.1897 (3)	0.6948 (3)	0.26569 (19)	0.0333 (4)
C3	0.3067 (3)	0.8671 (3)	0.6478 (2)	0.0390 (5)
H3A	0.4402	0.9359	0.6636	0.047*
H3B	0.2275	0.9267	0.5983	0.047*
C4	-0.0280 (3)	0.8118 (3)	0.7646 (2)	0.0346 (4)
C5	-0.3151 (3)	0.7494 (4)	0.8732 (3)	0.0488 (6)
H5A	-0.3432	0.8638	0.8978	0.073*
H5B	-0.3498	0.6812	0.9388	0.073*
H5C	-0.3881	0.6867	0.7856	0.073*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0507 (4)	0.0674 (4)	0.0306 (3)	0.0158 (3)	0.0153 (2)	0.0206 (3)
S2	0.0326 (3)	0.0578 (4)	0.0331 (3)	0.0132 (2)	0.0107 (2)	0.0168 (3)
S3	0.0393 (3)	0.0427 (3)	0.0300 (3)	0.0103 (2)	0.0079 (2)	0.0157 (2)
S4	0.0366 (3)	0.0623 (4)	0.0270 (3)	0.0115 (3)	0.0030 (2)	0.0107 (3)
S5	0.0446 (3)	0.0627 (4)	0.0328 (3)	0.0181 (3)	0.0012 (2)	0.0168 (3)
N1	0.0357 (9)	0.0483 (10)	0.0304 (8)	0.0113 (8)	0.0081 (7)	0.0145 (8)
N2	0.0385 (10)	0.0645 (12)	0.0333 (9)	0.0154 (9)	0.0056 (8)	0.0187 (9)
C1	0.0379 (13)	0.0657 (15)	0.0452 (12)	0.0161 (11)	0.0032 (10)	0.0193 (12)
C2	0.0388 (11)	0.0358 (9)	0.0276 (9)	0.0105 (8)	0.0077 (8)	0.0104 (8)
C3	0.0413 (11)	0.0417 (11)	0.0331 (10)	0.0045 (9)	0.0093 (9)	0.0116 (9)
C4	0.0385 (11)	0.0382 (10)	0.0290 (9)	0.0136 (8)	0.0061 (8)	0.0073 (8)
C5	0.0395 (13)	0.0686 (16)	0.0417 (12)	0.0180 (12)	0.0101 (10)	0.0137 (12)

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

S1—C2	1.6671 (18)	N2—C5	1.456 (3)
S2—C2	1.767 (2)	N2—H2	0.8600
S2—S3	2.0364 (8)	C1—H1A	0.9600
S3—C3	1.816 (2)	C1—H1B	0.9600
S4—C4	1.782 (2)	C1—H1C	0.9600
S4—C3	1.787 (2)	C3—H3A	0.9700
S5—C4	1.655 (2)	C3—H3B	0.9700
N1—C2	1.306 (3)	C5—H5A	0.9600

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N1—C1	1.453 (3)	C5—H5B	0.9600
N1—H1	0.8600	C5—H5C	0.9600
N2—C4	1.328 (3)		
C2—S2—S3	105.99 (7)	S1—C2—S2	113.24 (12)
C3—S3—S2	101.85 (7)	S4—C3—S3	107.88 (10)
C4—S4—C3	103.25 (10)	S4—C3—H3A	110.1
C2—N1—C1	123.90 (17)	S3—C3—H3A	110.1
C2—N1—H1	118.0	S4—C3—H3B	110.1
C1—N1—H1	118.0	S3—C3—H3B	110.1
C4—N2—C5	123.93 (18)	H3A—C3—H3B	108.4
C4—N2—H2	118.0	N2—C4—S5	125.43 (17)
C5—N2—H2	118.0	N2—C4—S4	109.93 (14)
N1—C1—H1A	109.5	S5—C4—S4	124.59 (12)
N1—C1—H1B	109.5	N2—C5—H5A	109.5
H1A—C1—H1B	109.5	N2—C5—H5B	109.5
N1—C1—H1C	109.5	H5A—C5—H5B	109.5
H1A—C1—H1C	109.5	N2—C5—H5C	109.5
H1B—C1—H1C	109.5	H5A—C5—H5C	109.5
N1—C2—S1	127.70 (16)	H5B—C5—H5C	109.5
N1—C2—S2	119.06 (14)		
C2—S2—S3—C3	-90.13 (11)	S2—S3—C3—S4	-177.57 (9)
C1—N1—C2—S1	-0.4 (3)	C5—N2—C4—S5	-2.4 (3)
C1—N1—C2—S2	179.97 (18)	C5—N2—C4—S4	175.1 (2)
S3—S2—C2—N1	-0.01 (19)	C3—S4—C4—N2	172.23 (16)
S3—S2—C2—S1	-179.71 (9)	C3—S4—C4—S5	-10.31 (17)
C4—S4—C3—S3	-83.86 (14)		

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 \cdots S3	0.86	2.50	3.073 (2)	125
N1—H1 \cdots S3 ⁱ	0.86	3.02	3.595 (2)	127
N2—H2 \cdots S1 ⁱⁱ	0.86	2.67	3.515 (2)	168

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

Fig. 1

