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Crystal structure of 3-[({[bis(2-cyanoethyl)-carbamothioyl]disulfanyl}methanethioyl)(2-cyano-ethyl) amino]propanenitrile

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Keywords: crystal structure; cyano derivatives; weak C—H···N hydrogen bonds; short intra-molecular contacts; twofold rotation symmetry.

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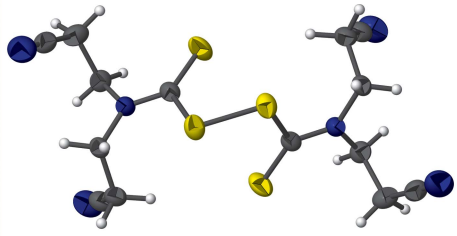
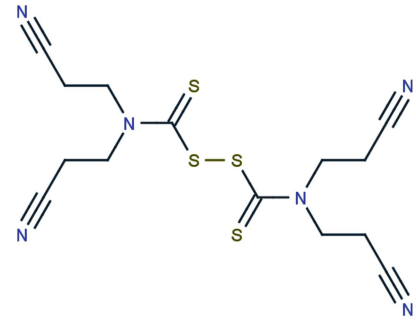
Structural data: full structural data are available from iucrdata.iucr.org

In the title compound, $C_{14}H_{16}N_6S_4$, the molecule resides on a twofold rotation axis, which runs through the central S—S bond. In the crystal, molecules are linked *via* weak C—H···N hydrogen bonds, forming $C(5)$ chains propagating in a helical arrangement along [010].

3D view



Chemical scheme



Structure description

In a continuation of the work in our laboratory on the crystal structure analysis of cyano derivatives, we have undertaken the single-crystal X-ray diffraction study of the title compound, and the results are presented herein.

The molecular structure of the title compound is illustrated in Fig. 1. The molecule resides on a crystallographic twofold rotation axis, which runs through the central S—S bond. The molecular structure maybe influenced by a series of very weak intramolecular C—H···S hydrogen bonds (Table 1).

In the crystal, weak C—H···N hydrogen bonds link the molecules, forming $C(5)$ chains propagating in a helical arrangement along [010]; see Fig. 2. The structure also forms a cavity consisting of 24 atoms between two molecules in an $R_2^2(24)$ graph-set motif.

Synthesis and crystallization

All chemicals were commercially available and analytical grade materials were used directly without further purification. A stoichiometric amount (0.1732 g, 2 mmol) of carbon disulfide, CS_2, was added dropwise to a methanol solution containing (0.2463 g, 2 mmol) 3,3′-azanediyldipropanenitrile and 0.24 g potassium hydroxide. The mixture was

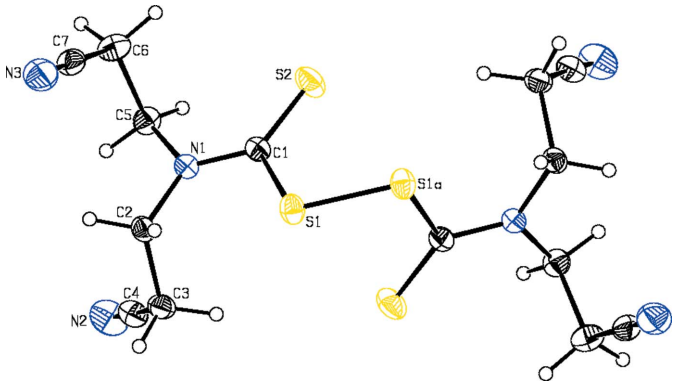


Figure 1
The molecular structure of the title compound, with the atom labelling. Displacement ellipsoids are drawn at the 30% probability level.

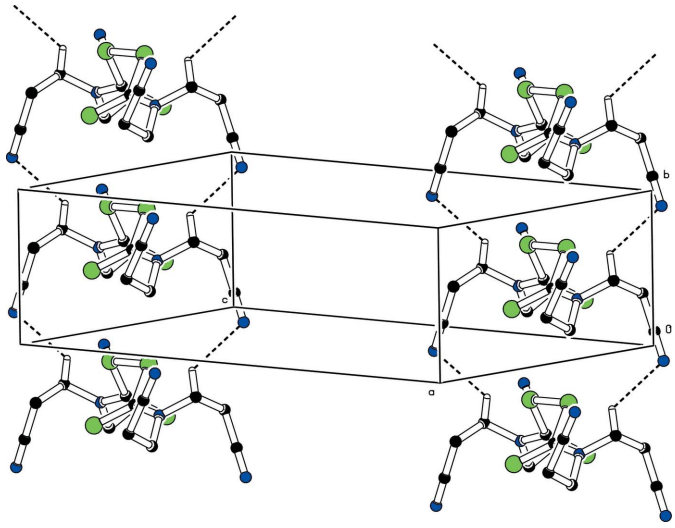


Figure 2
The crystal packing of the title compound. The weak C—H···N hydrogen bonds are shown as dashed lines (see Table 1). For clarity, H atoms not involved in these hydrogen bonds have been omitted.

stirred for about 25 minutes until a white precipitate appeared. The clear filtrate was then left at temperature of 278 K for crystallization. After few days, crystals suitable for X-ray analysis were collected (yield = 83%, m.p. 431 K). The presence of the C≡N groups was confirmed by FT–IR analysis.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2B···S1	0.97	2.46	2.857 (2)	105
C3—H3A···S1	0.97	2.84	3.332 (2)	112
C5—H5B···S2	0.97	2.69	3.028 (2)	101
C2—H2B···N2^{i}	0.97	2.55	3.202 (2)	125

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{14}H_{16}N_6S_4$
M_r	396.57
Crystal system, space group	Monoclinic, $C2/c$
Temperature (K)	293
a, b, c (Å)	15.4313 (7), 5.6117 (2), 22.8702 (12)
β (°)	108.713 (2)
V (Å^3)	1875.77 (15)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.52
Crystal size (mm)	0.30 × 0.20 × 0.20
Data collection	
Diffractometer	Bruker Kappa APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 1999)
T_{min}, T_{max}	0.81, 0.89
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	19984, 3347, 2569
R_{int}	0.024
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.766
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.037, 0.109, 1.11
No. of reflections	3347
No. of parameters	109
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.34, −0.27

Computer programs: *APEX2*, *SAINT* and *XPREP* (Bruker, 2004), *SHELXS97* (Sheldrick, 2008), *ORTEP-3 for Windows* (Farrugia, 2012), *SHELXL2014* (Sheldrick, 2015) and *PLATON* (Spek, 2009).

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full crystallographic data

IUCrData (2017). **2**, x170346 [https://doi.org/10.1107/S2414314617003467]

Crystal structure of 3-[({[bis(2-cyanoethyl)carbamothioyl]disulfanyl}methanethioyl)(2-cyanoethyl) amino]propanenitrile

A. S. Sonia, R. Baskaran and S. Selvanayagam

3-[({[bis(2-Cyanoethyl)carbamothioyl]disulfanyl}methanethioyl)(2-cyanoethyl)amino]propanenitrile

Crystal data

$C_{14}H_{16}N_6S_4$
M_r = 396.57
Monoclinic, $C2/c$
a = 15.4313 (7) Å
b = 5.6117 (2) Å
c = 22.8702 (12) Å
β = 108.713 (2)°
V = 1875.77 (15) Å^3
Z = 4
$F(000)$ = 824
D_x = 1.404 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 8307 reflections
θ = 2.3–31.7°
μ = 0.52 mm^{-1}
T = 293 K
Block, brown
0.30 × 0.20 × 0.20 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Radiation source: Sealed tube
ω and φ scan
Absorption correction: multi-scan (SADABS; Bruker, 1999)
T_{min} = 0.81, T_{max} = 0.89
19984 measured reflections
3347 independent reflections
2569 reflections with $I > 2\sigma(I)$
R_{int} = 0.024
θ_{max} = 33.0°, θ_{min} = 2.8°
h = −23→19
k = −8→8
l = −34→34

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.109
S = 1.11
3347 reflections
109 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0427P)^2 + 1.4682P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.34 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}

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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	−0.00264 (3)	0.57876 (7)	0.20581 (2)	0.03874 (11)
S2	0.13996 (3)	0.20336 (9)	0.26542 (2)	0.05086 (14)
N1	0.06850 (8)	0.2800 (2)	0.14508 (5)	0.0328 (2)
N2	−0.09703 (13)	−0.1278 (3)	0.02598 (9)	0.0644 (5)
N3	0.21226 (12)	0.6016 (3)	0.08156 (8)	0.0610 (4)
C1	0.07351 (10)	0.3344 (3)	0.20300 (6)	0.0325 (3)
C2	0.00524 (10)	0.3986 (3)	0.09077 (6)	0.0351 (3)
H2A	0.0289	0.3838	0.0565	0.042*
H2B	0.0027	0.5669	0.0997	0.042*
C3	−0.09148 (10)	0.2961 (3)	0.07169 (7)	0.0388 (3)
H3A	−0.1125	0.2922	0.1074	0.047*
H3B	−0.1322	0.3997	0.0411	0.047*
C4	−0.09592 (11)	0.0566 (3)	0.04630 (8)	0.0429 (3)
C5	0.12945 (11)	0.0991 (3)	0.13344 (8)	0.0389 (3)
H5A	0.1026	0.0367	0.0920	0.047*
H5B	0.1356	−0.0318	0.1622	0.047*
C6	0.22415 (11)	0.2006 (3)	0.14036 (9)	0.0487 (4)
H6A	0.2567	0.2279	0.1838	0.058*
H6B	0.2586	0.0851	0.1252	0.058*
C7	0.21877 (11)	0.4242 (4)	0.10651 (8)	0.0455 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0506 (2)	0.03350 (19)	0.03374 (19)	0.00673 (15)	0.01572 (16)	0.00523 (14)
S2	0.0572 (3)	0.0543 (3)	0.0332 (2)	0.0171 (2)	0.00349 (17)	0.00587 (17)
N1	0.0318 (5)	0.0356 (6)	0.0300 (5)	0.0003 (5)	0.0086 (4)	0.0007 (5)
N2	0.0730 (12)	0.0457 (9)	0.0650 (11)	−0.0021 (8)	0.0088 (9)	−0.0066 (8)
N3	0.0552 (9)	0.0645 (11)	0.0605 (10)	−0.0191 (8)	0.0146 (8)	0.0024 (9)
C1	0.0335 (6)	0.0312 (6)	0.0306 (6)	−0.0009 (5)	0.0071 (5)	0.0013 (5)
C2	0.0367 (7)	0.0390 (7)	0.0283 (6)	−0.0023 (6)	0.0084 (5)	0.0035 (5)
C3	0.0332 (7)	0.0430 (8)	0.0360 (7)	−0.0003 (6)	0.0054 (5)	−0.0027 (6)
C4	0.0407 (8)	0.0437 (8)	0.0386 (8)	−0.0027 (7)	0.0047 (6)	0.0008 (7)
C5	0.0408 (7)	0.0349 (7)	0.0422 (8)	0.0006 (6)	0.0150 (6)	−0.0045 (6)
C6	0.0360 (7)	0.0490 (9)	0.0610 (11)	0.0050 (7)	0.0155 (7)	−0.0001 (8)
C7	0.0346 (7)	0.0570 (10)	0.0456 (9)	−0.0093 (7)	0.0140 (6)	−0.0090 (8)

Geometric parameters (Å, º)

S1—C1	1.8201 (15)	C2—H2B	0.9700
S1—S1^{i}	1.9968 (7)	C3—C4	1.457 (2)
S2—C1	1.6405 (14)	C3—H3A	0.9700
N1—C1	1.3375 (18)	C3—H3B	0.9700
N1—C5	1.4651 (19)	C5—C6	1.529 (2)
N1—C2	1.4699 (18)	C5—H5A	0.9700

N2—C4	1.132 (2)	C5—H5B	0.9700
N3—C7	1.136 (3)	C6—C7	1.462 (3)
C2—C3	1.527 (2)	C6—H6A	0.9700
C2—H2A	0.9700	C6—H6B	0.9700
C1—S1—S1^{i}	102.62 (5)	C2—C3—H3B	109.2
C1—N1—C5	120.13 (12)	H3A—C3—H3B	107.9
C1—N1—C2	123.03 (12)	N2—C4—C3	177.8 (2)
C5—N1—C2	116.82 (12)	N1—C5—C6	111.78 (13)
N1—C1—S2	125.50 (11)	N1—C5—H5A	109.3
N1—C1—S1	111.98 (10)	C6—C5—H5A	109.3
S2—C1—S1	122.52 (8)	N1—C5—H5B	109.3
N1—C2—C3	113.23 (12)	C6—C5—H5B	109.3
N1—C2—H2A	108.9	H5A—C5—H5B	107.9
C3—C2—H2A	108.9	C7—C6—C5	112.02 (14)
N1—C2—H2B	108.9	C7—C6—H6A	109.2
C3—C2—H2B	108.9	C5—C6—H6A	109.2
H2A—C2—H2B	107.7	C7—C6—H6B	109.2
C4—C3—C2	112.20 (14)	C5—C6—H6B	109.2
C4—C3—H3A	109.2	H6A—C6—H6B	107.9
C2—C3—H3A	109.2	N3—C7—C6	177.1 (2)
C4—C3—H3B	109.2		
C5—N1—C1—S2	−3.8 (2)	C1—N1—C2—C3	−82.14 (17)
C2—N1—C1—S2	177.86 (11)	C5—N1—C2—C3	99.48 (15)
C5—N1—C1—S1	175.66 (10)	N1—C2—C3—C4	−69.60 (17)
C2—N1—C1—S1	−2.67 (17)	C1—N1—C5—C6	−81.15 (18)
S1^{i}—S1—C1—N1	170.16 (9)	C2—N1—C5—C6	97.28 (16)
S1^{i}—S1—C1—S2	−10.36 (10)	N1—C5—C6—C7	−48.7 (2)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2*B*···S1	0.97	2.46	2.857 (2)	105
C3—H3*A*···S1	0.97	2.84	3.332 (2)	112
C5—H5*B*···S2	0.97	2.69	3.028 (2)	101
C2—H2*B*···N2^{ii}	0.97	2.55	3.202 (2)	125

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