organic compounds

Bis[2-(1,3-benzothiazol-2-ylsulfanyl)-ethyl] ether

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The complete molecule of title compound, $C_{18}H_{16}N_2OS_4$, is generated by crystallographic twofold symmetry, with the O atom lying on the rotation axis. The dihedral angle between the ring systems is 80.91 (2)°. In the crystal, adjacent molecules are connected through π–π stacking interactions [centroid–centroid distance = 3.882 (2) Å], forming a three-dimensional network.

Related literature

For coordination polymers in supramolecular chemistry and crystal engineering, see: Robinson & Zaworotko (1995); Yaghi & Li (1996); Fujita *et al.* (1995); Tong *et al.* (2000); Bu *et al.* (2003); Long *et al.* (2004); Massue *et al.* (2007); Zou *et al.* (2004).
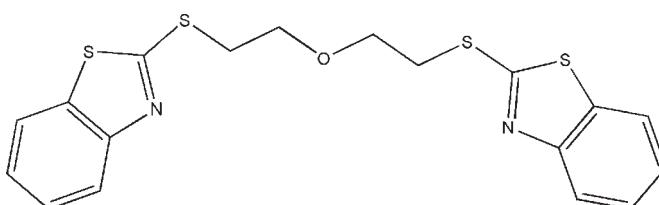
Experimental

Crystal data

$C_{18}H_{16}N_2OS_4$	$b = 4.7085$ (3) Å
$M_r = 404.57$	$c = 17.7866$ (15) Å
Monoclinic, $C2/c$	$\beta = 116.571$ (13)°
$a = 24.617$ (3) Å	$V = 1843.9$ (3) Å^3
$Z = 4$	$T = 293$ K
Cu $K\alpha$ radiation	$0.18 \times 0.15 \times 0.07$ mm
$\mu = 4.81$ mm^{-1}	

Data collection

Oxford Diffraction Xcalibur Sapphire3 diffractometer	2930 measured reflections
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2005)	1682 independent reflections
$T_{min} = 0.765$, $T_{max} = 1.000$	1353 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.020$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$	114 parameters
$wR(F^2) = 0.129$	H-atom parameters constrained
$S = 1.05$	$\Delta\rho_{max} = 0.27$ e Å^{-3}
1682 reflections	$\Delta\rho_{min} = -0.25$ e Å^{-3}

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2005); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG2684).

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supporting information

Bis[2-(1,3-benzothiazol-2-ylsulfanyl)ethyl] ether

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S1. Comment

Ligands containing thioether and nitrogenous heterocyclic groups are well established sources for biologically active complexes. In addition, this kind of ligands may form one- or multi-dimensional supramolecular structures *via* the intermolecule interactions such as hydrogen-bond or π-π stacking, attracting intense attention in the field of supramolecular chemistry and crystal engineering (Robinson *et al.*, 1995; Yaghi *et al.*, 1996; Fujita *et al.*, 1995; Tong *et al.*, 2000).

  Herein, we report the synthesis and structure of the title compound, namely bis[2-(benzothiazol-2-ylthio)ethyl]ether (Fig.1). As shown in Fig.2, a two-dimensional supramolecular network was formed by hydrogen bonds (Table 2) [Symmetry codes (i): *x*, -*y* + 1, *z* + 1/2] and S—S bonds of 3.575 (2) Å [Symmetry codes (ii): -*x* + 1/2, -*y* + 3/2, -*z* + 2], and there are also weak π-π stacking interactions between the phenyl rings and the thiazolyl rings of adjacent molecules with a centroid-centroid distances of 3.882 Å along *b* direction.

S2. Experimental

Bis(2-chloroethyl)ether (0.02 mol, 2.86 g) was added dropwise to a hot mixture solution (353 K) of 2-mercaptobenzo-thiazole (0.04 mol, 6.69 g), KOH (0.04 mol, 2.24 g) in ethanol (100 ml), and the mixture was further stirred at 353 K for 15 h. After cooling, the precipitate was filtered, washed with ethanol and water, and recrystallized from ethanol to obtain white powder. Yield: 56% (Bu *et al.*, 2003; Massue *et al.*, 2007; Long *et al.*, 2004). ^{1}H NMR (CDCl$_3$, 400 MHz): 3.56 (t, 4H), 3.89 (t, 4H), 7.25 (m, 2H), 7.39 (m, 2H), 7.70 (d, 2H), 7.82 (t, 2H). MS (ESI) m/z(%): 405.0 (M^{+1}).

S3. Refinement

The H atoms were placed at calculated positions in the riding model approximation (C—H 0.93 Å), with their temperature factors were set to 1.2 times those of the equivalent isotropic temperature factors of the parent atoms.
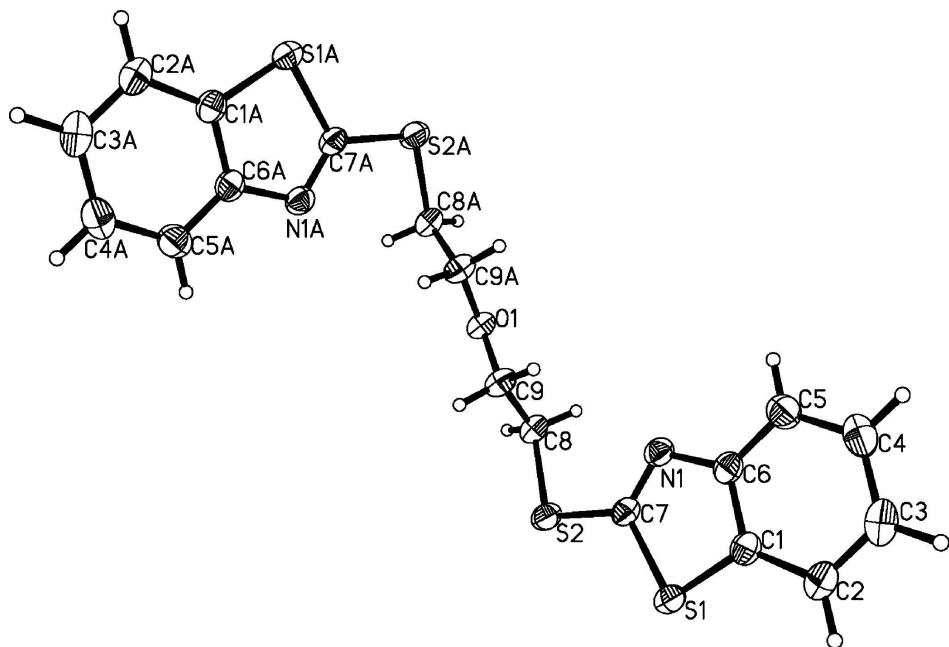
Figure 1

The structure of the title compound, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity.
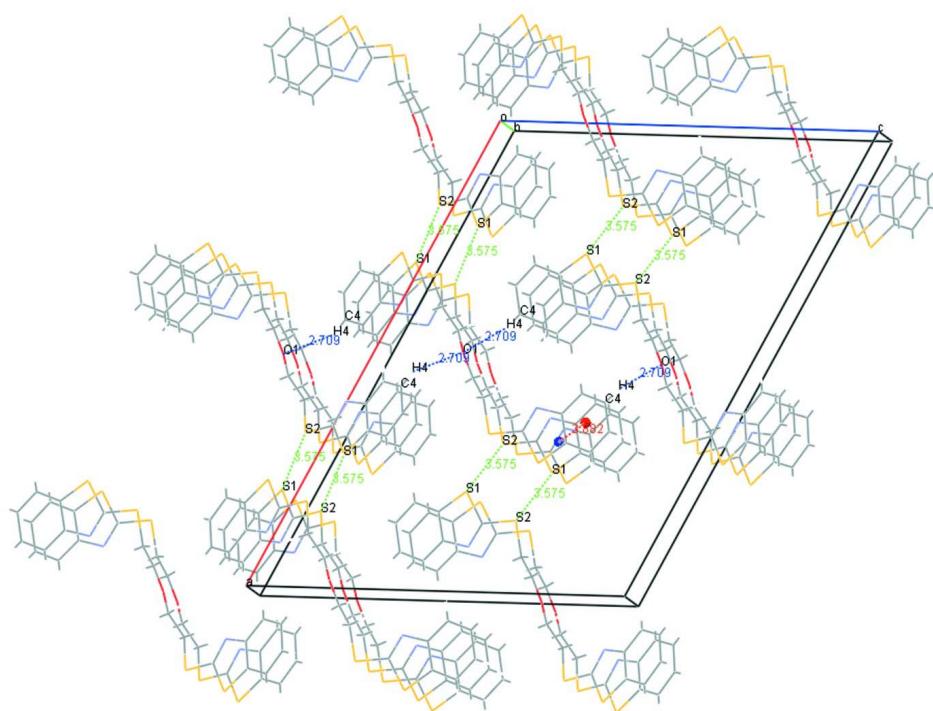
Figure 2

The three-dimensional structure by molecular packing, showing the hydrogen bonds as blue dashed lines [Symmetry codes: (i) x, $-y + 1$, $z + 1/2$], S—S bonds as green dashed lines and π-π stacking interactions as red dashed lines.

Bis[2-(1,3-benzothiazol-2-ylsulfanyl)ethyl] ether

Crystal data

$C_{18}H_{16}N_2OS_4$	$F(000) = 840$
$M_r = 404.57$	$D_x = 1.457$ Mg m^{-3}
Monoclinic, $C2/c$	Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å
Hall symbol: -C 2yc	Cell parameters from 1595 reflections
$a = 24.617$ (3) Å	$\theta = 2.8$–68.1°
$b = 4.7085$ (3) Å	$\mu = 4.81$ mm^{-1}
$c = 17.7866$ (15) Å	$T = 293$ K
$\beta = 116.571$ (13)°	Block, colourless
$V = 1843.9$ (3) Å^3	$0.18 \times 0.15 \times 0.07$ mm
$Z = 4$	

Data collection

Oxford Diffraction Xcalibur Sapphire3 diffractometer	2930 measured reflections
Radiation source: Enhance (Cu) X-ray Source	1682 independent reflections
Graphite monochromator	1353 reflections with $I > 2\sigma(I)$
Detector resolution: 16.0855 pixels mm^{-1}	$R_{int} = 0.020$
ω scans	$\theta_{max} = 68.1°$, $\theta_{min} = 2.8°$
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2005)	$h = -29 \rightarrow 25$
	$k = -5 \rightarrow 3$
$T_{min} = 0.765$, $T_{max} = 1.000$	$l = -21 \rightarrow 19$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.043$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.129$	
$S = 1.05$	H-atom parameters constrained
1682 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0876P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
114 parameters	
0 restraints	$(\Delta/\sigma)_{max} = 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.27$ e Å^{-3}
	$\Delta\rho_{min} = -0.25$ 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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.17154 (13)	0.1689 (5)	1.11310 (16)	0.0505 (6)
C2	0.18584 (15)	−0.0249 (6)	1.17798 (17)	0.0608 (7)
H2	0.2256	−0.0860	1.2098	0.073*
C3	0.13924 (18)	−0.1235 (7)	1.1936 (2)	0.0701 (8)

H3	0.1474	−0.2568	1.2359	0.084*
C4	0.08011 (16)	−0.0269 (8)	1.1470 (2)	0.0702 (8)
H4	0.0494	−0.0954	1.1591	0.084*
C5	0.06625 (15)	0.1676 (6)	1.0837 (2)	0.0614 (7)
H5	0.0266	0.2328	1.0534	0.074*
C6	0.11236 (12)	0.2665 (6)	1.06519 (15)	0.0489 (6)
C7	0.15597 (12)	0.4948 (6)	0.99910 (14)	0.0483 (6)
C8	0.09486 (13)	0.8627 (6)	0.86818 (16)	0.0532 (6)
H8C	0.0791	0.9199	0.9070	0.064*
H8B	0.0995	1.0323	0.8406	0.064*
C9	0.05001 (13)	0.6678 (5)	0.80325 (17)	0.0552 (6)
H9A	0.0683	0.5769	0.7712	0.066*
H9B	0.0370	0.5215	0.8300	0.066*
N1	0.10483 (10)	0.4522 (5)	1.00023 (13)	0.0507 (5)
S1	0.21965 (3)	0.32443 (16)	1.07717 (4)	0.0560 (2)
S2	0.16852 (3)	0.69930 (17)	0.92661 (4)	0.0592 (3)
O1	0.0000	0.8363 (5)	0.7500	0.0501 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0535 (14)	0.0516 (13)	0.0422 (12)	−0.0026 (11)	0.0176 (11)	−0.0037 (10)
C2	0.0671 (18)	0.0625 (16)	0.0465 (14)	0.0052 (13)	0.0197 (13)	0.0058 (12)
C3	0.094 (2)	0.0659 (17)	0.0546 (16)	−0.0017 (16)	0.0364 (17)	0.0077 (13)
C4	0.081 (2)	0.076 (2)	0.0661 (18)	−0.0114 (16)	0.0442 (17)	−0.0024 (15)
C5	0.0579 (16)	0.0686 (18)	0.0606 (17)	−0.0045 (13)	0.0290 (14)	−0.0061 (13)
C6	0.0530 (15)	0.0504 (13)	0.0395 (12)	−0.0021 (11)	0.0171 (11)	−0.0063 (10)
C7	0.0454 (13)	0.0524 (13)	0.0387 (11)	−0.0023 (10)	0.0112 (10)	−0.0007 (10)
C8	0.0561 (15)	0.0484 (13)	0.0442 (13)	0.0012 (11)	0.0127 (11)	0.0024 (10)
C9	0.0528 (15)	0.0482 (13)	0.0482 (13)	0.0051 (11)	0.0078 (12)	−0.0003 (11)
N1	0.0460 (11)	0.0559 (12)	0.0427 (10)	−0.0030 (9)	0.0132 (9)	−0.0023 (9)
S1	0.0438 (4)	0.0679 (5)	0.0484 (4)	0.0033 (3)	0.0136 (3)	0.0090 (3)
S2	0.0450 (4)	0.0713 (5)	0.0519 (4)	−0.0050 (3)	0.0132 (3)	0.0131 (3)
O1	0.0485 (14)	0.0462 (13)	0.0436 (12)	0.000	0.0099 (11)	0.000

Geometric parameters (Å, °)

C1—C2	1.387 (4)	C7—N1	1.284 (4)
C1—C6	1.396 (4)	C7—S2	1.744 (3)
C1—S1	1.739 (3)	C7—S1	1.755 (3)
C2—C3	1.376 (5)	C8—C9	1.501 (4)
C2—H2	0.9300	C8—S2	1.810 (3)
C3—C4	1.390 (5)	C8—H8C	0.9700
C3—H3	0.9300	C8—H8B	0.9700
C4—C5	1.372 (5)	C9—O1	1.414 (3)
C4—H4	0.9300	C9—H9A	0.9700
C5—C6	1.395 (4)	C9—H9B	0.9700
C5—H5	0.9300	O1—C9ⁱ	1.414 (3)

C6—N1	1.394 (4)		
C2—C1—C6	122.1 (3)	N1—C7—S1	116.8 (2)
C2—C1—S1	128.4 (2)	S2—C7—S1	116.50 (15)
C6—C1—S1	109.5 (2)	C9—C8—S2	112.65 (19)
C3—C2—C1	117.7 (3)	C9—C8—H8C	109.1
C3—C2—H2	121.1	S2—C8—H8C	109.1
C1—C2—H2	121.1	C9—C8—H8B	109.1
C2—C3—C4	121.0 (3)	S2—C8—H8B	109.1
C2—C3—H3	119.5	H8C—C8—H8B	107.8
C4—C3—H3	119.5	O1—C9—C8	107.0 (2)
C5—C4—C3	121.1 (3)	O1—C9—H9A	110.3
C5—C4—H4	119.4	C8—C9—H9A	110.3
C3—C4—H4	119.4	O1—C9—H9B	110.3
C4—C5—C6	119.1 (3)	C8—C9—H9B	110.3
C4—C5—H5	120.4	H9A—C9—H9B	108.6
C6—C5—H5	120.4	C7—N1—C6	110.1 (2)
N1—C6—C5	125.7 (2)	C1—S1—C7	88.23 (13)
N1—C6—C1	115.3 (2)	C7—S2—C8	101.30 (13)
C5—C6—C1	118.9 (3)	C9—O1—C9ⁱ	111.7 (3)
N1—C7—S2	126.7 (2)		

Symmetry code: (i) −x, y, −z+3/2.

Hydrogen-bond geometry (Å, º)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C4—H4⋯O1ⁱⁱ	0.93	2.71	3.358 (3)	128

Symmetry code: (ii) x, −y+1, z+1/2.