

Polymorphism of bis(1,3-benzothiazol-2-yl) trithio-carbonate

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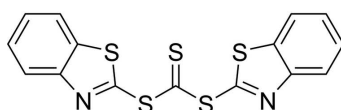
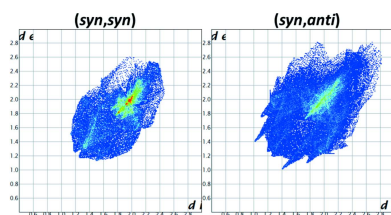
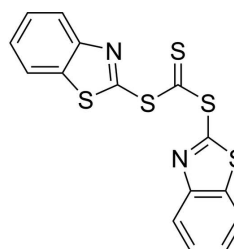
CCDC references: 2010358; 2010357

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The polymorphism of the title compound, $C_{15}H_8N_2S_5$, is reported, in which the (*syn,syn*) and (*syn,anti*) conformers simultaneously crystallized from a chloroform solution. The complete molecule of the (*syn,syn*) form is generated by a crystallographic twofold axis. The geometries of both conformers are compared in detail, revealing no significant differences in bond lengths, despite different bond angles because of the conformational changes. Analysis of the intermolecular interactions, aided by Hirshfeld surfaces, shows distinctive $S \cdots S$ and $S \cdots N$ contacts only for the (*syn,anti*) conformer. Aromatic π - π -stacking interactions are found for both conformers, which occur for the (*syn,anti*) conformer between pairs of molecules, but are continuous stacks in the (*syn,syn*) conformer. Non merohedral twinning was found for the crystal of the (*syn,anti*) conformer used for data collection.

1. Chemical context

Acyclic trithiocarbonates are important functional groups in several areas ranging from materials science and synthetic chemistry to pharmaceuticals (Kazemi *et al.*, 2018). Notably, their use as reagents in reversible addition-fragmentation chain-transfer (RAFT) free radical polymerization appears relevant since the relative stability of the conformers might have an influence on the stereochemistry of the obtained polymer (Huang *et al.*, 2018). Earlier studies on the conformational properties of perfluorodimethyl trithiocarbonate based on gas electron diffraction and Raman spectroscopy (Hermann *et al.*, 2000) show clear dependency of the solvent and aggregate state: The (*syn,syn*) conformer is predominant (84%) in the gas phase, as a liquid the distribution is almost equal [60% (*syn,syn*)], while in solution and with increasing polarity of the solvent, the ratio of the (*syn,anti*) conformer increases. The herein reported conformational polymorphism allows further structural comparison between trithiocarbonate conformers by X-ray diffraction analysis.

(*syn,syn*)(*syn,anti*)

2. Structural commentary

The (*syn, syn*) conformer crystallizes from chloroform solution in space group *Pbcn*. The asymmetric unit contains half of the molecule, with a crystallographic twofold axis passing through S3–C8 generating the complete molecule. The molecule is slightly twisted in a propeller-like shape, the twist introduced by the C7–S2–C8–S3 torsion angle of 24.46 (12)°, thus deviating from the idealized *syn* geometry of 0° (Fig. 1).

The (*syn, anti*) conformer also crystallizes from chloroform solution, but in space group *P1̄*. The *syn* and *anti* conformations of each half of the molecule are closer to the idealized geometry with torsion angles C7–S2–C8–S3 of 2.17 (13) and C9–S4–C8–S3 of –174.93 (9)°.

Interestingly, the thiocarbonyl and thiazol moieties in the (*syn, anti*) conformer are oriented almost perpendicular to each other, with S1–C7–S2–C8 and S5–C9–S4–C8 torsion angles close to 90° [–87.25 (10) and 104.26 (10)°, respectively]. In the (*syn, syn*) conformer, the thiocarbonyl and thiazol groups are almost in plane, apart from the propeller-like twist: the respective torsion angle S1–C7–S2–C8 is –2.4 (2)°, resulting in relative close proximity for the thiocarbonyl S1 and thiazol S3 atoms. This S1...S3 distance of 3.106 (1) Å, which is considerably shorter than the sum of van der Waals radii (3.78 Å; Alvarez, 2013), indicates possible attractive chalcogenic interactions. Comparable T-shaped geometries around sulfur were observed by our group for dihalosulfuranes (Talavera *et al.*, 2015; Peña *et al.*, 2017; Aversch *et al.*, 2019), where the interaction is even more pronounced because of the electronically depleted sulfur atoms.

The bond lengths in both conformers show no significant differences that would correspond to the changed bond angles in respect of hyperconjugative effects.

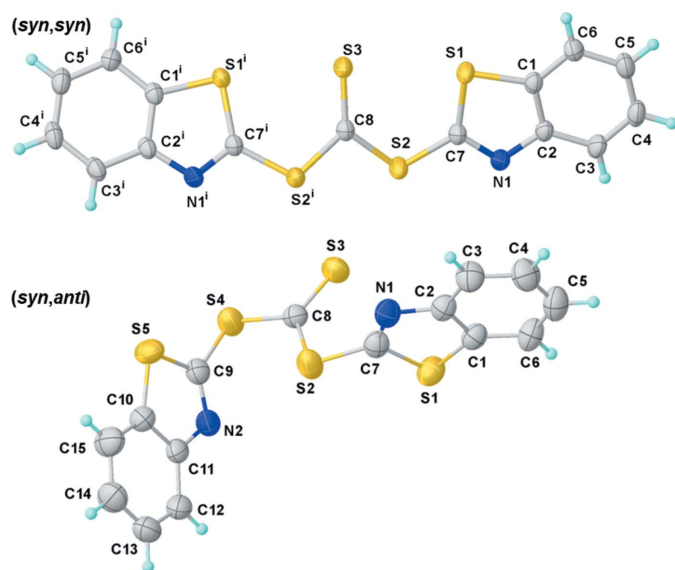


Figure 1
Molecular structures and labelling schemes for the (*syn, syn*) (top) and (*syn, anti*) (bottom) polymorphs with displacement ellipsoids at the 50% probability level. Symmetry code: (i) $-x, +y, \frac{1}{2} - z$.

Table 1
Hydrogen-bond geometry (Å, °) for the (*syn, anti*) conformer.

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C6–H6...N1 ⁱ	0.93	2.58	3.467 (2)	161
C15–H15...N2 ⁱⁱ	0.93	2.68	3.552 (2)	157

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

3. Supramolecular features

To investigate the supramolecular features, the Hirshfeld surface (Spackman & Jayatilaka, 2009) was calculated for both conformers using *CrystalExplorer17* (Turner *et al.*, 2017). The resulting Hirshfeld surfaces mapped over d_{norm} heatmaps for the (*syn, syn*) and (*syn, anti*) conformers are depicted in Fig. 2 and the corresponding fingerprint plots are shown in Fig. 3. Observation of the heatmap and the features of the fingerprint plots yields one apparent conclusion: the (*syn, syn*) conformer has no distinctive contacts while the surface for the (*syn, anti*)

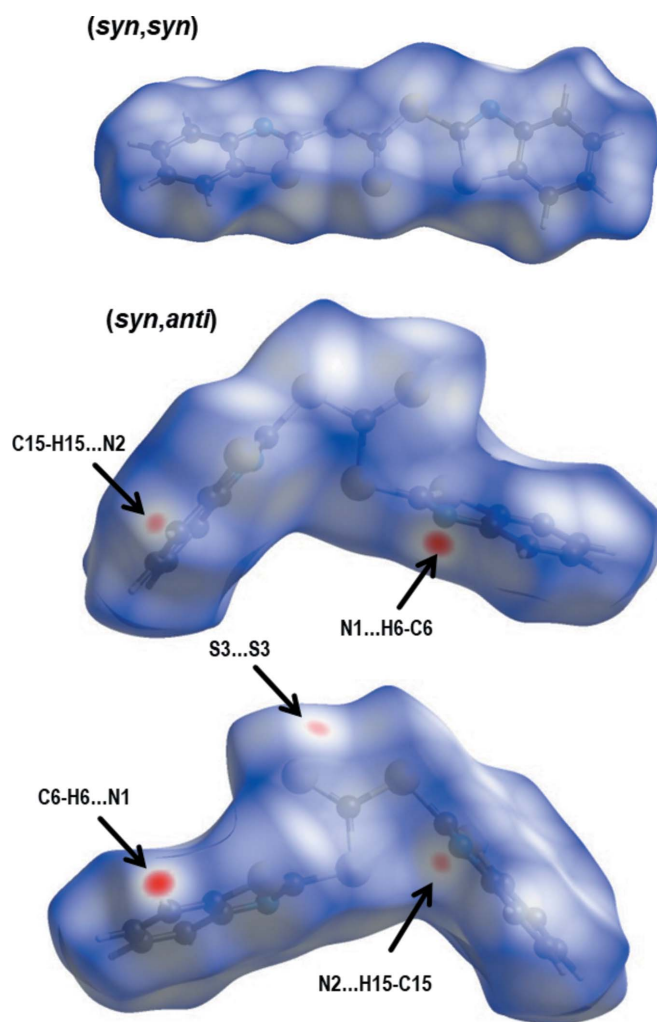


Figure 2
Hirshfeld surfaces mapped over d_{norm} for the (*syn, syn*) (top) and (*syn, anti*) (bottom) conformers in opposite views. Mapped ranges of 0.0097 to 1.0175 and –0.1520 to 1.2170 for (*syn, syn*) and (*syn, anti*), respectively.

Table 2

Relative element–element contributions to the Hirshfeld surface (in %). Asymmetric contacts include reciprocal contributions.

Contact	(<i>syn,syn</i>)	(<i>syn,anti</i>)
S··S	22.9	16.1
S··N	4.6	0.9
S··C	6.2	11.5
S··H	2.7	17.4
N··N	0.4	0.2
N··C	2.6	3.3
N··H	8.4	9.7
C··C	11.6	3.0
C··H	9.6	16.5
H··H	31.0	21.4

conformer features in total five hot spots, which reappear as sharp features in the fingerprint plot (Fig. 3). Those contacts are identified as two C–H··N hydrogen bonds (Table 1) between N1 and C6 and N2 and C15 with lengths of 3.467 (2) and 3.552 (2) Å, respectively. This is in the range of other C–H··N hydrogen bonds reported previously (Mambanda *et al.* 2007; Pingali *et al.*, 2014). The fifth contact is a symmetric S··S interaction between S3 and its adjacent symmetry-equivalent clone, with a distance of 3.509 (1) Å. The relative contributions of various contacts to the Hirshfeld surface are given in Table 2.

The Hirshfeld surface mapped over curvedness (Fig. 4) indicates π – π interactions by wide flat areas on one side of each benzothiazol unit. Packing diagrams of the (*syn,syn*) (Fig. 5) and (*syn,anti*) (Fig. 6) conformers show the parallel arrangement of adjacent benzothiazol groups, which come in

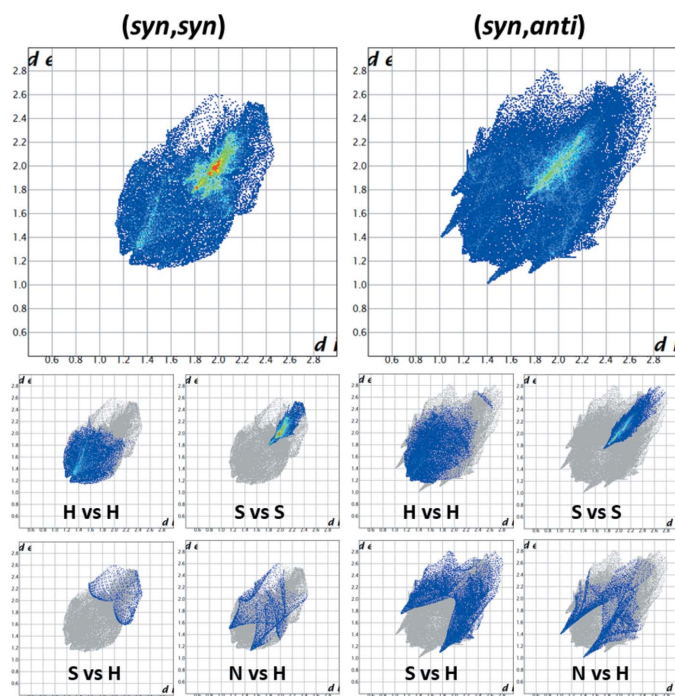


Figure 3 Full fingerprint plot (top) and decomposed plots (bottom) showing exclusive element element contacts.

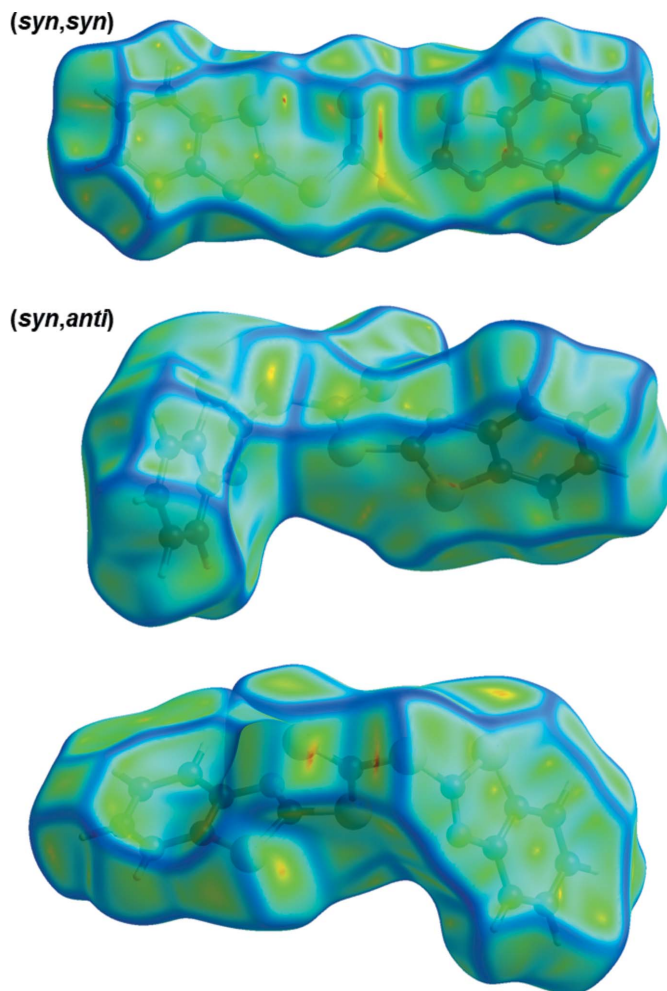


Figure 4 Hirshfeld surface mapped over curvedness for the (*syn,syn*) (top) and (*syn,anti*) (bottom) conformers in opposite views.

pairs (*syn,anti*) or in a continuous herringbone motif (*syn,syn*). The separation between the benzothiazol planes (defined by C1–C7/N1/S1 or C9–C15/N2/S5) are similar with distances of 3.54 Å in the (*syn,syn*) conformer and 3.43 and 3.58 Å in the (*syn,anti*) conformer.

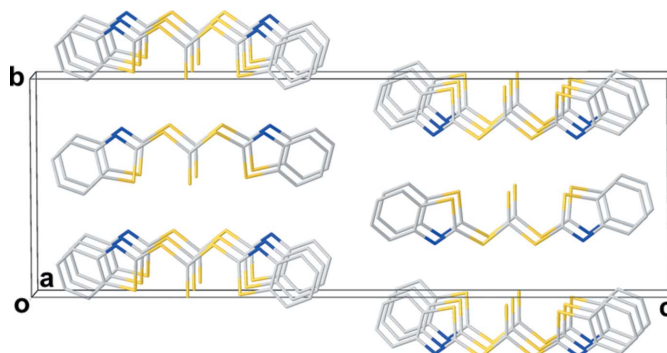


Figure 5 Packing diagram for (*syn,syn*) displaying the herringbone motif.

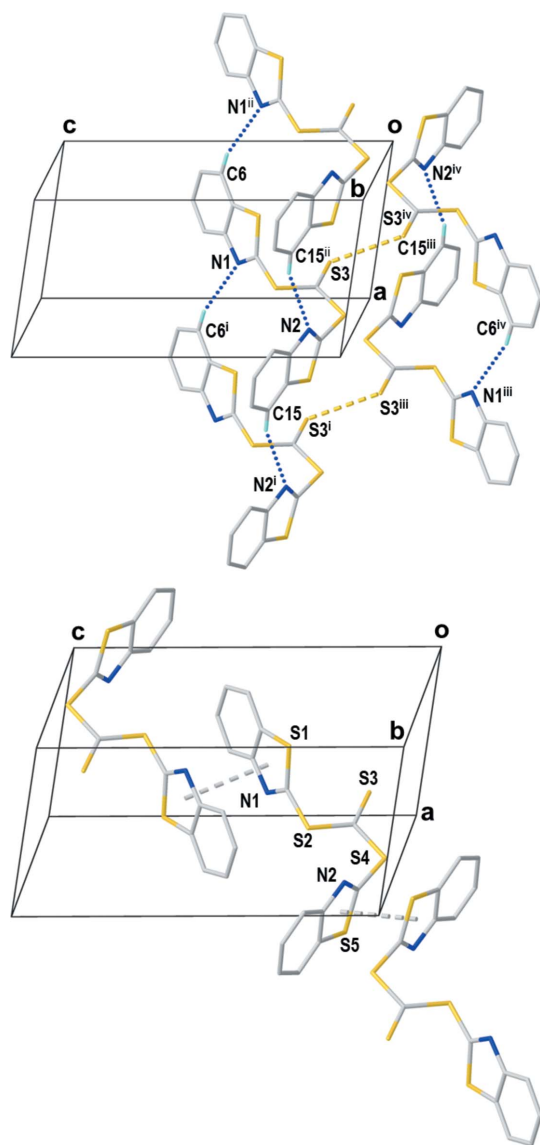


Figure 6
Packing diagram displaying all S...S contacts (yellow stippled bonds) and C—H...N hydrogen bonds (blue balled bonds) and separate packing diagram displaying π – π interactions (grey stippled bonds). Only hydrogen atoms participating in hydrogen bonds are shown. Symmetry codes: (i) $1 + x, +y, +z$; (ii) $-1 + x, +y, +z$; (iii) $2 - x, 1 - y, -z$; (iv) $1 - x, 1 - y, -z$.

4. Database survey

A search in the CSD (version 5.41, update of November 2019; Groom *et al.*, 2016) for non-cyclic and non-oxidized trithiocarbonates produced 20 results, of which only one (refcode XUBNAJ; Sotofte & Senning, 2001) adopts a (*syn,anti*) conformation. There is one outlier neither close to a (*syn,syn*) nor a (*syn,anti*) conformation, which is chemically a thioanhydride (XISSAU; Weber *et al.*, 2008). All other results are trithiocarbonates with a (*syn,syn*) conformation, which appears to be the predominant form. A substructure search for benzothiazoles and thiazoles yielded large numbers of hits (1500 and 2200, respectively). A comparable polymorphism with thiazolothiazols (Schneider *et al.*, 2015) was reported with

interplane separations around 3.45 Å, as well as arrangements in pairs of π – π interactions for one polymorph and a herringbone motif in the other, closely matching our observations.

5. Synthesis and crystallization

The title compound was initially isolated in small amounts as a side product and crystallized from chloroform solution in an NMR tube, where two crystalline species could be identified visually: (*syn,syn*) in the form of orange needles and (*syn,anti*) as orange blocks.

The synthesis of the title compound is based on a literature procedure (Runge *et al.*, 1962). Benzothiazole-2-thiol (500 mg, 2.99 mmol, 1.0 eq.) and sodium hydroxide (179 mg, 4.48 mmol, 1.5 eq.) were dissolved in water (30 ml). Thiophosgene (165 mg, 1.44 mmol, 0.48 eq.) was added dropwise at room temperature. After complete addition, the solution was stirred for 15 minutes. Brine solution was added, the reaction mixture extracted with ethyl acetate and the combined organic phases dried over sodium sulfate. The solvent was removed *in vacuo* to yield the crude product as an orange solid (518 mg). After recrystallization from boiling benzene solution the pure product was obtained as orange crystals (432 mg, 1.15 mmol, 77%).

The melting range is 420–423 K, as measured on a Büchi M-560.

NMR spectra recorded on a Bruker Avance III HD 300 and chemical shifts are given in parts per million. ^1H NMR (300 MHz, CDCl_3): 8.20–8.17 (*m*, 1H), 7.99–7.96 (*m*, 1H), 7.62–7.51 (*m*, 2H). ^{13}C -NMR (300 MHz, CDCl_3): 212.5 (C), 156.5 (C), 152.8 (C), 138.0 (C), 126.94 (CH), 126.85 (CH), 124.4 (CH), 121.7 (CH).

High-resolution mass spectrometry was carried out on a Bruker maXis ESI-QTOF-MS. Calculated for $\text{C}_{15}\text{H}_8\text{S}_5\text{N}_2+\text{H}^+$: 376.9364, found: 376.9364; calculated for $\text{C}_{15}\text{H}_8\text{S}_5\text{N}_2+\text{Na}^+$: 398.9183, found: 398.9185.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. All aromatic hydrogen atoms were placed geometrically ($\text{C}-\text{H} = 0.93$ Å) and refined using a riding model with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{iso}}(\text{C})$.

Non merohedral twinning was found for the crystal of the (*syn,anti*) conformer used for data collection. The twin domain transformation matrix was found to be (0.996, –0.141, –0.031/0.331, 0.977, –0.106/0.235, 0.130, 0.958). Data integration was carried out using both domains with a final twin batch scale factor of 0.1211 (17).

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Table 3
Experimental details.

	(<i>syn,syn</i>)	(<i>syn,anti</i>)
Crystal data		
Chemical formula	C ₁₅ H ₈ N ₂ S ₅	C ₁₅ H ₈ N ₂ S ₅
<i>M_r</i>	376.53	376.53
Crystal system, space group	Orthorhombic, <i>Pbcn</i>	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	299	299
<i>a</i> , <i>b</i> , <i>c</i> (Å)	3.9458 (15), 11.434 (3), 33.366 (11)	6.4976 (5), 9.5593 (12), 13.1962 (11)
α , β , γ (°)	90, 90, 90	80.576 (5), 82.312 (3), 86.288 (5)
<i>V</i> (Å ³)	1505.4 (9)	800.55 (14)
<i>Z</i>	4	2
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm ⁻¹)	0.76	0.72
Crystal size (mm)	0.24 × 0.07 × 0.02	0.44 × 0.35 × 0.28
Data collection		
Diffractometer	Bruker D8 Venture Dual Source	Bruker D8 Venture Dual Source
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2016)	Multi-scan (<i>TWINABS</i> ; Bruker, 2012)
<i>T</i> _{min} – <i>T</i> _{max}	0.248, 0.336	0.256, 0.372
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	17286, 2147, 1708	4846, 4846, 4296
<i>R</i> _{int}	0.048	–
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.699	0.714
Refinement		
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.051, 0.110, 1.10	0.036, 0.099, 1.03
No. of reflections	2147	4846
No. of parameters	101	200
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.32, –0.34	0.45, –0.43

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b) and *OLEX2* (Dolomanov *et al.*, 2009).

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supporting information

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Polymorphism of bis(1,3-benzothiazol-2-yl) trithiocarbonate

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Computing details

For both structures, data collection: *APEX3* (Bruker, 2016); cell refinement: *SAINTE* (Bruker, 2016); data reduction: *SAINTE* (Bruker, 2016); program(s) used to solve structure: *ShelXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

Bis(1,3-benzothiazol-2-yl) trithiocarbonate (ss)

Crystal data

$C_{15}H_8N_2S_5$

$M_r = 376.53$

Orthorhombic, *Pbcn*

$a = 3.9458$ (15) Å

$b = 11.434$ (3) Å

$c = 33.366$ (11) Å

$V = 1505.4$ (9) Å³

$Z = 4$

$F(000) = 768$

$D_x = 1.661$ Mg m⁻³

Melting point: 420 K

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 744 reflections

$\theta = 2.4$ – 23.7°

$\mu = 0.76$ mm⁻¹

$T = 299$ K

Needle, orange

$0.24 \times 0.07 \times 0.02$ mm

Data collection

Bruker D8 Venture Dual Source
diffractometer

Detector resolution: 8.33 pixels mm⁻¹

φ and ω scans

Absorption correction: multi-scan
(SADABS; Bruker, 2016)

$T_{\min} = 0.248$, $T_{\max} = 0.336$

17286 measured reflections

2147 independent reflections

1708 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.048$

$\theta_{\max} = 29.8^\circ$, $\theta_{\min} = 2.4^\circ$

$h = -5 \rightarrow 5$

$k = -15 \rightarrow 15$

$l = -46 \rightarrow 46$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.051$

$wR(F^2) = 0.110$

$S = 1.10$

2147 reflections

101 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0292P)^2 + 2.5718P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.32$ e Å⁻³

$\Delta\rho_{\min} = -0.34$ 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.3107 (2)	0.53882 (6)	0.33530 (2)	0.03516 (19)
S2	−0.0018 (2)	0.75692 (6)	0.29112 (2)	0.0406 (2)
S3	0.000000	0.52046 (9)	0.250000	0.0464 (3)
N1	0.2014 (7)	0.7473 (2)	0.36435 (6)	0.0339 (5)
C1	0.4357 (7)	0.5675 (2)	0.38429 (7)	0.0303 (5)
C2	0.3531 (7)	0.6823 (2)	0.39456 (7)	0.0303 (5)
C3	0.4219 (8)	0.7232 (3)	0.43318 (7)	0.0380 (7)
H3	0.364207	0.798967	0.440712	0.046*
C4	0.5772 (8)	0.6486 (3)	0.45974 (8)	0.0417 (7)
H4	0.626489	0.674805	0.485467	0.050*
C5	0.6622 (8)	0.5349 (3)	0.44906 (8)	0.0419 (7)
H5	0.766095	0.486440	0.467776	0.050*
C6	0.5954 (8)	0.4927 (3)	0.41122 (8)	0.0365 (6)
H6	0.654756	0.416888	0.403921	0.044*
C7	0.1712 (7)	0.6830 (2)	0.33240 (7)	0.0308 (5)
C8	0.000000	0.6615 (3)	0.250000	0.0302 (8)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0508 (4)	0.0307 (3)	0.0240 (3)	0.0060 (3)	−0.0060 (3)	−0.0048 (2)
S2	0.0647 (5)	0.0311 (3)	0.0261 (3)	0.0092 (4)	−0.0079 (3)	−0.0031 (2)
S3	0.0809 (9)	0.0299 (5)	0.0284 (4)	0.000	−0.0129 (5)	0.000
N1	0.0472 (14)	0.0301 (11)	0.0244 (9)	0.0004 (11)	−0.0001 (10)	−0.0024 (8)
C1	0.0335 (14)	0.0346 (13)	0.0228 (10)	−0.0035 (11)	0.0007 (10)	−0.0013 (9)
C2	0.0366 (15)	0.0326 (13)	0.0216 (10)	−0.0048 (12)	0.0010 (10)	−0.0016 (9)
C3	0.0514 (18)	0.0395 (15)	0.0231 (11)	−0.0053 (13)	0.0025 (11)	−0.0053 (10)
C4	0.0486 (18)	0.0530 (18)	0.0235 (11)	−0.0101 (15)	−0.0047 (12)	−0.0022 (11)
C5	0.0489 (18)	0.0495 (17)	0.0275 (12)	−0.0040 (15)	−0.0064 (12)	0.0057 (12)
C6	0.0428 (16)	0.0357 (14)	0.0310 (12)	0.0030 (13)	−0.0057 (11)	0.0010 (10)
C7	0.0388 (15)	0.0318 (12)	0.0218 (10)	−0.0001 (12)	−0.0002 (10)	−0.0009 (9)
C8	0.035 (2)	0.0332 (18)	0.0227 (14)	0.000	−0.0008 (14)	0.000

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

S1—C1	1.739 (2)	C2—C3	1.397 (3)
S1—C7	1.741 (3)	C3—H3	0.9300
S2—C7	1.755 (3)	C3—C4	1.375 (4)
S2—C8	1.753 (2)	C4—H4	0.9300

S3—C8	1.612 (4)	C4—C5	1.389 (4)
N1—C2	1.388 (3)	C5—H5	0.9300
N1—C7	1.300 (3)	C5—C6	1.377 (4)
C1—C2	1.395 (4)	C6—H6	0.9300
C1—C6	1.392 (4)		
C1—S1—C7	87.88 (12)	C5—C4—H4	119.2
C8—S2—C7	108.23 (13)	C4—C5—H5	119.4
C7—N1—C2	109.4 (2)	C6—C5—C4	121.1 (3)
C2—C1—S1	110.02 (19)	C6—C5—H5	119.4
C6—C1—S1	128.3 (2)	C1—C6—H6	121.2
C6—C1—C2	121.7 (2)	C5—C6—C1	117.6 (3)
N1—C2—C1	115.2 (2)	C5—C6—H6	121.2
N1—C2—C3	125.1 (2)	S1—C7—S2	128.53 (14)
C1—C2—C3	119.7 (2)	N1—C7—S1	117.46 (19)
C2—C3—H3	120.9	N1—C7—S2	114.0 (2)
C4—C3—C2	118.3 (3)	S2—C8—S2 ⁱ	103.00 (19)
C4—C3—H3	120.9	S3—C8—S2	128.50 (10)
C3—C4—H4	119.2	S3—C8—S2 ⁱ	128.50 (10)
C3—C4—C5	121.6 (2)		
S1—C1—C2—N1	-1.3 (3)	C4—C5—C6—C1	-0.8 (5)
S1—C1—C2—C3	178.1 (2)	C6—C1—C2—N1	178.7 (3)
S1—C1—C6—C5	-178.4 (2)	C6—C1—C2—C3	-1.9 (4)
N1—C2—C3—C4	-179.3 (3)	C7—S1—C1—C2	1.6 (2)
C1—S1—C7—S2	176.9 (2)	C7—S1—C1—C6	-178.3 (3)
C1—S1—C7—N1	-1.8 (2)	C7—S2—C8—S2 ⁱ	-155.54 (12)
C1—C2—C3—C4	1.4 (4)	C7—S2—C8—S3	24.46 (12)
C2—N1—C7—S1	1.3 (3)	C7—N1—C2—C1	0.0 (4)
C2—N1—C7—S2	-177.49 (19)	C7—N1—C2—C3	-179.3 (3)
C2—C1—C6—C5	1.6 (4)	C8—S2—C7—S1	-2.4 (2)
C2—C3—C4—C5	-0.6 (5)	C8—S2—C7—N1	176.3 (2)
C3—C4—C5—C6	0.3 (5)		

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

(sa)

Crystal data

$C_{15}H_8N_2S_5$

$M_r = 376.53$

Triclinic, $P\bar{1}$

$a = 6.4976$ (5) Å

$b = 9.5593$ (12) Å

$c = 13.1962$ (11) Å

$\alpha = 80.576$ (5)°

$\beta = 82.312$ (3)°

$\gamma = 86.288$ (5)°

$V = 800.55$ (14) Å³

$Z = 2$

$F(000) = 384$

$D_x = 1.562$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 1193 reflections

$\theta = 3.2$ – 27.5 °

$\mu = 0.72$ mm⁻¹

$T = 299$ K

Block, yellow

$0.44 \times 0.35 \times 0.28$ mm

Data collection

Bruker D8 Venture Dual Source
diffractometer
Detector resolution: 8.33 pixels mm⁻¹
 φ and ω scans
Absorption correction: multi-scan
(*TWINABS*; Bruker, 2012)
 $T_{\min} = 0.256$, $T_{\max} = 0.372$

4846 measured reflections
4846 independent reflections
4296 reflections with $I > 2\sigma(I)$
 $\theta_{\max} = 30.5^\circ$, $\theta_{\min} = 2.9^\circ$
 $h = -9 \rightarrow 9$
 $k = -13 \rightarrow 13$
 $l = 0 \rightarrow 18$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.099$
 $S = 1.03$
4846 reflections
200 parameters
0 restraints
Primary atom site location: dual

Hydrogen site location: inferred from
neighbouring sites
H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0452P)^2 + 0.2258P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.45 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.43 \text{ e } \text{\AA}^{-3}$

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.

Refinement. Refined as a 2-component twin.

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	0.28033 (7)	0.51733 (5)	0.34242 (3)	0.05338 (11)
S2	0.69953 (8)	0.63001 (5)	0.25025 (3)	0.05403 (12)
S3	0.61181 (7)	0.42429 (4)	0.11132 (3)	0.05159 (11)
S4	0.85868 (7)	0.66560 (5)	0.02663 (3)	0.05264 (11)
S5	1.22828 (7)	0.78128 (5)	0.09888 (4)	0.05328 (11)
N1	0.6295 (2)	0.39444 (15)	0.39055 (10)	0.0471 (3)
N2	0.8599 (2)	0.90383 (14)	0.11309 (11)	0.0448 (3)
C1	0.2690 (2)	0.36628 (18)	0.43444 (11)	0.0437 (3)
C2	0.4716 (2)	0.31514 (17)	0.45002 (11)	0.0433 (3)
C3	0.5015 (3)	0.1931 (2)	0.52121 (15)	0.0561 (4)
H3	0.634842	0.158220	0.532571	0.067*
C4	0.3300 (3)	0.1255 (2)	0.57426 (15)	0.0611 (4)
H4	0.348063	0.043560	0.621611	0.073*
C5	0.1300 (3)	0.1771 (2)	0.55856 (14)	0.0617 (5)
H5	0.016856	0.129419	0.596057	0.074*
C6	0.0959 (3)	0.2970 (2)	0.48879 (14)	0.0560 (4)
H6	-0.038178	0.330852	0.478180	0.067*
C7	0.5497 (2)	0.49964 (18)	0.33205 (12)	0.0453 (3)
C8	0.7176 (2)	0.56406 (15)	0.13211 (11)	0.0400 (3)
C9	0.9663 (2)	0.79599 (16)	0.08213 (12)	0.0441 (3)
C10	1.1930 (2)	0.93342 (17)	0.15548 (12)	0.0452 (3)

C11	0.9856 (2)	0.98336 (15)	0.15608 (11)	0.0400 (3)
C12	0.9199 (3)	1.10581 (17)	0.19921 (13)	0.0492 (3)
H12	0.782958	1.140853	0.199684	0.059*
C13	1.0611 (3)	1.17301 (19)	0.24069 (15)	0.0579 (4)
H13	1.018665	1.253812	0.270076	0.070*
C14	1.2667 (3)	1.1223 (2)	0.23954 (17)	0.0642 (5)
H14	1.359240	1.169973	0.268185	0.077*
C15	1.3362 (3)	1.0030 (2)	0.19685 (17)	0.0623 (5)
H15	1.474206	0.969922	0.195698	0.075*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0471 (2)	0.0600 (3)	0.0492 (2)	0.00577 (17)	-0.00451 (16)	-0.00160 (17)
S2	0.0664 (3)	0.0563 (2)	0.04205 (19)	-0.02084 (19)	-0.00072 (17)	-0.01342 (17)
S3	0.0573 (2)	0.0457 (2)	0.0549 (2)	-0.00929 (17)	-0.00458 (17)	-0.01626 (17)
S4	0.0636 (3)	0.0529 (2)	0.04214 (19)	-0.01454 (18)	0.00143 (17)	-0.01137 (16)
S5	0.0464 (2)	0.0507 (2)	0.0647 (3)	0.00660 (16)	-0.00631 (18)	-0.01861 (19)
N1	0.0411 (6)	0.0555 (8)	0.0454 (7)	-0.0049 (5)	-0.0061 (5)	-0.0085 (6)
N2	0.0414 (6)	0.0412 (6)	0.0500 (7)	-0.0037 (5)	-0.0032 (5)	-0.0031 (5)
C1	0.0414 (7)	0.0533 (8)	0.0368 (6)	-0.0001 (6)	-0.0034 (5)	-0.0104 (6)
C2	0.0403 (7)	0.0512 (8)	0.0398 (7)	-0.0029 (6)	-0.0050 (5)	-0.0107 (6)
C3	0.0498 (9)	0.0597 (10)	0.0568 (9)	0.0001 (7)	-0.0107 (7)	-0.0010 (8)
C4	0.0674 (11)	0.0609 (11)	0.0515 (9)	-0.0092 (9)	-0.0069 (8)	0.0035 (8)
C5	0.0565 (10)	0.0774 (13)	0.0486 (9)	-0.0169 (9)	0.0034 (7)	-0.0048 (8)
C6	0.0412 (8)	0.0773 (12)	0.0479 (8)	-0.0053 (7)	-0.0005 (6)	-0.0082 (8)
C7	0.0459 (7)	0.0518 (8)	0.0396 (7)	-0.0065 (6)	-0.0033 (6)	-0.0116 (6)
C8	0.0399 (6)	0.0392 (7)	0.0414 (7)	0.0004 (5)	-0.0050 (5)	-0.0086 (5)
C9	0.0461 (7)	0.0412 (7)	0.0433 (7)	-0.0057 (6)	-0.0019 (6)	-0.0031 (6)
C10	0.0419 (7)	0.0450 (8)	0.0484 (8)	-0.0005 (6)	-0.0028 (6)	-0.0089 (6)
C11	0.0408 (7)	0.0359 (6)	0.0400 (6)	-0.0027 (5)	0.0003 (5)	-0.0003 (5)
C12	0.0485 (8)	0.0396 (7)	0.0558 (9)	0.0005 (6)	0.0021 (7)	-0.0052 (6)
C13	0.0664 (11)	0.0457 (8)	0.0616 (10)	-0.0068 (8)	0.0019 (8)	-0.0141 (7)
C14	0.0614 (11)	0.0643 (11)	0.0728 (12)	-0.0137 (9)	-0.0090 (9)	-0.0236 (9)
C15	0.0449 (9)	0.0680 (12)	0.0792 (13)	-0.0016 (8)	-0.0109 (8)	-0.0242 (10)

Geometric parameters (Å, °)

S1—C1	1.7264 (17)	C3—C4	1.374 (3)
S1—C7	1.7368 (16)	C4—H4	0.9300
S2—C7	1.7610 (16)	C4—C5	1.389 (3)
S2—C8	1.7620 (15)	C5—H5	0.9300
S3—C8	1.6194 (15)	C5—C6	1.374 (3)
S4—C8	1.7468 (15)	C6—H6	0.9300
S4—C9	1.7685 (16)	C10—C11	1.400 (2)
S5—C9	1.7395 (16)	C10—C15	1.393 (2)
S5—C10	1.7299 (16)	C11—C12	1.402 (2)
N1—C2	1.391 (2)	C12—H12	0.9300

N1—C7	1.289 (2)	C12—C13	1.371 (3)
N2—C9	1.295 (2)	C13—H13	0.9300
N2—C11	1.383 (2)	C13—C14	1.390 (3)
C1—C2	1.404 (2)	C14—H14	0.9300
C1—C6	1.394 (2)	C14—C15	1.378 (3)
C2—C3	1.393 (2)	C15—H15	0.9300
C3—H3	0.9300		
C1—S1—C7	88.65 (8)	N1—C7—S2	123.20 (12)
C7—S2—C8	100.30 (7)	S3—C8—S2	126.96 (9)
C8—S4—C9	103.88 (7)	S3—C8—S4	117.64 (9)
C10—S5—C9	88.70 (7)	S4—C8—S2	115.36 (8)
C7—N1—C2	109.59 (13)	S5—C9—S4	119.69 (9)
C9—N2—C11	109.89 (13)	N2—C9—S4	123.63 (12)
C2—C1—S1	109.38 (12)	N2—C9—S5	116.68 (12)
C6—C1—S1	129.40 (13)	C11—C10—S5	109.30 (11)
C6—C1—C2	121.22 (16)	C15—C10—S5	129.31 (13)
N1—C2—C1	115.14 (14)	C15—C10—C11	121.39 (15)
N1—C2—C3	125.11 (15)	N2—C11—C10	115.42 (13)
C3—C2—C1	119.75 (15)	N2—C11—C12	125.09 (14)
C2—C3—H3	120.7	C10—C11—C12	119.49 (15)
C4—C3—C2	118.58 (17)	C11—C12—H12	120.6
C4—C3—H3	120.7	C13—C12—C11	118.85 (16)
C3—C4—H4	119.4	C13—C12—H12	120.6
C3—C4—C5	121.28 (18)	C12—C13—H13	119.5
C5—C4—H4	119.4	C12—C13—C14	121.06 (17)
C4—C5—H5	119.3	C14—C13—H13	119.5
C6—C5—C4	121.36 (17)	C13—C14—H14	119.3
C6—C5—H5	119.3	C15—C14—C13	121.41 (18)
C1—C6—H6	121.1	C15—C14—H14	119.3
C5—C6—C1	117.80 (16)	C10—C15—H15	121.1
C5—C6—H6	121.1	C14—C15—C10	117.79 (17)
S1—C7—S2	119.43 (10)	C14—C15—H15	121.1
N1—C7—S1	117.24 (12)		
S1—C1—C2—N1	0.14 (17)	C7—N1—C2—C1	-0.64 (19)
S1—C1—C2—C3	-179.90 (13)	C7—N1—C2—C3	179.42 (16)
S1—C1—C6—C5	179.91 (14)	C8—S2—C7—S1	-87.25 (10)
S5—C10—C11—N2	-0.09 (16)	C8—S2—C7—N1	97.19 (14)
S5—C10—C11—C12	179.50 (12)	C8—S4—C9—S5	104.26 (10)
S5—C10—C15—C14	-178.84 (16)	C8—S4—C9—N2	-74.91 (15)
N1—C2—C3—C4	-179.78 (17)	C9—S4—C8—S2	7.06 (11)
N2—C11—C12—C13	178.98 (15)	C9—S4—C8—S3	-174.93 (9)
C1—S1—C7—S2	-176.51 (10)	C9—S5—C10—C11	-0.52 (12)
C1—S1—C7—N1	-0.69 (13)	C9—S5—C10—C15	178.99 (19)
C1—C2—C3—C4	0.3 (3)	C9—N2—C11—C10	0.89 (18)
C2—N1—C7—S1	0.87 (17)	C9—N2—C11—C12	-178.67 (15)
C2—N1—C7—S2	176.52 (11)	C10—S5—C9—S4	-178.11 (10)

C2—C1—C6—C5	0.2 (3)	C10—S5—C9—N2	1.12 (13)
C2—C3—C4—C5	-0.5 (3)	C10—C11—C12—C13	-0.6 (2)
C3—C4—C5—C6	0.5 (3)	C11—N2—C9—S4	177.86 (11)
C4—C5—C6—C1	-0.4 (3)	C11—N2—C9—S5	-1.34 (17)
C6—C1—C2—N1	179.88 (15)	C11—C10—C15—C14	0.6 (3)
C6—C1—C2—C3	-0.2 (2)	C11—C12—C13—C14	0.6 (3)
C7—S1—C1—C2	0.26 (12)	C12—C13—C14—C15	0.0 (3)
C7—S1—C1—C6	-179.44 (17)	C13—C14—C15—C10	-0.6 (3)
C7—S2—C8—S3	2.17 (13)	C15—C10—C11—N2	-179.64 (16)
C7—S2—C8—S4	179.97 (9)	C15—C10—C11—C12	0.0 (2)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C6—H6 \cdots N1 ⁱ	0.93	2.58	3.467 (2)	161
C15—H15 \cdots N2 ⁱⁱ	0.93	2.68	3.552 (2)	157

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