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A second polymorph of 3*H*-1,2-benzodithiole-3-thione

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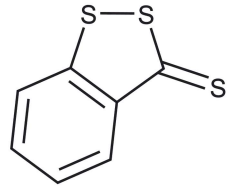
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $C_7H_4S_3$, is crystallizes in the monoclinic space group $P2_1/n$; it is the second polymorph, the first having been reported recently in space group $C2/c$ [Boukebbous *et al.* (2016) *IUCrData*, **1**, x161688]. The molecule displays an almost planar geometry with two fused rings [S10—C3—C4—C9 torsion angle = 0.2 (5)°]. In the crystal, short S···S [3.555 (1) and 3.503 (1) Å] contacts and π–π aromatic stacking [shortest centroid–centroid separation = 4.006 (5) Å] sustain the three-dimensional molecular packing.

3D view

Chemical scheme



Structure description

The title compound is a derivative of the 1,2-dithiole-3-thione family, which has attracted much interest because of the important bioactive properties and potential applications (Li *et al.*, 2016, Russell *et al.*, 2015), (Wallace *et al.*, 2007). Recrystallization of *3H*-1,2-benzodithiole-3-thione in toluene solution leads to a monoclinic polymorph in the space group *C*2/*c* (Boukebbous *et al.*, 2016) whereas recrystallization in diethyl ether solution leads to a second polymorph in the monoclinic system, and space group $P2_1/n$ (the present work). The *3H*-1,2-benzodithiole-3-thione molecule is composed of an aromatic ring fused with five-membered ring that containing two S atoms and thione functional groups (Fig. 1). The molecule displays an almost planar geometry with two fused rings [S10—C3—C4—C9 = 0.2 (5)°] with bond lengths of 2.064 (1), 1.738 (4), 1.726 (4) and 1.645 (3) Å for S1—S2, C5—S1, C3—S2 and C3—S10 bonds, respectively, and values of 94.0 (1) and 98.3 (1)° observed for angles C5—S1—S2 and S1—S2—C3, respectively. The angle S2—C3—C4 [113.1 (2)°] deviates from the expected value of 120° for a Csp^2 atom (C3═S10 bond). Likewise, a minor deviation (about 3°) is observed for the angles S1—C5—C4 and C5—C4—C3 from the expected value of 120°.

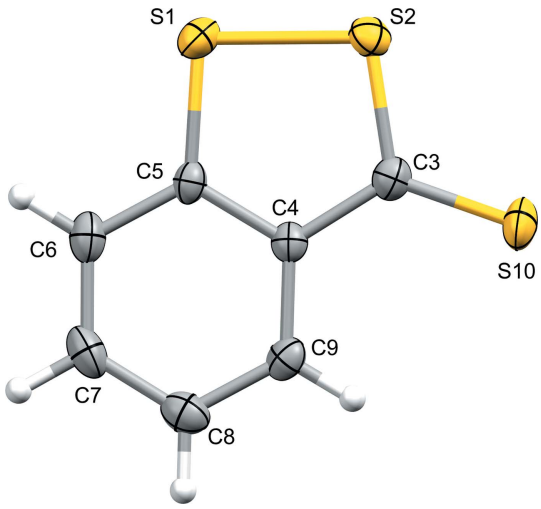


Figure 1
The molecular structure of the title compound, with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radius.

In the crystal (Figs. 2, 3 and 4), short S···S [S10···S1 = 3.555 (1) and S10···S2 = 3.503 (1) Å] contacts are observed. Moreover, parallel displaced π–π aromatic stacking interactions [shortest centroid-to-centroid separation = 4.006 (5) Å] linking adjacent molecules into a three-dimensional network are observed.

Synthesis and crystallization

The synthesis of 4.5-benzo-3*H*-1.2-dithiole-3-thione was based on a previously reported method (Klingsberg & Schreiber, 1962). To a xylene solution (150 ml) of 2,2-dithiodibenzoic acid (10 g, 0.033 mol), phosphorus pentasulfide (10 g, 0.04 mol) dissolved in xylene was added. The mixture was stirred for 1 h at reflux. The orange precipitate that formed was washed successively with distilled water and cold ethanol at 273 K and dried at room temperature for several hours. The recrystallization process was performed from diethyl ether solution by slow evaporation and red needles in a yield of 80% were obtained.

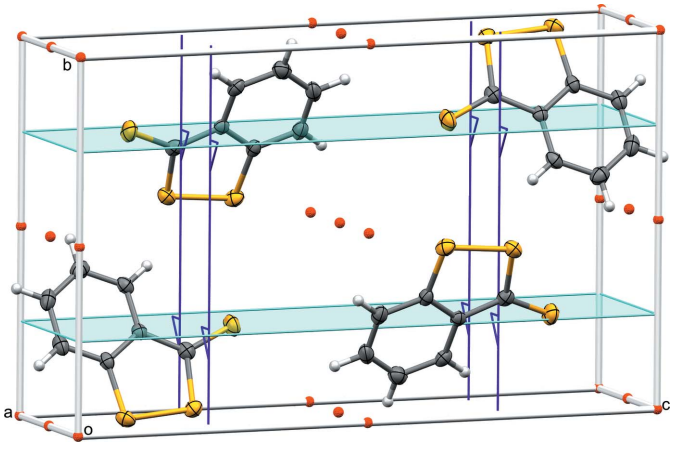


Figure 2
A view of the packing of the title compound, with displacement ellipsoids drawn at the 50% probability level. The inversion centre at [0,0,0] with symmetry operation $(-x, -y, -z)$ is shown as orange dots. The twofold screw axis in the [010] direction at $(\frac{1}{4}, y, \frac{1}{4})$, with symmetry operation $(\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z)$, is shown as purple lines. The glide plane perpendicular to [010] with glide component $[\frac{1}{2}, 0, \frac{1}{2}]$ and symmetry operation $(\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$ is shown as light-blue planes.

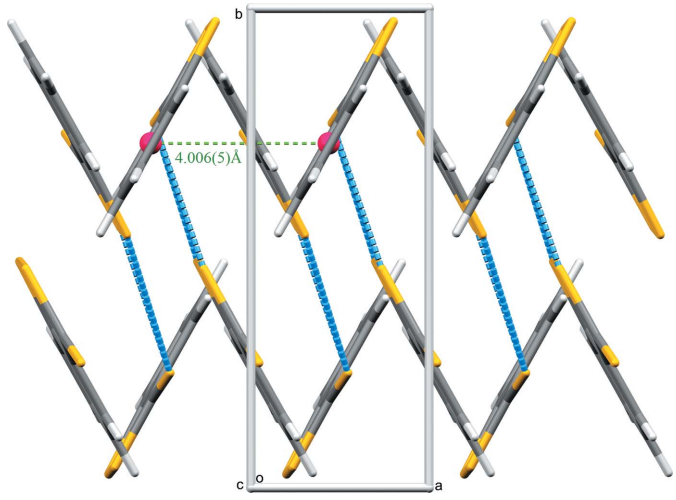


Figure 3
A view along the *c* axis of the molecular packing. The van der Waals interactions are shown as dashed blue lines. Centroids are shown as purple dots.

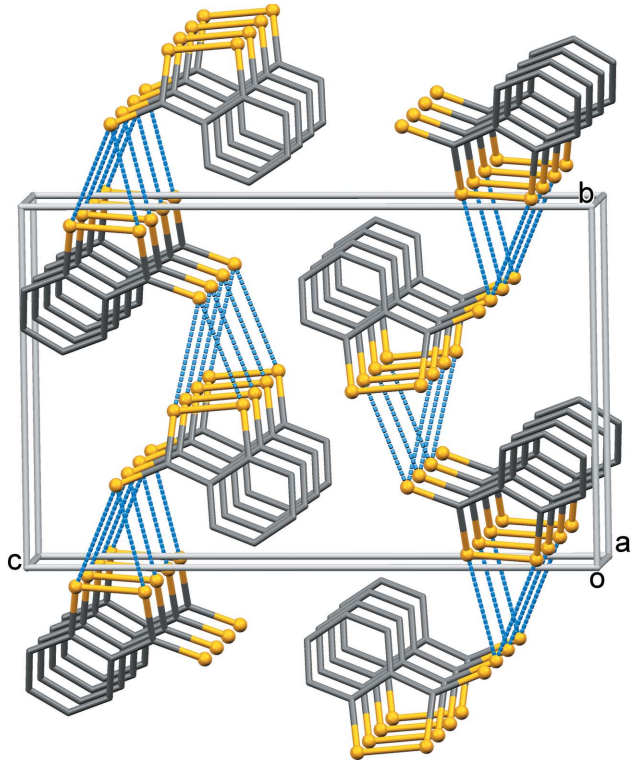


Figure 4
A view along the *a* axis of the molecular packing. S···S contacts are shown as dashed blue lines. H atoms have been omitted for clarity.

Table 1
Experimental details.

Crystal data	
Chemical formula	$C_7H_4S_3$
M_r	184.31
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	150
a, b, c (Å)	4.0062 (9), 10.739 (2), 17.178 (3)
β (°)	95.237 (18)
V (Å^3)	736.0 (3)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.91
Crystal size (mm)	0.52 × 0.10 × 0.06
Data collection	
Diffractometer	Rigaku OD Xcalibur Atlas Gemini ultra
Absorption correction	Analytical [*CrysAlis PRO* (Rigaku OD, 2015), based on expressions derived by Clark & Reid (1995)]
T_{min}, T_{max}	0.724, 0.947
No. of measured, independent and observed [$I > 2.0\sigma(I)$] reflections	6569, 1832, 1482
R_{int}	0.053
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.694
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.046, 0.101, 1.02
No. of reflections	1826
No. of parameters	91
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.77, −0.65

Computer programs: *CrysAlis PRO* (Rigaku OD, 2015), *SIR97* (Altomare *et al.*, 1999), *CRYSTALS* (Betteridge *et al.*, 2003) and *CAMERON* (Watkin *et al.*, 1996).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C—H in the range 0.93–0.98 and N—H in the range 0.86–0.89 Å) and U_{iso}(H) (in the range 1.2–1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints. (Cooper *et al.*, 2010).

Acknowledgements

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full crystallographic data

IUCrData (2016). **1**, x161799 [https://doi.org/10.1107/S2414314616017995]

A second polymorph of 3*H*-1,2-benzodithiole-3-thione

Khaled Boukebbous, El Adoui Laifa, Aimery De Mallmann and Mostafa Taoufik

(I)

Crystal data

$C_7H_4S_3$
M_r = 184.31
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
a = 4.0062 (9) Å
b = 10.739 (2) Å
c = 17.178 (3) Å
β = 95.237 (18)°
V = 736.0 (3) Å^3
Z = 4
$F(000)$ = 376
D_x = 1.663 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 1997 reflections
θ = 4.0–28.7°
μ = 0.91 mm^{-1}
T = 150 K
Needle, red
0.52 × 0.10 × 0.06 mm

Data collection

Rigaku OD Xcalibur Atlas Gemini ultra diffractometer
Radiation source: fine-focus sealed X-ray tube, Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 10.4685 pixels mm^{-1}
ω scans
Absorption correction: analytical [CrysAlis PRO (Rigaku OD, 2015), based on expressions derived by Clark & Reid (1995)]
T_{min} = 0.724, T_{max} = 0.947
6569 measured reflections
1832 independent reflections
1482 reflections with $I > 2.0\sigma(I)$
R_{int} = 0.053
θ_{max} = 29.6°, θ_{min} = 3.1°
h = −5→5
k = −14→14
l = −23→23

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.101
S = 1.02
1826 reflections
91 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: difference Fourier map
H-atom parameters constrained
Method, part 1, Chebychev polynomial, (Watkin, 1994, *P*rince, 1982) [*w*eight] = 1.0/[A_0*T_0(x) + A_1*T_1(x) ··· + A_{n-1}]*T_{n-1}(x)] where A_i are the Chebychev coefficients listed belo*w* and x = *F* /*F*max Method = Robust Weighting (*P*rince, 1982) W = [*w*eight] * [1-(delta*F*/6*sigma*F*)^2]^2 A_i are: 950. 0.135E + 04 758. 229.
$(\Delta/\sigma)_{max}$ = 0.0002003
$\Delta\rho_{max}$ = 0.77 e Å^{-3}
$\Delta\rho_{min}$ = −0.65 e Å^{-3}

Special details

Experimental. The crystal was placed in the cold stream of an Oxford Cryosystems open-flow nitrogen cryostat (Cosier & Glazer, 1986) with a nominal stability of 0.1K.
Cosier, J. & Glazer, A.M., 1986. J. Appl. Cryst. 105-107.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.3003 (2)	0.52792 (8)	0.39805 (5)	0.0270
S2	0.2657 (2)	0.54353 (8)	0.27784 (5)	0.0258
C3	0.0569 (8)	0.6841 (3)	0.26919 (19)	0.0228
C4	−0.0083 (8)	0.7372 (3)	0.34414 (18)	0.0199
C5	0.1038 (8)	0.6697 (3)	0.41121 (18)	0.0211
C6	0.0514 (9)	0.7144 (4)	0.48597 (19)	0.0271
C7	−0.1163 (9)	0.8257 (4)	0.4917 (2)	0.0303
C8	−0.2306 (9)	0.8936 (4)	0.4254 (2)	0.0302
C9	−0.1787 (8)	0.8500 (3)	0.3520 (2)	0.0238
S10	−0.0445 (3)	0.73941 (10)	0.18088 (5)	0.0327
H61	0.1275	0.6685	0.5306	0.0328*
H71	−0.1565	0.8563	0.5416	0.0356*
H81	−0.3459	0.9684	0.4305	0.0358*
H91	−0.2554	0.8942	0.3071	0.0286*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0281 (4)	0.0246 (4)	0.0274 (4)	0.0007 (3)	−0.0027 (3)	0.0049 (3)
S2	0.0258 (4)	0.0255 (4)	0.0256 (4)	−0.0001 (3)	0.0007 (3)	−0.0043 (3)
C3	0.0195 (14)	0.0253 (16)	0.0231 (15)	−0.0043 (13)	−0.0010 (12)	0.0012 (13)
C4	0.0195 (14)	0.0208 (15)	0.0195 (14)	−0.0047 (12)	0.0014 (11)	0.0001 (12)
C5	0.0202 (14)	0.0249 (16)	0.0178 (14)	−0.0044 (13)	−0.0003 (12)	0.0021 (12)
C6	0.0288 (17)	0.0327 (18)	0.0197 (15)	−0.0087 (15)	0.0012 (13)	0.0022 (14)
C7	0.0315 (18)	0.037 (2)	0.0236 (16)	−0.0089 (16)	0.0090 (14)	−0.0076 (15)
C8	0.0275 (17)	0.0282 (18)	0.0357 (19)	−0.0018 (15)	0.0076 (15)	−0.0047 (15)
C9	0.0204 (15)	0.0251 (17)	0.0260 (16)	−0.0030 (13)	0.0029 (13)	0.0058 (13)
S10	0.0417 (5)	0.0381 (5)	0.0175 (4)	−0.0030 (4)	−0.0016 (3)	0.0039 (4)

Geometric parameters (Å, º)

S1—S2	2.0637 (13)	C6—C7	1.379 (5)
S1—C5	1.738 (4)	C6—H61	0.938
S2—C3	1.726 (4)	C7—C8	1.394 (5)
C3—C4	1.453 (4)	C7—H71	0.945
C3—S10	1.645 (3)	C8—C9	1.378 (5)
C4—C5	1.400 (4)	C8—H81	0.935
C4—C9	1.403 (5)	C9—H91	0.935
C5—C6	1.404 (5)		

S2—S1—C5	93.97 (11)	C5—C6—H61	120.2
S1—S2—C3	98.33 (12)	C7—C6—H61	121.4
S2—C3—C4	113.1 (2)	C6—C7—C8	121.4 (3)
S2—C3—S10	118.2 (2)	C6—C7—H71	119.5
C4—C3—S10	128.7 (3)	C8—C7—H71	119.2
C3—C4—C5	117.1 (3)	C7—C8—C9	120.2 (3)
C3—C4—C9	123.6 (3)	C7—C8—H81	120.1
C5—C4—C9	119.3 (3)	C9—C8—H81	119.7
C4—C5—S1	117.5 (2)	C4—C9—C8	119.8 (3)
C4—C5—C6	120.8 (3)	C4—C9—H91	119.0
S1—C5—C6	121.7 (3)	C8—C9—H91	121.2
C5—C6—C7	118.4 (3)		