IUCrData

ISSN 2414-3146

3*H*-1,2-Benzodithiole-3-thione

Khaled Boukebbous,[a]* El Adoui Laifa[a] and Aimery De Mallmann[b]

[a]Department of Chemistry, University of Constantine, BP, 325 Route de Ain El Bey, Constantine 25017, Algeria, and [b]C2P2 (CNRS-UMR 5265), COMS group, Lyon 1 University, ESCPE Lyon, 43 Boulevard du 11 Novembre 1918, Villeurbanne 69626, France. *Correspondence e-mail: boukebbous.khaled@gmail.com

Received 20 October 2016
Accepted 20 October 2016

Edited by W. T. A. Harrison, University of Aberdeen, Scotland

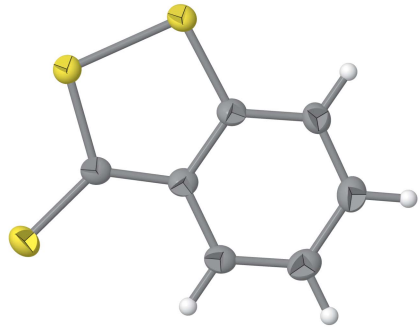
Keywords: crystal structure; dithiolethione derivatives; sulfur organic compounds; heterocyclic compounds.

CCDC reference: 1510917

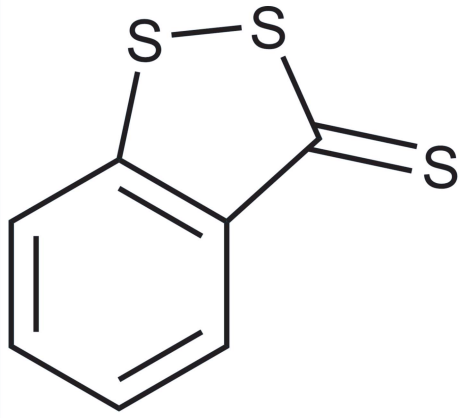
Structural data: full structural data are available from iucrdata.iucr.org

The almost planar (r.m.s. deviation = 0.034 Å) title compound, $C_7H_4S_3$, was synthesized by reacting 2,2-dithiodibenzoic acid with phosphorus pentasulfide in xylene solution. In the crystal, short S···S [3.3727 (14), 3.3765 (13) and 3.4284 (13) Å] contacts and aromatic π–π stacking [shortest centroid–centroid separation = 3.618 (2) Å] are observed.

3D view



Chemical scheme



Structure description

The title compound belongs to the 1,2-dithiole-3-thione family, which has attracted recent interest because of the bioactive properties and potential applications of its members (Li *et al.*, 2016; Russell *et al.*, 2015).

The title compound is composed of a benzene ring fused with a five-membered ring containing two S atoms and a thione functional group (Fig. 1). The geometry of the molecule is almost planar (r.m.s. deviation = 0.034 Å), with bond lengths of 2.064 (1), 1.751 (3), 1.732 (3) and 1.654 (4) Å for S1—S2, C5—S1, C3—S2 and C3—S10, respectively. Furthermore, bond angles of 93.62 (12) and 98.24 (12)° are observed for C5—S1—S2 and S1—S2—C3, respectively. The S2—C3—C4 angle [113.5 (2)°] deviates from the expected value of 120° for a Csp^2 atom (C3═S10); similarly, minor deviations of −3° are observed for the angles S1—C5—C4 and C5—C4—C3 from the expected value of 120° (C4═C5).

In the crystal, short S···S [3.3727 (14), 3.3765 (13) and 3.4284 (13) Å] contacts and aromatic π–π stacking [shortest centroid–centroid separation = 3.618 (2) Å] are observed (Figs. 2 and 3).

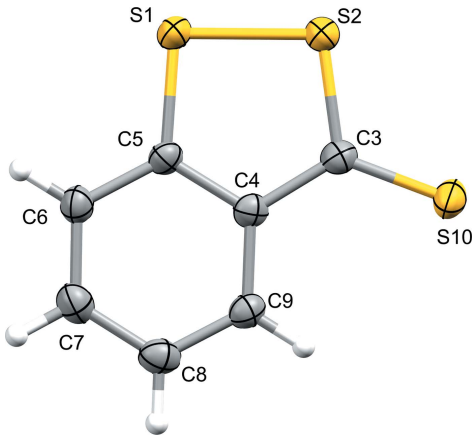


Figure 1
The title compound, with displacement ellipsoids drawn at the 50% probability level.

Synthesis and crystallization

The synthesis of 3*H*-1,2-benzodithiole-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) was added phosphorus pentasulfide (10 g, 0.04 mol) dissolved in xylene. The mixture was stirred for 1 h under reflux. The orange precipitate which formed was washed with distilled water and cold ethanol at 273 K successively and dried at room temperature for several hours. The recrystallization process was performed from toluene solution and red plates in a yield of 80% were obtained.

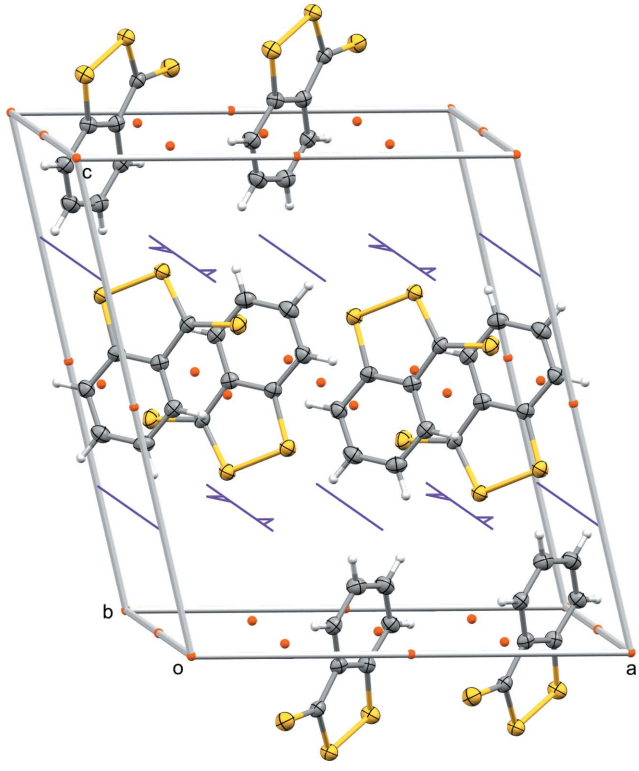


Figure 2
The crystal packing of the title compound, with displacement ellipsoids drawn at the 50% probability level. Inversion centres at [0,0,0] and [1/4,1/4,0] with symmetry operations of $(-x, -y, -z)$ and $(\frac{1}{2} - x, \frac{1}{2} - y, -z)$, respectively, are shown as orange dots. Rotation and screw axes in the [010] direction at $(0, y, 1/4)$ and $(1/4, y, 1/4)$ with symmetry operations of $(-x, y, \frac{1}{2} - z)$ and $(\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z)$, respectively, are shown as purple lines.

Table 1
Experimental details.

Crystal data	
Chemical formula	$C_7H_4S_3$
M_r	184.28
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	150
a, *b*, *c* (Å)	13.1921 (9), 7.5999 (5), 15.2507 (11)
β (°)	105.223 (7)
V (Å^3)	1475.36 (18)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.91
Crystal size (mm)	0.37 × 0.16 × 0.14
Data collection	
Diffractometer	Oxford Diffraction Xcalibur Atlas Gemini ultra
Absorption correction	Multi-scan [empirical absorption correction using spherical harmonics (Clark & Reid, 1995)]
T_{min}, T_{max}	0.602, 0.815
No. of measured, independent and observed [$I > 2.0\sigma(I)$] reflections	17502, 1969, 1784
R_{int}	0.070
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.696
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.059, 0.174, 1.04
No. of reflections	1965
No. of parameters	91
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.80, −0.67

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

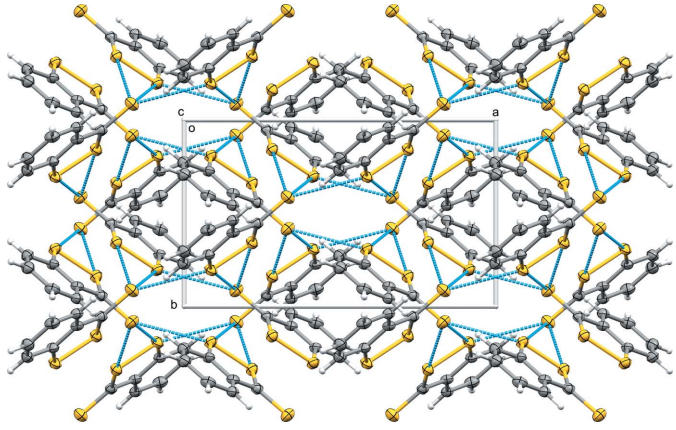


Figure 3
A view along the *c* axis of the packing. The shortest van der Waals interactions are shown as dashed blue lines.

with soft restraints on the bond lengths and angles to regularize their geometry (C—H = 0.93–0.98 Å and N—H = 0.86–0.89 Å) and U_{iso}(H) values (in the range 1.2–1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints.

Acknowledgements

We are grateful to The French National Center for Scientific Research (CNRS) for financial support.

References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.

Betteridge, P. W., Carruthers, J. R., Cooper, R. I., Prout, K. & Watkin, D. J. (2003). *J. Appl. Cryst.* **36**, 1487.

Clark, R. C. & Reid, J. S. (1995). *Acta Cryst.* A**51**, 887–897.

Klingsberg, E. & Schreiber, A. M. (1962). *J. Am. Chem. Soc.* **84**, 2941–2944.

Li, K. R., Yang, S. Q., Gong, Y. Q., Yang, H., Li, X. M., Zhao, Y. X., Yao, J., Jiang, Q. & Cao, C. (2016). *Sci. Rep.* **6**, 13.

Rigaku OD (2015). *CrysAlis PRO*. Rigaku Oxford Diffraction, Yarnton, Oxfordshire, England.

Russell, G. K., Gupta, R. C. & Vadhanam, M. V. (2015). *Mutat. Res./ Fundam. Mol. Mech. Mutagen.* **774**, 25–32.

Watkin, D. J., Prout, C. K. & Pearce, L. J. (1996). *CAMERON*. Chemical Crystallography Laboratory, Oxford, England.

full crystallographic data

IUCrData (2016). **1**, x161688 [https://doi.org/10.1107/S2414314616016886]

3*H*-1,2-Benzodithiole-3-thione

Khaled Boukebbous, El Adoui Laifa and Aimery De Mallmann

(I)

Crystal data

$C_7H_4S_3$
M_r = 184.28
Monoclinic, *C*2/*c*
Hall symbol: -C 2yc
a = 13.1921 (9) Å
b = 7.5999 (5) Å
c = 15.2507 (11) Å
β = 105.223 (7)°
V = 1475.36 (18) Å^3
Z = 8
F(000) = 752
D_x = 1.659 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 16526 reflections
θ = 3.4–29.4°
μ = 0.91 mm^{-1}
T = 150 K
Plate, red
0.37 × 0.16 × 0.14 mm

Data collection

Oxford Diffraction 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: multi-scan
Empirical absorption correction using spherical harmonics, (Clark & Reid, 1995)
T_{min} = 0.602, T_{max} = 0.815
17502 measured reflections
1969 independent reflections
1784 reflections with $I > 2.0\sigma(I)$
R_{int} = 0.070
θ_{max} = 29.6°, θ_{min} = 3.1°
h = −17→18
k = −10→10
l = −20→20

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.174
S = 1.04
1965 reflections
91 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: difference Fourier map
H-atom parameters constrained
Method = Modified Sheldrick $w = 1/[\sigma^2(F^2) + (0.09P)^2 + 10.33P]$, where $P = (\max(F_o^2,0) + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.0003912
$\Delta\rho_{max}$ = 0.80 e Å^{-3}
$\Delta\rho_{min}$ = −0.67 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 0.1 K.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.58588 (7)	0.30591 (11)	0.64939 (6)	0.0267
S2	0.71762 (6)	0.15998 (11)	0.71004 (6)	0.0256
C3	0.7343 (3)	0.0566 (4)	0.6136 (2)	0.0236
C4	0.6570 (3)	0.1061 (4)	0.5317 (2)	0.0227
C5	0.5785 (3)	0.2235 (4)	0.5407 (2)	0.0234
C6	0.4972 (3)	0.2718 (5)	0.4651 (2)	0.0272
C7	0.4986 (3)	0.2065 (5)	0.3811 (3)	0.0310
C8	0.5770 (3)	0.0912 (5)	0.3711 (2)	0.0304
C9	0.6559 (3)	0.0407 (4)	0.4456 (2)	0.0248
S10	0.83218 (7)	−0.08475 (12)	0.62490 (6)	0.0310
H91	0.7081	−0.0376	0.4393	0.0301*
H81	0.5773	0.0501	0.3136	0.0362*
H71	0.4450	0.2388	0.3300	0.0373*
H61	0.4433	0.3466	0.4714	0.0335*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0287 (4)	0.0234 (4)	0.0270 (4)	0.0048 (3)	0.0053 (3)	−0.0032 (3)
S2	0.0261 (4)	0.0260 (4)	0.0238 (4)	0.0021 (3)	0.0049 (3)	−0.0008 (3)
C3	0.0255 (15)	0.0216 (14)	0.0255 (15)	−0.0018 (12)	0.0101 (12)	0.0000 (11)
C4	0.0284 (15)	0.0155 (13)	0.0247 (15)	−0.0022 (11)	0.0075 (12)	0.0000 (11)
C5	0.0273 (15)	0.0174 (14)	0.0252 (15)	−0.0007 (11)	0.0062 (12)	−0.0024 (11)
C6	0.0274 (16)	0.0236 (16)	0.0290 (16)	0.0032 (12)	0.0046 (13)	0.0017 (12)
C7	0.0323 (18)	0.0271 (17)	0.0297 (17)	−0.0013 (14)	0.0015 (13)	0.0022 (13)
C8	0.0389 (19)	0.0250 (16)	0.0273 (16)	−0.0036 (14)	0.0088 (14)	−0.0023 (13)
C9	0.0288 (16)	0.0190 (14)	0.0281 (15)	−0.0013 (12)	0.0101 (12)	−0.0008 (12)
S10	0.0310 (5)	0.0303 (5)	0.0329 (5)	0.0098 (3)	0.0105 (4)	0.0044 (3)

Geometric parameters (Å, º)

S1—S2	2.0644 (12)	C6—C7	1.379 (5)
S1—C5	1.751 (3)	C6—H61	0.935
S2—C3	1.731 (3)	C7—C8	1.394 (5)
C3—C4	1.440 (5)	C7—H71	0.937
C3—S10	1.653 (3)	C8—C9	1.379 (5)
C4—C5	1.401 (5)	C8—H81	0.932
C4—C9	1.401 (5)	C9—H91	0.934
C5—C6	1.401 (5)		
S2—S1—C5	93.62 (12)	C5—C6—H61	120.9
S1—S2—C3	98.24 (12)	C7—C6—H61	120.6
S2—C3—C4	113.5 (2)	C6—C7—C8	121.3 (3)
S2—C3—S10	118.5 (2)	C6—C7—H71	119.2
C4—C3—S10	128.0 (3)	C8—C7—H71	119.5

C3—C4—C5	117.1 (3)	C7—C8—C9	120.4 (3)
C3—C4—C9	123.5 (3)	C7—C8—H81	120.1
C5—C4—C9	119.4 (3)	C9—C8—H81	119.5
S1—C5—C4	117.5 (2)	C4—C9—C8	119.6 (3)
S1—C5—C6	121.7 (3)	C4—C9—H91	119.7
C4—C5—C6	120.8 (3)	C8—C9—H91	120.7
C5—C6—C7	118.4 (3)		