

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

4,6,7,9,10,12,13,15-Octahydro-2H-1,3-dithiolo[4,5-*i*][1,4,7,12]dioxadithiacyclo-tetradecine-2-thione

Rui-Bin Hou,^a Bao Li,^b Tie Chen,^a Bing-Zhu Yin^{a*} and Li-Xin Wu^b

^aKey Laboratory of Organism Functional Factors of Changbai Mountain, Yanbian University, Ministry of Education, Yanji 133002, People's Republic of China, and

^bState Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University, Changchun 130012, People's Republic of China
Correspondence e-mail: zqcong@ybu.edu.cn

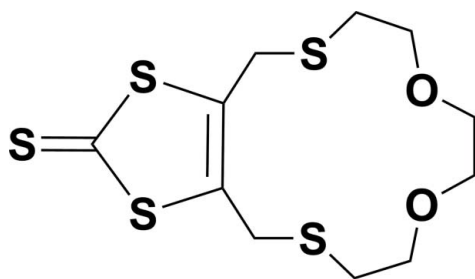
Received 21 July 2009; accepted 24 July 2009

Key indicators: single-crystal X-ray study; $T = 291$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.034; wR factor = 0.088; data-to-parameter ratio = 19.6.

In the title molecule, $\text{C}_{11}\text{H}_{16}\text{O}_2\text{S}_5$, the two S atoms from the macrocycle are situated on opposite sides of the mean plane of the five-membered ring, deviating from it by 1.288 (3) and 1.728 (3) Å. In the crystal, weak intermolecular C—H \cdots S and C—H \cdots O hydrogen bonds link the molecules into layers parallel to (100). The crystal studied was a racemic twin.

Related literature

For crown ether annulated 1,3-dithiol-2-thiones, see: Hansen *et al.* (1992); Trippé *et al.* (2002). For details of the synthesis, see: Chen *et al.* (2005). For a related structure, see: Hou *et al.* (2009)



Experimental

Crystal data

$\text{C}_{11}\text{H}_{16}\text{O}_2\text{S}_5$
 $M_r = 340.54$
Monoclinic, $P2_1$
 $a = 8.9201$ (18) Å

$b = 8.5317$ (17) Å
 $c = 10.128$ (2) Å
 $\beta = 97.00$ (3)°
 $V = 765.0$ (3) Å³

$Z = 2$
Mo $K\alpha$ radiation
 $\mu = 0.75$ mm⁻¹

$T = 291$ K
 $0.13 \times 0.12 \times 0.11$ mm

Data collection

Rigaku R-Axis RAPID diffractometer
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)
 $T_{\min} = 0.909$, $T_{\max} = 0.922$

7527 measured reflections
3221 independent reflections
3100 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.028$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.088$
 $S = 1.06$
3221 reflections
164 parameters
1 restraint

H-atom parameters constrained
 $\Delta\rho_{\max} = 0.58$ e Å⁻³
 $\Delta\rho_{\min} = -0.22$ e Å⁻³
Absolute structure: Flack (1983);
1359 Friedel pairs
Flack parameter: 0.42 (9)

Table 1

Hydrogen-bond geometry (Å, °).

D—H \cdots A	D—H	H \cdots A	D \cdots A	D—H \cdots A
C7—H7A \cdots S1 ⁱ	0.97	2.86	3.695 (3)	145
C10—H10A \cdots O2 ⁱⁱ	0.97	2.51	3.317 (3)	140

Symmetry codes: (i) $x - 1, y, z - 1$; (ii) $-x + 1, y + \frac{1}{2}, -z + 1$.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97*.

The authors acknowledge financial support from the National Natural Science Foundation of China (grant No. 20662010), the Specialized Research Fund for the Doctoral Program of Higher Education (grant No. 2006184001) and the Open Project of the State Key Laboratory of Supramolecular Structure and Materials, Jilin University.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2592).

References

- Chen, T., Liu, W. J., Cong, Z. Q. & Yin, B. Z. (2005). *Chin. J. Org. Chem.* **25**, 570–575.
Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
Hansen, T. K., Jørgensen, T., Stein, P. C. & Becher, J. (1992). *J. Org. Chem.* **57**, 6403–6409.
Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
Hou, R., Li, B., Yin, B. & Wu, L. (2009). *Acta Cryst.* **E65**, o1057.
Rigaku (1998). *RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan.
Rigaku/MS (2002). *CrystalStructure*. Rigaku/MS, The Woodlands, Texas, USA.
Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
Trippé, G., Levillain, E., Le Derf, F., Gorgues, A., Sallé, M., Jeppesen, J. O., Nielsen, K. & Becher, J. (2002). *Org. Lett.* **4**, 2461–2464.

supporting information

Acta Cryst. (2009). E65, o2042 [doi:10.1107/S1600536809029468]

4,6,7,9,10,12,13,15-Octahydro-2*H*-1,3-dithiolo[4,5-*i*][1,4,7,12]dioxadithia-cyclotetradecine-2-thione

Rui-Bin Hou, Bao Li, Tie Chen, Bing-Zhu Yin and Li-Xin Wu

S1. Comment

In the context of redox-responsive ligands, TTF is an ideal redox-active unit in view of its unique π -electron donating properties. Attachment of ligands such as crown ethers to TTF in many cases results in the electrochemical tunable ligands (Trippé *et al.*, 2002). Crowned 1,3-dithiolo-2-thiones, important precursors to TTF derivatives, have also attracted attention (Hansen *et al.*, 1992). In this paper, we report the crystal structure of the title compound.

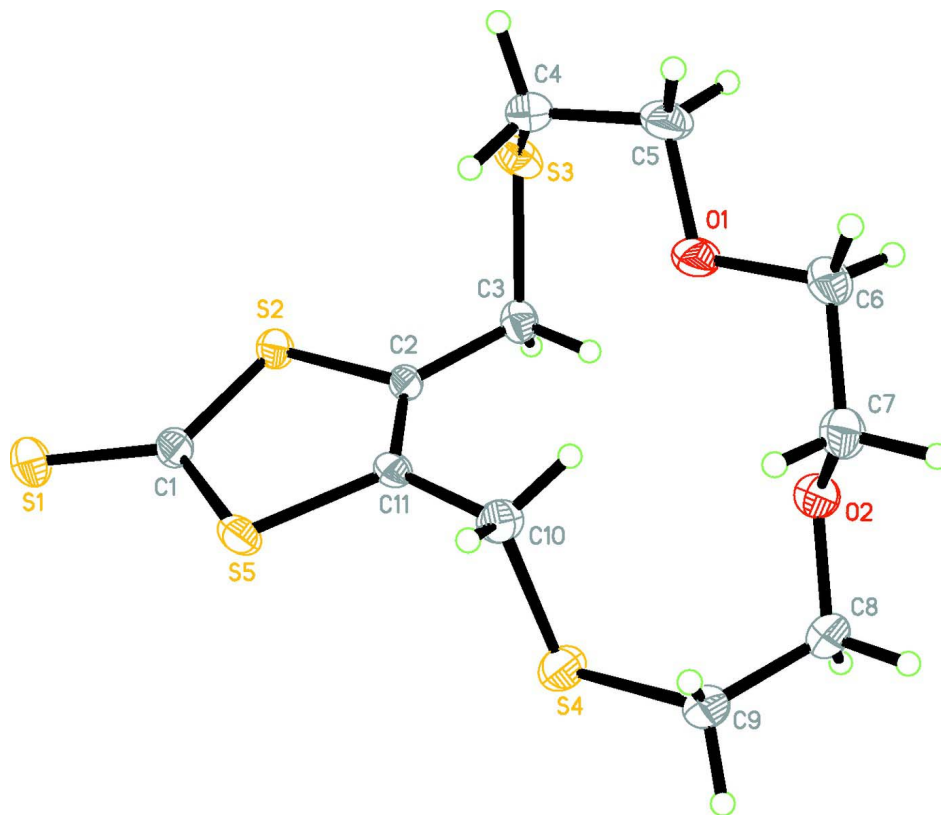
In the title compound (Fig. 1), all bond lengths and angles are normal and comparable with those reported for the related structure (Hou *et al.*, 2009). In the crystal, weak intermolecular C—H \cdots S and C—H \cdots O hydrogen bonds (Table 1) link the molecules into layers parallel to $(a+c)b$ plane.

S2. Experimental

The title compound was prepared according to the literature (Chen *et al.*, 2005) and single crystals suitable for X-ray diffraction were prepared by slow evaporation a mixture of dichloromethane and petroleum (60–90 °C) at room temperature.

S3. Refinement

Carbon-bound H-atoms were placed in calculated positions with C—H 0.97 Å and were included in the refinement in the riding model with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$. The refined value of Flack parameter of 0.42 (9) suggests that the crystal studied was a racemic twin.

**Figure 1**

The molecular structure of the title compound showing the atomic numbering. Displacement ellipsoids of non-H atoms are drawn at the 30% probability level.

4,6,7,9,10,12,13,15-Octahydro-2H-1,3-dithiolo[4,5-*i*][1,4,7,12]dioxadithiacyclotetradecine-2-thione

Crystal data

$C_{11}H_{16}O_2S_5$

$M_r = 340.54$

Monoclinic, $P2_1$

Hall symbol: $P\ 2yb$

$a = 8.9201\ (18)\ \text{\AA}$

$b = 8.5317\ (17)\ \text{\AA}$

$c = 10.128\ (2)\ \text{\AA}$

$\beta = 97.00\ (3)^\circ$

$V = 765.0\ (3)\ \text{\AA}^3$

$Z = 2$

$F(000) = 356$

$D_x = 1.478\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 7211 reflections

$\theta = 3.1\text{--}27.5^\circ$

$\mu = 0.75\ \text{mm}^{-1}$

$T = 291\ \text{K}$

Block, yellow

$0.13 \times 0.12 \times 0.11\ \text{mm}$

Data collection

Rigaku R-Axis RAPID
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω scans

Absorption correction: multi-scan
(*ABSCOR*; Higashi, 1995)

$T_{\min} = 0.909$, $T_{\max} = 0.922$

7527 measured reflections

3221 independent reflections

3100 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.028$

$\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 3.1^\circ$

$h = -11 \rightarrow 11$

$k = -11 \rightarrow 10$

$l = -13 \rightarrow 11$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.088$
 $S = 1.06$
 3221 reflections
 164 parameters
 1 restraint
 Primary atom site location: structure-invariant
 direct methods
 Secondary atom site location: difference Fourier
 map

Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0508P)^2 + 0.1939P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.58 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.22 \text{ e } \text{\AA}^{-3}$
 Absolute structure: Flack (1983); 1359 Friedel
 pairs
 Absolute structure parameter: 0.42 (9)

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.9104 (3)	0.5403 (4)	1.0514 (2)	0.0344 (5)
C2	0.6930 (2)	0.4126 (3)	0.8914 (2)	0.0264 (5)
C3	0.5748 (3)	0.2952 (3)	0.8447 (2)	0.0342 (5)
H3A	0.6206	0.1920	0.8492	0.041*
H3B	0.5391	0.3164	0.7521	0.041*
C4	0.3178 (3)	0.4733 (4)	0.8901 (3)	0.0406 (6)
H4A	0.2524	0.4990	0.9568	0.049*
H4B	0.3929	0.5556	0.8915	0.049*
C5	0.2242 (3)	0.4741 (4)	0.7555 (3)	0.0445 (7)
H5A	0.1638	0.3795	0.7439	0.053*
H5B	0.1566	0.5637	0.7482	0.053*
C6	0.2480 (3)	0.4848 (4)	0.5262 (3)	0.0426 (6)
H6A	0.1704	0.5650	0.5179	0.051*
H6B	0.2005	0.3842	0.5047	0.051*
C7	0.3637 (3)	0.5190 (4)	0.4329 (3)	0.0418 (6)
H7A	0.3150	0.5253	0.3421	0.050*
H7B	0.4128	0.6185	0.4558	0.050*
C8	0.5855 (3)	0.4162 (4)	0.3590 (3)	0.0427 (7)
H8A	0.5382	0.4495	0.2722	0.051*
H8B	0.6331	0.3156	0.3480	0.051*
C9	0.7060 (3)	0.5337 (4)	0.4090 (3)	0.0470 (7)
H9A	0.6589	0.6351	0.4175	0.056*
H9B	0.7765	0.5438	0.3438	0.056*

C10	0.6889 (3)	0.5696 (4)	0.6801 (2)	0.0381 (6)
H10A	0.6885	0.6826	0.6690	0.046*
H10B	0.5861	0.5322	0.6586	0.046*
C11	0.7448 (2)	0.5293 (3)	0.8207 (2)	0.0290 (5)
O1	0.3233 (2)	0.4825 (3)	0.65686 (18)	0.0432 (5)
O2	0.4715 (2)	0.3969 (2)	0.44464 (17)	0.0385 (4)
S1	1.03598 (9)	0.58767 (12)	1.17933 (8)	0.0558 (2)
S2	0.78149 (7)	0.39272 (8)	1.05411 (6)	0.03282 (15)
S3	0.41352 (8)	0.29178 (9)	0.93755 (8)	0.04456 (18)
S4	0.80970 (8)	0.48036 (12)	0.56811 (7)	0.0539 (2)
S5	0.89230 (7)	0.64009 (8)	0.90156 (7)	0.03733 (16)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0240 (11)	0.0456 (15)	0.0325 (11)	0.0034 (10)	-0.0003 (9)	-0.0064 (11)
C2	0.0195 (10)	0.0336 (13)	0.0252 (10)	0.0033 (8)	-0.0005 (8)	-0.0022 (9)
C3	0.0310 (12)	0.0346 (13)	0.0356 (12)	0.0012 (10)	-0.0020 (9)	-0.0022 (11)
C4	0.0330 (13)	0.0503 (17)	0.0400 (13)	0.0006 (12)	0.0105 (10)	-0.0063 (12)
C5	0.0259 (12)	0.0616 (19)	0.0473 (15)	0.0072 (12)	0.0094 (11)	0.0041 (14)
C6	0.0275 (13)	0.0597 (19)	0.0388 (13)	0.0049 (12)	-0.0030 (10)	0.0054 (13)
C7	0.0369 (14)	0.0520 (17)	0.0346 (12)	0.0011 (12)	-0.0028 (11)	0.0071 (12)
C8	0.0417 (15)	0.0582 (19)	0.0283 (11)	-0.0032 (13)	0.0048 (10)	0.0000 (12)
C9	0.0413 (15)	0.069 (2)	0.0313 (12)	-0.0104 (14)	0.0065 (11)	0.0044 (13)
C10	0.0318 (13)	0.0507 (16)	0.0315 (12)	0.0060 (11)	0.0028 (10)	0.0054 (11)
C11	0.0184 (10)	0.0390 (13)	0.0292 (11)	0.0012 (9)	0.0020 (8)	-0.0002 (10)
O1	0.0233 (8)	0.0716 (14)	0.0349 (9)	0.0071 (9)	0.0045 (7)	0.0047 (9)
O2	0.0346 (10)	0.0433 (11)	0.0377 (9)	-0.0016 (8)	0.0049 (7)	0.0018 (9)
S1	0.0336 (4)	0.0887 (7)	0.0416 (4)	-0.0110 (4)	-0.0092 (3)	-0.0101 (4)
S2	0.0298 (3)	0.0407 (3)	0.0267 (3)	-0.0002 (2)	-0.0015 (2)	0.0031 (2)
S3	0.0319 (3)	0.0508 (4)	0.0507 (4)	-0.0110 (3)	0.0041 (3)	0.0134 (3)
S4	0.0314 (3)	0.0975 (7)	0.0325 (3)	0.0086 (4)	0.0027 (3)	-0.0032 (4)
S5	0.0254 (3)	0.0466 (4)	0.0399 (3)	-0.0089 (3)	0.0031 (2)	0.0025 (3)

Geometric parameters (Å, °)

C1—S1	1.656 (3)	C6—H6A	0.9700
C1—S2	1.708 (3)	C6—H6B	0.9700
C1—S5	1.730 (3)	C7—O2	1.413 (4)
C2—C11	1.341 (4)	C7—H7A	0.9700
C2—C3	1.489 (3)	C7—H7B	0.9700
C2—S2	1.747 (2)	C8—O2	1.424 (3)
C3—S3	1.812 (3)	C8—C9	1.511 (4)
C3—H3A	0.9700	C8—H8A	0.9700
C3—H3B	0.9700	C8—H8B	0.9700
C4—C5	1.510 (4)	C9—S4	1.815 (3)
C4—S3	1.805 (3)	C9—H9A	0.9700
C4—H4A	0.9700	C9—H9B	0.9700

C4—H4B	0.9700	C10—C11	1.490 (3)
C5—O1	1.414 (3)	C10—S4	1.824 (3)
C5—H5A	0.9700	C10—H10A	0.9700
C5—H5B	0.9700	C10—H10B	0.9700
C6—O1	1.409 (3)	C11—S5	1.741 (2)
C6—C7	1.510 (4)		
S1—C1—S2	124.03 (17)	C6—C7—H7A	110.0
S1—C1—S5	123.24 (18)	O2—C7—H7B	110.0
S2—C1—S5	112.70 (14)	C6—C7—H7B	110.0
C11—C2—C3	127.4 (2)	H7A—C7—H7B	108.4
C11—C2—S2	115.48 (18)	O2—C8—C9	113.8 (2)
C3—C2—S2	117.08 (18)	O2—C8—H8A	108.8
C2—C3—S3	114.98 (18)	C9—C8—H8A	108.8
C2—C3—H3A	108.5	O2—C8—H8B	108.8
S3—C3—H3A	108.5	C9—C8—H8B	108.8
C2—C3—H3B	108.5	H8A—C8—H8B	107.7
S3—C3—H3B	108.5	C8—C9—S4	113.3 (2)
H3A—C3—H3B	107.5	C8—C9—H9A	108.9
C5—C4—S3	115.9 (2)	S4—C9—H9A	108.9
C5—C4—H4A	108.3	C8—C9—H9B	108.9
S3—C4—H4A	108.3	S4—C9—H9B	108.9
C5—C4—H4B	108.3	H9A—C9—H9B	107.7
S3—C4—H4B	108.3	C11—C10—S4	110.08 (18)
H4A—C4—H4B	107.4	C11—C10—H10A	109.6
O1—C5—C4	108.3 (2)	S4—C10—H10A	109.6
O1—C5—H5A	110.0	C11—C10—H10B	109.6
C4—C5—H5A	110.0	S4—C10—H10B	109.6
O1—C5—H5B	110.0	H10A—C10—H10B	108.2
C4—C5—H5B	110.0	C2—C11—C10	125.7 (2)
H5A—C5—H5B	108.4	C2—C11—S5	116.22 (18)
O1—C6—C7	107.8 (2)	C10—C11—S5	118.0 (2)
O1—C6—H6A	110.1	C6—O1—C5	113.3 (2)
C7—C6—H6A	110.1	C7—O2—C8	113.1 (2)
O1—C6—H6B	110.1	C1—S2—C2	98.09 (12)
C7—C6—H6B	110.1	C4—S3—C3	103.16 (13)
H6A—C6—H6B	108.5	C9—S4—C10	99.88 (14)
O2—C7—C6	108.3 (2)	C1—S5—C11	97.47 (13)
O2—C7—H7A	110.0		

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C7—H7A \cdots S1 ⁱ	0.97	2.86	3.695 (3)	145
C10—H10A \cdots O2 ⁱⁱ	0.97	2.51	3.317 (3)	140

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