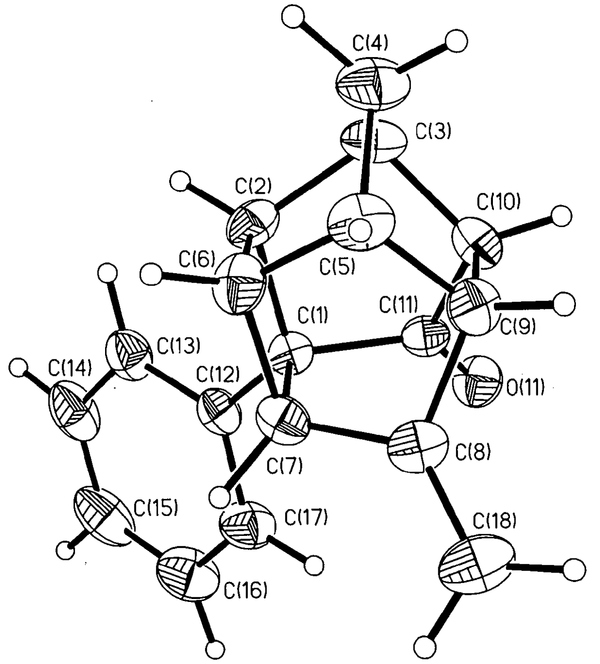

Fig. 1. Compound (2*a*) with thermal ellipsoids at the 30% probability level. H atoms are shown as spheres of arbitrary size.

products (Mehta, Srikrishna, Reddy & Nair, 1981) have been discussed.

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Structure of 1,7,10,16-Tetraoxa-4,13-dithiacyclooctadecane-2,6-dione at 163 K

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Abstract. $C_{12}H_{20}O_6S_2$, $M_r = 324{\cdot}41$, triclinic, $P\bar{1}$, $a = 8{\cdot}7876\,(13)$, $b = 8{\cdot}6117\,(12)$, $c = 11{\cdot}855\,(2)$ Å, $\alpha = 90{\cdot}391\,(12)$, $\beta = 118{\cdot}85\,(2)$, $\gamma = 97{\cdot}823\,(10)^\circ$, $V = 775{\cdot}8\,(2)$ Å^3, $Z = 2$, $D_x = 1{\cdot}389$ g cm^{-3}, $\lambda(\text{Mo }K\alpha) = 0{\cdot}71069$ Å, $\mu = 3{\cdot}476$ cm^{-1}, $F(000) = 344$, $R = 0{\cdot}0407$ for 2274 reflections ($F \geq 4\sigma_F$). The macrocycle backbone forms an elliptical cavity with approximate $C2$ symmetry despite the presence of the carbonyl groups. The conformation, beginning at O1, is $(ag^-g^+,\ g^+aa,\ ag^+a)_2$; all C—S—C—C fragments are *gauche* whereas all C—O—C—C fragments are *anti*. Differences in torsion angles related by the pseudo-twofold axis are less than 17° (r.m.s. deviation: 9·5°). The macrocycle is not planar; the S atoms are 1·1702 (7) and 1·1289 (7) Å out of the mean plane of the 18 backbone atoms and pointed out of the cavity [the dihedral angles between the C—S—C fragments and the backbone mean plane are 114·43 (11) and 115·91 (13)°]. Two H atoms are inside the cavity. The carbonyl O atoms are 0·184 (2) and 0·847 (2) Å out of the plane. The average C—C, C—O(ether) and C—S bond distances are 1·504 (16), 1·424 (8) and 1·814 (11) Å. Bonds in the ester portions are also normal.

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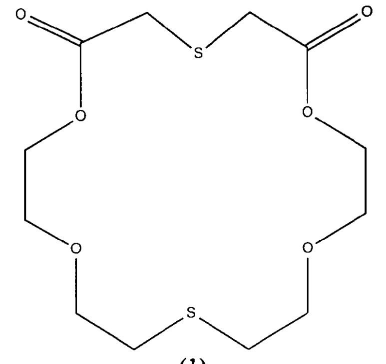
Experimental. The title compound (1) was prepared by the reaction of thiodiglycol dichloride and 1,4,10,13-tetraoxa-7-thiatridecane under high dilution conditions and was crystallized from chloroform/ether solution as white platelets (Maas, Bradshaw, Izatt & Christensen, 1977). A summary of data collection and structural refinement is given in Table 1. Unit-cell parameters were obtained by least-squares refinement of the setting angles of 15 reflections with $25{\cdot}0 < 2\theta < 34{\cdot}2°$. A Syntex $P2_1$ autodiffractometer with a graphite monochromator and a Syntex LT-1 inert-gas (N_2) low-temperature delivery system was used for all measurements. Data reduction was carried out as described by Riley & Davis (1976). Stability correction was based on intensities of four check reflections which were measured every 96 reflections. Absorption corrections were based on crystal-size measurements. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = \sigma_F^{-2}$, $\sigma_F = F\sigma_I/2I$, and $\sigma_I = [N_{\rm pk} + N_{\rm bg1} + N_{\rm bg2} + (0{\cdot}04I)^2]^{1/2}$.



(1)

Table 1. *Summary of data collection and refinement*

(*a*) Data collection (163 K)	
Mode	ω scan
Scan range (°)	1·0
Background	Stationary counts 1° before and after the $K\alpha$ peak for total scan time
Scan rate (°min^{-1})	1·5–5·0
Exposure time (h)	20
Stability correction range on *I*	0·925–1·036
Check reflections	$00\bar{3}$, 020, 400, 222
2θ range (°)	4·0–50·0
Range in *hkl*, min.	0, − 10, − 14
max.	10,10,11
Total reflections, measured, unique	2375, 2375
Crystal dimensions (mm)	0·29 × 0·24 × 0·16
Crystal volume (mm^3)	0·0104
Transmission-factor range	0·918–0·950
(*b*) Structure refinement	
Reflections used ($F \geq 4\sigma_F$)	2274
No. of variables	261
Goodness of fit, *S*	1·816
R, *wR*	0·0407, 0·0512
R for all data	0·0538
Max. shift/e.s.d.	0·0003
Extinction parameter	1·8 (12) × 10^{-7}
Max., min. density in difference Fourier map (e Å^{-3})	0·50, −0·26

Table 2. *Fractional atomic coordinates and equivalent isotropic temperature factors*

$$U_{\rm eq} = (1/3)\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	$U_{\rm eq}$(Å^2)
O1	0·6763 (2)	0·7401 (2)	0·0503 (2)	0·0281 (8)
C2	0·7885 (3)	0·8451 (3)	0·0329 (2)	0·0261 (10)
C3	0·9507 (3)	0·7796 (3)	0·0589 (3)	0·0301 (12)
S4	1·10455 (8)	0·79414 (8)	0·23187 (7)	0·0320 (3)
C5	1·0050 (3)	0·6395 (3)	0·2878 (3)	0·0268 (11)
C6	1·0107 (3)	0·4756 (3)	0·2454 (3)	0·0275 (11)
O7	0·9847 (2)	0·3715 (2)	0·3199 (2)	0·0329 (8)
C8	0·9746 (4)	0·2070 (3)	0·2824 (3)	0·0373 (14)
C9	0·8991 (4)	0·1098 (4)	0·3524 (3)	0·042 (2)
O10	0·7251 (3)	0·1365 (2)	0·3093 (2)	0·0393 (9)
C11	0·6409 (5)	0·0495 (4)	0·3714 (4)	0·046 (2)
C12	0·4792 (5)	0·1231 (4)	0·3460 (3)	0·046 (2)
S13	0·52869 (9)	0·30501 (9)	0·44476 (7)	0·0367 (3)
C14	0·6154 (4)	0·4532 (3)	0·3735 (3)	0·0334 (12)
C15	0·4724 (4)	0·5078 (4)	0·2543 (3)	0·0371 (13)
O16	0·5532 (2)	0·6292 (2)	0·2093 (2)	0·0342 (8)
C17	0·4324 (3)	0·6667 (3)	0·0837 (3)	0·0315 (12)
C18	0·5243 (3)	0·7965 (3)	0·0453 (3)	0·0296 (12)
O19	0·7616 (2)	0·9767 (2)	0·0026 (2)	0·0352 (9)
O20	1·0322 (3)	0·4402 (2)	0·1567 (2)	0·0435 (10)

The structure was solved in space group *P*1 starting with three S atoms whose coordinates were deduced from a sharpened Patterson map. The structure was augmented with 37 additional non-H atoms *via* two subsequent difference maps. Severe correlation of parameters and strange relationships between corresponding bond lengths of the two molecules prompted a search for a center of inversion that would relate the two molecules. Thus, the origin was shifted to coincide with the inversion center and the refinement was continued in space group $P\bar{1}$ with one molecule per asymmetric unit. 20 H atoms were located in a ΔF map as peaks of 0·52–1·19 e Å^{-3} at $R = 0{\cdot}072$. All atomic positional parameters, anisotropic thermal parameters for non-H atoms and isotropic thermal parameters for H atoms were refined by full-matrix least squares [*SHELX*76 (Sheldrick, 1976)] except that a single isotropic thermal parameter for the H atoms attached to C12 (H12*A* and H12*B*) was refined since refinement of an individual *U* for H12*A* resulted in a negative value. Scattering factors and anomalous-dispersion corrections for all non-H atoms were taken from *International Tables for X-ray Crystallography* (1974); H-atom scattering factors were taken from Stewart, Davidson & Simpson (1965). Atomic parameters are listed in Table 2;* bond lengths, bond angles, torsion

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* Tables of anisotropic thermal parameters, H-atom parameters, bond lengths and angles involving H atoms, least-squares planes and structure-factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52441 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

angles and selected interatomic distances are given in Table 3. Atom labeling is shown in Fig. 1. Packing of the unit cell is illustrated in Fig. 2. Principal computer programs are given by Gadol & Davis (1982). Figures were drawn with *ORTEP*II (Johnson, 1976); least-squares planes were calculated with *PLANES* (Cordes, 1983).

Table 3. *Bond lengths* (Å), *bond angles* (°) *and torsion angles* (°)

1	2	3	4	1—2	1—2—3	1—2—3—4
C2	O1	C18	C17	1·337 (3)	116·5 (2)	−172·9 (2)
C3	C2	O1	C18		111·2 (2)	171·9 (2)
O19	C2	C3	S4			97·4 (3)
O19	C2	O1	C18	1·211 (3)	123·5 (3)	−6·7 (4)
S4	C3	C2	O1	1·823 (3)	110·7 (2)	−81·2 (2)
C5	S4	C3	C2	1·798 (3)	102·72 (13)	75·1 (2)
C6	C5	S4	C3	1·511 (4)	114·3 (3)	70·2 (2)
O7	C6	C5	S4		110·3 (3)	161·3 (2)
O20	C6	O7	C8			−3·1 (4)
O20	C6	C5	S4	1·199 (4)	126·1 (3)	−19·9 (4)
C8	O7	C6	C5	1·459 (3)	115·5 (3)	175·7 (3)
C9	C8	O7	C6	1·490 (6)	107·1 (3)	−165·2 (3)
O10	C9	C8	O7	1·413 (4)	109·1 (3)	64·4 (3)
C11	O10	C9	C8	1·427 (5)	113·6 (3)	−179·5 (3)
C12	C11	O10	C9	1·532 (6)	107·8 (3)	164·0 (3)
S13	C12	C11	O10	1·820 (4)	114·4 (2)	−77·2 (3)
C14	S13	C12	C11	1·815 (4)	104·9 (2)	75·9 (3)
C15	C14	S13	C12	1·501 (4)	112·2 (2)	78·8 (3)
O16	C15	C14	S13	1·432 (4)	107·8 (2)	177·3 (2)
C17	O16	C15	C14	1·423 (3)	111·5 (2)	168·8 (3)
C18	C17	O16	C15	1·492 (5)	108·3 (2)	178·4 (3)
O1	C18	C17	O16	1·457 (4)	106·8 (2)	58·1 (3)
C3	C2	O19		1·497 (4)	125·3 (3)	
O7	C6	O20		1·336 (4)	123·6 (3)	

Interatomic distances between S and O atoms in the macrocyclic ring

1	2	1···2	1	2	1···2
O1	S4	3·272 (2)	O1	O7	4·665 (3)
O1	O10	6·015 (3)	O1	S13	6·509 (2)
O1	O16	2·711 (3)	S4	O7	3·939 (2)
S4	O10	6·474 (2)	S4	S13	7·509 (2)
S4	O16	4·737 (2)	O7	O10	2·789 (3)
O7	S13	4·868 (3)	O7	O16	4·308 (3)
O10	S13	3·315 (3)	O10	O16	4·666 (3)
S13	O16	4·019 (2)			

Related literature. As seen in other noncomplexed thia-oxa macrocyclic polyethers (Huffman, Campbell, Dalley & Larson, 1981; Dalley, Larson, Smith, Matheson, Izatt & Christensen, 1981; Barnes, Paton, Prout, Turner & Schroth, 1988), the S atoms in (1) point away from the cavity. The elliptical form of the cavity is similar to that of 18-crown-6 (Maverick, Seiler, Schweizer & Dunitz, 1980; Dunitz & Seiler, 1974) and thia-18-crown-6 (which is isomorphous to 18-crown-6) (Huffman *et al.*, 1981) although these structures have centers of inversion. Hexathia-18-crown-6 (Hartman, Wolf, Foxman & Cooper, 1983) is also elliptical. The C—O—C—C and C—S—C—C conformations are all *anti* and all *gauche*, respectively, consistent with the observation by Hartman *et al.* (1983) that the vast majority of the C—O—C—C conformations found in the literature are *anti* whereas all C—S—C—C conformations are *gauche*. 7,16-Dithia-18-crown-6, the non-carbonyl analog of (1), is elliptical with a center of inversion (Dalley *et al.*, 1981).

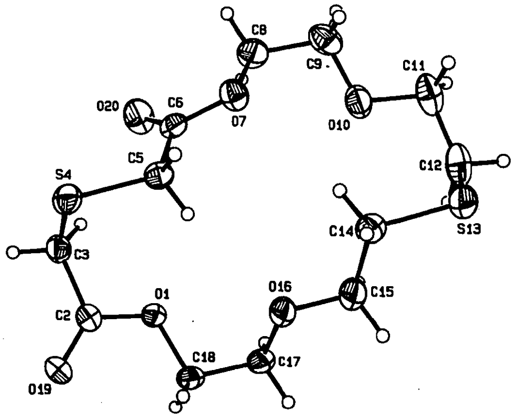

Fig. 1. Thermal-ellipsoid plot of (1) illustrating atom labeling and ellipsoidal conformation of the macrocycle. Some short C—H···O intramolecular contacts which may affect the molecular conformation include H3*B*···O20 [2·51 (3) Å], H5*B*···O1 [2·55 (3) Å] and H14*A*···O10 [2·48 (3) Å]. Thermal ellipsoids are drawn at the 50% probability level.

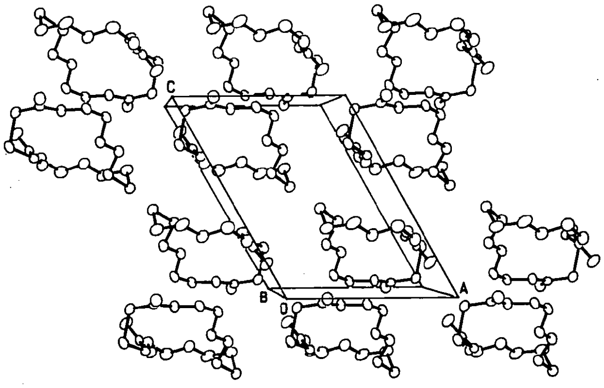

Fig. 2. Crystal packing diagram of (1) viewed approximately perpendicular to the *ac* plane. H atoms have been omitted for clarity. Closest intermolecular contacts are O19···H8*B* [2·47 (3) Å], O19···H3*A* [2·51 (3) Å] and O20···H3*B* [2·61 (3) Å].

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Structure of 1,2,3,5,6,10b*α*-Hexahydro-6*β*-hydroxy-4*α*-methyl-6*α*-phenylpyrrolo[2,1-*a*]isoquinolinium Iodide

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Abstract. $C_{19}H_{22}NO^+.I^-$, $M_r = 407{\cdot}30$, orthorhombic, *Pbca*, $a = 13{\cdot}687\,(2)$, $b = 14{\cdot}056\,(2)$, $c = 18{\cdot}055\,(4)$ Å, $V = 3473{\cdot}3$ Å^3, $Z = 8$, $D_x = 1{\cdot}558$ Mg m^{-3}, $\lambda(\text{Cu } K\alpha) = 1{\cdot}5418$ Å, $\mu = 14{\cdot}64$ mm^{-1}, $F(000) = 1632$, $T = 293\,(1)$ K, $R = 0{\cdot}0689$ for 1762 observed reflections with $I > 3\sigma(I)$. The six-membered central ring is in a distorted chair conformation and the five-membered ring is *cis*-fused to it. The planes of the phenyl rings are inclined at 111·9 (3)°. The I atom and the O atom of the hydroxy group are in van der Waals contact [I···H(O1) 2·57 Å, I···HO1—O(1) 163·0°].

Experimental. The preparation of the title compound has been described elsewhere (Sorgi, Maryanoff, McComsey, Graden & Maryanoff, 1989). Colorless crystals were obtained by slow crystallization at room temperature from a mixture of methanol:2-propanol. An elongated needle of approximate size 0·16 × 0·22 × 0·40 mm was used for data collection. Accurate cell dimensions and a crystal-orientation matrix were determined on an Enraf–Nonius CAD-4 diffractometer by a least-squares refinement of the setting angles of 25 reflections in the θ range 20–30°. Intensity data were collected by the ω–2θ scan method with ω-scan width $(0{\cdot}60 + 0{\cdot}14\tan\theta)°$ and variable scan speed of 1·3–5·5° min^{-1} using graphite-monochromatized Cu $K\alpha$ radiation with indices h 0 to 16, k 0 to 16 and l 0 to 21 in the θ range 5–65°. The intensities of three standard reflections measured every 2 h showed no evidence of crystal decay. Intensities of 3399 reflections were measured, 1762 had $I > 3\sigma(I)$, and were used in the structure solution and refinement. Data were corrected for Lorentz and polarization factors and for empirical absorption (North, Phillips & Mathews, 1968); maximum and minimum transmission coefficients were 1·00 and 0·33, respectively.

The structure was solved by the heavy-atom method. Refinement of the structure was by full-matrix least-squares calculations on F's, initially with isotropic and finally with anisotropic temperature factors for the non-H atoms. At an intermediate stage in the refinement a difference map revealed all H atoms which were included in subsequent cycles at geometrically idealized positions (C—H 0·95 Å), with an overall isotropic temperature factor. Refinement converged with $R = 0{\cdot}069$ and $wR = [\sum w\Delta^2/\sum F_o^2]^{1/2} = 0{\cdot}093$. Max. shift/e.s.d. was less than 0·01, $S = 1{\cdot}596$, $w = 1/[\sigma^2(F_o) + 0{\cdot}10(F_o)^2]$, min. and max. electron density in the final difference map being −0·39 and 0·43 e Å^{-3}, respectively. Scattering factors were those of Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965) and allowance was made for anomalous dispersion (Cromer & Liberman, 1970). All computer programs used were part of the Enraf–Nonius *Structure Determination Package* (B. A. Frenz & Associates Inc., 1985), and the figures were plotted using *ORTEP* (Johnson, 1976).

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