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The Structure of 1,4,7,10,13-Pentaoxa-14,16-cyclohexadecanedione*

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Abstract. $C_{11}H_{18}O_7$, monoclinic, $P2_1/c$, $a = 9{\cdot}332$ (2), $b = 13{\cdot}749$ (4), $c = 12{\cdot}858$ (4) Å, $\beta = 127{\cdot}60$ (2)°, $Z = 4$, $D_c = 1{\cdot}33$ Mg m^{-3}. The ether O atoms point into the interior of the ring and form a nearly regular pentagonal cavity. The carbonyl O atoms point out of the ring.

Introduction. There is considerable interest in cyclic polyethers because of their ability to selectively complex alkali and alkaline-earth cations. It has been found that the selectivity of the ethers is affected by such structural features as the size of the ether, the number, type and arrangement of the potential donor atoms, and the groups which are substituted on the ether. The title compound is of considerable interest in that it has carbonyl O in addition to ether O atoms, a situation also found in valinomycin and other naturally occurring molecules. This study was initiated to determine the conformation of the potential ligand with particular interest in the positions of the carbonyl O atoms.

The title compound was synthesized by S. F. Nielsen (Bradshaw *et al.*, 1976). Preliminary crystallographic data for the compound were obtained using a precession camera. The data indicated that the material crystallized in the monoclinic space group $P2_1/c$. A crystal, shaped to a sphere of diameter 0·37 mm, was mounted on a Syntex $P\bar{1}$ autodiffractometer. Intensity data were collected on that instrument utilizing Mo $K\alpha$ radiation (0·71073 Å) and a graphite monochromator. Accurate lattice parameters were obtained by a least-squares refinement of the 2θ measurements of 15 reflections. A total of 2439 independent reflections were measured to a 2θ limit of 50° ($\sin\theta/\lambda = 0{\cdot}595$ Å^{-1}). These data included 116 systematically extinct reflections, $0k0$, $k = 2n + 1$ and $h0l$, $l = 2n + 1$, and 488 reflections which were considered unobserved as $I < 2\sigma(I)$. During the data collection five check reflections were measured every 95 reflections and these showed no significant change. The data were collected using a $\theta/2\theta$ scan procedure, measuring backgrounds on both sides of the scan with the total background count time being equal to the total scan time.

The trial structure was obtained using direct methods. An E map calculated from the most consistent set of signs from *MULTAN* (Germain, Main & Woolfson, 1971) revealed a chemically reasonable model with peaks for the 18 non-hydrogen atoms. This model was refined using a full-matrix least-squares procedure (Busing, Martin & Levy, 1962). The H atom positions were obtained from a ΔF map. A weighted least-squares refinement of all atomic positions with anisotropic thermal parameters for non-hydrogen atoms and isotropic for H gave a weighted R of 0·027 and an unweighted R = 0·055. The shifts of the parameters of the non-hydrogen atoms in the final cycle were all less than two tenths of their uncertainties and the shifts of the parameters of the H atoms were less than 0·65 of their uncertainties. Final positional parameters are listed in Table 1.† All the data were used in the refinement with the exception of the $10,0,\bar{6}$

Table 1. *Non-hydrogen atomic positions in fractional coordinates* ($\times 10^5$) *for* 1,4,7,10,13-*pentaoxa*-14,16-*cyclohexadecanedione*

	x	y	z
O(1)	21218 (13)	2535 (7)	41168 (9)
C(2)	5260 (25)	−2780 (14)	37544 (20)
C(3)	−318 (24)	−9434 (14)	26496 (19)
O(4)	12629 (15)	−16989 (8)	31282 (10)
C(5)	7722 (29)	−24460 (13)	21982 (19)
C(6)	4608 (27)	−21032 (14)	9603 (17)
O(7)	20338 (15)	−16169 (8)	13036 (10)
C(8)	18105 (28)	−11772 (13)	2143 (17)
C(9)	33710 (27)	−5009 (13)	7234 (18)
O(10)	31853 (15)	3020 (7)	13304 (10)
C(11)	46466 (25)	9681 (13)	19051 (18)
C(12)	44350 (29)	17155 (12)	26513 (17)
O(13)	47221 (14)	12299 (7)	37681 (9)
C(14)	44961 (20)	17771 (11)	45141 (14)
C(15)	47088 (21)	12041 (11)	56014 (15)
C(16)	29611 (20)	7807 (10)	52154 (14)
O(17)	41485 (18)	26285 (8)	43339 (12)
O(18)	23916 (15)	8849 (9)	58304 (11)

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† Lists of structure factors, thermal parameters and H atom positional parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34529 (17pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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reflection. This reflection was omitted because of an apparent instrument malfunction in setting its φ angle. The weights were based on counting statistics with allowance for some experimental error, $\sigma(F) = \frac{1}{2}F\sigma(I)/I$ (Stout & Jensen, 1968). Atomic scattering factor tables for O and C were obtained from Cromer & Waber (1965), and that for H was taken from *International Tables for X-ray Crystallography* (1968).

Table 2. *Bond distances* (Å), *angles* (°) *and torsion angles* (°)

1	2	3	4	1–2	1–2–3	1–2–3–4
O(1)	C(2)	C(3)	O(4)	1·457 (3)	107·88 (23)	70·1 (2)
C(2)	C(3)	O(4)	C(5)	1·491 (3)	109·05 (13)	173·0 (2)
C(3)	O(4)	C(5)	C(6)	1·418 (2)	114·33 (12)	59·3 (3)
O(4)	C(5)	C(6)	O(7)	1·424 (2)	114·64 (16)	56·2 (2)
C(5)	C(6)	O(7)	C(8)	1·508 (4)	108·84 (14)	−173·8 (2)
C(6)	O(7)	C(8)	C(9)	1·416 (3)	113·16 (13)	167·0 (2)
O(7)	C(8)	C(9)	O(10)	1·419 (3)	108·33 (14)	−69·6 (2)
C(8)	C(9)	O(10)	C(11)	1·500 (3)	108·04 (22)	177·2 (1)
C(9)	O(10)	C(11)	C(12)	1·422 (3)	112·73 (18)	−173·3 (1)
O(10)	C(11)	C(12)	O(13)	1·419 (2)	108·40 (21)	68·1 (2)
C(11)	C(12)	O(13)	C(14)	1·499 (3)	107·50 (14)	−176·8 (1)
C(12)	O(13)	C(14)	C(15)	1·453 (3)	115·92 (13)	176·5 (1)
O(13)	C(14)	C(15)	C(16)	1·333 (2)	112·51 (13)	−90·6 (2)
C(14)	C(15)	C(16)	O(1)	1·509 (3)	113·18 (12)	53·5 (2)
C(15)	C(16)	O(1)	C(2)	1·502 (3)	112·18 (19)	173·0 (1)
C(16)	O(1)	C(2)	C(3)	1·336 (2)	115·84 (18)	−170·7 (1)

Distances and angles involving the carbonyl O atoms

O(17)–C(14)–O(13)–C(12)	1·199 (2)	123·70 (19)	−2·9 (2)
O(17)–C(14)–C(15)–C(16)	*a*	123·78 (20)	88·8 (2)
O(18)–C(16)–C(15)–C(14)	1·200 (3)	124·32 (14)	−127·8 (2)
O(18)–C(16)–O(1)–C(2)	*a*	123·49 (16)	−5·6 (2)

The C–H average bond distance is 1·02 (3) Å.

(*a*) Listed earlier in the table.

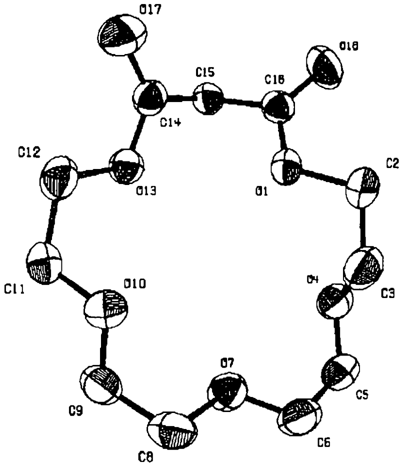

Fig. 1. *ORTEP* (Johnson, 1965) drawing of 1,4,7,10,13-pentaoxa-14,16-cyclohexadecanedione with 50% probability thermal ellipsoids for atoms. The hydrogen atoms are omitted.

Table 3. *Distances* (Å) *between ring oxygen atoms*

O(1)···O(4)	2·867 (2)	O(4)···O(10)	4·603 (2)
O(1)···O(7)	4·398 (2)	O(4)···O(13)	4·906 (2)
O(1)···O(10)	4·262 (3)	O(7)···O(10)	2·841 (2)
O(1)···O(13)	3·036 (2)	O(7)···O(13)	4·686 (2)
O(4)···O(7)	2·845 (2)	O(10)···O(13)	2·832 (2)

Discussion. The conformation of the molecule and the atom labels are given in Fig. 1. The bond lengths, bond angles and torsion angles are listed in Table 2. The bond lengths indicate that the molecule consists of an ester portion, atoms C(2), O(1)···O(13), C(12), and an ether portion, atoms C(2), C(3)···C(11), C(12). The bond lengths within the ester portion agree well with chemically similar bonds of esters previously studied (for examples, see Kroon & Kanters, 1973; Kanters, Doesberg & Koops, 1977). The C–C and C–O bond lengths [averaging 1·500 (7) and 1·420 (3) Å, respectively] of the ether portion are typical of those found in other cyclic polyethers (Dalley, 1978).

The presence of the two ester groups in the ring apparently causes it to assume a conformation in which all the ether O atoms are directed into the interior of the ring. The ether O atoms form a nearly regular pentagonal cavity. The distances between nonadjacent O atoms range from 4·262 to 4·906 Å (see Table 3), while the distances between adjacent O atoms which are separated by two C atoms are about 2·8 Å, the sum of the van der Waals radii for two O atoms (Pauling, 1960). In the ether portion of the molecule all the O–C–C–O torsion angles have values near 60°. The C–O–C–C torsion angles also have low strain values. This conformation, which is shown in Fig. 1, is similar to that found in the ligands of cyclic polyether cation complexes in which the cation is located in the cavity (Dalley, 1978). A similar conformation is also observed in the structure of 1,4,7,10,13,16-hexaoxa-2,6-cyclooctadecanedione, another cyclic ether with two ester groups (Dalley & Larson, 1979).

Least-squares planes were calculated for the two ester groups and for the ether O atoms of the ring. The two ester groups are planar with the carbonyl O atoms pointing out of the cavity. The deviations of the ring O atoms from the least-squares plane calculated for these atoms are O(1) +0·35, O(4) −0·15, O(7) −0·15, O(10) +0·37, O(13) −0·43 Å. The standard deviation of the distances of the atoms from the plane is 0·35 Å. The two carbonyl O atoms are on the same side of this plane with O(17) and O(18) being 0·62 and 0·23 Å out of the plane, respectively.

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cis-2,4,9-Trimethylthioxanthene 10-Oxide

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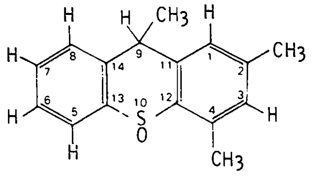
Abstract. $C_{16}H_{16}OS$, monoclinic, Cc, $Z = 4$, $M_r = 256{\cdot}36$, $a = 12{\cdot}122$ (1), $b = 14{\cdot}654$ (2), $c = 7{\cdot}734$ (1) Å, $\beta = 102{\cdot}94$ (1)°, $V = 1339{\cdot}0$ (3) Å^3, $D_x = 1{\cdot}272$ Mg m^{-3}, $\lambda(\text{Cu } K\alpha) = 1{\cdot}5418$ Å, $\mu(\text{Cu } K\alpha) = 1{\cdot}950$ mm^{-1}; final residual $R = 0{\cdot}039$. The 9-methyl and 10-oxide groups are both in the boat–axial conformation with respect to the central thioxanthene ring.

Introduction. Single crystals of *cis*-2,4,9-trimethylthioxanthene 10-oxide (I) were prepared by oxidation of the corresponding sulfide followed by recrystallization from a 1:1 mixture of benzene:hexane solution.† The unit-cell parameters were obtained by measuring the 2θ values of 15 reflections. The space group, Cc or $C2/c$, was deduced from systematic absences (hkl absent with $h + k$ odd and $h0l$ absent with l odd). The intensity data were collected on a Syntex $P2_1$ automatic diffractometer with a crystal approximately $0{\cdot}18 \times 0{\cdot}24 \times 0{\cdot}75$ mm. A $\theta/2\theta$ scanning mode with graphite-monochromated Cu $K\alpha$ radiation was used to measure 1118 independent reflections with 2θ values below 130°; of these, 1105 reflections were considered as observed by the criterion $I > 3{\cdot}0\sigma(I)$, where $\sigma(I)$ was determined from counting statistics. The intensity data were reduced to structure amplitudes by the application of Lorentz and polarization factors, but no absorption corrections were applied.



(I)

The structure was determined by the application of direct methods with the weighted multisolution tangent-refinement program *MULTAN* (Germain, Main & Woolfson, 1971). The space group was deduced to be Cc, since there are four molecules in a unit cell and the molecule does not possess any center of symmetry or twofold axis. The normalized structure factors were also shown to have a noncentrosymmetric distribution; the ratios between $\langle E\rangle$, $\langle E^2\rangle$, and $\langle E^2 - 1\rangle$ are 0·894, 1·000, and 0·707 respectively. The E map

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† Details will be published elsewhere.

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