

## SHORT STRUCTURAL PAPERS

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*Acta Cryst.* (1974). B30, 2739

## 1,4,7,10,13,16-Hexaoxacyclooctadecane

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**Abstract.**  $C_{12}H_{24}O_6$ , orthorhombic, *Pbca*,  $a=8.295$  (4),  $b=20.230$  (10),  $c=8.490$  (4) Å,  $M=264.32$ ,  $Z=4$ ,  $D_x=1.23$  g cm $^{-3}$ , m.p. 39°. The molecule has a crystallographic centre of symmetry, and the conformation of the 18-membered ring is approximately described in terms of (*ap, ap, ap*), (*ap, +sc, ap*), (*ap, -sc, +sc*) partial conformations of the three successive non-equivalent -O-CH $_2$ -CH $_2$ -O- units.

**Introduction.** The compound was recrystallized from ethanol, and crystals for X-ray analysis were sealed in capillaries to prevent sublimation. In spite of their low melting point the crystals yield X-ray diagrams extending to the limit of Cu *K*α radiation at room tem-

perature. Intensity measurements were made from a crystal of dimensions 0.35 × 0.35 × 0.35 mm with a four-circle diffractometer (Hilger and Watts Y290, graphite monochromator, Mo *K*α radiation,  $\theta/2\theta$  scan, background measurements at beginning and end of each scan). 1400 reflexions were measured out to  $\sin \theta/\lambda=0.83$  Å $^{-1}$ . The structure was solved by direct methods and refined by least-squares analysis, with three kinds of weighting scheme: (*a*) unit weights, (*b*) experimental weights, *i.e.* weights based on counting statistics with allowance for various kinds of experimental error, (*c*) experimental weights modified by multiplication by a function  $\exp(r \sin^2 \theta/\lambda^2)$  with  $r > 0$ . Modified weighting schemes of this kind have several advantages (Dunitz & Seiler, 1973) but they may not be suitable for optimizing hydrogen-atom parameters. Consequently, with weighting scheme (*c*) the hydrogen positions were recalculated from time to time from stereochemical considerations but held constant during each refinement cycle. Table 1 lists coordinates of C and O atoms taken from the final cycle (*c*) with  $r=36$  Å $^2$ , Table 2 the corresponding vibrational tensor components. Positions of hydrogen atoms are given in Table 3. The final *R* was 0.052 (0.022, weighted).<sup>\*</sup> Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962).

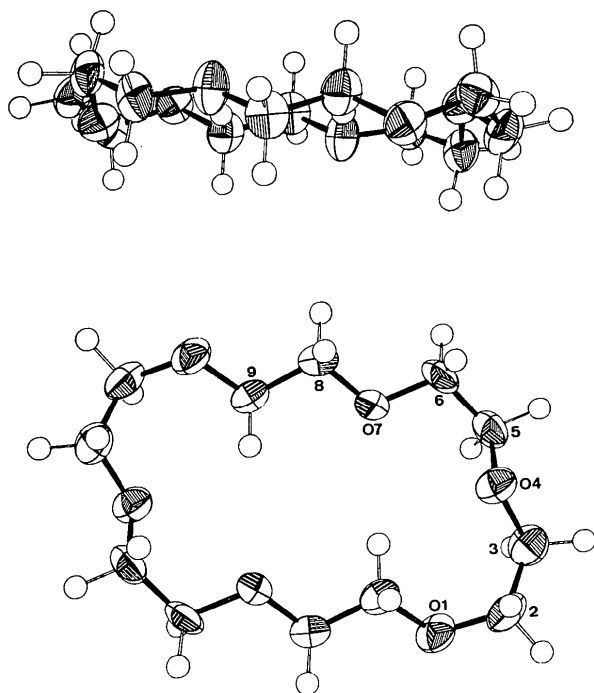


Fig. 1. Bottom: molecule viewed in the direction normal to its mean plane, showing atom numbering. Top: view along a direction in the mean plane. The vibration ellipsoids are drawn at the 50% probability level (Johnson, 1965).

Table 1. Fractional coordinates (and estimated standard deviations) of the carbon and oxygen atoms

	Values are $\times 10^4$ .		
	<i>x</i>	<i>y</i>	<i>z</i>
O(1)	-134 (2)	-1339 (1)	-2583 (1)
C(2)	-165 (2)	-1938 (1)	-1724 (2)
C(3)	1167 (2)	-2009 (1)	-529 (2)
O(4)	863 (1)	-1616 (1)	807 (1)
C(5)	2254 (2)	-1437 (1)	1646 (2)
C(6)	1857 (2)	-888 (1)	2784 (1)
O(7)	1490 (2)	-320 (1)	1901 (1)
C(8)	978 (2)	216 (1)	2833 (1)
C(9)	793 (2)	794 (1)	1734 (1)

<sup>\*</sup> A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30556 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Vibration-tensor components ( $\text{\AA}^2$ ) for the carbon and oxygen atoms*

Values are  $\times 10^3$ .

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
O(1)	74	55	48	3	7	-5
C(2)	70	48	58	-10	4	-11
C(3)	73	57	60	11	2	-9
O(4)	57	58	52	2	0	-6
C(5)	61	54	61	8	-8	3
C(6)	70	58	48	3	-12	6
O(7)	88	52	42	4	-9	0
C(8)	77	53	43	0	-5	-2
C(9)	82	50	43	4	1	-3

Table 3. *Fractional coordinates of the hydrogen atoms calculated assuming local  $C_{2v}$  symmetry of the methylene groups with  $C-H=1.04 \text{ \AA}$ ,*

$H-C-H=109^\circ$   
Values are  $\times 10^3$ .

	$x$	$y$	$z$
H(2)	-125	-197	-111
H(2)*	-6	-233	-250
H(3)	225	-185	-104
H(3)*	126	-250	-18
H(5)	312	-127	86
H(5)*	268	-184	226
H(6)	285	-80	350
H(6)*	87	-102	346
H(8)	182	32	370
H(8)*	-14	11	336
H(9)	3	67	81
H(9)*	193	92	130

**Discussion.** The conformation of the uncomplexed hexaether is shown in Fig. 1. The three  $-O-CH_2-CH_2-O-$  subunits that make up the asymmetric unit of the structure are clearly different. In the nomenclature of Klyne & Prelog (1960) the subunit  $-O(1)C(2)C(3)O(4)-$  is  $-sc, +sc, app$ ,  $-O(4)C(5)C(6)O(7)-$  is  $app, -sc, ap$  and  $-O(7)C(8)C(9)O(1')-$  is  $ap, ap, ap$ . The actual values of the torsion angles are given in Table 4, with bond distances and angles. The conformation proposed by Dale & Kristiansen (1972) on the basis of the infrared spectrum of the crystalline hexaether is not in agreement with our findings.

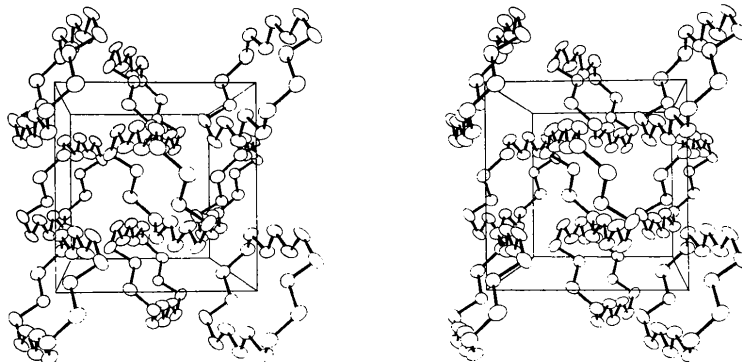
Table 4. *Bond distances ( $\text{\AA}$ ), bond angles ( $^\circ$ ) and torsion angles ( $^\circ$ ) in the centrosymmetric 18-membered ring*

Atoms				Distance	Angle	Torsion angle
1	2	3	4	2-3	1-2-3	1-2-3-4
C(9')	O(1)	C(2)	C(3)	1.414	113.3	-79.7
O(1)	C(2)	C(3)	O(4)	1.506	114.6	75.4
C(2)	C(3)	O(4)	C(5)	1.408	111.0	-155.2
C(3)	O(4)	C(5)	C(6)	1.403	114.0	165.8
O(4)	C(5)	C(6)	O(7)	1.509	109.6	-67.6
C(5)	C(6)	O(7)	C(8)	1.405	107.9	175.5
C(6)	O(7)	C(8)	C(9)	1.407	113.3	174.7
O(7)	C(8)	C(9)	O(1')	1.505	106.4	174.7
C(8)	C(9)	O(1')	C(2')	1.426	109.1	170.1

The mean C-C and C-O bond distances, 1.507 and 1.411  $\text{\AA}$  respectively, are both short compared with the corresponding distances in gaseous 1,4-dioxane, 1.523 and 1.423  $\text{\AA}$  respectively (Davis & Hassel, 1963). The refinements with the other weighting systems led to even shorter distances (1.492  $\text{\AA}$ ) for the C-C bonds and slightly longer ones (1.419  $\text{\AA}$ ) for the C-O bonds.

These apparently anomalous bond distances may be due to shortening effects from curvilinear motions of the atoms arising from internal molecular vibrations. Some of the vibration tensors are quite anisotropic, *e.g.* O(7), and analysis in terms of rigid-body motion (Schomaker & Trueblood, 1970) does not lead to good agreement between observed and calculated tensor components;  $\langle (\Delta U_{ij})^2 \rangle^{1/2} = 0.0044 \text{ \AA}^2$ ,  $\langle \sigma^2(U_{ij}) \rangle^{1/2} = 0.0006 \text{ \AA}^2$ . Fig. 1 suggests that each atom has a tendency to vibrate most strongly in a direction normal to the plane formed by it and its two bonded neighbours. Corrections for these motions should tend to make the bond distances longer but they are of uncertain magnitude and have not been applied.

The bond angles at carbon cover a range from 106.4 to 114.6° (mean 109.8°) whereas those at oxygen vary only from 113.3 to 114.0° (mean 113.5°). The two largest C-C-O angles occur at C(2) and C(3), just where some angle widening might be expected because of the *gauche* effect (Bartell, 1959). It is interesting that the two longest C-O bonds, 1.414 and 1.426  $\text{\AA}$ , also occur in this 'strained' part of the molecule. The other

Fig. 2. Stereoscopic view of the crystal structure looking along the  $b$  axis. The  $c$  axis is vertical, the  $a$  axis horizontal.

four C–O bonds lie in a very narrow range, 1.403–1.408 Å.

A stereoscopic drawing (Johnson, 1965) of the molecular packing is shown in Fig. 2. The planar zigzag segments of molecules related by the operation  $x \rightarrow \frac{1}{2} + x, y \rightarrow y, z \rightarrow \frac{1}{2} - z$  run antiparallel to one another, leading to electrostatically favourable dipole-dipole interactions.

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## Hydrated Sodium Thiocyanate Complex of 1,4,7,10,13,16-Hexaoxacyclooctadecane

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**Abstract.**  $C_{12}H_{24}O_6 \cdot NaNCS \cdot H_2O$ , monoclinic,  $P2_1/c$ ,  $a = 12.316$  (6),  $b = 13.737$  (7),  $c = 11.215$  (6) Å,  $\beta = 105.32$  (11)°,  $M = 363.40$ ,  $Z = 4$ ,  $D_x = 1.32$  g cm<sup>-3</sup>. The hexaether adopts a highly irregular conformation in which five approximately coplanar atoms surround the sodium cation. A distorted pentagonal bipyramidal coordination of the cation is completed by the remaining oxygen of the hexaether and by a water molecule.

**Introduction.** Intensity measurements were made from a crystal of dimensions 0.4 × 0.4 × 0.4 mm with a four-circle diffractometer (Hilger and Watts Y290, graphite monochromator, Mo  $K\alpha$  radiation,  $\theta/2\theta$  scan, background measurements at beginning and end of each scan). 3160 reflexions were measured out to  $\sin \theta/\lambda = 0.62$  Å<sup>-1</sup>. The structure was solved by direct methods and refined by least-squares with the modified weighting system described by Dunitz & Seiler (1973). Methylene hydrogen positions were calculated from stereochemical considerations but were held constant during refinement. The two hydrogen atoms of the H<sub>2</sub>O molecule were located from an ( $F_o - F_c$ ) synthesis but not subsequently refined. Table 1 lists coordinates of heavy atoms from the final cycle with  $r = 36$  Å<sup>2</sup>, Table 2 the corresponding vibration tensors. Hydrogen positions are given in Table 3. The final  $R$  was 0.081 (0.053, weighted).\* Atomic scattering factors were

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30557 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

### References

- BARTELL, L. E. (1959). *J. Amer. Chem. Soc.* **81**, 3497–3498.  
 DALE, J. & KRISTIANSEN, P. O. (1972). *Acta Chem. Scand.* **26**, 1471–1478.  
 DAVIS, M. & HASSEL, O. (1963). *Acta Chem. Scand.* **17**, 1181.  
 DUNITZ, J. D. & SEILER, P. (1973). *Acta Cryst.* B**29**, 589–595.  
*International Tables for X-ray Crystallography* (1962). Vol. III, pp. 202–216. Birmingham: Kynoch Press.  
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.  
 KLYNE, W. & PRELOG, V. (1960). *Experientia*, **16**, 521–523.  
 SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* B**24**, 63–76.

Table 1. Fractional coordinates (and estimated standard deviations) of the non-hydrogen atoms

	Values are × 10 <sup>4</sup> .		
	<i>x</i>	<i>y</i>	<i>z</i>
Na	2800 (0)	–580 (0)	1356 (0)
O(1)	2454 (1)	–2452 (1)	1046 (1)
C(2)	1306 (1)	–2739 (1)	650 (2)
C(3)	696 (1)	–2243 (1)	1471 (1)
O(4)	793 (1)	–1226 (1)	1343 (1)
C(5)	376 (1)	–710 (1)	2233 (1)
C(6)	454 (1)	358 (1)	2007 (1)
O(7)	1606 (1)	583 (1)	2121 (1)
C(8)	1785 (1)	1594 (1)	2076 (2)
C(9)	2996 (1)	1748 (1)	2063 (1)
O(10)	3293 (1)	1199 (1)	1121 (1)
C(11)	2785 (2)	1542 (1)	–100 (2)
C(12)	3037 (2)	829 (2)	–992 (2)
O(13)	2502 (1)	–65 (1)	–799 (1)
C(14)	2715 (2)	–856 (2)	–1518 (2)
C(15)	3871 (2)	–1299 (2)	–1031 (2)
O(16)	4127 (1)	–1458 (1)	276 (1)
C(17)	4252 (1)	–2446 (2)	679 (2)
C(18)	3137 (2)	–2970 (1)	423 (2)
N	6364 (2)	–776 (2)	4593 (3)
C	7296 (1)	–768 (1)	4558 (1)
S	8612 (0)	–770 (0)	4535 (0)
O(HOH)	3977 (1)	–589 (1)	3349 (1)

taken from *International Tables for X-ray Crystallography* (1962).

**Discussion.** The structural unit, with atom numbering, is shown in Fig. 1. Although 13 of the 18 ring-members are arranged as in the symmetrical  $D_{3d}$  conformation observed in the K<sup>+</sup> complex (Seiler, Dobler & Dunitz,