

Crystal Conformation of 1,4,8,11-Tetraoxacyclotetradecane at $-150\text{ }^{\circ}\text{C}$

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As part of a study of conformational problems in tetraoxacyclodecanes the 1,4,8,11-tetraoxacyclotetradecane, $\text{C}_{10}\text{H}_{20}\text{O}_4$, has been synthesized.¹ No definite conclusions about the ring conformation could be drawn on basis of NMR-data, and the crystal structure is now reported.

The crystals belong to the monoclinic system with space group $P2_1/n$, cell dimensions $a=8.026(1)\text{ \AA}$, $b=9.033(1)\text{ \AA}$, $c=15.711(2)\text{ \AA}$, $\beta=102.64(1)^{\circ}$, and $Z=4$ ($D_m=1.20\text{ g cm}^{-3}$, $D_x=1.22\text{ g cm}^{-3}$).

With $2\theta_{\text{max}}=50^{\circ}$ and $\text{MoK}\alpha$ -radiation 1966 independent reflections were measured on an automatic fourcircle diffractometer at $-150\text{ }^{\circ}\text{C}$. Using an observed-unobserved cutoff at 2.5 (I) 1683 reflections were recorded as observed. No corrections for absorption or secondary extinction were applied (crystal size $0.45 \times 0.60 \times 0.25\text{ mm}^3$).

The structure was solved by direct methods² and refined by full-matrix least-squares technique.^{3,*} Hydrogen atom positions were calculated. Anisotropic temperature factors were introduced for O and C atoms and weights in least-squares were

* All programs used (except those for phase determination) are included in this reference.

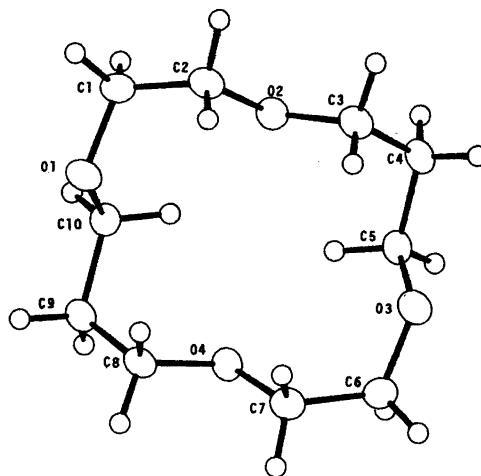


Fig. 1. Schematic drawing of the molecule.

calculated from the standard deviations in intensities, $\sigma(I)$, taken as

$$\sigma(I) = [C_T + (0.02C_N)^2]^{\frac{1}{2}}$$

where C_T is the total number of counts and C_N the net count. The form factors used were those of Hanson *et al.*⁴ except for hydrogen.⁵ The final R -value was 2.9% (weighted value $R_w=3.4\%$) for 1683 observed reflections.

Final fractional coordinates together with the thermal parameters are listed in Table 1. The principal thermal vibration ellipsoids for oxygen

Table 1. Final fractional coordinates and thermal parameters with estimated standard deviations. The expression for anisotropic vibration is $\exp[-2\pi^2(h^2a^{*2}U_{11} + \dots + 2klb^*c^*U_{23})]$. Atom Hmn is bonded to Cm.

ATOM	X	Y	Z	U11	U22	U33	U12	U13	U23
O1	.0431(10)	.0760(10)	.0023(6)	.0223(5)	.0278(5)	.0314(5)	.0029(4)	.0003(4)	-.0071(4)
O2	-.1444(10)	.0776(10)	.7307(5)	.0254(5)	.0229(5)	.0249(5)	.0011(4)	.0042(4)	-.0013(4)
O3	.1304(11)	.04027(10)	.09131(5)	.0264(5)	.0271(5)	.0267(5)	-.0009(4)	.0031(4)	.0056(4)
O4	.3100(10)	.0603(9)	.7700(5)	.0240(5)	.0264(5)	.0222(5)	-.0035(4)	.0034(4)	-.0005(4)
C1	-.1330(10)	.7005(10)	.0910(6)	.0217(7)	.0335(6)	.0297(7)	.0040(6)	.0049(6)	-.0069(6)
C2	.1701(11)	.7030(10)	.0934(6)	.0226(7)	.0249(7)	.0313(7)	.0025(6)	.0022(6)	-.0008(6)
C3	.1975(11)	.7430(10)	.0946(6)	.0259(7)	.0249(7)	.0290(7)	.0043(6)	.0032(6)	.0040(6)
C4	-.1009(11)	.0217(10)	.0903(6)	.0260(7)	.0267(7)	.0215(7)	.0001(6)	-.0004(6)	.0037(6)
C5	.0041(10)	.0409(10)	.0100(6)	.0260(7)	.0224(7)	.0200(7)	-.0009(6)	.0035(6)	.0015(6)
C6	.3001(11)	.0902(10)	.0032(6)	.0243(7)	.0323(6)	.0200(8)	.0005(6)	.0003(6)	.0022(6)
C7	.3709(11)	.0430(10)	.7147(6)	.0250(7)	.0205(6)	.0301(7)	-.0033(6)	.0050(6)	.0033(6)
C8	.3004(10)	.0103(10)	.0001(6)	.0192(7)	.0200(6)	.0261(7)	-.0018(6)	.0000(6)	-.0043(6)
C9	.0001(10)	.0002(10)	.0917(6)	.0243(7)	.0247(7)	.0223(7)	.0020(6)	.0003(6)	-.0010(6)
C10	.00017(10)	.00999(10)	.00030(6)	.0255(7)	.0222(7)	.0223(7)	-.0007(6)	.0047(6)	-.0025(6)

ATOM	X	Y	Z	B	ATOM	X	Y	Z	B
H11	-.1663(17)	.7700(10)	.9340(9)	2.1(3)	H12	-.2037(10)	.0174(10)	.0099(6)	2.2(3)
H21	.0000(17)	.0022(10)	.0010(6)	1.7(3)	H22	-.2076(10)	.0315(10)	.7931(9)	2.2(3)
H31	.0001(10)	.0147(10)	.0507(6)	1.9(3)	H32	-.2001(10)	.7992(10)	.6369(9)	2.1(3)
H41	-.1004(10)	.0000(10)	.0300(9)	1.0(3)	H42	-.2001(10)	.0404(10)	.5911(6)	2.1(3)
H51	.0012(10)	.0400(10)	.0720(6)	1.3(2)	H52	.0351(10)	.5100(10)	.0720(6)	1.2(2)
H61	.0090(17)	.0370(10)	.0044(6)	1.9(3)	H62	.0099(10)	.0400(10)	.0100(6)	1.9(3)
H71	.3400(10)	.7020(10)	.7212(6)	1.7(3)	H72	.0010(10)	.0320(10)	.7247(9)	2.2(3)
H81	.3000(10)	.7211(10)	.0030(6)	1.6(3)	H82	.0003(10)	.0120(10)	.0004(6)	1.9(3)
H91	.0000(17)	.0000(10)	.0000(6)	1.0(3)	H92	.1100(10)	.0100(10)	.0100(6)	1.7(3)
H101	.0373(10)	.0033(10)	.0340(6)	1.6(3)	H102	.0431(10)	.5100(10)	.0360(6)	1.1(2)

Table 2. Bond distances, bond angles, and dihedral angles with estimated standard deviations.

DISTANCE (Å)			DISTANCE (Å)		
O1 - C1	1.426(1)	O1 - C10	1.434(1)		
O2 - C2	1.420(1)	O2 - C3	1.425(1)		
O3 - C5	1.433(1)	O3 - C6	1.426(2)		
O4 - C7	1.422(2)	O4 - C8	1.425(1)		
C1 - C2	1.503(2)	C3 - C4	1.509(2)		
C4 - C5	1.514(2)	C6 - C7	1.506(2)		
C8 - C9	1.500(2)	C9 - C10	1.514(2)		

ANGLE (°)			ANGLE (°)		
O1 - C1 - C2	112.9(1)	C1 - O1 - C10	113.7(1)		
O1 - C10 - C9	107.7(1)	O2 - C2 - C1	109.5(1)		
C2 - O2 - C3	112.4(1)	O2 - C3 - C4	100.0(1)		
O3 - C5 - C4	107.4(1)	C5 - O3 - C6	114.2(1)		
O3 - C6 - C7	113.2(1)	O4 - C7 - C8	110.1(1)		
C7 - O4 - C8	111.0(1)	O4 - C8 - C9	108.7(1)		
C3 - C4 - C5	113.0(1)	C8 - C9 - C10	112.6(1)		

DIHEDRAL ANGLE (°)			
C10 - O1 - C1 - C2	-92.7(1)		
O2 - C2 - C1 - O1	75.9(1)		
C3 - O2 - C2 - C1	-175.0(1)		
C4 - C3 - O2 - C2	179.0(1)		
O2 - C3 - C4 - C5	-64.0(1)		
C3 - C4 - C5 - O3	-70.0(1)		
C6 - O3 - C4 - C5	167.0(1)		
C7 - C6 - O3 - C4	-89.1(1)		
O4 - C7 - C6 - O3	77.1(1)		
C8 - O4 - C7 - C6	-172.2(1)		
C9 - C8 - O4 - C7	176.9(1)		
O4 - C8 - C9 - C10	-64.7(1)		
C8 - C9 - C10 - O1	-69.3(1)		
C9 - C10 - O1 - C1	169.4(1)		

and carbon atoms were calculated from the thermal parameters of this table, and the maximum r.m.s. amplitudes range from 0.16 to 0.20 Å.

Bond distances, bond angles and dihedral angles may be found in Table 2. The standard deviations, given in parentheses, are estimated from the correlation matrix of the final least-squares refinement cycle.

Fig. 1 is a schematic drawing of the molecule, indicating the numbering of atoms.

For cyclotetradecane itself, the "rectangular" diamond-lattice conformation has the lowest calculated enthalpy⁶ as well as being the observed one in liquid and solution.⁷ Recently it has been shown that it also is the experimental crystal conformation.⁸ Furthermore, this centrosymmetric "rectangular" conformation is indeed the preferred one in the crystals of 1,3,8,10-tetraoxacyclotetradecane.⁹

However, it turned out that the ring skeleton of the present compound has a conformation with approximate two-fold rotational symmetry (Fig. 1).

From Table 2 it may be seen that the distances O1-C10 [1.434(1) Å] and O3-C5 [1.433(1) Å] seem to be somewhat longer than the other six (mean value 1.424 Å). The same effect, but less pronounced, is seen for C9-C10 [1.514(2) Å] and C4-C5 [1.514(2) Å] compared to the average value of the other four (1.506 Å).

Bond distances and angles agree within error limits with corresponding values for 1,3,8,10-tetraoxacyclotetradecane,⁹ and also with those of 1,5,9,13-tetraoxacyclohexadecane.¹⁰ In 1,3,8,10-

tetraoxacyclotetradecane the shortest intra-molecular nonbonded H...H contact is 2.19 Å, while in the present compound no such contacts shorter than 2.4 Å occur. No short inter-molecular distances are observed.

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1. Borgen, G. and Dale, J. *To be published.*
2. Germain, G., Main, P. and Woolfson, M. M. *Acta Crystallogr. A* 27 (1971) 368.
3. Groth, P. *Acta Chem. Scand.* 27 (1973) 1837.
4. Hanson, H. P., Herman, F., Lea, J. D. and Skillman, S. *Acta Crystallogr.* 17 (1964) 1040.
5. Stewart, R. F., Davidson, E. R. and Simpson, W. T. *J. Chem. Phys.* 42 (1965) 3175.
6. Dale, J. *Acta Chem. Scand.* 27 (1973) 1115.
7. Borgen, G. and Dale, J. *Chem. Commun.* (1970) 1340.
8. Groth, P. *Acta Chem. Scand. A* 30 (1976) 155.
9. Bassi, W. I., Scordamaglia, R. and Fiore, L. *J. Chem. Soc. Perkin Trans. 2* (1972) 1726.
10. Groth, P. *Acta Chem. Scand.* 25 (1971) 725.

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