

Crystal Conformation of 1,4,7,10-Tetraoxacyclododecane at $-150\text{ }^\circ\text{C}$

P. GROTH

Department of Chemistry, University of Oslo,
Oslo 3, Norway

As part of a study of conformational problems of tetraoxacycloalkanes 1,4,7,10-tetraoxacyclododecane has been synthesized.¹ In five known complexes with this cyclomer three different ring conformations occur. In $\text{Na}(\text{C}_8\text{H}_{16}\text{O}_4)_2\text{Cl}\cdot 5\text{H}_2\text{O}$,² $\text{Na}(\text{C}_8\text{H}_{16}\text{O}_4)_2\text{OH}\cdot 8\text{H}_2\text{O}$ ³ and $\text{Ca}(\text{C}_8\text{H}_{16}\text{O}_4)\text{Cl}_2\cdot 8\text{H}_2\text{O}$,⁴ the ring symmetry is C_4 . In $\text{Cu}(\text{C}_8\text{H}_{16}\text{O}_4)\text{Cl}_2$ ⁵ it is C_s and in $\text{Mg}(\text{H}_2\text{O})_6\text{Cl}_2\cdot \text{C}_8\text{H}_{16}\text{O}_4$ ⁶ a C_i geometry is obtained. For $\text{C}_8\text{H}_{16}\text{O}_4$ itself no definite conclusions about the ring conformation could be drawn on the basis of NMR-data, and the crystal structure is now reported.

The crystals belong to the triclinic system with space group $P1$, cell dimensions (for Dirichlet's reduced cell) $a=4.704(3)\text{ \AA}$, $b=7.282(4)\text{ \AA}$, $c=7.520(5)\text{ \AA}$, $\alpha=64.10(5)^\circ$, $\beta=85.12(5)^\circ$, $\gamma=76.52(4)^\circ$, and $Z=1$ ($D_x=1.30\text{ g cm}^{-3}$). The melting point was $\sim 0\text{ }^\circ\text{C}$ and the density was not measured.

With $2\theta_{\text{max}}=50^\circ$, $\text{MoK}\alpha$ -radiation, and an observed-unobserved cutoff at $2.5\sigma(I)$, 715 independent reflections were recorded as observed on an automatic four-circle diffractometer at $-150\text{ }^\circ\text{C}$ (the crystals were grown at $-10\text{ }^\circ\text{C}$ and rapidly transferred into the cold stream). No corrections for absorption or secondary extinction were applied (crystal size $0.3\times 0.4\times 0.4\text{ mm}$).

The structure was solved by direct methods⁷ (assuming space group $P1$) and refined by full-matrix least squares technique.⁸ After three cycles of isotropic refinement, the correlation matrix strongly

indicated a centrosymmetric structure, and coordinates were transformed to $P1$. Hydrogen atom positions were calculated. Anisotropic temperature factors were introduced for O and C atoms and weights in least squares were calculated from the standard deviations in intensities, $\sigma(I)$, taken as

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

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.*⁹ except for hydrogen.¹⁰ The final R -value was 3.0% (weighted value 3.8%) for 715 observed reflections.

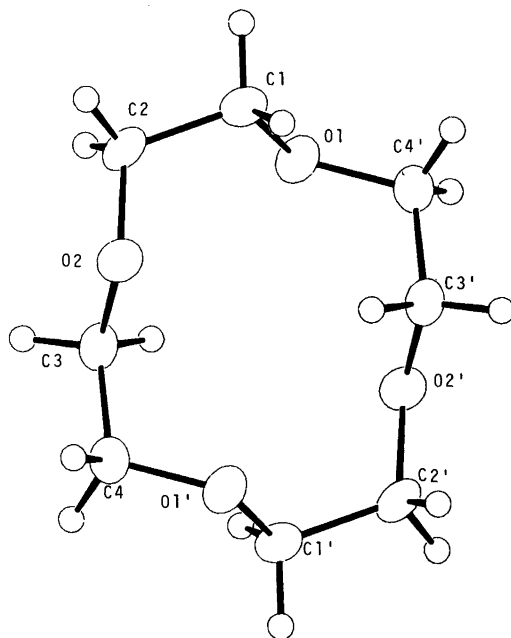


Fig. 1. Schematic drawing of the molecule.

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 H_{m} is bonded to C_{m} .

ATOM	X	Y	Z	U11	U22	U33	U12	U13	U23
O1	.07414(19)	-.20086(13)	.31532(12)	.0309(5)	.0297(5)	.0286(5)	-.0138(4)	.0053(4)	-.0156(4)
O2	.16359(18)	.22456(13)	.02679(12)	.0265(5)	.0311(5)	.0237(5)	-.0101(4)	.0037(3)	-.0127(4)
C1	.31396(20)	-.10086(21)	.31200(20)	.0263(7)	.0323(7)	.0233(7)	-.0103(5)	-.0001(5)	-.0125(6)
C2	.21132(30)	.12415(21)	.23625(18)	.0306(7)	.0330(7)	.0240(7)	-.0141(6)	.0044(5)	-.0176(6)
C3	-.13687(27)	.28583(21)	-.03263(19)	.0247(7)	.0250(7)	.0308(7)	-.0065(5)	.0038(5)	-.0155(6)
C4	-.10293(32)	.36594(20)	-.25370(20)	.0344(7)	.0219(6)	.0303(7)	-.0086(5)	.0000(5)	-.0107(6)

ATOM	X	Y	Z	B	ATOM	X	Y	Z	B
H11	.4624(31)	-.1340(20)	.2274(20)	1.7(3)	H12	.3919(29)	-.1665(21)	.4497(21)	1.8(3)
H01	.3713(31)	.1770(21)	.2625(20)	2.1(3)	H22	.0303(31)	.1585(21)	.3040(20)	1.9(3)
H31	-.0308(30)	.3962(22)	.0050(19)	1.8(3)	H32	-.2313(30)	.1668(22)	.0354(19)	1.8(3)
H41	-.0103(31)	.4051(22)	-.3162(21)	1.9(3)	H42	-.3580(32)	.4506(23)	-.3013(20)	2.2(3)

Table 2. Bond distances, bond angles, and dihedral angles with estimated standard deviations. Left columns: present compound. Right columns: $\text{Mg}(\text{H}_2\text{O})_6\text{Cl}_2\text{C}_8\text{H}_{16}\text{O}_4$.

Distance	(Å)	(Å)	Distance	(Å)	(Å)
O1—C1	1.430(1)	1.428(2)	O1—C4'	1.431(2)	1.428(2)
O2—C2	1.429(1)	1.435(2)	O2—C3	1.423(2)	1.430(2)
C1—C2	1.502(2)	1.495(3)	C3—C4	1.505(2)	1.494(3)
Angle	(°)	(°)	Angle	(°)	(°)
O1—C1—C2	110.3(1)	110.5(1)	C1—O1—C4'	113.1(1)	113.0(1)
O2—C2—C1	111.9(1)	111.7(2)	C2—O2—C3	114.1(1)	116.4(2)
O2—C3—C4	108.5(1)	108.0(2)	C3—C4—O1'	112.3(1)	112.1(2)
Dihedral angle			(°)	(°)	
C4'—O1—C1—C2			140.2(1)	116.8(2)	
C3—O2—C2—C1			102.7(1)	98.0(2)	
C4—C3—O2—C2			-173.6(1)	-147.3(2)	
O2—C2—C1—O1			-75.4(1)	-83.1(2)	
O2—C3—C4—O1			74.5(1)	71.0(2)	
C3—C4—O1'—C1'			85.2(1)	91.1(2)	

Final fractional coordinates together with the thermal parameters are listed in Table 1. The principal thermal vibration ellipsoids for oxygen and carbon atoms were calculated from the thermal parameters of this table, and the maximum r.m.s. amplitudes range from 0.184 to 0.200 Å.

Bond distances, bond angles and dihedral angles may be found as the left columns of Table 2. The standard deviations, given in parentheses, are estimated from the correlation matrix of the final least squares refinement cycle. The right columns show corresponding values for the $\text{C}_8\text{H}_{16}\text{O}_4$ ring in the $\text{Mg}(\text{H}_2\text{O})_6\text{Cl}_2$ complex⁶ (after turning the molecules to their best fit). Fig. 1 is a schematic drawing of the molecule giving a view of its C_i geometry and indicating the numbering of atoms.

As may be seen from Table 2, corresponding bond distances of the two rings are equal within error limits. Also the angles agree closely except for C2—O2—C3, which is somewhat larger for the complexed ring. However, for dihedral angles the deviations are considerable. In particular the angles at C1—O1 and C3—O2 are about 25° larger in the cyclomer itself than in the hydrogen-bonded ring of the complex.

C—H bond distances range from 0.99 to 1.01 Å and no short inter-molecular distances are observed.

Acknowledgement. The author thanks Dr. G. Borgen for preparing the crystals.

1. Borgen, G. and Dale, J. *To be published.*
2. van Remoortere, F. P. and Boer, F. P. *Inorg. Chem.* 13 (1974) 2071.
3. Boer, F. P., Neuman, M. A., van Remoortere, F. P. and Steiner, E. C. *Inorg. Chem.* 13 (1974) 2826.
4. North, P. P., Steiner, E. C., van Remoortere, F. P. and Boer, F. P. *Acta Crystallogr. B* 32 (1976) 370.
5. van Remoortere, F. P., Boer, F. P. and Steiner, E. C. *Acta Crystallogr. B* 31 (1975) 1420.
6. Neuman, M. A., Steiner, E. C., van Remoortere, F. P. and Boer, F. P. *Inorg. Chem.* 14 (1975) 734.
7. Germain, G., Main, P. and Woolfson, M. M. *Acta Crystallogr. A* 27 (1971) 368.
8. Groth, P. *Acta Chem. Scand.* 27 (1973) 1837.
9. Hanson, H. P., Herman, F., Lea, J. D. and Skillman, S. *Acta Crystallogr.* 17 (1964) 1040.
10. Stewart, R. F., Davidson, E. R. and Simpson, W. T. *J. Chem. Phys.* 42 (1965) 3175.

Received February 2, 1978.