

Crystal Structure of the (1:1) Complex between 1,4,7,10,13,16,19-Hepta-oxacycloicosane and *p*-Methoxybenzenediazonium Tetrafluoroborate at -150°C

P. GROTH

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

Aryldiazonium salts complex 18-crown-6 and other macrocyclic polyethers with large enough potential cavities.¹ In these complexes the N_2^+ group projects into the hole and the complex is considerably more stable and soluble in organic media than is the uncomplexed salt in water. In particular it has been shown² that the 21-crown-7 complex with *p*-methoxybenzenediazonium tetrafluoroborate is more stable than the corresponding complex with 18-crown-6. Although the crystal structure of the 18-crown-6 complex with toluenediazonium tetrafluoroborate has been cited,³ it is, to the best of the author's knowledge, not yet published. In order to obtain structural evidence for this type of complex, and to determine the conformation of the cyclic heptaether, a crystal structure analysis of $(\text{CH}_2\text{CH}_2\text{O})_7 \cdot \text{CH}_3\text{OC}_6\text{H}_4\text{N}_2\text{BF}_4$ has been carried out.

The crystals are triclinic with space group $P\bar{1}$ and cell dimensions (for Dirichlet's reduced cell) $a = 8.081(2)$, $b = 12.555(3)$, $c = 13.093(3)$ Å, $\alpha = 81.08(2)$, $\beta = 84.55(2)$, $\gamma = 86.00(2)^\circ$. There are two formula units in the cell ($D_x = 1.35$ g/cm³, $D_m = 1.31$ g/cm³). 3548 observed reflections were recorded on an automatic fourcircle diffractometer at $ca. -150^\circ\text{C}$ ($2\theta_{\text{max}} = 50^\circ$, MoK α -radiation). No corrections for absorption or secondary extinction were made (crystal size $0.3 \times 0.2 \times 0.4$ mm).

The structure was solved by direct methods⁴ and refined by full-matrix least squares technique.^{5*} Weights in least squares were obtained from the standard deviations in intensities, $\sigma(I)$, taken as $\sigma(I) = [C_T + (0.02 C_N)^2]^{1/2}$ where C_T is the total number of counts, and C_N the net count. Methyl hydrogen atom positions were not determined. Anisotropic temperature factors were introduced for all non-hydrogen atoms. The final R -value was 4.2% ($R_w = 4.3\%$) for 3548 observed reflections. The maximum r.m.s. amplitudes ranged from 0.22 to 0.53 Å for the tetrafluoroborate anion, while the others lay between 0.17 and 0.24 Å.

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

Table 1. Final fractional coordinates with estimated standard deviations. Hn1 and Hn2 are bonded to Cn. Hn is bonded to Cn in the benzene ring.

ATOM	X	Y	Z
O1	.17916(17)	.74153(11)	.76549(10)
C1	.28834(27)	.07429(18)	.79767(17)
C2	.27039(27)	.06953(18)	.91297(17)
O2	.14998(17)	.15017(11)	.94122(10)
C3	.11823(26)	.13928(18)	1.05089(16)
C4	.09737(27)	.13279(18)	1.07935(16)
O3	-.15413(17)	.22783(11)	1.04671(10)
C5	-.27592(29)	.28737(18)	1.10487(16)
C6	-.43860(28)	.29206(18)	1.06078(16)
O4	-.47656(17)	.35373(11)	.96040(10)
C7	-.53466(26)	.38418(17)	.92251(16)
C8	-.55830(27)	.43452(17)	.81154(16)
O5	-.50896(18)	.35179(11)	.75154(10)
C9	-.46851(26)	.39082(16)	.64466(15)
C10	-.47977(25)	.30334(16)	.58432(15)
O6	-.36358(17)	.21444(11)	.61809(10)
C11	-.37342(25)	.12473(16)	.56579(16)
C12	-.27327(26)	.03062(16)	.61735(16)
O7	-.19547(17)	.05774(10)	.61671(10)
C13	.00250(28)	-.13469(16)	.64421(16)
C14	.16324(27)	.00178(17)	.66827(16)
N1	-.23877(25)	.14345(16)	.84829(15)
N2	-.17054(23)	.21257(15)	.80716(14)
C15	-.09665(25)	.30039(16)	.75425(16)
C16	-.17294(26)	.39558(17)	.79614(16)
C17	-.02712(26)	.48399(16)	.74100(16)
C18	.06317(26)	.47477(16)	.64615(15)
C19	.07803(25)	.37672(16)	.60670(15)
C20	.00171(26)	.28353(16)	.65938(16)
O8	.14102(17)	.55579(11)	.53533(10)
C21	.12579(28)	.66145(17)	.61643(18)
B	.35085(35)	.26953(21)	.33313(21)
F1	.26370(16)	.22642(10)	.42763(9)
F2	.49394(19)	.18824(15)	.31840(13)
F3	.41117(34)	.35899(14)	.33279(15)
F4	.24912(17)	.26575(13)	.25327(10)
H211	.0049(25)	.6956(16)	.6357(15)
H212	.1974(27)	.6435(17)	.6776(16)
H213	.1733(27)	.7967(17)	.5587(17)
H11	.3125(24)	.1451(17)	.7645(16)
H12	.3833(23)	.0214(15)	.7731(14)
H21	.3819(24)	.0813(16)	.9328(15)
H22	.2360(25)	-.0034(16)	.7455(15)
H31	.2250(25)	.1737(16)	1.0832(15)
H32	.0653(25)	.0796(16)	1.0731(15)
H41	.0573(23)	.3032(15)	1.0437(14)
H42	.0017(24)	.2322(15)	1.1560(15)
H51	-.2363(24)	.3627(15)	1.1016(15)
H52	-.2830(24)	.2524(16)	1.1775(15)
H61	-.5261(26)	.3274(17)	1.1053(16)
H62	-.4710(25)	.2132(16)	1.0570(15)
H71	-.6477(27)	.4361(15)	.9663(14)
H72	-.6516(24)	.3173(15)	.9275(15)
H81	-.4734(24)	.4833(15)	.9030(15)
H82	-.6661(25)	.4722(16)	.7902(15)
H91	-.3549(21)	.4212(13)	.6325(13)
H92	-.5486(23)	.4508(15)	.6125(14)
H101	-.4567(23)	.3289(15)	.5086(14)
H102	-.5972(24)	.2740(15)	.5977(14)
H111	-.3291(24)	.1435(15)	.4913(14)
H112	-.4928(23)	.1037(15)	.5706(14)
H121	-.2787(23)	-.0341(14)	.5727(14)
H122	-.3199(23)	.0099(14)	.6917(14)
H131	.0237(24)	-.0732(15)	.5858(15)
H132	-.0502(24)	-.0307(15)	.7068(15)
H141	.2034(22)	.0695(14)	.6116(13)
H142	.2494(24)	-.0538(16)	.6736(15)
H16	-.1672(25)	.3974(16)	.3612(16)
H17	-.0387(24)	.5522(16)	.7667(15)
H19	.1438(24)	.3740(16)	.5416(15)
H20	.0045(26)	.2719(17)	.6322(16)

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

DISTANCE	(Å)	DISTANCE	(Å)
O1 - C1	1.421(3)	O1 - C14	1.424(2)
C1 - C2	1.495(3)	C2 - O2	1.421(3)
O2 - C3	1.422(2)	C3 - C4	1.493(3)
C4 - O3	1.422(3)	O3 - C5	1.423(3)
C5 - C6	1.436(3)	C6 - O4	1.417(3)
O4 - C7	1.427(3)	C7 - C8	1.495(3)
C8 - O5	1.414(2)	O5 - C9	1.424(2)
C9 - C10	1.493(3)	C10 - O6	1.425(2)
O6 - C11	1.422(2)	C11 - C12	1.493(3)
C12 - O7	1.422(2)	O7 - C13	1.425(2)
C13 - C14	1.491(3)	N1 - N2	1.099(2)
N2 - C15	1.389(3)	C15 - C16	1.385(3)
C15 - C20	1.394(3)	C16 - C17	1.375(3)
C17 - C18	1.396(3)	C13 - C19	1.403(3)
C19 - C20	1.365(3)	O8 - C21	1.440(3)
B - F1	1.367(3)	B - F2	1.372(3)
B - F3	1.353(3)	B - F4	1.374(3)

ANGLE	(°)	ANGLE	(°)
O1 - C1 - C2	108.9(2)	C1 - O1 - C14	112.9(2)
O1 - C14 - C13	108.7(2)	C1 - C2 - O2	109.9(2)
C2 - O2 - C3	110.8(2)	O2 - C3 - C4	110.2(2)
C3 - C4 - O3	110.4(2)	C4 - O3 - C5	111.0(2)
O3 - C5 - C6	109.9(2)	C5 - C6 - O4	103.9(2)
C6 - O4 - C7	112.6(2)	O4 - C7 - C8	108.5(2)
C7 - C8 - O5	108.0(2)	C8 - O5 - C9	112.3(2)
O5 - C9 - C10	108.2(2)	C9 - C10 - O6	109.3(2)
C10 - O6 - C11	111.7(2)	O6 - C11 - C12	109.5(2)
C11 - C12 - O7	109.5(2)	C12 - O7 - C13	111.9(2)
O7 - C13 - C14	108.9(2)	N1 - N2 - C15	179.2(2)
N2 - C15 - C16	118.0(2)	N2 - C15 - C20	117.9(2)
C15 - C16 - C17	118.0(2)	C16 - C15 - C20	124.9(2)
C15 - C20 - C19	117.1(2)	C16 - C17 - C18	119.5(2)
C17 - C18 - C19	120.8(2)	C17 - C18 - O8	124.5(2)
C18 - C19 - C20	120.5(2)	C19 - C18 - O8	114.2(2)
C18 - O8 - C21	119.0(2)	F1 - B - F2	109.0(2)
F1 - B - F3	110.7(2)	F1 - B - F4	110.0(2)
F2 - B - F3	108.2(2)	F2 - B - F4	109.4(2)
F3 - B - F4	109.4(2)		

DIHEDRAL ANGLE	(°)
C14 - O1 - C1 - C2	-156.3(2)
O1 - C1 - C2 - O2	-68.0(2)
C1 - C2 - O2 - C3	173.9(2)
C2 - O2 - C3 - C4	173.2(2)
O2 - C3 - C4 - O3	67.4(2)
C3 - C4 - O3 - C5	158.0(2)
C4 - O3 - C5 - C6	173.3(2)
O3 - C5 - C6 - O4	-66.3(2)
C5 - C6 - O4 - C7	-165.9(2)
C6 - O4 - C7 - C8	-172.1(2)
O4 - C7 - C8 - O5	74.0(2)
C7 - C8 - O5 - C9	-175.8(2)
C8 - O5 - C9 - C10	-159.5(2)
O5 - C9 - C10 - O6	-60.9(2)
C9 - C10 - O6 - C11	177.8(2)
C10 - O6 - C11 - C12	-169.6(2)
O6 - C11 - C12 - O7	-58.1(2)
C11 - C12 - O7 - C13	-167.9(2)
C12 - O7 - C13 - C14	-165.2(2)
O7 - C13 - C14 - O1	72.3(2)
C13 - C14 - O1 - C1	177.6(2)

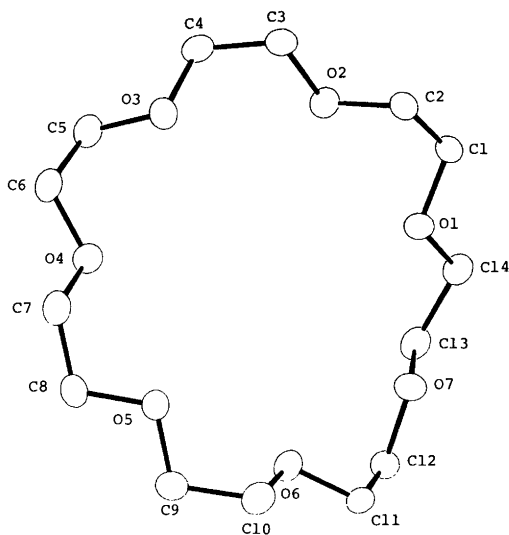


Fig. 1. Schematic drawing of the cyclic heptaether.

Final fractional coordinates with estimated standard deviations are listed in Table 1. Bond distances and angles and dihedral angles may be found in Table 2.

Fig. 1 is a schematic drawing illustrating the ring conformation. The torsional angles of Table 2 show that the 21-membered ring has a non-angular conformation, which may be obtained through ring expansion of the D_{3d} conformation observed for the cyclic hexaether in some complexes of 18-crown-6.⁶

From the stereoscopic view of the complex (Fig. 2) it may be seen that the $-\overset{+}{N}2 \equiv N1$ group actually

penetrates the ring. The seven other oxygen atoms are far from coplanar. Deviations from the least squares plane are:

$D(O_n)$ (Å)	$n =$	1	2	3	4
	$=$	-0.02	-0.48	0.44	0.09
		5	6	7	
		-0.30	-0.07	0.33	

The nitrogen atom distances from this plane are 0.91 Å and -0.20 Å for N1 and N2, respectively. Nitrogen oxygen distances are:

$N1-O_n$ (Å)	$n =$	1	2	3	4
	$=$	3.371	3.481	3.102	3.415
$N2-O_n$ (Å)	$=$	3.243	3.248	3.187	3.355
		5	6	7	
		3.455	3.245	3.433	
		3.223	3.046	3.382	

It is clear that the crown's hole generously accommodates the diazonium group, whose cylindrical diameter may be estimated to about 2.4 Å.¹ In fact, none of the N-O contacts may be characterized as "short due to strong interactions". It is not clearly understood why the present complex should be more stable than that of the 18-crown-6, where the ring would be expected to enclose more tightly the rod-like cation.

Bond distances and angles of Table 2 have normal values within estimated limits of error.

Lists of thermal parameters and observed and calculated structure factors are available from the author.

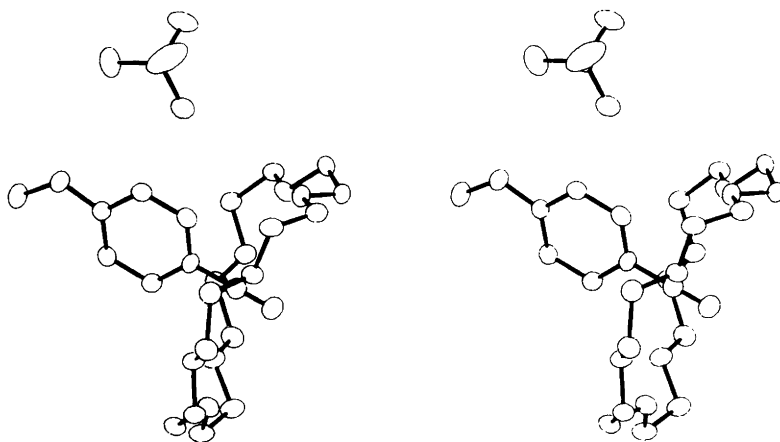


Fig. 2. Stereoscopic view of the complex.

Acknowledgement. The author thanks Dr. J. Krane for preparing the crystals.

1. Gokel, G. W. and Cram, D. J. *Chem. Commun.* (1973) 481.
2. Krane, J. *Personal communication.*
3. Haymore, B. L. and Hoffman, J. C. *Presented at Fourth Symposium on Macrocyclic Compounds, Provo, Utah, August 1980.*
4. Germain, G., Main, P. and Woolfson, M. M. *Acta Crystallogr. A* 27 (1971) 368.
5. Groth, P. *Acta Chem. Scand.* 27 (1973) 3131.
6. Dunitz, J. D., Dobler, M., Seiler, P. and Phizackerley, R. P. *Acta Crystallogr. B* 30 (1974) 2733.

Received May 26, 1981.