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The Structure of Benzo-15-crown-5 (6,7,9,10,12,13,15,16-Octahydrobenzo[1,4,7,10,13]pentaoxacyclopentadecin) at −150° C

BY I. R. HANSON

Molecular Structures Department, Rothamsted Experimental Station, Harpenden, Hertfordshire AL5 2JQ, England

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Abstract. $C_{14}H_{20}O_5$, $M_r = 268 \cdot 4$, orthorhombic, *Pbca*, $a = 20 \cdot 111$ (4), $b = 16 \cdot 515$ (3), $c = 8 \cdot 354$ (2) Å, $U = 2774 \cdot 6$ Å^3 (at −150°C), λ(Mo $K\alpha$) = 0·71069 Å, $Z = 8$, $D_m = 1 \cdot 234$ (20°C), $D_c = 1 \cdot 285$ g cm^{-3} (−150°C), μ(Cu $K\alpha$) = 7·66 cm^{-1}, $F(000) = 1152$. The structure was solved by direct methods from observations collected photographically and measured by a microdensitometer. Full-matrix refinement reduced R to 0·053 for 1134 reflections.

Introduction. The crystal structures of several complexes of benzo-15-crown-5 with cations have been determined (Bush & Truter, 1972; Mallinson & Truter, 1972; Owen & Wingfield, 1976; Cradwick & Poonia, 1977) and one compound crystallized with a hydrated molecule of benzo-15-crown-5 of solvation (Cradwick & Poonia, 1977). These coordinated molecules all have different conformations of the macrocyclic ether. For comparison we have determined the structure of the unsolvated molecule crystallized from cyclohexane and hexanol by Poonia (1975) and subsequently, to give crystals large enough for the present work, from methylene dichloride/carbon tetrachloride by Wingfield (1976).

The crystals were colourless plates and one, 0·275 × 0·45 × 0·45 mm, was mounted in turn about the c and b axes and cooled in a stream of nitrogen gas. Equi-inclination Weissenberg photographs were taken with Ni-filtered Cu $K\alpha$ radiation for $h0l$–$h2l$ and $hk0$–$hk5$.

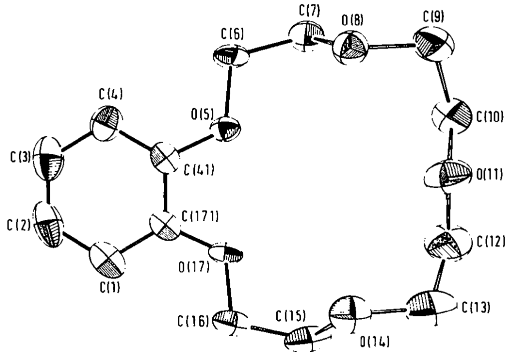

Fig. 1. An *ORTEP* drawing showing the numbering of the C and O atoms and their ellipsoids of vibration at the 50% probability level. H atoms are designated with the same numbers as the corresponding C atoms; those in methylene groups are distinguished by *A* and *B*.

Table 1. *Fractional coordinates* (×10^4) *and vibration parameters*

For hydrogen atoms U_{iso} is shown (×10^3 Å^2); for carbon and oxygen the anisotropic parameters have been deposited (see footnote on p. 1027).

	x	y	z	U_{iso}
C(1)	1141 (2)	2771 (3)	5524 (6)	–
H(1)	1218 (24)	2250 (33)	6036 (63)	67 (15)
C(2)	501 (3)	3096 (4)	5381 (8)	–
H(2)	174 (27)	2855 (33)	5855 (65)	70 (17)
C(3)	387 (3)	3790 (4)	4602 (8)	–
H(3)	−16 (29)	3999 (32)	4561 (65)	70 (17)
C(4)	903 (2)	4217 (3)	3910 (6)	–
H(4)	812 (21)	4804 (29)	3381 (57)	56 (14)
C(41)	1547 (2)	3917 (2)	4051 (5)	–
C(171)	1665 (2)	3186 (2)	4831 (5)	–
O(5)	2101 (1)	4287 (2)	3454 (4)	–
C(6)	2046 (2)	5114 (3)	2962 (7)	–
H*A*(6)	1731 (23)	5169 (28)	2017 (65)	61 (14)
H*B*(6)	1836 (19)	5420 (25)	3772 (52)	32 (12)
C(7)	2724 (2)	5415 (3)	2624 (6)	–
H*A*(7)	2706 (18)	5933 (27)	2116 (53)	44 (12)
H*B*(7)	2953 (20)	5028 (27)	1921 (51)	41 (12)
O(8)	3078 (1)	5497 (2)	4090 (4)	–
C(9)	3776 (3)	5615 (3)	3893 (8)	–
H*A*(9)	3839 (18)	5984 (25)	3035 (51)	35 (12)
H*B*(9)	3920 (24)	5902 (31)	4888 (66)	65 (17)
C(10)	4149 (2)	4842 (3)	3706 (7)	–
H*A*(10)	4616 (21)	5031 (26)	3403 (49)	44 (12)
H*B*(10)	3984 (19)	4465 (26)	2717 (59)	46 (13)
O(11)	4104 (2)	4409 (2)	5158 (4)	–
C(12)	4323 (3)	3609 (3)	5020 (8)	–
H*A*(12)	3997 (26)	3283 (33)	4160 (66)	72 (17)
H*B*(12)	4860 (24)	3615 (29)	4673 (57)	62 (13)
C(13)	4154 (3)	3160 (3)	6520 (7)	–
H*A*(13)	4312 (22)	3562 (33)	7507 (72)	69 (15)
H*B*(13)	4431 (23)	2640 (29)	6522 (55)	51 (13)
O(14)	3475 (2)	2979 (2)	6773 (4)	–
C(15)	3233 (3)	2286 (3)	5945 (8)	–
H*A*(15)	3467 (23)	2193 (32)	4964 (77)	62 (17)
H*B*(15)	3336 (24)	1785 (32)	6492 (65)	66 (15)
C(16)	2498 (3)	2311 (3)	5922 (6)	–
H*A*(16)	2281 (23)	2375 (29)	6896 (67)	55 (16)
H*B*(16)	2315 (21)	1845 (27)	5527 (57)	45 (13)
O(17)	2314 (1)	2955 (2)	4877 (3)	–

Intensities were measured by the SRC Microdensitometer Service. Lp corrections and interlayer scaling (Hamilton, Rollett & Sparks, 1965) were applied (Owen, 1975). Accurate unit-cell dimensions were obtained from 25 reflections on a CAD-4 diffractometer with Mo *Kα* radiation, the crystal being cooled in a nitrogen gas stream. The structure was solved by *SHELX* (Sheldrick, 1976) from 395 *E* values and the first map showed all but two of the non-hydrogen atoms; the numbering scheme is shown in Fig. 1. The H atoms were located in a difference electron density map and their inclusion reduced *R* to 0·076. Full-matrix refinement with isotropic parameters for H atoms and anisotropic values for the others was carried out by the program *SHELX*. Scattering factors were taken from Cromer & Mann (1968). The weighting scheme was $w = 2{\cdot}59/\sigma_F^2$ where $\sigma_F^2 = 2{\cdot}48 - 0{\cdot}083|F_o| + 0{\cdot}00372|F_o|^2$ and *R'* was 0·069. Final parameters are in Table 1.*

Discussion. Bond lengths and angles and their standard deviations calculated by *SHELX* are in Table 2, the torsion angles in the macrocyclic ring in Table 3, and the mean planes through the benzene ring and the O atoms in Table 4.

There are no significant differences between the bond lengths and angles of this molecule and any of the coordinated ones. Even at −150°C the atoms have significant mean-square amplitudes of vibration (Fig. 1 and Table 1) so the possibility that the apparent shortening of the C–C bonds is due to libration has not been eliminated; Goldberg (1975) found it to persist in a low-temperature investigation of a more favourable complex of 18-crown-6 which showed small vibrational amplitudes. The torsion angles are different from any found hitherto and show an approximate plane of symmetry through O(11) and the midpoints of C(41)–C(171) and C(2)–C(3).

The C–H bond lengths as refined are, as usual, shorter than those obtained by neutron diffraction; the mean C_{sp^2}–H is 0·95 Å and the mean C_{sp^3}–H is 1·005 Å; the difference, although in the expected direction, is not statistically significant. Angles involving H atoms are not reported; for H–C–H the standard deviation is 3·5° and for O–C–H and C–C–H it is 2·5°.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33209 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Bond lengths* (Å) *and bond angles* (°)

C(1)–C(2)	1·399 (8)	C(41)–O(5)	1·366 (5)	C(1)–H(1)	0·97 (5)	C(10)–H*A*(10)	1·02 (4)
C(1)–C(171)	1·385 (6)	C(171)–O(17)	1·360 (5)	C(2)–H(2)	0·87 (6)	C(10)–H*B*(10)	1·09 (5)
C(2)–C(3)	1·337 (9)	C(6)–O(5)	1·431 (5)	C(3)–H(3)	0·88 (6)	C(12)–H*A*(12)	1·11 (6)
C(3)–C(4)	1·381 (7)	C(7)–O(8)	1·423 (6)	C(4)–H(4)	1·08 (5)	C(12)–H*B*(12)	1·12 (5)
C(4)–C(41)	1·392 (6)	C(9)–O(8)	1·427 (6)	C(6)–H*A*(6)	1·02 (5)	C(13)–H*A*(13)	1·10 (6)
C(41)–C(171)	1·392 (6)	C(10)–O(11)	1·411 (6)	C(6)–H*B*(6)	0·94 (4)	C(13)–H*B*(13)	1·02 (5)
		C(12)–O(11)	1·398 (6)	C(7)–H*A*(7)	0·96 (5)	C(15)–H*A*(15)	0·96 (6)
C(6)–C(7)	1·478 (6)	C(13)–O(14)	1·414 (6)	C(7)–H*B*(7)	0·98 (5)	C(15)–H*B*(15)	0·97 (5)
C(9)–C(10)	1·489 (7)	C(15)–O(14)	1·423 (6)	C(9)–H*A*(9)	0·95 (4)	C(16)–H*A*(16)	0·93 (5)
C(12)–C(13)	1·495 (8)	C(16)–O(17)	1·425 (5)	C(9)–H*B*(9)	1·00 (5)	C(16)–H*B*(16)	0·91 (5)
C(15)–C(16)	1·479 (8)						
Average	1·485						

C(2)–C(1)–C(171)	118·3 (5)	O(5)–C(41)–C(171)	114·8 (4)	C(10)–O(11)–C(12)	112·8 (4)
C(3)–C(2)–C(1)	121·9 (5)	O(5)–C(41)–C(4)	124·7 (4)	O(11)–C(12)–C(13)	109·1 (5)
C(4)–C(3)–C(2)	120·9 (5)	C(41)–O(5)–C(6)	117·9 (3)	C(12)–C(13)–O(14)	116·7 (5)
C(41)–C(4)–C(3)	118·7 (5)	O(5)–C(6)–C(7)	107·7 (4)	C(13)–O(14)–C(15)	115·3 (4)
C(171)–C(41)–C(4)	120·5 (4)	C(6)–C(7)–O(8)	109·2 (4)	O(14)–C(15)–C(16)	109·0 (4)
C(41)–C(171)–C(1)	119·7 (4)	C(7)–O(8)–C(9)	114·0 (4)	C(15)–C(16)–O(17)	106·8 (4)
O(17)–C(171)–C(41)	114·9 (3)	O(8)–C(9)–C(10)	113·0 (4)	C(16)–O(17)–C(171)	118·5 (3)
O(17)–C(171)–C(1)	125·4 (4)	C(9)–C(10)–O(11)	108·1 (4)		

Table 3. *Torsion angles* (°) *in the macrocyclic ring* (*estimated standard deviations are about* 0·4°)

O(17)–C(171)–C(41)–O(5)	0		
C(171)–C(41)–O(5)–C(6)	−166	C(16)–O(17)–C(171)–C(41)	−167
C(41)–O(5)–C(6)–C(7)	171	C(15)–C(16)–O(17)–C(171)	−170
O(5)–C(6)–C(7)–O(8)	−71	O(14)–C(15)–C(16)–O(17)	70
C(6)–C(7)–O(8)–C(9)	167	C(13)–O(14)–C(15)–C(16)	−163
C(7)–O(8)–C(9)–C(10)	−85	C(12)–C(13)–O(14)–C(15)	81
O(8)–C(9)–C(10)–O(11)	−66	O(11)–C(12)–C(13)–O(14)	72
C(9)–C(10)–O(11)–C(12)	168	C(10)–O(11)–C(12)–C(13)	−171

Table 4. *Mean planes through groups of atoms and deviations* (Å) *of atoms from the planes*

Designations in italics are of atoms excluded from the calculation of the plane.

Plane *A* (benzene ring)

$$-0{\cdot}1294x - 0{\cdot}5045y - 0{\cdot}8536z + 6{\cdot}5428 = 0$$

C(1)	−0·002 (5)	C(2)	−0·005 (6)
C(3)	0·002 (7)	C(4)	0·006 (5)
C(41)	−0·012 (4)	C(171)	0·010 (4)
O(5)	*−0·039* (*3*)	*O(17)*	*0·001* (*3*)

Plane *B* (O atoms)

$$0{\cdot}3868x - 0{\cdot}3085y - 0{\cdot}8399z + 3{\cdot}6020 = 0$$

O(5)	0·119 (3)	O(8)	−0·328 (3)
O(11)	0·405 (3)	O(14)	−0·320 (3)
O(17)	0·123 (3)		

Plane *A*/Plane *B* 31°

Table 5. *Intermolecular distances* (Å) *for X*···*X less than* 3·5 Å *and X*··· H *less than or equal to* 3·0 Å

		A → *B*	*B* → *A*
C(1)···H*A*(9)	2·94	(I)	(II)
C(2)···H*A*(9)	3·00	(I)	(II)
C(2)···H*B*(13)	2·94	(IX)	(VIII)
C(41)···H*A*(7)	2·98	(I)	(II)
C(171)···H*A*(7)	2·71	(I)	(II)
C(17)···H*A*(16)	2·90	(IV)	(III)
O(5)···C(16)	3·47	(IV)	(III)
O(8)···C(6)	3·40	(I)	(II)
O(8)···H*A*(6)	2·71	(I)	(II)
O(8)···H*B*(16)	2·65	(VI)	(VII)
O(11)···H(4)	3·00	(I)	(II)
O(11)···C(6)	3·38	(I)	(II)
O(11)···H*A*(6)	2·39	(I)	(II)
O(11)···H*A*(10)	2·99	(V)	(V)
O(14)···C(6)	3·46	(I)	(II)
O(14)···H*A*(7)	2·99	(I)	(II)
O(14)···H*A*(15)	2·68	(III)	(IV)
O(17)···H*A*(7)	2·62	(I)	(II)
O(17)···C(16)	3·25	(IV)	(III)
O(17)···H*A*(16)	2·55	(IV)	(III)

Roman numerals refer to the following equivalent positions relative to the coordinates in Table 1 at *x*,*y*,*z*

(I)	$\frac{1}{2}-x$,	$1-y$,	$\frac{1}{2}+z$	(VI)	$\frac{1}{2}-x$,	$\frac{1}{2}+y$,	z
(II)	$\frac{1}{2}-x$,	$1-y$,	$-\frac{1}{2}+z$	(VII)	$\frac{1}{2}-x$,	$-\frac{1}{2}+y$,	z
(III)	x,	$\frac{1}{2}-y$,	$\frac{1}{2}+z$	(VIII)	$\frac{1}{2}+x$,	$\frac{1}{2}-y$,	$1-z$
(IV)	x,	$\frac{1}{2}-y$,	$-\frac{1}{2}+z$	(IX)	$-\frac{1}{2}+x$,	$\frac{1}{2}-y$,	$1-z$
(V)	$1-x$,	$1-y$,	$1-z$	(X)	$\frac{1}{2}+x$,	y,	$\frac{1}{2}-z$

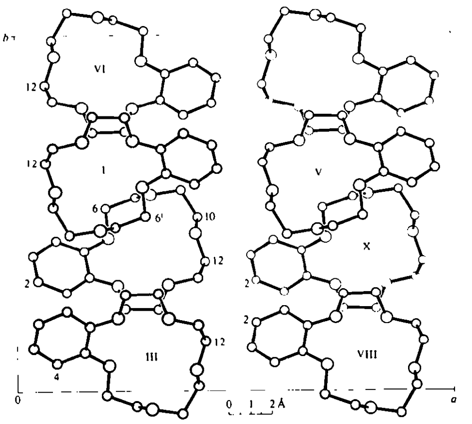

Fig. 2. The structure projected down the *c* axis. The designations of certain atoms are shown as numbers only. Molecules are identified by Roman numerals (as defined in Table 5). Molecules in relations (II) and (IV) are beneath (I) and (III) respectively, while (VII) and (IX) are outside the unit cell shown.

From the packing diagram (Fig. 2) the reason for ready cleavage perpendicular to the *a* axis is clear; shortest contacts are 2·5 Å between H*A*(13) and H(2^{VIII}) and 2·61–2·65 Å for H*B*(13) and H(2^{VIII}) and H(2^{X}). Other intermolecular contacts are given in Table 5. There are no intermolecular H···H contacts less than 2·4 Å. In the *bc* plane the most significant contacts are C—H···O ones; the shortest (2·37 Å) with C(6)—H*A*(6)···O(11^{II}) 166° is comparable with those, 2·32 and 2·49 Å, holding the dimethyl acetylenedicarboxylate ester to 18-crown-6 (Goldberg, 1975); for the other four such contacts in the range 2·55 to 2·68 Å the angles at H range from 145 to 172°. The benzene rings are not stacked parallel; H(1) is approximately equidistant from C(4), C(41) and C(171) of molecule (III).

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