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

W–Cl(1)	2·451 (2)	W–Cl(2)	2·349 (2)
W–Cl(3)	2·347 (2)	W–Cl(4)	2·345 (3)
W–Cl(5)	2·345 (2)	W–N	1·741 (4)
N–C(1)	1·365 (8)	C(1)–C(2)	1·390 (13)
C(1)–C(6)	1·387 (10)	C(2)–C(3)	1·346 (13)
C(3)–C(4)	1·399 (13)	C(4)–C(5)	1·363 (17)
C(4)–C(7)	1·481 (14)	C(5)–C(6)	1·380 (13)
P–C(11)	1·790 (4)	P–C(21)	1·793 (4)
P–C(31)	1·776 (4)	P–C(41)	1·822 (5)
C(41)–C(42)	1·494 (6)		
Cl(1)–W–Cl(2)	85·8 (1)	Cl(1)–W–Cl(3)	87·1 (1)
Cl(2)–W–Cl(3)	89·8 (1)	Cl(1)–W–Cl(4)	87·4 (1)
Cl(2)–W–Cl(4)	173·1 (1)	Cl(3)–W–Cl(4)	88·4 (1)
Cl(1)–W–Cl(5)	85·4 (1)	Cl(2)–W–Cl(5)	90·6 (1)
Cl(3)–W–Cl(5)	172·4 (1)	Cl(4)–W–Cl(5)	90·3 (1)
Cl(1)–W–N	174·8 (2)	Cl(2)–W–N	90·9 (2)
Cl(3)–W–N	97·0 (2)	Cl(4)–W–N	95·9 (2)
Cl(5)–W–N	90·6 (2)	W–N–C(1)	170·8 (5)
N–C(1)–C(2)	121·3 (6)	N–C(1)–C(6)	120·4 (8)
C(2)–C(1)–C(6)	118·2 (7)	C(1)–C(2)–C(3)	122·8 (8)
C(2)–C(3)–C(4)	119·0 (10)	C(3)–C(4)–C(5)	118·6 (8)
C(3)–C(4)–C(7)	120·0 (10)	C(5)–C(4)–C(7)	121·4 (9)
C(4)–C(5)–C(6)	122·7 (9)	C(1)–C(6)–C(5)	118·5 (9)
C(11)–P–C(21)	107·3 (2)	C(11)–P–C(31)	110·6 (2)
C(21)–P–C(31)	109·2 (2)	C(11)–P–C(41)	111·3 (2)
C(21)–P–C(41)	109·9 (2)	C(31)–P–C(41)	108·5 (2)
P–C(11)–C(12)	120·5 (1)	P–C(11)–C(16)	119·4 (1)
P–C(21)–C(22)	121·4 (1)	P–C(21)–C(26)	118·5 (1)
P–C(31)–C(32)	120·2 (1)	P–C(31)–C(36)	119·4 (1)
P–C(41)–C(42)	112·0 (4)	C(41)–C(42)–C(43)	120·2 (2)
C(41)–C(42)–C(47)	119·8 (2)		

reported by Bradley, Errington, Hursthouse, Short, Ashcroft, Clark, Nielson & Rickard (1987); it suffered from disorder in both the solvent molecules and the *p*-tolyl substituent, giving results consistent with, but less precise than, those presented here.

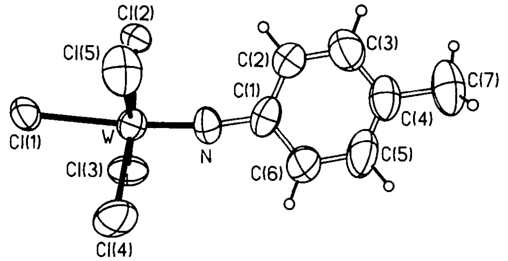

Fig. 1. Structure of the anion, with the atom-numbering scheme. Thermal motion is shown by ellipsoids at the 40% probability level.

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References

Bradley, D. C., Errington, R. J., Hursthouse, M. B., Short, R. L., Ashcroft, B. R., Clark, G. R., Nielson, A. J. & Rickard, C. E. F. (1987). *J. Chem. Soc. Dalton Trans.* pp. 2067–2075.

Clegg, W. (1981). *Acta Cryst.* A**37**, 22–28.

Hong, W. & Robertson, B. E. (1985). *Structure & Statistics in Crystallography*, edited by A. J. C. Wilson, pp. 125–136. New York: Adenine Press.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 99, 149. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Sheldrick, G. M. (1985). *SHELXTL. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data,* revision 5. Univ. of Göttingen, Federal Republic of Germany.

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Reinvestigation of the Structure of Dibenzo-12-crown-4 Ether*

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Abstract. $C_{16}H_{16}O_4$, $M_r = 272{\cdot}30$, orthorhombic, *Pbca*, $a = 6{\cdot}9774\,(2)$, $b = 13{\cdot}0730\,(3)$, $c = 14{\cdot}6363\,(3)$ Å, $V = 1335{\cdot}06$ Å^3, $Z = 4$, $D_x = 1{\cdot}355$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\bar{\alpha}) = 1{\cdot}54178$ Å, $\mu = 0{\cdot}076$ cm^{-1}, $F(000) = 576$, room temperature, $R = 0{\cdot}038$ for all 1400 unique reflections. The structure of 6,7,14,15-tetrahydrodibenzo[*b,h*]-[1,4,7,10]tetraoxacyclododecin (dibenzo-12-crown-4 ether) was redetermined in order to provide more complete and reliable data for structural comparison purposes. In addition to better residuals, this reinvestigation has yielded more precise structural parameters (C—C and C—O bond-length and -angle e.s.d.'s 0·0017 Å, 0·1°, and C—H bond-length and -angle e.s.d.'s of 0·02 Å, 1°) than the previous results of Hughes & Nowell [*J. Chem. Res.* (*M*) (1978), pp. 1534–1556] ($R = 0{\cdot}086$, C—C and C—O bond-length and -angle e.s.d.'s of 0·004 Å, 0·3° and C—H bond-length and -angle e.s.d.'s of 0·03 Å, 2°). The molecule

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Table 1. *Atomic parameters and B_{iso} values* (Å^2)

E.s.d.'s. refer to the last digit printed. B_{iso} is the mean of the principal axes of the thermal ellipsoid.

	x	y	z	B_{iso}
O1	0·22827 (15)	0·53695 (5)	0·50955 (6)	3·74 (4)
O2	0·02387 (14)	0·46679 (6)	0·35527 (6)	3·63 (4)
C1	−0·21548 (17)	0·37667 (8)	0·43880 (7)	2·99 (4)
C2	−0·08001 (19)	0·37825 (8)	0·36844 (8)	3·01 (4)
C3	−0·05578 (21)	0·29301 (10)	0·31351 (9)	3·78 (5)
C4	−0·16463 (24)	0·20540 (10)	0·32846 (10)	4·23 (5)
C5	−0·29954 (22)	0·20371 (10)	0·39742 (11)	4·16 (5)
C6	−0·32556 (21)	0·28918 (9)	0·45246 (10)	3·67 (5)
C7	0·22787 (20)	0·45739 (11)	0·36514 (9)	3·72 (5)
C8	0·30039 (20)	0·54686 (10)	0·41857 (9)	3·62 (5)
H3	0·043 (3)	0·2960 (10)	0·2655 (12)	4·1 (3)
H4	−0·1394 (23)	0·1473 (12)	0·2909 (12)	4·3 (3)
H5	−0·375 (3)	0·1416 (15)	0·4067 (12)	5·0 (4)
H6	−0·416 (3)	0·2891 (11)	0·5008 (13)	4·9 (4)
H71	0·287 (3)	0·4596 (11)	0·3049 (12)	4·4 (3)
H72	0·261 (3)	0·3909 (13)	0·3962 (11)	4·3 (3)
H81	0·434 (3)	0·5456 (12)	0·4178 (11)	3·9 (3)
H82	0·2509 (22)	0·6162 (11)	0·3917 (10)	3·0 (3)

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

O1—C8	1·4295 (15)	C4—H4	0·954 (17)
O2—C2	1·3793 (15)	C5—C6	1·3894 (20)
O2—C7	1·4359 (17)	C5—H5	0·977 (20)
C1—O1′	1·3619 (13)	C6—H6	0·948 (21)
C1—C2	1·3980 (17)	C7—C8	1·4952 (19)
C1—C6	1·3921 (17)	C7—H71	0·975 (18)
C2—C3	1·3844 (17)	C7—H72	1·007 (17)
C3—C4	1·3915 (21)	C8—H81	0·931 (19)
C3—H3	0·982 (18)	C8—H82	1·046 (15)
C4—C5	1·380 (3)		
C1′—O1—C8	117·71 (9)	C6—C5—H5	121·2 (11)
C2—O2—C7	115·79 (9)	C1—C6—C5	120·35 (14)
O1′—C1—C2	116·16 (10)	C1—C6—H6	118·4 (9)
O1′—C1—C6	124·43 (11)	C5—C6—H6	121·2 (9)
C2—C1—C6	119·41 (11)	O2—C7—C8	108·73 (10)
O2—C2—C1	118·08 (10)	O2—C7—H71	109·2 (11)
O2—C2—C3	122·02 (12)	O2—C7—H72	110·4 (11)
C1—C2—C3	119·89 (11)	C8—C7—H71	107·8 (9)
C2—C3—C4	120·30 (14)	C8—C7—H72	111·2 (10)
C2—C3—H3	117·9 (8)	H71—C7—H72	109·5 (13)
C4—C3—H3	121·7 (8)	O1—C8—C7	107·29 (10)
C3—C4—C5	120·02 (12)	O1—C8—H81	111·2 (10)
C3—C4—H4	117·6 (10)	O1—C8—H82	108·2 (8)
C5—C4—H4	122·3 (10)	C7—C8—H81	108·6 (10)
C4—C5—C6	120·01 (13)	C7—C8—H82	111·7 (8)
C4—C5—H5	118·9 (11)	H81—C8—H82	109·9 (13)
C1′—O1—C8—C7	−157·1 (1)	C8—O1—C1′—C2′	155·1 (1)
C8—O1—C1′—C6′	−24·3 (1)	C7—O2—C2—C1	119·4 (1)
C7—O2—C2—C3	−61·7 (1)	C2—O2—C7—C8	−136·8 (1)
C6—C1—C2—O2	178·6 (1)	C6—C1—C2—C3	−0·4 (1)
O1′—C1—C2—O2	−2·0 (1)	O1′—C1—C2—C3	179·1 (2)
C2—C1—C6—C5	0·8 (1)	O1′—C1—C6—C5	−178·6 (2)
C2—C1—O1′—C8′	−155·1 (1)	C6—C1—O1′—C8′	24·3 (1)
O2—C2—C3—C4	−179·4 (2)	C1—C2—C3—C4	−0·5 (1)
C2—C3—C4—C5	1·0 (1)	C3—C4—C5—C6	−0·6 (1)
C4—C5—C6—C1	−0·3 (1)	O2—C7—C8—O1	67·7 (1)
C1—O1′—C8′—C7′	157·1 (1)	C7′—O2′—C2′—C1′	−119·4 (1)
C7′—O2′—C2′—C3′	61·7 (1)	C2′—O2′—C7′—C8′	136·8 (1)
O1—C1′—C2′—O2′	2·0 (1)	O1—C1′—C2′—C3′	−179·1 (2)
C6′—C1′—C2′—O2′	−178·6 (1)	C6′—C1′—C2′—C3′	0·4 (1)
O1—C1′—C6′—C5′	178·6 (2)	C2′—C1′—C6′—C5′	−0·8 (1)
O2′—C2′—C3′—C4′	179·4 (2)	C1′—C2′—C3′—C4′	0·5 (1)
C2′—C3′—C4′—C5′	−1·0 (1)	C3′—C4′—C5′—C6′	0·6 (1)
C4′—C5′—C6′—C1′	0·3 (1)	O2′—C7′—C8′—O1′	−67·7 (1)

Symmetry code: (′) $-x$, $1-y$, $1-z$.

has a crystallographic center of symmetry and a 'deep step' shape. The presumed '*trans*' torsion angles about the two C1—O1 bonds, |155·1 (1)|°, which are closer to the ideal value of 180° than the torsion angles about the C2—O2 bonds, |119·4 (1)|°, are accompanied by O1—C1—C_r angles that are much more asymmetric than the O2—C2—C_r angles, where C_r is an aromatic C atom. C—O—C_r angle values indicate also that the O1 atoms [C8—O1—C1, 117·71 (9)°] are more sp^2-hybridized than their O2 counterparts [C7—O2—C2, 115·79 (9)°] which show a large departure from the expected value of 120° for an ideal planar trigonal geometry. So, structural distortions at C1 and C2, observed mainly in the O1—C1—C_r and C7—O2—C2—C_r torsion angles respectively, are also indicative of conformational strain in dibenzo-12-crown-4 ether.

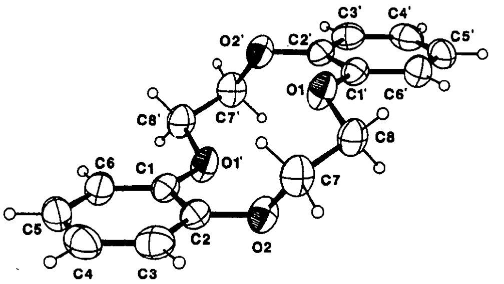

Fig. 1. View of the molecule showing the numbering scheme.

Experimental. Dibenzo-12-crown-4 ether prepared as described elsewhere (Buchanan, Kirby & Charland, 1988*a*). Crystals were obtained from hexane/CH_2Cl_2. A nearly cube-shaped specimen, dimensions 0·3 × 0·3 × 0·25 mm, was chosen for X-ray work. Cell parameters derived from least-squares refinement of 40 centered reflections, $90 \leq 2\theta \leq 98°$, on a Nonius CAD-4 diffractometer controlled by the *NRCCAD* software (Le Page, Gabe & White, 1987). Intensity data collected with $\omega/2\theta$ scan mode, graphite-monochromated Cu $K\alpha$ radiation. Three standard reflections monitored at regular intervals did not vary significantly. $2\theta_{\text{max}} = 152°$. Index range for unique data: $0 \leq h \leq 8$, $0 \leq k \leq 16$, $0 \leq l \leq 18$. 1775 reflections collected from the octants hkl and $\bar{h}\bar{k}\bar{l}$. Symmetry-related reflections were averaged ($R_{\text{int}} = 0{\cdot}012$). The unique set consisted of 1400 unique reflections which were all used for structure solution and refinement. Structure solved by direct methods using *MULTAN* (Germain, Main & Woolfson, 1971). The H atoms were located on the next D map. $\sum w(|F_o| - |F_c|)^2$ minimized where $w = F_o$, for $F_o < 6$, and $0{\cdot}4F_o$, for $F_o \geq 6$ (Hughes weighting scheme). Final full-matrix least-squares refinement with non-H atoms refined anisotropically and H atoms isotropically converged to $R = 0{\cdot}038$, $wR = 0{\cdot}046$ and $S = 1{\cdot}6$ for 124 parameters. Secondary-extinction coefficient $1{\cdot}38\,(5) \times 10^{-6}$.

$\Delta/\sigma_{\max} < 0{\cdot}01$, maximum and minimum heights in final ΔF map $+0{\cdot}17$ and $-0{\cdot}12\ \text{e}\ \text{Å}^{-3}$. The atomic scattering factors were from *International Tables for X-ray Crystallography* (1974). Computations performed with *NRCVAX* (Gabe, Lee & Le Page, 1985). The final positional and thermal parameters for the atoms are given in Table 1 while bond distances and angles, and torsional angles are listed in Table 2.* The numbering scheme used is shown in the *ORTEP*II (Johnson, 1976) drawing of Fig. 1.

Related literature. In their previous report (Hughes & Nowell, 1978), the authors discussed torsional angles about the C_r–O bonds to show the strain in dibenzo-12-crown-4 ether. Related structural studies include dicyclohexyl derivatives of the 14-crown-4 ether (Buchanan, Kirby & Charland, 1988*b*), 12-crown-4 ether (Buchanan, Kirby & Charland, 1988*a*) and 13-crown-4 ether families (Buchanan, Kirby & Charland, 1988*c*).

References

Buchanan, G. W., Kirby, R. A. & Charland, J.-P. (1988*a*). *J. Am. Chem. Soc.* Submitted.

Buchanan, G. W., Kirby, R. A. & Charland, J.-P. (1988*b*). *J. Am. Chem. Soc.* **110**, 2477–2483.

Buchanan, G. W., Kirby, R. A. & Charland, J.-P. (1988*c*). In preparation.

Gabe, E. J., Lee, F. L. & Le Page, Y. (1985). *Crystallographic Computing* 3, edited by G. Sheldrick, C. Kruger & R. Goddard, pp. 167–174. Oxford: Clarendon Press.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

Hughes, D. L. & Nowell, I. W. (1978). *J. Chem. Res.* (*M*), pp. 1534–1556.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Le Page, Y., Gabe, E. J. & White, P. S. (1987). *Acta Cryst.* A**43**, C-271.

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* Lists of observed and calculated structure factors and anisotropic temperature factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51295 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of a Hetero-Diels–Alder Adduct

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Abstract. (6a*RS*,8*RS*,10a*RS*)-4,6,6a,7,8,9,10,10a-Octahydro-2,4,6,6,8-pentamethyl-1*H*-[2]benzopyrano-[3,4-*d*]pyrimidine-1,3(2*H*)-dione, $C_{16}H_{24}N_2O_3$, $M_r = 292{\cdot}38$, triclinic, $P\bar{1}$, $a = 7{\cdot}759\ (1)$, $b = 8{\cdot}313\ (2)$, $c = 12{\cdot}985\ (2)$ Å, $\alpha = 90{\cdot}08\ (2)$, $\beta = 98{\cdot}38\ (2)$, $\gamma = 113{\cdot}24\ (2)^\circ$, $V = 759{\cdot}8$ Å^3, $Z = 2$, $D_x = 1{\cdot}274$ Mg m^{-3}, $\lambda(\text{Mo}\ K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}08$ mm^{-1}, $F(000) = 316$, $T = 298$ K, $R = 0{\cdot}050$ for 2229 observed reflections. The structure was investigated to determine the relative configuration which could not be established unambiguously by NMR. The *trans*-fused cyclohexane ring adopts a chair conformation, whereas the dihydropyran ring takes a twisted half-chair form.

Experimental. Crystal size $0{\cdot}2 \times 0{\cdot}4 \times 0{\cdot}8$ mm. Stoe–Siemens four-circle diffractometer, monochromated Mo $K\alpha$ radiation, profile-fitting mode involving variable scan width and speed (Clegg, 1981). 3914 reflections measured, $2\theta_{\max} = 50^\circ$, $h\ -9\rightarrow 9$, $k\ -9\rightarrow 9$, $l\ 0\rightarrow 15$, three check reflections with no significant intensity change. 2668 unique reflections ($R_{\text{int}} = 0{\cdot}059$), of which 2229 with $F > 4\sigma(F)$ were used for all calculations [*SHELXS*86 (Sheldrick, 1985); *SHELX*76 (Sheldrick, 1976)]. Cell constants refined from $\pm 2\theta$ values of 36 reflections in the range 20–25°. Absorption correction was not necessary. Extinction correction was performed yielding a secondary-extinction coefficient x of $0{\cdot}013\ (3)$, where $F_c^* = F_c\ (1 +$

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