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Structure of Dibenzo-54-crown-18*

BY J. VAN EERDEN, A. ROOS AND S. HARKEMA

Chemical Physics Laboratory, University of Twente, PO Box 217, 7500 AE Enschede, The Netherlands

AND P. D. J. GROOTENHUIS AND D. N. REINHOUDT

Organic Chemistry Laboratory, University of Twente, PO Box 217, 7500 AE Enschede, The Netherlands

Abstract. $C_{44}H_{72}O_{18}$, $M_r = 889 \cdot 05$, monoclinic, $P2_1/c$, $a = 27 \cdot 441$ (2), $b = 8 \cdot 9808$ (4), $c = 9 \cdot 3493$ (4) Å, $\beta = 90 \cdot 296$ (4)°, $V = 2304 \cdot 0$ (4) Å^3, $Z = 2$, $D_x = 1 \cdot 28$ g cm^{-3}, $\lambda(Cu\,K\alpha) = 1 \cdot 5418$ Å, $\mu = 7 \cdot 8$ cm^{-1}, $F(000) = 960$, $T = 161$ K, final $R = 4 \cdot 1\%$ for 2228 observed reflections. The molecule has a centre of symmetry. It consists of two benzo moieties connected by two parallel, helical polyether bridges, with the torsion angle sequence ag^-g^+ $(ag^-a)_7$. Shortest non-bonded contacts are $3 \cdot 5$ Å for non-H atoms.

Experimental. Dibenzo-54-crown-18† was formed as a by-product during the synthesis of benzo-27-crown-9† (Talma, van Vossen, Sudhölter, van Eerden & Reinhoudt, 1986) and obtained as colorless crystals after chromatography, m.p. 351–353 K. 80 MHz ^{1}H NMR (CDCl$_3$, Me$_4$Si as an internal standard): δ 6·90 (s, 8 H, ArH), 4·16 (m, 8 H, ArOCH$_2$), 3·84 (m, 8 H, ArOCH$_2$CH$_2$), 3·7–3·6 (m, 48 H, OCH$_2$); 50 MHz ^{13}C NMR (CDCl$_3$, Me$_4$Si): δ 148·96 (s, Ar-1,

Ar-2), 121·56 (d, Ar-4, Ar-5), 114·83 (d, Ar-3, Ar-6), 70·82, 70·54, 69·78, 68·92 (t, CH$_2$). Mass spectrum: m/e 888·472 (M^+; calcd 888·472). Elemental analysis for $C_{44}H_{72}O_{18}$, found: C 59·24, H 8·31%, calculated: C 59·44, H 8·16%. D_m not determined.

Intensities measured at 161 K on a Philips PW 1100 diffractometer (Cu $K\alpha$ radiation, graphite monochromator); crystal dimensions 0·10 × 0·40 × 0·40 mm. Lattice parameters determined by least squares from 25 reflections ($6 \cdot 5 < \theta < 20°$). A total of 3430 unique reflections up to $\theta = 60°$ ($-30 \leq h \leq 30$, $0 \leq k \leq 10$, $0 \leq l \leq 10$) measured in the $\theta/2\theta$ scan mode [scan speed 0·05° s^{-1}, scan width (1·1 + 0·2tanθ)°]; 2228 reflections considered observed $[F_o^2 > 3\sigma(F_o^2)]$. The intensity variation of three standard reflections, measured every hour, was less than 1%.

Structure solved with *MULTAN* (Germain, Main & Woolfson, 1971) and refined by full-matrix least squares. After convergence of the isotropic refinement an empirical absorption correction ($\mu = 7 \cdot 8$ cm^{-1}; correction factors 0·67–1·70) using the *DIFABS* procedure (Walker & Stuart, 1983) was applied, upon which R_{int} (F) of 153 pairs of symmetry-related reflections was reduced from 12·2 to 2·0%. Refinement was continued with anisotropic thermal parameters for the non-H atoms. H atoms located on

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difference Fourier maps and included in the refinement. Weights for each reflection in the refinement (on F) calculated from $w = 4F_o^2/\sigma^2(F_o^2)$, $\sigma^2(F_o^2) = \sigma^2(I) + (pF_o^2)^2$; the value of the instability factor p was determined as 0·04. The total number of parameters refined was 425: scale factor, isotropic extinction parameter (final value 8×10^{-7}), positional parameters,

anisotropic thermal parameters for non-H atoms and isotropic thermal parameters for H atoms. Refinement converged at $R = 4·1\%$, $wR = 4·8\%$, $(\Delta/\sigma)_{max} = 0·01$. Largest peak on final difference Fourier map 0·2 e Å^{-3}. All calculations were done using *SDP* (B. A. Frenz & Associates Inc., 1983). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Atomic parameters of non-H atoms are in Table 1.* Bond distances and angles for non-H atoms and torsion angles in the macrocycle are in Table 2. Atom numbering is shown in Fig. 1, unit-cell contents in Fig. 2.

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters for non-H atoms

$B_{eq} = \frac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$

	x	y	z	$B_{eq}(\text{Å}^2)$
C(1)	−0·4268 (1)	−0·0183 (3)	0·0932 (3)	3·10 (6)
O(2)	−0·40735 (7)	0·0305 (2)	−0·0334 (2)	3·48 (4)
C(3)	−0·4157 (1)	0·1840 (3)	−0·0715 (3)	3·76 (6)
C(4)	−0·3726 (1)	0·2377 (3)	−0·1534 (3)	3·84 (7)
O(5)	−0·32989 (7)	0·2406 (2)	−0·0672 (2)	4·42 (5)
C(6)	−0·3008 (1)	0·1092 (3)	−0·0754 (3)	3·75 (6)
C(7)	−0·2728 (1)	0·0891 (3)	0·0592 (3)	3·54 (6)
O(8)	−0·23711 (7)	0·2024 (2)	0·0726 (2)	3·53 (4)
C(9)	−0·2062 (1)	0·1775 (3)	0·1927 (3)	3·54 (6)
C(10)	−0·1710 (1)	0·3036 (3)	0·2048 (3)	3·48 (6)
O(11)	−0·13817 (6)	0·3008 (2)	0·0884 (2)	3·68 (4)
C(12)	−0·1061 (1)	0·4245 (3)	0·0916 (3)	3·48 (6)
C(13)	−0·0756 (1)	0·4261 (3)	−0·0400 (3)	3·56 (6)
O(14)	−0·04155 (7)	0·3082 (2)	−0·0373 (2)	3·74 (4)
C(15)	−0·0121 (1)	0·3097 (3)	−0·1614 (3)	3·87 (6)
C(16)	0·0223 (1)	0·1829 (3)	−0·1611 (3)	4·14 (7)
O(17)	0·05964 (7)	0·2039 (2)	−0·0565 (2)	4·00 (4)
C(18)	0·0940 (1)	0·0861 (3)	−0·0583 (3)	4·25 (7)
C(19)	0·1316 (1)	0·1074 (3)	0·0538 (3)	4·53 (7)
O(20)	0·16461 (7)	0·2222 (2)	0·0171 (2)	3·82 (4)
C(21)	0·1994 (1)	0·2462 (4)	0·1292 (3)	4·34 (7)
C(22)	0·2358 (1)	0·3596 (3)	0·0853 (3)	4·34 (7)
O(23)	0·26871 (7)	0·2966 (2)	−0·0145 (2)	3·69 (4)
C(24)	0·3082 (1)	0·3935 (3)	−0·0419 (3)	3·88 (7)
C(25)	0·3418 (1)	0·3271 (3)	−0·1485 (3)	3·60 (6)
O(26)	0·36385 (6)	0·1963 (2)	−0·0881 (2)	3·27 (4)
C(27)	0·40305 (9)	0·1375 (3)	−0·1599 (3)	2·86 (5)
C(28)	0·4194 (1)	0·1867 (3)	−0·2916 (3)	3·79 (6)
C(29)	0·4595 (1)	0·1198 (3)	−0·3541 (3)	4·64 (7)
C(30)	0·4838 (1)	0·0078 (4)	−0·2883 (3)	4·59 (7)
C(31)	0·4675 (1)	−0·0436 (3)	−0·1573 (3)	3·84 (7)

Table 2. Bond distances (Å) and angles (°) for non-H atoms and torsion angles (°) in the macrocycle

C(1)−O(2)	1·373 (3)	O(17)−C(18)	1·418 (3)
O(2)−C(3)	1·442 (3)	C(18)−C(19)	1·479 (4)
C(3)−C(4)	1·492 (4)	C(19)−O(20)	1·416 (4)
C(4)−O(5)	1·419 (4)	O(20)−C(21)	1·430 (3)
O(5)−C(6)	1·427 (3)	C(21)−C(22)	1·486 (4)
C(6)−C(7)	1·482 (4)	C(22)−O(23)	1·420 (3)
C(7)−O(8)	1·417 (3)	O(23)−C(24)	1·414 (3)
O(8)−C(9)	1·422 (3)	C(24)−C(25)	1·486 (4)
C(9)−C(10)	1·493 (4)	C(25)−O(26)	1·436 (3)
C(10)−O(11)	1·416 (3)	O(26)−C(27)	1·377 (3)
O(11)−C(12)	1·417 (3)	C(27)−C(28)	1·385 (4)
C(12)−C(13)	1·491 (4)	C(27)−C(1^i)	1·398 (4)
C(13)−O(14)	1·413 (3)	C(28)−C(29)	1·385 (4)
O(14)−C(15)	1·418 (3)	C(29)−C(30)	1·353 (4)
C(15)−C(16)	1·478 (4)	C(30)−C(31)	1·385 (4)
C(16)−O(17)	1·426 (3)	C(31)−C(1^i)	1·388 (4)

O(2)−C(1)−C(27^i)	116·6 (2)	C(16)−O(17)−C(18)	111·6 (2)
O(2)−C(1)−C(31^i)	124·2 (2)	O(17)−C(18)−C(19)	110·9 (2)
C(27^i)−C(1)−C(31^i)	119·2 (2)	C(18)−C(19)−O(20)	111·5 (2)
C(1)−O(2)−C(3)	117·2 (2)	C(19)−O(20)−C(21)	111·0 (2)
O(2)−C(3)−C(4)	108·0 (2)	O(20)−C(21)−C(22)	110·4 (2)
C(3)−C(4)−O(5)	111·7 (2)	C(21)−C(22)−O(23)	109·8 (2)
C(4)−O(5)−C(6)	114·5 (2)	C(22)−O(23)−C(24)	111·4 (2)
O(5)−C(6)−C(7)	110·1 (2)	O(23)−C(24)−C(25)	110·6 (2)
C(6)−C(7)−O(8)	110·0 (2)	C(24)−C(25)−O(26)	109·0 (2)
C(7)−O(8)−C(9)	111·5 (2)	C(25)−O(26)−C(27)	116·8 (2)
O(8)−C(9)−C(10)	108·9 (2)	O(26)−C(27)−C(28)	124·7 (2)
C(9)−C(10)−O(11)	110·0 (2)	O(26)−C(27)−C(1^i)	116·1 (2)
C(10)−O(11)−C(12)	111·5 (2)	C(28)−C(27)−C(1^i)	119·2 (2)
O(11)−C(12)−C(13)	109·9 (2)	C(27)−C(28)−C(29)	119·9 (3)
C(12)−C(13)−O(14)	110·6 (2)	C(28)−C(29)−C(30)	121·4 (3)
C(13)−O(14)−C(15)	111·0 (2)	C(29)−C(30)−C(31)	119·3 (3)
O(14)−C(15)−C(16)	111·0 (2)	C(30)−C(31)−C(1^i)	120·8 (3)
C(15)−C(16)−O(17)	110·8 (2)		

C(1)−O(2)−C(3)−C(4)	147·8	C(15)−C(16)−O(17)−C(18)	−177·8
O(2)−C(3)−C(4)−O(5)	−65·5	C(16)−O(17)−C(18)−C(19)	−178·2
C(3)−C(4)−O(5)−C(6)	93·6	O(17)−C(18)−C(19)−O(20)	−73·7
C(4)−O(5)−C(6)−C(7)	−152·9	C(18)−C(19)−O(20)−C(21)	177·4
O(5)−C(6)−C(7)−O(8)	−68·1	C(19)−O(20)−C(21)−C(22)	176·2
C(6)−C(7)−O(8)−C(9)	−173·8	O(20)−C(21)−C(22)−O(23)	−74·5
C(7)−O(8)−C(9)−C(10)	−177·5	C(21)−C(22)−O(23)−C(24)	−170·9
O(8)−C(9)−C(10)−O(11)	−67·8	C(22)−O(23)−C(24)−C(25)	−179·0
C(9)−C(10)−O(11)−C(12)	176·3	O(23)−C(24)−C(25)−O(26)	−65·5
C(10)−O(11)−C(12)−C(13)	−174·3	C(24)−C(25)−O(26)−C(27)	−167·3
O(11)−C(12)−C(13)−O(14)	−70·3	C(25)−O(26)−C(27)−C(1^i)	174·6
C(12)−C(13)−O(14)−C(15)	−179·4	O(26)−C(27)−C(1^i)−O(2^i)	−2·4
C(13)−O(14)−C(15)−C(16)	−177·8	C(27)−C(1^i)−O(2^i)−C(3^i)	−153·4
O(14)−C(15)−C(16)−O(17)	−71·6		
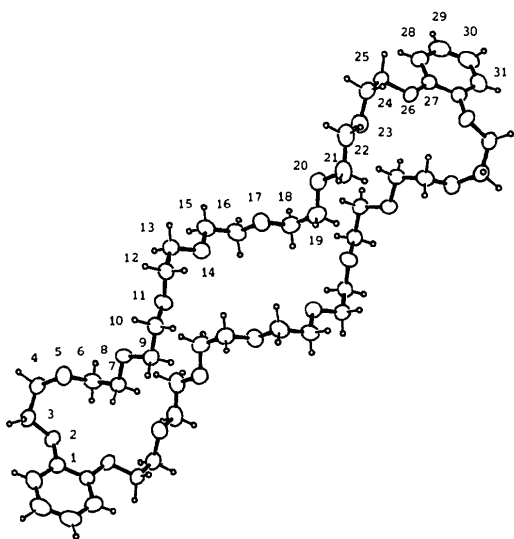
Fig. 1. View of the molecule with the atom numbering.

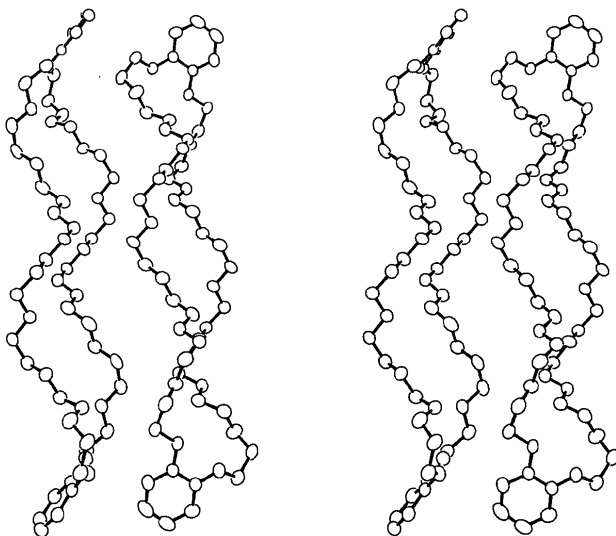Symmetry code: (i) −x, −y, −z.

Fig. 2. Stereoscopic view of the unit-cell contents; H atoms omitted for clarity.

Related literature. Crystal structures of dibenzo-24-crown-8 (Hanson, Hughes & Truter, 1976) and dibenzo-30-crown-10 (Bush & Truter, 1972) and the complexation of guanidinium perchlorate with benzo

crown ethers (de Boer, Uiterwijk, Geevers, Harkema & Reinhoudt, 1983) have been reported.

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Structure of Bruceine B Hydrate

BY JUDITH L. FLIPPEN-ANDERSON, R. GILARDI AND C. GEORGE

Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, DC 20375, USA

Abstract. $C_{23}H_{28}O_{11}.H_2O$, $M_r = 498.48$, monoclinic, $P2_1$, $a = 8.696$ (3), $b = 11.493$ (5), $c = 11.601$ (3) Å, $\beta = 100.7$ (1)°, $V = 1139.3$ (3) Å^3, $Z = 2$, $D_x = 1.45$ Mg m^{-3}, $\lambda(Mo\ K\alpha) = 0.71069$ Å, $\mu = 0.13$ mm^{-1}, $F(000) = 528$, $T = 295$ K, final $R = 0.037$, $wR = 0.033$, for 1423 independent reflections. Overall the molecule has an extended conformation. The only evidence of strain is in the five-membered ring where the average intra-ring bond angle for junction atoms is only 99.7°. Packing is dominated by hydrogen bonding involving all possible H atoms. The ether O atom in the five-membered ring has two intermolecular O$\cdots$O approaches slightly less than van der Waals separations.

Experimental. The title compound (I), purified and crystallized from medicinal plant, *Brucea javanica*, has

(I)
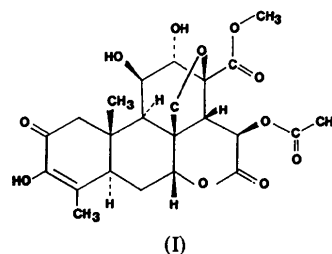
been found to be an active anti-malarial agent (Pavanand *et al.*, 1986). Crystal dimensions 0.15 × 0.10 × 0.25 mm, automated Nicolet R3m diffractometer with incident-beam monochromator. 25 centered reflections within $15 \le 2\theta \le 23°$ used for determining lattice parameters. $(\sin\theta/\lambda)_{max} = 0.538$ Å^{-1}, range of *hkl*: $-9 \le h \le 4$, $-13 \le k \le 0$, $-12 \le l \le 12$. Standards