Crystal and Molecular Structure of 6,7,9,10,12,13,20,21,23,24,26,27-Dodecahydrodibenzo[*b*,*n*][1,4,7,10,13,16,19,22]octaoxacyclotetracosin (Dibenzo-24-crown-8)

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The crystal structure of the title compound (I) has been determined from 1 080 diffractometer observations by direct methods. There are two centrosymmetric molecules in a monoclinic unit cell having a = 9.187(2), b = 4.913(2), c = 26.462(5) Å, β = 104.93°, and space group $P2_1/c$. Full-matrix refinement of the parameters of all atoms gave R 0.11.

Dimensions of the molecule are compared with those of other macrocyclic ethers and of the complexes of dibenzo-24-crown-8 with a sodium and with a potassium salt. Significant differences are found in the torsion angles, the unusual ones in the uncomplexed molecule are correlated with packing interactions.

THE macrocyclic polyether, dibenzo-24-crown-8 (I), originally synthesised by Pedersen [1] has been shown to form complexes with sodium and potassium in stoicheiometries dependent on the anion and solvent.[2] For two complexes [$(KNCS)_2$(I)][3] and [(Na 2-nitrophenolate)$_2$(I)],[4] the crystal structures have already been determined. We report here the crystal structure of the uncomplexed molecule and compare its dimensions and conformation with those of the complexes, and with other uncomplexed crown molecules and consider whether the torsion angles can be correlated with packing interactions.

Preliminary *X*-ray investigation showed that there were two molecules in a monoclinic unit cell having space group $P2_1/c$; the molecules must therefore be centro-

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[1] C. J. Pedersen, *J. Amer. Chem. Soc.*, 1967, **89**, 7017.

[2] N. S. Poonia and M. R. Truter, *J.C.S. Dalton*, 1973, 2062.

[3] M. Mercer and M. R. Truter, *J.C.S. Dalton*, 1973, 2469.

[4] D. L. Hughes, *J.C.S. Dalton*, 1975, 2374.

symmetric. Intensities were collected on a four-circle diffractometer. The phase problem was solved by direct methods. The designations of the atoms are shown in Figure 1 and the co-ordinates and vibration parameters of those in the asymmetric unit are in Tables 1 and 2.

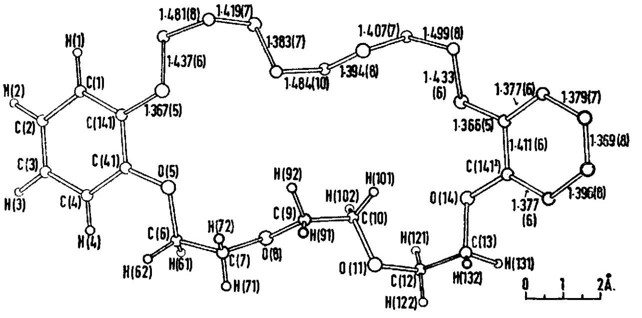


FIGURE 1 The molecule of dibenzo-24-crown-8 showing the designations of the atoms; those with the superscript I are centrosymmetrically related to those without. Bond lengths (Å) and standard deviations are displayed

TABLE 1

Fractional atomic co-ordinates ($\times 10^4$) and isotropic vibration parameters (B Å^2)

	x	y	z	B
C(1)	1 158(7)	5 836(14)	1 726(2)	*
C(2)	1 095(8)	4 094(15)	2 137(3)	*
C(3)	2 230(8)	2 278(15)	2 334(2)	*
C(4)	3 454(6)	2 149(12)	2 124(2)	*
C(41)	3 572(6)	3 862(11)	1 724(2)	*
C(141)	2 399(6)	5 733(11)	1 525(2)	*
O(5)	4 734(4)	3 936(7)	1 490(1)	*
C(6)	5 848(7)	1 838(15)	1 635(3)	*
C(7)	7 051(7)	2 533(21)	1 367(3)	*
O(8)	6 594(4)	1 798(8)	836(2)	*
C(9)	7 074(12)	3 589(18)	503(3)	*
C(10)	6 888(10)	2 362(18)	−22(3)	*
O(11)	8 140(4)	767(9)	−5(1)	*
C(12)	8 096(8)	−685(16)	−472(3)	*
C(13)	8 609(7)	895(13)	−871(2)	*
O(14)	7 402(3)	2 679(7)	−1 124(1)	*
H(1)	257(60)	7 108(126)	1 579(20)	10(2)
H(2)	282(40)	4 343(80)	2 283(14)	3(1)
H(3)	2 152(52)	987(108)	2 614(19)	7(2)
H(4)	4 255(42)	954(80)	2 257(15)	3(1)
H(61)	5 482(57)	−50(118)	1 537(20)	8(2)
H(62)	6 306(45)	1 924(89)	2 019(18)	4(1)
H(71)	7 911(46)	1 556(85)	1 498(16)	4(1)
H(72)	7 423(72)	4 542(152)	1 452(27)	12(3)
H(91)	8 055(60)	4 678(124)	692(22)	10(2)
H(92)	6 456(61)	5 108(119)	507(22)	8(2)
H(101)	6 859(54)	3 973(115)	−259(21)	8(2)
H(102)	6 052(67)	1 300(136)	−130(26)	10(3)
H(121)	7 017(49)	−1 404(92)	−620(17)	6(1)
H(122)	8 702(49)	−2 133(105)	−375(18)	6(2)
H(131)	8 857(45)	−143(84)	−1 146(16)	4(1)
H(132)	9 586(57)	2 084(115)	−711(20)	8(2)

* Anisotropic vibration parameters are in Table 2.

A complete molecule is obtained by operation of the centre of symmetry at ($\frac{1}{2}, \frac{1}{2}, 0$). Bond lengths and angles are in Figure 1 and Table 3.

DISCUSSION

The value of R, 0.11, after full-matrix, least-squares refinement is high for a structure determination from intensities collected on a diffractometer. A much lower R value could be obtained by inclusion of only half the reflections, *i.e.* those with $I \geqslant 2\sigma(I)$, but this reduced the ratio of observations-to-parameters to only 3 : 1.

TABLE 2

Anisotropic vibration parameters ($\times 10^3$ Å^2) of the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + 2U_{12}kha^*b^* + U_{22}k^2b^* + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + U_{33}l^2c^{*2})]$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	48(4)	60(4)	64(4)	0(4)	12(4)	−17(4)
C(2)	58(5)	80(5)	70(5)	−10(4)	29(4)	−20(4)
C(3)	72(5)	65(5)	64(5)	−12(4)	29(4)	1(4)
C(4)	48(4)	54(4)	55(4)	2(4)	9(3)	8(4)
C(41)	42(4)	43(4)	50(4)	−7(3)	8(3)	−5(3)
C(141)	52(4)	37(4)	45(4)	−5(3)	5(3)	−2(3)
O(5)	55(2)	63(3)	57(2)	6(2)	21(2)	14(2)
C(6)	46(4)	72(6)	66(5)	11(4)	13(4)	3(4)
C(7)	47(5)	123(7)	72(5)	9(5)	17(4)	−8(5)
O(8)	93(3)	106(4)	64(3)	−29(3)	37(3)	−6(3)
C(9)	145(8)	81(7)	87(6)	8(6)	57(6)	−7(5)
C(10)	106(7)	84(6)	79(6)	7(6)	36(5)	18(5)
O(11)	53(3)	108(3)	63(3)	16(2)	−1(2)	−12(3)
C(12)	74(5)	68(5)	59(5)	12(4)	−2(4)	−2(5)
C(13)	63(5)	51(4)	52(4)	3(4)	4(4)	10(4)
O(14)	47(2)	49(2)	61(3)	9(2)	6(2)	10(2)

TABLE 3

Molecular geometry

(*a*) Bond angles (°), with standard deviations in parentheses

C(2)–C(1)–C(141)	118.8(6)	C(6)–C(7)–O(8)	110.4(6)
C(1)–C(2)–C(3)	121.1(6)	C(7)–O(8)–C(9)	114.1(6)
C(2)–C(3)–C(4)	119.8(7)	O(8)–C(9)–C(10)	110.9(7)
C(3)–C(4)–C(41)	121.0(6)	C(9)–C(10)–O(11)	107.7(7)
C(4)–C(41)–C(141)	118.7(5)	C(10)–O(11)–C(12)	114.8(5)
C(1)–C(141)–C(41)	120.6(6)	O(11)–C(12)–C(13)	114.5(6)
C(4)–C(41)–O(5)	126.1(5)	C(12)–C(13)–O(14)	107.6(5)
C(141)–C(41)–O(5)	115.2(5)	C(13)–O(14)–C(141$^{\mathrm{I}}$)	118.0(4)
C(41)–O(5)–C(6)	116.5(4)	O(14)–C(141$^{\mathrm{I}}$)–C(41$^{\mathrm{I}}$)	114.8(5)
O(5)–C(6)–C(7)	105.8(6)	O(14)–C(141$^{\mathrm{I}}$)–C(1$^{\mathrm{I}}$)	124.6(5)

(*b*) Bond lengths (Å) involving hydrogen atoms

H(1)–C(1)	1.03(6)	H(91)–C(9)	1.06(5)
H(2)–C(2)	0.93(3)	H(92)–C(9)	0.94(5)
H(3)–C(3)	0.99(5)	H(101)–C(10)	1.01(5)
H(4)–C(4)	0.94(4)	H(102)–C(10)	0.91(6)
H(61)–C(6)	1.00(5)	H(121)–C(12)	1.03(4)
H(62)–C(6)	1.00(4)	H(122)–C(12)	0.90(4)
H(71)–C(7)	0.91(4)	H(131)–C(13)	0.96(4)
H(72)–C(7)	1.05(7)	H(132)–C(13)	1.06(5)

(*c*) Bond angles (°) involving hydrogen atoms, differing by $> 1\ \sigma$ from 120° [for C(2)] or 109.5°

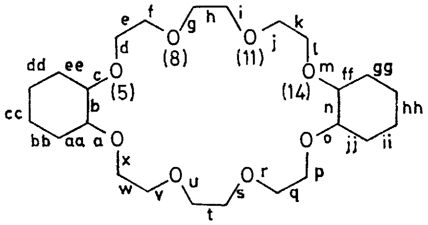
C(1)–C(2)–H(2)	116(3)	H(91)–C(9)–H(92)	92(5)
O(5)–C(6)–H(61)	115(3)	C(9)–C(10)–H(101)	104(3)
O(8)–C(7)–H(71)	105(3)	C(9)–C(10)–H(102)	114(4)
O(8)–C(7)–H(72)	117(4)	O(11)–C(12)–H(122)	106(3)
H(71)–C(7)–H(72)	102(4)	C(12)–C(13)–H(131)	116(3)
O(8)–C(9)–H(92)	102(4)	C(12)–C(13)–H(132)	113(3)
O(8)–C(9)–H(91)	113(3)	O(14)–C(13)–H(131)	106(2)
C(10)–C(9)–H(91)	122(3)	H(131)–C(13)–H(132)	105(4)
C(10)–C(9)–H(92)	114(4)		

Internal evidence suggests that the structure is correct. For example, the benzene ring is planar with a maximum deviation of 0.008 Å; O(5) and O(14$^{\mathrm{I}}$) are also in this plane, deviating from it by −0.002 and 0.008 Å respectively. The refined hydrogen-atom positions give mean bond lengths for C(sp^2)–H of 0.97 and for C(sp^3)–H of 0.99 Å; both are reasonable values for measurements by *X*-ray methods, and deviations from ideal bond angles are small, as shown in Table 3.

The bond lengths and angles are similar to those found in other macrocyclic ethers;[5-8] in particular the aliphatic C–C bonds (mean 1.488 Å), are shorter than the standard single-bond length (1.54 Å).[9] Possible reasons for this have been discussed[3,10] and the effect shown to persist at liquid-nitrogen temperature for the ring 18-crown-6 in its adduct with dimethyl acetylenedicarboxylate.[11] The C(sp^3)–O bond lengths about O(8) and O(11) (mean 1.401 Å) are also shorter than the standard value (1.426 Å), while for O(5) and O(14) the mean C(sp^2)–O and C(sp^3)–O bond lengths differ significantly, being 1.366 and 1.435 Å. The variations in bond lengths round the benzene ring are consistent with an apparent shortening in the outer ones resulting from libration; they fall into the pattern of those in other benzo-crown compounds.[5]

TABLE 4

Torsion angles (°) in the rings of free dibenzo-24-crown-8 (I), and in complexes with potassium and sodium salts. The bonds of the polyether ring are designated as illustrated. Some oxygen atoms are numbered and refer only to the present work. Pairs of symmetry-related bonds (s.r.b.) are shown. The sign of the torsion angle is reversed on inversion through the centres of symmetry in (I) and [(KNCS)$_2$(I)]; it is unchanged by rotation about the two-fold axis in [(Na 2-nitrophenolate)$_2$(I)]



	(I)		[(KNCS)$_2$(I)]		[(Na 2-nitrophenolate)$_2$(I)]	
Bond	Angle	S.r.b.	Angle	S.r.b.	Angle	S.r.b.
a	174.6(5)	m	174.0(8)	m	−170.7(4)	o
b	0.6(7)	n	0.0(11)	n	2.1(6)	n
c	−172.3(5)	o	−174.8(8)	o	−177.0(4)	m
d	−174.8(5)	p	165.0(8)	p	−179.6(4)	l
e	−78.1(7)	q	67.1(10)	q	−61.1(6)	k
f	144.0(7)	r	93.8(10)	r	−157.4(7)	j
g	166.0(7)	s	83.6(10)	s	−179.9(8)	i
h	−84.1(8)	t	60.6(12)	t	117.3(10)	
t	84.1(8)	h	−60.6(12)	h	138.8(4)	
u	−176.6(6)	i	−95.3(10)	i	178.6(4)	s
v	−84.5(7)	j	−169.2(8)	j	−175.6(4)	r
w	78.0(7)	k	−67.6(10)	k	−59.9(6)	q
x	177.3(5)	l	−164.7(8)	l	−174.6(4)	p
aa	1.2(9)	ff	−0.5(16)	ff	−0.5(8)	jj
bb	1.0(10)	gg	−1.1(20)	gg	−1.3(9)	ii
cc	−0.3(10)	hh	2.8(20)	hh	1.2(9)	hh
dd	1.3(10)	ii	−2.8(19)	ii	−0.3(9)	gg
ee	−1.1(9)	jj	1.0(15)	jj	−0.6(8)	ff

From the spread of the values about the mean, estimates of the standard deviations in individual values can be obtained. These are 0.009 and 0.014 Å for aliphatic C–C bonds and for C–O bonds at O(8) and O(11), respectively, whereas from the correlation coefficients obtained by inversion of the full least-squares matrix the values are 0.008—0.010 Å and 0.007—0.008 Å, as shown in Figure 1. Although in this structure the pairs of bonds C(7)–O(8), C(12)–O(11) and O(8)–C(9), C(10)–O(11) appear to give a consistent pattern, the first two being larger than the second two, this is not found in the complexes[3,4] or in the corresponding bonds in dibenzo-30-crown-10;[5] it is best interpreted as an indication that standard deviations may be underestimated by the least-squares procedure and in the discussion which follows we consider differences of 4 σ as significant.

The torsion angles (Table 4) show reasonable values for the standard deviations, as judged by those round the benzene rings. There are some significant departures from the values (180 or 60°) which correspond to minimum conformational energy and maximum H · · · H contact distances. In fact, the conformational energy of this molecule is higher[12] than that for the two complexes so far studied by *X*-ray crystal-structural analysis. Intramolecular contacts do not explain the conformation. The general shape of the molecule (Figure 1), like those of the other uncomplexed macrocyclic ethers,[5-8] tends towards one with the [CH_2CH_2O]$_n$ moieties parallel; the presence of the benzene rings limits the flexibility so that the shortest contact across the ring between the centrosymmetrically related halves of the molecule, from H(92) to H(102^I), is 2.87 Å, which is larger than the sum of the

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[5] M. A. Bush and M. R. Truter, *J.C.S. Perkin II*, 1972, 345.

[6] J. D. Dunitz, M. Dobler, P. Seiler, and R. P. Phizackerley, *Acta Cryst.*, 1974, **B30**, 2733.

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[8] P. R. Mallinson, *J.C.S. Perkin II*, 1975, 266.

[9] *Chem. Soc. Special Publ.*, No. 18, 1965.

[10] J. D. Dunitz and P. Seiler, *Acta Cryst.*, 1973, **B29**, 589.

[11] I. Goldberg, *Acta Cryst.*, 1975, **B31**, 754.

[12] J. D. Owen, 1975, personal communication.

TABLE 5

Selected intra- and inter-molecular contacts (Å)

(*a*) Intramolecular distances <2.5 Å, between hydrogen atoms on different carbon atoms

H(1) $\cdots$ H(131$^{\rm I}$)	2.16	H(62) $\cdots$ H(72)	2.40
H(1) $\cdots$ H(132$^{\rm I}$)	2.37	H(72) $\cdots$ H(91)	2.24
H(1) $\cdots$ H(2)	2.30	H(72) $\cdots$ H(92)	2.44
H(2) $\cdots$ H(3)	2.38	H(91) $\cdots$ H(101)	2.50
H(3) $\cdots$ H(4)	2.36	H(92) $\cdots$ H(101)	2.23
H(4) $\cdots$ H(61)	2.50	H(92) $\cdots$ H(102)	2.48
H(4) $\cdots$ H(62)	2.19	H(102) $\cdots$ H(121)	2.20
H(61) $\cdots$ H(71)	2.39	H(122) $\cdots$ H(131)	2.30
H(62) $\cdots$ H(71)	2.27	H(122) $\cdots$ H(132)	2.47

(*b*) Shortest distances across the polyether ring

O(5) $\cdots$ H(101$^{\rm I}$)	3.37	H(92) $\cdots$ H(102$^{\rm I}$)	2.87
C(10) $\cdots$ H(92$^{\rm I}$)	3.25		

(*c*) Selected intermolecular distances

H(101) $\cdots$ H(121$^{\rm III}$), H(121) $\cdots$ H(101$^{\rm VIII}$)	2.48
H(102) $\cdots$ H(102$^{\rm II}$)	2.55
C(41) $\cdots$ C(13$^{\rm II}$), C(13) $\cdots$ C(41$^{\rm II}$)	3.50
C(4) $\cdots$ C(141$^{\rm VIII}$), C(141) $\cdots$ C(4$^{\rm III}$)	3.55
C(1) $\cdots$ C(3$^{\rm III}$), C(3) $\cdots$ C(1$^{\rm VIII}$)	3.57
H(131) $\cdots$ C(1$^{\rm II}$), C(1) $\cdots$ H(131$^{\rm II}$)	3.19
H(131) $\cdots$ C(2$^{\rm II}$), C(2) $\cdots$ H(131$^{\rm II}$)	3.27
H(131) $\cdots$ C(3$^{\rm II}$), C(3) $\cdots$ H(131$^{\rm II}$)	3.22
H(131) $\cdots$ C(4$^{\rm II}$), C(4) $\cdots$ H(131$^{\rm II}$)	3.06
H(131) $\cdots$ C(41$^{\rm II}$), C(41) $\cdots$ H(131$^{\rm II}$)	2.98
H(131) $\cdots$ C(141$^{\rm II}$), C(141) $\cdots$ H(131$^{\rm II}$)	3.05
O(11) $\cdots$ C(12$^{\rm VII}$), C(12) $\cdots$ O(11$^{\rm VII}$)	3.36
O(11) $\cdots$ C(13$^{\rm VII}$), C(13) $\cdots$ O(11$^{\rm VII}$)	3.37
H(2) $\cdots$ H(3$^{\rm IV}$), H(3) $\cdots$ H(2$^{\rm VI}$)	2.46
H(3) $\cdots$ H(62$^{\rm IX}$), H(62) $\cdots$ H(3$^{\rm V}$)	2.49
H(3) $\cdots$ H(72$^{\rm IX}$), H(72) $\cdots$ H(3$^{\rm V}$)	2.50
C(3) $\cdots$ C(6$^{\rm IX}$), C(6) $\cdots$ C(3$^{\rm V}$)	3.62
C(4) $\cdots$ C(13$^{\rm II}$), C(13) $\cdots$ C(4$^{\rm II}$)	3.69
C(41) $\cdots$ C(12$^{\rm II}$), C(12) $\cdots$ C(41$^{\rm II}$)	3.63
C(141) $\cdots$ C(12$^{\rm II}$), C(12) $\cdots$ C(141$^{\rm II}$)	3.67
C(141) $\cdots$ C(13$^{\rm II}$), C(13) $\cdots$ C(141$^{\rm II}$)	3.69
C(10) $\cdots$ C(12$^{\rm III}$), C(12) $\cdots$ C(10$^{\rm VIII}$)	3.87
C(12) $\cdots$ C(12$^{\rm VII}$)	3.80

Roman numeral superscripts refer to the following equivalent positions relative to the co-ordinates in Table 1 at x, y, z:

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

van der Waals radii. If packing effects were responsible for the conformation we would expect the hydrogen atoms involved in short intramolecular H $\cdots$ H contacts [Table 5(*a*)], *i.e.* H(62), H(102), H(121), H(131), and possibly H(72), H(91), H(92), and H(101), to have closer intermolecular contacts than the hydrogen atoms H(61), H(71), H(122), and H(132) not so involved, and there is some evidence for this in Table 5(*c*). The molecular packing is shown in Figure 2.

Along the *b* axis stacking of the molecules gives minimum H $\cdots$ H contacts between methylene groups H(101) and H(121) of 2.48 Å and minimum C $\cdots$ C contacts between C(41) and C(13) of 3.50 Å. The stacking of the benzene rings gives separations of 3.55 and 3.57 Å between C(4) and C(141), and between C(1) and C(3). There is also a neat packing of H(131) almost equidistant from all six carbon atoms of one benzene ring. Along the *a* and *c* axes contacts are between glide-related molecules which are tilted in opposite directions along *b* so that normals to the benzene rings are approximately perpendicular (85.9°); this allows the hydrogen atoms of the benzene rings to form the packing contacts, the incoming hydrogen atom being on the opposite side from H(131). The minimum is 2.46 Å between H(2) and H(3), while H(3) also contacts H(62) and H(72) in another glide-related molecule.

EXPERIMENTAL

Crystals were obtained by recrystallisation from methylene dichloride–ethanol, and well-formed needles were extracted from a mixture of these and amorphous material. The crystal chosen for intensity measurements was a short needle 0.10 × 0.22 × 0.13 mm mounted with the long (*b*) axis approximately coincident with the ϕ axis of a Picker four-circle automatic diffractometer. Accurate cell dimensions were obtained by least-squares refinement from the 2θ settings of 25 manually-centred reflections.

Crystal Data.—$C_{24}H_{32}O_8$, M 448.5. Monoclinic, a = 9.187(2), b = 4.913(2), c = 26.462(5) Å, β = 104.93(1)°, U = 1 154.0 Å^3, D_m = 1.276 (flotation), Z = 2, D_c = 1.298 g cm^{-3}, $F(000)$ = 480, m.p. 103—104° (lit.,[1] 103—104°.* Space group $P2_1/c$ uniquely determined; molecular symmetry required, a centre of inversion. Mo-$K\bar{\alpha}$ radiation, Zr filtered; λ(Mo-$K\bar{\alpha}$) = 0.710 69 Å ≡ 10^{-10} m); μ(Mo-$K\bar{\alpha}$) =

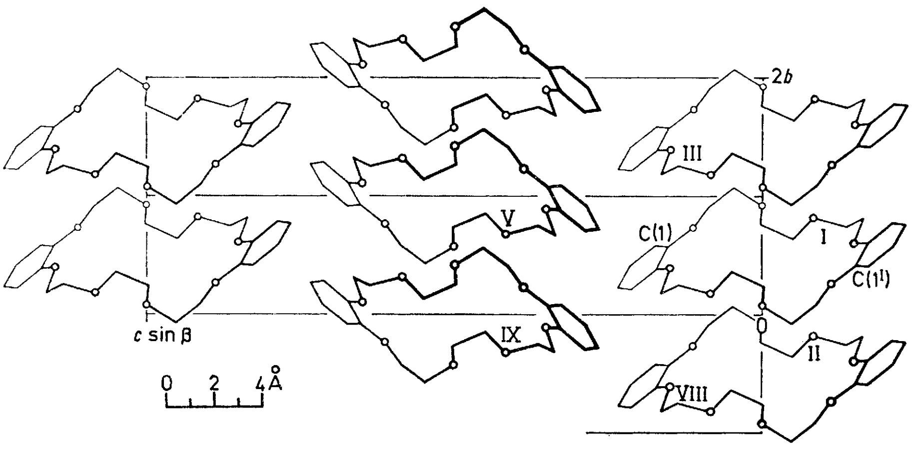

FIGURE 2 The crystal structure viewed along the [100] axis. Roman numeral superscripts are defined in Table 5; positions IV and VI are eclipsed by V and IX respectively, while VII is nearer the reader than II

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* Owing to a typographical error, the m.p. of dibenzo-24-crown-8 is incorrect in ref. 1. The m.p. should read 103—104°.

0.90 cm^{-1} calculated from values in ref. 13. Single-crystal diffraction intensities measured by counter.

Intensities were collected in shells of reciprocal space from 2θ 2.5° to 40°; individual reflections were measured up to four times, and the results of repetitive measurements averaged. A standard reflection, $(51\bar{5})$, measured after every 20 reflections showed no evidence for crystal decomposition. Scans at 0.5° min^{-1} were made from 0.5° below the Mo-K_{α_1} to 0.6° above the K_{α_2} peak in the θ—2θ mode, and backgrounds were counted for 25 s at the ends of each scan. Lorentz and polarisation factors (*LP*) were applied, and standard deviations were calculcated from the formula $\sigma^2_{(F)} = \sigma^2(I)/4.I.LP$ where $\sigma^2(I)$ = total count + (0.25 × background sum) × (scan time/background time)^2. Of 1 080 unique reflections measured, 552 were considered unobserved either because the intensity (I) was <0 (in which case, it was set to 1.0), or if the intensity was $<2\sigma(I)$.

Structure Determination.—The K curve method[14] was used to calculate E values for all reflections. The signs of reflections having $|E| \geqslant 1.8$ were obtained from a multisolution method using the Σ_2 triplet relationships in the sequence of programs described in ref. 15; the starting set comprised the three origin-defining reflections and five other reflections whose signs were systematically varied for 32 sets of signs. The three sets with highest consistency indices were extended to include reflections having $|E| \geqslant 1.4$, and E maps were calculated; the third one revealed all the carbon and oxygen atom positions. Structure factors were calculated and R was reduced from 0.47 to 0.21 in the first cycle of isotropic refinement. A Fourier difference synthesis revealed the hydrogen atoms in positions close to those expected to complete tetrahedral or trigonal bonding about carbon atoms. Refinement by full-matrix least-squares, allowing anisotropic vibration for carbon and oxygen atoms, with scattering factors from ref. 16, and isotropic vibration for hydrogen atoms, with scattering factors from ref. 17, gave a final R value of 0.11 for all reflections, and of 0.03 for the 528 observed reflections. The function minimised by the program NUCLS[18] was $\Sigma W(|F_o| - |F_c|)^2$ with the weighting scheme $W = W$ (counting)/(0.241 + 0.062 $|F_o|$); the final R' was 0.04. Measured and calculated structure factors are listed in Supplementary Publication No. SUP 21692 (6 pp., 1 microfiche).* Bond lengths and angles, with errors, were calculated by the program ORFFE,[18] from the variance–covariance matrix of the final cycle of refinement of the atomic co-ordinates. Torsion angles, mean planes through groups of atoms, and inter- and intramolecular contacts were calculated on an IBM 1130 computer.[19]

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* See Notice to Authors in *J.C.S. Perkin II*, 1975, Index issue.

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