Crystal Structures of Complexes between Alkali-metal Salts and Cyclic Polyethers. Part IV.[1] The Crystal Structures of Dibenzo-30-crown-10 (2,3:17,18-dibenzo-1,4,7,10,13,16,19,22,25,28-decaoxacyclotriaconta-2,17-diene) and of its Complex with Potassium Iodide

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The crystal structures of the title compounds have been determined from *X*-ray diffractometer observations. The molecules of the cyclic ether are centrosymmetric with $Z = 2$ in a monoclinic unit cell having $a = 16{\cdot}960$, $b = 8{\cdot}920$, $c = 9{\cdot}096$ Å, $\beta = 90{\cdot}03°$, and space group $P2_1/c$. They form loops approximately parallel to the *a* axis. The structure was solved by the iterative application of Sayres' equation, and refined by least-squares methods to *R* 0·056 for 1414 independent observations.

In the complex $Z = 4$ in an orthorhombic unit cell having $a = 19{\cdot}576$, $b = 12{\cdot}405$, and $c = 12{\cdot}965$ Å with space group *Pnna*. The structure was solved by conventional Patterson and Fourier methods and refined by least-squares techniques to *R* 0·046 for 1102 independent observations. Each potassium ion lies on a two-fold axis, and is enclosed by a ligand molecule wrapped round to give ten K–O distances in the range 2·850(6)—2·931(6) Å. The iodide ions also lie on two-fold axes and are not in contact with potassium. The packing of the complex cations and the iodide ions is a distorted sodium chloride structure.

Bond lengths and angles in the complexed and free molecules are the same; the conformations are different. Four of the C–C–O–C angles change from *trans* in the free molecule to *gauche* in the complex; the remaining torsion angles are of the same type in both forms but corresponding ones differ by as much as 30° and the sign may be reversed.

EXPERIMENTS on cation transport with mitochondria[2] and with artificial[3] and natural membranes[4] showed that much higher concentrations of macrocyclic polyethers than of naturally occurring cyclic antibiotics were required to produce comparable effects. Three cyclic antibiotics with strong selectivity for potassium have been shown to form crystalline complexes with the potassium ion enclosed by oxygen atoms at the corners of octahedra (enniatin B[5] and valinomycin[6]) or of a cube (nonactin).[7] By contrast the cyclic ether complexes of known structure derived from dibenzo-18-crown-6[8-10] or benzo-15-crown-5[1] have the ether oxygens arranged in a plane round the cation with the axial positions available for interaction with solvent and anion.

To discover whether a larger ether could enclose a potassium ion we determined the crystal structure of the complex formed between potassium iodide and dibenzo-30-crown-10 and, as described in a preliminary report,[9] found the ligand was wrapped round the cation 'like the seam of a tennis ball'.[7] Stability-constant measurements[11] for a series of macrocyclic ethers indicated that complete enclosure of the cation is also found in solution with this ligand, which gives a particularly high ratio for the stability constant of the potassium compared with that for the sodium complex.

Dibenzo-30-crown-10 is systematically named 2,3:17,18-dibenzo-1,4,7,10,13,16,19,22,25,28-decaoxacyclotriaconta-2,17-diene and is shown with the crystallographic numbering of the atoms in Figure 1.

We now report determinations of the crystal structures of the potassium iodide complex and of the macrocyclic ether itself, and compare the dimensions and conformations of the two forms.

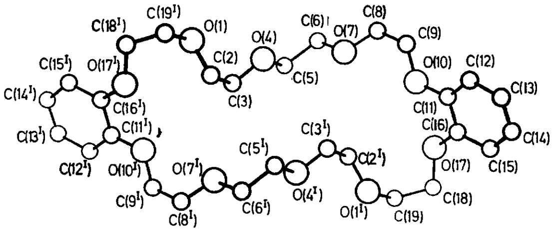

FIGURE 1 Dibenzo-30-crown-10 showing the designations of the atoms. The Roman superscript I denotes relation by a crystallographic element of symmetry. (In the drawing the conformation of an uncomplexed molecule is shown so the symmetry element is a centre)

The potassium iodide complex crystallises in the orthorhombic system with the potassium and iodide ions on crystallographic two-fold axes. The cyclic ether is wrapped round the potassium (Figure 2). The macrocyclic ether gives monoclinic crystals in which the molecules are necessarily centrosymmetrical (Figure 3).

In Table 1, the bond lengths and angles in the complex and the ligand are given; corresponding ones are the same within experimental error, except for small variations of angles in the ether chains. In both forms the benzene ring is planar, maximum deviations being 0·014 Å in the free and 0·015 Å in the complexed molecule. O(10) and O(17) are on opposite sides of this

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[1] Part III, M. A. Bush and M. R. Truter, preceding paper.

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[6] M. Pinkerton, L. K. Steinrauf, and P. Dawkins, *Biochem. Biophys. Res. Chem.*, 1969, **35**, 512.

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[8] D. Bright and M. R. Truter, *J. Chem. Soc.* (*B*), 1970, 1544.

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[11] H. K. Frensdorff, *J. Amer. Chem. Soc.*, 1971, **93**, 600.

plane by 0·055 and 0·025 Å, respectively, in the free molecule and 0·056 and 0·077 Å, respectively, in the complex.

The difference between the two forms is one of conformation. Torsion angles for both forms are given in Table 2. These show two features also found in the other cyclic ethers. One is that the torsion angle about the aliphatic C–C bond is *ca.* 60° corresponding to the *gauche* conformation, the other is that the C–C–O–C torsion angles are often close to 180 °. The main differences are that the four angles, about C(19$^{\mathrm{I}}$)–O(1) and C(3)–O(4) and the symmetry-related pairs, are *trans*, when uncomplexed, and *gauche* in the complex; there are also changes of sign for eight angles. Further, angles of the same type (*i.e. trans* or *gauche*) may differ by up to 30°.

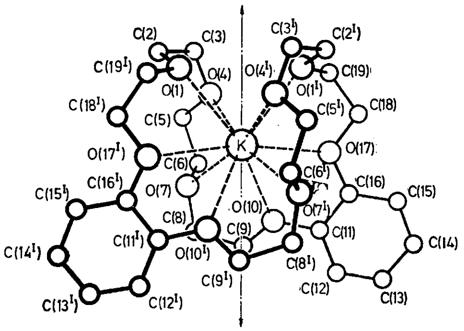

FIGURE 2 One complex cation (dibenzo-30-crown-10)-potassium; the crystallographic two-fold axis shown by the arrows relates the halves of the ligand

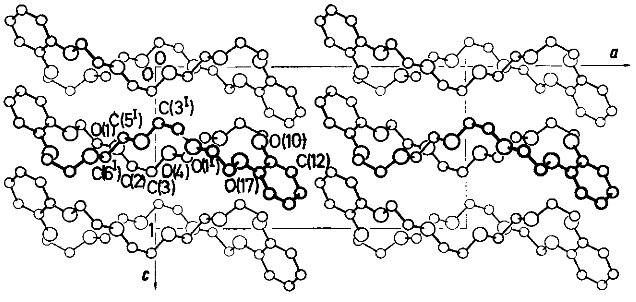

FIGURE 3 The structure of dibenzo-30-crown-10 projected along the [*b*] axis. The designations of some of the atoms are shown, those with Roman numeral superscripts, I, are related to those without by the centre of symmetry at 0, $\frac{1}{2}$, $\frac{1}{2}$. Molecules in heavy lines have their centres at $y = \frac{1}{2}$, those in lighter lines have their centres at $y = 0$

The conformation of an uncomplexed cyclic ether determined by crystal structure analysis may be a consequence of the crystal packing and lattice energy as well as of the conformational energy of the molecule. The conformation of a complexed ether, however, is also a function of the interactions it makes with the metal ion. This may be the most important factor as the conformation of the complexed form of the ether ' dibenzo-18-crown-6 ' has been found to be essentially the same in three different crystal packing environments.[8,10]

TABLE 1

Bond lengths (Å) and bond angles (°) in the complexed and free molecules. Here as elsewhere numbers in parentheses are the standard deviations, in the least significant digits

(*a*) Distances

	Complexed	Uncomplexed
O(1)–C(2)	1·39(1)	1·407(4)
C(2)–C(3)	1·51(1)	1·484(6)
C(3)–O(4)	1·40(1)	1·413(4)
O(4)–C(5)	1·42(1)	1·409(4)
C(5)–C(6)	1·48(1)	1·475(5)
C(6)–O(7)	1·42(1)	1·422(4)
O(7)–C(8)	1·43(1)	1·408(4)
C(8)–C(9)	1·50(1)	1·482(5)
C(9)–O(10)	1·41(1)	1·424(4)
O(10)–C(11)	1·37(1)	1·364(4)
C(11)–C(12)	1·40(1)	1·375(5)
C(12)–C(13)	1·36(1)	1·376(5)
C(13)–C(14)	1·40(1)	1·351(6)
C(14)–C(15)	1·36(1)	1·369(6)
C(15)–C(16)	1·37(1)	1·379(5)
C(16)–C(11)	1·39(1)	1·395(4)
C(16)–O(17)	1·35(1)	1·358(4)
O(17)–C(18)	1·42(1)	1·422(4)
C(18)–C(19)	1·48(1)	1·486(5)
C(19)–O(1$^{\mathrm{I}}$)	1·41(1)	1·405(4)

(*b*) Angles

C(19$^{\mathrm{I}}$)–O(1)–C(2)	115·4(8)	111·6(3)
C(3)–O(4)–C(5)	114·9(8)	112·3(3)
C(6)–O(7)–C(8)	114·4(7)	114·5(3)
C(9)–O(10)–C(11)	117·3(7)	118·3(3)
C(16)–O(17)–C(18)	118·8(7)	118·2(3)
O(1)–C(2)–C(3)	109·4(9)	110·6(3)
C(2)–C(3)–O(4)	112·8(9)	110·3(3)
O(4)–C(5)–C(6)	109·6(9)	111·0(3)
C(5)–C(6)–O(7)	108·3(9)	109·6(3)
O(7)–C(8)–C(9)	115·5(8)	112·5(3)
C(8)–C(9)–O(10)	109·3(8)	108·6(3)
O(17)–C(18)–C(19)	110·3(8)	108·3(3)
C(18)–C(19)–O(1$^{\mathrm{I}}$)	114·3(9)	110·6(3)
O(10)–C(11)–C(12)	123·6(9)	124·8(3)
O(17)–C(16)–C(15)	125·2(9)	125·6(4)
O(10)–C(11)–C(16)	116·9(8)	115·8(3)
O(17)–C(16)–C(11)	115·1(8)	115·7(3)
C(11)–C(12)–C(13)	119·5(10)	120·6(4)
C(12)–C(13)–C(14)	120·6(10)	120·1(4)
C(13)–C(14)–C(15)	119·7(10)	120·3(4)
C(14)–C(15)–C(16)	120·9(10)	120·9(4)
C(15)–C(16)–C(11)	119·7(9)	118·7(4)
C(16)–C(11)–C(12)	119·5(9)	119·4(3)

TABLE 2

Torsion angles (°)

	Complexed	Uncomplexed
C(18$^{\mathrm{I}}$)–C(19$^{\mathrm{I}}$)–O(1)–C(2)	79	177
C(19$^{\mathrm{I}}$)–O(1)–C(2)–C(3)	−176	−175
O(1)–C(2)–C(3)–O(4)	62	−72
C(2)–C(3)–O(4)–C(5)	85	177
C(3)–O(4)–C(5)–C(6)	−169	−180
O(4)–C(5)–C(6)–O(7)	69	−70
C(5)–C(6)–O(7)–C(8)	172	−169
C(6)–O(7)–C(8)–C(9)	62	95
O(7)–C(8)–C(9)–O(10)	44	−67
C(8)–C(9)–O(10)–C(11)	178	148
C(9)–O(10)–C(11)–C(16)	147	−154
O(10)–C(11)–C(16)–O(17)	−4	−2
C(11)–C(16)–O(17)–C(18)	−174	−174
C(16)–O(17)–C(18)–C(19)	175	165
O(17)–C(18)–C(19)–O(1$^{\mathrm{I}}$)	62	63

The dimensions in Table 1 are in good agreement with the corresponding ones found previously,[1,8,10] and in all it appears that the bond *e* (see Figure 4) is shorter than the other aromatic C–C bonds. The standard deviations of the mean bond length, however, when calculated on the basis of the spread of the individual values about this mean, indicate that the difference is not significant.

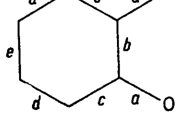

FIGURE 4 Diagram of a 'catechol' ring defining the different categories of bonds

The mean values (Å) with their estimated standard deviations and the number of bonds averaged are: *a* 1·36 ± 0·02, 20; *b* 1·40 ± 0·02, 10; *c* 1·39 ± 0·02, 20; *d* 1·39 ± 0·02, 20; and *e* 1·35 ± 0·03, 10.

In the complex, all ten oxygen atoms of the cyclic ether interact with the potassium ion, the distances (Table 3) ranging from 2·850(6)—2·931(6) Å mean 2·881 Å. This is a relatively compact arrangement for such a high co-ordination number; distances up to 3·06 Å are sometimes included for co-ordination numbers of eight or more. It compares with the compact eight-co-ordination by nonactin,[7] in which K–O ranges from 2·75 to 2·83 Å, mean 2·798 Å, and the increase in mean radius with co-ordination number agrees with the known trend.[12] The angles subtended at potassium between pairs of adjacent ether oxygen atoms are 53° for O(10)–K–O(17) and 58—60° for the remainder. Despite the crystallographic two-fold symmetry the ten atoms are not arranged in any of the regular geometrical figures discussed by King.[13] There is no set of five coplanar oxygen atoms: this is the only cyclic ether complex so far found which does not contain five or six coplanar oxygen atoms. The K–O–C angles are similar to the Na–O–C angles in the dibenzo-18-crown-6 [10] and the benzo-15-crown-5 [1] complexes and approximate to trigonal at the catechol oxygen atoms and tetrahedral at the others.

TABLE 3

Environment of the potassium ion

(*a*) Distances (Å)			
K–O(1)	2·850(6)	K–O(10)	2·895(6)
K–O(4)	2·879(6)	K–O(17)	2·931(6)
K–O(7)	2·850(6)		
(*b*) Angles (°) subtended by O–C–C–O			
O(1)–K–O(4)	60	O(10)–K–O(17)	53
O(4)–K–O(7)	59	O(17)–K–O(1^{I})	60
O(7)–K–O(10)	58		
(*c*) Angles (°) across the two-fold axis			
O(1)–K–O(1^{I})	76	O(10)–K–O(10^{I})	75
O(4)–K–O(4^{I})	118	O(17)–K–O(17^{I})	168
O(7)–K–O(7^{I})	127		

The packing of the complex is shown in Figure 5. It approximates to that of sodium chloride. The potassium ions are at: 0·508, ¼, ¼; 0·492, ¾, ¾; 0·008, ¼, ¾; and −0·008, ¾, ¼, giving a distorted face-centred cube. The iodide ions occupy the octahedral holes in this lattice but are displaced alternately above and below the centre points by *x*/*a* 0·17. There are no intermolecular distances <3·5 Å between non-hydrogen atoms; of the 26 contacts in the range 3·5—4·0 Å only one is to the iodide ion, that from C(18^{VIII}) at 3·95 Å.

As shown in Figure 3, the crown molecule consists of loops which are packed parallel to one another, somewhat similar to the loops of large saturated cyclic hydrocarbons, *e.g.* cyclotetratriacontane,[14] $[CH_2]_{34}$. Unlike the hydrocarbon however, the cyclic ether has no intramolecular contacts shorter than the sum of the van der Waals' radii. There are no unusual features about the packing; if hydrogen atoms are excluded there

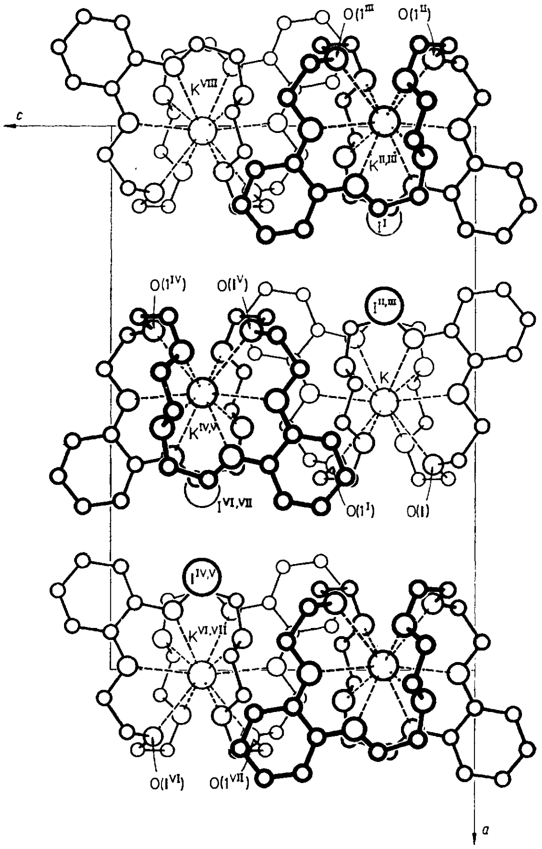

FIGURE 5 The structure of the (dibenzo-30-crown-10) potassium iodide complex projected along the *b* axis. Roman numeral superscripts refer to the equivalent positions relative to the molecular co-ordinates *x*, *y*, *z* shown in Table 4:

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

If the iodide ions were moved 3·3 Å along *a* to cover or be eclipsed by the potassium in the projection, the ions would occupy the same relative positions as in the sodium chloride lattice

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[12] R. D. Shannon and C. T. Prewitt, *Acta Cryst.*, 1969, *B*25, 925.

[13] R. B. King, *J. Amer. Chem. Soc.*, 1970, **92**, 6460.

[14] H. F. Fay and B. A. Newman, *Acta Cryst.*, 1968, *B*24, 615.

are three intermolecular distances <3·5 Å and all are contacts to oxygen atoms. These contacts are 3·34 Å between O(7) and C(19) in molecules related by translation along the *b* axis and 3·48 and 3·31 Å between C(15) and O(10) and O(17) respectively of molecules related by the *c* glide.

The difference in conformation found here is large compared with that found in the only naturally occurring compounds for which the crystal structures of free molecule [15] and complex [16] are known, monesin. Monesin is an acid held by hydrogen bonding into a cyclic form; it encloses an alkali metal (or silver) to form a neutral complex by changes in hydrogen bonding and by changes of not more than 17° in any dihedral angle. Monesin is not highly selective for potassium, in contrast with the neutral compounds valinomycin, enniatin-B, and nonactin. Hydrogen bonding is partly responsible for the conformation of valinomycin but not for that of the other two.

EXPERIMENTAL

(*a*) (*Dibenzo*-30-*crown*)-10-*potassium Iodide*

Synthesis.[17]—Potassium iodide (0·166 g) and dibenzo-30-crown-10 (0·55 g, giving a slight excess over a 1 : 1 ratio) were dissolved in methanol (20 ml) and set aside for a few hours. Some crystals of the ligand were deposited and removed by filtration. The filtrate was set aside overnight and gave colourless crystals of the *complex*, m.p. 116—118 °C (Found: C, 48·2; H, 5·7; I, 18·6. Calc. for $C_{28}H_{40}IKO_{10}$: C, 48·3; H, 5·8; I, 18·2%). As with the other aromatic crown compounds [18] a band at 965 cm^{-1} in the i.r. spectrum of dibenzo-30-crown-10 is absent in that of the complex. No bands appear in the hydroxy-stretching region, indicating that there is no solvation.

X-*ray Diffraction*.—Preliminary photographs showed that the crystal system was orthorhombic and the general conditions in reflections of $0kl$, $k + l = 2n$; $h0l$, $h + l = 2n$; $hk0$, $h = 2n$; $h00$, $h = 2n$; $0k0$, $k = 2n$, and $00l$, $l = 2n$ determined the space group as *Pnna*. The crystal density indicated $Z = 4$, hence the asymmetric unit comprised only one half of the formula unit so that the potassium ion and the iodide ion must each be situated either on a two-fold axis or on a centre of symmetry.

Crystal Data.—$C_{28}H_{40}IKO_{10}$, $M = 702{\cdot}7$, Orthorhombic, $a = 19{\cdot}576(6)$, $b = 12{\cdot}405(6)$, $c = 12{\cdot}965(4)$ Å, $U = 3148{\cdot}3$ Å^3, $D_m = 1{\cdot}51$ g cm^{-3}, $Z = 4$, $D_c = 1{\cdot}48$ g cm^{-3}, $F(000) = 1440$. Space group *Pnna* (D_{2h}^{6}, No, 52) uniquely determined. Mo-K_{α} radiation, $\lambda(K_{\alpha,1})$ 0·7093, $\lambda(K_{\alpha,2})$ 0·7135 Å (1 Å = 10^{-10} m), μ(Mo-$K_{\alpha,1}$) = 12·1 cm^{-1}, no correction applied. Molecular symmetry, two-fold axis.

The crystal used for the intensity determinations had dimensions 0·14 × 0·16 × 0·19 mm and was cut from a much larger one. It was set up on a Picker four-circle diffractometer with the *b* axis offset by *ca.* 15° from the ϕ axis, to reduce the chance of monitoring simultaneous reflections.* The centred positions of 12 reflections having a mean 2θ value of 30° were used to refine the orientation angles and unit-cell parameters.[19] Reflection intensities were measured for the *hkl* quadrant out to a 2θ value of 51° by the 2θ—θ scan method with a scan for each reflection from $2\theta\ \text{calc}_{(K\alpha1)} - 0{\cdot}5°$ to $2\theta\ \text{calc}_{(K\alpha2)} + 0{\cdot}5°$ at a rate of 0·5 °/min. Stationary background counts were monitored at the 2θ limits of the scans for 25 s each. The intensities of three standard reflections (6,0,0, 0,4,2, and 0,1,3) were measured every 50 reflections and the results used to place all the observations on a common scale. The observations were corrected for Lorentz and polarisation factors and reflections for which $I \leqslant 3\sigma_I$ (with σ_I derived as in ref. 8) were rejected; this produced 1102 independent structure amplitudes.

The mean value of $|F_o|$ for reflections having $h + l$ even was three times that for those having $h + l$ odd, thus suggesting that the iodide ions occupied the special positions '*d*' of the space group,[20] *i.e.* situated on two-fold axes parallel to the *a* axis. A three-dimensional Patterson synthesis verified this and yielded the co-ordinates of the iodide ions. Subsequent electron-density syntheses revealed the positions of all the remaining non-hydrogen atoms with the complex lying on the same two-fold axis as the iodide ion. Three cycles of full-matrix least-squares refinement [19] with scattering factors taken from ref. 21 carried out on the positional and isotropic vibrational atomic parameters and on one overall scale-factor, resulted in a conventional *R* of 0·075. Hydrogen atom co-ordinates were calculated [22] assuming C–H 0·95 Å and these were included in all further structure-factor calculations with scattering factors from ref. 23 and with isotropic temperature factors set at 5·0 Å^2. A weighting scheme of $\sigma = \dfrac{1}{w^2} = \sigma_{(\text{counting statistics})} + A|F_o| + B|F_o|^2$ was chosen and the coefficients *A* and *B* modified throughout the refinement such that $\Sigma w\Delta^2/n$ was reasonably constant when analysed in systematic ranges of $|F_o|$ and sin θ. Two cycles of refinement, with the scattering curve of iodide ion corrected for the effects of anomalous dispersion,[24] produced an *R* value of 0·052 and a subsequent electron-density difference synthesis showed peaks of 0·8 eÅ^{-3} near the iodide ion and smaller random peaks of <0·4 eÅ^{-3} elsewhere. The iodide ion was allowed an anisotropic vibration parameter whereupon two further cycles resulted in convergence at *R* 0·048 and R' $\{= (\Sigma w[|F_o| - |F_o|]^2/\Sigma w|F_o|^2)^{\frac{1}{2}}\}$ of 0·064. The structure refinement was concluded. Atomic co-ordinates and vibration parameters are in Table 4. Observed and calculated structure factors are listed in Supplementary Publication No. 20284 (17 pp., 1 microfiche).† An analysis of the agreement index for $h + l$ even or odd is given in Table 5.

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* On a mount designed by R. H. B. Mais and P. G. Owston, Imperial Chemical Industries Ltd.

† For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

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Table 4

Atomic co-ordinates ($\times 10^4$) and isotropic vibration parameters ($\times 10^2$) for the complex

	x/a	y/b	z/c	$B/Å^2$
I	1697(1)	2500(0)	2500(0)	*
K	5085(1)	2500(0)	2500(0)	292(5)
O(1)	6232(3)	2658(5)	1154(5)	331(13)
O(4)	5840(3)	0597(5)	1935(5)	363(14)
O(7)	4439(3)	0790(5)	1402(5)	345(14)
O(10)	3909(3)	1360(5)	3303(5)	315(13)
O(17)	4935(3)	1536(5)	4551(5)	296(13)
C(2)	6483(5)	1709(9)	0736(8)	439(24)
C(3)	6494(5)	0845(9)	1559(9)	445(25)
C(5)	5471(5)	−0170(9)	1343(8)	413(22)
C(6)	4752(5)	−0195(9)	1690(8)	410(22)
C(8)	3719(5)	0822(8)	1565(8)	371(22)
C(9)	3492(4)	0707(8)	2668(8)	359(22)
C(11)	3762(5)	1380(8)	4335(7)	279(19)
C(12)	3100(6)	1276(9)	4735(9)	432(24)
C(13)	3002(6)	1330(9)	5773(9)	463(25)
C(14)	3553(5)	1501(9)	6441(8)	414(23)
C(15)	4196(5)	1579(8)	6050(8)	362(21)
C(16)	4312(4)	1509(7)	5007(7)	276(18)
C(18)	5529(5)	1560(9)	5185(8)	362(22)
C(19)	6151(5)	1486(8)	4546(8)	393(22)
H(1,2) †	6910	1761	0406	500
H(2,2)	6161	1431	0194	500
H(3,3)	6757	1183	2116	500
H(4,3)	6734	0251	1324	500
H(5,5)	5665	−0857	1376	500
H(6,5)	5447	0051	0627	500
H(7,6)	4746	−0300	2451	500
H(8,6)	4518	−0836	1431	500
H(9,8)	3491	0292	1127	500
H(10,8)	3552	1519	1320	500
H(11,9)	3543	−0068	2838	500
H(12,9)	3017	0855	2726	500
H(13,12)	2715	1163	4271	500
H(14,13)	2545	1246	6052	500
H(15,14)	3470	1534	7181	500
H(16,15)	4585	1623	6540	500
H(17,18)	5501	0973	5703	500
H(18,18)	5544	2214	5605	500
H(19,19)	6101	0798	4192	500
H(20,19)	6529	1402	5012	500

* Anisotropic vibration parameters ($\times 10^4$) in the form:

$$\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)].$$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
I	26(1)	57(1)	61(1)	0(0)	0(0)	11(1)

† Hydrogen atom parameters were not refined. In the atom labelling, the number after the comma is that of the carbon atom to which the hydrogen is bonded.

Table 5

Variation of R with $|F_o|$ for the complex

$\|F_o\|$	R $h + l = 2n$	R $h + l = 2n + 1$
13·3—25·5	0·119	0·091
25·5—29·8	0·101	0·084
29·8—34·1	0·080	0·073
34·1—39·3	0·066	0·058
39·3—45·5	0·067	0·050
45·5—53·0	0·059	0·038
53·0—65·3	0·036	0·029
65·3—88·2	0·033	0·067
88·2—134·9	0·031	0·058
>134·9	0·030	0·017

(*b*) *Dibenzo*-30-*crown*-10

The compound [18] was recrystallised from methanol. Preliminary *X*-ray photographs showed that the crystals are monoclinic with space group $P2_1/c$. Density determination indicated $Z = 2$, so that the molecule must be centrosymmetric. The crystal used for the collection of intensities had dimensions 0·40 × 0·35 × 0·20 mm and was cut from a much larger one. It was set up on the diffractometer using 13 reflections having a mean 2θ value of 21° and observations were collected for the reflections of types *hkl* and *hkl* out to a 2θ value of 52° using the procedure

Table 6

Atomic co-ordinates ($\times 10^4$) and vibration parameters for the uncomplexed molecule. For the hydrogen atoms co-ordinates were not refined and all were assigned an isotropic temperature factor $\exp(-4{\cdot}5 \sin^2\theta/\lambda^2)$.

	x/a	y/b	z/c
O(1)	−1229(2)	2063(2)	5029(3)
C(2)	−0732(3)	1546(4)	6160(5)
C(3)	−0116(3)	2676(5)	6503(4)
O(4)	0446(1)	2731(3)	5359(2)
C(5)	1026(2)	3836(4)	5605(4)
C(6)	1601(2)	3872(4)	4391(4)
O(7)	2080(2)	2563(2)	4444(3)
C(8)	2739(3)	2598(4)	3504(4)
C(9)	3463(2)	3118(4)	4260(4)
O(10)	3366(1)	4656(2)	4640(2)
C(11)	3720(2)	5167(4)	5891(4)
C(12)	4382(2)	4548(4)	6519(5)
C(13)	4682(2)	5114(6)	7812(5)
C(14)	4326(3)	6286(6)	8477(4)
C(15)	3678(3)	6946(4)	7850(4)
C(16)	3367(2)	6408(4)	6552(4)
O(17)	2729(1)	6976(2)	5840(2)
C(18)	2393(2)	8330(4)	6378(4)
C(19)	1855(3)	8935(4)	5232(4)
H(1,2)	−0485	0640	5863
H(2,2)	−1037	1359	7018
H(3,3)	0136	2420	7401
H(4,3)	−0358	3635	6609
H(5,5)	1288	3644	6491
H(6,5)	0772	4792	5654
H(7,6)	1923	4737	4472
H(8,6)	1333	3899	3469
H(9,8)	2629	3246	2700
H(10,8)	2829	1612	3129
H(11,9)	3910	3016	3620
H(12,9)	3557	2543	5118
H(13,12)	2806	9034	6579
H(14,13)	2116	8135	7256
H(15,14)	2150	9085	4361
H(16,15)	1660	9868	5572
H(17,18)	4619	3707	6048
H(18,18)	5157	4676	8232
H(19,19)	4524	6654	9395
H(20,19)	3445	7797	8309

Anisotropic vibration parameters ($\times 10^4$) of the form

$$\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O(1)	0055(1)	0134(4)	0179(4)	0003(2)	0008(2)	0044(3)
C(2)	0061(2)	0194(7)	0186(6)	0036(3)	0040(3)	0071(6)
C(3)	0059(2)	0239(8)	0124(5)	0047(3)	0004(3)	0029(5)
O(4)	0055(1)	0176(4)	0140(3)	−0002(2)	0018(2)	−0019(3)
C(5)	0060(2)	0163(6)	0145(6)	0023(3)	−0016(3)	−0021(5)
C(6)	0051(2)	0127(5)	0179(6)	−0003(3)	−0011(3)	−0009(5)
O(7)	0061(1)	0114(3)	0223(4)	0008(2)	0032(2)	0015(3)
C(8)	0073(2)	0106(5)	0177(6)	−0003(3)	0021(3)	−0032(5)
C(9)	0063(2)	0126(5)	0175(6)	0012(3)	0029(3)	−0014(5)
O(10)	0064(1)	0111(3)	0151(4)	0011(2)	0001(2)	−0026(3)
C(11)	0043(2)	0120(5)	0137(5)	−0004(3)	0022(3)	0011(5)
C(12)	0048(2)	0160(6)	0198(7)	0004(3)	0021(3)	0023(5)
C(13)	0051(2)	0239(9)	0230(8)	−0022(4)	−0019(4)	0061(7)
C(14)	0076(3)	0232(9)	0164(7)	−0049(4)	−0023(4)	0018(7)
C(15)	0063(2)	0171(6)	0146(6)	−0028(3)	0013(3)	−0023(5)
C(16)	0042(2)	0133(6)	0137(5)	−0014(3)	0017(3)	0003(4)
O(17)	0051(1)	0120(3)	0169(4)	0007(2)	0009(2)	−0036(3)
C(18)	0052(2)	0123(5)	0224(7)	−0007(3)	0027(3)	−0042(5)
C(19)	0063(2)	0104(5)	0238(7)	0009(3)	0044(3)	0001(5)

described earlier. The standard reflections were 4,0,0, 0,1,4, and 1,5,0. The intensities were corrected for Lorentz and polarisation effects and those reflections for which $I \leqslant 2\sigma_I$ were rejected from the data set; this produced 1414 independent observations.

The structure was solved by the programme REL which applies Sayres' equation interatively to the E value triplets; the use of this programme has been reported previously.[25] E values were first computed [19] for all reflections; 233 of these were $>1{\cdot}30$ and these were used as input data for REL. Sixteen possible sets were produced; the set having the highest consistency index (0·81) also converged in the fewest cycles (7) and an E map based on these phases clearly showed all the non-hydrogen atom positions.

Three cycles of full-matrix least-squares refinement were carried out on the positional and isotropic vibrational atomic parameters and on one overall scale-factor to give R 0·24. The weighting scheme was applied as described for the complex. Two more cycles of refinement with the atoms allowed anisotropic vibration parameters reduced R to 0·12. Four more cycles were carried out in which the hydrogen atoms were included in the structure-factor calculations at positions calculated from the parameters of the previous cycle assuming C–H 0·95 Å, and isotropic temperature factors of 4·5 Å^2. Convergence was obtained at R and R' 0·056. A final electron-density difference synthesis showed only random fluctuations between $+0{\cdot}2$ and $-0{\cdot}2$ eÅ^{-3}. Atomic co-ordinates and vibration parameters are given in Table 6.

Crystal Data.—$C_{28}H_{40}O_{10}$, $M = 536{\cdot}7$, Monoclinic, $a = 16{\cdot}960(11)$, $b = 8{\cdot}920(9)$, $c = 9{\cdot}096(6)$ Å, $\beta = 90{\cdot}03(2)°$, $U = 1376{\cdot}0$ Å^3, $D_m = 1{\cdot}31$ g cm^{-3}, $Z = 2$, $D_c = 1{\cdot}30$ g cm^{-3}, $F(000) = 576{\cdot}0$. Space group, $P2_1/c$ (C^5_{2h}, No, 14), Mo-K_α radiation; μ(Mo-K_α) = 5·3 cm^{-1}. No correction applied. Molecular symmetry, centre.

Computing.—Full-matrix least-squares, some three-dimensional Fourier syntheses and the sign determinations were carried out on the London University CDC 6600 computer.[19] This was also used to calculate bond lengths and angles with their standard deviations derived from the variance–covariance matrix. Intermolecular distances and angles, torsion angles, and planes through groups of atoms, were calculated on the IBM 1130 computer.[22]

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