Structures of Two Isomeric Macrobicyclic Polyethers,* $C_{28}H_{42}O_8$, and the Potassium Perchlorate Complex of One

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Abstract

Isomer *A* of the compound 21,22,23,24,25,26,29,30, 31,32,33,34-dodecahydro-1,4,7,14,17,20,28,35-octa-oxa[2³,²⁹.2¹⁸,³⁴][7.7]orthocyclophane, $C_{28}H_{42}O_8$, crystallizes in $P2_1/a$ with $Z = 4$ in a unit cell having $a = 15\cdot613$ (2), $b = 21\cdot492$ (4), $c = 8\cdot021$ (1) Å, $\beta = 96\cdot99$ (2)°, $V = 2671\cdot4$ Å³. Anisotropic full-matrix refinement gave $R = 0\cdot038$ for 2163 reflections. The *cis* H atoms on the two cyclohexane/14-crown-4 ring junctions are on opposite sides so the relative configuration is $21R$, $26S$, $29S$ and $34R$. Isomer *B* is triclinic, $a = 8\cdot842$ (2), $b = 16\cdot702$ (6), $c = 10\cdot050$ (3) Å, $\alpha = 114\cdot10$ (3), $\beta = 98\cdot97$ (2), $\gamma = 91\cdot22$ (2)°, $V = 1332\cdot2$ Å³, with two molecules in $P\bar{1}$. $R = 0\cdot035$ for 2666 reflections. The *cis* H atoms on the two cyclohexane/14-crown-4 ring junctions are on the same side (relative configuration $21R$, $26S$, $29R$ and $34S$) and opposite to that of the $OCH_2CH_2OC_6$-$H_4OCH_2CH_2O$ bridge. The (1:1) complex of isomer *B* with potassium perchlorate is monoclinic with $Z = 4$ in $P2_1/c$, $a = 10\cdot990$ (2), $b = 14\cdot317$ (2), $c = 19\cdot583$ (3) Å, $\beta = 90\cdot64$ (2)°, $V = 3081\cdot1$ Å³. $R = 0\cdot074$ for 2795 reflections. In the complexed ion pair the K⁺ ion is coordinated by seven atoms of the ligand with K–O in the range 2·670–2·853 (4) Å, and one O atom of the perchlorate ion at 2·922 (10) Å; the eighth O atom of the ligand is at 3·145 (4) Å from the K⁺ ion. The complexed isomer *B* differs in conformation from that of the uncomplexed form. For all three compounds intensities were measured on an Enraf–Nonius CAD-4 diffractometer.

Introduction

Three isomeric macrobicyclic polyethers, *A*, *B* and *C*, have been synthesized and shown to have markedly different formation constants for complexing alkali-metal cations (Bandy, Parsons & Truter, 1981). The isomer with the highest complexing power, *B*, is purified by isolation of its crystalline complex with potassium perchlorate (Parsons, 1981). That with the lowest complexing power for alkali-metal cations, isomer *C*, crystallizes as a 1:1 adduct from methanol but unsolvated from ethanol; its crystal structure was reported briefly (Bandy *et al.*, 1981) and will be reported in detail in the following paper (Bandy, Hughes & Truter, 1982). We now describe the crystal structures of isomers *A* and *B* and of the potassium perchlorate complex of *B*. The structural formula and atom-numbering scheme for the isomeric polyethers are shown in Fig. 1. The cyclohexane entities were obtained (Bandy *et al.*, 1981) by reduction of the dibenzo-14-crown-4 diol with a catalyst which gives mainly *cis* addition. This means that both H atoms at the ring junctions are on the same side of the molecule and may be on either side with respect to O(4) and O(17) which
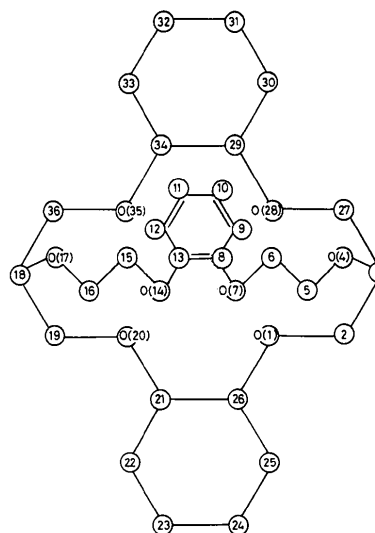

Fig. 1. Designations of the atoms. Numbers indicate C atoms; the H atoms, not shown, have the same number as the C atom, those of CH_2 groups being distinguished as H(*n*)a and H(*n*)b.

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are bridged by the benzene-ring-containing fragment to give the bicyclic molecule. We used crystal structure determination to establish the relative configurations of the isomers. We have found isomer B to have all four H atoms on the opposite side from the bridge and isomer A to have one pair of ring-junction H atoms on each side of the molecule. Investigation of the $KClO_4$ complex allows the changes in the ligand on complex formation to be studied, and provides comparison with the potassium complex of a similar macrobicyclic molecule in which all the six-membered rings are benzene (Hanson & Truter, 1981). The crystals are unsolvated so we hoped to avoid the problems encountered with disordered water in the potassium chloride complex of the all-benzo compound.

Experimental

Compounds were synthesized as described (Parsons, 1981) and form colourless crystals. Preliminary X-ray photographs indicated the space group and gave approximate unit-cell dimensions. Unit-cell dimensions quoted in the *Abstract* were obtained from 25 accurately positioned reflections of high θ value on the Enraf–Nonius CAD-4 diffractometer. A Guinier powder photograph was taken and indexed to show that the sample was of one phase and that the single crystal was representative of the bulk.

Intensities were collected on the CAD-4 diffractometer at 295 K using ω–2θ scans. Table 1 gives the values of the ω angle and of the horizontal aperture at the detector. For isomer A some observations in the $0kl$ zone were repeated with the ω angle $(0.6 + 0.35 \tan \theta)°$ to avoid overlap. The maximum time allowance for each measurement was 90 s. Three orientation-control reflections were measured after every 100 reflections and two intensity-control reflec-

tions (indices in Table 1) measured after every 3600 s exposure. In no case did the standards change significantly over the total period of exposure of the crystal.

The total number of independent observations for each structure, N_I, is given in Table 1 together with the number, N_F, used in the structure determination; these reflections were selected after application of Lorentz and polarization corrections, on the criterion that $|F| > 4\sigma(F)$.

All the structures were solved by direct methods with *SHELX* (Sheldrick, 1976). For isomer A the space group was determined uniquely; all the C and O atoms appeared in an E map (517 reflections with $E_{min} = 1.2$). Isotropic least-squares refinement and a difference synthesis revealed many of the H atoms in positions close to their calculated positions (C–H 0.98 Å). The latter were included with a common isotropic temperature factor in further refinement which, with the allowance of anisotropic vibration for the O atoms, led to an R value of 0.066. Individual isotropic vibration parameters for the H atoms did not reduce R. When the C atoms were allowed anisotropic vibration parameters R fell to 0.038 and the standard deviation in chemically equivalent bond lengths, calculated from the spread about the mean, was reduced from 0.017 to 0.011 Å.

Refinement converged with the R value, maximum shift and highest peak in the final difference map quoted in Table 1. The weighting scheme (Table 1) was satisfactory; there was no systematic variation in R with $\sin \theta/\lambda$ or $|F|$. Atomic coordinates are in Table 2.*

* Lists of structure factors, anisotropic vibration parameters, H-atom coordinates and deviations of atoms from selected mean planes for all three compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36948 (53 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Additional crystal data and experimental conditions*

	Isomer A	Isomer B	Isomer $B.KClO_4$
M_r	506·6	506·6	645·2
D_m (Mg m^{-3})	1·26	1·28	1·39
D_c (Mg m^{-3})	1·260	1·263	1·392
$F(000)$	1096	548	1364
λ(Mo $K\alpha_1$) (Å)	0·70926	0·70926	0·70926
μ(Mo $K\alpha$) (mm^{-1})	0·085	0·085	0·315
Crystal dimensions (mm)	0·25 × 0·23 × 0·30	0·23 × 0·20 × 0·25	0·33 × 0·28 × 0·41
ω scan angle (°)	1·2 + 0·35tan θ	0·75 + 0·35tan θ	0·8 + 0·35tan θ
Aperture (mm)	1·4 + 2·5tan θ	1·5 + 4·0tan θ	1·05 + 2·5tan θ
Range of θ (°)	1·75 to 22	1·0 to 23	1·4 to 22
Intensity control	$\bar{2}63, \bar{3}31$	$1\bar{3}2, 47\bar{2}$	$25\bar{5}, 2\bar{2}2$
N_I	3528	3983	4218
N_F	2163	2666	2795
R	0·0376	0·0352	0·074
w	1·2589/$\sigma^2_{(F)}$	0·7245/$\sigma^2_{(F)}$	5·7292/$\sigma^2_{(F)}$
Shift/e.s.d.	0·037	0·063	0·099
Maximum residual peak (e Å^{-3})	0·127	0·175	0·92

Table 2. *Atomic coordinates* $(\times 10^4)$ *and* U_{eq} *values* $(\mathring{A}^2 \times 10^3)$ *for isomer A*

$$U_{eq} = \tfrac{1}{3}\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* (\mathbf{a}_i \cdot \mathbf{a}_j).$$

	x	y	z	U_{eq}
O(1)	−1718 (1)	956·3 (8)	1986 (2)	44·2 (7)
C(2)	−1478 (2)	800 (1)	374 (3)	44 (1)
C(3)	−736 (2)	1198 (1)	−64 (3)	36 (1)
O(4)	37 (1)	958·7 (8)	842 (2)	43·1 (7)
C(5)	798 (2)	1045 (1)	85 (3)	43 (1)
C(6)	1543 (2)	931 (1)	1408 (3)	49 (1)
O(7)	2315 (1)	994·2 (9)	623 (2)	54·6 (8)
C(8)	3070 (2)	811 (1)	1555 (4)	46 (1)
C(9)	3531 (2)	336 (1)	942 (4)	54 (1)
C(10)	4316 (2)	158 (2)	1752 (5)	65 (2)
C(11)	4648 (2)	455 (2)	3199 (5)	68 (2)
C(12)	4192 (2)	930 (2)	3855 (4)	58 (1)
C(13)	3401 (2)	1108 (1)	3047 (4)	48 (1)
O(14)	2918 (1)	1583 (1)	3594 (2)	57·8 (8)
C(15)	3031 (2)	1720 (1)	5360 (4)	60 (1)
C(16)	2234 (2)	2044 (1)	5757 (4)	57 (1)
O(17)	1545 (1)	1616·6 (8)	5493 (2)	49·5 (8)
C(18)	697 (2)	1853 (1)	5507 (3)	41 (1)
C(19)	132 (2)	1298 (1)	4956 (3)	43 (1)
O(20)	−750 (1)	1464·3 (8)	4978 (2)	47·8 (8)
C(21)	−1320 (2)	948 (1)	4955 (3)	44 (1)
C(22)	−2193 (2)	1194 (1)	5272 (4)	52 (1)
C(23)	−2836 (2)	668 (1)	5378 (4)	61 (1)
C(24)	−2896 (2)	260 (1)	3816 (4)	56 (1)
C(25)	−2014 (2)	21 (1)	3486 (4)	49 (1)
C(26)	−1392 (2)	558 (1)	3346 (3)	41 (1)
C(27)	−893 (2)	1865 (1)	384 (3)	43 (1)
O(28)	−292 (1)	2275·2 (8)	−241 (2)	40·9 (7)
C(29)	−180 (2)	2850 (1)	670 (3)	39 (1)
C(30)	−246 (2)	3384 (1)	−562 (4)	51 (1)
C(31)	481 (2)	3365 (1)	−1660 (3)	58 (1)
C(32)	1353 (2)	3365 (1)	−608 (4)	63 (1)
C(33)	1431 (2)	2832 (1)	652 (4)	52 (1)
C(34)	697 (2)	2847 (1)	1730 (3)	41 (1)
O(35)	790 (1)	2323·1 (8)	2827 (2)	44·1 (7)
C(36)	504 (2)	2423 (1)	4417 (3)	45 (1)

For isomer *B* structure determination followed the same pattern as for isomer *A*. The *E* statistics indicated the centrosymmetric space group *P*1̄; the first *E* map from 523 reflections (E_{min} = 1·3) showed all C and O atoms. H atoms were located in a difference map; their coordinates were obtained by calculation (C−H = 0·98 Å). For final full-matrix refinement they were given a common isotropic temperature factor, 0·057 (1) Å², while C and O atoms were allowed anisotropic vibration. Table 1 gives details at convergence. Atomic coordinates are in Table 3.

For the KClO₄ complex of isomer *B* we could not solve the structure from the Patterson synthesis. The sixth *E* map with 503 reflections (E_{min} = 1·3) revealed the K, Cl, five O and twenty C atoms. The remaining non-hydrogen atoms were located by successive isotropic refinements and difference syntheses which indicated anisotropic vibration for K and the ClO₄⁻ ion. Refinement with H atoms in calculated positions, C−H = 0·98 Å, with a common isotropic temperature

factor, the C and O atoms of the ligand with isotropic vibration parameters and the K atom and the atoms of the ClO₄⁻ ion with anisotropic vibration parameters gave R = 0·089. Attempts to fit the electron density to a model with the ClO₄⁻ ion disordered in two positions about the Cl—O(51) bond were not successful. All H-atom positions were checked in a difference map. In the final full-matrix refinement, O atoms of the ligand, and C atoms of the cyclohexane rings were also allowed anisotropic refinement; the common isotropic vibration parameter for the H atoms was 0·072 (3) Å². Convergence details are in Table 1. Atomic coordinates are in Table 4.

The computer programs involved were the CAD-4 processing program (Hursthouse, 1976) and *SHELX* (Sheldrick, 1976) for structure determination using the scattering factors for C, O, Cl and H included in that program and for K⁺ the analytical coefficients in *International Tables for X-ray Crystallography* (1974).

Table 3. *Atomic coordinates* $(\times 10^4)$ *and* U_{eq} *values* $(\mathring{A}^2 \times 10^3)$ *for isomer B*

U_{eq} is defined in Table 2.

	x	y	z	U_{eq}
O(1)	11613 (2)	2345·7 (9)	5266 (1)	40·6 (6)
C(2)	11927 (3)	3281 (1)	5904 (2)	45 (1)
C(3)	10800 (2)	3699 (1)	5138 (2)	37·0 (9)
O(4)	9318 (2)	3355·8 (9)	5137 (2)	47·5 (7)
C(5)	8075 (3)	3864 (1)	5042 (3)	50 (1)
C(6)	6676 (3)	3243 (1)	4481 (3)	55 (1)
O(7)	5313 (2)	3656 (1)	4234 (2)	49·3 (7)
C(8)	5015 (2)	3699 (1)	2877 (2)	38 (1)
C(9)	5067 (3)	4506 (1)	2817 (3)	51 (1)
C(10)	4681 (3)	4556 (2)	1468 (3)	59 (1)
C(11)	4267 (3)	3804 (2)	187 (3)	57 (1)
C(12)	4201 (3)	2992 (1)	242 (2)	47 (1)
C(13)	4541 (2)	2933 (1)	1585 (2)	36 (1)
O(14)	4382 (2)	2172·8 (9)	1781 (1)	44·6 (7)
C(15)	4252 (3)	1341 (1)	534 (2)	45 (1)
C(16)	5745 (2)	1121 (1)	1 (2)	41 (1)
O(17)	6807 (2)	1077·9 (9)	1178 (1)	43·7 (7)
C(18)	8318 (2)	868 (1)	889 (2)	36·8 (9)
C(19)	9293 (2)	1142 (1)	2414 (2)	38 (1)
O(20)	10823 (2)	946 (1)	2193 (1)	43·6 (7)
C(21)	11929 (3)	941 (1)	3395 (2)	39 (1)
C(22)	11366 (3)	446 (1)	4222 (2)	46 (1)
C(23)	12737 (3)	322 (2)	5223 (3)	60 (1)
C(24)	13577 (3)	1208 (2)	6295 (2)	59 (1)
C(25)	14074 (3)	1738 (2)	5492 (2)	52 (1)
C(26)	12718 (2)	1846 (1)	4445 (2)	39 (1)
C(27)	11095 (2)	3485 (1)	3587 (2)	39 (1)
O(28)	9991 (2)	3851·2 (9)	2862 (1)	40·7 (7)
C(29)	10071 (3)	3656 (1)	1350 (2)	39 (1)
C(30)	8681 (3)	4013 (1)	787 (2)	53 (1)
C(31)	8561 (3)	3828 (2)	−846 (3)	68 (1)
C(32)	8568 (3)	2850 (2)	−1796 (3)	61 (1)
C(33)	9997 (3)	2513 (1)	−1230 (2)	48 (1)
C(34)	10127 (2)	2679 (1)	398 (2)	36·2 (9)
O(35)	8910 (2)	2209·5 (8)	640 (1)	35·3 (6)
C(36)	8943 (3)	1279 (1)	−26 (2)	37·6 (9)

Table 4. *Atomic coordinates* $(\times 10^4)$ *and isotropic thermal parameters* $(\mathrm{\AA}^2 \times 10^3)$ *for isomer* $B.\mathrm{KClO_4}$

U_{eq} values (defined in Table 2) are marked with an asterisk.

	x	y	z	U_{iso}/U_{eq}
K	7694 (1)	1845 (1)	1217·8 (7)	64·5 (6)*
O(1)	6271 (3)	1764 (3)	2356 (2)	54 (2)*
C(2)	4989 (6)	1764 (5)	2220 (3)	67 (2)
C(3)	4649 (6)	2203 (4)	1533 (3)	57 (2)
O(4)	5252 (4)	1676 (3)	1025 (2)	57 (2)*
C(5)	4916 (6)	1883 (5)	337 (3)	65 (2)
C(6)	5572 (6)	1241 (5)	−127 (4)	71 (2)
O(7)	6843 (4)	1450 (3)	−109 (2)	58 (2)*
C(8)	7589 (6)	946 (5)	−530 (3)	56 (2)
C(9)	7169 (7)	291 (5)	−1011 (3)	71 (2)
C(10)	8011 (7)	−168 (5)	−1403 (4)	77 (2)
C(11)	9192 (7)	−6 (5)	−1350 (4)	77 (2)
C(12)	9643 (7)	663 (5)	−868 (3)	65 (2)
C(13)	8821 (6)	1112 (5)	−467 (3)	56 (2)
O(14)	9152 (4)	1771 (3)	23 (2)	60 (2)*
C(15)	10419 (6)	1945 (5)	122 (3)	62 (2)
C(16)	10563 (6)	2704 (5)	628 (3)	63 (2)
O(17)	10092 (3)	2415 (3)	1262 (2)	50 (1)*
C(18)	10298 (6)	3037 (4)	1821 (3)	50 (2)
C(19)	9855 (6)	2558 (4)	2451 (3)	54 (2)
O(20)	8571 (3)	2461 (3)	2412 (2)	50 (2)*
C(21)	8016 (5)	2140 (4)	3021 (3)	46 (2)*
C(22)	8363 (6)	1121 (5)	3165 (4)	69 (3)*
C(23)	7719 (7)	752 (6)	3790 (4)	97 (4)*
C(24)	6369 (6)	881 (6)	3722 (4)	78 (3)*
C(25)	6047 (6)	1907 (5)	3598 (3)	65 (3)*
C(26)	6647 (5)	2255 (4)	2951 (3)	49 (2)*
C(27)	4891 (6)	3235 (5)	1479 (3)	59 (2)
O(28)	6160 (3)	3391 (3)	1431 (2)	52 (2)*
C(29)	6478 (6)	4353 (4)	1342 (3)	51 (2)*
C(30)	6513 (6)	4599 (5)	586 (3)	60 (3)*
C(31)	6897 (7)	5613 (5)	492 (4)	75 (3)*
C(32)	8075 (7)	5829 (5)	866 (4)	75 (3)*
C(33)	8007 (6)	5557 (4)	1618 (3)	61 (3)*
C(34)	7672 (6)	4532 (4)	1701 (3)	49 (2)*
O(35)	8551 (4)	3927 (3)	1401 (2)	52 (2)*
C(36)	9734 (6)	3997 (4)	1700 (3)	58 (2)
Cl	6986 (2)	−983 (2)	1612 (1)	79·6 (9)*
O(51)	5764 (5)	−871 (5)	1784 (3)	122 (3)*
O(52)	7171 (9)	−1719 (6)	1224 (6)	228 (6)*
O(53)	7389 (9)	−181 (7)	1286 (7)	249 (7)*
O(54)	7683 (9)	−1006 (9)	2150 (5)	241 (7)*

These programs were run on the ICL System 4 in Rothamsted Experimental Station. For molecular geometry Owen's (1981) program on the Prime 550 computer was used.

Results and discussion

Bond lengths for the organic molecules are in Table 5. Also shown are mean values for the C_{sp^3}—C_{sp^3} and C_{sp^3}—O bond lengths with, in parentheses, the standard deviation in the mean and, in square brackets, the e.s.d. in an individual value which is approximately twice that given by inversion of the least-squares matrix.

Despite the larger R value, results for the complex are as consistent as for the uncomplexed molecules. The indication that the difference between the observed and calculated model is not entirely random as assumed in ΔF is quite usual. In the *Discussion* this will be allowed for.

The mean values for corresponding bonds, including C_{sp^2}—C_{sp^2} and C_{sp^2}—O, are not significantly different in all three compounds nor are individual values with σ as derived from the spread. All the C_{sp^3}—C_{sp^3} bonds, not only those between two O atoms, are shorter than the standard value of 1·54 Å. Even with a cautious approach for the σ values, there are highly significant differences in the bond angles at O(20) and C(21).

Stereoviews of each of the three molecules are shown in Fig. 2. All the cyclohexane rings are in the more stable chair form and, as expected, the H atoms at the ring junctions are *cis*; taken together this means that at each ring junction one O atom is axial and one equatorial. If we consider a plane defined as the bridgehead C(3) and C(18) plus the ring-junction atoms C(21), C(26), C(29) and C(34), then the atoms O(4) to O(17) in the bridge are on one side. In isomer *A*, O(1) and O(20) are on the opposite side to the bridge and have the *anti* configuration, while O(28) and O(35) are on the same side with the *syn* configuration; O(1) and O(28) are the axial substituents of the cyclohexano rings. In isomer *B*, and its complex with KClO$_4$, by the same criterion, O(1), O(20), O(28) and O(35) are all *syn*, O(1) and O(35) are axial. For each structure the relative configurations, as seen in the stereoviews, can also be expressed quantitatively in terms of four planes through groups of atoms: (i) O(1), O(20), O(28), O(35), (ii) the benzene ring and also C(6), O(7), O(14), and C(15), (iii) and (iv) the best planes through the cyclohexane rings. C atoms in the cyclohexane rings are at approximately ±0·24 Å from the mean planes, and axial O atoms are 1·6 Å from these planes. Angles between the normals to the planes are in Table 6.

The striking difference between the uncomplexed isomer *B* and the other two compounds is in the relative orientation of the planes (i) and (ii). This is a consequence of the differences in torsion angles (Table 7); C(5)—C(6)—O(7)—C(8) and C(13)—O(14)—C(15)—C(16) are approximately *gauche* in isomer *B* and *trans* in isomer *A* and the complex. The complex differs from isomers *A* and *B* [torsion angles C(6)—O(7)—C(8)—C(9) and C(12)—C(13)—O(14)—C(15)] in such a way that C(6), O(7), O(14) and C(15) are nearly coplanar with the benzene ring in the complex but not in the other compounds. Differences around O(35) for isomer *A* compared with isomer *B* are mainly attributable to it being equatorial instead of axial. At O(28) there are more subtle differences and both the O(28)—C(29) torsion angles are more than 30° from the sterically more favourable ±60 or 180° for isomer

Table 5. *Bond lengths (Å) and angles (°) for the ligand*

Table 5 *(cont.)*

	Isomer A	Isomer B	Isomer B.KClO$_4$
O(1)–C(2)	1·429 (3)	1·427 (2)	1·430 (8)
O(1)–C(26)	1·431 (3)	1·433 (2)	1·419 (7)
C(2)–C(3)	1·515 (3)	1·517 (3)	1·529 (9)
C(3)–O(4)	1·426 (3)	1·419 (2)	1·419 (7)
C(3)–C(27)	1·507 (4)	1·516 (3)	1·506 (9)
O(4)–C(5)	1·411 (3)	1·418 (3)	1·422 (7)
C(5)–C(6)	1·496 (4)	1·475 (3)	1·485 (9)
C(6)–O(7)	1·433 (3)	1·439 (3)	1·429 (8)
O(7)–C(8)	1·374 (3)	1·380 (2)	1·375 (7)
C(8)–C(9)	1·373 (4)	1·375 (3)	1·403 (9)
C(8)–C(13)	1·399 (4)	1·396 (3)	1·378 (9)
C(9)–C(10)	1·370 (4)	1·382 (3)	1·376 (9)
C(10)–C(11)	1·370 (5)	1·372 (3)	1·321 (10)
C(11)–C(12)	1·384 (4)	1·380 (3)	1·431 (10)
C(12)–C(13)	1·378 (4)	1·380 (3)	1·365 (9)
C(13)–O(14)	1·372 (3)	1·370 (2)	1·392 (7)
O(14)–C(15)	1·437 (3)	1·428 (2)	1·425 (7)
C(15)–C(16)	1·493 (4)	1·499 (3)	1·478 (9)
C(16)–O(17)	1·412 (3)	1·418 (2)	1·413 (7)
O(17)–C(18)	1·418 (3)	1·432 (2)	1·426 (7)
C(18)–C(19)	1·516 (4)	1·516 (3)	1·498 (8)
C(18)–C(36)	1·515 (4)	1·511 (3)	1·526 (8)
C(19)–O(20)	1·424 (3)	1·428 (3)	1·419 (7)
O(20)–C(21)	1·422 (3)	1·433 (2)	1·422 (7)
C(21)–C(22)	1·512 (4)	1·516 (3)	1·534 (9)
C(21)–C(26)	1·531 (4)	1·518 (3)	1·517 (8)
C(22)–C(23)	1·519 (4)	1·524 (3)	1·515 (9)
C(23)–C(24)	1·522 (4)	1·519 (3)	1·499 (10)
C(24)–C(25)	1·523 (4)	1·518 (3)	1·529 (10)
C(25)–C(26)	1·522 (4)	1·533 (3)	1·520 (8)
C(27)–O(28)	1·423 (3)	1·423 (2)	1·416 (7)
O(28)–C(29)	1·435 (3)	1·431 (2)	1·432 (7)
C(29)–C(30)	1·511 (3)	1·509 (3)	1·524 (8)
C(29)–C(34)	1·521 (4)	1·525 (3)	1·503 (8)
C(30)–C(31)	1·519 (4)	1·526 (3)	1·523 (10)
C(31)–C(32)	1·511 (4)	1·519 (3)	1·513 (10)
C(32)–C(33)	1·523 (4)	1·518 (3)	1·527 (9)
C(33)–C(34)	1·516 (4)	1·529 (3)	1·522 (8)
C(34)–O(35)	1·426 (3)	1·426 (2)	1·429 (7)
O(35)–C(36)	1·418 (3)	1·422 (2)	1·424 (7)

Mean

	Isomer A	Isomer B	Isomer B.KClO$_4$
C$_{sp^3}$–C$_{sp^3}$	1·515 (2) [9]	1·516 (3) [12]	1·514 (3) [12]
C$_{sp^3}$–O	1·425 (2) [8]	1·427 (2) [6]	1·423 (2) [6]

	Isomer A	Isomer B	Isomer B.KClO$_4$
C(26)–O(1)–C(2)	116·2 (2)	116·4 (2)	115·5 (5)
O(1)–C(2)–C(3)	111·7 (2)	111·5 (2)	113·3 (6)
C(2)–C(3)–O(4)	107·6 (2)	105·5 (2)	106·7 (5)
C(2)–C(3)–C(27)	109·3 (2)	110·4 (2)	115·0 (6)
C(27)–C(3)–O(4)	112·0 (2)	112·6 (2)	112·9 (5)
C(3)–O(4)–C(5)	116·0 (2)	117·3 (2)	115·8 (5)
O(4)–C(5)–C(6)	107·2 (2)	105·9 (2)	109·1 (6)
C(5)–C(6)–O(7)	107·2 (2)	112·4 (2)	109·7 (6)
C(6)–O(7)–C(8)	116·5 (2)	114·9 (2)	117·7 (5)
O(7)–C(8)–C(9)	118·1 (3)	119·5 (2)	124·0 (6)
O(7)–C(8)–C(13)	122·5 (3)	120·2 (2)	116·5 (6)
C(13)–C(8)–C(9)	119·4 (3)	120·1 (2)	119·4 (7)
C(8)–C(9)–C(10)	121·1 (4)	119·8 (2)	118·4 (7)
C(9)–C(10)–C(11)	119·7 (3)	120·4 (2)	122·6 (8)
C(10)–C(11)–C(12)	120·4 (3)	120·0 (2)	120·1 (8)
C(11)–C(12)–C(13)	119·9 (3)	120·3 (2)	117·9 (7)
C(12)–C(13)–C(8)	119·5 (3)	119·3 (2)	121·6 (7)
C(8)–C(13)–O(14)	117·0 (3)	115·6 (2)	115·4 (6)
C(12)–C(13)–O(14)	123·5 (3)	125·0 (2)	123·1 (6)
C(13)–O(14)–C(15)	117·5 (2)	119·5 (2)	117·4 (5)
O(14)–C(15)–C(16)	107·5 (3)	112·6 (2)	108·5 (5)
C(15)–C(16)–O(17)	107·7 (2)	107·5 (2)	109·7 (5)
C(16)–O(17)–C(18)	117·4 (2)	116·4 (2)	115·8 (4)
O(17)–C(18)–C(19)	103·1 (2)	104·2 (2)	107·2 (5)
O(17)–C(18)–C(36)	114·0 (2)	115·0 (2)	112·5 (5)
C(36)–C(18)–C(19)	113·6 (2)	113·2 (2)	113·9 (5)
C(18)–C(19)–O(20)	109·2 (2)	106·7 (2)	109·4 (5)
C(19)–O(20)–C(21)	114·2 (2)	119·4 (2)	115·0 (4)
O(20)–C(21)–C(22)	107·6 (2)	115·0 (2)	110·7 (5)

	Isomer A	Isomer B	Isomer B.KClO$_4$
O(20)–C(21)–C(26)	114·8 (2)	113·8 (2)	108·9 (5)
C(26)–C(21)–C(22)	111·0 (2)	111·8 (2)	111·4 (5)
C(21)–C(22)–C(23)	111·4 (2)	109·0 (2)	111·2 (6)
C(22)–C(23)–C(24)	111·0 (2)	110·4 (2)	110·9 (6)
C(23)–C(24)–C(25)	111·7 (3)	111·8 (2)	111·0 (7)
C(24)–C(25)–C(26)	110·9 (2)	111·8 (2)	110·2 (5)
C(21)–C(26)–O(1)	107·4 (2)	108·0 (2)	107·5 (5)
C(25)–C(26)–O(1)	109·8 (2)	110·5 (2)	113·4 (5)
C(25)–C(26)–C(21)	109·5 (2)	109·0 (2)	109·1 (5)
C(3)–C(27)–O(28)	111·8 (2)	109·7 (2)	109·5 (5)
C(27)–O(28)–C(29)	113·5 (2)	115·9 (2)	113·7 (5)
O(28)–C(29)–C(30)	109·1 (2)	105·6 (2)	110·4 (5)
O(28)–C(29)–C(34)	109·1 (2)	113·6 (2)	108·7 (5)
C(34)–C(29)–C(30)	110·7 (2)	112·0 (2)	112·5 (5)
C(29)–C(30)–C(31)	111·2 (2)	112·2 (2)	110·3 (6)
C(30)–C(31)–C(32)	111·2 (2)	111·2 (2)	111·9 (6)
C(31)–C(32)–C(33)	111·4 (3)	109·7 (2)	111·4 (6)
C(32)–C(33)–C(34)	110·0 (2)	112·6 (2)	111·2 (6)
C(33)–C(34)–C(29)	111·9 (2)	110·2 (2)	109·0 (5)
C(29)–C(34)–O(35)	111·4 (2)	107·4 (2)	107·2 (5)
C(33)–C(34)–O(35)	107·9 (2)	112·4 (2)	112·1 (5)
C(34)–O(35)–C(36)	114·6 (2)	113·7 (2)	113·9 (4)
O(35)–C(36)–C(18)	109·5 (2)	110·5 (2)	111·5 (5)

A. Unfavourable angles of this kind occur at O(1)–C(2) in all the compounds. The possibility that they are compensated for by C—H···O hydrogen bonding is worth consideration.

Because the H-atom positions are calculated, distances involving them are treated only as indicators, and the corresponding C···O or C···C distances are quoted. In isomer *A* there are three intramolecular H···O distances less than 2·5 Å; the C···O distances are C(5)···O(28) 3·137 (3), C(19)···O(4) 3·365 (3) and C(6)···O(14) 2·956 (3) Å. The shortest calculated H···H contact is 2·28 Å between H(5)*b* and H(33)*b*. The packing arrangement is shown in Fig. 3; there are only two pairs of H···H contacts calculated at less than 2·4 Å; these are between H(18) and H(31)*b* at *x, y, z* + 1 and between H(31)*b* and H(36)*a* at *x, y, z* − 1. There is no intermolecular C—H···O bonding; the shortest such contact is 2·96 Å, H(25)*b*···O(17¹).

In isomer *B* there are two intramolecular C—H···O contacts less than 2·5 Å; C(6)···O(14) = 2·974 (3) and C(5)···O(28) = 2·965 (3) Å; the minimum calculated H···H distance is 2·33 Å from H(19)*b* to H(27)*a*. The packing of isomer *B* is shown in Fig. 4. The shortest C—H···O distance is 3·353 (3) Å between C(9) and O(7¹) [and O(7)···C(9¹)], the calculated H···O being 2·47 Å. O(14) contacts a ring-junction hydrogen H(26¹¹¹) at 2·57 Å, with the O(14)···C(26¹¹¹) distance 3·467 (2) Å, so this cannot be considered a hydrogen bond. There are two calculated H···H distances less than 2·4 Å: 2·39 Å for H(10)···H(11¹¹) and 2·26 Å for H(24)*b*···H(12¹ⱽ).

In the potassium complex there are no short intramolecular contacts; the minimum H···O is H(16)*a*···O(35) 2·70 Å with C(16)···O(35)

3·218 (8) Å. Fig. 5 shows the packing in the complex. There are two calculated intermolecular distances less than 2·4 Å: H(22)a···H(33¹)b and H(23)b···H(36¹)a. There are no distances less than 3·5 Å between non-hydrogen atoms; there are ten interactions from perchlorate O atoms to H atoms in the range 2·56 to 3·0 Å. The complex seems slightly less efficiently packed than the uncomplexed molecules. For each of the three isomers, A, B and C, the volume occupied per molecule is 668 ± 2 Å³; in the KClO₄ complex of isomer B the additional volume corresponds to 104 Å³ per KClO₄ entity compared with 90·4 Å³ in crystalline KClO₄ (Greenberg & Walden, 1940). However, the packing interactions do not seem likely to be strong enough to account for unfavourable torsion angles.

Table 6. Angles (°) between normals to planes through various groups of atoms

Plane (i):	O atoms of 14-crown-4 ring [O(1)O(20)O(28)O(35)]
Plane (ii):	benzene ring C(8)–C(13)
Plane (iii):	cyclohexane ring C(21)–C(26)
Plane (iv):	cyclohexane ring C(29)–C(34)

Planes	Isomer A	Isomer B	Isomer B.KClO₄
(i)–(ii)	83·8 (1)	17·5 (1)	92·4 (1)
(i)–(iii)	60·3 (1)	37·3 (1)	31·6 (3)
(i)–(iv)	44·0 (1)	23·5 (1)	34·5 (3)
(ii)–(iii)	48·9 (1)	33·7 (1)	99·7 (2)
(ii)–(iv)	72·6 (1)	36·3 (1)	80·5 (2)
(iii)–(iv)	85·3 (1)	60·5 (1)	65·9 (2)

Deviations of the atoms from these planes have been deposited.

Comparison of the torsion angles in isomer B and its complex shows that the following have changed their type trans/gauche: C(3)–C(27), C(5)–C(6), C(6)–O(7), O(7)–C(8), O(14)–C(15), C(18)–C(19), O(20)–C(21), and O(28)–C(29). The addition of potassium has induced a more symmetrical conformation with C(3) and C(18) further apart and some O atoms closer together; for example, O(1)···O(7) from 6·12 to 4·90 Å, O(1)···O(28) from 4·27 to 2·95 Å, and O(14)···O(20) from 6·10 to 4·83 Å.

The environment of the K⁺ ion is shown in Fig. 2(c) and the dimensions of the K···O contacts are in Table 8. The K⁺ ion is approximately coplanar with O(1), O(4), O(7), O(14), O(17) and O(20) and receives additional interaction, on one side from a perchlorate O [curiously this is not the one with the lowest vibration O(51), but is O(53)] and, on the other, unsymmetrically from two O atoms on a cyclohexane ring.
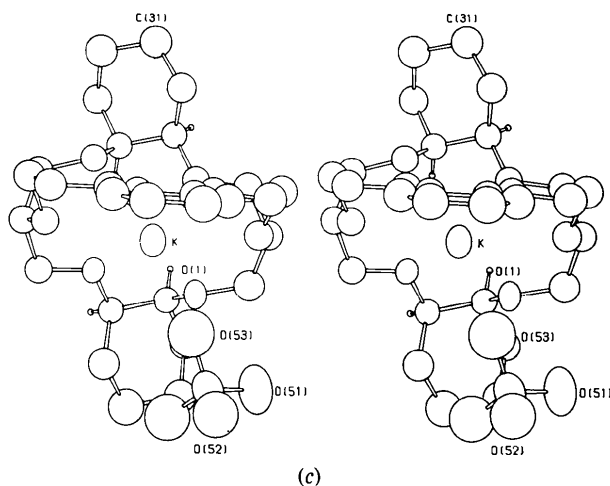

(a)

(b)

Fig. 2. Stereopairs drawn normal to the plane through O(1), O(20), O(28), and O(35) with the C(3)–O(4) and C(18)–O(17) bonds towards the reader. O atoms of the bicyclic molecules are shown as vibration ellipsoids while the C atoms are shown as circles corresponding to the equivalent isotropic vibration; sizes represent the 50% confidence level. H atoms at the cyclohexane ring junctions are depicted with arbitrary radii, others are omitted. (a) Isomer A. (b) Isomer B.

(c)

Fig. 2 (cont.) (c) Isomer B.KClO₄, with the K⁺ ion and Cl atoms shown as vibration ellipsoids. For clarity the O atoms of the perchlorate ion have been shown as equivalent isotropic circles for O(52), O(53) and O(54) and only O(51), which is not disordered, is shown as an ellipsoid.

Table 7. *Torsion angles* (°)

	Isomer A	Isomer B	Isomer B.KClO₄
C(26)–O(1)–C(2)–C(3)	–99·7 (2)	110·6 (2)	120·1 (6)
C(21)–C(26)–O(1)–C(2)	152·4 (2)	–158·4 (2)	177·7 (5)
C(25)–C(26)–O(1)–C(2)	–88·6 (3)	82·5 (2)	57·0 (7)
O(1)–C(2)–C(3)–O(4)	77·7 (3)	51·6 (2)	59·2 (7)
O(1)–C(2)–C(3)–C(27)	–44·0 (3)	–70·2 (2)	–66·8 (7)
C(2)–C(3)–O(4)–C(5)	151·0 (2)	155·7 (2)	171·1 (5)
C(27)–C(3)–O(4)–C(5)	–88·9 (3)	–83·9 (2)	–61·6 (7)
C(2)–C(3)–C(27)–O(28)	–170·6 (2)	177·6 (2)	73·0 (7)
O(4)–C(3)–C(27)–O(28)	70·3 (3)	60·1 (2)	49·8 (7)
C(3)–O(4)–C(5)–C(6)	164·4 (2)	158·4 (2)	–176·9 (5)
O(4)–C(5)–C(6)–O(7)	177·7 (2)	–176·3 (2)	–68·0 (7)
C(5)–C(6)–O(7)–C(8)	–170·0 (2)	84·7 (2)	–177·6 (5)
C(6)–O(7)–C(8)–C(9)	119·0 (3)	–114·9 (2)	5·0 (9)
C(6)–O(7)–C(8)–C(13)	–64·2 (4)	70·4 (3)	–175·4 (6)
O(7)–C(8)–C(9)–C(10)	175·7 (3)	–176·2 (2)	179·9 (6)
C(13)–C(8)–C(9)–C(10)	–1·2 (5)	–1·4 (4)	0·3 (10)
O(7)–C(8)–C(13)–C(12)	–175·3 (3)	177·9 (2)	–178·8 (6)
O(7)–C(8)–C(13)–O(14)	2·6 (4)	1·0 (3)	0·4 (9)
C(12)–C(13)–C(8)–C(9)	1·5 (5)	3·2 (3)	0·9 (10)
C(9)–C(8)–C(13)–O(14)	179·3 (3)	–173·8 (2)	–179·9 (6)
C(8)–C(9)–C(10)–C(11)	0·1 (5)	–0·9 (4)	–0·9 (12)
C(9)–C(10)–C(11)–C(12)	0·6 (5)	1·4 (4)	0·4 (12)
C(10)–C(11)–C(12)–C(13)	–0·3 (5)	0·5 (4)	0·7 (11)
C(11)–C(12)–C(13)–C(8)	–0·8 (5)	–2·7 (4)	–1·3 (10)
C(11)–C(12)–C(13)–O(14)	–178·5 (3)	173·9 (2)	179·5 (6)
C(8)–C(13)–O(14)–C(15)	154·9 (3)	–165·7 (2)	178·1 (6)
C(12)–C(13)–O(14)–C(15)	–27·4 (4)	17·5 (3)	–2·8 (9)
C(13)–O(14)–C(15)–C(16)	–157·3 (2)	73·1 (2)	176·4 (5)
O(14)–C(15)–C(16)–O(17)	65·9 (3)	61·2 (2)	63·1 (7)
C(15)–C(16)–O(17)–C(18)	–169·2 (2)	179·6 (2)	172·9 (5)
C(16)–O(17)–C(18)–C(19)	172·5 (2)	163·1 (2)	–174·0 (5)
C(16)–O(17)–C(18)–C(36)	49·0 (3)	38·5 (3)	60·1 (6)
O(17)–C(18)–C(19)–O(20)	177·7 (2)	180·0 (2)	–67·2 (6)
C(36)–C(18)–C(19)–O(20)	–58·5 (3)	–54·4 (2)	58·0 (7)
O(17)–C(18)–C(36)–O(35)	46·5 (3)	55·3 (2)	42·1 (7)
O(35)–C(36)–C(18)–C(19)	–71·2 (3)	–64·4 (2)	–80·2 (6)
C(18)–C(19)–O(20)–C(21)	–163·0 (2)	–165·7 (2)	–171·3 (5)
C(19)–O(20)–C(21)–C(22)	170·8 (2)	46·7 (3)	–68·4 (6)
C(19)–O(20)–C(21)–C(26)	–65·1 (3)	–84·1 (2)	168·9 (5)
O(20)–C(21)–C(22)–C(23)	–176·5 (2)	167·6 (2)	–176·7 (5)
C(26)–C(21)–C(22)–C(23)	57·2 (3)	–60·5 (3)	–55·4 (7)
O(20)–C(21)–C(26)–O(1)	–61·2 (3)	70·7 (2)	56·3 (6)
O(20)–C(21)–C(26)–C(25)	179·6 (2)	–169·2 (2)	179·6 (5)
O(1)–C(26)–C(21)–C(22)	61·0 (3)	–61·7 (2)	–66·1 (6)
C(25)–C(26)–C(21)–C(22)	–58·1 (3)	58·4 (2)	57·3 (7)
C(21)–C(22)–C(23)–C(24)	–54·7 (3)	57·9 (3)	54·4 (8)
C(22)–C(23)–C(24)–C(25)	54·1 (3)	–55·8 (3)	–56·6 (8)
C(23)–C(24)–C(25)–C(26)	–56·1 (3)	54·5 (3)	59·3 (8)
C(24)–C(25)–C(26)–O(1)	–60·3 (3)	64·0 (3)	60·9 (7)
C(24)–C(25)–C(26)–C(21)	57·3 (3)	–54·6 (3)	–58·8 (7)
C(3)–C(27)–O(28)–C(29)	–156·3 (2)	–176·4 (2)	177·0 (5)
C(27)–O(28)–C(29)–C(30)	–131·6 (2)	173·0 (2)	–89·8 (6)
C(27)–O(28)–C(29)–C(34)	107·3 (2)	50·0 (2)	146·4 (5)
O(28)–C(29)–C(30)–C(31)	–64·2 (3)	–177·9 (2)	–177·9 (5)
C(34)–C(29)–C(30)–C(31)	55·8 (3)	–53·8 (3)	–56·3 (7)
O(28)–C(29)–C(34)–C(33)	64·6 (3)	172·6 (2)	–179·1 (5)
O(28)–C(29)–C(34)–O(35)	–56·3 (3)	49·8 (2)	59·4 (6)
C(33)–C(34)–C(29)–C(30)	–55·5 (3)	53·1 (2)	58·3 (7)
C(30)–C(29)–C(34)–O(35)	–176·4 (2)	–69·7 (2)	–63·3 (6)
C(29)–C(30)–C(31)–C(32)	–56·3 (3)	55·3 (3)	53·1 (8)
C(30)–C(31)–C(32)–C(33)	55·5 (3)	–55·9 (3)	–53·7 (8)
C(31)–C(32)–C(33)–C(34)	–54·6 (3)	57·1 (3)	56·0 (8)
C(32)–C(33)–C(34)–C(29)	54·7 (3)	–55·6 (3)	–57·5 (7)
C(32)–C(33)–C(34)–O(35)	177·6 (2)	64·2 (2)	61·0 (7)
C(29)–C(34)–O(35)–C(36)	–89·3 (3)	–172·1 (2)	–178·5 (5)
C(33)–C(34)–O(35)–C(36)	147·6 (2)	66·5 (2)	61·9 (6)
C(34)–O(35)–C(36)–C(18)	–175·8 (2)	148·0 (2)	135·8 (5)

Complex formation also induced a more symmetrical conformation for the macrobicyclic polyether in which all six-membered rings are benzene (Hanson & Truter, 1981). In that complex a noncrystallographic plane of symmetry passes through the midpoints of two bonds in each benzene ring: C(8)–C(13), C(10)–C(11) and C(26)–C(21), C(24)–C(23), C(29)–C(34) and C(31)–C(32). (The corresponding symmetry is not possible with cyclohexane rings in the
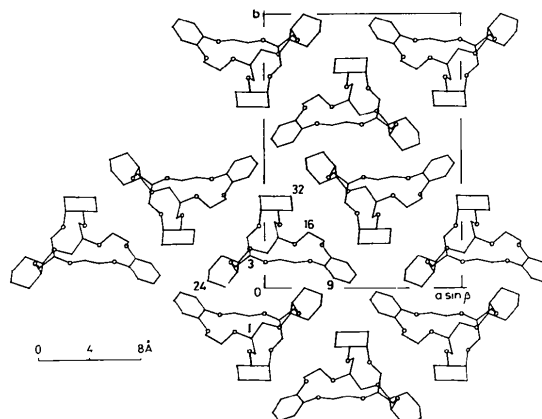

Fig. 3. Packing of isomer A viewed down c; O atoms are indicated as circles, and H atoms are omitted. Some atoms of the crystal-chemical unit are numbered. I indicates the molecule at –x, –y, 1 – z.
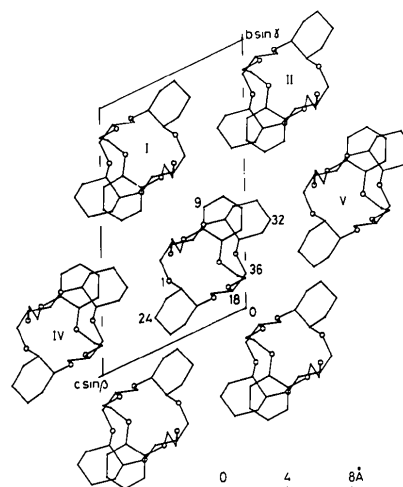

Fig. 4. Packing of isomer B viewed down a. Roman numerals denote the molecules at the following positions compared with the atomic coordinates in Table 3: (I) 1 – x, 1 – y, 1 – z; (II) 1 – x, 1 – y, –z; (III) x – 1, y, z; (IV) x + 1, y, z + 1; (V) x – 1, y, z – 1.

chair form.) The K⁺ ion is nearly centrally situated in an end-capped trigonal prism, the capping atoms O(4) and O(7) (both C_{sp^3}–O) being at 2·687 (7) Å and the others (C_{sp^2}–O) at 2·733 (5) Å, and has no interactions with the anion or solvent (Hanson & Truter, 1981). The all-benzo ligand has a slightly higher formation constant for KBr in methanol solution, 5·7 × 10⁸ l mol⁻¹ (Hanson, Parsons & Truter, 1979) than the dicyclohexano isomer B, 1·5 × 10⁸ l mol⁻¹ (Bandy et al., 1981). Complete enclosure of the metallic cation is correlated with high formation constants.

The six approximately coplanar O atoms deviate from a regular hexagon as shown by the angles (Table 8), ranging from 54·4 (1)° for O(7)–K–O(14) to
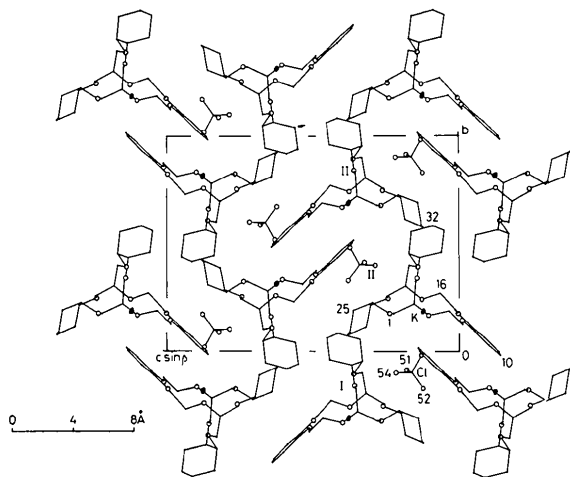
Fig. 5. Packing of isomer $B.KClO_4$ viewed down a. K^+ ions are indicated by full circles, O atoms by open circles; H atoms are omitted; bonds to K^+ ions are not shown. The designations of some atoms of the crystal-chemical unit are given. I indicates the K complex at $2 - x, y - \frac{1}{2}, \frac{1}{2} - z$, and II the perchlorate ion and the K complex at $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$.

Table 8. *Environment of the* K^+ *ion in the isomer* $B.KClO_4$ *complex*

(a) K—O bond lengths (Å)

K⋯O(1)	2·740 (4)	K⋯O(20)	2·670 (4)
K⋯O(4)	2·717 (4)	K⋯O(28)	2·816 (4)
K⋯O(7)	2·809 (4)	K⋯O(35)	3·145 (4)
K⋯O(14)	2·853 (4)	K⋯O(53)	2·922 (10)
K⋯O(17)	2·760 (4)		

(b) Angles (°) subtended at potassium in the form Oa—K—Ob; all e.s.d.'s are 0·1°, except those involving O(53) which are 0·2–0·3°

Ob Oa	O(1)	O(4)	O(7)	O(14)	O(17)	O(20)	O(28)	O(35)
O(4)	62·4							
O(7)	123·8	62·3						
O(14)	175·4	116·5	54·4					
O(17)	122·7	166·5	113·4	59·4				
O(20)	60·3	119·9	171·9	122·0	62·6			
O(28)	64·2	59·9	95·8	119·6	109·6	79·7		
O(35)	96·9	113·2	113·1	87·6	55·3	58·8	54·4	
O(53)	81·6	78·7	78·8	93·8	113·7	109·2	134·8	165·8

(c) Angles (°) at the coordinated O atoms

K—O(1)—C(2)	114·8 (4)	K—O(17)—C(18)	110·6 (3)
K—O(1)—C(26)	118·9 (3)	K—O(20)—C(19)	115·4 (3)
K—O(4)—C(3)	108·9 (3)	K—O(20)—C(21)	118·2 (3)
K—O(4)—C(5)	111·0 (4)	K—O(28)—C(27)	118·5 (3)
K—O(7)—C(6)	112·4 (4)	K—O(28)—C(29)	126·2 (3)
K—O(7)—C(8)	117·8 (4)	K—O(35)—C(34)	114·8 (3)
K—O(14)—C(13)	116·4 (4)	K—O(35)—C(36)	112·7 (3)
K—O(14)—C(15)	116·0 (4)	K⋯O(53)—Cl	151·5 (6)
K—O(17)—C(16)	114·7 (4)		

62·6° for O(17)—K—O(20); the smallest value at the chelated benzene ring is to be expected. The K—O-(aromatic) bonds are longer than the other four. The K^+ ion is out of the six-O-atom plane towards the perchlorate O(53) and the K—O(53) direction is 31 (1)° from the normal to the six-O-atom plane. The K—O(35) and K—O(28) directions are at 33·7 (1) and 19·9 (2)° to this normal. Although these two O atoms are attached to sp^3 C atoms, the K—O distances are as

long as, or longer than, the K—O(aromatic) distances. The six O atoms are in an 18-membered ring, and each pair is separated by only two C atoms, giving five-membered chelate rings, while those on the second cyclohexane ring are separated from O(1) and O(20) by three C atoms. The 18-membered ring is comparable with benzo-18-crown-6, an entity having one O—C—C—O torsion angle constrained to 0°. Of five compounds containing this entity complexed to an alkali metal or an alkaline-earth metal, all have the other C—C torsion angles approximately ±60° and all but one C—O torsion angle approximately 180°; for three of these compounds the exceptional angle is in the position corresponding to O(1)—C(2) and is 103·4° in rubidium thiocyanate–4-nitrobenzo-18-crown-6 (Hlavatá, Hašek & Huml, 1978), 102° in barium perchlorate–benzo-18-crown-6 dihydrate and 95° in strontium perchlorate–benzo-18-crown-6 trihydrate (Hughes, Mortimer & Truter, 1978). For the other two compounds the exceptional angle corresponds to C(6)—O(7) at 100·6° in rubidium thiocyanate–benzo-18-crown-6 (Hašek & Huml, 1978), and to C(3)—O(4) at 79·9° in caesium thiocyanate–4-nitrobenzo-18-crown-6 (Hašek, Hlavatá & Huml, 1977). In the present complex C(26)—O(1)—C(2)—C(3) is 120·1°. Because the eighteen torsion angles in an 18-membered ring are not independent, constraint of one to 0° results in another of 0° [as found incidentally in dibenzo-18-crown-6 and the all-benzo bicyclic ligand (Hanson & Truter, 1981)], or of 120° as here. Similarly, the bond angles and torsion angles in the cyclohexane rings are not independent (Dunitz, 1970). Thus the unfavourable torsion angle is a consequence of the size of and substitution in the macrocyclic ring, not a result of CH⋯O bonding.

For the pairs of axial and equatorial O atoms on the cyclohexane rings there are striking differences in K—O distances, K—O(1) being 0·070 (4) Å longer than K—O(20) and K—O(35) being 0·329 (4) Å longer than K—O(28). A similar effect was found in the crystal structure of the only dicyclohexano-18-crown-6 complex to be published in full to date: the *cis anti-cis* isomer is coordinated to a Na^+ ion at a centre of symmetry (Mercer & Truter, 1973). The three independent Na—O distances are 2·967 (4) Å to the axial and 2·682 (4) Å to the equatorial O atoms of the cyclohexane ring, and 2·676 (4) Å to the CH_2—O—CH_2 groups. The authors suggested that the longer bond was associated with the cation⋯O direction being 'tetrahedral' as opposed to 'trigonal', 'trigonal' being in the C—O—C plane and along the bisector of the angle.

Geometrical considerations do not seem to explain the differences in bond length and/or relative electronegativity of the axial and equatorial O atoms in the isomer $B.KClO_4$ complex. As the angles at the coordinated O atoms show (Table 8), those at O(1) and O(20) do not differ significantly, while those at O(28)

Table 9. *Dimensions in the perchlorate ion in the isomer B.KClO₄ complex*

Cl–O(51)	1·397 (6) Å	O(51)–Cl–O(52)	112·7 (5)°
Cl–O(52)	1·316 (7)	O(51)–Cl–O(53)	109·2 (5)
Cl–O(53)	1·388 (8)	O(51)–Cl–O(54)	111·5 (6)
Cl–O(54)	1·297 (8)	O(52)–Cl–O(53)	110·3 (7)
		O(52)–Cl–O(54)	110·8 (7)
		O(53)–Cl–O(54)	101·9 (8)

and O(35) are nearly 'trigonal' and 'tetrahedral' respectively. Steric hindrance may account for the relatively longer C_{axial}–M bonds and a possible explanation is provided in a paper describing the structures of the complexes of the *cis anti cis* and *cis syn cis* isomers of dicyclohexano-18-crown-6 with dimethylthallium picrate (Hughes & Truter, 1982).

Where formation constants in solution have been measured (Frensdorff, 1971; Izatt *et al.*, 1976) the *cis syn cis* isomer gives larger values than the *cis anti cis* isomer, *i.e.* that with the four cyclohexano ring-junction O atoms on the same side of the ring has a greater ratio for the rate of formation/rate of dissociation. Similarly, in this series of three macrobicyclic polyethers, *A*, *B* and *C*, the isomer *B* with the highest formation constant is that with the ring-junction H atoms on the same side of the molecule and away from the bridging O atoms. We originally suggested (Bandy *et al.*, 1981) that this isomer had the most electronegative cavity, *i.e.* postulating a slight repulsion from ring-junction H atoms towards an incoming cation. A similar argument is consistent with the observed formation constants for dicyclohexano-18-crown-6. However, kinetic measurements of the monocyclic systems (Dye, 1979) and of the bicyclic cryptates (Cox, García-Rosas & Schneider, 1981) all agree that selectivity results from differences in the rate of decomplexation, so that the highest formation constant is found for the complex least likely to interact with the solvent; so the cause may be that in the complex there are only H atoms on one surface.

The apparent geometry of the perchlorate ion (Table 9) is reasonably tetrahedral but the short bonds are the result of libration and/or disorder. Analyses of the vibration parameters showed that the anion could not be treated as a rigid body. Treatment of O(51), which has minimum vibration along the Cl–O bond, as riding on the Cl atom increases the bond length by 0·005 Å.

Conclusion

The relative configurations of two isomeric compounds have been determined by crystal structure analysis. Neither is optically active. At each cyclohexane ring junction one C atom is *R* and the other *S*; operation of a plane or centre of symmetry converts these to *S* and *R* respectively, while the axial or equatorial substitution of the O atoms is retained.

However, in solution, inversion of the cyclohexane ring can invert this substitution so that the molecules are superimposable on their mirror images. Complex formation with a chiral entity might freeze-in one absolute configuration.

The similarity in the melting points of the isomers is consistent with the purely van der Waals contacts in their packing.

Alkali-metal cations form complexes with much greater stability constants with isomer *B* than with isomer *A* (Bandy *et al.*, 1981). This can be correlated with the configuration, that of isomer *B* having all the ring-junction H atoms directed away from the cavity.

In the crystal, isomer *B* forms a complex with a potassium perchlorate ion-pair so that the K^+ ion is not completely enclosed by the ligand. This contrasts with the behaviour of the macrobicyclic compound having three benzene-ring substituents which completely encloses the K^+ ion and has an even higher formation constant (Hanson *et al.*, 1979).

Usually O atoms attached to aliphatic C atoms are more electronegative than those attached to aromatic C atoms, so this observation is unexpected. The weaker bonding is probably correlated with the longer K–O bonds to the O atoms in the axial positions relative to cyclohexane rings.

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The Structures of the Isomer C of the Macrobicyclic Polyether (21S,26R,29S,34R)-21,22,23,24,25,26,29,30,31,32,33,34-Dodecahydro-1,4,7,14,17,20,28,35-octaoxa-[2³,²⁹anti.2¹⁸,³⁴anti][7.7]orthocyclophane at 295 K and of its Methanol Complex at 295 and 123 K

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Abstract

Crystals of the title compound, $C_{28}H_{42}O_8$, have cell dimensions $a = 14.832$ (4), $b = 12.806$ (2), $c = 14.555$ (2) Å, $\beta = 103.88$ (1)°, $V = 2683.8$ (9) Å³; $P2_1/a$, $Z = 4$. $R = 0.036$ for 2546 reflections. Its 1:1 methanol complex crystallizes with $a = 14.520$ (2), $b = 15.391$ (3), $c = 12.754$ (2) Å, $\beta = 95.02$ (2)°, $V = 2839.3$ (9) Å³ at 295 K, and $a = 14.353$ (3), $b = 15.279$ (2), $c = 12.659$ (5) Å, $\beta = 95.00$ (2)°, $V = 2765.3$ (13) Å³ at 123 K; space group $P2_1/n$, $Z = 4$. $R = 0.040$ for 2071 reflections at 295 K and 0.033 for 2060 reflections at 123 K. The structures were solved by direct methods and refined with anisotropic vibration for O and C atoms. The macrobicyclic molecule consists of a dicyclohexano-14-crown-4 ring bridged by an $OCH_2CH_2OC_6H_4OCH_2CH_2O$ group. In isomer C the four cis H atoms at the cyclohexano ring junctions are on the same side of the 14-crown-4 entity as the bridge. The conformation of the molecule is essentially unchanged in the methanol complex where the methanol hydroxy group forms a weak bifurcated hydrogen bond to the O atoms on the aromatic ring.

Introduction

Three isomeric macrobicyclic polyethers, *A*, *B* and *C*, differing only in the configurations of the ring-junction C atoms of the cyclohexano groups, have been synthesized and found to have greatly different formation constants for complexation with alkali metals. Although they had diagnostically different infrared spectra, the relative configurations were established only by crystal structure determination of all three isomers (Bandy, Parsons & Truter, 1981). The structural formula and numbering of the atoms in these molecules are shown in Fig. 1. The hydrogenation of aromatic rings to form the cyclohexyl groups at an early stage of the synthesis gives mainly cis addition at the ring junctions, and the H atoms on C(21) and C(26) are therefore on the same side of the molecule; they can be either on the same side as, or on the opposite side to, the bridge atoms O(4) and O(17). The situation is the same for the H atoms on C(29) and C(34).

In the present paper we describe the crystal structure of the isomer *C*, having all four H atoms |H(21), H(26), H(29), and H(34)| on the same side as O(4) and O(17). This isomer has the lowest formation constant (although the value of $|KL|/|K||L|$ in methanol at 298 K is 10^4 l mol⁻¹) and has not yielded suitable crystalline complexes with metal salts. The unsolvated compound crystallizes from ethanol. From methanol, solvated crystals are obtained with stoichiometry 1:1; they show a sharp band in the IR spectrum at 3555 cm⁻¹, instead of the broad bands at lower frequencies usually found in hydrogen-bonded compounds. This appears to be an example of 'molecular recognition' by the guest, methanol, of the host macrobicyclic com-