

Crystal Structure of Two Bridged Macrobicyclic Polyethers, 1,5,12,16,23,26,29-Hepta-oxa[7^{3,14}][5.5]orthocyclophane and 1,5,12,16,23,26,29,32-Octaoxa[10^{3,14}][5.5]orthocyclophane

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The crystal structures of the two title compounds (1) and (2) have been solved by direct methods from diffractometer data. Both compounds crystallise in the rhombohedral space group $R\bar{3}$, and the obverse hexagonal cell was used in each case. The cell dimensions found were $a = 33.569(11)$, $c = 9.182(5)$ Å for compound (1) and $a = 34.772(7)$, $c = 9.743(2)$ Å for (2), and $Z = 18$. The structures have been refined to $R = 0.040$ for the 3 204 observations of (1), and $R = 0.084$ for the 1 621 observed planes in (2). The molecules have similar shapes and can be considered best as bridged analogues of the monocyclic crown ethers, benzo-15-crown-5 and benzo-18-crown-6, respectively. They each show an open face containing several oxygen atoms which would be available to complex with cations. The packing of the molecules in the crystals is very similar, in each case, one benzene ring being 'stacked' above that in a neighbouring molecule.

A SERIES of novel bridged macrocyclic polyethers has been developed in these laboratories and shown to form complexes with alkali metal cations in aqueous solution.¹ These complexes have high formation constants in both water and methanol solutions, and representative structures for complexes with alkali metals² and organic molecules³ have been reported. These have shown that these molecules are best considered as crown ethers with a bridge containing a benzene ring. Thus the two title compounds (1) and (2) may be considered as bridged benzo-15-crown-5 and bridged benzo-18-crown-6 molecules, respectively.

The structure found for (1) (Figure 1) in its hydrogen-bonded complex with naphthalene-2,3-diol³ shows the crown molecule contains a fairly good plane of five oxygen atoms O(1), O(23), O(26), O(29), and O(16). The hydrogen atoms of a molecule of water are close to four of these oxygen atoms, and the oxygen atom of the water accepts a hydrogen bond from one of the hydroxy-groups on the naphthalenediol.

The structure of (3), an analogue of (2) (see Figure 1), with a benzene ring in the bridge, has been determined in crystals of the free ligand,⁴ and complexed with KCl. \cdot n H₂O.^{2,4} The structure of the former shows one of the benzene rings is disordered, and the conformation is different from that in the complex, with some of the hydrogen atoms pointing into the cavity.⁴

The structures of the molecules of (1) and (2) are reported here as part of a study of the conformational changes which occur on complexation. The structures were solved by direct methods from diffractometer data,

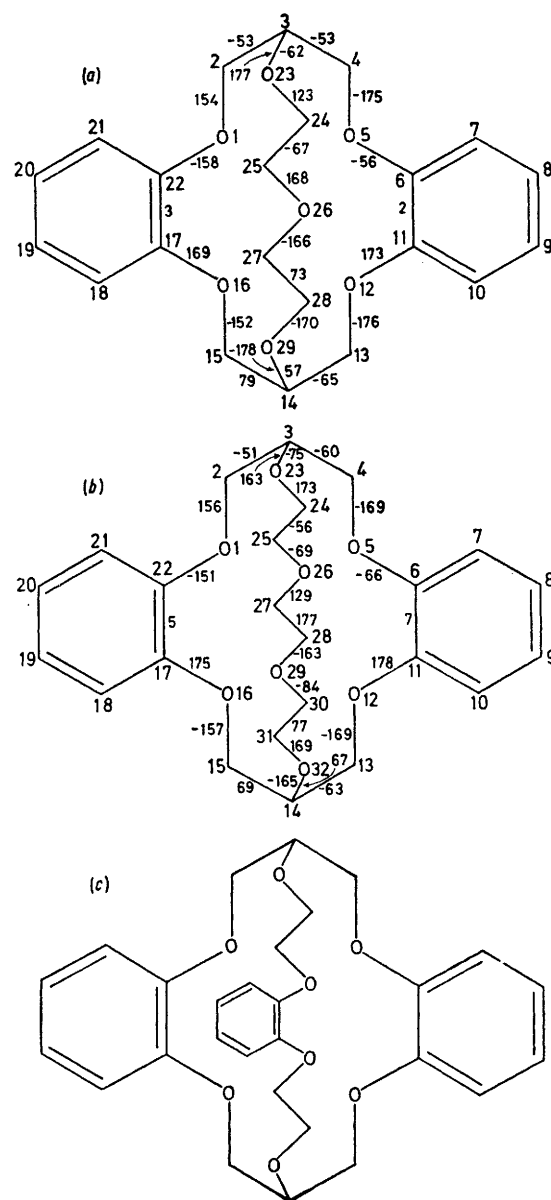


FIGURE 1 (a) 1,5,12,16,23,26,29-Hepta-oxa[7^{3,14}][5.5]orthocyclophane (1), showing the atom numbering and torsion angles. Angles not on the Figure are O(1)–C(2)–C(3)–O(23) 66.3°, O(12)–C(13)–C(14)–O(29) 56.2°, O(23)–C(3)–C(4)–O(5) –170.5°, O(29)–C(14)–C(15)–O(16) –47.9° (e.s.d.s of torsion angles are 0.1 or 0.2°). (b) 1,5,12,16,23,26,29,32-Octaoxa[10^{3,14}][5.5]orthocyclophane. (2), showing the atom numbering and torsion angles. Angles not on the Figure are O(1)–C(2)–C(3)–O(23) 68.9°, O(12)–C(13)–C(14)–O(32) 61.0°, O(23)–C(3)–C(4)–O(5) –179.2°, O(32)–C(14)–C(15)–O(16) –57.2° (e.s.d.s of torsion angles are 0.5–1.0°). (c) 1,4,7,14,17,20,28,35-Octaoxa[2^{3,29}, 2^{18,34}][7.7]orthocyclophane (3)

and the final least-squares refined parameters are shown in Tables 1 and 2. The shapes of the molecules are very similar and are shown in Figures 2–5.

RESULTS AND DISCUSSION

The two compounds form crystals with the same space group and similar cell dimensions. The molecules pack

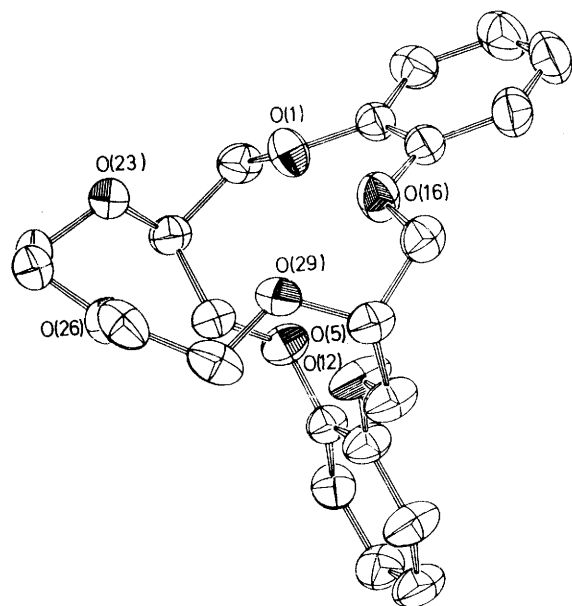


FIGURE 2 One molecule of (1) showing the 50% thermal ellipsoids

in very similar ways (see Figure 6) and they have similar shapes. They both show one open-face which contains easily accessible oxygen atoms. The remaining surfaces of the molecule are made up mainly of hydrogen atoms.

The bond lengths and angles (Tables 3 and 4) are similar to those found in other crown ethers and their complexes and show the same peculiarities. Thus the $\text{CH}_2\text{-CH}_2$ bonds tend to be shorter than expected, especially those around the aliphatic 'bridge'. Also

around the O(5)-C(6) bond. In each molecule, this bond length is longer than the other three similar bonds. This is coupled with an increased O(5)-C(6)-C(11) bond angle to a value greater than 120° , and a corresponding decrease in the O(5)-C(6)-C(7) angle. The three other bond angles equivalent to O(5)-C(6)-C(11) in these molecules are all less than 120° , in accord with those observed in other crown ether structures. These deviations are all greater than eight times the e.s.d. for (1) but, though still present in (2), are probably not significant in this case. These deviations are probably due to the lack of conjugation of the p -orbitals on O(5) as a result of the small torsion angle (-60°) about the

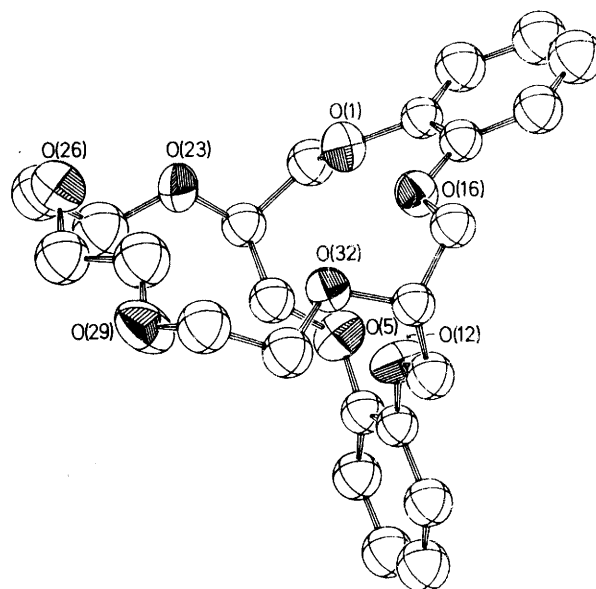


FIGURE 3 One molecule of (2) showing the 50% thermal ellipsoids

O(5)-C(6) bond. Small torsion angles corresponding to these were also found in the naphthalenediol complex of (1)³ and in the free ligand structure of (3),⁴ and again

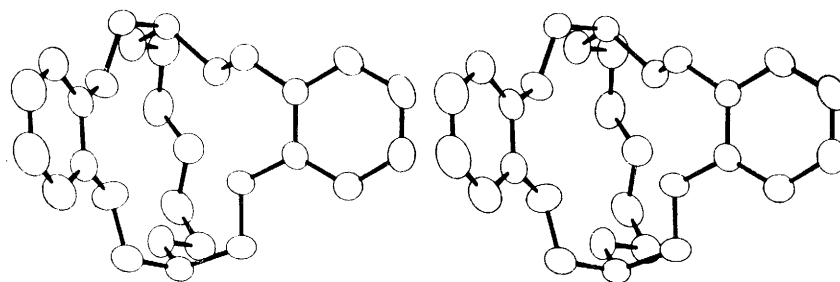


FIGURE 4 Stereopair of the molecule of (1)

the aromatic bonds C(8)-C(9) and C(19)-C(20) are much shorter than expected. The shortening of these two types of bond persists even when the crystal structure is determined at low temperature,^{5,6} and remains one of the unexplained features of crown ethers.

An interesting exception to the expected geometry is

the nearby geometry is affected. In both cases the change in the bond angles is more significant than the change in the O(5)-C(6) bond length.

Also of interest are the C(2)-C(3) bond lengths and equivalents. In both molecules these are slightly longer than the other CH_2CH_2 bonds, but still shorter than the

expected value. This feature is also present in the other structures so far determined which contains a carbon bridgehead atom.^{3,4}

The torsion angles (Figure 1) are mainly as expected,

contains four notable torsion angles, including a value of 177° about the C(27)–C(28) bond. This causes the hydrogen atoms on C(28) to point into the cavity of the molecule. This section of the molecule can be considered to

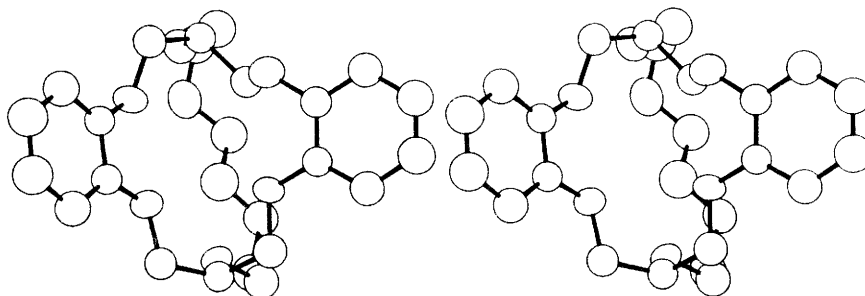


FIGURE 5 Stereopair of the molecule of (2)

close to $\pm 60^\circ$ about C–C bonds and 180° about C–O bonds. The only deviations in (1) are the -56° about O(5)–C(6), discussed above, and a value of 123° about O(23)–C(24). The overall shape of the molecule is very similar to that of the naphthalenediol complex, and may be considered as a benzo-15-crown-5 molecule bridged

form a benzo-18-crown-6 fragment with the benzene ring C(17)–C(22). No structure has so far been reported for uncomplexed benzo-18-crown-6, and in all the complexes so far found with metallic cations, all the oxygen atoms point into the cavity.⁸

Both molecules show an open face containing oxygen

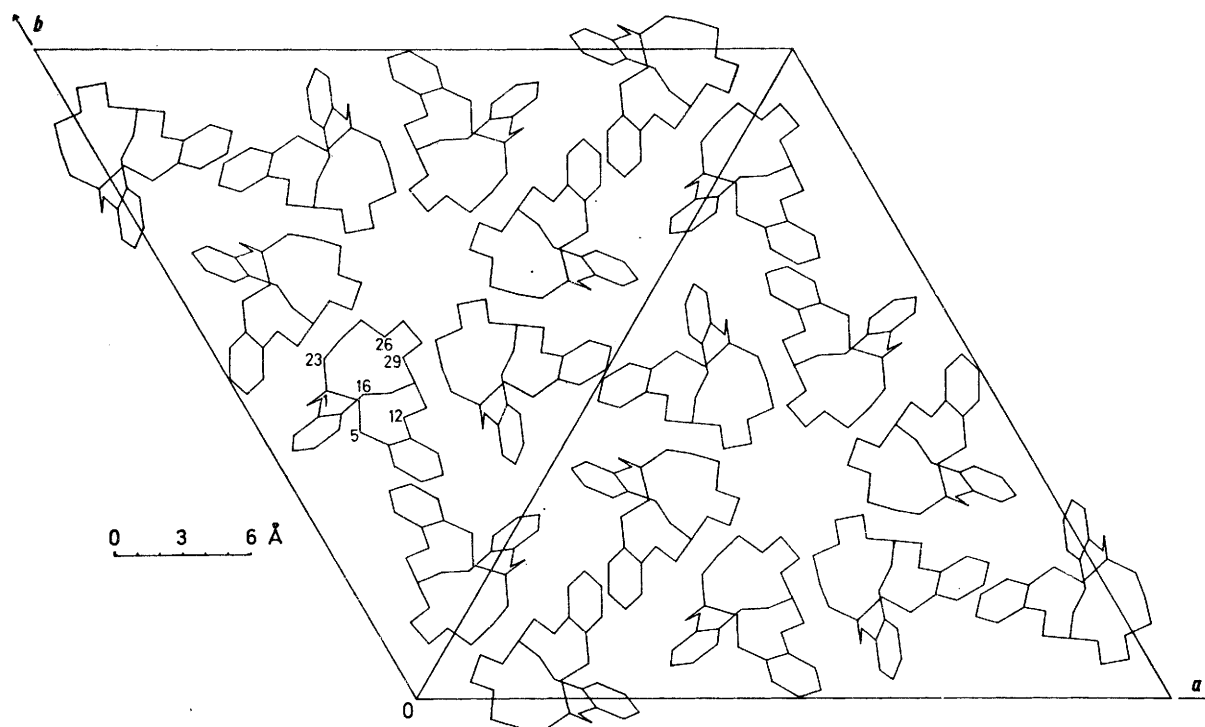


FIGURE 6 The hexagonal unit cell of (1) viewed down the crystallographic c axis, positive z towards the reader

by the benzene ring containing fragment, C(4)–C(13). Only small changes in a few torsion angles are necessary to bring the benzo-15-crown-5 section into the regular conformation found in its complex with $\text{Mg}(\text{NCS})_2$.⁷ The molecule of (2) takes up a similar shape to that of (1), but there are more deviations from the expected torsion angles. The aliphatic chain of atoms O(23)–O(32)

atoms, four in the case of (1) and five in (2). The conformation of the uncomplexed molecule of (3) which is found in the crystals,⁴ also has five oxygens in an open face, but they are not the same atoms as those in (2). This is because the conformations are very different. Notably the torsion about C(27)–C(28) is *trans* in (2), but is constrained to be *cis* by the benzene ring in (3).

Although the torsion angles about bonds involving the bridgehead atom C(14) are similar in (2) and (3), those about the other bridgehead, C(3), are very different in each case. The torsion angle C(17)–C(22)–O(1)–C(2)

TABLE 1

(a) Fractional co-ordinates ($\times 10^5$) for the non-hydrogen atoms of (1)

Atom	<i>x</i>	<i>y</i>	<i>z</i>
O(1)	10 712(4)	46 355(4)	29 809(11)
C(2)	8 330(5)	45 334(6)	43 300(16)
C(3)	11 958(5)	47 543(5)	54 964(16)
C(4)	15 544(5)	46 070(5)	53 688(17)
O(5)	13 174(3)	41 133(3)	53 413(12)
C(6)	15 935(5)	39 174(5)	53 551(16)
C(7)	15 040(6)	35 869(5)	63 894(16)
C(8)	17 441(6)	33 507(6)	64 150(17)
C(9)	20 854(7)	34 552(6)	54 133(19)
C(10)	21 838(7)	37 914(6)	43 736(19)
C(11)	19 395(6)	40 204(5)	43 219(17)
O(12)	20 025(4)	43 422(4)	32 987(12)
C(13)	23 850(6)	44 913(6)	23 480(18)
C(14)	24 237(6)	48 735(6)	13 699(16)
C(15)	20 220(6)	47 177(6)	3 421(17)
O(16)	16 498(4)	46 943(4)	11 428(12)
C(17)	12 082(5)	43 978(5)	7 601(17)
C(18)	10 625(7)	41 567(6)	−5 401(18)
C(19)	5 953(7)	38 712(6)	−7 862(20)
C(20)	2 808(7)	38 275(6)	2 381(21)
C(21)	4 222(6)	40 707(5)	15 389(19)
C(22)	8 841(5)	43 551(5)	18 000(16)
O(23)	14 062(4)	52 389(4)	52 886(11)
C(24)	17 520(6)	55 263(6)	63 097(19)
C(25)	21 937(6)	58 376(6)	55 553(20)
O(26)	23 760(4)	55 778(4)	49 401(12)
C(27)	27 453(6)	58 227(6)	39 534(19)
C(28)	28 238(6)	54 856(7)	31 309(18)
O(29)	24 596(4)	52 609(4)	21 219(11)

(b) Fractional co-ordinates ($\times 10^4$) for the hydrogen atoms of (1)

Atom	<i>x</i>	<i>y</i>	<i>z</i>
H(2)A	627	4 661	4 349
H(2)B	654	4 200	4 478
H(3)	1 057	4 661	6 465
H(4)A	1 763	4 721	6 207
H(4)B	1 731	4 730	4 469
H(7)	1 266	3 517	7 123
H(8)	1 671	3 110	7 144
H(9)	2 260	3 292	5 432
H(10)	2 430	3 867	3 667
H(13)A	2 667	4 606	2 925
H(13)B	2 344	4 232	1 746
H(14)	2 710	4 963	841
H(15)A	1 936	4 414	−53
H(15)B	2 105	4 938	−459
H(18)	1 287	4 188	−1 278
H(19)	490	3 700	−1 702
H(20)	−48	3 623	54
H(21)	195	4 040	2 265
H(24)A	1 649	5 712	6 836
H(24)B	1 801	5 333	7 002
H(25)A	2 413	6 057	6 259
H(25)B	2 138	6 006	4 783
H(27)A	2 668	5 999	3 274
H(27)B	3 024	6 033	4 494
H(28)A	2 827	5 260	3 803
H(28)B	3 118	5 646	2 613

is -84° in (3), which prevents O(1) forming part of the open face. In (2), it is the *trans*-disposition about C(27)–C(28) which prevents O(29) forming part of the open face. Thus the conformations of (2) and (3), though superficially similar, do in fact have few features in common.

The mean planes shown in Table 5 indicate again how these molecules are related to the monocyclic crowns. In (1) the deviations of the oxygen atoms O(1), O(23),

O(26), O(29), and O(16) from their mean plane are similar in magnitude and direction to those found⁷ for the benzo-15-crown-5 molecule complexed with Mg(NCS)₂, though the angle between this plane and the benzene

TABLE 2

(a) Fractional co-ordinates ($\times 10^4$) and isotropic temperature factors ($\times 10^3 \text{ \AA}^2$) for the non-hydrogen atoms of (2)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
O(1)	1 028(1)	4 516(1)	2 653(4)	
C(2)	756(2)	4 354(2)	3 849(7)	61(2)
C(3)	1 051(2)	4 533(2)	5 088(7)	55(2)
C(4)	1 440(2)	4 446(2)	5 031(7)	58(2)
O(5)	1 261(2)	3 978(1)	4 972(5)	
C(6)	1 563(2)	3 836(2)	5 158(7)	54(2)
C(7)	1 497(2)	3 560(2)	6 278(7)	66(2)
C(8)	1 767(2)	3 375(3)	6 431(8)	73(2)
C(9)	2 083(3)	3 451(3)	5 525(8)	77(2)
C(10)	2 158(2)	3 731(2)	4 401(7)	65(2)
C(11)	1 902(2)	3 933(2)	4 225(7)	50(2)
O(12)	1 956(1)	4 214(1)	3 181(4)	
C(13)	2 313(2)	4 328(2)	2 254(7)	64(2)
C(14)	2 388(2)	4 706(2)	1 317(7)	52(2)
C(15)	2 008(2)	4 608(2)	380(7)	57(2)
O(16)	1 640(1)	4 570(1)	1 128(4)	
C(17)	1 226(2)	4 335(2)	583(7)	51(2)
C(18)	1 129(2)	4 150(2)	−731(7)	67(2)
C(19)	678(3)	3 907(3)	−1 111(9)	82(2)
C(20)	358(3)	3 852(3)	−266(8)	80(2)
C(21)	451(3)	4 046(2)	1 041(8)	70(2)
C(22)	890(2)	4 291(2)	1 440(7)	49(2)
O(23)	1 213(2)	4 992(2)	5 129(4)	
C(24)	1 396(3)	5 199(3)	6 441(8)	86(3)
C(25)	1 597(3)	5 671(3)	6 341(9)	88(3)
O(26)	1 925(2)	5 881(2)	5 354(5)	
C(27)	2 328(3)	5 892(3)	5 551(8)	82(3)
C(28)	2 441(3)	5 729(3)	4 281(9)	89(3)
O(29)	2 839(2)	5 760(2)	4 427(5)	
C(30)	3 051(3)	5 738(3)	3 204(8)	80(2)
C(31)	2 914(2)	5 289(2)	2 702(8)	71(2)
O(32)	2 498(1)	5 100(1)	2 047(4)	

(b) Fractional co-ordinates ($\times 10^3$) for the hydrogen atoms of (2)

Atom	<i>x</i>	<i>y</i>	<i>z</i>
H(2)A	54	446	385
H(2)B	60	403	386
H(3)	88	438	591
H(4)A	162	457	585
H(4)B	162	459	421
H(7)	126	350	695
H(8)	172	318	722
H(9)	226	331	564
H(10)	239	379	374
H(13)A	258	442	278
H(13)B	225	407	169
H(14)	264	475	75
H(15)A	192	433	−10
H(15)B	210	485	−29
H(18)	136	419	−136
H(19)	60	378	−203
H(20)	5	367	−56
H(21)	21	401	165
H(24)A	162	512	673
H(24)B	116	509	712
H(25)A	173	580	723
H(25)B	136	574	614
H(27)A	256	620	574
H(27)B	230	570	633
H(28)A	245	591	350
H(28)B	221	542	413
H(30)A	299	589	248
H(30)B	337	589	337
H(31)A	289	510	348
H(31)B	313	530	205

ring C(17)–C(22) is much smaller at 5° . In contrast, for (2) the deviations of the oxygen atoms O(1), O(23), O(26), O(29), O(32), and O(16) from their mean plane

are much larger than those found for benzo-18-crown-6 molecules.⁸

There are several short intramolecular contacts in both these molecules due to the conformation around the O(5)-C(6) bond. This causes one hydrogen atom on

respectively. The overlap is small and slightly different in each case.

The ease with which these molecules form complexes

TABLE 4
Bond angles (°)

TABLE 3 Bond lengths (Å)			TABLE 4 Bond angles (°)		
	(1)	(2)		(1)	(2)
O(1)-C(2)	1.420(2)	1.429(7)	C(22)-O(1)-C(2)	121.1(1)	120.4(5)
C(2)-C(3)	1.509(2)	1.503(9)	O(1)-C(2)-C(3)	106.4(1)	108.1(5)
C(3)-C(4)	1.517(2)	1.528(8)	C(2)-C(3)-C(4)	111.2(1)	112.3(6)
C(4)-O(5)	1.436(2)	1.423(7)	C(2)-C(3)-O(23)	106.5(1)	107.2(5)
O(5)-C(6)	1.379(2)	1.376(7)	C(4)-C(3)-O(23)	109.9(1)	109.5(5)
C(6)-C(7)	1.375(2)	1.396(9)	C(3)-C(4)-O(5)	107.8(1)	107.7(5)
C(6)-C(11)	1.402(2)	1.389(8)	C(4)-O(5)-C(6)	115.7(1)	115.4(5)
C(7)-C(8)	1.385(2)	1.385(9)	O(5)-C(6)-C(7)	117.6(1)	117.2(6)
C(8)-C(9)	1.371(2)	1.330(9)	O(5)-C(6)-C(11)	123.2(1)	122.2(6)
C(9)-C(10)	1.386(2)	1.402(9)	C(7)-C(6)-C(11)	119.1(1)	120.3(7)
C(10)-C(11)	1.377(2)	1.392(8)	C(6)-C(7)-C(8)	121.3(1)	119.2(7)
C(11)-O(12)	1.366(2)	1.356(7)	C(7)-C(8)-C(9)	119.5(1)	121.4(8)
O(12)-C(13)	1.421(2)	1.423(7)	C(8)-C(9)-C(10)	119.9(2)	120.2(8)
C(13)-C(14)	1.518(2)	1.512(8)	C(9)-C(10)-C(11)	120.8(2)	120.3(7)
C(14)-C(15)	1.509(2)	1.497(8)	C(6)-C(11)-C(10)	119.3(1)	118.5(7)
C(15)-O(16)	1.418(2)	1.420(7)	C(6)-C(11)-O(12)	116.2(1)	117.4(6)
O(16)-C(17)	1.355(2)	1.359(7)	C(10)-C(11)-O(12)	124.4(1)	124.1(6)
C(17)-C(18)	1.387(2)	1.397(9)	C(11)-O(12)-C(13)	117.2(1)	117.7(5)
C(17)-C(22)	1.400(2)	1.381(8)	O(12)-C(13)-C(14)	110.0(1)	111.9(5)
C(18)-C(19)	1.388(3)	1.407(9)	C(13)-C(14)-C(15)	113.1(1)	115.0(6)
C(19)-C(20)	1.366(3)	1.321(9)	C(13)-C(14)-O(29)	114.7(1)	
C(20)-C(21)	1.390(2)	1.400(10)	C(15)-C(14)-O(29)	105.8(1)	
C(21)-C(22)	1.376(2)	1.382(8)	C(13)-C(14)-O(32)		112.6(5)
C(22)-O(1)	1.366(2)	1.365(7)	C(15)-C(14)-O(32)		107.8(5)
C(3)-O(23)	1.426(2)	1.405(7)	C(14)-C(15)-O(16)	107.8(1)	111.1(5)
O(23)-C(24)	1.427(2)	1.449(8)	C(15)-O(16)-C(17)	121.1(1)	119.4(5)
C(24)-C(25)	1.490(3)	1.428(10)	O(16)-C(17)-C(18)	126.1(2)	125.1(6)
C(25)-O(26)	1.410(2)	1.388(8)	O(16)-C(17)-C(22)	114.0(1)	114.5(6)
O(26)-C(27)	1.419(2)	1.393(8)	C(18)-C(17)-C(22)	119.9(1)	120.4(7)
C(27)-C(28)	1.489(3)	1.495(10)	C(17)-C(18)-C(19)	119.3(2)	117.3(7)
C(28)-O(29)	1.414(2)	1.341(8)	C(18)-C(19)-C(20)	120.5(2)	121.9(8)
O(29)-C(30)		1.423(8)	C(19)-C(20)-C(21)	120.7(2)	121.5(8)
C(30)-C(31)		1.472(9)	C(20)-C(21)-C(22)	119.5(2)	118.1(7)
C(31)-O(32)		1.406(7)	O(1)-C(22)-C(17)	113.9(1)	115.1(6)
O(32)-C(14)		1.418(7)	O(1)-C(22)-C(21)	125.9(1)	124.1(6)
O(29)-C(14)	1.423(2)		C(17)-C(22)-C(21)	120.0(1)	120.8(7)
			C(3)-O(23)-C(24)	117.0(1)	114.6(5)
			O(23)-C(24)-C(25)	110.9(1)	110.5(7)
			C(24)-C(25)-O(26)	109.9(1)	117.0(7)
			C(25)-O(26)-C(27)	114.9(1)	117.9(6)
			O(26)-C(27)-C(28)	108.6(1)	109.1(7)
			C(27)-C(28)-O(29)	107.7(1)	109.7(7)
			C(28)-O(29)-C(30)		116.5(6)
			O(29)-C(30)-C(31)		115.7(7)
			C(30)-C(31)-O(32)		110.9(6)
			C(28)-O(29)-C(14)	117.5(1)	
			C(31)-O(32)-C(14)		113.3(5)

C(4) to become fairly close to some oxygen atoms, though in no case is the angle at C(4)-H(4)B...O indicative of a strong hydrogen bond type of interaction (see Table 6).

The only intermolecular interaction of note is the partial stacking of the C(6)-C(11) benzene ring with a centrosymmetrically related equivalent at $1/3 - x$, $2/3 - y$, $2/3 - z$ (Table 6 and Figure 6). The two rings are parallel and 3.72 and 3.66 Å apart in (1) and (2),

with monovalent cations may be explained by the flexibility of the aliphatic chain, which can take up a conformation shown in these structures in which one

TABLE 5
Deviations (Å) from mean planes of selected atoms

	C(6)	C(7)	C(8)	C(9)	C(10)	C(11)
(a) Benzene ring						
(1)	-0.001(2)	0.008(2)	-0.008(2)	0.000(2)	0.007(2)	-0.007(2)
(2)	-0.013(7)	0.000(7)	0.011(8)	-0.007(8)	-0.006(7)	0.016(7)
(b) Benzene ring						
(1)	-0.005(2)	0.003(2)	0.002(2)	-0.004(2)	0.002(2)	0.002(2)
(2)	-0.017(7)	0.006(7)	0.010(8)	-0.013(8)	0.001(8)	0.014(7)
(a) Oxygen atoms						
(1)	-0.116(1)	0.142(1)	-0.126(1)	0.073(1)		0.027(1)
(2)	-0.008(4)	0.574(5)	-0.649(5)	0.313(6)	0.063(4)	-0.294(4)
(d) Interplanar angles (°)						
(1)	(a) - (b)	(a) - (c)	(b) - (c)			
(2)	85	86	5			
	71	92	-19			

face of the molecule exposes several oxygen atoms. On addition of the cation of the correct size, it would be possible for this chain to change to a conformation which could effectively protect the cation from solvent and

TABLE 6

(a) Selected intramolecular contacts

	H...O distance (Å)		C-H...O angle (°)	
	(1)	(2)	(1)	(2)
H(4)A...O(23)	2.69	2.62	63	66
H(4)A...O(26)	2.82		95	
H(4)B...O(1)	2.49	2.47	96	99
H(4)B...O(12)	2.20	2.36	120	116
H(4)B...O(23)	2.56	2.60	70	67
H(4)B...O(26)	2.61		109	
H(2)A...O(23)	2.51	2.48	70	70
H(28)B...O(32)		2.72		108

Other contacts (Å)

(1)		(2)	
C(4)...H(24)B	2.62	C(4)...H(24)A	2.68
H(4)A...H(24)B	2.12	H(4)A...H(24)A	2.12
H(4)A...C(24)	2.72	H(4)A...C(24)	2.75
C(13)...H(28)A	2.61	C(13)...H(31)A	2.71
H(13)A...H(28)A	2.14	H(13)A...H(31)A	2.18
H(13)A...C(28)	2.74	H(13)A...C(31)	2.65
O(1)...O(16)	2.51	H(4)B...H(28)B	2.58
O(1)...O(23)	2.75	H(24)A...H(27)B	2.25
O(23)...O(26)	2.88	O(1)...O(16)	2.52
O(26)...O(29)	2.86	O(1)...O(23)	2.81
O(29)...O(16)	2.58	O(23)...O(26)	2.84
		O(26)...O(29)	3.52
		O(29)...O(32)	3.05
		O(32)...O(16)	2.76

(b) Selected intermolecular contacts (Å)

(1)		(2)	
O(1)...H(13)B ^I	2.64	H(2)A...H(7) ^{II}	2.42
H(2)A...H(7) ^{II}	2.47	H(2)B...H(20) ^{VIII}	2.49
H(4)A...H(24)A ^{III}	2.51	H(4)A...H(25)B ^{III}	2.49
H(7)...H(8) ^{IV}	2.54	H(8)...H(8) ^{IV}	2.51
H(8)...H(15)A ^V	2.58	H(15)B...O(26) ^{VI}	2.51
H(15)B...H(25)B ^{VI}	2.30	H(25)A...O(29) ^{VII}	2.68
H(25)A...H(27)B ^{VII}	2.56	H(27)A...H(27)B ^{VII}	2.59
H(27)A...H(28)B ^I	2.57	H(28)A...H(30)B ^{IX}	2.39
O(29)...H(28)B ^I	2.64		

Roman numerals superscripts identify the atom related to that at x, y, z by the transformations

I	$y - \frac{1}{3}, -x + y + \frac{1}{3}, -z + \frac{1}{3}$
II	$-y + \frac{1}{3}, x - y + \frac{2}{3}, z - \frac{1}{3}$
III	$x - y + \frac{2}{3}, x + \frac{1}{3}, -z + \frac{1}{3}$
IV	$-x + \frac{1}{3}, -y + \frac{2}{3}, -z + \frac{1}{3}$
V	$-x + \frac{1}{3}, -y + \frac{2}{3}, -z + \frac{1}{3}$
VI	$x - y + \frac{2}{3}, x + \frac{1}{3}, -z + \frac{1}{3}$
VII	$y - \frac{1}{3}, -x + y + \frac{1}{3}, -z + \frac{1}{3}$
VIII	$-x + y - \frac{1}{3}, -x + \frac{1}{3}, z + \frac{1}{3}$
IX	$-x + y, -x + 1, z$

make release very difficult. We are attempting to find suitable crystalline complexes of (1) and (2) for comparison with the structures for the free ligands.

EXPERIMENTAL

Crystal Data.—(1), $C_{22}H_{26}O_7$, $M = 402.5$. Hexagonal needles, $a = 33.569(11)$, $c = 9.182(5)$ Å, $U = 8\,961$ Å³, $D_m = 1.34$, $Z = 18$, $D_c = 1.34$ g cm⁻³, $F(000) = 3\,888$, space group $R\bar{3}$ (C_{2h}^2 , no. 148), hexagonal axes, corresponding rhombohedral cell $a = 19.621$ Å, $\alpha = 117.61^\circ$, no molecular symmetry required, Mo- K_α radiation, graphite monochromator, $\lambda = 0.710\,7$ Å, $\mu = 0.94$ cm⁻¹, no absorption correction applied.

(2), $C_{24}H_{30}O_8$, $M = 446.5$. Hexagonal needles, $a = 34.772(7)$, $c = 9.743(2)$ Å, $U = 10\,202$ Å³, $D_m = 1.31$ g cm⁻³, $Z = 18$, $D_c = 1.31$ g cm⁻³, $F(000) = 4\,284$, space group $R\bar{3}$ (C_{2h}^2 , no. 148), hexagonal axes, corresponding rhombohedral cell $a = 20.336$ Å, $\alpha = 117.50^\circ$, no molecular symmetry required, Mo- K_α radiation, graphite monochromator, $\lambda = 0.710\,7$ Å, $\mu = 0.92$ cm⁻¹, no absorption correction applied.

Data Collection.—Crystals of both compounds were prepared by Dr. D. G. Parsons.^{1,9} A crystal of (1), with dimensions $0.48 \times 0.19 \times 0.33$ mm was mounted on an Enraf-Nonius CAD4 diffractometer. Accurate cell dimensions were obtained from the settings of 23 high angle planes, and intensity data were collected using symmetric ω —2 θ scans. Three standard reflections were measured every 2 h of exposure time, and showed no systematic variation in intensity during the data collection. Intensities were collected for all the planes with both h and $k \geq 0$ up to a maximum 2θ of 54° . Equivalent reflections were averaged to give 4 331 unique planes, 3 204 of which had $I \geq 2\sigma(I)$ and were classed as observed. The structure solution and initial refinement were carried out using the 1 656 observed planes with $2\theta \leq 40^\circ$.

The crystal of (2) which was used for data collection was $0.19 \times 0.19 \times 0.52$ mm. The rhombohedral axial system was used for the data collection, structure solution and refinement, and conversion to the hexagonal axes was carried out at a later stage. The settings of 18 high angle planes were used to refine accurate cell dimensions. The intensity data were collected using conditions similar to those used for (1). The two standard reflections, which were measured every 2 h exposure time, showed no significant variation during the data collection. Intensities were collected for all planes with $|h|, |l| < |k|$ up to a maximum 2θ of 40° . Equivalent reflections were then averaged to give 2 123 unique planes, of which 1 621 had $I \geq 2\sigma(I)$ and were classed as observed.

Structure Determination.—The two structures were solved using multi-solution direct methods.¹⁰ The best set of phases for (1) gave an E map which showed the whole molecule except for one missing atom. This was found on the subsequent Fourier map. In the case of (2), the second-best set of phases showed the whole molecule on the E map, with no missing atoms. Full matrix refinement was carried out¹⁰ with the hydrogen atoms in positions calculated from the geometry of the rest of the molecule, with a C-H distance of 0.98 Å, and a common isotropic temperature factor. This refined to $U_{iso} = 0.059(1)$ Å² for (1), and 0.093(4) Å² for (2). All the non-hydrogen atoms in (1) were given anisotropic temperature factors, but because of the shortage of observations in (2), only the oxygen atoms were so refined.

The refinement of (2) in the rhombohedral cell gave rise to many large correlation coefficients and bond length e.s.d.s ca. 0.02 Å. At the suggestion of Dr. R. O. Gould, the atomic parameters and Miller indices were transformed to correspond with the hexagonal axes. Refinement for two cycles gave the same R indices, and all the parameters (including the anisotropic temperature factors) changed very little. The number and magnitude of the correlation coefficients were much reduced, and the bond length e.s.d.s became ca. 0.009 Å. This much more satisfactory setting was therefore used from the beginning when the crystals of (1) became available.

The conventional agreement indices were $R = 0.040$

and $R' = 0.040$ for (1) using weights calculated from the counting statistics. In the case of (2), a satisfactory weighting scheme using the expression weight $\propto 1/[\sigma^2(F_0) + 0.000191 F_0^2]$ gave $R = 0.084$ and $R' = 0.087$ for the agreement indices. A final difference map for each compound showed only peaks $< 0.5 \text{ eÅ}^{-3}$, due to the inadequate description of the thermal motion of the atoms in (2), and peaks $< 0.35 \text{ eÅ}^{-3}$ midway along some of the C-C bonds in (1).

Scattering factors were calculated using the analytical approximation coefficients given in Table 2.2B of ref. 11. Geometry calculations were carried out on an IBM 1130 computer,¹² and the Figures drawn using ORTEP.¹³ Observed and calculated structure factors are listed in Supplementary Publication No. SUP 22904 (35 pp.).*

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1979, Index Issue.

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