

with a 'face-to-face' arrangement of the dianhydromannitolo residues, can be readily appreciated. Interestingly, the four C—O bonds [*e.g.* C(1)—O(2) *etc.*] that link the rigid portions of DD-(3) all adopt (Fig. 1) *gauche* geometries in contrast to the *anti*\* arrangements normally associated with polyether molecules (Goldberg, 1980, 1984). The two methoxy methyl groups adopt conformations about the C(aryl)—O bonds corresponding to minimum conjugation of these groups with the aromatic rings. The angles between the mean planes of C(14)—O(39)—C(40) and C(29)—O(34)—C(35) and the mean planes of their respective aryl rings are 88 (1) and 83 (1)°, respectively. Surprisingly, the two methyl groups are directed away from the central cavity region of the macrocycle rather than helping to fill it. The molecule has diastereotopic faces with the two aryl methoxy groups both lying on the more hindered face. The two aryl groups are tilted slightly with respect to each other with a cleft angle of 34 (1)° between the mean planes of the aromatic rings. Significantly, the shapes of the two dianhydromannitolo residues match (Table 2) each other very closely (equivalent torsional angles within 5°) in DD-(3), whereas this is not the case in DD-(2), which displays (Crawshaw *et al.*, 1986) internal differences between equivalent torsional angles of just greater than 50°.

There are four intermolecular contacts of less than 3.4 Å. The shortest of these is 3.22 (1) Å between C(38) and O(8) with an associated H...O distance of 2.45 Å.

\* In the context of this and the following paper '*gauche*' and '*anti*' are synonymous with synclinal and antiperiplanar, respectively.

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## Structure of a Chiral Macrobicyclic Crown Ether, 1,4:1',4':3,6:3',6'-Tetraanhydro-2,2':5,5'-O-[2,2'-(3,6-dioxaoctane-1,8-diylidioxy)bis(1,3-phenylene)tetrakis(methylene)]di-D-mannitol Dichloromethane Solvate

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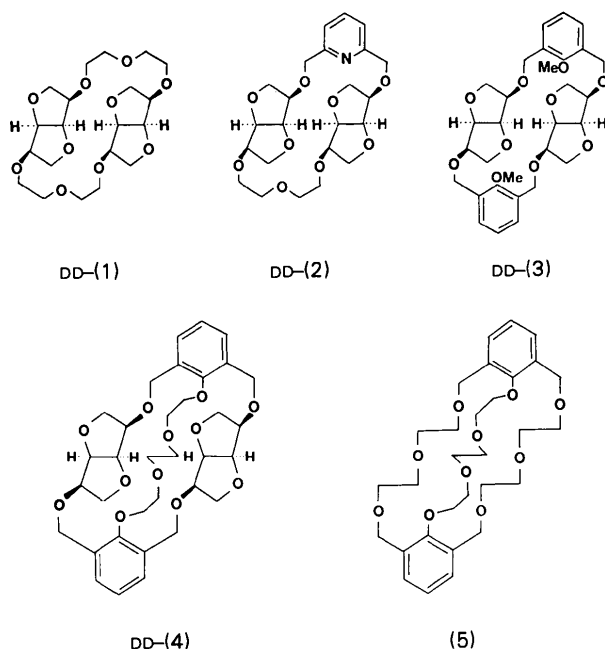
(Received 30 July 1985; accepted 23 December 1985)

**Abstract.** C<sub>34</sub>H<sub>42</sub>O<sub>12</sub>·CH<sub>2</sub>Cl<sub>2</sub>, *M<sub>r</sub>* = 727.63, orthorhombic, *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, *a* = 12.337 (2), *b* = 15.538 (2), *c* = 18.191 (4) Å, *V* = 3487 Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* =

1.39 g cm<sup>-3</sup>, λ(Cu Kα) = 1.54178 Å, μ = 22.1 cm<sup>-1</sup>, *F*(000) = 1536, room temperature, *R* = 0.049 for 2414 unique observed reflections. The chiral macrobicyclic

DD-(4) has gross conformational features similar to those of the macrocycles 1,4:1',4':3,6:3',6'-tetraanhydro-2,2':5,5'-bis(*O*-oxydiethylene)di-*D*-mannitol [DD-(1)] and 1,4:1',4':3,6:3',6'-tetraanhydro-5,5'-*O*-oxydiethylene-2,2'-*O*-[pyridine-2,6-diy]bis(methylene)]-di-*D*-mannitol [DD-(2)] in so far as the dianhydromannitolo units adopt a 'face-to-back' geometry with respect to each other. The central bridging polyether chain directs its O atoms into a potential molecular cavity and in so doing is reminiscent of the receptor 2,2'-(3,6-dioxaoctane-1,8-diyldioxy)-1,1':3,3'-bis(2,5,8-trioxanonane-1,9-diy)bis(phenylene) (5) when it is involved in complexing cationic rhodium complexes containing *cis*-diammine ligands. A hydrophilic cavity can be created in DD-(4) by a modest conformational change which affords a 'face-to-face' orientation of the two dianhydromannitolo units.

**Introduction.** Recently, we have reported on the X-ray crystal structures of DD-(1) (Metcalf, Stoddart, Jones, Crawshaw, Quick & Williams, 1981; Metcalf, Stoddart, Jones, Crawshaw, Gavuzzo & Williams, 1981), DD-(2) (Crawshaw, Stoddart & Williams, 1986*a*), and DD-(3) (Crawshaw, Stoddart & Williams, 1986*b*). Whereas in DD-(1) and DD-(2), the dianhydromannitolo units adopt a 'face-to-back' conformation, in DD-(3) they assume a 'back-to-back' conformation. With the objective of constructing a more rigid chiral cavity, DD-(4) has been synthesized (Crawshaw, 1982) employing a procedure similar to that reported (Alston, Slawin, Stoddart & Williams, 1984) for the achiral receptor (5). In this paper, we describe the X-ray crystal structure of the macrobicyclic compound DD-(4).



**Experimental.** Single crystals of DD-(4) [found:  $M$  (high-resolution mass spectrometry), 642.2674;  $C_{34}H_{42}O_{12}$  requires  $M$ , 642.2676], suitable for X-ray crystallography, were grown at room temperature from dichloromethane-hexane and had m.p. >523 K and  $[\alpha]_D^{20} = +203.3^\circ$  [ $CH_2Cl_2$ , 0.12 g dm<sup>-3</sup>]. The crystals were subsequently found to be solvated with one molecule of dichloromethane for each molecule of DD-(4). Crystal size 0.2 × 0.3 × 0.4 mm. Refined unit-cell parameters obtained by centring 22 reflections. Nicolet *R3m* diffractometer. 2663 independent reflections ( $\theta \leq 58^\circ$ ) measured,  $CuK\alpha$  radiation (graphite monochromator,  $\omega$  scan. 2414 [ $|F_o| > 3\sigma(|F_o|)$ ]) considered observed, index range  $h$  0/13,  $k$  0/16,  $l$  0/19; two check reflections measured every 50 reflections, net count constant; data brought to uniform scale, Lorentz and polarization corrections, no absorption correction. Several attempts at conventional multiple-solution tangent refinement using a series of different both automatically selected and hand-chosen starting sets failed to produce recognizable structural fragments. Structure ultimately solved by resorting to random-start tangent refinement and  $\Delta E$  map recycling; non-H atoms refined anisotropically; positions of H atoms calculated ( $C-H = 0.96 \text{ \AA}$ ), assigned isotropic thermal parameters,  $U(H) = 1.2 U_{eq}(C)$ , allowed to ride on parent C atoms. Empirical extinction correction applied [ $x = 0.0029(4)$ ]. Refinement using  $F$  magnitudes by block-cascade full-matrix least squares;  $R = 0.049$ ;  $wR = 0.055$  [ $w^{-1} = \sigma^2(F) + 0.0012F^2$ ].  $(\Delta/\sigma)_{max} = 0.035$ ; residual electron density in difference map within  $-0.44$  and  $+0.39 \text{ e \AA}^{-3}$ ; atomic scattering factors and dispersion corrections from *International Tables for X-ray Crystallography* (1974). Computations carried out on an Eclipse S140 computer using *SHELXTL* program system (Sheldrick, 1983).

**Discussion.** Table 1\* lists the fractional atomic coordinates of the non-H atoms, Table 2 the bond lengths and angles and selected C—C and C—O torsional angles associated with the dianhydromannitolo rings.

The structure of DD-(4) is illustrated in Fig. 1 which includes the atomic-numbering scheme and gives the torsion angles for a selected macrocyclic periphery and the bridging polyether chain. Fig. 2 shows a space-filling representation of the molecule.

The  $CH_2Cl_2$  solvent molecule, although well removed from the molecular cavity of DD-(4), is involved in two comparatively short C...O intermolecular contacts of

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters, and a figure of a skeletal representation of DD-(4) and the  $CH_2Cl_2$  molecule have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42740 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

3.09 (1) and 3.34 (1) Å to O(25) and O(8), respectively. The minimum associated H...O(25) and H...O(8) distances are 2.57 and 2.51 Å, respectively. These could be considered as indicating possible weak C—H...O interactions. The structure is loosely packed with only one intermolecular contact, namely C(41)...O(5) = 3.30 (1) Å, between molecules of DD-(4) of less than 3.4 Å.

The two dianhydromannitolo residues in DD-(4), by adopting a 'face-to-back' conformation as in DD-(2) (Crawshaw *et al.*, 1986a), give rise to the potential central cavity being filled by one [C(20) to C(27)] of the two carbohydrate units. The bridging polyether chain retains, with minor perturbations, a conventional all-*gauche* geometry (Goldberg, 1980). This is in contrast with the conformation assumed by the equivalent bridging polyether chain in free (5) (Alston *et al.*, 1984), which is folded in such a way as to fill partially

the central cavity of the molecule. However, on complexation with [Rh(cod)(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> (cod = 1,5-cyclo-octadiene), this bridging polyether chain in complexed (5) reverts to a geometry that matches closely the one

Table 1. Atom coordinates ( $\times 10^4$ ) and equivalent isotropic temperature factors ( $\text{Å}^2 \times 10^3$ )

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub> <sup>*</sup>
C(1)	6682 (4)	1949 (3)	8600 (3)	57 (2)
O(2)	7016 (2)	1536 (2)	7939 (2)	51 (1)
C(3)	6412 (3)	1771 (3)	7310 (3)	54 (2)
C(4)	6546 (4)	1075 (3)	6742 (3)	60 (2)
O(5)	7518 (2)	1269 (2)	6363 (2)	56 (1)
C(6)	7507 (4)	2179 (3)	6253 (3)	54 (1)
C(7)	6873 (4)	2558 (3)	6905 (3)	56 (2)
O(8)	7612 (3)	3056 (2)	7319 (2)	62 (1)
C(9)	8672 (4)	2740 (3)	7174 (3)	59 (2)
C(10)	8633 (4)	2550 (3)	6362 (3)	57 (2)
O(11)	9507 (3)	2001 (2)	6168 (2)	64 (1)
C(12)	9928 (4)	2111 (3)	5456 (3)	64 (2)
C(13)	11102 (4)	1840 (3)	5476 (2)	50 (1)
C(14)	11477 (5)	1131 (3)	5083 (3)	68 (2)
C(15)	12528 (5)	850 (4)	5151 (3)	78 (2)
C(16)	13213 (4)	1266 (3)	5622 (3)	64 (2)
C(17)	12897 (4)	1973 (3)	6021 (2)	49 (1)
C(18)	13674 (4)	2395 (3)	6552 (3)	62 (2)
O(19)	13646 (2)	2006 (2)	7265 (2)	58 (1)
C(20)	12853 (4)	2319 (3)	7747 (3)	51 (1)
C(21)	13254 (4)	2261 (4)	8534 (3)	66 (2)
O(22)	12330 (3)	2263 (3)	8982 (2)	71 (1)
C(23)	11392 (4)	2030 (3)	8553 (2)	52 (1)
C(24)	11788 (3)	1826 (3)	7795 (2)	48 (1)
O(25)	11989 (3)	912 (2)	7775 (2)	59 (1)
C(26)	11700 (4)	552 (3)	8462 (3)	66 (2)
C(27)	10924 (4)	1177 (3)	8810 (2)	55 (2)
O(28)	10915 (3)	1033 (2)	9577 (2)	70 (1)
C(29)	10208 (4)	1602 (4)	9963 (3)	69 (2)
C(30)	9026 (4)	1369 (3)	9856 (2)	52 (1)
C(31)	8565 (4)	694 (3)	10247 (2)	62 (2)
C(32)	7509 (5)	454 (3)	10144 (3)	67 (2)
C(33)	6893 (4)	877 (3)	9629 (3)	62 (2)
C(34)	7310 (4)	1548 (3)	9214 (2)	51 (1)
C(35)	8383 (4)	1805 (3)	9364 (2)	48 (1)
O(36)	8792 (3)	2501 (2)	8982 (2)	52 (1)
C(37)	8644 (5)	3303 (3)	9360 (3)	73 (2)
C(38)	8809 (6)	4031 (3)	8862 (4)	92 (2)
O(39)	9843 (3)	4060 (2)	8578 (2)	69 (1)
C(40)	10064 (6)	4869 (3)	8260 (3)	90 (3)
C(41)	10954 (5)	4860 (4)	7761 (3)	83 (2)
O(42)	10756 (3)	4372 (2)	7136 (2)	73 (1)
C(43)	11567 (5)	4428 (3)	6619 (3)	79 (2)
C(44)	11461 (6)	3782 (3)	6030 (3)	74 (2)
O(45)	11509 (3)	2958 (2)	6352 (2)	51 (1)
C(46)	11834 (4)	2273 (3)	5929 (2)	44 (1)
Cl(1)	14665 (2)	-816 (1)	6897 (1)	158 (1)
Cl(2)	14814 (2)	-120 (1)	8337 (1)	116 (1)
C(47)	14013 (5)	-233 (3)	7566 (3)	74 (2)

\* Equivalent isotropic *U* defined as one third of the trace of the orthogonalized *U*<sub>*ij*</sub> tensor.

Table 2. Bond lengths (Å), bond angles (°) and selected torsional angles (°)

C(1)—O(2)	1.424 (6)	C(1)—C(34)	1.495 (6)
O(2)—C(3)	1.414 (5)	C(3)—C(4)	1.505 (7)
C(3)—C(7)	1.537 (7)	C(4)—O(5)	1.416 (6)
O(5)—C(6)	1.428 (5)	C(6)—C(7)	1.537 (7)
C(6)—C(10)	1.518 (7)	C(7)—O(8)	1.414 (6)
O(8)—C(9)	1.422 (6)	C(9)—C(10)	1.507 (7)
C(10)—O(11)	1.420 (6)	O(11)—C(12)	1.404 (6)
C(12)—C(13)	1.509 (7)	C(13)—C(14)	1.392 (7)
C(13)—C(46)	1.396 (6)	C(14)—C(15)	1.374 (9)
C(15)—C(16)	1.365 (8)	C(16)—C(17)	1.374 (7)
C(17)—C(18)	1.511 (7)	C(17)—C(46)	1.402 (6)
C(18)—O(19)	1.431 (6)	O(19)—C(20)	1.401 (5)
C(20)—C(21)	1.517 (7)	C(20)—C(24)	1.523 (6)
C(21)—O(22)	1.400 (6)	O(22)—C(23)	1.443 (6)
C(23)—C(24)	1.497 (6)	C(23)—C(27)	1.520 (7)
C(24)—O(25)	1.442 (6)	O(25)—C(26)	1.416 (6)
C(26)—C(27)	1.503 (7)	C(27)—O(28)	1.413 (5)
O(28)—C(29)	1.426 (6)	C(29)—C(30)	1.515 (7)
C(30)—C(31)	1.388 (7)	C(30)—C(35)	1.375 (6)
C(31)—C(32)	1.368 (8)	C(32)—C(33)	1.373 (7)
C(33)—C(34)	1.386 (7)	C(34)—C(35)	1.409 (6)
C(35)—O(36)	1.382 (5)	O(36)—C(37)	1.435 (6)
C(37)—C(38)	1.463 (8)	C(38)—O(39)	1.378 (8)
O(39)—C(40)	1.410 (6)	C(40)—C(41)	1.424 (9)
C(41)—O(42)	1.389 (7)	O(42)—C(43)	1.377 (7)
C(43)—C(44)	1.474 (7)	C(44)—O(45)	1.409 (5)
O(45)—C(46)	1.373 (5)	Cl(1)—C(47)	1.716 (6)
Cl(2)—C(47)	1.725 (6)		
O(2)—C(1)—C(34)	107.0 (4)	C(1)—O(2)—C(3)	114.5 (3)
O(2)—C(3)—C(4)	108.2 (4)	O(2)—C(3)—C(7)	113.5 (4)
C(4)—C(3)—C(7)	101.6 (4)	C(3)—C(4)—O(5)	106.0 (4)
C(4)—O(5)—C(6)	105.7 (3)	O(5)—C(6)—C(7)	106.1 (4)
O(5)—C(6)—C(10)	110.5 (4)	C(7)—C(6)—C(10)	102.7 (4)
C(3)—C(7)—C(6)	104.6 (4)	C(3)—C(7)—O(8)	114.8 (4)
C(6)—C(7)—O(8)	107.0 (4)	C(7)—O(8)—C(9)	107.7 (3)
O(8)—C(9)—C(10)	102.8 (4)	C(6)—C(10)—C(9)	103.4 (4)
C(6)—C(10)—O(11)	115.7 (4)	C(9)—C(10)—O(11)	109.7 (4)
C(10)—O(11)—C(12)	115.9 (4)	O(11)—C(12)—C(13)	107.4 (4)
C(12)—C(13)—C(14)	121.9 (4)	C(12)—C(13)—C(46)	120.0 (4)
C(14)—C(13)—C(46)	118.0 (4)	C(13)—C(14)—C(15)	121.3 (5)
C(14)—C(15)—C(16)	119.4 (5)	C(15)—C(16)—C(17)	122.3 (5)
C(16)—C(17)—C(18)	120.3 (4)	C(16)—C(17)—C(46)	117.9 (4)
C(18)—C(17)—C(46)	121.7 (4)	C(17)—C(18)—O(19)	112.4 (4)
C(18)—O(19)—C(20)	116.0 (3)	O(19)—C(20)—C(21)	110.1 (4)
O(19)—C(20)—C(24)	117.7 (4)	C(21)—C(20)—C(24)	101.4 (4)
C(20)—C(21)—O(22)	106.5 (4)	C(21)—O(22)—C(23)	109.8 (3)
O(22)—C(23)—C(24)	106.8 (4)	O(22)—C(23)—C(27)	110.9 (4)
C(24)—C(23)—C(27)	102.9 (4)	C(20)—C(24)—C(23)	103.1 (4)
C(20)—C(24)—O(25)	110.1 (3)	C(23)—C(24)—O(25)	106.7 (3)
C(24)—O(25)—C(26)	108.9 (3)	O(25)—C(26)—C(27)	106.0 (4)
C(23)—C(27)—C(26)	101.1 (4)	C(23)—C(27)—O(28)	116.4 (4)
C(26)—C(27)—O(28)	108.6 (4)	C(27)—O(28)—C(29)	113.1 (4)
O(28)—C(29)—C(30)	112.2 (4)	C(29)—C(30)—C(31)	120.6 (4)
C(29)—C(30)—C(35)	121.4 (4)	C(31)—C(30)—C(35)	118.0 (4)
C(30)—C(31)—C(32)	121.7 (5)	C(31)—C(32)—C(33)	119.4 (5)
C(32)—C(33)—C(34)	121.6 (5)	C(1)—C(34)—C(33)	121.8 (4)
C(1)—C(34)—C(35)	120.9 (4)	C(33)—C(34)—C(35)	117.2 (4)
C(30)—C(35)—C(34)	121.9 (4)	C(30)—C(35)—O(36)	120.2 (4)
C(34)—C(35)—O(36)	117.9 (4)	C(35)—O(36)—C(37)	113.2 (3)
O(36)—C(37)—C(38)	110.9 (5)	C(37)—C(38)—O(39)	112.8 (5)
C(38)—O(39)—C(40)	111.3 (4)	O(39)—C(40)—C(41)	113.7 (5)
C(40)—C(41)—O(42)	113.0 (5)	C(41)—O(42)—C(43)	113.4 (4)
O(42)—C(43)—C(44)	112.9 (5)	C(43)—C(44)—O(45)	108.2 (4)
C(44)—O(45)—C(46)	118.9 (3)	C(13)—C(46)—C(17)	121.0 (4)
C(13)—C(46)—O(45)	121.1 (4)	C(17)—C(46)—O(45)	117.6 (4)
Cl(1)—C(47)—Cl(2)	111.2 (3)		
C(1)—O(2)—C(3)—C(4)	-158.9 (4)	C(18)—O(19)—C(20)—C(21)	-148.7 (4)
O(2)—C(3)—C(4)—O(5)	-84.8 (4)	O(19)—C(20)—C(21)—O(22)	-158.1 (4)
C(3)—C(4)—O(5)—C(6)	-41.7 (4)	C(20)—C(21)—O(22)—C(23)	19.1 (5)
C(4)—O(5)—C(6)—C(7)	30.2 (4)	C(21)—O(22)—C(23)—C(24)	3.2 (5)
O(5)—C(6)—C(7)—O(8)	114.5 (4)	O(22)—C(23)—C(24)—O(25)	92.4 (4)
C(6)—C(7)—O(8)—C(9)	-23.8 (5)	C(23)—C(24)—O(25)—C(26)	2.2 (5)
C(7)—O(8)—C(9)—C(10)	39.4 (5)	C(24)—O(25)—C(26)—C(27)	21.4 (5)
O(8)—C(9)—C(10)—O(11)	-163.0 (3)	O(25)—C(26)—C(27)—O(28)	-158.7 (4)
C(9)—C(10)—O(11)—C(12)	-148.2 (4)	C(26)—C(27)—O(28)—C(29)	179.4 (4)

we observe (Figs. 1 and 2) for free DD-(4). It is interesting to note that like the two methoxy methyl groups in DD-(3) (Crawshaw *et al.*, 1986*b*), the analogous pair of *O*-methylene groups [at C(37) and C(44)] in DD-(4) are directed away from the central cavity with their O—CH<sub>2</sub> bonds approximately orthogonal to the mean planes of the aryl rings. The same stereochemical arrangement of these groups is present (Alston *et al.*, 1984) in [Rh(cod)(NH<sub>3</sub>)<sub>2</sub>·(5)]<sup>+</sup>

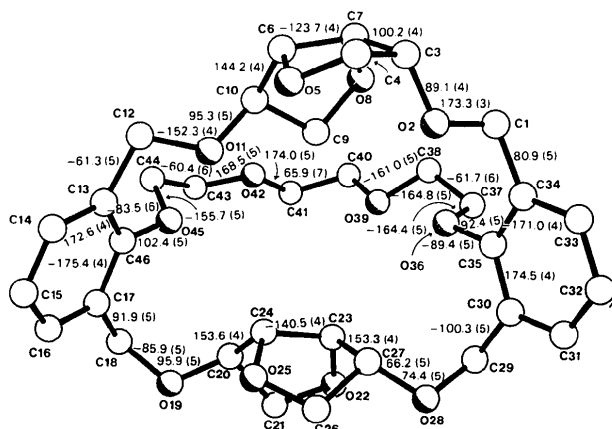


Fig. 1. Ball-and-stick representation of the structure of DD-(4) showing the atomic-numbering scheme and the torsional angles (°) around the macrocyclic periphery.

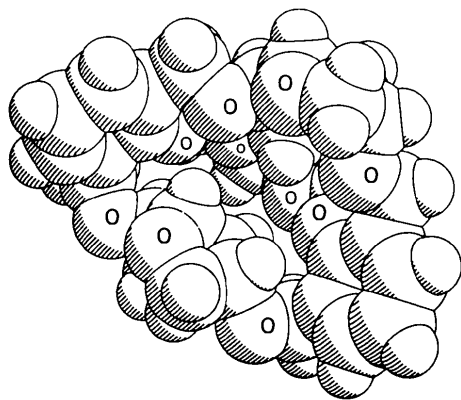


Fig. 2. A space-filling representation of DD-(4) corresponding to the skeletal view in Fig. 1.

whereas, in free (5), one of the O—CH<sub>2</sub> bonds, whilst still essentially orthogonal to the plane of its associated aryl ring, is directing the methylene group into the central cavity.

As in DD-(2) (Crawshaw *et al.*, 1986*a*), where the dianhydromannitolo residues also adopt a 'face-to-back' conformation, there are major differences (*ca* 60°) between equivalent torsional angles (Table 2) in the two residues. A consequence of the concave face of the dianhydromannitolo unit being oriented towards the centre of the macrocycle is the simultaneous directing inwards of O(2) and O(11) and an *anti* geometry about the C(1)—O(2) and O(11)—C(12) bonds. In contrast, the torsional angles about the C(18)—O(19) and O(28)—C(29) bonds are approximately *gauche* with the O atoms [O(19) and O(28)] being oriented away from the cavity. Clearly, a 'face-to-face' arrangement of the two dianhydromannitolo units in DD-(4) would result in all the O atoms being directed into the cavity, thus creating a hydrophilic pocket ideally suited for binding substrates.

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