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The crystal structure of 6^I-(6-aminohexyl)amino-6^I-deoxycyclomaltoheptaose

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Abstract

The monosubstituted cyclomaltoheptaose derivative, 6^I-(6-aminohexyl)amino-6^I-deoxycyclomaltoheptaose, crystallizes in the orthorhombic space group $P2_12_12_1$ with $a = 32.513(2)$, $b = 15.3871(9)$, $c = 15.2645(9)$ Å, $V = 7636.6(8)$ Å^3 and $Z = 4$. The macrocycles are spirally aligned along the twofold screw axis parallel to the c crystal axis forming polymeric-like columns. The 6-aminohexyl chain enters the cavity of an adjacent cyclomaltoheptaose moiety in the column from the secondary side and its extremity protrudes from the primary side of the latter. All the atoms of the chain exhibit high thermal motion.

Keywords: Cyclodextrin; Crystal structure; Synthesis; 6^I-(6-Aminohexyl)amino-6^I-deoxycyclomaltoheptaose; β-Cyclodextrin; Monosubstituted cyclomaltoheptaose

1. Introduction

Cyclomaltooligosaccharides (cyclodextrins, CDs) are of interest for modelling enzyme mechanisms and catalysis [1]. In order to improve their catalytic and complex-formation ability, modified CDs have been prepared by introducing more reactive groups into the macrocyclic ring [2]. Cyclomaltoheptaose (β-CD) is cheaper than the others, so its derivatives are of increasing interest. X-Ray analysis of monosubstituted cyclomaltoheptaoses (MCDs) have shown that a single molecule may behave both as a host and as

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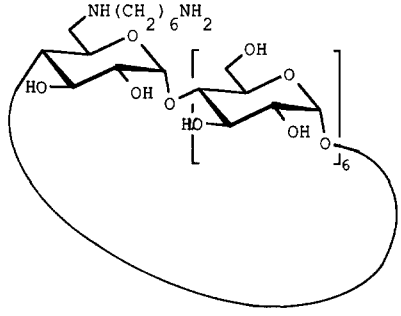
a guest [3–6] simultaneously. Each substituent group, having the role of the guest, is enclosed in the cavity of a neighboring MCD macrocycle which is the host. Thus, the inclusion formation for MCDs is much the same as for the parent CD [7]. We now report the synthesis and crystal structure analysis of 6^I-(6-aminohexyl)amino-6^I-deoxycyclomaltoheptaose (**1**). This compound is currently in use in our laboratory as a spacer system for the attachment of biologically active molecules to β-CD. The fact that the spacer-arm is orientated out of the cavity of the parent macrocycle is favorable for the interactions of such molecules with biological receptors and such interactions are under investigation.



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2. Experimental

6^I-(6-Aminohexyl)amino-6^I-deoxycyclomaltoheptaose (**1**).—To 1,6-hexanediamine from Aldrich Chemical Co., (50 mL, 0.43 mol) at 60 °C, was added (6^I-*O*-*p*-tolylsulfonyl)-cyclomaltoheptaose (2 g, 1.5 mmol), prepared by a known procedure [8] and the resultant solution heated, with stirring, at 80 °C for 12 h. The hot solution was poured into EtOH (500 mL) and the precipitate was filtered and washed with acetone (3 × 50 mL). The product was suspended in EtOH (50 mL) and refluxed for 6 h, to remove included 1,6-hexanediamine. Then, it was filtered and the solid was dried in vacuo to yield the title compound (500 mg, 48%); $[\alpha]_D^{25}$ + 118.8°. Anal. Calcd for $C_{48}H_{82}N_2O_{34} \cdot 10H_2O$: C, 40.85%; H, 7.28%; N, 1.98%. Found: C, 40.76%; H, 7.37%; N, 2.02%. Recrystallization was carried out by slow evaporation (2 months) of an aq soln that yielded crystal platelets from which X-ray data were collected. However their quality was low and they cracked immediately outside the mother liquor.

X-Ray measurements.—A crystal of dimensions 0.15 × 0.35 × 0.7 mm, covered with some mother liquor, sealed in a Lindemann glass capillary, was used for X-ray data collection. In preliminary Weissenberg and precession photographs, the systematic absences $h00$: $h = 2n$; $0k0$: $k = 2n$ and $00l$: $l = 2n$ and the Laue class *mmm* suggested the space group to be $P2_12_12_1$. The unit cell parameters were determined from 32

independent reflections. Intensity data were collected on a Syntex $P2_1$ diffractometer, upgraded with CRYSTAL LOGIC, with Ni-filtered Cu $K\alpha$ radiation with a θ–2θ scan mode up to 106° in 2θ, at $T = 295(2)$ K. A scan speed of 3.0°(2θ) min^{-1} was used with a scan width of 1.9°(2θ) plus the α_1–α_2 divergence. Of 5140 reflections collected, 4950 were unique and 2587 were considered as observed with $|F_o| \geq 4.0\sigma(|F_o|)$. The stability of the crystal was monitored by three standard reflections measured every 100 reflections. A 8.5% total decay in standard intensities was taken into account during data reduction. The intensities were corrected for Lorentz and polarization effects but not for absorption since the variation of the intensity as a function of Ψ was less than 4%.

Crystal data.—From the final results, the composition inferred was $C_{48}H_{82}N_2O_{34} \cdot 9.68H_2O$. The final lattice parameters were as follows: orthorhombic, space group $P2_12_12_1$, $a = 32.513(2)$, $b = 15.3871(9)$, $c = 15.2645(9)$ Å, $V = 7636.6(8)$ Å^3, $Z = 4$ and $D_{calc} = 1.222$ Mg m^{-3}.

Determination of the structure and refinement.—The skeleton atoms of β-CD moiety of the isomorphous structure of $6^I,6^{IV}$-di-*S*-(*tert*-butylthio)-$6^I,6^{IV}$-dithiocyclomaltoheptaose [4] were used as initial coordinates. The coordinates of the C-6 atoms, the hydroxyl oxygens, the substituent chain and the water molecules have been located by subsequent difference electron density maps, $\Delta\rho$. The refinement has been performed initially with a modified version of SHELX76 [9]. The coordinates of the 6-aminohexyl chain atoms have been optimized by fitting in a difference electron density map using the Molecular Graphics Program "O" [10] on an Indy Silicon Graphics workstation. Subsequently the structure has been refined by SHELXL93 [11] using unit weights, as giving a satisfactory analysis of variance and extinction correction [extinction coefficient 0.0020(3)]. Eleven reflections showing poor agreement for potential systematic errors, were given zero weight during final refinement cycles.

The occupancy factors of the oxygen atoms of the water molecules were refined. The total number of refined parameters was 472. Anisotropic thermal parameters have been used only for the O-4 and O-5 atoms. The small number of observations obtained leads to a small ratio of observed reflections to parameters, and does not allow the use of anisotropic refinement for all the non-H atoms. Hydrogen atoms linked to carbon atoms of the β-CD were used at calculated positions with C–H distance 0.98 Å for the secondary and 0.97 Å for the tertiary, while their thermal parameters have been set to $1.2 \times U_{iso}$ of the isotropic thermal parameter of the corresponding C atom. Scattering factors were taken from International Tables for X-ray Crystallography (1974) [12]. The structure was refined to $R = 0.127$ for the 2587 observed reflections and 0.184 for all data. The maximum and minimum peaks, observed in the final $\Delta\rho$ map, were 0.431 and -0.298 e A^{-3}. Four hydrogen atoms belonging to water molecules have been found by $\Delta\rho$ maps but their coordinates have not been refined. A list of the positional and isotropic or equivalent thermal parameters is given in Table 1 [1].

[1] Lists of the anisotropic thermal parameters of the O-4 and O-5 atoms, positional and thermal parameters of the H-atoms, bond lengths and angles and observed and calculated structure factors have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1E2, UK.

Table 1
Atomic coordinates (Å $\times 10^4$), equivalent isotropic displacement parameters (Å$^2 \times 10^3$) and occupancy factors (K) for **1**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor. Asterisks mark the anisotropically refined atoms

	x	y	z	U(iso/eq)	K
O-41	1644(4)	4287(7)	3144(8)	110(4)	*
C-11	367(6)	4883(13)	3493(13)	106(5)	
C-21	1239(6)	5506(12)	2840(13)	107(6)	
C-31	1582(5)	6033(11)	2493(11)	97(5)	
C-41	1791(5)	6480(11)	3274(11)	97(5)	
C-51	1906(5)	5873(11)	3970(11)	92(5)	
O-51	1557(4)	5343(7)	4245(8)	110(4)	*
O-21	1048(4)	007(9)	2166(10)	140(5)	
O-31	1441(4)	6667(8)	1855(8)	123(4)	
C-61	2040(6)	6281(12)	4804(11)	110(6)	
N-1	2190(5)	5667(11)	5471(12)	134(6)	
C-18	2230(15)	6148(30)	6360(25)	326(23)	
C-28	2159(18)	5513(42)	7122(29)	456(42)	
C-38	1764(15)	5267(34)	7282(32)	327(26)	
C-48	1582(23)	5564(51)	8056(40)	494(53)	
C-58	1501(24)	6345(51)	8362(41)	557(45)	
C-68	1450(27)	6781(37)	9290(52)	673(49)	
N-2	1372(23)	6115(51)	10098(41)	545(39)	
O-42	2165(3)	6880(7)	2899(8)	103(3)	*
C-12	2207(6)	7781(12)	3008(12)	104(5)	
C-22	2305(5)	8159(11)	2126(11)	93(5)	
C-32	2684(5)	7834(11)	1781(11)	94(5)	
C-42	3045(5)	8011(11)	2384(10)	86(4)	
C-52	2930(5)	7638(11)	3285(10)	89(5)	
O-52	2544(4)	7969(7)	3587(7)	105(4)	*
O-22	1960(4)	7996(8)	1538(8)	122(4)	
O-32	2784(3)	8260(7)	946(7)	103(3)	
C-62	3233(6)	7860(12)	4009(12)	107(6)	
O-62	3245(4)	8783(8)	4152(8)	119(4)	
O-43	3406(3)	7599(6)	2072(7)	93(3)	*
C-13	3767(5)	8063(12)	2067(11)	92(5)	
C-23	3931(5)	8099(11)	1147(11)	100(5)	
C-33	4048(5)	7208(11)	846(11)	98(5)	
C-43	4335(5)	6764(11)	1474(11)	94(5)	
C-53	4143(6)	6796(12)	2362(12)	106(5)	
O-53	4067(3)	7659(7)	2610(7)	103(4)	*
O-23	3623(4)	8503(8)	588(8)	114(4)	
O-33	4234(4)	7271(8)	−33(9)	128(4)	
C-63	4476(8)	6439(15)	3115(16)	142(8)	
O-63A	4282(6)	6472(13)	3944(14)	145(7)	0.73
O-63B	4769(17)	6878(35)	2915(35)	35(16)	0.27
O-44	4394(3)	5899(7)	1177(8)	108(4)	*
C-14	4806(7)	5619(15)	941(15)	131(7)	
C-24	4828(6)	5211(12)	96(13)	115(6)	
C-34	4590(6)	4416(11)	52(12)	100(5)	
C-44	4690(6)	3769(11)	721(11)	101(5)	
C-54	4656(6)	4227(13)	1631(13)	118(6)	
O-54	4902(4)	4980(8)	1632(11)	131(5)	*
O-24	4719(4)	5856(9)	−495(9)	136(5)	

Table 1 (continued)

	x	y	z	U(iso/eq)	K
O-34	4636(4)	4050(9)	−772(9)	129(4)	
C-64	4822(7)	3570(15)	2383(16)	142(8)	
O-64A	4660(7)	3788(15)	3273(15)	107(7)	0.50
O-64B	5236(21)	3706(42)	2128(43)	137(20)	0.20
O-64C	5031(13)	4254(27)	3045(28)	127(13)	0.30
O-45	4387(3)	3095(6)	728(7)	89(3)	*
C-15	4519(5)	2262(11)	524(10)	85(5)	
C-25	4280(5)	1874(11)	−181(11)	95(5)	
C-35	3836(5)	1818(11)	85(11)	102(5)	
C-45	3804(4)	1272(10)	930(9)	76(4)	
C-55	4090(5)	1624(11)	1598(11)	96(5)	
O-55	4501(3)	1731(7)	1275(8)	102(3)	*
O-25	4294(4)	2454(9)	−945(9)	128(4)	
O-35	3590(4)	1361(8)	−588(8)	117(4)	
C-65	4109(6)	1066(12)	2428(12)	118(6)	
O-65	4226(4)	231(10)	2234(10)	107(4)	
O-46	3388(3)	1281(6)	1219(6)	81(3)	*
C-16	3200(5)	480(11)	1396(11)	87(5)	
C-26	2782(5)	434(11)	854(11)	94(5)	
C-36	2487(5)	1133(11)	1202(10)	88(5)	
C-46	2451(5)	1050(11)	2169(10)	86(5)	
C-56	2852(5)	1057(11)	2644(10)	90(5)	
O-56	3106(3)	384(6)	2286(6)	82(3)	*
O-26	2894(3)	595(7)	−29(7)	99(3)	
O-36	2097(4)	1010(7)	807(8)	112(4)	
C-66	2815(5)	839(10)	3627(11)	96(5)	
O-66	2624(3)	29(8)	3773(8)	106(4)	
O-47	2202(3)	1771(6)	2441(7)	96(3)	*
C-17	1862(6)	1651(15)	3033(14)	117(6)	
C-27	1479(6)	1955(14)	2640(15)	130(7)	
C-37	1494(6)	2925(12)	2505(13)	114(6)	
C-47	1593(6)	3361(12)	3321(12)	112(6)	
C-57	2008(5)	3036(11)	3715(12)	98(5)	
O-57	1960(4)	2093(8)	3815(10)	127(4)	*
O-27	1428(4)	1526(9)	1814(10)	145(5)	
O-37	1097(5)	3198(10)	2200(10)	147(5)	
C-67	2127(6)	3355(13)	4581(13)	127(6)	
O-67	2507(4)	3089(9)	4873(9)	136(4)	
W-22	3365(8)	518(16)	5922(15)	241(9)	1.00
W-23	3972(8)	9455(17)	−816(18)	252(10)	0.96
W-31	4134(9)	2019(20)	7397(20)	188(11)	0.60
W-34	455(18)	1323(40)	1489(40)	322(25)	0.55
W-35	3893(22)	381(43)	7810(43)	377(31)	0.62
W-37	4703(19)	7079(46)	6742(44)	315(28)	0.48
W-62	957(5)	495(12)	8980(12)	182(6)	0.98
W-622	4086(10)	876(21)	5022(21)	297(14)	0.94
W-631	662(8)	1939(17)	9742(17)	185(9)	0.70
W-632	241(12)	4353(25)	199(25)	234(15)	0.64
W-64	5492(18)	7400(40)	426(38)	278(25)	0.46
W-65	5247(8)	4808(17)	4096(18)	202(10)	0.75
W-67	2845(11)	4742(23)	5375(21)	327(15)	1.00

3. Discussion

The numbering scheme of compound **1** is given in Fig. 1 [13]. C-*mn* or O-*mn* denotes the *m*th atom within the *n*th glucopyranose residue (G-*n*). All the atoms exhibit high thermal motion, their thermal parameters $U = B/8\pi^2$ being about 0.09 Å^2, for the atoms of the β-CD skeleton and 0.45 Å^2, for the chain and water oxygens, a usual feature of the CD structures [6].

The molecular conformation.—The oxygen atoms of the primary hydroxyl groups O-63 and O-64 are disordered over two and three sites (occupancy factors: 0.73 for the

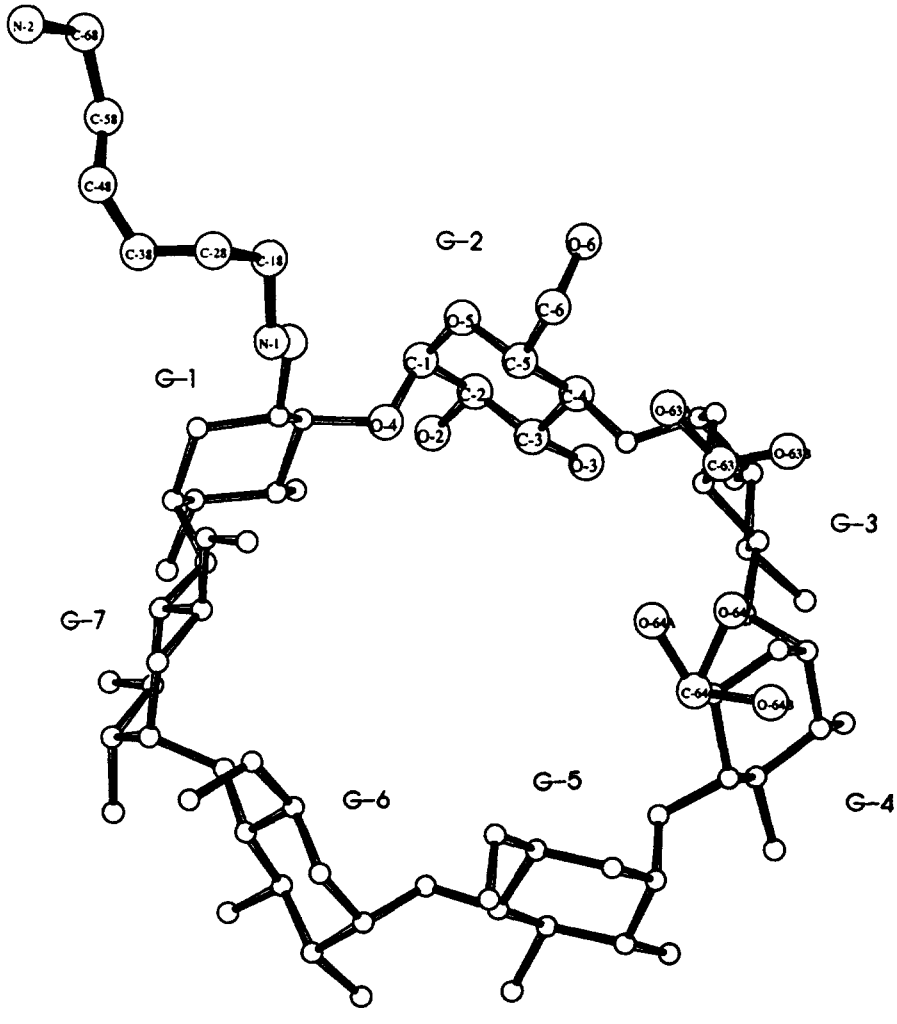

Fig. 1. An ORTEP molecular structure and numbering scheme for **1**.

Table 2
Selected torsion angles in degrees, with standard deviations in parentheses, and the tilt angles, formed between the O-4n and the O-4($n+1$)–C-1n–C-4n–O-4n mean planes

	G-1	G-2	G-3	G-4	G-5	G-6	G-7
C-41–C-51–C-61–N-1	−174.7(1.6)						
O-51–C-51–C-61–N-1	63.8(1.9)						
C-4–C-5–C-6–O-6		63.3(1.9)	−179.5(1.7)A 50.4(3.3)B	−158.2(1.8)A 74.3(3.3)B 145.3(2.2)C	58.0(2.1)	56.5(1.9)	−176.3(1.6)
O-5–C-5–C-6–O-6		−59.2(1.7)	62.2(2.1)A −69.9(3.1)	82.7(2.2)A −44.8(3.4)B 26.2(2.5)C	−67.7(1.9)	−61.7(1.9)	66.5(2.0)
Tilt angles	5.7	1.6	14.5	9.4	2.0	7.2	20.8

Table 3
Selected hydrogen bonds for 6^1-(6-aminohexyl)amino-6^1-deoxycyclomaltoheptaose (**1**)

H-bonds of the primary hydroxyl groups with a gauche–gauche *orientation*		
O-62 · · · W-62 = 2.83	C-62–O-62 · · · W-62 = 128	
O-65 · · · W-65 = 2.73	C-65–O-65 · · · W-65 = 124	
O-65 · · · W-62 = 2.95	C-65–O-65 · · · W-62 = 96	
O-62 · · · O-66 = 2.84	C-62–O-62 · · · O-66 = 128	O-62 · · · O-66–C-66 = 108
O-63B · · · O-64B = 2.81	C-63–O-63B · · · O-64B = 124	O-63B · · · O-64B–C-64 = 82
O-64B · · · O-65 = 3.09	C-64–O-64B · · · O-65 = 124	O-64B · · · O-65–C-65 = 143
O-64C · · · O-65 = 2.88	C-64–O-64C · · · O-65 = 127	O-64C · · · O-65–C-65 = 139
O-62 · · · O-36 = 2.78	C-62–O-62 · · · O-36 = 104	O-62 · · · O-36–C-36 = 137
O-66 · · · O-26 = 2.66	C-66–O-66 · · · O-26 = 135	O-66 · · · O-26–C-26 = 115
H-bonds of the primary hydroxyl groups with a gauche–trans *orientation*		
O-63A · · · W-631 = 2.74	C-63–O-63A · · · W-631 = 114	
O-63A · · · W-632 = 2.77	C-63–O-63A · · · W-632 = 94	
O-64A · · · W-65 = 2.77	C-64–O-64A · · · W-665 = 107	
O-64A · · · W-64 = 2.96	C-64–O-64A · · · W-64 = 120	
O-67 · · · W-67 = 2.88	C-67–O-67 · · · W-67 = 100	
O-67 · · · O-32 = 2.75	C-67–O-67 · · · O-32 = 96	O-67 · · · O-32–C-32 = 96
N-1 · · · W-67 = 2.57	C-61–N-1 · · · W-67 = 126	C-18–N-1 · · · W-67 = 104
H-bonds of the last chain atom		
N-2 · · · O-31 = 2.82	C-68–N-2 · · · O-31 = 121	N-2 · · · O-31–C-31 = 117
N-2 · · · W-67 = 2.90	C-68–N-2 · · · W-67 = 105	

major site of O-63; for the A, B and C sites of O-64 the occupancies were set to 0.50, 0.20 and 0.30 in order to have similar U values).

The main features of the β-CD moiety are common to all MCD structures. The conformation of the β-CD macrocycle is much the same as in the dimeric β-CD structures [14]. The substitution does not seem to affect the macrocycle geometry that much. However, in the present structure, the observed dispersion of the values of the corresponding bond lengths and angles of the glucopyranose residues is greater.

The primary hydroxyl groups of the G-2, G-5, G-6, and the B sites of the G-3 and G-4 residues have a *gauche–gauche* orientation pointing outwards of the β-CD cavity. They form hydrogen bonds with water molecules or other hydroxyl groups. The remaining groups having a *gauche–trans* orientation point inside the cavity forming hydrogen bonds with water molecules. The substituent group has also a *gauche–trans* orientation; the amine group points inwards and forms a strong H-bond with a water molecule (Tables 2 and 3).

The glycosidic O-4 atoms are lying in a plane within 0.16 Å. The tilt angles of glucopyranose residues, defined as the angles between the above O-4 plane and the individual O-4(n + 1)–C-1n–C-4n–O-4n planes, range between 1.6° and 20.8° (Table 2). All the tilt angles are positive. This is not true for all MCD structures. In 6-*O*-[(*R*)-2-hydroxypropyl]β-CD and 6-*O*-[(*S*)-2-hydroxypropyl]β-CD [6] the residue carrying the substituent group has an opposite tilt angle from the others. The hydroxypropyl groups in these two structures are rather short and the oxygen atom forms strong

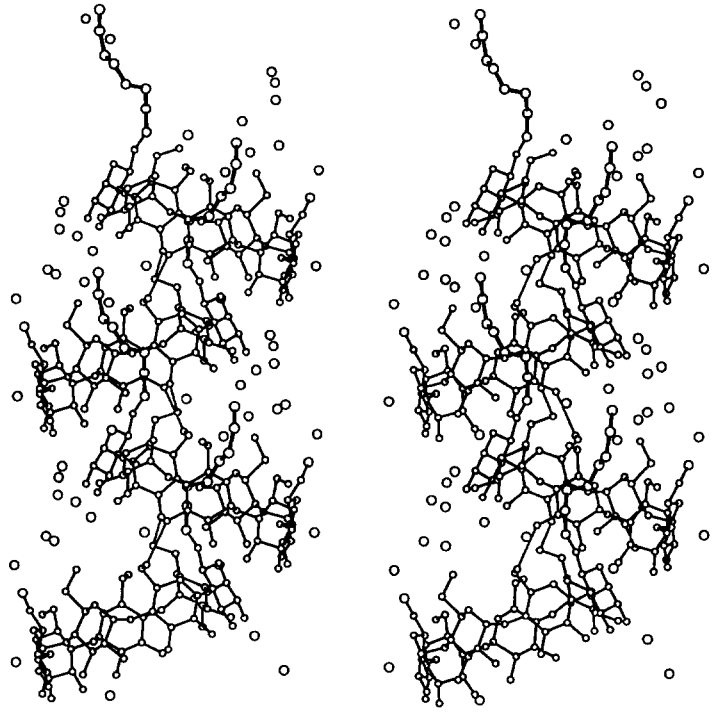

Fig. 2. A stereoview of the compound's polymeric-like columns.

hydrogen bonds with O-6 atoms of adjacent MCD and water molecules. So, the corresponding D-glucose residue is forced to flip over.

In the present structure, the flexible long substituent group enters the cavity of an adjacent host β-CD from the secondary hydroxyl side, traverses this macrocycle cavity, and its hydrophilic extremity comes out of its primary face into the hydrophilic intermolecular region of the column (see below) while its hydrophobic part is buried inside the hydrophobic cavity of the host β-CD. Its flexibility allows the chain to be accommodated nearly parallel to the approximate sevenfold axis of the host molecule. The N-1 atom is found near the secondary hydroxyl group rim of host β-CD and forms a strong hydrogen bond with W-67 (Table 3). The extreme atom of the substituent chain N-2, is also hydrogen bonded to a W-67 water molecule translated along the polymeric-like column, as well as to O-31 of a MCD macrocycle, related to the one to which the substituent is bonded by a whole translation along the *c* axis. The high thermal parameters of the chain atoms, close to the end, C-68 and N-2, imply a disorder. Attempts to find two sites using Molecular Graphics failed. Between the substituent chain and the MCD cavity, only three contacts less than 4.0 Å have been observed (C-58 · · · O-64A = 3.78 Å; C-68 · · · O-67 = 3.51 Å; N-2 · · · O-67 = 3.86 Å).

Molecular packing.—The macrocycles are spirally aligned along the twofold screw axis parallel to the *c* crystal axis (Fig. 2) forming screw channels [14]. The adjacent macrocycles of the columns are bound together by two hydrogen bonds formed between

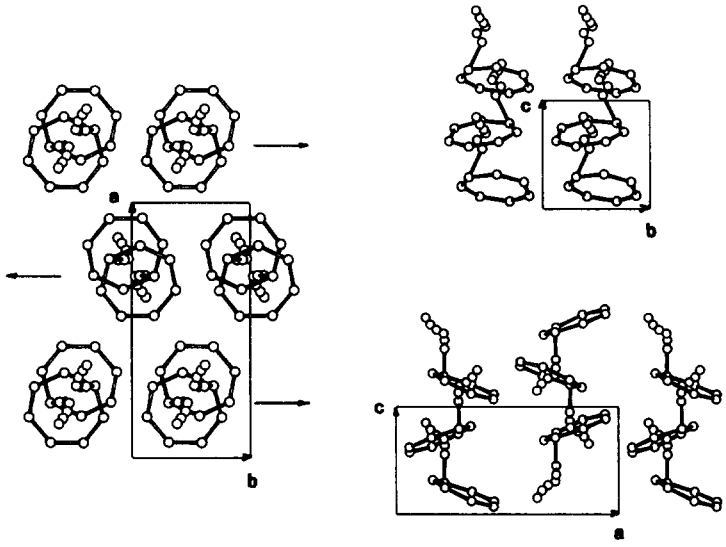

Fig. 3. Projection of the molecules on the crystal planes. Each of them is represented by its O-4 atoms and the atoms of the substituent chain.

primary and secondary hydroxyl groups (O-32 · · · O′-67; O-36 · · · O′-62; see Table 3). As a consequence, polymeric-like columns are formed [5,6]. The least-squares planes of the O-4 glucosidic atoms of two successive macrocycles of the same column form a dihedral angle of 43.3° while each of them forms an angle of 21.65° with the (001) crystal plane. Thus, the molecular packing has the appearance of a distorted, herringbone structure [15]. The above dihedral angles are smaller than the corresponding ones in the two hydroxypropyl β-CDs [6] (60° and 30° respectively) where the shorter and bulkier substituent group forces the whole molecule to rotate more with respect to each other than in the present structure and to translate also along the *b* axis. The present structure is isomorphous with two other structures [6^{I}-*S*-(*tert*-butylthio)-6^{I}-dithiocyclomaltoheptaose; $6^{I},6^{IV}$-di-*S*-(*tert*-butylthio)-$6^{I},6^{IV}$-dithiocyclomaltoheptaose] [3,4], where the *tert*-butylthio group being hydrophobic is accommodated inside the cavity of an adjacent macrocycle. On the contrary, the presence of a bulky phenyl group as a substituent group in phenylthio- and phenylsulfinyl-β-CD [5] gives rise to quite different cell dimensions and, notably, a different space group for one of them. Outside the columns is a hydrophilic pocket formed by three successive macrocycles of the same column filled with 9.68 water molecules, distributed over 13 sites (Fig. 2).

The MCD columns are stacked parallel along the *b* crystal axis and anti-parallel along the *a* axis (Fig. 3). Between parallel polymeric columns are two hydrogen bonds (O-26 · · · O′-66; O-62 · · · O′-66; Table 3). Between the adjacent anti-parallel polymeric columns, hydrogen bonds (O-63B · · · O′-64B and O-65 · · · O′-64B) including disordered O-6*n* atoms are formed. A further stabilization of the structure is due to a network of hydrogen bonds including water molecules.

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