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The crystal structure of the inclusion complex of cyclomaltoheptaose (β-cyclodextrin) with 4-*tert*-butylbenzoic acid

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ABSTRACT

The crystal of the 1:1 complex of cyclomaltoheptaose (β-cyclodextrin, βCD) with 4-*tert*-butylbenzoic acid is triclinic $P1$ with $a = 18.244(3)$, $b = 15.476(3)$, $c = 15.417(2)$ Å; $\alpha = 102.94(1)$, $\beta = 113.08(1)$, $\gamma = 99.69(2)°$; $V = 3740(1)$ Å^3; and $Z = 2$. The final R was determined to be 0.0932 for 8111 observed reflections (Mo$K\alpha$ radiation). Two independent molecules of βCD form a dimer, via hydrogen bonds involving the O-3*n* atoms, that encloses two molecules of 4-*tert*-butylbenzoic acid. The guest molecules penetrate the βCD cavities to different depths. There are 26.8 water molecules, distributed over 30 sites, which form a dense water network surrounding the dimers.

INTRODUCTION

Cyclodextrin (cyclomalto-oligosaccharide) complexes have been used for the study of noncovalent interactions which govern supramolecular chemistry. In an effort to determine the role of the nature of the guest molecule in the structure of the CD complexes, we have undertaken a systematic investigation of a series of βCD complexes, where only the polarity and/or the hydrogen-bonding ability of the guest varies.

The crystal structure of βCD with 4-*tert*-butylbenzoic acid is the third compound in the series, the other two being the complexes with 4-*tert*-butylbenzyl alcohol[1] and 4-*tert*-butyltoluene[2].

EXPERIMENTAL

Preparation of crystals and X-ray measurements.—The complex of βCD with 4-*tert*-butylbenzoic acid was formed immediately after the addition of an ethanolic solution of the guest molecule to an aqueous solution of βCD. The host–guest ratio was approximately 1:2. The complex dissolved on heating to 70°C with

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addition of a few drops of ethanol, and the solution was allowed to cool slowly. Six days later, colorless crystals were formed. Crystallographic data were collected from a well-formed, prismatic crystal ($0.7 \times 0.5 \times 0.3$ mm) sealed in a glass capillary to prevent loss of the water of crystallization.

One hemisphere of data ($2° < 2\theta < 55°$) was collected at 22°C on a CAD4 diffractometer with beta-filtered Mo$K\alpha$ radiation. The scan mode was $\omega/2\theta$ with scan angle $0.96 + 0.35 \tan \theta$ (degrees); horizontal scan aperture 1°, and vertical aperture 1.3° (3 and 4 mm at a distance of 173 mm from the crystal respectively). The scan speed was adapted per reflection to obtain a σ value of 2% but not taking longer than 60 s. The decay of the crystal was monitored by three standard reflections, but no decay was observed. Data were corrected for Lorentz and polarisation effects. No absorption correction was applied ($\mu = 0.82$ cm^{-1}). Of the 17729 reflections measured, 8111 with $F_o > 5\sigma(F_o)$ were considered as observed.

Crystal data.—From the final results, the composition inferred was $(C_{42}H_{70}O_{35}) \cdot (C_{11}H_{14}O_2) \cdot (H_2O)_{13.4}$. Final lattice parameters, as determined from 25 reflections ($18° < 2\theta < 36°$)[3], were: triclinic, space group $P1$; $a = 18.244(3)$, $b = 15.476(3)$, $c = 15.417(2)$ Å; $\alpha = 102.94(1)$, $\beta = 113.08(1)$, $\gamma = 99.69(2)°$; $V = 3740(1)$ Å^3; $Z = 2$; $d_{calcd} = 1.37$ g/cm^3.

Determination of the structure and refinement.—The structure was solved by using the coordinates of βCD molecules from the isomorphous crystal structure of a complex of βCD with 1-adamantanecarboxylic acid[4]. By difference Fourier calculations, 28 water positions were revealed. The structure was allowed to refine isotropically by unit-weight, full-matrix least-squares (SHELX76)[5] techniques, minimizing $(F_o - F_c)^2$, to $R = 13.6$. At this stage, the first guest molecule was completely located, while the second was still ambiguous. Anisotropic thermal parameters were assigned to all O-2, O-3, and O-6, and to the water molecules which behaved well during the refinement. Hydrogen atoms were calculated for all carbon atoms (C–H distance, 1.08 Å); only the positions of two hydroxyl hydrogen atoms were found but not refined. From the residual electron density, two more water positions and most of the second guest were located (two methyl carbon atoms and two carbon atoms belonging in the phenyl group were calculated at ideal positions). The guest molecules were allowed to refine isotropically by considering the phenyl groups as ideal hexagons and setting distance and angle constraints to *tert*-butyl and carboxyl groups. This process converged to $R = 0.0932$ and $R_w = 0.1044$ for all observed reflections $F_o > 5\sigma(F_o)$, while $R = 11.55$ and $R_w = 11.82$ for the reflections with $F_o > \sigma(F_o)$. Maximum and minimum values in the final difference-electron-density map were 0.86 and -0.52, respectively. The sum of the refined parameters was 1131. The final atomic coordinates are listed in Table I *.

* Atomic coordinates for this structure have been deposited with the Cambridge Crystallographic Data Centre. The coordinates may be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

TABLE I

Positional ($\times 10^4$) and thermal parameters ($U^2 = B/8\pi^2$, $\times 10^3$) of the nonhydrogen atoms with ESDs in parentheses, and the occupation factors (K) for the water and the guest molecules in the βCD–4-*tert*-butylbenzoic acid complex

Atom	x	y	z	U [a]	K
1C-11	2140(10)	380(10)	2560(10)	57	
1C-21	2837(9)	390(10)	2240(10)	52	
1O-21	3558(6)	342(7)	2967(8)	57 *	
1C-31	2971(9)	1270(10)	1910(10)	43	
1O-31	3596(7)	1267(8)	1569(9)	77	
1C-41	2171(8)	1260(10)	1130(10)	42	
1O-41	2313(6)	2138(6)	933(7)	41	
1C-51	1485(9)	1190(10)	1450(10)	48	
1O-51	1399(6)	397(6)	1764(7)	45	
1C-61	600(10)	980(10)	500(10)	66	
1O-61	8(8)	910(10)	810(10)	119 *	
1C-12	2134(8)	2150(10)	−50(10)	42	
1C-22	2911(9)	2720(9)	−10(10)	46	
1O-22	3573(6)	2312(7)	306(8)	58 *	
1C-32	3119(8)	3691(9)	650(10)	40	
1O-32	3850(5)	4264(6)	672(7)	47 *	
1C-42	2404(8)	4095(8)	250(10)	33	
1O-42	2581(5)	4970(6)	925(7)	38	
1C-52	1585(9)	3456(9)	140(10)	46	
1O-52	1451(6)	2510(6)	−431(7)	42	
1C-62	821(9)	3760(10)	−430(10)	47	
1O-62	759(6)	3752(8)	−1397(8)	64 *	
1C-13	2477(8)	5721(9)	560(10)	38	
1C-23	3293(8)	6461(9)	1070(10)	41	
1O-23	3901(6)	6136(6)	872(7)	45 *	
1C-33	3564(8)	6867(9)	2160(10)	36	
1O-33	4306(5)	7641(6)	2628(7)	41 *	
1C-43	2858(8)	7230(9)	2290(10)	36	
1O-43	3072(5)	7560(6)	3317(6)	35	
1C-53	2063(9)	6430(10)	1760(10)	48	
1O-53	1858(6)	6063(6)	718(7)	45	
1C-63	1320(10)	6780(10)	1810(10)	63	
1O-63	1238(7)	7523(9)	1410(10)	85 *	
1C-14	3095(8)	8474(9)	3740(10)	39	
1C-24	3925(8)	8954(9)	4620(10)	38	
1O-24	4583(5)	8977(6)	4348(7)	44 *	
1C-34	4033(8)	8474(9)	5410(10)	36	
1O-34	4771(5)	8943(7)	6275(7)	43 *	
1C-44	3298(8)	8470(10)	5670(10)	42	
1O-44	3343(6)	7878(6)	6273(7)	43	
1C-54	2451(8)	8062(9)	4730(10)	37	
1O-54	2432(6)	8507(6)	3991(7)	43	
1C-64	1740(10)	8220(10)	4970(10)	55	
1O-64	1851(7)	9171(8)	5398(9)	70 *	
1C-15	3307(9)	8220(10)	7180(10)	50	
1C-25	4088(9)	8190(10)	8020(10)	48	
1O-25	4816(6)	8713(7)	8050(7)	49 *	
1C-35	4089(9)	7190(10)	7910(10)	47	
1O-35	4806(6)	7148(7)	8732(7)	48 *	
1C-45	3296(8)	6672(9)	7880(10)	39	

TABLE I (continued)

Atom	x	y	z	U [a]	K
1O-45	3272(6)	5711(6)	7677(7)	42	
1C-55	2550(9)	6750(10)	7040(10)	48	
1O-55	2595(6)	7721(7)	7169(8)	54	
1C-65	1720(10)	6320(10)	6990(20)	84	
1O-65	1760(10)	6630(10)	7970(20)	150 *	
1C-16	3195(8)	5275(9)	8370(10)	36	
1C-26	3888(8)	4823(9)	8680(10)	36	
1O-26	4675(6)	5503(6)	9172(7)	39 *	
1C-36	3797(8)	4105(9)	7790(10)	40	
1O-36	4449(5)	3653(7)	8080(8)	46 *	
1C-46	2960(8)	3391(9)	7310(10)	35	
1O-46	2855(5)	2778(6)	6412(7)	37	
1C-56	2271(8)	3856(9)	7090(10)	37	
1O-56	2414(6)	4602(6)	7949(7)	43	
1C-66	1400(9)	3190(10)	6740(10)	46	
1O-66	1413(7)	2788(7)	7499(9)	64 *	
1C-17	2655(9)	1810(10)	6280(10)	45	
1C-27	3331(9)	1430(10)	6100(10)	46	
1O-27	4124(6)	1910(7)	6937(8)	48 *	
1C-37	3312(8)	1540(10)	5150(10)	41	
1O-37	3907(6)	1160(6)	4951(7)	44 *	
1C-47	2459(9)	1020(10)	4310(10)	44	
1O-47	2428(5)	1171(6)	3412(7)	41	
1C-57	1800(9)	1380(10)	4530(10)	47	
1O-57	1856(6)	1346(7)	5463(8)	52	
1C-67	880(10)	730(10)	3820(10)	65	
1O-67	779(7)	−183(8)	3872(9)	66 *	
2C-11	6833(7)	1227(8)	5113(9)	28	
2C-21	6137(7)	1066(8)	5375(9)	31	
2O-21	5340(6)	760(6)	4515(7)	41 *	
2C-31	6206(8)	1915(9)	6130(10)	39	
2O-31	5559(6)	1754(7)	6424(7)	48 *	
2C-41	7049(8)	2191(9)	7030(10)	39	
2O-41	7151(5)	3075(6)	7690(6)	37	
2C-51	7740(8)	2306(9)	6700(10)	40	
2O-51	7599(5)	1478(6)	5927(7)	39	
2C-61	8622(9)	2430(10)	7590(10)	48	
2O-61	8606(6)	1708(8)	8003(8)	60 *	
2C-12	7337(9)	3140(10)	8700(10)	46	
2C-22	6696(8)	3453(9)	8930(10)	39	
2O-22	5895(6)	2802(6)	8295(7)	47 *	
2C-32	6688(8)	4409(9)	8830(10)	36	
2O-32	6089(5)	4738(6)	9086(7)	40 *	
2C-42	6547(8)	5075(8)	9540(10)	35	
2O-42	7554(6)	5946(6)	9361(7)	42	
2C-52	8204(9)	4710(10)	9310(10)	49	
2O-52	8143(6)	3793(6)	9343(7)	43	
2C-62	9120(10)	5290(10)	10130(10)	55	
2O-62	9219(6)	5235(7)	11070(8)	52 *	
2C-13	7856(8)	6739(9)	10210(10)	41	
2C-23	7152(8)	7233(9)	10050(10)	39	
2O-23	6423(6)	6644(7)	9944(7)	51 *	
2C-33	7000(8)	7582(9)	9160(10)	40	

TABLE I (continued)

Atom	x	y	z	U [a]	K
2O-33	6405(6)	8072(7)	9036(8)	59 *	
2C-43	7833(9)	8200(10)	9330(10)	45	
2O-43	7703(6)	8441(6)	8459(7)	41	
2C-53	8517(8)	7697(9)	9540(10)	39	
2O-53	8582(6)	7343(6)	10334(7)	44	
2C-63	9360(10)	8330(10)	9850(10)	65	
2O-63	9580(7)	9075(8)	10700(10)	78 *	
2C-14	7914(8)	9396(9)	8540(10)	41	
2C-24	7127(8)	9561(9)	7800(10)	39	
2O-24	6467(6)	9382(7)	8062(7)	49 *	
2C-34	6913(8)	8971(9)	6760(10)	35	
2O-34	6216(6)	9149(7)	6052(7)	48 *	
2C-44	7655(8)	9210(9)	6540(10)	37	
2O-44	7446(6)	8575(6)	5594(7)	43	
2C-54	8434(9)	9110(10)	7320(10)	45	
2O-54	8579(6)	9631(6)	8311(7)	47	
2C-64	9234(9)	9510(10)	7240(10)	49	
2O-64	9309(7)	10434(8)	7260(10)	78 *	
2C-15	7564(9)	8920(10)	4880(10)	48	
2C-25	6756(9)	8600(10)	3950(10)	45	
2O-25	6126(6)	8919(6)	4140(7)	48 *	
2C-35	6488(9)	7570(10)	3480(10)	43	
2O-35	5746(6)	7278(7)	2567(7)	47 *	
2C-45	7194(8)	7300(9)	3300(10)	36	
2O-45	6954(6)	6297(6)	2900(7)	42	
2C-55	7996(9)	7650(10)	4250(10)	50	
2O-55	8180(6)	8622(7)	4662(8)	52	
2C-65	8740(10)	7450(20)	4110(20)	83	
2O-65	8830(10)	7770(10)	3380(20)	136 *	
2C-16	6955(8)	5896(9)	1980(10)	35	
2C-26	6123(8)	5190(9)	1320(10)	37	
2O-26	5458(6)	5614(6)	1161(7)	46 *	
2C-36	6021(8)	4434(9)	1790(10)	41	
2O-36	5263(6)	3723(6)	1142(8)	51 *	
2C-46	6735(8)	4023(9)	1940(10)	39	
2O-46	6668(6)	3394(6)	2491(7)	42	
2C-56	7567(8)	4761(9)	2520(10)	41	
2O-56	7595(6)	5501(6)	2086(7)	43	
2C-66	8300(10)	4400(10)	2530(10)	56	
2O-66	8177(7)	3975(8)	1566(9)	76 *	
2C-17	6708(9)	2470(10)	2130(10)	49	
2C-27	5946(9)	1820(10)	2000(10)	51	
2O-27	5205(7)	1950(7)	1318(8)	56 *	
2C-37	5928(9)	1910(10)	2970(10)	46	
2O-37	5129(9)	1233(7)	2852(8)	52 *	
2C-47	6726(9)	1770(10)	3680(10)	46	
2O-47	6758(5)	1941(6)	4653(7)	40	
2C-57	7502(9)	2470(10)	3800(10)	51	
2O-57	7430(7)	2353(7)	2787(8)	57	
2C-67	8340(10)	2310(20)	4400(20)	86	
2O-67	8310(10)	1370(20)	3990(20)	220 *	
1W-61	−940(10)	2000(10)	0(10)	116 *	1.00
1W-62	460(20)	5300(20)	8180(20)	196 *	1.00

TABLE I (continued)

Atom	x	y	z	U [a]	K
1W-63	820(30)	7050(30)	−570(30)	274	0.89
1W-64	1880(20)	9930(20)	7210(20)	228 *	1.00
1W-66	660(10)	920(10)	6910(20)	148 *	1.00
1W-67A	10(30)	9730(30)	5010(40)	205	0.56
1W-67B	400(8)	8451(10)	2222(9)	70	1.00
1W-21	4070(30)	9130(20)	1870(30)	272 *	0.80
1W-22	3530(20)	910(20)	8470(20)	238 *	1.00
1W-23	4730(20)	−2360(10)	580(20)	190 *	1.00
1W-25	5850(20)	−320(20)	190(30)	243 *	1.00
1W-27	4840(10)	630(10)	7580(10)	134 *	1.00
1W-31	4040(20)	60(30)	130(30)	280	0.97
2W-62A	70(20)	3880(20)	1370(20)	183 *	1.00
2W-62B	−316(8)	6870(10)	2560(10)	81 *	1.00
2W-66	7900(10)	2090(10)	740(10)	120 *	1.00
2W-67A	−510(40)	630(40)	5170(50)	208	0.44
2W-67B	8460(40)	720(60)	2200(60)	535	1.00
2W-22	5080(20)	2430(10)	−610(10)	152 *	1.00
2W-23	5980(30)	−2120(20)	1030(30)	177 *	0.61
2W-24	6450(20)	1100(20)	−710(20)	191 *	1.00
2W-25	5420(20)	−640(20)	2450(20)	141 *	0.85
2W-27	4850(60)	430(30)	−420(40)	326 *	0.68
W-1	1660(40)	8900(50)	8470(60)	438	0.88
W-2	20(30)	7780(30)	7750(40)	401	1.00
W-3	−510(40)	2370(40)	2790(40)	472 *	1.00
W-4	8580(40)	−510(30)	2290(40)	373 *	0.99
W-5	6760(40)	−440(40)	1730(50)	300	0.67
W-6	3510(30)	8720(30)	330(40)	300	0.76
W-7	1340(70)	8440(80)	−530(90)	547	0.70
1C-1	5310(30)	4920(40)	4820(40)	487	1.00
1C-2	5770(50)	4300(50)	5360(60)	605	1.00
1C-3	5070(50)	4940(60)	3740(40)	611	1.00
1C-4	6000(40)	5780(40)	5620(50)	407	1.00
1C-5	4500(30)	4630(50)	4940(40)	387	1.00
1C-6	3930(30)	3890(50)	4110(40)	629	1.00
1C-7	3150(30)	3960(50)	3530(40)	766	1.00
1C-8	2930(30)	4770(50)	3780(40)	1055	1.00
1C-9	3500(30)	5510(50)	4620(40)	847	1.00
1C-10	4290(30)	5440(50)	5200(40)	635	1.00
1C-11	1910(30)	4460(40)	3480(80)	787	1.00
1O-1	1360(30)	4890(40)	3330(50)	554	1.00
1O-2	1270(40)	3600(40)	3070(50)	684	1.00
2C-1	7660(50)	5460(60)	5760(70)	572	0.90
2C-2	7440(50)	6270(50)	6320(70)	548	0.90
2C-3	7980(60)	5140(70)	6750(70)	680	0.90
2C-4	6730(40)	5030(60)	4970(60)	434	0.90
2C-5	8500(30)	5650(60)	5660(40)	409	0.90
2C-6	8780(30)	4930(60)	5280(40)	574	0.90
2C-7	9540(30)	5140(60)	5260(40)	318	0.90
2C-8	10030(30)	6050(60)	5610(40)	794	0.90
2C-9	9750(30)	6770(60)	5980(40)	577	0.90
2C-10	8990(30)	6560(60)	6010(40)	605	0.90
2C-11	10310(50)	5990(60)	4700(60)	878	0.90
2O-1	10440(20)	5950(20)	3920(20)	240	0.90

[a] Asterisks mark the anisotropic atoms $U = 1/3(U_{11} + U_{22} + U_{33})$.

DISCUSSION

The numbering scheme adopted for the complex is given in Fig. 1: C-*mn* or O-*mn* denotes the *m*th atom within the *n*th glucosidic residue (G − *n*). The number 1 or 2 preceding the atoms denotes the crystallographically independent βCD complex molecules 1 or 2, respectively. These form a head-to-head dimer via 1O-3*n* ··· 2O-3(8 − *n*) hydrogen bonds. Two guest molecules are accommodated in the cavity of the βCD dimer (Fig. 2). Bond lengths and bond angles of the two βCD and guest molecules are given in Table II. The pyranose rings have the $^4C_1$ conformation. Apart from 1G-1, in all residues the primary hydroxyl groups have the *gauche–gauche* orientation [mean torsion angles C-4–C-5–C-6–O-6 and O-5–C-5–C-6–O-6, 55.9(9)° and −64.7(8)°, respectively] and point out of the cavity; 1O-61 points inwards, with the 1C-61–1O-61 bond *gauche* to the 1C-51–1O-51 bond (torsion angle 62°) and *trans* to the 1C-4–1C-5 bond (torsion angle 179°).

As is shown in Table III, the sevenfold symmetry of the βCD molecule is well maintained; the O-4*n* ··· O-4(*n* + 1) average distance is 4.37(2) Å while the mean value of the angle O-4(*n* − 1) ··· O-4*n* ··· O-4(*n* + 1) is 128.6(4)°, equal to the angle of the regular heptagon. Moreover, deviations of the O-4*n* atoms from their optimum plane are very small. The value of the dihedral angles between the O-4*n* optimum plane and the planes through the atoms C-2, C-3, C-5, and O-5 [average 84.1(5)°] indicate that the primary and secondary rims of the βCD cavity have little difference in diameter. The conformation of the βCD macrocycle is stabilized

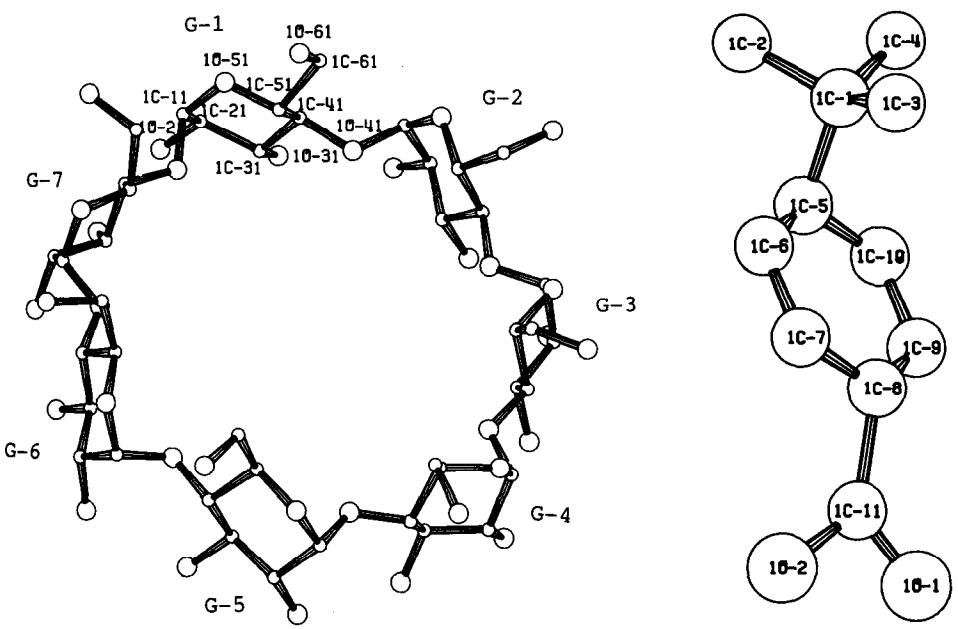

Fig. 1. The numbering scheme in the βCD and *tert*-butylbenzoic acid molecules.

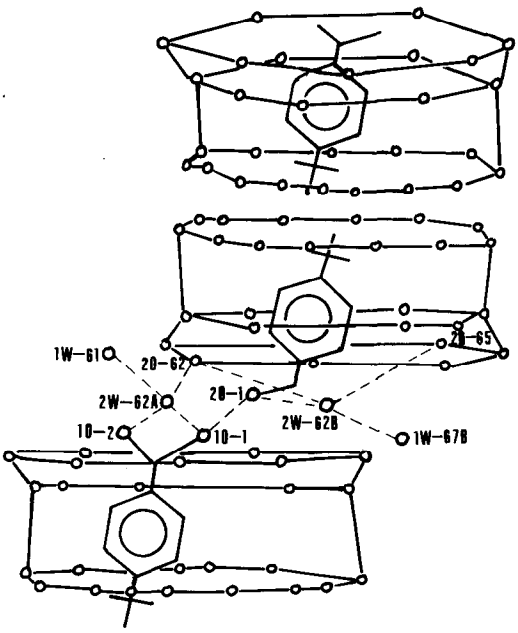

Fig. 2. Schematic drawing of the dimer and the hydrogen bonds in the interface between the dimers.

through strong intramolecular hydrogen bonds connecting the O-3n with O-2(n + 1) atoms of two neighboring glucosidic units. The O-3n $\cdots$ O-2(n + 1) distances [average 2.78(0) Å] and the angles C-3n–O-3n $\cdots$ O-2(n + 1) and O-3n $\cdots$ O-2(n + 1)–C-2(n + 1) [average 117.0(2)° and 119.5(3)°, respectively] lie within the normal values for hydrogen bonds. The βCD dimer is formed by means of strong intermolecular hydrogen bonds between 1O-3n $\cdots$ 2O-3(8 − n) with average distance 2.79(2) Å. The angles 1C-3n–1O-3n $\cdots$ 2O-3(8 − n) and 1O-3n $\cdots$ 2O-3(8 − n)–2C-3(8 − n) have mean values 118.4(6)° and 117.9(3)°, respectively (see Table IV). This does not apply to the interactions 1O-2n $\cdots$ 2O-2(8 − n), where all the distances are greater than 3.5 Å. The distances 1O-2n $\cdots$ 2O-3(8 − n) and 1O-3n $\cdots$ 2O-2(8 − n) have average values 3.10(3) and 3.10(2) Å, respectively, and they could indicate weak hydrogen bonding. However, although the angles 1C-2n–1O-2n $\cdots$ 2O-3(8 − n) and 1O-3n $\cdots$ 2O-2(8 − n)–2C-2(8 − n) have mean values 113.0(4)° and 113.3(5)°, respectively, the high values of the angles 1O-2n $\cdots$ 2O-3(8 − n)–2C-3(8 − n) and 1C-3n–1O-3n...2O-2(8 − n) [average 161.2(9) and 163.8(13)°, respectively] exclude such a possibility.

The dimers form layers almost parallel to the *bc* plane with their axis forming an angle of 19.2° with the crystallographic *a* axis (see Fig. 3). The relative average shifting of two dimers in consecutive layers is 6.0(0) Å, almost equal to the inner diameter of the βCD cavity at the primary edge. This type of packing, where the sevenfold axis of a dimer is located near the rim of the dimer below, has been classified as intermediate (IM)[1]. There are direct H-bonds between primary

TABLE II

Bond distances (Å) and angles of the βCD–4-*tert*-butylbenzoic acid complex

βCD of molecule 1							
Bond [a]	G-1	G-2	G-3	G-4	G-5	G-6	G-7
C-1–C-2	1.52(3)	1.52(2)	1.50(2)	1.50(2)	1.53(2)	1.51(2)	1.54(2)
C-1–O-5	1.44(2)	1.42(2)	1.41(2)	1.42(2)	1.40(2)	1.42(2)	1.42(1)
C-2–C-3	1.57(2)	1.50(2)	1.50(2)	1.53(2)	1.52(2)	1.49(2)	1.51(2)
C-2–O-2	1.38(2)	1.42(2)	1.40(2)	1.41(2)	1.41(2)	1.42(1)	1.43(1)
C-3–C-4	1.48(2)	1.52(2)	1.55(2)	1.55(2)	1.51(2)	1.51(2)	1.51(2)
C-3–O-3	1.43(2)	1.45(2)	1.44(1)	1.40(1)	1.44(2)	1.45(2)	1.42(2)
C-4–C-5	1.52(3)	1.57(2)	1.52(2)	1.55(2)	1.52(2)	1.52(2)	1.52(2)
C-4–O-4	1.46(2)	1.41(2)	1.42(2)	1.44(2)	1.44(2)	1.41(2)	1.44(2)
C-5–C-6	1.61(2)	1.54(2)	1.56(3)	1.51(3)	1.51(3)	1.55(2)	1.59(2)
C-5–O-5	1.42(2)	1.45(2)	1.45(2)	1.45(2)	1.46(2)	1.45(2)	1.41(2)
C-6–O-6	1.34(3)	1.45(2)	1.43(2)	1.42(2)	1.45(4)	1.44(2)	1.42(2)
O-4–C-1″	1.42(2)	1.41(2)	1.40(2)	1.41(2)	1.43(2)	1.43(2)	1.42(2)
Angle [a]							
C-1–C-2–C-3	109(1)	108(1)	112(1)	109(1)	109(1)	109(1)	109(1)
C-2–C-3–C-4	109(1)	110(1)	108(1)	108(1)	109(1)	111(1)	108(1)
C-3–C-4–C-5	113(1)	110(1)	108(1)	112(1)	110(1)	110(1)	111(1)
C-4–C-5–O-5	110(1)	110(1)	110(1)	111(1)	109(1)	112(1)	112(1)
C-5–O-5–C-1	115(1)	114(1)	113(1)	113(1)	113(1)	114(1)	114(1)
O-5–C-1–C-2	110(2)	111(1)	111(1)	112(1)	111(2)	110(1)	111(1)
C-1–C-2–O-2	113(2)	111(1)	111(1)	112(2)	111(2)	110(1)	110(1)
C-3–C-2–O-2	113(1)	112(1)	112(1)	111(1)	111(1)	113(1)	112(1)
C-2–C-3–O-3	109(1)	110(1)	112(1)	111(1)	110(1)	110(1)	110(1)
C-4–C-3–O-3	112(1)	109(1)	108(1)	108(1)	111(1)	109(1)	109(1)
C-4–C-5–C-6	110(1)	111(1)	110(1)	111(1)	114(2)	114(1)	114(1)
O-5–C-5–C-6	104(1)	107(1)	107(1)	106(1)	105(2)	107(1)	100(1)
C-5–C-6–O-6	108(2)	110(2)	111(2)	112(1)	110(1)	109(1)	112(1)
C-3–C-4–O-4	107(1)	110(1)	109(1)	106(1)	108(1)	109(1)	108(1)
C-5–C-4–O-4	108(1)	108(1)	109(1)	108(1)	108(1)	109(1)	109(1)
C-2–C-1–O-4′	107(1)	108(1)	109(1)	109(1)	109(1)	108(1)	109(1)
O-5–C-1–O-4′	111(1)	111(1)	111(1)	112(1)	111(1)	111(1)	110(1)
C-4–O-4–C-1″	120(1)	119(1)	119(1)	117(1)	118(1)	118(1)	118(1)

4-tert-Butylbenzoic acid of molecule 1

Bond		Angle	
C-1–C-2	1.55(11)	C-2–C-1–C-3	129(7)
C-1–C-3	1.56(10)	C-2–C-1–C-4	90(4)
C-1–C-4	1.54(7)	C-2–C-1–C-5	97(6)
C-1–C-5	1.56(9)	C-3–C-1–C-4	113(6)
C-8–C-11	1.68(7)	C-3–C-1–C-5	110(5)
C-11–O-1	1.28(8)	C-4–C-1–C-5	118(6)
C-11–O-2	1.44(7)	C-7–C-8–C-11	108(5)
		C-9–C-8–C-11	122(6)
		C-8–C-11–O-1	134(6)
		C-8–C-11–O-2	135(6)
		O-1–C-11–O-2	90(4)

hydroxyl groups of dimers in the same *bc* layer translated along the *c* axis (1O-62 ··· 1O-66, 2.76 Å; and 2O-62 ··· 2O-66, 2.93 Å), or along the *b* axis (1O-64 ··· 1O-67, 2.91 Å; and 2O-64 ··· 2O-61, 2.79 Å). There is also an interlayer

TABLE II (continued)

βCD of molecule 2							
Bond [a]	G-1	G-2	G-3	G-4	G-5	G-6	G-7
C-1–C-2	1.48(2)	1.48(3)	1.57(2)	1.55(2)	1.50(2)	1.51(2)	1.49(2)
C-1–O-5	1.38(1)	1.45(1)	1.40(2)	1.41(2)	1.41(2)	1.38(2)	1.38(2)
C-2–C-3	1.50(2)	1.52(2)	1.53(2)	1.51(2)	1.50(2)	1.52(2)	1.48(3)
C-2–O-2	1.44(1)	1.43(1)	1.41(2)	1.41(2)	1.43(2)	1.44(2)	1.43(2)
C-3–C-4	1.52(2)	1.52(2)	1.54(2)	1.54(2)	1.53(2)	1.50(2)	1.53(2)
C-3–O-3	1.42(2)	1.43(2)	1.40(2)	1.43(2)	1.42(2)	1.42(1)	1.44(2)
C-4–C-5	1.53(2)	1.53(2)	1.54(2)	1.53(2)	1.51(2)	1.52(2)	1.55(2)
C-4–O-4	1.44(2)	1.43(2)	1.42(2)	1.42(2)	1.45(2)	1.45(2)	1.44(2)
C-5–C-6	1.60(2)	1.59(2)	1.50(2)	1.56(3)	1.53(3)	1.54(3)	1.53(3)
C-5–O-5	1.45(2)	1.41(2)	1.42(2)	1.45(2)	1.42(2)	1.45(2)	1.48(2)
C-6–O-6	1.41(2)	1.42(2)	1.40(2)	1.40(2)	1.37(4)	1.40(2)	1.44(4)
O-4–C-1″	1.43(2)	1.42(2)	1.43(2)	1.40(2)	1.42(2)	1.44(2)	1.44(2)
Angle [a]							
C-1–C-2–C-3	111(1)	111(1)	110(1)	108(1)	112(1)	110(1)	111(1)
C-2–C-3–C-4	109(1)	108(1)	108(1)	110(1)	108(1)	108(1)	109(2)
C-3–C-4–C-5	110(1)	109(1)	112(1)	111(1)	111(1)	112(1)	111(1)
C-4–C-5–O-5	110(1)	112(1)	110(1)	110(1)	109(1)	112(1)	107(1)
C-5–O-5–C-1	113(1)	115(1)	117(1)	115(1)	115(1)	114(1)	115(1)
O-5–C-1–C-2	113(1)	110(1)	110(1)	110(1)	110(1)	111(1)	113(2)
C-1–C-2–O-2	112(1)	110(1)	111(1)	111(1)	111(1)	111(1)	112(2)
C-3–C-2–O-2	111(1)	111(1)	112(1)	113(1)	112(1)	111(1)	110(2)
C-2–C-3–O-3	111(1)	112(1)	111(1)	110(1)	111(1)	111(1)	111(1)
C-4–C-3–O-3	110(1)	109(1)	111(1)	109(1)	111(1)	109(1)	109(1)
C-4–C-5–C-6	112(1)	112(1)	113(1)	112(1)	114(1)	113(1)	115(2)
O-5–C-5–C-6	105(1)	105(1)	107(1)	105(1)	108(1)	105(1)	106(2)
C-5–C-6–O-6	112(1)	109(1)	111(2)	110(1)	111(2)	111(1)	109(1)
C-3–C-4–O-4	108(1)	107(1)	108(1)	107(1)	108(1)	106(1)	110(1)
C-5–C-4–O-4	108(1)	110(1)	109(1)	109(1)	111(1)	110(1)	107(1)
C-2–C-1–O-4′	107(1)	109(1)	107(1)	107(1)	109(1)	107(1)	107(1)
O-5–C-1–O-4′	111(1)	109(1)	111(1)	112(1)	111(1)	113(1)	110(1)
C-4–O-4–C-1″	117(1)	117(1)	119(1)	119(1)	118(1)	118(1)	119(1)

4-*tert*-Butylbenzoic acid of molecule 2			
Bond		Angle	
C-1–C-2	1.56(14)	C-2–C-1–C-3	90(8)
C-1–C-3	1.62(15)	C-2–C-1–C-4	91(6)
C-1–C-4	1.57(9)	C-2–C-1–C-5	120(6)
C-1–C-5	1.59(11)	C-3–C-1–C-4	119(8)
C-8–C-11	1.67(13)	C-3–C-1–C-5	99(6)
C-11–O-1	1.29(11)	C-4–C-1–C-5	132(8)
		C-7–C-8–C-11	97(5)
		C-9–C-8–C-11	125(8)
		C-8–C-11–O-1	173(7)

[a] Single primes denote the $n-1$ residues; double primes denote the $n+1$ residues.

H-bond between 1O-61 and the 2O-63 (2.76 Å) of the dimer at the layer below translated along all axes.

There are 26.8 water molecules distributed over 30 sites; 23 of the latter are hydrogen-bonded to oxygen atoms of the βCD hydroxyl groups and they have been

TABLE III

Parameters describing the conformation of the βCD macrocycle

Residue	D [a]	ϕ [b]	d [c]	a [d]	D_3 [e]
Molecule 1					
G-1	4.33	125.8	0.01	84	2.77
G-2	4.48	130.8	−0.02	86	2.82
G-3	4.29	128.7	0.02	81	2.77
G-4	4.39	127.4	−0.02	85	2.81
G-5	4.32	128.6	0.01	81	2.77
G-6	4.42	129.7	−0.01	86	2.69
G-7	4.35	129.0	0.00	86	2.80
Molecule 2					
G-1	4.38	128.7	0.01	86	2.74
G-2	4.39	130.0	−0.02	86	2.80
G-3	4.31	126.3	0.00	83	2.79
G-4	4.47	129.3	0.02	85	2.82
G-5	4.30	129.3	−0.02	81	2.78
G-6	4.39	127.9	0.00	85	2.81
G-7	4.33	128.5	0.01	81	2.76

[a] Distances between the atoms O-4n ··· O-4(n + 1). [b] Angles between the atoms O-4(n − 1) ··· O-4n ··· O-4(n + 1). [c] Deviations (Å) from the least-squares optimum plane of the seven O-4n atoms. [d] Dihedral angle between the O-4n plane and the optimum plane through C-2n, C-3n, C-5n, and O-5n. [e] Hydrogen-bond distances between atoms O-3n ··· O-2(n + 1).

labelled by the number of the closest oxygen atom to which they are bonded. Two separate sub-networks are formed, one involving hydrogen bonds with primary and another with secondary hydroxyl groups (see Table IV). None of the primary hydroxyl groups links to a water site of the secondary sub-network and vice versa. The coordinates of 26 water positions are very close to those of the isomorphous complex of βCD with 1-adamantanecarboxylic acid. This is in agreement with what has been noted[1] about the quasi-invariant water network in βCD complexes. Table IV indicates that the pseudo-twofold symmetry of the dimer is extended to the H-bonding with water molecules fairly well.

The two guest molecules are accommodated in the βCD dimer with the 4-*tert*-butyl groups buried in the βCD cavity at the secondary hydroxyl side and the carboxyl groups being at the primary edge. The two guests penetrate the βCD cavities to a different depth. The first, which was readily located at the beginning of the refinement, is almost completely enclosed while the second is partly outside (see Fig. 2). The second guest seems to be more mobile and therefore less bound to the βCD, a fact that was reflected in our difficulty in locating it and in our inability to find one of the oxygens of the carboxyl group. The two independent guests of adjacent dimers interact through hydrogen bonds (1O-1 ··· 2O-1 distance, 2.82 Å), and each one is also H-bonded to a water molecule (distances: 1O-1 ··· 2W-62A = 2.92, 1O-2 ··· 2W-62A = 2.92, 2O-1 ··· 2W-62B = 2.85 Å). Although the second guest was expected to be sufficiently stabilized via the hydrogen

bonds of its carboxyl group, this is not so. Therefore, we are justified in suggesting that the stability of the guest inside the host depends more on the hydrophobic interactions than on the H-bonding capacity of the polar groups. The polar groups, on the other hand, seem to determine the packing mode. In the present complex,

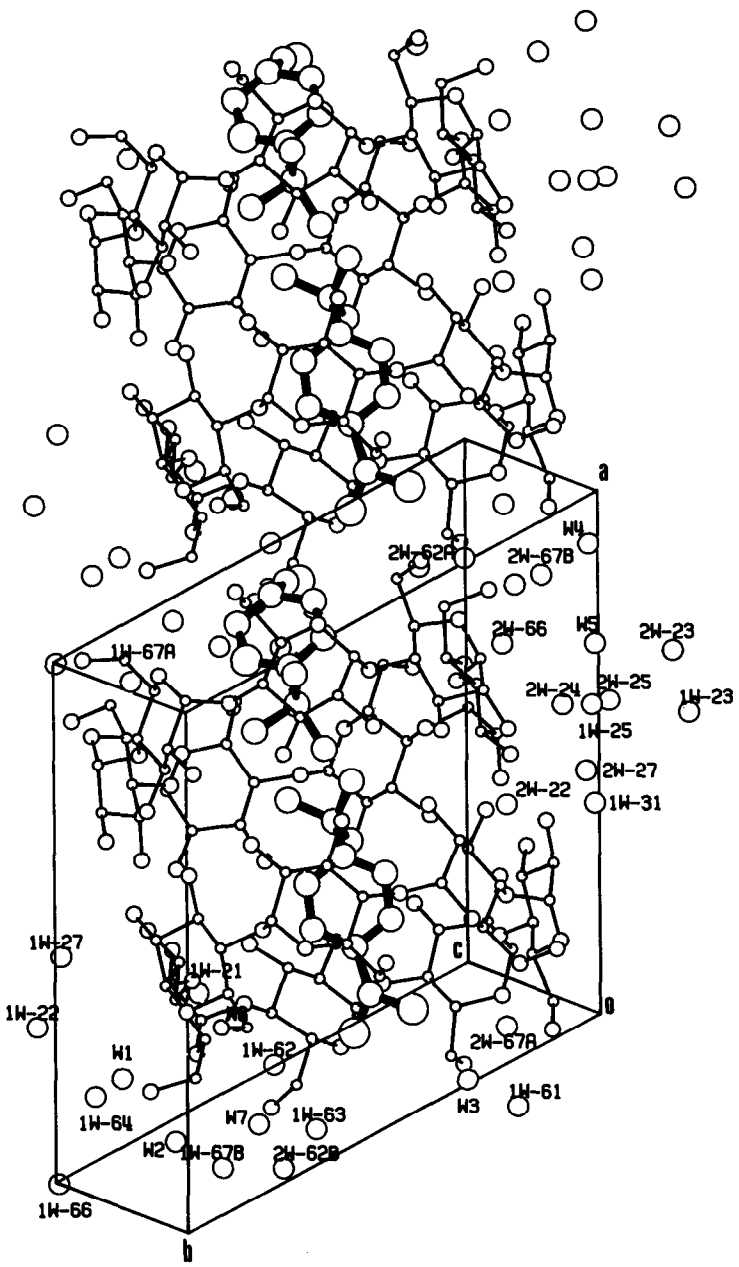

Fig. 3. ORTEP diagram[6] of the unit cell showing the intermediate packing.

the strong interaction of the carboxyl groups of the crystallographically independent guests probably forces the dimers to come close and form a packing type intermediate to the chessboard type existing in the complex of βCD with 4-*tert*-butylbenzyl alcohol[1] and to the channel type existing in the complex of βCD with

TABLE IV

Intermolecular hydrogen bonds of the βCD–4-*tert*-butylbenzoic acid complex

Intradimer			
Residue	Distance (Å)	Angle (°)	Angle (°)
	1O-3*n* · · ·	1C-3*n*–1O-3*n* · · ·	1O-3*n* · · ·
	2O-3(8 – *n*)	2O-3(8 – *n*)	2O-3(8 – *n*)–2C-3(8 – *n*)
G-1	2.86	120.4	118.0
G-2	2.72	119.9	115.9
G-3	2.81	116.9	118.2
G-4	2.77	115.8	118.3
G-5	2.83	118.4	118.4
G-6	2.78	118.5	118.2
G-7	2.80	119.1	118.5

With water molecules			
Molecule 1		Molecule 2	
Distance (Å)		Distance (Å)	
1O-61 · · · 1W-61	2.76	2O-61 · · · 1W-61	2.76
1O-62 · · · 1W-62	2.68	2O-62 · · · 2W-62A	2.82
		· · · 2W-62B	2.74
1O-63 · · · 1W-63	2.71	2O-63 · · · 1W-67	2.72
· · · 1W-67	2.73		
1O-64 · · · 1W-64	2.74	2O-64 · · · 1W-66	2.76
1O-65 · · · 1W-62	3.04	2O-65 · · · 2W-62B	2.73
		· · · 2W-67B	3.19
1O-66 · · · 1W-66	2.75	2O-66 · · · 2W-66	2.79
1O-67 · · · 1W-67A	2.66	2O-67 · · · 2W-67A	2.84
· · · 1W-67B	2.67	· · · 2W-67B	2.91
1O-21 · · · 1W-21	2.77		
1O-22 · · · 1W-22	3.11	2O-22 · · · 2W-22	2.74
1O-23 · · · 1W-23	2.78	2O-23 · · · 2W-23	2.70
		2O-24 · · · 2W-24	2.90
1O-25 · · · 1W-25	2.92	2O-25 · · · 2W-25	2.72
· · · 2W-27	3.07		
1O-27 · · · 1W-27	2.71	2O-27 · · · 2W-27	2.94
		· · · 1W-31	2.98
1O-31 · · · 1W-31	3.04		
1O-33 · · · 1W-21	2.83		
1O-34 · · · 1W-27	2.86		
1O-35 · · · 1W-23	2.84	2O-35 · · · 2W-23	2.89
· · · 2W-23	3.13	· · · 1W-23	3.14
1O-36 · · · 2W-22	3.11	2O-36 · · · 2W-22	2.85
		2O-37 · · · 2W-25	3.06
1O-1 · · · 2W-62A	2.93	2O-1 · · · 2W-62B	2.85
1O-2 · · · 2W-62A	2.92	1O-1 · · · 2O-1	2.82

TABLE IV (continued)

Among water molecules			
Distance (Å)		Distance (Å)	
1W-61 ··· 2W-66	2.78	1W-25 ··· 2W-27	2.31
··· 2W-62A	2.93	··· W-5	2.35
1W-62 ··· 1W-63	2.78	··· 2W-24	3.08
1W-63 ··· W-2	2.94	1W-27 ··· 2W-24	2.94
··· W-7	2.20	··· 2W-27	3.10
1W-64 ··· 1W-22	2.76	1W-31 ··· 2W-27	2.13
··· 1W-66	2.86	··· W-6	2.30
··· W-1	2.90	2W-66 ··· 2W-24	2.59
1W-66 ··· 2W-67A	2.57	2W-67A ··· 1W-67A	1.80
··· 1W-67A	2.75	2W-67B ··· W-3	2.56
1W-67B ··· 2W-62B	2.82	2W-67B ··· W-4	1.91
1W-21 ··· W-6	2.30	2W-67B ··· W-5	3.05
··· 2W-25	2.22	2W-22 ··· 2W-27	3.08
1W-22 ··· 2W-27	2.72	2W-23 ··· W-5	2.47
··· 2W-22	2.95	2W-24 ··· 2W-27	3.05
··· 1W-31	3.03	2W-25 ··· W-5	3.06
1W-23 ··· 2W-23	2.04	W-1 ··· W-2	2.76
··· W-6	2.92	W-1 ··· W-7	2.02
··· 2W-25	3.12	W-2β ··· W-7	2.70
		W-4 ··· W-5	3.10

4-*tert*-butyltoluene[2]. It is also possible that the strong association of the carboxyl groups pulls one of the acids out of the βCD cavity.

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