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

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ABSTRACT

The crystal of the 1:1 complex of 4-*tert*-butyltoluene with cyclomaltoheptaose (β-cyclodextrin, βCD) is triclinic $P1$ with $a = 15.562(2)$, $b = 15.564(4)$, $c = 15.835(3)$ Å, $\alpha = 102.11(2)$, $\beta = 102.15(1)$, $\gamma = 103.64(2)°$, $V = 3505(1)$ Å^3, and $Z = 2$. The two independent βCD molecules in the asymmetric unit form a dimer by hydrogen bonding involving HO-3, which accommodates two molecules of the guest. The hydrophobic guests are enclosed completely in the βCD cavities with the *tert*-butyl groups in the hydrophobic region beneath the primary hydroxyl groups. The aromatic rings have two orientations and their toluene methyl moieties could not be located but were calculated to be at the interface of the two monomers. The dimers form channels along the c axis. The inter-dimer space is filled with 17 molecules of water distributed over 25 sites. A dense network of hydrogen bonds is formed, involving the βCD hydroxyl groups and water molecules.

INTRODUCTION

The cyclomalto-oligosaccharides (cyclodextrins, CDs) and their inclusion complexes are used as models for the study of non-covalent intermolecular interactions and enzyme mechanisms, and for microencapsulation of substances that are volatile, sensitive, active, toxic, etc.[1]. Therefore, it is important to elucidate the forces which are responsible for the formation of the host–guest complexes. Analysis of crystal structures provides some insight into the interactions of CDs and substrate molecules[2,3].

Interpretation of structural data is accomplished best by comparisons of members of series of related compounds. The crystal structure of the 4-*tert*-butyltoluene–βCD complex is the second in a systematic crystallographic investigation of βCD inclusion complexes, the first being that of 4-*tert*-butylbenzyl alcohol[3]. The only variant is the polarity of the guest.

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EXPERIMENTAL

Preparation of crystals and X-ray measurements. — To an aqueous solution of βCD was added 4-*tert*-butyltoluene until the host:guest ratio was 1:10. The complex precipitated instantly but, on heating to 75°, it redissolved. An additional 10-fold excess of 4-*tert*-butyltoluene was added and the solution was allowed to cool slowly (5 days) to give colorless prismatic crystals.

Measurements were performed on a crystal (0.25 × 0.25 × 0.5 mm) sealed in a glass capillary to prevent loss of water. Final lattice parameters were determined from 15 reflections, $16° < 2\theta < 20°$, centered on a Syntex $P2_1$ diffractometer with Nb-filtered Mo-K_α radiation. A hemisphere of data $3° < 2\theta < 45°$ was collected by θ–2θ scan rates in the range 1.0–10°/min and a scan width of 1.8° plus the α_1–α_2 divergence. The background was measured at the start and end of each scan for 25% of the scan time of each reflection. The decay of the crystal was monitored by three standard reflections ($17° < 2\theta < 21°$) measured every 67 reflections, but no decay of their intensities was observed. The intensities were corrected for Lorentz and polarisation effects. No absorption correction was considered to be necessary ($\mu = 0.82$ cm^{-1}). Of 9641 reflections measured, 5956 with $|F_0| > 5\sigma(|F_0|)$ were considered as observed and were used in the refinement of the structure.

Crystal data. — From the final results, the composition inferred was $(C_{42}H_{70}O_{35})_2 \cdot (C_{11}H_{16})_2 \cdot (H_2O)_{17}$. The final lattice parameters were as follows: triclinic, space group *P*1, $a = 15.562(2)$, $b = 15.564(4)$, $c = 15.835(3)$ Å, $\alpha = 102.11(2)$, $\beta = 102.15(1)$, $\gamma = 103.64(2)°$, $V = 3505(1)$ Å^3, $Z = 2$, and $D_{calc} = 1.37$ g/cm^3.

Determination of the structure and refinement. — The initial solution of the structure was obtained by the "search-for-a-fragment-of-known-geometry" method[4] (program PATSEE). As the initial fragment, the co-ordinates of the 98 skeleton atoms of the βCD dimer from the complex of βCD with 3,3-dimethylbutylamine[5] were used. The best solution of this method gave the correct structure. Extensive use of Fourier techniques was made in order to locate the remaining 56 atoms of the βCD dimer as well as the 24 most prominent water positions. After the location of the above atoms and the *tert*-butyl group of the two guest molecules, refinement started by unit-weight, full-matrix, least-squares (SHELX76)[6] techniques, minimising $\sum(F_0 - F_c)^2$. Subsequent difference-electron-density Fourier maps revealed the positions of one more water molecule and of the phenyl atoms of the guest but not of the toluene methyl groups. The guest occupancy factor was refined initially but, since its value was close to unity, it was set at 1 and was not refined. Toward the end of the refinement, the phenyl groups were considered as regular hexagons of bond lengths 1.395 Å and were refined as rigid groups. In addition, carbon atoms were introduced at calculated positions corresponding to the toluene methyl groups. At this stage, calculated hydrogen atoms (C–H distance 0.96 Å) linked only to carbon atoms were used; only the positions of 3 hydroxyl hydrogen atoms were located but they were not refined.

Up to this stage, isotropic thermal parameters were used and the refinement had converged to $R = 0.1117$ and $R_w = 0.1211$ for the observed reflections. The refinement was then continued by assigning anisotropic temperature factors to the hydroxyl oxygen atoms and most of the water oxygen atoms (the refinement did not converge when the isotropic temperature factor of the water oxygen atoms was $> \sim 0.25$). The anisotropic refinement, involving only βCD and water atoms, converged to $R = 0.0989$ and $R_w = 0.1089$ for observed reflections and $R = 0.1397$ and $R_w = 0.1334$ for all reflections. Some residual electron density, close to the aromatic atoms, was assumed to correspond to a second position of the aromatic rings. Based on this residual density, a model was examined with two sites for the aromatic moiety of the guests. Sites A were the result of the previous refinement, and sites B had phenyl rings as regular hexagons and calculated positions for the methyl carbon atoms of the toluene group. Their relative occupancies were determined in the subsequent least-squares refinement of the guest, where the phenyl groups were refined as rigid groups. This process converged to $R = 0.0953$ and $R_w = 0.1009$. Maximum and minimum values in the final difference-electron-density map were 0.38 and -0.95 eÅ^{-3}, respectively. The sum of the refined parameters was 1078. The final atomic co-ordinates are listed in Table I*.

DISCUSSION

The numbering scheme adopted for the complex is given in Figs. 1 and 2: 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 independent βCD complex molecules 1 or 2, respectively. Two crystallographically independent molecules of the complex form a head-to-head dimer by means of 1O-3*n* ··· 2O-3(8-*n*) hydrogen bonds. Two guest molecules are accommodated in the cavity of the βCD dimer, the toluene moieties of which are disordered and occupy positions A and B (Figs. 1 and 2).

Bond lengths and bond angles of the two independent βCD and guest molecules are given in Table II. The pyranose rings have the $^4C_1$ conformation. With the exception of units 1G-1 and 2G-4, 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, 57° and −60°, respectively) and point out of the cavity. In unit 1G-1, the C-61–O-61 bond is *gauche* to the C-51–O-51 bond (torsion angle O-5–C-5–C-6–O-6 = 71°) and *trans* to the C-41–C-51 bond (torsion angle C-4–C-5–C-6–O-6 = −175°) and points outwards. In unit 2G-4, the atom 2O-64 is disordered having a *gauche–gauche* major orientation (A), with an occupation factor 0.64 pointing

* Tables of positional and isotropic thermal parameters for hydrogen atoms, thermal parameters for non-hydrogen atoms, and torsion angles of the βCD dimer are deposited with, and can be obtained from, Elsevier Science Publishers B.V., BBA Data Deposition, P.O. Box, 1527 Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/498/*Carbohydr. Res.*, 229 (1992) 1–15.

TABLE I

Positional ($\times 10^4$) and thermal parameters ($U^2 = B/8\pi^2$, $\times 10^3$) of the non-hydrogen atoms with ESD's in parentheses, and the occupation factors (K) for the water molecules in the βCD–4-*tert*-butyltoluene complex

Atom	x	y	z	U^a	K
1C-11	4480(10)	8260(10)	7340(10)	59	
1C-21	4770(10)	8650(10)	6660(10)	51	
1C-31	5730(10)	8570(10)	6640(10)	43	
1C-41	6370(10)	9020(10)	7560(10)	41	
1C-51	6030(10)	8620(10)	8260(10)	51	
1C-61	6620(20)	9370(20)	9310(20)	93	
1O-21	4153(9)	8244(8)	5806(8)	63*	
1O-31	6059(9)	8992(8)	6017(8)	64*	
1O-41	7248(8)	8894(7)	7561(7)	45	
1O-51	5108(9)	8690(8)	8211(8)	56	
1O-61	6390(30)	9010(30)	9970(30)	309*	
1C-12	8030(10)	9640(10)	7920(10)	52	
1C-22	8570(10)	9690(10)	7220(10)	66	
1C-32	8890(10)	8840(10)	6990(10)	45	
1C-42	9450(10)	8760(10)	7840(10)	44	
1C-52	8900(10)	8740(10)	8520(10)	59	
1C-62	9430(20)	8700(20)	9430(20)	90	
1O-22	7986(9)	9780(9)	6410(8)	71*	
1O-32	9414(9)	8889(9)	6366(8)	67*	
1O-42	9673(8)	7921(7)	7640(7)	45	
1O-52	8613(9)	9572(8)	8696(8)	59	
1O-62	10160(10)	9410(10)	9830(10)	111*	
1C-13	10620(10)	7930(10)	7860(10)	47	
1C-23	10780(10)	7350(10)	7020(10)	44	
1C-33	10220(10)	6360(10)	6800(10)	43	
1C-43	10430(10)	5980(10)	7610(10)	43	
1C-53	10280(10)	6590(10)	8430(10)	42	
1C-63	10650(10)	6330(10)	9280(10)	55	
1O-23	10594(9)	7768(8)	6314(7)	57*	
1O-33	10401(8)	5847(8)	6068(7)	57*	
1O-43	9823(8)	5101(8)	7386(8)	51	
1O-53	10832(8)	7555(8)	8621(7)	47	
1O-63	11610(10)	6440(10)	9463(9)	83*	
1C-14	10200(10)	4370(10)	7490(10)	52	
1C-24	9840(10)	3620(10)	6650(10)	57	
1C-34	8840(10)	3250(10)	6410(10)	46	
1C-44	8560(10)	2900(10)	7150(10)	48	
1C-54	8940(10)	3620(10)	8020(10)	54	
1C-64	8780(20)	3350(20)	8870(20)	123	
1O-24	10155(9)	3966(8)	5955(8)	60*	
1O-34	8499(9)	2491(8)	5557(7)	54*	
1O-44	7596(8)	2585(7)	6946(7)	47	
1O-54	9925(9)	4007(9)	8189(8)	64	
1O-64	9000(20)	2640(20)	8920(10)	187*	
1C-15	7150(10)	1640(10)	6930(10)	47	
1C-25	6460(10)	1190(10)	6040(10)	54	
1C-35	5710(10)	1680(10)	5920(10)	42	
1C-45	5270(10)	1660(10)	6670(10)	45	
1C-55	6000(10)	2090(10)	7580(10)	50	

TABLE I (continued)

Atom	x	y	z	U^a	K
1C-65	5660(20)	2010(20)	8380(20)	82	
1O-25	6863(9)	1144(8)	5327(7)	58*	
1O-35	5019(9)	1184(9)	5094(7)	62*	
1O-45	4659(8)	2227(7)	6598(7)	46	
1O-55	6727(8)	1659(8)	7647(7)	51	
1O-65	5250(10)	1020(10)	8290(10)	116*	
1C-16	3740(10)	1880(10)	6590(10)	57	
1C-26	3130(10)	1910(10)	5790(10)	58	
1C-36	3190(10)	2870(10)	5740(10)	45	
1C-46	3010(10)	3410(10)	6630(10)	46	
1C-56	3650(10)	3310(10)	7430(10)	55	
1C-66	3480(20)	3720(20)	8340(20)	110	
1O-26	3253(9)	1420(8)	4986(8)	62*	
1O-36	2532(9)	2942(8)	4996(8)	61*	
1O-46	3171(8)	4349(8)	6633(7)	50	
1O-56	3574(9)	2338(9)	7384(8)	64	
1O-66	2540(20)	3360(20)	8310(20)	238*	
1C-17	2460(10)	4750(10)	6700(10)	41	
1C-27	2310(10)	5210(10)	5950(10)	46	
1C-37	3190(10)	5960(10)	6070(10)	44	
1C-47	3460(10)	6600(10)	6970(10)	44	
1C-57	3540(10)	6150(10)	7700(10)	42	
1C-67	3670(10)	6760(10)	8650(10)	60	
1O-27	2041(8)	4568(8)	5106(8)	53*	
1O-37	3065(9)	6425(8)	5366(8)	63*	
1O-47	4349(7)	7265(7)	7105(7)	44	
1O-57	2704(8)	5421(8)	7551(7)	47	
1O-67	2940(10)	7190(10)	8631(9)	91*	
1C-1	6755(8)	5605(8)	8080(7)	18	
1C-3	7740(20)	6060(30)	8690(30)	303	
1C-4	6040(20)	5920(30)	8510(30)	237	
1C-5	6590(40)	4680(20)	8320(40)	208	
1C-2A	6790(40)	5660(30)	7130(10)	386	0.57
1C-6A	6270(40)	6210(30)	6820(10)	392	0.57
1C-7A	6400(40)	6530(30)	6080(10)	402	0.57
1C-8A	7050(40)	6300(30)	5650(10)	457	0.57
1C-9A	7560(40)	5750(30)	5960(10)	418	0.57
1C-10	7430(40)	5430(30)	6700(10)	519	0.57
1C-11A	7380(40)	6830(30)	5190(10)	400	0.57
1C-2B	6250(40)	5090(40)	7090(20)	214	0.43
1C-6B	5540(40)	5300(40)	6570(20)	234	0.43
1C-7B	5220(40)	4880(40)	5640(20)	173	0.43
1C-8B	5630(40)	4250(40)	5250(20)	113	0.43
1C-9B	6340(40)	4040(40)	5770(20)	191	0.43
1C-10B	6660(40)	4460(40)	6700(20)	231	0.43
1C-11B	5300(40)	3820(40)	4290(20)	240	0.43
2C-11	3150(10)	6970(10)	2210(10)	67	
2C-21	2760(10)	6640(10)	2940(10)	55	
2C-31	2850(10)	5690(10)	2940(10)	39	
2C-41	2390(10)	5060(10)	2020(10)	49	
2C-51	2790(10)	5410(10)	1320(10)	51	
2C-61	2310(20)	4860(30)	290(20)	125	

(continued)

TABLE I (continued)

Atom	x	y	z	U^a	K
2O-21	3192(9)	7290(8)	3784(8)	62*	
2O-31	2452(8)	5363(8)	3587(8)	59*	
2O-41	2544(8)	4164(8)	2056(7)	50	
2O-51	2751(8)	6329(8)	1374(8)	52	
2O-61	1530(30)	4830(20)	230(20)	180*	
2C-12	1770(10)	3400(10)	1710(10)	48	
2C-22	1750(10)	2880(10)	2390(10)	47	
2C-32	2590(10)	2540(10)	2600(10)	52	
2C-42	2690(10)	1980(10)	1760(10)	44	
2C-52	2700(10)	2540(10)	1080(10)	53	
2C-62	2740(20)	2060(20)	140(20)	87	
2O-22	1650(10)	3436(9)	3181(9)	76*	
2O-32	2560(10)	2012(8)	3249(8)	71*	
2O-42	3520(8)	1759(7)	1947(7)	43	
2O-52	1874(8)	2821(8)	915(8)	56	
2O-62	2040(10)	1280(10)	−230(10)	104*	
2C-13	3510(10)	790(10)	1720(10)	45	
2C-23	4070(10)	660(10)	2580(10)	44	
2C-33	5050(10)	1220(10)	2780(10)	37	
2C-43	5460(10)	1020(10)	2000(10)	38	
2C-53	4830(10)	1150(10)	1170(10)	44	
2C-63	5100(10)	770(10)	310(10)	56	
2O-23	3651(9)	822(8)	3276(7)	60*	
2O-33	5587(9)	1030(8)	3541(7)	60*	
2O-43	6317(8)	1611(7)	2198(7)	47	
2O-53	3883(8)	603(7)	992(7)	44	
2O-63	4990(10)	−160(10)	122(8)	76*	
2C-14	7040(10)	1210(10)	2080(10)	57	
2C-24	7800(10)	1560(10)	2990(10)	56	
2C-34	8230(10)	2610(10)	3220(10)	43	
2C-44	8570(10)	2900(10)	2470(10)	50	
2C-54	7760(20)	2460(20)	1570(10)	76	
2C-64	8140(20)	2670(20)	760(20)	104	
2O-24	7449(9)	1277(8)	3646(7)	56*	
2O-34	8937(8)	2904(8)	4023(7)	51*	
2O-44	8862(8)	3846(7)	2653(7)	45	
2O-54	7399(9)	1492(9)	1375(9)	63	
2O-64A	8750(20)	2370(20)	680(10)	130*	0.64
2O-64B	7610(30)	2050(30)	0(30)	104	0.36
2C-15	9780(10)	4300(10)	2660(10)	47	
2C-25	10230(10)	4980(10)	3550(10)	48	
2C-35	9770(10)	5740(10)	3680(10)	46	
2C-45	9740(10)	6140(10)	2910(10)	44	
2C-55	9320(10)	5410(10)	2010(10)	52	
2C-65	9450(20)	5770(20)	1230(10)	73	
2O-25	10282(8)	4546(8)	4270(7)	57*	
2O-35	10243(9)	6423(8)	4512(7)	54*	
2O-45	9189(8)	6766(7)	2995(7)	46	
2O-55	9764(8)	4700(8)	1964(7)	49	
2O-65	10400(20)	6160(10)	1300(10)	131*	
2C-16	9540(10)	7700(10)	2980(10)	60	
2C-26	9510(10)	8330(10)	3820(10)	50	

TABLE I (continued)

Atom	x	y	z	U [a]	K
2C-36	8540(10)	8240(10)	3830(10)	41	
2C-46	8030(10)	8420(10)	2980(10)	47	
2C-56	8160(10)	7810(10)	2170(10)	61	
2C-66	7720(20)	7930(20)	1240(20)	105	
2O-26	10009(8)	8186(9)	4632(8)	67*	
2O-36	8469(9)	8894(9)	4602(8)	62*	
2O-46	7076(8)	8237(7)	2945(7)	46	
2O-56	9074(9)	7866(8)	2214(8)	59	
2O-66	8050(20)	8910(20)	1320(10)	222*	
2C-17	6680(10)	8950(10)	2880(10)	46	
2C-27	6210(10)	9100(10)	3650(10)	46	
2C-37	5450(10)	8210(10)	3520(10)	49	
2C-47	4800(10)	7970(10)	2620(10)	39	
2C-57	5280(10)	7920(10)	1900(10)	48	
2C-67	4650(10)	7760(10)	980(10)	58	
2O-27	6858(9)	9375(8)	4507(7)	57*	
2O-37	4997(8)	8343(9)	4225(8)	60*	
2O-47	4180(8)	7098(8)	2489(8)	51	
2O-57	6012(8)	8725(8)	2064(8)	52	
2O-67	4220(10)	8500(10)	1000(10)	84*	
2C-1	5790(40)	4680(30)	1400(10)	128	
2C-3	5230(40)	5210(30)	890(10)	271	
2C-4	6810(40)	4830(30)	1440(10)	322	
2C-5	5420(40)	3660(30)	860(10)	208	
2C-2A	5520(40)	4870(60)	2280(30)	333	0.61
2C-6A	5570(40)	5680(60)	2900(30)	388	0.61
2C-7A	5340(40)	5650(60)	3690(30)	445	0.61
2C-8A	5050(40)	4810(60)	3880(30)	400	0.61
2C-9A	5000(40)	4000(60)	3270(30)	376	0.61
2C-10A	5230(40)	4030(60)	2470(30)	415	0.61
2C-11A	4800(40)	4850(60)	4680(30)	400	0.61
2C-2B	6250(70)	5020(70)	2420(20)	236	0.39
2C-6B	5830(70)	4160(70)	2510(20)	274	0.39
2C-7B	6140(70)	3930(70)	3310(20)	446	0.39
2C-8B	6860(70)	4560(70)	4010(20)	485	0.39
2C-9B	7280(70)	5420(70)	3910(20)	275	0.39
2C-10B	6970(70)	5650(70)	3120(20)	545	0.39
2C-11B	7170(70)	4320(70)	4830(20)	736	0.39
1W-62A	520(30)	9410(30)	1640(20)	195*	0.64
W-62A	1940(10)	9480(10)	−190(10)	110*	1.01
W-62B	70(20)	1340(20)	−40(30)	230*	0.71
1W-65	3400(20)	130(10)	7820(20)	91*	0.75
1W-66	950(40)	2080(50)	7860(70)	436*	0.57
1W-67	3220(10)	9060(10)	8930(10)	99*	0.93
1W-21	3780(10)	9530(10)	5030(20)	145*	0.98
1W-22	9280(30)	1000(20)	5800(40)	275*	0.74
1W-23A	2290(30)	8820(30)	6320(30)	179*	0.66
1W-23B	1980(40)	7820(50)	5480(70)	400*	0.63
1W-24	670(20)	2550(20)	5050(40)	155*	0.54
1W-26	1410(30)	360(30)	3650(30)	211	0.69
W-26	1690(40)	−200(40)	4910(40)	216	0.53
2W-62A	1940(30)	860(20)	7910(20)	166*	0.65

(continued)

TABLE I (continued)

Atom	x	y	z	U [a]	K
2W-64	8700(50)	500(50)	480(50)	248	0.51
2W-65	1300(10)	8030(10)	1800(10)	109*	0.87
2W-66	−570(50)	430(40)	1870(40)	230*	0.48
2W-67	2370(10)	8210(10)	640(10)	96*	1.02
2W-21	1920(20)	7700(20)	4510(20)	122*	0.95
2W-22	480(40)	2170(40)	3670(50)	258*	0.47
2W-23	2630(30)	9150(20)	3290(20)	139*	0.52
2W-24	8890(20)	750(20)	4460(30)	158*	0.70
2W-26	1040(40)	−70(40)	5890(40)	143	0.41
1W-W	360(60)	670(60)	3300(60)	328	0.57
2W-W	760(50)	1090(60)	6390(70)	357*	0.49

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

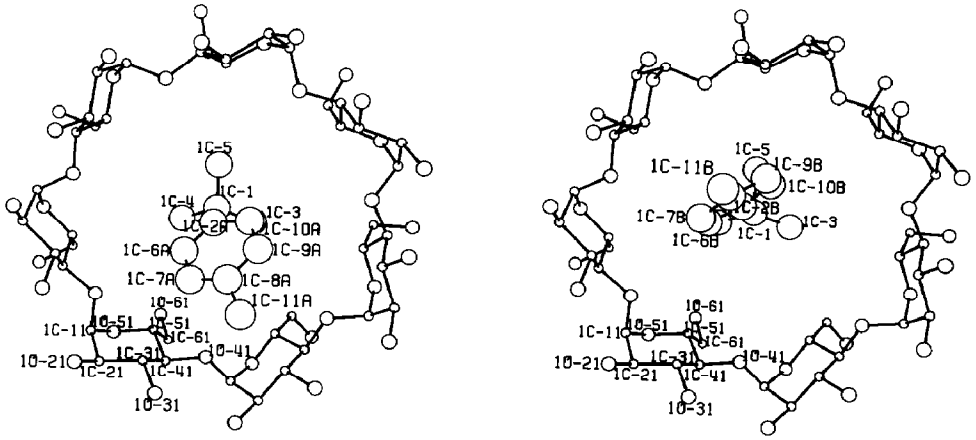

Fig. 1. The structure and numbering scheme of molecule 1 of the βCD–4-*tert*-butyltoluene complex: the two orientations of the toluene moiety are designated A and B.

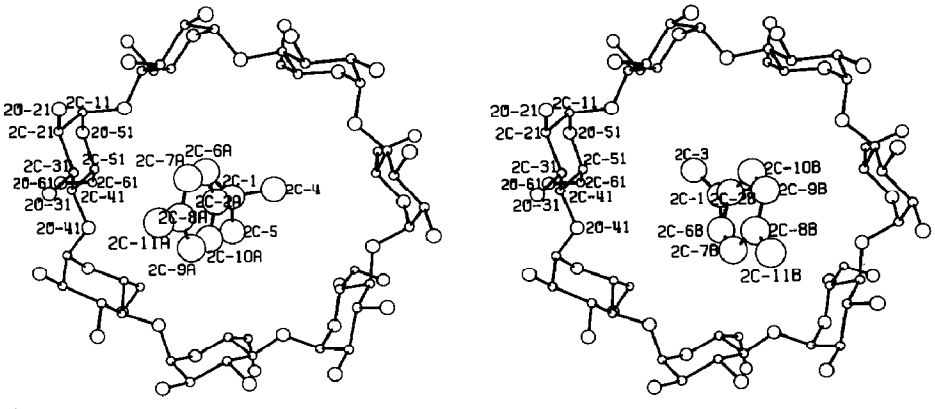

Fig. 2. The structure and numbering scheme of molecule 2 of the βCD–4-*tert*-butyltoluene complex: the two orientations of the toluene moiety are designated A and B.

TABLE II

Bond distances (Å) and angles (°) of the βCD–4-*tert*-butyltoluene 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	1.43(3)	1.52(3)	1.54(2)	1.48(2)	1.49(2)	1.42(3)	1.52(3)
C-1–O-5	1.43(2)	1.40(2)	1.46(2)	1.44(2)	1.42(2)	1.42(2)	1.43(2)
C-2–C-3	1.52(3)	1.53(3)	1.51(2)	1.46(2)	1.55(3)	1.49(3)	1.52(2)
C-2–O-2	1.40(2)	1.45(2)	1.42(2)	1.44(2)	1.39(2)	1.42(2)	1.40(2)
C-3–C-4	1.49(2)	1.48(2)	1.53(2)	1.49(3)	1.48(3)	1.59(2)	1.48(2)
C-3–O-3	1.42(2)	1.41(2)	1.39(2)	1.49(2)	1.44(2)	1.43(2)	1.45(2)
C-4–C-5	1.51(3)	1.51(3)	1.52(2)	1.50(2)	1.54(2)	1.50(2)	1.47(3)
C-4–O-4	1.42(2)	1.42(2)	1.38(2)	1.40(2)	1.44(2)	1.42(2)	1.47(2)
C-5–C-6	1.72(3)	1.53(3)	1.51(3)	1.54(4)	1.49(3)	1.55(4)	1.55(2)
C-5–O-5	1.45(2)	1.46(3)	1.48(2)	1.45(2)	1.44(2)	1.48(2)	1.45(2)
C-6–O-6	1.36(6)	1.30(3)	1.41(2)	1.24(5)	1.49(3)	1.43(4)	1.44(3)
O-4–C-1″	1.38(2)	1.43(2)	1.41(2)	1.46(2)	1.40(2)	1.40(2)	1.47(2)

Angle[a]	G-1	G-2	G-3	G-4	G-5	G-6	G-7
C-1–C-2–C-3	110(2)	111(2)	110(1)	112(1)	109(1)	113(1)	109(1)
C-2–C-3–C-4	109(1)	108(1)	111(1)	111(1)	109(1)	108(1)	109(1)
C-3–C-4–C-5	112(1)	110(1)	110(1)	111(1)	110(1)	109(1)	114(1)
C-4–C-5–O-5	109(1)	110(1)	112(1)	110(1)	112(1)	112(1)	110(1)
C-5–O-5–C-1	113(1)	111(1)	112(1)	115(1)	114(1)	112(1)	113(1)
O-5–C-1–C-2	113(1)	108(1)	111(1)	108(1)	112(1)	113(2)	109(1)
C-1–C-2–O-2	113(1)	109(1)	108(1)	108(1)	113(1)	114(2)	111(1)
C-3–C-2–O-2	111(1)	110(1)	114(1)	113(1)	111(1)	108(1)	112(1)
C-2–C-3–O-3	112(1)	112(1)	109(1)	111(1)	108(1)	115(1)	110(1)
C-4–C-3–O-3	109(1)	110(1)	111(1)	110(1)	108(1)	107(1)	112(1)
C-4–C-5–C-6	108(1)	114(2)	111(1)	118(2)	115(1)	115(2)	116(1)
O-5–C-5–C-6	100(1)	106(2)	103(1)	107(2)	104(2)	105(2)	103(1)
C-5–C-6–O-6	111(2)	114(2)	112(1)	111(2)	108(2)	110(2)	110(1)
C-3–C-4–O-4	109(1)	107(1)	107(1)	111(1)	107(1)	109(1)	109(1)
C-5–C-4–O-4	109(1)	109(1)	110(1)	110(1)	108(1)	111(1)	108(1)
C-2–C-1–O-4′	111(1)	109(1)	108(1)	109(1)	108(1)	111(1)	108(1)
O-5–C-1–O-4′	110(1)	113(1)	111(1)	110(1)	109(1)	110(1)	110(1)
C-4–O-4–C-1″	120(1)	120(1)	118(1)	119(1)	120(1)	118(1)	122(1)

4-tert-*Butyltoluene of molecule 1*

Bond		Angle	
C-1–C-2A	1.54(3)	C-2A–C-1–C-3	106(2)
C-1–C-3	1.54(3)	C-2A–C-1–C-4	121(3)
C-1–C-4	1.53(4)	C-2A–C-1–C-5	121(3)
C-1–C-5	1.53(4)	C-3–C-1–C-4	112(2)
C-1–C-2B	1.54(3)	C-3–C-1–C-5	98(3)
C-8A–C-11A	1.31(6)	C-4–C-1–C-5	95(3)
C-8B–C-11B	1.45(3)	C-1–C-2A–C-6A	112(3)
		C-1–C-2A–C-10A	125(3)
		C-7A–C-8A–C-11A	118(4)
		C-9A–C-8A–C-11A	118(4)
		C-1–C-2B–C-6B	125(3)
		C-1–C-2B–C-10B	115(3)

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	1.54(3)	1.48(3)	1.54(2)	1.56(2)	1.48(2)	1.49(3)	1.55(3)
C-1–O-5	1.39(2)	1.45(2)	1.41(2)	1.45(3)	1.38(2)	1.38(2)	1.39(2)
C-2–C-3	1.52(3)	1.51(3)	1.50(2)	1.55(2)	1.51(3)	1.50(3)	1.54(2)
C-2–O-2	1.41(2)	1.44(2)	1.40(2)	1.37(2)	1.44(2)	1.45(2)	1.42(2)
C-3–C-4	1.49(2)	1.49(2)	1.52(2)	1.50(3)	1.48(3)	1.54(2)	1.47(2)
C-3–O-3	1.43(2)	1.45(2)	1.44(2)	1.41(2)	1.43(2)	1.46(2)	1.45(2)
C-4–C-5	1.52(3)	1.53(3)	1.55(2)	1.58(2)	1.52(2)	1.50(2)	1.50(3)
C-4–O-4	1.48(2)	1.41(2)	1.36(2)	1.39(2)	1.45(2)	1.43(2)	1.41(2)
C-5–C-6	1.60(4)	1.54(3)	1.53(3)	1.59(4)	1.49(3)	1.56(3)	1.50(2)
C-5–O-5	1.43(2)	1.44(2)	1.45(2)	1.42(2)	1.44(2)	1.40(2)	1.41(2)
C-6–O-6A	1.19(6)	1.34(3)	1.38(2)	1.16(5)	1.43(3)	1.45(4)	1.46(3)
C-6–O-6B				1.33(5)			
O-4–C-1″	1.39(2)	1.47(2)	1.43(3)	1.43(2)	1.44(2)	1.40(2)	1.53(2)

Angle[a]	G-1	G-2	G-3	G-4	G-5	G-6	G-7
C-1–C-2–C-3	110(2)	113(2)	109(1)	110(1)	112(1)	110(1)	108(1)
C-2–C-3–C-4	109(1)	110(1)	113(1)	112(1)	110(1)	109(1)	109(1)
C-3–C-4–C-5	111(1)	109(1)	108(1)	108(1)	113(1)	109(1)	112(1)
C-4–C-5–O-5	110(1)	110(1)	112(1)	113(1)	110(1)	114(1)	112(1)
C-5–O-5–C-1	117(1)	114(1)	114(1)	113(2)	115(1)	114(2)	115(1)
O-5–C-1–C-2	111(1)	107(1)	112(1)	110(1)	112(1)	112(1)	109(1)
C-1–C-2–O-2	110(1)	108(1)	110(1)	110(1)	112(1)	114(1)	112(1)
C-3–C-2–O-2	113(1)	111(1)	115(1)	114(1)	113(1)	109(1)	112(1)
C-2–C-3–O-3	110(1)	113(1)	109(1)	109(1)	111(1)	112(1)	109(1)
C-4–C-3–O-3	110(1)	110(1)	108(1)	112(1)	111(1)	108(1)	112(1)
C-4–C-5–C-6	118(2)	117(2)	111(1)	109(2)	113(1)	116(2)	113(1)
O-5–C-5–C-6	105(2)	105(2)	104(1)	108(2)	104(2)	106(2)	108(1)
C-5–C-6–O-6A	101(2)	111(2)	113(1)	112(3)	112(2)	106(2)	109(1)
C-5–C-6–O-6B				108(3)			
C-3–C-4–O-4	106(1)	109(1)	110(1)	110(1)	107(1)	108(1)	108(1)
C-5–C-4–O-4	110(1)	109(1)	109(1)	111(1)	109(1)	111(1)	109(1)
C-2–C-1–O-4′	107(1)	107(1)	105(1)	107(1)	108(1)	109(1)	108(1)
O-5–C-1–O-4′	109(1)	108(1)	110(1)	110(1)	110(1)	111(1)	112(1)
C-4–O-4–C-1″	116(2)	119(1)	117(1)	120(1)	121(1)	117(1)	120(1)

4-tert-Butyltoluene of molecule 2

Bond		Angle	
C-1–C-2A	1.53(6)	C-2A–C-1–C-3	99(4)
C-1–C-3	1.54(7)	C-2A–C-1–C-4	118(4)
C-1–C-4	1.54(8)	C-2A–C-1–C-5	113(4)
C-1–C-5	1.54(6)	C-3–C-1–C-4	120(4)
C-1–C-2B	1.55(4)	C-3–C-1–C-5	108(3)
C-8A–C-11A	1.39(7)	C-4–C-1–C-5	98(4)
C-8B–C-11B	1.45(9)	C-1–C-2A–C-6A	132(5)
		C-1–C-2A–C-10A	107(5)
		C-7A–C-8A–C-11A	115(6)
		C-9A–C-8A–C-11A	124(6)
		C-1–C-2B–C-6B	90(5)
		C-1–C-2B–C-10B	147(4)

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

TABLE III

Parameters describing the conformation of the βCD macrocycle

Residue	D_4[a]	ϕ[b]	d[c]	a[d]	D_3[e]
Molecule 1					
G-1	4.37	128.5	−0.04(5)	85	2.84
G-2	4.39	127.8	0.05(5)	83	2.81
G-3	4.39	128.7	0.01(5)	87	2.82
G-4	4.37	129.2	−0.04(5)	83	2.79
G-5	4.46	128.5	0.00(5)	98	2.84
G-6	4.31	127.2	0.06(5)	100	2.80
G-7	4.44	130.0	−0.03(5)	84	2.79
Molecule 2					
G-1	4.34	128.4	−0.01(5)	93	2.84
G-2	4.35	128.2	0.03(5)	98	2.80
G-3	4.42	129.0	0.00(5)	84	2.80
G-4	4.36	128.4	−0.03(5)	78	2.79
G-5	4.43	129.0	0.01(5)	80	2.82
G-6	4.28	127.8	0.04(5)	83	2.76
G-7	4.48	129.2	−0.04(5)	89	2.75

[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).

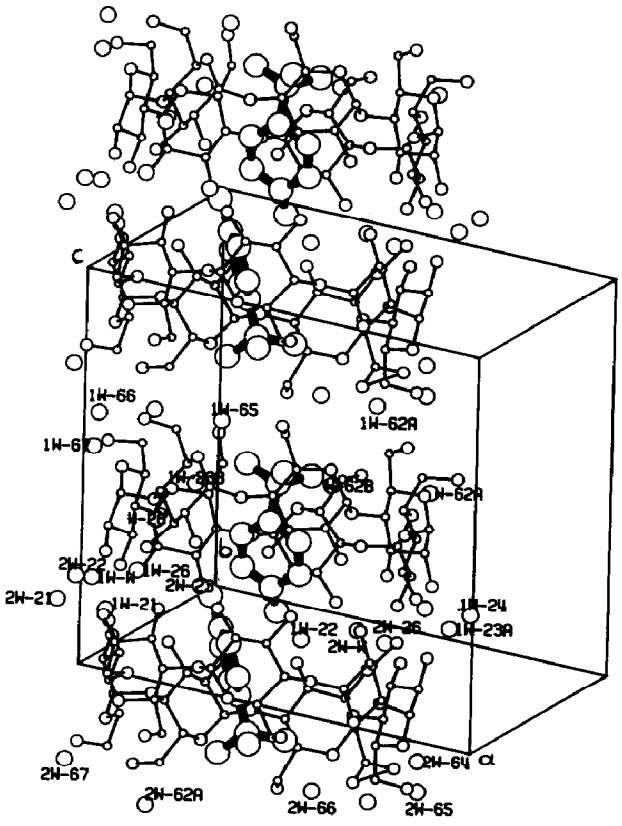

Fig. 3. ORTEP[7] diagram of the unit cell showing the channel packing: guests are depicted in orientation A.

outwards and a minor one (B) pointing inwards (torsion angles C-4–C-5–C-6–O-6 and O-5–C-5–C-6–O-6, 157° and 34°, respectively).

Both βCD monomers show seven-fold symmetry as shown by the O-4n ··· O-4(n + 1) distances and O-4(n-1) ··· O-4n ··· O-4(n + 1) angles, as well as in the small deviations of the O-4n atoms from their optimum plane shown in Table III along with some other relevant parameters. The similarity of the two independent βCD molecules is striking and is extended to the strong intramolecular hydrogen bonds (H-bonds) between the O-3 of one glucosidic unit and the O-2 of the next

TABLE IV

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

Intradimer

Residue	Distance (Å) 1O-3n ··· 2O-3(8-n)	Angle (°) 1C-3n–1O-3n ··· 2O-3(8-n)	Angle (°) 1O-3n ··· 2O-3(8-n)–2C-3(8-n)
G-1	2.80	117.3	119.3
G-2	2.87	116.5	118.2
G-3	2.78	119.2	116.8
G-4	2.81	117.6	118.0
G-5	2.76	116.9	118.7
G-6	2.85	116.9	116.8
G-7	2.78	118.0	118.8

With water molecules

Molecule 1		Molecule 2	
Distance (Å)		Distance (Å)	
1O-62 ··· 1W-62A	2.80	2O-62 ··· 2W-62A	2.84
··· W-62A	2.76	··· W-62A	2.80
··· W-62B	3.02	··· W-62B	3.14
1O-63 ··· 2W-67	2.79	2O-63 ··· 1W-67	2.82
		2O-64 ··· 2W-64	2.85
1O-65 ··· 1W-65	2.74	2O-65 ··· 2W-65	2.77
1O-66 ··· 1W-66	2.65	2O-66 ··· 2W-66	2.64
1O-67 ··· 1W-67	2.75	2O-67 ··· 2W-67	2.71
1O-21 ··· 1W-21	2.67	2O-21 ··· 2W-21	2.63
1O-22 ··· 1W-22	2.89	2O-22 ··· 2W-22	2.70
1O-23 ··· 1W-23A	2.76	2O-23 ··· 2W-23	2.72
1O-23 ··· 1W-23B	2.78		
1O-24 ··· 1W-24	2.75	2O-24 ··· 2W-24	2.73
1O-26 ··· 1W-26	3.02	2O-26 ··· 2W-26	2.88
··· W-26	2.99	··· W-26	3.08
1O-32 ··· 2W-26	2.99	2O-32 ··· 1W-26	3.02
1O-34 ··· 1W-22	2.92	2O-34 ··· 2W-22	2.99
1O-35 ··· 1W-21	2.80	2O-35 ··· 2W-21	2.88
		··· 1W-23B	2.90
1O-36 ··· 1W-24	2.84	1O-36 ··· 2W-24	2.87
1O-37 ··· 1W-23B	3.02		
1WW ··· 1W-26	1.8	2WW ··· 2W-26	2.1
··· 2W-22	2.2	··· 1W-22	2.2
··· 2W-66	2.3	··· 1W-66	2.4
··· 1W-62A	3.0	··· 2W-62A	2.9

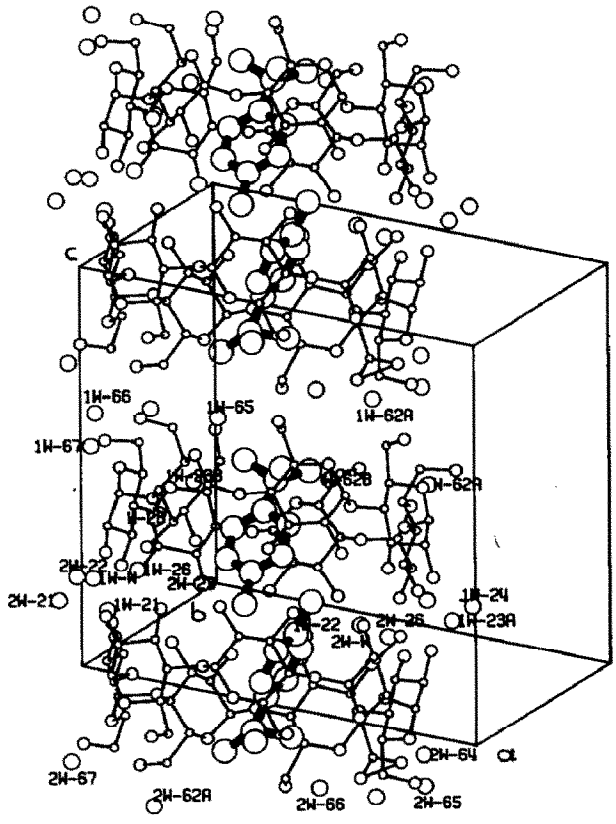

Fig. 4. ORTEP [7] diagram of the unit cell showing the channel packing: guests depicted are in orientation B.

(Table III). The average distances O-3n ··· O-2(n + 1) are 2.81 and 2.79 Å for molecules 1 and 2, respectively. The angle C-3n–O-3n ··· O-2(n + 1) and O-3n ··· O-2(n + 1)–C-2(n + 1) have average values 116.8° and 117.9°, respectively, for molecule 1 and 116.6° and 118.5°, respectively, for molecule 2. Generally, the geometries of the βCD molecules in the dimeric complexes, where the monomers are crystallographically independent, are similar[3] (see also Table II).

The dimers are formed by H-bonding between the 1O-3n and 2O-3(8-n) atoms of two adjacent crystallographically independent βCD molecules. Table IV shows the intradimer H-bond distances and the corresponding angles. As observed for other βCD complexes[3,5], the distances 1O-2n ··· 2O-3(8-n) and 1O-3n ··· 2O-2(8-n) are in the range (3.02–3.23 Å; average, 3.09 Å) of weak H-bonds. However, although the angles C-2n–O-2n ··· O-3(8-n) could indicate H-bonding (average, 113.6°), the angles O-2n ··· O-3(8-n)–C-3(8-n) have high values (average, 162.8°), thereby excluding such possibility. By the same argument, there are no 1O-2n ··· 2O-2(9-n) H-bonds.

The molecular packing is displayed in Figs. 3 and 4. The molecules form a channel along the c axis. The centre of each dimer projected on the O-4n plane of

the dimer below is displaced by 2.96 Å. The axis of the βCD dimer forms an angle of 10.8° with the crystallographic *c* axis; therefore, it is approximately perpendicular to the crystallographic (*ab*) plane. If the transformation $a' = a + b$, $b' = b - a$, $c' = c$ is performed, a pseudo-C dimeric layer is created with cell dimensions $|a'| = 19.24$ and $|b'| = 24.467$ Å, $\alpha = \gamma = 90°$, and $\beta = 109.87°$. The above cell dimensions are nearly equal to those of $C222_1$ and $C2$ structures of the βCD complexes[3]. The structures of all the dimeric complexes, determined up to now, can be considered to consist of centered or pseudo-centered dimeric layers of unit area $\sim 19 \times 24$ Å^2.

There are 17 water molecules per βCD dimer distributed over 25 molecular sites (denoted in Figs. 3 and 4 by W) and 23 are within H-bonding distance from the oxygen atoms of the βCD hydroxyl groups. The water sites have been labelled by the number of the closest oxygen atoms to which they are H-bonded (Table IV). It is assumed that distances O · · · W of 2.50–3.14 Å and angles C-O · · · W of 90–130° indicate H-bonding. The latter is higher (143–154°) in only 5 instances of the 40 indicated in Table IV (1O-66 · · · 1W-66, 2O-66 · · · 2W-66, 1O-32 · · · 2W-26, 2O-32 · · · 1W-26, and 2O-35 · · · 1W-23B). However, those too are accepted as H-bonds on account of the usual disorder of the water molecules and the inability to locate the H-atoms. Table IV indicates that the pseudo two-fold symmetry of the dimer is extended to the H-bonding fairly well, even to the two water molecules 1WW and 2WW which are H-bonded only to other water molecules.

The H-bonds form two water networks, one linking the primary hydroxyl groups between two adjacent dimeric layers and the other linking the secondary hydroxyl groups of the dimers of the same layer (Fig. 3). There are also H-bonds between primary hydroxyl groups of adjacent dimers either in the same channel: 1O-64 · · · 2O-64A, 1O-64 · · · 2O-64B, and 1O-61 · · · 2O-66 (3.0, 3.1, and 3.0 Å, respectively), or of adjacent channels in different layers: 1O-61 · · · 2O-63 and 1O-63 · · · 2O-61 (2.8 and 3.0 Å, respectively), or in the same layer: 1O-63 · · · 1O-67 and 2O-63 · · · 2O-67 (2.8 and 2.9 Å, respectively).

Two guest molecules are buried inside the cavity of the βCD dimer with the *tert*-butyl groups in the hydrophobic regions beneath the primary hydroxyl groups. The aromatic ring occupies two sites A and B (Figs. 1 and 2) with relative occupancies 0.57/0.43 for the guest of molecule 1 and 0.61/0.39 for that of molecule 2. The carbon atoms of the phenyl groups were located, but the latter were considered ideal during the refinement procedure. The flexibility of this part of the molecule can be explained by the inability to form H-bonds and it is well represented in its thermal parameters (Table I).

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