The Structure of the Cyclodextrin Complex. V. Crystal Structures of α-Cyclodextrin Complexes with *p*-Nitrophenol and *p*-Hydroxybenzoic Acid

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α-Cyclodextrin (α-CDx) forms a 1: 1 complex with *p*-nitrophenol (*p*-NP) and *p*-hydroxybenzoic acid (*p*-HB). The crystal structures were determined by the X-ray method. The crystals of both complexes are orthorhombic, and the space group is $P2_12_12_1$ with $Z=4$. The cell dimensions are $a=13.455(1)$, $b=15.296(1)$, and $c=24.740(3)$ Å for the *p*-NP complex, and $a=13.356(1)$, $b=15.342(1)$, and $c=24.896(2)$ Å for the *p*-HB complex. The crystal structures were determined on the basis of the isomorphous structure of the *p*-iodophenol complex by using 4811 reflections for the *p*-NP complex and 4692 reflections for the *p*-HB complex, and refined by the block-diagonal least-squares method to the final *R*-values of 0.066 and 0.067 respectively. In both complexes, the guest molecule is included in the α-CDx cavity, and the α-CDx ring is deformed from the regular hexagonal symmetry as a result of the inclusion of the planar molecule. The nitrophenyl or carboxyphenyl group is located in the cavity, while the phenolic hydroxyl group protrudes from the secondary hydroxyl side of the cavity. Several intermolecular hydrogen-hydrogen contacts shorter than the ideal van der Waals contact are observed between α-CDx and guest molecules, indicating that the guest molecule is rigidly fixed in the cavity. The nitro or carboxyl group is situated on the O(6) side and is hydrogen-bonded to water or a hydroxyl group of the adjacent α-CDx molecule. The geometry of the complex gives a reasonable model for the α-CDx-substrate complex in the hydrolysis of *p*-nitrophenyl acetate and *p*-carboxyphenyl acetate catalyzed by α-CDx.

α-Cyclodextrin (α-CDx) forms a number of inclusion complexes with a variety of molecules and ions,[1] and the inclusion process affects the reactivity of the guest molecule.[2] A remarkable stereospecific acceleration is caused by α-CDx in the hydrolysis of substituted phenyl esters.[3] The rate of phenol-release from *meta*-substituted phenyl esters is greatly enhanced, whereas the rate of phenol-release from the corresponding *para*-isomers is only slightly enhanced. It has been emphasized that the magnitude of the rate acceleration does not parallel the stabilities of the α-CDx-ester complex, but depends on the geometry of the complex. Moreover, the stereospecificity of the rate accerelation has been interpreted on the basis of the interaction of the secondary hydroxyl groups of α-CDx with the carbonyl carbon of the substrate in the α-CDx cavity.

The crystal structures of many α-CDx complexes have been determined by the X-ray method.[4-16] In the complexes with *p*-iodoaniline (*p*-IA)[14,15] and *p*-iodophenol (*p*-IP),[16] the hydrophobic iodophenyl group is located in the α-CDx cavity, while the amino or hydroxyl group protrudes from the secondary hydroxyl side. *p*-Nitrophenol (*p*-NP) and *p*-hydroxybenzoic acid (*p*-HB) forms a 1: 1 complex with α-CDx. In this case, the nitro or carboxyl group has been expected, from the kinetic study of the α-CDx-catalyzed hydrolysis of *p*-nitrophenyl acetate and *p*-carboxyphenyl acetate,[3] to be situated on the O(6) side of the cavity. The X-ray analysis of α-CDx complexes with *p*-NP and *p*-HB was carried out in order to investigate the geometry of the complexes in relation to the catalytic property of α-CDx.

Experimental

A yellowish and plate-like crystal of the α-CDx–*p*-NP complex was prepared by cooling an aqueous solution containing α-CDx and *p*-NP in a 1: 1 molar ratio. The crystals of the α-CDx–*p*-HB complex, which were obtained by the same procedure, are colorless needles. The determination of the lattice parameters and the intensity measurements were carried out on a Rigaku automatic four-circle diffractometer with graphite-monochromated Cu*K*α radiation. Intensity data were collected up to 150 ° in 2θ by using the 2θ-ω scan technique. 5765 independent reflections for the *p*-NP complex and 5410 for the *p*-HB complex were obtained, but reflections with $|F_o|<3\sigma(F)$, 954 for the *p*-NP complex and 718 for the *p*-HB complex, were treated as unobserved. No correction was made for absorption and extinction. The crystal data are shown in Table 1.

Table 1. Crystal data

	α-Cyclodextrin–*p*-nitrophenol $C_{36}H_{60}O_{30}\cdot C_6H_5NO_3\cdot 3H_2O$	α-Cyclodextrin–*p*-hydroxybenzoic acid $C_{36}H_{60}O_{30}\cdot C_7H_6O_3\cdot 3H_2O$
Molecular weight	1166.0	1165.0
Crystal system	Orthorhombic	Orthorhombic
Cell dimensions	*a* 13.455(1)Å	13.356(1)Å
	b 15.296(1)Å	15.342(1)Å
	c 24.740(3)Å	24.896(2)Å
Cell volume	*V* 5092.1(8)Å^3	5101.4(6)Å^3
Space group	$P2_12_12_1$	$P2_12_12_1$
	Z 4	4
Density	D_m 1.53 g cm^{-3}	1.53 g cm^{-3}
	D_x 1.52	1.52

Determination and Refinement of the Structure

The crystals of the α-CDx–*p*-NP complex and the α-CDx–*p*-HB complex are isomorphous with the crystals of the α-CDx–*p*-IA complex[14,15] and the α-CDx–*p*-IP complex.[16] A set of coordinates of α-CDx found in the α-CDx–*p*-IP complex was used to calculate the initial phases for the *p*-NP complex and the *p*-HB complex. The phases were refined by the block-diagonal least-squares method. Then, an electron-density map was

TABLE 2. FINAL ATOMIC PARAMETERS ($\times 10^4$) FOR THE NON-HYDROGEN ATOMS

The anisotropic thermal factors are of the form: $\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{23}kl+B_{31}lh)]$. OC indicates the occupancy factor of the disordered atom.

α-Cyclodextrin-*p*-Nitrophenol Complex

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{31}	OC
C(1,G1)	1491(5)	-491(4)	6957(3)	44(4)	29(3)	11(1)	-2(6)	2(3)	0(4)	
C(2,G1)	1237(5)	-1215(4)	6562(3)	42(4)	28(3)	10(1)	-10(6)	1(3)	-1(4)	
C(3,G1)	1880(5)	-1131(4)	6061(2)	44(4)	22(3)	8(1)	-4(5)	-2(3)	-7(3)	
C(4,G1)	1749(5)	-214(4)	5813(2)	35(4)	19(2)	10(1)	-1(5)	3(3)	0(3)	
C(5,G1)	1988(6)	474(4)	6239(3)	62(5)	21(3)	11(1)	2(6)	-3(3)	-4(4)	
C(6,G1)	1794(8)	1400(5)	6037(3)	134(9)	20(3)	14(1)	3(9)	10(4)	-16(6)	
O(2,G1)	1434(5)	-2034(3)	6830(2)	85(4)	27(2)	10(1)	-42(5)	9(2)	-16(3)	
O(3,G1)	1549(4)	-1750(3)	5658(2)	82(4)	21(2)	10(1)	-9(5)	-2(2)	-15(3)	
O(4,G1)	2456(4)	-138(3)	5378(2)	39(3)	31(2)	7(1)	2(4)	6(2)	-1(2)	
O(5,G1)	1349(4)	332(3)	6702(2)	58(3)	28(2)	9(1)	23(5)	-5(2)	0(3)	
O(6,G1)	826(5)	1510(4)	5815(3)	101(6)	45(3)	23(1)	75(7)	17(3)	6(5)	
C(1,G2)	2089(5)	122(4)	4857(3)	39(4)	29(3)	10(1)	5(6)	10(3)	-2(3)	
C(2,G2)	2297(5)	-625(4)	4469(2)	45(4)	25(3)	9(1)	-12(6)	3(3)	-9(3)	
C(3,G2)	3422(5)	-795(4)	4453(3)	46(4)	20(2)	10(1)	-11(6)	-8(3)	2(3)	
C(4,G2)	3931(5)	42(4)	4290(2)	37(4)	15(2)	9(1)	4(5)	3(2)	2(3)	
C(5,G2)	3646(5)	803(4)	4664(3)	45(4)	19(3)	13(1)	2(6)	-8(3)	3(4)	
C(6,G2)	4042(6)	1672(4)	4468(3)	60(5)	17(3)	22(2)	-3(6)	-5(4)	13(5)	
O(2,G2)	1745(4)	-1393(3)	4615(2)	58(3)	35(2)	10(1)	-43(5)	5(2)	-10(3)	
O(3,G2)	3662(4)	-1442(3)	4049(2)	62(4)	20(2)	14(1)	-10(5)	-12(2)	16(3)	
O(4,G2)	4980(3)	-123(3)	4351(2)	32(2)	21(2)	8(1)	11(4)	4(2)	-1(2)	
O(5,G2)	2577(3)	887(3)	4688(2)	35(3)	20(2)	13(1)	7(4)	8(2)	7(3)	
O(6,G2)	3798(5)	1817(4)	3909(3)	70(4)	34(3)	26(1)	2(6)	31(3)	12(4)	
C(1,G3)	5630(5)	84(4)	3915(2)	36(4)	24(3)	7(1)	1(5)	5(3)	0(3)	
C(2,G3)	6263(5)	-729(4)	3808(2)	37(4)	24(3)	7(1)	1(5)	0(3)	-1(3)	
C(3,G3)	6798(5)	-974(4)	4318(2)	40(4)	14(2)	9(1)	16(5)	-2(2)	2(3)	
C(4,G3)	7374(5)	-207(4)	4560(2)	36(4)	20(2)	8(1)	6(5)	3(3)	-4(3)	
C(5,G3)	6767(5)	652(4)	4570(2)	37(4)	18(2)	8(1)	-5(5)	-1(3)	1(3)	
C(6,G3)	7410(6)	1456(4)	4658(3)	52(5)	18(2)	14(1)	-6(6)	-4(3)	-9(4)	
O(2,G3)	5628(3)	-1436(3)	3625(2)	40(3)	26(2)	9(1)	-3(4)	-7(2)	-2(2)	
O(3,G3)	7487(4)	-1693(3)	4229(2)	42(3)	20(2)	11(1)	6(4)	-5(2)	0(3)	
O(4,G3)	7597(3)	-477(3)	5100(2)	34(3)	27(2)	7(1)	-3(4)	4(2)	-5(2)	
O(5,G3)	6269(3)	777(3)	4063(2)	43(3)	19(2)	9(1)	4(4)	8(2)	-1(2)	
O(6,G3)	8221(4)	1501(3)	4293(2)	60(4)	37(3)	18(1)	-41(5)	12(3)	-1(3)	
C(1,G4)	8568(5)	-320(4)	5311(2)	37(4)	28(3)	9(1)	-9(6)	-10(3)	-3(3)	
C(2,G4)	8888(6)	-1150(4)	5622(3)	53(5)	28(3)	8(1)	20(6)	-7(3)	-11(4)	
C(3,G4)	8302(6)	-1253(4)	6134(2)	58(5)	17(2)	9(1)	5(6)	-3(3)	-13(4)	
C(4,G4)	8309(5)	-426(4)	6474(2)	45(4)	17(2)	8(1)	1(5)	-4(3)	1(3)	
C(5,G4)	7913(5)	334(4)	6117(2)	51(4)	16(2)	8(1)	3(5)	-3(3)	4(3)	
C(6,G4)	7960(7)	1215(4)	6414(3)	90(6)	15(3)	10(1)	8(7)	-5(3)	-14(4)	
O(2,G4)	8778(4)	-1905(3)	5276(2)	79(4)	31(2)	11(1)	40(5)	-16(2)	-14(3)	
O(3,G4)	8761(4)	-1949(3)	6432(2)	80(4)	19(2)	12(1)	24(5)	2(2)	-1(3)	
O(4,G4)	7650(3)	-576(3)	6915(2)	35(3)	22(2)	7(1)	-7(4)	-3(2)	-1(2)	
O(5,G4)	8580(3)	417(3)	5658(2)	42(3)	24(2)	9(1)	-13(4)	-1(2)	1(2)	
O(6A,G4)	9053(14)	1458(9)	6516(6)	119(15)	28(6)	17(3)	-9(16)	-23(7)	12(11)	0.4
O(6B,G4)	7400(6)	1851(4)	6087(3)	40(5)	12(3)	9(1)	5(6)	3(3)	-2(4)	0.6
C(1,G5)	8019(5)	-417(4)	7442(2)	45(4)	19(2)	9(1)	0(6)	0(3)	-3(3)	
C(2,G5)	7801(5)	-1234(4)	7793(2)	41(4)	21(3)	10(1)	13(5)	-4(3)	-2(3)	
C(3,G5)	6674(5)	-1391(4)	7829(3)	44(4)	21(3)	9(1)	1(6)	4(3)	2(3)	
C(4,G5)	6147(5)	-561(4)	8013(2)	34(4)	22(3)	9(1)	-1(5)	4(3)	-4(3)	
C(5,G5)	6457(5)	239(4)	7677(2)	28(3)	23(3)	10(1)	2(5)	3(3)	-3(3)	
C(6,G5)	6055(5)	1098(4)	7895(3)	48(4)	19(3)	12(1)	16(6)	-3(3)	2(4)	
O(2,G5)	8280(4)	-1972(3)	7559(2)	58(3)	25(2)	13(1)	25(5)	-2(2)	5(3)	
O(3,G5)	6476(4)	-2082(3)	8202(2)	70(4)	23(2)	14(1)	-7(5)	13(2)	14(3)	
O(4,G5)	5108(3)	-715(3)	7930(2)	34(3)	31(2)	8(1)	-3(4)	-4(2)	2(2)	
O(5,G5)	7524(3)	316(2)	7674(2)	39(3)	16(2)	8(1)	4(4)	-6(2)	-3(2)	
O(6,G5)	6211(4)	1168(3)	8466(2)	44(3)	33(2)	14(1)	9(5)	-16(2)	-4(3)	
C(1,G6)	4440(5)	-589(4)	8362(2)	45(4)	27(3)	7(1)	4(6)	7(3)	5(3)	
C(2,G6)	3740(5)	-1378(4)	8361(3)	46(4)	24(3)	12(1)	-3(6)	9(3)	-3(4)	
C(3,G6)	3239(5)	-1438(4)	7812(3)	39(4)	22(3)	12(1)	-11(6)	6(3)	-3(4)	
C(4,G6)	2734(5)	-563(4)	7682(2)	31(4)	22(3)	9(1)	-4(5)	-1(3)	-1(3)	
C(5,G6)	3404(5)	238(4)	7767(2)	45(4)	18(2)	8(1)	-6(5)	-4(3)	-3(3)	
C(6,G6)	2812(6)	1087(4)	7751(3)	61(5)	23(3)	14(1)	1(6)	1(3)	-11(4)	
O(2,G6)	4261(4)	-2155(3)	8493(3)	55(4)	29(2)	26(1)	1(5)	18(3)	-19(4)	
O(3,G6)	2522(4)	-2126(3)	7821(2)	55(3)	20(2)	17(1)	-26(5)	6(2)	-10(3)	
O(4,G6)	2500(3)	-599(3)	7117(2)	33(3)	24(2)	8(1)	0(4)	-3(2)	-3(2)	
O(5,G6)	3880(3)	185(3)	8291(3)	41(3)	25(2)	7(1)	1(4)	-6(2)	-1(2)	
O(6,G6)	1870(4)	1025(4)	8007(2)	65(4)	37(3)	17(1)	30(5)	-8(3)	9(3)	
C(1,NP)	5286(6)	-2209(4)	6068(3)	50(5)	23(3)	13(1)	10(6)	8(3)	16(4)	
C(2,NP)	5046(7)	-1823(5)	6563(3)	81(6)	32(3)	10(1)	1(8)	1(3)	16(5)	
C(3,NP)	4917(7)	-938(5)	6589(3)	78(6)	35(3)	11(1)	-11(8)	-5(3)	20(5)	
C(4,NP)	5059(5)	-437(4)	6125(3)	41(4)	25(3)	9(1)	-4(6)	1(3)	-4(3)	
C(5,NP)	5302(6)	-804(5)	5636(3)	75(6)	30(3)	11(1)	-2(7)	2(3)	10(4)	
C(6,NP)	5415(7)	-1709(5)	5604(3)	70(6)	41(4)	11(1)	12(8)	-2(4)	19(5)	
N(NP)	4967(5)	517(4)	6160(3)	57(4)	28(3)	15(1)	-2(6)	-6(3)	-3(4)	
O(1,NP)	5430(4)	-3091(3)	6074(2)	71(4)	26(2)	16(1)	16(5)	9(3)	29(3)	
O(2,NP)	4742(6)	849(4)	6597(3)	144(7)	31(3)	21(1)	-5(7)	-11(3)	29(5)	
O(3,NP)	5149(6)	951(4)	5748(2)	121(6)	33(3)	17(1)	-1(7)	16(3)	3(5)	
O(W1)	5077(6)	-1109(5)	2510(3)	80(5)	74(4)	16(1)	-6(8)	16(4)	-18(4)	
O(W2A)	4859(6)	-1541(6)	9688(3)	48(5)	79(5)	25(2)	27(9)	28(5)	23(5)	0.8
O(W2B)	3571(25)	-2527(19)	9381(12)	84(25)	45(15)	20(6)	9(33)	44(16)	18(21)	0.2
O(W3A)	190(14)	-1713(13)	7923(8)	75(13)	87(12)	29(4)	12(21)	-10(12)	8(13)	0.4
O(W3B)	9798(7)	-2574(7)	8219(4)	57(7)	58(5)	19(2)	30(10)	-11(5)	-20(6)	0.6

α-Cyclodextrin-*p*-Hydroxybenzoic Acid Complex

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{31}	OC
C(1,G1)	1502(5)	-473(4)	6944(3)	46(4)	31(3)	11(1)	-6(6)	-2(3)	11(4)	
C(2,G1)	1260(5)	-1199(4)	6549(3)	46(4)	27(3)	12(1)	-9(6)	1(3)	-14(4)	
C(3,G1)	1892(5)	-1114(4)	6044(2)	49(4)	29(3)	9(1)	0(6)	-4(3)	-9(3)	
C(3,G1)	1737(5)	-206(4)	5803(2)	42(4)	27(3)	9(1)	-4(6)	-1(3)	3(3)	
C(5,G1)	1968(6)	496(5)	6227(3)	80(6)	32(3)	10(1)	-14(7)	-6(3)	12(4)	
C(6,G1)	1702(8)	1408(5)	6021(3)	123(9)	30(3)	16(1)	-26(9)	-1(4)	10(6)	
O(2,G1)	1447(4)	-2016(3)	6812(2)	85(4)	30(2)	11(1)	-34(5)	2(2)	-25(3)	
O(3,G1)	1564(4)	-1739(3)	5652(2)	87(4)	23(2)	12(1)	8(5)	-3(2)	-15(3)	
O(4,G1)	2434(4)	-122(3)	5366(2)	42(3)	39(2)	10(1)	6(5)	1(2)	2(3)	
O(5,G1)	1334(4)	334(3)	6686(2)	73(4)	28(2)	11(1)	17(5)	-2(2)	12(3)	
O(6,G1)	732(5)	1467(4)	5771(3)	108(6)	50(3)	26(1)	68(7)	17(4)	18(5)	
C(1,G2)	2043(5)	139(5)	4854(3)	44(5)	43(4)	12(1)	16(7)	5(3)	1(4)	
C(2,G2)	2234(6)	-597(5)	4462(3)	52(5)	38(3)	11(1)	-3(7)	3(3)	-6(4)	
C(3,G2)	3346(5)	-780(4)	4435(3)	50(4)	24(3)	11(1)	4(6)	-2(3)	-1(4)	
C(4,G2)	3891(5)	39(4)	4278(2)	46(4)	16(2)	10(1)	10(5)	-1(2)	3(3)	
C(5,G2)	3637(6)	799(4)	4650(3)	51(5)	22(3)	16(1)	13(6)	-7(3)	14(4)	
C(6,G2)	4041(7)	1665(5)	4463(4)	83(7)	34(4)	29(2)	8(9)	-7(5)	11(7)	
O(2,G2)	1663(4)	-1357(4)	4605(2)	62(4)	55(3)	10(1)	-48(6)	1(3)	-14(3)	
O(3,G2)	3569(4)	-1420(3)	4025(2)	76(4)	23(2)	14(1)	-4(5)	-7(2)	7(3)	
O(4,G2)	4933(3)	-149(3)	4329(2)	44(3)	26(2)	7(1)	13(4)	6(2)	2(2)	
O(5,G2)	2549(4)	900(3)	4679(2)	50(3)	28(2)	17(1)	23(5)	5(2)	12(3)	
O(6,G2)	3805(7)	1813(4)	3906(4)	142(8)	46(3)	47(2)	8(9)	43(5)	8(8)	
C(1,G3)	5589(5)	55(4)	3905(2)	52(4)	28(3)	7(1)	13(6)	4(3)	5(3)	
C(2,G3)	6225(5)	-762(4)	3802(2)	49(4)	24(3)	9(1)	-4(6)	2(3)	3(3)	
C(3,G3)	6786(5)	-995(4)	4317(2)	47(4)	19(2)	10(1)	-3(5)	1(3)	3(4)	
C(4,G3)	7364(5)	-221(4)	4543(2)	52(4)	24(3)	7(1)	-15(6)	2(3)	-3(3)	
C(5,G3)	6744(6)	622(4)	4555(2)	63(5)	24(3)	9(1)	1(6)	3(3)	-4(4)	
C(6,G3)	7387(7)	1433(4)	4640(3)	88(6)	22(3)	14(1)	-19(7)	-1(3)	-16(5)	
O(2,G3)	5606(3)	-1465(3)	3626(2)	41(3)	29(2)	9(1)	3(4)	-8(2)	2(2)	
O(3,G3)	7465(4)	-1708(3)	4232(2)	46(3)	21(2)	11(1)	0(4)	1(2)	-4(3)	
O(4,G3)	7590(4)	-467(3)	5090(2)	47(3)	30(2)	8(1)	-5(4)	1(2)	-5(2)	
O(5,G3)	6242(4)	745(3)	4046(2)	61(3)	23(2)	10(1)	-1(4)	10(2)	-3(3)	
O(6,G3)	8192(4)	1497(4)	4260(2)	68(4)	50(3)	18(1)	-43(6)	11(3)	-3(4)	
C(1,G4)	8572(5)	-339(4)	5288(2)	41(4)	35(3)	10(1)	-6(6)	-7(3)	-7(3)	
C(2,G4)	8875(6)	-1169(4)	5593(3)	60(5)	30(3)	11(1)	14(6)	-9(3)	-13(4)	
C(3,G4)	8296(6)	-1261(4)	6118(3)	60(5)	22(3)	13(1)	5(6)	-9(3)	-10(4)	
C(4,G4)	8368(5)	-422(4)	6447(2)	48(4)	24(3)	9(1)	-6(6)	-4(3)	3(3)	
C(5,G4)	7985(5)	336(4)	6102(2)	62(5)	22(3)	9(1)	-6(6)	-2(3)	4(4)	
C(6,G4)	8063(7)	1216(4)	6389(3)	93(7)	16(3)	14(1)	-4(7)	-8(3)	-7(5)	
O(2,G4)	8741(5)	-1933(3)	5270(2)	87(5)	43(3)	12(1)	46(6)	-17(3)	-23(3)	
O(3,G4)	8749(4)	-1964(3)	6409(2)	92(4)	22(2)	11(1)	19(5)	1(2)	-1(3)	
O(4,G4)	7723(3)	-544(3)	6899(2)	38(3)	27(2)	10(1)	-4(4)	-5(2)	-5(2)	
O(5,G4)	8627(4)	396(3)	6527(2)	52(3)	32(2)	10(1)	-34(5)	-4(2)	2(3)	
O(6A,G4)	9128(6)	1450(5)	6509(3)	82(6)	33(3)	15(1)	33(8)	-18(4)	5(5)	0.7
O(6B,G4)	7442(15)	1861(9)	6098(7)	90(15)	22(6)	17(3)	-34(17)	-25(8)	29(12)	0.3
C(1,G5)	8111(5)	-382(4)	7419(3)	56(5)	27(3)	10(1)	1(6)	-3(3)	-6(4)	
C(2,G5)	7910(6)	-1193(5)	7764(3)	55(5)	32(3)	11(1)	11(7)	0(3)	-5(4)	
C(3,G5)	6782(6)	-1353(4)	7814(3)	68(5)	20(3)	11(1)	3(6)	1(3)	-4(4)	
C(4,G5)	6231(5)	-541(4)	7993(2)	50(4)	21(3)	11(1)	-7(6)	-2(3)	-11(4)	
C(5,G5)	6532(5)	265(4)	7663(3)	43(4)	27(3)	11(1)	-3(6)	-1(3)	-3(4)	
C(6,G5)	6119(5)	1117(4)	7882(3)	49(5)	27(3)	14(1)	10(6)	3(3)	-1(4)	
O(2,G5)	8380(4)	-1939(3)	7535(2)	77(4)	36(2)	14(1)	40(5)	-7(3)	-9(3)	
O(3,G5)	6593(4)	-2041(3)	8189(2)	75(4)	28(2)	17(1)	5(5)	16(2)	1(3)	
O(4,G5)	5188(4)	-691(3)	7895(2)	44(3)	35(2)	8(1)	-10(4)	-3(2)	-4(2)	
O(5,G5)	7625(4)	345(3)	7653(2)	43(3)	22(2)	12(1)	2(4)	-9(2)	-2(3)	
O(6,G5)	6262(4)	1174(3)	8454(2)	44(3)	41(2)	16(1)	18(5)	-19(3)	-5(3)	
C(1,G6)	4491(6)	-617(5)	8325(3)	60(5)	33(3)	9(1)	-15(7)	1(3)	2(4)	
C(2,G6)	3829(6)	-1433(5)	8294(3)	65(5)	39(3)	14(1)	-40(7)	6(4)	-14(4)	
C(3,G6)	3286(6)	-1434(5)	7762(3)	51(5)	30(3)	14(1)	-25(6)	4(3)	3(4)	
C(4,G6)	2766(5)	-570(4)	7652(2)	44(4)	27(3)	10(1)	-14(6)	-5(3)	9(3)	
C(5,G6)	3434(5)	219(4)	7748(2)	49(4)	32(3)	9(1)	-8(6)	-6(3)	-6(4)	
C(6,G6)	2858(6)	1076(5)	7738(3)	64(6)	35(3)	17(1)	-7(7)	-1(4)	-13(5)	
O(2,G6)	4465(5)	-2187(3)	8349(3)	103(5)	29(2)	29(1)	-19(6)	11(3)	-41(5)	
O(3,G6)	2574(4)	-2136(3)	7769(2)	74(4)	34(2)	16(1)	-43(5)	3(3)	-5(3)	
O(4,G6)	2510(3)	-575(3)	7091(2)	38(3)	38(2)	8(1)	-14(4)	-8(2)	-1(2)	
O(5,G6)	3912(4)	147(3)	8275(2)	56(3)	32(2)	8(1)	-2(5)	-8(2)	-6(3)	
O(6,G6)	1907(4)	1012(4)	7994(2)	70(4)	56(3)	16(1)	20(6)	-22(3)	12(3)	
C(1,HB)	5261(5)	-2175(4)	6073(3)	38(4)	29(3)	12(1)	-10(6)	3(3)	15(4)	
C(2,HB)	5110(6)	-1737(5)	6552(3)	56(5)	44(4)	10(1)	8(7)	11(3)	16(4)	
C(3,HB)	5032(7)	-847(5)	6558(3)	80(6)	39(3)	9(1)	14(8)	-8(3)	9(4)	
C(4,HB)	5151(6)	-366(5)	6092(3)	53(5)	39(3)	11(1)	-1(7)	-9(3)	-1(4)	
C(5,HB)	5268(7)	-797(5)	5604(3)	85(6)	36(3)	8(1)	-17(8)	1(3)	4(4)	
C(6,HB)	5334(6)	-1708(5)	5592(3)	73(6)	43(4)	10(1)	-29(8)	-6(3)	17(4)	
C(7,HB)	5177(7)	602(5)	6103(3)	91(7)	39(4)	14(1)	7(9)	-13(4)	2(5)	
O(1,HB)	5368(4)	-3057(3)	6079(2)	68(4)	34(2)	15(1)	9(5)	4(3)	32(3)	
O(2,HB)	5168(7)	969(4)	6561(2)	205(9)	31(3)	16(1)	35(9)	-9(3)	9(6)	
O(3,HB)	5312(7)	1017(4)	5676(2)	181(8)	48(3)	13(1)	-72(9)	14(3)	-5(5)	
O(W1)	5047(6)	-1151(5)	2507(3)	81(5)	101(5)	18(1)	-39(9)	27(4)	-28(4)	
O(W2A)	4932(7)	-1677(10)	9690(4)	45(6)	222(14)	22(2)	31(16)	69(9)	0(6)	0.7
O(W2B)	3716(12)	-2467(10)	9383(8)	40(11)	34(8)	25(4)	19(15)	13(9)	23(11)	0.3
O(W3A)	277(7)	-1713(8)	7950(5)	60(7)	113(8)	36(3)	-14(12)	-26(8)	35(7)	0.7
O(W3B)	9798(15)	-2594(13)	8201(7)	71(14)	58(10)	18(4)	29(21)	-4(10)	-7(12)	0.3

TABLE 3. FRACTIONAL COORDINATES ($\times 10^3$) AND ISOTROPIC THERMAL FACTORS ($B/\text{Å}^2$) FOR HYDROGEN ATOMS

α-Cyclodextrin-*p*-Nitrophenol Complex

	x	y	z	B		x	y	z	B
H(C1,G1)	109(6)	-48(5)	735(3)	2.8	H(C5,G4)	710(6)	18(5)	598(3)	2.5
H(C2,G1)	42(6)	-116(5)	644(3)	2.6	H(O2,G4)	866(7)	-180(5)	484(3)	3.1
H(C3,G1)	275(6)	-128(5)	618(3)	2.6	H(O3,G4)	867(6)	-209(6)	680(3)	3.1
H(C4,G1)	93(6)	-15(5)	563(3)	2.2	H(C1,G5)	882(6)	-23(5)	741(3)	2.0
H(C5,G1)	285(6)	44(5)	636(3)	2.9	H(C2,G5)	809(6)	-117(5)	823(3)	2.2
H(C6A,G1)	238(7)	157(6)	575(3)	4.0	H(C3,G5)	632(6)	-153(5)	741(3)	2.4
H(C6B,G1)	185(7)	185(6)	638(4)	4.0	H(C4,G5)	631(6)	-49(5)	843(3)	2.1
H(O2,G1)	100(6)	-230(6)	654(3)	3.2	H(C5,G3)	616(6)	12(5)	726(3)	2.4
H(O3,G1)	193(6)	-203(6)	565(3)	3.1	H(C6A,G5)	645(6)	160(5)	769(3)	2.6
H(C1,G2)	128(6)	29(5)	490(3)	2.5	H(C6B,G5)	528(6)	118(5)	780(3)	2.6
H(C2,G2)	207(6)	-45(5)	406(3)	2.5	H(O2,G5)	900(6)	-218(5)	779(3)	2.9
H(C3,G2)	367(6)	-102(5)	486(3)	2.4	H(O3,G5)	670(6)	-213(6)	849(3)	3.2
H(C4,G2)	371(6)	17(5)	386(3)	1.8	H(O6,G5)	574(6)	127(6)	865(3)	3.2
H(C5,G2)	389(6)	67(5)	507(3)	2.6	H(C1,G6)	481(6)	-50(5)	875(3)	2.3
H(C6A,G2)	485(6)	168(5)	458(3)	3.2	H(C2,G6)	315(6)	-133(5)	868(3)	2.7
H(C6B,G2)	379(7)	214(5)	471(3)	3.2	H(C3,G6)	384(6)	-158(5)	750(3)	2.5
H(O2,G2)	192(6)	-160(6)	501(3)	3.1	H(C4,G6)	199(6)	-52(5)	792(3)	2.2
H(O3,G2)	308(6)	-134(5)	415(3)	2.9	H(C5,G6)	399(6)	24(5)	743(3)	2.2
H(C1,G3)	527(6)	29(5)	356(3)	2.1	H(C6A,G6)	329(6)	161(5)	796(3)	3.1
H(C2,G3)	679(6)	-58(5)	351(3)	2.3	H(C6B,G6)	273(6)	124(6)	730(3)	3.1
H(C3,G3)	624(6)	-116(5)	466(3)	2.2	H(O2,G6)	491(7)	-215(6)	825(3)	3.8
H(C4,G3)	809(6)	-10(5)	433(3)	2.1	H(O3,G6)	224(7)	-214(6)	751(3)	3.1
H(C5,G3)	624(6)	59(5)	492(3)	1.9	H(O6,G6)	170(7)	112(6)	837(3)	3.8
H(C6A,G3)	765(6)	144(5)	503(3)	2.8	H(C2,NP)	495(7)	-215(6)	699(3)	3.7
H(C6B,G3)	695(6)	199(5)	462(3)	2.8	H(C3,NP)	480(7)	-64(6)	701(4)	3.8
H(O2,G3)	502(6)	-152(5)	379(3)	2.4	H(C5,NP)	534(7)	-49(6)	520(3)	3.4
H(O3,G3)	775(6)	-169(5)	386(3)	2.4	H(C6,NP)	561(7)	-207(6)	523(3)	3.5
H(O6,G3)	824(7)	170(6)	407(4)	4.0	H(O1,NP)	535(7)	-330(6)	567(4)	3.9
H(C1,G4)	910(6)	-18(5)	502(3)	2.4	H(OA,W1)	465(7)	-87(6)	266(4)	5.0
H(C2,G4)	971(6)	-109(5)	572(3)	2.6	H(OB,W1)	522(7)	-123(6)	281(4)	5.0
H(C3,G4)	739(6)	-138(5)	605(3)	2.2	H(OA,W2A)	480(8)	-152(7)	994(4)	6.1
H(C4,G4)	910(6)	-33(5)	667(3)	1.9					

α-Cyclodextrin-*p*-Hydroxybenzoic Acid Complex

	x	y	z	B		x	y	z	B
H(C1,G1)	95(6)	-46(5)	731(3)	3.0	H(C5,G4)	707(6)	22(5)	599(3)	2.6
H(C2,G1)	43(6)	-117(5)	645(3)	2.8	H(O2,G4)	865(7)	-177(6)	501(3)	3.6
H(C3,G1)	276(6)	-126(5)	613(3)	2.7	H(O3,G4)	868(6)	-198(5)	679(3)	3.1
H(C4,G1)	92(6)	-10(5)	565(3)	2.5	H(C1,G5)	895(6)	-24(5)	739(3)	2.6
H(C5,G1)	278(6)	49(6)	635(3)	3.8	H(C2,G5)	815(6)	-115(5)	817(3)	2.9
H(C6A,G1)	238(7)	160(6)	582(3)	4.2	H(C3,G5)	648(6)	-153(5)	743(3)	2.9
H(C6B,G1)	172(7)	181(6)	634(3)	4.2	H(C4,G5)	641(6)	-44(5)	843(3)	2.3
H(O2,G1)	122(6)	-246(6)	659(3)	3.2	H(C5,G5)	623(6)	19(5)	723(3)	2.8
H(O3,G1)	196(6)	-228(6)	568(3)	3.3	H(C6A,G5)	646(6)	163(5)	770(3)	3.3
H(O6,G1)	31(7)	162(6)	619(4)	5.3	H(C6B,G5)	534(6)	114(5)	778(3)	3.3
H(C1,G2)	121(6)	37(5)	488(3)	3.5	H(O2,G5)	906(6)	-205(5)	779(3)	3.5
H(C2,G2)	189(6)	-43(5)	407(3)	3.2	H(O3,G5)	646(7)	-219(6)	868(3)	3.9
H(C3,G2)	360(6)	-99(5)	481(3)	2.4	H(O6,C5)	575(6)	131(5)	861(3)	3.3
H(C4,G2)	369(5)	21(5)	385(3)	2.0	H(C1,G6)	494(6)	-54(5)	867(3)	2.8
H(C5,G2)	399(6)	68(5)	507(3)	3.3	H(C2,G6)	326(6)	-141(6)	861(3)	3.7
H(C6A,G2)	492(7)	174(6)	457(4)	5.3	H(C3,G6)	393(6)	-157(5)	745(3)	2.8
H(C6B,G2)	363(7)	227(6)	469(4)	5.3	H(C4,G6)	207(6)	-48(5)	791(3)	2.7
H(O2,G2)	166(6)	-138(6)	500(3)	3.5	H(C5,G6)	407(6)	23(5)	743(3)	2.5
H(O3,G2)	341(6)	-192(5)	417(3)	3.1	H(C6A,G6)	329(7)	161(6)	793(3)	4.0
H(C1,G3)	514(6)	28(4)	356(3)	2.6	H(C6B,G6)	272(7)	125(6)	729(3)	4.0
H(C2,G3)	674(6)	-63(5)	346(3)	2.6	H(O2,G6)	489(7)	-267(6)	818(4)	5.4
H(C3,G3)	621(6)	-116(5)	461(3)	2.6	H(O3,G6)	224(7)	-202(6)	751(3)	3.9
H(C4,G3)	807(6)	-13(5)	432(3)	2.4	H(O6,G6)	177(7)	113(6)	831(3)	4.6
H(C5,G3)	616(6)	59(5)	492(3)	2.9	H(C2,HB)	503(6)	-209(5)	695(3)	3.3
H(C6A,G3)	768(6)	146(6)	498(3)	3.6	H(C3,HB)	492(6)	-52(5)	698(3)	3.7
H(C6B,G3)	696(6)	205(6)	462(3)	3.6	H(C5,HB)	527(6)	-39(5)	525(3)	3.5
H(O2,G3)	500(6)	-152(5)	381(3)	2.4	H(C6,HB)	538(6)	-204(6)	523(3)	3.6
H(O3,G3)	792(6)	-154(5)	384(3)	2.5	H(O1,HB)	576(6)	-327(6)	577(3)	3.5
H(O6,G3)	890(7)	170(6)	414(4)	4.7	H(O2,HB)	432(8)	111(6)	671(4)	5.8
H(C1,G4)	916(6)	-19(5)	496(3)	2.8	H(OA,W1)	473(7)	-91(6)	266(4)	5.6
H(C2,G4)	971(6)	-115(5)	567(3)	2.8	H(OB,W1)	540(7)	-126(6)	273(4)	5.6
H(C3,G4)	736(6)	-140(5)	600(3)	2.8	H(OA,W2A)	493(7)	-142(6)	996(4)	5.0
H(C4,G4)	920(6)	-29(5)	663(3)	2.4					

calculated. The guest molecule and water molecules were found on the map. The hydrogen atoms were found on a difference-Fourier map. In both complexes, O(6,G4), O(W2), and O(W3) were revealed to be statistically disordered. The occupancy was estimated on the electron-density map, but they were not refined. The refinement of the crystal structures was carried out by the block-diagonal least-squares method. The quantity minimized was $\sum w(|F_o|-|F_c|)^2$, with $w=1.0$ for the all reflections used. The thermal factors of the hydrogen atoms were not refined, but they were fixed as equal to the isotropic ones of the carbon or oxygen atoms to which the hydrogen atoms are bonded. The final R-values were 0.066 for the p-NP complex and 0.067 for the p-HB complex. The atomic scattering factors were taken from "International Tables for X-ray Crystallography."[17] The atomic parameters are listed in Tables 2 and 3. The observed and calculated structure factors are given in Table 4.*

Description of the Structure and Discussion

The structure and numbering schemes of the complexes are shown in Figs. 1 and 2. The atom numbering for α-CDx is the same as that used in the p-IA complex[14] and the p-IP complex.[16] The bond distances, angles, and conformation angles are shown in Figs. 3—6 and Tables 5* and 6. The geometrical data for the complex are shown in Tables 7 and 8. The crystal structure and hydrogen-bonding schemes are given in Figs. 7—9 and Table 9.

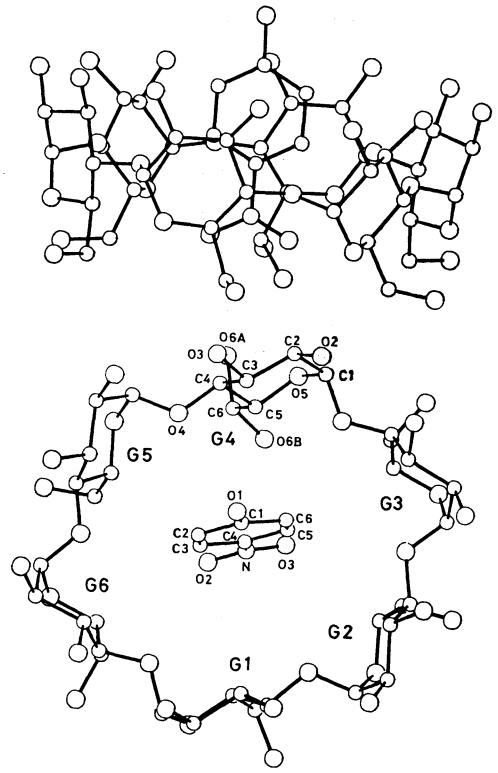

Fig. 1. The structure and numbering scheme of the α-cyclodextrin–p-nitrophenol complex.

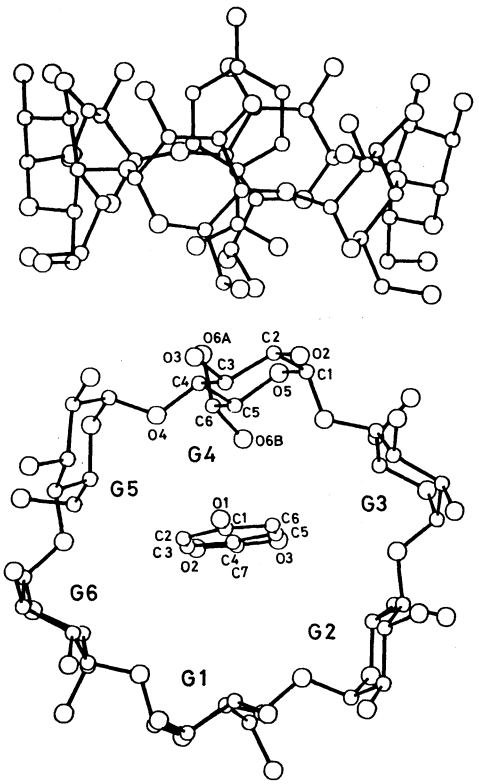

Fig. 2. The structure and numbering scheme of the α-cyclodextrin–p-hydroxybenzoic acid complex.

Structure of α-CDx. In both the α-CDx–p-NP complex and the α-CDx–p-HB complex, the conformation of α-CDx is nearly identical with the conformation found in the complexes with p-IA and p-IP. The distances of the C(1)–C(2) and C(4)–C(5) bonds are slightly longer than the C(2)–C(3) and C(3)–C(4) distances, while the contrary tendancy is observed in α-D-glucose monohydrate.[18] The C(4)–O(4) bond of the glycosidic linkage is longer than the C(1)–O(4) bond. In the pyranose ring, the C(5)–O(5) bond is longer than the C(1)–O(5) bond; a similar effect is observed in α-D-glucose monohydrate. The C(1)–O(5)–C(5) angles are in good agreement with the values found in the α-D-glucose derivatives[18,19] and in the maltose derivatives.[20-22] The α-1,4-linking oxygen angles of C(4)–O(4)–C(1′) are a little larger than those found in the maltose derivatives, but such large values are commonly observed in other α-CDx complexes.

A small conformational difference is observed among the glucose residues. One of the indices which represent the conformational change of glucose residues is the O(4)···O(4′) distance.[23] The O(4)···O(4′) distance in the p-NP complex and the p-HB complex (Table 7) are quite small compared with that found in α-D-glucose monohydrate. This may be due to the cyclic structure of α-CDx. The distance of the C(4) atom from the plane through C(2), C(3), C(5), and O(5) also indicates the conformational change in the pyranose ring (Table 8). The C(4) atom approaches to the plane slightly when the O(4)···O(4′) distance is shortened.

* Tables 4 and 5 are kept in the office of The Chemical Society of Japan (Document No. 7707).

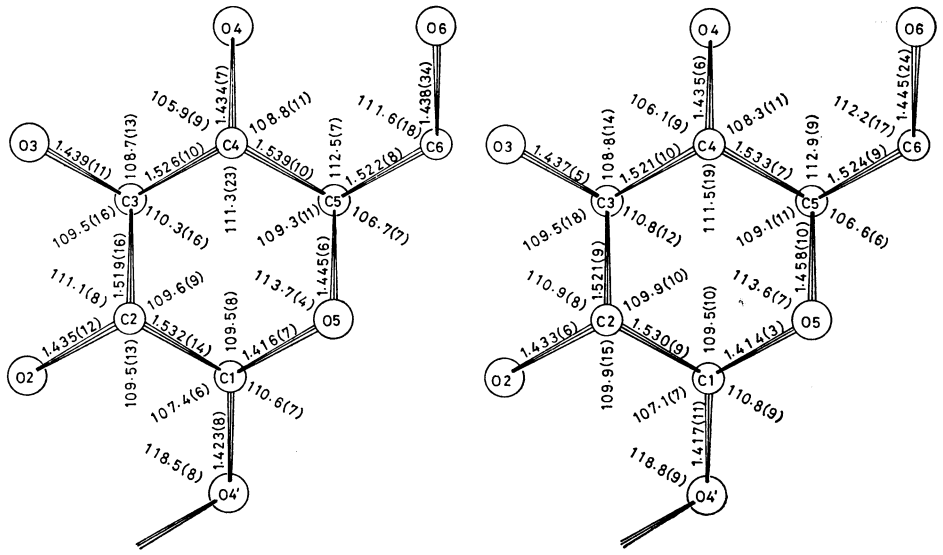

Fig. 3. Average bond distances and angles for the glucose residue in the α-cyclodextrin–*p*-nitrophenol complex (left) and the α-cyclodextrin–*p*-hydroxybenzoic acid complex (right). Standard deviations given in parentheses were estimated according to $\sigma=[\sum_{i=1}^{6}(x_i-\bar{x})^2/5]^{1/2}$, where x_i is the bond distance or angle in the i-th glucose residue and $\bar{x}$ is the average value.

Table 6. Conformation angles (ϕ/°) in α-cyclodextrin

A prime (′) indicates the atom in the adjacent glucose residue.

	G1	G2	G3	G4	G5	G6	AVERAGE
α-Cyclodextrin–*p*-Nitrophenol Complex							
C(1)-C(2)-C(3)-C(4)	-56.0	-57.2	-52.5	-51.1	-52.6	-54.2	-53.9
C(2)-C(3)-C(4)-C(5)	56.0	55.2	45.1	56.0	50.5	48.9	52.0
C(3)-C(4)-C(5)-O(5)	-57.0	-54.0	-44.8	-60.6	-53.0	-48.4	-53.0
C(4)-C(5)-O(5)-C(1)	62.3	56.8	57.3	65.4	60.9	57.0	60.0
C(5)-O(5)-C(1)-C(2)	-62.5	-60.9	-66.4	-60.3	-63.5	-65.5	-63.2
O(5)-C(1)-C(2)-C(3)	57.9	60.1	61.8	51.2	58.0	63.1	58.7
O(4′)-C(1)-C(2)-O(2)	56.9	64.7	64.6	52.7	59.7	66.5	60.9
O(2)-C(2)-C(3)-O(3)	69.4	62.1	65.0	67.1	66.2	61.9	65.3
O(3)-C(3)-C(4)-O(4)	-67.9	-67.9	-71.6	-67.9	-70.4	-73.5	-69.9
O(4)-C(4)-C(5)-C(6)	68.0	71.5	79.8	68.1	71.1	75.9	72.4
O(5)-C(5)-C(6)-O(6)	-67.4	-70.0	-69.2	-50.9*	-73.8	-81.6	-68.8
				74.2**			
C(4)-C(5)-C(6)-O(6)	51.7	50.6	51.9	65.5*	47.3	39.0	51.0
				-169.4**			
C(2)-C(1)-O(4′)-C(4′)	-131.9	-118.0	-129.1	-137.5	-129.3	-135.1	-130.2
O(5)-C(1)-O(4′)-C(4′)	108.3	122.0	113.2	101.4	112.2	106.0	110.5
C(1)-O(4′)-C(4′)-C(3′)	122.4	127.2	129.9	136.6	128.0	126.9	128.5
C(1)-O(4′)-C(4′)-C(5′)	-115.7	-114.9	-110.4	-101.8	-115.3	-112.6	-111.8
α-Cyclodextrin–*p*-Hydroxybenzoic Acid Complex							
	G1	G2	G3	G4	G5	G6	AVERAGE
C(1)-C(2)-C(3)-C(4)	-55.6	-57.0	-52.0	-51.4	-51.3	-50.3	-52.9
C(2)-C(3)-C(4)-C(5)	55.2	54.3	46.0	56.5	48.7	47.9	51.4
C(3)-C(4)-C(5)-O(5)	-56.7	-52.8	-46.9	-60.9	-51.2	-49.6	-53.0
C(4)-C(5)-O(5)-C(1)	62.7	57.0	59.1	64.4	60.4	58.7	60.4
C(5)-O(5)-C(1)-C(2)	-63.0	-61.4	-66.7	-59.0	-63.9	-64.6	-63.1
O(5)-C(1)-C(2)-C(3)	57.7	60.3	61.0	51.5	57.9	59.4	58.0
O(4′)-C(1)-C(2)-O(2)	58.8	66.1	63.7	53.0	59.5	59.6	60.1
O(2)-C(2)-C(3)-O(3)	67.4	62.1	63.4	65.2	65.4	68.4	65.3
O(3)-C(3)-C(4)-O(4)	-67.9	-67.3	-72.4	-68.4	-72.4	-73.9	-70.4
O(4)-C(4)-C(5)-C(6)	69.9	71.6	79.8	66.9	71.9	73.8	72.3
O(5)-C(5)-C(6)-O(6)	-70.5	-71.5	-67.1	-54.9*	-75.2	-81.3	-72.4
				77.2**			
C(4)-C(5)-C(6)-O(6)	46.7	49.0	53.4	62.9*	46.2	39.7	49.7
				-165.0**			
C(2)-C(1)-O(4′)-C(4′)	-130.3	-117.5	-131.3	-135.2	-128.8	-132.4	-129.2
O(5)-C(1)-O(4′)-C(4′)	111.4	123.5	111.2	103.3	113.7	117.1	113.4
C(1)-O(4′)-C(4′)-C(3′)	122.1	127.8	130.6	133.7	128.8	123.7	127.8
C(1)-O(4′)-C(4′)-C(5′)	-116.4	-113.6	-108.9	-105.6	-114.2	-116.1	-112.5

* The angles of O(5,G4)-C(5,G4)-C(6,G4)-O(6A,G4) and C(4,G4)-C(5,G4)-C(6,G4)-O(6A,G4).
** The angles of O(5,G4)-C(5,G4)-C(6,G4)-O(6B,G4) and C(4,G4)-C(5,G4)-C(6,G4)-O(6B,G4).

Table 7. Geometrical data for α-cyclodextrin

I. Distances (l/Å) between glycosidic oxygen atoms in the *p*-NP complex (A) and in the *p*-HB complex (B).

	A	B
O(4, G1)–O(4, G6)	4.361	4.351
O(4, G1)–O(4, G2)	4.241	4.219
O(4, G2)–O(4, G3)	4.016	4.053
O(4, G3)–O(4, G4)	4.493	4.509
O(4, G4)–O(4, G5)	4.249	4.201
O(4, G5)–O(4, G6)	4.049	4.103
Average value	4.235	4.239
O(4, G1)–O(4, G4)	7.984	8.055
O(4, G2)–O(4, G5)	8.902	8.923
O(4, G3)–O(4, G6)	8.457	8.418
Average value	8.457	8.465

II. Torsion-angle index[a] (ϕ/°) in the *p*-NP complex (A) and in the *p*-HB complex (B).

Residue	Index A	Index B	Residue	Index A	Index B
G1	125.7	127.1	G4	111.4	108.9
G2	125.8	128.6	G5	131.5	133.6
G3	148.1	145.9	G6	142.5	135.5
			Average value	130.8	129.9

a) The torsion-angle index is defined as follows: $|\phi(C(1)-C(2))|+|\phi(C(2)-C(3))|+|\phi(C(5)-O(5))|+|\phi(O(5)-C(1))|-|\phi(C(3)-C(4))|-|\phi(C(4)-C(5))|$, if the conformation angle of C(1)–C(2)–C(3)–C(4) is expressed as ϕ(C(2)–C(3)).

The conformation angles in the G4 residue, which gives the largest O(4)···O(4′) distance are in agreement with those of α-D-glucose monohydrate within 3.0° in the *p*-NP complex and within 4.0° in the *p*-HB complex. A small difference in the pyranose-ring conformation is observed between the G3 residue and the G4 residue. The C(3)–C(4)–C(5)–O(5) conformation angle of the G3 residue is greater by 15.8° in the *p*-NP complex and by 14.0° in the *p*-HB complex than the values found in the G4 residue. The change in the pyranose-ring conformation is also clearly shown by means of the torsion-angle index defined by French and Murphy.[23] The torsion-angle indices in the *p*-NP complex and the *p*-HB complex, except for that in the G4 residue, are

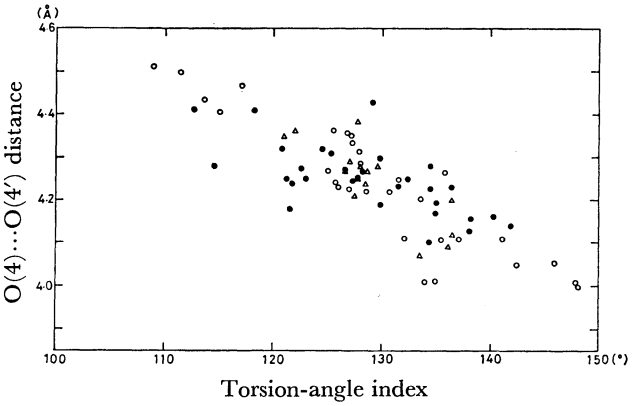

Fig. 4. Plot of the O(4)···O(4') distance against the torsion-angle index in the α-cyclodextrin complexes with *para*-disubstituted benzenes (○), the complexes with the cage-type structure (●), and the complexes with the channel-type structure (△).

greater than that found in α-D-glucose monohydrate. The glucose residue, which has a small O(4)—O(4') distance, gives a large torsion-angle index, and *vice versa*. The value found in the G3 residue is considerably larger than the values of 112.6—134.6° found in the α-CDx–water complex. This suggests that the pyranose ring changes its conformation when α-CDx includes the planar molecule.

The O(4)···O(4') distance is plotted against the torsion-angle index for the three types of crystal structures in Fig. 4. In the complexes with *para*-disubstituted benzenes, a correlation similar to that found in mono-, di-, and trisaccharides[23] is found between the two variables, while in the complexes with the cage-type structure[4–8] or the channel-type structure[9–12] the correlation is not clear. In the channel-type structure, the O(4)···O(4') distance and the torsion-angle index are found in a relatively small region, although the dimension and shape of the guest molecule are quite flexible. This indicates that the geometrical freedom of the pyranose ring is restricted not only by the guest molecule, but also by the crystal structure.

The α-CDx ring shows a distorted hexagon. The diagonal distances measured between the glycosidic oxygen atoms vary from 7.984 to 8.902 Å in the *p*-NP complex and from 8.055 to 8.923 Å in the *p*-HB complex (Table 7). On the other hand, the PSNa complex[12] gives 8.40—8.59 Å, showing a nearly regular hexagon. A distorted hexagon was also observed in the other α-CDx complexes with phenyl derivatives. The planarity of the six O(4) atoms is quite good (Table 8).

TABLE 8. LEAST-SQUARES PLANES AND DEVIATIONS OF ATOMS FROM THE PLANE (*l*/Å)
An asterisk (*) indicates an atom not included in the plane.

I. α-Cyclodextrin–*p*-nitrophenol complex.

(i) The plane through C(2), C(3), C(5), and O(5). The plane equation is of the $AX+BY+CZ=D$ form.

Residue	*A*	*B*	*C*	*D*
G1	0.8120	−0.1425	0.5660	10.7960
G2	0.0029	−0.2186	0.9758	11.0176
G3	0.8801	0.1257	−0.4578	2.9684
G4	0.8015	0.1501	0.5789	17.4115
G5	0.0166	0.1393	0.9901	19.0157
G6	0.8920	−0.0991	−0.4411	−4.4224

Deviations of atoms from the plane.

Residue	C(1)*	C(2)	C(3)	C(4)*	C(5)	O(5)
G1	−0.682	−0.009	0.009	0.699	−0.009	0.010
G2	−0.676	−0.012	0.011	0.660	−0.012	0.013
G3	−0.768	−0.004	0.004	0.559	−0.004	0.004
G4	−0.638	−0.039	0.039	0.723	−0.040	0.041
G5	−0.698	−0.015	0.014	0.630	−0.015	0.016
G6	−0.716	−0.004	0.003	0.592	−0.004	0.004

(ii) The plane through six O(4) atoms.

$0.0432X+0.9942Y+0.0988Z=1.1267$

O(4, G1)	0.121	O(4, G4)	0.133
O(4, G2)	0.040	O(4, G5)	0.022
O(4, G3)	−0.163	O(4, G6)	−0.152

(iii) The benzene plane.

$0.9711X+0.1004Y+0.2163Z=9.8172$

C(1, NP)	−0.001	C(6, NP)	−0.004
C(2, NP)	0.008	N(NP)*	0.050
C(3, NP)	−0.010	O(1, NP)*	0.053
C(4, NP)	0.004	O(2, NP)*	0.040
C(5, NP)	0.004	O(3, NP)*	0.133

II. α-Cyclodextrin–*p*-hydroxybenzoic acid complex,

(i) The plane through C(2), C(3), C(5), and O(5), The plane equation is of the $AX+BY+CZ=D$ form.

Residue	*A*	*B*	*C*	*D*
G1	0.8205	−0.1266	0.5574	10.6892
G2	0.0136	−0.2242	0.9744	11.0791
G3	0.8777	0.1223	−0.4633	2.7799
G4	0.8255	0.1224	0.5510	17.2970
G5	0.0327	0.1384	0.9898	19.2449
G6	0.8854	−0.0630	−0.4606	−4.8608

Deviations of atoms from the plane.

Residue	C(1)*	C(2)	C(3)	C(4)*	C(5)	O(5)
G1	−0.685	−0.013	0.012	0.693	−0.013	0.014
G2	−0.686	−0.009	0.008	0.644	−0.009	0.009
G3	−0.721	−0.011	0.010	0.571	−0.011	0.011
G4	−0.629	−0.033	0.032	0.720	−0.033	0.034
G5	−0.698	−0.020	0.019	0.610	−0.020	0.021
G6	−0.685	−0.017	0.016	0.587	−0.017	0.017

(ii) The plane through six O(4) atoms.

$0.0422X+0.9950Y+0.0908Z=1.0190$

O(4, G1)	0.145	O(4, G4)	0.145
O(4, G2)	0.011	O(4, G5)	0.004
O(4, G3)	−0.154	O(4, G6)	−0.152

(iii) The benzene plane.

$0.9892X+0.0585Y+0.1345Z=8.7861$

C(1, HB)	0.003	C(6, HB)	0.007
C(2, HB)	0.003	C(7, HB)*	0.151
C(3, HB)	−0.018	O(1, HB)*	0.067
C(4, HB)	0.027	O(2, HB)*	0.326
C(5, HB)	−0.021	O(3, HB)*	0.225

The intramolecular O(2)···O(3) hydrogen bonds are observed between the adjacent glucose residues (Table 9). Not all of these hydrogen bonds are oriented in the same direction, but both O(2)→O(3) and O(3)→O(2) hydrogen bonds are found. In the G4 and G6 residues, both of the secondary hydroxyl groups act as donors, but in the G1 residue, they are acceptors. The O(2) hydroxyl group in the G2 and G3 residues donates the hydrogen atom. O(2,G4)···O(3,G3) in the *p*-NP complex and O(2,G6)···O(3,G5) in the *p*-HB complex are rather doubtful hydrogen bonds since the O–H···O angles are too small.

Structures of p-*NP and* p-*HB.* The bond distances and angles in *p*-NP (Fig. 5) are in good agreement with those found in the crystal structure of *p*-NP.[24,25] The inequality in the C(2)–C(1)–O(1) and C(6)–C(1)–O(1) angles which is found in *p*-NP is not found in *p*-HB (Fig. 6). The bond distances of C(7)–O(2) and C(7)–O(3) in *p*-HB agree with those found in *p*-chlorobenzoic acid.[26] In both *p*-NP and *p*-HB, the benzene ring shows a good planarity (Table 8).

α-CDx-Guest Interaction. The nitrophenyl or carboxyphenyl group is located in the α-CDx cavity, while the phenolic hydroxyl group protrudes from the O(2),

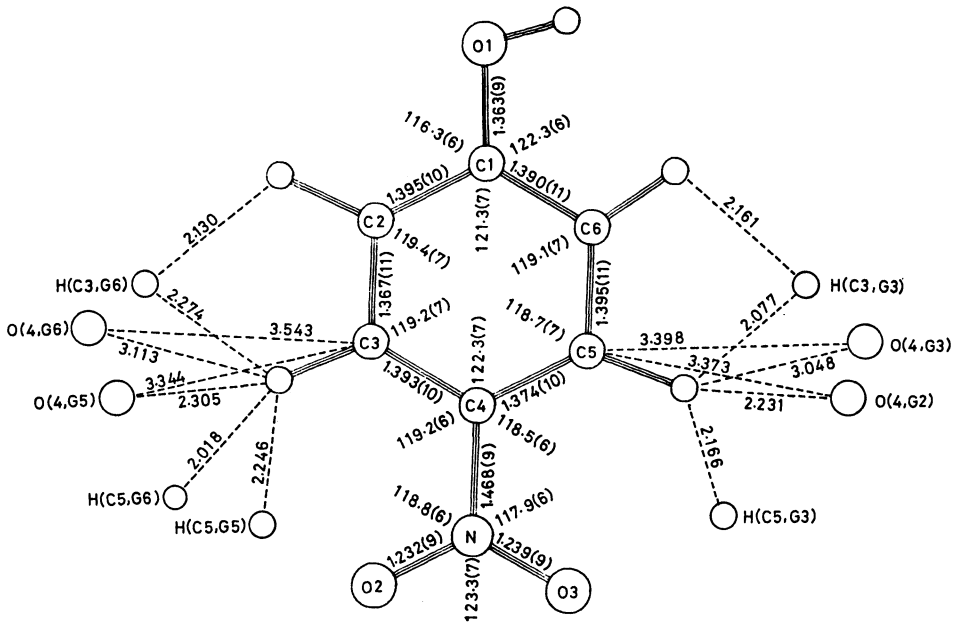

Fig. 5. Bond distances (l/Å) and angles (ϕ/°) in *p*-nitrophenol. Intermolecular distances between *p*-nitrophenol and α-cyclodextrin are shown by dashed lines.

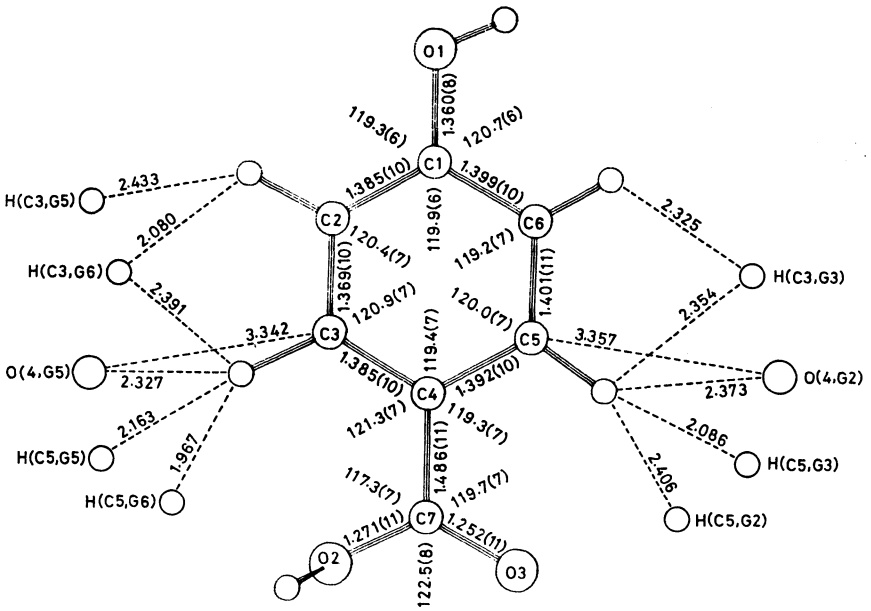

Fig. 6. Bond distances (l/Å) and angles (ϕ/°) in *p*-hydroxybenzoic acid. Intermolecular distances between *p*-hydroxybenzoic acid and α-cyclodextrin are shown by dashed lines.

Table 9. Hydrogen bond distances (l/Å) and angles (ϕ/°)

α-Cyclodextrin-*p*-Nitrophenol Complex

O	H	O		DISTANCE O-H	H···O	O···O	ANGLE O-H···O
O(3,G6)	H(O3,G6)	O(2,G1)		0.852	2.015	2.860	171.2
O(2,G2)	H(O2,G2)	O(3,G1)		1.054	1.693	2.650	148.6
O(2,G3)	H(O2,G3)	O(3,G2)		0.921	1.943	2.847	166.6
O(2,G4)	H(O2,G4)	O(3,G3)		1.104	2.189	2.736	107.8
O(3,G4)	H(O3,G4)	O(2,G5)		0.942	1.960	2.863	159.9
O(2,G6)	H(O2,G6)	O(3,G5)		1.052	2.116	3.068	149.3
O(W1)	H(OB,W1)	O(2,G3)		0.791	2.111	2.901	176.6
O(2,G5)	H(O2,G5)	O(W3B)		1.174	1.620	2.771	165.1
O(2,G6)		O(W2B)				2.453	
O(2,G5)	H(O2,G5)	O(W3A)	(a)	1.174	1.783	2.751	136.0
O(6,G1)		O(6A,G4)	(b)			2.950	
O(W2A)	H(OA,W2A)	O(6,G1)	(c)	0.628	2.326	2.938	165.4
O(6,G6)	H(O6,G6)	O(3,G2)	(c)	0.931	1.826	2.753	173.5
O(6A,G4)		O(W1)	(d)			2.774	
O(3,G5)	H(O3,G5)	O(6,G3)	(d)	0.787	2.201	2.871	143.3
O(W1)	H(OA,W1)	O(6,G6)	(e)	0.771	2.236	2.897	144.3
O(6,G2)		O(W3A)	(e)			2.800	
O(6,G2)		O(W3B)	(f)			2.798	
O(3,G3)	H(O3,G3)	O(6,G5)	(f)	0.972	1.889	2.697	138.7
O(6,G3)		O(W2A)	(f)			2.764	
O(1,NP)	H(O1,NP)	O(2,G2)	(g)	1.045	2.057	2.580	108.1
O(6,G2)		O(6A,G4)	(h)			2.861	
O(6,G2)		O(6B,G4)	(h)			2.773	
O(2,G1)	H(O2,G1)	O(2,G3)	(i)	1.004	2.036	2.814	132.6
O(3,G1)	H(O3,G1)	O(3,G3)	(i)	0.667	2.114	2.709	149.3
O(3,G2)		O(3,G4)	(i)			2.737	
O(W1)		O(W3B)	(i)			2.730	
O(6,G1)		O(W3B)	(j)			2.894	
O(6B,G4)		O(2,G6)	(j)			2.896	
O(6,G5)	H(O6,G5)	O(1,NP)	(j)	0.798	1.969	2.730	159.3
O(3,NP)		O(W2B)	(j)			2.914	

α-Cyclodextrin-*p*-Hydroxybenzoic Acid Complex

O	H	O		DISTANCE O-H	H···O	O···O	ANGLE O-H···O
O(3,G6)	H(O3,G6)	O(2,G1)		0.792	2.046	2.824	167.3
O(2,G2)	H(O2,G2)	O(3,G1)		0.986	1.715	2.674	163.2
O(2,G3)	H(O2,G3)	O(3,G2)		0.936	1.991	2.897	162.4
O(2,G4)	H(O2,G4)	O(3,G3)		0.716	2.491	3.114	146.6
O(3,G4)	H(O3,G4)	O(2,G5)		0.944	1.908	2.845	171.5
O(2,G6)	H(O2,G6)	O(3,G5)		1.018	2.474	2.878	102.9
O(W1)	H(OB,W1)	O(2,G3)		0.740	2.279	2.926	146.7
O(2,G5)	H(O2,G5)	O(W3B)		1.126	1.643	2.709	155.7
O(2,G6)		O(W2B)				2.795	
O(2,G5)	H(O2,G5)	O(W3A)	(a)	1.126	1.746	2.757	146.7
O(6,G1)	H(O6,G1)	O(6A,G4)	(b)	1.218	1.778	2.824	140.3
O(W2A)	H(OA,W2A)	O(6,G1)	(c)	0.784	2.196	2.851	141.4
O(6,G6)	H(O6,G6)	O(3,G2)	(c)	0.839	1.879	2.718	180.0
O(3,G5)	H(O3,G5)	O(6,G3)	(d)	1.246	1.863	2.808	128.1
O(6A,G4)		O(W1)	(d)			2.756	
O(W1)	H(OA,W1)	O(6,G6)	(e)	0.686	2.338	2.886	138.2
O(6,G2)		O(W3A)	(e)			2.682	
O(6,G2)		O(W3B)	(f)			2.829	
O(3,G3)	H(O3,G3)	O(6,G5)	(f)	1.174	1.563	2.706	162.6
O(6,G3)	H(O6,G3)	O(W2A)	(f)	1.037	2.087	2.739	118.6
O(2,G1)	H(O2,G1)	O(2,G3)	(g)	0.928	1.916	2.809	160.8
O(3,G1)	H(O3,G1)	O(3,G3)	(g)	0.995	1.699	2.685	170.3
O(6,G2)		O(6A,G4)	(h)			2.891	
O(6,G2)		O(6B,G4)	(h)			2.730	
O(W1)		O(W3B)	(i)			2.629	
O(1,HB)	H(O1,HB)	O(2,G2)	(i)	0.978	1.634	2.588	163.9
O(3,G2)	H(O3,G2)	O(3,G4)	(i)	0.876	2.281	2.715	110.5
O(3,HB)		O(W2B)	(j)			2.667	
O(6,G1)	H(O6,G1)	O(W3B)	(j)	1.218	1.939	3.023	145.6
O(6,G5)	H(O6,G5)	O(1,HB)	(j)	0.816	1.941	2.736	164.5
O(2,G6)	H(O2,G6)	O(2,HB)	(k)	1.018	2.183	2.880	124.1

Code	Symmetry Operator	Code	Symmetry Operator
None	x, y, z	f	$3/2-x$, $-y$, $1/2+z$
a	$1+x$, y, z	g	$1/2+x$, $-1/2-y$, $1-z$
b	$-1+x$, y, z	h	$-1/2+x$, $1/2-y$, $1-z$
c	$1/2-x$, $-y$, $1/2+z$	i	$-1/2+x$, $-1/2-y$, $1-z$
d	$3/2-x$, $-y$, $1/2+z$	j	$1-x$, $1/2+y$, $3/2-z$
e	$1/2-x$, $-y$, $-1/2+z$	k	$1-x$, $-1/2+y$, $3/2-z$

O(3) side. The relative orientation of the guest molecule in the cavity is similar to that found in the *p*-IA complex and the *p*-IP complex. In the channel-type structure and the cage-type structure, the hydroxyl group or sulfonato group of the guest molecule is hydrogen-bonded to the primary hydroxyl group with the *gauche-trans* conformation. However, in the complexes with *p*-NP and *p*-HB, the nitro or carboxyl group does not form the hydrogen bond with O(6B,G4), although the C(6,G4)–O(6B,G4) bond shows the *gauche-trans* conformation. It is noteworthy that the location of the benzene ring is the same as in the other α-CDx complexes with the aromatic guest molecule, such as *p*-IA,[14,15] *p*-IP,[16] Methyl Orange,[10] and BSNa.[11] This may be due to the fact that this position is sterically most favorable for the benzene ring. The plane of the guest molecule is nearly parallel to the longest diagonal line which passes through O(4,G2) and O(4,G5). The benzene ring makes angles of 80.6 and 83.6° against the plane through the six O(4) atoms in the *p*-NP complex and the *p*-HB complex respectively, while in the BSNa complex the benzene plane is perpendicular to the O(4) plane. The distances of O(4,G2)···C(5,NP), O(4,G5)···C(3,NP), O(4,G2)···C(5,HB), and O(4,G5)···C(3,HB) are in good agreement with the corresponding distances found in the *p*-IA complex, the *p*-IP complex, and the BSNa complex. Several hydrogen-hydrogen contacts shorter than the ideal van der Waals contact[27] are found between α-CDx and the benzene ring, as is shown in Figs. 5 and 6. This indicates that the guest molecule is tightly packed in the α-CDx ring. The hydrogen atoms attached to C(3) and C(5) of α-CDx are located inside the cavity, and are in contact with the guest molecule. The six hydrogen atoms bonded to C(5) form a neck of the cavity. The C(4)–C(7) bond of *p*-HB and C(4)–N bond of *p*-NP are located at the neck, showing a good fit of the guest molecule to the cavity. A similar geometrical fitness is observed in the complexes with *p*-IA, *p*-IP, Methyl Orange, and iodine.[4]

In the *p*-IA complex and the *p*-IP complex, the iodine atom is found at the position where the nitro or carboxyl group is located. In this case, the inclusion of the iodophenyl group has been interpreted as being mainly due to the hydrophobic interaction, since the interior of the cavity is relatively hydrophobic. It has also been shown by the theoretical calculation of the complex formation energy[11] that the inclusion of the hydrophobic group gives a more stable complex than the inclusion of the hydrophilic group when the guest molecule consists of hydrophobic and hydrophilic groups. In the complexes with *p*-NP and *p*-HB, the nitro or carboxyl groups are hydrophilic, and they form hydrogen bonds with water and the hydroxyl group of the adjacent α-CDx molecule (Table 9). It is geometrically possible that the *p*-NP and *p*-HB molecules are situated upside down in the cavity, that is, the nitro or carboxyl group protrudes from the secondary hydroxyl side of the cavity, and the phenolic hydroxyl group is situated at the primary hydroxyl side in the cavity. However, this structure may be unfavorable in view of the fit of the guest molecule to the α-CDx cavity. The guest molecule seems to be more loosely packed in the cavity. Moreover, the phenolic hydroxyl group can not be in contact with water or hydroxyl groups outside the cavity, since it is buried in the cavity. Thus, the geometry of inclusion may be determined by the fit of the guest molecule and the hydrogen bonds.

Crystal Structure and Hydrogen Bonds. The α-CDx molecules are arranged nearly parallel to the ac plane, forming a molecular layer (Fig. 7). The least-squares plane through the six O(4) atoms makes an angle of 6.2° in the *p*-NP complex and one of 5.7° in the *p*-HB complex against the ac plane. This type of the crystal structure is different from the cage-type structure,[4–8] since both ends of the cavity are open to the space between the layers. The α-CDx molecule, which lies in the next layer, is slipped so that the overlap of the annular aperture is quite small. Therefore, this arrange-

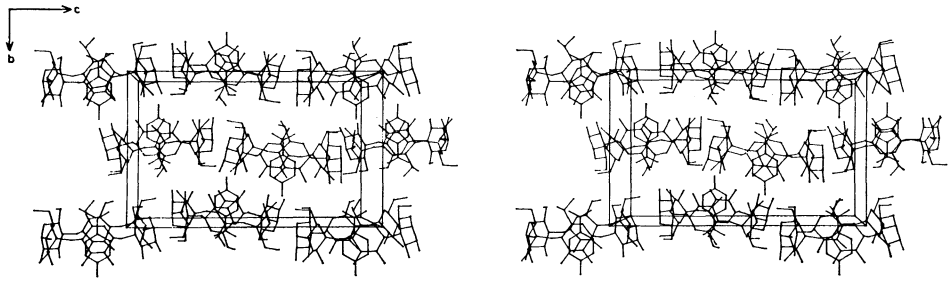

Fig. 7. A stereo drawing of the packing of the complex, viewed down along the a axis.

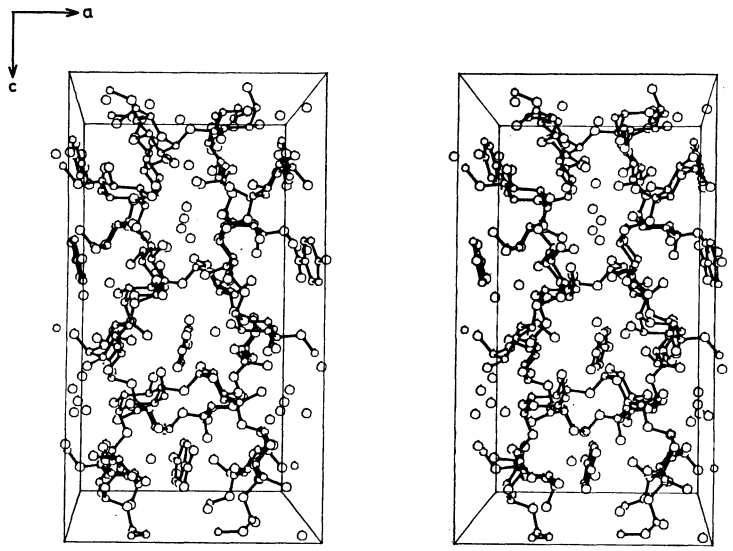

Fig. 8. A stereo drawing of the crystal structure of the α-cyclodextrin–*p*-nitrophenol complex, viewed down along the b axis.

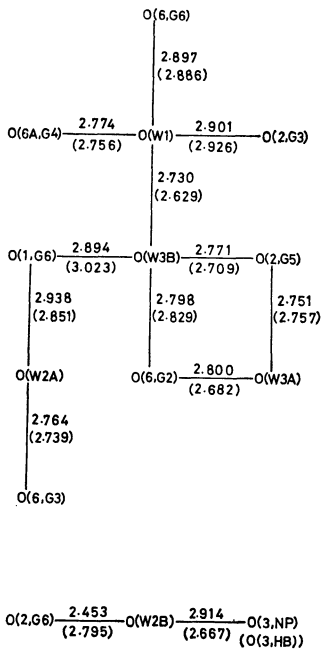

Fig. 9. A hydrogen-bonding scheme involving water molecules in the α-cyclodextrin complexes with *p*-nitrophenol and *p*-hydroxybenzoic acid. Hydrogen bond distances (*l*/Å) in the *p*-hydroxybenzoic acid complex are shown in parentheses.

ment of α-CDx molecules does not form a continuous channel such as is found in the channel-type structure.[9–12] The guest molecules are situated nearly parallel to the bc plane. The empty space between the α-CDx molecules is filled with three water molecules, two of which are statistically disordered.

A complete explanation of the hydrogen-bonding scheme is impossible since not all of the hydrogen atoms have been determined, but intermolecular oxygen-oxygen contacts less than 3.0 Å were considered as hydrogen bonds. All of the primary or secondary hydroxyl groups except for O(2,G4) and O(3,G6) are involved in the intermolecular hydrogen bonds in both the *p*-NP complex and the *p*-HB complex (Table 9). The phenolic hydroxyl groups of *p*-NP and *p*-HB donate the hydrogen atom to the O(2,G2) of α-CDx in the next layer, and accept it from O(6,G5) of the symmetry-related α-CDx by the two-fold screw axis parallel to the b axis. The hydrogen bonds of the same type are also found in the *p*-IA complex,[14,15] and the *p*-IP complex.[16] However, different hydrogen bonds are observed between the α-CDx and guest molecules. The carboxyl group of *p*-HB forms the two hydrogen bonds with O(W2B) and O(2,G6) in the next layer, while the nitro group is hydrogen-bonded to only O(W2B). In the *p*-IA complex and the *p*-IP complex, O(W2) is not disordered, but occupies the same position as O(W2A). Therefore, the hydrogen bonds involving

O(W2B) are not found in these complexes. O(W1) forms the four hydrogen bonds with O(2,G3), O(6A,G4), O(6,G6), and O(W3A), as is shown in Fig. 9. Both O(W3A) and O(W3B) are hydrogen-bonded to O(2,G5) and O(6,G2).

Structure and Catalytic Ability of α-CDx. α-CDx catalyzes the hydrolysis of *p*-nitrophenyl acetate and *p*-carboxyphenyl acetate.[3] The reaction mechanism has been interpreted on the basis of the α-CDx-substrate inclusion complex and the nucleophilic attack of the secondary hydroxyl group on the carbonyl carbon atom of the substrate. The structures of the *p*-NP complex and the *p*-HB complex support this reaction mechanism. If the *p*-nitrophenyl group or *p*-carboxyphenyl group is included in the same manner as in the crystal, the carbonyl group of the ester will be situated near the secondary hydroxyl side of α-CDx. However, the carbonyl carbon atom is expected for geometrical considerations to be more than 5 Å apart from the secondary hydroxyl groups. The phenyl group is rigidly fixed in the cavity so that the severe restriction is imposed on the translational and rotational freedom of the included substrate. Therefore, a considerable strain energy may be required to the α-CDx molecule to bring the carbonyl group in close contact with the secondary hydroxyl groups. As has been suggested by VanEtten *et al.*,[3] this seems to be the reason why the catalytic ability of α-CDx is low in the hydrolysis of *para*-substituted phenyl acetates.

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