The Structure of the Cyclodextrin Complex. I. The Crystal and Molecular Structure of the α-Cyclodextrin-*p*-Iodoaniline Complex

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The crystal structure of the α-cyclodextrin–*p*-iodoaniline complex [$(C_6H_{10}O_5)_6 \cdot C_6H_6NI \cdot 3H_2O$] has been determined by the X-ray method. The space group is $P2_12_12_1$ with unit cell dimensions of $a=13.659(2)$, $b=15.413(3)$, and $c=24.486(5)$ Å. The structure was solved by the heavy-atom method and refined by least-squares techniques. The final R-value was 0.072. The *p*-iodoaniline molecule is included in the cavity with its axis coincident with the axis of α-cyclodextrin; the iodobenzene group is situated in the cavity, while the amino group sticks out from the cavity. The shortest contact between the α-cyclodextrin molecule and the "guest" *p*-iodoaniline molecule is 3.25 Å, indicating that the latter is rigidly fixed in the cavity of the former. The distances between the amino group and the hydroxyl group are greater than 4.0 Å; this fact well explains why the catalytic ability of α-cyclodextrin is low in the hydrolysis of *para*-substituted phenyl esters.

Cyclodextrins, which are cyclic α-1,4-linked D-glucose oligomers, form a number of inclusion compounds both in crystalline states and in an aqueous solution with a variety of "guest" molecules,[1-3] such as paraffins, alkyl halides, halogens, and aromatic compounds. X-Ray analyses of the α-cyclodextrin complex with potassium acetate,[4] iodine,[5] and water[6] have proved that the "guest" molecule is included in the cavity of α-cyclodextrin.

Cyclodextrins catalyze the hydrolysis of phenyl esters.[7] Bender and his co-workers suggested[8] that the hydrolysis occurs when the phenyl group is bound in the cavity of cyclodextrins and that the relative rates of reactions are controled by the stereo-specific complexing ability. The evidence for the formation of the inclusion compounds with aromatic molecules has been obtained from NMR,[9] kinetic,[10] and X-ray[2] studies, but the geometry of inclusion is yet unknown. The present paper will deal with the detailed crystal and molecular structure of the α-cyclodextrin–*p*-iodoaniline-(α-CDx–*p*-IAN) complex. A short communication has already been published.[11]

Experimental

Crystals of the α-CDx–*p*-IAN complex were prepared by mixing of a hot aqueous solution containing 10% α-CDx with *p*-IAN. They are colorless prisms elongated along the a-axis. The space group was determined by an inspection of the Weissenberg and oscillation photographs. The density was measured by the flotation method in a mixture of carbon tetrachloride and tetrabromoethane. The unit cell parameters and intensities were measured on a Rigaku AFC four-circle diffractometer with a specimen with dimensions of $0.2\times0.4\times0.7$ mm, using a graphite monochromatized Mo$K\alpha$ radiation ($\lambda=0.70926$ Å) and the ω-scanning mode. During the data collection the crystal turned blue, but no significant intensity change in the standard reflections was observed. 5007 independent reflections were obtained up to 50° in 2θ. No correction was made for absorption and extinction. The crystal data are shown in Table 1.

TABLE 1. CRYSTAL DATA

$(C_6H_{10}O_5)_6 \cdot C_6H_6NI \cdot 3H_2O$	
Molecular weight	1245.9
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Z	4
Cell dimensions	$a=13.659(2)$Å
	$b=15.413(3)$
	$c=24.436(5)$
Cell volume	5144.4 Å^3
Density	$D_o=1.602$ g·cm^{-3}
	$D_x=1.610$

Determination and Refinement of the Structure

The crystal structure of the α-CDx–*p*-IAN complex was solved by the heavy-atom method using 1171 reflections with $2\theta\leqq30°$. The position of the iodine atom was deduced from a Patterson synthesis. An outline of the structure of the complex was obtained

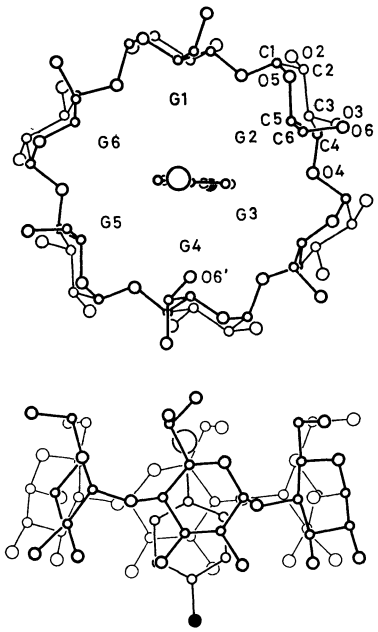

Fig. 1. Structure of the α-cyclodextrin–*p*-iodoaniline complex. The circles, in order of decreasing size, represent iodine, oxygen, and carbon atoms, and the black dots indicate nitrogen atoms.

TABLE 2. ATOMIC COORDINATES AND ANISOTROPIC TEMPERATURE FACTORS ($\times 10^4$) WITH STANDARD DEVIATIONS

The temperature factor expression used was $\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+hkB_{12}+klB_{23}+lhb_{31})]$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{31}
G1C(1)	1536(10)	-600(9)	6875(6)	34(8)	38(7)	15(3)	2(13)	7(7)	1(8)
G1C(2)	1319(11)	-1335(10)	6500(5)	51(10)	47(8)	7(2)	-28(15)	3(7)	0(8)
G1C(3)	1946(12)	-1252(8)	5978(6)	66(11)	18(5)	13(3)	9(13)	17(6)	2(9)
G1C(4)	1774(10)	-363(9)	5711(5)	31(8)	37(7)	10(2)	1(12)	9(7)	-1(7)
G1C(5)	1980(11)	374(8)	6156(6)	56(10)	26(6)	11(2)	7(12)	5(7)	-5(9)
G1C(6)	1743(15)	1281(10)	5938(6)	121(17)	36(7)	12(3)	14(19)	19(8)	3(12)
G1O(2)	1578(9)	-2123(6)	6782(4)	91(9)	30(5)	12(2)	-45(11)	9(5)	-14(7)
G1O(3)	1621(8)	-1913(6)	5603(4)	67(7)	25(4)	12(2)	-34(10)	1(5)	-3(6)
G1O(4)	2440(6)	-274(6)	5288(3)	26(5)	36(4)	9(2)	-1(8)	11(5)	-6(5)
G1O(5)	1366(8)	213(7)	6620(4)	60(7)	49(5)	10(2)	50(11)	9(5)	4(6)
G1O(6)	773(11)	1325(8)	5712(5)	128(12)	63(7)	18(2)	103(16)	24(7)	11(9)
G2C(1)	2083(11)	-33(10)	4765(6)	44(9)	42(7)	11(3)	-1(14)	9(7)	1(8)
G2C(2)	2367(10)	-753(10)	4368(5)	32(8)	45(8)	11(2)	-16(14)	8(7)	-4(8)
G2C(3)	3483(10)	-869(9)	4346(5)	41(8)	23(5)	12(2)	-5(13)	-9(7)	3(7)
G2C(4)	3917(9)	40(8)	4212(5)	29(7)	23(6)	12(2)	1(10)	8(6)	3(7)
G2C(5)	3578(9)	737(8)	4604(6)	25(6)	28(3)	3(11)	-5(7)	11(8)	
G2C(6)	3909(14)	1643(9)	4434(7)	76(13)	19(6)	28(4)	-15(15)	11(8)	-2(12)
G2O(2)	1960(7)	-1565(6)	4548(4)	44(6)	36(5)	10(2)	-16(9)	4(5)	1(5)
G2O(3)	3754(7)	-1435(6)	3919(4)	53(7)	24(4)	17(2)	4(9)	-4(5)	1(6)
G2O(4)	4952(8)	-78(5)	4291(3)	29(5)	34(4)	7(1)	10(11)	5(4)	1(6)
G2O(5)	2519(7)	760(5)	4595(4)	48(6)	21(4)	14(2)	24(8)	15(4)	7(6)
G2O(6)	3797(9)	1776(7)	3854(6)	82(9)	47(6)	32(3)	17(13)	41(8)	30(10)
G3C(1)	5647(9)	137(9)	3862(6)	32(8)	37(6)	11(2)	8(12)	4(7)	11(8)
G3C(2)	6276(9)	-672(8)	3776(5)	40(8)	40(7)	6(2)	-9(12)	5(7)	8(8)
G3C(3)	6791(8)	-879(9)	4279(5)	22(7)	35(6)	8(2)	-13(12)	13(7)	2(6)
G3C(4)	7338(9)	-118(9)	4531(5)	19(7)	43(7)	10(2)	2(12)	-1(7)	8(7)
G3C(5)	6727(11)	719(9)	4545(5)	59(10)	33(7)	8(2)	-10(14)	-1(6)	-2(8)
G3C(6)	7284(13)	1526(10)	4621(6)	67(11)	37(7)	13(3)	-22(16)	0(8)	-5(10)
G3O(2)	5678(7)	-1370(6)	3580(4)	46(6)	36(5)	11(2)	4(9)	-16(5)	-4(5)
G3O(3)	7495(7)	-1583(6)	4224(4)	43(6)	32(4)	13(2)	16(9)	-11(5)	8(6)
G3O(4)	7590(6)	-360(6)	5081(3)	28(6)	37(5)	5(1)	-1(8)	7(4)	-3(4)
G3O(5)	6219(7)	836(6)	4037(3)	40(6)	25(4)	11(2)	1(9)	10(4)	5(5)
G3O(6)	8113(8)	1601(8)	4272(5)	54(7)	54(6)	21(2)	-32(12)	15(7)	5(7)
G4C(1)	8546(10)	-207(9)	5270(5)	29(8)	36(7)	12(3)	5(12)	-1(7)	2(8)
G4C(2)	8901(10)	-1014(10)	5566(5)	39(8)	48(8)	9(2)	19(14)	-5(8)	11(7)
G4C(3)	8273(10)	-1180(8)	6079(5)	34(8)	25(6)	14(3)	8(11)	-15(6)	1(7)
G4C(4)	8330(10)	-388(9)	6433(5)	41(9)	31(6)	10(2)	-2(12)	7(7)	-3(8)
G4C(5)	7946(11)	389(9)	6111(5)	55(10)	35(7)	11(3)	-3(13)	-24(7)	8(8)
G4C(6)	8055(15)	1266(9)	6436(9)	117(16)	23(6)	14(3)	-27(17)	2(7)	-20(12)
G4O(2)	8834(7)	-1741(7)	5190(4)	49(7)	48(5)	9(2)	34(10)	-12(5)	0(6)
G4O(3)	8700(8)	-1892(6)	6368(4)	60(7)	38(5)	13(2)	29(10)	-8(5)	-1(6)
G4O(4)	7672(6)	-564(5)	6879(3)	31(5)	22(4)	7(1)	-8(7)	-1(4)	10(5)
G4O(5)	8569(7)	512(6)	5631(4)	45(6)	36(5)	13(2)	-37(9)	3(5)	2(6)
G4O(6)	9154(21)	1421(16)	6488(10)	66(20)	26(12)	10(5)	-56(27)	0(13)	-11(16)
G4O(6')	7438(13)	1914(11)	6121(6)	69(12)	52(9)	13(3)	-10(18)	0(9)	12(11)
G5C(1)	7994(10)	-412(8)	7419(5)	38(8)	19(6)	14(3)	-9(11)	-12(6)	-13(8)
G5C(2)	7739(10)	-1213(8)	7761(5)	35(8)	31(6)	8(2)	13(12)	1(6)	-8(7)
G5C(3)	6646(10)	-1327(7)	7791(5)	48(9)	30(6)	7(2)	17(13)	6(6)	1(8)
G5C(4)	6136(10)	-516(8)	7964(5)	36(8)	25(6)	10(2)	-7(11)	1(6)	-3(7)
G5C(5)	6433(10)	250(10)	7607(6)	33(8)	45(8)	14(3)	12(14)	-7(8)	16(8)
G5C(6)	6064(12)	1138(9)	7810(6)	57(10)	26(6)	15(3)	14(13)	-9(7)	-7(9)
G5O(2)	8231(8)	-1943(6)	7534(4)	53(7)	30(5)	14(2)	30(9)	-2(5)	13(6)
G5O(3)	6413(8)	-2034(6)	8170(4)	62(7)	33(5)	15(2)	3(10)	11(5)	14(7)
G5O(4)	5118(7)	-656(5)	7881(3)	34(6)	36(4)	10(1)	9(10)	-9(4)	10(6)
G5O(5)	7520(7)	330(6)	7643(3)	50(6)	25(4)	7(1)	-17(9)	-6(4)	0(5)
G5O(6)	6146(8)	1196(7)	8399(4)	61(8)	47(6)	20(2)	15(11)	-31(6)	-11(7)
G6C(1)	4431(10)	-490(9)	8310(5)	41(9)	37(7)	7(2)	1(13)	-4(7)	-6(7)
G6C(2)	3778(11)	-1272(8)	8336(5)	50(9)	22(5)	8(2)	12(12)	10(6)	-3(8)
G6C(3)	3302(10)	-1415(9)	7779(6)	41(9)	28(6)	14(3)	-11(13)	1(7)	13(8)
G6C(4)	2774(10)	-566(8)	7613(5)	42(9)	29(6)	7(2)	10(12)	6(6)	16(7)
G6C(5)	3409(10)	259(8)	7647(5)	37(8)	15(5)	10(2)	7(11)	2(6)	10(7)
G6C(6)	2836(12)	1085(9)	7605(6)	60(11)	29(7)	17(3)	20(14)	-3(7)	12(9)
G6O(2)	4312(8)	-2014(6)	8490(4)	64(8)	25(4)	19(2)	0(10)	17(5)	-1(7)
G6O(3)	2587(8)	-2080(6)	7808(4)	53(7)	26(4)	20(2)	-25(10)	4(5)	1(7)
G6O(4)	2537(6)	-666(6)	7052(3)	35(5)	32(4)	8(1)	-1(8)	4(4)	11(5)
G6O(5)	3889(7)	272(6)	8190(3)	47(6)	29(4)	11(2)	21(9)	-6(5)	6(5)
G6O(6)	1932(9)	1042(7)	7890(5)	79(8)	34(5)	22(2)	42(12)	-5(6)	1(8)
BC(1)	5045(13)	-438(7)	6080(5)	48(8)	27(5)	15(3)	-13(16)	-4(6)	-6(10)
BC(2)	5013(14)	-977(8)	6527(5)	64(9)	32(6)	12(2)	-24(20)	-1(7)	-18(11)
BC(3)	5007(14)	-1876(8)	6436(5)	65(10)	41(6)	8(2)	27(20)	-2(6)	-5(11)
BC(4)	5089(11)	-2198(7)	5896(5)	34(8)	28(5)	10(2)	-29(14)	1(5)	-10(9)
BC(5)	5121(12)	-1622(9)	5494(6)	50(10)	45(7)	11(2)	8(17)	-4(7)	9(10)
BC(6)	5111(11)	-736(8)	5552(5)	46(9)	33(6)	10(2)	1(15)	-3(6)	9(9)
I	4987(1)	924(1)	6209(0)	86(1)	35(0)	20(0)	-6(1)	-1(1)	-2(1)
N	5155(9)	-3103(6)	5794(4)	41(8)	27(4)	10(2)	-16(11)	-4(5)	-2(7)
WO(1)	5009(12)	-999(8)	2501(5)	79(8)	84(7)	21(2)	-29(21)	17(7)	-24(9)
WO(2)	4949(11)	-1499(9)	9632(5)	72(9)	99(9)	23(3)	-3(20)	0(8)	-14(11)
WO(3)	95(29)	-1900(24)	7870(13)	74(24)	105(23)	28(7)	-50(52)	-33(22)	4(28)
WO(3')	9701(18)	-2620(14)	8260(9)	101(21)	62(12)	32(6)	-17(26)	-19(14)	-29(17)

from an electron density map calculated with the phases based on the iodine atom; the positions of the *p*-IAN molecule and six glucose residues were located, but the least-squares refinement of the atomic parameters was unsuccessful. The positions and orientations of the *p*-IAN molecule and six glucose residues except O(6) atoms were refined by the block-diagonal rigid-body least-squares technique.[4] The O(6) atoms and water molecules were found on a difference-Fourier map. The refinement was continued by the block-diagonal least-squares method. In these refinements, two of the oxygen atoms, G4O(6) and WO(3), were found to be disordered. The occupancies were estimated by assuming that the magnitude of the isotropic thermal factor of an occupant is the same as that of the other. They are 0.35, 0.65, 0.60, and 0.40 for G4O(6), G4O(6'), WO(3), and WO(3') respectively. The final *R*-value was 0.072. The weighting schemes are as follows: $w=0.0$ for $F_o<3\sigma(F)$, and $w=1.0$ for $F_o\geqq 3\sigma(F)$. The anomalous dispersion terms were ignored. The atomic scattering factors were taken from the "International Tables for X-ray Crystallography."[12] The atomic coordinates and the anisotropic temperature factors are listed in Table 2. The observed and calculated structure factors are listed in Table 4.[13] The computation was done on a HITAC 8450 computer in this Institute.[14]

Results and Discussion

Conformation of Glucose Residues. The structure of the α-CDx–*p*-IAN complex is illustrated in Fig. 1 with the absolute configuration corresponding to D-glucose. The average bond distances and angles in the glucose residues are normal (Fig. 2), varying in the ranges of ±0.05 Å and ±3° respectively (Table 3[13]). The valence angles of the α-1,4-linking oxygen atoms are 119—121°. These rather large angles are commonly observed in the α-CDx complexes: 118.8—119.4° in the potassium acetate complex, 116—122° in the iodine complex, and 116.2—119.4° in the water complex. In di-saccharides, α,α-trehalose[15] and β-maltose[16] give 115.8° and 117.2° respectively.

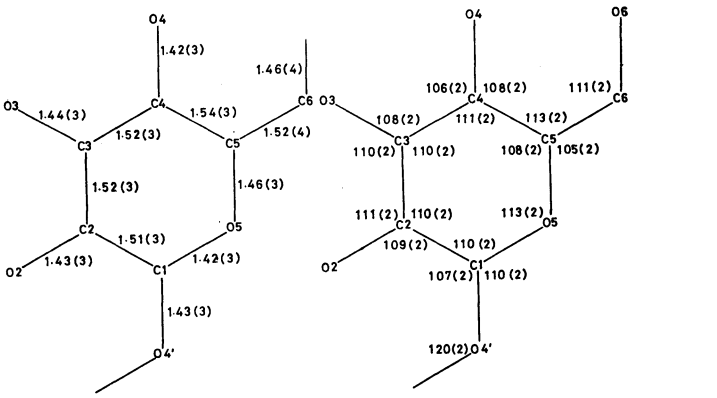

Fig. 2. Average bond distances and angles for the D-glucose residues with standard deviations.

Each glucose residue has the C1-chair conformation. The conformation angles around the pyranose ring vary from 45° to 66°. This range is similar to that found in the α-CDx–iodine complex (45—66°),[5] although it is rather wider than that of 52—66° in the α-CDx–potassium acetate complex,[4] that of 49—65° in the α-CDx–water complex,[6] and those found in di- and tri-saccharides.[15,17,18] In the G4 residue, the primary hydroxyl group takes two orientations: G4O(6) and G4O(6'). The former corresponds to a *gauche-gauche* conformation, and the latter to a *gauche-trans* conformation (Table 5). A similar disorder of the O(6) atom has been found in 1-kestose.[18] Both of those conformations have been found in the α-CDx–water complex, but in the α-CDx–potassium acetate complex the *gauche-gauche* conformation is not found because of the molecular packing and hydrogen bonds.

The macro-cyclic conformation of the α-CDx ring is described by the conformation angles including C(1)–O(4*)–C(4*) linkages. The C(1)–O(4*)–C(4*)–C(3*) and C(1)–O(4*)–C(4*)–C(5*) conformation angles are 123—132° and 104—115° respectively, while in the α-CDx–water complex they are 116.6—170.4° and

Table 5. Selected conformation angles (ϕ/°)

The angle was measured between projections of bonds *h–i* and *j–k* along the bond *i–j*. An asterisk (*) denotes the atom in the adjacent glucose residue.

h *i* *j* *k*	G1	G2	G3	G4	G5	G6
C(1)-C(2)-C(3)-C(4)	−56	−54	−52	−57	−51	−55
C(2)-C(3)-C(4)-C(5)	55	54	47	60	53	51
C(3)-C(4)-C(5)-O(5)	−56	−57	−45	−62	−57	−50
C(4)-C(5)-O(5)-C(1)	61	61	53	63	64	55
C(5)-O(5)-C(1)-C(2)	−63	−63	−61	−60	−64	−63
O(5)-C(1)-C(2)-C(3)	58	60	58	57	56	62
O(4*)-C(1)-C(2)-O(2)	54	59	64	57	61	64
O(2)-C(2)-C(3)-O(3)	70	69	65	66	65	66
O(3)-C(3)-C(4)-O(4)	−71	−71	−70	−68	−68	−73
O(4)-C(4)-C(5)-C(6)	68	73	79	71	72	77
O(5)-C(5)-C(6)-O(6)	−67	−76	−74	−76	−76	−80
O(5)-C(5)-C(6)-O(6′)	—	—	—	51	—	—
C(4)-C(5)-C(6)-O(6)	52	43	48	66	40	39
C(4)-C(5)-C(6)-O(6′)	—	—	—	−167	—	—
O(5)-C(1)-O(4*)-C(4*)	104	120	114	105	108	107
C(2)-C(1)-O(4*)-C(4*)	−134	−121	−127	−135	−132	−132
C(1)-O(4*)-C(4*)-C(3*)	123	129	126	134	132	129
C(1)-O(4*)-C(4*)-C(5*)	−115	−114	−115	−104	−112	−112

Table 6. Least-squares planes and deviations of atoms from the plane (*d*/Å)

(1) *p*-Iodoaniline

$0.9977X+0.0209Y+0.0648Z+7.8202=0$

BC(1)	0.009	BC(5)	−0.017
BC(2)	0.023	BC(6)	0.009
BC(3)	−0.031	N	0.031
BC(4)	−0.021	I	−0.003

(2) Six O(4) atoms

$0.0052X+0.9984Y+0.1020Z+0.8866=0$

G1O(4)	0.028	G4O(4)	0.018
G2O(4)	0.097	G5O(4)	0.108
G3O(4)	−0.119	G6O(4)	−0.132

Table 7. Selected intramolecular distances (*d*/Å)

(1) Between glucose residues			
G1O(3)–G2O(2)	2.68	G4O(3)–G5O(2)	2.92
G2O(3)–G3O(2)	2.76	G5O(3)–G6O(2)	2.98
G3O(3)–G4O(2)	3.00	G6O(3)–G1O(2)	2.87
(2) Between *p*-iodoaniline and glucose residues			
G1O(4)–BC(6)	3.78	G4O(4)–BC(2)	3.78
G2C(3)–BC(5)	3.72	G4O(6′)–I	3.70
G2O(4)–BC(6)	3.25	G5C(3)–BC(2)	3.85
G2O(4)–BC(5)	3.73	G5C(5)–BC(2)	3.78
G2C(3)–BC(6)	3.70	G5O(4)–BC(3)	4.00
G3C(3)–BC(5)	3.83	G5C(5)–BC(2)	3.99
G3C(3)–BC(6)	3.84	G5O(4)–BC(2)	3.35
G5C(5)–BC(6)	4.00	G5C(4)–BC(2)	3.90
G3O(4)–BC(6)	3.63	G6C(3)–BC(2)	3.91

69.3—129.7° respectively. This suggests that the α-CDx ring becomes more symmetrical when a bulky group is included. The six O(4) atoms are near the least-squares plane as is shown in Table 6. The r.m.s. displacement of the atoms from the plane is 0.10 Å, compared to that of 0.13 Å in the α-CDx–iodine complex. The distance between the O(2) and O(3) atoms of adjacent glucose residues corresponds to the acceptable one for the hydrogen bond (Table 7).

Structure of p-*Iodoaniline.* The bond distances and angles of *p*-IAN are shown in Fig. 3. The I–C(1) distrance is in agreement with that of 2.09 Å found in *o*-iodobenzonitrile.[19] The N–C(4) distance is longer than that of 1.371 Å in *N,N*-dimethyl-*p*-nitroaniline[20] and that of 1.358 Å in *p*-nitroaniline.[21] The planarity of *p*-IAN is good, as is shown in Table 6.

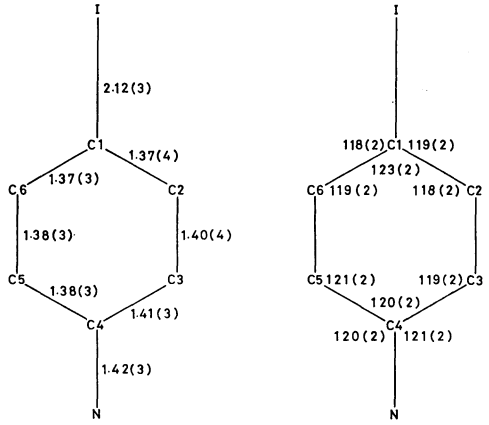

Fig. 3. Bond distances and angles with standard deviations in *p*-iodoaniline.

Geometry of Inclusion. As is shown in Fig. 1, the *p*-IAN molecule is included in the cavity of α-CDx, although the amino group sticks out. This suggests that the cavity is hydrophobic in nature and that α-CDx binds the hydrophobic portion of *p*-IAN. Selected intramolecular distances in the complex are shown in Table 7. The shortest interatomic distance of 3.25 Å, which is the distance between G2O(4) and BC(6), suggests that the "guest" molecule is rigidly fixed in the cavity. The iodine atom and G4O(6′) are in van der Waals contact. The amino nitrogen atom

TABLE 8. INTERMOLECULAR DISTANCES LESS THAN 3.0 Å AND ANGLES

The letters in parentheses denote the symmetry operations.

Distances (d/Å)			Angles (φ/°)	
G1O(2)–G3O(2)	(g)	2.77	G1C(2)–G1O(2)–G3O(2)	116
G1O(3)–G3O(3)	(g)	2.64	G1O(3)–G3O(3)–G3C(3)	109
G1O(6)–G4O(6)	(b)	2.92	G1C(6)–G1O(6)–G4O(6)	117
G1O(6)–WO(2)	(c)	2.83	G1C(6)–G1O(6)–WO(2)	136
G2O(2)–N	(g)	2.66	G2C(2)–G2O(2)–N	115
G2O(3)–G4O(3)	(h)	2.67	G2O(3)–G4O(3)–G4C(3)	128
G2O(3)–G6O(6)	(c)	2.75	G2C(3)–G2O(3)–G6O(6)	117
G2O(6)–WO(3)	(c)	2.85	G2C(6)–G2O(6)–WO(3)	141
G2O(6)–WO(3′)	(d)	2.83	G2C(6)–G2O(6)–WO(3′)	119
G2O(6)–G4O(6)	(i)	2.94	G2C(6)–G2O(6)–G4O(6)	113
G2O(6)–G4O(6′)	(i)	2.74	G2C(6)–G2O(6)–G4O(6′)	98
G3O(2)–WO(1)		2.85	G3C(2)–G3O(2)–WO(1)	110
G3O(3)–G5O(6)	(d)	2.81	G3C(3)–G3O(3)–G5O(6)	111
G3O(6)–WO(2)	(d)	2.80	G3C(6)–G3O(6)–WO(2)	124
G3O(6)–G5O(3)	(d)	2.85	G3O(6)–G5O(3)–G5C(3)	111
G4O(6)–WO(1)	(f)	2.80	G4C(6)–G4O(6)–WO(1)	116
G5O(2)–WO(3)	(a)	2.68	G5C(2)–G5O(2)–WO(3)	107
G5O(2)–WO(3′)		2.88	G5C(2)–G5O(2)–WO(3′)	112
G5O(6)–N	(j)	2.67	G5C(6)–G5O(6)–N	119
WO(1)–WO(3′)	(g)	2.86		
G6O(6)–WO(1)	(e)	2.82	G6C(6)–G6O(6)–WO(1)	99

Symmetry code	Symmetry operator		
	x,	y,	z
a	$1+x$,	y,	z
b	$-1+x$,	y,	z
c	$1/2-x$,	$-y$,	$-1/2+z$
d	$3/2-x$,	$-y$,	$-1/2+z$
e	$1/2-x$,	$-y$,	$1/2+z$
f	$3/2-x$,	$-y$,	$1/2+z$
g	$-1/2+x$,	$-1/2-y$	$1-z$
h	$1/2+x$,	$-1/2-y$,	$1-z$
i	$-1/2+x$,	$1/2-y$,	$1-z$
j	$1-x$,	$1/2+y$,	$3/2-z$

is apart more than 4.0 Å from any atom in α-CDx.

Crystal Structure. The crystal structure is shown in Figs. 4 and 5. The packing scheme of α-CDx is depicted in Fig. 6. Molecular layers composed of α-CDx are stacked along the b-axis in the crystal. The cavities of α-CDx do not form continuous channels which are found in the α-CDx–potassium acetate complex, since adjacent layers are each slipped by about half a molecule along the c-axis. The *p*-IAN molecule is so bulky that the amino group sticks out from the open end of the cavity. In the iodine and water complexes, the "guest" molecule is enclosed in the cavity, both ends of which are closed by the adjacent α-CDx molecules.

Intermolecular distances of less than 3.0 Å are shown in Table 8. Although the hydrogen atoms are not located, O···O and O···N distances less than 3.0 Å are taken as hydrogen bonds since the C–O···O and C–O···N angles are in the usual range for hydrogen bonds. The hydrogen-bonding network is formed in the crystal. The nitrogen atom forms hydrogen bonds with G2O(2) and G5O(6) in the adjacent layer. WO(1) forms hydrogen bonds with G4O(6), G3O(2), G6O(6), and WO(3), while both WO(3) and WO(3′) are hydrogen-bonded to G2O(6) and G5O(2). WO(2), which is separated from the other water molecules, is hydrogen-bonded to G3O(6) and G1O(6).

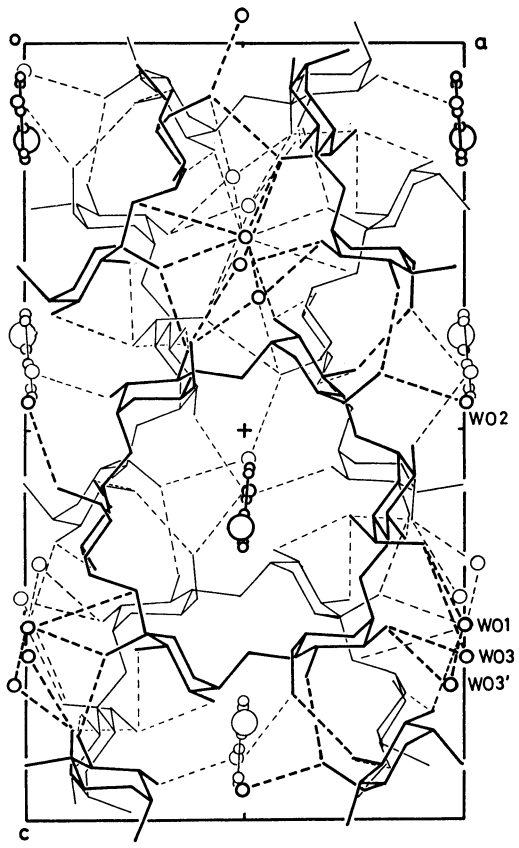

Fig. 4. Crystal structure viewed along the b-axis. Atoms represented by circles are those in *p*-iodoaniline and water molecules, and dashed lines indicate intermolecular distances less than 3.1 Å.

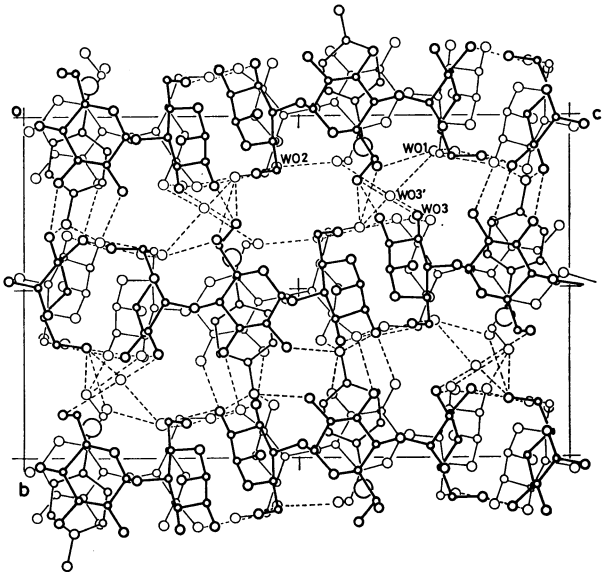

Fig. 5. Crystal structure viewed along the a-axis. Dashed lines indicate intermolecular distances less than 3.1 Å.

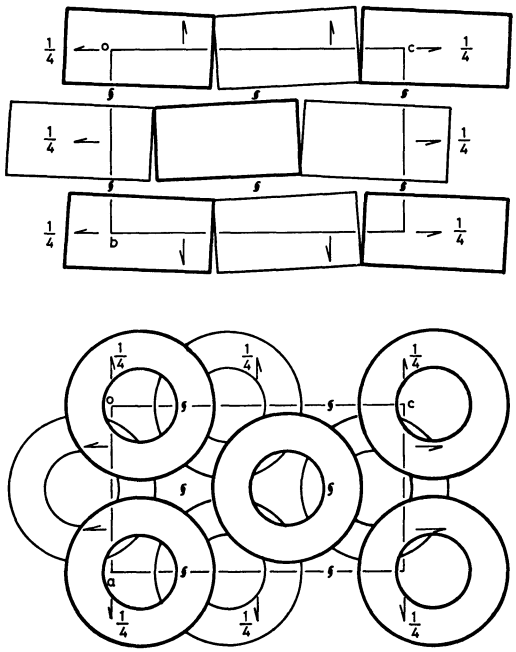

Fig. 6. The packing shemes of α-CDx in the crystal.

Between the layers, G1O(2), G1O(3), and G2O(3) form hydrogen bonds with G3O(2), G3O(3), and G4O(3) respectively.

Catalytic Property of α-Cyclodextrin. The cyclodextrin-catalyzed reactions have been interpreted in terms of the formation of inclusion compounds as intermediates. In the α-CDx–water complex, two of the primary hydroxyl groups of α-CDx have the *gauche-trans* conformation and form hydrogen bonds with water molecules in the cavity. In an aqueous solution, α-CDx seems to have a similar structure.[6] The cavity of α-CDx will release the water molecules when a "guest" molecule is included. Furthermore, the α-CDx ring will become more symmetrical and the *gauche-trans* conformation may turn to the *gauche-gauche* conformation, as in the iodine and *p*-IAN complexes.

It has been proved that the secondary hydroxyl group of α-CDx are catalytically reactive in the hydrolysis of substituted phenyl esters, and that the relative rates of the hydrolysis of *meta*-substituted phenyl esters are about 10^2 times faster than that of *para*-substituted phenyl esters. The structure of the α-CDx–*p*-IAN complex suggests that the hydrolysis of *para*-substituted phenyl esters will hardly occur if a substrate is included in the same manner as that of the *p*-IAN complex, since the distance between the secondary hydroxyl groups of α-CDx and the amino group of *p*-IAN is greater than 4.0 Å. On the other hand, *meta*-substituted phenyl esters must be in close contact with the secondary hydroxyl groups, judging from the inspection of molecular models, so the reaction will occur readily.

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