The Structure of the Cyclodextrin Complex. XXII. Crystal Structures of Hexakis(2,6-di-*O*-methyl)-α-cyclodextrin Complexes with 1-Propanol and Iodine. Evidence for the Formation of Iodine-Host Charge-Transfer Complex

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Crystal structures of hexakis(2,6-di-*O*-methyl)-α-cyclodextrin complexes with 1-propanol and iodine were determined by X-ray analysis. Crystals of both complexes are isomorphous and the space group is $P2_1$ with cell dimensions: a=14.136(2), b=10.680(1), c=21.479(2) Å, and β=106.00(1)° for the 1-propanol complex and a=14.124(2), b=10.667(2), c=21.443(3) Å, and β=106.29(1)° for the iodine complex. The structures were solved by the R-map method combined with the rigid-body least-squares technique and refined by the block-diagonal least-squares method to the R-value of 0.058 for the 1-propanol complex and 0.094 for the iodine complex. The host molecules are arranged in a herring-bone fashion to form a typical cage-type packing structure. Both guest molecules are included within the "cage" which is created by the block of both ends of the annular host cavity by adjacent molecules. The 1-propanol molecule is in van der Waals contact with the inside wall of the host cavity, whereas the iodine molecule forms a charge-transfer complex with an O(3)H hydroxyl group of the adjacent host.

Methylated cyclodextrins have been extensively investigated because of their unique characteristics different from native cyclodextrins and wide possibilities in the field of industrial application.[1,2] Since the reactivity of hydroxyl groups of cyclodextrins differs among O(2)H, O(3)H, and O(6)H, two kinds of methylated cyclodextrins, per(2,6-di-*O*-methyl)cyclodextrins and per(2,3,6-tri-*O*-methyl)cyclodextrins, have been prepared and provided for the investigation of their inclusion phenomena.[3,4] In the former, all O(2)H and O(6)H hydroxyl groups are methylated, while O(3)H hydroxyl groups remain as a functional group. The intramolecular O(2)···H–O(3) hydrogen bonds maintain the round structure of the molecule.[5] In contrast, the latter derivatives have no hydroxyl groups and are highly soluble in usual organic solvents. The X-ray analysis has demonstrated that the macrocyclic conformation of cyclodextrins is markedly affected by the permethylation which blocks the formation of intramolecular hydrogen bonds.[6] The macrocyclic ring becomes more flexible and more distorted than the unmodified cyclodextrin ring. The changes in shape and size of the host cavity, thus derived by the methylation, affect the mode of host-guest interaction and the high conformational flexibility of the host molecule enables the induced-fit conformational change in the complex formation.[7]

Recently, we have reported the crystal structure of hexakis(2,6-di-*O*-methyl)-α-cyclodextrin (DM-α-CDx) complex with 3-iodopropionic acid.[8] The DM-α-CDx molecule has a macrocyclic conformation similar to the conformation of α-cyclodextrin, but the guest 3-iodopropionic acid is included in a manner different from that observed in the α-cyclodextrin complex. The X-ray analysis of the DM-α-CDx complexes with iodine and 1-propanol has been undertaken for the further investigation of the structure of this partially methylated α-cyclodextrin and its host-guest interaction. A short communication on these structures has been published.[9]

Experimental

Preparation of Crystals and X-Ray Measurements. DM-α-CDx was purchased from Toshin Chemical Co. Ltd. and crystallized from hot water. The DM-α-CDx complex with iodine was prepared at 50 °C by standing an aqueous solution of DM-α-CDx saturated with iodine. Crystals were thin needles with brown color and metallic luster. The 1-propanol complex was crystallized in colorless prisms by the slow evaporation at 50 °C from a 20% 1-propanol solution. Both crystalline complexes were stable in air at room temperature. Diffraction experiments were carried out on a Nicolet P3/F diffractometer with graphite-monochromated Cu $K\alpha$ radiation (λ=1.5418 Å). Lattice parameters were determined by using 25 reflections with 2θ value between 35° and 40°. Intensity data were collected by using θ–2θ scan mode and 4299 (1-propanol complex) and 2823 (iodine complex) reflections with $|F_o| \geqq 3\sigma(F)$ were obtained up to 118° in 2θ and used for the structure determination and refinement. No corrections were made for absorption or extinction effects.

Crystal Data. (1) Iodine Complex. $C_{48}H_{84}O_{30}\cdot I_2$, F.W.=1395.0. Monoclinic, space group $P2_1$, Z=2, a=14.124(2), b=10.667(2), c=21.443(3) Å, β=106.29(1)°, V=3103.9(9) Å^3, D_x=1.493 g cm^{-3}.

(2) 1-Propanol complex. $C_{48}H_{84}O_{30}\cdot C_3H_8O$, F.W.=1201.3. Monoclinic, space group $P2_1$, Z=2, a=14.136(2), b=10.680(1), c=21.479(2) Å, β=106.00(1)°, V=3117.1(6) Å^3, D_x=1.280 g cm^{-3}.

Structure Determination and Refinement. The first attempt to solve the structure of the iodine complex was unsuccessuful because of the poor resolution of the electron-density map calculated by using phases with the contribution from iodine only. The orientation of the DM-α-CDx molecule of the 1-propanol complex was roughly estimated from the Patterson map. Then, the position of the molecule was determined by the *R*-map method. The position and orientation of each 2,6-di-*O*-methylglucose unit were corrected by the rigid-body least-squares method. Successive Fourier and difference Fourier syntheses revealed the full structure of the 1-propanol complex. Coordinates of hydrogen atoms of methine and methylene groups were calculated and those of methyl and hydroxyl groups were estimeted from the difference-Fourier map, and these hydrogen atoms were included in the least-squares refinement with the isotropic temperature factor of attached heavy atoms. The block-diagonal least-squares refinement of the structure achieved the *R*-value of 0.058. The unit weight was applied for all the reflections. The structure of the iodine complex was determined by using the DM-α-CDx coordinates of the 1-propanol complex and refined by the block-diagonal least-squares method with the isotropic temperature factors to the *R*-value of 0.094. Final atomic coordinates are given in Tables 1 and 2. Tables of observed and calculated structure factors, anisotropic temperature factors, and atomic parameters of hydrogen atoms are deposited to the Office of the Editor of Bull. Chem. Soc. Jpn. (Document No. 8936). The computation was carried out on a FACOM M-780 computer at the RIPS computer center of AIST (Tsukuba) by using programs developed in the author's laboratory.

Results and Discussion

Conformation of DM-α-CDx. The DM-α-CDx molecules has a round structure with a pseudo-hexagonal symmetry. The macrocyclic conformation is essentially same in both complexes. Bond distances and angles are in good agreement with those of α-cyclodextrin in its complexes with 1-propanol[10] and iodine.[11] All 2,6-di-*O*-methylglucose units have the $^4C_1$ chair conformation. The pyranose conformation is not significantly affected by the methylation of

Table 1. Atomic Coordinates and Temperature Factors of the 1-Propanol Complex

Atom	$x/10^{-4}$	$y/10^{-4}$	$z/10^{-4}$	$B_{eq}/Å^2$	Atom	$x/10^{-4}$	$y/10^{-4}$	$z/10^{-4}$	$B_{eq}/Å^2$
C(1,G1)	4185(5)	176(8)	2885(4)	4.2	C(3,G4)	−3087(5)	−103(8)	773(3)	3.4
C(2,G1)	4320(5)	−1252(8)	2961(4)	4.1	C(4,G4)	−2926(5)	1298(8)	872(3)	3.4
C(3,G1)	3464(6)	−1772(8)	3183(4)	4.1	C(5,G4)	−2847(5)	1737(7)	1562(3)	3.4
C(4,G1)	3399(5)	−1081(8)	3793(4)	3.7	C(6,G4)	−2923(6)	3155(9)	1609(4)	4.4
C(5,G1)	3339(5)	331(8)	3696(4)	3.9	C(7,G4)	−4842(6)	−2250(10)	533(5)	5.5
C(6,G1)	3381(6)	1103(9)	4296(4)	4.8	C(8,G4)	−4557(8)	3911(14)	1362(6)	7.9
C(7,G1)	4741(6)	−2935(9)	2321(5)	5.2	O(2,G4)	−4040(4)	−1841(6)	1031(2)	4.2
C(8,G1)	4201(12)	1335(19)	5364(6)	12.5	O(3,G4)	−3323(4)	−409(6)	105(2)	4.4
O(2,G1)	4331(4)	−1717(6)	2336(3)	4.7	O(4,G4)	−2009(3)	1511(5)	717(2)	3.5
O(3,G1)	3622(5)	−3073(6)	3329(3)	5.8	O(5,G4)	−3634(3)	1226(5)	1780(2)	3.7
O(4,G1)	2507(3)	−1553(5)	3904(2)	3.7	O(6,G4)	−3751(4)	3663(6)	1135(3)	5.0
O(5,G1)	4175(4)	715(6)	3478(3)	4.2	C(1,G5)	−1400(5)	−2055(9)	3928(3)	3.8
O(6,G1)	4157(5)	702(8)	4801(3)	6.7	C(2,G5)	−2042(5)	−2953(8)	3442(4)	3.9
C(1,G2)	2011(5)	2642(8)	855(4)	3.9	C(3,G5)	−2275(5)	−2434(8)	2760(4)	3.5
C(2,G2)	2649(5)	1577(8)	716(4)	3.9	C(4,G5)	−2724(5)	−1121(8)	2733(3)	3.3
C(3,G2)	2885(5)	644(8)	1270(4)	3.8	C(5,G5)	−2039(5)	−287(7)	3255(3)	3.4
C(4,G2)	3314(5)	1308(7)	1910(3)	3.5	C(6,G5)	−2445(5)	1011(8)	3317(4)	4.2
C(5,G2)	2670(5)	2424(8)	1999(4)	3.8	C(7,G5)	−2131(8)	−5200(10)	3482(6)	6.9
C(6,G2)	3099(6)	3220(9)	2597(4)	4.8	C(8,G5)	−3709(7)	2062(11)	3584(7)	7.5
C(7,G2)	2585(8)	1018(11)	−366(5)	6.1	O(2,G5)	−1547(4)	−4111(6)	3496(3)	4.8
C(8,G2)	4562(9)	4159(13)	3222(6)	8.9	O(3,G5)	−2934(4)	−3252(5)	2323(3)	4.3
O(2,G2)	2130(4)	979(6)	130(2)	4.5	O(4,G5)	−2797(3)	−657(5)	2100(2)	3.3
O(3,G2)	3571(4)	−248(6)	1157(3)	4.6	O(5,G5)	−1860(3)	−879(5)	3885(2)	3.7
O(4,G2)	3314(3)	399(5)	2399(2)	3.5	O(6,G5)	−3351(4)	897(6)	3464(3)	4.9
O(5,G2)	2495(4)	3235(5)	1448(3)	4.0	C(1,G6)	2488(5)	−1844(9)	4543(4)	4.2
O(6,G2)	4080(5)	3530(7)	2617(4)	7.1	C(2,G6)	2026(6)	−3144(9)	4528(4)	4.2
C(1,G3)	−1897(5)	2551(8)	345(4)	3.8	C(3,G6)	982(5)	−3101(8)	4073(4)	3.7
C(2,G3)	−1434(6)	2128(9)	−173(4)	4.3	C(4,G6)	409(5)	−2054(8)	4290(3)	3.4
C(3,G3)	−390(6)	1678(9)	136(3)	4.0	C(5,G6)	961(5)	−802(8)	4350(4)	3.8
C(4,G3)	201(5)	2678(8)	587(4)	3.6	C(6,G6)	458(6)	181(9)	4668(4)	4.8
C(5,G3)	−324(5)	3044(8)	1092(3)	3.6	C(7,G6)	2852(15)	−5117(16)	4602(12)	15.7
C(6,G3)	162(6)	4070(9)	1531(4)	4.5	C(8,G6)	540(9)	2071(11)	4075(5)	7.0
C(7,G3)	−2409(9)	1361(11)	−1177(5)	7.6	O(2,G6)	2613(4)	−3998(7)	4277(3)	5.6
C(8,G3)	257(15)	4850(20)	2587(7)	13.9	O(3,G6)	527(4)	−4284(6)	4126(3)	4.5
O(2,G3)	−2019(4)	1154(6)	−528(2)	4.9	O(4,G6)	−498(3)	−1957(5)	3764(2)	3.3
O(3,G3)	62(4)	1431(7)	−375(3)	5.2	O(5,G6)	1921(4)	−969(6)	4776(2)	4.0
O(4,G3)	1112(3)	2087(5)	911(2)	3.6	O(6,G6)	899(4)	1394(6)	4662(3)	5.7
O(5,G3)	−1288(4)	3486(5)	750(2)	3.7	C(1,PR)	−22(15)	−561(22)	2092(11)	17.1
O(6,G3)	−173(7)	4011(11)	2094(4)	9.7	C(2,PR)	−315(13)	−1567(21)	1463(13)	16.6
C(1,G4)	−3698(5)	−94(8)	1746(4)	3.6	C(3,PR)	526(13)	−1849(41)	1789(13)	26.4
C(2,G4)	−3926(5)	−510(8)	1054(4)	3.7	O(1,PR)	336(15)	465(23)	2460(7)	26.6

a) $B_{eq}=4/3\sum a_i a_j B_{ij}$, where a_i and a_j are lattice parameters and B_{ij} is the anisotropic temperature factor.

Table 2. Atomic Coordinates and Temperature Factors of the Iodine Complex

Atom	$x/10^{-3}$	$y/10^{-3}$	$z/10^{-3}$	$B/\text{Å}^2$	Atom	$x/10^{-3}$	$y/10^{-3}$	$z/10^{-3}$	$B/\text{Å}^2$
C(1,G1)	416(2)	21(3)	288(1)	4.2	C(2,G4)	−393(2)	−53(2)	107(1)	3.8
C(2,G1)	430(2)	−127(3)	296(1)	5.0	C(3,G4)	−308(2)	−14(3)	80(1)	3.7
C(3,G1)	342(2)	−179(3)	316(1)	4.9	C(4,G4)	−292(2)	132(3)	89(1)	4.5
C(4,G1)	343(2)	−110(3)	380(1)	4.6	C(5,G4)	−282(2)	170(3)	160(1)	4.6
C(5,G1)	332(2)	30(3)	369(1)	4.0	C(6,G4)	−288(2)	315(3)	165(1)	4.7
C(6,G1)	342(2)	105(3)	429(1)	5.9	C(7,G4)	−485(2)	−232(3)	51(1)	6.3
C(7,G1)	470(2)	−300(4)	232(2)	7.3	C(8,G4)	−458(3)	390(4)	140(2)	9.4
C(8,G1)	424(4)	145(6)	535(2)	13.4	O(2,G4)	−404(1)	−184(2)	103(1)	4.9
O(2,G1)	430(1)	−171(2)	231(1)	5.0	O(3,G4)	−328(1)	−39(2)	11(1)	5.5
O(3,G1)	357(1)	−308(2)	329(1)	6.2	O(4,G4)	−201(1)	153(2)	74(1)	4.1
O(4,G1)	250(1)	−158(2)	391(1)	4.1	O(5,G4)	−364(1)	121(2)	180(1)	3.9
O(5,G1)	417(1)	69(2)	348(1)	4.7	O(6,G4)	−376(1)	365(2)	116(1)	7.4
O(6,G1)	415(2)	68(2)	480(1)	7.5	C(1,G5)	−141(2)	−208(2)	395(1)	3.9
C(1,G2)	195(2)	271(3)	86(1)	4.7	C(2,G5)	−205(2)	−294(3)	347(1)	3.9
C(2,G2)	263(2)	163(2)	71(1)	3.4	C(3,G5)	−225(2)	−249(3)	278(1)	4.4
C(3,G2)	285(2)	73(3)	124(1)	4.9	C(4,G5)	−271(2)	−115(2)	277(1)	3.2
C(4,G2)	330(2)	135(3)	192(1)	4.2	C(5,G5)	−204(2)	−32(3)	328(1)	4.3
C(5,G2)	265(2)	242(3)	200(1)	5.1	C(6,G5)	−242(2)	101(3)	334(1)	6.3
C(6,G2)	309(2)	316(3)	262(1)	4.7	C(7,G5)	−215(3)	−528(4)	349(2)	8.1
C(7,G2)	259(2)	106(3)	−36(1)	6.0	C(8,G5)	−372(2)	210(3)	357(2)	6.9
C(8,G2)	458(3)	414(4)	326(2)	9.5	O(2,G5)	−155(1)	−412(2)	352(1)	5.4
O(2,G2)	208(1)	110(2)	14(1)	5.2	O(3,G5)	−290(1)	−323(2)	233(1)	4.8
O(3,G2)	350(1)	−22(2)	114(1)	5.8	O(4,G5)	−281(1)	−69(1)	212(1)	3.1
O(4,G2)	330(1)	41(2)	239(1)	4.3	O(5,G5)	−187(1)	−88(2)	390(1)	4.4
O(5,G2)	248(1)	323(2)	147(1)	4.9	O(6,G5)	−334(2)	87(2)	348(1)	7.6
O(6,G2)	407(2)	353(3)	265(1)	8.5	C(1,G6)	254(2)	−184(3)	456(1)	5.2
C(1,G3)	−196(2)	259(3)	33(1)	6.2	C(2,G6)	200(2)	−312(3)	455(1)	5.3
C(2,G3)	−149(2)	225(3)	−17(1)	5.0	C(3,G6)	99(2)	−308(2)	408(1)	3.1
C(3,G3)	−41(2)	178(2)	14(1)	3.7	C(4,G6)	40(2)	−206(2)	431(1)	3.4
C(4,G3)	18(2)	277(2)	57(1)	3.9	C(5,G6)	96(2)	−78(3)	433(1)	4.1
C(5,G3)	−38(2)	308(3)	108(1)	4.6	C(6,G6)	48(2)	22(3)	465(1)	5.3
C(6,G3)	11(2)	420(3)	142(1)	4.9	C(7,G6)	294(3)	−510(6)	470(2)	12.8
C(7,G3)	−243(2)	141(3)	−119(2)	6.9	C(8,G6)	54(2)	201(4)	403(2)	7.6
C(8,G3)	20(3)	510(6)	259(2)	12.3	O(2,G6)	262(1)	−400(2)	430(1)	6.7
O(2,G3)	−203(1)	122(2)	−52(1)	5.9	O(3,G6)	52(1)	−427(2)	416(1)	5.9
O(3,G3)	2(1)	156(2)	−39(1)	5.2	O(4,G6)	−47(1)	−198(2)	378(1)	3.7
O(4,G3)	107(1)	214(2)	90(1)	4.4	O(5,G6)	194(1)	−97(2)	479(1)	4.8
O(5,G3)	−134(1)	354(2)	75(1)	4.6	O(6,G6)	89(1)	141(2)	459(1)	6.8
O(6,G3)	−20(2)	420(3)	210(1)	9.1	I(1)	21.8(0.2)	−3.0(0.3)	271.8(0.1)	8.6[a]
C(1,G4)	−369(2)	−12(3)	177(1)	4.2	I(2)	3.5(0.2)	−164.4(0.3)	133.8(0.1)	7.3[a]

a) B_{eq} value.

O(2)H and O(6)H hydroxyl groups. The endo-cyclic torsion angles are confined to near ±60° and their absolute values vary in the range from 53° to 64° in the increasing order of C(2)-C(3)-C(4)-C(5), C(1)-C(2)-C(3)-C(4), C(3)-C(4)-C(5)-O(5), O(5)-C(1)-C(2)-C(3), C(4)-C(5)-O(5)-C(1), and C(5)-O(5)-C(1)-C(2). The torsion angle index is distributed in the range 119—139° in the 1-propanol complex and 124—145° in the iodine complex (Table 3). As shown in Fig. 1, the torsion-angle index is linearly correlated with the distance between O(4) and O(4′) of adjacent 2,6-di-*O*-methylglucose unit. The strong correlation is indicated by the correlation factor of −0.91. A similar correlation is found in α-cyclodextrin[12] but permethylated α-cyclodextrin shows no such correlation. The C(6)-O(6) bond shows two types of orientation, gauche-gauche (to the C(5)-O(5) bond and C(4)-C(5) bond, respectively) and gauche-trans. The former is

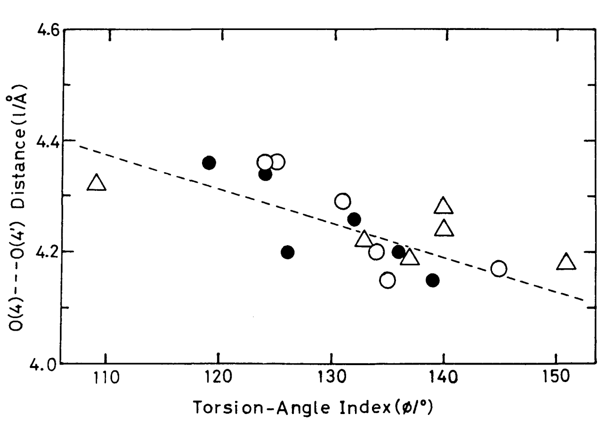

Fig. 1. Plot of the O(4)···(4′) distance between the adjacent units against the torsion-angle index in the DM-α-CDx complexes with 1-propanol (○), iodine (●), and 3-iodopropionic acid (△).

found in the G1, G2, G4, and G5 units and the C(6)–O(6) bond in the G3 and G6 units have the latter conformation. The methyl groups attached to O(2) point away from the center of macrocycle with the average torsion angels, C(1)–C(2)–O(2)–C(7) and C(3)–C(2)–O(2)–C(7), of 135° and −105°, respectively, in the 1-propanol complex. The C(8)H_3O(6) methoxyl group in the G1, G2, G3, and G5 units is trans to the C(5)–C(6) bond, whereas the methoxyl group in the G6 unit is nearly gauche and oriented to the inside of the macrocycle. The torsion angles involving the glycosidic linkage, C(4)–O(4)–C(1′)–C(2′), C(4)–O(4)–C(1′)–O(5′), C(3)–C(4)–O(4)–C(1′), and C(5)–C(4)–O(4)–C(1′), having average values of −136°, 106°, 133°, and −111°, respectively, are in good agreement with those found in *α*-cyclodextrin.

The six glycosidic O(4) atoms are coplanar within the deviation of 0.15 Å from their least-squares plane. As indicated by the tilt angle, which is distributed around 15° (Table 3), the 2,6-di-*O*-methylglucose units are not normal to the O(4) plane but incline with their O(6) side toward the inside of the macrocycle. Therefore, the O(6) side of the DM-*α*-CDx molecule is narrower than the O(2), O(3) side. The average tilt angle is larger than that (12°) found in the 3-iodopropionic acid complex.[8] The 3-iodopropionic acid molecule is bulkier than 1-propanol and iodine molecules and occupies the full space of the host cavity. In contrast, in the complexes with 1-propanol and iodine, the guest molecules are too small to fill the host cavity, therefore, the 2,6-di-*O*-methylglucose unit much more inclines so as to reduce the empty space at the O(6) side.

The inclination of 2,6-di-*O*-methylglucose unit is restricted by the O(2)···H–O(3′) hydrogen bond between adjacent units. As shown in Table 4, all O(3)H hydroxyl groups are hydrogen-bonded to adjacent O(2) and maintain the O(2)···O(3′) distance in the range 2.87—3.17 Å. These hydrogen bonds keep the tilt-angle within a limited range and maintain the round structure of DM-*α*-CDx. The importance of intramolecular hydrogen bonds can be demonstrated by the comparison with the structure of permethylated *α*-cyclodextrins (Table 5) in which the macrocyclic ring is free from the conformational restriction imposed by the O(2)···O(3′) hydrogen bonds and therefore higly flexible.

Host-Guest Interaction. In both DM-*α*-CDx complexes, the guest molecule is fully included within the host cavity as shown in Fig. 2. The inclusion feature of these complexes resembles to the structure of corresponding *α*-cyclodextrin complexes, but some significant differences are observed. The 1-propanol molecule is located near the O(2), O(3) side of DM-*α*-CDx and in van der Waals contact with the inside wall of the cavity (Fig. 2A). The methyl group attached to O(6,G6) is located at the O(6) end of the cavity and seems to prevent the further penetration of 1-propanol.

Table 3. Torsion-Angle Index and Tilt-angle of DM-*α*-CDx Complexes with 1-Propanol (I) and Iodine (II) (ϕ/°)

	Torsion-angle index[a]		Tilt-angle[b]	
	I	II	I	II
G1	132	131	8.0	9.8
G2	126	134	11.4	12.0
G3	119	125	21.3	21.4
G4	139	145	11.9	11.7
G5	124	124	14.3	12.8
G6	136	135	20.4	21.5

a) The torsion-angle index is defined as: $\Phi=|\phi(\mathrm{C(1)}\text{–}\mathrm{C(2)})|+|\phi(\mathrm{C(2)}\text{–}\mathrm{C(3)})|+|\phi(\mathrm{C(5)}\text{–}\mathrm{O(5)})|+|\phi(\mathrm{O(5)}\text{–}\mathrm{C(1)})|-|\phi(\mathrm{C(3)}\text{–}\mathrm{C(4)})|-|\phi(\mathrm{C(4)}\text{–}\mathrm{C(5)})|$. b) The tilt angle is defined as an angle made by the plane through six O(4) atoms and the plane through C(1), C(4), O(4), and O(4′) of each 2,6-di-*O*-methylglucose unit.

Table 4. Hydrogen Bond Distances (l/Å) and Angles (ϕ/°) in the 1-Propanol Complex

	Distance O···O	Angle O···H–O
O(2,G1)···H–O(3,G2)	2.92(1)	145(4)
O(2,G2)···H–O(3,G3)	2.87(1)	168(4)
O(2,G3)···H–O(3,G4)	3.07(1)	161(4)
O(2,G4)···H–O(3,G5)	3.17(1)	137(4)
O(2,G5)···H–O(3,G6)	2.88(1)	155(4)
O(2,G6)···H–O(3,G1)	2.96(1)	151(4)

Table 5. Comparison of the Geometrical Data of the Macrocycle Among *α*-CDx, DM-*α*-CDx, and TM-*α*-CDx

	α-CDx[a]	DM-*α*CDx[b]	TM-*α*-CDx[c]
Radius of the O(4) hexagon (l/Å)	4.23(5)	4.25(7)	4.29(23)
O(4)···O(4′) distance (l/Å)	4.24(7)	4.25(8)	4.30(14)
O(2)···O(3′) distance (l/Å)	2.97(9)	2.98(12)	3.39(12)
O(4) angle (ϕ/°)	119(1)	119(1)	118(1)
Planarity of the O(4) hexagon (l/Å)[d]	0.102	0.111	0.132
Torsion-angle index (ϕ/°)	131(4)	129(8)	137(12)
Tilt angle (ϕ/°)	13(10)	15(6)	18(12)

a) *α*-Cyclodextrin-1-propanol complex, see Ref. 10. b) Present work, 1-propanol complex. c) Permethylated *α*-cyclodextrin complex with D-mandelic acid, see Ref. 6. d) The root-mean-square deviation of O(4) atoms from the least-squares plane through six O(4) atoms.

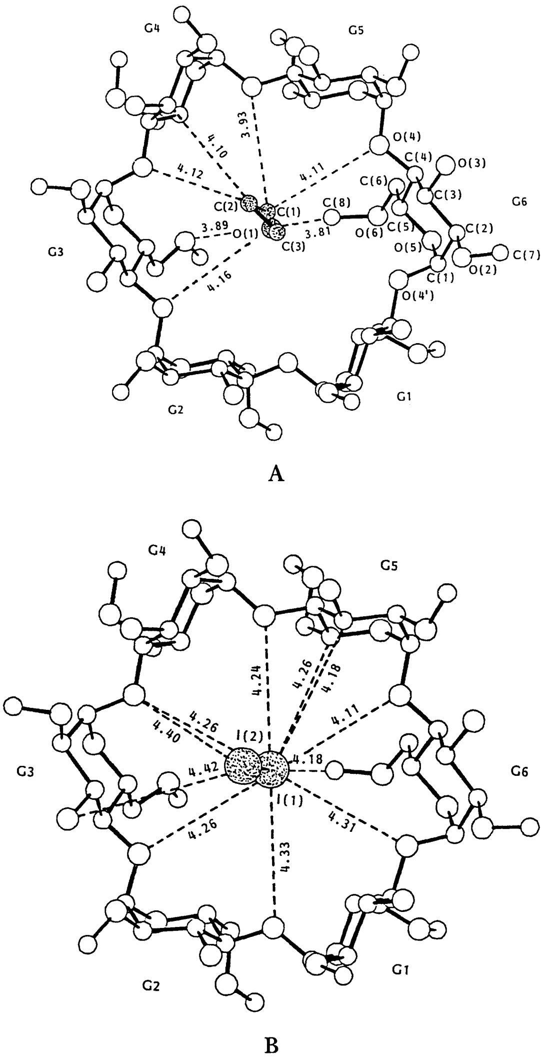

Fig. 2. Intermolecular distances between DM-α-CDx and guest in the 1-propanol complex (A) and the iodine complex (B).

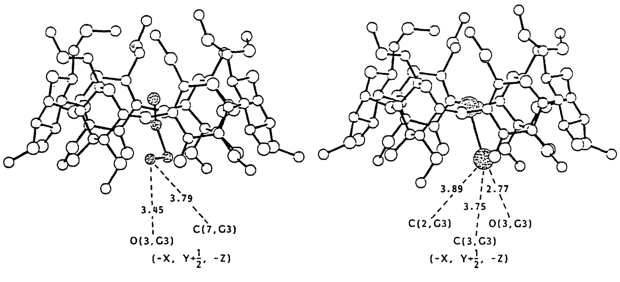

Fig. 3. Intermolecular distances between the guest and symmetry related host molecules. 1-Propanol (left) and iodine (light) molecules are shaded.

At the O(2), O(3) side, the 1-propanol molecule is also in van der Waals contact with the adjacent DM-α-CDx molecule (Fig. 3). The relatively large temperature factor of 1-propanol indicates that the guest molecule is loosely bound to the host cavity.

The iodine atom occupies the same position as that of 1-propanol and is in van der Waals contact with the host DM-α-CDx molecule (Fig. 2B). A significant short contact is observed between the I(2) iodine atom and an O(3) oxygen atom of the adjacent DM-α-CDx (Fig. 3). The interatomic distance of 2.77 Å is too short for van der Waals contact but in good agreement with the intermolecular I···O distance (2.81 Å) found in the charge-transfer complex of iodine with dioxane.[13] The geometry involving the I(2)···O(3) contact is shown in Fig. 4. The I(2)···O(3) distance and I(1)–I(2)···O(3) angle suggest the formation of charge-transfer complex between the DM-α-CDx and iodine.

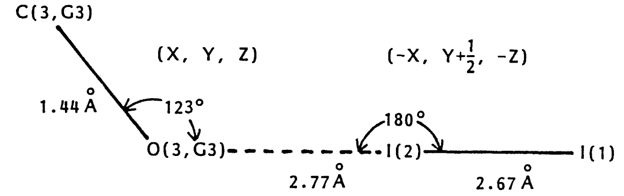

Fig. 4. The geometrical data of the charge-transfer interaction between DM-α-CDx and iodine.

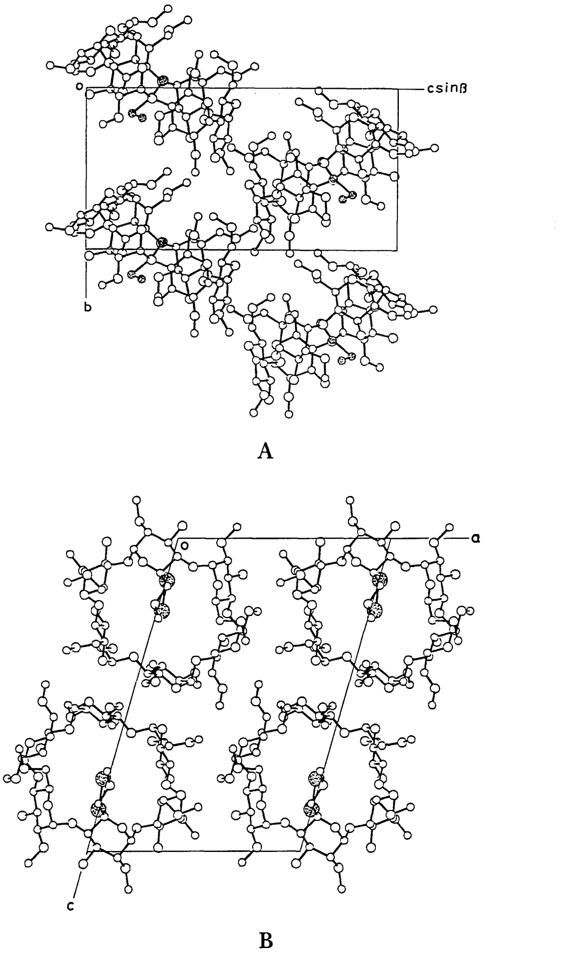

Fig. 5. Crystal structure of the DM-α-CDx complex with 1-propanol viewed along the *a* axis (A) and the iodine complex viewed along the *b* axis (B).

A short I···O contact is also observed between an iodine atom and a hydroxyl group in the α-cyclodextrin complex with iodine, but the formation of the charge-transfer complex is doubtful because of the relatively long I···O distance (3.01 Å).[11)]

Crystal Packing. Crystal structures are shown in Fig. 5. DM-α-CDx molecules are arranged in a herring-bone fashion along the b axis and form a typical cage-type packing structure. Both ends of the host cavity are blocked by adjacent DM-α-CDx molecules (Fig. 5A) and the guest molecule is accommodated in each isolated "cage". Another cage-type packing structure is observed in the DM-α-CDx complexes with 3-iodopropionic acid.[8)] However, the space group ($P2_12_12_1$) and the molecular arrangement differ from the present complexes. In contrast, α-cyclodextrin complexes with 1-propanol,[10)] iodine,[11)] and 3-iodopropionic acid[14)] crystallize in the space group $P2_12_12_1$ having the same packing. This suggests that DM-α-CDx distinguishes 3-iodopropionic acid from 1-propanol and iodine in the crystalline state.

References

1) D. Duchene, "Cyclodextrins and Their Industrial Uses," Editions de Sante, Paris (1987).

2) J. Szejtli, "Cyclodextrin Technology," Kluwer Academic Publishers, Dordrecht (1988).

3) B. Casu, M. Reggiani, and G. R. Sanderson, *Carbohydr. Res.*, **76**, 59 (1979).

4) J. Szejtli, A. Liptak, I. Jodal, P. Fugedi, P. Nanasi, and A. Neszwelyi, *Starch/Staerke*, **32**, 165 (1980).

5) K. Harata, *Bull. Chem. Soc. Jpn.*, **61**, 1939 (1988).

6) K. Harata, K. Uekama, M. Otagiri, and F. Hirayama, *J. Inclusion Phenom.*, **1**, 279 (1984).

7) K. Harata, K. Uekama, M. Otagiri, and F. Hirayama, *Bull. Chem. Soc. Jpn.*, **60**, 497 (1987).

8) K. Harata, *Carbohydr. Res.*, **192**, 33 (1989).

9) K. Harata, *Chem. Lett.*, **1986**, 2057.

10) W. Saenger, R. K. McMullan, J. Fayos, and D. Mootz, *Acta Crystallogr., Sect. B*, **30**, 2019 (1974).

11) R. K. McMullan, W. Saenger, J. Fayos, and D. Mootz, *Carbohydr. Res.*, **31**, 211 (1973).

12) K. Harata, *Bull. Chem. Soc. Jpn.*, **50**, 1416 (1977).

13) O. Hassel, *Acta Chem. Scand.*, **19**, 2259 (1965).

14) K. Harata, K. Uekama, M. Otagiri, and F. Hirayama, *Nihon Kagaku Kaishi*, **1983**, 173.