The Structure of the Cyclodextrin Complex. IV. The Crystal Structure of α-Cyclodextrin–Sodium 1-Propanesulfonate Nonahydrate

Kazuaki HARATA

Research Institute for Polymers and Textiles, Sawatari-4, Kanagawa-ku, Yokohama 221

(Received October 20, 1976)

α-Cyclodextrin, which is a cyclic oligosaccharide consisting of six D-glucose residues, forms a 1 : 1 complex with sodium 1-propanesulfonate. The crystal structure was determined by the X-ray method. The crystal is orthorhombic, and the space group is $P2_12_12$ with cell dimensions of $a=21.608(2)$, $b=16.700(2)$, and $c=8.302(1)$ Å, and $Z=2$. The structure was solved on the basis of 2219 diffractometer data and refined by the block-diagonal least-squares method to the final R-value of 0.077. The α-cyclodextrin molecule is nearly hexagonal with diagonal distances of 8.40—8.59 Å between the glycosidic oxygen atoms. The framework of the crystal is built up of a stack of α-cyclodextrin rings along the c axis in head-to-tail arrangement, with channel-type structure. The adjacent α-cyclodextrin molecules along the channel are linked by six O(3)···O(6) hydrogen bonds. The guest 1-propanesulfonate anions are located in channels, having statistical disorder. The primary hydroxyl groups of α-cyclodextrin exhibit *gauche-trans* conformation, and they form hydrogen bonds with the sulfonato group resulting in oxygen-oxygen distances of 2.72—2.80 Å. The propyl group is in contact with the O(2), O(3) side of the α-cyclodextrin ring. The sodium ion is located outside the channel, and is surrounded by five oxygen atoms which form a distorted trigonal bipyramid.

α-Cyclodextrin (α-CDx) is a cyclic oligosaccharide consisting of six D-glucose residues. It has a cylindrical cavity with a diameter of about 5 Å and a height of 8 Å in the center of the molecule. At both ends of the cavity, the hydroxyl groups are located, while in the interior of the ring the twelve C–H groups are oriented to the center of the cavity. Therefore, the cavity is of relatively hydrophobic nature. α-CDx forms a number of inclusion complexes with a variety of guest molecules which range from polar ones, such as potassium acetate, to non-polar ones, such as the rare gases.[1-4] The complexing ability has been considered to be largely determined by the relative size of the guest molecule. Recent X-ray analyses have revealed that the guest molecules are situated in the interior of the cavity, and that the macro-cyclic conformation of the α-CDx ring changes with the dimension and the shape of the guest molecule.[5-16] The α-CDx ring in the 1-propanol complex[8] is nearly hexagonal, but remarkable deformation of the α-CDx ring is observed in the water complex.[6]

α-CDx has been used as an enzyme model,[3] since it exhibits catalytic properties for some chemical reactions. The interaction between α-CDx and the guest molecule is of interest in relation to the enzyme-substrate interaction. Saenger and his coworkers[6-9] have proposed the inclusion mechanism on the basis of the fact that the driving force for the complex formation is derived from the difference between the conformational energy of α-CDx for the "tense" state and that for the "relaxed" state. On the other hand, a theoretical calculation of the complex formation energy[15] has shown that the stability of the complex is mainly determined by the difference between the solvation energy for the complexed state and that for the uncomplexed state, and that the inclusion of the hydrophobic group gives a more stable complex than does the inclusion of the hydrophilic group. Sodium 1-propanesulfonate (PSNa) consists of a hydrophobic propyl group and a hydrophilic sulfonato group. An X-ray analysis of the α-CDx–PSNa complex was performed to investigate the conformation of α-CDx and the interaction between α-CDx and PSNa, in comparison with those of other α-CDx complexes.

Experimental

Crystals of the α-CDx–PSNa complex were obtained by cooling an aqueous solution containing α-CDx and PSNa with a 1 : 1 molar ratio. These are colorless and orthorhombic prisms elongated along the c axis. The density was measured by the flotation method in a mixture of chloroform and dioxane. The diffraction measurements were carried out with the crystal enclosed in a quartz capillary containing a small amount of water, since the crystal decomposes in air. The crystal data are given in Table 1. The intensity data were obtained on a Rigaku automatic four-circle diffractometer using graphite monochromatized Cu$K\alpha$ radiation and the θ-2θ scan technique. 2570 independent reflections were obtained up to 120° in 2θ, but 351 reflections with $|F_o|<3\sigma(F)$ were treated as unobserved, where $\sigma(F)$ is the standard deviation estimated from counting statistics. No correction was made for absorption and extinction.

Table 1. Crystal data

$C_{36}H_{60}O_{30}\cdot C_3H_7SO_3Na\cdot 9H_2O$,		Orthorhombic
Molecular weight		1281.1
Cell dimensions	a	21.608(2) Å
	b	16.700(2)
	c	8.302(1)
Cell volume	V	2995.7 Å^3
Space group		$P2_12_12$
	Z	2
Density	D_m	1.42 g cm^{-3}
	D_x	1.42

Determination and Refinement of the Structure

The crystal structure of the α-CDx–PSNa complex was solved on the basis of the assumption that the location of the α-CDx molecule is same as that of the isomorphous crystal of the sodium benzenesulfonate (BSNa) complex[15]. The atomic parameters of α-CDx were refined by the block-diagonal least-squares method, starting from those of the BSNa complex. Then, a

Fourier map was calculated, and the PSNa and water molecules were found from it. The 1-propanesulfonate anion is statistically disordered on the two-fold axis. Unreasonably short intermolecular distances were found for Na···O(W6), O(W3)···O(W6), O(W5)···O(W7), and O(W6)···O(W7), indicating that the locations of these atoms are statistically disordered. An average population of 0.5 is assigned to the sodium ion, since there are only two PSNa molecules per unit cell in spite of the four equivalent positions. The population of O(W6) is also 0.5 since the O(W6) atom occupies the position when the sodium ion is absent. Then, the abnormally short distances for O(W3)···O(W6), O(W5)···O(W7), and O(W6)···O(W7) can be reasonably interpreted by assigning 0.5 to the respective occupancies of O(W3), O(W5), and O(W7). The 27 hydrogen atoms were found on the difference-Fourier map. A refinement of the atomic parameters was carried out by the block-diagonal least-squares method. The isotropic thermal factors of hydrogen atoms were taken to be equal to those of the carbon or oxygen atoms to which the hydrogen atoms are bonded, and were not refined. The final R-value is 0.077 for the 2219 reflections. The quantity minimized was $\sum w(|F_o|-|F_c|)^2$ with $w=1.0$ for all reflections used. The atomic scattering factors were taken from "International Tables for X-ray Crystallography."[17] The atomic parameters are shown in Tables 2 and 3. The observed and calculated structure factors are given in Table 4.*

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

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

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{31}
C(1,G1)	1541(4)	2457(6)	3331(12)	12(2)	19(4)	66(15)	-5(5)	7(13)	-5(10)
C(2,G1)	1272(5)	2873(6)	4301(13)	14(3)	25(4)	78(16)	-2(6)	-7(15)	7(11)
C(3,G1)	586(4)	2620(7)	4986(13)	9(2)	32(5)	71(15)	-1(6)	-36(15)	5(10)
C(4,G1)	240(4)	2831(6)	3450(12)	13(2)	25(4)	62(14)	-2(5)	-2(15)	10(11)
C(5,G1)	556(4)	2412(6)	1986(12)	10(2)	25(4)	56(15)	-7(5)	-1(14)	11(10)
C(6,G1)	269(5)	2690(7)	409(12)	14(2)	37(5)	59(15)	-2(6)	21(16)	-12(10)
O(2,G1)	1619(3)	2675(4)	6208(9)	16(2)	30(3)	82(11)	7(4)	-15(11)	-22(8)
O(3,G1)	313(3)	3043(5)	6284(9)	16(2)	41(4)	61(11)	4(4)	-18(12)	7(8)
O(4,G1)	-362(3)	2473(4)	3632(8)	7(1)	23(3)	85(11)	-1(3)	15(10)	6(7)
O(5,G1)	1198(3)	2673(4)	1943(8)	11(2)	28(3)	64(11)	5(4)	9(10)	7(7)
O(6,G1)	518(4)	2235(5)	-905(9)	20(2)	47(4)	59(11)	-2(5)	-16(12)	1(8)
C(1,G2)	2469(5)	-504(7)	3323(13)	13(3)	29(5)	79(16)	7(6)	25(15)	12(12)
C(2,G2)	2614(5)	24(7)	4743(12)	12(2)	24(4)	81(16)	9(6)	5(17)	-6(11)
C(3,G2)	2116(5)	646(6)	4949(13)	10(2)	26(4)	67(15)	-2(5)	-5(15)	-8(11)
C(4,G2)	2058(4)	1139(6)	3384(13)	11(2)	28(4)	84(17)	-1(5)	24(16)	7(11)
C(5,G2)	1942(5)	589(7)	1953(14)	16(3)	28(5)	83(17)	14(6)	9(16)	10(12)
C(6,G2)	1974(6)	1024(7)	357(13)	30(4)	30(5)	42(15)	7(7)	-11(15)	2(13)
O(2,G2)	2685(4)	-451(4)	6175(9)	23(2)	27(3)	97(12)	-6(4)	32(12)	-22(10)
O(3,G2)	2263(3)	1200(4)	6228(9)	19(2)	30(3)	65(11)	2(4)	6(11)	-3(8)
O(4,G2)	1503(3)	1619(4)	3609(9)	9(1)	16(2)	92(11)	2(3)	17(10)	4(7)
O(5,G2)	2429(3)	-20(5)	1906(8)	16(2)	27(3)	72(10)	9(4)	-3(12)	30(8)
O(6,G2)	1817(5)	536(5)	-935(10)	46(3)	40(4)	87(13)	0(6)	15(13)	21(12)
C(1,G3)	888(5)	-2963(6)	3306(14)	13(2)	23(4)	89(17)	0(5)	14(15)	0(11)
C(2,G3)	1319(5)	-2885(6)	4769(12)	17(3)	26(4)	58(15)	4(6)	34(14)	-3(11)
C(3,G3)	1497(5)	-2002(6)	4977(12)	15(3)	22(4)	44(14)	-1(5)	0(13)	-12(10)
C(4,G3)	1797(4)	-1699(6)	3434(12)	11(2)	26(4)	53(15)	3(5)	11(14)	11(10)
C(5,G3)	1371(5)	-1831(6)	1963(12)	18(3)	19(4)	41(14)	1(5)	-1(13)	8(11)
C(6,G3)	1689(5)	-1651(7)	395(13)	21(3)	36(5)	57(16)	-3(7)	23(16)	6(12)
O(2,G3)	1014(3)	-3194(5)	6152(10)	16(2)	37(4)	108(13)	1(4)	58(13)	-1(9)
O(3,G3)	1939(3)	-1921(5)	6247(9)	15(2)	42(4)	52(10)	1(4)	29(11)	-13(8)
O(4,G3)	1874(3)	-586(4)	3646(8)	14(2)	15(2)	57(10)	0(3)	2(9)	19(8)
O(5,G3)	1200(3)	-2680(4)	1904(8)	11(2)	24(3)	63(10)	8(4)	-17(10)	0(7)
O(6,G3)	1271(4)	-1704(5)	-913(9)	26(2)	47(4)	72(12)	-6(5)	8(13)	-6(10)
Na	3521(5)	-95(7)	671(11)	33(3)	36(4)	108(14)	12(6)	13(16)	30(12)
S	0(-)	0(-)	-1164(6)	26(1)	33(2)	160(8)	5(3)	0(-)	0(-)
O(1,PS)	44(18)	-785(12)	-683(39)	113(15)	21(8)	477(78)	-88(20)	5(45)	-8(72)
O(2,PS)	530(12)	378(32)	-722(38)	28(7)	393(58)	359(70)	-196(37)	40(117)	5(40)
O(3,PS)	-501(19)	399(19)	713(40)	132(21)	119(22)	369(75)	205(37)	63(72)	82(70)
C(1,PS)	0(-)	0(-)	-3205(32)	119(21)	205(37)	94(38)	-14(52)	0(-)	0(-)
C(2,PS)	222(37)	-93(75)	-4268(45)	102(46)	214(54)	208(67)	150(94)	-29(176)	144(87)
C(3,PS)	148(12)	5(62)	-6157(33)	18(13)	128(22)	159(44)	32(54)	-21(103)	4(32)
O(W1)	3582(5)	1315(6)	887(12)	49(4)	40(4)	149(17)	-36(7)	-9(15)	-38(14)
O(W2)	3311(4)	-1572(6)	774(11)	32(3)	47(4)	124(15)	33(6)	-4(14)	18(11)
O(W3)	1229(10)	4898(11)	2170(23)	47(7)	31(8)	219(37)	15(13)	-19(31)	-189(29)
O(W4)	0(-)	5000(-)	3400(33)	157(17)	49(9)	471(64)	17(23)	0(-)	0(-)
O(W5)	4685(11)	-355(15)	3114(42)	39(7)	63(13)	558(88)	-41(16)	48(63)	-98(50)
O(W6)	3872(12)	-177(13)	647(43)	37(8)	37(11)	632(97)	25(16)	44(60)	80(52)
O(W7)	4135(9)	-297(12)	2994(33)	28(5)	52(10)	394(60)	-14(12)	85(44)	-51(34)

TABLE 3. FRACTIONAL COORDINATES ($\times 10^3$) AND ISOTROPIC THERMAL FACTORS OF HYDROGEN ATOMS

The thermal factors are equal to those of the adjacent carbon or oxygen atoms.

	x	y	z	B/Å^2
H(C1, G1)	196(5)	262(6)	300(15)	1.7
H(C2, G1)	129(5)	362(6)	462(13)	2.7
H(C3, G1)	53(5)	188(6)	521(14)	2.2
H(C4, G1)	17(4)	357(5)	343(12)	1.6
H(C5, G1)	55(4)	171(6)	217(12)	1.8
H(C6A, G1)	34(4)	345(6)	18(12)	1.9
H(C6B, G1)	−19(5)	262(7)	41(15)	1.9
H(O2, G1)	175(5)	222(7)	621(15)	2.7
H(O3, G1)	35(6)	287(8)	704(17)	2.5
H(C1, G2)	280(5)	−95(6)	302(14)	2.3
H(C2, G2)	313(6)	19(8)	457(15)	3.0
H(C3, G2)	159(5)	35(7)	530(14)	2.2
H(C4, G2)	247(4)	146(6)	304(12)	2.4
H(C5, G2)	144(5)	28(7)	205(14)	2.3
H(C6A, G2)	240(4)	126(6)	−3(13)	3.1
H(C6B, G2)	168(6)	142(7)	33(16)	3.1
H(O2, G2)	251(6)	−79(7)	623(16)	2.6
H(O3, G2)	222(6)	100(7)	726(16)	2.7
H(C1, G3)	77(6)	−370(7)	295(16)	3.3
H(C2, G3)	167(5)	−328(6)	450(13)	2.8
H(C3, G3)	108(5)	−157(6)	529(13)	2.4
H(C4, G3)	222(5)	−194(6)	319(14)	1.9
H(C5, G3)	98(5)	−137(7)	213(15)	1.5
H(C6A, G3)	204(4)	−201(6)	3(12)	2.0
H(C6B, G3)	182(5)	−111(7)	40(15)	2.0
H(O2, G3)	67(5)	−316(5)	613(14)	2.9
H(O3, G3)	178(6)	−186(7)	708(16)	2.4

Description and Discussion of the Structure

The structure and numbering scheme of the α-CDx–PSNa complex are shown in Fig. 1. The α-CDx molecule is nearly hexagonal. The 1-propanesulfonate anion is located in the channel which is formed by the stacking of the α-CDx rings (Fig. 2). Bond distances, angles, and conformation angles are given in Table 5. The geometrical data describing the macro-cyclic conformation of α-CDx ring are shown in Tables 6 and 7. The crystal structure and hydrogen-bonding scheme are shown in Figs. 4—7.

Bond Distances and Angles. The bond distances and angles for α-CDx in the present complex are not significantly different from those for the potassium acetate (ACK) complex,[13] the Methyl Orange complexes,[14] and the BSNa complex[15] which have channel-type structures. The average bond lengths for the three glucose residues are in good agreement with the average values for the α-D-glucose residues given by Arnott and Scott.[18] However, regarding bond angles, the average value for C(3)–C(4)–O(4) in α-CDx is 105.2°, which is smaller than the Arnott and Scott value of 110.4°. The C(1)–O(4′)–C(4′) angles of 117.5—119.0° are larger than those for the disaccharides.[18] These C(3)–C(4)–O(4) and C(1)–O(4′)–C(4′), however, are commonly observed in α-CDx complexes.

The abnormally short bond length and large angles are found in the 1-propanesulfonate anion (Fig. 3). This may be due to the disorder of the anion on the two-fold axis. The C(1, PS) atom is found to lie on the two-fold axis, but the thermal factor is relatively

* Table 4 is kept as a Document at the office of The Chemical Society of Japan. (Document No. 7706).

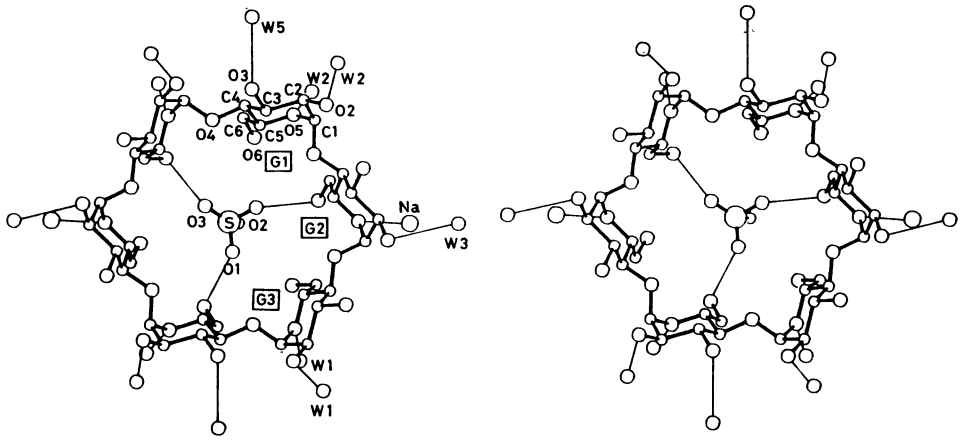

Fig. 1. A stereoview of the α-CDx–PSNa complex. Intermolecular O···O and O···Na contacts less than 3.0 Å are shown with thin lines. W1, W2, W3, and W5 denote oxygen atoms in water molecules.

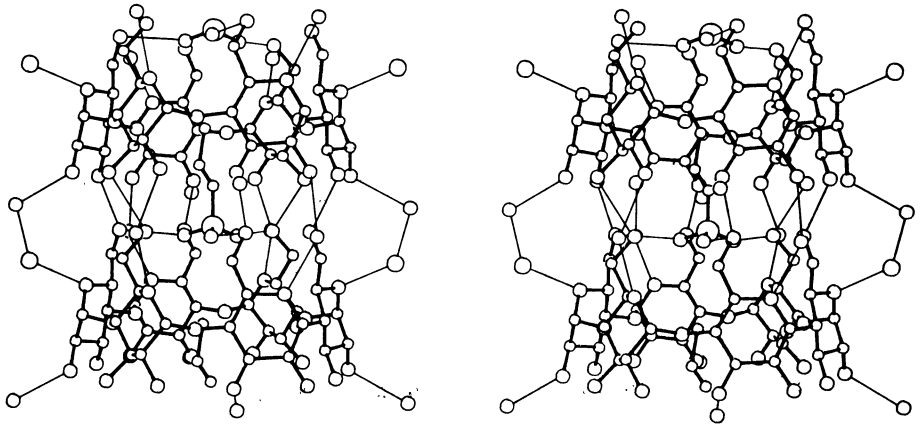

Fig. 2. A stereoview showing the stacking feature of α-CDx molecules. Intermolecular O···O and O···Na contacts less than 3.0 Å are shown with thin lines. Circles, in order of decreasing size, represent sulfur, sodium, oxygen, and carbon atoms.

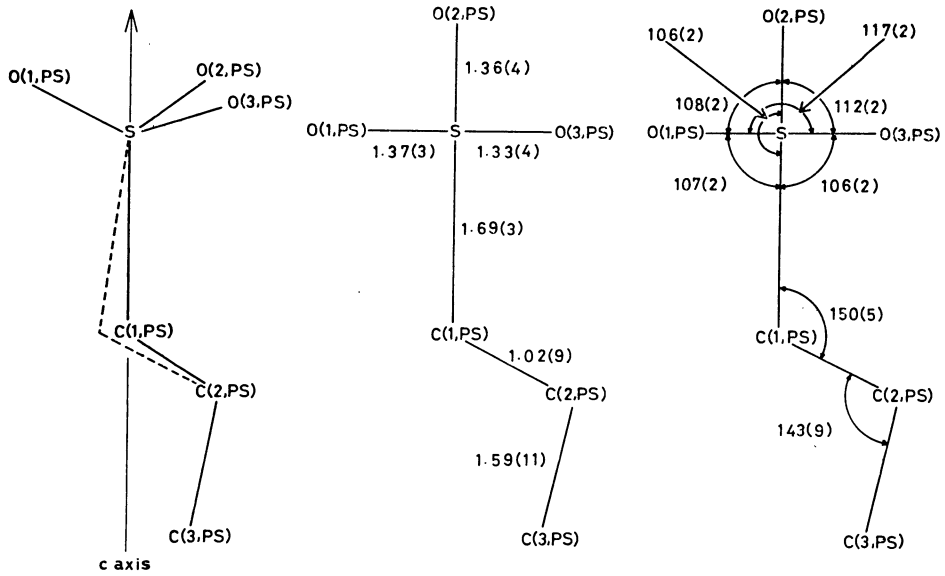

Fig. 3. Bond distances (l/Å) and angles (ϕ/°) in the 1-propanesulfonate anion. The short C(1,PS)–C(2,PS) distances and large valence angles of C(1,PS) and C(2,PS) are due to the small displacement of C(1,PS) from the c axis, as shown with the broken line.

TABLE 5. BOND DISTANCES (l/Å), ANGLES (ϕ/°), AND CONFORMATION ANGLES (ϕ/°) IN α-CYCLODEXTRIN

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

	G1	G2	G3	AVERAGE
C(1)-C(2)	1.520(14)	1.505(15)	1.537(15)	1.521
C(1)-O(5)	1.418(12)	1.430(13)	1.425(12)	1.424
C(1)-O(4′)	1.420(12)	1.438(12)	1.426(12)	1.428
C(2)-C(3)	1.547(15)	1.506(15)	1.534(14)	1.529
C(2)-O(2)	1.427(13)	1.438(13)	1.420(13)	1.428
C(3)-C(4)	1.520(14)	1.543(15)	1.523(14)	1.529
C(3)-O(3)	1.418(13)	1.443(13)	1.429(12)	1.430
C(4)-C(5)	1.560(14)	1.522(15)	1.545(14)	1.542
C(4)-O(4)	1.439(12)	1.456(12)	1.428(12)	1.441
C(5)-C(6)	1.522(15)	1.512(16)	1.502(15)	1.512
C(5)-O(5)	1.453(12)	1.464(13)	1.467(12)	1.461
C(6)-O(6)	1.434(13)	1.389(15)	1.415(14)	1.413

	G1	G2	G3	AVERAGE
C(2)-C(1)-O(5)	109.6(8)	109.0(8)	109.3(8)	109.3
C(2)-C(1)-O(4′)	107.3(8)	106.3(8)	106.6(8)	106.7
O(5)-C(1)-O(4′)	110.6(8)	109.3(8)	110.0(8)	110.0
C(1)-C(2)-C(3)	108.8(8)	110.2(9)	108.8(8)	109.3
C(1)-C(2)-O(2)	110.5(8)	110.3(8)	109.1(8)	110.0
C(3)-C(2)-O(2)	111.0(8)	111.2(8)	112.0(8)	111.4
C(2)-C(3)-C(4)	108.9(8)	109.3(8)	109.4(8)	109.2
C(2)-C(3)-O(3)	109.8(8)	111.7(8)	110.0(8)	110.5
C(4)-C(3)-O(3)	108.5(8)	107.2(8)	107.8(8)	107.8
C(3)-C(4)-C(5)	109.5(8)	110.5(9)	111.3(8)	110.4
C(3)-C(4)-O(4)	105.1(8)	104.7(8)	105.9(8)	105.2
O(5)-C(4)-O(4)	106.9(8)	107.3(8)	107.9(8)	107.4
C(4)-C(5)-C(6)	110.8(8)	112.8(9)	112.5(9)	112.0
C(4)-C(5)-O(5)	107.6(8)	108.7(9)	108.3(8)	108.2
C(6)-C(5)-O(5)	106.1(8)	106.1(9)	106.2(8)	106.1
C(5)-C(6)-O(6)	109.8(8)	112.6(10)	111.1(9)	111.2
C(1)-O(5)-C(5)	113.8(7)	114.5(8)	114.3(7)	114.2
C(1)-O(4′)-C(4′)	118.3(7)	119.0(7)	117.5(7)	118.3

	G1	G2	G3	AVERAGE
C(1)-C(2)-C(3)-C(4)	-57.3	-57.3	-57.1	-57.2
C(2)-C(3)-C(4)-C(5)	57.3	55.4	55.6	56.1
C(3)-C(4)-C(5)-O(5)	-57.7	-54.2	-54.4	-55.4
C(4)-C(5)-O(5)-C(1)	61.8	59.0	59.1	60.0
C(5)-O(5)-C(1)-C(2)	-63.5	-61.4	-62.6	-62.5
O(5)-C(1)-C(2)-C(3)	59.0	59.4	59.7	59.4
O(4′)-C(1)-C(2)-O(2)	61.0	64.9	63.2	63.0
O(2)-C(2)-C(3)-O(3)	62.2	61.6	64.2	62.7
O(3)-C(3)-C(4)-O(4)	-68.8	-68.3	-67.8	-68.3
O(4)-C(4)-C(5)-C(6)	73.5	74.9	72.7	73.7
O(5)-C(5)-C(6)-O(6)	69.8	66.1	67.1	67.7
C(4)-C(5)-C(6)-O(6)	-173.7	-175.0	-174.5	-174.4
C(2)-C(1)-O(4′)-C(4′)	-129.1	-132.1	-128.9	-130.0
O(5)-C(1)-O(4′)-C(4′)	111.4	110.5	112.7	111.5
C(1)-O(4′)-C(4′)-C(3′)	129.0	130.0	131.2	130.1
C(1)-O(4′)-C(4′)-C(5′)	-113.6	-110.7	-112.5	-112.3

TABLE 6. LEAST-SQUARES PLANES AND DEVIATIONS OF ATOMS (d/Å)

An asterisk (*) indicates an atom related by the two-fold symmetry.

(1) The plane through six O(4) atoms

$0.0000X + 0.0000Y + 1.0000Z = 3.0127$

O(4, G1)	0.003	O(4, G1)*	0.003
O(4, G2)	−0.017	O(4, G2)*	−0.017
O(4, G3)	0.014	O(4, G3)*	0.014

(2) Planes through C(2), C(3), C(5), and O(5) atoms in glucose residues

(i) G1 residue

$-0.2915X + 0.9491Y - 0.1197Z = 3.2812$

C(2, G1)	−0.007	O(5, G1)	0.007
C(3, G1)	0.006	C(1, G1)	−0.689[a]
C(5, G1)	−0.007	C(4, G1)	0.712[a]

(ii) G2 residue

$0.6815X + 0.7194Y - 0.1342Z = 3.3449$

C(2, G2)	0.004	O(5, G2)	−0.005
C(3, G2)	−0.004	C(1, G2)	−0.686[a]
C(5, G2)	0.004	C(4, G2)	0.676[a]

(iii) G3 residue

$0.9613X - 0.2399Y - 0.1352Z = 3.3559$

C(2, G3)	0.004	O(5, G3)	−0.004
C(3, G3)	−0.004	C(1, G3)	−0.697[a]
C(5, G3)	0.004	C(4, G3)	0.672[a]

a) Atoms not included in the plane.

TABLE 7. GEOMETRICAL DATA FOR THE CONFORMATION OF α-CYCLODEXTRIN

Asterisks (*) and primes (′) indicate atoms related by two-fold symmetry and atoms in the adjacent glucose residues, respectively.

Guest	Residue	Torsion-angle index (°)	O(4)···O(4′) distances (Å)	O(4)···O(4*) distances (Å)	O(2)···O(3′) distances (Å)
ACK	G1	127.1	4.29	8.31	2.82
	G2	136.3	4.20	8.50	2.85
	G3	127.9	4.25	8.67	2.86
	Average	130.4	4.25	8.49	2.85
BSNa	G1	122.0	4.36	8.19	2.83
	G2	136.4	4.12	8.52	2.93
	G3	128.1	4.28	8.81	2.85
	Average	128.8	4.25	8.51	2.87
MONa[a]	G1	127.8	4.38	8.08	2.84
	G2	133.5	4.07	8.56	2.87
	G3	129.6	4.28	8.82	2.78
	Average	130.3	4.24	8.49	2.83
MOK[b]	G1	121.0	4.35	8.06	2.84
	G2	136.1	4.09	8.54	2.89
	G3	128.7	4.28	8.84	2.81
	Average	128.6	4.24	8.48	2.85
PSNa	G1	126.6	4.27	8.40	2.83
	G2	127.5	4.21	8.45	2.94
	G3	128.5	4.24	8.59	2.88
	Average	127.5	4.24	8.48	2.88

a) Methyl Orange sodium salt. b) Methyl Orange potassium salt.

large (the isotropic thermal factor is 13.2 Å^2). The short C(1, PS)–C(2, PS) distance and large angles for S–C(1, PS)–C(2, PS) and C(1, PS)–C(2, PS)–C(3, PS) are reasonably explained as being due to a slight deviation of the C(1, PS) atom from the fwo-fold axis, as shown in Fig. 3, although this was not resolved on the electron-density map.

Conformation of α-Cyclodextrin. Each glucose residue is in a C1 chair conformation, and is α-1,4-linked. The primary hydroxyl groups show a *gauche-trans* conformation. None of the conformation angles in the glucose residues deviates from the mean value of the three glucose residues by more than 2.3°. The conformation angles in the pyranose ring are in good agreement with the Arnott and Scott values.[18] The α-CDx ring in the PSNa complex is more symmetrical than those in the ACK,[13] Methyl Orange,[14] and BSNa[15] complexes. The diagonal distances between the glycosidic oxygen atoms are 8.40, 8.45, and 8.59 Å (Table 7). In the Methyl Orange complexes and the BSNa complex, the α-CDx rings are elliptical due to the inclusion of the planar group; the O(4, G3)···O(4*, G3) distances are longer than the O(4, G1)···O(4*, G1) distances by 0.6—0.8 Å. The conformation angles involving C(1)–O(4′)–C(4′) linkages are in good agreement with each other for complexes having a channel-type structure. Therefore, the distortion of the α-CDx ring is not described by the conformation angles involving the glycosidic linkages.

French and Murphy[19] have discussed the deformation of the pyranose ring of the α-D-glucose residue in terms of the O(1)···O(4) distance and the torsion-angle index; the torsion-angle index is defined by $|\phi(C(1)-C(2))|+|\phi(C(2)-C(3))|+|\phi(C(5)-O(5))|+|\phi(O(5)-C(1))|-|\phi(C(3)-C(4))|-|\phi(C(4)-C(5))|$ when the torsion-angle of C(1)–C(2)–C(3)–C(4) is expressed by $\phi(C(2)-C(3))$. They have also shown that the O(1)···O(4) distance is closely related to the torsion-angle index. The O(4)···O(4′) distances in the PSNa complex are 4.24±0.03 Å, and this value agrees with 4.25 Å predicted for the α-CDx having regular hexagonal symmetry.[20] In the Methyl Orange complexes and the BSNa complex, the O(4)···O(4′) distances in the G2 residues are shorter by 0.24—0.31 Å than those in the G1 residues, although the average values are close to 4.25 Å. The different conformations of the pyranose ring result in different torsion-angle indices. In the PSNa complex, the torsion-angle indices are 126.6—128.5°. In the Methyl Orange complexes and the BSNa complex, the torsion-angle indices of the G2 residues are greater by 4.7—15.1° than those of the G1 residues. Therefore, the elliptical structure of α-CDx in the Methyl Orange complexes and the BSNa complex is ascribed to a deformation of the pyranose rings, that is, a difference between the conformation angles in the pyranose rings. No significant difference was observed for the O(2)···O(3′) distances, indicating that the distortion of the α-CDx ring does not affect the intramolecular hydrogen bonds in complexes with channel-type structures.

Geometry of Inclusion. α-CDx molecules are stacked in a head-to-tail arrangement, and form endless channels along the c axis. The α-CDx molecule has two-fold symmetry, but the asymmetric 1-propanesulfonate anion is located in a channel with statistical disorder on the two-fold axis. The anion is in contact with two α-CDx molecules. The propyl group contacts with the O(2), O(3) side of the α-CDx ring (Fig. 2). The sulfonato group is hydrogen-bonded to three of the primary hydroxyl groups, O(6*, G1), O(6, G2), and O(6*, G3) with oxygen-oxygen distances of 2.72, 2.80, and 2.75 Å, respectively. A different hydrogen-bonding contact was observed in the BSNa complex.[15] The sulfonato group forms hydrogen bonds with four of the primary hydroxyl groups, O(6, G1), O(6, G3), O(6*, G1), and O(6*, G3), with the respective distances being 2.80, 2.86, 2.71, and 2.86 Å. The primary hydroxyl groups of the G2 residues in the BSNa complex do not form hydrogen bonds because of the elliptical structure of α-CDx. In the ACK complex and the Methyl Orange complexes, the primary hydroxyl groups are also hydrogen-bonded to the ionized group of the guest molecule. It is noted that the sulfonato group and the acetate ion are nearly trigonal. The trigonal group fits well into the O(6) side of the α-CDx ring, as is shown in Figs. 1 and 2.

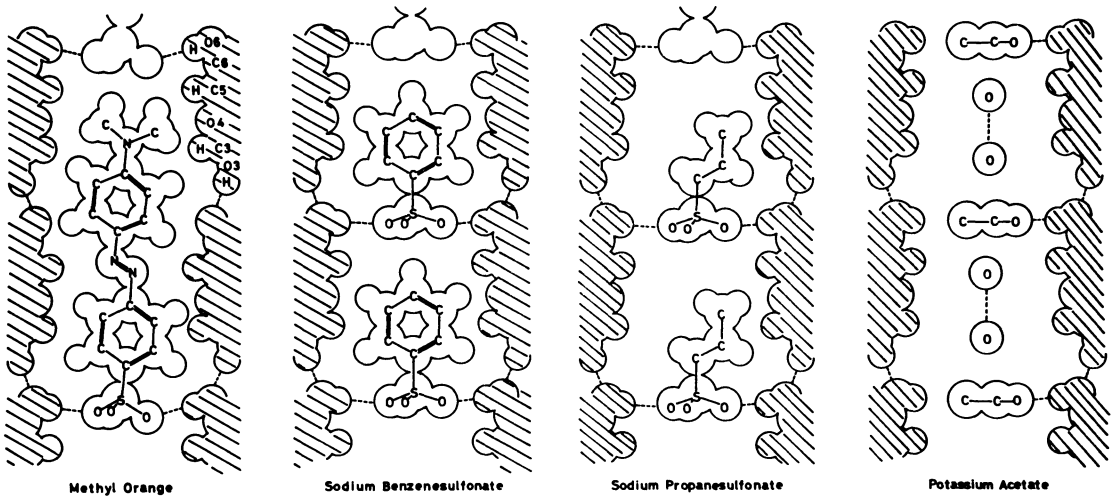

Fig. 4. A comparison of the arrangements of guest molecules in the channel. Broken lines denote hydrogen bonds.

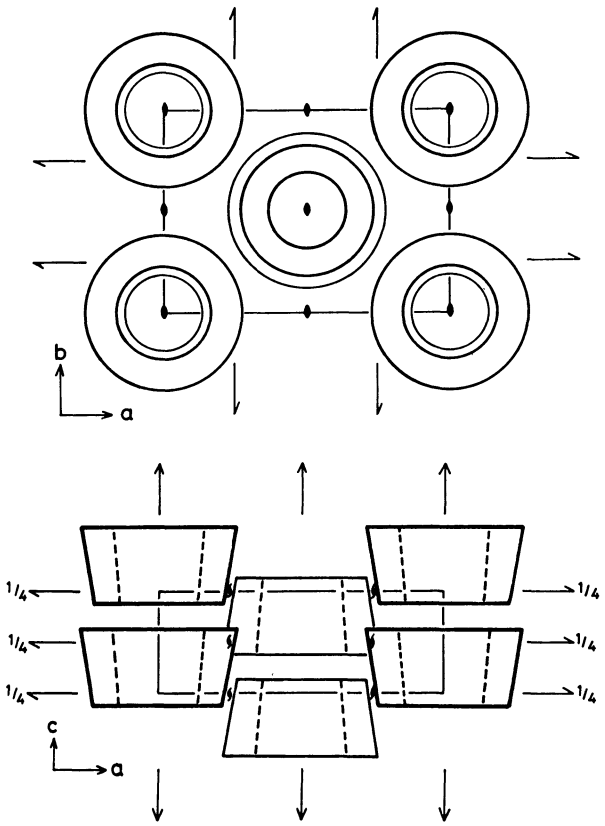

Fig. 5. A packing feature of α-CDx molecules in the crystal.

Schematic drawings of the arrangements of the guest molecules in the channel are shown in Fig. 4. A long molecule, as well as a small molecule, can be situated in the channel. In the ACK complex,[13] the acetate anion is so small that the empty space in the cavity is filled with two water molecules. On the other hand, a long guest anion extends through two α-CDx rings in the Methyl Orange complexes. For bulky guest molecules, the suitability of the guest molecule to the cavity may determine the geometry of the complex. In the interior of the cavity, the C(3)–H and C(5)–H groups are oriented at the center of the α-CDx cavity. The circle composed of six hydrogen atoms attached to the C(5) atoms forms the neck of the cavity. In the Methyl Orange complexes, the azo group is situated at the neck, but in the other complexes the guest molecules are not located at the neck. The conformation of the α-CDx ring in cage-type structures[5–9] changes remarkably with the dimension and the shape of the guest molecule. In channel-type structures,[13–15] however, the conformation change is quite small. This may be due to the fact that the framework of the α-CDx ring is held together by the hydrogen bonds between the α-CDx molecules and between α-CDx and the ionized group.

Crystal Structure and Hydrogen Bonds. The framework of the crystal is built up of endless cylinders formed by stacks of the α-CDx rings, as is shown in Fig. 5. The space outside the channel is filled with cations and water molecules (Fig. 6). The two adjacent α-CDx molecules are linked by O(2, G3)···O(W1)···O(5, G3), O(2, G1)···O(W2)···O(5, G1), and O(2, G2)···O(W3)···Na···O(5, G2) linkages except for O(3)···O(6) hydrogen bonds. The sodium ion is surrounded by five oxygen atoms, O(W1), O(W2), O(W3), O(W7), and O(5, G2), which form a distorted trigonal bipyramid (Fig. 7). The Na···O distance varies from 2.36 to 2.58 Å. These values are in good agreement with those of 2.34—2.55 Å found for the BSNa complex.[15] In the ACK complex[13] and the Methyl Orange complexes,[14] the cations are surrounded by six oxygen atoms which form a distorted octahedron (Fig. 8).

The hydrogen-bonding scheme is similar to that of the BSNa complex (Fig. 9). In the G1 residue, O(2, G1) and O(5, G1) are hydrogen-bonded to O(W2), while O(3, G1) is bonded to O(W5). Both of O(2,G3)

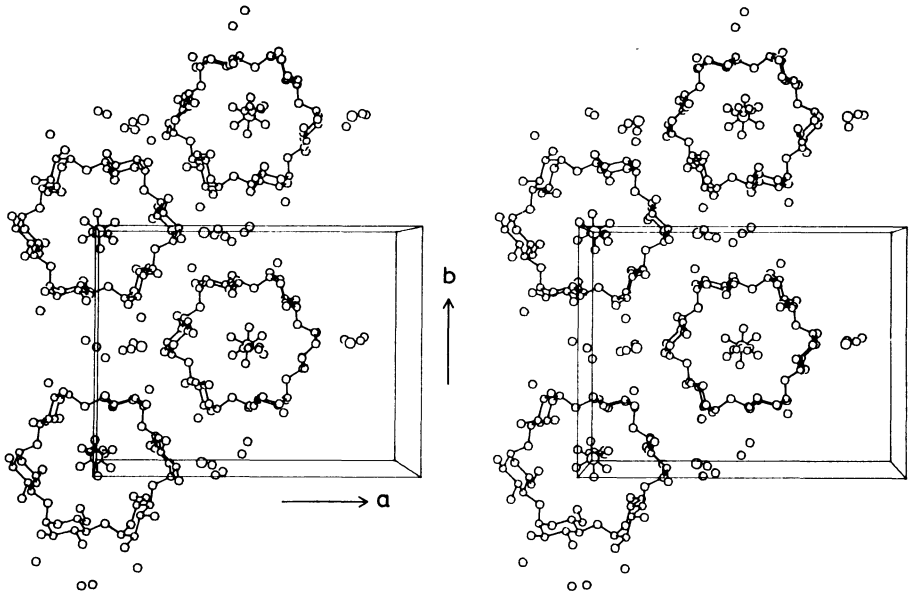

Fig. 6. A stereoview of the crystal structure viewed along the c axis.

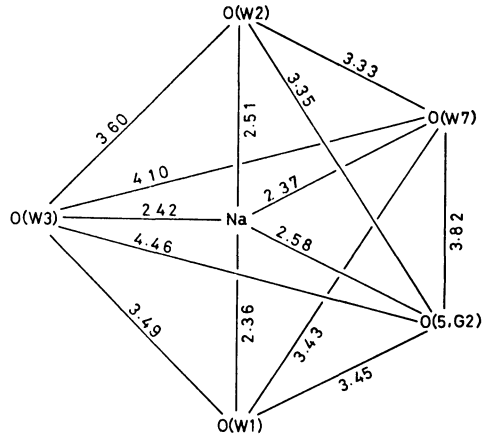

Fig. 7. Geometry of the sodium-ion coordination shell.

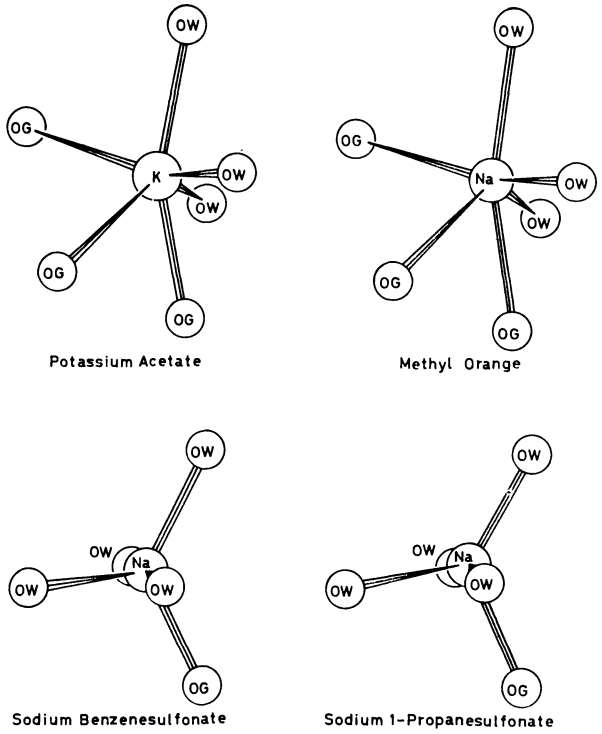

Fig. 8. Comparison of the geometry of the coordinations of alkali metal ions in the α-CDx complexes with the channel-type structure. OW and OG indicate oxygen atoms in water and glucose residue, respectively.

and O(5, G3) in the G3 residue form hydrogen bonds with O(W1). In the G2 residue, only O(2, G2) is involved in the hydrogen-bonding with water. The primary hydroxyl groups do not form hydrogen bonds with water, but they form hydrogen bonds with O(3) atoms in the adjacent α-CDx molecule.

Conclusions

So far, three channel-type structures with head-to-tail arrangement of α-CDx have been revealed; the ACK complex,[13] the Methyl Orange complex,[14] and the BSNa complex.[15] The PSNa complex has been

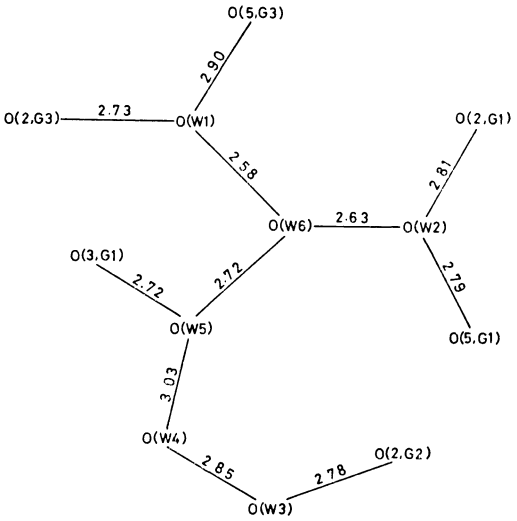

Fig. 9. The hydrogen-bonding scheme in crystals of α-CDx-PSNa nonahydrate.

shown to have the same crystal structure. It is noteworthy that these complexes crystallize in approximately isomorphous structures, although the shapes and dimensions of the guest molecules are quite different. The adjacent α-CDx molecules along the channel are connected by O(3)···O(6) hydrogen bonds. The hexagonal structure of α-CDx may be stabilized by hydrogen-bonding with the ionized group, which has a trigonal structures. The change in the macro-cyclic conformation of α-CDx, which is caused by the inclusion of the planar group, affects the lattice parameters. The elliptical α-CDx ring is parallel to the ac plane, and the long axis is oriented along the a axis. Therefore, the *a* dimensions of crystals of the Methyl Orange complexes and the BSNa complex are longer by 0.22—0.51 Å than that of the PSNa complex, while the *b* dimensions are shorter by 0.17—0.34 Å.

Another type of channel-type structure has been found in the α-CDx–polyiodide complexes.[16] In this case, the α-CDx molecules are arranged in a head-to-head fashion, that is, the O(2), O(3) side of the α-CDx ring is facing the same side of the adjacent α-CDx ring, and the O(6) side is facing the O(6) side. The conformation of the primary hydroxyl groups is *gauche-gauche*, and thus, these groups cannot form hydrogen bonds including the guest molecule. In the channel, the guest molecules are arranged with statistical disorder, forming an infinite polyiodide chain.

In both types of channel-type structures, the guest anions are included in the cavity, but the cations are located outside the α-CDx ring. This may be due to the fact that the α-CDx cavity has a relatively positively-charged character. The interior of the cavity contains C(3)–H, C(5)–H, H–C(6)–H, and O(4) whose charges were estimated to be 0.11, 0.14, 0.14, and −0.25, respectively.[15] Moreover, the C(3)–H and C-(5)–H groups are oriented to the center of the α-CDx ring. Therefore, it appears that the inclusion of an anion is more favorable than the inclusion of a cation. Outside the channel, the oxygen atoms surrounding the

TABLE 8. INTERMOLECULAR DISTANCES (l/Å) LESS THAN 3.0 Å

O (6, G2) -O (2, PS)	2.80	O (3, G1) -O (6, G1)	(i)	2.73
O (5, G2) -Na	2.58	O (3, G2) -O (6, G2)	(i)	2.78
O (W1) -Na	2.36	O (3, G3) -O (6, G3)	(i)	2.79
O (W2) -Na	2.51	O (6, G1) -O (1, PS)	(ii)	2.72
O (W7) -Na	2.37	O (6, G3) -O (3, PS)	(ii)	2.75
O (W1) -O (W6)	2.58	O (5, G1) -O (W2)	(iii)	2.79
O (W2) -O (W6)	2.63	O (W3) -O (W6)	(iii)	2.35[a]
O (W3) -O (W4)	2.85	O (2, G1) -O (W2)	(iv)	2.81
O (W5) -O (W6)	2.72	O (3, G1) -O (W5)	(iv)	2.72
O (W6) -Na	0.77[a]	Na -O (W3)	(v)	2.42
O (W5) -O (W7)	1.20[a]	O (5, G3) -O (W1)	(v)	2.90
O (W6) -O (W7)	2.04[a]	O (2, G2) -O (W3)	(vi)	2.78
		O (2, G3) -O (W1)	(vi)	2.73

Symmetry code	Symmetry operator		
None	x,	y,	z
i	x,	y,	$1+z$
ii	$-x$,	$-y$,	z
iii	$1/2-x$,	$1/2+y$,	$-z$
iv	$1/2-x$,	$1/2+y$,	$1-z$
v	$1/2-x$,	$-1/2+y$,	$-z$
vi	$1/2-x$,	$-1/2+y$,	$1-z$

a) The distance between disordered atoms.

cation form the coordination shell.

The geometry of the PSNa complex is similar to that of the BSNa complex. The hydrophobic propyl group is in contact with the O(2), O(3) side of the α-CDx ring, while the sulfonato group is hydrogen-bonded to the primary hydroxyl groups. When we consider a structure in an aqueous solution, the solvation effect is important as has been shown in a previous paper.[15] The transfer of the propyl group from the water environment to the interior of the cavity will reduce the solvation energy of PSNa, since the propyl group may be more likely to be found in the hydrophobic and nonpolar cavity than in the water environment. When the sulfonato group is included in the cavity, it may form hydrogen bonds with the primary hydroxyl groups. But, as has been suggested by Griffiths and Bender,[3] the hydrogen bonds do not appear to be important in the stabilization of the complex, since the sulfonato group may be hydrogen-bonded to water molecules in the uncomplexed state. Therefore, the inclusion of the propyl group will give a more stable complex than the inclusion of the sulfonato group in an aqueous solution.

The author would like to acknowledge the helpfull suggestions of Dr. Alfred D. French. The author also wishes to thank Dr. Hisashi Uedaira for supporting this study and for useful discussions. The stereoviews were drawn on a Hewlett-Packard 7200A graphic plotter. The computation was done on a HITAC 8450 computer in this laboratory.

References

1) J. A. Thoma and L. Stewart, "Starch: Chemistry and Technology," Vol. I, ed by R. L. Whistler and E. F. Pashall, Academic Press, New York (1965), pp. 209—249.
2) D. French, M. L. Levine, J. H. Pazur, and E. Norberg, *J. Am. Chem. Soc.*, **71**, 353 (1949).
3) D. W. Griffiths and M. L. Bender, *Adv. Catal.*, **23**, 209 (1973).
4) R. K. McMullan, W. Saenger, J. Fayos, and D. Mootz, *Carbohydr. Res.*, **31**, 37 (1973).
5) R. K. McMullan, W. Saenger, J. Fayos, and D. Mootz, *Carbohydr. Res.*, **31**, 211 (1973).
6) P. C. Manor and W. Saenger, *J. Am. Chem. Soc.*, **96**, 3630 (1974).
7) W. Saenger and M. Noltemeyer, *Chem. Ber.*, **109**, 503 (1976).
8) W. Saenger, R. K. McMullan, J. Fayos, and D. Mootz, *Acta Crystallogr., Sect. B*, **30**, 2019 (1974).
9) B. Hingerty and W. Saenger, *J. Am. Chem. Soc.*, **98**, 3357 (1976).
10) K. Harata, *Bull. Chem. Soc. Jpn.*, **48**, 2409 (1975).
11) W. Saenger, K. Beyer, and P. C. Manor, *Acta Crystallogr., Sect. B*, **32**, 120 (1976).
12) K. Harata, *Carbohydr. Res.*, **48**, 265 (1976).
13) A. Hybl, R. E. Rundle, and D. E. Williams, *J. Am. Chem. Soc.*, **87**, 2779 (1965).
14) K. Harata, *Bull. Chem. Soc. Jpn.*, **49**, 1493 (1976).
15) K. Harata, *Bull. Chem. Soc. Jpn.*, **49**, 2066 (1976).
16) M. Noltemeyer and W. Saenger, *Nature (London)*, **259**, 629 (1976).
17) "International Tables for X-Ray Crystallography," Vol. IV, Birmingham, Kynoch Press (1974), pp. 72—75.
18) S. Arnott and W. E. Scott, *J. Chem. Soc., Perkin Trans. 2*, **1972**, 324.
19) A. D. French and V. G. Murphy, *Carbohydr. Res.*, **27**, 391 (1973).
20) A. D. French and V. G. Murphy, Annual Meeting of Japanese Starch Society, Tokyo (1976).