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The Structure of the Cyclodextrin Complex. IX. The Crystal Structure of *α*-Cyclodextrin-*m*-Nitroaniline (1:1) Hexahydrate Complex

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The crystal structure of α-cyclodextrin–*m*-nitroaniline hexahydrate complex was determined by X-ray analysis. The crystal is monoclinic and the space group is $P2_1$ with $Z=2$. The cell dimensions are: $a=8.054(1)$, $b=13.508(1)$, $c=25.331(2)$ Å, and $\beta=103.90(1)$°. The structure was solved by an inspection of a Patterson map and by a trial-and-error method. The refinement was done by the block-diagonal least-squares method to the final *R*-value of 0.11 for 2351 reflections ($\sin\theta/\lambda<0.49$). α-Cyclodextrin molecules are stacked along the a axis in the head-to-tail fashion to form a channel-type structure. Most of the primary hydroxyl groups of α-cyclodextrin are in a *gauche-gauche* conformation and linked by hydrogen bonds directly or through water molecules to the secondary hydroxyl groups of the next α-cyclodextrin molecule along the channel. The guest *m*-nitroaniline molecules are linearly arranged in the channel. The α-cyclodextrin ring includes the nitrophenyl group, while the amino group protrudes outside from the secondary hydroxyl side of α-cyclodextrin and is hydrogen-bonded to a primary hydroxyl group of the next α-cyclodextrin molecule. Along the channel, *m*-nitroaniline molecules are linked to each other by a weak N–H···O hydrogen bond between the amino group and the nitro group. Columns formed by the stack of α-cyclodextrin are closely packed in the crystal, and intermolecular spaces are filled with water molecules which form many hydrogen bonds with each other and with α-cyclodextrin.

Cyclodextrins form a number of inclusion complexes with a variety of guest molecules. Cyclodextrin complexes with aromatic guests have been intensively studied, mainly in relation to an enzyme model.[1] Crystal structures of α-cyclodextrin complexes with *m*- and *p*-nitrophenols[2,3] have well interpreted the stereospecific acceleration of the hydrolysis rate of nitrophenyl acetates. α-Cyclodextrin also catalyzes hydrolysis of nitroacetanilides, and it has shown to act as a true catalyst in that case.[4]

Several α-cyclodextrin complexes with para-disubstituted benzenes have been investigated by the X-ray method.[2,3,5–7] The benzene ring has been found at the same position in those complexes in spite of various substituents. On the other hand, among the α-cyclodextrin complexes with meta-isomers, only the structure of a 1:2 complex with *m*-nitrophenol has been determined.[2] In the present work, we investigated the crystal structure of the α-cyclodextrin–*m*-nitroaniline complex. Unlike the *m*-nitrophenol complex, the *m*-nitroaniline complex gives a 1:1 host-guest stoichiometry; therefore, the inclusion geometry of the complex is of particular interest, for comparison with the *m*-nitrophenol complex as well as in relation to the catalytic reaction.

Experimental

Crystals of α-cyclodextrin–*m*-nitroaniline (1:1) hexahydrate complex were prepared by slowly cooling a hot aqueous solution of α-cyclodextrin saturated with *m*-nitroaniline. They are orange prisms elongated along the a axis. The determination of the lattice parameters and the intensity measurement were carried out on a Rigaku automatic four-circle diffractometer with graphite-monochromated Mo *Kα* radiation. The crystal was sealed in a quartz capillary with a drop of mother liquor since the crystal breaks up in air. 2677 independent reflections were obtained up to 40° in 2θ by using an ω-scan technique. But 324 reflections with $|F_o|<3\sigma(F)$ were treated as unobserved. No corrections were made for absorption and extinction.

Crystal Data: $C_{36}H_{60}O_{30}\cdot C_6H_7N_2O_2\cdot 6H_2O$, *F. W.*$=1220.1$, monoclinic, space group $P2_1$, $Z=2$, $a=8.054(1)$, $b=13.508(1)$, $c=25.331(2)$Å, $\beta=103.90(1)$°, $V=2675.1$ Å^3, $D_X=1.515$, $D_O=1.50$ g·cm^{-3}.

Determination and Refinement of the Structure

A Patterson map showed that the α-cyclodextrin ring is located nearly perpendicular to the a axis. The position and orientation of the molecule were determined by the trial-and-error method. At this stage, the position and orientation of each glucose residue were refined by the rigid-body least-squares method. *m*-Nitroaniline and water molecules were found on Fourier and difference-Fourier maps. Two primary hydroxyl groups (O(6,G2) and O(6,G3)) of α-cyclodextrin were found to be disordered. Their occupancies were estimated from an electron-density map, but they were not refined. The refinement of atomic parameters was carried out by the block-diagonal least-squares method by using isotropic temperature factors. The quantity minimized was $\sum w(|F_O|-|F_C|)^2$, with $w=1.0$ for all the reflections used. The final *R*-value was 0.11. The atomic scattering factors were taken from "International Tables for X-Ray Crystallography."[8] The atomic parameters are listed in Table 1. A table of observed and calculated structure factors and a table of bond distances, angles, and conformation angles in α-cyclodextrin are kept at the office of The Chemical Society of Japan (Document No. 8028).

Description and Discussion of the Structure

Structure of α-Cyclodextrin. The structure and the numbering scheme of the α-cyclodextrin–*m*-nitroaniline hexahydrate complex are shown in Fig. 1. The average bond distances and angles over six glucose residues are given in Fig. 2. These values are in good agreement

TABLE 1. FINAL POSITIONAL ($\times 10^4$) AND THERMAL PARAMETERS
Estimated standard deviations are given in parentheses. OC indicates an occupancy factor for disordered atom.

	x	*y*	*z*	*B*	*OC*
C(1,G1)	1882(26)	4734(—)	1106(8)	4.9(5)	
C(2,G1)	603(24)	4298(16)	1398(8)	4.2(4)	
C(3,G1)	985(22)	4629(14)	1993(7)	3.3(4)	
C(4,G1)	2854(22)	4453(14)	2263(7)	3.4(4)	
C(5,G1)	3981(24)	4892(16)	1941(8)	4.3(4)	
C(6,G1)	5981(29)	4679(19)	2153(10)	6.4(6)	
O(2,G1)	-1110(18)	4652(12)	1130(6)	5.7(3)	
O(3,G1)	-82(17)	4146(11)	2273(5)	4.7(3)	
O(4,G1)	3174(14)	4917(9)	2787(5)	3.2(2)	
O(5,G1)	3539(17)	4432(11)	1402(5)	5.2(3)	
O(6,G1)	6283(24)	3714(15)	2177(8)	9.0(5)	
C(1,G2)	2711(30)	8268(20)	303(10)	6.7(6)	
C(2,G2)	840(28)	7886(19)	74(9)	6.0(6)	
C(3,G2)	552(28)	7076(18)	485(9)	5.6(5)	
C(4,G2)	1943(27)	6227(17)	582(9)	5.3(5)	
C(5,G2)	3738(24)	6688(16)	708(8)	4.2(4)	
C(6,G2)	5017(33)	5912(22)	640(11)	7.8(7)	
O(2,G2)	-382(23)	8636(15)	72(8)	8.3(5)	
O(3,G2)	-1008(25)	6549(17)	226(8)	9.8(5)	
O(4,G2)	1654(17)	5753(12)	1069(5)	5.4(3)	
O(5,G2)	3871(18)	7477(12)	335(6)	5.7(3)	
O(6A,G2)	5112(81)	5658(54)	225(24)	9.3(17)	0.3
O(6B,G2)	6758(35)	6265(22)	797(11)	9.0(7)	0.7
C(1,G3)	4456(29)	11206(18)	1729(9)	5.9(5)	
C(2,G3)	2628(35)	11171(22)	1329(11)	8.2(7)	
C(3,G3)	2062(30)	10129(20)	1203(10)	6.6(6)	
C(4,G3)	3338(26)	9652(17)	930(8)	5.1(5)	
C(5,G3)	5074(25)	9690(16)	1318(8)	4.4(4)	
C(6,G3)	6467(30)	9244(20)	1061(9)	6.2(5)	
O(2,G3)	1604(24)	11672(16)	1666(8)	8.9(5)	
O(3,G3)	475(24)	10204(16)	807(8)	9.3(5)	
O(4,G3)	2750(17)	8684(11)	824(6)	5.2(3)	
O(5,G3)	5567(17)	10697(12)	1466(6)	5.3(3)	
O(6A,G3)	6606(43)	9690(28)	663(14)	7.7(9)	0.5
O(6B,G3)	8046(37)	9379(25)	1422(12)	6.1(7)	0.5
C(1,G4)	6158(26)	10870(17)	3911(8)	5.2(5)	
C(2,G4)	4543(26)	11513(17)	3630(8)	5.1(5)	
C(3,G4)	3789(24)	11185(16)	3059(8)	4.3(4)	
C(4,G4)	5272(26)	11190(16)	2721(8)	4.8(5)	
C(5,G4)	6754(24)	10586(16)	3033(8)	4.5(4)	
C(6,G4)	8305(31)	10671(21)	2760(10)	7.0(6)	
O(2,G4)	3349(18)	11400(12)	3963(6)	5.9(3)	
O(3,G4)	2455(18)	11856(12)	2804(6)	5.5(3)	
O(4,G4)	4435(16)	10693(11)	2233(5)	4.5(3)	
O(5,G4)	7378(18)	10933(11)	3579(6)	5.4(3)	
O(6,G4)	8696(20)	11695(13)	2727(7)	7.1(4)	
C(1,G5)	5889(22)	7247(14)	4688(7)	3.4(4)	
C(2,G5)	4735(24)	8022(15)	4858(7)	3.9(4)	
C(3,G5)	4455(22)	8840(13)	4458(7)	3.0(4)	
C(4,G5)	6105(21)	9329(14)	4368(7)	3.0(4)	
C(5,G5)	7230(22)	8476(14)	4236(7)	3.4(4)	
C(6,G5)	9144(31)	8792(19)	4194(10)	6.7(6)	
O(2,G5)	3204(16)	7517(11)	4883(5)	4.5(3)	
O(3,G5)	3501(17)	9665(11)	4651(5)	4.8(3)	
O(4,G5)	5538(15)	9870(9)	3884(5)	3.6(3)	
O(5,G5)	7461(15)	7713(10)	4642(5)	4.0(3)	
O(6,G5)	9889(22)	9269(15)	4664(7)	7.9(4)	
C(1,G6)	3908(22)	4368(15)	3245(7)	3.6(4)	
C(2,G6)	2815(23)	4543(15)	3680(7)	3.8(4)	
C(3,G6)	3015(20)	5630(15)	3861(6)	2.6(3)	
C(4,G6)	5809(20)	5650(13)	3861(6)	2.9(3)	
C(5,G6)	5008(22)	5865(14)	4072(7)	3.5(4)	
C(6,G6)	7715(24)	5864(14)	3728(8)	4.0(4)	
O(2,G6)	1063(15)	4351(10)	3435(5)	3.7(3)	
O(3,G6)	2229(16)	5726(10)	4308(5)	4.3(3)	
O(4,G6)	5000(13)	6910(9)	4159(4)	2.8(2)	
O(5,G6)	5627(14)	4629(9)	3468(5)	3.5(3)	
O(6,G6)	8611(17)	5373(11)	4194(5)	5.1(3)	
C(1,NP)	306(26)	7559(17)	2187(8)	5.0(5)	
C(2,NP)	1943(24)	7444(16)	2085(8)	4.2(4)	
C(3,NP)	3231(22)	7824(15)	2528(7)	3.7(4)	
C(4,NP)	1303(28)	8363(19)	3055(9)	8.3(5)	
C(5,NP)	3028(35)	8301(24)	2956(11)	5.7(7)	
C(6,NP)	55(31)	7981(20)	2652(10)	6.7(6)	
N(1,NP)	-1139(18)	7185(12)	1767(6)	7.5(3)	
N(2,NP)	5013(27)	7709(17)	2453(8)	3.7(6)	
O(1,NP)	5270(18)	7316(12)	2041(6)	5.6(3)	
O(2,NP)	6199(19)	7983(13)	2831(6)	6.4(4)	
O(W1)	-18(29)	1398(18)	4696(9)	11.4(6)	
O(W2)	352(21)	2497(14)	3734(7)	7.3(4)	
O(W3)	3699(25)	3175(16)	215(8)	9.6(5)	
O(W4)	6428(20)	3295(14)	1086(7)	7.0(4)	
O(W5)	8099(23)	3295(15)	4331(7)	8.4(5)	
O(W6)	8243(38)	11863(26)	1130(12)	16.9(10)	

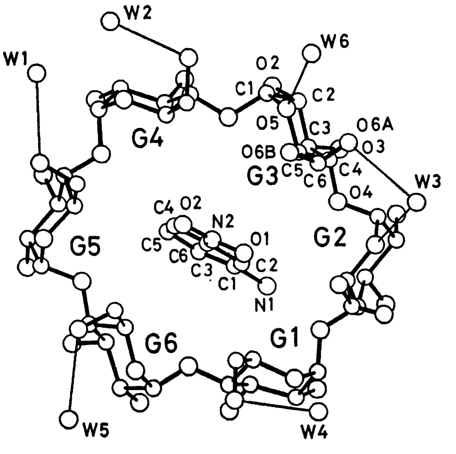

Fig. 1. Structure and numbering scheme of α-cyclodextrin-*m*-nitroaniline hexahydrate complex. O6A and O6B indicate disordered primary hydroxyl groups with *gauche-gauche* and *gauche-trans* conformations respectively. Water molecules are denoted by W1, W2, W3, W4, W5, and W6. Thin lines indicate intermolecular contacts less than 3.0 Å.

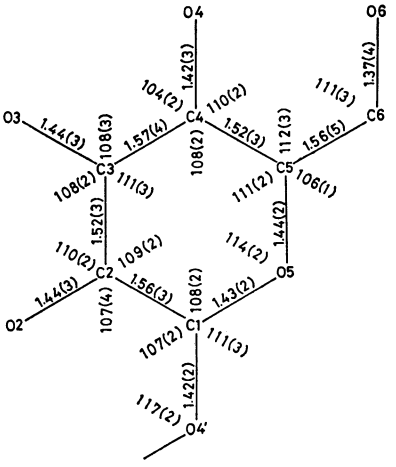

Fig. 2. Average bond distances (l/Å) and angles (ϕ/°) over six glucose residues. Standard deviations in parentheses were estimated according to the equation $\sigma=[\sum_{i=1}^{6}(x_i-\bar{x})^2/5]^{1/2}$, where x_i referes to the bond distance or angle in the i-th residue and $\bar{x}$ is the average value.

with those of other α-cyclodextrin complexes.[2,3,5–7] The primary hydroxyl groups in G2 and G3 residues are statistically disordered, and show *gauche-gauche* (O(6A)) and *gauche-trans* (O(6B)) conformations, while the others are in the *gauche-gauche* conformation. The geometrical data for the α-cyclodextrin ring are given in Tables 2 and 3. The α-cyclodextrin ring is elliptically distorted owing to the inclusion of the planar molecule, and elongated along the guest plane. The difference in the longest and shortest diagonal distances, which are measured between glycosidic oxygen atoms, is 0.99 Å. This value is nearly the same as the corresponding values found in the α-cyclodextrin complexes with para-disubstituted benzenes,[3] but is larger than the value found in the *m*-nitrophenol complex (0.40 Å).[2] The O(4)···O(4) distances between adjacent glucose residues and the torsion-angle indices indicate that the distortion of the pyranose ring is smaller than that

TABLE 2. GEOMETRICAL DATA FOR α-CYCLODEXTRIN RING

I. O(4)···O(4) distances.[a]

Distance(l/Å)		Distance(l/Å)	
O(4,G1)···O(4,G2)	4.38	O(4,G5)···O(4,G6)	4.10
O(4,G1)···O(4,G6)	4.36	O(4,G1)···O(4,G4)	8.03
O(4,G2)···O(4,G3)	4.14	O(4,G2)···O(4,G5)	8.99
O(4,G3)···O(4,G4)	4.43	O(4,G3)···O(4,G6)	8.55
O(4,G4)···O(4,G5)	4.21		

a) Estimated standard deviations are between 0.03 and 0.04 Å.

II. O(2)···O(3) distances between adjacent glucose residues.[b]

Distance(l/Å)		Distance(l/Å)	
O(2,G1)···O(3,G2)	3.45	O(2,G3)···O(3,G4)	2.81
O(3,G1)···O(2,G6)	2.74	O(2,G4)···O(3,G5)	2.91
O(2,G2)···O(3,G3)	2.80	O(2,G5)···O(3,G6)	2.84

b) Estimated standard deviations are between 0.03 and 0.04 Å.

III. Torsion-angle indices and tilt-angles for glucose residue.

Residue	Torsion-angle index (φ/°)	Tilt-angle (φ/°)
G1	132	17.6
G2	140	19.7
G3	120	10.1
G4	124	9.9
G5	126	11.2
G6	121	18.5

observed in the complexes with para-disubstituted benzenes.[3] Five O(2)···O(3) distances between adjacent glucose residues are in the range capable of hydrogen-bond formation (from 2.74 to 2.91 Å), while the O(2,G1)···O(3,G2) distance of 3.45 Å indicates no hydrogen bond. The six glycosidic oxygen atoms (O(4)) are in the same plane within the deviation of 0.16 Å. The tilt-angle of the glucose residue, which is measured between the plane through the six O(4) atoms and the plane through the O(4*), C(1), C(4), and O(4) atoms, is in the range from 9.9 to 19.7°. These values are relatively larger than those found in the α-cyclodextrin complexes with para-disubstituted benzenes (average value of 11.3°)[9] and *m*-nitrophenol (average value of 10.7°).[2]

TABLE 3. LEAST-SQUARES PLANES AND DEVIATIONS OF ATOMS FROM THE PLANE

The plane equation is of the $AX+BY+CZ=D$ form, where X, Y, and Z are the coordinates in Å units along the a, b, and c* axes, respectively.

I. The plane through the six O(4) atoms

$0.982X-0.187Y-0.038Z=-0.730$

O(4,G1)	0.07	O(4,G4)	−0.02
O(4,G2)	−0.16	O(4,G5)	−0.08
O(4,G3)	0.13	O(4,G6)	0.05

II. *m*-Nitroaniline

$0.036X+0.888Y-0.459Z=6.565$

C(1,NP)	0.00	C(6,NP)	−0.04
C(2,NP)	0.02	N(1,NP)	−0.01
C(3,NP)	0.01	N(2,NP)	0.01
C(4,NP)	0.08	O(1,NP)	0.01
C(5,NP)	−0.01	O(2,NP)	−0.07

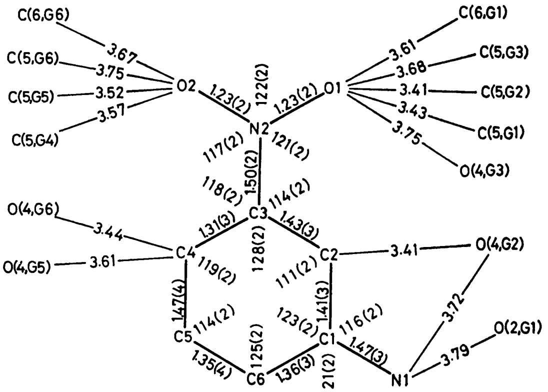

Fig. 3. Bond distances (l/Å) and angles (φ/°) in *m*-nitroaniline and selected intermolecular distances (l/Å) between *m*-nitroaniline and α-cyclodextrin. Estimated standard deviations in *m*-nitroaniline are given in parentheses, and those for intermolecular distances are in the range from 0.03 to 0.04 Å.

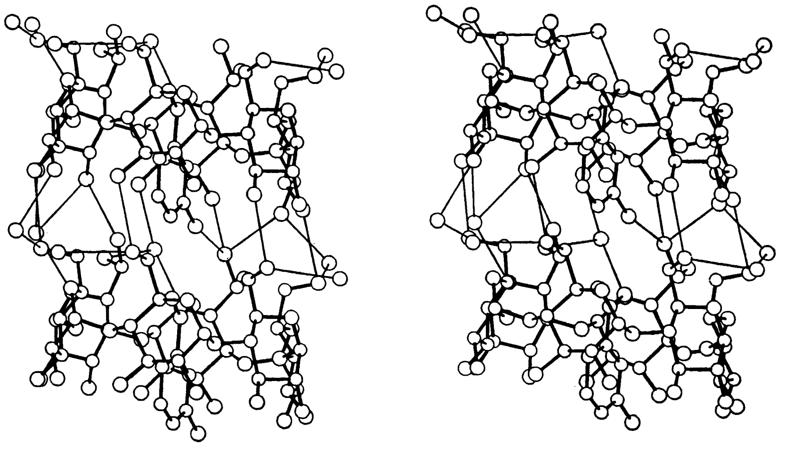

Fig. 4. A stereo-drawing of the packing feature of the complex with associated water molecules. Thin lines denote intermolecular contacts less than 3.0 Å.

Geometry of Inclusion. Figure 3 shows bond distances and angles in *m*-nitroaniline, and selected intermolecular distances between *m*-nitroaniline and α-cyclodextrin. α-Cyclodextrin molecules are stacked in head-to-tail fashion to form an endless channel, in which *m*-nitroaniline molecules are arranged as shown in Fig. 4. The nitrophenyl group is inserted into the α-cyclodextrin ring, while the amino group protrudes outside from the secondary hydroxyl side of α-cyclodextrin and forms a hydrogen bond with the primary hydroxyl group (O(6B,G2)) of the next α-cyclodextrin molecule. The nitrophenyl plane faces the G3 and G6 residues, and makes an angle of 83.5° with the plane through the six O(4) atoms. The shortest intermolecular distance is 3.41 Å, found in O(4,G2)···C(2,NP), and C(5,G2)···O(1,NP) contacts. The nitro group is surrounded by hydrogen atoms of C(5) methine groups and C(6) methylene groups. This inclusion geometry of the nitrophenyl group is quite similar to that found in the α-cyclodextrin–*p*-nitrophenol complex,[3] although the orientation of the nitrophenyl plane is slightly changed. In the *m*-nitroaniline complex, the nitrophenyl plane is parallel to the C(4)···C(4) diagonal of α-cyclodextrin, while the nitrophenyl group in the *p*-nitrophenol complex is parallel to the C(2)···C(2) diagonal. α-Cyclodextrin forms a 1:2 crystalline complex with *m*-nitrophenol[2] and also has a head-to-tail channel-type structure. Although one *m*-nitrophenol is located outside the α-cyclodextrin column, the other one is arranged in the channel. In that case, only the nitro group is inserted into the α-cyclodextrin ring, and therefore, the *m*-nitrophenol molecule is more loosely bound than the *m*-nitroaniline molecule.

In the *m*-nitroaniline complex, guest molecules are linearly arranged in the channel (Fig. 4). Some short contacts are observed between neighboring *m*-nitroaniline molecules: N(1,NP)···O(1,NP) distance of 3.14 Å and C(6,NP)···O(2,NP) distance of 3.24 Å. The O···N distance suggests a weak N–H···O hydrogen bond. The short C···O distance also shows that the *m*-nitroaniline molecules are very closely packed in the channel. Such short contacts were not observed in the *m*-nitrophenol complex.[2] The *m*-nitrophenol molecule is more tilted with respect to the channel axis, and the repetition unit along the channel (8.15 Å) is longer than that found in the *m*-nitroaniline complex (8.05 Å). As the result, the adjacent *m*-nitrophenol molecules are apart by 3.40 Å which is found between the phenolic hydroxyl group and the nitro group.

The tight packing of the guest *m*-nitroaniline molecule seems to affect its electronic state. Crystals of *m*-nitroaniline are dark yellow. When it forms the crystalline complex with α-cyclodextrin, the color changes to bright orange. This typical color change associated with the complex formation has been observed in the α-cyclodex-

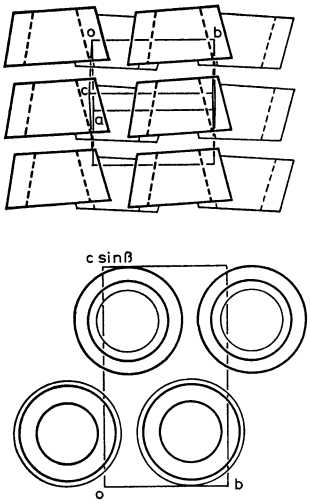

Fig. 5. Schematic drawings of the packing feature of α-cyclodextrin in the crystal.

TABLE 4. INTERMOLECULAR DISTANCES LESS THAN 3.0 Å

Distance(l/Å)	Code	Distance(l/Å)	Code
O(2,G1)···O(2,G7)	2.78 (c)	O(2,G4)···O(W2)	2.77 (b)
O(2,G1)···O(W4)	2.68 (c)	O(3,G4)···O(6,G4)	2.99 (c)
O(3,G1)···O(6,G1)	2.94 (c)	O(6,G4)···O(W2)	2.80 (e)
O(6,G1)···O(W1)	2.85	O(2,C5)···O(W5)	2.68 (h)
O(2,G2)···O(W3)	2.67 (f)	O(3,G5)···O(6,G5)	2.97 (c)
O(3,G2)···O(6B,G2)	2.60 (c)	O(5,G5)···O(W1)	2.92 (h)
O(5,G2)···O(W3)	2.82 (g)	O(6,G5)···O(W1)	2.88 (e)
O(6A,G2)···O(6A,G3)	2.68 (i)	O(2,G6)···O(W2)	2.72
O(6B,G2)···N(1,NP)	2.91 (a)	O(3,G6)···O(6,G6)	2.90 (c)
O(2,G3)···O(W6)	2.72 (c)	O(6,G6)···O(W5)	2.87
O(3,G3)···O(6B,G3)	2.99 (c)	O(W1)···O(W2)	2.93
O(3,G3)···O(W6)	2.93 (c)	O(W2)···O(W5)	2.84 (c)
O(5,G3)···O(W6)	2.83	O(W3)···O(W4)	2.72
O(6,G3)···O(W3)	2.99 (g)	O(W4)···O(W6)	2.61 (d)

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

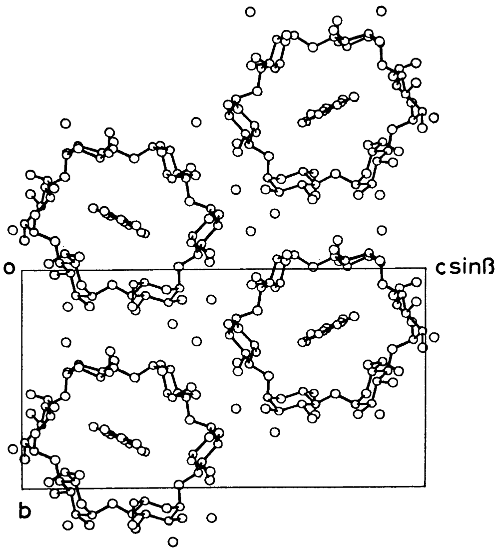

Fig. 6. Crystal structure viewed down along the a axis.

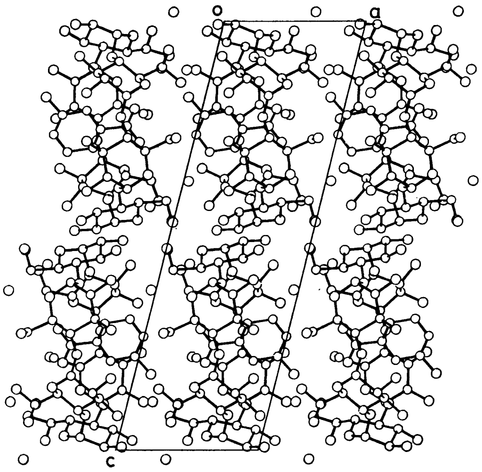

Fig. 7. Crystal structure viewed down along the b axis.

trin–polyiodide complexes,[10] where the extensive delocalization of electrons has been suggested as an explanation. In the *m*-nitroaniline complex, the charge-transfer may also occur through the hydrogen bond between the amino group and the nitro group.

Crystal Structure. Schematic drawings of the packing features of α-cyclodextrin molecules in the crystal are shown in Fig. 5. Projections of the crystal structure are given in Figs. 6 and 7. Intermolecular distances less than 3.0 Å are given in Table 4. Most of these contacts are considered to be hydrogen bonds. α-Cyclodextrin molecules are stacked along the a axis in head-to-tail fashion, thus forming an endless column. The packing of α-cyclodextrin molecules differes from other head-to-tail channel-type structures with the space group of $P2_12_12$,[2,11] in which the α-cyclodextrin molecule is located on the two-fold axis. On the other hand, the α-cyclodextrin ring in the *m*-nitroaniline complex is not perpendicular to the channel axis, but makes an angle of 79.0°. Owing to such a tilt of the α-cyclodextrin ring and the *gauche-gauche* conformation of the primary hydroxyl groups, intermolecular contacts between α-cyclodextrin molecules are quite different from those found in the $P2_12_12$ crystals. The adjacent α-cyclodextrin molecules along the channel are linked by O(2)···water···O(6) hydrogen bonds for G1, G4, and G6 residues and O(2)···water···O(5) hydrogen bonds for G2 and G3 residues, as well as by O(3)···O(6) hydrogen bonds for each glucose residue (Fig. 4). The O(2)···water···O(5) hydrogen bond is observed when the primary hydroxyl group is in the *gauche-trans* conformation. Neighboring α-cyclodextrin columns are closely packed in the crystal (Fig. 6) and are linked by hydrogen bonds directly or through water molecules. On the other hand, such close packing is not found in the $P2_12_12$ crystals, in which there is a sufficient intermolecular space to accommodate a part of the guest molecules. Water molecules fill intermolecular spaces. They are separated into two groups. W1, W2, and W5 are located in the space encircled by G4, G5, and G6 residues. They are connected to each other by a W1···W2···W5 hydrogen-bonding linkage. On the other hand, W3, W4, and W6, which are also linked by hydrogen bonds, are surrounded by G1, G2, and G3 residues.

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