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# The Structure of the Cyclodextrin Complex. XIII. Crystal Structure of β-Cyclodextrin-1,4-Diazabicyclo[2.2.2]octane Complex Tridecahydrate

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The crystal structure of β-cyclodextrin–1,4-diazabicyclo[2.2.2]octane complex tridecahydrate was determined by the X-ray method. The crystal is monoclinic with the space group $P2_1$, $Z=2$, $a=15.395(2)$, $b=16.598(1)$, $c=15.441(2)$ Å, and $\beta=117.35(1)°$. The structure was solved by inspection of a Patterson map and a trial-and-error method combined with the rigid-body least-squares technique and refined by the block-diagonal least-squares method to the final $R$-value of 0.048 for 5649 reflections ($\sin\theta/\lambda<0.61$). The β-cyclodextrin molecule is in the shape of a distorted and truncated heptagonal pyramid. Two of seven primary hydroxyl groups are in a *gauche-trans* conformation, the others being in a *gauche-gauche* conformation. Secondary hydroxyl groups form intramolecular hydrogen bonds between adjacent glucose residues. The guest 1,4-diazabicyclo[2.2.2]octane is almost fully included in the cavity of β-cyclodextrin. Its methylene groups are in van der Waals contact with the methine groups and the glycosidic oxygen atoms at the interior surface of β-cyclodextrin, while two nitrogen atoms form hydrogen bonds with a water molecule and a secondary hydroxyl group of the neighboring β-cyclodextrin. β-Cyclodextrin molecules are arranged nearly parallel to the crystallographic ac plane to form a corrugated sheet of molecular layer. All of the thirteen water molecules fill vacant spaces between the molecular layers, forming a hydrogen-bond network in the crystal.

β-Cyclodextrin forms many crystalline inclusion complexes with a variety of guest molecules. Crystals of uncomplexed β-cyclodextrin[1)] and its ethanol complex[2)] have a cage-type structure in which β-cyclodextrin molecules are arranged in a zigzag mode. Crystal structures of the complexes with 1-propanol[3)] and some benzene derivatives[4)] consist of a dimer unit formed by two β-cyclodextrin molecules with their secondary hydroxyl sides facing each other. In this paper, we present a crystal structure of the β-cyclodextrin-1,4-diazabicyclo[2.2.2]octane (1,4-DO) complex; its molecular packing is different from those found previously. The host-guest geometry of the complex is interesting in relation to the 1,4-DO catalyzed hydrolysis of acyl-β-cyclodextrin.

## Experimental

β-Cyclodextrin and 1,4-DO in a 1 : 1 molar ratio were dissolved in a hot aqueous solution, and the solution was allowed to stand at room temperature. Colorless and prismatic crystals were obtained. Lattice parameters and reflection intensities were measured on a Nicolet P3/F diffractometer with graphite-monochromated Cu *Kα* radiation. The crystal was sealed in a quartz capillary with a drop of mother liquor since it breaks up in air. 5649 independent reflections with $|F_o|\geqq 3\sigma(F)$ were collected up to 140° in $2\theta$ by using $\theta$-$2\theta$ scan mode. No corrections were made for absorption or extinction effect.

*Crystal Data*: $C_{42}H_{70}O_{35}\cdot C_6H_{12}N_2\cdot 13H_2O$, $F.W.=1481.4$ monoclinic, space group $P2_1$, $Z=2$, $a=15.395(2)$, $b=16.598(1)$, $c=15.441(2)$ Å, $\beta=117.35(1)°$, $V=3504.7(7)$ Å$^3$, $D_x=1.404$, $D_m=1.40$ g cm$^{-3}$.

## Determination and Refinement of the Structure

A Patterson map showed that the *pseudo* heptagonal axis of β-cyclodextrin makes an angle of *ca.* 10° against the crystallographic b axis. The rotation around the molecular axis and the translational parameters along the a and c axes were determined by a trial-and-error method. After the correction of the position and orientation of each glucose residue by the rigid-body least-squares technique, atomic parameters were refined by the block-diagonal least-squares method. Successive Fourier and difference-Fourier syntheses revealed the positions of 1,4-DO and hydrated water molecules. An occupancy factor of disordered water molecules (W10A and W10B) was estimated from an electron-density map, but it was not refined. Hydrogen atoms were found on a difference-Fourier map. Further refinement of the structure by the block-diagonal least-squares method converged the $R$-value to 0.048. The quantity minimized was $\sum w(|F_o|-|F_c|)^2$ with $w=1.0$ for all the reflections. Atomic scattering factors were taken from the "International Tables for X-Ray Crystallography."[6)] Final atomic coordinates and $B_{eq}$ of non-hydrogen atoms are given in Table 1. Tables of the observed and calculated structure factors, anisotropic temperature factors, atomic parameters of hydrogen atoms, bond distances, angles, and conformation angles of β-cyclodextrin are kept at The Chemical Society of Japan (Document No. 8232). The computation was carried out on a FACOM M-200 computer at the RIPS Center, Tsukuba.

## Description and Discussion of the Structure

*Outline of the Structure.* A numbering scheme of the β-cyclodextrin–1,4-DO complex is shown in Fig. 1. β-Cyclodextrin is in the shape of a distorted and truncated heptagonal pyramid with the wide aperture at the secondary hydroxyl side and the smaller aperture at the primary hydroxyl side. The guest 1,4-DO molecule is situated in the β-cyclodextrin cavity at the secondary hydroxyl side (Fig. 2). β-Cyclodextrin molecules are arranged nearly parallel to the ac plane and form a corrugated sheet of molecular layers (Fig. 3). All the water molecules are located outside the β-cyclodextrin

Table 1. Final atomic coordinates ($\times 10^4$) and $B_{eq}$ ($B$/Å$^2$) of non-hydrogen atoms[a,b)]

| | $x$ | $y$ | $z$ | $B_{eq}$/Å$^2$ |
|---|---|---|---|---|
| C(1,G1) | 3272(4) | 2895(4) | -187(4) | 2.79 |
| C(2,G1) | 2705(4) | 3679(4) | -383(4) | 3.15 |
| C(3,G1) | 1909(4) | 3621(3) | -65(4) | 3.05 |
| C(4,G1) | 1262(4) | 2893(3) | -532(4) | 2.75 |
| C(5,G1) | 1885(4) | 2133(3) | -334(4) | 2.80 |
| C(6,G1) | 1302(4) | 1395(3) | -877(5) | 3.78 |
| O(2,G1) | 3367(3) | 4313(3) | 146(3) | 3.69 |
| O(3,G1) | 1313(3) | 4334(2) | -356(3) | 3.65 |
| O(4,G1) | 645(2) | 2823(3) | -77(2) | 2.92 |
| O(5,G1) | 2614(2) | 2256(2) | -668(3) | 2.89 |
| O(6,G1) | 762(3) | 1517(3) | -1895(3) | 3.99 |
| C(1,G2) | 6500(4) | 2208(3) | 3062(4) | 2.66 |
| C(2,G2) | 6351(4) | 3058(3) | 2630(4) | 2.55 |
| C(3,G2) | 5267(4) | 3238(3) | 2075(4) | 2.51 |
| C(4,G2) | 4783(3) | 2600(3) | 1282(4) | 2.26 |
| C(5,G2) | 4974(3) | 1763(3) | 1742(3) | 2.40 |
| C(6,G2) | 4590(4) | 1088(3) | 1008(4) | 3.04 |
| O(2,G2) | 6849(3) | 3634(2) | 3384(3) | 3.11 |
| O(3,G2) | 5135(3) | 4021(2) | 1654(3) | 3.08 |
| O(4,G2) | 3749(2) | 2761(2) | 838(2) | 2.51 |
| O(5,G2) | 6013(3) | 1637(2) | 2302(2) | 2.52 |
| O(6,G2) | 4961(3) | 1150(3) | 317(3) | 3.60 |
| C(1,G3) | 6940(4) | 1437(4) | 6586(4) | 3.43 |
| C(2,G3) | 7575(4) | 2094(4) | 6456(4) | 3.71 |
| C(3,G3) | 7053(4) | 2470(4) | 5449(4) | 3.17 |
| C(4,G3) | 6736(4) | 1807(4) | 4666(4) | 2.84 |
| C(5,G3) | 6132(4) | 1169(4) | 4868(4) | 3.10 |
| C(6,G3) | 5922(5) | 447(4) | 4191(5) | 4.51 |
| O(2,G3) | 7814(3) | 2689(3) | 7194(3) | 4.43 |
| O(3,G3) | 7726(3) | 3004(3) | 5325(3) | 4.15 |
| O(4,G3) | 6128(2) | 2179(2) | 3748(2) | 2.63 |
| O(5,G3) | 6684(3) | 852(2) | 5838(3) | 3.39 |
| O(6,G3) | 5295(3) | -117(3) | 4327(3) | 4.33 |
| C(1,G4) | 4370(4) | 1782(3) | 7958(4) | 2.89 |
| C(2,G4) | 5249(4) | 2345(4) | 8371(4) | 2.91 |
| C(3,G4) | 5623(4) | 2464(4) | 7630(4) | 2.98 |
| C(4,G4) | 5843(4) | 1652(4) | 7326(4) | 3.04 |
| C(5,G4) | 4947(4) | 1110(3) | 6952(4) | 3.17 |
| C(6,G4) | 5161(5) | 255(4) | 6763(5) | 4.48 |
| O(2,G4) | 4973(3) | 3096(3) | 8640(3) | 3.76 |
| O(3,G4) | 6517(3) | 2932(3) | 8047(3) | 3.70 |
| O(4,G4) | 6090(3) | 1806(2) | 6539(2) | 2.96 |
| O(5,G4) | 4631(3) | 1046(2) | 7704(3) | 3.17 |
| O(6,G4) | 4268(4) | -204(3) | 6289(4) | 5.50 |
| C(1,G5) | 623(4) | 2569(3) | 5944(4) | 2.64 |
| C(2,G5) | 1298(4) | 3193(3) | 6677(4) | 2.78 |
| C(3,G5) | 2336(4) | 3096(3) | 6811(4) | 2.55 |
| C(4,G5) | 2673(4) | 2235(3) | 7116(4) | 2.36 |
| C(5,G5) | 1955(4) | 1641(3) | 6360(4) | 2.49 |
| C(6,G5) | 2177(4) | 760(3) | 6662(4) | 2.95 |
| O(2,G5) | 952(3) | 3987(2) | 6325(3) | 3.38 |
| O(3,G5) | 2993(3) | 3615(2) | 7568(3) | 3.01 |
| O(4,G5) | 3606(2) | 2160(2) | 7124(2) | 2.44 |
| O(5,G5) | 983(2) | 1787(2) | 6262(3) | 2.58 |
| O(6,G5) | 2158(3) | 631(2) | 7571(3) | 3.03 |
| C(1,G6) | -1416(4) | 2984(3) | 2116(4) | 2.59 |
| C(2,G6) | -1223(4) | 3727(3) | 2761(4) | 2.60 |
| C(3,G6) | -290(4) | 3604(3) | 3720(4) | 2.70 |
| C(4,G6) | -340(4) | 2820(3) | 4194(4) | 2.35 |
| C(5,G6) | -492(4) | 2128(3) | 3479(4) | 2.46 |
| C(6,G6) | -538(4) | 1301(3) | 3868(4) | 3.21 |
| O(2,G6) | -1128(3) | 4409(2) | 2251(3) | 3,06 |
| O(3,G6) | -211(3) | 4281(2) | 4343(3) | 3.21 |
| O(4,G6) | 604(2) | 2730(2) | 5028(2) | 2.28 |
| O(5,G6) | -1420(2) | 2270(2) | 2621(2) | 2.50 |
| O(6,G6) | -1302(3) | 1245(3) | 4146(3) | 3.93 |
| C(1,G7) | -372(4) | 2645(4) | -682(4) | 2.85 |
| C(2,G7) | -980(4) | 3380(4) | -683(4) | 3.10 |
| C(3,G7) | -801(4) | 3544(3) | 347(4) | 2.73 |
| C(4,G7) | -1008(4) | 2795(3) | 774(4) | 2.55 |
| C(5,G7) | -445(4) | 2063(3) | 699(4) | 3.22 |
| C(6,G7) | -775(6) | 1282(4) | 963(5) | 5.37 |
| O(2,G7) | -740(3) | 4057(3) | -1108(3) | 4.01 |
| O(3,G7) | -1443(3) | 4188(2) | 316(3) | 3.53 |
| O(4,G7) | -690(2) | 2645(2) | 1794(2) | 2.52 |
| O(5,G7) | -624(3) | 1972(2) | -305(3) | 3.14 |
| O(6,G7) | -1851(5) | 1196(4) | 255(5) | 8.40 |
| N(1,DO) | 2623(4) | 2495(4) | 3387(4) | 5.11 |
| C(2,DO) | 3623(8) | 2447(7) | 3568(12) | 13.85 |
| C(3,DO) | 4228(7) | 3170(7) | 4232(10) | 11.82 |
| N(4,DO) | 3591(4) | 3738(3) | 4336(4) | 3.99 |
| C(5,DO) | 3127(9) | 3373(8) | 4855(8) | 11.37 |
| C(6,DO) | 2607(8) | 2572(7) | 4336(7) | 9.25 |
| C(7,DO) | 2175(9) | 3235(6) | 2825(8) | 8.87 |
| C(8,DO) | 2839(9) | 3967(6) | 3386(8) | 9.16 |
| O(W1) | -2759(3) | 251(3) | 2793(4) | 4.78 |
| O(W2) | -708(5) | 179(7) | 7692(5) | 11.02 |
| O(W3) | -3126(4) | 682(4) | 880(4) | 6.12 |
| O(W4) | -3426(4) | 3894(4) | 49(4) | 6.14 |
| O(W5) | -1645(5) | 4293(4) | 6761(5) | 8.61 |
| O(W6) | 6034(6) | 4465(4) | 7630(5) | 8.86 |
| O(W7) | 3448(6) | 154(6) | 4376(5) | 10.13 |
| O(W8) | 1652(6) | 1073(4) | 2499(6) | 10.03 |
| O(W9) | 1825(6) | 5294(4) | 1266(4) | 7.92 |
| O(W10A) | 619(5) | 5685(4) | 3996(5) | 4.95 |
| O(W10B) | -1246(12) | 311(11) | 5556(12) | 5.83 |
| O(W11) | 390(5) | 4638(4) | 7541(4) | 8.86 |
| O(W12) | 3825(3) | 39(3) | 8941(3) | 3.42 |
| O(W13) | 2395(5) | 394(4) | 1303(5) | 7.07 |

a) Occupancy factors of O(W10A) and O(W10B) are 0.7 and 0.3, respectively. b) $B_{eq}=8\pi^2(u_1^2+u_2^2+u_3^2)/3$, where $u_i$ is the root-mean-square deviation in the $i$-th principal axis of the thermal ellipsoid.

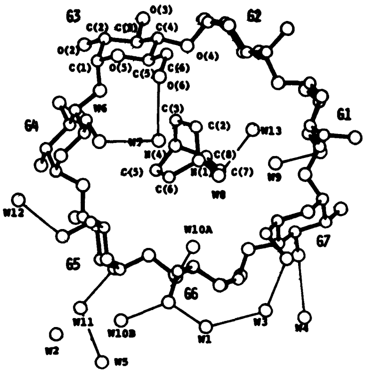

Fig. 1. A numbering scheme of β-cyclodextrin-1,4-DO complex tridecahydrate.

cavity. They fill the intermolecular space and form the hydrogen-bond network in the crystal.

*Conformation of β-Cyclodextrin.* β-Cyclodextrin consists of seven α-1,4-linked D-glucose residues of the $^4C_1$ chair conformation. Except for the orientation of the C(6)–O(6) bonds, the conformations of seven glucose residues are nearly identical with each other. The primary hydroxyl groups show two different types of conformations (Fig. 1). In G3 and G4 residues, they are inclined toward the β-cyclodextrin axis, having a *gauche-trans* conformation. This conformation is held by the hydrogen-bonds linking these hydroxyl groups through the W7 water molecule. The other primary hydroxyl groups in a *gauche-gauche* conformation turn away from the center of the β-cyclodextrin ring.

Average bond distances and angles for seven glucose residues are shown in Fig. 4. Characteristics similar to those found in α-cyclodextrin complexes[7)] are also observed in them; the C(2)–C(3) and C(3)–C(4) bonds are slightly shorter than the C(1)–C(2) and C(4)–C(5) bonds, and the C(3)–C(4)–O(4) angle is smaller than the ideal tetrahedral angle. This indicates that the glucose conformation is only slightly affected by the size of the macrocyclic ring. A significant difference is observed in the glycosidic oxygen angle between α- and β-cyclodextrin. The average value of 117.4° is smaller than the corresponding angle of α-cyclodextrin (118—119°), but it is in good agreement with the angle of

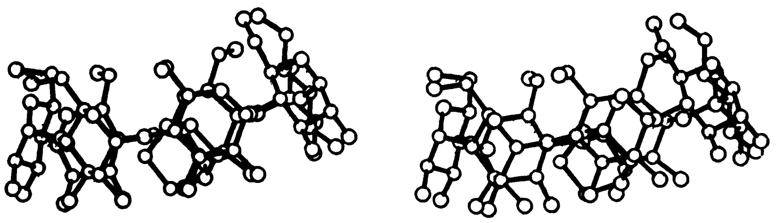

Fig. 2. A stereo-drawing of a side-view of the complex.

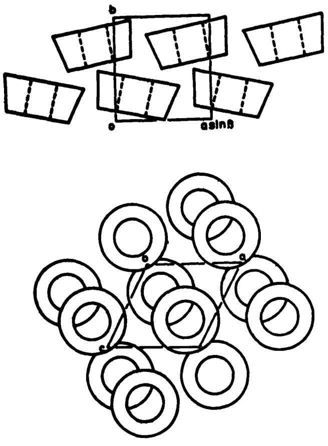

Fig. 3. An illustration of the packing feature of β-cyclodextrin in the crystal.

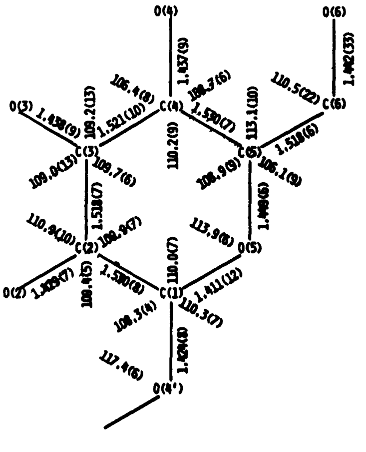

Fig. 4. Average bond distances and angles over seven glucose residues.
Standard deviations in parentheses were estimated according to the equation: $\sigma=[\sum_{i=1}^{7}(x_i-\bar{x})^2/6]^{1/2}$, where $x_i$ referes to the bond distance or angle in the $i$-th glucose residue, and $\bar{x}$ is the average value.

disaccharides.[8-10] Distances between glycosidic oxygen atoms of adjacent glucose residues are in the range 4.25—4.46 Å. The average value of 4.36 Å is larger than that of the α-cyclodextrin complexes (4.23—4.25 Å). The torsion-angle indices[11] (Table 2) vary from 111.0° to 126.6°. A linear correlation between these values and O(4)···O(4) distances is shown in Fig. 5. Although the torsion-angle index and O(4)···O(4) distances are limited to a rather small region, the correlation is stronger than that found in the α-cyclodextrin complexes.

Seven glycosidic oxygen atoms form a distorted heptagon. The distances between the center of gravity of the seven O(4) atoms and each individual O(4) atom are in the range 4.91—5.10 Å with an average value of 5.02 Å. These O(4) atoms are roughly coplanar with a maximum deviation of 0.26 Å from their least-squares plane (Table 3). This deviation is larger than that observed in the β-cyclodextrin complexes which have a head-to-head dimer-type arrangement. The tilt-angles[12] of glucose residues were measured as the angle made by the O(4) plane and the plane through C(1), C(4), O(4), and O(4') of each residue. Since the β-cyclodextrin ring is distored from the regular heptagon, the tilt-angles are not the same but vary within the

TABLE 2. GEOMETRICAL DATA FOR β-CYCLODEXTRIN

I. Radius of the O(4) heptagon.
The radius is measured from the center of gravity of seven O(4) atoms to each O(4) atom.

| Residue | Radius $l$/Å | Residue | Radius $l$/Å |
|---|---|---|---|
| G1 | 5.10 | G5 | 5.10 |
| G2 | 5.00 | G6 | 4.97 |
| G3 | 4.91 | G7 | 4.94 |
| G4 | 5.09 | Average | 5.02 |

II. O(4)···O(4) distance between adjacent glucose residues.

| | Distance $l$/Å | | Distance $l$/Å |
|---|---|---|---|
| O(4,G1)···O(4,G2) | 4.32 | O(4,G5)···O(4,G6) | 4.36 |
| O(4,G2)···O(4,G3) | 4.41 | O(4,G6)···O(4,G7) | 4.46 |
| O(4,G3)···O(4,G4) | 4.38 | O(4,G7)···O(4,G1) | 4.25 |
| O(4,G4)···O(4,G5) | 4.35 | Average | 4.36 |

III. Tilt-angle and torsion-angle index.[a,b]

| Residue | Tilt-angle $\phi$/° | Torsion-angle index $\phi$/° |
|---|---|---|
| G1 | 7.5 | 125.0 |
| G2 | 2.8 | 119.3 |
| G3 | 21.1 | 122.0 |
| G4 | 15.8 | 124.3 |
| G5 | 5.7 | 120.8 |
| G6 | 3.9 | 111.0 |
| G7 | 23.1 | 126.6 |
| Average | 11.4 | 121.3 |

a) The tilt-angle is defined as an angle between the O(4) plane and the plane through C(1), C(4), O(4), and O(4') of each glucose residue (see Ref. 12). b) The torsion-angle index is defined as: $|\phi(C(1)\text{–}C(2))|+|\phi(C(2)\text{–}C(3))|-|\phi(C(3)\text{–}C(4))|-|\phi(C(4)\text{–}C(5))|+|\phi(C(5)\text{–}O(5))|+|\phi(O(5)\text{–}C(1))|$, where $\phi(C(1)\text{–}C(2))$ is the conformation angle of O(5)–C(1)–C(2)–C(3) (see Ref. 11).

Table 3. Least-squares plane through seven O(4) atoms
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.
$0.107X+0.984Y+0.144\,Z=4.966$
Atomic deviations

| Residue | Distance $l$/Å | Residue | Distance $l$/Å |
|---|---|---|---|
| G1 | −0.26 | G5 | 0.02 |
| G2 | 0.26 | G6 | 0.20 |
| G3 | 0.06 | G7 | −0.05 |
| G4 | −0.22 | | |

Table 4. Bond distances and angles in 1,4-DO
I. Bond distances

| Distance | $l$/Å | Distance | $l$/Å |
|---|---|---|---|
| N(1,DO)-C(2,DO) | 1.44(3) | N(4,DO)-C(8,DO) | 1.44(2) |
| N(1,DO)-C(6,DO) | 1.48(2) | C(2,DO)-C(3,DO) | 1.57(3) |
| N(1,DO)-C(7,DO) | 1.48(2) | C(5,DO)-C(6,DO) | 1.57(3) |
| N(4,DO)-C(3,DO) | 1.42(2) | C(7,DO)-C(8,DO) | 1.57(3) |
| N(4,DO)-C(5,DO) | 1.43(3) | | |

II. Bond angles

| Angle | $\phi$/° |
|---|---|
| C(2,DO)-N(1,DO)-C(6,DO) | 108(1) |
| C(2,DO)-N(1,DO)-C(7,DO) | 109(1) |
| C(6,DO)-N(1,DO)-C(7,DO) | 107(1) |
| C(3,DO)-N(4,DO)-C(5,DO) | 109(1) |
| C(3,DO)-N(4,DO)-C(8,DO) | 109(1) |
| C(5,DO)-N(4,DO)-C(8,DO) | 108(1) |
| C(3,DO)-C(2,DO)-N(1,DO) | 110(2) |
| C(2,DO)-C(3,DO)-N(4,DO) | 110(2) |
| C(5,DO)-C(6,DO)-N(1,DO) | 110(2) |
| C(6,DO)-C(5,DO)-N(4,DO) | 110(2) |
| C(8,DO)-C(7,DO)-N(1,DO) | 108(2) |
| C(7,DO)-C(8,DO)-N(4,DO) | 112(2) |

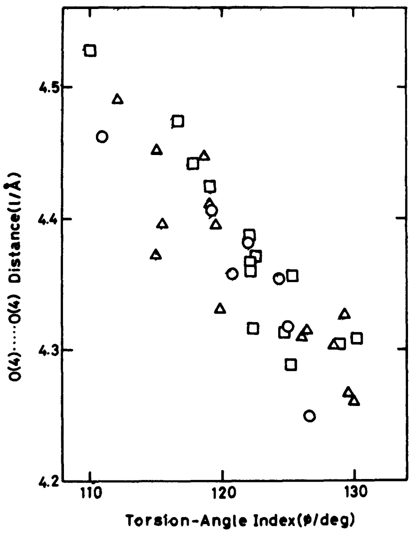

Fig. 5. Plot of the O(4)⋯O(4) distance against the torsion-angle index in $\beta$-cyclodextrin complexes with 1,4-DO (○) and 1-propanol (stable form △, unstable form □, see Ref. 13).

range 2.8—23.1°. The G2 and G6 residues are roughly perpendicular to the O(4) plane, while the G3 and G7 residues are inclined by angles of 21.2° and 23.1°, respectively, with the primary hydroxyl side nearer to the molecular axis.

*β-Cyclodextrin-Guest Interaction.* The guest 1,4-DO is situated near the secondary hydroxyl side in the $\beta$-cyclodextrin cavity, as shown in Figs. 1 and 2. The N(1) atom is located near the center of the cavity, while the N(4) atom located at the open end of the cavity is in contact with the neighboring $\beta$-cyclodextrin. The molecular axis through N(1) and N(4) does not coincide with the $\beta$-cyclodextrin axis, but inclines with the N(4) atom toward the G3 residue. The open space at the primary hydroxyl side is filled with three water molecules (W7, W8, and W13).

Bond distances and angles in 1,4-DO are shown in Table 4. The lengths of the chemically equivalent six C–N bonds vary from 1.40 Å to 1.48 Å with an average value of 1.45 Å, and the three C–C bonds are 1.57 Å. The C–N–C and C–C–N angles are in the range of 107—109° and 108—112°, respectively, and the corresponding average values are 108° and 110°. Figures 1 and 2 show that the hydrophobic methylene groups of 1,4-DO are in contact mainly with the hydrophobic surface in the host cavity. Most of these methylene

Table 5. Hydrogen bond distances ($l$/Å) and angles ($\phi$/°) and intermolecular distances less than 3.0 Å

| | | | | Distance | | | Angle |
|---|---|---|---|---|---|---|---|
| O | H | O | | O-H | H···O | O···O | O-H···O |
| O(2,G1) | -H(O2,G1) | O(3,G2) | | 1.00 | 1.72 | 2.691 | 163 |
| O(3,G1) | -H(O3,G1) | O(W9) | | 1.05 | 1.76 | 2.760 | 158 |
| O(6,G1) | -H(O6,G1) | O(6,G5) | (d) | 1.15 | 1.97 | 3.015 | 160 |
| O(2,G2) | -H(O2,G2) | O(6,G4) | (h) | 1.02 | 2.14 | 2.780 | 119 |
| O(6,G2) | -H(O6,G2) | O(W12) | (d) | 1.17 | 1.61 | 2.750 | 163 |
| O(2,G3) | -H(O2,G3) | O(3,G4) | | 0.81 | 2.10 | 2.882 | 162 |
| O(3,G3) | -H(O3,G3) | O(2,G2) | | 0.82 | 2.10 | 2.861 | 154 |
| O(6,G3) | -H(O6,G3) | N(4,DO) | (k) | 0.91 | 1.95 | 2.750 | 146 |
| O(2,G4) | -H(O2,G4) | O(3,G5) | | 0.89 | 1.96 | 2.853 | 180 |
| O(3,G4) | -H(O3,G4) | O(W6) | | 0.67 | 2.04 | 2.647 | 161 |
| O(6,G4) | -H(O6,G4) | O(W7) | | 0.88 | 1.82 | 2.693 | 153 |
| O(2,G5) | -H(O2,G5) | O(W11) | | 0.89 | 1.76 | 2.633 | 166 |
| O(3,G5) | -H(O3,G5) | O(W1) | (g) | 0.90 | 1.92 | 2.763 | 155 |
| O(6,G5) | -H(O6,G5) | O(W12) | | 0.84 | 1.82 | 2.654 | 172 |
| O(3,G6) | -H(O3,G6) | O(2,G5) | | 0.92 | 1.95 | 2.789 | 151 |
| O(6,G6) | -H(O6,G6) | O(W10A) | (k) | 0.88 | 1.90 | 2.726 | 156 |
| O(6,G6) | -H(O6,G6) | O(W10B) | | 0.88 | 1.80 | 2.642 | 159 |
| O(2,G7) | -H(O2,G7) | O(3,G1) | | 0.98 | 1.93 | 2.861 | 158 |
| O(3,G7) | -H(O3,G7) | O(2,G6) | | 0.91 | 1.92 | 2.822 | 171 |
| O(6,G7) | -H(O6,G7) | O(W9) | (i) | 1.21 | 1.69 | 2.800 | 149 |
| O(W1) | -H(1,W1) | O(6,G6) | | 0.93 | 1.89 | 2.749 | 163 |
| O(W1) | -H(2,W1) | O(5,G2) | (b) | 1.05 | 1.90 | 2.851 | 149 |
| O(W3) | -H(1,W3) | O(W1) | | 1.15 | 1.88 | 2.833 | 137 |
| O(W3) | -H(2,W3) | O(6,G7) | | 0.74 | 2.17 | 2.692 | 128 |
| O(W4) | -H(1,W4) | O(3,G7) | | 0.63 | 2.49 | 2.928 | 129 |
| O(W4) | -H(2,W4) | O(2,G4) | (e) | 0.60 | 2.19 | 2.763 | 161 |
| O(W5) | -H(1,W5) | O(2,G3) | (b) | 1.02 | 2.27 | 2.957 | 123 |
| O(W5) | -H(2,W5) | O(W11) | | 1.35 | 2.03 | 2.850 | 113 |
| O(W6) | -H(2,W6) | O(W13) | (h) | 0.99 | 1.95 | 2.698 | 130 |
| O(W7) | -H(1,W7) | O(W5) | (j) | 1.20 | 1.79 | 2.889 | 150 |
| O(W7) | -H(2,W7) | O(6,G3) | | 1.19 | 1.91 | 2.914 | 139 |
| O(W8) | -H(1,W8) | N(1,DO) | | 0.98 | 1.85 | 2.792 | 160 |
| O(W9) | -H(1,W9) | O(W2) | (g) | 1.14 | 2.16 | 2.850 | 116 |
| O(W10A) | -H(1,W10A) | O(3,G6) | | 0.74 | 2.11 | 2.825 | 163 |
| O(W10A) | -H(2,W10A) | O(W2) | (g) | 1.10 | 2.02 | 2.801 | 125 |
| O(W11) | -H(1,W11) | O(3,G1) | (c) | 1.11 | 1.90 | 2.928 | 153 |
| O(W12) | -H(1,W12) | O(3,G2) | (k) | 0.68 | 2.10 | 2.759 | 164 |
| O(W12) | -H(2,W12) | O(W4) | (j) | 0.83 | 1.88 | 2.703 | 171 |
| O(W13) | -H(1,W13) | O(W8) | | 1.25 | 1.95 | 2.817 | 122 |
| O(2,G1) | | O(W3) | (f) | | | 2.696 | |
| O(5,G5) | | O(W10A) | (k) | | | 2.947 | |
| O(6,G5) | | O(2,G6) | (k) | | | 2.665 | |
| O(3,G6) | | O(W10B) | (g) | | | 2.767 | |
| O(2,G7) | | O(W5) | (d) | | | 2.952 | |
| O(3,G3) | | O(W5) | (a) | | | 2.909 | |

Symmetry code

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

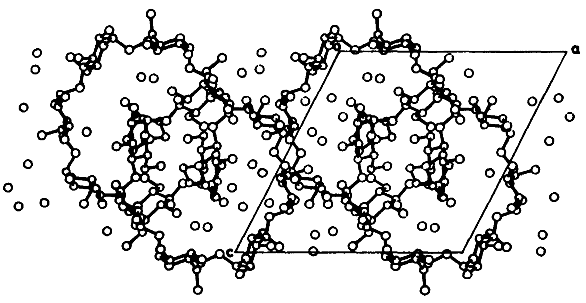

Fig. 6. The crystal structure viewed down along the b axis.

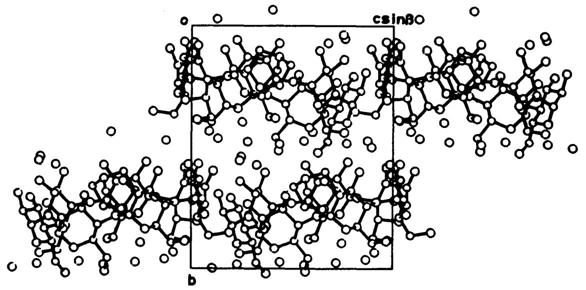

Fig. 7. The crystal structure viewed down along the a axis.

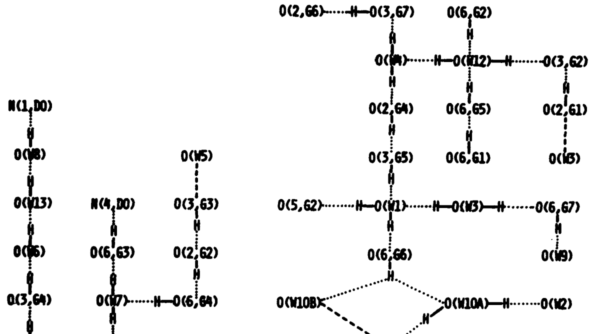

Fig. 8. A schematic representation of the hydrogen-bond network in the crystal. Dashed lines denote intermolecular contacts less than 3.0 Å.

groups are in van der Waals contact with the C(3) and C(5) methine groups and the O(4) atoms of β-cyclodextrin, although the C(8) methylene group located near the open end of the cavity is in contact with the neighboring β-cyclodextrin. The hydrophilic nitrogen atoms are not in contact with the host molecule, but instead are hydrogen-bonded to water or to a hydroxyl group lying outside the cavity.

*Molecular Packing and Hydrogen Bonds.* β-Cyclodextrin is located with its molecular axis making an angle of 10.3° with the b axis. The molecules arranged parallel to the ac plane form the corrugated molecular layers, of which the crystal is constructed. The intermolecular spaces between these layers are filled by water molecules which link these layers by hydrogen-bond bridges. A similar molecular packing has been observed in the α-cyclodextrin complexes with *para*-disubstituted benzenes,[7] but this is the first one found in the β-cyclodextrin complex. Other β-cyclodextrin complexes whose structures have been determined have a channel-type structure with head-to-head dimer-type packing or a cage-type structure in which the molecules are arranged in a zigzag mode. The crystal structure of the present β-cyclodextrin complex may belong to a modified cage-type structure. But unlike the typical cage-type structure, both ends of the β-cyclodextrin cavity are not completely blocked by neighboring β-cyclodextrin molecules, as shown in Fig. 3. Although the guest 1,4-DO is almost fully inserted into the host cavity, the C(8)–H bonds protrude outside the cavity. This may prevent the close contact between β-cyclodextrin molecules, and causes β-cyclodextrin to be packed more loosely, as indicated by the comparison of cell volumes between uncomplexed β-cyclodextrin (3070.3 Å$^3$) and the present complex (3504.7 Å$^3$).

Figure 8 shows the hydrogen-bond network in the crystal. Hydrogen-bond distances and angles are given in Table 5. Adjacent glucose residues in β-cyclodextrin are linked by O(2)–H···O(3) or O(3)–H···O(2) hydrogen bonds. Both the O(2) and the O(3) hydroxyl groups of the G3 and G7 residues donate hydrogen atoms to the hydroxyl groups of the adjacent residues, while those of the G2 and G5 residues only act as hydrogen acceptors.

Neighboring β-cyclodextrin molecules are linked by hydrogen bonds directly or through water molecules. N(1) and N(4) atoms of 1,4-DO act as hydrogen acceptors; thus, they are the terminal points of the hydrogen-bond chains. Of thirteen water molecules, the W10 water molecule is disordered, having a major position W10A of occupancy 0.7 and a minor position W10B of occupancy 0.3. There are two pairs and three trios of water molecules, in which individual water molecules are linked to each other by hydrogen bonds: O(W1)···H–O(W3), O(W9)–H···O(W2)···H–O(W10A), O(W4)···H–O(W12), O(W7)–H···O(W5)–H···O(W11), and O(W6)–H···O(W13)–H···O(W8). An infinite hydrogen-bond chain consists of a repetition unit comprising five hydroxyl groups and five water molecules: [···H–O(6,G7)···H–O(W3)–H···O(W1)–H···O(6,G6)–H···O-(W10A)–H···O(3,G6)–H···O(2,G5)–H···O(W11)–H···O(3,G1)–H···O(W9)···]. W2 links this chain and that related by the translation along the *z* direction (*x*, *y*, 1+*z*) by the O(W10A)–H···O(W2)···H–O(W9) bridge.

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