May, 1982] © *1982 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***55***, *1367—1371 (1982)* 1367

# The Structure of the Cyclodextrin Complex. XII. Crystal Structure of α-Cyclodextrin–1-Phenylethanol (1 : 1) Tetrahydrate

Kazuaki HARATA

*Research Institute for Polymers and Textiles, 1-1-4, Yatabe-Higashi, Tsukuba, Ibaraki 305*

(Received August 1, 1981)

The crystal structure of the α-cyclodextrin–1-phenylethanol (1:1) tetrahydrate, $C_{36}H_{60}O_{30}\cdot C_8H_{10}O\cdot 4H_2O$, was determined by the X-ray method. The crystal is monoclinic, the space group being $P2_1$ with $Z=2$; the cell dimensions are $a=8.176(1)$, $b=23.930(2)$, $c=13.853(1)$ Å, and $\beta=106.69(1)°$. The structure was solved by means of the Patterson map and the trial-and-error method combined with the rigid-body least-squares technique. Refinement was carried out by the block-diagonal least-squares method to the final $R$-value of 0.040 for 3565 reflections. α-Cyclodextrin molecules are stacked along the a axis in the head-to-tail fashion to form a channel-type structure, and are tilted by 17.0° against the channel axis. Owing to the lateral shift of α-cyclodextrin ring parallel to the molecular plane, neighboring α-cyclodextrin molecules along the channel are linked by only one weak hydrogen bond. The 1-phenylethanol molecule is sandwiched between stacked α-cyclodextrin molecules. $S$-(−) and $R$-(+) isomers of 1-phenylethanol are each located at the same position with the statistical disorder of the hydroxyl group with the occupancy of 0.5. Columns formed by the stack of α-cyclodextrin are closely packed, being linked with one another by many hydrogen bonds. Water molecules are located in two kinds of intermolecular spaces between α-cyclodextrin columns.

Cyclodextrins form diastereoisomers with optically active guests since they consist of optically active glucose residues. On this basis, complexation of cyclodextrins has been applied as a method for resolution of racemic molecules.[1] We have investivated the host-guest stereospecificity in the complex formation of cyclodextrins with benzene derivatives by the X-ray method.[2] In this paper, we deal with the α-cyclodextrin complex with racemic 1-phenylethanol to investigate the interaction with optically active molecules.

## Experimental

α-Cyclodextrin was dissolved in a hot aqueous solution saturated with 1-phenylethanol to prepare a 5% solution, and then the solution was allowed to stand at 40 °C. Colorless plate-like crystals were obtained. Measurements of lattice parameters and reflection intensities were carried out on a Nicolet P3/F diffractometer with graphite-monochromated Cu $K\alpha$ radiation. By the $\theta$-$2\theta$ scan mode, 3565 independent reflections with $|F_o|\geqq 3\sigma(F)$ were obtained up to 115° in $2\theta$. No corrections were made for absorption and extinction effects.

*Crystal Data*: $C_{36}H_{60}O_{30}\cdot C_8H_{10}O\cdot 4H_2O$; F.W.=1239.1; monoclinic; space group $P2_1$; $Z=2$; $a=8.176(1)$, $b=23.930(2)$, $c=13.853(1)$ Å, $\beta=106.69(1)°$; $V=2596.2$ Å$^3$; $D_x=1.585$ and $D_m=1.577$ g cm$^{-3}$.

## Determination and Refinement of the Structure

The orientation of α-cyclodextrin in a unit cell was deduced by inspection of a Patterson map. The position of the molecule was determined by the trial-and-error method. The positional and orientational parameters of each glucose residue were corrected by the rigid-body least-squares method. 1-Phenylethanol and water molecules were found on Fourier and difference-Fourier maps. Both $S$-(−) and $R$-(+) isomers of 1-phenylethanol are found with the statistical disorder of the hydroxyl group. The occupancy was estimated from an electron-density map but not refined. Hydrogen atoms were found on a difference-Fourier map. Refinement of the structure was carried out by the block-diagonal least-squares method. The quantity minimized was $\Sigma w(|F_o|-|F_c|)^2$ with $w=1.0$ for all the reflections. The final $R$-value was 0.040. The atomic scattering factors were taken from the "International Tables for X-Ray Crystallography."[3] Final atomic coordinates are given in Table 1. Tables of anisotropic temperature factors of non-

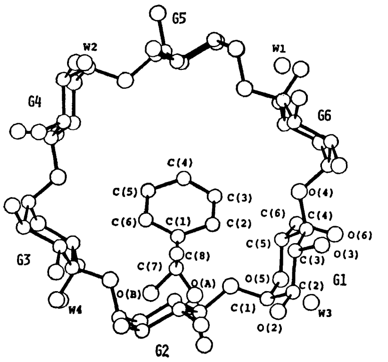

Fig. 1. A numbering scheme of the α-cyclodextrine–1-phenylethanol (1:1) tetrahydrate.
O(A) and O(B) denote disordered hydroxyl groups, corresponding to $S$-(−) and $R$-(+) isomers, respectively. Water molecules are denoted by W1, W2, W3, and W4.

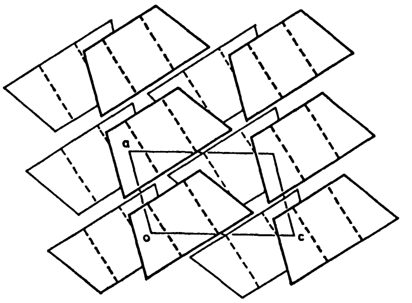

Fig. 2. A packing feature of α-cyclodextrin molecules viewed down along the b axis.

TABLE 1. FRACTIONAL COORDINATES ($\times 10^4$) AND $B_{eq}$[a)] ($B$/Å$^2$) OF NON-HYDROGEN ATOMS[b)]

| | $x$ | $y$ | $z$ | $B_{eq}$ | | $x$ | $y$ | $z$ | $B_{eq}$ |
|---|---|---|---|---|---|---|---|---|---|
| C(1,G1) | -809(7) | 1144(2) | -315(4) | 2.61 | O(3,G4) | 805(5) | 4588(2) | 4557(3) | 3.82 |
| C(2,G1) | -1855(7) | 762(2) | 150(4) | 2.66 | O(4,G4) | 1998(4) | 4291(2) | 2852(2) | 2.31 |
| C(3,G1) | -1062(7) | 743(2) | 1284(4) | 2.63 | O(5,G4) | 5816(4) | 4078(2) | 4991(3) | 2.61 |
| C(4,G1) | 800(6) | 581(2) | 1543(4) | 2.26 | O(6,G4) | 5911(8) | 4898(3) | 3378(5) | 4.52 |
| C(5,G1) | 1785(7) | 942(2) | 979(4) | 2.58 | C(1,G5) | 5097(7) | 1659(2) | 6254(4) | 2.46 |
| C(6,G1) | 3564(7) | 726(3) | 1088(5) | 4.15 | C(2,G5) | 4091(8) | 2006(2) | 6812(4) | 3.43 |
| O(2,G1) | -3551(5) | 977(2) | -79(3) | 3.24 | C(3,G5) | 3520(7) | 2553(2) | 6248(4) | 3.30 |
| O(3,G1) | -2002(5) | 346(2) | 1693(3) | 3.49 | C(4,G5) | 5070(7) | 2869(2) | 6096(4) | 2.51 |
| O(4,G1) | 1486(4) | 694(2) | 2603(3) | 2.36 | C(5,G5) | 6110(6) | 2483(2) | 5612(4) | 2.67 |
| O(5,G1) | 901(4) | 946(2) | -87(3) | 2.59 | C(6,G5) | 7770(7) | 2735(3) | 5550(5) | 3.30 |
| O(6,G1) | 3533(6) | 150(2) | 759(3) | 5.25 | O(2,G5) | 2678(6) | 1681(2) | 6864(3) | 4.86 |
| C(1,G2) | -1687(7) | 3342(2) | -764(4) | 2.49 | O(3,G5) | 2724(6) | 2909(2) | 6814(4) | 5.21 |
| C(2,G2) | -3264(7) | 2998(2) | -810(4) | 2.49 | O(4,G5) | 4390(4) | 3316(1) | 5405(3) | 2.31 |
| C(3,G2) | -2760(7) | 2448(2) | -225(4) | 2.72 | O(5,G5) | 6531(5) | 1971(2) | 6176(3) | 2.52 |
| C(4,G2) | -1437(7) | 2144(2) | -616(4) | 2.32 | O(6,G5) | 8921(6) | 2850(2) | 6518(3) | 3.92 |
| C(5,G2) | 75(6) | 2523(2) | -607(4) | 2.48 | C(1,G6) | 2402(7) | 267(2) | 3237(4) | 2.56 |
| C(6,G2) | 1317(7) | 2262(2) | -1111(4) | 2.88 | C(2,G6) | 1724(7) | 235(2) | 4155(4) | 2.83 |
| O(2,G2) | -4404(5) | 3309(2) | -407(3) | 3.32 | C(3,G6) | 2025(7) | 790(2) | 4705(4) | 2.65 |
| O(3,G2) | -4257(5) | 2122(2) | -375(3) | 3.54 | C(4,G6) | 3882(7) | 958(2) | 4964(7) | 2.47 |
| O(4,G2) | -827(5) | 1689(2) | 78(3) | 2.46 | C(5,G6) | 4567(7) | 933(2) | 4043(4) | 2.50 |
| O(5,G2) | -539(5) | 3033(2) | -1157(3) | 2.71 | C(6,G6) | 6464(7) | 1016(2) | 4293(4) | 3.24 |
| O(6,G2) | 466(5) | 2064(2) | -2112(3) | 3.03 | O(2,G6) | -57(5) | 108(2) | 3801(3) | 3.73 |
| C(1,G3) | 1623(7) | 4723(2) | 2127(4) | 2.50 | O(3,G6) | 1490(5) | 726(2) | 5597(3) | 4.08 |
| C(2,G3) | -299(7) | 4794(2) | 1756(4) | 2.85 | O(4,G6) | 4007(4) | 1534(1) | 5295(3) | 2.26 |
| C(3,G3) | -1109(7) | 4242(2) | 1337(4) | 2.75 | O(5,G6) | 4172(5) | 393(2) | 3560(3) | 2.58 |
| C(4,G3) | -362(7) | 4052(2) | 498(4) | 2.54 | O(6,G6) | 7361(5) | 708(2) | 5158(3) | 3.75 |
| C(5,G3) | 1597(7) | 4052(2) | 827(4) | 2.53 | C(1,PE) | -3629(8) | 2492(3) | 2297(4) | 4.00 |
| C(6,G3) | 2318(8) | 3971(3) | -66(5) | 3.70 | C(2,PE) | -2796(10) | 1981(3) | 2505(5) | 5.21 |
| O(2,G3) | -916(5) | 4965(2) | 2587(3) | 3.14 | C(3,PE) | -1141(11) | 1952(4) | 3031(6) | 6.92 |
| O(3,G3) | -2915(5) | 4295(2) | 940(3) | 3.81 | C(4,PE) | -203(9) | 2420(6) | 3364(5) | 7.81 |
| O(4,G3) | -939(5) | 3485(2) | 258(3) | 2.58 | C(5,PE) | -1000(13) | 2948(5) | 3149(7) | 8.28 |
| O(5,G3) | 2236(5) | 4578(2) | 1294(3) | 2.62 | C(6,PE) | -2705(11) | 2974(3) | 2604(6) | 5.90 |
| O(6,G3) | 1390(6) | 4280(2) | -935(3) | 4.04 | C(7,PE) | -5505(9) | 2506(5) | 1712(5) | 6.87 |
| C(1,G4) | 4975(7) | 3870(2) | 5679(4) | 2.54 | C(8,PE) | -6628(9) | 2505(4) | 2432(5) | 5.81 |
| C(2,G4) | 3436(7) | 4237(2) | 5646(4) | 2.59 | O(A,PE) | -6080(11) | 2225(5) | 998(7) | 5.86 |
| C(3,G4) | 2193(7) | 4222(2) | 4587(4) | 2.55 | O(B,PE) | -6016(11) | 2881(5) | 1027(7) | 5.37 |
| C(4,G4) | 3123(7) | 4404(2) | 3832(4) | 2.45 | O(W1) | -762(6) | 985(2) | 7150(3) | 4.24 |
| C(5,G4) | 4776(7) | 4078(2) | 3945(4) | 2.68 | O(W2) | -600(6) | 3928(2) | 7115(3) | 4.16 |
| C(6,G4) | 5868(8) | 4318(3) | 3331(5) | 4.01 | O(W3) | 4409(12) | 489(7) | -1628(10) | 22.98 |
| O(2,G4) | 2623(5) | 4060(2) | 6372(3) | 3.08 | O(W4) | 4845(8) | 4221(2) | -1740(4) | 5.92 |

a) $B_{eq}=8\pi^2(u_1{}^2+u_2{}^2+u_3{}^2)/3$, where $u_i$ is the root-mean-square deviation in the $i$-th principal axis of the thermal ellipsoid. b) Occupancy of each of O(A,PE) and O(B,PE) is 0.5.

hydrogen atoms, atomic parameters of hydrogen atoms, observed and calculated structure factors, bond distances, angles, and conformation angles in α-cyclodextrin are kept at The Chemical Society of Japan (Document No. 8218). The calculations were performed on a FACOM M-200 computer at the RIPS Center, Tsukuba.

## Description and Discussion of the Structure

*Outline of the Structure.* Structure and numbering scheme of the complex are shown in Fig. 1. A packing feature of α-cyclodextrin in the crystal is illustrated in Fig. 2. α-Cyclodextrin molecules are stacked with a head-to-tail mode along the a axis. The molecules are laterally shifted to each other parallel to the molecular plane. Both *S*-(−) and *R*-(+) isomers of the guest 1-phenylethanol molecule are sandwiched at the same position with a statistical disorder of the hydroxyl group by the two adjacent α-cyclodextrin molecules along the channel.

*Conformation of α-Cyclodextrin.* Average bond distances and angles over six glucose residues are shown in Fig. 3. Geometrical data of α-cyclodextrin ring are given in Tables 2 and 3. Average bond distances and angles are in good agreement with those of the α-cyclodextrin–benzaldehyde complex[2)] having a similar crystal structure. All primary hydroxyl groups are in a *gauche-gauche* conformation; average conformation angles of O(5)–C(5)–C(6)–O(6) and C(4)–C(5)–C(6)–O(6) are −71.7° and 50.0°, respectively. Distances between adjacent glycosidic oxygen atoms (O(4)) are in the range from 4.17 to 4.31 Å with the average value of 4.23 Å. Torsion-angle indexes of glucose residues lie in rather a narrow region (124.5—137.5), indicating that the conformation of each pyranose ring is nearly identical.

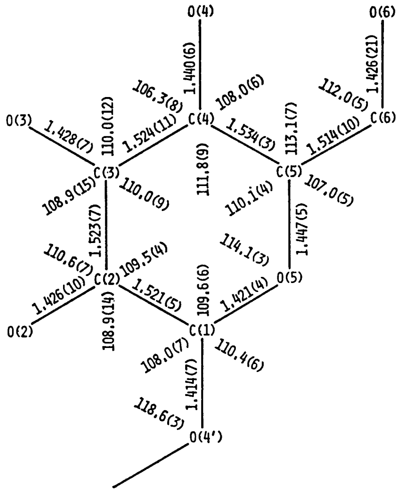

Fig. 3. Average bond distances and angles over six glucose residues in α-cyclodextrin.
Standard deviations in parentheses were estimated according to the equation: $\sigma=[\sum_{i=1}^{6}(x_i-\bar{x})^2/5]^{1/2}$ where $x_i$ referes to bond distance or angle in $i$-th glucose residue and $\bar{x}$ is the average value.

Diagonal distances measured between glycosidic oxygen atoms and the good planarity of these atoms (Table 3) show that the α-cyclodextrin ring is a nearly regular hexagon although the G1···G4 distance is slightly larger than the G2···G5 distance. Distances between O(2) and O(3) of adjacent glucose residues

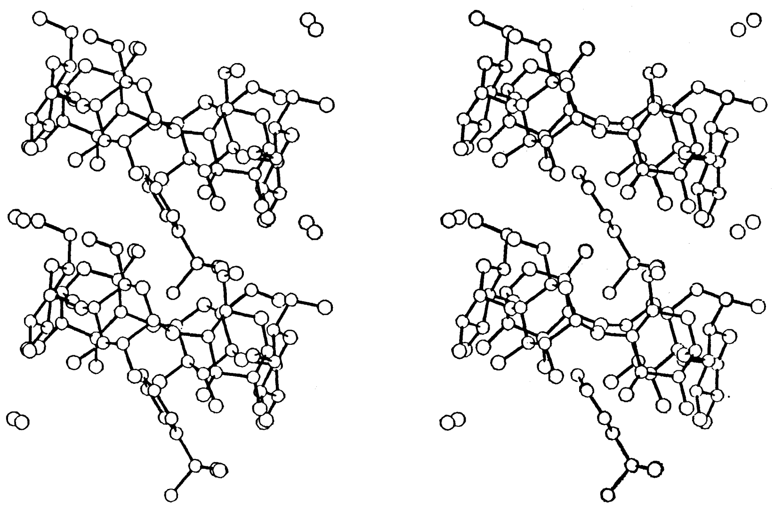

Fig. 4. A stereo-drawing of stacking feature of α-cyclodextrin.

TABLE 2. SELECTED GEOMETRICAL DATA FOR α-CYCLODEXTRIN RING

I. O(4)···O(4) distances

| Distance ($l$/Å) | | Distance ($l$/Å) | |
|---|---|---|---|
| O(4,G1)···O(4,G2) | 4.21 | O(4,G5)···O(4,G6) | 4.27 |
| O(4,G1)···O(4,G6) | 4.22 | O(4,G1)···O(4,G4) | 8.62 |
| O(4,G2)···O(4,G3) | 4.31 | O(4,G2)···O(4,G5) | 8.35 |
| O(4,G3)···O(4,G4) | 4.18 | O(4,G3)···O(4,G6) | 8.40 |
| O(4,G4)···O(4,G5) | 4.22 | | |

II. Torsion-angle index[a)] and tilt angle[b)]

| Residue | Torsion-angle index($\phi$/°) | Tilt-angle($\phi$/°) |
|---|---|---|
| G1 | 131.2 | 14.6 |
| G2 | 124.5 | 8.1 |
| G3 | 137.5 | 11.5 |
| G4 | 132.5 | 8.7 |
| G5 | 130.4 | 4.1 |
| G6 | 132.9 | 10.1 |

a) The torsion-angle index is defined as: $|\phi(\mathrm{C(1)\text{-}C(2)})| + |\phi(\mathrm{C(2)\text{-}C(3)})| + |\phi(\mathrm{C(5)\text{-}O(5)})| + |\phi(\mathrm{O(5)\text{-}C(1)})| - |\phi(\mathrm{C(3)\text{-}C(4)})| - |\phi(\mathrm{C(4)\text{-}C(5)})|$. b) The tilt-angle is defined as the 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 glucose residue.

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

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

| | | | |
|---|---|---|---|
| I. The plane through six O(4) atoms | | | |
| $0.956X-0.016Y-0.292Z=-0.887$ | | | |
| O(4,G1) | 0.023 | O(4,G4) | 0.097 |
| O(4,G2) | 0.117 | O(4,G5) | 0.044 |
| O(4,G3) | −0.177 | O(4,G6) | −0.104 |
| II. The benzene plane | | | |
| $-0.517X-0.041Y+0.855Z=4.354$ | | | |
| C(1,PE) | 0.014 | C(6,PE) | −0.011 |
| C(2,PE) | −0.009 | C(7,PE) | 0.022 |
| C(3,PE) | −0.001 | C(8,PE) | 1.462 |
| C(4,PE) | 0.004 | O(A,PE) | −0.664 |
| C(B,PE) | 0.001 | O(B,PE) | −0.716 |

vary in the range from 2.81 to 3.04 Å. These hydroxyl groups form a round circle with six intramolecular O(2)···O(3) hydrogen bonds. Significant conformational differences in the macrocyclic ring, compared with the benzaldehyde complex,[2)] are observed in the tilt-angles of glucose residues against the least-squares planes through six O(4) atoms, in spite of the similarity in the molecular packing. The tilt-angles of the 1-phenylethanol complex (4.1—14.6°) are smaller than those values of the benzaldehyde complex (10.9—19.9°). This may be interpreted in terms of differences in the molecular packing and intermolecular hydrogen bonds. As will be discussed later, the more tilted orientation of glucose residue in the benzaldehyde complex is held by intermolecular hydrogen bonds along the channel. In the 1-phenylethanol complex, however, the small tilt of glucose residue may be preferable to form hydrogen bonds with neighboring α-cyclodextrin molecules arranged in sheets parallel to the molecular plane.

*α-Cyclodextrin–Guest Interaction.* Bond distances and angles in 1-phenylethanol and intermolecular distances between 1-phenylethanol and α-cyclodextrin are shown in Fig. 5. The planarity of the phenyl group is quite good (Table 3). The hydroxyl group of 1-phenylethanol is statistically disordered with the same occupancy; O(A) and O(B) belong to *S*-(−) and *R*-(+) isomers, respectively. The C(7)–O(A) and C(7)–O(B) bonds are significantly short, and the C(1)–C(7)–O(A) and C(1)–C(7)–O(B) angles are somewhat large. This may be interpreted in terms of the thermal displacement and/or slight disorder of 1-phenylethyl moiety as discussed by Kim and Rosenstein.[4)] The relatively large temperature factor indicates that the position of the 1-phenylethyl moiety of the two isomers is slightly shifted to each other in the asymmetric environment although such small disorder is not resolved on the electron-density map.

1-Phenylethanol is sandwiched between adjacent α-

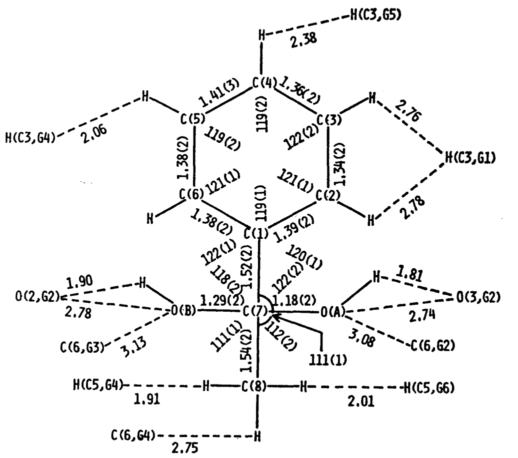

Fig. 5. Bond distances and angles in 1-phenylethanol and selected intermolecular distances between 1-phenylethanol and $\alpha$-cyclodextrin.

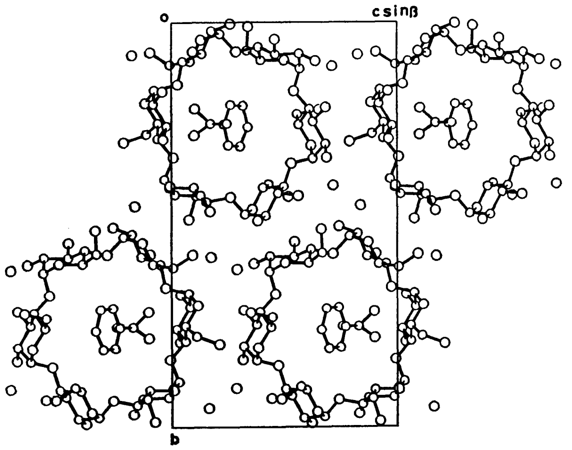

Fig. 6. Crystal structure viewed down along the a axis.

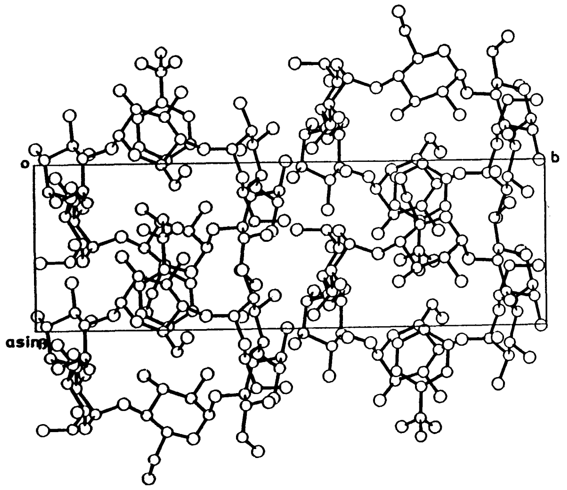

Fig. 7. Crystal structure viewed down along the c axis.

cyclodextrin molecules stacked along the channel (Fig. 4). The phenyl group is in contact with the secondary hydroxyl side of $\alpha$-cyclodextrin, while the ethanol moiety is located at the O(6) side of the next $\alpha$-cyclodextrin. The phenyl plane makes an angle of 42.0° with the plane through the six O(4) atoms. O(A) and O(B) hydroxyl groups form O(A)–H···O(3,G2) and O(B)–H···O(2, G2) hydrogen bonds, respectively. The C(7)–C(8) bond is inserted into the next $\alpha$-cyclodextrin from the primary hydroxyl side. This type of the host-guest interaction has not yet been found. In the $\alpha$-cyclodextrin complexes with other benzene derivatives,[2] the benzene ring is included at the O(2), O(3) side nearly parallel to the $\alpha$-cyclodextrin axis. In the 1-phenylethanol complex, however, such inclusion geometry may be unfavorable since the hydrogen bonds involving O(A) and O(B) should be broken to include the phenyl group parallel to the $\alpha$-cyclodextrin axis, and moreover, such parallel inclusion may cause steric hindrance between the C(8) methyl group of 1-phenylethanol and C(6) methylene groups of the next $\alpha$-cyclodextrin. Somewhat short contacts involving hydrogen atoms are found between $\alpha$-cyclodextrin and 1-phenylethanol; H(C3,G4)···H(C5,PE) (2.06 Å), H(C5,G4)···H(C8, PE) (1.91 Å), H(C5,G6)···H(C8,PE) (2.01 Å), and C(6,G4)···H(C8,PE) (2.75 Å). This suggests that the guest 1-phenylethanol molecule is bound in the channel by hydrogen bonds and the van der Waals force.

*Molecular Packing and Hydrogen Bonds.* Projections of crystal structure are shown in Figs. 6 and 7. $\alpha$-Cyclodextrin molecules are stacked along the a axis forming an endless column. Since the $\alpha$-cyclodextrin ring is tilted by 17.0° against the plane perpendicular to the channel axis, the rings are laterally shifted to each other parallel to the molecular plane. Except for a weak O(3,G5)–H···O(6,G5) hydrogen bond, no intermolecular hydrogen bonds along the column are formed. Most of the intermolecular hydrogen bonds are found between neighboring $\alpha$-cyclodextrin molecules arranged parallel to the molecular plane. In other channel-type structures,[2] the stacked $\alpha$-cyclodextrin molecules are linked by many hydrogen bonds along the column. In those complexes, the inclination and lateral shift of the $\alpha$-cyclodextrin ring are so small that the hydrogen bonds cannot be broken; in the benzaldehyde complex, the glucose residues are remarkably tilted to compensate the effect of the molecular shift on the hydrogen bond formation. Moreover, $\alpha$-cyclodextrin molecules belonging to different columns are linked with one another by hydrogen-bond bridges involving water molecules rather than by direct hydrogen bonds. In contrast to those complexes, $\alpha$-cyclodextrin columns in the 1-phenylethanol complex are linked mainly by direct hydrogen bonds, and as the result, they are more closely packed in the crystal as indicated by the comparison of cell volumes; 2645.1 Å$^3$ in the benzaldehyde complex and 2596.3 Å$^3$ in the 1-phenylethanol complex. Between columns, adjacent glucose residues are faced to each other as shown in Fig. 6. The G1 and G3 residues are linked by the O(3,G3)–H···O(6,G1) and O(6, G3)–H···O(3,G1) hydrogen bonds. Two hydrogen bonds, the O(6,G2)–H···O(6,G5) and O(2,G5)–H··· O(6,G2), are also found between the G2 and G5 residues, but only the O(2,G6)–H···O(3,G4) hydrogen bond is formed between the G4 and G6 residues.

Table 4. Hydrogen-bond distances ($l$/Å) and angles ($\phi$/°)

| | | | | DISTANCE | | | ANGLE |
|---|---|---|---|---|---|---|---|
| O | H | O | CODE | O-H | H•••O | O•••O | O-H•••O |
| O(2,G1) | -H(O2,G1) | O(W3) | (b) | 0.96 | 1.64 | 2.583 | 171 |
| O(3,G1) | -H(O3,G1) | O(2,G6) | | 0.87 | 2.09 | 2.952 | 171 |
| O(2,G2) | -H(O2,G2) | O(W4) | (b) | 1.19 | 1.65 | 2.811 | 163 |
| O(3,G2) | -H(O3,G2) | O(2,G1) | | 0.99 | 1.82 | 2.806 | 180 |
| O(6,G2) | -H(O6,G2) | O(6,G5) | (e) | 0.94 | 1.79 | 2.713 | 166 |
| O(2,G3) | -H(O2,G3) | O(W1) | (h) | 0.82 | 2.00 | 2.773 | 157 |
| O(3,G3) | -H(O3,G3) | O(2,G2) | | 0.98 | 2.12 | 3.037 | 157 |
| O(3,G3) | -H(O3,G3) | O(6,G1) | (f) | 0.98 | 2.13 | 3.049 | 156 |
| O(6,G3) | -H(O6,G3) | O(3,G1) | (f) | 1.10 | 1.86 | 2.858 | 150 |
| O(2,G4) | -H(O2,G4) | O(3,G5) | | 0.88 | 2.02 | 2.817 | 151 |
| O(3,G4) | -H(O3,G4) | O(2,G3) | | 1.13 | 1.72 | 2.835 | 172 |
| O(6,G4) | -H(O6,G4) | O(2,G3) | (a) | 0.84 | 2.58 | 3.097 | 121 |
| O(2,G5) | -H(O2,G5) | O(6,G2) | (c) | 0.89 | 1.87 | 2.756 | 170 |
| O(3,G5) | -H(O3,G5) | O(6,G5) | (b) | 1.19 | 2.05 | 3.021 | 136 |
| O(6,G5) | -H(O6,G5) | O(W2) | (a) | 1.02 | 1.70 | 2.703 | 166 |
| O(2,G6) | -H(O2,G6) | O(3,G4) | (j) | 1.00 | 1.85 | 2.809 | 159 |
| O(3,G6) | -H(O3,G6) | O(2,G5) | | 0.81 | 2.08 | 2.875 | 169 |
| O(A,PE) | -H(OA,PE) | O(2,G2) | | 1.07 | 1.81 | 2.743 | 144 |
| O(B,PE) | -H(OB,PE) | O(2,G2) | | 1.04 | 1.90 | 2.870 | 154 |
| O(W1) | -H(1,W1) | O(6,G2) | (c) | 0.78 | 2.09 | 2.850 | 168 |
| O(W1) | -H(2,W1) | O(6,G6) | (b) | 1.09 | 1.79 | 2.824 | 156 |
| O(W2) | -H(1,W2) | O(6,G3) | (c) | 1.20 | 1.68 | 2.851 | 165 |
| O(W2) | -H(2,W2) | O(2,G4) | | 0.97 | 2.63 | 3.108 | 111 |
| O(W3) | -H(1,W3) | O(6,G4) | (i) | 0.91 | 1.86 | 2.753 | 164 |
| O(W4) | -H(1,W4) | O(6,G1) | (g) | 0.69 | 2.34 | 2.740 | 119 |
| O(W4) | -H(2,W4) | O(2,G4) | (d) | 0.86 | 1.92 | 2.750 | 162 |

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

In the crystal, the hydrogen-bond network is built up of branched chains and circles of hydrogen bonds as shown in Fig. 8. Six intramolecular hydrogen bonds are observed between adjacent glucose residues. Except for the O(2,G4)–H···O(3,G5) hydrogen bond, the O(3) hydroxyl groups act as a hydrogen donor (Table 4). The G4 residue donates hydrogen atoms to the G3 and G5 resiues, while the G5 residue accepts two hydrogen atoms from the G4 and G6 residues. O(2,G4), O(3,G5), O(6,G5), and O(W2) from a four membered hydrogen-bond circle. O(2,G2), O(3,G3), O(6,G1), and O(W4) also form a cyclic hydrogen bond, although O(3,G3) donates a hydrogen atom to O(2,G2) and O(6,G1), forming weak bifurcated hydrogen bonds.[5] Water molecules are located in two kinds of intermolecular spaces as shown in Fig. 6; W1 and W3 are located in one space, while W2 and W4 are in the other space. W2 and W4 are linked by the O(W2)–H···O(2,G4)···H–O(W4) hydrogen-bond bridge. W1 forms three hydrogen bonds with O(2,W3), O(6,G2), and O(6,G6), linking three columns surrounding it. W4 forms similar tripod-like hydrogen bonds with each of O(6,G1), O(2,G2), and O(2,G4) in different columns. W3 links two columns with the O(2,G1)–H···O(W3)–H···O(6,G4) hydrogen-bond bridge. Unlike these three water molecules, W2 links α-cyclodextrin rings along the column axis with the O(6,G5)–H···O(W2)–H···O(2,G4) hydrogen-bond bridge, and is also hydrogen-bonded to O(6,G3) of the neighboring column.

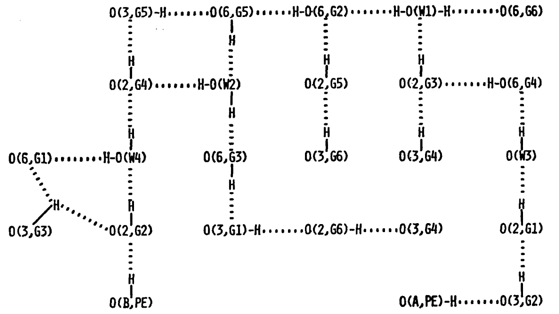

Fig. 8. A schematic representation of hydrogen-bond network.

## References

1) F. Cramer and W. Dietsche, *Chem. Ber.*, **92**, 378 (1959); H. P. Benshop and G. R. Van der Berg, *J. Chem. Soc., Chem. Commun.*, **1970**, 1431; M. Mikolajczyk, J. Drabowicz, and F. Cramer, *ibid.*, **1971**, 317; *J. Am. Chem. Soc.*, **100**, 2510 (1978).

2) K. Harata, K. Uekama, M. Otagiri, F. Hirayama, and H. Ogino, *Bull. Chem. Soc. Jpn.*, **54**, 1954 (1981), and references therein.

3) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham (1974), Vol. IV, pp. 72—75.

4) S. H. Kim and R. D. Rosenstein, *Acta Crystallogr.*, **22**, 648 (1967).

5) G. A. Jeffrey and S. Takagi, *Acc. Chem. Res.*, **11**, 264 (1978).