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Carbohydrate Research 260 (1994) 169–179

CARBOHYDRATE RESEARCH

Crystal structure of a complex of α-cyclodextrin with 2-fluoro-4-nitrophenol · $3H_2O$

Motonari Shibakami *, Akira Sekiya

National Institute of Materials and Chemical Research, Higashi 1-1, Tsukuba, Ibaraki 305, Japan

(Received June 15th, 1993; accepted February 21st, 1994)

Abstract

The crystal structure of a complex of α-cyclodextrin (α-CD) with 2-fluoro-4-nitrophenol · $3H_2O$ has been determined by the X-ray diffraction technique. The complex crystallizes in space group $P2_12_12_1$ with cell dimensions: $a = 13.431(3)$, $b = 15.299(4)$, $c = 24.780(5)$ Å. The structure was solved by direct methods and refined to $R = 6.7\%$ for 4483 reflections. The crystal structure is isomorphous to the α-CD–4-nitrophenol · $3H_2O$ complex. The phenyl group is inside the cavity, so that the O-4 hexagon of the α-CD is distorted in a systematic manner: the longest diagonal [O-4(G2) · · · O-4(G5)] is in the direction of the benzene ring. The phenolic OH group protrudes from the secondary OH side of the cavity and the NO_2 group is situated on the primary OH side. The hydrophobic F atom is statistically disordered over two sites and is located in the hydrophilic space, just beyond the rim of the secondary OH side of the cavity.

1. Introduction

α-Cyclodextrin (α-CD, cyclomaltohexaose), a cyclic oligosaccharide consisting of six α-(1 → 4)-linked D-glucopyranosyl residues, forms inclusion complexes with a wide variety of "guest" molecules fitting inside the α-CD cavity [1]. The inner surface of the cavity is dominated by H atoms and glycosidic O atoms and is, therefore, relatively hydrophobic. Since α-CD has attracted great attention as a model enzyme [1] and enzymes recognize slight structural changes, it was attractive to investigate how a slight change in the substrate affects its interaction with α-CD. Although many crystal structures of α-CD complexes have been determined

* Corresponding author.

SSDI 0008-6215(94)00075-Q

by the X-ray method, only a few attempts have been made on this point. In a previous paper [2], we reported the structures of α-CD complexes with 2- and 4-fluorophenol (2-FPhOH and 4-FPhOH, respectively). These analyses demonstrated that, in both complexes, the F atom changes enormously the guest orientation inside the cavity as compared with α-CD–4-iodophenol [3]. It is, therefore, of interest to study the interaction between α-CD and other organofluorine compounds.

We now report the crystal structure of the α-CD–2-fluoro-4-nitrophenol(2-FNPH) · $3H_2O$ inclusion complex, which demonstrates that the structure is highly isomorphous to the α-CD–4-nitrophenol(4-NPH) · $3H_2O$ complex [4]. That is, the F atom does not cause an observable change in the guest orientation, in contrast to α-CD–2-FPhOH and α-CD–4-FPhOH.

2. Experimental

α-CD was obtained from Tokyo Chemical Industry Co., Ltd. and further purified by recrystallization from water. 2-FNPH was prepared by the method of Brown et al. [5].

The pale-yellow prismatic crystals of the title complex were obtained from an aqueous solution containing α-CD and 2-FNPH in a 1 : 1 molar ratio. A well-shaped crystal with dimensions of $0.45 \times 0.40 \times 0.30$ mm was mounted on a Mac Science MXC18 automated four-circle diffractometer and studied with graphite-monochromated Cu$K\alpha$ radiation ($\lambda = 1.5418$ Å). The crystal was stable in air and did not decompose during data collection. Accurate unit-cell parameters were determined by a least-squares fit of 20 centred reflections in the 2θ range 56–60°. Intensities were measured by the ω–2θ scan technique with a scan rate of 8° min^{-1} in ω and a scan width of $\Delta(\omega) = (1.38 + 0.30 \tan \theta)°$. Background intensities were measured for 1/2 of the peak scanning time at each side of a scan. Three standard reflections were remeasured after every 100 reflections; no significant loss of intensity was observed throughout data collection. 4699 independent reflections were collected with 2θ up to 130° ($\sin \theta/\lambda = 0.583$ Å^{-1}) and an index range of $h = 0$ to 15, $k = 0$ to 17, $l = 0$ to 28. Corrections for Lorentz and polarization effects were applied to the intensity data; analytical absorption and extinction corrections [6] were carried out.

The structure was solved by direct methods using MULTAN 78 [7]. Two O atoms [O-6(G4) and O(W3)] and the F atom [F-1(2-FNPH)] are statistically disordered. The structure was refined by full-matrix least-squares using F^2. 4483 observed reflections [$|F_o| > 3\sigma(F)$] were included in the refinement; the function minimized was $\Sigma w(|F_o|^2 - |F_c|^2)^2$. On the difference Fourier maps, most H atoms were not found at the expected positions. This is probably due to the thermal vibration of the 2-FNPH molecule. The weighting scheme used was $w = [\sigma(F_o)^2 + 0.0004|F_o|^2]^{-1}$. The number of observations per refined parameter is 4483/764 = 5.87 and $S = 3.24$. The final R and R_w values are 0.067 and 0.090, respectively. The $(\Delta/\sigma)_{max}$ of non-H atoms in the final refinement cycle is 0.12.

Table 1
Positional parameters and equivalent isotropic thermal parameters for α-CD–2-FNPH complex

Atom	x	y	z	B_{eq} [a]	OC [b]
F-1(2-FNPH)	0.5100(4)	0.2295(2)	0.8024(1)	4.3(1)	0.67
F-2(2-FNPH)	0.5592(7)	0.2074(5)	0.9820(3)	6.4(3)	0.33
O-1(2-FNPH)	0.5432(2)	0.3076(2)	0.8944(1)	4.39(8)	
O-2(2-FNPH)	0.4808(4)	−0.0850(2)	0.8395(2)	6.9(1)	
O-3(2-FNPH)	0.5092(4)	−0.0968(2)	0.9243(1)	6.0(1)	
N(2-FNPH)	0.4974(3)	−0.0529(2)	0.8833(1)	3.90(9)	
C-1(2-FNPH)	0.5305(3)	0.2202(3)	0.8940(2)	3.4(1)	
C-2(2-FNPH)	0.5106(3)	0.1792(3)	0.8452(2)	3.6(1)	
C-3(2-FNPH)	0.4984(4)	0.0912(3)	0.8415(2)	3.7(1)	
C-4(2-FNPH)	0.5063(3)	0.0417(3)	0.8874(2)	3.22(9)	
C-5(2-FNPH)	0.5245(3)	0.0795(3)	0.9368(2)	3.7(1)	
C-6(2-FNPH)	0.5342(4)	0.1684(3)	0.9398(2)	4.2(1)	
C-1(G1)	0.1532(3)	0.0503(3)	0.8047(2)	3.06(9)	
C-2(G1)	0.1287(3)	0.1234(3)	0.8443(2)	3.4(1)	
C-3(G1)	0.1904(3)	0.1134(3)	0.8949(2)	2.92(9)	
C-4(G1)	0.1769(3)	0.0231(3)	0.9186(2)	2.97(9)	
C-5(G1)	0.1992(3)	−0.0461(3)	0.8765(2)	3.3(1)	
C-6(G1)	0.1830(5)	−0.1382(3)	0.8965(2)	5.4(2)	
O-2(G1)	0.1589(3)	0.1754(2)	0.9343(1)	4.01(8)	
O-3(G1)	0.1482(3)	0.2043(2)	0.8177(1)	4.58(9)	
O-4(G1)	0.2454(2)	0.0139(2)	0.9626(1)	3.12(6)	
O-5(G1)	0.1376(2)	−0.0316(2)	0.8299(1)	3.71(7)	
O-6(G1)	0.0877(4)	−0.1519(3)	0.9182(2)	6.3(1)	
C-1(G2)	0.2072(4)	−0.0120(4)	1.0137(2)	2.9(1)	
C-2(G2)	0.2267(5)	0.0626(4)	1.0534(2)	3.1(2)	
C-3(G2)	0.3386(5)	0.0790(4)	1.0558(2)	3.0(1)	
C-4(G2)	0.3923(4)	−0.0047(4)	1.0711(2)	2.5(1)	
C-5(G2)	0.3632(5)	−0.0810(4)	1.0345(3)	3.0(2)	
C-6(G2)	0.4027(6)	−0.1686(4)	1.0534(3)	4.2(2)	
O-2(G2)	0.1738(4)	0.1384(3)	1.0384(2)	4.0(1)	
O-3(G2)	0.3629(4)	0.1435(3)	1.0960(2)	4.0(1)	
O-4(G2)	0.4960(3)	0.0127(3)	1.0654(2)	2.8(1)	
O-5(G2)	0.2557(3)	−0.0890(3)	1.0313(2)	3.1(1)	
O-6(G2)	0.3785(4)	−0.1816(4)	1.1100(2)	5.4(2)	
C-1(G3)	0.5623(4)	−0.0097(4)	1.1079(2)	2.7(1)	
C-2(G3)	0.6258(4)	0.0714(4)	1.1190(2)	2.7(1)	
C-3(G3)	0.6801(4)	0.0966(4)	1.0682(2)	2.4(1)	
C-4(G3)	0.7374(4)	0.0195(4)	1.0435(2)	2.7(1)	
C-5(G3)	0.6765(5)	−0.0654(4)	1.0420(2)	2.9(1)	
C-6(G3)	0.7386(5)	−0.1466(4)	1.0325(3)	3.5(2)	
O-2(G3)	0.5631(3)	0.1425(3)	1.1372(2)	3.2(1)	
O-3(G3)	0.7478(3)	0.1678(3)	1.0769(2)	3.0(1)	
O-4(G3)	0.7592(3)	0.0468(3)	0.9896(1)	2.7(1)	
O-5(G3)	0.6256(3)	−0.0787(3)	1.0927(2)	3.0(1)	
O-6(G3)	0.8211(4)	−0.1528(4)	1.0691(2)	4.8(1)	
C-1(G4)	0.8566(4)	0.0310(4)	0.9689(2)	2.9(1)	
C-2(G4)	0.8877(5)	0.1141(4)	0.9381(2)	3.3(2)	
C-3(G4)	0.8302(5)	0.1255(4)	0.8858(2)	3.0(2)	
C-4(G4)	0.8319(4)	0.0422(4)	0.8526(2)	2.6(1)	
C-5(G4)	0.7922(5)	−0.0322(4)	0.8866(2)	2.9(1)	
C-6(G4)	0.7944(6)	−0.1202(4)	0.8580(2)	3.7(2)	

Table 1 (continued)

Atom	x	y	z	B_{eq} [a]	OC [b]
O-2(G4)	0.8754(4)	0.1898(3)	0.9717(2)	4.6(1)	
O-3(G4)	0.8763(4)	0.1952(3)	0.8565(2)	4.1(1)	
O-4(G4)	0.7676(3)	0.0591(3)	0.8077(2)	2.8(1)	
O-5(G4)	0.8567(3)	−0.0414(3)	0.9334(2)	3.2(1)	
O-6A(G4)	0.903(2)	−0.148(1)	0.8476(8)	8.3(7)	0.35
O-6B(G4)	0.7394(5)	−0.1839(4)	0.8906(2)	3.6(2)	0.65
C-1(G5)	0.8032(4)	0.0420(4)	0.7550(2)	2.8(1)	
C-2(G5)	0.7836(4)	0.1238(4)	0.7206(2)	2.9(1)	
C-3(G5)	0.6716(5)	0.1395(4)	0.7152(2)	2.9(1)	
C-4(G5)	0.6186(4)	0.0562(4)	0.6981(2)	2.8(1)	
C-5(G5)	0.6485(4)	−0.0230(4)	0.7316(2)	2.8(1)	
C-6(G5)	0.6080(5)	−0.1088(4)	0.7109(2)	3.2(1)	
O-2(G5)	0.8308(4)	0.1968(3)	0.7440(2)	3.6(1)	
O-3(G5)	0.6504(4)	0.2085(3)	0.6781(2)	4.0(1)	
O-4(G5)	0.5136(3)	0.0724(3)	0.7061(2)	2.9(1)	
O-5(G5)	0.7556(3)	−0.0305(3)	0.7322(2)	2.9(1)	
O-6(G5)	0.6197(4)	−0.1164(3)	0.6530(2)	3.8(1)	
C-1(G6)	0.4459(4)	0.0578(4)	0.6632(2)	2.9(1)	
C-2(G6)	0.3747(5)	0.1357(4)	0.6630(3)	3.3(2)	
C-3(G6)	0.3255(5)	0.1438(4)	0.7182(2)	2.9(1)	
C-4(G6)	0.2753(4)	0.0565(4)	0.7321(2)	2.7(1)	
C-5(G6)	0.3417(4)	−0.0235(4)	0.7234(2)	2.6(1)	
C-6(G6)	0.2839(5)	−0.1087(4)	0.7258(3)	3.7(2)	
O-2(G6)	0.4265(4)	0.2137(3)	0.6483(2)	4.6(1)	
O-3(G6)	0.2533(4)	0.2116(3)	0.7169(2)	3.9(1)	
O-4(G6)	0.2521(3)	0.0616(3)	0.7883(2)	2.8(1)	
O-5(G6)	0.3904(3)	−0.0198(3)	0.6714(2)	2.90(9)	
O-6(G6)	0.1895(4)	−0.1031(3)	0.6999(2)	4.5(1)	
OW1	0.0147(5)	−0.1581(6)	1.0317(3)	7.9(2)	
OW2	−0.0040(5)	−0.1070(5)	0.7468(2)	6.3(2)	
OW3A	0.9800(6)	0.2599(6)	0.6733(3)	5.8(3)	0.66
OW3B	1.020(2)	0.174(2)	0.709(1)	8.3(8)	0.34

[a] $B_{eq} = (8\pi^2/3)[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(bb^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + 2U_{23}bb^*cc^* \cos\alpha]$.

[b] OC, Occupancy. Blank space means occupancy is 1.0.

The peaks in the final $\Delta\rho$ map were between 0.55 and -0.28 eÅ^{-3}. The atomic scattering factors were taken from International Tables [8]. The final positional parameters are listed in Table 1 *.

* The observed and calculated structure factors, H-atom coordinates, and anisotropic thermal parameters have been deposited with the Cambridge Crystallographic Data Centre. The data may be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

3. Results and discussion

The molecular structure of α-CD–2-FNPH, as drawn by ORTEP [9], and the numbering scheme are presented in Fig. 1. A stereoscopic view is presented in Fig. 2. The cell dimensions are the same within 0.04 Å as that of the isomorphous α-CD–4-NPH. Bond distances and valence angles for α-CD show the normal values for the standard α-CD inclusion complexes within expected values [10]. Intermolecular distances are tabulated in Table 2.

(a) Structure of α-CD. — As shown in Fig. 1, all glucose residues are in the $^4C_1$ chair conformation. The ring of intramolecular hydrogen bonds between O-2 and O-3′ of adjacent glucosyl residues is formed with mean O-2 · · · · O-3′ distances of 2.91(16) Å. Several parameters and geometry show that the macrocyclic conformation of the α-CD is nearly identical with that found in α-CD–4-NPH. First, the interglucosidic torsion angles φ(O-4 · · · · C-1–O-4′–C-4′) and φ′(C-1–O-4′–C-4′ · · · · O-4″) for α-CD–2-FNPH and α-CD–4-NPH, which describe the rotation of connected glucose residues about the C-1–O-4′–C-4′ linkage [11], are shown in Table 3; the good agreement of φ and φ′ values between the two complexes indicates that each glucose chair of α-CD–2-FNPH is tilted towards the viewer at almost the same angle as that observed in α-CD–4-NPH. Secondly, geometrical data for the hexagon described by the O-4 atoms are tabulated in Table 4. Both O-4 hexagons are distorted in a systematic manner: the longest diagonal [O-

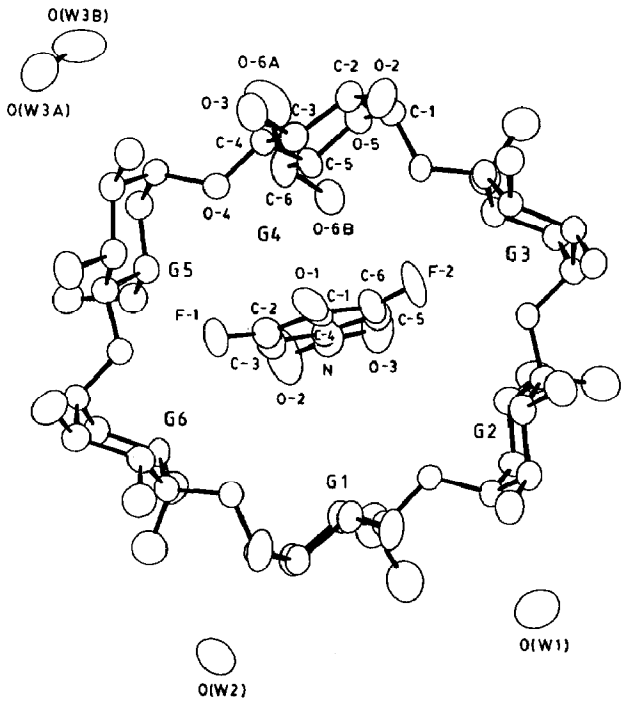

Fig. 1. Structure and numbering scheme of the α-CD–2-FNPH · $3H_2O$ complex.

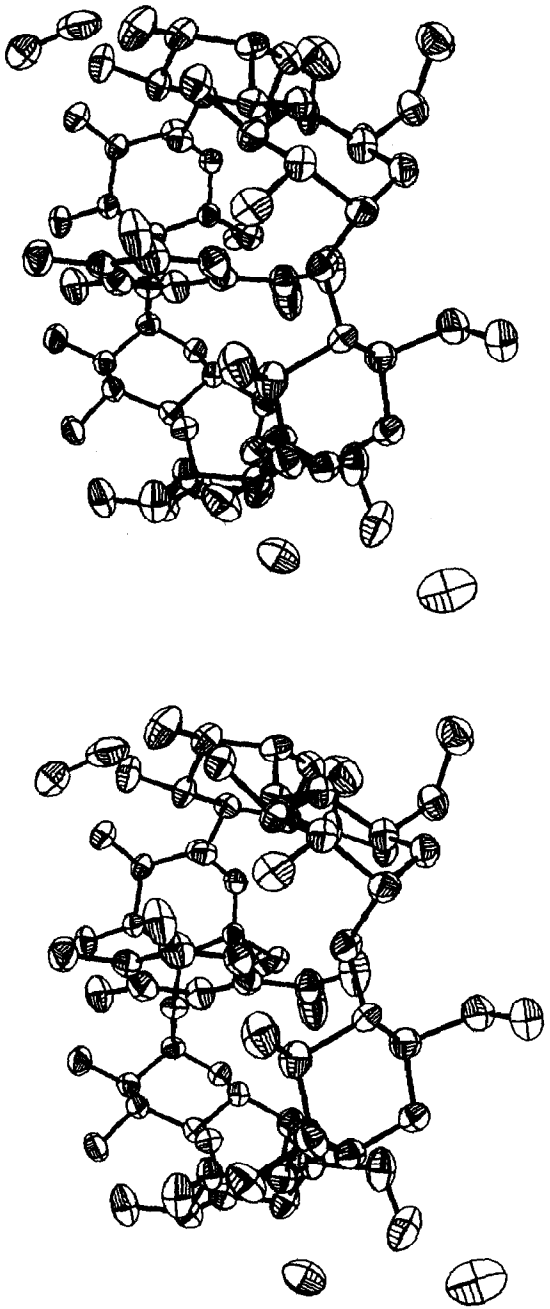

Fig. 2. Stereo view of the α-CD–2-FNPH·$3H_2O$ complex.

Table 2
Intermolecular distances (Å) for the α-CD–2-FNPH complex

Atom	Atom	SOC [a]	Distance
F-1(2-FNPH)	C-6(G5)	(2)	2.957(9)
F-2(2-FNPH)	O-2(G2)	(3)	2.84(1)
O-1(2-FNPH)	O-2(G2)	(3)	2.547(7)
O-1(2-FNPH)	O-6(G5)	(2)	2.749(7)
O-2(G1)	O-2(G3)	(4)	2.827(6)
O-3(G1)	O-3(G3)	(4)	2.691(6)
O-6(G1)	OW3A	(5)	2.88(1)
O-3(G2)	O-6(G6)	(6)	2.739(7)
O-3(G2)	O-3(G4)	(4)	2.740(6)
O-6(G2)	OW3A	(7)	2.80(1)
O-6(G2)	OW3B	(7)	2.81(3)
O-6(G2)	O-3(G4)	(8)	2.779(8)
O-6(G2)	O-6A(G4)	(8)	2.82(2)
O-2(G3)	OW2	(6)	2.881(7)
O-3(G3)	O-6(G5)	(7)	2.708(6)
O-6(G3)	OW1	(9)	2.761(9)
O-6(G3)	O-3(G5)	(7)	2.857(7)
O-3(G4)	O-2(G6)	(5)	2.890(8)
O-6A(G4)	OW2	(9)	2.86(2)
OW2	OW3A	(5)	2.79(1)

Code No.	Symmetry operator				Code No.	Symmetry operator			
2	−1.0	0.0	0.0	1.0000	6	−1.0	0.0	0.0	0.5000
	0.0	1.0	0.0	0.5000		0.0	−1.0	0.0	0.0000
	0.0	0.0	−1.0	1.5000		0.0	0.0	1.0	0.5000
3	1.0	0.0	0.0	−0.5000	7	−1.0	0.0	0.0	1.5000
	0.0	−1.0	0.0	0.5000		0.0	−1.0	0.0	0.0000
	0.0	0.0	−1.0	2.0000		0.0	0.0	1.0	0.5000
4	1.0	0.0	0.0	−0.5000	8	1.0	0.0	0.0	−0.5000
	0.0	−1.0	0.0	0.5000		0.0	−1.0	0.0	−0.5000
	0.0	0.0	−1.0	2.0000		0.0	0.0	−1.0	2.0000
5	−1.0	0.0	0.0	1.0000	9	1.0	0.0	0.0	1.0000
	0.0	1.0	0.0	−0.5000		0.0	1.0	0.0	0.0000
	0.0	0.0	−1.0	1.5000		0.0	0.0	1.0	0.0000

[a] SOC, Symmetry operator code.

4(G2) ··· O-4(G5)] is in the direction of the benzene ring as seen in Fig. 1. From a comparison between these values of two α-CD complexes, it is evident that the hexagon geometries are similar to each other. Thirdly, as shown in Fig. 1, all the primary OH groups except the disordered one point away from the centre of the molecule. Similar disorder was found in the α-CD–4-NPH complex.

(b) Structure of 2-FNPH. — The F atom is statistically disordered over two sites: F-1 (2-FNPH), 0.67; F-2 (2-FNPH), 0.33; which indicates that there are two guest orientations in the cavity. The angles of C-2–C-1–O-1 and C-6–C-1–O-1 are 118.5(6) and 123.8(6)°, respectively. Such an inequality of angle was also found in the 4-NPH molecule of the α-CD–4-NPH complex.

Table 3
Interglucosidic torsion angles (°) of the α-CD macrocycles

	α-CD–2-FNPH	α-CD–4-NPH
Angle φ	O-4 · · · C-1–O-4′–C-4′	
G1 · · · G2	−178.6	−178.7
G2 · · · G3	168.7	170.8
G3 · · · G4	160.9	160.8
G4 · · · G5	168.3	169.8
G5 · · · G6	161.5	163.7
G6 · · · G1	165.2	165.8
Angle φ′	C-1–O-4′–C-4′ · · · O-4″	
G1 · · · G2	−172.8	−173.0
G2 · · · G3	−168.5	−169.8
G3 · · · G4	−163.1	−162.8
G4 · · · G5	−170.5	−171.9
G5 · · · G6	−168.9	−170.9
G6 · · · G1	−176.2	−176.3

(c) Interaction between α-CD and 2-FNPH. — As can be seen from Fig. 2, 2-FNPH binds fully in the α-CD cavity in a similar manner to 4-NPH: the nitrophenyl group is located in the α-CD cavity while the OH group protrudes from the secondary OH side. The F atom is located in the hydrophilic space: slightly beyond the rim of the secondary OH group side, although the F atom is essentially hydrophobic. This geometry of the benzene ring inside the cavity is similar to that of other aromatic guests [12]. Thus, it appears that this position is sterically most favorable for the benzene ring. The relative geometry of the guest inside the cavity can be described by some of the intermolecular distances between host and guest. The intermolecular distances of C-3(2-FNPH) · · · O-4(G5), C-3(2-FNPH) · · · O-4(G6), C-5(2-FNPH) · · · O-4(G2), and C-5(2-FNPH) · · · O-4(G3) are 3.370, 3.585, 3.365, and 3.438 Å, respectively; the corresponding distances for the α-CD–4-NPH complex were 3.344, 3.543, 3.373, and 3.398 Å, respectively. This good agreement indicates that the orientation of 2-FNPH inside the cavity is very close to that of 4-NPH found in the α-CD–4-NPH complex.

Table 4
Distances (Å) between the O-4 atoms in the α-CD complexes

	α-CD–2-FNPH	α-CD–4-NPH
O-4(G6) · · · O-4(G1)	4.381	4.361
O-4(G1) · · · O-4(G2)	4.218	4.241
O-4(G2) · · · O-4(G3)	4.042	4.016
O-4(G3) · · · O-4(G4)	4.515	4.493
O-4(G4) · · · O-4(G5)	4.167	4.249
O-4(G5) · · · O-4(G6)	4.136	4.049
O-4(G1) · · · O-4(G4)	8.022	7.984
O-4(G2) · · · O-4(G5)	8.953	8.902
O-4(G3) · · · O-4(G6)	8.445	8.457

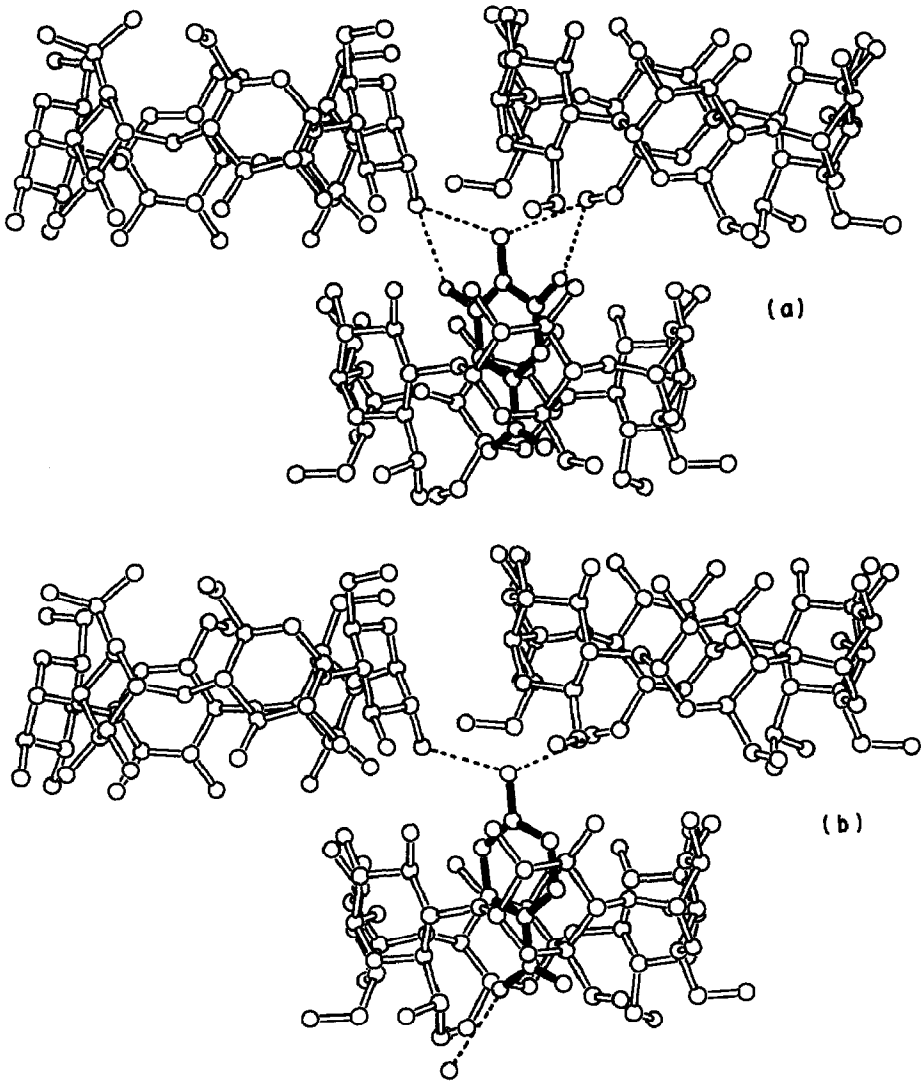

Fig. 3. Schematic representation of hydrogen bonding around the guest molecules, using CHARON [13]: (a) α-CD–2-FNPH complex, (b) α-CD–NPH complex [4]. The hydrogen bonds are shown by dotted lines. Several guest and water molecules are omitted for clarity.

A detailed discussion of hydrogen bonding is not so easy, since all the H atoms have not been determined experimentally. Thus, hydrogen bonds were analyzed in an intermolecular distance range of 2.20–3.00 Å, and intermolecular O ··· O and/or O ··· F contacts less than 3.00 Å were regarded as hydrogen bonds. Table 2 lists all the intermolecular hydrogen bonds. A schematic representation of hydrogen bonding around the guest molecule is shown in Fig. 3. The OH group of 2-FNPH is hydrogen-bonded to the primary and secondary OH groups of adjacent

α-CD molecules. An intermolecular hydrogen bond between the F atom and the secondary OH group of the enclosing α-CD cannot be observed. By contrast, between the F atom and the OH group of a symmetry-related α-CD molecule, a C–F ··· H–O type intermolecular hydrogen bond is formed. In our discussion of the guest orientation of α-CD–2-FPhOH and α-CD–4-FPhOH [2], we concluded that the C–F ··· H–O type intermolecular hydrogen bond determines the guest geometry inside the cavity. In contrast to those complexes, the intermolecular hydrogen bond in α-CD–2-FNPH cannot cause an observable change in guest orientation as compared with the α-CD–4-NPH complex. The O atom of the NO_2 group is not hydrogen-bonded to any atom; the O atom was hydrogen-bonded to one of the water molecules in α-CD–4-NPH.

(d) Hydrogen bonds. — As seen in Table 2, all the OH groups except for O-2(G4), O-2(G5), and O-3(G6) of α-CD are involved in intermolecular hydrogen bonds. The hydrogen-bonding network of α-CD–2-FNPH is not always in agreement with that found in α-CD–4-NPH. For example, O-3(G4) of α-CD–4-NPH was hydrogen-bonded only to O-3(G2); that of α-CD–2-FNPH is hydrogen-bonded to O-6(G2) and O-2(G6) besides O-3(G2) of symmetry-related α-CD molecules.

The interstices between the α-CD molecules are filled with three water molecules, one of which [O(W3)] is statistically disordered, probably in order to fill the empty space between α-CD molecules. The water molecules are hydrogen-bonded to the primary and/or secondary OH groups of host molecules, as seen in Table 2. There is no water molecule within the cavity.

Acknowledgment

We thank Mr. H. Inoue, Mac Science Co., Ltd. for assistance in the X-ray analysis.

References

[1] M.L. Bender and M. Komiyama, *Cyclodextrin Chemistry*, Springer-Verlag, 1978.
[2] M. Shibakami and A. Sekiya; *J. Chem. Soc. Chem. Commun.*, (1992) 1742–1743.
[3] K. Harata, *Carbohydr. Res.*, 48 (1976) 265–270.
[4] K. Harata, *Bull. Chem. Soc. Jpn.*, 50 (1977) 1416–1424.
[5] I. Brown, G. Eglinton, and M. Martin-Smith, *Spectrochim. Acta*, 18 (1962) 1593–1602.
[6] C. Katayama, *Acta Crystallogr., Sect. A*, 42 (1986) 19–23.
[7] P. Main, S.E. Hull, L. Lessinger, G. Germain, J.P. Declercq, and M.M. Woolfson, MULTAN-78, A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data, Universities of York, UK, and Louvain, Belgium, 1978.
[8] *International Tables for X-ray Crystallography*, Vol. IV, The Kynoch Press, Birmingham, UK, 1974.
[9] C.K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, USA, 1976.
[10] For example, (a) W. Saenger, P.K. McMullan, J. Fayos, and C. Mootz, *Acta Crystallogr., Sect. B*, 32 (1976) 2019–2028; (b) R. Hingerty and W. Saenger, *J. Am. Chem. Soc.*, 98 (1976) 3357–3365.

[11] W. Saenger, K. Beyer, and P.C. Manor, *Acta Crystallogr., Sect. B*, 32 (1976) 120–128.
[12] For example, (a) K. Harata, *Bull. Chem. Soc. Jpn.*, 48 (1975) 2409–2413; (b) K. Harata, *ibid.*, 49 (1976) 2066–2072.
[13] J.W. Lauher, CHARON, A Graphics Program for Postscript Printers, The Research Foundation of the State University of New York, 1989.