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Neutron Diffraction Study of the Hydrogen Bonding in β-Cyclodextrin Undecahydrate at 120 K: From Dynamic Flip-Flops to Static Homodromic Chains[†]

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Abstract: A neutron diffraction study of the β-cyclodextrin undecahydrate (β-CD·11H_2O) crystallized from D_2O was carried out at 120 K. Its composition is $(C_6H_7O_5D_3)_7\cdot 11D_2O$, with space group $P2_1$ and cell constants (120 K) $a = 21.617$ (4) Å, $b = 10.026$ (2) Å, $c = 14.891$ (4) Å, $\beta = 112.52$ (2)°, 5746 neutron data, and $\lambda = 1.2639$ Å. All H and D atoms are located, and the structure is refined to $R = 4.9\%$ for 5245 observations. The water positions are fully occupied except one (0.64), in contrast to the room-temperature structure where only three molecules are fully occupied and the remaining nine are distributed over 16 sites; i.e., upon cooling, water molecules have moved physically into lower energy positions. This is accompanied by ordering of the OH groups so that the 18 flip-flop hydrogen bonds of type O–($^1/_2$H)---($^1/_2$H)–O in the room-temperature structure have disappeared at 120 K and the ordered O–H---O bonds form extended patterns with homodromic arrangement, indicating (i) the strong influence of the cooperative effect and (ii) the dynamic nature of the flip-flop disorder. Besides infinite homodromic chains and a network in the *b,c* plane, a homodromic five-membered ring consisting of water molecules is located in the β-CD cavity. It is connected with a four-membered ring formed by flip-flop bonds between two water molecules and two β-CD hydroxyls. This flip-flop ring is not found at room temperature and probably exists because it is at the junction of several homodromic chains which would be interrupted if it were not of the flip-flop type.

Cyclodextrins (CD) are a family of macrocyclic oligosaccharides consisting of six (α-CD), seven (β-CD), or eight (γ-CD) D-glucose units linked by α(1–4) interglucose bonds, Figure 1. They accommodate guest molecules of suitable size in their central cavities, thereby forming inclusion complexes which can be obtained in crystalline form.[1,2] If cyclodextrins are crystallized from pure water, the corresponding hydrates are produced with water molecules included in the cavities and also located in interstices between the cyclodextrin macrocycles. Owing to the occurrence of one primary and two secondary hydroxyl groups per glucose, in conjunction with the water molecules numerous O–H---O hydrogen bonds can form in these crystal structures. They give rise to complicated patterns made up exclusively from hydrogen-bonded hydroxyl groups and water molecules. These have been studied by X-ray and neutron diffraction experiments in α-CD·6H_2O (form I,[3] form II[4]), in α-CD·7.57H_2O,[5] in β-CD·11H_2O,[6-8] and in γ-CD·18H_2O.[9-11]

In the crystal structures of α-CD·6H_2O (form I and form II) and of α-CD·7.57 H_2O, the most prominent hydrogen-bonding motifs are rings formed by four or more directly linked O–H---O–H---O–H--- interactions. Depending on the direction of the O–H bonds in these rings, three different cases can be distinguished where hydrogen bonds O–H---O in a cycle are running in the same direction (homodromic), in opposite directions (antidromic), and in random orientation (heterodromic),[12,13] Figure 2. In addition, these crystal structures display infinite, chainlike arrangements with homodromic orientation, which together with the preferred occurrence of homodromic rings indicate the influence of the cooperative effect.[14-18] This effect occurs because an O–H group is polarized if engaged in a hydrogen bond and it becomes simultaneously a better acceptor and a better donor so that chainlike structures O–H---O–H---O–H are preferred.

In the hydrate crystal structures of α-CD, all water molecules are well-ordered except for the 2.57 water molecules included in the cavity of α-CD·7.57H_2O, which are distributed statistically over four sites. The situation is even more complex in the crystal structure of the undecahydrate of the higher homologue β-CD. X-ray and neutron diffraction studies have shown that the 11 water molecules are statistically disordered over 16 positions, of which only 3 are fully occupied. Besides 35 hydrogen bonds of type O–H---O, there are 18 of type O–($^1/_2$H)---($^1/_2$H)–O per asymmetric unit.[8] In the latter, oxygen atoms are separated by normal distances, in the range 2.7–3.0 Å, and the two H-atom sites are statistically half-filled, with the occupation parameters adding up to 1.0 within the limits of accuracy. The H---H separation of ~1 Å is so short that these H-positions are mutually exclusive and we have to assume that we observe an average over two states where hydrogen atoms are in one or the other position.

$$\text{O–H---O} \rightleftharpoons \text{O---H–O}$$

In the β-CD·11H_2O crystal structure, several of these O–($^1/_2$H)---($^1/_2$H)–O hydrogen bonds are interconnected to form larger systems and an infinite chain. If in such systems H-atoms change position from one state to another, *all* the H-atoms in the associated O–($^1/_2$H)---($^1/_2$H)–O bonds have to move in a con-

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[†] Dedicated to Professor G. A. Jeffrey on the occasion of his 70th birthday. Part 23 of the series "Topography of Cyclodextrin Inclusion Complexes". For part 22 see: Saenger, W. *J. Inclusion Phenom.* **1984**, *2*, 445–454.

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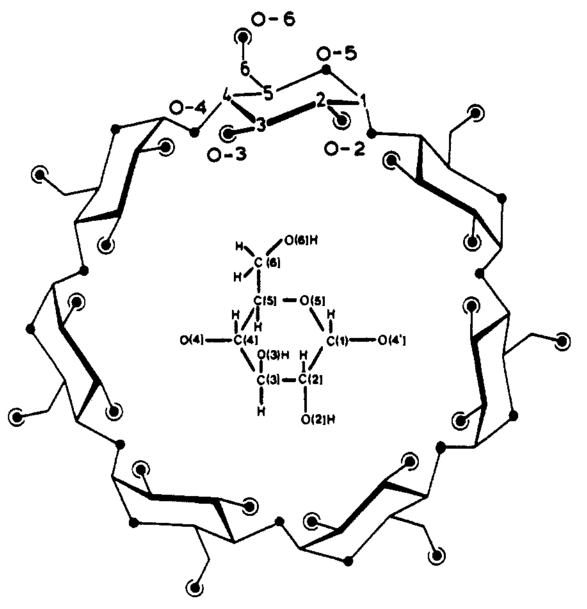

Figure 1. Chemical structure of β-cyclodextrin (β-CD). Hydroxyl groups are indicated by (⊙), and the insert describes the atomic numbering scheme.

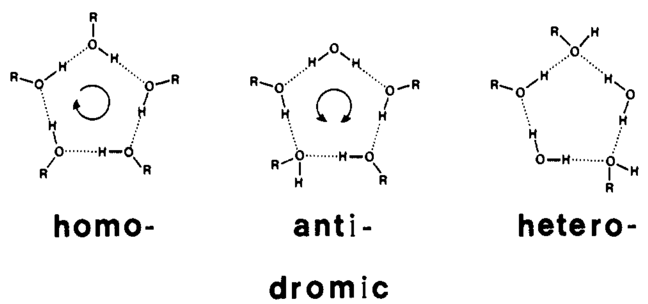

Figure 2. Illustration of the different possible hydrogen-bond orientations in rings composed of O–H---O bonds. The same nomenclature is used for chainlike structures.[12,13]

certed mode. Therefore, the term "flip-flop hydrogen bonds" was introduced for these O–($^1/_2$H)---($^1/_2$H)–O interactions.[19] Because the two states of a flip-flop hydrogen bond are energetically equivalent or nearly so, they should be favored entropically with respect to individual O–H---O hydrogen bonds.

The question arises whether we actually see, in the crystal structure analysis, *dynamic* or *static* disorder. If dynamic disorder occurs, it could be due either to rotation of hydroxyl groups (conformational change) as in (1) or to jumping of hydrogen atoms across O–H---O bonds (configurational change) as in (2).

conformational change


(1)

configurational change

$$\overleftarrow{\mathrm{H{-}O}}\cdots\overleftarrow{\mathrm{H{-}O}}\cdots\overleftarrow{\mathrm{H{-}O}} \rightleftharpoons \mathrm{H}\cdots\overrightarrow{\mathrm{O{-}H}}\cdots\overrightarrow{\mathrm{O{-}H}}\cdots\mathrm{O} \qquad (2)$$

In both cases, we would observe the time average over two different states in equilibrium. If static disorder is considered, at least two kinds of unit cells or domains exist in the crystal which exhibit one flip-flop state or the other, and the X-ray or neutron diffraction experiment sees the space average.

A preliminary answer to the question of static or dynamic disorder was obtained from calorimetric measurements with crystalline powder of β-CD·11H_2O.[20] If cooled down to ~100 K and then slowly heated to room temperature, an exothermic process was observed at 227 K. This finding was tentatively interpreted as an ordering of dynamically disordered flip-flops into one or the other form. In order to test this view, a neutron diffraction study of β-CD·11D_2O below this transition temperature was carried out. If static disorder prevails, the O–($^1/_2$H)---($^1/_2$H)–O flip-flops observed at room temperature should not disappear upon cooling, and in case of dynamical transform, all or at least some of the flip-flops should transform into one of the two states O–H---O and O---H–O. In this paper, the results of the low-temperature neutron diffraction study on β-CD·11D_2O are described and evidence for dynamic disorder is presented.

Table I. Crystallographic Data for β-CD·11H_2O[a]

	room temp (293 K)			low temp (120 K)
	X-ray[b]	neutron[c]	neutron[d]	neutron[d]
a, Å	21.29 (2)	21.261 (6)	21.268 (11)	21.617 (4)
b, Å	10.33 (1)	10.306 (3)	10.314 (6)	10.026 (2)
c, Å	15.10 (2)	15.123 (4)	15.082 (8)	14.891 (4)
β, deg	112.3 (5)	112.3 (5)	112.40 (3)	112.52 (2)
V, Å	3072.5	3065.8	3067.5	2981.3
d, g/cm^3		1.462	1.462	1.505

[a] Space group $P2_1$. [b] Lindner and Saenger, 1982. [c] Betzel et al., 1984. [d] This work.

Experimental Section

Commercially available β-CD (Serva, Heidelberg) was dissolved in D_2O and the solvent removed in a rotary evaporator. This process was repeated 5 times in order to remove all exchangeable H-atoms and hence eliminate their incoherent scattering contribution. A large crystal of dimensions 2.1 × 2.2 × 2.4 mm was finally grown from a hot, saturated solution which was cooled slowly in a Dewar filled with hot water. Because β-CD·11D_2O crystals tend to crack when left without mother liquor, the crystal was fixed in a quartz capillary with some quartz wool, and a drop of mother liquor was placed at one end of the capillary which was then sealed with a two-component adhesive suitable for low-temperature work.

The neutron diffraction measurements were performed on the four-circle instrument D8 at the ILL high-flux reactor, Grenoble, using a wavelength of 1.2639 Å. The unit cell parameters were first measured at room temperature and are consistent with those determined earlier with a conventional X-ray source (Table I). The heat shields of the DISPLEX cryorefrigerator were then mounted, and the temperature was slowly lowered to 120 K (ca. 1 °C/min). Data were collected at 120 K, and two reflections (400 and 002) which displayed substantially different intensities at room temperature and at 120 K were chosen to monitor the transition point when the crystal was slowly heated after data collection was terminated. This proved to be more successful, and at 203 ± 0.5 K, a transition was observed which could be reproduced by repeated temperature variations. The change in transition temperature from the anticipated 227 K (for H_2O) to 203 K (for D_2O) is best explained as an effect of H/D exchange.

The 120 K cell parameters of β-CD·11D_2O are presented in Table I. When the crystal is cooled, *a* increases by 0.35 Å whereas *b* and *c* decrease by 0.29 and 0.19 Å, respectively, leading to an overall volume change of −86.2 Å^3, which apparently occurs close to the transition point. Reflection intensity data were collected in several shells up to $2\theta = 52°$ by employing the ω–θ step scan technique with small steps in the background to avoid reflection overlap. In the last shell from 48° to 52°, only intensities $I > 10\sigma_I$ (after a prescan) were measured. In total, 5746 reflections were collected, of which 501 are considered unobserved ($I < 2\sigma_I$) after the usual systematic corrections were made.

Structure Determination and Refinement. The positions of glucose carbon and oxygen atoms determined in the X-ray study[6] were used to initate full-matrix least-squares refinement using the XRAY 76 system.[21] These and all subsequent refinements were based on $|F_{hkl}|$ and on σ_F obtained from counting statistics. Scattering lengths of C, O, H, and D atoms were 0.66484, 0.5805, −0.37409, and 0.6674, respectively.[22]

As refinement proceeded, all C–H hydrogen atoms were located in Fourier maps. They showed up as negative peaks at their expected positions. The assignment of the remaining positive peaks in difference Fourier maps to deuterium and water oxygen atoms proved more complicated in some instances. The reason is that the neutron scattering

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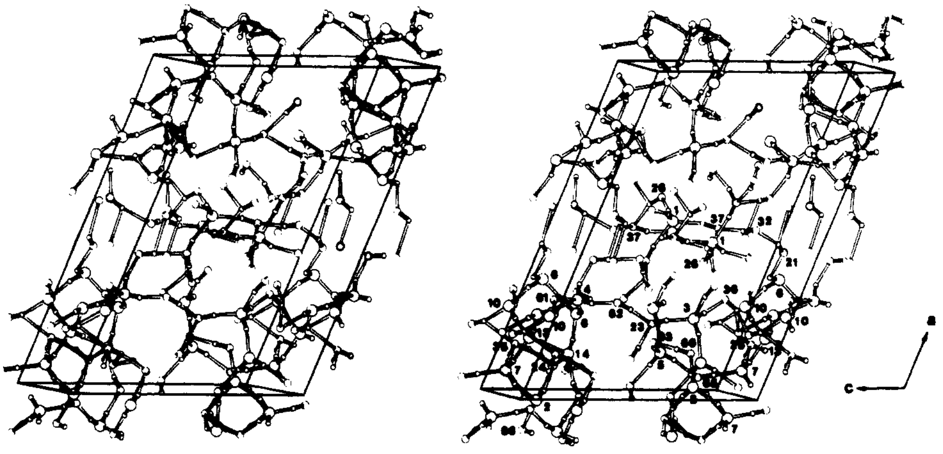


Figure 3. Stereoview (along *b*) of the unit cell contents of β-CD·11H_2O, with all β-CD carbon and C–H hydrogen atoms omitted for clarity. Covalent O–D bonds shown by solid lines, hydrogen bonds by open lines. Circles in increasing size represent D, O (hydroxyl), and O (water) atoms. Individual atoms denoted by two numbers are β-CD hydroxyls (e.g., 24 is O(2)4, i.e., oxygen 2 in glucose number 4), and water oxygen atoms are called, for example, 7 or 10 for W7 and W10.

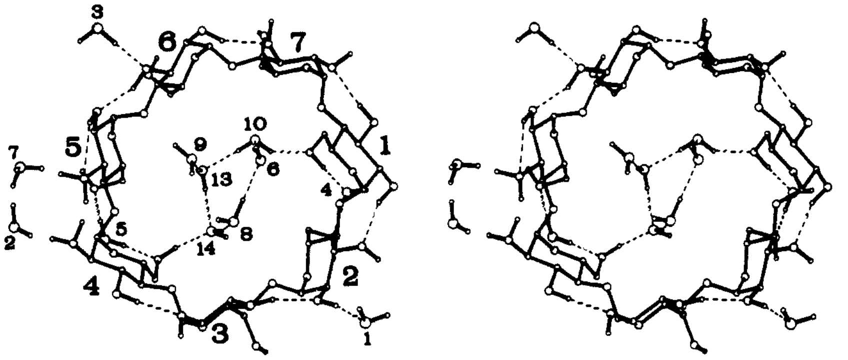


Figure 4. Stereoview of the covalent structure of β-CD (solid lines) and associated hydrogen bonds (dashed lines) as determined at 120 K. D, C, and O atoms are indicated by circles with increasing radii; C–H hydrogens are omitted for clarity. Individual glucoses are numbered at the periphery of the molecule (large numbers); hydrogen-bonded water molecules are denoted by small numbers. The flip-flop quadrilateral ring to the left is composed of O(2)4, O(3)5, W7, and W2, and the homodromic pentagonal ring in the cavity of β-CD is formed by water molecules W8, W6, W10, W13, and W14.

lengths of D and O are nearly identical, and in the case of disordered O and D atoms, they can be confused. Consideration of contact and bond distances, however, helped to clarify such situations.

After the isotropic refinement had converged at $R = 15\%$ where R is defined as $\sum|(|F_o| - |F_c|)|/\sum|F_o|$, the thermal parameters were varied anisotropically. Additional cycles of difference Fourier maps and least-squares refinement allowed positioning of all deuterium and water oxygen atoms. Problems arose with the bond parameters and some U_{ij}'s of water 6. All attempts to overcome this proved to be unsuccessful, probably because the difference peaks were due to only partial H/D exchange. In the final stages of the refinement, all occupation parameters of deuterium and of water oxygen atoms were released and parameters for C and H atoms were kept at 1.0. Because occupation parameters and temperature factors were heavily correlated, a damping factor of 0.3 was used. After three cycles of refinement, the occupation parameters were fixed (and reset to 1.0 if refinement indicated insignificant deviations from full occupancy) and all the other parameters released again in a few final cycles.

The function minimized was $\sum w||F_o| - |F_c||^2$ with a weighting scheme $w = {}^1/_{\sigma^2(F)}$ and an observation/parameter ratio of 3.1. Extinction does not play a significant part in this structure analysis as indicated by the largest difference between $|F_o|$ and $|F_c|$ of only −3.24; therefore, no extinction correction was included.

The least-squares refinement converged at $R = 4.9\%$, with a difference Fourier map showing only two minor peaks in the region of water 6, which could not be assigned on the basis of stereochemical considerations. The occupancy factors of the water oxygen atoms add up to 11.6 compared with 11.0 found in the room-temperature crystal structure.

Results

(a) Fully Ordered Water Molecules and Hydroxyl Groups at 120 K. Experimental results of the present study are summarized in Tables II–V, which give details of covalent and hydrogen-bonding geometry in β-CD·11D_2O, and in Figures 3 and 4. As expected, the covalent bond distances, angles, and torsion angles in the β-CD molecules at 120 K are similar to, but better defined than, the room-temperature data derived from X-ray and neutron diffraction studies.[6,8] A major difference is that the primary hydroxyl group O(6)2 is statistically disordered over two sites at room temperature, with the higher occupied site (0.54 (2)) in g/t conformation exhibiting a higher temperature factor *B* (14.1 Å^2) than the lower occupied g/g site (0.46 (2), $B = 6.3$ Å^2). In the 120 K study, the latter is now fully occupied at the expense of the former; i.e., as expected the less well-defined site with the higher temperature factor disappears at low temperature.

A striking difference between the room-temperature neutron crystal structure analysis of β-CD·11D_2O and the low-temperature study concerns the degree of ordering of certain atoms. In general the water molecules and hydroxyl hydrogen atoms at room temperature are disordered whereas they are ordered at low temperature, or more specifically it follows that:

Room Temperature. All water molecule oxygens are *disordered* except W1, W2, and W4, and all water and hydroxyl hydrogens are *disordered* except O(6)1–D, O(6)3–D, O(6)4–D, O(6)5–D, and O(6)6–D.

Low Temperature. All water molecules and O–D hydrogens are *ordered* except water W8 (occupation 0.64) and hydrogens of W2, W7, O(2)4, and O(3)5.

Although the hydrogen-bonding scheme in β-CD·11D_2O at 120 K looks clearer compared with the one at room temperature, it is still very complex, Figure 3. If analyzed in detail there are, however, several well-defined motifs in which almost all of the O–D---O hydrogen bonds are engaged in systematic, homodromic arrangements; see Figures 4–7. In the following, fully occupied exchanged hydrogen positions are identified by D whereas the

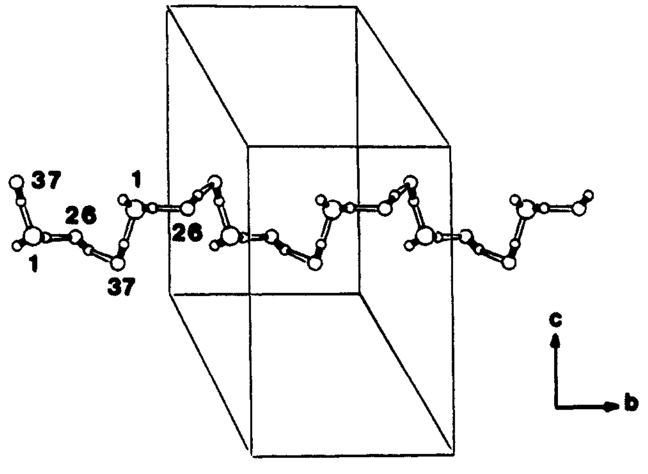


Figure 5. View of the homodromic chain in the *b* direction which resulted, at 120 K, from a chain in which all hydrogen bonds are of the flip-flop type at room temperature. Atoms are drawn as described in Figure 3.

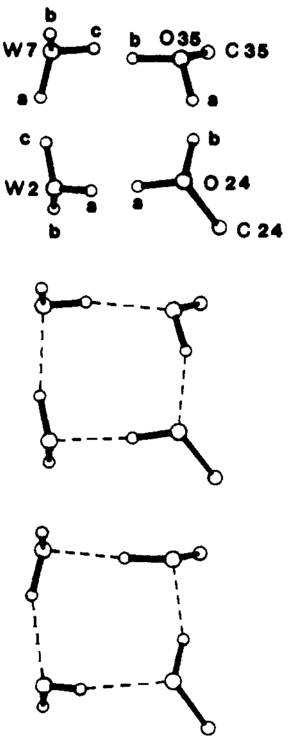


Figure 6. Four-membered flip-flop ring (top; see also Figures 3 and 4) representing an average over two homodromic rings where hydrogen bonds run in clockwise (center) and anticlockwise sense (bottom).

hydrogen atoms engaged in flip-flops and therefore partially (~ 0.5) occupied are denoted *D*.

(b) Almost Fully Satisfied Hydrogen-Bonding Potentials. All of the water and hydroxyl hydrogen atoms are engaged in D---O interactions. The water oxygen atoms all accept two hydrogen bonds, and the hydroxyl groups accept one bond except O(2)3, O(2)4, and O(3)7 which accept two bonds and O(3)4 and O(6)7 which have no hydroxyl hydrogens closer than 3.2 Å. All of the O(4) ether-like oxygen atoms are involved in intramolecular three-center bonds[16,23,24] (see Table V), and there are two additional contacts to ether-like oxygens O(5), $\mathrm{OW1{-}D_B{-}{-}{-}O(5)7}$ (1.865 Å) and $\mathrm{OW9{-}D_A{-}{-}{-}O(4)6}$ (2.04 Å), the latter involving a contact between an enclosed water molecule W9 and the surrounding β-CD.

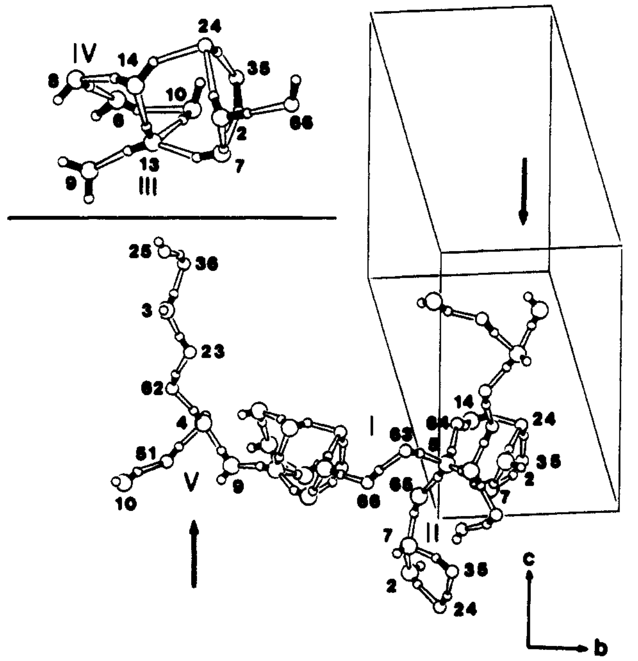


Figure 7. Five situations (I–V described in paragraph (e)) where symmetry-related flip-flop rings are connected by homodromic chains. Large arrows indicate symmetry-related infinite chains running in the *c* direction. The insert, top left, gives a closeup view at a slightly different orientation of the five-membered homodromic ring formed by water molecules W6→W10→W13→W14→W8→W6 etc. and of the four-membered flip-flop ring formed by two water molecules and two hydroxyl groups, W7←→W2←→O(2)4←→O(3)5←→etc. See also Schemes I–III where a simplified version of this picture is given.

(c) Homodromic Chain along *b*. In the room-temperature crystal structure of β-CD·11D$_2$O, an infinite chain of flip-flop hydrogen bonds extends along the 2_1 screw axis at $x = z = {}^1/_2$.[8] The chain consists of one water molecule and two secondary hydroxyl groups from the same β-CD molecule.

$$\leftrightarrow[D\text{–}\mathrm{OW1}\text{–}D\leftrightarrow D\text{–}\mathrm{O(2)6}\text{–}D\leftrightarrow D\text{–}\mathrm{O(3)7}\text{–}D]_\infty\leftrightarrow D\text{–}\mathrm{OW1}\text{–}D\leftrightarrow$$

At 120 K, this flip-flop chain no longer exists but is now changed to an infinite chain of O–D---O hydrogen bonds in homodromic arrangement, Figure 5.

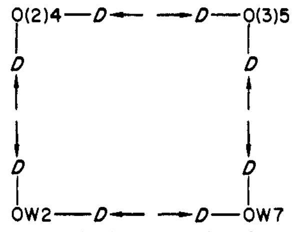
$$\rightarrow[\mathrm{OW1{-}D_A}\rightarrow\mathrm{O(2)6{-}D}\rightarrow\mathrm{O(3)7{-}D}]_\infty\rightarrow\mathrm{OW1{-}D_A}\rightarrow$$

This chain is in hydrogen-bonding contact with a number of other hydroxyl groups and forms three-center bonds with two ether-type oxygens O(4) and O(5).

$\mathrm{O(2)2{-}D}\rightarrow\mathrm{OW1}$, $\mathrm{O(3)2{-}D}\rightarrow\mathrm{O(3)7}$;

$\mathrm{OW1{-}D_B}\rightarrow\mathrm{O(5)7}$; $\mathrm{O(2)6{-}D}\rightarrow\mathrm{O(4)7}$ (three-center[15,16])

(d) A Four-Membered Ring Composed Entirely of Flip-Flops (Figures 4 and 6). The most remarkable feature in the crystal structure of β-CD·11D$_2$O at 120 K is a four-membered ring in which all the hydrogen bonds are flip-flops.



At room temperature, the hydrogen bonds involving O(2)4 are also flip-flops but those to water W7 are of the normal O–D---O type and arranged in a homodromic sense, OW2–*D*---OW7–*D*---O(3)5. The reason for the formation of this flip-flop ring at 120 K must be an energetical advantage compared with the room-temperature structure. This advantage could be due to the fact that at 120 K, W7 is fully occupied, whereas at room tem-

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Table II. Fractional Atomic Coordinates and Average Isotropic Temperature Factors[a]

atom	x	y	z	U_{eq},[b] 10^2 Å^2	atom	x	y	z	U_{eq},[b] 10^2 Å^2
C11	0.5471 (2)	0.5379 (–)	0.0850 (3)	1.0 (1)	C54	0.9473 (2)	–0.1102 (4)	0.3466 (3)	1.0 (1)
H11	0.5469 (4)	0.6138 (9)	0.1406 (6)	2.8 (3)	H54	0.9060 (4)	–0.0774 (8)	0.2786 (5)	2.3 (2)
C21	0.4760 (2)	0.5093 (4)	0.0134 (3)	1.3 (1)	O54	0.9965 (2)	–0.1783 (5)	0.3206 (3)	1.2 (1)
H21	0.4528 (4)	0.6039 (9)	–0.0209 (6)	2.7 (3)	C64	0.9838 (2)	0.0069 (4)	0.4074 (3)	1.7 (1)
O21	0.4354 (2)	0.4598 (6)	0.0614 (4)	1.8 (1)	H64A	1.0279 (4)	–0.0283 (9)	0.4698 (6)	2.9 (3)
D21	0.4620 (3)	0.3971 (6)	0.1115 (4)	3.6 (2)	H64B	0.9507 (5)	0.057 (1)	0.4355 (7)	4.0 (3)
C31	0.4790 (2)	0.4138 (4)	–0.0654 (3)	1.1 (1)	O64	1.0077 (3)	0.0964 (5)	0.3541 (4)	2.3 (2)
H31	0.5003 (4)	0.3167 (9)	–0.0299 (6)	2.4 (3)	D64	0.9696 (3)	0.1496 (6)	0.3153 (5)	4.1 (2)
O31	0.4134 (2)	0.3949 (5)	–0.1356 (3)	1.5 (1)	C15	0.8645 (2)	–0.2405 (4)	–0.1189 (3)	0.9 (1)
D31	0.4171 (2)	0.3353 (6)	–0.1851 (4)	3.1 (2)	H15	0.8724 (4)	–0.2522 (9)	–0.1883 (6)	2.6 (3)
C41	0.5243 (2)	0.4715 (4)	–0.1119 (3)	1.0 (1)	C25	0.8605 (2)	–0.3770 (4)	–0.0765 (3)	1.1 (1)
H41	0.5007 (4)	0.5605 (8)	–0.1560 (6)	2.4 (2)	H25	0.9060 (4)	–0.4332 (9)	–0.0714 (6)	2.7 (3)
O41	0.5318 (2)	0.3678 (5)	–0.1745 (3)	1.2 (1)	O25	0.8023 (2)	–0.4421 (5)	–0.1406 (3)	1.3 (1)
C51	0.5924 (2)	0.5101 (4)	–0.0373 (3)	1.3 (1)	D25	0.7913 (3)	–0.5160 (6)	–0.1087 (4)	3.4 (2)
H51	0.6197 (4)	0.4180 (9)	–0.0030 (6)	2.6 (3)	C35	0.8610 (2)	–0.3618 (4)	0.0254 (3)	0.9 (1)
O51	0.5847 (2)	0.5952 (5)	0.0360 (3)	1.4 (1)	H35	0.8147 (4)	–0.3122 (8)	0.0219 (6)	2.2 (2)
C61	0.6330 (2)	0.5915 (5)	–0.0818 (3)	1.8 (1)	O35	0.8614 (3)	–0.4896 (5)	0.0668 (4)	1.5 (2)
H61A	0.6353 (4)	0.541 (1)	–0.1462 (7)	3.6 (3)	D35A[e]	0.8776 (5)	–0.481 (1)	0.1380 (8)	2.9 (4)
H61B	0.6077 (5)	0.687 (1)	–0.1095 (7)	3.4 (3)	D35B[f]	0.8918 (5)	–0.552 (1)	0.0537 (7)	2.6 (4)
O61	0.6990 (2)	0.6110 (6)	–0.0164 (4)	2.4 (2)	C45	0.9220 (2)	–0.2809 (4)	0.0879 (3)	1.0 (1)
D61	0.6982 (3)	0.6748 (6)	0.0343 (4)	3.8 (2)	H45	0.9687 (4)	–0.3343 (8)	0.0966 (6)	2.4 (2)
C12	0.6903 (2)	0.2803 (4)	0.4120 (3)	1.1 (1)	O45	0.9170 (2)	–0.2626 (4)	0.1788 (3)	1.0 (1)
H12	0.7145 (4)	0.2902 (9)	0.4909 (5)	2.4 (2)	C55	0.9210 (2)	–0.1463 (4)	0.0386 (3)	1.0 (1)
C22	0.6136 (2)	0.2777 (4)	0.3795 (3)	1.1 (1)	H55	0.8745 (4)	–0.0938 (8)	0.0322 (6)	2.2 (2)
H22	0.6016 (4)	0.3578 (9)	0.4187 (5)	2.4 (2)	O55	0.9209 (2)	–0.1710 (5)	–0.0570 (3)	1.4 (1)
O22	0.5963 (2)	0.1525 (5)	0.4086 (3)	1.5 (1)	C65	0.9800 (2)	–0.0582 (4)	0.0940 (3)	1.4 (1)
D22	0.5535 (3)	0.1586 (5)	0.4141 (3)	3.0 (2)	H65A	0.9791 (5)	0.028 (1)	0.0478 (7)	3.8 (3)
C32	0.5774 (2)	0.2993 (4)	0.2701 (3)	0.9 (1)	H65B	0.9737 (4)	–0.0217 (9)	0.1593 (6)	3.0 (3)
H32	0.5832 (4)	0.2099 (8)	0.2318 (6)	2.2 (2)	O65	1.0420 (2)	–0.1256 (5)	0.1262 (4)	2.0 (1)
O32	0.5076 (2)	0.3160 (5)	0.2455 (3)	1.5 (1)	D65	1.0510 (2)	–0.1557 (5)	0.0697 (4)	3.5 (2)
D32	0.5027 (2)	0.3867 (6)	0.2867 (4)	3.5 (2)	C16	0.6659 (2)	0.0516 (4)	–0.3569 (3)	1.0 (1)
C42	0.6071 (2)	0.4172 (4)	0.2348 (3)	1.1 (1)	H16	0.6429 (4)	0.0984 (8)	–0.4289 (5)	2.1 (2)
H42	0.5979 (4)	0.5126 (9)	0.2660 (6)	2.9 (3)	C26	0.6595 (2)	–0.0996 (4)	–0.3644 (3)	1.0 (1)
O42	0.5749 (2)	0.4174 (4)	0.1310 (3)	1.1 (1)	H26	0.6787 (4)	–0.1354 (9)	–0.4183 (6)	2.6 (2)
C52	0.6827 (2)	0.3949 (4)	0.2681 (3)	1.2 (1)	O26	0.5906 (2)	–0.1378 (5)	–0.4014 (3)	1.4 (1)
H52	0.6913 (4)	0.2989 (9)	0.2384 (6)	2.6 (3)	D26	0.5679 (2)	–0.0771 (5)	–0.3735 (4)	2.9 (1)
O52	0.7103 (2)	0.3920 (5)	0.3730 (3)	1.2 (1)	C36	0.6989 (2)	–0.1614 (4)	–0.2667 (3)	1.0 (1)
C62	0.7196 (2)	0.5020 (4)	0.2374 (3)	1.8 (1)	H36	0.6760 (4)	–0.1348 (8)	–0.2124 (5)	2.3 (2)
H62A	0.7729 (4)	0.480 (1)	0.2676 (7)	3.5 (3)	O36	0.6985 (2)	–0.3015 (5)	–0.2774 (3)	1.4 (1)
H62B	0.7017 (4)	0.499 (1)	0.1572 (6)	3.2 (3)	D36	0.7302 (3)	–0.3406 (5)	–0.2162 (4)	3.2 (2)
O62	0.7073 (2)	0.6329 (5)	0.2614 (4)	1.7 (1)	C46	0.7710 (2)	–0.1104 (4)	–0.2292 (3)	1.0 (1)
D62	0.7282 (3)	0.6476 (5)	0.3311 (4)	3.3 (2)	H46	0.7957 (4)	–0.1437 (8)	–0.2777 (5)	2.2 (2)
C13	0.8578 (2)	–0.1245 (4)	0.4994 (3)	1.0 (1)	O46	0.8048 (2)	–0.1685 (5)	–0.1358 (3)	1.1 (1)
H13	0.8957 (4)	–0.1872 (9)	0.5555 (5)	2.3 (2)	C56	0.7728 (2)	0.0420 (4)	–0.2254 (3)	1.0 (1)
C23	0.7873 (2)	–0.1607 (4)	0.4901 (3)	1.0 (1)	H56	0.7503 (4)	0.0769 (8)	–0.1734 (5)	2.4 (2)
H23	0.7848 (4)	–0.1500 (9)	0.5629 (5)	2.4 (2)	O56	0.7333 (2)	0.0899 (4)	–0.3199 (3)	1.0 (1)
O23	0.7731 (2)	–0.2939 (5)	0.4571 (3)	1.4 (1)	C66	0.8421 (2)	0.0998 (5)	–0.1976 (3)	1.6 (1)
D23	0.7614 (2)	–0.3467 (5)	0.5050 (4)	3.1 (2)	H66A	0.8726 (4)	0.070 (1)	–0.1225 (6)	3.4 (3)
C33	0.7371 (2)	–0.0641 (4)	0.4218 (3)	1.0 (1)	H66B	0.8390 (4)	0.208 (1)	–0.1991 (7)	3.3 (3)
H33	0.7371 (4)	–0.0772 (9)	0.3486 (6)	2.7 (3)	O66	0.8740 (2)	0.0541 (5)	–0.2588 (4)	2.0 (2)
O33	0.6728 (2)	–0.0909 (5)	0.4212 (3)	1.4 (1)	D66	0.8629 (3)	0.1124 (6)	–0.3148 (4)	3.5 (2)
D33	0.6472 (2)	–0.0075 (6)	0.4058 (3)	2.8 (2)	C17	0.5106 (2)	0.3957 (4)	–0.2736 (3)	1.1 (1)
C43	0.7572 (2)	0.0782 (4)	0.4542 (3)	1.0 (1)	H17	0.4777 (4)	0.4840 (8)	–0.2941 (5)	2.2 (2)
H43	0.7524 (4)	0.0948 (8)	0.5250 (5)	2.1 (2)	C27	0.4743 (2)	0.2706 (4)	–0.3303 (3)	1.1 (1)
O43	0.7115 (2)	0.1610 (5)	0.3816 (3)	1.2 (1)	H27	0.4546 (4)	0.2955 (8)	–0.4085 (6)	2.4 (2)
C53	0.8298 (2)	0.1056 (4)	0.4661 (3)	0.9 (1)	O27	0.4217 (2)	0.2355 (5)	–0.3004 (3)	1.5 (1)
H53	0.8330 (4)	0.0992 (9)	0.3930 (6)	2.5 (2)	D27	0.3820 (2)	0.2804 (5)	–0.3441 (4)	2.7 (1)
O53	0.8733 (2)	0.0082 (5)	0.5303 (3)	1.2 (1)	C37	0.5239 (2)	0.1557 (4)	–0.3111 (3)	1.0 (1)
C63	0.8550 (2)	0.2401 (4)	0.5090 (3)	1.3 (1)	H37	0.5391 (4)	0.1256 (8)	–0.2334 (6)	2.4 (2)
H63A	0.9082 (4)	0.2490 (9)	0.5210 (7)	3.5 (3)	O37	0.4945 (2)	0.0404 (5)	–0.3663 (5)	1.0 (1)
H63B	0.8271 (4)	0.3181 (8)	0.4582 (6)	2.8 (3)	D37	0.4805 (2)	0.0648 (5)	–0.4364 (4)	2.9 (2)
O63	0.8468 (2)	0.2518 (5)	0.6000 (3)	1.7 (1)	C47	0.5855 (2)	0.1989 (4)	–0.3294 (3)	0.9 (1)
D63	0.8646 (3)	0.3379 (6)	0.6287 (4)	3.3 (2)	H47	0.5721 (4)	0.2143 (8)	–0.4079 (5)	2.0 (2)
C14	0.9730 (2)	–0.2935 (4)	0.2645 (3)	0.8 (1)	O47	0.6328 (2)	0.0932 (4)	–0.2967 (3)	0.9 (1)
H14	1.0147 (4)	–0.3311 (9)	0.2455 (5)	2.4 (2)	C57	0.6155 (2)	0.3263 (4)	–0.2755 (3)	1.0 (1)
C24	0.9498 (2)	–0.3972 (4)	0.3215 (3)	1.2 (1)	H57	0.6345 (4)	0.3068 (8)	–0.1972 (5)	2.3 (2)
H24	0.9934 (3)	–0.4225 (9)	0.3881 (5)	2.4 (2)	O57	0.5654 (2)	0.4280 (4)	–0.2994 (3)	1.1 (1)
O24	0.9271 (2)	–0.5132 (5)	0.2651 (3)	1.3 (1)	C67	0.6720 (2)	0.3792 (4)	–0.3010 (3)	1.2 (1)
D24A[c]	0.9653 (5)	–0.558 (1)	0.2565 (8)	3.1 (4)	H67A	0.7158 (4)	0.3102 (9)	–0.2731 (7)	3.3 (3)
D24B[d]	0.8982 (5)	–0.491 (1)	0.2003 (6)	2.9 (3)	H67B	0.6885 (4)	0.4742 (9)	–0.2620 (7)	3.0 (3)
C34	0.8954 (2)	–0.3366 (4)	0.3479 (3)	1.0 (1)	O67	0.6496 (2)	0.3974 (5)	–0.4023 (3)	2.0 (1)
H34	0.8514 (4)	–0.3161 (9)	0.2802 (6)	2.4 (2)	D67	0.6833 (3)	0.4510 (5)	–0.4139 (4)	3.6 (2)
O34	0.8772 (2)	–0.4286 (5)	0.4056 (3)	1.7 (1)	OW1	0.5246 (2)	–0.3769 (5)	–0.4441 (3)	1.7 (1)
D34	0.8437 (3)	–0.3877 (5)	0.4244 (4)	3.0 (2)	DW1A	0.5544 (3)	–0.2987 (5)	–0.4227 (4)	2.9 (2)
C44	0.9183 (2)	–0.2041 (4)	0.4014 (3)	1.2 (1)	DW1B	0.5481 (2)	–0.4459 (5)	–0.3981 (4)	3.3 (2)
H44	0.9560 (4)	–0.2260 (9)	0.4750 (5)	2.4 (2)	OW2	1.0286 (4)	–0.6427 (8)	0.2278 (7)	3.2 (2)
O44	0.8608 (2)	–0.1430 (4)	0.4072 (3)	1.1 (1)	DW2A[g]	0.9998 (8)	–0.612 (1)	0.2490 (9)	3.9 (4)

Table II (Continued)

atom	x	y	z	U_{eq},[b] 10^2 Å^2	atom	x	y	z	U_{eq},[b] 10^2 Å^2
DW2B	1.0630 (3)	−0.5775 (7)	0.2364 (4)	4.0 (2)	DW7C[j]	0.9091 (5)	−0.623 (1)	0.0442 (8)	3.0 (4)
DW2C[h]	1.0068 (6)	−0.663 (1)	0.159 (1)	4.7 (6)	OW8[k]	0.2450 (7)	−0.397 (2)	0.805 (1)	4.2 (6)
OW3	0.7534 (2)	−0.4225 (5)	−0.3983 (4)	2.1 (1)	DW8A[l]	0.2778 (6)	−0.367 (1)	0.868 (1)	4.8 (5)
DW3A	0.7374 (2)	−0.3735 (5)	−0.3557 (4)	3.3 (2)	DW8B[m]	0.2529 (7)	−0.494 (2)	0.807 (1)	8.3 (7)
DW3B	0.7993 (2)	−0.4516 (5)	−0.3566 (4)	3.5 (2)	OW9	0.7539 (4)	−0.0494 (7)	0.0020 (7)	5.1 (3)
OW4	0.2953 (3)	0.3109 (6)	−0.1213 (5)	2.6 (2)	DW9A	0.7626 (3)	−0.1137 (8)	−0.0402 (5)	5.6 (2)
DW4A	0.3413 (3)	0.3428 (6)	−0.1082 (4)	4.3 (2)	DW9B	0.7392 (3)	−0.1018 (7)	0.0451 (6)	6.6 (3)
DW4B	0.2866 (3)	0.2542 (6)	−0.1773 (4)	3.8 (2)	OW10	0.2604 (4)	−0.142 (1)	0.0535 (6)	5.4 (3)
OW5	0.8854 (2)	−0.5010 (5)	−0.3052 (3)	2.0 (1)	DW10A	0.2605 (3)	−0.0638 (8)	0.0167 (5)	5.0 (2)
DW5A	0.9227 (3)	−0.4624 (6)	−0.3191 (4)	4.0 (2)	DW10B	0.2250 (7)	−0.193 (1)	0.018 (1)	13.3 (6)
DW5B	0.9062 (3)	−0.5426 (5)	−0.2414 (4)	3.5 (2)	OW13	0.8316 (5)	0.169 (1)	0.0509 (8)	7.7 (4)
DW6	0.3468 (8)	0.660 (2)	−0.004 (2)	16.3 (8)	DW13A	0.8079 (4)	0.0873 (8)	0.0440 (6)	6.7 (3)
DW6A	0.359 (1)	0.595 (2)	0.041 (1)	16.7 (7)	DW15B	0.8459 (5)	0.1754 (9)	0.1126 (9)	8.0 (4)
DW6B	0.3204 (6)	0.715 (2)	0.0309 (9)	12.5 (6)	OW14	0.8818 (3)	0.2221 (8)	0.2543 (7)	5.7 (3)
OW7	0.9357 (3)	−0.6923 (5)	0.0364 (4)	2.9 (2)	DW14A	0.8869 (4)	0.3163 (9)	0.2766 (6)	6.8 (3)
DW7A[i]	0.9772 (4)	−0.688 (1)	0.0981 (7)	3.3 (4)	DW14B	0.8368 (7)	0.193 (1)	0.2430 (7)	10.5 (5)
DW7B	0.9057 (3)	−0.7619 (6)	0.0396 (6)	5.6 (2)					

[a] All occupation factors P are 1.0 except for the hydrogen atoms in flip-flop bonds and for OW8. Hydrogen atoms in C–H groups are called H; deuterium-exchanged hydrogens are called D. The y coordinate of atom C11 was held fixed during refinement. In the text, atom numbers are in parentheses; e.g., C63 is designated C(6)3, i.e., carbon atom C(6) of glucose number 3. [b] U_{eq} obtained from the anisotropic temperature factors, $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*a_ia_j$. [c] $P = 0.49$ (2). [d] $P = 0.49$ (2). [e] $P = 0.49$ (2). [f] $P = 0.48$ (2). [g] $P = 0.47$ (2). [h] $P = 0.49$ (2). [i] $P = 0.49$ (2). [j] $P = 0.48$ (2). [k] $P = 0.64$ (2). [l] $P = 0.61$ (2). [m] $P = 0.64$ (2).

Scheme I[27]

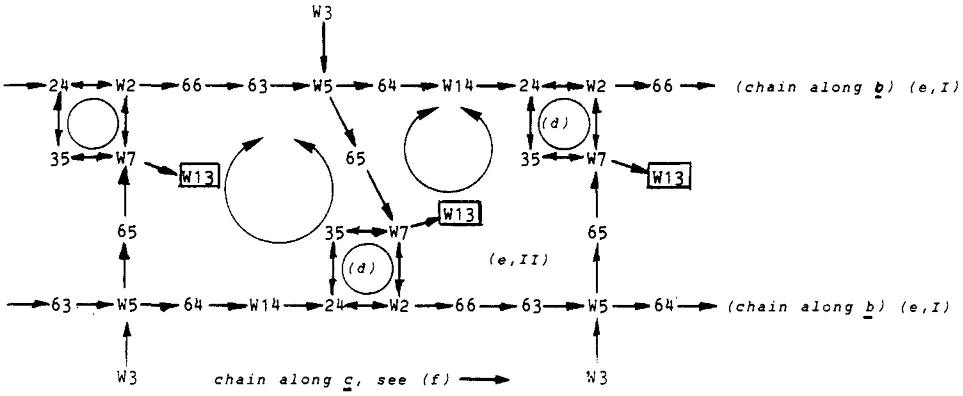
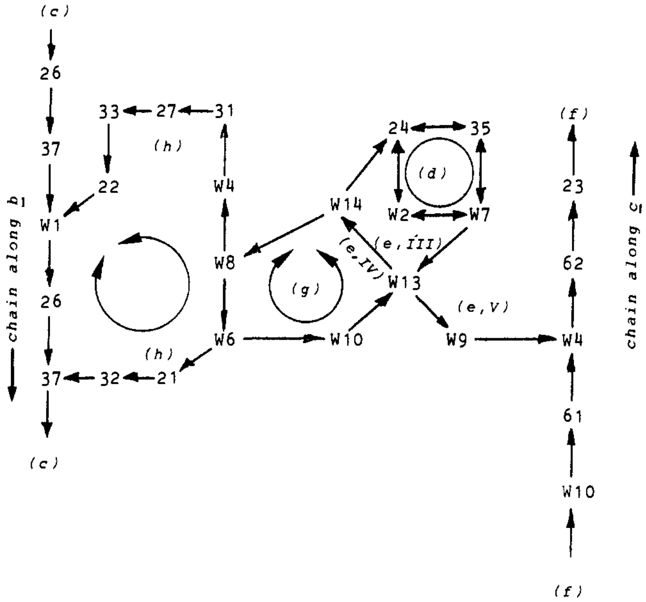


Table III. Bond Lengths (Å) and Angles (deg) of the Water Molecules[a]

OW1–DW1A	0.986 (7)	DW1A–OW1–DW1B	103.8 (5)
OW1–DW1B	0.970 (7)		
OW2–DW2A	0.85 (2)	DW2A–OW2–DW2B	110 (1)
OW2–DW2B	0.96 (1)	DW2A–OW2–DW2C	110 (1)
OW2–DW2C	0.97 (2)	DW2B–OW2–DW2C	109 (1)
OW3–DW3A	0.964 (8)	DW3A–OW3–DW3B	105.3 (6)
OW3–DW3B	0.992 (6)		
OW4–DW4A	0.989 (9)	DW4A–OW4–DW4B	102.1 (9)
OW4–DW4B	0.967 (9)		
OW5–DW5A	0.986 (8)	DW5A–OW5–DW5B	105.3 (6)
OW5–DW5B	0.975 (7)		
OW6–DW6A	0.90 (2)	DW6A–OW6–DW6B	94 (2)
OW6–DW6B	1.06 (3)		
OW7–DW7A	1.009 (9)	DW7A–OW7–DW7B	111.5 (9)
OW7–DW7B	0.964 (9)	DW7A–OW7–DW7C	103 (1)
OW7–DW7C	0.94 (1)	DW7B–OW7–DW7C	94 (1)
OW8–DW8A	0.98 (2)	DW8A–OW8–DW8B	103 (1)
OW8–DW8B	0.99 (3)		
OW9–DW9A	0.97 (1)	DW9A–OW9–DW9B	105 (1)
OW9–DW9B	0.97 (1)		
OW10–DW10A	0.96 (1)	DW10A–OW10–DW10B	109 (1)
OW10–DW10B	0.90 (1)		
OW13–DW13A	0.95 (2)	DW13A–OW13–DW13B	98 (2)
OW13–DW13B	0.85 (2)		
OW14–DW14A	0.99 (1)	DW14A–OW14–DW14B	109 (1)
OW14–DW14B	0.97 (2)		

[a] Standard deviations are given in parentheses. Mean values are calculated according to $\bar{l} = \sum_i X_i/N$ where X_i = observations, and standard deviations are obtained with $\sigma_l = [\sum_i(X_i - \bar{X})^2/(N - 1)]^{1/2}$.

Scheme II[27]



perature its occupation is only 78%. Also, the room temperature site W5C disappears upon cooling to 120 K so that W2 looses a flip-flop hydrogen-bonding site and instead engages in flip-flop bonding to W7. Moreover, the flip-flop ring is at the juntion of several homodromic rings and infinite chains which run through the flip-flop rings and therefore are part of it.

(e) The Flip-Flop Ring as a Versatile Junction between Several Homodromic Chains and Rings. The flip-flop ring has various connections with "outside" water molecules and hydroxyl groups and acts as a center for multiple hydrogen-bond donor and acceptor sites (Figure 7 and Schemes[27] I and II). These functions

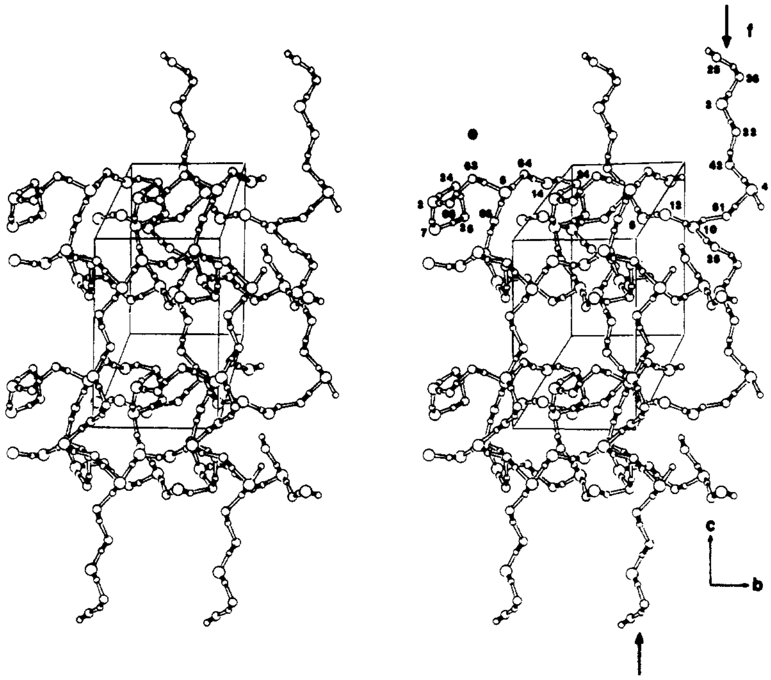


Figure 8. Stereoview of the homodromic network of O–D---O hydrogen bonds in the *b,c* plane; see also Scheme III. The arrows indicate infinite, screw symmetry related chains in the *c* direction, which are cross-linked by short homodromic chains formed exclusively by water molecules W10, W13, W9, and W4. The network is composed of meshes with 22 O–D groups in antidromic arrangement, with water molecules W4 acting as the double acceptor and W10 as the double donor. Letters indicate paragraphs in this text which describe chains (arrows) and the flip-flop ring.

are probably responsible for the occurrence of the flip-flop ring because a simple homo- or antidromic ring could not serve so many purposes. The connections are as follows: (I) An infinite homodromic chain in the *b* direction links two translation-related flip-flop rings at *x,y,z* and at *x,y* + 1,*z*; see Scheme I and Figure 7.

→[O(2)4-D_B→O(3)5-D_B→OW7-D_A→
OW2-D_B→O(6)6-D→O(6)3-D→OW5-$\mathrm{D_A}$→
O(6)4-D→OW14$\mathrm{D_A}]_\infty$→O(2)4-D_B→

This situation is shown in Figure 7. If the hydrogen bonds in the flip-flop ring run in the other direction, the sequence from O(2)4 to OW2 is short-cut.

→[O(2)4-D_A→OW2-D_B→O(6)6-D-]→etc.

(II) A homodromic chain connects flip-flop rings related by the screw axis at *x,y,z* and at *-x,y* + $^1/_2$,*-z*; see Scheme I.

→[OW7-D_A→OW2-$\mathrm{D_B}$→O(6)6-D→
O(6)3-D→OW5-$\mathrm{D_B}$→O(6)5-D$]_\infty$→OW7-D_A→

(III) A homodromic bridge connects diagonally opposite corners of the flip-flop ring to form a homodromic ring. The sequence displayed in Figure 7 is

→[O(2)4-D_B→O(3)5-D_B→OW7-D_B→OW13-$\mathrm{D_B}$→
OW14-$\mathrm{D_A}]_\infty$→O(2)4-D_B→

or if the hydrogen bonds in the flip-flop ring are oriented in the other direction

→[O(2)4-D_A→OW2-D_C→OW7-D_B→OW13-$\mathrm{D_B}$→
OW14-$\mathrm{D_A}]_\infty$→O(2)4-D_A→

(IV) Water molecules W13 and W14 of the homodromic bridge (III) are part of a five-membered homodromic ring described in (g); see Scheme II.

(V) The flip-flop ring is connected to infinite homodromic chains in *b* and *c* directions (see (c) and (f)), as shown in Scheme II.

OW7-D_B→OW13-$\mathrm{D_B}$→OW14-$\mathrm{D_B}$→OW8-$\mathrm{D_B}$→OW4-$\mathrm{D_A}$→
O(3)1-D→O(2)7-D→O(3)3-D→
O(2)2-D→OW1-$\mathrm{D_A}$→etc., chain (see (c))

OW7-D_B→OW13-$\mathrm{D_A}$→OW9-$\mathrm{D_B}$→OW4-$\mathrm{D_B}$→
etc., chain (see (f))

The chain along *c* (see (f)) is also connected in another way with the flip-flop ring; see Schemes I and III.

---chain(see (f))–OW3-$\mathrm{D_B}$→OW5-$\mathrm{D_A}$→
O(6)4-D→OW14-$\mathrm{D_A}$→O(2)4-D_B
→O(3)5-D_B→OW7-D_B→etc. (see above)

(f) An Infinite Homodromic Chain along *c* and a Homodromic Network in the *b,c* Plane. A homodromic chain composed of three water molecules and of five hydroxyl groups is formed along the *c* direction; see Figure 8 and Scheme III.

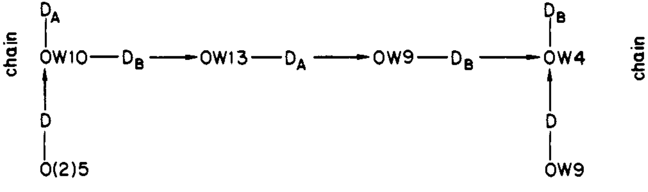
→[O(2)5-D→OW10-$\mathrm{D_A}$→O(6)1-D→
OW4-$\mathrm{D_B}$→O(6)2-D→O(2)3-D→OW3-$\mathrm{D_A}$→O(3)6-D$]_\infty$→
O(2)5-D→

This chain involves three different β-CD molecules which contribute (i) O(6)1, O(6)2, (ii) O(2)3, and (iii) O(3)6, O(2)5. Associated with the chain are a number of other hydrogen-bonding donors and acceptors in homodromic arrangements, of which only some are outlined here, e.g.,

OW4-$\mathrm{D_A}$→O(3)1-D→O(2)7-D→O(3)3-D→O(2)2→etc.

OW3-$\mathrm{D_B}$→OW5-$\mathrm{D_A}$→O(6)4-D→OW14-$\mathrm{D_A}$→
O(2)4 (flip-flop ring)

These infinite homodromic chains along *c*, related by translation along *b*, are connected by short, homodromic links consisting of water molecules.



As indicated in Scheme III, the homodromic chains along *c* and the links in the *b* direction form a network in the *b,c* plane.

Table IV. Hydrogen Bond Parameters[a]

	symop[b]	O–D	D- - -O	O- - -O	O–D- - -O
		A. Hydroxyl Donors			
O(2)1–D(2)1- - -O(3)2	*x,y,z*	0.976 (7)	2.027 (7)	2.959 (7)	158.8 (7)
O(3)1–D(3)1- - -O(2)7	*x,y,z*	0.975 (8)	2.023 (8)	2.991 (8)	171.6 (6)
O(6)1–D(6)1- - -OW4	15	0.994 (9)	1.850 (9)	2.836 (9)	170.9 (7)
O(2)2–D(2)2- - -OW1	15	0.963 (8)	1.938 (8)	2.875 (8)	163.7 (5)
O(3)2–D(3)2- - -O(3)7	15	0.969 (8)	1.932 (8)	2.892 (7)	170.7 (6)
O(6)2–D(6)2- - -O(2)3	2	0.972 (8)	1.847 (7)	2.807 (7)	169.0 (6)
O(2)3–D(2)3- - -OW3	4	0.996 (8)	1.695 (8)	2.681 (8)	169.7 (5)
O(3)3–D(3)3- - -O(2)2	*x,y,z*	0.981 (8)	1.954 (8)	2.913 (7)	165.2 (6)
O(6)3–D(6)3- - -OW5	1	0.975 (8)	1.855 (8)	2.816 (8)	168.1 (7)
disO(2)4–D(2)4A- - -OW2	*x,y,z*	0.99 (1)	1.79 (2)	2.78 (1)	174.0 (9)
disO(2)4–D(2)4B- - -O(3)5	*x,y,z*	0.954 (9)	1.84 (1)	2.754 (7)	160 (1)
O(3)4–D(3)4- - -O(2)3	*x,y,z*	0.964 (8)	2.004 (8)	2.967 (8)	176.4 (6)
O(6)4–D(6)4- - -OW14	*x,y,z*	0.967 (8)	1.906 (9)	2.848 (9)	164.0 (8)
O(2)5–D(2)5- - -OW10	18	0.959 (8)	2.05 (1)	2.98 (1)	161.8 (6)
disO(3)5–D(3)5A- - -O(2)4	*x,y,z*	0.98 (1)	1.81 (1)	2.754 (7)	159 (1)
disO(3)5–D(3)5B- - -OW7	*x,y,z*	0.98 (1)	1.77 (1)	2.733 (8)	167 (1)
O(6)5–D(6)5- - -OW7	11	0.980 (9)	1.75 (1)	2.726 (9)	173.8 (6)
O(2)6–D(2)6- - -O(3)7	*x,y,z*	0.971 (8)	2.011 (7)	2.935 (7)	158.3 (4)
O(3)6–D(3)6- - -O(2)5	*x,y,z*	0.989 (6)	1.840 (6)	2.770 (6)	155.4 (6)
O(6)6–D(6)6- - -O(6)3	6	0.971 (8)	1.828 (8)	2.783 (8)	167.2 (6)
O(2)7–D(2)7- - -O(3)3	15	0.968 (6)	1.829 (7)	2.761 (6)	160.9 (6)
O(3)7–D(3)7- - -OW1	16	1.000 (8)	1.836 (8)	2.817 (8)	166.3 (5)
O(6)7–D(6)7- - -OW3	2	0.973 (8)	1.921 (8)	2.863 (7)	162.4 (6)
		B. Water Donors			
OW1–DW1A- - -O(2)6	*x,y,z*	0.986 (7)	1.767 (7)	2.736 (7)	166.4 (5)
OW1–DW1B- - -O(5)7	8	0.970 (7)	1.865 (7)	2.793 (7)	159.1 (7)
OW2–DW2A- - -O(2)4	*x,y,z*	0.85 (2)	1.95 (2)	2.78 (1)	164 (1)
OW2–DW2B- - -O(6)6	13	0.96 (1)	1.831 (8)	2.79 (9)	175.5 (9)
OW2–DW2C- - -OW7	*x,y,z*	0.97 (2)	1.91 (2)	2.83 (1)	158 (2)
OW3–DW3A- - -O(3)6	*x,y,z*	0.964 (8)	1.828 (8)	2.785 (8)	171.4 (6)
OW3–DW3B- - -OW5	*x,y,z*	0.992 (6)	1.789 (7)	2.766 (6)	167.6 (7)
OW4–DW4A- - -O(3)1	*x,y,z*	0.989 (9)	1.833 (9)	2.773 (8)	157.5 (7)
OW4–DW4B- - -O(6)2	18	0.967 (9)	1.786 (9)	2.730 (9)	164.3 (6)
OW5–DW5A- - -O(6)4	13	0.986 (8)	1.867 (9)	2.850 (9)	174.2 (6)
OW5–DW5B- - -O(6)5	13	0.975 (7)	1.849 (7)	2.815 (7)	170.4 (7)
OW6–DW6A- - -O(2)1	*x,y,z*	0.90 (3)	2.07 (2)	2.69 (2)	125 (3)
OW6–DW6B- - -OW10	2	1.06 (3)	2.05 (2)	3.06 (2)	160 (2)
OW7–DW7A- - -OW2	*x,y,z*	1.009 (9)	1.88 (1)	2.83 (1)	156 (1)
OW7–DW7B- - -OW13	8	0.967 (9)	1.81 (1)	2.72 (1)	156.2 (8)
OW7–DW7C- - -O(3)5	*x,y,z*	0.94 (1)	1.80 (1)	2.733 (8)	176.6 (9)
OW8–DW8A- - -OW6	7	0.98 (2)	1.94 (2)	2.91 (2)	170 (2)
OW8–DW8B- - -OW4	7	0.99 (3)	2.25 (2)	3.17 (2)	155 (1)
OW9–DW9A- - -O(4)6	*x,y,z*	0.97 (1)	2.04 (1)	2.93 (1)	151.9 (9)
OW9–DW9B- - -OW4	18	0.97 (1)	1.80 (1)	2.77 (1)	174.5 (8)
OW10–DW10A- - -O(6)1	18	0.96 (1)	1.96 (1)	2.81 (1)	146.4 (7)
OW10–DW10B- - -OW13	18	0.90 (1)	1.87 (2)	2.75 (1)	165 (1)
OW13–DW13A- - -OW9	*x,y,z*	0.95 (2)	1.75 (1)	2.68 (1)	166 (1)
OW13–DW13B- - -OW14	*x,y,z*	0.85 (2)	2.00 (2)	2.85 (2)	171 (1)
OW14–DW14A- - -O(2)4	2	0.99 (1)	1.96 (1)	2.81 (1)	143 (1)
OW14–DW14B- - -OW8	14	0.97 (2)	1.86 (2)	2.80 (1)	163 (1)

[a] Distances in Å, angles in deg, standard deviations in parentheses. [b] 1 = $x,y+1,z+1$; 2 = $x,y+1,z$; 4 = $x,y,z+1$; 6 = $x,y,z-1$; 7 = $x,y-1,z-1$; 8 = $x,y-1,z$; 11 = $2-x,y+{}^1/_2,-z$; 13 = $2-x,y-{}^1/_2,-z$; 14 = $1-x,y+{}^1/_2,1-z$; 15 = $1-x,y+{}^1/_2,-z$; 16 = $1-x,y+{}^1/_2,-1-z$; 18 = $1-x,y-{}^1/_2,-z$.

Each of the meshes of the network forms a large antidromic ring of 22 water molecules and hydroxyl groups where waters W10 act as a double donor and W4 as a double acceptor.

(g) Water Molecules in the β-CD Cavity: A Homodromic, Five-Membered Ring. At room temperature, the cavity of the β-CD macrocycle is filled by 6.13 water molecules distributed statistically over 8 different sites. Only W4 is fully occupied, and the other seven positions (W6, W8, W9, W10, W12, W13, and W14) are in the range 0.53 (2)–0.89 (2), average occupation 0.77. At 120 K, the situation is changed. From the eight room-temperature water sites, W12 is unoccupied, and the other positions are fully occupied except W8 (occupancy 0.64 (2)). Five of these water molecules are arranged in a homodromic, pentagonal ring, Figure 9 and Scheme II.

$$\rightarrow \mathrm{OW6\text{-}D_B} \rightarrow \mathrm{OW10\text{-}D_B} \rightarrow \mathrm{OW13\text{-}D_B} \rightarrow \mathrm{OW14\text{-}D_B} \rightarrow \mathrm{OW8\text{-}D_A} \rightarrow$$

This ring again displays a number of hydrogen-bonding contacts to hydroxyl groups and other water molecules which are also enclosed in the cavity, e.g., OW6–D$_A$→O(2)1, OW8-D$_B$→OW4, O(2)5–D→OW10–D$_A$→O(6)1 (this is part of the chain along *c*, see (f)), OW13–D$_A$→OW9, OW7–D$_B$→OW13, O(6)4–D→OW14, and OW14–D$_A$→O(2)4. Some of these contacts (with

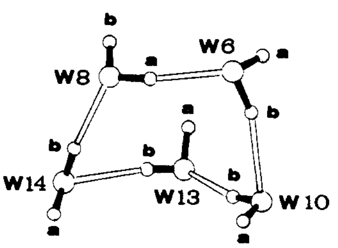


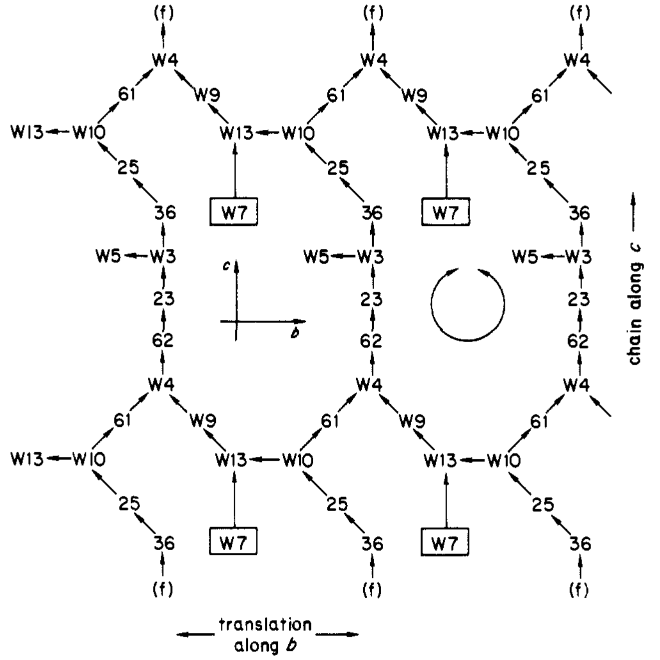
Figure 9. Pentagonal, homodromic ring found in the cavity of β-CD drawn in another orientation than Figure 4. All water sites are fully occupied except W8 (occupancy 0.64), whereas at room temperature none of them are fully occupied. See also Scheme II for the integration of this ring into the general hydrogen-bonding system.

Table V. Bifurcated Hydrogen Bonds

O-D---A	symop	O---A	D---A	O-D	O-D---A	A---D---A	SUM[a]
O(2)1-D---O(3)2	*x,y,z*	2.959 (7)	2.027 (7)	0.976 (7)	158.8 (7)	79.8 (2)	
O(4)2	*x,y,z*	2.820 (7)	2.355 (7)		108.4 (6)		347.0
O(3)1-D---O(2)7	*x,y,z*	2.991 (8)	2.023 (8)	0.975 (8)	171.6 (6)	75.0 (3)	
O(4)1	*x,y,z*	2.844 (7)	2.445 (7)		104.1 (4)		350.7
O(6)1-D---OW4	15	2.836 (9)	1.850 (9)	0.994 (9)	170.9 (7)	92.2 (3)	
O(5)1	*x,y,z*	2.866 (8)	2.590 (8)		95.8 (5)		358.9
O(3)3-D---O(2)2	*x,y,z*	2.913 (7)	1.954 (8)	0.981 (8)	165.2 (6)	77.3 (3)	
O(4)3	*x,y,z*	2.794 (7)	2.301 (8)		110.1 (5)		352.6
O(2)4-D_B---O(3)5	*x,y,z*	2.754 (7)	1.84 (1)	0.954 (9)	160 (1)	82.7 (4)	
O(4)5	*x,y,z*	2.792 (7)	2.37 (1)		106.4 (7)		349.1
O(3)4-D---O(2)3	*x,y,z*	2.967 (8)	2.004 (8)	0.964 (8)	176.4 (6)	73.8 (2)	
O(4)4	*x,y,z*	2.887 (7)	2.509 (7)		103.3 (5)		353.5
O(3)5-D_A---O(2)4	*x,y,z*	2.754 (7)	1.81 (1)	0.98 (1)	159 (1)	83.4 (4)	
O(4)5	*x,y,z*	2.806 (7)	2.34 (1)		107.7 (8)		350.1
O(2)6-D---O(3)7	*x,y,z*	2.935 (7)	2.011 (7)	0.971 (8)	158.3 (4)	83.0 (3)	
O(4)7	*x,y,z*	2.746 (6)	2.228 (6)		112.2 (5)		353.5
O(3)6-D---O(2)5	*x,y,z*	2.770 (6)	1.840 (6)	0.989 (6)	155.4 (6)	80.8 (2)	
O(4)6	*x,y,z*	2.793 (6)	2.352 (6)		106.1 (4)		342.5
OW2-D_C---OW7	*x,y,z*	2.83 (1)	1.91 (2)	0.97 (2)	158 (2)	83 (1)	
O(5)5	13	3.14 (2)	2.56 (2)		118 (1)		359.0
OW7-D_A---OW2	*x,y,z*	2.83 (1)	1.88 (1)	1.01 (1)	156 (1)	90.3 (5)	
O(5)5	13	3.003 (7)	2.51 (1)		109.7 (9)		356.0

[a] "SUM" gives the sum of angles with D as apex; SUM = (O-D---A_1) + (O-D---A_2) + (A_1---D---A_2). Ideally, SUM should be 360°, i.e., atom D and ligands are coplanar.[15]

Scheme III[27]



O(6)1 and O(6)4 are with the surrounding β-CD; the others are with other water molecules in the cavity. They all contribute to the stability of the pentagon and fix it in the β-CD cavity.

It is remarkable that at room temperature, the water sites of the pentagon are only partially filled and have oxygen occupation factors of W6 (0.88), W8 (0.53), W10 (0.81), W13 (0.68), and W14 (0.62) (standard deviation is 0.02 for these five values). Because all water sites except W8 are fully occupied at 120 K, this could imply that water molecules from the surrounding mother liquor penetrate into the crystal. A more likely explanation is that water molecules from very disordered sites not located in the room-temperature crystal structure move into the partially occupied sites to fill them completely.

(h) Three-Center Interglucose O-D---O Hydrogen Bonds. In Table V, the geometries of the intramolecular, interglucose hydrogen bonds are described. It is noteworthy that in all cases there are *intra*molecular contacts to the adjacent glucosyl O(4) links which are shorter than the "ideal" van der Waals D---O distance of 2.6 Å. These D---O(4) separations are always longer than the interglucose D---O(2) or D---O(3) hydrogen bonds formed by the same hydrogen atoms so that the three-center (bifurcated) interactions are unsymmetrical, with the major component formed by O(2)---O(3) hydrogen bonds and the minor component by a bond to the glycosyl O(4) atom. This, however, is not surprising because the hydroxyl oxygen is a much stronger hydrogen-bond acceptor compared with the ether-like O(4) oxygen. As required for three-center hydrogen bonds,[15,16] hydrogen and associated oxygen atoms are coplanar, as indicated by the sum of angles at the hydrogen atoms. It is always close to 360°, with the lowest value being 337.7° for O(3)1-D(---O(2)7)---O(4)1 with a long D---O(4) distance of 2.52 Å.

Discussion

The crystal structure of β-CD·11D_2O was studied at 120 K in order to decide whether the flip-flop disorder observed in the room-temperature structure of β-CD·11D_2O is of a static or of a dynamic nature. The disappearance of all but two of the eighteen flip-flop hydrogen bonds and the formation of a new quadrilateral flip-flop cycle at 120 K clearly indicate that the flip-flop disorder is dynamic.

Another conclusion drawn on the basis of the 120 K crystal structure of β-CD·11D_2O is that the cooperative effect has an influence on the formation of hydrogen bonds and that in case of several interconnected O-D---O bonds it determines their orientation. The crystal of β-CD·11D_2O was cooled from room temperature to 120 K so slowly that O-D groups and water moelcules had time to reorient and to adopt positions of minimum energy (shock-freezing would probably preserve the room-temperature structure, or a closely related structure). The result is striking because the whole crystal structure now consists of chainlike arrangements →O-D→O-D→O-D→ with homodromic orientation of the hydroxyl groups. Formation of antidromic systems is much less frequent and only observed with water molecules which act as double acceptors. In hydrogen-bonding patterns of this complexity, antidromic arrangements cannot be avoided for structural reasons; the heterodromic arrangement is not observed at all. These findings suggest that the cooperative effect determines the geometry (direction) of O-H---O hydrogen bonds if more extended hydrogen-bonded systems can form. In fact, quantum chemical calculations have demonstrated that in "infinite" chainlike or cyclic structures, the homodromic arrangement of O-H groups is about 10-26% more stable compared with the same number of individual O-H---O hydrogen bonds.[25,26]

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(25) Lesyng, B.; Saenger, W. *Biochim. Biophys. Acta* **1981**, *678*, 408-413.

It is also surprising to find that at 120 K all water oxygen positions in β-CD$\cdot$11D$_2$O are fully occupied except W8 (0.64), whereas at room temperature with composition β-CD$\cdot$11D$_2$O most of them are only statistically filled or distributed over several sites. This suggests that water molecules have physically moved upon cooling, and the same holds for hydroxyl hydrogens engaged in flip-flops that disappeared at 120 K.

The difference of 0.6 water molecules in the two crystal structures determined at room temperature and at 120 K cannot be accounted for by errors in refinement because standard deviations of occupation factors are only of the order ±0.02. The possibility that a second modification of β-CD hydrate of composition β-CD$\cdot$12D$_2$O was unwittingly used at 120 K can be discounted since it would show up in differences in unit cell constants.[20] We have to assume therefore that the 0.6 water molecule discrepancy is due to spurious water sites which did not show up clearly enough in the Fourier maps calculated with room-temperature data.

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Registry No. β-CD$\cdot$11H$_2$O, 85490-99-9.

Supplementary Material Available: Listing of atomic coordinates and anisotropic temperatures for all atoms, individual bond lengths, valence angles, torsion angles, and structure amplitudes (39 pages). Ordering information is given on any current masthead page.

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(26) Köhler, J.; Lesyng, B.; Saenger, W., unpublished results.

(27) Shown are hydrogen-bond patterns occurring in the crystal structure of β-CD$\cdot$11D$_2$O at 120 K. Because the total scheme is too complicated to be shown in one picture, it is broken up into three different schemes. In these, hydrogen bonds O–D---O are indicated by arrows pointing in the direction donor → acceptor, water molecules are denoted by W, and hydroxyl groups by two numbers, e.g., 64 means O(6)4, i.e., hydroxyl O(6) of glucose number 4 in the β-CD macrocycle. The flip-flop ring is indicated by a circle, homodromic rings by circular, one-headed arrows, and antidromic rings by circular, two-headed arrows. Water molecules W7 and W13 occur in all three schemes and are the points where the hydrogen-bonding systems are joined to form a complex three-dimensional structure. Letters in parentheses refer to paragraphs in the text.

Photofragmentation and Photosubstitution Kinetics of Dodecacarbonyltriosmium

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Abstract: The 436-nm photochemical kinetics of reactions of $Os_3(CO)_{12}$ in benzene with 1-octene and $P(OEt)_3$ have been studied under a wide variety of conditions. Reaction with 1-octene leads to fragmentation of the cluster whereas that with $P(OEt)_3$ leads to substitution. Both reactions proceed through the same intermediate which is shown to be a reactive isomer of $Os_3(CO)_{12}$, i.e., absorption of 436-nm radiation does not induce cluster fragmentation or CO dissociation. Since the reactivity of this intermediate with halocarbons is very low it is most probably not a diradical formed by homolysis of an Os–Os bond, although such a diradical could be a primary photoproduct that reacts very rapidly to form the more long-lived isomer. A possible structure for the isomer involves a CO that bridges two Os atoms (not otherwise bonded to each other), one of those Os atoms having a vacant coordination site. Attack at this site by a wide variety of donor molecules (CO, diglyme, and probably the benzene solvent, as well as the reactant molecules 1-octene and $P(OEt)_3$) can cause concerted reversion of the intermediate to $Os_3(CO)_{12}$. The fact that 1-octene and $P(OEt)_3$ can induce this reversion, in addition to causing forward reaction to form products, could well be the reason why the limiting quantum yields, found at high [1-octene] ($\phi_{\text{lim}} = 0.0320 \pm 0.0004$) or [$P(OEt)_3$] ($\phi_{\text{lim}} = 0.0456 \pm 0.0010$), are so low; i.e., the low quantum yields could be a reflection of the particular thermal reactivity pattern of the intermediate rather than of the photophysical behavior of $Os_3(CO)_{12}$. It is also the reason why limiting quantum yields are dependent on the nature of the ligand, a phenomenon also characteristic of the photokinetics of $Ru_3(CO)_{12}$.

The photochemical kinetics of dinuclear metal carbonyls have received considerable attention[1] since the pioneering work of Wrighton[2] but corresponding studies of metal carbonyl clusters are still quite rare. Photofragmentation is the predominant overall process in reactions of $Fe_3(CO)_{12}$ and $Ru_3(CO)_{12}$ with CO,[3-6] PPh_3,[3,4] and alkenes,[3-5,7] although the primary photoproduct from $Ru_3(CO)_{12}$ has been shown to be a reactive isomeric form of the cluster.[6] Very low quantum yields (0.001) for reactions of $Ru_3(CO)_{12}$ with halocarbons[5,6] have cast doubt on the earlier suggestion[3] that photolysis leads to homolysis of a Ru–Ru bond, and an alternative isomeric form has been proposed.[5,6] By contrast, $Os_3(CO)_{12}$ does not form $Os(CO)_5$ on photolysis under as much as 6 atm of CO,[3,8] and it undergoes simple photosubstitution with P donors.[3,8] No quantum yields were determined but reactions were reasonably fast. Again, quantum yields for reactions with halocarbons were very low ($\lesssim$0.002 at 313 nm) and it was suggested[8] that the major process caused by photolysis was CO dissociation. On the other hand, photolysis of $Os_3(CO)_{12}$ in the presence of alkenes does lead to fragmentation[3,9] with quantum yields of ca. 0.03.[3] We have undertaken kinetic studies designed to show more clearly the type of intermediates generated by photolysis of metal carbonyl clusters and report here the photofragmentation kinetics of reaction of $Os_3(CO)_{12}$ with 1-octene and the photosubstitution kinetics of its reaction with $P(OEt)_3$.

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