particular phenomenon will be given in a forthcoming paper (Ottersen & Almlöf, 1980).

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Topography of Cyclodextrin Inclusion Complexes. XII.* Hydrogen Bonding in the Crystal Structure of α-Cyclodextrin Hexahydrate: The Use of a Multicounter Detector in Neutron Diffraction

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Abstract

In the crystalline complex α-cyclodextrin hexahydrate, $C_{36}H_{60}O_{30}.6H_2O$, orthorhombic, space group $P2_12_12_1$, $Z = 4$, $a = 14{\cdot}858$ (3), $b = 34{\cdot}038$ (7), $c = 9{\cdot}529$ (2) Å, thirty hydroxyl hydrogen atoms are present, including one which is disordered (occupancies 0·92:0·08) and could not be located with certainty from X-ray counter data. 851 low-angle neutron data were measured using a conventional four-circle diffractometer with a graphite monochromator ($\lambda = 2{\cdot}384$ Å) and a neutron flux rate of $6{\cdot}4 \times 10^4$ n mm^{-2} s^{-1}. Further, 1957 high-angle neutron data were collected by means of the multicounter device 'hedgehog'. This instrument contains 100 BF_3 counters mounted on rotatable and extendable arms on the inside of a sphere, at the centre of which is installed a conventional Eulerian cradle holding the sample crystal. With the application of a modified Laue method, integration is over wavelength rather than over crystal rocking motion; a wavelength band of $1{\cdot}275 < \lambda < 1{\cdot}31$ Å, a Cu-crystal monochromator, and a neutron flux of $2{\cdot}4 \times 10^4$ n mm^{-2} s^{-1} were used. Details of the measurement and of the data reduction are given, and the refinement process, including combined neutron and a new set of 4268 X-ray data, is described. *R* factors are

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[*] For part XI, see *Proceedings of the International Symposium on Biomolecular Structure, Conformation, Function and Evolution*, Madras 1978, to be published. For part X, see Saenger, Noltemeyer, Manor, Hingerty & Klar (1976) and Cramer, Bergmann, Manor, Noltemeyer & Saenger (1976).

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12·0% for 2808 neutron data (8·8% for the 1963 'observed' data) and 3·7% for all X-ray data. The geometry of the α-cyclodextrin molecule as obtained from the X-ray data and the hydrogen-bonding scheme are described in detail and geometrical data for the hydrogen bonds are given in histograms.

Introduction

α-Cyclodextrin (α-CD) is a doughnut-shaped molecule composed of six α-(1→4)-linked glucoses. Owing to its particular geometry, α-CD as a 'host' is able to form inclusion complexes with 'guest' molecules small enough to fit into its 5 Å wide aperture (Saenger, 1976). Of special interest is the structure of the 'empty' α-CD crystallizing from aqueous solution as a hexahydrate with two water molecules entrapped within the cavity and the remaining four water molecules located outside the 'host'. The crystal structure of this complex had been solved earlier from X-ray counter data (Manor & Saenger, 1974) but, since not all of the 30 hydroxyl H atoms could be located with certainty, a detailed neutron diffraction study was carried out.

In the present article both the neutron and a repeated X-ray data collection are described with emphasis on the presentation of 'hedgehog', a multicounter neutron diffractometer developed at the Institut Laue–Langevin (ILL), Grenoble. Details are given of the structure refinement which finally gave the locations of all the H atoms and allowed the discovery of disorder in one hydroxyl group not evident with the previous X-ray data. Further, the crystal structure, molecular geometry and hydrogen bonding in α-CD hexahydrate will be discussed.

Neutron measurement

The neutron diffraction measurements were performed on two diffractometers installed at the high-flux reactor of the ILL. The low-resolution data were obtained on a classical four-circle diffractometer (D16), whereas the high-resolution reflections were measured on an unconventional multicounter apparatus ('hedgehog', D6). This partitioning of the experimental work between two instruments was done because the multicounter device does not easily allow for measurement of reciprocal-lattice points with low d^* values, but it is advantageous for treating in a short time the numerous data with high d^* values by the application of a simultaneous detection technique described below.

The sample crystal used in both neutron measurements was needle-shaped and elongated along **c** with dimensions 1·2 × 1·5 × 6 mm, corresponding to a crystal volume of 11 mm^3. The crystal was fixed in a thin-walled quartz-glass capillary with **c** in the direction of the goniometer-head axis.

Measurements with D16

D16 is a classical four-circle diffractometer. It is installed at a neutron guide oriented towards the 'cold source' of the reactor. As the use of the classical diffractometer is aimed only at measuring the inner shell in reciprocal space, the choice of D16 operating at a wavelength of 2·384 Å was a convenient solution: the measurement of reflections corresponding to a periodicity of 34 Å was possible without resolution problems. Furthermore, relaxed collimation conditions allowed for a high flux at the sample position (6·4 × 10^4 n mm^{-2} s^{-1}, graphite monochromator).

980 reflections were measured in the θ–2θ-scan mode with reflection 600 as a standard monitored after every 100 reflections. Each scan consisted of 48 points, the measuring time per point being 10 s.

Data reduction of the reflection profiles to structure amplitudes and assignment of standard deviations were performed by conventional procedures. No corrections were applied for neutron absorption. Symmetry-related reflections were combined and averaged, resulting in a data set of 851 independent reflections.

D6 measurements ('hedgehog')

The measurement with the multicounter device 'hedgehog' (D6) had simultaneously a practical and a methodological aspect: The first aspect was the interest shown in several features of the α-CD structure which could only be clarified by a large number of neutron diffraction intensities. The methodological aim was to use the somewhat unconventional and new type of instrument for the first time for the determination of a complex crystal structure and to find out during this application where the measuring procedure was already reliable and where improvements were needed.

The basic feature of this device is the gain in measuring time obtained by the simultaneous measurement of many Bragg reflections by many individually movable counters arranged on a spherical shell. A prerequisite for simultaneous detection is the availability of simultaneously active reflections. It can be fulfilled by employing the modified Laue method proposed by Maier-Leibnitz (1967), where a curved monochromator focuses a small wavelength band on to the sample. This wavelength band corresponds in reciprocal space to an active volume (Fig. 1). All reciprocal-lattice points lying within the active volume reflect simultaneously. Furthermore, as the reciprocal-lattice points (even taking into consideration a certain extension corresponding to mosaicity of the sample)

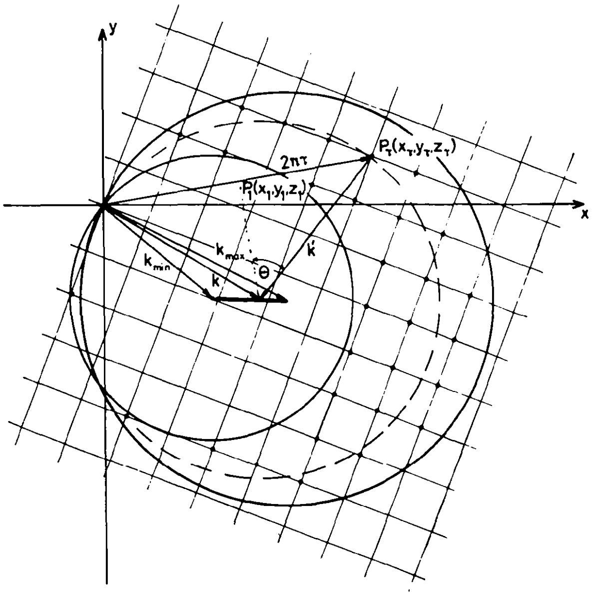

Fig. 1. Modified Laue method in reciprocal space. $k_{\min}$ and $k_{\max}$ are the limiting wavevectors of the active volume; k' is the wavevector reflected by the reciprocal-lattice point P_τ.

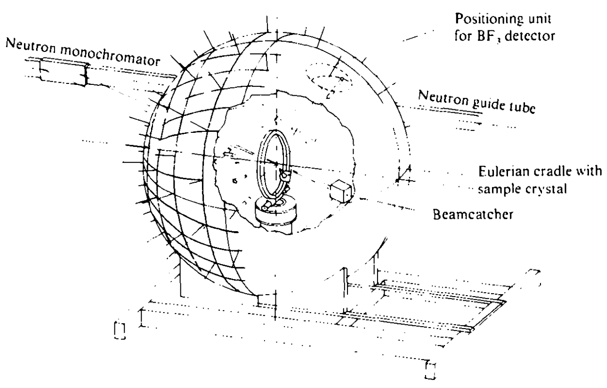

Fig. 2. Schematic drawing of the neutron diffraction instrument D6 ('hedgehog') with 100 movable detectors installed on the inside of a spherical shell. The sample crystal is mounted on a Eulerian cradle located at the centre of the sphere.

can be completely embedded in the active volume, the reflected intensity corresponds directly to an integrated intensity. A mechanical scan, as normally used in monochromatic techniques to sweep the reciprocal-lattice point through the Ewald sphere and to sum the intensities to obtain the integrated intensity, is not needed.

The instrument consists of 100 BF_3 detectors mounted on the inside of a metallic sphere with a radius of 850 mm (Fig. 2). Each counter can move within a circular region by means of two stepping motors. In all available positions the counters are oriented towards the centre of the sphere, where the sample is mounted on a Eulerian cradle with the conventional degrees of freedom ω, χ, φ. All positioning and data-handling procedures are treated by a small on-line computer. A detailed description of the instrument and of the measuring methods has been given by Klar (1973).

The monochromator was a curved Cu crystal with the (200) planes in reflection position:

dimensions of the crystal slab	120 × 20 × 4 mm
angle between surface and (200) planes	7 °
radius of curvature	6·30 m
focal distance	1·70 m
dimensions of focal spot	25 (vert.) × 11 (horiz.) mm
flux at the focal spot	$2{\cdot}43 \times 10^4$ n mm^{-2} s^{-1}
reflected wavelength band	$1{\cdot}275 < \lambda < 1{\cdot}31$ Å.

The curvature of the crystal slab was obtained by elastic deformation (Hohlwein, 1975). The monochromator together with its support and the micrometric screws for the determination were placed within the axis of a thermal-neutron guide.

A series of 428 measuring cycles were performed. These cycles were carried out with different orientations. In most cases the orientation differences were 0·75° in φ, while $\chi = 0°$ or $\chi = 90°$. Due to the shape of the active volume and because of the spatial detection system an ordered way of registering intensities as in ordinary diffractometry (by rows) or in the Weissenberg technique (by layer lines) is only approximately possible. Therefore a number of symmetry-related reflections outside the asymmetric unit under consideration were observed. For the same reasons multiple measurements of the same reflection under different geometrical conditions did occur.

For the measurements a program was used (Klar, 1975) which determines for every given orientation of the sample all simultaneously active reflections as well as their spherical coordinates. Furthermore, it allocates the reflections to the different counters and determines the step numbers for setting the counters on the allocated reflection. In average situations about 65 reflections were simultaneously active, 27 of them being observable with the counter system.

After positioning of the counters and the Eulerian cradle according to the calculated angles, the counting time was started. A typical counting time was 20 min, which corresponds to a total cycle time of about 27 min including setting times of the diffractometer. During the measuring time neither the counters nor the cradle was moving, the mechanical scan of the classical diffractometer being replaced by the integration over the wavelength.

During the counting time of 20 min those detectors which were not positioned on a reflection observed an average background of 1·2 counts s^{-1}. The background level increased slightly with 2θ. About 25% of this background came from the exterior (neighbouring experiments, monochromator shielding) and 75% was created in the diffractometer itself (mainly incoherent hydrogen scattering in the sample and air scattering in the flight path near the sample). Strong reflections like 600 had counting rates of up to 47 counts s^{-1}, mean reflections were in the range 10–40 counts s^{-1} and the majority of the reflections had intensities between the background level of 1·2 and 10 counts s^{-1}.

Data reduction was performed with a program (Klar, 1975) which transforms the observed intensities into squares of structure factors and derives e.s.d.'s. It scales for the monitor counting rate, for the different efficiencies of the counters, and for inhomogeneities in the intensity distribution of the wavelength band reflected by the monochromator. The background correction for an individual reflection is done by subtracting the mean counting rate observed on the detectors neighbouring the detector which recorded the reflection under consideration. The basic assumption involved in this procedure is the slow spatial variation of the background level.

The Lorentz factor which has to be applied is very different from those encountered in classical diffraction methods. These differences arise from the detection of reflections lying outside the equatorial plane and from the integration over wavelength instead of over crystal rotation. These characteristics introduce into the Lorentz-factor equation a supplementary parameter ψ describing together with the Bragg-angle θ the spherical coordinates of the reflected beam. They imply, furthermore, the monochromator take-off angle θ_M *via* the definition $\operatorname{tg} \nu = 2 \operatorname{tg} \theta_M$ (Thomas, 1972). With these parameters the Lorentz factor for the modified Laue method is (Klar, 1973): $L = 1/(\sin^2 \theta \cos \nu + \sin \theta \cos \psi \sin \nu \cos \theta)$. This formula can be transformed into the expression given by Hohlwein (1977). The numerical values of L exhibit an asymptotic behaviour for $\theta \rightarrow 90°$, showing the power of the modified Laue method in the high-angle region.

The 428 measuring cycles yielded 11 229 intensities. About 1000 values with F_o differing more than 3σ from symmetry-equivalent F_o's were excluded from further treatment. Then averages were made if a reflection had been measured several times, reducing the number to 9·620. Finally, symmetry-related reflections were combined giving 1957 independent reflections.

The analysis of symmetry-related or repeatedly measured reflections yielded several indications which were helpful from the methodological point of view: One of these indications is that intensities with Lorentz factors > 5 (in the neighbourhood of the focal position) should be excluded from further treatment. In this region the active volume is very narrow and the wavelength integration is not perfect. Several other more technical improvements appeared to be necessary and are already implemented or in progress (background correction, counter alignment, homogeneity of counter efficiency over the window).

X-ray measurements

As the earlier X-ray structure determination of α-CD hexahydrate converged at $R = 6\%$ it was decided to recollect the data. The new data set was measured from a crystal 0·2 × 0·3 × 0·5 mm mounted with **c** along the φ axis of an automated Stoe four-circle diffractometer equipped with a fine-focus Cu tube (Ni-filtered) operated at 40 kV, 30 mA. Each reflection was scanned for 64 s in the 2θ–θ mode and stationary background counts were measured for 8 s on both sides of each scan. 4268 reflections were measured up to a glancing angle of $2\theta = 125°$. An absorption curve established by rotating the crystal through φ at 10° intervals and measuring the intensity of the 002 reflection as a function of φ allowed the data to be corrected for absorption (North, Phillips & Matthews, 1968). Further, the data were corrected for the usual Lorentz, polarization and background effects. E.s.d.'s were derived with 1% allowance for machine instability (Stout & Jensen, 1968).

Analysis of data

Initially only the 851 reflections from the four-circle device D16 were available. On the basis of this data set a neutron difference synthesis was calculated with the C and O coordinates of the previous X-ray study (Manor & Saenger, 1974) and the geometrically determined H atoms. This map revealed all the 18 hydroxyl H and most of the 12 water H atoms. Another difference map yielded the rest of the water H atoms, except those of waters *A* and *B*, the included waters, which were ill defined due to high temperature factors. With all the atoms included the structure was refined to an $R = 6{\cdot}7\%$.

Attention was now shifted to the new absorption-corrected X-ray data. With only the C and O atoms from the previous paper, anisotropic refinement gave an $R = 7{\cdot}8\%$. When the geometrically determined C—H hydrogen atoms were included, R dropped to 5·4%. A difference map at this point located 21 out of 30 hydroxyl H atoms which were consistent with the neutron results. When these atoms were included R was 4·6% and another difference map indicated four more H atoms and a low-occupancy (8%) O(6)1*B*, which had been missed with the earlier less-accurate X-ray data. R was then 4·2% with only the H atoms of waters *A* and *B* ambiguous, since they could not be clearly seen, except for H20*B* (for nomenclature see *Results*).

Preliminary data were then available from 'hedgehog', D6. Because of geometrical problems in the alignment of the experimental device, a selection criterion was used to filter the correctly measured data points. These data were compared to the structure factor listing on the basis of the currently available coordinates and temperature factors. A reflection, if 'observed', was accepted if it deviated by <30% from the calculated value or, if 'unobserved', by 3 units in F and, as stated previously, if the Lorentz factor was ≤ 5. When only the more reliable data were used the remaining uncertain H atoms on waters A and B were found and included in the refinement. R from these preliminary data in addition to that from D16 was 16% for all the data and 12% for the 'observed'. For C and O atoms only the coordinates were varied, while the anisotropic temperature factors from the X-ray data were used as fixed quantities and for the H atoms both isotropic temperature factors and coordinates were varied. A listing of the correctly and incorrectly measured reflections was returned to Grenoble and this enabled a more accurate alignment of the apparatus.

The results for the previously undetermined H atoms for waters A and B were then included in the X-ray data. This data set was corrected for secondary extinction by the graphical method (Stout & Jensen, 1968). A few reflections which could not be adequately corrected for extinction or were obvious measurement errors were deleted with a final R of 3·7% for all the data and 3·6% for those data with $I > 3\sigma_I$.

More accurately measured neutron data were then available from 'hedgehog'. The selection criterion was modified so that a reflection was used only if it deviated by not more than 1·5 units in F (for weak 'observed' and 'unobserved') and if $||F_o| - |F_c||/|F_o|$ did not exceed 0·20 (for 'observed' only), a somewhat stricter criterion than before. This procedure yielded 1957 reflections which were combined with the D16 data to refine the final neutron parameters. As before, the C and O coordinates were allowed to vary while their anisotropic temperature factors were held fixed from the X-ray result and the H atoms were refined with isotropic B's. An attempt was made to refine all the atoms anisotropically but this resulted in non-positive-definite temperature factors and was abandoned. The final R for all 2808 neutron reflections was 12·0% while for 1963 'observed' reflections it was 8·8%. A few reflections were excluded due to obvious secondary extinction.

Results

The final atomic parameters resulting from this combined X-ray and neutron study are presented in

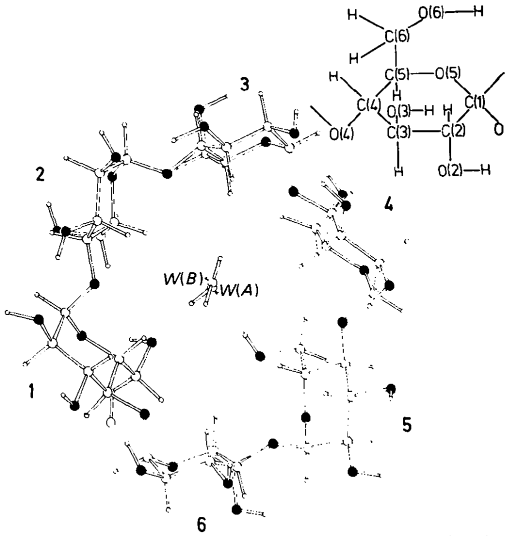

Fig. 3. A view of the α-CD molecule with water molecules $W(A)$, $W(B)$ complexed. The atom numbering in the glucose and the glucose numbering in the α-CD macrocycle refer to the scheme described under *Results*. Hydrogen bonds are indicated by broken lines. The dotted line between glucoses 4 and 5, 2·845 Å, is too long to be called a hydrogen bond.

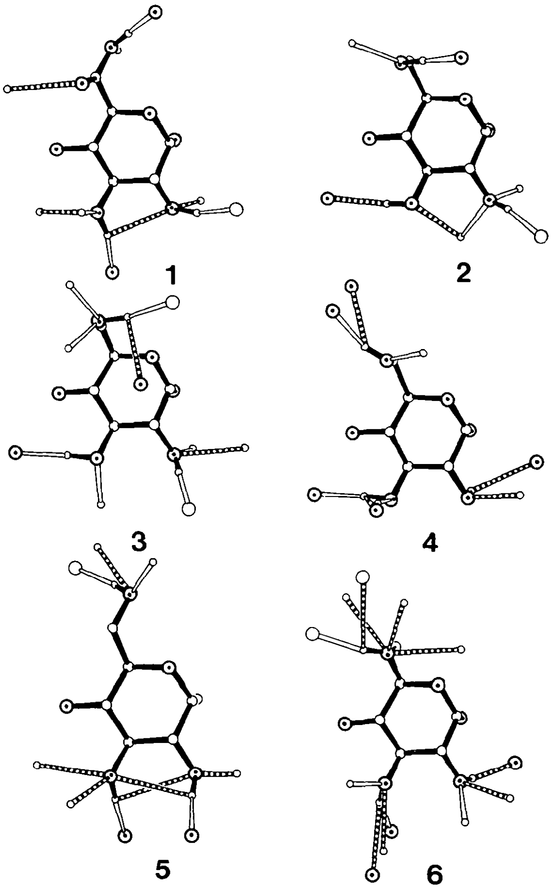

Fig. 4. The six chemically identical glucose units, projected on the plane defined by C(1), C(3), C(5). ○ H, ○ C, ⊙ hydroxyl O of α-CD, O water O atoms. Contacts <2·0 Å are indicated by double lines; broken lines mark contacts <3·0 Å.

Table 1. *Fractional atomic coordinates* (× 10⁴) *of* C, O, H *and isotropic temperature factors* [*exp*$(-B\sin^2\theta/\lambda^2)$] *for α-CD hexahydrate*

Temperature factors are multiplied by 10. Values for C and O atoms are converted from anisotropic temperature factors which are deposited with the data file. Isotropic *B*'s of H atoms are refined with neutron data. The C and O parameters are from X-ray data while the values for H are from neutron results.

	x	*y*	*z*	*B* (Å²)		*x*	*y*	*z*	*B* (Å²)
C(1)1	7799 (2)	2315 (1)	92 (4)	28	HC(1)1	7460 (9)	2612 (3)	−153 (19)	27 (3)
C(2)1	8361 (2)	2166 (1)	−1134 (4)	28	HC(2)1	8840 (11)	2404 (4)	−1571 (20)	42 (3)
O(2)1	7796 (1)	2054 (1)	−2268 (3)	34	HC(3)1	8562 (12)	1545 (4)	−638 (23)	48 (4)
C(3)1	8942 (2)	1816 (1)	−705 (3)	26	HC(4)1	9977 (12)	2116 (5)	399 (22)	37 (4)
O(3)1	9593 (1)	1725 (1)	−1756 (2)	30	HC(5)1	8343 (13)	1796 (5)	2036 (24)	49 (5)
C(4)1	9450 (2)	1904 (1)	640 (3)	25	HC(6)1	9741 (15)	1932 (6)	3481 (28)	99 (7)
O(4)1	9874 (1)	1542 (1)	1073 (3)	27	HC(6)1	9619 (12)	2418 (5)	2919 (24)	33 (4)
C(5)1	8816 (2)	2049 (1)	1785 (4)	29	HC(1)2	3781 (10)	1937 (4)	1608 (20)	41 (3)
O(5)1	8357 (1)	2393 (1)	1256 (3)	29	HC(2)2	4413 (10)	2124 (4)	−614 (18)	30 (3)
C(6)1	9277 (3)	2172 (1)	3126 (4)	41	HC(3)2	6015 (10)	1524 (4)	135 (20)	31 (3)
C(1)2	4514 (2)	1884 (1)	1495 (3)	24	HC(4)2	6107 (12)	2444 (4)	−83 (22)	46 (4)
C(2)2	4721 (2)	1843 (1)	−52 (4)	26	HC(5)2	6147 (8)	1928 (3)	2612 (17)	22 (3)
O(2)2	4300 (1)	1492 (1)	−589 (2)	29	HC(6)2	5943 (10)	2585 (4)	3736 (10)	36 (3)
C(3)2	5731 (2)	1813 (1)	−278 (3)	25	HC(6)2	6967 (11)	2503 (4)	2980 (21)	40 (4)
O(3)2	5900 (2)	1843 (1)	−1748 (2)	35	HC(1)3	3951 (9)	586 (4)	6076 (19)	31 (3)
C(4)2	6225 (2)	2136 (1)	495 (3)	23	HC(2)3	3043 (11)	793 (4)	3986 (22)	47 (4)
O(4)2	7158 (1)	2025 (1)	436 (3)	27	HC(3)3	4809 (9)	803 (4)	2573 (19)	28 (3)
C(5)2	5936 (2)	2177 (1)	2027 (3)	25	HC(4)3	3570 (9)	1465 (4)	3358 (19)	29 (3)
O(5)2	4966 (1)	2215 (1)	2067 (2)	25	HC(5)3	5310 (10)	1350 (4)	4646 (21)	37 (3)
C(6)2	6317 (2)	2535 (1)	2754 (3)	30	HC(6)3	4854 (13)	1841 (5)	6275 (24)	56 (4)
O(6)2	6242 (1)	2890 (1)	1962 (3)	34	HC(6)3	4873 (11)	2016 (5)	4489 (22)	44 (4)
C(1)3	4250 (2)	750 (1)	5249 (3)	24	HC(1)4	7681 (11)	−152 (4)	7435 (20)	40 (4)
C(2)3	3732 (2)	682 (1)	3906 (4)	24	HC(2)4	6138 (11)	−343 (4)	6870 (21)	37 (4)
O(2)3	3786 (1)	269 (1)	3592 (3)	30	HC(3)4	6410 (9)	157 (4)	4276 (18)	23 (3)
C(3)3	4154 (2)	924 (1)	2755 (3)	24	HC(4)4	5159 (10)	293 (4)	6664 (20)	35 (3)
O(3)3	3643 (2)	886 (1)	1479 (2)	31	HC(5)4	6813 (8)	743 (3)	5796 (17)	17 (2)
C(4)3	4210 (2)	1356 (1)	3198 (3)	23	HC(6)4	6712 (11)	1084 (4)	8066 (22)	45 (4)
O(4)3	4790 (1)	1533 (1)	2169 (2)	25	HC(6)4	5865 (13)	1222 (5)	6700 (24)	64 (5)
C(5)3	4629 (2)	1409 (1)	4640 (3)	25	HC(1)5	11317 (7)	531 (3)	5328 (16)	16 (2)
O(5)3	4215 (1)	1149 (1)	5653 (2)	26	HC(2)5	10454 (12)	4 (5)	6613 (22)	53 (4)
C(6)3	4550 (2)	1815 (1)	5257 (4)	31	HC(3)5	9316 (11)	−19 (4)	4088 (20)	35 (3)
O(6)3	3639 (2)	1944 (1)	5408 (3)	35	HC(4)5	8923 (11)	159 (4)	7211 (20)	37 (3)
C(1)4	7306 (2)	38 (1)	6717 (3)	24	HC(5)5	8883 (13)	718 (5)	4657 (24)	59 (4)
C(2)4	6585 (2)	−210 (1)	6001 (3)	24	HC(6)5	8928 (11)	899 (4)	7787 (22)	43 (4)
O(2)4	6974 (1)	−529 (1)	5246 (3)	32	HC(6)5	7977 (12)	923 (4)	6817 (23)	53 (4)
C(3)4	5989 (2)	51 (1)	5091 (3)	22	HC(1)6	11120 (11)	1794 (4)	614 (20)	37 (3)
O(3)4	5285 (1)	−174 (1)	4468 (2)	27	HC(2)6	11860 (12)	1140 (4)	716 (22)	48 (4)
C(4)4	5619 (2)	388 (1)	5963 (3)	22	HC(3)6	10121 (11)	774 (5)	1205 (23)	55 (4)
O(4)4	5158 (1)	635 (1)	4988 (2)	24	HC(4)6	11605 (8)	797 (4)	3204 (17)	21 (2)
C(5)4	6396 (2)	618 (1)	6603 (3)	23	HC(5)6	9991 (13)	1286 (5)	3693 (24)	56 (4)
O(5)4	6915 (1)	354 (1)	7483 (2)	25	HC(6)6	10814 (13)	1220 (5)	5808 (23)	53 (4)
C(6)4	6122 (2)	970 (1)	7462 (4)	29	HC(6)6	10935 (11)	1698 (5)	5040 (22)	42 (4)
O(6)4	5428 (2)	874 (1)	8428 (3)	35	HO(2)1	7663 (14)	2324 (5)	−2813 (26)	74 (5)
C(1)5	10600 (2)	476 (1)	5150 (3)	27	HO(3)1	9310 (11)	1647 (4)	−2641 (21)	39 (4)
C(2)5	10399 (2)	52 (1)	5509 (3)	28	HO(6)1	8611 (12)	2540 (5)	4374 (22)	41 (4)
O(2)5	10977 (2)	−205 (1)	4746 (3)	39	HO(2)2	3771 (10)	1567 (4)	−1047 (19)	35 (3)
C(3)5	9409 (2)	−47 (1)	5264 (3)	24	HO(3)2	6450 (11)	1896 (4)	−1941 (22)	58 (5)
O(3)5	9207 (1)	−436 (1)	5743 (3)	32	HO(6)2	5686 (10)	3000 (4)	1976 (18)	42 (3)
C(4)5	8818 (2)	238 (1)	6075 (3)	25	HO(2)3	3285 (12)	169 (4)	3302 (21)	53 (4)
O(4)5	7895 (1)	173 (1)	5664 (2)	24	HO(3)3	3945 (11)	1098 (4)	760 (20)	53 (4)
C(5)5	9085 (2)	660 (1)	5738 (4)	27	HO(6)3	3369 (13)	1787 (5)	6250 (24)	64 (5)
O(5)5	10034 (1)	711 (1)	5989 (2)	27	HO(2)4	7411 (12)	−413 (4)	4713 (21)	53 (4)
C(6)5	8649 (2)	961 (1)	6677 (4)	38	HO(3)4	4852 (10)	15 (4)	4047 (20)	41 (4)
O(6)5	8841 (2)	1348 (1)	6174 (3)	41	HO(6)4	5037 (10)	1089 (4)	8521 (20)	39 (4)
C(1)6	10818 (2)	1537 (1)	1217 (3)	27	HO(2)5	11048 (9)	−449 (3)	5254 (18)	30 (3)
C(2)6	11154 (2)	1152 (1)	623 (3)	27	HO(3)5	9351 (10)	−618 (4)	5003 (20)	50 (4)
O(2)6	10925 (2)	1110 (1)	−808 (3)	37	HO(6)5	8388 (11)	1429 (4)	5711 (21)	49 (4)
C(3)6	10783 (2)	808 (1)	1504 (3)	25	HO(2)6	10348 (11)	1229 (4)	−1034 (22)	55 (4)
O(3)6	11174 (2)	452 (1)	1016 (3)	32	HO(3)6	10740 (13)	309 (4)	530 (23)	57 (5)
C(4)6	10978 (2)	855 (1)	3049 (3)	23	HO(6)6	12182 (13)	1153 (4)	5678 (24)	71 (5)

Table 1 (*cont.*)

	x	*y*	*z*	*B* (Å^2)		*x*	*y*	*z*	*B* (Å^2)
O(4)6	10457 (1)	550 (1)	3702 (2)	25	H201	2446 (7)	551 (3)	7470 (16)	20 (2)
C(5)6	10733 (2)	1275 (1)	3576 (3)	26	H201′	1719 (11)	843 (4)	8017 (21)	45 (4)
O(5)6	11082 (1)	1570 (1)	2634 (2)	28	H202	3240 (11)	80 (4)	8452 (22)	44 (4)
O(6)6	12088 (2)	1339 (1)	4962 (3)	46	H202′	3125 (10)	−139 (4)	6982 (20)	43 (4)
C(6)6	11144 (2)	1391 (1)	4978 (4)	31	H203	2817 (13)	2082 (4)	3913 (22)	54 (4)
O(6)1*A*	8607 (2)	2239 (1)	4191 (3)	43	H203′	1899 (14)	1976 (5)	3272 (23)	67 (5)
O(6)1*B*	10274 (19)	2396 (7)	2749 (29)	42	H204	2304 (17)	1759 (6)	8048 (30)	122 (8)
W(1)	2232 (2)	836 (1)	7403 (3)	40	H204′	2536 (10)	1359 (4)	7730 (21)	43 (4)
W(2)	2803 (1)	39 (1)	7703 (3)	35	H20*A*	7725 (16)	1811 (6)	4515 (29)	114 (8)
W(3)	2434 (2)	2185 (1)	3273 (3)	58	H20*A*′	7187 (12)	1427 (5)	3891 (23)	58 (5)
W(4)	2800 (2)	1628 (1)	7901 (3)	44	H20*B*	6498 (17)	860 (6)	2216 (29)	98 (7)
W(*A*)	7344 (2)	1573 (1)	4632 (3)	70	H20*B*′	7449 (16)	906 (5)	1658 (28)	85 (6)
W(*B*)	7041 (3)	1006 (1)	2388 (5)	107	HC16*B*1	9049 (114)	2281 (46)	4190 (216)	42 (10)

Table 2. *Bond distances* (Å) *and angles* (°)

E.s.d.'s given in parentheses were obtained from the least-squares correlation matrix. Mean values for rows and columns are presented together with σ, calculated from $\sigma = [\Sigma_{i=1}^{m} (y_i - \bar{y})^2/m - 1]^{1/2}$, where $\bar{y}$ = mean value of observations y_i, m = number of observations.

	Glucose unit							
	1	2	3	4	5	6	Mean	σ
Bond lengths								
C(1)–C(2)	1·524 (5)	1·513 (5)	1·511 (5)	1·525 (4)	1·514 (4)	1·514 (4)	1·517	0·006
C(2)–C(3)	1·526 (4)	1·520 (4)	1·509 (4)	1·526 (4)	1·526 (4)	1·542 (4)	1·525	0·011
C(3)–C(4)	1·516 (5)	1·512 (4)	1·532 (4)	1·518 (4)	1·520 (4)	1·510 (4)	1·518	0·008
C(4)–C(5)	1·524 (5)	1·528 (4)	1·519 (4)	1·523 (4)	1·521 (4)	1·557 (4)	1·529	0·014
C(5)–C(6)	1·509 (5)	1·509 (5)	1·508 (5)	1·507 (4)	1·507 (5)	1·521 (5)	1·510	0·005
Mean	1·520	1·516	1·516	1·520	1·518	1·529	1·520	
σ	0·007	0·008	0·010	0·008	0·007	0·020		
C(1)–O(5)	1·410 (4)	1·420 (4)	1·412 (3)	1·424 (4)	1·411 (4)	1·411 (4)	1·415	0·006
C(1)–O(4)′	1·412 (4)	1·416 (4)	1·426 (3)	1·409 (4)	1·418 (4)	1·409 (4)	1·415	0·006
C(2)–O(2)	1·421 (4)	1·441 (4)	1·438 (3)	1·423 (4)	1·425 (4)	1·413 (4)	1·427	0·011
C(3)–O(3)	1·426 (4)	1·426 (4)	1·439 (4)	1·426 (4)	1·434 (4)	1·422 (4)	1·429	0·006
C(4)–O(4)	1·446 (4)	1·437 (3)	1·438 (4)	1·430 (4)	1·443 (4)	1·438 (4)	1·439	0·006
C(5)–O(5)	1·447 (4)	1·447 (4)	1·447 (4)	1·450 (4)	1·441 (4)	1·444 (4)	1·446	0·003
C(6)–O(6)	1·441 (5)	1·430 (4)	1·430 (4)	1·420 (4)	1·432 (4)	1·414 (4)	1·428	0·010
Mean	1·429	1·431	1·433	1·426	1·429	1·422	1·428	
σ	0·016	0·011	0·011	0·012	0·012	0·014	0·014	
Bond angles								
C(1)–C(2)–C(3)	111·4 (3)	110·2 (3)	108·7 (2)	109·8 (3)	111·5 (3)	109·7 (3)	110·2	1·1
C(2)–C(3)–C(4)	111·7 (3)	111·3 (3)	110·3 (2)	109·8 (2)	109·7 (2)	112·4 (3)	110·9	1·1
C(3)–C(4)–C(5)	111·2 (3)	113·4 (2)	112·7 (2)	109·4 (2)	110·2 (3)	111·6 (2)	111·4	1·5
C(4)–C(5)–C(6)	114·5 (3)	114·0 (3)	115·4 (3)	114·9 (3)	113·8 (3)	115·3 (3)	114·7	0·7
Mean	112·2	112·2	111·8	111·0	111·3	112·3	111·8	
σ	1·5	1·8	2·9	2·6	1·8	2·3		
C(2)–C(1)–O(5)	110·1 (3)	110·6 (2)	111·1 (2)	107·2 (2)	107·2 (3)	109·6 (3)	109·3	1·7
C(2)–C(1)–O(4)′	108·4 (3)	107·8 (2)	107·0 (2)	111·0 (2)	111·0 (3)	107·2 (3)	108·7	1·8
C(1)–C(2)–O(2)	110·4 (3)	109·5 (2)	107·3 (2)	110·5 (3)	110·5 (3)	111·7 (3)	110·0	1·5
C(3)–C(2)–O(2)	109·3 (3)	109·0 (2)	111·0 (2)	111·6 (3)	111·6 (3)	111·3 (3)	111·6	1·2
C(2)–C(3)–O(3)	111·4 (3)	108·0 (2)	110·2 (2)	110·9 (2)	110·9 (2)	108·8 (2)	110·0	1·3
C(4)–C(3)–O(3)	107·4 (2)	110·0 (2)	110·4 (2)	108·0 (2)	108·0 (2)	109·4 (2)	108·9	1·2
C(3)–C(4)–O(4)	106·9 (2)	104·9 (2)	104·3 (2)	108·2 (2)	108·2 (2)	104·0 (2)	106·1	1·9
C(5)–C(4)–O(4)	110·0 (2)	109·4 (2)	108·8 (2)	109·6 (2)	109·6 (2)	113·5 (2)	110·2	1·7
C(4)–C(5)–O(5)	107·7 (3)	108·3 (2)	111·0 (2)	108·4 (2)	109·6 (2)	110·8 (2)	109·3	1·4
C(6)–C(5)–O(5)	106·5 (3)	106·9 (2)	105·6 (3)	108·8 (2)	103·8 (2)	102·7 (3)	105·7	2·2
C(5)–C(6)–O(6)	109·0 (3)	114·2 (3)	113·2 (3)	111·5 (3)	110·0 (3)	110·9 (3)	111·5	1·9
Mean	108·8	109·0	109·1	109·6	109·1	109·1	109·2	
σ	1·6	2·3	2·7	1·6	2·2	3·3		
C(4)–O(4)–C(1)′	118·1 (2)	118·3 (2)	119·3 (2)	120·1 (2)	116·6 (2)	117·9 (2)	118·4	1·2
C(1)–O(5)–C(5)	113·5 (2)	113·1 (2)	113·0 (2)	112·9 (2)	114·9 (2)	116·1 (2)	113·9	1·3
Mean	115·8	115·7	116·2	116·5	115·8	117·0	116·2	
σ	3·3	3·7	4·5	5·1	1·2	1·3		
O(5)–C(1)–O(4)′	110·2 (3)	110·9 (2)	110·2 (2)	111·2 (2)	111·2 (2)	111·7 (2)	110·9	0·6

Table 2 (*cont.*)

Geometrical data involving hydrogen atoms

	Glucose					
	1	2	3	4	5	6
Bond distances						
C(1)–H(1)	1·15 (1)	1·11 (2)	1·06 (2)	1·09 (2)	1·09 (1)	1·14 (2)
C(2)–H(2)	1·16 (2)	1·19 (1)	1·09 (2)	1·15 (2)	1·07 (2)	1·05 (2)
C(3)–H(3)	1·08 (2)	1·14 (1)	1·07 (1)	1·06 (2)	1·13 (2)	1·03 (2)
C(4)–H(4)	1·09 (2)	1·20 (2)	1·03 (1)	1·01 (2)	1·13 (2)	0·96 (1)
C(5)–H(5)	1·14 (2)	1·06 (1)	1·03 (1)	1·08 (1)	1·09 (2)	1·11 (2)
C(6)–H(6)1	1·12 (2)	1·10 (2)	1·07 (2)	1·12 (2)	1·16 (2)	1·10 (2)
C(6)–H(6)2	1·00 (2)	0·99 (2)	1·11 (2)	1·19 (2)	1·01 (2)	1·09 (2)
O(2)–HO(2)	1·07 (2)	0·93 (2)	0·86 (2)	0·91 (2)	0·97 (1)	0·97 (2)
O(3)–HO(3)	0·98 (2)	0·86 (2)	1·09 (2)	0·99 (2)	0·96 (2)	0·93 (2)
O(6)–HO(6)	1·03 (2)	0·91 (1)	1·04 (2)	0·94 (1)	0·85 (2)	0·94 (2)

Bond distances and angles for water molecules

W(1)–H201	1·02 (1)	103 (1)	*W*(4)–H204	0·87 (2)	99 (2)
H201′	0·96 (2)		H204′	1·01 (2)	
W(2)–H202	0·97 (2)	105 (1)	*W*(*A*)–H20*A*	1·00 (2)	120 (2)
H202′	1·03 (2)		H20*A*′	0·89 (2)	
W(3)–H203	0·91 (2)	102 (2)	*W*(*B*)–H20*B*	0·96 (2)	103 (2)
H203′	1·07 (2)		H20*B*′	0·98 (3)	

	Glucose					
	1	2	3	4	5	6
Bond angles						
H–C(1)–C(2)	112 (1)	108 (1)	110 (1)	108 (1)	109 (1)	110 (1)
H–C(1)–O(5)	105 (1)	107 (1)	107 (1)	109 (1)	113 (1)	108 (1)
H–C(1)–O(4)′	112 (1)	112 (1)	112 (1)	109 (1)	106 (1)	110 (1)
H–C(2)–C(1)	112 (1)	107 (1)	111 (1)	107 (1)	111 (1)	109 (1)
H–C(2)–O(2)	106 (1)	110 (1)	114 (1)	107 (1)	111 (1)	109 (1)
H–C(2)–C(3)	107 (1)	112 (1)	104 (1)	108 (1)	101 (1)	106 (1)
H–O(2)–C(2)	104 (1)	108 (1)	114 (1)	104 (1)	110 (1)	113 (1)
H–C(3)–C(2)	113 (1)	112 (1)	107 (1)	106 (1)	104 (1)	106 (1)
H–C(3)–O(3)	102 (1)	110 (1)	108 (1)	108 (1)	112 (1)	102 (1)
H–C(3)–C(4)	112 (1)	106 (1)	111 (1)	111 (1)	112 (1)	118 (1)
H–O(3)–C(3)	112 (1)	113 (1)	105 (1)	107 (1)	108 (1)	109 (1)
H–C(4)–C(3)	108 (1)	110 (1)	110 (1)	112 (1)	105 (1)	108 (1)
H–C(4)–O(4)	108 (1)	111 (1)	120 (1)	107 (1)	111 (1)	108 (1)
H–C(4)–C(5)	112 (1)	108 (1)	102 (1)	114 (1)	113 (1)	111 (1)
H–C(5)–C(4)	107 (1)	110 (1)	113 (1)	111 (1)	107 (1)	107 (1)
H–C(5)–O(5)	113 (1)	110 (1)	107 (1)	111 (1)	114 (1)	113 (1)
H–C(5)–C(6)	108 (1)	107 (1)	104 (1)	103 (1)	109 (1)	108 (1)
H–C(6)–C(5)	109 (1)	109 (1)	113 (1)	110 (1)	105 (1)	108 (1)
	107 (1)	112 (1)	106 (1)	108 (1)	114 (1)	100 (1)
H–C(6)–O(6)	109 (1)	106 (1)	106 (1)	108 (1)	114 (1)	113 (1)
	111 (1)	106 (1)	107 (1)	109 (1)	111 (1)	114 (1)
H–C(6)–H	111 (2)	109 (1)	111 (1)	108 (1)	102 (1)	103 (1)
H–O(6)–C(6)	106 (1)	114 (1)	106 (1)	109 (1)	108 (1)	110 (1)

C–C–O–H torsion angles (°) for glucose

	Glucose					
	1	2	3	4	5	6
H–O(2)–C(2)–C(1)	84 (1)	100 (1)	138 (1)	−50 (1)	154 (1)	−34 (1)
H–O(2)–C(2)–C(3)	−154 (1)	−139 (1)	−103 (1)	74 (1)	−81 (1)	89 (1)
H–O(3)–C(3)–C(2)	−63 (1)	163 (1)	173 (1)	169 (1)	−85 (1)	−107 (1)
H–O(3)–C(3)–C(4)	176 (1)	42 (1)	51 (1)	47 (1)	154 (1)	129 (1)
H–O(6)–C(6)–C(5)	−111 (1)	78 (1)	73 (1)	−145 (1)	99 (1)	−119 (1)

Table 3. *Distances* (Å) *and angles* (°) *for the hydrogen bonding and the water coordination*

(*a*) Geometry of hydrogen-bonding interactions. Average e.s.d.'s are 0·01 Å for O–H and H···O, 0·003 Å for O···O and 1° for O–H···O angles.

Donor	Acceptor	O–H	O···O	∠O–H···O	H···O
O(2)1	*W*(3)	1·07	2·813	166	1·76
2	*W*(4)	0·93	2·692	169	1·77
3	*W*(2)	0·86	2·718	179	1·85
4	O(3)5	0·91	3·367	118	2·85
5	O(3)3	0·97	2·902	169	1·95
6	O(3)1	0·97	3·021	150	2·14
O(3)1	O(6)5	0·98	2·606	158	1·67
2	O(2)1	0·86	2·949	175	2·09
3	O(2)2	1·09	3·016	171	1·93
4	O(2)3	0·99	2·816	161	1·86
5	O(6)4	0·96	2·716	169	1·77
6	O(3)4	0·93	2·788	163	1·89
O(6)1*A*	O(6)3	1·03	2·807	177	1·77
2	O(3)1	0·91	2·785	171	1·89
3	*W*(4)	1·04	2·889	166	1·87
4	O(2)2	0·94	2·850	160	1·95
5	*W*(*A*)	0·85	2·773	176	1·92
6	*W*(1)	0·94	2·897	169	1·97
W(1)	*W*(2)	1·02	2·857	176	1·84
W(1)′	O(2)6	0·96	2·747	152	1·86
W(2)	O(2)5	0·97	2·719	174	1·75
W(2)′	O(3)6	1·03	2·773	169	1·75
W(3)	O(6)3	0·91	2·831	171	1·93
W(3)′	O(6)6	1·07	3·339	117	2·72
	O(6)1*B*		3·327	107	2·85
W(4)	O(6)2	0·87	2·840	169	1·98
W(4)′	*W*(1)	1·01	2·867	171	1·87
W(*A*)	O(6)1*A*	1·00	2·974	173	1·98
W(*A*)′	*W*(*B*)	0·89	2·915	167	2·04
W(*B*)	O(3)5	0·96	3·108	145	2·27
W(*B*)′	O(2)4	0·98	2·991	160	2·05

(*b*) Coordination of water molecules. Distances marked with an asterisk are too long to be considered as hydrogen bonds and can only be regarded as van der Waals contacts. Angles involving these bonds are also marked with an asterisk.

A–*B*–*C*	*A*–*B*	*B*–*C*	∠*A*–*B*–*C*
O(2)6–*W*(1)–O(6)6	2·747	2·897	104
– –*W*(2)		2·857	118
– –*W*(4)		2·867	77
O(6)6– –*W*(2)			132
– –*W*(4)			66
W(2)– –			142
O(2)3–*W*(2)–O(2)5	2·718	2·719	116
– –O(3)6		2·773	115
– –*W*(1)		2·857	98
O(2)5– –O(3)6			100
– –*W*(1)			94
O(3)6– –			133
O(2)1–*W*(3)–O(6)3	2·813	2·831	113
– –O(6)6		3·339*	171*
– –O(6)1*B*		3·327*	86*
O(6)3– –O(6)6			60*
– –O(6)1*B*			141*
O(6)6– –			96*
O(2)2–*W*(4)–O(6)2	2·692	2·840	139
– –O(6)3		2·889	98
– –*W*(1)		2·867	100
O(6)2– –O(6)3			100
– –*W*(1)			108
O(6)3– –			110
O(6)5–*W*(*A*)–O(6)1*A*	2·773	2·974	77
– –*W*(*B*)		2·915	109
– –O(2)1		3·440*	61*
O(6)1*A*– –*W*(*B*)			120
– –O(2)1			69*
W(*B*)– –			167*
O(2)4– –O(3)5	2·991	3·108	67
– –*W*(*A*)		2·915	142
O(3)5– –			151

Table 1.* Parameters of C and O atoms were refined with X-ray data and H atom parameters were obtained from the neutron data. Interatomic distances and angles are entered in Table 2; the hydrogen bonding is described in Table 3 and in Figs. 3 and 4. The numbering scheme denotes first the kind of atom, in parentheses is given the corresponding atom position within a glucose, the number after the parentheses describes which one of six glucoses is meant according to Fig. 3. Hydration water O atoms are numbered *W*(1) to *W*(4) and the two included water atoms are *W*(*A*), *W*(*B*). For further information concerning torsion angles, molecular packing, and detailed geometry of α-CD see Manor & Saenger (1974), Saenger (1976), and Saenger, Noltemeyer, Manor, Hingerty & Klar (1976).

Discussion of results

(*a*) *Disorder of* O(6)1

In the previous X-ray study (Manor & Saenger, 1974) all the atoms were found to be well ordered with occupancy indices 1·0. With the improved new X-ray data it was observed from a difference Fourier map calculated near the end of the least-squares refinement (R = 4·8%) that the hydroxyl O(6)1 of glucose 1 is twofold disordered, a major O(6)1*A* site occupied at 92% and a minor O(6)1*B* site filled to only 8%. The H atom attached to site O(6)1*B* at 8% could not be located and this O atom appears not to be involved in hydrogen-bond contacts (Table 3).

(*b*) *Bond angles and distances*

E.s.d.'s in bond angles and distances are smaller than in the previous X-ray study but the general distribution is comparable (Table 2). The C–H and O–H lengths are on average 1·10 and 0·95 Å, the latter significantly longer than the 0·890 (9) Å from 45 X-ray crystal structures of polyalcohols and saccharides (Kroon, Kanters, van Duijneveldt-van der Rijdt, van Duijneveldt & Vliegenthardt, 1975). This discrepancy may be explained by the fact that bond distances derived from X-ray data may appear to be shortened. In α-CD $6H_2O$, bond angles confined by C–H or by O–H bonds are close to tetrahedral with no significant differences if C–H or O–H is involved.

(*c*) *Torsion angles*

Differences in equivalent angles C–C–O–H in the six glucoses are due to hydrogen bonds to neigh-

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34995 (38 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

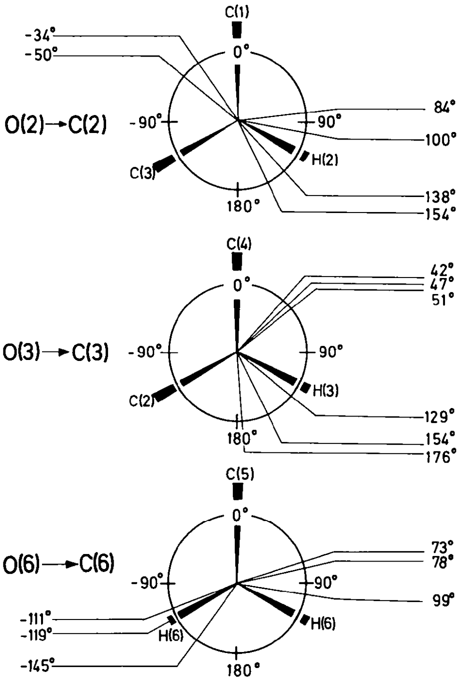


Fig. 5. Newman projections of torsion angles C—C—O—H, viewed down the O—C vector. The hydroxyl H is staggered with C but can be eclipsed with H.

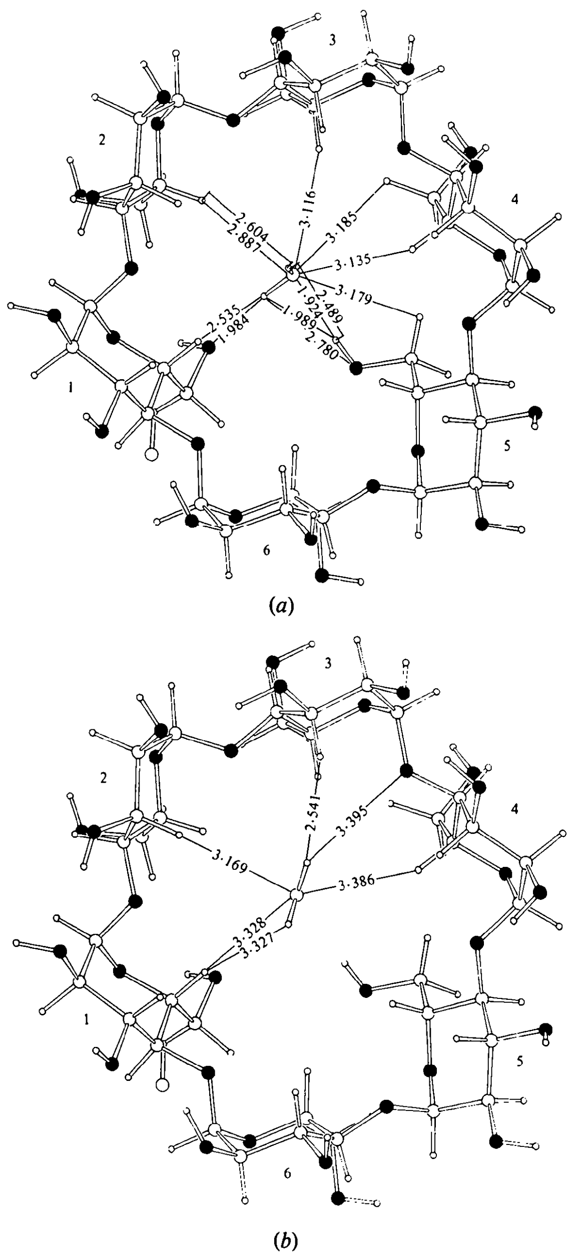
bouring or water O atoms; see the projections, Fig. 4, and the conformational wheels, Fig. 5. From the latter we find that staggered arrangements for C—C—O—H are preferred and that H atoms at both ends of the four-atom chain do not present severe hindrance, *i.e.* angles H—C—O—H can be eclipsed.

(*d*) *Close contacts between host and guest molecules*

In Fig. 6(*a*) and (*b*) are described distances <3·4 Å, from atoms of the included water molecules *W*(*A*) (Fig. 6*a*) and *W*(*B*) (Fig. 6*b*) to atoms lining the α-CD cavity. These distances must be compared with van der Waals radii for H, 1·2 Å, and for O, 1·4 Å (*Handbook of Chemistry and Physics*, 1972). Van der Waals contacts should be close to 2·4 Å for H···H and 2·6 Å for H···O.

Fig. 6(*a*) demonstrates that both water molecules are not located at the centre of the α-CD molecule but are moved by ~0·6 Å towards glucose 3 (Manor & Saenger, 1974). Water *W*(*A*) is held by hydrogen bonds with hydroxyls O(6)1*A* and O(6)5 and by contacts to C(5)–H and to C(6)–H hydrogens of glucoses 1 to 5, but not to glucose 6.

The H atom attached to O(6)5 has short contacts with the O atom of *W*(*A*), 1·92 Å (hydrogen bond), and with one of the H atoms of *W*(*A*), 1·99 Å, a distance less than the van der Waals contact of 2·4 Å, indicating a rather short H···H interaction.



(*a*)

(*b*)

Fig. 6. Close contacts (Å) between (*a*) water molecule *W*(*A*) and (*b*) water molecule *W*(*B*) and the surrounding α-CD molecule.

All the other *W*(*A*)···H—C(5) and, in the case of glucose 4, *W*(*A*)···H—C(6) distances are close to or exceed the theoretical value of 2·6 Å.

The contacts *W*(*A*)···H—C(5)1 and ···H—C(5)2, 2·54 and 2·89 Å, are significantly shorter than the other contacts to H—C(5) and H—C(6) hydrogen atoms, 3·12 to 3·19 Å.

Water molecule *W*(*B*) is only in van der Waals contact with glucoses 1 to 4 of the α-CD cavity, Fig.

6(*b*). It is situated near the O(2),O(3) rim of α-CD and, therefore, in contact mainly with hydrogens H—C(3). All H···H distances, from 2·54 to 3·40 Å, exceed the sum of the van der Waals radii. These relatively loose van der Waals contacts and the long hydrogen bonds with H···O distances >2·0 Å to hydroxyl groups *W*(*A*), O(2)4 and O(3)5, Table 3, suggest rather large thermal motion for water *W*(*B*). The molecule with most extensive vibration is *W*(*B*), followed by *W*(*A*), some O(6) hydroxyls and by the other water molecules. The C—O skeleton of the α-CD molecule shows little vibration, the exocyclic O(2), O(3) and C(6) displaying slightly more motion than the glucose-ring atoms.

(*e*) *Hydrogen bonds*

In this crystal structure, six primary and twelve secondary hydroxyl groups and six water molecules are able to act as donors for 30 hydrogen bonds. Table 3 lists 31 hydrogen bonds which fall into two classes. Those with H···O distances from 1·67 to 2·27 Å are shorter than the sum of the van der Waals radii, 1·2 Å for H and 1·4 Å for O, and satisfy the classical criteria for hydrogen bonds. The 'long' hydrogen bonds with H···O distances between 2·72 and 2·85 Å should be considered with reservation because the geometries of the respective O—H···O groups are unfavourable, especially if the angles at H, between 107 and 118°, are considered. For the bond O(2)4—H···O(3)5, this geometry is determined by the rotation of glucose 5 relative to the neighbouring glucoses 4 and 6 while the bond *W*(3)—H′···O(6)6 and O(6)1*B* represents a bifurcated hydrogen bond, the only one occurring in this crystal structure. If we apply Allinger's (1976) concept of van der Waals potential-minimum radii, 1·50 Å for H and 1·65 Å for O, the cut-off limit of 3·15 Å for an H···O interaction would still be greater than 2·72 to 2·85 Å and these hydrogen-bonding interactions, although weak, could be called 'existent'.

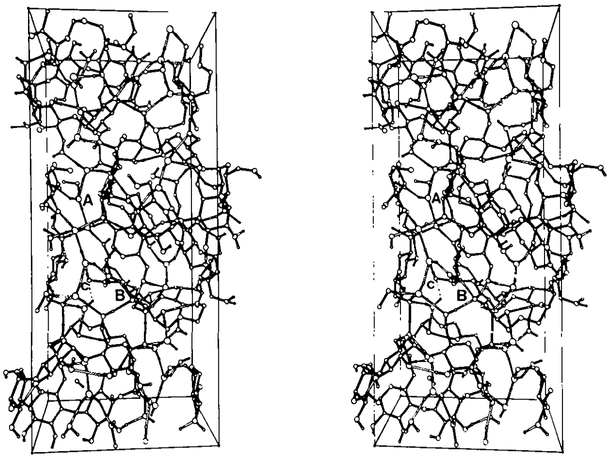


Fig. 7. A stereoplot describing the packing of α-CD molecules in the unit cell (Johnson, 1965). H···O hydrogen-bonding distances <2·3 Å are indicated by double lines. Circular hydrogen bonds are indicated by *A*, *B*, *C*. *A* represents the homodromic circle (I) described in Saenger (1979), while *B* and *C* are the antidromic circles (II) and (III). The stippled line in circle *C* represents the long *W*(3)H···O(6)6 hydrogen bond, which is bifurcated.

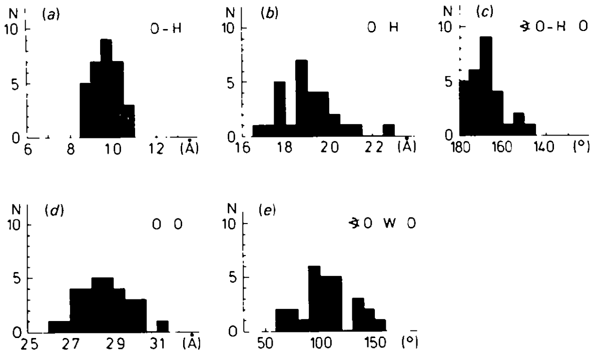


Fig. 8. Histograms to describe the distribution of bond angles and distances found for the 30 hydrogen bonds in this crystal structure.

A stereodiagram showing the packing and the hydrogen bonds is given in Fig. 7 (Johnson, 1965). In Fig. 8 the data entered in Table 3 are described in the form of histograms. It is not surprising to find that the histogram for the covalent H—O distances shows a rather narrow distribution. All the other histograms in Fig. 8 displaying data with non-bonded interactions indicate a broader distribution but compared with similar histograms derived from X-ray data (Kroon *et al.*, 1975) the distribution here is more narrow and confined, probably due to the rather accurate positioning of H atoms. Only the O···O histograms are comparable because O atoms in normal X-ray analyses and in this study are located with similar precision.

The spatial distribution of hydroxyl or water O atoms around water molecules tries to satisfy tetrahedral geometry but is in obvious conflict with packing requirements, Table 3(*b*) and Fig. 7. The best tetrahedra are established around *W*(2) and *W*(4) but the tetrahedron around *W*(1) is badly distorted. *W*(3) has only two hydrogen-bonded neighbours, O(2)1 and O(6)3, while O(6)6 and O(6)1*B* (at 8% occupancy) are 'loosely bonded' and the bonding angles vary between 60 and 171°. The included water molecules *W*(*A*) and *W*(*B*) have only three hydrogen-bonded partners. For *W*(*A*), the angle O(6)5—*W*(*A*)—O(6)1*A*, 77°, is clearly determined by geometrical restrictions imposed by the orientation of the two glucoses in the α-CD molecule while the other two angles to *W*(*B*), 109 and 120°, are roughly tetrahedral. For *W*(*B*), the angles between coordinated hydroxyls can no longer be called tetrahedral because their sum amounts to 360°: the ligands are in a planar arrangement.

At first sight, the hydrogen-bonding scheme, Table 3 and Fig. 7, appears rather unsystematic. However, if we follow the hydrogen bonds from one hydroxyl group to the next, we find chain-like structures of the type O—H···O—H···O—H··· which in some cases close up to form circles comprising five and six OH groups (Saenger, 1979). Similar endless chains have been observed previously in carbohydrate crystal structures (Jeffrey & Takagi, 1978; Jeffrey & Lewis, 1978; Jeffrey, Gress & Takagi, 1977). Theoretically, they have been explained on the basis of quantum-chemical calculations as being due to the 'cooperative effect' (Del Bene & Pople, 1973; Frank & Wen, 1957) which renders the hydroxyl group a stronger donor/acceptor if it already accepts/donates a hydrogen bond.

As reported for other crystal structures of α-CD (Saenger, 1976) the acetal oxygens O(4) and O(5) are not involved in hydrogen bonds. The recent X-ray analysis (Lindner & Saenger, to be published) of a second modification of $(\alpha\text{-CD})_2.6H_2O$, however, demonstrated that in α-CD such interactions, at least to O(5), are indeed possible, in agreement with the rare observation of such hydrogen bonds in crystal structures of individual glucoses (Jeffrey & Takagi, 1978).

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The Structure of 4-(3-Indolyl)butyric Acid

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Abstract

$C_{12}H_{13}NO_2$ crystallizes in the monoclinic space group $P2_1/c$ with $a = 21{\cdot}003$ (3), $b = 5{\cdot}114$ (1), $c = 9{\cdot}918$ (2) Å, $\beta = 93{\cdot}278$ (6)°, $Z = 4$. The structure was solved by direct methods and refined to $R = 0{\cdot}056$ for 1729 counter reflections. O—H···O bonds of length 2·644 Å are observed.

Introduction

The best established and most widely occurring natural auxin is indolylacetic acid (IAA). Homologues of IAA

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* Contribution No. 515.

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