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The crystal structure of the α-cellobiose·2 NaI·2 H_2O complex in the context of related structures and conformational analysis

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Abstract

The crystal structure of β-D-glucopyranosyl-(1→4)-α-D-glucopyranose (α-cellobiose) in a complex with water and NaI was determined with Mo K_α radiation at 150 K to $R = 0.027$. The space group is $P2_1$ and unit cell dimensions are $a = 9.0188$, $b = 12.2536$, $c = 10.9016$ Å, $\beta = 97.162°$. There are no direct hydrogen bonds among cellobiose molecules, and the usual intramolecular hydrogen bond between O-3–H and O-5′ is replaced by a bridge involving Na^+, O-3, O-5′, and O-6′. Both Na^+ have sixfold coordination. One I^- accepts six donor hydroxyl groups and three C–H···I^- hydrogen bonds. The other accepts three hydroxyls, one Na^+, and five C–H···I^- hydrogen bonds. Linkage torsion angles $\phi_{O\text{-}5}$ and $\psi_{C\text{-}5}$ are -73.6 and $-105.3°$, respectively ($\phi_H = 47.1°$ and $\psi_H = 14.6°$), probably induced by the Na^+ bridge. This conformation is in a separate cluster in ϕ, ψ space from most similar linkages. Both C-6–O–H and C-6′–O–H are gg, while the C-6′–O–H groups from molecules not in the cluster have gt conformations. Hybrid molecular mechanics/quantum mechanics calculations show < 1.2 kcal/mol strain for any of the small-molecule structures. Extrapolation of the NaI cellobiose geometry to a cellulose molecule gives a left-handed helix with 2.9 residues per turn. The energy map and small-molecule crystal structures imply that cellulose helices having 2.5 and 3.0 residues per turn are left-handed.

Keywords: α-Cellobiose; Cellulose; Mercerization; Modeling; QM/MM; Salt complex; Crystal structure

1. Introduction

Substantial progress has been made in determining the structure of exceptionally crystalline samples of cellulose.[1] However, many questions about cellulose structure remain when it is in industrial and biological environments where it has lesser or altered crystallinity. Therefore, it is important to understand its intrinsic shape, its degree of flexibility, and the environmental effects on these properties. One way to increase this understanding is to continue to study di- and oligosaccharides as model compounds.

Cellobiose, the smallest molecule that contains the linkage and repeated glucose rings of cellulose, has been studied by X-ray crystallography[2–4] in the usual β-anomeric form and by NMR spectroscopy.[5] About 30 years ago, the preparation of microcrystalline α-cellobiose was reported, along with a crystalline NaI complex.[6] However, structures were not determined. This paper reports the structure of a salt complex from that work. In addition to its implications for the shape properties of cellulose, interactions with Na^+ ions in this complex provide insight on mercerization, a poorly understood commercial treatment of cotton cellulose with NaOH.

Because each experiment determines one, or at most a few, molecular shapes, data from other molecules that have small chemical differences from cellobiose are also useful in understanding cellulose. The variations in constitution inevitably cause differences in the crystal

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lattice, and therefore in the external forces on the molecule. Such changes are not expected however, to have major consequences for the intramolecular forces that determine the linkage conformations. Therefore, the distribution of shapes from related structures should result in a better understanding of cellulose. To that end, we have taken 20 other related molecules from the literature, including methyl cellotrioside[7] and cellotetraose,[8] the two molecules closest to cellulose that have been determined so far.

Another way to determine likely shapes is to use computerized molecular modeling.[9–12] Although results have been inconsistent,[13] ideally, calculations provide a rationale for the experimental observations. The convergence of information from experiments and calculations on models in this work allows us to comment on a number of proposed cellulose structures.

Table 1
Crystal data and structure refinement for α-cellobiose·2 NaI·2 H_2O complex

Empirical formula	$C_{12}H_{26}I_2Na_2O_{13}$
Formula weight	678.11
Temperature (K)	150(2)
Wavelength (Å)	0.71073
Crystal system, space group	monoclinic, $P2_1$
Unit cell dimensions	
a (Å)	9.0188(4)
b (Å)	12.2536(6)
c (Å)	10.9016(5)
α (°)	90
β (°)	97.162(1)
γ (°)	90
V (Å^3)	1195.37(10)
Z, D_{Calcd} (Mg/m^3)	2, 1.884
Absorption coefficient (mm^{-1})	2.722
$F(000)$	660
Crystal size (mm)	$0.2 \times 0.2 \times 0.5$
θ Range for data collection (°)	1.88–34.75
Limiting indices	$-14 \le h \le 14$, $-19 \le k \le 19$, $-17 \le l \le 17$
Reflections collected/unique	19869/9474 [$R_{int} = 0.0265$]
Completeness to $\theta = 34.75$ (%)	94.8
Absorption correction	empirical
Max and min transmission	1.000000 and 0.719225
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	9474/58/355
Goodness-of-fit on F^2	0.818
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0272$, $wR_2 = 0.0460$
R indices (all data)	$R_1 = 0.0461$, $wR_2 = 0.0476$
Absolute structure parameter	0.004(11)
Largest difference peak and hole (e/Å^3)	0.939 and −0.695

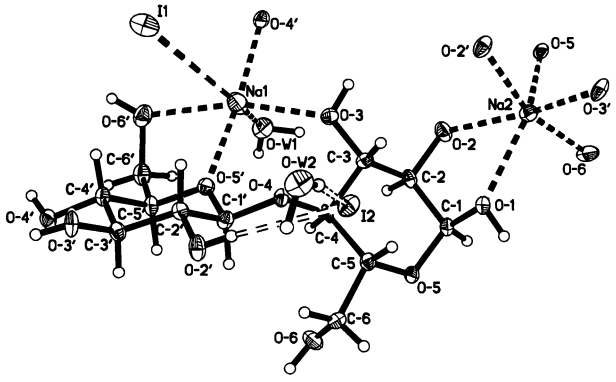

Fig. 1. ORTEP plot for the asymmetric unit of the α-cellobiose·2 NaI·2 H_2O complex. The heavy atoms are shown at 50% probability. Atoms from adjacent asymmetric units that complete the coordination around the Na^+ ions are also shown. Interactions with the Na^+ are shown as dashed and filled lines, and two hydrogen bonds (from O-2′ and from O-W2) to the I-2 ion are shown as unfilled dashed lines.

2. Results and discussion

Table 1 gives the details of the determination. The atoms of the asymmetric unit are shown in Fig. 1, with the non-hydrogen atoms represented as 50% probability thermal ellipsoids. Three projections of the crystal packing are given in Fig. 2. The cellobiose molecules take a zig–zag pattern in the c-axis projection, with parallel channels that contain water and ions. In the b-axis projection, the water molecules are in a channel that is centered in the unit cell, with the cellobiose molecules forming the borders of the channel. The projection along the a-axis shows the separation of the cellobiose molecules.

Both glucose rings have the usual $^4C_1$ shapes. Cremer–Pople puckering[14] amplitudes are 0.601 and 0.606 Å for the α- (reducing) and β- (nonreducing) pyranosyl rings, respectively, within the range of usual values. The θ puckering parameters of 6.5 and 0.5° are also normal, with the β-ring approaching the status of 'perfect' chair. Bond lengths are ordinary. C–O bond lengths involving the ring and glycosidic oxygen atoms are given in Table 2. The glycosidic C-1–O-1 bond of the α-ring is seven σ longer than its counterpart C-1′–O-4 bond, confirming experimental and theoretical observations of the anomeric effect.[15] The C-5′–C-6′ bond, at 1.499(4) Å, is slightly shorter than the other C–C bonds. To learn whether there is an intrinsic reason for this, an energy minimization with B3LYP/6-31G* quantum mechanics was performed with all torsion angles restrained to their crystallographic values. The calculated C-5′–C-6′ distance was 0.028 Å larger than observed; the biggest discrepancy, suggesting that the shortness is unexpected.

Linkage conformation.—Fig. 3 shows the distribution in ϕ, ψ space of the conformations of various β-(1→4)-linked compounds that are listed in Table 3. The contours in Fig. 3 are for a computed potential energy surface (see Section 4). The labels for the points are 'refcodes' from the Cambridge Structural Database (CSD).[16]

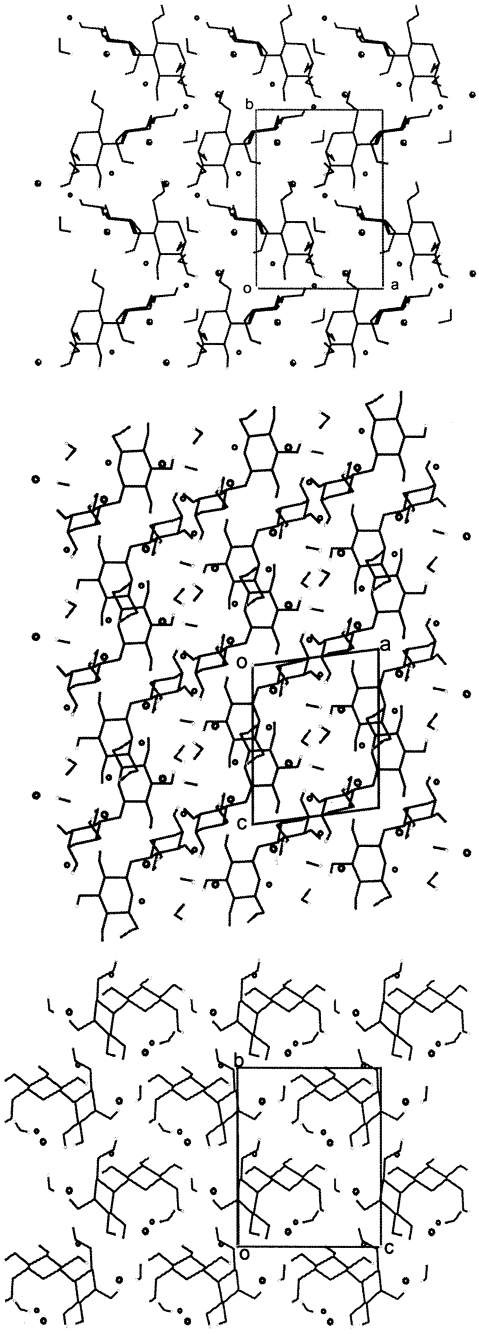

Fig. 2. Crystal packing in α-cellobiose·2 NaI·2 H_2O complex. Top: Projection along the *c*-axis. Center: projection along the *b*-axis. Bottom: Projection along the *a*-axis. Methine hydrogen atoms are not shown. The larger spheres are I^- and the smaller ones are Na^+.

Table 2
C–O bond lengths and their standard deviations that involve the ring oxygen and glycosidic and aglycon carbon atoms

α-Configured ring		β-Configured ring	
C-1–O-1	1.419(4)	C-1′–O-4	1.390(3)
C-1–O-5	1.423(3)	C-1′–O-5′	1.440(3)
O-5–C-5	1.452(3)	O-5′–C-5′	1.438(3)
C-4–O-4	1.441(3)		

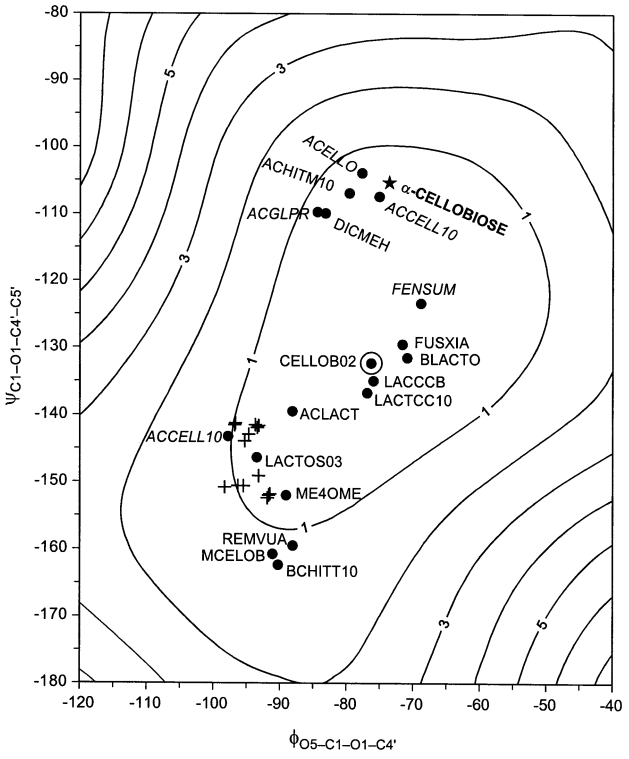

Fig. 3. A potential energy surface calculated for β-cellobiose. The contours are labeled in kcal/mol and the conformations for the observed crystal structures are noted with various symbols. ★ represents the conformation in α-cellobiose·2 NaI·2 H_2O complex. The + signs indicate conformations found in the crystal structures of methyl cellotrioside and cellotetraose, and the circled dot ⊙ denotes the conformation of β-cellobiose. See Table 3 for conversions of the REFCODES to chemical names. REFCODES in *italic* indicate structures whose hydroxyl groups are completely substituted with larger groups. ME4OME is not an official REFCODE.

Linkage torsion angles for α-cellobiose, $\phi_{O\text{-}5}$ and $\psi_{C\text{-}5}$, are -73.6 and $-105.3°$, respectively ($\phi_H = 47.1°$ and $\psi_H = 14.6°$). That linkage geometry is in an apparent cluster that includes the linkages of *N*,*N*′-diacetyl-α-chitobiose monohydrate (ACHITM10)[17] and 4-*O*-β-D-galactopyranosyl-α-D-mannopyranose ethanol solvate (DICMEH).[18] Similar geometries are also found for the linkage closer to the 'reducing' end of peracetylated β-cellotriose (ACCELL10)[19] and for the linkages in peracetylated β-cellobiose (ACELLO)[20] and 6-trityl cellobiose heptaacetate (ACGLPR).[21]

Table 3
Torsion angles in the interresidue linkages, and O-3···O-5′ and O-3···O-6′ distances for α-cellobiose and some related molecules (arranged in increasingly negative values of $\psi_{C\text{-}5}$)

Compound	Reference	REFCODE	$\phi_{O\text{-}5}$ (°)	$\psi_{C\text{-}5}$ (°)	O-3···O-5′ distance (Å)	Possibility of H-bond	O-6′ configuration	O-3···O-6′ (Å)	H···O-6′ (Å)	O-6 configuration
Cellobiose octaacetate	20	ACELLO	−77.7	−103.9	3.32	no	−70.9 gg			40.9 gt
α-Cellobiose·2 NaI·2 H_2O			−73.6	−105.3	3.31	yes	−59.5 gg	4.60		−57.0 gg
α-*N*,*N*′-Diacetylchitobiosamine	17	ACHITM10	−79.6	−106.9	3.31	yes	−65.5 gg	4.83		−74.6 gg
Cellotriose undecaacetate ('nonreducing')	19	ACCELL10	−75.1	−107.4	3.27	no	−64.4 gg			59.6 gt
6′-*O*-Trityl-α-cellobiose heptaacetate	21	ACGLPR	−84.4	−109.7	3.34	no	46.3 gt			
4-*O*-β-D-Galactosyl-α-D-mannose	23	DICMEH	−83.2	−109.9	3.24	yes	73.8 gt	5.26		−74.0 gg
Methyl hepta-*O*-nitro-β-cellobioside	49	FENSUM	−68.8	−123.4	2.89	no	62.3 gt			−76.8 gg
Methyl 6,6′-dinitro-β-cellobioside	24	FUSXIA	−71.6	−129.5	2.68	yes	64.3 gt	3.26	3.57 [d]	64.9 gt
β-Lactose	25	BLACTO	−70.9	−131.5	2.71	yes	50.5 gt	3.30	2.76	72.6 gt
β-Cellobiose	4	CELLOB02	−76.3	−132.3	2.77	yes	48.7 gt	3.10	2.64	70.5 gt
Lactose $CaBr_2$·7 H_2O	35	LACCCB	−76.0	−134.9	2.76	yes	62.4 gt	3.41	2.88	61.9 gt
Lactose $CaCl_2$·7 H_2O	36	LACTCC10	−76.9	−136.7	2.75	yes	59.8 gt	3.37	2.89	63.8 gt
N-Acetyl lactosamine·H_2O	29	ACLACT	−88.1	−139.5	2.79	yes	66.8 gt	3.26	2.67	−56.0 gg
Cellotriose acetate ('reducing')	19	ACELL10	−97.8	−143.2	3.03	no	−52.2 gg			−64.4 gg
α-Lactose	41	LACTOS03	−93.5	−146.3	2.81	yes	58.3 gt	3.33	2.71	63.4 gt
Methyl cellotrioside (average of 8)	7	TAQYAL	−94.4	−146.4	2.864	yes	61.9 gt	3.30	[c]	60.1 gt
Cellotetraose (average of 6)	8	ZILTUJ	−94.4	−146.8	2.875	yes	63.1 gt	3.34	[c]	59.7 gt
Methyl 4-*O*-methyl-β-D-glucosyl-β-D-glucose	23	ME4OME [a]	−89.1	−152.0	2.81	yes	59.0 gt	3.16	2.51	−54.3 gg
Lactosylurea·2 H_2O	27	REMVUA	−88.1	−159.5	2.74	yes	57.0 gt	3.01	2.38	−56.0 gg
Methyl β-cellobioside MeOH	22	MCELOB	−91.1 [b]	−160.7 [b]	2.76	yes	52.4 gt	2.91	2.25	−55.1 gg
N,*N*′-Diacetyl-β-chitobiose·3 H_2O	28	BCHITT10	−90.3	−162.3	2.80	yes	58.5 gt	2.88	2.28	−60.6 gg

The O-5–C-5–C-6–O-6 torsion angles are also given.
[a] ME4OME is not an official REFCODE.
[b] Converted from the inadvertently reported L enantiomer.
[c] Hydrogen positions were not well determined in these structures.
[d] See text for a discussion of possible incorrect hydrogen atom position.

The ϕ torsion angle in α-cellobiose is very similar to that found in β-cellobiose (CELLOB02),[4] while ψ differs by 28°. Both ϕ and ψ angles for methyl cellobioside in the methanol adduct (MCELOB)[22] differ considerably from those in α-cellobiose by 18 and 55°, respectively. Methyl 4-*O*-methyl-β-cellobioside[23] (ME4OME) also differs by 16 and 47°, respectively. The 29° range of observed ϕ values in Table 3 is half of the 58° range of ψ values, presumably because the exo-anomeric effect[15] deepens the energy well for ϕ.

The missing O-3–H···O-5′ hydrogen bond.—The O-3–H···O-5′ hydrogen bond that is found for most β-(1→4)-linked moieties is not found in any of the structures clustered in Fig. 3 with α-cellobiose. (Three of those structures have no hydroxyl groups for forming hydrogen bonds.) All structures near α-cellobiose have O-3···O-5′ distances (Table 3) that are too long to be high-quality hydrogen bonds. Even when the O-3–H atoms are present and bonding is chemically feasible, they are not oriented in such a way that they could donate to O-5′. In α-cellobiose, that hydrogen bond is replaced by a bridge involving Na^+-1 (Figs. 1 and 4). Na^+-1 also interacts with O-6′ of the same molecule. In ACHITM10,[17] O-3 is a donor and an acceptor for hydrogen bonds with other *N*,*N*′-diacetyl-α-chitobiose molecules. In DICMEH,[23] O-3 donates its proton to another disaccharide and accepts one from water of hydration. Except for the structures in the cluster with α-cellobiose, all chemically able molecules do form O-3–H···O-5′ hydrogen bonds. (The FUSXIA[24] paper mentions this hydrogen bond but its possibly erroneous H-3 coordinates do not support it. The O-3···O-5′ and···O-6′ distances of FUSXIA are very similar to its hydrogen-bonded neighbor in ϕ, ψ space, BLACTO.[25])

O-6 conformations.—Table 3 also lists the conformations of both O-6 groups. The α-cellobiose and ACHITM10[17] structures have O-6′ in gg positions, whereas all of their hydroxylated counterparts on the rest of the surface have O-6′ in the gt conformation. In DICMEH,[23] O-6′ is gt, possibly because the gg position is 'forbidden' for galactose residues.[26] The dispositions of the O-6 hydroxyl groups on the reducing residues are also listed in Table 3. Those groups in the cluster with α-cellobiose are all gg, as are those in the ME4OME,[23] REMVUA,[27] MCELOB,[22] and BCHITT10[28] subgroup. With the exception of ACLACT,[29] the rest are gt. It is thought that the O-6 groups in native cellulose I have tg conformations.[30]

The gt conformation of O-6′, when coupled with suitable ϕ and ψ values, can lead to a hydrogen bond between O-3–H and O-6′. It is usually the minor component of a three-centered hydrogen bond also involving O-5′. Values of the O-3···O-6′ distance are also in Table 3. REMVUA, MCELOB and BCHITT10, at the bottom of Fig. 3, have the shortest O-3–H···O-6′ distances. Because all structures that have the O-3···O-5′ hydrogen bond also have O-6′ in the gt conformation, even the long O-3–H···O-6′ interactions may be stabilizing the gt orientations.

Other non-bonded interactions.—Fig. 4 shows the complexation around each of the ions and the water molecules, and the geometries are listed in Table 4. Besides the lack of the O-3···O-5′ hydrogen bond in this α-cellobiose structure, there is no direct hydrogen bonding among the carbohydrate molecules. The only other example with no inter-carbohydrate hydrogen bonding that we found is the hydrated $CaBr_2$ complex of α-galactose (CAGALA10).[31] In many carbohydrate structures, the hydroxyl groups participate in long, donor–acceptor chains.[32] In α-cellobiose, the I^- are chain terminators. They accept six hydroxyl hydrogens from the cellobiose and three others from the water molecules.

Intramolecular hydrogen bonds (Fig. 4, upper left) include O-3′–H···O-4′, O-2′–H···O-4, and O-3–H···O-2, all of which are routinely found in gas-phase computer models of carbohydrates. They can have only modest stabilizing ability because of their long (2.50–2.61 Å) H···O distances and small (95–107°) O–H···O angles. All of these hydroxyls also donate to I^- or water.

The 12 O···Na^+ distances have a narrow range (2.27–2.50 Å). Besides replacing the O-3–H···O-5′ and O-3–H···O-6′ hydrogen bonds, Na^+-1 interacts with O-4′ on a neighboring cellobiose, a water and I^--1. Retention of the α configuration may be explained by the complexation of Na^+-2 with O-1 and its adjacent O-2. Na^+-2 also interacts with O-2′ and O-3′ on one neighboring cellobiose, and O-5 and O-6 on a third.

Interactions with I^- include eight apparent C–H···I^- hydrogen bonds. Otherwise the coordination of those ions is meager, especially to I^--1. A search of the CSD found 14,869 C–H···I^- distances of less than 3.70 Å in 1525 crystal structures. The distribution peaked between 3.3 and 3.4 Å so our distances of 3.09–3.43 Å are fairly short. A somewhat similar situation was found with the NaI sucrose complex,[33] where seven interactions with C–H, ranging from 3.18 to 3.77 Å, completed the coordination of the iodides. C–H···I bonding to neutral iodine was recently confirmed,[34] and classification of the present interactions with I^- as hydrogen bonds seems appropriate.

Other salt complexes of β-(1→4)-linked disaccharides, e.g., heptahydrated β-lactose complexed with $CaBr_2$ (LACCCB)[35] and $CaCl_2$ (LACTCC10),[36] have conformations that are nearly identical to CELLOB02[4] (Fig. 3). Unlike the NaI complex of α-cellobiose, these structures have O-3–H···O-5′ hydrogen bonds, perhaps because there is only one cation per disaccharide. In crystalline NaI–sucrose,[33] some inter-sucrose hydrogen bonding exists. Again, with two sucrose molecules for every three Na^+ and I^- ions, there is a higher ratio of sucrose to ions than in the α-cellobiose complex. The

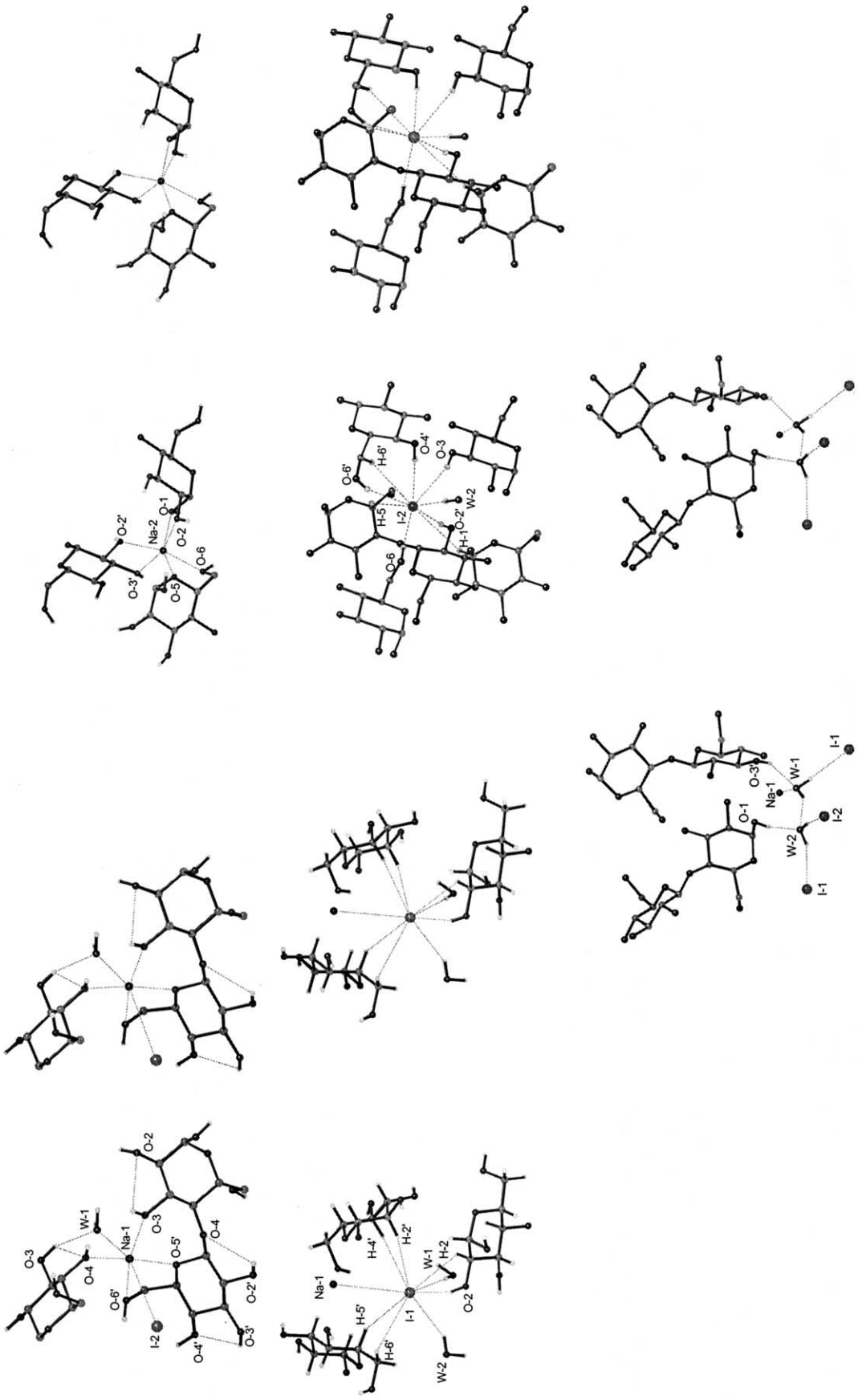

Fig. 4. Interactions of the carbohydrate and guest molecules, drawn as stereo pairs. Upper left: atoms surrounding Na^+-1 and the intramolecular hydrogen bonds, which are of low quality. Also shown is a hydrogen bond from O-3–H to W-1. Upper right: atoms surrounding Na^+-2. Center left: atoms surrounding I^--1. Center right: atoms surrounding I^--2. Lower center: the atoms interacting with the water molecules.

three Na^+ ions are coordinated by 8, 7, and 7 oxygen atoms, and the I^- ions are coordinated with 5, 5 and 6 O–H groups besides the above-mentioned C–H groups.

Relationship to the energy surface.—The observed ϕ and ψ values for α-cellobiose are within the 1 kcal/mol contour (0.57 kcal/mol) around the global minimum in Fig. 3. The small (114.3°) experimental glycosidic bond angle also suggests that there is minimal strain between the residues in the α-cellobiose conformation. CELLOB02[4] is nearer to the global minimum (0.15 kcal/mol). Only five of the 33 points are outside the 1 kcal/mol contour, and the highest corresponding energy, for BCHITT10,[28] is 1.18 kcal/mol. The average energy of all the points in Table 3 on the hybrid surface in Fig. 3 is 0.62 kcal/mol. The conformations for methyl cellotrioside and cellotetraose were averaged in Table 3 in consideration of proposed crystal field effects (see below). Treating the TAQYAL[7] and ZILTUJ[8] linkages as 14 independent values raises the average to 0.73 kcal/mol.

We considered other energy surfaces, including non-hybrid MM3 surfaces that were calculated for β-cellobiose with dielectric constants (ϵ) of 1.5 and 7.5.[37] The $\epsilon = 1.5$ MM3 surface ascribes 2.5–4.0 kcal/mol to the structures in the cluster with α-cellobiose, mostly because they lack the O-3–H···O-5′ hydrogen bond that lowers the energy of the other structures. This surface is less predictive for crystalline cellobiose conformations than in Fig. 2 because of the distribution of structures on the surface.[38] The structures in the cluster with

Table 4
Details of the coordinations

Na-1···O-4′ # 1	2.275(3)	Na-2···O-3′	2.357(2)	
Na-1···O-3	2.293(3)	Na-2···O-2′	2.377(2)	
Na-1···O-5′	2.325(3)	Na-2···O-1 # 3	2.492(2)	
Na-1···O-6′	2.345(3)	Na-2···O-2 # 3	2.306(2)	
Na-1···O-W1	2.499(3)	Na-2···O-5 # 4	2.460(2)	
Na-1···I-1	3.895(2)	Na-2···O-6 # 4	2.390(2)	
D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	<(DHA)
O-2–H-2A···I-1	0.84(3)	2.64(3)	3.441(2)	160(4)
O-W1–H-W1A···I-1	0.92(2)	2.74(3)	3.621(3)	161(3)
O-W2–H-W2A···I-1 # 3	0.85(3)	2.77(4)	3.534(3)	149(5)
O-W2–H-W2B···I-2	0.87(3)	2.63(3)	3.477(2)	167(6)
O-2′–H-2′A···I-2	0.81(2)	2.81(2)	3.613(2)	171(3)
O-3–H-3A···I-2 # 2	0.87(3)	3.01(3)	3.841(2)	161(4)
O-6-H-6A···I-2 # 3	0.83(2)	2.72(2)	3.548(2)	171(3)
O-4′–H-4′A···I-2 # 7	0.84(4)	2.64(4)	3.474(2)	176(3)
O-6′–H-6′A···I-2 # 7	0.85(3)	3.07(4)	3.701(2)	133(4)
C-2–H-2···I-1	1.00(3)	3.14(3)	3.784(3)	124(2)
C-2′–H-2′···I-1 # 4	1.03(3)	3.25(3)	4.190(3)	152(2)
C-4′–H-4′···I-1 # 4	0.99(3)	3.25(3)	4.135(3)	150(2)
C-5′–H-5′···I-1 # 10	1.07(3)	3.09(3)	3.882(3)	131(2)
C-6′–H-6′···I-1 # 10	0.90(3)	3.43(3)	3.738(4)	103(2)
C-1–H-1···I-2 # 9	0.95(3)	3.39(3)	4.167(3)	141(2)
C-5–H-5···I-2	1.04(2)	3.25(2)	4.038(3)	133(2)
C-6′–H-6′···I-2 # 7	0.90(3)	3.18(3)	3.844(3)	132(2)
O-3–-H-3A···O-2	0.87(3)	2.60(4)	2.818(3)	95(3)
O-2′–-H-2′A···O-4	0.81(2)	2.59(3)	2.843(3)	100(3)
O-3′–-H-3′A···O-4′	0.86(3)	2.49(4)	2.864(3)	107(3)
O-1–H-1A···O-W2 # 5	0.86(2)	1.94(2)	2.775(3)	164(3)
O-3′–H-3′A···O-W1 # 6	0.87(3)	2.12(3)	2.901(3)	149(3)
O-W1–H-W1B···O-W2 # 8	0.89(3)	2.07(5)	2.825(4)	142(6)

Symmetry transformations used to generate equivalent atoms: # 1, $-x$, $y-1/2$, $-z-1$; # 2, $-x$, $y-1/2$, $-z$; # 3, $-x$, $y+1/2$, $-z$; # 4, $x+1$, y, z; # 5, $x-1$, y, z; # 6, $-x$, $y+1/2$, $-z-1$; # 7, x, y, $z-1$; # 8, $x-1$, y, $z-1$; # 9, $x-1$, y, z; # 10, $-x-1$, $y+1/2$, $-z-1$.

α-cellobiose are the only ones over 2 kcal/mol, and there is a substantial area of unoccupied ϕ, ψ space with comparable energies.

On the MM3-only map with $\epsilon = 7.5$, the 1 kcal/mol contour surrounds all of the structures and their average energy would be only 0.29 kcal/mol, increased to 0.31 kcal with separate consideration of each TAQYAL and ZILTUJ linkage. Choosing between the MM3 $\epsilon = 7.5$ map and the hybrid map with its higher energy was difficult. Ultimately, the hybrid map was preferred because of that method's success for sucrose,[39] where MM3 alone was not satisfactory. Also, Fig. 3 is very similar to our earlier hybrid map that accounted well for most linkage conformations from cellodextrins and lactose molecules that are guests in crystalline proteins.[40] Fig. 3's average energy of 0.62 kcal/mol is closer to the average hybrid energy for several disaccharides[38] and to *RT*, the ideal gas constant times the room temperature. The value of *RT*, 0.59 kcal/mol at 300 K, is the expected average deformation energy for molecules in an ideal gas. By that criterion, the value of 0.3 kcal/mol for the MM3-only surface suggests that it is too flat.

Despite its 20° increments of ϕ and ψ and neglect of explicit environmental effects and entropy in the calculations, Fig. 3 appears to be accurate enough to be used for some general predictions about cellulose (next paragraph). However, the surface does not show individual wells for the cluster around α-cellobiose and the cluster that includes the structures near LACTOS03.[41] There is enough chemical heterogeneity in these clusters that the packing forces invoked below seem unlikely to account for all of the preference for these regions. For this reason, even better energy calculations may be useful. More crystal structures would also help decide if the clusters are real or if they result from the limited number of samples.

Implications for cellulose.—The known crystal forms of pure cellulose have two residues per turn. Small molecule analogs for that shape of cellulose include ME4OME,[23] TAQYAL,[7] and ZILTUJ.[8] They have pseudo twofold screw symmetry and efficient packing. The flat shapes, molecular pseudosymmetry, and tight clustering of the cellotrioside and cellotetraose conformations may result from this packing.[42] Construction of a cellulose chain by propagating the geometry of the nonreducing residue of our α-cellobiose structure, its observed glycosidic angle and its ϕ and ψ values, gives a left-handed helix with about 2.9 residues per turn. Thus, this structure, along with some of the other crystal structures and the energy surface can clarify the structures of some existing cellulose complexes and derivatives with 2.5 and 3.0 residues per turn. The rise per residue for these structures is similar to that for the twofold structures, about 5 Å.

Soda cellulose II,[43] β-(1→4)-xylan hydrate,[44] cellulose tripropionate,[45,46] and 6-*O*-acetyl-2,3-*O*-dipropionyl[47] cellulose are among the crystalline cellulose derivatives or analogs with three residues per turn. While this number of residues per turn is reliably indicated by their fiber-diffraction patterns, the details of the structures come from modeling studies. Left-handed conformations are proposed for the first three. Soda cellulose II is of special interest here because it is a complex of cellulose with Na^+ ions, possibly similar to the complex of cellobiose with NaI. The ϕ and ψ values proposed for soda cellulose II,[43] −90.3 and −81.9° (after conversion to our definitions), correspond to more than 3 kcal/mol in Fig. 3. That high energy, we think, is a consequence of the early modeling. Small adjustments to the linkage and monomeric geometries of our extrapolated model above would permit an exact threefold helix with a lower energy and would not destroy the ability to complex Na^+ with the O-3, O-5′ and O-6′ atoms. The ϕ and ψ values for the proposed xylan structure,[44] −58.3 and −114.2°, are within the 1 kcal/mol contour in Fig. 3, not so far from NaI cellobiose. The proposed tripropionate conformation[45,46] has ϕ and ψ values of −50.4 and −127.8°, again near the 1 kcal/mol contour in Fig. 3.

The proposed acetyl dipropionyl[47] helix was based on a finding that the global minimum on an MM2 surface corresponded to a right-handed structure, with ϕ and ψ values of −99.6 and 58.5°. Those values correspond to a collapsed helical form, not the extended form found by fiber diffraction. Those authors kept the right-handed result when building the extended helix model, with ϕ and ψ values of −142.7 and −178.3°. That conformation corresponds to more than 5 kcal/mol on the full version (not shown) of Fig. 3. A left-handed structure, such as proposed for the cellulose triproprionate or xylan hydrate is more likely. This is particularly so because of the proximity of left-handed models to three acetylated structures (ACELLO, ACCELL10 and ACGLPR.)

Trinitrocellulose,[48] with 2.5 residues per turn was also proposed to be right-handed. We constructed models based on their published glucose residue geometry and obtained ϕ and ψ values of −106.6 and −177.5°. This point falls near the 3 kcal/mol contour in Fig. 2. Using the same monomeric coordinates and 116.5° glycosidic bond angle, we also built a left-handed helix, with ϕ and ψ values of −66.7 and −132.0°, very close to the FUSXIA (6,6′-dinitrocellobiose) and FENSUM (methyl hepta-*O*-nitrocellobioside)[49] conformations. Based on this analogy to the nitrated cellobiose crystal structures and the lower potential energy for the linkage, it seems that a left-handed helix is more probable for nitrocellulose.

3. Conclusions

In this work, the structure of α-cellobiose·2 NaI·2 H_2O was determined and compared with a number of

related structures and with a hybrid energy surface. Based on this information, we speculated on the chirality of some cellulosic structures that had been studied previously by fiber diffraction.

Unlike almost all carbohydrate crystal structures, there was no direct intermolecular hydrogen bonding among the α-cellobiose molecules, and unlike most analogs of cellobiose, there was also no interresidue hydrogen bonding. Instead, the hydroxyl groups interact with the ions and complexed water. One of the main findings of this work was the interaction of one Na^+ with O-3, O-5′, and O-6′ to replace the usual interresidue hydrogen bond. By accepting nine water and hydroxyl protons, the iodides act as 'chain terminators' and the usual long chains of hydrogen bonds do not even get started. Despite these O–H···I^- hydrogen bonds and one Na^+, the coordination spheres of the I^- were completed by a total of eight C–H···I^- hydrogen bonds. Similar bonds were proposed previously for NaI sucrose.

Our structure has a linkage conformation similar to those for two molecules that do not, and three that cannot, form the usual inter ring O-3–H···O-5′ hydrogen bond. Those conformations are clustered in a part of ϕ, ψ space that is separate from the other small-molecule structures. We also found a substantial correlation of the orientations of O-6 groups with the position in ϕ, ψ space. In the structures that do have the O-3···O-5′ hydrogen bond, O-6′ invariably took the gt conformation. This could be accounted for by O-3 donating its proton, not only to O-5′, but also to O-6′ even when the distance is longer than usually thought appropriate for hydrogen bonding. No reason was found for O-6 groups on the reducing-residue to have gg orientations at the upper and lower ends of the range of two values, and mostly gt orientations in the middle.

The isolated-molecule, potential-energy calculations were able to rationalize the observed crystal structures to a substantial extent. The observations corresponded to an average of 0.62 kcal/mol on our hybrid surface, with a maximum of 1.18 kcal/mol. Fiber diffraction studies had proposed 2.5-and threefold structures for two cellulose derivatives and a complex that had energies of 3–5 kcal/mol on this same surface. The NaI cellobiose structure from the present work extrapolated to a left-handed helix with 2.9 residues per turn and was considered to be a good analog for the threefold soda cellulose II structure. Similar analogs were found for nitrocellulose and 6-*O*-acetyl dipropionyl cellulose, and corresponding energies for the new conformations were less than 1 kcal/mol.

4. Experimental

The sample preparation was the same as previously described,[6] with the exception of additional filtering of the reaction mixture before allowing it to stand undisturbed for 3 weeks. The sample was stored in a stoppered test tube inside a desiccator for 30 years, during which time it apparently gained two water molecules of hydration as it was originally nearly anhydrous (0.7% water). Perhaps this happened when the desiccator and test tube were opened over the years. Subsequent analyses show that the dihydrate can form at 30% rh. At 25% rh and 24 °C, the moisture content was 6.2% (the dihydrate would be 5.3%) and after 24 h at 15%, the moisture had dropped to 5.7%. The crystal was colorless.

A single crystal suitable for data collection was isolated from the sample and mounted on a Bruker SMART single crystal diffractometer with a 1K CCD detector. The crystal was cooled to 150(2) K in a stream of cold nitrogen gas and X-ray data were collected using Mo K_α radiation. The structure was solved by direct methods and optimized by full-matrix least-squares refinement of F^2 including all observations. Two slack restraints were imposed on the least-squares refinement to improve the refinement of the hydrogen atom positions. All O–H bond distances were restrained to be equal within a standard deviation of 0.04, and the H···H distances within the two water molecules were restrained to a distance corresponding to a 105° H–O–H bond angle within a standard deviation of 5°. Other details of the data collection and refinement are included in Table 1. Final atomic coordinates are given in Tables 5 and 6.

Details of the construction of the hybrid energy surfaces are in Ref. 38. Briefly, the map was made by subtracting the MM3 energy for an analog of cellobiose based on linked tetrahydropyran molecules from the MM3 energy for β-cellobiose at each ϕ, ψ point. A value of $\epsilon = 3.5$ was used in the MM3 disaccharide calculations, causing the hydrogen bonding strength to be 45% of its vacuum-phase value. The B3LYP/6-311 + + G**//B3LYP/6-31G* energy for the analog was then added. This essentially gives the torsional energies from quantum mechanics and the non-bonded energies from molecular mechanics. The full surface is similar to one presented in Ref. 40 that used less complete HF/6-31G* theory for the analog calculations. Also, the new torsional definitions were based on the O-5′ and C-5 atoms, instead of the C-1′–H and C-4–H atoms. Energies were calculated at increments of 20°.

The structures plotted in Fig. 3 were selected based on the degree of analogy to cellobiose. Omitted were deoxy molecules, as well as molecules that had alternate configurations for ring atoms near the linkage such as the mannose dimer and trimer. Still, these omitted structures had conformations that were quite similar to the ones that were included. Another cellobiose derivative, RIKMON (*O*-(2,3,6-tri-*O*-benzoyl-4-deoxy-4-*C*-ethynyl-β-D-glucopyranosyl)-(1 → 6)-4,5,8-tri-*O*-acetyl-

Table 5
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$)

	x	y	z	U_{eq}
C-1	−4481(3)	7611(3)	36(3)	14(1)
O-1	−3831(2)	7122(2)	1156(2)	18(1)
C-2	−4144(3)	6886(2)	−1012(3)	14(1)
O-2	−4634(2)	5797(2)	−833(2)	20(1)
C-3	−2477(3)	6888(3)	−1125(3)	15(1)
O-3	−2197(3)	6214(2)	−2150(2)	22(1)
C-4	−2023(3)	8052(3)	−1343(2)	13(1)
O-4	−450(2)	8075(2)	−1461(2)	13(1)
C-5	−2336(3)	8729(2)	−218(3)	14(1)
O-5	−3926(2)	8682(2)	−122(2)	14(1)
C-6	−1959(4)	9930(3)	−283(3)	18(1)
O-6	−2841(2)	10386(2)	−1347(2)	23(1)
C-1′	−74(3)	8735(3)	−2413(3)	14(1)
C-2′	1621(3)	8866(2)	−2260(3)	13(1)
O-2′	2113(2)	9447(2)	−1160(2)	19(1)
C-3′	2048(3)	9521(3)	−3347(3)	15(1)
O-3′	3628(2)	9655(2)	−3201(2)	19(1)
C-4′	1461(3)	8939(3)	−4547(3)	14(1)
O-4′	1801(2)	9611(2)	−5547(2)	18(1)
C-5′	−228(3)	8798(3)	−4615(3)	15(1)
O-5′	−549(2)	8179(2)	−3559(2)	15(1)
C-6′	−932(3)	8202(3)	−5741(3)	21(1)
O-6′	−420(3)	7104(2)	−5793(2)	25(1)
O-W1	−3918(3)	6495(2)	−5171(2)	32(1)
O-W2	5342(3)	8243(2)	3176(2)	26(1)
Na-1	−1338(2)	6406(1)	−4032(1)	32(1)
Na-2	4563(1)	10162(1)	−1165(1)	16(1)
I-1	−7057(1)	5836(1)	−3534(1)	28(1)
I-2	1683(1)	8118(1)	1733(1)	19(1)

Table 6
Hydrogen coordinates ($\times 10^3$) and isotropic displacement parameters ($Å^2 \times 10^3$) [a]

	x	y	z	U_{eq}
H-1B	−553(4)	771(3)	−3(3)	17
H-1A	−412(3)	757(2)	168(3)	20(9)
H-2B	−463(3)	716(2)	−183(3)	8(7)
H-2A	−531(4)	565(4)	−141(3)	58(14)
H-3B	−190(4)	656(3)	−46(3)	18
H-3A	−231(5)	552(2)	−200(4)	53(14)
H-4	−266(3)	835(2)	−213(3)	15
H-5	−181(3)	840(2)	60(2)	1(7)
H-6C	−217(3)	1024(2)	39(3)	8(7)
H-6B	−80(3)	997(2)	−31(3)	9
H-6A	−258(3)	1101(2)	−152(3)	9(8)
H-1′	−59(4)	948(3)	−239(3)	17
H-2′A	195(4)	910(3)	−56(3)	26(10)
H-2′B	207(3)	809(3)	−223(2)	16
H-3′A	384(4)	1000(3)	−385(3)	38(11)
H-3′B	161(3)	1021(3)	−337(3)	13(8)
H-4′B	200(3)	824(3)	−461(2)	12(8)
H-4′A	181(4)	926(3)	−621(4)	39(12)
H-5′	−78(3)	956(2)	−456(3)	0(7)
H-6′A	34(4)	697(4)	−616(4)	64(16)
H-6′C	−192(3)	803(3)	−572(2)	13(7)
H-6′B	−71(3)	857(2)	−641(3)	9(8)
H-W1A	−455(4)	636(3)	−459(3)	44(12)
H-W1B	−456(6)	696(5)	−557(6)	170(30)
H-W2A	538(7)	894(2)	322(6)	120(20)
H-W2B	441(4)	813(6)	291(5)	170(30)

[a] Water molecule excepted, A designates hydroxyl hydrogen atoms; B designates methine hydrogens; C designates the second methine hydrogen atoms on C-6 and C-6′.

3,7-anhydro-1,1,2,2-tetradehydro-1,2-dideoxy-1-*C*-(trimethylsilyl)-D-*glycero*-D-*gulo*-octitol disaccharide), has a ψ value of about $-300°$.[50] Its conformation falls in a secondary minimum just under 3 kcal/mol on the full range energy surfaces (not shown).

5. Supplementary material

The data were deposited at the Cambridge Structural database (Accession number CCDC 179392). Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

6. Note added in proof

The molecular conformation of methyl-β-lactoside in its methanol solvate crystal structure (Stenutz, R.; Shang, M.; Serianni, A. S. *Acta Crystallogr. Sect. C*, **1999**, *55*, 1719–1721) is very similar to those in REMVUA,[27] MCELOB[22] and BCHITT 10.[28] This includes the O-6 and O-6′ orientations.

B. Philipp, J. Kunze and A. Brant (*J. Appl. Polym. Sci., Appl. Polym. Symp.* **1983**, *37*, 393–405) showed that the solid state NMR peaks for C-2 and C-3 of cellulose were affected more by the presence of Na^+ ions than was the signal for C-6. This confirmed earlier findings by S.P. Rowland, *Cell. Chem. Technol.*, **1980**, *14*, 423–439. Those findings were based on cellulose derivatization in an alkaline medium.

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