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THE CRYSTAL STRUCTURES OF OCTYL α-D-GLUCOPYRANOSIDE MONOHYDRATE AND HEMIHYDRATE: MESOGENIC STRUCTURES WITH INTERDIGITIZING ALKYL CHAINS*

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ABSTRACT

The crystal structure of octyl α-D-glucopyranoside monohydrate, $C_{14}H_{28}O_6 \cdot H_2O$, is monoclinic, *C*2, with $Z = 4$, $a = 17.896(2)$, $b = 5.154(1)$, $c = 18.303(2)$ Å, $\beta = 90.30(1)°$. The hemihydrate, $C_{14}H_{28}O_6 \cdot 0.5\ H_2O$, is also monoclinic, *C*2, with $Z = 4$, $a = 15.190(5)$, $b = 5.136(3)$, $c = 19.944(7)$, $\beta = 92.74(3)°$. The crystal structures were solved using SHELXTL and refined to *R* values of 0.037 and 0.052 for 1224 and 1231 observed structure amplitudes, respectively. The crystal structures have bilayer head-to-head molecular packing with interdigitizing alkyl chains similar to those observed in other long-chain alkyl pyranosides. The carbohydrate moieties are hydrogen-bonded in infinite chains which exclude the ring and glycosidic oxygen atoms. Both crystal structures transform to a smectic A liquid crystal at 72.3°, which has a clearing point at 116.5°.

INTRODUCTION

The octyl D-glucopyranosides are members of a large class of amphiphilic carbohydrates which possess lyotropic and thermotropic liquid crystal properties[1,2]. The β anomer, in particular, has a variety of biochemical uses: it is a nonionic detergent for solubilizing cell-membrane proteins[3,4]. It has been substituted for phospholipids in reconstituting catalytic activity[5–7]. It has also been shown to be an effective agent for facilitating the crystallization of a number of proteins, transfer RNA's, and protein-nucleic acid complexes[8]. Hitherto, the β anomer has proved more difficult to obtain as crystals suitable for X-ray analysis than the α anomer, which forms two crystalline hydrates.

An electron-diffraction study of both the α and β anomers has been reported, and endothermic transitions to the liquid crystal phase at ~70° were observed[9].

The present work forms part of a general study of the crystal structures of

*Dedicated to Dr. R. Stuart Tipson.

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carbohydrate mesogens aimed at correlating their mesogenic property with the balance between the hydrophilic (hydrogen-bond) and hydrophobic (van der Waals) forces between the molecules in the crystal.

EXPERIMENTAL

Acicular crystals of the monohydrate were obtained from methanol–water solution; those of the hemihydrate from methanol, 2-propanol, and water solution. The diffraction data were measured on a Nicolet P-3 diffractometer using graphite-monochromated Cu$K\alpha$ radiation for the monohydrate and graphite-monochromated Mo$K\alpha$ radiation for the hemihydrate in the θ–2θ scan mode. The structures were solved using direct methods and were refined by a least squares procedure using a "blocked cascade" algorithm (SHELXTL, Version 4)*. The

TABLE I

CRYSTAL STRUCTURE AND REFINEMENT DATA FOR OCTYL α-D-GLUCOPYRANOSIDE MONOHYDRATE AND HEMIHYDRATE

	$C_{14}H_{28}O_6 \cdot H_2O$	$C_{14}H_{28}O_6 \cdot 0.5\,H_2O$
Space group	$C2$; $Z = 4$	
Cell dimensions a (Å)	17.896(2)	15.190(5)
b (Å)	5.154(1)	5.136(3)
c (Å)	18.303(2)	19.944(7)
β (deg)	90.30(1)	92.74(3)
V (Å^3)	1688.2(4)	1554.2(10)
Crystal dimensions (mm)	0.62 × 0.25 × 0.13	0.59 × 0.15 × 0.08
D_m (g/cc)	1.205	1.259
D_c (g/cc)	1.221	1.288
Radiation	graphite-monochromated Cu$K\alpha$	graphite-monochromated Mo$K\alpha$
Cell dimensions based on 25 reflections	$20 < \theta < 25°$	$10 < \theta < 15°$
Absorption (cm^{-1})	$\mu_{CuK\alpha} = 7.70$	$\mu_{MoK\alpha} = 0.94$
Intensity measured by $\theta/2\theta$ scans on Nicolet P-3 diffractometer	2695 intensities; 1304 unique, 80 considered unobserved with $F_o < 2.5\sigma(F_o)$	1605 intensities; 1541 unique, 310 considered unobserved with $F_o < 2.5\sigma(F_o)$

No absorption or extinction corrections applied. Structures solved by SHELXTL-83, with 243 (monohydrate) and 283 (hemihydrate) E values greater than 1.40. Refinement by SHELXTL-83 with the block cascade least-squares algorithm $R = [\omega(|kF_o^2| - |F_c^2|)]$, with $\omega = \sigma^{-2}$, $\sigma = \sigma + gF^2$, based on counting statistics. All hydrogen-atom positions located on difference Fourier maps and parameters refined isotropically.

Final agreement factors:		
$R(F^2)$	0.037	0.052
$R_w(F^2)$	0.041	0.051
G (goodness of fit)	1.057	0.976
No. of parameters	309	301

*SHELXTL is the primary system for structure determination on the Nicolet Crystallographic Systems.

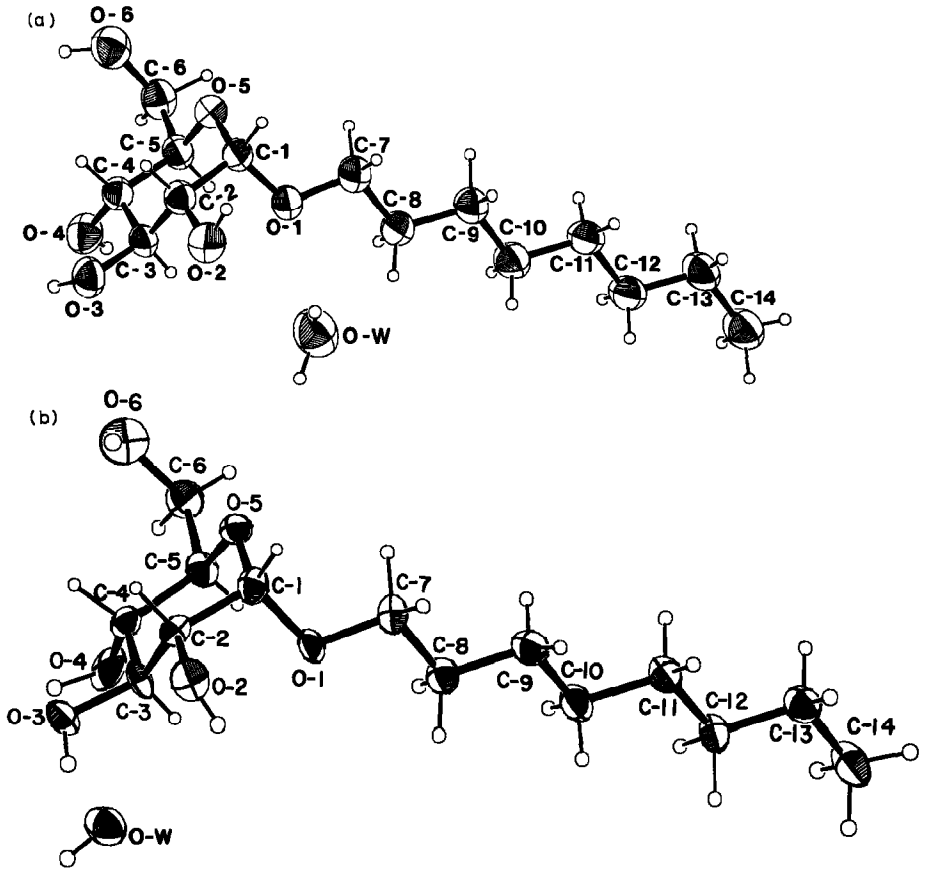

Fig. 1. Atomic notation and thermal ellipsoids, at 50% probability, for octyl α-D-glucopyranoside: (a), in the monohydrate; (b), in the hemihydrate.

carbon and oxygen atoms were refined with anisotropic temperature factors. All hydrogen atoms were located on difference maps and refined with isotropic temperature factors. The crystal densities were measured by flotation in hexane–carbon tetrachloride mixtures. Crystal and refinement data are given in Table I. The atomic notation and thermal ellipsoids are shown in Fig. 1, atomic positional parameters are listed† in Table II, and valence bond lengths in Table III.

†Tables of anisotropic temperature factors, bond and torsion angles, and observed and calculated structure factors are deposited with and can be obtained from: Elsevier Science Publishers B.V., BBA Data Deposition, P. O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/376/*Carbohydr. Res.*, 169 (1987) 1–11.

TABLE II

ATOMIC POSITIONAL PARAMETERS AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS FOR THE CRYSTAL STRUCTURE OF OCTYL α-D-GLUCOPYRANOSIDE MONOHYDRATE AND HEMIHYDRATE

Atom[a]	x/a	y/b	z/c	U_{eq} (Å^2)
C-1	1890(1) × 10^{-4}	4951(6) × 10^{-4}	3408(1) × 10^{-4}	44(1) × 10^{-1}
	3475(3)	11404(10)	8148(2)	28(1)
C-2	1826(1)	4195(6)	4215(1)	44(1)
	3726(2)	10951(9)	8880(2)	22(1)
C-3	1281(1)	1987(6)	4304(1)	42(1)
	3281(3)	8479(10)	9116(2)	26(1)
C-4	528(1)	2749(6)	3972(1)	42(1)
	2299(3)	8669(9)	8976(2)	26(1)
C-5	643(1)	3520(6)	3175(1)	45(1)
	2061(3)	9449(9)	8249(2)	28(1)
C-6	−66(2)	4457(7)	2789(2)	55(1)
	1103(3)	10155(10)	8134(2)	35(1)
C-7	2554(2)	3490(7)	2355(2)	52(1)
	3773(3)	9751(10)	7073(2)	32(1)
C-8	2754(2)	994(6)	1982(2)	50(1)
	3847(3)	7186(10)	6723(2)	30(1)
C-9	3149(2)	1393(7)	1255(2)	56(1)
	3814(3)	7381(11)	5953(2)	36(2)
C-10	3331(2)	−1159(7)	880(2)	57(1)
	3768(3)	4818(10)	5602(2)	34(1)
C-11	3689(2)	−833(7)	132(2)	56(1)
	3737(3)	5022(10)	4836(2)	32(1)
C-12	3872(2)	−3383(7)	−239(2)	57(1)
	3736(3)	2446(10)	4474(2)	31(1)
C-13	4262(2)	−3060(7)	−969(2)	61(1)
	3729(3)	2687(10)	3712(2)	36(2)
C-14	4479(2)	−5631(7)	−1313(2)	71(1)
	3720(4)	81(12)	3352(2)	47(2)
O-1	2207(1)	2850(4)	3037(1)	46(1)
	3809(2)	9345[b]	7779(1)	27(1)
O-2	2539(1)	3404(5)	4496(1)	58(1)
	4653(2)	10945(7)	9007(1)	36(1)
O-3	1216(1)	1374(5)	5057(1)	58(1)
	3432(2)	8109(7)	9821(1)	31(1)

TABLE II *(continued)*

Atom[a]	x/a	y/b	z/c	U_{eq} (Å^2)
O-4	11(1)	671(5)	4032(1)	58(1)
	1885(2)	6220(8)	9065(2)	43(1)
O-5	1171(1)	5612[b]	3134(1)	46(1)
	2550(2)	11681(6)	8046(1)	27(1)
O-6	−385(1)	6668(5)	3127(1)	70(1)
	855(2)	12285(7)	8534(2)	43(1)
O-W	3378(1)	−370(7)	3778(1)	85(1)
	5000[b]	4960(11)	10000[b]	42(2)
H–C-1	219(1) × 10^{-3}	641(5) × 10^{-3}	330(1) × 10^{-3}	20(5) × 10^{-1}
	375(2)	1311(9)	789(2)	26(10)
H–C-2	167(1)	573(6)	453(1)	45(7)
	352(2)	1241(7)	914(1)	22(8)
H–C-3	144(1)	60(4)	409(1)	15(5)
	353(2)	729(7)	892(1)	26(8)
H–C-4	29(1)	416(6)	424(1)	44(7)
	208(3)	1006(10)	933(2)	41(12)
H–C-5	83(1)	200(5)	294(1)	33(6)
	216(3)	808(9)	800(2)	28(11)
H-1–C-6	15(1)	498(8)	228(2)	71(9)
	70(3)	851(13)	828(2)	61(16)
H-2–C-6	−46(2)	312(7)	273(2)	60(9)
	94(3)	1040(13)	771(2)	64(16)
H-1–C-7	214(2)	462(8)	204(2)	77(10)
	428(3)	1087(10)	693(2)	29(12)
H-2–C-7	301(1)	460(8)	242(2)	70(9)
	315(3)	1078(11)	693(3)	45(13)
H-1–C-8	234(2)	−5(8)	190(2)	67(9)
	436(2)	614(8)	691(2)	30(9)
H-2–C-8	303(2)	−22(7)	233(2)	59(8)
	339(2)	604(10)	683(2)	32(11)
H-1–C-9	363(2)	240(9)	135(2)	89(12)
	436(2)	826(9)	582(2)	23(11)
H-2–C-9	277(2)	264(10)	90(2)	101(13)
	335(2)	825(7)	585(1)	36(8)
H-1–C-10	288(2)	−219(8)	79(2)	72(10)
	428(3)	382(11)	571(2)	50(14)

TABLE II *(continued)*

Atom[a]	x/a	y/b	z/c	U_{eq} (Å^2)
H-2–C-10	371(2)	−212(8)	126(2)	71(9)
	324(3).	376(9)	572(2)	33(12)
H-1–C-11	334(1)	16(7)	−11(3)	60(9)
	422(3)	616(10)	470(2)	39(13)
H-2–C-11	418(1)	24(7)	14(1)	57(8)
	316(3)	591(11)	466(2)	41(13)
H-1–C-12	424(1)	−442(6)	9(1)	55(7)
	428(2)	121(8)	464(2)	31(9)
H-2–C-12	334(1)	−434(7)	−34(2)	73(9)
	326(3)	127(10)	466(2)	31(11)
H-1–C-13	468(2)	−207(9)	−93(2)	88(11)
	327(3)	377(12)	354(2)	55(15)
H-2–C-13	383(2)	−211(10)	−124(2)	93(11)
	423(2)	378(9)	359(2)	36(10)
H-1–C-14	402(1)	−672(7)	−139(2)	67(9)
	421(3)	−121(13)	353(2)	67(17)
H-2–C-14	486(2)	−690(8)	−103(2)	79(10)
	384(3)	27(12)	288(2)	60(16)
H-3–C-14	480(2)	−536(12)	−164(2)	119(14)
	323(4)	−87(15)	353(3)	101(23)
H–O-2	277(2)	471(12)	444(3)	113(17)
	498(4)	975(14)	888(3)	85(20)
H–O-3	73(2)	64(10)	513(2)	123(14)
	385(2)	728(8)	990(2)	31(9)
H–O-4	−2(2)	−37(9)	371(2)	64(11)
	188(3)	598(11)	953(2)	46(13)
H–O-6	−84(4)	637(14)	339(5)	148(20)
	129(5)	1327(20)	873(4)	112(28)
H-1-W	366(2)	105(9)	401(2)	62(10)
	−6(3)	903(10)	1033(2)	35(15)
H-2-W	351(3)	−168(12)	417(3)	126(16)

[a]First line of each entry, monohydrate; second line, hemihydrate. Estimated standard deviations given in parentheses refer to the last significant digit. $U_{eq} = {}^1/_3\Sigma\Sigma U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$. [b]Fixed parameters.

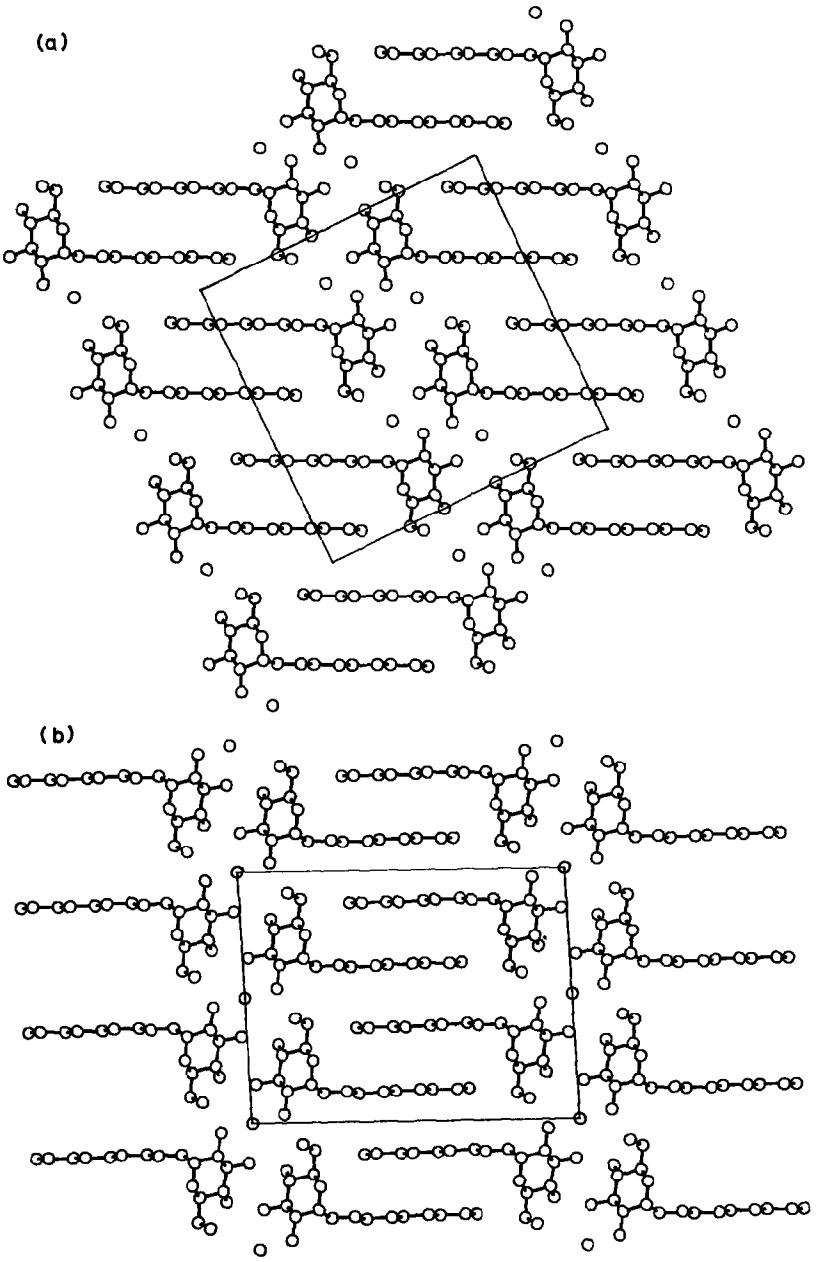

Fig. 2. Molecular packing in the crystal structures of octyl α-D-glucopyranoside, viewed down the *b* axis: (a), in the monohydrate; (b), in the hemihydrate.

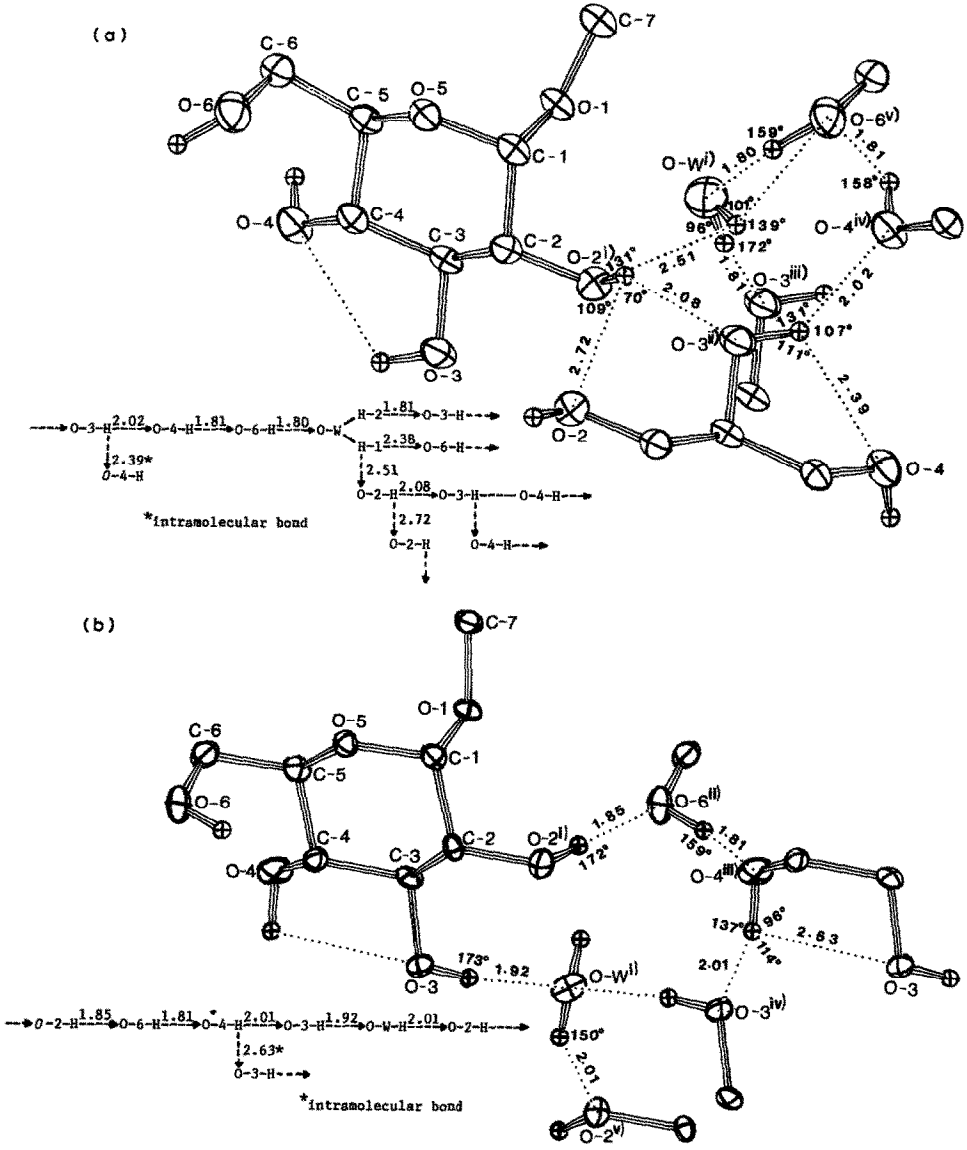

Fig. 3. Hydrogen-bonding in the crystal structures of octyl α-D-glucopyranoside. The H---O distances and O–H---O angles were obtained by normalizing the covalent O–H distances to the standard value of 0.97 Å (ref. 12). Upper figure (a), in the monohydrate. The symmetry code is: (i), x, y, z; (ii), $\frac{1}{2} - x$, $\frac{1}{2} + y$, $1 - z$; (iii), $\frac{1}{2} - x$, $-\frac{1}{2} + y$, $1 + z$; (iv), $\frac{1}{2} + x$, $\frac{1}{2} + y$, z; (v), $\frac{1}{2} + x$, $-\frac{1}{2} + y$, z. Lower figure (b), in the hemihydrate. The symmetry code is: (i), x, y, z; (ii), $\frac{1}{2} + x$, $-\frac{1}{2} + y$, z; (iii), $\frac{1}{2} + x$, $\frac{1}{2} + y$, z; (iv), $1 - x$, y, $2 - z$.

TABLE III

BOND LENGTHS IN OCTYL α-D-GLUCOPYRANOSIDE MONOHYDRATE AND HEMIHYDRATE[a]

Bond	*Monohydrate*	*Hemihydrate*
C-1–C-2	1.532(3)	1.510(5)
C-2–C-3	1.508(4)	1.523(6)
C-3–C-4	1.527(3)	1.507(6)
C-4–C-5	1.526(3)	1.532(6)
C-5–C-6	1.528(4)	1.506(6)
C-1–O-1	1.399(3)	1.397(5)
C-1–O-5	1.421(3)	1.416(5)
C-2–O-2	1.432(3)	1.418(4)
C-3–O-3	1.419(3)	1.427(4)
C-4–O-4	1.420(3)	1.421(6)
C-5–O-5	1.436(3)	1.434(5)
C-6–O-6	1.419(4)	1.416(6)
C-7–O-1	1.436(3)	1.422(5)
C-7–C-8	1.500(4)	1.497(7)
C-8–C-9	1.525(4)	1.538(6)
C-9–C-10	1.520(5)	1.491(7)
C-10–C-11	1.523(4)	1.530(6)
C-11–C-12	1.516(5)	1.507(7)
C-12–C-13	1.520(4)	1.524(6)
C-13–C-14	1.518(5)	1.519(8)

[a]Distances in Å. Estimated standard deviations, given in parentheses, refer to the last significant digit.

DISCUSSION

The molecular packing, shown in Fig. 2, is typical of all the long-chain alkyl pyranosides hitherto studied[1,2]. The carbohydrate moieties are hydrogen-bonded to form layers, two molecules wide. The alkyl chains, which extend from these layers, are interdigitated. In the hemihydrate, the axis of the fully extended alkyl chains is 90° to the plane of the bilayer. In the monohydrate, the inclination angle is about 25°.

The hydrogen-bonding is shown in Fig. 3. In the hemihydrate, it consists of symmetry-related infinite chains which intersect at the water molecules which are on the two-fold axis of symmetry. The ring and glycosidic oxygen atoms are excluded from the hydrogen-bonding.

The hydrogen-bonding in the monohydrate is more complex. There are infinite chains of two-center bonds which include one of the water OH groups. The other water OH group forms infinite chains involving three-center bonds. The water molecule accepts one two-center bond and donates one two-center and one three-center bond. As in the hemihydrate, the ring and glycosidic oxygen atoms are not involved in the hydrogen-bonding. Both hydrogen bonding schemes are consistent with those observed in other carbohydrate crystal structures[10].

The conformations of the molecules are almost identical, as shown by the best-fit superposition presented in Fig. 4. In both, the pyranoside rings are $^4C_1$ with puckering parameters[11] of Q = 0.586 Å, 0.549 Å, θ = 0°, 7° for the monohydrate and hemihydrate, respectively. The pyranose ring in the monohydrate is a relatively rare example of an ideal $^4C_1$ chair. The glycosidic torsion angles, O-5–C-1–O-1–C-7, are *g/t*, 81.3° and 68.7°, respectively. The primary alcohol orientation is *g/g* with O-5–C-5–C-6–O-6 equal to −61.4° and −62.7°, respectively. The alkyl chains are fully extended. There are no abnormal features in the bond lengths, shown in Table III, or in the bond and torsion angles.

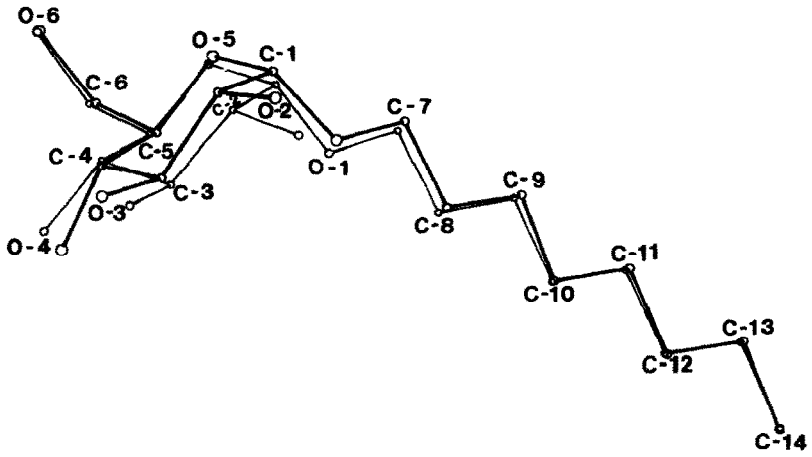

Fig. 4. Comparison of the molecular conformations of octyl α-D-glucopyranoside in the monohydrate (heavy line) and the hemihydrate (light line).

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