Table 2. *Average bond lengths* (Å) *for chemically equivalent bonds in compounds* (1) *and* (2)

Bond type	Number	Average length	Range
S—C	4	1·808 (10)	1·798–1·820
O—C in pyranose ring	4	1·428 (6)	1·421–1·435
O—C in 5-rings	12	1·416 (8)	1·405–1·430
C—C in pyranose ring	8	1·518 (7)	1·504–1·528
C—C in 5-rings	6	1·516 (10)	1·500–1·528
O—C (ester)	12	1·439 (8)	1·425–1·449
O—C (acetate)	12	1·338 (14)	1·318–1·356
C=O in acetyl groups	12	1·184 (15)	1·150–1·203
$C—CH_3$	16	1·482 (20)	1·452–1·536
C—C (other)	6	1·508 (11)	1·496–1·523

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Structure of Anhydrous Octyl α-D-Glucopyranoside. A Comparison with its Hemi- and Monohydrate

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Abstract. $C_{14}H_{28}O_6$, $M_r = 292{\cdot}37$, monoclinic, $P2_1$, $a = 5{\cdot}140\ (2)$, $b = 7{\cdot}604\ (2)$, $c = 19{\cdot}939\ (4)$ Å, $\beta = 92{\cdot}18\ (2)°$, $V = 778{\cdot}7\ (2)$ Å^3, $Z = 2$, $D_x = 1{\cdot}25$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}5418$ Å, $\mu = 1{\cdot}05$ cm^{-1}, $F(000) = 320$, $T = 293$ K, $R = 0{\cdot}049$ for 1682 observed reflections $[I > \sigma(I)]$. The conformation of octyl α-D-glucopyranoside in the anhydrous crystal is similar to the conformation in the hemihydrate and monohydrate crystals of the same compound. The structure consists of alternating regions of polar and nonpolar groups, resulting from the close packing of fully extended hydrocarbon chains between hydrogen-bonded layers of glucopyranoside rings. The packing is strictly analogous to that in the anhydrous decyl homologue. The hydrogen-bonding scheme between the polar groups in anhydrous octyl α-D-glucopyranoside greatly resembles the hydrogen bonding in the hemihydrate crystal, but differs from that in the monohydrate crystal. The octyl chain packing is different from the chain packing in both the hemihydrate and monohydrate crystals.

Introduction. A new method for the preparation of alkyl α-D-glucopyranosides (alkyl = octyl, decyl, dodecyl) by selective crystallization from a mixture with the β-anomer has recently been developed (Straathof, Romein, van Rantwijk, Kieboom & van Bekkum, 1987). In order to achieve crystallization in the presence of traces of water, further improvement of this method is under study (Straathof, van Bekkum & Kieboom, 1988). Elucidation of the crystal structures of alkyl D-glucopyranosides might result in an optimization of the crystallization step, thus making octyl α-D-glucopyranoside much better available. Knowledge of the crystal structure will also be of importance to the study of alkyl α-D-glucopyranosides as liquid crystals (Jeffrey, 1986, and references cited therein) and membrane protein solubilizing detergents (Dorset & Rosenbusch, 1983, and references cited therein).

Recently, we solved the crystal structure of octyl α-D-glucopyranoside monohydrate (van Koningsveld, Jansen & Straathof, 1986). Simultaneously, Jeffrey, Yeon & Abola (1987) submitted a paper describing the identical structure. They also described a hemihydrate, which, like the monohydrate, consisted of alternating regions of polar and nonpolar groups, resulting from the close packing of fully extended hydrocarbon chains between hydrogen-bonded layers of glucopyranoside rings. In this paper the crystal structure of anhydrous octyl α-D-glucopyranoside is reported and compared with the hemihydrate and monohydrate crystals of the same compound and with the anhydrous decyl homologue (Moews & Knox, 1976).

Experimental. Octyl α-D-glucopyranoside monohydrate (Straathof *et al.*, 1987) was recrystallized from

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ethyl acetate. Anhydrous crystals were only obtained upon addition of zeolite K-A, which adsorbed the dissolved water. An irregular-shaped crystal (maximum dimensions ~0·4 × 0·3 × 0·1 mm) was cut from a larger plate. Enraf–Nonius CAD-4 diffractometer, graphite monochromator, Cu$K\alpha$ radiation. Cell dimensions from setting angles of 25 reflections with $23{\cdot}5 \leq \theta \leq 39{\cdot}5°$. 1760 unique reflections surveyed to $\theta_{\max} = 76{\cdot}25°$; h: 0→6, k: 0→9, l: −25→25; 1690 reflections with $I > \sigma(I)$. Three reference reflections monitored periodically showed no significant variation in intensity. No absorption correction. Structure determined by direct methods. H atoms located in a difference Fourier synthesis but included, except for the H atoms bonded to O, in idealized positions [d(C—H) = 0·96 Å]. Least-squares calculations on F with anisotropic thermal parameters for C and O atoms and fixed isotropic thermal parameters for C and O atoms and fixed isotropic values for H atoms. Absolute configuration chosen to be consistent with the configuration of the skeleton in previous analysis (Jeffrey *et al.*, 1987). Convergence at $R = 0{\cdot}049$, $wR = 0{\cdot}058$, $w = 1/\sigma^2(F_o)$, $S = 28{\cdot}7$ for 192 variable and 1747 observations [1682 with $I > \sigma(I)$ plus those for which $F_c > F_o$; eight strong reflections left out of final refinement cycles]; $(\Delta/\sigma)_{\max} = 0{\cdot}1$ [for y of H(20)]. Final ΔF synthesis has $\rho < 0{\cdot}25$ e Å^{-3}. All calculations performed on the Delft University Amdahl 470/V7B computer with programs of the *XRAY*72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) and *MULTAN* (Germain, Main & Woolfson, 1971) packages. Atomic scattering factors from *XRAY*72.

Table 1. *Atomic coordinates* (×10^4) *and equivalent isotropic thermal parameters* (Å^2×10^3)

$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

	x	y	z	U_{eq}
C(1)	1344 (6)	2843 (6)	1650 (1)	29 (1)
C(2)	1908 (6)	2717 (6)	906 (1)	30 (1)
C(3)	4286 (6)	3822 (6)	768 (1)	31 (1)
C(4)	3913 (6)	5690 (6)	1006 (1)	28 (1)
C(5)	3187 (6)	5731 (6)	1736 (1)	31 (1)
C(6)	2467 (8)	7554 (6)	1978 (2)	39 (1)
C(7)	2945 (7)	1902 (6)	2717 (1)	37 (1)
C(8)	5494 (7)	1565 (6)	3091 (2)	39 (1)
C(9)	5231 (7)	1484 (7)	3844 (2)	40 (1)
C(10)	7804 (6)	1404 (7)	4241 (2)	39 (1)
C(11)	7565 (7)	1410 (7)	4993 (2)	40 (1)
C(12)	10131 (6)	1413 (7)	5393 (2)	39 (1)
C(13)	9868 (7)	1458 (7)	6145 (2)	43 (1)
C(14)	12447 (8)	1464 (8)	6541 (2)	55 (2)
O(1)	3430 (4)	2091 (5)	2017 (1)	32 (1)
O(2)	2337 (6)	946 (5)	704 (1)	44 (1)
O(3)	4602 (8)	3813*	59 (1)	52 (1)
O(4)	6282 (5)	6641 (5)	949 (1)	37 (1)
O(5)	934 (5)	4627 (5)	1833 (1)	31 (1)
O(6)	457 (5)	8378 (5)	1582 (1)	43 (1)

Calculated atomic coordinates (×10^3) and (fixed) isotropic thermal parameters (Å^2×10^3) for H atoms involved in hydrogen bonding. The O—H distance is normalized to 0·97 Å (Jeffrey & Lewis, 1978).

	x	y	z	U
H(20)	196	11	105	61
H(30)	561	484	−6	61
H(40)	605	721	52	61
H(60)	−111	767	151	61

* Fixed parameter.

Discussion. Fig. 1, drawn with *ORTEP* (Johnson, 1965), shows the molecular conformation and atom labeling. Atomic coordinates are listed in Table 1 and molecular dimensions in Table 2.* Besides the O(3)—H distance, no abnormal features in bond lengths and valence angles were found. From the ΔF map the (disordered?) position of the H atom bonded to O(3) could not be located accurately, resulting in a rather short O—H distance of 0·46 Å. The conformation is similar to those of the hemi- and monohydrate (Jeffrey *et al.*, 1987), and the anhydrous decyl compound (Moews & Knox, 1976). The alkyl chain is fully extended and the pyranoside ring is slightly flattened with respect to the ideal chair conformation.

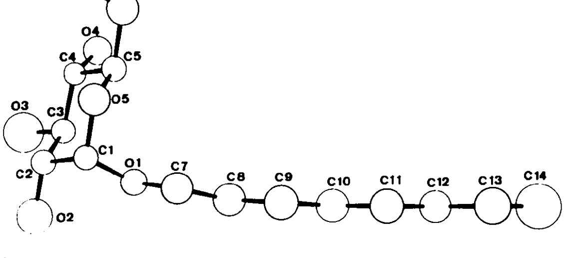

Fig. 1. Atomic notation and thermal ellipsoids, at 50% probability, for anhydrous octyl α-D-glucopyranoside.

The molecular packing is illustrated in Fig. 2(*a*). The structure consists of alternating regions of polar and nonpolar groups, and is strictly analogous to that of the decyl compound. The lengthening of the *c* axis in the decyl compound with respect to the octyl compound is caused by the longer alkyl chain. The other cell dimensions are hardly affected (Table 3).

The cell dimensions of anhydrous octyl α-D-glucopyranoside ($Z = 2$) show a remarkable correspondence to those of the hemihydrate ($Z = 4$): *a* of the anhydrous crystal is equal to *b* of the hemihydrate, *b* of the anhydrous crystal is equal to 0·5*a* of the hemihydrate, and the *c* axes are the same in both crystals. This indicates an equivalent total void volume per octyl α-D-glucopyranoside molecule (Table 3). The anhydrous crystal (Fig. 2*a*) can be transformed to the hemihydrate crystal (Fig. 2*b*) by a rotation of 180°

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* Lists of coordinates of H atoms, except those involved in hydrogen bonding, structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44765 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Molecular geometry*

(*a*) Bond lengths (Å)

C(1)—C(2)	1·525 (4)	C(5)—O(5)	1·449 (5)
C(2)—C(3)	1·517 (5)	C(6)—O(6)	1·422 (5)
C(3)—C(4)	1·512 (6)	C(7)—O(1)	1·434 (4)
C(4)—C(5)	1·518 (4)	C(7)—C(8)	1·504 (5)
C(5)—C(6)	1·518 (6)	C(8)—C(9)	1·515 (4)
C(1)—O(1)	1·398 (4)	C(9)—C(10)	1·515 (5)
C(1)—O(5)	1·422 (6)	C(10)—C(11)	1·510 (4)
C(2)—O(2)	1·425 (6)	C(11)—C(12)	1·515 (5)
C(3)—O(3)	1·428 (4)	C(12)—C(13)	1·512 (5)
C(4)—O(4)	1·425 (5)	C(13)—C(14)	1·516 (5)

(*b*) Bond angles (°)

O(1)—C(1)—C(2)	108·3 (3)	C(4)—C(5)—C(6)	113·3 (3)
O(1)—C(1)—O(5)	111·9 (3)	C(4)—C(5)—O(5)	110·0 (3)
O(5)—C(1)—C(2)	110·2 (3)	O(5)—C(5)—C(6)	106·3 (3)
C(1)—C(2)—C(3)	109·1 (3)	C(5)—C(6)—O(6)	114·0 (3)
C(1)—C(2)—O(2)	111·7 (3)	C(1)—O(5)—C(5)	113·1 (3)
O(2)—C(2)—C(3)	109·7 (3)	C(1)—O(1)—C(7)	113·1 (2)
C(2)—C(3)—C(4)	110·5 (3)	O(1)—C(7)—C(8)	108·5 (3)
C(2)—C(3)—O(3)	107·5 (3)	C(7)—C(8)—C(9)	112·9 (3)
O(3)—C(3)—C(4)	109·6 (3)	C(8)—C(9)—C(10)	114·2 (3)
C(3)—C(4)—C(5)	111·1 (3)	C(9)—C(10)—C(11)	114·6 (3)
C(3)—C(4)—O(4)	109·5 (3)	C(10)—C(11)—C(12)	114·9 (3)
O(4)—C(4)—C(5)	108·0 (3)	C(11)—C(12)—C(13)	114·4 (3)
		C(12)—C(13)—C(14)	114·0 (3)

(*c*) Selected torsion angles (°) (e.s.d.'s ~ 0·4°)

O(5)—C(1)—C(2)—C(3)	58·3	O(1)—C(7)—C(8)—C(9)	4·4
C(1)—C(2)—C(3)—C(4)	54·9	C(7)—C(8)—C(9)—C(10)	8·2
C(2)—C(3)—C(4)—C(5)	53·6	C(8)—C(9)—C(10)—C(11)	2·8
C(3)—C(4)—C(5)—O(5)	54·1	C(9)—C(10)—C(11)—C(12)	2·6
C(4)—C(5)—O(5)—C(1)	59·1	C(10)—C(11)—C(12)—C(13)	1·2
C(5)—O(5)—C(1)—C(2)	61·7	C(11)—C(12)—C(13)—C(14)	0·1

(*d*) Hydrogen-bonding scheme

The H···*Y* distances (Å) and *X*—H···*Y* angles (°) were obtained by normalizing the covalent *X*—H distances to the standard value of 0·97 Å (Jeffrey & Lewis, 1978).

X—H···*Y*	*X*···*Y*	*X*—H	H···*Y*	*X*—H···*Y*
O(2)—H(20)···O(6$^{\rm i}$)	2·817 (5)	0·97 (5)	1·87 (5)	165 (5)
O(3)—H(30)···O(2$^{\rm ii}$)	2·757 (4)	0·97 (7)	1·90 (5)	146 (10)
O(4)—H(40)···O(3$^{\rm ii}$)	2·627 (4)	0·97 (4)	1·69 (5)	160 (5)
O(6)—H(60)···O(4$^{\rm iii}$)	2·781 (4)	0·97 (5)	1·90 (4)	149 (4)

Symmetry code: (i) $x, y-1, z$; (ii) $-x+1, y+\frac{1}{2}, -z$; (iii) $x+1, y, z$.

around an axis parallel to **c** of one of the carbohydrate molecules in the anhydrous unit cell. In doing so, the system of voids of equivalent size between glucopyranoside layers in the anhydrous compound (hatched in Fig. 2*a*) is transformed into a system of alternating smaller and larger voids (hatched in Fig. 2*b*) without having any effect on the total void volume. The original voids as well as the smaller voids formed upon transformation are incapable of occluding water molecules. Upon incorporation of a water molecule in the larger voids, the hemihydrate structure is obtained, having infinite chains of hydrogen bonds in an order O—H(20)···O—H(60)···O—H(40)···O—H(30)···O—H(*w*)···O—H(20)···. A similar scheme, without O—H(*w*)···, is present in the anhydrous crystal (*cf.* Table 2*d* and Jeffrey *et al.*, 1987).

In the monohydrate a subcell very similar to the unit cell in the anhydrous and hemihydrate crystals can be outlined (see Fig. 2 and Table 3). The main difference from the hemihydrate structure can be described as a shift of neighbouring (201) layers, 8·011 Å thick. The hydrogen-bonding scheme in the monohydrate crystal is therefore different from those in the hemihydrate and anhydrate crystals.

The alkyl chain packing seems to be similar in Figs. 2(*a*), (*b*) and (*c*). However, in the anhydrous crystal the 2_1 axis is perpendicular to the alkyl chain plane whereas in the hemihydrate and monohydrate structures the 2_1

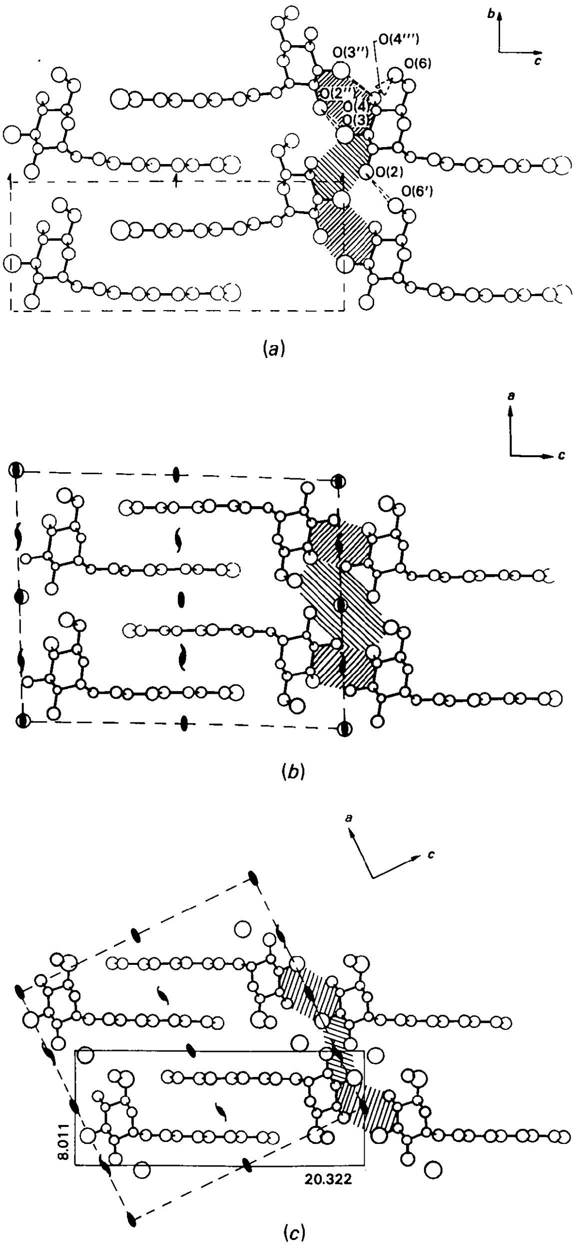

Fig. 2. Molecular packing in the crystal structures of octyl α-D-glucopyranoside: (*a*) in the anhydrous crystal, (*b*) in the hemihydrate crystal (Jeffrey *et al.*, 1987), (*c*) in the monohydrate crystal (subcell indicated by full lines). In the three structures, corresponding voids are hatched.

Table 3. *Comparison of anhydrous octyl* α-D-*glucopyranoside with the hemihydrate and the monohydrate, and with anhydrous decyl* α-D-*glucopyranoside*

	Space group	*a* (Å)	*b* (Å)	*c* (Å)	β (°)	*Z*	*V*/*Z* (Å^3)
Octyl							
$C_{14}H_{28}O_6$*	*P*2$_1$	5·140 (2)	7·604 (2)	19·939 (4)	92·18 (2)	2	389·4
$C_{14}H_{28}O_6$.0·5 H_2O†	*C*2	15·190 (5)	5·136 (3)	19·944 (7)	92·74 (3)	4	388·6
$C_{14}H_{28}O_6$.H_2O‡	*C*2	17·829 (3)	5·144 (2)	18·262 (4)	90·30 (2)	4	418·7
		(8·011)	(5·144)	(20·322)			
Decyl							
$C_{16}H_{32}O_6$§	*P*2$_1$	5·153 (2)	7·624 (4)	22·125 (7)	90·95 (4)	2	434·7

* This work.
† Jeffrey *et al.* (1987).
‡ Van Koningsveld *et al.* (1986). The subcell values are given within parentheses.
§ Moews & Knox (1976).

axis is parallel to the alkyl plane. Thus, all chains are parallel in the anhydrous crystal seen along **b**. The interwoven chains cross each other in both the hemihydrate and monohydrate crystals when viewed along **a**.

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Structure of *N,N*-Dimethyl-1,4-phenylenediamine

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Abstract. $C_8H_{12}N_2$, $M_r = 136·2$, monoclinic, *P*2/*c*, $a = 10·484$ (4), $b = 7·342$ (2), $c = 21·245$ (3) Å, $\beta = 90·90$ (2)°, $V = 1635·1$ (9) Å^3, $Z = 8$, $D_x = 1·106$ Mg m^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1·54178$ Å, $\mu(\mathrm{Cu}\,K\alpha) = 0·53$ mm^{-1}, $F(000) = 592$, $T = 295$ K, $R = 0·054$ for 2605 observed reflections $[F_o > \sigma(F_o)]$. Two independent molecules with almost the same geometries are included in the asymmetric unit. Amino and dimethylamino groups in the molecules adopt pyramidal structures. The angles between the bisector of the Me—N—Me angle and extension of the bond C(*ipso*)—N(dimethylamino) are 41·7 and 42·2° for the two molecules, respectively. Comparison with the molecular structure in the complex with 1,2,4,5-tetracyanobenzene revealed less contribution from a quinoidal form to the structures in free molecules. Hydrogen bonds were found between the H atoms of the amino groups and the N atoms in the amino and the dimethylamino groups.

Introduction. We have been interested in the substituent effect on the planarity of amino groups or dimethylamino groups in six-membered aromatics. The structure of one of them, the title compound, was determined by X-ray analysis.

The title compound is a strong electron donor and easily forms charge-transfer complexes with electron acceptors. We were interested in the effect of complex formation on the molecular structure of the donor. Therefore, the structure of the free molecule was compared with that in the complex with 1,2,4,5-tetracyanobenzene (Ohashi, 1973).

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