Supplementary Material Available. Table IV (atomic coordinates of the xylene solvate), Table V (bond distances and angles for the xylene solvate), and structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) University of Notre Dame; (b) Brooklyn College.
(2) D. A. Summerville and I. A. Cohen, *J. Am. Chem. Soc.*, **98**, 1747 (1976). A qualitative MO scheme for the complex is given for D_{4h} symmetry. This scheme is also applicable for the observed D_{4d} symmetry with minor changes in labeling.
(3) W. P. Griffith, *Coord. Chem. Rev.*, **8**, 369 (1972).
(4) $(FeTPP)_2O$: A. B. Hoffman, D. M. Collins, V. W. Day, E. B. Fleischer, T. S. Srivastava, and J. L. Hoard, *J. Am. Chem. Soc.*, **94**, 3620 (1972).
(5) $[Fe(ODM)]_2O$:[7] J. E. Kenney, J. W. Buchler, and W. R. Scheidt, to be submitted for publication.
(6) $[Fe(Proto\ IX\ DME)]_2O$:[7] L. J. Radonovich, W. S. Caughey, and J. L. Hoard, unpublished results.
(7) Abbreviations used: ODM, dianion of α,γ-dimethyloctaethylporphyrin; Proto IX DME, dianion of protoporphyrin IX dimethyl ester.
(8) N. F. M. Henry and K. Lonsdale, Ed., "International Tables for X-Ray Crystallography", Vol. I, 3d ed, Kynoch Press, Birmingham, England, 1969, pp 161–162.
(9) W. R. Scheidt, *J. Am. Chem. Soc.*, **96**, 84 (1974).
(10) A locally modified version of the Fourier program ALFF was used: C. R. Hubbard, C. O. Quicksall, and R. A. Jacobson, Report IS-2625, Ames Laboratory, Iowa State University, Ames, Iowa, 1971.
(11) A locally modified version of ORFLS was employed: W. R. Busing, K. O. Martin, and H. A. Levy "OR-FLS, a Fortran Crystallographic Least-Squares Program", Report ORNL-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.
(12) Atomic form factors were from D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968), with real and imaginary corrections for anomalous dispersion in the form factors of iron from D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).
(13) Scattering factor for hydrogen from R. F. Steward, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(14) R. Blessing, P. Coppens, and P. Becker, *J. Appl. Crystallogr.*, 7, 488 (1974).
(15) This absorption coefficient was calculated on the basis of 80% occupancy of the chloroform molecules, in agreement with the observed density.
(16) Supplementary material.
(17) C. K. Johnson, "ORTEP, A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations", Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.
(18) C. Maricondi, W. Swift, and D. K. Straub, *J. Am. Chem. Soc.*, **91**, 5205 (1969); E. B. Fleischer, and T. S. Srivastava, *J. Am. Chem. Soc.*, **91**, 2403 (1969); I. A. Cohen, *J. Am. Chem. Soc.*, **91**, 1980 (1969).
(19) P. D. W. Boyd and T. D. Smith, *Inorg. Chem.*, **10**, 2041 (1971).
(20) M. Ciechanowicz and A. C. Skapski, *J. Chem. Soc. A*, 1792 (1971).
(21) R. J. D. Gee and H. M. Powell, *J. Chem. Soc. A*, 1795 (1971).
(22) W. O. Davies, N. P. Johnson, P. Johnson, and A. J. Graham, *Chem. Commun.*, 736 (1969).
(23) J. Strähle, *Z. Anorg. Allg. Chem.*, **375**, 238 (1970).
(24) S. R. Fletcher and A. C. Skapski, *J. Chem. Soc., Dalton Trans.*, 1079 (1972); R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, **6**, 204 (1967); P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *ibid.*, **6**, 107 (1967).
(25) S. R. Fletcher, W. P. Griffith, D. Pawson, F. L. Phillips, and A. C. Skapski, *Inorg. Nucl. Chem. Lett.*, **9**, 1117 (1973); D. Bright and J. A. Ibers, *Inorg. Chem.*, **8**, 709 (1969).
(26) J. L. Hoard, *Ann. N.Y. Acad. Sci.*, **206**, 18 (1973); see also ref 27 and D. M. Collins, W. R. Scheidt, and J. L. Hoard, *J. Am. Chem. Soc.*, **94**, 6689 (1972).
(27) J. L. Hoard in "Porphyrins and Metalloporphyrins", K. M. Smith, Ed., Elsevier, Amsterdam, 1975, Chapter 8; W. R. Scheidt, in "The Porphyrins", D. Dolphin, Ed., Academic Press, New York, N.Y., in press.
(28) D. M. Collins, R. Countryman, and J. L. Hoard, *J. Am. Chem. Soc.*, **94**, 2066 (1972).
(29) R. G. Little, K. R. Dymock, and J. A. Ibers, *J. Am. Chem. Soc.*, **97**, 4532 (1975).
(30) K. M. Adams, P. G. Rasmussen, and W. R. Scheidt, to be submitted for publication.
(31) W. R. Scheidt and M. E. Frisse, *J. Am. Chem. Soc.*, **97**, 17 (1975).
(32) B. M. L. Chen and A. Tulinsky, unpublished results.
(33) L. J. Radonovich and J. L. Hoard, unpublished results.
(34) V. W. Day, B. R. Stults, E. L. Tasset, R. S. Marianelli, and L. J. Boucher, *Inorg. Nucl. Chem. Lett.*, **11**, 505 (1975).
(35) Similar Mn-N distances are observed in a six-coordinate Mn(III) porphyrin, J. F. Kirner and W. R. Scheidt, *Inorg. Chem.*, **14**, 2081 (1975).

The Crystal Structure of 1-Decyl α-D-Glucopyranoside: A Polar Bilayer with a Hydrocarbon Subcell[1]

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Abstract: A bilayer assembly of long polar molecules has been observed in the crystal structure of 1-decyl α-D-glucopyranoside, $C_{16}H_{32}O_6$. Alternating regions of polar and nonpolar groups result from the close packing of fully extended hydrocarbon chains between hydrogen-bonding layers of glucose rings. The chain packing, in which the planes of carbon–carbon bonds are parallel and equally spaced, is described by a new type of monoclinic subcell containing two CH_2 groups per asymmetric unit; its space group is $P2_1/m$ with $a_s = 4.64$ Å, $b_s = 7.63$ Å, $c_s = 2.54$ Å, and $\gamma_s = 90°$; the volume per CH_2 group is 22.4 Å.^{3} The main cell symmetry is $P2_1$ with $a = 5.153$ Å, $b = 7.624$ Å, $c = 22.125$ Å, $\beta = 90.95°$, and $Z = 2$; b is parallel to b_s. The structure was solved by direct phasing methods and least-squares refined to a residual of 9.3%.

Introduction

The synthesis of a series of *n*-alkyl derivatives of glucose, among them ethyl, *n*-hexyl, *n*-octyl, and *n*-decyl glucopyranoside, has been reported.[2] These uncharged polar molecules may serve as models for polar membrane components of similar topography. They share a number of properties with glyco- and phospholipids and, while simpler compounds, have been used for a number of physical studies. From a study of apparent molal volumes, Brown et al.[2] concluded that the alkyl glucopyranosides form micelles in aqueous solution; micelle formation was strongly dependent upon the structure of the sugar in that the β isomer was more soluble and formed micelles less readily than the α isomer. An investigation of the mechanism of micelle formation in the *n*-alkyl glucose derivatives (n = 6 to 10) has been carried out by Paul.[3] Recently, the solid *n*-alkyl pyranosides have been observed to form a thermotropic liquid crystal phase above 76 °C.[4]

Five of the homologous members of the *n*-alkyl series have been crystallized,[3] and we have now determined the crystal and molecular structure of 1-decyl α-D-glucopyranoside (**1**). The

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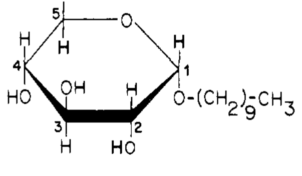

Table I. Fractional Coordinates ($\times 10^4$) and Anisotropic Temperature Factor Coefficients ($\times 10^3$)[a]

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	966 (12)	2930 (16)	8520 (3)	52 (3)	49 (4)	56 (4)	−4 (3)	4 (3)	3 (3)
C(2)	1729 (12)	3109 (16)	9181 (3)	49 (3)	57 (4)	63 (4)	5 (3)	−0 (3)	8 (3)
C(3)	4134 (12)	1994 (17)	9312 (3)	53 (3)	70 (4)	48 (3)	5 (3)	−2 (3)	3 (3)
C(4)	3667 (12)	120 (17)	9096 (3)	51 (4)	66 (4)	63 (4)	4 (3)	10 (3)	2 (4)
C(5)	2810 (13)	51 (16)	8440 (3)	55 (4)	64 (4)	59 (4)	6 (3)	6 (3)	7 (4)
C(6)	2027 (15)	−1714 (17)	8235 (3)	72 (4)	66 (4)	57 (4)	0 (4)	3 (3)	7 (4)
C(7)	2336 (12)	3892 (16)	7563 (3)	55 (3)	78 (5)	54 (4)	−6 (4)	6 (3)	0 (4)
C(8)	4821 (12)	4267 (18)	7228 (3)	54 (3)	80 (5)	62 (4)	−1 (4)	15 (3)	−6 (4)
C(9)	4364 (12)	4336 (17)	6549 (3)	52 (3)	79 (4)	61 (4)	−2 (4)	10 (3)	−1 (4)
C(10)	6883 (12)	4408 (17)	6194 (3)	53 (3)	75 (4)	64 (4)	1 (4)	10 (3)	−3 (4)
C(11)	6443 (12)	4417 (18)	5517 (3)	54 (3)	77 (5)	67 (4)	−1 (4)	18 (3)	0 (4)
C(12)	8973 (11)	4442 (16)	5157 (3)	50 (3)	70 (4)	69 (4)	−1 (4)	19 (3)	4 (4)
C(13)	8543 (12)	4402 (18)	4479 (3)	51 (3)	86 (5)	64 (4)	8 (4)	14 (3)	4 (4)
C(14)	11079 (11)	4403 (17)	4133 (3)	47 (3)	73 (4)	63 (4)	−1 (4)	12 (3)	−2 (4)
C(15)	10654 (12)	4368 (18)	3453 (3)	54 (3)	88 (5)	69 (4)	0 (4)	16 (3)	3 (4)
C(16)	13199 (14)	4320 (18)	3106 (3)	68 (4)	97 (6)	72 (5)	−8 (5)	22 (4)	4 (5)
O(1)	2974 (8)	3723 (14)	8186 (2)	50 (2)	69 (3)	48 (2)	−7 (2)	1 (2)	6 (2)
O(2)	2174 (9)	4854 (14)	9364 (2)	75 (3)	75 (4)	55 (3)	6 (3)	−12 (2)	−7 (3)
O(3)	4601 (10)	2003 (15)	9943 (2)	83 (3)	80 (4)	52 (2)	16 (3)	−11 (2)	−10 (3)
O(4)	6081 (7)	−818 (15)	9152 (2)	51 (2)	76 (3)	62 (3)	10 (2)	9 (2)	4 (2)
O(5)	552 (8)	1185 (14)	8359 (2)	46 (2)	66 (3)	59 (3)	2 (2)	3 (2)	4 (2)
O(6)	113 (9)	−2559 (14)	8585 (2)	56 (3)	59 (3)	82 (3)	−3 (2)	13 (2)	−5 (3)

[a] The expression is $T = \exp[-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl)]$.

crystal structure contains alternating layers of polar and nonpolar regions. The packing of the hydrocarbon portion of the molecules is not one of the commonly observed hydrocarbon packings, but rather a new type of long-chain hydrocarbon packing.

Experimental Section

Crystals of **1**, flat needles from anhydrous methanol, were kindly provided by C. H. Paul. The space group and lattice parameters were determined from Weissenberg and precession photographs and the lattice parameters refined by a least-squares fitting of diffractometer data for 12 reflections.

Crystal Data. $C_{16}H_{32}O_6$; mol wt = 320.4; $F(000) = 352$; monoclinic; $a = 5.153 \pm 0.002$ Å, $b = 7.626 \pm 0.004$ Å, $c = 22.125 \pm 0.007$ Å, $\beta = 90.95 \pm 0.04°$; $V = 869.3$ Å^3; $d_c = 1.220$ g cm^{-3} for $Z = 2$; $d_m = 1.22 \pm 0.01$ g cm^{-3} by flotation; linear absorption coefficient μ (Cu Kα) = 7.6 cm^{-1}; systematic extinctions: $0k0$ for k odd; space group $P2_1$ ($C_2{}^2$, no. 4).

A crystal measuring 0.5 × 0.25 × 0.06 mm was used for data collection. Intensity data were collected at room temperature with Cu Kα radiation on a Picker Corporation FACS-I four-circle diffractometer. An ω step scan technique designed by Cohen[5] was used employing 15 steps 0.04° apart and a counting time of 4 s for each step. Three standard reflections were monitored every 125 reflections, and no appreciable deterioration of the crystal was observed during data collection. Step data for each reflection was fitted to a Gaussian curve by the method of least-squares to produce background-corrected integrated intensities. Intensities for 1412 unique reflections were measured within the 2θ range 4 to 120°. The standard deviation of the intensity $\sigma(I_0)$ was assumed to be $[T + (0.05\,I_0)^2]^{1/2}$ where T is the total counts recorded during the scan and I_0 is the background-corrected integrated intensity. Those reflections which had background corrected intensities less than $4\sigma(I_0)$, 100 reflections in all, were treated as unobserved and assigned an intensity of $I_0 + 4\sigma(I_0)$. An empirical absorption correction was applied[6] and corrections were made for Lorentz-polarization effects.

Structure Determination and Refinement. The structure was solved by direct methods using MULTAN.[7] Normalized structure factors were calculated from the 1312 observed data and the 197 E values greater than 1.4 used to calculate an E map. The reflections used to fix the origin and enantiomorph were 2 1 6, 3 1 $\bar{4}$, and 2 2 13. The E map showed a nine-carbon portion of the hydrocarbon chain with the chain plane generally perpendicular to y. The structure solution was completed by tangent formula refinement based on the starting set of phases obtained from the chain fragment.

Least-squares refinement was carried out with the x-ray system of Stewart et al.[8] on an IBM 360 computer; tlhe quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$ where $w = \sigma^{-2}(F_o)$. On convergence of the refinement of the positions of the 22 atoms other than hydrogen, together with their isotropic temperature factors, the residual was 14.7%. Even though a difference map showed all of the hydrogen atoms along the hydrocarbon chain and four of the hydrogen atoms on carbon atoms of the sugar, all of the hydrogen atoms bonded to carbon were assigned ideal positions, and refinement continued for four cycles. The residual dropped to 10.3%, and a difference map was calculated to locate the hydrogen atoms bonded to oxygen atoms. Coordinates of these four hydrogen atoms were systematically determined as follows: A possible hydrogen atom position was calculated 1.02 Å from the oxygen atom with a C–O–H angle of 105°. This position was then rotated around the C–O bond at 5° intervals. The electron density at each of these positions was calculated by interpolation from the eight surrounding grid points. In addition, the distances and angles to possible hydrogen-bond acceptor atoms were calculated. With positions for these four hydroxyl hydrogen atoms now assigned, refinement continued. Hydrogen atoms were given the isotropic thermal parameters of the atoms to which they are bonded. Atoms other than hydrogen were given anisotropic temperature factors. Unobserved reflections were omitted from the refinement as were four strong, low-order reflections 001, 011, 10$\bar{2}$, and 021. After three additional cycles of refinement, the residual had dropped to 9.3% and parameter shifts were less than 0.5σ. The final atomic coordinates [with the D configuration at C(5)] are given in Tables I and II, observed and calculated structure factors have been deposited (see Supplementary Material).

Discussion of Results

Glucopyranose Ring. Figure 1 is a perspective view of the glucopyranose ring. The ring has a chair conformation ($^4C_1$) similar to that observed in other compounds containing the pyranose ring.[9] Bond distances and bond angles for the ring atoms (other than hydrogen) are given in Table III. The ring carbon–carbon bond distances in **1** are very similar to those in other glucopyranosides;[10-12] however, the exocyclic C(5)–C(6) bond distance is about 0.02 Å shorter than any so far observed. A shortening of the exocyclic C(5)–C(6) bond also occurs in 1-methyl α-D-glucopyranoside.[13] Fries et al.[10] have attributed this shortening either to the fact that the bond involves a primary and secondary carbon while the remainder of the ring carbon atoms are secondary carbons, or to thermal motion of the molecule. The latter explanation is more probable since

Table II. Fractional Coordinates ($\times 10^3$) of Hydrogen Atoms and Isotropic Temperature Factors ($\times 10^3$)[a]

Atom	x	y	z	U
H(C1)	−68	361	845	54
H(C2)	23	261	943	54
H(C3)	571	251	910	52
H(C4)	224	−42	935	55
H(C5)	439	46	819	52
H1(C6)	143	−166	780	65
H2(C6)	370	−252	826	65
H1(C7)	146	275	742	66
H2(C7)	103	490	752	66
H1(C8)	561	543	737	59
H2(C8)	619	329	733	59
H1(C9)	337	321	643	65
H2(C9)	330	539	646	65
H1(C10)	793	549	632	60
H2(C10)	803	331	631	60
H1(C11)	537	333	540	73
H2(C11)	538	551	541	73
H1(C12)	1005	552	528	58
H2(C12)	1008	334	529	58
H1(C13)	748	329	437	69
H2(C13)	747	548	436	69
H1(C14)	1216	549	425	59
H2(C14)	1218	331	426	59
H1(C15)	957	325	334	70
H2(C15)	958	544	333	70
H1(C16)	1436	541	322	76
H2(C16)	1435	323	324	76
H3(C16)	1297	430	266	76
H(O1)	129	558	903	63
H(O2)	450	69	1007	68
H(O3)	584	−170	951	57
H(O4)	−102	−157	874	64

[a] The expression used is $T = \exp(-8\pi^2 U \sin^2 \theta/\lambda^2)$.

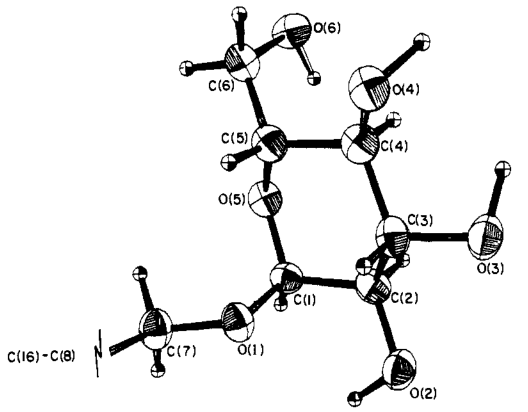

Figure 1. Perspective view of the sugar ring in **1** with the 1-decyl side chain omitted.

there seems no reason for the C(5)-C(6) bond to be shorter in the decyl derivative than it is in the methyl derivative.

The two ring C-O bond distances are markedly dissimilar while the anomeric C(1)-O(1) bond length is normal. This is in agreement with the observation that while free sugars have shortened anomeric bonds, glycosides substituted on the anomeric carbon do not have shortened anomeric bonds but instead show dissimilar O(5)-C(5) and O(5)-C(1) bond distances.[14,15] The anomeric bond is somewhat shorter, however, than the O-C bond to the side chain. The three exocyclic C-O bond distances, excluding the anomeric bond, have a mean value of 1.421 Å in good agreement with previously reported values.

Table III. Bond Distances (Å) and Angles (deg) in 1-Decyl α-D-Glucopyranoside[a]

Bond lengths			
C(1)-C(2)	1.515 (10)	O(1)-C(7)	1.419 (8)
C(2)-C(3)	1.527 (12)	C(7)-C(8)	1.516 (10)
C(3)-C(4)	1.525 (17)	C(8)-C(9)	1.519 (10)
C(4)-C(5)	1.511 (10)	C(9)-C(10)	1.529 (9)
C(5)-C(6)	1.474 (17)	C(10)-C(11)	1.511 (10)
C(5)-O(5)	1.459 (12)	C(11)-C(12)	1.540 (9)
O(5)-C(1)	1.393 (16)	C(12)-C(13)	1.513 (10)
C(1)-O(1)	1.416 (10)	C(13)-C(14)	1.525 (9)
C(2)-O(2)	1.408 (16)	C(14)-C(15)	1.519 (10)
C(3)-O(3)	1.412 (8)	C(15)-C(16)	1.530 (10)
C(4)-O(4)	1.439 (11)		
C(6)-O(6)	1.419 (11)		

Valence angles			
O(5)-C(1)-C(2)	111.7 (8)	C(1)-O(1)-C(7)	112.9 (5)
C(1)-C(2)-C(3)	109.3 (7)	O(1)-C(7)-C(8)	107.9 (5)
C(2)-C(3)-C(4)	109.8 (7)	C(7)-C(8)-C(9)	111.8 (5)
C(3)-C(4)-C(5)	112.1 (9)	C(8)-C(9)-C(10)	113.0 (5)
C(4)-C(5)-O(5)	108.5 (7)	C(9)-C(10)-C(11)	113.2 (5)
C(5)-O(5)-C(1)	114.6 (6)	C(10)-C(11)-C(12)	113.5 (5)
		C(11)-C(12)-C(13)	113.7 (5)
O(5)-C(1)-O(1)	112.7 (7)	C(12)-C(13)-C(14)	112.6 (5)
C(2)-C(1)-O(1)	106.5 (6)	C(13)-C(14)-C(15)	112.7 (5)
C(1)-C(2)-O(2)	113.6 (8)	C(14)-C(15)-C(16)	112.7 (5)
C(3)-C(2)-O(2)	110.1 (7)		
C(2)-C(3)-O(3)	108.0 (7)		
C(4)-C(3)-O(3)	109.8 (9)		
C(3)-C(4)-O(4)	107.9 (7)		
C(5)-C(4)-O(4)	107.7 (6)		
C(4)-C(5)-C(6)	113.7 (9)		
O(5)-C(5)-C(6)	106.8 (7)		
C(5)-C(6)-O(6)	115.9 (7)		

[a] Standard deviations are given in parentheses.

Table IV. A Comparison of Torsion Angles (deg) in the α-D-Glucopyranoside Rings of α-D-Glucose,[17] 1-Methyl α-D-Glucopyranoside,[13] and 1-Decyl α-D-Glucopyranoside[a]

Atoms	α-D-Glucose	1-Methyl α-D-glucopyranoside	1-Decyl α-D-glucopyranoside
O(5)C(1)-C(2)C(3)	54.1	58.2	56.5
C(1)C(2)-C(3)C(4)	−51.2	−55.6	−52.8
C(2)C(3)-C(4)C(5)	53.2	54.2	53.8
C(3)C(4)-C(5)O(5)	−57.5	−54.1	−54.1
C(4)C(5)-O(5)C(1)	62.2	58.0	58.3
C(5)O(5)-C(1)C(2)	−61.0	−60.1	−60.7
O(2)C(2)-C(1)O(1)	56.8	61.5	56.5
O(2)C(2)-C(3)O(3)	63.2	58.7	62.0
O(3)C(3)-C(4)O(4)	−65.4	−67.7	−69.1
O(4)C(4)-C(5)C(6)	62.9	64.3	68.7
O(5)C(5)-C(6)O(6)	−70.3	−73.5	−66.2
C(2)C(1)-O(1)C(7)	−163.2[b]	−175.6	−171.0
O(5)C(1)-O(1)C(7)	74.8[b]	63.0	66.2

[a] Zero angle is defined with front and rear bond superposed in projection down middle bond. Angle is positive if right-hand rotation of either bond is required for their superposition. [b] Calculated from the position of the hydrogen atom which corresponds to C(7).

The torsion angles in **1** are given in Table IV. The angles within the ring range from 53.4 to 61.1° and fall near the 55.8 to 61.7° range expected for an "ideal" sugar ring.[16] To see whether the long hydrocarbon chain at O(1) influences the ring conformation, the torsion angles are compared with the torsion angles observed for unsubstituted α-D-glucose[17] and 1-methyl

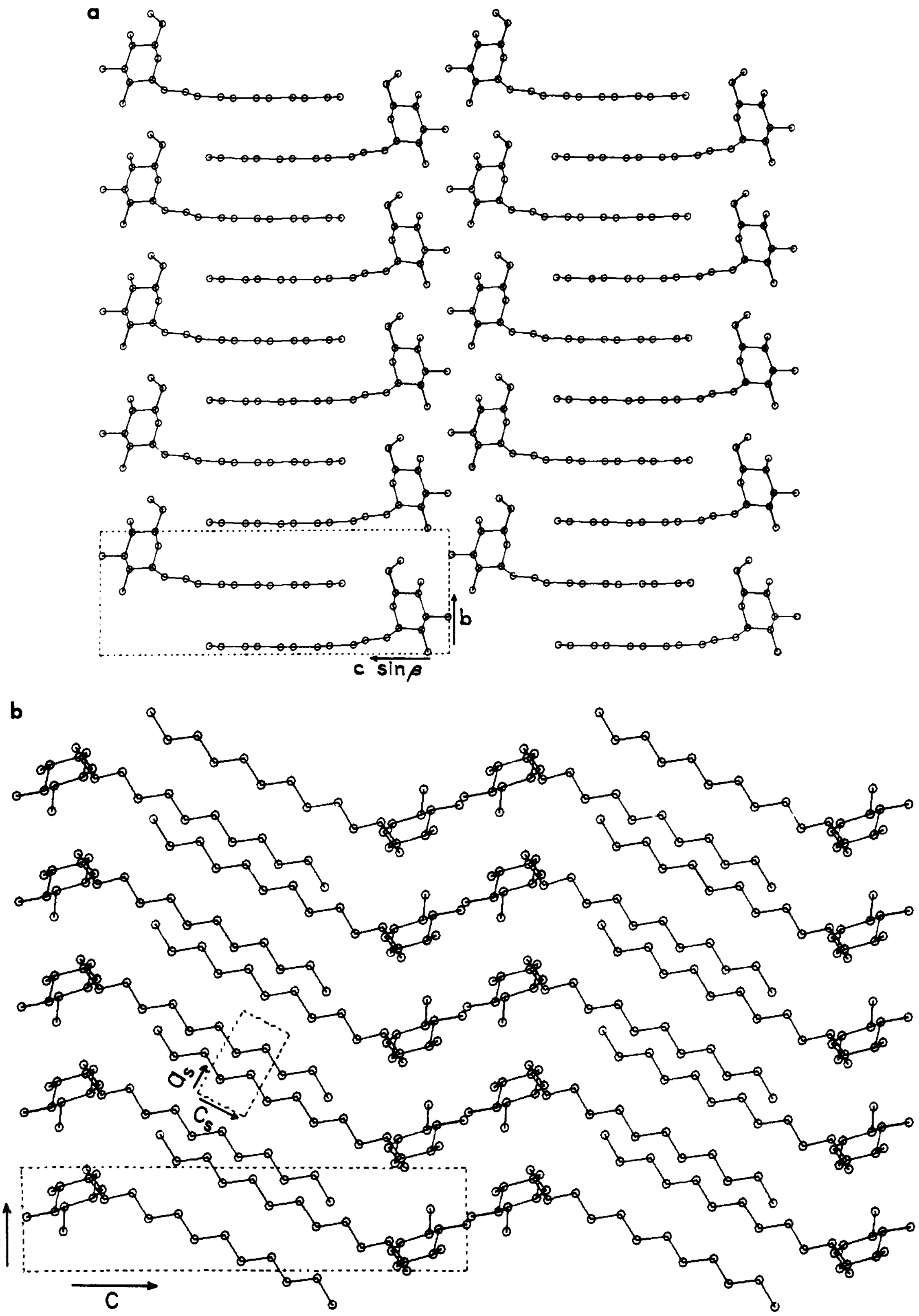

Figure 2. (a) Molecular packing projected along the *a* axis. The two bilayers shown extend outward from the page. (b) Molecular packing projected along *b*. The hydrocarbon subcell also appears in projection in this view. The subcell angle β_S, idealized to 90°, is actually 93°. Hydrogen atoms are not shown.

α-D-glucopyranoside.[13] The intra-ring torsional angles for the methyl and decyl derivatives are very similar and differ from the values for α-D-glucose by about the same amount and in the same direction; the largest difference (4°) is the torsion about the C(5)-O(5) bond. Torsion angles involving the extra-ring atoms of the substituted compounds differ by larger amounts up to 8°, this difference being in the exocyclic C(5)-C(6) bond, however. In the decyl sugar the O(2)C(2)-C(1)O(1) torsional angle (56.5°) is markedly less than the other decyl extra-ring torsional angles, an effect seen in glucose but not in the methyl sugar. These torsional angles indicate that the change from a methyl to a decyl substituent has little effect

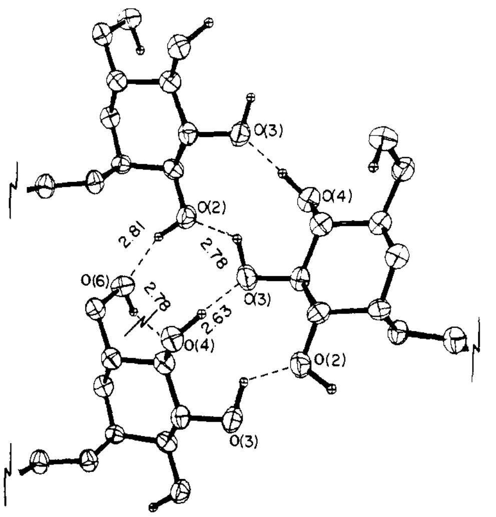

Figure 3. A closer view of Figure 2a showing hydrogen bonds linking the pyranoside heads of the molecules. The distances between oxygen atoms are indicated. The O(6)-H···O(4) hydrogen bond links two molecules separated out of the page along *a*. Hydrocarbon chains (not shown) lie horizontal.

Table V. Hydrogen-Bond Distances (Å) and Angles (deg) with Symmetry Code[a]

O-H(i)···O	O···O	H···O	O-H···O
O(2)-H···O(6)(ii)	2.81[b]	1.82	162
O(3)-H···O(2)(iii)	2.78[c]	2.20	113
O(4)-H···O(3)(iii)	2.63[c]	1.59	178
O(6)-H···O(4)(iv)	2.78[b]	1.85	151

[a] (i) x, y, z; (ii) $x, 1+y, z$; (iii) $1-x, y-\frac{1}{2}, 2-z$; (iv) $x-1, y, z$. [b] Hydrogen bonds *within* the polar surface (see text). [c] Hydrogen bonds bridging *across* two polar surfaces.

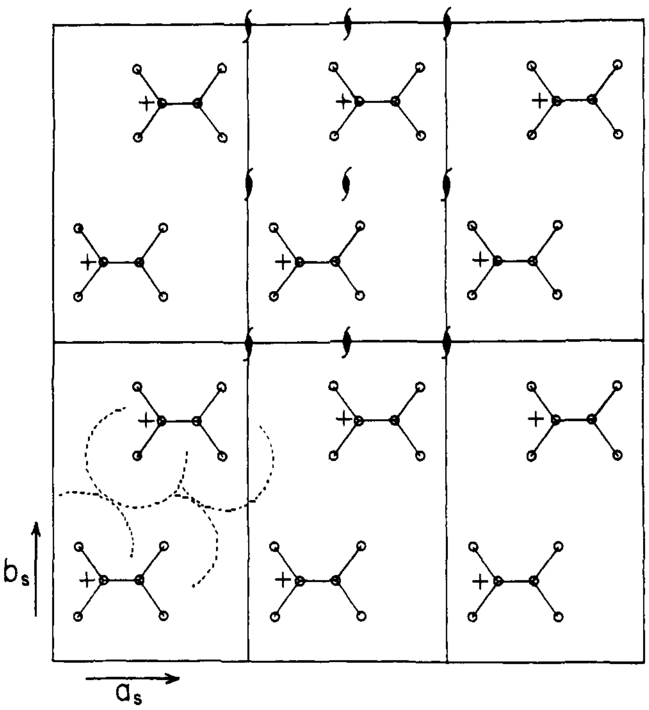

Figure 4. The idealized monoclinic subcell viewed along the hydrocarbon chain axis. Atom coordinates are given in the text. The CH_2 groups marked + are at the same height along c_s. The dotted circles indicate the expected intermolecular radius of a hydrogen atom, 1.17 Å.[20b]

on the conformation of the sugar ring, with changes occurring only in the exo- and extra-ring torsion angles.

Side Chain. The decyl side chain is fully extended and is generally trans to ring carbon C(2). Except for carbon atom C(7) nearest the ring, all carbon atoms in the chain are within 2° of the ideal trans configuration. The atom C(7) is 0.35 Å from the least-squares plane of the remaining chain carbon atoms C(8–16), of which none deviate more than 0.05 Å from their common plane. The average C–C bond distance in the chain is 1.522 Å, and the average bond angle is 113°. The ether angle at O(1) is 113°, which is 2° smaller than the angle at O(5) within the ring. A large twist (15°) about the O(1)–C(7) ether bond in the middle of the molecule may result from stresses imposed on the molecule by hydrogen bonding at one end and hydrocarbon packing at the other end.

Molecular Packing. The molecular arrangement in the crystal is shown in Figure 2. The polar sugar rings are bound together with hydrogen bonds while the decyl chains form a close hydrocarbon packing in which all the zig-zag chain planes are parallel (see below). The angle between the chain direction and the crystallographic *c* axis is 26° in the *ac* plane; the chain is nearly perpendicular to the *b* axis. This room temperature structure changes to a liquid crystalline structure at its mesophase transition point at 76 °C.[4]

Hydrogen Bonding. Hydrogen-bond dimensions are given in Table V. All of the hydrogen atoms belonging to the hydroxyl oxygen atoms are involved in hydrogen bonds, and each hydroxyl oxygen atom participates in two bonds; there are then eight hydrogen bonds per molecule (Figure 3). Two types of bond exist: four hydrogen bonds generally perpendicular to the chains hold the long molecules side-by-side to form a two-dimensional layer of sugar heads perpendicular to *c*; four other hydrogen bonds generally parallel to the chains bridge across two such sugar layers. Included in this latter set is the shortest (2.63 Å) and most linear (178°) of all the bonds, one between O(4) and O(3) of another ring.

Hydrocarbon Packing and Subcell. Long-chain hydrocarbons pack in a number of ways; Abrahamsson[18] and more recently Larsson[19b] have reviewed crystallographic studies of hydrocarbon chain packing. Kitaigorodskii[20] has analyzed possible stacking models of normal paraffins based on the requirements of close packing. The different kinds of packing have been described in terms of a "subcell" which describes the symmetry *only* of the hydrocarbon chain portion of a larger structure.[21] An averaging of all inter- and intra-chain distances is necessary, resulting in "idealized" subcell dimensions and symmetry. At least six different packing types have been found: $T_\parallel$, $M_\parallel$, $O_\parallel$, $O'_\parallel$, $O_\perp$, and $O'_\perp$, where symbols indicate the lattice symmetry of the subcells and whether the individual hydrocarbon chain *planes* are all parallel or whether every second chain plane is perpendicular to the planes of the others. The most widely occurring subcell is $O_\perp$, first described by Bunn,[22] with four methylene groups in an orthorhombic cell. Another common structure is $T_\parallel$ with two methylene groups in a triclinic subcell.[23] In both subcells the hydrocarbon chain *axes* are parallel, but in $O_\perp$ the chain plane of one molecule is perpendicular to the plane of the neighboring molecule; in $T_\parallel$ all chain planes are parallel.

All of the chain planes are parallel in the crystal structure of **1** (Figure 4), and the chain planes coincide to form equally spaced layers normal to the crystallographic *b* direction. Similar layers of hydrocarbon chain planes are observed in the $O'_\parallel$ packing of oleic acid[24] and in the $M_\parallel$ packing of 3-thiadodecanoic acid[25] and 1-monostearin.[19a] The parallel packing of the decyl chain planes differs from the $M_\parallel$ packing of the planes in 3-thiadodecanoic acid in the relationship between layers. In 3-thiadodecanoic acid a twofold screw axis is coincident with each chain axis, while in **1** a twofold screw axis is *between* chain axes rather than coincident with each axis.

The new subcell is outlined in Figure 2 and is best described as a distorted monoclinic cell (unique axis c_s) with idealized dimensions: $a_s = 4.64$ Å, $b_s = 7.63$ Å, $c_s = 2.54$ Å, and $\gamma_s = 90°$ with c_s lying along the chain direction and with b_s along b of the main cell. The space group is $P2_1/m$ ($C_{2h}{}^2$, no. 11) with four CH_2 groups per cell. The idealized subcell lattice with β_s set equal to 90° is shown in Figure 4. The fractional *xyz* coordinates of the two methylene groups in the asymmetric unit are:

C(+)	0.259	0.250	3/4
C	0.440	0.250	1/4
H(+)	0.132	0.359	3/4
H(+)	0.132	0.141	3/4
H	0.567	0.359	1/4
H	0.567	0.141	1/4

The volume per CH_2 group (22.4 $Å^3$) is 5% less than that observed in the other hydrocarbon chain packings mentioned above. The average value for the inter-chain hydrogen contacts calculated from these hydrogen positions is 2.38 Å.

Bilayer Structure. These long molecules crystallize easily to produce a bilayer structure in which the hydrocarbon chains interweave between two polar surfaces. The nature of the molecular packing invites speculation about which of two interactions is dominant in stabilizing the bilayer: the hydrogen-bonded head-to-head interactions along the surface, or the internal hydrophobic hydrocarbon interactions. Arguments can be made in support of either. For example, the importance of hydrogen bonding might be used to support the fact that the β anomer of **1** forms micelles less readily than **1**.[2] The hydrogen bonding in the bilayer structure (Figure 2) must in someway change if the sugar ring is moved to the β position of C(1); it is not certain the hydrocarbon packing must change.

We have observed that in **1** the hydrocarbon packing appears to be more "perfect" than the hydrogen-bonding network. That is, each hydrocarbon tail is within 1.5° of parallelism with its neighbors (Figure 2a); this parallelism is not required by space group symmetry. Further, the packing of chains is very close, giving a relatively small packing volume per CH_2 group. In contrast, most of the hydrogen bonds at the polar surface are severely bent from linearity. The single strong linear bond bridges *across* two bilayers rather than stabilizes head-to-head interactions *within* its own polar layer. Thus, in a real micelle this hydrogen bond either would not exist or would extend to a water molecule on the outside.

It should be cautioned that long-chain hydrocarbons can exist in several polymorphic modifications which correspond to different three-dimensional packings.[20b,26] This means that different hydrocarbon structures may differ by only small amounts in their free energies and that small stresses may be sufficient to form new packing structures. Thus, crystals of compound **1** assume a liquid crystalline structure when the temperature reaches 76 °C.[4] Isotropic melting does not occur until 138 °C. The packing of the hydrocarbon chains in membrane bilayers may well be influenced by similar stresses to produce new structures which differ from any so far studied crystallographically.

Supplementary Material Available: List of structure factors for 1-decyl α-D-glucopyranoside (10 pages). Ordering information is given on any current masthead page.

References and Notes

(1) This work was reported in part at a meeting of the American Crystallographic Association, March, 1975, Abstract B5. Financial support was provided by the National Institute of Allergies and Infectious Diseases (Grant No. AI-10925), U.S. Public Health Service. Computations were performed at the University of Connecticut Computer Center.

(2) G. M. Brown, P. Dubreuil, F. M. Ichhaporia, and J. E. Desnoyers, *Can. J. Chem.* **48**, 2525–2531 (1970).

(3) C. H. Paul, Ph.D. Thesis, University of Connecticut, Storrs, Conn., 1974.

(4) E. M. Barrall, Second New England Regional Liquid Crystal Conference, Harvard University, May, 1975.

(5) G. H. Cohen, National Institutes of Health, private communication, 1975.

(6) A. C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Crystallogr., Sect. A*, **24**, 351–359 (1968).

(7) G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. A*, **27**, 368–376 (1971).

(8) J. M. Stewart, G. J. Kruger, H. L. Ammon, C. Pickinson, and S. R. Hall, Technical Report TR-192, Computer Science Center, University of Maryland, 1972.

(9) G. Strahs, *Adv. Carbohydr. Chem.*, **25**, 53–107 (1970).

(10) D. C. Fries, S. T. Rao, and M. Sundaralingam, *Acta Crystallogr., Sect. B*, **27**, 994–1005 (1971).

(11) G. M. Brown and H. A. Levy, *Acta Crystallogr., Sect. B*, **29**, 790–797 (1973); J. C. Hanson, L. C. Sieker, and L. H. Jensen, *ibid.*, **29**, 797–808 (1973).

(12) D. C. Rohrer, *Acta Crystallogr., Sect. B*, **28**, 425–433 (1972).

(13) H. M. Berman and S. H. Kim, *Acta Crystallogr., Sect. B*, **24**, 879–904 (1968).

(14) H. M. Berman, S. S. G. Chu, and G. A. Jeffrey, *Science*, **157**, 1576–1577 (1967).

(15) G. A. Jeffrey, J. A. Pople, and L. Radom, *Carbohydr. Res.*, **25**, 117–131 (1972).

(16) S. H. Kim and G. A. Jeffrey, *Acta Crystallogr.*, **22**, 537–545 (1967).

(17) G. M. Brown and H. A. Levy, *Science*, **147**, 1038–1039 (1964).

(18) S. Abrahamsson, *Ark. Kemi*, **14**, 65–83 (1959).

(19) K. Larsson, (a) *Ark. Kemi*, **23**, 29–33 (1964); (b) *ibid.*, **23**, 35–56 (1964).

(20) A. I. Kitaigorodskii, (a) "Organic Chemical Crystallography", Consultants Bureau, New York, N.Y., 1957, pp 177–214; (b) "Molecular Crystals and Molecules", Academic Press, New York, N.Y., 1973, pp 48–62.

(21) V. Vand, *Acta Crystallogr.*, **4**, 104–105 (1951).

(22) C. W. Bunn, *Trans. Faraday Soc.*, **35**, 482–491 (1939).

(23) V. Vand and I. P. Bell, *Acta Crystallogr.*, **4**, 465–469 (1951).

(24) S. Abrahamsson and A. Westerdahl, *Acta Crystallogr.*, **16**, 404–409 (1963).

(25) S. Abrahamsson and I. Ryderstedt-Nahringbauer, *Acta Crystallogr.*, **15**, 1261–1268 (1962).

(26) V. Vand, *Acta Crystallogr.*, **7**, 697–700 (1954).