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CONFORMATION OF 1,2-*O*-(*S*)-(1-AMINOMETHYLETHYLIDENE)-α-D-GLUCOPYRANOSE AND 1,2-*O*-(*R*)-(1-*tert*-BUTOXYETHYLIDENE)-α-D-GLUCOPYRANOSE

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ABSTRACT

The crystal structures of 1,2-*O*-(*S*)-(1-aminomethylethylidene)-α-D-glucopyranose (**1**) and 1,2-*O*-(*R*)-(1-*tert*-butoxyethylidene)-α-D-glucopyranose (**2**) have been analysed by X-ray diffraction methods. The pyranoid rings in **1** and **2** have flattened $^4C_1$ conformations, the dioxolane ring in **1** has a half-chair $^1T_{O\text{-}1}$ conformation, and that in **2** a $^2T_{O\text{-}2}$ conformation distorted towards ^2E. The ^{1}H-n.m.r. spectra of **1** and **2** have been analysed by computer simulation. The computed best values of the vicinal coupling constants and the n.O.e. measurements can be interpreted in terms of a preponderant, distorted $^4C_1$ conformation in solution, although long-range H,H coupling and low-temperature ^{13}C-n.m.r. spectra suggest the presence of a conformational equilibrium.

INTRODUCTION

Numerous communications[1–12] have dealt with the conformation of 1,2-*O*-alkylidene-α-D-hexopyranoses both in the crystalline state and in solution. X-Ray crystallographic studies[7,8,10] have demonstrated that the conformation of the pyranoid ring of 3,4,6-tri-*O*-acetyl-1,2-*O*-ethylidene (*endo*-methyl) derivatives (**3**,**5**) of α-D-gluco- and α-D-allo-pyranose is a skew boat ($^OS_2$), whereas that of 3,4,6-tri-*O*-acetyl-1,2-*O*-(1-*tert*-butoxyethylidene)-α-D-galactopyranose (**6**) is a flattened chair ($^4C_1$), and the ^{1}H-n.m.r. spectra of these and other derivatives could be interpreted in terms of solution conformations similar to those in the solid state[10].

An X-ray crystallographic study of 1,2-*O*-(*S*)-(1-aminomethylethylidene)-α-D-glucopyranose hydroiodide (**1**-hydroiodide) indicated, however, that the conformation of the pyranoid ring in the solid state was a flattened chair and the ^{1}H-n.m.r. spectrum of **1** has been interpreted in terms of either a flattened chair[6] or a skew boat[2].

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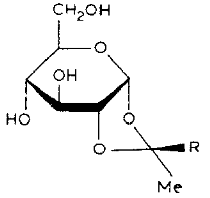
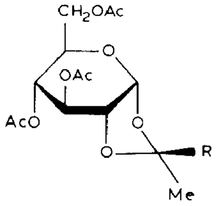
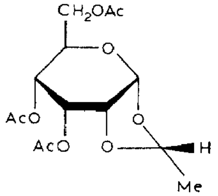
We now report the crystal structure and an n.m.r. study of **1** and 1,2-*O*-(*R*)-(1-*tert*-butoxyethylidene)-α-D-glucopyranose (**2**) as part of a series of studies on the conformation of pyranoid rings 1,2-*cis*-fused to five-membered rings[8-10,13].



1 R = CH_2NH_2
2 R = O^tBu



3 R = CN
4 R = OEt



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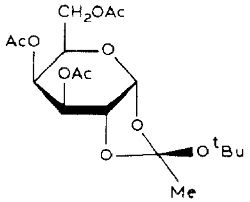

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RESULTS AND DISCUSSION

Fig. 1 shows **1** and **2** with the atomic numbering. The ring C–C bond-lengths in **2** (Table I) are shorter than those in **1**, which are similar to those in unsubstituted α-D-glucose[14]. Nevertheless, the values for **2** are within the range limits of the survey of pyranose rings given by Arnott and Scott[15]. The length of the bond C-5–C-6, which is usually lower than those for C–C bonds in the ring, is higher in **2** and near the upper limit of the above survey[15]. The C-5–O-5–C-1–O-1 sequence is similar in both compounds, the C-5–O-5 bond being longer than the C-1–O-5 bond with the C-1–O-1 bond intermediate. Angle C-5–O-5–C-1 is greater than angle O-5–C-1–O-1 and both are greater than tetrahedral. The angles C-4–C-5–C-6 and C-5–C-6–O-6 have increased values, whereas the value of the angle O-5–C-5–O-6 is decreased. The dioxolane ring in **1** has the usual values for bond lengths and angles[16,17].

The pyranoid rings in **1** and **2** have $^4C_1$ chair conformations flattened around the dioxolane ring fusion (Table II), in contrast to the $^{o}S_2$ skew conformation of 3,4,6-tri-*O*-acetyl-1,2-*O*-alkylidene-α-D-glucopyranoses in the solid state[7,8]. The conformation of **1** is similar to that[6] of **1**-hydroiodide and the conformation of **2** is similar to that[10] of **6**. The dioxolane ring in **1** has a $^1T_{O\text{-}1}$ half-chair conformation, whereas in **2** the half-chair $^2T_{O\text{-}2}$ is distorted towards an envelope ^2E. This situation produces different conformations for the C-8 and X substituents (see Table I for X

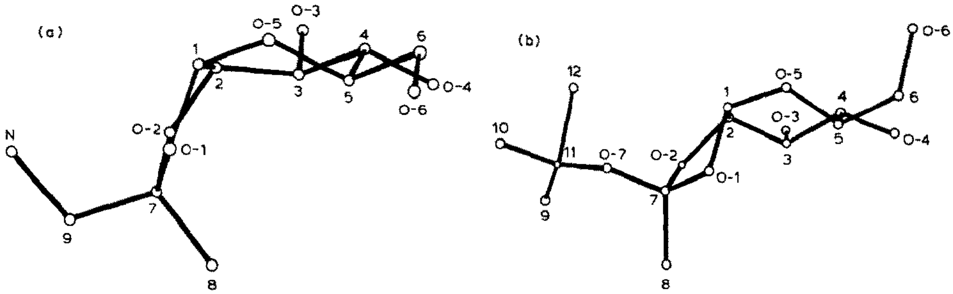

Fig. 1. The molecular structure with the atomic numbering for (*a*) **1** and (*b*) **2**.

and Y definitions, and see also torsion angles C-2/C-1–O-2/O-1–C-7–C-8/X in Table III. The different relative situations of the X-substituents are described by the torsion angles C-2–C-7–X–Y, O-1–C-7–X–Y, and O-2–C-7–X–Y. In Table III, the vicinal proton torsion-angles are also given.

A Table giving the H-bonding characteristics in both compounds has been deposited as supplementary material along with a Figure comparing the crystal packing of **1** with that of **1**-hydroiodide[6].

The ^{1}H-n.m.r. data for **1–3** are given in Table IV. The ^{1}H-n.m.r. spectra were analysed iteratively and the computed best values of the chemical shifts and coupling constants are given in Table IV, which also includes the values previously determined[10] for **3**. Table V gives the ^{13}C chemical shifts of **2**, which were assigned after selective irradiation in the proton spectrum.

The $J_{H,H}$ values are dependent on the solvent. The values of $J_{2,3}$ and $J_{3,4}$ are higher than those for **3**, the spectrum of which has been interpreted[2,9,10] as indicative of a major $^oS_2$ conformation in solution. The positive long-range $J_{2,4}$ coupling is only present in the spectrum of **2** in CD_3OD and this has been previously taken to indicate a planar arrangement of H-2 and H-4, and hence of a $^oS_2$ major conformation for the pyranoid ring in 3,4,6-tri-*O*-acetyl-1,2-*O*-alkylidene derivatives of α-D-allopyranose and α-D-glucopyranose[9,10]. Estimation of the vicinal-proton torsion angles from the vicinal couplings, using the generalised Karplus equation which takes into account the electronegativity and orientation of the substituents[18], is given in Table VI. The values shown are indicative of a major, flattened $^4C_1$ conformation of **1** in solution, similar to that found in the solid state; the flattening of the ring causes a decrease in the $J_{2,3}$ and $J_{3,4}$ values and hence the lowering of the dihedral angle. The spectrum of **2** in $CDCl_3$ could also be interpreted in terms of a flattened $^4C_1$ conformation, the axial–axial relationship of H-2,3 and H-3,4 being closer than in **1** in the resulting conformation. However, the spectrum of **2** in CD_3OD showed a large and positive long-range coupling between H-2 and H-4 indicative of a conformer with H-2,4 in planar orientation, although the values of $J_{2,3}$ and $J_{3,4}$ were similar to those for a solution in $CDCl_3$. The spectrum of **2** in 1:1 CD_3OD–$(CD_3)_2CO$ was very similar to that for CD_3OD. The

TABLE I

BOND DISTANCES (Å) AND BOND ANGLES (°)[a] FOR COMPOUNDS **1** AND **2**

Bond	**1**	**2**	*Angle*	**1**	**2**
Pyranoid ring					
C-1–C-2	1.533(4)	1.518(15)	C-1–C-2–C-3	117.5(2)	115.4(6)
C-2–C-3	1.534(3)	1.526(11)	C-2–C-3–C-4	114.7(2)	109.8(9)
C-3–C-4	1.522(4)	1.518(12)	C-3–C-4–C-5	110.7(2)	108.4(6)
C-4–C-5	1.526(4)	1.506(12)	C-4–C-5–O-5	108.2(2)	107.7(5)
C-5–O-5	1.439(2)	1.438(10)	C-2–C-1–O-5	115.9(2)	115.5(6)
C-1–O-5	1.393(3)	1.389(10)	C-1–O-5–C-5	115.7(2)	115.8(8)
Substituents					
C-3–O-3	1.415(4)	1.439(10)	C-2–C-3–O-3	107.0(2)	108.4(5)
C-4–O-4	1.415(3)	1.432(10)	C-4–C-3–O-3	111.1(2)	111.2(5)
C-6–O-6	1.408(4)	1.418(13)	C-3–C-4–O-4	105.9(2)	112.6(9)
C-5–C-6	1.515(4)	1.539(13)	C-5–C-4–O-4	112.0(2)	112.0(6)
			C-4–C-5–C-6	112.0(2)	114.6(6)
			O-5–C-5–C-6	107.1(2)	104.4(9)
			C-5–C-6–O-6	114.1(2)	112.7(6)
Dioxolane ring					
C-1–C-2	1.533(4)	1.518(15)	O-1–C-1–C-2	104.7(2)	101.5(9)
C-2–O-2	1.430(3)	1.459(10)	C-1–C-2–O-2	103.8(2)	102.6(6)
O-2–C-7	1.429(4)	1.405(8)	C-2–O-2–C-7	109.0(2)	107.1(7)
C-7–O-1	1.431(4)	1.392(11)	O-2–C-7–O-1	106.2(2)	107.8(5)
O-1–C-1	1.420(3)	1.425(10)	C-7–O-1–C-1	110.6(2)	104.7(5)
			O-5–C-1–O-1	111.4(2)	109.7(5)
			O-5–C-1–C-2	116.9(2)	115.5(6)
			C-3–C-2–O-2	111.2(2)	108.4(9)
			C-3–C-2–C-1	117.5(2)	115.4(6)
Aminomethylethylidene and butoxyethylidene substituents					
C-7–C-8	1.520(3)	1.508(18)	C-8–C-7–X	111.1(2)	111.8(6)
C-7–X	1.530(3)	1.403(9)	C-7–X–Y	114.4(2)	125.2(7)
X–Y	1.458(3)	1.465(8)	O-1–C-7–C-8	109.9(2)	107.6(6)
Y–C-9		1.491(20)	O-2–C-7–C-8	112.3(2)	110.3(10)
Y–C-10		1.501(18)	O-1–C-7–X	110.0(2)	105.7(9)
Y–C-12		1.526(15)	O-2–C-7–X	107.1(2)	113.3(5)
			X–Y–C-9		114.6(8)
			X–Y–C-10		102.4(8)
			X–Y–C-12		107.6(7)
			C-9–Y–C-10		111.7(10)
			C-10–Y–C-12		109.3(12)
			C-9–Y–C-12		110.8(10)

[a] E.s.d. values are given in parenthesis; X = C-9 and O-7, Y = N and C-11 for **1** and **2**, respectively.

^{13}C spectrum in this solvent mixture was recorded at temperatures down to $-120°$. As the temperature decreased, the peaks assigned to the carbons in the pyranoid ring gradually broadened but no coalescence temperature was reached. On the other hand, n.O.e. experiments with **2** in CD$_3$OD indicated the proximity of the *endo*-methyl group to H-5 (4%) and H-3 (5%), as expected for a major $^4C_1$ confor-

TABLE II

RING TORSION ANGLES (°)

Angles	*Compounds*			
	1	**2**	**1**-*Hydroiodide*	**6**
Pyranoid ring				
O-5–C-1–C-2–C-3	20.3(2)	33.1(9)	15.7(27)	35.7(12)
C-1–C-2–C-3–C-4	−19.7(2)	−39.7(7)	−23.8(25)	−46.7(11)
C-2–C-3–C-4–C-5	39.9(2)	56.4(8)	50.2(21)	59.2(10)
C-3–C-4–C-5–O-5	−61.2(2)	−66.7(8)	−66.5(19)	−61.5(9)
C-4–C-5–O-5–C-1	65.2(2)	61.3(6)	59.2(20)	53.7(10)
C-5–O-5–C-1–C-2	−44.0(2)	−44.3(9)	−37.0(24)	−40.2(11)
Dioxolane ring				
O-2–C-2–C-1–O-1	20.3(2)	32.2(5)	11.8(21)	32.7(9)
C-2–C-1–O-1–C-7	−9.3(2)	−40.6(6)	3.7(21)	−38.3(9)
C-1–O-1–C-7–O-2	−5.5(2)	34.3(6)	−18.0(20)	29.2(9)
C-1–C-7–O-2–C-2	19.4(2)	−12.5(8)	24.8(19)	−7.4(9)
C-7–O-2–C-2–C-1	−24.5(2)	−12.6(6)	−23.9(21)	−15.7(9)

TABLE III

SELECTED TORSION ANGLES (°)[a] INCLUDING PROTON LATERAL ANGLES

Angle	*Compound*	
	1	**2**
H-1–C-1–C-2–H-2	21(3)	23(7)
H-2–C-2–C-3–H-3	−136(3)	−152(7)
H-3–C-3–C-4–H-4	163(3)	−174(6)
H-4–C-4–C-5–H-5	179(3)	169(5)
H-5–C-5–C-6–H-6	−165(3)	60(6)
H-5–C-5–C-6–H-6′	75(3)	−56(7)
C-8–C-7–X–Y	−176.1(2)	−90.8(9)
O-1–C-7–X–Y	62.0(3)	152.4(6)
O-2–C-7–X–Y	−53.0(3)	34.6(10)
C-2–O-2–C-7–C-8	−100.8(2)	−129.6(7)
C-2–O-2–C-7–X	137.0(2)	104.2(7)
C-1–O-1–C-7–C-8	116.2(2)	153.2(7)
C-1–O-1–C-7–X	−121.1(2)	−87.2(6)

[a] E.s.d. values given in parenthesis; X = C-9 and O-7, Y = N and C-11 for **1** and **2**, respectively.

mation in solution. Thus, the major conformation of the pyranoid ring in **1** and **2** is a flattened $^4C_1$ similar to those found in the solid state, although the spectra of **2** in CD_3OD and in 1:1 CD_3OD–$(CD_3)_2CO$ suggest the presence of a skew conformer.

The above results show that the conformation of the pyranoid ring of these D-glucopyranose derivatives, both in the crystalline solid and in solution, is a flattened $^4C_1$ when the hydroxyl groups are unsubstituted, and $^oS_2$ in the acetylated

TABLE IV

^{1}H-N M R DATA[a] FOR **1–3** AT 360 MHz

Parameter	*Compound*			
	1[a]	**2**[b]		**3**[c,10]
Chemical shift (δ)				
H-1	5.649	5.512	5.690	5.803
H-2	4.114	4.101	4.318	4.390
H-3	3.842	3.738	3.993	5.213
H-4	3.468	3.386	3 776	4.916
H-5	3.702	3.468	3.615	3.906
H-6	3.703	3.543	3.841	4.193
H-6′	3.798	3.675	3.839	4.193
Coupling constant (Hz)				
$J_{1,2}$	4.9	5.1	5.1	5.2
$J_{1,3}$	−0.3	−0.4	−0.3	−0.4
$J_{1,5}$	−0.6	−0.6	−0.6	−0.7
$J_{2,3}$	4.8	3.9	4.0	3.0
$J_{2,4}$	0	0.9	0	0.9
$J_{3,4}$	6.1	4.2	4.1	2.8
$J_{4,5}$	8.7	9.3	8.5	9.5
$J_{5,6}$	5.5	5.9	3.1	—
$J_{5,6'}$	3.0	2 5	2 5	—
$J_{6,6'}$	−12.5	−11.9	−11.5	—

[a]CD_3OD. [b]Left-hand column for CD_3OD, right-hand column for $CDCl_3$. [c]In $CDCl_3$.

TABLE V

^{13}C-CHEMICAL SHIFT DATA[a] FOR **2**

Chemical shift (p.p.m.)	*Chemical shift (p.p.m.)*
121.93 C-7	74.05 C-3
98.44 C-1	70.40 C-4
77.65 C-2	63.16 C-6
75.45 C-11	30.49 Methyl groups
74.64 C-5	26.42 C-8

[a]In 1:1 CD_3OD–$(CD_3)_2CO$.

TABLE VI

VICINAL-PROTON TORSION ANGLES (°) AS DETERMINED FROM THE $J_{H,H}$ VALUES[20]

Angle	*Compound*		
	1[a]	**2**[b]	
H-1–C-1–C-2–H-2	39	37	37
H-2–C-2–C-3–H-3	−142(−55)	−136(−61)	−137(−60)
H-3–C-3–C-4–H-4	152(45)	140(59)	140(59)
H-4–C-4–C-5–H-5	159	167	157

[a]CD_3OD. [b]Left-hand column for CD_3OD, right-hand column for $CDCl_3$.

TABLE VII

CRYSTAL STRUCTURE PARAMETERS AT ROOM TEMPERATURE

Crystal data		
Formulae	$C_9H_{17}NO_6$ (**1**)	$C_{12}H_{22}O_7$ (**2**)
Crystal colour, habit, and size	Transparent, colourless, parallepipedic 0.36 × 0.21 × 0.06 mm	Same with dimensions: 0.27 × 0.22 × 0.35 mm
Symmetry	Monoclinic $P2_1$	Orthorhombic $P2_12_12_1$
Unit-cell dimensions (Å)	$a = 9.6926(5)$, $b = 8.2376(4)$, $c = 7.0159(3)$ $\beta = 105.997\ (4)°$	$a = 19.3634(11)$, $b = 12.0554(3)$, $c = 5.8866(1)$
Packing parameters	$V = 538.48(3)$ Å^3; $Z = 2$; $D_c = 1.450$ Mg.m^{-3} $M = 235.2$	$V = 1374.13(17)$ Å^3; $Z = 4$; $D_c = 1.345$ Mg.m^{-3} $M = 278.3$
Experimental data		
Technique	Four-circle Philips PW 1100 diffractometer; bisecting geometry	
Collection mode	$\omega/2\theta$; θ(Max.-Cu) = 67°	Same
No. of data collected	1037 independent 1026 observed; $2\sigma_c(I)$ criterion	723 independent 559 observed; $2\sigma_c(I)$ criterion
Stability from two standards	Monitored every 90 min; no variation	Same; 47% decay in 17 h
Solution and refinement		
Solution mode	MULTAN[25]	
Refinement mode	Least squares on F's, observed data only.	Full/2-blocks matrix.
Parameters	212 variables. About 5 reflex/variable. Final max. shift/error = 0.04	255 variables. About 2.2 reflex/variable. Final max. shift/error = 1.01
ω-Scheme	Empirical, to give no trends in $\langle\omega\Delta^2\rangle$ *vs.* $\langle F_0\rangle$ or $\langle \sin\theta/\lambda\rangle$	
Max. and min. thermal values	U_{11}(O-6) = 0.063, U_{11}(C-1) = 0.019 Å^2	U_{33}(C-12) = 0.151, U_{33}(O-5) = 0.023 Å^2
Difference synthesis	Final noise ±0.20 eÅ^3	Final noise ±0.14 eÅ^3
Final R and R_ω (obs. reflections)	0.033 and 0.029	0.039 and 0.046
Atomic scattering factors	From International Tables[23]	
Computing	X-Ray 70 System[24] on a UNIVAC 1100/80	

derivatives. The X-ray crystallographic study of **1** also indicates that crystallisation as the hydroiodide does not invert the solid state conformation. The n.m.r. study indicates that the major conformation of the pyranoid ring in solution must be a distorted chair, and the highly parametrised method described by Altona and Haasnoot[19] to calculate vicinal $J_{H,H}$ values in pyranoses gives couplings very different from those observed. These differences could be due to ring distortions[20]. However, it is possible that there is a minor contribution of skew forms in some solvents, giving rise to positive, long-range $J_{2,4}$ couplings.

EXPERIMENTAL

Materials. — 1,2-*O*-(*S*)-(1-Aminomethylethylidene)-α-D-glucopyranose (**1**) and 1,2-*O*-(*R*)-(1-*tert*-butoxyethylidene)-α-D-glucopyranose (**2**) were prepared by known procedures[21,22].

*X-Ray measurements**. — The characteristics of the crystal used for the data collection and those of the structure solution and refinement are given in Table VII. All hydrogen atoms were located by difference Fourier synthesis. Compound **2** decomposed readily and the sample was sealed into a Lindemann capillary. In spite of precautions, the rate of decay was fairly high and collection was stopped when about half the scheduled data had been collected.

N.m.r. data. — The ^{1}H-N.m.r. spectra (internal Me_4Si) were recorded at 360 MHz with a Bruker WP-360 spectrometer. Analyses were performed by using a PANIC program. The experimental and calculated spectra from the resulting best values matched satisfactorily. The ^{13}C-n.m.r. spectra (internal Me_4Si) were recorded at 75 MHz with a Varian XL-300 spectrometer.

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Supplementary material.* — Tables with final fractional co-ordinates for all atoms, thermal parameters, bond lengths and angles, the whole set of torsion angles, and the geometric characteristics of the H-bonds, a Figure comparing the packing differences between **1 and its hydroiodide, and the lists of observed and calculated structure factors for both compounds have been 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/307/*Carbohydr. Res.*, 139 (1985) 65–73.

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