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Conformation of 1,2-*O*-Alkylidene-α-D-hexopyranoses. Triacetylated Derivatives of D-Allose, D-Glucose, and D-Galactose

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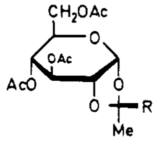
The crystal and molecular structures of 3,4,6-tri-*O*-acetyl-1,2-*O*-(*R*)-ethylidene-α-D-allopyranose (**5**) and 3,4,6-tri-*O*-acetyl-1,2-*O*-(*R*)-(1-*tert*-butoxyethylidene)-α-D-galactopyranose (**6**) have been determined, and the conformation of the pyranose and dioxolane rings are compared with those found for 3,4,6-tri-*O*-acetyl-1,2-*O*-(*S*)-(1-cyanoethylidene)-α-D-glucopyranose (**1**), the hydroiodide of 1,2-*O*-(*S*)-(1-aminoisopropylidene)-α-D-glucopyranose (**2**) and 3,4,6-tri-*O*-acetyl-1,2-*O*-(*S*)-(1-ethoxyethylidene)-α-D-glucopyranose (**3**). The solid-state conformation of the pyranose ring of **5** can be described as skew ($^3S_5$) and that of **6** as flattened chair ($^4C_1$). The ^{1}H NMR spectra of compounds **3**, **5**, **6**, and 3,4,6-tri-*O*-acetyl-1,2-*O*-(*R*)-(1-*tert*-butoxyethylidene)-α-D-glucopyranose (**7**) have been analyzed by iterative computer methods, and the computed best values of the coupling constants have been interpreted in terms of skew ($^3S_5$) average solution conformations for the D-gluco (**3** and **7**) and D-allo (**5**) derivatives and a distorted chair ($^4C_1$) conformation for the D-galacto compound. These assignments have been corroborated by NOE experiments on various derivatives.

The conformational analysis of six-membered rings fused to a dioxolane ring to form a bicyclo[4.3.0] system has been a subject of interest for several years. This feature is frequently encountered in carbohydrate chemistry, and the subject has been discussed in several reviews and articles.[1-3] There has been some uncertainty as to the effect of a 1,2-cis-fused dioxolane ring on the conformation of the glucopyranose ring of 1,2-*O*-alkylidene-α-D-glucopyranose derivatives. Thus Coxon and Hall,[4] on the basis of ^{1}H NMR data, assigned a skew conformation to the hexopyranose ring of 3,4,6-tri-*O*-acetyl-1,2-*O*-(*S*)-(1-cyanoethylidene)-α-D-glucopyranose (**1**) and some derivatives thereof which included 1,2-*O*-(*S*)-(1-aminoisopropylidene)-α-D-glucopyranose (**2**) (Chart I). Lemieux and Morgan,[5] however, deduced a flattened-chair conformation for the hexopyranose ring of 3,4,6-tri-*O*-acetyl-1,2-*O*-(*S*)-(1-ethoxyethylidene)-α-D-glucopyranose (**3**) and some related ortho esters from similar NMR evidence, and on the same basis flattened chair conformations have been reported for 1,2-*O*-(2-butylidene)-α-D-glucopyranose and related acetals[6] and for 3,4,6-tri-*O*-acetyl-1,2-*O*-(2-tetrahydrofuranylidene)-α-D-glucopyranose.[7] An X-ray crystallographic study of the hydroiodide of compound **2**[8] indicated that the conformation of the glucopyranose ring in the solid state could be described as a flattened chair. The crystal and molecular structure of ortho ester **3**[9,10] demonstrated, on the other hand, that the conformation of the glucopyranose ring might be better described as a skew boat.

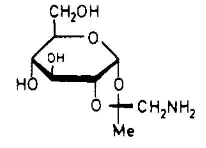
Chart I



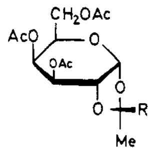
1 R=CN

3 R=OEt

7 R=O-*t* Bu

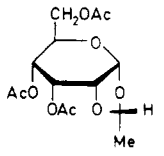


2



4 R=CN

6 R=O-*t* Bu



5

As part of a study of the reaction of acetobromoglucose and acetobromogalactose with metallic cyanides,[11-13] we have recently reported[11,14] the crystal and molecular structure of nitrile **1** and have found a nonchair conformation for the glucopyranose ring as previously proposed by Coxon and Hall[4] for this compound in solution and which is very similar to that reported for ortho ester **3** in the solid state.[9,10] The analysis of the ^{1}H NMR spectrum of nitrile **1** by an iterative method[13] has also shown that the average conformation of **1** in solution could be very similar to that found in the crystal while a similar analysis of the D-galactopyranose analogue (**4**) seemed to indicate[13] a distorted chair conformation of the galactopyranose ring. Skew and distorted chair conformations in solution have

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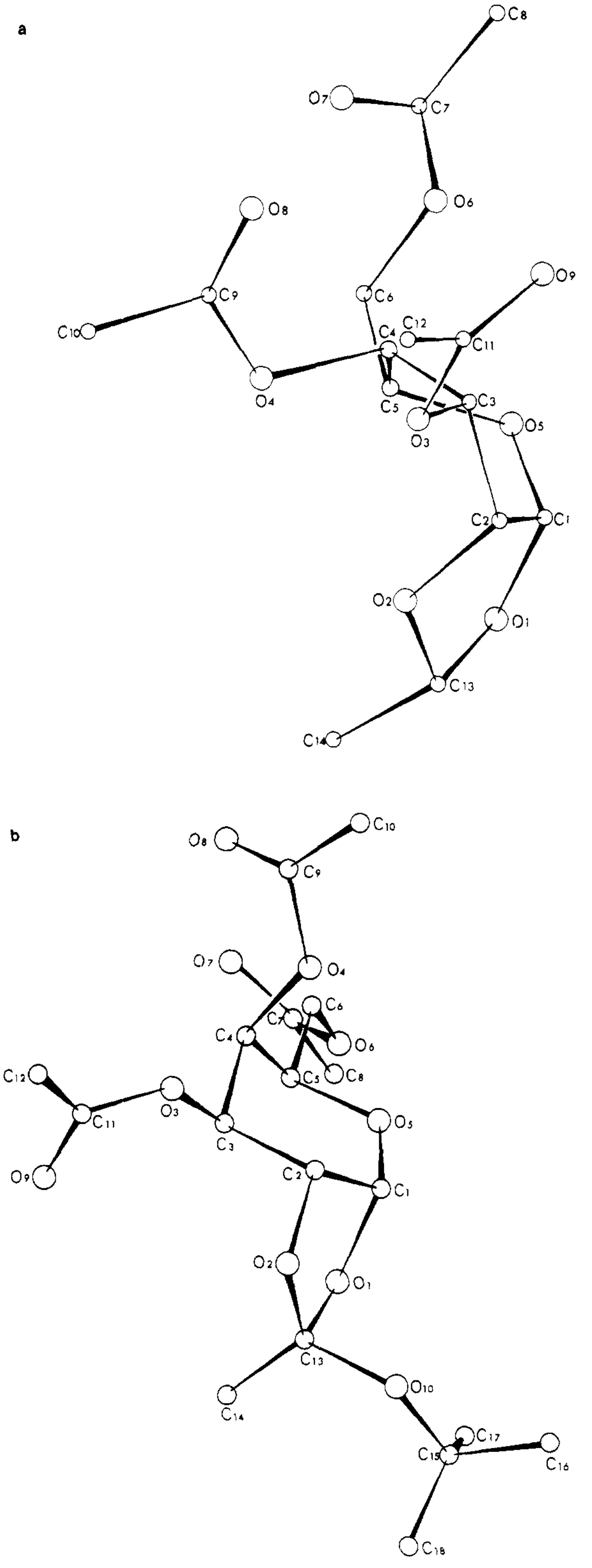

Figure 1. (a) Perspective view of 3,4,6-tri-*O*-acetyl-1,2-*O*-(*R*)-ethylidene-α-D-allopyranose (**5**). (b) Perspective view of 3,4,6-tri-*O*-acetyl-1,2-*O*-(*R*)-(1-*tert*-butoxyethylidene)-α-D-galactopyranose.

previously been assigned to 3,4,6-tri-*O*-acetyl-1,2-*O*-[1-(*tert*-butylperoxy)ethylidene]-α-D-gluco- and -galactopyranoses, respectively, by Schulz et al.[15] on the basis of the observed coupling constants in the ^{1}H NMR spectra.

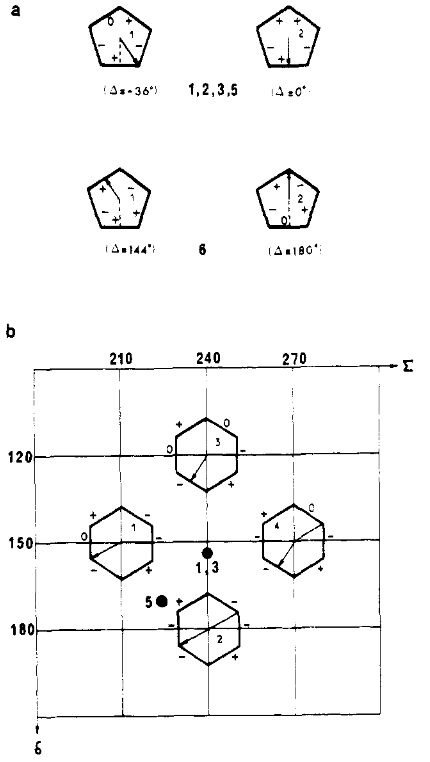

Figure 2. Nearest relevant forms for the conformations analyzed: (a) dioxolane; (b) pyranose rings.

As a contribution to the knowledge of the conformational effect of 1,2-cis-fused dioxolane rings on pyranose rings we report in this paper the crystal and molecular structure of 3,4,6-tri-*O*-acetyl-1,2-*O*-(*R*)-ethylidene-α-D-allopyranose (**5**) and 3,4,6-tri-*O*-acetyl-1,2-*O*-(*R*)-(1-*tert*-butoxyethylidene)-α-D-galactopyranose (**6**) and compare the conformations of these compounds with those found for the D-galactopyranose derivatives **1**,[14] the hydroiodide[8] of **2**, and **3**.[9,10] On the other hand we have analyzed the ^{1}H NMR spectra of compounds **5** and **6** and the D-glucopyranose derivatives **3** and **7** by iterative computer methods. The coupling constants deduced have been used with Karplus-type equations, as employed by Coxon,[17] Durette and Horton,[18] and Forrest[19] to estimate the torsion angles between adjacent protons. On the basis of these angles and NOE experiments, the average solution conformations of these derivatives have been determined.

Results and Discussion

Perspective views of 3,4,6-tri-*O*-acetyl-1,2-*O*-(*R*)-ethylidene-α-D-allopyranose (**5**) and 3,4,6-tri-*O*-acetyl-1,2-*O*-(*R*)-(1-*tert*-butoxyethylidene)-α-D-galactopyranose (**6**) are given in Figure 1a,b and the most relevant torsion angles, compared with those found for compounds **1**[14] and **3**[10] and for the hydroiodide of **2**,[8] are given in Table I. The conformations of the pyranose and dioxolane rings have been studied by following the criteria of Cano[20] and Altona,[21] respectively (Tables II and III).

The conformation of the dioxolane ring in all compounds but the D-galacto derivative **6** (see Figure 2a) can be described as almost an envelope at O(2) (relevant form with

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Table I. Experimental Torsion Angles (in Degrees) for the Pyranose and Dioxolane Rings

atoms	compd 1[14]	2 (hydroiodide)[8]	3[10]	5	6
	Pyranose Ring				
O(5)-C(1)-C(2)-C(3) = ϕ_0	−16.5	15.7	−15.9	−19.6	35.7
C(1)-C(2)-C(3)-C(4) = ϕ_1	42.4	−23.8	42.0	55.1	−46.7
C(2)-C(3)-C(4)-C(5) = ϕ_2	−14.9	50.2	−12.9	−30.7	59.2
C(3)-C(4)-C(5)-O(5) = ϕ_3	−38.7	−66.5	−40.2	−27.5	−61.5
C(4)-C(5)-O(5)-C(1) = ϕ_4	69.7	59.2	72.3	66.6	53.7
C(5)-O(5)-C(1)-C(2) = ϕ_5	−39.8	−37.0	−42.0	−40.8	−40.2
	Dioxolane Ring				
C(2)-O(2)-C(13)-O(1) = ϕ_0	−37.9	24.8	−33.3	−38.8	−7.4
O(2)-C(13)-O(1)-C(1) = ϕ_1	26.5	−18.0	23.0	25.5	29.2
C(13)-O(1)-C(1)-C(2) = ϕ_2	−4.8	3.7	3.8	−2.9	−38.3
O(1)-C(1)-C(2)-O(2) = ϕ_3	−16.8	11.8	−16.7	−20.4	32.7
C(1)-C(2)-O(2)-O(13) = ϕ_4	32.8	−23.9	31.0	35.9	−15.7

Table II. Conformational Parameters for the Pyranose Rings[a] and for the Dioxolane Rings[b] (All Values in Degrees)

parameters	compd 1	2 (hydroiodide)	3	5	6
	Pyranose Ring				
τ_m	12.4	42.1	14.0	4.9	49.5
q	55.5	26.2	56.3	60.5	13.4
$\Sigma/2$	119.8	165.9	119.9	112.9	195.1
$\delta/2$	77.1		75.6	85.4	
	Dioxolane Ring				
ϕ_m	−38.4	25.2	−34.6	−39.8	−38.4
Δ	−17.8	−20.8	−31.1	−26.3	157.8

[a] After Cano, Foces-Foces, and García-Blanco.[20] [b] After Altona, Geise, and Romers.[21]

$\Delta = -36°$) deformed toward a half chair ($\Delta = 0°$) at C(13)–O(2). The conformation of the dioxolane ring of the D-galacto derivative **6** is nearer to a half-chair conformation at O(1)–C(1) ($\Delta = 144°$) distorted toward an envelope at C(1) ($\Delta = 180°$).

With regard to the conformation of the pyranose ring (see Figure 2b), the tri-*O*-acetylated D-gluco derivatives **1** and **3** show almost identical conformations between diplanar (0,2)[20,22] [**1**(3) and **3**(3), $\Sigma = 240°$, $\delta = 120°$] and skew [**1**(2) and **3**(2), $\Sigma = 240°$, $\delta = 180°$]; for the value $\delta = 150°$ there could be assigned two more extreme conformations [**1**(1) and **3**(1), $\Sigma = 210°$ and $\delta = 150°$, and **1**(4) and **3**(4), $\Sigma = 270°$ and $\delta = 150°$]. The tri-*O*-acetyl-D-allo derivative **5** displays a conformation between monoplanar (0)[20,22] [**5**(1); $\Sigma = 210°$, $\delta = 150°$] and skew [**5**(2); $\Sigma = 240°$, $\delta = 180°$]. The tri-*O*-acetylated-D-galacto derivative has a distorted chair conformation and so does the D-gluco hydroiodide of **2**, both chairs being flattened around the same zone, the flattening being about twice for the hydroiodide of **2** than for **6**.

The ^{1}H NMR spectra of compounds **3** and **5**–**7** have been analyzed iteratively by means of a computer program. The computed best values obtained and those found in a previous work[13] for compounds **1** and **4** are given in Table IV. As previously deduced from a first-order analysis of the ^{1}H NMR spectrum of tri-*O*-acetylated-D-allo derivative **5**,[23] the computed coupling constants for this compound are indicative of a skew ($^3S_5$) average solution conformation of the pyranose ring. This average conformation must be very similar to that found in the solid state, the main argument being, as stated by Dick et al.,[23] the existence of the large and positive long-range coupling constant between protons H(2) and H(4). Comparison of the coupling constants computed for compound **5** with those reported by Coxon[24] for 3-*O*-benzoyl-1,2,4-*O*-benzylidene-α-D-ribopyranose, which is rigidly held in a skew conformation, shows a deviation of $J_{3,4}$ and $J_{4,5}$ and a smaller value of the long-range coupling $J_{2,4}$ in compound **5**. These variations could be accounted for by considering that the average skew conformation of the tri-*O*-acetyl-D-allo derivative **5** must be deformed, compared with the rigid molecule studied by Coxon,[24] in the region C(3)–C(5) in order to overcome the steric effect due to the proximity of the *endo*-methyl group. The spectroscopic parameters for the tri-*O*-acetyl-D-gluco derivatives **3** and **7** and those for the previously studied compound **1**[13] are also in agreement with a $^3S_5$ average solution conformation of the glucopyranose ring similar to that found for **1**[14] and **3**[9,10] in the solid state. In this case the computed coupling constants could be assigned to vicinal proton torsion angles which are either acute or obtuse, giving rise to skew[4] and distorted chair conformations,[5-7] respectively. However, the existence of a large and positive $J_{2,4}$ and NOE experiments with compound **7** indicated an arrangement of H(2) and H(4) very similar to that found in the tri-*O*-acetyl-D-allo derivative **5** and proximity of the *endo*-methyl group to the H(5) proton but not to proton H(3), respectively. Irradiation of the signal of the *endo*-methyl group induced an 11% increase of the integrated intensity of the signal assigned to proton H(5) and no change at all in that of the signal attributed to proton H(3) as was expected for a $^3S_5$ average conformation. The NOE observed on H(5) of the tri-*O*-acetyl-D-allo derivative **5** was a ~7% increase. Concerning the tri-*O*-acetylated-D-galacto derivative **6** and the previously studied compound **4**[13] the $J_{2,3}$ value of 6.5 Hz seems to indicate a conformational change in this region compared to the D-gluco derivatives **1**, **3**, and **7**. In this case, all the observed coupling constants could be interpreted in terms of a distorted chair average conformation (flattened $^4C_1$) as indicated by the crystal structure determination. In contrast to the D-gluco derivatives, NOE experiments clearly showed the proximity of the *endo*-methyl group to both H(5) (5% effect) and H(3) (7% effect) as expected for a chair conformation.

The torsion angles between vicinal protons as determined from X-ray data for compounds **1**,[14] **3**,[10] **5**, and **6**

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Table III. Calculated Torsion Angles for the Nearest Relevant Forms of the Pyranose and Dioxolane Rings

Pyranose Ring

	nearest relevant form							
	1(1)-3(1)	1(2)-3(2)	1(3)-3(3)	1(4)-3(4)	2(1)	5(1)	5(2)	6(1)
ϕ_0	0	−27.8	0	−24.9	36.6	0	−30.3	16.8
ϕ_1	39.2	55.5	27.8	39.2	−46.0	42.8	60.5	−23.6
ϕ_2	−24.9	−27.8	0	0	59.0	−27.1	−30.3	48.9
ϕ_3	−28.7	−27.8	−55.5	−53.6	−62.4	−15.7	−30.3	−67.4
ϕ_4	68.0	55.5	83.3	68.0	53.0	74.1	60.5	60.6
ϕ_5	−53.6	−27.8	−55.5	−28.7	−40.0	−58.4	−30.3	−35.3
nearest relevant $\Sigma/2$	105	120	120	135	195	105	120	165
nearest relevant $\delta/2$	75	90	60	75		75	90	

Dioxolane Ring

	nearest relevant form							
	1(1)-3(1)	1(2)-3(2)	2(1)	2(2)	5(1)	5(2)	6(1)	6(2)
ϕ_0	−38.4	−36.5	−11.9	0	−39.8	−37.9	25.2	24.0
ϕ_1	31.1	22.6	31.1	22.6	32.2	23.4	−20.4	−14.8
ϕ_2	−11.9	0	−38.4	−36.5	−12.3	0	7.8	0
ϕ_3	−11.9	−22.6	31.1	36.5	−12.3	−23.4	7.8	14.8
ϕ_4	31.1	36.5	−11.9	−22.6	32.2	37.9	−20.4	−24.0
nearest relevant Δ	0	−36	14.4	180	0	−36	0	−36

[a] Calculated by use of the values of the parameters τ_m, q, and ϕ_m of Table II. Compounds 1 and 3 are considered approximately equal. All values are in degrees.

Table IV. ^1H NMR Spectral Parameters, ν (δ) and J (Hz), at 100 MHz of Compounds 1 and 3-7

	compd					
parameter	1[13]	3	4[13]	5	6	7
ν_1	5.803	5.702	5.869	5.167	5.751	5.545
ν_2	4.390	4.322	4.322	3.703	4.249	4.213
ν_3	5.213	5.177	4.998	5.111	5.067	5.076
ν_4	4.916	4.896	5.401	5.394	5.425	4.805
ν_5	3.906	3.958	4.324	4.312	4.316	3.848
ν_6	4.193	4.178	4.140	4.173	4.133	4.089
ν_6'	4.193	4.199	4.165	4.135	4.162	4.097
$J_{1,2}$	5.2	5.2	4.9	5.5	4.8	5.1
$J_{1,3}$	−0.4	−0.3	−0.4	−0.2	−0.3	−0.4
$J_{1,4}$	−0.2	−0.1	−0.3	0.0	−0.2	−0.1
$J_{1,5}$	−0.7	−0.6	−0.7	−0.7	−0.5	−0.6
$J_{1,6}$		−0.3	0.0	−0.5	0.0	−0.4
$J_{1,6'}$		−0.1	0.0	0.0	0.0	−0.3
$J_{2,3}$	3.0	3.0	6.9	2.8	6.5	2.7
$J_{2,4}$	0.9	0.9	−0.3	1.0	−0.3	1.0
$J_{2,5}$	0.0	0.0	−0.1	0.0	0.0	0.0
$J_{2,6}$		0.0	0.0	0.0	0.0	−0.1
$J_{2,6'}$		0.0	0.0	0.0	0.0	−0.1
$J_{3,4}$	2.8	2.9	3.5	6.3	3.6	2.5
$J_{3,5}$	0.0	−0.3	−0.2	0.0	−0.2	−0.3
$J_{3,6}$		0.0	0.0	0.0	0.0	−0.2
$J_{3,6'}$		0.0	0.0	0.0	0.0	−0.2
$J_{4,5}$	9.5	9.5	2.0	7.5	2.6	9.6
$J_{4,6}$		−0.3	−0.4	−0.2	−0.3	−0.3
$J_{4,6'}$		0.0	0.0	−0.5	0.1	−0.2
$J_{5,6}$	8.4 ($J_{5,6'}$)	2.5	6.0	3.2	6.4	2.4
$J_{5,6'}$	8.4 ($J_{5,6}$)	5.9	7.0	6.3	6.9	5.8
$J_{6,6'}$		−12.1	−11.2	−12.0	−11.3	−12.3
rms error	0.06	0.06	0.07	0.06	0.07	0.08

Table V. Vicinal Proton Torsion Angles from X-ray Analysis (All Values in Degrees)

	compd			
atoms	1[14]	3[10]	5	6
H(1)-C(1)-C(2)-H(2)	−18 (5)	10	−13 (4)	24 (8)
H(2)-C(2)-C(3)-H(3)	−67 (6)	57	53 (4)	−167 (7)
H(3)-C(3)-C(4)-H(4)	95 (7)	95	−33 (4)	64 (7)
H(4)-C(4)-C(5)-H(5)	−148 (5)	168	−144 (4)	−53 (7)
H(5)-C(5)-C(6)-H(6)	50 (6)		60 (4)	175 (7)
H(5)-C(5)-C(6)-H(6)	−74 (6)		−67 (4)	40 (8)

are given in Table V, and the angles calculated from modified Karplus equations for compounds **1**,[13] **3**, **4**,[13] **5**, **6**, and **7** are shown in Table VI. Of the several modifications of the Karplus equation which have been used to approximately estimate the vicinal proton torsion angles from vicinal coupling constants and which take into account the electronegativity and steric arrangement of substituents, the treatment of Forrest predicts a gauche $^3J_{HH}$ coupling from observed values and includes well-proven substituent electronegativity effects. In almost

Table VI. Vicinal Proton Torsion Angles (in Degrees) for Compounds 1 and 3-7 Deduced from ^{1}H NMR

compd	ref	angle			
		H(1)C(1)C(2)H(2)	H(2)C(2)C(3)H(3)	H(3)C(3)C(4)H(4)	H(4)C(4)C(5)H(5)
1	17	36 (141)	51 (125)	52 (124)	
	18	34 (138)	61 (114)	62 (113)	179
	19	5	65	65	
3	17	36 (141)	51 (125)	52 (125)	
	18	34 (138)	60 (115)	61 (114)	175
	19	5	65	65	
4	17	38 (137)	150 (23)	47 (128)	58 (118)
	18	37 (135)	145 (25)	55 (119)	71 (103)
	19	14		50	48
5	17	34 (141)	52 (124)	28 (146)	155 (17)
	18	31 (141)	62 (112)	32 (140)	150 (18)
	19		55	33	
6	17	39 (137)	147 (26)	47 (129)	54 (123)
	18	38 (135)	142 (29)	54 (120)	64 (111)
	19	17		50	42
7	17	37 (138)	53 (123)	54 (122)	
	18	35 (137)	63 (112)	65 (110)	
	19	9	66	67	

Table VII. Crystal and Experimental Data and Structure-Refinement Parameters

	5	6
formula	$C_{14}H_{19}O_9$	$C_{18}H_{28}O_{10}$
system	monoclinic	orthorhombic
a, Å	11.6069 (7)	18.9424 (24)
b, Å	7.8888 (3)	12.5568 (9)
c, Å	9.2023 (3)	9.0214 (5)
β, deg	91.88 (1)	90
M_r	331.3	404.4
D_{exptl}, mg m^{-3}	1.306	1.252
space group	$P2_1$	$P2_12_12_1$
Z	2	4
cryst size, mm	0.13 × 0.27 × 0.43	0.10 × 0.30 × 0.30
stability	no variation detected	no variation when inside a capillary
technique and geometry	four-circle diffractometer, Philips Pw 1100 with graphite-monochromated radiation; bisecting geometry	
radiation	Cu $K\bar{\alpha}$	Mo $K\bar{\alpha}$
μ, cm^{-1}	9.36	0.96
total measurement up to a θ (deg) of	65	25
no. of independent rflctns	1551	2014
criterion of obsd rflctns	$I > 2\sigma(I)$	$I > 2\sigma(I)$
no. of obsd rflctns	1503	1265
solution	MULTAN system[26]	
refinement mode	on *F*'s less-than rflctns not used full matrix	block matrix
H atoms	from difference synthesis	
weighting scheme	empirical fit as to give no trends in $\langle w\Delta^2\rangle$ vs. F_0 or $(\sin\theta)/\lambda$	
R(obsd)	0.049	0.079
R_w(obsd)	0.057	0.089

every case this approach gives good agreement between angles determined by X-ray analysis and those calculated from coupling constants (see Tables V and VI). For torsion angles which were expected to be very different from 60°, the modifications of Durette and Horton[18] and Coxon[17] have been used.

From the X-ray diffraction and ^{1}H NMR results outlined above it could be concluded that the tri-*O*-acetylated-1,2-*O*-alkylidene-D-glucopyranose (**1**, **3**, **7**) and D-allopyranose (**5**) derivatives both in the solid state and in solution have a skew ($^3S_5$) conformation while the tri-*O*-acetylated-D-galacto derivatives (**4** and **6**) show a flattened chair (distorted $^4C_1$) conformation.

Experimental Section

Materials. 3,4,6-Tri-*O*-acetyl-1,2-*O*-(*S*)-(1-ethoxyethylidene)-α-D-glucopyranose (**3**) 3,4,6-tri-*O*-acetyl-1,2-*O*-(*R*)-ethylidene-α-D-allopyranose (**5**), 3,4,6-tri-*O*-acetyl-1,2-*O*-(*R*)-(1-*tert*-butoxyethylidene)-α-D-galactopyranose (**6**), and 3,4,6-tri-*O*-acetyl-1,2-(*R*)-(1-*tert*-butoxyethylidene)-α-D-glucopyranose (**7**) were prepared by known procedures.[5,23,25]

X-ray. The crystal and experimental data and refinement parameters are given in Table VII.

^{1}H NMR. The ^{1}H NMR spectra were recorded for solutions in $CDCl_3$ (compounds **3**, **6**, and **7**) or C_6D_6 (compound **5**) with Me_4Si as internal standard on a Varian XL-100 spectrometer in the frequency-sweep mode for both single- and double-resonance experiments. Spectral widths of 1.000 and 50 Hz were used for the measurements. Analyses of seven spin systems were performed by a Nicolet 1180 data system using an ITRCAL program. The experimental and calculated spectra from the resulting best values matched satisfactorily.

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Registry No. **1**, 61376-15-6; **2**·HI, 13078-67-6; **3**, 38081-38-8; **4**, 69927-13-5; **5**, 56687-80-0; **6**, 74035-78-2; **7**, 74035-79-3.

Supplementary Material Available: Bond distances, bond angles, and thermal parameters for compounds **5** and **6** (5 pages). Ordering information is given on any current masthead page.

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