

# CONFORMATIONAL ANALYSIS OF 1,2-ANHYDRO-3,4,6-TRI-*O*-BENZYL- $\alpha$ -D-GLUCOPYRANOSE AND $\beta$ -D-MANNOPYRANOSE

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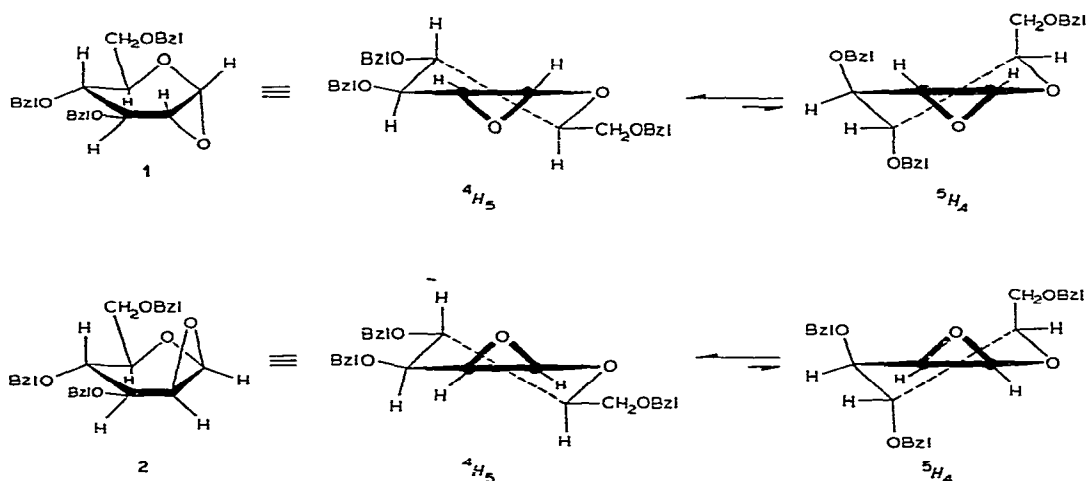
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## ABSTRACT

The  $^1\text{H}$ - and  $^{13}\text{C}$ -n.m.r. spectra of 1,2-anhydro-3,4,6-tri-*O*-benzyl- $\alpha$ -D-glucopyranose and  $\beta$ -D-mannopyranose were completely assigned by using single-frequency decoupling, off-resonance decoupling, and a spin-simulation program. The conformations of the two anhydro sugars were determined from their proton coupling-constants. The *gluco* isomer was found to be  $^4H_5$  (half-chair). The conformation of the *manno* derivative was found to be predominantly  $^4H_5$ , with some ring flattening.

## INTRODUCTION

1,2-Anhydro-3,4,6-tri-*O*-benzyl- $\alpha$ -D-glucopyranose<sup>1</sup> (**1**) and 1,2-anhydro-3,4,6-tri-*O*-benzyl- $\beta$ -D-mannopyranose<sup>2</sup> (**2**) have been prepared by Schuerch *et al.* for stereospecific polymerization. It is well known that conformational and configurational properties of a monomer play a major role in determining the rates and stereospecificity of a polymerization<sup>3</sup>. Earlier workers<sup>1-5</sup> have not studied conformational



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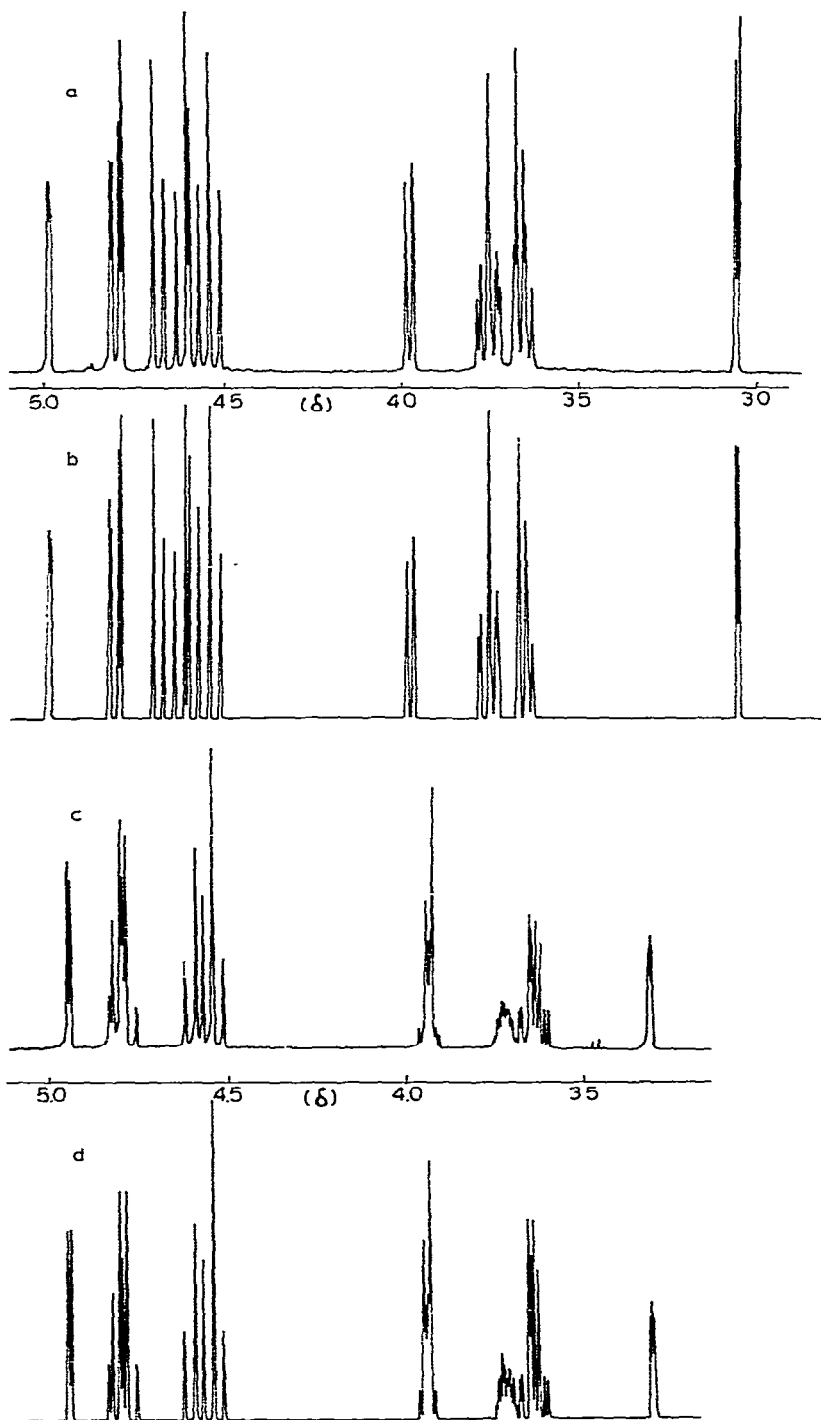


Fig. 1. (a)  $^1\text{H}$ -N.m.r. spectra of 1,2-anhydro-3,4,6-tri-*O*-benzyl- $\alpha$ -D-glucopyranose, (b) spin-simulation spectrum of a, (c) 1,2-anhydro-3,4,6-tri-*O*-benzyl- $\beta$ -D-mannopyranose, (d) spin-simulation spectrum of c.

properties of carbohydrate 1,2-oxiranes in great detail, and it was therefore our interest to carry out a comprehensive analysis of the oxiranes **1** and **2** by using  $^1\text{H}$ - and  $^{13}\text{C}$ -n.m.r. spectroscopy.

The conformation of 1,2-oxirane pyranoid sugars is similar to that of 1,2-unsaturated sugars, as shown by Dreiding models. Earlier studies<sup>6,7</sup> on 1,2-unsaturated pyranoid rings have established the conformation to be a half-chair ( $^4H_5$ ), with four of the ring atoms coplanar and the remaining two atoms above and below the plane.

The present report describes  $^1\text{H}$ - and  $^{13}\text{C}$ -n.m.r. studies of 1,2-oxiranes **1** and **2** in chloroform solution. Their chemical shifts and coupling constants are interpreted, and the influence of the oxirane ring on their conformation is discussed.

## RESULTS AND DISCUSSION

*General consideration of  $^1\text{H}$ -n.m.r. spectra.* —  $^1\text{H}$ -N.m.r.-spectral dispersions were insufficient for detailed analysis at 60 or 100 MHz, but the spectra at 400 MHz showed sufficient first-order character (see Fig. 1) to allow detailed interpretation for both compounds. Chemical shifts of protons of 1,2-oxiranes **1** and **2** are given in Table I, and their corresponding first-order coupling-constants are given in Table II.

It is well established in pyranoid ring-systems that vicinal pairs of protons in antiparallel (*ax-ax*) disposition give rise to large coupling-constants ( $\sim 9.5$  Hz), whereas those in *gauche* disposition give smaller values (1.0–2.0 Hz for *eq-eq*; 2.2–3.5 Hz for *ax-eq*)<sup>8</sup>. Variations are often observed and may be attributed to (a) the effect of substituent electronegativity, (b) the adoption of favored, lower-energy conformations (change of dihedral angles of vicinal protons from a nominal 60 or 180°), and (c) the incidence of conformational equilibria in which there is a time-

TABLE I

$^1\text{H}$  CHEMICAL SHIFTS ( $\delta$ ) FOR COMPOUNDS **1** AND **2**

Compound	H-1	H-2	H-3	H-4	H-5	H-6	H-6'	Benzyl methylene groups
<b>1</b>	4.99	3.06	3.98	3.65	3.74	3.77	3.66	4.81, 4.80, 4.68, 4.62, 4.59, 4.53
<b>2</b>	4.95	3.31	3.94	3.93	3.72	3.62	3.66	4.82, 4.81, 4.79, 4.61, 4.56, 4.53

TABLE II

$^1\text{H}$  COUPLING CONSTANTS (Hz) FOR COMPOUNDS **1** AND **2**

Compound	$J_{1,2}$	$J_{1,3}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{5,6'}$	$J_{6,6'}$	$J_{A,B}$ for benzyl $\text{CH}_2$
<b>1</b>	2.4	−1.0	0	7.8	7.8	2.1	1.7	−11.00	−10.8, −12.2, −12.2
<b>2</b>	2.9	0	1.7	4.9	9.8	4.9	2.0	−10.7	−11.7, −11.0, −11.9

averaging of the coupling constants from two or more rapidly equilibrating conformers<sup>9</sup>.

<sup>1</sup>H-N.m.r.-spectral assignments and conformational analyses. — 1,2-Anhydro-3,4,6-tri-O-benzyl- $\alpha$ -D-glucopyranose (**1**). The spectrum of **1** was assigned by comparison with the spectrum of 1,2-anhydro-3,4,6-tri-O-acetyl- $\alpha$ -D-glucopyranose<sup>5</sup> (**3**), by using single-frequency decoupling and by calculation of a theoretical spectrum using a spin-simulation program.

H-1 was assigned to the doublet of doublets at  $\delta$  4.99 ( $J_{1,2}$  2.4 Hz and  $J_{1,3}$   $-1.0$  Hz) and H-2 to the doublet at  $\delta$  3.06 ( $J_{1,2} = 2.4$  Hz), based on comparison to the chemical shifts of H-1 and H-2 in **3**. The assignments are also in agreement with the fact that oxirane rings cause a large, upfield shift of the attached protons<sup>10,11</sup>. H-3 was assigned to the doublet of doublets at  $\delta$  3.98 ( $J_{3,4}$  7.8 and  $J_{1,3}$   $-1.0$  Hz), as single-frequency irradiation of this peak caused collapse of the H-1 signal to a doublet.

The two remaining groups of multiplets, at  $\delta$  3.59–3.62 and 3.70–3.79, were found by integration to correspond to two protons each. Single-frequency decoupling of H-3 caused a change in the upfield multiplet, indicating that the H-4 signal was in this group. Based on the spectrum of **3**, in which H-5 resonates at  $\delta$  3.97, it was assumed that the H-5 signal of **1** would appear in the downfield multiplet. The two remaining protons (H-6 and H-6') were assigned to the downfield and upfield multiplets, respectively.

The chemical shifts of H-4, H-5, H-6, and H-6', together with their respective coupling constants, were determined by use of a spin-simulation program. The initial chemical-shift values of H-4 and H-6' were taken as the center of the multiplet ( $\delta$  3.61). The same method was used to attribute initial chemical shifts to H-5 and H-6 ( $\delta$  3.75). The trial coupling-constants,  $J_{4,5} = 8.7$ ,  $J_{5,6} = 4.2$ ,  $J_{5,6'} = 2.5$ , and  $J_{6,6'} = -11.0$  Hz, were taken from the <sup>1</sup>H spectrum of **3**. The values of chemical shifts and coupling constants were varied by an iterative procedure until the theoretical spectrum matched the observed one very closely. The values of the chemical shifts thus obtained were: H-4 at  $\delta$  3.65, H-5 at  $\delta$  3.74, H-6 at  $\delta$  3.77, H-6' at  $\delta$  3.66 ( $J_{4,5}$  7.8 Hz,  $J_{5,6}$  2.1,  $J_{5,6'}$  1.7, and  $J_{6,6'}$   $-11.0$  Hz). The group of peaks between  $\delta$  4.53 to 4.81 was assigned to the benzyl methylene protons. The individual AB pairs were readily assigned on the basis of their coupling constants (see Table I).

The conformation of **1** was determined from its coupling constants and by the calculation of bond angles according to the general Karplus equation<sup>8</sup> and a modified Karplus equation reported by Altona *et al.*<sup>12</sup> (see Tables II and III). The value of  $J_{1,2}$  (2.4 Hz) is in the typical range for epoxides and carbohydrate oxiranes in which the  $\phi_{1,2}$  is 0°. The  $J_{2,3}$  value was determined to be  $<0.5$  Hz, as single-frequency irradiation of H-3 caused no change in the H-2 signal. A value of  $<0.5$  Hz indicates a bond angle ( $\phi_{2,3}$ ) of  $\sim 90^\circ$ , and this is typical of a *trans* relationship between the quasiequatorial H-2 and the quasiallial H-3.

The value of  $J_{3,4}$  (7.8 Hz) gives  $\sim 157^\circ$  for the value of  $\phi_{3,4}$ . Typically  $J_{3,4}$  is<sup>13</sup>  $\sim 9.3$  Hz and  $\phi_{3,4}$  is  $180^\circ$  in glucopyranose derivatives. As H-3 is quasiallial because

TABLE III

BOND ANGLES (DEGREES) FOR COMPOUNDS 1 AND 2

Compound	Conformation	$\phi_{1,2}$	$\phi_{2,3}$	$\phi_{3,4}$	$\phi_{4,5}$
1	${}^1H_3^a$	0	90	170	180
	${}^4H_5^b$	54	78 or 99	157	157
	${}^4H_5^c$	<sup>d</sup>	76	161	151
	${}^5H_4^a$	0	75	80	50
2	${}^4H_5^a$	0	45	170	180
	${}^4H_5^b$	51	78	116	~180
	${}^4H_5^c$	<sup>d</sup>	77	131	180
	${}^5H_4^a$	0	35	85	45

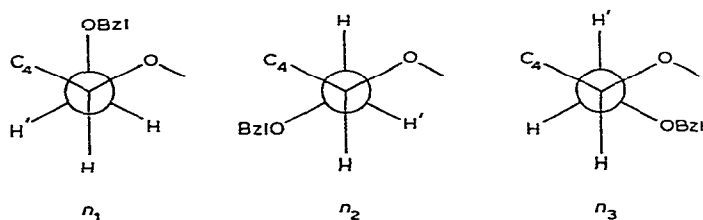
<sup>a</sup>Obtained from Dreiding models. <sup>b</sup>Calculated from the coupling constants by the Karplus equation<sup>8</sup>.<sup>c</sup>Calculated from the coupling constants by using a modified Karplus equation reported by Altona *et al.*<sup>12</sup>. <sup>d</sup>Equation reported by Altona *et al.*<sup>12</sup> not valid for planar portion of the ring.

of the adjacent epoxide ring, the values of both  $J_{3,4}$  and  $\phi_{3,4}$  will be somewhat lower.

The magnitude of  $J_{4,5}$  is also lower than would be predicted (9.7 Hz)<sup>13</sup> for a true *trans*-diaxial arrangement. The  $\phi_{4,5}$  value is calculated to be<sup>8</sup> 157°, or<sup>13</sup> 151°, indicating movement of either H-4 or H-5. Most probably, H-5 has moved outward because of 1,3-diaxial interaction with the lone pair of electrons on the oxirane ring.

The long-range coupling-constant  $J_{1,3}$  has an absolute value of 1.0 Hz. The sign could not be readily determined from the <sup>1</sup>H-n.m.r. spectrum. However, the predicted sign of  $J_{1,3}$  for an equatorial-axial arrangement would be negative (−0.56 Hz) for a saturated system<sup>14</sup>. Also, examining allylic systems<sup>3</sup>, the predicted  $J_{1,3}$  value for  $\phi_{1,3} = 90^\circ$  is −2.0 Hz. A  $J_{1,3}$  value of −1.0 Hz was also observed for substituted glucals<sup>7</sup>. Based on these observations, it is assumed that the sign of  $J_{1,3}$  is negative, and indeed, the calculated theoretical spectrum shows a much better fit when  $J_{1,3}$  is negative.

Based on the calculated bond-angles and those predicted from a Dreiding model of 1 (Table III), the most probable conformation of 1 is  ${}^4H_5$ , in which O-5-C-1-C-2-C-3 are coplanar, C-4 is slightly above the plane, and C-5 is slightly below. The C-4-C-5-O-5 position is very slightly flattened because of interaction between H-5 and the oxirane ring.

Fig. 2. The three staggered rotamers of the 5-CH<sub>2</sub>OBzl group in 1 and 2.

The favored conformation at 5-CH<sub>2</sub>-OBzl may be calculated from  $J_{5,6}$  and  $J_{5,6'}$ , as described by Vliegthart *et al.*<sup>15</sup>. The mol fractions of each of the three possible rotamers (see Fig. 2) were calculated to be  $n_1 = 0.94$ ,  $n_2 = 0.063$ , and  $n_3 = 0.001$ . Calculations of rotamer populations in other glucose derivatives, including 3 and 3,4,6-tri-*O*-benzyl-D-glucal<sup>16</sup>, indicate a preference for rotamer  $n_1$  but not to as large an extent as in **1**. The reason for this preference has not yet been explained.

*1,2-Anhydro-3,4,6-tri-O-benzyl-β-D-mannopyranose (2)*. — The anomeric proton (H-1) resonates as a doublet ( $J_{1,2}$  2.9 Hz) at  $\delta$  4.95. The  $J_{1,2}$  value is smaller than that predicted by the Karplus equation for  $\phi_{1,2}$  of 0°. The smaller value may be attributed to the shorter C-1–C-2 bond length and less sp<sup>3</sup> character in the bond. Smaller  $J_{1,2}$  values have also been observed in **1** and<sup>5</sup> **3**. H-2 was assigned to the highest-field ( $\delta$  3.31) doublet of doublets. The  $J_{2,3}$  value (1.7 Hz) is relatively small, as  $\phi_{2,3}$  is  $\sim 45^\circ$ . Interestingly,  $J_{1,3} = 0.0$  Hz in this derivative, in contrast to **1**. This difference may be due to the fact that the oxirane ring is *trans* to H-3. Values of  $J_{1,3} = 0.0$  Hz have been observed in other oxiranes. H-3 and H-4 have similar chemical shifts and could not be separated on a 400-MHz spectrum. The H-3 signal was identified as a quartet ( $\delta$  3.94) having  $J_{2,3}$  1.7 and  $J_{3,4}$  4.9 Hz. The chemical shift for H-3 was confirmed from the theoretical spectrum calculated by the spin-simulation program. H-3 becomes “quasial” (ax') because of the adjacent oxirane ring, and  $\phi_{3,4}$  is  $\sim 170^\circ$ . According to the modified Karplus equation<sup>12</sup>,  $J_{3,4}$  should be 9.5 Hz. A smaller  $J_{3,4}$  value indicates some distortion of the “half-chair” involving C-3–C-4 bonds.

The H-4 atom is axial and is *cis* to the oxirane ring. This orientation would result in an unfavorable 1,4 interaction and may result in some ring flattening at C-4. Also the ring-oxygen atom and the oxirane-ring oxygen atom have their dipole current in the same direction, and this may result in an unfavorable dipole–dipole repulsion and could cause some ring flattening at C-5. Ring flattening at both C-5 and C-4 would change  $\phi_{2,3}$ ,  $\phi_{3,4}$ ,  $\phi_{5,6}$ ,  $\phi_{5,6'}$  and, to some extent,  $\phi_{4,5}$ . This factor could explain the lower  $J_{2,3}$  and  $J_{3,4}$  values.

The H-5 signal appeared as an octet ( $\delta$  3.72) having  $J_{4,5}$  9.8,  $J_{5,6}$  4.9, and  $J_{5,6'}$  2.0 Hz. H-6 and H-6' appeared as an eight-line pattern for an AB portion of an ABX system. The spacings allowed determination of the first-order couplings;  $J_{5,6}$  2.0,  $J_{5,6'}$  4.9, and  $J_{6,6'}$  –10.7 Hz.

Calculation of the mol fraction of the three possible rotameric conformations of 5-CH<sub>2</sub>-OBzl gave  $n_1 = 0.637$ ,  $n_2 = 0.338$ , and  $n_3 = 0.025$  (see Fig. 2).

The benzyl methylene protons were assigned on the basis of their AB coupling constants, which are given in Table I and II.

<sup>13</sup>C Assignments and coupling constants. — Complete signal-assignments for the fully decoupled <sup>13</sup>C-n.m.r. spectra of **1** and **2** were not possible, as signals for C-1, C-2, C-3, C-4, C-5, C-6, and the three benzyl methylene groups were very close together. Only the aromatic (lowest field) and C-2 carbon atoms (highest field) were readily assigned. The C-6 and the benzyl methylene signals were assigned on the basis of off-resonance spectra. Unambiguous assignment of C-1, C-3, C-4, and C-5 was

TABLE IV

<sup>13</sup>C CHEMICAL SHIFTS (p.p.m.) AND COUPLING CONSTANTS (Hz) FOR COMPOUNDS 1 AND 2

Carbon atom	Chemical shift		<i>J</i> <sub>C,H</sub> coupling constant	
	1	2	1	2
C-1	77.52	78.72	212.0	214.8
C-2	52.47	54.28	179.0	179.9
C-3	79.12	79.33	139.8	140.4
C-4	74.46	78.18	150.1	149.6
C-5	69.61	76.11	150.8	148.5
C-6	68.43	68.85	143.8	143.2
Benzyl methylene groups	74.46	75.11	144.2	147.1
	73.61	73.58	138.1	144.4
	72.26	72.04	136.8	141.0

made by using an off-resonance, graphical procedure<sup>17</sup>, which can match a specific proton resonance to a particular carbon resonance. The procedure is essentially a series of off-resonance spectra obtained by varying the decoupler frequency. The chemical shifts of each peak of each carbon doublet was plotted against the decoupler frequency. Each carbon atom gives two straight lines that intersect at the resonance frequency of the proton attached to that carbon atom. If the proton spectrum is completely assigned, the carbon spectrum may then be completely assigned. In our case, we did not use graphical methods but instead used a computer program to calculate the straight lines via a least-squares method and then calculated the intercept. The results for **1** and **2** are shown in Table IV.

In **1**, C-2 was assigned to upfield peak at 52.47 p.p.m., as it is known that an oxirane ring causes a large upfield shift (~20 p.p.m.)<sup>18</sup>. The off-resonance spectrum of **1** indicated that the peaks at 68.43, 72.26, 73.61, and 74.46 p.p.m. arose from methylene carbon atoms (triplets) belonging to C-6 (68.43 p.p.m.) and the benzyl methylene groups. The remaining methine carbon atoms, at 79.12, 77.52, 74.46, and 69.61 p.p.m., were assigned by the off-resonance "graphical" procedure to C-3, C-1, C-4, and C-5, respectively. Similarly, C-2 in **2** was assigned to the peak at 54.28 p.p.m. and C-6 to the peak at 68.85 p.p.m. From the off-resonance spectrum of **2**, the benzyl methylene groups were assigned to the peaks at 75.11, 73.58, and 72.04 p.p.m. C-1, C-3, C-4, and C-5 atoms were assigned by the off-resonance, "graphical" procedure.

The fully proton-coupled <sup>13</sup>C-n.m.r. spectra of **1** and **2** gave the <sup>1</sup>*J*<sub>C,H</sub> coupling constants (see Table IV). The large coupling-constants for the peaks at 77.52 and 52.47 p.p.m. in **1** and at 78.72 and 54.28 p.p.m. in **2** confirmed that the oxirane ring was attached to these carbon atoms<sup>18</sup>. The remaining coupling-constants lie in the range expected for substituted sp<sup>3</sup>-hybridized carbons.

Comparing the chemical shifts of C-1 and C-2 in compound **1** to compound **2**, one may see that the axial arrangement of oxirane ring causes an upfield shift of C-1 and C-2 compared with the equatorial arrangement in **2**. The shift is in agreement

with other observations of carbohydrate derivatives in which axial groups cause an upfield shift whereas equatorial groups cause a downfield shift to the carbon atom.

*Conclusions.* — The conformation of **1** is  ${}^4H_5$  (a half-chair), with only slight distortion of the ring at C-5. The oxirane ring may be readily approached from either the top or bottom as in a polymerization, as all of the functional groups are either equatorial or quasiequatorial. The epoxide ring also should not have any added reactivity attributable to strain in the pyranose ring-system.

The mannose derivative **2** is also in a half-chair ( ${}^4H_5$ ) with considerable ring flattening at C-4 and C-5. The distortion may cause an increase in the reactivity of the oxirane ring due to torsional strain, and, since C-6 is more axial, approach to the oxirane ring from the top side may be sterically hindered.

Preliminary results of the cationic polymerization of **1** (ref. 19) and **2** (ref. 20) indicate that the polymerization is faster and the stereoregularity is higher for the glucose derivative **1** than for the mannose derivative **2**. The conformation of **2** may hinder the approach of the monomer to the growing end of the polymer. Increased reactivity of the oxirane group in **2** arising from the torsional strain may also allow the propagating oxonium ion to take on carbonium ion character and this planar intermediate can react to give either  $\alpha$  or  $\beta$  linkages.

Further polymerizations, and possibly copolymerizations of **1** and **2**, will be necessary to correlate the conformations of **1** and **2** completely with their polymerization rates and stereoregularity.

## EXPERIMENTAL

*General methods.* —  ${}^1\text{H}$ -N.m.r. spectra were recorded with a Bruker 400-MHz n.m.r. spectrometer in pulsed Fourier-transform mode, in chloroform-*d*, with tetramethylsilane as the internal standard. The accuracy of the coupling constants is  $\sim 0.25$  Hz.  ${}^{13}\text{C}$ -N.m.r. spectra were recorded with a Varian XL-100-15 spectrometer in pulsed Fourier, noise-decoupled transform mode in chloroform-*d*, with tetramethylsilane as internal standard. 1,2-Anhydro-3,4,6-tri-*O*-benzyl- $\alpha$ -D-glucopyranose<sup>2</sup> and  $\beta$ -D-mannopyranose<sup>1</sup> were crystallized from ether-petroleum ether and dried before use. Assignment of the  ${}^1\text{H}$ -n.m.r. spectra was made by use of a Varian spin-simulation program publication no. 87-131-214, program no. 994029-B, and by plotting the theoretical spectra on a Varian XL-100 X-Y plotter. The computer program for the calculation of the off-resonance "graphical" procedure were run on Apple II plus microcomputer with 48k of memory.

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