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Solid-State ^{13}C-NMR Study of Conformations of Oligosaccharides and Cellulose

Conformation of CH_2OH Group About the Exo-Cyclic C-C Bond

Fumitaka Horii, Asako Hirai and Ryozo Kitamaru

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan

SUMMARY

CP/DD/MAS ^{13}C NMR spectra have been obtained for different monosaccharides, oligosaccharides, and cellulose. It has been found that a simple linear relationship exists between the chemical shift of the CH_2OH carbon and the torsion angle χ about the exo-cyclic C-C bond. The chemical shifts fall into three groups of 60-62.6 ppm, 62.5-64.5 ppm, and 65.5-66.5 ppm, which are related to *gauche-gauche*, *gauche-trans*, and *trans-gauche* conformations, respectively. On the basis of these results the conformation of the CH_2OH carbon of cellulose is also discussed.

INTRODUCTION

High-resolution ^{13}C NMR spectra can be obtained even for solid organic compounds by employing proton dipolar decoupling(DD) and magic-angle spinning(MAS) mostly together with ^{13}C-^{1}H cross-polarization(CP) technique. In this case MAS removes the so-called chemical shift anisotropy and produces the high-resolution line corresponding to each conformer allowed in the solid state if no rapid molecular motion occurs. Therefore, so long as subsidiary effects such as packing(1) and hydrogen bonding(2-4) are not significant, solid-state chemical shifts will reflect the specific conformations of concerned carbons which are described by parameters such as torsion angles. In this paper we report a pronounced linear relationship between ^{13}C chemical shift of CH_2OH side group and the torsion angle about the exo-cyclic C-C bond for different monosaccharides, oligosaccharides, and cellulose. Similar relationships concerning β-1,4-glycosidic linkages will be published elsewhere.

RESULTS AND DISCUSSION

Figure 1 shows CP/DD/MAS ^{13}C NMR spectra of α-D-glucose, α-D-glucose·H_2O, and β-D-glucose crystals together with proton scalar-decoupled ^{13}C NMR spectrum of D-glucose in D_2O solution. Since the α- and β-anomers coexist in solution, the spectrum of the solution is composed of many resonance lines associated with both anomers(5). On the other hand, each solid spectrum contains a group of lines for either anomer as shown by broken lines in the figure, although the assignments of C2-C5 carbon lines are not well established at present. These results indicate that each solid sample comprises each pure anomer.

The assignment of the C6 line is relatively easy and reliable because the line is isolated from other lines and furthermore the spin-lattice relaxation time T_1 of the carbon is mostly shorter than those of the ring carbons(6). As seen in Figure 1, a large downfield shift of 2.4-2.9 ppm appears for the C6 line of the α-D-glucose crystal in comparison to those

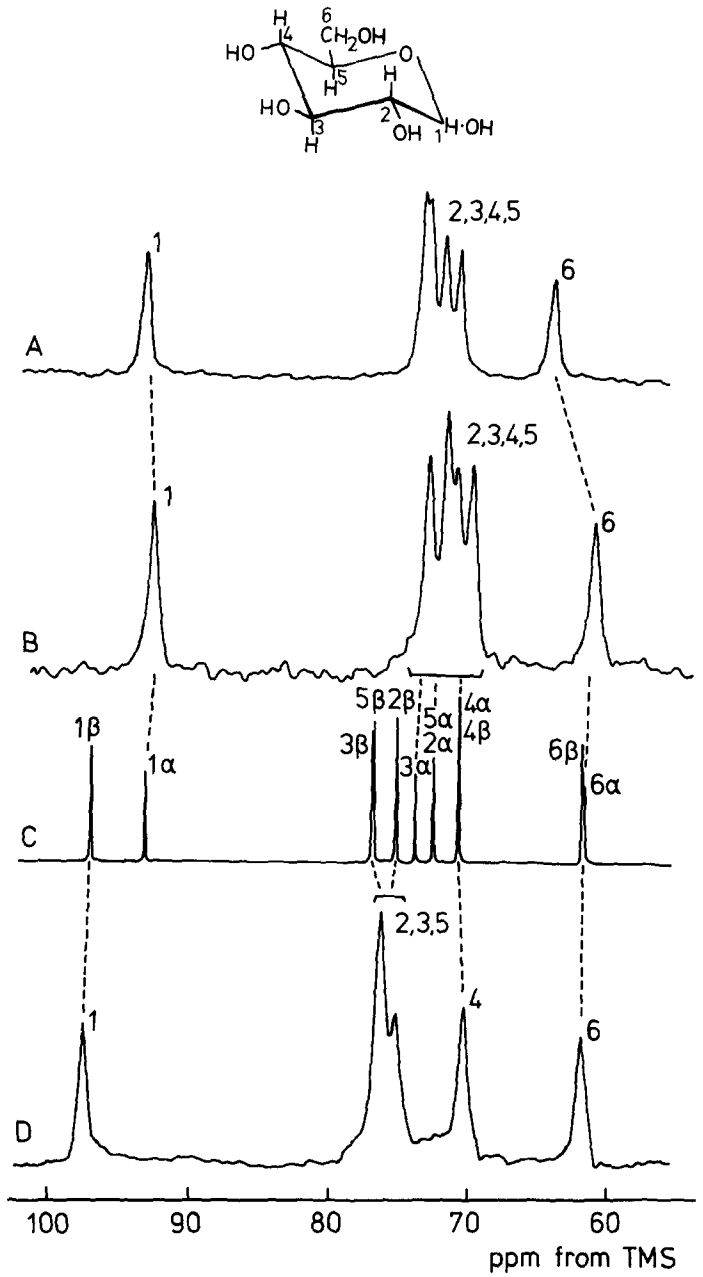

Figure 1 *25 MHz CP/DD/MAS and scalar-decoupled ^{13}C NMR spectra of D-glucose. A: α-D-glucose crystal, B: α-D-glucose·H_2O crystal, C: D-glucose in D_2O solution. D: β-D-glucose crystal.*

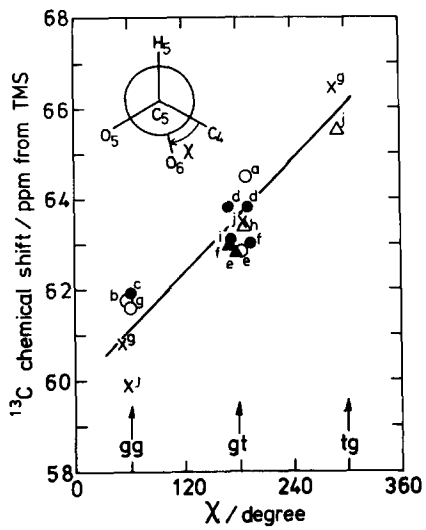

Figure 2 ^{13}C *chemical shifts of the* CH_2OH *carbons vs. torsion angles* χ *around the exo-cyclic C-C bonds. a: α-D-glucose, b: α-D-glucose·*H_2O*, c: β-D-glucose, d: β-D-cellobiose, e: α-D-lactose·*H_2O*, f: β-lactose, g: sucrose, h: α-melibiose·*H_2O*, i: β-methyl cellobioside·*CH_3OH*, j: raffinose·*$5H_2O$*;*
O: *α-glucopyranoses,*
●: *β-glucopyranoses,*
△: *α-galactopyranoses,*
▲: *β-galactopyranoses,*
X: *β-fructofuranoses*

of the α-D-glucose·H_2O as well as the β-D-glucose crystal and the solution. This suggests that the conformation about the C5-C6 bond of the α-D-glucose crystal is different from others. According to x-ray analyses(7-9) the conformations about the C5-C6 bond are *gauche-trans*, *gauche-gauche*, and *gauche-gauche* for the α-D-glucose, α-D-glucose·H_2O, and β-D-glucose crystals, respectively, where, for example, *gauche-trans* means that the C6-O6 bond is *gauche* to the C5-O5 bond and *trans* to the C4-C5 bond. It is, therefore, assumed that the chemical shifts of 64.5 ppm for the α-D-glucose and 61.6-61.9 ppm for the α-D-glucose·H_2O and β-D-glucose relate to the *gauche-trans* and *gauche-gauche* conformations, respectively.

In order to verify this assumption, the chemical shifts of the CH_2OH carbons of different monosaccharides and oligosaccharides are plotted in Figure 2 against torsion angles χ about the exo-cyclic C-C bonds which were determined by x-ray analyses(7-15). Although the samples involve mono- and oligosaccharides containing α- and β-glucopyranose, α- and β-galactopyranose, and β-fructofuranose rings, a simple linear relationship exists between the chemical shift and the torsion angle; the chemical shift increases with increasing χ, although above 300° the chemical shifts will decrease precipitously. It is, therefore, concluded that three preferred conformations of *gauche-gauche*(χ = 60°), *gauche-trans*(χ = 180°), and *trans-gauche*(χ = 300°) are reflected on the chemical shifts of 60-62 ppm, 62.5-64.5 ppm, and 65.5-66.5 ppm, respectively. In addition, the relatively large scattering of data within 2 ppm may be due to the difference in the chemical or stereospecific structure, or due to other additional effects such as packing(1) and hydrogen bonding(2-4). On the other hand, Saito et al.(16) have also pointed out that the ^{13}C chemical shift of the CH_2OH carbon in cyclohexa-amylose complexes with different low-molecular-weight compounds and amylose is qualitatively correlated with *gauche-gauche* or *gauche-trans* conformation. The conclusion obtained in our work is almost valid for those samples.

The assignment of the CH_2OH carbon line seems somewhat difficult for sucrose, melibiose·H_2O, and raffinose·$5H_2O$, because these samples contain the carbons with different conformations and the latter two samples further contain OCH_2 carbons in the 1-6 linkages. However, if such a linear relationship as shown in Figure 2 is assumed, their assignments are

Table 1 Conformations of the CH_2OH Groups of Cellulose in the Solid State

	^{13}C chemical shift /ppm	conformation	
		CP/DD/MAS NMR	X-ray
native cellulose			
crystalline	66.0-66.4	*trans-gauche*	*trans-gauche*
noncrystalline	63.4-63.9	*gauche-trans*	___
regenerated cellulose			
crystalline	63.9-64.3	*gauche-trans*	*gauche-trans* *trans-gauche*
noncrystalline	62.9-63.0	*gauche-trans*	___

straightforward. The chemical shift of the OCH_2 carbon of the 1-6 linkage was determined to be 65.5 ppm for both melibiose and raffinose crystals, suggesting that this agreement is due to almost the same conformation of the $O-CH_2-C$ bonds of them(13, 15). On the other hand, the solid spectrum of β-methyl cellobioside·CH_3OH crystal was devoid of the line corresponding to the CH_2OH carbon with the *gauche-gauche* conformation, whereas the line of the CH_2OH carbon with *gauche-trans* conformation as well as the lines of OCH_3 and CH_3OH carbons appeared at 63.1, 58.1, and 51.4 ppm, respectively. This means that the carbon with the *gauche-gauche* conformation may be so mobile that the efficiency of the CP between protons and ^{13}C nuclei is appreciably reduced. In addition, for commercial maltose monohydrate three lines appeared at 61.1, 64.1, and 66.4 ppm. Since β-maltose monohydrate (17, 18) and α-maltose(19) involve no CH_2OH carbons with *trans-gauche* conformation, the line at 66.4 ppm suggests the presence of a new type of the crystal structure.

The CP/DD/MAS ^{13}C spectra of native cellulose such as cotton and ramie contain two lines of the CH_2OH carbon(4, 20-22), which have already been assigned to the crystalline and noncrystalline components(23). Since their chemical shifts are 66.0-66.4 ppm and 63.4-63.9 ppm, the conformations are determined as *trans-gauche* and *gauche-gauche* for the crystalline and noncrystalline components, respectively, as shown in Table 1. The conformation of the crystalline component is in good accord with that determined by x-ray crystal analyses(24-26). On the other hand, the chemical shifts of the CH_2OH carbons of regenerated cellulose are 63.9-64.3 ppm and 62.9-63.0 ppm for the crystalline and noncrystalline components, respectively(4). Therefore, the conformation of the crystalline component is concluded to be *gauche-trans*, which conflicts with the conclusion by x-ray analyses(27, 28) permitting both of the *gauche-trans* and *trans-gauche* conformations. We think that the x-ray analyses must be revised for cellulose II crystal considering our NMR result. No appreciable difference in the CH_2OH conformation of the noncrystalline component appears for native and regenerated cellulose samples. However, the conformations of the β-1,4-glycosidic linkage are markedly different between the two samples as will be published elsewhere.

EXPERIMENTAL

β-D-glucose, β-D-cellobiose, and β-methyl cellobioside·CH_3OH were well

crystallized(29, 30). α-D-glucose, α-D-glucose·H_2O, β-maltose·H_2O, α-lactose·H_2O, β-lactose, sucrose, α-melibiose·H_2O, and raffinose·$5H_2O$ crystals were used as received from Nakarai Chem. Ltd., Japan. The high purity of these samples except for the β-maltose·H_2O was confirmed by their CP/DD/MAS ^{13}C NMR spectra as described for the D-glucose crystals.

25 MHz CP/DD/MAS ^{13}C NMR spectra were obtained with a JEOL JNM FX-100 spectrometer equipped with a CP/MAS unit(4, 31). The matched field strengths ν_{1H} and ν_{1C} were 69.4 kHz and the rate of the MAS was about 3.2 kHz. The ^{13}C chemical shifts were determined using the crystalline line of 33.6 ppm of polyethylene as an internal reference(4).

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