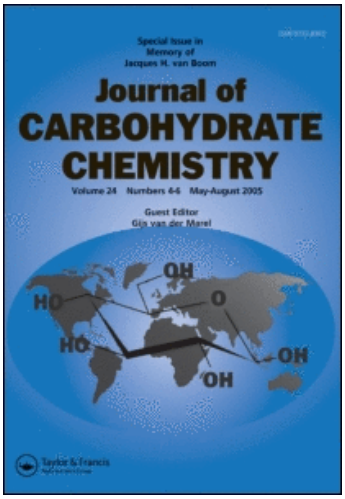

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INSIGHTS INTO THE LATTICE STRUCTURE OF CELLULOSE II FROM THE HIGH RESOLUTION CP/MAS SOLID STATE ^{13}C NMR SPECTRUM OF CELLOTETRAOSE

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ABSTRACT

The chemical shifts and multiplicities of the high-resolution ^{13}C CP/MAS NMR spectrum of cellulose II are quite diagnostic of the lattice structure of this polymorph. Particularly important is the chemical shift of C-1 and its clear splitting into two lines of equal intensity. Similar chemical shifts and multiplicities are seen in the spectrum of cellotetraose. Thus cellotetraose is considered to be a good model for the lattice structure of the polymer. A detailed investigation of the multiplicity of the C-1 resonance of cellotetraose shows that the two peaks are of equal intensity in this case also. Because of the limited number of repeat units in the tetramer, this observation implies that the unit cell contains two independent chains rather than a 'double' repeat unit. This gives support for a similar lattice structure, with two independent chains, for cellulose II itself.

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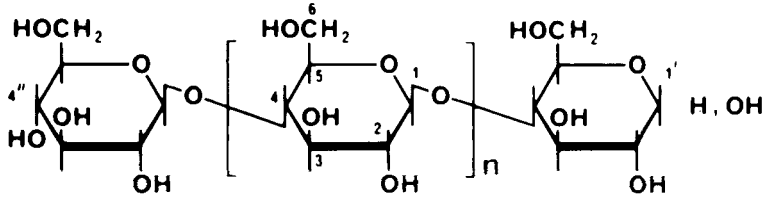
INTRODUCTION

Cellulose (1), the β-1,4-polymer of anhydroglucose exists in several polymorphic forms.[1,2] The naturally occurring form is



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cellulose I, while cellulose II is that usually obtained by regeneration from solution. There has been considerable discussion regarding the crystal structure of cellulose II and two models have been proposed.[3,4] In one, the unit cell is postulated to contain two independent chains,[3] while in the other, the chain conformation is thought to be such that a repeat unit containing two monomer units exists.[4] Since single crystals cannot be obtained, this problem cannot be solved by single-crystal diffraction techniques.

Information regarding the solid state structures of the cellulose polymorphs has been obtained from ^{13}C CP/MAS NMR spectroscopy.[4-7] In the case of cellulose II, Atalla and co-workers noted a 'doublet' structure for the C-1 resonance.[4] They postulated that this indicated the cellulose chain contained an alternation of conformationally different monomers and should be described by a 'double' repeat unit containing two monomers. This observation of the 'doublet' structure was confirmed by Fyfe, Marchessault and co-workers.[6,7] They showed that the multiplicities of the resonances due to C-1, and C-4 and the chemical shifts of C-1, C-4 and C-6 were particularly diagnostic of the cellulose II polymorph and reflected the unit cell configuration in a unique way. From a study of the cellulose II oligomers they further showed that these characteristic spectral

features are present in the spectra of cellotetraose and higher oligomers, and that these oligomers are good models for the structure of cellulose II itself.

In the present work we show that a choice between the two postulated crystal structures for cellulose II may be made from a detailed consideration of the ^{13}C CP/MAS NMR spectrum of cellotetraose.

RESULTS AND DISCUSSION

Figure 1 shows the ^{13}C CP/MAS spectra of cellulose II, cellotetraose and cellotriose. As can be seen, there is a very close correspondence between the spectra of cellulose II itself and cellotetraose, and both are quite different from that of cellotriose. The small 'doublet' splitting of C-4 seen in the cellulose spectrum is not observed in the cellotetraose spectrum, although the width of this resonance indicates the presence of more than one signal (the C-4 signal due to the reducing-end group must also be in this position). Otherwise, the two spectra are identical. In particular, the chemical shifts and the large 'doublet' splitting of C-1 are identical in both cases. There are two possible reasons why two peaks may be observed in solid-state NMR spectra, both due to effects of the crystal lattice. The unit cell might contain two crystallographically inequivalent sites, in principle yielding two signals for each resonance (as for 2,4-dinitrotoluene).[8a] However, the ^{13}C chemical shift difference resulting from this inequivalence might be too small to be observed for some resonances. Alternately, the site symmetry of the lattice might be lower than the molecular symmetry (as for the heptamethylbenzenium ion)[8b] giving more than one signal for some resonances. This latter effect is ruled out here as the cellulose monomer has no symmetry. Unfortunately, this by itself does not distinguish between the two possible unit cell structures as the site inequivalence induced by the crystal packing could exist either within a single chain or between chains. In the case of

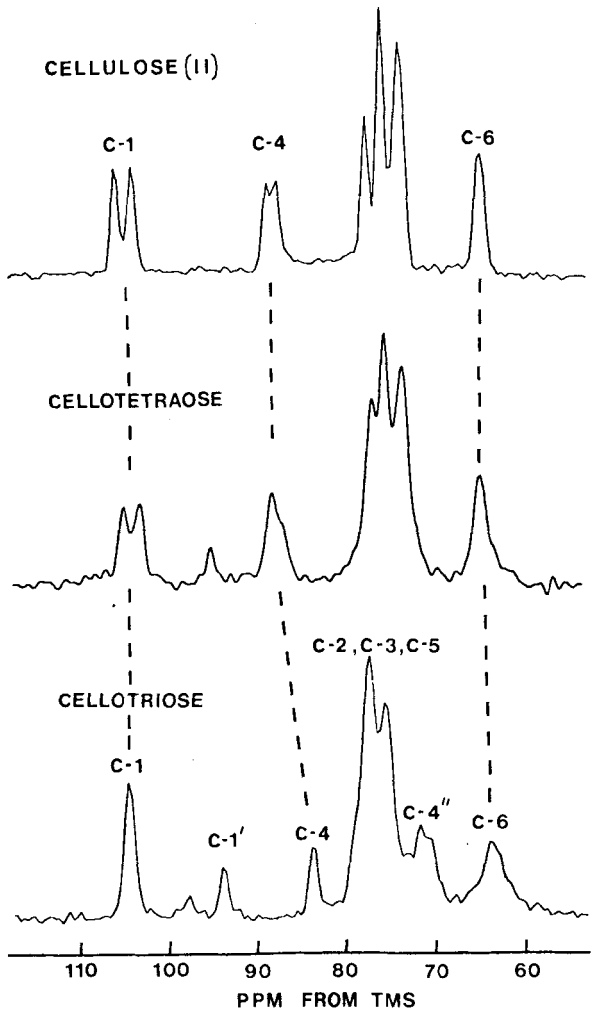

Figure 1. CP/MAS ^{13}C NMR spectra of cellulose oligomers and of a low-dp cellulose II sample. All spectra were recorded at 22.6 MHz using a 1-ms contact time τ_1 and a 1-s recycle delay time τ_2. Signals labelled C-1' and C-4" arise from the reducing and non-reducing groups of cellotriose respectively.

cellulose II, it is not possible to distinguish between these two possibilities, but such a distinction may be made for cellotetraose based on the relative intensities of the two signals.

Before considering the relative intensities, however, care must be taken to ensure that the spectra are quantitatively reliable. High resolution ^{13}C NMR spectra can be obtained from solid materials using a combination of high power decoupling, magic angle spinning, and cross-polarization (CP/MAS).[9] The CP/MAS experiment, shown in Figure 2, contains several variables which can affect the relative intensities of the different resonances. This may occur if different carbons in the system have different relaxation parameters or if the system is heterogeneous in nature. In the experiment, the proton magnetization is 'spin-locked' with a proton field H_H. During the spin-lock period magnetization is transferred to the carbon spin system by subjecting the carbon spins to an RF field H_c, such that the Hartman-

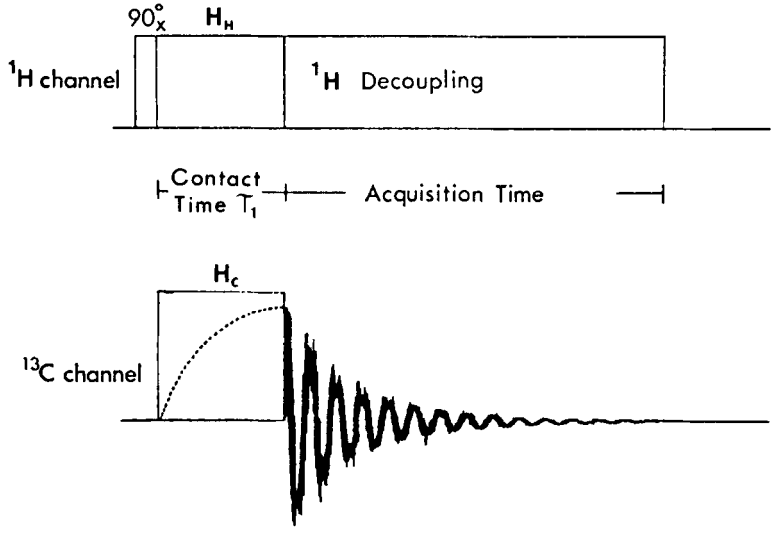

Figure 2. Schematic diagram of the cross-polarization ^{13}C NMR experiment.

Hahn condition $H_H\gamma_H = H_C\gamma_C$ is fulfilled. This gives rise to a maximum signal enhancement of $\gamma_H/\gamma_C = 4$. The ^{13}C signal is then observed during the acquisition time with high-power ^1H dipolar decoupling. During the 'spin-locking' period τ_1, the carbon magnetization will grow with a characteristic time constant T_{HC} and then decay according to the proton $T_{1\rho}$. Further, the carbon magnetization comes from the proton spin system and the reestablishment of the proton magnetization during the delay time τ_2 depends on the proton T_1 relaxation time. T_{HC} is affected by the local H-C dipolar interactions and may be different for different carbons in the system. In addition, although a single set of relaxation times is defined for all protons in a crystal, any sample heterogeneity on a macroscopic level can again cause differential effects in the ^{13}C spectrum. Figure 3 shows the effect on the cellotetraose spectrum of changing the contact time, τ_1, in the experiment. The absolute signal intensities change, but there is no differentiation in the relative peak intensities. Similarly, there is no change in relative peak intensities with variation in the delay time τ_2 of the experiment (Figure 4). Most importantly, the relative intensities of the two signals in the C-1 resonance are 1:1 in all of the spectra. As indicated above, this does not differentiate between the two possible mechanisms for the multiplicity in the case of cellulose II, but does in the case of cellotetraose due to the much smaller chain length. The two possible models for the cellotetraose unit cell configuration are represented schematically in Figure 5. Since the C-1 resonance of the reducing end group is clearly separated from those of the rest of the chain, the model with inequivalent sites within the chain (Figure 5A) should give two signals for the C-1 resonance in the ratio of 2:1. In contrast, the model where the inequivalent sites reside within two inequivalent chains (Figure 5B) should also yield two signals for the C-1 resonance, but now in the ratio of 1:1 (Similar effects will be seen in the spectra of higher oligomers, although the difference decreases with increasing chain length). The experimental results clearly favour a

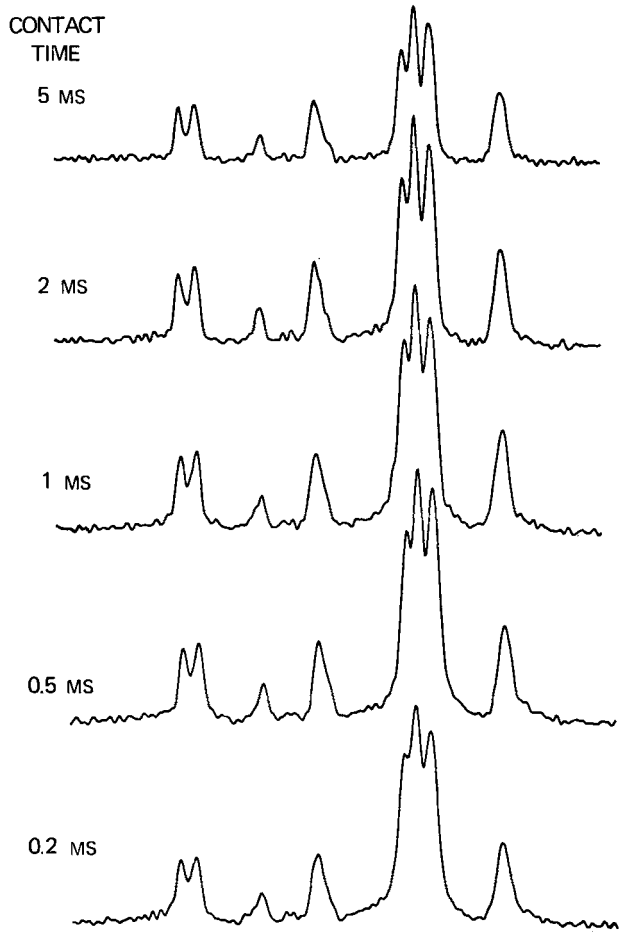

Figure 3. CP/MAS ^{13}C NMR spectra of cellotetraose obtained at 22.6 MHz using a variable contact time τ_1, and a 1-s recycle delay time τ_2. All spectra were plotted with -20Hz linebroadening.

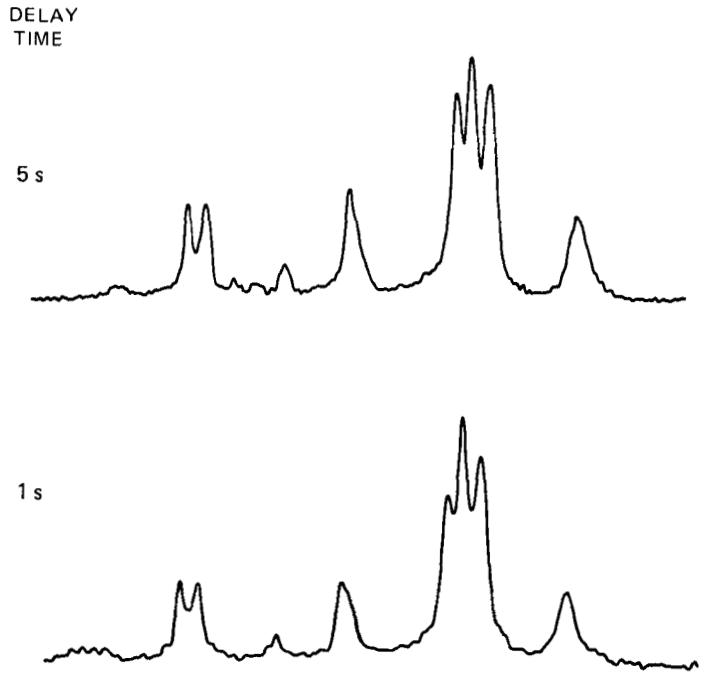

Figure 4. CP/MAS ^{13}C NMR spectra of cellotetraose obtained at 50.3 MHz using a variable recycle delay time τ_2, and a 1-ms contact time τ_1. All spectra were plotted with -40Hz linebroadening.

model for the cellotetraose crystal structure which contains two crystallographically inequivalent chains per unit cell.

However, a third possibility exists, not discussed to this point, which is a composite of the two models. Thus, a 1:1 doublet for C-1 will result from two chains if they contain between them equal amounts of the two repeat unit types. This could be an ordered structure in which the two chains mirror each other as in Figure 5C where the two repeat unit types still alternate (as in Figure 5A), but could also result from a random distribution of the two types over all the chains. If these were two crystallographically independent chains in addition, as suggested

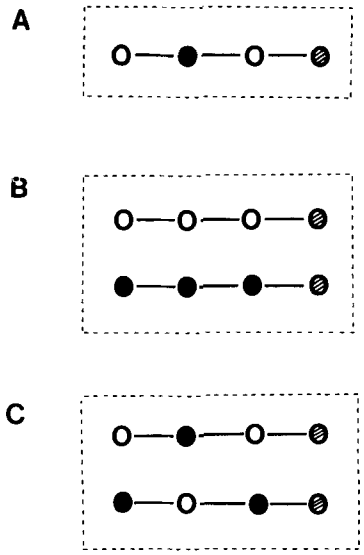

Figure 5. Two possible models for the cellotetraose unit cell. (A) Model with inequivalent sites within a single chain. (B) Model with two inequivalent chains. (C) Model with inequivalent chains where there are also two different monomer units within the chains. In (B) and (C) the chains may be parallel or anti-parallel. Closed and open circles represent monomer units in the inequivalent sites. Cross-hatched circles represent the reducing-end group which gives rise to a separate resonance for C-1 in the ^{13}C CP/MAS NMR spectrum.

by X-Ray data,[11] a multiplicity of four would be expected, but it is possible that the effect of chain inequivalence may be small and not be observed. From the NMR evidence alone it is not possible to rule out this model.

Thus, using ^{13}C CP/MAS NMR it is possible to eliminate some possible structures for cellotetraose. The close correspondence between the ^{13}C CP/MAS spectra of cellotetraose and cellulose II indicates clearly that cellotetraose is a sound model for the

cellulose II structure and extrapolation of the results of a single-crystal X-ray determined structure of cellotetraose to the cellulose II case is justifiable.

EXPERIMENTAL

^{13}C CP/MAS NMR spectra were obtained at 22.6 MHz using a Bruker CXP-100 spectrometer and at 50.3 MHz using a Bruker CXP-200 spectrometer with proton dipolar decoupling fields of approximately 15 Gauss. Cellotetraose was prepared according to the method of Whistler[10] by using direct acid hydrolysis of Whatman cellulose powder followed by chromatographic separation on carbon-Celite columns using ethanol-water eluants. The samples were then freeze-dried. Improvements in sample crystallinity were achieved by adding a few drops of water to the material. Cellulose II of low dp was prepared according to Atalla[4] by dissolving Avicel cellulose powder in 85% H_3PO_4 at room temperature and precipitating the filtered acid solution in a 10-fold excess of water after 11 days. The samples were characterized by melting point and high resolution ^{13}C NMR.

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