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Analysis

Solid State ^{13}C-NMR of Cellulose. A Relaxation Study

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SUMMARY

The ^{13}C spin-lattice relaxation times T_1 of hydrolysed cotton cellulose have been determined in the solid state. T_1 is between 202 and 266 seconds in the crystalline regions of the sample for all the carbons in the anhydroglucose unit and less than 15 seconds in the amorphous part. Based on the relaxation data, spectral assignment of the C2-C3-C5 region is proposed.

INTRODUCTION

Recently a number of papers have been published dealing with high resolution solid state ^{13}C NMR of cellulose and related compounds (1-9). Nevertheless the spectrum of the native cellulose has not been fully assigned and the line splittings remain largely unexplained. Figure 1A presents the resolution enhanced CP/DD/MASS ^{13}C NMR spectrum of cotton cellulose, hydrolysed in boiling 2.5 N HCl during 2 hours. It is obvious that the number of resonance lines exceeds the number of carbons in the glucopyranose ring. This may be caused by conformational differences of the glucose units in the cellulose crystals as well as in the noncrystalline parts. It has been shown earlier (2-5) that the broad lines at about 84 and 63 ppm are due to C4 and C6 resonances, respectively, in the less regular regions of the sample. Similarly, it must be noted that resonances at 105 ppm and 75 ppm contain besides the sharp lines much broader components from the above-mentioned less regular regions.

Horii *et al.* have proposed a simple relationship between the C6 carbon chemical shift and the CH_2OH group torsion angle about C-C bonds for different mono- and oligosaccharides in good agreement with X-ray data for native crystalline cellulose (6).

In spite of the efforts made, spectral assignment of the C2-C3-C5 region (71 to 76 ppm) has not been successful.

EXPERIMENTAL

To clarify this problem, we determined the spin-lattice relaxation times for all the resonances. This was done *via* cross polarization (CP) because of two obvious advantages: a CP experiment provides significant signal enhancement and the recycling delay is not determined by carbon, but by the much shorter proton relaxation time T_1. Taking into account that carbon T_1 is typically 250 s while proton T_1 is about 1.6 s in cellulose, the latter is of great importance. Even in the case of CP it takes about 100 hours to register one set of relaxation spectra, so it can be realised that it is almost impossible to measure those without using CP.

The pulse sequence used is given in Fig. 2. Cross polarization is acceptable, because we are not going to deal with the absolute, but only

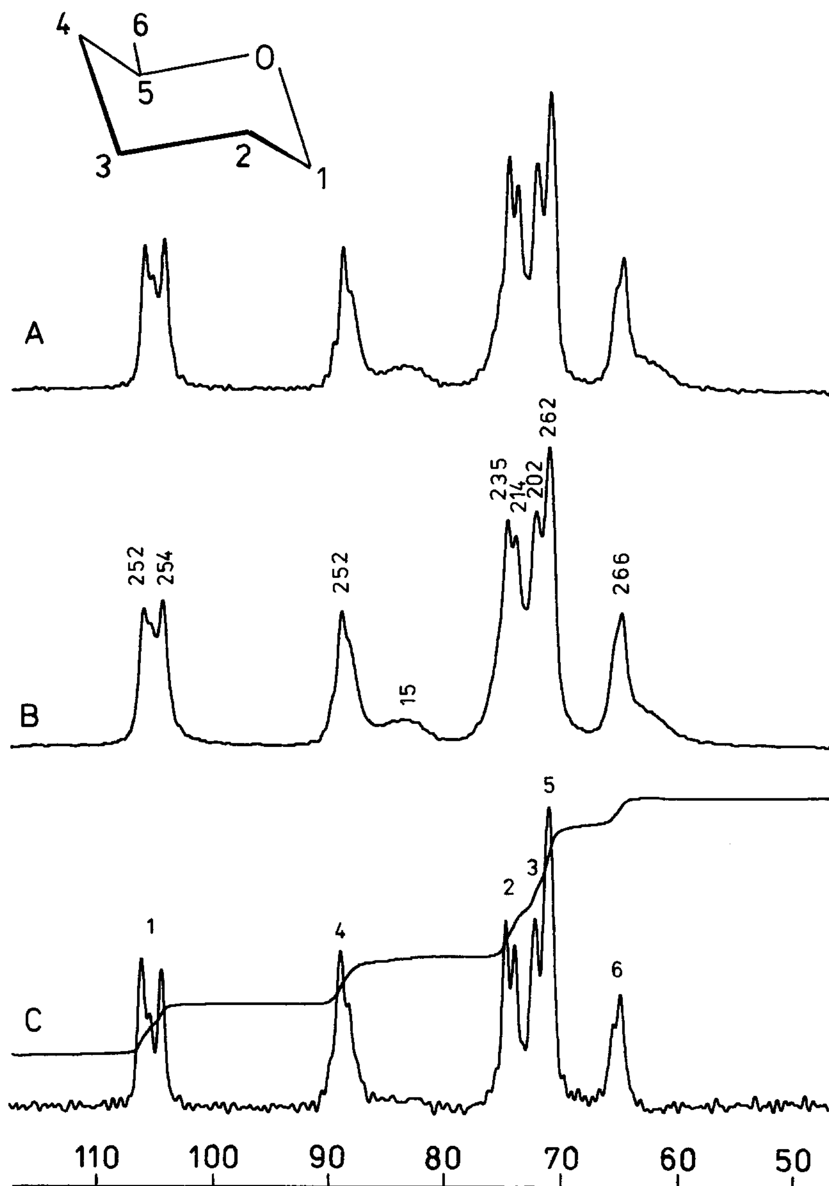

Figure 1. ^{13}C *MASS-spectra of cellulose I. A - hydrolysed cotton, B -* T_1 *relaxation times, C - the "crystalline part" of the spectrum A.*

relative intensities of the lines. Carbon relaxation is independent of the polarization process used.

Experiments were performed on a BRUKER CXP-200 spectrometer equipped with a 4.7 Tesla wide-bore Oxford superconducting magnet and a more stable home-built MASS unit of the double bullet design instead of the original mushroom-type rotor was used. Spinning frequency was routinely about 4 kHz. CP and decoupling radio frequency strengths were 50 kHz. Number of scans was limited by total duration of the experiment and was taken equal to 200

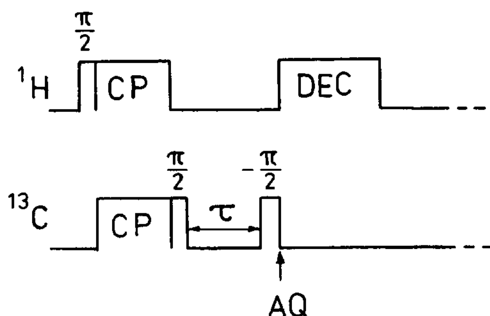

Figure 2 The pulse sequence used for the T_1 measurements.

and 140, respectively, for two sets of spectra. The waiting time τ was varied up to 700 seconds. Recycling delay was 8 seconds, equal to $5T_{1H}$.

To arrive at precise relaxation times, one must fit the relaxation curves by taking into account at least two exponential decay processes because of the presence of crystalline and amorphous components. This was complicated by the low signal-to-noise ratios of some lines. Therefore we determined the T_1 values for a tumefied cellulose sample which was completely amorphous. The data obtained are given in table 1.

Table 1. T_1 relaxation times for amorphous cellulose

Carbon number	1	2,3,5	4	6
Relaxation time T_1,s	12.0	8.1	12.4	0.5
Chemical shift, ppm	104.4	74.8	82.6	61.8

To avoid interference from amorphous regions, relaxation data for crystalline cellulose were evaluated using only spectra with $\tau \geq 100$ s, where the amorphous part was completely relaxed.

Figure 1B presents the computer-fitted carbon T_1 relaxation times for microcrystalline cellulose I. In marked contrast to Earl and VanderHart (2), we estimated that relaxation in the amorphous regions is very much faster than in the crystalline part, which indicates higher molecular mobility. This is probably caused by an irregular hydrogen bonding network. The broad C4 line at 84 ppm in hydrocellulose spectrum has a relaxation time rather close to that of the amorphous sample, which suggests that the structure and mobility of the less regular regions in hydrocellulose are similar to those of a totally amorphous sample. Difference between the two numbers (12.4 and 15 s) is due to the poor S/N ratio of the weak line.

DISCUSSION

In the crystalline part, C1, C4 and C6 have T_1 values very close to each other. Furthermore, the 71.4 ppm line in the central region also shows closely similar relaxation behaviour.

Crystalline cellulose I consists of parallel chains which are hydrogen-bonded into sheets. In those sheets all hydroxyl groups are linked through hydrogen bonds so that molecular motion is restricted (10, 11), which is also the reason for slow relaxation in comparison with the amorphous sample. In the glucose unit the C5 carbon is located between the C4 and C6 carbons and the ring oxygen. No known mechanism can cause C5 to relax faster than its neighbour. Obviously the 71.4 ppm line must be assigned to the C5 carbon. There is corroborating evidence to support the latter conclusion. C2 and C3 carbons have similar environments too. The remaining lines in the central region of the spectrum have also relaxation times relatively close to each other and differing from all the other T_1 values.

Further interpretation of the central region is complicated by the presence of a broad composite resonance from C2,3,5 at about 74.5 ppm, corresponding to regions with less regularity and persisting even in highly crystalline samples, for example in ramie cellulose (3). Nevertheless it is possible to cancel those broad lines with the same pulse sequence as described in Fig. 2. One must only know the spin-lattice relaxation time to calculate the proper waiting time so that the magnetization of the offending line goes through zero. Each different T_1 needs a different τ value to cancel the signal of the corresponding line. Figure 1C presents the spectrum of the same sample as Figure 1A, but with a delay of $\tau =$ $= 13.5$ seconds, optimized to cancel the signal of 2, 3 and 5 carbon of the amorphous part. One can also notice partial canceling of the amorphous part line at 84 ppm due to relatively close relaxation times of C2,3,5 and C4 carbons in the amorphous region. The same is true for the C1 signal. Amorphous C6 relaxes rather quickly, which results in intensity inversion at about 63 ppm.

The described method causes some intensity distortions. For the lines having relaxation times 202 and 262 seconds, the distortion produced by 13.5 s delay is about 1.6 per cent, small enough to neglect it. Comparison of the integral intensities in the central quartet allows assignment of the downfield two lines to the same carbon in the anhydroglucose unit. The ratio of intensities of those lines (75.1 and 74.2 ppm) to the remaining two (72.6 and 71.4 ppm) is about 1.23:2. The difference from the exactly 1:2 ratio can be due to the noncomplete canceling of the amorphous component, CP dynamics or linewidths differences (there is some overlapping of the lines). Splitting of the signal into two may be due to nonequivalent glucosidic linkages along the chain in analogy to the C1 splitting described by Atalla *et al.* (1). We assign the 75.1/74.2 doublet to the C2 carbon as the closest neighbour to C1. The final assignment is given in Fig. 1C.

It must be noted that the spectrum of the crystalline part of the sample (Fig. 1C) is very similar to that proposed by Atalla and VanderHart for the Iβ crystalline form of the cellulose I (12).

Relaxation times T_1 of cellulose II are also about 250÷300 seconds, but differences in the C2-C3-C5 region are even less.

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