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Synthesis of methyl 4′-*O*-methyl-β-D-cellobioside-$^{13}C_{12}$ from D-glucose-$^{13}C_6$. Part 2: Solid-state NMR studies

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Abstract—Double Quantum (DQ) NMR, which utilizes the magnetic dipole interaction between the ^{13}C atoms, was used for the complete assignment of the ^{13}C NMR resonances to the corresponding carbon ring positions for the monoclinic and triclinic allomorphs of methyl 4′-*O*-methyl-β-D-cellobioside-$^{13}C_{12}$(**1-$^{13}C_{12}$**), a cellodextrin model compound of cellulose ^{13}C-perlabeled at the cellobiose core. The through-space interactions were used to identify the direct chemical bonds between adjacent carbon atoms in the rings. More importantly, the ^{13}C NMR signals of the carbon sites C1′ and C4 involved in the glycosidic bond were identified. This allowed for the complete ^{13}C chemical shift assignment, that when combined with the X-ray crystallography data provides a complete characterization.

Keywords: Cellodextrins; Cellulose; Model compounds; Solid-state NMR; Glycosidic bond; ^{13}C Isotopic labeling

1. Introduction

The allomorphism of cellulose, the exact structure of the respective hydrogen bond networks and the changes of these networks upon swelling and dissolution processes are current 'hot topics' in cellulose chemistry and major challenges in polysaccharide analytics today. One way to tackle these problems is to use cellulose model compounds, from which the analytical results may be transferred to the polymer. This approach allows both: deriving first results on the polymer by analogy and sharpening the analytical tools with the help of 'easy-to-study' model compounds.

The disaccharide methyl 4′-*O*-methyl-β-D-cellobioside (**1**) was the first oligosaccharide model compound for cellulose to be found to crystallize also in two allomorphs.[1,2] Solid-state NMR characterization verified a significant effect of the crystal packing on the ^{13}C chemical shifts; even though the conformation of the individual molecules was quite similar in both crystalline phases as shown by XRD, their solid-state NMR chemical shifts showed appreciable differences.[2] The complete assignment of the NMR resonances to specific carbon atoms in the glucopyranose units requires that (i) the two subsets of six NMR resonances, belonging to either glucopyranose moiety, must be distinguished from each other and that (ii) in a subsequent step the C1′ and C4 resonances involved in the glycosidic bonds must be identified. This is the aim of the present paper.

It should be noted that the first task has already been solved in the past by various groups using ^{13}C-enriched

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cellulose samples and two-dimensional (2D) Double Quantum (DQ) NMR experiments based on homonuclear *J*-couplings.[3–10] However, no information is obtained on the glycosidic bond this way.

Considering that the assignment of glucopyranose units in cellulose allomorphs[11] is still a challenge and a matter of debate, it seemed indispensable that such a basic problem was solved for a relatively simple cellulosic model compound before the complex polymer case is addressed. The synthesis of **1-$^{13}C_{12}$**, a compound fully ^{13}C-labeled in both glucopyranose units, has been described.[12] We now focus on the complete assignment of all ^{13}C resonances to their specific positions in the glucopyranose units, including the direct observation of the glycosidic bond, that is, the identification of the C-4 and C-1′ atoms of the adjacent glucopyranose moiety, in both crystallographic modifications—the stable monoclinic $P2_1$ allomorph and the metastable triclinic $P1$ allomorph—of this cellulosic model compound.

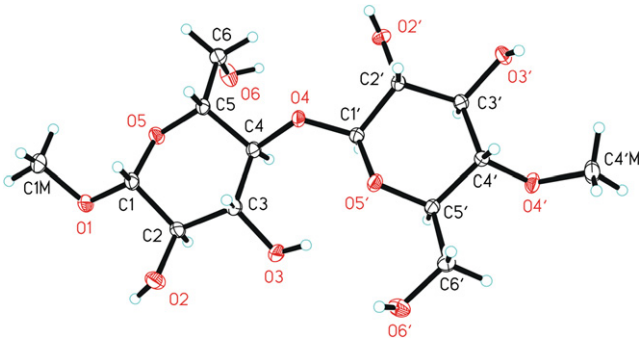

Figure 1. Thermal ellipsoid plots (60% ellipsoids) and crystallographic atom labeling of methyl 4′-*O*-methyl-β-D-cellobioside-$^{13}C_{12}$ (**1-$^{13}C_{12}$**).

2. Results and discussion

The molecular structure of compound **1-$^{13}C_{12}$** in its monoclinic phase[1,2] is shown in Figure 1 along with the crystallographic atom labeling, which is used in the following. Figure 2 displays the crystallographic packing along the *b*-axis.

The ^{13}C CPMAS NMR spectra of the monoclinic phase of the non-labeled model compound methyl 4′-*O*-methyl-β-D-cellobioside (**1**) and its labeled counterpart, methyl 4′-*O*-methyl-β-D-cellobioside-$^{13}C_{12}$ (**1-$^{13}C_{12}$**), are shown in Figure 3 (upper and middle row) together with the triclinic allomorph of **1-$^{13}C_{12}$** (lower row).[1,2] Narrow ^{13}C peaks with a line width at half-height of about 0.2 ppm (30 Hz) are observed for the non-labeled cellobioside (top-row spectrum) proving the high crystallinity of this sample. All of the 14 expected resonances are observed in this spectrum: 12 for the carbons in the two glucopyranose units and two for the methyl groups. These methyl resonances (C1M, C4′M) can be easily identified using different and, in particular, short CP times of about 0.5 ms. As the methyl groups rotate, the heteronuclear ^{1}H–^{13}C-dipole interaction within the methyl group is smaller than the corresponding coupling of the CH and CH_2 units. Consequently, the C1M and C4′M methyl carbon signal intensities are smaller for short CP times. These peaks are found at 55.7 ppm (right line) and at 61.4 ppm (third line from the right). All 12 carbon resonances of the glucopyranose rings are resolved. The pairs of the C1, C4, and C6 carbons can be assigned readily as shown in Figure 3 by comparing their chemical shifts with the well established assignment of celluloses.[8,13–15] However, without additional information it cannot be decided, which of these peaks represent the C1, C4, C6, or C1′, C4′, C6′ sites in the structure.

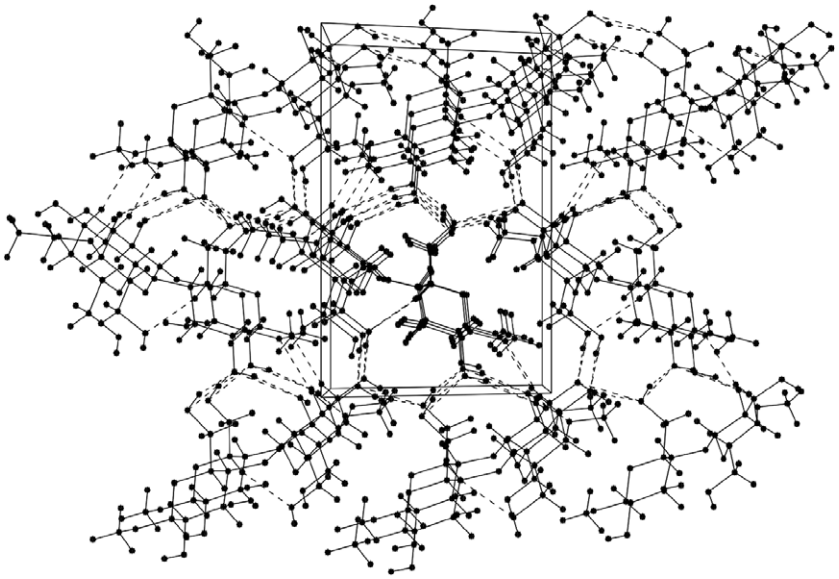

Figure 2. Crystal packing diagram of methyl 4′-*O*-methyl-β-D-cellobioside-$^{13}C_{12}$ (**1-$^{13}C_{12}$**), monoclinic allomorph, along the *b*-axis.