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Preliminary communication

Two, novel applications of Fourier Transform spectroscopy

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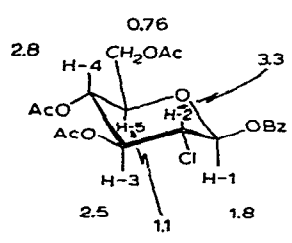
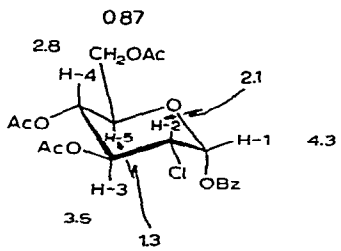
In a recent communication[1], we described, for the first time, two stereospecific dependencies for the longitudinal relaxation times (T_1-values) of the anomeric protons of pyranoid carbohydrates. We now provide important evidence concerning the mechanism responsible for these dependencies, illustrate its generality to positions other than the anomeric centre, and describe a novel method for simplifying the proton nuclear magnetic resonance (^{1}H n.m.r.) spectra of carbohydrates.

Measurement of the T_1-values of each proton of 3,4,6-tri-*O*-acetyl-1-*O*-benzoyl-2-chloro-2-deoxy-β-D-glucopyranose[2] (**1**, m.p. 160–161°) and of the corresponding α-D anomer[2] (**2**, m.p. 153–154°) was readily accomplished† and gave the data shown below



1



2

Intercomparisons of these data confirm[1] that, for an axially oriented proton, the most-important relaxation pathways involve either *1,3,5-triaxial*, or *vicinal–gauche*, interactions; for an equatorially oriented proton, only *vicinal–gauche* interactions are effective. Thus, the inversion of configuration at C-1 in going from **1** to **2** increases significantly the

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† Relaxation times were measured with a Varian XL-100 (15) spectrometer fitted with a Varian Fourier Transform system and a Varian 620L(16K) computer. A 3-pulse sequence (180°–90°–90°) was used; this displays the spectrum in the form (M_0–M_t). The samples were examined as 0.1M solutions in benzene-d_6 which were thoroughly degassed to remove dissolved oxygen.

relaxation times of both H-1 *and, importantly, H-3;* the relaxation time of H-5 is less influenced because its dominant relaxation pathway is *via* the H-6 nuclei. The *vicinal–gauche* effect is clearly shown by the values for the H-2 resonances, that for **2** being significantly the shorter. The *reciprocity* of these effects, which we could not previously examine, and the fact that they depend on inter-nuclear distance, support the contention that their dominant source is dipole–dipole relaxation. The identity of the T_1-values of the H-4 resonances encourages us to believe that it will be possible to develop empirical rules whereby T_1-values can be used as the basis for configurational assignments.

It is well known that full analysis of the ^{1}H n.m.r. spectra of monosaccharides is often complicated by the overlap of the H-5 and H-6 resonances with other ring protons. The extreme rapidity of the spin-lattice relaxation of these three protons suggested a way by which it might be possible to eliminate their resonances from an otherwise normal spectrum. In a T_1 determination[3], the delay time between the initial 180°-pulse and the subsequent 90°-monitoring pulse is varied. By chosing an appropriate delay time, it is possible to arrange for the signal of the proton that is relaxing most rapidly to decay to zero intensity, *while the other protons still have detectable intensity.* The two spectra shown in Fig.1 clearly illustrate the effectiveness of this approach. It is possible to see in the lower trace all four of the H-2 transitions, even though these same transitions are partially obscured in the normal spectrum.

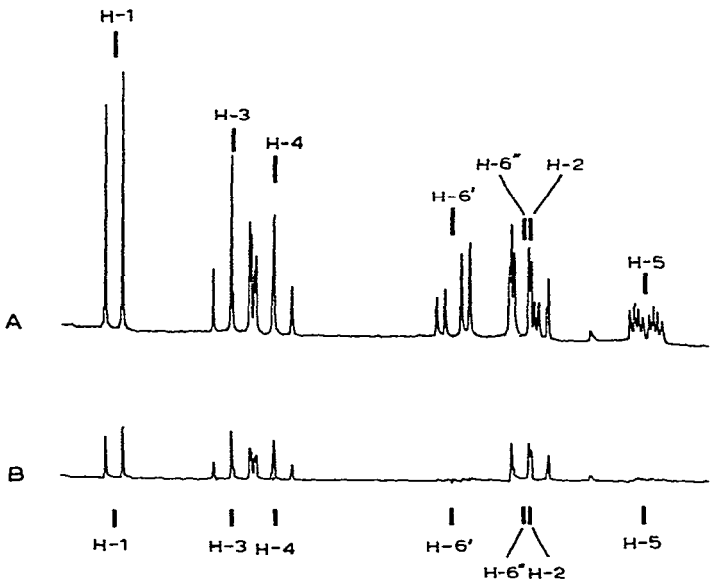

Fig.1. Partial 100-MHz proton resonance spectrum of a degassed solution of 3,4,6-tri-*O*-acetyl-1-*O*-benzoyl-2-chloro-2-deoxy-β-D-glucopyranose (**1**) in deuteriobenzene. The normal Fourier Transform spectrum is shown in A. The spectrum in the lower trace was run with a delay time of 3.0 sec between the 180° and 90° pulses.

We believe that the two applications of Fourier Transform n.m.r. spectroscopy illustrated here will further extend the already considerable potential of ^{1}H n.m.r. spectroscopy as a tool for studying carbohydrate derivatives.

ACKNOWLEDGMENTS

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