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Preliminary communication

Carbon-13 spin–lattice relaxation-times of some carbohydrate derivatives

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An understanding of ^{13}C spin–lattice relaxation-times (T_1 values) of carbohydrate derivatives is fundamental to the efficient measurement of ^{13}C n.m.r. spectra by the Fourier-transform (F.t.) method, and it also provides unique new insight into the microdynamics of the motion of carbohydrate molecules in solution. Some of these points will now be illustrated with respect to the four D-glucopyranose derivatives (**1**–**4**) whose T_1 values are summarized in Table I.

The practical relevance is that an approximate magnitude of the carbon-13 T_1-value is needed in order that a suitable time for the interval between successive (90°) pulses may be selected; ideally, this delay should be no less than five T_1 periods. Too short a time leads to progressive saturation of those resonances having the longer T_1 values, with the result that their intensities in the final spectrum are low; in the limit, such resonances can entirely disappear from the spectrum, and this is a common occurrence for carbon atoms that bear no directly bonded hydrogen substituent, such as a carbonyl carbon atom, or a carbon atom bearing a deuterium atom. Proper use of carbon-13 signal integrals[1], to determine compositions of mixtures, also requires a knowledge of the ^{13}C relaxation-times and relaxation-mechanisms. It is important to note (see Table I) that the T_1 values increase with decrease in concentration[2], but are not significantly affected by degassing to remove dissolved oxygen. On the other hand, the T_1 values are quite sensitive to temperature changes[3], so that temperature control is normally required if reproducible data are to be obtained; this is especially important because the noise-modulated, proton decoupling so widely used tends to warm the sample.

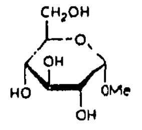
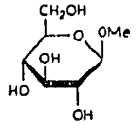
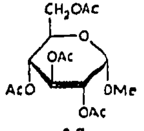
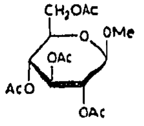
The relaxation of a single ^{13}C nucleus by a set of N_H directly bonded protons, operating *via* the intramolecular dipole–dipole mechanisms, has the form[4]

$$1/T_1 \propto N_H \cdot \gamma_C^2 \cdot \gamma_H^2 \cdot \tau_C \cdot (r_{C-H})^{-6} \qquad (1)$$

where γ_C and γ_H are the magnetogyric ratios of ^{13}C and ^{1}H, respectively, r_{C-H} is the carbon–hydrogen bond-length, and τ_C is the motional correlation-time of the carbon nucleus. That this is the dominant mechanism for the relaxation of compounds **1**–**4** is con-

TABLE I

CARBON-13 SPIN-LATTICE RELAXATION-TIMES[a] (sec) AND n.O.e. FACTORS[b] (%, in parentheses) FOR MOLAR SOLUTIONS[c], MEASURED AT 39° WITH A VARIAN CFT-20 (16K) SPECTROMETER[d]

Compound	*Solvent*	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*OMe*	*C=O*	*CH$_3$-CO-*
 1[e]	D_2O, not degassed	1.1	1.0	1.2	0.9	1.1	0.62	3.4	–	–
	D_2O, degassed	1.1 (105)	1.0 (94)	1.1 (96)	1.0 (96)	1.2 (95)	0.47 (100)	3.4 (95)	–	–
	D_2O (0.5M), not degassed	1.4	1.3	1.6	1.3	1.3	1.0	3.5	–	–
 2[e]	D_2O not degassed	1.2 1.2[f]	1.1 1.1[f]	1.1 1.2[f]	1.0 1.2[f]	1.1 1.2[f]	0.65 0.57[f]	3.2 3.4[f]	–	–
 3[e,g]	$CDCl_3$, not degassed	0.60	0.65	0.62	0.64	0.65	0.33	2.3	12.3[h]	2.4
	$CDCl_3$, degassed	0.60	0.67	0.70	0.60	0.69	0.36	2.3	15.2[h]	2.2
 4[e]	$CDCl_3$, not degassed	0.50 (90)	0.48 (90)	0.45 (100)	0.43 (100)	0.46 (100)	0.29 (100)	1.7 (100)	12.5[h] (70)	1.9 (90)

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[a] Using the spin-inversion, recovery method[7(a)]; 6–10 data points were determined for each resonance, and the T_1 values were calculated from the semi-log plots, using a least-squares-fit, computer program. For the carbonyl carbon atoms the progressive-saturation method[7(b),(c)] was used. [b] Determined by gated decoupling[8]. [c] A volume of 2.0 ml of solution was used for each experiment. [d] Operating with a 90° pulse of 20 μsec, at least 100 transients with a pulse interval of 15 sec, a sensitivity-enhancement factor of –0.4, and 8k data points over a sweep-width of 1.5 kHz to ensure accurate line-determinations. Line intensities were used for the T_1 experiments, whereas integrated areas were used in the n.O.e. determinations. [e] For peak assignments, see ref. 9. [f] Measured with 1.0 ml of solution, and a vortex plug to fill, precisely, the receiver coil. [g] For a revised peak-assignment, see ref. 10. [h] Average for 3 resonances for 3, and 4 resonances for 4.

firmed by the high values for the nuclear Overhauser enhancement (n.O.e.) factors[5] found for 1 and 4.

For each sugar, the close similarity* of the T_1 values of the individual ring-carbon atoms (C-1—C-5) indicates that (*a*) these carbon atoms have closely similar correlation-times, all other parameters in equation (*1*) being identical, and, hence, (*b*) each molecule tumbles isotropically in solution. That the T_1 value of C-6 is approximately half that of the ring-carbon atoms (*a*) is in accord[6] with the fact that this atom bears two hydrogen substituents and, importantly, (*b*) implies that its correlation time is not seriously influenced by rotation about the C-5—C-6 bond. In marked contrast, the T_1 values of the glycosidic methyl carbon atoms of compounds 1—4, and of the acetate methyl carbon atoms of compounds 3 and 4, are approximately three times longer than those of the ring-carbon atoms, rather than being a third of their value; this indicates[6] that these carbon atoms undergo essentially free rotation in solution. That the T_1 values of the carbonyl atoms of 3 and 4 are so much longer than any others reflects the fact that these carbon atoms bear no hydrogen substituents; even so, their n.O.e. factors indicate that they still acquire most of their relaxation from protons in the same molecule. Not surprisingly, the relaxation of these carbonyl carbon atoms was found to be influenced by degassing, the T_1 values then increasing by ~20%.

Although the T_1 values that are given here now provide for a rational basis for the use of carbon-13 F.t. measurements, it is clear that many further studies will be needed in order to permit full delineation of the microdynamics of sugar conformations.

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REFERENCES

1 G. C. Levy and G. L. Nelson, *Carbon-13 Nuclear Magnetic Resonance for Organic Chemists*, Wiley—Interscience, New York, 1972, pp. 29–31.
2 A. Allerhand, D. Doddrell, and R. Komoroski, *J. Chem. Phys.*, 55 (1971) 189–198.
3 I. M. Armitage, H. Huber, D. H. Live, H. Pearson, and J. D. Roberts, *J. Magn. Resonance*, 15 (1974) 142–149.
4 J. H. Noggle and R. E. Schirmer, *The Nuclear Overhauser Effect: Chemical Applications*, Academic Press, New York, 1971, p. 45 and references cited thereon.
5 Ref. 1, p. 30, and references cited thereon.
6 Ref. 1, p. 186, and references cited thereon.
7 (a) R. L. Vold, J. S. Waugh, M. P. Klein, and D. E, Phelps, *J. Chem. Phys.*, 48 (1968) 3831–3832. (b) R. Freeman and H. D. W. Hill, *ibid.*, 54 (1971) 3367–3377. (c) R. Freeman, H. D. W. Hill, and R. Kaptein, *J. Magn. Resonance*, 7 (1972) 82–98.
8 R. Freeman, H. D. W. Hill, and R. Kaptein. *J. Magn. Resonance*, 7 (1972) 327–329.
9 K. Bock and C. Pedersen, *J. Chem. Soc. Perkin II*, (1974) 293–297, and references cited therein.
10 K. Bock and C. Pedersen, *Acta Chem. Scand.*, in press.

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*The experimental error for each value is at least ±5%, and for the shorter T_1-values of the C-6 resonances, it is higher.