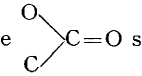
A Comparison of the Nuclear Magnetic Resonance Spectra of Acetylated Monosaccharides in Deuteriobenzene and Deuteriochloroform

By M. H. FREEMANTLE and W. G. OVEREND*

[*Chemistry Department, Birkbeck College* (*University of London*), *Malet Street, London, W.C.*1]

LARGE aromatic solvent induced shifts (ASIS)[1] in n.m.r. spectroscopy have now been observed in a series of acetylated monosaccharides and acetylated methyl glycosides. The results listed in the Table are typical of those noted in our work. The internal shifts of the ring proton from acetoxy-proton resonances are larger in C_6D_6 than in $CDCl_3$, leading to improved resolution. The magnitude and direction of the individual ASIS $\Delta^{\mathrm{CDCl_3}}_{\mathrm{C_6D_6}}$ ($\delta_{\mathrm{CDCl_3}} - \delta_{\mathrm{C_6D_6}}$) values for pyranose derivatives depend on the configuration and conformation (Table).

There are several contributions to these solvent shifts.[2] However, a comparatively large and perhaps dominant contribution is attributable to the magnetic anisotropic character of the benzene molecule and our discussion is restricted to this contribution. Williams *et al.*[3] have developed a model to explain anisotropic shifts in steroids and aromatic solutes and this has been adapted to account for the anisotropic factor in the ASIS of acetylated saccharides. It is assumed that (i) a 1 : 1 non-planar, non-random, transient "collision complex" is formed at the electron-deficient carbon of the carbonyl group of the acetate in such a way that the benzene molecule is as far away as possible from the oxygen of the carbonyl group; (ii) the complex may be represented by a time-averaged model of all possible rotamers of the acetate group and all locations of the complexing benzene molecule; (iii) contributions to the anisotropic shift due to association at other less electron-deficient sites are relatively small and so can be ignored; and (iv) the anisotropy of a benzene molecule may be attributed to a "ring current"[4] and a shielding envelope results. As a tentative model we assume that for each acetate group the benzene molecule is inclined towards the Me-group and is in a plane approximately at right angles to the plane of the  $\overset{\mathrm{O}}{\underset{\mathrm{C}}{>}}\mathrm{C{=}O}$ system. On the basis of this model the magnitude and direction of the benzene anisotropic contribution

Values of $\Delta^{CDCl_3}_{C_6D_6}$ (p.p.m.) *for* C-1 *substituents of some acetylated derivatives of monosaccharides**

	Orientation of substituent					
	Axial			Equatorial		
Derivative	H	OAc	OMe	H	OAc	OMe
Penta-*O*-acetyl-α-D-glucopyranose		+0·45		−0·24		
Penta-*O*-acetyl-β-D-glucopyranose	−0·11				+0·36	
1,2,3,4-Tetra-*O*-acetyl-6-deoxy-6-iodo-α-D-glucose		+0·50		−0·16		
1,3,4,6-Tetra-*O*-acetyl-2-deoxy-β-D-*arabino*-hexose	+0·10				+0·37	
1,2,3,4-Tetra-*O*-acetyl-6-deoxy-α-D-glucose		+0·42		−0·27		
Methyl tetra-*O*-acetyl-α-D-glucopyranoside			+0·41			
Methyl tetra-*O*-acetyl-β-D-glucopyranoside						+0·28
Methyl 2,3,4-tri-*O*-acetyl-6-deoxy-6-iodo-α-D-glucoside			+0·39			
Methyl 2,3,6-tri-*O*-acetyl-4-deoxy-α-D-*xylo*-hexoside			+0·35			
Tetra-*O*-acetyl-β-D-*xylo*-pyranose	−0·17				+0·38	
Penta-*O*-acetyl-α-D-galactopyranose		+0·41				

* All n.m.r. measurements were made with a Varian A-60 instrument and refer to 0·3M solutions at ambient temperature with Me_4Si as internal standard.

to a specific $\Delta^{CDCl_3}_{C_6D_6}$ value will depend on the average location of the benzene molecule with respect to the carbonyl group and thus the accessibility of the carbonyl group, and on contributions by similar associations at other sites in the solute molecule.

To a gross first approximation all contributions other than that due to the above association can be ignored. In this case the model accounts reasonably well for the trends observed. However, because of the number of parameters, approximations, and assumptions involved, it would seem unwise to use this model more rigorously.

The main value of these studies with respect to the n.m.r. spectroscopy of carbohydrates lies in the relation and use of the observed trends in $\Delta^{CDCl_3}_{C_6D_6}$ in connexion with configurational and conformational studies.

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