Stereospecific Contact Interactions in the Nuclear Magnetic Resonance Spectra of Polyol–Lanthanide Complexes

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Summary Addition of lanthanide ions to polyols in aqueous solution causes shifts in their ^{1}H n.m.r. spectra which are interpreted as being due to contact and pseudo-contact interactions; the contact interaction is greatest when the bonds connecting the proton and the cation form a planar zig-zag arrangement.

Although the effects of lanthanide shift reagents on ^{1}H n.m.r. spectra are attributed mainly to pseudo-contact interactions,[1] it is now realized that contributions from contact interactions are not insignificant at those nuclei which are only a few bonds away from the complexing site.[2] We now report instances in which the contact interactions on protons are particularly strong and are recognized to have a steric specificity.

When diamagnetic cations form complexes with polyols in aqueous solutions, small downfield shifts of the n.m.r. signals ('diamagnetic shifts') are observed.[3] Complexing of polyols with lanthanide cations causes shifts whose direction and magnitude appear puzzling.[4] From many results obtained here recently we present those relevant to *epi*-inositol and 1,6-anhydro-β-D-allopyranose. Complexing in these compounds occurs at an axial–equatorial–axial sequence of three oxygen atoms.[5] The lanthanide-induced shifts are interpreted as being caused by a combination of diamagnetic shifts, pseudo-contact shifts in the usual

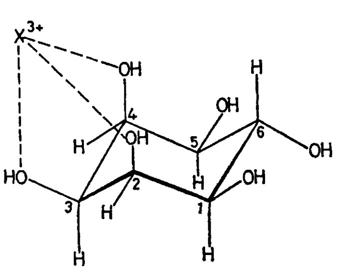
Table 1

Lanthanide-induced chemical shifts (p.p.m.) in the spectrum of *epi*-inositol (**1**)[a]

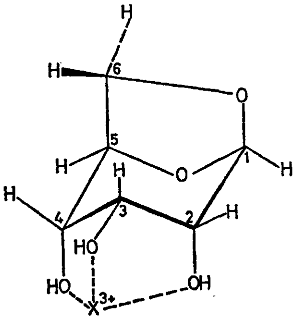
Cation	H-1,5	H-2,4	H-3	H-6
La^{3+}	0·2	0·25	0·55	0·05
Pr^{3+}	−1·05	−2·05	2·05	−3·5
Nd^{3+}	0·3	−1·10	6·1	−1·65
Eu^{3+}	−0·35	1·6	−7·2	1·65
Tb^{3+}	−18	−19	−35	−19
Yb^{3+}	−0·25	−2·05	−4·8	4·45

[a] N.m.r. spectra were measured with a JNM-4H-100 spectrometer at 100 MHz in D_2O solutions at 25°. The lanthanides were added as nitrates or chlorides. Only the relative values of the shifts with each metal are significant; the absolute values are only approximate since they were calculated with the use of an association constant ($K = 10$ mol^{-1} l) which is not accurately known. Positive values indicate downfield shifts.

direction (*i.e.*, that observed with shift reagents in organic solvents), and contact shifts which are in the opposite direction (except for Tb, Dy, Ho). In the spectra of complexes of *epi*-inositol (**1**) (Table 1) the shifts of H-6 (which is connected by the greatest number of bonds to the cation) are regarded as being representative of pseudo-contact effects, while those of H-3 show the greatest contact contribution.



(1)



(2)

This interpretation is based on the following arguments. (i) The direction and magnitude of the shifts of H-6 are typical of those caused by pseudo-contact interaction.[1,6] (ii) The relative shift of H-3 is largest in europium and neodymium complexes and comparatively small in praseodymium and ytterbium complexes, an order theoretically derived[7] and experimentally found[8] for contact interactions. (iii) The direction of contact interaction (as determined on ^{17}O of water in aqueous solutions of lanthanide perchlorates[9]) is opposite to that of the pseudo-contact interaction, except for Tb, Dy, and Ho; with these metals we have found all shifts to be in the same direction. (iv) Opposite shifts are observed of the protons connected to the complexing site by the smallest number of bonds.

The 1,6-anhydro-sugars present further relevant information; data on 1,6-anhydro-*β*-D-allopyranose (**2**) are shown in Table 2. Of the seven protons only one or three show shifts in the opposite direction, and these are the ones which are connected by only three bonds to the cation. The shift ratio of these signals varies strongly with the nature of the cation but that of most of the other protons is independent of the cation, as it should be for pseudo-contact shifts.[10] The contact shift contribution is greater in the europium than in the praseodymium complex.

TABLE 2

Lanthanide-induced chemical shifts in the spectrum of 1,6-anhydro-*β*-D-allopyranose (**2**)

Cation	H-1	H-2	H-3	H-4	H-5	$H\text{-}6_{exo}$	$H\text{-}6_{endo}$
Eu^{3+}	2·0	*c.* −0·3	−6·35	*c.* −0·3	2·0	0·1	0·7
Pr^{3+}	−2·7	*c.* −0·2	2·0	*c.* −0·2	−2·4	−1·0	*c.* −1·1

This appears to be the first reported occurrence of strong contact interactions in lanthanide-induced proton shifts of saturated organic compounds. Inspection of the shifts shows that contact interaction depends on the spatial arrangement, as observed and theoretically justified by Morishima and his co-workers[11] on amine–$Ni(acac)_2$ complexes. The interaction occurs most strongly through saturated bonds when the resonating nucleus, the lanthanide cation, and the intervening atoms are in a plane (that is, the bonds form an antiparallel zig-zag). In the complexes of *epi*-inositol (**1**), H-2 and H-3 are both connected through three bonds to the cation and are approximately equidistant from it; yet the contact interaction on these protons is very different. The bonds connecting H-3 to the cation are in a plane, those of H-2 are not. One bond further away, H-1 and H-5 in *epi*-inositol clearly show contact interaction, but H-1 and H-5 in 1,6-anhydro-*β*-D-allopyranose do not; they are not in a planar zig-zag. Contact interaction is detectable even over five intervening bonds, provided that they form a planar zig-zag: $H\text{-}6_{exo}$ (but not $H\text{-}6_{endo}$) in 1,6-anhydro-*β*-D-allopyranose displays a contact effect. Similar stereospecificity of the contact interaction can also be discerned in some ^{13}C spectra.[2,12]

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