Application of Lanthanide Induced Shift Reagents to Organic Cations by Outer Sphere Complexation

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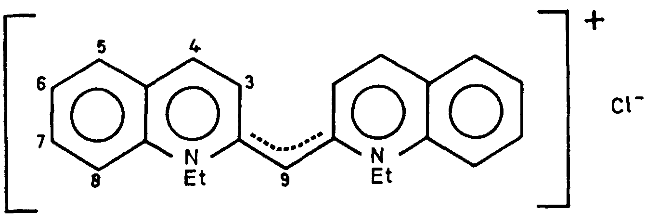
Summary Lanthanide ion shift reagents are effective in causing induced shifts in the proton resonance spectra of organic cations such as cyanine dyes, quinolinium, and quaternary ammonium salts, which apparently interact with the reagent by forming contact ion pairs.

The application of lanthanide induced shift (LIS)[1] reagents for the simplification of the n.m.r. spectra of organic solutes has grown recently. The applications reported, however, have been limited to those organic compounds which possess one or more groups such as hydroxy, keto, amino, carboxy, *etc.*, that are capable of direct binding to the lanthanide ions.[2] We describe here an unreported class of organic solutes which can be studied with LIS reagents.

In the course of studying the cationic dye, 1,1′-diethyl-2,2′-cyanine (pseudoisocyanine) chloride (Ia) we considered the use of LIS reagents for simplifying the complicated aromatic band. Although no example of an LIS effect with organic cations was known, we hoped that it could be observed with this class of compounds and examined deuteriochloroform solutions of (Ia) in the presence of Eu(fod)$_3$. We observed that resonances of all the protons of (Ia) were moved increasingly to lower applied field with addition of the reagent. The chemical shift changes, $\Delta\delta$, of assigned resonances were determined for 3×10^{-3}M-solutions of (Ia) in which the reagent: substrate ratio, R, was varied. Data were obtained at 100 MHz with a Varian HA-100 spectrometer which was modified for pulsed (Fourier transform) operation. The low dye concentration is a consequence of the sparing solubility of (I) in CDCl$_3$ and required time averaging of *ca.* 3000 pulses for a good signal: noise ratio.

The lanthanide induced shifts that we find for (Ia) are of the order of -1 to -2 p.p.m. for $R \geqslant 1{\cdot}0$, smaller than usually observed for various directly bonded Eu(fod)$_3$

adducts[2,3] but adequate to enable the analysis of the simplified (Ia) aromatic proton spectrum. At $R = 2{\cdot}4$, $-\Delta\delta$ is 2·0, 1·6, 2·6, 1·8, and 2·4 p.p.m. for the 3,3′; 4,4′; 9; CH_3, and CH_2 protons, respectively. The reagent $Pr(fod)_3$ was also effective in shifting the resonances of (Ia) in $CDCl_3$ solution. As for directly bound ligands,[2] $Pr(fod)_3$ caused shifts of opposite sign and was more effective than $Eu(fod)_3$.



(Ia)

We also have observed LIS's with *N*-ethylquinolinium iodide in $CDCl_3$. A substrate concentration of 4×10^{-3}M and *ca.* 0·5 equiv. of $Eu(fod)_3$ reagent gave a shift of the methyl signal of −0·73 p.p.m. which is close to that found for (Ia) under similar conditions.

The dye and quinolinium salt, in addition to being cations, are also aromatic and, thus, π-electron interactions could be important. We, therefore, examined solutions of tetraethylammonium chloride, for which no such bonding interaction of the cation with the reagent could take place. At a substrate concentration of 4×10^{-3}M with 2·3 equiv. of $Eu(fod)_3$, we found induced shifts of −3·86 and −7·52 p.p.m. for the methyl and methylene protons, respectively.

We suggest that the observation of LIS effects with organic cations such as (Ia) could result only if the cation participates in an outer sphere complex;[4] the dye counterion, Cl^- in the case of (Ia), complexes directly with europium(III). The dye–$Eu(fod)_3$ interaction is then a consequence of contact ion pairing between the dye and its counterion. It is well known that solvents of low dielectric constant, such as $CDCl_3$, facilitate ion pairing.[4,5]

Since this hypothesis requires inner sphere complex formation by the dye counterion (anion), it can be tested by measuring shifts for solutions of (Ib, c, and d) in which the dye counterion is Br^-, I^-, and SO_4^{2-}, respectively. The $Eu(fod)_3$ induced shifts for the methyl protons of these dye–anion combinations were obtained and are given for $R = 2{\cdot}0$ in the Table.

The data in the Table demonstrate clearly that the anion plays an important role in determining the magnitude of the induced shifts. The organic cation structure is identical in (Ia—d) and, we believe, precludes direct dye–metal ion complexation.

TABLE

$Eu(fod)_3$ *induced shift of methyl resonances at* $R = 2$ *for various pseudoisocyanine dyes in* $CDCl_3$[a]

Dye	Anion	Methyl Δδ (p.p.m.)[b]
(Ia)	Cl^-	−1·7
(Ib)	Br^-	−0·71
(Ic)	I^-	−0·30
(Id)	SO_4^{2-}	−1·72[c]

[a] [Dye] = 3×10^{-3}M. All shifts are referenced to internal Me_4Si. [b] The chemical shift of the methyl resonance in the absence of $Eu(fod)_3$ was −1·68 ± 0·01 p.p.m. for (Ia—d). [c] [Dye] = 5×10^{-4}M.

The overall stability of an $Eu(fod)_3$–dye adduct will be determined by several potentially important equilibria. These include (1) $Eu(fod)_3$ complex formation with the anion, (2) the association of the organic cation with the bound anion, and (3) dye–anion pair formation. The observed variation in LIS magnitude ($Cl^- > Br^- > I^-$) could result from differences in the stability constants,[6] K_1K_2/K_3, as well as the metal–ligand distances. Preliminary studies on (Ia) indicate the stability constants may be very large (*i.e.* $>10^2$).

These results show a new application of the lanthanide shift reagents and suggest their use in studies of such organic cationic species as quaternary ammonium, pyridinium, quinolinium, pyrylium, *etc.* Our results also show that competition from outer co-ordination sphere binding must be considered when polyfunctional organic cations are studied using shift reagents.

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