Cation–Anion Association in Iminium Salts. Use of Europium Complexes as ¹H N.M.R. Auxiliary Compounds

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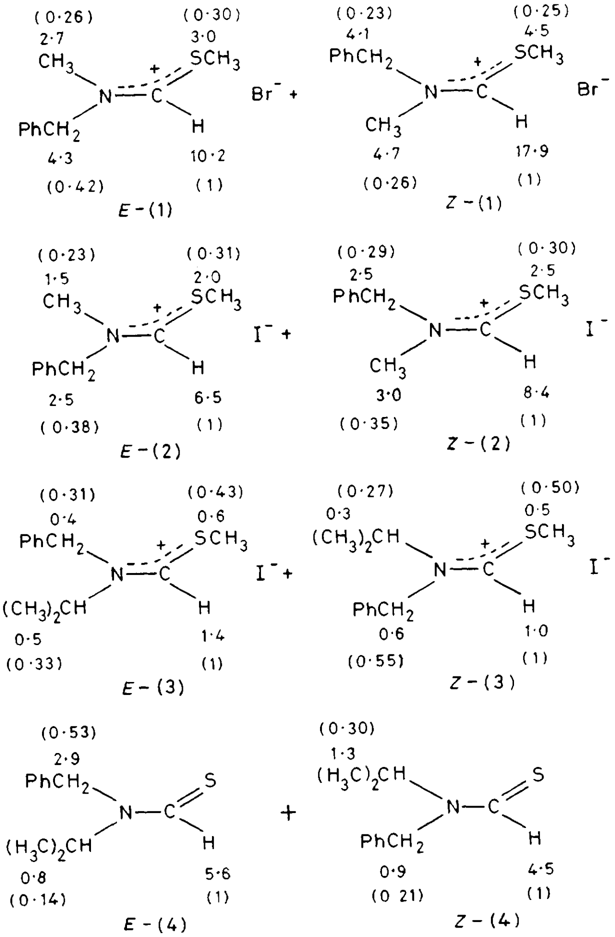
Summary The cations of the iminium salts (**1**)—(**3**) show characteristic ¹H n.m.r. shifts induced by $Eu(fod)_3$; (+)-$Eu(hfbc)_3$ generates unequal shifts for enantiotopic groups in the cations of (**3**) and (**5**).

THE ability of functional groups with lone pairs to interact with lanthanoid shift reagents has led to successful solutions of many structural problems by n.m.r. spectroscopy. Normally, anions also show this ability,[1–4] but this has not yet found further application. We now present some results showing that the use of auxiliary compounds can be helpful for the study of ionic systems. The iminium salts[5] (**1**), (**2**), and (**3**) (Scheme) exist as mixtures of *E*- and *Z*-isomers. ¹H Nuclear Overhauser measurements showed that the *E*-isomer of the iodide (**2**) predominated over the *Z*-isomer, and this is presumably also true for the bromide (**1**). The *E*-configuration was attributed to the major isomer of the iodide (**3**) by comparison with the equilibrium mixture of the corresponding bromide,[6] the isomers of which were assigned by considering the size of interacting substituents.



SCHEME. $Eu(fod)_3$-induced ¹H shifts, $\Delta\delta$ p.p.m., and relative induced ¹H shifts (ref. 7) (in parentheses), extrapolated to $[Eu(fod)_3]:[substrate] = 1$, in $CDCl_3$ at 30 °C. (**1**) and (**2**): 0·25 mol/l; (**3**) and (**4**): 0·15 mol/l.

Increasing quantities of tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dionato)europium(III), $Eu(fod)_3$, were added successively to solutions of (**1**), (**2**), and (**3**) in $CDCl_3$. The proton shifts of the cations were plotted *vs.* the concentration ratio $r = [Eu(fod)_3]:[salt]$ and the induced shifts were extrapolated to $r = 1$. In order to compare more effectively the $\Delta\delta$-values so obtained,

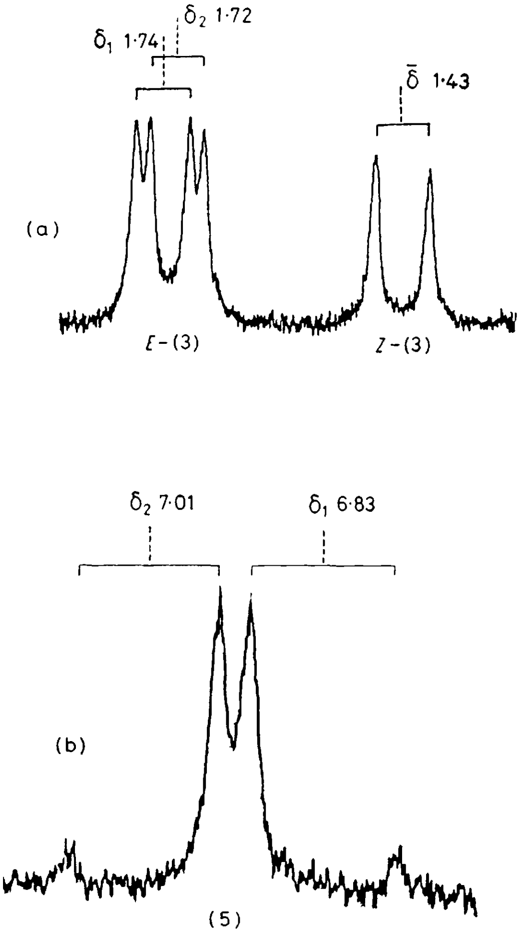
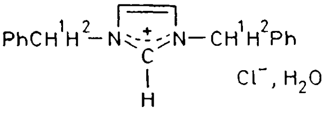


FIGURE. (a) Isopropyl methyl protons of (**3**) in $CDCl_3$ (0·16 mol/l; 33 °C) at 100 MHz. $[E\text{-}(3)]:[(Z\text{-}(3)] = 1{\cdot}85$; $[(+)\text{-}Eu(hfbc)_3]:[(3)] = 0{\cdot}78$; $^3J = 5{\cdot}6$ Hz (H_3C–CH); (b) methylene protons of (**5**) (monohydrate) in $ClCH_2CH_2Cl$ (0·1 mol/l; 33 °C) at 60 MHz; $[(+)\text{-}Eu(hfbc)_3]:[(5)] = 0{\cdot}6$; $^2J = 14{\cdot}8$ Hz (H^1–C–H^2); δ-values in p.p.m.

relative induced shifts[7] were calculated by defining $\Delta\delta$-(CH–S) ≡ 1 (Scheme).

Since direct complexation of the europium atom with the lone pairs of the sulphur atom must be considered, the Scheme includes the thioamide (**4**) for which interaction on sulphur has to be assumed.[8] Thus, the relative induced shift for CH_2 in *E*-(**4**) (0·53) is much larger than in *Z*-(**4**) (0·21), the same being true for CH_3 in *Z*-(**4**) (0·30) and *E*-(**4**) (0·14). This order is reversed for the corresponding iminium salt (**3**); *i.e.* the CH_2 group in *E*-(**3**) shows a much lower value (0·31) than in *Z*-(**3**) (0·55) where it is remote from sulphur. Therefore, the effect of direct complexation to sulphur in (**3**), if any, is hidden by the effect of a stronger interaction which is not located at sulphur. Thus, the induced proton shifts for our cations should be primarily due to the existence of 'paramagnetic artificial anions;' the cation and the anion are, at least statistically, very close to one another and the lanthanoid atom is co-ordinated to the anion. This interpretation is supported by the larger $\Delta\delta$-values obtained for (**1**), containing Br^-, compared with (**2**), containing I^-.

The interaction between the lanthanoid shift reagent and the cation was proved independently by using the optically active auxiliary compound (+)-tris[3-(heptafluorobutyryl)-D-camphorato] europium(III), (+)-Eu(hfbc)$_3$. Thus the enantiotopic isopropyl methyl groups in *E*-(**3**) are rendered anisochronous by 0·018 p.p.m., whereas no such effect is seen for *Z*-(**3**) (Figure). The splitting is absent in the presence of the racemic auxiliary compound[9] (±)-Eu(hfbc)$_3$. The geminal methylene protons did not show unequal shifts, probably because their environments differ less than do the environments of the protons of geminal methyl groups.[†] Similar consequences of association, including the absence of the splittings when (±)-Eu(hfbc)$_3$ was used, were noted for the corresponding bromide,[6] and the imidazolium salt[10] (**5**) (Figure). These selective shifts at prochiral sites are in agreement with the above assumption of a close cation–anion–europium complex. This phenomenon is related to the fact that enantiotopic groups in tertiary sulphonium[2] and quaternary ammonium[2,11] cations display unequal ^1H shifts in the presence of optically active anions.



(**5**)

Information about the structure of cation–anion association complexes and the location of the europium atom should be available from further comparisons of $\Delta\delta$-values, including the ones for $R_2N^+{=}CH_2X^-$.

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[†] The behaviour of (**4**) was significantly different; the isopropyl methyl protons of *Z*-(**4**) were rendered anisochronous by 0·046 p.p.m. while the methylene protons of *E*-(**4**) appeared as an AB system: $\delta_A - \delta_B = 0{\cdot}046$ p.p.m.; $^2J = 5{\cdot}8$ Hz {$r = [(+)\text{-Eu(hfbc)}_3]/[(\mathbf{4})] = 0{\cdot}82$; $c = 0{\cdot}15$ mol/l in $CDCl_3$, $T = 35$ °C}.

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