An Upfield Carbon-13 Shift Induced by Tris(dipivalomethanato)europium

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Summary A ^{13}C diamagnetic shift of the C(2) of primary amines is induced by the paramagnetic shift reagent $Eu(dpm)_3$.

IN the course of studies on the use of the paramagnetic shift reagent[1,2] tris(dipivalomethanato)europium on ^{13}C chemical shifts of compounds of biological importance, an *upfield* shift in the C(2) resonance signal was noted for Pr^nNH_2, Bu^nNH_2, and n-$C_5H_{11}NH_2$. Further, the upfield shift in the C(2) resonance signal cannot be explained satisfactorily by an exclusive pseudocontact interaction.

TABLE

^{13}C *Chemical shifts induced by* $Eu(dpm)_3$

Compound	^{13}C Shift [a](p.p.m.)[c] C(1)	C(2)	C(3)	C(4)	C(5)
Bu^nNH_2	$-16{\cdot}72$[b]	$+2{\cdot}16$	$-1{\cdot}61$	$-1{\cdot}30$	—
Bu^nNH_2 (protons)	$-4{\cdot}95$[d]	$-3{\cdot}14$[d]	$-1{\cdot}79$[d]	$-0{\cdot}95$[d]	—
Pr^nNH_2	$-25{\cdot}68$	$+3{\cdot}45$	$-2{\cdot}70$	—	—
n-$C_5H_{11}NH_2$	$-26{\cdot}54$	$+3{\cdot}24$	$-2{\cdot}69$	$-1{\cdot}94$	$-1{\cdot}19$
Bu^nOH	$-12{\cdot}44$	$-3{\cdot}03$	$-1{\cdot}95$	$-1{\cdot}19$	—

[a] Using a 4*K* data set chemical shifts are accurate to $\pm 0{\cdot}10$ p.p.m.; [b] Induced chemical shifts are measured: −downfield; +upfield; [c] Solutions 0·17M amine and 0·07M $Eu(dpm)_3$ (0·4 equiv.) in $CHCl_3$ with Me_6Si_2 as internal standard; [d] Refers to induced proton shift at this position.

The ^{13}C resonance signals were assigned by off-resonance techniques, and, in the case of Bu^nNH_2, a complete assignment of the proton chemical shifts (Table) was made by double resonance techniques. Confirmation of the individual ^{13}C assignments was made using selective proton decoupling.

The induced shifts for all compounds studied are given in the Table. The induced shifts for Bu^nOH are also included. The shifts are not extrapolated to equimolar amounts of amine and shift reagent and the magnitude of the shifts was found to decrease as the ratio of $Eu(dpm)_3$ to amine decreases.

Assuming a Eu–N distance of 3 Å, a C(1)–N–Eu angle of 109°, a N–Eu–C(1) angle of 25°, and a normal zig-zag conformation for the alkyl chain, then the C(2)–N–Eu angle cannot be greater than 54° 44′.

In addition, the ratio K_C/K_H, where K_C is the constant for ^{13}C in equation 1, below, and K_H is the constant for protons, is independent of magnetogyric effects and does not predict a negative value for C(2).[3,4]

The C(2) signal for Bu^nNH_2 is shifted downfield in the presence of $Pr(fod)_3$, whereas the other signals undergo the expected upfield shift.

Upfield proton shifts in $Eu(dpm)_3$ complexes have been reported.[5,6] In all cases the upfield shifts were attributed to the fact that the affected proton protruded into the positive cone of anisotropy inherent in the pseudocontact term of McConnell and Robertson:[3]

$$\Delta\delta = \frac{K(3\cos^2\phi_i - 1)}{r_i^3} \qquad (1)$$

for the *i*th nucleus.

Pseudocontact interaction between Eu^{III} and ^{13}C has been reported.[4,7] A contact mechanism for ^1H shifts induced by Eu^{III} has been ruled out.[2,6,8] However, a contact mechanism has been suggested to explain the upfield shift of ^{31}P signals in the presence of I.[9] In this regard, ^{13}C studies using bis(acetylacetonato)Ni^{II} [10] have shown that the C(2) shift is of opposite sign to the C(1) shift with Pr^nNH_2[11] and piperidine.[12]

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