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EU(FOD)$_3$ INDUCED SHIFTS IN A HETERONUCLEAR BICYCLIC AMINE

L. W. Morgan and M. C. Bourlas

Philip Morris Research Center, Richmond, Virginia U. S. A.

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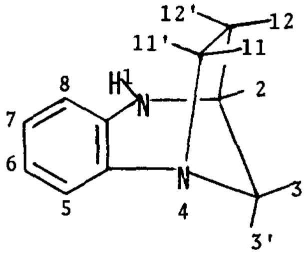
The application of tris(dipivalomethanato)europium, Eu(dpm)$_3$, to organic molecules bearing a lone pair on oxygen, and nitrogen is known to induce paramagnetic shifts in the PMR spectrum.[1,2] We report here an application of the fluorinated reagent, (europium tris 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4, 5-octanedione) Eu(fod)$_3$, in an investigation of the bicyclic benzo[b]-1,4-diazobicyclo[3,2,1] octane (I). We feel this structure should be ideal for the investigation of paramagnetic induced shifts and should provide a favorable means of comparing the proposed shift mechanisms.



(I)

PMR spectra were obtained at 60 MHz in CDCl$_3$ and the shift reagent to substrate molar ratio was varied between 0.18 and 0.82. Resulting downfield shifts were found to be directly proportional to the shift reagent concentration and the magnitude of induced shifts to be distance dependent (Table I). The relative magnitudes of the observed shifts indicate that coordination occurs exclusively at the bridgehead nitrogen.

Table I. Slope of the Line Induced Shift versus Mole Ratio

Proton at	R[a]	Δδ/ΔM[b]
C-11	2.04 Å	6.38
C-11'	---	---
C-3	2.10	5.74
C-3'	2.16	5.32
C-5	2.40	2.95
C-12	3.28	2.94
C-2	3.52	2.30
C-12'	3.34	2.14
C-8	4.68	1.40
C-6	4.48	0.97
C-7	5.32	0.52

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[a] Distance in angstroms measured from proton to periphery of electron pair at the bridgehead nitrogen.

[b] Slope of the plot of induced shift vs. mole ratio.

The PMR spectrum of benzo[b]-1,4-diazobicyclo[3,2,1] octane is complex and not easily interpreted. However, the addition of Eu(fod)$_3$ makes possible the assignments of all protons and vicinal and geminal coupling constants.

The individual aromatic protons (6.3 - 7.2 δ) become clearly discernible at a mole ratio of 0.56. Protons 5 and 8 each appears as a doublet showing both ortho and meta splitting.

$J_{5,6} = J_{6,7} = 7.8$ cps

$J_{5,7} = J_{6,8} = 1.9$ cps

Protons 6 and 7 each is a triplet showing ortho and meta splitting.

The two methylene groups bonded to the bridgehead nitrogen separate at a mole ratio of 0.180. The two protons in the 3 position are an AB quartet (5.19 and 5.42 δ) revealing the geminal coupling constant, $J_{3,3'} = 11$ cps. At slightly lower field (5.60 δ) the protons at position 11 appear as an A_2 B_2 triplet with the vicinal coupling, $J_{11,12} = 8$ cps.

The methine proton (3.82 δ) in the 2 position appeared as two doublets and remained unchanged throughout the study. Since the methine proton is positioned between the two methylene groups (Positions 12 and 3), assignment of the observed coupling constants can be made only by determining the dihedral angles between the methine proton and the methylene protons. The Newman projections for these angles indicate that the angles H_2-C-C-H_3 and H_2-C-C-H_{12} are of similar magnitude due to the degree of freedom in the bridge bonds. This angle appears to have a range between 32 - 48°. Similarly, the angles H_2-C-C-H_3' and H_2-C-C-H_{12}' exhibit a range of 72 - 88°. Assuming Karplus behavior,[3] one would expect two observable couplings, $J_{2,3} = J_{2,12}$ between 6 and 8.8 cps and $J_{2,3'} = J_{2,12'} = 3$ cps. The coupling constants actually observed were measured to be $J_{2,3} = J_{2,12} = 6$ cps and $J_{2,3'} = J_{2,12'} = 3$ cps. These assignments are justified both by the Karplus equation and the analysis of the patterns for the protons in positions 3 and 12. This evidence further supports the assignment of the geminal coupling constant made above ($J_{3,3'} = 11$ cps) since the two vicinal coupling constants $J_{2,3}$ and $J_{2,3'}$ cannot be observed due to severe line broadening in the protons adjacent to the site of coordination. On the other hand, the assignment of the vicinal coupling $J_{11,12} = 8$ cps can also be justified since the angle is about 120° for both $H_{11'}$-C-C-H_{12} and H_{11}-C-C-H_{12}' and Karplus behavior is therefore likely.

Paramagnetic shifts induced by the lanthanides are thought to occur via a pseudocontact interaction dependent upon angle and distance through space.[1,2] However, there is some question whether a contact interaction through bonds is in order when considering protons only two or three bonds from the coordination site.[4] The unique positioning of the protons in the compound discussed here warrants an investigation and discussion of the methods used to verify the pseudocontact effect.

Hinckley found that the pseudocontact effect is best represented by a plot of induced shift versus the cubed reciprocal distance between a proton and the position of the lanthanide ion. Cockerill,[5] et al. also consider the pseudocontact shift to be the major interaction; however, they choose to represent this by a plot of the slope ($\Delta\delta/\delta M$) of induced shift versus the mole ratio against the squared reciprocal distance from a proton to the periphery of the lone pair at which complexation occurs.

These two proposals were investigated by preparing graphs of induced shift versus $1/R^3$ and $\Delta\delta/\Delta$ M versus $1/R^2$.[6] Fits by least squares indicated that correlation of induced shift versus $1/R^3$ is improved considerably by omission of those points representing protons which are two or three bonds from the coordination site. A plot of $\Delta\delta/\Delta M$ versus $1/R^2$ (using all points) compares favorably with the above plot. The results obtained thus indicate that the pseudocontact nature of the interaction can be well represented by either of the two methods. Angular effects may also lend to the observed deviations.[7] However, the fact that the correlation of Hinckley's plot improves with omission of the protons close to the site of complexation indicates that contact shift interaction through bonds is a necessary consideration when the proton is two or three bonds from the coordination site.

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