

DIAMAGNETIC CORRECTIONS TO PARAMAGNETIC LANTHANIDE INDUCED NMR SHIFTS

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Chemical shift changes induced by shift reagents such as $\text{Eu}(\text{dpm})_3$ have generally been thought to be purely dipolar in origin.¹ A few reports also suggest contact shift contributions to the observed lanthanide induced shifts (LIS), especially with pyridines and related heterocycles.² Only occasionally has mention been given to the diamagnetic contribution to the LIS.³ The success of most attempts to interpret LIS in terms of molecular geometry, assuming only pseudocontact contributions, supports the contention that other contributions are generally small. We, however, recently encountered difficulty in the analysis of LIS⁴, and therefore were led to consider correcting these shifts for a diamagnetic contribution. An estimate of the magnitude of this correction can be obtained by measuring the LIS produced by $\text{La}(\text{dpm})_3$, $\text{Lu}(\text{dpm})_3$ or similar reagents. We wish to report some observations using the former material.

Perhaps the most interesting observation is the effect of $\text{La}(\text{dpm})_3$ on the geminal proton coupling constants of camphor. Shapiro *et al.*⁵ have noted that the α -geminal proton coupling constant ($^2J_{\text{HH}}$) at C_3 of camphor linearly increased in magnitude (became more negative) upon addition of $\text{Eu}(\text{dpm})_3$ or $\text{Eu}(\text{fod})_3$. However, $^2J_{\text{HH}}$ at sites more remote to C_2 showed no such effect. They suggested that this effect was probably due to the Lewis acid nature of the substrate. There are other literature^{2d,6} reports of lanthanide induced coupling constant changes which have been ascribed to conformational changes, contact shifts, and chemical-exchange spin-decoupling. If Shapiro's suggestion is correct, one would expect to find a similar effect induced by the nonparamagnetic $\text{La}(\text{dpm})_3$. Indeed, we find, at the maximum achievable ρ of 0.31, that $^2J_{\text{HH}}(\text{C} - 2)$ increases by 0.8 Hz from -17.8 to -18.7 which compares with a similar increase of 0.5 Hz induced by $\text{Eu}(\text{dpm})_3$ at $\rho=0.3$. It is interesting to also note that the vicinal coupling constant between the endo protons at C-2 and C-3 of exo, exo-2,3-camphandiol was unaffected ($^2J=7.0$ Hz) by $\text{La}(\text{dpm})_3$.

Table I reports our observations on five simple substrates. With ethanol the $\text{La}(\text{dpm})_3$ induced shifts for OH are about 2% of those induced by $\text{Eu}(\text{dpm})_3$ and about 0.1% for CH_2 ,⁶ while the methyl remained unshifted. Similarly with dimethyl sulfoxide the shifts were about 2.5% of those induced by $\text{Eu}(\text{dpm})_3$.⁷ As expected the interaction of diethyl ketone with $\text{La}(\text{dpm})_3$ was weaker than with ethanol and dimethyl sulfoxide. In fact, it was so much so that we were only able to dissolve 0.22 mol of reagent/mol of ketone in an 1.1 M CDCl_3 solution. No appreciable (<2 Hz) shifts were observed. With diethyl amine we were able to dissolve up to 0.65 mol $\text{Ln}(\text{dpm})_3$, but surprisingly no appreciable shifts were observed. It is known that the reagent-substrate complex is sensitive to steric effects such that secondary amines for example shift considerably less than primary amines.⁸ This is probably an important factor in our observation with diethyl amine. For *exo,exo*-2,3-camphandiol the $\text{La}(\text{dpm})_3$ shifts induced to the endo protons at C-2 and C-3 in CCl_4 are 2% of those induced by $\text{Eu}(\text{dpm})_3$. The methyl resonances remained unchanged.

Table I

Substrate	Solvent	Shifts Extrapolated to $\rho=1$ (proton) ppm		
ethanol	CDCl_3	1.06 (OH)	0.13 (CH_2)	0.0 (CH_3)
dimethyl sulfoxide	CCl_4	0.14 (CH_3)		
3-pentanone	CDCl_3^a	0.0 (CH_2) ^a	0.0 (CH_3) ^a	
diethylamine	CDCl_3	0.0 (CH_2) ^b	0.0 (CH_3) ^b	
<i>exo,exo</i> -2,3-camphandiol	CCl_4	0.33 (C_2H) ^c	0.33 (C_3H) ^c	0.0 (CH_3 's)

^a $\text{La}(\text{dpm})_3$ is much less soluble in 3-pentanone/ CDCl_3 than in ethanol/ CDCl_3 or DMSO/CCl_4 .

The maximum ratio of shift reagent to substrate (ρ) we achieved was 0.22, at which no appreciable shifts were observed.

^bNo appreciable shifts were observed up to $\rho=0.65$.

^cShift vs. ρ plots exhibited substantial curvature. The reported value is extrapolated from measurements at $\rho < 0.33$.

In general attempts to analyze LIS using the McConnell-Robertson equation, have resulted in best least squares fits in which the metal to donor atom distance is too large by about 0.5-1.0 Å.^{4b,9} Such is the case with pyridine (Table II) and we therefore attempted to correct the $\text{Eu}(\text{dpm})_3$ for a diamagnetic contribution by subtracting the $\text{La}(\text{dpm})_3$ shifts obtained under comparable conditions^{10a} to see what effect this would have on the quality of the fits.^{10b} Upon inspection of Table II one notices only a small improvement in the agreement factor⁹ and a modest (0.1-0.3 Å) improvement in the bond length. The expected bond lengths would be ca 2.5 Å.¹¹ Thus it would appear that only part of the reason for obtaining longer bond lengths lies in the uncorrected nature of shifts.

Our tentative conclusion is that $\text{Ln}(\text{dpm})_3$ corrections will generally be quite small and for saturate compounds limited to nuclei 1, 2 or 3 bonds removed from the site of coordination. Since it is so readily accomplished, we suggested that the diamagnetic corrections be checked, at least in a preliminary way, even though in most cases such corrections can safely be ignored.

Table II

Reagent	Solvent	Shift			Agreement Factor (%R)	d(N-Ln)A
		H ₂	H ₃	H ₄		
Eu(dpm) ₃ ^a	CCl ₄	25.9	9.0	8.2	2.57	3.33
La(dpm) ₃ ^b	CCl ₄	-0.28	+0.02	-0.06		
"Corrected shifts":		25.62	9.02	8.14	2.27	3.25
Eu(dpm) ₃ ^c	CDCl ₃	12.16	4.46	3.86	1.20	3.07
La(dpm) ₃	CDCl ₃	-0.16	+0.16	+0.11		
"Corrected shifts":		12.00	4.62	4.97	0.79	2.76
Yb(dpm) ₃ ^a	CCl ₄	90.0	35.0	28.0	0.66	2.91

^aPyridine concentration was reported to be 0.1-0.2M with a maximum shift reagent substrate ratio of 0.6. Data from reference 2a.

^bThe pyridine concentration was 0.14M and with a shift reagent ratio of 0.5.

^cThe pyridine concentration was reported to be ca. 0.5M and with a maximum shift reagent substrate ratio of 0.2. Data from reference 2d.

^dThe pyridine concentration was 0.69M with a shift reagent substrate ratio of up to ca. 0.3.

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