

LANTHANIDE SHIFT REAGENTS III: ERRORS RESULTING
FROM THE NEGLECT OF ANGLE DEPENDENCE¹

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The utility of the lanthanide shift reagents (LSR) in nmr structure investigations has been amply demonstrated². Although early workers³ noted an apparent correlation of the induced shift with $1/r^3$, several groups⁴ have subsequently illustrated the importance of the angle factor in the McConnell-Robertson pseudo-contact equation⁵ ($\Delta H = K [3 \cos^2 \phi - 1]/r^3$; ϕ and r are illustrated in the Figure) for stereochemical studies of the lanthanide chelate-substrate complex. In some instances, omission of the angle term can lead to incorrect proton assignments in the shifted nmr spectrum and to an erroneous picture of the solution complex. A case in point is the work of Wolkowski⁶ on the Yb(dpm)₃ shifted spectrum of fluorenone (1), which has been often quoted in the chemical literature as a representative example of a linear, "angle-less" $\log(\Delta H) - \log(r)$ relationship (the correlation was obtained using a Yb...O distance, r' , of 1.5 Å and θ of 0°; see Figure).

As part of a comprehensive study of LSR-substrate interactions, we have investigated the Yb(dpm)₃ and Eu(dpm)₃ shifted spectra of 1, as well as the Eu(fod)₃ spectra of 1 and of the four symmetrically substituted dimethylfluorenones. The proton assignments in a Eu(dpm)₃ shifted spectrum of 1 were

Table 1. Yb(dpm)₃-Fluorenone NMR Shift Data

	r'	θ	H1	H2	H3	H4
Original assignment ⁶			δ20.4	8.0	6.2	6.6
Calculated shifts ^a	1.5Å	0°	12.0	5.1	8.8	15.2
Reassigned data			20.4	6.2	6.6	8.0
Calculated shifts ^{a,12}	2.37	0	20.5	5.4	6.1	9.2

(a) Nmr shifts calculated using the Yb location defined by r' and θ ¹¹.

determined by decoupling experiments,^{7,8} which lead to a reassignment of the Yb induced shifts (Table 1). Not only are the original assignments for H2, H3 and H4 reversed, but the Yb...O distance of 1.5Å is clearly too short for a connection of this kind⁹. The calculated values of the induced shifts¹¹, obtained with a Yb location of $r' = 1.5\text{\AA}$ and $\theta = 0^\circ$, did not correlate with either set of proton assignments. The more likely Yb location¹² of $r' = 2.37\text{\AA}$ ($\theta=0^\circ$) gave calculated shifts (Table 1)¹¹ which are in good agreement with the reassigned shifts. Finally, the $\log(\Delta H_{Yb})-\log(r)$ relationship is not linear if the correct shift assignments are used. Von Ammon and Fischer² have suggested that large deviations from linearity in the $\log(\Delta H)-\log(r)$ relationship may be expected for ϕ 's in the 50-60° range. However, we have found that the logarithmic relationship is not linear even in the Yb...O = 2.37Å case where the largest ϕ is 41.5° (for H1; the H2 ϕ is 41.2°).

Table 2. Apparent Eu Locations from the Eu(fod)₃ NMR Shift Data

Fluorenone	1,8-Dimethyl-fluorenone	2,7-Dimethyl-fluorenone	3,6-Dimethyl-fluorenone	4,5-Dimethyl-fluorenone
r'	3.2(Å)	3.7	3.2	3.5
θ	31°	31	28	32

We have developed a least-squares method¹³ which uses the McConnell-Robertson equation, the nmr shift data and the substrate geometry to determine the "best" position for the Ln center in the LSR-substrate complex. The values of r' and θ from calculations on a series of Eu(fod)₃-fluorenone and dimethylfluorenone data are given in Table 2. The Eu...O distances, average 3.3Å, are in the range expected for labile LSR...O=C complexes based on known Eu-O distances from solid state X-ray crystallographic studies¹⁰. The Eu...O=C angle ($\theta \approx 30^\circ$) is probably determined by a balance of (a) steric forces acting between the Eu reagent and the substrate C atom skeleton, for which the "best" θ would be 0°, and (b) orbital directional effects which would favor alignment of the Eu...O vector with the O atom's unshared pair of electrons at $\theta = 60^\circ$. The θ differences between the Yb(dpm)₃ and Eu(fod)₃ analyses may be due in part to the greater lateral bulk of the dpm ligand relative to the fod group.

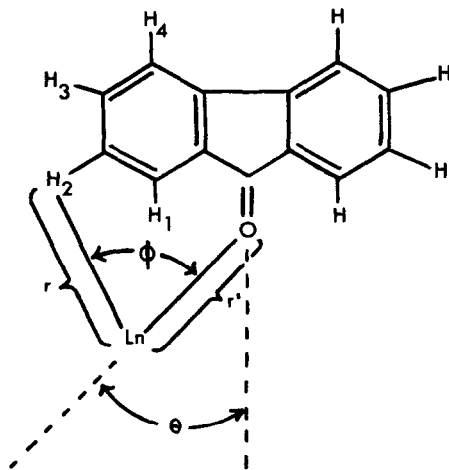


Figure. A representation of the Ln-fluorenone complex

In summary, we have demonstrated the

value of including, and the danger of excluding, the pseudo-contact equation's angle term in LSR calculations in the fluorenone system. Moreover, these conclusions should be valid for most molecular geometries. The determination of the solution stereochemistry of an LSR-substrate complex by an "angle-less" shift analysis should be done cautiously, and the results should be accepted only after an adequate evaluation of the consequences of angle neglect has been made.

References

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- 7) The shifted spectrum of l_1 (.43 molar equiv. $\text{Eu}(\text{dpm})_3$) showed a pair of doublets ($J=7$ Hz) at δ 10.0 and δ 8.48 and a multiplet (AB portion of ABXY multiplet) at δ 7.60 to 8.32. Irradiation of the multiplet at δ 7.66 caused the doublet at δ 10 to collapse to a singlet while the doublet at δ 8.48 only broadened slightly. Similarly irradiation of the multiplet at δ 7.98 caused the doublet at δ 8.48 to collapse to a broad singlet whereas the resonance at δ 10.0 remained a slightly broadened doublet. The most shifted proton can be confidently assigned to H_1 since the most shifted proton in the $\text{Eu}(\text{fod})_3$ treated spectrum of 2,7-dimethylfluorenone is a singlet. When $\text{Yb}(\text{dpm})_3$ is used, line broadening masks the splitting in the spectrum of l_1 at high $\text{Yb}(\text{dpm})_3/l_1$ ratios. However, at low $\text{Yb}(\text{dpm})_3/l_1$ ratios, it can clearly be seen that the first two protons resolved from the aromatic multiplet are doublets.
- 8) The first two peaks resolved from the aromatic multiplet of 1-indanone on treatment with $\text{Yb}(\text{dpm})_3$ are also doublets indicating these published assignments⁶ are also incorrect. We have not investigated the $\text{Yb}(\text{dpm})_3$ spectra of any other ketones.
- 9) $\text{Eu}\cdots\text{O}$ distances in the 2.40-2.60Å range have been found in several X-ray crystallographic studies of $\text{Eu}(\text{III})$ chelates¹⁰. Since the ionic radius of

Yb(III) is ca. 0.1\AA less than the Eu(III) value (D.G. Karraker, J. Chem. Ed., 47, 424 (1970)), the minimum value for the Yb...O distance in a LSR-substrate solution complex can be set at ca. 2.3\AA .

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- 11) The shifts (ΔH_C), initially computed using $K=1$ in the McConnell-Robertson equation, were placed on the same scale as the experimental shifts (ΔH_S) by multiplication of the ΔH_C 's by S : $S = \Sigma \Delta H_O / \Sigma \Delta H_C$.
- 12) This location represents a minimum in the function $\sum_{i=1}^6 [R_{O,i} - R_{C,i}(r', \theta)]^2$, where the R_O 's are the ratios of the observed shifts and the R_C 's are the ratios of the calculated shifts¹³.
- 13) H.L. Ammon, P.H. Mazzocchi, W.J. Kopecky, Jr., H.J. Tamburin and P.L. Watts, J. Amer. Chem. Soc., (in press). The method is given in detail in this paper.