

A SIMPLE GRAPHICAL METHOD FOR ANALYSIS OF LANTHANIDE INDUCED SHIFTS

Richard M. Wing,* Thomas A. Early

University of California, Riverside, California 92502

and J. John Uebel*

University of New Hampshire, Durham, New Hampshire 03824

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The McConnell, Robertson equation¹ (1) has been extensively used in quanti-

$$\Delta H_i/H = k(3 \cos^2 \theta_i - 1) \cdot R_i^{-3} \quad (1)$$

tative interpretations of lanthanide induced shifts (LIS). It is common practice, for reasons of simplicity and rapidity of computation, to ignore angular dependencies and analyze the LIS using the radial term only.^{2,3} It is clear, however, that omission of the angular term leads to poor fits⁴ as well as incorrect assignments in a number of cases.⁵ The use of LIS for structural and conformational analysis, of course, requires averaging the contributions of all the various site and rotamer populations extant in solution.⁵ Although a full analysis of the problem can be readily accomplished by any of several optimization techniques, the computational requirements are generally large. Therefore, we would like to present a graphical method whose merit is extreme simplicity with little sacrifice of accuracy.

At the heart of this method is a map of the dipolar field for an axially symmetric lanthanide complex (equation (1)) drawn to the same scale as standard Dreiding models, figure 1. The method is best illustrated using pyridine and cis-4-t-butylcyclohexanol as examples. The analysis of pyridine is straightforward, since symmetry requirements place the metal on its C₂ axis. One therefore positions the molecule on the graph such that the C₂ axis coincides with the principal magnetic axis (X) and the nitrogen lies about 3.0 ± 0.5 Å away from the metal. The relative shifts are then read directly from the plot and scaled to match the observed shifts (Table I).

The analysis of cis-4-t-butylcyclohexanol is a bit more complex. For this molecule the rotamer averaged field must have a mirror plane coincident with the molecular mirror plane. Once again we position the coordination site (OH) about 3.0 ± 0.5 Å from the metal with a metal-oxygen-carbon bond angle of about 125 ± 15°. We also require that the metal oxygen bond coincide with the principal magnetic axis. One next estimates the proton coordinates X_i and r_i, where X_i

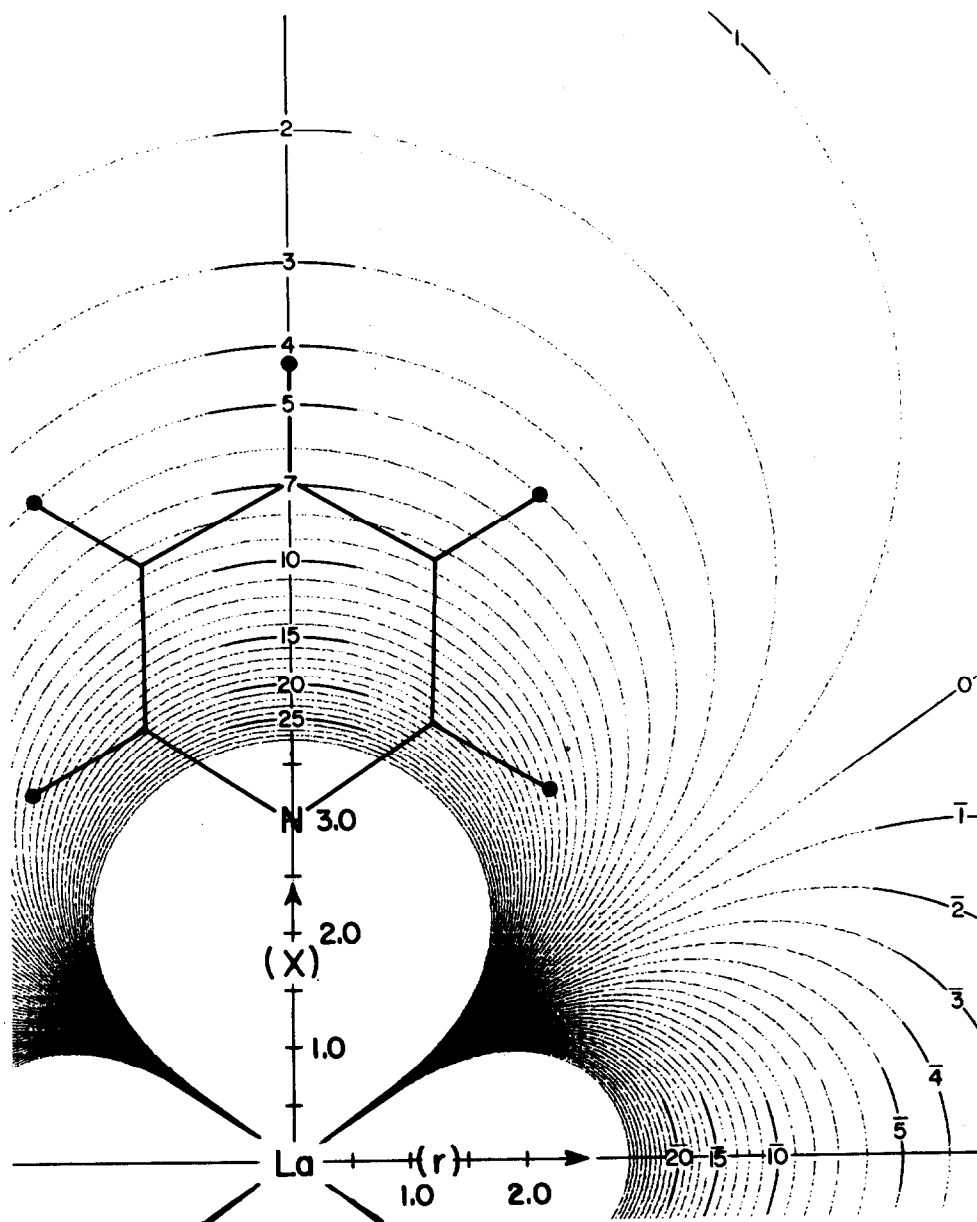


Figure 1: Map of the Dipolar Field; $(3\cos^2\theta - 1) \cdot R^{-3}$ where $X = R\cos\theta$ and $R^2 = X^2 + r^2$. Pyridine has been placed on the map as discussed in example 1. Full size copies of this map are available from the authors.

Table I

	H ₁	H ₂	H ₃	R(%) ^d			
Pyridine:^a							
observed	90.0	35.1	28.0				
calculated	88.8	34.9	29.4	1.8(at 3 Å, 180°)			
cis-4-t-Butylcyclohexanol:^b	H _{1e}	H _{2e}	H _{2a}	H _{3a}	H _{3e}	H _{4a}	t-Bu
observed	24.7	14.9	8.2	13.6	6.7	6.5	2.8
calculated	23.1	14.4	9.0	14.4	6.7	6.5	2.9
							6.0(at 3 Å, 110°)
1-Adamantanol:^c	H ₂	H ₃	H ₄	H ₄			
observed	268	81	87	cis	66		
calculated	257	82	93	trans	70		7.6(at 2.3 Å, 180°)

^a C. Beaute, Z. W. Walkowski, and N. Thoai, Tetrahedron Lett., 817 (1971).

^b P. V. Demarco, T. K. Elzey, R. B. Lewis and E. Wenkert, J. Amer. Chem. Soc., 92, 5736 (1970).

^c G. H. Wahl and M. R. Peterson, Jr., Chem. Commun., 1167 (1970).

^d $\bar{R}^2 = \frac{\sum (\text{shift observed} - \text{shift calculated})^2}{\sum (\text{shift observed})^2}$; $\bar{R}(\%) = 100 \bar{R}$

is the projected distance along the principal magnetic axis (X) and r_i is the perpendicular distance from X_i to H_i (figure 2). These cylindrical coordinates

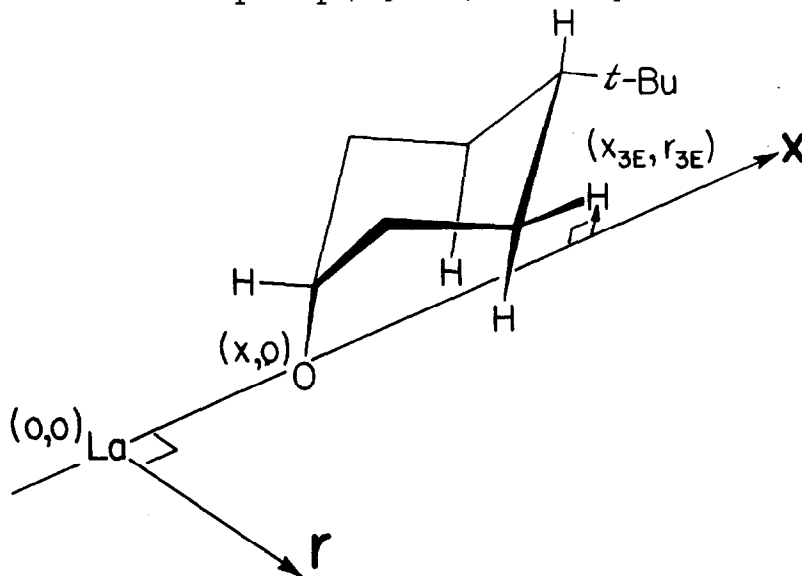


Figure 2: Coordinate system for using the dipolar field map with non-planar molecules.

are then plotted on the dipolar field map to obtain the relative shifts. Adjustment of the coordination distance and the metal-oxygen-carbon bond angle to optimize the fit is straightforward. The results for pyridine, cis-4-t-butylcyclohexanol and 1-adamantanol are given in Table I.

We feel this graphical method represents a useful laboratory aid and for many applications may be a satisfactory substitute for computer optimized fits.^{4,6}

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