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ANGULAR DEPENDENCY OF LANTHANIDE-INDUCED SHIFTS IN PROTON NUCLEAR MAGNETIC RESONANCE SPECTRA.

ANALYSIS OF RIGID BICYCLIC ETHERS.

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The magnitude of a lanthanide-induced pseudo-contact shift can be expressed as[1]

$$\Delta\delta_i = \delta_i[Eu \neq 0] - \delta_i[Eu = 0] = k(3\cos^2\theta_i - 1)(\frac{1}{R_i^3})$$

where δ_i is the chemical shift of the ith proton, k represents[2] a collection of constants, θ is an internuclear angle, and R_i is the proton-europium distance. The rough correlation of the paramagnetic shift with $\frac{1}{R_i^3}$ is already quite well established.[3] The angular dependency, which should be smaller,[4] has been more difficult to evaluate, owing largely to uncertainties in vector distances and angles in non-rigid molecules or systems with flexible coordination sites. There is evidence available, however, that suggests that this dependency can be detected[1,5] and inclusion of the $3\cos^2\theta - 1$ factor should improve $\Delta\delta_i$ correlations.[6]

The above uncertainties can be circumvented to some extent in the rigid bicyclic ethers 1, 2, and 3 where the coordination site is locked in the skeletal system and distances and angles can be estimated with the aid of Dreiding models. For the present pseudo-contact correlations we have taken a value of 3.0 Å for the oxygen-europium distance,[3d] and we have placed the europium in the plane defined by the oxygen atom and the two adjacent carbon atoms. The observed values for the tris(dipivalomethanato)europium (III) induced shifts for the protons in 1, 2, and 3 are listed in Table 1.

Two least square plots were made for each compound, one of $\Delta\delta_i$ versus $\frac{1}{R_i^3}$ and the other $\Delta\delta_i$ versus $(3\cos^2\theta_i - 1)(\frac{1}{R_i^3})$. The hydrogens on the carbons bearing oxygen (H_1 & H_4 in 1 and 2, and H_5 & H_6 in 3) were deleted from these plots owing to an apparent but expected[4a] contact contribution. The inclusion of the angular dependency factor produces a distinct improvement in the correlation as can be seen by comparison of the standard deviations in Table 2.

TABLE 1

^{1}H nmr spectra[a] of $CDCl_3$ solutions of 1, 2, and 3

1,4-Dihydronaphthalene-1,4-*endo*-oxide (1)[7]

	H_1 & H_4	H_5 & H_6	H_A	H_B
$\Delta\delta_i$[b]	9.2 ppm	3.7 ppm	2.2 ppm	1.2 ppm
R_i	4.0 Å	5.8 Å	6.3 Å	7.7 Å
θ^c	31°	23°	32°	33°

1,2,3,4-Tetrahydronaphthalene-1,4-*endo*-oxide (2)[8]

	H_1 & H_4	H_5 & H_{6x}	H_{5n} & H_{6n}	H_A	H_B
$\Delta\delta_i$[b]	8.2 ppm	4.3 ppm	3.4 ppm	2.0 ppm	1.0 ppm
R_i	4.1 Å	5.0 Å	6.1 Å	6.5 Å	7.9 Å
θ^c	30°	29°	15°	29°	31°

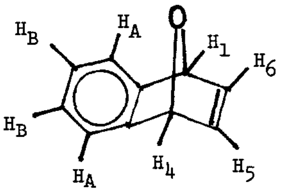
Benzonorbornadiene-*exo*-oxide (3)[9]

	H_1 & H_4	H_5 & H_6	H_A	H_B	H_{7s}	H_{7a}
$\Delta\delta_i$[b]	3.9 ppm	9.3 ppm	1.4 ppm	0.89 ppm	3.1 ppm	6.9 ppm
R_i	5.6 Å	5.0 Å	8.4 Å	9.8 Å	5.9 Å	4.2 Å
θ^c	28°	17°	18°	9°	27°	34°

(a) Spectra were obtained on Varian A-60 D.

(b) $\Delta\delta_i = \delta_i\ \mathrm{Eu} = 0.2 - \delta_i\ \mathrm{Eu} = 0$ ·

(c) θ = O-Eu-H_i bond angle.



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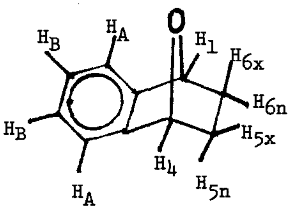

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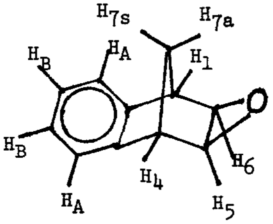

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TABLE 2

Plots of $\Delta\delta_i$ versus $\frac{1}{R_i^3}$

Compound	Slope	Standard Deviation
1	12.9	0.37
2	8.2	0.53
3	8.0	0.56

Plots of $\Delta\delta_i$ versus $(3\cos^2\theta - 1)(\frac{1}{R_i^3})$

Compound	Slope	Standard Deviation
1	7.3	0.033
2	6.4	0.076
3	7.6	0.12

The self-consistency of this data suggests that the assumed orientation of europium is probably close to being correct. Refinement of a larger quantity of data of this type hopefully can better define this parameter.

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