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CALCULATION OF LANTHANIDE N M R SHIFT DEPENDENCE ON PROTON DISTANCE
AN ANALYTICAL APPROACH

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In our recent investigations of europium shifts in the N M R spectrum of an alkaloid lactam Lupanine /1/ we have found like Cockerill /2,3/ that induced shift $\Delta\delta$ of a given proton is directly proportional to the inverse square of its distance R from the complexation site :

$$\Delta\delta = K\,R^{-n} \quad ,n = 2 \qquad K = \text{constant}$$

Many other authors preferred n = 3 , assuming pseudocontact nature of the phenomenon and basing on the graphic analysis of experimental data /4,5,6/. This discrepancy led us to a closer analysis of the calculation methods used. There are two of them :

1. The n value is adopted that gives straight line corellation between $\Delta\delta$ and R^{-n} . This may lead to confusion if there are few experimental points measured with large errors, which is frequently the case.
2. Plot of log $\Delta\delta$ vs. log R is a straight line for every R^{-n} type relationships. The slope of this line is equal to n /7/, and may be calculated from $\Delta\delta$ and R values for any two protons 1 and 2 :

$$n = \frac{\log\Delta\delta_1 - \log\Delta\delta_2}{\log R_2 - \log R_1}$$

Possibilities of approach 2. were not fully realized up to now.

We report here the application of this method to analysis of experimental results obtained by different authors /Table I/.

TABLE I

Author	Ref.	Reagent	Compound	− n as stated by the author	− n calculated as described	Distance from lanthanide ion to coordinating atom
P. Belanger	8	Eu/DPM/$_3$	cyclohexanones	3	0.2 − 0.8	no precise data
P. Belanger	8	Pr/DPM/$_3$	cyclohexanones	3	1 − 3	no precise data
A.F. Cockerill	2	Eu/DPM/$_3$	adamantanols	2	1.9 − 2.1	distances were measured from oxygen lone pair perimeter
A.F. Cockerill	2	Eu/DPM/$_3$	adamantanols	2	1.8 − 2.1	
A.F. Cockerill	2	Eu/DPM/$_3$	adamantanols	2	2.1 − 2.4	
A.F. Cockerill	2	Eu/DPM/$_3$	adamantanols	2	1.8 − 2.6	as above
A.F. Cockerill	2	Eu/DPM/$_3$	cyclopentanol	2	1.3 − 1.7	as above
P.V. Demarco	7	Eu/DPM/$_3$	cyclic alcohols	2.2	2.2	distances were measured from oxygen atom
C.C. Hinckley	4	Eu/DPM/$_3$ x 2Py	cholesterol	3	2.5 − 3.0	no precise data
G.H. Wahl Jun.	9	Eu/DPM/$_3$	adamantanols	not stated	0.6 − 1.8	equal to the sum of the two covalent radii
Z.W. Wolkowski	6	Yb/DPM/$_3$	quinuclidine	3	1.7	3 ± 0.3 A
Z.W. Wolkowski	6	Yb/DPM/$_3$	pyridine	3	2.1	3 ± 0.3 A
Z.W. Wolkowski	10	Yb/DPM/$_3$	indanone	not stated	1.6	1.5 A
Z.W. Wolkowski	10	Yb/DPM/$_3$	fluorenone	not stated	1.5	1.5 A
Z.W. Wolkowski	11	Eu/DPM/$_3$	oximes	2.3	2.3	distances were measured from oxygen atom
present authors	1	Eu/DPM/$_3$	lactam	2	1.82 − 2.06	as above

It is evident that n value calculated by a straightforward method frequently differs largely from that adopted by the author. These differences are probably due to :

- Uncertain interpretation of the results obtained by graphic analysis
- Improper positioning of lanthanide ion, from which distances are measured, errors in distance measurements and assumed geometry of the substrate. Sometimes authors do not specify precisely lanthanide position from which measurements were made.
- Angular factor $/3\cos^2\chi - 1/$ in the equation

  $$\Delta\delta = \frac{3\cos^2\chi - 1}{R^3}K$$

  where χ is lanthanide - electron donor - proton internuclear angle, is considered constant by most workers. It has been argued that in fact time averaged χ differs only slightly from proton to proton in the donor /14/, however Briggs's full calculations seem to prove the contrary /13/.
- It is possible that not only pseudocontact but also contact and other interactions contribute significantly to the observed lanthanide shift, especially in the case of very close to coordination site or sterically screened protons /9,15/.

These factors explain also large differences between n calculated from different sets of protons in the same molecule.

Too little is known about the nature of lanthanide paramagnetic shifts in the N M R spectra of organic molecules to allow drawing definite structural conclusions from crude approximations, that do not reflect the complex nature of interactions. Presented above comparision fully supports our opinion /1/ that better results are obtained for n = 2 rather than n = 3 and distances measured from the periphery of free electron pair /2/ or oxygen atom /1,7,11/.

Computer optimalization of lanthanide position by minimalization of $/n_{calc.} - 2/$ for every compound studied should give a corellation greatly simplyfying N M R signal assignment, but even without it very useful results are obtained /2,3/.

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