ical shifts and coupling constants were found[4] to be dependent on the concentration of HF. Addition of HF results in a shift[4] to higher field for both the doublet and quartet and at the same time an increase in the vicinal H–H coupling constant. We have previously reported that addition of HF to the equilibrating system **5** $\rightleftharpoons$ **6** produces just such a spectrum.[4] In this case, swamping the system with fluoride ion destroys ion **3** by the formation of **4**, which rapidly produces **5** at the higher temperature (−50°).

The observations of the ethylenechloronium ion (**1**) as a stable, well defined ion has substantial importance not only in regard with its intermediacy in electrophilic chlorine addition to ethylene, but ion (**1**) also may play an important role in the mechanism of β-chloroethylation reactions,[9] as well in biological alkylating systems involving precursors to incipient β-chloroethyl cations. These aspects will be discussed separately.

Acknowledgment. Support of our work by the National Science Foundation and the National Institutes of Health is gratefully acknowledged.

---

(9) G. A. Olah and S. J. Kuhn, *J. Org. Chem.*, **29**, 2317 (1964).

(10) Postdoctoral research associate, 1971–1973.

George A. Olah,* David A. Beal, Philip W. Westerman[10]
Department of Chemistry, Case Western Reserve University
Cleveland, Ohio 44106

Received February 5, 1973

Evaluation of Lanthanide-Induced Carbon-13 Contact *vs.* Pseudocontact Nuclear Magnetic Resonance Shifts[1]

Sir:

The apparent pseudocontact nature of the dispersal of proton resonances of molecules in the presence of lanthanide chelates is proving quite useful as a tool for structure identification,[2] and criteria for testing the validity of signal assignments have been devised.[3] The utilization of the pseudocontact model for lanthanide-separated carbon-13 spectra is complicated for amine[4] and pyridine base[5] adducts of $Eu(DPM)_3$ by the presence of a large Fermi contact contribution to the observed, induced chemical shifts. Since carbon-13 spectra contain unique information about carbocyclic molecular structure, we have investigated methods to obviate the "contact shift effect." Our initial approach has been to assay the magnitude of the problem by obtaining correlated carbon-13 and proton nmr spectra of isoquinoline in the presence of eight of the non-isotropically paramagnetic tris(dipivaloylmethane)-lanthanide chelates and to factor the apparent contact and pseudocontact contributions.

Correlation of carbon and proton spectra was effected by performing both measurements on the same solutions of a lanthanide–DPM chelate and isoquinoline. Experimental details as well as the computational procedure for analyzing the induced chemical shift data may be summarized.

Lanthanide-induced ${}^{13}C$ and ${}^{1}H$ shifts are treated as follows: (i) the europium location is mapped *vs.* the agreement factor R for the ${}^{1}H$ data;[2,3] (ii) the scale factor K, used to match experimental to calculated ${}^{1}H$ shifts, was recorded; (iii) the carbon pseudocontact shift values for each europium location are computed using K; (iv) a difference spectrum (${}^{13}C_{obsd} - {}^{13}C_{calcd} = {}^{13}C_{diff}$) was generated for the carbon spectrum. A survey of the carbon difference maps for the eight lanthanides revealed differences in the internal contact shift ratios, but no reversal of the sign ordering pattern of the shifts. For present purposes, it is convenient to ameliorate these differences by calculating, for each metal chelate, an average $\delta_{contact}/\delta_{pseudocontact}$ for the heterocyclic ring carbons proximate to the lanthanide (C-1,3,4,9,10), the contact shifts in the distal aromatic fragment (C-5,6,7,8) being small. These average terms, recorded in Table I, are indices of the contact shift induced by a particular lanthanide and provide a basis for ranking the reagents as usable heteronuclear shift reagents.

Table I. Average Values for $\delta_{contact}/\delta_{pseudocontact}$ in the Nitrogen Ring of Isoquinoline *vs.* $LAN(DPM)_3$

Eu = 0.80	Er = 0.25	Ho = 0.19	Dy = 0.13
Nd = 0.70	Tb = 0.21	Pr = 0.15	Yb = 0.05

Several assumptions bear on the validity of this evaluation. First, the McConnell–Robertson[6] equation on which we base our analysis requires axial symmetry of the lanthanide paramagnetism, a condition which is only approximately correct.[7] Second, our computational procedure for locating the lanthanide and constructing the difference map places the heterocyclic nitrogen on the principal symmetry axis of the chelate, a situation which is also nearly correct, *a fortuori*.[8] Finally, the pseudocontact description of the induced proton shifts is not rigorously justified.[9] The combined inaccuracies introduced by these assumptions are manifest as imprecision in the location of the lanthanide (Table II). The variations of the locations are not of great concern since we are able, in our simple scheme, to note that the magnitude of the "contact shift effect" on lanthanide-dispersed ${}^{13}C$ spectra is not a sensitive function of the lanthanide position.

From Table II it is perceived that the lanthanides can be grouped into several sets according to their aptitude at inducing contact shifts. Isoquinoline complexed to $Eu(DPM)_3$ has by far the largest contact shifts, followed by the $Nd(DPM)_3$ adduct. The chelates of Dy, Ho, Tb are intermediate in this contribution, while Er, Pr spectra are less affected by spin delocalization induced chemical shifts. It is abundantly clear that to obtain lanthanide-dispersed spectra, certainly for nitro-

---

(1) Part IV of the series "Interpretation of the Pseudocontact Model for Nuclear Magnetic Resonance Shift Reagents."

(2) M. R. Willcott, III, R. E. Davis, and R. E. Lenkinski, *J. Amer. Chem. Soc.*, **94**, 1742 (1972). Programs are available on request from the authors (R. E. D.).

(3) R. E. Davis and M. R. Willcott, III, *J. Amer. Chem. Soc.*, **94**, 1744 (1972).

(4) G. E. Hawkes, C. Marzin, S. R. Johns, and J. D. Roberts, *J. Amer. Chem. Soc.*, **95**, 1661 (1973).

(5) O. A. Gansow, P. A. Loeffler, R. E. Davis, M. R. Willcott, III, and R. E. Lenkinski, *J. Amer. Chem. Soc.*, **95**, 3390 (1973).

(6) H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, **29**, 1361 (1958).

(7) W. D. Horrocks and J. D. Sipe, III, XIIIth Experimental NMR Conference, 1972, Abstract 5.2, p 32.

(8) J. D. Roberts, R. A. Smith, M. Christl, D. Leibfritz, C. Marzin, G. E. Hawkes, S. R. Johns, R. A. Cooper, and D. W. Roberts, ref 7, Abstract 6.1.

(9) The present authors will soon publish an analysis of contact *vs.* pseudocontact shifts induced by lanthanides in proton nmr.

Table II. Minimum Proton R Factors and Lanthanide Nitrogen Distances

	R_H	d, A	$R_{C\ and\ H}$
Eu	3.0	3.2	47.7
Nd	4.8	3.3	46.8
Er	1.1	3.0	17.6
Tb	1.5	2.6	26.9
Ho	1.3	2.6	33.3
Pr	2.0	2.5	11.6
Dy	1.8	2.7	30.0
Yb	1.4	3.1	4.0

gen heterocycles, with the least contact shift perturbation, Yb(DPM)$_3$ is the chelate of choice. In fact, applying the R factor method to simultaneously fit *both* carbon-13 and proton shift data for isoquinoline Yb(DPM)$_3$ solutions results in a minimum R factor of 4.0%, well within the accuracy of the two sets of experimental data.[10] Neglecting the C-1, C-3 resonances (those most affected by contact shifts) produced a carbon-13 difference map indistinguishable from the experimental data scatter.

We list the following positive features concerning Yb(DPM)$_3$.[11] (i) The induced shifts are downfield, facilitating interpretation of spectra. (ii) Little line broadening of either the carbon or proton resonances is observed. (iii) The proton shifts detected are *ca.* 300% larger than for Eu(DPM)$_3$ at equal chelate concentrations. (iv) Yb(DPM)$_3$ is suitable for use to determine structural features from dispersed carbon-13 spectra, Eu(DPM)$_3$ is just as certainly not useful. Further experiments exploring the utility of correlated, dispersed carbon-13 and proton spectra are in progress.

Acknowledgments. We gratefully acknowledge research support from The Robert A. Welch Foundation (Grants C-386, E-183 and F-233) and from the National Institutes of Health (AM-14305).

---

(10) For even Pr(DPM)$_3$ or Er(DPM)$_3$, R factors of 11.6 and 17.6% are observed using both carbon and proton shift data (see $R_{C\ and\ H}$ values in Table II).

(11) M. Witanowski, L. Stefaniak, H. Janazewski, and Z. W. Wolkowski, *Tetrahedron Lett.*, 1653 (1971); Z. W. Wolkowski, *ibid.*, 821 (1971).

(12) John Simon Guggenheim Fellow, 1972–1973.

Otto A. Gansow,* Paul A. Loeffler
Department of Chemistry, Rice University
Houston, Texas 77001

Raymond E. Davis
Department of Chemistry, University of Texas
Austin, Texas 78712

M. R. Willcott, III,[12] Robert E. Lenkinski
Department of Chemistry, University of Houston
Houston, Texas 77004

Received June 27, 1972

Evidence for Europium-Induced Fermi Contact Shifts in Carbon-13 Nuclear Magnetic Resonance Spectra

Sir:

Notwithstanding the caution voiced by Weissman that both contact and pseudocontact shifts are to be expected in molecules coordinated to europium shift reagents,[1] numerous workers have applied a simplified form of the McConnell–Robertson relationship for pseudocontact interaction[2] as the sole interpreter of lanthanide induced shifts in rigid organic molecules. In the iterative computational schemes employed, the pseudocontact model reproduces proton shift behavior to a high degree of precision,[3–7] but duplication of ^{13}C data by this model *seems* less satisfactory.[8,9] The following extension of our computational procedure[6] to ^{13}C and ^{1}H spectra of pyridine bases coordinated to Eu(DPM)$_3$ includes a general method for obtaining the ratio of pseudocontact to measured ^{13}C nmr shifts, as well as a direct comparison between the applicability of a simplified pseudocontact model to both ^{13}C and ^{1}H Eu(DPM)$_3$ shifted spectra.

The rationale for this approach requires matching ^{13}C and ^{1}H spectral behavior. Correlation of the 100-MHz ^{1}H data (Varian HA-100) and 22.265-MHz ^{13}C data (Bruker HFX-90) was achieved by using the same sample for both measurements. The data were reduced using linear plots of shift perturbation *vs.* Eu(DPM)$_3$ extrapolated to 1:1 Eu(DPM)$_3$:substrate ratio. All chemical shifts were expressed in ppm from internal (CH$_3$)$_4$Si (^{13}C, ^{1}H). The samples were 0.5 *M* in substrate with Eu(DPM)$_3$ varying from 0.0 to 0.3 *M*. These extrapolated values, for three different nitrogen heterocyclic compounds, are recorded in Table I.

The correlated ^{13}C and ^{1}H isotropic shifts were treated in the following way: (i) the europium location was mapped *vs.* the agreement factor, R, for the ^{1}H data;[6] (ii) the scale factor, K, used to match experimental to calculated ^{1}H shifts, was recorded; (iii) the carbon pseudocontact shift values for each europium location were computed using this scale factor; and (iv) a difference spectrum ($^{13}C_{obsd} - {}^{13}C_{calcd} = {}^{13}C_{diff}$) was generated for the carbon spectrum. Pyridine can be used to illustrate this procedure. Systematic variation of the europium location over the surface of spheres of radius 2.0–5.0 Å centered on the pyridine nitrogen in 0.1 Å steps showed a decrease in the R factor from 18.8% (2.25 Å) to 0.9% (2.7 Å), followed by an increase to 5.0% (4.0 Å). Over the range 2.6–3.0 Å, numerous regions were found for the lanthanide which gave R factors of less than 2%. The best agreement, R = 0.9% was noted at 2.7 Å.[10] At this location, a difference spectrum ($^{13}C_{obsd} - {}^{13}C_{calcd} = {}^{13}C_{diff}$) was obtained; it is included in Table I. Corresponding

---

(1) S. I. Weissman, *J. Amer. Chem. Soc.*, **93**, 4928 (1971).

(2) H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, **29**, 1361 (1958).

(3) C. D. Barry, A. C. T. North, J. A. Glasel, R. J. P. Williams, and A. V. Xavier, *Nature (London)*, **232**, 236 (1971).

(4) S. Farid, A. Ateya, and M. Maggio, *Chem. Commun.*, 1285 (1971).

(5) J. Briggs, F. A. Hart, and G. P. Moss, *Chem. Commun.*, 1506 (1970).

(6) M. R. Willcott, III, R. E. Lenkinski, and R. E. Davis, *J. Amer. Chem. Soc.*, **94**, 1742 (1972). Programs are available on request from the authors (R. E. D.).

(7) R. E. Davis and M. R. Willcott, III, *J. Amer. Chem. Soc.*, **94**, 1744 (1972).

(8) J. Briggs, F. A. Hart, G. P. Moss, and E. W. Randall, *Chem. Commun.*, 364 (1971).

(9) O. A. Gansow, M. R. Willcott, and R. E. Lenkinski, *J. Amer. Chem. Soc.*, **93**, 4295 (1971).

(10) We anticipated the europium would lie along the C$_2$ axis through the nitrogen atom of pyridine. However, the minimum R factors were obtained when the Eu atom was displaced *ca.* 20° from the C$_2$ axis and *ca.* 10° from the plane of the ring. This unexpected result may be an artifact of our computational approach, or it may be due to experimental error or a combination of both factors. In any event, the europium angular location was found to influence the R factor much less than the Eu–N distance.