predicted by HMO theory to have $DE_\pi = 1.88\beta$, and might thus be expected to be *ca.* 2 kcal/mol less stable than a similarly substituted 3-vinylpentadienyl anion. It is not clear which of the maxima adjacent to VII is 22 kcal/mol above V_{cis}, but the higher one must be. The value for the activation energy for $V_{trans} \rightarrow V_{cis}$ is calculated from the observed half-life of 30 min at 140° for the $V_{trans} \rightarrow$ VI conversion, and the last activation energy in the sequence is assumed to have about the same value as the heptatrienyl–cycloheptadienyl anion cyclization.[9] Apparently 2- and 3-vinylpentadienyl anions suitably substituted for these sigmatropic rearrangements will best be prepared below room temperature.

Acknowledgments. We gratefully acknowledge financial support from the Petroleum Research Fund, administered by the American Chemical Society, the Sloan Foundation (Fellowship to R. B. B.), and the National Science Foundation (Grants No. GU-1534 and GP-21115).

R. B. Bates,* S. Brenner, C. M. Cole
Department of Chemistry, University of Arizona
Tucson, Arizona 85721

Received September 20, 1971

Iron(II) Phthalocyanines as Nuclear Magnetic Resonance Shift Reagents for Amines[1]

Sir:

The known existence of a large ring current in the phthalocyanine ring[2] and the known ability of the iron in iron(II) phthalocyanine to complex amines[3] suggested that this phthalocyanine might function as a useful nmr shift reagent for amines. This possibility has been investigated and it has been found that, in fact, iron(II) phthalocyanine does serve as an efficient and convenient shift reagent for amines.[4] It has also been found that through ligand exchange the complexes of iron(II) phthalocyanine with certain amines can sometimes function as convenient shift reagents for other amines.

These iron(II) phthalocyanine reagents are complementary to the group IV metal phthalocyanine reagents previously reported[6–10] because they bind the species of interest in a different way, *i.e.*, by coordinate covalent bonds rather than by simple covalent bonds. They are also complementary to the lanthanide reagents[11,12] since they are applicable to a much narrower range of bases than the lanthanide reagents. This specificity is expected to be of value in studies of polyfunctional compounds.

The use of iron(II) phthalocyanine as a shift reagent is illustrated by work carried out on methylamine and *n*-butylamine. In the case of methylamine the free amine was condensed in large excess on iron phthalocyanine and the excess amine allowed to evaporate off. The product when dissolved in deuteriobenzene gave, as is seen in Figure 1, a well-resolved A_2X_3 spectrum. In the case of *n*-butylamine a slight excess of the free amine in benzene was allowed to react with iron(II) phthalocyanine at room temperature overnight. The product was isolated by evaporation and purified by fractional precipitation from ether with hexane. A deuteriochloroform solution of it gave, as Figure 2 shows, a spectrum with well-resolved multiplets for each type of proton. For both complexes the areas of the resonances were consistent with a 2:1 ratio between amine and phthalocyanine.

An illustration of the use of the amine complexes of iron(II) phthalocyanine as shift reagents is provided by work done with the bis-*n*-butylamine complex. Here several successive additions of pyridine were made to a dilute deuteriochloroform solution of the *n*-butylamine complex, and after each addition a 100-MHz Fourier transform spectrum was taken. Each of these spectra showed resonances attributable to the bispyridine complex, the bis-*n*-butylamine complex, and what is presumed to be the monopyridine–mono-*n*-butylamine complex. The resonances of the pyridyl protons of the bispyridyl complex and the mixed complex overlapped partially in the case of the 2,6 protons and fully in the case of the 3,5 and 4 protons. Over the range studied the pyridyl protons showed no concentration dependence.

Similarly the addition of *n*-propylamine to a deuteriochloroform solution of the *n*-butylamine complex gave a solution showing the methyl resonance of complexed *n*-propylamine. The other amine resonances were, of course, overlapped by the *n*-butylamine resonances. (This overlap could have been alleviated or avoided by using other suitable complexes as reagents, for example, suitable aromatic amine complexes.)

That iron(II) phthalocyanines can function well as qualitative shift reagents is dependent on a number of factors besides those already mentioned. Of importance, since both iron(II) phthalocyanine itself and iron(III) species in general are paramagnetic,[5] is the low solubility of iron(II) phthalocyanine in organic solvents and its resistance to oxidation by air to iron(III) species. Also important is the rate of the iron–amine exchange in the complexes—slow enough to preclude broadening and shifting of the amine resonances but fast enough to permit convenient interchange of one ligand for another. The slowness of the N–H exchange rate and the rapidity of the N relaxation rate are also of significance since they preclude substantial N–H resonance broadening.[13,14]

---

[1] Support for this work was provided by National Science Foundation Grant No. GP-22739 and by an NDEA Fellowship. The work was presented in part at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971.

[2] T. R. Janson, A. R. Kane, J. F. Sullivan, K. Knox, and M. E. Kenney, *J. Amer. Chem. Soc.*, **91**, 5210 (1969).

[3] P. A. Barrett, D. A. Frye, and R. P. Linstead, *J. Chem. Soc.*, 1157 (1938).

[4] Although iron(II) phthalocyanine is paramagnetic, its bisamine complexes are diamagnetic.[5] Paramagnetism thus plays no role in the functioning of iron(II) phthalocyanine as a shift reagent for amines.

[5] A. B. P. Lever, *Advan. Inorg. Chem. Radiochem.*, 7, 27 (1965).

[6] J. E. Maskasky and M. E. Kenney, *J. Amer. Chem. Soc.*, **93**, 2060 (1971).

[7] A. R. Kane, J. F. Sullivan, D. H. Kenny, and M. E. Kenney, *Inorg. Chem.*, **9**, 1445 (1970).

[8] A. R. Kane, R. G. Yalman, and M. E. Kenney, *ibid.*, 7, 2588 (1968).

[9] J. N. Esposito, L. E. Sutton, and M. E. Kenney, *ibid.*, **6**, 1116 (1967).

[10] J. N. Esposito, J. E. Lloyd, and M. E. Kenney, *ibid.*, **5**, 1979 (1966).

[11] C. C. Hinckley, *J. Amer. Chem. Soc.*, **91**, 5160 (1969).

[12] A recent note listing many lanthanide shift reagent papers is W. De W. Horrocks, Jr., J. P. Sipe III, and J. R. Luber, *ibid.*, **93**, 5258 (1971).

[13] Other examples of rapid ^{14}N relaxation have been known for some time: G. V. D. Tiers and F. A. Bovey, *J. Phys. Chem.*, **63**, 302 (1959).

[14] Ruthenium(II) phthalocyanine[15] has properties similar to those of

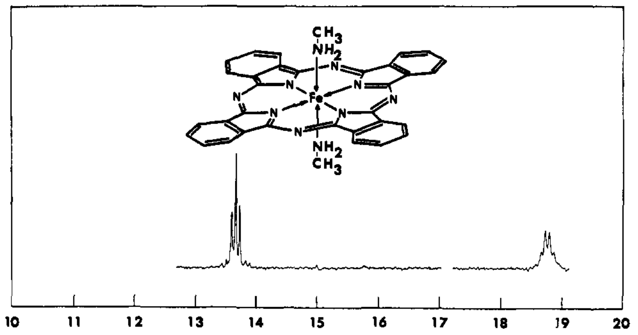

Figure 1. The 100-MHz Fourier transform spectrum of the bis-methylamine complex of iron(II) phthalocyanine in deuteriobenzene.

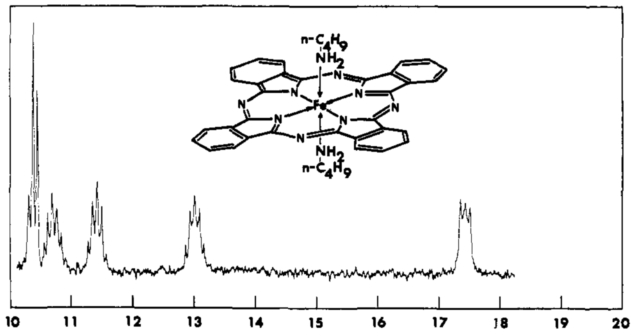

Figure 2. The 100-MHz continuous wave spectrum of the bis-*n*-butylamine complex of iron(II) phthalocyanine in deuteriochloroform.

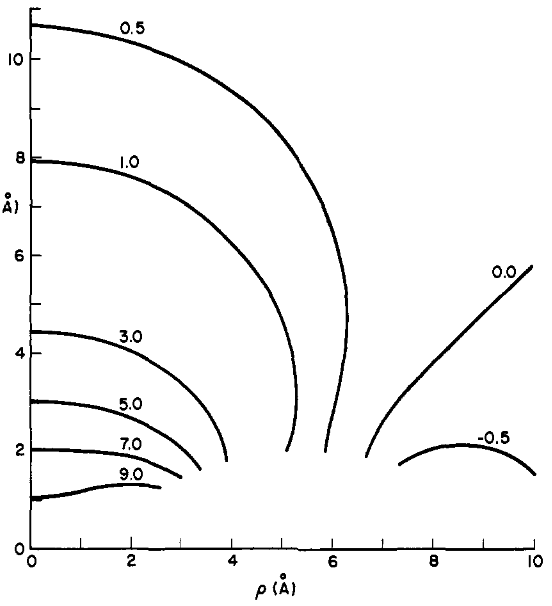

Figure 3. The average isoshielding lines of the phthalocyanine ring in parts per million as developed for the silicon phthalocyanine ring. The ordinate represents the distance from the ring center along the fourfold axis and the abscissa represents the distance from the ring center in the ring plane.[17]

To find out whether or not the type of data provided by these shift reagents could also be used for quantitative purposes, several trial structure parameter calculations were carried out. The data used in these calculations were those for the bis-4-methylpyridine adduct of iron(II) phthalocyanine and for free 4-methylpyridine ($CDCl_3$). The ring current equation used was that developed earlier for silicon phthalocyanines.[2,17] This equation, shown in graphical form in Figure 3, was not modified for these calculations because the separation between the 3,6 and the 4,5 phthalocyanine multiplets for silicon phthalocyanines, ~1.34 ppm, was found to be very similar to that for iron(II) phthalocyanine amine complexes, ~1.35 ppm.[18]

In one calculation the differences between the resonance positions of the three amine protons for the free and complexed amine were used to determine the amine Fe–N bond length in the complex. The value obtained, 1.94 Å, Table I, is in good agreement with the value predicted for this type of bond, 1.92 Å,[19] and the value found for the iron–amine nitrogen bond length in the tetrakis-4-methylpyridine complex of iron(II) phthalocyanine, 2.00 Å.[20] Of particular importance to this use of these shift reagents is the concentration independence of the incremental shifts, the consistency of the ring current effect of the phthalocyanine ring, and the required octahedral geometry at the iron.

Table I

	Incremental shifts, ppm			Bond length, Å
	$H_{2,6}$	$H_{3,5}$	CH_3	Fe–N
Obsd	6.47	2.30	1.30	
Calcd	6.41	2.44	1.41	1.94[a]

[a] Esd 0.04.

Acknowledgment. The contributions of Professor Kerro Knox and Dr. Thomas R. Janson to the program used in making the calculations are gratefully acknowledged.

---

iron(II) phthalocyanine and can also act as a shift reagent for amines.[16]

(15) P. C. Krueger and M. E. Kenney, *J. Inorg. Nucl. Chem.*, **25**, 303 (1963).

(16) J. E. Maskasky, Ph.D. Thesis, Case Western Reserve University, Cleveland, Ohio, 1972, p 111.

(17) T. R. Janson, Ph.D. Thesis, Case Western Reserve University, Cleveland, Ohio, 1971; University Microfilms T.R. 72-00051, p 8.

(18) This separation is assumed to be sensitive to changes in the ring current of phthalocyanines.

(19) J. L. Hoard, "Structural Chemistry and Molecular Biology," A. Rich and N. Davidson, Ed., W. H. Freeman, San Francisco, Calif., 1968, p 579.

(20) T. Kobayashi, F. Kurokawa, T. Ashida, N. Uyeda, and E. Suito, *Chem. Commun.*, 1631 (1971).

Joe E. Maskasky, J. Robert Mooney, Malcolm E. Kenney*
Chemistry Department, Case Western Reserve University
Cleveland, Ohio 44106

Received December 4, 1971

Laser Raman Spectra of Aqueous Lysozyme Denatured by Lithium Bromide

Sir:

Investigation by Raman spectroscopy of the structural changes in the lysozyme molecule denatured by thermal means is difficult because of the optical inhomogeneity produced by heating concentrated solutions of this enzyme.[1] Although chemical denatura-

---

(1) R. C. Lord and N. T. Yu, *J. Mol. Biol.*, **50**, 509 (1970).