evaluated by sum of the squares of the deviations of the calculated from the observed concentrations at each data point.

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Electronic Effects in Transition Metal Porphyrins. The Reactions of Imidazoles and Pyridines with a Series of Para-Substituted Tetraphenylporphyrin Complexes of Chloroiron(III)

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Abstract: Equilibrium constants for addition of Lewis bases to TPPFeCl in chloroform and several other solvents have been measured by visible spectral techniques. The equilibria observed are: TPPFeCl + 2B $\rightleftharpoons$ $[TPPFeB_2]^+Cl^-$ (β_2), where the product is an ion pair, and in some cases: TPPFeCl + B $\rightleftharpoons$ TPPFeClB(K_1), where the product may either be the six-coordinate or the five-coordinate $[TPPFeB]^+Cl^-$ ion pair. Increased solvent polarity causes β_2 to increase for B = *N*-methylimidazole more than for B = imidazole. The hydrogen bonding capabilities of N–H as compared with N–R imidazoles appear to stabilize the product of reaction 1 by about 3 log units in β_2. This suggests that Fe–N_{Im} bond strength in heme proteins may be significantly strengthened by weakening of the N–H bond of the histidine and further increased if this N–H proton can be transferred to some adjacent basic protein residue. The steric effect of addition of a methyl group to the 2 carbon of imidazole is approximately equal to the effect on β_2 of the loss of N–H···Cl^- hydrogen bonding. The basicity of B also has a dramatic effect upon β_2 within each class of B (imidazoles, pyridines). The addition of two B was also investigated as a function of para substituent, X, on the four phenyl rings of TPPFeCl for B = *N*-methylimidazole. A Hammett relationship between log β_2 and σ_X is observed, with ρ −0.39. The sign of ρ is opposite those observed for the reactions of (*p*-X)TPPM complexes (M = Ni^{2+}, VO^{2+}, Co^{2+}). This is because the product of the reaction contains a positively charged center (Fe), which is stabilized by electron-donating groups on the porphyrin ring.

Introduction

The physical properties (electronic,[1,2] NMR,[3-8] ESR,[9] Mössbauer[10,11] spectra, magnetic moments[12]) and reactions of ferric porphyrins have been studied by many investigators. The great interest in ferric porphyrins stems in part from the unique and sometimes puzzling variation in physical properties and chemical reactivity with changes in porphyrin substituents and/or axial ligands, and also from the desire to understand the mode of action of the iron porphyrin center in the ubiquitous heme proteins. In all of the heme proteins investigated to date, the heme moiety is bound to the protein by at least one coordinate covalent bond between iron and the "aromatic" nitrogen of a histidine residue of the protein. In some cases there are additional covalent or coordinate covalent linkages as well, as in the cytochromes *b* and *c*, but the iron-imidazole linkage is common to all those where axial ligands have been identified. The cytochromes b_2 and b_5, which are low on the electron-transport chains of yeasts and mammals, respectively, both appear to have two imidazoles coordinated to the heme iron.[13,14]

One is thus led to the question of why imidazole should be the ligand of choice for hemes rather than some other Lewis base, for example, a pyridine. As more data have become available, in recent years, the question of why Fe(III)-porphyrin-imidazole complexes are so much more stable, purer in magnetic state, and generally much more well defined in physical properties than the corresponding pyridine complexes has arisen.[7] The underlying question of the nature of the difference in electronic properties between pyridines and imidazoles, which gives rise to such different behavior of these ligands toward Fe(III) porphyrins nags investigators of these systems, and conflicting opinions as to the π-donor/π-acceptor character of these two classes of bases have been expressed.[10,15]

Several studies of the axial ligation reactions of Fe(III) porphyrins have already been reported.[16-22] The data available suggested that the equilibrium constant for addition of two imidazole molecules to PFeCl is very dependent upon solvent and that more extensive studies were required to define the electronic, steric, and solvation factors which affect complex stability. Such factors have been investigated in the work described herein.

Two steps of axial ligand (B) addition to Fe(III) porphyrins are possible. The first step is the formation of the 1:1 complex:

$$\mathrm{PFeCl} + \mathrm{B} \overset{K_1}{\rightleftharpoons} \mathrm{PFeClB} \qquad (1)$$

which may either be the six-coordinate model complex of ferrihemoglobin chloride or ferrimyoglobin chloride, or the five-coordinate $\mathrm{PFeB^+Cl^-}$ ion pair. (Although other anions could be utilized in addition to chloride, such investigations have been undertaken only to a limited extent in this work.) The distinction between these two possible coordination numbers and, indeed, the potential interconversion between these two forms of the 1:1 complex is made difficult due to the intervention of the second step of axial ligand addition to form the 2:1 complex:

$$\mathrm{PFeClB} + \mathrm{B} \overset{K_2}{\rightleftharpoons} \mathrm{PFeB_2{}^+Cl^-} \qquad (2)$$

since, as we shall see, the stepwise constant, K_2, is in general larger than K_1. In fact, as we shall also see, formation of the 1:1 complex is not always detectable, leading to the frequent experimental observation of addition of two ligands in an apparent single step:

$$\mathrm{PFeCl} + 2\mathrm{B} \overset{\beta_2}{\rightleftharpoons} \mathrm{PFeB_2{}^+Cl^-} \qquad (3)$$

Equation 3 is the sum of (1) and (2), and $\beta_2 = K_1K_2$. The product of reactions 2 and 3 is usually an ion pair,[17,20,22] which, in the stoichiometry found for the equilibrium constants K_2 and β_2, behaves as one unit rather than as two ions. (In a few cases of this study the stoichiometry found for the reactions indicates that the product behaves as separated ions; these special cases will be discussed below.)

In an attempt to determine the effect of electron-withdrawing or -donating groups on the porphyrin ring upon the equilibrium constant β_2, we have investigated reaction 3, and where possible 1, for P = octaethylporphyrin (OEP), tetraphenylporphyrin (TPP), and a series of para-substituted tetraphenylporphyrins [(p-X)TPP], and B = N-methylimidazole, in chloroform and several other solvents. The results are compared with those obtained for other systems, in which equilibrium constants for axial ligand addition [to (p-X) TPPM, where M = $\mathrm{VO^{2+}}$,[23] $\mathrm{Co^{2+}}$,[24] $\mathrm{Ni^{2+}}$ [23]] or redox potentials [of $\mathrm{H_2}$(p-X)TPP[25] and its $\mathrm{Co^{2+}}$ [24] and $\mathrm{Ni^{2+}}$ [26] complexes] have been found to obey Hammett relationships:[27]

$$\log (K^{\mathrm{X}}/K^{\mathrm{H}}) = 4\sigma\rho \qquad (4a)$$

or

$$E_{1/2}{}^{\mathrm{X}} - E_{1/2}{}^{\mathrm{H}} = 4\sigma\rho_{\mathrm{EMF}} \qquad (4b)$$

Observation of such a relationship allows quantification of the sensitivity of the reaction to electronic effects of porphyrin substituents within a series of structurally very similar porphyrin complexes, and comparison of the sensitivity parameter, ρ, for the reactions of several metals will hopefully lead to a better understanding of the complex electronic interactions between the metal, the porphyrin ring, and the axial ligands.

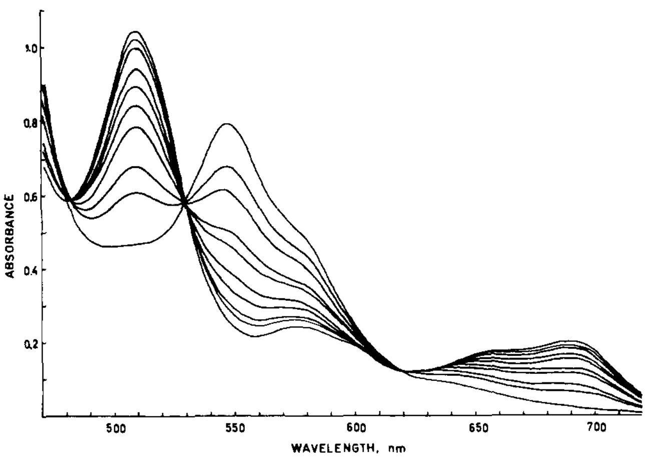


Figure 1. Visible spectral changes observed upon addition of N-methylimidazole to an 8.4×10^{-5} M solution of TPPFeCl in chloroform.

Experimental Section

The free porphyrins, $\mathrm{H_2OEP}$ and the series of $\mathrm{H_2}$(p-X)TPP, and their Fe(III) complexes were synthesized as described previously.[5,28,29] The final products, OEPFeCl and the series of (p-X)TPPFeCl, were recrystallized from benzene (Aldrich Reagent) before use. The mass spectrum of TPPFeCl showed no evidence of the presence of μ-oxo dimer [$\mathrm{(TPPFe)_2O}$], and extinction coefficients of all ν_3 bands of (p-X)TPPFeCl complexes were within experimental error of $1.24 \times 10^4\ \mathrm{M^{-1}\ cm^{-1}}$. Replacement of chloride by bromide or iodide ion was accomplished according to published procedures.[30]

Spectroscopic grade chloroform, benzene, dimethylformamide, and dichloromethane (Aldrich Gold Label or Mallinckrodt SpectrAR) were utilized for all spectral studies without further treatment, except for dimethylformamide, which was dried over molecular sieves (Linde 4A). Amines (Aldrich, except for 5-Cl-N-MeIm and 4-MeIm, K and K Laboratories) were distilled or recrystallized from benzene (Aldrich Reagent) shortly before use.

Spectrophotometric measurements were made on a Cary 14 spectrophotometer equipped with a thermostated cell compartment attached to a circulating constant-temperature bath, which controlled the temperature within the cuvette at 25.0 ± 0.2 °C in the cell compartment. For measurement of equilibrium constants and extinction coefficients, 1-mm, 10-mm, and 10-cm path length cuvettes were utilized as required. Equilibrium constants were typically measured from the absorbances of $\sim 8 \times 10^{-5}$ M (p-X)TPPFeCl solutions to which aliquots of amine stock solutions had been added.[31]

ESR spectra of several $\mathrm{TPPFeB_2{}^+Cl^-}$ complexes in chloroform glasses were recorded at liquid nitrogen temperature on a Varian E-12 ESR spectrometer. Varian weak pitch (g = 2.0027) was used as field-frequency calibrant, and the field sweep width was calibrated by use of an NMR gaussmeter, Alpha Model AL 675.

Results

In Figure 1 are shown the typical spectral changes which take place in the visible region when amines (in this case N-methylimidazole) are added to TPPFeCl. The isosbestic point at 520 nm is sharp for all amines. However, that at 480 nm in some cases shows clear evidence of two isosbestic points: one at low ratios of amine to Fe(III) and a second, nearby, at higher ratios; that at ~620 nm is lost for hindered bases and pyridines (crossover points spread over as much as 30 nm in a progressive manner as amine concentration is increased). The absorption maxima, extinction coefficients, and peak half-widths at 75% height for TPPFeCl and its amine adducts in $\mathrm{CHCl_3}$ are listed in Table I. The frequencies of the electronic transitions are clearly a function of the amine utilized, as will be discussed more fully in the Discussion section.

Table I. Absorption Maxima, Extinction Coefficients, and Band Half-Widths at 75% Height for TPPFeCl and Series of its Bis(amine) Complexes[a]

Base[b]	ν_1[c] $10^{-3}(\epsilon_1)$[d] (Δ)[e]	ν_2[c] $10^{-3}(\epsilon_2)$[d] (Δ)[e]	ν_3[c] $10^{-3}(\epsilon_3)$[d] (Δ)[e]	ν_4[c] $10^{-3}(\epsilon_4)$[d] (Δ)[e]		ν_5[c] $10^{-3}(\epsilon_5)$[d] (Δ)[e]		ν_6[c] (ϵ_6)[d] (Δ)[e]	ν_7[c] (ϵ_7)[d] (Δ)[e]
None	23.96[f] (99.1) (0.62)		19.61 (12.0) (0.59)	17.36 (2.98) (0.64)	15.15 (2.52) (0.64)	14.50 (2.82) (0.34)		11.42 (501) (0.97)	
Im	23.96 (154) (0.45)	21.81 (20.8) (0.42)	18.21 (9.04) (0.52)	17.24 (5.51) (0.36)	15.71 (1.30) (0.49)			8.59 (211) (1.00)	6.86 (198) (0.55)
4-MeIm	23.92 (165) (0.42)	21.88 (24.8) (0.44)	18.20 (9.14) (0.53)	17.20 (5.42) (0.39)	15.70 (1.39) (0.41)			8.83 (181) (0.95)	6.97 (180) (0.50)
4-PhIm	23.94 (156) (0.43)	21.74 (21.8) (0.42)	18.21 (9.25) (0.55)	17.18 (5.54) (0.37)	15.72 (1.69) (0.48)			8.56 (198) (0.98)	6.70 (188) (0.56)
2-MeIm	23.92 (107) (0.61)	21.55 (23.4) (0.54)	17.68 (6.75) (0.80)	16.60 (5.01) (0.42)			13.09 (0.132) (Infl)	9.07 (188) (0.70)	7.60 (240) (0.44)
5,6-Me_2Bzim	23.92[g] (73) (0.84)	19.69 (7.19) (1.10)	17.91 (8.10) (0.78)	16.84 (5.97) (0.50)	15.38 (1.49) (Sh)			8.89 (200) (0.65)	7.33 (249) (0.36)
N-MeIm	23.96 (156) (0.42)	21.65 (16.9) (0.35)	18.25 (9.04) (0.56)	17.25 (5.64) (0.35)	15.71 (1.54) (0.56)			8.52 (205) (0.88)	6.58 (185) (0.52)
5-Cl-*N*-MeIm	23.95 (164) (0.45)	21.74 (15.0) (sh)	18.22 (7.06) (0.52)	17.36 (4.51) (0.34)	15.74 (0.44) (0.50)			8.08 (208) (0.94)	6.02 (183) (0.33)
1,2-Me_2Im	24.01[h] (114) (0.58)	19.92 (6.06) (0.91)	17.54 (6.41) (0.36)	16.39 (3.24) (0.28)		14.53 (1.17) (0.26)	13.13 (0.327) (0.46)	11.52 (195) (1.26)	
2-MeBzim	24.04 (117) (0.68)	19.74 (7.01) (0.73)	17.53 (6.20) (0.35)	16.39 (3.23) (0.31)	15.29 (1.50) (Sh)	14.53 (1.45) (0.28)	13.11 (0.340) (0.45)	11.43 (216) (1.02)	
4-NMe_2Py	24.01 (143) (0.58)	21.41 (20.1) (0.52)	17.99 (9.11) (0.72)	16.81 (6.39) (0.54)	15.43 (2.42) (Sh)			8.66 (204) (0.57)	7.08 (229) (0.50)
3,4-Lut	23.46 (153) (0.43)		18.85 (12.26) (0.30)	17.76 (5.19) (0.37)	16.39 (1.52) (0.30)	14.49 (0.55) (sh)	13.01[i] (0.31)[i] (sh)[i]	7.62 (60) (sh)	6.20 (51) (0.49)
Py	23.64 (136) (0.47)	19.55 (7.68) (sh)	18.83 (7.94) (0.77)	17.24 (4.28) (0.42)	15.47 (1.04) (sh)	14.41 (0.99) (0.34)	~10.67 (0.22) (0.91)	7.55 (77) (sh)	6.20 (80) (0.38)

[a] Solvent = $CHCl_3$, T = 25 °C. [b] Abbreviations used: Im = imidazole; 4-MeIm = 4-methylimidazole; 4-PhIm = 4-phenylimidazole; 2-MeIm = 2-methylimidazole; 5,6-Me_2Bzim = 5,6-dimethylbenzimidazole; *N*-MeIm = *N*-methylimidazole; 5-Cl-*N*-MeIm = 5-chloro-*N*-methylimidazole; 1,2-Me_2Im = 1,2-dimethylimidazole; 2-MeBzim = 2-methylbenzimidazole; 4-NMe_2Py = 4-dimethylaminopyridine; 3,4-Lut = 3,4-lutidine (3,4-dimethylpyridine); and Py = pyridine. [c] Frequency, in kK. [d] Extinction coefficient, in $M^{-1}cm^{-1}$. [e] Band half-width at 75% height, in kK. [f] Shoulders at 26.37 kK (ϵ 54.4 × 10^3), (Δ 1.68 kK) and 28.90 kK (ϵ 36.9 × 10^3), (Δ 1.13 kK). [g] Shoulder at 21.55 kK (ϵ 31.8 × 10^3), (Δ 0.78 kK). [h] Shoulder at 21.55 kK (ϵ 17.3 × 10^3), (Δ 0.45 kK). [i] Additional shoulder at 11.64 kK (ϵ 196), (Δ 0.50 kK).

The spectral changes upon addition of varying amounts of amine provided from two to four wavelengths at which equilibrium constants could be calculated.[31] Typically, calculations were done on absorbance data taken at 510 nm and the wavelength maximum of the product (point of ν_3, Table I), which is 547.5 nm in Figure 1. In addition, where possible, calculations were also done from the data of 690 nm and that of ν_4 (575 nm in Figure 1). Plots of log $(A - A_0/A_c - A)$ vs. log [B] were constructed,[33] where A is the absorbance at the wavelength of interest, A_0 is the absorbance of (*p*-X)TPPFeCl in the absence of base B, and A_c is its absorbance in the presence of a large excess of base B, sufficient to form the complex to ~99%. Such a plot of the data of Figure 1 is shown in Figure 2, and the results for all complexes of this study are summarized in Tables II, III, and IV. For addition of one base molecule, log K_1 is estimated from the intercept of the portion of the graph which yields a slope of 1.0, and log β_2 is obtained from the intercept of the portion of the graph which yields a slope of 2.0. The data for calculations done at four wavelengths are included in Figure 2, and error limits established by the ranges of log $(A - A_0/A_c - A)$ for each [B]. In many cases, only the data at 510 nm yielded an initial slope of 1.0. For convenience, the values of log K_1 and log β_2 have been obtained from the x intercept in Figure 2, rather than the more common y-intercept extrapolation.

The assumption made in the determination of log K_1 in Figure 2 is that A_c for the 1:1 complex is similar to A_c for the 2:1 complex. This is probably not true, except, perhaps, at 510 nm, but in the absence of spectral data for the isolated 1:1 complexes, it is the only reasonable assumption which can be made. That the spectra of the 1:1 and 2:1 complexes are at least similar at 510 nm is suggested by the behavior of isosbestic points, discussed above. Typically, only two or three data points, for different log [B] values, were available for drawing the slope = 1.0 line. Thus, the values of log K_1 should be considered as only rough estimates, and the reliability of the values of K_1 (Tables II–IV) is of the order of a factor of 2.

The method of calculation of β_2 is based on the stoichiometry

Table II. Solvent and Concentration Effects on the Binding of Imidazoles to Iron(III) Porphyrins

Solvent	Porphyrin[a]	Base	T, °C	$[\mathrm{PFeCl}]_o$, M	E_T[b]	D[c]	K_1, M^{-1}	β_2, M^{-2}	β_{2D}, M^{-1}
Benzene	TPPFeCl	Im	25	8.0×10^{-6}	34.5	2.3		(4.6×10^4)[d]	
		N-MeIm	25	8.0×10^{-6}	34.5	2.3	1.3 ± 0.2	5.8 ± 0.8	
Chloroform	TPPFeCl	Im	25	5.4×10^{-5}	39.1	4.8		$(1.58 \pm 0.17) \times 10^6$	
		Im	25	7.6×10^{-7}	39.1	4.8		$(1.70 \pm 0.46) \times 10^6$	
		2-MeIm	25	5.4×10^{-5}	39.1	4.8	16 ± 3	$(3.30 \pm 0.50) \times 10^3$	
		N-MeIm	25	6.6×10^{-3}	39.1	4.8	10 ± 2	$(1.50 \pm 0.25) \times 10^3$	
		N-MeIm	25	8.4×10^{-5}	39.1	4.8	9 ± 2	$(1.50 \pm 0.24) \times 10^3$	
		N-MeIm	25	7.6×10^{-7}	39.1	4.8			$(1.6 \pm 0.3) \times 10^{-3}$
	TPPFeBr	N-MeIm	25	5.7×10^{-5}	39.1	4.8	$>1 \times 10^6$[e]	$>2.5 \times 10^7 (K_2' = 25\ M^{-1})$[e]	
	TPPFeI	N-MeIm	25	8.0×10^{-5}	39.1	4.8	$>1 \times 10^5$[e]	$>1 \times 10^7 (K_2' = 100\ M^{-1})$[e]	
	DPFeCl	Im[f]	30	$\sim 10^{-4}$[f]	39.1	4.8		2.8×10^6[f]	
Dichloromethane	TPPFeCl	Im[g]	30	1.6×10^{-4}[g]	41.1	9		4.8×10^5[g]	
		2-MeIm	25	7.0×10^5	41.1	9	22 ± 12	$(3.68 \pm 0.79) \times 10^3$	
		N-MeIm	25	7.0×10^{-5}	41.1	9	88 ± 12	$(1.0 \pm 0.2) \times 10^4$	0.53 ± 0.03
		N-MeIm	25	8.1×10^{-7}	41.1	9			0.42 ± 0.04
	DPFeCl	Im[h]	30	h	41.1	9		7.75×10^5[h]	
Acetone	TPPFeCl	Im[g]	30	1.6×10^{-4}[g]	42.2	20.7		6.6×10^5[g]	
		Im[i]	30	4.9×10^{-5}[i]	42.2	20.7		5.5×10^4[i]	
Dimethylformamide		Im	25	2.3×10^{-4}	43.8	37		$(3.07 \pm 0.56) \times 10^5$	
		N-MeIm	25	2.3×10^{-4}	43.8	37	126	$(6.11 \pm 0.54) \times 10^4$	
		N-MeIm	25	7.6×10^{-7}	43.8	37			$(1.5 \pm 0.3) \times 10^{-3}$
	TPPFeI	N-MeIm	25	2.0×10^{-4}	43.8	37		$\sim 6.3 \times 10^5$	
	DPFeCl	Im[f]	30	$\sim 10^{-4}$[f]	43.8	37		5.6×10^5[f]	

[a] TPP = tetraphenylporphyrin, DP = deuteroporphyrin IX. [b] Taken from ref 40. [c] "Handbook of Chemistry and Physics", 50th ed, Chemical Rubber Co., Cleveland, 1969. [d] β_2 estimated from $\sqrt{\text{“}\beta_4\text{”}}$ (see text). [e] Apparent values or lower limits; see Results section. [f] Reference 20. [g] Reference 17. [h] Reference 18. [i] Reference 19.

Table III. Equilibrium Constants for Addition of Amines to Fe(III) Porphyrins in $CHCl_3$ at 25 °C

Porphyrin ligand	Amine	$pK_a\ (BH^+)$	K_1, M^{-1}	β_2, M^{-2}
OEPFeCl	Im	6.65[a,b]		$(1.07 \pm 0.09) \times 10^6$
	N-MeIm	7.33[a]		$(6.75 \pm 1.05) \times 10^3$
	$1,2\text{-}Me_2Im$	7.85	~2 ± 1	~8 ± 2
TPPFeCl	Im	6.65[a,b]		$(1.58 \pm 0.17) \times 10^6$
	4-MeIm	7.22[a,b]		$(1.00 \pm 0.10) \times 10^6$
	4-PhIm	5.70[a,b]		$(1.26 \pm 0.09) \times 10^5$
	2-MeIm	7.56[a,b]	16 ± 3	$(3.30 \pm 0.50) \times 10^3$
	$5,6\text{-}Me_2Bzim$	5.68[a,b]		$(2.10 \pm 0.20) \times 10^3$
	2-MeBzim	5.89[a,b]	~14 ± 10	~160 ± 150
	N-MeIm	7.33[a]	9 ± 2	$(1.50 \pm 0.24) \times 10^3$
	5-Cl-N-MeIm	4.75[c]		8.4 ± 0.8
	$1,2\text{-}Me_2Im$	7.85	3.4 ± 1.3	9.3 ± 1.1
	$4\text{-}Me_2NPy$	9.70[d]	51 ± 12	$(2.63 \pm 0.12) \times 10^3$
	3,4-Lut	6.46[a]	~4 ± 4	~25 ± 15(?)[e]
	Py	5.17[a]	~0.2 ± 0.2	~0.5(?)[e]

[a] A. Albert, *Phys. Methods Heterocycl. Chem.* **1**, 1963. [b] Corrected for the presence of two protons in the conjugate acid (log 2). [c] G. G. Gallo, C. R. Pasqualucci, P. Radaelli, and G. C. Lancini, *J. Org. Chem.*, **29**, 862 (1964). [d] A. Albert, *Phys. Methods Heterocycl. Chem.*, **3** (1971). [e] See discussion.

of eq 3, that is 3 mol of reactants forming 1 mol of product. Thus the product behaves as one unit, an "associated" ion pair, and β_2 has units of M^{-2}.[34] Measurement of β_2 for addition of N-methylimidazole as a function of total [TPPFeCl], with chloroform as solvent, indicates that at concentrations greater than 10^{-5} M, β_2 and K_1 are constants (Table II), while at lower concentrations of TPPFeCl, β_2 varies as the concentration of base varies. At [TPPFeCl] = 7.6×10^{-7} M the spectrophotometric data are consistent with the product being separated ions:

$$\mathrm{TPPFeCl} + 2N\text{-}\mathrm{MeIm} \overset{\beta_{2D}}{\rightleftharpoons} \mathrm{TPPFe}(N\text{-}\mathrm{MeIm})_2^+ + \mathrm{Cl}^- \tag{5}$$

with $\beta_{2D} \sim 1.6 \times 10^{-3}\ M^{-1}$ (Table II). This allows calculation of $K_{\mathrm{diss}}^{\mathrm{LS}}$, the dissociation constant for the ion-paired product: $K_{\mathrm{diss}}^{\mathrm{LS}} = \beta_{2D}/\beta_2 = 1.1 \times 10^{-6}$ M. This places an upper limit on the tendency of TPPFeCl to dissociate into $TPPFe^+$ and Cl^-, $K_{\mathrm{diss}}^{\mathrm{HS}} < 10^{-6}$ M. Indeed, this is supported by the fact that β_2 for addition of N-MeIm (this work, Table II) or N-methylbenzimidazole[22] is larger for TPPFeBr than for TPPFeCl, in agreement with the expectation that the Br^- complex should dissociate more readily than TPPFeCl.

With regard to the dissociation of TPPFeX, NMR studies have previously shown extensive dissociation of the bromide and iodide complexes, but not the chloride, at higher concentrations (~2×10^{-2} M)[32] than those employed for visible

Table IV. Equilibrium Constants for Addition of *N*-Methylimidazole to Para-Substituted TPPFeCl Complexes in $CHCl_3$ at 25 °C[a]

Para subst	σ[b]	Est. K_1, M^{-1}	β_2, M^{-2}
OCH_3	−0.268	38 ± 23	(3.6 ± 0.6) × 10^3
CH_3	−0.170	20 ± 5	(2.70 ± 0.19) × 10^3
H	0	9 ± 2	(1.50 ± 0.24) × 10^3
F	0.062	14 ± 7	(1.00 ± 0.10) × 10^3
Cl	0.227	22 ± 10	(0.71 ± 0.08) × 10^3
		Slope = −0.39 (eq 4a)	

[a] Solvent, $CHCl_3$. [b] Taken from ref 27.

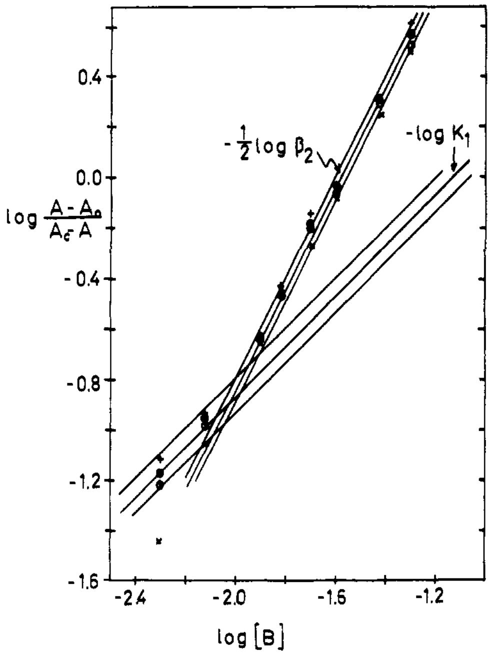


Figure 2. Method of analysis of absorbance data for the reaction of *N*-methylimidazole with TPPFeCl in chloroform; 510 nm (x), 547.5 nm (●), 575 nm (+), 690 nm (O).

spectral measurements (~8 × 10^{-5} M). Thus, the extent of dissociation appears to increase in the order Cl^- ≪ Br^-, I^- [32] The present studies show that TPPFeBr and TPPFeI have similar visible absorption spectra at 10^{-5} to 10^{-4} M concentration in chloroform, suggesting that they are similarly dissociated. (TPPFeBr: ν_3 19.55 kK, ϵ 11.5 × 10^3; ν_4 17.18, ϵ 2.84 × 10^3; ν_5 15.20, ϵ 3.88 × 10^3; ν_5' 14.41, ϵ 2.47 × 10^3. TPPFeI: ν_3 19.53, ϵ 11.1 × 10^3; ν_4 17.18, ϵ 2.23 × 10^3; ν_5 15.08, ϵ 4.71 × 10^3; ν_5' 14.27, ϵ 2.14 × 10^3.) In particular, for both TPPFeBr and TPPFeI, ν_5 is more intense than ν_5', whereas the reverse is true for TPPFeCl. The ν_5 bands of the bromide and iodide show major changes in intensity upon addition of only 1 equiv of *N*-methylimidazole, such that $\epsilon_5 \sim \epsilon_5' \sim 1.9 \times 10^3$. Further change in the intensity of these bands requires a 100-fold increase in [*N*-MeIm]. Under the same conditions, ν_3 increases in intensity upon addition of 1 equiv and then decreases again as more *N*-methylimidazole is added. Values of K_1 of $\geq 10^6$ and $\geq 10^5$ M^{-1} (bromide and iodide, respectively, Table II) can be estimated from samples containing less than 1 equiv of *N*-MeIm, but since each of these values are lower limits, no conclusion can be drawn as to the relative sizes of K_1 for these two complexes.

The bis adducts give identical spectra, slightly different from that of TPPFe(*N*-MeIm)$_2^+$$Cl^-$ (Table I), in that a second ν_3 band is observed. (TPPFe(*N*-MeIm)$_2^+$$Br^-$ ν_3' 19.42, ϵ 6.28 × 10^3; ν_3 18.23, ϵ 8.40 × 10^3; ν_4 17.18, ϵ 4.81 × 10^3; ν_5 15.50, ϵ 1.08 × 10^3.) The equilibrium constant for the second step of complex formation can be estimated from spectral changes which occur when more than 1 equiv of *N*-MeIm are added to TPPFeBr or TPPFeI. In the iodide complex case, the plot of log ($A - A_0/A_c - A$) vs. log [*N*-MeIm] is linear with a slope of 1.0 throughout the concentration range 6.3 × 10^{-5} to 7.6 × 10^{-2} M *N*-MeIm, whereas the same plot for the bromide complex is curved, with the minimum and maximum slopes <1.0 and 2.0, respectively. It is reasonable to interpret these results as indicating that the iodide complex is initially fully dissociated, so that the spectral changes above 1 equiv of *N*-MeIm are indicative of the reaction of the dissociated form of the mono-base complex:

$$\mathrm{TPPFeB^+ + B \overset{K_2'}{\rightleftharpoons} TPPFeB_2^+} \qquad (6)$$

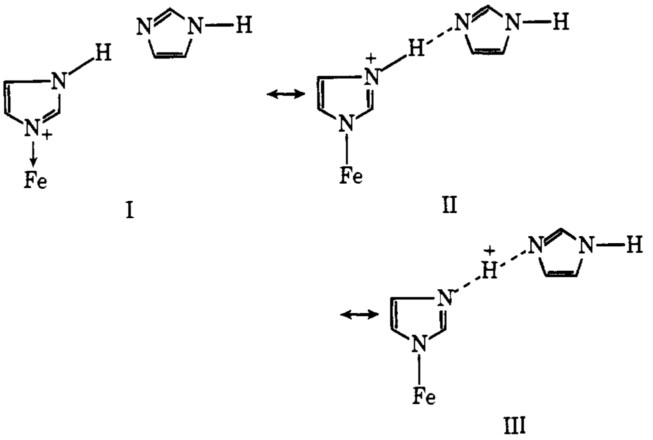
whereas the bromide complex may not be fully dissociated, and spectral changes may be due to a combination of reactions 2, 5, and 6. Since the visible spectra of TPPFeBr and the mono-amine adduct [TPPFeBr(*N*-MeIm) and/or TPPFe(*N*-MeIm)$^+$] are very similar, detection of the presence of more than two species in the solution is not possible by visible spectral techniques. Thus, the apparent K_2' for the bromide complex is probably less reliable than the corresponding value for the iodide complex (Table II).

Discussion

Effect of Solvent on β_2. Previous studies[35,36] of the effect of solvent on the reactions of several Fe(II) porphyrins with substituted pyridines led to the conclusion that ΔH and ΔS were strongly dependent on solvent (CCl_4, $CHCl_3$, C_6H_6). However, a more recent study of one of these systems [DPDMEFe(II) + 2Py in benzene][37] gives a vastly different value of β_2 (1.3 × 10^8 M^{-2} [37] as compared with 57 M^{-2} [36]). This recent report calls into question both the validity of the method of production of Fe(II) in the earlier study (addition of hydrazine monohydrate to a solution of the corresponding chloroiron(III) porphyrin complex)[35] and the conclusions concerning the effect of solvent on the thermodynamic parameters derived therefrom. In view of the latter findings,[37] there is no reason to believe that an equilibrium system is better characterized by ΔH than by ΔG measurements, and, in fact, both cases have been documented.[38] In the present study, equilibrium constants have been used to characterize the PFeX-ligand system rather than ΔH and ΔS values because K_{eq} measures the balance of enthalpy and entropy effects. Furthermore, K_{eq} is statistically more reliable than a ΔH determined from temperature variation of the equilibrium constant, which is in turn more reliable than the ΔS derived from this ΔH and log K_{eq} at a given temperature. Though direct calorimetric measurement of ΔH values as a function of solvent, along with the ΔG measurements of this work, might reveal the role of solvation (in terms of ΔS) in determining the stability of the complex, we suspect that ΔS values will be relatively constant for reactions within one solvent and differ by some constant amount from one solvent to another.

Most of the equilibrium constants of this study were measured in chloroform solution, usually considered to be a fairly good H-bonding solvent.[39] Although chloroform might H bond to the amines and thus invalidate β_2 as a thermodynamic constant, this effect is expected to be small for the amines of this study, which are less basic than aliphatic amines such as piperidine and thus less susceptible to strong solvent H-bonding interactions. In contrast to this potential drawback, *because* chloroform is capable of H bonding, it is better able to reduce self-association of imidazole and other N-H imidazoles in solution. Such self-association is evident in nonpolar, non-

H-bonding solvents such as benzene, *o*-dichlorobenzene, and bromobenzene, where β_2 for the reaction of TPPFeCl with imidazole depends upon the concentration of imidazole.[17] Our own studies of this reaction in benzene yielded data at four wavelengths which, when analyzed by the log-log method, gave a slope of 4.12 ± 0.10 and an intercept (log β_4?) of 9.21 ± 0.16. These data indicate that four molecules of imidazole react with one molecule of TPPFeCl to yield a species whose visible spectrum in benzene is identical with that of $\text{TPPFe(Im)}_2{}^+\text{Cl}^-$ in chloroform. Although it has been suggested that the additional imidazole molecules may interact with the porphyrin ring of $\text{TPP(Im)}_2{}^+\text{Cl}^-$ to form π complexes,[18] an alternative explanation is that the additional imidazoles are H bonded to the liganded imidazoles. Since the N-H bond of the imidazole ligand should become more polar upon formation of the Fe-N bond, this more polar bond could be better stabilized in the nonpolar benzene solvent by H bonding to a second imidazole:



Forms II and III are expected to be highly favored in the Fe(III) system because they allow delocalization of the positive charge on Fe to one or the other of the two imidazole ligands, or partially to each. (Only one imidazole ligand is shown in structures I-III.)

In order to compare the "β_4" obtained for the reaction of imidazole with TPPFeCl in benzene with β_2 values for reaction 3, it seems reasonable to assume, as suggested by structures II and III, that the reaction in benzene might be viewed as that of two imidazole dimers reacting with TPPFeCl to produce the adduct:

$$2\text{Im}\cdots\text{Im} + \text{TPPFeCl} \overset{\beta_4}{\rightleftharpoons} \text{TPPFe(Im}\cdots\text{Im)}_2{}^+\text{Cl}^- \quad (7)$$

where the chloride ion is probably H bonded to one of the imidazole N-H groups. Since the quantity used in calculating β_4 is the molar concentration of imidazole, irrespective of its state of aggregation, reaction 7 predicts that the equilibrium constant β_4 will have inverse fourth power dependence on imidazole concentration. If the imidazole were not dimerized and the reaction were (3), β_2 should equal $(\beta_4)^{1/2}$. Thus, in Table II, $(\beta_4)^{1/2}$ is entered as the β_2 for this system. As such, it is much smaller than β_2 for reaction 3 in more polar solvents (Table II).

In more polar solvents, imidazole is apparently sufficiently depolymerized so as to yield β_2 according to eq 3. The size β_2 does not vary greatly among the solvents investigated in this study (CHCl_3, DMF) or by others (CH_2Cl_2, CH_3COCH_3),[17] but is largest in chloroform (Table II), although chloroform is the least polar of these four solvents.[40] This may suggest that the H-bonding capability of CHCl_3[39] allows more complete depolymerization of imidazole, and thus allows it to be more readily available for complex formation with TPPFeCl than in slightly more polar solvents which do not have H-bonding capabilities.

A value of $\beta_2 = 9.75 \times 10^5\ \text{M}^{-2}$ for the reaction of TPPFeCl with imidazole in DMF has been reported,[21] but the temperature of the measurement was not listed; thus direct comparison with the results found in this work is not possible.

A clear distinction must be made between the nature of the solvation of N-H and N-R imidazoles and their PFe(III) complexes. The first class is capable of self-association by H bonding, and delocalization of the positive charge upon bonding to Fe(III), through a weakening of the N-H bond, whereas the N-R imidazoles are not. Thus it is not surprising that TPPFeCl reacts with *N*-methylimidazole in benzene solution to yield a clearly defined K_1 and β_2 (Table II). The 250-fold decrease in β_2 on going from chloroform to benzene (Table II) is a measure of the effect of solvent polarity upon reaction 3, independent of the more complex processes expected to be involved in the reactions of N-H imidazoles.

In more polar solvents (CHCl_3, CH_2Cl_2, DMF), both K_1 and β_2, for B = *N*-methylimidazole, increase as solvent polarity increases (Table II). In fact, even including the nonpolar benzene solvent data, log K_1 and log β_2 each increase fairly linearly with the solvent polarity parameter E_T:[40] $\log K_1 = -7.35 + 0.216\,E_T$; $\log \beta_2 = -12.66 + 0.403\,E_T$. E_T should be a considerably better indicator of solvent polarity in this system than the commonly quoted dielectric constant (Table II), because (a) it is not a bulk solvent property, but rather an experimental measure of molecular interaction between solvent and solute, and (b) it is determined by use of an indicator (pyridinium *N*-phenolbetaine), which is similar in size to the porphyrins of this study and which also involves ion pairs (internal in this case).[40]

The effect of solvent polarity on $\beta_{2\text{D}}$, eq 5, is not simple. The value of $\beta_{2\text{D}}$ increases on going from CHCl_3 to CH_2Cl_2, but decreases again on going to DMF (Table II). This may be symptomatic of conflicting roles of DMF molecules in (a) separating ion pairs (due to greater solvent polarity) and (b) competing with *N*-methylimidazole for vacant coordination sites on TPPFe^+. The first should increase and the second decrease the apparent $\beta_{2\text{D}}$.

Effect of Base on β_2. The data of Table III may be divided into three categories for purposes of this discussion: N-H imidazoles, N-R imidazoles, and pyridines. With this division in mind, a number of intercomparisons may be made. First, among nonhindered amines, there is a rough correlation between the basicity of the amine and the value of log β_2. Within each of the three classes, log β_2 varies ~0.8 log unit per $\text{p}K_\text{a}$ unit of the conjugate acid of B. Specifically, for N-H imidazoles (4-PhIm, 4-MeIm, Im), $\log \beta_2 = 0.74 + 0.77\ \text{p}K_\text{a}(\text{BH}^+)$; for N-R imidazoles (5-Cl-*N*-MeIm, *N*-MeIm), $\log \beta_2 = -3.20 + 0.87\ \text{p}K_\text{a}(\text{BH}^+)$; for pyridines ($\text{4-NMe}_2\text{Py}$, 3,4-Lut, Py), $\log \beta_2 = -4.51 + 0.81\ \text{p}K_\text{a}(\text{BH}^+)$. Thus, substituting R for H on the "aliphatic" nitrogen of imidazole decreases log β_2 by approximately 3.3 log units on the average, while changing B from an N-R imidazole to a pyridine decreases log β_2 further by about 1.7 log units. Looking at imidazoles only, we see that loss of the favorable charge delocalization through N-H bond weakening in products containing N-H imidazoles has a most dramatic effect (~3.3 log units) upon β_2. Clearly, the dominating feature of reaction 3 is stabilization of the product ion pair, which is more easily accomplished when the amine is an N-H imidazole. This fact suggests that partial dissociation (or weakening of the bond) of the N-H proton helps to stabilize the Fe(III) product, and that deprotonated imidazole-Fe(III) complexes would be extremely stable in biological systems. This lends credence to the suggestion[41,42] that hydrogen bonding of the proximal histidine imidazole proton to a neighboring peptide group would increase the basicity of this imidazole, thus increasing the oxygen affinity.

Such hydrogen bonding or deprotonation of histidine imidazole N-H groups should also have dramatic effects upon redox potentials and may be important in determining the positions of various cytochromes in the electron transport chain or the properties of "high pH" forms of cytochrome *c* and others.

The effect of bulky groups adjacent to the aromatic nitrogen of N-H and N-R imidazoles is clearly evident when we compare β_2 for imidazole, 2-methylimidazole, and 5,6-dimethylbenzimidazole, or *N*-methylimidazole and 1,2-dimethylimidazole; log β_2 decreases by 2.7-2.9 (N-H) or 2.2 (N-R) upon addition of a bulky group. That this effect is not apparent in 4-substituted imidazoles is probably due to the fact that there is rapid and facile tautomerism of the proton between the 1 and 3 nitrogens of N-H imidazoles, and only the nonhindered tautomer is competitive in binding to TPPFeCl. If the tautomers are of approximately equal stability, little steric effect will be detected in reaction 3.

It is interesting to note that the steric hindrance of a methyl group and the α-CH of a fused benzo ring are similar (2-methylimidazole and 5,6-dimethylbenzimidazole, Table III). It is also interesting to note that although two hindered bases can indeed be added to TPPFe(III), only the monoamine complex of Fe(II), TPPFe(2-MeIm), is stable in the solid state[43] and in solution.[44,45] The present result of formation of stable 2:1 complexes of hindered imidazoles with Fe(III) porphyrins suggests that there must be some reason other than steric hindrance for the fact that the corresponding Fe(II) porphyrins do not achieve this stoichiometry.[22]

The effect of the loss of H bonding of N-H imidazoles in $CHCl_3$ (Im vs. *N*-MeIm) is about equal to the effect of addition of a methyl group adjacent to the bonding nitrogen (Im vs. 2-MeIm or *N*-MeIm vs. 1,2-Me_2Im, Table III). Thus H bonding and steric effects have approximately equal weight in this system.

The values of β_2 obtained in this study, Tables III and IV, are in very good agreement with a smaller group obtained by an NMR technique.[22] The NMR method was sensitive to quantitative measurement of β_2 only, although existence of 1:1 complexes could be detected.[22,46] Large constants, such as β_2 for imidazole and 4-methylimidazole, cannot be determined by the NMR technique.[22]

The similar β_2 values observed for OEPFeCl + 2B and the corresponding TPPFeCl reactions (B = Im, *N*-MeIm, 1,2-Me_2Im, Table III) suggest that the nitrogen atoms of OEP are similar in basicity to those of TPP.

Effect of Phenyl Substituents, X, on β_2. In Table IV are listed the values of K_1 and β_2 for reaction of (*p*-X)TPPFeCl with *N*-methylimidazole. A plot of log β_2^X vs. $4\sigma_X$ (eq 4a) is shown in Figure 3. Clearly β_2 is a function of the electron-donating/withdrawing characteristics of X. However, the dependence is opposite that for (*p*-X)TPPM reactions with Lewis bases, where M is in the +2 oxidation state or is bonded to a nondissociable anion which neutralizes the charge.[23,24] That is, the Hammett ρ value is negative for the Fe(III) system, but positive for the V(IV),[23] Co(II),[24] and Ni(II)[23] reactions with Lewis bases. The negative ρ value is another way of saying that electron-donating groups favor the reaction. Thus, the stabilization of the positive charge on Fe(III) in the product, (*p*-X)TPPFe$B_2^+Cl^-$, by electron-donating X groups, is more important than the attraction between Lewis base and the electropositive reaction center of the reactant, (*p*-X)TPPFeCl, a center made more positive by electron-withdrawing groups. The latter effect, which we shall call the "Lewis acid contribution", is the only effect contributing to the Hammett relationship for the reaction of V(IV), Co(II), and Ni(II) porphyrins with axial bases, and for the Ni(II) reaction $\rho = +0.33$,[23] whereas in the Fe(III) case ρ is composed not only of this "Lewis acid contribution", but also the "charge contribution": stabilization of the positive charge of Fe(III).

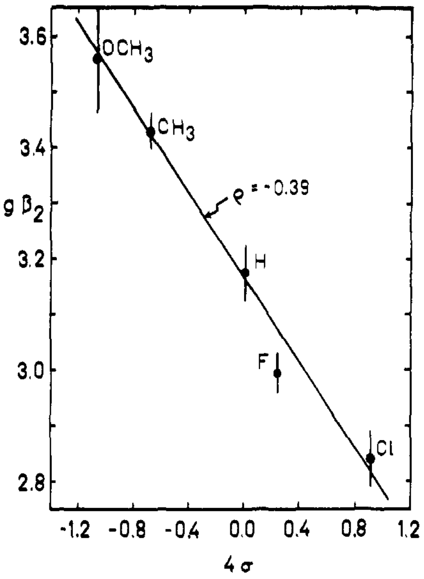


Figure 3. Hammett plot for the reaction of *N*-methylimidazole with (*p*-X)TPPFeCl in chloroform solution.

Utilizing the composite $\rho = -0.39$ (Table II) and the Lewis acid contribution estimated from the Ni(II) reaction with two piperidines, $\rho = +0.33$, we estimate that the charge contribution has $\rho \sim -0.7$. Thus, stabilization of the ion-paired product clearly dominates the reactions of para substituted TPP complexes of Fe(III), and undoubtedly Co(III) and other +3 metals which add two ligands.

Effect of Base on the Electronic Spectra of TPPFe$B_2^+Cl^-$. The data of Table I indicate that the absorption maxima of N-H and N-R bis(imidazole) complexes of TPPFeCl are reasonably constant, as long as no hindering groups are present. However, sterically hindered imidazoles produce complexes in which the absorption maxima are shifted in approximately the order expected for the degree of steric hindrance provided by the base. Thus, 5,6-dimethylbenzimidazole $\leqslant$ 2-methylimidazole $<$ 1,2-dimethylimidazole $<$ 2-methylbenzimidazole. Although this trend does not follow quantitatively the size of β_2, it does follow qualitatively.

Smith and Williams[1] have noted a correlation between energy and intensity of the bands near 20 kK and 16 kK (ν_3 and ν_4 of Table I) for high spin PFe(III) complexes. We find a similar correlation for ν_3 for low-spin TPPFe$B_2^+Cl^-$ complexes, as shown in Figure 4, except that ϵ_3 shifts in the opposite direction with changes in ν_3 for low-spin complexes than it does for high-spin PFe(III) complexes.[1] Other bands show nonlinear correlations between ν and ϵ.

The near infrared bands (ν_6, ν_7) may possibly be d-d transitions, since their intensities are within the range generally expected for such transitions[2] (Table I; note that ϵ_6 and ϵ_7 are not multiplied by 10^{-3} and are thus in the general range ~200 M^{-1} cm^{-1}). Smith and Williams[1] do not mention observing the peak corresponding to ν_7 in their low-spin natural porphyrin complexes. Shifts in the position of ν_6 and ν_7 parallel those of ν_3 and ν_4, which may indicate some configuration interaction between the electronic states involved.[1,2] These absorptions are not present in complexes of the hindered imidazoles, except for 2-methylimidazole (Table I).

The highly hindered imidazoles, 1,2-Me_2Im and 2-MeBzim, have a curiously sharp, low-intensity bump at 13.1 kK, not observed for other imidazoles or pyridines. The 2-MeIm complex has an inflection point at the same position. Because this peak is a sharp, low-intensity shoulder on the side of a peak at ~15 kK, and because its width is not consistent with others classified as ν_6, it is classified under ν_5. In these same com-

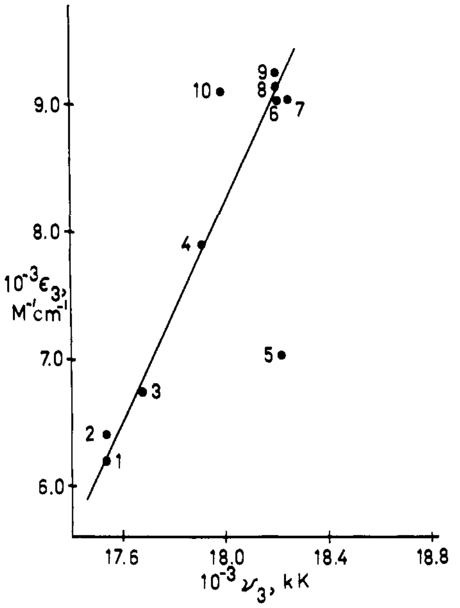


Figure 4. Correlation between energy and intensity of the ν_3 band of $TPPFeB_2^+Cl^-$. Solvent = chloroform. Bases are: 1 = 2-MeBzim; 2 = 1,2-Me$_2$Im; 3 = 2-MeIm; 4 = 5,6-Me$_2$Bzim; 5 = 5-Cl-*N*-MeIm; 6 = Im; 7 = *N*-MeIm; 8 = 4-MeIm; 9 = 4-PhIm; 10 = 4-NMe$_2$Py.

plexes, the major ν_5 absorption is broad and ill defined, sometimes split into two equal intensity peaks (2-MeBzim), similar to those observed for the high-spin TPPFeCl. These observations raise the question as to whether complexes of the highly hindered imidazoles may be intermediate or high spin or have a low-energy intermediate or high-spin excited state. It may be that the trends in ν_3, ν_4, and the presence or absence of the low-intensity bump at 13.1 kK and ν_6 and ν_7 may be measures of the spin state of these bis(amine) complexes and thus, for hindered imidazoles, measures of the length of the Fe-N bonds. Indeed, preliminary studies of the low-temperature ESR spectra of these complexes show that nonhindered imidazoles and 4-dimethylaminopyridine give typical low-spin g values ($g_1 \sim 2.9$, $g_2 \sim 2.3$, $g_3 \sim 1.5$), while hindered imidazoles, including 2-methylimidazole, and pyridine and 3,4-lutidine give "high-spin" spectra ($g_1 \sim 8.7$, $g_2 \sim 4.3$, $g_3 \sim 3.8$). However, the g values are quite dependent upon solvent and are under further investigation.[47] Magnetic susceptibility measurements on chloroform solutions of TPPFe(2-MeIm)$_2^+$Cl$^-$ by the NMR technique indicate that this complex is low spin at and below −25 °C,[22] even though it gives a "high-spin" ESR spectrum at 77 K.[47] At present we are left with the question of the spin state of hindered imidazole (and low basicity pyridine) complexes of TPPFe(III), and whether there may be a relationship between bond length and magnetic moment of $TPPFeB_2^+Cl^-$ complexes. Further studies which should help to answer this question are underway.

Abbreviations

P	porphyrin ligand with unspecified substituents
TPP	*meso*-tetraphenylporphyrin
(*p*-X)TPP	*meso*-tetra-(*p*-X-phenyl)porphyrin
DP	deuteroporphyrin IX
DPDME	deuteroporphyrin IX dimethyl ester
OEP	octaethylporphyrin
B	unspecified Lewis base
Im	imidazole
N-MeIm	*N*-methylimidazole
2-MeIm	2-methylimidazole
1,2-Me$_2$Im	1,2-dimethylimidazole
4-MeIm	4-methylimidazole
4-PhIm	4-phenylimidazole
5,6-Me$_2$Bzim	5,6-dimethylbenzimidazole
5-Cl-*N*-MeIm	5-chloro-*N*-methylimidazole
Py	pyridine
4-Me$_2$NPy	4-dimethylaminopyridine
3,4-Lut	3,4-lutidine (3,4-dimethylpyridine)
DMF	*N*,*N*-dimethylformamide
K_1	defined by eq 1
K_2	defined by eq 2
β_2	defined by eq 3
β_{2D}	defined by eq 5
K_2'	defined by eq 6
M	molar concentration, moles per liter
E_T	solvent polarity parameter (see text)
D	dielectric constant of the solvent

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Electrochemical Reduction of *sym*-Dibenzocyclooctatetraene, *sym*-Dibenzo-1,5-cyclooctadiene-3,7-diyne, and *sym*-Dibenzo-1,3,5-cyclooctatrien-7-yne

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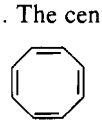
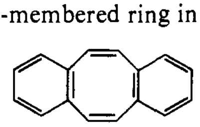
Abstract: A study of the electroreduction of *sym*-dibenzocyclooctatetraene (DBCOT), *sym*-dibenzo-1,5-cyclooctadiene-3,7-diyne (DBCOD) and *sym*-dibenzo-1,3,5-cyclooctatrien-7-yne (DBCOM) in DMF–TBAP solutions was carried out to investigate the effects of differences in the structure of the central eight-membered ring on the electrochemical behavior. The reversible half-wave potentials ($E_{1/2}^{r}$), heterogeneous electron-transfer rate constants (k_s), transfer coefficients, and pseudo-first-order rate constants of the following chemical reactions were determined by cyclic voltammetric–digital simulation techniques. The results are consistent with reduction of tub-shaped DBCOT to a planar radical anion and dianion and of planar or almost planar DBCOM and DBCOD to planar radical anions. Estimates of the energy of the conformational change were obtained by comparison of $E_{1/2}^{r}$ to calculated energies of the lowest unoccupied molecular orbital and from the k_s values.

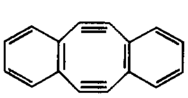
The electrochemical behavior of cyclooctatetraene (COT) and related compounds and the electron spin resonance (ESR) of the associated radical anions have been the subjects of numerous investigations.[2-8] The general picture which emerges is that reduction of the tub-shaped COT produces a planar or nearly planar radical anion ($COT\cdot^-$); the large change in molecular geometry leads to a high activation energy and hence slow electron-transfer rates. The second reduction step to the dianion involves only small changes in geometry and hence more rapid electron transfer. A more detailed explanation of the experimental results requires taking account of solvation changes, ion pairing effects, and following protonation reactions.



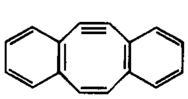
COT



DBCOT



DBCOD



DBCOM

Recently, Wong, Garratt, and Sondheimer[9] reported the synthesis of *sym*-dibenzo-1,5-cyclooctadiene-3,7-diyne (DBCOD) and *sym*-dibenzo-1,3,5-cyclooctatrien-7-yne (DBCOM). The central eight-membered ring in these compounds was reported to be planar, based on the NMR and electronic spectra, and this was confirmed for DBCOD by x-ray crystallography.[10] On the contrary, *sym*-dibenzocyclooctatetraene (DBCOT) is tub shaped, by analogy to COT, while its dianion was reported to be planar, based on the NMR spectra.[11] We thought it of interest to compare the electrochemical behavior of DBCOT, which shows a large structural change on reduction, with that of DBCOD and DBCOM, which presumably do not. We describe here studies of the electroreduction of these compounds in DMF solutions by cyclic voltammetry (CV) and other electrochemical techniques and report the reversible half-wave potentials ($E_{1/2}^{r}$), rate constants for heterogeneous electron transfer (k_s), transfer coefficients (α), and estimates of the half-lives of the radical anions and dianions ($t_{1/2}$).

Experimental Section

Chemicals. DBCOT was obtained by photoisomerization of dibenzobarrelene.[12] DBCOD was prepared in London by dehydrobromination of 3,4,7,8-tetrabromo-*sym*-dibenzo-1,5-cyclooctadiene,[9] sent to Austin, and used after removing polymerized products by passing a pentane solution through a short alumina column. DBCOM was prepared by dehydrobromination of 7,8-dibromo-*sym*-dibenzo-1,3,5-cyclooctatriene.[9] The product was purified by column chromatography and showed the reported uv spectrum. *N,N*-Dimethylformamide (DMF) and tetrabutylammonium perchlorate (TBAP) were purified as previously described.[13]

Electrochemical Measurements. Solutions were prepared under a helium atmosphere in a Vacuum/Atmosphere Corp. (Hawthorn, Calif.) glove box. All experiments were carried out under a nitrogen atmosphere with positive pressure. The nitrogen gas (prepurified grade) was further purified by passing it over hot copper wire and a Drierite column. Dissolved oxygen in the solution was removed by bubbling nitrogen gas through the solution. A spherical platinum electrode sealed in glass was used as the working electrode in the measurement of electrochemical kinetic parameters. The electrode was polished smooth with 0.5-μm alumina polishing powder before each use. The electrode area, as determined from electrochemical measurements with phthalonitrile, whose diffusion coefficient has been determined at a mercury electrode,[13] was 0.177 cm^2. A mercury pool was used as the counter electrode. An aqueous saturated calomel