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Electronic Effects in Transition Metal Porphyrins. 9. Effect of Phenyl *Ortho* Substituents on the Spectroscopic and Redox Properties and Axial Ligand Binding Constants of Iron(III) Tetraphenylporphyrinates

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To obtain a better understanding of the effects of *ortho*-halogen and related substituents on the phenyl rings of $TPPH_2$ and (TPP)Fe(III) complexes, a series of unsymmetrically substituted tetraphenylporphyrins have been synthesized. In each of these complexes one phenyl ring bears halogen(s) on one (or both) *ortho* position(s), while the other three phenyl rings carry *para*-methoxy substituents. The free-base porphyrins were characterized by UV−visible and ^1H NMR spectroscopy. The resonance of the pyrrole protons closest to the phenyl ring bearing the *ortho* substituent, H_a, of the free-base porphyrins shows a progressive shift to higher shielding as the atomic radius and Hammett substituent constant σ_p of the substituent increases. However, the fact that 2,6-substitution has a similar effect as 2-substitution suggests that size effects are more important than through-bond electronic effects. Equilibrium constants, β_2^{III}, for addition of *N*-methylimidazole to the series of complexes (o-X)(p-OCH_3)$_3$(TPP)FeCl and (2,6-X_2)(p-OCH_3)$_3$(TPP)FeCl were measured in chloroform at 25 °C. $\log(\beta_2^{III})$ increases in the order $F < Cl < Br < I < F_2 < CF_3 < Cl_2 < Br_2$, and all β_2^{III} values for mixed substituent porphyrins except the monofluoro-containing complex are larger than the β_2^{III} for the reaction between the symmetrical non-*ortho*-substituted parent compound, (p-OCH_3)$_4$(TPP)FeCl, and NMeIm. Hence, *ortho*-halogen and -CF_3 substituents increase the values of β_2^{III} in order of increasing size, with the 2,6-disubstituted phenyls causing an increase of β_2^{III} by more than a factor of 2 over that for 2-substituted phenyls. In the strongly solvating solvent dimethylformamide, where dissociation of the anion has already taken place, the opposite order of $\log(\beta_2^{III})$ is observed ($F > CF_3 > Cl_2 \gg p\text{-}OCH_3$). Both sets of equilibrium constant data suggest that *ortho*-halogens and -CF_3 groups are electron donating, which we believe is due to direct overlap between the electron clouds of the halogens and the π system of the porphyrin. This direct overlap of electron clouds decreases the Lewis acidity of Fe(III), *both* making it easier for Cl^- to dissociate from the Fe^+Cl^- starting material in $CHCl_3$ *and* making the complex less stable; the former contribution is more important in $CHCl_3$, while the latter becomes evident in DMF. The ^1H NMR spectra of the same series of low-spin Fe(III) complexes show a decrease in the spread of the pyrrole-H resonances in the order of $Cl_2 > F_2 > Br_2 \gg F > Cl > Br \sim CF_3 \gg I$. This order suggests that the apparent electron-donating characteristics of the substituents decrease in the listed order, which is quite different from that derived from the values of $\log(\beta_2^{III})$ measured in chloroform solution. The differences probably result from the fact that these two physical properties are sensing different effects of the *ortho* substituents: $\log(\beta_2^{III})$ values probe changes in the σ basicity of the pyrrole nitrogens and hence the Lewis acidity of the metal, while the spread of pyrrole-H resonances probes changes in the π electron density distribution in the e(π) orbitals and/or differences in the energy separation of those two orbitals of the porphyrin ring.

Introduction

The degree and mode of transmission of electronic effects between various points on the porphyrin ring and the central metal via the σ and π orbitals of the four porphyrin nitrogens have long been of interest to those who have investigated the physical properties and chemical reactions of metalloporphyrinates.[4−31] Because of the high aromaticity of the porphyrin ring system, electron-donating or -withdrawing substituents on the periphery of the molecule have been shown to affect the basicity of the porphyrin nitrogens,[4,5] the rate of N−H tautomerism in porphyrin free-bases,[6b,21a,23] the chemical shifts of pyrrole and NH protons in free-base tetraphenylporphyrins,[20a,24] rates of phenyl ring rotation[21b,c,25] and porphyrin ring inversion[22]

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in metalloporphyrinates, visible absorption spectra,[19b] spin states,[28] EPR parameters,[29] NMR isotropic shifts,[20b,c,25,26] metal nucleus NMR chemical shifts,[30,31] rate[7d,12b] and equilibrium[7e−15] constants for axial ligation, reduction potentials[7b,c,8d,11,15−18] of both porphyrin ring and metal redox reactions, and metal incorporation rates.[7f,g,19] In most of the systems studied (except refs 9, 14, 20, 21c, and 29), symmetrically substituted tetraphenylporphyrins having either *meta* or *para* substituents on the phenyl rings have been investigated, and it has usually been found that the above physical properties correlate with the Hammet σ constants of the substituents:

$$P(\mathrm{X}) - P(\mathrm{H}) = 4\sigma_{\mathrm{X}}\rho \tag{1}$$

Here P(X) and P(H) are the observed physical property of the tetraphenylporphyrins having substituent X and H, respectively, σ_X is the Hammett substituent constant of X, and ρ describes the sensitivity of the property being studied to the electron-withdrawing or -donating properties of X.[32] These linear free energy relationships have been useful in predicting the possible effects of new substituents on the reactivity of the porphyrin or metalloporphyrinate.

The effect of electron-donating and -withdrawing substituents on the equilibrium constants for the binding of axial ligands to metalloporphyrinates has been studied by a number of research groups.[7e−15] It has been shown that for a wide range of (tetrakis-(substituted phenyl)porphyrinato)metal(II) complexes in noncoordinating solvents (benzene, toluene, or chloroform), including Zn(II),[13,14] Ni(II),[8a] Co(II),[8b−d] Fe(II),[17b] and VO^{2+},[8a] that the ρ values are positive in all cases for the reactions

$$(\mathrm{X})_4\mathrm{TPPM} + \mathrm{L} \text{ or } 2\mathrm{L} \rightleftarrows (\mathrm{X})_4\mathrm{TPPML} \text{ or } (\mathrm{X})_4\mathrm{TPPML}_2 \tag{2}$$

This could be called the "Lewis acid effect", and it arises from a decrease or increase in Lewis acidity of the metal center in response to the electron-donating or -withdrawing, respectively, abilities of the phenyl *meta* or *para* substituents. In contrast, for iron(III) porphyrinates in chloroform or dichloromethane solution,[9] binding of two neutrally charged ligands to the metal requires dissociation of the chloride anion in these solvents and creates a net positive charge on iron(III):

$$(\mathrm{X})_4(\mathrm{TPP})\mathrm{FeCl} + 2\mathrm{L} \rightleftarrows [(\mathrm{X})_4(\mathrm{TPP})\mathrm{FeL}_2]^+\mathrm{Cl}^- \tag{3}$$

This contribution from charge separation and formal charge stabilization creates the opposite linear free energy dependence, and a value of $\rho = -0.39$ was reported for a series of symmetrical (tetrakis(*p*-substituted phenyl)porphinato)iron chloride complexes, $(p\text{-X})_4(\mathrm{TPP})\mathrm{FeCl}$,[9] indicating that electron-donating groups favor the formation of the complex in these solvents. This finding was at that time explained in terms of the stabilization of the positive charge on Fe(III) in the product. However, Brewer and Brewer later determined the equilibrium constants for the same set of *para*-substituted (tetraphenylporphyrinato)iron(III) chlorides with *N*-methylimidazole in dimethyl sulfoxide (DMSO) and found that $\rho = +0.11$.[10] DMSO is a coordinating solvent which binds to Fe(III) to create a bis(DMSO) complex,[33] whereas chloroform is noncoordinating, and the "charge stabilization of the product" observed by Walker *et al.*[9] had already occurred in the DMSO solvent before the addition of *N*-methylimidazole. This positive value of ρ observed in DMSO, together with the negative value observed in chloroform, suggest that the Hammett ρ value for *charge separation* in this system, ρ_{charge}, is approximately -0.5.[11]

The above considerations suggest that although it was not realized at the time of our earlier work on Fe(III) porphyrinates,[9,11] a more unifying approach to understanding the effects

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of substituents on the equilibrium constants for binding axial ligands to substituted (TPP)FeCl derivatives is to consider *both* the effect of these substituents on the ability to break the (TPP)Fe$^+$Cl$^-$ ionic bond and create the charge separated ion pair *and* the ability to stabilize the positive charge on Fe(III) in the product. From this viewpoint it is evident that the negative slope ($\rho = -0.39$) of eq 1 can be explained by the fact that electron-withdrawing substituents have a greater effect on stabilizing the *reactant*, $(X)_4$(TPP)FeCl, than they do in stabilizing the product, $[(X)_4(TPP)Fe(L)_2{}^+]Cl^-$, and that, at least for symmetrically substituted (tetrakis(*m*- or *p*-X-phenyl-substituted)porphyrinato)iron(III) complexes, the effect of electron-donating and -withdrawing substituents is no different than it is for any M(II) porphyrinate, except that we must include the *large* effect of breaking the (TPP)Fe$^+$Cl$^-$ bond and separating the charges on the two resulting ions, at least to the distance necessary to form the associated ion pair, $[(X)_4(TPP)FeL_2]^+Cl^-$.

Investigations of the sensitivity of reactions and physical properties to the electronic effects of substituents have been extended by this research group in studies of unsymmetrically *meta*- and *para*-phenyl-substituted derivatives of free-base,[20a] Zn(II),[14,16,20a] and Fe(III)[9b,15,20b,c,29b] tetraphenylporphyrinates. We have found that the pyrrole-H chemical shifts of free-base derivatives of the series (*m*- or *p*-X)$_x$(*m*- or *p*-Y)$_y$TPPH$_2$ ($x + y = 4$) behave according to eq 4.

$$P(\mathrm{X,Y}) - P(\mathrm{H}) = (\sum \sigma_{\mathrm{X,Y}})\rho \qquad (4)$$

The effect of a unique phenyl substituent was found to be felt largely at the closest pyrrole-H position, H$_a$, and the effect is attenuated by more than a factor of 10 at the next pyrrole-H position, H$_b$, arguing against direct conjugation between the phenyl carrying the substituent and the porphyrin ring.[20a] These results indicate that for free-base porphyrins, the transmission of the electronic effects of *meta* and *para* phenyl substituents is overwhelmingly inductive in nature and probably includes σ and π induction but not π conjugation.[20a] For Zn(II) complexes of unsymmetrically substituted tetraphenylporphyrins, it was found that equilibrium constants for addition of a 3-picoline ligand strictly obey eq 4,[14] with the same value of ρ as found for the symmetrically substituted derivatives, eq 1.[13,14] Thus, the Lewis acid Zn(II) appears to average the electronic properties of phenyl substituents, independent of whether they are the same or different.

In contrast to the results found for metal-free and Zn(II) complexes, the proton NMR spectra of Fe(III) complexes of unsymmetrically substituted tetraphenylporphyrinates provide evidence of π spin delocalization that is sensitive to the *difference* in electron-donating and -withdrawing properties of the substituents,[20b,c] while EPR *g* values were found not to be differently sensitive to unsymmetrical as compared to symmetrical substitution.[29b] The equilibrium constants, β_2^{III}, for addition of two *N*-methylimidazole (NMeIm) ligands to unsymmetrically substituted derivatives of (TPP)FeCl,[9b]

$$(X)_x(Y)_y(\mathrm{TPP})\mathrm{FeCl} + 2\mathrm{NMeIm} \rightleftarrows [(X)_x(Y)_y(\mathrm{TPP})\mathrm{Fe(NMeIm)_2}]^+\mathrm{Cl}^- \quad \beta_2^{\mathrm{III}} \qquad (5)$$

exhibit a complex behavior that is different from that of the symmetrically substituted (TPP)FeCl derivatives investigated earlier.[9a] This behavior suggests direct conjugation of the fourth phenyl ring in the symmetrical product complexes, $[(X)_4(TPP)Fe(NMeIm)_2]^+Cl^-$, or the "least willing" phenyl in the unsymmetrical product complexes, $[(X)_x(Y)_y(TPP)Fe(NMeIm)_2]^+Cl^-$, to remove the formal positive charge on Fe(III) in the product[9b] or, as we should now also consider, conjugation of the "most willing" phenyl ring in the unsymmetrical reactants to allow dissociation of the anion. Although we cannot separate the effects of unsymmetrical substitution of the previously studied complexes on the reactant and product of eq 5 without additional experiments, it remains true that there is a large difference in the equilibrium constants of unsymmetrically and symmetrically substituted derivatives of (TPP)FeCl in chloroform solution.[9b] In contrast, the Fe(III/II) reduction potentials of the low-spin, bis-NMeIm complexes of substituted TPP derivatives vary according to eq 4, independent of whether the porphyrin is symmetrically or unsymmetrically substituted.[16] Thus, unsymmetrically substituted porphyrin complexes of Fe(III) exhibit mixed behavior with regard to the effect of unsymmetrical substitution on linear free energy relationships.

Although substituent effects have been discussed for (tetraphenylporphyrinato)iron(III) complexes and are known to modulate the electronic properties of the porphyrin ring (ref 53 and references therein), the effects of *ortho* substituents on the physical and chemical properties of these complexes are nonconclusive. On one hand, there is evidence that the electronic effects of *ortho* substituents are much smaller than those of their *meta* and *para* counterparts.[53,54] On the other hand, there is considerable scattered evidence that the effects of *ortho* substituents are profound. For example, Longo and

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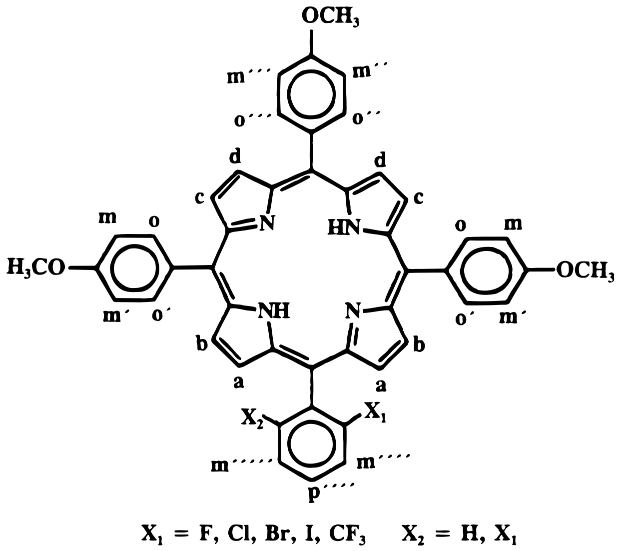

Figure 1. Structures of the unsymmetrically substituted porphyrins of this study. When $X_2 = X_1$, $o = o'$, $m = m'$, $o'' = o'''$, $m'' = m'''$, and $m'''' = m''''$.

co-workers showed some time ago that this is the case for free-base porphyrins,[37] and both (tetramesitylporphinato)iron(III) chloride, (TMP)FeCl,[11,35,36] and perchlorate, (TMP)FeOClO$_3$,[11,36] and (tetrakis(2,6-dichlorophenyl)porphinato)iron(III) perchlorate, (2,6-Cl$_2$)$_4$(TPP)FeOClO$_3$,[11,34,36] form bis-axial ligand complexes that are orders of magnitude more stable than those of related (TPP)Fe^{III} systems, despite the so-called "hindered" nature of the tetrakis(di-*ortho*-substituted)tetraphenylporphyrinate ligand. Bruice and co-workers[38] have also noted the particular stability of axial ligand complexes of (tetrakis(2,6-dibromo-3-sulfophenyl)porphyrinato)iron(III), (2,6-Br$_2$-3-SO$_3^-$)$_4$(TPP)Fe^{III}, and (tetrakis(2,6-dichloro-3-sulfophenyl)porphyrinato)iron(III), (2,6-Cl$_2$-3-SO$_3^-$)$_4$(TPP)Fe^{III}. The structures of five bis(pyridine) complexes of (TMP)FeOClO$_3$ show that the porphyrin ring prefers to undergo severe S_4 ruffling in order to bind the planar pyridine ligands in mutually perpendicular planes over the *meso* positions to produce low-spin Fe(III) complexes,[39a,b] but the porphyrin ring of the bis(*N*-methylimidazole) complex of (TMP)Fe^{III} is planar, with the axial ligands in parallel planes.[39a]

In the present study we have attempted to quantify the electronic effect(s) of *ortho*-phenyl substitution on the spectroscopic, redox, and ligand binding properties of tetraphenylporphyrins and their Fe(III) complexes. Because of the potential interaction of the steric[39a,b] and electronic effects of *ortho* substituents in symmetrical tetrakis(*ortho*-X-phenyl)porphyrins and their metal complexes, we have utilized TPP derivatives having only one *ortho*-substituted phenyl ring (either 2- or 2,6-substituted) and *N*-methylimidazole as the axial ligands, so that ruffling of the porphyrinate ring should not be required. We have used a large range of *ortho* substituents in the hope of obtaining a clear set of trends. For reason of more facile separation of the various porphyrins synthesized by column chromatography, the other three phenyl rings are *para*-methoxy (p-OCH$_3$) substituted, as shown in Figure 1. We will show below that the properties of the free-base porphyrins and their low-spin iron(III) analogues are mainly influenced by the size of the substituent.

Experimental Section

Substituted benzaldehydes (*o*-F, *o*-Cl, *o*-Br, *o*-CF$_3$, 2,6-F$_2$, 2,6-Cl$_2$, p-OCH$_3$) and *ortho*-iodobenzyl alcohol (Aldrich) were used as received. Pyrrole (Aldrich) was distilled before use. Trifluoroacetic acid (Aldrich) (100 mL) and trifluoroacetic anhydride (Aldrich) (1 mL) were refluxed under argon for several hours to remove traces of water and then distilled and stored under argon. All solvents used for synthesis and chromatography were obtained from Fisher (Optima) and used as received for porphyrin synthesis. Dimethylformamide (Burdick and Jackson), which was used for electrochemical studies, was used as received and stored under argon. Spectroscopic grade chloroform (Aldrich) was used for measurement of equilibrium constants; a fresh bottle was used for each day's experiments. *N*-Methylimidazole (Aldrich) was distilled prior to use.

The *ortho*-iodobenzaldehyde was prepared from *ortho*-iodobenzyl alcohol by oxidation with pyridinium chlorochromate[40] (Aldrich). 2,6-Dibromobenzaldehyde was prepared as reported elsewhere.[36,41,42] The synthesis and purification of the series of free-base porphyrins used in this study were carried out as reported previously[20a,43] or by slight modification of the Lindsey method utilizing dry dichloromethane as solvent and trifluoroacetic acid as catalyst. For the latter method, the total concentrations of pyrrole and benzaldehydes (0.75 anisaldehyde, 0.25 (*o*-X or 2,6-X$_2$)benzaldehyde) were each 1×10^{-2} M, with optimum yields occurring at reaction volumes of 100 mL.[43] Crude purification to remove tar was accomplished by column chromatography with Florisil (Baker) as the stationary phase and dichloromethane as the mobile phase. Further purification to remove remaining tar and chlorins, and to separate porphyrin isomers, was accomplished by column chromatography using silica gel (WR Grace, 60−200 mesh) as the stationary phase and toluene as the mobile phase. The desired isomer in each case was the fifth band that was eluted from the column. Isomer structure and purity was confirmed by NMR spectroscopy. 1-D ^{1}H NMR spectra of the free-base porphyrins were obtained at room temperature on a Bruker WM-250 spectrometer; 2-D spectra and 1-D spectra at low temperatures were obtained on a Bruker AM-500 NMR spectrometer. NMR data for the free-base porphyrins are summarized in Table 1. UV−visible spectra of all of the complexes were identical: Soret, 422 nm; IV−I bands, 516−518, 552−554, 592−594, and 648−650 nm. These values are slightly shifted from those of (TPP)H$_2$: 418, 516, 550, 590, and 648 nm.

Iron was inserted into the series of free-base porphyrins by adding an 8-fold molar ratio of anhydrous FeCl$_2$ (Alfa) dissolved in the minimum volume of 3:1 CHCl$_3$/MeOH to a solution of ~10 mg of the phenyl *ortho*-substituted porphyrin in 100 mL of CHCl$_3$.[44] After being refluxed overnight, the reaction mixture was washed repeatedly with water to extract any unreacted iron salts until the aqueous phase was clear. The organic phase was evaporated to dryness and heated (60 °C) under vacuum for 30 min. The resulting Fe(III) porphyrinate was then redissolved in 25 mL of dry CH$_2$Cl$_2$, HCl gas was bubbled through for 1 min, and the sample was then evaporated to dryness and dried at 60 °C under vacuum for 30 min. Samples were stored under argon until use.

Reduction potentials of the high- and low-spin Fe(III) porphyrins were measured by cyclic voltammetric techniques utilizing a three-electrode system with a Princeton Applied Research (PAR) model 173 potentiostat/galvanostat and a PAR model 276 computer interface module. The working electrode was a platinum disk (BAS) that was polished on 0.05 μm alumina, rinsed repeatedly with distilled water and reagent grade methanol, sonicated for 5 min, rinsed again with methanol, and air-dried before use. A platinum wire served as the counter electrode. The reference electrode consisted of a silver wire and silver nitrate (0.01 M) with 0.10 M tetrabutylammonium perchlorate (TBAP) in dimethylformamide (DMF) and was prepared freshly for each experiment. DMF solutions for electrochemical investigations were approximately 2.5×10^{-4} M in metalloporphyrinate and 0.10 M in TBAP electrolyte. For each run, 20 mL of the 0.10 M TBAP solution was placed in the water-jacketed electrochemical cell (Princeton Applied Research) maintained at 25 ± 0.1 °C and deaerated prior to the voltammetric run by purging with argon gas presaturated with DMF and was maintained under an argon atmosphere. The cyclic voltammogram of this blank was first recorded, and then the solid chloroiron(III) porphyrinate was added, dissolved, and again purged with argon gas. For each Fe(III) porphyrinate, the Fe(III/II) CV wave was recorded in the absence of added ligand and in the presence of 0.05 and 0.1 M

Table 1. ^{1}H NMR Chemical Shifts[a] of Free-Base Porphyrins, (o-X)(p-OCH$_3$)$_3$TPPH$_2$ or (2,6-X$_2$)(p-OCH$_3$)$_3$TPPH$_2$

X	σ_p[b]	H$_a$[c]	H$_b$[c]	H$_{c,d}$[c]	H$_{o'}$[c]	H$_{m'}$[c]	H$_{p'}$[c]	H$_{m''}$[c]	H$_o$(OCH$_3$)[c]	H$_m$(OCH$_3$)[c]	−OCH$_3$[c]	N−H[c]
F	0.06	8.82 (4.7 Hz)	8.91 (4.7 Hz)	8.89	8.15 (7.8 Hz)	7.59 (7.7 Hz)	7.83 (8.7, 7.5 Hz)	7.55 (8.7 Hz)	8.13 (m)	7.30 (7.6 Hz)	4.08 (2:1)	−2.79
Cl	0.23	8.71 (4.8 Hz)	8.90 (4.8 Hz)	8.89	8.13 (7.4, 1.5 Hz)	7.69 (7.3, 1.3 Hz)	7.78 (8.0, 1.4 Hz)	7.85 (8.6, 1.1 Hz)	8.16 (m, b) (8.5 Hz), 8.14 (d, s), 8.10 (m, b) (8.5 Hz)	7.30 (8.6 Hz)	4.07 (2:1)	−2.75
Br	0.23	8.70 (4.7 Hz)	8.90 (4.7 Hz)	8.89	8.18 (7.3, 1.8 Hz)	7.73 (7.3, 1.8 Hz)	7.70 (7.7, 1.8 Hz)	8.04 (7.6, 1.8 Hz)	8.16 (b) (8.2 Hz), 8.13 (d, s) (7.1 Hz), 8.10 (b) (7.8 Hz)	7.31 (8.5 Hz)	4.086 (1), 4.082 (2)	−2.76
I	0.18	8.66 (4.6 Hz)	8.90 (4.6 Hz)	8.89	8.20 (7.3, 1.5 Hz)	7.77 (7.5, 1.3 Hz)	7.52 (7.8, 1.2 Hz)	8.32 (8.1, 1.5 Hz)	8.17 (b) (7.4 Hz), 8.13 (d, s) (8.3 Hz), 8.08 (b) (7.7 Hz)	7.31 (8.2 Hz)	4.08	−2.74
CF$_3$	0.54	8.55 (4.8 Hz)	8.84 (4.8 Hz)	8.86	8.16 (8.1 Hz)	7.92 (7.8 Hz)	7.83 (6.9 Hz)	8.05 (8.1 Hz)	8.19 (b) (8.1 Hz), 8.11 (d, s) (8.1 Hz), 8.06 (b) (8.1 Hz)	7.28 (8.1 Hz)	4.091 (2), 4.097 (1)	−2.79
2,6-F$_2$	0.12[d]	8.80 (4.7 Hz)	8.89 (4.7 Hz)	8.85		7.76 (7.3 Hz)	7.36 (7.3 Hz)	7.76 (7.3 Hz)	8.10 (d, s) (8.1 Hz)	7.25 (8.1 Hz)	4.09	−2.75
2,6-Cl$_2$	0.46[d]	8.63 (4.6 Hz)	8.87 (4.6 Hz)	8.83		7.78 (8.0 Hz)	7.66 (8.0 Hz)	7.78 (8.0 Hz)	8.11 (d, s) (8.5 Hz), 8.09 (d, s) (8.5 Hz)	7.26 (8.5 Hz)	4.05	−2.67
2,6-Br$_2$	0.46[d]	8.63 (4.8 Hz)	8.89 (4.8 Hz)	8.84		8.10 (8.3 Hz)	7.52 (8.3 Hz)	8.10 (8.3 Hz)	8.13 (d, s) (8.4 Hz), 8.02 (d, s) (8.4 Hz)	7.26 (8.4 Hz)	4.08	−2.63

[a] Solvent = CDCl$_3$, ambient temperature. [b] Hammett σ_{para} constants. [c] Chemical shifts (ppm) referenced to CHCl$_3$ (7.24 ppm); in parentheses, J coupling constant. Chemical shifts ±0.02 ppm; coupling constants ±0.3 Hz. [d] For two substituents, $2\sigma_p$.

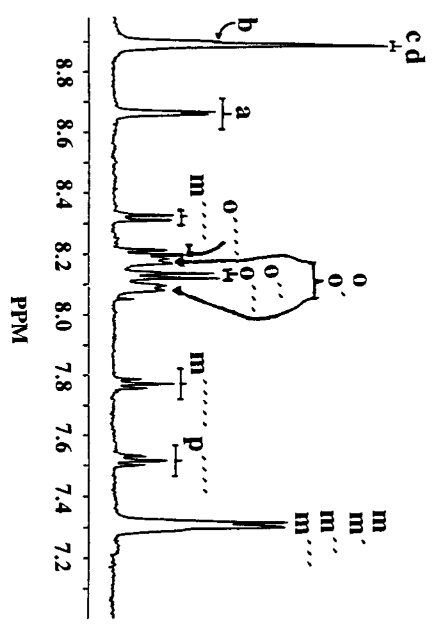

Figure 2. Aromatic region of the ^{1}H NMR spectrum of (o-I)(p-OCH$_3$)$_3$(TPP)H$_2$ in CD$_2$Cl$_2$ at 20 °C. Resonance assignments with respect to the structure of Figure 1 are marked.

N-methylimidazole. Following measurement of the Fe(III)/Fe(II) wave without and with ligand, ferrocene (5.2×10^{-4} M) was added to the solution and the Fe(III)/Fe(II) and ferrocene waves were rerecorded to provide an internal standard. Half-wave potentials were calculated from the midpoint of the cathodic and anodic peak potentials, $E_{p,c}$ and $E_{p,a}$, respectively.

UV−visible spectroscopic measurements were carried out utilizing a Hewlett-Packard 8451A spectrophotometer equipped with a water-jacketed cuvette attached to a circulating constant-temperature bath, set such that the temperature in the cell was 25.0 ± 0.2 °C. Measurement of equilibrium constants was carried out as described previously.[9] The wavelengths used for calculation of equilibrium constants were the visible λ_{max} values of the starting material, PFeCl (514 and 698 nm), and the product, [PFe(NMeIm)$_2$]$^+$Cl$^-$ (552 and 580 nm). One-dimensional proton NMR spectra of the paramagnetic Fe(III) complexes were obtained at 33 °C on a General Electric GN-300, a Bruker AM-250, or a Bruker DRX-300 spectrometer.

Results and Discussion

In this work we have carried out four different sets of measurements on mono(2- or 2,6-halogen phenyl) derivatives of tetraphenylporphyrin or their iron complexes. These four sets of measurements are (1) the ^{1}H NMR shifts of the free-base porphyrins, (2) the equilibrium constants, β_2^{III}, for binding two *N*-methylimidazole ligands to the (TPP)FeCl derivatives in chloroform solution, (3) the equilibrium constants, β_2^{III} and β_2^{II}, for binding two *N*-methylimidazole ligands to the (TPP)-FeOClO$_3$ derivatives or their Fe(II) counterparts, respectively, in dimethylformamide solution, and (4) the ^{1}H NMR shifts of the pyrrole-H protons of the unsymmetrically substituted [(TPP)-Fe(NMeIm)$_2$]$^+$ complexes in CDCl$_3$. In each case, *ortho*-halogen and -CF$_3$ substituents are found to behave differently than would be expected for the same substituent in the *meta* or *para* position, and in general the behavior is profoundly different and appears to correlate best with substituent size. While each set of measurements could have been presented as a separate publication, we have chosen to present all four sets in a single paper in order to avoid duplication of the discussion. The results of each set of measurements will be presented and discussed in separate sections, and then a final summary and discussion of the four sets of measurements will be presented.

Proton NMR Studies of the Metal-Free *Ortho*-Substituted TPPs. Resonance assignments, as shown in Figure 2 for (o-I)(p-OCH$_3$)$_3$(TPP)H$_2$, were accomplished by 2-D ^{1}H NMR (COSY) techniques (not shown). It should be noted that the chemical shifts of the o-H and, to a lesser extent, the m-H of the (p-OCH$_3$)-substituted phenyl rings of the unsymmetrically substituted porphyrin free base are sensitive to the mono-*o*-iodo substituent (Figure 2) and that rotation of the (p-OCH$_3$)-substituted phenyl rings is fairly slow on the NMR time scale at 500 MHz and ambient temperatures, as observed previously.[21a] The separate, broadened *o*- and *o′*-H resonances of the phenyl rings on either side of the *ortho*-iodophenyl group of the compound shown in Figure 2 are spread further apart for the *o*-CF$_3$ derivative and are more closely spaced for the smaller substituents, suggesting *either* that the solvation of the porphyrin is different on the two sides of the porphyrin plane as the substituent becomes larger *or* that a single bulky *ortho* substituent distorts its *meso*-carbon–phenyl ring bond out of the porphyrin plane by an increasing amount as the size of the single *ortho* substituent increases. It is well-known that phenyl ring rotation requires severe distortion of the porphyrin ring,[21b,c,25,45] and such distortion would be expected to be much more difficult if one phenyl ring has one or both *ortho* positions substituted by atoms larger than a proton. From the line broadening of the *o,o′*-H in Figure 2, a rate of phenyl rotation at room temperature of $\sim$3–5 s^{-1} can be estimated. (To our knowledge, this is the first example of estimation of the rate of phenyl rotation in a free-base porphyrin.) This is as slow or slower than the rates of phenyl rotation of a series of (tetrakis(*p*-phenyl-substituted)porphyrinato)metal complexes (excluding p-NEt$_2$), where the metal center is (InCl)$^{2+}$ ($k_{298} = 3-7$ s^{-1}),[21c] (TiO)$^{2+}$ ($k_{298} = 8-32$ s^{-1}),[21c] and (GaCl)$^{2+}$ ($k_{298} = 62-336$ s^{-1}),[21b] but faster than the rates of phenyl rotation of a series (RuL(CO))$^{2+}$ complexes ($k_{298} = 0.15-0.24$ s^{-1}).[21c] The rates of phenyl rotation reported for these particular metal TPP derivatives correlate fairly well with the expected ability of the porphyrin core to distort from planarity;[21c] the Ru(II) 6-coordinate porphyrinates are believed to be most rigid,[21b,c] and the porphyrinates of the small Ga(III) most flexible.[21b] The free-base porphyrins of this study should be considerably less rigid than any metalloporphyrin, and hence the slow rate of phenyl rotation of the two p-OCH$_3$-substituted phenyl rings on either side of the *o*-iodophenyl ring (Figure 2) testifies to significant loss of flexibility of the porphyrin core in this mono-*ortho*-substituted derivative of TPPH$_2$.

The pattern of pyrrole-H resonances observed for the free-base porphyrins of this study, a pair of AB doublets and a singlet, all in the 8.5–8.9 ppm region, is that expected for a free-base tetraphenylporphyrin having one unique substituted phenyl.[20a] Furthermore, in each case, one of the AB doublets has nearly the same chemical shift as the singlet, while the other has a smaller chemical shift, as shown in Figure 2. This is the pattern that has been observed previously for unsymmetrically *meta*- or *para*-substituted TPPH$_2$s in which one phenyl ring carries a substituent that is electron-withdrawing relative to the other three,[20a] although as will be discussed below, these *ortho*-halogen or -CF$_3$ substituents do not otherwise behave as though they are electron-withdrawing. This pyrrole-H resonance pattern identifies the doublet at higher shielding (smaller chemical shift) as being due to the protons nearest the unique phenyl, H$_a$, while the doublet at lower shielding is due to H$_b$ and the singlet to H$_c$ and H$_d$.[20a] The similarity in chemical shift of H$_b$, H$_c$, and H$_d$ for each of the free-base porphyrins of this study indicates that the effect of the single *ortho* substituent or the 2,6-substituents on one phenyl ring is felt only in very close proximity to the unique substituent, and thus, its effects are quite localized.

As summarized in Table 1, the H$_a$ pyrrole resonance shows a progressive shift to higher shielding as *o*-F is replaced by Cl, Br, I, and CF$_3$ or as 2,6-F$_2$ is replaced by 2,6-Cl$_2$ and 2,6-Br$_2$, while the H$_b$, H$_c$, and H$_d$ resonances do not vary nearly as much as the heavier halogens and CF$_3$ are substituted for fluorine. The difference in shift of the two AB doublets, $\delta(\mathrm{H_b}) - \delta(\mathrm{H_a})$, is probably a better measure of the relative electronic effects of the *ortho*-halogen or -CF$_3$ as compared to *para*-methoxy substituents. This chemical shift difference increases in the order $\mathrm{F_2} = \mathrm{F} < \mathrm{Cl} < \mathrm{Br} < \mathrm{I} = \mathrm{Cl_2} < \mathrm{Br_2} < \mathrm{CF_3}$, which, at least among the singly *ortho*-substituted compounds, is approximately in the order of the through-bond electron-withdrawing tendencies of the substituents if they were in the *para* position of the unique phenyl ring[32] *and also* in the order of increasing size of a single substituent. The trends of the 2,6-disubstituted free-base porphyrins of this series are in the same direction, but are not additive, based on the shifts observed for the mono-*ortho*-substituted series. This suggests that substituent *size* is more important than through-bond electron-withdrawing ability. Recent investigation of the *o*-CH$_3$ analogue of the free-base porphyrins of this study shows the same AB doublet structure, with H$_a$ shifted to higher shielding, and it falls very close to *o*-Cl in the above series of chemical shift differences of the two AB doublets.[46] This result strongly supports the importance of substituent *size*, since CH$_3$ is an electron-*donating* substituent when in the *para* position, though slightly less electron donating than a methoxy group, hence suggesting it should exhibit a much smaller separation of the AB doublets than has been observed for any of the *ortho*-halogen derivatives of this study, if through-bond electronic effects were most important.

As will be discussed elsewhere,[46] the pyrrole-H shifts seem to follow the same trend as discussed by Ghosh.[54] Phenyl rings bearing electron-withdrawing substituents seem to behave as local dipoles with the local dipole moment being directed away from the porphyrin ring in the case of *meta*- and *para*-substituted tetraphenylporphyrins and toward the center of the porphyrin macrocycle in the case of *ortho*-substituted TPPs. Using this rationale, a phenyl ring bearing an electron-withdrawing substituent will increase the electron density (or π density) at the pyrrole H$_a$ positions due to the local dipole moment, thereby shifting the pyrrole protons H$_a$ to higher shielding as the electron-withdrawing power of the substituent increases.

The chemical shifts of NH protons of porphyrin free-bases are expected to be affected both by the σ-donor properties (basicity) of the porphyrin nitrogens and the strength of the ring current that gives rise to the large shift of these protons to higher shielding. At very low temperatures (−90 °C) the ^{1}H NMR spectra of the NH protons of the unsymmetrically substituted porphyrin free bases show two resonances due to the two chemical environments of the NH protons (spectra not shown), as expected, on the basis of the structure shown in Figure 1 and the fact that the protons are expected to be on opposite rather than adjacent nitrogens.[22b,23,47] For singly *ortho*-substituted derivatives at −90 °C in CD$_2$Cl$_2$, the separation of the two resonances increases in the order $\mathrm{F} < \mathrm{Cl} < \mathrm{Br} < \mathrm{I}$ (6, 17, 23, and 35 Hz at 500 MHz, respectively), and the chemical shifts of the resonances at lower shielding are more strongly affected by the halogen than those at higher shielding. Thus, it is likely that the NH resonance at lower shielding is that due to the proton bound to the nitrogen of one of the pyrrole rings adjacent to the phenyl ring bearing the unique substituent.[20a] Its progressive shift to lower shielding is partially consistent with the electron-withdrawing characteristics of the halogen if it were a *para* substituent ($\mathrm{F} < \mathrm{I} < \mathrm{Cl} = \mathrm{Br}$) but is more consistent with the increase in size of the halogen and, hence, potential direct electron density transfer between the halogen and the π system of the porphyrin (see below). An increase in

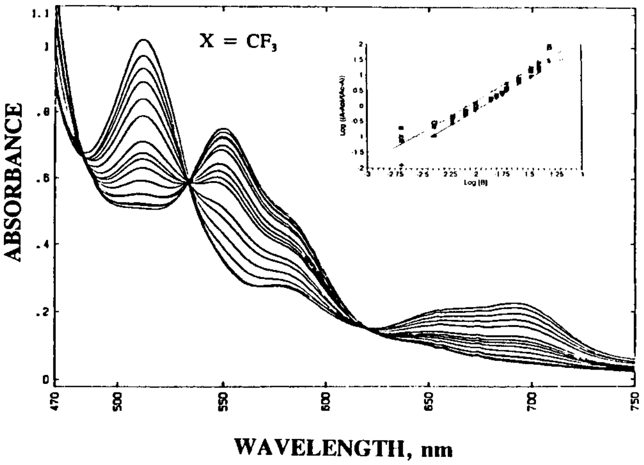

Figure 3. Progressive change in the UV–vis spectra of $[(o\text{-CF}_3)(p\text{-OCH}_3)_3(\text{TPP})\text{FeCl}]$ as the concentration of NMeIm is increased. Solvent = $CHCl_3$; temperature = 25.0 °C. Insert: Plot of eq 9 for the spectrophotometric data, showing the intercept $(\log(\beta_2^{III}))$.

π electron density in the region of the unique substituent *may* be accompanied by a decrease in σ donor strength at the nitrogen or, more likely, a decrease in ring current at the N–H position. The increase in π density would also agree with the phenyl ring bearing the substituent behaving as a local dipole. Either would cause a shift of that NH resonance to lower shielding. The lower sensitivity of the NH resonance at higher shielding to the nature of the halogen substituent suggests that the effect of the *ortho* substituents is attenuated significantly as the distance from the unique phenyl increases.

Spectrophotometric Determination of Equilibrium Constants, β_2^{III}, for Addition of *N*-Methylimidazole to the Chloroiron(III) Complexes Having *ortho*-Halogen Substituents (Solvent = Chloroform). Although the addition of axial ligands, L, to (TPP)FeCl might be expected to occur in a stepwise fashion,

$$(\text{TPP})\text{FeCl} + \text{L} \rightleftarrows (\text{TPP})\text{Fe(L)(Cl)} \quad K_1^{III} \tag{6}$$

$$(\text{TPP})\text{Fe(L)(Cl)} + \text{L} \rightleftarrows [(\text{TPP})\text{Fe(L)}_2]^+\text{Cl}^- \quad K_2^{III} \tag{7}$$

it has previously been shown that, for L = NMeIm in low-dielectric solvents such as chloroform and methylene chloride, the intermediate, 1:1 complex is seldom detected, and thus the overall equation

$$(\text{TPP})\text{FeCl} + 2\text{L} \rightleftarrows [(\text{TPP})\text{Fe(L)}_2]^+\text{Cl}^- \quad \beta_2^{III} = K_1^{III}K_2^{III} \tag{8}$$

best describes the observed reaction.[9] In chloroform solution the product of the reaction, $[(\text{TPP})\text{Fe(L)}_2]^+\text{Cl}^-$ (eqs 7 and 8), behaves as one unit—that is, the chloride ion forms an associated ion pair with $[(\text{TPP})\text{Fe(L)}_2]^+$.[9] The same is found in the present cases of the $[(o\text{-X})(p\text{-OCH}_3)_3(\text{TPP})\text{Fe(NMeIm)}_2]^+\text{Cl}^-$ complexes, as is discussed further below.

In Figure 3 is shown a typical example of the electronic spectral changes that occur when *N*-methylimidazole is added in a stepwise fashion to one of the *ortho*-substituted (TPP)FeCl derivatives of this study, in this case $(o\text{-CF}_3)(p\text{-OCH}_3)_3$(TPP)FeCl. Equilibrium constants were determined from the least-squares intercepts of the equation[9]

$$\log\{(A_i - A_0)/(A_c - A_i)\} = \log(\beta_2^{III}) + n \log[\text{NMeIm}]_i \tag{9}$$

Table 2. Equilibrium Constants, β_2^{III}, for Addition of *N*-Methylimidazole to the Series of $[(o\text{-X})(p\text{-OCH}_3)_3(\text{TPP})\text{FeCl}]$ and $[(2,6\text{-X}_2)(p\text{-OCH}_3)_3(\text{TPP})\text{FeCl}]$ in Chloroform and Derived Hammett σ Constants for the *Ortho* Substituents

X	β_2^{III}, M^{-2}	$\log(\beta_2^{III})$	$\Sigma\sigma$(calc)	$\sigma_{o\text{-X}}$(calc)
o-F	3 310	3.52	−0.75	−0.05
o-Cl	4 370	3.64	−1.45	−0.65
o-Br	5 010	3.70	−1.87	−1.07
o-I	5 500	3.74	−2.10	−1.30
o-CF_3	6 110	3.79	−2.42	−1.62
2,6-F_2	8 320	3.92	−3.15	−2.35
2,6-Cl_2	10 500	4.02	−3.90	−3.10
2,6-Br_2	10 650	4.03	−3.90	−3.10
p-OCH_3	3 600[15]	3.56[15]	−1.07[32]	−0.268[32]
4 *p*-H	1 500[15]	3.18[15]	0.00[32]	0.00[32]

where A_0 and A_c are the absorbances of the starting material to which no ligand and a large excess of ligand (0.1 M in the case of NMeIm) has been added, respectively, A_i is the absorbance of each solution to which varying concentrations of *N*-methylimidazole, $[\text{NMeIm}]_i$, have been added, and *n*, the number of ligands added, is allowed to be a variable. Absorbance values at each of four wavelengths (512, 550, 574, and 690 nm) were utilized to calculate the Beer's law function on the left side of eq 9. As was the case in the previous study,[9] the constants are not so large as to require correction of $[\text{NMeIm}]_i$ for the amount of ligand utilized in formation of the complex. The values of $\log(\beta_2^{III})$ obtained by this procedure are listed in Table 2. As observed previously,[9] at low concentrations of the ligand, the values of $\log\{(A_i - A_0)/(A_c - A_i)\}$ at the wavelength maxima of the starting material fell below the best-fit lines of slope 2 (indicating two ligands added), yielding an approximate slope of 1 (indicating one ligand added). Derived $\log(K_1^{III})$ values obtained from the intercept of this line of slope 1 range from 10 to 75 and indicate order-of-magnitude values for the stabilities of the 1:1 complexes, as discussed previously.[9a]

As is evident from the results presented in Table 2, all but one of the (*o*-X)- or $(2,6\text{-X}_2)(p\text{-OCH}_3)_3$(TPP)FeCl complexes of this study have equilibrium constants for addition of two *N*-methylimidazole ligands that are larger than those for the symmetrically substituted parent complex, $[(p\text{-OCH}_3)_4(\text{TPP})\text{FeCl}]$; only the mono-*o*-F complex has a slightly smaller equilibrium constant. As we have shown previously,[9] electron-donating substituents on the phenyl rings of the porphyrinate moiety favor the formation of the complex (eq 8); i.e., the Hammett ρ value is negative. As discussed in the Introduction, we must view the negative $\rho = -0.39$,[9] eq 1, as arising from the larger sensitivity of the reaction to the effect of electron-donating and -withdrawing substituents on the energetics of breaking the $(\text{TPP})\text{Fe}^+\text{Cl}^-$ bond to produce separated ions than on the energetics of stabilizing the iron(III) center of the product, which carries a formal positive charge. For the reaction of eq 8, the equilibrium constants increase in the order *o*-F < *p*-OCH_3 < *o*-Cl < *o*-Br < *o*-I < 2,6-F_2 < *o*-CF_3 < 2,6-Cl_2 ~ 2,6-Br_2 (Table 2). Thus, all *ortho*-halogen and -CF_3 substituted and disubstituted complexes of this study except *o*-F appear to be more strongly electron-donating, if through-bond transmission of the substituent effect is considered, than is the fourth *para*-OCH_3 substituent, and *ortho*-F is only slightly less electron-donating than this substituent. Therefore, *ortho*-halogens and the CF_3 group have considerably different through-bond electronic effects (if that is what is being measured) than do the same substituents in *para* positions, for which Hammett σ values have been reported: +0.06 (*p*-F), +0.18 (*p*-I), +0.23 (*p*-Cl, *p*-Br), and +0.54 (*p*-CF_3),[32] as compared to −0.27 (*p*-OCH_3). Rather than Hammett σ_p values, the above order correlates fairly

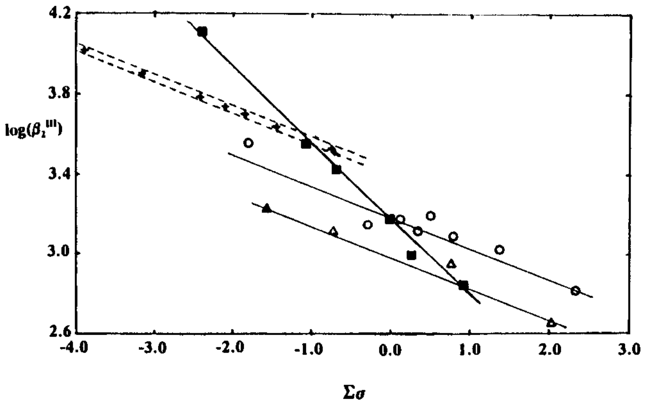

Figure 4. Plot of log(β_2^{III}) vs $\sum\sigma$ for reaction 6 for symmetrical[9a] (filled squares) and unsymmetrical derivatives of (TPP)FeCl[9b] (open circles and triangles). The apparent $\sum\sigma$ values for the complexes of this study have been estimated by constructing bracketing dotted lines parallel to those for the formation of the complexes $[(p\text{-X})_n(p\text{-Y})_{4-n}(\text{TPP})\text{Fe}(\text{NMeIm})_2]^+$, where X = Cl (triangles) and H (circles) on either side of the position expected for the *p*-OCH_3 substituent, and then marking the values of log(β_2^{III}) for the complexes of this study at the positions where they intersect the midpoint of these bracketing lines. From these values of $\sum\sigma$, the apparent σ constants of the *ortho* substituents were calculated (last column of Table 2).

well with the increasing total "size" of the substituent(s), a conclusion similar to that reached for the spread of the AB doublets of the free-base porphyrins, Table 1.

If one wishes to quantitate the effect of *ortho* substituents in terms of apparent through-bond electron-donating character of the substituent, the results obtained herein, Table 2, can be compared to those obtained previously[9b] for unsymmetrically substituted (TPP)FeCl derivatives in which only *meta*- or *para*-phenyl substituents were present. In the previous study, as mentioned in the Introduction and summarized in Figure 4, it was found that unsymmetrically substituted derivatives behave differently than symmetrically, tetra-*para*-substituted derivatives $(p\text{-X})_4(\text{TPP})\text{FeCl}$. The three solid lines shown in Figure 4 summarize the previously observed correlation of equilibrium constant data with the sum of the Hammett σ constants ($\sum\sigma$) for the binding of *N*-methylimidazole to symmetrically $(\text{X})_4(\text{TPP})\text{FeCl}$ and unsymmetrically $(\text{X})_x(\text{Y})_y(\text{TPP})\text{FeCl}$ complexes in which the substituents were located on either *meta* or *para* positions of the phenyl rings.[9b] As was pointed out in that work,[9b] tetra-*meta*-substituted and unsymmetrically substituted complexes show a weaker dependence of the binding constant on the electron-donating or -withdrawing properties of the substituents than do tetra-*para*-substituted complexes. The log(β_2^{III}) values for $(m\text{-X})_4(\text{TPP})\text{FeCl}$ and $(p\text{-X})_x(p\text{-Y})_y(\text{TPP})\text{FeCl}$ reactions with NMeIm give rise to parallel lines of slope −0.18,[9b] with the line for the unsymmetrical porphyrin series passing through the point for the particular tetra-*para*-substituted "parent" complex ($\rho = -0.39^{9a}$). In the present case, $[(p\text{-OCH}_3)_4(\text{TPP})\text{Fe}(\text{NMeIm})_2]^+\text{Cl}^-$ is the parent complex, so we have drawn two dotted lines of slope −0.18 that bracket that point, which should then represent the expected behavior of the series of $[(o\text{-X})(p\text{-OCH}_3)_3(\text{TPP})\text{Fe}(\text{NMeIm})_2]^+\text{Cl}^-$ complexes of this study, if the inductive effect of the *ortho* substituent were the only contribution to the observed values of β_2^{III}. We have then placed crosses between these lines at the positions that correspond to their measured values of log(β_2^{III}) (Table 2). The values of $\sum\sigma$ for these complexes that are obtained in this manner are then listed in the next-to-last column, and the derived values of the Hammett σ constants for these *ortho*-halogen substituents are listed in the last column of Table 2. As is apparent from the negative signs, when analyzed in terms of their apparent inductive effect, *all ortho*-halogens and the -CF_3 group appear to be electron-donating when placed on a phenyl ring of $(\text{TPP})\text{Fe}^{III}$, and they appear to increase in their electron-donating tendency in the order *o*-F ≪ *o*-Cl < *o*-Br < *o*-I < 2,6-F_2 < *o*-CF_3 < 2,6-Cl_2 = 2,6-Br_2. The apparent Hammett σ constants derived in this manner for the three heavy *ortho*-halogens and the -CF_3 group are larger than for any of the non-H-bonding *meta* and *para* substituents investigated thus far in this laboratory,[9,48,49] and thus, the effects of *ortho* substituents on Fe(III) tetraphenylporphyrinates are profound, in contrast to the conclusions of Ghosh for free-base porphyrins.[54] Furthermore, two *ortho* substituents on a given phenyl ring appear to be far more strongly electron-donating than simply double the effect of one (2,6-Cl_2, $\sigma_o = -3.1$; 2-Cl, $\sigma_o = -0.65$). The magnitudes of these apparent σ_o values are too large to be explained in terms of through-bond inductive effects, and their signs are opposite those expected when compared to σ_p values for the same substituents.[32] We will return to alternative explanations of these data after considering the trends in log(β_2^{III}) and log(β_2^{II}) obtained for some of these complexes by electrochemical measurements in DMF.

Electrochemical Determination of the Equilibrium Constants β_2^{III} and β_2^{II} for Addition of *N*-Methylimidazole to the (Perchlorato)iron(III) Complexes Having *ortho*-Halogen or -CF_3 Substituents (Solvent = Dimethylformamide). As has been shown recently,[11] the equilibrium constants for formation of the bis(*N*-methylimidazole) complexes of iron porphyrinates can be measured in dimethylformamide from the ligand concentration dependence of the $E_{1/2}$ values for the $\text{Fe}^{III}/\text{Fe}^{II}$ and $\text{Fe}^{II}/\text{Fe}^{I}$ couples. We have used these same methods to study the unsymmetrically substituted iron porphyrinates in dimethylformamide solution:

$$\text{PFe(DMF)} + 2\text{L} \rightleftarrows \text{PFeL}_2 + \text{DMF} \quad \beta_2^{II} \tag{10}$$

$$[\text{PFe(DMF)}_2]^+\text{ClO}_4^- + 2\text{L} \rightleftarrows [\text{PFeL}_2]^+\text{ClO}_4^- + 2\text{DMF} \quad \beta_2^{III} \tag{11}$$

Here, β_2^{II} is the equilibrium constant for binding two ligands to the Fe(II) complex, while β_2^{III} is, as in the above eqs 8 and 9 and discussion, that for binding two ligands to the Fe(III) complex. If only one step of complex formation can be detected for each oxidation state, the reduction potential, measured as a function of the concentration of the ligand added to the solution, is given by

$$(E_{1/2})_c = (E_{1/2})_s - (2.303RT/nF)\log(\beta_p^{ox}/\beta_q^{red}) - (2.303RT/nF)\log[\text{L}]^{p-q} \tag{12}$$

where $(E_{1/2})_c$ is the reduction potential of the iron porphyrinate in the presence of a particular concentration of axial ligand, $(E_{1/2})_s$ is the reduction potential of the ligand-free iron porphyrinate starting material, n is the number of electrons involved in the reduction reaction ($n = 1$ in this case), F is the Faraday constant, β_p^{ox} and β_q^{red} are the equilibrium constants for binding p ligands to the oxidized state and q ligands to the reduced state of the complex, respectively, and [L] is the equilibrium concentration of axial ligand present upon each addition. If indeed there is only one detectable step of complex formation, in this case the bis-ligand complex, then p and q can only be 0 or 2 over the course of the titration, and as we find, β_2^{II} is smaller than β_2^{III} in all cases, a plot of $(E_{1/2})_c$ vs log [L] will be a curve that has as its steepest slope −2(0.0591) V at 25 °C.[11] A more

Table 3. log(β_2^{III}), log(β_2^{II}), and $E_{1/2}$ Values for [(*o*-X)- or (2,6-X_2)(*p*-OCH_3)$_3$(TPP)Fe(NMeIm)$_2$]$^{+/0}$ Complexes

X	log(β_2^{III})	log(β_2^{II})	$E_{1/2}$(DMF) (V vs SCE)	$E_{1/2}$(NMeIm) (V vs SCE)	ref
o-F	7.2 ± 0.2	6.3 ± 0.4	−0.068	−0.111	TW[a]
o-CF_3	6.6 ± 0.1	5.7 ± 0.1	−0.071	−0.114	TW[a]
2,6-Cl_2	6.3 ± 0.1	5.7 ± 0.1	−0.066	−0.096	TW[a]
4 *p*-OCH_3	6.5 ± 0.1	5.5 ± 0.1	−0.079	−0.135	TW[a]
4 *p*-H	7.2 ± 0.3	6.5 ± 0.2	−0.047	−0.089	11
4 2,6-F_2	6.2 ± 0.5	6.9 ± 0.5	0.033	0.093	11
4 2,6-Cl_2	7.1 ± 0.2	7.4 ± 0.2	−0.013	0.003	11
4 2,6-Br_2	7.7 ± 0.6	7.7 ± 0.5	−0.040	−0.040	11

[a] TW = this work.

complete equation is required if the values of K_1 and K_2 are similar for one or both oxidation states.[11] The data were analyzed both according to the simple eq 12 and the more complete treatment, for which a computer program that fits the dependence of $(E_{1/2})_c$ on log [L] to the stepwise constants for both oxidation states[11] was also used. The best values of log(β_2^{II}) and log(β_2^{III}) obtained are summarized in Table 3.

In dimethylformamide, Fe(III) porphyrinates are fully complexed by the solvent (high-spin bis-DMF complex,[33,55] eq 11), while Fe(II) porphyrinates form stable high-spin mono-DMF complexes,[55] eq 10. Thus the binding constants measured, β_2^{III} and β_2^{II}, are ligand replacement constants. As shown in Table 3, the equilibrium constants for both Fe(III) and Fe(II) are largest for the single *o*-F-phenyl-containing porphyrinate, smaller for the single *o*-CF_3-phenyl-containing porphyrinate, and smallest for the single 2,6-Cl_2-phenyl-containing porphyrinate. This order is close to opposite that expected based upon the electron-withdrawing properties of *para* substituents ($\sigma_p = 0.06$ (F), 0.23 × 2 (2 Cl), 0.54 (CF_3)), and the symmetrical complex, (*p*-OCH_3)$_4$(TPP)FeCl, has a binding constant very similar to that of the mono-2,6-Cl_2-phenyl derivative. From the data of Table 2 we have seen that for the 2,6-disubstituted phenyl complexes the effect is more than additive, so it is perhaps not surprising that the 2,6-Cl_2 derivative has a smaller binding constant than the *o*-CF_3 derivative.

At this point we must recall that Brewer and Brewer[10] found that, in the coordinating solvent DMSO, tetrakis(*para*-phenyl-substituted) derivatives of (TPP)FeCl react with *N*-methylimidazole according to eq 11 to produce complexes with values of β_2^{III} that increase as the electron-withdrawing nature of the substituents increases. The Hammett ρ value that they obtained for the series of substituents studied was +0.11.[10] Assuming a similar positive value of ρ in DMF, we must conclude that the apparent through-bond electron-withdrawing ability of the substituents increases in the order 2,6-Cl_2 ∼ *p*-OCH_3 < *o*-CF_3 < *o*-F or that the apparent electron-donating ability increases in the opposite order. Thus, the values of log(β_2^{III}) measured in DMF lead to the same conclusion as those measured in $CHCl_3$: If induction is considered to be the sole contributor to determining the size of β_2^{III}, *ortho*-halogens and the CF_3 group on a phenyl ring of a [(TPP)Fe(NMeIm)$_2$]$^+$ complex appear to behave as electron-donating substituents, and a 2,6-dihalogen-substituted phenyl ring appears to be more than twice as electron-donating as a single 2-halogen-substituted phenyl.

We feel that this apparent electron-donating character of 2- and 2,6-halogens may best be explained in terms of a direct transfer of electron density from the halogen to the iron *both* in the reactant, which results in a weakening of the (TPP)Fe$^+$Cl$^-$ ionic bond in $CHCl_3$, *and* in the product, which results in decreasing the Lewis acidity of iron(III) in both $CHCl_3$ and DMF. We further feel that this electron donation takes place through direct overlap of the electron cloud of the *ortho*-halogen(s) with the π system of the porphyrin ring. In support of this, Bocian and co-workers have recently reported EPR and resonance Raman evidence for direct porphyrin (π)−chlorine (p) orbital overlap in the π cation radicals of Zn(II) and Mg(II) tetrakis(2,6-dichlorophenyl)porphyrin, [(2,6-Cl_2)$_4$TPPZn]$^{\bullet+}$ and [(2,6-Cl_2)$_4$TPPMg]$^{\bullet+}$.[50] Longo and co-workers were actually the first to suggest the direct overlap of *ortho*-halogen substituents with the porphyrin π system,[37] and Bunnenberg, Djerassi, and co-workers considered, among other possibilities, similar explanations for the altered sign pattern of the MCD spectra of the free-base tetrakis(2,6-dihalophenyl)porphyrins.[51] Bruice and co-workers have also suggested the possibility of direct overlap of electron clouds.[38] As concluded by these workers, we believe that direct overlap of the electron cloud of the *ortho* substituent with the π system of the porphyrin ring must play a significant role, because of the much larger effect of the size of log(β_2^{III}) measured in $CHCl_3$, Table 2, on the presence of 2,6-dihalogens as compared to a single *ortho*-halogen (a factor of 2.5 for F, 2.4 for Cl, and 2.1 for Br, which result in much larger differences in the calculated values of $\sigma_{o\text{-X}}$, Table 2). Again it should be pointed out that monosubstitution at the *ortho* position(s) of the phenyl was used in this study specifically to *diminish* the importance of any so-called "steric hindrance" effect of the tetrakis(2,6-X_2phenyl) substituents, and hence we believe that the major effect being observed is a transmission of electron density from the *ortho* substituent(s) to the iron(III) center in both the (TPP)Fe$^+$Cl$^-$ reactant in $CHCl_3$ and the [(TPP)FeL$_2$]$^+$− anion product in both $CHCl_3$ and DMF, probably by direct overlap of the electron cloud of the *ortho* substituent with the π system of the porphyrin ring. Such overlap would be expected to be more significant when two *ortho* substituents are present on the same phenyl ring, because this ring will be unable to "bend" the *ortho* substituents out of the way of the π system, as would a phenyl ring that carries only one *ortho* substituent.

The values of log(β_2^{II}) reported in Table 3 mirror fairly closely the values and relative order of log(β_2^{III}), again indicating that *ortho* substituents appear to be electron-donating in the order *p*-OCH_3 > 2,6-Cl_2 ∼ *o*-CF_3 > *o*-F, or in terms of our hypothesis of direct overlap of the electron cloud of the *ortho* substituent, the largest substituents are best able to transmit electron density from the *ortho* substituent to the porphyrin ring. Hence, there does not appear to be a major difference in behavior of Fe(II) as compared to Fe(III), and the Lewis acidity of the metal increases as the size of the halogen decreases in both cases. In all cases log(β_2^{III}) is larger than log(β_2^{II}).

In comparing the present equilibrium constant data to those obtained for the binding of *N*-methylimidazole to symmetrically 2,6-disubstituted phenyl derivatives of (TPP)Fe^{III} such as [(2,6-Cl_2)$_4$(TPP)Fe(DMF)$_2$]$^+$$ClO_4^-$, [(2,6-$Br_2$)$_4$(TPP)Fe(DMF)$_2$]$^+$-$ClO_4^-$, and (tetramesitylporphyrinato)iron(III) perchlorate, [TMPFe(DMF)$_2$]$^+$$ClO_4^-$, in dimethylformamide,[11] we first note that the presence of large 2,6-dihalogen or CH_3 substituents causes strong enhancement in the size of log(β_2^{III}) for binding a series of pyridines of differing basicities, as well as *N*- and 2-methylimidazole. For NMeIm the values of log(β_2^{III}) are 7.7 (Br), 7.1 (Cl), and 7.9 (TMP),[11] so there is some stabilization of the symmetrical tetrakis(2,6-phenyl-substituted) complexes with respect to the compounds of this study listed in Table 3. While all other ligands are known to cause extreme ruffling of the porphyrinate ring,[39] there is no evidence that the bis(*N*-

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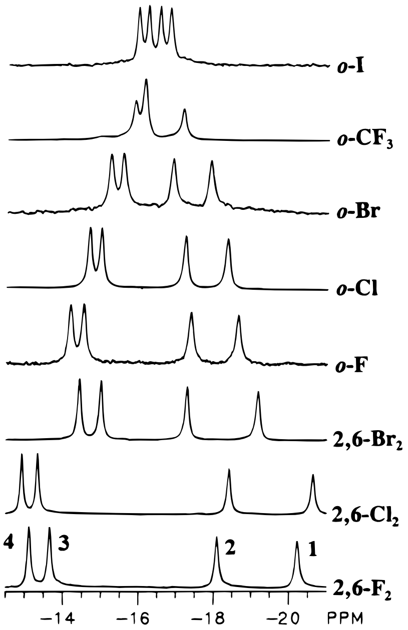

Figure 5. ^{1}H NMR spectra of the pyrrole-H resonances of the low-spin Fe(III) complexes [(*o*-X)- or (2,6-X_2)(*p*-OCH_3)$_3$(TPP)Fe(NMeIm)$_2$]$^+$-Cl^-, recorded at 33 °C in $CDCl_3$.

methylimidazole) complex of (TMP)Fe^{III} is ruffled,[39a] although one isomer of the 1-vinylimidazole complex of (2,6-Cl_2)$_4$(TPP)-Fe^{III} has the axial ligands in perpendicular planes[34] and *may* be slightly ruffled, and we observe both rhombic and "large g_{max}" EPR signals for [(2,6-Br_2)$_4$(TPP)Fe(NMeIm)$_2$]$^+$$ClO_4^-$,[56] the latter of which suggests the ligands are in perpendicular planes. Perpendicular ligand planes tend to cause the porphyrinate ring to ruffle,[57,58] so it is possible that part of the stabilization of the symmetrical tetrakis(2,6-phenyl-substituted) complexes of the previous study[42] is due to ruffling. Again, for the mono-2- or 2,6-phenyl-substituted complexes of the present study, there should be little need for ruffling of the porphyrinate ring. And while the 2-substituted phenyl ring may be able to distort the *meso*-C−phenyl bond out of the porphyrin plane to relieve steric interactions between the electron cloud of a single (large) *ortho*-halogen, the 2,6-disubstituted phenyl ring compounds cannot.

NMR Studies of the Low-Spin Fe(III) Complexes Having *ortho*-Halogen Substituents. The series of low-spin Fe(III) porphyrinate complexes, [(*o*-X)(*p*-OCH_3)$_3$(TPP)Fe(NMeIm)$_2$]$^+$-Cl^- and [(2,6-X_2)(*p*-OCH_3)$_3$(TPP)Fe(NMeIm)$_2$]$^+$$Cl^-$, formed by reaction 6 have been investigated by one-dimensional ^{1}H NMR spectroscopy in CD_2Cl_2 at room temperature. As in previously studied unsymmetrically substituted low-spin (TPP)Fe^{III} complexes, either three or four pyrrole-H resonances are observed in the −15 to −25 ppm region,[20b,c,26,44,59] as shown in Figure 5 for the complexes of this study. The pattern of two closely spaced or overlapping resonances at lower shielding (peaks 3 and 4) and two more widely spaced resonances at higher shielding (peaks 1 and 2) was observed previously among unsymmetrically substituted derivatives of [(TPP)Fe(NMeIm)$_2$]$^+$ having only *meta* or *para* substituents when one relatively electron-donating substituent was present.[20b,59c] On this basis, at least, it would appear that phenyl rings bearing *ortho* substituents behave as if they were electron-donating, except perhaps in the case of the monoiodo and *mono*-CF_3 complexes, where peak overlap makes the pattern less clear. In fact, it is curious to note that the separation of resonances 3 and 4 is almost the same for all of the complexes shown in Figure 5.

A much better understanding of the patterns of pyrrole-H resonances shown in Figure 5 could be obtained if the four pyrrole-H resonances could be assigned to the four unique types of protons, H_a−H_d. It has thus far not been possible to unambiguously assign the four resonances, but partial assignment shows that resonances 1,4 and 2,3 (or 1,3 and 2,4) are due to protons in individual pyrrole rings,[59b] as discussed further below. We have recently questioned[60] the data that resulted in our earlier assignments for *para*-substituted [(TPP)Fe(N-MeIm)$_2$]$^+$ complexes,[59c,d] since the cross peak pattern observed in the symmetrized NOESY maps of the complexes[59c,d] is not observed in phase-sensitive NOESY and steady-state NOE difference spectra.[60] However, recent one-and two-dimensional ^{1}H and ^{13}C NMR studies[46] appear to support the earlier assignments.[59c,d] For mono-*ortho*-substituted derivatives of [(TPP)Fe(NMeIm$_2$)]$^+$, H_a is the most upfield-shifted resonance,[46] thus allowing peaks 1−4 to be assigned to H_a, H_d, H_b, and H_c, respectively. This assignment is also consistent with the results of the earlier Hückel calculations.[59c]

We have previously shown by COSY techniques[59b] that the pyrrole-H coupling pattern of [(*o*-Cl)(*p*-OCH_3)$_3$(TPP)Fe-(NMeIm)$_2$]$^+$ is resonances 1,3 and 2,4 or large−small unpaired electron density in each case. These results confirm that spin delocalization occurs via the 3e(π) orbitals having nodes at opposite *meso* positions, by porphyrin → Fe π donation to the hole in the dπ orbitals of low-spin Fe(III). The *ortho*-fluoro, -chloro, and -bromo and the 2,6-difluoro and 2,6-dichloro complexes of this series show this same coupling pattern. In our earlier work, we found that the [(*o*-OEt)(TPP)Fe(NMeIm)$_2$]$^+$ complex and its *o*-OCH_2Ph and *o*-COOH analogues show the 1,4 and 2,3 coupling pattern,[59b] also a large−small pattern of electron density at the β-pyrrole positions. It was previously suggested that the 1,3 and 2,4 coupling pattern is indicative of modification of the electron density distribution in the 3e(π) orbitals at all four pyrrole positions and suggests at least some degree of π delocalization of the substituent effect[59b] while the 1,4 and 2,3 coupling pattern is indicative of modification of the electron density distribution at only the two closest pyrrole positions,[59b] and suggests mainly an inductive effect of the substituents that give that pattern. However, a more recent theoretical treatment of the Curie behavior of low-spin Fe(III) porphyrinates[61] shows that, depending on the energy separation of the two e(π) orbitals that are thermally occupied and the temperature at which the NMR spectrum was recorded, the relative shifts of H_b and H_c may be reversed. Hence, it is unlikely that the observation of a 1,3 and 2,4 coupling pattern for some complexes and a 1,4 and 2,3 coupling pattern for others provides any information concerning the "degree of localization" of the substituent effect, but rather, more likely, it provides information concerning the difference in energy, ΔE_π, of the two e(π) orbitals, as discussed further below.

As shown in Figure 5 and summarized in Table 4, the *ortho* substituent has a dramatic effect on the total spread of these

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Table 4. ^{1}H NMR Chemical Shifts[a] of the Pyrrole Protons of the Low-Spin Fe(III) Complexes $[(o\text{-X})(p\text{-OCH}_3)_3(\text{TPP})\text{Fe}(\text{NMeIm})_2]^+$ and $[(2,6\text{-X}_2)(p\text{-OCH}_3)_3(\text{TPP})\text{Fe}(\text{NMeIm})_2]^+$

X	H_1[b]	H_2[b]	H_3[b]	H_4[b]	δ_{av}[b]	$\Delta\delta$[b]	derived $\sigma_{(o\text{-X})}$[c]
o-F	−18.7	−17.4	−14.5	−14.2	−16.2	−4.5	−1.7
o-Cl	−18.4	−17.3	−15.0	−14.7	−16.4	−3.7	−1.3
o-Br	−17.9	−16.9	−15.5	−15.2	−16.4	−2.7	−0.9
o-CF_3	−17.2	−16.1	−16.1	−15.9	−16.3	−1.3	−0.3
o-I	−16.8	−16.5	−16.2	−16.0	−16.4	(−?)0.9	−0.1
2,6-F_2	−20.2	−18.1	−13.7	−13.1	−16.3	−7.1	−2.8
2,6-Cl_2	−20.9	−18.4	−13.4	−12.9	−16.4	−7.9	−3.1
2,6-Br_2	−19.2	−17.3	−15.0	−14.4	−16.5	−4.8	−1.8

[a] Measured in $CDCl_3$ at 33 °C. [b] Chemical shift (ppm) referenced to $CHCl_3$ at 7.25 ppm. [c] $\sigma_{o\text{-X}}$ for the phenyl *ortho* substituent determined from the observed $\Delta\delta$ (Figure 5) and the correlation line of Figure 6 (see text).

resonances. This total spread, $\Delta\delta$, decreases in the order $Cl_2 > F_2 > Br_2 \sim F > Cl > Br > CF_3 > I$. This is approximately the reverse of the order of the effect of the *ortho*-halogen substituent on the chemical shift difference of H_b and H_a in the free-base porphyrins, discussed above, and must arise from differences in the pattern of delocalized π electron density and/or differences in the energy of the two e(π) valence orbitals, ΔE_π,[61] in these low-spin Fe(III) complexes. This pattern of delocalized π electron density is indicative of unpaired electron delocalization into the modified e-symmetry filled π orbitals previously called the 3e(π) orbitals.[62] Mixing of these orbitals with the $^3/_4$-filled e-symmetry d_π orbitals, d_{xz} and d_{yz}, and, to a lesser extent, the empty porphyrin 4e(π) orbitals[62] produces a strongly bonding filled set, a weakly bonding, mainly metal-centered set containing one hole, and an empty antibonding set.[59c] The degeneracy of each of these sets of "e-symmetry" orbitals is lifted by the unsymmetrical substitution pattern, leaving one of the middle, mainly metal-centered set of orbitals to be the singly occupied molecular orbital (SOMO). The unpaired electron distribution in the two orbitals of the middle set, the SOMO and its slightly lower-in-energy filled counterpart, calculated from Hückel molecular orbital theory,[59c] has been shown to be satisfyingly consistent with the observed contact shifts of two unsymmetrically *para*-substituted [(TPP)Fe(NMeIm)$_2$]$^+$ isomers, and the same is true of the present *ortho*-phenyl substituent-containing complexes, for which the *ortho*-substituted phenyl ring is considered to be an electron-donating substituent.

For *para*- and *meta*-substituted iron(III) porphyrinates we have previously shown that a correlation exists between the spread of the pyrrole-H resonances in unsymmetrically substituted derivatives of [(TPP)Fe(NMeIm)$_2$]$^+$ and the difference in the electron-donating or -withdrawing effect of the substituents, as measured by the difference in the Hammett σ constants of the substituents.[20c] These data are summarized in Figure 6, where the spread of the pyrrole-H resonances of the series of $[(o\text{-X})\text{- or }(2,6\text{-X}_2)(p\text{-OCH}_3)_3(\text{TPP})\text{Fe}(\text{NMeIm})_2]^+$ complexes of this study (Figure 5, Table 4) has been marked as crosses on the correlation line of Figure 6 in each case. As is evident from the positions of these crosses, we find that the "apparent" Hammett σ constants for the *ortho*-halogen substituents are all negative. The derived apparent σ constants are summarized in the last column of Table 4. This order is entirely different (and not simply the reverse) from that found for either the H_b-H_a chemical shifts of the free-base porphyrins (Table 1) or the equilibrium constants for binding *N*-methylimidazole to the iron(III) porphyrins in $CHCl_3$ (Table 2) or DMF (Table 3). The large negative values of $\sigma_{o\text{-X}}$ derived from this procedure, some of which are similar in size to those derived from log(β_2^{III}) values measured in $CHCl_3$, Table 2 (although others are not), again support the conclusion that *ortho* substituents may behave as electron-donating substituents. Again, it should be noted that the order also correlates extremely well with the size of the substituent, though in the approximately opposite order, with one set for 2-X and another for 2,6-X_2 derivatives. However, the situation is more complex than for log(β_2^{III}) values, because the spread of the pyrrole-H resonances is not only determined by the electron-donating or -withdrawing characteristics of the unique substituent or, as we concluded above, by its size and the direct overlap of the electron cloud of the *ortho* substituent with the π system of the porphyrin but also by the relative populations of the two valence e(π) orbitals (which is in turn determined by the energy spacing between them, ΔE_π, as compared to kT).[61] Hückel calculations, where the energy of one *meso*-carbon orbital is adjusted up or down to simulate the electronic effect,[59c] and 2-level Curie dependence calculations[61] show that both of these factors are important, and they cannot be separated without carrying out extensive measurements of the temperature dependence of the pyrrole-H resonances of each complex, which we have not done. We may *suspect* that ΔE_π will increase with the size of the substituent, however, because large substituents can hinder the rotation of one (or both) axial ligands, but this does not explain why the separation $\Delta\delta$ is smaller for the 2,6-Br_2-substituted complex than for the 2,6-F_2-substituted complex.

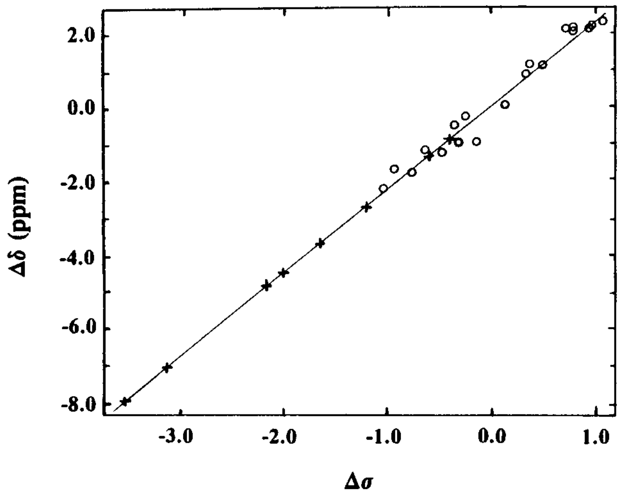

Figure 6. Plot of the difference in shift, $\Delta\delta$, between the most unique pyrrole-H resonance and its extreme vs $\Delta\sigma$, the difference in Hammett σ-constants of the two substituents. Data for $[(m\text{- or }p\text{-X})(m\text{- or }p\text{-Y})_3(\text{TPP})\text{Fe}(\text{NMeIm})_2]^+$ and the correlation line were taken from ref 20b, where the sign of $\Delta\delta$ was defined as positive when the pyrrole-H pattern was 1:1:(2) and negative when it was (2):1:1, where (2) represents the intensity of the two closely spaced resonances, which overlap at lower NMR field strength. On the basis of the observed $\Delta\delta$ (Figure 5), the compounds of this study have been placed on this line (crosses).

Summary

The NMR chemical shifts of the pyrrole protons H_a and H_b of the free-base porphyrins (Table 1) suggest that their separation depends on substituent size, while those of the corresponding low-spin Fe(III) complexes, especially the variation in the spread of the pyrrole-H resonances of these complexes (Figure 5, Table 4), indicate an order that is entirely different from either the

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(62) Longuet-Higgins, H. C.; Rector, C. W.; Platt, J. R. *J. Chem. Phys.* **1950**, *18*, 1174.

trends of the pyrrole-H resonances of the free-base porphyrins or the sizes of the equilibrium constants for binding *N*-methylimidazole to the high-spin Fe(III) derivatives, either in chloroform (Table 2) or DMF (Table 3). The equilibrium constants measured in both solvents confirm that *ortho*-halogen and -CF_3 substituents behave as though they are electron-donating, if the effect of the substituent is assumed to result entirely from through-bond inductive effects. All of these properties correlate well with the variation in size of the substituent(s), and the results are most consistent with the effect of the phenyl ring bearing the *ortho* substituent(s) behaving apparently as electron-donating, due to direct overlap of the electron cloud of the *ortho* substituent (which is expected to increase with its size) with the π system of the porphyrin ring.

It must also be mentioned that there are scattered pieces of data that suggest that *ortho*-halogens behave as electron-withdrawing substituents: In this work we have found that the pattern of free-base pyrrole-H resonances, with the H_a resonance shifted to higher shielding, is that expected for unsymmetrically substituted TPP derivatives in which one phenyl substituent is electron-withdrawing with respect to the other three,[20a] although we find that the resonance separation H_b-H_a increases in order of increasing substituent size (Table 1). The Fe^{III}/Fe^{II} reduction potentials of the complexes of the (tetrakis(2,6-X_2-phenyl)-porphyrinato)iron(III) in dimethylformamide shift negatively in the order F, Cl, Br, H, OCH_3, as do the Fe^{II}/Fe^{I} reduction potentials of the same complexes.[11] The Fe^{III}/Fe^{II} reduction potentials of the bis(*N*-methylimidazole) complexes also shift negatively in the same order,[11] suggesting in all three cases that reduction is thermodynamically favored by "electron-withdrawing substituents", although not in the order suggested by the σ_p values of these substituents. None of these trends in reduction potentials correlate with substituent size. A similar order was observed for cation radical species of some of the corresponding Zn(II) and Mg(II) complexes, where the reduction potentials from the cation radical to neutral porphyrin shift negatively in the order F, Cl, and H.[52] XPS and ab initio SCF calculations[53] and local density functional calculations[54] have also suggested that phenyl *o*-halogens appear to be electron-withdrawing but that local dipole effects may dominate the behavior of *ortho* substituents.[54] However, in the Zn(II) and Mg(II) complex study and in the XPS and calculations, *ortho*-fluoro and -chloro substituents have been considered together with perhalogenated phenyl rings, and it is not easy to relate these two types of substituted phenyl rings because of different substituent effects of *ortho*-, *meta*-, and *para*-halogens. As a result, we have only three data points for comparison, those for the TPP and tetrakis-(2,6-F_2) and -(2,6-Cl_2) derivatives, the latter two of whose Zn(II) cation radical reduction potentials are quite similar[52] and the latter two of whose calculated valence ionization potentials are almost identical.[54] It is to be hoped that additional studies of a wider range of *ortho*-halogen substituents will be carried out by these workers in order to more fully elucidate the effects of the whole class of phenyl *ortho* substituents.

The first question that must be addressed in correlating the data of this study is as follows: What is actually being measured in each case? In the case of the β_2^{III} values in the two different solvents, one which is noncoordinating and allows the anion to be coordinated to the metal in the starting material and the other of which is coordinating and has already accomplished the separation of the cation and anion, the opposite orders of log(β_2^{III}) can be attributed to a direct transfer of electron density from the halogen substituents to the π system of the porphyrin ring, which helps *both* to decrease the Lewis acidity of the metal in the (TPP)Fe^+Cl^- unit of the starting material, hence weakening that ionic bond, *and* to decrease the Lewis acidity of the metal in the product. The reaction (eqs 3 and 5) is much more sensitive to the direct transfer of electron density in the reactant than it is to the electron-donating properties of the substituents in the product.

In the case of the NMR experiments on the free-base porphyrins, we have used the H_b-H_a pyrrole proton resonance separation to attempt to quantify the asymmetry of the π electron cloud created by the difference in the effect of the *ortho*- or 2,6-halogens and the *para*-methoxy substituents. In the case of the NMR experiments on the low-spin Fe(III) complexes, we are using the pyrrole-H resonances of the porphyrin ring to measure the unpaired electron distribution in the e(π) filled porphyrin orbitals as a function of the 2- or 2,6-phenyl substituent. This distribution is a result of a combination of the modification in the electron density distribution in the e(π) orbital that is preferred for spin delocalization (the SOMO) and the energy separation between this half-filled orbital and the fully filled orbital, from which an electron can be excited to the SOMO, which is likely of the order of kT.[61] Hence, it is not surprising that the two sets of NMR measurements yield different orders of substituent effects.

The second question that arises concerning the electronic effects of *ortho* substituents in this system is as follows: Why are the trends observed in the spread of the pyrrole-H NMR resonances of the low-spin Fe(III) complexes ($Cl_2 > F_2 > Br_2 \sim F > Cl > Br > CF_3 > I$) so different from those observed for the size of log(β_2^{III}) measured in chloroform ($Br_2 > Cl_2 > CF_3 > F_2 > I > Br > Cl > F$) or DMF ($F > CF_3 > Cl_2$), when, for *meta*- and *para*-substituted derivatives of (TPP)Fe^{III}, both of these physical quantities were found to be functions of the Hammett σ_m- or σ_p-constants, respectively?[9,20b,c] To address this question we must remember that the spread of the pyrrole-H resonances measures the asymmetry in the unpaired electron density distribution in the e(π) orbitals[59c,62] *and, in addition, the difference in energy between the two formerly degenerate e(π) orbitals*, which will change the spread of the resonances as a function of temperature more than that expected on the basis of simple Curie behavior.[26,59c] On the other hand, the size of log(β_2^{III}) measures the combined σ and π electronic effects of substituents at the periphery of the porphyrin ring on the Lewis acidity of the metal. For *ortho* substituents, where there may indeed be varying degrees of direct overlap of the electron cloud of the halogen with the π system of the porphyrin as the size of the halogen(s) (or CF_3) increases in both the (TPP)-FeCl starting material and in the bis(NMeIm) complexes, there is no guarantee that the thermodynamic and spectroscopic properties will be correlated with each other, mainly because of the *extreme* sensitivity of the pyrrole-H shifts to changes in the π electron distribution in the SOMO. Furthermore, π electronic effects on the size of log(β_2^{III}) cannot be quantified on the basis of the spread of the pyrrole-H resonances alone, since the NMR contact shifts of the pyrrole protons sense *only* the electron density distribution in the e(π)-type SOMO and its slightly lower-energy filled e(π) partner and not that in the a_{1u}(π) or a_{2u}(π) orbitals, both of which are expected to be slightly lower in energy than the SOMO but still among the frontier orbitals of the Fe(III) porphyrinate. Hence, we cannot determine quantitatively the relative importance of σ, π, local dipole,[54] and direct electron cloud overlap effects on the values of log(β_2^{III}) and the spread of the pyrrole-H resonances of these low-spin Fe(III) complexes, but it is clear that the sum of these effects is profound. Future interpretations of the effects of phenyl *ortho* substituents of metallo-TPP complexes must be able to account for the extremely different trends in apparent $\sigma_{o\text{-X}}$ values of the large series of $[(o\text{-X or } 2,6\text{-X}_2)(p\text{-OCH}_3)_3\text{-}(\text{TPP})\text{Fe}(\text{NMeIm})_2]^+$ complexes of this study, obtained from these two sets of data (Tables 2 and 4).

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