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Electronic Effects in Transition-Metal Porphyrins. 4. Effect of Unsymmetrical Phenyl Substitution on the NMR Spectra of a Series of Metal-Free and Zinc Tetraphenylporphyrins

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The series of six metal-free porphyrins having all possible numbers of p-(diethylamino)phenyl and p-chlorophenyl groups, $H_2TPP(p\text{-Cl})_x(p\text{-NEt}_2)_y$ ($x + y = 4$; $x = 0$–4), have been synthesized and separated by chromatographic techniques. Their 250-MHz NMR spectra show patterns of pyrrole-H resonances which are fully consistent with the pattern of para phenyl substitution for each isomer. There are two regions of pyrrole-H resonances: one at 8.74–8.80 ppm and one at 8.92–9.04 ppm, for those protons immediately next to meso positions carrying a p-chlorophenyl or p-(diethylamino)phenyl group, respectively. The weighted average pyrrole resonance position of the six isomers shifts slightly upfield as the sum of the Hammett σ constants of the substituents increases and follows the same linear free energy correlation as do a series of $H_2(p\text{-R})_4$TPPs ($\rho_{\text{pyrrole-H}} = -0.0172$ ppm). However, while the weighted average pyrrole resonance position shifts upfield, the *individual* pyrrole-H resonances of the four unsymmetrical isomers shift *downfield* as the sum of the Hammett σ constants increases. These ring current shifts and those of the ortho phenyl protons are interpreted in terms of the electronic effects of phenyl substituents being transmitted to the porphyrin π system by a combination of σ and π *induction* rather than σ induction and π *conjugation*.

Introduction

The degree and mode of transmission of electron density to and from various points on the porphyrin ring through the σ- and π-orbital systems, the effects of changes in electron density upon the basicity of the four porphyrin nitrogens, and the reactivity and spectroscopic properties of the central metal ion, if present, have long been interests of those who have investigated the physical properties and chemical reactions of metalloporphyrins.[2–24] Early studies, mainly by Caughey and co-workers,[3–5,25] of such effects in the natural porphyrins and their metal complexes provided valuable information concerning the relative basicities of the free-base forms and the axial ligation properties of natural and modified natural porphyrins. Chemically modified derivatives of protoporphyrin IX complexes of iron have recently been extremely valuable in probing the active sites of various heme proteins by NMR spectroscopy,[25,26] in part because they produce varying degrees of asymmetry in the π-electron system of the porphyrin which are revealed by the pattern of unpaired electron delocalization of the low-spin iron(III) forms of these proteins.

Chemical modifications of protoporphyrin IX are typically made at the 2- and/or 4-pyrrole positions (Figure 1a). Thus substituents can interact directly with the π-electron system of the porphyrin ring, and the separation of resonance and inductive contributions to linear free energy relationships for natural porphyrins and their chemically modified relatives has not been possible. Furthermore, since naturally occurring porphyrins and their chemically modified derivatives are, by nature's design, of low molecular symmetry, it is difficult to quantitate the effect of substituents on orbital energies and the inherent symmetry of electron distribution in the porphyrin ring.

In the years since the original studies of Caughey and co-workers on the effects of substituents on the physical and chemical properties of natural porphyrins, a number of studies have been reported on related synthetic porphyrins, in particular tetraphenylporphyrins and their metal complexes.[9–24] These meso-substituted porphyrins (Figure 1b) are a totally synthetic family of molecules, which, although they cannot be substituted for heme in the proteins, have the advantage of allowing the systematic and quantitative study of the physical and chemical properties of the porphyrin nucleus because of the wide range of possible substituents that may be introduced onto the phenyl rings. They have the further advantage of high molecular symmetry, which simplifies the observed NMR spectra and the interpretation (in terms of

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(1) Recipient, NIH Research Career Development Award, 1976–1981.

(2) Falk, J. E. "Porphyrins and Metalloporphyrins"; Elsevier: New York, 1964; pp 28, 42, 69, 93.

(3) Caughey, W. S.; Deal, R. M.; McLees, B. D.; Alben, J. O. *J. Am. Chem. Soc.* **1962**, *84*, 1735–1736.

(4) Caughey, W. S.; Fujimoto, W. Y.; Johnson, B. P. *Biochemistry* **1966**, *5*, 3830–3843.

(5) McLees, B. D.; Caughey, W. S. *Biochemistry* **1968**, *7*, 642–652.

(6) Baker, E. W.; Storm, C. B.; McGrew, G. T.; Corwin, A. H., *Bioinorg. Chem.* **1973**, *3*, 49–60.

(7) Higginbotham, E.; Hambright, P. *Inorg. Nucl. Chem. Lett.* **1972**, *8*, 747–750.

(8) Worthington, P.; Hambright, P.; Williams, R. F. X.; Feldman, M. R.; Smith, K. M.; Langry, K. C. *Inorg. Nucl. Chem. Lett.* **1980**, *16*, 441–447.

(9) Williams, G. N.; Hambright, P. *Inorg. Chem.* **1978**, *17*, 2687–2688.

(10) Kirksey, C. H.; Hambright, P.; Storm, C. B. *Inorg. Chem.* **1969**, *8*, 2141–2144.

(11) Walker, F. A.; Hui, E.; Walker, J. M. *J. Am. Chem. Soc.* **1975**, *97*, 2390–2397.

(12) Walker, F. A.; Beroiz, D.; Kadish, K. M. *J. Am. Chem. Soc.* **1976**, *98*, 3484–3489.

(13) Walker, F. A.; Io, M.-W.; Ree, M. T. *J. Am. Chem. Soc.* **1976**, *98*, 5552–5560.

(14) Vogel, G. C.; Beckmann, B. A. *Inorg. Chem.* **1976**, *15*, 483–484.

(15) Jones, R. D.; Summerville, D. A.; Basolo, F. *J. Am. Chem. Soc.* **1978**, *100*, 4416–4424.

(16) Walker, F. A.; Barry, J. A.; Balke, V. L.; McDermott, G. A.; Wu, M. Z.; Linde, P. F. *Adv. Chem. Ser.*, in press.

(17) Kadish, K. M.; Morrison, M. M. *Bioinorg. Chem.* **1977**, *7*, 107–115 and references therein.

(18) Kadish, K. M.; Bottomley, L. A. *J. Am. Chem. Soc.* **1977**, *99*, 2380–2382.

(19) Kadish, K. M.; Bottomley, L. A.; Beroiz, D. *Inorg. Chem.* **1978**, *17*, 1124–1129.

(20) Rillema, D. P.; Nagle, J. K.; Barringer, L. F.; Meyer, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 56–62.

(21) Shears, B.; Shah, B.; Hambright, P. *J. Am. Chem. Soc.* **1971**, *93*, 776–778.

(22) Reid, J. B.; Hambright, P. *Inorg. Chem.* **1977**, *16*, 968–969.

(23) Meot-Ner, M.; Adler, A. D. *J. Am. Chem. Soc.* **1972**, *94*, 4763–4764.

(24) Meot-Ner, M.; Adler, A. D. *J. Am. Chem. Soc.* **1975**, *97*, 5107–5111.

(25) Wüthrich, K.; Shulman, R. G.; Wyluda, B. J.; Caughey, W. S. *Proc. Natl. Acad. Sci. U.S.A.* **1969**, *62*, 636–643.

(26) LaMar, G. N. In "Biological Applications of Magnetic Resonance"; Schulman, R. G., Ed.; Academic Press: New York, 1979; pp 305–343 and references therein.

0020-1669/82/1321-3342$01.25/0 © 1982 American Chemical Society

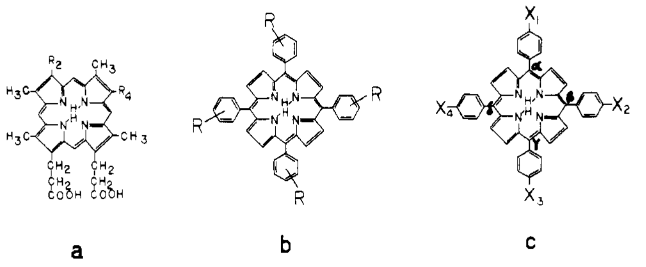

Figure 1. (a) Structure of protoporphyrin IX ($R_1 = R_2$ = vinyl) and its chemically modified derivatives (R_1, R_2 = H, CH_2CH_3, CHO, Br, etc.). (b) Structure of symmetrical tetraphenylporphyrins. (c) Structures of the six $H_2TPP(p\text{-}Cl)_x(p\text{-}NEt_2)_y$ isomers of this study: **1**, X_1–X_4 = Cl; **2**, $X_1 = NEt_2$, X_2–X_4 = Cl; **3**; X_1, $X_3 = NEt_2$, X_2, X_4 = Cl; **4**, X_1, $X_2 = NEt_2$, X_3, X_4 = Cl; **5**, X_1, X_2, $X_4 = NEt_2$, X_3 = Cl; **6**, X_1–$X_4 = NEt_2$. Note that the meso positions are labeled α, β, γ, δ to aid discussion in the text.

molecular orbital theory) of UV–visible, NMR, and other types of spectra which have therefore been investigated in detail. Such systematic investigations of these highly symmetrical compounds have allowed extraction of quantitative information such as the chemical shifts of pyrrole and N–H protons,[27,28] rates of phenyl rotation,[28-30] porphyrin inversion,[30,31] N–H proton tautomerism,[32,33] and evidence of atropisomerism of ortho-substituted derivatives.[34] Linear free energy relationships have been found for rate[9] and equilibrium[10-16] constants of axial ligand addition, including both Lewis base[10-16] and molecular oxygen[12,15] addition reactions, redox potentials[12,16-20] for both porphyrin ring and metal redox reactions, metal incorporation rates,[21-23] the energies of electronic absorptions,[24] etc. In almost all cases (except for ref 23, 24, and 30, as discussed below) the above quantities have correlated with the simple σ constants of the Hammett equation[35-37]

$$P_X = 4\sigma_X\rho \qquad (1)$$

where P_X is the observed physical property of a compound having substituent X, σ_X is the substituent constant of X as defined by the relative dissociation constants of a series of X-substituted benzoic acids,[35,36] and ρ describes the sensitivity of the property under study to the electron-withdrawing or -donating properties of X.

The question has often been raised as to whether the transfer of these electronic effects from meta- or para-X groups on the phenyl rings of TPP to the porphyrin ring is by inductive or resonance transfer or a combination of the two. Though most free energy relationships have related P_X to the original Hammett σ constants (eq 1), the rates of metal incorporation into the free-base porphyrins[23] and electronic absorption maxima of the totally protonated free-base porphyrins (known as the dications)[24] have been found to correlate with σ^+ [37] or $\sigma - \sigma^+$, indicating strong resonance coupling between phenyl and porphyrin rings. Rates of porphyrin inversion have been shown to be a nonlinear function of the original Hammett σ constants when the *p*-(diethylamino)phenyl substituent was included in the correlation.[30] Our own studies[16] of this latter substituent, however, have shown it to behave linearly with the Hammett σ constants for a number of "ground-state" or equilibrium properties such as reactions involving ligand addition to metalloporphyrins,[16] electrochemical redox potentials,[16] and, as summarized herein, NMR shifts of the various porphyrin protons, as well as proton isotropic shifts of low-spin iron(III) porphyrins[38,39] and the *g* anisotropy measured from EPR parameters,[16,40] discussed elsewhere.

Recent studies of photoisomerization of the "picket-fence porphyrin" have suggested that electronic excited states of porphyrin free bases may indeed have stronger resonance coupling between phenyl and porphyrin rings than do ground states.[41] This may account for the anomalies noted for activation energies of phenyl rotation, metal incorporation, and electronic spectra of the dications, or it may simply be that in each of these cases, but not others, the porphyrin ring is highly distorted from planarity, thus making direct resonance coupling possible.

For tetraphenylporphyrins in their ground electronic states, molecular models (CPK) suggest that because of steric interference between the β-pyrrole and ortho phenyl protons, the phenyl rings are constrained to being out of the plane of the porphyrin most of the time, and X-ray crystallographic structure determinations have confirmed this suggestion in numerous cases.[42] The barriers to rotation of the phenyl rings in Ru(III), In(III), and Ti(IV) TPPs have been determined by NMR techniques and are found to range from 11 to 17 kcal/mol,[30] relatively high energy barriers. These facts have suggested that the transfer of electronic effects from phenyl to porphyrin, and its consequent effect on "ground-state" (equilibrium) properties must be largely inductive. However, theoretical calculations of Wolberg[43] have suggested that in solution the phenyl rings can achieve positions nearly coplanar with the porphyrin ring and thereby allow significant resonance transfer of substituent effects. Such phenyl–porphyrin π-orbital overlap may explain kinetic results.[23,30] The question remains as to the importance of resonance to the equilibrium properties of metalloporphyrins and their free bases.

In a recent study of the effects of substituents on the equilibrium constants for complexation of piperidine to a series of V(IV) and Ni(II) porphyrins[11] it was found that there was evidence of almost equal contribution of resonance and (σ) inductive transfer,[11] although it was difficult to distinguish clearly between the possibility that the resonance portion of the transfer of electron-donating or -withdrawing effects of substituents from the para phenyl position to the metal center is by π induction or by moderate π conjugation as defined by Taft and co-workers.[44] Because of the inability to distinguish between π induction and moderate π conjugation in the Ni(II)-substituted TPPs, we have sought other systems which would allow such a distinction to be made. We have recently prepared the series of unsymmetrically phenyl-substituted tetraphenylporphyrins shown in Figure 1c, which provide

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(27) Janson, T. R.; Katz, J. J. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1979; Vol. IV, pp 1–59 and references therein.

(28) LaMar, G. N.; Walker, F. A. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1979; Vol. IV, pp 61–157 and references therein.

(29) Eaton, S. S.; Fishwild, D. M.; Eaton, G. R. *Inorg. Chem.* **1978**, *17*, 1542–1545.

(30) Eaton, S. S.; Eaton, G. R. *J. Am. Chem. Soc.* **1977**, *99*, 6594–6599 and references therein.

(31) LaMar, G. N.; Satterlee, J. D.; Snyder, R. V. *J. Am. Chem. Soc.* **1974**, *96*, 7137–7138. Snyder, R. V.; LaMar, G. N. *Ibid.* **1976**, *98*, 4419–4424.

(32) Storm, C. B.; Teklu, Y. *J. Am. Chem. Soc.* **1972**, *94*, 1745–1747.

(33) Eaton, S. S.; Eaton, G. R. *J. Am. Chem. Soc.* **1977**, *99*, 1601–1604.

(34) Walker, F. A.; Avery, G. L. *Tetrahedron Lett.* **1971**, 4949–4952.

(35) Hammett, L. P. *Trans. Faraday Soc.* **1938**, *34*, 156–165.

(36) Leffler, J. E.; Grunwald, E. "Rates and Equilibria of Organic Reactions"; Wiley: New York, 1963; pp 172, 173.

(37) Swain, C. G.; Lupton, E. C. *J. Am. Chem. Soc.* **1968**, *90*, 4328–4337.

(38) Walker, F. A.; Balke, V. L.; McDermott, G. A. *J. Am. Chem. Soc.*, **1982**, *104*, 1569–1574.

(39) Walker, F. A.; Benson, M., submitted for publication.

(40) Walker, F. A.; Reis, D.; Balke, V. L., submitted for publication.

(41) Freitag, R. A.; Mercer-Smith, J. A.; Whitter, D. G. *J. Am. Chem. Soc.* **1981**, *103*, 1226–1228.

(42) Meyer, E. F.; Cullen, D. L. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1979; Vol. III, pp 513–529 and references therein.

(43) Wolberg, A. *J. Mol. Struct.* **1974**, *21*, 61–66.

(44) Dayal, S. K.; Ehrenson, S.; Taft, R. W. *J. Am. Chem. Soc.* **1972**, *94*, 9113–9122.

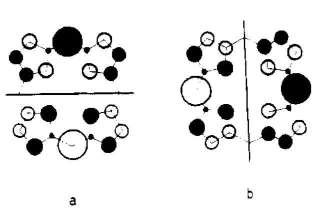

Figure 2. Electron density and nodal properties of the porphyrin 4e(π) orbitals,[46] which are the LUMOs of metal-free porphyrins and metalloporphyrins.[46,53] The light and dark shades represent orbital symmetry properties. The sizes of the circles depict the relative sizes of the squares of the atomic orbital mixing coefficients, c_i^2, for each atom and thus represent the relative electron density expected at that position. The 4e(π) orbitals shown in a and b are linear combinations of those shown in ref 46, which are appropriate for meso-substituted porphyrins. Compounds **2** and **3** are expected to utilize orbital a for resonance delocalization of para phenyl substituents while **5** is expected to utilize orbital b.

NMR evidence that the "resonance" contribution is that of π induction.

The reason that NMR spectroscopy should provide evidence for π conjugation in compounds such as those of Figure 1c, especially for compounds **2** and **5**, where three phenyl substituents are the same, may be understood if one considers the porphyrin π orbitals which are expected to be used for such π conjugation. The orbitals expected to be involved are the HOMO (for electron transfer from porphyrin to phenyl) and the LUMO (for electron transfer from phenyl to porphyrin). The HOMO is expected to be either A_{2u} or A_{1u} (typically the former)[45,46] and in either case a nondegenerate orbital of 4-fold symmetry,[45,46] whereas the LUMO is the degenerate E_g set which Longuet-Higgins et al.[46] call the 4e(π) orbitals. These orbitals are shown in Figure 2, redrawn from those shown earlier[45,46] as the hybrids of the original pair of 4e(π) orbitals; the hybrids are appropriate for meso-substituted porphyrins. In 4-fold symmetric TPP derivatives such as **1** and **6** of Figure 1c, the two 4e(π) vacant orbitals of Figure 2 are degenerate on the NMR time scale when N–H proton tautomerism is rapid (as it is at room temperature[32]). However, for compounds **2**, **3**, and **5** the molecular symmetry is lowered to 2-fold, and thus the degeneracy is expected to be lifted. This will cause one or the other of the 4e(π) orbitals to be favored for π conjugation. Orbital 2a should be favored for compounds **2** and **3**, while 2b is favored for compound **5**. Compound **4** would be expected to use one of the two original unhybridized 4e(π) orbitals[45,46] not shown in Figure 2.

Because of the 2-fold symmetric nature of the 4e(π) orbitals, placing one electron-donating substituent on the upper meso position (α) of Figure 2a (compound **2**; $X_1 = NEt_2$, X_2–X_4 = Cl) should place electron density not only at meso position α (top) but also at the γ position (bottom). Thus the pyrrole protons closest to meso position γ should feel a stronger ring current than those closest to meso positions β and δ, and NMR spectroscopy should give direct evidence of the importance of π conjugation. The preparation and investigation of the NMR spectra of the six compounds of Figure 1c and their Zn(II) complexes are the subject of this report.

Experimental Section

The compounds of Figure 1c were prepared by a variation of the Adler method:[47] 2 equiv of freshly distilled pyrrole (Eastman) and 1 equiv each of *p*-(diethylamino)benzaldehyde and *p*-chlorobenzaldehyde (both Aldrich) were refluxed together in propionic acid for 30 min. The reaction mixture was allowed to cool for 1 day. No crystals were obtained from the solution, and thus the product mixture plus side products were isolated by evaporating off the propionic acid, dissolving the resulting tarry solid in dichloromethane, and shaking with 6 M NH_4OH to remove traces of propionic acid and to deprotonate the diethylamino groups. The organic layer was then passed through a dry silica gel column (Baker chromatographic grade) to remove tar and side products. The column was eluted with dichloromethane, and the fractions were evaporated to dryness. The isomers **1**–**6** were separated on a gravity silica gel column packed with use of petroleum ether as solvent and eluted with 70% benzene–30% petroleum ether solution. The mass spectrum of compound **1** had peaks due to M^+, $M^+ - C_6H_4Cl$, $M^+ - 3C_6H_4Cl$, and the corresponding doubly charged ions; (diethylamino)phenyl-containing isomers were not sufficiently volatile for mass spectra to be obtained. All isomers gave satisfactory elemental analyses, although they tended to hold water and/or benzene of crystallization. Anal. Calcd for **1** (analyzed as the dihydrate, $C_{44}H_{30}N_4Cl_4O_2$): C, 67.0; H, 3.83; N, 7.10; Cl, 18.0; O, 4.1; N/Cl, 0.395. Found: C, 66.4; H, 3.90; N, 7.37; Cl, 18.4; O 3.9 (by difference); N/Cl 0.400. Calcd for **2** (analyzed as the monohydrate, benzene hemisolvate, $C_{51}H_{41}N_5Cl_3O$): C, 72.4; H, 4.88; N, 8.28; Cl, 12.6; O, 1.9; N/Cl, 0.658. Found: C, 73.1; H, 4.84; N, 8.54; Cl, 13.0; O, 0.5 (by difference); N/Cl, 0.658. Calcd for **4** (analyzed as the trihydrate, dibenzene solvate, $C_{64}H_{64}N_6Cl_2O_3$): C, 74.2; H, 6.23, N, 8.11; Cl, 6.84; O, 4.6; N/Cl, 1.19. Found: C, 74.7; H, 7.20; N, 7.43; Cl, 6.53; O, 4.1 (by difference); N/Cl, 1.14. Calcd for **5** (analyzed as the monohydrate, monobenzene solvate, $C_{62}H_{64}N_7ClO$): C, 77.7; H, 6.73; N, 10.2; Cl, 3.70; O, 1.7; N/Cl, 2.76. Found: C, 78.2; H, 6.99; N, 9.75; Cl, 3.58; O, 1.5 (by difference); N/Cl, 2.72. The presence of varying amounts of benzene and water of crystallization in individual preparations of each isomer was confirmed by NMR spectroscopy: peaks at 7.35 and ~1.3 ppm, respectively, could be decreased and eventually eliminated by repeated evaporation from $CDCl_3$.

The tetra-*p*-diethylamino isomer, compound **6**, was in small yield and did not elute well with the above solvent mixture. Quantity preparation of it was carried out by the Adler method[47] and purification accomplished by chromatography on silica gel with benzene as solvent. Spectroscopic properties of **6** in pyridine were similar to those reported by Datta-Gupta et al.[48] Anal. Calcd for **6** (analyzed as for the dihydrate, $C_{60}H_{70}N_8O_2$): C, 77.1; H, 7.54; N, 12.0, O, 3.4. Found: C, 77.8; H, 7.60; N, 11.1; O, 3.5 (by difference).

Zinc was inserted into several of the compounds by an adaptation of literature methods:[49] After the DMF solution cooled, an equal volume of dichloromethane was added and the mixture poured into a separatory funnel containing ca. 500 mL of H_2O. The organic layer was drawn off without shaking and then reintroduced into the separatory funnel in the presence of a fresh 500 mL of H_2O. It was shaken and separated and this step repeated two or three additional times to remove traces of DMF. The zinc complexes were chromatographed on silica gel with benzene as solvent.

Deuteriochloroform (Merck) was used as received. Several of the samples were evaporated from $CDCl_3$ before their NMR spectra were recorded to remove benzene of crystallization. Spectroscopic grade dichloromethane (Fisher) was used as solvent for UV–visible spectra.

The identity of the separated compounds was confirmed by NMR spectroscopy on a Varian EM-360 and where possible by mass spectrometry on a Du Pont 490B. UV–visible spectra were recorded on a Cary 17 spectrophotometer. Further NMR investigations were carried out on the 250-MHz spectrometer in the chemistry department at the University of California, Berkeley, CA.

Results

Table I lists the UV–visible spectral data obtained for compounds **1**–**6**. The UV–visible absorption maxima shift to longer wavelength as the number of diethylamino groups increases and will be discussed further in the Discussion section.

Figure 3 shows the aromatic region of the NMR spectra of **1**–**6**. The chemical shift and coupling data for β-pyrrole H, ortho and meta phenyl H, and N–H for **1**–**6**, H_2TPP, and several of its symmetrical derivatives and the Zn(II) complexes

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(45) Gouterman, M. *J. Chem. Phys.* **1959**, *30*, 1139–1161. Gouterman, M. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. III, pp 1–165.

(46) Longuet-Higgins, H. C.; Rector, C. W.; Platt, J. R. *J. Chem. Phys.* **1950**, *18*, 1174–1181.

(47) Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1967**, *32*, 476.

(48) Datta-Gupta, N.; Bardos, T. J. *J. Heterocycl. Chem.* **1966**, *3*, 495–502.

(49) Adler, A. D.; Longo, F. R.; Kampas, F.; Kim, J. *J. Inorg. Nucl. Chem.* **1970**, *32*, 2443–2448.

Table I. Absorption Maxima and Extinction Coefficients[a] of Tetraphenylporphyrin Free Bases in Methylene Chloride

compd	Soret shoulder	Soret	IV	III	II	I
1	402 (16.08)	418 (63.68)	514 (5.47)	548 (2.45)	589 (1.79)	648 (1.89)
2	405 sh	418 (53.0)[b]	516 (5.45)[b]	553 (3.22)[b]	589 (2.32)[b]	648 (1.57)[b]
3	*c*	416 (42.43)	518 (5.36)	568 (4.15)	588 (2.90)	653 (2.92)
4	*c*	410 (55.49)	514 (7.85)	559 (5.91)	583 (4.30)	649 (3.09)
5	414 (34.89)	440 (24.84)	521 (6.30)	573 (7.88)		661 (3.87)
6	421 (8.00)	445 (13.27)	530 (1.60)	585 (3.15)		672 (1.61)

[a] λ_{max} in nm; ϵ (in parentheses) in 10^3 M^{-1} cm^{-1}. [b] Extinction coefficients estimated. [c] Not observed.

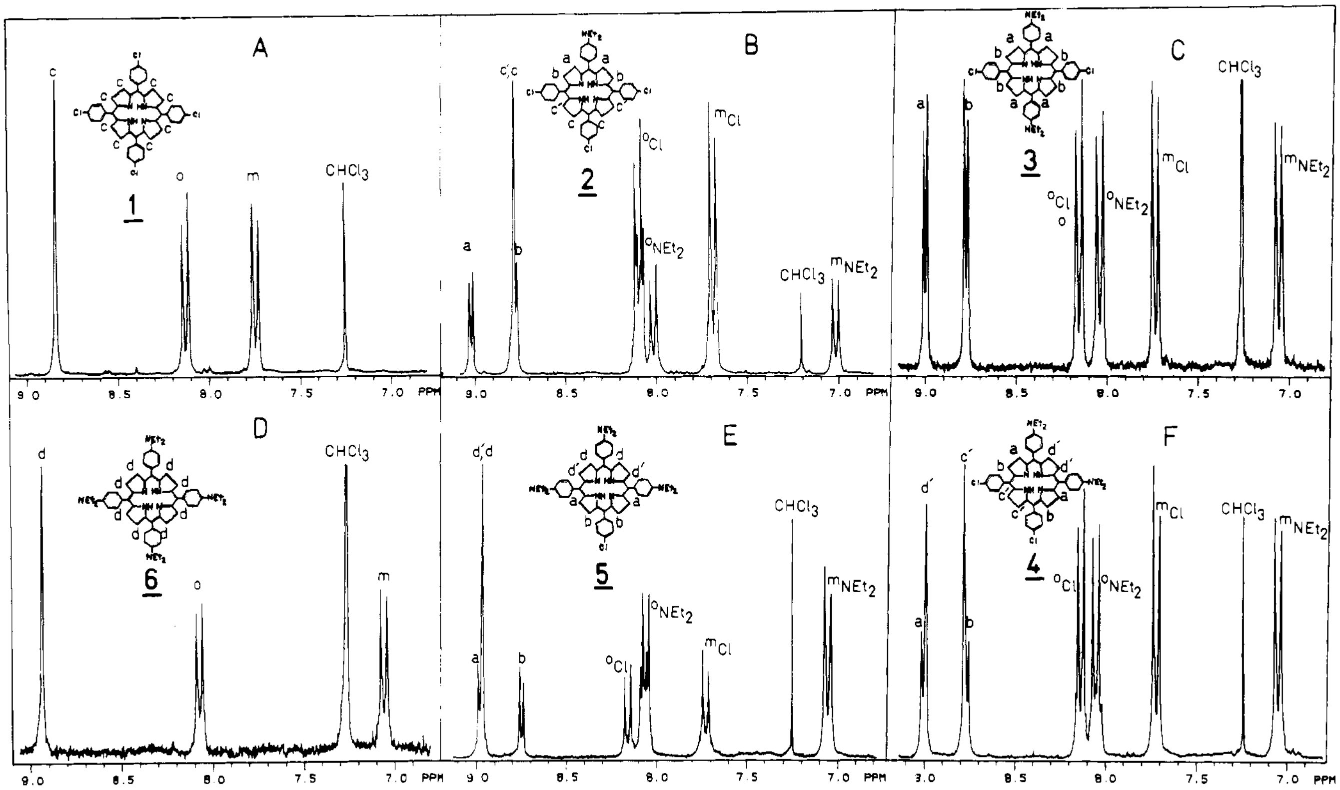

Figure 3. 250-MHz NMR spectra of the aromatic regions of the $H_2TPP(p\text{-}Cl)_x(p\text{-}NEt_2)_y$ series of compounds in $CDCl_3$ vs. Me_4Si. Symmetry labels a, b, c, c′, d, and d′ are discussed in the text.

of **2**, **4**, and **5** are summarized in Table II. Plots of the chemical shift data of Table II vs. the sum of the Hammett σ constants ($\sum\sigma$) of the phenyl substituents are shown in Figure 4.

Discussion

The electronic absorption spectra summarized in Table I for the six isomers of Figure 1c are listed with adoption of the numbering system (I–IV) for the visible bands used by Falk.[50] It has been shown by Gouterman[45] that the four visible bands of free-base porphyrins are due to the two possible transitions from A_{2u} to E_g porphyrin π orbitals each having a vibrational component. Bands I and III are ascribed to one transition (Q_x) and its vibrational component, and II and IV to the other transition (Q_y) and its vibrational component, respectively.[45] The energies Q_x and Q_y differ for the free-base porphyrins because the protons are fixed on two of the nitrogens during the time scale of the electronic absorption. The Soret band has been ascribed to the transition from A_{1u} to E_g,[45] and here the x and y components of E_g apparently do not lead to as large a separation in the energies of the two transitions. We observe "shoulders" on the Soret bands of four of the six isomers (not on **3** and **4**, Table I), and in one case (compound **5**), the intensities of "shoulder" and Soret bands are reversed. The cis (**4**) and trans (**3**) isomers of $(p\text{-}Cl)_2(p\text{-}NEt_2)(TPP)H_2$ do not exhibit shoulders. The energy difference between the "shoulder" and the Soret bands is approximately one-third that between I and III or II and IV in compounds **1** and **2**.

The visible bands I–IV, as well as the Soret, shift generally to longer wavelength as *p*-chloro groups are replaced by *p*-diethylamino groups. Furthermore, the relative intensities of bands I and IV change through the series in such a manner that there is a fair inverse correlation between ν_I or ν_{IV} and ϵ_I/ϵ_{IV} for compounds **1**–**6**. Similar trends are observed for the Zn(II) complexes of **1**–**6**, which will be discussed elsewhere.[51] Such correlations have been found previously for the α and β bands of metallotetraphenylporphyrins as the electronic properties of phenyl substituents[52] or electronegativities of axial ligands[53,54] are varied and have been correlated with changes in electron density in the porphyrin ring obtained from extended Hückel calculations on tin octaethylporphyrin dihalides (the halides are F, Cl, Br, and I).[54] Since band I of metal-free porphyrins is a component of what becomes the α band of metalloporphyrins, while band IV is a component of what becomes the β band, it is not surprising that the same general

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(50) Falk, J. E. "Porphyrins and Metalloporphyrins"; Elsevier: New York, 1964; pp 72–80, 89–93.

(51) McDermott, G. A.; Walker, F. A., manuscript in preparation.

(52) Shroyer, A. L. W.; Lorberau, C.; Eaton, S. S.; Eaton, G. R. *J. Org. Chem.* **1980**, *45*, 4296–4302.

(53) Nappa, M.; Valentine, J. S. *J. Am. Chem. Soc.* **1978**, *100*, 5075–5080.

(54) Gouterman, M.; Shcwarz, F. P.; Smith, P. D.; Dolphin, D. *J. Chem. Phys.* **1973**, *59*, 676–90.

Table II. Chemical Shifts of Tetraphenylporphyrin Protons[a]

compd	$\Sigma\sigma$[b]	pyrrole	*o*-phenyl	*m*-phenyl	N-H
$H_2(p\text{-}NO_2)_4TPP$	3.112	8.806	8.657 (8.7)	8.379 (8.7)	−2.95
H_2TPP	0.000	8.860	8.230 (7.0, 1.8)	7.758[c] (7.0)	−2.74
$H_2(p\text{-}CH_3)_4TPP$	−0.680	8.869	8.023 (7.7)	7.548 (7.7)	−2.78
$H_2(p\text{-}OCH_3)_4TPP$	−1.072	8.862	8.126 (8.4)	7.288 (8.4)	−2.75

$(p\text{-}Cl)_x(p\text{-}NEt_2)_y$TPP Isomers

compd	$\Sigma\sigma$	H_a	$H_{d',d}$	H_b	$H_{c',c}$	$o\text{-}H_{Cl}$	$o\text{-}H_{NEt_2}$	$m\text{-}H_{Cl}$	$m\text{-}H_{NEt_2}$	N-H
1	0.908				8.825	8.114 (8.0)		7.732 (8.0)		−2.86
2	−0.15	9.039 (4.8)		8.796 (4.8)	8.804	8.115 [2], 8.105 [1] (8.0)	8.030 (8.3)	7.705 (8.0)	7.037 (8.3)	−2.92
3	−1.21	8.988 (4.8)		8.763 (4.8)		8.145 (8.1)	8.030 (8.5)	7.726 (8.1)	7.046 (8.5)	−2.73
4	−1.21	9.005 (4.8)	8.898	8.765 (4.8)	8.780	8.134 (8.3)	8.052 (8.6)	7.720 (8.3)	7.050 (8.6)	−2.64
5	−2.26	8.967 (4.8)	8.952	8.737 (4.8)		8.145 (8.4)	8.059 [1], 8.045 [2] (8.5)	7.714 (8.4)	7.043 (8.5)	−2.56
6	−3.32		8.915				8.050 (8.5)		7.037 (8.5)	−2.52
Zn-1	0.908				8.932	8.132 (7.6)		7.740 (7.6)		
Zn-2	−0.15	9.123 (4.0)		8.885 (4.0)	8.891	8.123 [2], 8.116 [1] (8.3)	8.015 (8.0)	7.721 (8.3)	7.039 (8.0)	
Zn-4	−1.21	9.114 (4.0)	9.107	8.872 (4.0)	8.879	8.137 (8.3)	8.042 (8.7)	7.718 (8.3)	7.047 (8.7)	
Zn-5	−2.26	9.088 (4.8)	9.084	8.859 (4.8)		8.154 (8.2)	8.058 [1], 8.046 [2] (8.3)	7.712 (8.2)	7.045 (8.2)	
Zn-6	−3.32	9.059					8.067 (7.6)		7.061 (7.6)	

[a] Measured in $CDCl_3$, with Me_4Si as reference. Chemical shifts are in ppm, *J* coupling constants are in Hz, in parentheses, and relative intensities are shown in brackets. [b] Reference 36. The σ constant used for $-NEt_2$ is that of $-NMe_2$. [c] *p*-H at 7.769 ppm ($J = 7.0, 1.8$ Hz).

trends are observed for compounds **1–6**. However, although this general trend is followed, the appearance of the spectra (λ_{max}, ϵ; Table I) classifies them as belonging to one of three subgroups of very similar spectra: (a) those containing mostly chloro substituents (compounds **1** and **2**), (b) those containing equal numbers of chloro and diethylamino groups (compounds **3** and **4**), and (c) those containing mostly diethylamino groups (**5** and **6**). (Note that bands II and III have coalesced in these compounds.) The two compounds in each subgroup are more similar to each other in terms of the appearance of the visible spectral bands I–IV than they are to the next member of the series. Thus it appears that the effects of molecular symmetry cannot be clearly and simply utilized in explaining the electronic absorption bands, and therefore the *number* of diethylamino vs. chloro groups is the major perturbing factor on the electronic absorption spectra of this series of compounds.[55] This conclusion is quite different from that reached from study of the NMR spectra of isomers **1–6**, now to be discussed.

The aromatic regions of the 250-MHz NMR spectra of the six isomers of $H_2TPP(p\text{-}Cl)_x(p\text{-}NEt_2)_y$ of Figure 1c, numbered in order of their elution from the chromatography column, are shown in Figure 3. Also included in Figure 3 are symmetry labels for the types of pyrrole H. There are four possible types of pyrrole protons, based upon the identity of their nearest and next-nearest neighbors: H_a have *p*-(diethylamino)phenyl groups as nearest and *p*-chlorophenyl groups as next-nearest meso neighbors, while H_b have the reverse. H_c have *p*-chlorophenyl groups as both nearest and next-nearest meso neighbors, while H_d have *p*-(diethylamino)phenyl groups as both types of meso neighbors. Further subclassification of c and d can be made if third-nearest meso neighbors are considered: we define type c as those that have a *p*-chlorophenyl group as third-nearest neighbor (six atoms away from the carbon carrying H_c) and c′ as those that have a *p*-(diethylamino)phenyl in that position. Likewise, type d pyrrole protons are those which have a *p*-(diethylamino)phenyl group as the third-nearest meso neighbor, and d′ are those that have a *p*-chlorophenyl group in that position. The differentiation of c and c′ or d and d′ by NMR shift would be evidence of π conjugation, as suggested by Figure 2 and the discussion at the end of the Introduction. As it turns out, this subclassification of c, c′ and d, d′ is not necessary to explain the spectra of Figure 3, since their NMR shifts (c, c′ in **2** and d, d′ in **5**) are identical (see discussion below).

In a comparison of the pyrrole-H patterns and chemical shifts observed for the six compounds of Figure 3 and the chemical shift data for phenyl H and N–H presented in Table II, several conclusions can be drawn regarding the effect of electron-donating and -withdrawing substituents on the chemical shifts and splitting patterns of the pyrrole protons, as well as phenyl H and N–H.

Considering first the pyrrole protons, it is evident that para phenyl substituents in symmetrical tetrasubstituted H_2TPPs cause a slight upfield pyrrole-H shift if the substituent is electron withdrawing (*p*-Cl: $\sigma = +0.227^{36}$) (Figure 3A, Table II) and a downfield pyrrole-H shift if the substituent is electron donating (*p*-NEt_2: $\sigma \approx -0.83^{56}$) (Figure 3D, Table II) with respect to H_2TPP (*p*-H: $\sigma = 0.00^{36}$) (Table II). In fact, for a series of tetra-para-substituted TPPs, both pyrrole-H and N–H resonance positions vary linearly with the sum of the Hammett σ constants of the substituents (Figure 4).

The total chemical shift difference between tetra-*p*-chloro and tetra-*p*-diethylamino derivatives of H_2TPP is 0.090 ppm. The mixed phenyl-substituted isomers of Figure 3B,C,E,F have two pyrrole-H environments, on the basis of their observed chemical shifts, one (8.74–8.83 ppm) for those protons im-

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(55) It has been suggested (Gouterman, M., personal communication) that the reason that the electronic absorption spectra of metal-free porphyrins and metalloporphyrins do not appear to respond to the lowered symmetry inherent in unsymmetrically substituted porphyrins such as those of the present study is that the absorption bands are too broad to allow such effects to be observed. This broadening is, in the tetraphenylporphyrins, presumably due to the wide distribution of angles between phenyl and porphyrin planes that are present at the instant of electronic excitation and thus the wide range of potential resonance (whether by π induction or π conjugation) interactions between porphyrin and phenyl rings on the time scale of electronic spectroscopy.

(56) The σ constant for *p*-NEt_2 was assumed to be approximately equal to that for *p*-NMe_2.[36]

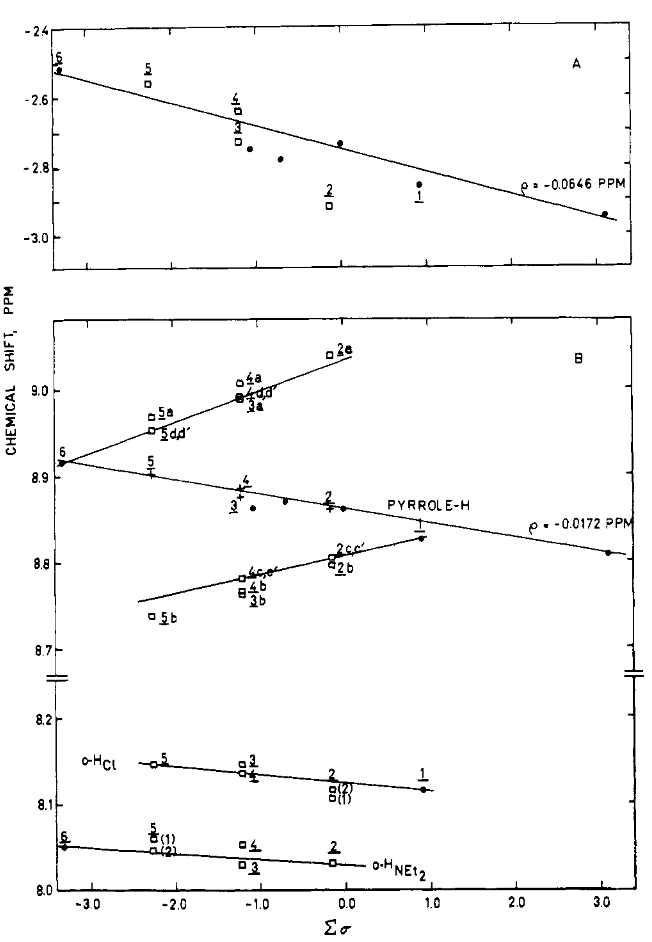

Figure 4. Linear free energy relationship between (A) N–H proton chemical shift or (B) pyrrole-H and ortho phenyl-H chemical shift and the sum of the Hammett σ constants ($\sum\sigma$) of the phenyl substituents. Legend: filled circles, chemical shifts of symmetrically tetra-para-substituted H_2TPPs; crosses, weighted average chemical shifts of pyrrole-H protons of unsymmetrically para-substituted H_2TPPs; squares, observed chemical shifts of unsymmetrically para-substituted H_2TPPs. Least-squares slopes (ρ) of the linear free energy relationships for pyrrole H and N–H are also given.

mediately next to meso positions carrying a *p*-chlorophenyl group (types b,c′,c, Figure 3B,C,E,F) and one (8.92–9.04 ppm) for those immediately next to meso positions carrying a *p*-(diethylamino)phenyl group (types a,d′,d, Figure 3B,C,E,F). The weighted average chemical shift of the pyrrole H of **2**–**5** lies on the same line as do the tetrasubstituted H_2TPPs discussed above (Figure 4), but the individual pyrrole H resonances of types b,c,c′ and a,d,d′ vary more in the opposite direction than does the average pyrrole-H resonance, when plotted against $\sum\sigma$ (Figure 4). The two lines b,c,c′ and a,d,d′ are nearly parallel, with an average separation of ca. 0.2 ppm. This separation we will call the "nearest-neighbor substituent effect". Our interpretation and explanation of the opposite slopes of the two individual lines b,c,c′ and a,d,d′ will be discussed below.

Pyrrole rings in which one proton is near a *p*-chlorophenyl (H_b) and the other is near a *p*-(diethylamino)phenyl (H_a) have their proton resonances split into an AB quartet, which is reduced almost to first order at 250 MHz (J = 4.8 Hz). The two nearly first-order doublets are centered slightly "outside" the resonance positions of the unsplit signals of $H_{c,c'}$ and $H_{d,d'}$ in isomers **2**, **4**, and **5**, with H_a being centered 0.015 ppm *downfield* from $H_{d,d'}$ in **4** and **5** and H_b centered 0.008–0.015 ppm *upfield* from $H_{c,c'}$ in **2** and **4** (see Figure 4). Thus H_a and H_b feel a slight (0.008–0.015-ppm) effect from the electron-donating or -withdrawing effect of their next-nearest neighbor. No splitting of H_c and $H_{c'}$ or H_d and $H_{d'}$ is observed at 250 MHz for compounds **2** and **5**, respectively, and therefore the electronic effect of the third-nearest meso neighbor is unmeasurably small at 250 MHz. Thus there is no evidence of π conjugation as suggested by Figure 2 and the last paragraph of the Introduction. Rather, the electronic effects of substituents on the meso phenyl rings on the pyrrole proton environments of the porphyrin attenuate rapidly, with the effect at H_b being less than a tenth of that at H_a in **2**. *No evidence exists in the pyrrole-H NMR patterns of Figure 3 of π delocalization of these effects to other pyrrole-H positions of the porphyrin ring.*

Further evidence for the lack of electron delocalization by direct π conjugation is found in the ortho phenyl-H resonances of compounds **2** and **5**. All ortho H in tetraphenylporphyrins and their diamagnetic metal complexes are subject to a deshielding effect (downfield shift) as a result of the porphyrin ring current, because the ortho phenyl protons lie outside the perimeter of the ring.[34] Because the expected electron density in the $4e(\pi)$ orbitals of Figure 2 is largest at the meso positions, placement of one electron-donating phenyl substituent at meso position α (compound **2**) should increase the electron density at the opposite (trans) meso position (γ) as compared to that at the cis (β and δ) meso positions. Thus the ortho phenyl H of the trans (γ) *p*-chlorophenyl group should be shifted further downfield than those of the cis (β and δ) *p*-chlorophenyl groups if π conjugation is important. Indeed, close scrutiny of the *o*-H_{Cl} doublets of **2** shows that two resonances do occur, of relative intensities 1:2. However, the *o*-H_{Cl} doublet of relative intensity 1 (γ) is slightly *upfield* of that of relative intensity 2 (β and δ), indicating that the *trans*- (γ) *p*-chlorophenyl group is subject to a *weaker* ring current than are the *cis*- (β and δ) *p*-chlorophenyl groups. Since this is in the opposite direction from that predicted above for direct π conjugation, the *o*-H resonance of the *trans-p*-chlorophenyl group of **2** (and likewise the *o*-H resonance of the *trans-p*-(diethylamino)phenyl group of **5**) provides further evidence of the lack of direct π conjugation. Instead, we see that the larger ring current at the cis (β and δ) meso positions, as evidenced by the slightly downfield positioning of the *o*-H peaks of the *cis-p*-chlorophenyl groups (Figures 3 and 4), is consistent with the conclusion reached above that the inductive effect felt at the pyrrole position closest to the unique substituent drops off rapidly as one progresses away from that meso position: Enough inductive effect reaches as far as the cis meso positions so as to make them *slightly* more electron rich than the trans meso position. In fact, some electron density may actually be "stolen" from the trans meso position, as discussed in the next paragraph.

Rather than direct π conjugation, the NMR shifts of the pyrrole protons (as well as the ortho phenyl H) of **1**–**6**, as summarized by Figure 4, give evidence of the importance of π induction: With a focus first on the pyrrole H, those adjacent to *p*-NEt_2-bearing phenyl groups are shifted *away* from the average line as the number of *p*-Cl-bearing phenyl groups increases (a,d,d′ line). Likewise, pyrrole H adjacent to *p*-Cl-bearing phenyl groups shift away from the average line as the number of *p*-NEt_2-bearing phenyl groups increases (b,c,c′ line). Thus, considering the effect from the *p*-NEt_2 point of view, the meso positions bearing the *p*-NEt_2 substituents appear to "rob" π-electron density (ring current) from distant parts of the π system to build up those regions closest to the *meso-p*-(diethylamino)phenyl substituents. Thus, for compound **2**, H_a feels a large ring current (larger than it should, according to the "average" behavior), while H_b and $H_{c,c'}$ have been "robbed": H_b, which is in the same pyrrole ring as H_a, has been robbed of slightly more electron density than $H_{c,c'}$. Proceeding through the series, we see the same behavior, scaled to the relative number of diethylamino and chloro groups, of compounds **3**, **4**, and **5**. For **5**, H_a still feels a larger ring current than it should, according to the behavior of **6**, **1**, and the other symmetrical H_2TPPs of Table II and Figure 4, but here it is joined by $H_{d,d'}$, so that the amount of electron density "robbed" from the H_b carbons is only about one-third of what it was in compound **2**. Note, however, that H_a, which is adjacent to H_b in the same pyrrole ring, still has a slightly greater downfield (ring current) shift than $H_{d,d'}$, thus indicating that the two meso positions adjacent to H_a are able to "rob" that meso position adjacent to H_b slightly better than the meso position opposite the *p*-chlorophenyl group. The same explanation accounts for the fact that the ortho H of the opposite (trans) phenyl group in **2** appears to have been "robbed" of a small amount of ring current and that of **5** appears to have slightly more than its β and δ neighbors.

The proton NMR spectra of compounds **1**–**6** appear to allow distinction between the two possible modes of transfer of resonance effects from phenyl substituents to the porphyrin ring which could not be distinguished in the Ni(II) and V(IV) TPP axial ligation studies:[11] Moderate conjugation must be ruled out on the basis of the pyrrole-H chemical shifts observed in **1**–**6**, leaving π induction as the major means of transfer of the resonance capability of X, when placed on a phenyl ring, into the porphyrin plane. In addition, σ induction is probably involved, as suggested from the Ni(II) and V(IV) ligation studies.[11]

The effect of substituting a diamagnetic metal (Zn^{2+}) for the two N–H protons on the patterns and chemical shifts of the protons of **1**–**6** is very small (Table II): The pyrrole-H protons are shifted ~0.09–0.13 ppm downfield, but the $H_{a,b}$ coupling constant remains the same, and $H_{c,c'}$ and $H_{d,d'}$ each remain equivalent. Linear relationships such as those shown in Figure 4 exist for Zn(II) complexes of **1**–**6**. Little effect on the phenyl protons is observed. Thus, the conclusions reached above concerning the importance of π induction and lack of importance of π conjugation appear to hold equally well for metal-free and diamagnetic metallotetraphenylporphyrins. (The effect of this π induction on the NMR spectra of paramagnetic metallotetraphenylporphyrins is, however, dramatic, as is discussed elsewhere.[38])

The effect of phenyl substitution on the N–H proton shifts of metal-free TPPs (Table II, Figure 4) provides further evidence for the lack of π conjugation between substituent X and the porphyrin ring. The N–H protons, which are inside the perimeter of the ring and thus experience a strong upfield ring current shift,[27,32,57] should be indicative of changes in the average strength of the ring current, since they exchange rapidly among the four porphyrin nitrogens at ambient temperatures.[32] The variation in N–H chemical shift is linear for symmetrical H_2TPPs, as well as for most of the unsymmetrical H_2TPPs of this series, and has the same sign slope (negative) as the line for the average pyrrole-H shifts for the same series of compounds. If the variation in N–H chemical shift were a ring current effect only, its slope should be *opposite* in sign from that of the pyrrole H. Since it is not, and since its magnitude is so much greater, it appears that the variation in N–H chemical shift among this series of compounds is overwhelmingly controlled by basicity effects (σ bonding). In this light, it may be that the deviation of compound **2** from the N–H linear free energy line is related to the unsymmetrical distribution of electron density at the porphyrin nitrogens of **2** which may stabilize the tautomer that has the two protons on adjacent rather than opposite[32,33] nitrogens. That **5** does not deviate significantly from the linear free energy correlation line may suggest more rapid proton tautomerism for **5** than for **2**. These possibilities are under further investigation.

Finally, the question might be raised as to whether the pyrrole protons are affected by changes in the ring current of the nearby phenyl groups caused by changes in para substituent, since the pyrrole-H protons are, on the average, situated *inside* the perimeter of the adjacent meso phenyl ring and thus potentially susceptible to an upfield shift due to the shielding ring current effect of the phenyl.[58] From the data presented in Figures 3 and 4 and Table II it appears that this is, at most, a minor factor affecting the chemical shift of the pyrrole protons, since the pyrrole-H protons adjacent to *p*-(diethylamino)phenyl groups are shifted *downfield* (i.e., responding to their being *outside* the perimeter of the porphyrin ring current loop, which we view as being particularly electron rich at the meso positions to which *p*-(diethylamino)phenyl groups are attached), rather than upfield, as they would be if they were responding to being inside the ring of the electron-rich *p*-(diethylamino)phenyl group.

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Registry No. **1**, 22112-77-2; Zn-**1**, 29116-33-4; **2**, 82044-64-2; Zn-**2**, 82044-65-3; **3**, 82044-66-4; **4**, 82044-67-5; Zn-**4**, 82044-68-6; **5**, 82044-69-7; Zn-**5**, 82044-70-0; **6**, 14609-52-0; Zn-**6**, 82044-71-1.

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(57) Abraham, R. J. *Mol. Phys.* **1961**, *4*, 145–152.

(58) Abraham, R. J.; Jackson, A. H.; Kenner, G. W.; Warburton, D. *J. Chem. Soc.* **1963**, 853–862.