Electronic Effects in Transition Metal Porphyrins. 5. Thermodynamics of Axial Ligand Addition and Spectroscopic Trends of a Series of Symmetrical and Unsymmetrical Derivatives of Tetraphenylporphinatozinc(II)

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The electronic spectra and equilibrium constants for addition of 3-picoline to a series of symmetrically and unsymmetrically phenyl-substituted ZnTPP derivatives have been measured. It is found that the α band energy varies slightly nonlinearly with the sum of the Hammett sigma constants of the substituents within the series $(p\text{-Cl})_x(p\text{-NEt}_2)_y$*TPPZn(II), while the smaller variation in the β band appears to be linear. The log of the intensity ratio of the α and β bands, log* A_β/A_α*, however, varies linearly with the band energies of both the α and β bands for both 4- and 5-coordinate complexes of unsymmetrical as well as symmetrical ZnTPP derivatives. Likewise, log* K_{eq} *for 3-picoline addition varies linearly with the sum of the Hammett sigma constants for all complexes investigated. Thus the electronic effects of unsymmetrically placed substituents are averaged by the metal Zn to yield a Lewis acid strength toward 3-picoline which is dependent only upon the sum of the electronic effects and not on the identity of the substituents or the symmetry of their distribution.*

Introduction

The degree and mode of transmission of electronic effects to and from various points on the porphyrin ring through the sigma and pi orbitals of the four porphyrin nitrogens to the central metal have long been an interest of those who have investigated the physical properties and chemical reactions of metalloporphyrins [2–32]. Because of the conjugated nature 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 [2, 4], the rate of N–H tautomerism in free base porphyrins [26, 27], the chemical shifts of pyrrole and N–H protons in tetrapehnylporphyrins [25, 28, 29], rates of phenyl rotation [29–31] and porphyrin inversion [31, 32] in metallotetraphenylporphyrins, visible absorption spectra [24], rate [9] and equilibrium [10–16] constants for axial ligation, redox potentials [12, 16–20] of both porphyrin ring and metal redox reactions, and metal incorporation rates [21–23]. In almost all cases involving symmetrical tetraphenylporphyrins and their metal complexes (except for references 23, 24 and 31) the above physical properties have been shown to correlate with the sigma constants of the Hammett equation [33–35],

$$P_x = 4\sigma_x\rho \qquad (1)$$

where P_x is the observed physical property of a compound having substituent X, σ_x is the Hammett substituent constant of X, and ρ describes the sensitivity of the property under study to the electron-withdrawing or -donating properties of X.

In the case of axial ligation reactions to the metallotetraphenylporphyrins, where $P_x = \log K_{eq}$, linear free energy relationships with the Hammett σ-constants have been shown to exist for the reactions of Lewis bases with V(IV) [11], Fe(II) [18], Fe(III) [13, 18], Co(II) [12], Ni(II) [11], and Zn(II) [14] complexes of symmetrically substituted tetraphenylporphyrins. For addition of one ligand to V(IV), Co(II), and Zn(II)TPPs, ρ values range from 0.113 to 0.188 [11, 12, 14], whereas for addition of two ligands to Ni(II), $\rho = 0.331$ [11] and to Fe(III), where the product is an ion pair, $\rho = -0.39$ [13]. Thus electron-withdrawing substituents favor axial ligation to +2 charged metals by making the metal a better Lewis acid, while the same electron-withdrawing substituents disfavor bis-axial ligation to +3 charged metals because a positive charge must be localized on the metal ion product [13].

Recently we have undertaken an investigation of the effects of unsymmetrical phenyl substitution on the physical properties and chemical reactivity of metal-free [25], Zn(II) [16, 25], and Fe(III) [16, 36] tetraphenylporphyrins. We have found that metal-free and Zn(II) derivatives of the series $H_2TPP(p\text{-Cl})_x(p\text{-NEt}_2)_y$, Fig. 1, behave according to equation (2),

$$P_{(X,Y)} = (\Sigma\sigma_{X,Y})\rho \qquad (2)$$

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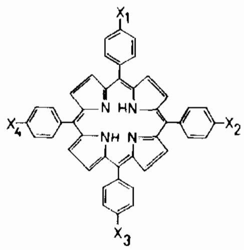
with respect to their weighted average pyrrole proton resonance position and also with respect to their individual pyrrole-H positions, although with ρ of opposite sign [25]. (Definitions in Equation 2 are as follows: $P_{(X,Y)}$ is the physical property of an unsymmetrically substituted tetraphenylporphyrin having various numbers of X and Y as its phenyl substituents, and $\Sigma\sigma_{X,Y}$ is the sum of the Hammett substituent constants for the number of X and Y present.) We have also shown that a large series of (m- or p-X) (m- or p-Y)$_3$TPPZn(II) complexes behave according to equation (2) with respect to electrochemical oxidation, but not reduction, of the porphyrin ring [16]. In terms of iron TPPs, we have shown that the average pyrrole–H isotropic shift of the slow-spin Fe(III) bis-N-methylimidazole complexes [36], as well as the average slopes and intercepts of the Curie plots [37], Fe(III)/(II) redox potentials [16], and g-anisotropies [16, 38] of unsymmetrically substituted Fe(III)TPPs behave according to equation (2), but that the difference in isotropic shift of the individual types of pyrrole–H in unsymmetrically substituted low-spin Fe(III)TPPs varies with $\sigma_X - \sigma_Y$ [36]. These results have been explained in terms of the electron density distribution in the porphyrin π orbital(s) being probed in each of these studies [16, 36–38]. In the case of axial ligation reactions of metallotetraphenylporphyrins, the effects of unsymmetrical substitution on the periphery of the molecule should be averaged at the metal center, and log K_{eq} should thus behave according to equation (2). We have tested this hypothesis for Zn(II) and Fe(III) derivatives of unsymmetrically substituted tetraphenylporphyrins and found it to hold for Zn(II) but not for Fe(III) [39]. The results of the Zn(II) study are the subject of this report.

Experimental

Preparation and characterization of the series of $H_2TPP(p\text{-}Cl)_x(p\text{-}NEt_2)_y$ isomers of Fig. 1 and their Zn(II) adducts has been reported previously [25]. Other Zn(II)TPP derivatives were prepared according to literature procedures [40, 41]. All ZnTPPs were chromatographed in subdued light shortly before use, with silica gel (Baker chromatographic grade) as stationary phase and benzene or benzene/petroleum ether (70/30) as moving phase. Following evaporation of the eluting solvent, the ZnTPPs were dried for at least one hour at 100 °C before use.

Toluene (MCB reagent grade) was distilled from sodium and stored over molecular sieves (Linde 4A). The ligand 3-picoline (Aldrich) was distilled and stored over molecular sieves.

The visible spectra were run on a Cary 17 recording spectrophotometer. Constant temperature (25.0 ± 0.1°) was maintained by circulating thermostatted bath water through a jacketed 1 cm cell containing the sample. The reference cell was not jacketed. Cells were allowed to equilibrate for at least five minutes before recording the spectra.



I $X_1 = X_2 = X_3 = X_4 = Cl$
II $X_1 = X_2 = X_3 = Cl,\ X_4 = NEt_2$
III $X_1 = X_3 = Cl,\ X_2 = X_4 = NEt_2$
IV $X_1 = X_2 = Cl,\ X_3 = X_4 = NEt_2$
V $X_4 = Cl,\ X_1 = X_2 = X_3 = NEt_2$
VI $X_1 = X_2 = X_3 = X_4 = NEt_2$

Fig. 1. Structures of the tetraphenylporphyrins of major interest to this study.

Stock solutions were prepared by volumetric dilutions of weighed amounts of the ZnTPP derivative and of a 1.00 mL amount of 3-picoline. Successive 1:10 dilutions of the base were made to obtain suitable concentrations. A fixed aliquot of porphyrin and the desired amount of base were mixed and diluted to 5.00 mL and the spectrum recorded after thermal equilibration. Data analysis was carried out according to methods described previously [42].

Results and Discussion

Positions and Intensities of the α and β Bands

Figure 2 shows a typical example of the change in the visible spectra of $(p\text{-}Cl)_4$TPPZn and $(p\text{-}NEt_2)_4$-TPPZn as a function of added 3-picoline. The existence of well-formed isosbestic points is typical of the entire series of complexes of this study, thus confirming that only one 3-picoline molecule is added in each case. Table I summarizes the values of $\bar{\nu}_{max}$ of the α and β bands of the 4- and 5-coordinate forms of the series of symmetrical and unsymmetrical ZnTPPs of this study and the ratio A_α/A_β observed for the two coordination numbers of the complexes. While the energy of the β (higher-energy) bands of both 4- and 5-coordinate forms of the ZnTPPs of this study vary linearly with $\Sigma\sigma_{X,Y}$, (where the σ-constant for p-NEt_2 is taken to be -0.60, based on arguments presented below) the α bands show clear curvature, for the unsymmetrically substituted complexes, as illustrated in Fig. 3.

It has been shown that the α band is a combination of bands I and III of the free base porphyrins and is a result of the (O–O) vibrational component of the electronic transition, which is vibrationally forbidden [43, 44]. As such, the intensities of bands I and III of the free bases, as well as the α bands of metalloporphyrins, depend upon changes in the peripheral symmetry of the molecule. The β band, however, is believed to be a combination of bands

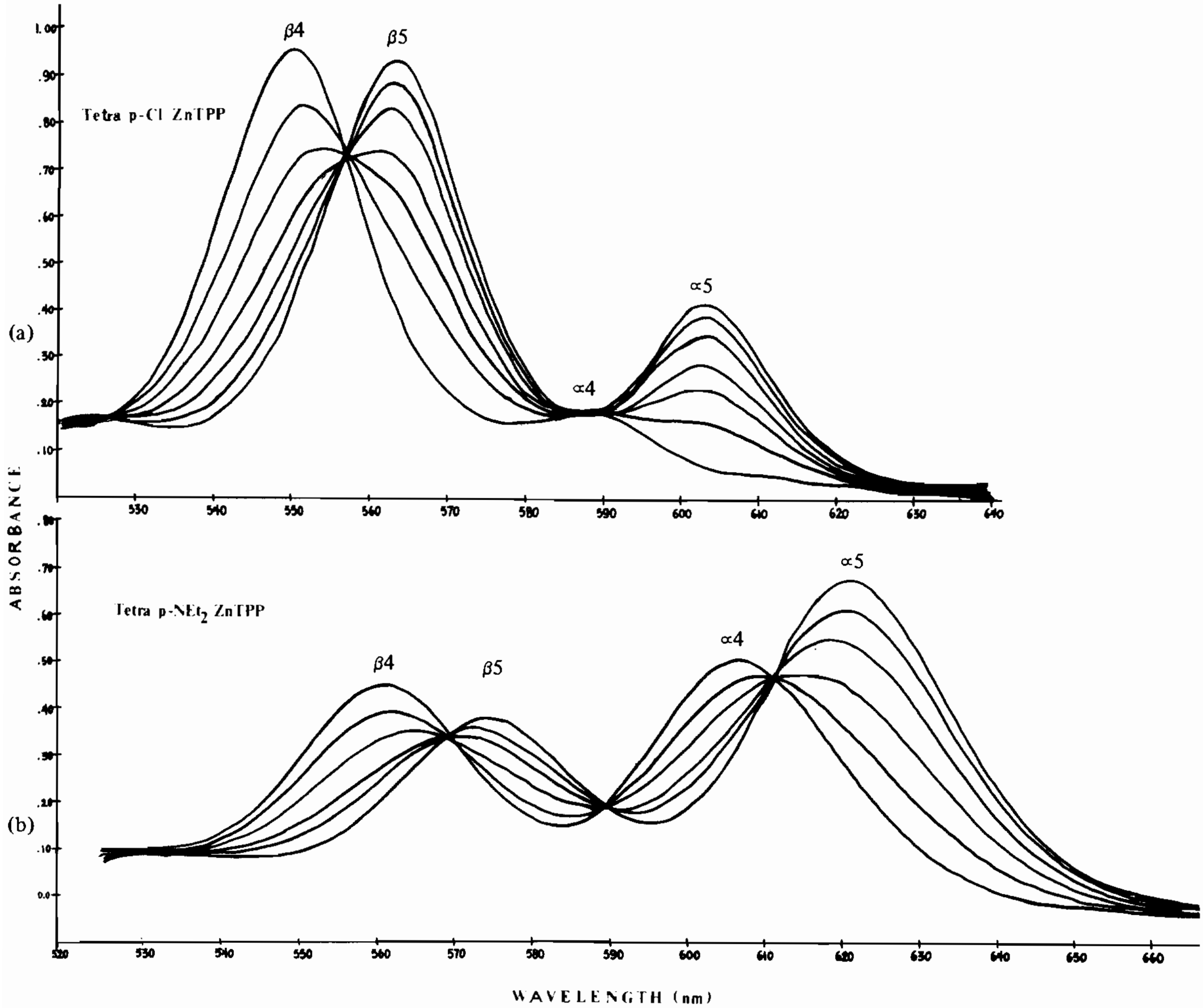


Fig. 2. Visible spectral changes observed upon addition of 3-picoline to (a) $(p\text{-Cl})_4$TPPZn, 4.11×10^{-5} *M* and (b) $(p\text{-NEt}_2)_4$-TPPZn, 4.15×10^{-5} *M* in toluene solution at 25.0 ± 0.1 °C.

TABLE I. Peak Positions and Intensity Ratios of the α and β Bands of 4- and 5-Coordinate ZnTPPs in Toluene.

Phenyl substituent(s)	$\Sigma\sigma$[a]	4-coord			5-coord		
		$\bar{\nu}_\alpha$[b]	$\bar{\nu}_\beta$[b]	$\frac{A_\beta}{A_\alpha}$	$\bar{\nu}_\alpha$[b]	$\bar{\nu}_\beta$[b]	$\frac{A_\beta}{A_\alpha}$
4 *m*-NO_2	2.840	16.72	18.08	6.63	16.58	17.73	3.48
4 *p*-Cl	0.908	17.01	18.19	5.00	16.59	17.76	2.19
1 *m*-$NHCOCH_3$	0.210	16.99	18.20	7.85	16.60	17.77	2.22
none	0.000	17.02	18.21	5.74	16.63	17.79	2.13
none	0.000	16.98[c]	18.20[c]	5.92[c]	16.61[c]	17.79[c]	2.31[c]
1 *p*-$NHCOCH_3$	−0.010		18.52		16.61	17.79	1.95
3 *p*-Cl, 1 *p*-NEt_2	0.08[d]	16.78	18.07	2.41	16.42	17.70	1.35
2 *p*-Cl, 2 *p*-NEt_2, *trans*	−0.75[d]	16.64	17.99	1.61	16.30	17.56	0.98
2 *p*-Cl, 2 *p*-NEt_2, *cis*	−0.75[d]	16.67	17.99	1.58	16.31	17.55	0.95
1 *p*-Cl, 3 *p*-NEt_2	−1.57[d]	16.59	17.93	1.24	16.22	17.53	0.77
4 *p*-NEt_2	−2.40[d]	16.49	17.83	0.89	16.11	17.44	0.60

[a] Taken from references 34 and 35. [b] $\bar{\nu}$ in kK. [c] Ref. 47. [d] The σ constant used for *p*-NEt_2 is −0.60 (see text).

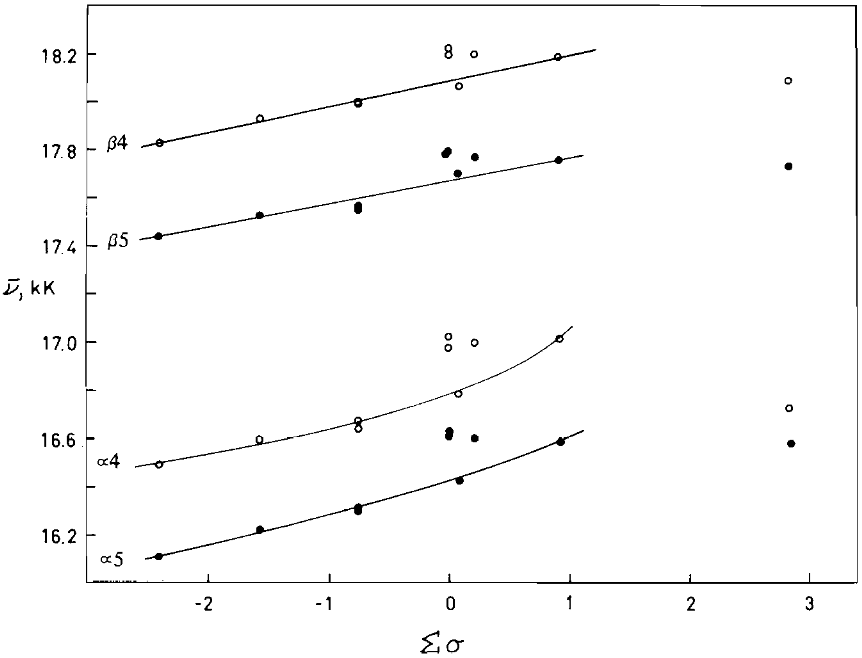


Fig. 3. Dependence of $\bar{\nu}_\alpha$ and $\bar{\nu}_\beta$ for both 4- and 5-coordinate ZnTPPs on the sum of the Hammett σ-constants of the substituents.

II and IV of the free bases, which are a result of the (O-1) vibrational component of the electronic transition [43, 44]. Since this transition is allowed, it is believed that the β band of metalloporphyrins should be less sensitive to peripheral changes in the molecule [43]. Such has previously been found to be the case for $Sn(Etio)X_2$, X = F, Cl, Br, I [45], and it is clearly the case in the present work, as evidenced by Fig. 3. First we should stress the fact that $\bar{\nu}_\alpha$ and $\bar{\nu}_\beta$ for both 4- and 5-coordinate forms of the complexes of this study shift to lower energy as the electron-donating nature of the combined substituents increases (as $\Sigma\sigma_{X,Y}$ decreases), and that both α and β shift to lower energy as one goes from the 4-coordinate ZnTPP form to the 5-coordinate 3-picoline adduct. Both of these phenomena can be explained in terms of Gouterman's conclusion that the shift in electron density from the metal to the periphery of the molecule results in spectral transitions which are shifted to lower energy [43]. Thus, when an axial ligand such as 3-picoline is added to the metalloporphyrin, electron density is added to the system. Some of this added electron density is transferred from the metal toward the periphery of the molecule, resulting in a shift to lower energy of the α and β bands. The ability of the electron density provided by the axial ligand to transfer from the metal toward the periphery depends upon the electronegativity of the metal. This electronegativity is influenced by the phenyl substituents: Those which contribute peripheral electron density will shift the α and β bands to lower energy. Such is the case of the compounds of this study (Fig. 3).

The fact that $\bar{\nu}_\alpha$ does not shift linearly with $\Sigma\sigma_{X,Y}$ for the unsymmetrically substituted ZnTPPs and their 3-picoline adducts may be related to the lower symmetry of the unsymmetrical ring systems of *2–5*, which could cause splitting of the π^* orbitals of the porphyrin (4e(π) in the terminology of Longuet-Higgins *et al.* [46], or $e_g(\pi^*)$ in the terminology of Gouterman [43]). Such splitting was postulated previously [16] to explain the fact that while the oxidation potentials (to form cation radicals and dications) of unsymmetrically substituted ZnTPPs behave no differently than their symmetrical counterparts, the reduction potentials (to form anion radicals and dianons) are more positive than their $\Sigma\sigma_{X,Y}$ would have predicted, in comparison to symmetrical counterparts. Since the electron(s) are added to the porphyrin LUMO, which is the 4e(π) (or $e_g(\pi^*)$) set [43–46], splitting of this set would make electron addition to the lower energy of the two more favorable than if the degeneracy of the orbitals had not been split. Since it is this same 4e(π) set which is the excited state for the electronic transitions of both the α and β bands [43–46], the same splitting could account for the lower energy, especially of the more sensitive α band, than predicted by the linear correlation of symmetrical ZnTPPs. However, one would have expected that such splitting of the 4e(π) orbitals would lead to a broadening or splitting of the α and β bands, and neither are observed.

Recently Nappa and Valentine showed [47] that the intensities of the α and β bands of ZnTPP, as well as their positions, varied with solvent and added axial ligand. They interpreted their results by theorizing that the axial ligand changed the electronegativity of the porphyrin which in turn caused a change in the intensity ratio of the α and β bands. They could not, however, rule out the possibility that the various axial ligands pulled the Zn(II) atom out of the porphyrin plane by different amounts and thereby produced an additional contribution to the varying intensity ratio. The present system provides an excellent opportunity to determine the effect of porphyrin electronegativity on the intensity ratio of the α and β bands for a series of 4-coordinate complexes in a common solvent and a series of 5-coordidinate complexes having a common fifth ligand. Qualitatively we note from Fig. 2 and Table I that the β band is taller for $(p\text{-Cl})_4$TPPZn and its 3-picoline adduct, while the α band is taller for $(p\text{-NEt}_2)_4$-TPPZn and its adduct.

Plots of A_β/A_α *vs.* $\bar{\nu}_\alpha$ and $\bar{\nu}_\beta$ show the general trend observed by Nappa and Valentine [47] but are curved. Thus, in Fig. 4 we have plotted log A_β/A_α *vs.* $\bar{\nu}_\alpha$ and $\bar{\nu}_\beta$ for 4- and 5-coordinate complexes of this study. The series of six isomers $(p\text{-Cl})_x(p\text{-NEt}_2)_y$-TPPZn fit this relationship with high linear correlation, while other *o*-, *m*- and *p*-substituted ZnTPP derivatives and the data of Nappa and Valentine [47] show a poorer fit. Thus, within a closely related series of metalloporphyrins, log A_β/A_α varies linearly with $\bar{\nu}_\alpha$ and $\bar{\nu}_\beta$. It is interesting to note that this correlation holds so well within a series of complexes belonging to different symmetry groups (*1* and *6*, D_{4h}, *2* and *5*, C_{2v}, *3*, D_{2h}, and *4*, C_{2v}, but with a different proper axis than *2* and *5*), when the intensities of the α and β bands are influenced by vibronic coupling [43, 44].

Equilibrium Constants for 3-Picoline Addition

The equilibrium constants for formation of the 5-coordinate 3-picoline adducts of *1*–*6* and several other symmetrically substituted ZnTPP derivatives at 25.0 ± 0.1 °C in toluene solution are listed in Table II and plotted *vs.* $\Sigma\sigma_{X,Y}$ in Fig. 5. The σ-constant for p-NEt$_2$ was taken to be −0.60 based upon the following arguments: 1) Though the σ-constant for p-NEt$_2$ is not available, that for p-NHEt is −0.61 [48], and that for -NHMe is −0.84 [48]. Making the alky chain longer reduces the magnitude of the σ-constant (−0.51 for $p\text{-NHC}_4\text{H}_9$ [48], presumably due to the more bulky alkyl group interfering with the lone pair orbital of nitrogen entering into conjugation with the aromatic ring. Adding the second alkyl group appears to reduce the magnitude of σ (p-NHMe, −0.84 [48]; p-NMe$_2$, −0.83 [33–35, 48]). Thus it would appear that σ for p-NEt$_2$ should be slightly less negative than −0.61. 2) In our previous studies involving the p-NEt$_2$ substituent in addition to a significant range of other substituents, the p-NEt$_2$ data point generally falls off the line of best fit when the σ-constant for p-NMe$_2$ is used (see for example reference 16, Figs. 3 and 8). Current studies of the Fe(III)TPP + N-MeIm system also strongly imply that log β_2 for the tetra-p-NEt$_2$ complex is more consistent with $\sigma = -0.60$ [49]. 3) With $\sigma = -0.60$ for p-NEt$_2$, the slope of the linear free energy plot of Fig. 5 more

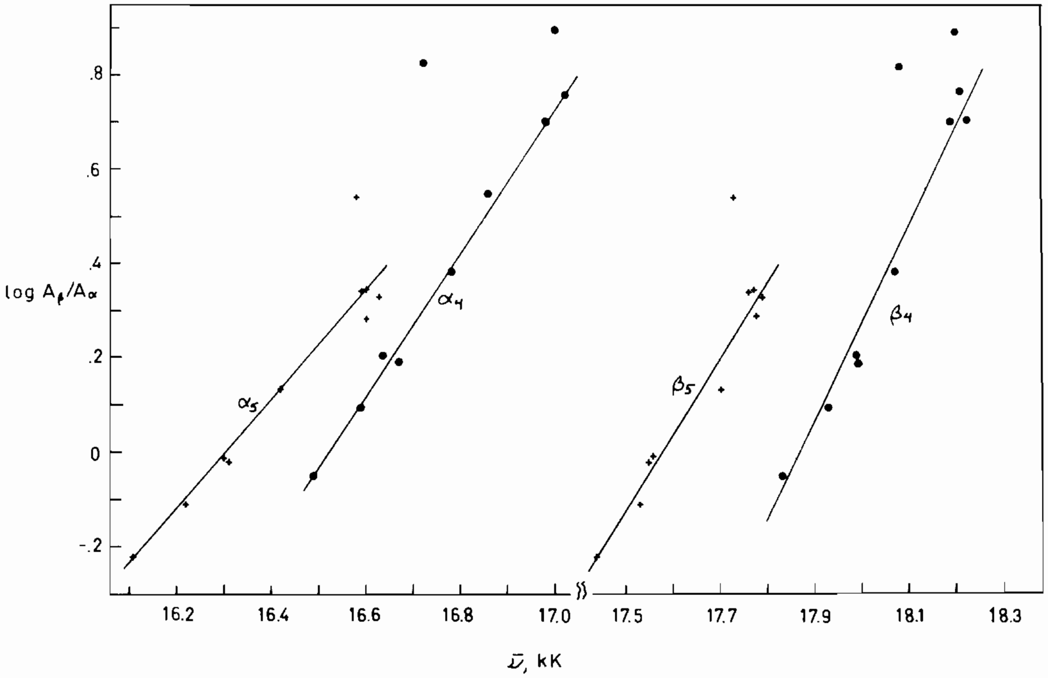


Fig. 4. Dependence of log A_β/A_α on $\bar{\nu}_\alpha$ and $\bar{\nu}_\beta$ for both 4- and 5-coordinate ZnTPP derivatives in toluene solution.

TABLE II. Equilibrium Constants for 3-Picoline Addition to a Series of ZnTPPs in Toluene Solution[a].

Phenyl substituents	$\Sigma\sigma$[b]	K_{eq}	Reference
4 m-NO_2	2.840	22,310 ± 4990	This work
4 p-Cl	0.908	10,280 ± 990	This work
1 o-$NHCOCH_3$	0.70[c]	9,060 ± 700	42
1 m-$NHCOCH_3$	0.210	4,140 ± 990	This work
3 p-Cl, 1 p-NEt_2	0.08[d]	7,120 ± 1,680	This work
none	0.000	6,850 ± 1,020	This work
none	0.000	4,850 ± 800	42
1 p-$NHCOCH_3$	−0.010	7,880 ± 1,410	This work
2 p-Cl, 2 p-NEt_2, *trans*	−0.75[d]	5,720 ± 980	This work
2 p-Cl, 2 p-NEt_2, *cis*	−0.75[d]	5,460 ± 1,200	This work
1 p-Cl, 3 p-NEt_2	−1.57[d]	3,450 ± 580	This work
4 p-NEt_2	−2.40[d]	2,560 ± 640	This work

[a] Temperature = 25.0 ± 0.1 °C. [b] Taken from references 34 and 35. [c] Estimated [16, 49]. [d] The σ-constant used for p-NEt_2 is −0.60 (see text).

closely approaches that found by Vogel and Beckman [14] for addition of pyridine to symmetrically *meta*- or *para*-substituted ZnTPPs in benzene solution at 25 °C. Since the equilibrium constants found by Vogel and Beckman for pyridine addition in benzene solution [14] are very similar to those for 3-picoline addition in toluene solution (Fig. 5), it is reasonable to expect the slopes (ρ) to be similar. (Use of $\sigma = -0.83$, the value for p-NMe_2 [33–35, 48], as we had done previously, yields $\rho = 0.150$.) This conclusion does appear to break down somewhat for the three most electron-withdrawing members of the earlier study (m-F, m-Cl, m-Br) [14], causing Vogel and Beckman's slope to be slightly larger than that of the present study (0.188 *vs.* 0.180). It is, however, most disconcerting to note the wide range of values obtained for the reaction of the parent compound, ZnTPP, with either 3-picoline or pyridine. Several previously reported values [10, 14, 50, 51] are included in Fig. 5 for comparison. The two values obtained in this laboratory for reaction of 3-picoline with ZnTPP in toluene, $K_{eq} = 4830\ M^{-1}$ [42] and 6350 M^{-1} (this work) differ by 40%. The same sample of ZnTPP was used in both cases, though it was freshly chromatographed and dried immediately before use in each case. Vogel and Beckman's value of K_{eq} for pyridine addition to ZnTPP in benzene was low compared to the other ZnTPP derivatives studied, and it and $(m\text{-}OCH_3)_4TPPZn$ were not included by them in their calculation of ρ [14]. Our present value for 3-picoline addition in toluene is also low compared to the other ZnTPP derivatives of this study. The only explanation for these anomalies which we can offer at the present time is that ZnTPP may more tenaciously hold a water ligand, due to more efficient crystal packing in the absence of appended m- or p-substituents, than do the substituted ZnTPPs, thus making drying temperature and length of time more critical for the parent complex than for its m- and p-substituted analogs. This is, however, not a particularly satisfying explanation.

It is clear from the data of Fig. 5 that all of the ZnTPP derivatives of this study (except for the

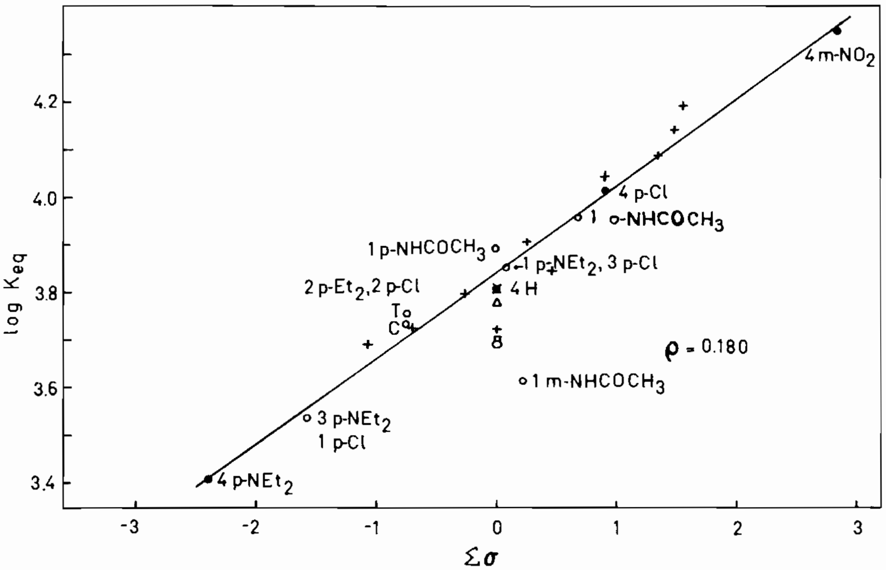


Fig. 5. Plot of log K_{eq} for ligand addition to ZnTPP derivatives *vs.* the sum of the Hammett σ-constants of the substituents. Circles: 3-picoline in toluene at 25.0 ± 0.1 °C (solid circles = symmetrically tetra-substituted, open circles = unsymmetrically substituted); crosses: pyridine in benzene at 25 °C, all compounds symmetrically substituted [14]; oval, ZnTPP + 3-picoline in toluene [42]; square, ZnTPP + pyridine in benzene [50]; triangle, ZnTPP + pyridine in benzene [10]; X, ZnTPP + pyridine in benzene [51].

mono-*m*-NHCOCH$_3$ derivative, discussed below) behave according to equation (2), irrespective of whether the four substituents are identical or are mixed. The slope of the linear correlation of log K_{eq} and $\Sigma\sigma_{X,Y}$, Fig. 5, is 0.180 ± 0.007. This value is compared to the ρ values for other ligand addition reactions to metallotetraphenylporphyrins in Table III. At least for those systems studied in toluene solution, it appears that the sensitivity of K_{eq} for single ligand addition increases with the number of d-electrons. This is probably mainly a result of the decreasing size of the metal ions as the first transition series is traversed. If so, one would expect such a correlation to exist within a specific type of base (pyridine or piperidine or imidazole) due to differences in the importance of σ and π bonding effects in each of these systems. However, not enough data are available for different types of bases and different metalloporphyrins to allow definitive conclusions to be drawn, and the differences observed so far are small.

We wish to stress the fact that unsymmetrically substituted ZnTPP derivatives behave no differently than their symmetrically substituted counterparts, *i.e.*, all ZnTPPs behave according to equation (2), where $P_{X,Y} = \log K_{eq}$ for 3-picoline addition. This adherence to equation (2) includes the mono-*o*-* and *p*-acetamido-substituted TPP derivatives of Zn(II), but not the mono *m*-acetamido derivative. We have previously reported that the Fe(III) derivatives of acetamido-substituted TPPs have been found to be anomalous in their nmr spectra [36], redox potentials [16], as well as equilibrium constants for addition of N-methylimidazole [49]. The *m*-acetamido substituent appears to be the 'most' anomalous, both for Zn(II) (Fig. 5) and Fe(III) [49]. Thus we conclude that except for the anomalous *m*-acetamido substituent, the hypothesis presented in the Introduction that electronic effects of unsymmetrically placed substituents should be averaged at the metal is upheld for the ZnTPP system. In contrast, for the Fe(III)TPP system, for which preliminary results have been discussed [16], this appears not to be the case: Unsymmetrically para-substituted derivatives of TPPFeCl have quite different values of β_2 for addition of two N-methylimidazoles than do their symmetrically substituted counterparts [16]. Further investigation of the Fe(III) system and exploration of the reasons for the fact that equation (2) is not obeyed is in progress [49].

Acknowledgements

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TABLE III. Summary of Hammett Rho Values for Ligand Addition to Metallotetraphenylporphyrins.

Metal	d-electron configuration	Ligand	#added	Solvent	K_H^{a}	ρ^{b}	Ref.
VO^{2+}	d^1	Piperidine	1	Toluene	0.40 M^{-1}	0.113 ± 0.003	11
Fe^{3+}	d^5	Pyridine	2	DMF	2.5 M^{-2}	−0.433	18
Fe^{3+}	d^5	N-Methylim.	2	CHCl$_3$	1500 M^{-2}	−0.39	13
Fe^{2+}	d^6	Pyridine	2	DMF	2.5 × 10^5 M^{-2}	0.127	18
Co^{2+}	d^7	Pyridine	1	Toluene	3680 M^{-1}	0.145 ± 0.017	12
Ni^{2+}	d^8	Piperidine	2	Toluene	0.38 M^{-2}	0.331 ± 0.005	11
Zn^{2+}	d^{10}	Pyridine	1	Benzene	5300 M^{-1}	0.188 ± 0.007	14
Zn^{2+}	d^{10}	3-Picoline	1	Toluene	6950 M^{-1}	0.180 ± 0.007	This work

^{a}Equilibrium constant for the parent (H-substituted) compound, taken as the intercept of the linear plot. ^{b}The rho value is calculated from equation 1 or 2, as appropriate.

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*The σ-constant for *o*-NHCOCH$_3$ is taken to be +0.7 based upon the redox potential of its low-spin Fe(III) complex [16].

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