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## Substituent Effects in Noncoplanar $\pi$ Systems. *ms*-Porphins

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**Abstract:** Visible and near ultraviolet absorption spectra of substituted *ms*-tetraphenylporphins, *ms*-tetraalkylporphins, and their acid dications show increasing bathochromic shifts relative to *ms*-tetraphenylporphin itself with increasing electron-donating power of the substituents. Simultaneous increases in the transition dipole ratios of the Q(0-0) and Q(0-1) band visible transitions and in the basicity of the pyrrole nitrogens are also observed in these same series. Changes of the largest magnitude are seen for the acid dications. Composite Hammett  $\sigma$  plots including both inductive and resonant terms correlate best for a predominantly resonant contribution. This indicates that resonance interactions may be strongly significant even for those instances where other physical data suggest that the phenyl and porphin  $\pi$  systems are very noncoplanar.

Because of its structural features, the *ms*-tetraphenylporphin molecule is a good model system for the study of substituent effects transmitted via composite  $\pi$  systems. Previous work by the present authors<sup>2a</sup> and others<sup>2b</sup> suggested that despite the noncoplanar configuration of the phenyl and porphin planes,<sup>3-5</sup> resonance-type substituent effects are predominant. Since these observations are in variance with some well-accepted notions on the requirements for resonance-type interactions, it appeared worthwhile to undertake further investigations on the effects of substituents on some features of the chemistry of *ms*-tetrasubstituted porphins. In the present work we investigated the effects of structural variation on the absorption spectra and basicity of meso-tetrasubstituted porphins and the possible implications thereof on the nature of the interactions of peripheral substituents with the porphin ring system.

### Experimental Section

The porphyrins were prepared and characterized by previously described methods.<sup>6,7</sup> Approximately  $2.0 \times 10^{-5} M$  solutions were prepared in DMF (Baker Spectroquality with 1% H<sub>2</sub>O). Changing from "dry" DMF to that containing 4% H<sub>2</sub>O produced no detectable effect on the spectra. Beer's law was obeyed in the concentration range  $10^{-4}$  to  $10^{-6} M$  indicating that aggregation effects on the absorption spectra under these conditions can be excluded. Fluorescence excitation spectroscopy of the solvents checked that no fluorescing impurities were present.

Acid dication solutions of about  $6.7 \times 10^{-6} M$  were prepared with 1.6 *M* HClO<sub>4</sub> including 3.9 *M* H<sub>2</sub>O in DMF. No detectable absorption due to the free bases could be observed at this acidity and further additions of acid did not cause any further detectable changes in the absorption spectra.

Visible and near ultraviolet absorption spectra were recorded on a Cary Model 14 spectrophotometer. Titrations with 70% aqueous HClO<sub>4</sub>, at 25°, were carried out on the DMF solutions in the 3 ml cuvette directly. Emission spectra were obtained on a Hitachi Perkin-Elmer Fluorescence Spectrophotometer Model MPF-2A.

### Results

Absorption spectra of the para-substituted *ms*-tetraphenylporphins, of two ortho-substituted *ms*-tetraphenylporphins, and of some *ms*-tetraalkylporphins are summarized in Table I.

As the electron-donating character of the substituent increases, the typical "etio" type spectrum as seen in T(*p*-CN)PP, with ( $\epsilon_I < \epsilon_{II} < \epsilon_{III} \leq \epsilon_{IV}$ ), gradually changes into a new type ( $\epsilon_{II} < \epsilon_I < \epsilon_{III} \leq \epsilon_{IV}$ ) as seen, in T(*p*-OH)PP, at the other extreme.<sup>17</sup>

In particular, the following gradual spectral changes are observed with increasing electron-donating power of the para substituents: (a) all peaks shift to the red, and (b) the ratios of the transition dipoles of the Q(0-0) (I and III peaks) to the Q(0-1) (II and IV peaks) bands,<sup>18</sup> correspondingly, increase markedly. This is mainly due to changes in the oscillator strengths of the 0-0 transitions, varying by about 100% between the two extreme members of the series, while the oscillator strengths of the 0-1 transitions only vary by about 20%.

Substituent effects on the spectra of the acid dications of the para-substituted compounds are parallel in all cases to the effects in the corresponding free bases (cf. Table II), with frequency shifts up to four times larger than in the free base spectra.

If direct steric interaction between substituents and the porphin ring, as, e.g., in T(*o*-CH<sub>3</sub>)PP or T(*o*-OC<sub>2</sub>H<sub>5</sub>)PP, is present, the peaks shift to the blue, and the oscillator strength ratios  $f_I/f_{II}$  and  $f_{III}/f_{IV}$  decrease. This effect of ortho substituents has been previously noted by other workers.<sup>8</sup>

Substituent induced changes in the absorption spectra of the tetraphenylporphins in several other solvents such as toluene, benzene, and CHCl<sub>3</sub> were similar in sign and magnitude to those measured in the *N,N*-dimethylformamide

Table I. Visible and Near Uv Spectra of *ms*-Tetraphenyl- and *ms*-Tetraalkylporphyrins in DMF<sup>a</sup>

No.	Compd	Peak No. I		Peak No. II		Peak No. III		Peak No. IV		Peak No. V (SORET)	
		$\lambda$ , nm	$f$	$\lambda$ , nm	$f$	$\lambda$ , nm	$f$	$\lambda$ , nm	$f$	$\lambda$ , nm	$f$
1	T( <i>p</i> -SO <sub>2</sub> CH <sub>3</sub> )PP	644.5	0.009	588.9	0.019	547.7	0.021	513.8	0.074	418.5	1.469
2	T( <i>p</i> -CN)PP	644.9	0.009	589.2	0.019	548.2	0.024	514.0	0.082	419.0	1.713
3	T( <i>p</i> -Cl)PP	646.1	0.010	589.7	0.019	548.9	0.026	514.0	0.083	417.9	1.812
4	T( <i>p</i> -Br)PP	646.2	0.011	590.0	0.020	548.9	0.026	514.6	0.078	418.3	1.652
5	TPP	646.6	0.015	589.8	0.017	548.1	0.025	513.8	0.076	416.7	1.712
6	T[ <i>p</i> -( <i>i</i> -C <sub>3</sub> H <sub>7</sub> )]PP	649.0	0.013	592.6	0.018	551.6	0.033	516.3	0.072	419.0	1.502
7	T( <i>p</i> -CH <sub>3</sub> )PP	648.9	0.013	592.2	0.017	550.5	0.030	515.2	0.073	418.4	1.712
8	T( <i>p</i> -OCH <sub>3</sub> )PP	651.4	0.015	594.5	0.015	555.0	0.040	517.9	0.068	421.3	1.691
9	T( <i>p</i> -CH <sub>2</sub> CONH)PP	651.5	0.016	594.8	0.016	555.9	0.041	518.5	0.066	420.0	1.462
10	T( <i>p</i> -OH)PP	653.2	0.017	596.0	0.016	557.7	0.045	519.5	0.062	422.7	1.555
11	T( <i>o</i> -CH <sub>3</sub> )PP	644.5	0.006	588.8	0.017	544.5	0.016	512.0	0.077	415.0	1.784
12	T( <i>o</i> -OC <sub>2</sub> H <sub>5</sub> )PP	651.6	0.013	591.3	0.019	546.2	0.021	513.4	0.081	418.0	1.544
13	T(CH <sub>3</sub> )P	662.4	0.010	603.4	0.009	552.6	0.018	518.8	0.040	413.0	0.828
14	T(C <sub>2</sub> H <sub>5</sub> )P	656.4	0.010	597.0	0.011	549.6	0.018	517.7	0.042	414.5	0.855
15	T(C <sub>3</sub> H <sub>7</sub> )P	656.8	0.010	598.5	0.010	551.1	0.018	518.9	0.042	415.3	0.886
16	T(C <sub>4</sub> H <sub>9</sub> )P	658.0	0.010	599.6	0.010	552.0	0.015	518.5	0.042	415.9	0.954
17	T(C <sub>8</sub> H <sub>17</sub> )P	658.3	0.011	599.9	0.010	552.1	0.020	519.0	0.046	416.2	1.172

$af = 4.32 \times 10^{-9} f \epsilon \bar{\nu}$  = oscillator strength. Error estimates:  $\lambda \pm 0.2$  nm;  $f \pm 5\%$ .

Table II. Visible and Near Uv Spectra of the Acid Dications of *ms*-Porphyrins

No.	Compd	Peak No. I		Peak No. II		Peak No. III (Soret)	
		$\lambda$ , nm	$f$	$\lambda$ , nm	$f$	$\lambda$ , nm	$f$
1	T( <i>p</i> -CN)PPH <sub>2</sub> <sup>2+</sup>	653.5	0.18	602.0	0.055	444.8	1.81
2	T( <i>p</i> -Cl)PPH <sub>2</sub> <sup>2+</sup>	661.0	0.24	610.0	0.038	443.6	1.97
3	T( <i>p</i> -Br)PPH <sub>2</sub> <sup>2+</sup>	661.6	0.25	610.0	0.038	444.8	2.01
4	TPPH <sub>2</sub> <sup>2+</sup>	658.8	0.24	608.0	0.038	441.7	1.94
5 <sup>a</sup>	T( <i>p</i> -CH <sub>3</sub> )PPH <sub>2</sub> <sup>2+</sup>	671.9	0.27			445.6	1.71
6 <sup>a</sup>	T[ <i>p</i> -( <i>i</i> -C <sub>3</sub> H <sub>7</sub> )]PPH <sub>2</sub> <sup>2+</sup>	670.7	0.27			445.1	1.77
7 <sup>a</sup>	T( <i>p</i> -OCH <sub>3</sub> )PPH <sub>2</sub> <sup>2+</sup>	694.7	0.38			452.5	2.02
8 <sup>a</sup>	T(CH <sub>2</sub> CONH)PPH <sub>2</sub> <sup>2+</sup>	695.7	0.46			458.0	1.96
9 <sup>a</sup>	T( <i>p</i> -OH)PPH <sub>2</sub> <sup>2+</sup>	707.9	0.47			455.4	1.88
10	T( <i>o</i> -CH <sub>3</sub> )PPH <sub>2</sub> <sup>2+</sup>	635.2	0.12	583.8	0.042	434.0	1.89
11	T( <i>o</i> -OC <sub>2</sub> H <sub>5</sub> )PPH <sub>2</sub> <sup>2+</sup>	651.1	0.18	597.0	0.037	446.9	1.91
12	T(CH <sub>3</sub> )PH <sub>2</sub> <sup>2+</sup>	630.7		582.8			
13	T(C <sub>2</sub> H <sub>5</sub> )PH <sub>2</sub> <sup>2+</sup>	627.5		590.9			
14	T(C <sub>3</sub> H <sub>7</sub> )PH <sub>2</sub> <sup>2+</sup>	629.2		582.3			
15	T(C <sub>4</sub> H <sub>9</sub> )PH <sub>2</sub> <sup>2+</sup>	630.5		582.8			
16	T(C <sub>6</sub> H <sub>13</sub> )PH <sub>2</sub> <sup>2+</sup>	630.8		583.9			
17	T(C <sub>7</sub> H <sub>15</sub> )PH <sub>2</sub> <sup>2+</sup>	631.0		583.5			
18	T(C <sub>8</sub> H <sub>17</sub> )PH <sub>2</sub> <sup>2+</sup>	630.0		584.2			

<sup>a</sup> Band II was too small to be resolved from band I in these compounds. Error estimates:  $\lambda \pm 0.2$  nm;  $f \pm 5\%$ .  $f = 4.32 \times 10^{-9} f \epsilon \bar{\nu}$ .

(hereafter DMF) solutions. Substituent effects due to changes in solvent-solute interactions upon substituents can therefore be ruled out. More significantly for the present purposes the absence of any significant effects on the effects of substitution shows that the observed substituent effects are truly intramolecular, and solvent-mediated transmission of substituent effect from the para-phenyl positions to the porphyrin ring can be ruled out.

The (0-0) transitions in the fluorescence spectra of tetraphenylporphyrins characteristically exhibit their maximum at a wavelength  $7 \pm 1$  nm longer than the corresponding 0-0 absorption peaks in all of the substituted TPP structures. Substituent induced shifts of the fluorescence spectra are thus equal within the experimental error limits to the shifts in the absorption spectra.

If electron-donating groups such as alkyl functions are substituted directly on the bridge carbons of porphyrin itself rather than on the phenyl substituents of TPP, a larger shift to the red and a larger increase in the ratios  $f_{III}/f_{II}$  and  $f_{III}/f_{IV}$  result. Thus, while T(*p*-CH<sub>3</sub>)PP and T[*p*-(*i*-C<sub>3</sub>H<sub>7</sub>)]PP are barely shifted from TPP, the tetraalkylporphyrins are the most red shifted of all the compounds examined. Within the tetraalkylporphyrin series, ethyl through *n*-octyl, a gradual

small shift to the red is observed as the alkyl chain length increases. However, tetramethylporphyrin is more red shifted than its position in this series would indicate. This may be indicative of a significant hyperconjugative effect for this molecule.<sup>9</sup> While large shifts are also seen for the acid dications of these tetraalkylporphyrins, we feel that the peaks are not well enough resolved to justify oscillator strength calculations on our present data.

Other differences between the spectra of the tetraalkylporphyrins and tetraphenylporphyrins are: in the tetraalkylporphyrins (i) the emission peak maxima of the 0-0 band are at a wavelength only  $2 \pm 1$  nm longer than the corresponding emission bands; (ii) distortion with broadening of the peak shapes is observed for band II; and (iii) the maxima of band I of the acid dications is at a shorter wavelength than in the free bases. It is interesting to note that in all these aspects T(*o*-CH<sub>3</sub>)PP behaves as the tetraalkylporphyrins rather than like the para-substituted tetraphenylporphyrins.

Effects on the observed acid dissociation constants show trends similar to the substituent-effected spectral shifts. The observed constant is defined as  $pK_{\text{obsd}} = -\log(\text{HClO}_4)_{1/2}$ , which is the midpoint concentration of the acid as obtained from a spectrophotometric titration with per-

Table III. Observed Dissociation Constants of Substituted *ms*-Tetraarylporphyrin Dications

Compd	$pK_{\text{Obsd}}$	Compd	$pK_{\text{Obsd}}$
T( <i>p</i> -CN)PP	0.62	T( <i>p</i> -OCH <sub>3</sub> )PP	2.31
T( <i>p</i> -Cl)PP	1.29	T( <i>p</i> -CH <sub>3</sub> CONH)PP	2.57
TPP	1.74	T( <i>p</i> -OH)PP	3.16
T( <i>p</i> -CH <sub>3</sub> )PP	1.85	T( <i>o</i> -CH <sub>3</sub> )PP	0.78
T[ <i>p</i> -( <i>i</i> -C <sub>3</sub> H <sub>7</sub> )]PP	2.16	T( <i>o</i> -OC <sub>2</sub> H <sub>5</sub> )PP	1.46

chloric acid. There is a marked progressive increase in  $pK_{\text{obsd}}$  in going from the electron-withdrawing T(*p*-CN)PP to the strongly electron-donating T(*p*-OH)PP (Table III).

## Discussion

(1) **The Theoretical Significance of the Spectral and Chemical Substituent Effects.** The direction of the trend of spectral shift observed in TPPH<sub>2</sub><sup>2+</sup> dications and free base tetraarylporphyrins in this work can be qualitatively interpreted on the basis of the four-orbital model of porphyrins<sup>10,11</sup> (Figure 1). For the  $a_{1u}$  orbitals the electron densities are largest on the pyrrole carbon atoms and the methene bridges lie on nodal planes. On the other hand, the  $a_{2u}$  electron densities are largest on the methene carbons and pyrrole nitrogens. (It should be pointed out that the  $a_{1u}$  and  $a_{2u}$  notations used in the above discussion are strictly applicable only for  $D_{4h}$  (TPPH<sub>2</sub><sup>2+</sup>) symmetries.) When the energies of the  $a_{1u}$  and  $a_{2u}$  orbitals are equal, mixing of the ( $a_{1u}e_g$ ) and ( $a_{2u}e_g$ ) configurations causes the transition dipoles of the state  $Q_1 = (1/\sqrt{2})(a_{1u}e_g - a_{2u}e_g)$  to vanish.<sup>11</sup>

Symmetrical substitution on the methene bridges affects mainly the  $a_{2u}$  orbital. It is expected that electron-donating substituents will raise the energy of this orbital by increasing its electron density. This will lead to a decrease in the energy of the transition and a concomitant increase in its oscillator strength due to the removal of the accidental degeneracy of the  $a_{2u}$  and  $a_{1u}$  orbitals. These predictions are consistently verified by the progressive shifts to longer wavelengths in the visible bands with increasingly stronger electron-donating substitution on the methene bridge carbon atoms, and the concomitant systematic changes in the oscillator strengths as observed.

The assumption that the intensity changes are due mainly to the raising of the  $a_{2u}$  orbital is supported by the monotonic relation between the transition dipole ratios and the frequency shifts as is predicted by the four-orbital model (cf. Figure 2). In all cases, intensities of the forbidden 0-0 transitions are affected much more significantly than those of the 0-1 bands, where perturbation by vibronic coupling has already removed the forbiddenness.<sup>11</sup>

The consistent correlation between the electron-donating efficiency of the para-phenyl substituents and the spectral shifts observed strongly indicates that the spectral changes observed are indeed determined by the effects of the substituents on the electron densities on the porphyrin ring. The spectral effects of the ortho-phenyl substituents can also be explained in a similar vein by the effects of the steric repulsion of the  $a_{2u}$  electrons toward the molecular periphery.

Although the differences between the spectra of porphyrin-TPP and *ms*-tetraalkylporphyrins were related earlier to the effects of substitution on  $a_{2u}$ - $a_{1u}$  degeneracy,<sup>10,11</sup> we feel that systematic data, like those in the present work, were necessary to substantiate those earlier speculations. Although the simple four-orbital model involves many approximations, it is seen to account satisfactorily for the substituent effects observed in the present work.

The raising of the electron density on the  $a_{2u}$  orbital by electron-donating substituents also explains well the increasing basicity of the pyrrole nitrogens with increasingly

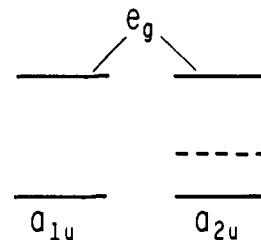


Figure 1. Schematic representation of the four-orbital model of  $D_{4h}$  symmetry with degenerate  $a_{1u}$  and  $a_{2u}$  orbitals. The broken line represents the shifted  $a_{2u}$  orbital level upon electron-donating meso substitution.

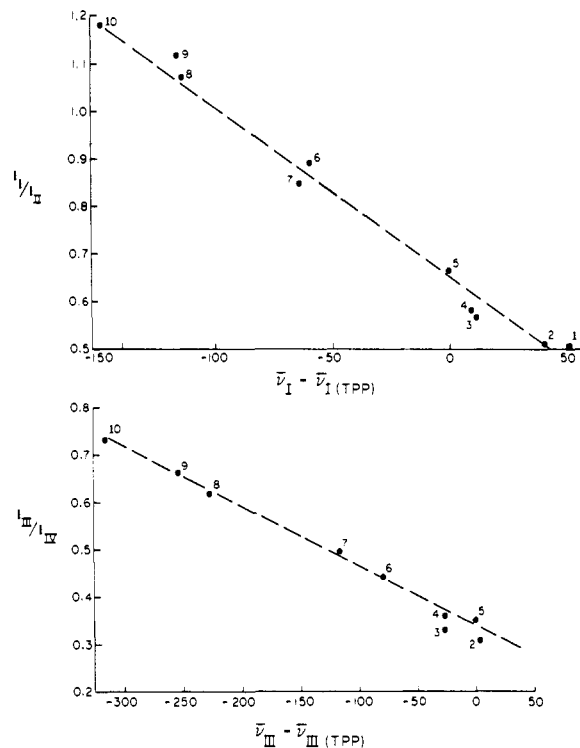


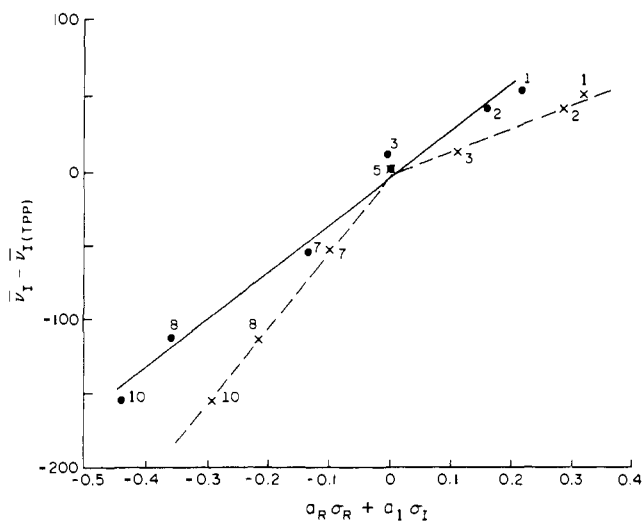
Figure 2. Correlation between frequency shifts ( $\nu_{T(p-X)PP} - \nu_{TPP}$  in  $\text{cm}^{-1}$ ) of the 0-0 bands and the ratios of the transition dipoles of the corresponding 0-0 and 0-1 transitions. Numbers relate to structures and spectral bands as listed in Table I.

stronger electron-donating para-substituents on the *ms*-phenyl groups (Table III).

Distortions of the band shapes of the tetraalkylporphyrins and the fluorescence data (vide supra) indicate more complex substitution effects in these molecules.

(2) **Transmission of Resonance and Inductive Substituent Effect in the Noncoplanar Phenyl-Porphyrin  $\pi$  System.** The main objective of the present study is to investigate the extent to which substituent effects due to fundamentally different physical interactions are propagated in a noncoplanar composite  $\pi$  system. Since the large body of experimental information on substituent effects is generally correlated in the framework of Hammett-type coefficients, we used this approach to interpret our data. The interpretation is, naturally, subject to the usual qualifications given for the quantitative value of this particular form of empirical data analysis.<sup>2a,12</sup>

For the free base spectra, the best correlation for the substituent-induced frequency or intensity-ratio shifts is given by the combination  $\sigma$  coefficient equation<sup>12,13</sup>  $a_R\sigma_R + a_I\sigma_I$  where  $a_R = 0.8$  and  $a_I = 0.2$  (cf. Figure 3) and where R signifies a resonance effect and I an inductive effect. The broken line in Figure 3 demonstrates that the linearity of



**Figure 3.** Correlation between frequency shifts ( $\nu_{\text{T}(p-x)\text{PP}} - \nu_{\text{TPP}}$  in  $\text{cm}^{-1}$ ) of the 0-0 band and combined Hammett coefficients:  $a_{\text{R}}\sigma_{\text{R}} + a_{\text{I}}\sigma_{\text{I}}$  for  $a_{\text{R}} = 0.6$ ,  $a_{\text{I}} = 0.4$  (X), and  $a_{\text{R}} = 0.8$ ,  $a_{\text{I}} = 0.3$  (●). The large deviation from linearity when the first combination of resonance and inductive coefficients is used demonstrates the sensitivity of the linear correlation observed to the type of substituent porphyrin interaction considered. Numbers relate to structures as listed in Table I.

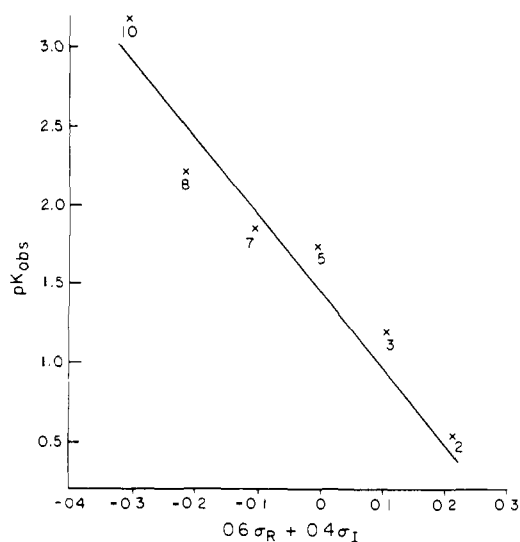
the Hammett-type plot is quite sensitive to the combination of the resonance ( $\sigma_{\text{R}}$ ) and inductive ( $\sigma_{\text{I}}$ ) coefficients used.<sup>19</sup> Such plots are therefore sensitive indicators of the nature of the substituent effects, as considered in the context of the Hammett-type coefficients. Subject to the quantitative validity of this type of combination coefficient analysis,<sup>12</sup> this particular situation clearly shows that an interpretation of unexpectedly large resonance-type interactions must be considered.

The plot of the shift of the basicity of the pyrrole nitrogens (i.e. of  $\text{p}K_{\text{obsd}}$ ) vs. the Hammett-type  $\sigma$  coefficient (Figure 4) gives best linearity when  $a_{\text{R}} = 0.6$  and  $a_{\text{I}} = 0.4$ . It is interesting to note that this result shows some decrease in the weight of the resonance interaction on the  $\text{p}K$  values as compared with the substituent effects on the frequency shifts in the free bases. Since crystal structure data<sup>15</sup> show that the diacid cations are considerably more coplanar than the free bases, this finding is contrary to classical expectations. (With respect to the plot in Figure 4 we should point out that no correction for the (unknown) acidity function of  $\text{HClO}_4$  in dimethyl sulfoxide was made.) In any event, the results indicate a predominantly resonance-type substituent effect on the  $\text{p}K$  values. Similarly, spectral shifts in the diacid cations correlate best with the ( $\sigma^+$ ,  $-\sigma$ ) coefficients, which correspond to resonance interactions.<sup>2a</sup> Correlation analysis of the substituent effects on the  $\text{p}K$  values and frequency shifts therefore indicate predominantly resonance-type interactions in the diacid cations, which are still significantly noncoplanar structures.

The experimental evidence on the nature of the interaction between the phenyl and porphyrin  $\pi$  system, and the effects of phenyl substituents on the chemistry of the porphyrin system in *meso*-tetraphenylporphyrins, may be summarized briefly as follows.

(i) Spectral shifts indicate that resonance effects (80-100) rather than inductive effects (0-20%) are predominantly transmitted from para-phenyl substituents to the porphyrin system in substituted free base TPP and  $\text{TPPH}_2^{2+}$  dications (present work and ref 2a).

(ii) Substituent effects on the kinetics of metal incorporation into substituted TPP structures indicate the predominance of resonance interactions.<sup>2a</sup>



**Figure 4.** Correlation between the observed dissociation constants of substituted *meso*-tetraphenylporphyrin dications and the combined Hammett coefficient  $0.6\sigma_{\text{R}} + 0.4\sigma_{\text{I}}$ . Numbers relate to structures as listed in Table I.

(iii) Substituent effects on the basicity of pyrrole nitrogens in TPP structures correlate to predominantly resonance-type interactions.

(iv) The unique mass spectrometric fragmentation patterns of metallo-TPP derivatives can be explained on the basis of the formation of fragment ions which are stabilized by aromatic structures, i.e., in which the number of electrons obeys the Hückel aromatic rule. This interpretation requires resonance interactions between the phenyl and porphyrin  $\pi$  systems.<sup>16</sup>

(v) Ir frequency changes in substituted CoTPP complexes in solutions exhibit resonance effects.<sup>2b</sup>

(vi) Kinetic catalysis efficiencies of substituted CoTPP in solutions and in the solid phase exhibit resonance interactions.<sup>2b</sup>

In summary, a variety of chemical evidence strongly indicates the transmission of interactions which are classically interpreted as resonance type from the phenyl groups to the porphyrin ring in *meso*-tetraphenylporphyrins. On the other hand, ample evidence exists that the phenyl and porphyrin planes are significantly noncoplanar in these molecules.<sup>3-5</sup> Angles of 60-85° between the phenyl and porphyrin planes were found in solids, and angles of about 40° were calculated recently by Wolberg for TPP in solution.<sup>2b</sup> Comparison of the structural and chemical properties of substituted TPP molecules therefore indicates a discrepancy with some generally accepted notions on the relation between structure and resonance effects. The behavior of these molecules indicates either that very significant resonance effects can be propagated in significantly noncoplanar  $\pi$  systems, or that substituent effects that are generally assumed to originate from resonance interactions may originate from intramolecular interactions of a different nature.

**Acknowledgment.** We wish to thank Dr. D. C. Mauzerall for advice, criticism, and the use of some of his equipment. We also thank Mrs. H. D. Meot-Ner for assistance in processing the data, Mr. N. Kagan for providing a sample of  $\text{T}(p\text{-SO}_2\text{CH}_3)\text{PP}$ , Ms. V. Varadi for technical assistance, and Ms. Y. Jarreau and G. Vella for preparation of the manuscript.

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- (17) Abbreviations used are TPP = *ms*-tetraphenylporphin, T(*p*-CN)PP = *ms*-tetra(*p*-cyano)phenylporphin, etc., T(CH<sub>3</sub>)P = *ms*-tetramethylporphin, etc., TPPH<sub>2</sub><sup>2+</sup> = acid dication of TPP, etc.,  $\epsilon$  = the absorption coefficient.
- (18) For identification of the spectral bands I-IV see Table I. The dipole strength ratios were calculated as  $(f_i/f_j)(\nu_{ij}/\nu_j)$ , where the oscillator strength is  $f = 4.32 \times 10^{-9} \int \epsilon_i d\nu$  and  $\bar{\nu}$  is the wave number.
- (19) For the present purposes we used the classical approach<sup>14</sup>  $\sigma_R = \sigma_D - \sigma_m$ ,  $\sigma_I = \sigma_m$  ( $\sigma_m$  and  $\sigma_D$  from ref 13). The use of  $\sigma'$  (obtained for substituted bicyclo compounds by J. D. Roberts and W. T. Moreland, *J. Am. Chem. Soc.*, **75**, 2167 (1953)) for  $\sigma_I$ , an approach preferred by several authors, does not significantly change the results when applied to our data, since  $\sigma_m$  and  $\sigma'$  are similar<sup>14</sup> for most of the substituents used in our work. In fact with any of the commonly used sets of  $\sigma_I$  and  $\sigma_R$  our results yield better linearity when predominantly resonance-type combination  $\sigma$  coefficients are used.

## Luminescence Studies on Several Tetraarylporphins and Their Zinc Derivatives

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**Abstract:** The fluorescence spectra and quantum yields were determined for a series of free base tetraarylporphins and their Zn derivatives in benzene. These porphins were substituted on positions 2, 3, and 4 of the phenyl rings. The heavy atom halogen substituents were found to quench fluorescence, especially when substituted at the 2-phenyl position. The quenching of the fluorescence was interpreted in terms of a heavy atom induced increase in intersystem crossing from S<sub>1</sub> to T<sub>n</sub>. The absorption and fluorescence (0-0) band intensities of the Zn derivatives were found to be reduced by the presence of an ortho substituent. A similar ortho substituent effect has previously been observed for free base tetraphenylporphins. We have identified a weak emission from the Zn tetraarylporphins at 560 nm as a fluorescence hot band. The phosphorescence spectra and relative quantum yields of phosphorescence were also determined for a number of the Zn derivatives in methylocyclohexane-isopentane glass at 77°K. Phosphorescent emission could not be detected from the free base tetraarylporphins.

The tetraarylporphins are an interesting class of synthetic porphyrins. Derivatives with symmetrical substitution on the phenyl rings are readily prepared by the Rothmund reaction using the appropriately substituted benzaldehyde.<sup>1</sup> Para substituted tetraarylporphins have been most extensively studied.<sup>1-3</sup> Para substituents have been found, in general, to have only a slight effect on the absorbance spectra of free base and metalloporphyrins. This lack of interaction between "para phenyl" substituents and the porphin  $\pi$  system is attributed to the large dihedral angle between the planes of the phenyl and porphin  $\pi$  systems.<sup>4</sup>

Kim, Leonard, and Longo<sup>1</sup> recently synthesized and studied a number of tetraarylporphins prepared from ortho-substituted benzaldehydes. They found that certain ortho substituents produced a marked reduction in the Q(0-0) band intensities of the free base. Ortho-substituted halogens were most effective while the ortho-methyl substituent produced little effect.

One part of the work reported in this paper is an extension of the investigation of ortho substituent effects to the metallotetraarylporphins, specifically the Zn derivatives.

Excited state processes in porphyrins are extremely important, especially those in biologically important porphyrins such as the chlorophylls.<sup>5,6</sup> The fluorescence yield of most porphyrins is less than 0.2.<sup>7,8</sup> Thus the excited state S<sub>1</sub> is primarily deactivated by radiationless decay. It appears fairly certain that the spin forbidden process S<sub>1</sub>  $\rightarrow$  T<sub>n</sub> is

the predominant route for radiationless deactivation of S<sub>1</sub> in porphyrins.<sup>9</sup>

In this paper we report a study of the halogen heavy atom effect on spin forbidden processes in free base and zinc tetraphenylporphin. The heavy atom effect on spin forbidden processes in porphyrins has been studied, for the most part, by substitution of various closed shell heavy metals into the porphyrin nucleus.<sup>10,11</sup> Gouterman et al.<sup>12</sup> have recently reported a study of the luminescence of group 4 metalloporphyrins. Both the effects of central metal and of axial ligands such as Cl, Br, and I were studied. They found that the extent of spin-orbit coupling depended much more on the nature of the ligand than on that of the metal. Solov'ev et al.<sup>13</sup> studied the effect of para-phenyl substituents Cl, Br, and I on the luminescence of free base, magnesium, and zinc tetraphenylporphin. They obtained fluorescence quantum yields as well as other luminescence data including relative increases in triplet-triplet absorption due to the various para substituents. Using the methods developed by Medinger and Wilkinson<sup>14</sup> they were able to calculate a quantum yield for triplet formation of 0.87 for free base tetraphenylporphin.

### Experimental Section

**Compounds and Solvents.** The free base tetraphenylporphin used in this study was prepared by Dr. E. Brown following the procedure of Adler et al.<sup>15</sup> All the substituted tetraphenylporphins were