result from increased covalency in the $(Me_5Cp)_2Mn$ system.

Conclusions

Our magnetic studies of decamethylmanganocene indicate that permethylation of the Cp ring results in exclusively low-spin behavior, in contrast to other manganocenes where high-spin states are thermally populated. From this result we conclude that the ligand field strength of the Cp ring is significantly enhanced by the complete replacement of the hydrogens with electron-donating methyl groups. The low-spin configuration of $(Me_5Cp)_2Mn$ renders it inert toward ring displacement and hydrolysis but the complex does undergo reversible oxidation and reduction to give low-spin 16- and 18-electron species for which no analogues exist in the other manganocenes. Further studies on other first-row transition-metal decamethylmetallocenes are now in progress.

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Substituent Effects in the Electroreduction of Porphyrins and Metalloporphyrins[1]

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Abstract: Electron affinities and electron transfer reactivities of selected mesotetraphenylporphyrin (TPP) moieties have been investigated by controlled potential coulometry, polarography, and cyclic voltammetry. The effect of β-pyrrole substituents (OEt, Cl, Br, SCN, CN, NO_2) on the electroreduction of TPP was remarkably large, accounting for polarographic half-wave potential ($E_{1/2}$) shifts as great as 0.35 V per substituent, which correlated linearly with Hammett's σ_p^-. Polysubstitution of cyano groups had an additive effect on $E_{1/2}$ shifts, but polysubstitution of bromine did not. Insertion of electroreducible cations, such as Mn(III), Fe(III), and Co(II), did not affect the magnitude of the substituent shifts observed on TPP per se. Substituent effects on the $E_{1/2}$ of the inserted metal were invariably smaller. Thus, the effect of β substitution on metalloporphyrins provides a simple diagnostic criterion for distinguishing between electron transfer implicating the central cation vs. electrons inserted into the porphyrin ligand.

A renaissance of interest in the electrochemistry of porphyrins and metalloporphyrins was engendered in the mid-1960s by several papers published in this journal.[5-8] An appreciable number of subsequent studies have been devoted to the electrooxidation–reduction of pyrrole-substituted porphyrins and of phenyl-substituted tetraphenylporphyrins and corresponding metalloporphyrins.[9-20] Classical literature on naturally occurring porphyrins contains indications that substituents affect redox behavior,[21] as indeed expected on theoretical considerations. Typically, electron-releasing substituents induce cathodic shifts of the reduction potentials whereas electron-withdrawing substituents exert the opposite effect. However, these potential shifts tend to be small in the case of natural porphyrins. Recently, several papers[16-18] have been devoted to the electrochemistry of synthetic phenyl-substituted tetraphenylporphins. Qualitatively, the same trends were observed as with the natural porphyrins, yielding Hammett-Taft linear free energy relationships. In metalloporphyrins, substituents on the porphyrin ligand have been reported to have little or no effect on the reduction potential of the inserted cation.[17b,22] To clarify the effect of substituents on the electroreduction of porphyrins, we decided to investigate pyrrole substitution with strong electron-withdrawing groups.[15] The relevant macrocycles are identified in Figure 1. Results are presented and discussed in this paper, including potential shifts as large as 1 V, which are unprecedented. Based on these

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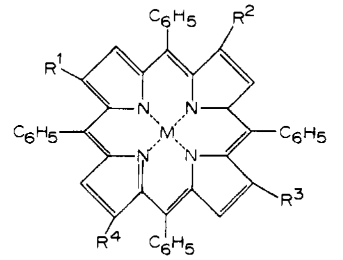

Name(*)	R^1	R^2	R^3	R^4	M
H_2TPP	H	H	H	H	H_2
$H_2TPP(X)$	X	H	H	H	H_2
$H_2TPP(Br)_{2ab}$	Br	Br	H	H	H_2
$H_2TPP(Br)_{2ac}$	Br	H	Br	H	H_2
$H_2TPP(Br)_3$	Br	Br	Br	H	H_2
CuTPP	H	H	H	H	Cu^{II}
CuTPP(X)	X	H	H	H	Cu^{II}
Mn $[TPP(CN)_4]Cl$	CN	CN	CN	CN	$Mn^{III}Cl$
Fe $[TPP(CN)_4]Cl$	CN	CN	CN	CN	$Fe^{III}Cl$
Co $TPP(CN)_3$	CN	CN	CN	H	Co^{II}
Co $TPP(CN)_4$	CN	CN	CN	CN	Co^{II}

* The groups shown in brackets are β-pyrrole-substituents, those without are bonded directly to the metal.

Figure 1. Notation used for identifying structural features of porphyrin moieties.

findings, a new, simple, and dependable criterion is described for localizing electron-transfer sites in metalloporphyrins, in order to differentiate between electroreduction of the inserted metal and electroreduction of the porphyrin ring.

Experimental Section

Electroanalytical Measurements. Polarography at the classical dropping mercury electrode (DME) was performed with the aid of a potentiostat (Model PRT 20-2X, supplied by S.O.L.E.A.-Tacussel, 69100 Villeurbanne, France), a voltage programmer (Model Servovit 2, supplied by S.O.L.E.A. Co.), an electronic millivoltmeter (S.O.L.E.A. Model S6B, input impedance 10^{12} Ω), and a recording microammeter (Model BGSO, supplied by Sefram Co., 75739 Paris Cedex 15). A Model PRG 4 instrument package (S.O.L.E.A.-Tacussel) was used for cyclic voltammetry at the dropping mercury electrode (DME). This was accomplished by appropriate current sampling on successive drops, while the potential was programmed by a triangular sweep. The procedure is equivalent to conventional cyclic voltammetry at Kemula's hanging drop mercury electrode.

Coulometry at controlled potential was performed at a mercury pool working cathode. A fritted glass barrier was interposed between the working electrode and a platinum foil counterelectrode.

A so-called "three-electrode" system was used in all electrochemical measurements, consisting of the appropriate indicator (or working) electrode (viz., the DME or a mercury pool), an auxiliary (or "counter"-) electrode, and a reference electrode. The latter was a conventional aqueous saturated calomel electrode (SCE), equipped with a salt bridge which consisted of DMF (containing 0.1 M TEAP) and water (saturated with KCl) separated by a porous glass frit septum. The electroreactive species (various porphyrins and metalloporphyrins) were dissolved in *N,N*-dimethylformamide (DMF), containing 0.1 M tetraethylammonium perchlorate (TEAP) as supporting electrolyte.

All electrochemical measurements were carried out at 25 °C. Potentials are referred to the SCE, using the sign convention of the International Union of Pure and Applied Chemistry (IUPAC),[23] i.e., the more reducing a potential, the more negative its assignment.

Materials. DMF and TEAP were purified as described in a previous communication.[15] The porphyrins $H_2TPP(Br)$, $H_2TPP(Br)_2$, $H_2TPP(Br)_3$, $H_2TPP(OEt)$, $H_2TPP(\text{2-py}^+)\cdot ClO_4^-$, and $H_2TPP(CN)$ were prepared by known procedures.[24,25] Other porphyrins and metalloporphyrins were synthesized as outlined below, separated (and purified) on columns of silica gel (Merck silica gel 60, 70-230 mesh) or alumina (activity grade I-II, Merck standardized), and authenticated by spectroscopy (using a Cary Model 118 spectrophotometer, supplied by Varian, Palo Alto, Calif.), mass spectrometry (Model 9000 mass spectrometer, supplied by LKB-Produkter AB, Bromma, Sweden), and elemental analysis (performed by the Service Central de Microanalyse du CNRS, Division de Strasbourg, France).

2-Chlorotetraphenylporphine, $H_2TPP(Cl)$. H_2TPP (200 mg) plus 400 mg of *N*-chlorosuccinimide were refluxed for 2 h in 60 mL of 1,2-dichloroethane. Solvent was evaporated and the residue washed with MeOH, dissolved in 1:1 cyclohexane-toluene, and chromatographed on 300 g of silica gel using the same eluent, yielding a first fraction (21 mg) of dichlorinated products which were discarded. The second fraction (98 mg), which was the desired product, was recrystallized from CH_2Cl_2-MeOH. Visible spectrum peaks in CH_2Cl_2: λ 417 nm (ε 356 000), 517 (22 300), 552 (7200), 595 (6500), 651 (5300). Mass spectrum: *m/e* 648 (M^+, reference), 613 (− Cl, 32%, m* 578.5). Anal. Calcd for $C_{44}H_{29}N_4Cl$: C, 81.40; H, 4.50; N, 8.62. Found: C, 81.51; H, 4.11; N, 8.89.

Copper 2-Thiocyanatotetraphenylporphine, CuTPP(SCN). $(SCN)_2$ was prepared by adding 1.6 g of bromine to 1.52 g of NH_4SCN in 15 mL of AcOH; 650 mg of CuTPP in 60 mL of CH_2Cl_2 was subsequently added. The mixture was stirred at room temperature for 40 min, washed with water, and dried over Na_2SO_4. The organic layer was evaporated and the residue dissolved in toluene and chromatographed on 100 g of silica gel (eluent toluene). The first fraction was unreacted starting material; the second fraction was the desired product (304 mg). CuTPP(SCN) was recrystallized from CH_2Cl_2-MeOH. Visible spectrum in CH_2Cl_2: λ 415 nm (ε 340 000), 542 (20 000), 575 (4650). Mass spectrum: *m/e* 732 (M^+, reference), 707 (86%), 705 (90%), 674 (− SCN, 52%, m* 622). Anal. Calcd for $C_{45}H_{27}N_5SCu$: C, 73.70; H, 3.71; N, 9.55; S, 4.37. Found: C, 73.09; H, 3.72; N, 9.57; S, 4.51.

2-Thiocyanatotetraphenylporphine, $H_2TPP(SCN)$. CuTPP(SCN) (50 mg) was dissolved in 5 mL of concentrated sulfuric acid, stirred for 3 min at room temperature, poured into concentrated aqueous ammonia, and extracted in CH_2Cl_2. The organic solvent layer was evaporated to dryness and the residue recrystallized from CH_2Cl_2-MeOH, yielding 34 mg of $H_2TPP(SCN)$. Visible spectrum in CH_2Cl_2: λ 420 nm (ε 302 000), 519 (20 800), 554 (4600), 595 (6000), 652 (5700). Mass spectrum: *m/e* 671 (M^+, reference), 646 (47%), 644 (49%), 613 (− SCN, 59%, m* 561). Anal. Calcd for $C_{45}H_{29}N_5S$: C, 80.51; H, 4.35; N, 10.43; S, 4.77. Found: C, 79.47; H, 4.30; N, 10.59; S, 4.39.

Copper 2-Nitrotetraphenylporphine, $CuTPP(NO_2)$. $Cu(NO_3)_2\cdot 6H_2O$ (500 mg) in 50 mL of Ac_2O was added to 550 mg of CuTPP dissolved in a mixture of 500 mL of chloroform plus 10 mL of acetic acid. The reaction mixture was stirred at 30-35 °C for 1 h, at which time no more starting material was detectable by TLC. The solution was subsequently washed with water and aqueous K_2CO_3, dried over Na_2SO_4, and concentrated in vacuo. Methanol was added yielding 400 mg of $CuTPP(NO)_2$. Spectrum in CH_2Cl_2: λ 420 nm (ε 186 000), 547 (13 000), 582 (8400). Mass spectrum: *m/e* 720 (M^+, reference), 690 (97%), 675 (85%). Anal. Calcd for $C_{44}H_{27}N_5O_2Cu$: C, 73.27; H, 3.77; N, 9.71. Found: C, 73.83; H, 3.77; N, 10.06.

2-Nitrotetraphenylporphine, $H_2TPP(NO_2)$. $CuTPP(NO_2)$ (200 mg) in 6 mL of concentrated sulfuric acid was poured into concentrated aqueous ammonia and extracted with chloroform. The extract was dried over sodium sulfate and evaporated to dryness. The residue was dissolved in toluene and eluted with the same solvent through a column of 200 g of alumina. The major eluted fraction was again evaporated to dryness and the residue recrystallized from a CH_2Cl_2-MeOH solvent mixture yielding 140 mg of $H_2TPP(NO_2)$. Spectrum in CH_2Cl_2: λ 426 nm (ε 216 000), 527 (15 000), 565 (4000). Mass spectrum: *m/e* 659 (M^+, reference), 629 (23%), 613 (− NO_2, 54%, m* 561.5). Anal. Calcd for $C_{44}H_{29}N_5O_2$: C, 80.10; H, 4.44; N, 10.61; O, 4.85. Found: C, 75.23; H, 4.66; N, 10.44; O, 4.52. Note: The low carbon value is accounted for by analytical difficulties encountered by other authors in porphyrin analysis.[40]

Copper 2-Bromotetraphenylporphine, CuTPP(Br). This metalloporphyrin was prepared from $H_2TPP(Br)$ and copper acetate in chloroform-MeOH. Spectrum in CH_2Cl_2: λ 416 nm (ε 405 000), 541 (19 500), 575 (3300). Mass spectrum: *m/e* 753, 755 (M^+, 65% and 100%), 674 (60%). Anal. Calcd for $C_{44}H_{27}BrN_4Cu$: C, 69.98; H, 3.60; N, 7.42. Found: C, 68.92; H, 3.52; N, 7.46.

Copper 2-Cyanotetraphenylporphine, CuTPP(CN). This metalloporphyrin was prepared from $H_2TPP(CN)$ by the same procedure as CuTPP(Br). Spectrum in CH_2Cl_2: λ 420 nm (ε 465 000), 510

(5600), 545 (21 000), 583 (12 500). Mass spectrum: *m/e* 700 (M^+, reference), 622 (13%). Anal. Calcd for $C_{45}H_{27}N_5Cu$: C, 77.07; H, 3.88; N, 9.99. Found: C, 76.98; H, 3.96; N, 10.20.

Chloromanganese(III) Tetracyanotetraphenylporphine, Mn[TPP(CN)$_4$]Cl. $(CN)_4TPP$[24] (200 mg) and 500 mg of manganese acetate were dissolved in DMF and refluxed for 0.5 h. The solvent was evaporated in vacuo. The residue was dissolved in chloroform and chromatographed on 120 g of silica gel. Elution with $CHCl_3$-MeOH (95:5) yielded successive fractions of the starting material (72 mg) and of Mn[TPP(CN)$_4$]Cl. The eluate was shaken for 48 h with 2 M HCl in excess. Evaporation of the organic layer and recrystallization from CH_2Cl_2-petroleum ether (bp 40-60 °C) yielded 61 mg of product. Spectrum in CH_2Cl_2: λ 400 nm (ϵ 65 000), 510 (130 000), 610 (11 800), 675 (14 000), 713 (21 200). Anal. Calcd for $C_{48}H_{24}ClN_8Mn$: C, 71.78; H, 3.0; N, 13.96. Found: C, 71.06; H, 3.06; N, 14.15.

Chloroiron(III) Tetracyanotetraphenylporphine, Fe[TPP(CN)$_4$]Cl. This metalloporphyrin was prepared by a procedure entirely analogous to the one used in synthesizing Mn[TPP(CN)$_4$]Cl. Spectrum in CH_2Cl_2: λ 433 nm (ϵ 89 000), 675 (19 400). Mass spectrum: *m/e* 768 (− Cl. 100%), 743 (78%). Anal. Calcd for $C_{48}H_{24}ClN_8Fe$: C, 71.70; H, 3.01; N, 13.95. Found: C, 71.09; H, 3.33; N, 13.98.

Cobalt(II) Tetra- and Tricyanotetraphenylporphine, CoTPP(CN)$_4$ and CoTPP(CN)$_3$. Cobaltous acetate (600 mg) dissolved in 40 mL of MeOH was added to 530 mg of TPP(Br)$_4$ in 400 mL of $CHCl_3$. Successive evaporation, addition of MeOH, and filtration yielded CoTPP(Br)$_4$; 530 mg of that product and 1 g of CuCN were refluxed in 35 mL of pyridine for 18 h under an atmosphere of nitrogen. The solvent was evaporated to dryness and the residue extracted with chloroform and chromatographed on 400 g of silica gel. Gradient elution was employed, using chloroform containing ethyl acetate in amounts increasing from 2 to 3%. Successive fractions yielded CoTPP(CN)$_3$ and CoTPP(CN)$_4$. Both compounds were recrystallized from MeOH and authenticated as follows.

CoTPP(CN)$_3$. Spectrum in CH_2Cl_2: λ 433 nm (ϵ 108 000), 612 (14 800), 635 (13 600). Mass spectrum: *m/e* 746 (M^+, reference, 100%), 721 (6%). Anal. Calcd for $C_{47}H_{25}N_7Co{\cdot}2H_2O$: C, 72.12; H, 3.73; N, 12.53. Found: C, 70.88; H, 3.67; N, 12.60.

CoTPP(CN)$_4$. Mass spectrum: *m/e* 771 (M^+, reference, 100%), 746 (47%), 721 (35%). Anal. Calcd for $C_{48}H_{24}N_8Co{\cdot}3H_2O$: C, 69.81; H, 3.67; N, 13.57. Found: C, 69.03; H, 3.73; N, 13.66.

Results

Comparison of Substituent Effects in Compounds of the Type $H_2TPP(X)$ and CuTPP(X). A typical polarogram of $H_2TPP(Br)$ is illustrated in Figure 2. It is qualitatively similar to the previously reported[6,7,10] current-voltage curves of H_2TPP and CuTPP exhibiting four successive reduction waves, implicating the porphyrin ring. In all instances, the first two waves were diffusion controlled and approximated a Nernst-reversible one-electron transfer each, under the experimental conditions normally prevailing in steady-state dc polarography at the DME (i.e., when the potential was scanned at a rate of 1-2 mV/s). These conclusions were substantiated as follows.

1. Coulometry at controlled potential yielded current-time integrals corresponding to 1 Faraday/mol of porphyrin; the relevant current-time curves decayed exponentially which indicated the *absence of* complications due to *chemical reaction kinetics.*

2. Plots of log i_d vs. log h (where i_d denotes the relevant—appropriately corrected—limiting current and h the mercury pressure effective on the DME) yielded slopes of 0.5, as expected when diffusion control prevails.

3. Classical polarographic wave analysis plots of the quantity log $(i_d - i)/i$ vs. the potential (E) of the DME yielded reciprocal slopes approximating the "Nernst slope" of (RT/F) ln 10 = 0.06 V at 25 °C.

The heights (diffusion currents) of the first two waves (identified by Roman numerals I and II in Figure 2) were equal and yielded consistent polarographic diffusion coefficients. In contradistinction, the heights of waves III and IV were greater by a factor of 1.7 each and exhibited an evidently "irreversible" (drawn-out) analytical geometry. The shape of wave IV tended to be ill defined. In view of this situation, the emphasis in this paper is placed on the quantitative characterization of waves I and II.

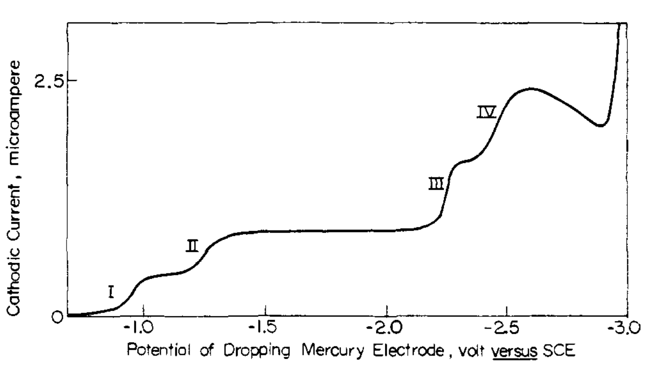

Figure 2. Polarogram of 0.0023 M $H_2TPP(Br)$ in DMF. Supporting electrolyte: 0.1 M TEAP. Waves identified by Roman numerals in order of increasing cathodic character.

Cyclic voltammetry yielded four reduction peaks, but only two converse reoxidation peaks which corresponded to waves I and II of Figure 2. The peak separation ($\Delta E_p = E_{p,a} - E_{p,c}$) was approximately $2.2RT/F$ = 57 mV at relatively slow potential scan rates ($v < 0.1$ V/s) and increased when $0.1 < v < 100$ V/s. Electrochemical rate constants were estimated by Nicholson's method[26] for the first two electroreduction processes (i.e., those which occurred most readily, at least negative potentials) of the moieties $H_2TPP(X)$.

Findings were qualitatively similar in the presence of the substituents X = H, Br, Cl, CN, NO_2, and OEt, and relevant data are summarized in Tables I and II. On the other hand, the electrochemical behavior of the moieties $H_2TPP(py^+)$, $CuTPP(py^+)$, $H_2TPP(SCN)$, and $Cu^{II}TPP(SCN)$ was anomalous, and the appropriate data are presented in Table III. The salient qualitative features of pyridinium and thiocyanate substitution are outlined below.

1. A fifth electroreduction "step" appeared in solutions of $H_2TPP(py^+)$ and $CuTPP(py^+)$. This occurred "before" (i.e., at potentials less negative) the waves whose characteristics are summarized in Tables I and II (and exemplified in Figure 2) and corresponded to a Nernst reversible electroreduction of pyridinium ion, viz.

$$H_2TPP(py^+) + e = H_2TPP(py) \qquad E_{1/2} = -0.82 \text{ V} \quad (1)$$

$$CuTPP(py^+) + e = CuTPP(py) \qquad E_{1/2} = -0.91 \text{ V} \quad (2)$$

2. In the case of $H_2TPP(SCN)$ and CuTPP(SCN), a total of six reduction waves were observed. The first (least negative) among these had the analytic geometry of a Nernst-reversible one-electron transfer. Its half-wave potential was close to the first wave of H_2TPP and can therefore be reasonably assigned to an analogous electroreduction of the porphyrin ring.

Substituent Effects in the Series $H_2TPP(Br)_n$ and $Cu^{II}TPP(Br)_n$. To complement the picture of electrochemical behavior trends emerging from Tables I-III, several polysubstituted bromotetraphenylporphyrins were investigated. Qualitatively, current-voltage curves were similar to Figure 2. Quantitative data are summarized in Table IV.

Substituent Effects in the Compounds $Mn^{III}[TPP(CN)_4]Cl$, $Fe^{III}[TPP(CN)_4]Cl$, $Co^{II}TPP(CN)_3$ and $Co^{II}TPP(CN)_4$. Corresponding structures are identified in Figure 1. The electrochemical behavior of the relevant compounds is in striking contradistinction to $Cu^{II}TPP$ and its substituted analogues, where the copper is known[6,7] to remain in the divalent state, while the porphyrin ring undergoes stepwise electroreduction. In $Mn^{III}[TPP(CN)_4]Cl$, $Co^{II}TPP(CN)_3$, $Co^{II}TPP(CN)_4$, and $Fe^{III}[TPP(CN)_4]Cl$ we have identified three well-defined

Table I. Polarographic Half-Wave Potentials[a] (V) of Monosubstituted Porphyrin Moieties

electroreducible free base porphyrin	$E^{I}_{1/2}$	$E^{II}_{1/2}$	$E^{I}_{1/2} - E^{II}_{1/2}$	electroreducible metalloporphyrin	$E^{I}_{1/2}$	$E^{II}_{1/2}$	$E^{I}_{1/2} - E^{II}_{1/2}$
H_2TPP[b]	−1.08	−1.46	0.38	CuTPP	−1.20	−1.68	0.48
$H_2TPP(Br)$[c]	−0.97	−1.30	0.33	CuTPP(Br)	−1.12	−1.59	0.47
$H_2TPP(Cl)$[d]	−0.95	−1.28	0.33				
$H_2TPP(CN)$[e]	−0.84	−1.20	0.36	CuTPP(CN)	−0.94	−1.44	0.50
$H_2TPP(NO_2)$[f]	−0.73	−1.04	0.31	$CuTPP(NO_2)$	−0.87	−1.31	0.44
$H_2TPP(OEt)$[g]	−1.12	−1.46	0.34				

[a] Waves identified by Roman numerals in order of increasing cathodic character, as shown in Figure 2. [b] $E^{III}_{1/2} = -2.34$, $E^{IV}_{1/2} = -2.49$. [c] $E^{III}_{1/2} = -2.10$, $E^{IV}_{1/2} = -2.33$. [d] $E^{III}_{1/2} = 2.08$, $E^{IV}_{1/2} = -2.28$. [e] $E^{III}_{1/2} = -2.06$, $E^{IV}_{1/2} = -2.26$. [f] $E^{III}_{1/2} = -1.85$, $E^{IV}_{1/2} = -2.44$. [g] $E^{III}_{1/2} = 2.35$.

Table II. Electrochemical Rate Constants[a] (k_s) and Polarographic Diffusion Coefficients (D) of Monosubstituted Free Base Porphyrins

electroreactive moiety	$D \times 10^6$, cm^2/s	$k_s \times 10^2$, cm/s	
		wave I	wave II
H_2TPP	1.0	1.0	0.8
$H_2TPP(Br)$	1.5	3.7	4.6
$H_2TPP(Cl)$	1.2	3.1	3.5
$H_2TPP(CN)$	1.9	1.2	0.7
$H_2TPP(NO_2)$	1.8	5.8	4.1
$H_2TPP(OEt)$	1.3	1.4	2.3

[a] Effective at the relevant conditional standard ("formal") potential.

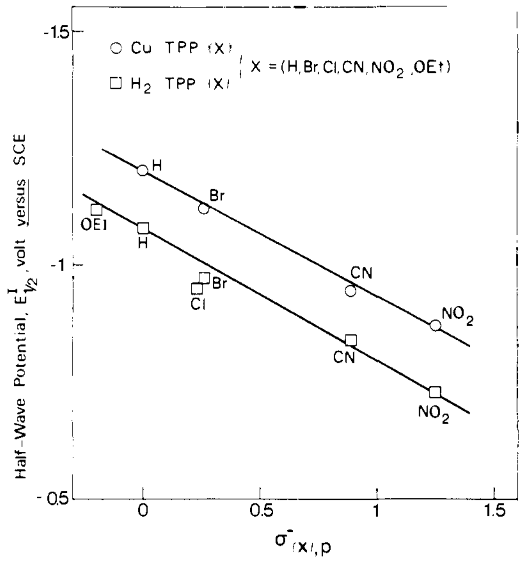

Figure 3. Plot of half-wave potentials of wave I vs. Hammett's σ_p^-

voltammetric reduction waves, one of which implicates a change in the oxidation state of the metal. Results are summarized in Table V.

Discussion

Interpretative comments are offered below, in the context of the results presented in Tables I-V. The discussion will be focused on the two monoelectronic reduction steps corresponding to waves I and II in Figure 2, which (1) occur at the least negative potentials; (2) yield well-defined Nernst-reversible classical dc polarograms; (3) are known[10-20] to implicate the porphyrin ring in the reactions

$$\text{TPP-moiety} + e = \text{anion radical} \quad (3)$$

$$\text{anion radical} + e = \text{dianion} \quad (4)$$

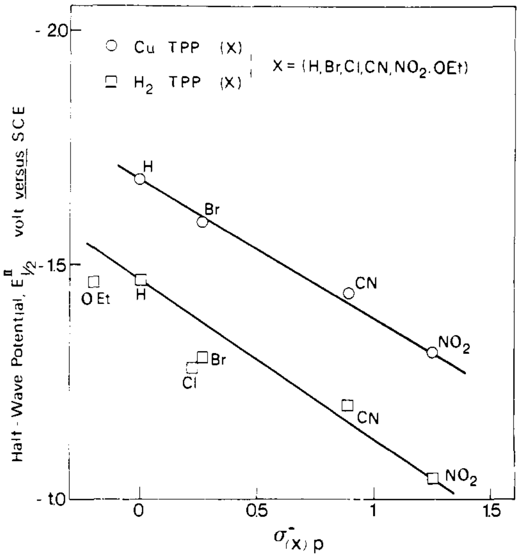

Figure 4. Plot of half-wave potentials of wave II vs. Hammett's σ_p^-.

In general agreement with previously published findings emanating from several laboratories, it is apparent that in monosubstituted TPP moieties electron-withdrawing groups facilitate reactions 3 and 4 by shifting each of the relevant half-wave potentials (i.e., $E^{I}_{1/2}$ on the one hand and $E^{II}_{1/2}$ on the other hand) to more positive (more anodic) values. The sequence[27] which transpires from Tables I and III is

$$\text{OEt} < \text{H} < \text{Br} < \text{Cl} < \text{SCN} < \text{CN} < \text{NO}_2 \quad (5)$$

This series is accounted for by classical intramolecular interactions. Indeed, the maximum potential shift (0.35 V) was engendered by the substituent with the greatest electron affinity, viz., NO_2. This is due to a corresponding change in the energy level of the lowest unoccupied molecular orbital (LUMO), because the substituent's electron-withdrawing effect produces a concomitant decrease in the electron density of the conjugated tetrapyrrole ring system. The potential shifts in series 5 evidently parallel the electron-withdrawing character of the substituents. The only *electron-releasing* group in that series, OEt, produced—as expected—the opposite effect, viz., a cathodic potential shift. Remarkably, the insertion of divalent copper (which was electroinactive under the experimental conditions) in the tetrapyrrole ring did *not affect* the substituent *shifts* in series 5 (even though copper did have an appreciable effect on the absolute values of the half-wave potentials, vide infra); this is reasonable, because the LUMO energy level change is thermodynamically equivalent to an enhancement of electron affinity of the porphyrin ring, regardless of copper insertion. At this point, it is worthwhile to observe that, for a given electron-withdrawing substituent, the

Table III. Data Illustrating the Anomalous Electrochemical Behavior of Pyridinium and Thiocyanato Substituted Porphyrins and Metalloporphyrins[a]

electroreactive moiety	half-wave potentials				rate parameters		
	$E^{py^+ \rightarrow py}$	$E^{I}_{1/2}$	$E^{II}_{1/2}$	$E^{I}_{1/2} - E^{II}_{1/2}$	$D \times 10^6$	$k^{I}_{s} \times 10^2$	$k^{II}_{s} \times 10^2$
$H_2TPP(py^+)$	−0.82	−1.06	−1.62	0.56	1.5	1.3	2.7
$H_2TPP(py^+)$	−0.91	−1.17	−1.62	0.45			
$H_2TPP(SCN)$[b]		−0.89	−1.15	0.26	1.3	5.6	
$CuTPP(SCN)$[c]		−1.05	−1.33	0.28			

[a] Roman numeral superscripts identify (in order of increasing cathodic character) successive electroreduction steps implicating the tetrapyrrole porphyrin ring. [b] $E^{III}_{1/2} = -1.26$, $E^{IV}_{1/2} = -1.62$, $E^{V}_{1/2} = -2.35$, $E^{VI}_{1/2} = -2.45$. [c] $E^{III}_{1/2} = -1.47$, $E^{IV}_{1/2} = -1.90$, $E^{V}_{1/2} = -2.35$, $E^{VI}_{1/2} = -2.50$.

Table IV. Electroreduction Parameters of Polysubstituted Bromotetraphenylporphyrins[a]

electroreactive moiety	half-wave potentials			rate parameters		
	$E^{I}_{1/2}$	$E^{II}_{1/2}$	$E^{I}_{1/2} - E^{II}_{1/2}$	$D \times 10^6$	$k^{I}_{s} \times 10^2$	$k^{II}_{s} \times 10^2$
H_2TPP[b]	−1.08	−1.46	0.38	1.0	1.0	0.8
$H_2TPP(Br)$[b,c]	−0.97	−1.30	0.33	1.5	3.7	4.6
$H_2TPP(Br)_{2,ab}$[c]	−0.87	−1.16	0.29			
$H_2TPP(Br)_{2,ac}$	−0.86	−1.14	0.28	1.6	1.0	0.8
$H_2TPP(Br)_3$[d]	−0.80	−1.05	0.25			

[a] See footnote *a*, Table III. [b] Data repeated from Tables I and II, in order to facilitate comparison. [c] $E^{III}_{1/2} = -2.11$, $E^{IV}_{1/2} = -2.30$. [d] $E^{III}_{1/2} = -2.18$, $E^{IV}_{1/2} = -2.36$.

Table V. Monoelectronic Reduction Waves of Metalloporphyrin Moieties Depicted in Figure 2

compound	1st wave			2nd wave			3rd wave		
	reduction site[a]	$E_{1/2}$	$\Delta E_{1/2}$ per cyano	reduction site[a]	$E_{1/2}$	$\Delta E_{1/2}$ per cyano	reduction site[a]	$E_{1/2}$	$\Delta E_{1/2}$ per cyano
$Mn^{III}TPPCl$	$Mn^{III} \rightarrow Mn^{II}$	−0.220	0.052	porphyrin ring	−1.320	0.24	porphyrin ring	−1.760	0.26
$Mn^{III}TPP(CN)_4Cl$		−0.010			−0.360			−0.730	
$Fe^{III}TPPCl$	$Fe^{III} \rightarrow Fe^{II}$	−0.170	0.013	$Fe^{II} \rightarrow Fe^{I}$	−1.040	0.20	porphyrin ring	−1.700	0.24
$Fe^{III}TPP(CN)_4Cl$		−0.120			−0.260			−0.730	
$Co^{II}TPP$	$Co^{II} \rightarrow Co^{I}$	−0.820		porphyrin ring	−1.920				
$Co^{II}TPP(CN)_3$		−0.420	0.13		−1.100	0.27			
$Co^{II}TPP(CN)_4$	*b*	−0.265	0.16		−0.850	0.25			

[a] Assigned in references 7, 13, and 39. [b] A Co(III)–Co(II) wave might have been observed at more positive potentials in solutions containing $Co^{III}TPP$ moieties.

observed anodic shift of the reduction potential (facilitating reduction) is at least five times larger when pyrroles, instead of phenyls, are substituted in tetraphenylporphyrins. For instance, in the first reduction step, four cyano groups induce the shift $\Delta E_{1/2} = +0.96$ V (referred to the half-wave potential of H_2TPP), when the pyrroles are substituted, and only $\Delta E_{1/2} = +0.17$ V when the phenyls are substituted.[15,17a] Plots[28] of the observed half-wave potential vs. Hammett's σ_p^- are shown in Figures 3 and 4.[29] They substantiate the prevalence of linear free energy relationships, viz.,

$$\Delta E_{1/2} = \rho_\pi \sigma_p^- \quad (6)$$

yielding

$$\text{from wave I, } \rho_\pi = +0.28 \pm 0.002 \text{ for } H_2TPP(X)$$
$$\text{and } +0.29 \pm 0.002 \text{ for } CuTPP(X) \quad (7)$$
$$\text{from wave II, } \rho_\pi = +0.32 \pm 0.002 \text{ for } H_2TPP(X)$$
$$\text{and } +0.29 \pm 0.002 \text{ for } CuTPP(X) \quad (8)$$

The rationale for using in eq 6 the parameters ρ_π and σ_p^- (rather than ρ and σ_p) is predicated on relevant fundamental considerations[30] and evidence available in the literature[9,31-34] that reductive electron transfer to porphyrins implicates directly the π-bonded ring system to which the β substituents are resonatively conjugated. Raman data[32] substantiating the prevalence of resonance interations are particularly convincing in this context. On the other hand, we now recognize that reliance on ρ and σ_p in two of our earlier papers[15,19] was in error, even though other authors have correctly used ρ and σ_p for *phenyl-substituted* moieties (where there are no resonant interactions between the π-electron system of the porphyrin ring and the substituents on the phenyls).

The positive assignments for ρ_π in eq 7 and 8 are consistent with the a priori plausible (and experimentally substantiated) enhancement of electron affinity in the presence of electron-withdrawing substituents, which engender a decrease of electron density in the porphyrin macrocycle. The ρ_π assignments obtained in the present study illustrate the drastic effect of *pyrrole substitution in porphyrins.* Analogous large effects—and excellent linearity with σ_p^-—have been substantiated by Pillsbury and Busch[36] for substituents directly bound to conjugated systems of other macrocycles. On the other hand, entirely different ρ values have been reported[16,17] for electron-withdrawing substituents on the peripheral phenyl groups of TPP, whose "efficiency" in lowering the electron density of the porphyrin ring core appears to be much smaller.

As far as sequential polysubstitution is concerned, the half-wave potential shifts in the bromo-TPP series (Table IV, columns 1-3) warrant a further comment. The relevant data are plotted in Figure 5. It is apparent that $E^{I}_{1/2}$ and $E^{II}_{1/2}$ shifted anodically, as a function of the number of bromine

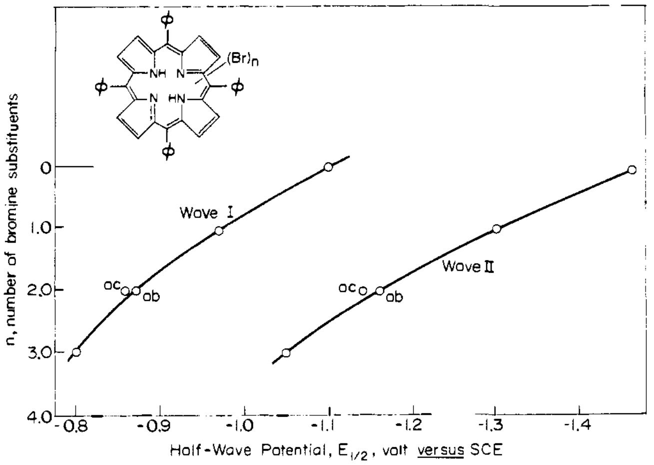

Figure 5. Plot of half-wave potentials as function of bromine substitution. The isomers ab and ac are identified in Figure 1.

substituents.[38] However, the shift was *nonlinear*, and decreased in magnitude as the number of bromines increased. This behavior is partly similar and partly at variance to that previously reported[15] in the polysubstituted cyano-TPP series. The similarity is qualitative in the sense that stepwise bromo and cyano substitution both produced anodic half-wave potential shifts. The difference is in the quantitative aspects of the half-wave potential shifts: each cyano substitution shifted $E^{I}_{1/2}$ and $E^{II}_{1/2}$ approximately by a constant 0.25 V; in contradistinction, the effect of bromo substitution was not only nonlinear, but also appreciably smaller, viz., 0.3-0.4 V for the cumulative effect of three bromine substituents vs. 0.75 for the cumulative shift by three cyano substituents. The nonadditivity of bromine substitution *cannot* be explained by polar or mesomeric interactions. However, it *can* reasonably be ascribed to steric interactions between the bromines and the phenyls in "peri" positions. These may minimize the effect of the phenyls which become more orthogonal and/or induce a deformation of the molecule (e.g., between pyrroles and meso bridges) which would tend to eliminate an eclipsed bromine-phenyl conformation. The steric hindrance (which tends to reduce potential shifts) can be expected to become gradually more effective when several bromine substituents are successively involved, and thus account for the observed nonlinearity in Figure 5. As in the cyanoporphyrin series[15] the anodic shift is larger for $H_2TPP(Br)_{2_{ac}}$ than for $H_2TPP(Br)_{2_{ab}}$, and again parallels an increased bathochromic shift in the visible part of the electronic spectra.

Insertion of copper, which is *not electroreducible*, in the monosubstituted porphyrins (Figures 3 and 4) did not modify the $E_{1/2}$ shifts engendered by the electron-withdrawing substituents on the periphery of the porphyrin ring: the effect was simply a constant (parallel) displacement of the Hammett plots. The insertion of *electroreducible cations* [e.g., Fe(III), Mn(III)] into our pyrrole-substituted cyanoporphyrins (Table V) yielded substituent effects on potential shifts, which depended on the electron acceptor site, viz., (a) when the porphyrinic macrocycle was electroreduced, the potential shift was *not affected* by the presence of the metal and remained a remarkably invariant (0.250 ± 0.002) V per cyano substituent; (b) when the inserted cation was electroreduced the potential shifts engendered by cyano substitution were unsystematically scattered and generally smaller [e.g., 0.013 V per cyano substituent in $Fe^{III}TPP(CN)_4Cl$].

The above "difference in sensitivity to β-pyrrole substitution" provides an interesting prima facie diagnostic criterion for identifying electron-acceptor sites in metalloporphyrins. Invariant half-wave potential shifts of +0.25 V per cyano substituents indicate electroreduction of the organic ligand, regardless of the electroreducibility of the inserted cation. On the other hand, potential shifts engendered by cyano substitution are smaller and scattered when an inserted metal is electroreduced. For optimum differentiation, reliance on the first (least cathodic) poloarographic half-wave potential is recommended.

In contradistinction to the drastic potential shifts, our β-pyrrole substituents did *not* change significantly the diffusion coefficients of the parent porphyrin moieties, nor their electroreduction rate constants. The relevant values, listed in Tables II-IV, are entirely comparable to those reported in the literature[16,37] for other porphyrins.

References and Notes

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