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trations of dissymmetric quencher molecules (CoNDP or CoNTP) in solution with a racemic excited-state population of luminophores (ΛLn* and ΔLn*) can produce substantial enantiomeric excess in the Ln* population via enantiodifferential rate processes for ΛLn* vs ΔLn* quenching. Evidence for the creation of an enantiomeric excess in the Ln* population is provided by circularly polarized luminescence measurements, and the rate of formation of this enantiomeric excess can be determined from time-resolved emission dissymmetry (g_{em}) measurements. Examples of CPL spectra generated by enantioselective quenching in Tb*–CoATP and Tb*–CoGTP systems are shown in Figures 2 and 3, and the values determined for several enantioselective quenching parameters (e.g., $k_{\delta q}$ and E_q) are summarized in Table I.

The enantioselective quenching results exhibit a number of interesting features, and we have identified and discussed these features in earlier parts of the paper. The most striking features are those reflected in the relative signs and magnitudes of E_q values determined for the six CoNTP and three CoNDP quencher complexes (see Table I and Figure 4). As illustrations, consider the following results for Tb* quenching: (a) CoATP quenches one enantiomer of Tb* 32% more efficiently than the other and CoGTP quenches one enantiomer of Tb* 16% more efficiently than the other, but CoATP and CoGTP have *opposite* enantiomeric preferences; (b) CoGTP and CoGDP show essentially identical quenching behavior, whereas CoATP and CoADP differ with respect to enantiomeric preference *and* the degree of enantioselective quenching. Interpretation of these results in terms of detailed structural or mechanistic models of intermolecular chiral discriminatory interactions is beyond the scope of the present work. Given the structural complexities of the systems and the subtleties of chiral discriminatory interactions, detailed interpretation of the results is a rather daunting task. However, this task will become easier as more enantioselective quenching studies are carried out on additional, structurally related systems. In our laboratory, we have begun a systematic study of *bidentate* Rh(H_2O)$_4$(nucleotide) and *tridentate* Rh(H_2O)$_3$(nucleotide) complexes as enantioselective quenchers of Eu* and Tb* luminescence. These complexes provide additional variations in stereochemical structure, and the replacement of Co(III) with Rh(III) provides an opportunity for examining how quenching is influenced by the electronic-state structure of the quencher metal.

Acknowledgment. This work was supported by grants from the National Science Foundation (CHE-8820180 to F.S.R.), the National Institutes of Health (DK 19419 to C.M.G.), and the Muscular Dystrophy Association of America.

Registry No. Tb(dpa)$_3^{3-}$, 38682-37-0; Eu(dpa)$_3^{3-}$, 38721-36-7; [Co(NH_3)$_4$(adp)], 63937-09-7; [Co(NH_3)$_4$(gdp)], 113903-18-7; [Co(NH_3)$_4$(idp)], 141345-92-8; [Co(NH_3)$_4$(atp)]$^-$, 63915-28-6; [Co(NH_3)$_4$(gtp)]$^-$, 141345-93-9; [Co(NH_3)$_4$(itp)]$^-$, 141345-94-0; [Co(NH_3)$_4$(ctp)]$^-$, 141345-95-1; [Co(NH_3)$_4$(utp)]$^-$, 141345-96-2; [Co(NH_3)$_4$(ttp)]$^-$, 141374-98-3.

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Unusual Behavior of 5,10,15,20-Tetraphenylporphine Diacid toward Oxygen Bronsted Bases

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Acid–base properties of 5,10,15,20-tetraphenylporphine diacid salts ($H_4TPP^{2+}(X^-)_2$) in the presence of neutral oxygen Bronsted bases have been studied in chloroform and nitrobenzene by visible and ^{1}H-NMR spectroscopy. The acid strength and the conformation of $H_4TPP^{2+}(X^-)_2$ are largely determined by the size and the nature of the counterion X^-. Localized negatively charged counterions, such as Cl^-, stabilize the protonated porphyrin by forming a strong tight-contact pair with the cationic porphyrin moiety, whereas delocalized negatively charged counterions, such as ClO_4^-, form a weak tight-contact pair and hence destabilize the porphyrin diacid by increasing its acidity. Defining the acidity by the concentration of Bronsted base required for half-neutralization of H_4TPP^{2+}(C50%), we find the acidity of $H_4TPP^{2+}(X^-)_2$ salts to be linearly correlated with both the size of the counteranion (r) and the chemical shift of the NH pyrrolic resonance of the porphyrin core (CS). Furthermore, the correlations of the acidity of $H_4TPP^{2+}(X^-)_2$ both with the pK_a of the neutral oxygen base solvents, measured in sulfuric acid–water solutions, and with the donicity number (D) of the oxygen Bronsted bases suggest that the mechanism of deprotonation of $H_4TPP^{2+}(X^-)_2$ is dependent upon both the basicity and the solvation power (donicity) of the Bronsted neutral oxygen base solvents.

Introduction

Porphyrins and metalloporphyrins have attracted the interests of chemists and biochemists alike, and their physical, chemical, and biological properties have been extensively studied over the last 50 years.[1] Little is known, however, about the chemistry of their mono- and diprotonated species, namely porphyrin acids (eqs 1 and 2). The X-ray crystal structures, as well as UV/vis and

$$H_2TPP \xrightarrow{H^+} H_3TPP^+ \tag{1}$$

$$H_3TPP^+ \xrightarrow{H^+} H_4TPP^{2+} \tag{2}$$

IR spectra, of a few porphine diacids[2] (5,10,15,20-tetra-4-pyridylporphine and 5,10,15,20-tetraphenylporphine[2a]) have been reported, as has the structure of a porphine monoacid salt (octaethylporphinium monoacid triiodide[2b]). It has been shown that the protonated octaethylporphyrin cation and triiodide counteranion ($(OEPH_4)^{2+}(I_3^-)_2$) are strongly associated through hydrogen bonding in chloroform, whereas in methanol the diprotonated species dissociates into monoprotonated porphyrin and HI.[2c] Our interest in the porphine diacids stems from observations in this laboratory that their treatment with the common organic solvents DMSO, DMF, Et_2O, etc. leads to their deprotonation.[3] Though

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(1) (a) Dolphin, D., Ed. *The Porphyrins*; Academic Press: New York, 1979. (b) Smith, K. M., Ed. *Porphyrins and Metalloporphyrins*; Elsevier Scientific Publishing Co.: Amsterdam, 1975.

(2) (a) Stone, A.; Fleischer, E. B. *J. Am. Chem. Soc.* **1968**, *90*, 2735. (b) Hirayama, N.; Takenaka, A.; Sasada, Y. *J. Chem. Soc., Chem. Commun.* **1974**, 330. (c) Ogoshi, H.; Watanabe, E.; Yoshida, Z. *Tetrahedron* **1973**, *29*, 3241.

(3) The same phenomenon was observed for dimeric porphyrins: (a) Bookser, B. C.; Bruice, T. C. *J. Am. Chem. Soc.* **1991**, *113*, 428. (b) Karaman, R.; Bruice, T. C. *J. Org. Chem.* **1991**, *56*, 3470–3472.

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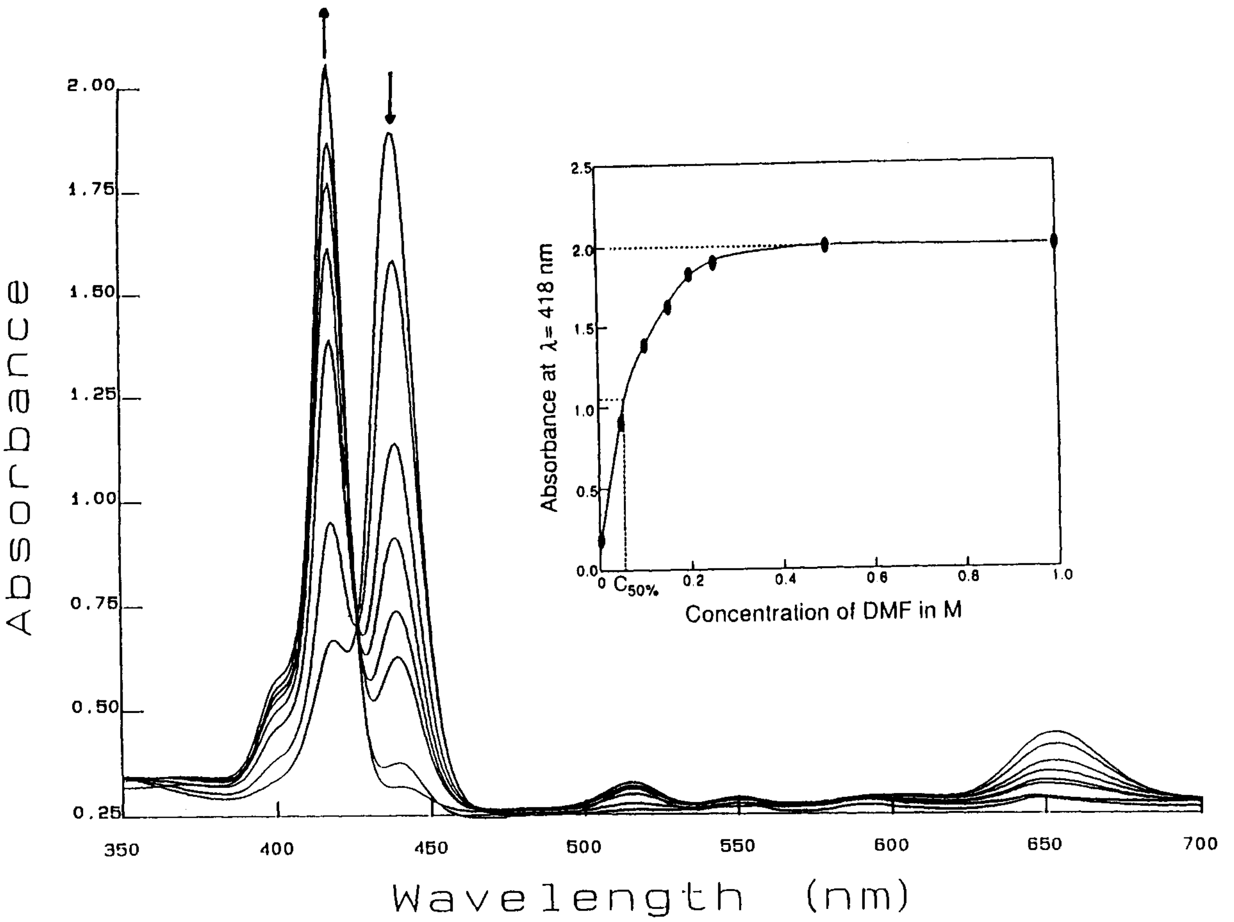

Figure 1. Repetitive spectral scan of $H_4TPP^{2+}(CF_3COO^-)_2$ in the titration with DMF. The arrows indicate the band direction upon addition of DMF. The Soret band at $\lambda = 418$ nm is for H_2TPP and that at $\lambda = 439$ nm is for $H_4TPP^{2+}(CF_3COO^-)_2$. The inset shows the accumulation of H_2TPP (absorbance at $\lambda = 418$ nm) on addition of DMF. Isosbestic point at $\lambda = 427.5$ nm shows that there is no accumulation of an intermediate (monoprotonated porphyrin).

the pK_a's of porphine diacids are comparable to that of protonated pyridine,[4] we find that the latter does not undergo proton dissociation in DMSO and DMF.

We describe in this paper the chemical behavior of 5,10,15,20-tetraphenylporphine diacid salts ($(H_4TPP)^{2+}(X^-)_2$) toward oxygen Bronsted bases and the effect of the nature of the counterion on the reactivity of the diacid. Furthermore, we discuss the relationship between the reactivity and the observed spectral properties (^{1}H-NMR and visible) in solution.

Experimental Section

Absorption spectra were recorded on a Cary 14 spectrophotometer interfaced to a Zenith computer equipped with OLIS (On-Line Instrument System Inc.) data acquisition and processing software. ^{1}H-NMR spectra were obtained on a Nicolet NT-300 spectrophotometer. The solvent used was $CDCl_3$ (pretreated with K_2CO_3 unless otherwise indicated). Chemical shifts (ppm) were referenced to Me_4Si. Tetraphenylporphyrin (H_2TPP) was purchased from Alfa Products Co. Trifluoroacetic acid, tetrabutylammonium iodide ($(n\text{-}Bu)_4N^+I^-$), tetraethylammonium bromide ($Et_4N^+Br^-$), benzyltriethylammonium chloride ($(PhCH_2)Et_3N^+Cl^-$), tetraethylammonium perchlorate ($Et_4N^+ClO_4^-$), acetophenone, nitrobenzene, and benzophenone were obtained from Aldrich Chemical Co. All other reagents were obtained commercially in high purity. Acetone, dimethyl sulfoxide (DMSO), and acetophenone were distilled from CaH_2.[5] Diethyl ether was distilled from $LiAlH_4$.[5] Absolute ethyl alcohol was distilled from Mg.[5] *N,N*-Dimethylformamide (DMF) was distilled and shaken with BaO, and the mixture was filtered.[6] Chloroform ($CHCl_3$) was distilled from K_2CO_3.[5] All the distilled solvents were stored over 3-Å molecular sieves.

Preparation of 5,10,15,20-Tetraphenylporphine Diacid Solutions ($H_4TPP^{2+}(X^-)_2$). A dry solution of 3.25×10^{-6} M tetraphenylporphyrin (H_2TPP) in chloroform or nitrobenzene was carefully titrated with dry trifluoroacetic acid until 95% of the H_2TPP was converted to $H_4TPP^{2+}(CF_3COO^-)_2$. The progress of the titration was followed by visible spectroscopy and was indicated by the disappearance of the absorption peak at $\lambda = 418$ nm, corresponding to H_2TPP, and the appearance of a new peak at $\lambda = 439$ nm, corresponding to $H_4TPP^{2+}(CF_3COO^-)_2$.

Reactions of 5,10,15,20-Tetraphenylporphine Diacid ($H_4TPP^{2+}(X^-)_2$) with Bronsted Bases. In a typical experiment, a dry Bronsted base (bases are listed in Table I) was added (via a gastight syringe) to a dry solution of $H_4TPP^{2+}(X^-)_2$ in chloroform, $CDCl_3$, or nitrobenzene (3.25×10^{-6} M for visible studies and 8×10^{-3} M for NMR studies). The progress of the reaction was followed by ^{1}H-NMR and visible spectroscopy.

^{1}H-NMR Experiments. ^{1}H-NMR spectra of $H_4TPP^{2+}(CF_3COO^-)_2$ in the presence of several counterions (Cl^-, Br^-, I^-, and ClO_4^-) were collected in dry $CDCl_3$ at 25 °C. The solutions were prepared by dissolving H_2TPP (5 mg, 0.008 mmol) in $CDCl_3$ (1 mL) and adding CF_3COOH (0.0162 mmol) and the appropriate counterion as the tetraalkylammonium salt ($(n\text{-}Bu)_4N^+I^-$, $Et_4N^+Br^-$, $(PhCH_2)Et_3N^+Cl^-$, or $Et_4N^+ClO_4^-$; 0.16 mmol).

Results

Acid-Base Equilibria of 5,10,15,20-Tetraphenylporphine Diacid with Bronsted Bases. We have investigated the deprotonation of the acid salt $H_4TPP^{2+}(CF_3COO^-)_2$ to provide H_2TPP in chloroform and nitrobenzene at 30 °C by the following Bronsted bases: DMSO, DMF, EtOH, Et_2O, acetone, acetophenone, and benzophenone. The concentrations of $H_4TPP^{2+}(CF_3COO^-)_2$ and H_2TPP were monitored at $\lambda = 439$ and 418 nm, respectively. A typical titration curve showing the disappearance of $H_4TPP^{2+}(CF_3COO^-)_2$ and the appearance of H_2TPP is depicted in Figure 1. Table I lists the C50% values determined for the various bases in chloroform and nitrobenzene [C50% is the base concentration needed

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(4) Stewart, R. *The Proton Applications to Organic Chemistry*; Academic Press: New York, 1985; pp 87-145.
(5) Perrin, D. D.; Armarego, W. L. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: Oxford, England, 1988.
(6) Thomas, A. B.; Rochow, E. G. *J. Am. Chem. Soc.* **1957**, *79*, 1843.

Table I. C50% Values of Bronsted Bases in the Titration of $H_4TPP^{2+}(CF_3COO^-)$, Their Measured pK_a and Calculated pK_{a3} Values, and Their Donicity Numbers (D)

Bronsted base	C50%, M in $CHCl_3$	C50%, M in nitrobenzene	pK_a[a]	pK_{a3}[b]	D[c]
DMF	0.082	0.069	−1.2	−10.51	30.9
DMSO	0.072	0.101	−1.54	−10.68	29.8
EtOH	0.449	0.673	−1.94	−11.50	
Et_2O	0.564	1.03	−2.39	−11.69	19.2
acetone	0.735	1.93	−3.06	−11.96	17.0
acetophenone	0.967	2.42	−3.46	−12.06	
benzophenone	1.563		−4.71		

[a] pK_a values taken from ref 8. [b] Calculated from eq 10. [c] Donicity numbers taken from ref 9.

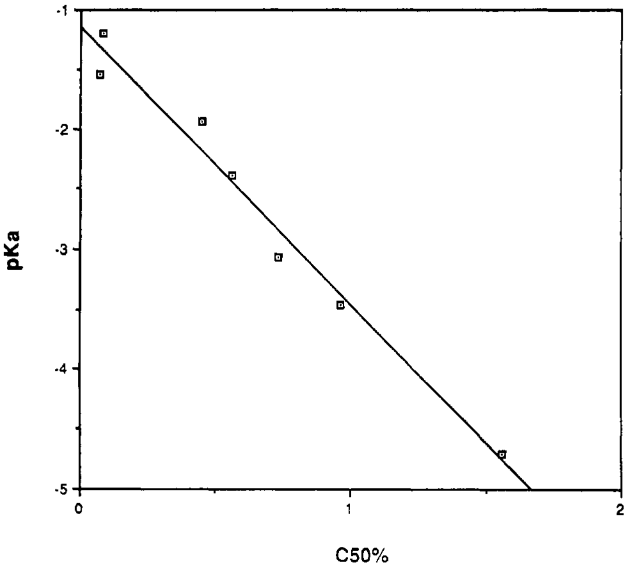

Figure 2. Plot of the measured pK_a values of Bronsted bases vs the C50% values (M) for the titration of $H_4TPP^{2+}(CF_3COO^-)_2$ (3.25×10^{-6} M in $CHCl_3$) with the bases. See eq 3.

to titrate 50% of $H_4TPP^{2+}(CF_3COO^-)_2$]. Also recorded in Table I are the pK_a values for the protonated solvent bases when determined in sulfuric acid–water solutions and in oleum mixtures using the x-acidity function.[7] It must be pointed out that the actual pK_a values in nonaqueous media such as nitrobenzene or chloroform will be different. However, since the listed pK_a values were measured in concentrated acid solutions to avoid deviations from ideality and since there are no reported pK_a values for all the bases studied in this work in nonaqueous systems, we believe that the use of these values as a basicity scale in chloroform or nitrobenzene is somewhat justified. The C50% data summarized in Table I were examined for linear relationships with the measured pK_a values of the oxygen Bronsted bases. They were found to follow reasonably well the simple expressions shown in eqs 3 and 4, where eq 3 is for the correlation in chloroform and eq 4

$$\mathrm{p}K_a = -1.15 - 2.31(\mathrm{C50\%}) \qquad R = 0.99 \qquad (3)$$

$$\mathrm{p}K_a = -1.33 - 0.90(\mathrm{C50\%}) \qquad R = 0.99 \qquad (4)$$

is for the correlation in nitrobenzene. The linear free-energy relationship in chloroform is shown graphically in Figure 2.

The position of the equilibrium of eq 5 is provided by the acid dissociation constants for H_4TPP^{2+}, H_3TPP^+, and oxybase·H^+ [K_{a1} (eq 6), K_{a2} (eq 7), and K_{a3} (eq 8), respectively], and its constant term (K_{eq}) is given in eq 9. The pK_{a3} values of oxybase·H^+ species in nitrobenzene (see Table I) were calculated from eq 10, where pK_{a1} and pK_{a2} are 4.38 and 3.85, respectively.[8] Comparison of oxybase·H^+ pK_{a3} values in nitrobenzene and pK_a values in sulfuric acid–water solutions establishes the linear relationship of eq 11.

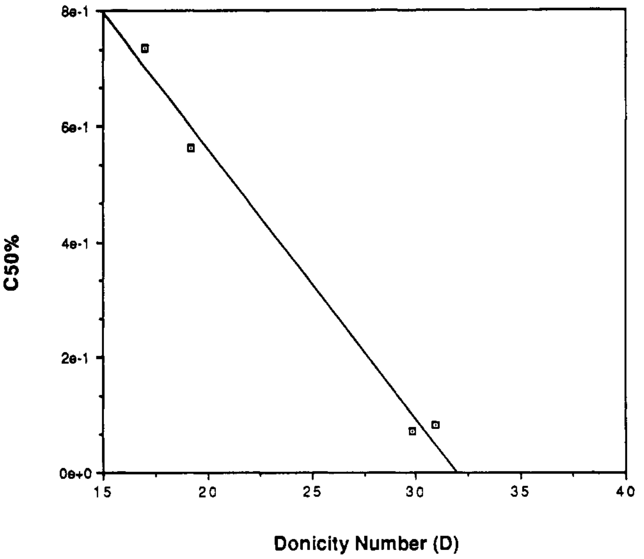

Figure 3. Plot of the C50% values (M) vs the donicity number of Bronsted bases (D) for the titration of $H_4TPP^{2+}(CF_3COO^-)_2$ (3.25×10^{-6} M in $CHCl_3$) with the bases. See eq 12.

$$H_4TPP^{2+} + \text{oxybase} \rightleftharpoons H_3TPP^+ + \text{oxybase}\cdot H^+ \qquad (5)$$

$$H_3TPP^+ + \text{oxybase} \rightleftharpoons H_2TPP + \text{oxybase}\cdot H^+$$

$$[H_4TPP^{2+}] = \frac{a_H[H_3TPP^+]}{K_{a1}} \qquad (6)$$

$$[H_3TPP^+] = \frac{K_{a1}a_H[H_2TPP]_T}{a_H^2 + K_{a1}a_H + K_{a1}K_{a2}} \qquad (7)$$

$$[H_2TPP]_T = [H_4TPP^{2+}] + [H_3TPP^+] + [H_2TPP]$$

$$[\text{oxybase}\cdot H^+] = \frac{a_H[\text{oxybase}]}{K_{a3}} \qquad (8)$$

$$K_{eq} = \frac{[H_2TPP][\text{oxybase}\cdot H^+]^2}{[H_4TPP^{2+}][\text{oxybase}]^2} \qquad (9)$$

$$K_{a3} = \left(\frac{K_{a1}K_{a2}}{K_{eq}}\right)^{1/2} \qquad (10)$$

$$\mathrm{p}K_a = 12.1 + 1.26(\mathrm{p}K_{a3}) \qquad R = 0.94 \qquad (11)$$

The discrepancy between the calculated and the measured pK_a values (see Table I) is attributed to the fact that the Bronsted bases studied here behave as bases and as solvating agents, especially when they are mixed with poor solvating agents such as chloroform and nitrobenzene. The solvation power (donicity) of the Bronsted bases does not depend on their dielectric constant, but on their ability to donate electrons to the cationic porphyrin (cation solvation) or accept electrons from the porphyrin counterions (anion solvation). The donor property of a solvent is measured by its "donicity".[9] We find the donicity numbers (D's) of some Bronsted bases studied (see Table I) bear linear relationships to the C50% values in chloroform and nitrobenzene, and the correlation results obtained are summarized in eqs 12 and 13,

$$\mathrm{C50\%} = 1.50 - 0.05D \qquad R = 0.99 \qquad (12)$$

$$\mathrm{C50\%} = 3.65 - 0.12D \qquad R = 0.95 \qquad (13)$$

respectively. The correlation results of eq 12 are illustrated

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(7) (a) Bagno, A.; Scorrano, G. *J. Am. Chem. Soc.* **1988**, *110*, 4577. (b) Bagno, A.; Scorrano, G.; Oferall, R. A. M. *Rev. Chem. Intermed.* **1987**, 314.

(8) Aronoff, S. *J. Phys. Chem.* **1958**, *62*, 428.

(9) (a) Gutmann, V. *Coordination Chemistry in Non-Aqueous Solutions*; Springer-Verlag: Berlin, 1968. (b) Szwarc, M. *Ions and Ion Pairs in Organic Reactions*; Szwarc, M., Ed.; Wiley: New York, 1972; Vol. 1, pp 1–26.

Table II. ^{1}H NMR Spectral Data for $H_4TPP^{2+}(X^-)_2$ (3.25×10^{-6} M) in $CDCl_3$, C50% (M) Values for the Titration with DMF, and *r* values (Å) for X^-

		chemical shifts, ppm					
X^-	C50%	NH	ortho proton	meta,para protons	β proton	r^a	r^b
ClO_4^-	0.036	−0.77	8.55	8.0	8.68		
CF_3COO^-	0.082	−0.65	8.55	8.0	8.66		
I^-	0.335	−0.60	8.60	8.0	8.59	2.05	2.16
Br^-	0.904	−0.22	8.58	7.99	8.54	1.80	1.95
Cl^-	1.451^c	0.24	8.55	7.99	8.52	1.64	1.81

^{a} Radius of X^- recommended by Gourary and Adrian.[12] ^{b} Radius of X^- recommended by Pauling.[13] ^{c} A similar value was obtained using a 3.25×10^{-6} M solution of $H_4TPP^{2+}(Cl^-)$ prepared by titrating a solution of H_2TPP in $CHCl_3$ with HCl gas.

graphically in Figure 3. As the measured pK_a values were earlier shown to correlate directly with the C50% values, the correlations in eqs 12 and 13 establish the relationship of all three data sets.

Effect of the Counterion on Acid–Base Equilibria of 5,10,15,20-Tetraphenylporphine Diacid. To investigate whether the counterion plays a role in determining the stability or the reactivity of the H_4TPP^{2+} moiety, titrations of 3.25×10^{-6} M solutions of $H_4TPP^{2+}(CF_3COO^-)_2$ by DMF were carried out in the presence of a large excess (8.3×10^{-3} M) of the following ammonium salts: $(n\text{-}Bu)_4N^+I^-$, $Et_4N^+Br^-$, $(PhCH_2)Et_3N^+Cl^-$, and $Et_4N^+ClO_4^-$. It should be mentioned that attempts to conduct titration measurements in the presence of tetrabutylammonium fluoride failed, since deprotonation of $H_4TPP^{2+}(CF_3COO^-)_2$ occurred upon the addition of the fluoride salt. This is because of the high basicity of the fluoride anion.[10] The C50% values obtained from these experiments are listed in Table II. Also included are the ^{1}H-NMR data for the protonated species in $CDCl_3$.

The effect of the counterion on the ^{1}H-NMR chemical shift of the protons of its nearby cation is determined by the size and the electronic charge of the anion.[11] To examine the relationship between the sizes of the counterions of the protonated porphyrin species, $H_4TPP^{2+}(X^-)_2$, and their observed ^{1}H-NMR spectra, the values of the radii (*r*, Å) of the halogen counterions were plotted against the chemical shifts of the NH resonances (CS), and the correlation results were found to follow the simple expressions depicted in eqs 14 and 15, where eq 14 is for the *r* values rec-

$$\mathrm{CS} = 3.47 - 2.00r \qquad R = 0.98 \tag{14}$$

$$\mathrm{CS} = 4.45 - 2.35r \qquad R = 0.99 \tag{15}$$

ommended by the Adrian and Gourary[12] and eq 15 is for those recommended by Pauling.[13] Furthermore, the acidities of $H_4TPP^{2+}(X^-)_2$ as reflected by the C50% values were examined for a linear relationship with the NH resonances (CS), and the correlation results obtained are depicted in eq 16 and illustrated graphically in Figure 4.

$$\mathrm{CS} = -0.78 - 0.676(\mathrm{C50\%}) \qquad R = 0.99 \tag{16}$$

Discussion

Aronoff[8] carried out spectrophotometric titrations of tetraphenylporphyrin in nitrobenzene using as titrant a solution of perchloric acid in dioxane. He found that H_2TPP undergoes two successive protonation processes that lead to the mono- and the diprotonated species, H_3TPP^+ and H_4TPP^{2+}, respectively. The pK_a values calculated for the mono- and the diprotonated species are pK_{a1} = 4.38 and pK_{a2} = 3.85, respectively. From these reported pK_a values it is apparent that neither the mono- nor the diprotonated tetraphenylporphyrin species is a strong acid. One might expect that deprotonation of H_3TPP^+ and H_4TPP^{2+} would require a stronger base than the neutral oxygen Bronsted bases employed in this study. Examination of the results shown in Table I and summarized in eqs 3 and 4 indicates that this is not the case. Weak bases, such as benzophenone and acetophenone, react with $H_4TPP^{2+}(X^-)_2$ to give H_2TPP, presumably through the monoprotonated H_2TPP (H_3TPP^+). However, throughout this study, no evidence for the intermediacy of $H_3TPP^+(X^-)$ was obtained. In order to understand this unique phenomenon, we investigated the following points: (1) the conformational structure of $H_4TPP^{2+}(X^-)_2$ in organic solvents and the effect of the nature of the counterion on its acidity (pK_a); (2) the conformational changes of $H_4TPP^{2+}(X^-)_2$ upon titration with a Bronsted base.

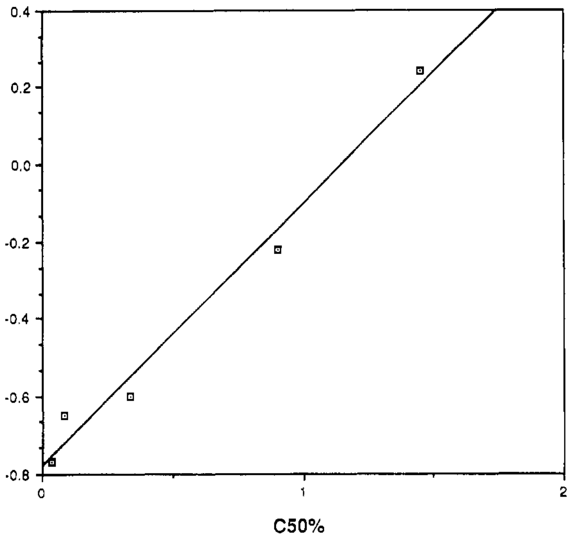

Figure 4. Plot of the chemical shifts of the NH resonances in ppm (CS) vs the C50% values (M) for the titration of $H_4TPP^{2+}(X^-)_2$ (3.25×10^{-6} M in $CHCl_3$) with DMF. See eq 16.

(1) Effect of the Counterion on the Acidity of 5,10,15,20-Tetraphenylporphine Diacid. Examination of Table II indicates a number of pronounced systematic relationships whose significance may be understood. Most significant is the marked relationship between the size of the counteranion (X^-) and the ability of X^- to stabilize the diprotonated species. Whereas counterions with localized negative charges, such as Cl^-, stabilize the protonated species, counterions with delocalized negative charges, such as CF_3COO^- and ClO_4^-, tend to destabilize it by enhancing its acidity. This conclusion is based on the amount of DMF needed to titrate 50% of a 3.25×10^{-6} M solution of H_4TPP^{2+} (C50%) in the presence of the different counterions (see column 2 in Table II). This is not surprising, since it is known that, in solvents of low or moderate polarity, such as chloroform or nitrobenzene, ions are extensively associated into pairs and the reactivity of the ion is significantly dependent on the counterion.[9b]

Inspection of the ^{1}H-NMR spectral data in Table II indicates that NH resonances of the diprotonated porphyrin, $H_4TPP^{2+}(X^-)_2$, in the presence of the more localized negatively charged counterions, such as Cl^-, are more deshielded than those of the porphyrin in the presence of delocalized ones, such as CF_3COO^- and ClO_4^-.[14] The deshielding is attributed to the electronic effect of the negatively charged counterion on its nearby cation. In the case of $H_4TPP^{2+}(Cl^-)_2$, the NH resonance is significantly deshielded because the ions exist mainly as strong tight-contact ion pairs and thereby the Cl···H distance is relatively short, whereas, in the case of $H_4TPP^{2+}(ClO_4^-)_2$, the NH resonance is less deshielded since the H···ClO_4 distance is longer because the population consists mainly of weak tight-contact ion pairs.

The acidity of a diprotonated porphyrin is determined by the magnitude of the equilibrium constant (K_{eqa}) for its dissociation (eq 17). The acid strength of H_4TPP^{2+} with bulky counterions, as in $H_4TPP^{2+}(ClO_4^-)_2$, is greater than that with small counterions,

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(10) The pK_a of HF is 3.18: Perrin, D. D. *Ionization Constants of Inorganic Acids and Bases in Aqueous Solutions*, 2nd ed.; Pergamon Press: Oxford, England, 1982.

(11) McKeever, D. In *Ions and Ion Pairs in Organic Chemistry*; Szwarc, M., Ed.; Wiley: New York, 1972; Vol. 1, pp 263–287.

(12) Gourary, B. S.; Adrian, F. J. *Solid State Phys.* **1960**, *12*, 127.

(13) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

(14) Similar changes in the ^{1}H-NMR spectra of octaethylporphyrin diacids were observed.[3c]

$$(H_4TPP^{2+},X^-)_{tight} \overset{K_{eq}}{\rightleftharpoons} (H_4TPP^{2+} + X^-)_{free} \tag{17}$$

as in $H_4TPP^{2+}(Cl^-)_2$, because of greater dissociation into free ions. The correlation results depicted in eq 16 and illustrated in Figure 4 indicate clearly the linear relationship between the closeness of the ion pairs, as reflected by the chemical shifts of the NH resonances (CS), and the reactivity or the acid strength of the protonated species (C50%). The results summarized in eqs 14 and 15 indicate that the chemical shift of the NH resonance of the diprotonated porphyrin (CS) is linearly correlated with the size of the counterion (r). The deshielding effect of a large counterion, such as I^-, on the NH resonance of H_4TPP^{2+} is less than that of a small counterion, such as Cl^-. This is because small counterions bind strongly to the cation and large counterions prefer the formation of a weak tight-contact pair with less association between the ions.

The effect of the counterion on the chemical shifts of the pyrrolic β and the phenyl protons of $H_4TPP^{2+}(X^-)_2$ is not very significant, since the counterion is localized far from the environment of these protons. An inverse relationship is seen to exist between the size of X^- and the chemical shift of the pyrrolic β protons (see column 6 in Table II). From the ^{1}H-NMR data it is difficult to distinguish whether the deshielding effect of the counterions on the NH resonances is only a result of the distance between the counterion and the pyrrolic NH protons or a result of both the change in the conformation of the porphyrin core and the NH$\cdots$X distance.

(2) Effect of the Nature of the Added Bronsted Base on the Acidity of 5,10,15,20-Tetraphenylporphine Diacid. On the basis of the results described in the previous section, changes in the environment are expected to drastically affect the acidities of the protonated tetraphenylporphyrin species. Chloroform and nitrobenzene are electron-deficient solvents, and their association with the protonated tetraphenylporphyrin species is likely to be weak. In contrast, Bronsted bases, such as those listed in Table I, are capable of associating with protons through hydrogen bonding, and their addition to solutions of $H_4TPP^{2+}(X^-)_2$ in such solvents as chloroform and nitrobenzene is expected to lead to changes in the ionic nature of the protonated species from that of tight-contact pairs (H_4TPP^{2+},X^-), in which the protonated porphyrin is associated with its counterion by hydrogen bonding, to that of solvent-separated ion pairs (H_4TPP^{2+},B,X^-), in which one or more molecules of the Bronsted base solvent separate the ions.[15] The solvation ability of a certain solvent is measured by the donicity number.[9] Bronsted bases with high donicity numbers are strong solvating agents and are expected to coordinate strongly with the ions of the contact pair. An increase in the strength of the solvation power provides the driving force for the dissociation of the solvent-separated ion pair into free ions. Therefore, the dissociation of the ion pairs in good solvating agents such as Bronsted bases with high donicity numbers is more extensive than that in poor coordinating solvents such as weak Bronsted bases. The increase in the fraction of free ions causes an enhancement in the acid strength of the protonated species. It is found that the values of C50% are a linear function (eqs 12 and 13) of the literature[9] donicity numbers (Figure 3). The results of Figure 3 indicate clearly the linear relationship between the acid strength of the diprotonated porphyrin as measured by the amount of Bronsted base needed in the titration (C50%) and the solvation power (donicity number) of the Bronsted base.

Inspection of Table I indicates that the directly determined pK_a values of the Bronsted bases in sulfuric acid–water solutions (−1.2 to −4.71; see column 4) are much greater than the calculated pK_{a3} values from eq 10 (−10.51 to −12.06; see column 5). This is because in low dielectric solvents, such as chloroform and nitrobenzene, ions are strongly associated into pairs. Because the acid dissociation constant K_{eq} is defined in terms of dissociation of ions (see eqs 5 and 9), the calculated equilibria do not reflect true pK_a values, since upon the addition of a Bronsted base to the protonated porphyrin the equilibrium position changes with respect to the new species formed. The changes in the equilibria are dependent on the nature of the added Bronsted base and on the number of the base molecules participating in the solvation of the new ionic species. Furthermore, the slope of eq 11 indicates that the relative basicities of the Bronsted bases listed in Table I are about the same in nitrobenzene and in concentrated sulfuric acid–water solutions. This is because all the bases studied are neutral oxygen Bronsted bases.[16] Comparisons of eqs 3 and 4 indicate that the basicities of the Bronsted bases are lower in nitrobenzene than in chloroform. This might be attributed to the fact that nitrobenzene has a higher dielectric constant and a higher dipole moment than chloroform[17] and hence its association with the Bronsted base is stronger, which results in leveling the basicity of the Bronsted base.

In order to better understand the nature and the modes of the interaction between the Bronsted base and the protonated species, an 8×10^{-3} M solution of $H_4TPP^{2+}(CF_3COO^-)_2$ in $CDCl_3$ was titrated with dry DMSO-d_6 while the reaction was monitored by ^{1}H-NMR spectroscopy. Addition of a small amount of DMSO-d_6 caused broadening and downfield shifting of the NH resonance (0.8 ppm) without significantly affecting other resonances. Addition of more DMSO-d_6 resulted in the formation of H_2TPP. The change in the chemical shift and the shape of the NH resonance could be attributed to an interaction between the protonated porphyrin and DMSO-d_6. This is also confirmed by the slight change in the visible absorption of the QI band (2–3 nm) upon the addition of the base.

Conclusions

The following salient points emerge from this work: (1) The acid strength of $H_4TPP^{2+}(X^-)_2$ is largely affected by the nature of the counterion X^-. (2) The mechanism for the deprotonation of $H_4TPP^{2+}(X^-)_2$ by Bronsted bases is dependent upon both (a) the basicity and (b) the solvation power (donicity number[9]) of the added Bronsted base. (3) The correlation results of eq 12 serve to establish a quantitative scale for the solvation power (donicity number) of the Bronsted bases studied in this work. (4) The chemical shift of the NH resonance of $H_4TPP^{2+}(X^-)_2$ is a good index for estimating the effect of X^- on the acid strength of H_4TPP^{2+}. (5) Throughout this work, no evidence for the accumulation of the monoprotonated porphyrin, $H_3TPP^+(X^-)$, was found on neutralization of the diprotonated species. This could be attributed to the similarity of the pK_a values of $H_4TPP^{2+}(X^-)_2$ and $H_3TPP^+(X^-)$, as was suggested by others.[18]

Registry No. $H_4TPP^{2+}(ClO_4^-)_2$, 22124-45-4; $H_4TPP^{2+}(CF_3CO_2^-)_2$, 59973-30-7; $H_4TPP^{2+}(I^-)_2$, 141346-29-4; $H_4TPP^{2+}(Br^-)_2$, 141346-30-7; $H_4TPP^{2+}(Cl^-)_2$, 141346-31-8; DMSO, 67-68-5; DMF, 68-12-2; EtOH, 64-17-5; Et_2O, 60-29-7; acetone, 67-64-1; acetophenone, 98-86-2; benzophenone, 119-61-9.

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(15) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*; Harper and Row: New York, 1987.

(16) Bell, R. P. *The Proton in Chemistry*, 2nd ed.; Cornell University Press: Ithaca, NY, 1973; p 56.

(17) The dielectric constant and the dipole moment of nitrobenzene are 34.82 and 4.22 D, respectively, and those of chloroform are 4.806 and 1.01 D, respectively: Weast, R. C., Ed. *Handbook of Chemistry and Physics*, 69th ed.; CRC Press: Boca Raton, FL, 1988–1989; Tables E50, E51, and E60.

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