A Proton NMR Study of the Reactions with Acid of *meso*-Tetraphenylporphyrins with Various Numbers of 4-Dimethylamino Groups†

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Proton NMR spectroscopy has been used to study the protonation of *meso*-tetraphenylporphyrins with zero, one, or four para dimethylamino substituents. Changes in the spectra are similar for corresponding protons through this series of compounds. We give the following interpretations. The internal pyrrolenine nitrogen atoms always add two protons before any peripheral dimethylamino groups react. There is no evidence for a monoprotonated intermediate between the free base and diprotonated porphyrin in the chloroform–trifluoroacetic acid solvent system used. The chemical shifts of the NMR signals of the internal N–H protons are strongly acid-dependent and suggest a loss of aromatic ring current at the porphyrin core at intermediate acid concentrations. Changes in chemical shifts of protons on the periphery of these aromatic systems are much smaller and in the opposite sense. The signals of the pyrrole H_β protons move discontinuously upfield upon diprotonation and then drift continuously downfield as acid concentration is increased beyond that required for diprotonation. These changes are also in the directions to be expected if aromatic ring currents of the porphyrin decrease to a minimum at the acid concentration at which the internal nitrogen atoms are fully protonated. We suggest that this is due to the known distortion from planarity of the diprotonated tetraarylporphyrin aromatic system. Signals of protons attached to the meso-substituted aromatic rings move unidirectionally downfield as acid concentration increases.

The changes in optical spectra of porphyrins on addition of acid have been used extensively to follow the evolution of solute species as basic sites are protonated.[1] Careful analysis of the shapes of these spectrophotometric titration curves can establish the sequence of distinguishable states and in favorable cases the number of protons added if successive sets of isosbestic points can be identified. However, there can be problems in determining the concentration of free acid in the nonaqueous solvents generally used for these studies. Furthermore, if several competing basic sites are available, the spectrophotometric data can at best tell only indirectly which sites are protonated. Although proton NMR spectra of porphyrins have been routinely recorded as a step in characterization, they often have not been used to count the number of protons at specific basic sites in these molecules, by integration of appropriate NMR signals. Also, with some exceptions, the spectra have been run only in a nonpolar neutral solvent or in trifluoroacetic acid but not at intermediate acid concentrations.[2] The expectation has been that porphyrins without basic groups on the periphery of the ring system will add two protons on the two pyrrolenine nitrogen atoms which lack them in the free base. This expectation was confirmed by early acid–base titrations[3] and NMR studies[4] which have been interpreted as demonstrations of diprotonation.

In this paper we report proton NMR studies on *meso*-tetraphenylporphyrin with from zero to four para dimethylamino substituents. The data are interpreted in terms of the order in which basic groups are protonated, of the existence of significant concentrations of intermediates at the various stages of protonation, and of the changes in the characteristics of the aromatic system as protonation occurs. These results are correlated with optical spectrophotometric titration data described in the preceding paper.[5]

† We dedicate this paper to the memory of Professor Gerhard L. Closs, in recognition of his important contributions to structure determinations of porphyrins by NMR and to many other areas of physical–organic chemistry.

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Experimental Section

The proton NMR spectra were run on a Bruker AM-400 spectrometer operating in the Fourier transfer mode at 400 MHz, at ambient temperature. In order to correlate these spectra with the sample identity established by optical spectrophotometry[5] (using the absorption maxima and isosbestic points) as acid concentration was increased, it was desirable to confirm the maxima without sample dilution. This was usually possible by the use of spectrophotometer cell spacers which reduced the solution light path length to 0.05 mm; these produced on-scale spectra (except for the Soret peaks) with 0.002 M NMR samples. This is the minimum practical concentration at which NMR spectra can be obtained without excessive base-line roll or instrument noise spikes. For good integration results, it is essential to correct the spectrum base line before integration, and it is much better to use 0.01 M porphyrin solutions. We have assumed that the identity of optical spectra obtained at 0.01–0.002 M concentration with the cell spacer and at 10^{-5}–10^{-6} M without a spacer indicates that there is negligible solute aggregation in these samples over this concentration range. The spectrophotometer used was a Cary Model 17D, and the porphyrin preparations were the same as those studied in the previous paper.[5]

Deuteriochloroform was used as the solvent and trifluoroacetic acid (TFA) as the acid at variable concentration, in these experiments. Conventional 99.8 atom % $CDCl_3$ gives a signal for residual $CHCl_3$ an order of magnitude more intense than the lines in more dilute samples under our conditions, and this intense line creates difficulties in phasing the FID and sometimes conceals solute signals. This problem was evaded by using "100%" $CDCl_3$ (Aldrich) as the solvent for our later spectra. This gives a solvent $CHCl_3$ line with about the same intensity as the solute signals. The chemical shift scale was calibrated by setting this solvent signal at $\delta = 7.26$ ppm. TMS was usually not added; if it was present, the chemical shift calibration against that signal was not significantly different. It proved to be impossible to reach a predetermined protonation step by addition of a calculated TFA volume, due to solvent evaporation as samples were cycled between NMR tubes and spectrophotometer cells. The optical spectra[5]

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were thus necessary to identify (and if necessary to adjust) the stage of protonation observed by NMR.

Sample preparation is straightforward for tetraphenylporphyrin $TPPH_2$ [$=(DMA)_0PH_2$][5] and for ((dimethylamino)phenyl)triphenylporphyrin $(DMA)_1PH_2$, but tetrakis(4-(dimethylamino)phenyl)porphyrin $(DMA)_4PH_2$ is essentially insoluble, as reported, in $CDCl_3$ and other solvents investigated. It is adequately soluble as the diprotonated species $(DMA)_4PH_4^{2+}$ and at higher protonated stages through $(DMA)_4PH_6^{4+}$. Furthermore, the fully protonated $(DMA)_4PH_8^{6+}$ is soluble in TFA but negligibly soluble when $CDCl_3$ is also present. The NMR spectrum of the free base was obtained by treating a solution of the diprotonated species with ethylenediamine. Solute gradually aggregated and eventually separated from this initially clear solution, but it was possible to obtain an adequate (but very noisy) spectrum during this slow formation of solid. The validity of this spectrum is confirmed by the identical aromatic region published for the more soluble tetrakis(4-(diethylamino)phenyl)porphyrin.[7] Our spectrum contains extra unidentified weak lines which probably arise from the suspended solids in this sample. The unsymmetrically-substituted porphyrin $(DMA)_1PH_2$ is adequately soluble in $CDCl_3$.

$CHCl_3$ and $CDCl_3$ are known to take up water from glass surfaces to give an NMR signal at about 1.54 ppm; this can be avoided by careful drying of all apparatus. We concluded that maintaining adequate dryness through successive additions of acid was impossible when cell spacers were used for the spectrophotometric confirmation of identity and allowed water to accumulate in the solvent. This reacts slowly with $CHCl_3$ to give an acid reported[8] to be HCl. Consequently, our porphyrin solutions in $CDCl_3$ often contained small amounts of the diprotonated base in amounts determined by the basicity of the porphyrin, when the free base was dissolved in $CDCl_3$.

Results

In the case of tetraphenylporphyrin, $TPPH_2$, and its diprotonated form $TPPH_4^{2+}$, our chemical shift data for the aromatic protons do not differ significantly from the values reported[9] earlier. We also agree with the line assignments given there. With smaller amounts of TFA than the 2 equiv per mole of $TPPH_2$ required to convert the porphyrin completely to $TPPH_4^{2+}$, the NMR spectra contain superimposed signals of both $TPPH_2$ and $TPPH_4^{2+}$ at their normal chemical shift values; there are no lines at intermediate positions which could be attributed to a monoprotonated intermediate; see Figure 1, spectra A, B, and C. (At the acid concentration of Figure 1C, the signals for the β pyrrole and the ortho phenyl protons overlap.) When the concentration of TFA is increased beyond this minimum required for formation of $TPPH_4^{2+}$, all of the aromatic proton signals move downfield continuously with increasing acid concentration to limiting values in solvent TFA (Figure 1 spectra D and E). They also broaden significantly in solvent TFA.

The signal for the internal N–H protons is strongly acid-sensitive: that for $TPPH_2$ appears upfield at –2.77 ppm (due to the ring current) in $CDCl_3$ solution (Figure 2A), at +0.35 ppm with 2 equiv of TFA in $CDCl_3$ (Figure 2C), and at –1.94 ppm in TFA solvent (Figure 2E). Thus, in TFA solution this signal has returned almost to the position observed for the free base in $CDCl_3$. Our chemical shifts in TFA solvent are not as negative as some published values, possibly due to the accumulation of water in our solvent. Integrations of these N–H lines (using the signals for the 28 aromatic protons as an internal standard) give averaged values of 1.99 protons for $TPPH_2$ and 4.01 protons for $TPPH_4^{2+}$; errors in individual determinations are estimated to be within ±10%. At acid concentrations intermediate to complete formation of $TPPH_4^{2+}$, separate N–H signals for both free base and diprotonated species are observed (Figure 2B) consistent with the reported[10] slow proton exchange between $TPPH_2$ and $TPPH_4^{2+}$; in this case the integrations over the two N–H lines

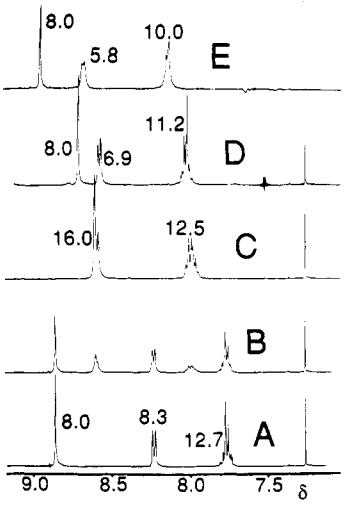

Figure 1. Effect of TFA concentration on the chemical shifts of aromatic proton lines of 0.01 M $TPPH_2$ in $CDCl_3$. The approximate concentrations of total TFA added for the spectra shown and the solute species present are as follows: spectrum A, 0 M, PH_2; B, 0.01 M, $PH_2 + PH_4^{2+}$; C, 0.025 M, PH_4^{2+}; D, 0.10 M, PH_4^{2+}; E, 100% CF_3COOD/CF_3COOH, PH_4^{2+}. Integrals of lines or multiplets relative to the pyrrole H_β line set at 8.0 are given beside the lines. The lines at 7.26 ppm are due to $CHCl_3$ in the solvent.

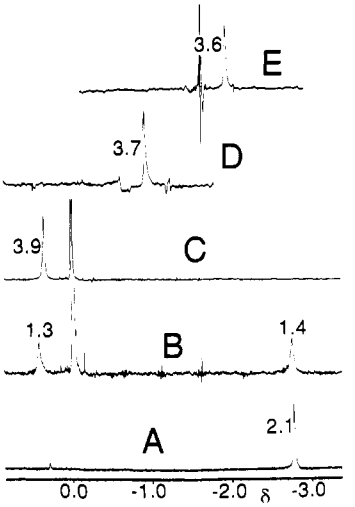

Figure 2. Effect of acid concentration on the chemical shift of internal N–H proton lines of $TPPH_2$. These lines are generally broader than the C–H NMR lines, probably due to the ^{14}N nuclear quadrupole relaxation. Acid concentrations and species present are as given for Figure 1. The intense line at zero ppm in two samples is due to 1% TMS present in the $CDCl_3$ solvent.

are less precise, with errors estimated at ±20%. No signals are observed which could be assigned to a protonation intermediate between $TPPH_2$ and $TPPH_4^{2+}$.

We call attention to the contrasting motions of the β pyrrole and the N–H signals as the solvent for $TPPH_2$ becomes increasingly acid. Conversion of the free base with H_β at 8.83 ppm to diprotonated $TPPH_4^{2+}$ moves the H_β signal upfield ca. 0.25 ppm, while the N–H signal moves downfield about 3.0 ppm. Both changes are discontinuous and are in the directions to be expected if the aromatic ring current decreases with the diprotonation, although their magnitudes differ by a factor of 10. When TFA concentrations are increased beyond that necessary to form $TPPH_4^{2+}$, these NMR signals again move continuously in opposite directions which are the reverse of the original changes: H_β downfield by 0.35 ppm and N–H upfield ca. 2.5 ppm. The aromatic proton signals also broaden significantly, so that the phenyl ring multiplets lose much of their structure in TFA solution. We surmise, but have at this time inadequate data to prove, that these changes are connected with distortions of the porphyrin

TABLE I: Effect of Acid Concentration on Chemical Shifts (δ, ppm) of Proton NMR Lines of *N,N*-Dimethyl-*p*-toluidine[a]

	center of aromatic doublets			
solvent	meta[b]	ortho[b]	$-N(CH_3)_2$	Ar–CH_3
$CDCl_3$	7.059	6.700	2.904	2.260
0.10 M TFA	7.424	7.334	3.250	2.408
TFA	7.472	7.431	3.435	2.474

[a] Amine concentration is ca. 0.014 M. [b] Ring positions relative to the $-N(CH_3)_2$ group.

aromatic ring system from nominal planarity as TFA concentration increases. The same pattern of chemical shift changes is also observed for the dimethylamino substituted porphyrins studied.

Abraham and co-workers,[10] in a C-13 NMR study in $CDCl_3$/TFA solution, also observed no monoprotonated $TPPH_2$. We call attention to Aronoff's[3] spectrophotometric titration of $TPPH_2$ in nitrobenzene solution; this system does give an intermediate spectrum attributed to monoprotonated $TPPH_3^+$. We propose that this species, which is not observed in $CDCl_3$ solution, is stabilized by a polar solvent. We have not studied solvent effects on the protonation.

The other porphyrin samples studied contain meso-bonded phenyl rings which are substituted by *N,N*-dimethylamino groups at one or more 4-positions. We selected *N,N*-dimethyl-*p*-toluidine (Aldrich) as a model compound for these rings. The NMR spectra (Table I) contain the expected single lines for the ring methyl and *N*-methyl protons, and a pair of doublets for the ortho coupled protons of the aromatic ring. Doublet separation is 8.7 Hz, in the expected range. The NMR signal for the protons ortho to the strongly electron-donating $-N(CH_3)_2$ group is expected to be upfield relative to the meta proton signal. Tables of the effects of substitution on aromatic proton chemical shifts[11] lead us to expect a downfield shift of up to 1 ppm upon conversion of $-N(CH_3)_2$ to $-NH^+(CH_3)_2$, for the ring protons ortho to these groups. Available data do not permit a prediction for the meta protons, except that the change will be smaller. The observed values are $\Delta\delta = +0.63$ ppm (assigned to the ortho protons) and +0.37 ppm (assigned to the protons meta to the substituent). The increment in chemical shift on changing the solvent from 0.10 M TFA in $CDCl_3$ (where the basic groups are fully protonated) to pure TFA is $\Delta\delta = +0.10$–0.05 ppm; this is attributed to a specific solvent effect in TFA. An effect of this type has been postulated for ^{13}C NMR.[12] No N–H signal is observed for the protonated substituents, presumably due to fast exchange with the TFA added. The methyl proton signal of the $-N(CH_3)_2$ groups confirms this: separate $-N(CH_3)_2$ and $-NH^+(CH_3)_2$ signals are never observed. This line is sensitive to excess acid; the chemical shift is 2.90 ppm in $CDCl_3$, 3.25 ppm in 0.10 M TFA/$CDCl_3$ (where complete protonation is expected), and 3.44 ppm in pure TFA-*d*. All of these effects of added acid in *N,N*-dimethyl-*p*-toluidine are exactly paralleled by those of *meso*-(p-(dimethylamino)phenyl) groups on a porphyrin ring.

The second symmetrically-substituted porphyrin investigated in this work is $(DMA)_4PH_2$. It was impossible to obtain evidence on an intermediate between this substance and diprotonated $(DMA)_4PH_4^{2+}$ by the addition of less than 2 equiv of acid, due to the low solubility of the free base. There are substantial changes in the chemical shifts of aromatic protons as the diprotonation takes place (Figure 3, spectra A and B); the pyrrole H_β signal moves upfield from 8.84 ppm by 0.6 ppm, and the two aromatic proton doublets move downfield by 0.15–0.35 ppm. All of these changes are in the same directions as those observed for the corresponding protons upon diprotonation of $TPPH_2$. The NMR spectra, particularly the position of the $-N(CH_3)_2$ line discussed below, show that protonation of the internal pyrrolenine nitrogen atoms precedes protonation of any of the dimethylamino groups. As increments of TFA are added to diprotonated $(DMA)_4PH_4^{2+}$

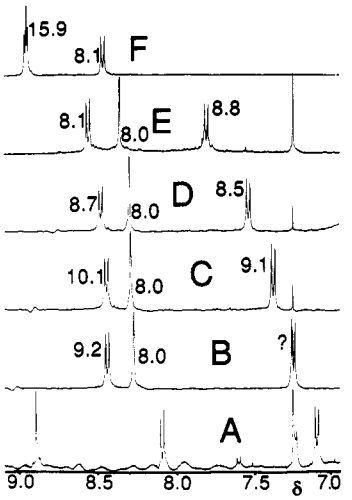

Figure 3. Effect of TFA concentration on the chemical shifts of aromatic proton lines of 0.005 M $(DMA)_4PH_2$ solutions in $CDCl_3$. The total concentrations of acid in the $CDCl_3$ solution for the spectra shown are not exactly known, since the free base already dissolves in "100%" $CDCl_3$ as $(DMA)_4PH_4^{2+}$. The TFA concentrations were adjusted to give individual solute species identified by spectrophotometry. The approximate concentrations of total TFA added and the solute species present for the spectra shown are as follows: spectrum A, 0 M, treated with ethylenediamine, PH_2; B, 0.00003 M, PH_4^{2+}; C, 0.001 M, PH_5^{3+}; D, 0.008 M, PH_6^{4+}; E, 0.20 M, PH_7^{5+}; and F, pure TFA-*d*, PH_8^{6+}.

to protonate successively the four dimethylamino groups, only gradual small shifts downfield are observed in the aromatic proton signals; these are continuous changes which depend upon the amount of TFA added; see Figure 3 spectra C,D, and E. They are followed by larger downfield shifts when the solvent is changed to neat TFA (Figure 3F).

The internal N–H proton line is at –2.6 ppm (very rough, due to poor S/N) in the free base, but its integral value is uncertain because the sample is so dilute. Upon formation of $(DMA)_4PH_4^{2+}$, this line shifts downfield to 1.34 ppm and integrates to 4 ± 1 protons. As the TFA concentration is increased to protonate the dimethylamino groups, the internal N–H signal gradually moves upfield to +0.77 ppm at the stage of $(DMA)_4PH_7^{5+}$; it then jumps to –1.3 ppm upon formation of fully protonated $(DMA)_4PH_8^{6+}$ in TFA solvent. Only at this stage of complete protonation does the solution color change from some shade of brown to green.

The sharp signal due to the methyl protons of the $-N(CH_3)_2$ groups moves discontinuously from 3.20 to 3.32 ppm upon diprotonation of the internal nitrogen atoms. After this diprotonation is complete, this signal (which never shows splitting due to protonation of the dimethylamino nitrogens) gradually moves downfield from 3.32 to 3.86 ppm over the TFA concentration range over which these four external basic groups are protonated. Meaningful integration of the internal N–H signals is impossible for this system as the free base, as $(DMA)_4PH_7^{5+}$, or as the fully protonated $(DMA)_4PH_8^{6+}$ in CF_3COOD/CF_3COOH. Because of the very poor signal to noise in these spectra, we do not show them as a figure. No signal for the N^+H protons of the protonated peripheral dimethylamino groups is observed, consistent with fast exchange between these proton positions and the pool of excess TFA present; the acid gives a strong (weighted average) signal.

The unsymmetrically-substituted porphyrin $(DMA)_1PH_2$ exhibits some characteristics of both of the symmetrical systems already considered, upon addition of protons. The NMR spectra (Figures 4 and 5) are complicated, since there are two types of meso phenyl groups, but it is usually possible to pick out the two doublet signals due to protons on the para-disubstituted phenyl ring. In the porphyrin free base, these are centered at 8.09 and 7.11 ppm (Figure 4A); in the diprotonated intermediate they are centered at 8.6 (?) and 7.30 ppm (Figure 4C); and in fully

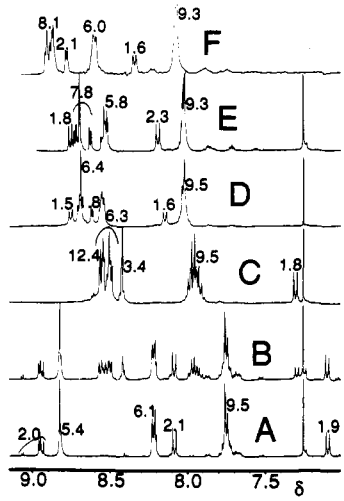

Figure 4. Effect of TFA concentration on the chemical shifts of aromatic proton lines of 0.005 M $(DMA)_1PH_2$ in $CDCl_3$. The total concentrations of TFA added for the spectra shown are as follows: spectrum A, 0 M, PH_2; B, 0.0020 M, $PH_2 + PH_4^{2+}$; C, 0.010 M, PH_4^{2+}; D, 0.11 M, PH_5^{3+}; E, 0.25 M, PH_5^{3+}; F, CF_3COOD/CF_3COOH, PH_5^{3+}.

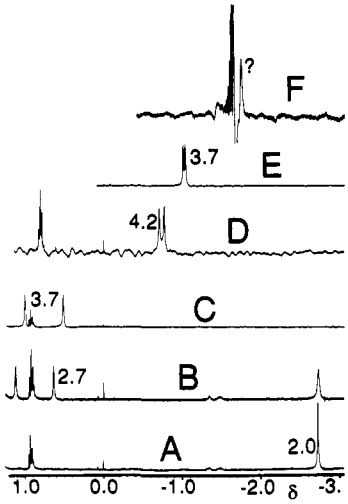

Figure 5. Effect of TFA concentration on the chemical shifts of internal N–H proton lines of $(DMA)_1PH_2$. Acid concentrations and species present are as given for Figure 4.

triprotonated $(DMA)_1PH_5^{3+}$ they are centered at 8.8 and 8.22 ppm (Figure 5D). The positions of this last pair of doublets are strongly dependent upon the concentration of excess TFA present (Figure 5 spectra E and F). It is also possible to identify the other aromatic proton lines when the solute consists of a single species. At intermediate concentrations of added acid, when both free base and diprotonated or both diprotonated and triprotonated porphyrins are present, complete assignment of the spectra in the aromatic proton region has not been possible. It is quite likely that no intermediate species $(DMA)_1PH_3^+$ is present. A major pyrrole H_β line which integrates for 5 or 6 protons moves discontinuously upfield from 8.82 to 8.42 ppm upon diprotonation (Figure 4 spectra A–C). (We omit discussion of the weak lines at $\delta > 8.9$ ppm (Figure 4 spectra A and B); these seem to be due to two of the H_β protons, but we cannot identify them securely in the proton spectra at higher acid concentrations.) This conclusion is reinforced by the positions of the pair of doublets which arise from the para disubstituted ring. They are not observed at intermediate positions at any stage of the addition of TFA up to 0.01 M, which produces $(DMA)_1PH_4^{2+}$ (Figure 4 spectra A–C), and the spectrum shows all of the lines of both the free base and the diprotonated species (Figure 4B). The absence of monoprotonated intermediate is confirmed by behavior of the methyl proton signal from the $-N(CH_3)_2$ group; this is at 3.24 ppm before the addition of acid and at 3.36 ppm (discontinuous change) for the diprotonated species. At intermediate concentrations of added TFA, both lines appear with intensities determined by the relative concentrations of free base and diprotonated porphyrin. Both signals are sharp, and there is no signal at any intermediate position. When more TFA is added after protonation of the dimethylamino group, this signal moves continuously downfield to 3.68 ppm in 0.10 M TFA and to 3.85 ppm in the pure acid as solvent. As in the case of $TPPH_4^{2+}$, there is broadening of the H_β and the phenyl ring protons in solvent TFA; this is particularly striking in the loss of structure in the phenyl ring multiplets. In this case, the doublets of the single disubstituted phenyl ring also broaden to a degree which is obvious.

The internal protons on this free base give a signal at −2.7 ppm, (Figure 5A). In principle, there can be four different pairs of pyrrole H_β protons in this system. In the absence of further information we do not at this time offer an explanation for the observation of a single N–H proton line. Addition of TFA splits this signal into two of equal area at chemical shifts +1.01 and +0.52 ppm in the diprotonated system (Figure 5C). This pair of signals, together with that at −2.7 ppm, all appear when mixtures of $(DMA)_1PH_2$ and $(DMA)_1PH_4^{2+}$ are present (Figure 5B). With addition of more TFA, the signals of the internal N–H protons gradually move upfield and merge (Figure 5 spectra D and E). In pure TFA, there is a single line at −1.76 ppm (Figure 5F), but the area is meaningless due to equilibration with the CF_3COOH/CF_3COOD solvent mixture used. The two N–H signals are attributed to two structurally inequivalent pyrrole rings in this unsymmetrically substituted $(DMA)_1PH_4^{2+}$. The two pyrrole rings bonded to the meso carbon to which the substituted phenyl ring is attached constitute one set, and the two remaining pyrrole rings the second set in the diprotonated system. The separation of these N–H lines diminishes after the dimethylamino group is protonated. Integration of the internal N–H signals with the $N(CH_3)_2$ proton signal as the internal reference, gives 2.0 protons for the free base, 2.7 protons at the intermediate stage illustrated in Figure 5B, and 3.7 protons for both $(DMA)_1PH_4^{2+}$ and $(DMA)_1PH_5^{3+}$.

Discussion

The ground-state NMR spectra as function of degree of protonation and excess TFA are closely consistent for the three porphyrins investigated and for the model compound, *N,N*-dimethyl-*p*-toluidine. This constitutes very strong evidence for the main interpretation given in the previous paper, that the optical spectra of partially protonated *meso*-(aminophenyl)porphyrins and related hyperporphyrins involve formation of charge-transfer *excited* states.[5]

In addition, the NMR data support the following conclusions.

1. The shift of solution color to green and the reappearance of a porphyrin-D_{4h} spectrum with a very intense near-UV Soret band and two bands in the visible region occur only after complete protonation of all basic centers in the molecule, including any external dimethylamino groups that are present.

2. There is no evidence for an intermediate protonation stage between free base and diprotonated porphyrin. This is consistent with the absence of isosbestic points to define the monoprotonated porphyrin in the optical spectra.[5] The N–H lines at all acid concentrations are somewhat broader than normal C–H line widths, possibly due to the ^{14}N nuclear quadrupole relaxation.

3. The changes in chemical shift of the internal N–H protons with increasing acidity are very large—3–4 ppm. In the free base, this N–H signal is at −2.6 to −2.8 ppm and integrates to two protons. Diprotonation moves the signal downfield to the range +1.3 to +0.4 ppm, with an integral for four protons. This occurs at the minimum acid concentration (up to about 0.01 M, dependent upon porphyrin structure) which produces diprotonation. As the TFA concentration is increased beyond this

minimum value, the signal for these N–H protons gradually moves back upfield and is close to the free base value in pure TFA solution. These effects of excess acid on the chemical shift of the N–H protons are observed for all of the diprotonated porphyrins studied, including $TPPH_4^{2+}$, so they are not dependent upon the presence of dimethylamino groups. We are not aware that they have been reported previously, probably because porphyrin NMR spectra have generally been run only in $CDCl_3$ or in TFA solution, so the effects of intermediate acid concentrations have not been observed.

4. The proton NMR spectra indicate that most of the possible proton exchange processes for these systems are fast on the NMR time scale determined by the frequency separation of the lines for the two sites. As was reported very early in porphyrin NMR studies,[10] exchange between free base and diprotonated base is slow. Tautomeric exchange of protons between pairs of internal nitrogen atoms is fast at room temperature. Additional possible exchanges involve the peripheral dimethylamino groups. The observation of single *N*-methyl proton signals which gradually move downfield as TFA is added to protonate these nitrogen atoms requires that exchange between $-N(CH_3)_2$ and $-NH^+(CH_3)_2$ be fast. No signal for N–H on protonated amino groups is ever observed; this is interpreted as the result of fast exchange with the pool of excess TFA, with the N–H incorporated into the more intense TFA signal at these relatively high acid concentrations.

Changes in the chemical shifts of the aromatic protons with increasing acidity are in the opposite directions and much smaller than those for the N–H line. Thus, the pyrrole H_β line moves upfield by 0.25–0.60 ppm upon conversion of PH_2 to PH_4^{2+}. As still more TFA is added, this line reverses direction to move downfield, eventually to a somewhat larger chemical shift than that of the free base PH_2. The signals of the meso-substituted aromatic rings move downfield throughout the increase in acidity. All of these aromatic proton lines broaden significantly as the solvent becomes neat TFA. This change is particularly striking in the loss of structure of the multiplets due to meso phenyl ring protons.

A recent publication by Gunter and Robinson[13] reports their study of $(DMA)_4PH_2$ and some of its protonated forms. These authors emphasize the conversion of their samples to a blue nonporphyrin "oxidation product" in the presence of oxygen and acid and report a spectrum consisting of two very broad bands in the visible region and a narrower third peak at ca. 435 nm. We find that formation of this substance occurs under much more restricted conditions than their report implies: our solutions of $(DMA)_4PH_4^{2+}$, $(DMA)_4PH_5^{3+}$, and $(DMA)_4PH_6^{4+}$ appear to be perfectly stable in $TFA/CDCl_3$ solutions in which these solutes are in equilibrium with the acid present; this requires acid concentrations up to ca. 8×10^{-3} M. The fully protonated form, $(DMA)_4PH_8^{6+}$, is soluble and stable in pure TFA. Thus, the reactive species appears to be $(DMA)_4PH_7^{5+}$, which should be at maximum concentration (but in equilibrium with the PH_6^{4+} and PH_8^{6+} species) in the region around 0.05 M TFA. A solution of the porphyrin in $TFA/CDCl_3$, when acidified further to reach this acid concentration, usually produces a green oil which is soluble in TFA and has the spectrum of $(DMA)_4PH_8^{6+}$. The very dilute residual solution is bluish and has the optical spectrum reported[13] for the "oxidation product". These results are not fully reproducible and seem to depend upon the rate and concentration at which TFA is added to the partly acidified porphyrin solution. NMR spectra of $(DMA)_4PH_8^{6+}$ in TFA/CD_2Cl_2 or $TFA/CDCl_3$ contain weak (since most of the solute oils out) doublets for the ring protons of the meso 1,4-disubstituted phenyl rings. Occasionally still weaker doublets appear at chemical shifts in the range 6.8–8.2 ppm; these are unassigned. Gunter and Robinson did not fully characterize their "oxidation product", but their structure is probably correct by analogy with the established structure of the purple oxidation product from tetrakis(3,5-di-*tert*-butyl-4-(hydroxyphenyl))porphyrin in basic solution.[14]

Gunter and Robinson[13] attribute the large downfield shift of the N–H signal upon diprotonation of $(DMA)_4PH_2$ to a "decrease of ring current of the macrocyclic system". This cannot be correct as stated. The downfield position of the β pyrrole protons of porphyrins, (ca. $\delta = 9$ ppm) and of the peripheral protons of other aromatic systems is attributed to deshielding which is produced by the magnetic field of the circulating π electrons. Diprotonated porphyrins also give H_β signals at a chemical shift of ca. 9 ppm, and this is not the result of near contact with the meso phenyl rings in the compounds we consider here, since porphine is also reported to give H_β signals at 9.74 ppm in the free base[15] and at 9.94 ppm in the diprotonated system.[4] Thus it appears that the β protons are subject to the ring current in both the free base and its diprotonated form. The internal N–H protons are a different matter: here the effect of the ring current in the free base is additional shielding of these protons, which consequently appear far upfield. It is this effect of the ring current which is (partially?) lost in the diprotonated porphyrins. This could result from geometric distortion of the porphyrin ring by twisting or by rocking the four pyrrole rings to accommodate four protons and the double positive electric charge, but it is not clear how this distortion could move these protons so far as to be outside the field produced by the ring current. The available crystallographic data indicate that $TPPH_4^{2+}$ is more distorted out of the average porphine plane[16] than is $TPPH_2$,[17] and they also suggest that the porphyrin macrocycle is readily distorted out of planarity. Alternatively, the downfield shift of the N–H signal on diprotonation might result from a direct decrease in ring current at the interior of the ring system which is not dependent upon geometric distortion. In either case, the evidence is that the effect of ring current on the peripheral protons is not greatly disturbed through these changes.

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References and Notes

(1) A review of studies of acid–base properties of porphyrins is given by Hambright: Hambright, P. In *Porphyrins and Metalloporphyrins*; Smith, K. M., Ed.; Elsevier: Amsterdam, 1975; pp 234–238.

(2) Proton NMR studies of porphyrins are reviewed by Janson and Katz: Janson, T. R.; Katz, J. J. *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1979; Volume IV, Chapter 1.

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

(4) Abraham, R. J.; Jackson, A. H.; Kenner, G. W. *J. Chem. Soc.* **1961**, 3468.

(5) A spectrophotometric study of the same porphyrins considered here has been reported by Ojadi, E. C. A.; et al. *J. Phys. Chem.*, preceding paper in this issue.

(6) Datta-Gupta, T. J.; Bardos, T. J. *J. Heterocycl. Chem.* **1966**, *3*, 497.

(7) Walker, F. A.; Balke, V. L.; McDermott, G. A. *Inorg. Chem.* **1982**, *21*, 3342.

(8) Baskerville, C.; Hamor, W. H. J. *Ind. Eng. Chem.* **1912**, *4*, 278.

(9) Behere, D. V.; Mitra, S. *Ind. J. Chem.* **1982**, *21A*, 966.

(10) (a) Abraham, R. J.; Hawkes, G. E.; Smith, K. M. *Tetrahedron Lett.* **1974**, 71. (b) Storm, C. B.; Teklu, Y.; Sokolski, E. A. *Ann. N. Y. Acad. Sci.* **1973**, *206*, 631.

(11) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; John Wiley and Sons: New York, 1981; p 231.

(12) Abraham, R. J.; Hawkes, G. E.; Hudson, M. F.; Smith, K. M. *J. Chem. Soc., Perkin Trans. 2*, **1975**, 204.

(13) Gunter, M. J.; Robinson, B. C. *Austr. J. Chem.* **1989**, *42*, 1897.

(14) (a) Milgrom, L. R. *Tetrahedron* **1983**, *39*, 3895. (b) Traylor, T. G.; Nolan, K. B.; Hildreth, R. *J. Am. Chem. Soc.* **1983**, *105*, 6149.

(15) Solovev, K. N.; Mashenkov, V. A.; Gradyushko, A. T.; Turkova, A. E.; Lezina, V. P. *J. Appl. Spectrosc. USSR* **1970**, *13*, 1106.

(16) Stone, A.; Fleischer, E. B. *J. Am. Chem. Soc.* **1968**, *90*, 2735.

(17) (a) Hamor, M. J.; Hamor, T. A.; Hoard, J. L. *J. Am. Chem. Soc.* **1964**, *86*, 1938. (b) Silvers, S. L.; Tulinsky, A. *J. Am. Chem. Soc.* **1967**, *89*, 3331.