Effects of Acid on Line Widths in the Proton NMR Spectra of Porphyrins Not Substituted at the *meso*-Positions

Abolfazl Seyed Sadjadi,[1] Robert I. Walter,* and John S. Harwood

Chemistry Department (m/c 111), University of Illinois at Chicago, 845 West Taylor Street, Chicago, Illinois 60607

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It was shown in earlier work that the proton NMR spectra of some *meso*-tetraarylporphyrins in deuterochloroform−trifluoroacetic acid solutions show little dependence of signal line widths upon acid concentration, but chemical shifts (particularly of the N-H signal) are strongly acid dependent. In contrast, the corresponding NMR spectra of *meso*-unsubstituted coproporphyrin I tetramethyl ester in deuterochloroform solution show weak signals assigned to porphyrin N−H and to O−H (water impurity in solvent). Addition of trifluoroacetic acid at mole ratios TFA:$COPH_2$ as low as 0.05 produces simultaneous broadening of these signals, both of which become too broad to observe at normal instrument gain and room temperature when this mole ratio exceeds 0.3. Additional acid causes the N−H signal to narrow again and then reappear as a very broad line when the TFA:$COPH_2$ ratio exceeds 2. It gradually narrows and moves upfield as the TFA concentration increases further. Within the same range of TFA:$COPH_2$ concentration ratios, the narrow H(*meso*) signal also broadens to about 35 Hz and then narrows again while it moves significantly downfield. We propose that an acid species catalyzes proton exchange between $COPH_2$ and $COPH_4^{++}$ in the intermediate rate region to produce these line width effects, which are also seen with other *meso*-unsubstituted porphyrins under the same conditions. These two structural classes of porphyrins also display characteristic differences in the optical spectra of their diprotonated dications: $COPH_4^{++}$ and the dications of other porphyrins unsubstituted on the four *meso*-positions give red-purple solutions with band intensities II > I for the two bands in the visible region. Dications of *meso*-tetraarylporphyrins give green solutions with relative band intensities I < II, as pointed out over 25 years ago by Fleischer. The catalytic acid species may be the much discussed monoprotonated monocation $COPH_3^+$, but the spectra reported here give no information on its structure or identity.

An early generalization on the qualitative behavior of porphyrin free bases with acid was proposed by Fleischer,[2,3] who pointed out for the limited number of cases then investigated that *meso*-tetraaryl-substituted porphyrins are green in acid solution, while porphyrins without this substitution are red-purple in acid. The two-band visible spectra of the acid solutions account for the different colors. *meso*-Substituted porphyrins have band intensities I > II, while those without *meso*-substituents have II > I. Studies by a variety of acid titration methods have led to persistent proposals that the diprotonated dication PH_4^{++} is formed through an intermediate monoprotonated[4] species PH_3^+. Other investigators have claimed the formation of PH_4^{++} without the appearance of a monoprotonated intermediate stage.[5] There seems to be no widely accepted unifying principle to explain these results, but note that all of the porphyrins reported in ref 4 are *meso*-unsubstituted. Proton NMR studies on organic-soluble porphyrins have typically been carried out in solvents such as $CDCl_3$ or CF_3COOH (TFA). The data obtained thus apply to the porphyrin free base PH_2[6] or to the diprotonated dication PH_4^{++}.[7] We have found[5c] that useful additonal information about these systems can be obtained at the intermediate acid concentrations achieved with these solvents mixed in various ratios. Our earlier study[5b] was carried out on porphyrins which contain four phenyl (or substituted phenyl) groups bonded at the four *meso*-positions of the porphyrin. Those samples showed only minor changes in NMR line widths with TFA concentration. This report is concerned with similar studies applied to porphyrins not substituted in the four *meso*-positions, with confirmatory evidence from optical spectroscopy. In these cases, there are very large variations in the NMR linewidths at intermediate acid concentrations and room temperature.

Optimum samples for these studies provide symmetry of substitution at the β-pyrrole positions to minimize the number of NMR signals and absence of substituents on the periphery of the porphyrin ring, which would interact strongly with the porphyrin π electron system and thus complicate interpretation of the spectra. The selection of samples for these studies also involves practical considerations of availability and of solubility. In practice, these restrictions limit the sample selection to relatively few compounds. We have used coproporphyrin I tetramethyl ester for most experiments. Here, the symmetry of substitution around the porphyrin ring simplifies the NMR spectrum, and the four ester groups confer good solubility in $CDCl_3$. The series of compounds derived chemically from protoporphyrin IX fails the symmetry test, but this disadvantage is limited by the fact that most side chains on these porphyrins derived from natural products are seen as alkyl groups by the π system and produce closely spaced line groups in the NMR spectra.

Experimental Section

The proton NMR spectra were run as before[5c] on a Bruker AM 400 spectrometer equipped with a Bruker BVT-1000 temperature control unit and operated at 400 MHz in the Fourier transform mode. Porphyrin concentrations were usually 0.01 M but were as low as 0.008 M with the less soluble octaethylporphyrin. The solvent was Aldrich "100%" $CDCl_3$; this still

* Corresponding author. Fax: (312) 996-0431.

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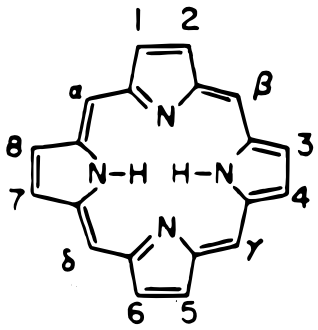
contains enough $CHCl_3$ to give an easily detectable proton NMR signal used to set the chemical shift scale. A broad signal at 1.53 ppm is assigned to water. Some of this is present in every solvent sample, and variable additional amounts are picked up from glassware surfaces. The presence and relative amounts of these impurities vary with the solvent batch number and its history after opening the ampule. Water can be removed from the solvent by drying with P_2O_5, but this cannot be used with the porphyrin solutions, which deposit a large amount of porphyrin on the surface of the drying agent. Dry solutions quickly pick up water from glass surfaces. TFA from Aldrich was used without further treatment. The ionization behavior of TFA in the TFA/$CDCl_3$ solvent systems is not known. Consequently, we report the molar concentration of total TFA added to the various samples, based upon the measured volumes and known density, with no attempt to partition the TFA between molecular acid and various ionized forms. In some samples there is also a sharp signal at 2.17 ppm, which we assign to acetone impurity. Some of this is present in the $CDCl_3$ solvent, but when higher concentrations occur, it probably is introduced by incomplete drying of glassware after an acetone rinse. In our experience, NMR data are more reliable (due to viscosity effects?) if not recorded too close to the freezing point of the solvent, and CD_2Cl_2 affords an extra 30° in the liquid range before it freezes. Thus, spectra recorded in CD_2Cl_2 solution below ambient temperature were helpful in establishing proton exchange patterns. Bruker instrument software was used to control pulse sequences, data acquisition, and data analysis for the 1-D NOE difference and the phase-sensitive NOESY (referred to as EXSY when used to investigate chemical exchange) experiments used to identify unambiguously exchange processes in these samples.

Optical spectra were recorded on a Cary 17D spectrophotometer using either separately diluted solutions with porphyrin concentration 5×10^{-5} to 1×10^{-4} M in methylene chloride (this solvent is superior to $CHCl_3$ at low $COPH_2$ concentrations because it does not introduce oxidation inhibitor) or with the 0.01 M NMR samples (in $CDCl_3$) and a 0.05 mm cell spacer. Identity of the optical spectra recorded under these different conditions was taken to show that there are negligible differences between these solvents, and no significant aggregation of solute at the higher concentrations. Conventional volumetric methods are not suitable to make up solutions to known concentrations in the volatile solvents used, particularly at low TFA concentrations. Consequently, Hamilton microliter syringes were used to measure liquid volumes for the dilutions, to minimize evaporation.

Coproporphyrin I tetramethyl ester ($COPH_2$) and octaethylporphyrin ($OEPH_2$) were purchased from Aldrich. Mesoporphyrin IX dimethyl ester ($MEPH_2$) was prepared from hemin by the classical procedure[8] and recrystallized from $CHCl_3$/MeOH. Figure 1 illustrates the structures and necessary nomenclature for the compounds considered here.



Substitutions at Numbered Positions

$COPH_2$		$MEPH_2$
methyl	1	methyl
Pr	2	ethyl
methyl	3	methyl
Pr	4	ethyl
methyl	5	methyl
Pr	6	Pr
methyl	7	Pr
Pr	8	methyl

Figure 1. Structures and nomenclature of the various porphyrins considered. The four *meso*-positions are labeled with Greek letters and are the sites of phenyl substitution in *meso*-tetraphenylporphyrin. The eight numbered exterior positions are all substituted by ethyl groups in $OEPH_2$. They are substituted as shown in the figure in $COPH_2$ and in $MEPH_2$. The substituent Pr is $-CH_2CH_2COOCH_3$ in these compounds.

Results

The proton NMR spectra of 0.01 M $COPH_2$ solutions in $CDCl_3$ recorded at 293 K with various concentrations of added TFA are shown in Figure 2. We have used the conventional proton assignments for this solute in $CDCl_3$[6] and in TFA[7] solution. Signals in the range 3.0−4.7 ppm arise from aliphatic protons on substituents on the porphyrin ring. These show substantial changes in line widths and shapes with TFA concentration, but are otherwise little affected, and are not considered further. Useful information is available from signals of *meso*- and N−H protons, particularly from spectra recorded at lower temperatures; even a decrease to 260 K slows exchange processes significantly. Spectra recorded on $COPH_2$ as the free base in $CDCl_3$ are omitted; they show no significant changes (other than increasingly negative chemical shift for the N−H signal) down to 220 K. Spectra at TFA concentrations equal to 0.003, 0.025, and 0.20 M are shown over the low-temperature range in Figure 3. The results identify exchange processes which lead to the major line width changes and are confirmed by the data from exchange experiments.

The signals of greatest interest given by solutions of the free base in $CDCl_3$ (spectrum 2A) appear at 10.06 ppm (H(*meso*)), 1.53 ppm (O−H from water in the solvent), and at −3.87 ppm (N−H). Changes in chemical shift and line width with increasing acidity are clearly displayed by the NMR signal assigned to the *meso*-protons. This moves gradually downfield from 10.06 ppm in $CDCl_3$ to 10.86 ppm in 2.0 M TFA solution; the chemical shift changes most rapidly over the acid concentration range 0.001−0.015 M. This line is sharp (width ∼2 Hz) in $CDCl_3$ solution or with TFA concentration 0.020 M or higher. Within this range of acid concentrations and at room temperature, the H(*meso*) signal gradually broadens to 33−35 Hz in the TFA concentration range 0.003−0.010 M, and subsequently again sharpens to ca. 2 Hz in 0.025 TFA. A 1-D NOE difference experiment confirms that exchange occurs between the states which give these *meso*-signals: when the sample is irradiated at either the H(*meso*) frequency in $CDCl_3$ solution or that in 0.025 M TFA, *both* lines are eliminated from the spectrum. The former sample (no added TFA) must arise from *meso*-protons in the free base. We will argue below that diprotonation to $COPH_4^{++}$ is complete before the TFA concentration reaches 0.025 M.

The signal for the N−H protons has a line width of 22 Hz in the free base and integrates to 1.9 protons relative to the H(*meso*) line set at 4.0. Part of this width arises from room-temperature exchange between O−H and N−H, as demonstrated by a 2D EXSY experiment which shows off-diagonal peaks at the frequencies of both of these signals. The N−H signal moves downfield and broadens further at TFA concentrations as low as 0.0005 M and becomes too broad at room temperature to observe at reasonable instrument gain when TFA exceeds 0.003 M. It does not reappear until the acid concentration reaches 0.02 M; this very broad signal then gradually narrows and moves upfield as TFA concentration increases further. The N−H signal can be seen through this range of TFA concentrations by increasing gain on the instrument display by a factor of about 100. However, both the position and the area of this greatly amplified signal are affected significantly by the very large base

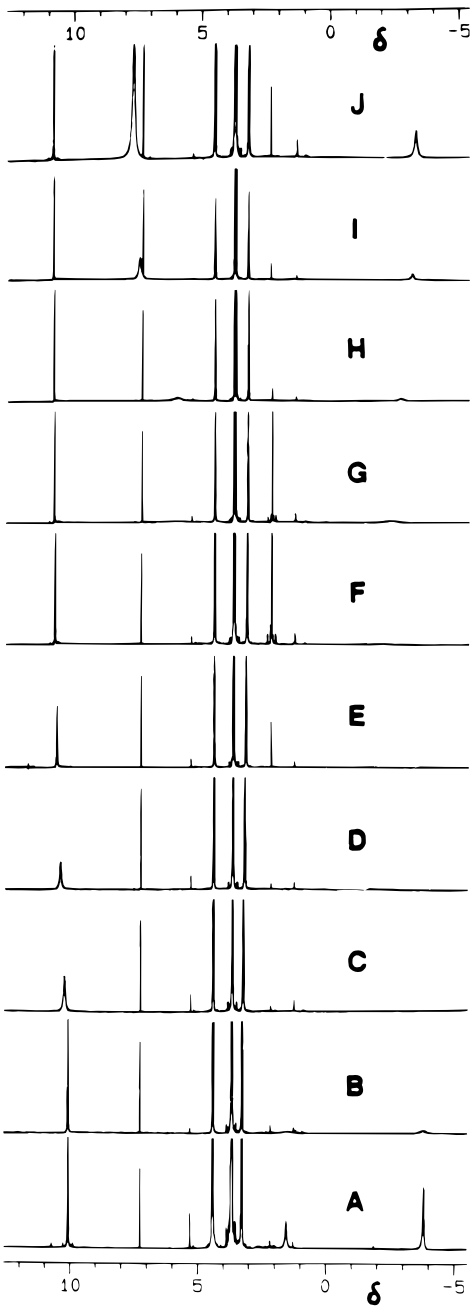


Figure 2. Proton NMR spectra of 0.01 M $COPH_2$ in $CDCl_3$ solution with the indicated concentrations of total TFA, from 0 to 0.200 M. The acid concentrations are curve A, 0; B, 0.001 M; C, 0.005 M; D, 0.010 M; E, 0.015 M; F, 0.020 M; G, 0.025 M; H, 0.075 M; I, 0.140 M; J, 0.200 M. Signals for the beta methyl and ester groups at 3.0−4.6 ppm are truncated, as are narrow *meso*-lines, in order to display the weak O−H and N−H signals at reasonable intensities.

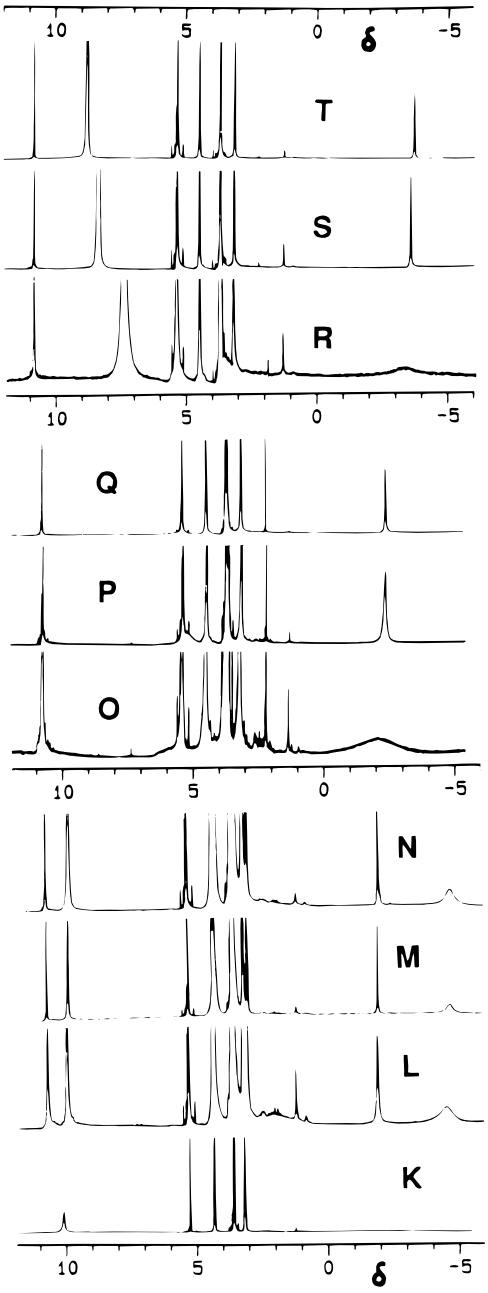


Figure 3. Proton NMR spectra of 0.01 M $COPH_2$ in CH_2Cl_2/TFA solutions at various temperatures. Spectra K, L, M, N in 0.003 M TFA at 293, 258, 223, and 203 K, respectively. Spectra O, P, Q in 0.025 M TFA at 293 (plotted at very high instrument gain), 260, and 240 K, respectively. Spectra R, S, T in 0.20 M TFA at 293 (plotted at very high instrument gain), 263, and 243 K, respectively. Again, the intense peaks are truncated.

line corrections required at this high gain. Within this region, the signal appears broadest (roughly 500 Hz) and farthest downfield ($\delta = -1.8$ ppm) at 0.010 M TFA.

These line width variations are eliminated by recording the spectra at reduced temperature (Figure 3). At the lowest TFA concentration studied, 0.003 M, the available acid can convert only a fraction of the 0.01 M $COPH_2$ to the dication $COPH_4^{++}$. (We argue below that the monocation $COPH_3^+$ could be present at most only at low concentration.) When the probe temperature is lowered as little as 30°, the proton exchange rate is lowered out of the intermediate rate region which produces line broadening (spectra K, L, M, N, Figure 3), and two signals appear. The narrower, at −1.92 ppm (field-dependent) is assigned to the dication, and the broader (∼300 Hz) is assigned to N−H in the free base. In support of these assignments, we argue that the ionic charge on the dication should move that signal downfield, the larger N−H integral (very rough due to the broad line) must be assigned to the free base for consistency with the *meso*-proton integrals, and that the broad signal disappears when TFA concentration exceeds 0.025 M.

The spectra recorded at 0.025 M TFA (O, P, Q, Figure 3) again show strong narrowing of the N−H signal upon cooling, but this time only a single somewhat broad signal appears, at approximately the chemical shift assigned to the dication. The average integral gives 3.9 protons. Spectra recorded in excess acid (0.2 M; R, S, T, Figure 3) again show a single N−H signal which is still narrower and displaced further upfield in the more strongly acid solution. Integration gives 4.0 protons. The broad

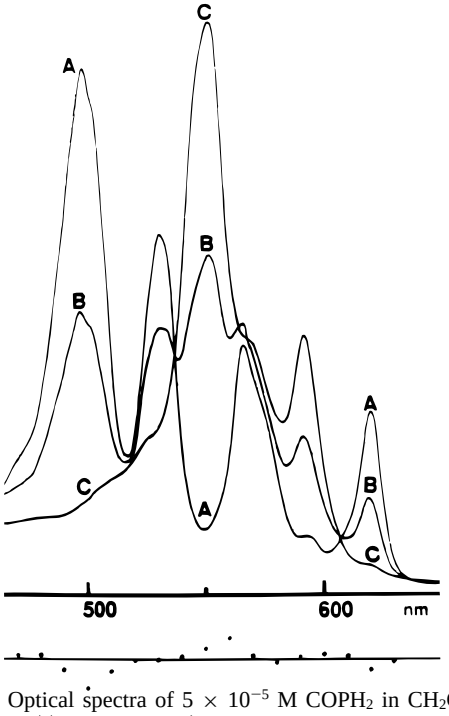


Figure 4. Optical spectra of 5×10^{-5} M $COPH_2$ in CH_2Cl_2 (curve A), of $COPH_4^{++}$ in 1.2×10^{-4} M TFA in CH_2Cl_2 (curve C), and of the intermediate stage in 5×10^{-5} M TFA in CH_2Cl_2 (curve B). Assignments of the species which produce curves A and C are consistent with integration values for the N−H NMR signals. Curve B is close to the mean of A and C: the differences $B - (A + C)/2$ are plotted below the wavelength scale of the spectra with the same vertical scale.

signals which appear at 7.4−9.1 ppm (strongly temperature-dependent) are assigned to excess TFA. Protonation of the core nitrogen atoms does not proceed beyond formation of the diprotonated dication in these solutions: in pure TFA solvent, the N−H signal has also been reported[7] to integrate to four protons. Thus the experimental evidence is that $COPH_2$ adds only two protons in $CDCl_3$/TFA solutions to give $COPH_4^{++}$.

The signal at 1.53 ppm due to water in the solvent also broadens and then disappears in phase with the N−H signal upon addition of TFA. It probably reappears as a combined (due to fast exchange) TFA/H_2O line as the concentration of TFA in the system increases above 0.025 M, but we have been unable to demonstrate this. This combined signal then moves downfield to 11.4 ppm in 2.0 M TFA in $CDCl_3$. Note that independent experiments with TFA in (wet) $CDCl_3$ give the same results for the O−H signal; thus porphyrin is not required to broaden the O−H signal. A 1-D NOE experiment conducted on a 0.003 M TFA solution of $COPH_2$ in $CDCl_3$ at 260 K shows exchange between the O−H and the two types of N−H protons.

The optical spectra of $COPH_2$ in methylene chloride solutions to which variable amounts of TFA are added show that acid converts the 4-band visible spectrum of $COPH_2$ through intermediate stages to a two-band absorption with the relative intensities II > I and red-purple color consistent with Fleischer's proposal.[2,3] This two-band spectrum undergoes only minor changes in positions, intensities, and line widths when a large excess of acid is added, so it seems reasonable to attribute it to diprotonated $COPH_4^{++}$, consistent with the integration results from NMR. Three of these spectra are shown in Figure 4.

Isosbestic points are observed in these spectra at 537 and 606 nm, and these do not change position over the entire range of TFA concentrations which converts the $COPH_2$ spectrum to that of $COPH_4^{++}$. At intermediate stages of the acid titration there is no shift of the isosbestic points to indicate the formation of two successive protonated species.[7] Thus there is no independent experimental evidence to support the assignment of a spectrum to monoprotonated porphyrin. The assignments of curves A and C to $COPH_2$ and to $COPH_4^{++}$ are unambiguous, on the basis of the N−H NMR integration data, but with uncertainty over the correct minimum acid concentration at which to observe C. Curve B was recorded with acid and porphyrin free base in 1:1 stoichiometric ratio, so the concentration of any intermediate $COPH_3^+$ should be near its maximum. Curve B resembles various reported spectra of proposed intermediates[4] in porphyrin acidification. However, if B is compared with $(A + C)/2$, the former is largely accounted for as the average absorption by a mixture of $COPH_2$ and $COPH_4^{++}$; the differences are plotted at the bottom of Figure 4.

Spectrum B crosses over a narrow section of C at 565 nm. This feature is reproducible but is affected by the concentration of TFA in excess of 0.02 M, which changes both the bandwidth and the level of the shoulder of the intense peak at 552 nm in C. Perhaps these variations are due to a shift in isosbestic points which reflects the presence of a monoprotonated porphyrin monocation in the solution. It is also possible that they are due to changes in solvent properties as the TFA concentration increases. In any case the spectrum in Figure 4B is largely determined by the species $COPH_2$ and $COPH_4^{++}$, and the monocation is at best only a minor solution component. Both solvent effects on the stabilization of PH_3^+ (maximum stability in H_2O, lower stability in nonpolar solvent[5b,10]) and the low concentration of PH_3^+ attained[5,10] have been proposed by previous authors. Note that the N−H line broadening reaches its maximum in the TFA concentration range which should give the maximum concentration of $COPH_3^+$.

Discussion

Some of the possible proton exchange modes by porphyrin solutions have already been studied: tautomeric exchange of protons between the two pairs of nitrogen atoms across the PH_2 core was first proposed by Becker, Bradley, and Watson.[6] Many investigators have shown this exchange to be fast on the NMR time scale. Diprotonated $COPH_4^{++}$ has been shown to exchange with the free base $COPH_2$ rather slowly on the NMR time scale;[9] it seems likely that this rate is solvent-dependent. When TFA is added to a $CDCl_3$ solution of $COPH_2$ at room temperature, the somewhat broad NMR lines assigned to N−H broaden further upon addition of much less than equimolar (to $COPH_2$) TFA and eventually cannot be seen at normal instrument gain. This acid-dependent broadening reaches its maximum over the acid concentration range 0.005−0.015 M, so the concentration of any protonation intermediate should be greatest with porphyrin concentration about 0.01 M. Further addition of acid protonates the remaining basic sites on nitrogen to destroy any intermediate stage. In the diprotonated dication, the acid-dependent NMR signal returns to approximately the position and line width of the N−H signal of the free base. This appears to be an example of NMR line broadening by proton exchange in the intermediate rate region, where the exchange rate depends upon TFA concentration. The results already described indicate that the exchange involves N−H in both the free base and the dication, as well as O−H.

The NMR signal of the C-H protons at the *meso*-positions also broadens in the same intermediate acid concentration range. Proton exchange by the C−H is not expected; we attribute these line width effects to $COPH_2$−$COPH_4^{++}$ exchange which involves nitrogen atoms which are nearby but not directly bonded to the protons which produce the H(*meso*) NMR signal. Thus, this exchange is the same process which broadens the N−H signals.

NMR signals of the alkyl group protons are only weakly affected by these changes in acid concentration. The line widths of signals of protons covalently bonded to side chains on the porphyrin ring system all are in the range 2.0−2.5 Hz. There are somewhat abrupt changes in these signals as the temperature is lowered; these are attributed to changes in rotational narrowing as solvent viscosity changes. The signals of solutes such as chloroform or acetone which exist as free molecules independent of the porphyrin are narrower: in the range 1.0−1.5 Hz. This difference is attributed to faster tumbling in solution by these small solute molecules.

We consider now the nature of the reaction(s) which convert $COPH_2$ to $COPH_4^{++}$. For the solvents $CDCl_3$ and CD_2Cl_2 (which are assumed to behave identically) and TFA as the acid, the two-proton addition is confirmed by the N−H integrations at 260 K and below. The reduced temperature is necessary to reduce the exchange broadening of the NMR signal observed near the equivalence point for TFA at 293 K. The integration data indicate four equivalent N−H protons in 0.025 M TFA, with no indication that an intermediate protonation stage intervenes in the two-proton addition to $COPH_2$. The crossover at 565 nm of optical spectra B and C in Figure 4 is reproducible and could reflect the presence of a monoprotonated intermediate at low concentrations; it might also be due to changes in solvent properties as the concentration of TFA increases. In any case, the data provide no evidence on the structure of any intermediate. Our data show that the N−H integral value remains unchanged at 4.0 protons at TFA concentrations up to 2.0 M. Abraham and co-workers[7] have reported that the value is still four protons for $COPH_4^{++}$ dissolved in pure TFA. It hardly need be pointed out that diprotonation without a monoprotonated intermediate would be very unusual, although the absence of (inability to detect) an intermediate has been invoked by previous authors[5] for a variety of porphyrins. A monoprotonated species could function as a proton exchange catalyst and thus explain the appearance of exchange-induced line broadening at very low TFA concentrations.

We have not attempted to determine the minimum TFA concentration (between 0.020 and 0.025 M) at which the formation of $COPH_4^{++}$ is complete. This of course bears on the question whether the diprotonation proceeds stoichiometrically or reaches an equilibrium state dependent upon reactant concentrations and the strengths of the acids and bases involved.

We have carried out our most complete investigation on $COPH_2$, with the results reported above. $OEPH_2$ and $MEPH_2$ have also been investigated, and the results completely parallel those for $COPH_2$. In fact, the parallel is quantitative for the optical spectra: the porphyrin free bases all have absorption maxima close to 495, 531, 564, and 617 nm, with intensities IV > III > II > I, and brownish-purple solutions. The acid solutions of PH_4^{++} absorb at 552 and 592 nm, with intensities II > I; these solutions are red-purple. Isosbestic points for all three systems are close to 604 and 536 nm in TFA/CH_2Cl_2 solvent, throughout the full range of acid concentrations which converts to PH_2 to PH_4^{++}. We have avoided substituents on the β-pyrrole positions which would interact strongly with the π-electron system of the porphyrin ring and cause variations in these parameters; all of the substituents used here are seen as alkyl groups by the π system. The NMR spectra of course reflect differences in the porphyrin substituents by differences in their chemical shifts, but broadening of the *meso*- and the N−H proton signals occurs in all cases.

These results contrast sharply with the analogous optical data for the *meso*-tetraarylporphyrins reported earlier.[5b] In those cases, the free base absorption maxima are at 513, 547, 590, and 644 nm for *meso*-tetraphenylporphyrin. The maxima for the diprotonated dication are at 600 and 650 nm, with II < I. Solutions of these dications are deep green. Few data are available on meso-tetrasubstituted porphyrins with less bulky groups than aromatic rings. Albers and Knorr, and Moet-Ner and Adler have reported[11] a few *meso*-tetraalkylporphyrins. Three of the four bands for the free bases are within 5 nm of the corresponding maxima for the tetraphenyl compound; band I shifts 10−15 nm. Band I of the diprotonated dication shifts more: up to 50 nm longer wavelength for strong π-donating substituents,[11] with a change away from the clear green color toward greyish.

The behavior of the $COPH_2$ NMR spectra at low TFA concentration reported here—particularly the line width effects—is also quite different from that observed earlier for *meso*-tetraarylporphyrins.[5c] The latter showed distinct, somewhat broad, signals for the N−H protons in PH_2 and PH_4^{++}. Both of these signals appeared at all intermediate acid concentrations with intensity ratios proportional to the relative concentrations of these species in the samples as acidification proceeded. There were only small changes in line width with TFA concentration; the N−H signal in $CDCl_3$ solution broadens about 2-fold at the intermediate TFA concentrations which give approximately equal concentrations of PH_2 and PH_4^{++}, then returns to the original line width (ca. 20 Hz) when conversion to PH_4^{++} nears completion. We attribute this minor broadening to slow PH_2−PH_4^{++} exchange.[9] In no case was there either a unique NMR or an optical signal which could be attributed to a monoprotonated species. All of these effects were observed with 0.01 M porphyrin solutions of both tetraphenylporphyrin and with a number of *para*-substituted derivatives.

Fleischer[3] has reviewed crystallographic studies on porphyrins and proposed a model for the effect of bulky substituents on their protonation, including the failure of monoprotonation in *meso*-tetraarylporphyrins. Unfortunately, there are no direct studies of porphyrin structures in solution, so the extent to which Fleischer's model, based upon crystallographic data, is applicable to porphyrin solutions is unknown. The buckled macrocycles observed in crystals of diprotonated *meso*-tetraarylporphyrins probably exercise significant control over some porphyrin reactions and may be the source of the differences reported here.

Conclusions

We have shown that *meso*-tetraarylporphyrins and three *meso*-unsubstituted porphyrins behave differently at low concentrations of TFA in a low-polarity solvent with respect to proton NMR line width changes, solution colors, and order of intensities of the two bands in the optical spectrum of the diprotonated dications. Division into two behavioral classes determined by *meso*-substituted or by *meso*-free structures is consistent with a good deal of previously uncorrelated data on reactions of porphyrins with acid and on their optical spectra. We suggest that these two classes of porphyrin behavior are general, but modified—in some cases strongly—by π-interactive substituents on the periphery of the porphyrin macrocycle. These π interactions have not been extensively studied.

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