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Aggregation in High-Spin Ferric Complexes of Tetraarylporphyrins. Structure Determination Using Intermolecular Electron–Nuclear Dipolar Relaxation

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Abstract: The ^{1}H NMR spectra of the high-spin ferric halide complexes of tetra-*p*-tolylporphyrins are shown to exhibit concentration-dependent line width and chemical shifts indicative of significant aggregation in solution. The degree of aggregation is shown to increase with solvent dielectric constant in chloroform-*d*, methylene chloride-d_2, and toluene-d_8, and with halide ion in a given solvent in the order I > Br > Cl. The intermolecular paramagnetic dipolar relaxation is shown to be highly stereospecific, permitting a qualitative description of the structure of the proposed dominant dimer at intermediate concentrations. The structure consists of pairs of overlapping pyrroles in contact on the side of the porphyrin opposite to the out-of-plane iron. At higher concentrations, additional aggregated species exist. The results indicate that intermolecular paramagnetic dipolar relaxation may serve as a very useful tool for elucidating the solution structure of porphyrin aggregates.

One of the characteristic properties of porphyrins and metalloporphyrins is the tendency to dimerize or aggregate in solution. Two general types of aggregates have been characterized,[1,2] those involving the formation of a covalent bond linking the porphyrins within an aggregate via either a bridging ligand, metal–metal bond, or intermolecular coordination of basic side chains, and those based on van der Waals interactions involving primarily the porphyrin π systems. The covalently linked aggregates have been generally easier to characterize and much more work has been devoted to their study than to the van der Waals aggregates.[1,2] Particularly little is known about the factors influencing the noncovalent porphyrin interactions in nonaqueous systems. It is precisely these van der Waals π–π interactions in a hydrophobic environment between the porphyrin π cloud and aromatic amino acid side chains which are important in all known hemoproteins.[3]

Although the tendency for natural porphyrin derivatives to aggregate in a noncovalent manner is well recognized, it has been generally accepted[1] that the more or less perpendicular orientation of the phenyl groups in the synthetic *meso*-

tetraarylporphyrin systems prevents the necessarily close contact (~3.5-4.5 Å) characteristic of π-π donor-acceptor complexes.[1,4] The near-perpendicular orientation[5] of the phenyl groups results from the sizable barrier to rotation arising from steric interaction between the *o*-H and pyrrole H.

The view that the perpendicular phenyl groups provide intermolecular steric constraints to the formation of stable noncovalent dimers is supported indirectly by a number of observations. Thus, while the zinc(II) complexes of octaethylporphyrin, OEPZn,[6] and the cation radical, OEP^+Zn,[7] dimerized significantly, the analogous compounds of tetraphenylporphyrin, TPPZn and TPP^+Zn, do not. The ability to photochemically form the metal-metal bond in $(OEPRu)_2$ but not in $(TPPRu)_2$ was also attributed to the phenyl groups.[8] Lastly, the interplane separation[9] in the covalent oxo-bridged dimer, $(TPPFe)_2O$, is larger than that in the analogous dimer of protoporphyrin dimethyl ester.[10] No noncovalent aggregates of TPP derivatives in nonaqueous solvents have been characterized to date.

The determination of the structure of porphyrin aggregates not involving covalent bonds has relied primarily on magnetic resonance methods.[11-14] In diamagnetic systems, ^1H NMR intermolecular ring current shifts have been utilized extensively, leading to proposed structures consisting of overlapping parallel π planes spaced some 8-10 Å apart.[1,11] Electron spin resonance studies of paramagnetic systems, on the other hand, have provided very direct evidence for much shorter metal-metal spacings (~4 Å) for Cu(II) and vanadyl porphyrins.[12,13] The apparent discrepancies between the EPR- and NMR-determined interplane spacings for very similar porphyrin complexes has been suggested to arise from inadequacies in the ring current models.[13] Detection of dimerization or aggregation by ESR, on the other hand, requires that the metals, rather than just the π clouds, get quite close to each other,[12,13] which may not be the situation in all forms of aggregates.[14]

We had shown[14] earlier that information on the extent of aggregation and the nature of the structure of the aggregate can be inferred from proton relaxation[15] studies in paramagnetic metalloporphyrins, and that the interpretation of relaxation data in terms of structure might be subject to fewer uncertainties than in the case of ring current shifts.[1,11] Paramagnetic dipolar relaxation, which is generally dominant for protons within a complex,[15] is given, in the applicable limit $\omega_S{}^2\pi^2 \gg 1$, by

$$\pi\delta_m = T_2{}^{-1} = \frac{7}{15}\gamma^2 g^2 \beta^2 S(S+1) r^{-6}\tau_c = Kr^{-6}\tau_c \quad (1)$$

where the δ_m is the line width in the monomeric species in hertz, T_2 is the spin-spin relaxation time, γ is the proton magnetogyric ratio, β is the Bohr magneton, r is the metal-proton distance, and τ_c is the correlation time modulating the dipolar interaction. In the case of well-resolved proton spectra for complexes[15], $\tau_c = T_{1e}$, where T_{1e} is the electron spin-lattice relaxation time.

Under conditions of a rapid equilibrium between monomeric and, for example, dimeric species, the averaged T_2 or line width, δ_0, in the absence of exchange contributions, is given[16] by

$$\delta_0 = (\pi T_2)_0{}^{-1} = f_m\delta_m + f_d\delta_d \quad (2)$$

where f_m and f_d are the fractions of porphyrin complexes as monomers and dimers, respectively, and the dimer line width, δ_d, is given by

$$\delta_d = \delta_d(\text{intra}) + \delta_d(\text{inter}) \quad (3)$$

where δ_d(intra) and δ_d(inter) are the intramolecular and intermolecular contributions to the paramagnetic relaxation, respectively. Under favorable cases, where τ is not significantly affected by the extent of aggregation,[14] $\delta_d(\text{intra}) = \delta_m$. δ_d(inter) is given by an expression similar to eq 1, namely

$$\pi\delta_d(\text{inter}) = Kr'^{-6}\tau_c \quad (4)$$

where r' is the distance between a proton on one complex and the iron in the other porphyrin complex. By rearranging eq 2, 3, and 4 we can obtain the following:

$$\delta_0 - \delta_m = f_d\delta_d(\text{inter}) \quad (5)$$

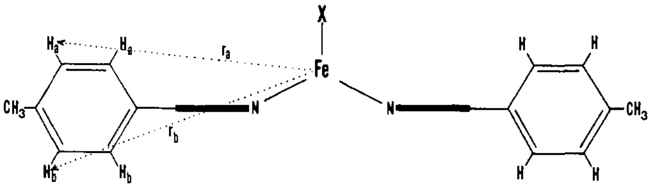

Figure 1. Side view of tetraphenylporphyriniron(III) chloride depicting the out-of-plane displacement of the iron and the perpendicular orientation of the phenyl rings.

This last equation predicts that the observed line width increases with concentration since f_d increases with concentration. Moreover, the ratios of the concentration-dependent contribution to the line widths for two nonequivalent protons in a complex will yield the relative values of r'^{-6}, i.e.

$$(\delta_0 - \delta_m)_i/(\delta_0 - \delta_m)_j = r'_i{}^{-6}/r'_j{}^{-6} \quad (6)$$

This ratio of distances will permit determination[14] of the "average" structure in solution. Structures determined in this fashion should be reliable since they depend on only one parameter (r) in contrast to the number of parameters required for ring current calculations.[11] Recent studies in our laboratory on low-spin ferric biscyano complexes of natural porphyrins have shown[14,17] that intermolecular paramagnetic relaxation can indeed yield information on dimerization and lead to the characterization of novel types of aggregates.

In this study we will demonstrate that intermolecular dipolar relaxation can be used to elucidate the structure of aggregates involving high-spin iron halide complexes of the synthetic porphyrin,[18] tetra-*p*-tolylporphyrin, designated PFeX, where X is the halide, in nonaqueous solution. These complexes have been well characterized[18] and their ^1H NMR traces have been recorded.[19-22] The x-ray crystal structure of tetraphenylporphyrin iron chloride, TPPFeCl, has been reported,[23] and the general features of this structure are depicted in Figure 1. The aspects of note for this study are the sizable (0.38 Å) displacement of the ferric ion out of the plane in the direction of the chloride, and the general perpendicular orientation of the four phenyl rings. These phenyl rings actually exhibit small degrees of tilt of ~20° from the perpendicular, but severe steric interactions prevent any stable rotamer with much larger tilting.

Our relaxation study will demonstrate that, contrary to the general view,[1,6-8] not only are the TPP-type complexes aggregated in nonaqueous solution, but the aggregation is stereospecific and highly sensitive to both axial ligand and solvent.

Experimental Section

The ferric chloride complex of tetra-*p*-tolylporphyrin, PFeCl, was prepared by the standard method,[18,20] and the bromide, iodide, and azide salts were prepared by a metathesis, as described earlier.[19,21,22] The purity of all complexes was verified as ≥99% by the previously characterized ^1H NMR spectra.[20-22] Trinitrobenzene, TNB, was recrystallized from ethanol prior to use.

Chloroform-*d* and methylene chloride-d_2 solutions were prepared approximately 40 mM by careful weighing of PFeX into 0.40 mL of

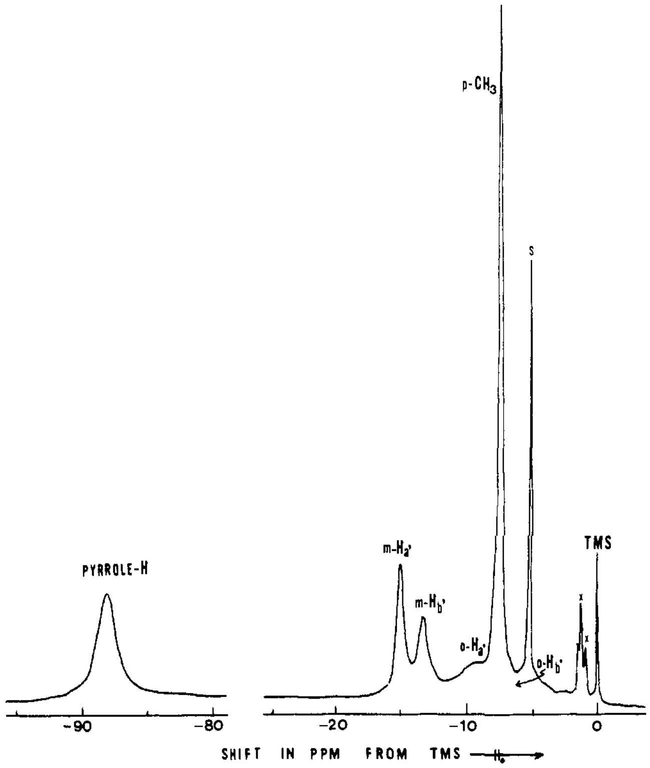

Figure 2. ^{1}H NMR trace of a 43.6 mM tetra-*p*-tolylporphyriniron(III) bromide, PFeBr, solution in CD_2Cl_2 at 0 °C. The subscripts a′ and b′ refer to low- and high-field signals, respectively: x = impurities.

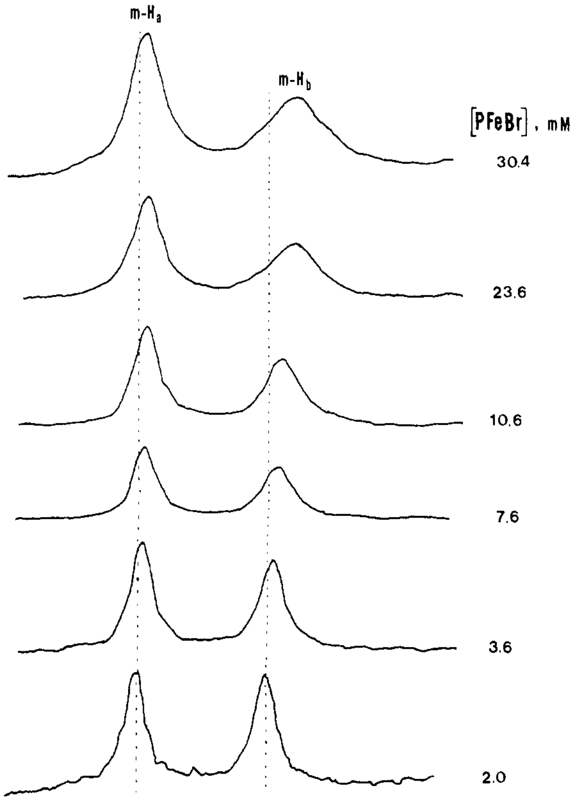

Figure 3. *m*-H region of the proton trace of tetra-*p*-tolylporphyriniron(III) bromide, PFeBr, in CD_2Cl_2 at −30 °C as a function of concentration. Both the shifts and line broadening are readily observed.

solvent. Dilution studies were carried out by incremental addition of pure solvent until the low concentration prevented resolution of the peaks of interest. The observed line width directly yielded δ_0 in eq 6. The effect of TNB was observed by adding increasing increments of solid, weighed TNB to a solution of known [PFeX]. TNB was added until the PFeX line widths became independent of added TNB. The proton line width for all resolved peaks were measured for all samples. The effect of added TNB to a solution was to break up aggregation (vide infra) as evidenced by the decrease in line widths to those typical for the very dilute PFeX samples. The line width in the presence of TNB therefore provided a direct determination of δ_m (eq 6) at any [PFeX]. Only a small effect of [PFeX] on δ_m was noted, which is consistent with nonspecific intermolecular relaxation. The line width data as function of [PFeX] were collected in the temperature range 0 to −30 °C in order to suppress kinetic broadening of the *m*-H signals due to phenyl group rotation[21] and dissociative porphyrin inversion.[22]

The ^{1}H NMR spectra were recorded on a JEOL PS-100/EC-100 FT NMR spectrometer operating at 99.5 MHz. A typical spectrum consisted of 100–5000 transients obtained with a 20-μs 90° pulse using 8K points over a 20-kHz bandwidth. T_1 values were determined by the conventional 180°-*t*-90° pulse sequence.[24] Line widths are defined as full width at half-length, and are given in hertz. Sufficient signal/noise was attainable so that the line width for all resolved peaks could be determined with uncertainties ≤5%. Chemical shifts are referenced to the internal calibrant, Me_4Si, and are reported in parts per million.

Results and Discussion

A typical ^{1}H NMR trace for PFeX is illustrated in Figure 2 for X = Br in CD_2Cl_2 solution; all peaks have been assigned previously.[19-22] The spectra for X = Cl, Br, and I are very similar, except that the phenyl protons exhibit a slight downfield bias in the order I > Br > Cl, as may be expected from their variations in zero-field splitting parameters.[19] The pair of *m*-H peaks, labeled *m*-$H_{a'}$, and *m*-$H_{b'}$ (as well as the pair of *o*-H peaks, one of which is not resolved), arise due to the slow phenyl group rotation and the nonequivalence of the two sides of the porphyrin plane,[20,21] as depicted in Figure 1. The two *m*-H peaks exhibit different line widths, as shown in Figure 2. Originally this appeared to be explainable by the known structure of the complex,[23] where the out-of-plane iron is closer to *m*-H_a than *m*-H_b in Figure 1. Since the intramolecular dipolar relaxation[15] varies as r^{-6}, it is expected that the line widths differ so that $\delta_m(m\text{-}H_a) > \delta_m(m\text{-}H_b)$. Closer investigation, however, reveals a more complex origin. In Figure 3 we plot the portion of the trace containing the two *m*-H peaks of PFeBr in CD_2Cl_2 as a function of PFeBr concentration. From this it is clear that the relative line widths depend on concentration, with the upfield *m*-$H_{b'}$ much more affected than the downfield *m*-$H_{a'}$. Although line widths in paramagnetic complexes generally increase slightly with increased concentration owing to nonspecific intermolecular relaxation, the significantly different relaxation of the two nonequivalent peaks within a complex argues strongly for specific interactions between complexes. In fact, the greater broadening of one *m*-H indicates that interaction is also stereospecific,[14] with the approach of a second complex favoring one of the two sides of the porphyrin plane.

In order to eliminate any sort of line broadening effect due to chemical exchange, and to demonstrate that the concentration-dependent contribution to the line width arises from intermolecular dipolar relaxation,[15] we determined the T_1's for the two *m*-H peaks via a 180°-*t*-90° pulse sequence.[24] The usual plot[24] of ln $[(A_\infty - A_t)/A_\infty]$ vs. *t* is shown in Figure 4. The T_1's, 8.5 ± 0.8 and 6.6 ± 0.6 ms, have the same relative values as do the T_2's (from $T_2^{-1} = \pi\delta$), which are 7.1 ± 0.5 and 5.4 ± 0.4 ms, respectively. The near identity of T_1 and T_2 for both *m*-H peaks is in agreement with dominant dipolar relaxation for both the intra- and intermolecular contributions.[15,19] The ratio $T_1/T_2 = 1.3 \pm 0.2$ is within experimental error of the ratio expected[15,19] when $\omega_S{}^2\tau^2 \gg 1$, i.e., 7/6.

In Figure 5 we present the effect of concentration on both line widths (A) and shifts (B) of PFeI in $CDCl_3$ at −26 °C. This complex has inherent line widths[19] small enough to permit resolution of the maximum number of peaks. All peaks ex-

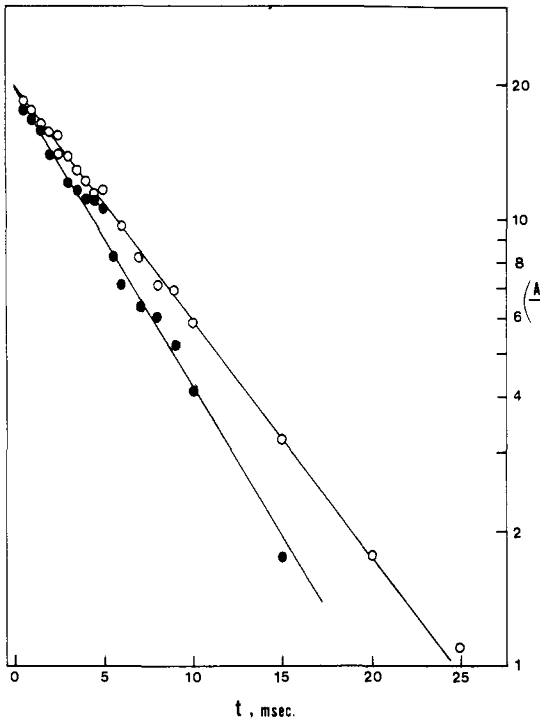

Figure 4. Plot of ln $(A_t - A_\infty)/A_\infty$ vs. t from a 180°-t-90° pulse FT NMR T_1 determination. A_t, A_∞ are in arbitrary units; m-H$_{a'}$, -○-; m-H$_{b'}$, -●-.

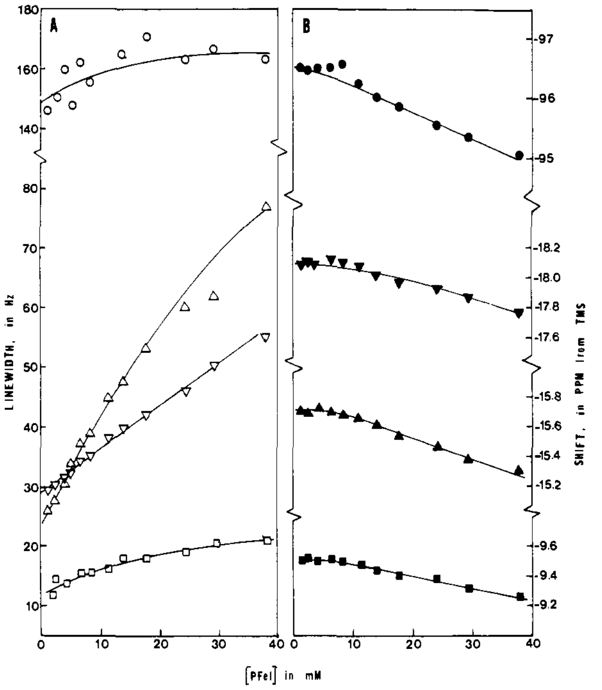

Figure 5. Plot of line widths (A) and chemical shifts (B) as a function of concentration of tetra-p-tolylporphyriniron(III) iodide in $CDCl_3$ at −30 °C: -○-, -●-, pyrrole-H; -▽-, -▼-, m-H$_{a'}$; -△-, -▲-, m-H$_{b'}$; -□-, -■-, p-CH_3.

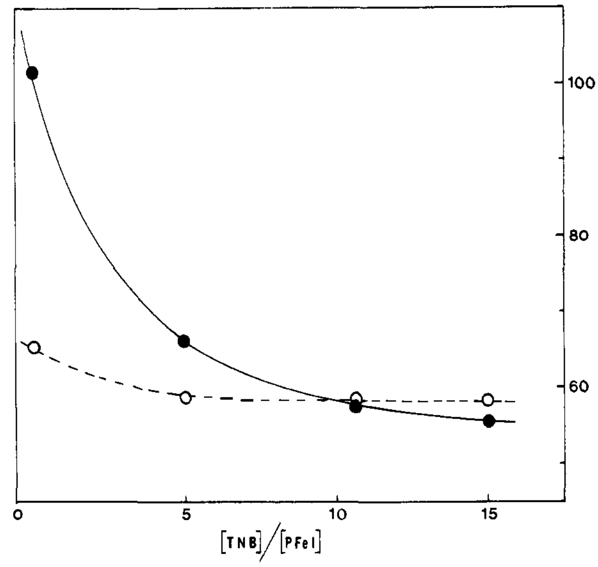

Figure 6. Plot of m-H$_{a'}$, -○-, and m-H$_{b'}$, -●-, line width as a function of mole ratio of trinitrobenzene, TNB, to tetra-p-tolylporphyriniron (III) iodide, PFeI, at −5 ° in CD_2Cl_2; [PFeI] = 36 mM.

hibited downfield shifts upon dilution which are consistent with intermolecular ring currents from some form of π stacking at higher concentrations.[11] Figure 5 also shows that, although all lines become somewhat narrower upon dilution, the effect is much greater for the m-H's. (Actually the effect appears to be greatest for the o-H's, but the wider of the two o-H's is too broad to detect at even moderate concentrations.) The behavior of the m-H line widths is particularly interesting since the relative order of line widths is *reversed at high and low concentrations.*

Based on the reasonable assumption that the low concentration traces represent the monomeric complexes, this change in the pattern of m-H line widths allows us to draw two important conclusions. Firstly, the low concentration line width ratios lead to the assignment of the downfield resonance, m-H$_a{}'$, to the m-H$_a$ on the same side of the porphyrin plane as the ferric ion, and the m-H$_b{}'$ peak to the m-H$_b$ in Figure 1. Secondly, the broader upfield peak at higher concentration proves that the iron of one porphyrin (and hence the whole complex) approaches the second complex on the side of the porphyrin plane *opposite* to that where the iron protrudes (vide infra).

Confirmation for the intermolecular origin of the excessive m-H$_{b'}$ broadening is obtained from studies of the effect of trinitrobenzene, TNB, on the line widths of the subject complexes. Previous work[25] with porphyrins of low-spin Co(II) has demonstrated that the introduction of TNB breaks up aggregation by the formation of π complexes between TNB and the metalloporphyrin. We have characterized[26] the TPPCo–TNB complex in detail elsewhere. Addition of TNB to a solution of PFeX at high concentration resulted in the decrease of line widths with relative effects very similar to those caused by dilution (Figure 5). The effect of TNB on the m-H line widths of PFeI in CD_2Cl_2 at −5 °C is illustrated in Figure 6. Again, the breaking up of the aggregate yields a reversal of the relative m-H$_{a'}$ and m-H$_{b'}$ line widths, leading to the assignment of the downfield peak to m-H$_a$ in Figure 1.

At low concentrations, where the dilution studies indicate negligible aggregation, addition of TNB has no detectable effect on line widths, although some small shifts are observed due to the ring currents induced by the TNB. The presence of the TNB interaction is also confirmed by the observation of a broadening and ring current shift of the TNB signal.[25,26] Thus the addition of TNB provides a convenient and reliable method for estimating the line width for all protons in the complex at a certain concentration under conditions of negligible aggregation; hence by this method we can always estimate δ_d(intra) in eq 3.

Several attempts were made to interpret the concentration-dependent shift and line width data in terms of an equilibrium constant for a dimer or trimer using conventional methods.[11] However, in no case were we able to obtain a fit with resonable parameters. The poor fits which were obtained tended to have very small equilibrium constants and unrea-

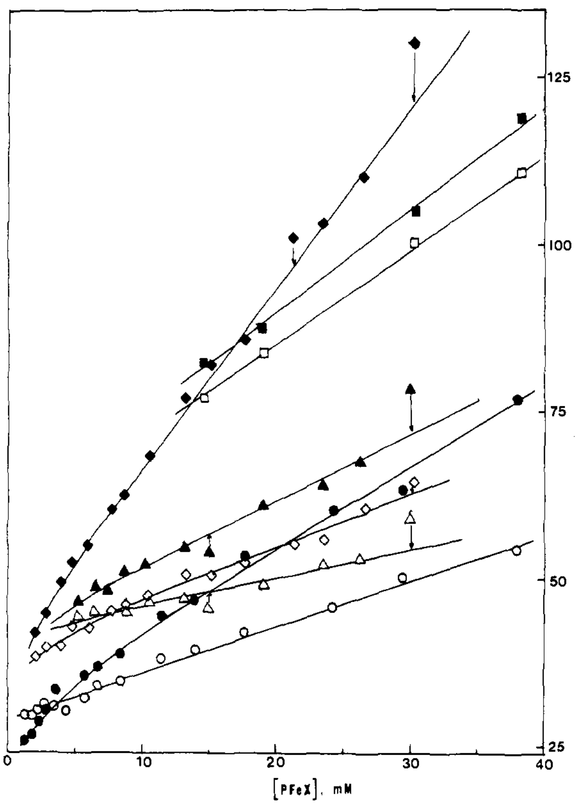

Figure 7. Graph of m-H$_{a'}$ (open markers) and m-H$_{b'}$ (darkened markers) line widths for tetra-p-tolylporphyriniron(III) halide, PFeX, vs. concentration at −30 °C: -◇-, -◆-, X = Br in CD_2Cl_2; -△-, -▲-, X = Br in $CDCl_3$; -□-, -■-, X = Cl in $CDCl_3$; -○-, -●-, X = I in $CDCl_3$.

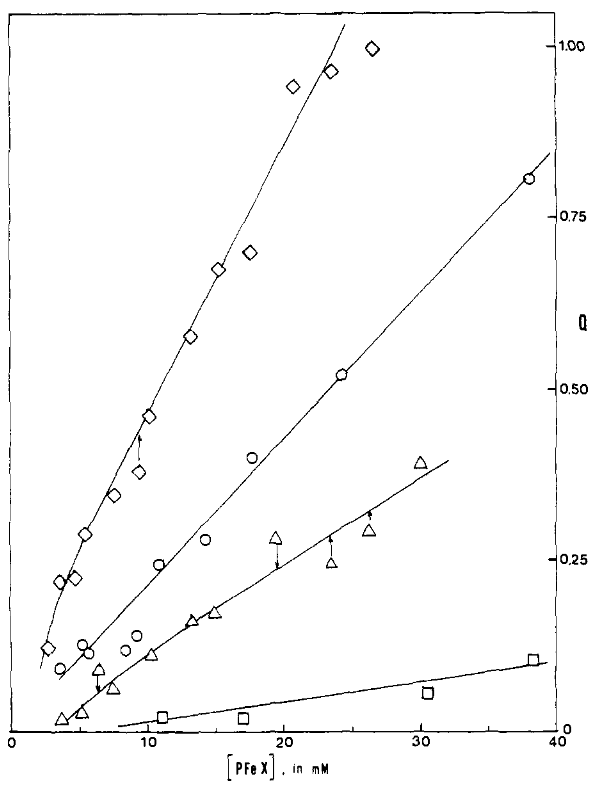

Figure 8. Graph of $Q = [\delta_0(m\text{-H}_{b'}) - \delta_0(m\text{-H}_{a'})]/\tfrac{1}{2}[\delta_m(m\text{-H}_{a'}) + \delta_m(m\text{-H}_{b'})]$, as defined in eq 7, vs. tetra-p-tolylporphyriniron(III) halide, PFeX, concentration at −30 °C. The slope of this line is a qualitative measure of the relative magnitudes of stereospecific intermolecular vs. intramolecular dipolar relaxation, and hence a qualitative index of the degree of aggregation: -◇-, X = Br in CD_2Cl_2; -△-, X = Br in Cdcl$_3$; -□-, X = Cl in $CDCl_3$; -○-, X = I in $CDCl_3$.

sonably larger dimer shifts and line widths (i.e., shift >50 ppm). The fits did not improve assuming higher degrees of aggregation. Further attempts at providing a quantitative index of the extent and manner of aggregation were abandoned when a detailed analysis of the intermolecular contribution to the line widths indicated that there must exist at least two unrelated structures for aggregates in solution (vide infra).

Axial Ligand and Solvent Effects on Aggregation. Comparison of the concentration dependence of the line widths of PFeX for different X in different solvents reveals that similar aggregates are formed in all cases but to an apparently different degree. In Figure 7 we present the data for the two m-H peaks in PFeX, X = Cl, Br, and I, in $CDCl_3$ and also PFeBr in CD_2Cl_2, all at −30 °C. It is obvious in this figure that the difference in the m-H$_{a'}$ and m-H$_{b'}$ line widths for PFeBr is much larger in CD_2Cl_2 than $CDCl_3$ at the same concentration and temperature, suggesting more extensive aggregation in the former solvent. Similarly, the rate of divergence with concentration of the two m-H line widths is greatest for PFeI and least for PFeCl in $CDCl_3$.

The degree of difference in aggregation, although not definable by equilibrium constants, can be better represented than by the data in Figure 7 simply by recognizing that the inherent line width for monomeric PFeX differs significantly with X, as discussed in detail previously.[19] A qualitative index of the average degree of aggregation could be represented by the ratio, Q, of the difference in the m-H$_{a'}$ and m-H$_{b'}$ line widths to that of the average m-H line width in the absence of aggregation,[27] i.e.

$$Q = [\delta_0(m\text{-H}_{b'}) - \delta_0(m\text{-H}_{a'})]/\tfrac{1}{2}[\delta_m(m\text{-H}_a) + \delta_m(m\text{-H}_b)] \quad (7)$$

This ratio, Q, will provide the measure of the important intermolecular relative to intramolecular relaxation, and eliminates the difference in intrinsic line width[19] for monomeric PFeX.

The aggregation parameter, Q, for the same systems represented in Figure 7 is plotted again for PFeX in Figure 8. The relative slopes of the lines in this figure indicate that the degree of aggregation at −30 °C definitely increases in the order I > Br > Cl in the same solvent, and is larger in CD_2Cl_2 than in $CDCl_3$ for the same complex. The number of complexes compared is further extended by the room temperature data listed in Table I. Here we present line width data for the two m-H's peaks at comparable concentrations in three solvents and for X = Cl, Br, and I, as well as N_3. The parameter, Q, in the last column again leads to the same trend of aggregation with X as determined at −30 °C, with azide somewhere between Cl and Br.[19] Also, these 25 °C data indicate increased aggregation in the order $CD_2Cl_2 > CDCl_3 >$ toluene-d_8.

It should be mentioned that the relative degrees of aggregation in Table I, as defined by Q, are not as reliable as those obtained at lower temperature, because it is known[21,22] that both the m-H's experience line broadening from chemical exchange mechanisms. Thus PFeCl exhibits m-H line broadening due to phenyl rotation,[21] while PFeI exhibits line broadening arising from porphyrin inversion by a dissociative mechanism.[22] Both of the effects[21,22] are totally suppressed below −20 °C. However, since both dynamic mechanisms broaden the two m-H peaks equally, the difference in line width, as indexed by Q, will still reflect the degree of aggregation. The line width contribution for the monomer in the absence of exchange at room temperature is obtained by extrapolating the data obtained at low temperatures. The data in Table I clearly demonstrate that TPP-type complexes do aggregate in solution at ambient temperatures. Although aggregation is barely detectable for PFeX in $CDCl_3$, it is very

Table I. Line Width Data for the *m*-H Signals in PFeX[a]

X	[PFeX], mM	Solvent (ϵ)[b]	Line width, δ^a		δ_m(av)[c]	Q^d
			m-H$_{a'}$	*m*-H$_{b'}$		
Cl	2.32	$CDCl_3$ (4.8)	63.4	65.6	56.5	0.04
Br	26.6	$CDCl_3$ (4.8)	48.5	56.4	36.2	0.22
I	16.9	$CDCl_3$ (4.8)	55.7	66.0	27.5	0.38
N_3	23.4	$CDCl_3$ (4.8)	68.4	74.7	55.1	0.11
Cl	21.8	CD_2Cl_2 (8.1)	73.4	90.2	57.5	0.29
Br	25.3	CD_2Cl_2 (8.1)	50.2	69.2	36.5	0.52
I	19.7	CD_2Cl_2 (8.1)	47.3	66.0	27.7	0.68
Br	25.2	$CD_3C_6D_5$ (2.8)	41.4	41.2	39.5	0.00

[a] In hertz at 25 °C. [b] ϵ = dielectric constant of solvent. [c] $\delta_m(\text{av}) = \frac{1}{2}[\delta_m(m\text{-H}_a) + \delta_m(m\text{-H}_b)]$, obtained from addition of TNB. [d] Defined in text in eq 7.

Table II. Meta Proton Line Widths as a Function of Concentration in PFeBr[a]

[PFeX], mM	Observed line width, $\delta_0{}^b$		Monomer line width, $\delta_m{}^b$		$\delta_0 - \delta_m{}^{b,c}$		$\frac{(\delta_0 - \delta_m)_a}{(\delta_0 - \delta_m)_b}$[d]
	m-H$_{a'}$	*m*-H$_{b'}$	*m*-H$_{a'}$	*m*-H$_{b'}$	*m*-H$_{a'}$	*m*-H$_{b'}$	
36	110	193	48.7	46.9	61.	146	2.4
30	65	130	47.9	46.1	17	84	5.0
24	55.8	103	46.9	45.1	8.9	57.9	6.5
21	55.3	100	46.4	44.6	8.9	56.4	6.4
16	50.3	81.8	45.1	43.3	5.2	38.5	7.4
8.9	45.8	62.7	43.4	41.5	2.4	21.2	8.8
7.6	45.1	60.4	42.9	41.1	2.2	19.3	8.8
4.8	42.9	52.7	41.6	39.8	1.3	12.9	9.9

[a] In CD_2Cl_2 solution at −30 °C. [b] Line widths in hertz. [c] Line broadening attributable to aggregation. [d] Ratio of intermolecular dipolar relaxation rates, i.e., eq 6.

noticeable for PFeI in all solvents at 20–25 mM. Dilution studies indicate that the aggregation becomes undetectable by the *m*-H line width in $CDCl_3$ at $\leq$15 mM for PFeCl, $\leq$5 mM for PFeBr, and $\leq$1 mM for PFeI; lower concentrations would pertain for CD_2Cl_2 solution. Our present results suggest that particular care must be exercised in monitoring aggregation in the case of the iodine salts of the ferric porphyrin, especially in solvents with dielectric constants >10.

The trend in the degree of aggregation with solvent follows an established pattern[1] in nonaqueous systems, with the aggregation increasing with solvent dielectric constant, ϵ, which are also listed in Table I. The apparent increase in the degree of aggregation with halide ion represents the first characterization of a systematic trend with axial ligand in isostructural complexes. We suggest that the effect of X is primarily due to the increased charge donation to the ferric ion in the order I > Br > Cl, which serves to increase the polarizability of the porphyrin π cloud. A direct effect of the halide ion does not seem likely in view of the proposed structure of the aggregate which has off-centered π stacking of two porphyrin planes on the sides opposite that containing the halogen (vide infra).

Structure of the Aggregate. The existence of only a single type of aggregate in solution requires[14,15,26] that $(\delta_0 - \delta_m)_i/(\delta_0 - \delta_m)_j$ in eq 6 is independent of the concentration. In such a case, the relative magnitudes of the intermolecular contributions to the broadening for nonequivalent protons will yield a unique solution structure of the aggregate.[14] In the case of the present complexes, however, analysis of the line widths reveals that the ratios in eq 6 are not independent of concentration. A typical set of such data is presented in Table II for PFeBr in CD_2Cl_2 at −30 °C, where it is evident that this ratio varies from ~10 at low concentrations and decreases at higher concentrations. Hence, at least two different species, in addition to the monomer, must exist at higher concentrations. This finding is consistent with our inability to define a simple equilibrium constant for the aggregation.

The tendency for *m*-H$_{b'}$ to be broadened much more severely than *m*-H$_{a'}$ via intermolecular relaxation does permit some qualitative conclusions about the structure of the aggregate which predominates at low concentration. Since *m*-H$_{b'}$ is broadened ~6–10 times more than *m*-H$_{a'}$ (Table II), we can conclude that the presumed dimer involves π–π stacking of some form on the side of the porphyrin opposite to that containing the halogen. Inspection of space-filling molecular models[28] reveals that, in spite of the phenyl groups, relatively close approach of parallel π planes can occur in a number of cases. With the ~30° oscillatory mobility for the phenyl groups, interplane spacings of 4.5–5.5 Å can be achieved. Although these spacings are not as short as those associated with tight π–π stacking,[3,4] they may be close enough to permit reasonable interaction between π systems.

Three idealized candidates were considered as plausible models for a solution dimer: (a) total overlap of the π system of both porphyrins, with the meso positions staggered to minimize intermolecular phenyl steric effects, (b) a one pyrrole over one pyrrole overlap resulting from a 2–4-Å slip of porphyrins with eclipsed phenyl groups along the N–Fe–N direction of one complex relative to the other, and (c) a two over two pyrrole overlap resulting from a 4–5-Å slip along an axis 45° to the N–Fe–N axis of the two porphyrins with eclipsed phenyl groups. In each of these systems 20–30° phenyl group tilting permits a ~5 Å interplane separation.

Model (a) can be clearly eliminated on the basis of two observations: it predicts intermolecular line broadening approximately proportional to the intramolecular line broadening, and also predicts that the maximum increase in line width for any signal upon aggregation is 60%. Both predictions are completely contrary to observation. Model (b) can similarly be eliminated on the basis that it predicts the largest intermolecular line broadening, by a factor of 2, for the pyrrole H's. As illustrated in Figure 5 for PFeI,the pyrrole H is little affected by intermolecular relaxation.

Model (c) presents us with the most realistic candidate, since it places one phenyl group over the metal, as depicted in Figure 9. Estimates of the average relative values of r^{-6} per set of equivalent protons in the monomer yields predicted relative

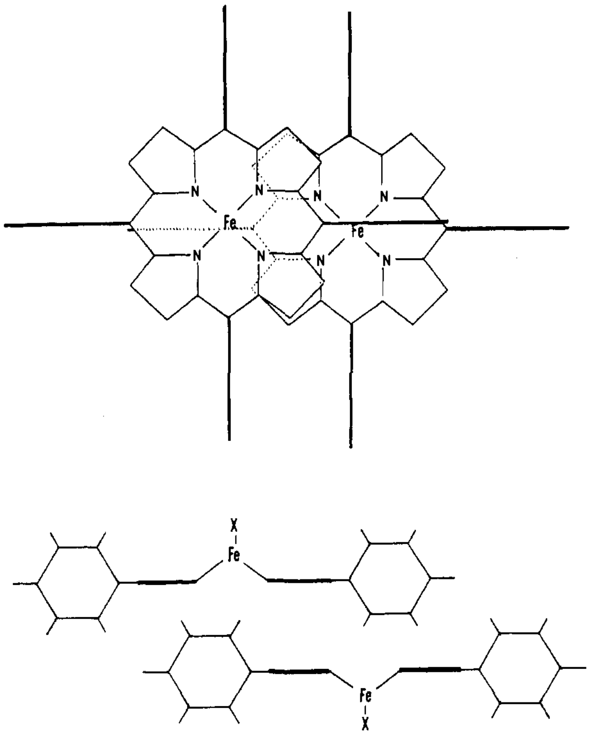

Figure 9. Qualitative features of the proposed dimer structure constituting the dominant aggregate at intermediate concentrations of complex.

intermolecular line broadening of o-H$_{b'}$ > m-H$_{b'}$ ≫ o-H$_{a'}$ > pyrrole-H ~ m-H$_{a'}$ ~ p-CH$_3$, in agreement with a dominant effect on the m-H$_{b'}$ and o-H$_{b'}$ peaks. No attempt was made to define the structure more quantitatively in terms of the intermolecular spacing or the degree of slip of the two prophyrin planes because of the presence of other structures in solution. We can conclude, however, that the low concentration intermolecular relaxation is consistent with predominantly a dimer having the structure[29] depicted in Figure 9.

At higher concentrations, the difference between m-H$_{a'}$ and m-H$_{b'}$ intermolecular line broadening decreases, indicating that possibly trimers or higher aggregates are formed which are not as stereospecific as the dimer described above. Although a more quantitative description of the solution structure is not feasible with the presently available data, our studies do demonstrate that TPP complexes aggregate in solution and that the intermolecular paramagnetic dipolar relaxation[14] provides a valuable new probe for assessing the structure of van der Waals π complexes of metalloporphyrins in solution. The full scope and utility of this method will become more evident upon completing a related study of dimerization in low-spin, ferric biscyano complexes of natural porphyrin derivatives, where it will prove possible to define the aggregate as a simple dimer involving overlap of single pyrroles in the two porphyrins.[30]

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(27) The ratio $\delta_d(m\text{-H})/\delta_m(m\text{-H})$ may appear to serve as just as valid an index of intermolecular relative to intramolecular dipolar relaxation. However, our index in eq 7 emphasizes the contribution of the dominant dimer at intermediate concentrations for which m-H$_a$ and m-H$_b$ are relaxed very differently.
(28) CPK Atomic Models, Schwarz-BioResearch, Orangeburg, N.Y., were employed.
(29) An estimate to the lower limit of the degree of dimerization can be made by assuming the closest possible approach between the iron and m-H$_b$ (2.8 Å). Scaling the relative values of r^{-6} and the known intramolecular line width, δ_d(inter) for m-H$_b$ ~ 10 kHz is obtained. The observed δ_d ~ 80 Hz for PFeI in CD$_2$Cl$_2$ at −30 ° thus indicates ~1% dimer formation. Since the iron and m-H$_b$ are unlikely to be in such a close contact, the actual extent of dimerization must be much larger.
(30) D. B. Viscio and G. N. La Mar, to be published.