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NMR Studies of Low-Spin Ferric Complexes of Natural Porphyrin Derivatives. 2. Determination of the Dimer Structure of the Biscyano Complex Using Intermolecular Paramagnetic Dipolar Relaxations

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Abstract: The ^{1}H NMR spectra of 2,4-dibromodeuteroporphinatoiron(III) dicyanide recorded below −40 °C exhibit significant concentration-dependent line widths and longitudinal relaxation rates. These intermolecular paramagnetic dipolar relaxation rates are highly regioselective and permit determination of the solution structure of the dimer which consists of the overlap of a single pyrrole from each porphyrin. The contact is highly stereospecific, involving the overlap of pyrrole I of one porphyrin with pyrrole IV of the other porphyrin complex within the dimer. The ≤4 Å spacing between essentially parallel porphyrin planes is consistent with a π–π complex. Since the π contact in the dimer involves the pyrroles suggested to be the best π acceptor (I) and best π donor (IV) based on spin density asymmetry, donor/acceptor π–π interactions are proposed as contributing to the dimer stability.

Introduction

The dimerization of metalloporphyrins in solution is a well-documented phenomenon[1] whose study has been pursued, in part, in order to gain insight into the unusual properties of the large polarizable π-electron systems. The characterization of the dimer structures in solution has relied primarily on the analysis of intermolecular ^{1}H NMR ring current shifts in the case of diamagnetic porphyrins,[2] and intermolecular electron-spin dipolar interactions in paramagnetic complexes.[3] We wish to demonstrate here that intermolecular paramagnetic dipolar relaxation[4,5] can also be profitably utilized for structure analysis, and that this method is particularly well suited for probing highly stereospecific interactions between porphyrins within a dimer.

Although the ^{1}H NMR spectra of the 2,4-substituted deuteroporphyrin iron(III) dicyanide complexes[6] ($S = \frac{1}{2}$) were found to be concentration independent in methanol at ambient temperatures,[7] spectra recorded below −40 °C exhibited significant concentration-dependent line positions as well as line widths. Computer analysis of the concentration-dependent shifts was shown to be consistent with an equilibrium involving solely monomer and dimer,[8] and equilibrium constants in the range 5–50 L mol^{-1} were found for various R, with 2,4-dibromodeuteroporphyrin iron(III) dicyanide exhibiting the largest degree of dimerization.

Solution ESR of these low-spin ferric complexes cannot be resolved,[9] and analysis of the concentration-dependent NMR shifts is not possible because the dimer shifts arise from the sum of intermolecular positive ring-current shifts and negative paramagnetic dipolar shifts which cannot be readily separated.

The observed stereospecific intermolecular relaxation, however, is due exclusively to paramagnetic dipolar relaxation (vide infra) caused by the second iron atom in the dimer. This intermolecular relaxation contribution is proportional to r_1^{-6},

the distance to the second iron atom, and should be of utility in elucidating the structure of the dimer. A preliminary report[5] on the qualitative structure determination of the dimer of protoporphyrin iron(III) dicyanide in $C^2H_3O^2H$ has already been presented. We will explore here the utility of intermolecular dipolar T_1 relaxation as a tool for determining the solution dimer structure of 2,4-dibromodeuteroporphyrin iron-(III) dicyanide.

The qualitative aspects of the observed stereospecific intermolecular relaxation are found to be the same in all complexes with electron-withdrawing substituents at the 2,4 position.[7,8] The dibromo complex was chosen for detailed study because its thermodynamics of dimerization could be characterized most readily,[8] its proton spectrum is the best resolved in the critical methyl region,[7] permitting accurate T_1 determinations, and the absence of protons in the 2,4 substituents permits the resolution of all nonequivalent protons in the complex over the widest range of temperature and concentration.

In addition to assessing the use of intermolecular dipolar relaxation as a solution structure tool for porphyrin dimers, we are interested in determining if the major interaction between the porphyrins involves the contact of the two π systems suggestive of π–π donor–acceptor interaction,[10] and whether the asymmetry characterized by the spread of the methyl contact shifts, as discussed in part 1 of this study,[7] plays a major role in controlling the stereospecificity of the π contacts.

Principles

The observation of concentration-dependent relaxation rates will yield data which can be used to determine relaxation rates in the pure dimer. For the system in rapid exchange on the NMR time scale (only one set of resonances was observed) between the monomer and dimer, the observed relaxation rates,

$R_{1,2} = T_{1,2}^{-1}$, are given by[11,12]

$$R_1 \text{ (obsd)} = f^M R_1^M = f^D R_1^D \qquad (1)$$

$$R_2 \text{ (obsd)} = f^M R_2^M + f^D R_2^D$$
$$+ (f^M)^2 (f^D)^2 (\Delta^2 \omega_{MD}) (\tau_M + \tau_D) \qquad (2)$$

where f^M and f^D, R_1^M and R_1^D, R_2^M and R_2^D, τ_M and τ_D, and $\Delta\omega_{MD}$ are the fractional populations, longitudinal relaxation rates, transverse relaxation rates, lifetimes, and difference in chemical shifts of the monomer and dimer, respectively. R_2 (obsd) is not necessarily a weighted average like R_1 (obsd) but may have an additional exchange broadening term dependent on the square of the chemical shift difference. This renders R_2 (obsd) only qualitatively useful (vide infra) for a structure determination. Hence, R_1 (obsd) will be used for the quantitative determination of the dimer structure.

The intramolecular relaxation in the monomer is the sum of a contact contribution and a dipolar contribution:[12]

$$R_1^M = R_{1,con}^{M,intra} + R_{1,dip}^{M,intra} \text{ with} \qquad (3)$$

$$R_{1,con}^{M,intra} = BA^2 f(\tau_c) \qquad (4a)$$

$$R_{1,dip}^{M,intra} = Cr^{-6} f'(\tau_c) \qquad (4b)$$

where $B = 2S(S + 1)/3\hbar^2$, $C = 2S(S + 1)\gamma_N^2 g^2 \beta^2 / 15$, A is the contact coupling constant, r is the intramolecular Fe–H distance, and $f(\tau_c)$ and $f'(\tau_c)$ are functions of the correlation time, τ_c. Similar equations hold for R_2 relaxation.

For the dimer, similar relaxation expressions would describe the intramolecular relaxation, $R_1^{D,intra} = R_{1,con}^{D,intra} + R_{1,dip}^{D,intra}$, except that the correlation time, τ_c', may be different from that of the monomer. In addition the second iron would produce an *inter*molecular dipolar contribution given by[4,12]

$$R_{1,dip}^D = Cr_1^{-6} f'(\tau_c') \qquad (4c)$$

where r_1 is the intermolecular Fe–H distance. Knowledge of both the intramolecular and intermolecular dipolar contributions makes possible the determination of r_1, since

$$R_{1,dip}^{D,inter} / R_{1,dip}^{D,intra} = r_1^{-6} / r^{-6} \qquad (5)$$

where r can be determined from known X-ray crystal structures of monomeric metalloporphyrins.[13]

Experimental Section

2,4-Dibromodeuteroporphyrin iron(III) chloride and the dimethyl ester derivative were synthesized and the cyanide complexes, 2,4-dibromodeuteroporphyrin iron(III) dicyanide (2,4-B_2DC) and 2,4-dibromodeuteroporphyrin dimethyl ester iron(III) dicyanide (2,4-B_2DEC), were prepared[7] in $C^2H_3O^2H$. The ^1H NMR spectra have the same ionic strength dependence with LiCl and KCN.[8] Hence the ionic strength was maintained at 0.33 M at all porphyrin concentrations with excess KCN.

^1H NMR spectra (100 MHz) were obtained on a JEOL PFT-100 pulsed FT NMR spectrometer as described previously,[7] and 270-MHz spectra were recorded on a Bruker WH-270 FT NMR spectrometer, using 16K points over a 7-kHz bandwidth. Temperature was maintained with a JEOL-JNM-VT-3C variable temperature control unit and measured using the chemical shift difference of the resonances of a standard methanol sample using calibration curves of Van Geet.[14] Relaxation rates, $R_1 = T_1^{-1}$, were measured using a standard 180°-τ-90° inversion recovery experiment[15] where τ is the delay time between the 180° and 90° pulses.

Results

Although the NMR spectra of 2,4-B_2DC in $C^2H_3O^2H$ at 25 °C are concentration independent, below −40 °C the NMR spectra exhibit large concentration-dependent line widths and chemical shifts as illustrated in Figure 1 by the 100-MHz ^1H NMR trace of 2,4-B_2DC at −65 °C at 0.0012 M, A, and 0.035 M, B. The insert in B illustrates the meso-H region at 0.035 M at 270 MHz. Figure 1 clearly shows that 8-CH₃ and 1-CH₃
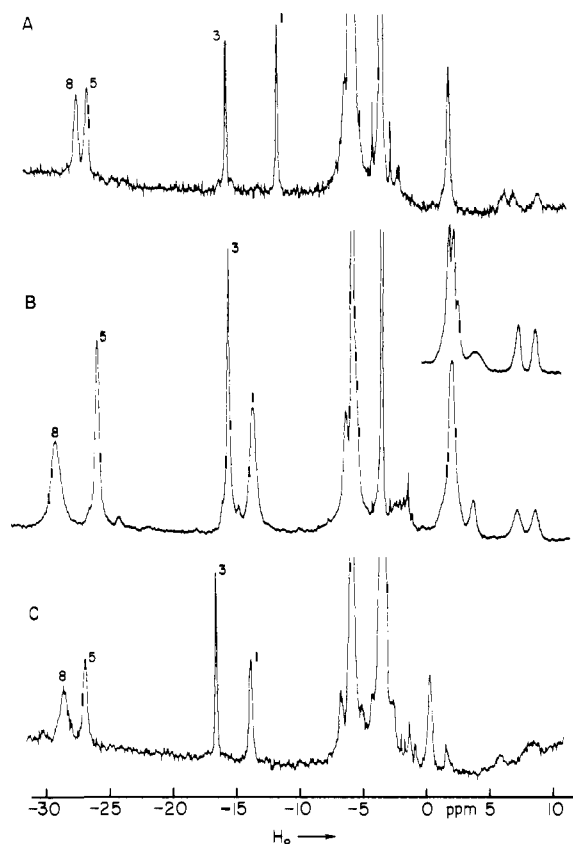

Figure 1. 100-MHz ^1H NMR spectra in $C^2H_3O^2H$ at −65 °C: A, 0.0012 M 2,4-B_2DC; B, 0.035 M 2,4-B_2DC; C, 0.0015 M 2,4-B_2DEC. Insert in B is a 270-MHz expansion of the meso-H region of 2,4-B_2DC.

exhibit dramatic line-width increases as concentration increases, while 5-CH₃ and 3-CH₃ exhibit insignificant line-width changes. Moreover, 8-CH₃, 1-CH₃, and δ-meso-H have been shown to exhibit the largest concentration-dependent shifts.[8] Included in Figure 1 is the spectrum of 0.0012 M 2,4-B_2DEC, C, at 100 MHz, illustrating that the ester complex dimerizes in a manner similar to the acid complex.

Figure 2 shows the methyl region of 0.0012 M, A, and 0.035 M, B, 2,4-B_2DC as a function of the delay time, τ, in a 180°-τ-90° inversion recovery experiment at −62 °C. A plot of ln $(A_\infty - A_\tau)$ vs. τ, where A_τ is the resonance height at time τ, should yield a straight line with a slope[15] of $-R_1$ as given in Figure 3A,B. In Figure 4 we plot ln R_1 vs. reciprocal temperature for 0.0012 M, A, and 0.035 M, B, 2,4-B_2DC.

Discussion

Monomer Relaxation. Thermodynamic studies[8] have shown that at 0.0012 M, essentially only monomer exists in solution for 2,4-B_2DC; thus

$$R_1(0.0012 \text{ M}) = R_1^M \qquad (6)$$

The plot of ln $(A_\infty - A_\tau)$ vs. τ for the monomer, as illustrated in Figure 3A, yields the T_1 values for the methyl resonances. Since electron relaxation in the low-spin ferric porphyrin complexes is very fast ($\sim 10^{-13}$ s),[9] $f(\tau_c) \sim 10\tau_{1e}$,[12] where τ_{1e} is the electron longitudinal relaxation. τ_{1e} can be expressed by[16]

$$\tau_{1e} \sim \tau_e^\circ e^{-V/kT} \qquad (7)$$

where V would be the activation energy for the physical motion governing the electron relaxation. Thus a plot of ln R_1 vs. T^{-1} should yield a straight line with slope $-V/k$. as illustrated in Figure 4A for 0.0012 M 2,4-B_2DC. Since the slopes for all four
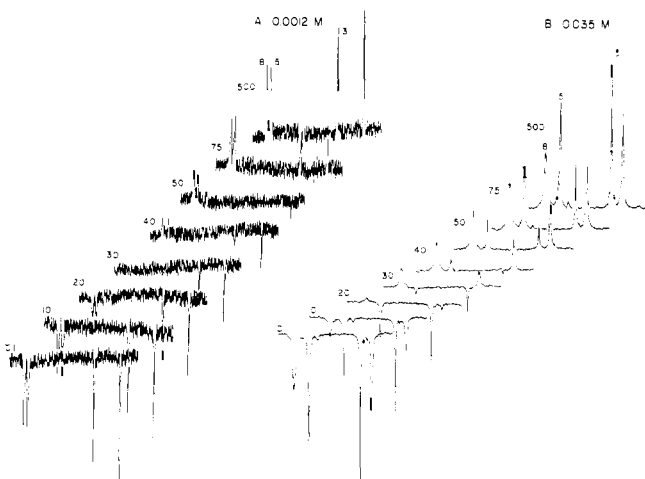
Figure 2. 100-MHz ^{1}H NMR spectra of 2,4-B$_2$DC in C^{2}H$_3$O^{2}H at −62 °C as a function of τ in a 180°-τ-90° inversion recovery experiment: A, 0.0012 M; B, 0.035 M.

Figure 4. Plot of ln R_1 vs. T^{-1} for 2,4-B$_2$DC: A, 0.0012 M; B, 0.035 M; $\triangle$, 1-CH$_3$; $\square$, 3-CH$_3$; O, 5-CH$_3$; $\diamond$, 8-CH$_3$.
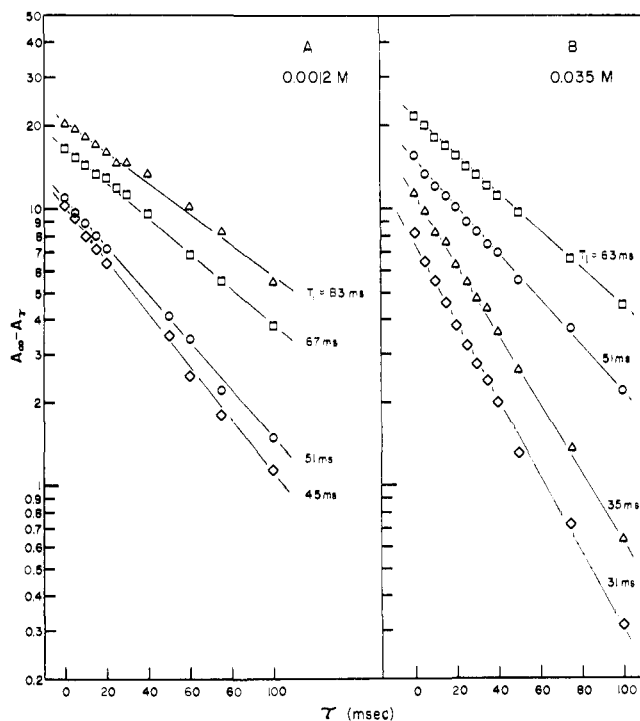
Figure 3. Plot of ln $(A_\infty - A_\tau)$ vs. τ at −62 °C for 2,4-B$_2$DC: A, 0.0012 M; B, 0.035 M; $\triangle$, 1-CH$_3$; $\square$, 3-CH$_3$; O, 5-CH$_3$; $\diamond$, 8-CH$_3$.

methyl resonances are identical, i.e., identical V, their relaxation must be controlled by the same process, as expected for a monomer species. Figures 2A and 3A illustrate that the methyl R_1^M's and line widths have similar behavior, with R_1^M's and line widths increasing with increasing downfield shift.[7] An earlier study[7] of 2,4-substituted deuteroporphyrin iron(III) dicyanide complexes showed that the relaxation is predominantly dipolar for methyl resonances whose chemical shift is upfield of −15 ppm. Thus R_1^M(1-CH$_3$) is essentially completely dipolar in nature, and since r^{-6} (X-CH$_3$) is independent of X, we thus have

$$R_{1,dip}^{M,intra} \text{ (X-CH}_3) = R_1^M(1\text{-CH}_3) \quad \text{where X} = 3, 5, 8 \quad (8)$$

Additional relaxation of the 3,5,8-CH$_3$ resonances is due necessarily to a contact contribution[7,12] ($\propto A^2$) which will increase with increasing overall downfield shift.
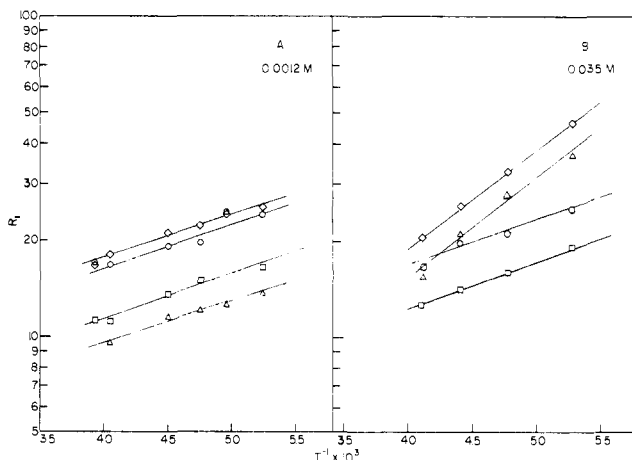
Dimer Relaxation. Examination of Figure 3, illustrating ln $(A_\infty - A_\tau)$ vs. τ, shows that 5-CH$_3$ and 3-CH$_3$ have similar T_1's at both 0.0012 and 0.035 M, whereas the T_1's for 8-CH$_3$ and 1-CH$_3$ have decreased substantially going from 0.0012 to 0.035 M. Moreover, the T^{-1} dependence of the observed ln R_1 at 0.035 M, as illustrated in Figure 4B, shows that 5-CH$_3$ and 3-CH$_3$ have identical slopes which are unchanged from the values at 0.0012 M. The data in both Figures 3 and 4 thus indicate that 5-CH$_3$ and 3-CH$_3$ experience solely intramolecular relaxation in the dimer, i.e.

$$R_1^D(\text{X-CH}_3) = R_1^{D,intra} (\text{X-CH}_3) \qquad \text{where X} = 5,3$$

Figure 4 also shows that the T^{-1} dependences of 3-CH$_3$ and 5-CH$_3$ at 0.035 and 0.0012 M have identical slopes though the lines at 0.035 M are ~10% higher at all temperatures. This is probably due to differences in τ_0 (eq 7) for the monomer and dimer and would affect all four methyl groups identically. It can be taken into consideration for 8-CH$_3$ and 1-CH$_3$ by scaling to 3-CH$_3$ via

$$R_1^{D,intra} (\text{X-CH}_3) = R_1^M(\text{X-CH}_3) \frac{R_1^{D,intra}(3\text{-CH}_3)}{R_1^M(3\text{-CH}_3)} \quad (9)$$

$$X = 8,1$$

Since the scalar contribution to $R_1^{D,intra}$ (1-CH$_3$) is negligible, as found in the monomer (eq 8), we have

$$R_1^{D,intra} (1\text{-CH}_3) = R_{1,dip}^{D,intra} \quad (10)$$

Unlike 5-CH$_3$ and 3-CH$_3$, the slopes of the ln R_1 vs. T^{-1} plots for 8-CH$_3$ and 1-CH$_3$ have increased substantially at 0.035 M owing to an additional relaxation contribution whose effect increases with decreasing temperature (i.e., increasing extent of dimerization). However, a quantitative expression for the dimer relaxation of 8-CH$_3$ and 1-CH$_3$ cannot be made until a qualitative picture of the dimer is obtained.

Figures 2 and 3 illustrate that the resonance line widths parallel the R_1's, with the narrowest resonance having the smallest R_1 and the broadest resonance having the largest R_1.[7] Hence line widths can be utilized for a qualitative determination of the structure.[17]

Dimer Structure Determination. Qualitative Aspects. Coordination of heme substituents to the iron atoms as the mode of dimer formation[18] can be eliminated since the axial cyanide ligands remain coordinated at all times.[19] Participation of the carboxylate groups can also be ruled out since 2,4-B$_2$DEC dimerizes in an identical manner as 2,4-B$_2$DC as illustrated in C of Figure 1, with the 1,8-CH$_3$ again narrowing as concentration decreases.
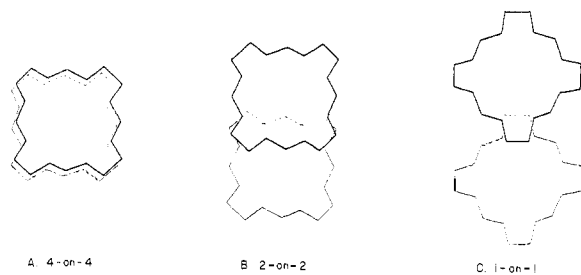
Figure 5. Limiting types of π-π porphyrin dimers: A, 4 on 4 overlap; B, 2 on 2 overlap; C, 1 on 1 overlap.

Figure 6. Schematic of 2,4-B_2DC dimer giving distances and parameters relevant to the solution dimer structure.

Using the line widths, $\delta_{1/2} \propto r^{-6}$, a qualitative picture of the porphyrin–porphyrin interaction within the dimer can be obtained. Three limiting types of porphyrin interactions are illustrated in Figure 5. A is complete overlap (4 on 4) of the porphyrins, B is overlap of 2 pyrroles (2 on 2) of each porphyrin, and C is overlap of 1 pyrrole (1 on 1) of each porphyrin.

The 4 on 4 dimer, A, can be eliminated since all methyl groups would be equidistant from the second iron atom and would exhibit identical line width increases from the intermolecular relaxation. 8-CH_3 and 1-CH_3 must be close to a second iron while 5-CH_3 and 3-CH_3 are far from a second iron. This occurs with porphyrin overlap of pyrroles I and IV as illustrated by the two interactions in Figures 5B,C. The 2 on 2 dimer, B, can be eliminated since the δ-meso-H would always be closest to the second iron and would exhibit line width or R_1 increases ~two times that observed for 8-CH_3 and 1-CH_3. The 100-MHz spectrum at 0.035 M (Figure 1) clearly shows no increase in line widths of any of the meso-H resonances at conditions where 8-CH_3 and 1-CH_3 exhibit substantial line width of R_1 increases. Thus any meso H must be farther from the second iron than both 8-CH_3 and 1-CH_3.[21] This leaves the most stereospecific dimer structure, C, involving overlap of pyrrole I of one porphyrin and pyrrole IV of the other porphyrin in the dimer.

Quantitative Aspects. For the 1 on 1 overlap dimer, $R_1{}^D$ for 8-CH_3 or 1-CH_3 is

$$R_1{}^D = \frac{1}{2}R_{1,dip}^{D,inter} + R_{1,dip}^{D,intra} + R_{1,con}^{D,intra} \qquad (11)$$

The $\frac{1}{2}$ factor arises because each dimer has two 8-CH_3's and two 1-CH_3's, with only one of each pair close to the second iron. These two types of methyls are in rapid exchange. All methyls on pyrroles not in contact in the dimer experience negligible intermolecular relaxation.

Substituting $R_1{}^D$ into eq 1 and defining $R_1(obsd) = R_1(0.035 \text{ M})$, we obtain

$$R_{1,dip}^{D,inter}(X\text{-}CH_3) = \frac{2}{f^D}R_1^{obsd}(X\text{-}CH_3) - \frac{2f^M}{f^D}R_1^M(X\text{-}CH_3)$$
$$-2R_{1,dip}^{D,intra}(X\text{-}CH_3) - 2R_{1,con}^{D,intra}(X\text{-}CH_3) \qquad (12)$$

where X = 8,1.

Figure 6 represents the dimer with relevant distances labeled. In the temperature range -60 to -70 °C, K ranges from 38 to 52 L mol^{-1}.[8] Published X-ray structure gives $r(8) = r(1) = 6.1$ Å.[13] Equations 5, 10, and 11 yield $r_1(1) = 4.8 \pm 0.2$ Å and $r_1(8) = 5.2 \pm 0.4$ Å for the above temperature range.[21] Hence the limit of interplanar separation is $\gtrsim 5$ Å. These are the only quantitative data that can be calculated. The angle between the $r_1(8)$-$r(1)$ plane and the $r_1(1)$-$r(8)$ plane cannot be determined from presently available data. Thus all other determinations require qualitative consideration of the known monomer structure and van der Waals radii.

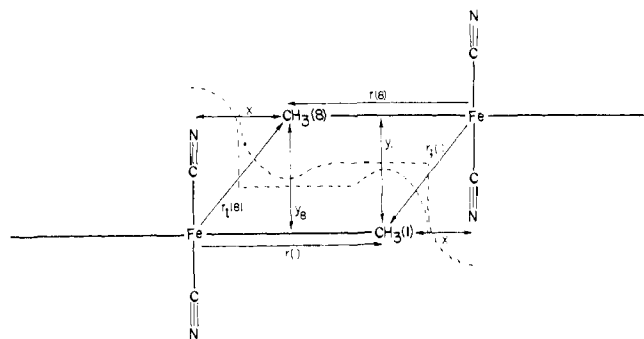Intermolecular steric interactions between coordinated cyanide and methyls require an interplanar spacing less than either $r_1(1)$ or $r_1(8)$. Consideration of van der Waals contacts[22] dictates that x in Figure 6 be ≥ 3.0 Å, yielding $y_8 \leq 4.2 \pm 0.5$, $y_1 \leq 3.7 \pm 0.3$ Å for an average interplanar spacing ≤ 4 Å.[23] The intermolecular interaction between cyanide and a methyl cannot be solvent separated since this requires $x > 5$ Å and would impose $y_8, y_1 < 1$ Å, which is less than the minimum van der Waals contact of the porphyrins π planes (~3.5–3.6 Å).[22] Assuming that the porphyrin core can be represented by a disk 15 Å in diameter and 3.5 Å thick (van der Waals radii), the limitations imposed by y_1 and y_8 dictate that the maximum angle between the π planes is 7°. The overlap of pyrroles I and IV is approximately 50% and may account for the low temperatures required to stabilize the dimer.

Thus the present study demonstrates that intermolecular paramagnetic dipolar relaxation can be usefully employed for elucidating the structure of porphyrin aggregates in solution. This method is particularly useful for the iron porphyrins since all but one of the oxidation/spin states are paramagnetic and only one exhibits a resolved solution ESR spectrum.

The interplanar separation of ≤ 4.0 Å is consistent with spacings of π-π complexes as determined by ESR of dimeric cupric and vanadyl porphyrins (3.4–4.4 Å)[3] and X-ray structure of 2,4-diacetyldeuteroporphyrin dimethyl ester nickel(II) (~3.5 Å).[25] The dominant role of π-π interaction is also emphasized by the observation that the dimer structure is essentially unaltered upon esterification of the acid side chains[26] (i.e., compare B and C in Figure 1). The overlap of pyrroles I and IV supports a donor/acceptor stabilizing interaction in the formation of the dimer as suggested by the analysis of the methyl contact shifts, with pyrrole I as the acceptor and pyrrole IV as the donor.[7] Although all four pyrroles could participate in a donor/acceptor interaction, only one dimer structure could be detected. With a limit of 5% for the population of a second dimer structure involving other pyrroles, at least 1 kcal/mol difference in ΔH for the predominant structure and any secondary structures must exist.[27]

Since the strength of a donor/acceptor interaction is dependent on the relative donor and/or acceptor abilities[10] of the moieties in a complex, the dimerization thermodynamics and degree of stereospecificity may be expected to be dependent on the 2,4 substituents which can change the π-cloud electron distribution. This suggestion is supported in part 3[8] which investigates the thermodynamics of dimerization.

Dimer and Monomer Lifetimes. The observation of magnetic field dependent line widths of 1-CH_3 and 8-CH_3[28] and δ-meso-H can provide information on the kinetics of monomer–dimer exchange. From Figure 1 the δ-meso-H at 100 MHz has the same line width as the other meso H's. However, at 270 MHz δ-meso-H exhibits substantially increased line width relative to the other meso-H signals. Since the relative $\Delta\omega_{MD}$ for meso H are[8] α:β:δ 1:2:5.4, δ-meso-H would have $\geq$seven times greater exchange broadening than any other meso H.

Thus the difference in δ-meso-H line width and any other meso is proportional to $\tau_M + \tau_D$ (eq 2). At -70 °C, $K = 51.5$ L mol^{-1}, $\Delta\omega = 7.89 \times 10^3$ rad s^{-1}, $\Delta\delta_{1/2} = 90$ Hz, yielding $\tau_M = 2.4 \times 10^{-7}$ s, $\tau_D = 1.2 \times 10^{-5}$ s. These lifetimes are consistent with lifetimes determined for other porphyrin dimers[29] (10^{-4}–10^{-8} s).

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(19) Cyanide is in slow exchange at 25 °C (H. Goff, *J. Am. Chem. Soc.*, **99**, 7723–7725 (1977)) and hence is in slow exchange at lower temperatures. Monocyanide complexes exhibit NMR spectra distinct from those of the dicyanide complexes and are easily identified. No monocyanide species were noted in these studies.
(20) The 1 on 1 pyrrole overlap (C) places the closest meso H at least twice as far from the iron as either 1- or 8-CH$_3$, indicating an intermolecular dipolar relaxation contribution to any meso H of ≤0.03 of that of 1,8-CH$_3$.
(21) At higher temperatures, the fraction of dimer, f^D, is so small that the calculation of intermolecular relaxation rates is the small difference between two large numbers which has very large uncertainties. Analysis of data at lower temperatures is precluded owing to severe overlap of methyl resonances which interferes with T_1 and T_2 determinations. Higher field strengths were of little value in improving resolution owing to the increasing contribution of chemical exchange to the line widths.
(22) The following van der Waals radii were used: aromatic C, 1.5–1.6 Å; methyl group, 1.5–2.0 Å; and bromine, 2.0 Å.
(23) The analysis assumes that the magnetic moment of 2,4-B$_2$DC is isotropic. However, 2,4-B$_2$DC has approximate axial symmetry and the relaxation must be described by expressions derived by H Sternlicht, *J. Chem. Phys.*, **42**, 2250–2251 (1965). However, assuming a moderate axial g tensor anisotropy for these complexes in methanol (G. N. La Mar, J. Del Gaudio, and J. S. Frye, *Biochem. Biophys. Acta*, **498**, 422 (1977)), use of the Sternlicht equation resulted in less than 3% changes in the computed r_i. Hence anisotropic effects in the relaxation are negligible.
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(27) All other complexes exhibit signs of decreased stereospecificity with 2,4-A$_2$DC exhibiting evidence of a second dimer structure involving pyrrole II below -50 °C (see ref 8).
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NMR Studies of Low-Spin Ferric Complexes of Natural Porphyrin Derivatives. 3. Thermodynamics of Dimerization and the Influence of Substituents on Dimer Structure and Stability

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Abstract: The low-temperature ^{1}H NMR spectra of 2,4-disubstituted deuteroporphyrin iron(III) dicyanide complexes in methanol exhibit concentration-dependent chemical shifts and line widths. Computer analysis of the dilution shifts shows they are consistent with exclusively a monomer–dimer equilibrium. Thermodynamic parameters for the dimerization of the 2,4-dibromo complex are consistent with an associative process with $\Delta H° = 3.4$ kcal/mol and $\Delta S° = -8.9$ eu. The ionic strength and solvent dependence of the extent of dimerization are similar to that observed for other porphyrin aggregations and support a π–π interaction. As the 2,4 substituent becomes more electron withdrawing and the unpaired electron spin distribution becomes more asymmetric, the extent of dimerization increases. Since overlap involves pyrroles having the greatest difference in unpaired electron spin density, this suggests a π donor–acceptor interaction as contributing to the stability of the dimer. The properties of the electronic asymmetry of protoporphyrin suggest that the asymmetry may play an important role in the stability of the heme–apoprotein interactions.

Introduction

The interest in π–π interactions of porphyrins stems from the possible roles of such interactions in the stabilization and function of hemoproteins.[1] Changes in these π contacts have also been suggested as a possible trigger in the cooperative O_2 binding of hemoglobin.[2] Porphyrins readily form π–π complexes with organic aromatic molecules[2] and other porphyrins