Aryl Ring Rotation in Porphyrins. A Carbon-13 NMR Spin−Lattice Relaxation Time Study

Lori Noss, Paul A. Liddell, Ana L. Moore,* Thomas A. Moore,* and Devens Gust*

Center for the Study of Early Events in Photosynthesis, Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287-1604

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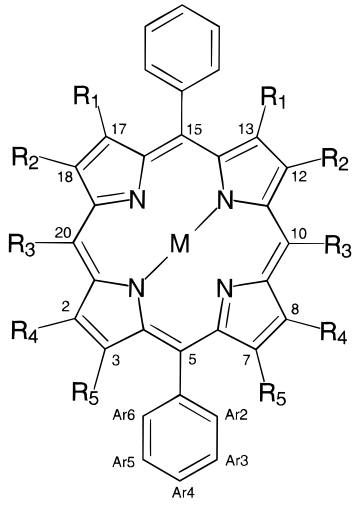
Overall tumbling and internal rotational motions in porphyrins bearing *meso* aryl substituents and, in some cases, flanking alkyl groups at the β-pyrrolic positions have been determined using ^{13}C spin−lattice relaxation time measurements. In deuteriochloroform solution at 303 K, the overall reorientation of all three porphyrins investigated occurs with diffusion coefficients of $\sim 1 \times 10^9$ s^{-1}. In porphyrins with only hydrogen at the β-pyrrolic positions, the *meso* phenyl rings undergo rotations about their single bonds to the porphyrin with diffusion coefficients of $\sim 4 \times 10^9$ s^{-1}. Introduction of methyl substituents at the β-pyrrolic positions adjacent to the phenyl rings reduces these motions, but only to $\sim 1 \times 10^9$ s^{-1}. Thus, significant internal motions are present in both types of molecules. These motions occur on the time scale of many photoinduced electron and energy transfer processes in porphyrins covalently linked to electron or energy donors or acceptors through *meso* aryl groups. Thus, the internal librational motions may affect rates of photoinduced electron and energy transfer, even in relatively "rigid" molecular constructs.

Introduction

Synthetic *meso*-polyarylporphyrins are important constituents of many molecular and supramolecular model systems for photosynthetic electron and energy transfer, where they stand in for naturally occurring porphyrins and chlorophylls found in reaction centers and other components of the photosynthetic apparatus.[1−8] The aryl groups of such porphyrins serve as convenient points of attachment for various electron or energy donor and acceptor moieties. The aryl rings serve a structural role by providing a linkage that separates the porphyrin chromophore from the π-electron systems of attached donors and acceptors. In most cases, they also mediate the actual transfer of electrons, triplet excitation energy, and sometimes singlet excitation energy[9] through a superexchange mechanism, which involves mixing of aryl bridge wave functions with those of the adjacent moieties.

The role of $\pi-\pi$ overlap between the porphyrin macrocyclic ring and the attached *meso* aryl groups has always been problematic. If the aryl rings of a *meso*-polyarylporphyrin such as **1** were coplanar with the macrocycle, then conjugation would be complete, and the aryl rings would be part of the porphyrin chromophore. For steric reasons, this is not the case. In the solid state, the dihedral angle between the plane of the porphyrin and the plane of the aryl group is usually between 60° and 90°.[10−14] Calculations[15] and NMR studies in solution[16,17] have estimated the angle to be about 45°. At angles between 0° and 90°, conjugation between the two π-electron systems would be partial. The angle of rotation of the aryl ring can affect energy and photoinduced electron transfer rates in several ways. In the equilibrium conformation, the angle will determine the degree of orbital overlap of the π-electrons, which in turn will affect the rate of transfer, because the rate is a function of the orbital overlap between the donor and the acceptor. In addition, rotational motions about the single bond joining the aryl group to the macrocycle will modulate the orbital overlap and could thus affect, or even determine, the rate of transfer. Finally, for donor or acceptor groups joined to the porphyrin through the aryl carbon atoms ortho or meta to the point of attachment, rotations can alter both the dihedral angles and the distances separating the various donor and acceptor moieties. Electron transfer rate constants can also depend strongly on these parameters. Thus, an understanding of the aryl rotational motions is crucial to understanding the electron and energy transfer processes.



1: $R_1 = R_2 = R_4 = R_5 = H$, $R_3 =$  , $M = H_2$

2: $R_1 = R_5 = CH_3$, $R_2 = R_4 = CH_2CH_3$, $R_3 = H$, $M = H_2$

3: $R_1 = R_2 = R_3 = H$, $R_4 = (CH_2)_5CH_3$, $R_5 = CH_3$, $M = Zn$

Numerous investigators have prepared photosynthetic model systems in which the *meso* aryl groups are flanked by methyl, ethyl, or other alkyl groups at the "β-pyrrolic" positions on the porphyrin periphery (cf. porphyrin **2**).[12−14,18−29] Molecular modeling and some X-ray crystal structure determinations suggest that the β-alkyl groups force the aryl rings into a position perpendicular to the (idealized) porphyrin plane. If this were the case, and if the rings do not deviate from that position, then

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TABLE 1: Selected Carbon-13 Chemical Shifts and Spin−Lattice Relaxation Times for Porphyrins 1−3 in Deuteriochloroform at 303 K

	porphyrin 1[a]		porphyrin 2		porphyrin 3	
carbon	δ (ppm)	T_1 (s)	δ (ppm)	T_1 (s)	δ (ppm)	T_1 (s)
2, 8	131.1	0.45 ± 0.03				
3, 7	131.1	0.45 ± 0.03				
10, 20			96.5	0.52±0.01	101.9	0.38 ± 0.02
12, 18	131.1	0.45 ± 0.03			131.9	0.40 ± 0.01
13, 17	131.1	0.45 ± 0.03			130.8	0.40 ± 0.01
5Ar2,6	134.6	0.72 ± 0.01	133.1	0.58 ± 0.01	133.4	0.48 ± 0.01
15Ar2,6	134.6	0.72 ± 0.01	133.1	0.58 ± 0.01	134.6	0.61 ± 0.01
5Ar3,5	126.7	0.72 ± 0.01	127.6	0.57 ± 0.01	127.6	0.46 ± 0.01
15Ar3,5	126.7	0.72 ± 0.01	127.6	0.57 ± 0.01	126.6	0.60 ± 0.01
5Ar4	127.7	0.46 ± 0.01	128.3	0.46 ± 0.01	128.3	0.39 ± 0.01
15Ar4	127.7	0.46 ± 0.01	128.3	0.46 ± 0.01	127.4	0.41 ± 0.01

[a] For porphyrin **1**, the chemical shifts and T_1 values for the carbon atoms of the phenyl groups at the 10- and 20-positions are identical to those reported for the corresponding carbon atoms of the phenyl rings at the 5- and 15-positions, for reasons of symmetry.

the porphyrin and its attached aryl rings would form a rigid molecular framework with no $\pi-\pi$ interaction between the rings and the macrocycle, and the question of π-delocalization onto the aryl rings would be settled.

Given the single bond joining an aryl ring to the macrocycle and the notorious flexibility of molecular species, the assumption of rigidity for porphyrins with β-alkyl groups is suspect. If aryl rotation does occur, and occurs on a time scale comparable to or faster than electron or energy transfer, then the ambiguities discussed above in connection with porphyrins such as **1** are also present in structures related to **2**.

Carbon-13 nuclear magnetic resonance spectroscopy can yield detailed information about overall and internal motions of molecules in solution. As will be discussed in detail below, dipole−dipole spin−lattice relaxation of a ^{13}C nucleus by a directly bonded hydrogen is a function of the time scale of reorientation of the internuclear vector with respect to the spectrometer magnetic field. Thus, motional information may be extracted from experimentally determined dipole−dipole spin−lattice relaxation times (T_1^{DD}). In this paper, we report the results of such investigations on *meso*-tetraphenylporphyrin **1** and porphyrins **2** and **3**, which feature alkyl groups that flank the phenyl rings.

Results and Discussion

Synthesis. Porphyrin **1** is a known compound. Compounds **2** and **3** were synthesized by an application of the MacDonald [2+2] condensation, as described in the Experimental Section.

Chemical Shift Assignments. The numbering system used to identify the various carbon atoms in the porphyrins is indicated on the structural drawing. The ^{1}H and ^{13}C NMR spectra were assigned by a combination of COSY, NOESY, HMQC, and one-dimensional experiments. The relevant ^{13}C chemical shifts appear in Table 1, and the ^{1}H NMR data are given in the Experimental Section.

^{13}C Spin−Lattice Relaxation Time Measurements. The T_1 measurements were made at 11.7 T in degassed deuteriochloroform solution at 303 ± 0.5 K. Measurements were repeated at least six times for each molecule. Compounds **1** and **2** were measured at 0.024 and 0.0092 M, and identical results were obtained at the two concentrations, within experimental error. The concentration for **3** was 0.0082 M. The inversion−recovery (*D*-180-*t*-90-FID) pulse sequence was employed (see Experimental Section). The T_1 values for the monoprotonated carbon atoms of **1**−**3** are reported in Table 1, along with the standard deviations in the measurements.

Theoretical Framework for Analysis. As the theoretical principles used to interpret the T_1 data have been thoroughly discussed in the literature, only a brief summary of the approach used here will be given. Following excitation, ^{13}C nuclei relax by interaction with local magnetic fields which have motional components at the Larmor frequency. Relaxation mechanisms that may be of importance for molecules such as **1**−**3** include dipole−dipole, spin rotation, chemical shift anisotropy, and scalar coupling. In practice, the dipole−dipole mechanism often dominates for carbon atoms directly bonded to hydrogen, and this has been shown to be the case for porphyrins such as **1**−**3** under the experimental conditions used in this study.[30] Relaxation arises from the interaction of the ^{13}C nuclear magnetization with that of an attached proton, modulated by molecular motions that change the orientation of the C−H internuclear vector relative to the external magnetic field provided by the spectrometer. Under these conditions, the dipole−dipole spin−lattice relaxation time, T_1^{DD}, for a ^{13}C nucleus is given[31] by eq 1,

$$1/T_1^{DD} = 0.1N\gamma_H^2\gamma_C^2\hbar^2 r^{-6}[J_0(\omega_H - \omega_C) + 3J_1(\omega_C) + 6J_2(\omega_H + \omega_C)] \quad (1)$$

where N is the number of directly attached hydrogens, γ_H and γ_C are the magnetogyric ratios of hydrogen and carbon, r is the internuclear distance, ω_H and ω_C are the Larmor frequencies of hydrogen and carbon, and the $J(\omega)$ are spectral density functions describing molecular reorientational motions.

For a rigid, isotropically rotating molecule, the spectral density functions in eq 1 may be expressed[31] according to eq 2. The

$$J_i(\omega) = \tau_c/(1 + \omega^2\tau_c^2) \quad (2)$$

molecular reorientation is given in terms of a single rotational correlation time τ_c, which is sometimes more conveniently expressed as the rotational diffusion constant D ($\tau_c = 1/6D$). For this situation, eq 1 becomes

$$1/T_1^{DD} = 0.1N\gamma_H^2\gamma_C^2\hbar^2 r^{-6}\left[\frac{\tau_c}{1 + (\omega_H - \omega_C)^2\tau_c^2} + \frac{3\tau_c}{1 + \omega_c^2\tau_c^2} + \frac{6\tau_c}{1 + (\omega_H + \omega_C)^2\tau_c^2}\right] \quad (3)$$

When the overall rotation of the molecule is isotropic, but internal rotations such as those around carbon−carbon single bonds also contribute to relaxation, the important motions include not only the tumbling of the molecule about its center of mass (D_0) but also rotations about single bonds joining the chain of atoms separating the carbon of interest from the center

TABLE 2: Calculated Isotropic Diffusion Coefficients for Porphyrins 1−3 in Deuteriochloroform at 303 K

	porphyrin **1**[a]		porphyrin **2**		porphyrin **3**	
carbon	D_0 (s^{-1})[b]	D_1 (s^{-1})	D_0 (s^{-1})[b]	D_1 (s^{-1})	D_0 (s^{-1})[b]	D_1 (s^{-1})
2, 8	1.4×10^9					
3, 7	1.4×10^9					
10, 20			1.7×10^9		1.2×10^9	
12, 18	1.4×10^9				1.2×10^9	
13, 17	1.4×10^9				1.2×10^9	
5Ar2,6	(1.5×10^9)	4.3×10^9	(1.5×10^9)	1.5×10^9	(1.2×10^9)	1.1×10^9
15Ar2,6	(1.5×10^9)	4.3×10^9	(1.5×10^9)	1.5×10^9	(1.2×10^9)	3.7×10^9
5Ar3,5	(1.5×10^9)	4.3×10^9	(1.5×10^9)	1.3×10^9	(1.2×10^9)	8.4×10^8
15Ar3,5	(1.5×10^9)	4.3×10^9	(1.5×10^9)	1.3×10^9	(1.2×10^9)	3.6×10^9
5Ar4	1.5×10^9		1.5×10^9		1.2×10^9	
15Ar4	1.5×10^9		1.5×10^9		1.3×10^9	

[a] For porphyrin **1**, the diffusion coefficients for the carbon atoms of the phenyl groups at the 10- and 20-positions are identical to those for the corresponding carbon atoms of the phenyl groups at the 5- and 15-positions, for reasons of symmetry. [b] D_0 values in parentheses are those used to calculate D_1 values for rotation about the single bond joining the phenyl ring to the macrocycle.

of mass. There are several models for treating the effects of such motions on relaxation. In this analysis, internal rotations will be considered as rotational diffusion motions about the bond axes.[31−34] In this case, the spectral densities are given by eq 4,

$$J_i(\omega) = \sum_{a,b,...x} |d_{ab}(\beta_a)|^2 |d_{bc}(\beta_b)|^2 \ldots |d_{nx}(\beta_n)|^2 |d_{x0}(\beta_x)|^2 \times [\tau/(1 + \omega^2\tau^2)] \quad (4)$$

where

$$\tau = (6D_0 + a^2D_a + b^2D_b + \ldots + x^2D_x)^{-1} \quad (5)$$

The $d_{ij}(\beta_i)$ are the reduced second-order Wigner rotation matrices,[32−34] the β_i are the angles between successive axes of rotation (i.e., bonds), and β_x is the angle between the final rotational (bond) axis and the C−H internuclear vector for the two nuclei in question. The D_i values are the diffusion constants for each of the single bonds about which internal rotation occurs, and D_0 is the diffusion coefficient for the overall isotropic motion. Symmetry considerations allow the 5 × 5 matrices that arise from a treatment using the Wigner rotation matrices to be replaced by 3 × 3 matrices.[32] The resulting spectral density functions are given[32−34] by

$$J_i(\omega) = \sum_{a,b,...x} B_{ab}B_{bc} \ldots B_{hx}B_{x0}\left[\frac{\tau}{1 + \omega^2\tau^2}\right] \quad (6)$$

where B_{ij} are elements of a 3 × 3 matrix and the sum is run from 0 to 2 over all the indexes.

An additional complication occurs when the motions of the molecule are no longer isotropic. A special case involves approximation of the overall molecular tumbling as that of an axially symmetric body such as an ellipsoid of revolution, with rotational diffusion constants $D_{||}$ (for rotation about the major axis) and $D_\perp$ (for rotation perpendicular to that axis). In this case, the spectral density functions are given[17] by eq 7, where

$$J_i(\omega) = \sin^4\beta\,\frac{\tau^2}{1 + \omega^2{\tau_2}^2} + \sin^2 2\beta\,\frac{\tau_1}{1 + \omega^2{\tau_1}^2} + \frac{1}{3}(3\cos^2\beta - 1)^2\,\frac{\tau_0}{1 + \omega^2{\tau_0}^2} \quad (7)$$

β is the angle between the major axis and the C−H vector. In this case, the correlation times are related to the diffusion constants by eqs 8−10.

$$\tau_2 = (2D_\perp + 4D_{||})^{-1} \quad (8)$$

$$\tau_1 = (5D_\perp + D_{||})^{-1} \quad (9)$$

$$\tau_0 = (6D_\perp)^{-1} \quad (10)$$

Porphyrins as Isotropic Rotors. The T_1 data for **1**−**3** were first interpreted in terms of eqs 3−6, which require that the molecule rotate isotropically about its center of mass. Under these conditions, the carbon−hydrogen bond vectors for all of the hydrogen-bearing carbon atoms on the periphery of the porphyrin macrocycle reorient with a diffusion coefficient D_0, the overall tumbling rate of the molecule, as the macrocyclic framework is assumed to be rigid. The same motions will relax the carbons at the 4-positions of the aryl rings attached to the macrocycle (Ar4), as internal oscillations of the phenyl groups about their single bonds will have no effect on this C−H bond vector. Application of the equations requires knowledge of the carbon−hydrogen bond lengths. We chose a value of 1.09 Å for all bond lengths, although strictly speaking these lengths cannot all be exactly equal. Equation 3 yielded the values for D_0 reported in Table 2.

Having obtained values for the rates of overall tumbling of the molecules, we went on to calculate the diffusion coefficients for rotations about the single bonds joining the phenyl rings to the porphyrin macrocycle (D_1) using eqs 3−6. These values can be extracted from the T_1 data for the Ar2,6 and Ar3,5 carbon atoms (Table 1), because these relaxation times are affected not only by overall tumbling of the molecule but also by internal rotational motions about the single bond in question. For each porphyrin, the D_0 values used in these calculations were the average of those found for the Ar4 carbons, because the carbon−hydrogen bond lengths for these carbons are expected to most closely approximate those for the Ar2,6 and Ar3,5 carbon atoms. The results appear in Table 2.

Porphyrins as Anisotropic Rotors. Using ^{113}Cd NMR spectroscopy, Ellis and co-workers have shown that for the pyridine complex of **1** metalated with cadmium the molecule does not tumble completely isotropically.[17] Rather, rotational diffusion about an axis through the center of the porphyrin and orthogonal to the porphyrin plane ($D_{||}$) occurs 3.2 ± 0.8 times faster than rotation perpendicular to this axis ($D_\perp$). Although this anisotropy is relatively small, we also analyzed the spin−lattice relaxation time results for **1**−**3** under these conditions using the equations discussed earlier. Values for $D_{||}$ (=3.2$D_\perp$) were calculated from the T_1 values for the Ar4 carbons and the carbon atoms rigidly fixed to the porphyrin skeleton, and the values obtained for the Ar4 carbons were used in the calculation

TABLE 3: Calculated Anisotropic Diffusion Coefficients for Porphyrins 1−3 in Deuteriochloroform at 303 K

	porphyrin **1**[a]			porphyrin **2**			porphyrin **3**		
carbon	$D_{\|}$ (s^{-1})[b]	$D_{\perp}$ (s^{-1})[b]	D_1 (s^{-1})	$D_{\|}$ (s^{-1})[b]	$D_{\perp}$ (s^{-1})[b]	D_1 (s^{-1})	$D_{\|}$ (s^{-1})[b]	$D_{\perp}$ (s^{-1})[b]	D_1 (s^{-1})
2, 8	2.4×10^9	7.4×10^8							
3, 7	2.4×10^9	7.4×10^8							
10, 20				2.9×10^9	8.9×10^8		1.9×10^9	5.9×10^8	
12, 18	2.4×10^9	7.4×10^8					2.0×10^9	6.3×10^8	
13, 17	2.4×10^9	7.4×10^8					2.0×10^9	6.2×10^8	
5Ar2,6	(2.4×10^9)	(7.6×10^8)	3.8×10^9	(2.5×10^9)	(7.7×10^8)	1.9×10^9	(2.0×10^9)	(6.4×10^8)	1.4×10^9
15Ar2,6	(2.4×10^9)	(7.6×10^8)	3.8×10^9	(2.5×10^9)	(7.7×10^8)	1.9×10^9	(2.0×10^9)	(6.4×10^8)	3.2×10^9
5Ar3,5	(2.4×10^9)	(7.6×10^8)	3.8×10^9	(2.5×10^9)	(7.7×10^8)	1.8×10^9	(2.0×10^9)	(6.4×10^8)	1.2×10^9
15Ar3,5	(2.4×10^9)	(7.6×10^8)	3.8×10^9	(2.5×10^9)	(7.7×10^8)	1.8×10^9	(2.0×10^9)	(6.4×10^8)	3.0×10^9
5Ar4	2.4×10^9	7.6×10^8		2.5×10^9	7.7×10^8		2.0×10^9	6.1×10^8	
15Ar4	2.4×10^9	7.6×10^8		2.5×10^9	7.7×10^8		2.0×10^9	6.6×10^8	

[a] For porphyrin **1**, the diffusion coefficients for the carbon atoms of the phenyl groups at the 10- and 20-positions are identical to those for the corresponding carbon atoms of the phenyl groups at the 5- and 15-positions, for reasons of symmetry. [b] $D_{\|}$ and $D_{\perp}$ values in parentheses are those used to calculate D_1 values for rotation about the single bond joining the phenyl ring to the macrocycle.

of D_1 values for the Ar2,6 and Ar3,5 carbon atoms. The results appear in Table 3.

Discussion

Isotropic Rotation. For porphyrin **1**, the T_1 values for the carbons of the porphyrin macrocycle bearing one hydrogen atom and for the carbons at the 4-positions of the aryl rings are identical, within experimental error, as expected for an isotropically rotating rigid body. The T_1 value for the Ar4 carbons yields an overall reorientation rate D_0 of 1.5×10^9 s^{-1}. In porphyrin **2**, the T_1 values for the Ar4 carbons yielded a D_0 value identical to that found for **1**, whereas the 10,20 carbons of **2** gave a slightly higher value (1.7×10^9 s^{-1}). In zinc porphyrin **3**, the two different Ar4 carbons and the three different sets of hydrogen-bearing carbons on the porphyrin macrocycle all had the same T_1 value within experimental error. The average D_0 value for **3** is 1.2×10^9 s^{-1}. Thus, the overall reorientational motions of porphyrins **1**−**3** are essentially identical. The isotropic D_0 values are very similar to that reported previously for the zinc analog of **1** (1.3×10^9 s^{-1}).[30]

Turning now to the librational motions about the single bonds joining the phenyl groups to the macrocycle, it is evident from the data in Table 1 that the T_1 values for the Ar2,6 and Ar3,5 carbon atoms of **1** are significantly greater than those for the Ar4 carbons and the proton-bearing carbons on the macrocycle. This indicates that the carbon−hydrogen internuclear vectors are reorienting relative to the external magnetic field not only due to overall tumbling of the molecule but also due to librations around the single bonds joining the phenyl groups to the macrocycle. The overall more rapid motions of these carbon−hydrogen bond vectors make dipole−dipole relaxation less efficient. The D_1 value for diffusion about the single bonds to the phenyl groups of **1** is 4.3×10^9 s^{-1}. This is very similar to the value of 2.9×10^9 s^{-1} found for the zinc analog of **1**[30] and the value of 2.2×10^9 s^{-1} determined for the pyridine adduct of the cadmium analog of **1**.[17]

Porphyrin **2** differs from **1** in that the two phenyl groups are flanked by methyl groups. Table 1 shows that even with the steric hindrance imposed by these groups, the T_1 values for the Ar2,6 and Ar3,5 carbon atoms are still significantly greater than those for the Ar4 and macrocyclic carbons. Thus, the flanking alkyl groups do not eliminate rapid rotational motions. Quantitatively, the average D_1 value for librations about the single bond of the phenyl group is 1.4×10^9 s^{-1} (Table 2). Thus, the steric hindrance reduces the librational motions by only a factor of about 3. The molecule is only slightly more "rigid" than the less hindered analog **1**.

In this connection, it is clear that the librational motions in question cannot be complete 360° rotations of the phenyl rings. As mentioned above, in porphyrins such as **1** the phenyl rings make angles of ∼45° or greater with the porphyrin macrocyclic plane in solution. The equilibrium angle is that which best balances repulsive forces due to steric interactions of the phenyl groups with the hydrogen atoms at the β-pyrrolic positions (which are minimized in the orthogonal conformation), attractive forces between these two regions, and conjugative interactions between the phenyl group and the macrocycle (which are maximized in a planar conformation).

Rotation from the equilibrium position into the plane is a high-energy process, for steric reasons. In metalated porphyrins, barriers to rotation of phenyl groups through the plane in the range 14−18 kcal/mol have been reported.[35,36] Motions that achieve this rotation are much too slow to affect carbon-13 relaxation. Thus, the librational motions of interest are those that move the plane of the phenyl ring through an arc centered at the orthogonal orientation. In the case of relatively unhindered porphyrins such as **1**, this arc must cover angles of roughly ±45° from the orthogonal conformation, and the calculated D_1 value represents oscillatory motion through this arc.

For porphyrins such as **2** that feature flanking alkyl groups, steric hindrance between these groups and the phenyl rings will constrict the size of this arc and thus decrease the D_1 value. In the case of **2**, this decrease is observed, but is relatively small. The data do not allow us to discriminate between a situation similar to **1**, where two conformational minima are located on either side of the orthogonal arrangement, and a single conformation with a minimum at the orthogonal orientation that undergoes rotational excursions on either side of this minimum.

An additional feature that may contribute to the facile rotation of the phenyl rings in **2** is distortion of the macrocycle from planarity. Porphyrins with large substituents at both the *meso* and β positions tend to distort significantly,[37−40] and this could lower the rotational barrier for the phenyl rings. For example, the macrocycle of the dication of **1**, which bears four protons instead of two on the central nitrogen atoms, is significantly distorted, with the pyrrole rings tilted at angles of ∼33° relative to the mean porphyrin plane.[41,42] In a closely related porphyrin dication, the barrier for rotation of the aryl rings through the mean porphyrin plane is reduced by 2.9 kcal/mol, relative to the free base form.[43]

In the case of zinc porphyrin **3,** it is clear from the T_1 data in Table 1 that the less hindered phenyl ring at position 15 undergoes librations about its bond to the macrocycle that are large enough to significantly increase the relaxation times of the Ar2,6 and Ar3,5 carbon atoms relative to those at Ar4 and on the macrocycle itself. Table 2 shows that this increase gives rise to a D_1 value of about 3.7×10^9 s^{-1}, which is slightly smaller than the corresponding value for **1.** In the case of the

more hindered phenyl ring at position 5, the average T_1 for the Ar2,6 and Ar3,5 carbon atoms is 0.47 s, whereas the T_1 for the corresponding Ar4 carbon is 0.39 s. Thus, there is detectable internal motion about the single bond linking the phenyl group at the 5-position to the macrocycle. The D_1 value for this motion is $\sim 1 \times 10^9$ s^{-1}, which is about one-quarter of the corresponding value for the less hindered phenyl group at the 15-position. Thus, the effect of alkyl group hindrance is comparable in zinc porphyrin **3** and free base porphyrins **1** and **2**.

The average diffusion constants of both the less and more hindered phenyl groups of **3** are slightly smaller for the zinc porphyrin than for comparable phenyl groups in the free base forms. This is likely due to a stiffening of the porphyrin skeleton resulting from introduction of the metal and/or changes in the degree of nonplanarity of the porphyrin skeleton.[35−40]

Anisotropic Rotation. Treating the porphyrins as anisotropic rotors with internal motions has very little effect on the calculated D_1 values for rotation of the phenyl rings (Table 3). Thus, the conclusions presented above for the isotropic case apply equally well to the anisotropic analysis.

Conclusions

These results show that the introduction of methyl groups at the β-pyrrolic positions flanking *meso* aryl substituents on porphyrin macrocycles results in steric hindrance to librational motions of the aryl groups around the single bonds joining them to the macrocycle. However, the effect is relatively small, and librational motions still occur at rates comparable to or greater than overall reorientation of the macrocycle. Diffusion constants for the oscillatory motions are $\sim 1 \times 10^9$ to 4×10^9 s^{-1}. Thus, the distribution of motional frequencies describing the librations is comparable to the rate constants for photoinduced electron transfer often observed in porphyrin-based electron donor−acceptor systems.[1−7] The observed D_1 values are substantially larger than rate constants for charge recombination in some of these systems and larger than some rates of triplet−triplet energy transfer from porphyrins to carotenoids or other acceptors.[9,44]

Because these librations necessarily modify the $\pi-\pi$ overlap between the macrocycle and the aryl rings, they may affect the rates of photoinduced electron or energy transfer when such transfer is mediated by the bonds of the covalent linkage joining the donor and acceptor. In addition, donors or acceptors linked to *meso* aryl rings through positions other than the 4-position will undergo changes in their angular relationship to the porphyrin macrocycle as a result of these oscillations and possibly changes in the distances separating them from other donor or acceptor moieties. Donor−acceptor systems based upon porphyrins bearing *meso* aryl rings flanked by alkyl groups are certainly more conformationally constrained than many other donor−acceptor species, and rotations of the aryl rings are more hindered than those of their counterparts that lack the flanking alkyl groups. However, even these molecules are far from being "rigid" in the same sense that rigidity is imparted by double bonds or some bicyclic systems.

The magnitude of the effect of these internal motions on electron and energy transfer rate constants will depend on the details of the system. In a companion study, it was found that introduction of methyl substituents at porphyrin β-pyrrolic positions adjacent to aryl rings bearing electron donor or acceptor groups reduces electron transfer rate constants by a factor of $\sim$1/5.[45]

Experimental Section

Synthesis. *Porphyrin **1** (5,10,15,20-tetraphenylporphyrin)* was purchased from Aldrich Chemical Co., treated with 2,3-dichloro-5,6-dicyanobenzoquinone to remove any chlorin impurity, and purified by chromatography before use.

*2,8,12,18-Tetraethyl-3,7,13,17-tetramethyl-5,15-diphenylporphyrin (**2**)* was prepared in 80% yield from benzaldehyde and bis(4-ethyl-3-methyl-2-pyrrolyl)methane using the method of Maruyama and co-workers:[46] ^{1}H NMR (300 MHz, $CDCl_3$) δ −2.41 (1H, br s, 2NH), 1.77 (12H, t, J = 8 Hz, 2-CH_3, 8-CH_3, 12-CH_3, 18-CH_3), 2.49 (12H, s, 3-CH_3, 7-CH_3, 13-CH_3, 17-CH_3), 4.02 (8H, q, J = 8 Hz, 2-CH_2, 8-CH_2, 12-CH_2, 18-CH_2), 7.73 (4H, m, 5Ar3,5-H, 15Ar3,5-H), 7.79 (2H, m, 5Ar4-H, 15Ar4-H), 8.07 (4H, d, J = 8 Hz, 5Ar2,6-H, 15Ar2,6-H), 10.23 (2H, s, 10-CH, 20-CH); MS (FAB) *m/z* 631.3778 (calcd for $(M+H)^+$, 631.3722); UV/vis (CH_2Cl_2) 408, 508, 540, 576, 628 nm.

*Benzyl Pyrrole-2-carboxylate (**4**).* A mixture of pyrrole-2-carboxylic acid (11.11 g, 0.10 mol), dimethylformamide (150 mL), and potassium carbonate (15.2 g, 0.11 mol) was stirred under a nitrogen atmosphere for 15 min. Benzyl bromide (14.3 mL, 0.12 mol) was added to the resulting suspension, and the mixture was stirred for 29 h. The reaction mixture was then poured into 400 mL of diethyl ether, washed five times with water, and washed once with aqueous sodium chloride. The organic layer was separated, the solvent was removed by distillation at reduced pressure, and the residue was recrystallized from a mixture of dichloromethane and hexane to yield pure **4**. The crude material remaining in the mother liquor was chromatographed on silica gel (hexane/ethyl acetate, 4:1) and combined with the recrystallized material to produce a total of 19.10 g (95% yield) of fibrous white crystalline **4**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.31 (2H, s, CH_2), 6.27 (1H, dd, J = 6.3, 2.5 Hz, 4-H), 6.96 (2H, m, 5-H, 3-H), 7.38 (5H, m, Ar-H), 9.17 (1H, br s, NH); MS *m/z* 201 (M^+).

*Benzyl 5-Formylpyrrole-2-carboxylate (**5**).* An 11.2 mL (0.12 mol) portion of $POCl_3$ was added dropwise to 23 mL (0.3 mol) of dimethylformamide at 5−10 °C under a nitrogen atmosphere. Stirring for 30 min produced the Vilsmeier reagent. A 12.07 g (0.06 mol) portion of **4** was dissolved in 250 mL of 1,2-dichloroethane, the solution was cooled to −20 °C, and the Vilsmeier reagent was added dropwise over 12−15 min. The reaction mixture was stirred at 0 °C for 3 h and then at room temperature for 27 h. Aqueous sodium bicarbonate was added, and the mixture was stirred for an additional 16 h. The organic layer was separated and washed with water, and the solvent was evaporated under reduced pressure. The residue was dissolved in 200 mL of diethyl ether and washed with water (×5) and aqueous sodium chloride solution. Drying the solution over $MgSO_4$ and filtering gave a clear yellow solution that was concentrated by evaporation at reduced pressure and chromatographed on silica gel (hexane/ethyl acetate/dichloromethane, 70:15:15) to yield 8.66 g of **5** (63% yield) and 4.54 g of benzyl 4-formylpyrrole-2-carboxylate (**6**) (33% yield): ^{1}H NMR of **5** (300 MHz, $CDCl_3$) δ 5.32 (2H, s, CH_2), 6.93 (2H, m, 3-H, 4-H), 7.36 (5H, m, Ar-H), 9.63 (1H, s, CHO), 9.86 (1H, br s, NH); MS *m/z* 229 (M^+); ^{1}H NMR of **6** (300 MHz, $CDCl_3$) δ 5.34 (2H, s, CH_2), 7.39 (5H, m, Ar-H), 7.56 (2H, m, 3-H, 5-H), 9.77 (1H, br s, NH), 9.85 (1H, s, CHO).

*Benzyl 5-(Hydroxymethylphenyl)pyrrole-2-carboxylate (**7**).* A solution of 11.5 g (0.05 mol) of **6** in 200 mL of tetrahydrofuran was cooled to 0 °C under a nitrogen atmosphere, and 50 mL (0.10 mol) of phenylmagnesium chloride (2M) in tetrahydrofuran was added dropwise over 10 min. The reaction mixture was stirred for 15 min at 0 °C and poured into a mixture of ice, citric acid, and dichloromethane. The mixture was stirred until the ice melted, the organic layer was separated, and the aqueous phase was extracted twice with dichloromethane. The combined

extracts were washed with water and aqueous sodium bicarbonate, and the resulting solution was dried over anhydrous sodium sulfate and filtered. Distillation of the solvent under vacuum gave 14.31 g of **7** as a pale yellow solid (93% yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.77 (1H, d, J = 4 Hz, OH), 5.27 (2H, s, CH_2), 5.87 (1H, d, J = 4 Hz, 4-CH), 5.96 (1H, dd, J = 3, 4 Hz, CH), 6.88 (1H, dd, J = 3, 4 Hz, 3-CH), 7.33 (10H, m, Ar2-H, Ar5-H), 9.47 (1H, br s, NH); MS *m/z* 307 (M^+).

*1,9-Bis(carbobenzoxy)-5-phenyldipyrromethane (**8**).* To a stirred mixture of **7** (3.10 g, 10.0 mmol) and **4** (2.1 g, 10.0 mmol) in 60 mL of dichloromethane under a nitrogen atmosphere was added 1.90 g (10.0 mmol) of *p*-toluenesulfonic acid. After stirring the mixture for 30 min, it was diluted with dichloromethane, washed with water, washed with aqueous sodium bicarbonate, and dried over anhydrous sodium sulfate. The solvent was removed from the resulting solution by distillation at reduced pressure, and the residue was chromatographed on silica gel (hexane/ethyl acetate, 83:17) to give 4.25 g of **8** (87% yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.19 (4H, s, 1-CO_2CH_2, 9-CO_2CH_2), 5.46 (1H, s, 5-CH), 5.88 (2H, m, 2-H, 8-H or 3-H, 7-H), 6.80 (2H, m, 3-H, 7-H or 2-H, 8-H), 7.34 (15H, m, Ar-H), 9.77 (2H, br s, NH); MS *m/z* 490 (M^+).

*5-Phenyldipyrromethane (**9**).* A mixture of **8** (5.00 g, 10.2 mmol) and 0.5 g of 10% palladium on carbon in 100 mL of tetrahydrofuran was stirred under an atmosphere of hydrogen for 14 h. The catalyst was removed by filtration through Celite, and the filtrate was concentrated by evaporation of the solvent under reduced pressure. The resulting solid was dissolved in a solution of sodium hydroxide (8.2 g, 0.2 mol) in 100 mL of ethylene glycol, and the solution was heated at 185 °C under a nitrogen atmosphere for 1 h. The cooled solution was mixed with toluene and water, and the aqueous phase was extracted with toluene four times. The combined organic extracts were washed with aqueous sodium chloride, and the toluene was distilled at reduced pressure to produce **9**, which was used in later reactions without further purification: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.47 (1H, s, 5-H), 5.93 (2H, m, 1-H, 9-H or 3-H, 7-H), 6.17 (2H, m, 2-H, 8-H), 6.70 (2H, m, 3-H, 7-H or 1-H, 9-H), 7.28 (5H, m, Ar-H), 7.91 (2H, br s, NH); MS *m/z* 222 (M^+).

*Ethyl 3,5-Dimethyl-4-(1-hexenyl)pyrrole-2-carboxylate (**10**).* A 120 mL portion (0.24 mol) of pentylmagnesium bromide in diethyl ether was added dropwise to a solution of 20 g (0.10 mol) of ethyl 3,5-dimethyl-4-formylpyrrole-2-carboxylate in 250 mL of tetrahydrofuran under a nitrogen atmosphere and cooled in an ice bath. When addition was complete, the mixture was stirred at ambient temperature for 30 min and poured over ice. The layers were separated, and the aqueous layer was extracted four times with 120 mL portions of diethyl ether. The solvent was distilled from the combined extracts at reduced pressure to yield crude ethyl 3,5-dimethyl-4-(1-hydroxyhexyl)pyrrole-2-carboxylate, which was dissolved in 250 mL of dichloromethane. This solution was mixed with 150 mL of 3 M hydrochloric acid and stirred for 25 min. The organic layer was separated, and the aqueous phase was washed twice with 100 mL portions of dichloromethane. The combined organic extracts were washed with aqueous sodium bicarbonate, dried over anhydrous sodium sulfate, and filtered. Evaporation of the solvent at reduced pressure yielded a pale yellow solid, which was recrystallized from methanol to give **10** in 91% yield: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.93 (3H, t, J = 7 Hz, 6′-CH_3), 1.35 (3H, t, J = 7 Hz, 2-CH_3), 1.42 (4H, m, 4′-CH_2, 5′-CH_2 or 3′-CH_2), 2.19 (2H, m, 3′-CH_2 or 4′-CH_2 or 5′-CH_2), 2.29 (3H, s, 5-CH_3 or 3-CH_3), 2.36 (3H, s, 3-CH_3 or 5-CH_3), 4.30 (2H, q, J = 7 Hz, CO_2CH_2), 5.74 (1H, td, J = 16.5, 7 Hz, 2′-H), 6.21 (1H, dd, J = 16.5, 1 Hz, 1′-CH), 8.68 (1H, br s, NH); MS *m/z* 249 (M^+).

*Ethyl 3,5-Dimethyl-4-hexylpyrrole-2-carboxylate (**11**).* A mixture of **10** (5.0 g, 20 mmol) and 0.50 g of 5% palladium on carbon in 80 mL of ethyl acetate was stirred under 50 psi of hydrogen for 24 h. The catalyst was removed by filtration and washed with dichloromethane/methanol (9:1). The solvent was distilled from the combined filtrates at reduced pressure to give **11** (5.0 g, 99% yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (3H, t, J = 7 Hz, 6′-CH_3), 1.29 (3H, m, 2-CH_3), 1.37 (8H, m, 2′-CH_2 3′-CH_2 4′-CH_2 5′-CH_2), 2.19 (3H, s, 5-CH_3 or 3CH_3), 2.26 (3H, s, 3-CH_3 or 5-CH_3), 2.34 (2H, t, J = 7 Hz, 1′-H), 4.29 (2H, q, J = 7 Hz, 2- CH_2), 8.56 (1H, br s, NH); MS *m/z* 251 (M^+).

*Benzyl 3,5-Dimethyl-4-hexylpyrrole-2-carboxylate (**12**).* A mixture of benzyl alcohol (800 mL) and sodium metal (0.64 g, 28 mmol) was stirred under nitrogen until all the sodium had reacted, and 70.0 g (0.278 mol) of **11** was then added. The solution was stirred at 90 °C under a pressure of 16 mmHg for 19 h. The solution was cooled, and 24 mL of acetic acid was added. Distillation of the solvent at reduced pressure gave a white solid, which was dissolved in dichloromethane. The solution was washed with water, dried over anhydrous sodium sulfate, and filtered, and the solvent was removed by distillation at reduced pressure. Recrystallization of the residue from dichloromethane/hexane yielded **12.** Additional material was obtained by chromatography of the residue in the mother liquor on silica gel (dichloromethane/hexane, 3:1) to yield a total of 84.1 g of **12** (96% yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.85 (3H, br t, J = 7 Hz, 6′-CH_3), 1.25 (6H, s, 3′-CH_2 4′-CH_2 5′-CH_2), 1.37 (2H, m, 2′-CH_2), 2.15 (3H, s, 5-CH_3 or 3-CH_3), 2.25 (3H, s, 3-CH_3 or 5-CH_3), 2.31 (2H, t, J = 7 Hz, 1′-CH_2), 5.26 (2H, s, CO_2CH_2), 7.35 (5H, m, Ar-H), 8.52 (1H br s, NH); MS *m/z* 313 (M^+).

*Benzyl 4-Hexyl-5-carbomethoxy-3-methylpyrrole-2-carboxylate (**13**).* A solution of 600 mL of carbon tetrachloride and 31.35 g (0.100 mol) of **12** was stirred and cooled to 0 °C under a nitrogen atmosphere. A 32.1 mL portion (0.400 mol) of sulfuryl chloride was added dropwise at a rate of 8.8 mL/h. After completion of the addition, the reaction mixture was stirred for 8 h, the solvent was distilled under vacuum, and residual liquids were removed by codistillation with 200 mL of benzene. The resulting yellow-orange oil was dissolved in 500 mL of methanol, and 100 g of sodium acetate was added. The suspension was warmed at 50 °C under a nitrogen atmosphere for 5 h, and the reaction mixture was mixed with dichloromethane and water and aqueous sodium bicarbonate. The organic layer was separated, dried over anhydrous sodium sulfate, and filtered, and the solvent was removed by distillation at reduced pressure. Chromatography of the residue on silica gel (hexane/ethyl acetate, 85:15) gave 24.75 g of **13** (69% yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (3H, t, J = 7 Hz, 6′-CH_3), 1.30 (6H, br s, 3′-CH_2, 4′-CH_2, 5′-CH_2), 1.46 (2H, m, 2′-CH_2), 2.28 (3H, s, 3-CH_3), 2.71 (2H, t, J = 7 Hz, 1′-CH_2), 3.87 (3H, s, CO_2CH_3), 5.33 (2H, s, CO_2CH_2), 7.38 (5H, m, Ar-H), 9.35 (1H, br s, NH); MS *m/z* 357 (M^+).

*Methyl 3-Hexyl-4-methylpyrrole-2-carboxylate (**14**).* A mixture of 40.0 g (0.112 mol) of **13** and 2 g of 10% palladium on charcoal in 400 mL of tetrahydrofuran was stirred under a positive hydrogen atmosphere for 5 h. The catalyst was removed by filtration through Celite and washed with a mixture of tetrahydrofuran and methanol (4:1). Distillation of the solvent from the combined filtrates at reduced pressure gave 4-hexyl-5-carbomethoxy-3-methylpyrrole-2-carboxylic acid, which was dissolved in 400 mL of water containing 18.23 g (0.217 mol)

of sodium bicarbonate. The solution was heated to 70 °C, 350 mL of 1,2-dichloroethane was added, and the mixture was stirred as 34.4 g (0.136 mol) of iodine was added in small portions. When addition was complete, the solution was heated at reflux for 40 min. After treating the cooled reaction mixture with aqueous sodium bisulfite, the organic layer was separated and the aqueous phase extracted with dichloromethane. The combined organic extracts were washed with an aqueous solution of sodium bicarbonate and sodium bisulfite, dried over anhydrous sodium sulfate, and filtered. The solvent was distilled from the filtrate at reduced pressure to yield a yellow fibrous material, which was added to a mixture of 500 mL of methanol, 75 g of sodium acetate, and 70 mg of PtO_2. The suspension was stirred under a positive pressure of hydrogen gas for 21 h. The solvent was distilled under reduced pressure, and the residue dissolved in a mixture of water and dichloromethane. The organic layer was separated, dried over sodium sulfate, and filtered, and the solvent was distilled under reduced pressure. Chromatography of the residue on silica gel (hexane/diethyl ether 85:15) gave **14** in quantitative yield based on **13**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (3H, br t, $J = 7$ Hz, 6′-CH_3), 1.32 (6H, br s, 3′-CH_2, 4′-CH_2, 5′-CH_2), 1.50 (2H, m, 2′-CH_2), 2.03 (3H, s, 4-CH_3), 2.72 (2H, t, $J = 8$ Hz, 1′-CH_2), 3.8 (3H, m, CO_2CH_3), 6.66 (1H, d, $J = 2$ Hz, CH), 8.27 (1H, br s, NH); MS *m/z* 223 (M^+).

*Benzyl 3-Hexyl-4-methylpyrrole-2-carboxylate (**15**).* Metallic sodium (0.23 g, 0.010 mol) was dissolved in 500 mL of benzyl alcohol, and 23 g (0.10 mol) of **14** was added. The solution was heated at 90 °C for 15 h under the vacuum from an aspirator. The solvent was distilled under reduced pressure and the residue was chromatographed on silica gel (hexane/ethyl acetate, 85:15). The product was recrystallized from dichloromethane and hexane to give 29.11 g of **15** (94% yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.86 (3H, m, 6′-CH_3), 1.25 (6H, m, 3′-CH_2, 4′-CH_2, 5′-CH_2), 1.46 (2H, m, 2′-CH_2), 2.02 (3H, s, 3-CH_3), 2.70 (2H, t, $J = 8$ Hz, 1′-CH_2), 5.29 (2H, m, CO_2-CH_2), 6.65 (1H, d, $J = 3$ Hz, CH), 7.37 (5H, m, Ar-H), 8.72 (1H, br s, NH); MS *m/z* 299 (M^+).

*Benzyl 5-Formyl-3-hexyl-4-methylpyrrole-2-carboxylate (**16**).* A Vilsmeier reagent was formed by adding 10.6 mL (0.114 mol) of $POCl_3$ dropwise to 24 mL of dimethylformamide at 0 °C and stirring the resulting solution for 30 min. The reagent was added dropwise to a solution of 17.0 g (0.057 mol) of **15** in 300 mL of 1,2-dichloroethane at 0 °C under a nitrogen atmosphere. The mixture was stirred for 10 min, warmed to room temperature, and stirred for an additional 30 min. The solution was cooled in an ice bath, aqueous sodium acetate was added, and the resulting mixture was stirred for 14 h. The organic layer was separated and washed with aqueous sodium bicarbonate, and the solvent was distilled at reduced pressure. The residue was redissolved in diethyl ether, washed four times with water, washed with aqueous sodium chloride, dried over anhydrous magnesium sulfate, and filtered. The solvent was removed by distillation at reduced pressure, and the resulting yellow solid recrystallized from dichloromethane and hexane to give 17.86 g of **16** (96% yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.87 (3H, m, 6′-CH_3), 1.25 (6H, m, 3′-CH_2, 4′-CH_2, 5′-CH_2), 1.45 (2H, m, 2′-CH_2), 2.30 (3H, s, 4-CH_3), 2.69 (2H, t, $J = 8$ Hz, 1′-CH_2), 5.32 (2H, m, CO_2CH_2), 7.40 (5H, m, Ar-H), 9.44 (1H, br s, NH), 9.77 (1H, s, CHO); MS *m/z* 327 (M^+).

*Benzyl 3-Hexyl-5-(hydroxymethylphenyl)-4-methylpyrrole-2-carboxylate (**17**).* A solution of **16** (6.55 g, 0.020 mol) in 150 mL of tetrahydrofuran was stirred at 0 °C under a nitrogen atmosphere, and 20 mL of a 2.0 M solution of phenylmagnesium chloride in tetrahydrofuran (0.040 mol) was added dropwise. After stirring the mixture for 20 min, it was poured over a mixture of ice, diethyl ether, and citric acid and stirred. The organic layer was separated, and the aqueous phase extracted twice with 80 mL of diethyl ether. The combined organic extracts were washed with aqueous sodium bicarbonate and aqueous sodium chloride, dried over sodium sulfate, and filtered, and the solvent was distilled at reduced pressure to give 7.85 g of **17** as a white solid (96% yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.85 (3H, t, $J = 7$ Hz, 6′-CH_3), 1.22 (6H, m, 3′-CH_2, 4′-CH_2, 5′-CH_2), 1.41 (2H, m, 2′-CH_2), 1.88 (3H, s, 4-CH_3), 2.38 (1H, d, $J = 3$ Hz, OH), 2.65 (2H, m, 1′-CH_2), 5.25 (1H, d, $J = 8$ Hz, $CO_2CH\mathit{H}$), 5.26 (1H, d, $J = 8$ Hz, $CO_2C\mathit{H}H$), 5.90 (1H, d, $J = 3$ Hz, CH), 7.35 (10H, m, Ar-H), 8.97 (1H, br s, NH); MS *m/z* 405 (M^+).

*1,9-(Dibenzyloxycarbonyl)-2,8-dihexyl-3,7-dimethyl-5-phenyldipyrromethane (**18**).* To a stirred solution of 3.00 g (10.0 mmol) of **15** and 4.06 g (10.0 mmol) of **17** in 60 mL of dichloromethane was added 1.9 g (10.0 mmol) of *p*-toluenesulfonic acid. The pink solution was stirred for 30 min, diluted with dichloromethane, washed with aqueous sodium bicarbonate and aqueous sodium chloride, dried over sodium sulfate, and filtered. The solvent was distilled at reduced pressure, and the residue was chromatographed on silica gel (hexane/ethyl acetate, 85:15) to give 6.56 g of **18** (95% yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.85 (6H, t, $J = 6$ Hz, 6″-CH_3, 6′-CH_3), 1.22 (12H, m, 3″-CH_2, 3′-CH_2, 4″-CH_2, 4′-CH_2, 5″-CH_2, 5′-CH_2), 1.43 (4H, m, 2″-CH_2, 2′-CH_2), 1.76 (6H, s, 3-CH_3, 7-CH_3, 2.66 (4H, m, 1″-CH_2, 1′-CH_2), 5.23 (4H, s, 1-CO_2CH_2, 9-CO_2CH_2), 5.47 (1H, s, 5-CH), 7.08−7.35 (15H, m, 1Ar-H, 5Ar-H, 9Ar-H), 8.25 (2H, br s, NH); MS *m/z* 686 (M^+).

*1,9-Diformyl-2,8-dihexyl-3,7-dimethyl-5-phenyldipyrromethane (**19**).* A 6.0 g (8.73 mmol) portion of **18** and 0.6 g of 10% palladium on carbon were added to 100 mL of tetrahydrofuran, and the suspension was stirred under a positive pressure of hydrogen for 16 h. The catalyst was removed by filtration through Celite, and the residue was washed with tetrahydrofuran/methanol (4:1). The solvent was removed by distillation at reduced pressure. The residue was dissolved in 50 mL of dimethylformamide, purged of oxygen with nitrogen gas, and heated at reflux for 4 h. The reaction mixture was cooled to 0 °C under a nitrogen atmosphere, and a Vilsmeier reagent prepared from 4.07 mL (43.7 mmol) of $POCl_3$ and 7.3 of mL dimethylformamide was added. The resulting mixture was stirred at 0 °C for 20 min and at room temperature for 1 h. The solution was diluted with 100 mL of 1,2-dichloroethane, and aqueous sodium bicarbonate was added. After stirring the mixture for 16 h, the organic layer was separated and the aqueous phase extracted twice with dichloromethane. The combined extracts were washed with aqueous sodium bicarbonate and aqueous sodium chloride to yield **19** (3.60 g, 87%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (6H, t, $J = 7$ Hz, 6″-CH_3, 6′-CH_3), 1.31 (12H, br s, 3″-CH_2, 4″-CH_2, 5″-CH_2, 3′-CH_2, 4′-CH_2, 5′-CH_2), 1.54 (4H, m, 2″-CH_2, 2′-CH_2), 1.85 (6H, s, 7-CH_3, 3-CH_3), 2.66 (4H, m, 1″-CH_2, 1′-CH_2), 5.58 (1H, s, 5-CH), 7.07−7.30 (5H, m, Ar-H), 9.27 (2H, br s, NH), 9.44 (2H, s, CHO); MS *m/z* 474 (M^+).

*2,8-Dihexyl-3,7-dimethyl-5,15-diphenylporphyrin (**20**).* To a mixture of 0.48 g (1.00 mmol) of **19** and 0.23 g (1.00 mmol) of **9** in 350 mL of dichloromethane under a nitrogen atmosphere was added 8.0 g of *p*-toluenesulfonic acid (azeotropically dried three times with 200 mL portions of toluene) in 20 mL of methanol. The dark red reaction mixture was stirred at room temperature for 19 h, and 20 mL of methanol and excess zinc acetate were added. The mixture was refluxed for 5 h and stirred at room temperature for 14 h. After addition of 2,3-

dichloro-5,6-dicyanobenzoquinone (1.0 g, excess) the mixture was stirred for an additional 5 h. The mixture was washed with water, 10% hydrochloric acid, aqueous sodium bicarbonate (×3), and aqueous sodium chloride. The solvent was distilled at reduced pressure, and the residue chromatographed on silica gel (dichloromethane/hexane, 2:1) to give 0.210 g of **20** (32% yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ −3.03 (1H, s, NH), −2.54 (1H, s, NH), 0.91 (6H, t, J = 7 Hz, 6′-CH_3, 6″-CH_3), 1.37 (4H, m, 5′-CH_2, 5″-CH_2), 1.48 (4H, m, 4′-CH_2, 4″-CH_2), 1.72 (4H, m, 3′-CH_2, 3″-CH_2), 2.16 (4H, m, 2′-CH_2, 2″-CH_2), 2.47 (6H, s, 8-CH_3, 12-CH_3), 3.97 (4H, t, J = 8 Hz, 1′-CH_2, 1″-CH_2), 7.78 (6H, m, 20Ar3,4,5-H, 10Ar3,4,5-H), 8.08 (2H, d, J = 7 Hz, 10Ar2,6-H), 8.28 (2H, dd, J = 4, 7 Hz, 20Ar2,6-H), 9.07 (2H, d, J = 4 Hz, 18-CH, 2-CH), 9.37 (2H, d, J = 4 Hz, 17-CH, 3-CH), 10.24 (2H, s, 5-CH, 15-CH); MS (FAB) *m/z* 659.4120 (calcd for $(M+H)^+$, 659.4035); UV/vis (CH_2Cl_2) 406, 506, 538, 576, 630 nm. Porphyrin **20** was quantitatively converted to zinc 2,8-dihexyl-3,7-dimethyl-5,15-diphenylporphyrin (**3**) by stirring a dichloromethane solution with zinc acetate and purifying the crude product by chromatography on silica gel (dichloromethane/hexane, 2:1).

NMR Spectroscopy. Chemical shift assignments were made using Varian Unity 500 or 400 MHz spectrometers. Spin−lattice relaxation time measurements were made at 11.7 T on the Varian Unity-500 spectrometer. The sample temperature was 303.0 ± 0.5 K. Samples were dissolved in deuteriochloroform, transferred to 10 mm NMR tubes, and degassed under vacuum using four freeze−thaw cycles. The tubes were then sealed. The T_1 measurements were made using the *D*-180-*t*-90-FID inversion−recovery pulse sequence with a relaxation delay D at least 10 times the longest T_1 value of interest, and a minimum of 13 t values. Relaxation times were calculated by fitting the data with eq 11, where A and B are constants and I

$$I = A + B_{\exp}(-t/T_1) \tag{11}$$

is the peak intensity for the spectrum obtained at time t. To verify the 90° pulse tip angle and other parameters, T_1 measurements were also made on freshly prepared solutions of dioxane in D_2O. The results were consistent with literature reports.[47]

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References and Notes

(1) Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res.* **1993**, *26*, 198−205.
(2) Gust, D.; Moore, T. A. *Adv. Photochem.* **1991**, *16*, 1−65.
(3) Gust, D.; Moore, T. A. *Top. Curr. Chem.* **1991**, *159*, 103−151.
(4) Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435−461.
(5) Osuka, A.; Maruyama, K.; Nataga, N.; Asahi, T.; Yamazaki, I.; Tamai, N. *J. Am. Chem. Soc.* **1990**, *112*, 4958−4959.
(6) Maruyama, K.; Osuka, A.; Mataga, N. *Pure Appl. Chem.* **1994**, *66*, 867−872.
(7) Connolly, J. S.; Bolton, J. R. In *Photoinduced Electron Transfer, Part D*; Fox, M. A., Channon, M., Eds.; Elsevier: Amsterdam, 1988; pp 303−393.
(8) Rabanal, F.; DeGrado, W. F.; Dutton, P. L. *J. Am. Chem. Soc.* **1996**, *118*, 473−474.
(9) Gust, D.; Moore, T. A.; Moore, A. L.; Devadoss, C.; Liddell, P. A.; Hermant, R.; Nieman, R. A.; Demanche, L. J.; DeGraziano, J. M.; Gouni, I. *J. Am. Chem. Soc.* **1992**, *114*, 3590−3603.
(10) Hoard, J. L. *Science* **1971**, *174*, 1295−1302.
(11) Hoard, J. L. In *Porphyrins and Metalloporphyrins*; Smith, K. M., Ed.; Elsevier: New York, 1975; pp 317.
(12) Sessler, J. L.; Johnson, M. R.; Creager, S. E.; Fettinger, J. C.; Ibers, J. A. *J. Am. Chem. Soc.* **1990**, *112*, 9310−9329.
(13) Krieger, C.; Weiser Juergen; Staab, H. A. *Tetrahedron Lett.* **1985**, *26*, 6055−6058.
(14) Krieger, C.; Dernbach, M.; Voit, G.; Carell, T.; Staab, H. A. *Chem. Ber.* **1993**, *126*, 811−821.
(15) Schrijvers, R.; Van Dijk, M.; Sanders, G. M.; Sudholter, E. J. R. *Recl. Trav. Chim. Pays-Bas* **1994**, *113*, 351−354.
(16) Chachaty, C.; Gust, D.; Moore, T. A.; Nemeth, G. A.; Liddell, P. A.; Moore, A. L. *Org. Magn. Reson.* **1984**, *22*, 39−46.
(17) Jakobsen, H. J.; Ellis, P. D.; Inners, R. R.; Jensen, C. F. *J. Am. Chem. Soc.* **1982**, *104*, 7442−7452.
(18) Zindel, J.; Lightner, D. A. *J. Heterocycl. Chem.* **1995**, *32*, 1219−1223.
(19) Sessler, J. L.; Johnson, M. R.; Lin, T.-Y.; Creager, S. E. *J. Am. Chem. Soc.* **1988**, *110*, 3659−3661.
(20) Sessler, J. L.; Johnson, M. R.; Lin, T.-Y. *Tetrahedron* **1989**, *45*, 4767−4784.
(21) Heitele, H.; Pollinger, F.; Kremer, K.; Michel-Beyerle, M. E.; Futscher, M.; Voit, G.; Weiser, J.; Staab, H. A. *Chem. Phys. Lett.* **1992**, *188*, 270−278.
(22) Wasielewski, M. R.; Niemczyk, M. P.; Svec, W. A.; Pewitt, E. B. *J. Am. Chem. Soc.* **1985**, *107*, 5562−5563.
(23) Sakata, Y.; Tsue, H.; O'Neil, M. P.; Wiederrecht, G. P.; Wasielewski, M. A. *J. Am. Chem. Soc.* **1994**, *116*, 6904−6909.
(24) Tsue, H.; Nakashima, S.; Goto, Y.; Tatemitsu, H.; Misumi, S.; Abraham, R. J.; Asahi, T.; Tanaka, Y.; Okada, T.; Mataga, N.; Sakata, Y. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 3067−3075.
(25) Osuka, A.; Maruyama, K.; Yamazaki, I.; Tamai, N. *J. Chem. Soc., Chem. Commun.* **1988**, 1243−1245.
(26) Osuka, A.; Maruyama, K. *J. Am. Chem. Soc.* **1988**, *110*, 4454−4456.
(27) Osuka, A.; Kobayashi, F.; Maruyama, K. *Chem. Lett.* **1990**, 1521−1524.
(28) Osuka, A.; Nagata, T.; Maruyama, K.; Mataga, N.; Asahi, T.; Yamazaki, I.; Nishimura, Y. *Chem. Phys. Lett.* **1991**, *185*, 88−94.
(29) Osuka, A.; Yamada, H.; Maruyama, K.; Mataga, N.; Asahi, T.; Ohkouchi, M.; Okada, T.; Yamazaki, I.; Nishimura, Y. *J. Am. Chem. Soc.* **1993**, *115*, 9439−9452.
(30) Li, S.; Swindle, S. L.; Smith, S. K.; Nieman, R. A.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Phys. Chem.* **1995**, *99*, 3371−3378.
(31) Levy, G. C.; Axelson, D. E.; Schwartz, R.; Hochmann, J. *J. Am. Chem. Soc.* **1978**, *100*, 410−424.
(32) London, R. E.; Avitabile, J. *J. Chem. Phys.* **1976**, *65*, 2443−2450.
(33) Levine, Y. K.; Partington, P.; Roberts, G. C. K. *Mol. Phys.* **1973**, *25*, 497−514.
(34) Levine, Y. K.; Birdsall, N. J. M.; Lee, A. G.; Metcalfe, J. C.; Partington, P.; Roberts, G. C. K. *J. Chem. Phys.* **1974**, *60*, 2890−2899.
(35) Eaton, S. S.; Eaton, G. R. *J. Am. Chem. Soc.* **1977**, *99*, 6594−6599.
(36) Eaton, S. S.; Eaton, G. R. *J. Am. Chem. Soc.* **1975**, *97*, 3660−3666.
(37) Barkigia, K. M.; Berber, M. D.; Fajer, J.; Medforth, C. J.; Renner, M. W.; Smith, K. M. *J. Am. Chem. Soc.* **1990**, *112*, 8851−8857.
(38) Renner, M. W.; Barkigia, K. M.; Zhang, Y.; Medforth, C. J.; Smith, K. M.; Fajer, J. *J. Am. Chem. Soc.* **1994**, *116*, 8582−8592.
(39) Regev, A.; Galili, T.; Medforth, C. J.; Smith, K. M.; Barkigia, K. M.; Fajer, J.; Levanon, H. *J. Phys. Chem.* **1994**, *98*, 2520−2526.
(40) Gentemann, S.; Medforth, C. J.; Forsyth, T. P.; Nurco, D. J.; Smith, K. M.; Fajer, J.; Holten, D. *J. Am. Chem. Soc.* **1994**, *116*, 7363−7368.
(41) Stone, A.; Fleischer, E. B. *J. Am. Chem. Soc.* **1968**, *90*, 2735−2748.
(42) Fleischer, E. B. *Acc. Chem. Res.* **1970**, *3*, 105−112.
(43) Dirks, J. W.; Underwood, G.; Matheson, J. C.; Gust, D. *J. Org. Chem.* **1979**, *44*, 2551−2555.
(44) Gust, D.; Moore, T. A.; Moore, A. L.; Krasnovsky, A. A., Jr.; Liddell, P. A.; Nicodem, D.; DeGraziano, J. M.; Kerrigan, P.; Makings, L. R.; Pessiki, P. J. *J. Am. Chem. Soc.* **1993**, *115*, 5684−5691.
(45) Kuciauskas, D.; Liddell, P. A.; Hung, S.-C.; Lin, S.; Stone, S.; Seely, G. R.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Phys. Chem.* **1997**, *101B*, 429−440.
(46) Osuka, A.; Nagata, T.; Kobayashi, F.; Maruyama, K. *J. Heterocycl. Chem.* **1990**, *27*, 1657−1659.
(47) Armitage, I. M.; Huber, H.; Live, D. H.; Pearson, H.; Roberts, J. D. *J. Magn. Reson.* **1974**, *15*, 142−149.