Conformational Dynamics of α,β,γ,δ-Tetraarylporphyrins and Their Dications[1]

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Rotational isomerism in several tetraarylporphyrin free bases and the corresponding dications has been studied by using dynamic ^{1}H NMR spectroscopy. The average free energy of activation for rotation of a single aryl ring for the stereoisomers of α,β,γ,δ-tetrakis(2-methoxyphenyl)porphyrin is $\Delta G^{\ddagger}_{433}$ = 25.9 kcal/mol. The barrier for the corresponding dication is $\Delta G^{\ddagger}_{388}$ = 23.0 kcal/mol. For α,β,γ,δ-tetrakis(2,4-dimethoxyphenyl)porphyrin and its dication, the rotational barriers are $\Delta G^{\ddagger}_{433}$ = 25.2 and $\Delta G^{\ddagger}_{388}$ = 21.8 kcal/mol, respectively. These results shed light on the questions of the degree of distortion of the porphyrin macrocycle in solution and the orientation of the aryl rings relative to the mean porphyrin plane.

It has recently been pointed out that, although the structure of prophyrins in the solid state has been extensively investigated, "relatively little is known about the stereochemistry and rigidity of the macrocycle in solution".[2] This situation has been somewhat alleviated in the case of metalloporphyrins by the work of Eaton and co-workers.[3] These investigators have obtained information concerning the dynamic stereochemistry and flexibility of metalated tetraphenylporphyrins and their para-substituted analogues from dynamic nuclear magnetic resonance studies of complexes with different axial ligands to the metal on the two sides of the metalloporphyrin plane. In these and other metalated tetraarylporphyrins the four aryl rings make angles of ~60–90° with the plane of the porphyrin macrocycle in the solid state,[4] and aryl ring rotation is slow on the NMR time scale at low temperatures. Thus, the two ortho (and two meta) hydrogen atoms on an aryl ring are diastereotopic and give rise to anisochronous resonances in the ^{1}H NMR spectrum. As the temperature is increased, rotation of the rings becomes more rapid, and line-shape analysis of the resulting partially averaged spectra yields kinetic information concerning the rotational process.

The solution structure and conformational dynamics of free-base tetraarylporphyrins and their dications are also of considerable interest. In particular, there has been speculation concerning the degree of planarity of the porphyrin macrocycle, the degree of rotation of the aryl rings out of the porphyrin plane in the ground state, and the effects of this rotation on resonance interactions between the rings and the porphyrin macrocycle.[5] The approach employed by Eaton and co-workers is, of course, not applicable to porphyrin free bases and dications because ligation to a central metal cannot be used as a means of rendering the two faces of the porphyrin diastereotopic. However, the required reduction in symmetry can be attained by eliminating the local C_2 axes of the aryl rings through substitution at ortho and/or meta positions. Rotational isomerism has been detected in a number of ortho-substituted tetraarylporphyrin free bases and metal complexes.[3f,h,5b,6] Unfortunately, in those cases where rotational isomers were observed by NMR spectroscopy,[3f,h,6] the energy barriers to rotation of the aryl rings proved too high to measure under the experimental conditions and only lower limits were obtained. Indeed, the only kinetic parameters available for ortho-substituted tetraarylporphyrins are estimates for α,β,γ,δ-tetrakis(2-hydroxyphenyl)porphyrin and its copper complex which were obtained through separation of the isomers by thin-layer chromatography.[5b] No rotational barriers for tetraarylporphyrin dications have been reported. Perusal of the studies mentioned above suggested that rotational barriers for ortho-substituted tetraarylporphyrins and dications might be measurable by NMR methods under favorable conditions. The results reported below reveal that this is in fact the case.

Results

α,β,γ,δ-Tetrakis(2-methoxyphenyl)porphyrin. A previously known ortho-substituted porphyrin, α,β,γ,δ-tetrakis(2-methoxyphenyl)porphyrin (1), was prepared as reported in the literature,[8] and its 100-MHz ^{1}H NMR

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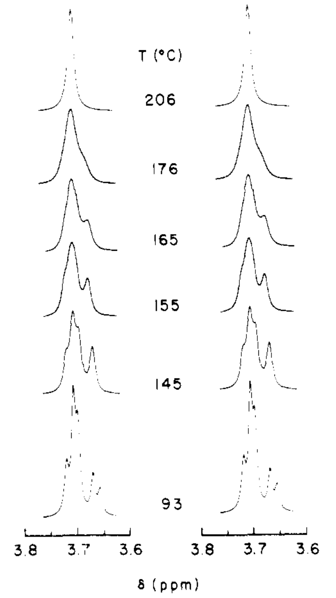

Figure 1. Experimental (left) and computer-simulated (right) ^{1}H NMR spectra of the ortho methoxy groups of 1 in nitrobenzene-d_5 solution at selected temperatures.

spectrum in nitrobenzene-d_5 solution was determined. Figure 1 shows the spectra for the methoxy region at selected temperatures. The multiple resonances observed at low temperatures indicate some form of isomerism. In order that these results can be interpreted, the stereochemistry of ortho-substituted tetraarylporphyrins must be discussed.

Although X-ray studies indicate that in the solid state the phenyl rings of tetraphenylporphyrins and their derivatives are, in general, neither coplanar with nor exactly perpendicular to the mean porphyrin plane,[4,5c] the NMR studies cited above are all consistent with structures in which the four aryl rings are rapidly oscillating through the perpendicular orientation and are thus effectively perpendicular on the NMR time scale. Granted such a conformation, a free-base porphyrin such as 1 in which each aryl ring bears the same ortho substituent would be expected to exist in four diastereomeric conformations[5b,6a] on the NMR time scale when rotation of the aryl rings is slow, but exchange of the two central hydrogen atoms among the four nitrogen atoms is fast:[7] a structure with C_{4v} symmetry, a C_s structure, a D_{2d} structure, and a C_{2h} conformation (Figure 2). If all of these isomers were present in detectable amounts, one would expect the ^{1}H NMR spectrum of 1 to feature six resonances in the methoxy region: three arising from the C_s isomer which has three sets of diastereotopic methoxy groups, and one from each of the other isomers, each of whose methoxy groups is equivalent or enantiotopic.

The spectrum at 93 °C (Figure 1) is consistent with this interpretation. Five resonances are observed at δ 3.66, 3.67, 3.70, 3.71, and 3.72. The NMR results do not allow unambiguous assignment of these resonances to the four expected isomers. However, the three resonances for the C_s isomer are necessarily present in the ratio 1:2:1. Given this constraint, the following assignments can be made: δ 3.66 (C_{4v}), δ 3.67 (C_s), δ 3.70 (C_s), δ 3.71 (C_s and C_{2h}, accidentally isochronous), and δ 3.72 (D_{2d}). Calculations[9] using these values of chemical shift and a ratio of intensities of 0.08:0.13:0.27:0.13:0.24:0.15 for the six resonances, respectively, yield a simulated spectrum which is an adequate match for the experimental result (Figure 1). This ratio of intensities is very close to that expected statistically.[5b,6a] These assignments are by no means unique (see Experimental Section). However, they are consistent with the experimental results and, as will be shown below, they are sufficient for the purposes of this study.

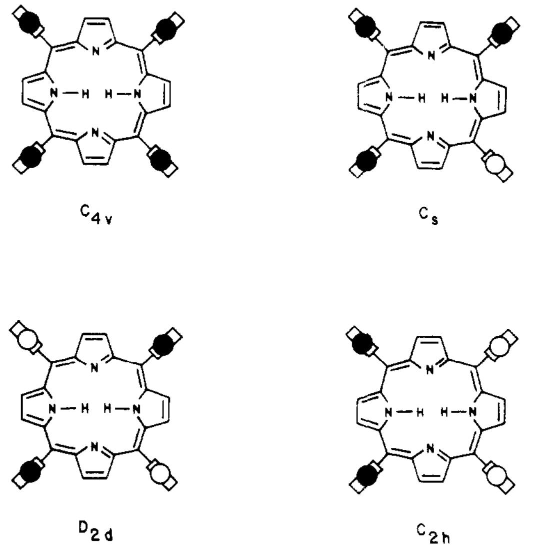

Figure 2. Schematic representation of the rotational stereoisomers of 1. A solid circle represents an ortho methoxy group above the plane of the paper, whereas a hollow circle denotes such a group below this plane. Point-group notations define the effective point group when exchange of the central protons among the four nitrogen atoms is rapid on the NMR time scale.

As shown in Figure 1, the spectrum of 1 is altered upon warming the solution. The spectral changes are reversible and must arise from conformational changes. As the temperature is raised above 90 °C, the chemical shift of the resonance at δ 3.66 increases, and at 145 °C this resonance and that at δ 3.67 have become accidentally isochronous. More significantly for the present study, all resonances have broadened slightly at 145 °C. The broadening becomes more apparent at higher temperatures, and by 206 °C all resonances have coalesced to a single peak which is again becoming narrow. This coalescence behavior is a result of stereoisomerization processes which are becoming rapid on the NMR time scale.

Stereoisomerizations of the four isomers of 1 occur by rotations of the aryl rings by $\sim\pi$ rad about the bonds to the macrocycle, and analysis of the coalescence behavior yields kinetic information concerning these rotations. Inspection of Figure 2 reveals that the C_s isomer may be converted to any of the other isomers by a rotation about a suitable aryl ring–macrocycle bond. Each of the other isomers can be converted only to the C_s form by a single rotation. Thus, there are six rate constants for isomerization with which one must be concerned. Since the system is at equilibrium, the rate constants for isomerization of the C_{4v}, D_{2d}, and C_{2h} isomers may be derived from the remaining three rate constants by the constraints imposed by the relative populations. However, the rate constants for isomerization of the C_s form are not so constrained and will, in principle, differ from one another. As a first attempt at analysis, it was assumed that the rates of rotation of each of the four aryl groups in the C_s isomer are equal. This is reasonable, since examination of molecular models suggests that there is no significant direct steric interaction between aryl groups, and the orientation of one aryl group therefore has little influence on the

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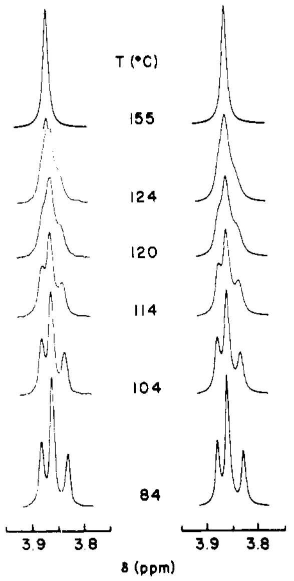

Figure 3. Experimental (left) and computer-simulated (right) ^1H NMR spectra of the ortho methoxy groups of **2** in nitrobenzene-d_5 solution at selected temperatures.

rotation of another. Line shapes were calculated[9] for **1** at different isomerization rates by using the above assumption and the assignment scheme described earlier (see Experimental Section). The resulting curves, shown on the right side of Figure 1, are reasonable matches for the experimental spectra. Rate constants for each isomerization were obtained for each temperature, and application of the Eyring equation yielded free energies of activation for isomerization. The free energies of activation for rotation of a single aryl ring differed slightly for each isomer as required by the population differences but all were within ±0.2 kcal/mol of an average value of $\Delta G^{\ddagger}_{433}$ = 25.9 kcal/mol (see Experimental Section).

Upon treatment with acid, tetraarylporphyrin free bases form diprotonated dications in which all four central nitrogen atoms bear hydrogen atoms. As will be discussed in detail below, the dication of tetraphenylporphyrin in the solid state exhibits pseudo S_4 symmetry,[5a] and the macrocyclic ring is no longer essentially planar, as it is in the free base. If these conformational differences are maintained in solution as has been suggested,[5a,c] they should be reflected in a change in the barrier to rotation of the aryl rings.

The dication of tetrakis(2-methoxyphenyl)porphyrin (**2**) was prepared by treatment of a nitrobenzene-d_5 solution of **1** with a large excess of trifluoroacetic acid. The ^1H NMR spectrum of this solution at 80 °C featured three resonances in the methoxy region at δ 3.83, 3.86, and 3.88 in the ratio of intensities of 0.22:0.53:0.25, respectively (Figure 3). A dication **2** in which rotation of the aryl groups is slow on the NMR time scale but inversion of the macrocycle is fast[10] would be expected to give rise to six methoxy resonances, as was the case with **1**. The observation of three resonances is consistent with this expectation if some of the resonances are accidentally isochronous. In fact, the observed spectrum can readily be simulated in a manner similar to that described for **1** (see Figure 3 and Experimental Section). As illustrated in Figure 3, the resonances in the methoxy region of the spectrum of **2** broaden when the sample is heated and coalesce to a singlet at 118 °C. Since the ranges of ortho methoxy group chemical shifts observed for **1** and **2** are comparable, this much lower coalescence temperature for **2** suggests that the barriers to rotation of the aryl groups of **2** are also much lower than those for **1**. Indeed, a line-shape analysis similar to that carried out for **1** (see Experimental Section) yields an average free energy of activation for rotation of one aryl ring of $\Delta G^{\ddagger}_{388}$ = 23.0 kcal/mol.

The large difference in free energies of activation for aryl ring rotation between **1** and **2** (~3 kcal/mol) signifies a profound structural change in the molecule upon protonation. It is tempting to ascribe this difference to differences in steric hindrance due to conformational changes. However, resonance interactions must also be taken into account. Aryl group substituents in the para position have recently been found to affect the barriers to phenyl ring rotation in metalated tetraarylporphyrins.[3g,h] In order to assess the contribution of resonance effects to the results for **1** and **2**, we prepared a second porphyrin, having an additional methoxy group in the para position of each aryl ring.

α,β,γ,δ-Tetrakis(2,4-dimethoxyphenyl)porphyrin (3). Porphyrin **3** was prepared by a route similar to that employed for **1** (see Experimental Section). The ^1H NMR spectrum of a nitrobenzene-d_5 solution of **3** featured five resolved resonances in the ortho methoxy region at 116 °C and in fact was nearly identical with that of **1**, with a few minor differences in chemical shifts and intensities. Coalescence behavior similar to that of **1** was observed upon heating, and a line-shape analysis parallel to that described for **1** yielded an average barrier to rotation of an aryl ring of $\Delta G^{\ddagger}_{433}$ = 25.2 kcal/mol (see Experimental Section).

The dication of **3** (**4**, prepared by addition of excess trifluoroacetic acid) yielded, at 68 °C, a three-line spectrum in the ortho methoxy region similar to that of **2**. Line-shape analysis of the coalescence behavior (see Experimental Section) gave an average rotational barrier of $\Delta G^{\ddagger}_{388}$ = 21.8 kcal/mol.

Discussion

Separation of Steric and Resonance Effects. The differences among the energies of activation reported above are the result of both the steric and electronic contributions of the substituents on the aryl rings. If these contributions can be separated, a more revealing interpretation of the results may be achieved. The electronic effects of the methoxy substituents may in turn be subdivided into inductive and resonance contributions. To a first approximation, inductive effects would be expected to contribute roughly equally to the stabilization of the ground and transition states for any of the molecules studied and will therefore be neglected. Resonance interactions, on the other hand, would be expected to stabilize a transition state for aryl ring rotation, where the aryl group and the mean porphyrin plane are approximately coplanar, relative to the ground state where the dihedral angle is large. In addition, the electron-donating methoxy group would be expected to stabilize the positively charged dication to a greater extent than the neutral free-base porphyrin. Thus, the difference in free energies of activation for **1** and **2** (2.9 kcal/mol) is expected to contain a significant resonance contribution. The magnitude of this contribution may be roughly estimated by a consideration of the results for **3** and **4**, as well as those

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[9] The computer program used for line-shape analysis is based on one originated by M. Saunders (Saunders, M. In "Magnetic Resonance in Biological Systems"; Ehrenberg, A., Malmström, C., Vänngård, T., Eds.; Pergamon Press: New York, N.Y., 1967; p 85).

[10] (a) Published results[5a,i] suggest that inversion due to proton exchange would be rapid on the NMR time scale in the temeprature range of interest (~100–200 °C).

for **1** and **2**. The para methoxy group decreases the free-energy difference between the ground state and the transition state for the free base by 0.7 kcal/mol, whereas the corresponding barrier for the dication is reduced by 1.2 kcal/mol. The contribution of the para methoxy group can only be electronic, and the effect of this group is therefore qualitatively as predicted from the above considerations.

Since the addition of a para methoxy group lowers the rotational barrier for the dication ~0.5 kcal/mol more than it lowers the free energy of activation for the free base, the resonance contribution to barrier lowering in the dication (relative to the free base) of a para methoxy group is ~0.5 kcal/mol. Although the separation of steric and electronic effects of ortho substituents has been the subject of much debate, there are a number of studies which suggest that the resonance contributions of a substituent in the ortho and para positions are about equal.[11] Granted this approximation, it may be estimated that the ortho methoxy groups of **2** lower the barrier to rotation of an aryl group by about 0.5 kcal/mol relative to **1** through resonance interactions. Therefore, roughly 2.4 kcal/mol of the decrease in energy of activation is due to steric effects.

Steric Effects. As mentioned above, the dication of $\alpha,\beta,\gamma,\delta$-tetraphenylporphyrin assumes a distorted conformation in the solid state. The pyrrole rings are alternately tilted up and down at angles of ~33° from the mean porphyrin plane.[5a] A result of this distortion is that the steric hindrance preventing the meso aryl groups from lying in the mean porphyrin plane is greatly lessened, and these rings now make an angle of ~21° with this plane,[5c] as contrasted with an angle of ~60° for the free base.[12] It has been suggested that a similar distortion of the macrocycle occurs in solution and that the resulting increased overlap of the π systems of the aryl rings and macrocycle accounts for the green color of tetraarylporphyrin dications[5a,c] (the free base is purple in solution). This change in structure has also been suggested as an explanation for the instability of porphyrin monocations relative to dications[5a] and the relatively slow exchange of protons between porphyrins and their dications.[13]

An examination of molecular models suggests that the major steric interactions which occur on rotation of the aryl rings toward the plane of a porphyrin free base are between the β-pyrrole hydrogens and the ortho phenyl substituents. This interpretation is borne out by molecular mechanics calculations.[5e] Furthermore, this interaction may be relieved in part by a distortion of the porphyrin ring in the manner observed in the dication. Thus, the ground-state conformation of the dication may be considered to be a crude steric model for a distorted macrocycle intermediate in structure between the ground state and the transition state for phenyl ring rotation in the free base. In addition, the actual transition states for phenyl rotation in the free base and the dication would be expected to feature a somewhat similar degree of distortion of the macrocycle. Another way of stating this point is that if the distortion of the macrocycle in the dication results in rotation of the aryl rings toward the mean porphyrin plane, then, to a crude approximation, rotation of an aryl ring in the free base would be expected to lead to a distortion of the porphyrin macrocycle of the same kind as that seen in the ground state of the dication. If one accepts this rough analogy, then the energy required to deform the nearly planar free-base macrocycle to the extent seen in the dication can be estimated to be about 2.4 kcal/mol.

The above value is admittedly a very crude measure of the deformability of the porphyrin macrocycle in solution. However, it is hoped that it will be of some utility, since estimates of this quantity are not easily obtained experimentally. The ease of deformation of porphyrins is of interest in a number of contexts, including the question of the mechanism of oxygen binding and the cooperative effect in hemoglobin.[14]

Thus, the results for **1**–**4** are consistent with the hypothesis that dications of tetraarylporphyrins are highly distorted in solution as well as in the solid state. The estimated barriers to rotation of the phenyl rings of **1** and **3** are slightly higher than the value of 24.0 kcal/mol which was estimated for tetrakis(2-hydroxyphenyl)porphyrin at 23 °C.[5b] Although a comparison is somewhat dangerous due to the large temperature difference, this result is reasonable because a methoxy group might be expected to be somewhat more bulky than a hydroxy group. The copper complex of tetrakis(2-hydroxyphenyl)porphyrin, on the other hand, has a barrier to aryl ring rotation (25.4 kcal/mol)[5b] which is comparable to those observed for **1** and **3**. This undoubtedly reflects a greater rigidity of the metal complex, compared to the free base.[5b] The relatively high barriers to rotation measured for metalated tetraarylporphyrins which have only hydrogen in the ortho positions may also be ascribed in part to this effect.[3]

Resonance Effects. Comparison of the results for **3** and **4** with those for **1** and **2** shows that resonance stabilization of the transition state for aryl ring rotation occurs in both the free bases and the dications. As expected, this stabilization is more effective for the dication than for the free base, as illustrated by the fact that the additional para methoxy group in **3** and **4** lowers the barrier for the free base by 0.7 kcal/mol, whereas it lowers that for the dication by 1.2 kcal/mol. This finding is consistent with the suggestion that the color of the dication is the result of enhanced resonance interactions between the aryl groups and macrocycle.[5a,c] Recent results of Meot-Ner and Adler, based on Hammett-type free-energy relationships, have been interpreted to suggest that, contrary to expectations, resonance interactions may be more important in the free base than in the dication.[5f] The results given above offer no support for this possibility, but it must be remembered that these results are concerned in part with transition states for aryl ring rotation, rather than ground states or electronic excited states.

The directions of the substituent effects on the rotational barriers observed for the free bases **1** and **3** and the dications **2** and **4** are the same as those measured for metalated porphyrins,[3g,h] where electron-donating substituents also lowered the free energy of activation for rotation. Although the magnitudes of these effects are roughly comparable in the three systems, the lowering appears to be greatest for the dications.

Experimental Section

Elemental analyses were performed by Galbraith Laboratories, Inc. ^{1}H NMR spectra were obtained on a Bruker WH-90 or Varian XL-100 spectrometer and refer to ~20% solutions in $CDCl_3$ with tetramethylsilane as an internal reference unless specified

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(11) See, for example: (a) Shorter, J. In "Advances in Linear Free Energy Relationships"; Chapman, N. B., Shorter, J., Eds.; Plenum Press: New York, N.Y., 1972; p 71. (b) Charton, M. *Can. J. Chem.* **1960**, *38*, 2493. (c) Brown, H. C.; Smoot, C. R. *J. Am. Chem. Soc.* **1956**, *78*, 6255. (d) Taft, Jr., R. W. *Ibid.* **1952**, *74*, 3120.

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(13) Abraham, R. J.; Hawkes, G. E.; Smith, K. M. *Tetrahedron Lett.* **1974**, 71.

(14) For a concise discussion of this problem, see ref 4b.

otherwise. Variable-temperature NMR studies were carried out in nitrobenzene-d_5 solution on a Varian XL-100 continuous-wave spectrometer with a variable-temperature accessory. Temperature measurements were calibrated by using an ethylene glycol standard and the temperature–shift correlations of Van Geet.[15]

α,β,γ,δ-Tetrakis(2-methoxyphenyl)porphyrin (1) was prepared as described in the literature.[8] At 93 °C the spectrum of the methoxy region of 1 featured resonances at δ 3.66, 3.67, 3.70, 3.71, and 3.72 in the ratio of intensities of 0.08:0.13:0.27:0.37:0.15. These resonances were assigned to the four stereoisomers as described in the text. The chemical shifts were temperature dependent in the region 40–130 °C, and the temperature dependence was extrapolated into the region of coalescence. For the line-shape analysis,[9] the relationships of the rate constants for isomerization were derived as discussed in the text, and the relative exchange probabilities for the six resonances were assigned in accord with these relationships. The resulting calculated line shapes were compared visually with the experimental spectra, and adequate matches were obtained (Figure 1). Thus, the resonance assignments and the assumption of approximately equal rates of rotation for the four aryl rings of the C_s isomer at a given temperature are consistent with the experimental data. The rate constants obtained from the line-shape analysis were used to calculate free energies of activation for rotation of a single aryl ring in each isomer. These barriers were all within ±0.2 kcal/mol of an average value of $\Delta G^{\ddagger}_{433}$ = 25.9 kcal/mol.

α,β,γ,δ-Tetrakis(2-methoxyphenyl)porphyrin dication (2) was prepared by addition of excess trifluoroacetic acid to a nitrobenzene-d_5 solution of 1. ^{1}H NMR resonances in the methoxy region were observed at δ 3.83, 3.86, and 3.88 in a ratio of 0.22:0.53:0.25, respectively. These were assigned as follows: δ 3.83 (C_{4v} and C_s), δ 3.86 (C_s and C_{2h}), and δ 3.88 (C_s and D_{2d}). The relative populations of the resonances were assigned as 0.10:0.12:0.25:0.28:0.12:0.13, respectively. Line-shape analysis performed as described for 1 yielded the results given in the text.

As mentioned above, the assignments of resonance positions and populations to individual isomers given for 1 and 2 (as well as 3 and 4; see below) are not unique, and other assignments would also be consistent with the results and in some cases would yield slightly different energies of activation for each isomerization. However, since these population and chemical shift differences are small and have relatively little effect on the free energies of activation, the average rotational barrier for an aryl ring would be only slightly affected by different assignment patterns. For example, since only three resonances were observed for **2**, a variety of assignments are possible, The population ratios used were chosen because they are very near the statistically expected ratios.[6a] Ratios very close to the statistical ones are found for other ortho-substituted porphyrins,[5b,6a] as well as for 1 (see above), whose spectrum has only one accidental isochrony and may therefore be assigned with less ambiguity. If the relative populations are alternatively assigned as 0.02:0.20:0.40:0.13:0.20:0.05, respectively, the ratio of isomers is far from statistical. However, a fair fit to the experimental line shapes may be obtained, and the rate data yield an average value of $\Delta G^{\ddagger}_{388}$ = 22.7 kcal/mol for the rotation of one aryl ring. Similarly, if one chooses a different assignment pattern wherein all the resonances for the C_s isomer appear at a single frequency (δ 3.83 (C_{4v} and D_{2d}), δ 3.86 (C_s), δ 3.88 (C_{2h})), line-shape analysis yields a rather poor fit to the experimental spectra, but even this assignment pattern yields an average barrier for rotation of a single aryl ring of $\Delta G^{\ddagger}_{388}$ = 23.4 kcal/mol. Finally, simply treating the spectrum as three coalescing resonances where each of the outer lines exchanges with the central resonance yields an average free energy of activation for exchange of $\Delta G^{\ddagger}_{388}$ = 22.8 kcal/mol.

Thus, the values for free energies of activation reported in the text are not as reliable as those which could be obtained if all resonances could be resolved and assigned with certainty. This is especially the case for **2** and **4**, whose spectra feature three accidental isochronies. However, even in the case of **2**, the alternative assignment patterns discussed above yield values for the free energy of activation for rotation which are within ±0.4 kcal/mol of the reported value, and the reported values are therefore judged to be useful estimates of the actual energy barriers. It should also be noted that much of the discussion in the text deals with differences in energies of activation between **1** and **3** and between **2** and **4**. The spectra for **1** and **3** are very similar in the ortho methoxy region, as are those for **2** and **4**. In addition, analogous assignments of resonance positions and populations were made within each pair. Thus, these differences are undoubtedly significant, even though the absolute values of the free energies of activation have rather large limits of error for a complete line-shape analysis.

α,β,γ,δ-Tetrakis(2,4-dimethoxyphenyl)porphyrin (3) was prepared from 2,4-dimethoxybenzaldehyde and pyrrole, using the method reported for 1:[8] ^{1}H NMR (CDCl$_3$) δ 3.56 (12 H, m, ortho OCH$_3$), 4.09 (12 H, m, para OCH$_3$), 6.90 (8 H, m, aromatic H), 7.89 (4 H, m, aromatic H), 8.74 (8 H, s, β-pyrrole H). Anal. Calcd for $C_{52}H_{46}N_4O_8$: C, 73.05; H, 5.42. Found: C, 72.78; H, 5.63.

At 116 °C the ^{1}H NMR spectrum of the ortho methoxy region in nitrobenzene-d_5 solution featured resonances at δ 3.72, 3.73, 3.76, 3.77, and 3.79. The ratios of intensities were 0.09:0.14:0.22:0.41:0.14, respectively. These resonances were assigned by using the same pattern as was employed for 1, and a line-shape analysis similar to that described for 1 yielded the results reported in the text.

α,β,γ,δ-Tetrakis(2,4-dimethoxyphenyl)porphyrin dication (4) was prepared by addition of a large excess of trifluoroacetic acid to a nitrobenzene-d_5 solution of **3**. The ^{1}H NMR spectrum of the ortho methoxy region at 68 °C featured resonances at δ 3.91, 3.95, and 3.98 in the ratio 0.18:0.52:0.30. These resonances were assigned by using the same pattern as was employed for **2**, and a line-shape analysis yielded the results reported in the text.

Registry No. 1, 29114-94-1; **2**, 70145-32-3; **3**, 70145-33-4; **4**, 70145-34-5; 2,4-dimethoxybenzaldehyde, 613-45-6; pyrrole, 109-97-7.

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