On the Negligible Impact of Ruffling on the Electronic Spectra of Porphine, Tetramethylporphyrin, and Perfluoroalkylporphyrins

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Abstract: In the first part of this paper, the syntheses, structural characterization, molecular modeling, and electronic spectra for planar and nonplanar perfluoroalkylated porphyrins, $(R_f)_4P$'s, are reported. These studies demonstrate that the intrinsic substituent effect of the perfluoroalkyl group on the long-wavelength electronic spectrum of porphyrins is substantial, and similar (in magnitude) to that of a phenyl ring. Moreover, it is shown that out-of-plane distortion of $(R_f)_4P$'s has a negligible impact on their electronic spectra. These data bolster the findings of our earlier work and demonstrate that nonplanarity of $(R_f)_4P$'s *does not result in a red-shift in their optical spectra*. In the second part of this paper, time-dependent density functional spectral calculations (B3LYP/6-311G*/TD) for porphine, 5,10,15,20-tetrakis(trifluoromethyl)porphyrin, and 5,10,15,-20-tetramethylporphyrin in a variety of ruffled conformations are reported. The results of these studies indicate that (1) substantial ruffling of porphyrins has a negligible effect upon their electronic spectra, (2) similarly small effects upon electronic spectra are predicted if electron-withdrawing or electron-releasing groups decorate the porphyrin periphery, (3) for sterically encumbered porphyrins, ruffling can actually result in hypsochromic shifts in various absorption bands, and (4) the bulk of the red-shift commonly thought to be due to nonplanar distortion actually arises from other substituent effects. These results pose serious challenges to previous theoretical and empirical studies that have sought to find a cause-and-effect relationship between nonplanarity and electronic spectra in porphyrins.

Introduction

Toward the goal of understanding the biological relevance of nonplanar distortion in protein-bound porphyrinoid pigments, considerable effort has been directed toward the synthesis and spectroscopy of highly substituted, conformationally constrained model compounds.[1−12] Such highly substituted porphyrins adopt nonplanar structures; two of the most common deformation modes[13] are shown in Figure 1, along with labeling schemes

Figure 1. Labeling diagram and two principal distortion modes for porphyrins. Closed and open circles represent displacement above and below the mean plane, respectively.

for the macrocycle. Numerous studies on *meso*-substituted, sterically encumbered nonplanar porphyrins demonstrate that these compounds exhibit bathochromically shifted absorption spectra relative to standard planar porphyrins such as 5,10,15,-20-tetraphenylporphyrin (TPP) and 2,3,7,8,12,13,17,18-octa-ethylporphyrin (OEP).[14] The number of such studies has grown to the point that it is generally accepted that a red-shift in the long-wavelength region of the optical spectrum is the signature of porphyrin ring distortion, as is clearly reflected in current reviews.[15−17] However, an often neglected potential pitfall in

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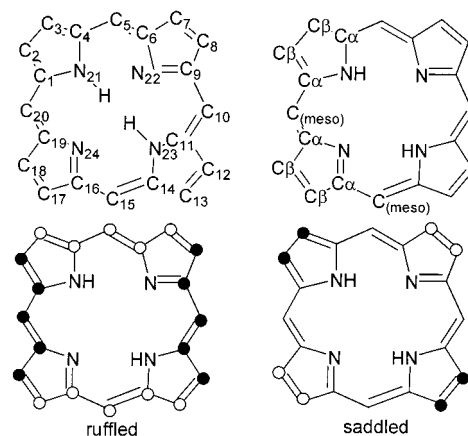(13) Scheidt, W. R.; Lee, Y. J. *Struct. Bonding* **1987**, *64*, 1−70.

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studying sterically encumbered model compounds is that substituents introduced to cause nonplanar macrocycle distortion perturb the electronic structure and deform the porphyrin ring in a manner that is distinct from nonplanarity. If these substituent effects are important, one can neither extrapolate the electronic effects of porphyrin ring distortion in models to those of their biologically relevant cognates nor logically infer a cause-and-effect relationship between nonplanarity and spectral properties. In this article we show conclusively that, for at least one common deformation mode, porphyrin ring ruffling, these hitherto neglected substituent effects both dwarf the stereoelectronic consequences of nonplanar distortion and are the principal, and perhaps only, cause of experimentally observed bathochromic spectral shifts previously thought to have their origins in nonplanarity. The logical relationship between ruffling and red-shifts is shown to be one of collateral contiguity rather than cause-and-effect.

5,10,15,20-Tetrakis(perfluoroalkyl)porphyrins, $(R_f)_4$P's, are unusual in that they possess highly distorted macrocycle conformations yet show ground- and excited-state electronic properties that are virtually identical to those of their planar counterparts, such as TPP.[18,19] The lowest energy absorption band ($Q_x(0,0)$) for 5,10,15,20-tetrakis(heptafluoropropyl)porphyrin, $(C_3F_7)_4$P, occurs at 647 nm in CH_2Cl_2, making $(C_3F_7)_4$P comparable to TPP (646 nm) in this regard. At the time these data were reported, it was noted that they were incompatible with the prevailing *Weltanschauung* that nonplanar distortion in porphyrins is equated with bathochromically shifted electronic spectra.[20] Furthermore, these data indicated that substituent effects were major factors contributing to the red-shift in other conformationally constrained porphyrin models and, by extension, raised questions regarding the biological relevance of current structure/optoelectronic property relationships derived from studies of nonplanar heme models.

In response, Parusel, Wondimagegn, and Ghosh have recently countered that $(R_f)_4$P's do, in fact, possess substantially red-shifted optical spectra resulting from their nonplanar macrocycle geometries.[21] After comparing the results of electronic spectral calculations of zinc porphine in its optimized, planar form and in two nonplanar geometries derived from optimized structures of zinc tetrakis(trifluoromethyl)porphyrin, they conclude that the reported absence of red-shifts in $(R_f)_4$P electronic spectra merely "stems from the questionable use of tetraphenylporphyrin" (instead of porphine [$Q_x(0,0) = 614$ nm]) "as a zero level for spectral shifts". This controversy concerning perfluoroalkylated porphyrins serves as a useful starting point to reexamine the spectroscopic consequences of ring distortion in these compounds, and in porphyrins generally.

It is a matter of simple empirical fact that the electronic spectra of ruffled $(R_f)_4$P's differ substantially from the electronic spectrum of the unsubstituted parent compound. The crux of the controversy lies in assigning the relative contributions of substituent effects and porphyrin ring ruffling to the observed difference. To draw these distinctions, one must first recognize that substituents have conformational consequences (such as rehybridization) that are distinct from nonplanarity. Sterically demanding substituents located at the porphyrin ring periphery introduce significant changes in the bond lengths and bond angles of the macrocycle; these bonding alterations occur regardless of whether the ring distorts from planarity. Relief of strain resulting from in-plane nuclear reorganization (IPNR) is the driving force for nonplanarity in highly substituted free base porphyrins. Importantly, nonplanarity induced by IPNR is not necessarily related to that observed in proteins, where nonbonded peptide−pigment interactions and contraction of the core around a metal ion lead to macrocycle distortion. It is difficult to delineate the relative impact of electronic substituent effects, nonplanarity, and IPNR induced by perfluoroalkyl groups in $(R_f)_4$P's upon spectroscopic properties directly; nevertheless, this problem may be approached empirically and theoretically, and both tacks are described below. The first part of this paper describes the syntheses, structural characterization, molecular modeling, and electronic spectra of planar and nonplanar perfluoroalkylated porphyrins. These studies enable empirical assessment of the electronic and steric substituent effects in the absence and in the presence of nonplanar distortion and serve to disentangle how IPNR, electronic substituent effects, and nonplanarity alter porphyrin spectroscopic properties. This work demonstrates that the intrinsic substituent effect of the perfluoroalkyl group on the long-wavelength electronic spectrum of porphyrins is substantial, and similar in magnitude to that of a phenyl ring. Moreover, it is shown that the out-of-plane distortion of $(R_f)_4$P's has a negligible impact on their electronic spectra. The second part of this paper reports theoretical studies likewise aimed at deconvolution of the substituent and conformational effects of the perfluoroalkyl substituent. We report time-dependent density functional calculations (B3LYP/6-311G*/TD) of optimized nonplanar $(R_f)_4$P in three nonplanar conformations. A comparison of these studies with similar studies of porphine (P) and 5,10,15,20-tetramethylporphyrin (TMP) indicates that the effect of porphyrin ruffling upon electronic spectra is generally small and can result in either bathochromic or hypsochromic shifts, depending upon the nature of the substituents. These data bolster the findings of our earlier work and demonstrate that nonplanarity of $(R_f)_4$P's *results in a negligible change in their optical spectra.* These data also indicate that increased ruffling can be correlated with hypsochromic shifts in sterically hindered ruffled model compounds, suggesting that observed bathochromic shifts commonly attributed to nonplanar distortion arise largely from IPNR. These studies help us explain why conflicting data are obtained from theoretical studies in this area, and they indicate that the majority of the differences in electronic spectra generally thought to be caused by ruffling of porphyrins may, in fact, be due to substituent artifacts which are absent in biology.

Syntheses

The syntheses of 5,15-bis(heptafluoropropyl)porphyrin ($(C_3F_7)_2$P) and 5,10,15-tris(heptafluoropropyl)porphyrin ($(C_3F_7)_3$P) are shown in Scheme 1. Following the MacDonald approach,[22,23] the syntheses employed substituted dipyrrylmethane derivatives to provide regiochemical control. The appropriate dipyrrylmethane precursors cyclize to por-

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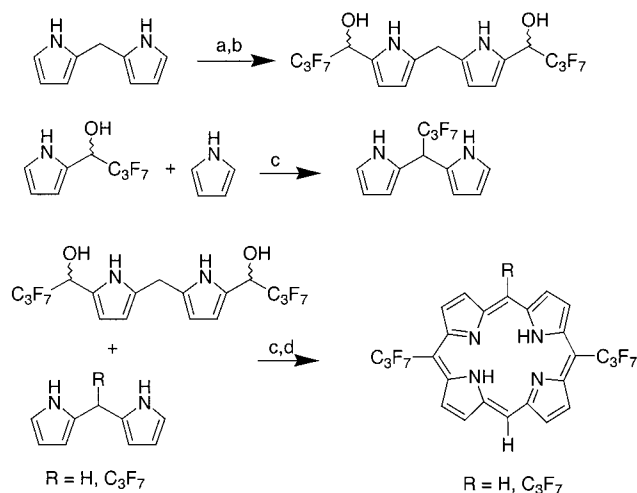
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Scheme 1[a]

[a] Conditions: (a) heptafluorobutyryl chloride, triethylamine, THF, 0 °C; (b) NaBH₄, MeOH; (c) pyrrole, *p*-toluenesufonic acid, benzene heated at reflux; (d) DDQ.

phyrinogens under typical dry, acidic conditions[18,24] and are subsequently oxidized with DDQ to give $(R_f)_2P$ and $(R_f)_3P$ in low (5%) but acceptable yield. Full experimental procedures are given in the Supporting Information.

Structure

Crystals of $(C_3F_7)_3P$ grown from CHCl₃ were suitable for X-ray diffraction. Perspective drawings from the crystal structure determination are shown in Figure 2.[25] The perfluoropropyl group at C10 is disordered due to equal occupancy of two possible extended conformations within the crystal lattice. This structure is quite informative in that half of the macrocycle is essentially flat and half adopts a modestly nonplanar geometry. The maximum deviation of the pyrrole carbons C7, C8, C12, and C13 from the mean porphyrin plane is 0.209 Å, and no other ring atom is displaced more than 0.11 Å. These data suggest that perfluoropropyl groups at the 5- and 15-postions do not provide sufficient steric bulk to cause the porphyrin ring to deviate from planarity, while introduction of the third *meso*-perfluoropropyl group buckles the ring. Examination of the C–C bond lengths and the internal bond angles at the *meso* positions provides evidence for this postulated additive steric effect. At the unencumbered *meso* carbon atom (C20), the average C–C bond length is 1.382(8) Å and the internal bond angle (C1–C20–C19) is 130.3(4)°. In contrast, the corresponding C–C bonds at the perfluoroalkylated positions are somewhat longer (>1.40 Å). In addition, the average internal bond angles are contracted dramatically at C5 and C15 (C4–C5–C6 = 124.0(4)°, C14–C15–C16 = 125.3(4)°), indicating that the pyrrole rings have rotated away from the bulky perfluoropropyl groups. While this steric pressure is accommodated at C2O by expanding the C19–C20–C1 bond angle, the presence of the perfluoroalkyl group at C10 causes additional angle strain, the ring buckles, and the C9–C10–C11 bond angle contracts to 127.3(4)°.

Molecular Modeling

Molecular modeling studies were conducted with four goals in mind: to verify that the X-ray structure of $(C_3F_7)_3P$ is a reasonably accurate description of a local conformational minimum, to determine the degree of nonplanarity caused by sequential perfluoroalkyl group substitution, to illustrate other conformational consequences of incorporating bulky substituents

in porphyrins, and to assess the accuracy of the DFT method employed to model the empirical geometries. Optimized geometries for porphine, $(C_2F_5)_1P$, $(C_2F_5)_2P$, $(C_2F_5)_3P$, and $(C_2F_5)_4P$ were obtained by using hybrid density functional calculations (B3LYP) and a minimal basis set (3-21G*).[26] The perfluoroalkyl groups were truncated to perfluoroethyl in order to conserve computational effort.

Two compounds from the homologous series, $(C_3F_7)_3P$[27] and $(C_3F_7)_4P$,[18] have been structurally characterized. A perspective drawing from the X-ray determination of ruffled $(C_3F_7)_4P$, drawn from the Cambridge Crystallographic database,[28] is shown in Figure 3, juxtaposed with the calculated, optimized ruffled structure. Both structures have similar core sizes (N–N_av = 4.06 Å calc; 4.08 Å X-ray), transannular distances (C5–C15 = 6.76 Å calc; 6.75 Å X-ray), and peripheral nonbonded H–F contacts (average = 2.15 Å calc; 2.24 Å X-ray). The graph showing the degree of nonplanarity of the porphyrin ring (maximum deviation = 0.498 Å calc; 0.493 Å X-ray) demonstrates that the DFT method employed provides a reasonable model of the structure of this compound using the small 3-21G* basis set.

The calculated structure of $(C_3F_7)_3P$ is shown in Figure 2 beside the crystal structure determination. The overall nonplanarity of the empirical structure is well described by the modeling; maximum displacements from the ring mean plane for the trisubstituted structures are 0.214 and 0.209 Å for the calculated and empirical structures, respectively. However, the type of distortion mode observed in the X-ray crystal structure is not reproduced well in the model, as is clear from inspection of the lower half of Figure 2. The shallowness of the conformational energy surface for the calculated porphyrin, along with the susceptibility of porphyrins to crystal packing distortions, makes the differences in the calculated and empirical geometries understandable. Given these variables, the modeling appears to mimic reasonably well the degree of nonplanar distortion seen for these perfluoroalkylated porphyrins.

The calculated structures of $(C_2F_5)_1P$ and $(C_2F_5)_2P$ demonstrate the striking degree of in-plane nuclear reorganization in the porphyrin ring caused by the bulky substituents (Figure 4). In these structures, introduction of a perfluoroethyl group at a *meso* position is associated with a significant contraction of the interior bond angles (C4–C5–C6) at the substituted positions: 122.9° for $(C_2F_5)_1P$ and 122.4° for $(C_2F_5)_2P$. The effect of these changes is to elongate the macrocycles along their C5–C15 axes. For $(C_2F_5)_1P$, the distance from C5 to C15 is 7.14 Å, while the distance from C10 to C20 is 6.65 Å. The ellipticity is slightly larger in $(C_2F_5)_2P$: C5–C15 is 7.26 Å and C10–C20 is 6.54 Å. Although considerable IPNR caused by the C_2F_5 groups is evident, the maximum and average deviations from the least-squares plane in these calculated structures are only 0.16 and 0.065 Å for $(C_2F_5)_1P$ and 0.09 and 0.049 Å for $(C_2F_5)_2P$, respectively. Given the reasonable degree of success of this theoretical method to mimic the out-of-plane distortion seen in $(C_3F_7)_3P$ and $(C_3F_7)_4P$, it is reasonable to consider $(C_3F_7)_2P$ to be essentially planar.

The modeling and structural studies described in this work are consistent with one another: as the number of appended *meso*-perfluoroalkyl groups increases from 2 to 4, the conformation of the porphyrin ring changes from planar (or nearly so), to slightly nonplanar, to substantially ruffled. Together with porphine, this set of molecules constitutes an appropriate

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(25) Crystal data for 5,10,15,-tris(heptafluoropropyl)porphyrin: $C_{32}H_{10}F_{28}N_4$ crystallizes in the monoclinic space group $P2(1)/c$ with $a = 17.4086(6)$ Å, $b = 18.4656(6)$ Å, $c = 9.1527(3)$ Å, $\alpha = 90°$, $\beta = 95.4050(10)°$, $\gamma = 90°$, $V = 2929.1(2)$ Å³, $Z = 4$, and $d_{calc} = 1.847$ Mg/m³. Refinement converged to $R_1 = 0.0759$ and $R_2 = 0.1023$.

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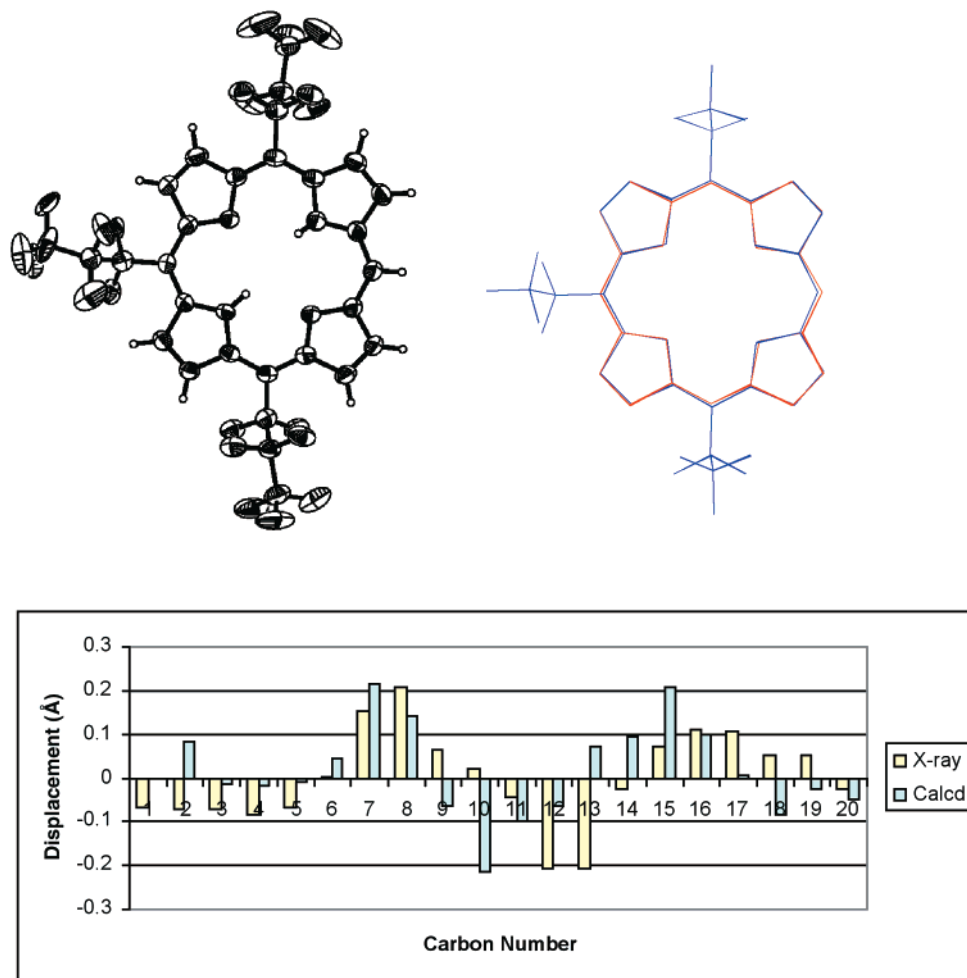
Figure 2. Comparison of X-ray and calculated structures for 5,10,15-tris(perfluoroalkyl)porphyrins. (Left) A perspective drawing of the X-ray crystal structure of $(C_3F_7)_3P$. (Right) The calculated structure of $(C_2F_5)_3P$ is shown in blue superimposed upon the calculated structure of porphine (shown in red). The graph at the bottom of the figure compares the out-of-plane displacements (in angstroms) at the macrocycle periphery for the X-ray (yellow) and calculated (blue) structures.

empirical instrument to extricate the effect of nonplanar distortion from other substituent effects in this system.

Optical Spectroscopy

The wavelengths for the $Q_x(0,0)$ transitions of porphine (614 nm, 2.02 eV), $(R_f)_2P$ (628 nm, 1.98 eV), $(R_f)_3P$ (636 nm, 1.95 eV), and $(R_f)_4P$ (647 nm, 1.92 eV) were determined from electronic spectra of the compounds in CH_2Cl_2. For comparison, the spectra of 5,15-diphenylporphyrin[29] (DPP) ($Q_x(0,0) = 629$ nm, 1.97 eV), 5,10,15-triphenylporphyrin ($Q_x(0,0) = 641$ nm, 1.93 eV),[30] and TPP ($Q_x(0,0) = 646$ nm, 1.92 eV) were recorded under identical conditions; the data are plotted in Figure 5. The addition of two perfluoroalkyl or two phenyl groups results in a similar red-shift in the electronic spectrum of porphine; significantly, neither of these compounds is substantially nonplanar. These data indicate that there is a considerable substituent effect associated with the perfluoroalkyl group that is independent of nonplanar conformational change and is similar in magnitude to that of a phenyl group. Further substitution (of either phenyl or perfluoroalkyl groups) leads to nearly linearly increasing bathochromic shifts in the $Q_x(0,0)$ absorption band; there is no obvious bathochromic shift attributable to the onset of nonplanar distortion. In summary, it appears that the

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substituent effect of a perfluoroalkyl at the porphyrin *meso* position upon the long-wavelength region of the optical spectrum is responsible for most, if not *all*, of the observed red-shift in the spectrum; any alteration of the long-wavelength electronic spectrum due to a conformational transition from planar to nonplanar perfluoroalkylated porphyrins is insignificant in comparison to other substituent effects. Furthermore, tetraphenylporphyrin seems an appropriate benchmark by which to gauge the spectral shifts in perfluoroalkylated porphyrins, since the impact of successive phenyl or perfluoroalkyl group substitution upon the macrocycle has a comparable effect on the spectroscopic properties. Given that nearly identical bathochromic shifts in the spectrum of porphine are observed for DPP and $(R_f)_2P$ in the absence of significant nonplanar distortion, and that nearly identical spectral shifts are recorded upon additional substitution (DPP → TPP and $(R_f)_2P$ → $(R_f)_4P$) that induces significant nonplanarity only in $(R_f)_4P$, it is clear that there are no empirical data here to support the notion that there is a significant red-shift in the optical spectrum due to nonplanar distortion of $(R_f)_4P$'s.

It is informative to analyze the analogous structural and spectroscopic data for the corresponding zinc(II) derivatives. $Zn(C_3F_7)_4P \cdot pyridine$ exhibits a ruffled structure in which the *meso* positions are displaced 0.405 Å, on average, from the mean porphyrin plane.[19] Despite this extensive ruffling, the longest-wavelength optical transition (THF, 652 nm, 1.902 eV) occurs
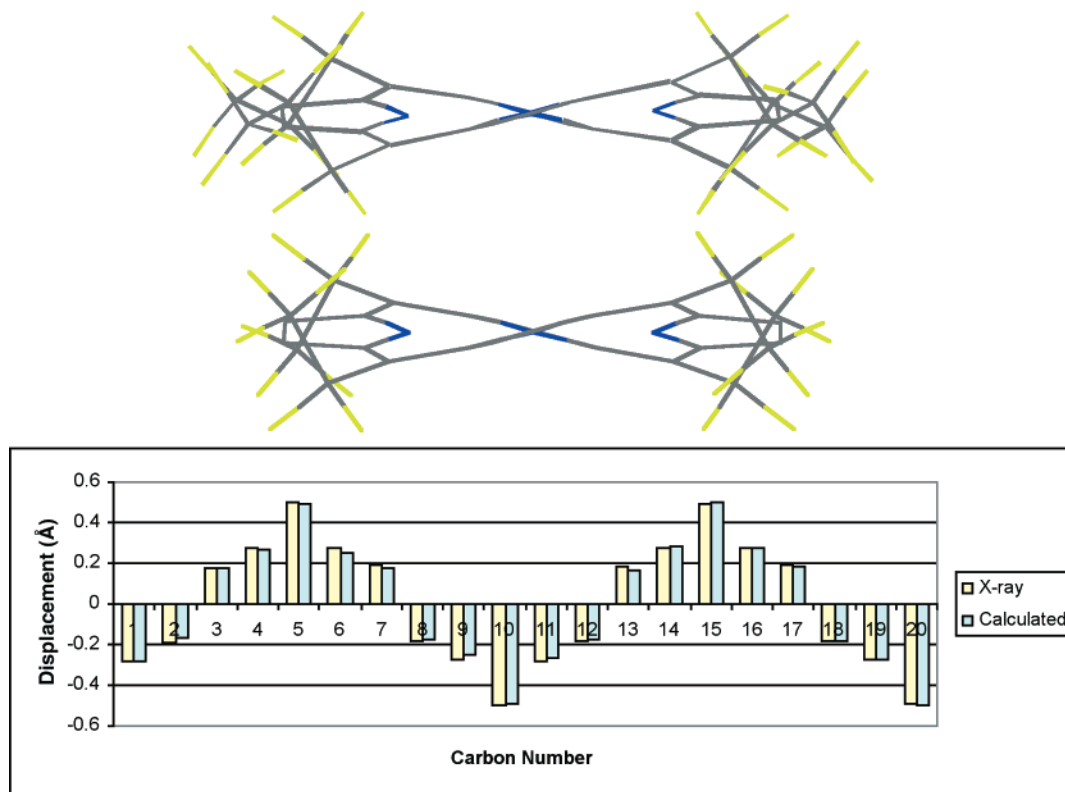
Figure 3. Comparison of the X-ray structure of $(C_3F_7)_4P$ (top) and calculated structure of $(C_2F_5)_4P$ (bottom) looking down the N22−N24 axis. Hydrogen atoms have been removed for clarity. The graph compares the out-of-plane displacements (in angstroms) at the macrocycle periphery for the X-ray (yellow) and calculated (blue) structures.
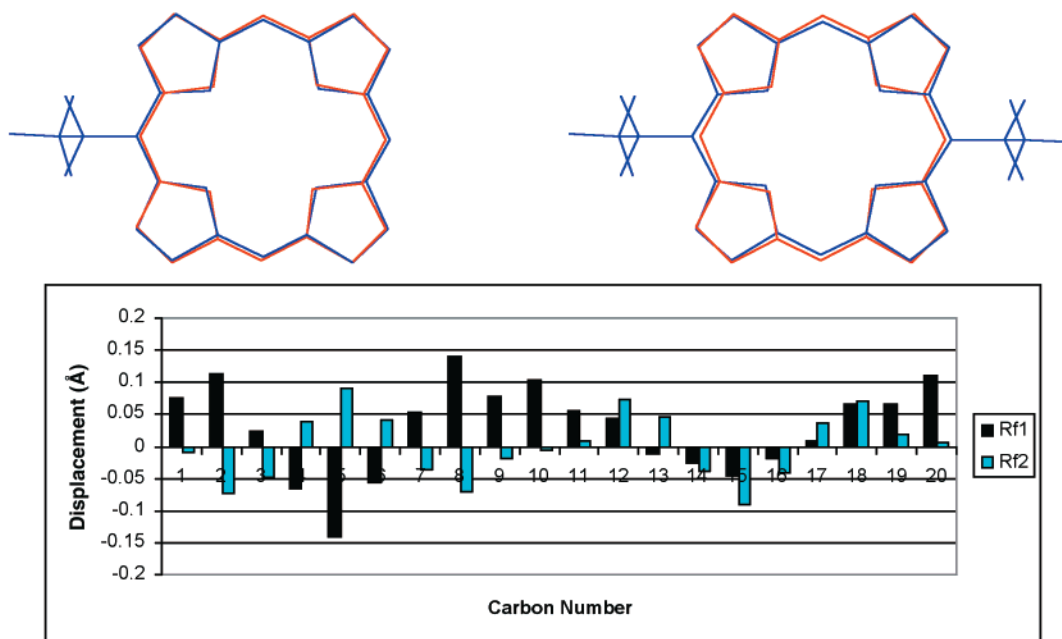

Figure 4. Calculated structures of $(C_2F_5)_1$ and $(C_2F_5)_2$. (Top) The structures overlaid upon the calculated structure of porphine. (Bottom) The degree of out-of-plane displacement (in angstroms) at each carbon atom in the porphyrin ring.

at precisely the same energy as the corresponding transition in (planar) ZnTPP under identical conditions (THF, 652 nm, 1.902 eV).[19] Thus, the distortion in the structure of $Zn(C_3F_7)_4P$ is not reflected in a red-shift versus the planar benchmark ZnTPP. Once again, the available empirical evidence does not support the argument that the electronic spectra of perfluoroalkylated porphyrins differ from the spectrum of porphine because of macrocycle nonplanarity. The observed spectral shift arises from substituent effects that are independent of nonplanar distortion;

the maxim that bathochromic optical absorption spectra are electronic signatures of nonplanar distortion holds neither for $(R_f)_4P$'s nor for $Zn(R_f)_4P$'s.

Density Functional Theory

In the empirical studies described above, the effect of a perfluoroalkyl group upon porphyrin optical spectroscopy was seen to be comparable to that of a phenyl group and largely independent of macrocycle conformation. However, due to the
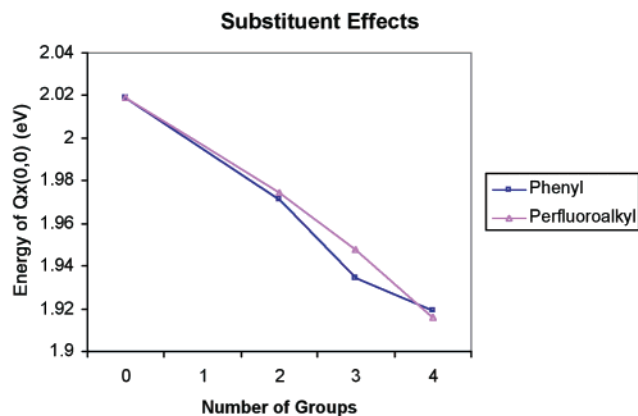
Figure 5. Plot comparing the impact of increasing substitution with phenyl or perfluoroalkyl groups upon the lowest energy electronic absorption band of porphine. Spectra were recorded in methylene chloride.

Table 1. Structural Details from B3LYP/6-311G* Calculations of P, TMP, and (CF$_3$)$_4$P

compd[a]	ruffling angle[b] (deg)	relative energy[c] (kcal/mol)	core size[d] (Å)	β-oop[e] (Å)	meso-oop[f] (Å)
(CF$_3$)$_4$P	28	0.28	4.09	0.179	0.497
(CF$_3$)$_4$P	34	0.00	4.06	0.218	0.590
(CF$_3$)$_4$P	40	0.31	4.02	0.254	0.678
TMP	14.2	0.00	4.13	0.095	0.250
TMP	28	0.97	4.07	0.182	0.470
TMP	40	3.95	4.00	0.254	0.656
P	0	0.00	4.15	0.000	0.000
P	28	4.59	4.08	0.180	0.445
P	40	9.82	4.01	0.252	0.629
P$_{(CF_3)_4P}$	28	8.07	4.09	0.179	0.497
P$_{(CF_3)_4P}$	34	10.22	4.06	0.218	0.590
P$_{(CF_3)_4P}$	40	12.46	4.02	0.254	0.678
P$_{TMP}$	14.2	3.15	4.13	0.095	0.250
P$_{TMP}$	28	6.48	4.07	0.182	0.470
P$_{TMP}$	40	11.63	4.00	0.254	0.656

[a] The first nine entries are full geometry optimizations. The structures featuring 28° and 40° ruffling angles were obtained by using dihedral constraints, as outlined in the text. For the final six entries, porphine was calculated in the conformations derived from the (CF$_3$)$_4$P and TMP optimizations after replacement of the substituents with hydrogen atoms, as described in the text. [b] Defined as the dihedral angle between *anti* pyrrole rings. The absolute value is reported. [c] Energies are calculated relative to that of the corresponding fully optimized, unconstrained compound. For porphine, the lowest energy structure was planar; for (CF$_3$)$_4$P and TMP, ruffled minimum energy conformations were obtained, as indicated. [d] The core size is defined as the average of the N21–N23 and N22–N24 distances. [e] The out-of-plane displacement at the porphyrin β positions was calculated by summing the distance of carbons 2, 3, 7, 8, 12, 13, 17, and18 from the porphyrin least-squares plane and dividing by 8. [f] The out-of-plane displacement at the porphyrin *meso* positions was calculated by summing the distance of carbons 5, 10, 15, and 20 from the porphyrin least-squares plane and dividing by 4.

disparate electronic nature of phenyl and perfluoroalkyl substituents and the divergent electronic ground and excited states of the resultant porphyrins, one could question whether the negligible impact of ruffling observed in these studies is an isolated and serendipitous occurrence, or is a manifestation of a more general phenomenon. To ascertain theoretically the effect of ruffling upon the electronic spectra of porphyrins generally, and (R$_f$)$_4$P's specifically, we performed higher level DFT geometry optimizations (B3LYP/6-311G*) and time-dependent density functional theory calculations (B3LYP/6-311G*/TD) on porphine (P), 5,10,15,20-tetramethylporphyrin (TMP), and a truncated perfluoroalkylated derivative, 5,10,15,20-tetrakis-(trifluoromethyl)porphyrin ((CF$_3$)$_4$P). The choice of trifluoromethyl instead of trifluoroethyl as the appended perfluoroalkyl group was made to facilitate comparison of these results with earlier work[21] and to save computational effort. All optimizations were performed without symmetry constraints; ruffled geometries were obtained by constraining four transannular dihedral angles (C1–N21–N23–C14, etc.) to either 28° or 40°. It deserves comment that the structures obtained from the 40° dihedral constraints exhibit more out-of-plane displacement than any ruffled porphyrin or metalloporphyrin yet observed in a protein crystal structure determination.

For porphine, the lowest lying planar structure and two ruffled conformations were fully optimized. The 28° structure obtained lies 4.60 kcal/mol above the energy of the planar ground state. The second, more highly ruffled structure (ruffling dihedral angle = 40°) was calculated to lie 9.82 kcal/mol above the planar ground state. Further structural data for these compounds are summarized in Table 1. Similar geometry optimizations were performed for TMP, with the exception that the optimized (unconstrained) ground-state structure was slightly ruffled (ruffling angle = 14.2°) due to steric interactions of the methyl substituents with the β-hydrogen atoms at the porphyrin periphery. The data are also summarized in Table 1. The relatively small energetic cost associated with ruffling TMP to a dihedral angle of 40° (3.96 vs 9.82 kcal/mol for P) indicates that there is an exchange of IPNR for torsional strain as the porphyrin is ruffled; nonplanar distortion alleviates IPNR, and the potential energy surface is shallower than that in the unsubstituted parent compound. For (CF$_3$)$_4$P, the ground-state optimized geometry is significantly more ruffled (ruffling angle = 34˚) than it is for the same calculation at a lower basis set. This ruffling angle is slightly larger than that seen in the available crystal structure determination (ruffling angle = 28°). Two additional optimized structures were obtained by using

transannular dihedral constraints of 40° (more ruffled) and 28° (less ruffled). Again, the shallowness of the potential energy surface is indicated by the small endotherms associated with macrocycle deformation.

Finally, we used the previously employed strategem[31] whereby the CF$_3$ groups from the three calculated ruffled structures of (CF$_3$)$_4$P were replaced by hydrogen atoms (C–H bond length = 1.08 Å) at the *meso* positions to yield porphine in the (CF$_3$)$_4$P geometry. Single-point calculations on P were performed at each geometry. An identical process was used to calculate P in the ruffled TMP geometries. The structural data for all of these calculations are summarized in Table 1.

Two parameters from Table 1 demonstrate that IPNR plays a significant role in the ruffled *meso*-substituted compounds TMP and (CF$_3$)$_4$P. First, the degree of out-of-plane distortion at the *meso* positions for TMP and (CF$_3$)$_4$P exceeds that seen in the comparably ruffled optimized structures of porphine. Second, porphine in its optimized ruffled geometry is significantly more stable than it is calculated to be in its corresponding TMP- or (CF$_3$)$_4$P-derived ruffled conformations. Although IPNR accounts for only roughly 20–40% of the total strain energy of porphine in the latter conformations, its effect on the spectroscopic properties of the distorted macrocycle is significant (vide infra).

(31) In ref 21, the authors state that "(t)he artificially ruffled conformation of ZnP was derived from the ruffled optimized geometry of ZnP(CF$_3$)$_4$ by replacing the CF$_3$ groups with H, with the H's lying exactly along the original C(meso)–C(CF$_3$) vectors and C(meso)–H bonds being set to 1.08." The authors then compare the calculated results from ruffled ZnP and planar (fully optimized) ZnP and attribute all of the difference in the electronic spectrum to nonplanar distortion.

Table 2.   Electronic Structure Calculations (B3LYP/6-311G*/TD) of $(CF_3)_4P$, TMP, and P

compd[a]	ruffling angle (deg)	energy (eV)				transition wavelengths[b] (nm)
		HOMO − 1	HOMO	LUMO	LUMO + 1	
$(CF_3)_4P$	28	−6.572	−6.354	−3.596	−3.544	567.0, 531.3, 404.9, 398.8
$(CF_3)_4P$	34	−6.570	−6.350	−3.602	−3.540	568.0, 532.6, 404.4, 397.9
$(CF_3)_4P$	40	−6.569	−6.346	−3.607	−3.537	569.0, 533.9, 404.0, 397.5
TMP	14.2	−5.418	−4.996	−2.401	−2.341	592.0, 547.0, 389.4, 373.8
TMP	28	−5.399	−4.983	−2.378	−2.343	591.7, 549.5, 390.2, 372.7
TMP	40	−5.375	−4.968	−2.350	−2.341	590.7, 551.9, 390.9, 373.8
P	0	−5.542	−5.407	−2.485	−2.472	543.9, 509.8, 372.3, 362.2
P	28	−5.522	−5.401	−2.483	−2.461	545.2, 511.9, 372.9, 362.9
P	40	−5.504	−5.396	−2.481	−2.453	546.5, 514.0, 373.7, 363.9
$P_{(CF_3)_4P}$	28	−5.476	−5.381	−2.492	−2.466	553.7, 519.9, 374.2, 361.8
$P_{(CF_3)_4P}$	34	−5.463	−5.374	−2.488	−2.456	554.1, 520.7, 374.3, 361.4
$P_{(CF_3)_4P}$	40	−5.455	−5.369	−2.487	−2.448	554.5, 521.6, 374.5, 361.5
P_{TMP}	14.2	−5.520	−5.424	−2.510	−2.486	548.2, 513.5, 375.7, 366.7
P_{TMP}	28	−5.503	−5.415	−2.508	−2.474	549.4, 515.3, 376.0, 366.7
P_{TMP}	40	−5.482	−5.405	−2.500	−2.464	550.8, 517.5, 376.9, 367.9

[a] Geometries are identical to those described in Table 1. [b] Calculation details are given in the Supporting Information.

Calculated Electronic Spectra

Electronic spectral calculations for all of the computed geometries are summarized in Table 2. It is evident from inspection of Table 2 that ruffling has a small impact on the electronic spectrum of porphine, even at relatively large deviations from planarity (0.65 Å = maximum displacement). The four frontier orbitals move to higher energy with increasing distortion, and modest bathochromic shifts are evident in the four calculated lowest lying electronic transitions. In contrast, TMP shows a more complicated electronic response to ruffling. The lowest lying transition exhibits a modest hypsochromic shift at large nonplanar deviation, while the remaining transitions either move steadily to lower energies or exhibit a nonlinear response to ruffling. The transitions of $(CF_3)_4P$ also exhibit a mixed response to ruffling: the low-energy Q-bands are shifted slightly to the red, while the higher energy bands move to the blue. Taken together, these spectral calculations predict that the impact of ruffling on the electronic spectra of porphyrins is extremely modest and can result in either slight bathochromic or hypsochromic shifts in various bands, depending upon the nature of the substituents.

To assign the relative importance of conformational and electronic effects to the differences between the electronic spectra of $(CF_3)_4P$ and porphine, it is important to note that, in addition to an electronic effect, the CF_3 substituent has a conformational effect (IPNR) that is distinct from nonplanarity. This fact is illustrated by comparing time-dependent density functional theory calculations on porphine in the $(CF_3)_4P$-derived geometries to those on porphine in its optimized, ruffled conformations (Table 2). For a measure of the electronic effect, one can compare the spectra of $(CF_3)_4P$ and P in identical conformations. For example, replacing the (CF_3) substituents with hydrogen atoms results in a 0.057 eV shift (from 569 to 554.5 nm) in the longest wavelength transition for the 40° structure and a 0.053 eV shift (from 567 to 553.7 nm) in the 28° structure. An estimate of the impact of IPNR on the electronic spectrum of $(CF_3)_4P$ can be made by comparing the spectra of porphine in the $(CF_3)_4P$-derived conformations to those of P in optimized structures with the same degree of ruffling. IPNR is responsible for a 0.033 eV shift (from 554.5 to 546.5 nm) in the 40° structure and a 0.035 eV shift (from 553.7 to 545.2 nm) in the 28° structure. Ruffling itself, as gauged by comparison of planar porphine to ruffled (optimized) porphine, accounts for only 0.011 and 0.005 eV shifts in the lowest wavelength transition energies in the 40° and 28° structures, respectively. These data show that red-shifts observed in the long-wavelength region of the spectrum of highly ruffled $(CF_3)_4P$ are largely due to electronic effects and IPNR; only 10% (or less) of the difference between the lowest lying transition energies of highly ruffled $(CF_3)_4P$ and planar P can be attributed to nonplanarity using this factoring methodology.

Similar conclusions can be drawn from studies of porphine in the TMP-derived ruffled geometries, except that reduced IPNR, due to the smaller steric demand of methyl compared to trifluoromethyl, results in smaller red-shifts in the spectra. Still, the spectral shifts due to IPNR dwarf those due to ruffling. It is consistent with the data presented here for TMP and $(CF_3)_4P$ to postulate that the importance of IPNR scales with the steric demand at the porphyrin *meso* position.

These studies show that IPNR is a major factor influencing the spectra of sterically encumbered porphyrins such as $(CF_3)_4P$. This in-plane nuclear reorganization was evident in the empirical and modeling studies in the first part of this article. Furthermore, it is consistent with basic notions of chemical bonding that bond and angle distortion derived from strain- and/or substituent-induced rehybridization should affect electronic transition energies.[32] These considerations help us explain why the impact of nonplanar distortion is often overestimated in theoretical studies in this area. It is imperative that the IPNR caused by the substituents be taken into account, yet this has not generally been done. Attributing to nonplanarity the difference in the calculated spectra of optimized porphine and porphine in a geometry derived from a highly substituted nonplanar porphyrin misses this key substituent effect and introduces significant errors that jeopardize the conclusions of such work.[31]

Taken together, the DFT studies outlined here should strike a tocsin for those attempting to derive general stereoelectronic relationships from highly substituted porphyrins. While easy access to nonplanar geometries is made available by sterically demanding substituents, the geometries so obtained necessarily incorporate a great deal of IPNR. Given that the impact of IPNR upon the electronic spectra of porphyrins is predicted to be far larger than that arising from ruffling, these studies suggest that sterically encumbered porphyrins, though fascinating molecules, are perhaps misleading structural models for assessing the impact of nonplanarity upon porphyrin electronic properties. Moreover, IPNR should be absent in biological systems where the pigment is not subject to such substituent-derived localized steric forces, nor does it generally possess the same type,

(32) Pauling, L.; Wilson, E. B. *Introduction to Quantum Mechanics with Applications to Chemistry*; McGraw-Hill: New York, 1935.

location, or number of peripheral substituent groups as seen in typical model systems.

Conclusions

In summary, several key conclusions may be drawn from this work: (1) the impact of ruffling on the electronic properties of perfluoroalkylated porphyrins is exceptionally modest; (2) large spectral deviations observed for sterically encumbered, ruffled, free base porphyrins may not be due to nonplanar distortion, but rather arise from substituent electronic effects and IPNR; (3) the impact of in-plane reorganization of the nuclear coordinates upon porphyrin electronic properties is large and has not been generally recognized previously; and, consequently, (4) the use of structure−spectroscopy relationships derived from the study of highly substituted, nonplanar porphyrin model compounds to interpret the structure of porphyrins in proteins is not currently justifiable.

The methods employed here can also be used to assess the impact of nonplanarity upon the electronic properties of metalated porphyrins and porphyrins with differing substitution patterns or distortion modes. We believe that the results presented here pose serious challenges to theoretical and empirical studies that have sought to find a cause-and-effect relationship between nonplanarity and electronic spectra in porphyrins. Claims that such a relationship exists need to be revisited.[15−17, 33]

Supporting Information Available: Experimental procedures and characterization data for $(C_3F_7)_3P$, $(C_3F_7)_2P$, and their precursors; computational details; X-ray structural information on $(C_3F_7)_3P$ (PDF, CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(33) For example, in ref 17 the author states, "An analysis of closely related species indicates a direct correlation of these bathochromic shifts with the degree of nonplanarity." He goes on to say, "Proof for the relationship between nonplanarity and absorption band shifts has been provided by several molecular orbital calculations."