Do Nonplanar Porphyrins Have Red-Shifted Electronic Spectra? A DFT/SCI Study and Reinvestigation of a Recent Proposal

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Abstract: It is commonly believed that nonplanar distortions of the porphyrin skeleton bring about significant red shifts in the electronic absorption spectra. However, based on absorption spectroscopy and semiempirical AM1 studies of *meso*-tetrakis(perfluoroalkyl)porphyrins, DiMagno and co-workers have challenged this notion. Here we present density functional theory based configuration interaction singles calculations which uphold the traditional view. Both ruffling and saddling deformations do bring about significant red shifts in the electronic spectra. Nonplanarity-induced destabilization of the porphyrin HOMOs appears to be the principal cause of these red shifts.

Introduction

Nonplanar conformations such as the ruffled and saddled conformations are well-established for both synthetic porphyrins and porphyrin-type cofactors of proteins (Figure 1).[1] Macrocycle nonplanarity is an important, biologically relevant aspect of many heme cofactors of hemoproteins,[2] the pigments of photosynthetic proteins,[3] and cofactor F_{430} of methylcoenzyme M reductase.[4] Two broad issues are of great interest in this connection: (a) What factors bring about and control the various types of nonplanar distortions? (b) What are the chemical and biological consequences of nonplanarity in terms of properties such as redox potentials, axial ligand affinities, and excited-state energetics? In recent years, we have used quantum chemical methods to address the first question in some detail: in particular, DFT calculations[5] have furnished a fairly comprehensive understanding of the factors controlling ruffling deformations of porphyrins.[6] Here we proceed to address the second question, especially to determine the effects of nonplanar distortions of the porphyrin skeleton on the electronic absorption spectra using fairly reliable quantum chemical methods.[7]

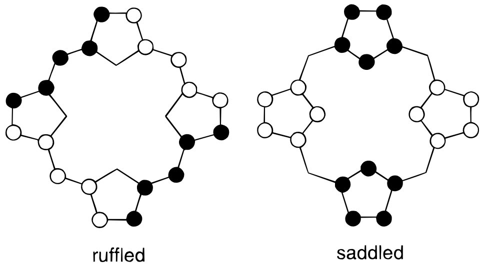

Figure 1. Schematic depiction of ruffled and saddled conformations. The filled and open circles indicate displacements on opposite sides of the mean plane of the porphyrin.

A specific motivation behind this study is as follows. On the basis of a large body of evidence,[1] most porphyrin researchers believe that nonplanar distortions exert a significant effect on the redox and spectroscopic properties of the porphyrin macrocycle. In particular, significant red shifts in the electronic absorption spectra often serve as a signature of porphyrin nonplanarity. However, based on absorption spectroscopy and semiempirical AM1 studies of *meso*-tetrakis(perfluoroalkyl)-porphyrins, DiMagno and co-workers challenged this prevailing view.[8] The Q and B (Soret) bands of β-octahalogeno-*meso*-tetraarylporphyrins exhibit large red shifts on the order of 30−52 nm, relative to the corresponding β-unsubstituted *meso*-tetraarylporphyrins.[9] DiMagno and co-workers argue as follows: “Saddle distortions allow (otherwise nearly orthogonal) aryl groups to rotate substantially into the plane of the [porphyrin] ring and interact more strongly with the π-system.” They “posit that the observed red shifts are not intrinsic to the ring distortion, but result from different substituent effects in planar and nonplanar conformations. This interpretation is bolstered by the observation that [*meso*-tetrakis(perfluoroalkyl)-porphyrins][10] and dodecaalkylporphyrins,[11] despite large nonplanar distortions, show small shifts in their absorption spectra.”

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Here we report DFT-based configuration interaction singles calculations (DFT/SCI) which show that nonplanar distortions do indeed bring about significant red shifts in the electronic absorption spectra,

Critique of Earlier Work

The following considerations prompted us to reinvestigate some of the conclusions reached by DiMagno and co-workers.

These authors compare the absorption spectra of the clearly nonplanar *meso*-tetrakis(perfluoroalkyl)porphyrins ($Q_x(0,0) = 648$ nm) and planar *meso*-tetraphenylporphyrin derivatives ($Q_x(0,0) = 652$ nm) and point out that the spectra of the former are blue-shifted relative to the latter compounds. While literally correct, this appears not to be a very meaningful comparison. In our opinion, the appropriate zero level for determining red shifts should be unsubstituted porphyrin ($Q_x(0,0) = 631$ nm),[12] not tetraphenylporphyrin, because the absorption spectrum of the latter compound is already rather red shifted relative unsubstituted porphyrin or β-octaethylporphyrin. In other words, DiMagno and co-workers' observation of "the absence of a red shift in the solution and solid-phase optical spectra" stems from the questionable use of tetraphenylporphyrin as the zero level for spectral shifts.

Second, the commonly accepted view is that nonplanar distortions engender red-shifted electronic absorption spectra by destabilizing the porphyrin HOMO, while not affecting the LUMOs significantly.[1a,13] DiMagno and co-workers present a series of AM1 calculations with systematically increasing saddling distortions and find that the HOMO is actually significantly stabilized by saddling. Moreover, AM1/CI calculations revealed a blue shift for the Q(0,0) energy with increasing saddling! These findings, clearly contrary to other classical work in this field, form the basis for DiMagno's proposal that nonplanar distortions do not bring about spectral red shifts. Here we report density functional theory calculations, including calculations of ionization potentials of nonplanar porphyrins, which uphold the traditional view that nonplanarity destabilizes the porphyrin HOMO.

DiMagno and co-workers point out that nonplanar dodecaalkylporphyrins exhibit "small red shifts in their absorption spectra" to bolster their claim that red shifts are not intrinsic to nonplanar distortions. However, an examination of the literature clearly shows that the optical spectra of saddled dodecaalkylporphyrins are indeed significantly red shifted relative to unsubstituted porphyrin and β-octaalkylporphyrin derivatives.[1a]

Molecular Geometries

We present density functional theory-based configuration interaction calculations with single excitations on unsubstituted zinc porphyrin (ZnP) and on the ruffled and saddled conformations of zinc *meso*-tetrakis(trifluoromethyl)porphyrins ($ZnP(CF_3)_4$). These structures are fully optimized at the DFT(PW91)/TZP level and taken from our previous work.[14] In addition, we also consider artificially ruffled and saddled geometries of ZnP, obtained as described below, to separate the influence of porphyrin nonplanarity from the electronic effects of peripheral substituents on the electronic spectra.

Elsewhere,[14] using geometry optimizations with DFT, we have shown that *meso*-tetrakis(perfluoroalkyl)porphyrins are conformationally flexible and can adopt ruffled, saddled, and intermediate structures, consistent with available crystallographic results. We quote here some relevant structural information from that study. The ruffled geometry of $ZnP(CF_3)_4$ is characterized by a ruffling torsion angle of 27°, displacements of 0.48 Å of the *meso* carbons from the mean porphyrin plane, and by relatively short Zn−N distances of 2.045 Å, which, overall, indicate a fairly strongly ruffled structure. The 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 Å. For the optimized saddled structure of $ZnP(CF_3)_4$, the saddling is rather mild: the β carbons of alternate pyrrole rings are displaced by +0.37 and −0.05 Å, relative to the Zn atom.

We chose not to derive the artificially saddled geometry of ZnP from the structure of saddled $ZnP(CF_3)_4$, as we feared that relatively mild saddling will not allow a clear evaluation of saddle distortions on the electronic spectra. Instead we took the highly saddled optimized geometry of zinc β-octamethyl-*meso*-tetraphenylporphyrin[15] and replaced the substituents with H's in the same manner as described above to generate an artificially saddled conformation of ZnP. The β-carbons in alternate pyrrole rings of this molecule are displaced by ±0.49 Å relative to the mean plane of the molecule. In other words, the maximum out-of-plane displacements of the porphyrin carbon atoms for the artifically ruffled and saddled conformations are similar, which was expected to allow a better comparison of the relative effects of ruffling versus saddling deformations on the electronic spectra of porphyrins.

Computational Details

The DFT/SCI calculations were performed using the method described by Grimme.[16] Elsewhere,[7a] we have observed that this method gives a good description of the excited states of different prototype porphyrins. The method is based on single-excitation configuration interaction (SCI) with the CI matrix elements modified and corrected empirically. The molecular orbital (MO) eigenvalues are taken from B3LYP DFT calculations for construction of the CI matrix. The calculations have been performed with the TURBOMOLE[17] suite of programs using valence double-ζ Gaussian basis sets (VDZP).[18] In addition, for each porphyrin system studied, the two lowest one-electron ionization potentials were evaluated using DFT(PW91)/(TZP) ΔSCF calculations and the ADF program system.[19]

Results and Discussion

Table 1 presents the DFT orbital energies and Table 2 the DFT/SCI energies and configurational composition of the different excited states. The excitation energies exhibit modest but significant variations among the different compounds. For example, the Q-bands of the nonplanar conformations of $ZnP(CF_3)_4$ (ruffled 2.13 eV, saddled 2.15 eV) are red shifted relative to those of ZnP (2.22 eV) by 0.07−0.09 eV or 18−24 nm (Table 2), consistent with experimental data on relevant compounds.[10b] From a comparison of these red shifts with those calculated for the appropriate artificially nonplanar conformations of ZnP, the red shifts of about 0.08 eV for the Q-bands of $ZnP(CF_3)_4$,

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Table 1. B3LYP/VDZP Orbital Energies in eV

	ZnP (D_{4h})	ruffled ZnP (D_{2d})	ruffled ZnP(CF$_3$)$_4$ (D_{2d})	saddled ZnP (D_{2d})	saddled ZnP(CF$_3$)$_4$ (C_{2v})
LUMO+2	−0.73 (a_{1u})	−0.81 (a_1)	−1.93 (a_1)	−0.85 (a_1)	−1.86 (a_1)
LUMO+1	−2.31 (e_g)	−2.33 (e)	−3.45 (e)	−2.35 (e)	−3.41 (b_2)
LUMO	−2.31 (e_g)	−2.33 (e)	−3.45 (e)	−2.35 (e)	−3.43 (b_1)
HOMO	−5.33 (a_{2u})	−5.30 (b_2)	−6.23 (b_1)	−5.26 (b_2)	−6.22 (a_2)
HOMO-1	−5.39 (a_{1u})	−5.34 (b_1)	−6.52 (b_2)	−5.34 (b_1)	−6.53 (a_1)
HOMO-2	−6.59 (a_{1g})	−6.51 (nb_1)[a]	−7.47 (nb_1)	−6.68 (nb_2)[a]	−7.48 (na_1)[a]

[a] *n* denotes the second highest occupied MO of a given symmetry.

Table 2. Excitation Energies in eV (nm), Oscillator Strengths, and Configurational Compositional of the Lowest Excited Singlet States of ZnP, Ruffled ZnP, Ruffled ZnP(CF$_3$)$_4$, Saddled ZnP, and Saddled ZnP(CF$_3$)$_4$

	symmetry	ΔE	f	main contributions			
ZnP							
Q	E_u	2.22 (558)	0.002	50% (a_{2u}−e_g)	49% (a_{1u}−e_g)		
B	E_u	3.92 (316)	1.729	38% (a_{2u}−e_g)	42% (a_{1u}−e_g)		
ruffled ZnP							
Q	E	2.16 (575)	0.003	49% (b_2−e)	50% (b_1−e)		
B	E	3.82 (325)	0.821	20% (b_2−e)	21% (b_1−e)	51% (nb_1−e)[a]	
ruffled ZnP(CF$_3$)$_4$							
Q	E	2.13 (582)	0.012	44% (b_2−e)	54% (b_1−e)		
B	E	3.72 (333)	0.223	6% (b_2−e)	5% (b_1−e)	85% (nb_1−e)[a]	
saddled ZnP							
Q	E	2.12 (585)	0.002	50% (b_1−e)	49% (b_2−e)		
B	E	3.74 (332)	1.403	51% (b_1−e)	48% (b_2−e)		
saddled ZnP(CF$_3$)$_4$							
Q_x	B_2	2.14 (578)	0.013	44% (a_1−b_2)	55% (a_2−b_1)		
Q_y	B_1	2.15 (576)	0.012	54% (a_2−b_2)	44% (a_1−b_1)		
B_y	B_1	3.78 (328)	1.164	27% (a_2−b_2)	29% (a_1−b_1)	16% (na_1−b_1)[a]	14% ($2na_1$−b_1)[a]
B_x	B_2	3.79 (327)	1.370	31% (a_1−b_2)	35% (a_2−b_1)	14% (na_1−b_2)[a]	10% ($2na_1$−b_2)[a]

[a] *n* and 2*n* denote the second and third highest MOs for a given symmetry species.

relative to ZnP, may be attributed, to a significant extent, to porphyrin nonplanarity and, to some extent, also to the electronic effects of the CF$_3$ groups. These red shifts are smaller than the difference of 52 nm between the Q(0,0) energies of zinc(II) tetrakis(pentafluorophenyl)porphyrin (ZnTPFPP, 544 nm) and of zinc(II) octa-β-bromotetrakis(pentafluorophenyl)porphyrin ZnBr$_8$TPFPP (596 nm), showing the importance of differences in substituent electronic effects between planar and saddled conformations.[9]

Compared to the Q-bands, the calculated B-band energies shift somewhat more among the different compounds studied, especially in response to ruffling. Relative to ZnP (3.92 eV), the B-band red shifts by 0.2 eV for the ruffled conformation of ZnP(CF$_3$)$_4$ (3.72 eV) and somewhat less for the saddled conformation (3.78 eV). For the B-bands, about half of these shifts are ascribable to nonplanarity and the other half to the electronic effects of the CF$_3$ groups. Thus, DiMagno and co-workers' suggestion that "the observed red shifts are not intrinsic to ... ring distortion" is untenable.

Why do the B-bands red shift more than the Q-bands in response to ruffling? The Q-bands of planar ZnP have a relatively pure four-orbital composition, i.e., involving the four frontier molecular orbitals.[20] Note from Table 1 that ruffling introduces considerable non-four-orbital character into the B-band, leaving the composition of the Q-band relatively unchanged. *meso*-Trifluoromethylation affects the composition of the Q- and B-bands significantly. The HOMO switches from a_{2u} to a_{1u} between ZnP and ZnP(CF$_3$)$_4$. For ZnP(CF$_3$)$_4$, we find that excitation out of the "a_{1u}-type" HOMO makes an increased contribution to the Q-band, relative to ZnP, resulting in increased oscillator strength for the fluorinated molecule (ZnP, 0.002; ZnP(CF$_3$)$_4$, 0.012). To the B-bands, *meso*-trifluoromethylation imparts significant to overwhelming non-four-orbital character (ruffled ZnP(CF$_3$)$_4$, 85%; saddled ZnP(CF$_3$)$_4$, 25−30%), which also results in a significant smaller oscillator strength (ZnP, 1.729; ruffled ZnP(CF$_3$)$_4$, 0.223; saddled ZnP(CF$_3$)$_4$, 1.164).

The Q-bands of the artificially ruffled and saddled conformations of ZnP are red shifted by 17 (0.06 eV) and 27 nm (0.09 eV), respectively, relative to planar ZnP. The B-bands of the artificially ruffled and saddled conformations of ZnP are red shifted by 9 (0.10 eV) and 16 nm (0.18 eV), respectively, relative to planar ZnP. These are significant red shifts indeed, approximately 30−50% of the red shift described above for ZnBr$_8$TPFPP. Thus, while DiMagno and co-workers correctly conclude that nonplanarity cannot explain the entire red shift observed for β-octahalogeno-*meso*-tetraarylporphyrins, nonplanarity does account for a substantial fraction of the red shift.

Finally, the two lowest IPs of planar ZnP are calculated to be 7.03 and 7.09 eV, which correspond to A_{2u}- and A_{1u}-type cation radical states, respectively. These IPs shift to 6.99 and 7.04 eV, respectively, for the artificially ruffled conformation and to 6.96 and 7.04 eV, respectively, for the artificially saddled conformation. We have shown elsewhere that nonlocal DFT gives essentially quantitatively correct valence IPs for porphyrins.[21] Thus, nonplanarity does indeed destabilize the porphyrin HOMOs.

Conclusion

On the basis of the absorption spectroscopy and semiempirical AM1 studies of *meso*-tetrakis(perfluoroalkyl)porphyrins, DiMagno and co-workers have challenged the commonly held view that nonplanar distortions bring about red shifts in the electronic spectra of porphyrins. Here we have presented density functional theory based configuration interaction singles calculations which uphold the traditional view that *nonplanarity does lead to significantly red-shifted electronic spectra*, while agree-

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ing with DiMagno and co-workers that *differences in substituent effects in planar versus nonplanar porphyrins may contribute equally or even more, relative to nonplanarity, to the observed red-shifted spectra of individual nonplanar porphyrins*. Presumably, the conclusions reached by DiMagno reflect shortcomings of the semiempirical theoretical methods they used. Both ruffling and saddling deformations do bring about significant red shifts in the electronic spectra. Nonplanarity-induced destabilization of the porphyrin HOMOs appears to be the principal cause of these red shifts.

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