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Do Nonplanar Distortions of Porphyrins Bring about Strongly Red-Shifted Electronic Spectra? Controversy, Consensus, New Developments, and Relevance to Chelatases

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Abstract: TDDFT calculations confirm a controversial proposal by DiMagno and co-workers that ruffling distortions, by themselves, do *not* bring about sizable red shifts in the electronic absorption spectra of “simple” nontransition-metal porphyrins. We now report that the same also holds for saddling distortions. The situation is more complex for transition metal porphyrins. For example, ruffling does bring about strong red shifts in the electronic spectra of nickel porphyrins because of a specific metal(d)−porphyrin(π) orbital interaction.

Introduction

Nonplanar distortions such as the ruffled and saddled conformations are well-established for both synthetic porphyrins as well as for porphyrin-type cofactors of proteins (Figure 1).[1,2] Two broad issues are of interest in relation to nonplanar conformations of porphyrins: (a) What factors bring about and control the various types of nonplanar distortions? (b) What are the chemical and biological consequences of nonplanarity for properties such as redox potentials, axial ligand affinities, and excited-state energetics? Much progress has been achieved in relation to both of these questions, not least by means of high-quality quantum chemical calculations.[3] However, in recent years, controversy has surrounded one of the best-known experimental signatures of nonplanar porphyrins, viz. their red-shifted optical spectra.[1,2] The specific question that has provoked controversy is the one posed in the title: Do nonplanar distortions such as ruffling or saddling bring about sizable red shifts in the electronic absorption spectra of porphyrins?

On the basis of a large body of evidence,[1,2] most porphyrin researchers believe that nonplanar distortions exert a significant effect on the redox and spectroscopic properties of porphyrins. However, in 1995, based on electronic absorption spectroscopy and semiempirical AM1 calculations of *meso*-tetrakis(perfluoroalkyl)porphyrins, DiMagno and co-workers challenged this prevailing view.[4] The Q and the 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. DiMagno and co-workers argued as follows:[4] “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 posited “that the observed red shifts are not intrinsic to 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 and dodecaalkylporphyrins, despite their large nonplanar distortions, show small shifts in their absorption spectra.”[4]

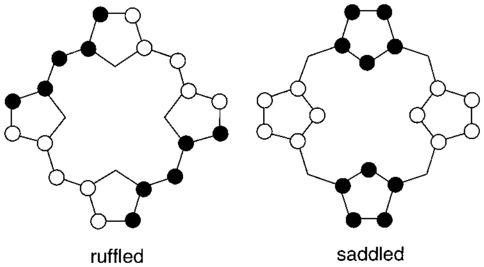

Figure 1. Schematic depiction of ruffled and saddled conformations. The filled and open circles indicate displacements on opposite sides of the mean plane of the porphyrin.

For five years, the proposal of DiMagno and co-workers was neither confirmed nor challenged; on the basis of personal conversations with other researchers in the field, we understood that these findings were viewed with considerable skepticism and, therefore, were often ignored. In 2000, one of us[5] published a reinvestigation of this proposal using DFT/SCI calculations and reached conclusions opposite to that of DiMagno and co-workers, i.e., consistent with the traditional view that nonplanar distortions do bring about sizable red shifts in porphyrin electronic spectra. In a typical calculation,[5] we took the highly saddled optimized geometry of zinc β-octamethyl-*meso*-tetraphenylporphyrin and replaced the peripheral substituents with

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(5) Parusel, A. B. J.; Wondimagegn, T.; Ghosh, A. *J. Am. Chem. Soc.* **2000**, *122*, 6371.

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hydrogens lying exactly along the original C(porphyrin)−substituent vectors, setting the C(porphyrin)−H bonds to 1.08 Å. DFT/SCI calculations[5] on the artificially saddled (D_{2d}) conformation of Zn porphine, thus obtained, yielded significantly red-shifted B- and Q-bands, relative to those of the optimized planar (D_{4h}) geometry of zinc porphine. Calculations such as these led us[5] to conclude that DiMagno and co-workers had reached an erroneous conclusion in their 1995 paper.[5] We wrote:[5] "Presumably, the conclusions reached by DiMagno and co-workers reflect shortcomings of the semiempirical methods they used."

But we were wrong, as shown by DiMagno and co-workers in 2001.[6] Using constrained optimizations of simple free-base porphyrins where the degree of ruffling was the only constraint—an approach different from ours[5]—DiMagno and co-workers[6] found little or no red shift in Q- and B-band energies calculated with time-dependent DFT(B3LYP)/6-311G* (TDDFT) calculations. This provokes two questions. How can we reconcile this finding with the incontrovertible fact that most nonplanar porphyrins do exhibit strongly red-shifted optical spectra? Second, given that both our[5] calculations and those of DiMagno and co-workers[6] are technically of high quality, what accounts for the dramatic difference in the results?

DiMagno and co-workers answered these questions satisfactorily. The main difference between our calculations[5] and those of DiMagno and co-workers[6] is that while we computed the electronic spectra of nonplanar porphine skeletons taken directly from the optimized structures of real nonplanar porphyrins, they carried out TDDFT calculations on fully optimized porphyrin structures, subject only to the constraint of various degrees of ruffling. DiMagno and co-workers showed convincingly that it is not ruffling itself but changes in bond lengths and angles induced by the substituents that bring about ruffling—what these authors call the in-plane nuclear reorganizations (IPNRs)—that play a key role in engendering the red shifts in the electronic spectra of nonplanar porphyrins.[6]

However, despite the convincing nature of the arguments made by DiMagno and co-workers,[6] skepticism persists vis-à-vis their thesis among many porphyrin researchers. Given the centrality of this issue to porphyrin-related research, we considered this to be a rather unsatisfactory state of affairs and decided to reinvestigate this issue via TDDFT calculations. Specifically, we wished to reconfirm the finding of DiMagno and co-workers[6] that it is indeed possible to significantly ruffle a porphyrin (at least, theoretically) without causing sizable red shifts in its electronic spectrum. We confirm here the essential correctness of this finding. Second, DiMagno and co-workers[6] did not address the influence of saddling on electronic absorption spectra in their studies. Is it possible to strongly "saddle" a porphyrin without engendering large red shifts in its optical spectrum? This is an important question because, if the answer is yes, it would significantly extend the thesis of DiMagno and co-workers. We shall see that the answer is indeed "yes".

Interestingly, although a certain closure has now been brought to the controversy surrounding the origin of red-shifted optical spectra of nonplanar porphyrins,[5,6] it is important not to oversimplify the problem.[6] Our calculations reveal some richly complex characteristics of transition metal porphyrins vis-à-vis this issue. We shall see that ruffling *does* induce sizable to strong red shifts in the electronic spectra of nickel porphyrins, which are some of the most widely studied metalloporphyrins in the context of porphyrin nonplanarity. The key to this finding lies in metal(d)−porphyrin(π) orbital interactions which are symmetry forbidden in planar metalloporphyrins but are switched on by ruffling. Thus, the question of whether nonplanar distortions bring about strongly red-shifted electronic spectra will have to be addressed carefully and systematically for a variety of transition metal porphyrins.

Results

Tables 1 and 2 present calculated TDDFT(PW91/TZP)[7] Q and B (Soret) transition energies, respectively, for the various molecules studied. The data lead to the following main conclusions. For free-base porphine [(P)H_2], zinc porphine [Zn(P)], and magnesium porphine [Mg(P)], ruffling results in small red shifts of Q and B (Soret) transition energies, up to 5−6 nm,[8] qualitatively consistent with the finding of DiMagno and co-workers. For free-base porphine [(P)H_2], Zn(P), and Mg(P), saddling also engenders small red shifts of the Q and B (Soret) transition energies, which significantly extends the finding of DiMagno and co-workers.[6]

In sharp contrast to these results, ruffling engenders sizable to strong red shifts of the Q and B transition energies of Ni(P) and Ni(Br_8P). Thus, for a 0.5 Å displacement of the meso carbons from the mean porphyrin plane (see Tables 1 and 2), the Q- and B-bands of Ni(P) red shift by 8 and 17 nm, respectively, relative to the planar geometry of Ni(P). Saddling has relatively little effect on the Q and B transition energies of Ni(P) and Ni(Br_8P).

To investigate the possible importance of the metal(d_{xy})−porphyrin(a_{2u}) antibonding interaction in other transition metal porphyrins, we also studied the effect of ruffling on the D_{2d} low-spin complex, Fe^{II}(P)(pyridine)$_2$ (where the two axial pyridine ligands lie in mutually perpendicular planes).[9] Interestingly, in this case, ruffling has little effect on the Q- and B-band energies.

An examination of the frontier MOs (Figure 2) of Ni(P) and Fe^{II}(P)(pyridine)$_2$ provides some clues to this question. For Ni(P), the "a_{2u}"−e_g HOMO-LUMO gap decreases rather sharply with ruffling, while the "a_{1u}"−e_g HOMO-LUMO gap remains relatively constant, which explains a net spectral red shift. For Fe^{II}(P)(pyridine)$_2$, in contrast, the "a_{2u}"−e_g HOMO-LUMO gap increases somewhat with ruffling, while the "a_{1u}"−e_g HOMO-

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[6] Wertsching, A. K.; Koch, A. S.; DiMagno, S. G. *J. Am. Chem. Soc*. **2001**, *123*, 3932.

[7] The ground-state and time-dependent DFT calculations were carried out with Slater-type valence triple-ζ plus polarization basis sets, the VWN local functional, the Perdew-Wang 1991 gradient corrections, a spin-restricted formalism, a fine mesh for numerical integration of matrix elements, full geometry optimizations, and the ADF program system. The theoretical methods used in ADF are discussed in the following papers: (a) Velde, G. T.; Bickelhaupt, F. M.; Baerends, E. J.; Guerra, C. F.; Van Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T. *J. Comput. Chem*. **2001**, *22*, 931. (b) van Gisbergen, S. J. A.; Snijders, J. G.; Baerends, E. J. *Comput. Phys. Commun*. **1999**, *118*, 119. The ADF program system was obtained from Scientific Computing and Modeling, Department of Theoretical Chemistry, Vrije Universiteit, 1081 HV Amsterdam, The Netherlands. The ruffled and saddled structures referred to in Tables 1 and 2 are fully optimized with the degree of ruffling or saddling, as measured by the *z* displacements mentioned in Tables 1 and 2, as the only constraints.

[8] These red shifts of 5−6 nm are slightly higher than those found by DiMagno and co-workers in ref 5, although we note that they have not studied exactly the same compounds as we have; they have studied free-base porphine, *meso*-tetramethylporphyrin, and perfluoroalkylated porphyrins but they have not investigated metal complexes of these ligands.

[9] For a theoretical study of the metal(d_{xy})−porphyrin(a_{2u}) orbital interaction in ruffled iron porphyrins, see: Ghosh, A.; Gonzalez, E.; Vangberg, T. *J. Phys. Chem. B* **1999**, *103*, 1363.

Table 1. Excitation Energies (in eV and nm), Oscillator Strengths, and Configurational Composition of the Lowest Excited Singlet States (i.e. the Q Bands) of Ruffled Ni(P), Mg(P), and $(P)H_2$ and Saddled Mg(P), Ni(P), $Mg(Br_8P)$, and $Ni(Br_8P)$[a]

		z (Å)	symmetry	Δ*E*/eV	Δ*E*/nm	*f*	main contribution	
$(P)H_2$	planar	0	B_{3u}	2.160	575	0.0009	63% ($b_{1u}-b_{2g}$)	36% (a_u-b_{3g})
			B_{1u}	2.294	541	0.0007	58% ($b_{1u}-b_{3g}$)	40% (a_u-b_{2g})
	ruffled	0.1	B_3	2.161	575	0.0008	62% (b_1-b_2)	37% ($a-b_3$)
			B_2	2.293	542	0.0007	58% (b_1-b_3)	40% ($a-b_2$)
	ruffled	0.2	B_3	2.159	575	0.0008	62% (b_1-b_2)	37% ($a-b_3$)
			B_2	2.292	542	0.0006	58% (b_1-b_3)	41% ($a-b_2$)
	ruffled	0.3	B_3	2.156	576	0.0007	62% (b_1-b_2)	37% ($a-b_3$)
			B_2	2.288	543	0.0005	58% (b_1-b_3)	41% ($a-b_2$)
	ruffled	0.4	B_3	2.153	576	0.0005	61% (b_1-b_2)	38% ($a-b_3$)
			B_2	2.283	544	0.0005	58% (b_1-b_3)	41% ($a-b_2$)
	ruffled	0.5	B_3	2.152	577	0.0003	61% (b_1-b_2)	38% ($a-b_3$)
			B_2	2.278	545	0.0004	57% (b_1-b_3)	41% ($a-b_2$)
Zn(P)	planar	0	E_u	2.291	542	0.00008	54% ($a_{2u}-e_g$)	44% ($a_{1u}-e_g$)
	ruffled	0.5	*E*	2.259	550	0.00025	53% (b_2-e)	46% (b_1-e)
	saddled	0.5	*E*	2.271	547	0.00005	54% (b_2-e)	44% (b_1-e)
Mg(P)	planar	0	E_u	2.243	554	0.00009	56% ($a_{2u}-e_g$)	42% ($a_{1u}-e_g$)
	ruffled	0.1	*E*	2.244	554	0.00008	56% (b_2-e)	42% (b_1-e)
	ruffled	0.2	*E*	2.241	554	0.00008	56%(b_2-e)	42% (b_1-e)
	ruffled	0.3	*E*	2.236	555	0.00004	56%(b_2-e)	42% (b_1-e)
	ruffled	0.4	*E*	2.229	557	0.00002	56% (b_2-e)	43% (b_1-e)
	ruffled	0.5	*E*	2.220	559	0.00002	55% (b_2-e)	43% (b_1-e)
	saddled	0.1	*E*	2.246	553	0.00008	56% (b_2-e)	42% (b_1-e)
	saddled	0.2	*E*	2.242	554	0.00008	56% (b_2-e)	42% (b_1-e)
	saddled	0.3	*E*	2.236	555	0.0001	57% (b_2-e)	42% (b_1-e)
	saddled	0.4	*E*	2.229	557	0.0001	57% (b_2-e)	42% (b_1-e)
	saddled	0.5	*E*	2.220	559	0.0002	57% (b_2-e)	42% (b_1-e)
$Mg(Br_8P)$	planar	0	E_{1u}	2.144	579	0.008	51% ($a_{1u}-e_g$)	45% ($a_{2u}-e_g$)
	saddled	0.1	*E*	2.143	579	0.008	51% (b_1-e)	45% (b_2-e)
	saddled	0.2	*E*	2.140	580	0.007	51% (b_1-e)	46% (b_2-e)
	saddled	0.3	*E*	2.137	581	0.007	51% (b_1-e)	46% (b_2-e)
	saddled	0.4	*E*	2.131	583	0.007	51% (b_1-e)	46% (b_2-e)
	saddled	0.5	*E*	2.124	585	0.006	51% (b_1-e)	46% (b_2-e)
Ni(P)	planar	0	E_u	2.405	516	0.002	50% ($a_{1u}-e_g$)	49% ($a_{2u}-e_g$)
	ruffled	0.1	*E*	2.404	517	0.002	50% (b_1-e)	49% (b_2-e)
	ruffeld	0.2	*E*	2.402	517	0.002	50% (b_1-e)	49% (b_2-e)
	ruffled	0.3	*E*	2.392	519	0.002	50% (b_2-e)	49% (b_1-e)
	ruffled	0.4	*E*	2.382	521	0.002	50% (b_2-e)	48% (b_1-e)
	ruffled	0.5	*E*	2.371	524	0.001	39% (b_1-e)	39% (b_2-e)
	saddled	0.1	*E*	2.407	516	0.002	50% (b_1-e)	49% (b_2-e)
	saddled	0.2	*E*	2.405	516	0.002	50% (b_1-e)	49% (b_2-e)
	saddled	0.3	*E*	2.402	517	0.002	50% (b_1-e)	49% (b_2-e)
	saddled	0.4	*E*	2.398	518	0.002	50% (b_1-e)	48% (b_2-e)
	saddled	0.5	*E*	2.392	519	0.002	50% (b_1-e)	49% (b_2-e)
$Ni(Br_8P)$	planar	0	E_{1u}	2.270	547	0.02	60% ($a_{1u}-e_g$)	37% ($a_{2u}-e_g$)
	ruffled	0.5	*E*	2.241	554	0.02	58% (b_1-e)	39% (b_2-e)
	saddled	0.1	*E*	2.270	547	0.02	61% (b_1-e)	37% (b_2-e)
	saddled	0.2	*E*	2.269	547	0.02	61% (b_1-e)	37% (b_2-e)
	saddled	0.3	*E*	2.266	548	0.02	61% (b_1-e)	37% (b_2-e)
	saddled	0.4	*E*	2.264	549	0.02	61% (b_1-e)	37% (b_2-e)
	saddled	0.5	*E*	2.259	550	0.02	60% (b_1-e)	37% (b_2-e)
$Fe^{II}(P)(py)_2$	ruffled	0	*E*	2.348	529	0.0002	62% (b_2-e)	36% (b_1-e)
	ruffled	0.26	*E*	2.359	527	0.00004	61% (b_2-e)	38% (b_1-e)
	ruffled	0.400	*E*	2.360	526	0.00003	59% (b_2-e)	40% (b_1-e)
	ruffled	0.500	*E*	2.359	526	0.00002	56% (b_2-e)	42% (b_1-e)
$[P^V(P)F_2]^+$	ruffled	0.700	*E*	2.311	537	0.0006	51% (b_1-e)	48% (b_2-e)
	ruffled	0.800	*E*	2.297	541	0.0007	52% (b_1-e)	47% (b_2-e)
	ruffled	0.878	*E*	2.282	544	0.0009	52% (b_1-e)	47% (b_2-e)
	ruffled	1.000	*E*	2.255	551	0.001	53% (b_1-e)	46% (b_2-e)
$Si^{IV}(P)F_2$	planar	0.000	E_u	2.287	543	3.22×10^{-7}	56% ($a_{2u}-e_g$)	43% ($a_{1u}-e_g$)
	ruffled	0.200	*E*	2.283	544	1.16×10^{-7}	56% (b_2-e)	43% (b_1-e)
	ruffled	0.400	*E*	2.270	547	7.89×10^{-7}	55% (b_2-e)	43% (b_1-e)
	ruffled	0.600	*E*	2.256	551	8.66×10^{-7}	54% (b_2-e)	45% (b_1-e)

[a] *z* refers to the displacement of the meso or *β* carbons from the mean porphyrin plane for ruffled or saddled porphyrins, respectively.

LUMO gap decreases with ruffling by a comparable amount, leading to little net red-shift in the Q- and B-bands. What accounts for this difference relative to the Fe(II) and Ni(II) cases? We do not have a clear answer yet but one possibility is that in the Ni(II) case, because of the shortness of the metal–nitrogen bonds compared to the Fe(II) case, a metal(d_{xy})–porphyrin(a_{2u})[10] antibonding interaction (which becomes symmetry-allowed in a ruffled porphyrin (Figure 3)) is particularly effective at raising the orbital energy of the a_{2u} HOMO.

Finally, we have found that increasing ruffling does red-shift the Q- and B-bands of the main-group complexes, $[P^V(P)F_2]^+$ and $[Si^{IV}(P)F_2]$.[11]

Table 2. Excitation Energies (in eV and nm), Oscillator Strengths, and Configurational Composition of the Singlet B (Soret) States of Ruffled Ni(P), Mg(P), and (P)H$_2$ and Saddled Mg(P), Ni(P), Mg(PBr$_8$), and Ni(PBr$_8$)[a]

		z (Å)	symmetry	*E*/eV	*E*/nm	*f*	main contribution			
(P)H$_2$	planar	0.000	B_{1u}	3.406	365	0.884	46% (a_u-b_{2g})	29% ($b_{1u}-b_{3g}$)	14% ($nb_{1u}-b_{3g}$)	
			B_{3u}	3.471	358	0.738	33% (a_u-b_{3g})	30% ($b_{1u}-b_{2g}$)	24% ($nb_{1u}-b_{2g}$)	
	ruffled	0.100	B_2	3.406	365	0.876	46% ($a-b_2$)	29% (b_1-b_3)	14% (nb_1-b_3)	
			B_3	3.471	358	0.736	32% ($a-b_3$)	30% ($nb1-b2$)	24% (b_1-b_2)	
	ruffled	0.200	B_2	3.405	365	0.856	45% ($a-b_2$)	28% (b_1-b_3)	14% (nb_1-b_3)	
			B_3	3.467	358	0.730	32% ($a-b_3$)	30% (nb_1-b_2)	24% (b_1-b_2)	
	ruffled	0.300	B_2	3.401	365	0.820	43% ($a-b_2$)	27% (b_1-b_3)	13% (nb_1-b_3)	
			B_3	3.458	359	0.719	32% ($a-b_3$)	29% (nb_1-b_2)	24% (b_1-b_2)	
	ruffled	0.400	B_2	3.394	366	0.766	40% ($a-b_2$)	26% (b_1-b_3)	13% (na_1-b_2)	11% (nb_1-b_3)
			B_3	3.448	360	0.706	32% ($a-b_3$)	29% (nb_1-b_2)	24% (b_1-b_2)	
	ruffled	0.500	B_2	3.388	367	0.686	36% ($a-b_2$)	24% (b_1-b_3)	22% (na_1-b_2)	
			B_3	3.435	362	0.690	31% ($a-b_3$)	27% (nb_1-b_2)	25% (b_1-b_2)	
Zn(P)	planar	0.00	E_u	3.315	354	0.565	34% ($a_{2u}-e_g$)	36% ($a_{1u}-e_g$)	14% ($na_{2u}-e_g$)	13% ($b_{2u}-e_g$)
	ruffled	0.500	E	3.276	358	0.593	38% (b_1-e)	36% (b_2-e)	13% (nb_2-e)	
	saddled	0.500	E	3.289	357	0.560	36% (b_1-e)	34% (b_2-e)	12% (nb_2-e)	
Mg(P)	planar	0.000	E_u	3.282	378	0.547	37% ($a_{1u}-e_g$)	31% ($a_{2u}-e_g$)	21% ($na_{2u}-e_g$)	
	ruffled	0.100	E	3.282	378	0.5496	37% (b_1-e)	31% (b_2-e)	21% (nb_2-e)	
	ruffled	0.200	E	3.278	379	0.5539	38% (b_1-e)	31% (b_2-e)	20% (nb_2-e)	
	ruffled	0.300	E	3.271	380	0.5602	38% (b_1-e)	32% (b_2-e)	20% (nb_2-e)	
	ruffled	0.400	E	3.261	381	0.5659	39% (b_1-e)	32% (b_2-e)	20% (nb_2-e)	
	ruffled	0.500	E	3.247	382	0.5732	40% (b_1-e)	33% (b_2-e)	19% (nb_2-e)	
	saddled	0.100	E	3.285	378	0.549	37% (b_1-e)	31% (b_2-e)	20% (nb_2-e)	
	saddled	0.200	E	3.279	379	0.545	37% (b_1-e)	31% (b_2-e)	20% (nb_2-e)	
	saddled	0.300	E	3.272	380	0.542	38% (b_1-e)	31% (b_2-e)	20% (nb_2-e)	
	saddled	0.400	E	3.263	381	0.538	37% (b_1-e)	31% (b_2-e)	19% (nb_2-e)	
	saddled	0.500	E	3.251	382	0.535	38% (b_1-e)	31% (b_2-e)	19% (nb_2-e)	
Mg(Br$_8$P)	planar	0	E_{4u}	3.098	401	1.158	49% ($a_{2u}-e_g$)	42% ($a_{1u}-e_g$)		
	saddled	0.100	E	3.097	401	1.153	49% (b_2-e)	42% (b_1-e)		
	saddled	0.200	E	3.092	402	1.149	49% (b_2-e)	42% (b_1-e)		
	saddled	0.300	E	3.089	402	1.139	49% (b_2-e)	42% (b_1-e)		
	saddled	0.400	E	3.080	403	1.129	48% (b_2-e)	42% (b_1-e)		
	saddled	0.500	E	3.070	405	1.114	48% (b_2-e)	43% (b_1-e)		
Ni(P)	planar	0	E_u	3.167	392	0.323	33% ($a_{2u}-e_g$)	33% ($a_{1u}-e_g$)	28% ($d_{xz}-d_{x^2-y^2}$)	
	ruffled	0.100	E	3.160	393	0.310	32% (b_2-e)	32% (b_1-e)	26% ($e-a_1$)	
	ruffled	0.200	E	3.145	395	0.284	31% (b_1-e)	30% (b_2-e)	21% ($e-a_1$)	21% (nb_2-e)
	ruffled	0.300	E	3.113	399	0.250	29% (b_1-e)	28% (b_2-e)	21% (nb_2-e)	21% ($e-a_1$)
	ruffled	0.400	E	3.078	403	0.220	29% (b_1-e)	29% (nb_2-e)	26% (b_2-e)	26% ($e-a_1$)
	ruffled	0.500	E	3.034	409	0.196	33% (nb_2-e)	29% (b_1-e)	24% (b_2-e)	24% ($e-a_1$)
	saddled	0.100	E	3.169	392	0.323	33% (b_2-e)	33% (b_1-e)	28% ($e-a_2$)	
	saddled	0.200	E	3.165	392	0.321	33% (b_2-e)	32% (b_1-e)	28% ($e-a_2$)	
	saddled	0.300	E	3.158	393	0.314	33% (b_2-e)	32% (b_1-e)	28% ($e-a_2$)	
	saddled	0.400	E	3.148	394	0.308	33% (b_2-e)	32% (b_1-e)	28% ($e-a_2$)	
	saddled	0.500	E	3.135	396	0.298	33% (b_2-e)	32% (b_1-e)	29% ($e-a_2$)	
Ni(Br$_8$P)	planar	0	E_{4u}	2.996	415	0.308	42% ($a_{2u}-e_g$)	21% ($a_{1u}-e_g$)	14% ($na_{2u}-e_g$)	
	ruffled	0.500	E	2.947	421	0.276	32% (b_2-e)	29% ($2ne-nb_1$)	18% (b_1-e)	
	saddled	0.100	E	2.997	414	0.309	42% (b_2-e)	21% (b_1-e)	14% (nb_2-e)	
	saddled	0.200	E	2.995	415	0.308	42% (b_2-e)	21% (b_1-e)	14% (nb_2-e)	
	saddled	0.300	E	2.993	415	0.306	41% (b_2-e)	21% (b_1-e)	15% (nb_2-e)	
	saddled	0.400	E	2.991	415	0.301	41% (b_2-e)	21% (b_1-e)	16% (nb_2-e)	
	saddled	0.500	E	2.985	416	0.294	40% (b_2-e)	20% (b_1-e)	17% (nb_2-e)	
Fe^{II}(P)(py)$_2$	planar	0	E	3.145	395	0.333	40% (b_1-e)	22% (b_2-e)		
	ruffled	0.260	E	3.153	394	0.353	41% (b_1-e)	24% (b_2-e)		
	ruffled	0.400	E	3.154	394	0.346	39% (b_1-e)	24% (b_2-e)		
	ruffled	0.500	E	3.151	394	0.346	36% (b_1-e)	24% (b_2-e)		
[(P)P^{V}F$_2$]$^+$	ruffled	0.700	E	3.409	364	0.805	47% (b_2-e)	45% (b_1-e)		
	ruffled	0.800	E	3.394	366	0.813	48% (b_2-e)	45% (b_1-e)		
	ruffled	0.878	E	3.376	367	0.808	48% (b_2-e)	45% (b_1-e)		
	ruffled	1.000	E	3.344	371	0.799	49% (b_2-e)	45% (b_1-e)		
PSi^{IV}F$_2$	planar	0	E_u	3.273	379	0.499	39% ($a_{1u}-e_g$)	26% ($a_{2u}-e_g$)	18% ($b_{2u}-e_g$)	
	ruffled	0.200	E	3.270	380	0.495	39% (b_1-e)	26% (b_2-e)	19% (a_2-e)	
	ruffled	0.400	E	3.250	382	0.434	35% (b_1-e)	30% (a_2-e)	22% (b_2-e)	
	ruffled	0.600	E	3.229	385	0.326	50% (a_2-e)	26% (b_1-e)	16% (b_2-e)	

[a] *z* refers to the displacement of the meso or β carbons from the mean porphyrin plane for ruffled or saddled porphyrins, respectively.

Discussion and Conclusion

We confirm the finding of DiMagno and co-workers that ruffling, *by itself*, does not engender significant red shifts in the Q- and B-band energies of simple porphyrins and metalloporphyrins, i.e., those that exhibit what Gouterman calls "normal" optical spectra. We have now extended this finding to the saddling case, i.e., saddling too, *by itself*, does not bring about significantly red-shifted optical spectra. The phrase "by itself" emphasizes that the red-shifted optical spectra exhibited by most nonplanar porphyrins do not actually result from

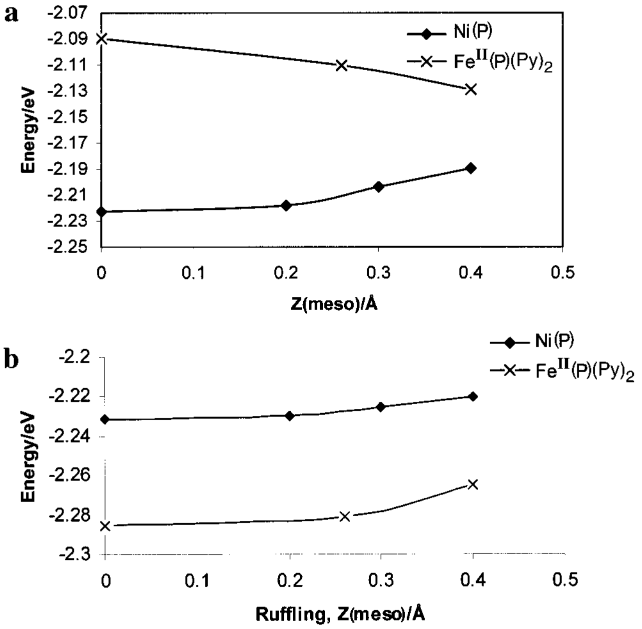

Figure 2. (a) The a_{2u}/e_g HOMO-LUMO gap as a function of the out-of-plane displacement of the meso carbons. (b) The a_{1u}/e_g HOMO-LUMO gap as a function of the out-of-plane displacement of the meso carbons.

nonplanarity, but from changes in bond distances and angles in the porphyrin skeleton—the IPNRs—brought about by substituents which also bring about the nonplanarity.[12] Thus, it is possible to significantly ruffle and saddle a porphyrin without engendering sizable red shifts in its optical spectrum. As DiMagno and co-workers[6] have pointed out, this may be of relevance to relatively "gentle" IPNR-free nonplanar distortion of a porphyrin cofactor within a protein matrix.

Some recent studies on chelatases may be of interest in this connection. Schultz[13] suggested that ferrochelatase catalyzes the insertion of iron into protoporphyrin IX by forcing the porphyrin into a distorted conformation. Recently, Spiro and co-workers[14] and Shelnutt and co-workers[15] have provided some resonance Raman evidence for porphyrin distortion in porphyrin−ferrochelatase complexes. Karger et al.[16] have studied the binding of deuteroporphyrin IX and the magnesium chelatase H subunit and report mild red shifts in the B- (2-4 nm) and Q-bands (4−9 nm) of the porphyrin on complexation with the protein. In light of this study, these red shifts are compatible with mild-to-significant distortion of the porphyrin ring on complexation with the chelatase.

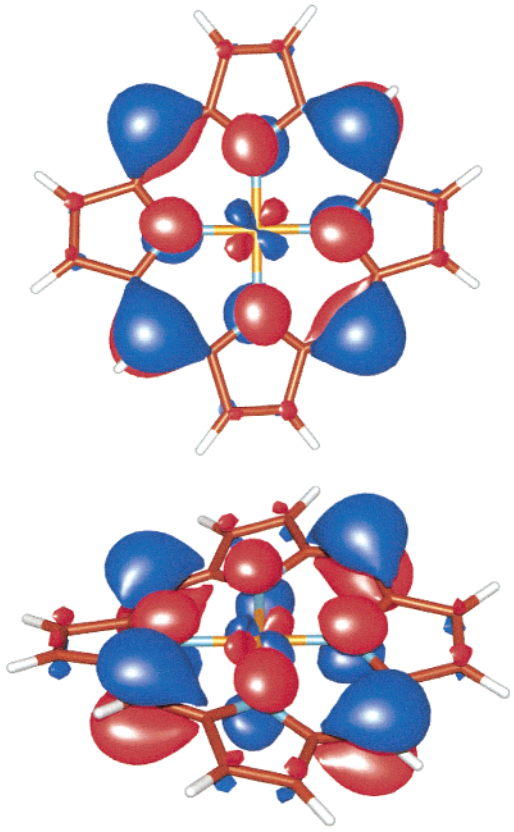

Figure 3. Two views of a_{2u} HOMO of ruffled Ni(P) showing the $d_{xy}-a_{2u}$ antibonding interaction.

For transition metal porphyrins, however, the question of whether nonplanar distortions bring about red shifts in the electronic spectra is a complicated one. Nonplanar distortions switch on specific metal(d)−porphyrin(π) orbital interactions and the influence of these on the electronic spectra remains to be systematically explored. In the case of nickel porphyrins, ruffling does bring about sizable red shifts in the electronic spectra.

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(10) Both the idealized ruffled and saddled conformations correspond to the D_{2d} point group. In this point group, the "a_{1u}" and "a_{2u}" porphyrin HOMOs (D_{4h} notation) transform as b_1 and b_2, respectively, for both ruffling and saddling. The metal "t_{2g}-type" d_{xy} orbital transforms as b_2 for the ruffled conformation and as b_1 for the saddled conformation, respectively. The metal "e_g-type" $d_{x^2-y^2}$ orbital transforms as b_1 for the ruffled conformation and as b_2 for the saddled conformation, respectively.

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(12) Some readers may take exception to the supposedly "academic" nature of this finding. What difference does it make, they may ask, whether the observed red-shifted spectra of nonplanar porphyrins results from nonplanarity or from other structural perturbations (i.e. the IPNRs) brought about by substituents that also bring about the nonplanarity? As DiMagno and co-workers have shown and as we confirm, it is possible to dissect the effects of nonplanarity from those of the IPNRs and this line of inquiry has led to a new understanding of the red-shifted optical spectra of many nonplanar porphyrins.

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