

A First-Principles Quantum Chemical Analysis of the Factors Controlling Ruffling Deformations of Porphyrins: Insights from the Molecular Structures and Potential Energy Surfaces of Silicon, Phosphorus, Germanium, and Arsenic Porphyrins and of a Peroxidase Compound I Model

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Abstract: Using nonlocal density functional theory calculations, we have examined several factors influencing ruffling deformations of porphyrin and porphyrazine complexes. Because a ruffling distortion is often a direct result of a small macrocycle core size, which, in turn, is brought about by complexation of a central ion with a small ionic radius, this study focuses on the conformations and potential energy surfaces of porphyrin complexes with small central ions (hereafter symbolized M) such as Si^{IV}, P^V, Ge^{IV}, and As^V. The optimized geometries exhibit ruffling torsion angles ranging from 0° for (P)Ge^{IV}F₂ and (P)Si^{IV}(C≡CPh)₂ to about 55° for [(P)P^VF₂]⁺. For relatively substantial ruffling distortions, a good linear correlation has been found between the ruffling torsion angle and the M–N distance for a wide variety of central ions including transition metals, for sterically unhindered porphyrins, and for a database including both experimental and optimized structures. The threshold between ruffling and planar structures is at M–N bond distances of 2.00–2.02 Å for sterically unhindered porphyrins and at 1.85–1.87 Å for porphyrazines. The calculations confirm an experimental observation that electron-withdrawing axial ligands lead to increased ruffling, especially for phosphorous and silicon porphyrins. The *ortho* hydrogens of axial phenyl ligands and the 2- and 6- hydrogens of axial pyridine ligands can sterically interfere with the porphyrin and contribute to ruffling. In addition to the M–N distance, a number of other geometrical parameters also vary systematically with the ruffling distortion. Thus, the C_α–C_{meso}–C_α angle decreases with ruffling and the C_βC_β distance and C_α–N–C_α angle increase with ruffling. These structural variations are reflected in a number of ruffling-sensitive vibrational frequencies. The ruffled D_{2d} geometries of [(P)P^VF₂]⁺ and [(P)P^VCl₂]⁺ are stabilized by 9.25 and 5.26 kcal/mol, respectively, relative to planar D_{4h} symmetry-constrained optimized geometries. In contrast, the ruffled D_{2d} geometries of [(Pz)P^VF₂]⁺ and of all the silicon complexes studied are more stable than the corresponding D_{4h} symmetry-constrained optimized geometries by less than 0.01 kcal/mol. This underscores the extreme softness of ruffling deformations and shows that even fairly large distortions, where the ruffling torsion angle changes by up to 25°, can occur with almost no expenditure of energy. Finally, through a reinvestigation of a recent study of a peroxidase compound I model, we have uncovered a heretofore unsuspected role of Fe(3d_{xy})-porphyrin(a_m) orbital interactions in macrocycle ruffling. Also seen for certain low-spin ferrihemes, this orbital interaction is not important for manganese porphyrins.

1. Introduction

In recent years, much attention has been devoted to the subject of nonplanar conformations of porphyrins and related macrocycles.^{1,2} A variety of conformations, including the ruffled, saddled, domed, and waved conformations have been characterized for synthetic porphyrins, with ruffling being the most commonly observed of these nonplanar distortions.^{1,2} Macrocycle nonplanarity is also an important structural feature of many heme cofactors of hemoproteins,³ the pigments of photosynthetic

proteins,⁴ and cofactor F₄₃₀ of methylcoenzyme M reductase.⁵ Two broad issues are of great interest in this connection: (a) What factors bring about and control the various types of nonplanar distortions? (b) How do nonplanar distortions influence such properties as redox potentials, axial ligand affinities, and excited-state energies and lifetimes? This work is concerned with the first of these issues: specifically, we have attempted to obtain a detailed understanding of the factors controlling ruffling distortions, based on first-principles quantum chemical studies of the potential energy surfaces of porphyrin complexes with small central ions (hereafter symbolized M) such as Si^{IV},

(1) (a) Shelnut, J. A.; Song, X.-Z.; Ma, J.-G.; Jia, S.-L.; Jentzen, W.; Medforth, C. J. *Chem. Soc. Rev.* **1998**, 27, 31. (b) Shelnut, J. A. In *The Porphyrin Handbook*; Kadish, K. M.; Smith, K. M.; Guilard, R., Eds.; Academic: New York, 2000; Vol. 7, pp 167–223.

(2) (a) Scheidt, W. R.; Lee, Y. J. *Struct. Bonding* **1987**, 64, 2. (b) Scheidt, W. R. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic: New York, 2000; Vol 3, pp 49–112.

(3) Hoffmann, B. M. In *The Porphyrins*; Dolphin, D., Ed.; Academic: New York, 1979; Vol VII, p 403.

(4) Barkigia, K. M.; Chantranupong, L.; Smith, K. M.; Fajer, J. *J. Am. Chem. Soc.* **1988**, 110, 7566.

(5) Telser, J. *Struct. Bonding* **1998**, 91, 31.

P^V, Ge^{IV}, and As^V (we distinguish between the porphyrin ligand and pentavalent phosphorus by the symbols (P) and P^V, respectively).

Until now, molecular mechanics (MM) calculations have played a crucial role in theoretical studies of porphyrin nonplanarity.^{1,2} A significant contribution of these calculations has been the decomposition of observed nonplanar distortions in synthetic and biological porphyrin systems in terms of displacements along various low-frequency normal modes of the porphyrin macrocycle.¹ However, because molecular mechanics and semi-empirical quantum mechanical techniques rely on empirical parameters, they can be inadequate for accurate conformational analyses of molecules with novel structural or electronic features. It is somewhat surprising, therefore, that there are extremely few nonempirical quantum mechanical studies of nonplanar distortions of porphyrins. At the time of initial submission of this paper, our recent theoretical study of low-spin six-coordinate hemes with axial pyridine ligands, model compounds of the cytochromes *b*, is the only published report of a nonempirical quantum mechanical geometry optimization of a significantly nonplanar porphyrin.⁶ What can account for the scarcity of such calculations? First, such calculations are reasonably expensive in terms of computational resources. Second, because of the softness of the potential energy surfaces associated with nonplanar distortions, geometry optimizations with standard convergence criteria often yield optimized geometries that are not reproducible. We speculate that these two factors, although hardly insurmountable, have so far discouraged serious first-principles theoretical studies of this important area.

The main goals of the present study, which uses nonlocal (NL) density functional theory (DFT)^{7,8} and high-quality basis sets, are as follows.

Because first-principles quantum chemical methods do not yet have a significant track record in describing nonplanar conformations of porphyrins, an early goal of this study was to establish such a track record and to compare various optimized ruffled structures with experiment.

Having convinced ourselves of the suitability of the NL-DFT method for studying this problem, we focused on more "chemical" issues: how is the degree of ruffling controlled by such factors as the size of the central coordinated ion and the electronic and steric character of the axial ligand? Do porphyrins have a tendency to ruffle?

Because of the greater accuracy of the NL-DFT approach, relative to MM and semiempirical chemical methods, an important goal was also to obtain accurate estimates of the energetics of ruffling distortions of various porphyrin complexes of interest.

We have also investigated the possible existence of vibrational signatures of macrocycle ruffling and the structural basis of such marker bands.

Finally, we have studied the origin of ruffling in a peroxidase compound I model and uncovered metal(d_{xy})-porphyrin(π) orbital interactions as a contributing factor.

Overall, although most of the results of this study were obtained from calculations on Si^{IV}, P^V, Ge^{IV}, and As^V complexes, both the fundamental questions posed and the conclu-

(6) Ghosh, A.; Gonzalez, E.; Vangberg, T. *J. Phys. Chem. B* **1999**, *103*, 1363. This paper presents a theoretical treatment of the possibility that metal-(d)-porphyrin(π) orbital interactions are important for ruffling, a topic not discussed further in this work.

(7) Ghosh, A. *Acc. Chem. Res.* **1998**, *31*, 189.

(8) Ghosh, A. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic: New York, 2000; Vol 7, pp 1–38.

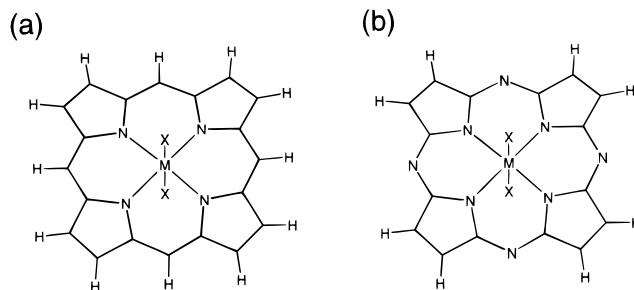


Figure 1. Schematic illustration of the structures studied, (a) (P)MX₂ and (b) (Pz)MX₂ where M = (P^V, Si^{IV}, As^V, Ge^{IV}), X = (F, Cl, Ph), (P) = porphyrinato, (Pz) = porphyrizinato, and Ph = phenyl.

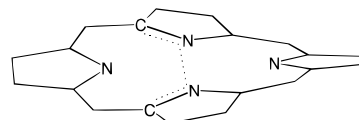


Figure 2. Definition of the C_α-N-N-C_α ruffling torsion angle.

sions reached in this study are of wide relevance to porphyrin chemistry and not just to specific classes of porphyrin complexes.

2. Methods

We used nonlocal density functional theory, the B3LYP exchange-correlation functional, the 6-311G(d,p) basis set, full geometry optimizations with tight criteria for forces on atomic nuclei, and analytical evaluation of frequencies at the optimized geometries, as implemented in the Gaussian98 program system.⁹ For reasons mentioned in the Introduction, the tight convergence criteria for geometry optimizations were an absolutely essential feature of these calculations. Figure 1 shows the various molecules studied in this work. Unless otherwise mentioned, all calculations were carried out with *D*_{2d} symmetry constraints.

3. Results and Discussion

Before discussing specific results, it is useful to define the ruffling distortion in a quantitative manner. In this work, we have chosen to use the torsion angle shown in Figure 2 as a quantitative measure of ruffling. Other commonly used measures of ruffling include the standard deviation for the displacement of the atoms in the C₂₀N₄ porphyrin macrocycle from the mean plane of the porphyrin or simply the mean displacement of the *meso* carbon atoms from the mean plane of the porphyrin. For all of the structures studied in this work, there is an almost exact linear dependence between the ruffling torsion angle and the other two measures of ruffling.

(a) Systematic Structural Variations. Table 1 presents selected geometrical parameters of the optimized structures of the various molecules studied in this work. While only one of the optimized porphyrazine structures is ruffled, the optimized porphyrin structures span the entire range of experimentally observed ruffling angles. The ruffling torsion angle correlates

(9) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. J. A.; E., S.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian98*, revision A.5; Gaussian, Inc.: Pittsburgh, PA, 1998. Additional technical details about the calculations are obtainable from the Gaussian98 program manual.

Table 1. Selected Geometry Parameters (Å, deg) for Various Optimized Structures^a

	ruffling	$C_{\alpha}-N-C_{\alpha}$	$C_{\alpha}-C_m-C_{\alpha}$ ($C_{\alpha}-N_m-C_{\alpha}$)	$C_{\beta}-C_{\beta}$	$C_{\alpha}-C_m$ ($C_{\alpha}-N_m$)	$C_{\alpha}-N$	M-N	M-axial
[(P)P ^V F ₂] ⁺	54.7120	106.5103	120.5264	1.3624	1.3812	1.3863	1.8533	1.6295
[(P)P ^V Cl ₂] ⁺	47.8151	106.2605	121.0132	1.3616	1.3786	1.3878	1.8793	2.1738
[(P)P ^V Ph ₂] ⁺	36.7332	106.9070	123.3414	1.3617	1.3857	1.3791	1.9553	1.8939
(P)Si ^{IV} F ₂	24.1533	105.8319	123.8829	1.3581	1.3833	1.3749	1.9699	1.6578
(P)Si ^{IV} Ph ₂	23.2694	106.9266	125.0671	1.3604	1.3907	1.3708	2.0077	1.9619
(P)Si ^{IV} Cl ₂	12.8012	105.4059	123.8487	1.3569	1.3792	1.3781	1.9754	2.2110
(P)Si ^{IV} (CCPh) ₂	0.0034	106.1032	124.9101	1.3585	1.3851	1.3737	2.0089	1.8759
(P)Ge ^{IV} F ₂	0.0003	106.9222	125.6747	1.3592	1.3871	1.3719	2.0308	1.7961
[(P)As ^V F ₂] ⁺	30.1220	106.0695	123.3991	1.3628	1.3818	1.3866	1.9566	1.7426
[(Pz)P ^V F ₂] ⁺	21.7297	105.3427	119.7944	1.3541	1.3112	1.3924	1.8470	1.6291
[(Pz)P ^V Cl ₂] ⁺	0.0069	105.2302	120.2883	1.3534	1.3092	1.3940	1.8670	2.1660
(Pz)Si ^{IV} F ₂	0.0008	106.4842	121.3834	1.3502	1.3213	1.3739	1.9079	1.6712
(Pz)Si ^{IV} Cl ₂	0.0010	106.1987	121.0572	1.3531	1.3184	1.3781	1.8978	2.2394

^a The rather excessive accuracy of these numerical results is intended to allow the interested reader to carry out various structure-frequency and other correlations of the type shown in Figures 3–6

monotonically with a number of geometrical parameters of the porphyrin ring. Thus, the $C_{\alpha}-N-C_{\alpha}$ angle increases with ruffling, while the $C_{\alpha}-C_{meso}-C_{\alpha}$ angle decreases with ruffling. Again, the $C_{\beta}-C_{\beta}$ and $C_{\alpha}-N$ distances increase with ruffling. (It should be pointed out that planar, unruffled structures do not fit these correlations.) As shown in Table 1, many of these structural variations are so small that they may not be detectable in crystallographic determinations of molecular structure. However, as will be discussed in Section 3(e), these structural differences do manifest themselves as ruffling-sensitive modes in the vibrational spectra of the molecules in question. The structural parameter showing the best and most obvious correlation with the torsion angle is the M–N_{porphyrin} distance or, in other words, the macrocycle core size. This is further discussed in the next section.

(b) Correlation of Ruffling with Macrocycle Core Size and Energetics of Ruffling. Very often, a ruffling distortion stems directly from a small macrocycle core size, which, in turn, results from complexation of an ion with a small ionic radius. For the different complexed ions studied, the P^V complexes exhibit the most extreme ruffling, which is over 50° for [(P)P^VF₂]⁺. These are followed by [(P)As^VF₂]⁺, with a ruffling angle of 30.1°, some of the silicon complexes, and the planar (P)Ge^{IV}F₂. These trends are more or less as expected from elementary considerations of ionic radii. Consistent with an old empirical observation by Hoard,¹⁰ our calculations indicate that the threshold between planar and nonplanar porphyrins appears to occur at an M–N_{porphyrin} distance in the range 2.00–2.02 Å.

To obtain an appreciation of the energetics of ruffling, we carried out relaxed potential energy scans on four species, [(P)P^VF₂]⁺, [(Pz)P^VF₂]⁺, (P)Si^{IV}F₂, (Pz)Si^{IV}F₂. In these calculations, the M–N_{porphyrin} distance was frozen at 3–4 different values above and below the potential energy minimum, while all other geometrical parameters were optimized. Figure 3 shows the approximately linear relationship between the ruffling angle and the M–N_{porphyrin} distance. Figure 4 shows the dependence of the molecular potential energies on the M–N_{porphyrin} distance. Except for the phosphorus porphyrins, which exhibit extreme ruffling, the energetic stabilization associated with ruffling, relative to planar D_{4h} optimized geometries, is exceedingly small. Thus, the ruffled D_{2d} geometries of [(P)P^VF₂]⁺ and [(P)P^VCl₂]⁺ are stabilized by 9.25 and 5.26 kcal/mol, relative to planar D_{4h} symmetry-constrained optimized geometries. In contrast, the ruffled D_{2d} geometries of [(Pz)P^VF₂]⁺ and of all the silicon complexes studied are stabilized relative to the corresponding D_{4h} symmetry-constrained optimized geometries

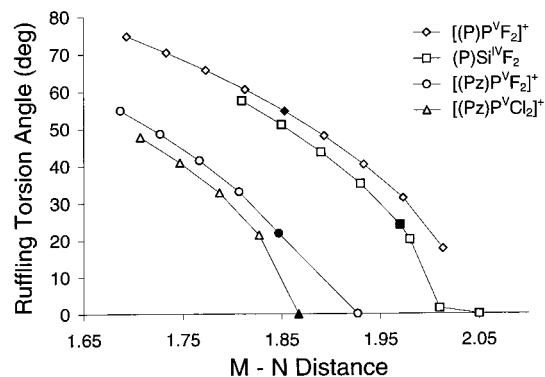


Figure 3. Variation of the ruffling torsion angle as a function of the M–N distance for [(P)P^VF₂]⁺, (P)Si^{IV}F₂, [(Pz)P^VF₂]⁺, and [(Pz)P^VCl₂]⁺, all other internal coordinates being fully optimized.

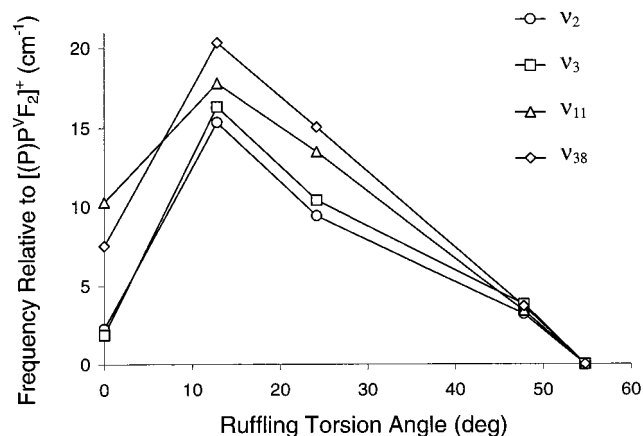


Figure 4. Correlation between selected vibrational marker bands and the ruffling torsion angle. From left to right, the molecules are (P)–Ge^{IV}F₂, (P)Si^{IV}Cl₂, (P)Si^{IV}F₂, [(P)P^VCl₂]⁺, and [(P)P^VF₂]⁺.

by less than 0.1 kcal/mol. This illustrates the extreme softness of ruffling distortions and explains why ruffling distortions are often observed for porphyrins in solution and in crystals even when there is no obvious driving force for ruffling but simply as a result of relatively weak intermolecular forces. This underscores the vulnerability of theoretical, particularly DFT, calculations on porphyrin nonplanarity to numerical errors involved in the computational methods.

(c) Comparison of Optimized and Crystallographic Ruffled Structures.

Given the extreme softness of ruffling distortions, can one expect any correlation between calculated and experimentally

(10) Hoard, J. L. *Science* **1971**, *174*, 1295.

Table 2. Selected Experimental Geometry Parameters (Å, deg) Averaged Over the "Symmetry Unique" Atoms

	ruffling	C _α -N-C _α	C _α -C _m -C _α	C _β -C _β	C _α -C _m	C _α -N	M-N	M-axial	ref
[(OEP)P ^V Cl ₂] ⁺	55.10	106.35	120.17	1.357	1.371	1.389	1.833	2.138	11
[(TPP)P ^V (OH) ₂] ⁺		107.5	120.5				1.89	1.595	12
(TPP)Si ^{IV} (Ph) ₂	29.46	106.05	122.57	1.341	1.398	1.374	1.970	1.947	19
(TTFP)Si ^{IV} F ₂	40.71	106.16	121.63	1.339	1.389	1.380	1.920	1.640	13
TTPSi ^{IV} F ₂	38.77	105.94	121.51	1.332	1.385	1.385	1.918	1.643	13
(TTP)Si ^{IV} (O ₃ SCF ₃) ₂	47.75	105.92	120.15	1.344	1.384	1.386	1.870	1.831	14
(OEP)Ge ^{IV} F ₂	27.31	106.36	125.47	1.371	1.385	1.375	1.986	1.790	15
(P)Ge ^{IV} (OMe) ₂	3.76	106.61	126.31	1.337	1.373	1.378	2.015	1.823	16
(TPP)Ge ^{IV} (OAc) ₂	2.36	106.52	123.35	1.348	1.379	1.388	1.963	1.873	17
(OEP)As ^V (Me)(OH)	8.32	105.93	126.38	1.357	1.375	1.386	2.003	1.825 (O) 1.870 (C)	18

observed ruffling torsion angles? Not surprisingly, the experimental crystallographic data presented in Table 2 show that one can only expect rather qualitative agreement between theory and experiment with regard to the ruffling torsion angle. Thus, consistent with our findings on [(P)P^VF₂]⁺ and [(P)P^VF₂]⁺, the phosphorous complex, [(OEP)P^VCl₂]⁺ exhibits the greatest ruffling distortion among the various relevant species that have been crystallographically characterized.¹¹ The tetraarylporphyrin silicon complexes exhibit somewhat more ruffling relative to the silicon complexes of unsubstituted porphyrin studied theoretically. Although the evidence is not conclusive, this may indicate that tetraarylporphyrin macrocycles may have a greater intrinsic tendency to ruffle relative to unsubstituted porphyrin. The ruffling torsion angles for the crystallographically characterized germanium complexes vary considerably from almost 0° to 27.3°.¹⁵⁻¹⁷

Overall, in view of the softness of ruffling deformations, it is futile to attempt to accurately reproduce solid-state ruffling distortions by molecular calculations. However, the calculations do confirm another aspect of the experimentally characterized ruffled structures in a quantitative manner: in general, the experimental structures quantitatively confirm the correlation between ruffling torsion angle and macrocycle core size that we have found in our calculations. To give an example, the optimized geometry of (P)Ge^{IV}F₂ is planar, whereas the experimental solid-state structure of (OEP)Ge^{IV}F₂ is significantly ruffled with a ruffling angle of 27.3°. However, if (P)Ge^{IV}F₂ is optimized with the Ge-N_{porphyrin} distances constrained to the value observed experimentally for (OEP)Ge^{IV}F₂, the optimization also reproduces the experimentally observed ruffling angle. This point is further illustrated by Figure 5.

Figure 5 shows a scatter plot of the ruffling angles (ρ) of various experimental and DFT optimized geometries versus the M-N distance (d). Some of the noteworthy points related to Figure 5 are as follows. For ruffling angles greater than 20°, there is a good linear correlation between ρ (deg) and d (Å). Clearly, this particular correlation between the ruffling angle and the M-N_{porphyrin} distance holds reasonably well for unsubstituted porphyrin and sterically unhindered porphyrins, but should not be expected to hold for a porphyrin ligand with an

inherently different tendency to ruffle such as dodecaphenylporphyrin. Figure 5 includes all ruffled structures optimized in our laboratory to date and pertinent crystallographic structures. A significant point is the diversity of central coordinated ions represented in Figure 5, which includes not only Si^{IV}, P^V, Ge^{IV}, and As^V, but also transition metal ions.²⁰ In other words, the ρ - d correlation obtained in this study applies very generally, well beyond the metalloid ions that have been the focus of this work. Finally, it is no surprise that in Figure 5, the data points are considerably more scattered for low-ruffling torsion angles, where the deformations are exceedingly soft, than for higher-ruffling angles, where the deformations are stiffer.

(d) Porphyrins versus Porphyrazines. Porphyrins and porphyrazines have inherently different tendencies to ruffle. The central cavity of porphyrazines, as measured by the distance between opposite central nitrogens, is about 0.2 Å smaller than the central cavity of an analogous porphyrin.^{21,22} Thus, the porphyrazine ligand can accommodate a smaller central ion than a porphyrin ligand without undergoing ruffling. Among the different porphyrazine complexes studied, only [(Pz)P^VF₂]⁺ is ruffled with a ruffling angle of 21.8° and a P^V-N bond distance of 1.847 Å, whereas [(Pz)P^VCl₂]⁺, with only a slightly longer P^V-N bond distance of 1.867 Å, is planar. Thus, the threshold for ruffling of the porphyrazine ligand appears to be at an M-N bond distance of 1.85–1.87 Å.

(e) Electronic Effects of Axial Ligands. Table 1 shows that complexes with fluorine axial ligands are, in general, significantly more ruffled than analogous complexes with chlorine axial ligands. This suggests that electron-withdrawing axial ligands promote ruffling in tetrapyrrole complexes. Such axial ligands also lead to a shortening of the M-N bond distances and, apparently, of the effective ionic radius of the central ion. A similar trend is also seen in the X-ray structures of silicon and phosphorus porphyrins where the degree of ruffling correlates with the electron-withdrawing ability of the axial ligands.¹⁹

(f) Steric Effects of Axial Ligands. Since phenyl groups are not particularly electron-withdrawing, one would expect, in view

(11) Yamamoto, Y.; Nadano, R.; Itagaki, M.; Akiba, K. *J. Am. Chem. Soc.* **1995**, *117*, 8287.

(12) Cowley, A. H.; Ebsworth, E. A. V.; Mehrotra, S. K.; Rankin, D. W. H.; Walkinshaw, M. D. *J. Chem. Soc., Chem. Comm.* **1982**, 1099.

(13) Kane, K. M.; Lemke, F. R.; Petersen, J. L. *Inorg. Chem.* **1997**, *36*, 1354.

(14) Kane, K. M.; Lemke, F. R.; Petersen, J. L. *Inorg. Chem.* **1995**, *34*, 4085.

(15) Guillard, R.; Barbe, J.; Boukhris, M.; Lecomte, C. *J. Chem. Soc., Dalton Trans.* **1988**, 1109.

(16) Mavridis, A.; Tulinsky, A. *Inorg. Chem.* **1976**, *15*, 2723.

(17) Lin, S. W. J. A.; Hong, T. N.; Tung, J. Y.; Chen, J. H. R. *Inorg. Chem.* **1997**, *36*, 3886.

(18) Satoh, W.; Nadano, R.; Yamamoto, Y.; Akiba, K. *J. Chem. Soc., Chem. Comm.* **1996**, 2451.

(19) Zheng, J. Y.; Konishi, K.; Aida, T. *Inorg. Chem.* **1998**, *37*, 2591.

(20) The optimized data on the Fe(III) complexes is taken from ref 6 and the data on Ni(III) complexes is taken from: Ghosh, A.; Wondimagegn, T.; Gonzalez, E.; Halvorsen, I. *J. Inorg. Biochem.*, in press.

(21) For a geometry optimization of porphyrazine, see: Ghosh, A.; Gassman, P. G.; Almlöf, J. *J. Am. Chem. Soc.* **1994**, *116*, 1932.

(22) (a) Shelnut, J. A.; Medforth, C. J.; Berber, M. D.; Barkigia, K. M.; Smith, K. M. *J. Am. Chem. Soc.* **1991**, *113*, 4077. Molecular mechanics calculations described in this paper revealed some of the same ruffling-sensitive structural features as identified in this paper. (b) Jentzen, W.; Simpson, M. C.; Hobbs, J. D.; Song, X.; Ema, T.; Nelson, N. Y.; Medforth, C. J.; Smith, K. M.; Veyrat, M.; Mazzanti, M.; Ramasseul, R.; Marchon, J.-C.; Takeuchi, T.; Goddard, W. A., III; Shelnut, J. A. *J. Am. Chem. Soc.* **1995**, *117*, 11085.

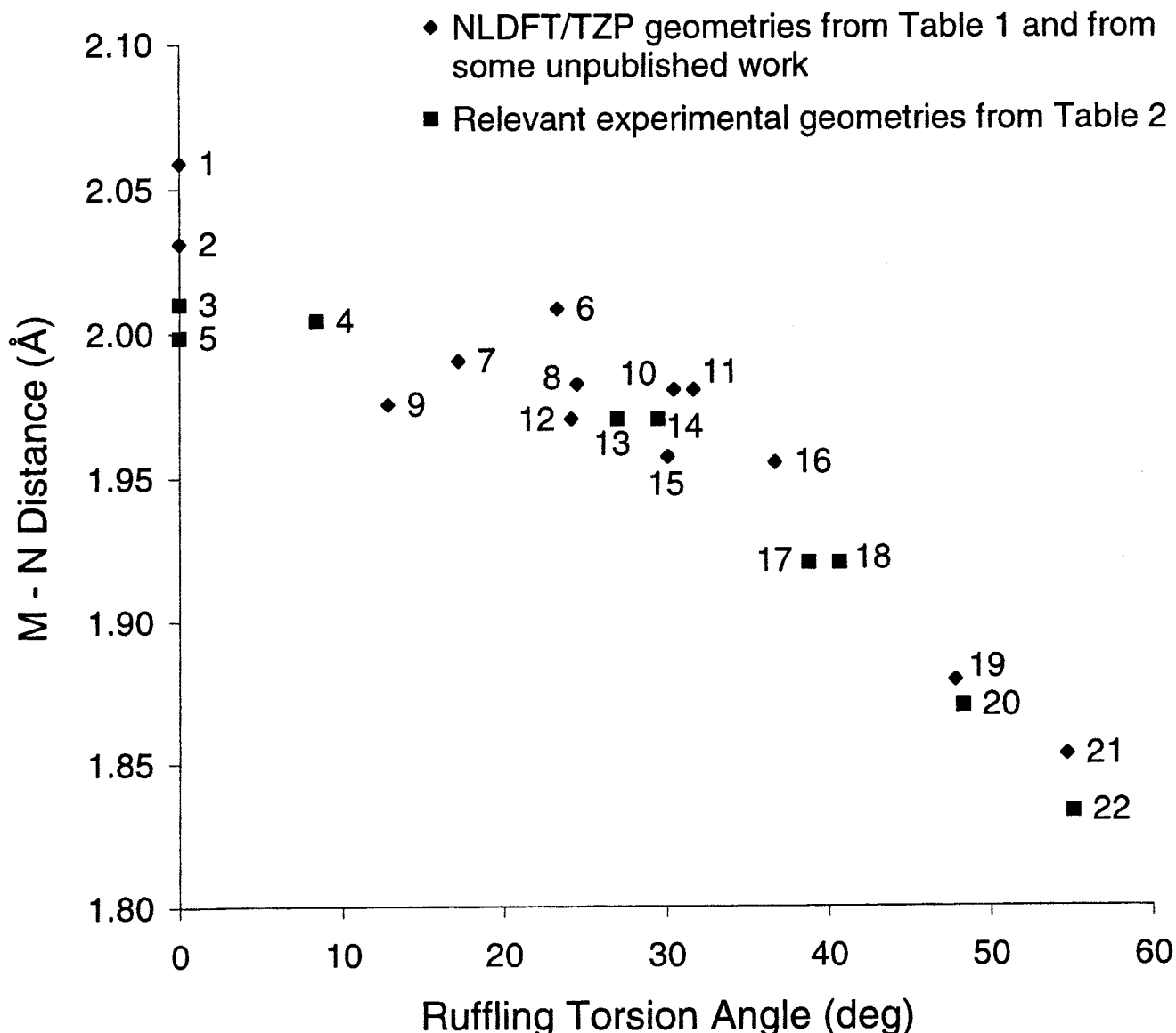


Figure 5. Relation between the ruffling torsion angle and the M–N distance for various optimized (Table 1), and experimental (Table 2) porphyrin structures, and some unpublished DFT structures on Fe(III)- and Ni(III)-metalloporphyrins. The molecules included in the scatter plot are: **1.** [(P)Ni^{III}(CN)₂]⁻, **2.** (P)Ge^{IV}F₂, **3.** (P)Ge^{IV}(OMe)₂, **4.** [(OEP)As^VMe(OH)]⁺, **5.** (TPP)Ge^{IV}(OAc)₂, **6.** (P)Si^{IV}Ph₂, **7.** [(P)Fe^{III}(py)₂]⁺, **8.** [(P)Ni^{III}(py)₂]⁺, **9.** (P)Si^{IV}Cl₂, **10.** [(P)Fe^{III}(py)₂]⁺, **11.** [(P)Fe^{III}(cypy)₂]⁺, **12.** (P)Si^{IV}F₂, **13.** (OEP)Ge^{IV}F₂, **14.** (TPP)Si^{IV}(Ph)₂, **15.** [(P)As^VF₂]⁺, **16.** [(P)P^VPh₂]⁺, **17.** [(TPP)Si^{IV}F₂]⁺, **18.** (TTFP)Si^{IV}F₂, **19.** [(P)P^VCl₂]⁺, **20.** (TPP)Si^{IV}(O₃SCF₃)₂, **21.** [(P)P^VF₂]⁺, **22.** [(OEP)P^VCl₂]⁺. For torsion angles greater than 20° there is a good linear correlation between the ruffling torsion angle (τ) and the M–N distance (d), $d = -0.0048\tau + 2.1101$, $R^2 = 0.9397$.

of the above discussion in section 3(e), that [(P)P^VPh₂]⁺ and (P)Si^{IV}Ph₂ would be relatively mildly ruffled. However, the optimized ruffling torsion angles of [(P)P^VPh₂]⁺ and (P)Si^{IV}Ph₂ are fairly large, 37.7 and 23.2°, respectively. Indeed, in apparent contradiction to the arguments in Section 3(e), (P)Si^{IV}Ph₂ is 11° more ruffled than (P)Si^{IV}Cl₂. Zheng and co-workers have suggested that the ruffling in (TPP)Si^{IV}Ph₂ is caused by steric repulsion between the *ortho* hydrogens of the phenyl groups and the porphyrin ring.¹⁹ The optimized structure of (P)Si^{IV}Ph₂ is consistent with this suggestion. Thus, the nearest contacts between an *ortho* phenyl hydrogen on one hand and porphyrin N, C_α, C_{meso} atoms on the other hand are 2.63, 2.79, and 2.86 Å, respectively. Lending further credence to the proposal of Zheng and co-workers is our finding that the porphyrin ligand in the optimized structure of (P)Si^{IV}(C≡CPh)₂, with sterically unhindered phenylethynyl ligands, is planar. These findings are relevant to analogous results for low-spin iron(III)⁶ and nickel(III)²⁰ porphyrins with axial pyridine ligands

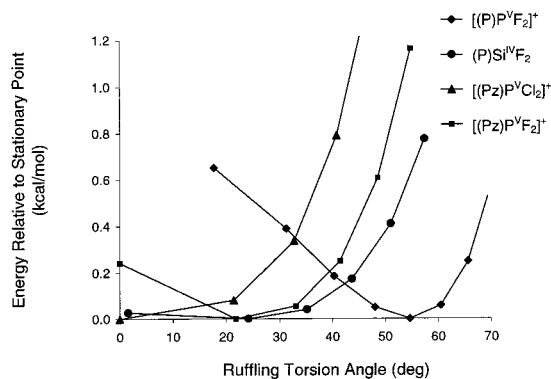
where the 2- and 6- hydrogens of the pyridine ligands appear to interact sterically with the porphyrin.

(g) Ruffling-Sensitive Vibrational Modes. Full vibrational analyses were carried out on five of the molecules studied, [(P)P^VF₂]⁺, [(P)P^VCl₂]⁺, (P)Si^{IV}F₂, (P)Si^{IV}Cl₂, and (P)Ge^{IV}F₂. No imaginary frequencies were found for any of these molecules, proving that the D_{2d} optimized structures are true minima at the level of theory used in this work. This result is nontrivial: it shows that the molecules have pure ruffled structures with no saddling. Mixed ruffling and saddling would have led to an S_4 point group symmetry.

Table 3 presents the frequencies of selected vibrational modes of these molecules along with their ¹⁵N₄ isotope shifts. As shown graphically in Figure 6, several of the frequencies appear to correlate with the ruffling torsion angle. Thus, the C_βC_β stretching frequencies ν_2 , ν_3 , ν_{11} , and ν_{38} decrease with increasing ruffling, as expected from increasing C_βC_β distances with increasing ruffling. The two modes ν_{18} and ν_{50} increase

Table 3. Selected Calculated Frequencies and $\Delta^{15}\text{N}_4$ Isotope Shifts in Parenthesis (cm^{-1})

mode	(P)P ^V F ₂ ⁺	(P)P ^V Cl ₂ ⁺	(P)Si ^{IV} F ₂	(P)Si ^{IV} Cl ₂	(P)Ge ^{IV} F ₂
			A ₁		
ν_2	1596.3 (0.3)	1599.5 (0.2)	1605.8 (0.5)	1611.5 (0.3)	1598.6 (0.6)
ν_3	1482.9 (0.2)	1486.7 (0.1)	1493.3 (0.7)	1499.0 (0.4)	1484.8 (1.1)
ν_4	1416.7 (8.6)	1404.5 (7.1)	1416.9 (8.8)	1414.0 (8.1)	1408.1 (8.7)
γ_{14}	94.7 (0.0)	82.2 (0.0)	41.9 (0.0)	14.1 (0.0)	43.7 (0.0)
			A ₂		
ν_{26}	1337.9 (5.4)	1339.3 (4.9)	1350.0 (5.40)	1351.5 (4.9)	1357.8 (5.6)
γ_{18}	62.7 (0.0)	58.1 (0.0)	55.4 (0.0)	54.3 (0.0)	58.5 (0.0)
			B ₁		
ν_{10}	1666.7 (0.3)	1677.2 (0.2)	1679.8 (0.1)	1692.4 (0.2)	1669.0 (0.1)
ν_{11}	1529.6 (0.1)	1533.0 (0.0)	1543.1 (0.1)	1547.0 (0.1)	1539.9 (0.1)
γ_{11}	669.7 (0.1)	672.1 (0.0)	679.8 (0.0)	685.2 (0.0)	682.6 (0.0)
ν_{18}	241.7 (1.4)	232.0 (1.4)	214.3 (1.4)	209.2 (1.4)	219.3 (1.4)
			B ₂		
ν_{30}	1114.9 (21.2)	1106.3 (21.7)	1088.1 (19.7)	1987.7 (20.5)	1084.7 (18.9)
ν_{33}	470.5 (1.1)	457.5 (0.0)	440.0 (0.0)	439.3 (0.0)	429.8 (0.0)
			E		
ν_{38}	1561.0 (1.3)	1564.6 (1.20)	1576.0 (1.2)	1581.2 (1.1)	1568.5 (1.4)
ν_{50}	520.9 (0.4)	487.0 (0.6)	459.2 (0.9)	448.5 (0.8)	439.0 (1.5)

**Figure 6.** Variation of the energy relative to stationary geometry as a function of the ruffling torsion angle for [(P)P^VF₂]⁺, (P)Si^{IV}F₂, [(Pz)P^VCl₂]⁺, and [(Pz)P^VF₂]⁺.

with ruffling. This too is understandable because these modes have a large M–N_{porphyrin} stretching component and the M–N_{porphyrin} distance contracts with increasing ruffling. In particular, these calculated results agree with the experimental observation by Shelnett, Smith, and co-workers that the structure-sensitive marker bands ν_2 and ν_3 decrease with decreasing macrocycle core size.²² The ruffling frequency itself, γ_{14} , increases significantly with increasing ruffling, presumably owing to increasing stiffness of the M–N_{porphyrin} bonds. In other words, the more strongly ruffled porphyrin structures occupy steeper potential energy wells, as far as the ruffling coordinate is concerned.

(h) Reinvestigation of a Peroxidase Compound I Model. (Note added in proof.) After this paper was submitted, Deeth published a paper on ruffling deformations of peroxidase compound I models wherein he described dramatic electronic consequences of porphyrin ruffling (described as saddle distortion in the paper).²³ The porphyrin ring in the optimized structure of [(P)Fe(O)(ImH)]⁺ (ImH = imidazole) was found to be significantly ruffled with ruffling dihedral angles of 38–39°. For such a high degree of ruffling, the Fe–N_{porphyrin} distances of 1.98 Å are fairly long, longer than that predicted by Figure 5, suggesting that an A_{2u} porphyrin cation radical has a greater tendency to ruffle relative to the corresponding nonradical porphyrin. Compared to a conformation of this molecule with

a planar porphyrin ring, the spin density profile of the ruffled conformation was found to be dramatically different. The porphyrin ring in the planar conformation appears to be a typical and full-fledged porphyrin “cation” radical. In contrast, the ruffled porphyrin ligand carries only about half an electron spin, with the spin population on the iron rising to 1.45, compared to an iron spin population of 1.05 for the planar conformation. The author does not offer any insights into the “mechanism” of this ruffling-induced electron redistribution. Whatever this “mechanism” may be, it must also explain another curious observation: in spite of the dramatic difference in iron spin population between the planar and ruffled conformations, the optimized Fe=O bond lengths are essentially identical, 1.64 Å, for both conformations.²³

Intrigued by these fascinating unexplained facets of Deeth’s results, we repeated his calculations and analyzed the results in some detail. We quantitatively reproduced the ruffling-induced changes in the spin density profiles as well as all structural features reported by Deeth. Our key new finding is that ruffling turns on a specific metal(*d_{xy}*)–porphyrin(*a_{2u}*) orbital interaction that is absent for the planar porphyrin conformation. In general, this is a weak orbital interaction because the metal *d_{xy}* orbital is σ whereas the *a_{2u}* orbital is π , with respect to reflection across the plane of the porphyrin. But, for *D_{2d}* ruffled (but not saddled) metalloporphyrins, both the *d_{xy}* and *a_{2u}* orbitals transform as *b₂*. This explains the significant spin populations of 0.12 per *meso* carbon and 0.06 per porphyrin nitrogen for the ruffled conformation of [(P)Fe(O)(ImH)]⁺.²³ Because the metal *d_{xy}* orbital is nonbonding with respect to the oxygen orbitals, it also becomes clear why the Fe=O bond distances are the same for the planar and ruffled conformations, despite the significant difference in iron spin populations. Elsewhere,⁶ we have characterized the *d_{xy}*–*a_{2u}* orbital interaction for low-spin six-coordinate ferrihemes with low-basicity pyridines as axial ligands. It appears that the *d_{xy}*–*a_{2u}* orbital interaction is uniquely important for hemes. In contrast, this orbital overlap is negligible for Mn(IV) porphyrins.²⁴ Are ruffling and the *d_{xy}*–*a_{2u}* orbital interaction important features of enzymatic compound I intermediates? Because natural β -substituted metalloporphyrins give rise to A_{1u}-type cation radicals,²⁵ the *d_{xy}*–*a_{2u}* orbital interaction probably does not play a significant role in determining the

(23) Deeth, R. J. *J. Am. Chem. Soc.* **1999**, *121*, 6074.(24) Ghosh, A.; Gonzalez, E. *Isr. J. Chem.* (Special Issue on Bioinorganic Chemistry; Gross, Z., Gray, H. B., eds.), in press.

conformation of the porphyrin macrocycle. However, regardless of the significance of this orbital interaction, the porphyrin ring may still be ruffled in a particular enzymatic compound I intermediate simply as a consequence of the softness of the ruffling deformation.

(i) Other Factors Controlling Ruffling. Certain other factors that have a strong influence on ruffling distortions, but which have not been discussed here, are as follows. Because all calculations in this work have used unsubstituted porphyrin and porphyrazine ligands, we have largely ignored the electronic and steric effects of peripheral substituents on ruffling. In as yet unpublished work, we have examined ruffling distortions of hydroporphyrins as a function of metal ion size: the essence of that study is that hydroporphyrins do have an enhanced tendency to ruffle relative to porphyrins and that Ni(II) hydroporphyrins are much more ruffled than analogous Zn(II) hydroporphyrins. Also not explored here is the issue of whether porphyrin cation and anion radicals have significantly different tendencies to undergo ruffling distortions relative to ordinary porphyrin ligands. We plan to explore these issues and report our results in the foreseeable future.

4. Conclusions

The main conclusions from this study are as follows.

(1) A variety of porphyrin molecules with small central ions such as Si^{IV}, P^V, Ge^{IV}, and As^V have been studied and frequency analyses show that the potential energy minima correspond to pure ruffled structures.

(2) Very often, a ruffling distortion is a direct result of a small macrocycle core size, which, in turn, is brought about by complexation of a central ion with a small ionic radius. For relatively substantial ruffling distortions, a good linear correlation has been found between the ruffling torsion angle and the M–N distance for a wide variety of central ions including transition metals, for a relatively sterically unhindered class of porphyrins, and for a database including both experimental and optimized structures.

(3) The threshold between ruffling and planar structures is at M–N bond distances of 2.00–2.02 Å for sterically unhindered porphyrins and at 1.85–1.87 Å for porphyrazines.

(4) The ruffled D_{2d} geometries of [(P)P^VF₂]⁺ and [(P)P^VCl₂]⁺

(25) Weiss, R.; gold, A.; Trautwein, A. X.; Ternier, J. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guillard, R., Eds.; Academic: New York, 2000; Vol. 4, Chapter 29.

are stabilized by 9.25 and 5.26 kcal/mol, respectively, relative to planar D_{4h} symmetry-constrained optimized geometries. In contrast, the ruffled D_{2d} geometries of [(Pz)P^VF₂]⁺ and of all the silicon complexes studied are more stable than the corresponding D_{4h} symmetry-constrained optimized geometries by less than 0.1 kcal/mol. This illustrates the extreme softness of ruffling deformations and shows that even fairly large distortions, where the ruffling torsion angle changes by up to 25°, can occur with almost no expenditure of energy.

(5) The calculations confirm an experimental observation that electron-withdrawing axial ligands lead to increased ruffling, especially for phosphorus and silicon porphyrins.

(6) The *ortho* hydrogens of axial phenyl ligands and the 2- and 6- hydrogens of axial pyridine ligands can sterically interfere with the porphyrin and contribute to ruffling.

(7) In addition to the M–N distance, a number of other geometrical parameters also vary systematically with the ruffling distortion. Thus, the C_α–C_{meso}–C_α angle decreases with ruffling and the C_βC_β distance and C_α–N–C_α angle increase with ruffling. These structural variations are reflected in a number of ruffling-sensitive vibrational frequencies.

(8) An iron(d_{xy})-porphyrin(a_{2u}) orbital interaction has been identified as a potential driving force for certain peroxidase compound I model compounds. Hitherto unsuspected for Fe(IV)–oxo porphyrins, this orbital interaction is well-known for certain low-spin six-coordinate ferrihemes.

(9) Finally, to our knowledge, this is the first major first-principles quantum chemical study of porphyrin ruffling. Given the great interest in theoretical modeling of nonplanar porphyrins and the considerable progress of molecular mechanics studies, it is somewhat surprising that first-principles calculations in this area have had such a slow start. Regardless, we hope this work proves that a variety of interesting issues related to porphyrin nonplanarity can be readily and very profitably studied with first-principles quantum chemical methods, particularly DFT.

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