J. Phys. Chem. A **2000,** *104,* 4606−4608

Conformational Flexibility of *meso*-Tetrakis(perfluoroalkyl)porphyrins: Energetics of Ruffling versus Saddling

Tebikie Wondimagegn and Abhik Ghosh*

Institute of Chemistry, University of Tromsø, N-9037 Tromsø, Norway

Received: January 5, 2000; In Final Form: February 28, 2000

To better understand the existence of multiple nonplanar conformations of certain porphyrins, we have carried out geometry optimizations with nonlocal density functional theory and triple-ζ plus polarization basis sets for the ruffled and saddled conformations of four metalloporphyrins, M(TCF_3P) and M(TC_2F_5P), where M is Ni and Zn, TCF_3P is *meso*-tetrakis(trifluoromethyl)porphyrin, and TC_2F_5P is *meso*-tetrakis(pentafluoroethyl)porphyrin. Short $F\cdots H_\beta$ contacts lead to strongly nonplanar geometries for every optimized structure. Ruffling is significantly favored over saddling for Ni(II) complexes, whereas the ruffled and saddled geometries are essentially equienergetic for Zn(II) complexes, consistent with experimental observation of both predominantly ruffled and saddled conformations for *meso*-tetrakis(perfluoroalkyl)porphyrins. Contrastingly, for dodecaphenylporphyrins, which generally exhibit saddled conformations, ruffling and saddling appear to be most competitive for Ni(II) complexes. Despite shorter $F\cdots H_\beta$ contacts in the TC_2F_5P complexes, the TCF_3P and TC_2F_5P complexes exhibit comparable nonplanar distortions for a particular metal.

Introduction

In a paper entitled “Conformational Flexibility in Dodecasubstituted Porphyrins”,[1] Smith and co-workers demonstrated that dodecaphenylporphyrins (DPPs) exhibit a variety of nonplanar conformations such as ruffled, saddled, and waved in the solid state. Although not recognized as such, the same phenomenon of conformational flexibility has also been found for *meso*-tetrakis(perfluoroalkyl)porphyrins.[2,3] Thus, crystallographic analyses revealed a ruffled conformation for free-base[2] *meso*-tetrakis(heptafluoropropyl)-porphyrin and a predominantly saddled conformation, with a mild degree of ruffling, for the cobalt(II)[3] complex of the same porphyrin. On the basis of recent successes with first-principles quantum chemical studies of nonplanar porphyrins[4,5] and hydroporphyrins,[6] we present here an initial density functional theory-based study of the energetics of ruffling versus saddling distortions in *meso*-tetrakis(perfluoroalkyl)porphyrins.[7]

Methods

For the calculations, we used the ADF[8] program system, PW91 functional, Slater-type triple-ζ plus polarization basis sets, a fine mesh for numerical evaluation of electron repulsion integrals, and tight convergence criteria for atomic forces and displacements in the geometry optimizations. Both ruffled (D_{2d}) and saddled (C_{2v}) conformations were optimized for M(TCF_3P) and M(TC_2F_5P), where M is Ni and Zn, TCF_3P is *meso*-tetrakis(trifluoro-methyl)porphyrin, and TC_2F_5P is *meso*-tetrakis(pentafluoroethyl)porphyrin. At this point, our computer resources have not permitted frequency analyses on the optimized structures. Indeed, in each case, the “pure” ruffled or saddled geometry may actually be a transition state, with some lower-symmetry conformation being the global minimum. The optimized geometries are shown in Figure 1.

Results

(a) Energetics of Ruffling Versus Saddling. For Ni(TCF_3P) and Ni(TC_2F_5P), the ruffled conformation was found to be favored over the saddled form by the relatively significant margins of 10.73 and 7.93 kcal/mol, respectively. In contrast, the ruffled conformations of Zn(TCF_3P) and Zn(TC_2F_5P) are favored over the saddled conformations by only 2.20 and 3.23 kcal/mol, respectively. In general, a close correlation exists between ruffling distortions and short $M-N_{porphyrin}$ distances.[5,9] It is thus reasonable that the small low-spin Ni(II) ion favors the ruffled conformation. However, the optimized data on the zinc porphyrins suggest that except for the smallest metal ions, the energies of the ruffled and saddled conformations are very delicately balanced.

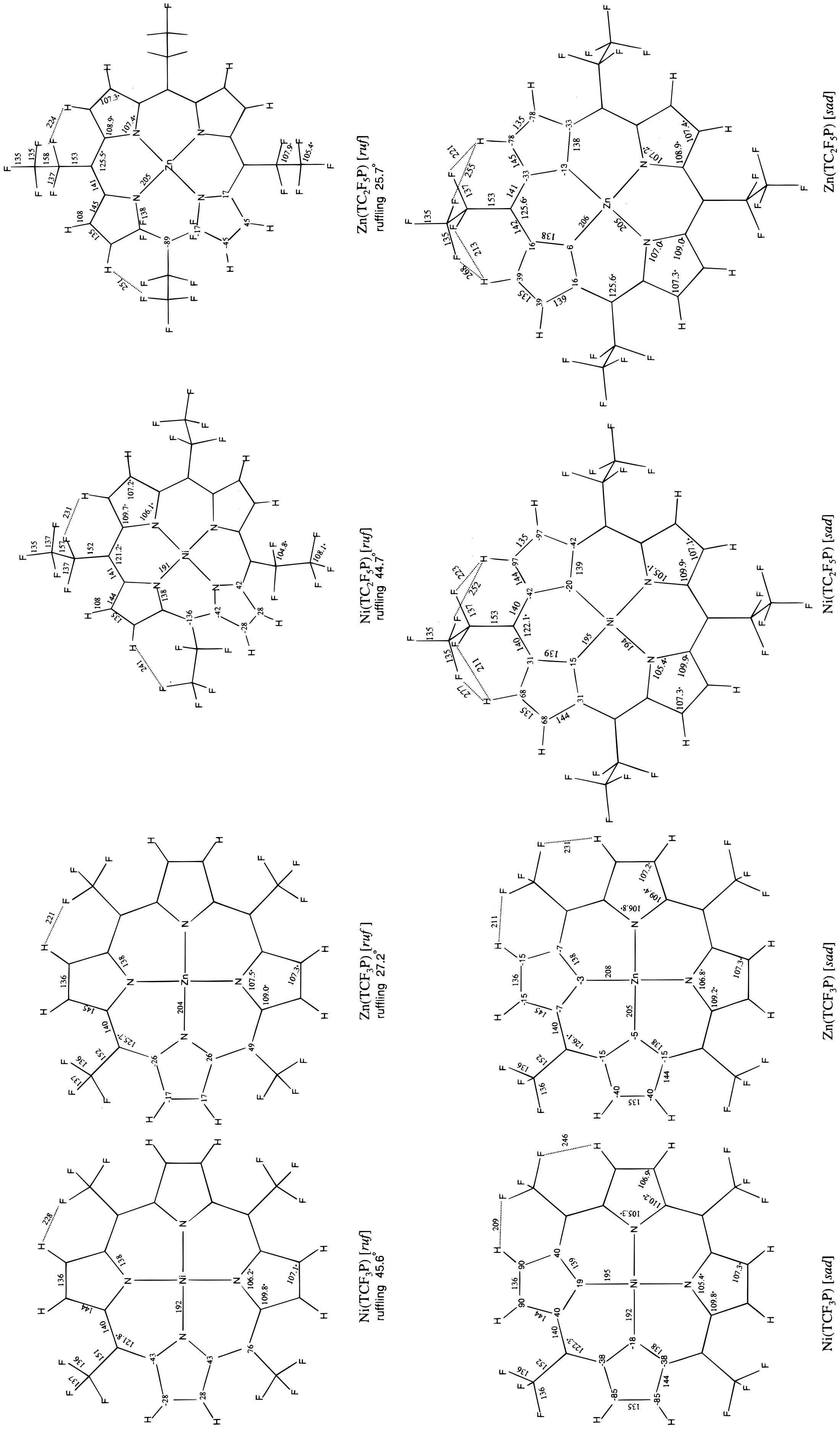
(b) Description of Optimized Geometries. For the ruffled conformations, the ruffling torsion angles[7] for Ni(TCF_3P) and Ni(TC_2F_5P) are 45.6 and 44.7°, respectively. These values are significantly higher than the ruffling angles of 27.2 and 25.7° for Zn(TCF_3P) and Zn(TC_2F_5P), respectively. These ruffling angles are consistent with metal-nitrogen distances of 192, 191, 204, and 205 pm for Ni(TCF_3P), Ni(TC_2F_5P), Zn(TCF_3P), and Zn(TC_2F_5P), respectively. Although all of the optimized geometrical parameters are generally in excellent agreement with the relevant experimental data,[1] a comment is in order on the short Ni−N distances, of around 190 pm, found in our calculations and experiments. In a study on metallohydroporphyrins, we have shown that peripheral substituents on the tetrapyrrole ring play a significant role in shortening the metal−nitrogen distances and that Ni(II) complexes of unsubstituted hydroporphyrins exhibit significantly longer Ni−N distances of 195−197 pm.[6]

The nonplanar distortions, given by z displacements in pm in Figure 1, refer to the mean N_4 plane for the ruffled porphyrins. For saddled porphyrins, they refer to a plane containing the metal and perpendicular to the molecular C_2 axis. As in the case of the ruffled conformations, the nonplanar distortions are signifi-

---

* To whom correspondence should be addressed. E-mail: abhik@chem.uit.no. Fax: +47 77644765.

10.1021/jp0000376 CCC: $19.00



Ni(TCF$_3$P) [*ruf*]
ruffling 45.6°

Zn(TCF$_3$P) [*ruf*]
ruffling 27.2°

Ni(TC$_2$F$_5$P) [*ruf*]
ruffling 44.7°

Zn(TC$_2$F$_5$P) [*ruf*]
ruffling 25.7°

Ni(TCF$_3$P) [*sad*]

Zn(TCF$_3$P) [*sad*]

Ni(TC$_2$F$_5$P) [*sad*]

Zn(TC$_2$F$_5$P) [*sad*]

Figure 1. Optimized geometries (pm, deg) of different metalloporphyrins studied.

cantly smaller for the Zn(II) complexes than for the Ni(II) complexes. Note the unusual mild doming in the saddled conformation of Zn(TCF_3P). It remains to be seen whether this is an artifact of the symmetry constraint used in the optimization.

The optimized structures (Figure 1) clearly demonstrate that the nonplanar distortions of *meso*-tetrakis(perfluoroalkyl)porphyrins result from short F$\cdots$$H_\beta$ contacts. The F$\cdots$$H_\beta$ contact distances are roughly comparable between the ruffled and the saddled conformations for any of the compounds studied. In other words, ruffling and saddling distortions appear to be comparably effective in alleviating F$\cdots$$H_\beta$ steric repulsions relative to a hypothetical planar conformation. Note also that each C_2F_5 group in the TC_2F_5P complexes has four relatively short F$\cdots$$H_\beta$ contacts compared to only two for each CF_3 group in the TCF_3P complexes. Yet the TCF_3P and TC_2F_5P complexes exhibit comparable nonplanar distortions for a particular metal. The clue to this paradox lies in the directionality or vectorial character of the F$\cdots$$H_\beta$ repulsions: the nonplanar distortions are governed by not only the number of short F$\cdots$$H_\beta$ contacts but also their exact orientations in space.

(c) Comparison of *meso*-Tetrakis(heptafluoropropyl)porphyrins and DPPs. How do the above results compare with relevant experimental results on conformational flexibility of porphyrins? Experimentally, the largest collection of data on conformational flexibility are available for the DPPs.[1] Although we have not studied multiple conformations of DPPs theoretically, we take the liberty of making some speculative remarks on the experimental DPP structures.

Crystallographic analysis of unsubstituted NiDPP revealed a strongly ruffled conformation, a deformation mode not previously observed for sterically crowded dodecasubstituted porphyrins.[1] In contrast, a fluorinated analogue of NiDPP, NiDPPF$_{24}$, exhibited a saddled conformation.[1] For another fluorinated derivative, NiDPPF$_{20}$, with *meso*-pentafluorophenyl groups, two crystalline forms were characterized that were found to have different proportions of ruffling and saddling, with one form more ruffled and the other more saddled.[1] The more ruffled and more saddled forms featured mean Ni−N distances of 189.2(3) and 191.6(3) pm, respectively. In other words, although short Ni−N bonds around 190 pm can occur for both ruffled and saddled porphyrins, the Ni−N bonds are slightly shorter in the ruffled conformation than in the saddled one for a particular peripheral substitution pattern. Thus, in contrast to Ni(II) *meso*-tetrakis(perfluoroalkyl)porphyrins, which appear to have the strongest preference for ruffled conformations, NiDPP derivatives appear to exhibit remarkable conformational flexibility. How can we explain this?

The fact that the majority of DPP derivatives exhibit saddled conformations[1] suggests that DPPs are inherently predisposed toward saddling rather than toward ruffling distortions. Only the very small Ni(II) ion appears to make ruffling energetically competitive with saddling. In contrast, *meso*-tetrakis(perfluoroalkyl)porphyrins do not seem to have an inherent preference for ruffling over saddling or vice versa and, thus, ruffling is significantly preferred for very small metal ions such as Ni(II). Additional calculations are underway to verify these speculative remarks.

Finally, to put the results in a broader perspective, we note that conformational flexibility is also known for other classes of nonplanar aromatics, the premier example being the bowl-to-bowl inversion of corannulene.[10]

In summary, *meso*-tetrakis(perfluoroalkyl)porphyrins are conformationally flexible, and ruffled, saddled, and intermediate conformations may be expected in crystallographic analyses of different metal complexes. Although they are well known for dodecasubstituted porphyrins, multiple nonplanar conformations are less known for *meso*-tetrasubstituted β-unsubstituted porphyrins.

Acknowledgment. This work was supported by the Norwegian Research Council, the VISTA program of Statoil (Norway), and a Senior Fellowship (A.G.) of the San Diego Supercomputer Center.

References and Notes

(1) Nurco, D. J.; Medforth, C. J.; Forsyth, T. P.; Olmstead, M. M.; Smith, K. M. *J. Am. Chem. Soc.* **1996**, *118*, 10 918.

(2) DiMagno, S. G.; Williams, R. A.; Therien, M. J. *J. Org. Chem.* **1994**, *59*, 6943.

(3) DiMagno, S. G.; Wertsching, A. K.; Ross, C. R. *J. Am. Chem. Soc.* **1995**, *117*, 8279.

(4) For definitions of "ruffling" and "saddling", as well as an introduction to the stereochemistry of porphyrins, see: Scheidt, W. R. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic: New York, 2000; Vol 3, Chapter 16, pp 49−112.

(5) (a) Ghosh, A.; Gonzalez, E.; Vangberg, T. *J. Phys. Chem. B* **1999**, *103*, 1363. (b) Vangberg, T.; Ghosh, A. *J. Am. Chem. Soc.* **1999**, *121*, 12 154.

(6) Wondimagegn, T.; Ghosh, A. *J. Phys. Chem. B*, submitted for publication.

(7) Ghosh, A. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic: New York, 2000; Vol 7, Chapter 47, pp 1−38. For a definition of ruffling torsion angles, see Figure 23, p 21.

(8) The ADF program is obtainable from: Scientific Computing and Modelling, Department of Theoretical Chemistry, Vrije Universiteit, 1081 HV Amsterdam, The Netherlands.

(9) Shelnutt, J. A.; Medforth, C. J.; Berber, M. D.; Barkigia, K. M.; Smith, K. M. *J. Am. Chem. Soc.* **1991**, *113*, 4077.

(10) Scott, L. T.; Hashemi, M. M.; Bratcher, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 1920.