

Density Functional Theory Analysis of Nickel Octaethylporphyrin Ruffling

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The results of density functional theory (DFT) energy calculations and geometry optimizations for selected planar and ruffled conformers of nickel octaethylporphyrin (NiOEP) are reported. Calculated geometric parameters show remarkably good agreement with experimental X-ray crystallography data. The tendency for ruffling of the porphyrin macrocycle to allow for a shorter Ni–N bond is accurately predicted by DFT calculations. Energy values indicate that ruffling of the macrocycle lowers the energy of the different conformers by about 0.2 kcal/mol.

Introduction

Metalloporphyrins have been extensively studied because they have important and diverse roles in biological systems including heme proteins,¹ cytochromes,² and photosynthetic active centers,³ and because they display unique photophysical and spectroscopic properties.⁴ Among different metalloporphyrins, nickel(II) porphyrins are considered to be exemplary systems for spectroscopic studies because they form stable nonfluorescent four-coordinate complexes without the complication of axial ligation.⁵ For many nickel(II) complexes, nearly complete vibrational assignment has been established on the basis of multiple isotope studies with infrared and multiple wavelength resonance Raman [RR] spectroscopy.^{6–8} In particular, nickel octaethylporphyrin, NiOEP (Figure 1), has been considered to be a good model for the heme prosthetic group because like all physiological porphyrins, the porphyrin macrocycle retains its 4-fold symmetry and has carbon substituents at the eight pyrrole positions. The eight ethyl substituents give rise to a high level of symmetry without being too sterically bulky. NiOEP has played a key role as a model system for spectroscopic characterization of heme proteins by RR spectroscopy.⁹ In this context, NiOEP has been used by many researchers as a primary model for the development of the empirical force field. In earlier studies Kitagawa and co-workers used NiOEP with several isotopomers to establish the vibrational assignment of certain in-plane vibrations of the porphyrin skeleton and to identify various over- and combination tones.⁶ Spiro and co-workers significantly extended and improved the quality of the empirical force field, resulting in development of a consistent porphyrin force field.⁷ The resulting force field was used to assign all in-plane vibrations^{7a,7b} with an attempt to characterize out-of-plane vibrations as well.^{7c}

NiOEP has interesting conformational properties because different orientations of the eight ethyl groups can generate a number of different conformers. Indeed, X-ray crystallography data has been published for three conformers of NiOEP. Meyer reported X-ray data for a tetragonal form of NiOEP,¹⁰ Cullen

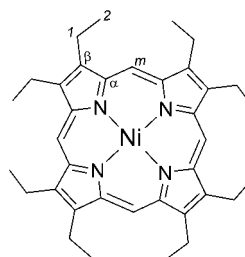


Figure 1. Structure of nickel octaethylporphyrin and its carbon atom labeling scheme.

and Meyer followed this with data for a triclinic form (later referred to as the triclinic A form),¹¹ and Shelnutz and co-workers reported X-ray data for a second triclinic form, called triclinic B.¹² It is well-known that nickel(II) porphyrins have a tendency to deviate from planarity.¹³ This deviation from planarity is attributed to the combination of the Ni–N bond being too short to fit the central cavity of a planar porphyrin and the presence of substituents on the periphery of the macrocycle.¹⁴ The bond shortening is accommodated by ruffling of the porphyrin ring, an effect which has been observed crystallographically and spectroscopically.^{12,14,15}

Although a large amount of experimental data has been reported for NiOEP, there has not been an attempt to characterize this system quantum mechanically. In this paper we report the results of density functional theory (DFT) energy calculations and geometry optimizations for selected planar and ruffled conformers of NiOEP. The ultimate goal of this project is to develop a high quality vibrational force field and establish definite vibrational assignment similar to those presented recently for nickel porphine (NiP)¹⁶ and nickel tetraphenylporphyrin (NiTPP).¹⁷ Contrary to these previously studied nickel porphyrins, the full structural and vibrational analysis of NiOEP presents a more complex problem than for other nickel systems because of the various possible ethyl group orientations. From a combinatorial point of view there are over 200 possible conformers of NiOEP with respect to ethyl orientation, of which about 25 are unique, nonredundant conformers. In this study we concentrate on the energies and geometries of four conformers (Figure 2). These conformers were chosen because X-ray crystallography data has been reported for three of them,^{10–12} and the fourth has been used as a model in other NiOEP

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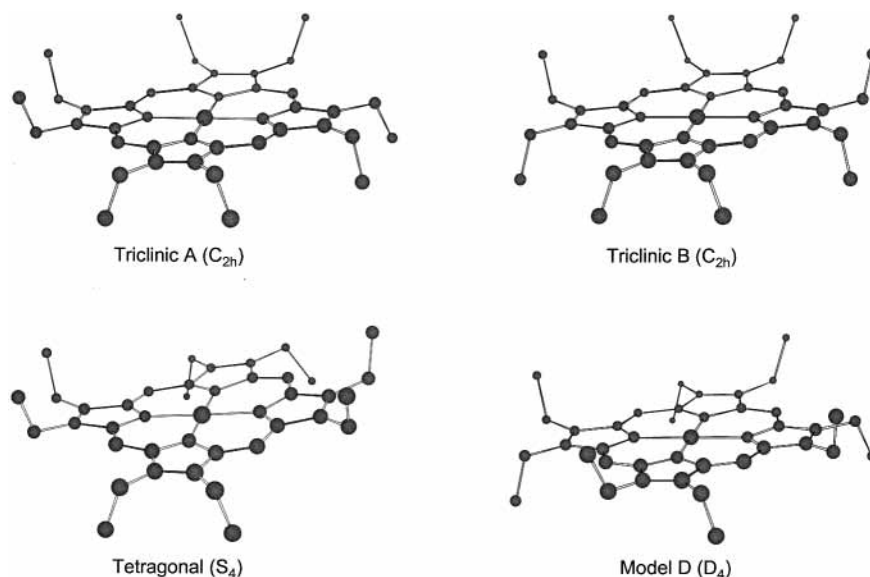


Figure 2. Structures of NiOEP conformers showing the orientation of the ethyl substituent groups.

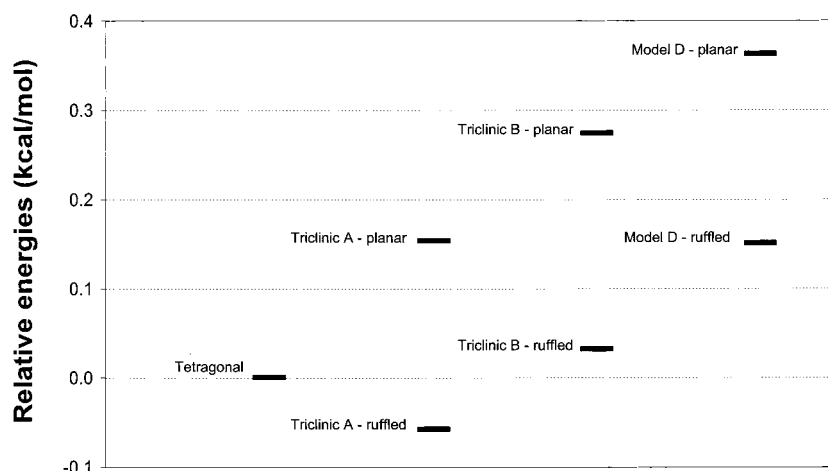


Figure 3. DFT optimized energies of NiOEP conformers relative to the tetragonal (S_4) conformer.

TABLE 1: Comparison of DFT Optimized Energy Values for NiOEP Conformers

conformer	symmetry	energy (a.u.)	energy relative to S_4		planar vs ruffled (kcal/mol)
			(10^{-4} a.u.)	(kcal/mol)	
tetragonal	S_4	-3125.819185	0.00	0.00	
triclinic A					
planar	C_{2h}	-3125.818939	2.46	0.15	0.21
ruffled	C_s	-3125.819278	-0.93	-0.06	
triclinic B					
planar	C_{2h}	-3125.818748	4.36	0.27	0.24
ruffled	C_2	-3125.819133	0.52	0.03	
model D					
planar	D_4	-3125.818606	5.78	0.36	0.21
ruffled	D_2	-3125.818945	2.40	0.15	

studies.^{7b} The detailed vibrational analysis will be presented in future publication.¹⁸

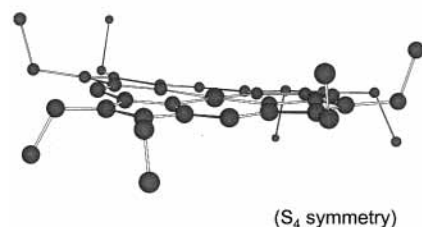
Computational Methods

Calculations reported in this paper were carried out using gradient-corrected density functional theory (DFT) with the Becke-Lee-Young-Parr composite exchange correlation functional (B3LYP) as implemented in the Gaussian¹⁹ suite of programs for electronic structure calculations. The B3-LYP level of theory with 6-31G(d) [for H, C, and N atoms] and Ahlrichs VTZ (for Ni)²⁰ basis sets, successfully used in previous

calculations on metalloporphyrins,^{16,17,21-23} was employed in the present study.

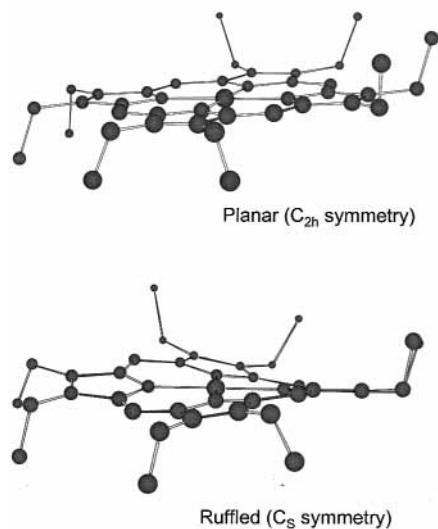
Results and Discussion

A. Energies. Table 1 summarizes the results of DFT optimized energy values for NiOEP conformers. These energies, relative to the energy calculated for the tetragonal conformer (S_4 symmetry), are plotted in Figure 3. Initially, geometries were optimized for four NiOEP conformers that correspond to tetragonal with S_4 symmetry, triclinic A and B forms with C_{2h} symmetry, and model D with D_4 symmetry²⁴ (Figure 2). The



Parameter	X-Ray ^{a,b}	DFT	
		Ruffled	
bond lengths (Å)			
Ni-N	1.929 (3)	1.970	
C _p -C _p	1.362 (5)	1.368	
C _α -C _β	1.449 (5)	1.450	
C _α -C _m	1.372 (2)	1.382	
C _α -N	1.386 (2)	1.376	
C _p -C ₁	1.501 (5)	1.504	
C ₁ -C ₂	1.537 (7)	1.542	
angles (deg)			
N-Ni-N	90.0	90.0	
Ni-N-C _α	127.4 (2)	127.7	
C _α -N-C _α	105.1 (3)	104.6	
N-C _α -C _m	124.0 (2)	124.9	
N-C _α -C _β	110.6 (2)	111.5	
C _p -C _α -C _m	125.0 (2)	123.5	
C _α -C _α -C _α	124.1 (2)	124.3	
C _α -C _β -C _β	106.8 (3)	106.2	
C _α -C _β -C ₁	124.9	125.2	
C _β -C _β -C ₁	128.2	128.5	
C _β -C ₁ -C ₂	112.8	113.6	
C _α -N-N-C _α ^c	32.8 ^d	8.4	
rms displacement ^e	29.8 ^e	11.8	

Figure 4. Comparison of calculated and experimentally determined structures of NiOEP, tetragonal conformer. ^aMeyer, E. F. *Acta Crystallogr.* **1972**, *B28*, 2162. ^bCullen, D. L.; Meyer, E. F. *J. Am. Chem. Soc.* **1974**, *96*, 2095. ^cThe torsional angle, in degrees, of the opposite pyrrole ring planes with respect to the N–Ni–N axis which connects them. ^dJentzen, W.; Turowska-Tyrk, I.; Scheidt, W. R.; Shelnutt, J. A. *Inorg. Chem.* **1996**, *35*, 3559. ^eThe root-mean-square out-of-plane displacement, in 10⁻² Å, following the definition in Jentzen et al. *Inorg. Chem.* **1996**, *35*, 3559.



Parameter	X-Ray ^a	DFT	
		Planar	Ruffled
bond lengths (Å)			
Ni-N	1.958 (2)	1.973	1.961
C _p -C _p	1.346 (2)	1.368	1.369
C _α -C _β	1.443 (3)	1.449	1.450
C _α -C _m	1.371 (4)	1.381	1.383
C _α -N	1.376 (6)	1.376	1.376
C _p -C ₁	1.495 (4)	1.504	1.504
C ₁ -C ₂	1.522 (5)	1.542	1.542
angles (deg)			
N-Ni-N	90.15 (9)	89.98	90.02
Ni-N-C _α	128.0 (2)	127.8	127.6
C _α -N-C _α	103.9 (4)	104.5	104.8
N-C _α -C _m	124.4 (3)	125.0	124.8
N-C _α -C _β	111.6 (3)	111.6	111.4
C _p -C _α -C _m	124.1 (4)	123.4	123.7
C _α -C _m -C _α	125.1 (1)	124.4	124.0
C _α -C _β -C _β	106.5 (4)	106.2	106.2
C _α -C _β -C ₁	125.5	125.3	125.3
C _β -C _β -C ₁	128.1	128.5	128.5
C _β -C ₁ -C ₂	113.5	113.8	113.7
C _α -N-N-C _α ^b	0.0 ^c	0.5	19.8
rms displacement ^d	1.8 ^e	1.1	18.4

Figure 5. Comparison of calculated and experimentally determined structures of NiOEP, triclinic A conformer. ^aCullen, D. L.; Meyer, E. F. *J. Am. Chem. Soc.* **1974**, *96*, 2095–2102. ^bThe torsional angle, in degrees, of the opposite pyrrole ring planes with respect to the N–Ni–N axis which connects them. ^cJentzen, W.; Turowska-Tyrk, I.; Scheidt, W. R.; Shelnutt, J. A. *Inorg. Chem.* **1996**, *35*, 3559. ^dThe root-mean-square out-of-plane displacement, in 10⁻² Å, following the definition in Jentzen et al. *Inorg. Chem.* **1996**, *35*, 3559.

lowest energy was found for the tetragonal S_4 conformer, though the energy difference between other conformers, i.e., planar triclinic A and B as well as planar model D, was found to be small in the range of 0.15–0.36 kcal/mol (Table 1, Figure 3).

For each conformer under consideration, frequency calculations were performed and analyzed. All harmonic frequencies for the optimized geometry for the tetragonal S_4 conformer were real, indicating that the optimized structure corresponds to a stable energy minimum (Figure 4). In the three other cases, one imaginary frequency was found which was associated with the planarity of the porphyrin core imposed by symmetry con-

straints. Interestingly, eigenvector analysis revealed that in all three cases the imaginary frequency was associated with ruffling of the porphyrin core. Consequently, each of these three optimized structures was distorted by lowering the symmetry of the initial structure along the eigenvector representing the imaginary frequency, and the resulting distorted structures were re-optimized and frequencies were recalculated. The final analysis of conformers show that for the planar triclinic A conformer with C_{2h} symmetry, the minimum energy corresponds to a ruffled structure with C_s symmetry (Figure 5). Similarly, the minimum corresponding to the triclinic conformer B (C_{2h}

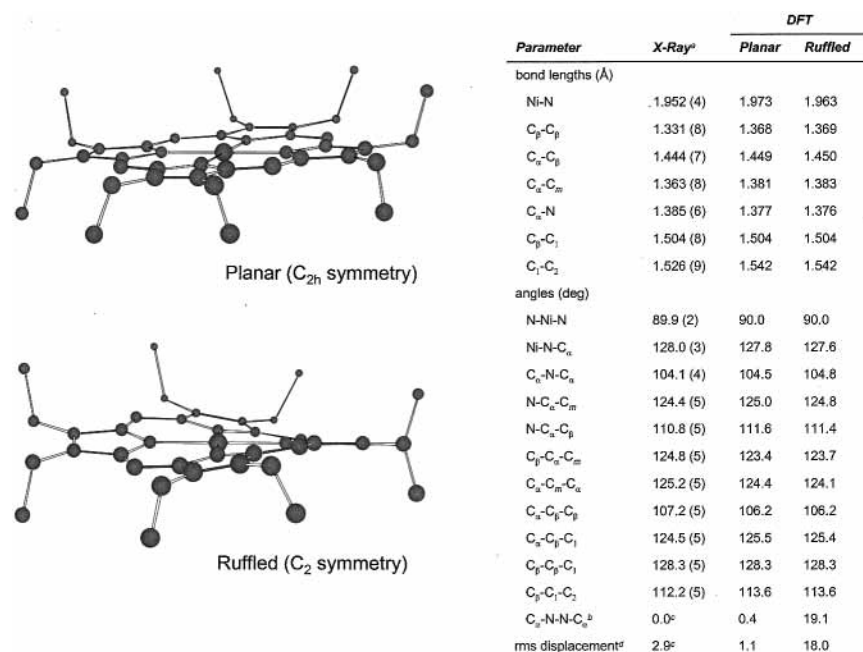


Figure 6. Comparison of calculated and experimentally determined structures of NiOEP, triclinc B conformer. ^a Brennan, T. D.; Scheidt, W. R.; Shelnut, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 3919. ^b The torsional angle, in degrees, of the opposite pyrrole ring planes with respect to the N–Ni–N axis which connects them. ^c Jentzen, W.; Turowska-Tyrk, I.; Scheidt, W. R.; Shelnut, J. A. *Inorg. Chem.* **1996**, *35*, 3559. ^d The root-mean-square out of plane displacement, in 10⁻² Å, following the definition in Jentzen et al. *Inorg. Chem.* **1996**, *35*, 3559.

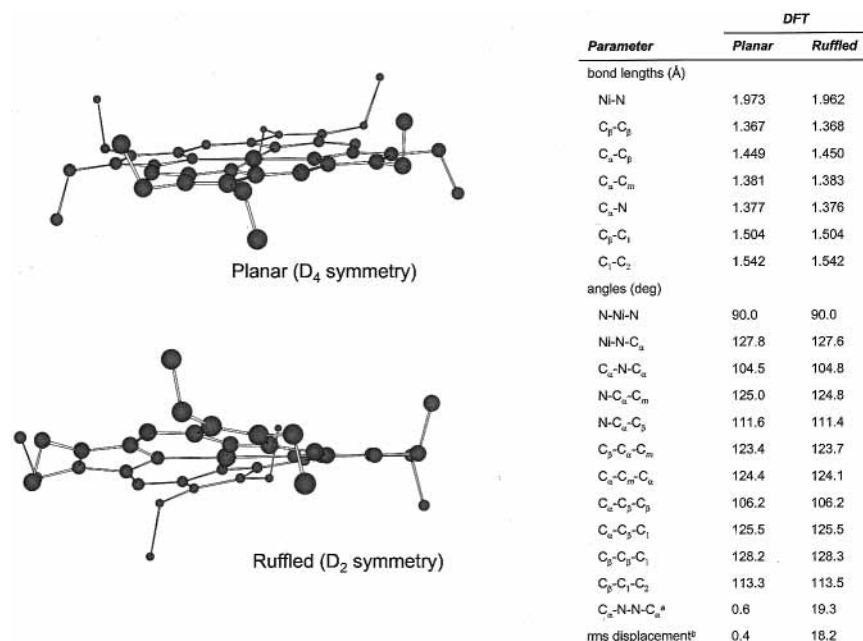


Figure 7. Comparison of calculated and experimentally determined structures of NiOEP, model D conformer. ^aThe torsional angle, in degrees, of the opposite pyrrole ring planes with respect to the N–Ni–N axis which connects them. ^bThe root-mean-square out-of-plane displacement, in 10⁻² Å, following the definition in Jentzen et al. *Inorg. Chem.* **1996**, *35*, 3559.

symmetry) has ruffled C₂ symmetry (Figure 6). The distortion of model D (D₄ symmetry) leads to a structure of D₂ symmetry with a ruffled porphyrin core (Figure 7). The ruffling of the porphyrin macrocycle accounts for about a 0.2 kcal/mol lowering of energy in each of the conformers. The ruffled forms of the triclinc conformers along with the tetragonal conformer, which is also ruffled, have energy values within a range of 0.09 kcal/mol (Figure 3) and are essentially degenerate. Upon correction for zero-point vibrational energy, these three conformers are all within 0.3 kcal/mol of each other.

In spectroscopic studies on the conformational properties of NiOEP in solution, Jentzen and co-workers^{15d} decomposed the

sublines of ν_{19} and ν_{10} on the polarized resonance Raman spectra for NiOEP and determined that the nonplanar conformer is favored energetically in CH₂Cl₂ and CS₂ solutions. Their experimentally obtained value of 0.7 kcal/mol is slightly higher but is of the same order of magnitude as that of the 0.2 kcal/mol calculated value.

B. Optimized Geometries. Values of the optimized geometrical parameters for each conformer together with available X-ray data are summarized in Figures 4–7. Table 2 gives values for two other nickel porphyrins: nickel porphine (NiP) and nickel tetraphenylporphyrin (NiTPP).

TABLE 2: Calculated and Experimentally Determined Geometries of NiP and NiTPP

parameter	NiP			NiTPP			
	X-ray ^b	DFT		X-ray ^e	DFT ^a		
		D_{4h} ^c	D_{2d} ^d		D_{4h}	D_{2d}	S_4
bonds lengths (Å)							
Ni–N	1.951 (2)	1.969	1.966	1.931 (2)	1.969	1.996	1.940
C_β – C_β	1.347 (3)	1.358	1.359	1.340 (4)	1.356	1.356	1.359
C_α – C_β	1.435 (4)	1.440	1.440	1.429 (3)	1.440	1.440	1.441
C_α – C_m	1.371 (3)	1.382	1.382	1.383 (3)	1.391	1.393	1.397
C_α –N	1.379 (2)	1.378	1.378	1.377 (3)	1.381	1.382	1.377
angles (deg)							
N–Ni–N	90.0 (1)	90.00	90.00	90.0 (2)	90.00	90.03	90.00
Ni–N– C_α	127.8 (2)	127.7	127.7	127.5 (2)	127.7	127.5	127.2
C_α –N– C_α	104.3 (2)	104.5	104.7	104.9 (2)	104.5	104.7	105.4
N– C_α – C_m	125.4 (3)	125.4	125.3	125.5 (2)	126.2	126.0	125.5
N– C_α – C_β	111.0 (3)	111.2	111.1	110.4 (2)	111.0	110.9	111.4
C_β – C_α – C_m	123.6 (2)	123.4	123.5	123.9 (2)	122.8	123.1	123.8
C_α – C_m – C_α	123.5 (2)	123.7	123.6	121.7 (2)	122.2	121.8	121.2
C_α – C_β – C_β	106.8 (2)	106.6	106.6	107.1 (2)	106.7	106.8	106.8
C_α –N–N– C_α ^f	1.7	0.00	11.78	nr ^g	0.00	0.00	32.22
rms displacement ^h	1.9	0.0	11.1	nr	0.0	21.4	32.2

^a Rush, T. S.; Kozłowski, P. M.; Piffat, C. A.; Kumble, R.; Zgierski, M. Z.; Spiro, T. G. *J. Phys. Chem. B* **2000**, *104*, 5020. ^b Jentzen, W.; Turowska-Tyrk, I.; Scheidt, W. R.; Shelnut, J. A. *Inorg. Chem.* **1996**, *35*, 3559. ^c This work. ^d Kozłowski, P. M.; Rush, T. S.; Jarzecki, A. A.; Zgierski, M. Z.; Chase, B.; Piffat, C.; Ye, B.-H.; Li, X.-Y.; Pulay, P.; Spiro, T. G. *J. Phys. Chem. A* **1999**, *103*, 1357. ^e Maclean et al. *Aust. J. Chem. A* **1996**, *49*, 1273. ^f The torsional angle, in degrees, of the opposite pyrrole ring planes with respect to the N–Ni–N axis which connects them.^g Not reported. ^h The root-mean-square out-of-plane displacement, in 10^{-2} Å, following the definition in Jentzen et al. *Inorg. Chem.* **1996**, *35*, 3559.

The DFT calculations for the planar and ruffled conformers of triclinic A, triclinic B, and model D show the expected decrease in the Ni–N bond length with the ruffling of the porphyrin macrocycle. Overall, the DFT calculations for bond lengths are in good agreement with reported experimental values. The experimental C_β – C_β , C_α –N, and C_1 – C_2 bond lengths are somewhat shorter than the corresponding calculated bond lengths for the tetragonal, triclinic A, and triclinic B conformers, and this can be attributed to crystal packing forces that are not present in the theoretical models.

For NiOEP, NiP, and NiTPP, the C_β – C_β bond length appears to be insensitive to ruffling. Additionally, the calculated C_β – C_β bond distances are larger for the NiOEP conformers than for the NiP and NiTPP conformers, which can be attributed to the fact that of the three molecules, only NiOEP has carbon substituents at the C_β position. Likewise, NiTPP has longer C_α – C_m bond distances than the other two molecules, and only NiTPP has carbon substituents at the C_m position.

The calculated bond angles also show good agreement with the data for the three conformers characterized experimentally. In general, the calculated C_α –N–N– C_α dihedral angles compare favorably with the reported experimental values. Calculations of the ruffled conformers give larger values for the C_α –N–N– C_α dihedral angles and root-mean-square out-of-plane displacements,²⁵ another measure of planarity of the porphyrin macrocycle, as compared to their planar counterparts, as expected. For the triclinic A and B conformers, the C_α –N–N– C_α dihedral angles found by X-ray are smaller than those calculated, and this may also be attributed to crystal packing forces. The C_α –N–N– C_α dihedral angle in the tetragonal conformer, however, does not follow this trend. This dihedral angle had a significantly smaller calculated value compared to experiment. This may be the result of comparing gas-phase calculations with solid-state X-ray data or of possible error in the calculated values, experimental values, or both. Closer analysis of the porphyrin skeleton bond lengths show that the experimental Ni–N bond length of the tetragonal conformer is significantly shorter, i.e., 1.929(3) Å, in comparison to the triclinic A and B conformers, which have Ni–N bond lengths of 1.958(2) and 1.952 (4) Å, respectively. The optimized

theoretical Ni–N bond lengths for the three conformers are consistent with values of 1.970, 1.961, and 1.963 Å. This similarity among the optimized conformers might indicate that the experimental Ni–N bond length was not determined accurately for the tetragonal conformer.

Conclusion

The values obtained through geometry optimization of NiOEP using density functional theory show remarkably good agreement with experimental X-ray results. As such, DFT appears to be a good choice for performing calculations on the complex structures of metalloporphyrins. DFT calculations show that three NiOEP conformers, which crystallize in alternative polymorphs, have essentially degenerate energy values. All investigated conformers show significant ruffling distortion. The origin of the ruffling distortion is attributed to the fact that the nickel ion is too small for the natural porphyrin cavity size, which has a 2.00 Å radius.¹³ With a distance shorter than 2.00 Å, the Ni–N bonds draw the pyrrole rings toward the center through a ruffling distortion of the macrocycle. Since the planar geometry maximizes the π overlap, the equilibrium structure would find a balance between the energy gain from shorter bonds and the energy penalty to the π system from ruffling. On the basis of present DFT calculations for NiOEP, the energy corresponding to this ruffling distortion can be accurately estimated to be equal to 0.2 kcal/mol.

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- (24) Because this work focuses on the comparison of theoretical values with experimental X-ray data, the crystallographic descriptions of the different conformers were used to identify the different conformers. Hence the conformer with S_4 symmetry is referred to as the tetragonal conformer, though the crystal structure was not involved in the DFT calculations. Likewise, the two conformers with C_{2h} (planar) symmetry are referred to as triclinic A and triclinic B as appropriate.
- (25) Root-mean-square out-of-plane displacements were calculated using the method described in ref 14.