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A Theoretical Study of Axial Tilting and Equatorial Asymmetry in Metalloporphyrin−Nitrosyl Complexes

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Produced in mammals by the heme protein nitric oxide synthase, NO binds to the heme cofactor of guanylate cyclase which catalyzes the conversion of GTP to cGMP. The production of cGMP regulates a variety of physiological functions includng vasodilation, inhibition of platelet aggregation, cell adhesion, neurotransmission, and penile erection.[1] The profound biological significance of NO, named "Molecule of the Year" by *Science* magazine in 1992,[2] has fueled renewed interest in fundamental chemical aspects of metal−nitrosyl complexes.[3]

The most important nitrosylmetalloporphyrins are $\{MNO\}^n$ systems with $n = 6$, 7 and 8, where M is a transition metal and n the total number of electrons in metal d and NO π^* orbitals combined.[4] These three cases are characterized by widely different MNO angles of approximately 180°, 140°, and 120°, respectively.[4] Representative examples of $n = 6$, 7, and 8 are given by ferriheme−NO complexes, ferroheme−NO complexes, and cobalt(II)−NO porphyrin complexes, respectively.[3] Early theoretical studies[5] provided a qualitatively satisfactory explanation of the wide variations in MNO angles: the most important metal bonding orbitals are the two d_π and the d_{z^2} orbitals; for $n \geq 7$, one of the d_π orbitals changes its bonding character from π to σ.

Recently, on the basis of extensive crystallographic analyses of metalloporphyrin−nitrosyl complexes, Scheidt and Ellison[6] appear to have uncovered another fundamental structural feature of metalloporphyrin−nitrosyl complexes, viz. tilting of the axial NO ligand and an asymmetrical distribution of the equatorial $M-N_P$ bond distances (where N_P denotes porphyrin nitrogen). The observed tilt of the NO ligand, across a number of five-coordinate iron(II)−NO porphyrin complexes, is about 6−8°.[7] In the cobalt case, best represented by Co(OEP)(NO), the axial tilt was smaller, about 2°.[8] The equatorial asymmetry, given by the difference between the mean lengths of the longer and shorter equatorial $M-N_P$ bonds, ranges from 0.025 ± 0.004 Å for Fe(OEP)(NO) to 0.015 ± 0.004 Å for Co(OEP)(NO), the shorter bonds always being on the same side as the NO ligand. It is a testament to these researchers' insight that they did not dismiss these subtle effects as artifacts of crystal packing forces.

Here we present an initial density functional theoretical study[9] of NO tilting and equatorial asymmetry. The calculations confirm that tilt and asymmetry are indeed molecular phenomena, manifestations of specific orbital interactions. The calculations also explain why the magnitude of equatorial asymmetry should track the magnitude of NO tilting and the tilt and asymmetry should be significantly lower in the cobalt case, relative to iron.

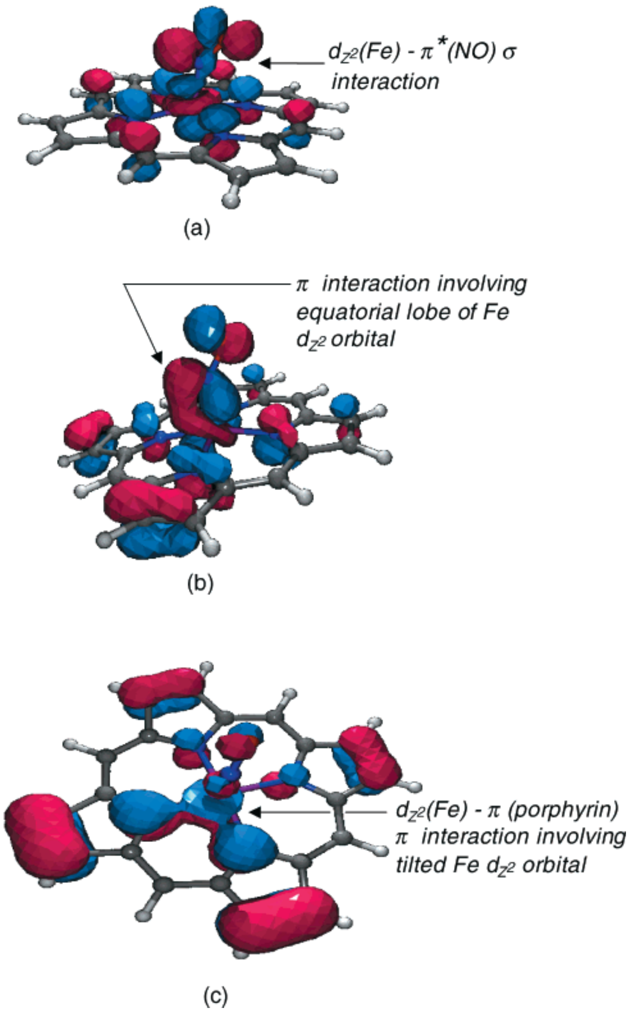

Figure 1. Some MOs relevent to NO tilting.

Table 1 presents key optimized geometry parameters of Fe(P)(NO) and Co(P)(NO) as well as relevant crystallographic results obtained by Scheidt and Ellison.[7,8] The calculated structural parameters are in generally excellent agreement with experiment,[7,8] which, along with a large database of nonlocal DFT structural data,[10,11] confirms the high quality of the optimized geometries. Relative to the normal to the mean porphyrin plane, the M−N(NO) vectors are tilted by 4.9 and 0.3° in Fe(P)(NO) and Co(P)(NO), respectively, in good agreement with experiment. The $Fe-N_P$ bonds in Fe(P)(NO) are 2.039 and 1.992 Å, which translate into a $\Delta(Fe-N_P)$ of 0.039 Å. The $Co-N_P$ bonds in Co(P)(NO) are 2.006 and 1.985 Å, which translate into a $\Delta(Co-N_P)$ of 0.021 Å. In other words, the calculated equatorial asymmetries mirror those observed experimentally.

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[9] The calculations used the PW91 exchange-correlation functional, triple-ζ plus polarization Slater-type basis sets, a fine mesh for numerical integrations, and tight criteria for atomic forces and displacements, as implemented in the ADF program system, obtained from: Scientific Computing and Modelling, Department of Theoretical Chemistry, Vrije Universiteit, 1081 HV Amsterdam, The Netherlands. The geometry optimizations used C_s symmetry constraints, with the M−N−O plane as the plane of symmetry. Both spin-restricted and spin-unrestricted calculations were carried out on all the molecules studied and, in each case, nearly identical final geometries were obtained.

[10] For reviews of DFT-based structural studies on porphyrins and metalloporphyrins, see: (a) 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. (b) Ghosh, A. *Acc. Chem. Res.* **1998**, *31*, 189.

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Table 1. Optimized and Crystallographic Structural Parameters (Å, deg) of M(P)(NO) Complexes

complex	M−N−O[a]	ΔM[b,c]	M−N(NO)[b]	N−O[b]	orientation[a,d]	tilt[a,e]	M−N$_P$[b] short	long	asymmetry	ref
					Optimized					
Fe(P)(NO)	143.75	0.237	1.692	1.184	45.0	4.9	1.992	2.031	0.039	this work
Co(P)(NO)	122.33	0.140	1.817	1.178	45.3	0.3	1.985	2.006	0.021	this work
					Experimental					
Fe(OEP)(NO) (P1)	14.74(8)	0.27	1.7307(7)	1.1677(11)	40.2	8.2	1.999(1)	2.020(4)	0.021	7
Fe(OEP)(NO) ($P2_1/c$)	144.4(2)	0.29	1.722(2)	1.167(3)	37.9	6.5	1.991(3)	2.016(1)	0.025	7
Co(OEP)(NO) (P1)	122.70(8)	0.16	1.8444(9)	1.1642(13)	45.0	2.2	1.977(1)	1.992(3)	0.015	8

[a] Values in degrees. [b] Value in Å. [c] Metal atom displacement from mean 24-atom porphyrin plane. [d] Dihedral angle between M−N−O and NP−M−N(NO) planes. [e] Deviation from normal to porphyrin plane.

Figure 1 depicts three molecular orbitals (MOs) of Fe(P)(NO) that appear to be relevant to tilting and asymmetry. Figure 1a depicts the open-shell, highest occupied MO, which, as expected,[5a] chiefly involves a d_{z^2}(metal)−π*(NO) σ antibonding interaction. Because an extra electron enters this MO in the cobalt case, we suspected that the detailed nature of the d_{z^2}(Fe)−π*(NO) orbital interactions should provide a clue to understanding the different degrees of tilting and asymmetry for the two metals. Figure 1b depicts a doubly occupied orbital involving *a heretofore unsuspected d_{z^2}(Fe)−π*(NO) π-interaction, which involves both lobes of the d_{z^2} orbital*: tilting clearly facilitates this interaction. In the cobalt case, this π interaction is absent because of the considerably smaller M−N−O angle, which provides a plausible explanation for the absence of significant tilting in the cobalt case. Tilting in the iron case is further strengthened by a d_{z^2}(Fe)−π(porphyrin) π-bonding interaction, as shown in Figure 1c. Finally, as suggested by Scheidt and Ellison,[6] we also find that tilting leads to slightly stronger basal σ interactions with the two porphyrin nitrogens in the same direction as the tilt than with those on the other side which explains why equatorial asymmetry tracks tilting.

In summary, DFT calculations confirm that NO tilting and equatorial asymmetry are truly molecular phenomena and not artifacts of crystal packing forces. The calculations reproduce the experimentally observed observed tilting and asymmetry in the cobalt and iron cases, provide a pictorial view of specific orbital interactions switched on by tilting, and qualitatively explain the significant difference in tilting and asymmetry between the two metals. Obviously, much more remains to be clarified about this effect. Ongoing work in our laboratory, focusing on potential energy surfaces[10a] and MO Walsh diagrams associated with NO tilting, will be reported in a full paper on this topic.

Table 2. Key Optimized Structural Parameters (Å, deg) of Two Isonitrosyl Complexes

complex	M−N$_P$ short	long	M−O(ON)	O−N	M−O−N	tilt
Fe(P)(ON)	1.989	2.015	1.796	1.177	144.6	3.8
Co(P)(ON)	1.982	1.992	1.956	1.166	126.3	0.3

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Note Added in Proof. While we were correcting the proofs of this work, another contribution appeared that reported an isonitrosyl linkage isomer, Fe(OEP)(ON), obtained as a low-temperature photoproduct derived from Fe(OEP)(NO).[12] Accordingly, we were interested in checking whether the phenomena of axial tilting and equatorial asymmetry extended to the isonitrosyl complexes as well. Geometry optimization of Fe(P)(ON) ($S = {}^1/_2$) and Co(P)(ON) ($S = 0$) at the same level of theory (PW91/TZP) as used for the nitrosyl complexes showed that these two complexes are 1.51 and 1.20 eV higher in energy relative to the corresponding nitrosyl complexes, respectively. Table 2 presents key optimized geometry parameters for the two isontrosyl complexes studied. As in the case of the nitrosyl complexes, the iron case features significant axial titling and equatorial asymmetry, not a surprising result, perhaps, in light of the expected qualitative similarity of all orbital interactions between isosteric nitrosyl and isonitrosyl complexes.

Supporting Information Available: The optimized coordinates of the different molecules studied are given herein (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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