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Density Functional Theory Calculations of the Lowest Energy Quintet and Triplet States of Model Hemes: Role of Functional, Basis Set, and Zero-Point Energy Corrections

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We investigated the effect of several computational variables, including the choice of the basis set, application of symmetry constraints, and zero-point energy (ZPE) corrections, on the structural parameters and predicted ground electronic state of model 5-coordinate hemes (iron(II) porphines axially coordinated by a single imidazole or 2-methylimidazole). We studied the performance of B3LYP and B3PW91 with eight Pople-style basis sets (up to 6-311+G*) and B97-1, OLYP, and TPSS functionals with 6-31G and 6-31G* basis sets. Only hybrid functionals B3LYP, B3PW91, and B97-1 reproduced the quintet ground state of the model hemes. With a given functional, the choice of the basis set caused up to 2.7 kcal/mol variation of the quintet−triplet electronic energy gap (ΔE_{el}), in several cases, resulting in the inversion of the sign of ΔE_{el}. Single-point energy calculations with triple-ζ basis sets of the Pople (up to 6-311G++(2d,2p)), Ahlrichs (TZVP and TZVPP), and Dunning (cc-pVTZ) families showed the same trend. The zero-point energy of the quintet state was ∼1 kcal/mol lower than that of the triplet, and accounting for ZPE corrections was crucial for establishing the ground state if the electronic energy of the triplet state was ∼1 kcal/mol less than that of the quintet. Within a given model chemistry, effects of symmetry constraints and of a “tense” structure of the iron porphine fragment coordinated to 2-methylimidazole on ΔE_{el} were limited to 0.3 kcal/mol. For both model hemes the best agreement with crystallographic structural data was achieved with small 6-31G and 6-31G* basis sets. Deviation of the computed frequency of the Fe−Im stretching mode from the experimental value with the basis set decreased in the order: nonaugmented basis sets, basis sets with polarization functions, and basis sets with polarization and diffuse functions. Contraction of Pople-style basis sets (double-ζ or triple-ζ) affected the results insignificantly for iron(II) porphyrin coordinated with imidazole. Poor performance of a “locally dense” basis set with a large number of basis functions on the Fe center was observed in calculation of quintet−triplet gaps. Our results lead to a series of suggestions for density functional theory calculations of quintet−triplet energy gaps in ferrohemes with a single axial imidazole; these suggestions are potentially applicable for other transition-metal complexes.

Introduction

Imidazole-coordinated ferrohemes (iron(II) porphyrins, Figure 1) play a critical role in oxygen metabolism, being responsible for O_2 transport (as prosthetic groups of hemoglobins), O_2 storage (in myoglobins), and respiratory O_2 reduction (in all terminal oxidases).[1] Dynamics of O_2 binding to the 5-coordinate heme and dissociation of O_2 from oxyheme are affected by the electronic state of the Fe center.[2−4] In native and mutant myoglobins and hemoglobins on- and off-rates of O_2 vary by >7 orders of magnitude.[5] Quantitative understanding of the contribution of the electronic factors to this variability is important for elucidating the precise biochemical roles of the corresponding hemoproteins under normal and pathological conditions, their catalytic cycles (e.g., for terminal oxidases), their evolutionary history, and their potential as pharmacological targets or for technological uses ex vivo. In addition, there is intense contemporary interest in synthetic monoimidazole-ligated iron(II) porphyrins as potential Pt-free catalysts for O_2 reduction in low-temperature fuel cells,[6] for noncryogenic air separation,[7] and as blood substitutes.[8]

As a result, there is a strong need for data on the electronic states of monoimidazole-ligated iron(II) porphyrins. Experimental measurements of the electronic ground state of such complexes are nontrivial as is the interpretation of the results. To date the ground states of only a few synthetic ferrohemes,[9−15] human deoxyhemoglobin,[9,16] and three different deoxymyoglobins[9,17,18] have been established. All complexes were reported to have the quintet ground state, but the population of d-orbitals remains subject to debate.[12−14,17] The interpretation of spectroscopic results is complicated by the presence of multiple excited states[11,12,19] of various multiplicities within a few kilocalories per mole of the ground state. Because of the experimental challenges, quantum-mechanical computations provide the only practical means of estimating the ground states of most iron(II) porphyrins coordinated by a single axial imidazole.

Density functional theory (DFT) methods have been successfully used in modeling of a wide range of transition-metal properties, from catalytic mechanisms[20] to various spectroscopic properties,[21] and are often the method of choice for transition-metal systems due to the favorable tradeoff between the accuracy and computational cost.[22] Ordering of spin states of iron porphyrins is a complex computational problem due to the presence of multiple closely spaced electronic states.[23−25] One of the more controversial computational issues is the relative energies of the lowest-lying triplet and quintet states of the heme: either of them has been reported to be the ground

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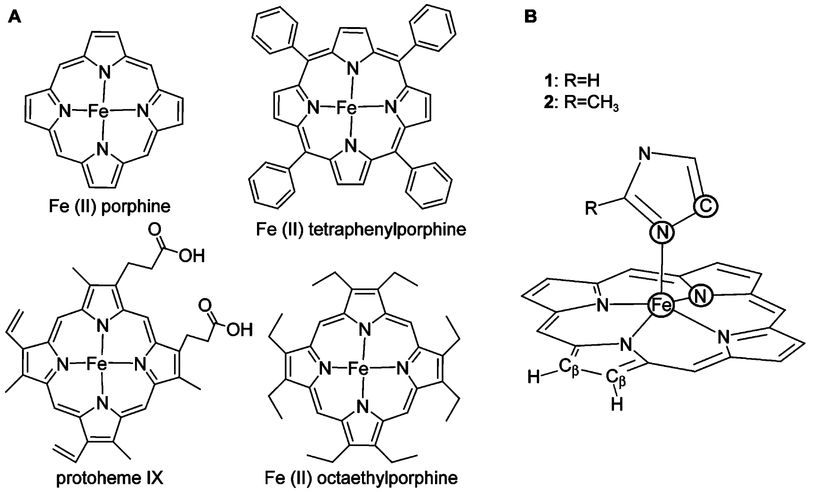

Figure 1. (A) Chemical structures and names of commonly encountered iron porphyrins. (B) Chemical structures of the two model hemes [Fe(por)(Im)], **1**, and [Fe(por)(2-MeIm)], **2,** studied by us. The circled atoms define the dihedral angle, D_{or}, used to characterize the orientation of imidazole in computed structures.

state.[2,3,23−29] The result partially depends on the functional used in computations: pure DFT methods usually overestimate the stability of low-spin states (i.e., triplet for 5-coordinate iron(II) porphyrin).[2,30] Hybrid functionals that contain a Hartree−Fock exact exchange term predict smaller quintet−triplet gaps than pure functionals do, often resulting in the quintet ground state, in agreement with experimental data. Relatively accurate predictions of hybrid functionals for spin-state splittings in transition-metal complexes are believed to originate from cancellation of errors of pure DFT that favors low-spin states and of the Hartree−Fock method that favors high-spin states.[30] In fact, the predicted $\Delta E = E(\text{high spin}) - E(\text{low spin})$ energy difference was found to decrease linearly with an increasing proportion of exact exchange in a given functional.[31,32] However, with the same B3LYP functional both the quintet[3,25] and the triplet[2,26] ground states have been calculated for monoimidazole-coordinated iron(II) porphyrins, suggesting that additional computational variables may affect the results.

The model chemistry that defines the result of a calculation is a combination of the method and the basis set, each introducing its own error. Generally, an improved description of electron density distribution with larger basis sets results in computed parameters that are closer to the experimental ones than those obtained with smaller basis sets, although exceptions are known.[33] The size of monoimidazole-ligated iron(II) porphyrins (at least 30 heavy atoms) and their open-shell electronic structure make calculations of equilibrium structural parameters and particularly of normal vibrational modes resource-intensive with basis sets larger than of triple-split-valence quality with augmentation. Basis set variations are known to yield chemically significant differences in relative energies and structural parameters of isomers of compounds of second-row elements,[34] and the calculated parameters of transition-metal complexes are likely to be at least as sensitive to the basis set, yet few studies examined systematically the basis set dependence of the properties of transition-metal derivatives.[2,35]

Among other computational variables that may affect the results are (1) vibrational zero-point energy (ZPE) corrections, (2) symmetry constraints, and (3, 4) specifically for the heme models, peripheral substituents of (3) porphine and (4) imidazole (Im), Figure 1.

(1) Contributions of vibrational zero-point energy (E_{ZPE}) may stabilize high-spin states by up to several kilocalories per mole relative to the lower spin states[36] and are of paramount importance in modeling any process in which the spin state changes, e.g., in spin-crossover materials.[37] The high cost of computing E_{ZPE} often prevents its inclusion in calculations of relative energies of the triplet and quintet states of hemes.

(2) It is typical to conduct computations on model [Fe(por)(Im)] complexes constrained to C_s symmetry with the mirror plane containing the Im ligand,[4,24,25] thereby preventing rotation of the Im about the Fe−N_{Im} bond.

(3) Only negligible differences were observed in computed structural and electronic properties of the FeN_5 core in Fe(II) complexes of porphine, tetraphenylporphine, octaethylporphine, or protoporphyrin IX (Figure 1A).[23,29]

(4) Although 2-methylimidazole (2-MeIm; Figure 1B) has been used extensively in biomimetic chemistry to model the “tense” state of deoxyhemoglobin and to enforce monoimidazole ligation of iron(II) porphyrins,[1,5] all reported computational studies but one[23] were done with iron porphyrins ligated by unsubstituted imidazole, [Fe(por)(Im)].[2,3,25−29] Whether computed electronic structures of [Fe(por)(2-MeIm)] and [Fe(por)(Im)] (Figure 1) are different is not known. Ferrohemes complexed by 2-MeIm are characterized by a larger displacement of Fe from the porphyrin plane compared to the Im-ligated analogues. In computations such larger displacements were shown to favor the quintet state over the triplet state.[23,24,27]

The objective of the study we report here was to quantify the sensitivity of the computed structural and vibrational parameters and the ground electronic states of two model heme complexes, [Fe(por)(Im)], **1**, and [Fe(por)(2-MeIm)], **2**, to the basis set, symmetry constraints, and inclusion of ZPE corrections. We expect that such information would provide some guidance in selecting computational variables to maximize the probability that the calculated properties of a monoimidazole-ligated iron(II) porphyrin are realistic. In our study we used basis sets of the 6-31G and 6-311G families of Pople and coworkers.[38−40] The inclusion of polarization (d or *) and diffuse (+) functions resulted in six basis sets (6-31G, 6-31G*, 6-31+G*, 6-311G, 6-311G*, and 6-311+G*) that were applied to whole complexes, and two mixed basis sets, M1 (6-31G* on Fe, 6-31G on all other atoms) and M2 (6-311G* on Fe, 6-31G* on all other atoms). We tested three hybrid functionals (B3LYP, B3PW91, B97-1) and two pure functionals (OLYP and TPSS). In addition, we carried out single-point energy calculations with the B3LYP functional and Pople-style basis sets up to 6-311++G(2d,2p), Ahlrichs-style basis sets up to TZVPP, and

Dunning's correlation-consistent cc-pVTZ basis set (see the Computational Details for further details). B3PW91 and popular B3LYP were previously shown to yield good results for model hemes.[2,24,25,41] TPSS, OLYP, and B97-1 were recommended in benchmarking studies of a number of transition-metal compounds[42] and specifically iron complexes,[36,43] including porphyrins,[44] but to the best of our knowledge have not been tested on model hemes. TPSS and OLYP are pure functionals and hence do not include the exact exchange term that is often considered necessary for accurate prediction of the spin state of iron porphyrins;[2,30,44] however, in several studies of spin-state splittings of Fe(II) complexes,[36,43] OLYP was found to provide results comparable in accuracy to hybrid functionals.

Computational Details

We calculated the lowest energy quintet and triplet states of [Fe(por)(Im)] (^{5}**1** and ^{3}**1**) and [Fe(por)(2MeIm)] (^{5}**2** and ^{3}**2**) (Figure 1). Unrestricted Kohn−Sham formalism was used in the calculations since only open-shell systems were investigated. All computations were done with Gaussian03 software[45] with default parameters for structure optimizations and vibrational analyses; tight SCF convergence criteria were used in all calculations, including single-point energy calculations. Symmetry constraints were not applied unless stated otherwise; the stability of wave functions was verified in all calculations. Vibrational analyses performed to obtain ZPE corrections confirmed the optimized structures to be the minimum-energy conformations rather than saddle points.

Basis Sets Used in Structure Optimizations and Vibrational Analysis. The contraction schemes used in double-split-valence (double-ζ) 6-31G and triple-split-valence (triple-ζ) 6-311G basis sets are described by Pople et al.[38−40] Polarized sets include one additional set of d-type functions on C and N atoms and one additional set of f-type functions on Fe.[39,40,46] Diffuse sets include one additional set of s- and p-functions on C and N atoms and one additional set of s-functions, two additional sets of p-functions, and one additional set of d-functions on Fe.[47,48] In Gaussian03 for Fe, the 6-311G basis set and its augmented versions imply the Wachters all-electron basis set[49] (contraction scheme (13s,9p,5d) → [9s,5p,3d]) with scaling factors of Raghavachari and Trucks;[50] diffuse d-functions for the Wachters basis set were optimized by Hay.[48] We used the original 6-31G* basis set[40] rather than the optimized version[51] 6-31G(d′) for Fe. One of the benchmarks in the development of the 6-31G(d′) basis set were results obtained with the 6-311G* basis set. The difference between quintet−triplet energy gaps calculated with 6-31G* and 6-311G* basis sets in this work was negligible, making 6-31G(d′) unnecessary for our purposes.

In Gaussian03, the default descriptions of d-functions in double-ζ and triple-ζ basis sets are different: Six Cartesian functions are used to describe valence and polarization d-shells in the 6-31G family of basis sets, while five pure d-functions are employed in the 6-311G family; seven pure f-functions are used in all cases. The Gaussian03 Gen keyword was used in cases of M1 and M2 mixed basis sets to assign different basis sets to different atomic centers, which defaults to a description with pure d-functions regardless of the number of contracted Gaussian functions in the valence shell. We tested the significance of using pure vs Cartesian d-functions in mixed basis sets and found insignificant differences in structural parameters and relative energies of quintet and triplet states (Table S1 in the Supporting Information). Hence, all results reported below refer to the default description in Gaussian03 (i.e., Cartesian d-functions for 6-31G contraction and pure d-functions for 6-311G contraction and mixed basis sets).

Basis Sets Used in Single-Point Energy Calculations. Additional single-point energy calculations were carried out with a number of basis sets developed by Pople et al.,[39,47,52] Ahlrichs et al.,[53,54] and Dunning et al.[55] Pople-style basis sets were of 6-311G quality with one (d or *) or two (2d) sets of polarization functions added to basis sets of heavy atoms and additional one (p) or two (2p) sets of p-type polarization functions added to basis sets of hydrogen atoms. In several computations basis sets of all atoms were augmented with diffuse functions (notation ++), which included a set of s-type diffuse functions on hydrogens in addition to diffuse functions on Fe, C, and N described earlier. The largest Pople-style basis set used was 6-311++G(2d,2p), i.e., the 6-311G basis set with a set of diffuse functions on each atom, two sets of polarization functions on non-hydrogen atoms, and two sets of polarization functions on hydrogen atoms.

Ahlrichs-style basis sets used were SVP[53] (double-ζ with one set of p-type polarization functions on Fe, d-type on C and N, and p-type on H), TZVP[54] (triple-ζ TZV with the same polarization functions as in SVP), and TZVPP[49,54,56] (TZV kernel with polarization functions of the triple-ζ correlation-consistent cc-pVTZ basis set of Dunning et al. on N, C, and H atoms[55] and polarization functions of p-type and f-type in the basis set of the Fe atom[56]). The correlation-consistent cc-pVTZ basis set of Dunning et al.[55] includes (2f,g) sets of polarization functions on the Fe atom, (2d,f) sets of polarization functions on C and N atoms, and (2p,d) sets of polarization functions on H atoms. Definitions of many basis sets are conveniently summarized in the Basis Set Exchange Database[57] and in the electronic resource provided by the University of Karlsruhe.[56]

Functionals. B3LYP and B3PW91 have the same exchange part (hybrid three-parameter Becke's functional[58]) and differ in their correlation functionals: empirical Lee, Yang, and Parr[58] (LYP) and nonempirical Perdew−Wang 1991[59] (PW91), respectively. B97-1 is a 10-parameter GGA hybrid functional derived by Becke[60] with the exact exchange contribution reoptimized by Handy et al.[61] OLYP is a combination of the LYP correlation functional and the optimized exchange OPTX functional.[62] TPSS[63] belongs to meta-GGA functionals that in addition to the electron density gradient take into account kinetic energy density and contains no empirical parameters.

Results and Discussion

Structural Parameters. We selected the following structural parameters for benchmarking geometry computations: bond length of Fe to the N atom of the axial imidazole, Fe−N$_{\mathrm{Im}}$; average distances of Fe to the four N atoms of the porphine, Fe−N$_{\mathrm{por}}$; displacement of Fe from the least-squares plane defined by these four N atoms, Fe−Ct. We compared average experimental values for two reported crystal structures of iron(II) porphyrins ligated with Im and nine reported crystal structures of iron(II) porphyrins ligated with 2-MeIm to those calculated for the quintet electronic states of [Fe(por)Im] (^{5}**1**) and [Fe(por)(2-MeIm)] (^{5}**2**), respectively. The corresponding crystal structure reference codes in the Cambridge Structural Database[64] are GAJHAA[65] and FUHVUZ[66] for Im-ligated structures and MIYZUP,[10] PVPORI20,[65] TALLAU,[12] TALLEY,[12] TALLIC,[12] TALLOI,[12] SEHPOL,[13] SEHPUR,[13] and MAQLEW[67] for 2-MeIm-ligated structures. We only used TALLEY, TALLOI, and SEHPOL structures to calculate the average Fe−N$_{\mathrm{Im}}$ distance in 2-MeIm-ligated complexes due to disordered positions of 2-MeIm in the other structures.

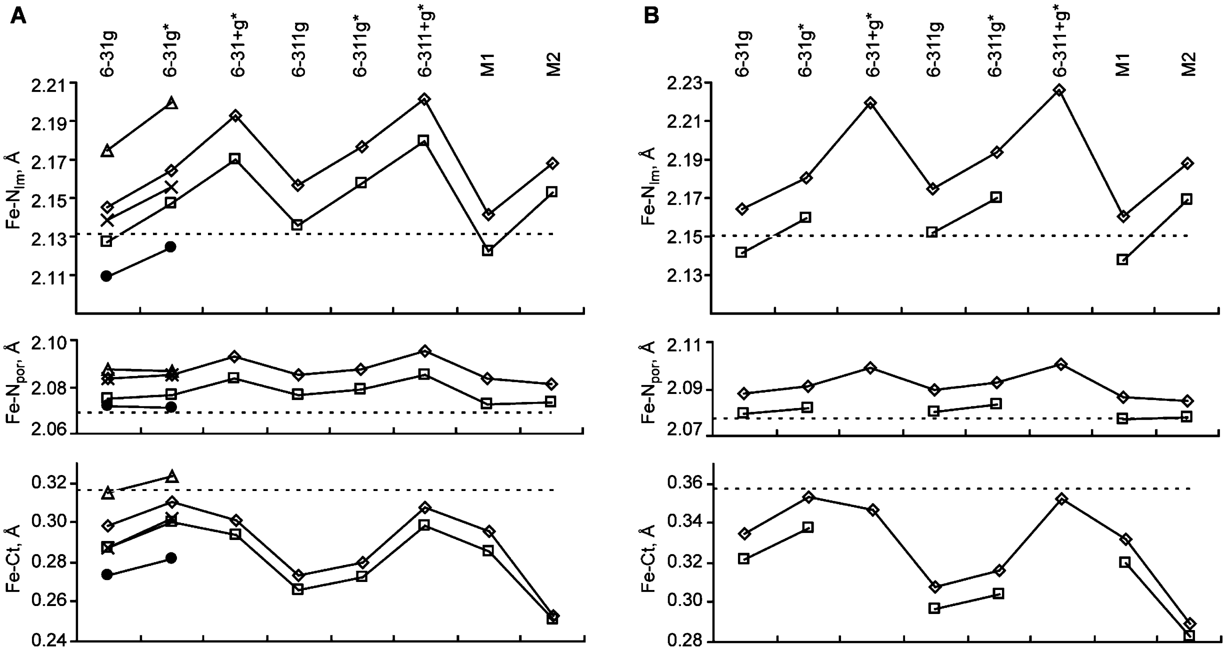

Figure 2. Calculated structural parameters in ^{5}**1** (A) and ^{5}**2** (B) with B3LYP (◇), B3PW91 (□), B97-1 (×), TPSS (●), and OLYP (△). Dashed horizontal lines indicate average parameters from single-crystal structures of two imidazole-ligated and nine 2-methylimidazole-ligated iron(II) porphyrins with various peripheral substituents. Calculations for ^{5}**2** with B3PW91 and basis sets augmented with polarization and diffuse functions were not performed due to computational cost.

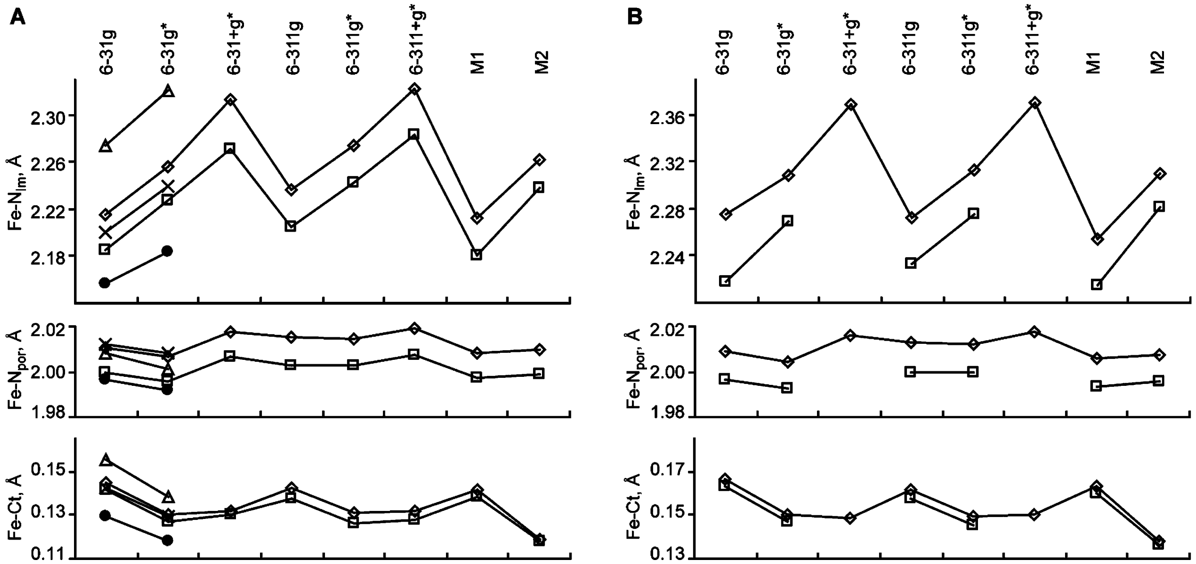

Figure 3. Calculated structural parameters in ^{3}**1** (A) and ^{3}**2** (B) with B3LYP (◇), B3PW91 (□), B97-1 (×), TPSS (●), and OLYP (△). Calculations for ^{3}**2** with B3PW91 and basis sets augmented with polarization and diffuse functions were not performed due to computational cost.

Combinations of B3LYP or B3PW91 with any basis set tested predicted the Fe$-$N$_{por}$ distances closest to the experimental values (maximum deviation <0.03 Å), followed by Fe$-$N$_{Im}$ distances (maximum absolute deviation <0.08 Å, maximum relative deviation 3.5%), Figure 2, Table 1. No functional/basis set combination correctly predicted *both* the Fe$-$N$_{Im}$ and the Fe$-$Ct separations. We found that Fe$-$Ct distances typically correlated with the Fe$-$N$_{Im}$ and Fe$-$N$_{por}$ bond lengths: correct predictions of the out-of-plane displacement were accompanied by overestimated Fe$-$N$_{Im}$ and Fe$-$N$_{por}$ distances and vice versa. It seems unlikely that these systematic deviations result from comparing distances between centroids of the electron density (the experimental values) to internuclear separations (the calculated values). The experimental values may be influenced by the secondary and tertiary coordination spheres of iron porphyrins in crystal structures, which are not accounted for in the calculations.

The variation of structural parameters of ^{5}**1** and ^{5}**2** with the basis set (Figure 2) is remarkably consistent for the B3LYP and B3PW91 functionals. For both functionals, the minimum total of the absolute deviations of the three calculated metric parameters from the average experimental values was observed with the smallest 6-31G and 6-31G* basis sets and their combination M1 (Table 1). Although B3LYP underestimated the average observed out-of-plane displacement less than B3PW91 did, it overestimated the Fe$-$N$_{Im}$ and Fe$-$N$_{por}$ bonds. B3LYP was found to overestimate bond lengths in a benchmarking study on a wide range of transition-metal systems.[42]

Structures obtained with triple-ζ basis sets manifested longer Fe$-$N$_{Im}$ and Fe$-$N$_{por}$ bonds and smaller out-of-plane displace-

TABLE 1: Selected Structural Parameters Calculated for Quintet 1 and 2 with Various Model Chemistries[a,b]

		6-31G	6-31G*	6-31+G*	6-311G	6-311G*	6-311+G*	M1	M2
^{5}**1**, B3LYP	$\mathrm{Fe-N_{Im}}$	2.145	2.164	2.193	2.157	2.176	2.202	2.142	2.168
	$\mathrm{Fe-N_{por}}$	2.083	2.085	2.093	2.085	2.088	2.095	2.083	2.081
	Fe−Ct	0.298	0.311	0.301	0.273	0.280	0.308	0.296	0.254
	deviation[c]	0.044	0.052	0.098	0.082	0.097	0.102	0.042	0.109
	D_{or} [d]	3.7	0.1	3.5	4.4	5.4	3.3	4.0	6.0
^{5}**1**, B3PW91	$\mathrm{Fe-N_{Im}}$	2.127	2.147	2.170	2.136	2.157	2.180	2.122	2.153
	$\mathrm{Fe-N_{por}}$	2.075	2.076	2.084	2.076	2.079	2.085	2.073	2.074
	Fe−Ct	0.288	0.301	0.294	0.266	0.272	0.298	0.285	0.252
	deviation[c]	0.035	0.035	0.073	0.059	0.077	0.080	0.040	0.088
	D_{or} [d]	4.1	5.0	3.7	4.5	5.7	3.4	3.9	6.1
^{5}**1**, B97-1	$\mathrm{Fe-N_{Im}}$	2.138	2.156						
	$\mathrm{Fe-N_{por}}$	2.084	2.085						
	Fe−Ct	0.288	0.302						
	deviation[c]	0.048	0.052						
	D_{or} [d]	0.0	0.0						
^{5}**1**, TPSS	$\mathrm{Fe-N_{Im}}$	2.109	2.124						
	$\mathrm{Fe-N_{por}}$	2.072	2.071						
	Fe−Ct	0.274	0.281						
	deviation[c]	0.064	0.041						
	D_{or} [d]	0.4	4.7						
^{5}**1**, OLYP	$\mathrm{Fe-N_{Im}}$	2.174	2.199						
	$\mathrm{Fe-N_{por}}$	2.088	2.087						
	Fe−Ct	0.315	0.323						
	deviation[c]	0.065	0.096						
	D_{or} [d]	0.0	0.0						
^{5}**2**, B3LYP	$\mathrm{Fe-N_{Im}}$	2.165	2.181	2.220	2.175	2.194	2.226	2.160	2.188
	$\mathrm{Fe-N_{por}}$	2.088	2.091	2.099	2.090	2.092	2.101	2.086	2.085
	Fe−Ct	0.335	0.353	0.347	0.308	0.316	0.353	0.332	0.289
	deviation[c]	0.048	0.048	0.101	0.086	0.100	0.104	0.044	0.113
	D_{or} [d]	28.8	30.1	11.1	32.8	33.3	10.5	31.5	34.0
^{5}**2**, B3PW91	$\mathrm{Fe-N_{Im}}$	2.142	2.159		2.151	2.170		2.138	2.169
	$\mathrm{Fe-N_{por}}$	2.079	2.082		2.080	2.083		2.077	2.078
	Fe−Ct	0.322	0.337		0.297	0.304		0.319	0.283
	deviation[c]	0.046	0.033		0.064	0.079		0.050	0.093
	D_{or} [d]	32.8	33.4		36.7	38.1		33.2	37.2

[a] Distances in angstroms, angles in degrees. [b] Average experimental structural parameters for Im-ligated hemes: $\mathrm{Fe-N_{Im}}$, 2.131 Å; $\mathrm{Fe-N_{por}}$, 2.069 Å; Fe−Ct, 0.316 Å. Average structural parameters for 2-MeIm-ligated hemes: $\mathrm{Fe-N_{Im}}$, 2.150 Å; $\mathrm{Fe-N_{por}}$, 2.077 Å; Fe−Ct, 0.357 Å. [c] Total of the absolute deviations of the three calculated metric parameters from the average experimental values. [d] The dihedral angle (D_{or}) is defined in Figure 1.

TABLE 2: Vibrational Frequencies of the Fe−Im Stretching Mode Calculated for ^{5}1 and ^{5}2 with Various Model Chemistries

		6-31G	6-31G*	6-31+G*	6-311G	6-311G*	6-311+G*	M1	M2
^{5}**1**	B3LYP	243	231	225	244	231	225	242	232
	B3PW91	246	231	227	247	232	227	245	232
	B97-1	245	232						
	TPSS	244	229						
	OLYP	233	220						
^{5}**2**	B3LYP	237	211[a]	220	237	225	220	235	228
	B3PW91	248	216[b]		252	227[c]		246	226

[a−c] Several close-lying vibrational modes met the structural criteria of Fe−Im bond elongation coupled with out-of-plane movement of Fe: (*a*) 219 cm^{-1}; (*b*) 221, 226, and 245 cm^{-1}; (*c*) 227, 232, and 249 cm^{-1}.

ments compared to those obtained with double-ζ basis sets with the same augmentation, resulting in larger total deviations. Both double-ζ and triple-ζ basis sets with diffuse and polarization functions overestimated $\mathrm{Fe-N_{por}}$ and especially $\mathrm{Fe-N_{Im}}$ bond lengths (maximum deviation of 0.071 Å for ^{5}**1** and 0.076 Å for ^{5}**2**) and appear poor choices for calculating equilibrium structural parameters.

The structural parameters of triplet [Fe(por)(Im)] (^{3}**1**) and [Fe(por)(2-MeIm)] (^{3}**2**) structures computed with various model chemistries are shown in Figure 3 and are listed in Table S2 in the Supporting Information. In agreement with other studies, the major change observed upon transition from the quintet to the triplet state was a pronounced (up to 0.18 Å) in-plane movement of the iron accompanied by a slight shortening of the $\mathrm{Fe-N_{por}}$ bonds. The concomitant lengthening of the $\mathrm{Fe-N_{Im}}$ bond was not sufficient to compensate for iron's in-plane movement, and the imidazole ligand is closer to the porphine in the triplet than in the quintet state for a given model chemistry.

Structural differences between [Fe(por)(Im)] and [Fe(por)-(2-MeIm)] in either spin state are probably driven to a large degree by steric repulsion between the porphine macrocycle and the methyl group of 2-MeIm. In [Fe(por)(2-MeIm)] the $\mathrm{Fe-N_{Im}}$ bond and the Fe−Ct distance were longer, the porphine was more distorted, and 2-MeIm was tilted with respect to the $\mathrm{Fe-N_{Im}}$ bond positioning the methyl group away from the porphyrin (Figure 4). The details of structural variations between **1** and **2** are somewhat different in the two spin states. With a given model chemistry the difference of the $\mathrm{Fe-N_{Im}}$ bond length between **2** and **1** was smaller in the quintet (by 0.018 Å on average) than in the triplet (by 0.042 Å on average) state. The increase in the Fe−Ct displacement, on the other hand, was

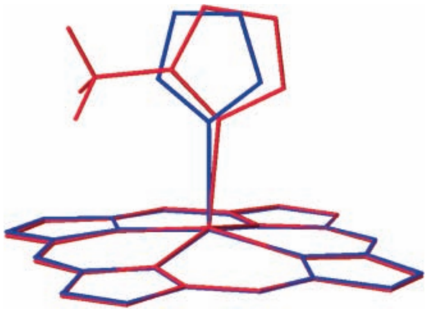

Figure 4. Structural differences between ^{5}**1** (blue) and ^{5}**2** (red) optimized at the B3LYP/6-31g level. Hydrogen atoms except those of the methyl group of 2-MeIm are omitted for clarity. The structures were superimposed using the four nitrogen atoms of the porphine.

more significant for quintets than for triplets, 0.037 and 0.020 Å on average, respectively.

As mentioned above, every model chemistry predicted smaller Fe−Ct distances in the triplet vs quintet states and a smaller difference in out-of-plane displacement of Fe between ^{3}**1** and ^{3}**2** than between ^{5}**1** and ^{5}**2**. This observation suggests that displacement of triplet Fe from the porphyrin plane is energetically costlier than the equal displacement of quintet Fe. As suggested previously[26] and confirmed in our studies, the $d_{x^2-y^2}$-orbital has antibonding character with respect to Fe−N$_{por}$ bonds and its population only in the quintet state favors longer Fe−N$_{por}$ and therefore longer Fe−Ct distances for quintet Fe than triplet Fe.

Free of symmetry constraints, our computations showed that the preferred orientation of the axial ligand was spin-state-dependent regardless of the model chemistry. In ^{3}**1** Im adopted a staggered orientation with respect to the N$_{por}$−Fe−N$_{por}$ diagonals (dihedral angle (D_{or}) of 44.6−44.9°, with the exception of OLYP/6-31G model chemistry that yielded a value of 36.2°, Table S2), whereas it was eclipsed in ^{5}**1** (D_{or} = 0.0−6.3°, Table 1). Nakashima et al.[3] obtained similar results with B3LYP and a mixed basis set with 6-31G* on Fe and porphine's N atoms and 6-31G on the other atoms. The difference in the ligand's orientation may result from greater steric repulsion between the porphine and the hydrogen atoms at Im's 2- and 4-positions in the triplet state due to the proximity of Im to the porphine in the triplet state. Qualitatively similar trends were observed in [Fe(por)(2-MeIm)] (D_{or} in ^{3}**2** is on average 9.7° larger than in ^{5}**2**); however, the fully eclipsed conformation was probably precluded by the bulk of the 2-methyl group.

Because for B3LYP and B3PW91 the experimental metric parameters were reproduced most successfully with the 6-31G and 6-31G* basis sets, we tested their performance with three more functionals (B97-1, TPSS, and OLYP) for predicting structures of ^{5}**1** and ^{3}**1** (Figures 2 and 3, Tables 1 and S2). Qualitatively similar trends were observed: (1) the triplet states manifested longer Fe−N$_{Im}$ and shorter Fe−Ct distances compared to the quintet state; (2) with B97-1 and OLYP and either basis set the closer the calculated Fe−Ct distance was to the experimental value, the farther off the Fe−N$_{Im}$ distance was; TPSS was an exception.

Among all five functionals in combination with 6-31G and 6-31G* basis sets, the sum of the absolute deviations of the three benchmark metrics was minimal for B3PW91/6-31G and B3PW91/6-31G*, in qualitative agreement with the findings of Strickland and Harvey.[2] The overall accuracies of B3LYP, B97-1, and TPSS with either 6-31G or 6-31G* and of OLYP/6-31G were comparable. Only TPSS slightly *under*estimated the Fe−N$_{Im}$ bond; it predicted the smallest out-of-plane displacements but accurate Fe−N$_{por}$ bond lengths. The Fe−Ct distances were best reproduced with the OLYP functional, but the Fe−N$_{Im}$ bonds were exceptionally long (maximum deviation of 0.043 and 0.068 Å with 6-31G and 6-31G* basis sets, respectively). On the basis of trends observed in variation of the Fe−N$_{Im}$ bond with the basis set for B3LYP and B3PW91, OLYP with larger basis sets seems unlikely to yield more realistic Fe−N$_{Im}$ distances.

Vibrational Frequency of the Fe−Im Stretching Mode. A characteristic spectral feature of 5-coordinate hemes is a vibrational mode at ~220 cm^{-1} assigned to stretching of the Fe−N$_{Im}$ bond that involves movement of Fe perpendicular to the porphyrin plane.[68] Comparing the DFT-calculated values for this vibration (Table 2) with the experimental values provides an additional benchmark of the quality of the computed structures. It must be noted here that for several combinations of method/basis set there were multiple vibrations in which a change of the Fe−N$_{Im}$ distance was coupled with out-of-plane displacement of Fe. In these cases the vibration with the lowest frequency was selected for benchmarking. Frequency calculations were carried out for an isolated molecule in the gas phase in harmonic approximation.

The frequencies of the Fe−N$_{Im}$ stretching mode computed for ^{5}**1** with B3LYP and B3PW91 functionals varied systematically with augmentation of the basis set; B3PW91 frequencies were marginally higher than those of B3LYP with a given basis set (Table 2). At the same augmentation the difference between vibrational frequencies calculated with double-ζ and triple-ζ basis sets did not exceed 1 cm^{-1}. Insensitivity of the frequencies to contraction could be specific to Pople-style basis sets: the previously reported frequencies of this vibrational mode in [Fe(por)(Im)] computed with B3LYP and Ahlrichs' VDZ (double-ζ) and VTZ (triple-ζ) basis sets were 249 and 234 cm^{-1}, respectively.[24] Frequencies calculated with basis sets without any additional functions exceeded the experimental value by as much as 26 cm^{-1}. The agreement of the experimental frequency with frequencies computed using basis sets with polarization functions was good, within 11 cm^{-1}, and addition of diffuse functions further improved the predictions to within 5−7 cm^{-1} of the experimental values.

Vibrational frequencies computed for ^{5}**2** were not as uniform as those for ^{5}**1**, probably due to the more complex vibrational structure. However, for a given functional, frequencies with the 6-31G basis set and 6-311G basis set were higher than those with, respectively, the 6-31G* and 6-311G* basis sets. With the B3LYP functional the frequencies obtained for ^{5}**1** were higher than those of ^{5}**2** for a given basis set; B3PW91 predicted higher frequencies for ^{5}**2** than for ^{5}**1** with nonaugmented basis sets and lower frequencies with basis sets containing polarization functions (Table 2).

The trend of decreasing Fe−N$_{Im}$ frequency in ^{5}**1** with the 6-31G* basis set compared with the 6-31G basis set was the same for all five functionals used in our work; frequencies computed with all functionals but OLYP differed insignificantly (243−246 cm^{-1} with the 6-31G basis set and 229−232 cm^{-1} with the 6-31G* basis set). OLYP's frequencies were ~10 cm^{-1} lower than those obtained with other functionals and in fact were closest to the experimental data (Table 2).

Among the functionals and basis sets we tested, B3LYP/6-31G* and B3PW91/6-31G* reproduced both the frequency of the Fe−N$_{Im}$ stretch and the geometric parameters with the best accuracy. The 6-31G basis set, while providing comparable agreement with the structural parameters, predicted the frequencies poorly. Of the two basis sets, 6-31G and 6-31G*, that we

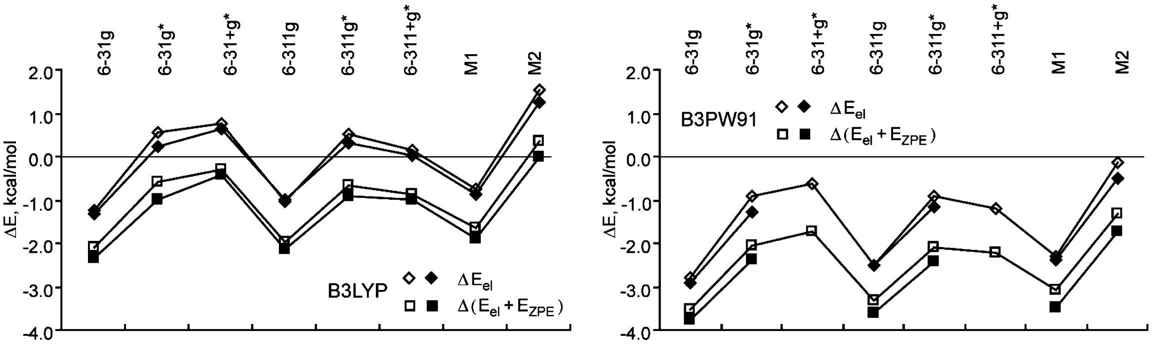

Figure 5. Basis set dependence of calculated energy differences between the quintet and triplet states of **1** (open symbols) and **2** (filled symbols). Full structure optimizations were carried out with each combination of functional/basis set.

TABLE 3: Values of ΔE_{el}, ΔE_{ZPE}, and ΔG_{corr} (kcal/mol) Calculated for 1 and 2 with Various Model Chemistries[a]

		6-31G	6-31G*	6-31+G*	6-311G	6-311G*	6-311+G*	M1	M2
[Fe(por)(Im)], B3LYP	ΔE_{el}	−1.2	+0.6	+0.8	−1.0	+0.5	+0.2	−0.7	+1.5
	ΔE_{ZPE}	−0.9	−1.2	−1.0	−0.9	−1.2	−1.0	−0.9	−1.1
	ΔG_{corr}	−1.7	−2.2	−1.3	−1.6	−2.2	−1.2	−1.8	−2.0
[Fe(por)(Im)], B3PW91	ΔE_{el}	−2.8	−0.9	−0.6	−2.5	−0.9	−1.2	−2.3	−0.2
	ΔE_{ZPE}	−0.7	−1.1	−1.1	−0.8	−1.2	−1.0	−0.8	−1.1
	ΔG_{corr}	−1.4	−2.2	−1.6	−1.5	−2.3	−1.4	−1.5	−1.9
[Fe(por)(Im)], B97-1	ΔE_{el}	−3.3	−1.4						
	ΔE_{ZPE}	−0.8	−1.1						
	ΔG_{corr}	−1.4	−1.9						
[Fe(por)(Im)], TPSS	ΔE_{el}	+10.2	+12.1						
	ΔE_{ZPE}	−0.9	−1.1						
	ΔG_{corr}	−1.7	−2.3						
[Fe(por)(Im)], OLYP	ΔE_{el}	−0.6	+1.2						
	ΔE_{ZPE}	−0.6	−0.4						
	ΔG_{corr}	−0.1	−1.0						
[Fe(por)(2-MeIm)], B3LYP	ΔE_{el}	−1.3	+0.3	+0.7	−1.0	+0.3	+0.1	−0.9	+1.3
	ΔE_{ZPE}	−1.0	−1.3	−1.1	−1.1	−1.2	−1.1	−1.0	−1.2
	ΔG_{corr}	−1.7	−2.2	−1.7	−2.3	−2.5	−2.1	−1.5	−2.2
[Fe(por)(2-MeIm)], B3PW91	ΔE_{el}	−2.9	−1.3		−2.5	−1.1		−2.4	−0.5
	ΔE_{ZPE}	−0.8	−1.2		−1.1	−1.3		−1.1	−1.2
	ΔG_{corr}	−0.9	−1.9		−2.0	−2.1		−2.1	−2.2

[a] Individual electronic energies, vibrational zero-point energies, and entropic and enthalpic contributions to ΔG_{corr} are listed in Tables S3 and S4 in the Supporting Information.

tested with B97-1 and TPSS, the 6-31G* basis set provided a better agreement with experimental structural parameters and the Fe−N_{Im} vibrational frequency. OLYP is a special case: its predictions were within 10 cm^{-1} of the experimental value with either basis set. Although the frequency calculated at the OLYP/6-31G* level was 220 cm^{-1}, in excellent agreement with experimental data, the structural parameters are the worst among all combinations of functionals with this basis set (Table 1).

Electronic Structure and Relative Energies of Triplet and Quintet 1 and 2. We found that both **1** and **2** had the following occupations of the metal d-orbitals: $(d_{xz},d_{yz})^3(d_{xy})^1(d_{z^2})^1(d_{x^2-y^2})^1$ and $(d_{xz},d_{yz})^3(d_{xy})^2(d_{z^2})^1(d_{x^2-y^2})^0$ in the quintet and triplet states, respectively. The *x*- and *y*-axes were selected to coincide with the N_{por}−Fe−N_{por} vectors but were not differentiated. Hence, only the combined electron population of the two orbitals d_{xz} and d_{yz} is listed, following Liao and Scheiner.[23] The above orbital populations correspond to the $^5A'$ and $^3A''$ states in the idealized C_s symmetry of **1** with the preferred orientation of Im maintained in each state. Available computational data[23,24] are in agreement on the above d-orbital occupation pattern of the lowest lying triplet state, but either the $(d_{xz},d_{yz})^3$ $(d_{xy})^1(d_{z^2})^1$ $(d_{x^2-y^2})^1$ [12,24,25] or the $(d_{xy})^2(d_{xz})^1(d_{yz})^1(d_{z^2})^1(d_{x^2-y^2})^1$ [14,17,23,25,69] configuration of the lowest energy quintet was suggested from experimental or computational investigation. The only published study[23] on [Fe(por)(2-MeIm)] found $(d_{xy})^2(d_{xz})^1(d_{yz})^1(d_{z^2})^1(d_{x^2-y^2})^1$ to be the lowest lying quintet state, albeit with structural parameters in poorer agreement with the experimental values than those obtained for the $(d_{xz},d_{yz})^3(d_{xy})^1(d_{z^2})^1(d_{x^2-y^2})^1$ state.

The quintet−triplet electronic energy gaps, $\Delta E_{\mathrm{el}} = E_{\mathrm{el}}^{\mathrm{quintet}} - E_{\mathrm{el}}^{\mathrm{triplet}}$ both in **1** and in **2** varied considerably with the basis sets for either B3LYP or B3PW91 (the maximum variation for a functional was 2.7 kcal/mol, Figure 5, Table 3). On the other hand, with the same model chemistry the difference in ΔE_{el} between **2** and **1** was 0.0−0.3 kcal/mol. While B3PW91 predicted negative values of ΔE_{el} in all cases, with B3LYP positive or negative values of ΔE_{el} were obtained for either heme, depending on the basis set. The zero-point energy difference, $\Delta E_{\mathrm{ZPE}} = E_{\mathrm{ZPE}}^{\mathrm{quintet}} - E_{\mathrm{ZPE}}^{\mathrm{triplet}}$, between the quintet and triplet states in all cases was approximately −1 kcal/mol (Table 3), which is comparable to ΔE_{el}. Inclusion of the ZPE correction resulted in the quintet ground electronic state being predicted by either functional and all basis sets except B3LYP/M2 (Figure 5).

It is generally accepted that the quintet−triplet electronic energy gap of the hemes must be near zero,[2,3,23−26] and it is surprising that vibrational corrections to the free energy have not been accounted for in comparing the relative free energies of the two states, since the values of the vibrational energy differences for spin states of Fe(II) complexes are known to be substantial.[32,36,70] Small absolute values of ΔE_{el} in 5-coordinate ferrohemes make the sign of computed ΔE_{el} values sensitive to both the functional and the basis set, which in turn makes the

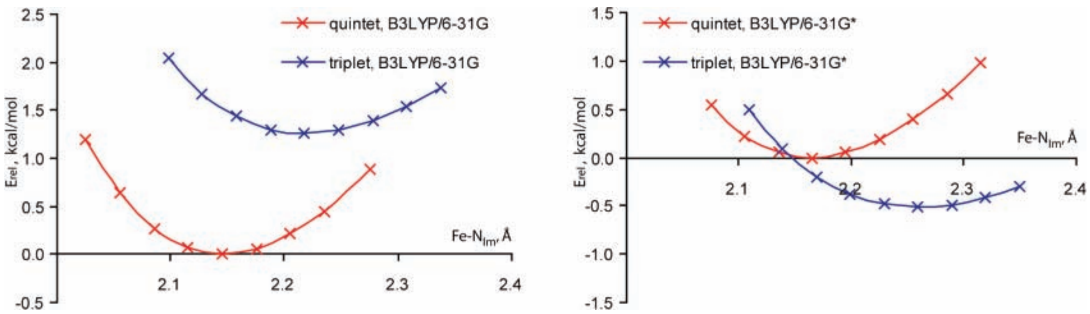

Figure 6. Electronic energy of quintet and triplet [Fe(por)(Im)] as a function of Fe−N$_{Im}$ distance model chemistries obtained in optimizations with constrained Fe−N$_{Im}$ distances. C_s symmetry with the preferred orientation of Im (eclipsed for quintet, staggered for triplet) was maintained for each state in constrained optimizations. E_{rel} is the energy relative to that of the quintet state fully optimized with a given model chemistry.

sign of the computed *free* energy differences sensitive to the inclusion of vibrational corrections.

Computations of ^{5}**1** and ^{3}**1** constrained to C_s symmetry with B3LYP/6-31G and B3LYP/6-31G* model chemistries (Table S5 in the Supporting Information) confirmed it to be an adequate approximation, with a <0.1 kcal/mol difference in the electronic energy and minor structural changes as reported previously,[4] provided imidazole was confined close to its preferred orientation in each spin state. However, symmetry-restricted optimizations may become misleading when imidazole is constrained to the *same* orientation in both spin states. The difference in electronic energy of ^{5}**1** with staggered and eclipsed imidazole was up to 0.5 kcal/mol (Table S6 in the Supporting Information), with the staggered rotamer probably being the transition state for rotation of imidazole about the Fe−N$_{Im}$ axis. Because this 0.5 kcal/mol energy difference is comparable to ΔE_{el} values obtained with B3LYP, optimizing the orientation of axial imidazole is likely important in estimating relative energies of the minimum-energy crossing points between quintets and spin states of lower multiplicity. Whereas the preferred orientation of imidazole in quintet [Fe(por)(Im)] is eclipsed, it is staggered in both the triplet and singlet[3] states. As expected, ΔE_{el} was fairly insensitive to distortion of the Fe−N$_{Im}$ distance away from its equilibrium values in the minimum-energy conformers of ^{5}**1** and ^{3}**1** (Figure 6): a 0.1−0.2 kcal/mol increase in electronic energy required a 0.03 Å displacement from the equilibrium distance, which greatly exceeded the 0.001−0.002 Å uncertainty of the computed parameters.

The dependence of the ΔE_{el} values on the basis set was identical for B3LYP and B3PW91. The two sets of values correlated linearly (Figure 7), ΔE_{el}(B3PW91/BS) = ΔE_{el}(B3LYP/BS) − 1.5 kcal/mol, where BS is any of the eight basis sets tested. The existence of such a linear correlation must be related to the additivity of the errors of the method and the basis set in the computed ΔE_{el}: the unit slope indicates that the basis set error with a given basis set is the same for both functionals and the value of the offset is the difference between the errors of the two functionals. A relatively small value of the offset, −1.5 kcal/mol, is expected: the two functionals have the same exchange part and differ only in the correlation part, and the exchange functional is known to be more important than the correlation functional in computing relative spin-state energies.[30]

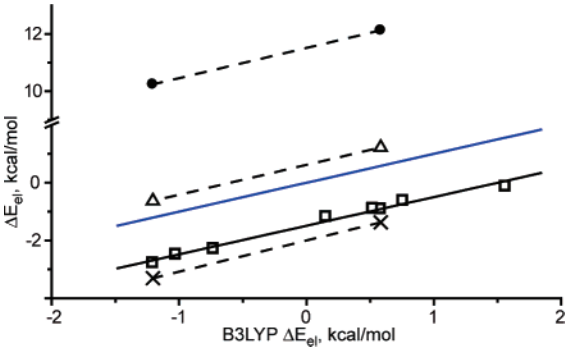

Figure 7. Electronic energy gaps calculated with B3PW91 (□), B97-1 (×), TPSS (●), and OLYP (△) versus those obtained with B3LYP. The solid blue line is ΔE_{el}(B3LYP/BS) vs ΔE_{el}(B3LYP/BS), i.e., the $x = y$ line. The solid black line is the least-squares linear fit of ΔE_{el}(B3PW91/BS) vs ΔE_{el}(B3LYP/BS); the resulting equation is ΔE_{el}(B3PW91/BS) = ΔE_{el}(B3LYP/BS) − 1.5 kcal/mol. Dashed lines serve as a guide to the eye.

We also computed ΔE_{el} and ΔE_{ZPE} values for **1** with the 6-31G and 6-31G* basis sets and the B97-1, OLYP, and TPSS functionals (Figure 6, Table 3). TPSS, despite providing acceptable geometric parameters, failed to describe adequately the spin-state energetics of [Fe(por)(Im)], predicting ΔE_{el} up to 12.1 kcal/mol. Such behavior is consistent with that reported for pure functionals BP86 and BLYP that were found to strongly favor the triplet state of model hemes while yielding structural parameters in good agreement with experimental data.[2,27] Since the ΔE_{ZPE} correction is −1 kcal/mol, TPSS predicted the triplet electronic state far below the quintet state. We did not test the possibility that TPSS predicts a singlet as the ground electronic state. The electronic energy gaps calculated with B97-1 were the lowest among the five functionals and negative, which could stem partially from its larger exchange admixture compared to that of other functionals (21% in B97-1,[60] 20% in B3LYP and B3PW91,[58] 0% in TPSS[63] and OLYP[62]). Increasing the fraction of exact exchange is known to shift electronic energy gaps toward states with higher spin.[30−32] Our results indicate that a 20% exact exchange admixture in the B3LYP formulation is barely sufficient to reproduce the experimentally observed quintet state and decreasing the admixture as recommended for other Fe(II) complexes[31,32] should result in the triplet ground state, contrary to experimental data.

Values of ΔE_{el} calculated with the pure OLYP functional (zero exact exchange) were only slightly larger than those obtained with hybrid B3LYP, representing a substantial improvement with respect to other pure functionals. However, the OLYP/6-31G* model chemistry failed to predict the quintet ground state due to the small value of ΔE_{ZPE} (−0.4 kcal/mol); ΔE_{ZPE} calculated at the OLYP/6-31G level, −0.6 kcal/mol, was also among the smallest obtained with any of the model chemistries tested in this work (Table 3). Although OLYP, unlike other pure functionals, was shown to provide accurate results for non-porphyrin iron(II) complexes,[36,43] its performance was deemed questionable in predicting relative spin-state energies of a number of iron porphyrin complexes.[44]

Remarkably, for all five functionals we tested the difference in the electronic energy gaps predicted with the 6-31G and

6-31G* basis sets was 1.8−1.9 kcal/mol, despite the different mathematical formulations of the functionals. This is likely a manifestation of the additivity of the errors of the method and the basis set for all tested functionals. If such additivity holds, it appears reasonable to speculate that the basis set dependence of ΔE_{el} values calculated with B97-1, OLYP, and TPSS functionals is similar to that found within the B3LYP and B3PW91 sets, but this assertion remains to be tested. Were it correct, ΔE_{el} calculated with one of the eight basis sets we used would differ from that calculated with B3LYP and the same basis set by ∼11.5 kcal/mol for TPSS, ∼0.6 kcal/mol for OLYP, and ∼−2.0 kcal/mol for B97-1. (We obtained these estimates using the average of two pairwise differences of ΔE_{el} values obtained with B3LYP and a given functional with the 6-31G basis set and with the 6-31G* basis set.) Consequently, both TPSS and B97-1 would maintain their respective preferences toward the triplet or quintet state even with the inclusion of ZPE corrections. The offset for OLYP was small and positive, and in combination with small negative values of its ΔE_{ZPE}, it does not allow an extrapolation of the predicted ground state to other basis sets.

Spin states of heme complexes have only been measured by NMR[14,17] or Mössbauer spectroscopies.[9,10,12,13,15,16,18] If one is interested in calculated ground-state multiplicities at cryogenic temperatures, relevant to low-temperature Mössbauer measurements, it is sufficient to consider only the $\Delta E_{\mathrm{el}} + \Delta E_{\mathrm{ZPE}}$ sum, which accounts for the vibrational energy at 0 K. For comparisons with experimental data collected at higher temperatures, thermal corrections to the free energy of the hemes have to be taken into account. Table 3 lists these corrections ($\Delta G_{\mathrm{corr}} = G_{\mathrm{corr}}^{\mathrm{quintet}} - G_{\mathrm{corr}}^{\mathrm{triplet}}$) at 298.15 K computed from partition functions of the two spin states in the ideal gas approximation,[71] neglecting the different molecular volumes of the two spin states.

Free energy corrections (ΔG_{corr}) account for both enthalpic and entropic terms, and the total free energy difference at 298.15 K is expressed as $\Delta G(298.15\ \mathrm{K}) = \Delta G_{\mathrm{corr}} + \Delta E_{\mathrm{el}}$. The values of ΔG_{corr} were more negative than the values of ΔE_{ZPE} for any tested model chemistry; i.e., the quintet state is favored more strongly over the triplet at room temperature than at 0 K. The numeric values of ΔG_{corr} were not as uniform across various model chemistries as those of ΔE_{ZPE}: unlike ΔE_{ZPE}, ΔG_{corr} includes a $-T\Delta S$ contribution, and available data[72] indicate that entropic corrections to thermodynamic parameters of spin-state transitions are more sensitive to the quality of the basis set than enthalpic ones.

Aside from the errors of the method and the basis set, one important source of potential discrepancies between experimental and calculated results could be the neglect of intermolecular interactions: we calculated the properties of isolated hemes in the gas phase, because accounting for solvent effects or for periodic solid-state conditions was prohibitively expensive computationally. The energy differences between the spin states of transition-metal complexes are routinely calculated in the gas phase.[36,70,72,73] The transferability of the resultant free energy differences between various spin states of iron(II) complexes to the complexes in condensed phases was analyzed by Casida et al.[36] Computed vibrational spectra (and hence vibrational energy)[72] and values of ΔS for quintet−singlet transitions[32,73] for a number of Fe(II) complexes in singlet and quintet states are in good agreement with the experimental data for crystalline solids. The calculated values of ΔE_{ZPE} for non-porphyrin iron(II) complexes in the quintet and singlet states typically range between 2.5 and 7 kcal/mol,[32,36,70] significantly higher than the ∼−1 kcal/mol of quintet−triplet gaps calculated for 5-coordinate ferrohemes in this work. The lower vibrational energy of states with higher multiplicity is believed to stem from population of metal-based antibonding orbitals.[36,74] There are zero, one, and two such orbitals in the singlet, triplet, and quintet states of Fe(II), accounting for the smaller magnitude of ΔE_{ZPE} in quintet/triplet pairs compared to quintet/singlet pairs.

TABLE 4: Values of ΔE_{el} for [Fe(por)(Im)] Calculated with the B3LYP Functional and Various Basis Sets Using Geometries Optimized at the B3LYP/6-31G Level

Augmented 6-311G Basis Set

diffuse function added	6-311G(d)[a]	6-311G(d,p)[b]	6-311G(2d)	6-311G(2d,2p)
none	0.5	0.5	1.2	1.2
+	0.1	0.2	0.7	0.6
++	0.1	0.2	0.7	0.6

Other Basis Sets

SVP	MVP[c]	TZVP	TZVPP	cc-pVTZ
−0.8	0.1	−0.1	0.3	2.6

[a] Alternative notation for the 6-311G* basis set. [b] Alternative notation for the 6-311G** basis set. [c] Mixed basis set with TZVP on Fe and SVP on other atoms.

Discussion of Basis Set Effects. We observed that calculated structural parameters of the $\mathrm{FeN_5}$ core were significantly more sensitive to basis set augmentation than structural parameters of the rest of the complex (maximum variations of 0.102 Å for $\mathrm{Fe-N_{Im}}$ and 0.007 Å for $\mathrm{C}_\beta-\mathrm{C}_\beta$ bond lengths in ^{5}**1**; β-carbons are defined in Figure 1). Bond lengths between atoms not involving Fe varied uniformly and predictably with augmentation. For example, polarization functions shortened the $\mathrm{C}_\beta-\mathrm{C}_\beta$ bonds by 0.005−0.007 Å, since polarization functions improve the description of orbital overlap, and the bonds elongated by 0.001−0.002 Å upon further addition of diffuse functions, which allow the electron density to localize farther from the nuclei. Fe−N bonds differed in how they were affected by augmentation, seemingly correlating with the character of the highest lying metal-based molecular orbital contributing to the Fe−N bond. The d_{z^2}-orbital is occupied in both states and is antibonding with respect to the $\mathrm{Fe-N_{Im}}$ bond;[26] basis set augmentation lengthened this bond in either spin state. On the other hand, addition of polarization functions shortened the $\mathrm{Fe-N_{por}}$ bond in triplets but elongated it in quintets. This behavior is consistent with the $\mathrm{d}_{x^2-y^2}$-orbital being antibonding with respect to the $\mathrm{Fe-N_{por}}$ bonds[26] and vacant in the triplet state, but occupied in the quintet.

Quintet−Triplet Energy Gaps Calculated with Other Basis Sets. To assess whether relatively large variations in calculated values of ΔE_{el} were caused in part by the small size of the basis sets used, we carried out single-point calculations with the B3LYP functional and various basis sets using geometries of ^{5}**1** and ^{3}**1** optimized at the B3LYP/6-31G level.[75] We used Pople-style 6-311G basis sets augmented up to the 6-311++G(2d,2p) size, Ahlrichs-style basis sets SVP (double-ζ), TZVP and TZVPP (triple-ζ), and Dunning's correlation-consistent cc-pVTZ (triple-ζ) basis set. The Ahlrichs and Dunning basis sets include polarization functions on all atoms. Calculated quintet−triplet electronic energy differences varied from −0.8 to 2.6 kcal/mol (Table 4); the lowest value was obtained with the SVP basis set and the highest with the cc-pVTZ basis set. Ahlrichs-style basis sets predicted gaps lower than those of the Pople-style basis sets. The values of ΔE_{el} calculated with triple-ζ plus polarization basis sets of Table 4 span the range of 2.7 kcal/mol, which is comparable to that obtained with double- and triple-ζ Pople-style basis sets used in full optimizations and computations of vibrational corrections. Recalling that electronic energy gaps calculated with the B3LYP and B3PW91 functionals correlated linearly with the offset of −1.5 kcal/mol, we anticipate positive ΔE_{el} values calculated at the B3PW91/cc-pVTZ level.

Values of ΔE_{el} calculated with Pople-style basis sets (Table 4) increased with increasing number of polarization functions on non-hydrogen atoms and decreased upon augmentation with diffuse functions. The addition of polarization and diffuse functions to basis sets of hydrogen atoms negligibly affected calculated energy differences, which is expected because hydrogen atoms are located on the periphery of the [Fe(por)-Im] complexes.

Changes in the values of ΔE_{el} computed with triple-ζ Ahlrichs basis sets TZVP and TZVPP were seemingly consistent with the trends observed for the Pople-style basis sets if the differences in the augmentation of the basis set on the Fe atom were considered, since there are important differences in the *types* of polarization functions defined in Pople-style and Ahlrichs-style basis sets for the Fe atom. Polarization functions in the TZVP basis set are of the p-type, while TZVPP has both a p-type set and an f-type set. ΔE_{el} computed with TZVPP was larger than that computed with TZVP; i.e., f-type polarization functions added to the Ahlrichs-style basis sets on Fe shifted electronic energy gaps toward the triplet state, as found for Pople-style basis sets.

The p-type polarization set of TZVP and TZVPP[56] is in fact a part of the diffuse set of orbitals for Fe used in Pople-style basis sets[57] (see the Computational Details for details of basis set definitions) and hence is present in all Pople-style basis sets that include a "+" or "++" in their definition. The results of Table 4 indicate that augmentation of Pople-style basis sets with diffuse functions shifted the electronic energy gaps toward the quintet state. This could partially account for the lower values of ΔE_{el} obtained with TZVPP and TZVPP than with the 6-311G-(d,p) and 6-311G(2d,2p) basis sets. These basis sets nominally belong to the same class, triple-ζ with polarization functions on all atoms, but Pople-style basis sets lack the p-type function on Fe that Ahlrichs-style basis sets have. Electronic energy gaps calculated with Pople-style basis sets involving diffuse functions were closer to those of Ahlrichs-style basis sets than in the absence of diffuse functions. For example, ΔE_{el} values calculated with the 6-311+G(d) basis set and TZVPP basis set, both of which include the additional p-type and f-type sets of functions on Fe, were 0.1 and 0.3 kcal/mol, respectively (Table 4). cc-pVTZ, another basis set of triple-ζ quality with polarization functions on all atoms, contains two sets of polarization f-functions and one set of g-functions and yielded the highest value of ΔE_{el} of all basis sets tested.

Behavior of Mixed Basis Sets. The parameters calculated with the M2 basis set (the combination of the 6-311G* set on Fe and the 6-31G* set on the ligands) fell significantly outside the range of values calculated with the other Pople-style basis sets used for structure optimizations with either B3LYP or B3PW91. The M2 basis set gave exceptionally short Fe−Ct distances (Figures 2 and 3, Tables 1 and S3) and the highest values of ΔE_{el} calculated with either functional and Pople-style basis sets for both **1** and **2** (Figure 5, Table 3). In contrast, electronic energy gaps predicted with the M1 basis set lay between those calculated with the 6-31G* and 6-31G sets. The inferior performance of the M2 set compared to all other Pople-style basis sets probably lies in the imbalanced description with too many basis functions on the Fe center compared to other atoms in the complex. As early as the 1960s large imbalanced (many basis functions on one atom, few on the other) basis sets were documented to predict molecular properties of diatomics less accurately than smaller but balanced basis sets did.[76] However, with few exceptions,[77] the problem of basis set balance has not been systematically studied for transition-metal complexes.

To verify whether a similar trend holds for other families of basis sets, we compared ΔE_{el} values from single-point energy calculations with the B3LYP functional in combination with the following Ahlrichs-style basis sets: double-ζ plus polarization (SVP), triple-ζ plus polarization (TZVP), and a mixed basis set (MVP) comprised of TZVP on Fe and SVP on lighter atoms (Table 4). The values of ΔE_{el} obtained with SVP, mixed MVP, and TZVP were −0.8, 0.1, and −0.1 kcal/mol, respectively. This behavior was qualitatively similar to the trend observed with the 6-31G*, M2, and 6-311G* basis sets of Pople et al.: the value of ΔE_{el} obtained with the mixed triple-ζ(Fe)/double-ζ(ligands) basis set was higher than with either a triple-ζ or a double-ζ basis set used on all atoms in the complex, although ΔE_{el} calculated with the MVP basis set was only marginally larger than that calculated with the TZVP basis set.

Using a better quality basis set on the metal center than on the ligands in the transition-metal complex is a common practice[2−4] (the so-called "locally dense basis set" approach). Our findings, however, show that it can worsen rather than improve predictions of spin-state ordering. The anomalous behavior of mixed basis sets with respect to predicted quintet−triplet electronic energy gaps in 5-coordinate iron porphyrins is supported by computations at the CCSD(T) level with correlation-consistent basis sets on complexes $[\mathrm{Fe(NHCHNH)_2(H_2O)}]$ and $[\mathrm{Fe(NH(CH_2)_3NH)^2(H_2O)}]$ reported by Strickland and Harvey in an interesting paper on binding of small ligands to heme.[2] For $[\mathrm{Fe(NHCHNH)_2(H_2O)}]$, values of ΔE_{el} calculated with mixed basis sets cc-pVQZ(Fe)/cc-pVTZ(ligands) and cc-pVTZ(Fe)/cc-pVDZ(ligands) were shifted towards the triplet state by 1.5 and 1.0 kcal/mol, respectively, relative to the value of ΔE_{el} obtained with the uniform cc-pVTZ basis set on the entire complex. Although only $[\mathrm{Fe(NHCHNH)_2(H_2O)}]$ could be studied with basis sets of larger than triple-ζ quality, the authors argued[2] that the variation of the gaps with the basis set was the same for both complexes even though the ΔE_{el} values for the two complexes calculated with a given basis set differed by ∼17.5 kcal/mol. Following this argument, a nonmonotonous behavior of ΔE_{el} calculated with mixed basis sets would be observed for $[\mathrm{Fe(NH(CH_2)_3NH)^2(H_2O)}]$ at the CCSD(T) level as well.

Summary

Our calculations showed that hybrid functionals B3LYP, B3PW91, and B97-1 and the pure functional OLYP predicted near-zero quintet−triplet electronic energy gaps of model heme compounds, while the pure TPSS functional significantly overestimated the stability of the triplet state. Among computed parameters that determine the free energy difference between the two spin states, i.e., enthalpic and entropic corrections and the electronic energy difference, the latter was most sensitive to the basis set. We observed variations of >2 kcal/mol in the values of ΔE_{el} computed with Pople-style basis sets of 6-31G and 6-311G quality with or without polarization and diffuse functions. Both positive and negative values were obtained with the B3LYP and OLYP functionals. Among triple-split-valence plus polarization basis sets of the Pople, Ahlrichs, and Dunning families, ΔE_{el} computed with the B3LYP functional ranged from

−0.1 to 2.6 kcal/mol, indicating that variability of the gaps is not a consequence of the relatively small sizes of the 6-31G, 6-31G*, and 6-31+G* Pople-style basis sets.

ZPE corrections typically stabilized the quintet state by ∼−1 kcal/mol and changed the multiplicity of the electronic ground state predicted from electronic energies alone from triplet to quintet in the case of B3LYP with the 6-31G*, 6-31+G*, 6-311G*, and 6-311+G* basis sets. The effects of symmetry constraints and of replacing imidazole with 2-methylimidazole, which increases the displacement of Fe from the porphyrin plane (so-called tense structure), were within 0.3 kcal/mol. Structural parameters of the FeN_5 core also showed a pronounced basis set dependence, and the best agreement with the experimental values were observed with the 6-31G or 6-31G* basis set. The calculated frequencies of the Fe−Im stretching mode for quintet [Fe(por)(Im)] were overestimated with all basis sets and relatively independent of the choice of the functional (with the exception of OLYP). Agreement with the experimental value, 220 cm^{-1}, systematically improved upon addition of polarization and diffuse functions, to a minimum absolute difference of 5−7 cm^{-1}, but at the same augmentation we observed only negligible differences between the frequencies calculated with the 6-31G and 6-311G families of basis sets. The computed Fe−Im stretching frequency in [Fe(por)(2-MeIm)] was more sensitive to the computational variables than the frequency in [Fe(por)(Im)].

Among the five functionals we tested, only hybrid B3LYP, B3PW91, and B97-1 uniformly predicted the quintet ground state of Fe in [Fe(por)(Im)] or [Fe(por)(2-MeIm)]. Pure and hybrid functionals reproduced the structural parameters of the FeN_5 core at comparable accuracy, with B3PW91 giving the smallest total absolute deviation. Although the OLYP-predicted electronic energy gaps were comparable to those obtained with B3LYP and presented an impressive improvement over those obtained with TPSS, OLYP significantly overestimated the Fe−N_{Im} bond lengths and yielded the smallest differences in zero-point energies of the quintet and triplet states of all functionals.

The following summary may provide guidance in calculating a reliable estimate of the multiplicity of the ground electronic state of new monoimidazole-ligated iron(II) porphyrins by DFT.

(1) Structures can be optimized with a small basis set (e.g., 6-31G*), with symmetry constraints if necessary, followed by the relaxation of the constraints to establish the magnitude of the change in the structural parameters.

(2) Basis set dependence of energy gaps can be tested by single-point energy calculations on these structures using larger basis sets. The resulting values will probably be close (within 0.1 kcal/mol in our tests) to those obtained from more time-consuming full optimization of quintet and triplet states with the larger basis sets.

(3) If the energy gaps are small and favor the lower spin state, ZPE corrections and potentially thermal corrections to enthalpy and entropy must be considered. Zero-point energy differences between the spin states as well as thermal corrections to enthalpy appear to be insensitive to the functional/basis set and can therefore be calculated with a small basis set, significantly decreasing the computational expense. Entropic corrections are more sensitive to the choice of the functional and the basis set and may require basis sets augmented with polarization and diffuse functions for computations.

Two of our findings may be of relevance to computational studies of spin-state energetics of other first-row transition-metal complexes. First, the lowest energy conformations of different spin states may differ in the relative orientation of the ligands and using explicit symmetry constraints may prevent these differences from being explored. Second, a "locally dense" basis set with a significantly larger basis set on the metal than on the ligands (mixed basis set M2) resulted in calculated geometric parameters and quintet−triplet energy gaps that deviated significantly more from the experimental values than those calculated with smaller basis sets (either mixed or uniform). The locally dense basis set approach is often thought to improve the overall description of the complex while minimizing the computational cost associated with larger basis sets, but its applicability for computing spin-state energy gaps must be validated individually for each system in question.

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Supporting Information Available: Tables S1−S8 (selected structural parameters, electronic energies, vibrational zero-point energies, thermal corrections to enthalpy and entropy for optimized structures) and Cartesian coordinates of optimized structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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