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fact that there is no apparent relationship between the site symmetry of the axial ligand (C_{2v} for py vs. $C_{\infty v}$ for CN$^-$) and the global pattern of the MCD spectra.

As the axial field strength increases, the dipole strength of the Q band decreases, as opposed to what was observed in the ZnTPP series. Such a behavior complies with a gradual displacement along the ν axis in the direction of the pivot point ω at a negative angle. The total distance spanned by the present ZnOEP system is calculated to be 6°, which is similar to the $\Delta\nu$ shift in the ZnTPP series. Estimated values of ω range between $-14.5°$ and $-12°$, depending on whether the ν origin is assigned to the uncoordinated ZnOEP or to ZnOEP(py). Corresponding r/R ratios vary between -0.26 and -0.21. These values are comparable to $r/R = -0.173$, which was obtained by Shelnutt from a spectral fit of OEP metalloporphyrins and related metallouroporphyrins.[8] Inserting reasonable values for the moment integrals in eq 21 yields at $\nu = \omega/2$ a minimal $\bar{\mathcal{B}}_0(\mathrm{G} \rightarrow \mathrm{Q})$ value of about $-6 \times 10^{-4}\ \hbar\ \mathrm{D}^2/\mathrm{cm}^{-1}$ (cf. Figure 3). Experimental values turn out to be larger, which again may be due to systematic errors in the extraction of the $\bar{\mathcal{B}}_0$ parameters.

(c) Conclusions. Axial substitution series have been related to small angular distortions around fixed positions in parameter space. The ZnTPP and ZnOEP series have similar $\Delta\nu$ spans but are located in different intervals of the ν axis. Each interval has its own characteristic correlations between the various optical parameters and the average axial field strength. While the ZnOEP data clearly lie in the $[\omega,0]$ interval close to the coordinate origin, the ZnTPP data fall entirely in the normal region at negative ν values. If one assumes similar ω angles for ZnTPP and ZnOEP, ν is found to increase upon replacement of *meso*-phenyl groups by *exo*-alkyl substituents, which is in agreement with the expected influence of ring substituents on the relative positions of the a_{1u} and a_{2u} orbitals[22] (see also section Ib).

As the MCD studies of Djerassi et al. illustrate,[27] complete fluorination[36] of the phenyl substituents in the ZnTPP compounds moves the entire ZnTPP series to the right and into the $[\omega,0]$ interval. The ZnTF$_5$PP thereby reaches an extreme $\bar{\mathcal{B}}_0(\mathrm{G} \rightarrow \mathrm{Q})$ value of $-44 \times 10^{-4}\ \hbar\ \mathrm{D}^2/\mathrm{cm}^{-1}$, which might very well set this compound in the minimum of the $\bar{\mathcal{B}}_0(\mathrm{G} \rightarrow \mathrm{Q})$ well. For $\omega < 0$ axial pyridine or cyanide coordination on ZnTF$_5$PP is expected to drive the system backwards toward the pivot point ω. Extremely low $\bar{\mathcal{D}}_0(\mathrm{G} \rightarrow \mathrm{Q})$ values of only 0.15 D^2 are indeed reported for ZnTF$_5$PP(py) and ZnTF$_5$PP(CN), confirming that these complexes enclose the ω point. Quite remarkably in these cases one also observes[27] inverted $\bar{\mathcal{A}}_1(\mathrm{G} \rightarrow \mathrm{Q})$ terms. Such sign inversion probably originates from specific vibronic intensity mechanisms, which have not been taken into account in the present model, and only show up around the pivot point where the classical dipole mechanisms tend to cancel.

Finally it should be pointed out that while the different location of different ring templates on the ν axis may indeed be related to the effect of the ring substituents on the HOMO splitting, it must be kept in mind that in principle these substituents may also change the moment integrals and the angle ω, thereby changing the position of the anomalous interval itself.

Further studies on analogous HgTPP and HgOEP compounds are currently in progress.

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Registry No. ZnTPP, 14074-80-7; ZnTPP(py), 24389-79-5; ZnTPP(CN), 67820-05-7; ZnOEP, 17632-18-7; ZnOEP(py), 54816-40-9; ZnOEP(CN), 99829-69-3.

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Preferred Orientation of Imidazole Ligands in Metalloporphyrins

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Abstract: Recent work has suggested that axial ligand orientation can affect the physicochemical properties of metalloporphyrins. Analysis of crystallographic data indicates that axial imidazole ligands in metalloporphyrins tend to prefer sterically unfavorable orientations that eclipse equatorial M–N$_\mathrm{p}$ bonds. Charge iterative extended Hückel theory calculations on electronic effects for a broad selection of representative systems indicate a previously unrecognized orientational preference in the M–N(imidazole) π bond which favors eclipsed orientations. Somewhat surprisingly, this π bond is found to be dominated by the metal pπ–imidazole pπ interaction. These theoretical results provide an explanation of the mystery of why the orientation effect seems to be insensitive to metal d^n configuration, spin state, oxidation state, and the presence or absence of a sixth axial ligand.

A number of mechanisms by which physicochemical properties of metalloporphyrins and hemoproteins might be "fine tuned" have been suggested. One of these concerns the orientation of the axial ligands. Geiger et al. have recently suggested[1] that magnetic properties in iron(III) derivatives can depend on the rotational orientation of the axial ligand(s) with respect to the equatorial M–N$_\mathrm{p}$ bonds of the porphyrin. This suggestion was based on the correlation of structure with spin state for two crystalline forms of $[\mathrm{Fe(OEP)((3\text{-}Cl)py)_2}]^+$[2,3] (with radically different electronic states) and the solid-state structure of high-spin $[\mathrm{Fe(OEP)(2\text{-}MeHIm)_2}]^+$.[1] Korszun et al.[4] have suggested that imidazole

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[1] Geiger, D. K.; Lee, Y. J.; Scheidt, W. R. *J. Am. Chem. Soc.* **1984**, *106*, 6336–6343.

[2] (a) Scheidt, W. R.; Geiger, D. K.; Haller, K. J. *J. Am. Chem. Soc.* **1982**, *104*, 495–499. (b) Scheidt, W. R.; Geiger, D. K.; Hayes, R. G.; Lang, G. *J. Am. Chem. Soc.* **1983**, *105*, 2625–2632.

[3] Abbreviations used: Porph, dianion of a generalized porphyrin; P, dianion of porphine; TPP, dianion of *meso*-tetraphenylporphyrin; OEP, dianion of octaethylporphyrin; Proto IX, dianion of protoporphyrin IX; TPivP, dianion of "picket fence" porphyrin; TPyP, dianion of tetra(4-*N*-methylpyridyl)porphine; TPP(Im), dianion of imidazole "tailed" *meso*-tetraphenylporphyrin; Im, generalized imidazole; HIm, imidazole; Im$^-$, imidazolate anion; 1-MeIm, 1-methylimidazole; 2-MeHIm, 2-methylimidazole; 1,2-Me$_2$Im, 1,2-dimethylimidazole; BzIm, benzimidazole; 4-MeHIm$^-$, 4-methylimidazolate; (3-Cl)py, 3-chloropyridine; THT, tetrahydrothiophene.

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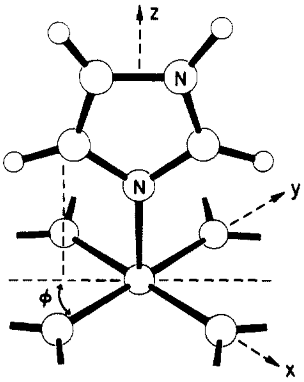

Figure 1. Figure illustrating the definition of the angle ϕ and the coordinate axis system used in the calculations.

orientation is a significant component in the regulation of midpoint potentials of heme proteins. Walker et al.[5] have been studying the possible effects of the relative axial ligand orientation on the EPR and NMR spectra of bis(imidazole)iron(III) porphyrinates as models of the cytochromes *b*. The apparent reality and importance of imidazole ligand orientation effects have led us to examine the factors that might direct such ligand orientations in metalloporphyrin derivatives.

A convenient measure of the orientation of imidazole ligands in metalloporphyrin complexes was introduced by Hoard.[6] He used the dihedral angle ϕ between the imidazole plane and a plane perpendicular to the porphinato core and passing through a porphinato nitrogen atom (Figure 1). A value of $\phi = 0°$ corresponds to the imidazole eclipsing the $M-N_p$ bonds and a value of 45° corresponds to a staggered conformation. Consideration of intramolecular nonbonded interactions between coordinated imidazole and porphinato atoms suggests[6] maximum steric repulsion at $\phi = 0°$ and minimum repulsion at $\phi = 45°$. This observation holds for both sterically hindered and unhindered imidazoles. However, even a casual examination of the orientation data available makes evident that the ϕ values do not tend toward 45° but rather toward smaller values. Hence, either nonbonded intramolecular interactions are insignificant or other factors are also involved in imidazole orientations. That nonbonded effects can play a significant stereochemical role comes from the classic analysis of Hoard et at.[6] They found for the structure of $[Fe(TPP)(HIm)_2]^+$ that the longer of the two $Fe-N_{ax}$ bonds is associated with the imidazole ligand having the smaller ϕ value. Indeed in all cases[7] of species where the two axial imidazoles have different M-N bond lengths, the longer bond is associated with the smaller ϕ value.

Intermolecular interactions (crystal packing effects) might also have an effect on orientation. However, the environments of imidazole ligands in the solid state appear to involve a large variety of nearest-neighbor intermolecular interactions. Thus we believe that the crystal packing effect on imidazole orientation would be random and consequently unimportant in defining a consistent orientational preference.

The imidazole-ligated metalloporphyrin derivatives are conveniently divided into two classes: five-coordinate M(Porph)(Im)[3] derivatives and six-coordinate M(Porph)(Im)(L) complexes, where L is either a second imidazole or another ligand. X-ray structure data for a number of both types are available. The average ϕ value for the five-coordinate complexes[8] is 10.4° with an estimated standard deviation (esd) of 7.3°. (The calculation of esd's gives a measure of the dispersion in the sample.) There are nine independent[9] values available: the maximum ϕ value is 23° and the minimum value is 4°. There are a total of 15 six-coordinate complexes.[10] For the 11 complexes most appropriately considered,[11] there are 14 independent values of the orientation angle. The average ϕ value is 16.2 (10.2) the values range from 1 to 39°. The observations for the two classes encompass complexes with d^4 to d^8 configurations and a variety of spin and oxidation states.

Further strong evidence for preferred orientations comes from the few available examples of duplicate or equivalent structures. The two cobalt(II) complexes, Co(TPP)(1-MeIm)[8e] and Co(OEP)(1-MeIm),[8f] have ϕ values of 4 and 10°, respectively. $[Fe(TPP)(BzIm)_2]^+$ [10d] and $[Fe(OEP)(2\text{-}MeHIm)_2]^+$,[10c] both high-spin ferric species, have $\phi = 10$ and 22°, respectively. Finally, there are three independent measurements of ϕ in the *same* complex, $[Fe(OEP)(2\text{-}MeHIm)]^+$,[8b] in different crystal forms: the three ϕ values are 4, 3, and 7°.

We interpret these data as suggesting that there is a preferred orientation for imidazole ligands: a tendency toward small ϕ values (0 to 20°). These orientation data clearly imply that nonbonded interactions, which should give ϕ's near 45°, are not the dominant factor. In this paper, we explore the remaining important factor likely to affect orientation, namely electronic effects. Theoretical calculations have been used with some success to examine a variety[12,13] of questions about metalloporphyrin electronic structure

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(8) In this footnote and the following one for the six-coordinate species a compound abbreviation is given, followed by the observed orientation angle in parentheses and then the literature citation. (a) [Mn(TPP)(1-MeIm)] (15°): Kirner, J. F.; Reed, C. A.; Scheidt, W. R. *J. Am. Chem. Soc.* **1977**, *99*, 2557–2563. (b) $[Fe(OEP)(2\text{-}MeHIm)]^+$ (4, 3, 7°): Scheidt, W. R.; Geiger, D. K.; Lee, Y. J.; Reed, C. A.; Lang, G. *J. Am. Chem. Soc.* **1985**, *107*, 5693–5699. (c) [Fe(TPP)(2-MeHIm)] (7°): Collman, J. P.; Kim, N.; Hoard, J. L.; Lang, G.; Radanovich, L. J.; Reed, C. A. "Abstracts of Papers", 167th National Meeting of the American Chemical Society, Los Angeles, CA, April 1974; American Chemical Society, Washington, DC.; INOR 29. (d) [Fe(TPivP)(2-MeHIm)] (23°): Jameson, G. B.; Molinaro, F. S.; Ibers, J. A.; Collman, J. P.; Brauman, J. I.; Rose, E.; Suslick, K. *J. Am. Chem. Soc.* **1978**, *102*, 3224–3237. (e) [Co(TPP)(1-MeIm)] (4°): Scheidt, W. R. *J. Am. Chem. Soc.* **1974**, *96*, 90–94. (f) [Co(OEP)(1-MeIm)] (10°): Little, R. G.; Ibers, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 4452–4463. (g) $[Co(TPP)(1,2\text{-}Me_2Im)]$ (20°): Dwyer, P. N.; Madura, P.; Scheidt, W. R. *J. Am. Chem. Soc.* **1974**, *96*, 4815–4819.

(9) An independent value refers to a crystallographically unique determination of ligand orientation; duplicate values required by crystallographic symmetry are not included in the averages.

(10) (a) $[Fe(TPP)(HIm)_2]^+$ (18,39°): ref 6. (b) $[Fe(Proto\ IX)(1\text{-}MeIm)_2]$ (3,16°): ref 7a. (c) $[Fe(OEP)(2\text{-}MeHIm)_2]^+$ (22°): ref 1. (d) $[Fe(TPP)(BzIm)_2]^+$ (10°): Levan, K. R.; Strouse, C. E. "Abstracts of Papers", American Crystallographic Association Summer Meeting, Snowmass, CO, Aug 1–5, 1983; Abstract H1. Levan, K. R.. Ph.D. Thesis, UCLA, 1984. (e) $[Fe(TPP)(2\text{-}MeHIm)_2]^+$ (32,32°): Kirner, J. F.; Hoard, J. L.; Reed, C. A. "Abstracts of Papers", 175th National Meeting of the American Chemical Society, Anaheim, CA, March 13–17, 1978; American Chemical Society: Washington, D.C., 1978; INOR 14. (f) $[Fe(TPP)(4\text{-}MeIm^-)_2]^-$ (1,17°): ref 7b. (g) [Fe(TPP)(NO)(1-MeIm)] (25°): Piciulo, P. L; Scheidt, W. R. *J. Am. Chem. Soc.* **1976**, *98*, 1913–1919. (h) $[Fe(TPivP)(1\text{-}MeIm)(O_2)]$ (20°): Jameson, G. B.; Rodley, G. A.; Robinson, W. T.; Gagne, R. R.; Reed, C. A.; Collman, J. P. *Inorg. Chem.* **1978**, *17*, 850–857. (i) $[Fe(TPivP)(2\text{-}MeHIm)(O_2)]$ (22°): ref 8d. (j) [Fe(TPP)(Im)(THT)] (4°): Mashiko, T.; Reed, C. A.; Kastner, M. E.; Haller, K. J.; Scheidt W. R. *J. Am. Chem. Soc.* **1981**, *103*, 5758–5767. (k) $[Mn(TPP)(Im^-)]_n$ (26,28°): Landrum, J. T.; Hatano, K.; Scheidt, W. R.; Reed, C. A. *J. Am. Chem. Soc.* **1980**, *102*, 6729–6735. (l) $[Ni(TPyP)(HIm)_2]$ (23°): Kirner, J. F.; Garofalo, J., Jr.; Scheidt, W. R. *Inorg. Nucl. Chem. Lett.* **1975**, *11*, 107–112. (m) $[Fe(TPP)(1\text{-}MeIm)_2]$ (10°): Steffen, W. L.; Chun, H. K.; Hoard, J. L.; Reed, C. A. "Abstracts of Papers", 175th National Meeting of the American Chemical Society, Anaheim, CA, March 13–17, 1978; American Chemical Society: Washington, D.C., 1978; INOR 15. (n) $[Mn(TPP)(1\text{-}MeIm)_2]^+$ (19°): *Ibid.* (o) $[Co(TPP)(HIm)_2]^+$ (42,43°): Lauher, J. W.; Ibers, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 4447–4451.

(11) One of the four complexes eliminated is $(Mn(TPP)(Im^-)]_n$, since even fitting the *porphyrin* components in this polymer is a difficult stereochemical challenge. The consequent effect on the imidazole orientation is unknown. In addition, $[Fe(TPivP)(2\text{-}MeHIm)(O_2)]$, $[Co(TPP)(HIm)_2]^+$, and $[Fe(TPP)(2\text{-}MeHIm)_2]^+$ were deleted. These are all of the low-spin complexes having especially difficult steric interactions. Despite this, two of the three still have rather small ϕ values (22. 32°). Inclusion of the angles for these four complexes increases the average ϕ for six-coordinate complexes to 21.2 (12.1)°.

and are the basis for the present study.

We have carried out a series of charge iterative extended Hückel calculations[12] for a number of representative complexes at various orientation angles. Calculations were carried on three five-coordinate systems: $[Fe(P)(2\text{-}MeHIm)]^+$, $[Fe(P)(2\text{-}MeHIm)]$, and $[Co(P)(HIm)]$ which logically represent all known electronic configurations of five-coordinate imidazole complexes. Calculations were also performed for four different six-coordinate $[M(P)(HIm)_2]$ complexes: high-spin d^5 $[Fe(P)(2\text{-}MeHIm)_2]^+$, low-spin d^5 $[Fe(P)(HIm)_2]^+$, low-spin d^6 $[Fe(P)(HIm)_2]$, and high-spin d^8 $[Ni(P)(HIm)_2]$, which encompass all known d^n configurations.[14] Finally $[Fe(P)(CO)(HIm)]$, an observed complex of unknown geometry, was investigated as representative of the several mixed ligand Fe(II) complexes. We thus note that the eight calculated species represent the entire set of imidazole complexes of known geometry. The porphine nucleus, rather than various substituted porphyrins, was used for computational efficiency and was considered to be the smallest reasonable model of the full complexes.

Results of the theoretical calculations are interpreted in terms of a weak π interaction between imidazole and metal, the magnitude of which is orientationally dependent and favors ϕ values near 0°. Somewhat surprisingly, this π bond is found to be dominated by the metal $p\pi$–imidazole $p\pi$ interaction. This explains why the orientation effect appears to be insensitive to metal d^n configuration. The observed orientations are the result of the competition between the π bonding and steric interaction. We envision that the two effects are energetically of comparable magnitude and thus lead to a total rotational potential function that varies modestly with orientation angle with a minimum generally occurring at small ϕ values.

Although this work focuses on imidazole complexes, similar conclusions may pertain to pyridine complexes as well. A survey of known pyridine adducts shows an average ϕ value of 17.9 (14.8)° for five-coordinate species and an average value of 28.5 (14.2)° for the six-coordinate derivatives. There is thus a preference toward small ϕ values even though it is expected that the nonbonded interactions leading to ϕ values near 45° are more pronounced for the pyridine derivatives.

Results and Discussion

Electronic effects were first explored by charge iterative extended Hückel (IEH) calculations on five-coordinate high-spin d^5 $[Fe(P)(2\text{-}MeHIm)]^+$ and d^6 $[Fe(P)(2\text{-}MeHIm)]$ and low-spin d^7 $[Co(P)(HIm)]$ as a function of ligand rotation angle. These three complexes were chosen as known examples of complexes having a partially filled $d\pi$ shell and a filled $d\pi$ shell, respectively. All sets of calculations started with $\phi = 4°$ (at or near the experimental geometry) and were followed by a series of 10° rotations of the ligand plane[15] around the $M\text{–}N_{ax}$ bond to ϕ of 44°. The expected periodicity (fourfold symmetry) was verified by extending the computations to $\phi < 0$ and $> 45°$. For all systems, the porphyrin frontier molecular orbital energy levels are essentially independent of the rotation. The energies of the MOs which are predominantly metal d in character show a small decrease in stability with increasing ϕ. The change in stability, however, similarly affects all d orbitals. In particular, no significant differentiation of the d_{xz} and d_{yz} orbital energies as a function of the rotation was observed.[16]

Table I. Orbital–Orbital Overlap Populations as a Function of Rotation Angle for Five-Coordinate Complexes

type	rotation, deg 4	14	24	34	44
High-Spin d^5 $[Fe(P)(2\text{-}MeHIm)]^+$					
Fe $p\pi$–Im $p\pi$	0.012	0.009	0.005	0.001	0.000
Fe $d\pi$–Im $p\pi$	0.005	0.004	0.003	0.002	0.001
High-Spin d^6 $[Fe(P)(2\text{-}MeHIm)]$					
Fe $p\pi$–Im $p\pi$	0.008	0.006	0.003	0.000	−0.001
Fe $d\pi$–Im $p\pi$	0.004	0.003	0.002	0.001	0.001
Low-Spin d^7 $[Co(P)(HIm)]$					
Co $p\pi$–Im $p\pi$	0.004	0.002	0.000	−0.002	−0.003
Co $d\pi$–Im $p\pi$	0.001	0.000	0.000	0.000	0.000
Low-Spin d^6 $[Fe(P)(CO)]$					
Fe $p\pi$–C $p\pi^a$	0.025				
Fe $d\pi$–C$p\pi^a$	0.073				
Low-Spin d^5 $[Fe(P)(CN)_2]^-$					
Fe $p\pi$–C $p\pi^a$	0.002				
Fe $d\pi$–C $p\pi^a$	0.008				

[a] For comparison only the p_x or d_{xz} component is given; there is, of course, a degenerate p_y or d_{yz} component.

It is widely recognized that the IEH method often gives a poor description of energetics but is frequently used successfully to monitor changes in charge distribution.[17] Consequently, we use the method only to examine trends in overlap populations. These provide a much clearer and more detailed picture of the bonding interactions of interest.

The most significant variation in bonding parameters, as a function of the rotation, is found for the metal π–imidazole π interactions.[18] The results are summarized in Table I. It is seen that the metal–imidazole π bond is stabilizing at small angles and becomes negligible or destabilizing at large angles. For the iron(II) and iron (III) complexes, the effect is seen in the Fe $p\pi$ and, to a lesser extent, in the Fe $d\pi$ interactions. The cobalt(II) species, with completely filled $d\pi$ orbitals, still shows a significant angular effect for the Co $p\pi$–imidazole π interaction, but not for Co $d\pi$. For all species, the σ interaction between metal and axial ligand is independent of ligand orientation as would be expected.

For comparison, orbital–orbital overlap populations were calculated in two metalloporphyrin complexes for which significant π bonding to the axial ligand is expected. The complexes chosen are five-coordinate Fe(P)(CO), whose structure is unknown, and $[Fe(P)(CN)_2]^-$, whose structure is known.[19] Fe(P)(CO) should represent a species with maximum π interaction and $[Fe(P)(CN)_2]^-$ a species with smaller but still significant π interactions. These expectations are indeed found in the overlap populations given in Table I. Quantitative comparison of the overlap populations of the reference complexes and the imidazole-ligated species support the reality of π interaction between metal and imidazole. One difference seen is in the relative magnitudes of the p and d contributions to the π bond in the imidazole complexes and the CO and cyanide reference species. These differences are wholly consistent with the expectation that imidazole is a good π donor while the reference ligands are π acceptors.

The question of preferred orientations in six-coordinate species was examined by a series of calculations on high-spin $[Fe(P)(2\text{-}MeHIm)_2]^+$ [10c] and $[Ni(P)(HIm)_2]$[10l] and low-spin $[Fe(P)(HIm)_2]$[10m] and $[Fe(P)(HIm)_2]^+$,[10a] which were chosen as known

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(12) (a) Zerner, M.; Gouterman, M. *Theor. Chim. Acta* **1966**, *4*, 44–63. (b) Antipas, A.; Buchler, J. W.; Gouterman, M.; Smith, P. D. *J. Am. Chem. Soc.* **1978**, *100*, 3015–3024.

(13) (a) Tatsumi, K.; Hoffman, R. *J. Am. Chem. Soc.* **1981**, *103*, 3328–3341. (b) Hanson, L. K.; Hoffman, B. M. *J. Am. Chem. Soc.* **1980**, *102*, 4602–4609. (c) Spangler, D.; Maggoria, G. M.; Shipman, L. L.; Christoffersen, R. E. *J. Am. Chem. Soc.* **1977**, *99*, 7478–7489. (d) Loew, G. H.; Kirchner, R. F. *Biophys. J.* **1978**, *22*, 179–189. (e) Dadieu, A.; Rohmer, M.-M.; Veillard, A. *Adv. Quantum Chem* **1982**, *16*, 43–97.

(14) The high-spin d^4 Mn(III) case should be electronically similar to the high-spin d^5 Fe(III) case since they differ only in the occupancy of the relatively inert $d_{x^2-y^2}$ orbital.

(15) The porphinato core geometry was held fixed since it is expected that the $M\text{–}N_p$ bond distances will not change if the spin state remains constant. Some small variation in porphinato core conformation might occur in response to nonbonded repulsion between the axial ligand and core atoms. These are expected to be small since these contacts remain near the sum of van der Waals radii for all rotations.

(16) For all five-coordinate complexes, the total energies typically vary by a few tenths of an electron volt as the imidazole ring rotates. The minimum occurs at small angles. Similar trends are shown for d orbital energies.

(17) (a) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397–1412. (b) Nelson, J. H.; Wheelock, K. S.; Cusachs, L. C.; Jonassen, H. B. *Inorg. Chem.* **1972**, *11*, 422–424.

(18) The metal orbitals with π symmetry toward the axial ligand are d_{xz} and p_x at $\phi = 0$, with d_{yz} and p_y mixing in at nonzero angles.

(19) Scheidt, W. R.; Haller, K. J.; Hatano, K. *J. Am. Chem. Soc.* **1980**, *102*, 3017–3021.

Table II. Orbital–Orbital Overlap Populations as a Function of Rotation Angle for Six-Coordinate Complexes

type	rotation, deg				
	0	11	22	33	45
High-Spin d^5 $[Fe(P)(2\text{-}MeHIm)_2]^+$					
Fe $p\pi$–Im $p\pi$	0.004	0.003	0.001	−0.001	−0.001
Fe $d\pi$–Im $p\pi$	0.000	0.000	0.001	0.001	0.001
High-Spin d^8 $[Ni(P)(HIm)_2]$					
Ni $p\pi$–Im $p\pi$	0.002	0.002	0.000	−0.001	−0.002
Ni $d\pi$–Im $p\pi$	0.000	0.000	0.000	0.000	0.000
type	rotation, deg				
	0	10	20	30	40
Low-Spin d^6 $[Fe(P)(HIm)_2]$					
Fe $p\pi$–Im $p\pi$	0.002	0.001	0.001	−0.004	−0.006
Fe $d\pi$–Im $p\pi$	0.002	0.002	0.001	0.000	−0.001
Low-Spin d^5 $[Fe(P)(HIm)_2]^+$					
(a) Rings $\parallel$, d_{xz} Hole Is $\perp$ to Rings[a]					
Fe $p\pi$–Im $p\pi$	0.005	0.004	0.001	−0.002	−0.005
Fe $d\pi$–Im $p\pi$	0.003	0.003	0.002	0.001	0.000
(b) Rings $\parallel$. d_{yz} Hole Is $\parallel$ to Rings[a]					
Fe $p\pi$–Im $p\pi$	0.005	0.004	0.001	−0.002	−0.005
Fe $d\pi$–Im $p\pi$	0.001	0.001	0.000	0.000	0.000
(c) Rings $\perp$, d_{yz} Hole $\parallel$ to Ring 1 and $\perp$ to Ring 2[a]					
Fe $p\pi$–Im^1 $p\pi$	0.005	0.004	0.001	−0.002	−0.005
Fe $d\pi$–Im^1 $p\pi$	0.001	0.001	0.000	−0.000	−0.001
Fe $p\pi$–Im^2 $p\pi$	0.005	0.003	0.001	−0.002	−0.005
Fe $d\pi$–Im^2 $p\pi$	0.003	0.003	0.003	0.002	0.002
Low-Spin d^6 $[Fe(P)(CO)(HIm)]$					
Fe $p\pi$–Im $p\pi$	0.003	0.002	−0.001	−0.003	−0.005
Fe $d\pi$–Im $p\pi$	0.002	0.001	0.001	−0.000	−0.001
Fe $p\pi$–C $p\pi$[b]	0.017	0.017	0.017	0.017	0.017
Fe $d\pi$–C $p\pi$[b]	0.056	0.056	0.056	0.056	0.056

[a] At $\phi = 0$. [b] For comparison only the p_x or d_{xz} component is given.

examples of complexes with partially and completely filled $d\pi$ shells. Calculations were performed for the observed orientation and other orientations between 0 and 45°. Most of the bis(imidazole) complexes either have required inversion centers or close approximations to inversion centers in the solid state. Hence, in the initial set of rotational calculations, the two imidazole ligands were required to retain an inversion center relationship (parallel orientation). In a second set of calculations, the two imidazole planes were required to have a constant dihedral angle of 90° (perpendicular orientation). In either system a rotational dependence of π overlap was found that favors small ϕ values. The overlap populations are summarized in Table II. Except for the low-spin iron(III) system which is described in more detail below, the overlap populations between metal and the two axial imidazole ligands are essentially identical irrespective of whether the imidazole planes are coplanar or perpendicular. Our calculations thus suggest that except for the low-spin iron(III) complexes and electronically similar systems[20] there is no significant electronic preference for coplanar vs. perpendicular orientations of the two imidazole planes. However, in all cases, the preference for small ϕ values remains.[21] As in the five-coordinate cases, the metal-ligand π interaction will be counteracted by steric effects favoring larger ϕ values. Because of the smaller nonbonded contact distances involved, we expect that the magnitude of the steric interaction is somewhat larger than in the five-coordinate systems. Thus, the energetic preference for a particular ligand orientation is likely to be less pronounced, especially in low-spin six-coordinate derivatives. This is consistent with the larger range of values and the larger average value of ϕ observed for the six-coordinate species.

Table III. Orbital–Orbital Overlap Populations as a Function of Rotation Angle in $[Fe(P)(2\text{-}MeHIm)]^+$ and the Related Model Complex $[Fe(NH_2)_4(2\text{-}MeHIm)]^-$

type	rotation, deg				
	4	14	24	34	44
$[Fe(P)(2\text{-}MeHIm)]^+$					
Fe $p\pi$–Im $p\pi$	0.012	0.009	0.005	0.001	0.000
Fe $d\pi$–Im $p\pi$	0.005	0.004	0.003	0.002	0.001
$[Fe(NH_2)_4(2\text{-}MeHIm)]^-$					
Fe $p\pi$–Im $p\pi$	0.004	0.003	0.000	−0.003	−0.004
Fe $d\pi$–Im $p\pi$	0.002	0.001	0.000	0.000	−0.001

The low-spin iron(III) system represents a unique case: these are the only known imidazole derivatives in which the two $d\pi$ orbitals are not equally populated. For this species there is, in principle, a distinction as to which $d\pi$ orbital contains the hole: d_{xz} or d_{yz}. Three possible combinations of geometry and electronic configuration were examined. As can be seen from an examination of the relevant portion of Table II, the Fe $p\pi$–Im $p\pi$ interactions are the same for all three combinations and show the ϕ dependence common to the other d^n systems. The magnitude of the Fe $d\pi$–Im $p\pi$ interaction does depend on the orientation of the imidazole rings with respect to the hole: having the ring(s) perpendicular to the hole leads to a larger $d\pi$ overlap population, especially at smaller ϕ values. The differences in Fe $d\pi$–Im $p\pi$ overlaps as a function of the relative orientation of the electron hole with the imidazole ring(s) are in complete agreement with that expected for π-donation from the imidazole ligand. The calculations for the low-spin d^5 bis(imidazole) complexes thus lead to two geometric predictions: both parallel imidazole rings and small ϕ values appear to be favored.

A final set of rotational calculations were performed for the molecule [Fe(P)(CO)(HIm)] (whose detailed molecular structure is unknown) to evaluate the effect of a strong trans π-bonding ligand on the Fe–imidazole π bond. Again the π interaction shows a strong rotational preference as shown in Table II. The decrease in the Fe–CO interaction in the six-coordinate species, compared to the five-coordinate complex, is a natural consequence of the increased Fe–C bond distance.

Near the end of our study, we became aware of a similar investigation by Veillard and co-workers,[22] who have reached somewhat different conclusions. Veillard et al. calculated the total ab initio energy for the model system $[Fe(NH_2)_4(HIm)]^{2-}$ in two spin states ($S = 0$ and $S = 2$) at 0 and 45°. They find very small differences in the total energy for the two orientations and conclude that "electronic factors do not appreciably favor one conformation over the other". We have repeated our calculation for $[Fe(P)(2\text{-}MeHIm)]^+$ using (as did Veillard et al.) four NH_2^- units as an approximation for the porphyrin ligand, i.e., $[Fe(NH_2)_4(2\text{-}MeHIm)]^-$, with rotations. We find that this model displays smaller π overlaps at all angles (Table III) than the corresponding full porphyrin molecule. This may explain why Veillard et al. appear to find a smaller effect of ligand rotation.

Concluding Remarks. The calculations reported herein show an electronic factor that favors small ϕ angles in imidazole-ligated metalloporphyrins, namely ϕ-dependent π-bonding. These results have several important general consequences. The fact that the metal $p\pi$–imidazole $p\pi$ interaction is larger than the metal $d\pi$–imidazole $p\pi$ is significant since the metal p orbital directions are fixed by their strong σ interaction with the phorphinato core. This leads to the conclusion that preferred ligand orientations will be largely independent of the d^n configuration, the oxidation state, and the spin state of the metal in the metalloporphyrin. They also suggest that there will be a preferred imidazole orientation irrespective of the presence or nature of a (trans) sixth ligand. All of these conclusions are in fact borne out by the current

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(20) A distinction appears possible for any complex having a metal with nonequally populated $p\pi$ or $d\pi$ orbitals.

(21) As in the five-coordinate case, the total energies for the six-coordinate species generally show a minimum at small angles. The exceptions are two low-spin systems where the energy is effectively constant as a function of ligand rotation and one which shows a minimum at high angle. However, as noted earlier,[17] the total energy is less useful than the overlap populations in the present context.

(22) Rohmer, M.-M.; Strich. A.; Veillard, A. *Theor. Chim. Acta* **1984**, *65*, 219–231.

experimental observations. Structure determinations of selected metalloporphyrins to further test these ideas are contemplated.

Computational Details

Calculations were carried out with the charge iterative extended Hückel method[12a] with standard atomic parameters.[12b] Initial coordinates for [Fe(P)(2-MeHIm)], [Fe(P)(2-MeHIm)]$^+$, [Co(P)(HIm)], [Fe(P)(2-MeHIm)$_2$]$^+$, [Fe(P)(HIm)$_2$], [Fe(P)(HIm)$_2$]$^+$, [Ni(P)(HIm)$_2$], and [Fe(P)(CN)$_2$]$^-$ were taken from their respective crystallographic structure determinations and transformed to the coordinate system shown in Figure 1. Peripheral groups of the porphyrins were replaced by hydrogen atoms with idealized C–H distances of 1.08 Å. All other C–H bond lengths were also idealized. Ligand rotations were made around the axial M–N(Im) bond and no additional idealization of geometry was imposed. For [Fe(P)(CO)], whose structure is unknown, a Fe–C bond distance[23] of 1.70 Å and an out-of-plane displacement of the iron atom of 0.21 Å was assumed. For [Fe(P)(CO)(HIm)], a planar porphyrin core, an in-plane iron atom and Fe–C and Fe–N(HIm) distances of 1.77 and 2.01 Å were assumed. For the [Fe(NH$_2$)$_4$(2-MeHIm)]$^-$ model calculation, H atoms were placed 1.02 Å along the N–C bonds of [Fe(P)(2-MeHIm)]$^+$. A reviewer has asked about the convergence of the calculations. The default criterion for convergence was to stop the calculation when all atomic charges change by less than 0.010 from one iteration to the next. Some exploratory calculations with a more strigent criterion of 0.005 showed that the reported overlap populations are indeed well converged.

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[23] This distance was estimated from the known structure of [Fe(OEP)(CS)] and discussion found in the following: Scheidt, W. R.; Geiger, D. K. *Inorg. Chem.* **1982**, *21*, 1208-1211.

Coordination Chemistry of Cyclamphosphorane. Access to Transition-Metal Cyclamphosphoranides. Crystal and Molecular Structure of CpMo(CO)$_2$(cyclamphosphoranide)

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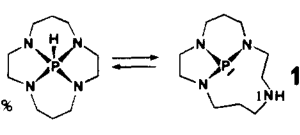
Abstract: In solution, cyclamphosphorane **1a** is in equilibrium with ca. 20% of the open cyclamphosphine form **1b**. This equilibrium can be shifted under the action of transition-metal derivatives to yield adducts of **1b**. Three situations were encountered: (i) With Fe(NO)$_2$(CO)$_2$, only phosphorus-bound adducts were formed; both Fe(NO)$_2$(CO)(**1b**) and Fe(NO)$_2$(**1b**)$_2$ were isolated. (ii) The phosphorus- and nitrogen-bound chelates **6** were obtained under the action of [Rh(CO)$_2$Cl]$_2$. (iii) With CpM(CO)$_3$Cl, a more complex situation was found: with M = W, one CO was substituted to yield a mixture of diastereoisomeric neutral P-bound cis adducts, **8**; under the action of NaBPh$_4$, the NH site quantitatively displaced the chloride ion to give a mixture of phosphorus- and nitrogen-bound diastereoisomeric salts, **10**; when M = Mo, the reaction yielded a 3:1 mixture of the neutral P-bound only and of the ionic P- and N-bound diastereoisomers; this mixture can also be quantitatively converted to the ionic diastereoisomeric chelates, **9**. Complexes **3** and **4**, which formally contain the cyclamphosphoranide ligand **13**, i.e., a 10-electron valence-shell, monoanionic, 4-coordinated phosphorus(III) species, were isolated in over 90% yields from the reaction of the cationic chelates **9** and **10** after abstraction of the N-borne proton by LiMe. Only one diastereoisomer (an enantiomeric pair) appears to form. The phosphoranides could not be obtained directly from LiMe and the neutral adducts **7a** or **8**, in which the NH site is not coordinated. The phosphoranides are thermally fairly stable (dec 150 and 200 °C) and only moderately air-sensitive. They are characterized by high-field ^{31}P chemical shifts, ca. 173 ppm upfield from those of their precursors **9** and **10**. Adduct **3**, (C$_5$H$_5$)Mo(CO)$_2$(C$_{10}$H$_{20}$N$_4$P), crystallized in the monoclinic space group $P2_1/n$ with a = 13.736 (1) Å, b = 9.354 (2) Å, c = 15.577 (2) Å, β = 113.05 (1)°, and Z = 4. Its most notable features are the 5-connected character (i.e., phosphoranide nature of the metal-bound phosphorus atom, with a short (2.44 Å) Mo–P bond), the coordination of a P-bound nitrogen atom to the same molybdenum (2.22 Å) to form a $\overset{M}{\text{P—N}}$ cycle, the long P–N bond within this cycle (1.85 Å) contrasting with the shortness of the other apical P–N bond (1.70 Å), which compares in length with the equatorial P–N bonds (1.67 and 1.70 Å), the close to planar configuration of the uncoordinated apical nitrogen atom, the close to bipyramidal arrangement of bonds around phosphorus in spite of the five cycles to which this phosphorus belongs, and the unusual "negative" distortion of this bipyramid on Berry's ideal trigonal-bipyramid/square-pyramid low-energy path.

Cyclamphosphorane **1a**[2] has many interesting features, among which are its polycyclic structure and its equilibrium with an open tautomeric form, **1b**, in solution (eq A). We reported recently



1a 80% **1b** 20%

that both the phosphorane form, **1a**, and the open phosphine form, **1b**, can exhibit bidentate behavior in the presence of diborane.[3] In the first case, **2a**, two BH$_3$ groups are coordinated on the two apical nitrogen atoms of the bipyramidal phosphorus center, while in the second case, **2b**, the BH$_3$ groups are linked one to the phosphine and the other to the secondary amine sites. The two adducts form simultaneously; then the first slowly converts to the second in the solution. We also briefly reported on the possibility of coordinating transition metals *across* a P–N bond of the closed cyclamphosphorane as in **3** and **4**.[4] It was therefore interesting

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