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Conformational preferences of the axial ligands in some metalloporphyrins. A theoretical study

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The conformational preferences of the axial ligands have been determined for several metalloporphyrins MPL and MPLL′ (M = Mo, Fe; P = porphine dianion; L and L′ being the axial ligands). For $MoP(C_2H_2)$ a qualitative analysis indicates that the conformation with the acetylenic bond eclipsing two Mo–N bonds will be favored. *Ab initio* SCF calculations indicate that:

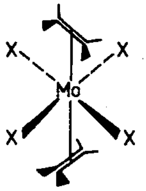
(i) iron porphyrins with an axial imidazole ligand show a flat potential energy curve for the rotation of the imidazole ligand;
(ii) iron porphyrins with a dioxygen ligand prefer the staggered conformation with the O–O bond projecting along the bisectors of the Fe–N bonds;
(iii) in the *cis*-dinitrosyl molybdenum porphyrin, the nitrosyl ligands should be eclipsed with respect to the $Mo–N_{pyr}$ bonds.

These theoretical predictions are compared with the experimental structures from the literature.

Key words: Conformation—metalloporphyrins.

1. Introduction

As part of our theoretical studies of the conformational preferences of organometallic molecules [1], we have previously studied the stereochemistry of *trans*-$MoX_4(C_2H_4)_2$ and $MoX_4(O_2)_2$ complexes [2]. Our prediction that the most stable conformation for $Mo(PH_3)_4(C_2H_4)_2$ and $Mo(CO)_4(C_2H_4)_2$ has the two ethylene ligands mutually perpendicular and eclipsing the equatorial bonds Mo–X



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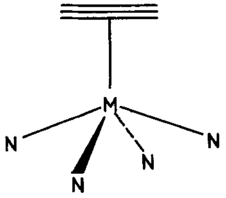
as in **1** was corroborated by the X-ray crystal structures reported later for the analogous systems *trans*-[$W(H_2CCHR)_2(CO)_4$] [3] and *trans*-[$Mo(C_2H_4)_2(PMe_3)_4$] [4]. In another d^6 complex $RuCl_2(CO)(C_2H_4)(PMe_2Ph)_2$ the ethylene ligand was found to eclipse the Ru–P bonds [5]. The orientation of the ethylene ligand in these systems is one feature of the sterochemistry of the hexacoordinate MX_4L_2 or MX_4LL' and five-coordinate MX_4L systems, when the ligands L and L′ lack the axial symmetry relatively to the coordination axis. Another example includes the stereochemistry of the oxygen adducts of the metalloporphyrins MPO_2 (P porphine dianion) which has been studied theoretically for the side-on and end-on coordination of dioxygen [6]. Here we report a theoretical study of the stereochemistry of several metalloporphyrins with various axial ligands: (i) an acetylene molecule as in **2**; (ii) an heterocyclic ligand such as the imidazole or pyridine molecules as in **3**; (iii) a dioxygen ligand coordinated end-on with different groups as the sixth ligand, as in **4**; (iv) two nitrosyl ligands cis to each other and on the same side of the macrocycle as in **5**. Our theoretical approach will be based either on a qualitative analysis of the metal–ligand interactions or on *ab initio* SCF calculations.



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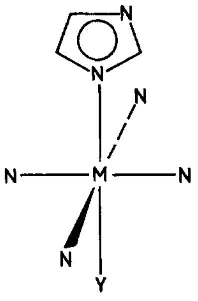

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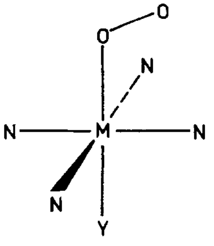

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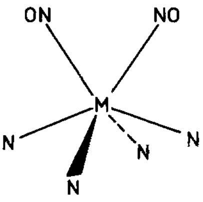

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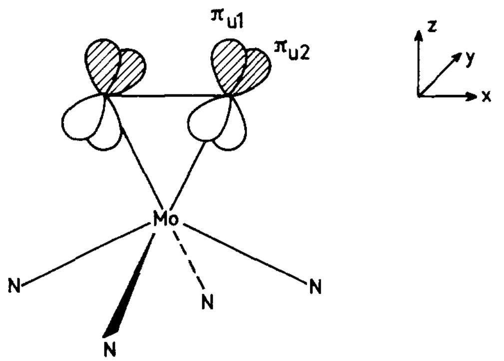
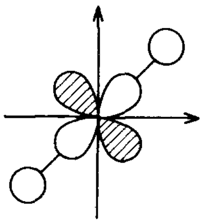


Fig. 1. The orbitals π_{u1} and π_{u2} of the acetylene ligand in $MoPC_2H_2$

2. The stereochemistry of $MoP(C_2H_2)$

Weiss et al. have reported the structure of a π-bonded diphenylacetylene adduct of a molybdenum(II)porphyrin [7]. In this system Mo(TTP)(PhC_2Ph), the acetylenic carbon-carbon bond eclipses two opposite Mo–N bonds. In the original paper [7], a qualitative analysis of the electronic structure was presented for this complex, which was assigned the ground state configuration $(xy)^2(xz)^2$ with the choice of axis of Fig. 1. This has been confirmed by extended Hückel calculations [8]. However no rationale has been given for the eclipsed conformation of the acetylene ligand.

A qualitative analysis of the metal-ligand interactions indicates that the eclipsed conformation should be more stable than the staggered one. To do this, one only needs to consider the differential effect of the interactions between the metal d_{xy} and $d_{x^2-y^2}$ orbitals and the ligand π_{u1} and π_{u2} (bonding), π_{g1} and π_{g2} (antibonding orbitals (Fig. 1) (one does not need to consider the interactions with the metal orbitals d_{z^2}, d_{xz} and d_{yz} since it is easily shown that their differential effect for the two conformations will be zero). Then one finds that the only non-zero interactions are a four-electron (4e) destabilizing interaction d_{xy}/π_{u1} **6** for the staggered conformation versus a pair of two-electron (2*e*) stabilizing interactions $d_{x^2-y^2}/\pi_{u1}$ **7** and d_{xy}/π_{g2} **8** in the eclipsed conformation (see Ref. 8 for a detailed interaction diagram for this conformation). Thus the net balance of the metal–ligand interactions favors the eclipsed conformation, in agreement with the experimental structure.



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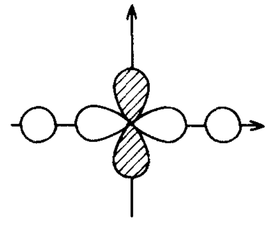

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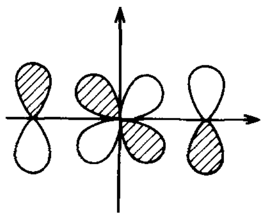

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This conclusion is valid for a d^4 system. For a closed-shell d^2 system we expect that the orbital d_{xy} will be empty, so that the only non-zero interactions will be a $2e$ stabilizing interaction d_{xy}/π_{u1} for the staggered conformation versus a $2e$ stabilizing interaction $d_{x^2-y^2}/\pi_{u1}$ for the eclipsed conformation. The first one should be larger (since the energy gap between d_{xy} and π_{u1} should be smaller than it is between $d_{x^2-y^2}$ and π_{u1}) and we predict that the staggered conformation will be slightly favored.

3. The stereochemistry of metal porphyrins with an axial imidazole ligand

Many structures of metalloporphyrins have been reported with an axial imidazole ligand, either five-coordinate MPIm or six-coordinate MPImL. In Table 1 we have summarized the values of the dihedral angle φ between the imidazole plane and a plane passing through the four-fold axis of the porphyrin and containing one pyrrole nitrogen (Fig. 2). $\varphi = 0°$ corresponds to the eclipsed conformation and $\varphi = 45°$ to the staggered conformation (which minimizes the steric interactions

Table 1. Experimental values of the dihedral angle φ as defined in Fig. 2

Porphyrin	φ	Contact (in Å)[a]	Reference
Co(1-MeIm)(TPP)	0°	2.62	10
Fe(1-MeIm)$_2$(PP–IX)	3°, 16°	2.5–2.6	11
Fe(C5Im)(TPP)(THT)	4°	2.55	12
[Fe(Im)$_2$(OEP)]$^+$	7°	2.34, 2.45	13
Fe(2-MeIm)(TPP)	7°		22
Fe(1-MeIm)$_2$(TPP)	10°, 10°		20
Co(1-MeIm)(OEP)	10°	2.8	14
Mn(1-MeIm)(TPP)	15°	>2.94	15
[Fe(Im)$_2$(TPP)]$^+$	18°, 39°	2.56	16
Fe(1-MeIm)(TpivPP)(O$_2$)	20°		21
Co(1,2-diMeIm)(TPP)	20°	2.57	17
Fe(2-MeIm)(TpivPP)(O$_2$)	22°		22
Fe(2-MeIm)(TpivPP)	23°		22
Fe(1-MeIm)(TPP)(NO)	25°		18
[Co(Im)$_2$(TPP)]$^+$	42°, 43°	2.57	19
Oxymb	~0°		23
Ferrocytochrome *c*	47°		24
Ferricytochrome *c*	51°		24

[a] Contact between the ligand and the atoms of the core.

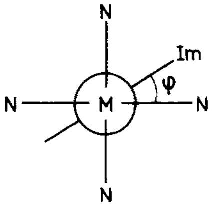


Fig. 2. The dihedral angle φ

between the hydrogen atoms of the imidazole ligand with the porphinato nitrogen atoms [9]). Experimental values of φ in Table 1 appear to be spread over the entire range 0°–45°, their density being somewhat higher in the range 0° to 25° (despite the fact that this usually leads to contacts in the range 2.5–2.6 Å which are well below the normal packing distance of 2.90 Å[16]). For this reason it has been stated in the literature that "the frequency of this alignment (of the two planes defining φ) suggests electronic considerations may be an important factor" [12]. Let us quote another statement from the literature: "It is not clear whether intramolecular or intermolecular packing forces or other factors predominate in determining the value of the orientation parameter φ for imidazole ligands" [18]. This has led us to study this problem at the molecular level, in other words we address the question of the preferred orientation of the imidazole ligand for an isolated molecule.

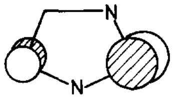
An *ab initio* SCF calculation [25] has been carried out for the model system $Fe(NH_2)_4Im$ (related models have been used previously by others [26, 27] and their merits and shortcomings have been discussed [26, 28]). The energy values of the two conformations, eclipsed and staggered, are reported in Table 2 for two different electronic configurations, the first one low-spin ($S = 0$) and the other one high-spin ($S = 2$). For the low-spin configuration, the energy is practically the same for the two conformations. For the high-spin configuration, the eclipsed conformation is hardly more stable, by less than one kcal/mole. This is at first surprising, since the eclipsed conformation has two short contacts of 2.52 Å and 2.58 Å (partly due to the fact that the iron atom sits in the plane of the NH_2 groups) while the contacts are much longer, 2.97 and 3.03 Å, for the staggered conformation. Anyway, our theoretical results are in good agreement with the experimental data of Table 1 for the following points: (i) the dispersion of the experimental values of the angle φ between 0° and 45° is certainly related to the shallow character of the potential energy surface as a function of the rotation angle; (ii) the short contacts in the range 2.5–2.6 Å which are found in a number of experimental structures corresponding to small values of φ do not lead to any significant destabilization of these conformations.

Why is the potential energy curve as flat as a function of the rotation angle? Let us consider the case of a low-spin ($S = 0$) Fe(II) porphyrin with the electronic configuration $d_{xy}^2 d_{xz}^2 d_{yz}^2$. The only metal-ligand interactions to be considered are those involving the π orbitals of the imidazole ligand and the d_{xy} and $d_{x^2-y^2}$ orbitals of the iron atom (since the orbital d_{z^2} and the pair of orbitals d_{xz} and

Table 2. Total energy (in a.u.) for the staggered and eclipsed conformations of $Fe(NH_2)_4(Im)$

Electronic configuration	Conformation	
	staggered	eclipsed
$(xy)^2(xz)^2(yz)^2 \quad S = 0$	−1708.80408	−1708.80410
$(yz)^2(xy)^1(xz)^1(z^2)^1(x^2-y^2)^1 \quad S = 2$	−1708.89385	−1708.89473

d_{yz} have the axial symmetry relatively to the rotation axis). Among the π orbitals of the imidazole group we need to consider only the components on the C_α carbons since (i) the π component on the coordinating nitrogen will have a zero interaction by symmetry with d_{xy} and $d_{x^2-y^2}$; (ii) the C_β and N_β atoms are further away from the iron atom and will give much smaller contributions because of the overlap factor in the interaction term [29]. Furthermore we shall restrict our analysis to the HOMO and LUMO π orbitals of imidazole (because of the energy denominator in the interaction term), respectively **9** and **10**. Then the only non-zero metal-ligand interactions will be:



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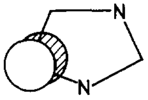

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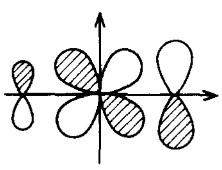
(i) for the eclipsed conformation (with the imidazole ligand in the xz plane), a $4e$ destabilizing interaction d_{xy}/HOMO **11** and a $2e$ stabilizing interaction d_{xy}/LUMO **12**. These two interactions will cancel approximately.



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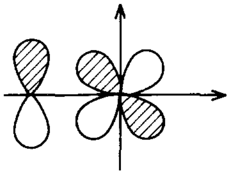

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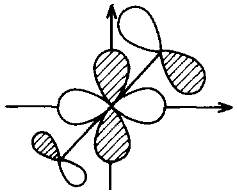
(ii) for the staggered conformation a $2e$ stabilizing interaction $d_{x^2-y^2}$/HOMO **13** which is expected to be small because of a large energy denominator.



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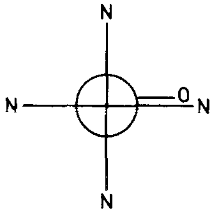
The balance is such that electronic factors do not appreciably favor one conformation over the other.

4. The stereochemistry of the iron porphyrins with a dioxygen ligand

Bent end-on geometry of the iron-dioxygen bond has been observed in oxyhemoglobin models [30], in oxymyoglobin [23, 31] and in the anion $[Fe(O_2)(SC_6HF_4)TPpivP]^-$ which is a model for the active site of oxycytochrome P450

[32]. The stereochemistry of these systems is further characterized by the orientation of the FeO_2 unit with respect to the porphyrin. The O–O bond may project either along the Fe–N bonds (eclipsed structure) as in **14** or along the Fe–C_{meso} bonds (staggered structure) as in **15**.



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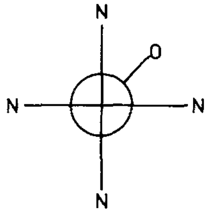

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The crystal structure of the dioxygen complex of the picket fence porphyrin shows a staggered structure of the Fe–O_2 unit as in **15** [30], whereas an eclipsed arrangement has been found in oxymyoglobin and explained on the basis of steric interactions between the dioxygen ligand and nearby residues of the globin [31]. In the crystal structure of the porphyrin anion $[Fe(O_2)(SC_6HF_4)TPpivP]^-$, the terminal oxygen atom occupies two sites: (i) minor site with a structure close to the staggered one (with an angle φ of 35°); (ii) a major site with an angle φ of 17° [32].

We had previously calculated the relative stabilities of the two conformations **14** and **15** for the five-coordinate model $FePO_2$ (considered as a model of $FePO_2Im$) [6]. The staggered conformation was found more stable than the eclipsed one by 6 kcal/mole. This greater stability of the staggered conformation was traced to the destabilization of the eclipsed structure through the steric interactions between the terminal oxygen atom and one of the porphinato nitrogen atom.

The experimental report of both staggered and eclipsed conformations for oxyheme systems and their models and the disorder of the dioxygen ligand over two positions for the cytochrome P450 model led us to study the influence of the *trans* axial ligand on the orientation of the dioxygen ligand.

Ab initio SCF calculations have been carried out [33] for the model systems $[Fe(NH_2)_4O_2L]^{2-}$ with L = none, NH_3 (used to mimic the imidazole ligand of the heme) and SH^- (used to mimic the thiolate ligand in the P450 complexes), the porphyrin cycle being now mimicked by four NH_2^- groups [34].

The relative stabilities of the two conformations, eclipsed and staggered, are reported in Table 3 for the different systems. The most stable conformation corresponds to the staggered structure **15** with the eclipsed structure **14** slightly higher in energy (by 2–3 kcal/mole). This confirms our previous results for the model system $FePO_2$ (although the energy difference is now somewhat smaller). This is also in agreement with the crystal structure of the dioxygen adduct of picket fence porphyrins [21, 22]. A low barrier has been found through INDO-SCF calculations for the system $FePO_2Im$, the staggered conformation being the most

Table 3. Relative stabilities (in kcal/mole) for the two conformations of $Fe(NH_2)_4O_2L$ calculated for the system $[Fe(NH_2)_4O_2L]^{2-}$ (comparable values were obtained for the neutral system $Fe(NH_2)_4O_2L$ for L = none and NH_3)

		Conformation	
L	Basis set	eclipsed	staggered
none	I	2.2	0
	II	2.4	0
NH_3	I	3.2	0
	II	2.6	0
SH^-	I	1.9	0
	II	2.5	0

stable [35] and for the system $FePO_2SCH_3^-$ with essentially free rotation of the terminal oxygen around the Fe–O axis [36].

We had previously traced the destabilization of the eclipsed orientation to the steric interactions between the terminal oxygen atom and one porphinato nitrogen [6]. In the present models $Fe(NH_2)_4O_2L$ (with L = none or NH_3), the O_β–N_p distance is 2.73 Å in the eclipsed structure and 2.92 Å in the staggered structure, to be compared to the sum of the Van der Waals radii, 2.90 Å. For the model system with $L = SH^-$, these distances increase respectively to 2.81 Å and 3.01 Å and one would expect a slight decrease in the computed barrier. Such a decrease is found when going from $L = NH_3$ to $L = SH^-$ with basis set I but is absent with basis set II. One possible explanation would be that the terminal oxygen atom is more negative with a thiolate ligand as the sixth ligand [37], with this negative charge resulting in increased steric interactions.

We have also calculated the potential energy curve as a function of the dihedral angle HSFeN for both orientations (eclipsed and staggered) of the dioxygen ligand. The results given in Table 4 correspond to an almost free rotation of

Table 4. Potential energy curve (in kcal/mole) calculated for the rotation of the SH^- group around the Fe–S axis (with BSI)

	Conformation of the dioxygen ligand	
φ	staggered	eclipsed
0°	1.5	0.6
45°	0.7	1.0
90°	0.5	1.2
135°	0	0.5
180°	0	0
225°	0	0.2
270°	0.4	0.6
315°	0.4	0.4

the thiolate ligand. The experimental structure [32] of the anion $[Fe(O_2)(SC_6HF_4)TPpivP]^-$ shows an almost eclipsed conformation of the dioxygen ligand (for the major site of the terminal oxygen atom) and a dihedral angle of the oxy and thiolate ligands close to 180°. This represents the conformation of minimum energy according to the results of Table 4.

5. The stereochemistry of the axial ligands in the cis-dinitrosyl molybdenum(II)porphyrin

X-ray structures of the dinitrosyl [38] and dicarbonyl [39] molybdenum(II)porphyrins $Mo(TTP)(NO)_2$ and $Mo(TTP)(CO)_2$ have revealed an unusual geometry such as **5**, with the two axial ligands cis to each other on the same side of the macrocycle. The stereochemistry of these systems corresponds to the axial ligand being eclipsed with respect to the pyrrolic nitrogens in the nitrosyl complex [38] but staggered in the carbonyl complex [39]. *Ab initio* SCF calculations have previously been reported [39] for $Mo(NH_2)_4(CO)_2$, a model of $Mo(TTP)(CO)_2$, and have reproduced the preferred staggered orientation. We hereafter report the results of similar *ab initio* SCF calculations for $Mo(NH_2)_4(NO)_2$ considered as a model of $Mo(TTP)(NO)_2$, in the two conformations eclipsed and staggered [40] (Fig. 3).

The computed total energies and formal electronic configurations for the ground state of this Mo(II) d^4 complex are given in Table 5. For both conformations the filled orbitals of the metal atom are those which point away from the ligands namely (i) d_{xy} and d_{Yz} for the staggered conformation: (ii) d_{xy} and d_{yz} for the eclipsed conformation (for more details, see Ref. [39]). The dinitrosyl complex

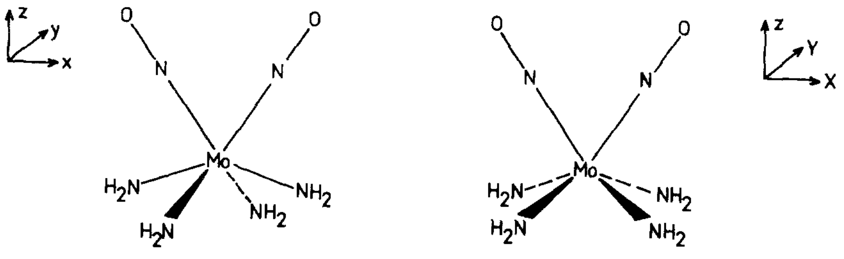


Fig. 3. Geometries of the two conformers (left, eclipsed; right, staggered) of $Mo(NH_2)_4(NO)_2$ (the x and y-axes pass through the amido nitrogens, whereas the X and Y-axes are the bisectors of the coordinate axes)

Table 5. Total energies (in a.u.) for the ground state of $Mo(NH_2)_4(NO)_2$

Conformation	Electronic configuration	Total energy
eclipsed	$(xy)^2(yz)^2(\pi_s^*)^2$	−4448.0180
staggered	$(xy)^2(Yz)^2(\tilde{\pi}_a^*)^2$	−4448.0150

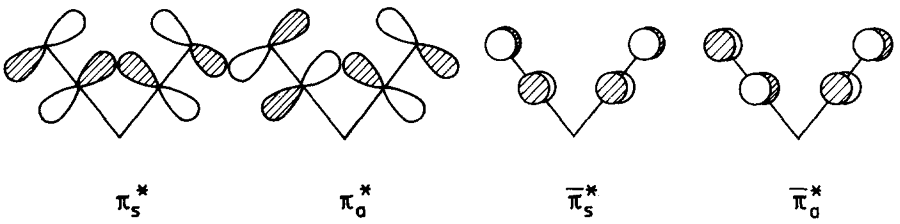
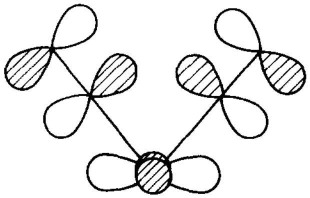


Fig. 4. The π^* orbitals of the dinitrosyl ligand

has one more occupied molecular orbital than the dicarbonyl complex, one among the four anti-bonding π^* orbitals of the nitrosyl ligands, namely π_s^*, π_a^*, $\bar{\pi}_s^*$ and $\bar{\pi}_a^*$ as represented in Fig. 4. The ground state of the eclipsed structure corresponds to the configuration with this π_s^* orbital doubly occupied, this configuration being energetically favored by a two electron stabilizing interaction between π_s^* and a combination of the empty metal orbitals $d_{x^2-y^2}$ and d_{z^2}. The two components of this interaction are shown in **16** and **17**. Other electronic configurations are energetically less favorable [42] since the occupation of the $\bar{\pi}_a^*$ orbital would yield a four-electron destabilizing interaction ($\bar{\pi}_a^* - d_{xy}$), as well as the occupation of the $\bar{\pi}_s^*$ orbital ($\bar{\pi}_s^* - d_{yz}$) while the occupation of the π_a^* orbital does not lead to any significant interaction with a metal d orbital but is unfavored by the anti-bonding interaction between the two nitrosyl groups. For the staggered conformation a similar analysis shows that the ground state configuration with the $\bar{\pi}_a^*$ orbital occupied is favored by the two-electron stabilizing interaction **18** ($\bar{\pi}_a^* - d_{x^2-y^2}$).



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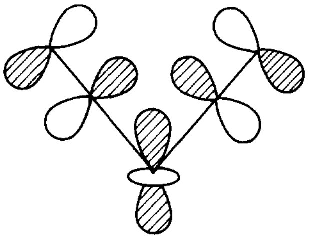

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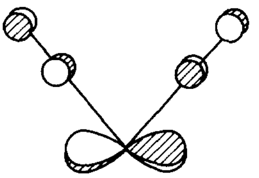

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From the results of Table 5, the eclipsed conformation turns out to be slightly more stable than the staggered one, by about 2 kcal/mole. This is in agreement with the experimental structure reported for $Mo(NO)_2(TTP)$ [38]. This agreement is probably not fortuitous, despite the many approximations of our theoretical treatment (choice of a simplified model, use of a limited basis set and neglect of the electronic correlation). For the system $Mo(NH_2)_4(CO)_2$ the staggered conformation was preferred and this was also in agreement with the experimental structure reported for the complex $Mo(CO)_2(TTP)$ [39].

The conformation of the dinitrosyl complex appears to be controlled by the electronic factors rather than by the steric factors. Examination of the interactomic distances in our model indicates a close contact of 2.39 Å in the eclipsed conformation between the nitrogen atoms of the nitrosyl and amido ligands while this contact is increased to 2.65 Å in the staggered conformation. The dominant metal-ligand interaction corresponds to two-electron stabilizing interactions, respectively **16** and **17** for the eclipsed conformation and **18** for the staggered one. However, the overlap term [29] should be larger for interactions **16** and **17**, leading to a greater stabilization of the eclipsed conformation. Thus electronic factors favor the eclipsed conformation while the steric factors favor the staggered conformation.

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    $\text{Fe–N}_{\text{amido}} = 1.97$ Å; $\widehat{\text{FeOO}} = 129°$
    $\text{Fe–L} = 2.07$ Å for $L = NH_3$; 2.37 Å for $L = SH^-$
    $\text{Fe–O} = 1.76$ Å for $L = NH_3$; 1.82 Å for $L = SH^-$
    $\text{O–O} = 1.22$ Å for $L = NH_3$; 1.30 Å for $L = SH^-$
34. We have resorted here to the model $(NH_2)_4^{4-}$ [27] rather than to the dianion $(NH_2)_4^{2-}$ since this latter one has one empty π orbital (of b_{2u} symmetry) which is artificially low when compared to the LUMO of the porphyrin cycle [28]. This results in a wrong electronic configuration for the system $[Fe(NH_2)_4(O_2)SH]^-$. No such problem is found with the model $(NH_2)_4^{4-}$ since all π orbitals of the imido ligands are occupied
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