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Iterative Extended Hückel Studies of Some Pyridine-Fe(II)-Porphin Complexes

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Iterative extended Hückel self-consistent charge calculations were performed for a number of conformations of Fe(II) porphin, a pyridine complex of Fe(II) porphin, and a pyridine-Fe(II)-porphin CO complex. For Fe(II) porphin, spin zero and spin 2 states were found to have their energy minimum in a planar conformation. Addition of the pyridine ligand results in an out-of-plane minimum energy conformation in the spin 2 case. Ligand bond formation is readily interpreted in terms of conventional chemical bonding theory. An energy-bond length curve was obtained for CO binding to pyridine-Fe(II)-porphin and found to be qualitatively reasonable.

Key words: Fe(II) porphin – Heme – CO-heme complex

1. Introduction

In recent years numerous approximate quantum mechanical studies of transition metal porphyrins have been reported [1–17], with particular attention given to iron-porphyrin complexes which simulate the active site of hemoglobin (Hb) and myoglobin (Mb). In these molecules the prosthetic group is iron protoporphyrin IX (heme), held in place by non-bonding interactions with the polypeptide backbone of the molecule and by coordinate bonding of the Fe atom to the β nitrogen of the imidazole ring of a histidine residue [18]. Perutz has proposed [19] that this latter interaction determines crucial features of the binding of ligands in both Hb and Mb and may be responsible for the cooperative effect in oxygen binding to Hb [20]. A number of recent papers [12, 15, 21] have dealt with the conformation of deoxy- and oxy-heme complexes and have attempted to identify the interactions responsible for the change in Fe position upon ligand binding. An

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interpretation of this change in terms of the electronic structure of the complex would contribute to our understanding of the kinetics of ligand binding in Hb and Mb as well as the equilibrium properties of these important bimolecules.

We report here results obtained in iterative extended Hückel, self-consistent charge (IEH-SCC) calculations on Fe(II)-porphin, a complex of Fe(II)-porphin with pryidine, and a complex of Fe(II) porphin with pyridine and CO. The latter two complexes were chosen to simulate the active site in unliganded (deoxy-) and in carboxy-Hb and Mb. The CO complexes of heme proteins have been the subject of numerous experimental static [22, 23] and dynamic [24] studies but have received somewhat less theoretical attention than O_2 complexes. As in much work in this area a porphin ($H_{12}C_{20}N_4$) ring was chosen to simulate the less symmetrical porphyrin group. The minimum symmetry treated was C_{2v} and the pyridine ligand was chosen as the closest approximation to an imidazole ring consistent with this symmetry. Several conformations of each complex were studied.

In earlier work [14], two of us calculated energies for numerous conformations of a CO–Fe(II) porphin complex using the simple extended Hückel procedure and constructed energy surfaces for two electronic states over a range of CO–Fe and Fe–porphin distances. Our calculation forced occupancy of the primarily Fe *d* molecular orbitals and resulted in energy surfaces for the S=0 and S=2 states of the system which were topologically reasonable but greatly exaggerated the dependence of the total energy on the system geometry. It was then conjectured that similar calculations using the IEH-SCC method and including a pyridine ligand would produce more reasonable results. While we have found this to be the case in a number of respects, difficulties were encountered in the present calculations which preclude the possibility of a comparably extensive study. These problems are described below and indicate some limitations of the form of IEH-SCC theory adopted here.

2. Method

We use the IEH-SCC method as described by Zerner *et al.* [1, 2]. The essence of the method is the prescription

$$\langle \chi_p | H_{\text{eff}} | \chi_q \rangle \equiv H_{pq} = \tfrac{1}{2}(H_{pp} + H_{qq}) S_{pq} [\kappa + (1-\kappa)\, \delta_{pq}]$$

for the matrix element of an effective one-electron Hamiltonian in the basis of atomic orbitals χ. Here H_{pp} and H_{qq} are valence state ionization potentials (VSIP) for the orbitals χ_p and χ_q, interpolated between values appropriate for neutral and ionic species on the basis of a Mulliken [25] population analysis, S_{pq} is the orbital overlap, and κ a parameter chosen by matching a computed property with the corresponding experimental value. We follow Zerner *et al.* [1, 2] in the choice of H_{pp}, κ, and single exponent Slater-type orbitals, with the single exception of the Fe 3*d* orbitals, for which we use the more accurate multiexponential functions of Watson [26].

The capabilities and limitations of extended Hückel methods are well known and require only brief comment here. The value chosen for κ (1.89) results in matching a difference in computed porphin π and π^* orbital energies to the known $\pi \rightarrow \pi^*$ transition energy [1]. It is reasonable, though by no means certain that other differences in computed orbital energies will also approximate the energies of the corresponding transitions. While the computed energies of occupied orbitals correlate reasonably well with orbital energies obtained in a self-consistent-field (SCF) calculation, the energies of the unoccupied orbitals will often be considerably lower than their SCF counterparts. Zerner *et al.* attribute this difference to the fact that in the SCF procedure unoccupied orbitals are determined in effect for the extra electron of a negatively charged species. Since, for $\kappa = 1.89$, unoccupied ligand orbitals lie lower in energy than their SCF counterparts one must remain alert to the possibility that IEH-SCC calculations with this value of κ may, in some cases, exaggerate the amount of charge transfer into these orbitals and yield misleading results.

Following Hoffmann [27] we will regard the sum of orbital energies (weighted by occupancy) as the approximate total energy of a given conformation of the system. Using this approach, Hoffman found that simple (non-iterative) extended Hückel calculations predicted reasonable geometries for a great many simple hydrocarbons and concluded that the neglect of nuclear–nuclear repulsion terms roughly compensated for the overestimation of electron–electron repulsion terms inherent in this procedure. While it is not certain that a similar near cancellation of errors will occur for an SCC calculation and for other types of molecular systems, it is reasonable to hope that the variation of total energy with conformation in the calculations presented here will have at least heuristic value.

Conformations may be compared with regard to the energies of individual orbitals, total energy, and charge distribution as determined from population analysis. While orbital energies and wavefunctions contain a great deal of information, it is difficult in some cases to interpret their variation with conformation, owing to the mixing of Fe, porphin, and ligand orbitals and to the redistribution of charge throughout the complex as the conformation changes. Nevertheless, it is generally possible to classify the computed orbitals as predominantly Fe, porphin, or ligand and in many cases to recognize their bonding or antibonding character. The total energy in an IEH-SCC calculation is a highly sensitive function of the net atomic charges assumed in forming the effective Hamiltonian. Iterations were continued until all atomic charges were constant to within ± 0.005 electrons and an extrapolation was made to determine the total energy. Finally, we note that the determination of a set of self-consistent charges is a highly appealing feature of the IEH-SCC method since it permits a numerical test of much qualitative chemical reasoning.

3. Ligands

Molecular orbital wavefunctions and orbital energies were determined for the isolated ligand molecules and were compared with the published results of SCF calculations done with comparable basis sets. The geometry of pyridine (C_5H_5N) was taken from the microwave structure determination by Bak *et al.* [28]. The energies obtained for occupied pyridine orbitals were in general agreement with those of Clementi [29]; the average disparity between corresponding occupied orbitals was about 3 eV. In contrast, the lowest unoccupied orbitals were computed to have energies some 10 eV below the corresponding SCF values. Surprisingly, the occupied orbital energies were in better general agreement with the SCF results than those of Rein *et al.* [30], who employed the Cusach's Hamiltonian [31] and a more sophisticated population analysis which preserved the orbital center of charge. The wavefunctions obtained for CO were in good qualitative agreement with the SCF orbitals determined by Ransil [32]. The computed energies of the four highest CO orbitals agree within 0.5 eV with the SCF energies while the lowest unoccupied orbital was some 15 eV below the SCF value.

3.1. *Fe(II)-Porphin*

The porphin ring was placed in the xy plane and assigned the same coordinates as in the D_{4h} planar projected geometry of Zerner *et al.* [1] with the exception of the nitrogens which were displaced slightly inward to provide a porphin hole radius of 2.03 Å. The $S=0\,{}^1A_1\,(d_{xy}^2 d_\pi^4)$ state and two $S=2$ states, ${}^5B_2(d_{xy}^2 d_\pi^2 d_{z^2} d_{x^2-y^2})$ and ${}^5E(d_{xy} d_\pi^3 d_{z^2} d_{x^2-y^2})$, were studied in separate IEH-SCC calculations for Fe positions ranging from in-plane to 1 Å away from the porphin plane. The term symbols used here are for C_{4v} symmetry. The correspondence between these symmetry designations and the more conventional D_{4h} symbols are given by

$$A_1 \rightarrow A_{1g}, A_{2u}; \qquad A_2 \rightarrow A_{2g}, A_{1u}; \qquad B_1 \rightarrow B_{1g}, B_{2u}; \qquad B_2 \rightarrow B_{2g}, B_{1u};$$

$$E \rightarrow E_g, E_u.$$

In the ${}^5E$ case the two d_π orbitals, d_{xz} and d_{yz}, were each assigned 1.5 electrons in the SCC procedure. The computed orbital energies were found to be only slightly dependent on the orbital populations. The orbital energies obtained for the Fe in plane and displaced 0.5 Å from the porphin plane are shown in Fig. 1 (for the ${}^1A_1$ state). The results of the Mulliken population analysis for all three states at these geometries are given in Table 1.

For all states considered the minimum energy conformation was that in which the Fe atom lies in the porphin plane (for the assumed porphin hole radius of 2.03 Å). While the antibonding nature of the $d_{x^2-y^2}$ orbital is apparent from Fig. 1, the remaining orbitals increase in energy as the Fe is displaced from the prophin plane reflecting bonding interactions which result in maximum charge transfer from the Fe to the porphin in the in-plane position. Our results are in disagreement with the frequently expressed view [19] that an $S=2$ Fe is too large to fit into the porphin center but are in accord with the results obtained by Olafson and Goddard [15] in *ab initio* calculations on a smaller model system. The in-plane position is, as expected, more strongly favored in the $S=0$ state than in the $S=2$ states, with about 4 eV required to displace the Fe by 0.5 Å for $S=0$ and 1 or 2 eV required for the $S=2$ states. If a phenomenological exchange correction of about -2.5 eV [2] is added to the energies of the $S=2$ state, it is found that the $S=0$ state has lower

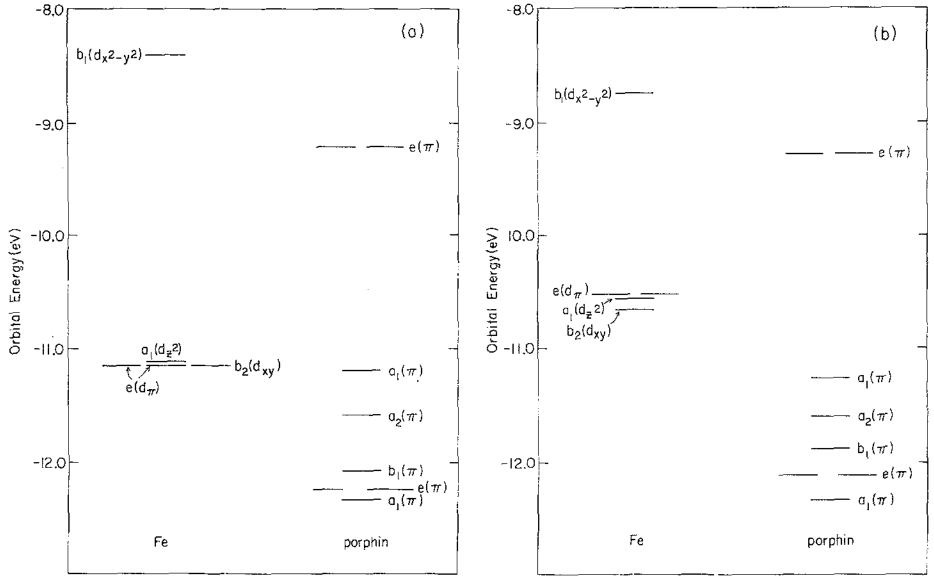

Fig. 1. Orbital energies (eV) for ${}^1A_1$ state of Fe(II)-porphin. (a) Fe in plane, (b) Fe 0.5 Å from porphin plane. Non-π porphin orbitals have been deleted for clarity. Non-Fe orbitals with energy less than −10 eV are fully occupied

Table 1. Population of Fe orbitals and net Fe charge for Fe(II) porphin

State	${}^1A_1$		${}^5B_2$		${}^5E$	
Fe position (Å)	0.0	0.5	0.0	0.5	0.0	0.5
$3d_{xy}$	2.00	2.00	2.00	2.00	1.07	1.03
$3d_{yz}$	1.95	1.96	1.18	1.17	1.61	1.58
$3d_{xz}$	1.95	1.96	1.18	1.17	1.61	1.58
$3d_{x^2-y^2}$	0.96	0.85	1.51	1.45	1.53	1.46
$3d_{z^2}$	0.17	0.39	1.09	1.31	1.10	1.38
$4s$	0.30	0.30	0.36	0.35	0.36	0.35
$4p_x$	0.14	0.14	0.15	0.12	0.16	0.14
$4p_y$	0.14	0.14	0.15	0.12	0.16	0.14
$4p_z$	0.14	0.09	0.15	0.10	0.15	0.10
net Fe charge	0.23	0.18	0.23	0.20	0.25	0.21

energy in the in-plane conformation but the $S=2$ states are lower with the Fe at 0.5 Å. The ${}^5B_2$ and ${}^5E$ states are very close in energy in the latter case.

3.2. *Pyridine-Fe(II)-Porphin*

The pyridine ring was placed in the yz plane ($z>0$), which contains two of the porphin N atoms. While it had been hoped [14] that the IEH-SCC method would permit the construction of energy surfaces for several states of the 5-coordinate complex as the Fe-porphin and Fe-pyridine distances were varied, we found that as the Fe was brought towards the pyridine the total energy decreased steadily and did not have a minimum for any reasonable Fe-pyridine separation. Examination of the wavefunctions obtained for small Fe-pyridine separation showed excessive delocalization of the Fe d electrons resulting in a high positive charge on the Fe atom. It is possible that more realistic results might have been obtained if inner shell orbitals on the Fe had been included [33], however part of the difficulty may be attributable to the very low (-8 eV) energies of the two lowest unoccupied pyridine orbitals (in the present parameterization) which would encourage excessive charge transfer to the pyridine ring. We did not explore these possibilities further in the present work but fixed the Fe-pyridine separation at 2.0 Å and maintained this separation as the Fe position was varied.

As in the preceding case the $S=0$ ${}^1A_1$ state $(d_{xy}^2 d_{xz}^2 d_{yz}^2)$ and two $S=2$ states ${}^5A_2(d_{xy}^2 d_{xz} d_{yz} d_{z^2} d_{x^2-y^2})$ and ${}^5B_1(d_{xy} d_{xz}^2 d_{yz} d_{z^2} d_{x^2-y^2})$ were studied in separate IEH-SCC calculations. The term symbols used here are for C_{2v} symmetry. The correspondence between these symmetry designations and the D_{4h} case is given by

$$A_1 \to A_{1g}, A_{2u}, B_{1g}, B_{2u}; \qquad A_2 \to A_{2g}, A_{1u}, B_{2g}, B_{1u}; \qquad B_1, B_2 \to E_g, E_u.$$

It was found in this case also that the individual orbital energies are not very sensitive to the orbital populations. The orbital energies obtained for the ${}^1A_1$ state are shown in Fig. 2 for the Fe in plane and for Fe 0.5 Å out of plane. The results of the population analyses are given in Table 2.

Examination of Fig. 2 and comparison with Fig. 1 permits a number of qualitative conclusions to be drawn. Binding of the pyridine ligand to Fe(II) porphin results in large measure from the formation of bonding and antibonding orbitals between a pyridine $a_1(\sigma)$ orbital (the N lone pair) and the Fe d_{z^2}. The energy of the bonding orbital, composed primarily of pyridine atomic orbitals, is about 1.5 eV lower than the orbital energy (-10.74 eV) obtained for free pyridine, while the energy of the antibonding combination, mainly Fe d_{z^2}, is somewhat over 1 eV higher than the corresponding orbital in Fe(II) porphin. The small splittings obtained between Fe d_{xz} and d_{yz} and between porphin $b_1(\pi)$ and $b_2(\pi)$ orbitals suggests that the pyridine π system is very little involved in the bonding and that an alternative orientation of the pyridine (rotated about the z axis) would yield quite similar results.

In the present case the minimum energy conformation occurs for the $S=0$ state when the Fe is in or quite close to the porphin plane and for the $S=2$ states when the Fe is from 0.3 to 0.5 Å out of plane. If a phenomenological [2] spin correction is made, it is found that the $S=0$ state lies lower in energy for the in-plane conformation but that the $S=2$ states have lower energy for the out-of-plane positions. The minimum energy state of the complex is an $S=2$ state, in accord with the familiar experimental results for Mb and Hb. The extrapolated total energies of the two $S=2$ states are too closely spaced to permit certain identification of the lower energy state.

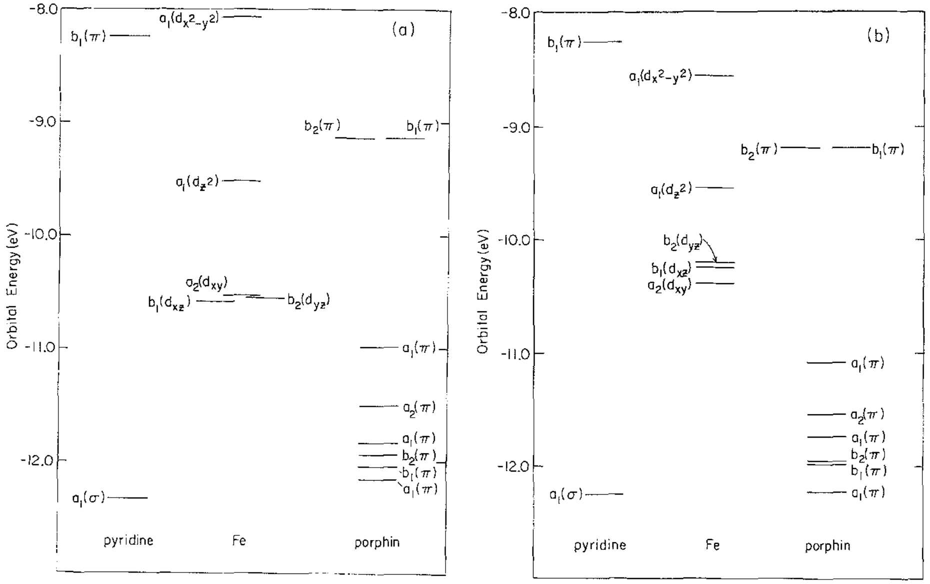

Fig. 2. Orbital energies (eV) for $^1A_1$ state of pyridine-Fe(II)-porphin. (a) Fe in plane, (b) Fe 0.5 Å from porphin plane. Non-π porphin orbitals have been deleted for clarity. Non-Fe orbitals with energy less than -10 eV are fully occupied

Table 2. Population of Fe orbitals and net Fe and C_5H_5N charges for pyridine-Fe(II)-porphin

State	$^1A_1$		$^5A_2$		$^5B_1$	
Fe position (Å)	0.0	0.5	0.0	0.5	0.0	0.5
$3d_{xy}$	2.00	2.00	2.00	2.00	1.05	1.03
$3d_{yz}$	1.92	1.94	1.14	1.17	1.18	1.21
$3d_{xz}$	1.89	1.89	1.10	1.16	1.93	1.93
$3d_{x^2-y^2}$	0.86	0.81	1.49	1.45	1.50	1.48
$3d_{z^2}$	0.62	0.56	1.37	1.34	1.39	1.38
$4s$	0.26	0.29	0.31	0.31	0.32	0.32
$4p_x$	0.11	0.13	0.13	0.12	0.13	0.16
$4p_y$	0.08	0.10	0.10	0.09	0.11	0.09
$4p_z$	0.08	0.11	0.17	0.17	0.17	0.18
net Fe charge	0.17	0.15	0.21	0.19	0.22	0.20
net C_5H_5N charge	0.31	0.24	0.25	0.25	0.25	0.25

Identication of the interactions responsible for the out-of-plane equilibrium position for the $S=2$ states of the 5-coordinate complex in contrast to the in-plane favored conformation of 4-coordinate Fe(II)-porphin is highly desirable. In their *ab initio* study Olafson and Goddard [15] examined the approach of an NH_3 molecule to 4 NH_2 groups arranged to simulate the porphin center in the absence of the Fe atom and found a considerable repulsive interaction between the NH_3 and NH_2 electrons. It is difficult to isolate this interaction when the Fe is present.

Comparison of Tables 1 and 2 suggests that an additional significant factor favoring the out-of-plane conformation for the 5-coordinate complex may be the transfer of charge from the pyridine to the Fe and porphin. As a result the Fe bears a smaller positive charge in the 5-coordinate case. In the IEH-SCC model the Fe orbitals have a higher energy (i.e., VSIP) when the pyridine is present, than when it is not, and as a result the bonding interaction with the porphin ring is lessened.

3.3. *Pyridine-Fe(II)-porphin-CO*

Our studies of this 6-coordinate complex were restricted to the $S=0\ {}^1A_1$ state and to conformations in which the Fe is in the porphin plane and the pyridine N is 2.0 Å away from the Fe. The CO was placed in an axial position and the CO bond length was fixed at the experimental value of 1.13 Å [34]. Computed orbital energies are shown in Fig. 3 for the representative [2, 35] Fe–C distance of 1.84 Å.

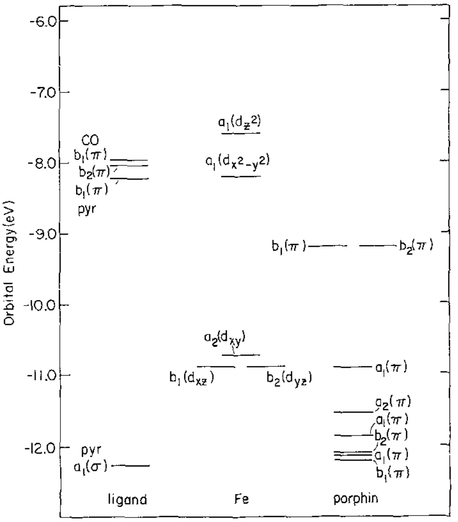

Fig. 3. Orbital energies (eV) for ${}^1A_1$ state of pyridine-Fe(II)-porphin-CO complex, Fe in porphin plane, Fe–C separation 1.84 Å. Non-π porphin orbitals have been deleted for clarity. Non-Fe orbitals with energy less than -10 eV are fully occupied

The principal bonding interactions are, as expected, between the highest occupied $a_1(\sigma)$ CO orbital and the Fe d_{z^2} and between the unoccupied b_1 and b_2 CO π orbitals and the Fe d_{xz} and d_{yz}. The σ bonding orbital has energy -14.25 eV compared with -13.71 eV for free CO while the d_{z^2} orbital is raised by about 2 eV with respect to the 5-coordinate in-plane configuration. The $b_1(d_{xz})$ and $b_2(d_{yz})$ levels are about 0.4 eV lower than in the 5-coordinate complex while the b_1 and b_2 CO π levels are at -7.98 eV and -8.04 eV compared with -8.83 eV in free CO. These interactions are reflected in the population analysis in which it is found that there are 0.85 electrons in the nominally unoccupied d_{z^2} orbital and 1.75 and 1.73 electrons in the d_{yz} and d_{xz} orbitals respectively (compare Table 2).

The energy level scheme of Fig. 3 is in accord with the failure of Churg and Makinen [23] to observe z polarized absorption (porphin π to Fe d_{z^2}) in the 33000–13000

cm^{-1} (1.6–4.1 eV) region. The 3.5 eV separation between the $d_\pi(d_{xz}, d_{yz})$ and d_{z^2} levels has implications for the mechanism of flash photolysis of MbCO. It is known from experiment [36, 37] that the CO–Fe bond in MbCO and HbCO is photolyzed with a quantum yield of order unity for photon energies greater than 2 eV. In the mechanism of Zerner *et al.* [2] the $\pi \rightarrow \pi^*$ transition is radiationlessly coupled to the $d_\pi \rightarrow d_{z^2}$ transition which induces the photolysis. Fig. 3 indicates that for the assumed geometry the $d_\pi \rightarrow d_{z^2}$ transition requires at least 1 eV greater energy than the lowest energy porphin $\pi \rightarrow \pi^*$ transition. Radiationless transitions need not be vertical, however, and if there is some conformation change following the $\pi \rightarrow \pi^*$ transition, the $d_\pi \rightarrow d_{z^2}$ transition may become energetically feasible. Our results do not support the suggestion [37] that the $\pi \rightarrow \pi^*$ state itself is antibonding for we find the energy of the $\pi \rightarrow \pi^*$ transition to be quite insensitive to the Fe–CO distance.

In Fig. 4 we show the variation of total energy with the Fe–C bond distance for the $^1A_1$ $(d_{xz}^2 d_{yz}^2 d_{xy}^2)$ state, for the arithmetic average (labelled ^3B) of the $^3B_1$ $(d_{xz} d_{yz}^2 d_{xy}^2 d_{z^2})$ and $^3B_2 (d_{xz}^2 d_{yz} d_{xy}^2 d_{z^2})$ states, and for the $^5A_2(d_{xz} d_{yz} d_{xy}^2 d_{x^2-y^2} d_{z^2})$ states. In the latter two cases the orbital energies of the $^1A_1$ state were used and exchange corrections [2] of −0.46 eV and −2.44 eV respectively were included.

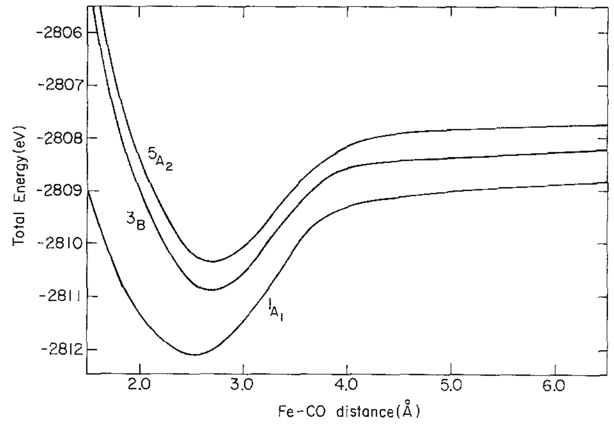

Fig. 4. Total energies for $^1A_1(d_{xz}^2 d_{yz}^2 d_{xy}^2)$ ground state, average of $^3B_1(d_{xz} d_{yz}^2 d_{xy}^2 d_{z^2})$ and $^3B_2(d_{xz}^2 d_{yz} d_{xy}^2 d_{z^2})$ states and $^5A_2(d_{xz} d_{yz} d_{xy}^2 d_{x^2-y^2} d_{z^2})$ state for pyridine-Fe(II)-porphin-CO complex as a function of Fe–C bond distance. The Fe is fixed in the porphin plane and the pyridine N is 2.0 Å away from the Fe. The CO is placed in an axial position and the CO bond length fixed at 1.13 Å

If one bears in mind the limitations of the method, such a diagram may be of heuristic value, even though such features as the equilibrium bond length may be rather unrealistic. It is reassuring to find a simple binding curve for the ground state ($^1A_1$) but perhaps surprising that these excited states (^3B and $^5A_2$) also show bonding character. If allowance is made for the relaxation of the Fe position as the CO leaves the molecule, as can be done for large Fe–CO separations using the results obtained for the in-plane and out-of-plane conformations of 5-coordinate pyridine Fe(II)-porphin, we find that the $^5A_2$ state becomes the ground state for large Fe–CO distances. Whether the $^5A_2$ state retains some bonding character in this case is uncertain. Our results suggest more strongly that the $^3B_1$ and $^3B_2$ states do retain some bonding character. If this is so, they may be significant intermediates in the CO binding process.

4. Conclusions

The results of IEH-SCC calculations on Fe(II)-porphin, pyridine-Fe(II)-porphin, and pyridine-Fe(II)-porphin-CO were found to be consistent with other models of heme proteins and their CO complexes and to be readily interpreted in terms of simple chemical bonding theory. While not quantitatively reliable, the dependence of the orbital energies and wavefunctions and the total energy on conformation obtained in the present parameterization is qualitatively reasonable and suggests that further studies at the level of IEH-SCC theory (perhaps with an alternative parameterization and the inclusion of some inner shells) may have heuristic value in the attempt to unravel the kinetics of ligand binding to home proteins.

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