Electronic Structure of Porphyrins. All Valence Electron Self-Consistent Field Molecular Orbital Calculations of Free Base, Magnesium, and Aquomagnesium Porphines

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Abstract: CNDO/2–SCF–MO calculations were carried out on free base, magnesium, and aquomagnesium porphines. Several aspects of the electronic structure, such as MO ordering and molecular charge distribution, are analyzed. Of particular interest is the ordering of the two highest occupied MO's, which in the present work is reversed from that obtained in other calculations. However, the ordering is consistent with available experimental data. The calculated ionization potentials are also in reasonable agreement with experiment. A large gap (*ca.* 3 eV) between the two highest occupied MO's and the next occupied MO was obtained in the present calculations. The implication of this energy gap to the electronic and spectral properties of porphyrins and the effect on metal–ligand bonding of including magnesium d orbitals are also discussed.

Porphyrins are some of the most ubiquitous compounds found in nature,[2,3] and they are important in a wide variety of biochemical processes from oxygen transport to the trapping and transduction of solar radiation into useful chemical energy.[4] A considerable number of theoretical investigations have been carried out on this important class of compounds.

Most of the studies utilized simple molecular orbital (MO) methods, which treated only π electrons.[5-14] Self-consistent field (SCF) calculations using the Pariser–Parr–Pople π-electron method were carried out by Kobayashi,[15] Weiss, *et al.*,[16] and Sundbom,[17] who also treated the nitrogen lone pair electrons explicitly. The most complete studies to date are those of Zerner and Gouterman[18,19] using a type of iterative extended Hückel theory (IEHT) which treats all valence electrons.

The present study is concerned with an examination of several aspects of the structural chemistry of porphine, magnesium porphine, and aquomagnesium porphine using the CNDO/2 all valence electron

SCF–MO method developed by Pople, Santry, and Segal.[20,21] Ground state properties are examined, and particular emphasis is placed on examination of the MO structure, electron populations, net atomic charges, metal–ligand bonding, and the importance of magnesium d orbitals to the bonding. Since only ground state properties are considered in the current study, the MO structure of the virtual orbitals is not discussed. Their structure will, however, be discussed in a forthcoming publication on the spectra of porphyrins. Several aspects of the geometric structure of the two magnesium porphine complexes are also examined. Where possible, comparisons to experimental data and Zerner and Gouterman's all valence electron IEHT calculations will be made,[18,19] although the calculation on the aquomagnesium porphine complex is the only one carried out to date.

Experimental Section

Procedure. As mentioned above, the present calculations were carried out using the CNDO/2 method.[20,21] Parameters for magnesium were taken from the work of Santry and Segal[22] and employed a basis consisting of 3s, 3p, and 3d orbitals.

The basic computer program used in the calculations was obtained from the Quantum Chemistry Program Exchange at Indiana University (QCPE 141). The program was suitably modified to handle up to 150 basis functions, and matrix diagonalization was performed using a modified Givens algorithm also available through the Quantum Chemistry Program Exchange (QCPE 62.3). All computations were performed on the Honeywell 635 computer at the University of Kansas Computation Center. Computational times ranged from a minimum of 0.8 hr for the in-plane magnesium porphine to 2.6 hr for aquomagnesium porphine.

The porphine ring geometry (see Figure 1) was taken from the paper by Zerner and Gouterman[18] and is based on the X-ray diffraction data of Hoard, Hamor, and Hamor[23] for tetraphenylporphine. The inner-ring hydrogens of the free base are located on opposite, rather than adjacent, nitrogens, as suggested by the studies of Silvers and Tulinsky.[24] Two configurations of the magnesium porphine complex were investigated: (1) the square planar (D_{4h}) complex and (2) the square pyramidal (C_{4v}) complex, where the magnesium atom lies 0.273 Å above the por-

(1) This work was supported in part by a USPHS Health Sciences Advancement Award (RR-06147) to the University of Kansas and by a grant from the General Research Fund of the University of Kansas.

(2) J. E. Falk, "Porphyrins and Metalloporphyrins," Elsevier, Amsterdam, 1964.

(3) An excellent review on porphyrin chemistry can be found in K. M. Smith, *Quart. Rev., Chem. Soc.*, 31 (1971).

(4) Porphyrin biochemistry is extensively reviewed in H. R. Mahler and E. H. Cordes, "Biological Chemistry," 2nd ed, Harper and Row, New York, N. Y., 1971.

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(19) M. Zerner and M. Gouterman, *Theor. Chim. Acta*, 8, 26 (1967).

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(22) D. P. Santry and G. A. Segal, *J. Chem. Phys.*, 47, 158 (1967).

(23) J. L. Hoard, M. J. Hamor, and T. A. Hamor, *J. Amer. Chem. Soc.*, 85, 2334 (1963).

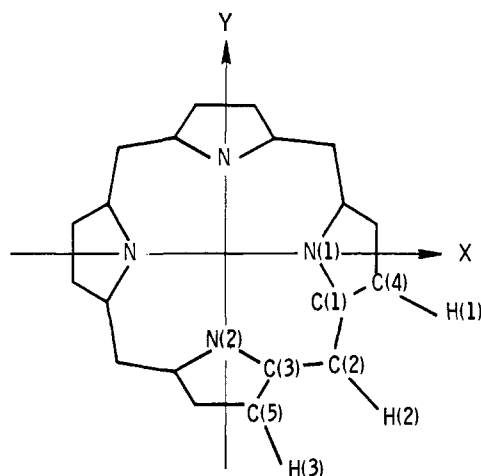(24) S. Silvers and A. Tulinsky, *J. Amer. Chem. Soc.*, 86, 927 (1964).

Figure 1. The basic porphine structure used in the calculations.

Table I. Theoretical Studies of the Water Proton Geometry in Aquomagnesium Porphine

Config[a]	Rel energy, kcal/mol
PU	0.00
PU*	0.18
PD	82.36
PD*	83.40

[a] See ref 27 for a discussion of the notation used.

porphyrin complex. The present calculations also indicate that the out-of-plane configuration is 9.74 kcal/mol more stable than the in-plane configuration.

The exact geometry of the protons in the water molecule of aquomagnesium porphine is not known, and calculations were carried out on four possible geometries. The results are summarized in Table I. While there is a rather large energy difference between the PU and PD configurations,[27] there is only a very small energy difference between the two conformers of a particular configuration (*i.e.*, PU and PU* or PD and PD*). While the PU configuration is certainly the most stable, there does not seem to be any real preference for either the PU or PU* conformations. Hence for convenience and conformity the PU conformation was used for all further analysis in the current study.

MO Structure and Bonding. Table II lists the symmetry and energy of the high lying MO's of the three porphine molecules, as well as the porphine dianion. Figure 2 shows the correlation among the MO's of the different molecules with respect to their particular molecular point groups. Figure 2 also shows the large energy gap between the two highest occupied MO's (HOMO and HOMO-1)[28] and the next highest occupied MO (HOMO-2). This gap (*ca.* 3 eV) is present in all four porphine species studied in Table II. It should be noted that, even in the case of the free base

Table II. Energies and Symmetries of the High Lying Occupied MO's of the Porphines Studied

Porphine free base (D_{2h})		Porphine dianion (D_{4h})		Magnesium porphine (D_{4h})		Magnesium porphine (C_{4v})		Aquomagnesium porphine (C_{2v})	
Orbital sym	Energy, eV	Orbital sym	Energy, eV	Orbital sym	Energy, eV	Orbital sym	Energy, eV	Orbital sym	Energy, eV
$a_u(\pi)$	−8.3399	$a_{2u}(\pi)$	+0.3809	$a_{1u}(\pi)$	−8.3589	a_2	−8.3671	a_2	−8.0949
$b_{1u}(\pi)$	−8.5875	$a_{1u}(\pi)$	−0.2939	$a_{2u}(\pi)$	−8.7997	a_1	−8.8161	a_1	−8.4160
$b_{3g}(\pi)$	−11.7901	b_{1g}	−3.8421	b_{1g}	−12.6200	b_1	−12.1411	a_1	−12.2499
a_g	−12.0377	$e_g(\pi)$	−4.0325	$b_{2u}(\pi)$	−12.6282	b_1	−12.6907	a_1	−12.4512
b_{2u}	−12.1656	e_u	−4.2420	e_u	−12.7914	e	−12.7996	b_2	−12.4921
$b_{1u}(\pi)$	−12.4295	$b_{2u}(\pi)$	−4.3672	$e_g(\pi)$	−13.1860	e	−13.1424	b_1	−12.4975
b_{1g}	−13.2513	a_{2g}	−5.3713	a_{2g}	−13.3547	a_2	−13.3492	b_2	−12.8186
b_{3u}	−13.3982	a_{1g}	−5.4719	$a_{2u}(\pi)$	−13.7302	a_1	−13.7356	b_1	−12.8512
$b_{2g}(\pi)$	−14.4131	$a_{2u}(\pi)$	−5.5454	a_{1g}	−14.6390	a_1	−14.6961	a_2	−13.0988
b_{2u}	−14.5029	b_{2g}	−6.5549	e_u	−14.7424	e	−14.7505	a_1	−13.3764
$b_{1u}(\pi)$	−14.7125	e_u	−6.6338	$e_g(\pi)$	−14.9546	e	−14.9464	a_1	−14.3505
b_{1g}	−14.7587	$e_g(\pi)$	−7.0773	b_{2g}	−15.0607	b_2	−15.0552	b_2	−14.4729
$b_{2g}(\pi)$	−14.7941	b_{1g}	−7.5589	b_{1g}	−15.5995	b_1	−15.5940	b_1	−14.4729
a_g	−14.9900	e_u	−7.8066	e_u	−16.2008	e	−16.2198	b_2	−14.7015
b_{3u}	−15.0635	b_{1g}	−8.8868	b_{1g}	−16.5981	b_2	−16.5899	b_1	−14.7015

phine plane. This distance was taken from the X-ray diffraction study of aquomagnesium tetraphenylporphyrin by Timkovich and Tulinsky.[25] The magnesium oxygen distance in the aquo-magnesium porphine complex was taken as 2.099 Å and was also obtained from the work of Timkovich and Tulinsky.[25] Finally, the geometry of the water molecule was taken from ref 26.

Results and Discussion

Geometric Structural Studies. While no specific experimental investigation on the structure of magnesium porphyrins has been carried out, the out-of-plane nature of the magnesium atom is at least tentatively confirmed by the previously cited X-ray study of Timkovich and Tulinsky[25] on the aquomagnesium

(25) R. Timkovich and A. Tulinsky, *J. Amer. Chem. Soc.*, **91**, 4430 (1969).
(26) "Table of Interatomic Distances," The Chemical Society, London, 1958, p M67.

where extensive mixing of the lower MO's occurs, there is essentially no change in the relative energy and ordering of the two highest filled MO's. A pictorial representation of these two MO's is given in Figure 3.

From the nodal structure of the "$a_{1u}(\pi)$" orbital[29]

(27) The notations PU and PD stand for the "proton-up" and "proton-down" configurations, respectively. In the PU configuration the two water protons lie above the oxygen with respect to the porphine plane. In the PD configuration the two protons lie below the oxygen. The unstarred or starred notation refers to whether the two protons lie in the *xz* plane or in a plane which bisects the *x* and *y* axes and contains the *z* axis, respectively (see Figure 1).
(28) HOMO = highest occupied MO.
(29) The quotation marks on the irreducible representations, *i.e.*, "$a_{2u}(\pi)$," signify the fact that the irreducible representation refers to the symmetry of the MO in the D_{4h} point group, which is the most symmetric configuration possible for the porphine moiety. The correlation of these MO's for different point groups is seen in Figure 2 and is discussed in H. H. Jaffe and M. Orchin, "Symmetry, Orbitals, and Spectra," Wiley, New York, N. Y., 1971, Appendix 1.

Table III. Comparison of the MO's of the Present Work with Other Calculations[a]

MO	Free base porphine (D_{2h})						Magnesium porphine (C_{4v})			
	Sundbom[b]		Zerner and Gouterman[c]		This work		Zerner and Gouterman[d]		This work	
HOMO	b_{1u}	−6.5767	b_{1u}	−11.66	a_u	−8.3399	b_1	−10.65	a_2	−8.3671
HOMO-1	a_u	−6.6719	a_u	−12.00	b_{1u}	−8.5875	a_1	−11.15	a_1	−8.8161
HOMO-2	b_{2g}	−8.4950			b_{3g}	−11.7901	a_2	−11.55	b_1	−12.1411

[a] All energies in eV. [b] π-electron SCF-MO calculation. For details see ref 17. [c] IEHT calculation. MO energies were estimated from Figure 2 of ref 18. [d] IEHT calculation. MO energies were estimated from Figure 4 of ref 19.
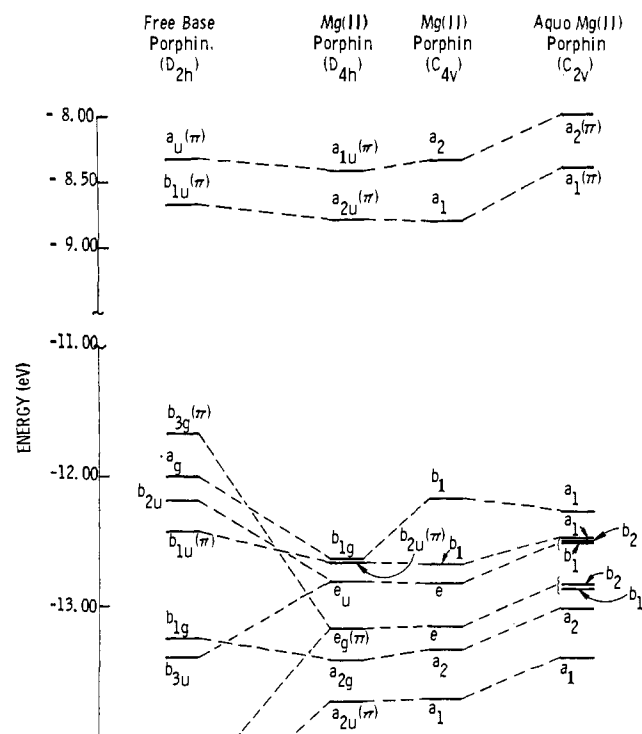

Figure 2. The correlations between high lying occupied MO's of the different molecules investigated.

HOMO "a_{1u} (π)"

HOMO-1 "a_{2u} (π)"

it is clear that the pyrrolic carbon p_π orbitals of the HOMO are nonbonding with respect to the inner ring nitrogens and the bridging meso carbons. Since the square of an MO coefficient indicates the contribution to the electron population of a particular basis orbital in that MO,[30] it follows that there is no electron population on the inner ring nitrogens and meso carbons of the HOMO. This fact has important implications in correlating MO structure with observed esr spectra, as will be seen shortly. In the case of the HOMO-1 there is considerable electron population in the nitrogen p_π orbitals (see Figure 3). Hence, it would be expected that addition of positively charged species, e.g., protons or a Mg(II) ion, near the ring nitrogens should differentially stabilize the "$a_{2u}(\pi)$" orbital of the dianion and perhaps even invert the MO ordering of these two orbitals. This is indeed found to be the case, as seen in Table II.

As seen in Table II and Figure 2, the p_π-p_π metal-ligand interaction in the Mg(II) complexes does not give rise to a large additional stabilization in the "$a_{2u}(\pi)$" orbital over that observed in the free base where
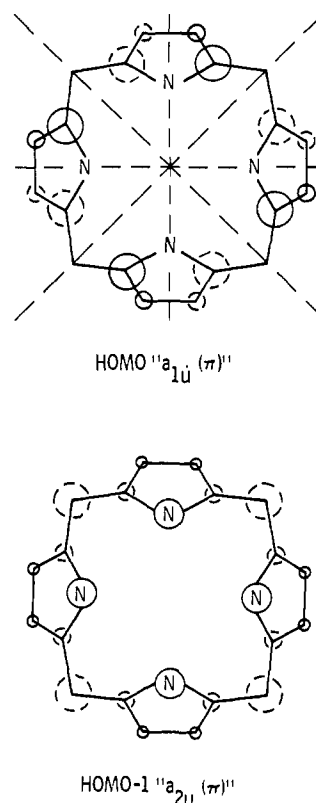
Figure 3. The atomic orbital (AO) structure of the porphine ring in the two highest occupied MO's of the molecules investigated. The size of the circles is approximately proportional to the AO coefficients. The view is looking down the positive z axis at the upper lobe of the p_π AO's. The solid lines indicate a positive value for the upper lobe while the dashed lines indicate a negative value. The straight dashed lines coincident with and bisecting the x,y axes represent the nodes of the "$a_{1u}(\pi)$" orbital.

such an interaction is not present. It should be kept in mind, however, that the energy of a particular MO depends not only on its bonding properties, but also on the average potential field produced by the electrons contained in the other MO's.

As is seen in Table III, discrepancies exist between the MO structure of the present work and those of previous workers. Unfortunately, very little experimental data are available for resolving the conflicting results unequivocally. For example, spectral data are not sufficient since they reflect the electronic structure of both the ground and excited states. However, studies of the cation radicals of magnesium porphyrins[31,32] indicate that the ground state is of $^2A_{1u}$ symmetry with an MO configuration of $a_{2u}{}^2a_{1u}{}^1$. This is

(30) As pointed out by Pople and Segal (J. A. Pople and G. A. Segal, J. Chem. Phys., 43, S136 (1965)) the assumption of neglect of differential overlap amounts to assuming the basis orbitals are orthonormal. Only in this case does the square of the MO coefficient equal the electron population of that particular basis orbital in the MO of interest.

(31) R. H. Felton, D. Dolphin, D. C. Borg, and J. Fajer, J. Amer. Chem. Soc., 91, 196 (1969).

(32) J. Fajer, D. C. Borg, A. Formin, D Dolphin, and R. H. Felton, J. Amer. Chem. Soc., 92, 3451 (1970).

Table IV. Comparison of Calculated and Experimental Ionization Potentials of Several Porphyrins

Molecule	Calcd, eV[a]	Expt, eV
Porphine	8.34[b]	7.42[e]
	6.58[c]	
	11.66[d]	
meso-Tetraphenylporphine		7.12[e]
Magnesium porphine	8.37[b]	
	10.65[c]	
Aquomagnesium porphine	8.10[b]	
Zinc tetraphenylporphine		6.82[e]
Copper tetraphenylporphine		7.05[e]

[a] Calculated ionization potentials were obtained using Koopman's theorem,[34] i.e., IP = $-E_{HOMO}$. [b] This work. See Tables II and III for values used. [c] See Table III and ref 17. [d] See Table III and ref 18 and 19. [e] A. Stanienda, Z. Naturforsch. B, 23, 1285 (1968).

altered between the two complexes, and there is a slight destabilization of all MO's except the "b_{1g}." This is due primarily to antibonding between the water and magnesium orbitals. Also the doubly degenerate "e_u" MO's slightly split, due to the lowered symmetry of the aqueous complex, into MO's of b_1 and b_2 symmetry, although the smallness of the splitting indicates a weak effect due to water complexation.

Ionization Potentials. Although very few ionization potentials of porphyrins are experimentally known, a few comparisons can be made. The data are summarized in Table IV. Examination of the table shows that the results of the current study are in reasonable agreement with experiment.

The chelation of divalent cations such as Zn(II) and Cu(II) is seen to only slightly shift the ionization

Table V. Electron Populations and Net Atomic Charges[a,b]

Atom[c]	Free base porphine (D_{2h})				Magnesium porphine (C_{4v})[d]				Aquomagnesium porphine (C_{2v})			
	σ	π	Total	At. charge	σ	π	Total	At. charge	σ	π	Total	At. charge
N(1)	3.475	1.625	5.100	−0.100	3.836	1.355	5.191	−0.191	3.822	1.369	5.191	−0.191
N(2)	3.994	1.303	5.297	−0.297	3.836	1.355	5.191	−0.191	3.821	1.369	5.190	−0.190
C(1)	2.880	1.001	3.881	0.119	2.903	0.964	3.867	0.133	2.905	0.964	3.869	0.131
C(2)	3.018	1.043	4.061	−0.061	3.015	1.041	4.056	−0.056	3.012	1.048	4.060	−0.060
C(3)	2.928	0.950	3.878	0.122	2.903	0.964	3.867	0.133	2.905	0.964	3.869	0.131
C(4)	3.010	1.022	4.032	−0.032	3.018	1.020	4.038	−0.038	3.019	1.023	4.042	−0.042
C(5)	3.018	1.020	4.038	−0.038	3.018	1.020	4.038	−0.038	3.019	1.023	4.042	−0.042
H(1)			0.986	0.014			0.999	0.001			1.002	−0.002
H(2)			0.989	0.011			0.990	0.010			0.993	0.007
H(3)			1.010	−0.010			0.999	0.001			1.002	−0.002
H_N			0.853	0.147								
Mg							1.820	0.180			1.948	0.053
O											6.190	−0.190
H_O											0.792	0.208

[a] An excellent discussion of the basis of and the method for computing electron populations and net atomic charges with CNDO/2 wave functions is found in J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970, p 87. [b] The σ- and π-electron populations refer only to the basis orbitals of the porphine ring. [c] See Figure 1 for the numbering of the porphine atoms. H_N represents the inner-ring protons, while O and H_O represent the oxygen and hydrogen atoms of the water moiety, respectively. [d] The electron populations and net atomic charges of the in-plane magnesium porphine complex are almost identical with those listed for the out-of-plane magnesium porphine complex. The largest deviation occurs on the Mg(II) ion and amounts to an increase of 0.017 electron from the data shown in this table.

consistent with the MO structure obtained in the present study if it is assumed that removal of an electron from the HOMO of "$a_{1u}(\pi)$" symmetry does not significantly alter the MO structure. As discussed earlier, the "$a_{1u}(\pi)$" orbital does not have any electron population on the pyrrolic nitrogens or meso carbons. Hence, it follows that the unpaired electron of the cation radical [magnesium porphine+] remaining in this MO should show no isotropic hyperfine coupling with either the pyrrolic nitrogens or methine protons. This is found to be the case experimentally.[31,32] A similar experimental result has also been found for the cation radical of the free base of tetraphenyl porphine.[33] While the above experimental results do not definitively confirm the calculated MO ordering, they provide strong evidence as to the correctness of the present results.

The bonding picture in aquomagnesium porphine complexes is essentially the same as that found in the out-of-plane magnesium porphine complexes. As can be seen from Figure 2, the MO ordering is not

(33) A. Wolberg and J. Manassen, J. Amer. Chem. Soc., 92, 2982 (1970).
(34) T. Koopmans, Physica (Utrecht), 1, 104 (1933).

potential of the corresponding free base porphyrin. This is in reasonable agreement with the results of the present calculations. The present calculations also predict a slightly lowered ionization potential for the aquomagnesium porphine complex, and, as discussed previously, the ionized electron comes from the porphine ligand MO of "$a_{1u}(\pi)$" symmetry.

Electron Populations and Atomic Charges. The electron populations and net atomic charges of the different porphines investigated in the current study are given in Table V. These results are qualitatively similar to those obtained by Zerner and Gouterman for the free base porphine[18] and the out-of-plane magnesium porphine,[19] except that the electron population on Mg(II) obtained in the present study is about 0.4 larger. This may be due in part to the greater out-of-plane distance (0.65 Å) used by Zerner and Gouterman in their calculatons. A comparison of the net atomic charges between magnesium porphine and aquomagnesium porphine shows that very little change occurs due to the binding of water. In fact, the only change which occurred was almost entirely localized to the pyrrolic nitrogens.

Table VI indicates the net charge on the porphine

Table VI. Ring Charge and Ring to Metal Charge Transfer[a]

Moiety	Magnesium porphine (C_{4v})	Aquomagnesium porphine (C_{2v})
Mg(II)	0.180	0.053
Porphine ring	−0.180	−0.279
H₂O		0.226
Amount of charge transfer	Ring → Mg(II) = 1.820	Ring → Mg(II) = 1.722 H₂O → Mg(II) = 0.226

[a] The values obtained in this table were calculated from the data of Table V.

ring and the amount of ligand to metal charge transfer that takes place when Mg(II) is chelated. The relatively higher energy (*i.e.*, lower ionization potential) of the HOMO of aquomagnesium porphine relative to that of magnesium porphine, coupled with its more negative ring charge, would indicate a greater ease of one-electron oxidation for the aqueous complex. This is further substantiated by the relatively lower ring → Mg(II) charge transfer of the aqueous complex, which is consistent with a weaker inductive effect due to the Mg(II) ion.[35] As pointed out by Fuhrhop, Kadish, and Davis[36] in their extensive studies of the redox behavior of metalloporphyrins, there seems to be a direct correlation with the strength of the inductive effect of the central metal and the magnitude of the redox potential. This is also consistent with the fact that the "$a_{1u}(\pi)$" HOMO (see Figure 3) is completely nonbonding with the central Mg(II) ion. Hence, changes in the energy and electronic structure, due to Mg(II) chelation, of this MO must be brought about inductively. The inductive effect can take place either through interactions with other MO's which are bonding with respect to the Mg(II) ion or through interaction of the "$a_{1u}(\pi)$" orbital with the effective charge on the Mg(II) ion.

Calculations are now being carried out on several reduced magnesium porphines, more closely analogous to chlorophyll, to see whether the binding of water produces similar electronic effects.

Summary and Conclusions

The present calculations are in excellent agreement with available experimental data with respect to the ordering of the "$a_{1u}(\pi)$" and "$a_{2u}(\pi)$" orbitals. Pre-

(35) Note that the increased ring charge of the aqueous complex is localized primarily on the pyrrolic nitrogens as discussed above.
(36) J. Fuhrhop, K. M. Kadish, and D. G. Davis, private communication.

vious calculations have obtained an inverted ordering from that obtained in this work.

Of special interest is the large energy gap between the chemically interesting HOMO and HOMO-1 and the considerably more stable (*ca.* 3 eV) HOMO-2. Even though, as shown in Figure 2, considerable rearrangement of the lower lying MO's takes place, the relative order and energy spacing of the two high lying "$a_{1u}(\pi)$" and $a_{2u}(\pi)$" orbitals remains essentially unchanged.

It may be anticipated that a similar, although not necessarily as large, energy gap would be present in other metalloporphyrins, since mixing of the two widely separated sets of MO's would require extremely strong interactions with the central metal ion. As discussed by Gouterman and coworkers,[9–11,18] the great similarity of metalloporphyrin spectra is probably due to the weak interaction of the various metal orbitals with the π orbitals of the porphine ligands. The essential "isolation" of the "$a_{1u}(\pi)$" and "$a_{2u}(\pi)$" orbitals from the lower lying filled MO's would also explain the relative effectiveness of the four orbital model[10,11] in treating metalloporphyrin spectra. The inductive effect of the central metal ion on the redox behavior of metalloporphyrins is also consistent with the large calculated energy gap.

The calculated ionization potentials are in reasonable agreement with available experimental data. The small change observed experimentally when divalent cations are introduced is also consistent with the large calculated energy gap. Electron populations and net atomic charges are also in close agreement with other all valence electron calculations, except that the Mg(II) ion has a slightly lower positive charge indicating a less ionic character to the Mg(II)–ligand bond. The calculations on the aquomagnesium porphine complex predict similar properties for the aqueous complex, although the ionization potential and the oxidation potential would be lowered.