J. Am. Chem. Soc. 1992, 114, 9538-9544

Magnesium Porphyrin Radical Cations: A Theoretical Study of Substituent Effects on the Ground State

A. Geoffrey Skillman,† **Jack R. Collins,*** **and Gilda H. Loew**

Contribution from the Molecular Research Institute, 845 Page Mill Road,
Palo Alto, California 94304. Received November 7, 1991

Abstract: Semiempirical (INDO) calculations have been performed to investigate the effect of substituents on the nature of the π cation radical states for a series of meso- and β-substituted four-coordinated Mg porphyrins. In particular, the effect of these substituents in modulating whether the ground state is a $^2A_{1u}$ or $^2A_{2u}$ π cation radical was determined. The β substituents were found to preserve the $^2A_{1u}$ ground state of the unsubstituted porphine with a modest (±3 kcal/mol) effect on the relative energies of the $^2A_{1u}$ and $^2A_{2u}$ states. In contrast, the effect of the meso substituents was more pronounced, leading to the $^2A_{2u}$ ground state in some instances. The calculated state orderings are in good agreement with known experimental results. A balance between the π effects and σ effects of the substituents explains the modulation of the state energy orderings in these substituted Mg(II) porphyrins.

Introduction

The ubiquity of metalloporphyrins in nature and their significance in biological functions has led to a great interest in their physical properties. This macrocycle, particularly important in biological oxidation–reduction reactions, forms the core of all heme proteins, with cation radicals identified as intermediates in many catalytic cycles. Enzyme systems whose reactive centers contain a porphyrin include the photosynthetic reaction center, hemoglobin and myoglobin, and the numerous cytochromes.[1] The diversity of function of these systems is displayed by their participation in the primary photosynthetic process, oxygen transport, electron transport, and the metabolism of drugs and xenobiotics.[1-4] Furthermore, porphyrins and their structural variants are used in broad technological applications such as electrophotographic photoreceptors, air deodorants, pigment preparations, and cancer diagnostics.[5] Future molecular electronic devices used in memory or logic applications could rely specifically on "tuning" the electronic properties of porphyrins and their π cation radicals.[43] Thus, the unique properties of these systems are fundamental to many aspects of biology, chemistry, physics, and technology.

The core of all porphyin systems is the tetrapyrrolic macrocyclic porphine (Figure 1). The diverse physical, chemical, and spectroscopic properties of the porphyrins can be modulated by small changes in this macrocyclic system through substitution at the β and meso positions (Figure 1), although in the naturally occurring proto-, deutero-, and mesoporphyrins, shown in Chart I, only the β position is substituted. Changes in the electronic structure and properties of porphyrins caused by these modifications can be an important factor in determining their unique functions and their diverse uses.

The extreme ease with which porphyrins form stable π cation radicals during the course of oxidation–reduction reactions and the modulation of this ability play a central role in a number of biochemical processes that utilize the porphyrins.[1-4] For example, π cation radical formation is critical to the photooxidation of chlorophyll in which magnesium porphyrins act as a source of electrons in the photosynthetic cycle.[2] Oxidative metabolism involving such heme proteins as the catalases, peroxidases, and cytochrome P450s also proceed via formation of the highly oxidized porphyrin–iron–oxo (compound-I) radical cation species.[4]

Efforts to characterize the various reactive intermediates formed in heme proteins have focused on spectroscopic properties as measured by their UV–visible,[3,8] NMR,[9-11] EPR,[12-14] MCD,[15] XAFS,[16,17] ENDOR,[18-20] Mössbauer,[13,21,22] and resonance Raman[23-26] spectra as well as on X-ray structure studies of the intermediates themselves.[27] The results of these experimental studies reveal the presence of two π radical cation species with different spectroscopic properties, corresponding to removal of an electron from either of the two high-lying porphyrin π molecular orbitals, a_{1u} or a_{2u}.[2,3,8] For example, low-temperature studies of the optical–UV spectra of horseradish peroxidase compound-I reconstituted with different porphyrins[28] reported a $^2A_{2u}$ ground state for protoporphyrin–HRP and a $^2A_{1u}$ "catalase-like" ground state for deuteroporphyrin–HRP. Reconstitution with modified porphyrins also affects the function of HRP. Experiments with

---

† Present address: University of California, San Francisco, Medical School.

(1) Poulos, T. L., Finzel, B. C. *Pept. Protein Rev.* **1984**, *4*, 115–171.

(2) Dolphin, D.; Felton, R. H. *Acc. Chem. Res.* **1974**, *7*, 26–32.

(3) Dolphin, D.; Muljiani, Z.; Rousseau, K.; Borg, D. C.; Fajer, J.; Felton. *Ann. N. Y. Acad. Sci.* **1973**, *206*, 177–198.

(4) Dawson, J. H. *Science* **1988**, *240*, 433–439.

(5) See, for example, any recent issue of *CA SELECTS*: *Porphyrins*, published by Chemical Abstracts Service.

(6) Loew, G. H. Theoretical Investigations of Iron Porphyrins; In *Iron Porphyrins*; Lever, A. B. P., Gray, H. G., Eds.; Addison-Wesley: Reading, MA, 1983.

(7) *The Porphyrins. Physical Chemistry, Part A*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. III.

(8) Gouterman, M. Optical Spectra and Electronic Structure of Porphyrins and Related Rings; In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. III.

(9) Morishima, I.; Takamuki, Y.; Shiro, Y. *J. Am. Chem. Soc.* **1984**, *106*, 7666–7672.

(10) Godziela, G. M.; Goff, H. M. *J. Am. Chem. Soc.* **1986**, *108*, 2237–2243.

(11) La Mar, G. N.; de Ropp, J. S.; Latos-Grazynski, L.; Balch, A. L.; Johnson, R. B.; Smith, K. M.; Parish, D. W.; Cheng, R. *J. Am. Chem. Soc.* **1983**, *105*, 782–787.

(12) Beinert, H. *Biochem. Soc. Trans.* **1985**, *13*, 542–547. Palmer, G. *Biochem. Soc. Trans.* **1985**, *13*, 548–560.

(13) Rutter, R.; Valentime, M.; Hendrich, M. P.; Hager, L. P.; Debrunner, P. G. *Biochemistry* **1983**, *22*, 4769–4774.

(14) Fajer, J.; Davis, M. S. Electron Spin Resonance of Porphyrin π Cations and Anions; In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. III.

(15) Browett, W. R.; Stillman, M. J.: *Inorg. Chim. Acta* **1981**, *49*, 69–77.

(16) Kau, K.; Svastits, E. W.; Dawson, J. H.; Hodgson, K. O. *Inorg. Chem.* **1986**, *25*, 4307–4309.

(17) Chance, B.; Powers, L.; Ching, Y.; Poulos, T.; Schonbaum, G. R.; Yamazaki, I.; Paul, K. G. *Arch. Biochem. Biophys.* **1984**, *235*, 596–611.

(18) Roberts, J. E.; Hoffman, B. M.; Rutter, R.; Hager, L. P. *J. Am. Chem. Soc.* **1981**, *103*, 7654–7656.

(19) Roberts, J. E.; Hoffman, B. M.; Rutter, R.; Hager, L. P. *J. Biol. Chem.* **1981**, *256*, 2118–2121.

(20) Sandusky, P. O.; Salehi, A.; Chang, C. K.; Babcock, G. T. *J. Am. Chem. Soc.* **1989**, *111*, 6437–6439.

(21) English, D. R.; Hendrickson, D. N.; Suslick, K. S. *Inorg. Chem.* **1983**, *22*, 368–370.

(22) Münck, E. Mössbauer Spectra of Hemes; In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. IV.

(23) Mizutani, Y.; Hashimoto, S.; Tatsuno, Y.; Kitagawa, T. *J. Am. Chem. Soc.* **1990**, *112*, 6809–6814.

(24) Oertling, W. A.; Salehi, A.; Chang, C. K.; Babcock, G. T. *J. Phys. Chem.* **1989**, *93*, 1311–1319.

(25) Czernuszewicz, R. S.; Macor, K. A.; Li, X.-Y.; Kincaid, J. R.; Spiro, T. G. *J. Am. Chem. Soc.* **1989**, *111*, 3860–3869.

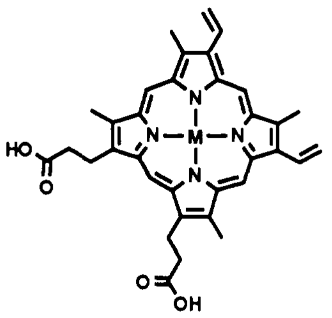
(26) Bangcharoenpaurpong, O.; Champion, P. M.; Martinis, S.; Sligar, S. *J. Chem. Phys.* **1987**, *87*, 4273.

(27) Edwards, S. L.; Xuong, N. H.; Hamlin, R. C.; Kraut, J. *Biochemistry* **1987**, *26*, 1503–1511.

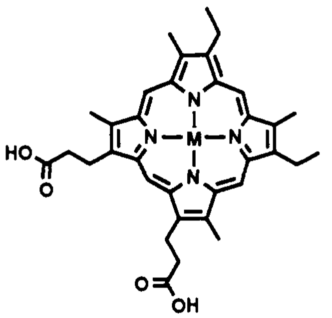
(28) DiNello, R. K.; Dolphin, D. *Biochem. Biophys. Res. Commun.* **1979**, *86*, 190–198.

0002-7863/92/1514-9538$03.00/0 © 1992 American Chemical Society

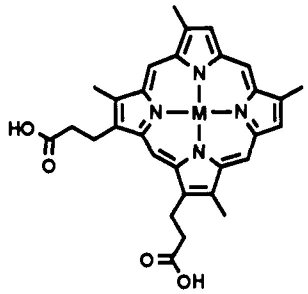
Chart I



Protoporphyrin IX



Mesoporphyrin IX



Deuteroporphyrin IX

modified heme groups[29] have shown that the enzymatic activity of HRP toward the oxidation of guaiacol decreased as the protoporphyrin was replaced by meso (92%), deutero (90%), monoester (18%), and diester (~0%) porphyrins.

Investigation of the effects of substituents on the electronic structure of porphyrin radical cations, independent of the effects induced by the protein, has been enhanced by the use of model compounds. Such systematic studies indicate that the substituents on the porphyrin ring are important factors in determining whether the ${}^2A_{1u}$ or ${}^2A_{2u}$ π cation radical will be formed.[2] For example, octaethylporphyrin (OEP) complexes with Mg(II) and Zn(II) form ${}^2A_{1u}$ π cation radicals, while tetraphenylporphyrin (TPP) complexes with these metals form ${}^2A_{2u}$ π cation radicals.[2,14] Evidence for these observations comes mainly from electron spin resonance (EPR) measurements. For example, tetraphenylporphyrin ($ZnTPP^{\bullet+}$) was also observed to have high spin density at the meso carbon with some delocalization onto the four phenyl groups.[14] EPR measurements for $Zn(OEP)^{\bullet+}$ revealed ~60% of the spin density on the α pyrrole carbons with the remainder split equally between the β and the meso carbons.[14] In addition, electronic spectra consistent with a ${}^2A_{1u}$ ground state have been observed for $[Mg^{II}OEP]^{\bullet+}ClO_4^-$ and $[Zn^{II}OEP]^{\bullet+}$, while a ${}^2A_{2u}$ ground state has been reported for $[Mg^{II}TPP]^{\bullet+}ClO_4^-$ and $[Zn^{II}TPP]^{\bullet+}ClO_4^-$.[2] EPR spectroscopy has shown $Zn(Me)_4P^{\bullet+}$ to have a ${}^2A_{2u}$ ground state with ~60% of the spin density on the meso carbons and ~30% on the nitrogens.[14] Similar results have been reported for other meso-substituted tetraalkylporphyrins.[14]

In addition to the ring substituents, several factors appear to determine the relative stability of the ${}^2A_{1u}$ vs ${}^2A_{2u}$ radical cations. Among these are the central metal[2] and variation of the fifth and sixth axial ligands.[14,30] Experiments with $[Co^{III}OEP]^{\bullet 2+}(Br^-)_2$ and $[Co^{III}OEP]^{\bullet 2+}(ClO_4^-)_2$ indicate that different counterions can also affect the ground state of these radical species, resulting in ${}^2A_{1u}$ and ${}^2A_{2u}$ states, respectively, when the central metal interacts strongly with the porphyrin orbitals.[38,39] Resonance Raman evidence[25] indicates that these two states can mix vibrationally in some transition-metal porphyrin systems, suggesting that the balance between these two states is quite delicate. Clearly, subtle interactions between several determinants moderate the ground state of the porphyrin radical cations.

Previous theoretical studies concerned with the effects of substituents on the a1u/a2u radical cation properties have been limited to IEHT calculations.[30] These calculations have mostly focused on the spin distribution in the porphyrin macrocycle and delocalization onto the substituents. More recent semiempirical[31] and ab initio[32] calculations on porphyrins have used the unsubstituted porphine macrocycle to model the electronic structure and properties of diverse porphyrins. In many of these cases, the ground state of the model porphine π cation (${}^2A_{1u}$) does not correspond to the experimentally determined one for the actual system of interest.[6,31] This discrepancy is often explained by the absence of porphyrin substituents in the porphine model. However, many electronic properties of interest are similar for the A_{1u} and A_{2u} states.[6]

In the study presented here, we have used the INDO/S semiempirical quantum mechanical method to systematically explore the effect of substituent variations on the relative stability of the ${}^2A_{1u}$ and ${}^2A_{2u}$ states of symmetrically substituted porphyrin π cation radicals. In order to focus on substituent effects, the coordinating metal, Mg(II), and the porphyrin macrocycle geometry were kept fixed and no axial ligands have been considered. To assess the reliability of the method to predict electronic properties of experimentally uncharacterized porphyrin systems, we have included compounds for which experiments have established the ground states. These are octaethylporphyrin (modeled here by $Mg^{II}P(CH_3)_8$), tetraphenylporphyrin ($Mg^{II}TPP$), and tetraalkylporphyrins (specifically $Mg^{II}P(CH_3)_4$), the first known to form ${}^2A_{1u}$ and the latter two ${}^2A_{2u}$ π cation radicals, respectively. In addition, experimental evidence suggests that the unsubstituted porphine forms the ${}^2A_{1u}$ radical cation.[40] To systematically investigate the electronic effects of various substituents on the stability of the ${}^2A_{1u}$ and ${}^2A_{2u}$ states, a series of porphyrins, symmetrically substituted with electron-withdrawing or -donating groups at either the meso or β positions, have been included in these calculations on the ground state of the radical cation.

Insights gained from these studies into the effect of substituents on the electronic properties and ground state of porphyrin cation radicals can be useful in three different ways: (1) for designing prosthetic groups with specific properties for use in reconstituted proteins and as model compounds; (2) for determining when unsubstituted porphine can be used to represent substituted analogues in theoretical studies, and (3) for selecting simple models that can be reliably used to mimic the effects of larger substituents found in heme proteins.

Methods

Semiempirical SCF calculations were performed to characterize the electronic structure and properties of a series of 11 symmetrically substituted Mg(II) porphyrins. Specifically, the effects

---

(29) Tamura, M.; Asakura, T.; Yonetani, T. *Biochim. Biophys. Acta* **1972**, *268*, 292–304.

(30) Fujita, I.; Hanson, L. K.; Walker, F. A.; Fajer, J. *J. Am. Chem. Soc.* **1983**, *105*, 3296–3300. Hanson, L. K. *Int. J. Quantum Chem. QBS* **1979**, *6*, 73–87.

(31) Loew, G. H.; Herman, Z. S.; Rohmer, M. M.; Goldblum, A.; Pudzianowski, A. *Ann. N. Y. Acad. Sci.* **1981**, *367*, 192–218. Edwards, W. D.; Weiner, B.; Zerner, M. C. *J. Am. Chem. Soc.* **1986**, *108*, 2196–2204. Edwards, W. D.; Zerner, M. C. *Can. J. Chem.* **1985**, *63*, 1763–1772. Axe, F. U.; Flowers, C.; Loew, G. H.; Waleh, A. *J. Am. Chem. Soc.* **1989**, *111*, 7333–7339. Waleh, A.; Ho, N.; Chantranupong, L.; Loew, G. H. *J. Am. Chem. Soc.* **1989**, *111*, 2767–2772.

(32) Yamamoto, S.; Kashiwagi, H. *Chem. Phys. Lett.* **1988**, *145*, 111–116. Yamamoto, S.; Teraoka; Kashiwagi, H. *J. Chem. Phys.* **1988**, *88*, 303–312. Dedieu, A.; Rohmer, M. M.; Veillard, A. *Adv. Quantum Chem.* **1982**, *16*, 43–95. Rawlings, D. C.; et al. *Int. J. Quantum Chem.* **1985**, *28*, 773, 797, 823. Ghosh, A.; et al. *Chem. Phys. Lett.* **1991**, *186*, 113.

(33) Timkovich, R.; Tulinsky, A. *J. Am. Chem. Soc.* **1969**, *91*, 4430–4432.

(34) Dewar, M. J. S.; Thiele, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899–4917. Stewart, J. J. P. MOPAC(5.0).

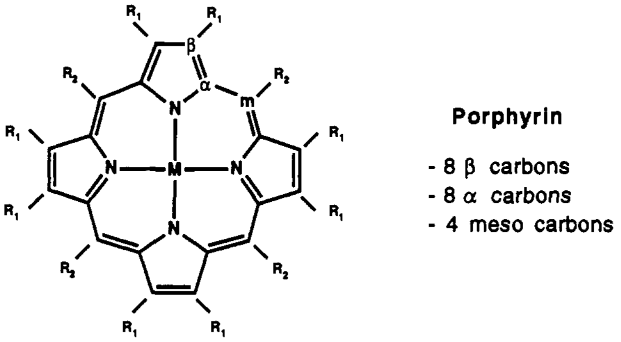
(35) Unpublished data.

(36) Ridley; Zerner, M. C. *Theor. Chim. Acta* **1976**, *42*, 223. Bacon, A.; Zerner, M. C. *Theor. Chim. Acta* **1979**, *53*, 21.

(37) Edwards, W. D.; Zerner, M. C. *Theor. Chim. Acta* **1987**, *72*, 347.

(38) Setsune, J.; Ikeda, M.; Kishimoto, Y.; Kitao, T. *J. Am. Chem. Soc.* **1986**, *108*, 1309.

(39) Gasyna, Z.; Browett, W. R.; Stillman, M. J. *Inorg. Chem.* **1988**, *27* 4619.



Porphine	R_1	R_2
MgP	H	H
Meso-Substituents		
MgP(NH2)4	H	NH2
MgP(C6H5)4	H	Phenyl
MgP(OH)4	H	OH
MgP(CH3)4	H	CH3
MgP(Cl)4	H	Cl
MgP(CN)4	H	CN
Beta-Substituents		
MgP(NH2)8	NH2	H
MgP(OH)8	OH	H
MgP(CH3)8	CH3	H
MgP(Cl)8	Cl	H
MgP(CN)8	CN	H

Figure 1. Nomenclature and substitution patterns of the 12 porphyrin systems studied here. All substituents were symmetrically substituted at either R_1 or R_2. $MgP(C_6H_5)_4$ is also commonly called MgTPP.

Table I. Porphyrin Core Geometry Used for All Complexes Studied

geometric parameter	value
rMg–N	2.05 Å
rN–C_α	1.38 Å
$r C_\alpha$–C_β	1.43 Å
∠Mg–C_m	3.45 Å
∠Mg–N–C_α	126:9°
∠N–C_α–C_β	109.9°

of ring substituents on the parent complex and the ground and first excited states of the Mg porphyrin radical cations were calculated. Two types of substituted rings were included: those fully substituted at the four meso carbons and those fully substituted at the eight β carbons (Figure 1). Five meso-($Mg(P)(X)_4$) compounds and the corresponding five β-($Mg(P)(X)_8$) compounds with the same substituents were included in this study with P = porphyrin and X = NH_2, OH, CH_3, Cl, and CN. In addition, porphine- and mesotetraphenylporphyrin (TTP) were also studied.

The core geometry of all of the model complexes studied here was based on the crystal structure[33] of [Mg(tetraphenylporphyrin)(aquo)•]$^+$, with the macrocycle regularized to have D_{4h} symmetry and the Mg atom moved into the plane of the ring (Table I). This model porphine core was used for all calculations, thus excluding the possible effect of macrocycle geometry on the electronic structure. The geometries of the substituted porphyrins were obtained by constrained optimizations using MNDO,[34] with only the structural parameters associated with the substituents allowed to optimize for each of the compounds. Beryllium was used as the central metal atom in these optimizations since MNDO does not contain parameters for Mg. Since a frozen macrocycle geometry was maintained during the optimizations, the substitution of Be for Mg should not significantly affect the resulting substituent geometries. For all compounds other than MgTPP, all non-hydrogen substituent atoms were forced to remain in the plane of the porphine ring, thus maintaining C_4 or C_{4v} symmetry. The resulting geometry was used for the neutral and radical cation calculations.

The ground- and excited-state electronic properties of the porphyrins were calculated using the INDO/S semiempirical method.[36,37] Self-consistent field (SCF) calculations were performed for each neutral compound and the corresponding $^2A_{1u}$ and $^2A_{2u}$ radical cations. The ROHF formalism[37] included in the program ZINDO was used for the open-shell calculations. The calculations were performed using C_{2v} and C_2 symmetries. Upon addition of substituents to the porphine macrocycle, the $^2A_{2u}$ and $^2A_{1u}$ states of porphine reduce to $^2A_1$ and $^2B_2$, respectively, for compounds possessing C_{2v} symmetry and to ^2A and ^2B for those possessing only a C_2 axis, e.g., MgTPP. However, as a convention, we have retained the $^2A_{1u}$ and $^2A_{2u}$ symmetry labels for all complexes studied, with the porphyrin macrocycle lying in the xy plane. Since the two states are in different representations in each of the point groups, the SCF formalism can be used to calculate the energy difference between the states for each of the different substituted porphryins. Calculations were considered to be converged when the energy difference between successive SCF cycles fell below 10^{-7} hartree. In all cases, the $^2A_{1u}$ and the $^2A_{2u}$ porphyrin cation radical states were found to be either the ground or first excited states.

The π and σ effects of each substituent were determined using the neutral, closed-shell, electronic properties of each substituted porphyin. The total π electron population (Table II; "total π") of the porphyrin macrocycle for each substituted porphyrin was compared with that of porphine to determine the π' effect of each substituent:

$$\pi_{\text{substituent}} = \sum\pi(C_\alpha,C_\beta,C_m,N,Mg)_{\text{substituted porphyrin}} - \sum\pi(C_\alpha,C_\beta,C_m,N,Mg)_{\text{porphine}} \quad (1)$$

The σ effect of each substituent was calculated from the change in the electron population of the σ orbitals (p_x,p_y,s) for the single carbon atom at which the substituents were attached (Table II, "σ") compared to the value for porphine.

$$\sigma_m = \sum\sigma_m(p_x,p_y,s)_{\text{meso-substituted porphyrin}} - \sum\sigma_m(p_x,p_y,s)_{\text{porphine}} \quad (2)$$

$$\sigma_\beta = \sum\sigma_\beta(p_x,p_y,s)_{\beta\text{-substituted porphyrin}} - \sum\sigma_\beta(p_x,p_y,s)_{\text{porphine}} \quad (3)$$

Multivariate regression analyses were performed separately for the meso-substituted and β-substituted porphyrins with the calculated energy differences $\Delta E = E(^2A_{2u}) - E(^2A_{1u})$ used as the dependent variable and the π and σ parameters used as the independent variables.

Results

Figure 2 depicts a representation of the a_{1u} and a_{2u} orbital densities for neutral, closed-shell, Mg porphine. Each scaled circle represents the magnitude of orbital density at its corresponding atom, and the shading represents the phase of the atomic orbital.

Table II lists the detailed results of calculations for each of the neutral parent substituted porphyrin systems studied and their $^2A_{2u}$ and $^2A_{1u}$ π cation radicals. The meso- and β-substituted porphyrins are each listed in order of decreasing relative stability of the $^2A_{2u}$ state. The column labeled "total π" gives the total number of electrons in the porphyrin π system, calculated from the Mulliken population analysis. The next five columns give the individual π electron densities of each of the atoms in the porphyrin macrocycle and Mg. The three columns labeled "σ" list the total σ electron densities for the carbon atoms in the macrocycle. The sum of the σ and π electron densities correspond to the total electron densities, and hence the charge, for C_m, C_α, and C_β. In the last four columns are the a_{2u} and a_{1u} orbital energies of the neutral parent compounds and the energy differences between the $^2A_{2u}$ and $^2A_{1u}$ π cation radical states, calculated by two different

---

(40) M. J. Crossley, private communication.

(41) Atamian, M.; Wagner, R. W.; Lindsey, J. S.; Bocian, D. F. *Inorg. Chem.* **1988**, *27*, 1510.

Table II. Calculated Electron Densities[a] and Orbital Energies of the Neutral Parent Porphyrins and the Relative Energies of the Resulting π Cation States

		porphyrin π					σ			orbital energies[b]		Δ energy	
compd	total π	Mg	N	C_m	C_α	C_β	C_m	C_α	C_β	a_{2u}	a_{1u}	ΔSCF[c]	$\Delta\epsilon$[d]
porphine	25.997	0.217	1.485	1.024	0.950	1.018	3.036	2.918	3.054	−0.249 07	−0.234 95	8.42	8.85
(NH2)4	26.303	0.235	1.476	0.973	1.004	1.030	2.907	2.881	3.050	−0.214 75	−0.238 73	−14.94	−15.03
TPP	26.065	0.225	1.478	0.980	0.979	1.022	3.000	2.900	3.056	−0.231 15	−0.238 89	−5.48	−4.85
(OH)4	26.147	0.223	1.486	0.995	0.983	1.017	2.818	2.888	3.052	−0.236 58	−0.242 60	−3.82	−3.78
(CH3)4	26.070	0.226	1.478	0.987	0.976	1.022	3.005	2.901	3.055	−0.233 93	−0.236 03	−2.01	−1.32
(Cl)4	26.043	0.207	1.498	1.057	0.949	1.003	2.820	2.890	3.055	−0.271 54	−0.256 92	8.56	9.17
(CN)4	25.867	0.199	1.491	1.046	0.937	1.003	2.897	2.918	3.056	−0.278 59	−0.264 80	9.33	8.65
(CN)8	25.838	0.202	1.478	0.995	0.949	1.014	3.042	2.907	2.913	−0.299 67	−0.290 88	5.22	5.51
(Cl)8	26.093	0.205	1.493	0.995	0.963	1.029	3.038	2.876	2.823	−0.287 04	−0.278 66	5.31	5.25
(OH)8	26.308	0.212	1.500	1.022	0.970	1.031	3.031	2.896	2.794	−0.252 28	−0.240 30	7.68	7.51
(NH2)8	26.501	0.217	1.504	1.047	0.968	1.042	3.022	2.903	2.877	−0.234 65	−0.220 56	9.69	8.83
(CH3)8	26.150	0.218	1.491	1.036	0.958	1.020	3.031	2.914	2.997	−0.242 27	−0.225 64	10.58	10.43

[a] Electron density values given in electrons. [b] Orbital energies of the a_{2u} and a_{1u} orbitals of the neutral parent compounds given in hartrees. [c] $\Delta\text{SCF} = E(^2A_{2u}) - E(^2A_{1u})$ calculated for each radical cation, in units of kcal/mol. A negative value indicates a $^2A_{2u}$ ground state. [d] $\Delta\epsilon = \epsilon(a_{2u}) - \epsilon(a_{1u})$ for neutral parent system, given in units of kcal/mol.

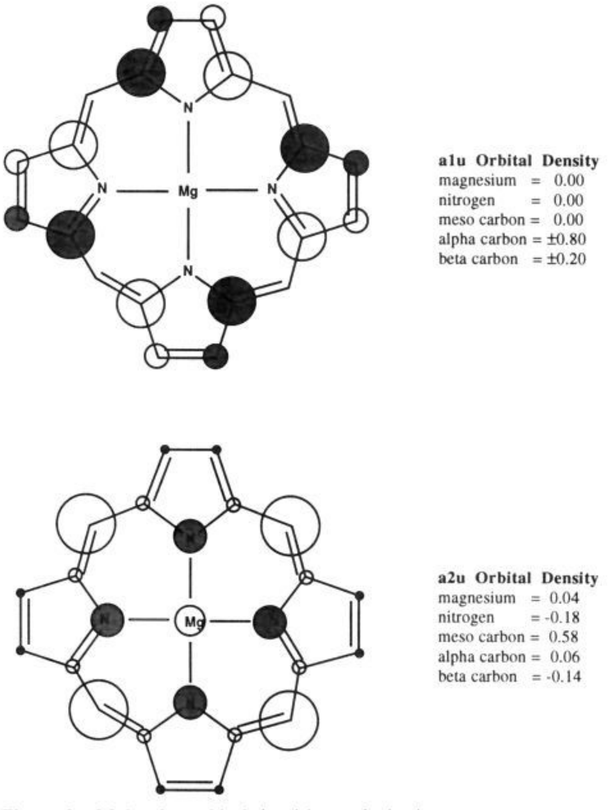


Figure 2. Molecular orbital densities and phasing of the a_{1u} and a_{2u} orbitals of neutral Mg porphine are shown. The circles are proportional to the square of the orbital coefficients at each atom. (The values given for the orbital densities were calculated as $\sum_i c_i^2$, where c_i is the atomic orbital coefficient and the summation includes all atoms of the group specified (e.g., all meso carbons). The signs for the phases were retained from the molecular orbital coefficients.)

methods. The column labeled ΔSCF gives the energy differences between the $^2A_{2u}$ and $^2A_{1u}$ states of the π cation radicals obtained from the restricted open-shell calculations. The last column lists the difference ($\Delta\epsilon$) between the a_{1u} and a_{2u} orbital energies of the neutral parent, which is an estimate of the energy difference between the two states assuming a "frozen orbital" (Koopmann's) approximation. The extent to which the values of $\Delta\epsilon$ and ΔSCF are different indicates the extent of orbital relaxation in the ionization process of forming the π cation radical from the neutral parent.

Table III lists the spin density distribution in the $^2A_{2u}$ and $^2A_{1u}$ states calculated for each compound. Specifically, the total spin density on the pyrrole nitrogens, on the meso, α, and β carbons, and on the substituents are given.

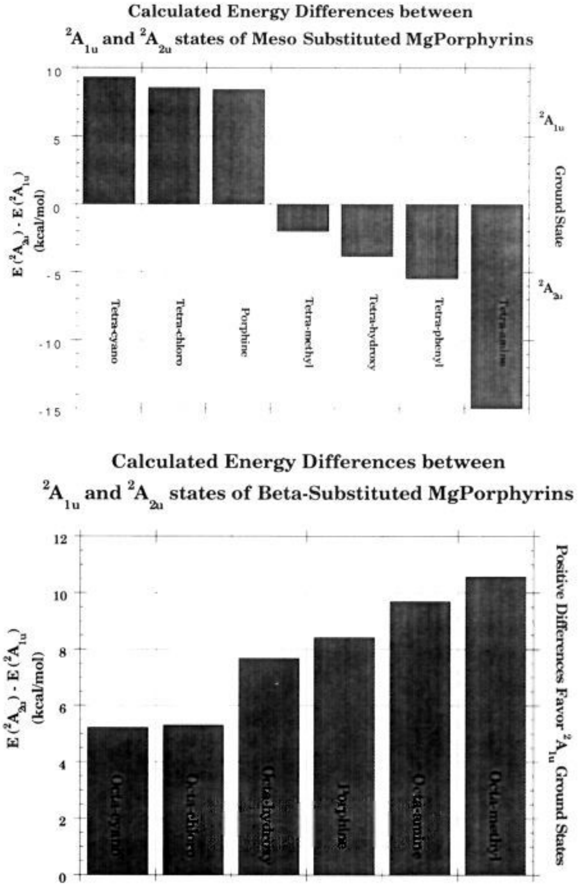


Figure 3. Graphical representation of the relative energy differences between the $^2A_{1u}$ and $^2A_{2u}$ π cation radical states for the meso (a) and β (b) substituents. Positive values indicate a $^2A_{1u}$ ground state, while a $^2A_{2u}$ ground state corresponds to a negative value.

Figures 3a and 3b show the trends in the $^2A_{1u}/^2A_{2u}$ state energy differences for the meso- and β-substituted porphyrins, respectively. Figure 4 shows plots of the calculated state energy differences versus those predicted from the regression analysis for the meso (4a) and β (4b) substituents. The final equations derived from the regression analysis are

$$\Delta E(\pi,\sigma) = -58.9\pi - 41.3\sigma - 1.95\ \text{kcal/mol} \quad \text{(meso)} \quad (4)$$

$$\Delta E(\pi,\sigma) = 8.6\pi + 22.6\sigma + 10.1\ \text{kcal/mol} \quad (\beta) \quad (5)$$

and have r^2 values of 0.92 and 0.93, respectively, for the meso and β substituents. These values correspond to 97 and 93% confidence levels, as defined by the F test with each variable being >90% significant by the Student t test.

Table III. Spin Density on Porphyrin Ring Atoms and Substituents in the $^2A_{1u}$ and $^2A_{2u}$ Cation Radical States of Substituted Mg^{2+} Porphyrins

unsubstituted Mg Porphine	N	subst	C_m	C_α	C_β
	0.19/0.00	0.00/0.00	0.61/0.00	0.05/0.80	0.12/0.20

meso-substituted compds	n $^2A_{2u}/^2A_{1u}$	subst $^2A_{2u}/^2A_{1u}$	C_m $^2A_{2u}/^2A_{1u}$	C_α $^2A_{2u}/^2A_{1u}$	C_β $^2A_{2u}/^2A_{1u}$
$MgP(NH_2)_4$	0.14/0.00	0.16/0.00	0.49/0.00	0.08/0.80	0.10/0.20
$MgP(C_6H_5)_4$	0.07/0.00	0.17/0.01	0.54/0.00	0.07/0.79	0.11/0.20
$MgP(OH)_4$	0.06/0.00	0.17/0.00	0.56/0.00	0.06/0.81	0.11/0.19
$MgP(CH_3)_4$	0.04/0.00	0.18/0.00	0.57/0.00	0.06/0.80	0.10/0.20
$MgP(Cl)_4$	0.17/0.00	0.03/0.00	0.60/0.00	0.05/0.81	0.13/0.19
$MgP(CN)_4$	0.16/0.00	0.12/0.00	0.54/0.00	0.04/0.81	0.11/0.19

β-substituted compds	N $^2A_{2u}/^2A_{1u}$	subst $^2A_{2u}/^2A_{1u}$	Cm $^2a_{2u}/^2A_{1u}$	C_α $^2A_{2u}/^2A_{1u}$	C_β $^2A_{2u}/^2A_{1u}$
$MgP(CN)_8$	0.19/0.00	0.03/0.05	0.59/0.00	0.05/0.76	0.12/0.19
$MgP(Cl)_8$	0.18/0.00	0.01/0.01	0.60/0.00	0.05/0.80	0.13/0.19
$MgP(OH)_8$	0.15/0.00	0.02/0.02	0.59/0.00	0.04/0.82	0.18/0.16
$MgP(NH_2)_8$	0.10/0.00	0.07/0.05	0.54/0.00	0.03/0.82	0.24/0.13
$MgP(CH_3)_8$	0.16/0.00	0.01/0.02	0.60/0.00	0.04/0.81	0.16/0.17

Discussion

To assess the reliability of the INDO method implemented by Zerner and co-workers, we have included four systems that have been experimentally characterized. In all cases, the calculated results are consistent with experiment. Porphine has been suggested to have a $^2A_{1u}$ ground state by studies of the reactivity of the oxidized system.[40] Our calculations result in the $^2A_{1u}$ ground state that is 8.4 kcal/mol more stable (Table II) than the $^2A_{2u}$ state for the regularized X-ray geometry of Mg(II) porphine given in Table I. For the substituted porphyrins, octamethylporphyrin is calculated to have a $^2A_{1u}$ ground state. This result can be compared with the octaethyl compound $Mg^{II}OEP^{\bullet+}$ considered the prototypical $^2A_{1u}$ radical cation,[2,14] since the effect of methyl and ethyl substituents should be very similar. Experimental studies have shown that the $Mg^{II}TPP$ π cation radical has an $^2A_{2u}$ ground state.[2,14] Our calculations are consistent with these results and predict the $^2A_{2u}$ state to be more stable by 5.5 kcal/mol for the $Mg^{II}TPP$ radical cations (Table II). Finally, $Mg^{II}P(C_3H_7)_4$ is known to have a $^2A_{2u}$ ground state,[2] and our results for $Mg^{II}P(CH_3)_4$ are consistent, with the $^2A_{2u}$ radical cation calculated to be more stable by 2.0 kcal/mol, since the larger alkyl chain is not expected to have a significant effect on the electronic properties of the system. This assumption is reinforced by the observation that $Zn^{II}P(CH_3)_4$ π cation radicals have $^2A_{2u}$ ground states[14] and that Zn and Mg porphyrin complexes yield similar results for the tetraphenyl- and octaethylporphyrin complexes. These results provide evidence that the method correctly predicts the effects of known substituents on the ground state of the cation radicals and should produce reliable results in predicting the effects of other substituents on these properties.

Porphine has often been used as a simple model for many substituted porphyrin compounds. In the present analysis, the unsubstituted Mg(II) porphine is used as the standard for comparing the properties of all of the substituted porphyrins. Therefore, electronic effects affecting the relative energies of the $^2A_{1u}$ and $^2A_{2u}$ π cation radical states, induced by the substituents, will be deduced by comparing the electronic properties of the substituted porphyrins with those of porphine.

As seen in Figure 3, substituents can significantly modulate the relative energies of the $^2A_{1u}$ and $^2A_{2u}$ states of the Mg(II) porphyrin π cation radicals. For each of the β-substituted compounds (Figure 3b), the $^2A_{1u}$ state remains the ground state, with the relative energy of the $^2A_{2u}$ state varying by ±3 kcal/mol compared to porphine. Interestingly, of all the β-substituted complexes in this study, the methyl substituent causes the greatest stabilization of the $^2A_{1u}$ state relative to $^2A_{2u}$. These results suggest that it may not be necessary to explicitly include substituents in theoretical studies if the system is symmetrically substituted only at the β position.

In contrast to the β-substituted complexes, meso substitution induces a larger perturbation on the magnesium porphyrins, with the calculated π cation ground state depending heavily on the substituent (Figure 3a). Specifically, for all but the most electron-withdrawing substituents, we find a $^2A_{2u}$ ground state for the meso-substituted porphyrins. This is consistent with recent experiments that show that many meso-substituted porphyrins, even alkyl/aryl hybrids, result in $^2A_{2u}$ π cation radicals. Most important for theoretical calculations, these results indicate that porphine is not a good model for meso-substituted porphyrins if properties that explicitly depend on the detailed nature of the ground-state π cation radical are of interest. One such property is the location of the unpaired spin density in these π cation radicals.

We see from Table III that the calculated unpaired spin density on the substituents is significantly only in the $^2A_{2u}$ ground state

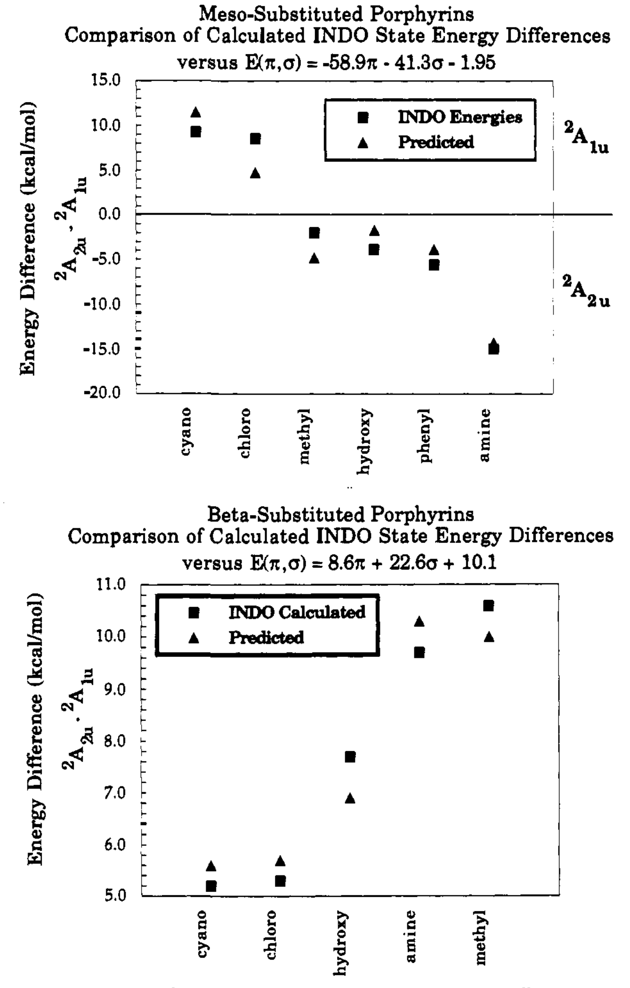


Figure 4. Graphical comparison of the quantum mechanically calculated values of the relative energy differences between the $^2A_{2u}$ and $^2A_{1u}$ π cation radical states (■) and those predicted from the regression analysis (▲) for the meso- and β-substituted porphyrins, respectively.

for meso-substituted porphyrins and that the β-substituted compounds show much less delocalization onto the substituents. These results are consistent with observed hyperfine interactions[14] between alkyl and phenyl substituents and the porphyin ring in EPR experiments of meso-substituted porphyrin π cations, each calculated to have $^2A_{2u}$ ground states. Our results are also consistent with the exceedingly small unpaired spin densities observed[14] on the pyrrole N and substituents for $Mg(OEP)^{\bullet +}$, which we find to have a $^2A_{1u}$ ground state. However, our results do not explain the anomalous spin density on the four meso carbons reported for the EPR experiments on $Mg(OEP)^{\bullet +}$, since, as seen in Figure 1, the a_{1u} orbital has no calculated density on the pyrrole nitrogens of meso carbons. Further, experimental studies to clarify the origin of this spin density in octaethylporphyrin systems has led to inconclusive results.[20,39] Therefore, the origin of these anomalous signals is still not clear in this case.

To understand the origin of the energy differences between the $^2A_{1u}$ and $^2A_{2u}$ π cation radical states induced by the substituents, we have compared the electronic properties of each of the substituted porphyrins with porphine. As shown in Table II, the energy difference between the $^2A_{2u}$ and $^2A_{1u}$ states (ΔSCF) of the π cation radicals closely parallels the relative energies of the highest occupied a_{1u} and a_{2u} orbitals of the neutral parent compound (Δε), indicating that orbital relaxation effects are small in Mg(II) porphyrins. Thus, substituent modulation of the relative a_{1u} and a_{2u} orbital energies in the parent compound appears to be a reliable indicator of the relative $^2A_{1u}$ and $^2A_{2u}$ state energies of the π cation radical. The ability of substituents to perturb the a_{1u} and a_{2u} π molecular orbitals of the porphyrin macrocycle can be manifest in two distinct ways: (1) a σ effect of the substituents can modify the effective nuclear charge felt by the porphyrin π orbitals and (2) substituent π electrons can delocalize into the porphyrin π orbitals and modify the electron distribution and orbital energies. The combined effects of these two types of perturbations should determine the relative stability of the highest occupied a_{1u} and a_{2u} orbitals and, hence, the ground state of the π cation radical.

A quantitative measure of both the π and σ effects has been developed to understand the changes induced by the substituents. Using eq 1, the change in the total π electron density on the porphyrin macrocycle upon substitution has been calculated for each complex. The σ effect of each substituent, measured as the change in electron density in the σ orbitals of the porphyrin atom with the substituent attached, has also been calculated using eqs 2 and 3. Table II lists the electron densities for the σ and π systems, used in eqs 1–3, of porphine and the substituted porphyrins. The ability of the changes in the π and σ electron densities to account for the relative energy differences of the $^2A_{1u}$ and $^2A_{2u}$ π cation radical states has been evaluated for performing separate multivariate linear regression analyses with the meso- and β-substituted porphyrins.

As shown in the results, the final equations derived from the regression analysis for the meso- (eq 4) and β- (eq 5) substituted complexes have a very good correlation between the calculated energy differences and the properties chosen to determine the π and σ effects of both types of substituents. The regression analyses yield a correlation between the π and σ electronic effects and the state energy differences that is statistically (>93%) significant for both the meso- and β-substituted cases. Further, both variables (π and σ) are needed to achieve this correlation. Figures 4a and 4b show the calculated energy differences between the $^2A_{1u}$ and $^2A_{2u}$ π cation radical states for the meso- and β-substituted porphines compared with those predicted by the corresponding equations (eqs 4 and 5). As can be seen from Figure 4, the regression equations, using calculated changes in the π and σ systems of the substituted neutral porphyrins, clearly reflect the overall trend in the calculated differences in state energies for the radical cations, indicating that the relative energies of the π cation radicals are modulated by these properties.

Meso substituents that increase the π electron density on the porphyrin tend to destabilize the a_{2u} orbital, thus favoring the $^2A_{2u}$ state. This effect is manifest in the regression results by a large negative coefficient for the π effect in the meso-substituted porphyrins. Electron donation to the porphyrin ring tends to destabilize the π orbitals due to increased electron repulsion between the porphyrin ring electrons and the substituents. The meso substituents have a large effect because of the large electron density of the a_{2u} orbital at the meso positions.

For the β-substituted porphyrins, the π interactions affect both the a_{1u} and a_{2u} orbitals (Table II), since each orbital has some small density at this position. Thus, the π interaction is not as strong for the β, compared to the meso, substituents. The small coefficient of the π effect in the regression analysis is consistent with the smaller π electron density at the beta position, and the positive sign indicates that substituents that donate electrons to the porphyrin π system preferentially destabilize the a_{1u} orbital, stabilizing the $^2A_{1u}$ ground state.

The σ effect induced by the substituents is due to their electrophilicity compared to the H atom in porphine. As seen in Table II, substituents containing electronegative atoms, such as CN, Cl, NH_2, and OH, tend to significantly decrease the σ electron density at the substituted position in the macrocycle. The resultant increase in effective nuclear charge stabilizes both the a_{1u} and a_{2u} orbitals, with respect to porphine, to varying degrees. This effect is reflected in the regression equations. The negative coefficient for the σ term in eq 4 and the positive coefficient in eq 5 indicate that electron withdrawal stabilizes the $^2A_{2u}$ state in the β- and the $^2A_{1u}$ state in the meso-substituted cases.

As evidenced by the regression equations, the calculated state energy differences depend on the combined magnitudes and effects of both the σ and π interactions. The π effects are most important when the substituent is at the meso carbon, as evidenced by the larger π coefficient with respect to the σ coefficient in the regression equation. As expected from the orbital densities, the σ effects are more dominant for the β substituents. Based on these results, we would predict that porphyrins symmetrically substituted at both the meso and β positions, such as Mg^{II} octachlorotetraphenylporphyrin, would greatly favor the $^2A_{2u}$ radical cation ground state. Experimental evidence from Zn^{II}octabromotetraphenylporphyrin[42] appears to confirm this prediction. Further evidence comes from tetraphenyl porphyrins singly substituted at the β position with different substituents.[43] Therefore, it appears that the ground state of these porphyrins can be preferentially selected by appropriate substitution at the meso and β positions.

In summary, meso substituents primarily affect the a_{2u} orbital and show little effect on the a_{1u} porphyrin π molecular orbital due to a symmetry node through the meso carbon. This difference is reflected in the lack of unpaired spin density on the meso substituent atoms in the $^2A_{1u}$ states and the significant spin density found on these atoms in the $^2A_{2u}$ states (Table III). For $Mg^{II}P(CN)_4$ and $Mg^{II}P(Cl)_4$, both the σ and π effects favor stabilizing the a_{2u} orbital over the a_{1u}, leading to these two complexes being the only meso-substituted compounds to have $^2A_{1u}$ ground states. For the β substituents, the interaction with the π system is via both the a_{1u} and a_{2u} orbitals, which have small orbital coefficients at this position. As a result, we expect π perturbation due to the C_β substituents to be, in general, smaller than that due to the meso substituents, leaving the ground state unchanged from the unsubstituted porphine. Finally, the regression analysis including the π and σ effects of the substituents on the relative state energies of the π cation radicals are able to simulate the calculated energy differences very well. In addition, this analysis also explains the physical origin of the π and σ effects of the substituents in modulating the ground states of the π cation radicals.

Conclusion

Semiempirical (INDO) calculations have been performed to investigate the effect of substituents on the nature of the π cation radical states for a series of meso- and β-substituted four-coordinated Mg porphyins. The method was found to agree with those

---

(42) Bhyrappa, P.; Krishnan, V. *Inorg. Chem.* **1991**, *30*, 239.

(43) Binstead, R. A.; Crossley, M. J.; Hush, N. S. *Inorg. Chem.* **1991**, *30*, 1259.

systems where the ground state of the π cation radical has been experimentally determined. The method was then used to determine the effect of substituents in cases where the ground state is unknown. Meso substituents that are electron donating lead to a $^2A_{2u}$ ground state, while those that are electron withdrawing lead to a $^2A_{1u}$ ground state. The β-substituted porphyrins maintained the $^2A_{1u}$ π cation radical ground state of the unsubstituted porphine and have a smaller effect on the relative energies of the $^2A_{1u}$ and $^2A_{2u}$ states compared to the meso substituents. Multivariate linear regression analyses, reflecting basic electronic principals, indicate that a balance between π effects, which tend to destabilize the a_{2u} and a_{1u} orbitals, and σ effects, which generally stabilize the orbitals, can explain the state energy orderings of the substituted Mg(II) porphyrins studied here. These states can be distinguished by experimental techniques such as NMR, EPR, and ENDOR that monitor the extent of unpaired spin on the substituents and porphyrin ring atoms. Since protoporphyin IX, the most commonly occurring porphyrin group in endogenous heme proteins, does not have meso substituents but has only β substituents, as do all the other naturally occurring porphyrins found in heme proteins, it would be expected to form $^2A_{1u}$ π cation states in the four-coordinate Mg(II) case. However, substitution of Fe for Mg and addition of axial ligands can be further modulators of these states and can lead to different ground states and properties. Future studies will address the role of these additional factors in determining the nature and selective stability of their π cation states.

Acknowledgment. We would like to thank Drs. Ping Du and Jack Fajer for helpful discussions during the course of this study. Support from the National Science Foundation (Grant No. DMB-9096181) for this work is gratefully acknowledged.

Ab-Initio Calculations on Vibronic Coupling in the Lower Triplet States of Pyrimidine

W. J. Buma,*,† M. C. J. M. Donckers,‡ and E. J. J. Groenen*,‡

Contribution from the Chemistry Department, University of California, Riverside, California 92521, and Center for the Study of Excited States of Molecules, Huygens Laboratory, University of Leiden, P.O. Box 9504, 2300 RA Leiden, The Netherlands.

Received February 28, 1992

Abstract: Ab-initio calculations at the UHF and CASSCF levels have been performed in which the geometry of pyrimidine in the $^3B_1(n\pi^*)$, $^3A_2(n\pi^*)$, and $^3A_1(\pi\pi^*)$ states has been optimized. The calculations clearly demonstrate the influence of vibronic coupling on the molecular and electronic structure of the molecule in these states. For the $n\pi^*$ states, conformations corresponding to minimum energy are found that deviate significantly from planar. For the $^3A_1(\pi\pi^*)$ state, vibronic coupling similar to that between the $^3B_{1u}$ and $^3E_{1u}$ states of benzene has been found. From the calculations, we deduce a dynamic out-of-plane distortion of the molecule in the $^3B_1(n\pi^*)$ state, which provides for a coherent description of the results of optical and magnetic-resonance data available for the lowest triplet state of pyrimidine. The out-of-plane distortions occurring in the $^3B_1(n\pi^*)$ and $^3A_2(n\pi^*)$ states conform to the increased antibonding character of the π-electron system upon $n\pi^*$ excitation.

Introduction

The class of azaaromatic molecules distinguishes itself from the hydrocarbon analogues by the presence of one or more nitrogen atoms in the conjugated system. The introduction of these nitrogen atoms leads to the occurrence of $n\pi^*$ excited states and modifies the electronic properties of the $\pi\pi^*$ excited states as compared to those of their hydrocarbon parent compounds. Extensive experimental and theoretical studies have been performed to characterize the low-lying excited states of azaaromatic compounds, as amply illustrated in a recent review.[1] For many such molecules, vibronic coupling has been invoked between $n\pi^*$ and $\pi\pi^*$ states as well as among $\pi\pi^*$ states in order to describe the properties of the excited states.

For pyridine, the simplest azaaromatic molecule, such studies have been problematic for a long time owing to its unfavorable emissive characteristics. Recently, we were able to unravel in great detail the molecular and electronic structure of pyridine in the lowest triplet state ($^3B_1(n\pi^*)$) by the application of electron spin echo (ESE) spectroscopy[2-5] and by ab-initio calculations.[6] From the observed nitrogen and deuterium hyperfine interactions, it was found that pyridine upon excitation adopts a boatlike structure in which the nitrogen and the para-carbon atoms are tilted by about 40 and 10°, respectively, with respect to the plane spanned by the ortho- and meta-carbon atoms. The nonplanar structure could be rationalized in terms of a strong vibronic coupling between the $^3B_1(n\pi^*)$ and $^3A_1(\pi\pi^*)$ states. In agreement with the vibronic coupling picture, the observed spin-density distribution reflected a state of both $n\pi^*$ and $\pi\pi^*$ character.

The experimentally determined molecular structure has subsequently beautifully been confirmed by theoretical studies performed by Nagaoka and Nagashima[7] and by us.[6] From our calculations, we concluded that the observed distortion could, besides in terms of vibronic coupling, be considered in terms of the increased antibonding character of the π-electron system upon $n\pi^*$ excitation. This suggested that the π^* orbital involved in the excitation might determine the character of the geometry relaxation. Indeed, our calculations showed that the nodal-plane structure of the $3b_1(\pi^*)$ orbital correlates very well with the way pyridine distorts in the lowest triplet state.

---

† University of California. Present address: Department of Physical Chemistry, University of Amsterdam, Nieuwe Achtergracht 127, 1018 WS Amsterdam, The Netherlands.

‡ University of Leiden.

(1) Innes, K. K.; Ross, I. G.; Moomaw, W. R. *J. Mol. Spectrosc.* **1988**, *132*, 492.

(2) Bos, F. C.; Buma, W. J.; Schmidt, J. *Chem. Phys. Lett.* **1985**, *117*, 203.

(3) Buma, W. J.; Groenen, E. J. J.; Schmidt, J. *Chem. Phys. Lett.* **1986**, *127*, 189.

(4) Groenen, E. J. J.; Buma, W. J.; Schmidt, J. *Isr. J. Chem.* **1989**, *29*, 99.

(5) Buma, W. J.; Groenen, E. J. J.; Schmidt, J.; de Beer, R. *J. Chem. Phys.* **1989**, *91*, 6549.

(6) Buma, W. J.; Groenen, E. J. J.; van Hemert, M. C. *J. Am. Chem. Soc.* **1990**, *112*, 5447.

(7) Nagaoka, S.; Nagashima, U. *J. Phys. Chem.* **1990**, *94*, 4467.

0002-7863/92/1514-9544$03.00/0