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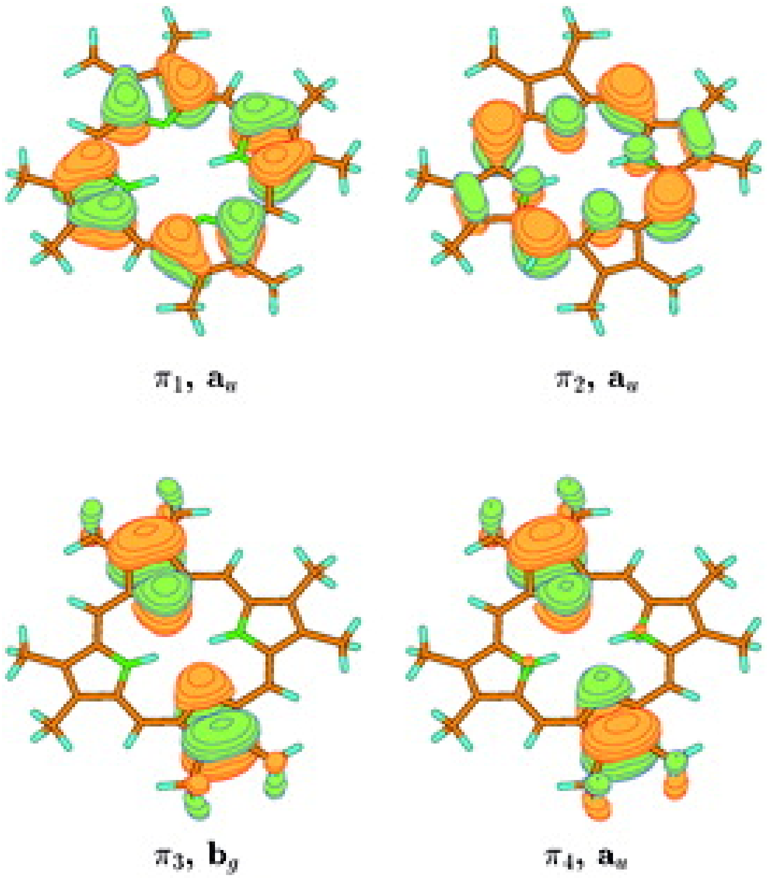

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Electron Propagator Calculations Show that Alkyl Substituents Alter Porphyrin Ionization Energies

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Porphyrins and metalloporphyrins are crucial participants in biochemical processes[1] that involve changes in oxidation states or electron transfer.[2] These macrocyclic species perform their functions in a variety of protein scaffolds that have subtle effects on their electron binding energies and, therefore, on their reactivity. Therefore, electron binding energies of isolated species are useful data for those who would understand or modify the diverse reactive capabilities of this ubiquitous class of molecules.

Ionization energies (IEs) of isolated molecules can be measured in gas-phase, ultraviolet photoelectron spectra (PES), but only results on free base porphine (H_2P) itself and a number of heavily substituted porphyrins and metalloporphyrins (usually, octaethyl and tetraphenyl derivatives) have been published. PES of H_2P[3] in the 6−14 eV range consist of four, well-separated bands. PES of octaethylporphyrin (OEP)[4] suggest that ethyl groups produce significant shifts to lower IEs for all peaks and split the ones that are nearly degenerate in H_2P by as much as 0.5 eV. Two peaks in the 6−7 eV region, which are no longer quasidegenerate, were assigned to ionizations from the pyrrolic moiety of the porphyrin. For OEP, the first two IEs occurred at 6.39 and 6.83 eV. In a recent re-evaluation[5] of the PES of OEP, the positions of the first two IEs were determined to be 6.24 and 6.49 eV, thus making the splitting of these levels much smaller. The first and second IEs were assigned to the OEP counterparts of H_2P ^2A_u and $^2B_{1u}$ cationic states, respectively. The larger reduction of the first IE (compared with that of H_2P) was explained by hyperconjugative delocalization of porphyrin π orbitals into alkyl σ orbitals.

There are many density functional studies of ground-state structures and spectra of porphyrins.[6,7] Good agreement with experimental IEs[3] was obtained[6] for the first two IEs of H_2P, which correspond to distinct irreducible representations. Variational calculations with a double-ζ basis set[8] and an equation-of-motion, coupled-cluster method with a sub-double-ζ basis[9] produced IEs that were in error by 0.3−0.9. A semiempirical electron propagator method also was used to calculate IEs of H_2P and a number of substituted porphyrins.[10] However, none of these approaches possesses predictive quality for making complete assignments of PES.

In contrast, ab initio electron propagator calculations in the partial third-order approximation (P3)[11] with triple-ζ plus polarization basis sets have been shown to give excellent agreement with experimental PES for organic molecules with heteroatom lone pairs and large π-electron systems.[12] Mistaken orderings of final states with lone pair σ and delocalized π holes that are predicted by Koopmans's theorem (KT) results are corrected in P3 calculations. In addition, mean absolute deviations from observed peaks below 20 eV are approximately 0.15 eV.

To facilitate spectral assignments that remain in doubt and to understand the effects of alkyl substitution on IEs and consequent reactivity trends, such as charge-transfer behavior and electrophilicity, the P3 method is applied presently to the vertical IEs of H_2P and octamethylporphyrin (OMP), which can be considered to be a close approximation to OEP. All calculations were performed with Gaussian 98.[13] B3LYP/6-311G** geometry optimizations[14,15] and subsequent harmonic frequency analysis confirmed D_{2h} and C_{2h} minima for H_2P and OMP, respectively.

H_2P IEs were calculated with the 6-311G** and 6-311G* basis sets; for OMP, the 6-311G* basis set was used. Propagator calculations in the latter case were made feasible by neglecting virtual Hartree−Fock (HF) orbitals with energies above 2.79 au. (The same approximation, which is necessary to ensure the quality of the results, is currently not feasible for OEP.) To every IE calculated with electron propagator theory, there corresponds a Dyson orbital (DO) which is defined by

$$\Phi_i^{\text{Dyson}}(x_1) = N^{-1/2} \int \Psi_{\text{molecule}}(x_1,x_2,x_3,...,x_N)\, \Psi_{i,\text{cation}}(x_2,x_3,x_4,...,x_N)\, \mathrm{d}x_2\mathrm{d}x_3\mathrm{d}x_4...\mathrm{d}x_N$$

where N is the number of electrons in the initial, uncharged state; i is the index of a final, cationic state, and x_j is the space-spin coordinate of the jth electron.[16] In the P3 approximation, each DO is proportional to a canonical HF orbital and has a normalization factor equal to the corresponding pole strength. Orbital plots were generated with Molden.[17] Contour values of ±0.03 were used for OMP DOs depicted in Figure 1.

P3 results (Table 1) are in excellent agreement with the peaks assigned to π levels in the PES of H_2P.[3] $^2B_{1u}$ and ^2A_u ionized states are predicted at 6.96 and 7.02 eV, respectively. A significant P3 correction to the KT prediction is observed for the latter state. High pole strength values of ~0.85 indicate the qualitative validity of the Koopmans approximation for the first two IEs. Corresponding DOs are delocalized extensively. The main contributions to the $5b_{1u}$ orbital pertain to meso-carbons; pyrrolic nitrogens participate slightly. In the $2a_u$ orbital, an antibonding pattern of π lobes on pyrrolic α-carbon atoms is observed. Two ionized states are predicted for the experimental plateau at ~8.4 eV: $^2B_{3g}$ at 8.30 eV and $^2B_{1u}$ at 8.48 eV. Electron density corresponding to the DOs is almost equally distributed between β-carbons and the dehydrogenated nitrogens of two, non-neighboring pyrrolic rings. Antibonding interactions between two π lobes on nitrogens in $3b_{3g}$ and a contrasting bonding pattern for the same atoms in $4b_{1u}$ split these two orbitals by a small amount.

The larger size of OMP prevents the use of the 6-311G** basis set that usually accompanies P3 calculations on organic molecules. Instead, the smaller, 6-311G* basis set was chosen. To make a consistent comparison, the first four IEs of H_2P also were calculated with the 6-311G* basis set. Variations in the P3 results for H_2P with respect to the basis set are less than 0.05 eV. These calculations were repeated with an active space of virtual orbitals that was reduced according to the same criterion (2.79 au) that was used in the case of OMP. Predictions for the first four IEs of H_2P calculated with the P3 method are smaller than the ones obtained with the larger basis set and with the full active space of virtual orbitals by

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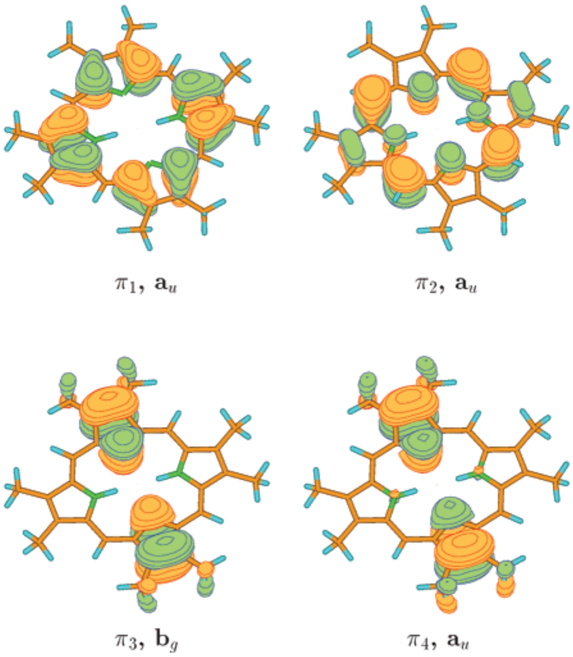

π_1, $\mathbf{a}_u$ π_2, $\mathbf{a}_u$

π_3, $\mathbf{b}_g$ π_4, $\mathbf{a}_u$

Figure 1. Dyson orbitals for the first four vertical ionization energies of OMP.

Table 1. Vertical Ionization Energies (eV)

H2P				OMP		
state	KT	P3	expt	state	KT	P3
^2A_u	6.14	7.02	7.1	^2A_u	5.63	6.34
$^2B_{1u}$	6.66	6.96	6.9	^2A_u	6.47	6.52
$^2B_{3g}$	9.13	8.30	8.4	^2B_g	8.49	7.49
$^2B_{1u}$	9.30	8.48	8.4	^2A_u	8.60	7.65

~0.1 eV. The order of final states is unaffected. In addition, the energy separations within nearly degenerate pairs and between these pairs are essentially the same. OMP calculations displayed in Table 1, therefore, employ the 6-311G* basis set, and the P3 results are obtained with the reduced active space of virtual orbitals.

The first two ionized states of OMP have ^2A_u symmetry, and the predicted splitting between them is 0.18 eV, a value which is larger than that obtained for H_2P. The DO for the first (π_1) IE has a pattern of out-of-phase combinations of π lobes on α- and β-carbons in each pyrrole ring and strongly resembles the a_u DO of H_2P. The other DO in this pair is similar to its b_{1u} π_2 counterpart in H_2P. The order of the first two ionized states is reversed compared with H_2P. Both levels are significantly destabilized by methyl substitution; the π_1 of OMP is ~0.7 eV higher than a_u of H_2P, while π_2 of OMP is only ~0.4 eV higher than the respective (b_{1u}) result of H_2P. This behavior is similar to the trends observed in comparing the experimental results for H_2P[3] and OEP,[5] where the shifts are 0.78 and 0.47 eV, respectively. Greater destabilization of the a_u orbital was attributed to larger hyperconjugation of the π lobes on pyrrole rings in the porphyrin moiety with the σ bonds of the alkyl groups.[5] When the contour value of the DO plots is changed to ±0.01, some pseudo-π density appears on the appropriate C−H bonds of the methyl groups in the case of OMP π_1.

Methyl substituent effects are somewhat larger for the second set of OMP π levels corresponding to a ^2B_g state and to another ^2A_u state. Their positions are shifted with respect to H_2P by ~0.8 eV. An energy gap of ~0.2 eV is predicted to lie between these two ionized states, and the spacing between the second and third final states is predicted to be ~1.0 eV. In the corresponding DOs of Figure 1, hyperconjugation is clearly seen in the antibonding interactions between methyl groups and neighboring lobes. For the four IEs, there is a correlation between the shift produced by alkyl substitution and the degree of hyperconjugation.

Comparison of the present results with PES experiments on OEP[4,5] favors the data of ref 5, where the energy difference between the two first IEs was only 0.25 eV.

Alkyl substitution at up to eight β positions can reduce various IEs of porphyrins by 0.4−0.8 eV and change the energy order of the two highest DOs by hyperconjugatively destabilizing them to different degrees. These effects will be stronger for orbitals with larger amplitudes on the β-carbons. Judicious substitutions, therefore, may tune the IEs and the consequent reactivity patterns that depend on charge-transfer capabilities and electrophilicity.

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Supporting Information Available: Complete ref 13. This material is available free of charge via the Internet at http://pubs.acs.org.

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