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Substituent Effects in Porphyrazines and Phthalocyanines[1]

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Abstract: *Ab initio* Hartree–Fock calculations with double-ζ basis sets have been carried out on a variety of free-base porphyrinic molecules. A comparative study is presented on the electronic structures of four unsubstituted parent tetrapyrroles, porphyrin, porphyrazine, tetrabenzoporphyrin, and phthalocyanine. The electronic influence of multiple peripheral fluoro, chloro, cyano, nitro, and trifluoromethyl groups on the orbital energies of the porphyrazine macrocycle has been calculated. Among the structurally perturbed phthalocyanines studied are hexadecafluorophthalocyanine, 2,3-naphthalocyanine, and tetrapyrazinoporphyrazine. Tetraazaporphyrins such as porphyrazines and phthalocyanines exhibit several important differences compared to the porphyrins, in both their electronic and geometric structures. An important structural consequence of *meso*-tetraaza substitution is the significantly smaller central hole in porphyrazine than in porphyrin. *meso*-Tetraaza substitution is predicted to result in a significant increase in the core ionization potentials of the central nitrogens of the porphyrin macrocycle. The first ionization potential of porphyrazine is also predicted to be significantly higher than that of porphyrin. Tetrabenzo annulation of porphyrin and porphyrazine results in a significant drop in their first ionization potentials (IPs). The additional linear annulation in 2,3-naphthalocyanine leads to a further lowering of the first IP. Suitable arrays of highly electronegative peripheral substituents are predicted to exert electronic effects of about 2 eV or more on the nitrogen 1s and valence ionization potentials of tetrapyrrolic ligands.

I. Introduction

The tetrapyrroles[2] have been at the focus of multidisciplinary interest for many decades. Porphyrins are not only important in biology, but they also have a rich coordination chemistry and applications in catalysis and materials science.[2] The abiological phthalocyanines[3] have numerous technological applications such as energy conversion,[4] electrophotography,[5] optical data storage,[6] gas sensors,[7] liquid crystals,[8] infrared dyes for laser technology,[9] and low-dimensional metals.[10] Porphyrins and phthalocyanines have also been of considerable interest to theoreticians and spectroscopists owing to their high symmetry, planarity, and electronic delocalization.[11] In contrast to the porphyrins and phthalocyanines, the porphyrazines have received negligible attention since their early syntheses[12] some decades ago. Only a trifling number of interesting discoveries involving porphyrazines have been made in recent years,[13–16] but it appears that these foreshadow a bright future for applications of these ligands. Thus, new substituted porphyrazines have been prepared via new routes from acyclic starting materials[13–15] or by electrophilic substitution of unsubstituted porphyrazine (PzH_2),[16] setting the stage for the availability of a wide array of substituted porphyrazines in the near future. At present, the chemistry of porphyrazines is wide open for exploratory research. The present theoretical work on porphyrazines is of an exploratory and predictive nature, with certain calculations being reported on hitherto unsynthesized porphyrazines.

All-electron *ab initio* Hartree–Fock (HF) self-consistent field (SCF) calculations have been carried out on various tetrapyrroles,

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yielding both core and valence orbital energies. Core orbital energies of the central nitrogens of tetrapyrroles, which reflect the electrostatic potential in the central metal-binding region, are known to be sensitive probes of the effects of peripheral substituents and other structural perturbations.[17,18] Core orbital energies obtained with double-ζ (DZ) basis sets have been previously found to provide very useful simulations of the X-ray photoelectron spectra (XPS) of tetrapyrroles.[17] The computed valence orbital energies, in particular those of the highest occupied molecular orbitals (HOMOs), are suitable for interpreting ultraviolet photoelectron spectra (UPS) and electrochemical oxidation potentials.[17,19]

This study presents the first *ab initio* calculations on parent PzH_2 and on substituted porphyrazines and phthalocyanines. A wealth of interesting electronic effects due to peripheral substitutions, *meso*-tetraaza substitution, and tetrabenzo annulation have been uncovered. Shifts of about 2 eV or more on the core orbital energies of the central nitrogens are predicted for certain porphyrazines with multiple, highly electronegative substituents. Significant electronic differences between porphyrin (PH_2, previously known as porphine[20]) and porphyrazine have been found with *ab initio* SCF calculations with full geometry optimizations and polarized basis sets. A calculation on 2,3-naphthalocyanine (2,3-NcH_2) reveals an extremely low first ionization potential (IP), a dramatic influence of linear benzo annulation on phthalocyanine (PcH_2). Because peripheral substituents in a phthalocyanine are further from the molecule's center than in a porphyrin, we wished to determine the possibility of significant modulation of the electrostatic potential in the central region of the phthalocyanine ring system by highly electronegative peripheral substituents. A calculation on hexadecafluorophthalocyanine ($PcF_{16}H_2$) has confirmed this.

This work reports some of the largest *ab initio* SCF calculations carried out to date, these being feasible owing to our use of the direct SCF method.[21] The smallest molecule studied in this work is PzH_2 ($C_{16}N_8H_{10}$) and among the largest are 2,3-NcH_2[22] ($C_{48}N_8H_{26}$) and $PcF_{16}H_2$[23] ($C_{32}N_8F_{16}H_2$). This study demonstrates that *ab initio* calculations on molecules containing more than 50 atoms are routinely possible with modern hardware and state-of-the-art computational methods.

II. Computational Details

Ab initio SCF calculations on molecules of the size considered here are not feasible using a conventional SCF scheme in which the number of integrals to be stored would be prohibitively large. We used the direct SCF[21] scheme, as implemented in the program system DISCO,[24] in which numerically insignificant integrals are screened out at an early stage of the calculations, while a much smaller number of "significant" integrals are recalculated in each SCF iteration. The direct SCF scheme is particularly well suited for the study of large symmetric molecules such as the porphyrins owing to the straightforward utilization of molecular symmetry for reducing the number of integrals to be computed. All calculations were carried out on Cray-2 and Cray-XMP computers.

A general contraction[25] scheme has been employed for all basis sets used in this work. The majority of *ab initio* SCF calculations carried out to date have used segmented basis sets. Although segmented contraction is easier to implement than general contraction, the latter results in a more flexible contracted basis set. The commonly used basis set in this investigation is of DZ quality: (3s)/[2s] for H, (6s3p)/[3s2p] for all first-row elements (C, N, O, F),[26] and (10s6p1d)/[5s4p1d] for Cl.[27] The polarized basis set (DZP) used to compare in detail the orbital energies of PH_2 and PzH_2 consists of (4s1p)/[3s1p] for H and (7s4p1d)/[4s3p1d] for C and N.[28]

The influence of electron correlation on the valence photoelectron spectra of selected tetrapyrroles is difficult to assess quantitatively, but previous semiempirical studies indicate that the effect is substantial.[29] The magnitude of these correlation effects can be estimated by comparing Hartree–Fock and local density functional (LDF) calculations. Density functional theory (DFT) constitutes a computationally expedient method for including electron correlation for large molecules.[30,31] The LDF calculations were carried out using the program system DMOL (Version 2.2).[32] The exchange-correlation functional due to von Barth and Hedin[33] was used in all LDF calculations. The numerical basis sets used were of "double numeric" plus polarization quality, and a very fine mesh was used for all calculations.

In general, the calculated IPs reported in this work are simply the sign-reversed orbital energies ($|\epsilon|$) obtained from the SCF calculations. These IPs refer to a frozen-orbital picture in which the (spin) orbitals are assumed to be identical in the neutral initial state and cationic final state,[34] and thus ignore the effects of orbital relaxation upon removal of the electron. These relaxation effects were examined for the first two UPS IPs of the parent molecules, PH_2, PzH_2, and PcH_2. The relaxation effect (e_{relax}) on a photoemission process is given by

$$e_{\text{relax}} = |\epsilon| - I_{\Delta\text{SCF}} > 0$$

where $I_{\Delta\text{SCF}}$ is the ΔSCF IP of the parent system, defined as the absolute value of the difference between the SCF total energies of the neutral and its cation. The relaxation energy, e_{relax}, is always positive, since an electronically relaxed cation is always lower in energy than a cationic final state in the frozen-orbital approximation. Relaxation energies for valence IPs are usually rather small (0.5–1.0 eV) but vary somewhat with the chemical environment. On the other hand, relaxation effects for core IPs are typically very large (~25 eV for N 1s). However, for a

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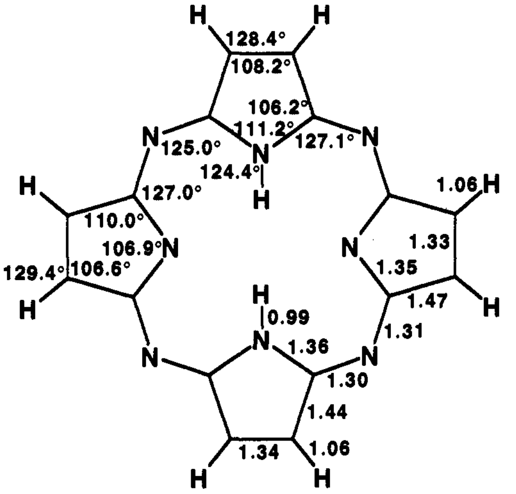


Figure 1. The SCF/DZ optimized geometry of PzH_2 obtained with a D_{2h} symmetry constraint. Distances are in angstroms and angles are in degrees.

particular element, relaxation effects for the core IPs are remarkably constant across different molecules, enabling the interpretation of electronic effects as small as 0.1 eV.

We have also performed ΔLDF calculations for two of the lowest IPs ($I_{\Delta\mathrm{LDF}}$) for PH_2, PzH_2, and PcH_2, in the same manner as in the ΔSCF calculations. Assuming that the difference between ΔSCF and ΔLDF IPs is due primarily to correlation effects included in the latter type of calculation, the effect of differential correlation ($e_{\Delta\mathrm{corr}}$) in the initial and final states is given by

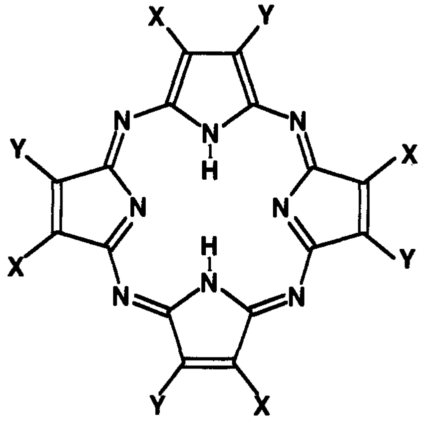
$$e_{\Delta\mathrm{corr}} = I_{\Delta\mathrm{LDF}} - I_{\Delta\mathrm{SCF}}$$

In general, one can assume that the correlation energy of a molecule scales with the number of electrons. Neglecting that effect in Hartree–Fock calculations thus leads to a smaller error for the cation than for the parent system, and the differential correlation effect on the IPs, $e_{\Delta\mathrm{corr}}$, is therefore usually positive. Values for $e_{\Delta\mathrm{corr}}$ are often of the order of +1 eV, although in this work, we shall encounter some exceptions in the case of the azaporphyrins. The ΔLDF IPs, which are generally in near-quantitative agreement with experiment, can be expressed as

$$I_{\Delta\mathrm{LDF}} = |\epsilon| - e_{\mathrm{relax}} + e_{\Delta\mathrm{corr}}$$

Geometry optimizations were carried out using SCF analytic gradients.[35] For molecules containing multiple fused rings, geometry optimization is often a traumatic procedure. The geometry of unsubstituted porphyrazine was optimized using "natural internal coordinates",[36] a prudent estimation of the initial nuclear Hessian, efficient optimization techniques,[37] and a D_{2h} symmetry constraint. The optimized geometry of porphyrazine is shown in Figure 1. Geometry optimizations of porphyrin at the SCF and correlated levels have already been reported.[38]

The SCF/DZ optimized structure of unsubstituted porphyrazine was also used as the core geometry of substituted porphyrazines. Bond distances and angles involving substituents were chosen to be the same as in our previous work on porphyrins.[17] The following substituted porphyrazines (Figure 2) were studied at the SCF/DZ level: octafluoroporphyrazine (PzF_8H_2), octachloroporphyrazine ($PzCl_8H_2$), octacyanoporphyrazine [$Pz(CN)_8H_2$], 2,7,12,17-tetrakis(trifluoromethyl)porphyrazine [$Pz(CF_3)_4H_2$], and two conformations of 2,7,12,17-tetranitroporphyrazine, with the nitro groups coplanar [c-$P(NO_2)_4H_2$] with and perpendicular [p-$P(NO_2)_4H_2$] to the plane of the porphyrazine ring. Octa- and tetrasubstituted porphyrazines were assigned D_{2h} and C_{2h} symmetries, respectively.



	X	Y
PzH_2:	H	H
PzF_8H_2:	F	F
$PzCl_8H_2$:	Cl	Cl
$Pz(CN)_8H_2$:	CN	CN
$Pz(CF_3)_4H_2$:	CF_3	H
$Pz(NO_2)_4H_2$:	NO_2	H

Figure 2. Structures of substituted porphyrazines studied.

The geometry of PcH_2 was adapted from a neutron diffraction study.[39] The geometry of tetrabenzoporphyrin[40] ($TBPH_2$) was chosen to be a hybrid between that of PH_2 and PcH_2. Similarly, unoptimized geometries were used for 2,3-NcH_2, $PcF_{16}H_2$, and tetrapyrazinoporphyrazine[41] ($TPyzPzH_2$). Except for the internal hydrogens, the skeletal geometries of $TBPH_2$, PcH_2, 2,3-NcH_2, $PcF_{16}H_2$, and $TPyzPzH_2$ (Figure 3) were idealized to D_{4h} symmetry, so that with the inclusion of the central hydrogens, the molecular geometries were D_{2h}. Because the positions of hydrogen atoms are poorly determined by crystallography, an N–H distance of 0.997 Å, a value taken from the fully optimized structure of PH_2,[31c] was adopted for all these molecules. The essential equality of the N–H distances in the optimized structures of PH_2 and PzH_2 suggests that this bond length is not particularly macrocycle sensitive. Atomic coordinates of PH_2, PzH_2, PcH_2, $TBPH_2$, 2,3-NcH_2, and $TPyzPzH_2$ are given in the supplementary material. All these molecules were studied at the SCF/DZ level.

III. Results and Discussion

A. Electronic Differences between Porphyrin and Porphyrazine. The electronic structure and physical and chemical properties of porphyrazines have been little explored compared to those of porphyrins. However, one indication that their electronic structures may be quite different is the far higher intensity of the visible (Q) absorption band of porphyrazines relative to porphyrins.[12,42,43] Here, we predict a number of electronic differences

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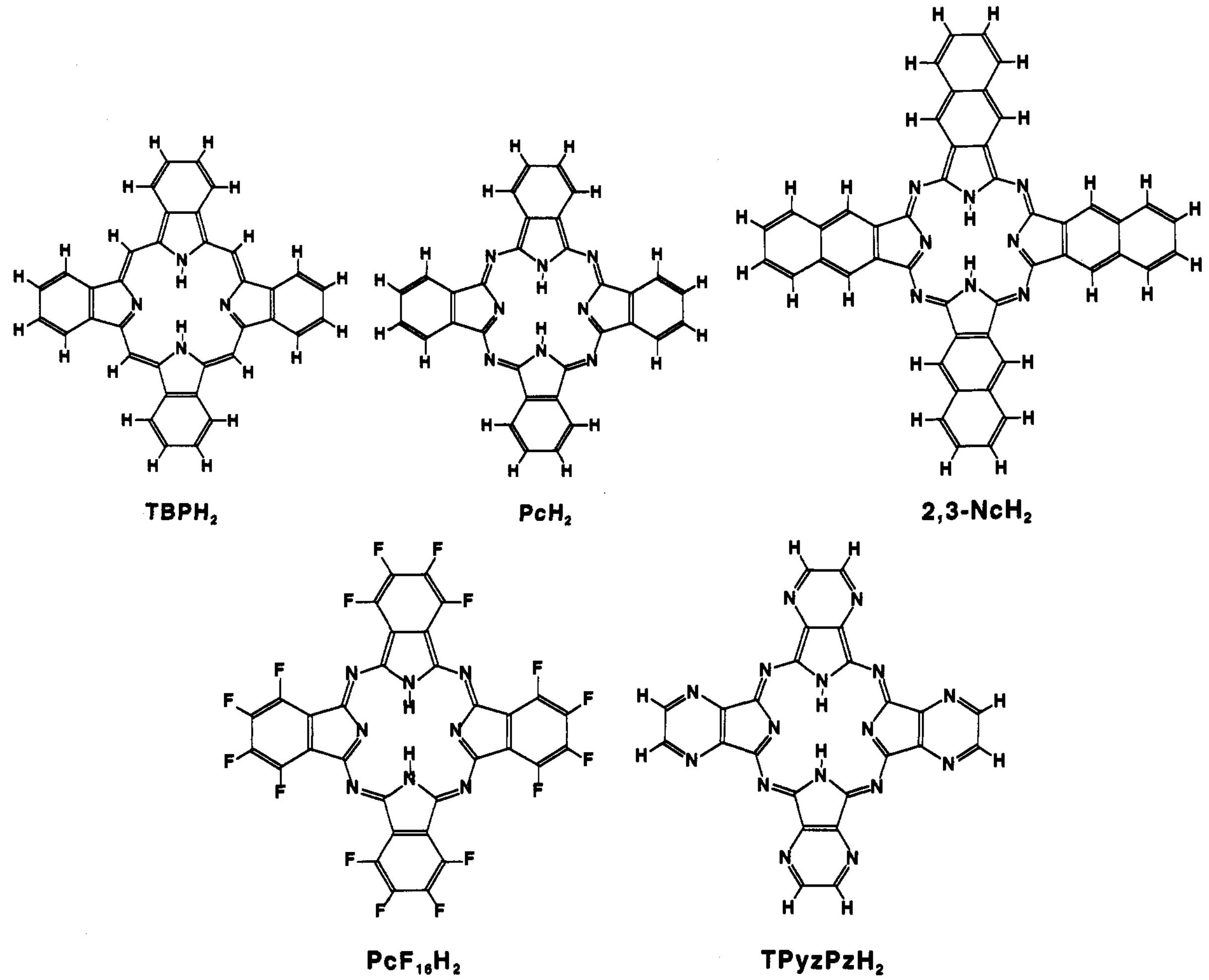

Figure 3. Structures of phthalocyanines and related molecules studied.

Table 1. Sign-Reversed Orbital Energies (eV) of PH_2 and PzH_2, Pertinent Experimental N 1s and Valence IPs, and the Shifts of the N 1s IPs (or Sign-Reversed Orbital Energies), relative to N2 (the Unprotonated Central Nitrogens) in PH_2

	DZ basis		DZP basis		experiment		
	PH_2	PzH_2	PH_2	PzH_2	PH_2	PEt_8H_2	$PzEt_8H_2$
			Orbital Energies				
N 1s[a]							
N1	424.39	424.92	424.39	424.81	400.05	399.75	399.95
N2	422.63	423.28	422.50	423.01	398.00	397.65	398.10
N3		424.14		423.88			398.75
			Shifts Relative to N2 in PH_2				
N 1s[a]							
N1	1.76	2.29	1.89	2.31	2.05	1.75	1.95
N2	0.00	0.65	0.00	0.51	0.00	−0.35	0.10
N3		1.51		1.38			0.75
			Valence Energies[c]				
a_u (HOMO)	6.20	6.53	6.05	6.25	6.9, 7.2[b,44a]	6.39, 6.83[44b]	
b_{1u}	6.52	8.73	6.69	9.03			
b_{2g}	9.07	9.82	9.25	9.83			
b_{1u}	9.30	10.04	9.41	10.04			
b_{3g}	10.20	10.82	10.09	10.80			

[a] N1, N2, and N3 are the central protonated, central unprotonated, and *meso* nitrogens, respectively. [b] The two lowest UPS IPs of PH_2 are yet to be definitively assigned.[19,31c] [c] The labeling of orbitals refers to representations of the D_{2h} point group.

between PH_2 and PzH_2 in quantitative terms. PH_2 and PzH_2 are isoelectronic, have nearly identical molecular shapes, and are expected to have nearly equal relaxation energies associated with photoelectron emission. Therefore, unless correlation effects are very different for the two systems, differences in XPS[17] and UPS spectral IPs[44a] between PH_2 and PzH_2 should be accurately given by differences in their computed SCF orbital energies. Table 1 presents sign-reversed orbital energies of the nitrogen 1s and the two HOMOs of PH_2 and PzH_2 for the DZ and DZP basis sets.

Table 1 shows that the maximum discrepancy between the orbital energies obtained with the DZ and DZP basis sets is 0.3 eV. A previous extensive study[17,19] of basis set effects on the orbital energies of PH_2 and substituted porphyrins showed that a DZ basis is generally sufficient for simulating the XPS and UPS of porphyrins.

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(44) (a) Dupuis, P.; Roberge, R.; Sandorfy, C. *Chem. Phys. Lett.* **1980**, *75*, 434. (b) Kitagawa, S.; Morishima, I.; Yonezawa, T.; Sato, N. *Inorg. Chem.* **1979**, *18*, 1345.

Both types of central nitrogens of PzH$_2$ are predicted to have significantly higher (by ~0.4 eV) 1s IPs than those of PH$_2$. In XPS studies of metalloporphyrins, we found that the influence of peripheral substituents on the core IPs of the central metal is comparable to substituent effects on the N 1s IPs.[45] A metal atom complexed to a porphyrazine is therefore expected to experience a significantly higher electrostatic potential than one complexed to a similarly substituted porphyrin. On the basis of electrostatics alone, one would naively expect a four-coordinate metalloporphyrazine to exhibit a higher affinity for axial ligands than an analogous metalloporphyrin. This has been experimentally confirmed for Fe^{II} complexes.[15b]

We know from previous work[17] that the Hartree–Fock approximation provides a good reproduction of the charge distribution in highly delocalized porphyrinic molecules. Differences in XPS core IPs (N 1s and C 1s) among different tetrapyrroles can be simulated with impressive accuracy by *ab initio* SCF calculations. For instance, the splitting of 1.9 eV between the computed (SCF/DZP) 1s orbital energies of the two types of central nitrogens in PH$_2$ is in essentially quantitative agreement with the experimental value of 2.0 eV.[17,19] This was the first finding[19] that suggested that *ab initio* SCF calculations should be useful for predicting or simulating the XPS of tetrapyrrolic materials. Subsequently, we found excellent agreement between theory and experiment for the core IPs of several other porphyrins.[17]

In the case of PzH$_2$, for which an XPS experiment has not yet been performed on a pure sample, our calculations predict that the peak due to the four *meso* nitrogens should fall between the peaks due to the two types of central nitrogens. Therefore, unmonochromatized X-radiation is unlikely to yield a well-resolved N 1s XPS of PzH$_2$. However, with monochromatized X-rays, one or more of the N 1s peaks of PzH$_2$ should be resolvable, allowing a comparison of the N 1s energies of PzH$_2$ and PH$_2$.

These expectations were confirmed by XPS measurements on octaethylporphyrazine (PzEt$_8$H$_2$) with monochromatized Al Kα radiation.[46] Using the notation of Table 1, the XPS N 1s IPs of PzEt$_8$H$_2$ are the following: 399.95 (N1), 398.1 (N2), and 398.75 eV (N3). These may be compared to the N 1s IPs of octaethylporphyrin (PEt$_8$H$_2$): 399.75 (N1) and 397.65 eV (N2). Thus, the average 1s IP of the central nitrogens is about 0.3 eV higher for PzEt$_8$H$_2$ than for PEt$_8$H$_2$, in agreement with the difference of about 0.4–0.5 eV between the computed 1s orbital energies of the central nitrogens (N1 or N2) of PH$_2$ and PzH$_2$. Note that the difference in the 1s IPs of two types of central nitrogens (N1 or N2) is slightly smaller in PzEt$_8$H$_2$ (1.85 eV) than in PEt$_8$H$_2$ (2.1 eV). This trend too is faithfully reproduced by the computed N 1s orbital energy splittings for PH$_2$ and PzH$_2$. Finally, the XPS signal due to the *meso* nitrogens (N3) is somewhat closer to N2 than N1, again in excellent agreement with computed results. The difference of about 25 eV between the XPS N IPs and the sign-reversed N 1s orbital energies is mostly ascribable to the large relaxation effects associated with core level photoemissions that we neglected in our calculations. As mentioned before,[17,19] this discrepancy is not a matter of concern in this case, since the isoelectronic molecules, PH$_2$ and PzH$_2$, are expected to have very similar relaxation effects for core photoemissions.

We have reported elsewhere[17] that β-octaethyl substitution in porphyrin lowers the absolute values of the XPS N 1s IPs by about 0.3 eV, in agreement with theoretical prediction. The effect of β-octaethyl substitution in porphyrazine may be expected to be similar: the predicted, experimental 1s IPs of the central nitrogens of unsubstituted PzH$_2$ are, therefore, 400.25 (N1) and 398.4 eV (N2). For comparison, the N 1s IPs of PH$_2$ are 400.05 (N1) and 398.0 eV (N2).

In the absence of relaxation and correlation effects, an ionization potential is simply equal to the sign-reversed SCF orbital energy, $|\epsilon|$ (Koopmans' theorem[34]). Koopmans' theorem is usually rather good for valence IPs, since e_{relax} and $e_{\Delta\mathrm{corr}}$ are small quantities of comparable magnitude, and roughly cancel each other. For core ionizations, however, very large relaxation effects, of the order of tens of electron volts, are involved, while the effect of differential correlation is only about 1 eV. Thus, the relaxation effect largely accounts for the difference of about 25 eV between the XPS N 1s IPs and the computed $|\epsilon|$ values. It is indeed possible to show this explicitly with ΔSCF calculations, i.e. by performing SCF calculations on the core-ionized states, for small molecules such as NH$_3$, H$_2$O, or HF,[47] but we found that such calculations on highly excited, core-ionized states of large molecules such as tetrapyrroles were not feasible. Fortunately, this breakdown of Koopmans' theorem does not seriously detract from the utility of HF calculations in simulating core level XPS spectra. For a particular element in a series of "related"[48] molecules, the contributions of the relaxation and correlation effects are often nearly constant so that the theoretical and experimental XPS spectra are related by a uniform shift of the energy scale.

Table 1 shows that the two highest occupied valence molecular orbitals (MOs) undergo rather different shifts in orbital energy as a result of *meso*-tetraaza substitution. Thus, the computed first IP of PzH$_2$ exceeds that of PH$_2$ by a modest amount (~0.3 eV), but the computed second IP of PzH$_2$ is drastically higher than that of PH$_2$ (by ca. 2.2 eV). In other words, the near-degeneracy of the a$_{\mathrm{u}}$ and b$_{1\mathrm{u}}$ HOMOs of porphyrins, which is embodied in Gouterman's four-orbital model for understanding the electronic spectra of porphyrins, does not hold for porphyrazines. This difference between PH$_2$ and PzH$_2$ has also been qualitatively reproduced by other, more approximate quantum chemical methods.[49] The large difference in the energy shifts of the highest occupied a$_{\mathrm{u}}$ and b$_{1\mathrm{u}}$ orbitals due to *meso*-tetraaza substitution can be qualitatively understood in terms of the nodal structures of these orbitals. The a$_{\mathrm{u}}$ HOMO of PH$_2$ has negligible amplitude at the *meso* positions, which explains the modest energy shift due to tetraaza substitution. The b$_{1\mathrm{u}}$ MO has large amplitudes at the *meso* positions, and this is responsible for the large shift in its orbital energy on *meso*-tetraaza substitution. This picture of the valence MO energies of PzH$_2$, unfortunately, happens to be simplistic.

Much caution is warranted in the prediction of the ultraviolet photoelectron spectrum of porphyrazine on the basis of the SCF valence orbital energies. Thus, although the a$_{\mathrm{u}}$ HOMO is well-separated from all other orbitals, the second highest occupied MO of b$_{1\mathrm{u}}$ symmetry has other occupied MOs of the same symmetry at slightly lower orbital energies. This raises the

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(45) Ghosh, A.; Gassman, P. G.; Almlöf, J. In *Proceedings of the Symposium on Surfaces in Biomaterials* 1991. Symposium Sponsor: Perkin-Elmer Corp., Eden Prairie, MN, October 11, 1991.

(46) Experimental details of the XPS measurements are described in ref 17. A Physical Electronics 5600 spectrometer, equipped with a monochromator, was kindly made available for these measurements by Peter Sobol of Physical Electronics Division, Perkin-Elmer Corp., Eden Prairie, MN. Details of the XPS study of PzEt$_8$H$_2$, along with XPS and X-ray-excited Auger electron spectral (XAES) data on metallooctaethylporphyrazines, will be described elsewhere (Ghosh, A.; Fitzgerald, J. to be submitted for publication).

(47) Mukhopadhyay, D., Jr.; Chaudhuri, R.; Mukherjee, D. *Chem. Phys. Lett.* **1990**, *172*, 515.

(48) The term "related" is applied somewhat loosely to (tetrapyrrole) molecules of similar size (e.g. TBPH$_2$ and PcH$_2$, but not PH$_2$ and PcH$_2$), containing the same or similar π-systems, and containing similar electronic environments around the atom undergoing core photoionization (e.g. N 1s IPs of PzH$_2$ and Pz(CF$_3$)$_4$H$_2$).

(49) Valence effective Hamiltonian (VEH) pseudopotential quantum chemical calculations on tetrapyrroles: (a) Ortí, E.; Brédas, J. L. *J. Chem. Phys.* **1988**, *89*, 1009. (b) Ortí, E.; Brédas, J. L. *Chem. Phys. Lett.* **1989**, *164*, 247. (c) Ortí, E.; Brédas, J. L. In *Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronics, and Molecular Electronics*; Bredas, J. L., Chance, R. R., Eds.; Kluwer Academic: Amsterdam, 1990; pp 517–530. (d) Ortí, E.; Piqueras, M. C.; Crespo, R.; Brédas, J. L. *Chem. Mater.* **1990**, *2*, 110. (e) Ortí, E.; Brédas, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 8669. The VEH method is described in: (f) Nicolas, G.; Durand, Ph. *J. Chem. Phys.* **1979**, *70*, 2020. (g) Nicolas, G.; Durand, Ph. *J. Chem. Phys.* **1980**, *72*, 453.

possibility that configuration interaction (CI) may play a significant role in determining the energies of the low-lying $^2B_{1u}$ states of the PzH_2 cation radical. If this is indeed the case, the energy difference between the first and second UPS IPs of PzH_2, which correspond to ^2A_u and $^2B_{1u}$ final states, respectively, will not be as large as implied by Table 1. For the PH_2 cation, the effect of CI on the lowest $^2B_{1u}$ state is likely to be much less severe than in PzH_2. These and other issues involving electron correlation are further pursued in section IIIE. However, from this discussion, we may expect that computed substituent effects on the IP ($|\epsilon|$) corresponding to the lowest ^2A_u final state (in which there should be no significant effects of near-degeneracy correlation) should be more reliable than those on higher valence IPs.

The LUMO energies obtained from *ab initio* SCF calculations are totally unreliable as estimates of electron affinities. Differences in LUMO energies may be useful for purely qualitative comparisons of molecules. The SCF/DZ LUMO energies of PH_2 and PzH_2 are +0.44 and –0.45 eV, respectively. Experimentally, the difference in reversible Fe^{III}/Fe^{II} redox potentials between $Fe(PzEt_8)(py)_2$ and $Fe(PEt_8)(py)_2$ (py = pyridine) is more than 400 mV.[15b] The better stabilization of the Fe^{II} oxidation state in the porphyrazine complex relative to the porphyrin is in accord with a lower LUMO energy of the porphyrazine ligand relative to the porphyrin or the porphyrazine ligand being a better π-acceptor.

B. The Molecular Geometry of Free-Base Porphyrazine. PzH_2 has a highly delocalized geometry.[50] Any two adjacent C_α–N_{meso} distances are found to be nearly identical. As is typical in tetrapyrroles,[51] the C_α–C_β bonds are long (1.44–1.47 Å in Figure 1) compared to typical aromatic C–C distances (~1.39 Å). The C_α–N–C_α internuclear angle subtended at a central protonated nitrogen is significantly larger (by about 4°) than that subtended at the unprotonated nitrogen. In all these features, the computed geometry of PzH_2 resembles the crystallographic geometry of PH_2.[43,52]

There is an important difference between the geometries of PH_2 and PzH_2. The C_α–N_{meso} distance in PzH_2 (about 1.31 Å in the SCF/DZ optimized structure) is significantly shorter than the C_α–C_{meso} distance in PH_2 (about 1.38 Å in the SCF/DZ optimized structure).[31c] This results in the central cavity of PzH_2 being significantly smaller than that of PH_2.[31c,53] Thus, the calculated distances between diagonally opposite, protonated, central nitrogens are 3.99 and 4.18 Å in the SCF/DZ optimized geometries of PzH_2 and PH_2, respectively.[31c] The calculated distances between the unprotonated central nitrogens are 3.86 and 4.04 Å for the SCF/DZ optimized geometries of PzH_2 and PH_2, respectively. It has been suggested[15b] that this geometric difference between porphyrins and porphyrazines is related to the different spin states of the iron(III) chloride complexes of octaethylporphyrin (PEt_8FeCl: $S = {}^5/_2$) and octaethylporphyrazine ($PzEt_8FeCl$: $S = {}^3/_2$).

C. Substituent Effects in Porphyrazines. The syntheses of several diversely substituted porphyrazines have recently been reported.[14] Tetrakis(*tert*-butyl)porphyrazine and magnesium porphyrazine undergo tetrabromination with *N*-bromosuccinimide[16a] and bromine,[16b] respectively. The tetrabromoporphyrazines are potentially transformable into other substituted porphyrazines *via* a variety of halogen substitution reactions, such as trifluoromethylation, etc. A general, high-yield route to octakis(alkylthio)porphyrazines has been devised.[13c–d] Using a convenient transformation of alkynes to substituted fumaronitriles and maleonitriles, Fitzgerald *et al.* have reported a synthesis of octaethylporphyrazine, which is a highly soluble porphyrazine.[15a,b] Finally, there are some scattered reports on the application of porphyrazines as transition-metal ligands in catalytic oxidation reactions of organic substrates.[54] It appears that after a prolonged period of stagnation there is a revival of interest in porphyrazines.

The subject of substituent effects in porphyrins is currently of wide interest. To a significant extent, this is due to the recent availability of several porphyrins bearing multiple electron-withdrawing groups.[55] Metal complexes of some electron-deficient porphyrins exhibit enhanced reactivity[56] and selectivity[57] as catalysts in various oxygenation reactions of organic substrates,[58] relative to metal complexes of the electron-rich tetraphenylporphyrin ($TPPH_2$) and PEt_8H_2. A notable discovery in this area was made by Traylor *et al.*,[57] who showed that *meso*-tetrakis(pentafluorophenyl)hemin ($TPFPPFe^{III}Cl$) and other electron-deficient hemin catalysts resulted in superb yields of epoxide products (86–100%!) in alkene epoxidations by hydrogen peroxide or organic hydroperoxides. Previous failures to obtain good yields of epoxides with hydroperoxides and relatively electron-rich hemins were convincingly ascribed to the putative ferryl intermediate ("compound I") preferring hydroperoxide oxidation over epoxidation. This preference is much less for electron-deficient ferryl intermediates which explains the excellent yields of epoxide obtained with catalysis by $TPFPPFe^{III}Cl$. So

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(50) Reference 15b describes the crystallographic structure of octaethylporphyrazinatoiron(III) chloride ($PzEt_8FeCl$) and compares it to that of protoporphyrin IX iron(III) chloride (ProtoP-IXFeCl). The crystallographic C_α–$(N/C)_{meso}$ distances in $PzEt_8FeCl$ and ProtoP-IXFeCl are 1.32 and 1.38 Å, respectively. The Fe–N distances in ProtoP-IXFeCl and $PzEt_8FeCl$ are 2.07 and 1.93 Å, respectively.

(51) See, e.g.: Tulinsky, A. *Ann. N.Y. Acad. Sci.* **1973**, *206*, 47. This paper describes the crystallographic structure of PH_2.

(52) For a discussion of the effect of electron correlation on the geometries of tetrapyrrole molecules, see ref 31c.

(53) Another reason for the smaller central hole of porphyrazine is the C_α–N_{meso}–C_α angle being slightly smaller than the C_α–C_{meso}–C_α angle in porphyrin. The C_α–$(N/C)_{meso}$–C_α angles are 121.3 and 125.9° in $PzEt_8FeCl$ and ProtoP-IXFeCl, respectively.[15b] In the D_{2h} SCF/DZ optimized structures,[44] the C_α–$(N/C)_{meso}$–C_α angles are 125.0 and 126.4 Å in PzH_2 and PH_2, respectively.

(54) Barkanova, S. V.; Zheltukhin, I. A.; Kaliya, O. L.; Kopranenkov, V. N.; Luk'yanets, E. A. In *Dioxygen Activation and Homogeneous Catalytic Oxidation*; Simándi, L. I., Ed.; Elsevier: Amsterdam, 1991.

(55) For an extensive list of references on porphyrins bearing electron-withdrawing substituents, see ref 17. Notable additional references include—Halogenated porphyrins: (a) Antonio, M. d'A.; Gonsalves, R.; Johnstone, R. A. W.; Pereira, M. M.; Shaw, J.; Sobral, A. J. F. N. *Tetrahedron Lett.* **1991**, *32*, 1355. (b) Bhyrappa, P.; Krishnan, V. *Inorg. Chem.* **1991**, *30*, 239. (c) Mandon, D.; Ochsenbein, P.; Fischer, J.; Weiss, R.; Jayaraj, K.; Austin, R. N.; Gold, A.; White, P. S.; Brigaud, O.; Battioni, P.; Mansuy, D. *Inorg. Chem.* **1992**, *31*, 2044. (d) DiMagno, S. G.; Lin, V. S.-Y.; Theiren, M. J. *J. Am. Chem. Soc.* **1993**, *115*, 2513. (e) Crossley, M. J.; Burn, P. L.; Chew, S. S.; Cuttance, F. B.; Newsom, I. A. *J. Chem. Soc., Chem. Commun.* **1991**, 1564. Trifluoromethylated porphyrins: (f) Yoshimura, T.; Kamada, H.; Toi, H.; Inaba, S.; Ogoshi, H. *Inorg. Chim. Acta* **1993**, *208*, 9. Octacarbomethoxyporphyrin: (g) Müller, F.; Karwe, A.; Mattay, J. *J. Org. Chem.* **1992**, *57*, 6080. Octakis (*N,N*-dialkylcarboxamido)porphyrins: (h) Kaesler, R. W.; LeGoff, E. *J. Org. Chem.* **1983**, *48*, 4399. Octamethoxyporphyrin: (i) Merz, A.; Schropp, R.; Lex, J. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 291. β-Octaethyl-*meso*-tetranitroporphyrin: (j) Zhu, N.-J.; Li, Y.; Wu, G.-Z.; Liang, X.-G. *Acta Chim. Sin.* **1992**, *50*, 249.

(56) (a) Traylor, P. S.; Dolphin, D.; Traylor, T. G. *J. Chem. Soc., Chem. Commun.* **1984**, 279. (b) Traylor, T. G.; Tsuchiya, S. *Inorg. Chem.* **1987**, *26*, 1338. (c) Tsuchiya, S.; Seno, M. *Chem. Lett.* **1989**, 263. (d) Wijesekera, T.; Matsumoto, A.; Dolphin, D.; Lexa, D. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1028. (e) Hoffmann, P.; Labat, G.; Robert, A.; Meunier, B. *Tetrahedron Lett.* **1990**, *31*, 1991. (f) Carrier, M-N.; Scheer, C.; Gouvine, P.; Bartoli, J-F.; Battioni, P.; Mansuy, D. *Tetrahedron Lett.* **1990**, *31*, 6645. (g) Ellis, P. E.; Lyons, J. E. *Coord. Chem. Rev.* **1990**, *105*, 181. (h) Bartoli, J. F.; Brigaud, O.; Battioni, P.; Mansuy, D. *J. Chem. Soc., Chem. Commun.* **1991**, 440. (i) Campestrini, S.; Robert, A.; Meunier, B. *J. Org. Chem.* **1991**, *56*, 3725. (j) Lyons, J. E.; Ellis, P. E. *Catal. Lett.* **1991**, *8*, 45. (k) Traylor, T. G.; Hill, K. W.; Fann, W.-P.; Tsuchiya, S.; Dunlap, B. E. *J. Am. Chem. Soc.* **1992**, *114*, 1308. (l) Hoffmann, P.; Robert, A.; Meunier, B. *Bull. Soc. Chim. Fr.* **1992**, *129*, 85. (m) Fujii, H. *J. Am. Chem. Soc.* **1993**, *115*, 4641.

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Table 2. Sign-Reversed SCF/DZ Orbital Energies (eV) of Substituted Porphyrazines

	PzH_2	PzF_8H_2	$PzCl_8H_2$	$Pz(CN)_8H_2$	$Pz(CF_3)_4H_2$	*c*-$Pz(NO_2)_4H_2$	*p*-$Pz(NO_2)_4H_2$
N 1s[a]							
N1	424.92	426.67	426.27	427.54	426.20	426.84	426.90
N2	423.28	425.06	424.68	425.98	424.61	425.27	425.31
N3	424.14	425.85	425.41	426.70	425.34	425.92	426.09
N4				425.83		423.13	432.20
N5				425.35		431.88	431.95
valence[b]							
a_u (HOMO)	6.53	8.23	7.72	9.02	7.86 (a_u)	8.46 (a_u)	8.48 (a_u)

[a] N1, N2, and N3 are the central protonated, central unprotonated, and *meso* nitrogens, respectively. Nitrogen atoms with peripheral substituents are referred to as N4 and N5. The N4 atoms are attached to the pyrrole rings containing the central protonated nitrogens (N1) and the N5 atoms are attached to the pyrrole rings containing the central unprotonated nitrogens (N2). [b] For the C_{2h} tetrasubstituted porphyrazines, the symmetry of the HOMO (a_u in C_{2h}) corresponds to a_u in D_{2h}.

far, this and other dramatic examples of substituent effects in porphyrins have been documented only at a descriptive level. A dissection of the electronic, steric, and solvent effects operating in these reactions is a complex, but important, problem. In our approach to this problem, we began[17] by evaluating the extent to which a porphyrin's peripheral substituents can modulate the electronic character of a coordinated metal ion. For example, we have found by XPS that the 1s IPs of the central nitrogens of $TPFPPH_2$ are about 0.9 eV higher than those of $TPPH_2$. We have also measured by XPS and theoretically calculated substituent effects on the N 1s and HOMO energies of a series of tetraphenylporphyrins. Here we extend this line of research to predict substituent effects in a variety of porphyrazine ligands (Table 2). The long-term aim of this research is to obtain correlations between the electronic structures and chemical reactivity patterns of tetrapyrrolic compounds.

Table 2 presents sign-reversed SCF/DZ orbital energies for several porphyrazines. Clearly, peripheral substituents can modulate the potential at the center of the porphyrazine macrocycle in a dramatic fashion. Thus, four peripheral nitro groups shift the 1s energies of the central nitrogens by about 2 eV, while four peripheral trifluoromethyl groups cause a shift of about 1.3 eV. Peripheral perchlorination shifts the 1s energies of the central nitrogens by about 1.35 eV, while peripheral perfluorination causes a shift of about 1.7 eV. The most dramatic shifts, of about 2.6 eV, are caused by octacyano substitution. This last result is reminiscent of an XPS study of the extremely electron-deficient β-octakis(*N*,*N*-diethylcarboxamido)porphyrin,[18,55h] for which the 1s IPs of the central nitrogens were found to be higher by 0.4 and 1.3 eV than those of $TPFPPH_2$ and $TPPH_2$, respectively. Thus, it appears that carboxyl-derived substituents are among the most effective in withdrawing electron density from the central region of tetrapyrroles. Porphyrins bearing carboxyl-derived substituents are known, but no porphyrazines with substituents such as $-CN$, $-CF_3$, $-CONR_2$, and $-CO_2R$ have been synthesized.[55] The recent synthetic approach to the porphyrazine ring system from alkyne starting materials may provide access to such high-potential porphyrazine ligands.[15a,b]

Table 2 shows that substituent effects on the highest occupied a_u orbital are about the same as those on the N 1s levels. Stabilization of the HOMO is related to an increase in the ligand's oxidation potential. The electron-deficient porphyrazines should therefore exhibit improved resistance toward oxidative degradation initiated by electron transfer from the macrocycle. A reason for choosing in Table 2 only the orbital energies of the highest occupied a_u orbitals from the entire valence orbital energy spectrum is that CI effects are likely to be severe for some of the other valence IPs. As mentioned before, Table 1 suggests that CI is likely to be important in determining the energies of the lowest $^2B_{1u}$ states of the PzH_2 cation.

Most of the porphyrazines listed in Table 2 have not yet been synthesized, although synthetic efforts are at present underway in a number of laboratories to synthesize these and/or very similar ligands. Indeed, our choice of substituted porphyrazines for this theoretical survey was dictated by considerations of synthetic accessibility. Our calculations should therefore be of considerable relevance to future experimental studies on electron-deficient porphyrazines. Among the substituted porphyrazines in Table 2, only $PzCl_8H_2$ is presently known, and experimental XPS and UPS studies of the substituent effect in this compound should provide a rigorous test for our computed results. It has not been possible at this point to report experimental photoelectron spectral data on any of the substituted porphyrazines listed in Table 2, and the data thus serve an essentially predictive and exploratory purpose.

In the absence of experimental data, the following question naturally arises: To what extent can we trust the calculated substituent effects on the N 1s orbital energies? In the past,[17] we have been able to reproduce substituent effects on the N 1s energies in a series of tetraphenylporphyrins. *Ab initio* SCF calculations also provided impressive simulations of the C 1s XPS of polyfluorinated porphyrins such as $TPFPPH_2$ and tetrakis-(4-(trifluoromethyl)phenyl)porphyrin. Our calculations have reproduced differences in XPS core IPs of different atoms of the same element within the same molecule. As an example,[17] the three different N 1s IPs of $PzEt_8H_2$ may be cited (see Table 2). On the basis of this experience, we may be quite optimistic about the reliability of our predictions on substituent effects on the N 1s IPs of porphyrazines.

D. Phthalocyanines and Related Molecules. Phthalocyanines have found a number of technical applications owing to their interesting optical, electronic, liquid crystalline, and other physical properties.[4-10] Theoretical calculations of high quality should be a useful exploratory tool for physical chemists and materials scientists working on these materials. Table 3 presents sign-reversed N 1s and valence orbital energies of various phthalocyanines and related molecules. The symmetry ordering of the five HOMOs is the same in all the molecules, except 2,3-NcH_2, for which the orbital symmetries are shown within parentheses.

The geometries of the molecules listed in Table 3 have not been optimized, but they have been obtained by idealization of crystallographic geometries. On the basis of our experience from similar, previous work on PH_2,[17] it is estimated that this assumption may cause inaccuracies of about 0.1 eV in the N 1s and valence orbital energies. The following points concerning Table 3 merit discussion.

We have recently carried out an XPS study of PcH_2 and $TBPH_2$ using monochromatized X-rays. The experimental N 1s IPs of PcH_2 are 399.8 (N1), 398.4 (N3), and 397.9 eV (N2). The XPS N 1s IPs of $TBPH_2$ are 399.6 (N1) and 397.6 eV (N2). The computed energy splittings between different types of nitrogen atoms in PcH_2 and $TBPH_2$ (Table 3) are in excellent agreement with the XPS energy splittings measured for both compounds. The XPS N 1s IPs of the central nitrogens of PcH_2 are higher than those of $TBPH_2$ by about 0.2–0.3 eV,[40] in agreement with the calculated results in Table 3. However, this last agreement may be a coincidence, since we have used non-optimized geometries for both PcH_2 and $TBPH_2$.

Table 3. Sign-Reversed Orbital Energies (eV) of Phthalocyanines and Related Systems and Some Pertinent XPS/UPS Data

	theory					experiment	
	$TBPH_2$	PcH_2	$PcF_{16}H_2$	$TPyzPzH_2$	2,3-NcH_2	$TBPH_2$	PcH_2
				N 1s Energies[a]			
N1	424.95	425.23	426.92	426.09	425.30	399.6	399.8
N2	422.99	423.31	425.05	424.25	423.44	397.6	397.9
N3		423.88	425.46	424.56	423.72		398.4
N4[b]				425.23			
N5[c]				424.82			
				Valence Energies			
a_u	5.23	5.41[d]	7.07	6.49	4.79 (a_u)		6.41[61]
b_{1u}	6.73	8.60[e]	10.21	9.28	7.72 (b_{3g})		
b_{2g}	8.54	8.81	10.56	9.95	7.74 (a_u)		
b_{1u}	8.77	8.97	10.73	10.67	7.87 (b_{2g})		
b_{3g}	8.74	9.28	10.74	10.69	8.51 (a_u)		

[a] N1, N2, and N3 are the central protonated, central unprotonated, and *meso* nitrogens, respectively. [b] These are the pyrazine nitrogens attached to the pyrrole rings with the protonated nitrogens. [c] These are the pyrazine nitrogens attached to the pyrrole rings with the unprotonated nitrogens. [d] The ΔSCF and ΔLDF values for this IP are 4.94 and 6.84 eV, respectively. [e] The ΔLDF value for this IP is 8.01 eV.

The valence orbital energy spectra of PcH_2 and $TBPH_2$ exhibit interesting differences. Thus, the computed first IP of PcH_2, according to Koopmans' theorem, is slightly higher than that of $TBPH_2$, which agrees qualitatively with a slightly higher electrochemical oxidation potential of PcH_2.[40c] Note that the gap between the SCF orbital energies of the two HOMOs (a_u and b_{1u}) in PcH_2 is very large (>3 eV), larger than the corresponding gaps in PH_2 and PzH_2.[59] However, as in the case of PzH_2, we should not expect the difference in the first two IPs of PcH_2 to be as large as 3 eV. Table 3 shows that the two highest occupied b_{1u} orbitals of PcH_2 are extremely close, which raises the possibility of strong CI effects in the lowest $^2B_{1u}$ states of the PcH_2 cation. The Hartree–Fock orbital energies, therefore, do not provide appropriate theoretical values for the IPs corresponding to these $^2B_{1u}$ final states. It would be naive, therefore, to attempt to quantitatively simulate the full valence band photoelectron spectra of tetrapyrroles using uncorrelated MO methods, be they approximate or *ab initio*.[49]

Peripheral perfluorination shifts the energies of both the 1s orbitals of the central nitrogens and the HOMO of PcH_2 by approximately 1.7 eV. However, because $PcF_{16}H_2$ is a significantly larger molecule than PcH_2, the relaxation effect may result in a somewhat smaller substituent effect to be found by photoelectron spectroscopy.

$TPyzPzH_2$, a compound that has been prepared recently,[41] is isoelectronic with PcH_2 or $TBPH_2$, and relaxation effects associated with photoemission should be nearly the same in all three compounds. Therefore, the photoelectron spectra of $TPyzPzH_2$ and PcH_2 should faithfully reproduce the differences in their computed IPs (Table 3). The 1s IPs of the central nitrogens of $TPyzPzH_2$ are predicted to be about 0.7–0.9 eV higher than those of PcH_2. The computed first IP of $TPyzPzH_2$ is higher than that of PcH_2 by about 1.1 eV. Several polyazaphthalocyanines are known.[60] This calculation demonstrates that ring aza substitution is an effective method for modulating the valence orbital energies and potential in the central region of the macrocyclic ligands.

Table 4. Ionization Potentials According to Koopmans' Theorem (|ε|), ΔSCF IPs ($I_{\Delta SCF}$), and ΔLDF IPs ($I_{\Delta LDF}$) for the Two Lowest-Energy Ionizations of PH_2, PzH_2, and PcH_2 as Well as an Analysis of Relaxation and Differential Correlation Effects

final state	molecule	|ε| (eV)	$I_{\Delta SCF}$ (eV)	$I_{\Delta LDF}$ (eV)	e_{relax} (eV)	$e_{\Delta corr}$ (eV)
^2A_u	PH_2	6.19	5.80	7.37	0.39	1.57
^2A_u	PzH_2	6.53	6.16	8.02	0.37	1.86
^2A_u	PcH_2	5.41	4.94	6.84	0.47	1.90
$^2B_{1u}$	PH_2	6.48	6.01	7.26	0.47	1.25
$^2B_{1u}$	PzH_2	8.73	8.23	8.57	0.50	0.34
$^2B_{1u}$	PcH_2	8.60	*a*	8.01	*a*	*a*

[a] These quantities could not be determined as the SCF calculation on the $^2B_{1u}$ cation of PcH_2 did not converge.

The series comprising PzH_2, PcH_2, and 2,3-NcH_2 was studied to examine the effect of linear benzo annulation. Clearly, linear benzo annulation leads to sharp drops in the first IPs. Thus, according to Koopmans' theorem, a very low first IP (|ε|) of 4.79 eV is calculated for 2,3-NcH_2. In general, as will be discussed in more detail in the next section, HF theory (Koopmans' theorem) underestimates the first IP of tetrapyrroles by roughly 1 eV.[17,19] Thus, the experimental UPS first IP of PcH_2 is 6.41 eV, the computed |ε| value being 5.41 eV.[61] The computed first IP of 2,3-NcH_2 is about 0.6 eV lower than that of PcH_2, from which we may estimate that the experimental first IP of 2,3-NcH_2 should be about 5.8 eV. This very low IP is probably intimately related to the photoconductivity of 2,3-NcH_2.

E. Relaxation and Correlation Effects. We have alluded in the previous sections to the possibility of strong CI effects on the energy of the lowest $^2B_{1u}$ states of the cations of PzH_2 and PcH_2. This implies that Hartree–Fock calculations should not be used to predict the ionization potentials corresponding to lowest $^2B_{1u}$ final states. Since the second highest occupied MO of many tetrapyrroles is of b_{1u} symmetry, this limits the application of Hartree–Fock calculations to predicting the orbital energy and shifts of the a_u HOMO. In this section, we therefore turn to other methods to better compute the second IPs of PzH_2 and PcH_2. Table 4 compares IPs according to Koopmans' theorem (|ε|), ΔSCF IPs ($I_{\Delta SCF}$), and ΔLDF IPs ($I_{\Delta LDF}$) for the two lowest-energy ionizations of PH_2, PzH_2, and PcH_2. Since ΔLDF IPs include both relaxation and correlation effects, they are usually the most accurate of the three types of IPs.[31c] The discrepancy between |ε| and ΔLDF IPs is analyzed in terms of relaxation (e_{relax}) and differential correlation ($e_{\Delta corr}$) contributions.

Several comments are warranted on the data in Table 4.

Note the constancy of the relaxation effect (0.4–0.5 eV) for all three molecules and for both ionizations. We reported relaxation energies for these ionizations of octamethylporphyrin and $TPPH_2$, and these too were in this range. In contrast, note the much greater variation in the differential correlation contribution.

The magnitudes of the relaxation and correlation contributions are very different for all three molecules, which appears to be a peculiarity of these aromatic tetrapyrroles. For the ionization corresponding to the lowest A_u final state, the correlation contribution exceeds the relaxation effect by over 1 eV. In addition, the ΔLDF first IPs exceed the experimental values by about 0.3 eV (for PH_2 and PcH_2), a very small discrepancy, considering the simplicity of the LDF exchange-correlation functional. This leads to the rule of thumb that Koopmans' theorem underestimates the first IPs of tetrapyrroles by roughly 1 eV.

In the case of PzH_2, note that the correlation contribution for the second IP is drastically lower than that for the first IP. While an exact value of $e_{\Delta corr}$ is not available for the second IP of PcH_2 (Table 4), the situation must be similar to that in PzH_2. If we

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(59) Qualitatively, this is in harmony with the assignment of the visible Q band of a D_{4h} Pc derivative such as ZnPc to a pure, doubly degenerate a_u (HOMO) → e_g (LUMO) transition. In contrast, the Q bands of porphyrins have a four-orbital constitution, since the two HOMOs are near-degenerate.

(60) (a) Linstead, R. P.; Noble, E. G.; Wright, J. M. *J. Chem. Soc.* **1936**, 1744. (b) Gal'pern, M. G.; Luk'yanets, E. A. *Zh. Obshch. Khim.* **1969**, *39*, 2536. (c) Gal'pern, M. G.; Luk'yanets, E. A. *Anilinokr. Prom.* **1972**, *No. 5*, 22. (d) Brach, P. J.; Grammatica, S. J.; Ossanna, O. A.; Weinberger, L. *J. Heterocycl. Chem.* **1970**, *7*, 1403. (e) Wöhrle, D.; Meyer, G.; Wahl, B. *Makromol. Chem.* **1980**, *181*, 2127. (f) Wöhrle, D.; Gitzel, J.; Okuro, I.; Aono, S. *J. Chem. Soc., Perkin Trans. II* **1985**, 1171. (g) Palacin, S.; Ruandel-Teixier, A.; Barraud, A. *J. Phys. Chem.* **1986**, *90*, 6237.

(61) Berkowitz, J. *J. Chem. Phys.* **1979**, *70*, 2819.

assume that e_{relax} equals 0.5 eV for the second IP of PcH_2 on the basis of the above-mentioned constancy of this quantity, $e_{\Delta corr}$ turns out to be close to 0.0 eV! In other words, the correlation energy of the $^2B_{1u}$ azaporphyrin (PzH_2 or PcH_2) cation is nearly equal to that of the azaporphyrin neutral. This unusual behavior is evidence for strong CI effects on the energy of the $^2B_{1u}$ cations of PzH_2 or PcH_2. No such severe effects of near-degeneracy correlation were found for the first two IPs of PH_2.[31c]

No UPS experiment on PzH_2 has been reported to date. The results of this section are of considerable predictive value for such an experiment. *Ab initio* Hartree–Fock theory, approximate MO calculations, as well as qualitative arguments based on the nodal structures of the highest occupied a_u and b_{1u} MOs suggest that the first and second IPs of PzH_2 should be drastically different. In contrast, ΔLDF calculations on PzH_2 predict a difference of merely 0.55 eV between the first two IPs. We naturally trust the ΔLDF prediction, since it accounts for both relaxation and correlation effects.

The difference between the ΔLDF first IPs of PH_2 and PzH_2 is about 0.76 eV, compared to a ΔSCF value of about 0.36 eV. (Note from Table 4 that the PH_2 and PzH_2 cation radicals have ground states of different symmetries at the LDF level: ^2A_u and $^2B_{1u}$ for PzH_2 and PH_2 cations, respectively.) We noted before that the first UPS IPs of PH_2 and PcH_2 are overestimated at the ΔLDF level by about 0.3 eV. Therefore, our best quantitative estimate of the experimental, first UPS IP of PzH_2 is 7.7 eV, compared to 6.9 eV for PH_2.

It may be of interest to note that ΔLDF calculations have yielded an excellent simulation of the UPS of porphyrin even beyond the second IP.[31c] In contrast, the Hartree–Fock approximation and Koopmans' theorem provide little guidance in assigning the UPS of porphyrins beyond the second IP.[29] However, the all-electron *ab initio* Hartree–Fock calculations have the important advantage that they provide excellent simulations of the core XPS of these large molecules.

IV. Conclusion

We have used direct electronic structure methods to carry out *ab initio* calculations on a variety of free-base porphyrazines and phthalocyanines using DZ or better basis sets. We have calculated the effects of different peripheral substitution patterns and structural perturbations on the energies of the nitrogen 1s and highest occupied MOs. The principal conclusions of this study are as follows.

1. Hartree–Fock calculations have been used to simulate the N 1s XPS of $PzEt_8H_2$ and PcH_2. We found excellent agreement between theoretical and experimental differences between the 1s energies of different types of nitrogens in these molecules. Considering that the N 1s and C 1s XPS of many other porphyrinic molecules have been accurately reproduced, we may expect that our predicted substituent effects on the 1s energies of the central nitrogens will agree with experimental data, when they become available.

2. Since much less is known about porphyrazines than about porphyrins, it was of interest to determine electronic differences between the parent compounds, PH_2 and PzH_2. The first UPS IP of PzH_2 is predicted to exceed that of PH_2 by about 0.3 eV at the SCF level ($|\epsilon|$ or ΔSCF) and by 0.76 eV at the ΔLDF level. This implies that the electrochemical oxidation potential of PzH_2 should be appreciably higher than that of PH_2. XPS measurements and Hartree–Fock calculations show that the average 1s IP of the central nitrogens of PzH_2 exceeds that of PH_2 by 0.3 eV. A metal ion complexed to a porphyrazine should therefore experience a higher potential than one complexed to an analogous porphyrin.

3. *Ab initio* SCF calculations show that suitable arrays of electron-withdrawing peripheral substituents can cause drastic shifts in the 1s IPs of the central nitrogens of porphyrazine or phthalocyanine ligands. Extremely active and robust metallotetrapyrrole catalysts for oxidation processes can be potentially derived from such high-potential ligands.

4. Linear benzo annulation (resulting in 2,3-NcH_2) was shown to result in a drastic drop in the first IP of PcH_2. Even longer linear benzo annulations may produce even more drastic drops in the first IPs. These results are clearly of great relevance to current research on semiconducting properties of phthalocyanines. A calculation on tetra(pyrazino)porphyrazine illustrated another approach to modulating the first IPs of phthalocyanines. The first IP of $TPyzPzH_2$, according to Koopmans' theorem, is over 1 eV higher than that of PcH_2. The 1s IPs of the central nitrogens of $TPyzPzH_2$ also exceed those of PcH_2 by over 1 eV. Peripheral substituents provide yet a third approach to tuning the electronic properties of phthalocyanines. Highly electron-deficient ligands related to $PcF_{16}H_2$ deserve attention as potential precursors of highly stable catalysts of oxidation processes.

5. A useful generalization can be made on the magnitude of relaxation effects on the first two IPs of tetrapyrroles. The relaxation energy, e_{relax}, is remarkably constant among different tetrapyrroles. For tetrapyrrolic molecules of widely different sizes, e_{relax} lies in the very short range of 0.4–0.6 eV. Disagreements between Hartree–Fock theoretical (Koopmans' theorem) and experimental substituent effects on the first IPs of tetrapyrroles should therefore be readily ascribable to the differential correlation effect.

6. Differential correlation effects on the lowest valence IPs varied a lot among tetrapyrroles. Calculations of substituent effects at the Hartree–Fock level should therefore be limited to comparing structures with very similar π-systems, for which the correlation effects are likely to be similar.

In summary, *ab initio* calculations have yielded valuable predictions, simulations, and insights related to substituent effects in porphyrazines and phthalocyanines.

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Supplementary Material Available: Tables of atomic coordinates of several tetrapyrrole geometries (5 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.