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Electronic Distinction between Porphyrins and Tetraazaporphyrins. Insights from X-ray Photoelectron Spectra of Free Base Porphyrin, Porphyrazine, and Phthalocyanine Ligands

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High-resolution nitrogen core X-ray photoelectron spectra are reported for free base octaethylporphyrin, octaethylporphyrazine, tetrabenzoporphyrin, and phthalocyanine. The spectra have been analyzed and assigned using all-electron *ab initio* Hartree−Fock calculations with basis sets of double-ζ or better quality. The results show that *meso*-tetraaza-substitution causes an increase of 0.2−0.45 eV in the core ionization potentials of the central nitrogens of porphyrin ligands, which implies a significantly more positive electrostatic potential in the central metal-binding region of a tetraazaporphyrin relative to a similarly substituted porphyrin.

Introduction

The subject of substituent effects in porphyrins is of considerable current interest. In particular, metalloporphyrins with novel substitution patterns are being intensively studied as catalysts in oxygenation reactions of hydrocarbons.[1] Many physical techniques, such as crystallography, spectroscopy, electrochemistry, and theoretical calculations, are being used to develop a deeper understanding of the electronic modulation of the porphyrin ligand by peripheral substituents.[2,3] Our recent investigations in this area have made extensive use of X-ray photoelectron spectroscopy (XPS).[4−6] These studies have shown that the core ionization potentials (IPs) of the central nitrogens are extremely sensitive to electronic effects exerted by peripheral substituents.[3,5,6] In addition to peripheral substitutions, skeletal substitutions such as *meso*-tetraaza-substitution constitute a well-known alternative avenue for modulating the electronic character of the porphyrin ring. It appeared likely that a comparative XPS study of porphyrins and tetraazaporphyrins would contribute to our understanding of the electronic differences between the two types of ligands.[7] Here we compare nitrogen core X-ray photoelectron spectra of free base octaethylporphyrin (PEt$_8$H$_2$), octaethylporphyrazine (PzEt$_8$H$_2$),[8] tetrabenzoporphyrin (TBPH$_2$), and phthalocyanine (PcH$_2$). The results reveal a significant modulation of the electrostatic potential in the central metal-binding regions of the macrocyclic ligands as a result of *meso*-tetraaza-substitution.

Methods

The XPS measurements were carried out with a Physical Electronics 5600 spectrometer, using monochromatized Al Kα X-rays of 500 W power. (Unmonochromatized X-rays do not result in the resolution necessary for a satisfactory analysis of the nitrogen 1s XPS of tetraazaporphyrins.) A tiny speck of material was rubbed with a flat-tipped quartz rod into an extremely thin, effectively conducting film on gold foil, so that the Au 4f$_{7/2}$ peak at 84.0 eV of the gold substratum could be used as a convenient external binding energy reference. There was no evidence of sample charging under these conditions, as the positions and shapes of the XPS peaks remained unchanged from run to run and also on flooding the samples with low-energy electrons from a neutralizer. The XPS data reported here were reproducible to within ±0.1 eV.

Each of the porphyrin and azaporphyrin compounds examined contains more than one type of nitrogen in its molecules. A meaningful comparison of the different nitrogen core spectra hinges upon our successful assignment of the different nitrogen 1s XPS peaks to the different nitrogens. For brevity, we will abbreviate the central protonated, central unprotonated, and *meso* nitrogens (if any) of these compounds as N1, N2, and N3, respectively. Recent advances in *ab initio* computational technology encouraged us to attempt to assign the nitrogen core XPS using all-electron Hartree−Fock (HF) self-consistent field (SCF) calculations. Use of the direct SCF method,[9] as implemented in the program system DISCO,[10] was critical for accomplishing the large calculations that are relevant to this study. All-electron HF SCF calculations, employing generally contracted[11] double-ζ plus polarization (DZP)[12] basis sets, were carried out on free base unsubstituted porphyrin (PH$_2$) and porphyrazine (PzH$_2$). The larger molecules, TBPH$_2$ and PcH$_2$, were studied with only unpolarized double-ζ (DZ)[13] basis sets.[14] We know from earlier theoretical studies[3,4] on

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(8) Of the four compounds studied by XPS, PzEt$_8$H$_2$ was prepared as follows, the other three compounds being commercially available: Fitzgerald, J.; Taylor, W.; Owen, H. *Synthesis* **1991**, 686.

(9) Almlöf, J.; Faegri, K.; Korsell, K. *J. Comput. Chem.* **1982**, *3*, 385.

(10) J. Almlöf, K. Faegri, M. Feyereisen, T. H. Fischer, K. Korsell, and H. P. Lüthi, DISCO, a direct SCF and MP2 code.

(11) General contraction: (a) Raffenetti, R. C. *J. Chem. Phys.* **1973**, *58*, 4452. (b) Schmidt, M. W.; Ruedenberg, K. *J. Chem. Phys.* **1979**, *71*, 3951.

(12) The DZP basis sets for C, N, and H were (7s4p1d)/[4s3p1d], (7s4p1d)/[4s3p1d], and (4s1p)/[3s1p]. The nonpolarization parts of these basis sets were obtained from: van Duijneveldt, F. B. *IBM Res. Rep.* **1971**, No. RJ945. The polarization exponents of C and N were obtained from: Roos, B.; Siegbahn, P. *Theor. Chim. Acta* **1970**, *17*, 199. A polarization p exponent of 0.8 was used for H.

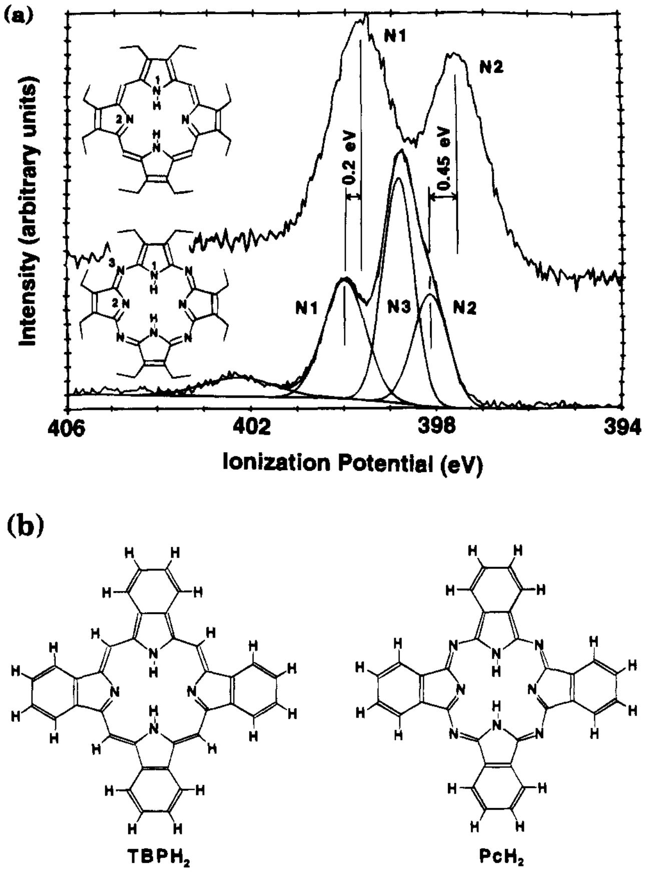

Figure 1. (a) The nitrogen 1s XPS of PEt_8H_2 (top) and $PzEt_8H_2$ (bottom). A curve-fit to the latter spectrum is also shown. Assignments of the different peaks to N1, N2, and N3 types of nitrogen are indicated. (b) Molecular structures of $TBPH_2$ and PcH_2.

porphyrins that the DZ basis sets used result in orbital energies that are close to the Hartree–Fock limit. The molecular geometries used for the compounds were obtained from earlier work.[15,16] The molecular geometries of PH_2 and PzH_2 were fully optimized using a D_{2h} symmetry constraint, but the geometries $TBPH_2$ and PcH_2 were not optimized.[16] An examination of the calculated nitrogen core orbitals and orbital energies readily enabled us to assign the composite XPS peaks to the different types of nitrogens in these molecules.[17]

Results

Figure 1 compares the nitrogen 1s XPS of PEt_8H_2 and $PzEt_8H_2$. Table 1 presents the experimental nitrogen 1s IPs of the four compounds studied by XPS. Table 2 presents the calculated nitrogen 1s orbital energies. Also indicated in Tables 1 and 2 are the energy splittings between the different nitrogen 1s energies. The qualitative shapes of the nitrogen 1s XPS of $TBPH_2$ and PcH_2, which are not shown here, are similar to those of PEt_8H_2 and $PzEt_8H_2$, respectively.

Table 1. Experimental Nitrogen 1s IPs (eV)

	IP			N 1s energy splitting		
compd	N1	N2	N3	N1–N2	N2–N3	N3–N1
PEt_8H_2	399.75	397.65		2.1		
$PzEt_8H_2$	399.95	398.1	398.75	1.85	0.65	1.2
$TBPH_2$	399.6	397.6		2.0		
PcH_2	399.8	397.9	398.4	1.9	0.5	1.4

Table 2. Calculated Sign–Reversed Nitrogen 1s Orbital Energies (eV)

		sign-reversed orbital energy			N 1s energy splittings		
compd	basis set	N1	N2	N3	N1–N2	N2–N3	N3–N1
PH_2	DZP	424.39	422.50		1.89		
PzH_2	DZP	424.81	423.01	423.88	1.80	0.87	0.93
$TBPH_2$	DZ	424.95	422.99		1.96		
PcH_2	DZ	425.23	423.31	423.88	1.92	0.57	1.35

Discussion

Several comments are in order concerning the experimental results.

A comparison of the data in Tables 1 and 2 reveals that the calculated, sign-reversed nitrogen 1s orbital energies differ from the experimental XPS IPs by approximately 25 eV. This discrepancy, while substantial, is not a matter of concern, since it stems largely from the neglect of relaxation effects in our calculations.[3,4] The relaxation effect is believed to be nearly identical (to within about 0.05 eV) across a series of related compounds such as the tetrapyrroles being studied.[3,5,18] Therefore, the experimental IPs and calculated orbital energies may be regarded as being related simply by a uniform shift of the energy scale.

The nitrogen 1s XPS of PEt_8H_2 shown in Figure 1 is typical of that of a free base porphyrin.[3,4] The two prominent nitrogen 1s peaks of PEt_8H_2 are separated by 2.1 eV, which agrees well with a calculated (HF/DZP) nitrogen 1s energy splitting of 1.89 eV for PH_2. The calculation enables us to assign the XPS peak with the higher IP to the central protonated nitrogens and the other peak to the central unprotonated nitrogens. As expected, this assignment also holds for $TBPH_2$.

The nitrogen 1s XPS of $PzEt_8H_2$ is somewhat more complicated. A free base porphyrazine has three types of nitrogens, but it appears from the XPS that only one kind of nitrogen is resolved on the high-IP side of the spectrum. The large unresolved peak on the low-IP side has a slight shoulder, but a *unique* deconvolution of this composite peak appeared to be impossible on the basis of the empirical results alone. The calculated core orbital energies of PzH_2 provided a means for obtaining a reasonable curve-fit to the experimental nitrogen 1s XPS of $PzEt_8H_2$. Making use of the calculated nitrogen 1s energy splitting pattern of PzH_2 (Table 2) and recalling that the distribution of N1, N2, and N3 is 1:1:2, we obtained an excellent curve-fit of the XPS, as shown in Figure 1. The experimental nitrogen 1s energy splittings of $PzEt_8H_2$ are 1.85

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(13) The DZ basis sets for C, N, and H were (6s3p)/[3s2p], (6s3p)/[3s2p], and (3s)/[2s], respectively, and were obtained from the compilation of van Duijneveldt.[12] The hydrogen exponents were multiplied by a scaling factor of 1.44. For molecular applications, a scaling factor of 1.2 is optimal for Slater-type orbital basis sets for hydrogen, which corresponds to a scaling factor of 1.44 for Gaussian basis sets.

(14) For all basis sets, the outermost s and p primitives were uncontracted so that they could constitute basis functions on their own.

(15) The optimized geometry of PH_2 was obtained from: Almlöf, J.; Fischer, T. H.; Gassman, P. G.; Ghosh, A.; Häser, M. *J. Phys. Chem.* **1993**, *97*, 10964.

(16) The optimized geometry of PzH_2 and the unoptimized geometries of $TBPH_2$ and PcH_2 were obtained from: Ghosh, A.; Gassman, P. G.; Almlöf, J. *J. Am. Chem. Soc.* **1994**, *116*, 1932.

(17) It is worth mentioning why we chose to perform our XPS measurements on the free bases rather than on metal complexes. Our choice stems from the fact that it was impossible to resolve the two types of nitrogen (*meso* and central) present in a metallotetraazaporphyrin such as $ZnPzEt_8$ or ZnPc. We know from XPS measurements on metalloporphyrins that the core IPs of both the metal and the central nitrogens shift by comparable amounts as a result of electronic effects of peripheral substituents. Therefore, XPS analyses of both the free bases and metallotetrapyrroles provide approximately the same information on the electrostatic potential in the central region of the macrocycle.

(18) The constancy of the relaxation effect has been verified by explicit calculations for the two lowest IPs of various tetrapyrrolic molecules.[3]

(N1−N2), 0.65 (N2−N3), and 1.2 eV (N1−N3), which are in impressive agreement with the calculated HF/DZP splittings of 1.80 (N1−N2), 0.87 (N2−N3), and 0.93 eV (N1−N3) for PzH_2.[19] The XPS of PcH_2 was curve-fit and assigned in the same manner using the calculated nitrogen 1s energy splitting pattern.

The core IPs of the central nitrogens of $PzEt_8H_2$ exceed those of PEt_8H_2 by 0.2 (for N1) to 0.45 eV (for N2). Similarly, the core IPs of the central nitrogens of PcH_2 exceed those of $TBPH_2$ by 0.2 (for N1) to 0.3 eV (for N2). The data indicate that *meso*-tetraaza-substitution results in a modest, but reproducible and significant, increase of roughly 200−450 mV in the electrostatic potential in the central region of the macrocycle. In other words, a metal ion bound to a tetraazaporphyrin is likely to experience a potential that is 200−450 mV more positive relative to the same ion bound to a similarly substituted porphyrin. This difference, although modest, can indeed cause significant differences in chemical behavior between porphyrins and tetraazaporphyrins.

Consistent with the more positive potential in the central region of tetraazaporphyrins, porphyrazines and phthalocyanines are better at stabilizing lower oxidation states of complexed metals (e.g. Fe^{II} versus Fe^{III}) relative to porphyrins bearing similar substituents. 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.[20] To take another example, the core IPs of the central nitrogens of $TPPH_2$ ($TPPH_2$ = tetraphenylporphyrin) are 399.5 (N1) and 397.4 eV (N2), which may be compared to 399.8 (N1) and 397.9 eV (N2) for PcH_2. Thus, a metal ion should experience a more positive potential when bound to Pc than when bound to TPP by a margin of ~300−500 mV. This is reflected in electrochemical data: one-electron electrochemical reduction of $(PcFe)_2O$ takes place at a potential that is approximately 400 mV less negative than in the case of $(TPPFe)_2O$.[21,22] The increased stabilization of Fe^{II} versus Fe^{III} by the Pc ligand, relative to a "low-potential" porphyrin ligand such as TPP, also manifests itself in an oxo-transfer reaction of $[PcFe^{III}(py)]_2O$:[20,21]

$$[PcFe^{III}(py)]_2O + PPh_3 \rightarrow 2PcFe^{II}(py) + OPPh_3$$

This type of reactivity is quite unusual for the (μ-oxo)diiron(III) unit, which is well-known for its stability.

In addition to correctly predicting the nitrogen 1s energy splitting patterns in the different porphyrinic molecules, our calculations succeed in reproducing the *difference* in core IPs of the central nitrogens of PEt_8H_2 and $PzEt_8H_2$ with high accuracy. In other words, the calculations can accurately predict the effect of *meso*-tetraaza-substitution on the potential at the center of the macrocyclic ligands. However, the calculated nitrogen 1s orbital energies of $TBPH_2$ and PcH_2 should not be quantitatively compared with each other and with those of PH_2 and PzH_2, since we used unoptimized geometries in the calculations on $TBPH_2$ and PcH_2. We know from experience[23] that the calculated nitrogen 1s energies are somewhat sensitive to small changes in the molecular geometries, differing by up to 0.3 eV between a calculation with a fully optimized geometry and one using a reasonable unoptimized geometry. Nevertheless, there is impressive agreement between experimental (Table 1) and calculated (Table 2) nitrogen 1s orbital energy splittings of $TBPH_2$ and PcH_2.

Mention should be made of a previous XPS study of PcH_2 by Niwa et al.[24] The nitrogen 1s IPs reported by these authors are not directly useful for precise comparison with our results, since they used a different binding energy reference. However, as in this work, they were successful in resolving the peak due to N1 and thus disproved suggestions[25] that each of the central hydrogens of PcH_2 is shared by (or bridging) two central nitrogens. Similarly, our XPS results on $PzEt_8H_2$ shows that the central hydrogens are not bridging, but are each attached to individual nitrogens.

Since the XPS results appear to be in general agreement with electrochemical redox potentials, it is worth noting the difference between the information provided by XPS and by electrochemistry. Because of the extremely localized, atom-centered nature of the hole due to core ionization, XPS core IPs reflect electrostatic potentials at individual atoms. In contrast, the holes due to valence ionizations are often highly delocalized so that electrochemical redox potentials and valence IPs do not generally reflect potentials at individual atoms. To illustrate the point, note that the nitrogen core IPs of PcH_2 exceed those of $TPPH_2$ by 0.3−0.5 eV but the first (i.e. lowest) IPs of PcH_2[26] and $TPPH_2$[27] are nearly identical, each being about 6.4 eV.

Finally, mention should be made of some electronic differences between porphyrins and tetraazaporphyrins that were uncovered by techniques other than photoelectron spectroscopy. For instance, the central metal-binding cavity in a tetraazaporphyrin is smaller than that of a porphyrin by about 20 pm.[15,20,28] Presumably, the smaller coordination sphere results in a stronger ligand field in a porphyrazine relative to a similarly substituted porphyrin. This is consistent with (octaethylporphyrazinato)-iron(III) chloride having a quartet ground state, whereas typical hemin chloride complexes are ground state sextets.[20] We will continue to study these and other electronic differences between porphyrins and tetraazaporphyrins.

Conclusion

High-resolution nitrogen 1s X-ray photoelectron spectra have been acquired for free base porphyrin, porphyrazine, and phthalocyanine ligands. The spectra were deconvoluted and assigned using all-electron *ab initio* HF calculations with extended basis sets. The overall agreement between theoretical and spectroscopic results was excellent. The results indicate that *meso*-tetraaza-substitution increases the potential in the

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(19) The small peak toward the high-IP end of the nitrogen 1s XPS of $PzEt_8H_2$ is believed to be a shake-up feature, resulting from a core-ionized valence-excited final state. A similar feature also exists in the XPS of PEt_8H_2, where it is less obvious.

(20) Fitzgerald, J.; Haggerty, B. S.; Rheingold, A. N.; May, L. *Inorg. Chem.* **1992**, *31*, 2006.

(21) Ercolani, C.; Gardini, M.; Pennesi, G.; Ross, G. *J. Chem. Soc., Chem. Commun.* **1983**, 549.

(22) Ercolani, C.; Floris, B. In *Phthalocyanines*; Leznoff, C. C., Lever, A. B. P., Eds.; VCH: New York, Vol. 2, 1993; pp 5−41.

(23) Ghosh, A. Unpublished results.

(24) Niwa, Y.; Kobayashi, H.; Tsuchiya, T. *J. Chem. Phys.* **1974**, *60*, 799.

(25) Schaffer, A. M.; Gouterman, M. *Theor. Chim. Acta* **1972**, *25*, 62. If each of the central hydrogens were symmetrically bridging between two central nitrogens, there would be only two types of nitrogens in a 1:1 ratio in PcH_2 or $PzEt_8H_2$, which is clearly inconsistent with the XPS data.

(26) Ultraviolet photoelectron spectrum of PcH_2: Berkowitz, J. *J. Chem. Phys.* **1979**, *70*, 2819.

(27) Ultraviolet photoelectron spectrum of $TPPH_2$: Khandelwal, C.; Roebber, J. L. *Chem. Phys. Lett.* **1975**, *34*, 355.

(28) For structures of analogous PEt_8 and $PzEt_8$ complexes, see the following: (a) PEt_8FeCl: Ernst, J.; Subramanian, J.; Fuhrhop, J.-H. *Z. Naturforsch., A* **1977**, *32A*, 1129. $PzEt_8FeCl$: Reference 21. (b) PEt_8RhCH_3: Takenaka, A.; Syal, S. K.; Sasada, Y.; Omura, T.; Ogoshi, H.; Yoshida, Z. *Acta Crystallogr., Sect. B* **1976**, *B32*, 62. $PzEt_8RhCH_3$: Ni, Y.; Fitzgerald, J. P.; Carroll, P.; Wayland, B. B. *Inorg. Chem.* **1994**, *33*, 2029.

central metal-binding regions of the ligands by about 200−450 mV, which is in agreement with the known chemical properties of porphyrins and tetraazaporphyrns. This work also demonstrates the growing role of modern quantum chemistry for accurate studies of molecules as large as porphyrins and phthalocyanines.

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