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Electronic Effects of Peripheral Substituents in Porphyrins: X-ray Photoelectron Spectroscopy and ab Initio Self-Consistent Field Calculations

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Abstract: The electronic effects of a wide variety of peripheral substituents in free base porphyrins have been evaluated using X-ray photoelectron spectroscopy (XPS) and all-electron ab initio calculations. Both methods have identified the 1s energies of the central nitrogens as excellent sensors of the electronic effects of peripheral substituents. Core level photoelectron spectra are reported for nine porphyrins, including unsubstituted porphyrin, octaethylporphyrin, and seven tetraphenylporphyrins. Substituents on the phenyl groups in tetraphenylporphyrins have been found to modulate the electronic environment of the central region of the porphyrin nucleus in a significant manner. Thus, between tetraphenylporphyrin and tetrakis(pentafluorophenyl)porphyrin, the XPS nitrogen 1s ionization potentials shift by 0.9 eV. Ab initio self-consistent field calculations were carried out on substituted porphyrins, with multiple alkyl, aryl, fluoro, chloro, bromo, cyano, and nitro groups, using basis sets of double-ζ quality. Calculations on selected porphyrins with larger, polarized basis sets suggest that both the absolute values of the orbital energies and the substituent effects are reasonably well-converged at the double-ζ level of basis sets. Very large substituent effects (up to 4.1 eV, relative to octamethylporphyrin, in our calculations) on the 1s energies of the central nitrogens of the porphyrin nucleus are predicted for certain arrays of electron-withdrawing peripheral substituents. Valence orbital energies have also been computed, and the differences in the ultraviolet photoelectron spectra of porphyrin and octaalkylporphyrins are well reproduced by the calculations. Suitable arrays of strongly electron-withdrawing substituents result in large stabilizations of the porphyrin π orbitals, which should translate into enhanced stability of the porphyrins toward oxidative degradation. The molecules studied by the ab initio calculations range in size from porphyrin, $C_{20}H_{14}N_4$, to β-octafluoro-*meso*-tetrakis(pentafluorophenyl)porphyrin, $C_{44}H_2F_{28}N_4$. Use of the direct SCF formalism, in which integrals do not need to be stored, has made these large calculations feasible. These calculations demonstrate that at present ab initio calculations can be performed routinely for molecules containing 50–100 atoms.

I. Introduction

A number of recent studies have demonstrated the importance of substituent effects in porphyrins.[1–6] Metal complexes of porphyrins bearing directly attached electron-withdrawing substituents (in particular halogenated porphyrins) have been found to have significantly better catalytic properties in various oxidation reactions than complexes of the more common tetraphenylporphyrin and octaethylporphyrin.[7,8] Two reasons have been suggested for this.[8] First, the electronegative substituents may activate the high-valent metal intermediate involved in these reactions. Second, by lowering the energy of the highest occupied molecular orbital (HOMO), they protect the porphyrin macrocycle from oxidative degradation. In addition, the steric effects of the peripheral substituents are also important: bulky substituents at appropriate positions prevent the formation of the catalytically inert μ-oxo dimers, and also sterically hinder electrophilic attack on the porphyrin.[9] In other studies, even remote substituents, such as those on the phenyl rings in tetraphenylporphyrins, have been found to modulate the electronic properties of the central region of the porphyrin macrocycle.[10]

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Table I. Basis Sets Used for Different Elements

element	set I	set II	set III
H(peripheral)[a]	(3s)/[2s][b]	(4s)/[3s][b,c]	(4s1p)/[3s1p][d]
H(central)[a]	(3s)/[2s][b]	(4s1p)/[3s1p][b–d]	(4s1p)/[3s1p][d]
C[a,e]	(6s3p)[3s2p]	(7s4p1d)[4s3p1d][f]	(7s4p1d)[4s3p1d][g]
N[a,e]	(6s3p)[3s2p]	(7s4p1d)[4s3p1d][h]	(7s4p1d)[4s3p1d][i]
O[a,e]	(6s3p)[3s2p]		(7s4p1d)[4s3p1d][j]
F[a,e]	(6s3p)[3s2p]	(7s4p1d)[4s3p1d][k]	(7s4p1d)[4s3p1d][k]
Cl[l]	(10s6p1d)/[4s3p1d][m]	(11s7p2d)/[5s4p2d][n]	
Br[o]	(13s9p5d)/[7s6p3d]		

[a] Basis sets for these elements were obtained from the compilation by van Duijneveldt.[26] [b] The s exponents were multiplied by a scaling factor of 1.44.[27] [c] The diffuse s exponent for H was 0.08.[28] [d] The polarization p exponent for H was 0.8.[29] [e] The outermost primitive s and p GTOs were "uncontracted", i.e., they constituted basis functions on their own. [f] The diffuse s and p exponents for C were 0.07 and 0.06, respectively,[28] and the d exponent was 0.8.[29] [g] The d exponent for C was 0.63. [h] The diffuse s and p exponents for N were 0.08 and 0.09, respectively,[28] and the d exponent was 1.0.[29] [i] The d exponent for N was 0.95. [j] The d exponent for O was 1.33. [k] The diffuse s and p exponents for F were 0.151 245 and 0.159 606,[28] respectively, in set II. The d exponent was 1.62 for both sets II and III.[29] [l] This sp basis of Cl was obtained from ref 30. [m] The d exponent of Cl in set I was 0.68.[29] [n] The diffuse s and p exponents for Cl were 0.080 266 and 0.069 285, respectively.[28] The d exponents of Cl in set II were 1.177 794 and 0.392 598. [o] This basis was obtained from ref 31.

We chose to evaluate the electronic effects of peripheral substituents on the electronic character of the atoms at the center of the porphyrin ring, separately from steric considerations and solvent effects, in two complementary ways: (1) core level X-ray photoelectron spectroscopy (XPS),[11,12] and (2) all-electron ab initio self-consistent field (SCF) calculations.[13] The 1s orbital energies of the central nitrogens in porphyrins provide a sensitive probe of the effects of peripheral substituents on the central region of the porphyrin ring. In this paper, we report ab initio SCF studies of substituent effects on a series of free-base porphyrins and a comparison of XPS and computed substituent effects for a series of tetraphenylporphyrins.

The unsubstituted parent compound, porphyrin (until recently known as porphin),[14] is a fairly large molecule by current standards of ab initio quantum chemistry, and many substituted porphyrins of experimental interest are beyond the reach of conventional ab initio methods. For this reason, in spite of the interest in porphyrins, there have been relatively few all-electron ab initio Hartree–Fock studies. Most of these calculations have been on the parent macrocycles such as porphyrin or chlorin, or on simple substituted analogues and metal complexes.[13] The subject of substituent effects in porphyrins has not been previously addressed by ab initio methods. In the present series of calculations, we have examined substituent effects due to multiple alkyl, aryl,[1] fluoro,[2] chloro,[3] bromo,[3] trifluoromethyl,[4] cyano,[5] and nitro[6] substituents. The size of the molecules studied in these calculations ranged from porphyrin, $C_{20}H_{14}N_4$, to 2,3,7,8,12,13,17,18-octafluoro-5,10,15,20-tetrakis(pentafluorophenyl)porphyrin, $C_{44}H_2F_{28}N_4$.

II. Experimental Methods

X-ray photoelectron spectra were obtained using Perkin-Elmer PHI 555, 5400, and 5600 spectrometers. Unmonochromatized magnesium or aluminum Kα radiation was generally used. Monochromatized Al Kα radiation was used in analyses requiring very high resolution. We used the lowest possible pass energies (10–25 eV, depending on the spectrometer) that were compatible with achieving a sufficiently high signal-to-noise ratio in a reasonable amount of time (at the most about 30 min of acquisition time per peak). The compounds examined showed no evidence of X-ray-induced damage for the lengths of time necessary for spectral acquisition. The spectrometers were calibrated so that the Au $4f_{7/2}$ and Cu $2p_{3/2}$ peaks of the clean, sputtered metals appeared at 84.00 and 932.65 eV, respectively.

The following free-base porphyrins were prepared according to known procedures and examined by XPS: porphyrin (PH_2),[15] 2,3,7,8,12,13,17,18-octaethylporphyrin (β-PEt_8H_2),[16] 5,10,15,20-tetraphenylporphyrin ($TPPH_2$),[17] 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin (TCl_2PPH_2),[18] 5,10,15,20-tetrakis(4-cyanophenyl)porphyrin ($TCNPPH_2$),[19] 5,10,15,20-tetrakis(4-(trifluoromethyl)phenyl)porphyrin (TCF_3PPH_2),[20] 5,10,15,20-tetrakis(4-nitrophenyl)porphyrin (TNO_2PPH_2),[19] and 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin (TF_5PPH_2).[21]

The XPS sample consisted of approximately 10 μg of the solid porphyrin rubbed into an extremely thin film on a piece (roughly 1 cm × 1 cm) of gold foil (0.1 mm thick) using a flat-tipped sapphire or quartz rod. The films, which appeared like a colored sheen on the gold, were so thin as to be effectively conducting, and there was no evidence of sample charging. This was judged from the following. For a particular sample, the XPS peak positions and shapes remained highly reproducible (±0.1 eV) from one run to another and from one spectrometer to another.

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Table II. List of Porphyrin Systems Studied, Number of Primitive and Contracted Basis Functions, and Number of Electrons

porphyrin and molecular symmetry	no. of basis functions		no. of electrons
	prim	contr	
Porphyrin and Octamethylporphyrin			
porphyrin ($\mathrm{PH_2}$), D_{2h}	402	244	162
2,3,7,8,12,13,17,18-octamethylporphyrin (β-$\mathrm{PMe_8H_2}$), D_{2h}	570	348	226
Tetraphenylporphyrins			
$\mathrm{TPPH_2}$, D_{2h}	810	492	322
$\mathrm{TPPH_2}$, C_{2v}	810	492	322
$\mathrm{TCl_2PPH_2}$, D_{2h}	1050	620	450
$\mathrm{TCNPPH_2}$, D_{2h}	918	556	370
$\mathrm{TCF_3PPH_2}$, $\mathrm{D_2}$	1038	628	450
$\mathrm{TNO_2PPH_2}$, D_{2h}	978	592	410
$\mathrm{TF_5PPH_2}$, D_{2h}	1050	632	482
Chlorinated Porphyrins			
5,10,15,20-tetrachloroporphyrin (m-$\mathrm{PCl_4H_2}$), D_{2h}	522	308	226
2,3,7,8,12,13,17,18-octachloroporphyrin (β-$\mathrm{PCl_8H_2}$), D_{2h}	642	372	290
dodecachloroporphyrin ($\mathrm{PCl_{12}H_2}$), D_{2h}	762	436	354
Brominated Porphyrins			
5,10,15,20-tetrabromoporphyrin (m-$\mathrm{PBr_4H_2}$), D_{2h}	650	396	298
2,3,7,8,12,13,17,18-octabromoporphyrin (β-$\mathrm{PBr_8H_2}$), D_{2h}	898	548	434
Fluorinated Porphyrins			
5,10,15,20-tetrafluoroporphyrin (m-$\mathrm{PF_4H_2}$), D_{2h}	450	272	194
2,7,12,17-tetrafluoroporphyrin (β-$\mathrm{PF_4H_2}$), C_{2h}	450	272	194
2,3,7,8,12,13,17,18-octafluoroporphyrin (β-$\mathrm{PF_8H_2}$), D_{2h}	498	300	226
dodecafluoroporphyrin ($\mathrm{PF_{12}H_2}$), D_{2h}	546	328	258
5,10,15,20-tetrakis(trifluoromethyl)porphyrin (m-$\mathrm{P(CF_3)_4H_2}$), D_2	630	380	290
2,7,12,17-tetrakis(trifluoromethyl)porphyrin (β-$\mathrm{P(CF_3)_4H_2}$), C_{2h}	630	380	290
2,3,7,8,12,13,17,18-octafluoro-5,10,15,20-tetrakis(pentafluorophenyl)porphyrin ($\mathrm{F_{28}TPPH_2}$), D_{2h}	1146	688	546
Cyanoporphyrins			
5,10,15,20-tetracyanoporphyrin (m-$\mathrm{P(CN)_4H_2}$), D_{2h}	510	308	210
2,3,7,8,12,13,17,18-octacyanoporphyrin (β-$\mathrm{P(CN)_8H_2}$), D_{2h}	618	372	258
dodecacyanoporphyrin ($\mathrm{P(CN)_{12}H_2}$), D_{2h}	726	436	306
2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetracyanoporphyrin ($\mathrm{PCl_8(CN)_4H_2}$), D_{2h}	750	436	338
Nitroporphyrins			
5,10,15,20-tetranitroporphyrin (m-$\mathrm{P(NO_2)_4H_2}$; coplanar), D_{2h}	570	344	250
5,10,15,20-tetranitroporphyrin (m-$\mathrm{P(NO_2)_4H_2}$; orthogonal), D_{2h}	570	344	250

In general, very sharp peaks were obtained. Thus, the full widths at half height of the nitrogen 1s peaks ranged from 0.8 to 1.3 eV, the lower end of this range being obtained with monochromatized X-rays. Flooding the sample with moderate levels of low-energy electrons using a charge neutralizer did not result in significant changes in peak positions or shapes. Finally, photoelectrons from the underlying gold were readily detectable. The $4f_{7/2}$ level at 84.00 eV of the gold substratum could therefore be used as an external binding energy reference. This method of correction for sample charging has been successfully used in other investigations.[11c,e,h,k,22]

III. Computational Methods

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 scheme,[23] 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.

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 different basis sets used in this work are shown in Table I. Set I, which is of double-ζ (DZ) quality, has been used for all the porphyrins that we have studied by computation in this study. The larger basis sets II and III have been used for a few selected porphyrins to obtain an estimate of the errors associated with the results obtained with set I. The basis sets for first-row elements (including hydrogen) were taken from a compilation by van Duijneveldt[26] for sets I, II, and III.[26] Polarization d functions were added for Cl and Br atoms. In all cases involving d orbitals, only the five "pure" spherical harmonic d functions were used, and the totally symmetric s components were projected out of the basis. The differences between sets I, II, and III are briefly as follows, with additional details given in Table I.

In set I, the (6s3p) primitive sets, used for the first-row atoms (C, N, O, F), are the smallest sets in van Duijneveldt's compilation having two Gaussian-type orbitals (GTOs) in the 2s valence region. For hydrogen, the exponents for the (3s) primitive set were multiplied by a scaling factor of 1.44.[27]

The nonpolarization part of basis set II is derived from set I by adding diffuse functions; a single polarization function is used on all first-row atoms except peripheral hydrogens. The compounds studied using basis set II are $\mathrm{PH_2}$, m-$\mathrm{PF_4H_2}$, and m-$\mathrm{PCl_4H_2}$.

Set III is not adapted from set I. Set III uses the larger (7s4p) primitive sets from van Duijneveldt's compilation for the first-row atoms

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[25] (a) Raffenetti, R. C. *J. Chem. Phys.* **1973**, *58*, 4452. (b) Schmidt, M. W.; Ruedenberg, K. *J. Chem. Phys.* **1979**, *71*, 3951.

[26] van Duijneveldt, F. B. IBM Research Report RJ945, 1971.

[27] The optimum scaling factor for a calculation on the hydrogen molecule is 1.2, when one uses an STO basis optimized for the hydrogen atom. This translates to a scaling factor of 1.44 for a GTO basis.

[28] The exponents of the diffuse functions in basis set II were obtained by dividing the exponents of the most diffuse s and p functions in basis set I by ~2.5–3.0.

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[30] Roos, B.; Siegbahn, P. *Theor. Chim. Acta* **1970**, *17*, 209.

[31] Dunning, T. H. *J. Chem. Phys.* **1970**, *53*, 2823.

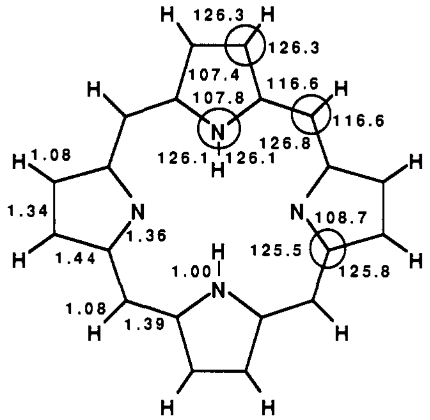

Figure 1. The molecular geometry of porphyrin. Except for the internal hydrogens, the distribution of the other nuclei has been assumed to conform to D_{4h} symmetry. Symmetry-distinct (according to D_{4h} symmetry) bond distances (in Å) and angles (in deg) are shown.

(C, N, O, F), in addition to polarization functions. A (4s1p)/[3s1p] basis was used for all hydrogens in set III. Set III does not have diffuse functions. The compounds studied using basis set III are PH_2, β-PF_8H_2, and *m*-$P(NO_2)_4H_2$ (the nitro groups were chosen perpendicular to the porphyrin ring).

In addition, porphyrin and tetraphenylporphyrin were studied with a fourth basis set, IV, which is essentially basis set II without the polarization functions. Set IV is thus a DZ basis set augmented with diffuse functions.

Table II lists the different porphyrins studied by the calculations and also some technical data about these calculations. Table II also lists the abbreviations of the names of the different porphyrins, which we will use hereafter. The numbers of basis functions listed in Table II refer to basis set I.

The calculations were carried out on Cray-2 and Cray-XMP computers at the Minnesota Supercomputer Center in Minneapolis and at the National Center for Supercomputing Applications in Urbana-Champaign.

The geometry used for the porphyrin ring in these calculations is very similar to that used in an early ab initio calculation on porphyrin[13a] and is shown in Figure 1. It is adapted from the X-ray diffraction investigation by Webb and Fleischer.[32] Except for the internal hydrogens, the distribution of the other nuclei was assumed to have D_{4h} symmetry. Since hydrogen positions are poorly resolved by X-ray diffraction studies, C–H distances of 1.08 Å were adopted. The positions of the internal hydrogens were optimized with basis set I and the equilibrium geometry was found to be a linear NH···HN arrangement with the N–H bond length equal to 0.997 Å. With the inclusion of the internal hydrogens, the optimized geometry of porphyrin had D_{2h} symmetry. Note that there are two types of central nitrogens in a free-base porphyrin, two "pyrrole-type" nitrogens each of which carries a hydrogen, and two "pyridine-type" nitrogens which do not carry hydrogens. This also results in two symmetry-distinct types of pyrrole rings, two types of α and β carbons, and two types of β hydrogens.

We preserved the geometry of the porphyrin skeleton in Figure 1 in the calculations on other substituted porphyrins. Unless otherwise mentioned, the positions and orientations of the substituents were obtained from the examination of atlases and tables of crystallographic data on molecules containing the same substituents.[33] The geometries of all porphyrins studied were constrained to D_{2h} symmetry, except as noted below. Using X to denote a β substituent and Y to denote a meso substituent, the C_α–C_β–C_X and C_α–C_{meso}–C_Y angles in the substituted porphyrins were chosen to be respectively equal to the C_α–C_β–H_β and C_α–C_{meso}–H_{meso} angles in porphyrin. A few bond lengths were optimized using basis set I, and these and some other geometrical details are noted below.

In β-PMe_8H_2, the methyl groups were oriented in order that they were bisected by the plane containing the porphyrin nucleus, as shown in Figure 2a. This resulted in the maximum possible symmetry, D_{2h}, for this compound. All internuclear angles subtended at the methyl carbons were chosen to be perfectly tetrahedral. The C_β–C_{Me} distance was assumed to be 1.50 Å and the C–H distances within the methyl groups were made equal to 1.09 Å.

The carbon–fluorine and carbon–chlorine bond lengths were optimized using basis set I in *m*-PF_4H_2 and *m*-PCl_4H_2, respectively, and the same bond lengths were also used for β-fluorinated and β-chlorinated porphyrins. The optimized C–F and C–Cl bond lengths are 1.366 and 1.767 Å, respectively. The carbon–bromine bond length was not optimized with basis set I. Instead, the value of 1.920 Å was adopted from a previous geometry optimization study of hexabromobenzene at the SCF level, which used basis sets comparable to the ones we have used in the present study.[35] The β-PF_4H_2 molecule was constrained to C_{2h} symmetry. The trifluoromethylated porphyrins, *m*-$P(CF_3)_4H_2$ and β-$P(CF_3)_4H_2$, were constrained to D_2 and C_{2h} symmetries, respectively, as shown in Figure 2b,c. All internuclear angles subtended at the trifluoromethyl carbons were chosen to be perfectly tetrahedral.

For the cyanoporphyrins, the $C_{porphyrin}$–C_{cyano} and C_{cyano}–N_{cyano} distances were assigned values of 1.43 and 1.16 Å, respectively, and a linear $C_{porphyrin}$–C_{cyano}–N_{cyano} arrangement was chosen.[33]

We studied two conformers of 5,10,15,20-tetranitroporphyrin (*m*-$P(NO_2)_4H_2$), both of D_{2h} symmetry, one in which the nitro groups and the porphyrin ring are coplanar (the "coplanar" form) and another in which the nitro groups and the porphyrin rings are perpendicular (the "perpendicular" form). The C_{meso}–N_{nitro} and the N_{nitro}–O distances were given values of 1.48 and 1.22 Å, respectively, and the C_{meso}–N_{nitro}–O and the O–N_{nitro}–O angles were chosen to be 118° and 124°, respectively.[33]

In the five tetraphenylporphyrins of D_{2h} symmetry listed in Table II, the phenyl groups were placed perpendicular to the plane containing the porphyrin nucleus.[34] Except for the linkage to the porphyrin nucleus, the benzene rings in the tetraphenylporphyrins were assumed to be regular hexagons with substituents placed radially outward at appropriate distances. The C_{meso}–C_{phenyl} bond length was chosen to be 1.509 Å and the C–C and C–H distances in the phenyl groups were chosen to be 1.39 and 1.09 Å, respectively.[34] The C–Cl distance in TCl_2PPH_2 and the C–F bond length in TF_5PPH_2 were chosen to be 1.735 and 1.369 Å, respectively.[35] The geometry of the cyano groups in $TCNPPH_2$ was assumed to be the same as in *m*-$P(CN)_4H_2$. The nitro groups in TNO_2PPH_2 (Figure 2d), were placed in the same planes as the phenyl rings to which they are bonded. Like *m*-$P(CF_3)_4H_2$, TCF_3PPH_2 was assigned a D_2-symmetric geometry, as shown in Figure 2e. The dimensions of the trifluoromethyl groups in TCF_3PPH_2 were assumed to be the same as in *m*-$P(CF_3)_4H_2$. A C_{2v} conformer of $TPPH_2$, shown in Figure 2f, in which the porphyrin–phenyl dihedral angle was assigned a value of 60°, was studied in order to estimate the effect of varying the porphyrin–phenyl dihedral angle.

IV. Results and Discussion

A. Basis Set Effects. At the beginning of our computational studies, we needed to determine possible basis set artifacts in the absolute values of the core and valence orbital energies, as well as in the substituent effects on these orbital energies. Two convenient criteria were available that helped us in the selection of the basis set to be used throughout the series of calculations. First, the valence electronic structure of porphyrins conforms to the four-orbital model,[36] according to which the two highest occupied MOs are closely spaced, and the two lowest virtual orbitals are also near-degenerate. These four orbitals are well-separated energetically from the remainder of occupied and virtual orbitals. The second criterion concerns the 1s energies of the central nitrogens of free-base porphyrins. We found from XPS on a large number of porphyrins that the energy difference ($\Delta\epsilon_{N,1s}$) between the 1s energies of the pyrrole-type and pyridine-type nitrogens is 2.1 ± 0.1 eV, and this value is largely independent of the peripheral substitution pattern. If a basis set is to describe substituent effects on the 1s energies of the central nitrogens in a reliable fashion, it should at least be able to describe $\Delta\epsilon_{N,1s}$ with resonable accuracy.

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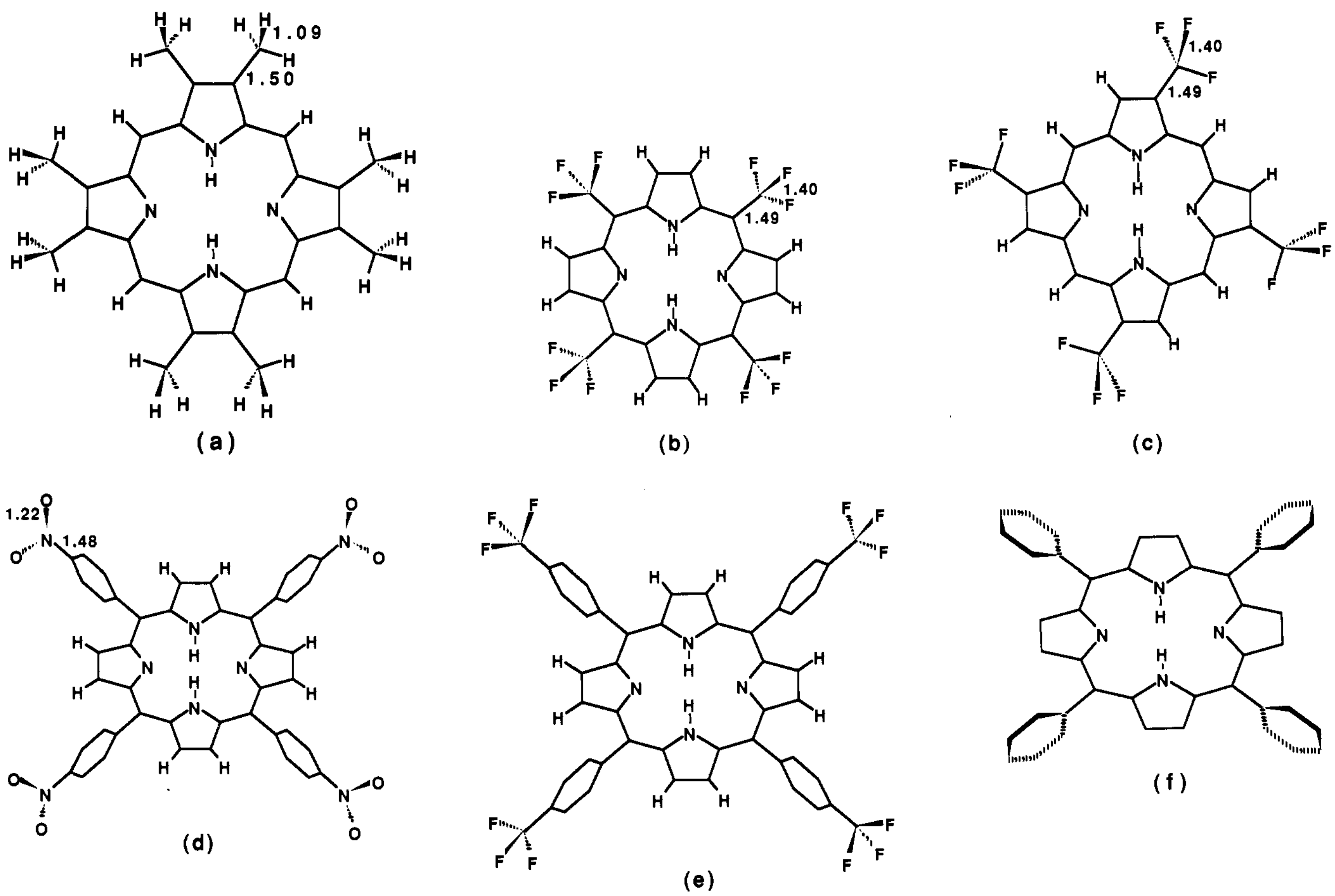

Figure 2. Geometries and conformations of selected substituted porphyrins: (a) PMe_8H_2, D_{2h}; (b) *m*-$P(CF_3)_4H_2$, D_2; (c) β-$P(CF_3)_4H_2$, C_{2h}; (d) TNO_2PPH_2, D_{2h}; (e) TCF_3PPH_2, D_2; (f) $TPPH_2$, C_{2v}. Some bond distances (in Å) are shown.

Table III. Comparison of the Selected Sign-Reversed Orbital Energies (eV) for Different Basis Sets (I, II, and III)

	PH_2			*m*-PF_4H_2		*m*-PCl_4H_2		β-PF_8H_2		*m*-$P(NO_2)_4H_2$	
	set I	set II	set III	set I	set II	set I	set II	set I	set III	set I	set III
orbitals											
N 1s	424.59	424.84	424.55	425.51	425.63	425.44	425.59	426.22	425.95	426.66	426.42
	422.49	422.69	422.38	423.42	423.51	423.33	423.45	424.16	423.80	424.52	424.21
valence											
a_u	6.23	6.22	6.13	7.15	7.02	6.96	6.89	7.84	7.48	8.01	7.73
b_{1u}	6.44	6.78	6.66	6.83	7.14	7.02	7.29	7.77	7.87	8.72	8.77
b_{2g}	8.89	9.07	8.99	9.52	9.62	9.44	9.56	10.07	10.07	10.59	10.55
b_{1u}	9.13	9.28	9.20	9.71	9.81	9.68	9.78	10.20	10.21	10.77	10.70
b_{3g}	10.16	10.20	10.12	10.65	10.66	10.31	10.34	11.41	11.33	11.93	11.83
b_{2g}	10.43	10.48	10.41	10.97	11.00	10.67	10.72	11.51	11.51	12.05	11.98

We have previously published an extensive study of basis set effects on the orbital energies of the parent compound, porphyrin.[37] The main conclusions of that study are as follows. Use of minimal basis sets resulted in unrealistically large $\Delta\epsilon_{N,1s}$ values. With basis sets of approximate DZ quality, the calculated value of $\Delta\epsilon_{N,1s}$ is essentially the same as the experimental value. A general contraction scheme gives somewhat better results for orbital energies than a segmented scheme (e.g. 3-21G). This difference becomes less pronounced as the basis set quality is improved to double-ζ with polarization (DZP) (e.g. with 6-31G* for the segmented set) or better. A DZ basis set with a general contraction scheme (basis set I) gave essentially converged Hartree–Fock limit values for all core orbital energies, and most valence orbital energies; for a few valence level orbitals of π symmetry, which had large amplitudes of d functions in calculations using polarized basis sets, the orbital energies obtained with the DZ basis set I differed from the DZP values by about 0.5 eV. In contrast, the absolute values of the core orbital energies obtained with the segmented 3-21G basis set differed considerably (by 1 eV or more) from the converged values, but the valence orbital energies were in good agreement with those obtained with basis set I.

Table IV. Basis Set Dependence of Substituent Effects

	rel N 1s energy (eV)		
porphyrin	set I	set II	set III
PH_2	0.0	0.0	0.0
m-PF_4H_2	−0.9	−0.8	
m-PCl_4H_2	−0.8	−0.7	
β-PF_8H_2	−1.6		−1.5
m-$P(NO_2)_4H_2$	−2.0		−1.8

To obtain an estimate of the basis set dependence of substituent effects, we initially studied PH_2, *m*-PF_4H_2, and *m*-PCl_4H_2 using the polarized basis set II, in addition to basis set I. Later, to make sure that the computed substituent effects were relatively free from basis set artifacts, even for arrays of extremely electron-withdrawing substituents, we performed SCF calculations on PH_2,

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Table V. Computed Nitrogen 1s Orbital Energies (eV) of Porphyrins

	$-\epsilon_{N-1s}$	
porphyrin	central nitrogens	substituents
Porphyrin and Octamethylporphyrin		
PH_2	424.59, 422.49	
β-PMe_8H_2	424.20, 422.09	
Tetraphenylporphyrins		
$TPPH_2$ (D_{2h})	424.46, 422.36	
$TPPH_2$ (C_{2v})	424.54, 422.45	
TCl_2PPH_2	424.56, 422.46	
$TCNPPH_2$	425.25, 423.15	424.20
TCF_3PPH_2	425.36, 423.27	
TNO_2PPH_2	425.48, 423.38	431.40
TF_5PPH_2	425.74, 423.63	
Chlorinated Porphyrins		
m-PCl_4H_2	425.44, 423.33	
β-PCl_8H_2	425.95, 423.93	
$PCl_{12}H_2$	426.54, 424.50	
Brominated Porphyrins		
m-PBr_4H_2	425.43, 423.33	
β-PBr_8H_2	425.86, 423.85	
Fluorinated Porphyrins		
m-PF_4H_2	425.51, 423.42	
β-PF_4H_2	425,41, 423.33	
β-PF_8H_2	426,22, 424.16	
$PF_{12}H_2$	427.12, 425.08	
m-$P(CF_3)_4H_2$	426.28, 424.10	
β-$P(CF_3)_4H_2$	425.73, 423.68	
$F_{28}TPPH_2$	427.15, 425.10	
Cyanoporphyrins		
m-$P(CN)_4H_2$	426.18, 424.03	424.73
β-$P(CN)_8H_2$	427.20, 425.21	425.80 (cyano N's on pyrrole rings with pyrrole-type N's), 425.44 (cyano N's on pyrrole rings with pyridine-type N's)
$P(CN)_{12}H_2$	428.24, 426.19	426.06 (cyano N's on pyrrole rings with pyrrole-type N's), 426.00 (N's of meso cyano groups), 425.69 (cyano N's on pyrrole rings with pyridine-type N's)
$PCl_8(CN)_4H_2$	427.13, 425.04	424.89
Nitroporphyrins		
m-$P(NO_2)_4H_2$ (coplanar)	426.69, 424.49	431.95
m-$P(NO_2)_4H_2$ (perpendicular)	426.95, 424.80	432.21

β-PF_8H_2, and m-$P(NO_2)_4H_2$ using the polarized basis set III. Table III provides a comparison of the absolute values of the energies of the nitrogen 1s and of the six highest occupied porphyrin π orbitals for the five porphyrins for different basis sets. In general, the orbital energies obtained using basis set I are in good agreement with those obtained using the larger basis sets II and III. From Table III, the maximum discrepancy in the orbital energies between the different basis sets is found to be 0.36 eV, and in most cases the discrepancy is much less.

Table IV provides a comparison of the nitrogen 1s energies of these five molecules for the different basis sets, with the nitrogen 1s energies of PH_2 chosen as the zero level for all basis sets. In other words, Table IV gives the substituent effects for the three basis sets. Although a free-base porphyrin has two different types of nitrogen, only one nitrogen 1s energy is entered in Table IV for each porphyrin, because the peripheral substituent effects are approximately (to within ±0.1 eV) the same for the two types of nitrogens. There is good agreement between the shifts obtained using basis sets I and those obtained using the larger sets, even for very strong substituent effects. These results suggest that substituent effects obtained using basis set I are reasonably well-converged. However, it should be noted that the substituent effects calculated using the larger sets are marginally, but systematically, lower than those obtained using set I.

B. Theoretical Nitrogen 1s Orbital Energies. In this paper, it is necessary to distinguish between orbital energies and ionization potentials (IPs). *We will reserve the term orbital energies for the eigenvalues of the SCF equations, and we will refer to XPS binding energies as ionization potentials.*

Table V lists the computed nitrogen 1s energies of the different porphyrins. The calculations show that the pyrrole-type porphyrin nitrogens have more negative 1s orbital energy (or higher XPS IPs) than the pyridine-type nitrogens. The energy difference $\Delta\epsilon_{N-1s}$ is extremely regular and lies in the 1.99–2.20 eV range for all the porphyrins studied in this work.

While it is intuitively obvious that peripheral substituents should perturb the energies of the delocalized porphyrin π orbitals, it is difficult to predict the extent of modulation of the electronic character of the central region of the porphyrin ring by substituents on the macrocycle's periphery. The results of our calculations suggest that a suitable array of substituents can cause a dramatic change in the electronic character of the atoms at the porphyrin's center. As shown in Table V, the calculated substituent effects span a very large range. Between octamethylporphyrin at the electron-rich end and dodecacyanoporphyrin at the electron-deficient end, the computed 1s energies of the central nitrogens change by 4.1 eV.

Table VI shows that for such high levels of peripheral substitutions as we have examined here, the substituent effects on the nitrogen 1s levels may not always be additive. In Table VI, X denotes a meso substituent and Y a β substituent. Thus, additivity holds well for fluorine substituents. An examination of Table V shows that the substituent effect in β-PF_8H_2 is almost exactly twice that in β-PF_4H_2. Chlorine substituent effects appear to be somewhat less additive. In contrast, the effects due to high levels of cyano substitution are calculated to be non-additive.

Table VII shows another interesting trend: our calculations predict that a particular substituent placed at a meso position exerts an approximately 20% larger substituent effect than when it is placed at a β position. Each of the substituent effects listed in Table VII are for a single substituent, that is, the substituent effects in meso-tetrasubstituted and β-octasubstituted porphyrins, relative to unsubstituted porphyrin, were divided by 4 and 8, respectively, to generate the values listed in Table VII. Because of the small difference between meso and β substituent effects, this trend in the theoretical results may be difficult to observe experimentally. The reason for this trend has not been established. A possible explanation may be that there is less bond distance alternation between the meso positions and the central nitrogens than between the β positions and the central nitrogens.[38]

Table VI. Investigation of the Additivity of Substituent Effects on the 1s Energies of the Central Nitrogens

	N 1s energy (eV) relative to unsubstituted porphyrin			
			$PX_4Y_8H_2$	
substituents	m-PX_4H_2	β-PY_8H_2	expected for perfect additivity	computed
X = Y = F	−0.92	−1.65	−2.54	−2.56
X = Y = Cl	−0.85	−1.36	−2.21	−1.97
X = Y = CN	−1.57	−2.61	−4.18	−3.68
X = CN, Y = Cl	−1.57	−1.36	−2.93	−2.54
X = C_6F_5, Y = F	−1.15	−1.65	−2.80	−2.56

Table VII. Meso versus β Substituent Effects (eV) per Substituent

substituent	meso	β
F	0.23	0.21
Cl	0.21	0.17
Br	0.21	0.16
CN	0.39	0.33
CF_3	0.42	0.29

Table VIII. XPS Core IPs (eV) for Free-Base Porphyrins

porphyrin	central N 1s	substituent N 1s	C 1s
PH_2	400.1, 398.1		284.8
β-PEt_8H_2	399.8, 397.7		285.0
tetraphenylporphyrins			
$TPPH_2$	399.5, 397.4		284.2
$TMeOPPH_2$	399.7, 397.6		not recorded
TCl_2PPH_2	400.05, 398.0		285.0
$TCNPPH_2$	400.2, 398.1	399.4	285.1
TCF_3PPH_2	400.2, 398.1		285.1, 292.7 (CF_3)
TNO_2PPH_2	400.2, 398.1	406.1	285.2
TF_5PPH_2	400.4, 398.2		285.1 (broad) 287.9 (C_6F_5)

Table IX. Comparison of XPS and Computed Substituent Effects on the 1s Energies (eV) of the Central Nitrogens in Tetraphenylporphyrins

	substituent effects	
porphyrin	XPS	computed
$TPPH_2$	0.0	0.00
TCl_2PPH_2	0.4	0.10
$TCNPPH_2$	0.6	0.79
TCF_3PPH_2	0.7	0.90
TNO_2PPH_2	0.7	1.01
TF_5PPH_2	0.9	1.27

An important concern in our calculations on the tetraphenylporphyrins was to determine if the porphyrin–phenyl dihedral angle played a major role in modulating the N 1s orbital energies. Although this issue has not been analyzed in detail in this paper, Table V shows that the two conformers of $TPPH_2$, which we have studied by SCF calculations, have very similar N 1s orbital energies.

Some of the porphyrins studied have more than two symmetry-unique types of nitrogen. The assignment of the 1s energies of these different nitrogens is shown in Table V. It can be seen that while the ionization potentials of nitro nitrogens are much higher than those of the central porphyrin nitrogens, the N 1s XPS peaks of the cyano groups may overlap with those of the porphyrin nitrogens. These cases are further discussed in the next section.

C. XPS Ionization Potentials. Table VIII lists the XPS N 1s IPs of several porphyrins as well as the positions of the C 1s peak maxima. Several points deserve comment. Between tetraphenylporphyrin and tetrakis(pentafluorophenyl)porphyrin the 1s IPs of the central nitrogens shift by 0.9 eV. This is a large shift considering that there are no electronegative atoms attached directly to the porphyrin periphery in these compounds. The experimental value of $\Delta\epsilon_{N,1s}$ (approximately 2.1 eV) is in excellent agreement with the theoretically predicted value.

Table IX compares the theoretical and experimental substituent effects on the 1s levels of the central nitrogens of several tetraphenylporphyrins, choosing the N 1s levels of unsubstituted tetraphenylporphyrin as the zero level. The positive numbers in this table signify that the N 1s orbital energies of the particular tetraphenylporphyrin in question are more negative (i.e., the IPs are more positive) than those of unsubstituted tetraphenylporphyrin. The agreement between the theoretical and computed substituent effects is qualitatively quite good.

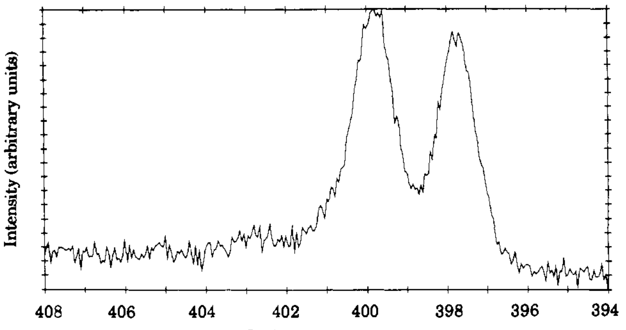

Figure 3. The N 1s XPS of β-PEt_8H_2.

There is a systematic difference of about 25 eV between the absolute values of the theoretical N 1s orbital energies (Table V) and experimental N 1s IPs (Table VIII). This discrepancy can be attributed to the neglect of relaxation and correlation energies in our calculations. It is now well-documented that relaxation accounts for the major part of this discrepancy, whereas differential electron correlation between the neutral and the core-ionized states is responsible for a small effect.[39] A ΔSCF IP is the difference between the SCF total energies of the neutral molecule and its ionized state. ΔSCF calculations of core IPs therefore yield results in good agreement with experimental gas-phase IPs.[40] We attempted to obtain ΔSCF estimates of the IPs by performing SCF calculations on N 1s core-ionized states of porphyrin, but these calculations could not be converged for the large molecules investigated here. Calculations of IPs have also been carried out at high levels of theory, including electron correlation, on smaller molecules, and experimental core ionization potentials have been accurately reproduced.[40,41] This work shows that the energy differences between, for instance, different types of carbon and nitrogen 1s IPs are very well reproduced by SCF calculations on the neutral molecules, and the DZ basis set I is essentially converged to the Hartree–Fock limit with respect to reproducing these effects. The substituent effects on the core energies, which are of interest here, are of the same nature, and should also be reliably described by the present calculations. The small discrepancies in Table IX should not be of great concern. Some possible factors contributing to the discrepancies include the neglect of relaxation and correlation effects in our calculations, the use of unoptimized or idealized molecular geometries, the neglect of porphyrin ruffling or buckling, intermolecular interactions in the solid state, the use of unpolarized basis sets, etc. The N 1s IPs of unsubstituted porphyrin (Table VIII) are about 0.5 eV more than those of tetraphenylporphyrin, a difference that is not matched in the computed N 1s orbital energies (Table V). A plausible explanation for this difference is that the larger molecule, tetraphenylporphyrin, has a larger relaxation energy than porphyrin.

Some further comments are warranted on the XPS of some individual porphyrins.

β-PEt_8H_2: Figure 3 shows the N 1s XPS of β-PEt_8H_2, a common synthetic model for the natural octasubstituted compounds. This is a typical N 1s XPS of a free-base porphyrin.

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(38) The difference in the amount of bond length alternation between the central nitrogens and the *meso* positions on the one hand and the β positions on the other can be checked either from Figure 1 of this paper or from the original crystallographic studies.[32]

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(41) The C 1s IPs of the CF_3 groups in TCF_3PPH_2 agree well with those of CF_3 groups in other molecules studied previously. Similarly, the pentafluorophenyl C 1s IPs in TF_5PPH_2 agree well with the C 1s IPs of hexafluorobenzene. Gelius, U.; Hedén, P. F.; Hedman, J.; Lindberg, B. J.; Manne, R.; Nordberg, R.; Nordling, C.; Siegbahn, K. *Phys. Scr.* **1970**, *2*, 70.

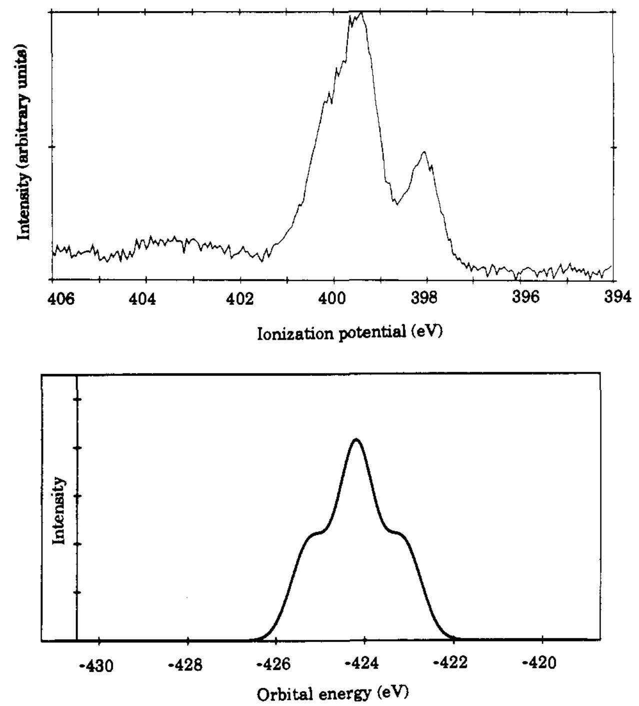

Figure 4. The (a, top) experimental and (b, bottom) simulated N 1s XPS of $TCNPPH_2$.

$TCNPPH_2$: The monochromatic N 1s XPS is shown in Figure 4. The three N 1s peaks could not be completely resolved. Using the computed energy differences between the three types of N 1s orbitals, however, a good Gaussian–Lorentzian curve-fit could be obtained for the composite N 1s signal. Use of a monochromator allows the clean resolution of the pyrrole-type N 1s peak, with the pyridine-type N 1s peak appearing as a shoulder on the cyano N 1s peak. Figure 4 also shows a "theoretical" N 1s XPS of $TCNPPH_2$, generated using the computed N 1s orbital energies. The intensity was represented by the expression $\exp[-(\epsilon - \epsilon_i)^2/\gamma]$, where ϵ_i's are the orbital energies, $\gamma = \omega^2/(4 \ln 2)$, and ω is the peak width at half-height ($\omega = 1.25$ eV in Figure 4), followed by a summation over the different ϵ_i eigenvalues. The experimental and computed N 1s XPS are quite similar. The calculated spectrum correctly places the cyano N 1s energies between the 1s energies of the two types of central nitrogens. However, while in the experimental spectrum the cyano N 1s peak is slightly closer to the central pyrrole-type N 1s peak (Table VIII) than to the pyridine-type central N 1s peak, the calculated cyano N 1s energies are exactly half-way between the two different central N 1s energies. This slight discrepancy is responsible for the difference in the shapes of the experimental and simulated spectra shown in Figure 4.

TNO_2PPH_2: The experimental and computed N 1s XPS are shown in Figure 5. Note the three cleanly resolved peaks. The experimental porphyrin $\Delta\epsilon_{N,1s}$ is 2.1 eV, and the difference between the nitro and the pyrrole-type N 1s peaks is 5.9 eV. Table V shows that the computed values of these energy differences are exactly the same as the experimental ones. This result shows that the DZ basis set we have chosen correctly describes large differences in the electronic environment.

TCF_3PPH_2: Except for the substituent effects of the trifluoromethyl groups, the N 1s XPS of this porphyrin is ordinary and is not shown here. In the C 1s spectrum, shown in Figure 6, the trifluoromethyl carbons appear as a fully resolved high-IP peak[41] and all the other carbons give rise to an unresolved peak. The latter peak, although composite, has a symmetrical appearance and appears to have a single maximum. The energy difference between the maxima of these two peaks was found to be 7.5 eV. To obtain a theoretical value for this energy difference, we used the computed C 1s orbital energies of TCF_3PPH_2 to produce a computed C 1s XPS, which is also shown in Figure 6. As can be seen from Figure 6, the shapes of the simulated and actual spectra agree qualitatively, and the theoretical value of the energy difference is 6.9 eV. The discrepancy of about 0.6 eV between the theoretical and experimental values of this difference is not unexpected, given the various factors not taken into account in our calculations.

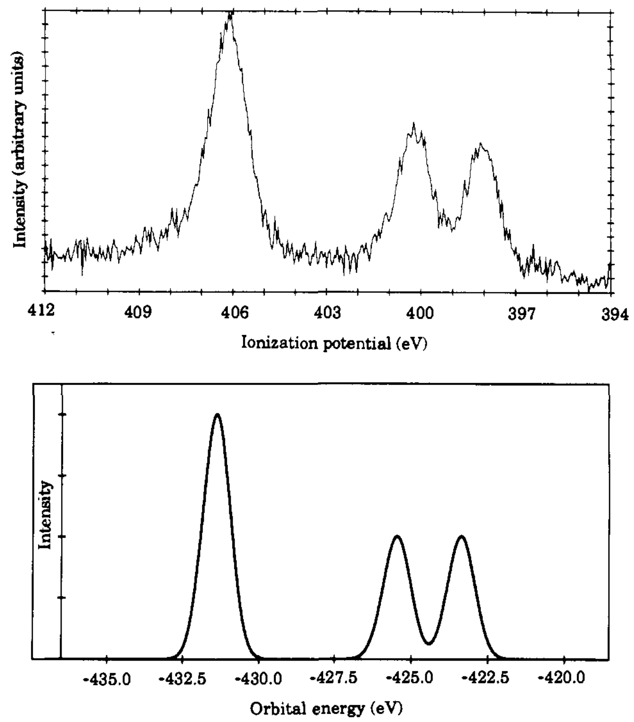

Figure 5. The (a, top) experimental and (b, bottom) simulated N 1s XPS of TNO_2PPH_2.

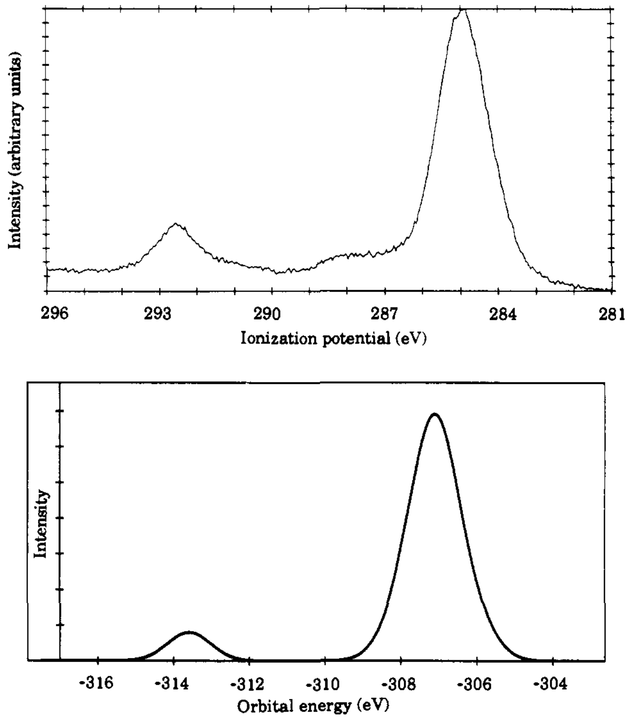

Figure 6. The (a, top) experimental and (b, bottom) simulated C 1s XPS of TCF_3PPH_2.

TF_5PPH_2: Except for the substituent effects exerted by the pentafluorophenyl groups, the N 1s spectrum is of the usual type. The C 1s spectrum, shown in Figure 7, consists of two resolved, composite peaks, the high-IP pentafluorophenyl carbons being clearly separated from the other carbons.[41] Figure 7 also shows the simulation of this spectrum using the computed C 1s orbital

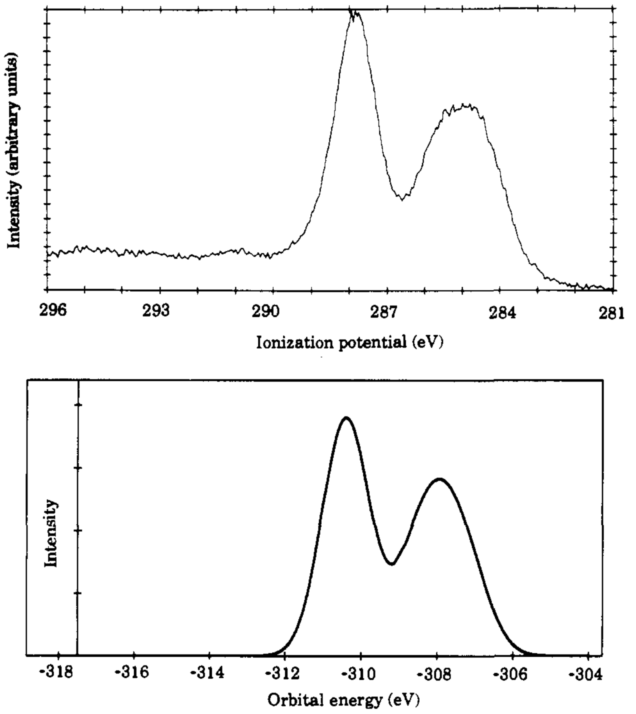

Figure 7. The (a, top) experimental and (b, bottom) simulated C 1s XPS of TF_5PPH_2.

energies. The simulation clearly reproduces the qualitative shape of the experimental C 1s spectrum. The experimental and calculated spectra show energy differences of about 2.8 and 2.5 eV, respectively, between the maxima of the two peaks. This level of agreement may be regarded as satisfactory, since in our calculations we have used idealized orientations of the pentafluorophenyl groups relative to the porphyrin core.

D. Valence Level Energies. Although our calculations gave complete energy eigenvalue spectra for the occupied orbitals, the focus of the present study was on the study of the 1s orbitals of the central nitrogens. Accordingly, before discussing our computed substituent effect data, we should define the scope of our valence level studies.

Valence level photoelectron spectroscopic data on porphyrins are scarce.[42] However, some pertinent data are discussed below. Also, a database of electrochemical oxidation potentials does not exist for a significant number of the porphyrins that we have studied by computation, and therefore we will not discuss electrochemical data in this paper. A large body of electrochemical work on substituent effects exists, however, for various peripheral substitution patterns not examined in our calculations.[3d,6f,43] Since virtual energies are unreliable as estimates of electron affinities, we will not discuss electron affinities or reduction potentials.[43j,44] Also not included in the scope of the present study is the question of precise symmetry ordering of the highest and second highest porphyrin MOs.[43o,45] We noted in a previous paper that a few porphyrin π MOs (e.g. the second highest occupied MO of unsubstituted porphyrin, of b_{1u} symmetry) had large amplitudes of d functions in calculations using polarized basis sets and the energy at the DZ level of basis sets was about 0.5 eV off from the DZP results, which can be taken as converged to the Hartree–Fock limit values. It is not surprising, therefore, that the symmetry ordering of the two HOMOs in m-PF_4H_2 switched on passing from basis set I to basis set II, although this did not happen for unsubstituted porphyrin. In line with the scope of the present study, we have not attempted to determine the ground states (A_u versus B_{1u} in the notation of D_{2h} symmetry) of porphyrin cation radicals for various substitution patterns.[46]

Table X. Comparison of Sign-Reversed Valence Level Orbital Energies (eV) of Porphyrin and Octaalkylporphyrins

computed levels			UPS peaks[a]	
PH_2	β-PMe_8H_2	symmetry	PH_2	β-PEt_8H_2
6.23	5.80	a_u	6.9	6.39
6.44	6.19	b_{1u}	7.2	6.83
8.89	8.18	b_{2g}	8.8	7.55 (sh), 7.80,
9.13	8.32	b_{1u}	9.1	8.13, 8.44
10.16	9.50	b_{3g}	10.0	9.33
10.43	9.58	b_{1u}	10.3	9.55
10.44	9.88	b_{3g}		9.68
10.46	9.96	b_{2g}		9.82

[a] See refs 42c and 42d.

Table XI. Comparison of the Sign-Reversed Computed Valence Level Orbital Energies (eV) and the UPS of Tetraphenylporphyrin

computed levels				
D_{2h}		C_{2v}		UPS peaks
6.13	a_u	6.08	a_1	6.39
6.23	b_{1u}	6.21	a_2	6.72
				7.71
8.69	b_{2g}	8.70	b_2	8.86
8.91	b_{1u}	8.84	b_1	broad peak[b]
9.14–9.29	8 orbitals[a]	8.91–9.45	8 orbitals[a]	broad peak[b]
9.95	b_{3g}	10.29	b_1	several peaks
10.24	b_{3g}	10.32	a_1	with IPs
10.25	b_{2g}	10.36	b_1	around 10
10.26	b_{1u}	10.51	b_2	eV[c]

[a] These eight closely spaced orbitals are the HOMOs of the symmetry-related phenyl groups (two per phenyl group). These orbitals correspond to the doubly degenerate HOMOs of benzene. [b] From an examination of the data in ref 42a and the UPS of toluene, this broad peak appears to result primarily from ionizations from the phenyl HOMOs. The spectra referred to in ref 42a for these two broad peaks are those of metallotetraphenylporphyrins. [c] See the spectra of metallotetraphenylporphyrins in ref 42a. The authors note that there is close resemblance between all spectra of the tetraphenylporphyrin derivatives (including that of the free base).

Our discussion of UPS data will be limited to those available for unsubstituted porphyrin, octaethylporphyrin, and tetraphenylporphyrin. We have already discussed the valence level orbital energies and UPS of unsubstituted porphyrin in a previous paper. In Table X we compare the valence level orbital energies of porphyrin and an octaalkylporphyrin in order to evaluate the effect of octaalkyl substitution on the highest occupied π orbitals.

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Table XII. Ionization Potentials (eV) and Relaxation Effects (eV) of Selected Porphyrins Obtained Using Basis Set I

orbital ionized	compd	ionization potentials Koopmans'	ionization potentials ΔSCF	ϵ_{relax}
a_u (HOMO)	PH_2	6.23	5.84	0.39
a_u (HOMO)	PMe_8H_2	5.80	5.31	0.49
a_u (HOMO)	$TPPH_2$ (D_{2h})	6.13	5.57	0.56
b_{1u} (second HOMO)	PH_2	6.44	5.97	0.47
b_{1u} (second HOMO)	PMe_8H_2	6.19	5.64	0.55
b_{1u} (second HOMO)	$TPPH_2$ (D_{2h})	6.23	5.57	0.66

For simplicity, we will compare our calculated orbital energies of octamethylporphyrin with the published UPS data for octaethylporphyrin.[42c] As in the case of PH_2, the UPS peaks occur in three clusters in the 5–11 eV range of IPs for β-PMe_8H_2, and our calculations have succeeded in qualitatively reproducing this pattern of energy levels. The two highest occupied MOs are seen to be well separated energetically from all other MOs, in agreement with the four-orbital model.[36] As for PH_2, the first ionization potential, according to Koopmans' theorem, of β-PMe_8H_2 is some 0.7 eV less than the experimental value. Interpretation of the four UPS peaks in the second region, and even pinpointing their exact positions, is difficult, as these peaks are not resolved (see Figure 2, ref 42c, for the photoelectron spectrum). Table X shows that the effect of octamethyl substitution on the two π HOMOs is about 0.5 eV (compared to 0.3 eV substituent effect for the N 1s levels of β-PEt_8H_2 relative to PH_2, from Table VIII).

Table XI shows a comparison of the computed valence level orbital eneriges of the D_{2h} and C_{2v} conformers of tetraphenylporphyrin and the UPS. Khandelwal and Roebber have studied the free-base and several metal complexes of tetraphenylporphyrin.[42a] While their paper does not show the actual UPS of the free-base in a diagram, the UPS of some metallotetraphenylporphyrins are shown in figures (Figures 1 and 2 in ref 42a). They note that there is a close resemblance of all the ultraviolet photoelectron spectra. When necessary, we will therefore refer to the metallotetraphenylporphyrin spectra shown in ref 42a for our discussion of the UPS of the free-base.

The experimental first ionization potential of tetraphenylporphyrin is 6.39 eV, about 0.5 eV less than that of porphyrin. As mentioned before in Section IVc, this difference is also seen in the N 1s IPs of the two compounds. Table XI shows that the computed HOMO energies of either conformer of $TPPH_2$ (D_{2h} or C_{2v}) do not match this difference. We attempted to shed some light on this discrepancy by considering two possibilities. First, we wanted to determine if basis set I was too small to provide a reasonable description of porphyrin–phenyl interactions. Calculations using the larger basis set IV did uncover a slight magnification of the substituent effect obtained with basis set I. Thus, for both the HOMO and the N 1s orbital energies, a tetraphenyl substituent effect of 0.2 eV was obtained with basis set IV, the effect being 0.1 eV with basis set I. Second, we considered the possibility that larger relaxation energies might be associated with photoelectron emissions from $TPPH_2$ than from PH_2. Calculations of the first and second IPs of PH_2, PMe_8H_2, and $TPPH_2$ by the ΔSCF method showed that relaxation is indeed larger for $TPPH_2$ than for PH_2 or PMe_8H_2. The results of these calculations are shown in Table XII. The relaxation energy, ϵ_{relax}, shown in Table XII is the absolute value of the difference between the ΔSCF and Koopmans' theorem IPs and it accounts for part of the 0.5-eV difference between the experimental IPs of the PH_2 and $TPPH_2$. Addition of diffuse functions to the DZ basis set I accounts for another 0.1 eV of the tetraphenyl effect. Therefore, our best theoretical estimate of the tetraphenyl substituent effect on the HOMO energies is approximately 0.4 eV. It is reasonable to expect similar relaxation effects for the N 1s ionizations, since the second highest occupied MO (b_{1u}) has substantial amplitude on the central nitrogens.

Within the 5–11 eV range of IPs in the UPS, the pattern of three clusters of peaks, mentioned above for PH_2 and PEt_8H_2, is complicated by the intervention of ionizations from the HOMOs of the phenyl groups of $TPPH_2$. Careful examination of the metallotetraphenylporphyrin spectra does, however, support our computed clustering pattern of the peaks for free-base tetraphenylporphyrin. As in other porphyrins, our calculations show that the two HOMOs are energetically well-separated from other occupied orbitals and this is corroborated in the UPS results. In Khandelwal and Roebber's work, the two closely spaced HOMOs are clearly resolved for (tetraphenylporphyrinato)zinc(II), whereas for (tetraphenylporphyrinato)magnesium(II), the two peaks overlap. The second region (from the low-IP end) in the UPS of the tetraphenylporphyrin derivatives is dominated by a broad and intense peak around 9 eV, which on the basis of the computed results shown in Table XI appears to arise from ionizations from the phenyl HOMOs. On the lower-IP side of this broad peak are some small peaks/shoulders, which appear to be associated with the third and fourth highest π MOs of the porphyrin core. Ionizations from the fifth to eighth highest MOs of the porphyrin core appear to be responsible for the small peaks around 10 eV on the higher-IP side of the intense peak around 9 eV.

Table XIII. Computed Sign-Reversed Energies (eV) and Symmetries of the Highest (HOMO) and Second Highest (SHOMO) Occupied MOs

porphyrin	$-\epsilon_{HOMO}$	$-\epsilon_{SHOMO}$
Porphyrin and Octamethylporphyrin		
PH_2	6.23 (a_u)	6.44 (b_{1u})
β-PMe_8H_2	5.80 (a_u)	6.19 (b_{1u})
Tetraphenylporphyrins		
$TPPH_2(D_{2h})$	6.13 (a_u)	6.23 (b_{1u})
$TPPH_2(C_{2v})$	6.08 (a_1)	6.21 (a_2)
TCl_2PPH_2	6.14 (a_u)	6.39 (b_{1u})
$TCNPPH_2$	6.90 (a_u)	7.06 (b_{1u})
$TCF_3PPH_2(D_2)$	7.02 (a)	7.19 (b_1)
TNO_2PPH_2	7.13 (a_u)	7.31 (b_{1u})
TF_5PPH_2	7.29 (a_u)	7.74 (b_{1u})
Chlorinated Porphyrins		
m-PCl_4H_2	6.96 (a_u)	7.02 (b_{1u})
β-PCl_8H_2	7.50 (a_u)	7.53 (b_{1u})
$PCl_{12}H_2$	7.68 (b_{1u})	8.01 (a_u)
Brominated Porphyrins		
m-PBr_4H_2	6.94 (a_u)	7.07 (b_{1u})
β-PBr_8H_2	7.40 (a_u)	7.46 (b_{1u})
Fluorinated Porphyrins		
m-PF_4H_2	6.83 (b_{1u})	7.15 (a_u)
β-$PF_4H_2(C_{2h})$	6.98 (a_u)	7.17 (a_u)
β-PF_8H_2	7.77 (b_{1u})	7.84 (a_u)
$PF_{12}H_2$	8.13 (b_{1u})	8,76 (a_u)
m-$P(CF_3)_4H_2(D_2)$	7.55 (a)	8.76 (b_1)
β-$P(CF_3)_4H_2(C_{2h})$	7.31 (a_u)	7.51 (a_u)
$F_{28}TPPH_2$	8.72 (b_{1u})	8.77 (a_u)
Cyanoporphyrins		
m-$P(CN)_4H_2$	7.57 (a_u)	8.11 (b_{1u})
β-$P(CN)_8H_2$	8.73 (b_{1u})	8.80 (a_u)
$P(CN)_{12}H_2$	9.60 (a_u)	9.65 (b_{1u})
$PCl_8(CN)_4H_2$	8.45 (a_u)	8.63 (b_{1u})
Nitroporphyrins		
m-$P(NO_2)_4H_2$ (coplanar)	7.52 (a_u)	8.98 (b_{1u})
m-$P(NO_2)_4H_2$ (perpendicular)	8.01 (a_u)	8.72 (b_{1u})

Table XIII shows the computed energies and symmetries of the two highest occupied porphyrin π MOs. In all cases, the two highest occupied MOs are well-separated energetically from the other MOs. Again, very large substituent effects can be seen. Between octamethylporphyrin and dodecacyanoporphyrin, the HOMO energy shifts by 3.83 eV. A less extreme but still very large stabilization (lowering of the orbital energy) of the HOMO is seen with many other substitution patterns.

The data shown in Table XIII are of potential value to an UPS investigation of substituent effects in porphyrins. Some reservations should be mentioned, however. First, from our basis set effect studies, we know that some valence level orbital energies do not reach the Hartree–Fock limit at the DZ quality of basis sets. Second, from the UPS results discussed above, the first IP of the porphyrins appears to be about 0.6–1.0 eV more than the computed Koopmans' IP, even at the Hartree–Fock limit. Third, many of the electron-deficient porphyrins currently known are sterically hindered dodecasubstituted porphyrins, which, on the basis of available crystallographic data,[6g,48] are probably highly buckled. In this survey of substituent effects, we have not studied any buckled porphyrins. From this point of view, fluoro and cyano substituents are among the least sterically demanding among electronegative substituents and, therefore, are the least likely to cause buckling. Fourth, there may be unexpectedly large relaxation energies associated with ionizations of certain substituted porphyrins. Some of these questions are currently being pursued in our laboratory.

V. Conclusions

XPS and all-electron ab initio SCF calculations have shown the 1s energies of the central nitrogens to be sensitive probes of the electronic effects of peripheral substituents in porphyrins. Estimates of substituent effects on the highest occupied π MOs have also been obtained. The results of our calculations have been found to be in generally good agreement with experiment. The present study shows that very large substituent effects are possible with suitable arrays of electronegative substituents. Effects of this magnitude should be responsible for a wide range of physical and chemical properties among the porphyrins.

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Unimolecular Chemistry of Protonated Ethyl Cyanide and Ethyl Isocyanide: An Experimental and Molecular Orbital Study

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Abstract: The unimolecular reactivity of both protonated forms of ethyl cyanide (**1**) and ethyl isocyanide (**2**) in the gas phase has been examined experimentally using deuterium labeling and mass analyzed ion kinetic energy spectrometry. It has been shown that both species isomerize into weak π-complexes between ethene and $HCNH^+$ (**3** and **4**), which may further dissociate or interconvert either by reorientation or by cycloaddition–cycloreversion. Relevant portions of the $C_3H_6N^+$ potential energy surface have been explored using ab initio molecular orbital calculations up to the MP2/6-311++G**//MP2/6-31G** + ZPE level. These data provide new examples of the 1,2 elimination processes which require the intermediacy of loosely bound ion–neutral complexes. This study is also of interest in interstellar and planetary atmosphere chemistry, particularly in view of the possible formation of ethyl isocyanide along with ethyl cyanide by dissociative recombination of both protonated forms **2** or **1**, respectively.

Introduction

The gas-phase chemistry of cyanides and isocyanides is of interest not only in fundamental organic chemistry but also in interstellar[1] and planetary high atmosphere[2] chemistry where it is generally agreed that they derive from dissociative recombination of their protonated counterparts[3]

$$MH^+ + e \rightarrow M + H^\cdot$$

$$(M = RCN \text{ or } RNC)$$

While a number of studies have been devoted to the protonated forms of HCN, HNC, CH_3CN, CH_3NC, *n*-C_3H_7CN, and *i*-C_3H_7CN,[4-20] the protonated ethyl cyanide and ethyl isocyanide have received less attention,[14,15,18,19,20] and, to date, no detailed examination of their unimolecular reactivity has been reported even though ethyl cyanide is among the 80 or so species yet identified in the interstellar media.[1]

This article presents the results of an experimental and theoretical investigation on the isomerisation and dissociation of

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