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Substituent Effects on Valence Ionization Potentials of Free Base Porphyrins: Local Density Functional Calculations and Their Relevance to Electrochemical and Photoelectron Spectroscopic Studies

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Abstract: Local density functional (LDF) calculations with polarized double-ζ basis sets have been used to calculate the two lowest one-electron ionization potentials (IPs) of a variety of free base porphyrins with multiple alkyl, aryl, fluoro, chloro, bromo, trifluoromethyl, cyano, and nitro substituents. For unsubstituted porphyrin (PH_2), β-octaalkylporphyrins, and *meso*-tetraphenylporphyrin ($TPPH_2$), LDF-ΔSCF calculations reproduce the lowest ultraviolet photoelectron spectral (UPS) IPs to within ~0.2 eV. The two lowest one-electron IPs of $TPPH_2$ are predicted to be lower than those of PH_2 by ~0.5 eV, in agreement with UPS experiments. *Ab initio* Hartree–Fock (HF) theory seriously underestimates this electronic effect of *meso*-tetraphenyl substitution. Both LDF and HF theories predict that substituents on the phenyl rings of $TPPH_2$ should strongly affect the lowest one-electron IPs of $TPPH_2$. Substitution of the *para* positions of the phenyl groups of $TPPH_2$ with $-CF_3$, $-CN$, or $-NO_2$ substituents should raise the lowest IP by 0.7–0.8 eV, while perfluorination of the phenyl rings should increase the lowest IP by ~0.95 eV. A comparison of the IPs of *ortho-*, *meta-*, and *para*-fluorinated $TPPH_2$ derivatives suggests that electron-withdrawing substituents at *meta* and *para* positions should exert significantly stronger electronic effects on the porphyrin ring than *ortho* substituents. *Ab initio* HF theory seriously overestimates the electron-withdrawing effect of peripheral halogen substituents. Provided there is no macrocycle buckling due to steric interactions among peripheral substituents, LDF theory predicts that *meso*-tetrahalogenation (with F, Cl, or Br) should have almost no influence on the lowest IP of PH_2, while β-octachlorination or octabromination should increase the lowest IP by ~0.4–0.5 eV. Electrochemical measurements support these LDF predictions. β-Octafluorination is predicted to exert an electronic effect of ~0.85 eV on the lowest IPs of PH_2, which is significantly larger than the electronic effect of β-octachlorination or octabromination. Substituents such as $-CF_3$, $-CN$, and $-NO_2$ exert far higher electronic effects than the halogens. For instance, LDF theory predicts that the lowest IP of *meso*-tetrakis(trifluoromethyl)porphyrin should exceed that of $TPPH_2$ by ~1.74 eV and that of *meso*-tetrakis(pentafluorophenyl)porphyrin by ~0.68 eV. Unlike the halogens, *meso*-tetrasubstitution with cyano groups should drastically increase the lowest IP of PH_2, by a margin of ~1.2 eV. β-Octacyano-substitution is predicted to have an electronic effect of >2.0 eV on the lowest IP of PH_2. *Meso*-tetranitrosubstitution is predicted to elevate the lowest IP of PH_2 by ~0.9–1.1 eV, depending on the conformation of the nitro groups. In general, *meso*-substituents exert stronger electronic effects than the same substituents placed at β-positions.

I. Introduction

Porphyrin ligands with multiple electron-withdrawing peripheral substituents are currently of interest as precursors to stable metalloporphyrin catalysts for a variety of hydrocarbon oxygenation reactions.[1] Electron-withdrawing substituents bring about an increase in the ionization potential (IP) of the porphyrin and thus protect the metalloporphyrin catalyst from oxidative destruction. There is considerable interest, therefore, in deepening our understanding of substituent effects on the IPs of porphyrins. An improved understanding should provide valuable guidelines for the design of new porphyrin ligands for a variety of applications.

Gas-phase photoelectron spectroscopy may be the ideal experimental tool for such a study, but gas-phase measurements may be difficult for some large porphyrin molecules. Moreover, the interpretation of electrochemical redox potentials may not be straightforward: for instance, it may be problematic to decide whether substituent effects on redox potentials faithfully reflect trends in gas-phase properties such as IPs and electron affinities (EAs) or are obscured by condensed-phase effects such as differential solvation between the oxidized and reduced states.

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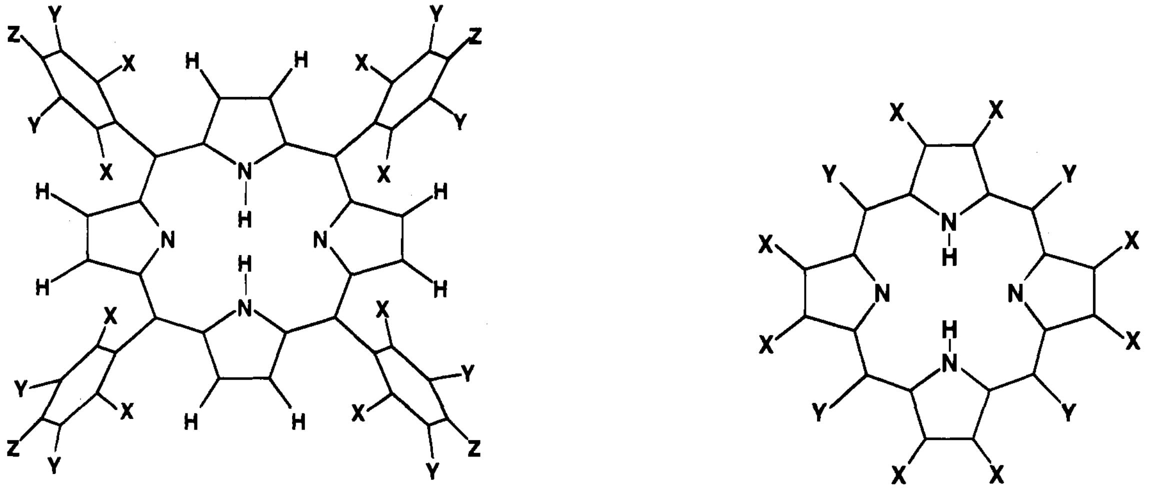

	X	Y	Z
$TPPH_2$	H	H	H
$TDCPPH_2$	Cl	H	H
o,o′-$TDFPPH_2$	F	H	H
m,m′-$TDFPPH_2$	H	F	H
p-$TFPPH_2$	H	H	F
p-TCF_3PPH_2	H	H	CF_3
p-$TCNPPH_2$	H	H	-CN
p-TNO_2PPH_2	H	H	$-NO_2$
$TPFPPH_2$	F	F	F

	X	Y
PH_2	H	H
PMe_8H_2	CH_3	H
m-PF_4H_2	H	F
β-PF_8H_2	F	H
$F_{28}TPPH_2$	F	C_6F_5
m-$P(CF_3)_4H_2$	H	CF_3
β-$P(CF_3)_8H_2$	CF_3	H
$PF_8(CF_3)_4H_2$	F	CF_3

	X	Y
m-PCl_4H_2	H	Cl
β-PCl_8H_2	Cl	H
m-PBr_4H_2	H	Br
β-PBr_8H_2	Br	H
m-$P(CN)_4H_2$	H	CN
β-$P(CN)_8H_2$	CN	H
m-$P(NO_2)_4H_2$	H	NO_2

Figure 1. Structures of selected compounds studied in this work. Double bonds are not shown.

Accordingly, it appeared worthwhile to apply high-quality theoretical methods as alternative probes of substituent effects in porphyrins.

We recently found that density functional theory (DFT)[2] constitutes an impressively accurate method for calculating valence IPs of porphyrins.[3,4] The calculated IPs agree with experiment to within ~0.2 eV.[3] Assuming that this error is a fairly systematic one across a variety of substituted porphyrins, *differences* between IPs of different molecules should be reproduced with even less error, i.e. with near-quantitative accuracy. This level of performance of DFT considerably exceeds that of *ab initio* Hartree–Fock theory[5,6] and stems from the fact that DFT effectively accounts for electron correlation.[7–9] Moreover, since DFT is far more computationally facile than conventional correlated *ab initio* methods, we have been able to assemble a large database of local density functional (LDF) valence IPs for molecules ranging in size from unsubstituted porphyrin to perfluorinated tetraphenylporphyrin. The results constitute an accurate and insightful overview of electronic effects of alkyl, aryl, fluoro, chloro, bromo, trifluoromethyl, cyano, and nitro substituents on the valence IPs of free base porphyrins.

II. Methods

The density functional calculations were performed with the DMol[10] program system using the local exchange-correlation functional due to von Barth and Hedin.[11] Numerically tabulated basis sets of double-ζ plus polarization ("DNP") quality were used.[11] An extremely fine mesh was used for the numerical integrations for calculating matrix elements.[12] All calculations were of the spin-unrestricted type. The IPs were calculated by a ΔSCF method, i.e. the total energy of the neutral porphyrin was subtracted from the energies of cationic doublet states of different symmetries. Since a many-electron wave function does not exist in the LDF formalism, one cannot impose orthogonality constraints between different states. Accordingly, the method inherently lacks the ability to describe excited states except in cases where such orthogonality to *all* lower states is ensured on symmetry grounds. Therefore, it was only possible to calculate the energetically lowest state for any particular symmetry species of the cation.

Figure 1 depicts the structures of the compounds studied in this work. The molecular geometries used in the present LDF calculations are the same as those used in our previous *ab initio* study.[6]

III. Results

Table 1 lists the names and abbreviations of the different porphyrins studied, their LDF IPs for the two lowest (^2A_u and

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[10] For a description of the DMol program, see: Delley, B. *J. Chem. Phys.* **1990**, *92*, 508. The DMol program is distributed by Biosym Technologies, Inc.: San Diego, CA.

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[12] For details, see: *DMol User Guide*; Biosym Technologies, Inc., 9685 Scranton Road, San Diego, CA 92121-2777.

Table 1. Calculated LDF/DZP and HF-KT/DZ Values of the Two Lowest IPs of Porphyrins[a] (Substituent Effects Arė Relative to Unsubstituted Porphyrin[b])

			IP (eV)				substituent effect (eV)[b]			
			LDF[c]		HF-KT[d]		LDF		HF-KT	
		molecular	final state		final stte		final state		final state	
compd	abbrev	point group	^2A_u	$^2B_{1u}$	^2A_u	$^2B_{1u}$	^2A_u	$^2B_{1u}$	^2A_u	$^2B_{1u}$
unsubstituted porphyrin	PH_2	D_{2h}	7.38	7.21	6.23	6.44	0.00	0.00	0.00	0.00
β-octamethylporphyrin	PMe_8H_2	D_{2h}	6.72	6.64	5.80	6.19	−0.66	−0.57	−0.43	−0.25
tetraphenylporphyrins										
meso-tetraphenylporphyrin	$TPPH_2$	D_{2h}	7.01	6.73	6.13	6.23	−0.37	−0.48	−0.10	−0.21
meso-tetrakis(2,6-dichlorophenyl)porphyrin	$TDCPPH_2$	D_{2h}	7.06	6.78	6.14	6.39	−0.32	−0.43	−0.09	−0.05
meso-tetrakis(2,6-difluorophenyl)porphyrin	*o,o′*-$TDFPPH_2$	D_{2h}	7.20	6.95	*e*	*e*	−0.18	−0.26	*e*	*e*
meso-tetrakis(4-fluorophenyl)porphyrin	*p*-$TFPPH_2$	D_{2h}	7.30	7.02	*e*	*e*	−0.08	−0.19	*e*	*e*
meso-tetrakis(3,5-difluorophenyl)porphyrin	*m,m′*-$TDFPPH_2$	D_{2h}	7.49	7.32	*e*	*e*	0.11	0.11	*e*	*e*
meso-tetrakis[4-(trifluoromethyl)phenyl]porphyrin	*p*-TCF_3PPH_2	D_2	7.73	7.45	7.02	7.19	0.35	0.24	0.79	0.75
meso-tetrakis(4-cyanophenyl)porphyrin	*p*-$TCNPPH_2$	D_{2h}	7.77	7.49	6.90	7.06	0.39	0.28	0.67	0.62
meso-tetrakis(4-nitrophenyl)porphyrin	*p*-TNO_2PPH_2	D_{2h}	7.81	7.52	7.13	7.31	0.43	0.31	0.90	0.87
meso-tetrakis(pentafluorophenyl)porphyrin	$TPFPPH_2$	D_{2h}	7.96	7.79	7.29	7.74	0.58	0.58	1.06	1.30
fluorinated porphyrins										
meso-tetrafluoroporphyrin	*m*-PF_4H_2	D_{2h}	7.87	7.29	7.15	6.83	0.49	0.08	0.92	0.39
β-octafluoroporphyrin	β-PF_8H_2	D_{2h}	8.22	8.07	7.84	7.77	0.84	0.86	1.61	1.33
β-octafluoro-*meso*-tetrakis(pentafluorophenyl)porphyrin	$F_{28}TPPH_2$	D_{2h}	8.51	8.38	8.77	8.72	1.13	1.17	2.54	2.28
meso-tetrakis(trifluoromethyl)porphyrin	*m*-$P(CF_3)_4H_2$	D_2	8.47	8.54	7.55	8.76	1.09	1.33	1.32	2.32
β-octakis(trifluoromethyl)porphyrin	β-$P(CF_3)_8H_2$	D_{2h}	8.90	8.48	*e*	*e*	1.52	1.27	*e*	*e*
β-octafluoro-*meso*-tetrakis(trifluoromethyl)porphyrin	$PF_8(CF_3)_4H_2$	D_2	9.19	9.05	*e*	*e*	1.81	1.84	*e*	*e*
chlorinated porphyrins										
meso-tetrachloroporphyrin	*m*-PCl_4H_2	D_{2h}	7.84	7.29	6.96	7.02	0.46	0.08	0.73	0.58
β-octachloroporphyrin	β-PCl_8H_2	D_{2h}	7.93	7.83	7.50	7.53	0.55	0.62	1.27	1.09
brominated porphyrins										
meso-tetrabromoporphyrin	*m*-PBr_4H_2	D_{2h}	7.80	7.23	6.94	7.07	0.42	0.02	0.71	0.63
β-octabromoporphyrin	β-PBr_8H_2	D_{2h}	7.76	7.69	7.40	7.46	0.38	0.48	1.17	1.02
cyanoporphyrins										
meso-tetracyanoporphyrin	*m*-$P(CN)_4H_2$	D_{2h}	8.64	8.44	7.57	8.11	1.26	1.23	1.34	1.67
β-octacyanoporphyrin	β-$P(CN)_8H_2$	D_{2h}	9.45	9.28	8.73	8.80	2.07	2.07	2.50	2.36
nitroporphyrins										
meso-tetranitroporphyrin (coplanar)	*m*-$P(NO_2)_4H_2$	D_{2h}	8.49	8.67	7.52	8.98	1.11	1.46	1.29	2.54
meso-tetranitroporphyrin (perpendicular)	*m*-$P(NO_2)_4H_2$	D_{2h}	8.51	8.11	8.01	8.72	1.13	0.90	1.78	2.28

[a] The two lowest IPs correspond to ^2A_u and $^2B_{1u}$ cationic final states of a D_{2h}-symmetric porphyrin. These states transform as A and B_1 for D_2 symmetry and as A_{1u} and A_{2u} for a typical D_{4h} symmetric metalloporphyrin (e.g. ZnP), respectively. [b] A substituent effect is defined here as the IP of a substituted porphyrin minus the IP of PH_2, for a particular type/symmetry of the final ionized state. [c] This work. [d] These data are quoted from ref 6. [e] Data unavailable or not obtained.

$^2B_{1u}$ in D_{2h}; A and B_1 in D_2) cationic final states, and the substituent effects relative to unsubstituted porphyrin for the two final state symmetries. Also shown for comparison, where available from older work,[6] are IPs obtained from Hartree–Fock (HF) calculations using Koopmans' theorem (KT).

IV. Discussion

A. Ultraviolet Photoelectron Spectra of PH_2, Octaalkylporphyrins, and $TPPH_2$. Gas-phase ultraviolet photoelectron spectral (UPS) data are scarce for porphyrins, but such data are available for PH_2,[13b] some octaalkylporphyrins,[13] and $TPPH_2$.[14,15] These data permit an evaluation of the performance of LDF theory in reproducing the *absolute values* of the lowest UPS IPs of porphyrins.

The calculated LDF values of the two lowest IPs of PH_2 are 7.21 and 7.38 eV, which agree to within 0.2–0.3 eV with the experimental UPS IPs of 6.9 and 7.2 eV.[13b] The difference in energy between the lowest ^2A_u and $^2B_{1u}$ states of the PH_2 cation is too small (~0.3 eV) for the present LDF calculations to reliably predict the precise energy ordering of these states. A more accurate method such as the CASPT2 technique may be useful for assigning the final state symmetries for the two lowest UPS IPs of PH_2.[16]

The two lowest UPS IPs of octaethylporphyrin (PEt_8H_2) are 6.39 and 6.83 eV,[13a] which agree to within 0.1–0.3 eV with calculated LDF values of 6.64 and 6.72 eV for PMe_8H_2. The calculated LDF values (6.73 and 7.01 eV) of the two lowest IPs of $TPPH_2$ are in similarly good agreement with experimental UPS values of 6.39 and 6.72 eV.[14] Notably, the LDF IPs accurately reproduce the electronic effects (~0.5 eV) of *meso*-tetraphenyl and β-octaethyl substitution on the two lowest one-electron IPs of PH_2. X-ray photoelectron spectroscopic (XPS) studies revealed a similar difference of ~0.6 eV between the core IPs of the central nitrogens of PH_2 and $TPPH_2$.[6,17] In contrast to the LDF and UPS results, HF theory predicted that *meso*-tetraphenyl substitution should have an effect of only 0.1–0.2 eV on the two lowest IPs of PH_2,[6] thus significantly underestimating the substantial electron-donating effect of the *meso*-phenyl groups.

Gouterman's four-orbital model[18] suggests that the two lowest one-electron IPs of porphyrins should be energetically well-separated from all higher IPs which has been found to be the case for PH_2, octaalkylporphyrins, and $TPPH_2$.[13,14] The experimental UPS values of the third lowest one-electron IPs of

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(13) (a) UPS of PEt_8H_2: Kitagawa, S.; Morishima, I.; Yonezawa, T.; Sato, N. *Inorg. Chem.* **1979**, *18*, 1345. (b) Dupuis, P.; Roberge, R.; Sandorfy, C. *Chem. Phys. Lett.* **1980**, *75*, 434. This article reports the UPS of free base PH_2 and etioporphyrins I–III, whose lower IPs, not unexpectedly, are essentially the same as those of PEt_8H_2.[13a]

(14) UPS of $TPPH_2$: Khandelwal, C.; Roebber, J. L. *Chem. Phys. Lett.* **1975**, *34*, 355.

(15) For LDF simulations of the lowest UPS IPs of free base phthalocyanine, see: Ghosh, A.; Gassman, P. G.; Almlöf, J. *J. Am. Chem. Soc.* **1994**, *116*, 1932

(16) For CASPT2 calculations on porphyrins, see, in addition to ref 8b: Merchán, M.; Ortí, E.; Roos, B. O. *Chem. Phys. Lett.* **1994**, *226*, 27.

PH_2 and $TPPH_2$ are 8.4 and 7.71 eV, respectively. LDF theory predicts that the cationic $^2B_{2g}$ states of PH_2 and $TPPH_2$ are higher in energy than the neutral ground state by 8.24 and 7.67 eV, respectively. This constitutes evidence that the third lowest cationic states of PH_2 and $TPPH_2$ are $^2B_{2g}$.[19] Once again, the results suggest that the error in LDF-ΔSCF values of IPs of porphyrins is no more than approximately 0.2 eV. The LDF IPs also reproduce the electronic effect of ~0.7 eV of *meso*-tetraphenyl substitution on the third lowest UPS IP of PH_2.

LDF theory also predicted that *meso*-tetrafluorination should have almost no effect on the lowest IPs and oxidation potentials of porphyrins, which was confirmed by electrochemical measurements.[4]

B. Substituent Effects in Tetraarylporphyrins. Electron-withdrawing substituents on the phenyl rings of iron and manganese tetraarylporphyrins enhance the stability and catalytic activity of the metalloporphyrin catalysts in a variety of hydrocarbon oxygenation reactions.[20] Thus, Fe^{III} and Mn^{III} complexes of the TPFPP ligand are significantly better catalysts of oxygenation reactions than analogous metallo-TPP complexes, the latter being readily degraded under the highly oxidizing conditions employed.[20] Suitably bulky *ortho* substituents on the phenyl rings may improve the performance of metallotetraarylporphyrin catalysts by preventing the formation of catalytically inactive *μ*-oxo metalloporphyrin dimers and by sterically protecting the porphyrin periphery from oxidative attack. A detailed analysis of the steric and electronic effects of substituents on the chemical reactivity of metallotetraarylporphyrin catalysts is an important and challenging problem of considerable current interest. Theoretical and photoelectron spectroscopic studies can contribute to this analysis by determining the purely electronic effects of peripheral substituents without interference from steric (as happens in studies of chemical reactivity) and solvent effects (as is possible in electrochemical investigations).

Table 2. Substituent Effects (eV) in *meso*-Tetraarylporphyrins Relative to $TPPH_2$

		substituent effect (eV)				
		LDF		HF-KT		XPS
		Final State		Final State		
compd	$\Sigma\sigma$	^2A_u	$^2B_{1u}$	^2A_u	$^2B_{1u}$	N 1s
$TPPH_2$	0.00	0.00	0.00	0.00	0.00	0.0
$TDCPPH_2$		0.05	0.05	0.01	0.16	0.3
o,o'-$TDFPPH_2$		0.19	0.22			
p-$TFPPH_2$	0.60	0.29	0.29			
m,m'-$TDFPPH_2$	2.72	0.48	0.59			
p-TCF_3PPH_2	2.12	0.72	0.72	0.89	0.96	0.65
p-$TCNPPH_2$	2.80	0.76	0.76	0.77	0.83	0.7
p-TNO_2PPH_2	3.24	0.80	0.79	1.00	1.08	0.75
$TPFPPH_2$		0.95	1.06	1.16	1.51	0.9

To facilitate a discussion of the influence of substituents on the phenyl rings on the lowest IPs of $TPPH_2$, Table 2 recasts the data on tetraarylporphyrins using $TPPH_2$ as the zero level for substituent effects (instead of PH_2). The data clearly show that substituents on the phenyl rings exert a strong influence on the valence IPs of the porphyrin ring. Replacement of the four *para* hydrogens of $TPPH_2$ by trifluoromethyl, cyano, and nitro substituents results in increments of ~0.7–0.8 eV in the two lowest LDF IPs of $TPPH_2$. Between $TPPH_2$ and $TPFPPH_2$, the two lowest IPs are predicted to differ by about 1 eV at the LDF level. Table 2 also includes previously reported XPS results[6] and which show that the calculated shifts of the LDF valence IPs are essentially equal to the substituent effects on the nitrogen core IPs.

Although HF theory seriously underestimates the influence of *meso*-tetraphenyl substitution on the IPs of PH_2, Table 2 shows that the HF values of electronic effects of substituents on the phenyl rings *relative to unsubstituted $TPPH_2$* are quite good, being only about 15% higher than substituent effects obtained with LDF calculations and XPS measurements. Indeed, HF theory provided rather accurate simulations of core level XPS of a series of tetraarylporphyrins.[6] However, we will see that for some other porphyrins (see e.g. section IVC) substituent effects calculated using HF theory are in poor agreement with experiment.

It is instructive to compare substituent effects on the LDF IPs of tetraarylporphyrins with those on experimental one-electron oxidation potentials. Kadish *et al.* obtained approximately linear Hammett plots of substituent-induced shifts in oxidation potentials ($\Delta E_{1/2}$) of free base tetraarylporphyrins versus the sum of substituent constants ($\Sigma\sigma$) for substituents on the phenyl rings.[21–23] The slopes (ϱ) of such plots were 0.065 and 0.054 V for dichloromethane and *n*-butyronitrile solvents, respectively. Table 2 includes values of $\Sigma\sigma$ for the tetraarylporphyrins that have only *meta* and *para* substituents. Figure 2 shows a Hammett plot of substituent-induced shifts in the lowest LDF IP of $TPPH_2$ versus $\Sigma\sigma$ for all the tetraarylporphyrins studied except those with *o,o'*-substitution. The cations of all the compounds included in this plot have $^2B_{1u}$

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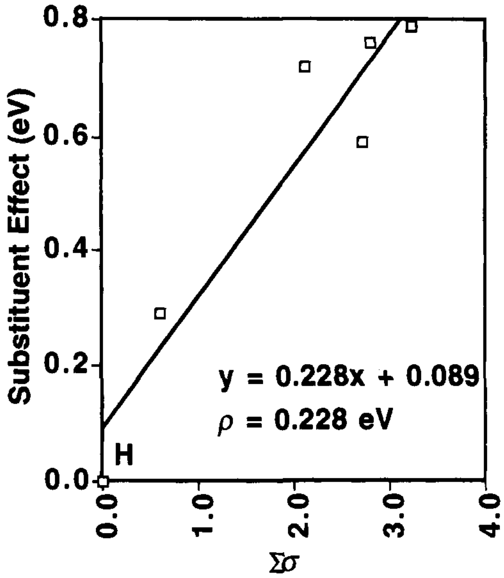

Figure 2. A Hammett plot of substituent effects (eV) on the lowest LDF IP of tetraarylporphyrins, which corresponds to a $^2B_{1u}$ final state. All substituent effects are relative to the lowest IP of $TPPH_2$ chosen as the zero level.

ground states at the present LDF level. The most interesting feature of this plot is that the slope, ϱ, is ~0.23 eV, which is considerably higher than the ϱ's of the electrochemical plots. Thus, *p*-fluoro and *p*-cyano substitution at all four *para* positions of $TPPH_2$ increases the electrochemical oxidation potential by ~0.1 and 0.2 V, respectively, but affects the LDF first IP by ~0.29 and 0.76 eV, respectively. What causes this discrepancy between electrochemical and LDF substituent effects? Is this a failure of LDF theory? While a definitive answer must await UPS measurements, two facts argue against this possibility. First, LDF theory has performed astonishingly well in reproducing the lowest one-electron IPs of porphyrins for which experimental UPS data are available. Second, as Table 2 shows, the calculated substituent effects on the lowest LDF IPs are very closely paralleled by substituent effects observed by XPS. This suggests that substituent effects on electrochemical oxidation potentials may not be linearly related to shifts in gas-phase IPs, especially where these shifts are very large. This is not particularly surprising since even a change of solvent can significantly affect the reaction constant ϱ for a particular electrochemical oxidation or reduction of a family of porphyrins. Overall, solvation appears to exert a "damping" effect on substituent effects observed in the gas phase.

The calculations on *o,o'*-$TDFPPH_2$, *m,m'*-$TDFPPH_2$, *p*-$TFPPH_2$, and $TPFPPH_2$ show that the electronic effects of successive fluorinations on the phenyl rings are additive. These calculations illustrate another interesting point: *m*- and *p*- fluoro substituents on the phenyl groups exert much larger electronic effects on the lowest IPs of porphyrins than *ortho* substituents. An examination of Mulliken atomic charges suggests a plausible explanation for this effect. Although the dihedral point groups of the porphyrins preclude overall molecular dipole moments, the fluorinated phenyl groups may be regarded as local dipoles. In the case of *m,m'*-$TDFPPH_2$ and *p*-$TFPPH_2$, the dipole moments associated with the phenyl rings are directed outward, i.e. away from the center of the porphyrin. In contrast, the dipole moments associated with the phenyl groups of *o,o'*-$TDFPPH_2$ are directed inward, which accounts for the much smaller electronic effects of *o*-fluoro substituents relative to *m*- and *p*-fluoro groups. Such an effect may also account for the very small difference (~0.05 eV) in the lowest LDF IPs of $TPPH_2$ and $TDCPPH_2$.

C. Halogenated Porphyrins. The first reports by Traylor[24] and Dolphin[25] on syntheses of β-octabromo- and β-octachloro-*meso*-tetraarylporphyrins marked the beginning of a virtual explosion of interest in this new class of ligands.[26] A number of studies suggested that the new β-octahalogeno ligands were significantly more resistant to oxidative degradation than their β-unsubstituted analogs. This is consistent with the intuitive expectation that multiple electronegative substituents such as halogens should increase the oxidation potential of the porphyrin macrocycle. However, examples are known where peripheral halogenation results in essentially no change in a porphyrin's oxidation potential.[27,28] These observations clearly warrant a detailed understanding of the electronic effects of peripheral halogenation on the electronic character of the ligand.

The LDF data in Table 1 shows that *meso*-tetrahalogenation has almost no effect on the lowest IP of PH_2, which corresponds to a $^2B_{1u}$ final state, but exerts a significantly stronger effect of ~0.4 eV on the second lowest IP, which corresponds to a ^2A_u final state. Experimentally, *meso*-tetrafluorination has a negligible effect on the one-electron oxidation potential of octaethylporphyrin,[28] in agreement with the LDF predictions, but contrary to the HF results (see Table 1).[4] In other words, the LDF calculations suggest that the ground state of *meso*-tetrafluoro-β-octaethylporphyrin cation must be $^2B_{1u}$, as it is for $[PF_4H_2]^+$ at the LDF level.

What accounts for the substantial difference in energy of ~0.6 eV between the two lowest LDF IPs of *meso*-tetrahalogenoporphyrins, compared to a difference of only ~0.2 eV for PH_2? Mesomeric electron donation from the halogens may provide a possible explanation. Such a +R effect would be expected to strongly stabilize the lowest $^2B_{1u}$ cationic state relative to the lowest ^2A_u state, since only the former has significant unpaired

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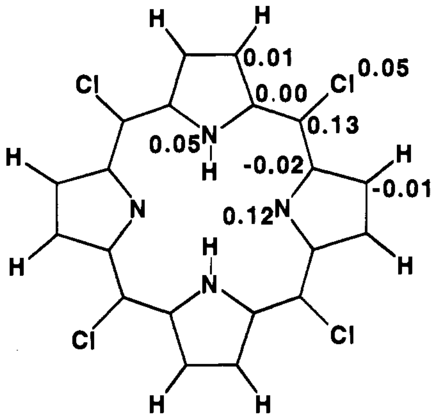

Figure 3. Spin populations on symmetry-distinct non-hydrogen atoms in the ground ($^2B_{1u}$) state of $[PCl_4H_2]^+$.

Table 3. XPS Core IPs (eV) of the Central Protonated and Unprotonated Nitrogens of Selected Free Base Porphyrins

	nitrogen 1s IP	
compd	protonated	unprotonated
$TPPH_2$	399.5	397.4
β-Br_8TPPH_2	399.9	397.75
$TDCPPH_2$	399.75	397.7
β-$Cl_8TDCPPH_2$	400.1	398.1

electron density at the *meso* positions. The LDF calculated spin density distributions of the $^2B_{1u}$ cationic states of *meso*-tetrahalogenoporphyrins supports this picture, the unpaired spin being considerably delocalized onto the halogen atoms. Figure 3 shows that in the ground ($^2B_{1u}$) state of $[m\text{-}PCl_4H_2]^+$ each chlorine atom carries a substantial spin population of 0.054, which is close to half of that at a *meso* carbon atom.

In an earlier *ab initio* HF theoretical study[6] of substituent effects in porphyrins, we predicted that β-octahalogenation should exert dramatic shifts of over 1 eV on the core and lowest valence IPs of porphyrins (see Table 1). However, we could not test this prediction against experimental results, since the appropriate physical measurements had not been reported at that time. Subsequently, the following measurements led us to question this HF-based prediction.

Nitrogen core X-ray photoelectron spectra were obtained for $TPPH_2$, $TDCPPH_2$, and their β-halogenated derivatives, β-Br_8TPPH_2[29] and β-$Cl_8TDCPPH_2$.[30,31] Differences between the nitrogen core IPs of the unhalogenated and halogenated porphyrins may be regarded as providing an estimate of the modulation of the electrostatic potential in the central region of the porphyrin as a result of β-halogenation. The results, shown in Table 3, indicate that β-octachlorination and octabromination affect the core IPs of the central nitrogens by only about ~0.4 eV, i.e. far less than the shifts in the HF nitrogen 1s orbital energies.[6]

Variations in gas-phase electron affinities (EAs) of hemins provide another sensitive probe of the electronic effects of substituents on the porphyrin ring.[32] β-Octachlorination of Fe(TDCPP)Cl and Fe(TPFPP)Cl affects the EAs of the two compounds by (0.72 ± 0.22) and (0.21 ± 0.06) eV, respectively.[32] The rather large uncertainty in the former number makes it difficult to analyze, but the latter number again suggests that the electronic effect of β-octachlorination, while significant, is considerably less than the HF prediction.

A comparison of our computed results on PCl_8H_2 and PBr_8H_2 with existing electrochemical data on β-polyhalogenated porphyrins is somewhat more involved. While we have assumed planar D_{2h} structures for PCl_8H_2 and PBr_8H_2, all known β-octachloro- and β-bromoporphyrins are also *meso*-tetraaryl-substituted and have severely buckled equilibrium geometries as a result of steric effects.[33,34] It is probably appropriate, therefore, to estimate the effect of β-octachloro and β-octabromo substitution alone on the lowest IP of PH_2 from the oxidation potential of the nearly planar 7,8,17,18-tetrahalogeno-5,10,15,20-tetramesitylporphyrin.[28] 7,8,17,18-Tetrachlorination or 7,8,17,18-tetrabromination increases the one-electron oxidation potential of tetramesitylporphyrin ($TMPH_2$) by 0.24 and 0.21 V, respectively. Assuming that the electronic effects of β-halogenation are additive, one would predict that β-octachlorination and β-octabromination should increase the oxidation potential of a porphyrin by 0.48 and 0.42 eV, respectively, in the absence of macrocycle buckling due to bulky *meso* substituents. These estimates are in excellent agreement with differences of 0.55−0.62 eV between the lowest LDF IPs of PH_2 and PCl_8H_2 and differences of 0.38−0.48 eV between the lowest LDF IPs of PH_2 and PBr_8H_2 (see Table 1). The LDF calculations also reproduce the electrochemical result that β-octachlorination exerts a very slightly larger electronic effect than β-octabromination.[28]

Overall, experimental measurements of the effects of β-octachloro or β-octabromo substitution on such properties as XPS IPs (Table 3),[29,30] gas-phase EAs,[32] and electrochemical oxidation potentials[25,28] are in excellent accord with LDF theoretical substituent effects of about 0.5 eV. The LDF and experimental results[25,27−30,32] also show that HF theory seriously overestimates the electronic effects of halogen substituents on the porphyrin ring.

Oxidation potentials of β-octachloro- and β-octabromo-*meso*-tetraarylporphyrins deserve an additional comment. Macrocycle buckling in these porphyrins results in a lowering of the first IP or of the oxidation potential[35] which may almost entirely offset the electron-withdrawing effect of β-octahalogenation.[28] However, macrocycle buckling does not mask the electronic influence of β-halogens on the nitrogen core IPs (as shown by the XPS results in Table 3),[30] reduction potentials,[25,28] or EAs.[28]

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[31] A Physical Electronics 5600 spectrometer was used for the XPS measurements. A tiny speck (~5 μg) of porphyrin was rubbed with a flat-tipped quartz rod into an extremely thin, effectively conducting film on gold foil, the Au $4f_{7/2}$ peak at 84.0 eV being used as a convenient external reference. Monochromatized Al Kα X-rays, of power 500 W, were used. Flooding the samples with low-energy electrons from a neutralizer did not change the positions or shapes of the XPS peaks, eliminating the need for any correction for sample charging. The data reported here are reproducible to within ±0.1 eV.

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This is consistent with the observation by Dolphin *et al.* that β-octachlorination of TPPFeCl increases the ring-centered oxidation potential by only ~100 mV, while lowering the reduction potential by ~400 mV.[25] Similarly, β-octachloro and β-octabromo substitution of $TMPH_2$ has essentially no effect on the oxidation potential but decreases the reduction potential by ~600 mV.[28] Accordingly, any extra stability of β-octachloro and β-octabromo derivatives of TPP, TMP, or TDCPP ligands or metal complexes toward oxidants, relative to the unhalogenated systems, probably owes more to the steric effects of the halogens than their modest electronic effects. Indeed, in certain cases, especially in the presence of a large excess of oxidant relative to the substrate, β-octachlorination or β-octabromination does not appear to confer any additional stability to a metallotetraarylporphyrin catalyst.[36] Thus, the LDF results and the experimental scenario, together, suggest that the design of the ultimate high-potential porphyrin ligands cannot rely on β-octachlorination or octabromination *alone*. However, β-halogenation of porphyrins with strongly electron-withdrawing *meso* substituents should constitute a promising approach to high-potential ligands and catalysts. Examples of such compounds include $Fe(\beta Cl_8TPFPP)Cl$[26m] and $Fe(\beta Br_8TPFPP)Cl$,[26l] which are superb catalysts of alkane hydroxylation with molecular oxygen in the absence of sacrificial reductants.[26aa,bb]

In contrast to chlorinated and brominated porphyrins, ring-fluorinated porphyrins have received relatively little attention.[26f,g,27,37] The LDF data in Table 1 show that β-octafluorination has an effect of ~0.85 eV on the lowest IPs of PH_2, which exceeds the substituent effects of β-octachlorination or β-octabromination by a significant margin of 0.3−0.4 eV. Moreover, since the steric bulk of fluorine is considerably less than that of other halogens, β-octafluoro-*meso*-tetraarylporphyrins should be less buckled than their chloro and bromo analogs. Thus, both electronic and conformational factors should be responsible for the lowest IPs or oxidation potentials of β-polyfluoro-*meso*-tetraarylporphyrins being higher than those of their chloro and bromo analogs. Assuming a D_{2h} structure of perfluorinated $TPPH_2$, LDF calculations predict (see Table 1) that substitution of all 28 peripheral hydrogens of $TPPH_2$ by fluorine should increase the first IP by 1.65 eV! At the HF level, the electronic effect of perfluorination of $TPPH_2$ is considerably more than the already large LDF value, but as discussed above, the LDF value is presumably trustworthy. Not surprisingly, $Fe(F_{28}TPP)Cl$ is reported to be a remarkably stable and efficient catalyst of hydrocarbon oxygenation, hydroxylating benzene and epoxidizing cyclooctene with high turnover numbers with 35% H_2O_2 without suffering any decomposition in 1−2 h.[37b]

Finally, note that for each of the compounds PF_8H_2, PCl_8H_2, and PBr_8H_2, the two lowest IPs are very close. Therefore, our calculations cannot predict with certainty the ground states, ^2A_u or $^2B_{1u}$, of the cation radicals of these compounds.

D. Trifluoromethylated Porphyrins. Although porphyrins with perfluoroalkyl groups have been known for some years, they have been largely ignored by both physical and synthetic chemists.[38] Recent *ab initio* HF calculations[6] and the present LDF study suggest that perfluoroalkylated porphyrins rank among the ultimate high-potential porphyrin ligands and, therefore, merit detailed experimental study.

The lowest LDF IP of *m*-$P(CF_3)_4H_2$ exceeds that of $TPPH_2$ by 1.74 eV. In other words, *m*-$P(CF_3)_4H_2$ is approximately as electron-deficient as $F_{28}TPPH_2$. Accordingly, a comparison of the performance of the relatively sterically unhindered Fe[*m*-$P(CF_3)_4$]Cl with that of $Fe(\beta X_8TPFPP)Cl$ (X = F, Cl, Br) in catalyzing hydrocarbon oxygenation may allow a dissection of the roles played by high molecular IPs and steric effects of β-halogens in protecting the porphyrin from oxidative degradation.

Electrochemical redox potentials of zinc *meso*-tetrakis(perfluoro-*n*-propyl)porphyrin [ZnP(*n*$C_3F_7)_4$] have been reported.[38i] The oxidation potential of this compound is ~0.67 V higher than that of ZnTPP, while the reduction potential of ZnP(*n*$C_3F_7)_4$ is lower than that of ZnTPP by the same amount. Large as these electrochemical substituent effects may be, they are far lower than substituent effects of ~1.74 eV that are predicted at the LDF level for the first IP. Photoelectron spectroscopic experiments on *meso*-tetrakis(perfluoro-*n*-alkyl)porphyrins are in progress to determine the accuracy of the LDF predictions.[39] Presumably, the smaller magnitudes of these electrochemical substituent effects, compared to LDF data, result from differential solvation energies of neutral and charged states of porphyrins.

The relative magnitudes of the two lowest IPs of *m*-$P(CF_3)_4H_2$ may deserve a comment. At the HF-KT level, the $^2B_{1u}$ state of [*m*-$P(CF_3)_4H_2]^+$ is higher in energy by over 1 eV than the ^2A_u state, in agreement with the intuitive expectation that strongly electron-withdrawing *meso* substituents should preferentially stabilize the highest occupied b_{1u} orbital, which has large amplitudes at the *meso* positions, relative to the highest occupied a_u orbital. The LDF results, which we tend to trust on the basis of their generally excellent agreement with experiment (as described in Section IVA), are somewhat unexpected: the two lowest vertical IPs of *m*-$P(CF_3)_4H_2$ are extremely close. However, both HF and LDF theories agree that the ground state of [*m*-$P(CF_3)_4H_2]^+$ is ^2A_u.

In view of the extreme electron-deficient character of *m*-$P(CF_3)_4H_2$, it was of interest to perform exploratory calculations on β-$P(CF_3)_8H_2$, a compound yet to be synthesized. Surprisingly, the lowest LDF IP of β-$P(CF_3)_8H_2$ is essentially the same as that of *m*-$P(CF_3)_4H_2$! Clearly, a *meso* trifluoromethyl group exerts a much stronger electron-withdrawing effect than one at a β position. As expected, the lowest IP of β-$P(CF_3)_8H_2$ corresponds to a $^2B_{1u}$ cationic final state, the ^2A_u state being higher by a margin of 0.4 eV.

Ono has reported electrochemical oxidation potentials of free base [$PMe_4(CF_3)_4H_2$] and zinc-complexed 2,7,12,17-tetramethyl-3,8,13,18-tetrakis(trifluoromethyl)porphyrin [$ZnPMe_4(CF_3)_4$].[38d] The one-electron oxidation potentials of these two compounds are higher than those of PEt_8H_2 and $ZnPEt_8$ by 0.24 and 0.33 V, respectively.[38d] Assuming perfect additivity of substituent effects, one would predict that the lowest IP of $PMe_4(CF_3)_4H_2$

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should equal the mean of those of β-PMe_8H_2 and β-$P(CF_3)_8H_2$, which is 7.56 eV. Explicit LDF calculations on $PMe_4(CF_3)_4H_2$ (C_{2h}) resulted in a value of 7.58 eV for the lowest IP, in excellent agreement with the predicted value. At the LDF level, the lowest IP of $PMe_4(CF_3)_4H_2$ exceeds that of β-PMe_8H_2 by 0.94 eV, which is considerably more than the substituent effect on the electrochemical oxidation potentials. Once again, it appears that electrochemical redox potentials do not reflect the intrinsic electronic effects of multiple, highly electron-withdrawing substituents such as trifluoromethyl groups. Gas-phase UPS measurements, where the cationic final states cannot be preferentially solvated as in electrochemistry, should reveal significantly larger substituent effects than observed by electrochemical measurements.

Chemists at the Sun Company (Marcus Hook, Pennsylvania) have reported perfluorination of the β-positions of *meso*-tetrakis(perfluoro-*n*-alkyl)porphyrins by controlled fluorination with F_2 diluted in N_2.[26g] The lowest LDF IP of such a porphyrin, exemplified by $PF_8(CF_3)_4H_2$ in this study, exceeds the lowest IPs of PH_2 and $TPPH_2$ by over 1.8 and 2.3 eV, respectively. Thus, there is little doubt about the stability of β-octafluoro-*meso*-tetrakis(perfluoro-*n*-alkyl)porphyrins toward oxidative degradation.

E. Cyanoporphyrins. In this study, we have selected cyanoporphyrins as the simplest representatives of a larger class of porphyrins bearing carboxyl-derived substituents such as $-CN$,[40] CO_2R,[41] $CONR_2$,[42,43] etc. Cyanoporphyrins are accessible from the corresponding bromoporphyrins *via* the Rosenmund−von Braun reaction. Callot was the first to prepare β-tetracyanoporphyrins by this method.[40a] A recent patent has reported high levels of β-polycyano substitution, resulting from subjecting β-octabromo-*meso*-tetraarylporphyrins to the Rosenmund−von Braun procedure.[40d] In view of the extreme electron-withdrawing power of cyano substituents, the polycyanoporphyrins deserve considerably more physicochemical study than reported to date.

At the LDF level, the two lowest one-electron IPs of *m*-$P(CN)_4H_2$, 8.44 and 8.64 eV, are about the same as those of *m*-$P(CF_3)_4H_2$. As in the case of *m*-$P(CF_3)_4H_2$, the LDF vertical IPs of *m*-$P(CN)_4H_2$ are very similar for the lowest ^2A_u and $^2B_{1u}$ final states. The lowest LDF IP of β-$P(CN)_8H_2$ is extremely high at 9.28 eV, which exceeds that of β-$P(CF_3)_8H_2$ by 0.8 eV. Thus, although CN^- is regarded as a pseudohalide, cyano substitution exerts a far more drastic effect on the IPs of PH_2 than does substitution with halogens. Clearly, polycyanoporphyrins are among the most electron-deficient porphyrins known.

Since HF theory is known to seriously overestimate the electron-withdrawing effects of peripheral halogen substituents on the valence IPs of PH_2 (see section IVD),[4] it is of interest to compare HF and LDF results on substituent effects due to peripheral cyano groups. Table 1 shows that unlike in the case of halogenated porphyrins, the HF-KT and LDF substituent effects are in rather good agreement for the two cyanoporphyrins studied, *m*-$P(CN)_4H_2$ and β-$P(CN)_8H_2$. Thus, the maximum discrepancy between the HF-KT and LDF values for the substituent effects due to polycyano substitution is only ~30% of the LDF substituent effects, compared to ≫100% for certain halogenated porphyrins. This observation appears to be quite suggestive, when we recall that HF theory provides a good description of the charge distribution in free base β-octaethylporphyrazine and phthalocyanine.[15,17n] We suggest that for tetrapyrroles containing only C, H, and N, HF theory can semiquantitatively reproduce experimentally observed substituent effects on the core and lowest valence IPs. In contrast, HF theory appears to grossly exaggerate the electron-withdrawing effects of substituents containing such highly electronegative atoms as F, Cl, Br, and O on the porphyrin nucleus.

F. Nitroporphyrins. Polynitroporphyrins have been known for a few years,[44] but their application to catalysis of hydrocarbon oxygenation is just beginning to be investigated. The oxo-bridged dimer of iron(III) β-octaethyl-*meso*-tetranitroporphyrin reportedly catalyzes the conversion of isobutane to *tert*-butyl alcohol with dioxygen as oxidant, giving 1600 turnovers in 5 h in benzene at 80 °C, conditions under which $Fe(PEt_8)Cl$ and $[Fe(PEt_8)]_2O$ are totally inactive.[44k] Similarly, polynitro derivatives of Fe(TDCPP)Cl and Fe(TPFPP)Cl catalyze alkane oxygenation with dioxygen without any sacrificial reductants.[44l]

LDF calculations have been carried out for two different conformations of *m*-$P(NO_2)_4H_2$, in which the nitro groups are coplanar and perpendicular to the porphyrin ring. The two lowest LDF IPs of the coplanar form, 8.49 and 8.67 eV, are similar to those of *m*-$P(CF_3)_4H_2$ and *m*-$P(CN)_4H_2$. For the coplanar form, the ground state of the cation is ^2A_u at the LDF level, as expected for extremely electron-withdrawing *meso* substituents. The results for the perpendicular form of *m*-$P(NO_2)_4H_2$ are rather different from those for the coplanar form. Thus, the lowest LDF IP (8.11 eV) of the perpendicular form is substantially lower than the second lowest IP (8.51 eV) and also significantly lower than the two lowest LDF IPs of the coplanar form. Moreover, the ground state of the perpendicular form of [*m*-$P(NO_2)_4H_2]^+$ is ^2A_u at the LDF level, instead of the expected $^2B_{1u}$! Examination of the spin density distributions of the cationic states reveals a conjugative interaction between the highest occupied σ (relative to the plane of the nitro group) orbital of the nitro group and the porphyrin's π-system, which is possible only for the perpendicular form. For the $^2B_{1u}$ cationic state of the perpendicular form, this interaction results in significant delocalization of the unpaired spin density and, therefore, of the positive charge onto the nitro groups, which explains the stability of the $^2B_{1u}$ state relative to the ^2A_u state.

As in the case of halogenated porphyrins[4] and unlike in the case of cyanoporphyrins, the HF substituent effects listed in Table 1 for *m*-$P(NO_2)_4H_2$ exceed the LDF values by over 100% of the latter. Presumably, this again reflects the fact that HF theory seriously overestimates the electron-withdrawing effects of the nitro oxygens on the rest of the molecule (as suggested in section IVE).

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Table 4. Electronic Effects (eV) of Substituents on the Two Lowest One-Electron IPs of PH_2 on a "per Substituent Basis"

	meso		β	
	final state		final state	
substituent	^2A_u	$^2B_{1u}$	^2A_u	$^2B_{1u}$
H	0.00	0.00	0.00	0.00
Me			−0.08	−0.07
Ph	−0.09	−0.12		
C_6F_5	0.145	0.145		
F	0.12	0.02	0.105	0.11
Cl	0.115	0.02	0.07	0.08
Br	0.105	0.005	0.05	0.06
CF_3	0.27	0.33	0.19	0.16
CN	0.315	0.31	0.26	0.26
NO_2 (coplanar)	0.28	0.365		
NO_2 (perp.)	0.28	0.22		

G. A Comparison of Different Substituents. Table 4 compares the effects of different substituents on the two lowest LDF IPs of PH_2 on a "per substituent" basis. The effects of individual *meso* and β substituents were obtained by dividing the total substituent effects in *meso*-tetrasubstituted and β-octasubstituted porphyrins (which are given in Table 1) by 4 and 8, respectively. All substituent effects are relative to hydrogen, unsubstituted porphyrin being taken as the zero level.

In terms of electron-withdrawing power, the substituents we have studied rank as follows (in decreasing order): $NO_2 \sim CN \sim CF_3 > C_6F_5 > F \geq Cl \sim Br > H > Me > Ph$. By and large, this order is intuitively expected. A number of other trends emerge from Table 4.

A substituent placed at a *meso* position generally exerts a higher electronic effect than the same substituent placed at a β-position. However, halogens are an exception to this generalization. As discussed above, *meso* halogens exert a near-zero effect on the lowest LDF IP of porphyrin, i.e. the IP that corresponds to the lowest $^2B_{1u}$ final state.

Contrary to HF results and, perhaps, to chemical intuition, β-octasubstitution with all the substituents studied results in nearly equal electronic effects on the two lowest LDF IPs of PH_2. Except for halogens, *meso* substituents too exert nearly equal effects on the two lowest LDF IPs of PH_2.

V. Summary and Conclusions

A comparison of LDF results with available UPS data suggests that the LDF approach reproduces the absolute values of the lowest one-electron IPs of porphyrins to within about 0.2 eV. Substituent effects on the IPs are probably reproduced with even higher accuracy. This level of accuracy exceeds by far that of HF calculations and shows that the computationally expedient LDF method provides a rather accurate description of the difference in correlation energy between the neutral and ionized states of porphyrin molecules. In a number of cases, substituent effects calculated with HF and LDF theories are quite different. For instance, HF theory seriously underestimates the substantial electron-donating effect of *meso*-tetraphenyl substitution and overestimates the electron-withdrawing effects of halogens. In contrast, LDF substituent effects are generally in near-quantitative agreement with experiment.

In view of the excellent performance of the LDF method, we have assembled a database of the lowest LDF IPs of a broad variety of substituted porphyrins. This should provide valuable guidance to experimentalists using peripheral substitutions to electronically tune the porphyrin ligand for specific applications. Specifically, our results are relevant to ongoing experimental work on electron-deficient porphyrins that are resistant to oxidative degradation. For instance, we have shown that β-octachlorination or β-octabromination brings about comparatively modest increments in the IPs of porphyrins. In contrast, substituents such as trifluoromethyl, cyano, and nitro exert drastic electron-withdrawing effects. Thus, porphyrins bearing these latter substituents, which to date have received relatively little attention, should have the maximum electronic protection against oxidative degradation. Overall, LDF calculations have provided an accurate and fairly comprehensive picture of substituent effects in porphyrins.

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