NEW MATERIALS DESIGN. FREE-BASE PORPHYRIN AND ITS *MESO*-TETRAHALOGENATED DERIVATIVES

Kiet A. Nguyen and Ruth Pachter

Air Force Research Laboratory, Materials & Manufacturing Directorate, Wright-Patterson Air Force Base, Ohio 45433

ABSTRACT

Ab initio electronic structure theory has been applied to predict the structures and electronic spectra of free-base porphyrin (PH_2) and its *meso*-tetrahalogenated derivatives (*m*-PX_8H_2; X = F, Cl, Br). Structures, singlet-triplet energy gaps, and electronic spectra are predicted using the B3LYP method in conjunction with the 6-31G(d) basis set and the effective core potentials/basis sets of Stevens et al. Minimum energy structures of the lowest triplet excited states (T_1) were found to retain D_{2h} symmetry with stretched C_β-C_β and C_β-C_m bond distances. We found that halogenation at the four *meso*-positions significantly changes the ground state excitation energies and the singlet-triplet gap for the free-base parent compound.

Keywords. Modeling and simulation of optical limiting materials; ab initio electronic structure; porphyrin derivatives; electronic spectra; molecular structures

INTRODUCTION

Halogenation leads to significant changes in physical and chemical properties of porphyrins (Figure 1) that can be exploited in a wide variety of applications. In previous studies, β-octahalogenation[1, 2] and *meso*-tetrahalogenation[3] have been shown to significantly increase the valence IPs of all octahalogenated free-base porphyrins in comparison to PH_2.

In view of the large increase in ionization potentials that may protect these halogenated dyes from oxidative destruction and photodegradations, *m*-PX_8H_2 deserves more photophysical study. Due to potential applications of porphyrins in photodynamic therapy,[4] optical storage,[5] and optical limiting,[6] a subject of interest has been the halogenation effect upon the ground and excited states spectra. This study examines the effects of *meso*-tetrahalogens upon the ground state spectra and the singlet-triplet (S_0–T_1) energy gaps.

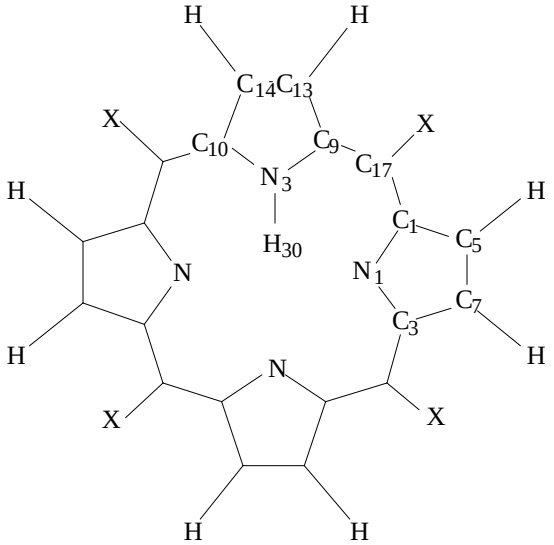

Figure 1: Porphyrin

Calculations using density functional theory (DFT) are carried out to predict the structures and electronic spectra of *m*-PX_8H_2 (X = F, Cl, Br). The structures and energetics of the corresponding triplet states of these compounds are also computed to predict the triplet energy levels that can be directly compared with experimental phosphorescence of PH_2 in order to establish structures of the triplet excited state. Previous attempts in synthesizing the free-base *meso*-tetrahalogenated derivatives have not been successful.[7-9] A direct comparison of the computed results to experiment, therefore, is not possible. However, *m*-PX_8H_2 can serve as simplified models of the known β-octaethyl-*meso*-tetra halogenatedporphyrins.[10] In addition, the computed results also provide preliminary assessments of the spectroscopic properties prior to synthesis.

COMPUTATIONAL METHODS

The structures of all porphyrins have been predicted using the Kohn-Sham (KS)[11] density functional theory. All calculations were carried out using the 6-31G(d)[12, 13] basis set (for carbon, hydrogen, and fluorine). Effective core potentials and basis sets of Stevens et al.[14, 15] were used for heavier elements. DFT calculations were carried out using Becke's three-parameter (B3LYP) hybrid functional.[16-18] Open-shell DFT calculations for the triplets were carried out using the unrestricted Hartree-Fock (UHF)[19]

formalism, while the restricted version (RHF)[20] was used for the closed-shell species. The structures were verified to be either minima or transition states by evaluating the appropriate matrix of energy second derivatives (Hessian). The excitation energy calculations were carried out using the time dependent density functional response theory (TDDFT)[21-23] as implemented in the Gaussian 98[24] program.

RESULTS AND DISCUSSION

Ground State Structures and Spectra

The computed structures and spectra of PH_2 and *meso*-PX_4H_2 are listed in Tables I and II. The computed structures and excitation energies for the Q and B bands of PH_2 have been reported in a previous study. Geometrical parameters and excitation energies of PH_2 are tabulated with *meso*-tetrahalogenated derivatives for the comparison of substituent effects. The ground state of all *meso*-PX_4H_2 species are predicted to have D_{2h} symmetry. In comparison with PH_2, changes in bond lengths of the porphyrin framework for all *meso*-PX_4H_2 are within 0.01 Å. All bond angles in *meso*-PX_4H_2 are within 2˚ of the corresponding angles in PH_2. The spectral shifts observed in *meso*-PX_4H_2, therefore, are largely of electronic origin. TDDFT reproduces the experimental excitation energies of PH_2 reasonably well up to the N bands (see Table II). Interestingly, the largest error of 0.3 eV comes from the Q_x band.

Upon fluorination, the Q band red-shifts about 0.1 eV. Chlorination and bromination also red-shift the Q bands (~ 0.2 eV). In comparison to β-octahalogenation,[2] the shifts exerted by *meso*-tetrahalogenation to the Q bands are about twice as large in energy. In contrast to large red-shifts (~ 0.4 eV) previously observed for β-octahalogenation for the B bands,[2] very small spectral shifts (0.04 eV to the blue for B_x, B_y is not shifted) are seen upon *meso*-tetrafluorination. However, the corresponding chlorination and bromination cause larger red-shifts (~ 0.2 eV) of the B bands. Similar spectral trends are also observed for the N bands. The *meso*-tetrafluorination of PH_2 causes slight shifts of 0.04 and 0.06 eV to the blue and red for the N_x and N_y band. Chlorination and bromination, however, red-shift the N bands by about 0.2-0.3 eV.

Triplet Excited State Structures and Energetics

For PH_2, the excited state structure was found to retain the D_{2h} symmetry with positive definite Hessian. The macrocyclic ring was also allowed to undergo two different distortions, C_{2h} and C_{2v}. However, these structures converged to the D_{2h} equilibrium geometry after the optimization. Among the noticeable structural changes upon going from the ground to the first triplet excited state (T_1) are the stretching (0.03 Å) of one of the C_β-C_β (C_{14}-C_{13}) and C_β-C_m (C_9-C_{17}) bonds and the shortening of one the C_α-C_β (C_9-C_{13}) bonds by the same amount (see Table 1). Other bond changes involve a slight (0.01 Å) increase and decrease in the N_1-C_3 distance and C_1-C_{17}, respectively. For PH_2, changes in bond angles are no larger than 1° upon going from the ground to the first triplet excited state. Energetically, T_1 lies 1.53 eV above the ground state on the classical potential energy surface (PES). Zero point corrections lower the $S_0 \rightarrow T_1$ splitting of PH_2 to 1.42 eV. These predicted excitation energies are in good agreement with the experimental phosphorescence value of 1.58 eV.[25].

Little changes in geometry are observed upon *meso*-halogenation. The minimum structures for all *meso*-PX_4H_2 were also found to have the D_{2h} symmetry with stretched C_β-C_β and C_β-C_m bond distances. The changes in the *meso*-PX_4H_2 skeletons upon going from S_0 to T_1 are essentially the same as the corresponding changes observed for PH_2 (see Table I). However, the electronic effects induced by *meso*-halogenation on the $S_0 \rightarrow T_1$ splittings are large. In contrast to β-octahalogenation where $S_0 \rightarrow T_1$ splitting is largely unaffected, *meso*-tetrahalogenation reduces the splitting by about 0.2 eV. There are little differences in $S_0 \rightarrow T_1$ splittings among the *meso*-PX_4H_2.

Table I. Geometries for the ground and triplet excited states of free-base *meso*-halogenated porphyrins

	PH_2		meso-PH_2F_4		meso-PH_2Cl_4		meso-PH_2Br_4	
	^1A_g	$^3B_{2u}$	^1A_g	$^3B_{2u}$	^1A_g	$^3B_{2u}$	^1A_g	$^3B_{2u}$
H_{30}-N_3	1.015	1.015	1.015	1.015	1.015	1.014	1.014	1.014
N_3-C_9	1.372	1.372	1.372	1.371	1.376	1.376	1.378	1.377
N_1-C_3	1.364	1.372	1.363	1.371	1.366	1.374	1.368	1.376
C_9-C_{13}	1.435	1.408	1.429	1.403	1.431	1.405	1.432	1.406
C_5-C_1	1.460	1.463	1.453	1.457	1.458	1.460	1.458	1.461
C_{14}-C_{13}	1.372	1.401	1.375	1.403	1.369	1.395	1.367	1.393
C_5-C_7	1.356	1.353	1.360	1.356	1.353	1.350	1.352	1.349
C_9-C_{17}	1.394	1.428	1.395	1.429	1.400	1.435	1.400	1.435
C_1-C_{17}	1.400	1.389	1.398	1.387	1.405	1.395	1.405	1.394
C_{13}-H	1.082	1.082	1.080	1.080	1.079	1.079	1.079	1.078
C_5-H	1.083	1.083	1.082	1.081	1.080	1.080	1.080	1.080
C_{17}-X	1.086	1.087	1.355	1.349	1.770	1.760	1.931	1.920
$\alpha(H_{30}$-N_3-$C_9)$	124.6	124.9	125.1	125.3	124.9	125.2	124.8	125.1
$\alpha(C_9$-N_3-$C_{10})$	110.9	110.3	109.9	109.4	110.2	109.7	110.4	109.8
$\alpha(C_1$-N_1-$C_3)$	105.4	105.4	104.5	104.4	104.9	104.8	105.0	105.0
$\alpha(N_3$-C_9-$C_{13})$	106.5	107.3	107.3	108.0	106.8	107.5	106.6	107.3
$\alpha(N_1$-C_1-$C_5)$	111.1	110.8	111.8	111.6	111.4	111.1	111.2	110.9
$\alpha(C_9$-C_{13}-$C_{14})$	108.0	107.6	107.8	107.3	108.1	107.7	108.2	107.8
$\alpha(C_1$-C_5-$C_7)$	106.2	106.5	105.9	106.2	106.2	106.5	106.3	106.6

$\alpha(N_3\text{-}C_9\text{-}C_{17})$	125.5	124.6	124.4	123.3	125.1	124.1	125.1	124.1
$\alpha(N_1\text{-}C_1\text{-}C_{17})$	125.5	125.1	123.8	123.6	124.1	123.9	124.0	123.8
$\alpha(C_9\text{-}C_{17}\text{-}C_1)$	127.1	128.1	129.0	130.1	128.3	129.2	128.5	129.4
$\alpha(C_9\text{-}C_{13}\text{-}H)$	124.3	124.9	124.5	125.1	124.7	125.4	124.8	125.5
$\alpha(C_1\text{-}C_5\text{-}H)$	125.4	125.2	125.7	125.6	126.0	125.9	126.1	125.9
$\alpha(C_9\text{-}C_{17}\text{-}X)$	115.9	115.0	114.7	113.4	114.9	113.9	114.8	113.8

Table II. Excitation energies (in eV) for free-base porphyrins[a]

	PH_2		PH_2F_4	PH_2Cl_4	PH_2Br_4
		Exp[b]			
$^1B_{1u}$ ($\pi \rightarrow \pi^*$)	2.28	1.98 (Q_x)	2.16	2.10	2.08
$^1B_{2u}$ ($\pi \rightarrow \pi^*$)	2.44	2.42 (Q_y)	2.35	2.27	2.25
$^1B_{1u}$ ($\pi \rightarrow \pi^*$)	3.34	3.33 (B_x)	3.37	3.17	3.13
$^1B_{2u}$ ($\pi \rightarrow \pi^*$)	3.51	3.33 (B_y)	3.52	3.34	3.29
$^1B_{2u}$ ($\pi \rightarrow \pi^*$)	3.77	3.65 (N_x)	3.79	3.58	3.54
$^1B_{1u}$ ($\pi \rightarrow \pi^*$)	3.87	3.65 (N_y)	3.81	3.65	3.60

[b]Data taken in gas phase.[26]

Table III. B3LYP/6-31G(d) adiabatic $S_0 \rightarrow T_1(^3B_{2u})$ excitation energies (in eV) for free-base porphyrins

System	ΔE	ΔH
PH_2	1.53	1.42[a]
β-PH_2F_8	1.62	1.41
β-PH_2Cl_8	1.52	1.50
β-PH_2Br_8	1.50	1.39
m-PH_2F_4	1.25	1.18
m-PH_2Cl_4	1.31	1.23
m-PH_2Br_4	1.32	1.24

[a] Experimental phosphorescence value of 1.58 eV[25].

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