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Ground and Triplet Excited Structures and Spectroscopic Properties of Halogenated Zinc *meso*-Tetraphenylporphyrin

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Structures of the ground and triplet excited state of zinc *meso*-tetraphenylporphyrin (ZnTPP) and its β-octahalogenated derivatives (ZnTPPX$_8$ with X = F, Cl, and Br) have been predicted using density functional theory (DFT) with Becke's three-parameter functional. The excitation energies, computed by singles CI and time-dependent DFT (TDDFT), are consistent with the observed trends, with TDDFT values in near quantitative agreement with experiment. For ZnTPPBr$_8$, we found that geometry distortion contributes about one-third of the redshifts observed for the Q and B bands in the ground-state spectrum. The results for ZnTPPX$_8$ and the nonphenylated ZnPX$_8$ provide insightful accounts of effects of phenyl, fluoro, chloro, and bromo substituents on the excitation energies of these systems. The computed singlet−triplet (S$_0$−T$_1$) splitting of ZnTPP is in excellent agreement with experiment. The S$_0$−T$_1$ splitting is predicted to be significantly (0.4−0.5 eV) redshifted upon β-chlorination and β-bromination.

I. Introduction

Free-base porphyrins and their metal analogues are an important class of materials that are being used as catalysts in industrial processes,[1−9] as photosensitizers in photodynamic therapy (PDT),[10] and as media for optical recording.[11] Porphyrins are also an important class of organic nonlinear optical (NLO) materials that can potentially be used as optical limiters that have a high transmission at normal light intensities and a low transmission at high-intensity light sources. Optical limiting properties in these compounds have been attributed to nonlinear absorption in which the induced excited state absorption cross section is much stronger than its ground state counterpart. Such nonlinear absorptions have been referred to as reverse saturable absorption (RSA). The mechanisms for achieving RSA have been shown to involve primarily the ground-state singlet−singlet ($S_0 \rightarrow S_1$) and triplet−triplet ($T_1 \rightarrow T_n$) absorptions and the singlet−triplet intersystem crossing in order to maintain sufficient triplet populations.[12] The triplet population can be effectively modulated by halogenation as reported by Bonnet et al. for a series of free-base octaalkylporphyrins.[13] Techniques such as heavy central atoms, halogens, and electron-donating auxochromes have been used to enhance optical limiting properties.[12,14] Octahalogenated *meso*-tetraphenylporphyrins[15−17] (Figure 1) exhibit pronounced changes from the unsubstituted porphyrin in conformations and in photophysical and chemical properties. The substitution of eight bromine atoms at the pyrrole rings in *meso*-tetraphenylporphyrins, for example, produced large ground-state spectral and oxidation potential shifts.[15] The increase in oxidation potentials provides extra stability toward oxidative destruction and photodegradation for halogenated porphyrins. For example, Su et al. have shown that zinc octabrominated *meso*-tetraphenylporphyrin exhibits the largest optical limiting enhancement among a large number of free-base and metalloporphyrins.[18] Thus, the ability of a given porphyrin to function as an oxidation catalyst or an optical limiting material is strongly dependent upon its electronic structure, which can be greatly altered by peripheral substituents.

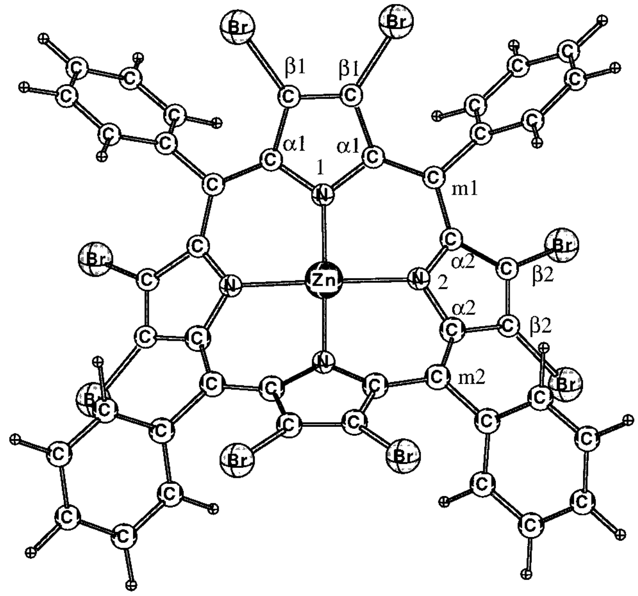

Figure 1. Labeling scheme zinc *meso*-tetraphenylporphyrins.

To shed more light on the effects of peripheral β-halogen substituents on zinc porphyrins that lead to the observed changes in photophysical properties, ab initio electronic structure calculations are carried out to examine the ground state (S$_0$) structures and spectra of zinc *meso*-tetraphenylporphyrin (ZnTPP) and its β-octahalogenated derivatives (ZnTPPX$_8$ with X = F, Cl, and Br). In addition, structures and energetics of the corresponding triplet (T$_1$) excited states of these species are also computed at the ab initio level of theory. In contrast to the common assumption that the severe nonplanar distortions observed from the X-ray crystal structures[16,19,20] are principally responsible for the large redshifted Soret and visible absorption bands of these porphyrins, we have found that geometry distortion contributes about one-third of the redshifts observed for the ground-state spectrum of β-ZnTPPBr$_8$. The results for

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TABLE 1: Geometry Parameters (in Angstroms and Degrees) for the Ground State Zinc *meso*-Tetraphenylporphyrins

	ZnTPP		$ZnTPPF_8$		$ZnTPPCl_8$		$ZnTPPBr_8$	
	exptl[a]	B3LYP	exptl[b]	B3LYP	exptl[c]	B3LYP	exptl[d]	B3LYP
Zn−N	2.037	2.055	2.059	2.062	2.032	2.047	2.030	2.044
$C_\beta-C_\beta$	1.349	1.361	1.337	1.357	1.337	1.371	1.353	1.373
$C_\alpha-C_m$	1.400	1.408	1.397	1.404	1.403	1.414	1.403	1.416
$\alpha(Zn-N-C_\alpha)$	126.3	126.4	127.3	126.0	125.3	123.5	123.6	122.8
$\alpha(C_\beta-C_\alpha-C_m)$	125.0	124.7	124.3	124.9	128.4	127.9	129.6	128.7
$\alpha(N-C_\alpha-C_m)$	126.3	125.9	125.5	126.8	124.2	124.0	123.5	123.3
DMP[f]		0.070		0.0		0.640		0.711

[a] Reference 54. [b] Experimental values are taken from the crystal structure of zinc β-octafluoro-*meso*-tetrakis(pentafluorophenyl)porphyrin.[20] [c] Experimental values are taken from the crystal structure of zinc β-octachloro-*meso*-tetrakis(pentafluorophenyl)porphyrin.[58] [d] Reference 16. [f] RMS deviation from the porphyrin skeleton (24 atoms) least-squares plane.

$ZnTPPX_8$ and the nonphenylated $ZnPX_8$[21] provide insightful accounts of effects of phenyl, fluoro, chloro, and bromo substituents on the excitation energies of these systems.

II. Computational Methods

Structures (verified by positive definite Hessians) of porphyrins were predicted using the Kohn−Sham (KS)[22] density functional theory (DFT). DFT calculations were carried out using Becke's three-parameter hybrid functional[23−25] (B3LYP). Throughout, the all-electron 6-31G(d)[26,27] basis set was used for carbon, nitrogen, fluorine, and hydrogen atoms; for heavier elements, we use the effective core potentials and basis sets of Stevens et al.[28,29] Open-shell DFT calculations for the triplets were carried out using the unrestricted SCF[30] formalism, while the restricted version[31] was used for the singlet species. Excitation energies were evaluated at the B3LYP structures using the time-dependent density functional response theory[32−36] (TDDFT) and singles CI[37] (CIS) method based on the B3LYP and Hartree−Fock wave functions, respectively. DFT and TDDFT with B3LYP functional have been shown to produce low-lying excitation energies that are in excellent agreement with experiment for porphyrins[21,36] and a variety of other systems.[38−51] Electronic structure calculations were carried out using the Gaussian 94[52] and Gaussian 98[53] programs.

III. Results and Discussion

The computed results are listed in Tables 1−5. We begin with the computed structures and compare them with available experimental data in order to establish their accuracy. The computed (verified by positive definite Hessians) and observed key geometric parameters for ground state are listed in Table 1. Four conformations were considered: planar (D_{4h}), ruffled (S_4), wave (C_i), and saddle (D_{2d}). However, we limit our discussion to the lowest energy conformation. This was found to be the saddle form for all $ZnTPPX_8$, except for $ZnTPPF_8$, in which the lowest energy conformation has D_{4h} symmetry. We note that these computed structures are in excellent agreement with X-ray structures for ZnTPP and two β-octahalogenated ($ZnTPPX_8$) derivatives, $ZnTPPBr_8$ and $ZnTPPF_8$. The lowest energy structure of ZnTPP is slightly saddled with the opposite phenyl rings gauche with one another by 11.9° (see Figure 1), in agreement with the X-ray structure reported by Scheidt et al.[54] For $ZnTPPF_8$, the computed structure is in better agreement with the nearly planar experimental structure of zinc β-octafluoro-*meso*-tetrakis(pentafluorophenyl)porphyrin[20] than the X-ray structure of $ZnTPPF_8$.[17] The ruffled structure reported by Leroy et al.[17] may be the result of (1) structural polymorphism, (2) the effects of ligation and crystal packing, or (3) a combination of 1 and 2. To investigate the effect of water ligation, geometry optimization of $(H_2O)ZnTPPF_8$ was also carried out. However, an addition of H_2O to $ZnTPPF_8$ produced little geometrical change. Since *meso*-tetraphenylporphyrins[55−57] are known to assume different conformations in the crystalline phase, including the ruffled one, their halogenated derivatives may also exhibit structural polymorphism. To our knowledge, no X-ray structure of $ZnTPPCl_8$ has been reported. However, a derivative, zinc β-octachloro-*meso*-tetrakis(pentafluorophenyl)porphyrin ($ZnTFPPCl_8$) has been synthesized and characterized.[58] The distortion in the computed structure of $ZnTPPCl_8$ is similar to that of the X-ray of $ZnTFPPCl_8$; the pyrrole rings are tilted to minimize repulsion between the chlorine atoms and the *meso*-phenyl groups upon chlorination. This resulted in an increase of the $\alpha(C_\beta-C_\alpha-C_m)$ angle and reductions of the $\alpha(N-C_\alpha-C_m)$ and $\alpha(Zn-N-C_\alpha)$ angles that are consistent with the X-ray structure of $ZnTFPPCl_8$ (see Table 1 and Figure 1).[58] Similarly, the computed structure of $ZnTPPBr_8$ was found to assume a saddle conformation with a slightly larger $\alpha(C_\beta-C_\alpha-$

TABLE 2: Excitation Energies (in eV) for Zinc Porphyrins[a]

system/transition	CIS	TDDFT	exptl
ZnTPP			
$^1E(\pi \rightarrow p^*)$	2.46 (2.54)	2.30 (2.44)	2.09,[b] 2.12[c] (2.23)
$^1E(\pi \rightarrow p^*)$	4.39 (4.74)	3.25 (3.54)	3.05,[b] 2.97[c] (3.18)
$ZnTPPF_8$			
$^1E_u(\pi \rightarrow \pi^*)$	2.53 (2.58)	2.39 (2.47)	2.15,[d] 2.16[e]
$^1E_u(\pi \rightarrow \pi^*)$	4.57 (4.85)	3.30 (3.41)	3.02,[d] 3.05[e]
$ZnTPPCl_8$			
$^1E(\pi \rightarrow \pi^*)$	2.28 (2.48)	2.08 (2.36)	1.92[f]
$^1E(\pi \rightarrow \pi^*)$	4.02 (4.56)	2.91 (3.26)	2.72[f]
$ZnTPPBr_8$			
$^1E(\pi \rightarrow \pi^*)$	2.23 (2.46)	2.00 (2.34)	1.89[g]
$^1E(\pi \rightarrow \pi^*)$	3.88 (4.48)	2.80 (3.18)	2.66[g]

[a] Computed with single CI (CIS) and time-dependent density functional theory (TDDFT); numbers in parentheses are computed/experimental excitation energies of the corresponding nonphenylated $ZnPX_8$ with D_{4h} symmetry and $^1E_u(\pi \rightarrow \pi^*)$ transitions;[21] experimental excitation energies of ZnP are from optical spectra in *n*-octane.[63] [b] From optical spectra in vapor phase at 445 °C, ref 64. [c] From optical spectra in CH_2Cl_2 at 25 °C, ref 64. [d] From optical spectra in $CHCl_3$, ref 17. [e] From optical spectra in CH_2Cl_2, ref 20. [f] From optical spectra in $CHCl_3$, ref 65. [g] From optical spectra in CH_2Cl_2, ref 15.

TABLE 3: B3LYP Sign Reversed Gouterman's Orbital Energies (in eV) for Zinc Tetraphenylporphyrins

	zinc porphyrin			
orbital[a]	ZnTPP	$ZnTPPF_8$[b]	$ZnTPPCl_8$	$ZnTPPBr_8$
HOMO-1 (b_1)	5.15	5.78	5.88	5.82
HOMO (b_2)	4.97	5.65	5.60	5.40
LUMO (e)	2.14	2.69	2.97	2.96
HOMO−LUMO	2.83	2.96	2.53	2.44

[a] Orbital symmetries are in parentheses. [b] Symmetries of the HOMO-1, HOMO, and the degenerate virtuals are a_{1u}, a_{2u}, and e_g, respectively.

TABLE 4: Geometry Parameters (in Angstroms and Degrees) for the T_1 Excited States of Zinc *meso*-Tetraphenylporphyrins

	ZnTPP	ZnTPPF$_8$	ZnTPPCl$_8$	ZnTPPBr$_8$
Zn−N$_1$	2.060	2.056	2.056	2.057
Zn−N$_2$	2.086	2.098	2.086	2.081
$C_{\beta1}$−$C_{\beta1}$	1.385	1.381	1.395	1.397
$C_{\beta2}$−$C_{\beta2}$	1.359	1.356	1.369	1.371
$C_{\alpha1}$−C_{m1}	1.439	1.437	1.444	1.446
$C_{\alpha2}$−C_{m2}	1.402	1.399	1.405	1.406
α(Zn−N$_1$−$C_{\alpha1}$)	125.8	123.4	119.7	118.8
α(Zn−N$_2$−$C_{\alpha2}$)	125.7	123.8	121.0	120.4
α($C_{\beta1}$−$C_{\alpha1}$−C_{m1})	124.8	125.8	128.6	129.3
α($C_{\beta2}$−$C_{\alpha2}$−C_{m2})	125.0	126.2	128.8	129.4
α(N$_1$−$C_{\alpha1}$−C_{m1})	125.2	125.4	122.3	121.5
α(N$_2$−$C_{\alpha2}$−C_{m2})	125.6	125.4	122.9	122.3
DMP[a]	0.229	0.458	0.761	0.813

[a] RMS deviation from the porphyrin skeleton (24 atoms) least-squares plane.

TABLE 5: $S_0 \rightarrow T_1$ Excitation Energies (in eV) for Zinc *meso*-Tetraphenylporphyrins[a]

		adiabatic		
system	vertical	ΔE	ΔH	exptl
ZnTPP	1.78	1.61	1.53	1.61,[b] 1.57[c]
ZnTPPF$_8$	1.87	1.60	1.55	
ZnTPPCl$_8$	1.49	1.21	1.16	
ZnTPPBr$_8$	1.41	1.13	1.09	1.70[d]

[a] Electronic states for the triplets are of $^3B_1$ symmetry. [b] From optical spectra in toluene, ref 60. [c] From optical spectra in toluene with 0.5% pyridine, ref 60. [d] From optical spectra in CHCl$_3$, ref 15.

C_m) and somewhat smaller α(N−C_α−C_m) and α(Zn−N−C_α) angles (Table 1). These changes in bond angles, a signal for nonplanar distortion, are also observed in the X-ray structure of ZnTPPBr$_8$.[16]

The observed and computed ground-state excitation energies of ZnTPP and ZnTPPX$_8$ are listed in Table 2. The corresponding energies for ZnP and ZnPX$_8$, computed previously[21] are also included (in parentheses) for comparison. For ZnTPPCl$_8$ and ZnTPPBr$_8$, the computed first excitation energies are redshifted about 0.2−0.3 eV from those of ZnTPP, while ZnTPPF$_8$ shows a slight blueshift of about 0.1 eV. Much larger redshifts (up to 0.5 eV) were observed for the Soret bands of ZnTPPX$_8$. These predicted trends are in excellent agreement with experiment (see Table 2). However, the absolute CIS excitation energies systematically overestimate the Q and B bands by about 15% and 30%, respectively. Except for the Soret band of ZnTPPF$_8$, the Q and B bands computed by CIS are within 0.1 eV of experiment after scaling (0.85 and 0.70). The TDDFT excitation energies are in excellent agreement with experiment without any scaling. The TDDFT results have an absolute mean deviation of 0.19 eV for ZnTPP and ZnTPPX$_8$. The quantitative improvement in accuracy of TDDFT over CIS at about the same computational cost for ZnTPPX$_8$ is consistent with our previous study of free-base and zinc porphin.[21]

The redshifts observed in the electronic spectrum of ZnTPPX$_8$ (X = Cl and Br) can be attributed partly to the conformational distortion which destabilizes the porphyrin HOMO and, to lesser extent, the LUMO. This results in the smaller HOMO−LUMO gaps (see Table 3). The computed B3LYP HOMO−LUMO gaps do correlate with the spectral trends for the $S_0 \rightarrow S_1$ and $S_0 \rightarrow T_1$ (see below) excitation energies of ZnTPPCl$_8$ and ZnTPPBr$_8$. Furthermore, an increase in the HOMO−LUMO gap of the planar ZnTPPF$_8$ is also consistent with its blueshifts in excitation energies. The effects of the halogen and phenyl groups, however, can be a significant factor in lowering the excitation energies of the Q and B bands. For example, the computed redshifts in the Q and B bands upon going from ZnP to ZnTPP are 0.11 and 0.21 eV, respectively (see Table 2). These predicted shifts are consistent with experiment. Conformational distortion is likely not a major cause of the redshifts in this case since the skeletal structure of ZnTPP is essentially planar. ZnTPP has the RMS deviation from the skeleton (24 atoms) least-squares plane of only 0.07 Å (see Table 1). It should be noted that the shifts in excitation energy of ZnTPPCl$_8$ and ZnTPPBr$_8$ relative to ZnTPP include the effects of halogens, conformational distortion, and the combined effects of phenyl and halogen. The energy shifts contributed by distortion can be obtained by subtracting the shifts induced by halogens from ZnPX$_8$ that have planar D_{4h} geometries. However, these distortion energy shifts contain the combined electronic effects of the phenyl and halogen groups. To quantify the effects of distortion alone, TDDFT excitation energy calculations for a modified ZnTPPBr$_8$ were carried out with all the bromo and phenyl substituents being replaced by hydrogens while retaining the distorted porphyrin skeleton. TDDFT excitation energy calculations with the modified structure yield the redshifts (relative to ZnTPP) of only 0.10 and 0.14 eV for the Q and B bands, respectively. The distortion in the macrocyclic ring of ZnTPPBr$_8$, therefore, accounts for only one-third of the redshift in the Q and B band. Apparently, the combined electronic effect of the bromo and phenyl groups is important and is the major factor for the redshift of the Q and B bands in ZnTPPBr$_8$.

A parallel study of ZnTPP and their halogenated derivatives has also been carried out for the lowest triplet excited states using the B3LYP DFT method. Since the ZnTPP lowest unoccupied molecular orbital (LUMO) is degenerate (e symmetry under D_{2d} point group), the lowest triplet excited state of ZnTPP (^{3}ZnTPP) undergoes a Jahn-Teller (J-T) distortion. The geometry search for ^{3}ZnTPP leads to a structure with C_{2v} symmetry ($^3B_1$) which is a verified minimum with all real frequencies. In comparison with the ground state, the J-T distorted structure of ^{3}ZnTPP has two stretched pyrrole C_β−C_β and C_α−C_m bonds, while the other C_β−C_β and C_α−C_m bonds remain essentially unchanged (cf., Tables 1 and 4 and Figure 1). This is consistent with the downshifts from the ground-state stretching frequencies involving the pyrrole C_β−C_β and C_α−C_m bonds in the ^{3}ZnTPP resonance Raman spectra, as reported by Reed et al.[59] The B3LYP $S_0 \rightarrow T_1$ adiabatic excitation energy for ZnTPP is also in excellent agreement with the phosphorescence value reported by Walters et al.[60] (see Table 5). The T_1 structures of ZnTPPX$_8$ were also found to have C_{2v} symmetry ($^3B_1$). In the T_1 state, ^{3}ZnTPPF$_8$ is significantly distorted from the planar D_{4h} structure, while the ^{3}ZnTPPCl$_8$ and ^{3}ZnTPPBr$_8$ structures maintain a pronounced saddle conformation similar to their ground-state structures. The stretching of C_β−C_β and C_α−C_m bonds apparently does not help in relieving the steric hindrance that is apparently responsible for the pronounced saddle conformation. Interestingly, the T_1 energy level of ^{3}ZnTPPF$_8$ is essentially identical to that of ^{3}ZnTPP. In contrast, the $S_0 \rightarrow T_1$ excitation energies of ZnTPPCl$_8$ and ZnTPPBr$_8$ are significantly redshifted from those of ZnTPP. Adiabatically, the $S_0 \rightarrow T_1$ gap of ZnTPP is decreased by 0.48 eV (to 1.13 eV) upon β-bromination. However, this is not in agreement with the emission spectrum of ZnTPPBr$_8$ obtained by Bhyrappa and Krishnan in CHCl$_3$.[15] Although these authors concluded that the phosphorescence spectrum of ZnTPPBr$_8$ is redshifted relative to ZnTPP, they reported the highest energy band (presumably T(0−0)) of 1.70 eV for ZnTPPBr$_8$. Since chlorinated solvents have been shown to react with photoexcited porphyrins,[61] this may be a primary source of the discrepancy between the computed and experimental results. The effects of solvation/ligation, however, cannot be ruled out. Although the computed B3LYP $S_0 \rightarrow T_1$ excitation energies for free-base TPP,[62] porphine,[21] and a variety of other systems[38−51] with similar basis sets are in excellent agreement with experiments and high-level ab initio calculations, new experiments on $ZnTPPX_8$ are needed to confirm the computed S_0-T_1 splittings because high-quality CASPT2 or coupled cluster (CCSD(T)) calculations are presently not practical for these $ZnTPPX_8$ systems. These methods scale-up to N,[7] where N is the number of basis functions, which is as high as 906 basis functions in this study.

IV. Conclusions

In summary, structures of the ground and triplet excited states have been predicted using DFT with the B3LYP functional. For the ground state, the CIS and TDDFT excitation energies are consistent with the observed trends, with TDDFT values in near quantitative agreement with experiment. In contrast to the common notion that nonplanar distortion principally redshifts the spectra of porphyrins, we have shown that it contributes only one-third of the redshifts observed for the ground-state spectrum of zinc β-$ZnTPPBr_8$. The spectroscopic data for $ZnTPPX_8$ and $ZnPX_8$ allow direct quantitative accounts for the effects of phenyl, β-halogen, and geometric distortion upon the basic zinc porphin chromophore. The computed S_0-T_1 splitting of ZnTPP is in excellent agreement with experiment. The S_0-T_1 splitting is predicted to be significantly (0.4−0.5 eV) redshifted upon β-chlorination and β-bromination. This is not in agreement with the experimental S_0-T_1 splitting of $ZnTPPBr_8$ which calls for new luminescence studies on $ZnTPPX_8$. The computed ionization potentials and triplet−triplet absorption spectra will be reported later.

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Supporting Information Available: A listing of optimized geometries (Cartesian coordinates) and total energies. This material is available free of charge via the Internet at http://pubs.acs.org.

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