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COMMENTS

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

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Recently Nguyen, Day, and Pachter published a paper concerning the structures and spectroscopic properties of halogenated zinc *meso*-tetraphenylporphyrins.[1] Structures of the ground and triplet excited state of zinc *meso*-tetraphenylporphyrin (ZnTPP) and its β-octahalogenated derivatives ($ZnTPPX_8$ with X = F, C1, and Br) were computed using density functional theory (DFT). The lowest energy conformation in the ground state was demonstrated to be the saddle form for all $ZnTPPX_8$, with the exception of $ZnTPPF_8$. The excitation energies computed by time-dependent DFT (TDDFT) were shown to be in near quantitative agreement with experiment. Although we evaluate the study highly, the logic employed for drawing out one of the major conclusions is considered to be questionable. In contrast to the common notion that nonplanar distortion is principally responsible for the redshifted B and Q absorption bands, they concluded that geometry distortion contributes only one-third of the redshifts observed for the ground-state spectrum of $ZnTPPBr_8$.

The excitation energy shifts are contributed by (a) conformational distortion, (b) the *meso*-phenyl groups, (c) the β-halogen groups, and (d) combined effects of nonplanar distortion, *meso*-tetraphenylation, and β-octahalogenation, as Nguyen et al. pointed out.[1] To quantify the effects of distortion alone, that is, contribution *a*, they carried out TDDFT excitation energy calculations for a modified $ZnTPPBr_8$ with all the bromo and phenyl substituents being replaced by hydrogens while retaining the distorted porphyrin skeleton; this imaginary complex is a distorted ZnP with the same distortion as $ZnTPPBr_8$. The computed values for the Q and B bands of normal ZnP, ZnTPP, distorted ZnP, and $ZnTPPBr_8$ are reproduced in column 2 of Table 1. The authors discussed the contribution of conformational distortion to total redshifts in $ZnTPPBr_8$ relative to ZnTPP, 0.30 and 0.45 eV for the Q and B bands, respectively. Adopting the difference between excitation energies, *E*, for ZnTPP and distorted ZnP, 0.10 and 0.14 eV for the Q and B bands, respectively, as the contribution of distortion, they asserted that distortion in the macrocyclic ring of $ZnTPPBr_8$ accounts for only one-third of the redshifts. This method of comparison is not valid for quantifying the effects of distortion alone: although ZnTPP has phenyl groups, distorted ZnP does not. The shifts of 0.10 and 0.14 eV in distorted ZnP are caused by contribution *a minus* contribution *b*. On the other hand, the shifts of 0.30 and 0.45 eV in $ZnTPPBr_8$ result from contributions *a*, *c*, and *d*, as illustrated in Figure 1. Thus, "one-third" corresponds to the fraction of $(a - b)/(a + c + d)$, not $a/(a + c + d)$.

TABLE 1: Excitation Energies and Redshifts (E and $-\Delta E$ in eV) for Zinc Porphyrins[a]

system/band	E	$-\Delta E$	contribution
ZnP			
Q	2.44	0	
B	3.54	0	
ZnTPP			b
Q	2.30	0.14	
B	3.25	0.29	
distd. ZnP[b]			a
Q	2.20	0.24	
B	3.11	0.43	
$ZnTPPBr_8$			$a + b + c + d$
Q	2.00	0.44	
B	2.80	0.74	

[a] Reproduced from ref 1. [b] Modified $ZnTPPBr_8$ with all the bromo and phenyl substiutents being replaced by hydrogens, with the distorted porphyrin skeleton being retained.

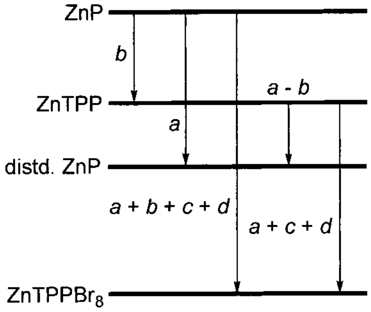

Figure 1. Schematic diagram of the shifts in transition energies for zinc porphyrins.

Because the redshifts upon going from normal ZnP to ZnTPP are regarded as being induced by phenyl groups, the shifts by contribution *b* are 0.14 and 0.29 eV for the Q and B bands, respectively, as shown in columns 3 and 4 of Table 1 and Figure 1. These values should be added to 0.10 or 0.14 eV to obtain the energy shifts contributed by distortion, and consequently, they are calculated to be 0.24 and 0.43 eV, coming back to the shifts in distorted ZnP with reference to normal ZnP. Thus, the values of the fractional contribution of geometry distortion, $a/(a + c + d)$, amount to 80 and 96% for the Q and B bands, respectively, of $ZnTPPBr_8$. Because the actual lowest energy structure of ZnTPP is slightly saddled,[1] the redshifts upon going from normal ZnP to ZnTPP include contribution by the slight distortion, a', in addition to *b*; the shifts of 0.14 and 0.29 eV correspond to $a' + b$. The shifts of 0.30 and 0.45 eV in $ZnTPPBr_8$ for $a + c + d$ are perhaps slightly underestimated, and 80 and 96% for $a/(a + c + d)$ slightly overestimated. An alternative way in which normal ZnP is taken as a reference may be adopted to evaluate the effects of distortion; the values

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of $-\Delta E$ listed in column 4 of Table 1, should be compared with one another. The shifts of 0.44 and 0.74 eV in ZnTPPBr$_8$ correspond to $a + b + c + d$, and the fractions of $a/(a + b + c + d)$ are calculated to be 55 and 58% for the Q and B bands, respectively.

In summary, geometry distortion contributes 55% to nearly 96% of the redshifts observed for the Q and B bands of ZnTPPBr$_8$, depending upon the reference complex; we must conclude that nonplanar distortion is the major factor for the redshifts.

References and Notes

(1) Nguyen, K. A.; Day, P. N.; Pachter, R. *J. Phys. Chem. A* **1999**, *103*, 9378.