Direct Porphyrin−Aryl Orbital Overlaps in Some *meso*-Tetraarylporphyrins

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Abstract: Several *meso*-tetraarylporphyrins with *ortho* substituents such as −Cl, −Br, and $-NO_2$ exemplify a hitherto unsuspected mesomeric interaction between the porphyrin and aryl groups. The interaction consists of direct orbital overlap between the porphyrin π system and the *ortho* substituents on the aryl groups. Interestingly, both the a_{1u} and a_{2u} HOMOs of the porphyrin ring have the correct symmetry for participation in this type of interaction. Nonlocal density functional calculations have been used to characterize and visualize the nature of this interaction. We have also investigated the effects of this interaction on porphyrin valence ionization potentials and the relative stabilities of the A_{1u} and A_{2u} cation radical states. An interesting consequence of this interaction is that the unpaired electron spin of porphyrin cation radicals can leak from the porphyrin macrocycle onto the aryl groups, an effect for which there is some experimental support from EPR measurements.

1. Introduction

For many years, there has been considerable interest in obtaining a detailed understanding of substitutent effects in porphyrins. An important motivation for this was the need to develop more efficient and oxidation-resistant metalloporphyrin-based catalysts for hydrocarbon functionalization.[1] Thus, we and others investigated the effects of peripheral substituents on the oxidation potentials and charge distributions of porphyrins using electrochemistry, photoelectron spectroscopy, theoretical, and other techniques.[2] A relatively comprehensive study[2] of the subject presents a unified view of a large body of substituent effect data obtained with different techniques. However, recent developments[3] emphasize the need for a deeper analysis of certain aspects of substituent effects in porphyrins, the topic of porphyrin−aryl interactions in *meso*-tetraarylporphyrins being a good example. A variety of multiporphyrin arrays with diarylacetylene linkers have been prepared that function as photon funnels, wires, optoelectronic gates, etc.[3] Porphyrin−aryl electronic interactions play a crucial part in the functioning of these molecular electronic devices. Against this background, the present report of a new pattern of porphyrin−aryl orbital overlap interactions may be of interest.

meso-Tetraarylporphyrins with *ortho* substituents on the aryl groups are a popular class of tetraarylporphyrins. Under the highly oxidizing conditions of hydrocarbon oxygenation experiments, these *ortho* substituents provide some steric protection to the porphyrin macrocycle against oxidative breakdown.[1] In the area of porphyrin-based molecular devices mentioned above, the *ortho* substituents have been exploited to lock the porphyrin and aryl units into perpendicular planes.[3] In contrast to these obvious steric effects, the electronic effects of *ortho* substituents in *meso*-tetraarylporphyrins have not been analyzed. A possibility that has not been considered so far is that *ortho* substituents on *meso*-aryl groups of porphyrins can come in such close proximity to the *meso*-carbons that they may engage in direct orbital overlap interactions with the porphyrin π-system. The resonance structures shown in Figure 1 suggest that the unpaired electron spin in tetraarylporphyrin cation radicals should leak from the porphyrin π system onto the *ortho* substituents on the aryl groups, an effect that should be experimentally testable. Density functional calculations of ionization potentials and unpaired spin distributions are used to characterize and visualize the nature of this orbital interaction.

Two recent studies led us to attempt to confirm the existence of and then to characterize the orbital interactions of the type mentioned above. First, in the course of a comparative study of electronic effects due to *ortho*, *meta*, and *para* substituents in tetraarylporphyrins, we found that *meso*-tetrakis(2,6-dinitrophenyl)porphyrin has an extremely low first ionization potential (IP) that is much lower than those of *meso*-tetrakis(3,5-dinitrophenyl)porphyrin and *meso*-tetrakis(4-nitrophenyl)porphyrin.[4] We later appreciated that this must be related to the proximity of the nitro groups and the porphyrin π-system in the case of the 2,6-dinitro system. Second, on the basis of EPR studies on *meso*-tetrakis(2,6-dichlorophenyl)porphyrin cation radicals, Bocian and co-workers concluded that the porphyrin-π and Cl-2p orbitals interact in these systems.[5] These authors pointed out that the porphyrin orbital involved in this interaction must be the a_{2u} HOMO of *meso*-tetrakis(2,6-dichlorophenyl)-porphyrin. Here we examine the nature of this interaction in various zinc *meso*-tetrakis(2,6-di-X-phenyl)porphyrin (ZnT-DXPP) cation radicals, where X = Cl (ZnTDCPP), Br (ZnT-DBPP), NO_2 ($ZnTDNO_2PP$), and CF_3 ($ZnTDCF_3PP$).

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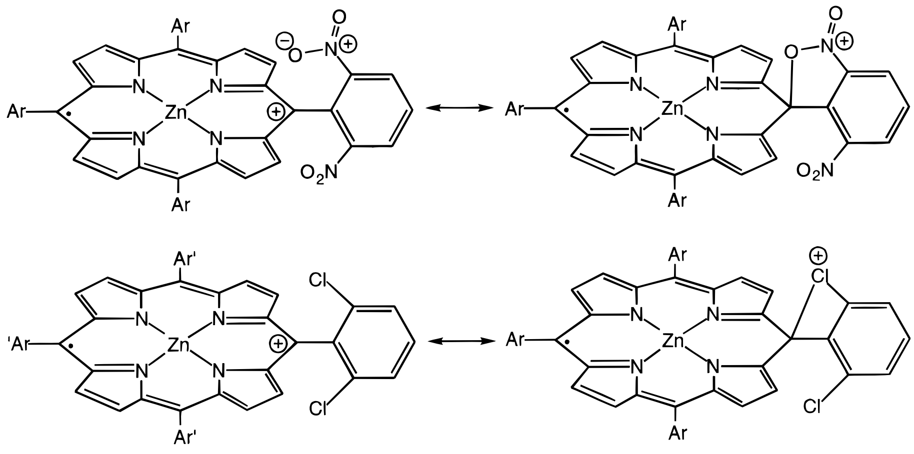

Ar = 2,6-dinitrophenyl, Ar' = 2,6-dichlorophenyl

Figure 1. Porphyrin−aryl mesomeric interactions in *meso*-tetraarylporphyrin cation radicals.

An important characteristic of the electronic structures of most common porphyrins is expressed by the so-called four-orbital model,[6] according to which the two HOMOs of common porphyrins are near-degenerate, as are the two LUMOs, and these four molecular orbitals are well-separated energetically from all other occupied and uncoccupied orbitals. For a D_{4h} metalloporphyrin, the two (porphyrin-based) HOMOs are typically a_{1u} and a_{2u} and the cation radicals derived from ionization of these two orbitals differ in energy by about 0.0−0.5 eV. Porphyrin cation radicals are of great mechanistic interest and are involved in the chemistry of the photosynthetic reaction center, the mechanisms of heme-based oxygenases and synthetic model compounds used as catalysts for hydrocarbon functionalization, and other processes. An important part of the characterization of these intermediates is the determination of their A_{1u} or A_{2u} nature, which can be done on the basis of their distinctive NMR, vibrational, and other properties. Over many years, much effort has been devoted to the prediction and understanding of the factors responsible for determining the ground states (A_{1u} or A_{2u}) of porphyrin cation radicals. We will see that the orbital interaction described here is an important factor that has not been considered so far as a determinant of the ground states common *meso*-tetraarylporphyrin cation radicals.

2. Theoretical Methods and Their Performance

Among nonempirical methods, nonlocal density functional theory (NLDFT) is probably the highest level of theory that is applicable to the molecules of interest here, which contain about 100 atoms each. Thus, we performed all calculations with spin-restricted NLDFT using the Vosko−Wilks−Nusair local functional,[7] gradient corrections due to Perdew and Wang,[8] Slater-type triple-ζ plus polarization (TZP) basis sets, a very fine mesh for numerical integrations, fully optimized geometries, and the ADF program system.[9] All optimizations used D_{4h} symmetry constraints, which requires the porphyrin and aryl planes to be orthogonal (where applicable), a reasonable assumption in view of the sterically hindered nature of the aryl groups. The energies of the cation radical states were computed via a ΔSCF procedure.

Some comments are worthwhile on the performance of first-principles methods in previous calculations of porphyrin cation radical states. Ab initio Hartree−Fock theory gives a fair picture of substituent effects for porphyrins that contain C, H, and N, but significantly poorer results for systems containing heteroatoms such as halogenated porphyrins. Local density functional (LDF) theory provides quantitatively correct substituent effects on valence IPs but the absolute values of the IPs are correct to about 0.2−0.3 eV, a small but not negligible error.[2] This level of performance falls just short of that required for an accurate theoretical assessment of the relative stability of A_{1u}- and A_{2u}-type porphyrin cation radicals as a function of peripheral substitution. Fortunately, we found that NLDFT reproduces the absolute values of four of the lowest IPs of porphine *quantitatively*, i.e., to about 0.1 eV,[10] which led us to expect that the method should furnish a good description of the energetics of the two lowest near-degenerate cation radical states of the porphyrins that are of interest here.

Table 1. The Two Lowest One-electron IPs (eV) of Zinc(II) Porphyrins

porphyrin	ionized state[a] $^2A_{2u}$	$^2A_{1u}$
ZnP	7.04 (7.02)	7.10 (7.05)
ZnTPP	6.57 (6.55)	6.72 (6.69)
ZnTDCF$_3$PP	6.85 (6.74)	7.06 (6.96)
ZnTDCPP	6.67 (6.65)	6.80 (6.76)
ZnTDBPP	6.62 (6.58)	6.74 (6.70)
ZnTDNO$_2$PP	6.50 (6.36)	6.98 (6.89)

[a] The data outside the parentheses show the two lowest one-electron *vertical* IPs (eV) of zinc(II) porphyrins. The data within parentheses refer to energies (eV) of geometry-relaxed $^2A_{2u}$ and $^2A_{1u}$ cation radical states of zinc porphyrins relative to the geometry-optimized neutral states.

3. Results and Discussion

The data (not in parentheses) in Table 1 consist of the two lowest vertical ionization potentials (IP) of the four zinc porphyrins mentioned above, of zinc porphin (ZnP), and of zinc tetraphenylporphyin (ZnTPP). The data in parentheses in Table 1 show the energies of the optimized structures of $^2A_{1u}$ and $^2A_{2u}$ cation radicals relative to the optimized structures of the respective neutral porphyrins, all optimizations being performed with D_{4h} symmetry contraints. Although the two sets of data give essentially the same information, together, they provide a "feel" for the energies associated with geometry relaxation for the different cation radical states: these are at the most 0.14 eV. Comparison with ultraviolet photoelectron spectroscopic data show that Table 1 correctly reproduces differences (ca. 0.55

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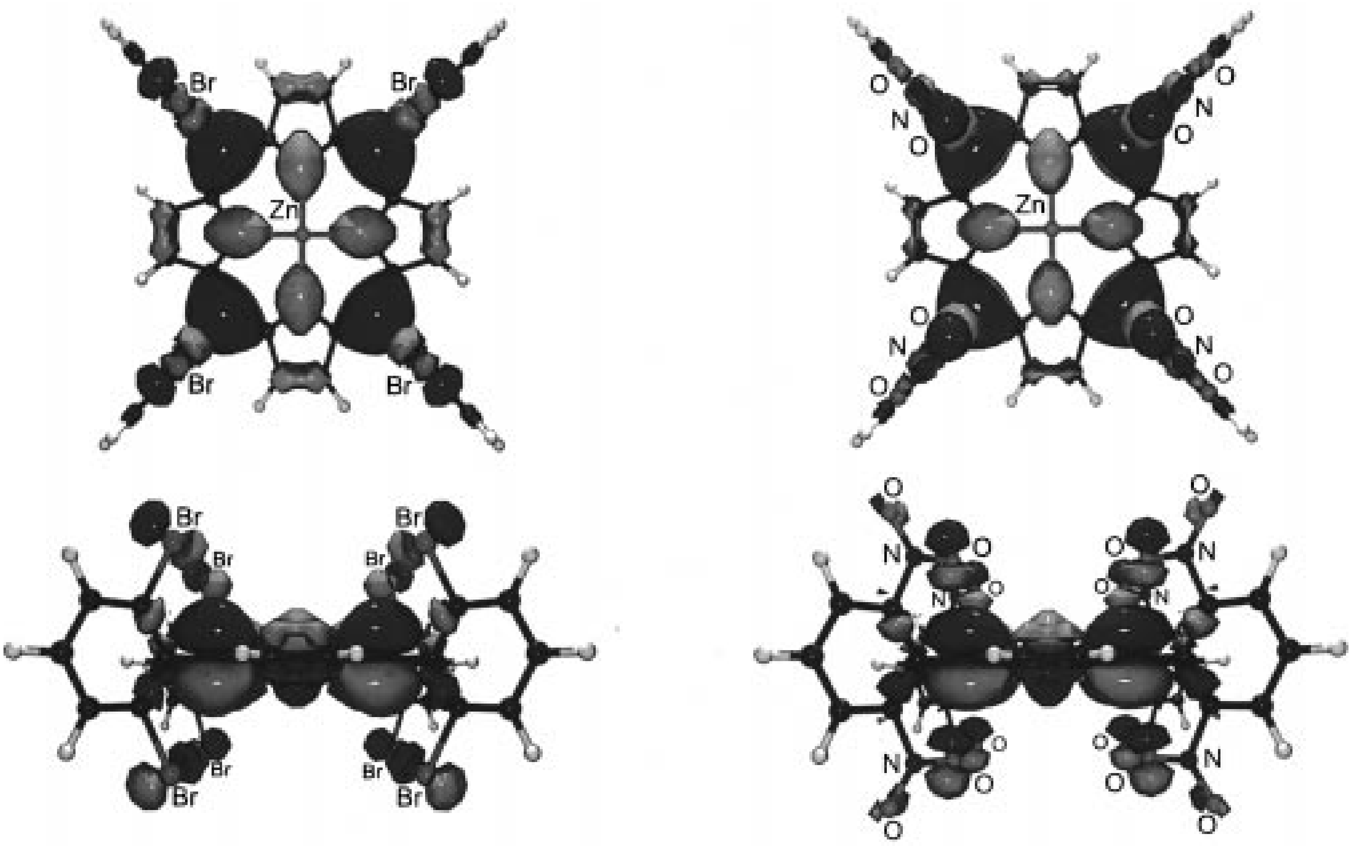

Figure 2. The singly occupied a_{2u} orbital of the ground states of ZnTDBPP$^{+\bullet}$ (left) and ZnTDNO$_2$PP$^{+\bullet}$ (right).

eV) in IPs between porphin and tetraphenylporphyrin systems.[11] For all compounds, the lowest IP corresponds to $^2A_{2u}$ ionized states.

Figure 2 depicts the singly occupied a_{2u} orbital of (the ground states of) ZnTDBPP$^{+\bullet}$ and ZnTDNO$_2$PP$^{+\bullet}$, these molecules being chosen as representative of all molecules studied. It is clear that the bromine and the nitro groups carry significant amplitudes of the a_{2u} orbital. Figure 3 presents the gross atomic spin populations for the ground states of all the metallotetraarylporphyrin cation radicals studied. The porphyrin−aryl orbital interaction is especially intense for ZnTDNO$_2$PP$^{+\bullet}$, presumably as a result of the short distance (2.60 Å, Figure 3) between the *meso* carbon and the nearest nitro oxygen as well as the highly electron-rich nature of nitro oxygens. Thus, each nitro oxygen closest to a *meso* carbon carries a rather high unpaired spin population (0.0216). This also explains the unusually low first IP of ZnTDNO$_2$PP as well as the relatively high stability of its $^2A_{2u}$ ionized state relative to the $^2A_{1u}$ state. The bromine and chlorine atoms in ZnTDBPP$^{+\bullet}$ and ZnTDCPP$^{+\bullet}$ also carry significant spin populations of 0.015 and 0.005, respectively, the larger population on the bromine clearly reflecting its larger atomic size. Each CF$_3$ group in ZnTDCF$_3$PP$^{+\bullet}$ carries a spin population of only about 0.003, reflecting the poor ability of CF$_3$ groups to mesomerically stabilize a cation radical. In other words, the eight *ortho* substituents in the ground $^2A_{2u}$ states of the cation radicals, ZnTDCF$_3$PP$^{+\bullet}$, ZnTDCPP$^{+\bullet}$, ZnTDBPP$^{+\bullet}$, and ZnTDNO$_2$PP$^{+\bullet}$, carry 1, 4, 9, and 17% of the total electron spin in the respective molecules.

For most of the compounds, the IP corresponding to the $^2A_{1u}$ ionized states are only a couple of tenths of an eV higher than the lowest IP. As pointed out above, the only exception is ZnTDNO$_2$PP for which the $^2A_{2u}$ ionized state is considerably more stable than the $^2A_{1u}$ state. Thus, the question arises as to why the porphyrin−aryl interaction of the type shown in Figure 2 does not significantly stabilize the $^2A_{2u}$ state relative to the $^2A_{1u}$ state for ZnTDCPP$^{+\bullet}$ and ZnTDBPP$^{+\bullet}$. An examination of the open-shell orbital in the $^2A_{1u}$ state for ZnTDCPP$^{+\bullet}$ and ZnTDBPP$^{+\bullet}$ (Figure 4) provides some insights. Figure 4 shows

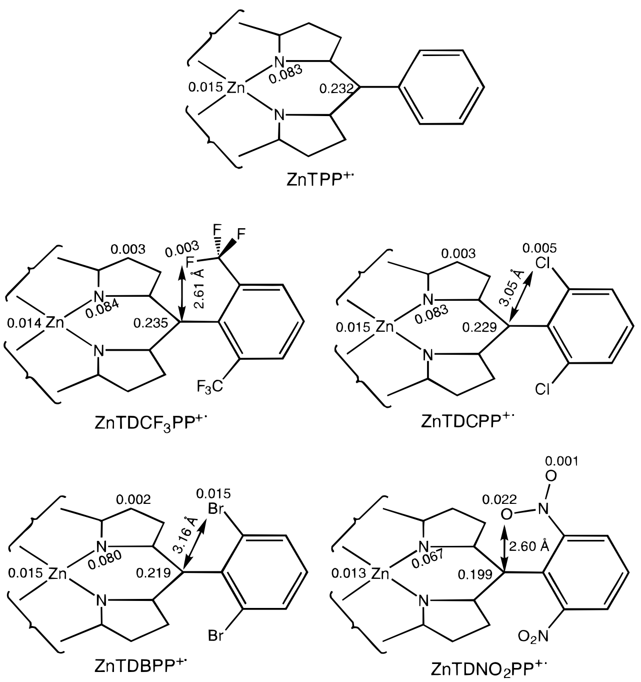

Figure 3. Unpaired electron spin populations in the ground states of zinc porphyrin cation radicals.

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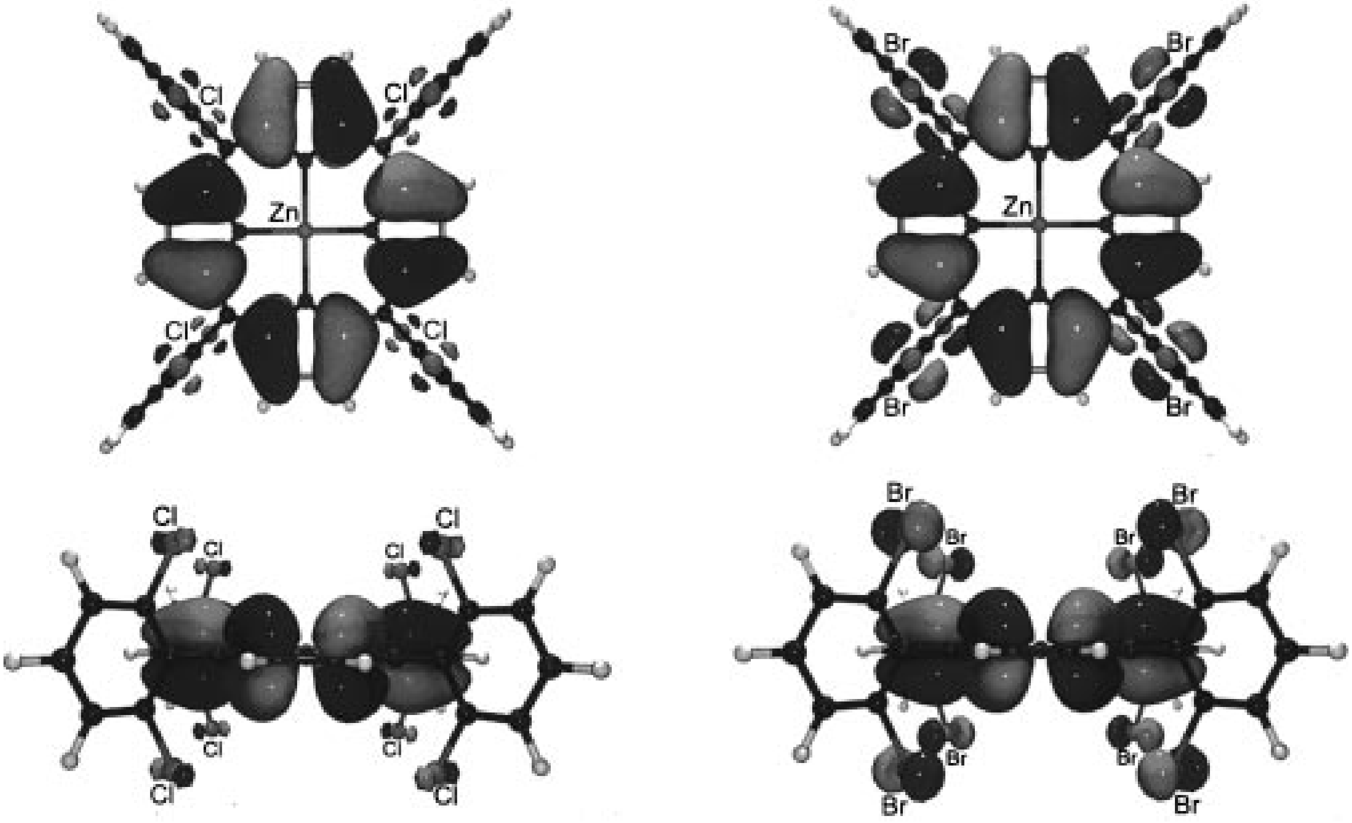

Figure 4. The singly occupied a_{1u} orbital of the $^2A_{1u}$ states of ZnTDCPP$^{+\bullet}$ (left) and ZnTDBPP$^{+\bullet}$ (right).

that these a_{1u} orbitals, too, feature porphyrin−aryl interaction. The lateral extent of the lone pairs of the chlorine and bromine atoms in these molecules is sufficient to permit an overlap with the porphyrin's a_{1u} orbital, which has the correct symmetry for such overlap. In contrast, since an oxygen atom is significantly smaller than Cl or Br, a similar a_{1u}−aryl orbital interaction is insignificant for the ZnTDNO$_2$PP system and therefore not shown in Figure 4.

In summary, we have shown the existence of, visualized, and characterized direct porphyrin−aryl orbital overlap interactions in some common *meso*-tetraarylporphyrins with *ortho* substituents. This represents a hitherto unsuspected "mechanism" by which peripheral substituents exert their electronic effects on the porphyrin macrocycle. These interactions have a significant effect on the relative energies of the $^2A_{2u}$ and $^2A_{1u}$ cation radical states and on the unpaired spin density distributions. In particular, the orbital overlaps described here may play a critical role in the functioning of porphyrin-based molecular electronic devices of the types mentioned in the Introduction.

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