Electronic Structures of Halogenated Porphyrins: Spectroscopic Properties of ZnTFPPX8 (TFPPX8 = Octa-.beta.-halotetrakis(pentafluorophenyl)porphyrin; X = Cl, Br)

ARTICLE *in* JOURNAL OF THE AMERICAN CHEMICAL SOCIETY · OCTOBER 1994

Impact Factor: 12.11 · DOI: 10.1021/ja00100a043

William A. Goddard

California Institute of Technology

J. Am. Chem. Soc. 1994, 116, 9730–9732

Electronic Structures of Halogenated Porphyrins: Spectroscopic Properties of $ZnTFPPX_8$ ($TFPPX_8$ = Octa-β-halotetrakis(pentafluorophenyl)porphyrin; X = Cl, Br)

Toshihiko Takeuchi, Harry B. Gray, and William A. Goddard III*

Contribution from the Materials and Molecular Simulations Center, Beckman Institute (139-74), Division of Chemistry and Chemical Engineering (Contribution No. 8767), California Institute of Technology, Pasadena, California 91125

Received May 12, 1993. Revised Manuscript Received April 4, 1994®

Abstract: We report here spectroscopic and theoretical (AM1) studies on zinc(II) octa-β-halotetrakis(pentafluorophenyl)-porphyrins ($ZnTFPPX_8$; X = Cl, Br) that show a red shift in the Soret and Q absorption bands attributable to substituent-induced saddling of the macrocycle. The electronic effect of the halogens is to reduce the energies of both the HOMOs and LUMOs; however, this stabilization of orbital energies is counteracted by the distortion of the macrocycle, which results in a large destabilization of the porphyrin HOMOs and a smaller destabilization of the LUMOs. The net result is a slight increase in stability of the HOMOs and a greater stabilization of the LUMOs. Lowering the energies of the porphyrin HOMOs is an important factor to consider in the development of robust porphyrin catalysts.

It is well-established that halogenation leads to dramatic changes in the spectroscopic properties of porphyrins.[1–4] Both the Soret and Q bands in the absorption spectrum of octa-β-bromotetrakis(pentafluorophenyl)porphyrin ($TFPPBr_8$) are strongly red-shifted relative to the corresponding bands in tetraphenylporphyrin (TPP). In our efforts to understand these and other unusual electronic structural features, we have done theoretical and experimental work on a $ZnTFPPX_8$ (X = H, Cl, Br) model system. Since the geometries of $ZnTFPPX_8$ molecules are very similar to those of β-alkyltetraphenylporphyrins,[5–10] we have attempted to determine the specific influence that the highly distorted porphyrin framework has on the electronic structures of these systems. Our findings have suggested possible reasons for the high activities and oxidative stabilities of the halogenated iron–porphyrin catalysts employed by Lyons and Ellis in the oxygenation of alkanes.[11]

The standard model for the interpretation of porphyrin spectra is due to Gouterman (the Four Orbital Model, or FOM).[12] Figure 1 shows the Gouterman orbitals for $ZnTFPPBr_8$; there are two nearly degenerate HOMOs (b1 and b2 with a_{2u} and a_{1u} symmetries in D_{4h}) and two nearly degenerate LUMOs (c1 and c2 with e_g symmetry in D_{4h}). The ground-state configuration is $(b1)^2(b2)^2$ and the excited states are given by eqs 1 and 2:

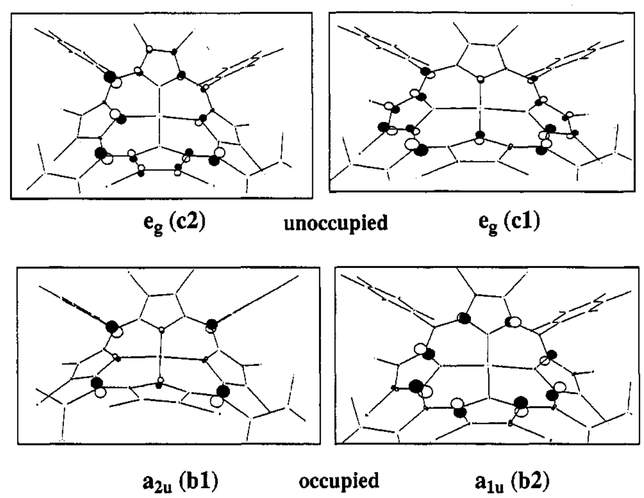

Figure 1. The Gouterman orbitals for $ZnTFPPBr_8$ from AM1 calculations.

$$\left.\begin{matrix} B_x \\ Q_x \end{matrix}\right\} = [(b1c2) \mp (b2c1)]/(2)^{1/2} \quad (1)$$

$$\left.\begin{matrix} B_y \\ Q_y \end{matrix}\right\} = [(b1c1) \pm (b2c2)]/(2)^{1/2} \quad (2)$$

where Q_x, Q_y are the states associated with the visible bands, and B_x, B_y correspond to the Soret bands. Elsewhere[13] we will report extensive *ab initio* HF, GVB-MCSCF, and configuration-interaction calculations that confirm the principal aspects of the FOM. Here we use this model with semiempirical AM1[14] calculations using MOPAC.[15] These calculations include full configuration interaction (CI) within the orbitals of the FOM.

* Author to whom correspondence should be addressed.

® Abstract published in *Advance ACS Abstracts*, October 15, 1994.

(1) Callot, H. J. *Bull. Soc. Chim. Fr.* **1974**, *8*, 1492. Corrections to the structures have been reported: Crossley, M. J.; Burn, P. L.; Chew, S. S.; Cuttance, F. B.; Newsom, I. A. *J. Chem. Soc., Chem. Commun.* **1991**, 1564.
(2) D'Souza, F.; Villard, A.; Caemelbecke, E. V.; Franzen, M.; Boschi, T.; Tagliatesta, P.; Kadish, K. M. *Inorg. Chem.* **1993**, *32*, 4042.
(3) Bhyrappa, P.; Krishnan, V. *Inorg. Chem.* **1991**, *30*, 239.
(4) Lyons, J. E.; Ellis, P. E.; Wagner, R. W.; Thompson, R. E.; Hughes, M. E.; Hodge, J. A.; Gray, H. B. *Am. Chem. Soc. Div. Petroleum Chem. Symp.* **1992**, April.
(5) Barkigia, K. M.; Chantranupong, L.; Smith, K. M.; Fajer, J. *J. Am. Chem. Soc.* **1988**, *110*, 7566.
(6) Barkigia, K. M.; Berber, M. D.; Fajer, J.; Medforth, C. J.; Renner, M. W.; Smith, K. M. *J. Am. Chem. Soc.* **1990**, *112*, 8851.
(7) Shelnutt, J. A.; Medforth, C. J.; Berber, B. D.; Barkigia, K. M.; Smith, K. M. *J. Am. Chem. Soc.* **1991**, *113*, 4077.
(8) Sparks, L. D.; Medforth, C. J.; Park, M. S.; Chamberlain, J. R.; Ondrias, M. R.; Senge, M. O.; Smith, K. M.; Shelnutt, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 581.
(9) Barkigia, K. M.; Renner, M. W.; Furenlid, L. R.; Medforth, C. J.; Smith, K. M.; Fajer, J. *J. Am. Chem. Soc.* **1993**, *115*, 3627.
(10) Senge, M. O. *J. Photochem. Photobiol. B: Biol.* **1992**, *16*, 3.
(11) Octa-β-bromo[tetrakis(pentafluorophenyl)porphyrinato]iron(III) chloride catalyzes the room-temperature conversion of isobutane to *tert*-butyl alcohol in the presence of oxygen at a rate of 190 mol of product per mol of catalyst per h with over 90% selectivity to the alcohol. Remarkably, this activity is unchanged after 74 h: Lyons, J. E.; Ellis, P. E. *Catal. Lett.* **1991**, *8*, 45.
(12) Gouterman, M. *J. Mol. Spectrosc.* **1961**, *6*, 138.
(13) Muller, R. P.; Takeuchi, T.; Ringnalda, M. N.; Goddard, W. A. *Ab Initio* GVB-MCSCF, and π-space Configuration Interaction Calculations of Porphyrins and Reduced Porphyrins: Quantitative Confirmation of the Gouterman Four Orbital Model, in preparation.
(14) Dewar, M. J. S.; Healy, E. F.; Stewart, J. J. P.; Zoebisch, E. G. *J. Am. Chem. Soc.* **1985**, *107*, 3902.
(15) Stewart, J. J. P. Program No. 581 (MOPAC) from the Quantum Chemistry Program Exchange (QCPE), Indiana University, Bloomington, IN.

0002-7863/94/1516-9730$04.50/0

Table 1. Excitation Energies for $ZnTFPPX_8$ from Theory (AM1) and Experiment

	λ (nm)		
	ZnTFPP	$ZnTFPPCl_8$	$ZnTFPPBr_8$
Q (visible)			
exper	544	575	596
theory (Q_x)	517	535	553
(Q_y)	516	533	548
B (Soret)			
exper	412	442	464
theory (B_x)	317	329	345
(B_y)	317	328	344

Table 2. Energies (eV) from AM1 Calculations

	ZnTFPP	$ZnTFPPCl_8$	$ZnTFPPBr_8$
	Orbital Energies, ϵ_i		
b2	−8.40	−8.87	−8.77
b1	−8.05	−8.67	−8.64
c1	−2.71	−3.34	−3.36
c2	−2.66	−3.30	−3.34
	Excitation Energies, E_{ij}		
b1 → c1	5.35	5.33	5.28
b1 → c2	5.39	5.37	5.30
b2 → c1	5.69	5.53	5.42
b2 → c2	5.74	5.57	5.44

The calculations were performed on a series of halogenated porphyrins: ZnTFPP, $ZnTFPPCl_8$, and $ZnTFPPBr_8$.[16–21] Examination of Table 1 shows that the calculations reproduce the experimental trends.[22] The absorption spectrum shifts to the red as the size of the Cβ substituents increases (H to Cl to Br). Thus, porphyrins with hydrogen at the β-pyrrolic positions exhibit the highest-energy transitions, whereas those compounds with bromine in the pyrrolic positions have the lowest-energy transitions.

In order to ascertain the electronic perturbations associated with this size-induced red-shifting, the FOM-MO transition energies were examined (Table 2). Note that these are simple MO excitation energies, whereas the theoretical values in Table 1 include CI. The results set out in Table 2 suggest that the red shifts in the absorption spectra are attributable to a decrease in the one-electron excitation energies. However, it is not clear from these data how the electronic and steric properties of the β-pyrrole substituents individually affect the orbital energies.

In order to estimate the component of the red-shifting that is sterically induced, the X atoms of $ZnTFPPX_8$ molecules were removed and replaced with X′ = Cl, Br, F, or CH_3, while retaining

(16) The $ZnTFPPX_8$ structures were assumed to be the same as those of the corresponding Cu compounds, where data for X = H, Cl, and Br are available.[17,18,20] For X = H and Br, the structures of the Cu and Zn derivatives are closely similar.[18–20]

(17) Schaefer, W. P.; Hodge, J. A.; Hughes, M. E.; Gray, H. B.; Lyons, J. E.; Ellis, P. E.; Wagner, R. W. *Acta Crystallogr., Sect. C* **1993**, *49*, 1342.

(18) Henling, L. M.; Schaefer, W. P.; Hodge, J. A.; Hughes, M. E.; Gray, H. B. *Acta Crystallogr., Sect. C* **1993**, *49*, 1743.

(19) Marsh, R. E.; Schaefer, W. P.; Hodge, J. A.; Hughes, M. E.; Gray, H. B. *Acta Crystallogr., Sect. C* **1993**, *49*, 1339.

(20) Schaefer, W. P.; Henling, L. M.; Hodge, J. A.; Grinstaff, M. W., in preparation.

(21) The structure of $NiTFPPBr_8$, which shows similar saddle distortions, has been reported: Mandon, D.; Ochesbein, P.; Fischer, J.; Weiss, R.; Jayaraj, K.; Austin, R. N.; Gold, A.; White, P. S.; Brigaud, O.; Battioni, P.; Mansuy, D. *Inorg. Chem.* **1992**, *31*, 2044. Also, see ref 18.

(22) H_2TFPP obtained from Aldrich was purified using techniques described earlier. (Kaizu, Y.; Misu, N.; Tsuji, K.; Kaneko, Y.; Kobayashi, H. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 103). $H_2TFPPCl_8$ (Wijesekera, T.; Matsumoto, A.; Dolphin, D.; Lexa, D. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1028) and $H_2TFPPBr_8$ (Ellis, P. E.; Lyons, J. E. *Coord. Chem. Rev.* **1990**, *105*, 181) were prepared according to literature procedures. All porphyrins were purified on a silica gel column (150 Å pore size and 75–150 μm particle size). ZnTFPP was eluted using dichloromethane/hexane (1/1 v/v), while $ZnTFPPCl_8$ and $ZnTFPPBr_8$ were eluted with dichloromethane/hexane (2/1 v/v). Absorption spectra were measured using a Cary 14 spectrophotometer. The porphyrin solutions were prepared by dissolving approximately 1.25 mg of porphyrin in 50 mL of methylcyclohexane followed by 20:1 solvent–solution dilution. Spectra were obtained at 25 °C.

Table 3. Evaluation of Energies (eV) for Various Cβ Substituents at Different Degrees of Distortion

Cβ substituent	orbital E (eV)	ZnTFPP structure	$ZnTFPPCl_8$ structure	$ZnTFPPBr_8$ structure
Cl	b2	−8.88	−8.87	−8.69
	b1	−8.72	−8.67	−8.52
	c1	−3.36	−3.34	−3.24
	c2	−3.32	−3.30	−3.21
	HOMO-LUMO gap (eV)[a]	2.45	2.33	2.24
Br	b2	−8.95	−8.93	−8.77
	b1	−8.80	−8.75	−8.64
	c1	−3.44	−3.41	−3.36
	c2	−3.40	−3.37	−3.34
	HOMO-LUMO gap (eV)[a]	2.37	2.32	2.24
CH3	b2	−8.28	−8.25	−8.13
	b1	−7.84	−7.77	−7.75
	c1	−2.60	−2.56	−2.55
	c2	−2.57	−2.51	−2.52
	HOMO-LUMO gap (eV)[a]	2.36	2.32	2.26
F	b2	−9.05	−8.88	−8.80
	b1	−8.96	−8.72	−8.69
	c1	−3.55	−3.36	−3.35
	c2	−3.50	−3.32	−3.32
	HOMO-LUMO gap (eV)[a]	2.68	2.40	2.19

[a] The HOMO-LUMO gap reported is the energy of the Q band transition from AM1 CI calculations.

the geometries of the respective compounds (and using the correct C–X′ bond distances). The effects of these replacements on MO excitation energies are given in Table 3. In each case, there are decreases in the transition energies as the porphyrin distorts. Since the nature of the substituent varies from an electron-donating CH_3 to a highly-electron-withdrawing F (while a net decrease in the HOMO-LUMO gap is evident for each substituent), we can conclude that distortion clearly induces red-shifting in porphyrin absorptions. Further examination of Table 3 shows that, as the porphyrin saddles, both the HOMO and LUMO energies increase. However, the HOMOs are destabilized more than the LUMOs, leading to red-shifts in the absorption spectra. These findings are consistent with earlier work done on β-alkylporphyrins.[5–9]

A good test of the electronic effect of the substituents can be obtained by maintaining a constant geometry while varying the substituents on the porphyrin skeleton. Calculation of transition energies upon constraint of the macrocycle to the planar ZnTFPP geometry (Table 3) yields HOMO-LUMO[23] gaps of −2.40 (ZnTFPP), −2.45 ($ZnTFPPCl_8$), −2.37 ($ZnTFPPBr_8$), and −2.36 eV ($ZnTFPPMe_8$), which are nearly the same for all of the β substituents. This suggests that a change in electronegativity at the Cβ positions equally stabilizes both the HOMOs and LUMOs, with a correspondingly small effect on the excitation energies. Furthermore, the HOMO-LUMO gaps of $ZnTFPPCl_8$, $ZnTFPPBr_8$, and $ZnTFPPMe_8$ similarly drop with increasing distortion from the planar structure. It also should be noted that although substituent electronic properties have little effect on the transition energies for substitution with X′ = H, Cl, Br, and Me, F is an exception; probably because of its powerful electron-withdrawing properties, it significantly perturbs the HOMO-LUMO gap.

The electronic effect of each halogen is to lower the energies of both the HOMOs and LUMOs of $ZnTFPPX_8$. However, the distortion of the porphyrin predominantly raises the energies of the HOMOs, so the net result is a large drop in the LUMO energies and a smaller drop in the HOMO energies upon halogenation of the porphyrin macrocycle. Furthermore, the HOMOs of $ZnTFPPBr_8$ should be destabilized with respect to $ZnTFPPCl_8$ since bromines are slightly less electronegative and add steric bulk to the ring, further distorting the porphyrin

(23) The lower Q band energy is a good estimate of the HOMO-LUMO gap.[6,9]

structure. Indeed, these predictions (Table 2) closely match the trends found in electrochemical experiments.[24]

Our model of steric and electronic effects should guide the design of novel porphyrins with specific properties. For example, since the spectral red-shift is highly sensitive to distortion of the porphyrin ring, porphyrin geometry can be qualitatively probed by absorption spectroscopy. The greater the red-shifting in the spectra, the greater the distortion of the porphyrin ring. Furthermore, decoupling of the electronic effects of the substituent from the distortion predicts that a planar porphyrin with electron-withdrawing substituents in β positions would show extremely high oxidation potentials, since the HOMOs are *not* destabilized due to distortion of the ring.[25] The stability with respect to oxidation is an important factor to consider in the design of porphyrin catalysts: lowering the energy of the porphyrin HOMOs should enhance catalyst lifetimes, because this type of electronic stabilization strongly disfavors oxidative destruction of the macrocycle.

Acknowledgment. We thank Eva Birnbaum, Paul Ellis, Mark Grinstaff, Mike Hill, Julia Hodge, and Jim Lyons for helpful comments. T.T. acknowledges a graduate fellowship from the Department of Defense. This work was supported by the Department of Energy, Morgantown Energy Technology Center, the Gas Research Institute, the Sun Company, Inc., and DOE-AICD. The facilities of the MSC are also supported by grants from NSF-CHE, NSF-DMR-MRG, NSF-ACR, Allied-Signal Corp., Asahi Chemical, Asahi Glass, BP America, Chevron, BF Goodrich, Xerox, and the Arnold and Mabel Beckman Foundation.

(24) The finding that the porphyrin LUMO is stabilized more than the HOMO is supported by electrochemical data (the oxidation and reduction potentials using cyclic voltammetry for ZnTFPP are 1.36 and –0.96, the potentials for $ZnTFPPCl_8$ are 1.62 and –0.47, while the potentials for $ZnTFPPBr_8$ are 1.58 and –0.49 V vs SCE): Hodge, J. A.; Hill, M. G.; Gray, H. B., in preparation.

(25) Saddle-shaped octa-β-halotetrakis(mesityl)porphyrin derivatives are easier to oxidize than the corresponding tetra-β-halogenated derivatives that are not saddle-shaped: Ochsenbein, P.; Ayougou, K.; Mandon, D.; Fischer, J.; Weiss, R.; Austin, R. N.; Jayaraj, K.; Gold, A.; Terner, J.; Fajer, J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 348.