

## X-ray Photoelectron Spectral Characterization of the Extremely Electron-Deficient Nature of $\beta$ -Octakis(*N,N*-diethylcarboxamido)porphyrin

Abhik Ghosh

Department of Chemistry, University of Minnesota,  
Minneapolis, Minnesota 55455

Received July 12, 1993

In the course of biomimetic studies on cytochrome P450 and related enzymes, synthetic metalloporphyrins have been studied as catalysts of various oxygenation reactions of organic compounds.<sup>1</sup> Metalloporphyrin catalysts, bearing multiple electronegative peripheral substituents, appear to be especially attractive, since they exhibit enhanced reactivity in hydrocarbon functionalization reactions and superb ruggedness in highly oxidized media, compared to catalysts based on common electron-rich porphyrins such as tetraphenylporphyrin and octaethylporphyrin.<sup>2</sup> However, the electronic nature of the modulation of metal-centered reactions of metalloporphyrins by electronegative peripheral substituents remains poorly understood. As a first step in this line of research, we have attempted to measure the extent of modulation of the electronic character of the central region of the porphyrin macrocycle by electron-withdrawing peripheral substituents. In this work, we have examined the influence of eight electron-withdrawing *N,N*-diethylcarboxamido substituents.

Most electron-deficient porphyrins are dodecasubstituted, with macrocycle buckling resulting from steric interactions between  $\beta$  and *meso* substituents.<sup>3</sup> Understanding the effect of electron-withdrawing substituents in such porphyrins is complicated by the fact that the buckling itself shifts the orbital energies of the porphyrin.<sup>4</sup> 2,3,7,8,12,13,17,18-Octakis(*N,N*-diethylcarboxamido)porphyrin<sup>5</sup> (ODCAPH<sub>2</sub>) is of interest, therefore, as one of the few *meso*-unsubstituted porphyrins bearing eight strongly electron-withdrawing  $\beta$ -substituents. Another valuable property of ODCAPH<sub>2</sub> is its solubility in water. Herein we demonstrate another interesting property of ODCAPH<sub>2</sub>, viz. its extremely electron-deficient nature.

We have demonstrated that the 1s ionization potentials (IPs) of the central nitrogens of the porphyrin ring are sensitive probes of the electronic influence of peripheral substituents.<sup>6</sup> Nitrogen 1s X-ray photoelectron spectra (XPS)<sup>7</sup> were acquired for ODCAPH<sub>2</sub> to determine the effect of the eight amido substituents. Figure 1 shows the N 1s XPS of ODCAPH<sub>2</sub>. The N 1s XPS of ODCAPH<sub>2</sub> is complicated by the presence of eight amide nitrogens in addition to the central nitrogens. Only one N 1s peak at

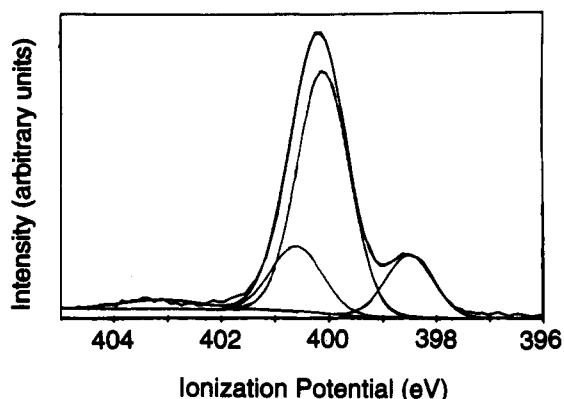


Figure 1. The N 1s XPS of 2,3,7,8,12,13,17,18-Octakis(*N,N*-diethylcarboxamido)porphyrin.

398.6 eV is resolved at the low-IP end of the spectrum, and the area of this peak is approximately 20% of that of the other more intense unresolved peak at higher IP. The resolved peak must therefore be due to one of the two types of central nitrogens. On the basis of all-electron *ab initio* calculations<sup>6</sup> and extensive XPS studies<sup>6</sup> on other porphyrins, we can confidently assign the peak at 398.6 eV to the central unprotonated nitrogens. Previous studies have shown that the 1s energy splitting between the two types of central nitrogens in a free-base porphyrin is remarkably constant at approximately 2.1 eV for any peripheral substitution pattern.<sup>6</sup> Therefore, another peak of the same size and shape as the resolved peak, but due to the protonated central nitrogens, was assumed to exist at 400.7 eV, i.e. at an IP of 2.1 eV higher than the resolved peak. The remainder of the composite N 1s signal was filled by a single peak due to the eight amide nitrogens, resulting in an excellent curve-fit. Curve-fitting resulted in an IP of 400.3 eV for the peak due to the eight amide groups.

The 1s IPs of the central nitrogens of ODCAPH<sub>2</sub> are the highest that have been recorded so far for any free-base porphyrin. Thus, they exceed corresponding IPs of tetraphenylporphyrin by 1.2 eV, those of tetrakis(2,6-dichlorophenyl)porphyrin by 0.8 eV, and those of tetrakis(pentafluorophenyl)porphyrin by 0.3 eV.<sup>6</sup> Among porphyrins whose central nitrogens may have even higher 1s IPs than ODCAPH<sub>2</sub> are octacarbethoxyporphyrin<sup>8</sup> and perfluorinated tetraphenylporphyrin.<sup>9</sup> In summary, ODCAPH<sub>2</sub> is a unique porphyrin ligand that is water soluble, *meso*-unsubstituted and therefore presumably possessing a planar equilibrium geometry, and also extremely electron deficient.

**Acknowledgment.** The author is grateful to Professor Eugene LeGoff of Michigan State University for the generous gift of samples of ODCAPH<sub>2</sub>, to Peter Sobol of Perkin-Elmer Corp. for XPS facilities, and to Prof. Jan Almlöf of the University of Minnesota for discussions.

- (1) Meunier, B. *Chem. Rev.* 1992, 92, 1411.  
 (2) (a) Traylor, T. G.; Tsuchiya, S. *Inorg. Chem.* 1987, 26, 1338. (b) Wijesekera, T.; Matsumoto, A.; Dolphin, D.; Lexa, D. *Angew. Chem. Int. Ed. Engl.* 1990, 29, 1028.  
 (3) Examples of nonplanar porphyrins: (a) Sparks, L. D.; Medforth, C. J.; Park, M.-S.; Chamberlain, J. R.; Ondrias, M. R.; Senge, M. O.; Smith, K. M.; Shelnut, J. A. *J. Am. Chem. Soc.* 1993, 115, 581. (b) Zhu, N.-J.; Li, Y.; Wu, G.-Z.; Liang, X.-G. *Acta Chim. Sin.* 1992, 50, 249. For a planar dodecasubstituted porphyrin, see: (c) Senge, M. O.; Medforth, C. J.; Sparks, L. D.; Shelnut, J. A.; Smith, K. M. *Inorg. Chem.* 1993, 32, 1716.  
 (4) (a) Barkigia, K. M.; Chantranupong, L.; Smith, K. M.; Fajer, J. *J. Am. Chem. Soc.* 1988, 110, 7599. (b) Gudowska-Nowak, E.; Newton, M. D.; Fajer, J. *J. Phys. Chem.* 1990, 94, 5795.  
 (5) Kaesler, R. W.; LeGoff, E. *J. Org. Chem.* 1983, 48, 4399.  
 (6) (a) Gassman, P. G.; Ghosh, A.; Almlöf, J. *J. Am. Chem. Soc.* 1992, 114, 9990. (b) Ghosh, A.; Gassman, P. G.; Almlöf, J. *Chem. Phys. Lett.* 1991, 186, 113.  
 (7) A Perkin-Elmer Physical Electronics 5600 XPS spectrometer was used for the XPS measurements. The XPS sample consisted of approximately 10  $\mu$ g of the porphyrin rubbed into an extremely thin, effectively conducting film on gold foil, the Au 4f<sub>7/2</sub> peak at 84.0 eV being used as a convenient external reference. Monochromatized Al K $\alpha$  X-rays, of power 600 W, were used. Flooding the sample with low-energy electrons from a neutralizer did not change the position or shape of the XPS peaks, eliminating the need for any correction due to sample charging.  
 (8) Müller, F.; Karwe, A. *Mattay, J. J. Org. Chem.* 1992, 57, 6080.  
 (9) Tsuchiya, S.; Seno, M. *Chem. Lett.* 1989, 263.