

Abstract No. bark34

### Structure of a Novel Tetracationic Porphyrin

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Beamline(s): X7B

**Introduction:** Exhaustive electro-oxidation of Zn-octaethylporphyrin (ZnOEP) in the presence of pyridine and  $\text{PF}_6^-$  affords in high yield the new tetracationic porphyrin **1**, in which the four meso protons of ZnOEP are replaced by four pyridinium groups linked by their nitrogens. The compound has been characterized by elemental analysis, NMR, and crystallography [1]. The latter confirms the preparative electrochemical methodology and molecular structure and shows the porphyrin skeleton adopts a severely nonplanar saddle conformation which minimizes steric crowding between the twelve peripheral substituents.

**Methods and Materials:** Crystals of **1** were grown from mixtures of acetonitrile, pyridine and ethanol. Over two hemispheres of data were collected at 100K by the rotation method using a MAR345 image plate detector. The data were processed and merged with Denzo/Scalepack [2]. The structure was solved by direct methods [3] and refined with the SHELXTL package [4].

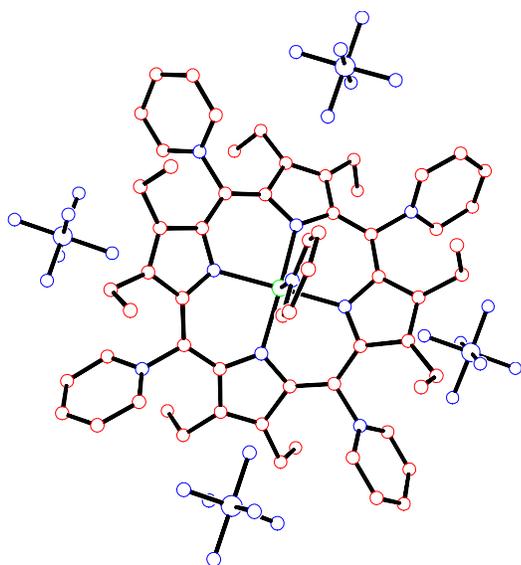
**Results:** The molecular structure of **1** is shown in Figure 1 and its severely saddled conformation is shown in Figure 2.

**Conclusions:** This determination provides an unambiguous identification of **1** and its extremely distorted conformation. Similar skeletal deformations are known to affect the photophysical and chemical properties of nonplanar porphyrins.

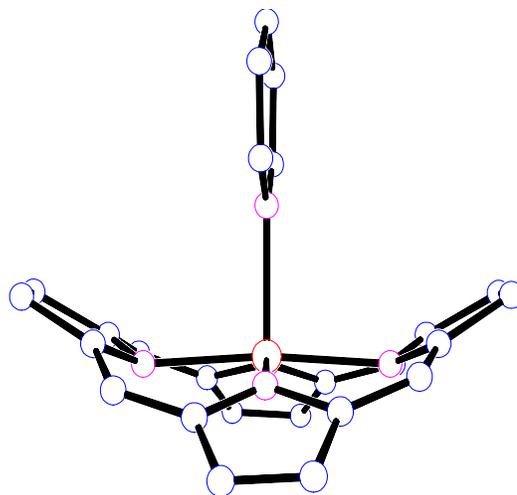
**Acknowledgments:** We thank Dr. Jonathan C. Hanson for assistance with the crystallographic data collection. The work at Brookhaven was supported by the Division of Chemical Sciences, Geosciences and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract DE-AC02-98CH10886.

#### References:

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**Figure 1.** Molecular structure of **1**, with its four  $\text{PF}_6^-$  counterions. The axial ligand is pyridine. Hydrogens have been removed for clarity.



**Figure 2.** Edge-on view of **1**, which illustrates the saddle conformation of the porphyrin skeleton and the orientation of the axial pyridine. The peripheral substituents, counterions and hydrogens have been removed for clarity.