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π-Extension in Expanded Porphyrins: Cyclo[4]naphthobipyrrole

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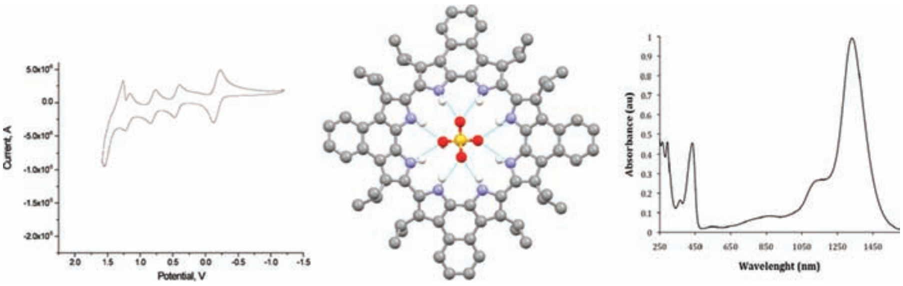
ABSTRACT



The π-extended cyclo[4]naphthobipyrrole 1a has been prepared *via* an Fe(III)-mediated oxidative cyclization of an alkyl-substituted naphthobipyrrole. The structure of this new expanded porphyrin, isolated as the deprotonated sulfate salt, was characterized by spectroscopic means, as well through a single crystal X-ray diffraction analysis. Salt 1a displays a total of four well-resolved redox waves as determined by cyclic voltammetry. It also displays bathochromically shifted near-IR absorption maxima compared to the diprotonated forms of nonannulated cyclo[8]pyrroles.

Over the past decade considerable effort has been devoted to the preparation of so-called π-extended porphyrins.[1] These annulated systems are generally characterized by optical absorption maxima that are bathochromically shifted relative to unfunctionalized porphyrins. This has made π-extended porphyrins of interest in a variety of application areas, including energy conversion[2] and oxygen sensing.[3] In parallel with this effort, considerable synthetic work has been focused on creating expanded porphyrins, oligopyrrolic macrocycles possessing a larger central core than found in porphyrins. Typically, this has been done by increasing the number of pyrrolic (or other heterocyclic) subunits within the macrocyclic ring and varying the relative connectivity between the pyrrolic constituents or by adjusting the number of bridging *meso* carbon atoms. Depending on the specific system in question, unusual metal coordination chemistry, anion binding features, redox behavior,

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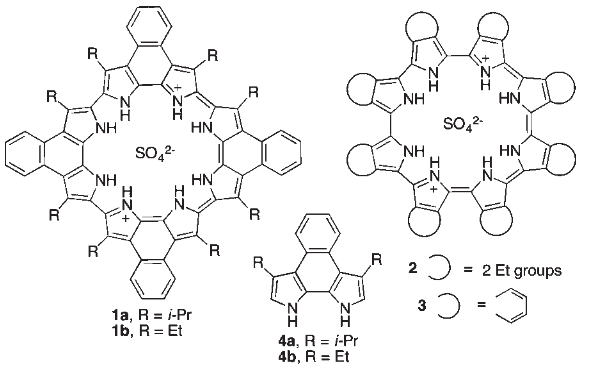

Figure 1. Structure of dialkylnaphthobipyrroles **4** and π-extended cyclo[4]naphthobipyrrole **1** and cyclo[8]isoindole **3**.

nonlinear optical properties, and electronic structure effects (e.g., Hückel vs Möbius aromaticity) have been noted.[4,5]

The attractive features of π-extended porphyrins and expanded porphyrins have provided an incentive to create new porphyrin analogues that combine key attributes from both approaches within a single chemical entity. This convergence has led recently to the synthesis of new chromophores that are both expanded and π-extended relative to normal porphyrins. Among the systems reported to date are benzosapphyrin,[6] benzoporphycenes,[7] tetrabenzocorrole,[8] and cyclo[8]isoindole.[9] Also known are naphthosapphyrin and naphthorubirin.[10] These latter systems, prepared in conjunction with the Lee and Panda groups, were made synthetically accessible by the availability of dinaphthobipyrroles.[11]

We have now found that this same precursor may be used to prepare cyclo[4]naphthobipyrroles, such as **1** (Figure 1).[12] This provides an entry into π-extended analogues of cyclo[8]pyrrole **2**, a system first reported by our group in 2002.[13] The present strategy relies on the oxidative coupling of bipyrrolic fragments in general accord with our original report. It thus provides a complement to the very recent efforts by Kobayashi, Okujima and co-workers involving the synthesis of cyclo[8]isoindole **3** (Figure 1). System **3**, the first π-extended cyclo[*n*]pyrrole to be reported in the literature,[9] displayed features expected for a π-extended cyclo[8]pyrrole, including a significant red shift in the optical absorption maxima (to ca. 1100 nm). Unfortunately, cyclo[8]isoindole **3** in its structurally characterized diprotonated form was found to deviate substantially from planarity. Presumably, this is the result of steric effects involving the adjacent fused benzene subunits on the isoindole units present in **3**. System **1** was expected to be relatively free from the latter distortions and thus be more planar. Nevertheless, it was expected to retain the unusual optical features noted in the case of **3** and in our original cyclo[8]pyrrole **2**. As detailed below, this proved to be the case.

Naphthobipyrroles of general structure **4**[11] are the product of a three-step scalable procedure. This accessibility led us to explore its behavior when subject to the oxidative cyclization conditions used to prepare **2**. In analogy to what proved true for diethylbipyrrole (and other dialkylpyrroles), treatment of **4a** with ferric chloride in 1 M sulfuric acid solution was found to give the desired cyclo[4]naphthobipyrrole in the form of its deprotonated sulfate salt (**1a**) as shown in Figure 1. However, important differences were noted. For instance, in contrast to what proved true in the case of diethylbipyrrole, which gave cyclo[8]pyrrole **2** in greater than 70% yield,[13] we were unable to optimize the yield of **1a** above 30%. On the other hand, whereas **2** was the exclusive product when diethylbipyrrole was subject to Fe(III)-mediated oxidation in the presence of sulfuric acid, peaks ascribable to a wide range of other products are seen in the mass spectrum after **4a** is subject to Fe(III)-mediated oxidation in the presence of sulfuric acid (Figures S4–S6). Unfortunately, efforts to isolate and characterize these byproducts, presumed to be cyclic and acyclic oligomers, have so far proved unsuccessful. The problems of separation were exacerbated in the case of **4b**; although evidence of cyclic products was seen by mass spectral analysis, product **1b** could not be isolated cleanly (Figure S7).

Macrocycle **1a** was characterized by standard spectroscopic and analytical means (cf. Supporting Information). The ^{1}H NMR spectrum ($CDCl_3$) was consistent with the presence of a diatropic current and thus provides support for the overall aromatic nature of cyclo[4]naphthobipyrrole. For instance, signals ascribable to the aromatic protons are seen at $\delta = 9.47$ and 7.96 ppm. In contrast to **2**, where the NH resonance appears in the $\delta = -1.6-0.6$ ppm region,[13] the signals for the pyrrolic hydrogen atoms of **1a** appear as a broadened singlet at 2.99 ppm. This downfield shift could reflect a variety of factors, including electronic effects, but is tentatively ascribed to the presence of a more robust hydrogen bonding network in **1a** as compared to **2**. Similar downfield shifts (to ca. 9–10 ppm) for the NH signals have been observed for dinaphthoporphycenes[11a] and dibenzoporphycenes,[14] as compared to the parent alkyl substituted porphycene (a species for which the NH resonances appear at 3.2 ppm).[15] Two doublets, corresponding to the methyl groups present in **1a**, are seen. This

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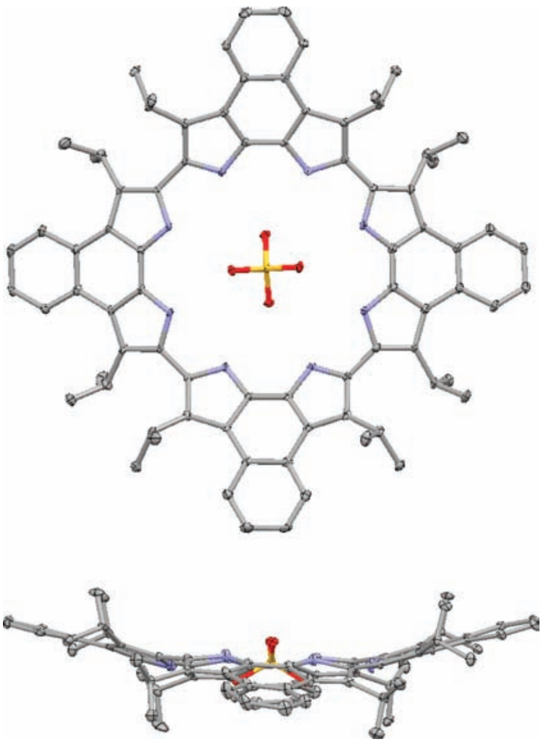

Figure 2. Two orthogonal views of the X-ray structure of **1a**. All hydrogen atoms are omitted for clarity. Thermal elipsoids were scaled to the 50% probability level.

doubling is consistent with a system with lowered symmetry and was taken as an indication that molecule **1a** is not planar.

Proof for this latter supposition came from a single crystal X-ray crystallographic analysis. The resulting structure (Figure 2) revealed that, in the solid state, macrocycle **1a** adapts a saddle-type conformation with alternating naphthobipyrrole subunits. The mean deviation of the nitrogen atoms from the central plane is 0.173(5) Å. This is, however, lower than the corresponding 0.608 Å deviation seen in the case of the π-annulated cyclo[8]pyrrole **3**.[9] We thus conclude that macrocycle **1a** is more planar than **3**. Finally, in accord with what is expected for cyclo[8]pyrroles produced via Fe(III)-mediated oxidative coupling in the presence of sulfuric acid, the X-ray structural analysis revealed a sulfate ion bound within the inner core of the diprotonated macrocycle. The eight NH···O interactions that are presumed to stabilize the bound anion are characterized by hydrogen bond lengths ranging from 1.93 to 1.99 Å.

Macrocycle **1a** displays light absorption properties similar to those of **2**.[13] For instance, both compounds display high extinction coefficients in the visible and near-IR regions, i.e., the B and L absorption bands, respectively. However, the spectral features of **1a** are bathochromically shifted by ca. 180 nm compared to **2** (Figure S8). In analogy to what proved true for the parent system **2** ($\tau_s = 0.7$ ps),[5d] the singlet excited state of **1a** was short-lived with the decay being fit to single exponential with a half-life of 0.5 ps. This correspondence was reflected in the two-photon absorption values (3030 GM for **2**; 3400 for **1a**).

Cyclic voltammetry[16] was used to probe what effect if any the presence of naphthobipyrrole fragments would have on the basic redox properties of the cyclo[8]pyrrole framework. The diprotonated form of **2**, studied previously,[17] is characterized by four oxidation waves with peak potentials at 0.52, 0.77, 1.14, and 1.30 V vs SCE in CH_2Cl_2, although the last two redox features were difficult to discern. A reversible reduction process was also seen at −0.08 V vs SCE in CH_2Cl_2 that involves twice the number of electrons per event as each of the oxidative waves. Grossly similar electrochemical behavior was seen for the diprotonated sulfate salt of **1a**. Specifically, two easily discernible reversible oxidation processes are observed at 0.61 and 0.98 V vs SCE, respectively, and one reversible reduction process at 0.01 V vs SCE is seen (Figure S1). As proved true for **2**, twice as many electrons were involved in the reduction process for **1a** as in the corresponding oxidation waves.[18] On the basis of the electrochemical measurements, therefore, we conclude that the net effect of naphthalene annulation in **1** is to make it somewhat harder to oxidize the macrocycle compared to **2**. However, the difference between the first oxidation and first reduction processes, a measure of the HOMO−LUMO gap, is virtually the same for these two cyclo[8]pyrrole systems.

To obtain further insights into the electronic features of macrocycle **1a**, TD-DFT methods were used to simulate the spectrum of **1a**; the predicted values were found to match well with those determined experimentally. This concordance is thought to reflect the fact that the lowest energy absorption feature is red-shifted due to the electronic contribution of a “naphthobridge”. This results in the degeneracy of the LUMO and LUMO+1 orbitals being broken. As such, broad and intensified NIR absorption bands are predicted on the basis of the TD-DFT calculations, as is indeed seen by experiment (Figures S11, S12). The effect of the naphthobridge is more pronounced in the case of the diprotonated form than for the neutral, or free-base, form. Such a finding is consistent with the greater symmetry and correspondingly larger number of resonance structures that can be written for the diprotonated form.

In conclusion, we have prepared and characterized a new π-extended cyclo[8]pyrrole derivative, namely cyclo[4]naphthobipyrrole, **1a**. This system is fully aromatic as inferred from its optical and NMR spectroscopic properties.

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(16) CV measurements were conducted in a 0.1 M $TBAPF_6-CH_2Cl_2$ solution with a platinum button electrode (Ø = 1 mm) used as the working electrode, and a platinum and silver wire as the counter and reference electrodes, respectively. Peak potentials were referenced against a ferrocene/ferrocenium couple used as an internal standard and then recalculated so as to be referenced vs SCE.

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(18) When scanned further in the positive direction two more oxidation features are observed at ca. 1.37 and 1.70 V vs SCE, respectively. The first of these is well-defined and involves the same number of electrons as the two other oxidation waves. However, the fourth redox peak is not well-resolved in this solvent system.

While the basic features of this new system match those of its parent **2**, a particularly intense near-IR absorption is seen in the case of **1a**. This feature and the reversible nature of the initial oxidation and reduction waves could make this new π-extended analogue of interest in terms of energy capture and storage applications.

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Supporting Information Available. Experimental procedures and characterization data of **1**. X-ray crystallographic data in CIF format (CCDC 840710). This material is available free of charge via the Internet at http://pubs.acs.org.