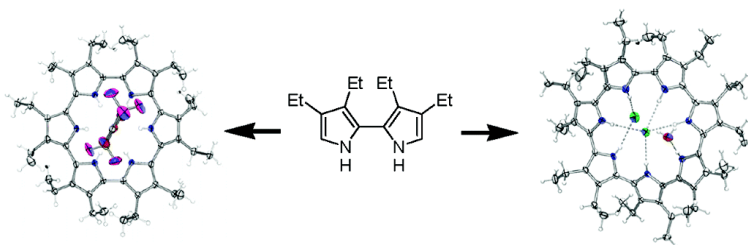


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Formation and Properties of Cyclo[6]pyrrole and Cyclo[7]pyrrole

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In recent years, expanded porphyrins have been attracting increasing attention.^{1–3} While sharing a number of attributes with porphyrins, the expanded porphyrins show unique features, such as the ability to bind anions⁴ or coordinate large cations in a 1:1 in-plane fashion,⁵ that have made them particularly attractive for study. This, in turn, has focused interest on new preparative methodologies, including oxidative couplings,^{5a–7} that might serve to extend the synthetic scope of more traditional cyclization strategies, such as those embodied in classic Rothmund-^{2,8} or MacDonald-type^{2,9} condensations, as well as newer McMurry-based couplings.² In the context of such efforts, we recently reported that 3,3',4,4'-tetraalkylbipyrroles (e.g., **2**) may be coupled under biphasic oxidative conditions (FeCl₃; dichloromethane–1 M aqueous sulfuric acid) to produce cyclo[8]pyrroles [30]octaphyrins(0.0.0.0.0.0.0.0) such as **1**.¹⁰ As inferred from simple molecular modeling studies, such macrocycles, which contain no meso bridges, were thought to represent the smallest possible “contracted” expanded porphyrins. However, much to our surprise, we have now succeeded in producing the smaller cyclo[6]- and cyclo[7]pyrrole analogues, title compounds **3** and **4**.

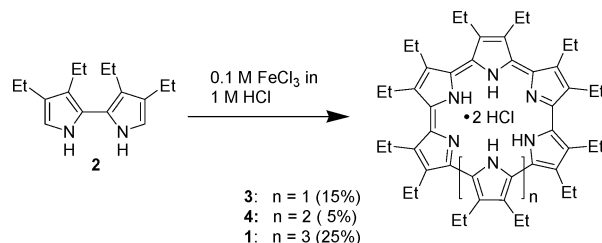
The synthesis of **3** and **4** was made possible by replacing the sulfuric acid by HCl in the Fe^{III}-mediated cyclization of **2**. Specifically, under these conditions, we found that two other meso-carbon-free macrocycles, namely, cyclo[6]pyrrole **3** (HCl salt of [22]hexaphyrin(0.0.0.0.0.0)) and cyclo[7]pyrrole **4** (HCl salt of [26]heptaphyrin(0.0.0.0.0.0.0.0)), were obtained in isolated yields of 15% and 5%, respectively, as well as the expected cyclo[8]pyrrole **1** (obtained in 25% yield; Scheme 1). Salts corresponding to **3** and **4** are found only in trace quantities when sulfuric acid is used, leading us to conclude that their formation is abetted by a specific anion effect.

Consistent with this supposition was the finding that using acids other than HCl led to either decomposition of the bipyrrole (in the case of nitric acid) or to significantly lower yields of **1** (e.g., 20% in the case of acetic acid).¹¹

The proton NMR spectrum of **3** and **4** revealed one upfield-shifted NH signal, at –1.34 ppm and –2.12 ppm for **3** and **4**, respectively. The ethyl groups are resolved into one chemically distinct triplet and a quartet, just as proved true for **1**. The high symmetry presumed for **3** and **4** is reflected in their ¹³C NMR spectra, which in the case of both compounds revealed only two signals in the alkyl region, as well as two signals in the aryl region. Thus, like **1**, compounds **3** and **4** are judged to be aromatic.

Structural proof for cyclo[*n*]pyrroles **3** and **4** was obtained from single-X-ray diffraction analyses of their diprotonated forms. In the case of **3a** (H₂**3**²⁺·2TFA^{2–}) and **4a** (H₂**4**²⁺·2Cl[–]·H₂O), the system shows a deviation of the pyrrole rings from 19 to 22.4°

Scheme 1



with respect to the mean macrocyclic plane (cf. Figure 1).¹² By contrast, **4a** exists in the form of a distorted bowl in the solid state (Figure 2). Six hydrogen-bonding interactions between NH···Cl are inferred in the solid state, with the resulting distances ranging from 2.31 to 2.66 Å. The torsional angles between the pyrrolic subunits range from 14 to 33°.¹³

Analogous those of cyclo[8]pyrrole **1**, the UV–vis spectra of both cyclo[6]pyrrole **3** and cyclo[7]pyrrole **4** (Figure 3) revealed unusual features. Specifically, these bis-HCl salts are characterized by weak Soret-like bands and very strong Q-type absorbances. While the Soret-like band exhibits a small red-shift as the size of the macrocycle grows, the position of the Q-type band shifts dramatically, namely from 792 to 936 to 1112 nm on going from **3** to **4** to **1**. Presumably, this reflects the increased size of the respective frameworks involved (the 4*n* + 2 peripheries increase from 22 to 26 to 30 π-electrons on moving from **3** to **4** to **1**).¹⁴

To gain further insights into the effect that increasing the conjugation path has on the energetics of this “matched set” of heteroannulenes, the electrochemical properties of cyclo[*n*]pyrroles **1**, **3**, and **4** were studied by cyclic voltammetry (CV) and spectroelectrochemistry. While **1** undergoes a two-electron reduction at a potential (vs SCE) of –0.08 V to produce a formally 32 π-electron antiaromatic species (cf. Table 1 for conditions), only one-electron reduction events are seen in the case of its smaller congeners (a single-electron process at –0.18 V in the case of **4** and two processes at –0.35 V and –0.48 V in the case of **3**). Importantly, however, all three cyclo[*n*]pyrroles proved much easier to reduce (by many hundreds of mV) than typical free-base porphyrins.¹⁵ Such a finding is completely consistent with the larger conjugation pathways present in **3**, **4**, and **1**.

In the case of cyclo[8]pyrrole **1**, it proved possible to observe four one-electron oxidation processes by CV (cf. Table 1). On the other hand, **3** and **4** were found to exhibit only two one-electron oxidation processes over the 800–1700 mV scan range. The energy difference between the first one-electron reduction and the first one-electron oxidation—in cases where both are reversible—is considered an indicator of the energy gap between the HOMO and the LUMO orbitals. The electrochemical results indicate that compared to porphyrins (2.25 ± 0.15 V)¹⁶ all three compounds show a dramatic

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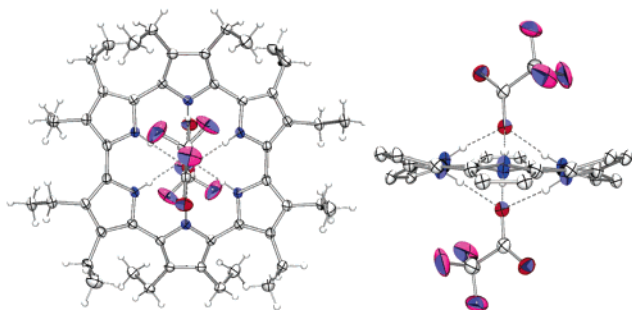


Figure 1. Top and side views of an ORTEP-POVray-rendered image of **3a**. The thermal ellipsoids are scaled to the 50% probability level. The six NH...O bonding interactions range from 1.99 to 2.10 Å.

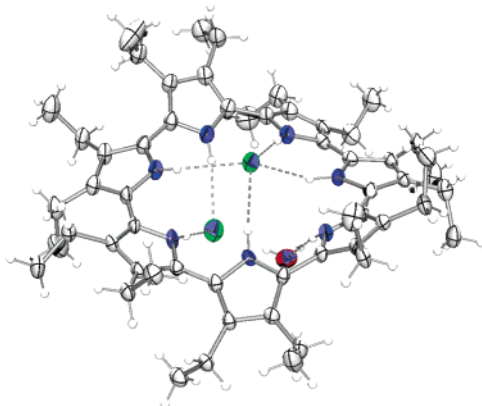


Figure 2. Illustration of an ORTEP-POVray rendered view of **4a**. The thermal ellipsoids are scaled to the 50% probability level.

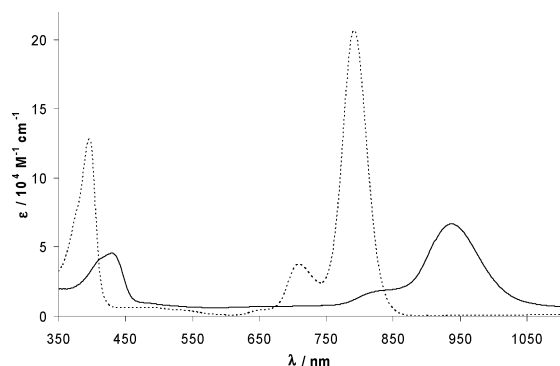


Figure 3. UV/vis spectra of **3** (···) and **4** (—) in methylene chloride. For **3**: λ_{\max} [nm] (ϵ in $\text{M}^{-1} \text{cm}^{-1}$) 397 (122 600), 708, 792 (206 400); for **4**: λ_{\max} [nm] (ϵ in $\text{M}^{-1} \text{cm}^{-1}$) 429 (44 300), 936 (66 700).

decrease (1.30 to 0.60 V) in this value. The larger the π system, the smaller the HOMO–LUMO gap, a key parameter that reaches a minimum in this series in the case of the 30 π -electron system of **1**. These findings match the decrease in the energy associated with the reversible uptake of one electron into the LUMO (ease of first reduction as noted above). Compounds **3**, **4**, and **1** thus stand as almost “textbook” examples of heteroaromatic compounds wherein the change in the conjugation pathway translates into readily quantifiable changes in spectroscopic characteristics. Accordingly, we are currently exploring whether the cyclo[*n*]pyrrole series can be extended to produce larger or smaller variants, as well as working to characterize oxidized and reduced forms of these macrocycles. In preliminary work, we have succeeded in obtaining a cyclo[12]-

Table 1. Half-wave Potentials (V vs SCE) of Cyclo[*n*]pyrroles in CH_2Cl_2 Containing 0.1 M Tetrabutylammonium Perchlorate

cmpd	oxidation				reduction		HOMO–LUMO gap (V)
	4th	3rd	2nd	1st	1st	2nd	
3	–	–	1.56 ^a	0.95	–0.35 ^b	–0.48 ^{a,c}	1.30
4	–	–	1.10 ^a	0.67	–0.18	–	0.85
1	1.30 ^a	1.14 ^a	0.77	0.52	–0.08 ^b	–	0.60

^a E_p at a scan rate of 0.1 V/s. ^b Two-electron process at a scan rate of 0.1 V/s. ^c A further reversible reduction with small peak current at –1.40 V can also be observed.

pyrrole derivative,¹⁷ albeit not in pure form, as well as a fully reduced, N-alkylated version of **1**.

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Supporting Information Available: Experimental details describing the synthesis and characterization of compounds **3** and **4** and cyclic voltammetric results (PDF). Crystallographic data (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (11) While the formation of the cyclo[6]pyrrole species **3** is easy to understand, the formation of the cyclo[7]pyrrole **4** is more difficult to rationalize. It could be the result of an attack by a bipyrrrole radical, generated in situ, on a 2,2'-bond of a bipyrrrole. Such a process would lead to the loss of one pyrrole unit and permit formation of **4**.
- (12) The structure for **3a** was refined on F^2 to an $R_w = 0.121$, with a conventional $R = 0.051$. For details, see Supporting Information.
- (13) The structure for **4a** was refined on F^2 to an $R_w = 0.198$, with a conventional $R = 0.078$. For details, see Supporting Information.
- (14) The intensity of the UV–vis bands was found to vary somewhat across the series ($\epsilon_{792 \text{ nm}} = 206\,400 \text{ M}^{-1} \text{cm}^{-1}$ vs $\epsilon_{936 \text{ nm}} = 66\,700 \text{ M}^{-1} \text{cm}^{-1}$ vs $\epsilon_{1112 \text{ nm}} = 132\,200 \text{ M}^{-1} \text{cm}^{-1}$ for the bis-HCl salts of **3**, **4**, and **1**, respectively); we rationalize this in terms of the varying, albeit small, deviations from planarity seen for these systems.
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