7190 *J. Am. Chem. Soc.* **2001,** *123,* 7190−7191

meso-Aryl-Substituted Expanded Porphyrins

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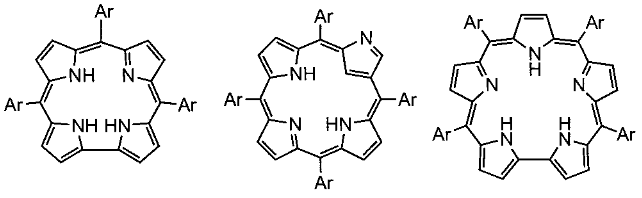
Received March 12, 2001

In recent years expanded porphyrins have emerged as a promising class of molecules in light of their optical, electrochemical, and coordination properties.[1] Continuing synthetic efforts have culminated in the developments of a variety of large pyrrole-containing macrocycles.[2] Nevertheless, the synthesis of *meso*-aryl-substituted expanded porphyrins with more than four pyrrolic subunits still remains an important subject, since they could be considered as the "legitimated" members of the expanded porphyrin family as judged from the wide use of *meso*-tetraaryl porphyrins. Recent findings of concurrent formation of variants such as corrole **1**,[3] *N*-confused porphyrin **2**,[4] and sapphyrin **3**[5] in the Rothemund-type porphyrin synthesis have tempted us to reinvestigate the cyclization reaction (Chart 1). Herein, we report a facile synthesis of a series of *meso*-aryl-substituted expanded porphyrins by the acid-catalyzed condensation of pentafluorobenzaldehdye and pyrrole.

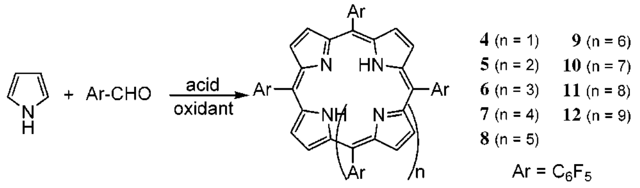
A series of *meso*-aryl-substituted expanded porphyrins were synthesized under the modified Lindsey conditions,[6] at relatively high concentration, 67 mM in both the reactants in CH_2Cl_2 with $BF_3 \cdot OEt_2$ (4.2 mM). After the oxidation with DDQ, repeated chromatography over a silica gel column led to isolation of distinct products including porphyrin **4** (11∼12%), *N*-fused pentaphyrin **NFP$_5$**[7] (14∼15%), hexaphyrin **6**[8] (16∼20%), heptaphyrin **7**[9] (4∼5%), octaphyrin **8** (5∼6%), nonaphyrin **9** (2∼3%), and even higher homologues,[10] as judged by their respective ^{1}H NMR and FAB-MS data (Scheme 1).

Chart 1



1 **2** **3**

Scheme 1



Among the new *meso*-aryl-substituted expanded porphyrins, X-ray crystal structures of free base octaphyrin **8**[11] and protonated nonaphyrin **9**[12] have been determined (Figures 1 and 2). The octaphyrin **8** adopts a twisted "figure-eight" conformation with near C_2 symmetry, consisting of two porphyrin-like tetrapyrrolic "hemi-macrocycles", in which the dipyrromethene units of the pyrrole rings **A** and **B** and of the pyrrole rings **C** and **D** are respectively nearly coplanar but the resulting two planes are canted by ca. 38°. The similar "figure eight" conformations have been observed in other octapyrrolic macrocycles.[1,13] The pyrrole interior C−N−C angles reveal an alternate location of amino-type (N(1), N(3), N(5), and N(7)) and imino-type (N(2), N(4), N(6), and N(8)) pyrrole rings. Additionally, the two C−C bond distances at the methene bridges reveal the bond alternation as shown in Chart 2a consistent with the above assignments, hence suggesting the 36π-electron nonaromatic system.

On the other hand, the X-ray structure of the nonaphyrin **9**-trifluoroacetate **9**·TFA shows a helical twisted conformation containing a near mirror plane with a large cleft wherein the TFA anion is tightly bound (Figure 2). The pyrrole interior C−N−C angles reveal a location of amino-type (N(1), N(2), N(4), N(5), N(6), N(7), and N(9)) and imino-type (N(3) and N(8)) pyrrole rings. Of the three pyrroles inverted, the two nitrogens (N(5) and N(6)) are pointing outward so as to flank the TFA anion through hydrogen bonding. The alternation of C−C bond distance is modest (<0.038 Å) compared with that of **8** (0.036−0.103 Å), suggesting the 42π-electron aromatic system (Chart 2b).

The ^{1}H NMR spectrum of **8** in $CDCl_3$ shows a C_2 symmetric signal pattern containing four pairs of doublets of the pyrrolic β-Hs in 7.67−6.11 ppm and two broad signals of the inner NHs at 13.25 and 8.59 ppm, also implying its nonaromatic nature. The ^{1}H NMR spectrum of **9**·TFA records C_2 symmetric signals: three pairs of doublets at 7.47, 6.64, and 6.21 ppm, a singlet at 4.43 ppm, and two pairs of doublets at 2.05 and 1.98 ppm for the

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(6) In the Lindsey method, the porphyrin yield was reported to be highest at 10 mM reactants and decline by about a factor of 2 at either 100 or 1 mM reactants at a fixed concentration of acid catalyst. Lindsey, J. S.; Schreiman, I. C.; Hsu, H. C.; Kearney, P. C.; Marguettaz, A. M. *J. Org. Chem.* **1987**, *52*, 827.

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(9) The structure of heptaphyrin **7** has not been determined yet. An initially isolated molecule with the parent ion peak at 1705 (calcd for $C_{77}H_{16}N_7F_{35}$ = 1706) was changed to a stable product **7-HF** (4−5%) whose mass was smaller than the former product by 20 mass units that corresponded to HF. Since the analogous *meso*-aryl-substituted heptaphyrin molecules obtained from the reaction of other 2,6-disubstituted arylaldehydes were stable, we believe that the initial product has a *meso*-aryl-substituted heptaphyrin core.

(10) The higher homologues such as decaphyrin **10** (ca. 0.1%, FAB-MS: *m*/*z* 2437, calcd for $C_{110}H_{25}N_{10}F_{50}$ = 2436, λ_{max} = 748 nm), undecaphyrin **11** (ca. 0.1%, *m*/*z* 2680, calcd for $C_{121}H_{28}N_{11}F_{55}$ = 2680, λ_{max} = 784 nm), and dodecaphyrin **12** (ca. 0.1%, *m*/*z* 2924, calcd for $C_{132}H_{30}N_{12}F_{60}$ = 2924, λ_{max} = 829 nm) were also isolated.

(11) Crystal data of **8**: $C_{94}H_{34}F_{40}N_8$, M_w = 2035.2(9), monoclinic, space group $P2_1/c$, a = 17.2198(18) Å, b = 16.2725(17) Å, c = 29.763(3) Å, β = 91.902(2)°, V = 8335.4(15) Å^3, Z = 4, D_{calc} = 1.622 g/cm^3, T = 100 K, crystal size 0.12 × 0.38 × 0.47 mm^3. $R1$ = 0.0984, $wR2$ = 0.2335 for 14195 reflections with $I > 2\sigma(I)$, GOF(on F^2) = 1.161.

(12) Crystal data of **9**·TFA: $C_{104}H_{32}F_{48}N_9O_2$, M_w = 2351.3(9), monoclinic, space group $P2_1/n$, a = 13.6250(11) Å, b = 30.814(3) Å, c = 22.7475(19) Å, β = 96.824(3)°, V = 9482.6(13) Å^3, Z = 4, D_{calc} = 1.647 g/cm^3, T = 103 K, crystal size 0.42 × 0.21 × 0.14 mm^3, $R1$ = 0.0663, $wR2$ = 0.1436 for 9930 reflections with $I > 2\sigma(I)$, GOF(on F^2) = 1.066.

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10.1021/ja0106624 CCC: $20.00

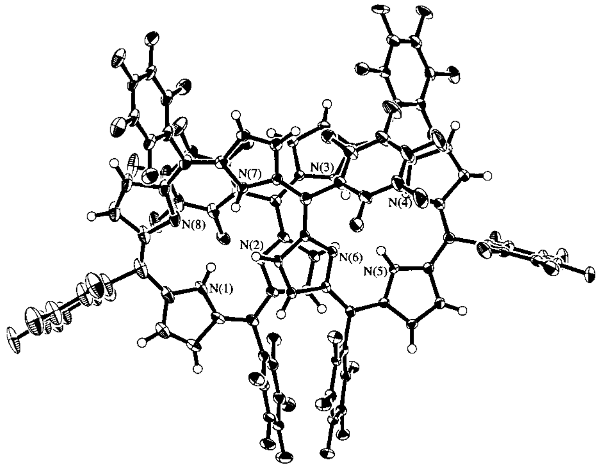


Figure 1. X-ray structure of octaphyrin **8**.

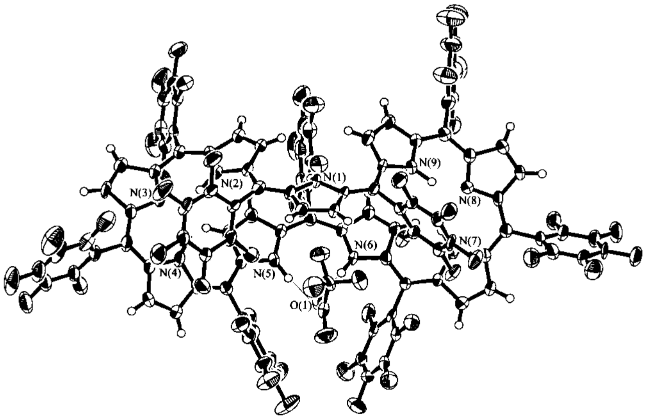
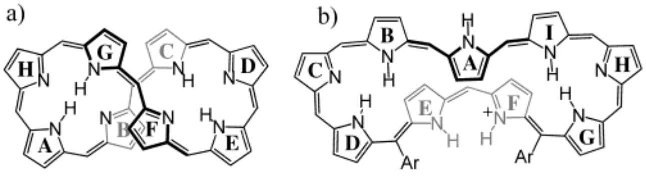


Figure 2. X-ray structure of nonaphyrin **9**-TFA complex.

Chart 2



pyrrole β-protons and three sets of broad 2H signals at 13.55, 5.52, and 4.85 ppm and a broad 1H signal at 4.98 ppm for the inner NHs. Markedly different chemical shifts particularly for the β-pyrrolic protons suggest the aromatic electronic character for **9**, in accord with its 42π-electron formulation. It thus may be reasonable to assign the upfield shifted β-signals and the downfield shifted NH signal for the inverted **E**- and **F**-rings. The coincidence of the solid-state and solution-state structures in the case of **9**·TFA may be owing to the stabilization imposed by the presumably strong hydrogen bonding between the TFA ion and two NH protons.

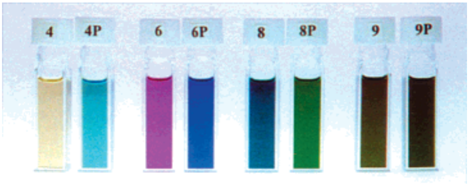


Figure 3. CH_2Cl_2 solutions of free base and protonated expanded porphyrins: porphyrin **4**, hexaphyrin **6**, octaphyrin **8**, and nonaphyrin **9**. **P**: protonated form in the presence of 1% TFA.

The expanded porphyrins show the respective bright colors in neutral and protonated forms (Figure 3). The absorption spectra of **8** and **9** display broad bands at 638 and 710 nm, respectively, which are considerably red-shifted compared with the Soret band of **4** (411 nm) and the Soret-like band of **6** (567 nm). Consistent with a notion that **8** may be a 36π nonaromatic molecule, treatment of **8** with DDQ in CH_2Cl_2 led to the appearance of an intense sharper band at 738 nm as well as Q-band-like small transitions centered at 1264 nm, as would be expected for a 34π-electron aromatic system. When $NaBH_4$ was added to a methanol solution of **8**, the similar nonaromatic to aromatic spectral changes were induced with the appearance of a sharp Soret-like band at 720 nm and Q-bands at 960, 1114, and 1242 nm, in line with formation of the 38π-electron aromatic system. In fact, this reduced **8** displays two sets of β-H signals at 2.79 and 2.53 ppm assignable to the inverted pyrrole, reflecting the presence of the aromatic ring current effect. Such facile redox interconversions, as seen also for hexaphyrin **6**,[8] might be an intrinsic property of *meso*-aryl-expanded porphyrins owing to a low energy barrier between aromatic and nonaromatic states as well as possible allowance of different conformations.

It is now evident that the slightly modified Rothemund−Lindsey method indeed provided a series of *meso*-aryl-substituted expanded porphyrins. The preparative procedure reported here is quite simple and appears to be general. Actually, we have found that a range of 2,6-disubstituted arylaldehydes may be used in place of pentafluorobenzaldehyde. These results may imply that the steric hindrance around the formyl group is crucial for the formation of the expanded porphyrins. Systematic studies on the expanded porphyrins could provide important information on the fundamental and interrelated questions of ring size, aromaticity, a multitude of oxidation states, and macrocycle conformation and stability, as well as an important entry into the development of new photosensitizers and chelating receptors for the complexation of anions and cations.

Acknowledgment. This work was supported by Grant-in-Aids for Scientific Research (Nos. 11233205 and 12440196) from the Ministry of Education, Science, Sports and Culture of Japan and by CREST (Core Research for Evolutional Science and Technology) and PRESTO (Precursory Research for Embryonic Science and Technology) of Japan Science and Technology Corporation (JST).

Note Added after ASAP. There were errors in Chart 1 in the version posted ASAP June 29, 2001; the corrected version was posted July 18, 2001.

Supporting Information Available: Synthetic procedures, spectral data, absorption spectra, and crystallographic data for **8** and **9**, spectroscopic data or **7** and **7-HF**, and absorption spectra of **10**, **11**, and **12** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA0106624