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Metalation of Expanded Porphyrins: A Chemical Trigger Used To Produce Molecular Twisting and Möbius Aromaticity[**]

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The concept of Möbius aromaticity, a postulate that states that aromatic characteristics will be observed for [4*n*]annulenes lying in a twisted Möbius strip, is a time-honored concept that is fascinating from both the theoretical and experiment standpoints,[1,2] since it provides a natural complement to the well-recognized idea of Hückel aromaticity that governs the properties of planar [$4n+2$]annulenes (Figure 1). Although first suggested by Heilbronner for a ground-state system early in 1964,[1] and later put forth as being relevant to certain transition states[3] and reactive intermediates,[4] real Möbius aromatic systems proved elusive until the recent seminal report by Herges and co-workers,[5] wherein the first example of a Möbius aromatic hydrocarbon was disclosed. This system was obtained by the strategic lateral combination of a normal, planar conjugated segment with a belt-shaped conjugated segment. Despite the laborious synthetic sequence required to obtain this particular product, the aromatic character of this macrocycle is not very strong, a finding consistent with the large dihedral angle (−107.7°) and small nucleus-independent chemical shift (NICS) value (−3.4 ppm).[6,7] Recently, however, it has been suggested on the basis of an extensive principal component analysis that Möbius twisted [16]annulenes should be more aromatic than the corresponding nontwisted isomers.[8] These studies have served to rekindle theoretical interest in Möbius aromatic molecules and underscore the need for further syntheses. In this context, the recent finding that a di-*p*-benzihexaphyrin(1.1.1.1.1.1), which is a hexapyrrolic "expanded porphyrin", exhibits a Möbius structure in the solid state, but shows a dynamic Hückel–Möbius topological interconversion in solution,[9] is interesting. Therefore, the need for a simple, versatile approach to obtain real Möbius aromatic systems with distinct aromatic characters remains.

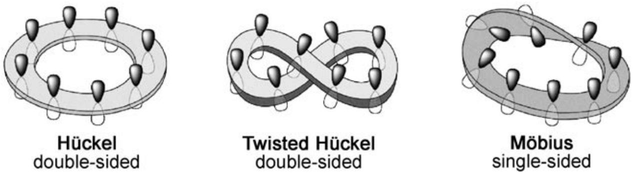

Figure 1. Schematic representation of the topologies of π-conjugated electron systems.

The synthesis of Möbius aromatic molecules is made inherently difficult by the need to accommodate two conflicting structural objectives, namely a twisted Möbius topology and an overall conjugated $4n$ π-electron periphery. The twisted nature of the Möbius topology necessitates the use of large annulenic systems to mitigate the distortion associated with molecular twists. Unfortunately, such systems often show considerable conformational flexibility, which makes "locking in" a twisted conformation difficult.

Recently, conjugated oligopyrrolic macrocycles, the so-called expanded porphyrins, have emerged as a new class of heteroannulene variants that display a range of interesting electronic and conformational characteristics,[10–12] including the formation of structures with figure-eight geometries.[13–15] These features led us to consider that, compared with more conventional annulenes, expanded porphyrins might have distinct advantages in the construction of Möbius-type aromatic systems. These include 1) an overall conformational flexibility, 2) an ability to invert, or "flip out", the constituent pyrrolic subunits under certain conditions, 3) the capacity to respond to two-electron oxidation and reduction through the facile release or capture of a pair of pyrrolic NH hydrogen atoms to balance the charge,[11] and 4) the possibility of

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"locking in" conformations through metalation, especially in those systems that permit the formation of both nitrogen–metal and carbon–metal bonds.[16,17] In spite of this promise, no general approach to Möbius-type aromatic systems involving expanded porphyrins has been reported. However, we have now found that Möbius aromatic molecules are formed readily and spontaneously upon subjecting several larger meso-substituted expanded porphyrins to metalation with Group 10 metals. As detailed below, this approach, which to the best of our knowledge is without precedent in the literature, is both simple and can potentially be generalized.

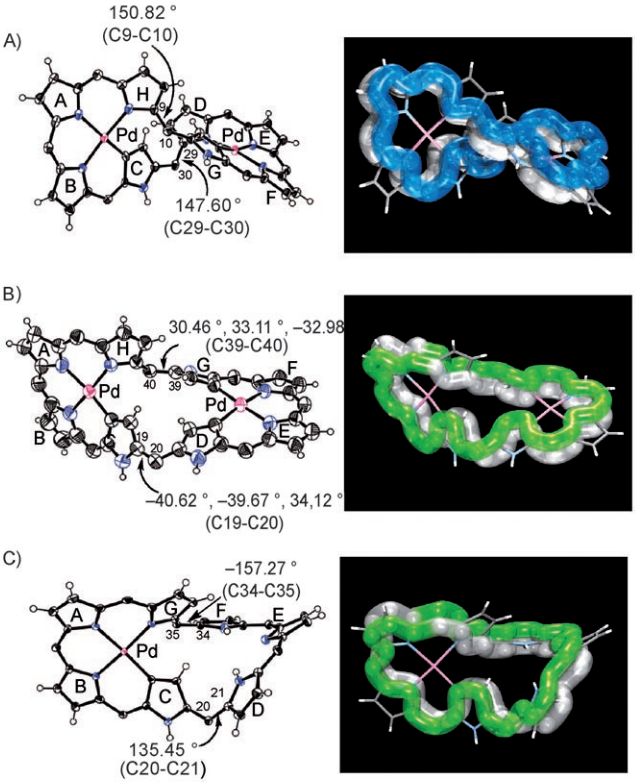
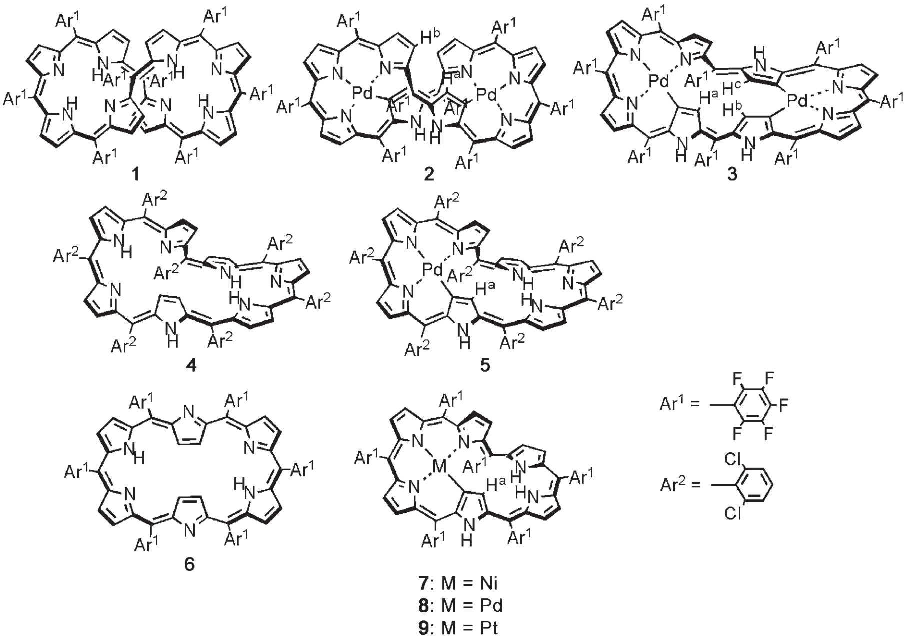


Figure 2. X-ray structures (left) and schematic representations of molecular topologies (right) of **2** (A), **3** (B), and **5** (C). The thermal ellipsoids are scaled to the 50% probability level and meso-aryl substituents are omitted for clarity. Dihedral angles at the most distorted points are also indicated; dihedral angles for the three molecules in crystal are shown for **3**.[19]

[36]Octaphyrin(1.1.1.1.1.1.1.1) **1** (Scheme 1), which has 36 π electrons within its conjugation pathway, is an intriguing expanded porphyrin that undergoes an unprecedented scission reaction to give two porphyrins upon metalation with two copper(II) ions.[18] In a continuation of this study, which has clear topological implications, we examined the metalation of **1** with palladium acetate. We found that heating this metal-free species in methanol in the presence of palladium acetate gave rise to the bispalladium(II) complexes **2** and **3** in yields of 51 and 20%, respectively. A single-crystal X-ray analysis revealed that **2** possesses a C_2-symmetric figure-eight structure with two inverted pyrrole rings. The two palladium atoms are each bound by three pyrrolic nitrogen atoms and a pyrrolic β-carbon atom, thereby resulting in a square-planar NNNC coordination environment, a mode of metal complexation that is new for octaphyrins (Figure 2). This structure is consistent with a 36-π-electron circuit within what can be considered a twisted double-sided (orientable) Hückel topology. As would be expected for such a formulation, protons H^a and H^b (see Scheme 1) which are located near the crossing point of the figure-eight structure resonate at $\delta = 17.14$ and 8.60 ppm, in the deshielded region. Such findings are consistent with a paratropic ring current. The UV/Vis absorption spectrum of **2** is ill-defined, with band features appearing at 413, 572, and 660 nm. We thus infer that **2** is largely antiaromatic in character, a conclusion that is supported by the finding of a very large calculated NICS value (+38.4 ppm) at the center of the molecule. By way of comparison, compound **1**, a system considered to be non-aromatic on the basis of its UV/Vis and ^{1}H NMR spectroscopic features, has a calculated NICS value of −2.1 ppm at its center.



Scheme 1. Expanded porphyrins and their Group 10 metal complexes.

In contrast to **2**, the structure of **3** was found to possess a twisted single-sided Möbius topology. The overall charge and bonding pattern are consistent with a system containing a 36-π-electron periphery that is defined by the two central Pd atoms coordinated in NNNC and NNCC modes (Figure 2). The greatest deviations from planarity are seen at the C19–C20 and C39–C40 bonds, sites that serve to connect the two relatively planar palladium-coordinating segments. However, even here the dihedral angles are rather modest (Figure 2 and Table 1), which allows for effective conjugation of the macrocycle. A distinct diatropic ring current is apparent in the ^{1}H NMR spectrum of **3**. Specifically, the outer pyrrolic β-CH signals appear in the deshielded region ($\delta = 8.19$–7.42 ppm), while the inner pyrrolic H^a, H^b, and H^c signals appear at $\delta = -1.77$, -2.93, and 0.24 ppm, each as a singlet. Thus, a large $\Delta\delta$ value of 11.12 ppm is observed, as would be expected for an aromatic system. The aromatic character proposed for **3** is also supported by its UV/Vis absorption spectrum, which reveals an intense Soret-like band at 735 nm and Q-like bands at 822, 1020, and 1143 nm. It is noteworthy that the ^{1}H NMR spectra of **2** and **3** are both somewhat independent of changes in either the temperature or solvent, a finding we interpret in terms of their robust structures which are made rigid by the two coordinated palladium atoms. This finding stands in contrast to what is seen in the case of **1**, which displays features that are considerably temperature and solvent dependent, as befits its conformational flexibility. The calculated NICS value at the center of macrocycle **3** is $\delta = -14.6$ ppm, thus providing support for the above assignment.

Table 1: Selected data.

Compound	ϕ [°][a]	$\Delta\delta$ [ppm][b]	NICS [ppm][c]	$\sigma^{(2)}$ [GM] (λ_{ex} [nm])[d]
1	−164.23, −159.69	1.56	−2.1	870 (1240)
2	150.82, 147.60	12.04	38.4	690 (1240)
3	−40.62, 30.46 −39.67, 33.11 34.12, −32.98	11.12	−14.6	6400 (1440)
4	–	–	−12.3	2600 (1240)
5	135.45, −157.27	9.97	−12.2	4200 (1300)
7	−45.83, −138.74	5.90	−15.7	5500 (1200)
8	−41.14, −134.13	7.05	−13.3	4000 (1200)
9	−39.92, −133.47	6.37	−11.9	4600 (1200)

[a] Dihedral angle at the two most distorted points; for **3**, the values of the three molecules in the crystal are shown. [b] Difference between the most upfield-shifted and the most downfield-shifted chemical shifts for β-CH signals in the ^{1}H NMR spectra recorded in $CDCl_3$ at room temperature. [c] Nucleus-independent chemical shift at the center of the macrocycles (see Table S3 in the Supporting Information) calculated by the GIAO method with the B3LYP functional and employing a basis set consisting of SDD for Ni, Pd, and Pt, and 6-31G(d) for C, H, and N, on the optimized structure models without aromatic substituents; NICS. [d] TPA cross-section value and wavelength determined in CH_2Cl_2 by the open-aperture Z-scan method.

The ^{1}H NMR spectrum of [32]heptaphyrin(1.1.1.1.1.1.1) **4**,[20] recorded at room temperature, revealed broad signals consistent with conformational flexibility. However, an analogous analysis carried out at low temperature was best interpreted in terms of the existence of several conformers with Möbius-type aromatic character (see Figures S4 and S16 in the Supporting Information). Metalation of **4** with palladium acetate in dichloromethane provided monopalladium complex **5** in 88 % yield. X-ray diffraction analysis of **5** revealed a twisted Möbius strip type structure, in which the Pd atom is bound to pyrrole rings A, B, C, and G in a square-planar CNNN coordination mode, while the rest of the pyrrole rings define a relatively planar segment. The dihedral angles between these two segments are characterized by only modest distortion (Table 1), as in the case of **3**. Thus, the organic framework present in **5** is best considered as a 32-π-electron conjugated macrocycle (Figure 2). The aromatic character of **5** is apparent from its ^{1}H NMR spectrum recorded at −60 °C, which is characterized by distinctly shielded signals ascribed to the H^a and NH protons at $\delta = -2.20$ ppm, and 0.07 and 3.84 ppm, respectively. Deshielded signals corresponding to the outer β and NH protons are seen in the range $\delta = 7.3$–8.0 ppm and at 9.44 ppm, respectively, which leads to a large $\Delta\delta$ value of $\delta = 9.97$ ppm (at room temperature) and $\delta = 10.21$ ppm (at −60 °C). The UV/Vis absorption spectrum of **5** exhibits a sharp Soret band at 663 nm, along with Q-like bands. In this case, the palladium metalation serves to "lock in" the Möbius structure, for which a NICS value of $\delta = -12.2$ ppm was calculated. Again, this is a value that supports the assignment of aromaticity.

As a new quantitative measure of aromaticity, we examined the two-photon absorption (TPA) cross-section ($\sigma^{(2)}$) by the open-aperture Z-scan method.[21] Since the $\sigma^{(2)}$ value is largely determined by the degree of electronic delocalization, large values for aromatic expanded porphyrins are routinely recorded.[22–24] The measurements were carefully performed in the near-infrared region (Table 1) to avoid any contribution from one-photon absorptions. The maximum $\sigma^{(2)}$ value of **3** was found to be 6400 GM, a value that is distinctly larger than those of **1** (870 GM) and **2** (690 GM), but comparable with those seen for Hückel aromatic molecules.[23] The maximum $\sigma^{(2)}$ values for **4** and **5** were found to be 2600 and 4200 GM, respectively, thus supporting the aromatic characters proposed for these macrocycles. These are the first TPA measurements of Möbius aromatic molecules and thus represent an important demonstration that $\sigma^{(2)}$ values may be used to quantify the extent of aromaticity regardless of the topology of the specific conjugated electronic circuit under consideration.

The demonstration that both octaphyrin and heptaphyrin can provide Möbius aromatic complexes led us to question whether the smaller, and inherently less flexible, hexaphyrin congener would also work in this capacity. This drove us to reexamine the metal complexes of [28]hexaphyrins (**7**, **8**, and **9**), which we previously found to form in good yields upon metalation of [26]hexaphyrin(1.1.1.1.1.1) **6** with Group 10 metals. Although we did not recognize the specific nature of these structurally characterized complexes at the time of initial publication,[17] we now appreciate that they all possess distinct Möbius topologies. Moreover, they all contain 28-π-electron peripheries and display diatropic ring currents, as evidenced by the fact that the signals for the inner β protons (H^a in Scheme 1) appear in a strongly shielded region at $\delta = 1.70$, 0.80, and 1.23 ppm, for **7**, **8**, and **9**, respectively, while the outer β protons resonate in the $\delta = 7.0–8.0$ ppm region. The maximum $\sigma^{(2)}$ values of these complexes have now been measured, and have been found to be rather large: 5500, 4000, and 4600 GM, respectively. These values coincide with those typically seen for Hückel-type aromatic expanded porphyrins, while the calculated NICS values are considerably negative (Table 1). These data are fully consistent with the Möbius aromaticity proposed for these complexes.

In summary, metal complexes **3**, **5**, **7**, **8**, and **9** are stable, conformationally locked Möbius aromatic molecules that display distinct aromaticity. The formation of such Möbius aromatic complexes is not only spontaneous, but is also surprisingly general upon metalation with Group 10 metals, as seen in the case of octaphyrin, heptaphyrin, and hexaphyrin. While requiring further study, we currently believe that the formation of Möbius-type aromatic systems under the conditions of metalation is driven by a need to relieve the internal strain that would accumulate upon the formation of complexes in the absence of twisting, with the energetic stabilization provided by Möbius-type aromatization. These results unambiguously validate the concept of Möbius aromaticity predicted by Heilbronner more than 40 years ago. Moreover, the ready availability of Möbius aromatic complexes from expanded porphyrins is expected to stimulate further studies in this area, including their applications in development of functional materials.

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