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Macrocycles

Möbius Aromatic Core-Modified Heterocyclic [20] Macrocycles (4.1.1) with a Protruding *N*-Methyl Pyrrole Ring

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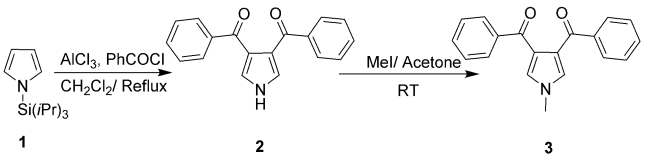
Dedicated to Professor Tavarekere K. Chandrashekar on the occasion of his 60th birthday

Abstract: Herein, we report the first synthesis of an unorthodox tripyrrane moiety from the regioselective β-benzoylation of pyrrole and the acid-catalyzed condensation of the desired precursors. A [3+1] Mac Donald type condensation strategy for this tripyrrane has led to the exclusive isolation of two hitherto-unknown aromatic [20] heterocyclic macrocycles (4.1.1).

Aromaticity continues to be the topic of numerous studies that are not only associated with its relevance in chemistry, biology, and technology, but also with the very concept itself.[1] Even though chemists are accustomed to thinking of nearly planar [4*n*+2] Hückel topology, recently, there has been an upsurge in interest in the exploration of twisted Möbius [4*n*] annulenes. According to Hückel Molecular Orbital (HMO) theory, in a fully delocalized system with 4*n*π electrons, Hückel topology predicts an open-shell electron configuration, whereas Möbius topology predicts a closed-shell structure.[2] Porphyrins and expanded porphyrins have been widely studied to probe subtle variations in aromaticity, antiaromaticity, and Möbius aromaticity.[3] Ever since the successful observation of Möbius topology in A,D-di-*p*-benziporphyrin,[4a] many new promising classes of expanded porphyrins have been rigorously investigated by inducing structural variations through metal coordination, temperature changes, solvent effects, protonation with an appropriate acid, and functionalization with *meso* or β substituents.[4] Notably, Rh(I) [24] N-fused pentaphyrin and Pd(II) [44] decaphyrin[5] are the smallest and largest Möbius aromatic macrocycles reported to date, respectively. The recent syntheses of many new and novel Möbius aromatic macrocycles have challenged the synthetic and theoretical chemists to quantify the smallest-possible porphyrin macrocycle with less than [24]π electrons in the conjugation pathway that could exhibit distinct metal-free Möbius aromaticity,[5c] not only from a synthetic point of view, but also from an understanding of the molecular and electronic structures of these macrocycles. Included in the continuing efforts to synthesize more and more such fascinating macrocycles has been the exploration of improved and new precursors. Herein, we report our first efforts towards the rational synthetic design and synthesis of an unprecedented tripyrrane moiety (**5**), which has led to the isolation of two hitherto-unknown [20] aromatic macrocycles **8** and **9**. These macrocycles have been synthesized by strategically bringing β,β-carbon atoms of *N*-methyl pyrrole ring into the core of the macrocycles.[6]

To synthesize the target macrocycles, we designed the three-step synthesis of (1-methyl-1H-pyrrole-3,4-diyl)bis(phenylmethanone) (**3**; Scheme 1) from pyrrole, in which bulky substituents on the nitrogen atom of the pyrrole moiety were employed to obstruct electrophilic attack at the α positions through significant steric and electronic effects. In this context, the report by Corey et al.[7a] was highly impactful, sparking the idea that triisopropylsilyl (TIPS)-pyrrole could act as a progenitor of β-substituted pyrrole **3** through kinetic electrophilic substitution of 1-(triisopropylsilyl) pyrrole. Thus, TIPS-pyrrole **1** was readily prepared in high yield from the sodium salt of pyrrole and triisopropylsilyl chloride.[7b] Following the literature procedure for the benzoylation of pyrrole,[7c] an excess use of $AlCl_3$ and benzoyl chloride upon refluxing for 72 hours, has led to the isolation of 3,4-dibenzoyl pyrrole **2** due to hydrogen chloride induced desilylation in 30% yield after flash column chromatography on silica gel. We attributed the high regioselectivity of this reaction to the fact that the regioselective step occurred before the desilylation of TIPS-pyrrole, which would have otherwise led to the formation of 2,4-dibenzoyl pyrrole. In the final step, N-methylation of compound **2** was performed by using methyl iodide to afford compound **3**. Both compounds **2** and **3** were thoroughly characterized by spectroscopy (see the Supporting Information, Figures S2, S3, and S11–S14) and by single-crystal X-ray structural analysis (Figure 1).[8]



Scheme 1. Regioselective β-benzoylation of the pyrrole ring.

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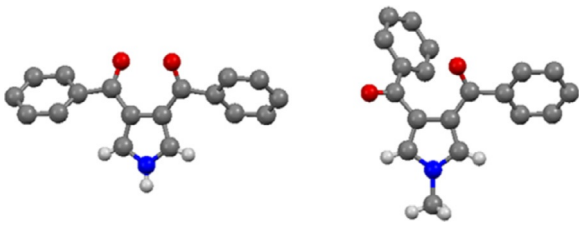
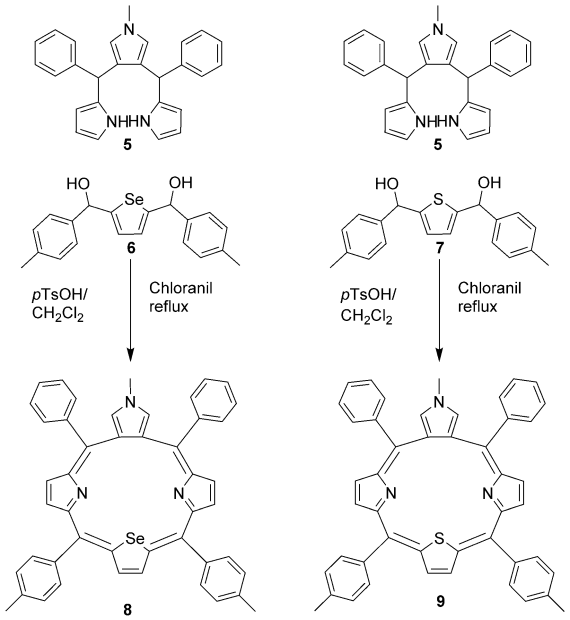


Figure 1. X-ray crystal structures of compounds 2 (left) and 3 (right).

Following reduction with lithium aluminum hydride, the corresponding dicarbinol (**4**) was obtained in quantitative yield, which was subsequently reacted with 80 equivalents of freshly distilled pyrrole to yield the desired precursor (**5**) in 70% yield (see the Supporting Information, Scheme S1). Notably, this is the first report for synthesis of tripyrrane **5**. Rational synthesis of macrocycles **8** and **9** entailed a [3+1] acid-catalyzed condensation of tripyrrane **5** with 2,5-bis(tolylhydroxymethyl)selenophene (**6**) or 2,5-bis(tolylhydroxymethyl) thiophene (**7**),[9] followed by oxidation with chloranil (Scheme 2).[10] The best yield was obtained with 0.1 equivalents of *p*-toluenesulfonic acid as a catalyst. Purification by column chromatography on basic alumina, followed by repeated column chromatography on silica gel (200–400 mesh) yielded macrocycles **8** and **9** as green solids in 10% and 8% yield respectively.

The structures of these new macrocycles were established by thorough spectroscopic analysis. Macrocycles **8** and **9** showed peaks for their parent ions at *m/z* 722.404 and 674.305, respectively, under positive-ionization conditions in MALDI-TOF mass spectrometer, thus confirming their compositions. The electronic absorption spectra of both the macrocycles in their free-base and protonated forms were porphyrin-like. The free-base forms of both macrocycles exhibited sharp



Scheme 2. Synthesis of macrocycles **8** and **9**.

absorption spectra in the Soret band region (456.41 nm for **8**; 451.28 nm for **9**), with well-defined Q-like bands (624.35 and 675.45 nm for **8**; 632.41 and 683.88 nm for **9**), which was attributed to the aromatic nature of these macrocycles. The heteroatom effect was clearly observed, by red-shift in the bands with a bigger heteroatom (Se vs S). As shown in Figure 2, protonation of both the macrocycles led to the generation of

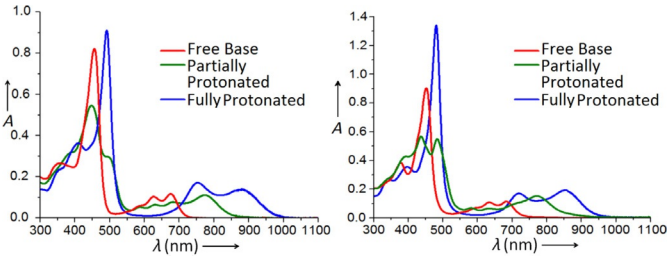
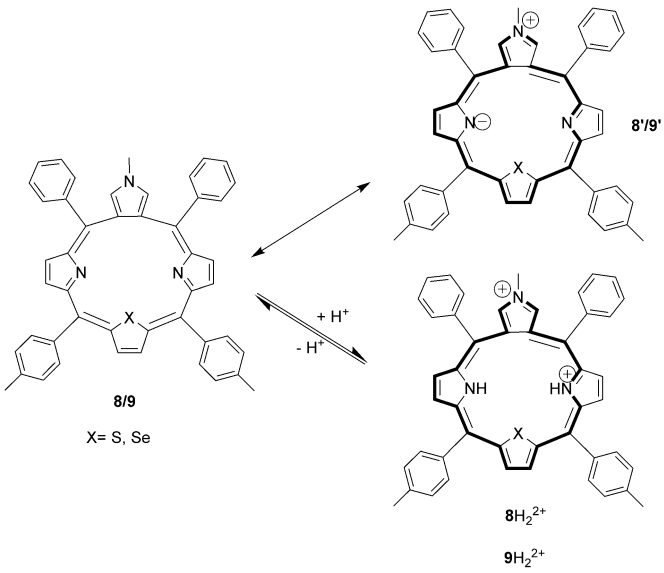


Figure 2. UV/Vis spectra of macrocycles **8** (left) and **9** (right).

sharp Soret bands with a red-shift of 30–35 nm (492.67 nm for **8**; 481.86 nm for **9**) and also red-shift in the Q-band region (750.73 and 883.88 nm for **8**; 719.97 and 855.67 nm for **9**), which typified the porphyrinic nature of these macrocycles with aromaticity.[3b] Titration of these macrocycles against trifluoroacetic acid was performed to isolate partially protonated and diprotonated states (see the Supporting Information, Figures S21 and S24).

The nonplanar structure of the macrocycles in their free-base form was preserved in the solution state, as confirmed by ^{1}H NMR spectra. For both the macrocycles, the unusual way of linking the *N*-methyl pyrrole moiety into the macrocyclic conjugation pathway accelerated a dynamic flipping of the heterocyclic rings, and so only broad peaks were observed at ambient temperature and no significant change in the spectroscopic pattern was observed upon lowering the temperature (see the Supporting Information, Figures S27 and S37). At 223 K, the free-base form of macrocycle **9** exhibited three correlations in the aromatic region (see the Supporting Information, Figure S38) between peaks at $\delta = 7.45$ and 7.79 ppm, $\delta = 7.52$ and 7.89 ppm, and $\delta = 7.65$ and 7.95 ppm. The correlation between the signals at $\delta = 2.56$ and 7.45 ppm clearly indicated that the signals at $\delta = 7.45$ and 7.79 ppm corresponded to the *m*-CH and *o*-CH protons of the *meso*-tolyl substituents, respectively. In the ROESY spectra of the free-base form of macrocycle **8** at 253 K (see the Supporting Information, Figure S29), the resolution of the spectra was too low to allow for conclusive assignment of all the peaks. However, the observation of methyl signal for the *N*-methyl pyrrole moiety at $\delta = 3.25$ ppm in the spectra of both the macrocycles in the free-base form, strongly downfield of the signal that regular N-substituted porphyrins usually exhibit (e.g., $\delta = -4.322$ ppm for NCH_3–TPPH),[11] and the observation of two closely spaced doublets at $\delta =$ 8.56 ppm, which could be assigned to the thiophene/selenophene β-CH protons, provided confirmation of the structures as shown in Scheme 3. The calculated $\Delta\delta$ value of 6.0 ppm suggested that the aromaticity in the free-base form was lower



Scheme 3. Charge-separated resonance structures (bold lines denote the delocalization pathways).

than that of an [18π] porphyrin system. Macrocycles **8** and **9** happened to be cross-conjugated systems, for which dipolar resonance contributors could be written (**8**′ and **9**′, respectively; Scheme 3); that imparted a degree of porphyrinoid aromaticity onto the macrocycles, thereby leading to the observation of a weak diatropic ring current in their ^{1}H NMR spectra. In other word, the charge separation in the dipolar resonance structure, as shown in Scheme 3, contributed to the reduced aromaticity.

Even though it was not possible to conclusively assign all of the peaks for the free-base form of both macrocycles, owing to dynamic conformational fluxionality, a profound change in spectroscopic pattern was observed in the fully protonated state by adding 10% trifluoroacetic acid in $CDCl_3$ (v/v) at 298 K. This change was owing to the fact that protonation constrained the conformational dynamics of the macrocycles, even at ambient temperature, thereby affording sharp signals. A representative ^{1}H NMR pattern of macrocycle **8** in its protonated form is shown in Figure 3. To differentiate between the heterocyclic β-CH protons and the *meso*-aryl CH protons, 2D NOESY spectra (see the Supporting Information, Figure S33) were recorded in addition to 2D COSY spectra (see the Supporting Information, Figure S32) at ambient temperature, because lowering the temperature led to coalescence of the signals and no conclusive results were obtained (see the Supporting Information, Figure S31). There were two 3H singlets at $\delta = 2.70$ and 2.71 ppm, which corresponded to the methyl peaks of the *meso*-tolyl rings. The tolyl *m*-CH protons were unequivocally assigned to the multiplet at $\delta = 7.61$–7.63 ppm, based on the correlation with the signals at $\delta = 2.70$–2.71 ppm in the 2D COSY spectra (see the Supporting Information, Figure S32). In turn, this multiplet showed a strong correlation with the broad signal at $\delta = 8.11$ ppm, thus allowing the assignment of the later signal as the *o*-CH protons of the tolyl substituents (see the Supporting Information, Figure S32). The peak at $\delta = -1.03$ ppm was unambiguously assigned as the NH proton of the pyrrole rings upon protonation, as confirmed by D_2O-exchange experiments (see the Supporting Information, Figure S46). Two overlapping doublets at $\delta = 8.94$ and 8.92 ppm, which exhibited dipolar coupling with the broad signal at $\delta = 8.11$ ppm in the 2D ROESY spectra (see the Supporting Information, Figure S33) without exhibiting any scalar coupling with any signal(s) in the shielded/deshielded regions, were unambiguously assigned to the β-CH protons of the selenophene. There were four well-resolved doublets at $\delta = 8.20$, 8.22, 8.38, and 8.55 ppm, which exhibited a typical COSY pattern for pyrrole β-CH protons (see the Supporting Information, Figure S32). The two sets of well-resolved doublets at $\delta = 8.22$ and 8.55 ppm were unequivocally assigned to the β-CH protons on the same pyrrole ring, owing to a correlation between them in the 2D COSY spectra (see the Supporting Information, Figure S32) and dipolar coupling between the signal at $\delta = 8.55$ ppm with the *o*-CH proton of the *meso*-tolyl substituent at $\delta = 8.11$ ppm in 2D ROESY spectra (see the Supporting Information, Figure S33). The doublet at $\delta = 8.38$ ppm exhibited dipolar coupling with the broad signal at $\delta = 8.21$ ppm in the 2D ROESY spectra (see the Supporting Information, Figure S33), whilst also exhibiting scalar coupling with the signal at $\delta = 8.20$ ppm in the 2D COSY spectra; thus, the doublets at $\delta = 8.38$ and 8.20 ppm corresponded to the β-CH atoms of the other pyrrole ring, thereby confirming the assignment of the later signal as the *o*-CH protons of the phenyl rings. The spatial proximity of the signal at $\delta = 3.56$ ppm and the signal at $\delta = 7.38$ ppm enabled us to identify a correlation in the 2D ROESY spectra (see the Supporting Information, Figure S33); thus, this later signal corresponded to both the α-CH protons of the *N*-methyl pyrrole ring. These observations were consistent with the prevalence of no pyrrole/thiophene ring-inversion, except the protruding *N*-methyl pyrrole ring. Our assignment of all of these peaks was further supported by 2D HSQC experiments (see the Supporting Information, Figure S35). To obtain a satisfactory interpretation of these surprising chemical shifts, we invoked a ring-current effect, because the manifestation of a porphyrin-like aromatic ring current is usually accounted for by the downfield shifts of the peripheral substituents and up field shifts of the inner NH/CH protons. The $\Delta\delta$ value—that is, the difference between the chemical shifts of the inner (NH/CH) and outer ring protons in the ^{1}H NMR spectrum—of 9.97 ppm implied a diatropic ring current for macrocycle **8** upon com-

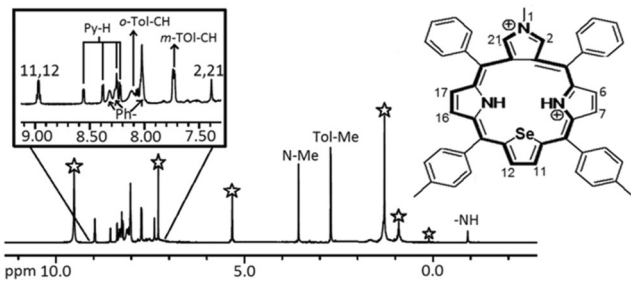


Figure 3. ^{1}H NMR spectra of macrocycle **8** in 10% $CF_3COOH/CDCl_3$ (v/v) at 298 K.

plete protonation.[12] The increased diatropic character compared to the free-base form was attributed to the favorable canonical form $\mathbf{8H_2}^{2+}$, which no longer required charge separation, as in structure **8′**, but instead mediated charge delocalization. In other word, the macrocyclic aromaticity was retained through a 20 π electron-delocalization motif. The magnetic inequivalency of the selenophene protons and the pyrrole ring protons unambiguously supported a lower symmetry of the macrocyclic ring in the diprotonated form.

The observation of four sets of signals for the β-CH protons of the two pyrrole rings but only one NH signal clearly indicated a much-faster NH tautomerization within the NMR timescale, which persisted even after lowering the temperature (see the Supporting Information, Figure S31). Another interesting observation was the isolation of a single signal for the α-CH protons of the *N*-methyl pyrrole ring. This result could be owing to the fact that the protruding *N*-methyl pyrrole ring deviated from the mean macrocyclic plane (defined by the six *meso*-carbon atoms) to the same extent on both sides and, hence, both the α-CH protons experienced the macrocyclic diamagnetic ring current to an equal extent. A similar spectroscopic observation was found for the macrocycle **9** upon complete protonation (see the Supporting Information, Figures S37–S45).

Given a low symmetry conformation with aromaticity in a [20] π-electron conjugation pathway, the macrocycles could not be planar and the preferred conformation could include a Möbius twist. Although this structure has not been confirmed by single-crystal X-ray diffraction analysis, DFT level optimized geometries revealed the presence of a characteristic Möbius twist in the *N*-methyl pyrrole linked region of the macrocycles in the free base as well as in the protonated state (see the Supporting Information, Figures S47 and S48). The nucleus-independent chemical shift, NICS(0), values[13] at the center of the macrocycles were $\delta = -4.7$ and -2.9 ppm (see the Supporting Information, Figures S49 and S50) for the free-base **8** and **9**, respectively, which accounted for the presence of a weak diatropic ring current, owing to dipolar resonance contribution (Scheme 3). Notably, the more aromatic character that was associated with the cross-conjugated arene unit (the NICS(0) value at the center of the *N*-methyl pyrrole ring was > -11 ppm; see the Supporting Information, Figures S49 and S50), the lower the aromaticity that would be present in the macrocycle.

Both macrocycles **8** and **9** were found to be robust towards electrochemical oxidation and reduction. Electrochemical studies were performed by using cyclic voltammetry and differential pulse voltammetry with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. Macrocycle **8** exhibited two irreversible oxidations at 0.776 and 1.104 V, followed by a quasireversible oxidation at 1.311 V, with an estimated HOMO–LUMO gap of 1.714 V. Macrocycle **9** exhibited two irreversible oxidation peaks at 0.714 and 1.089 V, followed by a reversible oxidation peak at 1.342 V, with an estimated HOMO–LUMO gap of 1.778 V (see the Supporting Information, Figure S51). The slightly narrower HOMO–LUMO gap for macrocycle **8** compared to macrocycle **9** also accounted for the red-shift in the electronic absorption spectrum of macrocycle **8**. Notably, [20] aromatic macrocycles **8** and **9** showed significantly narrower HOMO–LUMO gaps than the [18] tetraphenyl porphyrin (2.24 V) and the monothiatetraphenyl porphyrin (2.09 V),[14] thus suggesting a higher degree of delocalization of the π electrons in macrocycles **8** and **9**. This result was also reflected in the red-shift of the Soret and Q-bands in the UV/Vis spectra of the macrocycles **8** and **9**.

In conclusion, we have reported the first synthesis of an unconventional tripyrrane moiety from the regioselective β-benzoylated pyrrole. The unconventional 3,4-linkages of N-methyl pyrrole unit admirably served as incentive to two different types of highly stable [20] aromatic heteroannulenes. Most importantly, the presence of the "local" aromatic unit (considering 3,4-linkages of *N*-methyl pyrrole) in the macrocyclic core didn't quench the diatropic ring-current effect of the macrocycle, as confirmed by ^{1}H NMR spectra. To the best of our knowledge, these observations are unprecedented. The synthesis of more such structural variants is currently underway in our laboratory.

Experimental Section

Synthesis of Macrocycle 8

Tripyrrane **5** (2.29 g, 5.85 mmol) and 2,5-bis(tolylhydroxymethyl)selenophene (**6**; 2.17 g, 5.85 mmol) were added in CH_2Cl_2 (600 mL) and the mixture was stirred for 15 min under a nitrogen atmosphere to obtain a clear solution. Next, *para*-toluenesulfonic acid (0.1 g, 0.58 mmol) was added and the solution was stirred for 1 hr in the dark. Then, *p*-chloranil (4.32 g, 17.56 mmol) was added and the resulting mixture was heated at reflux for 1 hr in air and then stirred at RT for 10 h. After removal of the solvent from the crude mixture by rotary evaporation, the product was purified by column chromatography on basic alumina using 20% CH_2Cl_2/hexane followed by repeated column chromatography on silica gel using 40% CH_2Cl_2/hexane. Yield 43 mg (ca. 10%); ^{1}H NMR (500 MHz, 10% $CF_3COOH/CDCl_3$, 300 K): $\delta = -1.03$ (s, 2H; NH), 2.70 (s, 3H), 2.71 (s, 3H), 3.56 (s, 3H), 7.38 (br s, 2H), 7.61–7.67 (br s, 4H), 8.02–8.07 (br s, 6H), 8.11 (br s, 4H), 8.20 (d, $J = 4.5$ Hz, 1H), 8.21 (br s, 2H), 8.22 (d, $J = 4.5$ Hz, 1H), 8.31 (br s, 2H), 8.38 (d, $J = 4.5$ Hz, 1H), 8.55 (d, $J = 4.5$ Hz, 1H), 8.92–8.94 ppm (m, 2H); UV/Vis (CH_2Cl_2, 298 K): λ_{max} (ε) = 456.41 (74450), 584 (shoulder), 624.35 (9720), 675.45 nm (11000 $mol^{-1} dm^3 cm^{-1}$); UV/Vis (CH_2Cl_2, 1% TFA/CH_2Cl_2, 298 K): λ_{max} (ε) = 492.67 (82900), 750.73 (15540), 883.88 nm (12900 $mol^{-1} dm^3 cm^{-1}$); MS (MALDI): *m/z* calcd for $C_{47}H_{35}N_3Se$: 721.2; found:722.4.

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Keywords: core modification · heteroannulenes · Möbius aromaticity · regioselectivity · unorthodox tripyrranes

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