

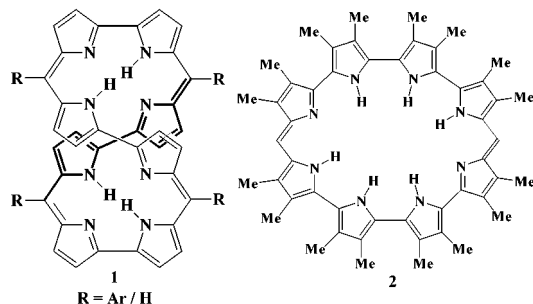
34 π Octaphyrin: First Structural Characterization of a Planar, Aromatic [1.0.1.0.1.0.1.0] Octaphyrin with Inverted Heterocyclic Rings

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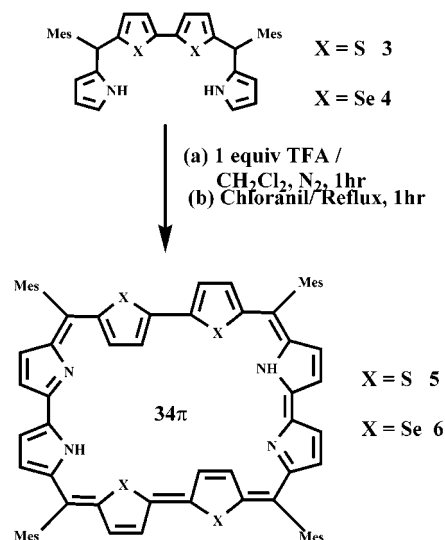
Octaphyrin is a cyclic molecule in which eight pyrrole rings are connected to each other through meso carbon bridges. A range of octaphyrins **1** containing 32 π , 34 π , and 36 π electrons are known, and all of them exhibit chiral figure-eight conformation and are nonaromatic.^{1,2} Very recently, Sessler and co-workers reported the synthesis of a 32 π octaphyrin **2** through an oxidative coupling reaction, which does not exhibit a figure-eight conformation.³ This has been attributed to the presence of only two meso carbons and a greater number of direct pyrrole–pyrrole links.



Synthesis of planar aromatic octaphyrins is still a challenge not only from the point of view of synthesis, but also from the point of validity of the (4n+2) Huckel rule for higher annulene systems. Herein we report on the successful synthesis of a planar modified octaphyrin, which exhibits aromaticity both in freebase and protonated forms, thus providing direct experimental evidence for validity of the Huckel rule.

We have recently made use of oxidative coupling reaction of a modified tripyrrane to synthesize 26 π rubyryns in which two direct pyrrole–pyrrole links were generated in the final step of the reaction.⁴ Sessler and co-workers following a similar methodology synthesized **2** using a quarterpyrrole precursor.³ In the

Scheme 1



present synthesis, our strategy was to use a modified 20,21-dithiatetrapyrromethane with two meso carbon bridges for the [4 + 4] coupling reaction. Thus, reaction of (5,15-dimesityl-20,21-dithio-1-norobilane) **3** in the presence of 1 equiv of trifluoroacetic acid (TFA) catalyst in methylene chloride under inert atmosphere followed by chloranil oxidation in air and chromatographic purification gave **5** as a lustrous bronze solid in 5% yield (Scheme 1). **6** was also synthesized by a similar procedure using **4** as the precursor in 5% yield.

The UV–visible spectrum of **5** in dry methylene chloride (Figure 1) exhibits a very intense Soret-type band [598 nm, (log ϵ = 4.95)] and a series of Q bands [754 (3.95), 835 (4.1) and 906 nm (3.85)], and on diprotonation these bands experience red-shifts which is typical of meso aryl porphyrins and expanded porphyrins⁵ [for [5.2H]²⁺, Soret band, 645 nm (log ϵ = 5.45), Q bands 794 (3.68), 873 (3.9) and 998 nm (4.57)]. The ϵ values for the most intense band goes up more than 3 times upon diprotonation, and the magnitude of these values are higher than those reported for other octaphyrins.^{1,2}

Detailed ¹H and 2D NMR studies have been performed in two different solvents (*d*₈-toluene and CDCl₃), between the temperature range 330–208 K to understand the dynamic structural behavior of **5** and **6** in solution. All of the assignments were based on the correlations seen in COSY and the NOESY spectra. The important feature of the NMR studies is the observation of two different conformers in solution, and separate set of peaks have been observed for both the conformers in the aromatic and the shielded region. Furthermore, in both the conformers, one thiophene ring of each bithiophene unit is inverted as inferred from the observation of β -CH protons of these rings in the shielded region. For example, for conformer I, in toluene-*d*₈ at 248 K, two sharp doublets appear at –5.3 and –5.89 ppm assigned to β -CH protons of the inverted thiophene rings and three sets of doublets in the region 11.5 to 10.1 ppm assigned to bipyrrrole and the noninverted thiophene β -CH protons. The pyrrole NH protons are observed as a broad singlet at –2.21 ppm. On the other hand conformer II showed a less planar structure relative to that of conformer I as inferred by the greater number of peaks observed. In this case four doublets (third and fourth are merging; refer to Supporting Information) are observed in the region –3.28 to –3.61 ppm in toluene-*d*₈ assigned to β -CH protons of the inverted thiophene

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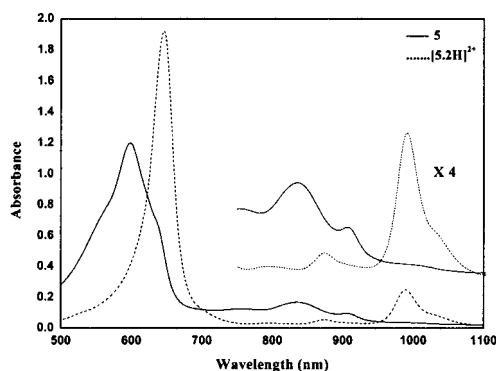


Figure 1. Electronic absorption spectra of **5** in freebase (—) and diprotonated (···) form in methylene chloride. The concentration for freebase is 1.35×10^{-5} M, and that for diprotonated is 6.76×10^{-6} M.

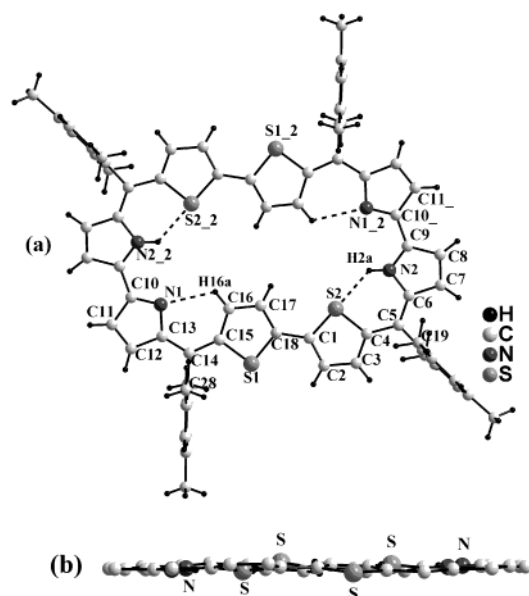


Figure 2. Crystal structure of **5**. (a) Top view (the dotted lines show the intramolecular hydrogen bonding); (b) side view showing the planarity of the molecule (mesityl rings and the hydrogens are removed for clarity).

rings. The two pyrrole NH protons now resonate as two broad singlets at -0.8 and -4.16 ppm, suggesting their magnetic inequivalence. In the aromatic region six sets of doublets were observed in the region 10.7 – 9.3 ppm assigned to the bipyrole and noninverted thiophene β -CH protons. An estimate of the apparent sustained diamagnetic ring current from the chemical shifts of the most shielded and the deshielded protons gave a value of $\Delta\delta = 17.32$ ppm for conformer I and 14.89 ppm for the conformer II in toluene- d_8 . These values are slightly higher than those observed for meso aryl 30π aromatic heptaphyrins⁶ and 26π aromatic rubeprins.⁴ Thus, ^1H NMR data in conjunction with UV–visible spectral data gives a strong evidence for the aromatic nature of **5** and **6**.

The confirmation of the planar structure for **5** came from the single-crystal X-ray analysis.⁷ The structure confirms (Figure 2) the inversion of one thiophene ring in each of the bithiophene units. The dihedral angle for the inverted thiophene with respect to the mean plane defined by four meso carbon atoms is 4.67° . The C_β – C_β distance of inverted thiophene and normal thiophene

shows small difference [$C(16)$ – $C(17)$ is 1.385 Å while $C(2)$ – $C(3)$ is 1.4 Å] suggesting a modified electron delocalization pathway. The C_β – C_β distance of pyrrole rings [$C(7)$ – $C(8)$ is 1.339 Å] is in the range observed for that of other aromatic rubeprins and saphyrins.⁴ The aromatic nature of **5** is evident from the observation of the C_α – C_β distance greater than the C_β – C_β distance for both the thiophene and pyrrole rings (1.385 vs 1.414 Å for thiophene and 1.337 vs 1.451 Å for pyrrole). The meso mesityl rings are exactly perpendicular to the mean plane of the meso carbon atoms (dihedral angles: 90.3° and 88.6°). There are two independent molecules in the asymmetric unit cell, and these are linked to each other through weak inter- and intramolecular hydrogen-bonding interactions (refer to Supporting Information for detailed structure). The planarity of the macrocycle excluding the meso phenyl ring is obvious from the side view (Figure 2). There are four intramolecular hydrogen-bonding interactions inside the cavity: two involving $C\text{--}H\cdots N$ (3.378 Å, $115.88(0)^\circ$) and two involving $N\text{--}H\cdots S$ (3.099 Å, $131.43(0)^\circ$). This structure corresponds to the planar conformer I observed in NMR studies. Two tautomers are possible in solution by shifting the pyrrole hydrogens. The conformer I corresponds to the tautomer where the hydrogens are placed on nitrogens adjacent to the noninverted heterocyclic rings (Scheme 1). In the second tautomer the hydrogens are on the pyrrole nitrogens which are adjacent to the inverted thiophene ring in which there will be repulsion between the $N\text{--}H$ proton and the inverted ring $C\text{--}H$ protons due to which the heterocyclic ring is tilted out of the porphyrin plane defined by the four meso carbons, thus making the ring nonplanar as observed in the X-ray structure (see the Supporting Information). NMR studies also justify such a conclusion where multiple sets of peaks are observed for NH and CH protons.

An attempt has been made to justify the observed inversion of thiophene rings in the structure by calculation of relative energies for the inverted and the noninverted structure by ab initio and semiempirical methods.⁸ The result shows that the inverted structure is more stable by 18.14 kcal/mol relative to the noninverted structure for freebase of **5**. For the diprotonated derivative, the calculation shows that the inverted structure is more stable by 9.26 kcal/mol with respect to the noninverted structure. We believe the absence of β -alkyl substituents in the pyrrole rings and the presence of strong intramolecular hydrogen-bonding interactions are responsible for the planar structure observed here in contrast to figure-eight octaphyrins. Thus, in summary, we have successfully synthesized planar 34π octaphyrins by a simple methodology using a single precursor, and the spectroscopic and structural data clearly suggest that the octaphyrins **5** and **6** are aromatic. To the best of our knowledge this is the first example of an aromatic planar 34π expanded porphyrin containing eight heterocyclic rings⁹

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Supporting Information Available: Experimental details describing the synthesis and characterization through ^1H , 2D and NOESY NMR, and FAB mass spectra for **5** (PDF) as well as an X-ray crystallographic file (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(7) X-ray data for **5** 90(2) K: black crystals, $C_{72}H_{62}N_4S_4$, $M_w = 1111.55$, size = $0.78 \times 0.70 \times 0.50$ mm³ triclinic space group $P-1$, $a = 15.3559(4)$ Å, $b = 21.8104(6)$ Å, $c = 23.3852(6)$ Å, $\alpha = 100.0340(10)^\circ$, $\beta = 100.7120(10)^\circ$, $\gamma = 107.4260(10)^\circ$, $V = 7117.4(3)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.097$ Mg/m³, $R = 0.0662$, $R_w = 0.1795$, GOF = 1.102.

(8) Ab initio calculations were done by Gaussian 94 using 3-21G* basis set. For semiempirical calculations Hyperchem 6.01 was used. The AM1 method was used, and the convergence criterion for SCF was 0.001. The RMS gradient of 0.1 kcal/mol was kept as termination criteria.

(9) There are two 34π aromatic porphyrins known in the literature thus far; one is [5.5.5.5] porphyrin and the other is [2.2.2.2.2.2]hexathiahexaphyrin. For details, see: Knobel, G.; Franck, B. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1170 and ref 2a.