Communication

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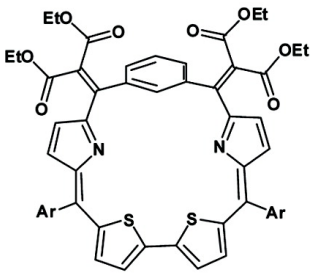

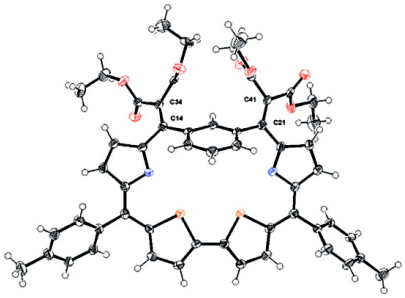

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Dithiabenzisapphyrin: A Core-Modified Sapphyrin Bearing Exocyclic Double Bonds at the *meso*-Positions

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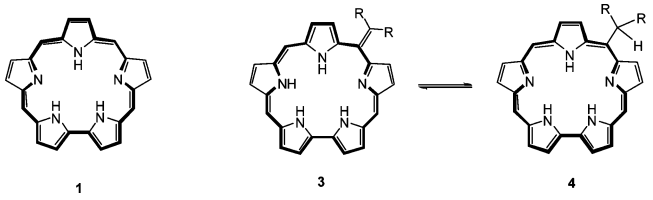
Sapphyrins **1**, the oldest known member of the expanded porphyrin family,[1] are among the most widely studied of the porphyrin analogues. This reflects both their venerable status and their potential applications in anion binding/sensing,[2,3] medicine,[4,5] and materials science.[6] Accordingly, many structural variants of sapphyrins have been reported, including *meso*-substituted sapphyrins,[7] β-substituted sapphyrins or carbasapphyrin,[8] N-confused analogues,[9] and core-modified sapphyrins where one or more of the pyrrole rings is replaced with another aromatic subunit.[10] In the case where the latter replacement involves benzene, the result is a system lacking in global aromaticity. Other sapphyrin derivatives are known wherein the primary conjugation pathway is interrupted as the result of serendipitous nucleophile insertion processes.[11] While these latter systems display interesting chemical and spectroscopic properties, we are not aware of any systematic efforts to control and modulate the conjugation pathways present in sapphyrins. One convenient approach to achieving this goal could be through the use of exocyclic double bonds at the *meso*-positions. We have recently found that *meso*-bisalkylidenyl porphyrins may be stabilized via the introduction of bulky substituents at the *meso*-(α)-positions[12] and wish to report here that this approach may be extended to produce a new class of nonaromatic *meso*-alkylidenyl dithiabenzisapphyrin derivatives (e.g., **2**).

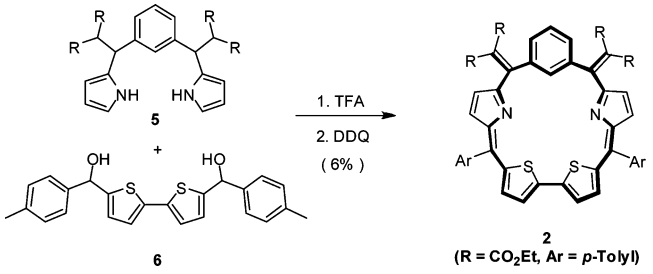
This system, wherein the presence of the exocyclic double bond at the *meso*-position(s) serves to disturb the full conjugation of the macrocycle, is to the best of our knowledge without precedent in the expanded porphyrin literature.[13] Unlike the fully conjugated parent sapphyrin system **1** that contains an aromatic 22 π-electron periphery, the putative structure **3**, which bears an exocyclic double bond at a *meso*-position, is not expected to exhibit global aromaticity due to the disrupted nature of the electronic pathway (Scheme 1). However, in principle, structure **4** can undergo tautomerization to produce structure **3**, an isomer that would be expected to display extensive conjugation. If the exocyclic double bond at the *meso*-position is structurally locked, this interconversion process could be impeded with the consequence that the macrocyclic structure would be maintained in the more conjugated form represented by structure **3**. In other words, the electronics of the system are potentially subject to chemical control.

On the basis of our prior studies of porphyrin derivatives, we appreciated that the use of bulky substituents at the *meso*-(α)-position might provide a means of accomplishing the structural locking needed to obtain macrocycles of generalized structure **3**. However, since the number of possible tautomeric forms increases with the number of protons inside the cavity, we also appreciated that it would be necessary to reduce the number of NH groups within the core if easy-to-analyze models for sapphyrins **3** and **4**

Scheme 1



Scheme 2



were to be obtained. These considerations led us to target the dithiabenzisapphyrin analogue **2** as a first generation model system with which to explore the effects of *meso* exocyclic methylene group functionalization within a sapphyrin-type core.

The synthesis of **2** is shown in Scheme 2. Precursor **5** was obtained from the reaction of tetraethyl-(2,2′-(1,3-phenylenebis-(methan-1-yl-1-ylidene))dimalonate with pyrrole in the presence of a Lewis acid catalyst, as described previously.[12] The bithiophene diol **6** was synthesized from bithiophene by treating with first *n*-butyllithium and then *p*-tolualdehyde.[12,13] Acid-catalyzed condensation of **5** with dicarbinol **6** in acetonitrile, followed by oxidation with DDQ, then afforded sapphyrin **2** in 6% yield. The ^{1}H NMR spectrum of **2** reveals no evidence of a macroaromatic ring current effect. For instance, the β-pyrrolic protons appear at 6.74 and 6.80 ppm as two sets of doublets (J = 4.5 Hz), as would be expected for a system that is nonaromatic.

The solid-state structure of **2** is shown in Figure 1. It reveals that the benzene moiety resides in an orientation that is almost inverted relative to the mean plane of the macrocycle, with an inward tilt angle relative to this plane of 37.3°. Both exocyclic double bonds are distorted from coplanarity. The dihedral angle (α) of the C14−C34 double bond is 16.2°, while that of the C21−C41 double bond is 9.5°.

These observations are consistent with the intuitively reasonable conclusion that the steric congestion between the *meso*-(α)-substituents and the benzene moiety within the macrocyclic ring serves to restrict the conformational mobility of the system and disrupt any putative extended conjugation within the system.

These electronic effects are reflected in the absorption spectrum of **2** taken in CH_2Cl_2 (cf. Figure 2). While a Soret and Q-like bands

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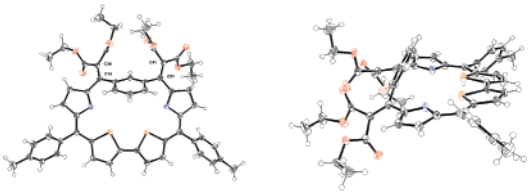

(a) (b)

Figure 1. Solid-state structure of **2** showing partial atom labeling scheme as deduced from X-ray diffraction analyses: (a) top view and (b) side view. The benzene ring is largely inverted and is tilted inward off the mean macrocycle plane by 37.3°. The thermal ellipsoids are scaled to the 50% probability level.

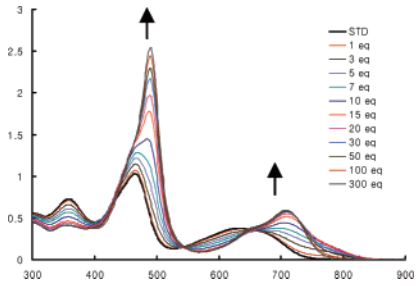

Figure 2. UV−vis titration of **2** with trifluoroacetic acid ([**2**] = 2.25 × 10^{-5} M in CH_2Cl_2, saturation at [**2**] + 300 equiv of TFA).

are observed at 465 and 630 nm, the intensities (ϵ = 44 700 and 13 200, respectively) are greatly reduced relative to what is normally seen for β-substituted sapphyrins.[14]

Titration of sapphyrin **2** with trifluoroacetic acid (up to 300 equiv) produces a gradual shift in the Soret-like band from 465 to 491 nm and a slightly greater change in the Q-band (final λ_{max} = 709 nm). The original free base spectrum is fully recovered upon addition of excess base (e.g., triethylamine), as would be expected for a reversible protonation−deprotonation process.

The addition of 7.0 equiv of acid to a dichloromethane solution of **2** resulted in the formation of diprotonated species. A 2D ^{1}H COSY spectrum obtained after addition of 7.0 equiv of trifluoroacetic acid at 233 K is consistent with protonation occurring at the pyrrolic nitrogen (Supporting Information). For example, the two proton resonance appearing at 13.35 ppm shows scalar coupling with β-pyrrolic hydrogens which appeared at 7.28 and 7.12 ppm. Interestingly, no couplings between the β-pyrrolic protons and the NH protons are observed. The unusual low field shift of the pyrrole N−H can be explained by additional hydrogen bonding with sulfur in the thiophene moiety. The protonation site observed in **2** is comparable with similar alkylidenyl porphyrin analogues reported previously.[12] The upfield shift of the aryl-H signals is in accord with a change in the tilt angle of the aryl portion of the molecule. Unlike other fully aromatic sapphyrins,[10,15] complete inversion of the phenyl group is likely to be difficult due to the bulky *meso*-alkylidenyl groups as well as the protons present in the core; nonetheless, a slight dynamic peak broadening was observed at low temperature.[16] Furthermore, the two sets of signals ascribed to the two ethoxy groups remain intact upon the addition of acid.

In summary, we have demonstrated that dithia analogues of *meso*-alkylidenyl sapphyrins can be prepared as stable species. The present first generation model, **2**, is nonplanar and characterized by a partially conjugated electronic structure. As such, it helps to define further the interplay between macroaromaticity and π-conjugation in porphyrinoid systems while serving to underscore the diverse nature of conjugation and aromaticity effects in expanded porphyrin chemistry.

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Supporting Information Available: Complete experimental details and corresponding spectral data are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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