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## Porphyrins Based on Thiophene

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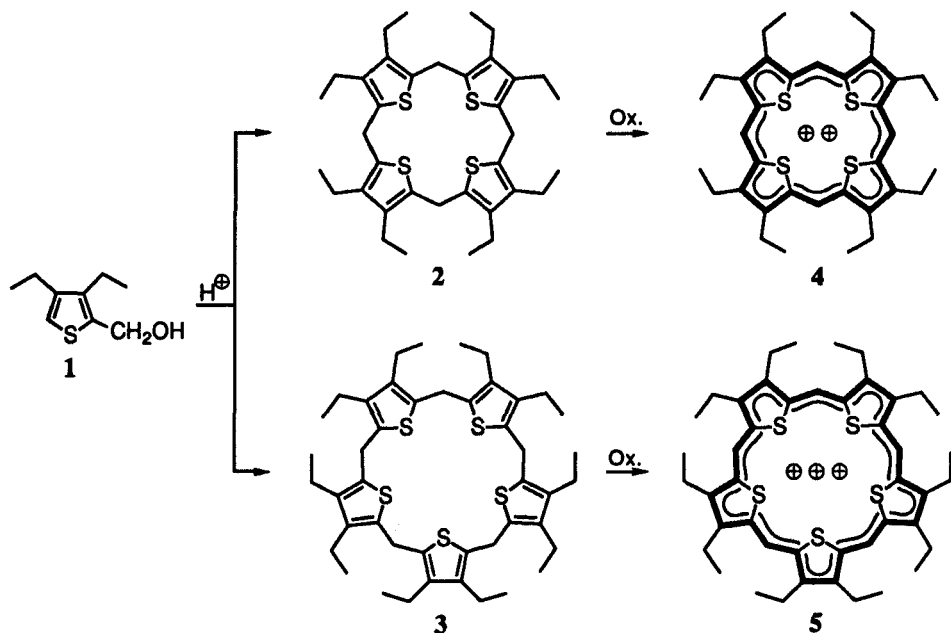
## PORPHYRINS BASED ON THIOPHENE

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**Abstract** The virgin field of "Porphyrins Based on Thiophene" is opened up by the biomimetic-type cyclocondensation of the  $\alpha$ -hydroxymethylthiophene **1**.

Guided conceptually by the [18]annulene model of porphyrin, we embarked some time ago on a systematic exploration of potentially aromatic porphyrin structural variants that could be expected to generate interdisciplinary interest. As a result, the porphycenes<sup>1</sup> and metalloporphycenes as well as the tetraoxa-,<sup>2</sup> tetrathia-<sup>3</sup> and tetraselenaporphyrin dications<sup>3</sup> were discovered.



The tetrathiaporphyrin dication (as its perchlorate salt), which was synthesized from furfuryl alcohol via tetraoxaporphyrinogen and tetrathiaporphyrinogen, qualifies as aromatic despite the fact that it deviates from planarity due to the steric interference of the four sulfur atoms<sup>3</sup>. As the development of the chemistry of the parent dication is hampered by poor solubility of the compound, efforts to employ its octaethyl derivative **4** suggested themselves.

In line with expectation, the octaethyltetrathiaporphyrin dication **4** (as its perchlorate salt), readily obtained from **1** by the two-step reaction sequence of acid-catalyzed cyclocondensation (to give **2** in 25% yield) and oxidation, proved to be amenable to the desired chemical exploration.

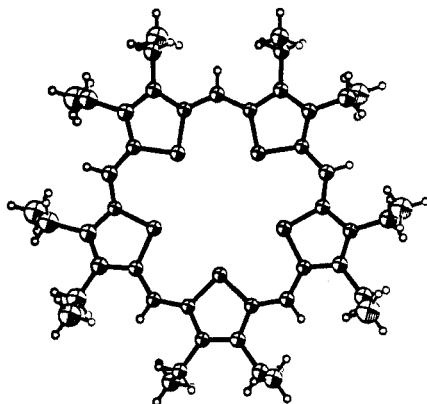
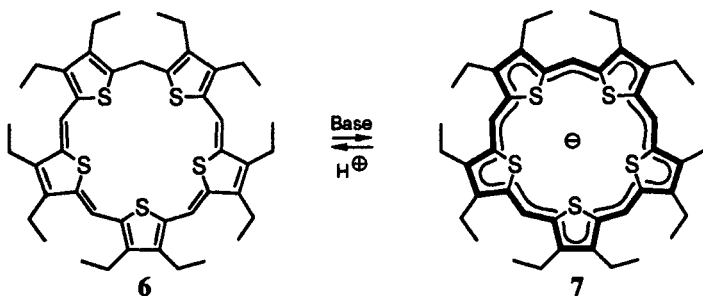


FIGURE 1 Molecular structure of **5** (as its hexachloroantimonate salt)

Surprisingly, the acid-catalyzed condensation of **1** afforded, in addition to **2**, the cyclic pentacondensation product **3** (in 20% yield). This finding turned out to be a great bonus since it led to the discovery of the novel pentathiapentaphyrin trication<sup>4</sup> **5** (as its hexachloroantimonate and as other salts) which, as inferred from its spectra, constitutes a  $22\pi$  Hückel-aromatic species. According to X-ray crystallographic analyses (performed on **5** with various counter anions) the trication **5** - in striking contrast to the parent tetrathiaporphyrin dication and to **4** - is planar (Figure 1).



The intriguing chemistry associated with **3** and **5** is reflected in the generation of unusual thiophene-based macrocycles, notably **6** and the  $26\pi$  Hückel-aromatic monoanion **7**.

## REFERENCES

1. E. Vogel, M. Köcher, H. Schmickler, J. Lex, *Angew. Chem. Int. Ed. Engl.*, **25**, 257 (1986); E. Vogel, *Pure Appl. Chem.*, **62**, 557 (1990).
2. E. Vogel, W. Haas, B. Knipp, J. Lex, H. Schmickler, *Angew. Chem. Int. Ed. Engl.*, **27**, 406 (1988); W. Haas, B. Knipp, M. Sicken, J. Lex, E. Vogel, *Angew. Chem. Int. Ed. Engl.*, **27**, 409 (1988); E. Vogel, *Pure Appl. Chem.*, **65**, 143 (1993).
3. E. Vogel, P. Röhrig, M. Sicken, B. Knipp, A. Herrmann, M. Pohl, H. Schmickler, J. Lex, *Angew. Chem. Int. Ed. Engl.*, **28**, 1651 (1989).
4. H. Rexhausen, A. Gossauer, *J. Chem. Soc. Chem. Commun.*, **1983**, 275.