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Notes

Crystal and Molecular Structure of 21-Thia-5,20-diphenyl-10,15-bis(*p*-nitrophenyl)porphyrin and 21,23-Dithiatetraphenylporphyrin. The Influence of Sulfur on the π-Delocalization Pattern

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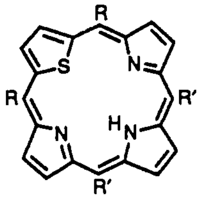
Introduction

Core modification of porphyrins by the introduction of various heteroatoms in place of the pyrrole nitrogen atoms allows for the preparation of a series of new heterocycles that have interesting properties both in terms of their aromatic character and their ability to bind metal ions. The series of sulfur-containing porphyrins, 1–4, constitute a group where the core size is systematically varied. The monothiaporphyrins 1 have been extensively studied as ligands and are capable of binding metal ions with coordination numbers of 4, 5, and 6.[1-5] In these, the thiophene ring binds the metal ion through a pyramidal sulfur atom. As a result the thiophene ring is sharply bent out of the mean plane of the porphyrin. Some properties of the 21,23-dithiaporphyrin 2 were reported by Ulman and co-workers.[6-13] The isomeric 21,22-dithiaporphyrin as well as the trithiaporphyrin cation 3 do not appear to have been prepared. Recently Vogel and co-workers have presented elegant work on the tetrathiaporphyrin dication 4.[14]



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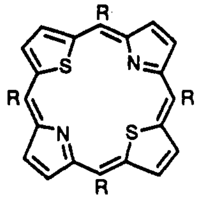

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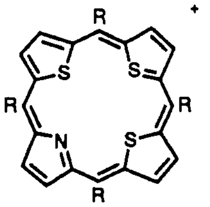

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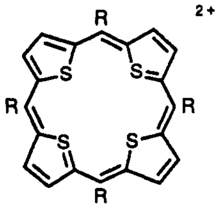

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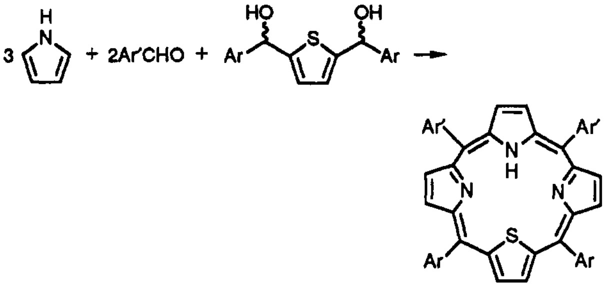
Here we report on structural studies of 1 and 2. Obtaining accurate structural information on these flat, disklike molecules presents some difficulties. Core modification alters the interior of these molecules while their external shape, which is responsible for crystal packing, remains relatively unaffected as long as the thiophene rings remain near the mean porphyrin plane. Consequently disorder frequently occurs in the solid state and as a result the structural information available is less precise.

Results

Structural Studies of 21-Thiaporphyrins. Previous structural work on STTPH (1, R = R' = p-$C_6H_4CH_3$) indicated that the molecule was planar, but the location of the sulfur atom was disordered with 38% occupancy of two sites trans to each other and 12% occupancy of the other two remaining sites.[1a] The synthetic route to the thiaporphyrin (reaction 2)[1b] allows for the introduction of



(1)

unsymmetrical substituents on the porphyrin periphery which have a structurally defined relationship to the location of the thiophene sulfur. These should introduce asymmetry into the molecular packing so that disorder is prevented. Two derivatives prepared for this purpose have been examined. Crystals of 21-thia-5,20-diphenyl-10,15-di-(p-tolylporphyrin SDPDTPH (1, R = C_6H_5, R' = p-$C_6H_5CH_3$) still show small signs of disorder which manisfest themselves in unusually small thermal parameters for the nitrogen atom trans to the thiophene sulfur and long C–N bonds for that pyrrole ring. Crystals of 21-thia-5,20-diphenyl-10,15-bis(p-nitrophenyl)porphyrin (1, R = C_6H_5, R' = p-$C_6H_4NO_2$), however, show no signs of disorder. Figure 1 gives relevant structural data for the thiaporphyrin core, which is slightly saddle shaped. This is best described by considering the dihedral angle between the plane of the four meso carbon atoms and the planes

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Table I. Bond Distances (Å) Relating to Delocalization Patterns in Thiaporphyrins

	pyrrole			thiophene		
	N–C_α	C_α–C_β	C_β–C_β	S–C_α	C_α–C_β	C_β–C_β
1 (R = Ph, R′ = *p*-NO_2Ph)	1.369 (6)	1.445 (6)	1.347 (5)	1.740 (4)	1.421 (4)	1.365 (7)
2 (R = Ph)	1.362 (5)	1.461 (6)	1.353 (5)	1.748 (4)	1.408 (6)	1.367 (7)
Ni^{II}(STPP)Cl[a]	1.383 (6)	1.457 (6)	1.380 (7)	1.744 (6)	1.412 (6)	1.370 (6)
TTP^{2+}[b]				1.725	1.412	1.363
TTPG[c]				1.725	1.359	1.420
thiophene[d]				1.714 (2)	1.370 (3)	1.423 (3)

[a] From ref 2. [b] Tetrathiaporphyrin dication, 4, from ref 14. [c] Tetrathiaporphyrinogen, from ref 14. [d] From ref 19.

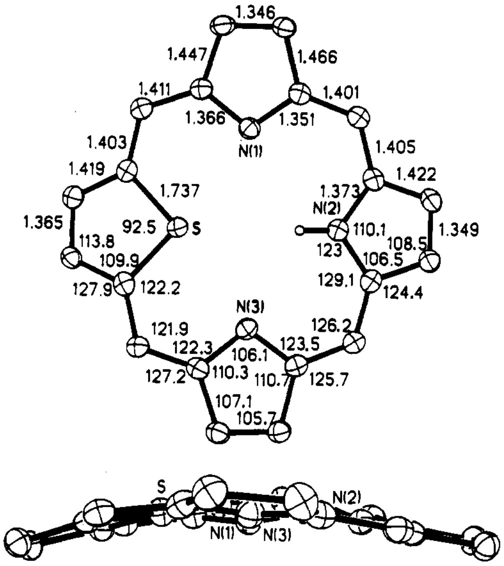

Figure 1. Top: dimensions within the core of 1 (R = C_6H_5, R′ = *p*-$C_6H_4NO_2$). The bond distances (Å) at the top and bond angles (deg) below are the average of the chemically equivalent parameters. Bottom: a view emphasizing the planar aspects of the thiaporphyrin.

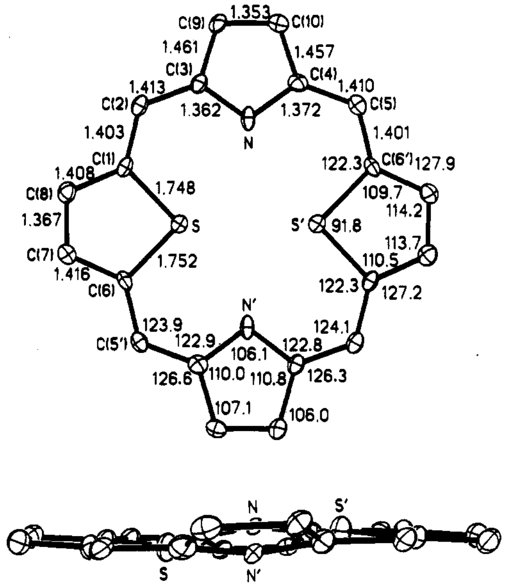

Figure 2. Top: dimensions within the core of 2 (R = C_6H_5). Bottom: a view emphasizing the planar nature of the dithiaporphyrin.

of the four five-membered rings. These are similar: thiophene, 14.1°; pyrrole (N(1)), −11.5°; pyrrole(N(2)), 10.0°; pyrrole (N(3)), −7.4°. The hydrogen atom bond to N(2) was located and refined. Its position is entirely consistent with previous ^{1}H NMR observations.[1] Because of the sulfur atom, the core size of the macrocycle is restricted: the nonbonded S–N(2) distance is 3.547 (8) Å while the nonbonded N(1)–N(3) distance (4.40 (1) Å) is somewhat longer than that in the tetragonal form (4.108 Å) or in the triclinic form (4.06, 4.20 Å) tetraphenylporphyrin.[15]

Structure of 21,23-Dithiatetraphenylporphyrin. Figure 2 gives the dimensions of the porphyrin core. Fortunately the molecule, which has a crystallographically imposed center of symmetry, is fully ordered. The deviations from planarity of the core, as expressed as the dihedral angle between the plane of the four meso carbons and the planes of the four-membered rings, are thiophene 4.9°, pyrrole (N) 12.9°. The nonbonded N···N′ distance is 4.65 (1) Å while the S···S′ distance is 3.069 (6) Å. (A S···S′ distance of 3.05 Å was quoted[11] from an unpublished structure (which gave no other information on the macrocycle) and an attractive S–S interaction was proposed for this molecule[11].) Notice that the S···S′ distance would be slightly shortened if the dithiaporphyrin were strictly planar. The S···S′ distance is considerably shorter than the sum of the van der Waals radii for two sulfur atoms (3.70 Å)[16] but longer than that of a typical S–S single bond (2.08 Å).[17] The cross-ring S···S distance (3.532 Å) in the dication 4[14] is much longer than the S···S distance in 2.

Conjugative Pathway and the Nature of S···S Interaction. Extensive delocalization exists throughout these macrocycles and extends to the thiophene fragment. Comparisons of bond distances within the pyrrole and thiophene portions of these and related macroycles are available in Table I.

Semiquantitative Fenske–Hall LCAO MO calculations[19] have been performed on these thiaporphyrins. These are approximate Hartree–Fock–Roothaan SCF LCAO molecular orbital calculations which depend only on the choice of wave functions and use the atomic coordinates (here for 1 and 2 with R = R′ = H) as input data. The characteristics of the bonding are presented as the Mulliken π overlap populations that are given in Table II. The values in that table correlate very well with the bond lengths shown in Table I.

There is an appreciable effect of the aromatic character of the macrocycle on the thiophene portion. The bond distances within the thiophene ring are altered as seen in Table I. Thus the C_α–C_β bond lengths in the 21-thiaporphyrin, its nickel complex, in dithiaporphyrin, and in the tetrathiaporphyrin dication are longer than the C_β–C_β distances whereas the reverse is true for thiophene[18] and tetrathiaporphyrinogen.[14] Thus the pattern of bond

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J. Org. Chem. **1991**, *56*, 4045–4048 **4045**

Table II. Two-Center Overlap Populations (Two-Center Population in Parentheses)

	SDPDPH	S_2TPP	thiophene
$N-C_\alpha$[a]	0.5174 (0.1049)	0.5342 (0.1069)	
$C_\alpha-C_\beta$[a]	0.5060 (0.0678)	0.4939 (0.0587)	
$C_\beta-C_\beta$[a]	0.6368 (0.2036)	0.6383 (0.1879)	
$S-C_\alpha$[b]	0.4653 (0.0689)	0.4558 (0.0699)	0.4639 (0.0830)
$C_\alpha-C_\beta$[b]	0.5457 (0.0951)	0.5451 (0.0999)	0.6362 (0.1912)
$C_\beta-C_\beta$[b]	0.6114 (0.1572)	0.6168 (0.1751)	0.5410 (0.1110)
$C_\alpha-C_m$[c]	0.5558 (0.1173)	0.5642 (0.1279)	
C_m-C_α[d]	0.5813 (0.1293)	0.5691 (0.1253)	
$S-S'$		0.0039 (0.0039)	

[a] The pyrroline moiety. [b] The thiophene moiety. [c] C_α from thiophene. [d] C_α from pyrroline.

lengths within the thiophene portion of these macrocycles is modified so that it conforms to the pattern seen in the pyrrole positions. However, the C_α–S bond length remains practically unchanged in all of these substances. These changes suggest that the π electron density has been altered within the thiophene portion so that it is increased in the C_β–C_β bond, decreased in the C_α–C_β bonds and unchanged in the C_α–S bonds. The overlap populations shown in Table II confirm this interpretation.

Comparison of the data for 1 and 2 indicates that whatever S···S interaction is present has negligible effect on the structure of the thiophene portion. The Mulliken overlap population data in Table II shows that there is a very small S···S overlap (0.0039) when d orbitals on sulfur are not included. When d orbitals are included, that overlap population increases only to a very small extent. For comparison we conducted a calculation for diatomic S_2 with the sulfur atoms separated by 3.06 Å (the S···S distance found in 2). The corresponding two-center overlap (0.1965) is considerably larger. We conclude that the S···S interaction is very weak in 2 and that it does not play a role in determining the delocalization pathway within the dithiaporphyrin.

The chemical shifts in the ^1H NMR spectra of dithiaporphyrin were discussed in terms of changes in the pathway of inner and outer aromaticity produced by specific core interaction,[9] but the structural results do not support this suggestion.

Experimental Section

Preparation of Compounds. Samples of 1 (R = C_6H_5, R' = *p*-$C_6H_5NO_2$)[1] and 2 (R = Ph)[6] were obtained by previously describe routes.

Crystal Structure Analysis. Dark blue prisms of 1 (R = C_6H_5, R' = *p*-$C_6H_4NO_2$ were obtained as a 0.5 M *n*-hexane solvate by diffusion of hexane into a dichloromethane solution of the macrocycle. Crystal data at 130 K: triclinic, space group $P\bar{1}$, a = 11.361 (3) Å, b = 12.708 (3) Å, c = 14.819 (4) Å; α = 108.91 (2)°; β = 93.84 (2); γ = 114.65 (2)°, Z = 2; R = 0.072; R_w = 0.081 for 5073 reflections with $I > 2\sigma I$ and 511 parameters.

Dark brown plates of 2 (R = C_6H_5) were obtained by crystallization of the macrocycle from a mixture of acetonitrile and dichloromethane. They form in the monoclinic space group $P2_1/c$ with a = 11.972 (5) Å, b = 11.607 (5) Å, c = 11.738 (4) Å, β = 103.36 (3)°, Z = 2 at 130 K. Refinement of 1753 reflections with $I > 2\sigma(I)$ and 217 parameters yielded R = 0.059, R_w = 0.051.

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Supplementary Material Available: Tables of atomic coordinates, bond distances bond angles, hydrogen atom coordinates, and thermal parameters for 1 (R = C_6H_5, R' - *p*-$C_6H_4NO_2$) and 2 (R = C_6H_5) and perspective views of the entire molecules 1 and 2 (18 pages). Ordering information is given on any current masthead page.

Unexpected Behavior of Dienol Thioethers Gives Versatile Access to a Large Set of Functionalized Dienes

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Thio dienol ethers are useful synthons of special interest in cycloaddition reactions and have been extensively studied throughout the literature in intra[1] and intermolecular[2] situations. Because of their substitution pattern and functionalities methoxy(phenylthio)butadienes have found several applications in the synthesis of natural products such as carvone[3] or eudesmane sesquiterpenes precursors.[4] Preparation of 1,4-disubstituted dienes is generally known to be complicated by both the nature of the substituents and control of the stereochemistry; the proposed route to these structures based upon conrotatory opening of appropriately substituted cyclobutenes[5] leads, in the case of 4-methoxy-1-(phenylthio)buta-1,3-diene, to a mixture of isomers.[6] Thus, the problem of an efficient stereocontrolled synthesis of this potent building block remains to be solved. We present in this work: (i) the first stereoselective access to 4-methoxy-1-(phenylthio)buta-1,3-diene based on 1,4-elimination of corresponding thioether acetal 4, (ii) the exceptional ability of nucleophilic additions to take place on such substrates, giving easy access to a large set of functionalized dienes.

As an extension of our previous studies on polyvinylogation reactions[7] and alkylation using thio enol ether derivatives,[8] we decided to investigate the possibilities of various vinylic thioethers as alkylating systems. The compounds studied have been conveniently prepared according to Scheme I. Crotonaldehyde (**1a**) or senecialdehyde (**1b**) are transformed into the corresponding silyl enol ethers **2a,b**[9] (62%, 74% yield, respectively), which, in turn, are brominated and then directly acetalized by methanol,[10] leading to allylic bromo acetals **3a,b** (60%, 89% respectively). Displacement of bromide by thiophenol/triethylamine[11] gives allylic thioethers 4 in 92% and 96% yields, respectively. The stereochemistry is completely controlled in crotonaldehyde derivatives at each step (*E* isomer only) while the corresponding intermediates from senecialdehyde are obtained as a mixture of isomers with the ratios reported in Scheme I.

When treated at low temperature (−60 °C) with strong bases such as alkyllithium or lithium amide reagents, allyl thioethers 4 undergo γ-elimination of the methoxy group,

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