Synthesis and X-Ray Crystal Structure of 27-Oxa-25,29-Dithiasapphyrin: Bithiophene-containing Sapphyrins Have an Inverted Structure

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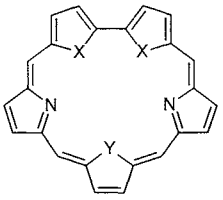
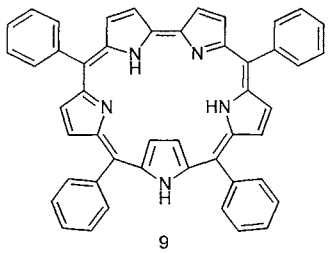
Acid-catalyzed condensation of 16-oxa-5,10,15,17-tetrahydrotripyrrin and 5,5'-bis(tolylhydroxymethyl)-2,2'-bithiophene gives 5,20-ditolyl-27-oxa-25,29-dithiasapphyrin. The X-ray crystal structure revealed this sapphyrin derivative has an O-inverted structure.

In recent years there has been considerable research directed towards the synthesis and study of macrocyclic system involving expanded porphyrins.[1] Sapphyrin, so-called due to their intense blue-green color, were the first known examples of the expanded porphyrins.[2] The system contains five pyrroles and possesses an overall aromatic 22 π-electron annulene framework. Heteroatom-substituted sapphyrins in which a furan, thiophene or selenophene moiety replaces one or more of the pyrrole rings are also reported.[3] Structures of sapphyrin and its heterologues are represented by generalized structure **1-8**. Recent studies have shown that inverted *meso*-tetraphenyl-sapphyrin **9** can be formed during the Rothemund synthesis of porphyrins.[4] Very recently we have synthesized and determined X-ray crystal structure of *meso*-tetraphenyl-trithiasapphyrin **10**.[5] The crystal structure revealed that the *meso*-tetraphenyl-trithiasapphyrin has a S-inverted structure. We have postulated this inversion of the thiophene moiety was induced by the large ring strain caused from a large C_α---C_α distance of bithiophene. In order to prove this postulation, we have synthesized and determined the structure of oxa-dithia-sapphyrin **11**, which has a furan opposite to the bithiophene moiety.



X=Y=NH	1
X=NH, Y=S	2
X=NH, Y=O	3
X=NH, Y=Se	4
X=NH, Y=O	5
X=Y=O	6
X=O, Y=NH	7
X=O, Y=S	8



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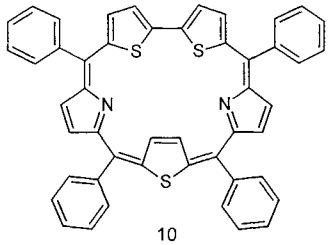

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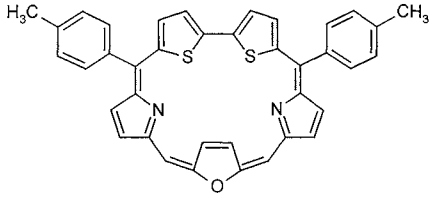

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Acid-catalyzed condensation of 16-oxa-5,10,15,17-tetrahydrotripyrrin[6] (0.3 g, 1.33 mmol) and 5,5'-bis(tolylhydroxymethyl)-2,2'-bithiophene[5] (0.54 g, 1.33 mmol) in CH_3CN (150 ml) conducted for 10 min, followed by oxidation with *p*-chloranil, yielded a product, 5,20-ditolyl-27-oxa-25,29-dithiasapphyrin. Catalytic amount (0.3 equivalent) of *p*-toluenesulfonic acid was used as an acid. The crude product was purified from silica gel chromatography with $CHCl_3$ as the eluent and recrystallized from chloroform/hexane to give a pure product in 6.5% yield.[7]

The electronic spectrum displayed a Soret absorption at 491 nm (log ε = 4.91), and Q bands occur at 599 (log ε = 4.03) and 646 (log ε = 3.90) nm, which is shorter than that of the trithiasapphyrin.[2] Usually the thia analogues of the sapphyrin exhibit more red-shifted Soret bands compared to the all nitrogen compound, while the oxa analogues exhibit the reverse effect. Typically, the electronic spectra of the sapphyrins and their heterologues are dominated by an intense Soret band in the 435-470 nm regions for the free base and less intense 2-5 Q bands in the 600-750 nm spectral regions.[2]

As is true for the aromatic macrocycles, the ^{1}H NMR spectrum of compound **11** reveals the upfield and downfield shifts for the internal ring protons and external ring protons characteristic of aromatic macrocycles. In the ^{1}H NMR spectrum of **11**, the furan's β-protons opposite to the bithiophene located at 0.97 ppm, which suggests that the compound **11** has a furan-inverted structure. Such a structure is consistent with the observation in the case of *meso*-tetraphenyl-trithiasapphyrin and *meso*-tetraphenyl-sapphyrin, wherein the thiophene ring and the pyrrole ring is rotationally inverted, respectively.[4,5] The β-protons of the inverted thiophene and pyrrole resonate at -0.78 ppm and -1.21 ppm, respectively.[4,5]

Support for the structural assignment was obtained from X-ray crystallographic analysis. Single crystals of the compound **11** for X-ray data were obtained by slow evaporation of benzene solution.[8] As illustrated in Figure 1, the oxygen atom of the furan is placed outside of the core of the macrocycle. The side view of the crystal structure (Figure 2) revealed the furan plane is tilted relative to the least-square plane defined by the atoms of the macrocyclic core[9] by 34.0(1)°. Large core deformation by the tilted furan may affect the electronic absorption to cause red shift of the Soret band. The Soret band of **11** at 491 nm is approximately 41 nm red-shifted relative to that of the free base form of the planar sapphyrin. N(1), N(2), S(1) and S(2) are nearly planar with a standard deviation of

0.0124 Å. The two tolyl rings are tilted by 50.1(1)° and 52.3(1)° relative to the same macrocyclic plane. Distances for C(1)-C(4) and C(21)-C(24) are equal to 2.506(5) and 2.503(5) Å, respectively, while distances for C(6)-C(9) and C(16)-C(19) are equal to 2.177(5) and 2.181(5) Å, respectively. The bithiophene unit incorporated into the sapphyrin ring instead of the bipyrrole unit increases the core size and hence may induce a ring strain to invert the furan ring. The compound **11** has a core size of 6.266(4) Å diameter. This diameter is similar to the core size (ca. 6.391 Å) of the trithiasapphyrin,[5] but larger than that (ca. 5.5 Å) of the sapphyrin.[2] The sapphyrin and its heterologues **1-8** do not have inverted structures. However, the *meso*-tetraphenylsapphyrin **9** proved to have a N-inverted structure, as evidenced by ^{1}H NMR spectroscopic analysis.[4] Sessler and coworkers have also synthesized *meso*-diarylsapphyrins, but they do not have inverted structures.[10] Therefore, in the case of sapphyrin, tetraaryl groups at the *meso* position may be necessary for the inversion of pyrrole unit opposite to the bipyrrole. However, the presence of tetraaryl groups at the *meso* position is not necessary for the bithiophene-containing sapphyrins to have the inverted structure.

In conclusion, the bithiophene-containing sapphyrins have the inverted structure due to the large ring strain, regardless of the presence of aryl groups at the *meso* position.

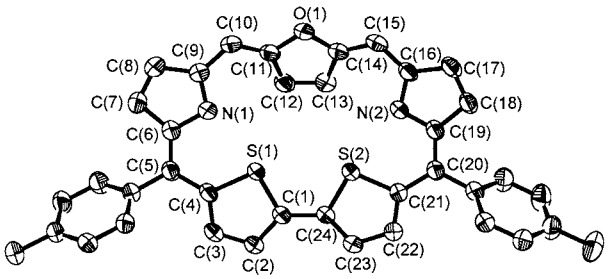

Figure 1. Top View of 5,20-ditolyl-27-oxa-25,29-dithiasapphyrin (ORTEP, 50% probability). All hydrogens and solvent atoms are excluded for clarity. Selected bond distances (Å): S(1)-C(1) 1.729(4), S(1)-C(4) 1.732(3), S(2)-C(24) 1.723(3), S(2)-C(21) 1.744(4), N(1)-C(6) 1.365(5), N(1)-C(9) 1.331(5), N(2)-C(16) 1.339(4), N(2)-C(19) 1.366(5), O(1)-C(11) 1.397(5), O(1)-C(14) 1.379(4).

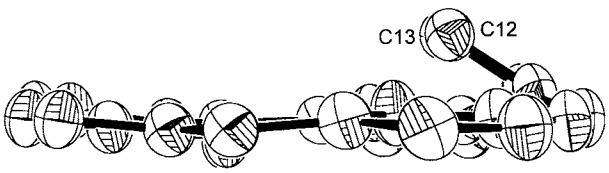

Figure 2. Side View of 5,20-ditolyl-27-oxa-25,29-dithiasapphyrin (ORTEP, 50% probability). All hydrogens, solvent atoms and two tolyl groups at the *meso* position are omitted for clarity.

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7 ^{1}H NMR ($CDCl_3$): δ 9.62 (d, 2H, bithiophene-H_β), 9.35(d, 2H, bithiophene-H_β), 8.80 (s, 2H, *meso*-H), 8.39 (d, 2H, pyrrole-H_β), 8.35 (d, 2H, pyrrole-H_β), 8.06 (b, 4H, *o*-phenyl), 7.57 (d, 4H, *m*-phenyl), 2.67 (s, 6H, CH_3), 0.97(s, 2H, furan-H_β). HR FAB-MS $(M+H)^+$: *m/z* 591.1566 (calcd for $C_{38}H_{26}N_2S_2+H^+$ 591.1565).

8 Crystal data for **11**·C_6H_6: $C_{44}H_{32}N_2OS_2$, *F. W.* = 668.79, triclinic, space group, $P\bar{1}$, a = 9.030(1), b = 10.448(1), c = 16.889(1) Å α = 98.72(1)°, β = 96.65(1)°, γ = 93.91(1)°, V = 1558.4(2) Å^3, Z = 2, D_{calcd} = 1.412 gcm^{-3}, F(000) = 688, GOF = 1.043. For 5465 unique observed reflections [I>2σ(I)] collected at 293 K, the final R value is 0.0687 (R value for all data = 0.0864). Anal calcd for $C_{38}H_{26}N_2S_2$·C_6H_6: C, 79.02; H, 4.82; N, 4.19%. Found: C, 78.87; H, 4.83; N, 4.21%.

9 The least-square plane defined by the atoms of the macrocyclic core refers to a plane containing C(1), C(4), C(5), C(6), C(9), C(10), C(15), C(16), C(19), C(20), C(21), and C(24) with a standard deviation of 0.0265.

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