Pergamon

Tetrahedron Letters 42 (2001) 3391–3394

TETRAHEDRON LETTERS

Characterization of a new *meso*-aryl rubyrin isomer: [26]hexaphyrin (1.1.1.0.1.0) with an inverted heterocyclic ring

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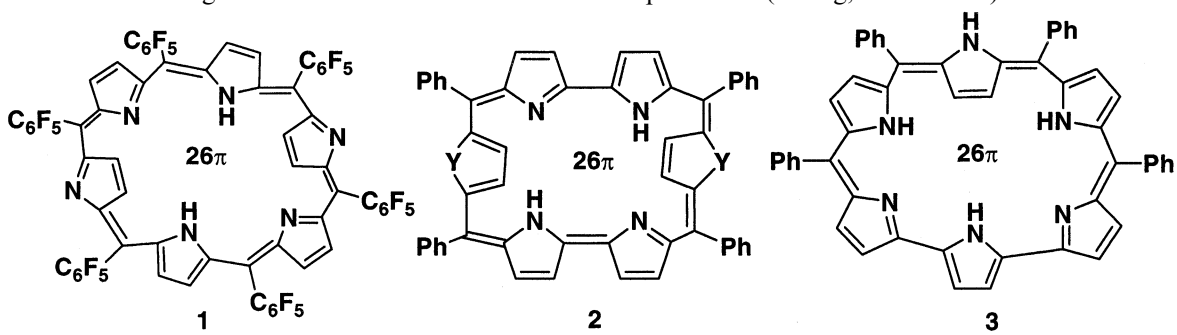
Received 11 January 2001; revised 8 March 2001; accepted 15 March 2001

Abstract—The synthesis and characterization of new aromatic 26π macrocycles obtained from the acid catalyzed 4+3 coupling reaction of core modified tripyrrane and tetrapyrrane are described.

Expanded porphyrins continue to be attractive synthetic targets because of their applications in the field of medicine, anion binding and molecular recognition.[1] Further interest in these systems is associated with their rich metallation chemistry and dynamic structural behavior.

Meso substituted hexaphyrin **1**[2] in particular and rubyrin **2**[3] in general adopt different conformations depending on the nature of the linkage, heteroatom and the state of protonation. For example, **2** exhibits a bis inverted structure in the freebase form and a planar structure in the diprotonated form, while **1** exhibits only a bis inverted structure in both the freebase and protonated forms. Very recently, Sessler and co-workers reported the synthesis of an isomer **3** of rubyrin in which only one pyrrole ring is inverted both in the freebase and the protonated forms.[4] The subtle nature of these structural changes is not well understood and hence there is a need for the synthesis of more structural variants. In this communication, we wish to report the synthesis of another isomer of rubyrin, where the six pyrrole/heterocyclic rings are linked in a [1.1.1.0.1.0] fashion, in which the heterocyclic ring opposite to the bithiophene/biselenophene unit remains inverted both in the freebase and the diprotonated form.

The synthesis is outlined in Scheme 1. Briefly, a [4+3] acid catalyzed oxidative coupling reaction of modified tetrapyrrane **4** and hetero tripyrrane **5** in dichloromethane followed by oxidation gave modified rubyrins **6** in about 3–5% yield, in addition to the expected heptaphyrins **7** in about 15–20% yield.[5] Specifically, in a typical reaction; **4a** (0.35 g, 0.73 mmol) with **5a** (0.29 g, 0.73 mmol) in dichloromethane under a nitrogen atmosphere was stirred in the presence of 2 equivalents (0.17 g, 1.46 mmol) of trifluoroacetic acid



Keywords: hexaphyrin; rubyrin; expanded porphyrin; macrocycle.

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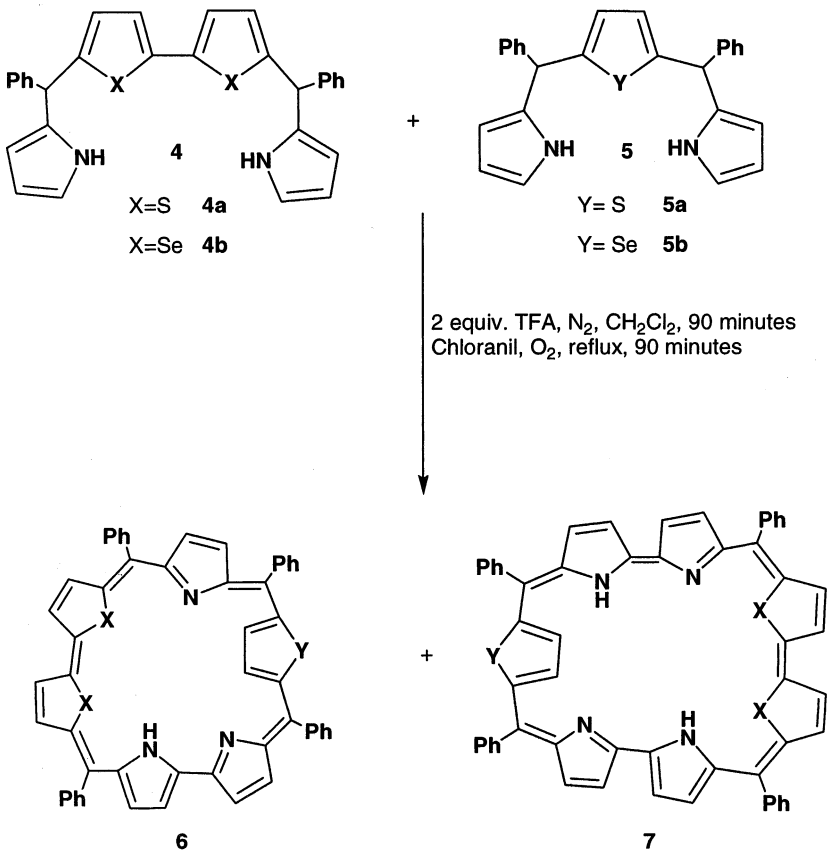
0040-4039/01/$ - see front matter
PII: S0040-4039(01)00451-8

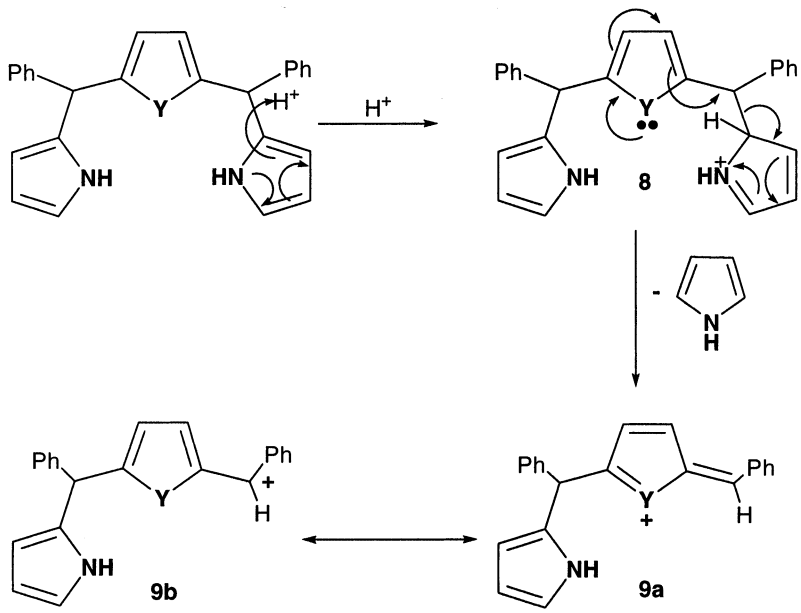


	X	Y	yield
6a	S	S	5%
6b	S	Se	4%
6c	Se	Se	3%
6d	Se	S	4%

	X	Y
7a	S	S
7b	S	Se
7c	Se	Se
7d	Se	S

Scheme 1.

for 30 min in the dark followed by oxidation with chloranil (0.36 g, 1.46 mmol) in the presence of oxygen under reflux for 90 min. After evaporation of the solvent, a column chromatographic purification using basic alumina (grade 3) gave a pink fraction upon elution with 1:3 petroleum ether:dichloromethane, which was identified as **6a** (5% yield) and another purple fraction eluted with 1:44 ethyl ace-

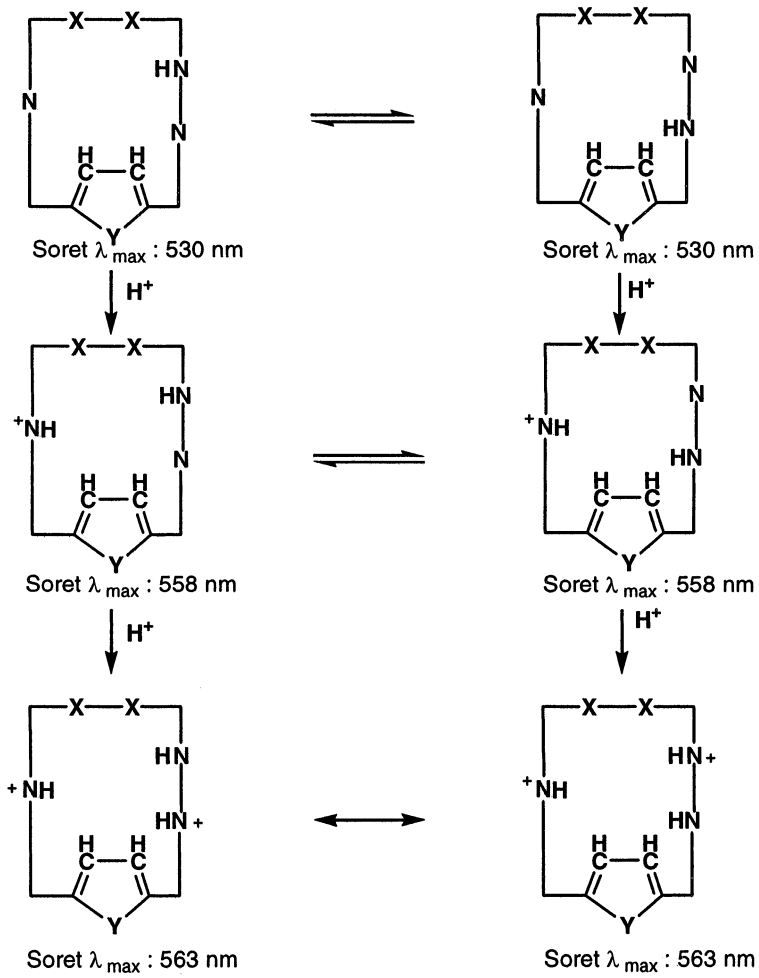


tate:dichloromethane identified as **7a** (16% yield). The formation of **6** was found to be dependent on the TFA concentration used. For example, the use of 1 equivalent of TFA gave the expected heptaphyrin **7** only, whilst 1.5 equivalents of TFA gave 1% of **6** in addition to **7**. Rubyrin **2** was also formed in the reaction and the yield of rubyrin decreases with increase in acid concentration.

It is known that the tripyrranes undergo fragmentation in the presence of an acid catalyst and the extent of fragmentation depends on the acid concentration. The formation of **6** in the reaction can be accounted for by assuming the acidolysis of modified tripyrranes **5** in the presence of TFA. Thus, protonation of **5** leads to an intermediate **8** which can fragment losing a pyrrole ring, thereby, giving rise to a second intermediate **9a**/**b**. Strong support for such a conclusion comes from recent work by Lash and co-workers who have suggested the formation of pyrrole and dipyrromethane-like intermediates in the acid catalyzed reaction of tripyrranes.[6] A similar acidolysis of dipyrromethane has been reported recently.[7] The intermediates **9a**/**b** can react with **4** to generate a porphyrinogen type intermediate which on oxidation can give core modified [26]hexaphyrin (1.1.1.0.1.0) **6**.

The composition of **6** was established from elemental analysis and mass spectroscopic data.[8] The UV–vis spectra of **6a**–**6d** show typical strong Soret type bands and four Q-bands confirming the porphyrinic nature of the macrocycles. The inversion of the heterocyclic ring was inferred in the free base form of **6** by observation of the β-CH proton resonance signals in the shielded region (for example, the chemical shifts of these protons for **6a** are −0.01 and −1.01 ppm). The inner NH signals are not observed at room temperature because of rapid tautomerism where the proton is exchanging sites between two bipyrrolic nitrogens. However, on complete protonation three distinct NH signals are observed at −1.3, −2.32, −5.37 ppm for **6a** confirming the aromatic nature of the macrocycle. $\Delta\delta$ values of 11.44 ppm for **6a** and 16.91 ppm for **6a·2H⁺** further ratifies the aromaticity of the macrocycle. Formation of mono and dicationic species of **6** upon careful titration of a dilute solution of TFA in methylene chloride was followed spectroscopically and distinct spectra were observed for both the species. The different protonation stages are summarized in Scheme 2.

In conclusion, the synthesis of a new isomer of modified rubyrin was achieved by an easy methodology. The new



Scheme 2.

rubyrin isomer **6** is different from rubyrin **2** in the following respects: (a) in **2**, the two heterocyclic rings which are linking the bipyrrole rings are inverted in the freebase while in **6** only one heterocyclic ring is inverted; (b) upon diprotonation, the heterocyclic ring remains inverted in **6** while the inverted rings undergo 180° ring flipping in **2**. These differences highlight the presence of subtle conformational effects in *meso*-aryl hexaphyrins.

Acknowledgements

T.K.C. is grateful to the Department of Science and Technology, New Delhi, India, for support of this work. S.K.P thanks the Council of Scientific and Industrial Research for the Senior research fellowship.

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8. Selected spectroscopic data:
   Compond **6a:** ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): 10.43–10.42 (m, 2H); 9.59 (d, 2H, $J=4.4$ Hz), 9.25–9.22 (m, 2H); 8.74 (d, 1H, $J=4.28$ Hz); 8.5–8.42 (m, 3H); 8.36–8.23 (m, 6H); 7.89–7.69 (m, 14H); −0.01 (d, 1H, $J=4.5$ Hz); −1.01 (d, 1H, $J=4.5$ Hz); UV–vis (CH_2Cl_2): λ_{max} nm ($\varepsilon\times10^{-4}$): 530 (11.83), 655 (0.75), 718 (0.76), 842 (0.24), 899 (0.27), 947 (0.28); ESMS: m/z (%): 796 (90) [M^+]; mp >250°C. Anal. calcd for $C_{52}H_{33}N_3S_3$: C, 78.4; H, 4.17; N, 5.28. Found: C, 78.38; H, 4.19; N, 5.26.
   Compound **6a·2H$^+$**: ^{1}H NMR (400 MHz, $CDCl_3$/TFA, 25°C): 11.54 (d, 1H, $J=4.4$ Hz); 11.34 (d, 1H, $J=4.4$ Hz); 10.67 (d, 1H, $J=4.8$ Hz); 10.62 (d, 1H, $J=4.8$ Hz); 10.48 (d, 1H, $J=4.4$ Hz); 10.45 (d, 1H, $J=5.2$ Hz); 9.84 (d, 1H, $J=4.8$ Hz); 9.72 (d, 1H, $J=4.8$ Hz); 9.58 (d, 1H, $J=5.2$ Hz); 9.51 (d, 1H, $J=4.8$ Hz); 8.93 (d, 2H, $J=7.2$ Hz); 8.84–8.82 (m, 2H); 8.76 (d, 2H, $J=6.8$ Hz); 8.66–8.64 (m, 2H); 8.18–7.93 (m, 12H); −1.3 (s, 1H), −2.32 (br.s, 1H), −3.3 (d, 1H, $J=5.2$ Hz); −3.43 (d, 1H, $J=5.2$ Hz); −5.37 (br.s, 1H); UV–vis (CH_2Cl_2/TFA): λ_{max} nm ($\varepsilon\times10^{-4}$): 563 (18.04), 751 (0.43), 846 (1.64), 911 (1.62).
   Compounds **6b–d** were also characterized thoroughly by UV–vis, NMR (1D and 2D) and FAB mass spectroscopic techniques and elemental analysis.