

Dithiaethyneazuliporphyrin - a contracted heterocarba-porphyrin†

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Received (in Austin, TX, USA) 27th April 2006, Accepted 9th June 2006

First published as an Advance Article on the web 4th July 2006

DOI: 10.1039/b605984h

Dithiaethyneazuliporphyrin, the first contracted carbaporphyrinoid, has been synthesized; the molecule contains an azulene moiety embedded in the [18]dithiacarbatriphyrin(4.1.1) macrocyclic framework.

Carbaporphyrinoids provide a unique macrocyclic platform which is suitable to explore organometallic chemistry in a peculiar porphyrin-like environment forcing unusual coordination geometry and/or oxidation states of metal ions.¹ Typically an internal carbon donor atom belongs to a carbo- or heterocycle while the (C/NNN) core becomes the denominator of the monocarbaporphyrinoid structure. A subsequent replacement of one of the pyrrolic nitrogens by a heteroatom (O, S, or Se) yields heterocarba-porphyrinoids.² Enlargement of the macrocycle accompanied by introduction of a carbon atom in place of a nitrogen afforded expanded carbaporphyrinoids.³ On the other hand, to the best of our knowledge, no contracted carbaporphyrinoids have been reported to date.

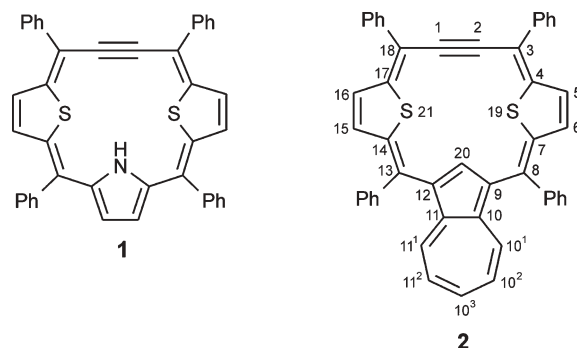
Dithiaethyneporphyrin **1**, reported recently, introduces a unique pattern for contracted porphyrins created by fusing the structural motifs of 21,23-dithiaporphyrin and acetylene.⁴ Actually, the molecule can be considered as a triphyrin – a contracted porphyrin analogue. Such systems have recently gained some attention.^{4,5} The synthetic route elaborated for dithiaethyneporphyrin **1**⁴ opens access to structure **2**, an unprecedented contracted heterocarba-porphyrinoid containing the (SCS) core, confined in the rather atypical frame of [18]triphyrin(4.1.1).

Here we report on the synthesis and characterization of the first contracted carbaporphyrinoid – dithiaethyneazuliporphyrin **2** (Scheme 1). The coordinating ability of **2** is exemplified by the formation of its ruthenium(II) complex (**4**).

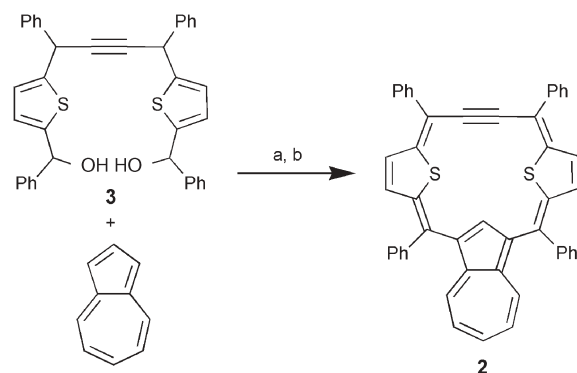
The contracted heterocarba-porphyrin **2** was obtained by a modification of the synthesis described for **1**. The synthetic strategy (Scheme 2) resembles the [3 + 1] approach using 1,4-bis(5-(phenylhydroxymethyl)thien-2-yl)-1,4-diphenyl-2-butyne **3**⁴ and azulene. This method relies on the known suitability of azulene as a substrate for Rothemund-type condensations (Scheme 2).⁶ **2** has been isolated in 15% yield.

The electronic spectrum of **2** (Fig. 1) contains broad absorption bands with relatively small extinction coefficients, suggesting a reduction in the aromatic character, which remains in contrast with the parent system **1**⁴ and dithiaporphyrin S₂TPP.⁷

The ¹H NMR spectrum of **2** shows an AB pattern (8.00, 7.91 ppm) assigned to the β protons of the thiophene rings



Scheme 1 Dithiaethyneporphyrin **1** and dithiaethyneazuliporphyrin **2**.



Scheme 2 Synthesis of dithiaethyneazuliporphyrin: (a) Et₂O:BF₃, RT, 1 h; (b) Et₃N, DDQ, RT, 20 min.

(Fig. 2A). The azulene moiety contributes the inner CH singlet at 5.57 ppm, upfield relative to the position of azulene (7.91 ppm) or tetra(*para*-tolyl)dithiadiazuliporphyrinogen (7.72 ppm)⁶ but

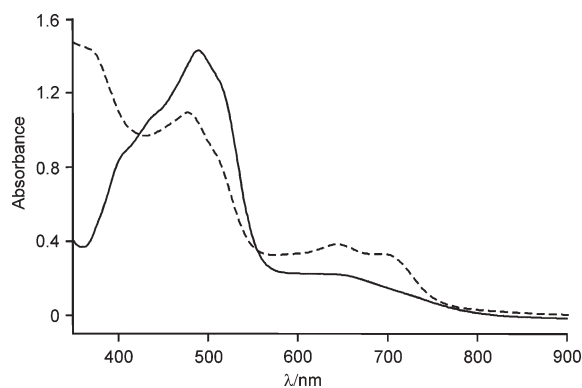


Fig. 1 Absorption spectra of **2** (solid line) and **4** (dashed line) in CHCl₃.

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† Electronic supplementary information (ESI) available: Experimental details and spectral data of **2** and **4**. See DOI: 10.1039/b605984h

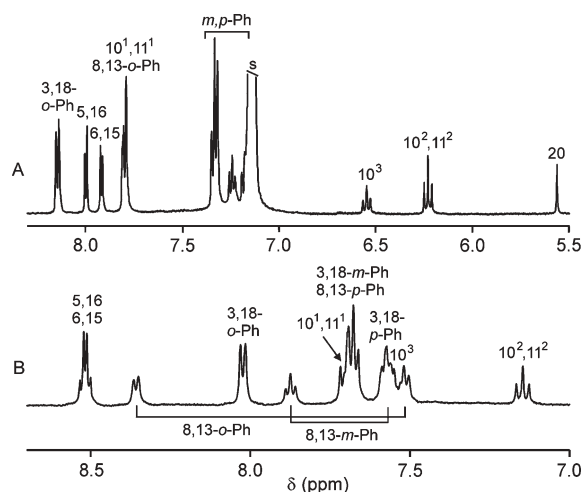
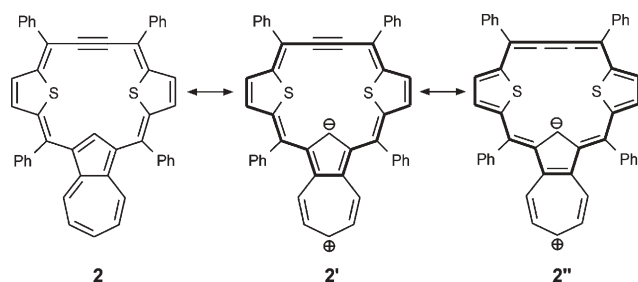


Fig. 2 ^1H NMR spectra of **2** (A; benzene- d_6 , 298 K) and **4** (B; CD_2Cl_2 , 220 K). Peak labels follow systematic position numbering or denote proton groups: *o*-, *m*-, *p*-Ph – *ortho*, *meta* and *para* positions of the *meso*-phenyls.

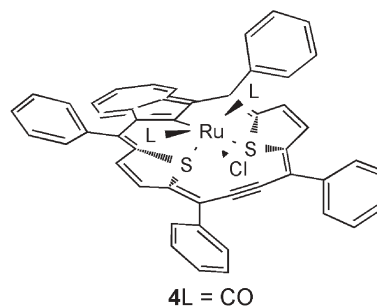
downfield with respect to *meso*- (3.35 ppm) or β -substituted monoazuliporphyrins (1.59 ppm).⁶ One can consider the ^1H NMR shifts of the internally located H(20) proton and the peripheral thiophene resonances as a convenient spectroscopic criterion of macrocyclic aromaticity. Thus the molecule **2** is only weakly aromatic, reflecting the limited contribution of the 18 π -electron delocalization pathway resulting from the input of the dipolar canonical structures **2'** and **2''**.

Two canonical structures of **2'** and **2''** define 18 π -electron macrocyclic delocalization pathways (Scheme 3). Accordingly, the electronic structure of **2** can be described as reflecting a combination of the acetylene ($=\text{C}-\text{C}\equiv\text{C}-\text{C}=\text{C}$) and cumulene ($-\text{C}=\text{C}=\text{C}=\text{C}-$) character of the C18–C1–C2–C3 fragment. The ^{13}C NMR chemical shift of carbon atoms C(1) and C(2) of the linker at **2** equals 106.1 ppm, upfield in relation to **1** (116.8 ppm).⁴ Thus the acetylene character of the $\text{C}_{\text{sp}}\text{C}_{\text{sp}}$ moiety of **2** prevails. The detected chemical shifts of **2** are fairly typical for acetylene-cumulene porphyrinoids⁸ and acetylene-cumulene dehydroannulenes.⁹

Reaction of **2** with $\text{Ru}_3(\text{CO})_{12}$ in chlorobenzene under reflux results in the formation of ruthenium(II) dithiaethyneazuliporphyrin ($\text{S}_2\text{EATPP})\text{Ru}^{\text{II}}(\text{CO})_2\text{Cl}$ (**4**). The relatively small yield reflects the inherent instability of the maternal macrocycle, which decomposes in the insertion conditions. Coordination of ruthenium is reflected in the substantial changes of the electronic



Scheme 3 Canonical structures of **2**.



Scheme 4 Coordination geometry of **4**.

spectrum in comparison to **2** (Fig. 1). Dithiaethyneazuliporphyrin acts as a monoanionic ligand forming the Ru–C(20) σ -bond. Accordingly, the unique H(20) resonance seen in the ^1H NMR spectrum of **2** is missing in the spectrum of **4**.

In contrast to ruthenium(II) 21,23-dithiaporphyrin¹⁰ ($\text{S}_2\text{TPP})\text{Ru}^{\text{II}}\text{Cl}_2$ and ruthenium(II) dithiaethneporphyrin⁴ ($\text{S}_2\text{ETPP})\text{Ru}^{\text{II}}(\text{CO})_2\text{Cl}$, molecule **4** preserves the C_s symmetry with a mirror plane passing through the ruthenium, chloride and coordinated azulene carbon as reflected by a single AB pattern assigned to the β protons of two thiophene rings (Fig. 2B). The geometry of **4**, inferred from the ^1H NMR spectroscopic pattern (Fig. 2B), reflects the balance between the constraints of the macrocyclic ligand and the requirements of ruthenium(II) for octahedral geometry (Scheme 4). The dithiaethyneazuliporphyrin molecule **2** has to distort to accommodate the $\text{Ru}(\text{CO})_2\text{Cl}$ moiety. The puckering of dithiaethyneazuliporphyrin and the difference in coordination above and below the porphyrin plane lower the symmetry with respect to the carbaporphyrinoid plane. Accordingly, two *ortho* and two *meta* resonances have been identified for one set of *meso* aryls (8,13-Ph) at 220 K.

In conclusion, dithiaethyneazuliporphyrin **2**, the original contracted carbaporphyrinoid, is a peculiar molecule combining three structural motifs: acetylene, azulene and thiophene moieties in a [18]triphyrin(4.1.1) frame.

We thank the Ministry of Scientific Research and Information Technology (Grant PBZ-KBN-118/T09/5) for financial support.

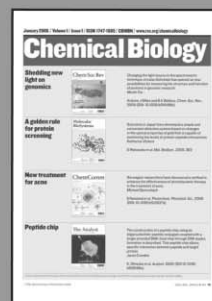
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