# Dithiaethyneazuliporphyrin - a contracted heterocarbaporphyrin†

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**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 (CNNN) 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 heterocarbaporphyrinoids.[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.

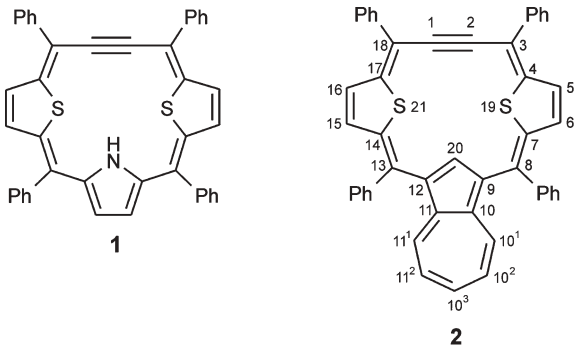
Dithiaethyneporphyrin **1**, reported recently, introduces a unique pattern for contracted porphyrins created by fusing the structural motifs of 21,23-dithiaporphyrin and acetylene.[4] Actually, the molecule can be considered as a triphyrin – a contracted porphyrin analogue. Such systems have recently gained some attention.[4,5] The synthetic route elaborated for dithiaethyneporphyrin **1**[4] opens access to structure **2**, an unprecedented contracted heterocarbaporphyrinoid 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**).

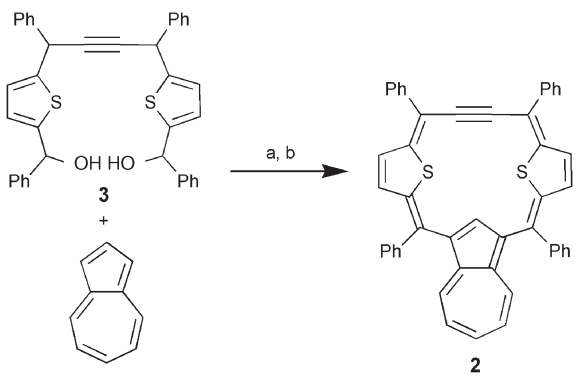
The contracted heterocarbaporphyrin **2** was obtained by a modification of the synthesis described for **1**. The synthetic strategy (Scheme 2) resembles the [3 + 1] approach using 1,4-bis(5-(phenylhydroxymethyl)thien-2-yl)-1,4-diphenyl-2-butyne **3**[4] and azulene. This method relies on the known 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 $S_2$TPP.[7]

The $^1$H 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) $Et_2O{:}BF_3$, RT, 1 h; (b) $Et_3N$, 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

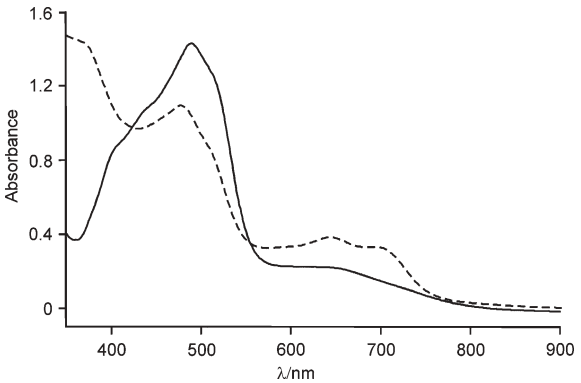



**Fig. 1** Absorption spectra of **2** (solid line) and **4** (dashed line) in $CHCl_3$.

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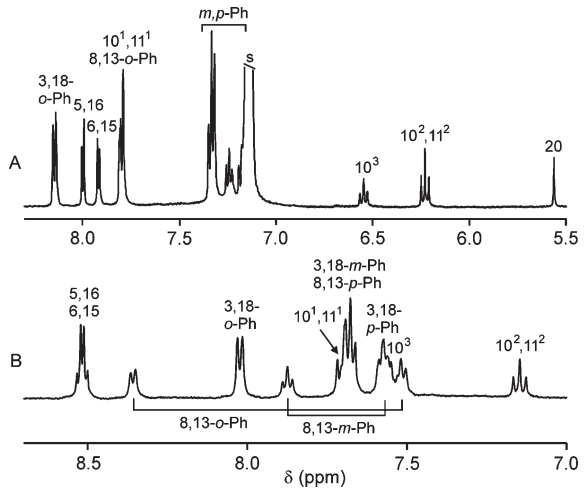
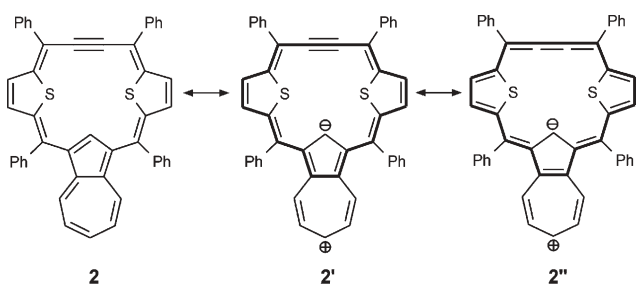



**Fig. 2** $^1$H NMR spectra of **2** (A; benzene-$d_6$, 298 K) and **4** (B; $CD_2Cl_2$, 220 K). Peak labels follow systematic position numbering or denote proton groups: *o*-, *m*-, *p*-Ph – *ortho*, *meta* and *para* positions of the *meso*-phenyls.

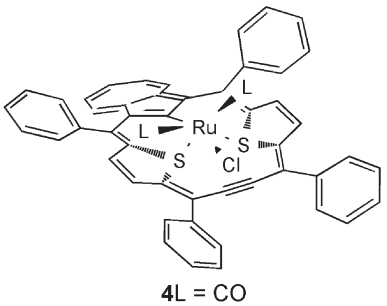
downfield with respect to *meso*- (3.35 ppm) or β-substituted monoazuliporphyrins (1.59 ppm).[6] One can consider the $^1$H NMR shifts of the internally located H(20) proton and the peripheral thiophene resonances as a convenient spectroscopic criterion of macrocyclic aromaticity. Thus the molecule **2** 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 (=C–C≡C–C=) and cumulene (–C=C=C=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 $C_{sp}C_{sp}$ moiety of **2** prevails. The detected chemical shifts of **2** are fairly typical for acetylene-cumulene porphyrinoids[8] and acetylene-cumulene dehydroannulenes.[9]

Reaction of **2** with $Ru_3(CO)_{12}$ in chlorobenzene under reflux results in the formation of ruthenium(II) dithiaethyneazuliporphyrin ($S_2$EATPP)$Ru^{II}(CO)_2Cl$ (**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 $^1$H NMR spectrum of **2** is missing in the spectrum of **4**.

In contrast to ruthenium(II) 21,23-dithiaporphyrin[10] ($S_2$TPP)$Ru^{II}Cl_2$ and ruthenium(II) dithiaethyneporphyrin[4] ($S_2$ETPP)$Ru^{II}(CO)_2Cl$, 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 $^1$H 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 $Ru(CO)_2Cl$ 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.

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