Porphyrinoids

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Annulation and Arylation Stabilize New Porphyrinoids

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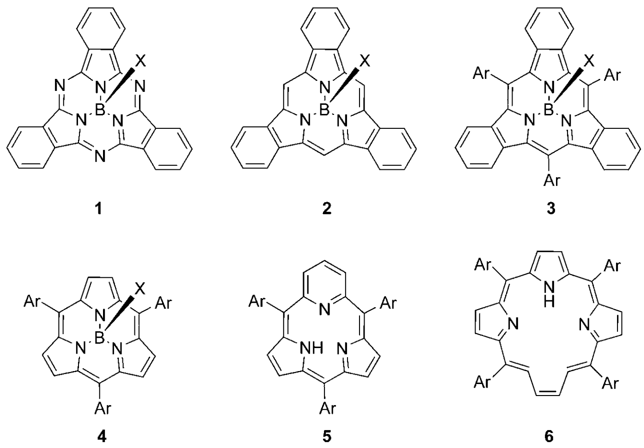
annulenes · azulenes · porphyrinoids · annulation

Dedicated to Professor Dieter Wöhrle on the occasion of his 70th birthday

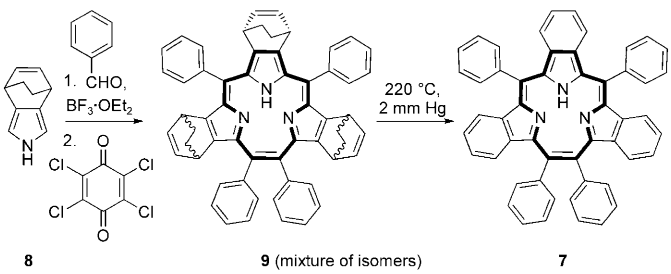
Porphyrin research keeps up in presenting astonishing results, which is aptly demonstrated by the synthesis of a new free-base (non-metalated) [14]triphyrin(2.1.1)[1] and the very recent formation of tetraazuliporphyrin tetracation.[2] Both compounds owe their stablity to annulation and arylation of the aromatic skeleton with other π-electron-rich rings. The functionalization of porphyrins clearly plays a dominant role in porphyrin chemistry as it delivers highly interesting materials with a broad range of applications.[3] However, from a more fundamental point of view, the amazing variety of porphyrin variants stemming from structural reorganization,[4] expansion,[5] contraction,[6] nitrogen atom replacement,[7] fusion, and combined variations[8] that have come to light over the past two decades show that it is still quite worthwhile to carry out basic research with this unique class of macrocycles.



Scheme 1. Examples of subporphyrins. X = for example, OH, OMe.

The contraction of the porphyrin system by the formal removal of a whole pyrrole ring delivers a new class of porphyrinoids, the aptly named "subporphyrins" or "triphyrins".[9] The first example came to light in 1972, when the attempted preparation of a phthalocyanine boron complex delivered boron subphthalocyanine **1** (X = for example, OH, OMe) instead (Scheme 1).[10] It took more than three decades for other subporphyrins to emerge, the next being tribenzosubporphyrin **2** in 2006,[11] which strongly resembles its early congener **1**. A tribenzotriphyrin **3** with aryl substituents in the *meso* positions was prepared in 2007 by an ingenious procedure that employed pyridinetri(*N*-pyrrolyl)borane as the precursor.[12] The non-benzannelated triaryl triphyrin **4** was prepared in 2007.[13] It is important to note that subporphyrins **1**–**4** and most others exist only as boron complexes with nonplanar, that is, dome-shaped conformations, as their synthesis is performed with boron compounds as templates. A removal of the boron ion is not possible, thus preventing the formation of other metal complexes (Scheme 1). Only a few subporphyrins were obtained as free bases when boron templation was synthetically unnecessary. Important examples are subpyriporphyrin **5**[14] and 21-vacataporphyrin **6**[15] (Scheme 1). Clearly, changing a pyrrole to a pyridine ring or enlarging the bridging units delivers enough stability for the free-base systems to be isolable.

In a joint contribution, the groups of Shen, Yamada, You, and Kobayashi prepared the planar, free-base, all-pyrrole tribenzotriphyrin **7**.[1] It is closely related to the abovementioned triaryl tribenzosupporphyrin **3**, but carries a (2.1.1) bridge pattern. A conceptual approach to **7** is to remove the quinone-like pyrrole moiety of tetraphenylporphyrin. The direct precursor of **7**, alkylated triphyrin **9**, is prepared by using quite ordinary conditions for the generation of tetraaryl porphyrins. $BF_3{\cdot}OEt_2$-catalyzed Rothemund/Lindsey condensation of norbornadiene-derived pyrrole **8** and benzaldehyde, followed by oxidation with *p*-chloranil, gave compound **9** in good yields (up to 35%; Scheme 2). The triphyrin(2.1.1) connectivity of **9** was evidenced by X-ray structural analysis, which clearly showed an unexpected double bond between two pyrrole-like rings. Furthermore, the central triphyrin unit of **9** is planar despite the substitution pattern; in contrast, the comparable 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetraphe-



Scheme 2. Synthesis of tribenzotriphyrin(2.1.1) **7**.

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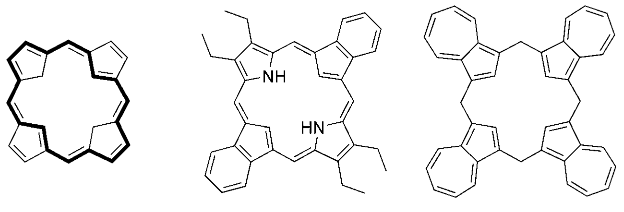
nylporphyrin has a strongly ruffled structure.[16] To conclude the synthesis, **9** was heated in vacuum to induce a retro-Diels–Alder reaction that liberated ethylene and formed the annulated benzene rings of **7**. The tribenzotriphyrin(2.1.1) structure of **7** was also unambiguously determined by X-ray structural analysis, which showed **7** to be also planar.[17] Again, the presence of the double-bond bridge confirms the structural assignment. In both **7** and **9**, the lengths of the three bonds of the two-carbon bridging units are equal and indicate the delocalization of the 14 π-electron system (bold lines in Scheme 2); tautomeric processes may also occur. The remarkable downfield positions of the signals for the inner NH protons (**7**: $\delta_{NH} = 8.16$; **9**: $\delta_{NH} = 7.68$) stem from strong NH···N interactions, which have also been observed in other porphyroids.[18]

The formation of triphyrin(2.1.1) **9** is quite astonishing and needs to be commented upon. First, it is not quite clear how the compound is formed: the authors offer no explanation, but participation of an azafulvene and/or azafulvenium cation in the cyclization procedure is likely.[19] Second, it is rather surprising that **9** or similar materials were not discovered earlier, although **8** has been used before in "normal" porphyrin syntheses.[20] In fact, the same reaction sequence was employed to prepare tetraaryl tetrabenzoporphyrins.[20] It seems that the discovery of **9** is a truly serendipitous event. This new triphyrin system may allow new, unique metal complexation behavior in subporphyrin chemistry, together with applications thereof, to be explored for the first time.

A highly sought-after compound in porphyrin chemistry is carbaphyrin **10**. This interest stems from **10** being a form of "missing link" between annulenes and porphyrins (indicated by bold lines in Scheme 3). Compound **10** can be envisioned

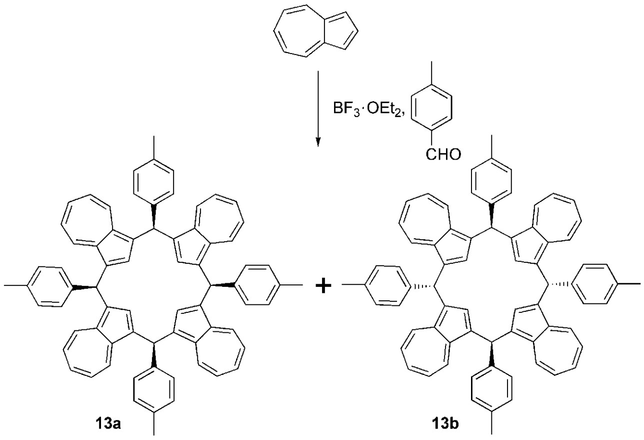


10 11 12

Scheme 3. Some porphyrinoids with N/CH replacement. Compound **10** not known to date.

conceptually by removing the inner nitrogen functionalities of porphyrin itself and replacing them with CH or CH_2 groups. To date, **10** has eluded all synthetic attempts, although some approaches to **10** have been made. Noteworthy are indene-derived porphyrin systems, such as **11**[21] and calix[4]azulene **12**,[22] which are all-carbon compounds with the same internal skeleton as **10**.

Very recently, in a new approach to **10**, Latos-Grażyński and co-workers prepared the tetraaryl congener **13** of **12** by simple Lindsey condensation of azulene with aryl aldehydes. This synthesis is in marked contrast to the formation of **12** from paraformaldehyde and azulene, which succeeded only with florisil as catalyst. Not unexpectedly, **13** (obtained in 97% yield!) turned out to be a mixture of stereoisomers, with two of the four possible isomers being predominant (**13a** and **13b**; Scheme 4). Interestingly, those two isomers turned out to be statistically the least likely of the four to form, **13a** with

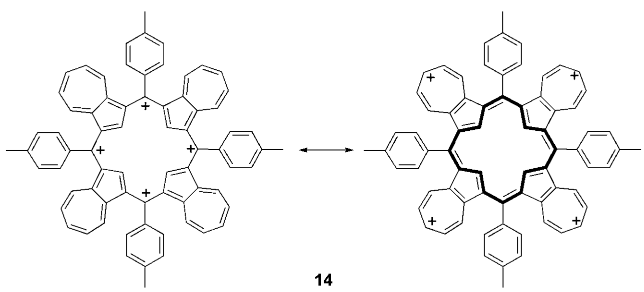


13a 13b

Scheme 4. Stereoisomers **13a** (αααα) and **13b** (αβαβ).

an αααα (12.5% probability) and **13b** with an αβαβ arrangement (12.5% probability) of the aryl groups.[23] The structures of both **13a** and **13b** were determined by X-ray crystallography; both isomers show that two opposing azulenes of the calix[4]azulene framework lie in one plane. In **13a**, the other pair points to one direction and forms a boat-like structure, whereas the other pair of azulenes in **13b** point up and down, giving rise to a chair-like situation.

A π system similar to that of **10** (a 18π main conjugation pathway) is not accessible by oxidation of **13** (or **12**) without introduction of either positive charges or sp^3-hybridized carbon atoms within the azulene submoieties and/or redistribution of hydrogen atoms to form both porphyrin-internal CH_2 units. Nevertheless, **13** contains the correct number of internal hydrogen atoms to be a precursor of a dehydroquatyrin derivative with a 16π main conjugation system (bold lines in Scheme 5), which is the oxidized congener of **10**. Formally, four hydrides have to be abstracted to attain this oxidation level. The oxidation of **13** (both isomers) with DDQ in dichloromethane was followed by ^{1}H NMR spectroscopy, and indicated the stepwise formation of mono-, di-, and trication. Only the addition of $HBF_4{\cdot}OEt_2$ finally yielded the



14

Scheme 5. Canonic structures of tetratolyltetraazuliporphyrin tetracation **14**. The 16π main conjugation pathway of dehydroquatyrin is shown in bold.

tetracation. Although an X-ray structural analysis has not yet been performed, the generation of tetracation **14** was unambiguously shown by NMR and UV/Vis spectroscopy.

Significant changes can be seen in the UV/Vis spectrum of **14**, for which the typical features of free azulene, such as those seen for **13a/b**, are replaced by intense absorptions in the visible region. The most intense band is located at 588 nm, which almost resembles the typical Soret band of expanded porphyrins, but comes closer to the spectroscopic features of azulene methylium salts. ^{1}H and ^{13}C NMR spectroscopy confirmed the assumed formation of tetracation **14**: the spectra are somewhat simpler than those of the precursor systems **13a/b**, and are consistent with effective D_{4h} or S_2 symmetries of **14**; DFT optimization clearly shows the latter to be the case. Interestingly, the internal protons of the azulene moieties resonate at $\delta = 11.34$ ppm, which thus means **14** is not aromatic. The strong downfield shift is most likely due to a combination of paratropicity (16π dehydroquatyrin) and positive charge distribution within the inner core of the molecule. Extensive use of NMR correlation spectroscopy allowed the assignment of all the carbon resonances. As a result, the charge distribution along the carbon skeleton was revealed, which was in agreement with DFT results. The canonic structure on the left side of Scheme 5 shows the predominant allocation of the charges. Chemical evidence for this assignment is the reaction of **14** with water, which results in the addition of a hydroxide ion to one of the *meso* positions.

The formation of tetracation **14** is an important step towards all-carbon porphyrins. Even without these prospects, **14** itself is a highly intriguing species that encompasses topics such as azulene, arene, calixarene, and carbocation chemistry. The calculated structure of **14** suggests its potential as anion receptor for weakly binding anions. Furthermore, the excellent accessibility of **14** and the variation of aryl groups, which allows the modification of the charge distribution, make applications of **14** and its congeners in molecular electronics likely.

Both contributions, namely tribenzotriphyrin[2.1.1] **7** and the tetraaryl tetraazuliporphyrin tetracation **14**, are strong additions to porphyrin chemistry. They will add further impetus to the field of unusual porphyrinoids with a vast potential for further developments with respect to their use as functional materials.

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[23] Typical annotation for porphyrin stereoisomers: α represents a substituent above and β below the porphyrin(ogen) plane.

