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How Should Aromaticity Be Described in Porphyrinoids?

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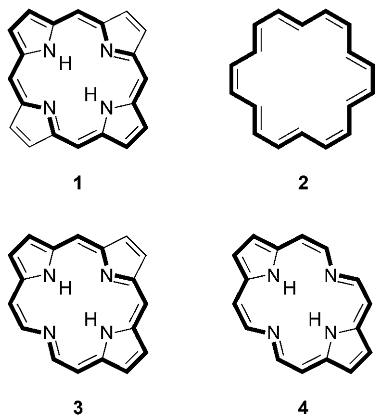
annulenes · aromaticity · conjugation · Hückel · porphyrinoids

Modern porphyrinoid chemistry has benefited particularly strongly from Hückels simple description of aromaticity, which explains the formation of stable aromatic compounds by the presence of $4n+2$ cyclic conjugated π electrons.[1] In the early 1930s porphyrins were already discussed as possible aromatic systems with aligned C–C bonds.[2] However, since the Hückel theory does not apply to polycyclic systems, it required the development and application of new analytical techniques, including single-crystal diffraction and NMR spectroscopy, to enforce this point of view. In particular, the similarity of the physical data obtained for **1** by these methods with those of the [18]annulene **2** reported by Sondheimers et al. in 1962[3] led to the general acceptance of the interpretation of porphyrin as a multiple-bridged aromatic diaza[18]annulene system.[4] The details of the electronic influence of the imino- and ethylidene bridges on the aromatic 18π system of the so-called main conjugation pathway of porphyrin (shown in bold in Scheme 1) have remained unclear until today. The porphyrin-like spectroscopic properties of chlorines and bacteriochlorins,[5] which contain one or two saturated ethylene bridges, respectively, were often highlighted in this context as proof of the viability of this aromaticity concept of porphyrinoids. In addition, the stable and aromatic bacteriophin **4**, a norporphyrin related to the natural, twofold hydrogenated system, could be prepared, while chlorophin **3** still awaits to be synthesized.[6]



Scheme 1. Comparison of porphyrin **1** with an 18π main conjugation pathway and Sondheimers [18]annulene **2**, as well as with the biomimetic norporphyrins **3** and **4**.

The physical meaning of main conjugation pathways and their verification by analytical methods are contentious. However, it is an undeniable fact that from this idea—appropriately entitled “*The porphyrins from the ‘annulenes chemist’s’ perspective*”[7]—started a revolution in porphyrinoid chemistry. Many of the contracted, isomeric, heteroatom-exchanged, inverted, and expanded porphyrinoids that have since been studied in many different areas have originally been derived from attempts to transfer the $(4n+2)$-π-electron rule of the annulenes to this class of natural products. Illustrative examples are the Hückel-aromatic subporphyrin **5**[8] and pentaphyrin **6**[9] with three and five C_4N units as well as 14 and 22 π electrons in the main conjugation pathway, respectively, and the currently much acclaimed Möbius aromatic compounds **7** and **8** from the class of expanded porphyrinoids (Scheme 2).[10–12]

Several exceptions are also known: The expanded porphyrins offer a particular wealth of stable macrocycles which, according to the Hückel rule, have to be classified as antiaromatic. Several polyenic representatives also show higher chemical stability than typical aromatic members, such as pentaphyrin **6** or hexaphyrin—a macrocycle containing six C_4N rings.[13] Consequently, theoretical approaches to describe the aromaticity in porphyrinoids on a quantitative basis now mainly concern magnetic properties, which are experimentally verifiable by NMR spectroscopy.[14–17] One such recent approach examines the local and global aromaticity in the porphyrin polycycle and comes to the conclusion that the 22 π electrons of all the 11 double bonds are necessary for the correct description of the magnetic properties of free-base porphyrin, and not only the 18 electrons of a single-stranded main conjugation pathway. The picture changes if metals are coordinated. In this case, an 18π main conjugation path of a 16-membered inner ring analogous to an [16]annulene dianion (Scheme 3) is sufficient to explain the observed spectroscopic data.[17] Thus, for free-base porphyrins the

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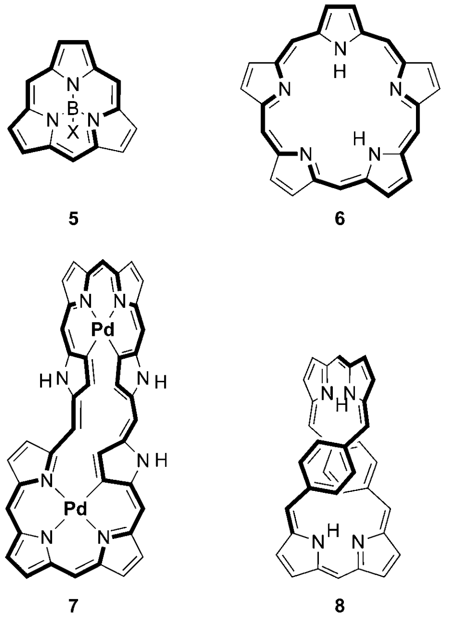
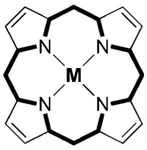


Scheme 2. Selected synthesized Hückel- and Möbius-aromatic porphyrinoids **5**–**8** from the annulene concept.

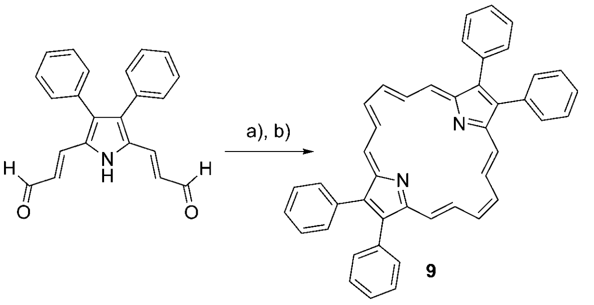


Scheme 3. 16-Membered inner conjugation pathway for metal porphyrins.

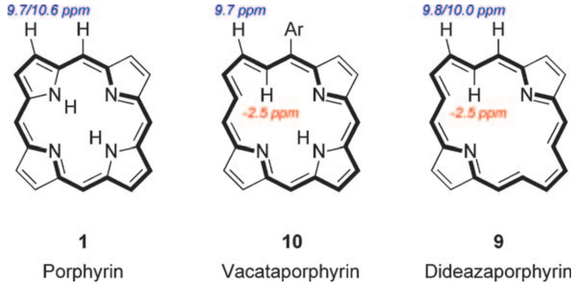
theoretical analysis differs from the simple and successful $(4n+2)\pi$ concept.

A new aromatic and polycyclic molecule has now re-ignited this discussion. Lash et al. recently reported the successful preparation of the annulene **9** by the McMurry coupling of a vinylogous pyrrole dialdehyde and subsequent oxidation of the intermediate macrocycle in air (Scheme 4).[18] Annulene **9** may be considered as either a diaza[18]annulene or a dideazaporphyrin. The spectroscopic properties of the new annulene are undoubtedly porphyrinoid in nature (Soret and Q bands in the optical spectra, and remarkable diatropic shifts in the ^{1}H NMR spectrum; see Scheme 5). A single-crystal X-ray diffraction analysis reveals aligned C–C bonds and an almost perfect planarity of the 18-membered ring of **9**, thus indicating a close relationship between the macrocycle and the "*pigments of life*".[19]

From a certain perspective, **9** may be regarded as the missing link in a series of porphyrin-type bridged annulenes, with the biological macrocycles chlorin and bacteriochlorin, as well as the artificial vacataporphyrin **10**[20] being the already known members (Scheme 5). The formal removal of two or one of the inner aza bridges results in a dynamic behavior of **9** and **10**, respectively (rotation of the ethylidene bridges in solution), and thus in the marked line broadening observed in their spectra. This behavior is also characteristic of [18]annulene. None of these compounds, however, can convincingly be described by the model of local and global aromaticity. The authors therefore come to the conclusion, that "*the essence of these properties* (the aromatic characteristics of porphyrins) *appears to be encapsulated in the diaza[18]annulene substructure*".



Scheme 4. Preparation of dideazaporphyrin **9** by McMurry coupling of a suitable dialdehyde; a) $TiCl_4$, Zn(Cu), THF, b) O_2.



Scheme 5. Comparison of the ^{1}H NMR chemical shifts of inner and outer C-bound protons in porphyrin **1**,[21] vacataporphyrin **10**, and dideazaporphyrin **9**.

The confrontation between different philosophies appears as the bottom line here. On one side is the fraction of preparative organic chemists, with their need for powerful, simple, and intuitive concepts such as aromaticity and electronegativity. On the other side are the advocates of chemistry as a physically exact science, who are not afraid to develop seemingly abstract and less-intuitive explanations for the sake of preciseness. The competition between the two fractions has always been stimulating and inspiring. The preparative fraction has now gained some more ammunition, and it will be interesting to see how the theoreticians reply.

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