

Carbaporphyrins and Beyond: The Quest for Quatyrin

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Carbaporphyrins are porphyrin analogues where one of the interior nitrogens has been replaced by a carbon atom. In addition to true carbaporphyrins, which possess a cyclopentadiene unit, many related systems are known including N-confused porphyrins, benziporphyrins, azuliporphyrins and tropiporphyrins. These monocarbaporphyrinoid systems have unique reactivity and unusual spectroscopic properties. They range from fully aromatic macrocycles that resemble the porphyrins to nonaromatic systems, and indeed antiaromatic systems have also been noted. Many of these systems are superior organometallic ligands that form complexes with many late transition metal ions under mild conditions. For instance, azuliporphyrins have been reported to form stable complexes with Ni(II), Pd(II), Pt(II), Ir(III), Rh(III) and Ru(II). Carbaporphyrins also form organometallic derivatives with Ag(III), Au(III) and Pd(II). Given the unique and insightful properties exhibited by monocarbaporphyrinoid systems, syntheses of dicarbaporphyrinoids and further heterocycle-diminished species have been investigated. In these studies, porphyrinoid systems with two pyrrolic units and two carbocyclic moieties have been prepared. These include structures with two azulenes, two indenenes, two cyclopentadiene rings, two benzenes, mixed benzene and azulene structures, and mixed indene and azulene macrocycles. These systems again demonstrate a wide range of aromatic properties and in some cases afford organometallic derivatives. The extent of aromatic character in these structures provides insights into the origins of aromaticity in the porphyrins. It is noteworthy that while some of these porphyrinoids retain highly diatropic characteristics, the stability of many dicarbaporphyrinoids is reduced compared to monoporphyrid systems. Hence, the pyrrole units in porphyrin appear to play an important role in stabilizing these macrocycles. Nevertheless, this work may lead to the development of synthetic routes to quatyrins, theoretically important hydrocarbon analogues of the porphyrins.