



21-Carba-23-oxaporphyrinoids and 21-oxo-21-carba-23-oxaporphyrinoids: macrocyclic π -conjugation involving the carbonyl moiety

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Streszczenie

A rational synthesis using the carba analogues of tripyrrane and 1,3-bis(arylhydroxymethyl)furan as synthons resulted in the formation of 21-carba-23-oxaporphyrin and 21-carba-23-oxachlorin. The molecular design preserves all essential virtues of the 21-oxaporphyrin architecture allowing for incorporation of a cyclopentadiene moiety into the macrocyclic framework. Protonation of the inner core carbon atom reveals its adjustable (trigonal *versus* tetrahedral) geometry. Oxygenation of 21-carba-23-oxachlorin and 21-carba-23-oxaporphyrin afforded aromatic 21-oxo-21-carba-23-oxachlorin and nonaromatic 21-oxo-21-carba-23-oxaporphyrin, respectively. NMR spectroscopy reveals the predominance of the keto tautomer over the hydroxy one. The aromaticity of 21-oxo-21-carba-23-oxachlorin, with a built-in cyclopentanone moiety, resulted from the predomination of the 18 π -electron delocalization assisted by the dipolar resonance contributors. In the case of 21-oxo-21-carba-23-oxaporphyrin incorporating cyclopentadienone, three major canonical structures imply the 20 π -electron antiaromaticity, 18 π -electron aromaticity, or local 4 π -electron antiaromaticity of the cyclopentadienone unit, which seem to contribute to the overall nonaromatic features. DFT optimized molecular models were used to evaluate the nucleus-independent chemical shifts, which are -12.9 for 21-oxo-21-carba-23-oxachlorin and -0.9 for 21-oxo-21-carba-23-oxaporphyrin consistent with magnetic properties reflected by ^1H NMR spectra.

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<https://www.rsc.org/>

