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Synthesis, spectroscopy, and photophysics of hemiporphycene and its oxygen-containing analogues

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Mimicking of porphyrinoids, ideal biocatalytic and energy converting systems, still remains out of reach of the researchers. Beyond potential applications resulting from their natural roles, porphyrinoids are also convenient models for investigation of such elementary chemical reactions as hydrogen or proton transfer and the associated interaction: a hydrogen bond.

The simplest representative of porphyrinoids, porphyrin, has been profoundly investigated in the context of intramolecular hydrogen bond and the process of hydrogen transfer. This high-symmetry molecule is built from four pyrrole and four methine bridges. The first objective of my PhD project was to elaborate the synthesis a structural isomer of porphyrin: hemiporphycene. This compound, similarly to porphyrin and another isomer – porphycene – possesses two intramolecular hydrogen bonds potentially involved in the tautomerization process relying on two hydrogens transfer. The substantial difference between the hemiporphycene and other known porphyrin isomers, as well as the main reason for interest in this compound, is the lower symmetry of hemiporphycene. The disrupted symmetry influences two intramolecular hydrogens bonds, making them chemically inequivalent, contrary to the case of porphyrin and porphycene bonds. The same influence of symmetry applies to the tautomeric forms – six different possible structures are distinguishable in the case of hemiporphycene. These structural properties make hemiporphycene a promising model system for the investigation of nonlinear hydrogen bonds and hydrogen transfer processes in the unsymmetrical potential.

The PhD thesis describes the multistep synthesis of unsubstituted hemiporphycene. Moreover, spectroscopic and photophysical properties of this compound are presented. The obtained results are compared with the characteristics of porphyrin and porphycene. The studies allowed to assign the structures of hemiporphycene tautomers interconverting at room temperature.

The structure of the macrocycle may be also disrupted by the substitution of one of the inner cavity nitrogen atoms by another element. The second objective of the thesis was to synthesize a series of hemiporphycene analogues containing one oxygen atom. The thesis describes the synthesis of four possible oxahemiporphycenes and presents their spectroscopic and photophysical characteristics. The stability tautomeric forms of oxahemiporphycenes has also been discussed.

The work carried out as a part of the doctoral studies resulted in the synthesis of a new class of porphyrinoids: oxahemiporphycenes. The elaborated synthetic strategies and protocols may be further adopted to the synthesis of other new macrocycles possessing low symmetry. The obtained compounds are currently being investigated in the regime of isolated molecules and in single molecule experiments.