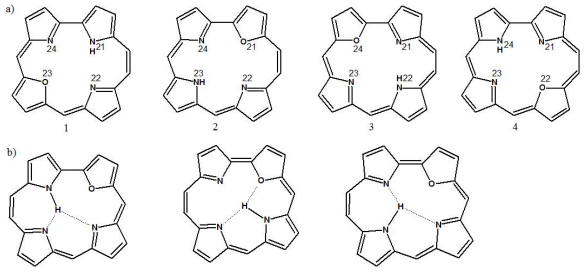
Hydrogen bond is an interaction widely found in nature. It has a great impact on biomolecules, being a key factor that determines the structure of proteins and DNA. It participates in proton transfer processes, the most elementary chemical reactions, of particular meaning also in physics, biology, and materials science. Studies on hydrogen bond physicochemistry allow better understanding of many complex processes, such as conformational changes of proteins and self-asembly of molecules.

Model systems, much simpler than those occurring in nature, are used for the investigation of hydrogen bond. The intramolecular hydrogen bonds in porphyrins make these compounds convenient models for studies of hydrogen bonding and proton transfer processes. Moreover, the strength of intramolecular hydrogen bonds in porphyrins can be easily tuned by changing N•••H-N distances and angles.

The novel structures proposed for the synthesis in this project are oxa- analogs of hemiporphycene (Scheme 1a). Formally, each of them may be represented by three tautomeric forms with the inner hydrogen residing on one of the three nitrogen atoms. (Scheme 1b). The main goal of the project is to elaborate a convenient synthetic approach to oxa- analogs of hemiporphycene and to identify equilibrium tautomeric forms by experimental methods supported by calculations. The influence of hydrogen bond energy, length, and geometrical arrangement on tautomeric equilibria will be discussed. The monooxa analogs of hemiporphycene have been chosen as model compounds for the investigation of intramolecular hydrogen bond due to diversity of possible hydrogen bond configurations. It is expected that the proposed structures will allow to expand the knowledge concerning the nature of hydrogen bond, especially in the poorly known aspect of angle-dependences on its energy. Moreover, spectral and photophysical studies of compounds 1-4 will provide a basis for the investigations of proton transfer processes kinetics and mechanisms in low symmetry systems.



Scheme 1. a) Monooxahemiporphycenes. b) Possible tautomers of 24-oxahemiporphycene 3