

Regioselective internal carbonylation of the 2-aza-21-carbaporphyrin: access to configurationally stable chiral porphyrinoids.

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Streszczenie

Reaction of paraformaldehyde with *meso*-tetraaryl-2-aza-21-carbaporphyrins (NCP) in the presence of a basic catalyst afforded fused lactam derivatives comprising a $>\text{C}=\text{O}$ bridge linking the internal carbon C21 with one of the internal nitrogens. The isomer **2** with C21–C(O)–N24 bridge is formed with about 9-fold molar excess over that with C21–C(O)–N22 bridge (**3**). The ^1H NMR and UV–vis spectral characteristics indicate aromatic character of the derivatives. For *meso*-tetrakis(3',5'-dimethoxy)- and *meso*-tetrakis(3',4',5'-trimethoxy)-21,24-carbonyl-NCP an efficient external ring fusion by linking C3, i.e., the external carbon of the *confused* pyrrole, with an ortho carbon of the adjacent aryl was observed under acidic conditions, yielding derivatives **4c** and **4d**, comprising a linear system of five fused rings. The chirality and configurational stability of these carbonylated systems were established by a chiral stationary phase HPLC and circular dichroism. The interaction of **2** with chiral acids and alcohols leading to the formation of diastereomers was observed by ^1H NMR. Slow racemization of **2** under acidic conditions was established by HPLC and ^1H NMR and a mechanism for this process was proposed.

Adres publiczny

<http://dx.doi.org/10.1021/jo500272t>

Strona internetowa wydawcy

<https://www.acs.org/content/acs/en.html>