

O-confused oxaporphyrin-an intermediate in formation of 3-substituted 2-oxa-21-carbaporphyrins.

Autorzy

Miłosz Pawlicki

Lechosław Latos-Grażyński

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Streszczenie

A condensation of 2,4-bis(phenylhydroxymethyl)furan with pyrrole and *p*-toluylaldehyde in the presence of ethanol formed 5,20-diphenyl-10,15-di(*p*-tolyl)-2-oxa-3-ethoxy-3-hydro-21-carbaporphyrin [(H,EtO)OCPH]H₂. The new carbaporphyrinoid has ¹H NMR features of an aromatic molecule, including the upfield shift of the inner H(21) atom (−5.48 ppm). Addition of acid removes the ethoxy substituent and converts [(H,EtO)OCPH]H₂ into the dication of “true” O-confused oxaporphyrin {[(H)OCPH]H₃}²⁺ via an exocyclic C(3)–O bond cleavage followed by an elimination of the ethoxy group as determined by ¹H NMR. Addition of ethanol, water, or pyrrole converts {[(H)OCPH]H₃}²⁺ into [(H,EtO)OCPH]H₂, [(H,OH)OCPH]H₂, or pyrrole appended O-confused porphyrin [(H,pyrrole)OCPH]H₂, respectively. The reaction of [(H,OEt)OCPH]H₂ with silver(I) acetate yields a stable Ag(III) complex [(H,OEt)OCP]Ag^{III} substituted at the C(3) position by the ethoxy group and hydrogen. Coordination through the nitrogen donors is reflected by the presence of ^{107/109}Ag scalar splitting seen for the selected β-H pyrrolic signals. Addition of TFA to [(H,OEt)OCP]Ag^{III} produces a weakly aromatic O-confused porphyrin complex {[(H)OCP]Ag^{III}}⁺. In the course of this reversible process the tetrahedral–trigonal rearrangements originate at the C(3) atom but extend its consequences on the whole structure. Insertion of silver into the hydroxy analogue of [(H,OEt)OCPH]H₂, i.e., [(H,OH)OCPH]H₂, was accompanied by ligand oxidation, yielding carbaporpholactone which contains the lactone functionality instead of the regular furan moiety embedded in the carbaporphyrin ligand of [(O)OCP]Ag^{III}. The structure was determined by X-ray crystallography. The macrocycle is only slightly distorted from planarity, and silver(III) is located in the NNNC plane.

Słowa kluczowe

Aromatic compounds, Ethanol, Macrocycles, Pyrroles,
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