Carbaporphyrinoids containing a pyridine moiety: 3-aza-*meta*-benziporphyrin and 24-thia-3-aza-*meta*-benziporphyrin.

Autorzy

Radomir Myśliborski

Lechosław Latos-Grażyński

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Streszczenie

6,11,16,21-Tetraaryl-3-aza-*m*-benziporphyrin, an analog of 5,10,15,20-tetraarylporphyrin with one of the pyrrole units replaced by a pyridine ring pointing outwards, linked at β,β′ positions, was formed by condensation of 3,5-bis[phenyl(2-pyrrolyl)methyl]pyridine, pyrrole and *p*-tolualdehyde catalyzed by TFA. The [3+1] approach, which involved a condensation of 3,5-bis[phenyl(2-pyrrolyl)methyl]pyridine with 2,5-bis[hydroxy(*p*-tolyl)methyl]thiophene was applied to afford 6,11,16,21-tetraaryl-24-thia-3-aza-*m*-benziporphyrin. Introduction of bulky substituents at *ortho* positions of *meso*-aryl compounds, adjacent to the pyridine ring, resulted in an increase in the yield of condensation. 3-Aza-*m*-benziporphyrins and 24-thia-3-aza-*m*-benziporphyrins have the ^{1}H NMR spectroscopic features of non-aromatic molecules. Crystal structures of 6,21-diphenyl-11,16-di-*p*-tolyl-3-aza-*m*-benziporphyrin and 6,21-diphenyl-11,16-di-*p*-tolyl-24-thia-3-aza-*m*-benziporphyrin were determined by X-ray crystallography. Both molecules show a similar degree of nonplanarity with the pyridine ring sharply tipped out of the N(23)X(24)N(25) plane, making room for the 6,21-phenyl groups which are almost coplanar with the macrocycle. The protonation of 6,21-diphenyl-11,16-di-*p*-tolyl-3-aza-*m*-benziporphyrin with trifluoroacetic acid proceeds stepwise, subsequently yielding two dicationic and one tricationic species. Protonated 6,21-diphenyl-11,16-di-*p*-tolyl-24-thia-3-aza-*m*-benziporphyrinreacts reversibly with water to give 6-hydroxy-6,21-diphenyl-11,16-di-*p*-tolyl-24-thia-3-aza-*m*-benziphlorin. The protonation of 6,21-dimesityl-11,16-di-*p*-tolyl-24-thia-3-aza-*m*-benziporphyrin initiates an unprecedented process, which converts the non-aromatic carbaporphyrinoid reversibly into the aromatic 2-hydroxy-6,21-dimesityl-11,16-di-*p*-tolyl-24-thia-3-aza-*m*-benzichlorin.