

Transformations of *N*-confused porphyrin triggered by insertion of silicon(IV).

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Streszczenie

N-confused porphyrin, 5,10,15,20-tetraaryl-2-aza-21-carbaporphyrin, dissolved in triethylamine reacts with dichloromethylsilane yielding the methylsilicon(IV) complex of 5,10,15,20-tetraaryl-2-aza-21-hydroxy-21-carbaporphyrin.

Addition of aldehydes or ketones (acetone, acetaldehyde, acetophenone, butanone, propanal, benzaldehyde, *p*-methylbenzaldehyde, *p*-methoxybenzaldehyde, terephthalaldehyde) into the insertion mixture triggered the profound transformation of *N*-confused porphyrin to form the methylsilicon(IV) complex of *N*-fused porphyrin derivative substituted at the inner C(9) position by a hydroxyalkyl moiety derived from aldehyde or ketone. The macrocycle is structurally related to an aromatic *N*-fused inner phlorin while the coordination polyhedron of bound silicon resembles the trigonal bipyramid. The macrocyclic ligand coordinates in the facial mode as the three pyrrolic nitrogen donors lie at the vertices of the single trigonal face. The meridional positions of the trigonal bipyramid are occupied by two pyrrolic nitrogen donors and a σ -methyl ligand. The coordination sphere is completed by apical coordination of the alkoxy oxygen atom derived from alkanal or alkanone. The incorporation of aldehydes and ketones is stereoselective. Acidic desililation of alkanal compounds yields two aromatic *N*-confused porphyrin derivatives, that is, 3-(1-hydroxyalkyl)-5,10,15,20-tetraaryl-2-aza-21-carbaporphyrin and its oxidation product 3-alkanoyl-5,10,15,20-tetraaryl-2-aza-21-carbaporphyrin. The acid triggered desililation of ketone derivatives produces the equimolar amounts of *N*-confused porphyrin and ketone. The first spectroscopically identified step involves the protonation of the C(7) position affording the non-aromatic silicon(IV) complex. The density functional theory (DFT) has been applied to model the molecular and electronic structure of all species identified in the course of silicon insertion into the *N*-confused and *N*-fused porphyrin.

Słowa kluczowe

Aldehydes, Ketones, Molecular structure, Pyrroles, Reaction products

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