

Influence of the benzyl-substitution in porphyrin macrocycles on its ability to extra-ligand axial coordination

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Keywords: zinc tetrabenzoporphyrin complexes, axial ligands, nitro-substitution, spectrophotometric titration.

Abstract

Axial coordination processes of the extra-ligands (pyridine (L1) and 1-methylimidazole (L2)) with zinc(II) tetrabenzoporphyrin (**I**) and its tetranitrosubstituted analogue were investigated in toluene by the spectrophotometric titration and computer simulating methods. The geometric optimization of the studied porphyrinic molecules and their pyridine and imidazole axial complexes was carried out by Gaussian Software using DFT B3LYP/6-31G(d,p) method. The formation of the stable axial complexes of **I** with L2 was confirmed by ¹H NMR spectroscopy data. It was established, that the expansion of the aromatic π -system by addition of extra cycles results in the increasing of the porphyrinic macrocycle ability to axial coordination with different organic basis, what is accompanied by bathochromic shifts of the absorbance bands in UV-vis spectra. According to the computer simulation data inner coordination core of the annulated Zn(II) porphyrin is more expanded in comparison with the Zn(II) tetraphenylporphyrin or Zn(II) octaethylporphyrin (**II**), what makes Zn-N bonds in coordination core more stretched and less strong. Weakening of the Zn-N bonds of **I** results in increasing of extra charge of zinc cation; the ability of **I** to axial coordination with extra imidazole and pyridine ligands increases. It was shown, that the influence of the nitro-substitution in tetrabenzoporphyrinic macrocycle on axial coordination process is more leveled, than the influence of the analogue substitution in octaethylporphyrin. The addition of four NO₂-substituents to tetrabenzoporphyrin macrocycle causes the deformation effect, which is less than for porphyrin **II**. The main factor, determined features of conformation structure of porphyrin molecule, is steric interaction between hydrogens of benzo-substituents and NO₂.

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