

SYNTHESIS OF UNSYMMETRICAL DERIVATES OF AZAPHTALOCYANINES II.

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Magnesium complexes of unsymmetrical azaphtalocyanines (AzaPc) of tetrapyrazinoporphyrazine type with one carboxylic acid were synthesized using statistical condensation of 5,6-bis(*tert*-butylsulfanyl)pyrazine-2,3-dicarbonitrile (A) and 6-(3-*tert*-butylsulfanyl-5,6-dicyanopyrazine-2-ylamino)hexanoic acid (B). These two products were chosen because each of them takes advantage of suitable properties to application of AzaPc in photodynamic therapy. These properties are demonstrated in final product too. Bulky *tert*-butylsulfanyl ensures good monomerisation of planar molecules of AzaPc in a solution and consequently allows efficient separation and purification. Positive influence of alkylsulfanyl substituent on singlet oxygen production has been already shown earlier. Carboxy group, that can be converted in other reactions (esterification, conjugation with biomolecules) brings into the AzaPc the modifiable moiety. The standard cyclization process in butanol in the presence of magnesium butanolate was applied. 2,2-dimethylpropane-1-thiol was liberated during the reaction. Probably, it was due to nucleophilic attack of butanolate on the aromatic pyrazine carbon adjacent to the alkylsulfanyl substituent leading to an exchange of alkylsulfanyl substituents for butoxy groups. The tetramerisation was performed using mixed condensation of two different precursors and a mixture of six possible isomers (AAAA, AAAB, AABB, ABAB, ABBB, BBBB) was obtained. They were detected on TLC but only unsymmetrical derivative of AAAB type was isolated using column chromatography on silica. The precursor B had to be esterified on butylester of 6-(3-*tert*-butylsulfanyl-5,6-dicyanopyrazine-2-ylamino)hexanoic before cyclotetramerization and the final AzaPc was again hydrolyzed to give AAAB in better purity. Optimal reaction conditions were found for hydrolysis. The final compound was characterized using IR, NMR, MS, UV-Vis spectroscopic methods.