

SYNTHESIS OF UNSYMMETRICAL DERIVATES OF AZAPHTALOCYANINES FOR THE THIRD GENERATION OF PHOTSENSITISERS AND SYNTHESIS OF THEIR PRECURSORS

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Unsymmetrical zinc complexes of azaphtalocyanines (AzaPc) of tetrapyrazinoporphyrazine type with one carboxylic acid (AAAB) were synthesized using statistical condensation of 5,6-bis(*tert*-butylsulfanyl)pyrazine-2,3-dicarbonitrile (A) with 6-(3-*tert*-butylsulfanyl-5,6-dicyanopyrazine-2-ylamino)hexanoic acid (B₁) or 3-(5,6-dicyano-3-methyl-pyrazine-2-ylsulfanyl)propionic acid (B₂). These precursors were chosen because each of them takes advantage of suitable properties to application of AzaPc in photodynamic therapy. These properties are demonstrated in final products 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 further functionalized (e.g. conjugation with biomolecules) brings into the AzaPc the modifiable moiety. The standard cyclization process with anhydrous zinc acetate was applied. The final compounds were characterized using IR, NMR, UV-Vis spectroscopic methods.

O-nitroanilin was chosen as a starting material for the synthesis of precursors of enlarged AzaPc (for example benzimidazoporphyrazines, chinoxalinoporphyrazines etc.). It was converted to 1,2-diaminofalonitril in four steps (oxidation of aminogroup, iodation, reduction of nitrogroups and substitution of iodine atoms by cyanogroups). This product can be used in different condensation reactions with vicinal diketones and thus it is a suitable compound to preparation of substituted chinoxaline-6,7-dicarbonitriles.