

SYNTHESIS OF UNSYMMETRICAL DERIVATES OF AZAPHTALOCYANINES VI.

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Aim of the work was to find optimal synthesis of azaphthalocyanines (AzaPcs) with different number of nitrogen-containing peripheral substituents. Zinc complexes (**2**) of AzaPc of tetrapyrazinoporphyrazine type were prepared by cyclization of precursor 5-(*tert*-butylsulfanyl)-6-(diethylamine)pyrazine-2,3-dicarbonitrile (**1**). Its R_f value corresponded exactly to the symmetrical 2,3,9,10,16,17,23,24-*oktakis(tert-butylsulfanyl)*-1,4,8,11,15,18,22,25-(octaaza)phtalocyaninato zinc(II) complex and they will not be isolatable from statistical mixture in future. Therefore, more polar precursor 5-(*tert*-butylsulfanyl)-6-(2-hydroxyethylmethylamine)pyrazine-2,3-dicarbonitrile (**6**) was synthesized for tetramerisation. Side product containing new morpholine ring was also isolated - 4-methyl-3,4-dihydro-2H-pyrazino[2,3-*b*][1,4]oxazine-6,7-dicarbonitrile (**5**) during preparation of (**6**). The cyclization of (**6**) in anhydrous zinc acetate and anhydrous dimethylformamide was unsuccessful. Serendipitously, we have uncovered that metal-free derivatives similar to my differ in R_f values. Therefore, mixture of 15 magnesium phtalocyanines complexes (**8-22**) including their isomers was obtained from the statistical synthesis of 5,6-(*tert*-butylsulfanyl)-2,3-dicarbonitrile (**7**) and dicarbonitrile (**1**) in magnesium butoxide at the 1:1 ratio. The central magnesium can be removed in acidic media (TFA) and several metal-free derivatives can be isolated by preparative TLC. The mixture of positional isomers is necessary to separate by column chromatography on silica.

Keywords: Azaphthalocyanine, tetrapyrazinoporphyrazine, statistical condensation, singlet oxygen.