

New Synthetic Method for Zinc Complexes of 20-Aryltetrabenzo[5,10,15]triazaporphyrin

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Zn^{II} complexes of 20-aryltetrabenzo[5,10,15]triazaporphyrin have been prepared using novel synthetic approach by interaction of phthalonitrile with quaternary triphenylphosphonium salts in the presence of zinc powder. The obtained compounds were characterized by mass-spectrometry, ¹H NMR and UV-vis spectroscopy.

Keywords: Tetrabenzotriazaporphyrins, Zn^{II} complexes, triphenylphosphonium salts.

Complexes of tetrabenzo[5,10,15,20]tetraazaporphyrins, known as phthalocyanines, are an important class of macrocyclic compounds, which due to their unique properties have found a wide range of applications. The close analogs of phthalocyanines are tetrabenzotriazaporphyrins, in which one of the *meso*-nitrogen atoms is substituted by a carbon atom. Tetrabenzo[5,10,15]triazaporphyrins are suggested as photoconducting materials,^[1] fluorescent markers in medicine,^[2,3] and gas sensors.^[4] These compounds remain much less synthetically available than phthalocyanines. The first report on the synthesis of tetrabenzo[5,10,15]triazaporphyrin by heating of the mixture of phthalonitrile, 3-methylenephthalimide and copper chloride at 250°C was published in 1938.^[5] One of the common methods of synthesis of tetrabenzo[5,10,15]triazaporphyrins, used up to now, is the interaction of phthalonitrile with organomagnesium reagents with following refluxing in highly boiling solvent.^[6,7] There is only one communication on the template synthesis of zinc complex of 20-phenyltetrabenzo[5,10,15]triazaporphyrin on the basis of interaction of 1,3-diiminoisoindoline with phenylacetic acid in the presence of template agent (zinc oxide).^[8] Here, we propose a new synthetic method for zinc complexes of 20-aryltetrabenzo[5,10,15]triazaporphyrins by the reaction of unsubstituted phthalodinitrile with quaternary salts of triphenylphosphonium in the presence of zinc powder at gradual heating from 200 to 300°C.[§]

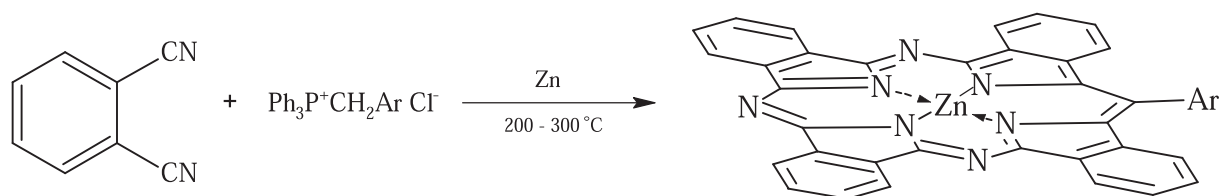
[§]*General procedure for zinc 20-(2-methylphenyl)tetrabenzo[5,10,15]triazaporphyrin.* The mixture of phthalodinitrile (0.64 g, 5.0 mmol), (2-methylbenzyl)triphenylphosphonium chloride (0.40 g, 1 mmol) and zinc powder (0.20 g, 3 mmol) under argon was placed in a bath at 200°C. The resulting yellow-orange melt soon became blue-green with following transformation into dark-blue crystalline mass. Then the temperature was raised to 300°C and the mixture was kept for 6 hours. After cooling, the resulting dark blue crystalline product was dissolved in hot tetrahydrofuran. The solution was filtered off to remove an admixture of zinc phthalocyanine, evaporated, and then chromatographed on a silica gel column (eluent – hexane:tetrahydrofuran 5:2). The collected blue-green zone was chromatographed repeatedly (silica gel, toluene:dioxane 10:1). The residue after evaporation of the solvent was crystallized from a tetrahydrofuran-methanol mixture to give blue-violet crystals which were dried under vacuum at 140°C. Yield: 0.072 g (11%).

It is known that phosphonium ylides react with aromatic nitriles in the presence of Lewis acids.^[9] Many metal cations, used in the classic template synthesis of phthalocyanines, simultaneously are the Lewis acids. Using the classical template method, but with the addition of the quaternary triphenylphosphonium salt as the source of the hydrocarbon radical, we have carried out the synthesis of 20-aryltetrabenzo[5,10,15]triazaporphyrin. Zinc has been chosen as the template agent, because, firstly, zinc salts are the classical Lewis acids, secondly, the zinc cation has a good template and coordination ability and, thirdly, it is known from the literature,^[8] that zinc complex of 20-phenyltetrabenzo[5,10,15]triazaporphyrin is readily soluble in organic solvents, which makes it possible to separate the reaction products by column chromatography. While the reaction proceeds the initial yellow-orange color inherent to phosphonium ylide melt, turns in 10-15 minutes into blue-green, with following further darkening and finally a dark-blue crystalline mass is obtained in the end of the synthesis.

After the separation of zinc phthalocyanine by filtration and chromatography only one metal complex - 20-aryltetrabenzo[5,10,15]triazaporphyrin was isolated. No di- and triarylsubstituted complexes were detected in the reaction products, which facilitates the isolation of the target products. In other methods, the formation of a mixture of mono-, di- and triarylated derivatives was observed.^[7,8]

The obtained compounds were characterized by MALDI-TOF spectrometry, ¹H NMR and UV-vis spectroscopy. The MALDI-TOF mass spectra of the obtained complexes contain the molecular ion peaks with isotopic distribution typical for zinc complexes. ¹H NMR spectra of the obtained zinc aryltetrabenzo[5,10,15]triazaporphyrin complexes are similar to that of the corresponding magne-

m/z (MALDI-TOF): 667 [M⁺]. UV-vis (THF) λ_{max} nm: 385, 442, 593, 646, 667. ¹H NMR ([D₆]DMSO, 363 K) δ_H ppm: 9.30-9.57 (m, 6H), 7.65-8.27 (m, 12H), 7.03 (d, 2H), 1.98 (s, 3H). Similarly the other zinc complexes of aryltetrabenzo[5,10,15]triazaporphyrin were obtained with the corresponding yields: 20-phenyl- (12%), 20-(3-methylphenyl)- (14%), 20-(4-methylphenyl)- (10%), 20-(4-methoxyphenyl)- (2%) tetrabenzo[5,10,15]triazaporphyrin complexes.



Ar: Ph (12%), p-CH₃Ph (10%), m-CH₃Ph (14%), o-CH₃Ph (11%), p-CH₃OPh (2%)

sium complexes.^[7,10] Unlike classical phthalocyanines they contain in a weak field at 9.30-9.60 ppm two multiplets corresponding to six aromatic protons in the α -position of the benzene rings adjacent to three *meso*-nitrogen atoms.

The UV-vis spectra of the synthesized compounds are characterized by the presence of intense absorption bands in the long-wave region (645-667 nm, *Q* bands) and less intense bands in the UV region (385-445 nm, *B* bands). The UV-vis spectra of the zinc complexes are similar to that of the corresponding magnesium derivatives.^[10] The nature of the aryl substituent in the zinc complex has a little effect on the spectral character and the maxima of the absorption bands in the UV-vis spectra. The value of the band maximum in the long-wave region (667 nm) corresponds to the maximum in the case of zinc phthalocyanine, but *Q* band is split due to reduced symmetry of the molecule. The spectra of isolated compounds are also characterized by the presence of the satellite in the Soret band region at 442-445 nm.

In this paper, we propose a new method for synthesis of zinc(II) complexes of 20-aryltetrabenzo[5,10,15]triazaporphyrins, which allowed to obtain the previously unknown compounds. The proposed method is simple and leads to formation of the target complexes as the only soluble reaction

products. In addition, the reagents used - phthalodinitrile, triphenylphosphine and benzylhalides - are the low cost products of large-capacity chemistry.

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