

## Reaction of 4-Phenylphthalimide with Naphthalene-1-acetic Acid in the Presence of Zinc(II) Acetate

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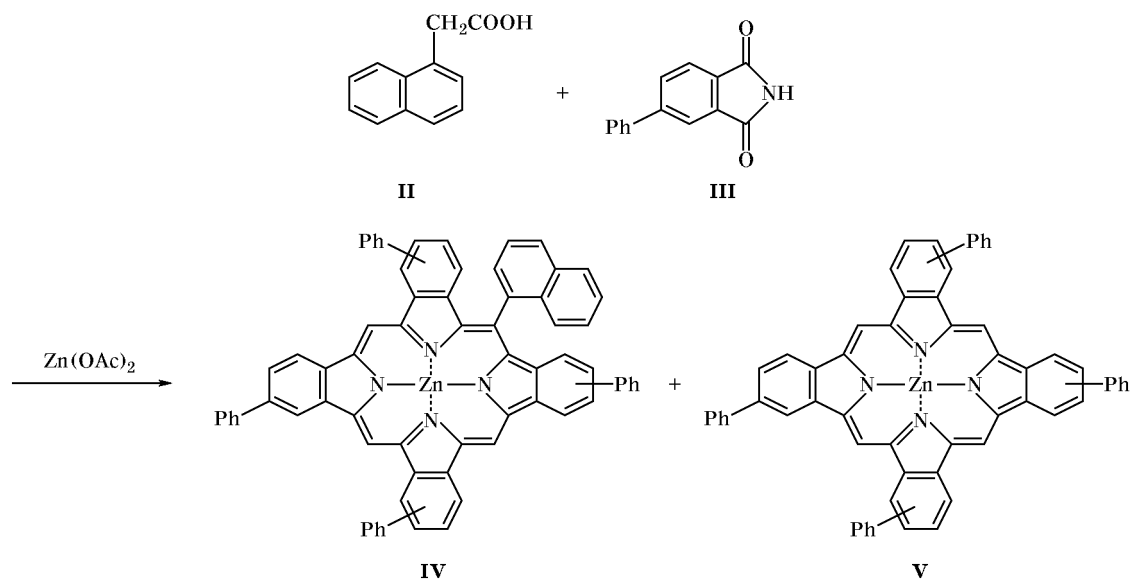
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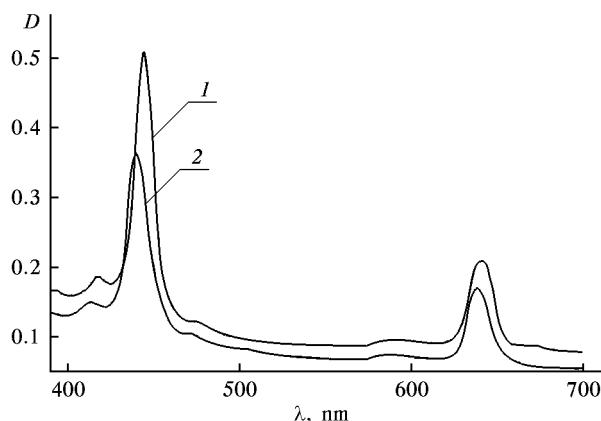
**Abstract**—The only porphyrin-like products formed in the reaction of 4-phenylphthalimide with naphthalene-1-acetic acid in the presence of zinc(II) acetate are zinc complexes of *meso*-mono(1-naphthyl)-4-tetraphenyl-tetrabenzoporphine and 4-tetraphenyltetrabenzoporphine.

*meso*-Tetraaryl-substituted tetrabenzoporphines were reported for the first time in 1981 [1]. They were synthesized by condensation of phthalimide with arylacetic acids in the presence of metal acetates. A more detailed study of this reaction [2] revealed formation of both *meso*-tetraaryltetrabenzoporphines and products containing one, two, and three *meso*-aryl groups. These results were explained by the presence in the reaction mixture of acetate ion which can be the source of methylene component. Later on, Luk'yanets *et al.* proposed a procedure for preparation of the zinc complex of *meso*-tetraphenyltetrabenzoporphine with the use of zinc hydroxide or formate [3]. This procedure ensured synthesis of the target compound containing almost no impurities of partially *meso*-substituted products.

We made an attempt to synthesize the zinc complex of *meso*-tetranaphthyl-4-tetraphenyltetrabenzoporphine (I) by fusion of naphthalene-1-acetic acid (II) with 4-phenylphthalimide (III) in the presence of zinc formate. As a result, we obtained a brown material in which even traces of the target product were not detected. However, by replacing zinc formate by zinc acetate we succeeded in isolating tetrabenzoporphines (the melt turned green). Chromatographic separation of the mixture gave two green products with different electron absorption spectra. Taking into account published data [4] and fast atom bombardment (FAB) mass spectra of the products, they were assigned the structures of zinc complexes of *meso*-mono(1-naphthyl)-4-tetraphenyltetrabenzoporphine (IV) and 4-tetraphenyltetrabenzoporphine (V) (Scheme 1).

Scheme 1.





Electron absorption spectra of the zinc complexes of (1) *meso*-mono(1-naphthyl)-4-tetraphenyltetrabenzoporphine (**IV**) and (2) 4-tetraphenyltetrabenzoporphine (**V**) in benzene.

The mass spectra contained no ion peaks with  $m/z$  1128, 1254, and 1380. This suggests that zinc complexes of *meso*-di-, tri-, and tetra(1-naphthyl)-4-tetraphenyltetrabenzoporphines were not formed.

Complexes **IV** and **V** are dark green crystalline substances which are better soluble in organic solvents (benzene, chloroform, and acetone) than unsubstituted tetrabenzoporphine due to the presence of bulky aryl groups. Figure shows the electron absorption spectra of compounds **IV** and **V**. As expected, the main absorption bands in the spectrum of **IV** are displaced by 4–5 nm to longer wavelengths, as compared with complex **V**. This may be explained by the positive inductive effect of the *meso*-substituent and possible distortion of the porphyrin macroring. An analogous pattern was observed previously for other *meso*-substituted tetrabenzoporphines [5].

Our results allow us to draw the following conclusion. Unlike unsubstituted phthalimide, the use of 4-phenylphthalimide (**III**) in the synthesis of *meso*-naphthyl-substituted tetrabenzoporphines leads to formation of a mixture of compounds **IV** and **V** containing no products with two or more *meso*-naphthyl groups. A probable reason is that the presence of an additional phenyl group in the phthalimide molecule gives rise to considerable steric hindrances which prevent formation of *meso*-polysubstituted products.

#### EXPERIMENTAL

The electron absorption spectra were measured on a Hitachi UV-2000 spectrophotometer. The fast atom bombardment mass spectra (*m*-nitrobenzyl alcohol matrix) were obtained on a Finnigan HSQ-30 mass spectrometer.

**Zinc complexes of *meso*-mono(1-naphthyl)-4-tetraphenyltetrabenzoporphine (**IV**) and 4-tetraphenyltetrabenzoporphine (**V**).** A mixture of 0.6 g of phthalimide **III**, 0.9 g of naphthalene-1-acetic acid (**II**), and 0.8 g of zinc(II) acetate dihydrate was heated for 30 min at 240°C. The temperature was raised to 350°C, and the mixture was kept for 30 min at that temperature. It was then cooled, ground, and subjected to column chromatography on aluminum oxide of activity grade II using benzene as eluent. From the first fraction we isolated 0.06 g (7% with respect to phthalimide **III** or 41% in the porphyrin mixture) of complex **IV** as a dark green powder,  $R_f$  0.52 (eluent benzene, Silufol). Electron spectrum (benzene),  $\lambda_{max}$ , nm ( $D/D_{max}$ ): 642 (1.0), 592 (0.46), 445 (2.45), 418 (0.89). Mass spectrum (FAB),  $m/z$ : 1003.1 [ $M+H$ ]<sup>+</sup>, 1002.1 [ $M$ ]<sup>+</sup>, 876.1 [ $M-C_{10}H_7$ ]<sup>+</sup>. Compound **IV** is readily soluble in DMF, benzene, toluene, and acetone and insoluble in water and dilute acids and alcohols.

The column was then eluted with benzene–acetone (10:1, by volume) to isolate the second fraction from which we obtained 0.11 g (12% with respect to phthalimide **III** or 59% in the porphyrin mixture) of complex **V** as a dark green powder,  $R_f$  0.26 (eluent benzene, Silufol). Electron spectrum (benzene),  $\lambda_{max}$ , nm ( $D/D_{max}$ ): 638 (1.0), 588 (0.43), 440 (2.55), 414 (0.88). Mass spectrum (FAB),  $m/z$ : 879.1 [ $M+3H$ ]<sup>+</sup>, 878.2 [ $M+2H$ ]<sup>+</sup>, 877.2 [ $M+H$ ]<sup>+</sup>, 876.2 [ $M$ ]<sup>+</sup>, 800.1 [ $M-C_6H_5$ ]<sup>+</sup>. Compound **V** is readily soluble in DMF, benzene, toluene, and acetone and insoluble in water and dilute acids and alcohols.

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