Russian Journal of Organic Chemistry, Vol. 38, No. 8, 2002, pp. 1200–1203. From Zhurnal Organicheskoi Khimii, Vol. 38, No. 8, 2002, pp. 1251–1254.

Synthesis and Properties of *meso*-Phenyl-Substituted Tetrabenzoazaporphins Magnesium Complexes

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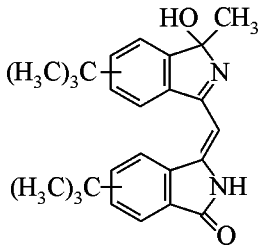
Received January 16, 2002

Abstract—Magnesium complexes of highly soluble *meso*-phenyl-substituted tetrabenzoazaporphins were prepared from 1,3-diiminoisoindoline and phenylacetic acid in the presence of magnesium oxide. Some physicochemical and spectral properties of the compounds were investigated.

Tetrabenzoazaporphines, structural analogs of phthalocyanines and tetrabenzoporphin, occupy intermediate position between these compounds. First information on substances from this group was published in 1938. In reaction between *o*-cyanoacetophenone and metallic iron in a low yield were obtained iron complexes of tetrabenzoporphin, tetrabenzomonoazaporphin, and tetrabenzodiazaporphin [1].



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Nearly simultaneously copper complexes of aza-substituted tetrabenzoporphins were prepared in similar low yields from 3-methylenephthalimide and phthalonitrile in the presence of copper chloride [2]. A method of building up a macroring starting with dimeric isoindologen with a fixed methylene bridge was suggested later [3]. As the starting dimeric compound was used 1-hydroxy-1-methyl-3-(1-oxo-6-*tert*-butylisoindolin-3-ylidenemethyl)-5-*tert*-butyl-1*H*-isoindole (**I**). The reaction of dimer **I** with a phthalonitrile in the presence of zinc acetate provided a mixture of tetrabenzoazaporphins. Its chromatographic separation on alumina furnished zinc complexes of di(4-*tert*-butylbenzo)dibenzomonoaza-, diaza-, triazaporphin. The yields of the complexes were respectively 0.7, 2.9, and 13.1%. The drawback of this method is the necessity of preliminary preparation of the initial compound **I**.

Thus all the above procedures have a number of significant drawbacks related to complications in the synthesis, low yield of the target products, and difficulties arising in separation of compounds mixture with different number of *meso*-nitrogen atoms. Publications treating soluble derivatives of tetrabenzoazaporphins mentioned only compounds with *tert*-butyl substituents attached to isoindole fragments; therewith the number of these publications is very limited [3, 4].

The solubility of tetrabenzoporphin azaderivatives may be increased by introduction of bulky substituents (e.g., phenyl) into the *meso*-position of the macroring. Up till now no such compounds have been described.

The goal of this study was development of synthetic procedure for *meso*-phenyl-substituted tetrabenzoporphins soluble in organic solvents, and investigation of some of their physicochemical and spectral properties.

We studied reaction with phenylacetic acid of 1,3-diiminoisoindoline (**II**) that possessed enhanced reactivity toward nucleophilic reagents and simultaneously was a source of *meso*-nitrogen. The magnesium oxide was used as template agent. The reaction of the compounds for 1 h at 280°C afforded a mixture of magnesium complexes of *meso*-monophenyl-tetrabenzotriazaporphin (**III**), *meso*-*trans*-(**IV**) and -*cis*-diphenyltetrabenzodiazaporphin (**V**), and *meso*-triphenyltetrabenzomonoazaporphin (**VI**).

The magnesium complexes of *meso*-phenyl-substituted tetrabenzoazaporphins are well soluble in organic solvents, and they were separated by column chromatography on aluminum oxide of *II* grade activity.

The homogeneity of compounds obtained was confirmed by TLC, and their structure was establish-

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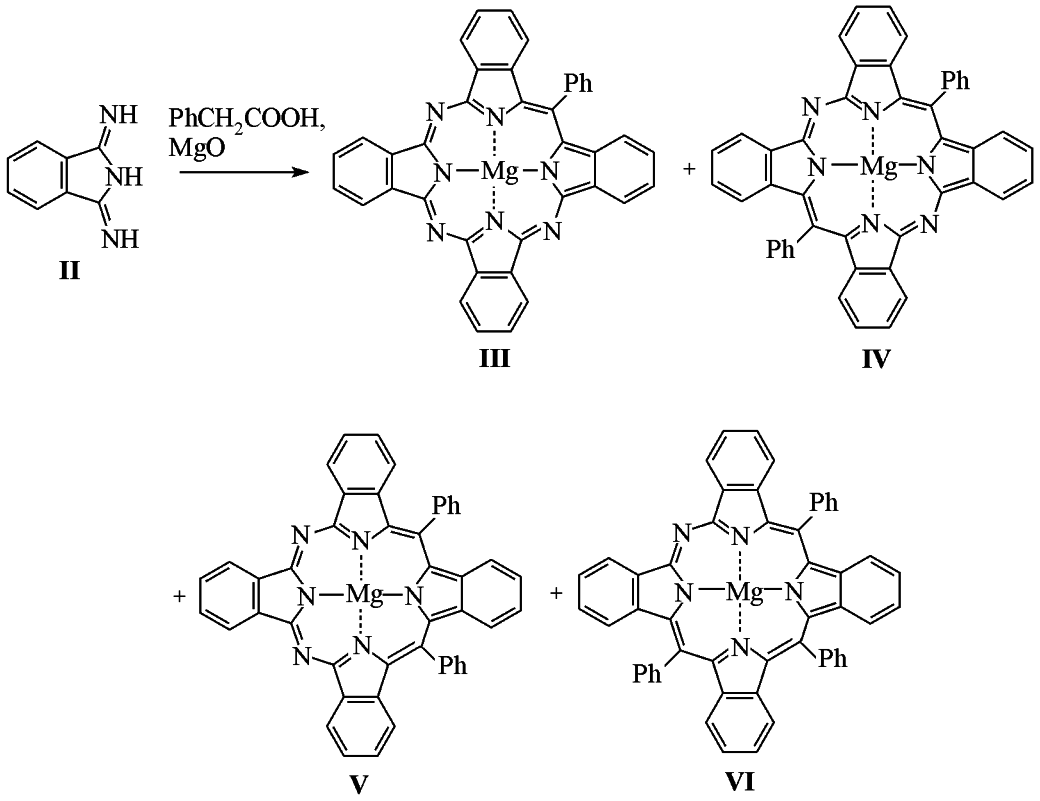

ed from the data of elemental analysis, electronic, and ^{1}H NMR spectra.

The compounds obtained are fine crystalline powders of blue (**III**) or green (**IV**–**VI**) color, soluble in benzene, chloroform, and acetone.

In the ^{1}H NMR spectra of compounds **III**–**VI** registered in deuterochloroform in the downfield region appeared the groups of signals belonging to the aromatic protons. The resonances of protons from isoindole fragments were observed at 8.60–7.90 ppm, and the signals from protons of phenyl substituents were present at 7.85–7.40 ppm. With growing number of *meso*-nitrogens the proton signals from isoindole fragments regularly shifted downfield, whereas the position of phenyl protons remained virtually unchanged. This fact may be rationalized as follows. With growing number of nitrogen atoms in

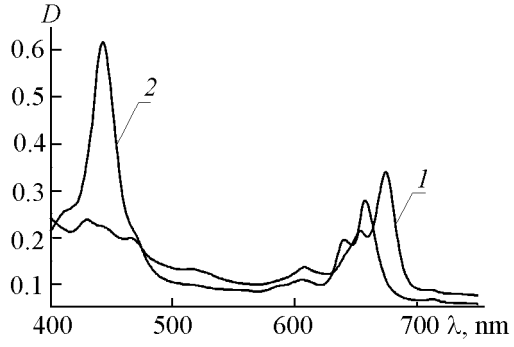

Fig. 1. Electron absorption spectra in benzene. (*1*) Magnesium *meso*-monophenyl-tetrabenzotriazaporphin (**III**). (*2*) Magnesium *meso*-triphenyltetrabenzomonoazaporphin (**VI**).

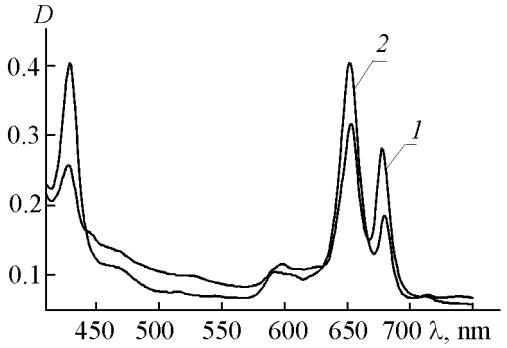

Fig. 2. Electron absorption spectra in benzene. (*1*) Magnesium *meso*-*cis*-diphenyltetrabenzodiazaporphin (**V**). (*2*) Magnesium *meso*-*trans*-diphenyltetrabenzodiazaporphin (**VI**).

the macroring its rigidity and π-deficiency increases. The phenyl substituents are not coplanar with the plane of the macroring and therefore the phenyl protons are less sensitive to the changes in the structure of the molecule.

Electron absorption spectra of compounds **III**–**VI** (Figs. 1, 2) contain characteristic bands in the longwave region of the spectrum (640–670 nm, Q-bands) and bands in the shortwave range (425–450 nm, B-bands). In going from the magnesium *meso*-tetraphenyltetrabenzoporphin [5] to its azaanalogs **III**–**VI** the electronic spectra suffer qualitative alterations: the longwave band undergoes red shift and is split in two components that may be ascribed to lower symmetry of the aza-substituted macroring. For instance, in the spectrum of compound **VI** (Fig. 1) is present a doublet at 658 and 641 nm, and the longwave component is very close in position to the absorption band of compound **IV**, and the shortwave component coincides with the absorption band of the magnesium *meso*-tetraphenyltetrabenzoporphin [6]. In the spectrum of compound **III** (Fig. 1) the longwave component at 675 nm coincides with the absorption band of the magnesium phthalocyanine [6].

Thanks to the good solubility of compounds **IV, V** in a wide range of organic solvents we succeeded in separation of their mixture by column chromatography. The electronic spectra of compounds **IV, V** are presented on Fig. 2. The spectra of *trans* (**IV**) and *cis* (**V**) isomers of magnesium *meso*-diphenyltetrabenzodiazaporphins are similar in position of the main absorption bands, but differ in their intensity. Thus in the spectrum of *cis*-isomer **V** the shortwave component of the Q-band is more intensive, whereas in the spectrum of *trans*-isomer **IV** the intensity of both components is approximately equal. This feature is also characteristic for electron absorption spectra of asymmetrically substituted phthalocyanines of AABB and ABAB types [7].

Gradual aza-substitution in magnesium *meso*-tetraphenyltetrabenzoporphin causes a shift of the shortwave Soret band in the UV region and its broadening. If in the spectrum of compound **VI** this shift is small and amounts to 3–4 nm, for compounds **III**–**V** the shift of Soret band is 14–16 nm. As should be expected, with growing aza-substitution the relative intensity of the Soret band decreases. In the spectrum of compound **VI** the intensity of this band is the greatest, in compounds **IV, V** the Q and Soret bands are of similar intensity, and in the spectrum of compound **III** the Q-band becomes the most strong. Similar trend was observed formerly in the magnesium complexes of unsubstituted tetrabenzoazaporphins [8].

Thus as a result of this research for the first time magnesium complexes of *meso*-phenyl-substituted tetrabenzoazaporphins were prepared that possessed high solubility. Also the effect of gradual aza-substitution on some physicochemical and spectral characteristics of the compounds was investigated.

EXPERIMENTAL

Electron absorption spectra of compounds obtained were measured on spectrophotometer Hitachi UV-2000. ^{1}H NMR spectra were registered on spectrometer Bruker AM-200.

1,3-Diiminoisoindoline (II) was prepared and purified by procedure described in [9].

Magnesium complexes of *meso*-phenyl-substituted tetrabenzoazaporphines III–VI. A mixture of 1.47 g (10 mmol) of 1,3-diiminoisoindoline (**II**), 0.68 g (5 mmol) of phenylacetic acid, and 0.4 g (10 mmol) of magnesium oxide was placed into a quartz tube and heated to 280°C for 1 h. Then the melt was cooled, ground, and subjected to column chromatography on aluminum oxide of *II* grade of activity (eluent benzene–acetone, 10 : 1 by volume). On removing solvent from the first collected fraction we obtained 0.14 g (11.4%) of powdery dark-green compound **VI**. Electron absorption spectrum (benzene), λ_{max}, nm (D/D_{max}): 658 (0.45), 641 (0.31), 607 (0.18), 443 (1.0). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 8.1–7.7 m (16H), 7.60–7.55 m (6H, *o*-C_6H_5), 7.50–7.40 m (9H, *m*, *p*-C_6H_5). Compound **VI** is well soluble in DMF, benzene, chloroform, acetone, insoluble in water, dilute acids and alkali. Found, %: C 84.20; H 4.40; N 9.40. $C_{53}H_{31}MgN_5$. Calculated, %: C 83.52; H 4.10; N 9.19.

The second fraction was eluted with a mixture benzene–acetone (5 : 1 by volume). After the fraction was subjected to chromatography on aluminum oxide for the second time with eluent benzene–ethyl acetate (5 : 1 by volume) we obtained 0.08 g (4.7%) of dark-green powdery compound **IV** and 0.05 g (30%) of dark-green powdery compound **V**.

Compound IV. Electron absorption spectrum (benzene), λ_{max}, nm (D/D_{max}): 679 (0.89), 652 (1.0), 592 (0.26), 429 (1.0). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.9–7.85 m (16H), 7.80–7.75 s (4H, *o*-C_6H_5), 7.65–7.55 m (6H, *m*, *p*-C_6H_5). Compound **IV** is well soluble in DMF, benzene, chloroform, acetone,

insoluble in water, dilute acids and alkali. Found, %: C 81.30; H 4.10; N 12.50. $C_{45}H_{26}MgN_6$. Calculated, %: C 80.42; H 3.81; N 12.25.

Compound V. Electron absorption spectrum (benzene), λ_{max}, nm (D/D_{max}): 677 (0.90), 653 (1.0), 597 (0.36), 428 (0.81). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.95–7.90 m (16H), 7.85– 7.84 m (4H, *o*-C_6H_5), 7.75–7.65 m (6H, *m*, *p*-C_6H_5). Compound **V** is well soluble in DMF, benzene, chloroform, acetone, insoluble in water, dilute acids and alkali. Found, %: C 79.90; H 4.15; N 12.80. $C_{46}H_{26}MgN_6$. Calculated, %: C 80.42; H 3.81; N 12.25.

Then with a mixture benzene–acetone (1 : 5) was eluted the third fraction which on removing the solvent furnished 0.26 g (8.5%) of compound **III** as dark-blue powder. Electron absorption spectrum (benzene), λ_{max}, nm (D/D_{max}): 675 (1.0), 655 (0.63), 609 (0.18), 465 (0.58), 431 (0.70). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 8.60–8.55 m (16H), 7.85–7.84 s (2H, *o*-C_6H_5), 7.65–7.60 m (3H, *m*, *p*-C_6H_5). Compound **III** is well soluble in DMF, benzene, chloroform, acetone, insoluble in water, dilute acids and alkali. Found, %: C 77.15; H 3.90; N 16.45. $C_{39}H_{21}MgN_7$. Calculated, %: C 76.55; H 3.46; N 16.02.

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