Russian Journal of General Chemistry, Vol. 75, No. 4, 2005, pp. 651–655. Translated from Zhurnal Obshchei Khimii, Vol. 75, No. 4, 2005, pp. 689–693.

meso-Phenyltetrabenzoazaporphyrins and Their Zinc Complexes. Synthesis and Spectral Properties

N. E. Galanin, E. V. Kudrik, and G. P. Shaposhnikov

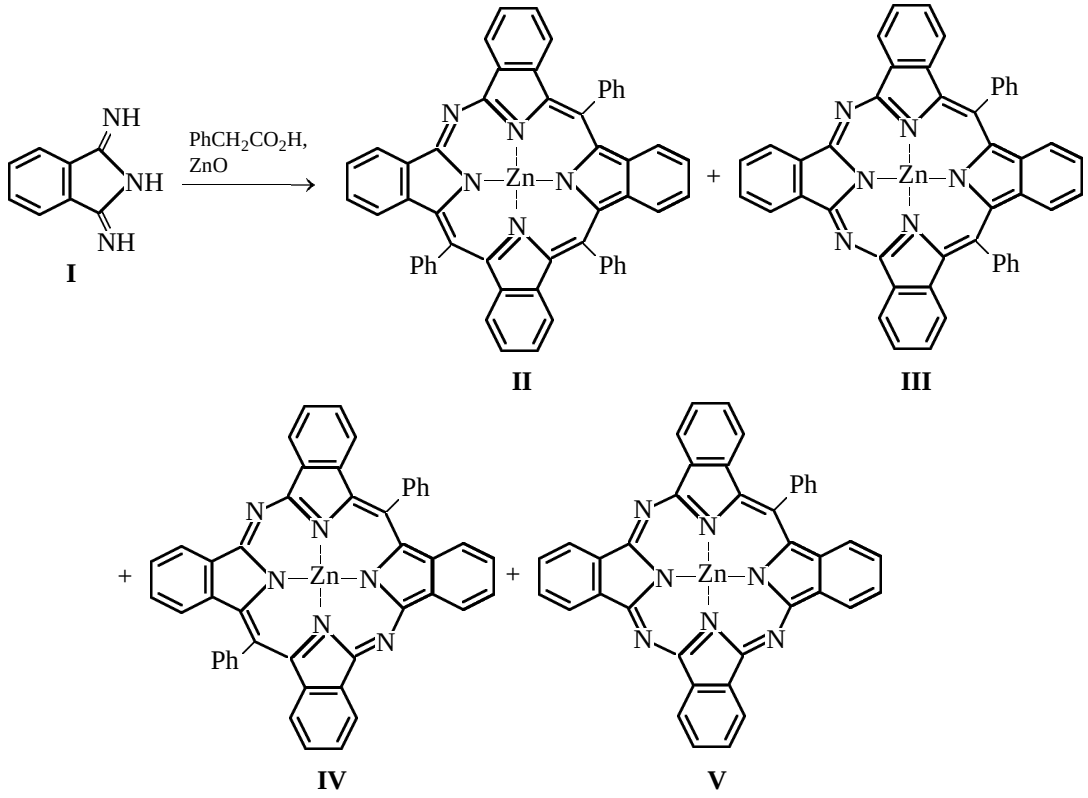
Ivanovo State University of Chemical Technology, Ivanovo, Russia

Received November 12, 2003

Abstract — Zinc complexes of *meso*-phenyltetrabenzoazaporphyrins were prepared by the reaction of isoindoline-1,3-diimine with phenylacetic acid in the presence of zinc oxide. Treatment of the products with sulfuric acid gave metal-free compounds.

Tetrabenzoazaporphyrins occupy an intermediate place between tetrabenzophorphyrin and phthalocyanine. These compounds present a theoretical interest and can be applied as, for example, phototransducers [1].

Previously we showed that template condensation of isoindoline-1,3-diimine (**I**) with phenylacetic acid in the presence of magnesium oxide gives rise to magnesium complexes of *meso*-phenyltetrabenzoazaporphyrins [2]. The present work is a continuation of the research into synthesis and spectral properties of *meso*-phenyltetrabenzoazaporphyrins and their zinc complexes. Zinc *meso*-phenyltetrabenzoazaporphyrins **II**–**V** were synthesized by the reaction of compound **I** with phenylacetic acid in the presence of zinc oxide by the following scheme.



1070-3632/05/7504-0651

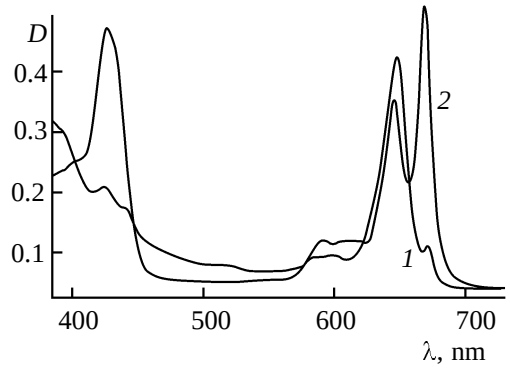


Fig. 1. Electronic absorption spectra of (*1*) zinc *meso*-triphenyltetrabenzoprophyrin (**V**) and (*2*) zinc *meso*-tetrabenzotriazaporphyrin (**V**) in toluene.

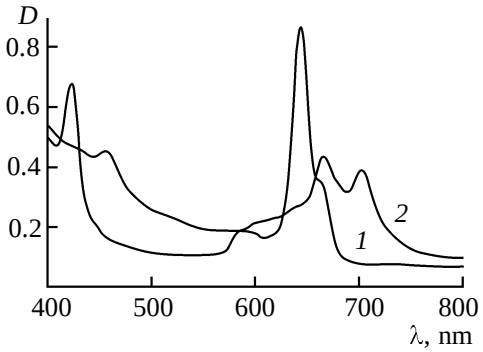


Fig. 2. Electronic absorption spectra of (*1*) zinc *meso-cis*-diphenyltetrabenzodiazaporphyrin (**III**) and (*2*) zinc *meso-trans*-diphenyltetrabenzodiazaporphyrin (**IV**) in toluene.

The mixture of zinc complexes **II**–**V** was separated by column chromatography on alumina. The complexes were then dissolved in concentrated sulfuric acid, and the solutions were left to stand for 2 h ay room temperature to obtain metal-free compounds **VI**–**VIII**. It was found that metal complex **V** under the synthesis conditions undergoes no demetalation, but is sulfurized at higher temperatures and longer exposure times. Purification of compounds **VI**–**VIII** was performed by column chromatography.

The purity of the products was confirmed by TLC, and their composition and structures were established by elemental analysis and ^{1}H NMR and electronic spectroscopy.

Compounds **II**–**VII** were obtained as powders. They are soluble in pyridine, DMF, DMSO, benzene, chloroform, acetone, and concentrated sulfuric acid.

The electronic absorption spectra of metal complexes **II**–**V** (Figs. 1 and 2) characteristically display both long-wave (703–644 nm, *Q* bands) and short-wave bands (421–455 nm, *B* bands). The spectral patterns, maxima positions, and relative intensity of principal bands are much dependent of the number of phenyl substituents. Thus in going from triphenyl-substituted azaporphyrin **II** to monophenyl derivative **V**, the relative intensity of the *Q* band increases, and the spectral pattern gets closer to that of the metal phthalocyanine. The band splitting is associated with the lower symmetry of the macroring. In the case of diphenyldiazaporphyrins, the spectra of the *cis* and *trans* isomers are different from each other. Thus, the *Q* band of *trans* isomer **IV** is split into two components and strongly shifted red compared to that of *cis* isomer **III**. The *Q* band of compound **III** is split only slightly and has a shoulder at 664 nm. The same pattern is also characteristic of unsymmetrically substituted phthalocyanines of the *AABB* type [3, 4]. Such spectral changes can, to a first approximation, be explained in terms of the popular Gouterman's model [5]. According to this model, long-wave bands in the electronic absorption spectra of porphyrins relate to transitions of the a_{1u} orbital to two perperdicular e_g^* orbitals that, in D_{4h} porphyrins (for instance, in their metal complexes), are degenerate. In lower symmetry porphyrins, these orbitals are no longer degenerate, and the *Q* bond is split into two components of close intensity. The magnitude of the splitting is highly sensitive to the nature of the macroring and, according to theoretical predictions, should be maximal in unsymmetrically substituted porphyrazines of the *ABAB* type and minimal in compounds of the *AABB* type. It is this pattern that is observed in our case.

Comparison of the electronic absorption spectra of zinc complexes **II**–**V** with the spectra of known magnesium *meso*-phenyltetrabenzoazaporphyrins [1] shows that substitution of zinc for magnesium radically changes the spectral pattern. Thus, principal absorption bands of zinc complexes **II**, **IV**, and **V** are shifted blue by 8–13 nm compared to respective bands of magnesium complexes, except for *cis* isomer **III**. In the latter case, considerable red shifts of absorption bands compared to magnesium *meso-trans*-diphenyltetrabenzodiazaporphyrin are observed (up to 26 nm for the Soret band and 24 nm for the long-wave component of the *Q* band). This observation is probably explained by a stronger planarity disturbance in the case of magnesium complexes because of the smaller size of magnesium ion compared to zinc ion. As a result, the HOMO energy increases, while the LUMO energy changes only slightly, thereby shifting the absorption bands red. With compound **III** that has a more planar structure, the opposite effect takes place. Having two mutually perpendicular symmetry axes,

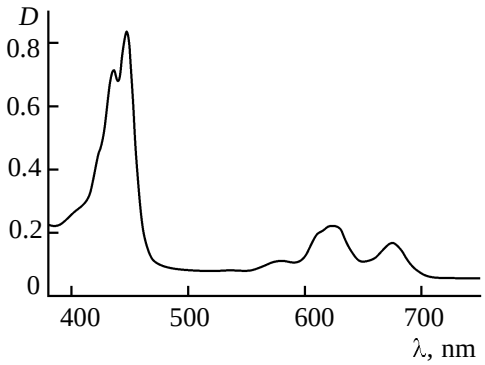


Fig. 3. Electronic absorption spectrum of *meso*-triphenyltetrabenzoazaporphyrin (**VI**) in toluene.

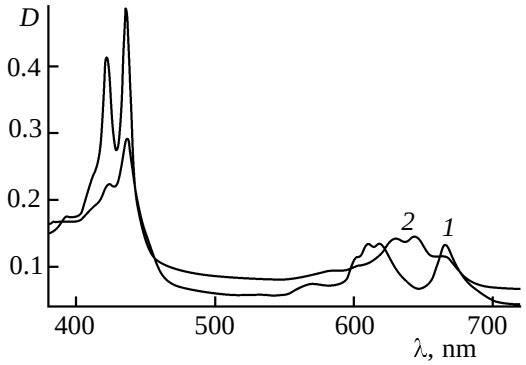


Fig. 4. Electronic absorption spectra of (*1*) *meso-cis*-diphenyltetrobenzodiazaporphyrin (**VII**) and (*2*) *meso-trans*-diphenyltetrobenzodiazaporphyrin (**VIII**) in toluene.

this molecule is strongly polarized, which results in splitting of the *Q* band into two components with their maxima at 703 and 697 nm (Fig 2, spectrum *2*). The planarity disturbance of the molecule of magnesium *meso-trans*-diphenyltetrabenzodiazaporphyrin renders it less polarized, as a result of which the *Q*-band maxima get closer together (679 and 652 nm).

In going from zinc complexes **II**–**V** to metal-free compounds **VI**–**VIII**, the spectral pattern becomes more intricate (Figs. 3 and 4). Since the symmetry of MOs is lowered, the Soret band is split into two components, which is also characteristic of *meso*-substituted tetrabenzoporphyrins [6, 7]. With *meso*-triphenyltetrobenzoazaporphyrin (**VI**), a red shift of absorption bands compared to diphenyl-substituted ligands **VII** and **VIII** is observed. Like with metal complexes **III** and **IV**, in the spectra of compounds **VII** and **VIII**, the degree of band splitting decreases in going from the *trans* to *cis* isomers. The general spectral patterns of the ligands, unlike metal complexes, are similar to those of *meso*-substituted tetrabenzoporphyrines. A possible explanation for this fact is that metal complexes of *meso*-phenyl-substituted tetrobenzoazaporphyrins are only slightly nonplanar, whereas metal-free compounds, in the absence of the stabilizing effect of the complexing metal, are much more distorted. The ligands are close in geometry to *meso*-substituted tetrabenzoporphyrins, which predetermines the similarity of their electronic absorption spectra.

The ^{1}H NMR spectra of the synthesized compounds in DMSO-d_6 contain two downfield multiplets at 8.6–7.5 and 8.0–7.0 ppm, assignable to 16 isoindole protons and phenyl protons, respectively.

In the spectra of metal-free compounds **VI** and **VIII**, the signals of endocyclic protons (Fig. 5) appear as singlets at –0.9 (**VI**) and –1.5 ppm (**VIII**). In the spectrum of *meso-cis*-diphenyldiazaporphyrin (**VII**), the signals of two endocyclic protons appear as two singlets at –1.0 and –1.6 ppm. The appearance of two proton signals in the latter case we relate to nonequivalence of the two endocyclic protons, associated with the unsymmetrical structure of molecule **VII**. A similar spectral pattern was previously observed with an unsymmetrical porphyrazine of the *AABB* type, containing 3,4-dicyano-1,2,5-thiadiazole and 2,3-dicyano-1,4-dipentoxyphthalodinitrile residues [3]; however, the spectrum of the latter compound, unlike what is observed with compound **VII**, two endocyclic proton signals appeared only on cooling of the $CDCl_3$ solution to –58°C.

The gradual upfield shifting of endocyclic proton signals with increasing number of aza groups can be explained by enhancing rigidity and, consequently, planarization of the azaporphyrin molecules.

EXPERIMENTAL

The electronic absorption spectra were measured on a Hitachi UV-2000 spectrophotometer in toluene. The ^{1}H NMR spectra were obtained on a Bruker AMD-300X spectrometer (300 MHz, TMS).

Isoindoline-1,3-diimine (**I**) was synthesized and purified as described in [8].

Zinc complexes of *meso*-phenyl-substituted tetrabenzoazaporphyrins II–V. A mixture of 1.47 g of isoindoline-1,3-diimine (**I**), 1.4 g of phenylacetic acid, and 0.4 g of zinc oxide was placed into a quartz tube and heated at 280°C for 1 h. The resulting melt was cooled, ground, refluxed for 10 min in 100 ml of 20% KOH, filtered off, washed with water to neutral washings, and dried. The residue was dissolved in acetone and subjected to chromatography on a column of alumina (activity grade II), eluent toluene–acetone,

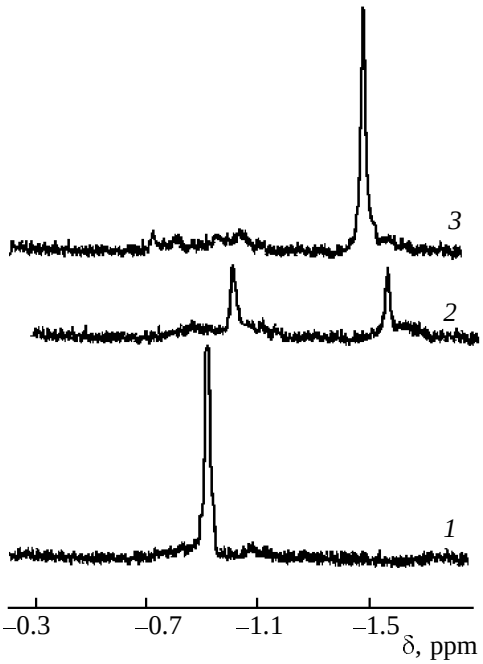


Fig. 5. ^{1}H NMR spectra of compounds (*1*) **VI**, (*2*) **VII**, and (*3*) **VIII** in DMSO-d_6.

10 : 1. Therewith, four bands formed, that contained zinc *meso*-triphenyltetrabenzoazaporphyrin (**II**), zinc *meso-cis*-diphenyltetrabenzodiazaporphyrin (**III**), zinc *meso-trans*-diphenyltetrabenzodiazaporphyrin (**IV**), and zinc *meso*-phenyltetrabenzotriazaporphyrin (**V**).

Zinc *meso*-triphenyltetrabenzoazaporphyrin (II). Yield 0.14 g (11%), R_f 0.76 (Silufol, chloroform). Electronic absorption spectrum (toluene), λ_{max}, nm (D/D_{max}): 672 (0.24), 648 (0.90), 600 (0.02), 427 (1.00). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 8.5–8.3 m (16H), 8.2–7.4 m (15H). Found, %: C 80.2; H 4.4; N 8.4. $C_{53}H_{31}N_5Zn$. Calculated, %: C 79.3; H 3.9; N 8.7.

Zinc *meso-cis*-diphenyltetrabenzodiazaporphyrin (III). Yield 0.03 g (2.5%), R_f 0.55 (Silufol, chloroform). Electronic absorption spectrum (toluene), λ_{max}, nm (D/D_{max}): 664 (0.34), 644 (1.00), 587 (0.02), 421 (0.78). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 8.3–7.6 m (16H), 7.5–7.2 m (10H). Found, %: C 76.4; H 4.1; N 11.2. $C_{46}H_{26}N_6Zn$. Calculated, %: C 75.9; H 3.6; N 11.6.

Zinc *meso-trans*-diphenyltetrabenzodiazaporphyrin (IV). Yield 0.07 g (4.5%), R_f 0.53 (Silufol, chloroform). Electronic absorption spectrum (toluene), λ_{max}, nm (D/D_{max}): 703 (0.73), 667 (0.82), 455 (1.00). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 8.1–7.8 m (16H), 7.7–7.2 m (10H). Found, %: C 74.2; H 3.8; N 10.8. $C_{46}H_{26}N_6Zn$. Calculated, %: C 75.9; H 3.6; N 11.6.

Zinc *meso*-phenyltetrabenzotriazaporphyrin (V). Yield 0.07 g (5%), R_f 0.26 (Silufol, chloroform). Electronic absorption spectrum (toluene), λ_{max}, nm (D/D_{max}): 669 (1.00), 645 (0.69), 597 (0.02), 440 (0.34), 425 (0.41). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 8.3– 7.8 m (16H), 7.5–7.1 m (5H). Found, %: C 72.3; H 4.5; N 14.8. $C_{39}H_{21}N_7Zn$. Calculated, %: C 71.8; H 3.2; N 15.1.

***meso*-Phenyl-substituted tetrabenzoazaporphyrins VI–VIII.** Zinc complex **II**–**V**, 0.1 g, was dissolved in 50 ml of conc. H_2SO_4, and the solution was left to stand at 20°C for 2 h, after which it was poured into 100 ml of water. The precipitate that formed was filtered off, washed with 100 ml of water and 50 ml of 10% ammonia, dried at 100°C, dissolved in acetone, and subjected to column chromatography on alumina (activity grade II) using as eluent toluene–acetone, 10 : 1 (v/v), to isolate compounds **VI**–**VIII**.

***meso*-Triphenyltetrabenzoazaporphyrin (VI).** Yield 0.07 g (73%), R_f 0.78 (Silufol, chloroform). Electronic absorption spectrum (toluene), λ_{max}, nm (D/D_{max}): 674 (0.20), 626 (0.27), 611 (0.24), 577 (0.13), 447 (1.00), 436 (0.86). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 8.6–8.2 m (16H), 8.0–7.2 m (15H), –0.9 s (2H). Found, %: C 85.2; H 4.40; N 9.2. $C_{53}H_{33}N_5$. Calculated, %: C 86.1; H 4.5; N 9.5.

***meso-cis*-Diphenyltetrabenzobenzodiazaporphyrin (VII).** Yield 0.06 g (62%), R_f 0.59 (Silufol, chloroform). Electronic absorption spectrum (toluene), λ_{max}, nm (D/D_{max}): 664 (0.40), 645 (0.50), 631 (0.49), 437 (1.00), 423 (0.77), 389 (0.58). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 8.2–7.6 m (16H), 7.5–7.1 m (10H), –1.0 s (1H), –1.6 s (1H). Found, %: C 82.2; H 4.8; N 13.1. $C_{46}H_{28}N_6$. Calculated, %: C 83.1; H 4.2; N 12.7.

***meso-trans*-Diphenyltetrabenzodiazaporphyrin (VIII).** Yield 0.05 g (54%), R_f 0.54 (Silufol, chloroform). Electronic absorption spectrum (toluene), λ_{max}, nm (D/D_{max}): 666 (0.27), 619 (0.28), 611 (0.28), 603 (0.23), 569 (0.14), 436 (1.00), 422 (0.85), 394 (0.36). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 8.1–7.7 m (16H), 7.6–7.2 m (10H), –1.5 s (2H). Found, %: C 84.8; H 4.5; N 12.3. $C_{46}H_{28}N_6$. Calculated, %: C 83.1; H 4.2; N 12.7.

REFERENCES

1. Shaposhnikov, G.P., Kulinich, V.P., and Maizlish, V.E., in *Uspekhi khimii porfirinov* (Advances in Porphyrin Chemistry), St. Petersburg: Nauchno-Issled. Inst. Khimii S.-Peterb. Gos. Univ., 1999, vol. 2, p. 190.

2. Galanin, N.E., Kudrik, E.V., and Shaposhnikov, G.P., *Zh. Org. Khim.*, 2002, vol. 38, no. 8, p. 1251.
3. Donazello, M., Ercolani, C., Gaberkorn, A., Kudrik, E., Menegetti, M., Marcolongo, G., Rizolli, C., and Stuzhin, P., *Chem. Eur. J.*, 2003, vol. 9, no. 17, p. 4009.
4. Kudrik, E.V., Nikolaev, I.Yu., and Shaposhnikov, G.P., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 2000, no. 12, p. 2062.
5. Gouterman, M., Wagniere, G., and Snyder, L.C., *J. Mol. Spectrosc.*, 1969, vol. 11, no. 2, p. 108.
6. Galanin, N.E., Kudrik, E.V., and Shaposhnikov, G.P., *Zh. Obshch. Khim.*, 2002, vol. 72, no. 7, p. 1198.
7. Galanin, N.E., Kudrik, E.V., and Shaposhnikov, G.P., *Zh. Obshch. Khim.*, 2000, vol. 70, no. 8, p. 1379.
8. Baumann, F., Binert, B., and Rosh, G.U.A., *Angew. Chem.*, 1956, vol. 68, no. 1, p. 133.