ISSN 1070-4280, Russian Journal of Organic Chemistry, 2006, Vol. 42, No. 4, pp. 603–606. © Pleiades Publishing, Inc., 2006.
Original Russian Text © N.E. Galanin, E.V. Kudrik, G.P. Shaposhnikov, 2006, published in Zhurnal Organicheskoi Khimii, 2006, Vol. 42, No. 4, pp. 619–623.

4-Tetraphenyl- and 4-Tetraphenoxy-Substituted *meso*-Tetraphenyltetrabenzoporphyrins. Synthesis and Spectral Properties

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

Ivanovo State University of Chemical Technology, pr. F. Engel'sa 7, Ivanovo, 153460 Russia
e-mail: ttoc@isuct.ru

Received April 25, 2005

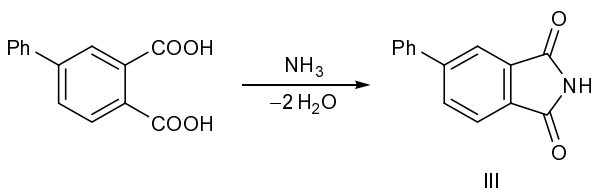
Abstract—The reactions of 4-phenyl- and 4-phenoxyphthalimide with benzoic acid in the presence of zinc(II) oxide gave zinc complexes of *meso*-tetraphenyltetra(4-phenylbenzo)porphyrin and *meso*-tetraphenyltetra-(4-phenoxybenzo)porphyrin, respectively, and the latter were treated with hydrochloric acid to isolate the corresponding metal-free porphyrins. Spectral properties of the complexes and ligands were studied.

DOI: 10.1134/S1070428006040191

We previously reported on the synthesis and properties of *meso*-tetraphenyltetrabenzoporphyrins having substituents in the isoindole fragments and metal complexes derived therefrom [1]. These compounds were prepared by template condensation of substituted phthalimides with benzoic acid in the presence of zinc acetate. It should be noted that the condensation with the use of zinc acetate as template agent led to formation of a mixture of products with different numbers of the *meso*-substituents [2, 3] and that the yield of the target *meso*-tetraphenyl derivatives was fairly poor. In order to avoid formation of partially *meso*-substituted products, it was proposed to use zinc oxide, hydroxide, or formate [4].

In the present work we synthesized zinc complexes of *meso*-tetraphenyltetra(4-phenylbenzo)porphyrin and *meso*-tetraphenyltetra(4-phenoxybenzo)porphyrin **I** and **II** by reactions of 4-phenylphthalimide (**III**) and 4-phenoxyphthalimide (**IV**), respectively, with benzoic acid (**V**) in the presence of zinc oxide. Imide **III** was prepared by passing dry ammonia through molten 4-phenylphthalic acid at 195°C until the mixture solidified (~10 min; Scheme 1). The structure of compound **III** was confirmed by the analytical data and ^{1}H NMR spectrum. The ^{1}H NMR spectrum of **III** contained a singlet at δ 10.33 ppm, corresponding to the NH proton. Protons in the fused benzene ring resonated as a multiplet at δ 7.93–7.75 ppm, and protons in the phenyl substituent gave a five-proton multiplet signal at δ 7.35–7.18 ppm.

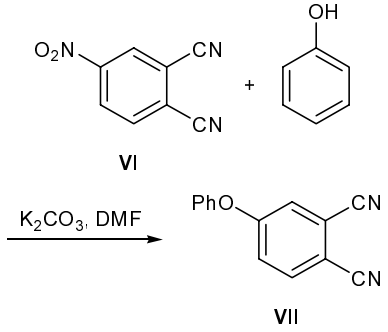
Scheme 1.



III

4-Phenoxyphthalimide (**IV**) was obtained from 4-nitrophthalonitrile (**VI**) [5]. Nucleophilic replacement of the nitro group in **IV** by the action of phenol in DMF in the presence of potassium carbonate gave 4-phenoxyphthalonitrile (**VII**) (Scheme 2).

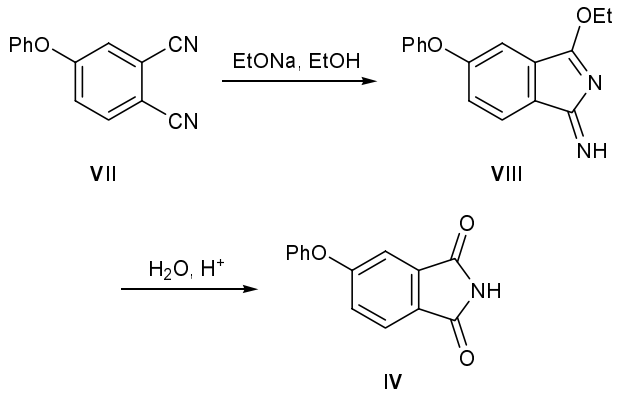
Scheme 2.



VII

Compound **VII** was treated with sodium ethoxide in ethanol, and the subsequent hydrolysis of 3-ethoxy-5-phenoxyisoindol-3-imine (**VIII**) with dilute nitric acid afforded phthalimide **IV** (Scheme 3). The struc-

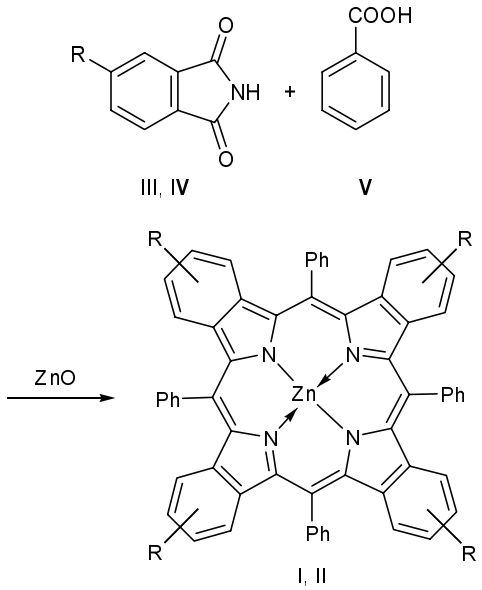
Scheme 3.



ture of compound **IV** was confirmed by the IR and ^{1}H NMR spectra and elemental analysis. Imide **IV** showed in the ^{1}H NMR spectrum a singlet from the NH proton at δ 10.46 ppm and two multiplets in the regions δ 7.94–7.68 (3H) and 7.35–7.15 ppm (5H), corresponding to aromatic protons in the isoindole fragment and phenoxy group, respectively.

Zinc complexes **I** and **II** were synthesized by heating imides **III** and **IV**, respectively with excess benzoic acid (**V**) in the presence of zinc(II) oxide (Scheme 4). The complexes were isolated from the reaction mixture by column chromatography on aluminum oxide. Treatment of solutions of complexes **I** and **II** in chloroform with concentrated hydrochloric acid gave the corresponding metal-free porphyrins **IX** and **X** which were purified by column chromatography.

Scheme 4.



I, **III**, R = Ph; **II**, **IV**, R = PhO.

Zinc complexes **I** and **II** and ligands **IX** and **X** are dark green substances which are readily soluble in a number of organic solvents. Their structure was confirmed by the analytical and spectral data (^{1}H NMR and electronic absorption spectroscopy). The ^{1}H NMR spectrum of zinc complex **I** lacked signals from *meso*-protons in the region δ 9–12 ppm, indicating the absence of partially *meso*-phenyl-substituted derivatives as impurity. The multiplet signal at δ 8.33–7.92 ppm was assigned to eight protons in the *para* positions of the phenyl substituents, signals from 32 *ortho*- and *meta*-protons appeared as a multiplet in the region δ 7.65–7.21 ppm, and 12 protons in the isoindole fragments resonated as a multiplet at δ 7.15–6.94 ppm. The ^{1}H NMR spectrum of **II** was quite similar to that of complex **I**. Likewise, the absence of signals from protons in the *meso* positions indicated exhaustive *meso*-substitution.

Unlike complexes **I** and **II**, metal-free compounds **IX** and **X** showed in the ^{1}H NMR spectra signals from the intracyclic NH protons at δ –0.9 and –0.3 ppm, respectively. According to published data [6], the NH signal of *meso*-tetraphenyltetrabenzoporphyrin is located at δ –1.12 ppm. The observed downfield shift of the corresponding signals in the ^{1}H NMR spectra of compounds **IX** and **X** indicates stronger distortion of the macroring in their molecules (especially in **X**), as compared to *meso*-tetraphenyltetrabenzoporphyrin.

The electronic absorption spectra of phenyl-substituted *meso*-tetraphenyltetrabenzoporphyrin **IX** and its zinc complex **I** (Fig. 1) are very similar to the spectra of *meso*-tetraphenyltetrabenzoporphyrin and its zinc complex [4]; the difference is observed only in positions of the absorption maxima. Introduction of four phenyl substituents into the isoindole fragments of (*meso*-tetraphenyltetrabenzoporphyrinato)zinc leads to a small red shift of the absorption maxima (by 6 nm for the Soret band and by 8 nm for the *Q* band), presumably due to participation of the phenyl substituents in conjugation with the macroring via partial overlap of their π-electron systems and stronger distortion of the macroring. The same applies to metal-free compound **IX**, for which the red shift of both absorption maxima is 5 nm.

A different pattern was observed with phenoxy-substituted analogs **II** and **X**. The effect of phenoxy substituents on the absorption spectra (Fig. 2) is much stronger, and the absorption maxima of phenoxy-substituted compounds **II** and **X** are located at shorter wavelengths, as compared to the corresponding maxima of *meso*-tetraphenyltetrabenzoporphyrin and

its zinc complex. The blue shift is 16 nm for the Soret band and 11 nm for the *Q* band of zinc complex **II**, while in the case of ligand **X** the shift is as large as 25 nm. Probably, distortion of the macroring in molecules **II** and **X**, caused by steric effect of the phenoxy substituents, is so strong that it leads to partial rupture of the conjugation system with reduction in the degree of aromaticity. This is indirectly supported by the ^{1}H NMR data. In order to substantiate this assumption, we performed AM1 semiempirical quantum-chemical calculations of the geometric structure of molecules **IX** and **X**. The calculated structure of molecule **X** (as PLUTO model) is shown in Fig. 3. It is seen that the macroring in molecule **X** is distorted to a strong extent. The angle characterizing deviation of the isoindole fragments from the average macroring plane reaches 48°. Obviously, this should lead to partial rupture of the conjugation system, which is responsible for the observed blue shift of the absorption maxima. Unlike compound **X**, the distortion of the macroring in molecule **IX** is weaker, and the angle between the isoindole fragments and the average macroring plane is 36°; therefore, the conjugation system in **IX** is not ruptured to an appreciable extent. Thus the results of calculations are very consistent with the experimental spectral patterns.

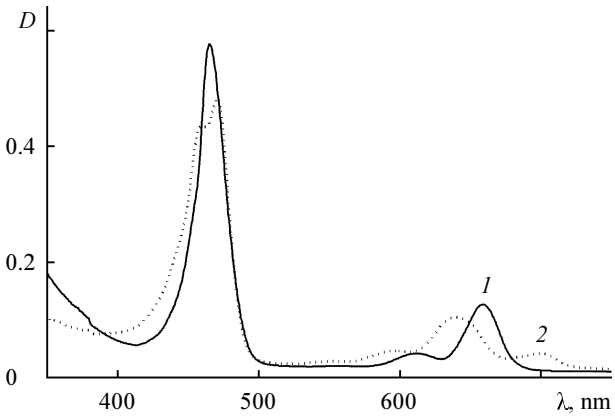


Fig. 1. Electron absorption spectra of compounds (*1*) **I** and (*2*) **IX** in benzene.

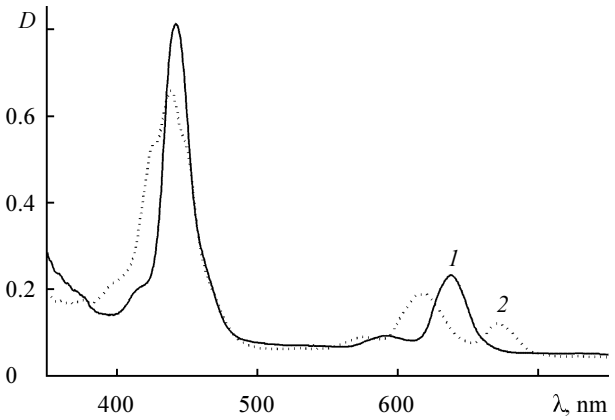


Fig. 2. Electron absorption spectra of compounds (*1*) **II** and (*2*) **X** in benzene.

Fig. 3. AM1 simulated structure of the molecule of $2^{2(3)},7^{2(3)},12^{2(3)},17^{2(3)}$-tetraphenoxy-5,10,15,20-tetraphenyltetrabenzoporphyrin (**X**).

EXPERIMENTAL

The electronic absorption spectra were recorded on a Hitachi UV-2000 spectrophotometer. The IR spectra (400–4000 cm^{-1}) were obtained in KBr on an Avatar 360 FT-IR spectrometer. The ^{1}H NMR spectra were measured on a Bruker WM-250 instrument (250 MHz) using TMS as internal reference.

4-Phenylphthalimide (III). Dry gaseous ammonia was passed through 1.5 g of molten 4-phenylphthalic acid at 195°C until the mixture solidified. The solid was cooled, powdered, and used in further synthesis without additional purification. Yield quantitative, light gray powder, mp 198–199°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 10.33 s (1H), 7.93–7.75 m (3H), 7.35–7.18 m (5H). Found, %: N 6.10. $C_{14}H_9NO_2$. Calculated, %: N 6.27.

4-Phenoxyphthalonitrile (VII). A mixture of 5 g (0.03 mol) of 4-nitrophthalonitrile (**VI**), 5 g (0.05 mol) of phenol, and 6 g (0.04 mol) of potassium carbonate in 50 ml of anhydrous DMF was stirred for 24 h at 100°C and poured into 200 ml of water. The precipitate was filtered off, washed with 200 ml of water, and dried. Yield 6.3 g (83%), white powder, mp 96–98°C. Found, %: C 76.4; H 3.7; N 12.6. $C_{14}H_8N_2O$. Calculated, %: C 76.2; H 3.6; N 12.7.

4-Phenoxyphthalimide (IV). Compound **VII**, 3 g (0.014 mol), was added at 15°C to a solution of sodium ethoxide prepared from 30 ml of ethanol and 0.5 g of metallic sodium. The mixture was stirred for 2 h and poured into 50 ml of 10% nitric acid. After

30 min, the precipitate was filtered off, washed with 150 ml of water, and dried. Yield 3.5 g (92%), white powder, mp 112–113°C. Compound **VII** is readily soluble in DMF, DMSO, and acetone and sparingly soluble in hot water. IR spectrum, ν, cm^{-1}: 3200 (N–H), 2936 (C–H), 1762 (C=O), 1043 (C–O). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 10.46 s (1H), 7.94–7.68 m (3H), 7.35–7.15 m (5H). Found, %: N 5.77. $C_{14}H_9NO_3$. Calculated, %: N 5.85.

($2^{2(3)}$,5,$7^{2(3)}$,10,$12^{2(3)}$,15,$17^{2(3)}$,20-Octaphenyltetrabenzoporphyrinato)zinc(II) (I). A mixture of 1 g (4.5 mmol) of 4-phenylphthalimide (**III**), 1.8 g (13 mmol) of benzoic acid (**V**), and 2.0 g (25 mmol) of zinc(II) oxide was heated for 30 min at 240°C; the temperature was then raised to 350°C, and the mixture was kept for an additional 30 min at that temperature. The resulting melt was cooled, pounded, and extracted with chloroform in a Soxhlet apparatus. The extract was evaporated to dryness, the residue (a dark green powder) was dissolved in benzene, and the solution was subjected to column chromatography on aluminum oxide (Brockmann activity grade II) using benzene as eluent. Yield 0.26 g (19%), dark green powder. The complex is readily soluble in DMF, DMSO, benzene, chloroform, and acetone and insoluble in water. Electronic absorption spectrum (benzene), λ_{max}, nm (D/D_{max}): 659 (0.22), 610 (0.01), 465 (1.00). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 8.33–7.92 m (8H), 7.65–7.21 m (32H), 7.15–6.94 m (12H). Found, %: C 84.13; H 4.75; N 4.55. $C_{84}H_{52}N_4Zn$. Calculated, %: C 85.30; H 4.43; N 4.74.

$2^{2(3)}$,5,$7^{2(3)}$,10,$12^{2(3)}$,15,$17^{2(3)}$,20-Octaphenyltetrabenzoporphyrin (IX). Complex **I**, 0.1 g, was dissolved in 10 ml of chloroform, 5 ml of concentrated hydrochloric acid was added, and the mixture was stirred for 1 h. The mixture was then diluted with water, and the organic phase was separated, washed with water, aqueous ammonia, and water again to pH 7, dried over $CaCl_2$, and subjected to column chromatography on aluminum oxide (Brockmann activity grade II) using benzene as eluent. Yield 0.08 g (76%), dark green powder. Compound **IX** is readily soluble in DMF, DMSO, benzene, chloroform, and acetone and insoluble in water. Electronic absorption spectrum (benzene), λ_{max}, nm (D/D_{max}): 702 (0.09), 640 (0.22), 595 (0.09), 472 (1.00), 458 sh. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 8.36–7.97 m (8H), 7.58–7.29 m (32H), 7.25–6.93 m (12H), –0.9 s (2H). Found, %: C 90.92; H 4.51; N 4.68. $C_{84}H_{54}N_4$. Calculated, %: C 90.13; H 4.86; N 5.01.

($2^{2(3)}$,$7^{2(3)}$,$12^{2(3)}$,$17^{2(3)}$-Tetraphenoxy-5,10,15,20-tetraphenyltetrabenzoporphyrinato)zinc(II) (II). A mixture of 1.2 g (5 mmol) of imide **IV**, 2.2 g (16 mmol) of benzoic acid **V**, and 0.6 g (7 mmol) of zinc(II) oxide was heated for 30 min at 240°C; the temperature was then raised to 350°C, and the mixture was kept for an additional 30 min at that temperature. The resulting melt was cooled, pounded, and extracted with chloroform in a Soxhlet apparatus. The extract was evaporated to dryness, the residue (a dark green powder) was dissolved in benzene, and the solution was subjected to column chromatography on aluminum oxide (Brockmann activity grade II) using benzene as eluent. Yield 0.25 g (18%), dark green powder. The complex is readily soluble in DMF, DMSO, benzene, chloroform, and acetone and insoluble in water. Electronic absorption spectrum (benzene), λ_{max}, nm (D/D_{max}): 640 (0.29), 592 (0.11), 443 (1.00). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 8.45–8.25 m (4H), 8.16–7.88 m (8H), 7.75–7.53 m (28H), 7.48–6.95 m (12H). Found, %: C 81.15; H 4.73; N 4.4. $C_{84}H_{52}N_4O_4Zn$. Calculated, %: C 80.92; H 4.20; N 4.49.

$2^{2(3)}$,$7^{2(3)}$,$12^{2(3)}$,$17^{2(3)}$-Tetraphenoxy-5,10,15,20-tetraphenyltetrabenzoporphyrin (X) was synthesized as described above for compound **IX** from 0.1 g of zinc complex **II**. Yield 0.07 g (72%), dark green powder. Compound **X** is readily soluble in DMF, DMSO, chloroform, benzene, and acetone and insoluble in water. Electronic absorption spectrum (benzene), λ_{max}, nm (D/D_{max}): 673 (0.18), 620 (0.29), 576 (0.13), 438 (1.00), 426 sh. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 8.58–8.35 m (4H), 8.19–7.68 m (8H), 7.74–7.59 m (28H), 7.47–6.98 m (12H), –0.3 s (2H). Found, %: C 86.10; H 4.37; N 4.43. $C_{84}H_{54}N_4O_4$. Calculated, %: C 85.26; H 4.60; N 4.73.

REFERENCES

1. Galanin, N.E., Kudrik, E.V., and Shaposhnikov, G.P., *Russ. J. Gen. Chem*., 1997, vol. 67, p. 1306.
2. Ichimura, K., Sakuragi, M., Morii, H., Yasuike, M., Fukui, M., and Ohno, O., *Inorg. Chim. Acta*, 1991, vol. 182, p. 83.
3. Ichimura, K., Sakuragi, M., Morii, H., Yasuike, M., Toba, Y., Fukui, M., and Ohno, O., *Inorg. Chim. Acta*, 1991, vol. 186, p. 95.
4. Luk'yanets, E.A., Dashkevich, S.N., and Kobayashi, N., *Russ. J. Gen. Chem*., 1993, vol. 63, p. 985.
5. Thiel, W. and Mayer, R., *J. Prakt. Chem*., 1986, vol. 328, p. 497.
6. Yasuike, M., Yamaoka, T., Ohno, O., Sakuragi, M., and Ichimura, K., *Inorg. Chim. Acta*, 1991, vol. 184, p. 191.