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meso-Quinolyl-substituted Tetrabenzoporphins. Synthesis and Properties

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Abstract—Prolonged heating of phthalimide with 2-methylquinoline in the presence of zinc oxide afforded zink complexes of *meso*-tri-, di- and monoquinolyltetrabenzoporphins. Alternative preparation methods were developed for some among these compounds. The corresponding porphins were prepared by treating complexes with hydrochloric acid. The spectral characteristics of compounds synthesized were investigated.

meso-Aryl-substituted tetrabenzoporphins are prepared by reaction of phthalimide with arylacetic acids in the presence of a template agent (zinc or cadmium com-pounds) under stringent conditions: at the temperature up to 380°C [1–5].

We developed a preparation method for zinc *meso*-tetra(2-quinolyl)tetrabenzoporphinate (**I**) by reaction of phthalimide with 2-methylquinoline in the presence of zinc oxide [6]. Heating the mixture at boiling point (248°C) for 12 h afforded compound **I** in a yield of about 15%.

It was presumable that a longer heating would lead to a better yield of complex **I**. However the boiling of the reagents mixture for 36 h did not provide the desired result On the contrary, the yeld of compound **I** reduced to 2.8%, and from the reaction mixture were isolated by column chromatography alongside compound **I** also zinc complexes of *meso*-tri(2-quinolyl)tetrabenzoporphin (**II**), *meso*-di(2-quinolyl)tetrabenzoporphin (**III**), and *meso*-(2-quinolyl)tetrabenzoporphin (**IV**).

Products of incomplete *meso*-aryl substitution in the tetrabenzoporphin form at the use as the template agent of metal acetates; therewith the acetate ion serves as a source of a methylene group [7]. The application of zinc oxide or hydroxide results in formation of solely zinc *meso*-tetraaryltetrabenzoporphinate [1]. The presence in the reaction mixture of compounds **II–IV** in our case is an uncommon fact that may be due to the thermal degradation of complex **I** for the prolonged heating results in decrease in its amount. A similar pattern was formerly observed at the study of oxidative degradation at heating of metal complexes of *meso*-tetraphenyltetrabenzoporphin [8]. It was established that the heating of the metal complex in air resulted in mass loss in the sample corresponding to the successive elimination of the *meso*-phenyl substituents. Thus the formation of compounds **II–IV** follows Scheme 1.

Therewith due to sterical hindrances the formation of zinc *meso*-*trans*-di(2-quinolyl)tetrabenzoporphinate (**III**) is more probable than of its *cis*-isomer. For instance, quantum-chemical calculations by the semiempirical AM1 procedure show that the enthalpy of formation ΔH_f for compound **III** is 1837.32 kJ mol^{-1}, by 37.46 kJ mol^{-1} less than for zinc *meso*-*cis*-di(2-quinolyl)tetrabenzoporphinate.

Complexes **II–IV** were isolated from the reaction mixture by column chromatography on alumina. It should be pointed out that the preparative separation of a mixture of four porphyrins **I–IV** is a difficulr problem. Therefore we developed selective preparation methods for tetra-benzoporphyrins **III** and **IV**.

One synthetic method for products of incomplete *meso*-aryl substitution in the tetrabenzoporphin is building up of a macroring from dimeric isoindologen with a fixed position of the methine group. It is known [4] that in the selective synthesis of zinc *meso*-diphenyltetrabenzo-porphinate a dimeric product can be used prepared by phthalimide condensation with acetic or malonic acid, 3-(3-oxo-2,3-dihydro-1*H*-1-isoindolylidenemethyl)-1*H*-1-isoindolone (**V**). We used this compound for preparation of zinc complex **III**. The reaction of dimer **V** with excess 2-methylquinoline in the presence of zinc oxide at 280°C within 30 min afforded compound **III** in an approximately 12% yield.

Porphyrin **III** was isolated from the reaction mixture by column chromatography. Besides a small amount of

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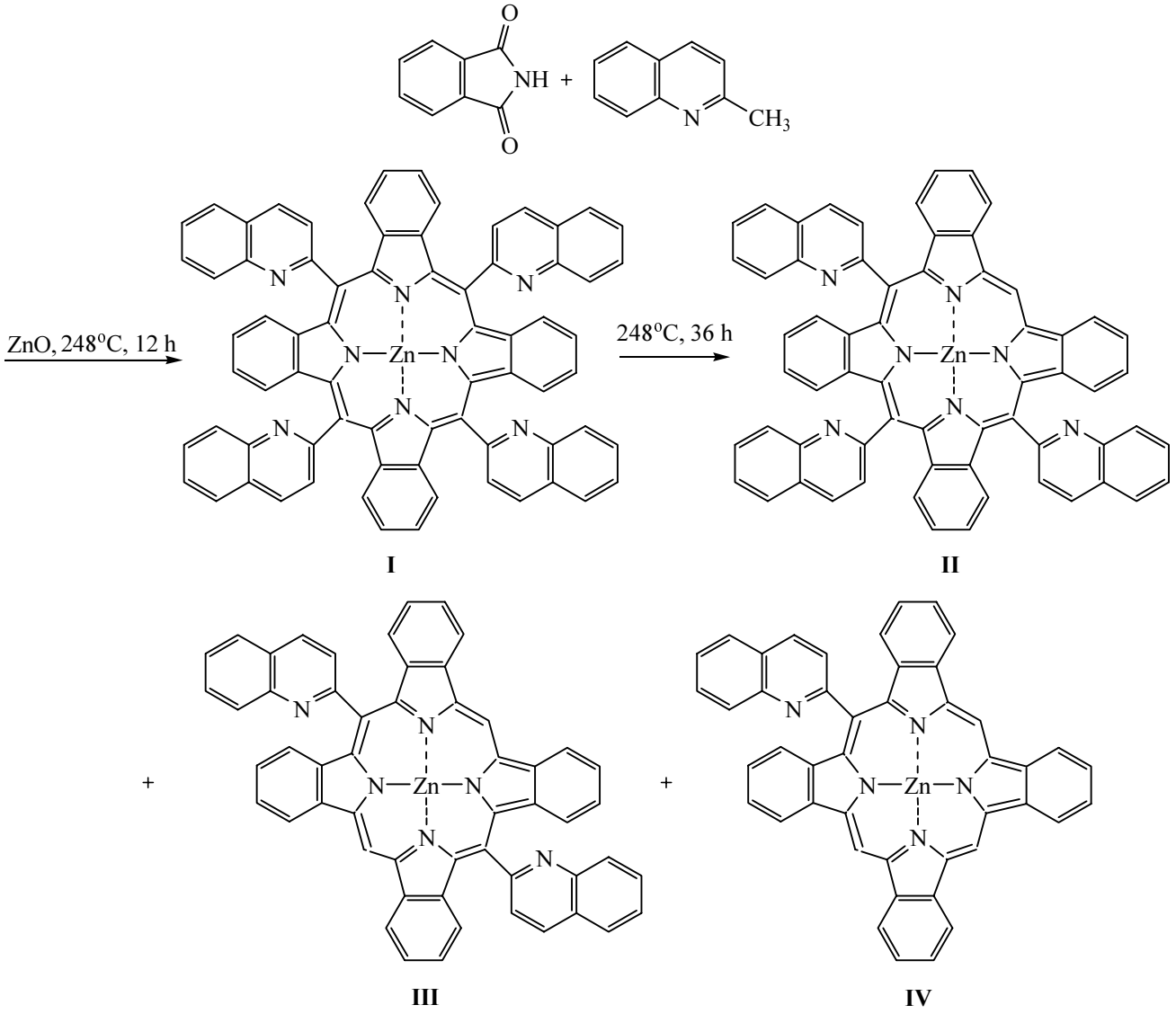
Scheme 1.



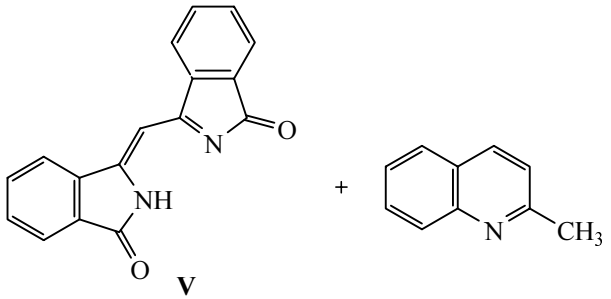
complex **IV** was isolated arising apparently due to elimination of one *meso*-substituent from molecule **III**.

It was shown formerly [7], that in the synthesis of *meso*-phenyl-substituted zinc tetrabenzoporphinates 3-benzylidenephthalimidine could be used.

By boiling equimolar quantities of phthalimide and 2-methylquinoline in trichlorobenzene for 5 h we prepared its quinolyl-substituted analog, 3-(2-quinolylmethylidene)-phthalimidine (**VI**) (Scheme 3).

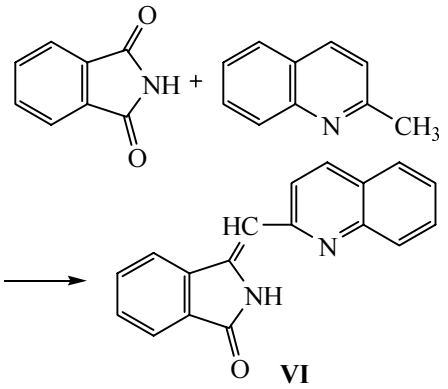
On completion of the reaction trichlorobenzene and un-reacted 2-methylquinoline were distilled off in a vacuum. Compound **VI** was isolated from the reaction mixture by column chromatography; its composition and structure were proved by elemental analysis, ^{1}H and ^{13}C NMR spectroscopy.

Scheme 2.



In the ^{1}H NMR spectrum of compound **VI** the most downfield signal appearing as broadened singlet at 11.36 ppm belonged to the imino group; a singlet from CH group proton is observed in the strongest field, at 6.95 ppm.

Scheme 3.



VI

The doublet in the region 8.40–8.35 ppm corresponds to the proton of the quinolyl substituent in the *para*-position with respect to nitrogen, and the doublet at 7.66–7.62 ppm originates from the proton in *meta*-position. The multiplet in the region 8.20–7.70 ppm corresponds to four protons of benzene ring attached to the quinolyl substituent, and to four protons of the isoindole moiety. The broadening of the signal of the imino group proton indicates that it is involved into a hydrogen bond with the nitrogen of the quinoline ring.

The heating at 300°C of a mixture of compound **VI** and excess phthalimide in the presence of zinc acetate for 20min afforded complex **IV** in about 10% yield.

Although the main reaction product was zinc tetrabenzoporphinate (**VII**), the chromatographic isolation of complex **IV** was easy due to its high solubility in organic solvents.

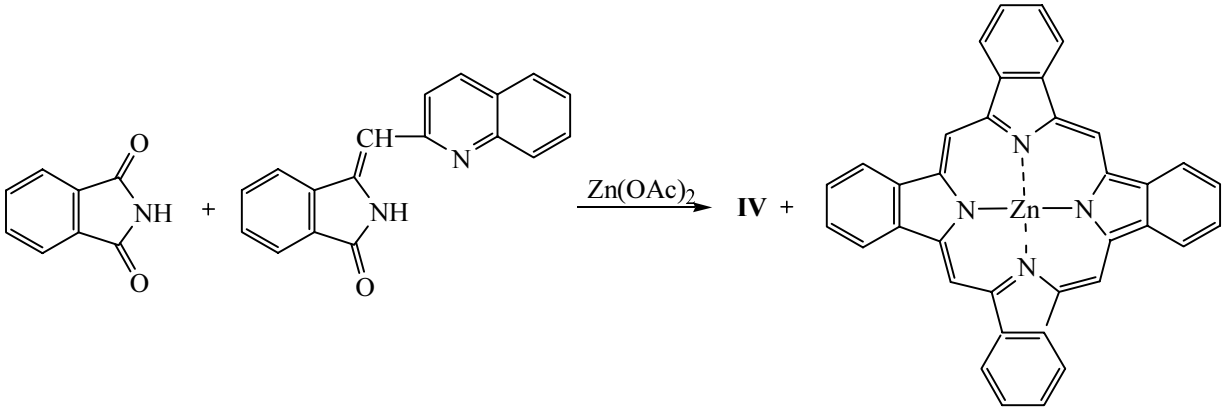
Metal complexes **II–IV** are dark-green crystalline substances, well soluble in benzene, chloroform, acetone, and DMF. Their homogeneity was proved by TLC, the composition and structure were confirmed by elemental analysis, electronic and ^{1}H NMR spectroscopy, and also by field desorption mass spectrometry. It should be noted that here the CHN-elemental analysis provided few information: the percent content of carbon, hydrogen, and nitrogen in going from tri- to (2-quinolyl)-substituted tetrabenzoporphins varied insignificantly (from 1 to 0.1%), therefore the most reliable for proving the structure of compounds **II–IV** were the mass spectra.

The electron absorption spectra of *meso*-heteryl-substituted zinc tetrabenzoporphinates **II–IV** (Fig. 1) have the same pattern as the respective spectra of *meso*-phenyl-substituted complexes: They contain a strong Soret band in the region 449–435 nm and a less strong Q-band in the region 643–630 nm. The comparison of spectral data obtained with those of *meso*-phenyl-substituted zinc tetrabenzoporphinates [3–5] shows that replacement of three phenyl substituent in the molecule of zinc *meso*-triphenyltetrabenzoporphinate by a 2-quinolyl groups caused simultaneous red shift of the absorption bands by 9–11 nm, and the analogous replacement in the zinc *meso*-monophenyltetrabenzoporphinate provided a red shift by 5–7 nm. The replacement in the zinc *meso*-diphenyl-tetrabenzoporphinate of the phenyl substituents by 2-quinolyl ones led to the red shift of the Soret band by 11 nm, and of Q-band only by 3 nm.

This spectral pattern may be due to stronger spatial distortion of molecules in compounds **II–IV** compared to the molecules of the *meso*-phenyl-sybstituted porphyrins caused by larger size of the quinoline fragments than that of benzene rings. Note also that on the spectra of compounds **II–IV** bands characterizing the absorption of the quinoline moieties appear in the region 314 nm

In the ^{1}H NMR spectra of the zinc complexes **II– IV** the most downfield signals in the region 9.80–9.30 ppm correspond to the methine group protons, and the signal

Scheme 4.



VI **VII**

shifts successively downfield as the number of the *meso*-substituents decreases. This fact is due to the lesser distortion of the macroring and consequently with growing deshielding of the methine group protons. The resonance of protons from the quinolyl moieties ins observed in a stronger field at 8.70–8.20 ppm, and the multiplets in the region 8.00–7.40 ppm belong to the protons in the isoindole fragments.

The metal-free porphyrins **VIII–X** were obtained by treating the acetone solutions of compounds **II–IV** by concn. hydrochloric acid. They were purified by column chromatography on alumina. The substances are green crystals well soluble in polar and nonpolar organic solvents. Their composition and structure were also derived from elemental analysis, electronic, ^{1}H NMR, and mass spectra.

The electron absorption spectra of porphyrins **VIII–X** (Fig. 2) also resemble the spectra of the corresponding *meso*-phenyl-substituted tetrabenzoporphins. In going from compound **VIII** to compound **X** the absorption bands simultaneously undergo a blue shift by 5–7 nm, and their splitting is increased.

In the ^{1}H NMR spectra of porphyrins **VIII–X** the most upfield signal in the region–0.99...–1.80 ppm belongs to the protons of the endocyclic imino groups, and with decrease in the number of the *meso*-substituents a successive upfield shift is observed due to flattening of the macroring

In the course of chromatography of porphyrins **VIII–X** and their metal complexes **II–IV** we observed their abnormal mobility in the column packed with alumina. It turned out that in contrast to the *meso*-phenyl-substituted tetrabenzoporphins the highest mobility corresponded to *meso*-mono(2-quinolyl)-substituted compounds **IV** and **X**, and the lowest to *meso*-tri(2-quinolyl)-substituted **II** and **VIII**. This phenomenon is apparently caused by coordination of the pyridine nitrogens in the *meso*-substituents to the aluminum atoms. Therefore with growing number of the *meso*-substituents the R_f value of the corresponding poephyrines decreases.

EXPERIMENTAL

Electron absorption spectra of compounds obtained were measured on a spectrophotometer Hitachi UV-2000, ^{1}H NMR spectra (200 MHz, internal reference HMDS) and ^{13}C NMR spectra (75 MHz) were registered on spectrometer Bruker AM-200 from solutions in DMSO-d_6. Field desorption mass spectra were obtained on JEOL JMS 700 instrument.

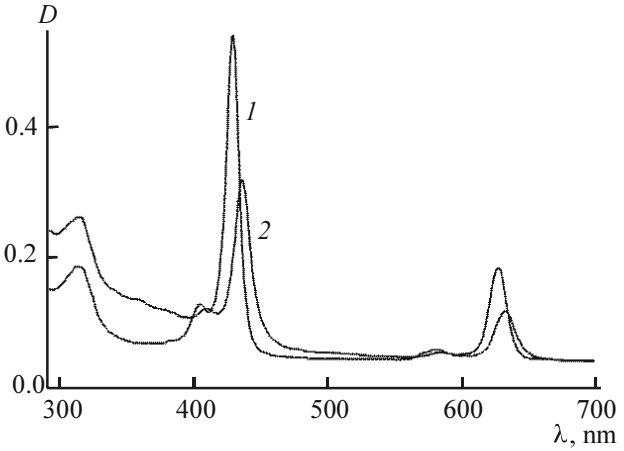


Fig. 1. Electron absorption spectra in chloroform solution: (*1*) compound **IV**; (*2*) compound **III**.

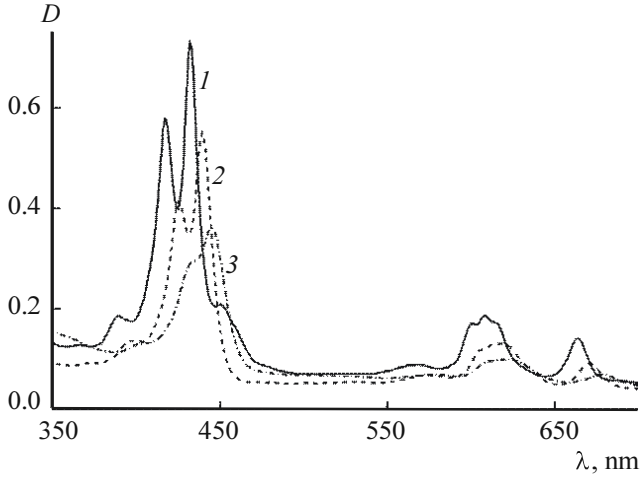


Fig. 2. Electron absorption spectra in chloroform solution: (*1*) compound **X**; (*2*) compound **IX**; (*3*) compound **VIII**.

3-(3-Oxo-2,3-dihydro-1*H*-1-isoindolylidenemethyl)-1*H*-1-isoindolone (**V**) was prepared and pyrified as described in [4].

***meso*-(2-Quinolyl)-substituted zinc tetrabenzoporphinates II–IV.** *a.* A mixture of 1 g of phthalimide (**I**), 0.3 g of zinc oxide, and 10 ml of 2-methylquinoline (**V**) was boiled for 36 h. The reaction mixture was cooled and subjected to chromatography on a column packed with aluminum oxide of II grade activity. By elution with a mixture benzene–hexane, 1:10 by volume, was separated excess 2-methylquinoline, then with a mixture chloroform–acetone, 10:1 by volume, was separated the green zone. On removing the solvent the residue was dissolved in chloroform and subjected to chromatography on a column packed with aluminum oxide of II grade activity, eluent chloroform–hexane, 1:1 by volume. The separation occurred into 4 green zones containing

respectively compounds **I–IV** which were dark green substances well soluble in benzene, acetone, and chloroform, insoluble in water. On removing the solvent compounds **II–IV** were isolated.

b. A mixture of 0.5 g (2 mmol) of compound **V**, 1.5 g (10 mmol) of 2-methylquinoline, and 0.2 g of zinc oxide was heated at 280°C for 30 min. The melt was cooled, crushed into powder, and the product was extracted by chloroform in a Soxhlet apparatus. The extract was evaporated to dryness, the dark-green powder obtained was dissolved in dichloromethane and subjected to chromatography on a column packed with aluminum oxide, eluent dichloromethane–benzene, 1:1 by volume. The main green zone was collected, and the solvent was evaporated to furnish 0.01 g (12%) of compound **III** whose properties were identical to the sample obtained by procedure *a*.

c. A mixture of 0.5 g (2 mmol) of compound **VI**, 1 g (7 mmol) of phthalimide, and 1 g of zinc acetate was heated at 300°C for 20 min. The melt was cooled, crushed into powder, and the product was extracted by chloroform in a Soxhlet apparatus. The extract was evaporated to dryness, the dark-green powder obtained was dissolved in dichloromethane and subjected to chromatography on a column packed with aluminum oxide, eluent dichloromethane. The main green zone was collected, and the solvent was evaporated to furnish 0.12 g (10%) of compound **IV** whose properties were identical to the sample obtained by procedure *a*.

Zinc *meso*-tri(2-quinolyl)tetrabenzoporphinate (II). Yield 0.07 g (4.8%), R_f 0.20 ($CHCl_3$, Silufol). Electron absorption spectrum ($CHCl_3$), λ_{max}, nm (D/D_{max}): 643 (0.32), 597 (0.15), 449 (1.00), 418 (0.45), 316 (0.88). ^{1}H NMR spectrum, δ, ppm: 9.30 s (1H), 8.66–8.25 m (18H), 7.95–7.65 m (16H). Mass spectrum, *m/z*: 954 $[M + H]^+$, 1907 $[2M + H]^+$. Found, %: C 80.25; H 3.4.02; N 10.16. $C_{63}H_{35}N_7Zn$. Calculated, %: C 79.31; H 3.70; N 10.28.

Zinc *meso*-di(2-quinolyl)tetrabenzoporphinate (III). Yield 0.10 g (6.7%), R_f 0.39 ($CHCl_3$, Silufol). Electron absorption spectrum ($CHCl_3$), λ_{max}, nm (D/D_{max}): 634 (0.36), 589 (0.07), 437 (1.00), 409 (0.38), 314 (0.82). ^{1}H NMR spectrum, δ, ppm: 9.45 s (2H), 8.66–8.45 m (12H), 7.90–7.60 m (16H). Mass spectrum, *m/z*: 826 $[M]^+$, 1653 $[2M + H]^+$. Found, %: C 78.20; H 3.50; N 10.45. $C_{54}H_{30}N_6Zn$. Calculated, %: C 78.43; H 3.66; N 10.17.

Zinc *meso*-(2-quinolyl)tetrabenzoporphinate (IV). Yield 0.05 g (3.4%), R_f 0.69 ($CHCl_3$, Silufol). Electron absorption spectrum ($CHCl_3$), λ_{max}, nm (D/D_{max}): 628 (0.37), 583 (0.08), 430 (1.00), 404 (0.23), 314 (0.26). ^{1}H NMR spectrum, δ, ppm: 9.78 s (3H), 8.70–8.55 m (6H), 8.00–7.75 m (16H). Mass spectrum, *m/z*: 700 $[M + H]^+$, 1400 $[2M + H]^+$. Found, %: C 78.01; H 3.80; N 10.15. $C_{45}H_{25}N_5Zn$. Calculated, %: C 77.24; H 3.60; N 10.01.

3-(2-Quinolylmethylidene)phthalimidine (VI). A mixture of 6 g (0.04 mol) of phthalimide, 5.7 g (0.04 mol) of 2-methylquinoline, and 20 ml of trichlorobenzene was boiled for 8 h, then the trichlorobenzene and unreacted 2-methylquinoline were distilled off in a vacuum. The residue was dissolved in chloroform and subjected to chromatography on a column packed with aluminum oxide (eluent chloroform) collecting the light-yellow zone. On removing the solvent 1.2 g (10.9%) of light-yellow powdery compound **VI** was obtained well soluble in benzene, acetone, chloroform, and DMF, insoluble in water. ^{1}H NMR spectrum, δ, ppm: 11.36 s (1H), 8.40–8.35 d (1H), 8.20–7.70 m (8H), 7.66–7.62 d (1H), 6.95 s (1H). ^{13}C NMR spectrum, δ, ppm: 169.25, 167.87, 155.79, 147.32, 138.60, 137.67, 134.30, 132.61, 130.31, 128.58, 127.75, 126.38, 123.26, 121.03, 102.41. Found, %: C 79.55; H 4.60; N 10.42. $C_{18}H_{12}N_2O$. Calculated, %: C 79.40; H 4.44; N 10.29.

***meso*-(2-Quinolyl)-substituted tetrabenzoporphins VIII–X.** In 5 ml of acetone was dissolved 0.05 g of zinc complex **II–IV**, 1 ml of concn. HCl was added, and the mixture was left standing for 1 h at 20°C. Then 5 ml of concn. NH_3 solution and 20 ml of chloroform was added, and the mixture was stirred for 5 min. The organic layer was separated, the solvent was evaporated, the residue was dissolved in chloroform and subjected to chromatography on a column packed with aluminum oxide of II grade activity (eluent benzene–chloroform, 1:1 by volume). Compounds **VIII–X** were isolated by removing the solvent.

***meso*-Tri(2-quinolyl)tetrabenzoporphin (VIII).** Yield 0.03 g (59%), R_f 0.25 ($CHCl_3$, Silufol). Electron absorption spectrum ($CHCl_3$), λ_{max}, nm (D/D_{max}): 679 (0.19), 622 (0.28), 583 (0.16), 444 (1.00), 433 sh, 401 (0.36). ^{1}H NMR spectrum, δ, ppm: 9.28 s (1H), 8.68–8.30 m (18H), 7.90–7.45 m (16H), –0.99 s (2H). Mass spectrum, *m/z*: 891 $[M]^+$, 1784 $[2M + H]^+$. Found, %: C 78.01; H 3.80; N 10.15. $C_{63}H_{37}N_7$. Calculated, %: C 84.82; H 4.18; N 11.00.

***meso*-Di(2-quinolyl)tetrabenzoporphin (IX).** Yield 0.04 g (72%), R_f 0.42 ($CHCl_3$, Silufol). Electron absorption

spectrum ($CHCl_3$), λ_{max}, nm (D/D_{max}): 671 (0.17), 616 (0.24), 603 sh, 565 (0.13), 439 (1.00), 425 (0.75) 397 (0.25). ^1H NMR spectrum, δ, ppm: 9.33 s (2H), 8.55–8.48 m (12H), 7.8 8–7.62 m (16H), –1.55 s (2H). Mass spectrum, *m/z*: 765 $[M + H]^+$, 1529 $[2M + H]^+$. Found, %: C 84.01; H 5.10; N 10.38. $C_{54}H_{32}N_6$. Calculated, %: C 84.79; H 4.22; N 10.99.

***meso*-(2-Quinolyl)tetrabenzoporphin (X).** Yield 0.03 s (57%), R_f 0.75 ($CHCl_3$, Silufol). Electron absorption spectrum ($CHCl_3$), λ_{max}, nm (D/D_{max}): 664 (0.19), 615 (0.24), 608 (0.25), 601 (0.23), 568 (0.12), 432 (1.00), 418 (0.79) 389 (0.25). ^1H NMR spectrum, δ, ppm: 9.73 s (3H), 8.75–8.52 m (6H), 7.88–7.45 m (16H), –1.80 s (2H). Mass spectrum, *m/z*: 638 $[M + H]^+$, 1277 $[2M + H]^+$. Found, %: C 85.35; H 4.75; N 10.66. $C_{45}H_{27}N_5$. Calculated, %: C 84.74; H 4.27; N 10.99.

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