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5,15-Dialkyl-Substituted Tetrabenzoporphyrins and Their Zinc Complexes. Synthesis and Spectral Properties

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Abstract—Reactions of phthalimide with capric and stearic acids gave 1-[1-(1-oxo-1*H*-isoindol-3-yl)nonylidene]-2,3-dihydro-1*H*-isoindol-3-one and 1-[1-(1-oxo-1*H*-isoindol-3-yl)heptadecylidene]-2,3-dihydro-1*H*-isoindol-3-one, respectively. The latter were heated with zinc(II) acetate to obtain zinc complexes of 5,15-dioctyl- and 5,15-dihexadecyltetrabenzoporphyrins. The same complexes were synthesized by reaction of 1-(1-oxo-1*H*-isoindol-3-ylmethylidene)-2,3-dihydro-1*H*-isoindol-3-one with capric or stearic acid in the presence of zinc(II) oxide. The corresponding free porphyrin ligands were obtained by treatment of the metal complexes with sulfuric acid.

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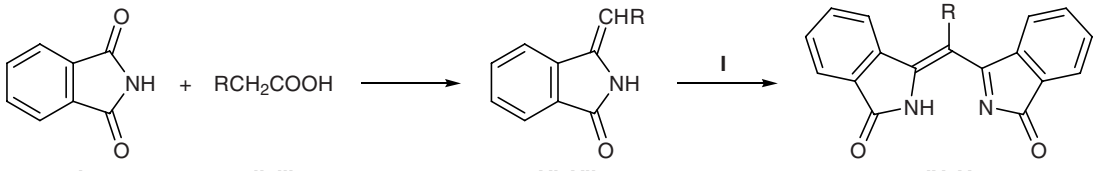
meso-Substituted tetrabenzoporphyrins constitute one of the most important groups of synthetic analogs of natural porphyrins. Among other factors, interest in these compounds is determined by their improved solubility in a number of organic solvents, which makes it possible to use chromatographic methods for their purification and considerably facilitates applied studies. Up to now, *meso*-aryl-substituted tetrabenzoporphyrins have been explored most thoroughly. They were proposed as dyes [1], photochromic light filters [2], and materials for photodynamic therapy of cancer [3, 4] and nonlinear optics [5]. On the other hand, publications on the synthesis of *meso*-alkyl-substituted tetrabenzoporphyrins are very few in number, though such compounds could attract interest from both theoretical and practical viewpoints.

First representatives of *meso*-tetraalkyl-substituted tetrabenzoporphyrins were synthesized in 1984 [6] by reaction of 3-alkylidenephthalimidines with zinc acetate in the presence of an organic base (tribenzylamine) under helium at 340°C. In this way, *meso*-tetramethyl-, *meso*-tetraethyl-, and *meso*-tetrapropyltetrabenzoporphyrin zinc complexes were obtained. However, the proposed procedure requires preliminary multistep preparation of the corresponding 3-alkylidenephthtalimidines, and the presence of four alkyl groups with a carbon chain no longer than three atoms only slightly improves the solubility of porphyrins in organic solvents.

Taking the above into account, we tried to synthesize readily soluble *meso*-tetraalkyl-substituted tetrabenzoporphyrins by reactions of phthalimide (**I**) with capric and stearic acids **II** and **III** in the presence of zinc(II) oxide and sodium hydroxide. The reactions were carried out at 320°C (1 h) under argon. However, no appreciable amounts of the target metal complexes were formed under these conditions, while the products were 1-[1-(1-oxo-1*H*-isoindol-3-yl)nonylidene]-

Scheme 1.



I **II**, **III** **VI**, **VII** **IV**, **V**

II, **IV**, **VI**, R = C_8H_{17}; **III**, **V**, **VII**, R = $C_{16}H_{33}$.

2,3-dihydro-1*H*-isoindol-3-one (**IV**) and 1-[1-(1-oxo-1*H*-isoindol-3-yl)heptadecylidene]-2,3-dihydro-1*H*-isoindol-3-one (**V**). Presumably, closure of porphyrin macroring is hampered for steric reasons: neither prolonged reaction nor elevated temperature (380°C) resulted in the formation of the desired complexes, but the amount of tars strongly increased. The reaction of imide **I** with carboxylic acids **II** and **III** is illustrated by Scheme 1. Obviously, compounds **IV** and **V** are formed by condensation of intermediate 3-alkylidenephthalimidines **VI** and **VII** with initial imide **I**. Compounds **IV** and **V** were isolated and purified by column chromatography on aluminum oxide. In addition, from the reaction mixtures we isolated small amounts of phthalimidines **VI** and **VII** as light yellow waxy substances which showed in the mass spectra peaks from the molecular ions with *m*/*z* 257 and 369, respectively. Compounds **IV** and **V** are dark red substances which are readily soluble in various organic solvents. Their structure was confirmed by the analytical data and electronic absorption, ^{1}H NMR, and mass spectra.

Introduction of an octyl or hexadecyl substituent into the molecule of 1-[(1-oxo-1*H*-isoindol-3-ylmethylidene]-2,3-dihydro-1*H*-isoindol-3-one (**VIII**) [7] leads to considerable changes in the electronic absorption spectrum. The spectrum of **VIII** contains three absorption bands in the visible region, while compound **IV** displays only two less resolved bands (Fig. 1). These findings suggest strong association of molecules **IV** in solution. In addition, the absorption maxima are displaced by 45–47 nm to shorter wavelengths, presumably due to distortion of planar structure of molecule **IV** having a bulky alkyl substituent. On the other hand, the electronic absorption spectra of compounds **IV** and **V** are almost similar (see Experimental), i.e., extension of the alkyl chain from 8 to 16 carbon atoms almost does not affect the absorption pattern.

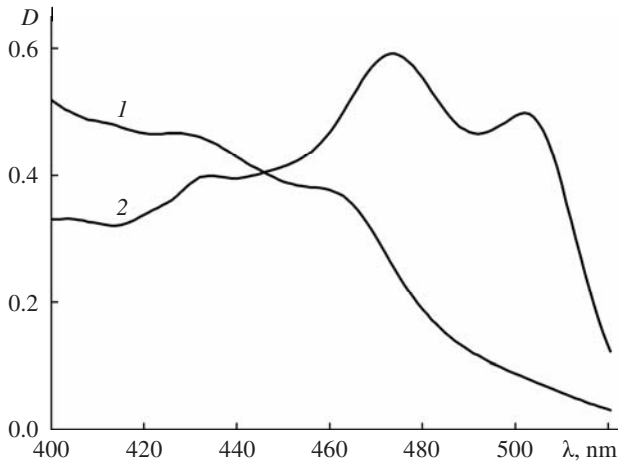


Fig. 1. Electronic absorption spectra of (*1*) compound **IV** in carbon tetrachloride and (*2*) compound **VIII** in acetone.

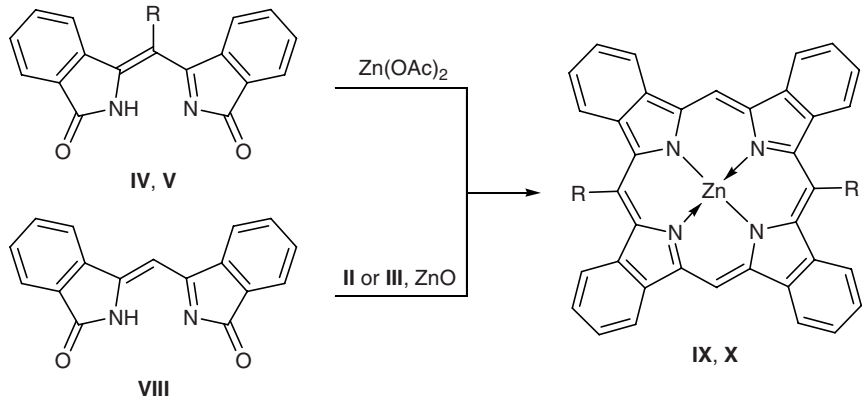
In the ^{1}H NMR spectrum of **IV**, the most downfield signal is a broadened singlet at δ 10.99 ppm, which belongs to the NH proton. Eight protons in the benzene rings of two isoindole fragments resonate as a multiplet at δ 7.84–7.22 ppm. The upfield region of the spectrum contains signals from protons in the alkyl substituent. Two protons of the α-methylene group give rise to a triplet at δ 2.26 ppm, a broadened singlet at δ 1.25 ppm belongs to 12 internal methylene protons, and signal from the terminal methyl group appeared as a triplet at δ 0.86 ppm. The ^{1}H NMR spectrum of **V** is qualitatively similar to the spectrum of **IV**, the only difference being the signal intensity ratio.

The mass spectrum (electron impact) of **IV** contained the molecular ion peak with *m*/*z* 386 (I_{rel} 25%), as well as peaks from fragment ions with *m*/*z* 371 (35%) $[M - CH_3]^+$ and 287 (33%) $[M - C_7H_{15}]^+$. The base peak in the spectrum, *m*/*z* 120, corresponds to the isoindole fragment. In the mass spectrum of **V** we observed the following ion peaks, *m*/*z*: 498 (I_{rel} 29%) $[M]^+$, 368, 331, 274, and others.

By heating compounds **IV** and **V** with excess zinc(II) acetate at 320°C for 30 min we obtained (5,15-dioctyltetrabenzoporphyrinato)zinc(II) (**IX**) and (5,15-dihexadecyltetrabenzoporphyrinato)zinc(II) (**X**), respectively. The same complexes were synthesized in another way, by reaction of 1-(1-oxo-1*H*-isoindol-3-ylmethylidene)-2,3-dihydro-1*H*-isoindol-3-one (**VIII**) [7] with acid **II** or **III** in the presence of zinc(II) oxide, the reaction temperature and time being the same (Scheme 2). Complexes **IX** and **X** were isolated from the reaction mixture and purified by chromatography on aluminum oxide using carbon tetrachloride–dioxane (2:1 by volume) as eluent. The free ligands, 5,15-dioctyltetrabenzoporphyrine (**XI**) and 5,15-dihexadecyltetrabenzoporphyrine (**XII**), were obtained by dissolution of complexes **IX** and **X** in 100% sulfuric acid; the solution was held for 2 h at 20°C and diluted with water. Porphyrins **XI** and **XII** were purified by column chromatography.

Compounds **IX**–**XII** are green substances that are readily soluble in a number of organic solvents. Their purity was checked by TLC, and the structure was confirmed by elemental analysis and ^{1}H NMR and electronic absorption spectroscopy. The ^{1}H NMR spectrum of complex **IX** contained a downfield singlet at

Scheme 2.



II, **IV**, **IX**, R = C_8H_{17}; **III**, **V**, **X**, R = $C_{16}H_{33}$.

δ 11.03 ppm from two *meso*-protons, a multiplet at δ 7.75–7.36 ppm from 16 protons in the isoindole fragments, a triplet at δ 2.77 ppm from four protons in the α-methylene groups of two alkyl substituents, a singlet at δ 1.36 ppm from 24 protons of the other methylene groups, and a triplet at δ 0.82 ppm from six protons of the terminal methyl groups in the alkyl substituents. The ^{1}H NMR spectra of ligands **XI** and **XII** resemble those of the corresponding zinc complexes **IX** and **X**; the difference is that the ligands display a singlet in a very strong field, at δ –2.41 and –2.35 ppm for **XI** and **XII**, respectively, which belongs to intracyclic NH protons.

The electronic absorption spectra of zinc complexes **IX** and **X** and ligands **XI** and **XII** (Fig. 2; see Experimental) are very similar with the spectra of tetrabenzoporphyrin and its zinc(II) complex [8]. Two main absorption bands (*Q* and Soret) are present in the visible region, and their position does not depend on the length of the *meso*-alkyl substituent. The Soret band in the spectra of complexes **IX** and **X** has its maximum at λ 427 nm, and the *Q*-band, at λ 626 nm. Metal-free compounds **XI** and **XII** are characterized by a small bathochromic shift of the absorption maxima (by 5–6 nm) relative to the corresponding maxima of tetrabenzoporphyrin. Thus introduction of two long-chain alkyl groups into the two opposite *meso*-positions of tetrabenzoporphyrin and its zinc complex almost does not affect the electronic absorption spectra. Obviously, alkyl groups, in contrast to phenyl [7, 9, 10], induce no distortion of the planar structure of the porphyrin macroring. According to the results of AM1 quantum-chemical calculations of molecule **XI**, the saddle-like distortion of the macroring is insignificant, and the isoindole fragments deviate from the macroring plane by an angle of no more than 12°. In addition, the planar structure of porphyrin molecules **XI** and **XII** follows from the position of the NH signals in the ^{1}H NMR spectra (see above); these signals are displaced only slightly downfield relative to the NH signal of tetrabenzoporphyrin (δ –2.53 ppm) [11] whose molecule is planar. It is known that strong deviations from planar structure induced by introduction of phenyl substituents into the *meso*-positions of tetrabenzoporphyrin lead to a considerable downfield shift of the NH protons [7, 10].

Thus we have synthesized in two ways tetrabenzoporphyrin derivatives with two long-chain alkyl substituents in the opposite *meso*-positions, which possess improved solubility in organic solvents. As follows from analysis of their spectral parameters and quantum-chemical calculations, molecules of the obtained compounds have planar structure.

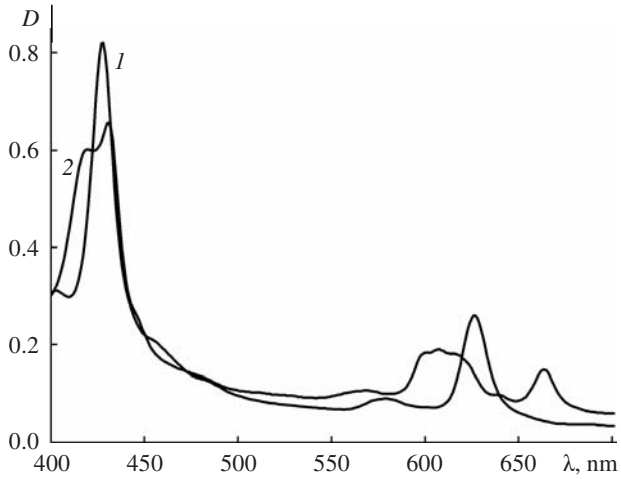


Fig. 2. Electronic absorption spectra of compounds (*1*) **IX** and (*2*) **XI** in carbon tetrachloride.

EXPERIMENTAL

The electronic absorption spectra were measured on a Hitachi UV-2000 spectrophotometer. The ^{1}H NMR spectra were recorded from solutions in $CDCl_3$ relative to tetramethylsilane (internal reference) on a Bruker AMD-200 instrument. The mass spectra were obtained on a Varian Saturn 2000R GC–MS system. The elemental compositions were determined using a FlashEA 1112 CHNS-O Analyzer.

Reaction of phthalimide with carboxylic acids in the presence of zinc(II) oxide (*general procedure*). A mixture of 0.01 mol of phthalimide (**I**), 0.02 mol of acid **II** or **III**, 0.5 g of zinc(II) oxide, and 0.2 g of sodium hydroxide was heated for 1 h at 320°C in a stream of argon. The mixture was cooled, excess acid **II** or **III** was removed by washing the mixture in succession with a 10% solution of potassium hydroxide and water. The residue was dissolved in 30 ml of chloroform, the solution was treated with 20 ml of 20% hydrochloric acid, the organic phase was separated, the solvent was removed, the residue was dissolved in carbon tetrachloride, the solution was applied to a column charged with aluminum oxide (Brockmann activity grade II), and the column was eluted with carbon tetrachloride to isolate the dark red zone.

1-[1-(1-Oxo-1*H*-isoindol-3-yl)nonylidene]-2,3-dihydro-1*H*-isoindol-3-one (IV) was synthesized from capric acid (**II**). Yield 0.61 g (32%), dark red powder readily soluble in benzene, carbon tetrachloride, and chloroform. Electronic absorption spectrum (CCl_4), λ_{max}, nm (D/D_{max}): 457 (0.87), 427 (1.00). ^{1}H NMR spectrum, δ, ppm: 10.99 s (1H), 7.84–7.22 m (8H), 2.26 t (2H), 1.25 s (12H), 0.86 t (3H). Mass spectrum (EI), *m*/*z* (I_{rel}, %): 386 $[M]^+$ (25), 371 (35), 287 (33), 120 (100). Found, %: C 78.22; H 6.85; N 7.16. $C_{25}H_{26}N_2O_2$. Calculated, %: C 77.69; H 6.78; N 7.25.

1-[1-(1-Oxo-1*H*-isoindol-3-yl)heptadecylidene]-2,3-dihydro-1*H*-isoindol-3-one (V) was synthesized from stearic acid (**III**). Yield 0.76 g (30%), dark red waxy material readily soluble in benzene, carbon tetrachloride, and chloroform. Electronic absorption spectrum (CCl_4), λ_{max}, nm (D/D_{max}): 458 (0.84), 426 (1.00). ^{1}H NMR spectrum, δ, ppm: 10.92 s (1H), 7.83–7.25 m (8H), 2.21 t (2H), 1.24 s (28H), 0.84 t (3H). Mass spectrum (EI), *m*/*z* (I_{rel}, %): 498 $[M]^+$ (29), 368 (38), 331 (32), 160 (100). Found, %: C 79.01; H 8.55; N 6.14. $C_{33}H_{42}N_2O_2$. Calculated, %: C 79.48; H 8.49; N 6.25.

5,15-Dialkyltetrabenzoporphyrin complexes IX and X (*general procedure*). *a*. A mixture of 0.01 mol of compound **IV** or **V** and 1.0 g of zinc(II) acetate dihydrate was heated to 320°C, kept for 30 min at that temperature, cooled, dissolved in carbon tetrachloride, and applied to a column charged with aluminum oxide (Brockmann activity grade II). The column was eluted with carbon tetrachloride–dioxane (2:1 by volume) to isolate the main green zone.

b. A mixture of 0.02 mol of compound **VIII**, 0.04 mol of acid **II** or **III**, and 0.4 g of zinc(II) oxide was heated to 320°C and kept for 30 min at that temperature. Complexes **IX** and **X** were isolated as described above in a.

(5,15-Dioctyltetrabenzoporphyrinato)zinc(II) (IX). Yield 0.18 g (37%) (*a*), 0.26 g (34%) (*b*), dark green powder readily soluble in benzene, chloroform, and carbon tetrachloride and poorly soluble in hexane and acetone. Electronic absorption spectrum (CCl_4), λ_{max}, nm (logε): 403 (4.58), 427 (5.01), 579 (4.05), 626 (4.51). ^{1}H NMR spectrum, δ, ppm: 11.03 s (2H), 7.75–7.36 m (16H), 2.77 t (4H), 1.36 s (24H), 0.82 t (6H). Found, %: C 78.41; H 7.15; N 6.84. $C_{52}H_{52}N_4Zn$. Calculated, %: C 78.23; H 6.56; N 7.02.

(5,15-Dihexadecyltetrabenzoporphyrinato)zinc(II) (X). Yield 0.23 g (37%) (*a*), 0.28 g (34%) (*b*), dark green waxy material readily soluble in benzene, chloroform, carbon tetrachloride, and hexane and poorly soluble in acetone. Electronic absorption spectrum (CCl_4), λ_{max}, nm (logε): 402 (4.59), 427 (5.02), 579 (4.03), 626 (4.50). ^{1}H NMR spectrum, δ, ppm: 11.12 s (2H), 7.77–7.41 m (16H), 2.75 t (4H), 1.33 s (56H), 0.85 t (6H). Found, %: C 80.22; H 8.76; N 5.12. $C_{68}H_{84}N_4Zn$. Calculated, %: C 79.85; H 8.28; N 5.48.

5,15-Dialkyltetrabenzoporphyrins XI and XII (*general procedure*). Complex **IX** or **X**, 0.1 g, was dissolved in 10 ml of 100% sulfuric acid, the solution was kept for 2 h at 20°C and diluted with 30 ml of water, and the precipitate was filtered off, washed on a filter with 50 ml of 20% aqueous ammonia and 100 ml of water, dried, and dissolved in carbon tetrachloride. The solution was applied to a column charged with aluminum oxide (Brockmann activity grade II), and the column was eluted with carbon tetrachloride–dioxane (2:1 by volume) to isolate the green zone.

5,15-Dioctyltetrabenzoporphyrin (XI) was synthesized from complex **IX**. Yield 0.07 g (78%), dark green powder readily soluble in benzene, chloroform, and carbon tetrachloride and poorly soluble in hexane and acetone. Electronic absorption spectrum (CCl_4), λ_{max}, nm (logε): 418 (4.87), 431 (4.91), 565 (4.14),

601 (4.35), 608 (4.38), 616 (4.35), 663 (4.27). ^{1}H NMR spectrum, δ, ppm: 11.05 s (2H), 7.76–7.33 m (16H), 2.76 t (4H), 1.32 s (24H), 0.84 t (6H), –2.41 s (2H). Found, %: C 85.22; H 7.35; N 6.70. $C_{52}H_{54}N_4$. Calculated, %: C 84.97; H 7.40; N 7.62.

5,15-Dihexadecyltetrabenzoporphyrin (XII) was synthesized from complex **X**. Yield 0.06 g (67%), dark green powder readily soluble in benzene, chloroform, carbon tetrachloride, and hexane and poorly soluble in acetone. Electronic absorption spectrum (CCl_4), λ_{max}, nm (log ε): 419 (4.86), 433 (4.90), 565 (4.15), 603 (4.35), 608 (4.37), 616 (4.35), 663 (4.28). ^{1}H NMR spectrum, δ, ppm: 11.05 s (2H), 7.78–7.43 m (16H), 2.72 t (4H), 1.30 s (56H), 0.86 t (6H), –2.35 s (2H). Found, %: C 85.20; H 10.12; N 4.62. $C_{68}H_{86}N_4$. Calculated, %: C 85.13; H 9.03; N 5.84.

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