

Stepwise Synthesis and Spectral Characteristics of *meso-trans*-Diphenyldi(1-naphthyl)tetrabenzoporphin and Its Zinc Complex

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Abstract—A reaction of phthalimide with phenylacetic acid in the presence of zinc oxide furnished 3-oxoisindolenyl-3'-oxoisindolinylidene-1,1'-benzylidene which at heating with 1-naphthylacetic acid in the presence of zinc oxide provided zinc *meso-trans*-diphenyldi(1-naphthyl)tetrabenzoporphin complex. Proceeding from this compound a *meso-trans*-diphenyldi(1-naphthyl)tetrabenzoporphin was prepared. The spectral characteristics of compounds obtained were studied.

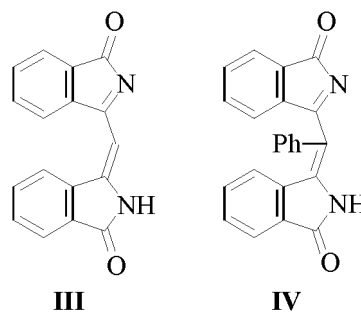
meso-Substituted tetrabenzoporphins and their metal complexes possess versatile valuable practical properties. For instance, some of this group compounds were suggested as fat-soluble dyes [1], photochrome filters [2], photosensitizers for generation of singlet oxygen in photodynamic therapy of cancer [3].

The symmetrically substituted *meso*-tetraaryltetrabenzoporphins are now studied in sufficient detail [4–6] in contrast to unsymmetrically substituted ones. Therewith the published information concerns only the products of incomplete *meso*-substitution in the tetrabenzoporphin [7–9]. We did not find any published data on the synthesis and characteristics of unsymmetrically substituted *meso*-tetraaryltetrabenzoporphins containing different aryl moieties in the *meso*-positions. However such compounds may be of practical use. The analysis of published data on the synthesis of *meso*-aryltetrabenzoporphins suggests that compounds of unsymmetrical structure are available only by stepwise condensation since the simultaneous heating of two arylacetic acids with phthalimide can afford a mixture of six possible tetrabenzoporphins which would provide great difficulties at preparative separation of the components.

On the basis of the above the target of this study was investigation of reaction products of phenylacetic acid and phthalimide, intermediates in the synthesis of *meso*-tetraphenyltetrabenzoporphin, and a development of a procedure for preparation of *meso-trans*-diphenyldi(1-naphthyl)tetrabenzoporphin (**I**) and its complex with zinc **II**.

It was formerly shown [8] that a selective synthesis of zinc *meso-trans*-diphenyltetrabenzoporphin

complex could be performed using the product of phthalimide condensation with acetic or malonic acids in the presence of metal acetates, 3-oxoisindolenyl-3'-oxoisindolinylidene-1,1'-methylidene (**III**).



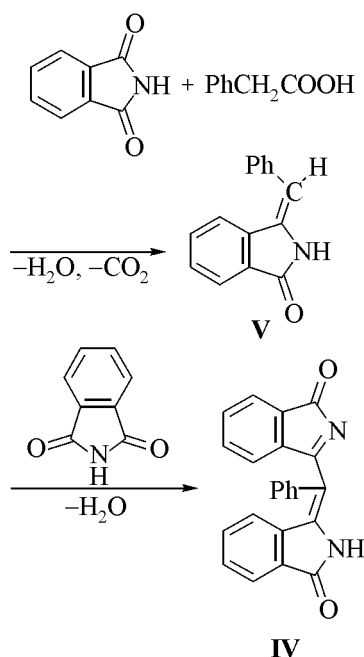
By the reaction between phthalimine and phenylacetic acid in the presence of zinc oxide at 230°C within 30 min we obtained a phenyl-substituted analog of compound **III**, 3-oxoisindolenyl-3'-oxoisindolinylidene-1,1'-benzylidene (**IV**).

Dimer **IV** formed through an intermediate stage of 3-benzylidenephthalimidine (**V**) along Scheme 1.

On completion of reaction the reaction mixture was cooled, treated with a solution of hydrochloric acid, and washed with hot water. Compound **IV** was isolated by column chromatography on alumina; besides the main product were isolated small amounts of 3-benzylidenephthalimidine (**V**), a light-yellow crystalline compound, and of *meso*-tetraphenyltetrabenzoporphin.

3-Oxoisindolenyl-3'-oxoisindolinylidene-1,1'-benzylidene (**IV**) is a red crystalline compound well soluble in polar and nonpolar organic solvents. Its

Scheme 1.



structure was confirmed by elemental analysis and electronic, vibration, and ^1H and ^{13}C NMR spectra.

In the electron absorption spectrum of compound **IV** in the visible region three absorption bands at 523, 489, 458 nm are present. The comparison of this spectrum with that of compound **III** [8] shows that introduction into the molecule of **III** of a phenyl substituent resulted in a blue shift of the absorption bands by 25 nm apparently because the planar structure of molecule **IV** is disrupted due to the steric effect of the phenyl substituent.

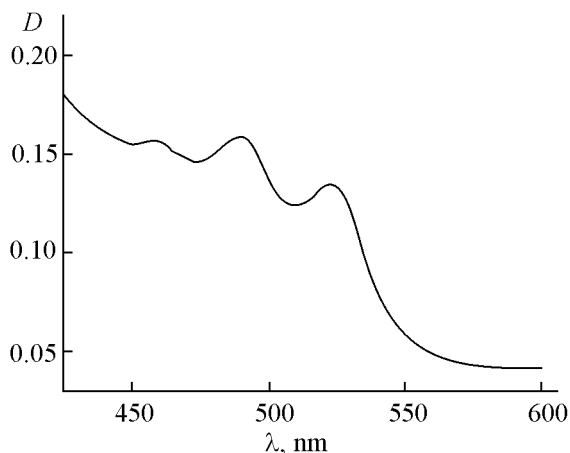


Fig. 1. Electron absorption spectrum of 3-oxoisindolenyl-3'-oxoisindolinylidene-1,1'-benzylidene (**IV**) in chloroform.

In the IR spectrum of compound **IV** appear absorption bands at 1766 and 1726 cm^{-1} evidencing the presence of C=O groups. The bands at 1363 and 1288 cm^{-1} belong to the stretching vibrations of the C=N bonds, that at 3181 cm^{-1} to the stretching vibrations of the N-H bond. It is important that the band of the stretching vibrations of the N-H bond is considerably shifted to high frequency region and appears in the same place as the analogous absorption in metal-free porphyrins. This result together with the ^1H NMR data permits a conclusion that dimer **IV** exists as a *cis*-isomer stabilized by formation of an intramolecular hydrogen bond N-H...N.

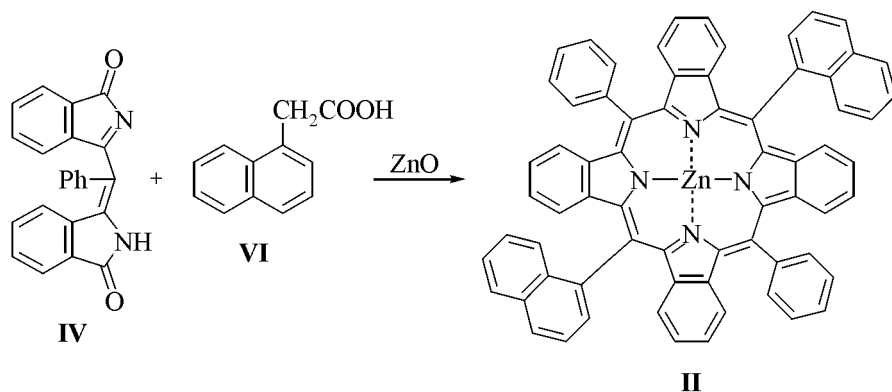
Thus in the ^1H NMR spectrum of compound **IV** the most downfield peak is the resonance of the proton from imide ring (a broadened singlet at δ 8.69 ppm). In the region 7.81–7.62 ppm appears a multiplet corresponding to three *o*- and *p*-protons of the phenyl substituent. The signals of two *m*-protons of the phenyl substituent are observed as a triplet at 7.59–7.52 ppm. The resonance of 8 protons from the isoindole fragments appears as a multiplet in the region 7.50–7.13 ppm.

In the spectrum of 3-benzylidenephthalimidine (**V**) the proton signal of the imide ring is observed as a singlet at 10.6 ppm. The upfield shift of the similar signal in the spectrum of compound **IV** and its broadening is due to the already mentioned possibility of formation of an intramolecular hydrogen bond with the nitrogen atom of the second isoindole fragment. To confirm this assumption we carried out quantum-chemical calculations of molecule **IV** by the semi-empirical AM1 method. The calculation results show that the distance from the hydrogen atom of the imide ring and the nitrogen of the imidine moiety is 2.44 Å, and thus the hydrogen bond formation is probable.

In the ^{13}C NMR spectrum of compound **IV** the most upfield signal at 106.46 ppm corresponds to the carbon linked to the carbonyl in the imide ring; the signal of the similar carbon from the imidine ring appears at 112.30 ppm. The carbon signals from atoms in the imide and imidine rings bonded to the benzylidene fragment are observed in the region 120.16 and 123.88 ppm respectively. The other carbon signals are seen in the region 128.13–138.99 ppm, and their assignment is difficult.

The zinc complex of *meso-trans*-diphenyldi(1-naphthyl)tetrabenzoporphin (**II**) was obtained by heating 3-oxoisindolenyl-3'-oxoisindolinylidene-1,1'-benzylidene (**IV**) with 1-naphthylacetic acid (**VI**) in the presence of zinc oxide at 340°C for 30 min according to the following Scheme 2.

Scheme 2.



The target metal complex **II** was isolated from the reaction mixture by column chromatography on aluminum oxide. As eluent was used a mixture chloroform-hexane, 1:5.

The synthesis of metal-free *meso-trans*-diphenyldi(1-naphthyl)tetrabenzoporphyrin (**I**) was performed by treating the zinc complex **II** with concn. Hydrochloric acid in chloroform. Then the reaction mixture was washed with ammonia solution and water till pH 7. The organic layer was separated, the solvent was evaporated, and the residue was subjected to chromatography on a column charged with silica gel using as eluent a mixture dichloromethane-ethanol, 100:1 by volume. Porphyrins **I** and **II** are dark-green substances, well soluble in various organic solvents. Their homogeneity was confirmed by TLC, the structure was proved by elemental analysis, by electronic and vibration spectroscopy, and by mass spectrometry.

The electron absorption spectrum of compound **II** (Fig. 2) has the pattern characteristic of tetrabenzoporphyrins metal complexes: In the visible region the spectrum contains two main absorption bands, a strong Soret band with a maximum at 463 nm and a less strong Q-band in the longwave region with a maximum at 654 nm. The comparison of the spectrum of compound **II** with that of zinc *meso*-tetraphenyltetrabenzoporphyrin [4] shows that replacement of two phenyl moieties by naphthyl ones results in a red shift of the maxima of the main absorption band by 35 nm.

This shift may be attributed to higher positive inductive effect of the *meso*-naphthyl substituents compared to phenyls.

As to the spectrum of metal-free porphyrin **I** (Fig. 3), therein significant changes are observed in the intensity ratio of the main absorption bands as compared to the spectrum of the *meso*-tetraphenyl-

tetrabenzoporphyrin [4]. For instance, the longwave component of the Q-band in the spectrum of porphyrin **I** (Fig. 3) has the same intensity as the short-wave component whereas in the spectrum of the

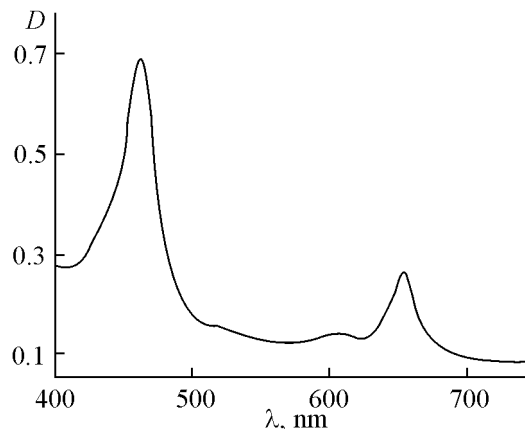


Fig. 2. Electron absorption spectrum of zinc *meso-trans*-diphenyldi(1-naphthyl)tetrabenzoporphyrin in chloroform.

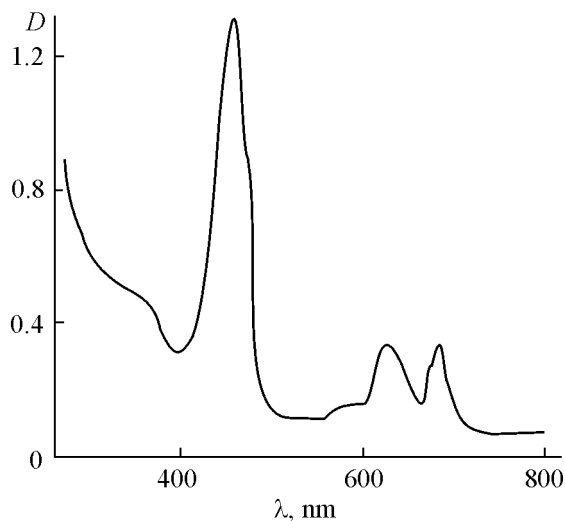


Fig. 3. Electron absorption spectrum of *meso-trans*-diphenyldi(1-naphthyl)tetrabenzoporphyrin in dichloromethane.

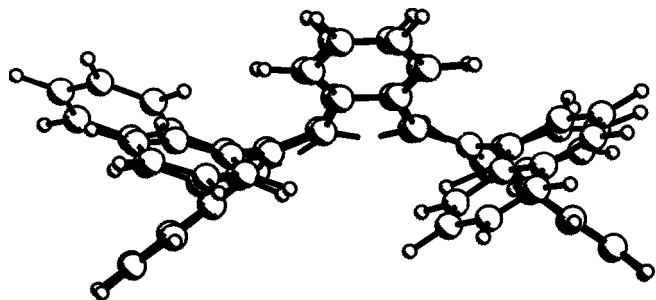


Fig. 4. Geometric structure of *meso-trans*-diphenyldi(1-naphthyl)tetrabenzoporphin (**I**) molecule according to AM-1 calculations.

meso-tetraphenyltetrabenzoporphin the intensity of the latter is notably smaller.

Besides in the spectrum of compound **I** as compared to the spectrum of *meso*-tetraphenyltetrabenzoporphin a significant blue shift (up to 18 nm) is observed of the main absorption bands. We believe that the cause of the above shift lies in the additional asymmetry and in the increased size of substituents in going from *meso*-phenyl to *meso*-naphthyl substituents that in the absence of the stabilizing effect of the metal complexing results in notable distortion of the porphyrin molecule accompanied with somewhat decreased macroring aromaticity.

Quantum-chemical calculations of *meso-trans*-diphenyldi(1-naphthyl)tetrabenzoporphin (**I**) molecule by AM-1 method support the above assumption. The results of calculations are presented on Fig. 4 as a PLUTO-model. As seen, the molecule of compound **I** is actually strongly distorted, and the latter fact governs its spectral characteristics. It should be also noted that in the electronic spectrum of porphyrin **I** on the spectral curve in the region 347 nm appears a shoulder characteristic of the absorption in the naphthalene moieties.

Thus we succeeded in the synthesis of *meso*-aryl substituted tetrabenzoporphins of unsymmetrical structure. The analysis of spectral data and quantum-chemical calculations permitted an assumption on nonplanar structure of porphyrins synthesized.

EXPERIMENTAL

Electronic spectra of compounds obtained were measured on spectrophotometer Hitachi UV-2000, IR spectra were recorded on spectrophotometer Avatar 360 FT-IR in the region 4004000 cm^{-1} from samples pelletized with KBr. ^1H NMR spectra (300 MHz, TMS) and ^{13}C NMR spectra (75 MHz) were register-

ed on spectrometer Bruker AMD-300X. BBA-mass spectra (in *m*-nitrobenzyl alcohol matrix) were measured on JEOL JMS 700 instrument.

3-Oxoisoindolenyl-3'-oxoisoindolinylidene-1,1'-benzylidene (IV). A mixture of 6 g of phthalimide, 2.5 g of phenylacetic acid, and 1.6 g of zinc oxide was heated in a test tube for 30 min at 240°C, then the melt was cooled, crushed, and boiled in a beaker with 100 ml of 10% hydrochloric acid for 5 min. Then the mixture was filtered, and the precipitate was washed on the filter with 200 ml of hot water. After drying the product was dissolved in chloroform and subjected to chromatography on a column charged with aluminum oxide of the **II** grade of activity (eluent chloroform). The main (second) bright-red zone was collected, the solvent was removed, and we obtained 1.6 g (24.9%) of compound **IV** as a dark-red powder. Electron absorption spectrum, λ_{max} , nm (**D**) (chloroform): 523 (0.134), 489 (0.158), 458 (0.156). ^1H NMR spectrum (CD_2Cl_2), δ , ppm: 8.69 s (1H), 7.81–7.62 m (3H), 7.59–7.52 t (2H), 7.50–7.13 m (8H). ^{13}C NMR spectrum (CD_2Cl_2), δ , ppm: 138.99, 136.15, 135.68, 135.60, 134.73, 133.63, 130.71, 129.86, 129.67, 128.13, 123.88, 120.16, 112.30, 106.46. IR spectrum, cm^{-1} (KBr pellets): 3181 (N–H), 2920 (C–H), 1766, 1726 (C=O), 1363, 1288 (C=N), 778, 616, 582. Well soluble in DMF, chloroform, benzene, acetone, insoluble in water, diluted acids and alkalis. Found, %: C 79.25; H 4.10; N 7.85. $\text{C}_{23}\text{H}_{14}\text{N}_2\text{O}_2$. Calculated, %: C 78.84; H 4.03; N 8.00.

From the first light-yellow zone on removing the solvent we isolated 0.07 g of 3-benzylidenephthalimidine (**V**). ^1H NMR spectrum (CD_2Cl_2), δ , ppm: 10.52 s (1H), 7.95 d (1H), 7.75 d (1H), 7.70–7.55 m (2H), 7.45–7.40 t (1H), 7.40–7.30 t (2H), 7.20–7.10 m (2H), 6.55 s (1H). A light-yellow powder, well soluble in DMF, chloroform, benzene, acetone, insoluble in water, diluted acids and alkalis. Found, %: C 81.80; H 5.70; N 6.25. $\text{C}_{15}\text{H}_{11}\text{NO}$. Calculated, %: C 81.43; H 5.01; N 6.33.

Zinc complex of *meso-trans*-diphenyldi(1-naphthyl)tetrabenzoporphin (II). A mixture of 0.35 g of compound **IV**, 0.25 g of 1-naphthylacetic acid (**VI**), and 0.2 g of zinc oxide was charged into a quartz test tube, and the mixture was heated for 30 min at 340°C. The melt was cooled, crushed, and extracted with benzene in a Soxhlet apparatus. The benzene extract was evaporated till dryness, the dark-green powder obtained was dissolved in chloroform and subjected to column chromatography on aluminum oxide of the **II** activity grade; elution with

a mixture chloroform-hexane (1:5 by volume). We collected the main green zone, the solvent was removed to obtain 0.10 g (21%) of compound **II** as a dark-green powder. Electron absorption spectrum, λ_{\max} , nm (log ϵ) (chloroform): 654 (4.41), 604 (3.12), 463 (4.98). Mass spectrum, m/z , BBA (%): 977.2 [$M+H$]⁺ (100). Rf 0.59 (chloroform, Silufol). Well soluble in DMF, chloroform, benzene, acetone, insoluble in water, diluted acids and alkalis. Found, %: C 83.80; H 4.50; N 5.65. C₆₈H₄₀N₄Zn. Calculated, %: C 83.47; H 4.12; N 5.73.

meso-trans-Diphenyldi(1-naphthyl)tetrabenzoporphin (I). In 10 ml of chloroform was dissolved 0.05 g of compound **II**, 5 ml of concn. HCl was added, and the mixture was stirred for 1 h. The mixture was diluted with water, washed with a solution of ammonia and water till neutral washings. The organic layer was separated, dried, the solvent was removed, the residue was dissolved in dichloromethane and subjected to chromatography on a column charged with silica gel L 40/100, elution with a mixture dichloromethaneethanol (100:1 by volume). We obtained 0.03 g (64%) of compound **I** as dark-green powder. Electron absorption spectrum, λ_{\max} , nm (log ϵ) (dichloromethane): 682 (4.01), 627 (4.01), 585 (3.28), 453 (4.91), 347 (4.12). Mass spectrum, m/z , BBA (%): 915.6 [$M+H$]⁺ (100). IR spectrum, cm⁻¹ (KBr pellets): 3184 (N-H), 2920 (C-H), 1384, 1352 (C=C), 1288 (C=N), 1086 (C-C), 1046, 879,

612. R_f 0.68 (chloroform, Silufol). Well soluble in DMF, chloroform, benzene, acetone, insoluble in water, diluted acids and alkalis. Found, %: C 90.10; H 4.95; N 5.90. C₆₈H₄₂N₄. Calculated, %: C 89.25; H 4.63; N 6.12.

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