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Synthesis and Spectral Properties of *meso*-Phenyltetrabenzoazaporphyrins Containing Triphenylmethyl Groups

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Abstract—4-(*p*-Triphenylmethylphenoxy)isoindoline-1,3-diimine was synthesized starting from 4-(*p*-triphenylmethylphenoxy)phthalodinitrile obtained by the reaction of 4-nitrophthalodinitrile with 4-(triphenylmethyl)phenol. The former was reacted with phenylacetic acid in the presence of zinc oxide to obtain zinc complexes of *meso*-phenyltetrabenzoazaporphyrins containing triphenylmethyl groups. Spectral properties of the synthesized compounds were studied.

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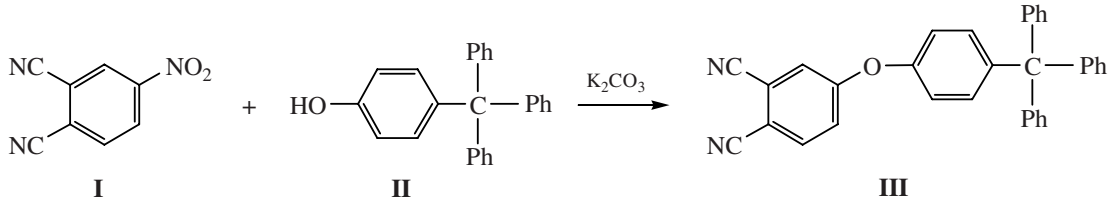
meso-Aryl-substituted tetrabenzoazaporphyrins relate a group of poorly studied tetrapyrrole derivatives. Actually, the synthesis and spectral properties have been reported only in [1–3], even though such compounds hold much promise. *meso*-Phenyltetrabenzoazaporphyrins characteristically exhibit enhanced solubility in organic solvents, which facilitates their chromatographic isolation. The solubility of *meso*-unsubstituted tetrabenzoazaporphyrins in organic solvents can be improved by introduction of bulky (for example, *tert*-butyl) substituents in the isoindole fragments of the macroring, as shown in [4]. *meso*-Aryl-substituted tetrabenzoazaporphyrins containing substituents in the isoindole fragments have never been reported.

At present both symmetrical [5, 6] and unsymmetrical [7] triphenylmethyl-substituted phthalocyanines are known. These phthalocyanines are quite interesting compounds, since triphenylmethyl substituents make them readily soluble in most organic solvents and, in addition, endow them with liquid crystal properties [8, 9]. At the same time, porphyrins containing such substituents are still unknown. In this connection we set ourselves the task to develop methods of synthesis of highly soluble *meso*-phenyltetrabenzoazaporphyrins containing triphenylmethyl substituents in the isoindole fragments and to study spectral properties of these compounds.

As the first step we synthesized 4-(*p*-triphenylmethylphenoxy)phthalodinitrile (**III**) via nucleophilic substitution of the nitro group in 4-nitrophthalodinitrile (**I**) by a 4-triphenylmethylphenol (**II**) residue (Scheme 1).

Dinitrile **III** is a light-yellow powder readily soluble in apolar organic solvents. Its structure was established by elemental analysis, vibrational spectroscopy, and mass spectrometry.

Scheme 1.



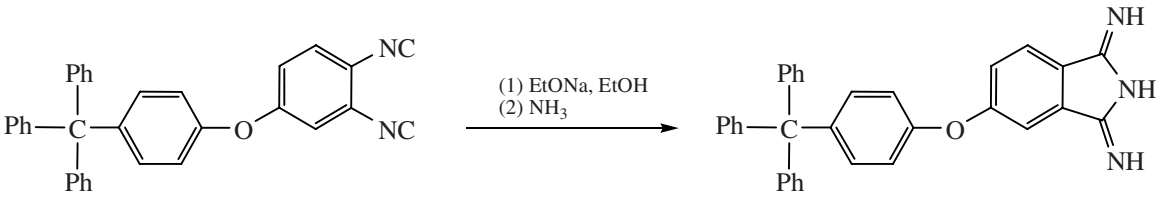
I **II** **III**

The IR spectrum of compound **III** shows an absorption band at 2232 cm^{-1}, corresponding to C≡N stretching vibrations. The bands at 1223 and 1211 cm^{-1} (C–O stretching vibrations) point to the presence of an ether group. Furthermore, the spectra show absorption bands due to stretching and bending vibrations of the C–H (2928 and 1489 cm^{-1}) and C=C (1595 cm^{-1}) bonds of the triphenylmethyl group.

The FAB (fast atom bombardment) mass spectrum of compound **III** contains molecular (*m/z* 462.1) and fragment ions {*m/z* 385.1 $[M - C_6H_5]^+$ and 307.2 $[M - 2C_6H_5]^+$}.

Dinitrile **III** was used to synthesize 4-(*p*-tiphenylmethylphenoxy)-1,3-diiminoisoindoline (**IV**). The synthesis of compound **IV** was performed by reacting dinitrile **III** with sodium ethylate in ethanol and subsequently treating the resulting dialkoxy derivative with ammonia at 60°C, according to Scheme 2.

Scheme 2.



III **IV**

Compound **IV** is a light blue powder readily soluble in apolar organic solvents. Its structure, too, elemental analysis, vibrational spectroscopy, and mass spec-trometry.

The IR spectrum of compound **IV** resembles that of compound **III** but lacks C≡N bands at 2232 cm^{-1} and contains a diffuse imino N–H band in the region of 3410 cm^{-1}.

The EI (electron impact) mass spectrum of compound **IV** contains deprotonated molecular {*m/z* 476 $[M - 3]^+$} and fragment ions {*m/z* 430 $[M - 2HCN - 5]^+$ and 283 $[M - HCN - NH - 2C_6H_5]^+$}.

By heating compound **IV** with excess phenylacetic acid in the presence of zinc oxide at 290°C for 40 min we synthesized zinc benzoazaporphyrinates **V–VIII** (Scheme 3).

Compounds **V–VIII** were isolated and purified by column chromatography. The are dark green (**V, VI**) and dark blue (**VII, VIII**) powders readily soluble in benzene and chloroform and fairly soluble in acetone and DMF. Unexpectedly, no *cis* isomer of *meso*-diphenyltetrabenzodiazaporphyrin was found in the mixture of azaporphyrins. This is probably explained by steric reasons.

The structure of compounds **V–VIII** was confirmed by elemental analysis, mass spectrometry, and electronic spectroscopy.

The MALDI–TOF mass spectra of compounds **V–VIII** contain molecular ions at *m/z* 2138, 2063, 1988, and 1913, and the isotope patterns are nicely consistent with calculation.

The electronic absorption spectrum of complex **V** (Fig. 1, spectrum *1*) shows a strong Soret band peaking at 470 nm and a *Q*-band split into two components of equal intensity (λ_{max} 645 and 679 nm). Such a splitting of the long-wave band is probably associated with decreased, due to aza substitution, symmetry of the HOMO. Comparison of the electronic absorption spectrum of compound **V** with the spectrum of zinc *meso*-triphenyltetrabenzomonoazaporphyrinate [2]

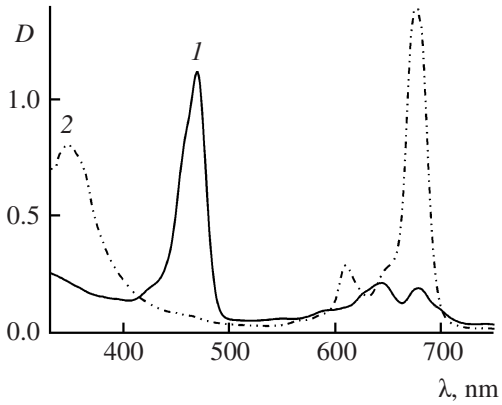
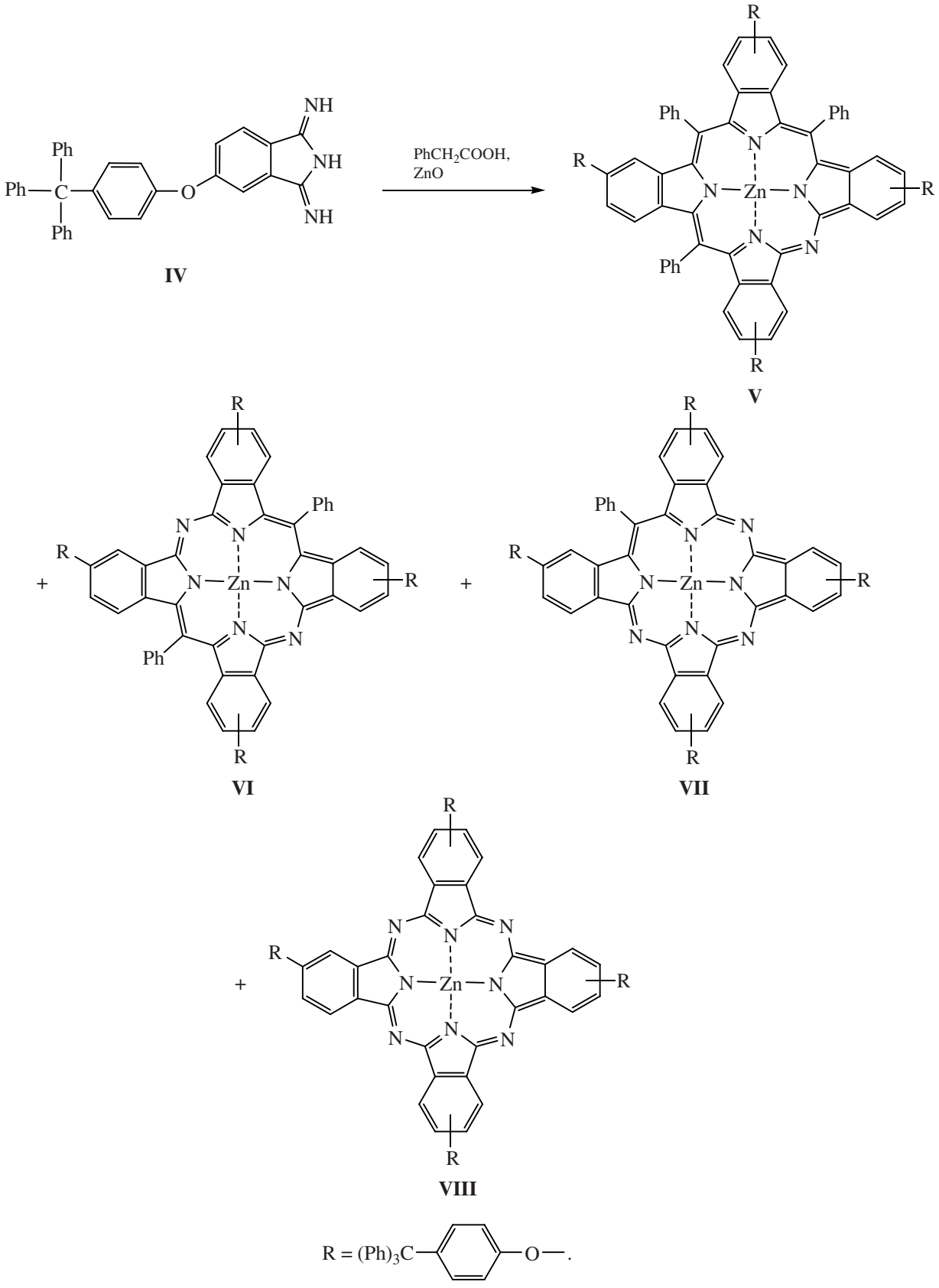


Fig. 1. Electronic absorption spectra in toluene: (*1*) **V** and (*2*) **VIII**.

Scheme 3.



shows that the four bulky substituents in the isoindole fragments results in a considerable (43 nm) bathochromic shift of the Soret band, whereas the *Q*-band maxima scarcely change their position but slightly lose in intensity. This fact can be explained in terms of a strong distortion of molecule **V** under the action of the triphenylmethylphenoxy substituents.

The Soret band in the electronic absorption spectrum of complex **VI** (Fig. 2, spectrum *1*) is shifted hypsochromically by 29 nm compared with that of compound **V**. The *Q*-band is split into three components, and, therewith, the long-wave component of the *Q*-band is in the same region as in the case of complex **V**, and the short-wave component of the *Q*-band of complex **V** at λ_{max} 645 nm splits into two components (λ_{max} 638 and 659 nm) in going to complex **VI**. Such a *Q*-band splitting is also characteristic of unsymmetrically substituted porphyrazins of ABAB type [10, 11]. Furthermore, compared to the spectrum of complex **V**, the relative intensity of the *Q*-band increases, which is explained by the fact that the HOMO (A_{1g}) and LUMO (E_u) get closer together becase of enhanced "rigidity" and aromaticity of the macroring.

In the electronic absorption spectrum of triazaporphyrin **VII** (Fig. 2, spectrum *2*), the relative intensity of the double-split *Q*-band which becomes stronger than the Soret band peaking at 441 nm. It should be noted that the strongest band in the spectrum of compound **VII** is the long-wave component of the *Q*-band, peaking at 680 nm, and its short-wave component suffers is bathochromically shifted by 11 nm from that of monoazaporphyrin **V**. Moreover, the spectrum of compound **VII** acquires a new band at λ_{max} 487 nm. The position and relative intensity of this band suggest that it is a charge-transfer band.

As to the electronic absorption spectrum of phthalocyanine **VIII** (Fig. 1, spectrum *2*), then in the character and maxima positions and intensities it fully identical to that reported in [8].

EXPERIMENTAL

The electronic absorption spectra were measured on a Hitachi UV-2001 spectrophotometer. The IR spectra were obtained on an Avatar 360 FT-IR spectrometer at 400–4000 cm^{-1} in films on a TlI glass. The mass spectra were registered on JEOL JMS 700 (FAB, matrix *m*-nitrobenzyl alcohol), Bruker Reflex **III** (MALDI–TOF, matrix ditranol), and **V**arian Saturn 2000R (EI, 70 eV) spectrometers. Elemental analysis was performed on a FlashEA 1112 CHNS-O analyzer.

4-Nitrophthalonitrile (**I**) and 4-(triphenylmethyl)-phenol (**II**) were synthesized by known procedures [12, 13].

4-(*p*-Triphenylmethylphenoxy)phthalodinitrile (III). A mixture of 2.6 g of 4-nitrophthalonitrile (**I**), 6.9 g of 4-(triphenylmethyl)phenol (**II**), 3.0 g of K_2CO_3, and 50 ml of DMF was stirred for 10 h at 110°C, cooled, and poured into 300 ml of water. The precipitate was filtered off, washed with water, dried in air at 80°C, and subjected to column chromatography on Brockmann grade II alumina (eluent benzene). Yield 4.8 g (69%), light-yellow powder, mp 216–218°C, readily soluble in benzene and chloroform and poorly soluble in acetone. R_f 0.59 (Silufol, chloroform). IR spectrum, ν, cm^{-1}: 2928, 2232 (C≡N), 1595 (C=C), 1489, 1386, 1223, 1211, 953, 748. FAB mass spectrum, *m/z*: 462.1 $[M]^+$, 385.1 $[M - C_6H_5]^+$, 307.2 $[M - 2C_6H_5]^+$. Found, %: C 86.22; H 5.05; N 5.88. $C_{33}H_{22}N_2O$. Calculated, %: C 85.68; H 4.80; N 6.06.

4-(*p*-Triphenylmethylphenoxy)isoindoline-1,3-diimine (IV). Dinitrile **III**, 4.0 g, was added to a solution of 0.5 g in 50 ml of ethanol. The suspension was stirred for 2 h at 20°C and then heated to 60°C. Dry ammonia was passed through the resulting solution for 3 h. After cooling, a precipitate formed and was filtered off, washed with 20 ml of acetone, and dried to obtain 2.3 g (55.5%), of diimine **III** as a light blue powder readily soluble in benzene, chloroform and poorly soluble in acetone. IR soectrum, ν, cm^{-1}: 3410 (N–H), 3087, 3055 (C–H), 3028, 1592 (C=C), 1487, 1280, 1250, 1213 (C–O), 1174 (C–O), 834, 750, 702.

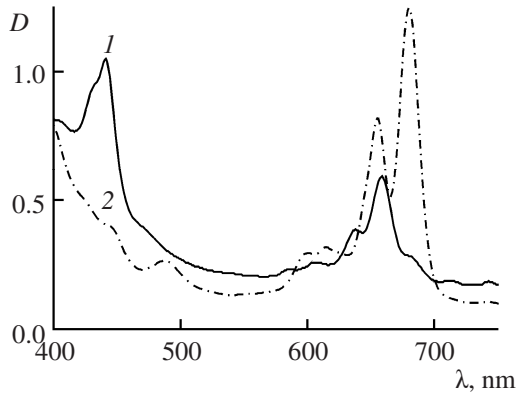


Fig. 2. Electronic absorption spectra in toluene: (*1*) **VI** and (*2*) **VII**.

Mass spectrum (EI), *m/z*: 476 $[M - 3]^+$, 430 $[M - 2HCN\text{-}5]^+$, 283 $[M - HCN - NH - 2C_6H_5]^+$. Found, %: C 83.01; H 5.10; N 8.22. $C_{33}H_{25}N_3O$. Calculated, %: C 82.65; H 5.25; N 8.71.

Condensation of diimine IV with phenylacetic acid in the presence of zinc oxide. A mixture of compound **IV**, 5.0 g of phenylacetic acid, and 1.0 g of zinc oxide was heated for 40 min at 290°C. The melt was cooled, ground, refluxed for 5 min in 100 ml of 10% KOH, and filtered. The solid matter was dissolved in 100 ml of water, dried, dissolved in toluene, and subjected to column chromatography on Brockmann grade II alumina (eluent toluene–acetone, 50:1 v/v). The mixture separated into 4 bands corresponding to compounds **V–VIII** which were eluted one after another.

Zinc *meso*-triphenyltetra{[(*p*-(triphenylmethyl)-phenoxy]benzo}azaporphyrinate V, yield 0.12 g (5.4%), dark green powder, readily soluble in toluene and chloroform and poorly soluble in acetone. R_f 0.84 (toluene, Silufol). Electronic absorption spectrum (toluene), λ_{max}, nm (D/D_{max}): 679 (0.17), 645 (0.19), 470 (1.00). Mass spectrum (MALDI–TOF), *m/z* (I_{rel}, %): 2138 $[M]^+$ (100). Found, %: C 86.02; H 4.99; N 2.87. $C_{153}H_{103}N_5O_4Zn$. Calculated, %: C 85.84; H 4.85; N 3.27.

Zinc *meso-trans*-Diphenyltetra{[(*p*-(triphenylmethyl)phenoxy}benzo]diazaporphyrinate VI, yield 0.08 g (3.71%), dark green powder, readily soluble in toluene and chloroform and poorly soluble in acetone. R_f 0.42 (toluene, Silufol). Electronic absorption spectrum (toluene), λ_{max}, nm (D/D_{max}): 680 (0.27), 659 (0.56), 638 (0.37), 440 (1.00). Mass spectrum (MALDI–TOF), *m/z* (I_{rel}, %): 2063 $[M]^+$ (100). Found, %: C 85.44; H 5.74; N 3.96. $C_{146}H_{98}N_6O4Zn$. Calculated, %: C 84.89; H 4.78; N 4.07.

Zinc *meso*-phenyltetra{[(*p*-(triphenylmethyl)phenoxy]benzo}triazaporphyrinate VII, yield 0.25 g (12.04%), dark blue powder, readily soluble in toluene and chloroform and poorly soluble in acetone. R_f 0.27 (toluene, Silufol). Electronic absorption spectrum (toluene), λ_{max}, nm (D/D_{max}): 680 (1.00), 655 (0.66), 614 (0.25), 600 (0.23), 488 (0.21), 440 (0.32). Mass spectrum (MALDI–TOF), *m/z* (I_{rel}, %): 1988 $[M]^+$ (100). Found, %: C 84.04; H 5.25; N 4.29. $C_{139}H_{93}N_7O_4Zn$. Calculated, %: C 83.87; H 4.71; N 4.93.

Zinc tetra{[(*p*-(triphenylmethyl)phenoxy]benzo}-teraazaporphyrinate VIII, yield 0.68 g (34.05%), blue powder, readily soluble in toluene and chloroform and poorly soluble in acetone. R_f 0.12 (toluene, Silufol). Electronic absorption spectrum (toluene), λ_{max}, nm (D/D_{max}): 676 (1.00), 610 (0.21), 348 (0.58). Mass spectrum (MALDI–TOF), *m/z* (I_{rel}, %): 1913 $[M]^+$ (100). Found, %: C 82.95; H 4.91; N 5.21. $C_{132}H_{88}N_8O_4Zn$. Calculated, %: C 82.77; H 4.63; N 5.85.

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