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# Synthesis and Spectral Properties of Porphyrazines with Unsymmetrical Structure Based on 3,6-Dipentoxyphthalodinitrile and 1,2-Diphenylfumarodintrile

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**Abstract**—Porphyrazines of unsymmetrical structure of $A_3B$, ABAB and AABB types were prepared by random condensation of 3,6-dipentyloxyphthalodinitrile (A component) with 1,2-diphenylfumarodinitrile (B component), and their spectral properties were investigated.

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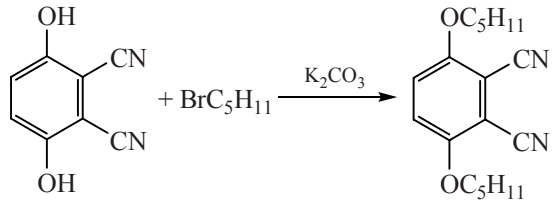
Substituted porphyrazines with unsymmetrical structure nowadays are intensively studied. This is related to the fact that the presence in a molecule of both electron-donor and electron-acceptor substituents simultaneously leads to a polarized electronic structure [1], and such compounds are promising for application in non-linear optics [2, 3]. Moreover, the unsymmetrical porphyrazines containing long alkyl substituents or bulky triphenylmethyl groups often possess the properties of liquid crystals [4–6]. The features of molecular and electronic structure of unsymmetrically substituted porphyrazine provide a possibility of their application to nano technology [7].

Among the numerous tetrapyrrole derivatives a great interest present the porphyrazines of unsymmetrical structure containing phenyl substituents or condensed benzene rings in the pyrrole fragments [8–10] owing to their specific electronooptical properties. The aim of this work is the development of methods for the synthesis of unsymmetrical phenyl-substituted porphyrazines containing strong electron-donor substituents in a fused benzene fragment, and the study of spectral properties of the synthesized compounds.

For the synthesis of porphyrazines of such structure the most often the method is used of random condensation of two *ortho*-dicarboxylic acid nitriles in the presence of a template agent [11, 12]. In this work as A component is chosen 3,6-dipentoxyphthalodinitrile (**I**), as B component 1,2-diphenylfumarodinitrile (**II**).

The choice of compound **I** is defined by the presence in its structure of two bulky pentoxy substituents that hinder sterically the formation of symmetrical octapentoxyphthalocyanine [13] and thus increase the process selectivity. Dinitrile **I** is obtained by alkylation of 3,6-dihydroxyphthalodinitrile (**III**) with 1-bromopentane in DMF in the presence of $K_2CO_3$.




**III** **I**

Compound **I** is a white powder, well soluble in benzene and chloroform and poorly soluble in DMF and acetone. Its composition and structure are confirmed by elemental analysis, data of vibration and $^1$H NMR spectroscopy, and mass-spectrometry.

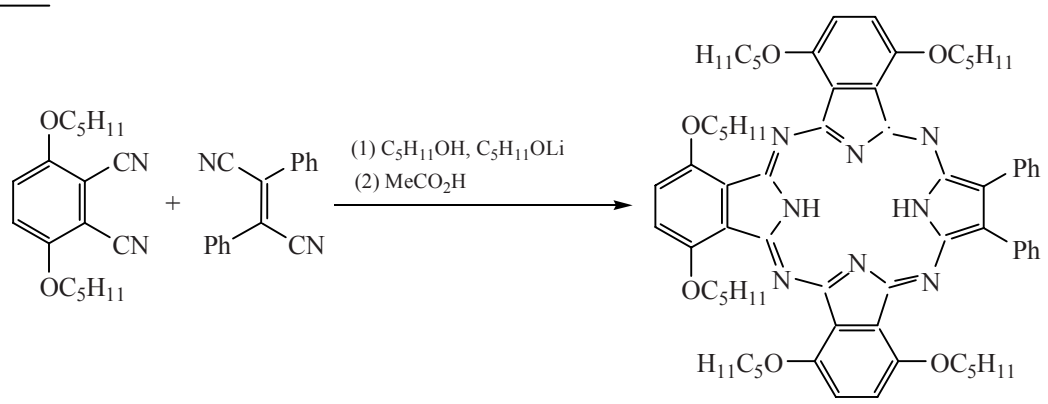
The IR spectrum of compound **I** contains a band at 2936 $cm^{-1}$ that corresponds to vibrations of C–H bonds in alkyl substituents, a band at 2304 $cm^{-1}$ charac-

terizing vibrations of cyano groups, bands at 1116 and 1080 $cm^{-1}$ that indicate the presence of C–O–C bonds. In the $^1H$ NMR spectrum of nitrile **I** at the most downfield singlet at 7.38 ppm corresponds to the resonance of two benzene ring protons, a multiplet in the region of 4.19–4.01 characterizes the resonance of four protons in the α-positions of alkyl groups, a multiplet at 1.95–1.89 ppm corresponds to the resonance of four protons in the β-positions, a multiplet at 1.49–1.24 ppm, the resonance of eight protons in γ- and δ-positions, and a singlet at 0.89 ppm, the resonance of six protons of terminal methyl groups. In the mass spectrum of compound **I** (ionization by electron impact) occurs a peak of molecular ion, *m/z* 300 $[M]^+$, and the peaks of the products of its fragmentation: *m/z* 273 $[M - HCN]^+$, 213 $[M - OC_5H_{11}]^+$, and 126 $[M - 2OC_5H_{11}]^+$.

Heating of the three-fold excess of nitrile **I** with compound **II** in boiling 1-pentanol in the presence of lithium 1-pentoxide followed by treatment with acetic acid leads, in accordance Scheme 1, to the formation of a mixture of 2,3-diphenyltri[(3,6-dipentoxy)benzo] porphyrazine (**IV**) ($A_3B$), 2,3,12,13-tetraphenyldi[(3,6-dipentoxy)benzo]porphyrazine (**V**) (ABAB) and 2,3,7,8-tetraphenyldi[(3,6-dipentoxy)benzo]porphyrazine (**VI**) (AABB). All these compounds were isolated and purified by column chromatography. Their composition and structure were elucidated by means of elemental analysis, vibration, electronic, and $^1H$ NMR spectroscopy.

In the IR spectra of porphyrazines **IV–VI** appear selected several common bands. The bands in the region of 3081–3076 $cm^{-1}$ correspond to N–H vibrations of endocyclic imino groups, the strong bands at 2954–2853 $cm^{-1}$ correspond to vibrations of C–H bonds in alkyl residues, the bands at 1731–1726, 1507–1488, 1271–1245 $cm^{-1}$ characterize vibrations of the bonds C=C and C=N in the macrocycles. The bands in the region 1161–1148 $cm^{-1}$ correspond to vibrations of $C_{Ar}$–O bonds, and those at 1060–1058 $cm^{-1}$, to $C_{Alk}$–O bonds.

In the $^1H$ NMR spectra of porphyrazines **IV–VI** there are three groups of signals that characterize resonance of the protons of endocyclic N–H groups, pentoxide substituents, and the protons of benzene rings, respectively. In going from compound **IV** to **VI** the positions of the signals vary insignificantly, only

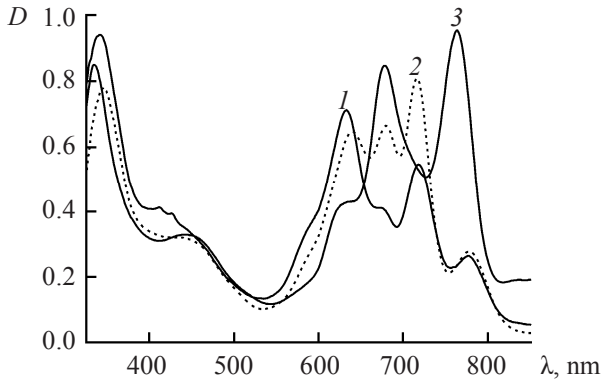


changes occur in their relative intensity. In the spectrum of porphyrazine **IV** the resonance of ten protons in two phenyl substituents appear as a multiplet at 7.73–7.45 ppm, a multiplet at 7.19–7.03 ppm characterizes the resonance of protons of benzene rings in the isoindole fragments. A multiplet at 3.56–3.50 ppm corresponds to the resonance of 12 protons of methylene groups in the α-positions of six pentoxide substituents, a multiplet at 2.01–1.97 ppm corresponds to the resonance of 12 protons in the β-positions, a multiplet at 1.48–1.33 ppm to the resonance of 24 protons in the γ- and δ-positions, a singlet at 0.97 ppm characterizes the resonance of 18 protons of terminal methyl groups. The resonance of two protons of endocyclic imino groups is registered as a broad singlet at –0.38 ppm

In the $^1$H NMR spectra of compounds **V** and **VI** relative intensity grows of the resonance signals of the protons in phenyl substituents and upfield shift occurs of the signals of protons of endocyclic imino groups. This fact indicates somewhat more planar structure of compounds **V** and **VI**.

Electron absorption spectra of compounds **IV**–**VI** show strong absorption in the region of 778–633 nm (*Q* bands) and in the region of 344–335 nm (Soret bands).

In the spectrum of porphyrazine **IV** ($A_3B$) (Fig. 1, curve *1*) the long-wave band is split into three components with the maxima at 777, 718 and 633 nm. The three-bands character of the spectrum in the long-wave region is typical for the metal free porphyrazine of $A_3B$ type, the most long-wave component of *Q* and as well as diffuse band in the region of 413 nm are the bands of charge transfer from the donor part of the molecule to the acceptor one [14], which in this particular case is diphenylpyrrole fragment. The Soret band has a maximum at 342 nm. The comparison of electron absorption spectrum of compound **IV** with that of similar structure 2,3-di(*m*-trifluoromethylphenyl)tribenzoporphyrazine [10] shows that the introduction of electron-donor substituents to benzene rings results in red shift of the long-wave *Q* band maximum by 85 nm, the middle component suffers a red shift by 64 nm, and the short-wave component remains in the same region. This observation points to the strong enhancing of HOMO energy at the introducing pentoxide substituents to 3 and 6 positions of isoindole fragments owing to significant contribution of atomic orbitals of the carbon atoms in these positions to its formation [15]. Besides, polarization of molecule of compound **IV** affects significantly its spectral properties. Judging from the data of semi-empirical AM1 quantum-chemical calculations, the dipole moment of compound **IV** molecule is 8.54 D that provides the observed value of the red shift of the *Q* band long-wave component.




Electron absorption spectra (solvent chloroform): (*1*) compound **IV**, (*2*) compound **V**, and (*3*) compound **VI.**

Electron absorption spectrum of compound **V** (ABAB) (Fig. 1, curve *2*) in the long-wave region contains four bands with the maxima at 778, 717, 680, and 640 nm. The increase in the number of bands results from the fact that due to decrease in symmetry of the macrocycle the two lowest molecular π* orbitals are no more degenerate. In the spectrum of compound **VI** (AABB) the number of bands in its electron absorption spectrum diminishes (Fig. 1, curve *3*). In the long-wave region occur only two bands with the maxima at 763 and 678 nm. In the region of 448 nm in the spectra of compounds **V** and **VI** there are two diffuse charge transfer bands and the Soret bands have maxima at 344 and 335 nm.

The data obtained fit well the Gouterman four orbital model [16], assuming that the number of bands in the electron absorption spectra of the unsymmetrically substituted porphyrazine *cis*-isomers (AABB) should be minimal, while that of the *trans*-isomer (ABAB) maximal. Just this picture is observed in our case.

## EXPERIMENTAL

The electronic absorption spectra of the obtained compounds were registered on a Hitachi UV-2001 spectrophotometer, the $^1$H NMR spectra were taken from solutions in $CDCl_3$ on a Bruker AMD-200

instrument (200 MHz, internal reference TMS), IR spectra were registered on an Avatar 360 FT-IR spectrophotometer in the region of 400–4000 $cm^{-1}$ from thin films, the mass spectrum was registered on a Varian Saturn 2000R chromato-mass sepctrometer. Elemetal analysis was carried out on a FlashEA 1112 CHNS–O Analyzer.

**1,2-Diphenylfumarodinitrile III** was prepared along the procedure [17].

**3,6-Dipentoxyphthalodinitrile (I)**. A mixture of 10 g (0.0625 mol) of 3,6-dihydroxyphthalodinitrile **II**, 45 ml (0.25 mol) of 1-bromopentane, 34.5 g (0.25 mol) of $K_2CO_3$ and 50 ml of DMF was stirred at 100°C for 20 h, then cooled, diluted with 100 ml of water, and the precipitate formed was filtered off, dried, and recrystallized from DMF. Yield 18 g (96%), white powder, mp 177°C. IR spectrum, ν, $cm^{-1}$: 3096, 3032, 2936, 2304, 1528, 1416, 1336, 1220, 1116, 1080, 832. The $^1H$ NMR spectrum, δ, ppm: 7.38 s (2H), 4.19–4.01 m (4H), 1.95–1.89 m (4H), 1.49–1.24 m (8H), 0.89 s (6H). The mass spectrum, *m/z* ($I_{rel.}$, %): 300 $[M]^+$ (45), 273 $[M - HCN]^+$ (52), 213 $[M - OC_5H_{11}]^+$ (100), 126 $[M - 2OC_5H_{11}]^+$ (88). Found, %: C 71.83; H 8.17; N 9.40. $C_{18}H_{24}O_2N_2$. Calculated, %: C 71.97; H, 8.05; N, 9.33.

**Condensation of 3,6-dipentoxyphthalonitrile (I) with 1,2-diphenylfumarodinitrile (III).** To a boiling solution of lithium 1-pentoxide in 1-pentanol prepared by dissolving 0.1 g of lithium in 20 ml of anhydrous 1-pentanol was charged 0.3 g (1.0 mmol) of compound **I**, after 15-min reflux was added 0.08 g (0.3 mmol) of compound **III** and boiling at reflux was continued for 4 h. The reaction mixture was cooled, 20 ml of acetic acid and 30 ml of water was then added, the precipitate separaterd was filtered off, washed on the filter with 30 ml of methanol, and dried. The product was dissolved in benzene and subjected to chromatography on a column with silica gel 60 (eluent benzene–hexane–chloroform, 5:10:1 by volume). The mixture separated into three zones containing, respectively, porphyrazines **IV**, **V** and **VI** that were eluted to complete washing out from the column. After removing the solvent we obtained the following products.

**2,3-Diphenyltri[(3,6-dipentoxy)benzo]porphyrazine (IV) ($A_3B$)**, yield 0.09 g (22%), green powder, well soluble in benzene, chloroform, poorly soluble in acetone. $R_f$ 0.87 (Silufol, $CHCl_3$). The electronic absorption spectrum ($CHCl_3$), $\lambda_{max.}$, nm ($D/D_{max.}$): 777 (0.28), 718 (0.58), 676 sh, 633 (0.71), 413 (0.44), 342 (1.00). The IR spectrum, ν, $cm^{-1}$: 3081, 2954, 2923, 2853, 1728, 1504, 1270, 1161, 1060, 807, 760, 722, 597. The $^1H$ NMR spectrum, δ, ppm: 7.73–7.45 m (10H), 7.19–7.03 m (6H), 3.56–3.50 m (12H), 2.01–1.97 m (12H), 1.48–1.33 m (24H), 0.97 s (18H), –0.38 s (2H). Found, %: C 74.44; H 7.66; N 9.12. $C_{70}H_{84}N_8O_6$. Calculated, %: C 74.18; H 7.47; N 9.89.

**2,3,12,13-Tetraphenyldi[(3,6-dipentoxy)benzo]-porphyrazine (V) (ABAB)**, yield 0.06 g (34%), green powder, well soluble in в benzene, chloroform, poorly soluble in acetone. $R_f$ 0.65 (Silufol, $CHCl_3$). The electronic absorption spectrum ($CHCl_3$), $\lambda_{max.}$, nm ($D/D_{max.}$): 778 (0.34), 717 (1.00), 680 (0.82), 640 (0.80), 448 (0.39), 344 (0.96). The IR spectrum, ν, $cm^{-1}$: 3079, 2948, 2855, 1731, 1496, 1271, 1161, 1050, 807, 722, 597. The $^1H$ NMR spectrum, δ, ppm: 7.75–7.42 m (20H), 7.18–7.08 m (4H), 3.55–3.51 m (8H), 2.02–1.96 m (8H), 1.49–1.30 m (16H), 0.96 s (12H), –0.77 s (2H). Found, %: C 77.12; H 6.77; N 9.91. $C_{68}H_{70}N_8O_4$. Calculated, %: C 76.81; H 6.64; N 10.54.

**2,3,7,8-Tetraphenyldi[(3,6-dipentoxy)benzo]porphyrazine (VI) (AABB)**, yield 0.04 g (25%), green powder, well soluble in в benzene, chloroform, poorly soluble in acetone. $R_f$ 0.54 (Silufol, $CHCl_3$). The electronic absorption spectrum ($CHCl_3$), $\lambda_{max.}$, nm ($D/D_{max}$): 763 (1.00), 678 (0.89), 628 sh, 442 (0.34), 335 (0.99). The IR spectrum, ν, $cm^{-1}$: 3076, 2953, 2861, 17329, 1488, 1245, 1152, 1058, 809, 733, 591. The $^1H$ NMR spectrum, δ, ppm: 7.78–7.41 m (20H), 7.16–7.09 m (4H), 3.54–3.49 m (8H), 2.10–1.98 m (8H), 1.48–1.35 m (16H), 0.97 s (12H), –0.81 s (2H). Found, %: C 76.55; H 6.98; N 9.85. $C_{68}H_{70}N_8O_4$. Calculated, %: C 76.81; H 6.64; N 10.54.

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