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Nucleophilic Substitution in 4-Bromo-5-nitrophthalodinitrile: X.[1] Synthesis of 4-(1-Benzotriazolyl)-5-(1(2)-naphthyloxy)-phthalodinitriles and Related Phthalocyanines

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Abstract—4-(1-Benzotriazolyl)-5-[1(2)-naphthyloxy]phthalodinitriles were obtained by nucleophilic substitution of bromine and nitro group in 4-bromo-5-nitrophthalodinitrile. These compounds were used for the synthesis of the corresponding octa-substituted phthalocyanines. Spectral data of the compounds obtained were examined.

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Phthalocyanines and related compounds for a long time have been used as high-grade organic dyes and pigments [2] and catalysts for various processes [3]. There are some approaches to their practical use as photosensitizers for tumor photodynamic therapy [4], mesomorphic materials [5], photoconverters [6] and in others branches of science and technology [7].

This report deals with synthesis and study of physicochemical properties of 4-(1-benzotriazolyl)-5-[1(2)-naphthyloxy]phthalodinitriles and phthalocyanines based on them.

In the first stage we synthesized the target phthalodintriles **IVa** and **IVb** using the known procedure [8, 9], by successive nucleophilic aromatic substitution of the bromine atom and nitro group in 4-bromo-5-nitrophthaloditrile **I**.

The compounds obtained were identified using ^{1}H, IR spectroscopy and elemental analysis data.

In the ^{1}H NMR spectrum of phthalodinitrile **IVa** there are signals at 8.73 and 8.14 ppm belonging to aromatic protons (positions *1* and *2*) of phthalodintrile and in the region of 8.23, 7.81, 7.55 and 8.08 ppm, to benzotriazole fragment protons (positions *3, 4, 5* and *6*) respectively. Signals of 1-naphthol protons are registered as a triplet at 8.17 ppm (position *13*), multiplets at 7.28 (position *7*), 7.04 (position *8*), 7.45 (position *9*), 8.43 (position *10*) and a doublet at 7.55 ppm (positions *11, 12*).

Signals location for benzotriazole and phthalodinitrile aromatic protons in the spectrum of 4-(1-benzotriazolyl)-5-(2-naphthyloxy)phthaloditrile **IVb** do not sufficiently change in comparison with the spectrum of 4-(1-benzotriazolyl)-5-(1-naphthyloxy) phthalodintrile **IVa**. 2-Naphthol fragment protons give a triplet signal at 7.33 ppm (position *13*), multiplets at 7.16 (position *7*), 7.67 (position *8*), 7.68 ppm (position *9*) and 7.45 ppm (position *10*) and a doublet at 7.87 ppm (positions *11, 12*).

In the IR spectra of **IVa** and **IVb** an absorption band at 2231 cm^{-1} was observed belonging to CºN bond vibrations [10]. Absorption bands in the range of 1200–1210 cm^{-1} are characteristic of Ar–O–Ar bonds vibrations, at 1040–1050 and 470–475 cm^{-1}, of benzotriazole C–N and N=N bonds [11].

Compounds **Va–VIa** free of metal were prepared by heating of the corresponding phthalodintriles at

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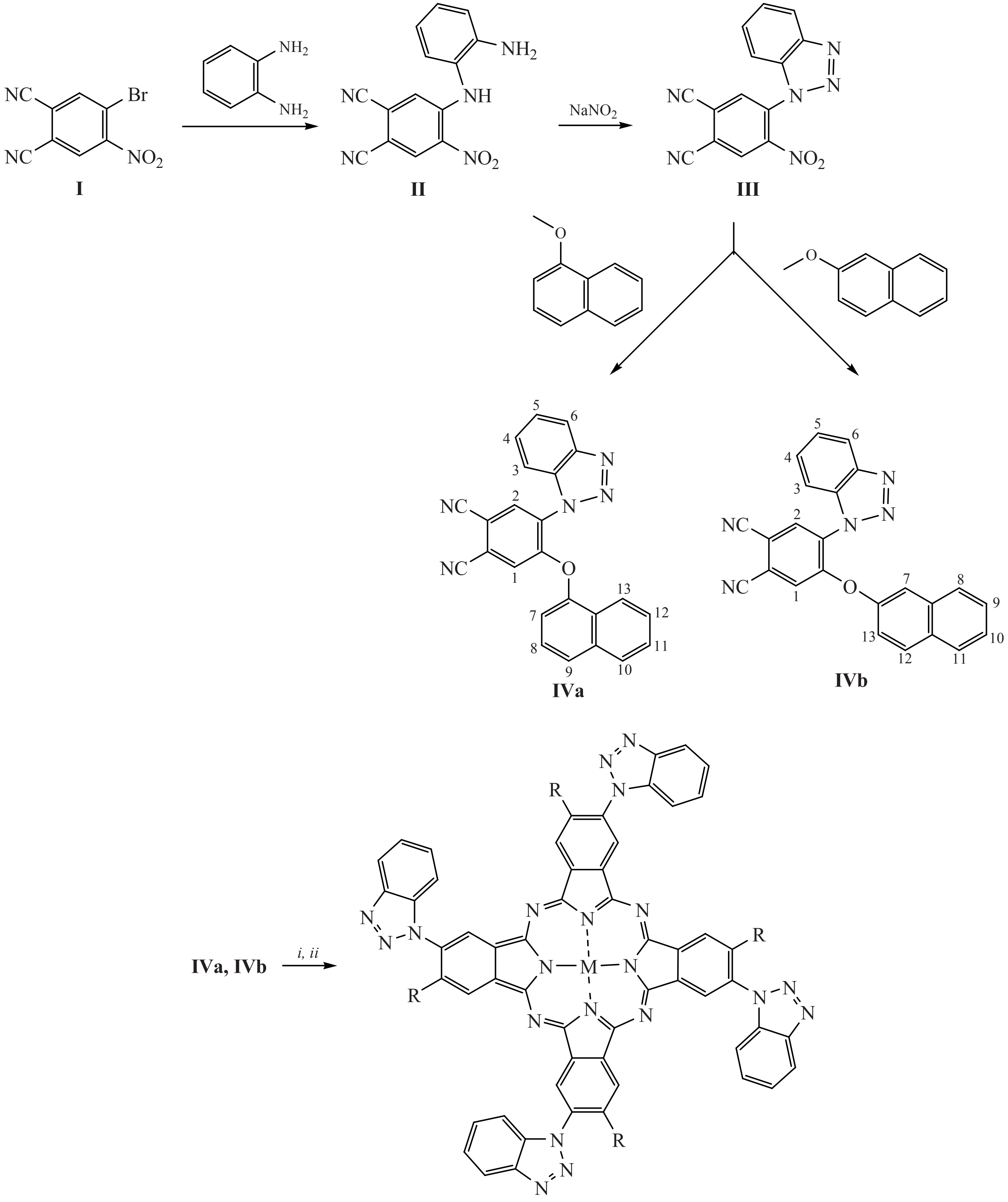
[1] For communication IX, see [1].



Va–Vc–VIa–VIc

(*i*) T = 220°C, urea; (*ii*) T = 200–210°C, $M(OAc)_2 \cdot nH_2O$; M = HH (**a**), Cu (**b**, n = 1), Ni (**c**, n = 6); R = 1-naphthol (**V**), 2-naphthol (**VI**).

220ºC for 2 h in the presence of urea (*i*), since in the absence of the latter reaction proceeds at high temperature and the target products yields are approximately three times lower. We emphasize that the unsubstituted phthalodintrile does not form phthalocyanine macrocycle under the conditions mentioned above. Probably, in this case positive result can be ascribed to the presence of basic benzotriazolyl groups in the initial precursor molecules. An indirect confirmation of the validity of this assumption is the fact that the unsubstituted phthalocyanine was obtained on the yield over than 50% by heating a mixture of unsubstituted phthalodintrile with urea in the presence of 1-benzotriazole in the molar ratio 4:1 (phthalodintrile:benzotriazole). However more detailed investigation is necessary for ascertaining the cause of this phenomenon.

Metal complexes **Vb**, **Vc**, **VIb** and **VIc** were synthesized by the nitrile method (*ii*) by reaction of phthalodintriles **IVa–IVb** with the corresponding metal acetates.

After the reaction completing, the products were carefully ground, washed with 5% hydrochloric acid and then with water to neutral pH, dried at 80°C, and extracted with chloroform. The final purification was carried out by column chromatography using Al_2O_3 as a sorbent and chloroform as an eluent.

The compounds obtained were identified by the data of elemental analysis, ^{1}H NMR, vibration and electronic spectroscopy.

In the ^{1}H NMR spectrum of tetra-4-(1-benzotriazolyl)-tetra-5-(2-naphthyloxy)phthalocyanine **VIa** there is a signal of transannular imino groups protons at –1.80 ppm, which is absent in the spectrum of compound **VIc**. The signals location in the spectra of benzotriazolyl-substituted phthalocyanines as a whole practically coincided with the described above spectrum of the initial phthalodintrile.

In the IR spectra of the synthesized compounds the absorption bands remained belonging to substituents bond vibrations and to those registered in the spectrum of the corresponding phthalodinitriles. In the spectra of metal-free phthalocyanines there are absorption bands in the region of 1012–1014 cm^{-1} characteristic for phthalocyanine ligands. Absorption at 3290–3340 cm^{-1} originates from NH-bonds vibra-tion of transannular imino groups [12] and is absent in the spectra of metal complexes.

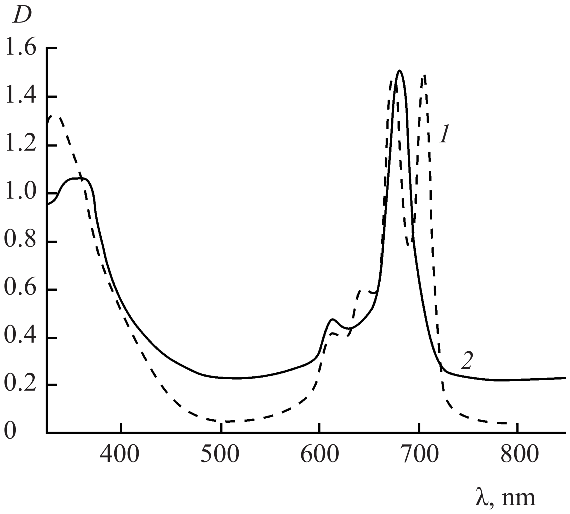


Fig. 1. Electronic spectra of tetra-4-(1-benzotriazolyl)-tetra-5-(2-naphthyloxy)phthalocyanine: (*1*) in DMF (2.20×10^{-5} mol l^{-1}) and (*2*) in chloroform (2.12×10^{-5} mol l^{-1}).

In the electronic spectra ($CDCl_3$) of not metal-containing compounds we observed two intensive long-wave absorption bands in the region of 671–672 and 707–709 nm that are characteristic of phthalocyanine ligands [7] (Fig. 1).

In DMF, a simplification of the electron spectrum is observed, which is characterized by the presence of a single *Q*-band at 683–684 nm in place of two long-wave bands. This indicates that phthalocyanine dianionic form with molecular symmetry D_{4h} is produced in the medium of basic solvent [13].

Analyzing the electronic spectra of tetra-4-(1-benzotriazolyl)-tetra-5-(1(2)-naphthyloxy)phthalocyanines metal complexes **Vb, VIc–VIb, VIc** (Fig. 2), we emphasize that in such organic solvents as DMF, chloroform, and carbon tetrachloride all the compounds are in the non-associated forms. The solvent nature effects on the first band location appears as a red shift of the first absorption band by 4–5 nm when DMF is replaced by chloroform.

The red shift of *Q*-band by 5–6 nm is also observed in passing from nickel complexes to copper phthalocyanines.

At the comparative analysis of the electronic spectra for metal complexes **Vb, Vc–VIb, VIc** and the corresponding tetra-4-(1-benzotriazolyl)metalphthalocyanines in organic solvents we noted that incurporation of 1- or 2-naphthol residue into *ortho*-position relative to 1-benzotriazole fragment causes a red shift of *Q*-band by 5 nm.

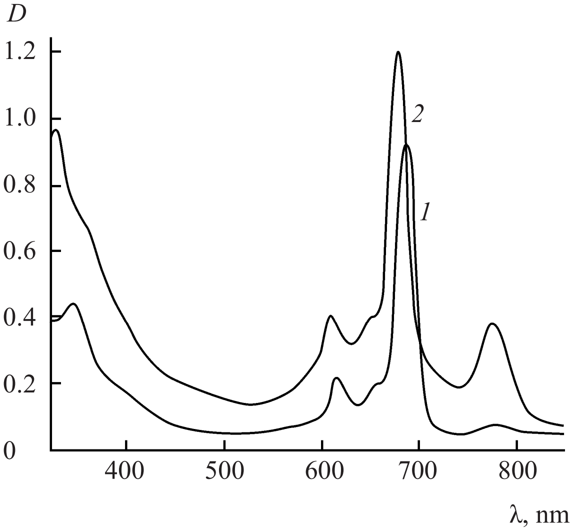


Fig. 2. Electronic spectra ($CDCl_3$) of: (*1*) copper 1-tetra-4-(1-benzotriazolyl)-tetra-5-(2-naphthyloxy)phthalocyanine (1.12×10^{-5} mol l^{-1}) and (*2*) nickel tetra-4-(1-benzotriazolyl)-tetra-5-(2-naphthyloxy)phthalocyanine (1.50×10^{-5} mol l^{-1}).

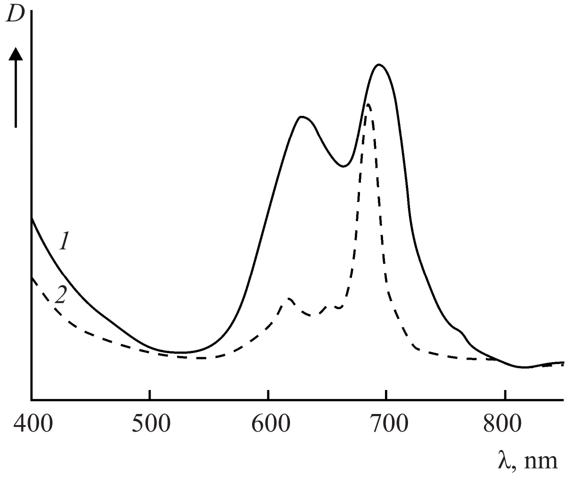


Fig. 3. Electronic spectra of water-soluble product obtained by sulfonation of copper tetra-4-(1-benzotriazolyl)-tetra-5-(2-naphthyloxy)phthalocyanine, (*1*) in water and (*2*) in DMF.

Furthermore, in the electronic spectra of copper and nickel complexes the additional absorption band in the long-wave region (765–775 nm) is observed. It is relatively weak in the case of copper phthalocyanines and more intensive in the case of nickel complexes (Fig. 2). This absorption band is absent in the spectra of metal-free compounds and it is its nature currently difficult to interpret.

On dissolving all the metal complexes in concentrated sulfuric acid followed by pouring into water we obtain products of dark green color, which lose the solubility in chloroform and others organic solvents except for DMF and acquire a solubility in water-base media. In DMF, the location and shape of absorption bands in the electron spectra are practically similar to the spectra of initial metal complexes. In visible region of spectrum of the water-based solutions two diffusion absorption bands are observed, the location and ratio of intensities of which depend on the phthalocyanine concentration in the solution (Fig. 3). This shows according to the published data that the compounds obtained are in associated forms in the water-base solutions [14].

In the IR spectra there are absorption bands in the region of 1190–1200 cm^{-1} belonging to sulfo groups [11]. This suggests that tetra-4-(1-benzotriazlyl)tetra-5-(naphthyloxy)phthalocyanines sulfonic acids are formed. By the elemental analysis data, in the course of the process mentioned above, a mixture of sulfonation products is formed, containing various number of sulfo groups, on the average 4–6 per molecule of the corresponding metal phthalocyanine. We failed to separate this mixture.

On studying the color properties of all the compounds obtained their ability was found to colorize waxes, fats, and polymeric materials into bright rich colors [9].

EXPERIMENTAL

The electron spectra were recorded on a HITACHI U-2001 spectrophotometer in DMF and chloroform at room temperature in the range of 325–900 nm. The IR spectra were registered on an Avatar 360 FT-IR ESP device in the range of 400–4000 cm^{-1} from films (chloroform) and pellets (KBr). The ^1H NMR spectra of phthalodinitriles were taken on a Bruker DRX-500 device in DMSO-d_6 relative to internal TMS; the ^1H NMR spectra of benzotriazolyl-substituted phthalocyanines were recorded on a Bruker AMD-200 device in $CDCl_3$. Elemental analysis was accomplished on a CHNS-O FlashEA (1112 series) elemental analyser.

4-Bromo-5-nitrophthalonitrile (I) was obtained by the known procedure [15].

4-(2-Aminophenylamino)-5-nitrophthalodinitrile (II) was prepared from 4-bromo-5-nitrophthalodinitrile **I** by the known procedure [16].

4-(1-Benzotriazolyl)-5-nitrophthalodinitrile (III) was prepared from compound **II** by procedure [16].

4-(1-Benzotriazolyl)-5-(1(2)-naphthyloxy)phthalodinitriles (IVa, IVb) were prepared by procedure [9].

Compound obtained are pale yellow needles, insoluble in water, well soluble in DMF, chloroform, acetone and benzene.

4-(1-Benzotriazolyl)-5-(1-naphthyloxy)phthalodinitrile (IVa). Yield 86%, mp 210–212°C. Found, %: C 77.10, H 4.72, N 15.40. $C_{24}H_{13}N_5O$. Calculated, %: C 76.47, H 4.65, N 15.37. ^{1}H NMR spectrum, δ, ppm: 8.73 s (1H, H^2), 8.23 d (1H, H^3), 8.14 s (1H, H^1), 7.81 d (1H, H^4), 7.55 t (1H, H^5), 8.08 t (1H, H^6), 7.28 m (1H, H^7), 7.04 m (1H, H^8), 7.45 m (1H, H^9), 8.43 m (1H, H^{10}), 7.55 d (2H, $H^{11,12}$), 8.15 t (1H, H^{13}).

4-(1-Benzotriazolyl)-5-(2-naphthyloxy)phthalodinitrile (IVb). Yield 87%, mp 209–212°C . Found, %: C 76.49, H 4.64, N 15.14. $C_{24}H_{13}N_5O$. Calculated, %: C 76.47, H 4.65, N 15.37. ^{1}H NMR spectrum, δ, ppm: 8.73 s (1H, H^2), 8.23 d (1H, H^3), 8.16 s (1H, H^1), 7.81 d (1H, H^4), 7.55 t (1H, H^5), 8.08 t (1H, H^6), 7.16 m (1H, H^7), 7.67 m (1H, H^8), 7.68 m (1H, H^9), 7.45 m (1H, H^{10}), 7.87 d (2H, $H^{11,12}$), 7.33 t (1H, H^{13}).

General procedure of synthesis of tetra-4-(1-benzotriazolyl)-tetra-5-(naphthyloxy)phthalocyanine ligands (Va, VIa). 100 mg (0.24 mmol) of the corresponding phthalonitriles was heated to 220°C for 2 h in the presence of 5 mg of urea. Purification of the target products was carried out by extraction with chloroform and then by column chromatography using Al_2O_3 and chloroform as eluent. The product was dried in a vacuum at 70ºC. The compounds obtained are powders of bright green color insoluble in water and well soluble in organic solvents.

Tetra-4-(1-benzotriazolyl)-tetra-5-(1-naphthyloxy)-phthalocyanine (Va) was prepared from 4-(1-benzotriazolyl)tetra-5-(1-naphthyloxy)phthalodinitrile **(IVa)**. Yield 89.6 mg (90%). Found, %: C 73.71, H 4.80, N 17.86. $C_{96}H_{54}N_{20}O_4$. Calculated, %: C 74.30, H 4.51, N 18.10. Electron spectrum, λ_{max}, nm (log ε): in chloroform 707 (4.90), 673 (4.88); in DMFA 681 (4.82).

Tetra-4-(1-benzotriazolyl)-tetra-5-(2-naphthyloxy)-phthalocyanine (VIa) was prepared from 4-(1-benzotriazolyl)tetra-5-(2-naphthyloxy)-phthalodinitrile **(IVb)**. Yield 91.1 mg (91%). Found, %: C 74.00, H 4.63, N 17.71. $C_{96}H_{54}N_{20}O_4$. Calculated, %: C 74.30, H 4.51, N 18.10. Electron spectrum, λ_{max}, nm (log ε): in chloroform 708 (4.92), 673 (4.90); in DMFA 681 (4.89). ^{1}H, NMR spectrum, δ, ppm: 8.70 s (4H, H^2), 8.13 s (4H, H^1), 8.05 s (4H, H^3), 7.90 s (4H, H^4), 7.57 t (4H, H^5), 7.57–7.20 m (32H, $H^{7–13}$), –1.80 s (2H, NH).

General procedure of synthesis of tetra-4-(1-benzotriazolyl)-tetra-5-(naphthyloxy)phthalocyanines metal complexes. A mixture of 50 mg (0.12 mmol) of phthalodinitriles **IVa, IVb** and 0.03 mmol of the corresponding metal acetate was heated to 200–220°C and kept at this temperature for 1–1.5 h. The phthalocyanines obtained were ground, washed with 5% hydrochloric acid solution and with water to pH = 7 and dried at 80°C . The target products were extracted with chloroform and purified by column chromatography using Al_2O_3 and chloroform as eluent.

Copper tetra-4-(1-benzotriazolyl)-tetra-5-(1-naphthyloxy)phthalocyanine (Vb) was prepared from 4-(1-benzotriazolyl)-5-(1-naphthyloxy)phthalodintrile **IVa** and 6 mg of copper acetate. Yield 31.0 mg (66%). Found, %: C 71.11, H 3.33, N 17.52. $C_{96}H_{52}N_{20}O_4Cu$. Calculated, %: C 71.49; H 3.28; N 17.38. Electron spectra, λ_{max}, nm (log ε): in chloroform 688 (4.93); in DMFA 684 (4.86)

Copper tetra-4-(1-benzotriazolyl)-tetra-5-(2-naphthyloxy)phthalocyanine (VIb) was prepared from 4-(1-benzotriazolyl)-5-(2-naphthyloxy)phthaloditrile **IVb** and 6 mg of copper acetamide. Yield 34.2 mg (71%). Found, %: C 70.01, H 3.37, N 17.95. $C_{96}H_{52}N_{20}O_4Cu$. Calculated, %: C 71.49; H 3.28; N 17.38. Electron spectra, λ_{max}, nm (log ε): in chloroform 688 (4.97); DMFA 684 (4.90).

Nickel tetra-4-(1-benzotriazolyl)-tetra-5-(1-naphthyloxy)phthalocyanine (Vc) was prepared from 4-(1-benzotriazolyl)-5-(1-naphthyloxy)phthalodintrile **IVa** and 8.5 mg of nickel acetate. Yield 12.3 mg (25%). Found, %: C 73.22, H 3.77, N 18.05. $C_{96}H_{52}N_{20}O_4Ni$. Calculated, %: C 71.71; H 3.33; N 17.53. Electron spectra, λ_{max}, nm (log ε): in chloroform 681 (4.80), 781 (4.36); in DMFA 681(4.83), 766 (4.27).

Nickel tetra-4-(1-benzotriazolyl)-tetra-5-(2-naphthyloxy)phthalocyanine (VIc) was prepared from 4-(1-benzotriazolyl)-5-(2-naphthyloxy)phthalodintrile **IVb** and 8.5 mg of nickel acetate. Yield 14.3 mg (29%). Found, %: C 71.78; H 4.08; N 17.80. $C_{96}H_{52}N_{20}O_4Ni$. Calculated, %: C 73.22, H 3.77, N 18.05. Electron spectrum, λ_{max}, nm (log ε): in chloroform 682 (4.86), 760 (4.37); in DMFA 678 (4.80), 776 (4.20). ^{1}H NMR spectrum, δ, ppm: 8.73 s (4H, H^2), 8.20 d (4H, H^3), 8.13 d (4H, H^1), 7.83 s (4H, H^4, J 7.9 Hz), 7.56 s (4H, H^5), 8.05 d (4H, H^6), 7.20 d (4H, H^7), 7.60 s (4H, H^8), 7.62 s (4H, H^9), 7.45 m (4H, H^{10}), 7.90 s (8H, H^{11,12}), 7.37 s (4H, H^{13}).

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REFERENCES

1. Fedotova, A.I., Maizlish, V.E., Shaposhnikov, G.P., Abramov, I.G., and Filimonov, S.N., *Zh. Obshch. Khim*., 2009, vol. 79, no. 5, p. 846.
2. Maizlish, V.E., Shaposhnikov, G.P., and Zhukova, Z.N., *Zh. Prikl. Khim*., 2002, vol. 70, no. 1, p. 153.
3. Maizlish, V.E. and Shaposhnikov, G.P., *Uspekhi khimii porfirinov* (Porphirin Chemistry), Saint-Petersburg: NII khimii S.-Peterb. Gos. Univ., 2004, p. 327.
4. Mironov, A.F., *Uspekhi khimii porfirinov* (Porphirin Chemistry), Saint-Petersburg: NII Khimii S.-Peterb. Gos. Univ., 1997, p. 357.
5. Usol'tseva, N.V., *Uspekhi khimii porfirinov* (Porphirin Chemistry), Saint-Petersburg: NII Khimii S.-Peterb. Gos. Univ., 1997, vol. 2, p. 142.
6. Simon, Zh., Andre, Zh.-Zh., *Molekulyarnye poluprovodniki. Fotoelektricheskie svoistva i solnechnye elementy* (Molecular Semiconductors. Photoelectric Properties and Solar Elements), Moscow: Mir, 1988, p. 342.
7. Berezin, B.D., *Koordinatsionnye soyedinenia porfirinov i ftalotsianina* (Porphirin and Phthalocyanine Coordination Compounds), Moscow: Nauka, 1978, p. 280.
8. Abramov, I.G., Smirnov, A.V., and Plakhtinskii, V.V., *Panorama sovremennoi khimii Rossii. Uspekhi v neftekhimicheskom sinteze polifunktsional'nykh aromaticheskikh soedinenii* (Panorama of Contemporary Chemistry of Russia. Progress in Petrochemical Synthesis of Polyfunctional Aromatic Compounds), Moscow: Khimiya, 2005, p. 85.
9. Znoiko, S.A., Maizlish, V.E., Shaposhnikov, G.P., Abramov, I.G., and Lyskov, V.B., RF Patent no. 2327720 2006144983; appl. 18.12.06; publ. 27.06.2008; *Byull. Izobret*., no. 18.
10. Rodionova, G.N., Boglayenkova, G.V., Mikhailenko, S.A., and Lukyanets, E.A., *Anilinokrasochnaya promyshlennost'* (Aniline-Dye Industry), Moscow: NIITEKHIM, 1974, no. 1, p. 3.
11. Daiyer, J.D., *Prilozheniya absorbtsionnoi spektroskopii organicheskikh soedinenii* (Application of Absorption Spectroscopy of Organic Compounds), Moscow: Khimiya, 1970, p. 164.
12. Sidorov, A.N. and Kotlyar, I.P., *Opt. i Spektr*., 1961, vol. 11, no. 2, p. 175.
13. Vul'fson, S.V., Lebedev, O.L., and Lukyanets, E.A., *Zh. Prikl. Spektr*., 1972, vol. 17, no. 5, p. 903.
14. Maizlish, V.E., Shirokov, A.V., Kudrik, E.V., and Shaposhnikov, G.P., *Zh. Obshch. Khim*., 2002, vol. 72, no. 10, p. 1740.
15. Shishkina, O.V., Maizlish, V.E., Shaposhnikov, G.P., Lyubimtsev, A.V., Smirnov, R.P., and Baran'ski, A., *Zh. Obshch. Khim*., 1997, vol. 67, no. 5, p. 842.
16. Abramov, I.G., Smirnov, A.V., Plakhtinskii, V.V., and Krasovskaya, G.G., *Mendeleev Commun*., 2002, no. 2, p. 72.