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Nucleophilic Substitution in 4-Bromo-5-nitrophthalodinitrile: VIII.[1] Synthesis of 4-(Benzotriazol-1-yl)-5-[4-(1-methyl-1-phenylethyl)phenoxy]phthalodinitrile and Phthalocyanines on Its Basis

S. A. Znoiko[a], V. E. Maizlish[a], G. P. Shaposhnikov[a],
I. G. Abramov[b], and M. N. Voron'ko[b]

[a] Ivanovo State Chemical Technological University,
pr. F. Engel'sa 7, Ivanovo, 153000 Russia
e-mail: ttoc@isuct.ru
[b] Yaroslavl State Technical University, Yaroslavl, Russia

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Abstract—Nucleophilic aromatic substitution of the bromine atom in 4-bromo-5-nitrophthalodinitrile by a 2-aminophenylamine residue followed by conversion of the resulting compound to 4-(1-benzothiazol-1-yl)-5-nitrophthalodinitrile and nucleophilic substitution of the nitro group by a 4-(1-methyl-1-phenylethyl)-phenoxy group gave 4-(benzotriazol-1-yl)-5-[4-(1-methyl-1-phenylethyl)phenoxy]phthalodinitrile. The latter product was reacted with certain metal acetates and chlorides to obtain the corresponding metal complexes of octasubstituted phthalocyanines. Spectral properties of the complexes were studied.

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Phthalocyanines and related compounds have long been used as high-class organic dyes and pigments [2] and effective desulfurization catalysts [3]. They are also known to be applied as catalysts in other processes, as well as materials for photodynamic therapy of cancer, optical discs, chemical sensors, etc. [4–8]. Heterocyclic compounds are of primary importance in many biological processes and are their key components. In particular, triazoles are bacterial antagonists that inhibit cell division, and they also possess herbicidal activity [9]. In view of the aforesaid, synthesis of phthalocyanines (Pc) containing such "small" heterocycles holds promise, but only few such compounds have been synthesized, mostly pyridyl-substituted Pc [10].

New substituted phthalocyanines are difficult to synthesize, not infrequently because of the lack of difficulties in preparation of starting phthalic acids or their derivatives, specifically phthalodinitriles. Previously we reported on a unique source of a variety of substituted phthalodinitriles, 4-bromo-5-nitrophthalodinitrile (**I**) [11], which exhibits high reactivity in aromatic nucleophilic substitution [12–14].

In the present work we made use of compound **I** to 4-(benzotriazol-1-yl)-5-[4-(1-methyl-1-phenylethyl)-phenoxy]phthalodinitrile (**IV**) and metal phthalocyanines on its basis.

The nucleophilic substitution of the bromine atom in 4-bromo-5-nitrophthalodinitrile (**I**) on the reaction of the latter with (2-aminophenyl)amine resulted in the synthesis of 4-[(2-aminophenyl)amino]-5-nitrophthalodinitrile (**II**) which reacted with sodium nitrite in the presence of acetic acid to form 4-(1-benzothiazol-1-yl)-5-nitrophthalodinitrile (**III**) [13]. The nucleophilic substitution of the nitro group under the action of 4-(1-methyl-1-phenylethyl)phenol in the presence of K_2CO_3 gave target phthalocyanogen **IV**.

Compounds **II**–**IV** were identified by elemental analysis and ^{1}H NMR (the numbering of protons in the compounds are given in the scheme) and vibrational spectroscopy.

The ^{1}H NMR spectrum of phthalodinitrile **IV** contains signals at 7.75 and 8.70 ppm, corresponding to the protons in the 1 and 2 positions of the phthalodinitrile benzene ring, and signals at 8.16, 7.80, 7.65, and 7.5 ppm, corresponding to the protons in the 3, 4, 5, and 6 positions of the benzotriazole fragment. The

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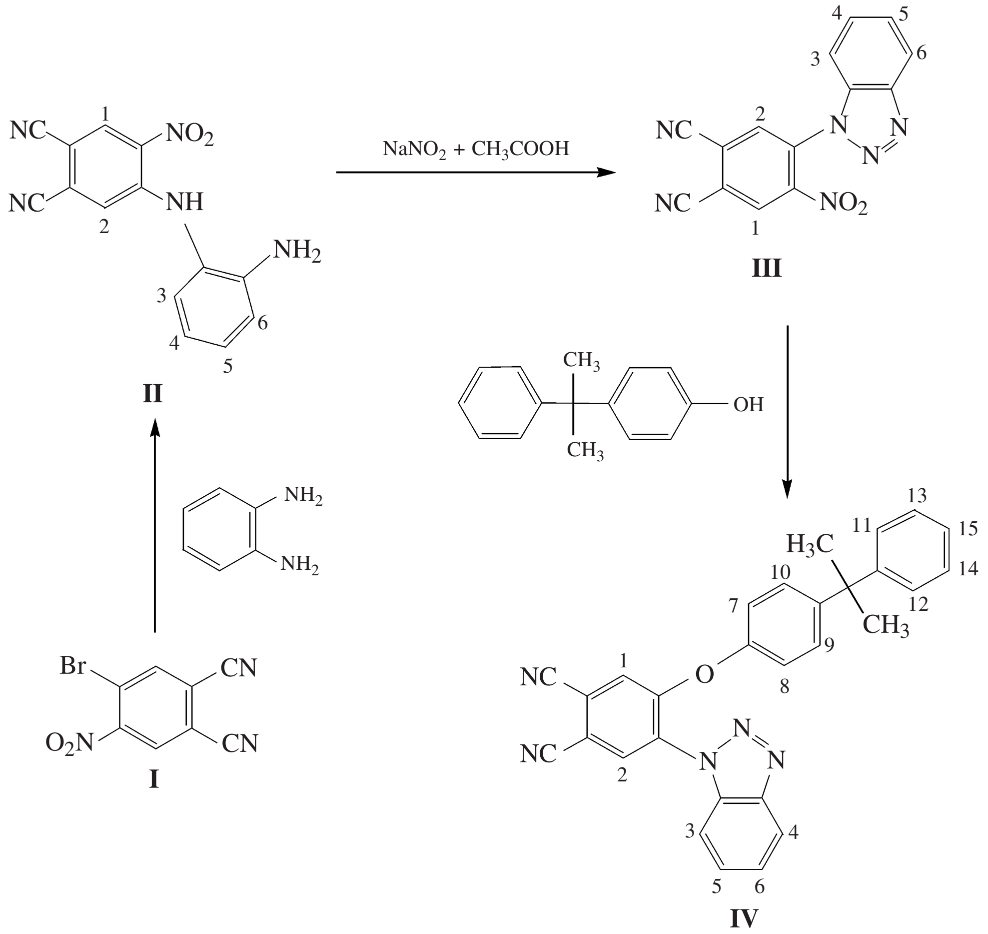
[1] For communication VII, see [1].



signals of the 4-(1-methyl-1-phenylethyl)phenoxy group appear as a multiplet at 7.20 ppm (positions 7–10 and 15), a triplet at 7.27 ppm (positions 13 and 14), and a doublet at 7.05 ppm (positions 11 and 12). The upfield singlet at 1.60 ppm belongs to six methyl protons.

The IR spectra of phthalodinitrile **IV** show bands characteristic of substituted phthalodinitriles [15] and indicative of the substituents present. The absorption bands characteristic of the C≡N bonds are observed at 2233 cm^{-1}, and those of the Ar–O–Ar bonds, at 1208 cm^{-1}. The stretching vibration bands of the methyl groups appear at 2874–3060 cm^{-1} [16].

Metal complexes **Va**–**Vd** were synthesized by the "nitrile" method from phthalodinitrile **IV** and acetates and chlorides of the corresponding metals.

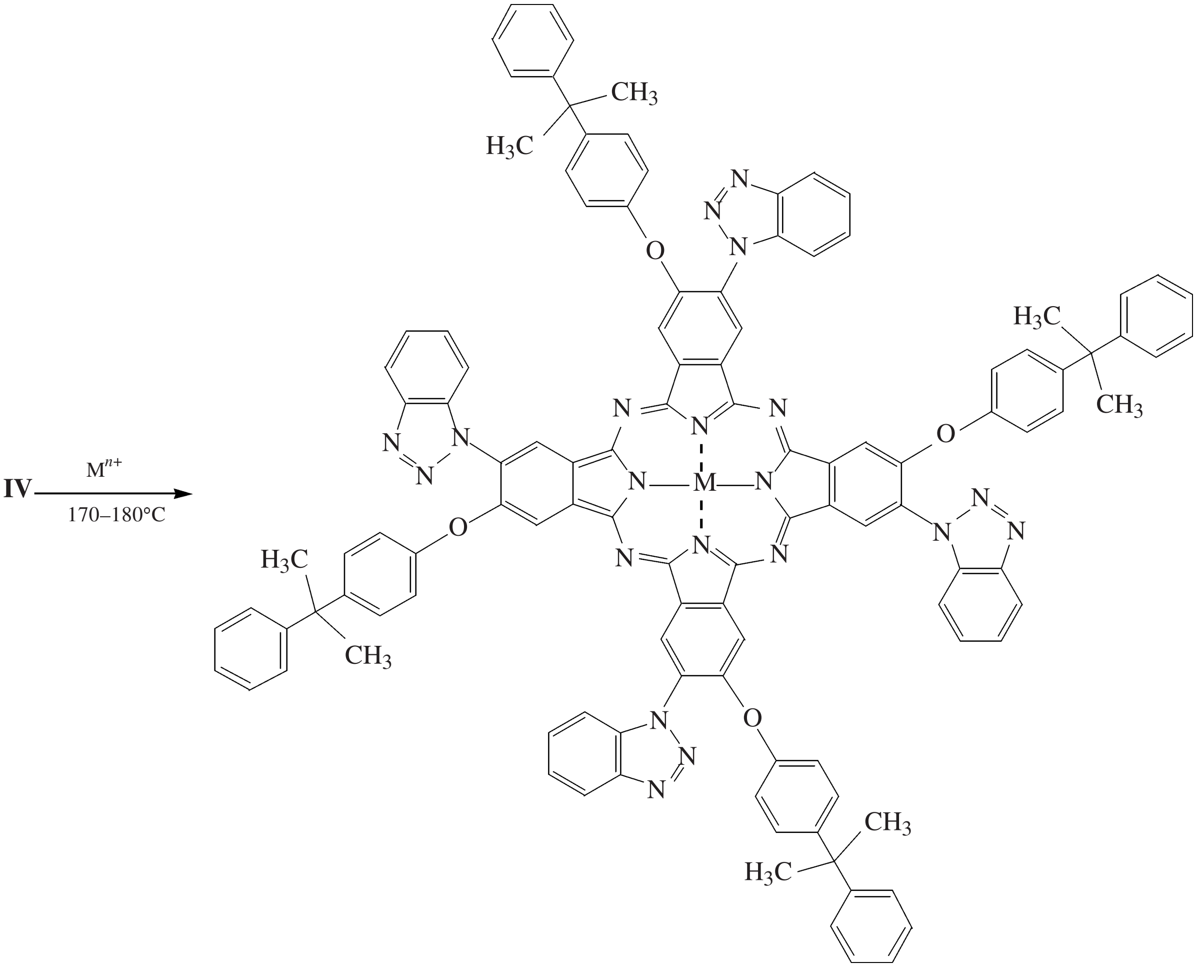
The presence in the phthalocyanine molecule of bulky 4-(1-methyl-1-phenylethyl)phenoxy groups weakens intermolecular interactions and enhances solubility in DMF and other organic solvents, specifically chloroform, benzene, and acetone. With this in mind, the target products were extracted with chloroform.

The purification technique was chosen depending on the individual features of each phthalocyanine.

Copper tetra[4-(benzotriazol-1-yl)]-tetra{5-[4-(1-methyl-1-phenylethyl)phenoxy]}phthalocyanine (**Va**) is soluble in concentrated hydrochloric acid and was purified by reprecipitation from this acid. Cobalt and nickel complexes **Vb** and **Vc**, respectively, were purified by treatment with aqueous acetone to remove unreacted phthalodinitrile. Final purification was performed by column chromatography on Al_2O_3 (eluent chloroform). The complexes were identified by elemental analysis and vibrational and electronic spectroscopy.

The IR spectrum of the copper complex contains almost all bands characteristic of phthalodinitrile **IV**, except for the C≡N bands at 2230–2240 cm^{-1}. The same is true of the IR spectra of the other metal phthalocyanines.

Analysis of the electronic absorption spectra shows that the solvent (DMS, chloroform) only slightly affects the position of the first band at 669–689 nm (see figure).



Va–Vd

M = Cu (**Va**), Co (**Vb**), Ni (**Vc**), Er (**Vd**); n = 2 (**Va–Vc**), 3 (**Vd**).

The influence of the central metal atom shows up in a bathochromic shift of the first band, whose magnitude increases in the series: Co < Ni < Cu < Er (in DMF) and Ni < Co < Cu and Er (in chloroform).

The Q band in the electronic absorption spectrum of cooper tetra[4-(benzothiazol-1-yl)]-tetra{5-[4-(1-methyl-1-phenylethyl)phenoxy]}phthalocyanine (**Va**) in DMF is shifted bathochromically compared with

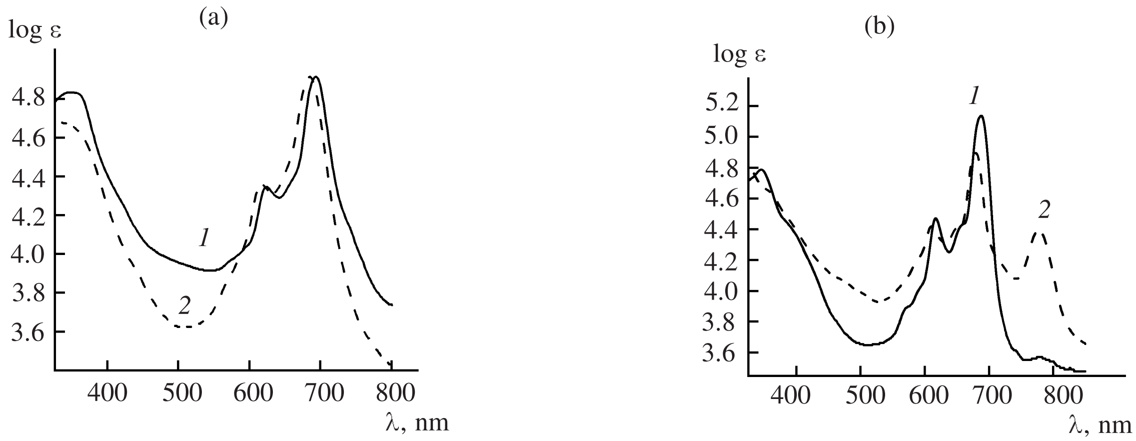


Fig. 1. Electronic absorption spectra in chloroform. (a): (*1*) Erbium complex **Vd** and (*2*) cobalt complex **Vb**; (b): (*1*) copper complex **Va** and (*2*) nickel complex **Vc**.

copper tetra[4-(benzothiazol-1-yl)]phthalocyanine (λ_{max} 679 nm).

It should be noted that the long-wave regions of the spectra of copper complex **Va** and nickel complex **Vc** (765–775 nm) contain an additional absorption band which is fairly weak for complex **Va** and stronger for complex **Vc** (see Fig. 1b).

EXPERIMENTAL

The electronic absorption spectra were taken in DMF and chloroform on a UV/VIS Perkin Elmer Spectrometer Lambda 200 spectrophotometer at room temperature in the range 325–900 nm. The IR spectra were obtained on an Avatar 360 FT-IR ESP instrument in the range 400–4000 cm^{-1} in thin films (chloroform) and KBr tablets. The ^1H NMR spectra were measured in 5% solutions in DMSO-d_6 on a Bruker DRX-500 instrument, internal reference TMS. Elemntal analysis was performed on a CHNS-O FlashEA Series 1112 instrument.

4-[(2-Aminophenyl)amino]-5-nitrophthalodinitrile (II). A mixture of 2.52 g of 4-bromo-5-nitrophthalodinitrile, 1.01 g of triethylamine, 1.81 g of 2-aminophenylamine, and 50 ml of propan-2-ol was refluxed for 2 h, and the precipitate that formed was filtered off. Yield 2.55 g (92%), mp 168–170°C. ^1H NMR spectrum, δ, ppm: 9.66 s (1H, NH), 8.70 s (1H, H^1), 7.12 t (1H, H^3, *J* 16 Hz), 7.05 d (1H, H^6, *J* 8 Hz), 6.93 s (1H, H^2), 6.85 d (1H, H^5, *J* 8 Hz), 6.75 t (1H, H^4, *J* 16 Hz), 5.15 s (2H, NH_2). Found, %: C 60.19; H 3.12; N 24.76. $C_{14}H_9N_5O_2$. Calculated, %: C 60.21; H 3.25; N 25.08.

4-(1-Benzothiazol-1-yl)-5-nitrophthalodinitrile (III). A solution of 7.60 g of $NaNO_2$ in 50 ml of water was added to a solution of 31.00 g of compound **II** in 300 ml of acetic acid. The reaction mixture was stirred at 70°C for 3 h. The precipitate that formed after cooling was filtered off, washed with 20 ml of acetic acid, and dried at 70°C. Yield 29.64 g (92%), mp 234–236°C. ^1H NMR spectrum, δ, ppm: 9.29 s (1H, H^1), 9.00 s (1H, H^2), 8.25 d (1H, H^3, *J* 8 Hz), 8.00 d (1H, H^4, *J* 8,1 Hz), 7.80 t (1H, H^5), 7.60 t (1H, H^6). Found, %: C 57.95; H 2.06; N 28.92. $C_{14}H_6N_6O_2$. Calculated, %: C 57.94; H 2.08; N 28.95.

4-(Benzotriazol-1-yl)-5-[4-(1-methyl-1-phenylethyl)phenoxy]phthalodinitrile (IV). Dimethylformamide, 30 ml, compound **III**, 2.9 g, 4-(1-methyl-1-phenylethyl)phenol, 2.12 g, and 1.38 g of K_2CO_3 were dissolved with stirring in 10 ml of water, and the solution was allowed to stand for 0.5 h at room temperature. The precipitate that formed was filtered off, washed with propan-2-ol (50 ml) and water (100 ml), and dried at 70°C. The precipitate looks like light yellow needles insoluble in water and readily soluble in DMF, chloroform, acetone, and benzene. Yield 3.84 g (87%), mp 209–212°C. ^1H NMR spectrum, δ, ppm: 8.70 s (1H, H^2), 8.16 d (1H, H^3, **J** 8 Hz), 7.85 s (1H, H^1), 7.8 d (1H, H^4, *J* 7.9 Hz), 7.65 t (1H, H^5), 7.5 t (1H, H^6), 7.27 t (2H, $H^{13,14}$), 7.20 m (4H, $H^{8-10,15}$), 7.05 d (2H, $H^{11,12}$, *J* 8.1 Hz), 1.60 s (6H). Found, %: C 76.49; H 4.64; N 15.14. $C_{35}H_{21}N_5O$. Calculated, %: C 76.47; H 4.65; N 15.37.

Metal complexes of tetra[4-(benzotriazol-1-yl)]-tetra{5-[4-(1-methyl-1-phenylethyl)phenoxy]}-phthalocyanine were prepared by the reactions of phthalodinitrile **IV** with metal acetates and chlorides. The mixture was heated at 200–220°C for 1–1.5 h. The reaction products were thoroughly ground, washed with 5% HCl, washed with water to neutral, dried at 80°C, and then extracted with chloroform. After removal of the solvent the products were purified with account for their individual features. The final purification was performed by chromatography on Al_2O_3 (eluent chloroform).

The resulting phthalocyanines are dark green or bluish green powders insoluble in water and readily soluble in DMF, chloroform, acetone, and benzene.

Copper tetra[4-(benzotriazol-1-yl)]-tetra{5-[4-(1-methyl-1-phenylethyl)phenoxy]}phthalocyanine (Va) was prepared from 47 mg of compound **IV** and 6 mg of copper acetate and purified by reprecipitation from conc. HCl. Yield 31 mg (60%). Electronic absorption spectrum, λ_{max}, nm (logε): in DMF: 613 (4.26), 684 (5.09); in chloroform: 617 (4.46), 688 (5.17), 771 (3.57). Found, %: C 72.26; H 4.18; N 15.00. $C_{116}H_{84}CuN_{20}O_4$. Calculated, %: C 73.85; H 4.46; N 14.85.

Cobalt tetra[4-(benzotriazol-1-yl)]-tetra{5-[4-(1-methyl-1-phenylethyl)phenoxy]}phthalocyanine (Vb) was prepared from 47 mg of compound **IV** and 7 mg of cobalt chloride and purified by treatment with aqueous acetone (1:10, v/v). Yield 38 mg (76.8%). Electronic absorption spectrum, λ_{max}, nm (logε): in DMF: 605 (4.51), 669 (4.90); in chloroform: 607 (4.25), 675 (4.90). Found, %: C 70.99; H 4.19; N 14.87. $C_{116}H_{84}CoN_{20}O_4$. Calculated, %: C 73.87; H 4.50; N 14.87.

Nickel tetra[4-(benzotriazol-1-yl)]-tetra{5-[4-(1-methyl-1-phenylethyl)phenoxy]}phthalocyanine (Vc) was prepared from 47 mg of compound **IV** and 7 mg of nickel acetate and and purified by treatment with aqueous acetone (1:10, v/v). Yield 11.3 mg (22%). Electronic absorption spectrum, λ_{max}, nm (logε): in DMF: 600 (4.57), 679 (4.91), 760 (4.41);

in chloroform: 605 (4.46), 676 (4.96), 771 (4.36). Found, %: C 70.19; H 4.30; N 14.23. $C_{116}H_{84}N_{20} \cdot NiO_4$. Calculated, %: C 74.10; H 4.51; N 13.85.

Erbium tetra[4-(benzotriazol-1-yl)]-tetra{5-[4-(1-methyl-1-phenylethyl)phenoxy]}phthalocyanine (Vd) was prepared from 56.4 mg of compound **IV** and 14 mg of erbium chloride. Yield 26 mg (48%). Electronic absorption spectrum, λ_{max}, nm (log ε): in DMF: 621 (4.16), 689 (4.87); in chloroform: 618 (4.21), 688 (4.92). Found, %: C 70.92; H 4.30; N 14.23. $C_{116}H_{84}ErN_{20}O_4$. Calculated, %: C 68.98; H 4.20; N 13.85.

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