ISSN 1070-3632, Russian Journal of General Chemistry, 2015, Vol. 85, No. 4, pp. 871–875. © Pleiades Publishing, Ltd., 2015.
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Nucleophilic Substitution in 4-Bromo-5-nitrophthalodinitrile: XII.[1] Synthesis and Properties of 4-(1-Benzotriazolyl)-, 4-Nitro-5-(4-nonylphenoxy)phthalonitriles and the Ligands Based on Them

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Received November 11, 2014

Abstract—4-Nitro- and 4-(1-benzotriazolyl)-5-(4-nonylphenoxy)phthalonitriles were prepared by nucleophilic substitution of bromine and nitro group in 4-bromo-5-nitrophthalonitrile. Based on the latter the corresponding octa-substituted phthalocyanines were synthesized. The spectral properties of the prepared compounds were investigated.

Keywords: 4-bromo-5-nitrophthalonitrile, nucleophilic substitution, metal-free phthalocyanine, electron absorption spectra

DOI: 10.1134/S1070363215040180

Phthalocyanine derivatives and their metal complexes attract interest of researches due to their wide use in various fields of science and technology [2–4]. The present report continued a series of reports on the synthesis and investigation of physicochemical properties of octa-substituted phthalocyanines [5–7]. Here we present data on the synthesis and investigation of the spectral properties of new 4-nitro- and 4-(1-benzotriazolyl)-5-(4-nonylphenoxy)phthalonitriles and phthalocyanines prepared therof.

Target phthalonitriles **II** and **III** were synthesized by the successive nucleophilic substitution of the bromine atom and nitro group in 4-bromo-5-nitrophthalodinitrile **I**.

The reaction of compound **I** with 4-nonylphenol in the presence of potassium carbonate in DMF at room temperature in 0.5 h afforded 4-nitro-5-(4-nonylphenoxy)phthalonitrile **II** in 94% yield. The latter reacted with 1*H*-benzotriazole in DMF at 70°C for 1 h to form compound **III** in 68% yield.

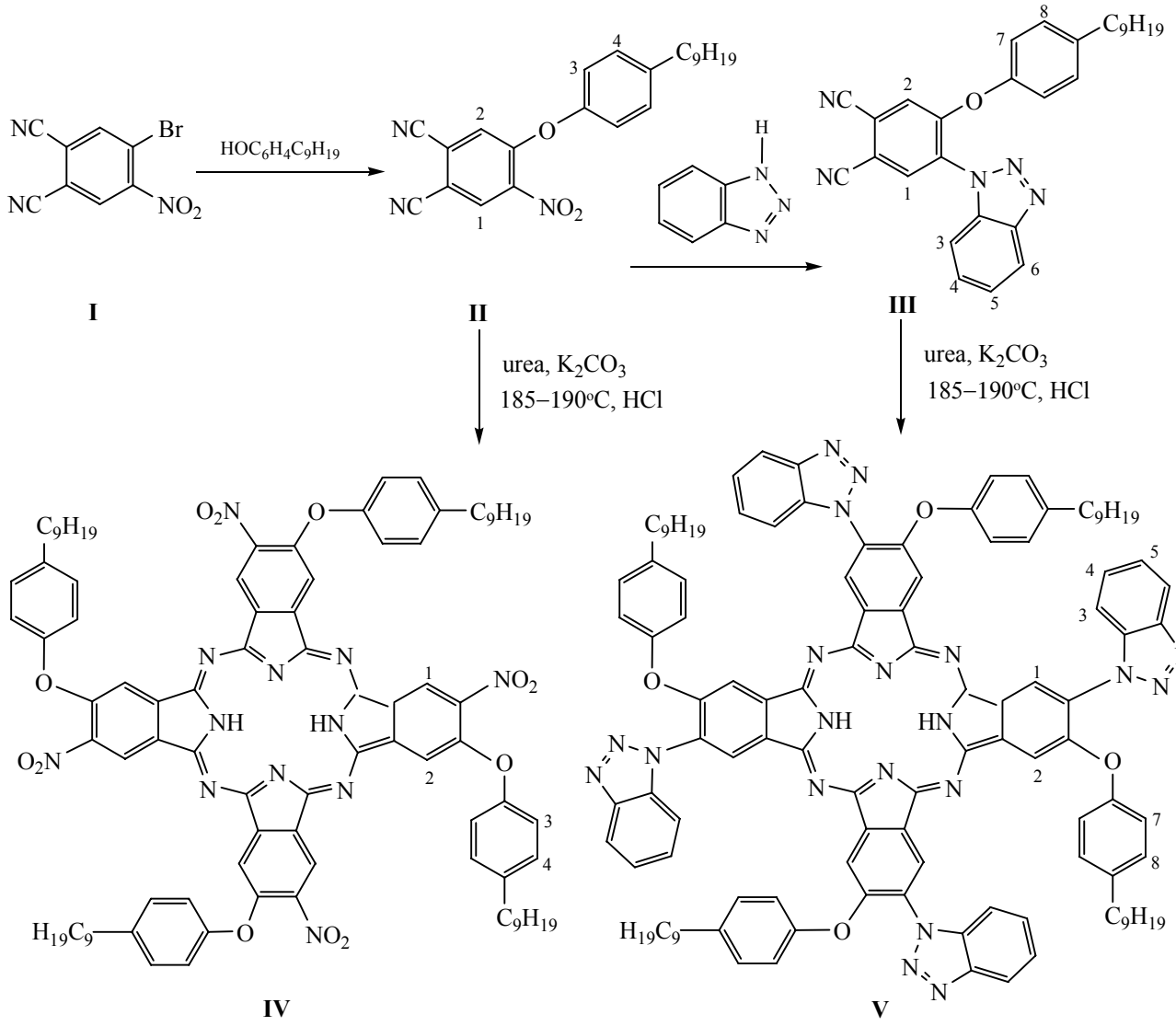
The obtained phthalonitriles were identified by ^{1}H NMR and IR spectroscopy, as well as by elemental analysis. Thus, in the ^{1}H NMR spectrum of compound **II** the signals of the *ortho*-protons to the nitro and phenoxy groups were shifted downfield to 8.84 and 7.90 ppm, respectively. The protons of nonyl fragment resonated at 7.18 ppm. The proton signals of the phenoxy group in the *ortho*-position to the bridging oxygen were observed at 6.70 ppm. The signals of methyl and methylene groups of the nonyl substituent appeared upfield.

In the ^{1}H NMR spectrum of compound **III** the signals of *para*-nonylphenoxy group were also observed but a singlet at 8.84 ppm disappeared confirming the substitution of the nitro group. Moreover, in the spectrum of compound **III** a signal at 8.69 ppm was registered which corresponded to the resonance of the proton of the phthalonitrile benzene ring located in the *ortho*-position to the benzotriazole substituent [1, 6]; the protons of the benzotriazole benzene ring resonated downfield at 8.23, 7.81, 7.55, and 8.05 ppm.

In the IR spectrum of phthalonitrile **II** the bands of stretching vibrations of C≡N bond (2234 cm^{-1}), methyl and methylene groups of the nonyl chain (2950 and 2880 cm^{-1}), symmetric (1365–1375 cm^{-1}) and asymmetric (1555–1565 cm^{-1}) vibrations of NO_2-group

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

Scheme 1.



I **II** **III** **IV** **V**

were observed [8]. In the IR spectrum of 4-(1-benzotriazolyl)-5-(4-nonylphenoxy)phthalonitrile **III** the absorption bands indicating the presence of nitro group disappeared completely that also confirmed the absence of the starting phthalonitrile **II** in the target product. In addition, the absorption bands of the fragments C–N and N=N of the benzotriazole substituent were registered [1, 6, 7] (Scheme 1).

Some phthalonitrile derivatives are known to form the corresponding metal-free phthalocyanines upon heating [7]. Similarly, phthalonitriles **II** and **III** heated at 135–145°C underwent transformation into the corresponding phthalocyanines **IV** and **V** in the yield of ≤45%. Electron absorption spectra of the solutions of the prepared phthalocyanines in chloroform contained two strong absorption bands at 673–676 and 708–710 nm that confirmed the formation of the corresponding metal-free phthalocyanines. The increase in the temperature up to 185–190°C did not lead to improvement of the yield of the target products.

However, the presence of urea and potassium carbonate allowed to increase the yield of tetra-4-nitro-5-(4-nonylphenoxy)phthalocyanine **IV** and tetra-4-(1-benzotriazolyl)tetra-5-(4-nonylphenoxy)phthalocyanine **V** up to 72 and 76%, respectively.

The structure of the prepared compounds was established by IR and NMR spectroscopy. In the ^{1}H NMR spectra of compounds **IV** and **V** the proton

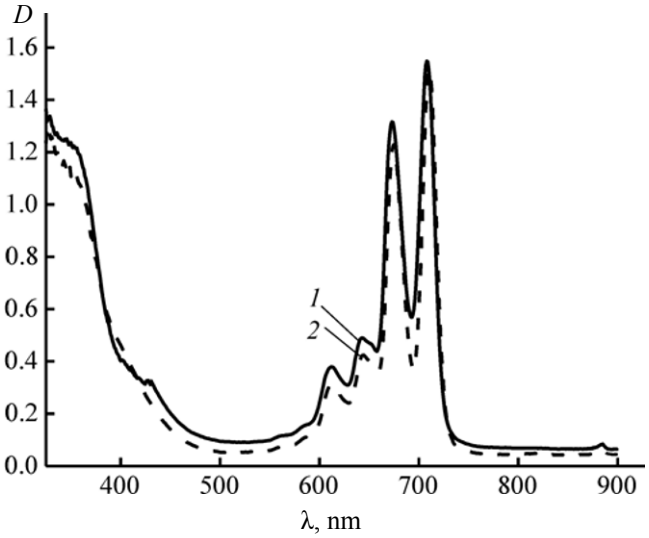


Fig. 1. Electron absorption spectra of compounds **IV** (*1*) and **V** (*2*) in chloroform ($c = 2.15 \times 10^{-5}$ mol L^{-1}).

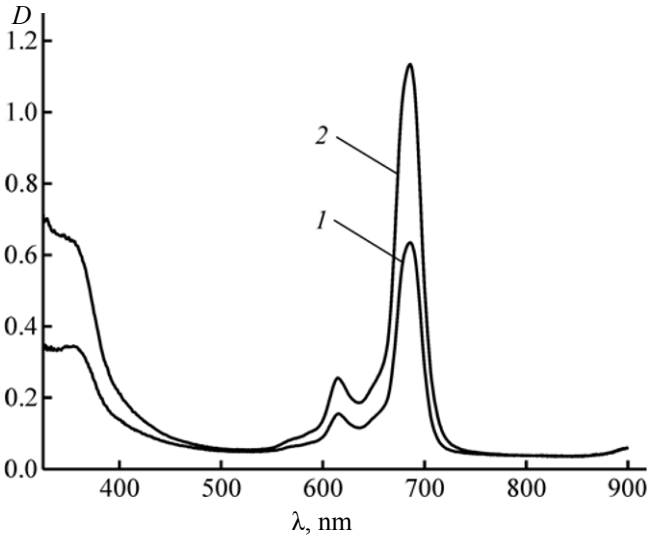


Fig. 2. Electron absorption spectra of compounds **IV** (*1*, $c = 0.98 \times 10^{-5}$ mol L^{-1}) and **V** (*2*, $c = 1.78 \times 10^{-5}$ mol L^{-1}) in DMF.

signals of *para*-nonylphenoxy groups, benzene rings of the phthalocyanine molecule, and benzotriazole substituents were registered. In the strongest field at –2.01 ppm the signal of the protons of endocyclic imino groups [7] was observed that proved the formation of the metal-free phthalocyanines.

In the IR spectra of compounds **IV** and **V** the absorption bands of the nitrile groups (2230–2240 cm^{-1}) disappeared, but the absorption bands in the range of 1012–1014 cm^{-1} arose which were specific for phthalocyanine ligands. The absorption in the region of 3290–3340 cm^{-1} corresponded to vibrations of N–H bonds of the endocyclic imino groups [8].

As was mentioned above, the electron absorption spectra of phthalocyanines **IV** and **V** contained two strong *Q*-bands in the long-wave region (Fig. 1) along with two absorption bands at 622 and 645 nm, which are characteristic of metal-free phthalocyanines [9]. In the near UV region the Soret band (345 nm) was registered. The replacement of the nitro group by the benzotriazolyl fragment led to an insignificant red shift of the *Q*-bands by 3 nm.

Comp. no.	ESP, λ, nm (log ε)		
	DMF	chloroform	H_2SO_4
IV	684 (4.78)	673 (4.74), 708 (4.84)	792, 829
V	686 (4.80)	676 (4.73), 710 (4.84)	809

Use of DMF as a solvent caused simplification of the absorption spectrum: a single *Q*-band was observed at 684 (**IV**) and 686 nm (**V**) (Fig. 2). This fact may be due to the deprotonation of the endocyclic nitrogen atoms and the formation of dianionic species of the phthalocyanine [10] that is characteristic of some metal-free phthalocyanines [11]. When passing from **IV** to **V** an insignificant red shift by 2 nm was observed.

In conc. sulfuric acid the spectral pattern typical of the benzotriazolyl-substituted phthalocyanines was observed [4, 5]: a strong diffuse absorption band in the long-wave region (700–850 nm) appeared.

The replacement of the nitro groups in compound **IV** by the benzotriazole substituents **V** caused a blue shift of the *Q*-band by 20 nm (Fig. 3).

Hence, two new phthalonitriles were prepared which contain electron-donor and electron-withdrawing substituents in an *ortho*-position to each other; the corresponding substituted phthalocyanine ligands were synthesized from the phthalonitriles. The replacement of the nitro groups by the benzotriazole substituents was proven to cause a red shift of the long-wave absorption bands in the electronic spectra registered in organic solvents and a blue shift in conc. sulfuric acid.

EXPERIMENTAL

Electron absorption spectra were recorded on a HITACHI U-2001 instrument at room temperature

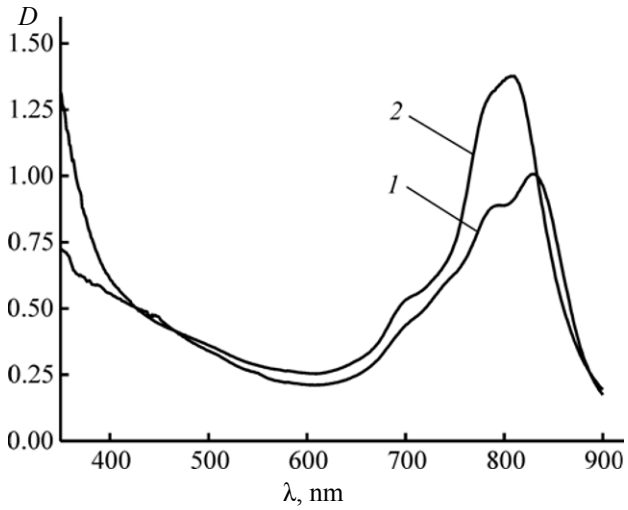


Fig. 3. Electron absorption spectra of compounds **IV** (*1*) and **V** (*2*) in conc. sulfuric acid.

within the range of wave lengths 325–900 nm. IR spectra were registered on an Avatar 360 FT-IR ESP spectrometer in the range of 400–4000 cm^{-1} from films (chloroform) or from KBr pellets. ^1H NMR spectra of the solutions in $CDCl_3$ were obtained on a Bruker DRX-500 spectrometer, internal reference TMS. Elemental analysis was done on a CHNS-O FlashEA analyzer of 1112 series.

All investigations were done with use of the equipment of the Centre of Joint Usage of Ivanovo State University of Chemistry and Technology.

4-Bromo-5-nitrophthalonitrile I was prepared by the known method [12].

4-Nitro-5-(4-nonylphenoxy)phthalonitrile (II). A solution of 1.19 g (1 mmol) of K_2CO_3 in 5 mL of water was added to a solution of 2.52 g (1 mmol) of compound **I** and 2.2 g (2.3 mL, 1 mmol) of 4-nonylphenol in 30 mL of DMF. The obtained mixture was stirred at 25°C for 30 min. The formed precipitate was filtered off, washed with 2-propanol and water, and dried in air at 70–80°C. Yield 3.67 g (94%). IR spectrum, ν, cm^{-1}: 3939, 3855, 3234 (C≡N), 1538 (N=O, as.), 1378 (N=O, s), 1215 (Ar–O–Ar). ^1H NMR spectrum, δ, ppm: 8.84 s (1H, H^1), 7.90 s (1H, H^2), 7.20–7.18 m (1H, H^4), 6.75–6.78 m (1H, H^3), 2.54, 1.75, 1.33–1.24 m (16H, CH_2), 0.88 s (3H, CH_3). Found, %: C 69.71; H 6.70; N 10.67. $C_{23}H_{25}N_3O_3$. Calculated, %: C 70.57; H 6.44; N 10.73.

4-(1-Benzotriazolyl)-5-(4-nonylphenoxy)phthalonitrile (III) was prepared similarly from 1.00 g (0.25 mmol) of compound **II** and 0.30 g (0.25 mmol) of 1*H*-benzotriazole. Yield 0.86 g (73%). IR spectrum, ν, cm^{-1}: 3942, 3880 (CH_2, CH_3), 3234 (CN), 1536 (NO_2, as.), 1362 (NO_2, s), 1212 (Ar–O–Ar), 1040 (N=N), 745 (C–N). ^1H NMR spectrum, δ, ppm: 8.69 s (1H, H^1), 8.18 s (1H, H^2), 8.25 s (1H, H^3), 7.78–7.81 m (1H, H^4), 7.55–7.51 m (1H, H^5), 8.03–8.08 m (1H, H^6), 7.11–7.08 m (1H, H^8), 6.57–6.61 m (1H, H^7), 2.54, 1.75, 1.33–1.24 m (16H, CH_2), 0.88 s (3H, CH_3). Found, %: C 75.25; H 6.60; N 15.02. $C_{23}H_{25}N_3O_3$. Calculated, %: C 75.14; H 6.31; N 15.11.

2,9,16,33-Tetra-4-nitro-3,10,17,24-tetra-5-(4-nonylphenoxy)phthalocyanine (IV). Thoroughly ground mixture of 0.32 g (0.2 mmol) of compound **II**, 0.05 g (0.8 mmol) of urea, and 0.05 g (0.36 mmol) of K_2CO_3 was heated at 185–190°C for 1.5–2 h. Then the reaction mixture was washed with diluted hydrochloric acid to remove products of urea decomposition, and with water till the negative reaction of washings for chloride anions with silver nitrate. The residue was dried in air at 70–80°C and purified by chromatography on aluminum oxide eluting with chloroform. Yield 0.23 g (72%), viscous dark green mass, insoluble in water, sparingly soluble in DMF, well soluble in chloroform. ^1H NMR spectrum, δ, ppm: 8.83 s (4H, H^1), 7.80 s (4H, H^2), 7.30–7.18 m (4H, H^4), 6.80–6.58 m (4H, H^3), 2.54, 1.75, 1.33–1.24 m (64H, CH_2), 0.90 s (12H, CH_3). Found, %: C 70.10; H 7.00; N 11.05. $C_{92}H_{102}N_{12}O_{12}$. Calculated, %: C 70.48; H 6.56; N 10.72.

2,9,16,23-Tetra-4-(1-benzotriazolyl)-3,10,17,24-tetra-5-(4-nonylphenoxy)phthalocyanine (V) was prepared similarly from 0.37 g (0.2 mmol) of compound **III**, 0.05 g (0.8 mmol) of urea, and 0.05 g (0.36 mmol) of K_2CO_3. Yield 76%, dark green solid, insoluble in water, sparingly soluble in DMF, well soluble in chloroform. ^1H NMR spectrum, δ, ppm: 8.69 t (4H, H^1), 8.18 m (4H, H^2), 8.23 s (4H, H^3), 7.78–7.81 m (4H, H^4), 7.55–7.51 m (1H, H^5), 7.91 s (4H, H^6), 7.11–7.08 m (4H, H^8), 6.57–6.61 m (4H, H^7), 2.54, 1.75, 1.33–1.24 m (64H, CH_2), 0.88 s (12H, CH_3). Found, %: C 74.20; H 6.56; N 14.90. $C_{116}H_{118}N_{20}O_4$. Calculated, %: C 75.05; H 6.41; N 15.09.

ACKNOWLEDGMENTS

This work was financially supported by the Russian Science Foundation (grant no. 14-23-00204) and the Ministry of Education and Science of Russia in the

frame of the basic part of the governmental task (contract no. 795).

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