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Synthesis and Properties of 4-[(*E*)-(4'-R-Phenyl)diazenyl]phthalonitriles and Cobalt Phthalocyanines Obtained Therefrom

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Abstract—The diazotization–azocoupling method has been utilized to prepare a series of previously unknown 4-[(*E*)-(4'-R-phenyl)diazenyl]phthalonitriles, which were further transformed into the corresponding cobalt phthalocyanines. The effect of the peripheral substitution of the phthalocyanine ligand on the spectral properties of the prepared compounds has been demonstrated.

Keywords: synthesis, chromophore, diazotization, azocoupling, phthalonitrile, phthalocyanine, electron absorption spectrum

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Phthalocyanines (Pc) are extremely interesting objects of fundamental and applied studies, owing to the unique stability as well as photochemical and electronic properties [1, 2]. Broadening of the light absorption range (in particular, via introduction of additional chromophore group at the periphery of the molecule [3–5]) has been among important issues of Pc investigations.

Our earlier studies in this direction have been described in [6–8]; here we report on the preparation of 4-[*(E)*-(4'-R-phenyl)diazenyl]nitriles **3a**–**3f** and the corresponding cobalt phthalocyanines **4a**–**4f**.

Starting 4-aminophthalonitrile **1** was prepared via reduction of 4-nitrophthalonitrile with tin(II) chloride in muriatic medium [9]. Compound **1** was further transformed into the diazonium salt **2** via treatment with sodium nitrite solution in aqueous sulfuric acid at cooling below 0°C [9]. The so formed unstable salt **2** was introduced (without isolation) into the azocoupling reaction with diphenylamine or 4-hydroxybenzoic acid (Scheme 1).

The pathway of the reaction with 4-hydroxybenzoic acid (the carboxy group substitution) has been earlier described in [10].

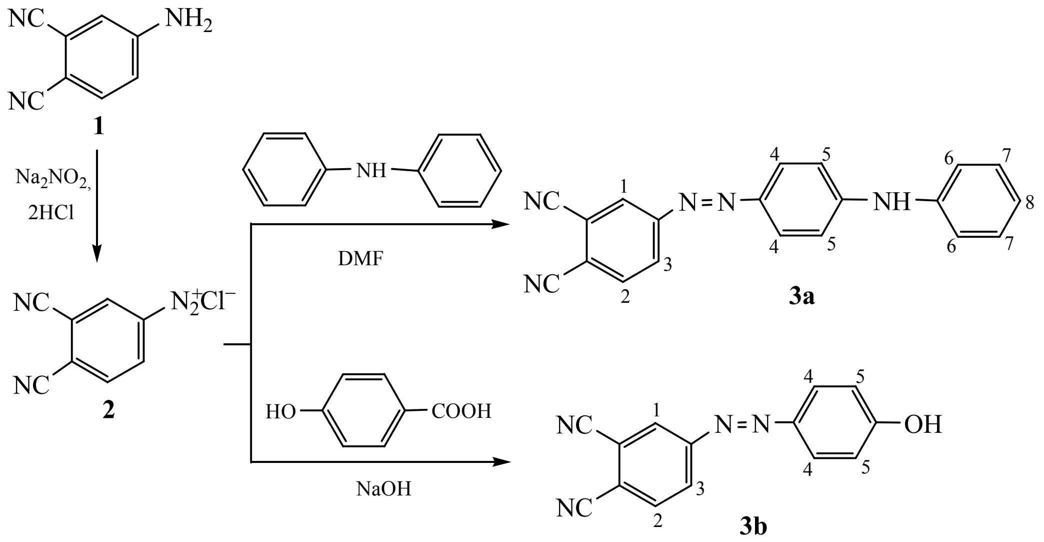
The dyes stability against photochemical decomposition is generally determined by the presence of the weak bonds (qiunoid fragments in the case of the phthalocyanines) and labile atoms (for instance, hydrogen atoms of amino and hydroxy groups) [10]. Hence, light resistance of the dye could be enhanced via acylation or alkylation of the hydroxy group of compound **3b** (Scheme 2).

In view of the poor stability of azo dyes in the hot aqueous alkali solutions, pyridine was used to bind hydrogen chloride evolving in the course of compound **3b** acylation [11]. Alkylation of compound **3b** with different alkyl bromides was performed in a DMF–water mixture in the presence of excess of potassium carbonate, the latter activating the phenol group and binding the evolving hydrogen bromide.

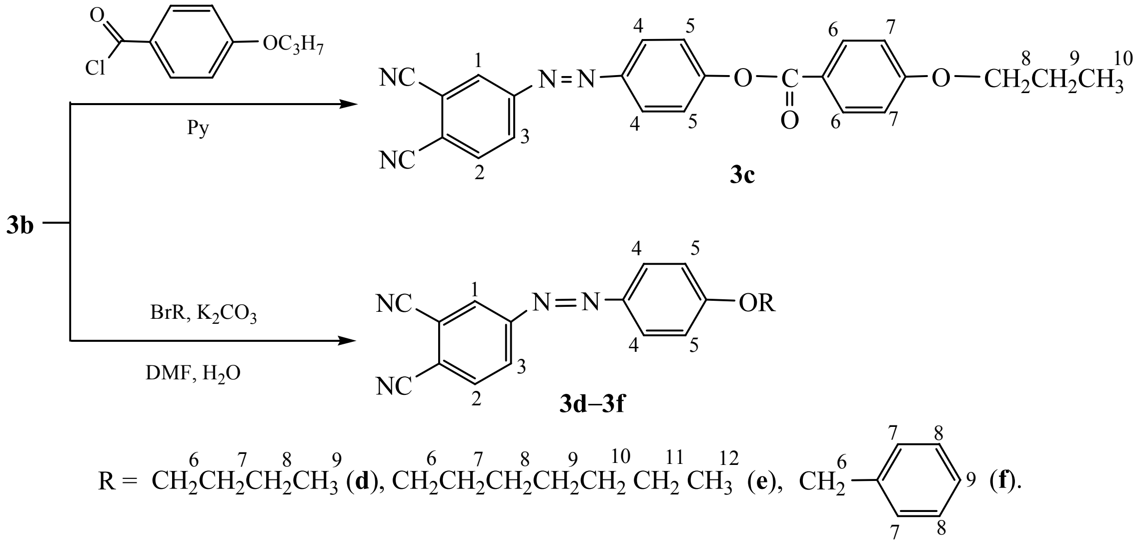
The prepared phthalonitriles **3a**–**3f** were red-orange powders, readily soluble in acetone, DMF, and chloroform. Alkylation or acylation of the hydroxy group of compound **3b** noticeably decreased the melting point of the modified phthalonitriles.

The prepared products were identified using the data of elemental analysis as well as IR, ^{1}H NMR, and electron absorption spectroscopy [12].

Scheme 1.



Scheme 2.



The absorbance band of nitrile group stretching vibrations characteristic of compound **1** was preserved in IR spectra of all prepared phthalonitriles **3a**–**3f** (2230–2240 cm^{-1}); on top of that, the products spectra contained the bands assigned to the N=N stretching vibrations (1608–1580 cm^{-1}) and aliphatic C–H stretching vibrations (2848–2930 cm^{-1}). Besides those common bands, the spectrum of compound **3a** contained the bands at 3414 and 1614 cm^{-1} (stretching vibrations and bending vibrations of the secondary amino group, respectively) and at 1387 cm^{-1} (the C–N stretching vibrations); the spectrum of phthalonitrile **3b** contained the absorption bands at 3500 and 1328 cm^{-1} (stretching vibrations and bending vibrations of hydroxy group, respectively); the spectra of compounds **3c**–**3f** contained a band at 1250–1257 cm^{-1} (the C–O–C stretching vibrations); the spectrum of compound **3c** contained an additional absorption band at 1729 cm^{-1} (the C=O bond stretching vibrations).

Good solubility of the prepared phthalonitriles in organic solvents (in particular, in chloroform) allowed their characterization by means of ^1H NMR spectroscopy. The registered spectra contained the signals of all protons of the structures corresponding to the

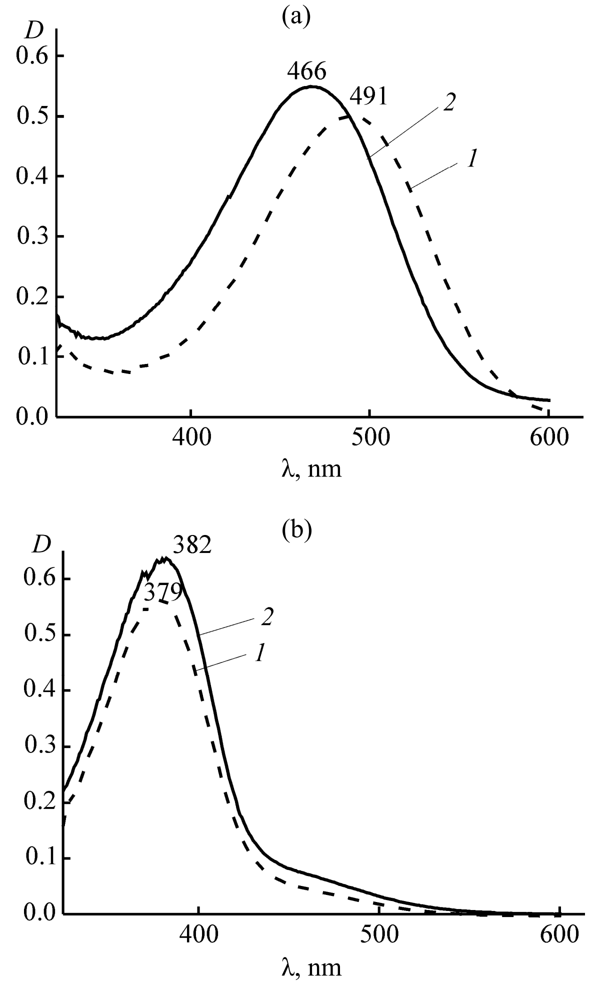


Fig. 1. Electron absorption spectra of solution of compounds (a) **3a** and (b) **3e** in (*1*) DMF and (*2*) chloroform.

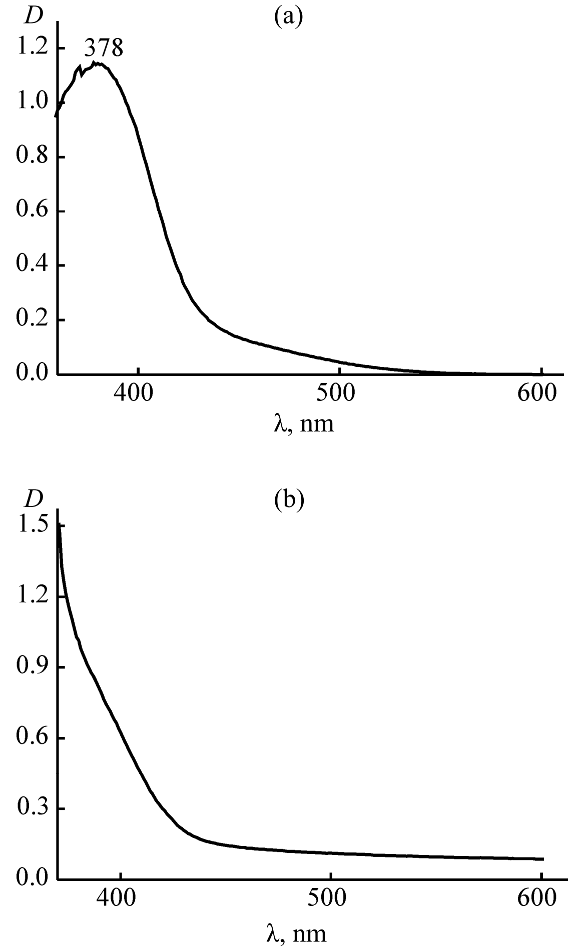


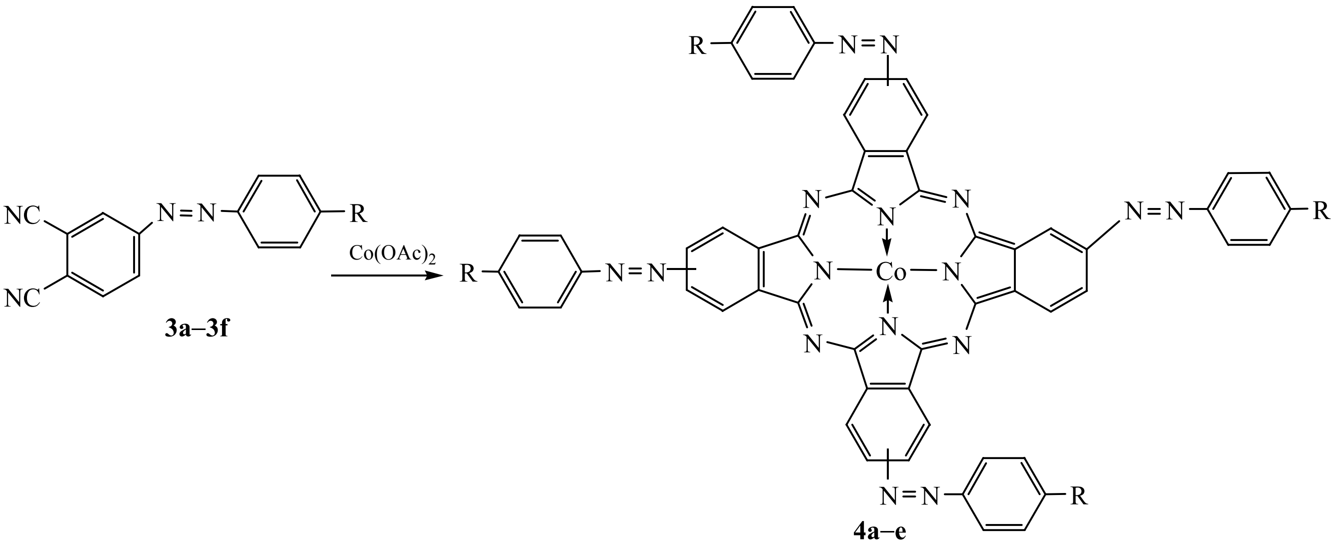
Fig. 2. Electron absorption spectra of ethanol solutions of initial compound (a) **3d** and (b) compound **3d** treated with tin(II) chloride.

expected products. For example, the spectrum of compound **3d** (the numbering of the protons is shown in the scheme) contained a triplet at 1.03 ppm (protons of the terminal methyl group), a multiplet at 1.58 ppm (the H^8 protons of the γ-methylene group), a multiplet at 1.85 ppm (the H^7 protons of the β-methylene group), a triplet at 4.11 ppm (the H^6 protons of the α-methylene group), a doublet at 7.06 ppm (the H^5 protons of the benzene ring in the *ortho*-position with respect to the alkoxy group), a multiplet at 7.98 ppm (the H^4 protons in the *ortho*-position with respect to the azo group), a multiplet at 7.96 ppm (the H^2 proton of the phthalonitrile fragment), and a multiplet at 8.19–8.28 ppm (the H^1 and H^3 protons of the phthalonitrile fragment).

Electron absorption spectra of compounds **3a**–**f** in organic solvents contained a strong band with a maximum at 378–491 nm assigned to the electronic transitions in the azo dye chromophore system. The band position was affected both by the compound structure and the solvent nature. In particular, the absorption band maximum of the nitrile **3a** was found at longer wavelength (the difference being up to 90 nm) in comparison with that of compounds **3b**–**3f** likely due to the strong electron-donor effect of the NHC_6H_5 group, a part of the chromophore system of compound **3a**. The absorption band of the solutions in chloroform of the nitriles containing the *O*-alkyl group (**3d**–**3f**) was observed at higher wavelengths than that of the solutions in DMF; in the cases of the nitriles **3a**–**3c**, the solvent effect was the opposite (Fig. 1).

The structure of the prepared nitriles was additionally confirmed by their reduction with tin(II) chloride in ethanol at room temperature. Azo dyes are

Scheme 3.



R = NHC_6H_5 (**a**), OH (**b**), $OCOC_6H_4OC_3H_7$ (**c**), OC_4H_9 (**d**), OC_7H_{15} (**e**), $OCH_2C_6H_5$ (**f**).

known to be split into a pair of the primary amines under these conditions [11]; the distinct band in the electron absorption spectrum of the solution simultaneously disappears. The similar behavior we observed, for example, in the case of compound **3d** (Fig. 2).

The prepared precursors **3a**–**3f** were further transformed into the corresponding phthalocyanines via the interaction with cobalt(II) acetate at 185–190°C [1, 2] (Scheme 3).

The products were dark-violet (**4a**) or green (**4b**–**4f**) powders. All prepared complexes were soluble in DMF, whereas the solubility in other organic solvents depended in the nature of the peripheral substituents. In particular, compound **4b** was partially soluble in aqueous alkali, and compounds **4c**–**4f** containing acyl or alkoxy moieties were insoluble in aqueous alkali but soluble in chloroform and acetone.

The composition and structure of the prepared phthalocyanines was confirmed by the data of elemental analysis as well as IR and electron absorption spectroscopy. Thus, the IR spectra contained the absorption bands typical of the phthalocyanines [14] along with the bands corresponding to the functional substituents of compounds **3a**–**3f**.

Electron absorption spectra of solutions of complexes **4a**–**f** in organic solvents contained strong

Basic parameters of electron absorption spectra of phthalocyanines **4a**–**4f**

Compound no.	λ_{max}, nm (D_{rel})^a		
	chloroform	DMF	H_2SO_4 (conc.)
4a	–^{b}	478 (1.00), 723 (0.48)	577 (1.00), 928 (0.91)
4b	–^{b}	370 (1.00), 703 (0.63)	477 (1.00), 831 (0.66)
4c	365 (1.00), 642 (0.40), 709 (0.27)	353 (1.00), 642 (0.49), 702 (0.57)	478 (0.88), 855 (1.00)
4d	360 (1.00), 650 (0.53), 707 (0.50)	364 (1.00), 652 (0.45) 703 (0.72)	483 (1.00), 887 (0.83)
4e	357 (1.00),645 (0.47), 707 (0.51)	360 (1.00), 640 (0.40), 703 (0.93)	484 (1.00), 868 (0.70)
4f	370 (1.00), 654 (0.50), 705 (0.47)	368 (1.00), 645 (0.47), 701 (0.90)	480 (1.00), 859 (0.69)
CoPc	–^{b}	660	790

[a] Intensities of the absorption bands are referenced to the strongest one. [b] Insoluble.

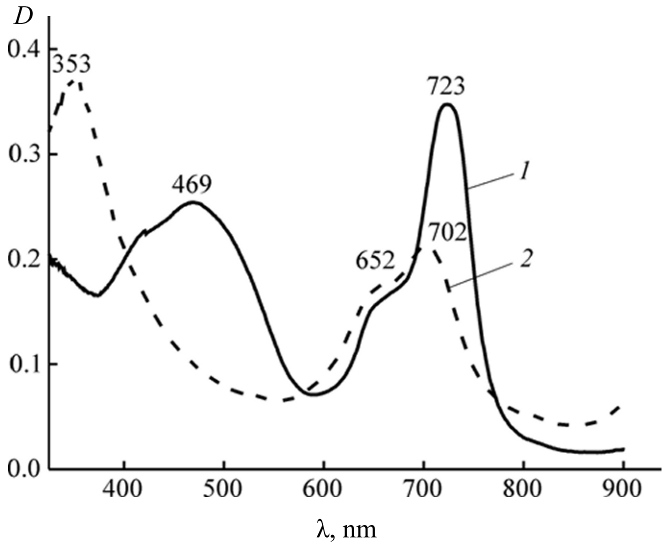


Fig. 3. Electron absorption spectra of compounds (*1*) **4a** and (*2*) **4c** solutions in DMF.

absorption bands at 650–730 nm (π–π* electronic transitions in the main conjugation path of the phthalocyanine macrocycle) and 360–486 nm (electronic transitions in the chromophore system of the azo dye) (see the table and Fig. 3); similar features have been earlier marked for the tetra-R-phenylazophenoxyphthalocyanines [8].

The azo chromophore nature strongly affected the absorption bands position. For instance, the *O*-alkylation resulted in a slight blue shift of the bands (cf. the data for compounds **4b** and **4d**); the wavelengths of the absorption bands in the spectrum of the complex containing the diphenylamine fragments (**4a**) were increased as compared to those in the spectrum of compound **4b**, by 100 and 20 nm (for the short-wave and long-wave bands, respectively) (see the table). The observed features were due to the strong electron-donor properties of the peripheral diphenylamine substituents.

The ratio of intensities of the main *Q* band and that at the range of vibrational satellite in the spectra of complexes **4** depended on the solvent nature: in the case of the solutions in chloroform the *Q* band was relatively stronger than in the case of the solutions in DMF (see the table). That was due likely to the change in the association behavior of the phthalocyanine molecules as a function of the solvent polarity. The low dielectric constant of non-polar and low-polar solvents weakens the solvent shielding of the intermolecular Pc–Pc interactions, thus enhancing the associates stability. The decrease in the amount of the π–π associates in the polar solvents like DMF results in weakening of the short-wave absorption band [14].

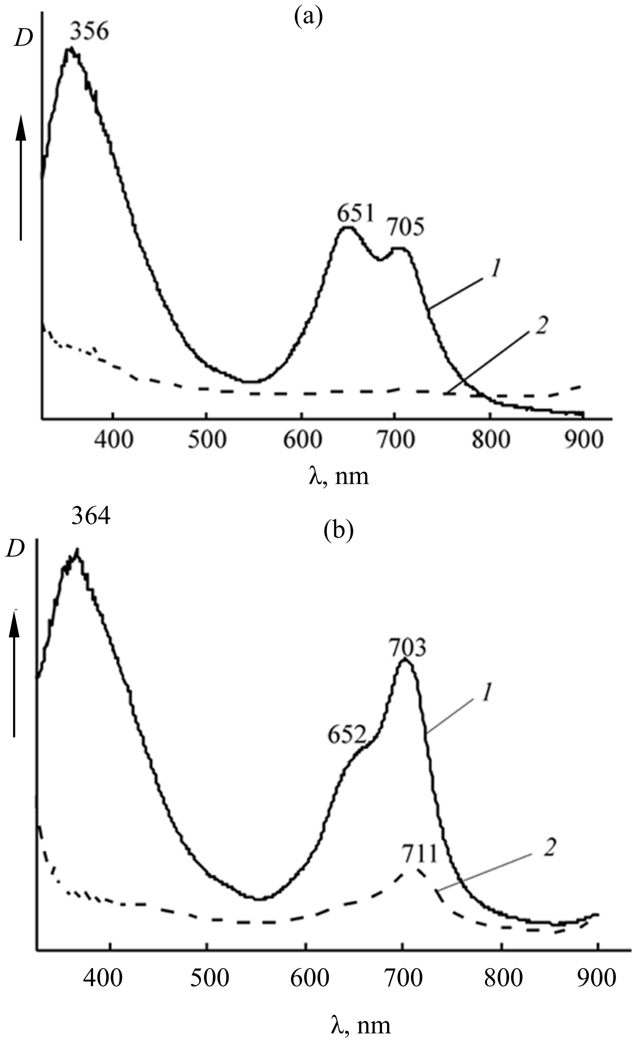


Fig. 4. Electron absorption spectra of compound **4d** solutions in (a) chloroform and (b) DMF (*1*) before and (*2*) after the treatment with $SnCl_2$.

Absorption bands of the solutions of all prepared phthalocyanines in concentrated sulfuric acid were observed at significantly longer wavelength as compared to the solutions in the organic solvents (see the table); that was due to the protonation of the nitrogen *meso*-atoms of the phthalocyanine macrocycle [15]. The shift of the bands position observed in this work was somewhat higher than that in the case of the non-substituted cobalt phthalocyanine, due likely to the protonation of the peripheral nitrogen atoms involved in the conjugation with the macrocycle. The most prominent red shift was observed in the case of compound **4a** containing peripheral fragments of the arylamine along with the azo groups.

Regardless of the solvent nature the absorption bands of the phthalocyanines prepared in this work were observed at longer wavelengths as compared to the earlier studied tetra-4-R-azophenoxyphthalocyanines [8]. That was ascribed to the conjugation of the azo dye with the macrocycle existing in compounds **4a**–**4f**, in contrast to the compounds containing the azo chromophore separated from the phthalocyanine ligand with a spacer (oxygen atom) [8].

Structures of the prepared cobalt phthalocyanines **4a**–**4d** were additionally confirmed by their reduction with tin(II) chloride in a chloroform–ethanol mixture at room temperature. The initially green mixture turned blue in the course of the process owing to the formation of the suspended reaction product insoluble in chloroform.

Let us consider the changes of the reaction mixture spectra after the reduction taking compound **4d** as an example (Fig. 4). The visible-range absorption was almost absent due to the product insolubility in chloroform. The absorption band found in the substrate spectrum at 364 nm (DMF) disappeared after the reduction, and the *Q* band suffered the red shift; those changes pointed at decomposition of the peripheral azo chromophores of the **4d** complex.

To conclude, we prepared a series of earlier unknown 4-[(*E*)-(4'-R-phenyl)diazenyl]phthalonitriles and the corresponding cobalt phthalocyanines. Comparative analysis of the electron absorption spectra of the prepared compounds revealed the influence of the peripheral substituents and the solvent nature on the chromophore properties.

EXPERIMENTAL

Electron absorption spectra of the solutions in DMF, chloroform, and concentrated sulfuric acid (325–900 nm) were recorded using a HITACHI U-2001 spectrophotometer at room temperature. IR spectra (from thin films of the solution in chloroform or KBr pellets; 400–4000 cm^{-1}) were recorded using an Avatar 360 FT-IR ESP spectrometer. ^{1}H NMR spectra (5 wt % solutions in $CDCl_3$, TMS as reference) were recorded using a Bruker DRX-500 spectrometer. Elemental analysis was performed using a CHNS-O FlashEA 1112 series elemental analyzer.

Physicochemical parameters of the prepared compounds were studied using the equipment installed at the Center for Joint Usage, Ivanovo State University of Chemistry and Technology.

4-[(*E*)-(4'-Anilinophenyl)diazenyl]phthalonitrile (3a). Diazotization of 0.6 g (0.0042 mol) of 4-aminophthalonitrile was performed as described in [9]. The so formed solution was added to a cooled solution of 0.71 g (0.0042 mol) of diphenylamine in 5 mL of DMF at vigorous stirring, maintaining the temperature of the mixture below 10–15°C. The reaction completion was monitored using a flow-out test with disodium 3-hydroxy-4-niroso-2,7-naphthalenedisulfonate (weakly acidic medium). The reaction mixture was diluted with 20 mL of water and 30 mL of ethyl acetate. The organic layer was separated using a separatory funnel, the solvent was distilled off, and the target product was extracted with chloroform and purified by column chromatography (M60 silica gel, chloroform as eluent). Yield 0.95 g (70 %), mp 166°C. IR spectrum (KBr), ν, cm^{-1}: 3414 br (NH), 2231 s (C≡N), 1614 s (NH), 1586 s (N=N), 1387 s (C–N). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 8.27 s (1H, H^1), 8.16 m (1H, H^3), 7.93 m (2H, H^4), 7.78 m (1H, H^2), 7.42 m (2H, H^5), 7.23 m (2H, H^7), 7.12 m (3H, H^{6,8}), 6.30 s (1H, NH). Electron absorption spectrum, λ_{max}, nm: 466 (chloroform); 491 (DMF). Found, %: C 73.45; H 4.01; N 19.76. $C_{20}H_{13}N_5$. Calculated, %: C 74.29; H 4.05; N 21.66.

4-[(*E*)-(4'-Hydroxyphanyl)diazenyl]phthalonitrile (3b). Diazotization of 0.6 g (0.0042 mol) of 4-aminophthalonitrile was performed as described in [9]. The so formed solution was added dropwise to a cooled solution of 1.2 g (0.0042 mol) of 4-hydroxybenzoic acid in 25 mL of 20 wt % aqueous solution of Na_2CO_3 at vigorous stirring, maintaining the temperature of the mixture below 8–10°C. The reaction completion was monitored using a flow-out test with disodium 3-hydroxy-4-niroso-2,7-naphthalenedisulfonate (neutral medium). The formed precipitate was filtered off, washed with water, and dried. The product was extracted with chloroform and purified by column chromatography (M60 silica gel, chloroform as eluent). Yield 1.8 g (86.5%), mp 190°C. IR spectrum (KBr), ν, cm^{-1}: 3500 br (OH), 2241 s (C≡N), 1581 s (N=N), 1328 s (OH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 8.75 s (1H, OH), 8.29 s (1H, H^1), 8.19 m (1H, H^3), 7.96 m (1H, H^2), 7.03 m (2H, H^4), 7.01 m (2H, H^5). Electronic absorption spectrum, λ_{max}, nm: 382 (chloroform); 385 (DMF). Found, %: C 66.93; H 4.00;

N 21.98. $C_{14}H_8N_4O$. Calculated, %: C 67.74; H 3.25; N 22.57.

4-{4'-[(*E*)-(4"-Propoxybenzoyl)oxyphenyl]diazenyl}-phthalonitrile (3c). A mixture of 0.3 g (0.002 mol) of 4-(4'-propoxy)benzoic acid and 0.6 mL (0.005 mol) of thionyl chloride was heated at 40–50°C at stirring till the gas evolution ceased (about 2 h). 0.9 g (0.0036 mol) of compound **3b** and 1 mL of pyridine were then added, and the reaction mixture was refluxed at 85°C during 2 h. The obtained mass was poured into water; the precipitate was filtered off, washed with water till neutral reaction of the washings, and dried. The product was extracted with chloroform and purified by column chromatography (M60 silica gel, chloroform as eluent). Yield 0.7 g (47%), mp 148°C. IR spectrum (KBr), ν, cm^{-1}: 2924 s, 2852 (CH), 2235 s (C≡N), 1729 s (C=O), 1267 s (Ar–O–Alk), 1608 s (N=N). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 8.28 s (1H, H^1), 8.19 m (1H, H^3), 7.97 m (2H, H^4), 7.95 m (1H, H^2), 7.49 m (2H, H^5), 7.03 m (2H, H^7), 6.22 m (2H, H^8), 1.61 m (2H, H^9), 0.90 m (3H, H^{10}). Electronic absorption spectrum, λ_{max}, nm: 380 (chloroform); 387 (DMF). Found, %: C 69.93; H 4.12; N 13.18. $C_{24}H_{18}N_4O_3$. Calculated, %: C 70.23; H 4.42; N 13.65.

4-[(*E*)-(4'-Alkoxyphenyl)diazenyl]phthalonitriles (3d–3f). A mixture of 30 mL of DMF, 0.5 g (0.002 mol) of compound **3b**, 0.375 g (0.0027 mol) of potassium carbonate, and 0.0019 mol of the corresponding alkyl bromide was heated on a boiling water bath during 2 h at stirring and then poured into 300 mL of water. In the cases of compounds **3d** and **3e** the formed oily layer was separated using a separatory funnel and extracted with acetone; the solvent was then distilled off. In the case of compound **3f**, the precipitate formed after pouring into water was separated, washed with water, and dried. The product was extracted with chloroform and purified by column chromatography (M60 silica gel, chloroform as eluent).

4-[(*E*)-(4'-Butoxyphenyl)diazenyl]phthalonitrile (3d). Yield 0.45 g (74%), mp 105°C. IR spectrum (KBr), ν, cm^{-1}: 2937 s, 2852 (CH), 2233 s (C≡N), 1601 s (N=N), 1257 s (C–O–C). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 8.28 m (1H, H^1), 8.19 m (1H, H^3), 7.98 m (2H, H^4), 7.96 m (1H, H^2), 7.06 m (2H, H^5), 4.11 m (2H, H^6), 1.85 m (2H, H^7), 1.58 m (2H, H^8), 1.03 m (3H, H^9). Electronic absorption spectrum, λ_{max}, nm: 383 (chloroform); 378 (DMF). Found, %: C 70.63; H 4.92; N 18.18. $C_{18}H_{16}N_4O$. Calculated, %: C 71.04; H 5.30; N 18.41.

4-[(*E*)-(4'-Heptyloxyphenyl)diazenyl]phthalonitrile (3e). Yield 0.4 g (57%), mp 131°C. IR spectrum (KBr), ν, cm^{-1}: 2923 s, 2854 (CH), 2230 s (C≡N), 1598 s (N=N), 1253 s (C–O–C). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 8.28 s (1H, H^1), 8.19 m (1H, H^3), 7.95 m (1H, H^2), 7.49 m (2H, H^4), 7.27 m (2H, H^5), 4.10 m (2H, H^6), 1.86 m (2H, H^7), 1.66 m (2H, H^8), 1.27 m (4H, H^{9,10}), 0.92 m (5H, H^{11,12}). Electronic absorption spectrum, λ_{max}, nm: 382 (chloroform); 380 (DMF). Found, %: C 70.10; H 5.41; N 17.73. $C_{21}H_{22}N_4O$. Calculated, %: C 72.81; H 6.40; N 16.17.

4-[(*E*)-(4'-Benzyloxyphenyl)diazenyl]phthalonitrile (3f). Yield 0.6 g (86%), mp 152°C. IR spectrum (KBr), ν, cm^{-1}: 2914 m (CH_2), 2228 s (C≡N), 1595 s (N=N), 1250 s (C–O–C). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 8.28 s (1H, H^1), 8.19 m (1H, H^3), 7.95 m (1H, H^2), 7.45 m (2H, H^4), 7.28 m (5H, H^{7,8,9}), 7.14 s (2H, H^5), 5.21 s (2H, CH_2). Electronic absorption spectrum, λ_{max}, nm: 382 (chloroform); 379 (DMF). Found, %: C 74.54; H 4.17; N 16.56. $C_{21}H_{14}N_4O$. Calculated, %: C 74.54; H 4.17; N 16.56.

Cobalt(II) tetra-4-[(*E*)-(4'-R-phenyl)diazenyl]-phthalocyanines (4a–4f). A mixture of 0.001 mol of the corresponding phthalonitrile **3a–3f** and 0.19 g (0.0003 mol) of cobalt(II) acetate was thoroughly ground, heated up to 185–190°C in a quartz ampule, and kept at this temperature till solidification of the reaction mass. The latter was then cooled down to ambient, ground, washed with 5 wt% aqueous hydrochloric acid till colorless washings and then with water till neutral reaction of the washings. The obtained solid substance was dried, extracted with DMF (**4a**, **4b**) or with a 5 : 1 chloroform–ethanol mixture (**4c–4f**), and purified by column chromatography [M60 silica gel; eluent: DMF (**4a, 4b**) or a 5 : 1 chloroform–ethanol mixture (**4c–4f**)].

Cobalt(II) tetra-4-[(*E*)-(4'-anilinophenyl)diazenyl]-phthalocyanine (4a). Yield 0.12 g (36%). IR spectrum (KBr), ν, cm^{-1}: 3409 br (NH), 1592 s (N=N). Found, %: C 69.86; H 4.02; N 20.02. $C_{80}H_{52}CoN_{20}$. Calculated, %: C 71.05; H 3.88; N 20.71.

Cobalt(II) tetra-4-[(*E*)-(4'-hydroxyphenyl)diazenyl]-phthalocyanine (4b). Yield 0.16 g (60.84%). IR spectrum (KBr), ν, cm^{-1}: 3400 br (OH), 1591 s (N=N), 1330 s (OH). Found, %: C 63.02; H 3.42; N 20.93. $C_{56}H_{32}CoN_{16}O_4$. Calculated, %: C 63.94; H 3.07; N 21.30.

Cobalt(II) tetra-4-{4'-[(*E*)-(4"-propoxybenzoyl) oxyphenyl]diazenyl}phthalocyanine (4c). Yield

0.29 g (68%). IR spectrum (KBr), ν, cm^{-1}: 2925 s, 2850 (CH), 1731 s (C=O), 1257 s (Ar–O–Alk), 1600 s (N=N). Found, %: C 67.61; H 4.55; N 13.03. $C_{84}H_{88}CoN_{16}O_4$. Calculated, %: C 67.80; H 4.27; N 13.18.

Cobalt(II) tetra-4-[(*E*)-(4'-butoxyphenyl)diazenyl]-phthalocyanine (4d). Yield 0.20 g (63.5%). IR spectrum (KBr), ν, cm^{-1}: 2924 s, 2859 s (CH), 1598 s (N=N), 1250 s (C–O–C). Found, %: C 67.36; H 5.12; N 17.36. $C_{72}H_{64}CoN_{16}O_4$. Calculated, %: C 67.76; H 5.05; N 17.56.

Cobalt(II) tetra-4-[(*E*)-(4'-heptyloxyphenyl)diazenyl]phthalocyanine (4e). Yield 0.23 g (64%). IR spectrum (KBr), ν, cm^{-1}: 2922 s, 2852 (CH), 1597 s (N=N), 1252 s (C–O–C). Found, %: C 69.79; H 6.59; N 15.43. $C_{84}H_{88}CoN_{16}O_4$. Calculated, %: C 69.84; H 6.14; N 15.51.

Cobalt(II) tetra-4-[(*E*)-(4'-benzyloxyphenyl)diazenyl]phthalocyanine (4f). Yield 0.22 g (62%). IR spectrum (KBr), ν, cm^{-1}: 2922 s (CH), 1601 s (N=N), 1249 s (C–O–C). Found, %: C 69.99; H 4.30; N 15.50. $C_{84}H_{56}CoN_{16}O_4$. Calculated, %: C 71.43; H 4.00; N 15.87.

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