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Synthesis and Properties of Phthalonitriles with an Azo Chromophore and Related Phthalocyanines

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Abstract—The 4-R-phenylazophenoxyphthalonitriles were synthesized by the reaction of 4-bromophthalonitrile with 4-R-phenylazophenols and were used to obtain tetra-R-phenylazophenoxyphthalocyanines and their metal complexes. The effect of substituents on the spectral and other properties of the synthesized compounds was established.

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The synthesis and properties of substituted phthalocyanines are described in literature in detail [1, 2]. One of the drawbacks of the majority of these compounds is a narrow color range, so the work aimed at extending the range of absorption of phthalocyanines is important and relevant. One of the directions in solving this problem is the introduction into the phthalocyanine molecule of a substituent with its proper chromophore system [3–5].

In continuation of our research in this direction [4, 5] we report here on the synthesis of nitriles **VII** and phthalocyanines **VIII–XI** based on them containing azo chromophores on the molecule periphery.



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Synthesis of nitriles **VIIa–VIIc** was carried out in accordance with the scheme above.

Diazotization of the substituted anilines **Ia–Ic** afforded diazo compounds **IIa–IIc**, which undergo the azo coupling with sodium *p*-hydroxybenzoate **III**. This reaction belongs to particular cases of the azo coupling and it proceeds with the replacement of a substituent (carboxyl group) [6]. By adding concentrated hydrochloric acid to a solution of a compound **IVa–IVc** respective dyes **Va–Vc** as a R-substituted phenylazophenols were isolated.

The nucleophilic substitution of the bromine atom in 4-bromophthalonitrile VI synthesized by the known method [7] by the appropriate azo dye residue (CHROM) in the DMF medium in the presence of K_2CO_3 afforded the corresponding new R-substituted phenylazophenoxyphthalonitriles VIIa–VIIc.

The choice of 4-bromophthalonitrile VI as a substrate for nucleophilic substitution reactions is defined by the fact that the electron-withdrawing substituent (C=N group) in the benzene ring causes polarization of the C–Br bond and the appearance of effective positive charge on the carbon atom bearing the bromine, which contributes to the easy replacement of the latter [8]. The role of potassium carbonate consists in the transformation of the CHROM–OH in bipolar ion with higher reactivity in the nucleophilic substitution reactions [9]. The choice of DMF as a solvent is due to the fact that in aprotic solvents dissolving well the source nitrile VI the reaction rate of nucleophilic substitution increases by 3-5 orders of magnitude over that performed in non-polar solvents [10].

Synthesized phthalonitriles **VIIa–VIIc** are powders of red-orange color, readily soluble in organic solvents (acetone, DMF, ethanol).

It is noted that the nature and the amount of the substituents R and R¹ in the phthalonitrile molecule affect the melting point of the substance. While the melting onset temperature of 4-[4'-(4"-methyl-phenylazo)phenoxy]phthalonitrile **VIIa** is 140°C, the introduction of an additional methyl group R¹ leads to a significant decrease in the melting temperature: 4-[4'-(2',4"-dimethylphenylazo)phenoxy]phthalonitrile **VIIb** melts at 43°C. Replacing the methyl group R by acylamino group also reduces the melting temperature to 108°C.

The identification of the compounds **VIIa–VIIc** was performed using data of elemental analysis, gas chromatography–mass spectrometry, IR, ¹H NMR, and





electron spectroscopy. Chromatograms of the phthalonitriles **VIIa** and **VIIb** contained single peaks indicating the absence of impurities. Mass spectra of nitriles **VIIa**, **VIIb** have the signals corresponding to the main molecular ion (m/z 338 and 352 in the mass spectra of **VIIa** and **VIIb**, respectively). Among the registered peaks of the products of their fragmentation, the principal are of m/z 247 and 219, corresponding to the 4-azophenoxyphthalonitrile and the residue of phenoxyphthalonitrile, respectively.

Comparing the IR spectra of the source and target phthalonitriles, the preservation should be noted of the bands at 2230–2232 cm⁻¹ corresponding to the stretching vibrations of the cyano group. In the spectra of each compound an absorption band appears in the range 1247–1250 cm⁻¹ characteristic of the Ar–O–Ar vibrations. In the region of 2919–2930 cm⁻¹ a band is observed corresponding to the stretching vibrations of CH bonds of methyl groups, and at 1592–1585 cm⁻¹, a band corresponding to stretching vibrations of the azo group (N=N). In the spectrum of nitrile **VIIc** there is an additional absorption band at 1671 cm⁻¹ corresponding to the C=O of the amide group and at 3307 cm⁻¹, characteristic of the secondary amine groups (Fig. 1) [11].

The good solubility of the synthesized phthalonitriles in organic solvents, particularly in chloroform, allowed us their study by ¹H NMR spectroscopy.



Thus, considering the ¹H NMR spectrum of compound **VIIa**, we note the following signals. A triplet at 2.48 ppm corresponds to the resonance of the three protons of the CH₃ groups. In a weak field there are two multiplets at 7.24–7.38 ppm corresponding to four protons (8–11) of benzene ring of the *p*-toluidine residue and two protons (4, 6) of the benzene ring in the *ortho* position to the oxygen atom of the phenoxy residue. The signals of three protons (1–3) of phthalonitrile are also the multiplets in a weak field at 7.78–7.88 ppm, and the most downfield is a multiplet at 8.3 ppm corresponding to the signals of protons (5, 7),

located in the *ortho* position to the azo group of the phenoxy residue.

By heating the synthesized phthalonitriles **VIIa**– **VIIc** with potassium carbonate playing the role of an alkaline agent [9] at 185–190°C and subsequent reprecipitation of the products obtained from concentrated sulfuric acid we isolated the corresponding tetra-R-phenylazophenoxyphthalocyanines **VIIIa**– **VIIIc**. The synthesis of metallocomplexes **IX–XI** was performed by reacting the phthalonitriles **VIIa–VIIc** with anhydrous cobalt, copper, and nickel chlorides at 185–190°C.



M = 2H (VIII), Co (IX), Cu (X), Ni (XI); $R = CH_3$, $R^1 = H$ (a); $R = CH_3$, $R^1 = CH_3$ (b); $R = NHCOCH_3$; $R^1 = H$ (c).

The phthalocyanines obtained were purified by reprecipitation from concentrated sulfuric acid followed by washing with organic solvents in a Soxhlet apparatus and finally by the column chromatography on silica gel M 60.

Phthalocyanines **VIII–XI** are green and blue-green powders. Their solubility in organic solvents depends on the nature and quantity of the substituents R and R¹. All compounds are soluble in DMF, the presence of methyl groups in the macromolecules **VIIIa**, **VIIIb– XIa**, **XIb** makes them soluble in chloroform, the compounds with acylamino groups **VIIIc–XIc** are soluble in acetone.

Identification of the obtained phthalocyanines was carried out using the data of elemental analysis, IR and electronic spectroscopy. In the IR spectra of the synthesized compounds **VIII–XI** the absorption band typical of the aryloxy-, methoxy- and azo-groups of the corresponding phthalonitriles were retained. In addition, in the IR spectra of substituted H_2Pc the presence of absorption bands at 1008 cm⁻¹ was noted characteristic of metal-free phthalocyanines [12].

The electron absorption spectra (EAS) of the synthesized phthalocyanines in organic solvents and sulfuric acid are presented in the table and Figs. 2-5. Spectral curves of tetra-R-phenylazophenoxyphthalocvanines VIIIa-VIIIc in organic solvents are characterized by a doublet in the long-wavelength region (Fig. 2, table), which is typical of the metal-free compounds and is due to the decrease in the molecular symmetry from D_{4h} to D_{2h} [13]. A distinctive feature of all spectra is the presence of a strong absorption band in the region of 341-367 nm originating from electronic transitions in the chromophore system of the azo dyes attached to the benzene rings of the phthalocyanine ligand (Fig. 2, table). In going from phthalocyanines VIIIa-VIIIc to their metallocomplexes IX-XI their symmetry increases from D_{2h} to D_{4h} , resulting in merging of two components of Qband into one [13], which is undergoes a red shift in comparison with the Q-band of the corresponding unsubstituted MPc (table, Fig. 3). The azo-chromophore nature virtually does not affect the position of the long-wavelength band in the EAS (Fig. 3, table).

SYNTHESIS AND PROPERTIES OF PHTHALONITRILES

Comp. no.	М	R, R ¹	$\lambda_{\max}, \operatorname{nm}(D/D_{\max})$			
			chloroform	DMF	acetone	Conc. H ₂ SO ₄
VIIIa	2Н	$R = CH_3,$ $R^1 = H$	345 (1.00), 702 (0.71), 666 (0.63), 641 (0.31), 607 (0.21)	349 (1.00), 698 (0.67), 670 (0.60), 641 (0.40), 610 (0.29)	_	468 (1.00), 891 (0.55), 836 (0.54)
VIIIb	2H	$R = CH_3,$ $R^1 = CH_3$	350 (1.00), 700 (0.92), 665 (0.82), 640 (0.34), 605 (0.29)	359 (1.00), 697 (0.76), 669 (0.72), 637 (0.41), 605 (0.28)	_	475 (1.00), 901 (0.60), 841 (0.57),
VIIIc	2H	$R = CH_3,$ $R^1 = NHCOCH_3$	_	366 (1.00), 700 (0.62), 669 (0.60), 635 (0.41), 610 (0.29)	367 (1.00), 699 (0.66) 667 (0.64), 639 (0.32), 610 (0.22)	470 (1.00), 873 (0.76), 817 (0.66), 767 (0.48)
IXa	Co	$R = CH_3,$ $R^1 = H$	341 (1.00), 674 (0.66), 613 (0.35)	345 (1.00), 666 (0.59), 603 (0.22)	_	472 (1.00), 818 (0.58)
IXb	Co	$R = CH_3,$ $R^1 = CH_3$	345 (1.00), 675 (0.65), 610 (0.29)	345 (1.00), 670 (0.65), 605 (0.21)	_	479 (1.00), 824 (0.44)
IXc	Co	$R = CH_3,$ $R^1 = NHCOCH_3$	_	365 (1.00), 667 (0.79), 605 (0.24)	365 (1.00), 665 (0.89), 600 (0.22)	472 (1.00), 802 (0.75), 710 (0.43)
Xa	Cu	$R = CH_3,$ $R^1 = H$	345 (1.00), 680 (0.65), 605 (0.25)	345 (1.00), 675 (0.55), 610 (0.21)	_	470 (1.00), 839 (0.82), 740 (0.35)
Xb	Cu	$R = CH_3,$ $R^1 = CH_3$	344 (1.00), 681 (0.99), 615 (0.31)	355 (1.00), 675.5 (0.71), 610 (0.52)	_	476 (1.00), 846 (0.88), 740 (0.39)
Xc	Cu	$R = CH_3,$ $R^1 = NHCOCH_3$	_	365 (1.00), 675 (0.71), 610 (0.26)	_	470 (1.00), 824 (0.72), 725 (0.20)
XIa	Ni	$R = CH_3,$ $R^1 = H$	351 (1.00), 671 (0.81), 616 (0.26)	341 (1.00), 672 (0.62), 616 (0.47)	_	470 (1.00), 814 (0.78), 722 (0.26)
XIb	Ni	$R = CH_3,$ $R^1 = CH_3$	340 (1.00), 675 (0.92), 610 (0.34)	363 (1.00), 673 (0.64), 605 (0.33)	_	480 (1.00), 821 (0.71), 727 (0.25)
XIc	Ni	$R = CH_3,$ $R^1 = NHCOCH_3$	-	350 (1.00), 677 (0.70), 610 (0.31)	_	470 (1.00), 800 (0.84), 705 (0.32)

The position of the absorption bands in the EAS of the synthesized phthalocyanines

The nature of the absorption bands and the ratio of their intensities in the spectra of the synthesized phthalocyanines point to the tendency of the metallocomplexes to association in solution (Fig. 4, table). It is



Fig. 2. Electron absorption spectrum of phthalocyanine **VIIIa** in chloroform.



important to note that the tendency to association of



Fig. 3. Electron absorption spectra in DMF: (1) IXb, (2) IXc.



Fig. 4. Electron absorption spectra of compounds (a) IXb and (b) XIa: (1) in chloroform, (2) in DMF.

phthalocyanine in aprotic solvents form extra-complexes with the solvent molecules as extraligands preventing the intermolecular interactions [14].

The comparative analysis of the EAS of phthalocyanines in DMF and chloroform (Fig. 4, table) shows that the nature of the solvent, in particular, its polarity also affects the propensity of the MPc molecules to the associative processes. The low dielectric permeability of nonpolar and low-polar solvents reduces the screening effect of the Pc–Pc intermolecular interaction by the solvent and, consequently, contributes to the formation of associates and increases their stability compared to solutions in polar solvent (DMF) [15].

Changing the solvent from DMF to chloroform results in a red shift of the long-wavelength band in the



spectra of all phthalocyanines save the nickel complexes (see the table). Thus, depending on the nature of the metal-chelating agent, in DMF a red shift is observed of the absorption bands in the sequence: $Co \rightarrow Ni \rightarrow Cu$. Replacing the solvent by chloroform alters the picture: $Ni \rightarrow Co \rightarrow Cu$ (see the table). The replacement of organic solvents by concentrated sulfuric acid is known to result in a significant red shift of the absorption bands due to the protonation of the phthalocyanine macroring at the nitrogen meso-atoms [16], which occurs in the spectra of all synthesized phthalocyanines. However, the shift in the case of the compounds synthesized by us is somewhat smaller than that of the unsubstituted phthalocyanines, and increases in the following order: VIIIc-XIc < VIIIa-XIa < VIIIb–XIb (Fig. 5, table). We believe that it due to the participation of the peripheral nitrogen atoms of acylamido and azo groups in the processes of protonation and simultaneous decrease in the degree of protonation of the meso-nitrogen atoms of the macroring.

Our studies of the synthesized phthalocyanines, which are well soluble in organic solvents, showed a possibility of their application as fat-soluble dyes for dyeing waxes, hydrocarbons, and plastics.

EXPERIMENTAL

The electron absorption spectra of the compounds obtained were measured on a Hitachi U-2001 spectrophotometer, the IR spectra were recorded on a spectrophotometer AVATAR 360 FT-IR in the 400– 4000 cm⁻¹ from thin films, the ¹H NMR spectra were taken on a Bruker AMD-200 instrument from solutions in CDCl₃, the mass spectra were measured on a Varian Saturn 2000K instrument. Elemental analysis was performed on a FlashEA 1112 CHNS-O Analyzer.

Synthesis of monoazodyes (general procedure) [6]. A porcelain beaker equipped with a stirrer and a thermometer was charged at stirring with 100 ml of water, 30 ml of concentrated hydrochloric acid (0.27 mol), and 0.1 mol of the corresponding substituted amine. The resulting solution was cooled to $0-3^{\circ}$ C in an ice-salt mixture. At this temperature was added at stirring dropwise from a dropping funnel 24 ml of 30% solution of sodium nitrite (0.13 mol). After completion of the sodium nitrite addition the stirring continued at $2-3^{\circ}$ C for 30 minutes. During the reaction an acidic environment was maintained by adding dropwise hydrochloric acid. The substituted phenyldiazonium chloride thus obtained was immediately used in the stage of azo coupling.

In a porcelain beaker equipped with a stirrer and a thermometer was placed 32 ml of 25% sodium carbonate solution (0.08 mol), 8.00 g (0.20 mol) of sodium hydroxide, and 13.80 g (0.10 mol) of p-hydroxybenzoic acid. The resulting solution was cooled to 8-10°C by adding ice. Then, at vigorous stirring was added dropwise from a dropping funnel a substituted phenyldiazonium chloride. The coupling was carried out at a temperature of 14-15°C in alkaline medium. After adding the total diazo component the stirring was continued for another 30 min. The resulting precipitate was filtered off on a Buechner funnel, washed with 15% hydrochloric acid and with water until neutral reaction. The resulting product was dried in air. The target compound was extracted in a Soxhlet apparatus with ethyl alcohol, ethanol was distilled off, and the dve was dried in air.

4-(4'-Methylphenylazo)phenol (Va) was obtained along the general procedure, using 10.70 g of *p*-toluidine. Yield 14.27 g (67.3%).

4-(2',4'-dimethylphenylazo)phenol (Vb) was obtained along the general procedure, using 12.4 ml of m-xylidine. Yield 17.08 g (75.60%).

4-(4'-Acetamidophenylazo)phenol (Vc) was obtained along the general procedure, using 15.00 g of *p*-aminoacetanilide. Yield 9.11 g (67.13%).

Synthesis of R-phenylazophthalonitriles (general procedure). A flask fitted with a stirrer, reflux condenser, and thermometer was charged with 30 ml of DMF, 2.07 g (0.01 mol) of 4-bromophthalonitrile

VI, 2.07 g (0.015 mol) of potassium carbonate, and 0.015 mol the corresponding R-phenylazophenol **Va–Vc**. The resulting mixture was heated while stirring to 140–145°C and kept at this temperature for 2 h. The reaction mixture was poured with stirring into 300 ml of water. The precipitate was filtered off, washed with 5% sodium hydroxide solution until the filtrate was colorless, and then with water until the filtrate was neutral. The resulting precipitate was dried in air. Final purification was performed by column chromatography on alumina using chloroform as eluent.

4-[4'-(4''-Methylphenylazo)phenoxy]phthalonitrile (VIIa) was obtained along the general procedure using 3.18 g of 4-(4'-methylphenylazo)phenol. Yield 3.25 g (64.20%), mp 140°C. IR spectrum (film): 2232 (C=N), 1247 (Ar–O–Ar), 1586 (N=N), 2920 (CH₃). Mass spectrum (m/z): 338. ¹H NMR spectrum (CDCl₃), δ , ppm: 8.03 m (2H, H^{5,7}), 7.88 m (2H, H^{1,3}), 7.78 s (2H, H²), 7.38 m (2H, H^{8,10}), 7.29 s (4H, H^{4,6}), 7.24 m (4H, H^{9,11}), 2.48 m (CH₃). Found, %: C 74.43, H 4.30, N 16.28. C₂₁H₁₄N₄O. Calculated, %: C 74.54, H 4.17, N 16.56.

4-[4'-(2',4''-Dimethylphenylazo)phenoxy]phthalonitrile (VIIb) was obtained along the general procedure using 3.39 g of 4-(2',4'-dimethylphenylazo) phenol. Yield 3.76 g (71.30%), mp 43°C. IR spectrum (film): 2231 (C=N), 1249 (Ar–O–Ar), 1586 (N=N), 2919 (CH₃). Mass spectrum (m/z): 352. Found, %: C 74.63, H 4.93, N 15.43. C₂₂H₁₆N₄O. Calculated, %: C 74.98, H 4.58, N 15.90.

4-[4'-(4"-Acetamidophenylazo)phenoxy]phthalonitrile (VIIc) was obtained along the general procedure using 4.15 g of 4-(4'-acetamidophenylazo)phenol. Yield 3.91 g (68.50%), mp 108°C. IR spectrum (film): 2230 (C \equiv N), 1249 (Ar–O–Ar), 1592 (N=N), 2929 (CH₃), 1671 (C=O), 3307 (N–H sec.). Found, %: C 68.96, H 4.74, N 18.87. C₂₂H₁₅N₅O₂. Calculated, %: C 69.28, H 3.96, N 18.36.

Synthesis of tetra-R-phenylazophenoxyphthalocyanines (general procedure). Thoroughly ground mixture of 0.001 mol of the corresponding R-phenylazophenoxyphthalonitrile VIIa–VIIc and 0.21 g (0.0015 mol) of potassium carbonate was placed in a glass tube, heated to 185–195°C, and maintained at this temperature for 1 h. After cooling, the reaction mixture was ground and dissolved in concentrated sulfuric acid. The resulting solution was poured on ice. The precipitate was filtered off on a glass frit filter and washed with water until neutral reaction. Then the obtained powder was washed with acetone in a Soxhlet apparatus, and the final purification was performed by column chromatography on silica gel M 60, using as eluent chloroform (**VIIIa**, **VIIIb**) or DMF (**VIIIc**).

Tetra-{4-[4'-(4"-methylphenylazo)phenoxy]}phthalocyanine (VIIIa) was obtained along the general procedure using 0.34 g of 4-[4-(4'-methylphenylazo)phenoxy]phthalonitrile. Yield 2.51 g (46.26%). Found, %: C 73.93, H 5.20, N 16.28. C₈₄H₅₈N₁₆O₄. Calculated, %: C 74.43, H 4.31, N 16.53. EAS in chloroform, λ_{max} , nm: 345, 607, 641, 666, 702; in DMF, λ_{max} , nm: 349, 610, 641, 670, 698; in concentrated sulfuric acid, λ_{max} , nm: 468, 836, 891.

Tetra-4-[4'-(2',4''-dimethylphenylazo)phenoxy]phthalocyanine (VIIIb) was obtained along the general procedure using 0.35 g of 4-[4'-(2',4''-dimethylphenylazo)phenoxy]phthalonitrile. Yield 2.54 g (44.95%). Found, %: C 74.54, H 4.93, N 16.29. C₈₈H₆₆N₁₆O₄. Calculated, %: C 74.88, H 4.71, N 15.88. EAS in chloroform, λ_{max} , nm: 350, 605, 640, 665, 700; in DMF, λ_{max} , nm: 359, 605, 637, 669, 697; in concentrated sulfuric acid, λ_{max} , nm: 475, 841, 901.

Tetra-4-[4'-(4"-acetamidophenylazo)phenoxy]phthalocyanine (VIIIc) was obtained along the general procedure using 0.81 g of 4-[4'-(4"-acetaminophenylazo)phenoxy]phthalonitrile. Yield 2.63 g (43.13%). Found, %: C 69.03, H 4.20, N 18.28. C₈₈H₆₂N₁₆O₈. Calculated, %: C 69.19, H 4.09, N 18.38. EAS in DMF, λ_{max} , nm: 366, 610, 635, 669, 700; in acetone, λ_{max} , nm: 369, 610, 639, 667, 699; in concentrated sulfuric acid, λ_{max} , nm: 470, 767, 817, 873.

Synthesis of metal complexes of tetra-R-phenylazophnoxyphthalocyanines (general procedure). In the glass tube was placed the required amount of a ground mixture of 0.001 mole of the corresponding Rphenylazophnoxyphthalonitrile VIIa–VIIc and 0.0015 mol of a metal chloride, the tube was heated to 185–195°C and maintained at this temperature for 1 h. After cooling, the reaction mixture was ground and dissolved in concentrated sulfuric acid. The resulting solution was poured on ice. The precipitate was filtered off on a glass frit filter, and washed with water until neutral reaction. Then the obtained powder was washed with acetone in a Soxhlet apparatus and the final purification was performed by column chromatography on silica gel, M 60, using as eluent chloroform (IXa, IXb-XIa, XIb) or DMF (IXc-XIc).

Tetra-{4-[4'-(4"-methylphenylazo)phenoxy]}cobalt phthalocyanine (IXa) was obtained along the general procedure using 0.34 g of 4-[4-(4'-methylphenylazo)phenoxy]phthalonitrile and 0.19 g of cobalt chloride. Yield 1.95 g (34.60%). Found, %: C 71.19, H 4.20, N 15.68. C₈₄H₅₆CoN₁₆O₄. Calculated, %: C 71.43, H 4.00, N 15.87. EAS in chloroform, λ_{max} , nm: 341, 613, 674; in DMF, λ_{max} , nm: 345, 603, 666; in concentrated sulfuric acid, λ_{max} , nm: 472, 818.

Tetra-4-[4'-(2',4''-dimethylphenylazo)phenoxy]phthalocyanine cobalt (IXb) was obtained along the general procedure using 0.35 g of 4-[4'-(2',4'-dimethylphenylazo)phenoxy]phthalonitrile and 0.19 g of cobalt chloride. Yield 2.06 g (32.56%). Found, %: C 71.14, H 4.13, N 15.29. $C_{88}H_{64}CoN_{16}O_4$. Calculated, %: C 71.98, H 4.39, N 15.26. EAS in chloroform, λ_{max} , nm: 345, 610, 675; in DMF, λ_{max} , nm: 345, 605, 670, in concentrated sulfuric acid, λ_{max} , nm: 479, 824.

Tetra-4-[4'-(4"-acetamidophenylazo)phenoxy]phthalocyanine cobalt (IXc) was obtained along the general procedure using 0.81 g of 4-[4'-(4"-acetamidophenylazo)phenoxy]phthalonitrile and 0.19 g of cobalt chloride. Yield 1.89 g (29.75%). Found, %: C 66.63, H 4.00, N 17.38. $C_{88}H_{60}CoN_{20}O_8$. Calculated, %: C 66.71, H 3.82, N 17.68. EAS in DMF, λ_{max} , nm: 365, 605, 667; in acetone, λ_{max} , nm: 365, 600, 665, in concentrated sulfuric acid, λ_{max} , nm: 472, 710, 802.

Tetra-{4-[4'-(4''-methylphenylazo)phenoxy]}copper phthalocyanine (Xa) was obtained along the general procedure using 0.34 g of 4-[4-(4'-methylphenylazo) phenoxy]phthalonitrile and 0.20 g of copper chloride. Yield 1.91 g (32.62%). Found, %: C 71.10, H 4.25, N 15.68. C₈₄H₅₆CuN₁₆O₄. Calculated, %: C 71.20, H 3.98, N 15.82. EAS in chloroform, λ_{max} , nm: 345, 613, 674; in DMF, λ_{max} , nm: 345, 610, 675; in concentrated sulfuric acid, λ_{max} , nm: 470, 740, 839.

Tetra-4-[4'-(2',4"-dimethylphenylazo)phenoxy]phthalocyanine copper (Xb) was obtained along the general procedure using 0.35 g of 4-[4'-(2',4"-dimethylphenylazo)phenoxy]phthalonitrile and 0.20 g of copper chloride. Yield 1.78 g (31.54%). Found, %: C 71.61, H 4.51, N 15.16. C₈₈H₆₄CuN₁₆O4. Calculated, %: C 71.75, H 4.38, N 15.21. EAS in chloroform, λ_{max} , nm: 344, 615, 681; in DMF, λ_{max} , nm: 355, 610, 675; in concentrated sulfuric acid, λ_{max} , nm: 476, 740, 846.

Tetra-4-[4'-(4"-acetamidophenylazo)phenoxy]phthalocyanine copper (Xc) was obtained along the general procedure using 0.81 g of 4-[4'-(4"-acetamidophenylazo)phenoxy]phthalonitrile and 0.20 g of copper chloride. Yield 1.99 g (35.30%). Found, %: C 66.58, H 4.10, N 17.42. $C_{88}H_{60}CuN_{20}O_8$. Calculated, %: C 66.51, H 3.81, N 17.63. EAS in DMF, λ_{max} , nm: 365, 610, 675; in concentrated sulfuric acid, λ_{max} , nm: 470, 725, 824.

Tetra-{4-[4'-(4"-methylphenylazo)phenoxy]}phthalocyanine nickel (XIa) was obtained along the general procedure using 0.34 g of 4-[4-(4'-methylphenylazo)phenoxy]phthalonitrile and 0.19 g of nickel chloride. Yield 1.93 g (30.54%). Found, %: C 71,40, H 4,20, N 15,67. C₈₄H₅₆N₁₆NiO₄. Calculated, %: C 71.45, H 4.00, N 15.87. EAS in chloroform, λ_{max} , nm: 351, 616, 671; in DMF, λ_{max} , nm: 341, 616, 672; in concentrated sulfuric acid, λ_{max} , nm: 470, 722, 814.

Tetra-4-[4'-(2',4"-dimethylphenylazo)phenoxy]phthalocyanine nickel (XIb) was obtained along the general procedure using 0.35 g of 4-[4'-(2',4"-dimethylphenylazo)phenoxy]phthalonitrile and 0.19 g of nickel chloride. Yield 1.39 g (23.70%). Found, %: C 71.91, H 4.50, N 15.06. $C_{88}H_{64}N_{16}NiO_4$. Calculated, %: C 71.99, H 4.39, N 15.26. EAS in chloroform, λ_{max} , nm: 340, 610, 675; in DMF, λ_{max} , nm: 363, 605, 673; in concentrated sulfuric acid, λ_{max} , nm: 480, 727, 821.

Tetra-4-[4'-(4"-acetamidophenylazo)phenoxy]phthalocyanine nickel (XIc) was obtained along the general procedure using 0.81 g of 4-[4'-(4"-acetamidophenylazo)phenoxy]phthalonitrile and 0.19 g of nickel chloride. Yield 1.66 g (28.43%). Found, %: C 66.50, H 4.07, N 17.452. $C_{88}H_{60}N_{20}NiO_8$. Calculated, %: C 66.72, H 3.82, N 17.68. EAS in DMF, λ_{max} , nm: 350, 610, 677; in concentrated sulfuric acid, λ_{max} , nm: 470, 725, 800.

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