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Phthalocyanines with Peripheral Azo Chromophores

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Abstract—Interaction of 4-halogenated phthalonitrile with arylazophenols provided 4-R-azophenoxyphthalonitriles that have been further transformed into tetra-4-(4'-arylazophenoxy)phthalocyanines and their metal complexes. Physicochemical properties of the prepared compounds were studied.

Keywords: phthalonitrile, phthalocyanine, azo chromophore, electron absorption spectrum, mesomorphism, thermooxidative decomposition

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Phthalocyanine (Pc) and its numerous derivatives have been intensively studied since 1930s. The interest to these compounds is due to their unique structure and the set of physicochemical properties [1, 2].

Chromophore system of phthalocyanines is characterized by a closed conjugation system including the 16-membered heterocycle of carbon and nitrogen atoms, resulting in deep blue color of the compounds. The narrow color spectrum of phthalocyanine is among the disadvantages of these unique compounds. In view of this, the studies aiming to extend the range of light absorption by compounds of the phthalocyanines family are of high importance. One of the possible approaches is the introduction of the substituents containing a proper chromophore system to the phthalocyanine molecules. The resulting compounds have been recognized as promising dyes, materials for solar energetics, microelectronics, and other related applications [3, 4].

Here we report on the synthesis and the study of hybrid phthalocyanines containing the chemically linked phthalocyanine and azo chromophores; such compounds have been poorly discussed in the literature so far [5–7].

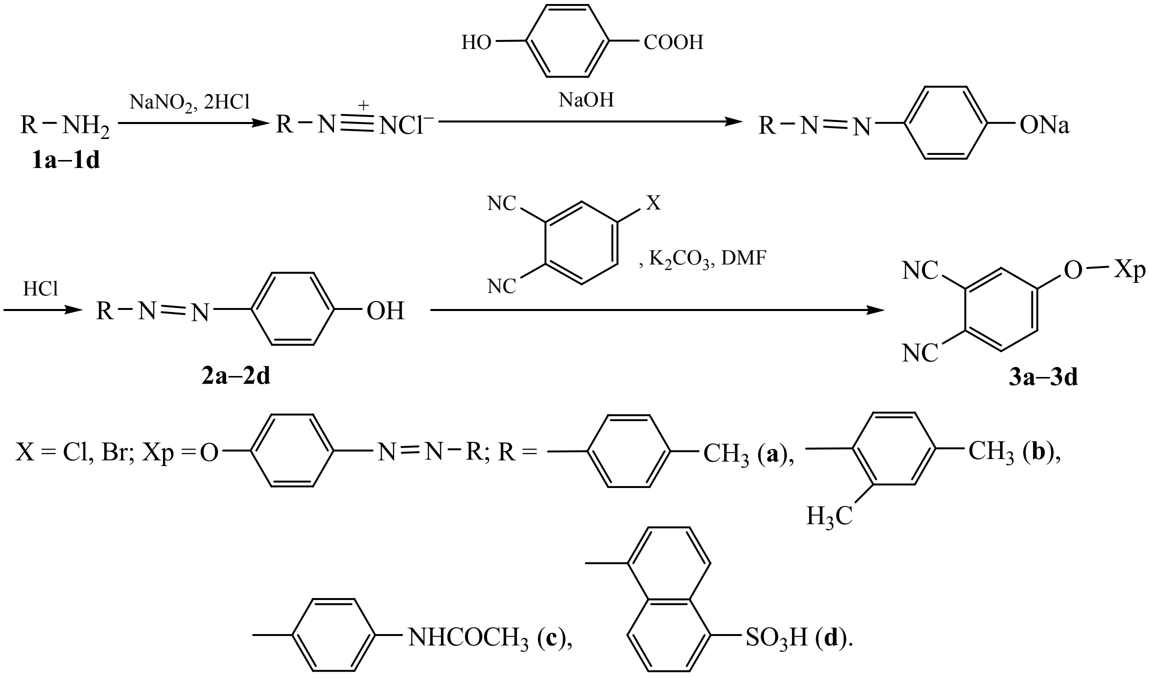
The nitrile route is among the efficient approaches to the preparation of substituted phthalocyanines [8]. In this work we used substituted nitriles as precursors of phthalocyanines. In particular, the diazotization of aryl-substituted aromatic amines **1a**–**1d** yielded the corresponding diazonium salts that were subjected to the *in situ* azocoupling with *p*-hydroxybenzoic acid in the alkaline medium. The nucleophilic substitution of the halogen atom in the 4-halogenated phthalonitrile with the azo dye fragment (Xp) via the known method [9] gave the corresponding 4-arylazophenoxyphthalonitriles **3a**–**3d** [10–12]. The purity and the structure of the products was confirmed by means of chromato–mass spectrometry as well as by ^{1}H NMR, IR, and electron absorption spectroscopy.

The prepared phthalonitriles **3a**–**3d** were yellow or red-orange powders, readily soluble in organic solvents (acetone, DMF, and ethanol); the presence of sulfo group in the aryl fragment of compound **3d** imparted the solubility in water.

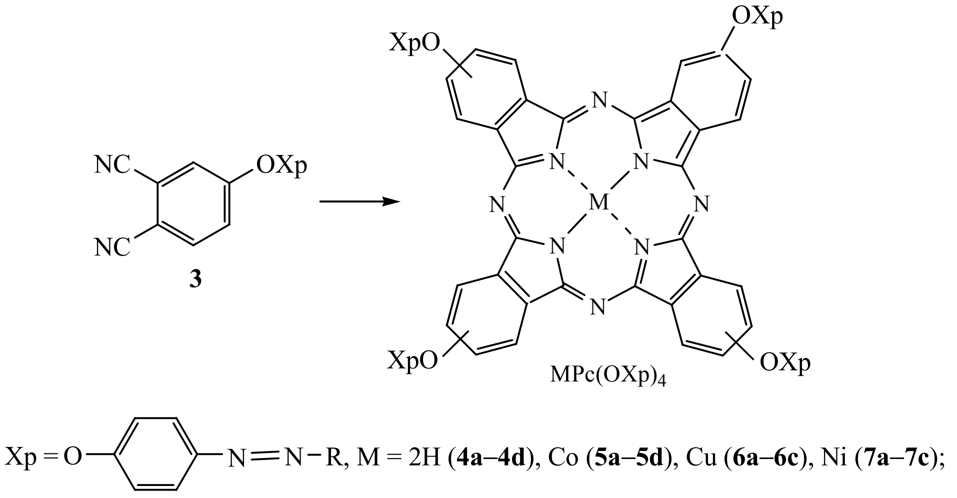
The nature of the substituent in the phthalonitrile molecule affected the melting point of the substance. In particular, 4-[4'-(4''-methylphenyl)azophenoxy]phthalonitrile **3a** started melting at 140°C; the introduction of an additional methyl group at the *p*-toluidine fragment significantly reduced the melting point of 4-[4'-(2'',4''-dimethylphenyl)azophenoxy]phthalonitrile **3b** to 43°C. The substitution of the methyl group in the *p*-toluidine fragment with acylamino group (**3c**) or naphthylsulfonic acid moiety (**3d**) resulted to the less prominent reduction of the melting point: to 108 and 120–125°C, respectively (Scheme 1).

Heating of the prepared phthalonitrile **3a**–**3d** following the procedure described in [13] resulted in

Scheme 1.



Scheme 2.



R = 4-$CH_3C_6H_4$ (**a**), 2,4-$(CH_3)_2C_6H_3$ (**b**), 4-$NHCOCH_3C_6H_4$ (**c**), 5-SO_3HNaph (**d**).

the corresponding tetra-4-(4'-arylazophenoxy)phthalocyanines **4a**–**4d** [10–12].

The metal complexes **5**–**7** were prepared via the interaction of phthalonitriles **3a**–**3d** with chlorides of cobalt, copper, or nickel at 185–190°C (see Scheme 2). In the case of the sulfo-containing phthalonitrile **3d**, only the cobalt complex **5d** was prepared, the copper and nickel complexes formed in trace amounts. A similar trend has been earlier observed for the other sulfo-containing substrates as well [13]; however, it has not been explained so far.

All prepared compounds **4**–**7** were soluble in DMF; due to the presence of methyl groups, compounds **4**–**7a**, **7b** were soluble in chloroform, whereas the acylamino groups of compounds **4**–**7c** enhanced their solubility in acetone, and compounds **4**–**5d** were soluble in DMSO and aqueous alkali solutions due to the presence of sulfo groups.

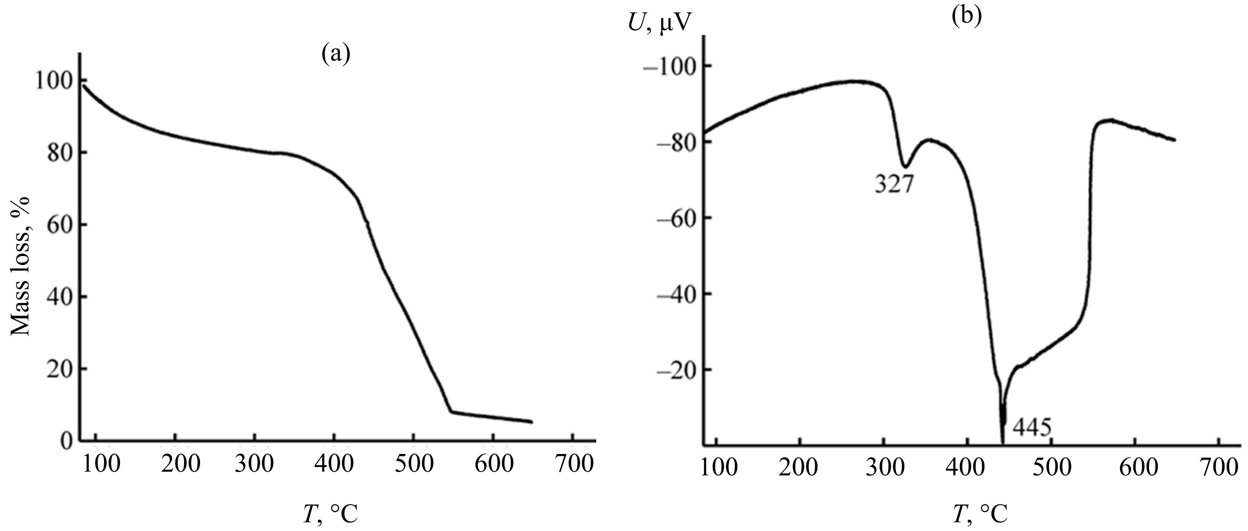


Fig. 1. Derivatogram of nickel tetra-4-[4'-(4''-methylphenylazo)phenoxy]phthalicyaninate **7a**. (a) TG and (b) DTG.

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

IR spectra of the synthesized phthalocyanines **4**–**7** contained the absorption bands characteristic of the aryloxy, methoxy, sulfo, and azo groups. Spectra of the sulfo-derivatives are less resolved as is typical of the sulfonic derivatives of phthalocyanine [1]. On top of that, IR spectra of the metal-free phthalocyanines **4a**–**4c** contained absorption band at 1008 cm^{-1}, typical of the metal-free phthalocyanines [14].

Basic parameters of thermooxidative decomposition of the studied compounds are summarized in Table 1. The behavior of phthalocyanines **4a**–**7a**, and **5d** was similar. Their heating in air up to 200°C resulted in slight (1–3%) mass loss corresponding to elimination of residual solvent; that was confirmed by the identity of IR spectra of the initial specimens and those annealed at 200°C. Further heating resulted in a multi-stage decomposition, as documented in the DTA traces (see the representative example in Fig. 1).

Table 1. Parameters of thermooxidative decomposition of the prepared phthalocyanines **4**–**7**

Comp. no.	Temperature of the fastest mass loss, °C	Temperature of the highest exothermic effect, °C
4a	400–555	515
5a	360–530	425
5d	355–590	510
6a	390–505	450
7a	380–560	445

In all cases, the heating at 350–590°C was accompanies with the loss of 65–70% of the mass, corresponding to the degradation of the phthalocyanine macrocycle. The highest thermal stability was observed in the case of cobalt tetra-4-[4'-(5''-sulfonaphthyl)azophenoxy]phthalocyaninate **5d** (Table 1).

Depending on the nature of the complex forming ion, the stability of the tetra-4-[4'-(4''-methylphenyl)-azophenoxy]phthalocyanines **5**–**7a** decreased in the Cu > Ni > Co series (Table 1). It is known that the metal–nitrogen covalent bonds in nickel and cobalt phthalocyaninates are weaker than in the corresponding copper complexes [15]. This is likely the reason of the lower thermal stability of the nickel **7a** and cobalt **5a** complexes than that of the copper one **6a**.

Electron absorption spectra of solutions of the tetra-4-(4'-arylazophenoxy)phthalocyanines **4**–**7** in organic solvents contained a doublet in the long-wavelength range, typical of the metal-free compounds and corresponding to the D_{2h} molecule symmetry [15]. Furthermore, all spectra contained a strong absorption band at 325–367 nm assigned to electronic transitions in the chromophore system of the azo dye linked to benzene rings of the phthalocyanine ligand (Table 2). Since the azo chromophore was not conjugated with the Pc macrocycle, the green color of the compounds was due to the combination of the absorptions from the phthalocyanine (blue) and the azo (yellow) chromophores separated by the oxygen spacer.

Table 2. Absorbance bands in electronic spectra of phthalocyanines **4**–**7**

Comp. no.	λ_{max}, nm (I_{rel})			
	chloroform	DMF	0.5 wt% NaOH in water	conc. H_2SO_4
4a	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)	[a]	468 (1.00), 891 (0,55), 836 (0.54)
4b	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)	[a]	475 (1.00), 901 (0.60), 841 (0.57),
4c	[a]	366 (1.00), 700 (0.62), 669 (0.60), 635 (0.41), 610 (0.29)	[a]	470 (1.00), 873 (0.76), 817 (0.66), 767 (0.48)
4d	[a]	672 (1.00), 698 (0.98), 325 (0.97), 645 sh (0.63)	622	524(1.00), 825(0.69)
5a	341 (1.00), 674 (0.66), 613 (0.35)	345 (1.00), 666 (0.59), 603 (0.22)	[a]	472 (1.00), 818; (0.58)
5b	345 (1.00), 675 (0.65), 610 (0.29)	345 (1.00), 670 (0.65), 605; (0.21)	[a]	479 (1.00), 824; (0.44)
5c	[a]	365 (1.00), 667 (0.79), 605; (0.24)	[a]	472(1.00), 802 (0.75), 710 (0.43)
5d	[a]	666 (1.00), 325 (0.98), 600 sh (0.27)	628(1.00), 675 (0.88)	811(1.00), 524(0.52)
6a	345 (1.00), 680 (0.65), 605 (0.25)	345 (1.00), 675 (0.55), 610 (0.21)	[a]	470 (1.00), 839 (0.82), 740 (0.35)
6b	344 (1.00), 681 (0.80) 615 (0.31)	355 (1.00), 675.5 (0.71), 610 (0.52)	[a]	476 (1.00), 846 (0.88), 740 (0.39)
6c	[a]	365 (1.00), 675(0.71), 610 (0.26)	[a]	470 (1.00), 824 (0.72), 725 (0.20)
7a	351 (1.00), 672 (0.77), 616 (0.26)	344 (1.00), 673 (0.52), 622 (0.45)	[a]	470 (1.00), 814 (0.78), 722 (0.26)
7b	340 (1.00), 675 (0.78), 610 (0.40)	363 (1.00), 673 (0.40),622; (0.30)	[a]	480 (1.00), 821 (0.71), 727 (0.25)
7c	[a]	350 (1.00), 677 (0.70), 610 (0.31)	[a]	470 (1.00), 800 (0.84), 705 (0.32)

[a] Insoluble.

As compared to the metal-free phthalocyanines, their metal complexes **5**–**7** exhibited the higher molecular symmetry (D_{2h} and D_{4h}, respectively); therefore, the two components of the *Q* band in the electron absorption spectra were merged [15], the resulting band being shifted to longer wavelength as compared to the *Q* band of the corresponding unsubstituted metal phthalocyaninate (Table 2). Noteworthily, the azo chromophore nature had practically no effect on the position of the long-wavelength absorption band.

When chloroform was used as solvent instead of DMF, the intensities of the major *Q* band and that in the range of the vibrational satellite were changed, the latter becoming stronger (Fig. 2, Table 2). The spectral changes were likely due to the different tendency of Pc to associate depending on the solvent polarity [16]. Association of the Co(II) complexes was weaker as compared to the similar complexes of Cu(II) and Ni(II), due to the stronger coordinating properties of cobalt ions. The cobalt phthalocyanines **5a**–**5d** formed

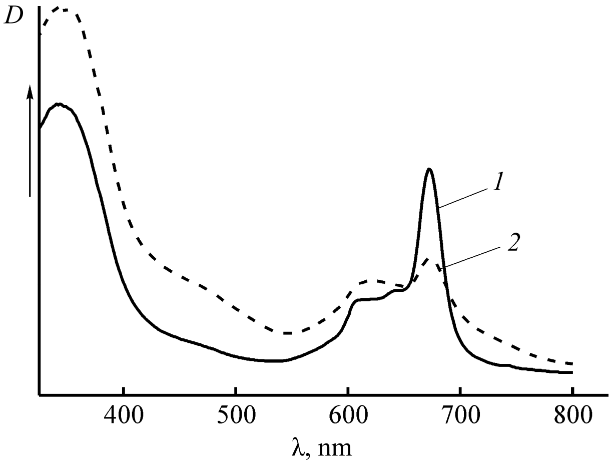


Fig. 2. Electronic absorption spectra of the complex **6b** in (*1*) chloroform and (*2*) in DMF.

the extraligand complexes with the solvent molecules, hindering the intermolecular interactions [16].

The same change of the solvent from DMF to chloroform resulted in the shift of the long-wavelength absorption band towards longer wavelength in all phthalocyanines excluding the nickel complexes (Table 2).

Sulfo groups present in the phthalocyanines **4–5d** provided for their solubility in aqueous alkaline media. When the 0.5 wt % NaOH aqueous solution was used as solvent instead of the organic ones, the long-wavelength absorption bands of the complexes were shifted towards shorter wavelength, due to the enhanced molecules association.

All the absorption bands in the spectra of the studied phthalocyanines dissolved in concentrated sulfuric acid exhibited the red shift as compared to the spectra in other solvents, due to protonation of the *meso* nitrogen atom in the macrocycle [15]. The shifts observed in this work were smaller as compared to the cases of unsubstituted phthalocyanines [1]. That was likely due to the participation of nitrogen atom of the acylamino and azo groups accompanied by the reduced degree of protonation of the *meso* nitrogen atoms.

The study of the synthesized tetraarylazophenoxyphthalocyanines **4** and their copper complexes **6** by means of polarization microscopy revealed the thermotropic mesomorphism only in the cases of tetra-4-[4'-(2",4"-dimethylphenyl)azophenoxy]phthalocyanine **4b** and its copper complex **6b**, the metal-free compound forming the mesophase at lower temperature [11]. Lyotropic properties were observed in all organosoluble compounds in the binary systems with a series of solvents (chloroform, toluene, and DMF), whereas compounds **4b** and **6b** were amphotropic discotics [11].

To conclude, the prepared phthalocyanines can be applicable as organosoluble dyes for waxes, hydrocarbons, and polymers; the sulfo-containing compounds can be used for green or green-blue coloring of protein and cellulose fibers [17–20].

EXPERIMENTAL

4-Arylazophenoxyphthalonitriles **3a–3d** and the corresponding substituted phthalocyanines **4–7** were prepared and purified as described elsewhere [10–12, 17–20].

Thermogravimetry studies were performed at the heating rate of 5 deg/min using a setup with a 1000D derivatograph as measuring unit. The scheme and the principle of the setup operation as well as the details of the data processing have been described earlier [21].

Electron absorption spectra of solutions of the studied compounds (10^{-4}–10^{-6} mol/L) were recorded using a Hitachi U-2001 spectrophotometer (250–900 nm, room temperature). IR spectra (KBr pellets) were recorded using an Avatar 360 FT–IR ESP spectrometer at 400–4000 nm^{-1}. ^{1}H NMR spectra ($CDCl_3$) were registered using a Bruker DRX-500 instrument. Elemental analysis was performed using a FlashEA 1112 CHNS–O Analyzer instrument.

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