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Synthesis and Properties of Cobalt(II) Tetrakis-[4,5-di(4'-carboxy)phenylene(oxy/sulfanyl/amino)]phthalocyanines

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Abstract—Phthalonitriles with fragments of 4-hydroxy, 4-mercapto and 4-aminobenzoic acids were synthesized by nucleophilic substitution in 4-bromo-5-nitrophthalonitrile. The synthesized phthalonitriles were used to prepare octasubstituted cobalt phthalocyanines by template synthesis. The spectral properties of the products were studied.

Keywords: 4-bromo-5-nitrophthalonitrile, benzoic acids, metal phthalocyanines, electronic absorption spectra

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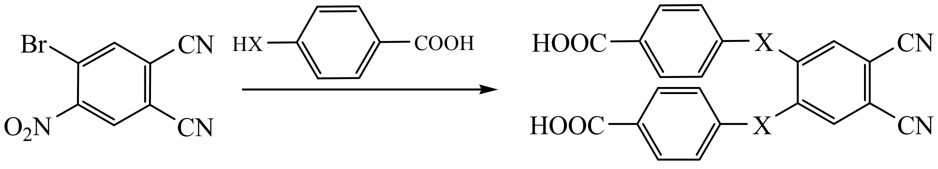
Carboxylic acids and their derivatives occupy special place among numerous substituted phthalocyanines because of their diverse potential uses in science and technics [1–10]. Over the past years phthalocyanines containing as substituents hydroxy- [1, 5, 8–10], amino [7,9], or mercaptobezoic acids [6, 9] have attracted attention of scientists and practitioners. It was found that some of such substituted macroheterocyclic compounds can find application as liquid crystalline [5] and medical materials [11], dyes and photo-sensitizers [6, 7, 12], as well as catalysts [13, 14]. Therewith, all publications dealt with either tetrasub-stituted phthalocyanines [1, 5–8, 13, 14] or octasubstituted phthalocyanines with 3,5-dicarboxyphenoxy fragments [2–4].

In the present work we synthesized 4,5-octasubstituted cobalt phthalocyanines containing as substituents *para*-substituted benzoic acid fragments and studied their spectral properties.

The starting 4,5-bis(4-carboxyphenoxy)- (**2**), 4,5-bis[(4-carboxyphenyl)sulfanyl]$^-$ (**3**), and 4,5-bis[4-carboxyphenyl)amino]phthalonitriles (**4**) were synthesized by the nucleophilic substitution of the bromo and nitro groups in 4-bromo-5-nitrophthalonitrile (**1**) by corresponding benzoic acid residues (Scheme 1). Like with other disubstituted phthalonitriles [1, 9], the synthesis was performed in aqueous DMF in the presence of potash. Since in the present work we substituted both the Br and NO_2 groups, the reaction mixture was heated at 80–90°C for 18–24 h. In the case of compound **4** containing *para*-aminobenzoic acid residues as substituents, the reaction was performed in the presence of trimethylamine.

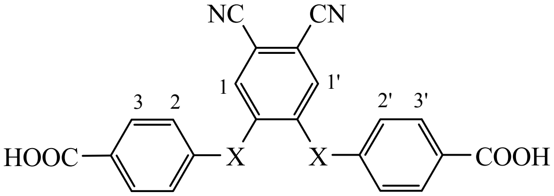
Scheme 1.



1 **2–4**

X = O (**2**), S (**3**), NH (**4**).

Table 1. Signal positions in the ^{1}H NMR spectra of compounds **2**–**4**



Atom no.	Signal position, δ, ppm					
	X = O (**2**)		X= S (**3**)		X= NH (**4**)	
	theory	experiment	theory	experiment	theory	experiment
$H^{1,1'}$	7.75	7.66	7.89	7.88	8.08	8.01
$H^{2,2'}$	6.96–7.00	6.96–7.06 *J* = 2.01 Hz	7.59–7.61	7.57–7.60 d *J* = 2.05 Hz	7.08–7.09	7.52–7.53 *J* = 2.05 Hz
$H^{3,3'}$	8.05–8.09	8.03–8.12 d *J* = 2.05 Hz	8.08–8.10	7.96–8.02 d *J* = 2.04 Hz	7.73–7.76	7.62–7.63 d *J* = 2.01 Hz
COOH	11.72	10.58 s	11.72	10.55 s	8.49	8.58 s
NH			–		8.49	8.51 s

Compounds **2** and **3** can also be synthesized by introducing the second benzoic acid to presynthesized 4-(4'-carboxyphenylsulfanyl)-5-nirophthalonitrile or 4-(4'-carboxyphenoxy)-5-nitrophthalonitrile [9]. Therewith, the two-stage synthesis requires isolation of the intermediate product, which increases the synthesis time and entails additional losses on purification. We failed to synthesize compound **4** from 4-(4'-carboxyphenylamino)-5-nitrophthalonitrile.

To isolate compounds **2** and **3**, the reaction mixture was poured into 5% aqueous HCl, and the precipitate that formed was filtered off and washed with acidic water. The yields of compounds **2** and **3** were 72 and 88%, respectively.

In the case of phthalonitrile **4**, the reaction mixture were poured into water, the target product was extracted with chloroform, and the organic layer was subjected to column chromatography on silica gel (eluent chloroform). The eluate was then evaporated, and phthalonitrile **4** was dried under vacuum at 70°C. The yield of the target product was 40%.

Compounds **2**–**4** were identified by elemental analysis, UV-Vis, ^{1}H NMR, and IR spectroscopy, and MALDI-TOF mass spectrometry.

The IR spectra of all the products contain the ν(C≡N) band at 2229–2237 cm^{-1} [15]. The position of this band depends on the nature of the bridging group, which reveals itself in a red shift of this band, increasing the following order of bridging groups:

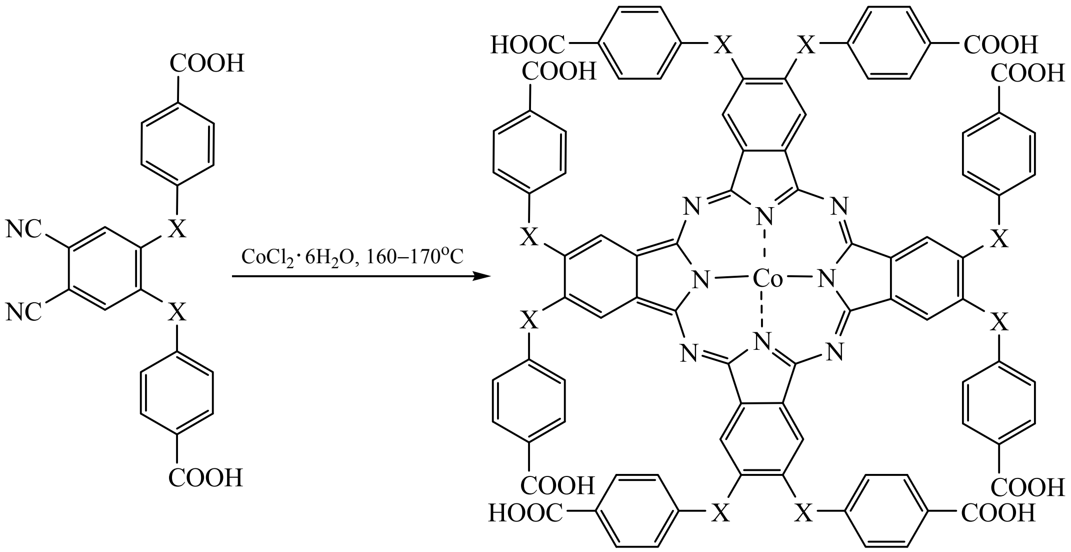
3 (X = S) < **4** (X = NH) < **2** (X = O).

The dependence of the ν(C≡N) band position on the nature of the bridging group was also observed in our previous work [9], where we synthesized phthalonitriles having the nitro group ortho to the corresponding benzoic acid fragment. However, in that case the red shift of this band varied in a different order of bridging groups:

(X = O) < (X = S) < (X = NH) [9].

Furthermore, the spectra of all the synthesized compounds display the ν(O–H) and ν(C=O) bands of the carboxyl groups of the benzoic acid fragments at 3417–3457 and 1706–1710 cm^{-1}, respectively [15]. The spectra of compounds **2**–**4** show no symmetric (1342–1352 cm^{-1}) and antisymmetric (1562–1565 cm^{-1}) vibration bands of the N=O bonds of the nitro groups [15], providing evidence for completion of nucleophilic substitution of the NO_2 group in compound **1**. The spectrum of phthalonitrile **3** contains the stretching vibration band of the Ar–S–Ar group at 1104 cm^{-1} [15], and the spectrum of phthalonitrile **4**, which contains a *para*-aminobenzoic acid fragment, shows the stretching (3195 cm^{-1}) and deformation (1604 cm^{-1}) vibration bands of the N–H bond of the secondary amino group. The spectrum of compound **2**

Scheme 2.



2–4 **5–7**

X = O (**2**, **5**), S (**3**, **6**), NH (**4**, **7**).

displays the stretching vibration band of the Ar–O–Ar band at 1220 cm^{-1} [15].

The positions of signals in the ^{1}H NMR spectra of compounds **2**–**4** in DMSO-d_6 are listed in Table 1.

The ^{1}H NMR spectra of compounds **2**–**4** display a downfield signal of the phthalonitrile benzene rings (Table 1). The position of this signal depends on the nature of the bridging group (Table 1) and shifta upfield in the following order:

4 (X = NH) < **3** (X = S) < **2** (X = O).

The downfield signals in the range 7.52–8.12 ppm belong to the benzene ring protons of the benzoic acid residues.

The COOH proton signals in the ^{1}H NMR spectra of compounds **2**–**4** are observed at 8.58–10.58 ppm. This fact implies that the target phthalonitriles are carboxylic acids rather than salts. The spectrum of compound **4**, which has two *para*-aminobenzoic acid fragments ortho to each other, shows a downfield (8.51 ppm) two-proton signal of the secondary amino group. The position of the benzene ring signals of the benzoic acid fragments located ortho to the bridging group, too, depend on the nature of this group. Thus, the signals shift upfield in the following order:

3 (X = S) < **4** (X = NH) < **2** (X = O) (Table 1).

Further evidence showing that compounds **2**–**4** are carboxylic acids rather than potassium salts comes from the MALDI–TOF mass spectra, which contain molecular ion peaks at *m/z* 399 (**2**), 431 (**3**), and 398 (**4**) (Fig. 1).

After isolation and identification the synthesized phthalonitriles were used as starting materials to obtain octasubstituted cobalt phthalocyanines **5**−**7**.

The synthesis was performed by the nitrile method, specifically, by heating the corresponding substituted phthalonitrile and cobalt chloride in the presence of urea at 160−170°C until the reaction mixture solidified (Scheme 2). After cooling down the solid material was ground and transferred onto a filter, successively washed with acidified water and acetone, and dried. The target compounds were extracted with DMF, and the solvent was removed to leave dry dark green powders insoluble in acetone and chloroform, readily soluble in water and aqueous alkaline solutions, and sparingly soluble in DMF.

Compounds **5**–**7** were identified by elemental analysis, UV-Vis and IR spectroscopy, and MALDI-TOF. mass spectrometry.

The mass spectral data are presented in Experimental and Fig. 2.

The IR spectra of the synthesized cobalt phthalocyanines show no $\nu(C\equiv N)$ band at 2225–2240 cm^{-1} [15], which suggests a lack of impurities of the starting compounds. The spectra of all of the synthesized

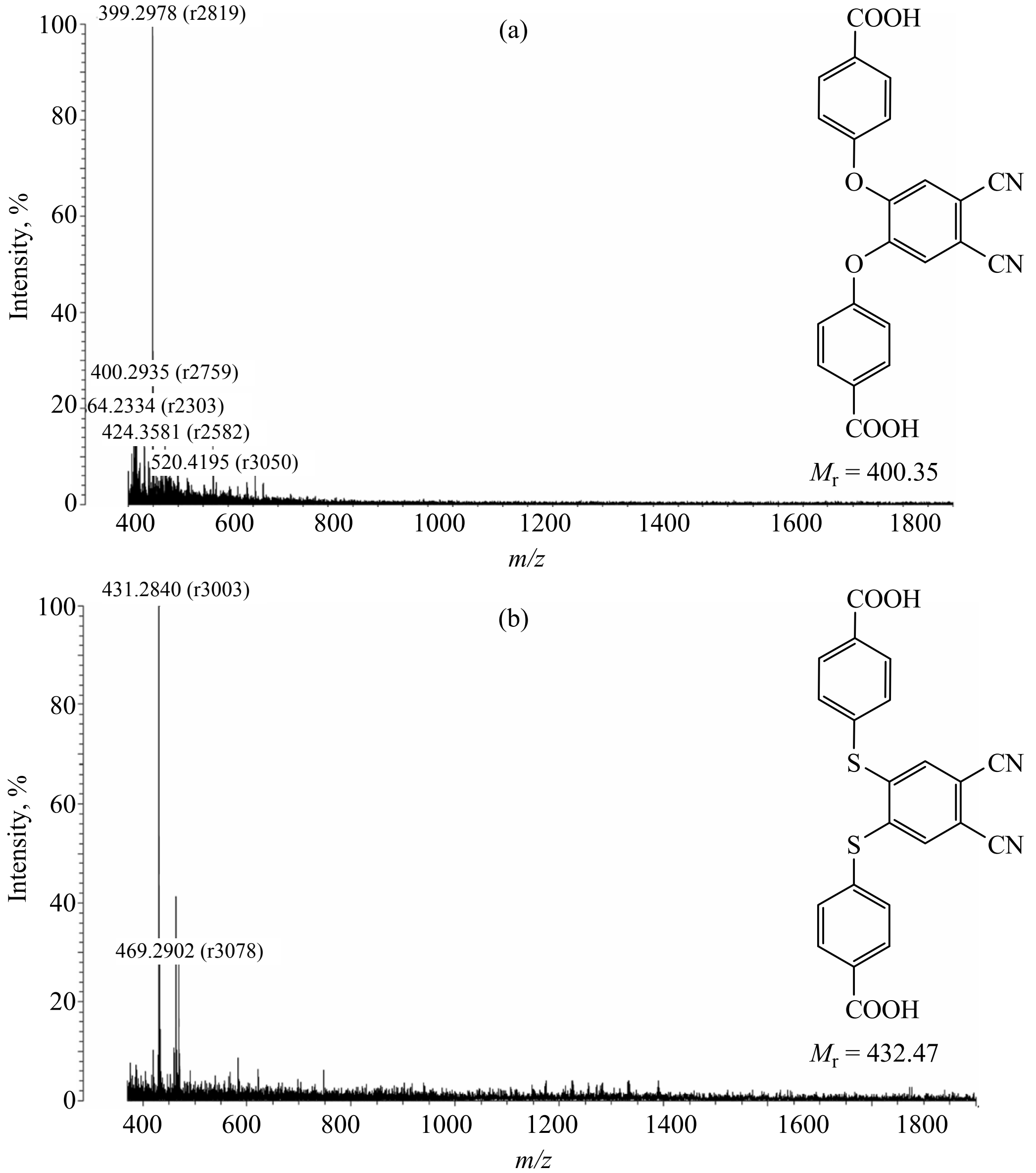


Fig. 1. MALDI-TOF mass spectra of compounds (a) **2** and (b) **3.**

phthalocyanines contain the stretching vibration bands of the functional groups, which were also observed in the IR spectra of phthalonitriles **2**–**4**. Therefore, we can conclude that phthalocyanines **5–7** contain the same functional groups.

Analyzing the UV-Vis spectra of compounds **5**–**7** both in aqueous alkali and in DMF we can note that the spectral curves are diffuse. Moreover, the Lambert–Bouguer–Beer law fails in this case. Consequently, cobalt phthalocyanines are present mostly in the associated form. The positions of the longwave absorption bands depend on the nature of the bridging heteroatom X (Table 2, Fig. 3). Thus, it was found that, at equal concentrations of DMF solutions, the red shift of the *Q* band decreases in the following order of compounds:

6 (X = S) < **5** (X = O) < **7** (X = NH).

Analyzing the spectral patterns (Fig. 2), we can draw a preliminary conclusion that the cobalt phthalocyanine containing mercaptobenzoic acid fragments (compound **6**) has the highest degree of association in DMF.

Diffuse longwave bands (λ_{max} 650–705 nm) are also observed in the UV-Vis spectra of aqueous alkaline solutions (5% aqueous ammonia), even when their

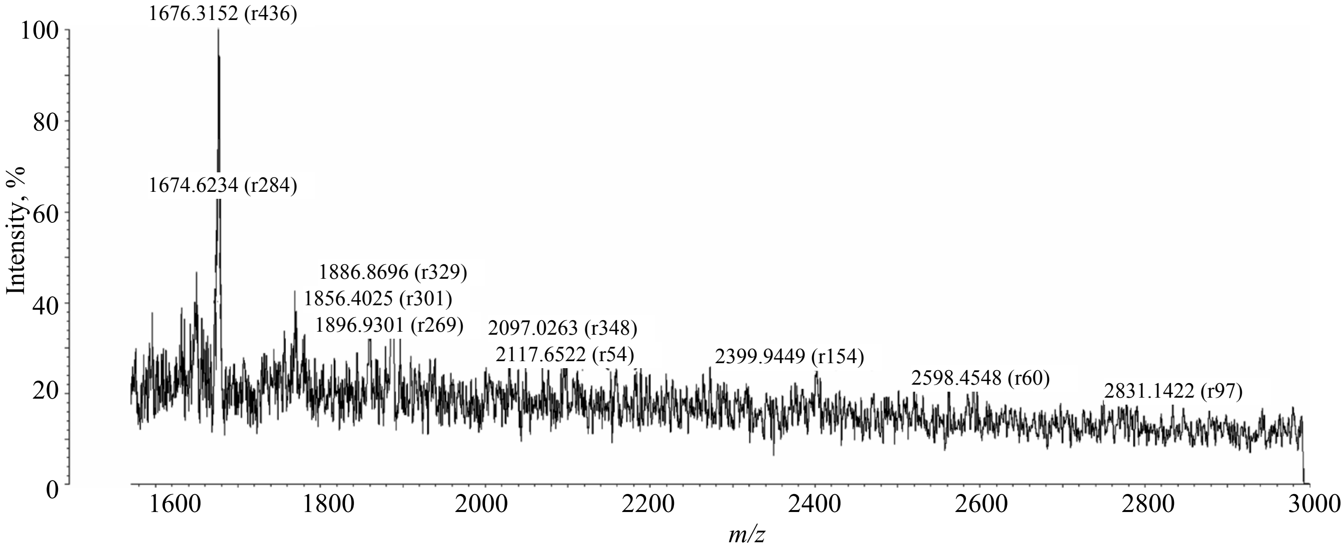


Fig. 2. Fragment of the MALDI-TOF mass spectrum of compound **5** in the m/z range 1600–3000.

concentrations are quite low (10^{-6}–10^{-3} M) (Fig. 4, Table 2). The spectra of phthalocyanines **6** and **7**, which contain 8 fragments of *p*-mercaptobenzoic and *p*-aminobenzoic acid fragments, display two maxima of equal intensity in the first case and with a much stronger longwave component in the second (Table 2).

In going to aqueous alkaline and organic solvents to conc. H_2SO_4, the longwave bands shift red (Table 2, Fig. 5). The replacement of the nitro group in cobalt tetra-4-(4'-carboxyphenylsulfanyl)-tetra-5-nitrophthalocyanine [9] by one more mercaprobenzoic acid fragment shifts the longwave absorption band in the UV-Vis spectrum in conc. H_2SO_4 by 180 nm (Table 2). In the case of compounds with hydroxyl- and aminobenzoic acid fragments such shift is not so large (40 and 22 nm, respectively).

As previously [1, 9], the position of the *Q* band and its red shift in going from DMF to conc. H_2SO_4 depend on the nature of the heteroatom bridging the benzoic acid and phthalocyanine components. The red shift of the *Q* band decreases in the following order (Table 2):

(**6**, X=S) > (**7**, X = NH) > (**5**, X = O).

Thus, the nucleophilic substitution of bromine in 4-bromo-5-nitrophthalonitrile by benzoic acid fragments allowed us to synthesize phthalonitrile containing 2 identical benzoic acid fragments located ortho to each other. The tetramerization of the synthesized phthalonitriles with cobalt chloride gave novel octasubstituted cobalt phthalocyanines.

The spectral properties of the synthesized compounds were studied. It was found that the position of

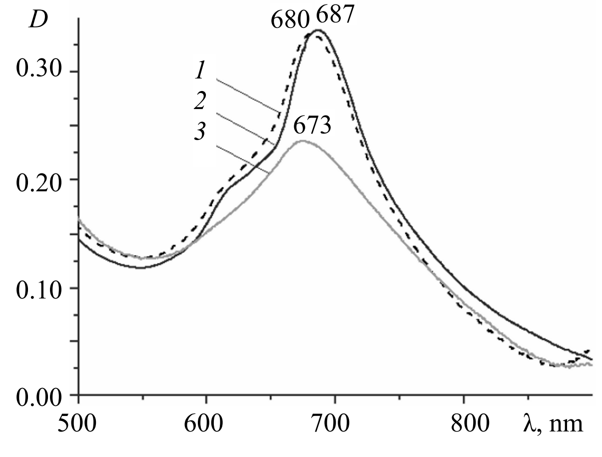


Fig. 3. Electronic absorption spectra of compounds (*1*) **5**, (*2*) **6**, and (*3*) **7** in DMF (0.45×10^{-5} M).

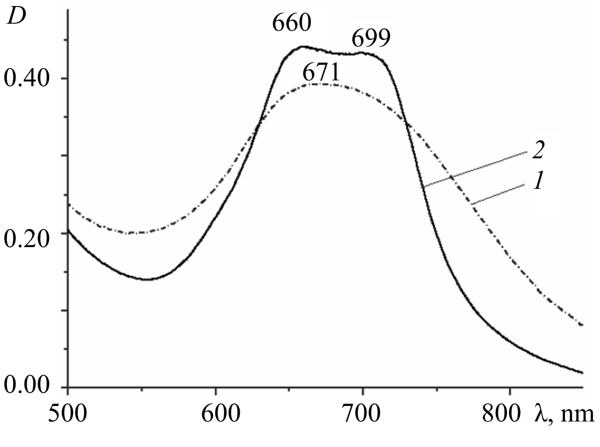


Fig. 4. Electronic absorption spectra of compounds (*1*) **5** and (*2*) **6** in 5 % aqueous NH_4OH (0.55×10^{-5} M).

the *Q* band and its red shift in going from DMF to conc. H_2SO_4 depends on the nature of the heteroatom bridging the benzoic acid and phthalocyanine fragments. The red shift of the *Q* band decreases in the following order:

(**7**, X=S) > (**8**, X = NH) > (**6**, X = O).

Similar trends we previously observed in the spectra of cobalt phthalocyanines combining the corresponding benzoic acid fragments and nitro groups [9].

EXPERIMENTAL

All analyses were performed using the equipment of the Center for Collective Use, Ivanovo State University of Chemical Technology.

Elemental analysis was performed on on a Thermo Scientific FlashEA 1112 CHNS-O analyzer.

The UV-Vis spectra were registered in DMF, aqueous ammonia, and conc. H_2SO_4 on a Hitachi U-2001 spectrophotometer at room temperature in the range 400–900 nm. The IR spectra were run in KBr pellets on an Avatar 360 FT-IR ESP spectrometer in the range 400–4000 cm^{-1}.

The ^{1}H NMR spectra were measured on a Bruker DRX-500 instrument in DMSO-d_6 against internal TMS.

The MALDI-TOF mass spectra were obtained on a Shimadzu Biotech Axima Confidence instrument in the negative (**2**, **3**) and positive (**4**–**7**) ion modes using α-cyano-4-hydroxycinnamic acid as a matrix. The samples were prepared by mixing solutions of compounds **2**–**4** in THF ($c = 10^{-4}$–10^{-5} M) or compounds **4**–**9** in DMF with a solution of the matrix (30 mg/mL) in THF.

4-Bromo-5-nitrophthalonitrile (**1**) was synthesized by the procedure described in [16]. The physicochemical characteristics of this product were well consistent with published data: mp 140–142°C. Found, %: 38.10; N 16.50; H 0.76. $C_8H_2BrN_3O_2$. Calculated, %: C 38.16; N 16.67; H 0.80.

Synthesis of 4,4'-[4,5-Dicyano-1,2-phenylenedi(oxy/sulfanyl/amino)]dibenzoic acids (2–4). *Method 1 (general procedure).* A solution of 5.52 g (0.04 mol) of anhydrous potassium carbonate in 7 mL of water was added to a solution of 2.52 g (0.01 mol) of 4-bromo-5-nitrophthalonitrile (**1**) and 0.02 mol of corresponding benzoic acid in 50 mL of DMF in a two-necked flask equipped with a reflux condenser. The resulting mixture was diluted with water, heated with stirring at 80–90°C for 24 h, and poured into acidified water. The solid target product was filtered off and washed with 5% aqueous HCl until colorless washings.

Table 2. Positions of the longwave absorption bands in the UV-Vis spectra of compounds **5**–**7** in different solvents

Comp. no.	UV-Vis spectrum, λ_{max} (intensity ratio)			
	X	DMF	NH_4OH (5%)	H_2SO_4
5	O	680	671	813
6	S	673	660; 699 (1.00 : 0.97)	993
7	NH	687	651; 701 (1.00 : 1.75)	829

4,4'-(4,5-Dicyano-1,2-phenylenedioxy)dibenzoic acid (2) was synthesized from 2.76 g of *para*-hydroxybenzoic acid. After the reaction had been complete, the reaction mixture was poured into 5% aqueous HCl, the precipitate that formed was filtered off, washed with 2% aqueous HCl, and dried in air at 70–80°C. Yield: 2.88 g (72% per **1**). Found, %:C 64.59; H 3.12; N 6.83. $C_{22}H_{12}N_2O_6$; Calculated, %: C 66.00; H 3.02; N 7.00. Mass spectrum, *m/z*: 399.30 $[M - H]^-$; calculated *M* 400.07. IR spectrum, ν, cm^{-1}: 3457 (OH); 2237 (C≡N); 1708 (C=O); 1220 (Ar–O–Ar). ^{1}H NMR spectrum, δ, ppm: 10.58 s (COOH, 2H); 7.66 s (H^1, 2H); 6.96–7.06 d (H^2, 4H, J = 2.01 Hz); 8.03–8.12 d (H^3, 4H, J = 2.05 Hz).

4,4'-(4,5-Dicyano-1,2-phenylenedisulfanyl)dibenzoic acid (3) was synthesized from 3.08 g of *para*-mercaptobenzoic acid and isolated by acidifying the

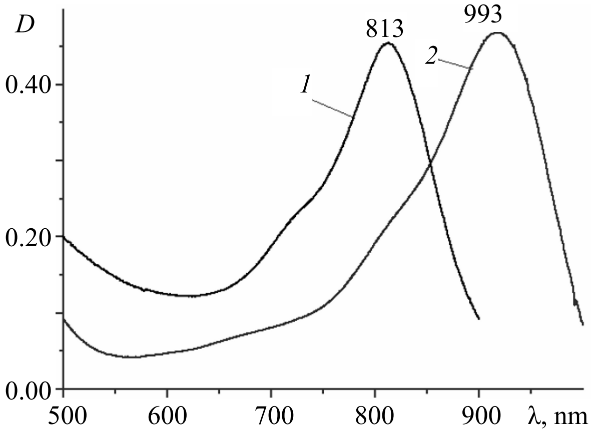


Fig. 5. Electronic absorption spectra of compounds (*1*) **5** and (*2*) **6** in H_2SO_4.

reaction mixture with 5% aqueous HCl, filtering off the precipitate that formed, washing it with 2% aqueous HCl, and drying in air at 70–80°C. Yield: 3.80 g (88% per **1**). Found, %: C 60.95; H 2.93; N 6.15; S 14.35. $C_{22}H_{12}N_2O_4S_2$. Calculated%: C 61.10; H 2.80; N 6.48; S 14.83. Mass spectrum, *m/z*: 431.28 $[M-H]^-$; calculated *M* 432.02. IR spectrum, ν, cm^{-1}: 3417 (OH); 2229 (C≡N); 1710 (C=O); 1104 (Ar–S–Ar). ^1H NMR spectrum, δ, ppm: 10.55 s (COOH, 2H); 7,88 s (H^1, 2H); 7.57–7.60 d (H^2, 4H; *J* = 2,05 Hz); 7.96–8.02 d (H^3, 4H; *J* = 2.04 Hz).

4,4'-(4,5-Dicyano-1,2-phenylenediamino)dibenzoic acid (4) was prepared from 2.74 g of *para*-aminobenzoic acid in the presence of 2 mL of trimethylamine. After the reaction had been complete, the reaction mixture was poured into water and diluted with chloroform. The chloroform layer was separated, and the solvent was removed by distillation. The residue was subjected to column chromatography on silica gel, eluent chloroform. The solvent was removed by distillation, and the product was dried in a vacuum at 70°C. Yield: 1.59 g (40% per **1**). Found, %: C 65.20; H 3.33; N 14.10; $C_{22}H_{14}N_4O_4$; Calculated %: C 66.33; H 3.54; N 14.06. Mass spectrum, *m/z*: 398.96 $[M+H]^+$; calculated *M* 398.38. IR spectrum, ν, cm^{-1}: 3418 (OH); 3195 (NH); 2234 (C≡N); 1706 (C=O); 1604 [$\delta(NH_{sec})$], [$\nu(NH_{sec})$]. ^1H NMR spectrum, δ, ppm: 8.58 s (COOH, 2H); 8.51 s (NH, 2H); 8.01 s (H^1, 2H); 7.52–7,53 d (H^2, 1H; *J* = 2.05 Hz); 7.62–7.63 d (H^3, 2H; *J* = 2.01 Hz).

Method 2 (general procedure). A solution of 0.14 g (0.1 mmol) of anhydrous potassium carbonate in 0.7 mL of water was added to a solution of 0.1 mmol of 4-(4,5-dicyano-2-nitrophenoxy)-, 4-(4,5-dicyano-2-nitrophenylsulfanyl)-, and 4-(4,5-dicyano-2-nitrophenylamino)benzoic acid, and 0.1 mmol of corresponding benzoic acid in 5 mL DMF in a two-necked flask equipped with a reflux condenser. The reaction mixture was stirred at 80–90°C for 24 h. The precipitate that formed was filtered off, washed with 5% aqueous HCl until colorless washings, and dried in air at 70–80°C.

Compound **4** could not be prepared by this method.

4,4'-(4,5-Dicyano-1,2-phenylenedioxy)dibenzoic acid (2) was synthesized from 0.31 g of 4-(4,5-dicyano-2-nitrophenoxy)benzoic acid and 0.14 g of *para*-hydroxybenzoic acid. After the reaction had been complete, the reaction mixture was poured into 5% aqueous HCl, the precipitate that formed was filtered off, washed with 2% aqueous HCl, and dried in air at 70–80°C. Yield 0.21 g (51% per **1**). Found, %: C 64.63; H 3.14; N 6.67; $C_{22}H_{12}N_2O_6$; Calculated, %: C 66.00; H 3.02; N 7.00. IR spectrum, ν, cm^{-1}: 3454 (OH); 2237 (C≡N); 1708 (C=O); 1220 (Ar–O–Ar).

4,4'-(4,5-Dicyano-1,2-phenylenedisulfanyl)dibenzoic acid (3) was synthesized from 0.33 g of 4-(4,5-dicyano-2-nitrophenoxy)benzoic acid and 0.15 g of *para*-mercaptobenzoic acid. After the reaction had been complete, the reaction mixture was acidified with 5% aqueous HCl, the precipitate that formed was filtered off, washed with 2% aqueous HCl, and dried in air at 70–80°C. Yield 0.27 g (62% per **1**). Found, %: C 60.90; H 2.90; N 6.24; S 14.52; $C_{22}H_{12}N_2O_4S_2$; Calculated, %: C 61.10; H 2.80; N 6.48; S 14.83. IR spectrum, ν, cm^{-1}: 3417 (OH); 2229 (C≡N); 1710 (C=O); 1104 (Ar–S–Ar).

Synthesis of cobalt octa-[4,5-(4-carboxyphenyl (oxy/sulfanyl/amino)]phthalocyanines 5–7 *(general procedure).* A fine mixture of 0.33 mmol of corresponding substituted phthalonitile, 54 mg (0.20 mmol) of cobalt chloride tetrahydrate, and 60 mg (1 mmol) of urea was heated at 160–170°C until solidification, after which it was ground, washed with acidified water and acetone, and dried in air at 70–80°C.

Cobalt octa-[4,5-(4-carboxyphenoxy)]phthalocyanine (5) was synthesized from 120 mg of phthalonitrile **2**. Yield 82 mg (68%). Found, %: C 63.10; H 3.04; N 6.55; $C_{88}H_{48}N_8O_{24}Co$; Calculated, %: C 63.66; H 2.91; N 6.75. Mass spectrum, *m/z*: 1676.17 $[M+O]^+$; calculated 1660.32. IR spectrum, ν, cm^{-1}: 3443 (OH); 1712 (C=O); 1224 (Ar–O–Ar).

Cobalt octa-[4,5-(4-carboxyphenylsulfanyl)]-phthalocyanine (6) was synthesized from 130 mg of phthalonitrile **3**. Yield 95 mg (73%). Found, %: C 59.17; H 2.82; N 6.10; $C_{88}H_{48}N_8O_{16}S_8Co$. Calculated, %: C 59.09; H 2.70; N 6.26. Mass spectrum, *m/z*: 1789.78 $[M+H]^+$; calculated *M* 1788.81. IR spectrum, ν, cm^{-1}: 3447 (OH), 1711 (C=O), 1104 (Ar–S–Ar).

Cobalt octa-[4,5-(4-carboxyphenylamino)]-phthalocyanine (7) was synthesized from 120 mg of phthalonitrile 4. Yield 49.4 mg (41%). Found, %: C 63.70; H 3.55; N 13.18. $C_{88}H_{56}N_{16}O_{16}Co$. Calculated, %: C 63.96; H 3.42; N 13.56. Mass spectrum, *m/z*: 1652.36 $[M+4H]^+$, calculated *M* 1651,33. IR spectrum, ν, cm^{-1}: 3413 (OH); 3172 (NH); 1703 (C=O); 1602 [$\delta(NH_{sec})$]; 1434 [$\nu(NH_{sec})$].

ACKNOWLEDGMENTS

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CONFLICT OF INTERESTS

No conflict of interests was declared by the authors.

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