

# Phthalonitriles Containing Ester Groups and Copper Phthalocyanines Based on Them

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**Abstract**—Phthalonitriles containing ester groups were obtained by acylation of 4-hydroxyphthalonitrile and esterification of 4-(*p*-carboxyphenoxy)phthalonitriles. On the basis of these phthalonitriles the respective copper phthalocyanines were synthesized. Spectral and some other physical and chemical properties of the synthesized compounds were investigated.

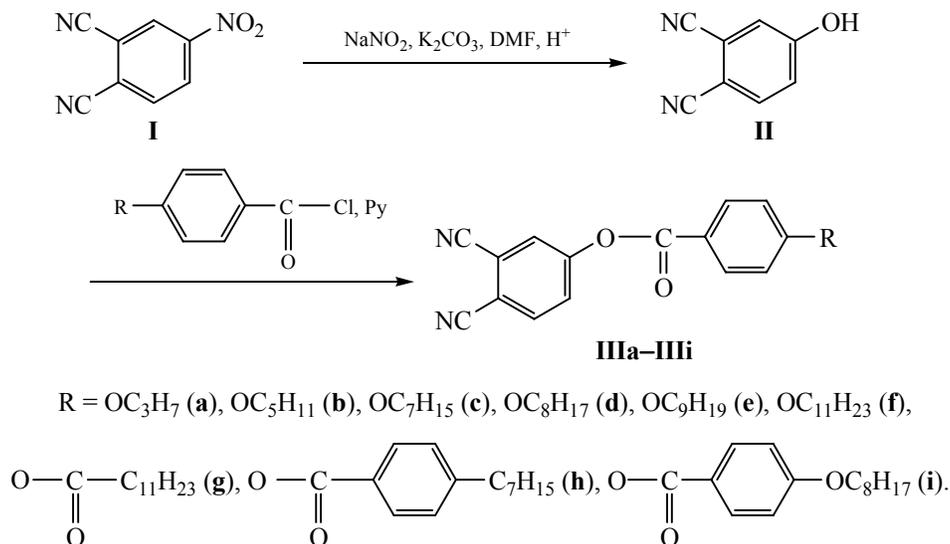
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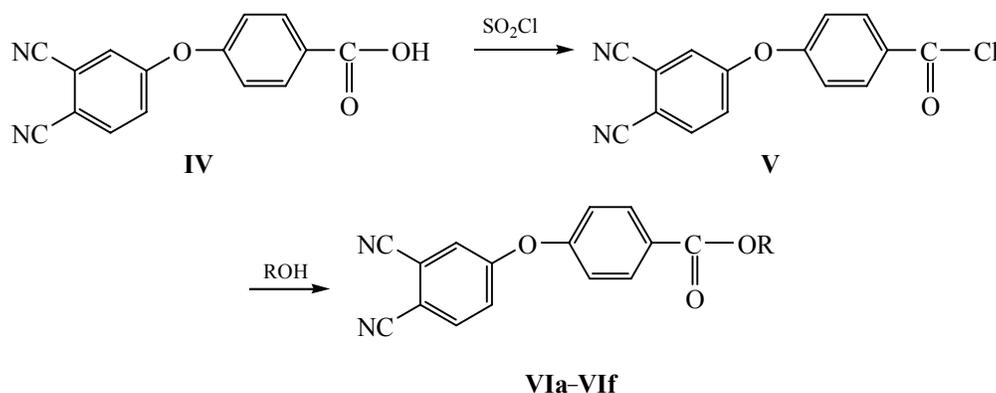
Complexes of phthalocyanines with metals (MPC) have valuable practical properties and can be used in various fields of science and technology. Each specific field of application requires well-defined properties that can be added to MPC by chemical modification. Phthalocyanines containing ether groups and well soluble in organic solvents are of definite interest. Already there is an evidence on the possibility of their practical use [1–4]. However, the information concerning the metal phthalocyanines containing ester groups is rather poor, although we believe that they can possess other valuable properties besides the solubility in organic solvents.

In this paper the synthesis and properties of substituted phthalonitriles containing ester groups and copper phthalocyanines based on them are considered.

Initial phthalonitriles were synthesized by two procedures.

By the first procedure, 4-nitrophthalonitrile (**I**) was transformed into a 4-hydroxyphthalonitrile (**II**) by the reaction of nucleophilic substitution [5]. Then the nitrile **II** was O-acylated in pyridine medium. As acylation agents substituted benzoic acid chlorides were used obtained by the interaction of respective acid with an excess of thionyl chloride. Thus a series of *R*-benzoyloxyphthalonitriles (**IIIa–IIIi**) was prepared [6].





R = C<sub>3</sub>H<sub>7</sub> (**a**), C<sub>4</sub>H<sub>9</sub> (**b**), C<sub>5</sub>H<sub>11</sub> (**c**), C<sub>7</sub>H<sub>15</sub> (**d**), C<sub>8</sub>H<sub>17</sub> (**e**), C<sub>9</sub>H<sub>19</sub> (**f**).

The optimized conditions of the acylation process found by applying mathematical modeling are as follows: the molar ratio of reagents 1:1, temperature 84 to 85°C, and the reaction time 17 h [7]. For the isolation of target compounds from the reaction mixtures we used the difference in the solubility in organic solvents of the original substances and the products obtained. To confirm individuality of the phthalonitriles we used the method of chromatography-mass spectrometry [6].

The (*p*-alkoxycarbonylphenoxy)phthalonitriles **VIa–VI f** were obtained by the second procedure. Initial 4-(*p*-carboxyphenoxy)phthalonitrile (**IV**) was synthesized by the reaction of 4-nitrophthalonitrile with *p*-hydroxybenzoic acid in DMF medium in the presence of potassium carbonate [8]. Then 4-(*p*-carboxyphenoxy)phthalonitrile (**IV**) was refluxed with an excess of thionyl chloride to obtain the corresponding chloride (**V**) and the latter was subjected to esterification. After the reaction completion, an excess of the alcohol used for the esterification was distilled off in a vacuum [9].

All synthesized phthalonitriles are powders (**IIIa–III f**, **VIc–VI f**) or waxy substances (**IIIg–III i**, **VIc–VI f**) of white to cream color. All compounds are readily soluble in organic solvents (chloroform, acetone) and insoluble in water and aqueous alkaline solutions.

The structure of the phthalonitriles obtained was confirmed by <sup>1</sup>H NMR and IR spectroscopy. In the <sup>1</sup>H NMR spectra of the synthesized nitriles in deuteriochloroform the signals of protons of alkoxy substituent were observed in the strong field. The signals positions do not depend on the nature of the hydrocarbon radical. In a weak field the signals occurred of the protons of benzene ring of the substituted benzoic acid

residue, and in the weakest field the signals of protons of the phthalonitrile fragment were present [6].

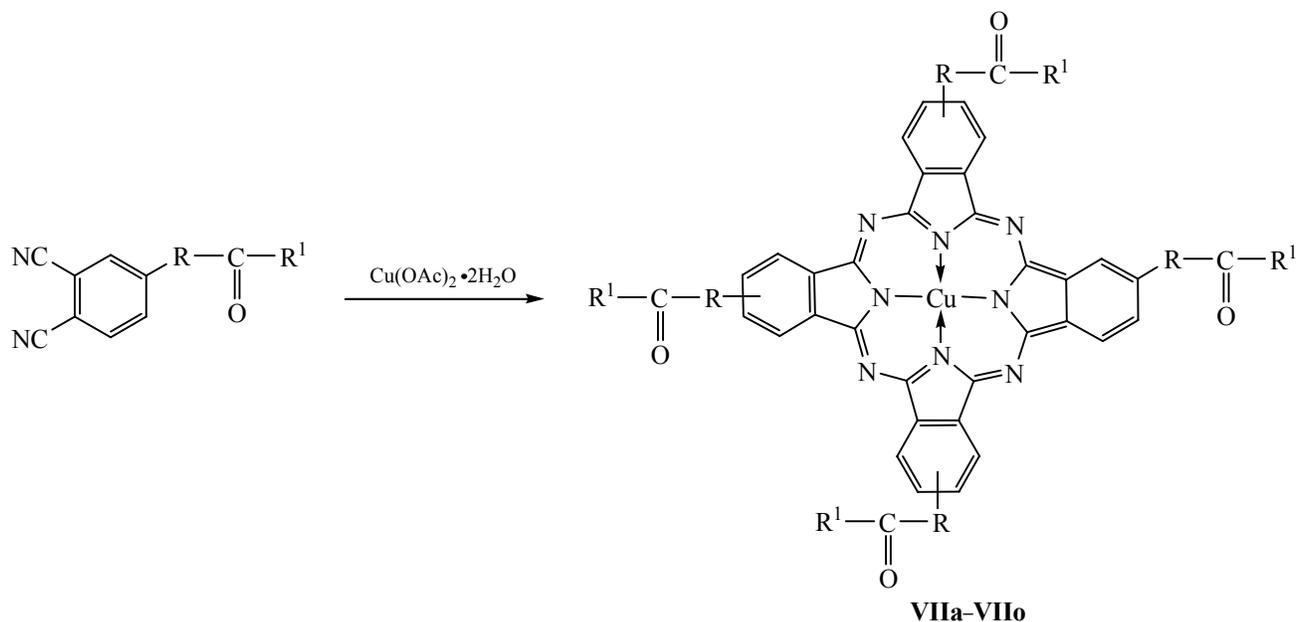
In the IR spectra of the synthesized phthalonitriles the absorption bands were observed characteristic of phthalonitriles [10]. In the region of 2232–2240 cm<sup>-1</sup> the spectra of all compounds contain absorption bands corresponding to vibrations of the nitrile group, and in the range of 1670–1750 cm<sup>-1</sup> the absorption bands appear characteristic of vibrations of the ester C=O bonds. In the spectra of (*p*-alkoxycarbonylphenoxy) phthalonitriles **VIa–VI f** in the region of 1244–1292 cm<sup>-1</sup> absorption appears due to the presence of aryloxy groups [11].

On the basis of the synthesized phthalonitriles respective copper phthalocyanines **VIIa–VII o** were synthesized by the “nitrile” method.

The synthesized compounds are powders of blue-green color whose physical and chemical properties are largely determined by the nature of functional substituents. The presence in their composition of ester groups with different alkyl chains imparts them with the solubility in organic solvents (chloroform, benzene, DMF). This allowed us to apply column chromatography on alumina for their purification.

In the IR spectra of the complexes the absorption bands were detected in the regions of 1612–1624, 1505–1524, 1342–1360, 1246–1288, 1170–1188, 1140–1150, 1116–1130, 1080–1092, 1048–1060, 910–950, 850–880, 770–780, and 734–736 cm<sup>-1</sup>, characteristic of phthalocyanines [12]. Besides, the spectra contained the absorption bands corresponding to the functional substituents.

The <sup>1</sup>H NMR spectra of the obtained complexes are similar in nature and contain the signals of aliphatic



R = O, R<sup>1</sup> = C<sub>6</sub>H<sub>4</sub>OC<sub>3</sub>H<sub>7</sub> (**a**), C<sub>6</sub>H<sub>4</sub>OC<sub>5</sub>H<sub>11</sub> (**b**), C<sub>6</sub>H<sub>4</sub>OC<sub>7</sub>H<sub>15</sub> (**c**), C<sub>6</sub>H<sub>4</sub>OC<sub>8</sub>H<sub>17</sub> (**d**), C<sub>6</sub>H<sub>4</sub>OC<sub>9</sub>H<sub>19</sub> (**e**), C<sub>6</sub>H<sub>4</sub>OC<sub>11</sub>H<sub>23</sub> (**f**),

C<sub>6</sub>H<sub>4</sub>OCOC<sub>11</sub>H<sub>23</sub> (**g**), C<sub>6</sub>H<sub>4</sub>OCOC<sub>6</sub>H<sub>4</sub>C<sub>7</sub>H<sub>15</sub> (**h**), C<sub>6</sub>H<sub>4</sub>OCOC<sub>6</sub>H<sub>4</sub>OC<sub>8</sub>H<sub>17</sub> (**i**); R = O—

R<sup>1</sup> = C<sub>3</sub>H<sub>7</sub> (**j**), C<sub>4</sub>H<sub>9</sub> (**k**), C<sub>5</sub>H<sub>11</sub> (**l**), C<sub>7</sub>H<sub>15</sub> (**m**), C<sub>8</sub>H<sub>17</sub> (**n**), C<sub>9</sub>H<sub>19</sub> (**o**).

protons in the strong field and aromatic protons in the weak field [6, 9].

In the <sup>1</sup>H NMR spectra of the synthesized compounds a downfield shift of the signals of aliphatic protons can be noted upon increase in their distance from the electron-acceptor carbonyl group, due to the rapid decrease in the negative inductive effect of the carboxy oxygen of the ester groups [13].

**Thermal stability.** Investigation of stability of the complexes **VIIa–VIIo** toward the thermo-oxidative degradation showed a similarity in their behavior. In the first phase upon heating in air to 175°C the TG curves registered a slight decrease in the mass of the samples. The additional examination by the IR and electron absorption spectroscopy (EAS) of the phthalocyanine samples before the DTA experiment and after heating to 180°C showed their identity. This observation suggests that the changes in the derivatograms do not relate to the processes of destruction of the MPC. At further heating the decomposition of compounds becomes complicated, as evidences the presence of several maxima in the DTA and DTG curves.

Analysis of the TG leads to the following assumptions. At heating from 180°C to 300–350°C

there is an intense weight loss of the samples. Analyzing the IR spectra of the samples after heating to 350°C and comparing them with the IR spectra of starting material we note a significant decrease in the intensity of the absorption bands characterizing vibrations of the functional substituents (C=O, C–H, etc.). The samples heated in this temperature range became practically insoluble in organic solvents. However, the EAS of the solutions in DMF have the form typical for metallophthalocyanines. These data suggest that the process of thermal degradation is associated with the changes in the substituents. The thermooxidative degradation of tetra-4-(*p*-alkoxycarbonylphenoxy)copper phthalocyanines **VIIj–VIIo** with the removal of ester groups occurs at temperatures around 280°C [9], in contrast to the complexes **VIIa–VIIi** for which this process takes place at 180°C.

At further heating (above 350°C) thermal oxidative destruction of the phthalocyanine macrocycle occurs to the formation of copper oxides. In general it is noted that the studied phthalocyanines are much less stable thermally than the copper phthalocyanines without substituents.

**The electron absorption spectra** of all complexes in organic solvents contain two absorption bands in the

Characteristics of electron absorption spectra of phthalocyanines

Comp. no.	R <sup>1</sup>	$\lambda_{\max}$ , nm ( $D/D_{\max}$ )	
		DMF	CHCl <sub>3</sub>
<b>VIIa</b>	H <sub>7</sub> C <sub>3</sub> OH <sub>4</sub> C <sub>6</sub>	671 (1.00), 610 (0.63)	673 (1.00), 610 (0.75)
<b>VIIb</b>	H <sub>11</sub> C <sub>5</sub> OH <sub>4</sub> C <sub>6</sub>	670 (1.00), 615 (0.74)	673 (1.00) 613, (0.76)
<b>VIIc</b>	H <sub>15</sub> C <sub>7</sub> OH <sub>4</sub> C <sub>6</sub>	671 (1.00), 671 (0.75)	673 (1.00), 611 (0.79)
<b>VIIId</b>	H <sub>17</sub> C <sub>8</sub> OH <sub>4</sub> C <sub>6</sub>	670 (1.00), 617 (0.75)	672 (1.00), 611 (0.77)
<b>VIIe</b>	H <sub>19</sub> C <sub>9</sub> OH <sub>4</sub> C <sub>6</sub>	671 (1.00), 615 (0.72)	672 (1.00), 614 (0.76)
<b>VIIIf</b>	H <sub>23</sub> C <sub>11</sub> OH <sub>4</sub> C <sub>6</sub>	670 (1.00), 612 (0.75)	672 (1.00), 617 (0.80)
<b>VIIg</b>	H <sub>23</sub> C <sub>11</sub> OCO <sub>4</sub> C <sub>6</sub>	672 (1.00), 611 (0.45)	672 (1.00), 616 (0.51)
<b>VIIh</b>	H <sub>15</sub> C <sub>7</sub> H <sub>4</sub> C <sub>6</sub> OCO <sub>4</sub> C <sub>6</sub>	670 (1.00), 618 (0.84)	672 (1.00), 614 (0.96)
<b>VIIi</b>	H <sub>18</sub> C <sub>8</sub> OH <sub>4</sub> C <sub>6</sub> OCO <sub>4</sub> C <sub>6</sub>	670 (1.00) 615 (0.86)	672 (1.00), 617 (0.93)
<b>VIIj</b>	H <sub>7</sub> C <sub>3</sub> O	678 (1.00), 614 (0.72)	679 (1.00), 612 (0.75)
<b>VIIk</b>	H <sub>9</sub> C <sub>4</sub> O	678 (1.00), 615 (0.74)	679 (1.00), 613 (0.78)
<b>VIIl</b>	H <sub>11</sub> C <sub>5</sub> O	679 (1.00), 614 (0.70)	679 (1.00), 612 (0.80)
<b>VIIm</b>	H <sub>15</sub> C <sub>7</sub> O	678 (1.00) 615 (0.72)	679 (1.00), 613 (0.87)
<b>VIIIn</b>	H <sub>17</sub> C <sub>8</sub> O	678 (1.00), 615 (0.74)	679 (1.00), 612 (0.85)
<b>VIIIo</b>	H <sub>19</sub> C <sub>9</sub> O	678 (1.00), 615 (0.70)	665 (1.00), 611 (0.86)

region of 600–700 nm, with the intensity ratio depending on the concentration of phthalocyanine in the solution (see the table and the figure). Upon dilution the intensity of the longwave band decreases to a lesser extent, than the shortwave band. This phenomenon and the observed changes in the intensity ratio of the absorption bands indicate a tendency of the metallocomplexes to association in solutions. In addition, the association is confirmed by the temperature dependence of the intensity ratio of the absorption bands and by the deviation from the Bouguer–Lambert–Beer law at the concentrations above  $10^{-7}$  mol l<sup>-1</sup> as well.

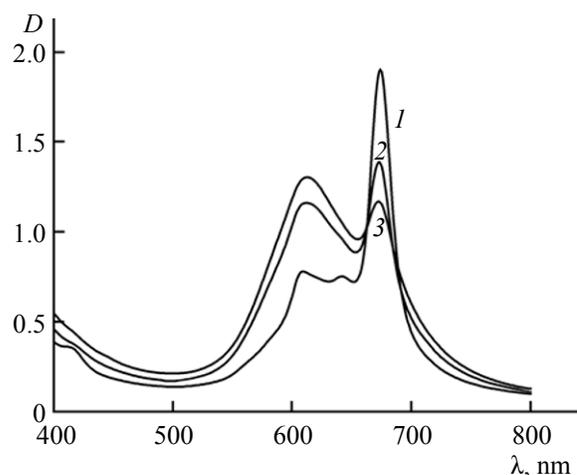
Proceeding from the structure of the synthesized complexes and the published data [14, 15], we can assume that in the solutions may form dimers, both due to hydrogen bonding between the peripheral substituents in the phthalocyanine molecules, and owing to  $\pi$ – $\pi$  interactions.

By an example of tetra-4-[(4'-heptyloxybezoyl)oxy] copper phthalocyanine (**VIIa**) we studied the processes of association of such complexes in benzene, *o*-xylene, and chloroform by the methods of calorimetric dilution and electron absorption spectroscopy. In the benzene, chloroform and *o*-xylene solutions at the concentration of the complex from  $5 \times 10^{-6}$  to  $7 \times 10^{-5}$  M there is a

monomer–dimer equilibrium with the dimerization of the  $\pi$ – $\pi$  type [16].

The position of the longwave band in the electron absorption spectra depends on the location of the ester group. When it is far from the macrocycle, the absorption occurs at longer wavelength (see the table).

For all the synthesized complexes we observed that the solvent nature does not affect the position of the absorption bands (see the figure).



Electron absorption spectra of compound **VIIc** in various solvents at the concentration  $5 \times 10^{-5}$  M: (1) *o*-xylene, (2) benzene, and (3) chloroform.

**The liquid crystal properties.** Study of the synthesized complexes using polarization microscopy revealed that they all exhibit thermotropic mesomorphism [9, 17, 18]. Comparing the data obtained for the tetra-4-[(*p*-alkoxycarbonyl)phenoxy]copper (**VIIj–VIIo**), and tetra-4-[(*R*-benzoyl)oxy]copper phthalocyanines (**VIIa–VIIi**) that differ from each other by the location of ester group, we can draw the following conclusions: (1) The increase in the number of carbon atoms in the alkyl chain decreases the phase transition temperatures of the complexes of both types, but the melting points of tetra-4-[(*p*-alkoxycarbonyl)phenoxy]copper phthalocyanines (**VIIj–VIIo**) with  $n > 7$  begin to grow, that is not observed for the compounds **VIIa–VIIi**. (2) At more distant location of the ester group from the macrocycle the temperature of transition of the phthalocyanines into the mesomorphic state raises.

It is also important to note that compounds **VIIIh** and **VIIIi** and the copper tetra-4-[(*p*-alkoxycarbonyl)phenoxy]phthalocyanines **VIIj–VIIo** are capable of vitrification with preservation of the mesophase texture that makes them promising for application in optoelectronics [2].

The tendency of compounds to the associative processes is a prerequisite for the formation by such substances of a liomesophase [2]. To test this assumption, we carried out a study of several synthesized copper complexes [9, 17, 18].

We found that among the tetra-4-[(*R*-benzoyl)oxy]copper phthalocyanines **VIIa–VIIi** only the complexes that include alkoxy groups (**VIIa–VIIf**, **VIIIi**) form liomesophase in a binary system with organic solvent. It should also be noted that these complexes can show the mesomorphism only with low-polarity and non-polar solvents (chloroform, benzene). In contrast to these compounds, copper tetra-4-[(*p*-alkoxycarbonyl)phenoxy]phthalocyanines **VIIj–VIIo** are capable to form liomesophase in binary systems with a wider range of organic solvents (chloroform, benzene, DMF, etc.).

The synthesized phthalocyanines are well soluble in organic solvents and can be used as a fat-soluble dyes for dyeing waxes, hydrocarbons, plastics, and rubber [19].

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