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Nucleophilic Substitution in 4-Bromo-5-nitrophthalodinitrile: V.[1] Synthesis of 5-Nitro-4-(4-R-phenoxy)phthalodinitriles and Phthalocyanines Derived from Them

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Abstract—A series of aryloxy-substituted phthalodinitriles were prepared by nucleophilic aromatic substitution of bromine in 4-bromo-5-nitrophthalodinitrile, and the corresponding phthalocyanines were synthesized. The physicochemical properties of phthalocyanines depend on the substituent in the aryl moiety.

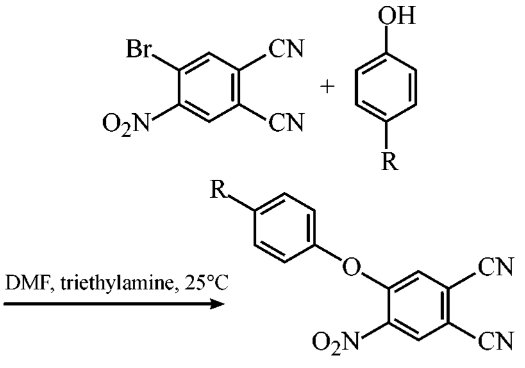
Phthalocyanines are widely used as organic dyes and pigments [2], catalysts of redox reactions [3], semiconductor materials [4], and gas sensors [5]. However, unsubstituted phthalocyanines are poorly soluble, which restricts their use.

Syntheses of soluble octasubstituted phthalocyanines were reported in numerous papers [6–9]. As a rule, compounds with identical substituents were prepared. Data on solubility in organic solvents of complexes with different peripheral substituents are scarce [1, 10–13]. This may be due to difficult availability of the corresponding initial compounds, disubstituted phthalocyanines.

We have reported previously on synthesis of 5-nitro-4-phenoxyphthalodinitrile by nucleophilic aromatic substitution of bromine in 4-bromo-5-nitrophthalodinitrile [14] and on preparation from this compound of metal phthalocyanines [12]. It was noted that bulky peripheral phenyl substituents make the phthalocyanines readily soluble in organic solvents.

Proceeding with these studies, with the aim to elucidate the effect of substituent in the phenyl rings on the physicochemical properties of phthalocyanines, we prepared a series of 5-nitro-4-(4-R-phenoxy)phthalodinitriles including 5-nitro-4-(4-*tert*-butylphenoxy)phthalodinitrile **II**, 5-nitro-4-(4-nitrophenoxy)phthalodinitrile **III**, and 5-nitro-4-(4-carboxyphenoxy)phthalodinitrile **IV**, and also the corresponding octasubstituted phthalocyanines.

Phthalodinitriles **II**–**IV** were prepared as follows:



II–IV

R = *t*-Bu (**II**), NO_2 (**III**), COOH (**IV**).

We showed previously that in 4-bromo-5-nitrophthalodinitrile **I** the halogen atom undergoes nucleophilic substitution first [1, 14–16]. This is due to the presence in the *o*-position of a strong electron acceptor, nitro group, decreasing the electron density on the carbon atom bound to bromine.

Attempts to prepare **II**–**IV** by the procedure used for preparing 5-nitro-4-phenoxyphthalodinitrile [14] failed. We succeeded in preparing **II**–**IV** by reaction of **I** with *p*-substituted phenols in the presence of triethylamine.

Compounds **II**–**IV**, recrystallized from ethanol, are yellow powders insoluble in water and soluble in benzene, acetone, chloroform, ethanol, and DMF.

After preparing and identifying dinitriles **II**–**IV**, we synthesized from them the corresponding octasubstituted phthalocyanines. Metal complexes **IIa**–**IIc**, **IIIa**, **IIIb**, and **IVa** were prepared by fusion with the corresponding metal acetates at 190–200°C for 1 h.

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[1] For communication IV, see [1].

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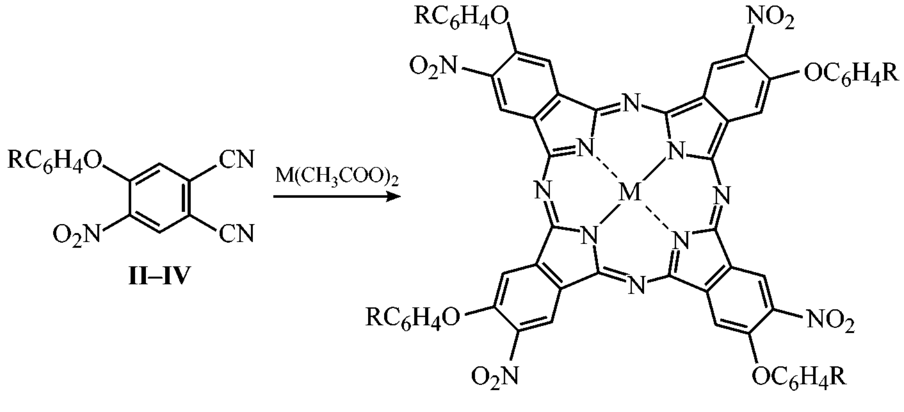
Metal-free tetra-5-nitrotetra-4-(4-*tert*-butylphenoxy)phthalocyanine **IId** was prepared by demetallation of its magnesium complex **IIc** (reprecipitation from concentrated sulfuric acid).



II–IV

IIa–IId, IIIa, IIIb, IVa

R = *t*-Bu (**II**), NO_2 (**III**), COOH (**IV**); M = Cu (**IIa**, **IIIa**), Co (**IIb**, **IIIb**, **IVa**), Mg (**IIc**), 2H (**IId**).

The choice of the purification procedure was governed by the specific features of the phthalocyanines. Compounds **IIa**–**IId**, which are soluble in chloroform, were purified by column chromatography (silica gel L 40/100, chloroform). Compounds **IIIa** and **IIIb** were purified by reprecipitation from concentrated sulfuric acid. Complex **IVa**, which is readily soluble in aqueous alkaline solutions, was purified by dissolution in 5% aqueous NaOH, followed by precipitation with aqueous HCl.

It should be noted that the nature of the substituent strongly affects the physicochemical properties of the complexes. For example, bulky *tert*-butyl groups increase the solubility of the complex, as compared to tetra-5-nitrotetra-4-phenoxyphthalocyanines, in chloroform, benzene, acetone, and DMF. On the contrary, electron-withdrawing nitro and carboxy groups at the 4-position decrease the solubility in chloroform and benzene. Previously a similar trend was observed for cobalt tetra-5-nitrotetra-4-(4-sulfophenoxy)phthalocyanine [12].

The electronic absorption spectra of the complexes are typical of phthalocyanines and contain two absorption bands at about 330 (Soret band) and 670–700 nm (*Q* band) (see table and figure).

Substituents in the 4-position of the phenyl ring affect the position of the long-wave band insignificantly. Four bulky electron-donating *tert*-butyl groups cause a slight bathochromic shift of the *Q* band relative to tetra-5-nitrotetra-4-phenoxyphthalocyanines, whereas electron-withdrawing substituents (NO_2, COOH) cause a weak hypsochromic shift (see table and figure). Apparently, the hypsochromic shift is due to a decrease in the electron-donor power of the phen-

Yields, position of the first absorption band in the electronic absorption spectra, and analytical data for tetra-5-nitrotetra-4-(4-R-phenoxy)phthalocyanines

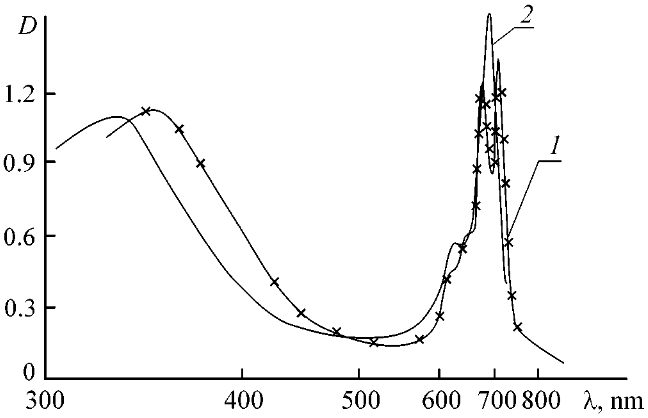
Comp. no.	Yield, %	λ_{max}, nm			Found, %			Formula	Calculated, %		
		H_2SO_4	DMF	chloroform	C	H	N		C	H	N
IIa	42	808	686	698	64.5	4.2	12.2	$C_{72}H_{60}CuN_{12}O_{12}$	64.1	4.5	12.5
IIb	38	784	677	686	64.1	4.3	12.3	$C_{72}H_{60}CoN_{12}O_{12}$	64.3	4.5	12.5
IIc	32	–	694	714	66.4	4.3	12.4	$C_{72}H_{60}MgN_{12}O_{12}$	66.1	4.6	12.8
IId	29	789, 817	694	683, 714	67.5	4.4	12.8	$C_{72}H_{62}N_{12}O_{12}$	67.2	4.8	13.1
IIIa	65	794	686	–	51.2	1.6	17.6	$C_{56}H_{24}CuN_{16}O_{20}$	51.5	1.8	17.2
IIIb	61	772	676	–	51.4	1.6	17.4	$C_{56}H_{24}CoN_{16}O_{20}$	51.7	1.9	17.2
IVa	54	774	668	–	55.2	2.4	12.7	$C_{60}H_{28}CuN_{12}O_{20}$	55.6	2.2	13.0

oxy group on introducing an electron-withdrawing substituent.

The electronic spectra of **IId** in organic solvents resemble those of tetra-5-nitrotetra-4-phenoxyphthalocyanine, i.e., in DMF there is a single strong absorption band in the visible range, whereas in chloroform a two-band pattern typical of metal-free phthalocyanines [17] is observed (see table and figure).

The spectra of **IIIa**, **IIIb**, and **IVa** in DMF are somewhat broadened, which may be due to their tendency to association.

As expected, in going from organic solvents to concentrated sulfuric acid the long-wave absorption band undergoes a significant bathochromic shift, which is due to protonation of the porphyrazine ring at the *meso* nitrogen atoms [18]; the effect of substituents on the position of the long-wave absorption band is similar to that observed in organic solvents (see table).



Electronic absorption spectra in chloroform: (*1*) tetra-5-nitrotetra-4-(4-*tert*-butylphenoxy)phthalocyanine **IId** (c 1.3 × 10^{-5} M) and (*2*) cobalt tetra-5-nitrotetra-4-(4-*tert*-butylphenoxy)phthalocyanine **IIb** (c 1.3 × 10^{-5} M).

EXPERIMENTAL

The electronic absorption spectra were taken on a Specord M-40 spectrometer at room temperature in the range 300–900 nm (solutions in DMF, $CHCl_3$, and concentrated H_2SO_4).

The melting points were determined with a Boetius heating stage.

4-Bromo-5-nitrophthalodinitrile **I** was prepared as described in [19].

5-Nitro-4-(4-R-phenoxy)phthalodinitriles II–IV (general procedure). To 30 ml of DMF at 20–25°C we added 3.6 mmol of dinitrile **I** and 5.4 ml of appropriate phenol, and then 5.4 mmol of triethylamine. The mixture was stirred for 6 h at room temperature. After reaction completion, the mixture was poured into 50 ml of a water–ice mixture. The precipitate was filtered off and washed with 5% alkali and water until the wash water became neutral and colorless. The completeness of removal of hydroxy compounds was checked by the negative reaction with a diazo compound. The reaction products were recrystallized from ethanol.

5-Nitro-4-(4-*tert*-butylphenoxy)phthalodinitrile II. Yellow powder soluble in ethanol, acetone, benzene, chloroform, and DMF. Yield 45%, mp 176–178°C. Found, %: C 67.8; H 4.4; N 13.3. $C_{18}H_{15}N_3O_3$. Calculated, %: C 67.3; H 4.7; N 13.1.

5-Nitro-4-(4-nitrophenoxy)phthalodinitrile III. Yellow powder soluble in ethanol, acetone, benzene, chloroform, and DMF. Yield 56%, mp 182–185°C. Found, %: C 51.1; H 1.6; N 17.5. $C_{14}H_6N_4O_5$. Calculated, %: C 51.5; H 1.9; N 17.2.

5-Nitro-4-(4-carboxyphenoxy)phthalodinitrile IV. Yellow powder soluble in ethanol, acetone, benzene, chloroform, and DMF. Yield 31%, mp 180–182°C. Found, %: C 58.6; H 2.5; N 13.3. $C_{15}H_7N_3O_5$. Calculated, %: C 58.3; H 2.2; N 13.0.

Tetra-5-nitrotetra-4-(4-R-phenoxy)phthalocyanines IIa–IId, IIIa, IIIb, and IVa (general procedure). A mixture of 0.62 mol of 5-nitro-4-(4-R-phenoxy)phthalodinitrile and 0.17 mmol of appropriate metal acetate was thoroughly ground, heated in a quartz ampule to 190–200°C, and kept at this temperature for 1 h. The cake was washed with dilute HCl until the filtrate became colorless and with water to remove chloride ions, and then dried at 60°C.

Metal-free phthalocyanine **IId** was prepared by demetallation of **IIc** (reprecipitation from concentrated sulfuric acid).

Compounds **IIa**–**IId** were extracted with chloroform, and the solvent was evaporated at reduced pressure. Refining was performed by column chromatography (silica gel L 40/100, chloroform). Complexes **IIIa** and **IIIb** were recrystallized from concentrated sulfuric acid with subsequent extraction of impurities with acetone. Compound **IVa** was purified by dissolution in 25 ml of 5% aqueous NaOH. The resulting green solution was filtered, and the filtrate was acidified with HCl to weakly acidic reaction. The blue-green precipitate was filtered off and washed with distilled water to neutral reaction.

The analytical data, yields of the compounds, and position of the Q band in the electronic absorption spectra are listed in the table.

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