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Phthalocyanines and Related Compounds: XLV.[1] Nucleophilic Substitution of Chlorine in Tetrachlorophthalonitrile: Synthesis of Aryloxy-Aubstituted Phthalonitriles and Phthalocyanines Derived from Them

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Abstract — Nucleophilic substitution of chlorine in tetrachlorophthalonitrile by the reaction with aryloxy anions is studied. Depending on the reactant ratio, the products of substitution of one, two, and/or three chlorine atoms are formed. Their tetramerization gives aryloxychloro-substituted phthalocyanines having the absorption band in the near-IR range.
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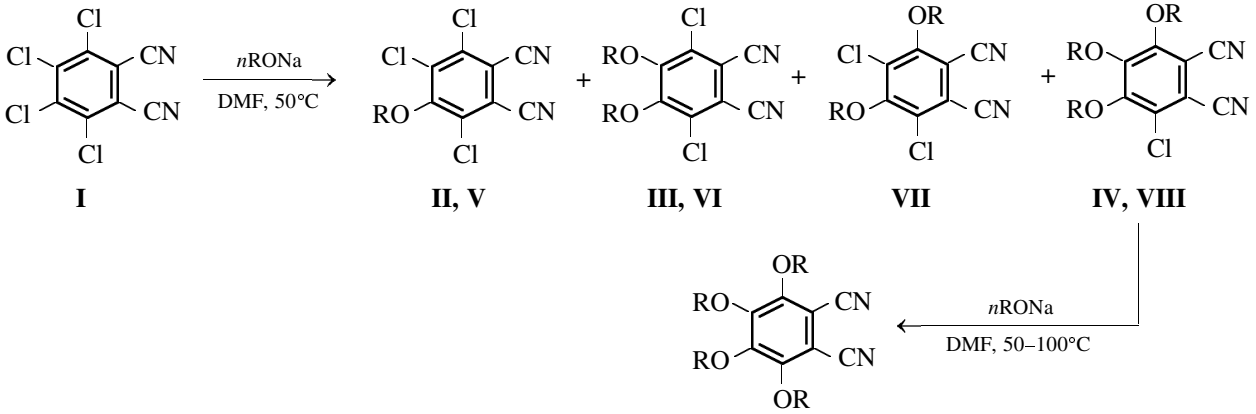
We have studied previously the reaction of tetrachlorophthalonitrile **I** with thiols [2]. We found that substitution of chlorine is regiospecific, with the 4-Cl atom replaced first and the 5-Cl atom, second. Depending on the reactant ratio, products with various degrees of substitution, up to tetrasubstituted compounds, can be prepared.

Proceeding with studies of the nucleophilic substitution in tetrachlorophthalonitrile, we examined its reactions with some O-nucleophiles, namely, with aryloxy and alkoxy anions at varied molar ratios of the reactants. The results of the reactions of dinitrile **I** with the above nucleophiles are shown in Scheme 1 and in Table 1.

Scheme 1.



R = Ph (**II**–**IV**), Py (**V**–**VIII**), Py = 3-pyridyl.

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

The reaction of dinitrile **I** with sodium phenolate was carried out at 50°C in DMF for 3 h at the reactant molar ratio varied from 1 : 1 to 1 : 4. In all the cases, the reaction mixture contained several products. All of them were isolated pure and characterized.

At 1 : 1 molar ratio, the conversion of phthalonitrile is incomplete. About 1/2 of the starting compound was recovered from the reaction mixture, and 30% of phenoxytrichlorophthalonitrile, the product of substitution of one chlorine with phenoxy group, was obtained. At 1 : 2 ratio, the amount of the recovered starting product **I** decreased to ~7%. The major reaction product was dinitrile **II** (53%), and only an insignificant amount (~10%) of the expected product of substitution of two chlorine atoms **III** was obtained. Compound **III** becomes the major product at 1 : 3 molar ratio of the reactants (yield 45%). In this case, the monosubstituted product **II** and a new product **IV** containing phenoxy groups (19 and 10% yields, respectively) were also obtained. We failed to obtain tetraphenoxyphthalonitrile, the product of complete substitution, at 1 : 4 molar ratio and the chosen temperature of 50°C. Although the yield of triphenoxyphthalonitrile increased considerably (up to 37%), product **III** with two phenoxy groups was isolated in this experiment in almost the same yield (31%).

An increase in the reaction temperature to the DMF boiling point at 1 : 4 molar ratio did not lead to the formation of the tetrasubstituted product either, although the yield of the trisubstituted product **IV** increased to 65%.

The reaction of dinitrile **I** with potassium 3-pyridolate in 1 : 2 molar ratio was carried out at 50°C for 3 h. However, contrary to the results obtained with thiols and phenol, four products were isolated and characterized in this case.

The major products were disubstituted compounds **VI** and **VII** isolated by column chromatography in a total yield of 38%. The monosubstituted product **V** was isolated in 13% yield, and the trisubstituted product **VIII**, in 9% yield (Table 2).

When dinitrile **I** and pyridolate were taken in 1 : 4 molar ratio, the same substances as in the previous case were isolated, but the major product was the trisubstituted compound **VIII**, whereas the content of disubstituted compounds **VI** and **VII** decreased considerably, and only traces of the monosubstituted compound were obtained. An increase in the temperature to ~100°C, similarly to the case of phenolate, led to an increase in the yield of the trisubstituted product **VIII** to 60%. However, this was accompanied by a considerable increase in the amount of tars contaminating the target product. Our attempt to substitute the last chlorine atom in dinitriles **IV** and **VIII** at 50°C led only to the recovery of the starting product, whereas at the solvent boiling point (~150°C) extensive tarring was observed.

Table 1. Yields of the aroxychloro-substituted phthalonitriles at various molar ratios of reactants[a]

RONa	Product	Dinitrile **I** : RONa molar ratio			
		1 : 1	1 : 2	1 : 3	1 : 4
R = Ph	**I**	48.3	6.7	–	–
	II	29.2	53.4[c]	19.2	[d]
	III	–	10.5[c]	45.3	30.5[c]
	IV	–	–	10.0	36.5[c]
R = Py[b]	**V**	[e]	13.0[c]	[e]	[d]
	VI		22.0[c]		7.8
	VII		16.2[c]		5.2
	VIII		9.1[c]		49.9[c]

[a] In all the cases, unless otherwise indicated, the yields of the products after their separation by preparative column chromatography (silica gel, elution with 1 : 2 benzene–hexane for R = Ph, with 2 : 1 benzene–ethyl acetate for R = 3-pyridyl) are presented. [b] Py = 3-pyridyl. [c] After crystallization from ethanol. [d] Traces, according to TLC. [e] The products were not isolated.

For all the compounds obtained, we recorded the ^{13}C NMR spectra. In the spectra of disubstituted compounds **III** and **VI**, as expected, the number of the carbon atom signals was twice smaller, which corresponds to the symmetric substitution. Similarly to 4,5-bis(phenylthio)-3,6-dichlorophthalinitrile formed regiospecifically from dinitrile **I** and thiophenol under the same conditions [2], we assumed that phthalonitriles **III** and **VI** were products of the substitution of two chlorine atoms in the symmetric positions 4 and 5 of tetrachlorophthalonitrile **I**. For the pyridyloxy-substituted dinitrile **VI**, this assumption was confirmed by single crystal X-ray diffraction.[2]

As already noted, the reaction of arylate ions, contrary to that of thiolate ones [2], does not lead to substitution of all the four chlorine atoms, which is evidently associated with a significant decrease in the electron deficiency of the phthalonitrile ring due to the effect of the already introduced three phenoxy groups and with the lower nucleophilicity of arylates as compared to thiolates. In the reactions with **I**, all the arylates under study, taken in any ratio to **I**,

[2] Detailed X-ray structural data will be published separately.

Table 2. Melting points, elemental analyses, and IR and mass spectral parameters of the phthalonitriles obtained

Product	mp, °C	Found, %				Formula	Calculated, %				ν, cm^{-1}	M^+
		C	H	Cl	N		C	H	Cl	N		
II	215–216	51.92 52.01	1.57 1.60	32.77 32.85	8.61 8.67	$C_{14}H_5Cl_3N_2O$	51.97	1.56	32.87	8.66	2241	322
III	131–133	62.91 62.99	2.62 2.63	18.56 17.63	7.30 7.36	$C_{20}H_{10}Cl_2N_2O_2$	63.01	2.64	18.60	7.35	2240	380
IV	162–164	71.09 71.15	3.44 3.47	8.00 8.11	6.37 6.44	$C_{26}H_{15}ClN_2O_3$	71.16	3.45	8.08	6.38	2239	438
V	218–219	48.02 48.10	1.19 1.23	32.75 32.83	12.87 12.94	$C_{13}H_4Cl_3N_3O$	48.11	1.24	32.77	12.95	2241	323
VI	260–262	56.43 56.48	2.06 2.10	18.48 18.55	14.61 14.67	$C_{18}H_8Cl_2N_4O_2$	56.42	2.10	18.50	14.62	2240	382
VII	252–253	56.36 56.45	2.05 2.08	18.45 18.55	14.59 14.65	$C_{18}H_8Cl_2N_4O_2$	56.42	2.10	18.50	14.62	2242	382
VIII	201–202	62.45 62.50	2.70 2.74	7.96 8.07	15.81 15.90	$C_{23}H_{12}ClN_5O_3$	62.52	2.74	8.02	15.85	2230	441

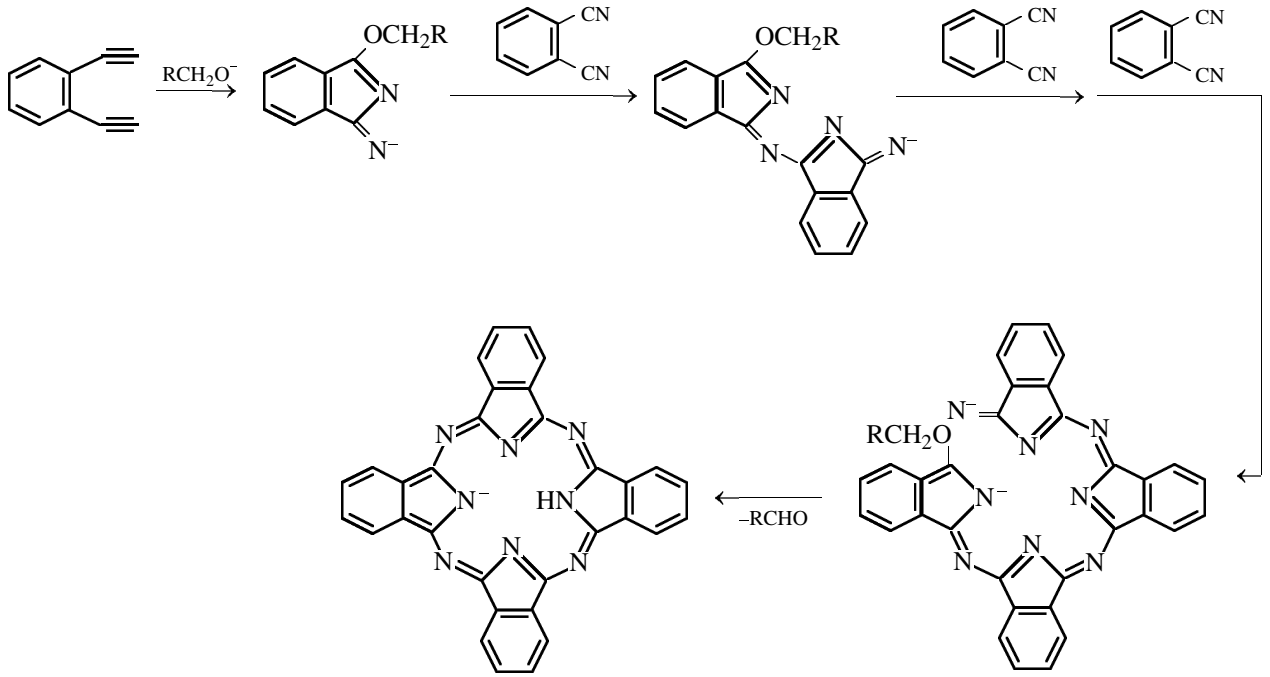
Table 3. ^{13}C NMR parameters of some phthalonitriles obtained (DMSO-d_6)

Product	δ_C, ppm
II	155.3 ($C_{Ar'}$–O), 151.7 (C_{Ar}–O), 136.6 (C_{Ar}–Cl), 134.9 (C_{Ar}–Cl), 132.1 (C_{Ar}–Cl), 130.2 ($C_{Ar'}$–H), 123.8 ($C_{Ar'}$–H), 117.2 (C_{Ar}–CN), 115.5 (C_{Ar}–CN), 114.9 ($C_{Ar'}$–H), 112.8 (CN), 112.5 (CN)
III	156.1($C_{Ar'}$–O), 152.6 (C_{Ar}–O), 135.8 (C_{Ar}–Cl), 131.0 ($C_{Ar'}$–H), 124.8 ($C_{Ar'}$–H), 116.4 (C_{Ar}–CN), 115.8 ($C_{Ar'}$–H), 113.5 (CN)
V	152.4 ($C_{Ar'}$–O), 150.6 (C_{Ar}–O), 143.0 ($C_{Ar'}$–H), 136.9 (C_{Ar}–Cl), 135.3 ($C_{Ar'}$–H), 134.7 (C_{Ar}–Cl), 131.8 (C_{Ar}–Cl), 126.2 ($C_{Ar'}$–H), 125.8 ($C_{Ar'}$–H), 117.4 (C_{Ar}–CN), 115.7 (C_{Ar}–CN), 112.7(CN), 112.5 (CN)
VI	152.1($C_{Ar'}$–O), 148.3 (C_{Ar}–O), 145.4 ($C_{Ar'}$–H), 137.7 ($C_{Ar'}$–H), 132.6 (C_{Ar}–Cl), 124.6 ($C_{Ar'}$–H), 122.7 ($C_{Ar'}$–H), 115.6 (C_{Ar}–CN), 112.9 (CN)
VII	152.9 ($C_{Ar'}$–O), 152.8 ($C_{Ar'}$–O), 152.2 (C_{Ar}–O), 152.0 (C_{Ar}–O), 145.6 ($C_{Ar'}$–H), 145.3 ($C_{Ar'}$–H), 137.9 ($C_{Ar'}$–H), 137.4 ($C_{Ar'}$–H), 130.7 (C_{Ar}–Cl), 130.1 (C_{Ar}–Cl), 125.0 ($C_{Ar'}$–H), 123.1 ($C_{Ar'}$–H), 122.4 ($C_{Ar'}$–H), 117.2 (C_{Ar}–CN), 112.9 (C_{Ar}–CN), 111.7 (CN), 110.5 (CN)

formed mixtures of substitution products, one of them being major. The necessity of the chromatographic separation significantly decreases the synthetic value of the reaction under investigation. An exception is the process carried out at 1 : 4 (or higher) molar ratio and elevated temperature, yielding tris(aryloxy)phthalonitrile, the product with the highest possible degree of substitution. Unfortunately, under more severe conditions (heating above 100°C), the specific reactivity of the *o*-located cyano groups toward nucleophiles causes the formation of significant amounts of oligomeric products.

In the case of thiolate anions [2]. substitution of two chlorine atoms proceeds regiospecifically in position 4 and then in position 5 of the phthalonitrile ring. As follows from the above data, the phenolate and 3-pyridolate ions also substitute the first chlorine atom in position 4 exclusively. This is also proved by the formation of only one monosubstituted product and of 4,5-bis(aryloxy)dichloro-substituted products **III** and **VI**. Substitution of the second chlorine atom with the phenoxy group, similarly to the reaction with thiolate anions, proceeds regiospecifically and yields symmetrical 4,5-diphenoxy-3,6-dichlorophthalonitrile **III**. At the same time, 3-pyridolate reacts to form both symmetrical and unsymmetrical disubstitution products. Presumably, this pattern is due to the steric hindrance to the attack of the adjacent position, created by the solvated nitrogen of the pyridyloxy group already introduced into phthalonitrile, but it does not alter the regioselective character of substitution.

Scheme 2.



It is known that addition of the alkoxide anion to *o*-located cyano groups of phthalonitrile leads to the formation of isoindole structures. Their oligomerization leads, in particular, to the formation of phthalocyanine [3] (Scheme 2).

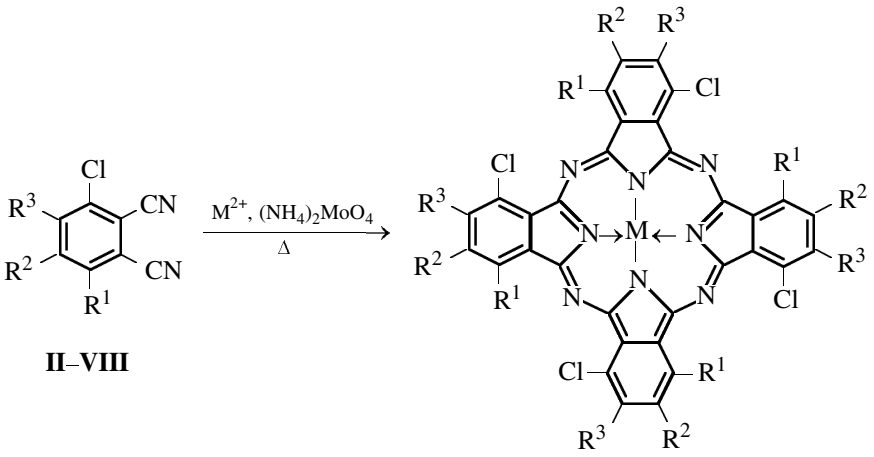
However, it was shown recently that all the four fluorine atoms of tetrafluorophthalonitrile can be substituted with alkoxy groups, in particular, with neopentoxy and hexoxy groups, under the action of a large excess of aliphatic alcohols in presence of potassium carbonate [4, 5]. Using the similar procedure, we performed the reaction of tetrachlorophthalonitrile with hexyl alcohol. An unseparable mixture of products formed. The same result was obtained when sodium alcoholates prepared beforehand (from hexanol, benzyl alcohol, and 2-dimethylaminoethanol) were brought into the reaction with **I** in 1 : 2 or 1 : 4 ratio in DMF at 50°C (no reaction was observed at lower temperature). According to the mass-spectral data, at 1 : 2 molar ratio the major component of the reaction mixture was the starting compound. It also contained unidentified products with high molecular weights and insignificant amounts of the monosubstitution products. Di- and trisubstituted products in 1 : 4 molar ratio were detected by mass spectrometry, in addition to large amounts of oligomers and products of addition to cyano groups (Scheme 2). In the IR spectra of the latter products, the absorption bands of cyano groups were absent (though we failed to obtain analytically pure samples). In the case of hexanol and 2-dimethylaminoethanol, traces of phthalocyanines were also obtained.

So significant difference between the results obtained for tetrafluorophthalonitrile [4, 5] and our data for tetrachlorophthalonitrile is apparently due to significantly stronger electron-acceptor power of fluorine compared to chlorine. This factor favors the successful competition of the aromatic nucleophilic substitution with alkoxides in tetrafluorophthalonitrile with the attack on cyano groups. In the reactions of tetrachlorophthalonitrile with alkoxides, the attack on cyano group evidently prevails.

The aryloxychloro-substituted phthalonitriles were used for preparing the substituted phthalocyanines under the standard conditions of template synthesis. They were fused with metal salts (cobalt chloride and zinc acetate) in the presence of ammonium molybdate. A small amount of *o*-dichlorobenzene was added to the reaction mixture for better homogenization. The reaction was carried out in the temperature range 140–210°C for 3 h with cobalt complexes and for 6 h with zinc complexes. Based on the structures of the starting phthalonitriles and the elemental analysis data, the compounds obtained were identified as **IX**–**XV** (Scheme 3, Table 4).

The complexes obtained **IX**–**XV** were purified first by multiple sequential extraction of impurities with boiling ethanol, benzene, and distilled water, and then

Scheme 3.



II–VIII **IX–XV**

$R^1 = R^2 = Cl$, $R^3 = PhO$ (**II, IX**), PyO (**V, XII**); $R^1 = Cl$, $R^2 = R^3 = PhO$ (**III, X**), PyO (**VI, XIII**); $R^2 = Cl$, $R^1 = R^3 = PyO$ (**VII, XIV**); $R^1 = R^2 = R^3 = PhO$ (**IV, XI**), PyO (**VIII, XV**); M = Co (**a**), Zn (**b**). Py = 3-pyridyl.

Table 4. Elemental analyses and positions of maxima (λ_{max}) of the long-wave absorption bands of the complexes obtained

Product	Found, %				Formula	Calculated, %				λ_{max}, nm (DMSO)
	C	H	Cl	N		C	H	Cl	N	
IXa	49.58 49.66	1.41 1.50	31.16 31.25	8.27 8.35	$C_{56}H_{20}Cl_{12}CoN_8O_4$	49.71	1.49	31.44	8.31	679
IXb	49.64 49.70	1.50 1.53	30.92 30.98	8.24 8.31	$C_{56}H_{20}Cl_{12}N_8O_4Zn$	49.47	1.48	31.29	8.24	690
Xa	60.82 60.90	2.51 2.55	17.66 17.74	7.00 7.08	$C_{80}H_{40}Cl_8CoN_8O_8$	60.67	2.55	17.91	7.08	690
Xb	60.48 60.56	2.51 2.54	17.63 17.72	7.01 7.10	$C_{80}H_{40}Cl_8N_8O_8Zn$	60.42	2.54	17.84	7.05	695
XIa	67.94 69.13	3.27 3.33	7.65 7.71	6.17 6.22	$C_{104}H_{60}Cl_4CoN_8O_{12}$	68.85	3.33	7.82	6.18	693
XIb	68.59 69.03	3.31 3.34	7.64 7.73	6.18 6.21	$C_{104}H_{60}Cl_4N_8O_{12}Zn$	68.60	3.32	7.79	6.15	700
XIIa	46.14 46.26	1.11 1.20	31.00 31.12	12.37 12.45	$C_{52}H_{16}Cl_{12}CoN_{12}O_4$	46.02	1.19	31.35	12.38	685
XIIb	46.94 47.01	1.12 1.17	30.90 30.98	12.29 12.37	$C_{52}H_{16}Cl_{12}N_{12}O_4Zn$	46.80	1.18	31.20	12.33	694
XIIIa	54.37 54.46	2.01 2.06	17.58 17.65	14.07 14.15	$C_{72}H_{32}Cl_8CoN_{16}O_8$	54.33	2.03	17.82	14.08	687
XIIIb	54.15 54.21	1.96 2.01	17.53 17.60	14.08 14.11	$C_{72}H_{32}Cl_8N_{16}O_8Zn$	54.11	2.02	17.75	14.02	703
XIVa	54.36 54.49	2.00 2.05	17.58 17.66	14.04 14.11	$C_{72}H_{32}Cl_8CoN_{16}O_8$	54.33	2.03	17.82	14.08	687
XIVb	54.16 54.22	1.95 2.02	17.50 17.60	14.03 14.09	$C_{72}H_{32}Cl_8N_{16}O_8Zn$	54.11	2.02	17.75	14.02	698
XVa	60.49 60.58	2.64 2.67	7.63 7.74	15.27 15.37	$C_{92}H_{48}Cl_4CoN_{20}O_{12}$	60.51	2.65	7.77	15.34	700
XVb	60.28 50.39	2.60 2.68	7.68 7.71	15.34 15.40	$C_{92}H_{48}Cl_4N_{20}O_{12}Zn$	60.29	2.64	7.74	15.29	713

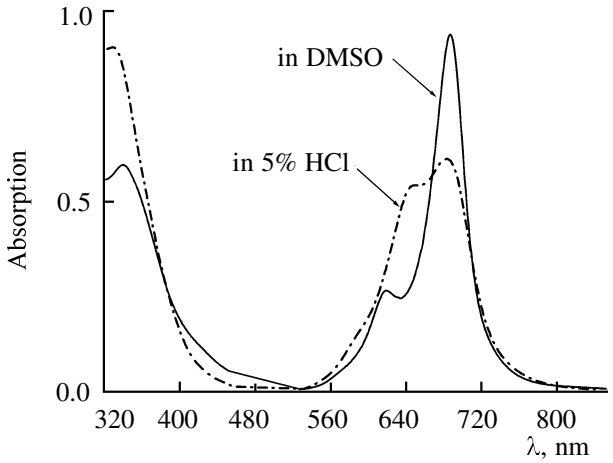


Fig. 1. Electronic absorption spectra of complex **XIIIa** in DMSO and in 5% aqueous HCl.

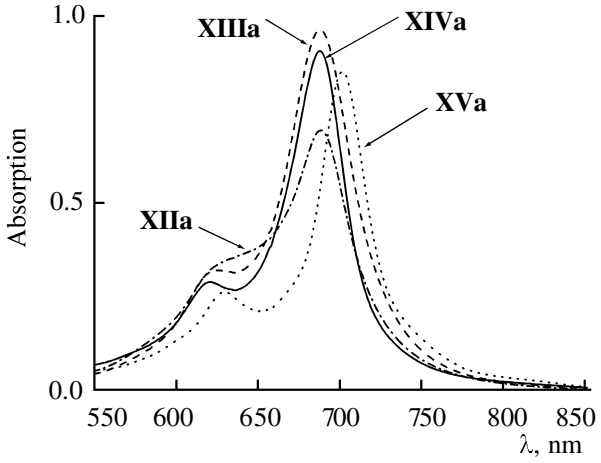


Fig. 2. Electronic absorption spectra of pyridyloxy-substituted cobalt complexes **XIIa**–**XVa** in DMSO.

by precipitation from DMSO with water in the case of phenoxy-substituted complexes **IX**–**XI**, or from 10% hydrochloric acid with ammonium hydroxide in the case of pyridyloxy-substituted phthalocyanines **XII**–**XV**, followed by washing of the precipitates with hot ethanol and water.

When purifying complex **XIIa**, we failed to dissolve the product obtained in 10% hydrochloric acid. The product was partially soluble only in 17% hydrochloric acid. In 36.5% acid, approximately 2/3 of the product dissolved. This solution was treated with ammonium hydroxide to precipitate the compound. The insoluble part of the reaction mixture was washed with concentrated hydrochloric acid and water to neutral pH and then was dissolved in hot DMSO and precipitated with water. As a result, two fractions of the product were obtained. Their analytical data were similar, which allowed us to consider them as two randomers of the cobalt complex **XIIa**.

Zinc complexes **XIIb**–**XVb** were additionally purified by column chromatography (silica gel column, elution with pyridine). After that, the products were precipitated from pyridine with the benzene–acetic acid mixture, washed with hot benzene, water, and ethanol, and dried. All the complexes obtained were blue-green powders insoluble in water and such organic solvents as hydrocarbons, alcohols, ketones, ethers, and esters. At the same time, all of them are soluble in aprotic polar solvents such as DMF and DMSO, and also in pyridine, due to coordination of the latter with the central metal atom. The solubility of the complexes obtained increased with the amount of the pyridyloxy groups in the macroring. The most soluble were dodecakis(aryloxy)tetrachlorophthalocyanines, which completely dissolved in DMF at 50°C. Tetrakis(aryloxy)dodecachlorophthalocyanines were the least soluble.

For all the complexes **IX**–**XV**, we recorded the electronic absorption spectra in DMSO (Figs. 1, 2). The electron absorption spectra of the pyridyloxy-substituted phthalocyanines were also recorded in 5% HCl. The general view of the electronic absorption spectrum in the range 300–850 nm is presented for **XIIIa** in Fig. 1. Similarly to all the other phthalocyanine complexes, two strong absorption bands are observed. The long-wave band (*Q* band) is located in the range 680–715 nm, and the short-wave band (Soret band), at about 350 nm. Note that the *Q* band of complex **XIIa** is poorly resolved, evidently because of the partial aggregation of molecules.

The general view of the electronic absorption spectra of complexes **XIII**–**XV** in 5% aqueous HCl is similar to that in DMSO, but the *Q* band is significantly broadened and split in two maxima at ~630 nm and ~680 nm related to the bands of the aggregated and monomeric species, respectively.

The *Q* band in the spectra of all the substituted cobalt and zinc phthalocyanines is significantly shifted bathochromically as compared to the unsubstituted analogs. In particular, for phenoxy-substituted cobalt complexes **IXa**–**XIa** the above-mentioned shift is 12, 23, and 26 nm, respectively, while for pyridyloxy-substituted complexes **XIIa**–**XIVa** it is 18–20 nm, and for **XVa**, 33 nm.

It is known that introduction of chlorine as well as alkoxy and aryloxy groups into the phthalocyanine macroring causes the bathochromic shift of the *Q*

band [6]. Comparing the spectral data for complexes we obtained with the published data on the octachloro- [7] and octakis(aryloxy/alkoxy)-substituted zinc, cobalt, and some other metal phthalocyanines [4, 8], we can note that eight aryloxy/alkoxy groups in the β-positions of the macroring cause the batochromic shift of the *Q* band by no more than 10 nm as compared to the unsubstituted analog, whereas eight chlorine atoms in α-positions of the phthalocyanine shift the band by ~30 nm. In the spectra of the complexes we obtained, each containing eight above-mentioned groups in the same positions, the *Q* band is shifted by only ~20 nm, contrary to the phenyl(alkyl)thio groups shifting the *Q* band by 60–70 nm [2]. Hence, the effect of substituents on the location of the *Q* band maximum is not additive. At the same time, in going from unsubstituted phthalocyanines to the analogs with eight alkoxy groups in *o*-positions of benzene rings, the bathochromic shift of the *Q* band maximum point is no less than 60 nm (λ_{max} 735–760 nm) [9, 10]. These data, together with the published data on hexadecakis(alkoxy/aryloxy)phthalocyanine metal complexes (λ_{max} 750–760 nm) [4, 5, 11], indicate that, with a large number of alkyl(aryl)thio [2] and alkoxy (aryloxy) substituents in the phthalocyanine macroring, the substituent effect is not additive. Thus, the results of this study, in combination with the previous data, allow the substituents to be ranked in the following order with respect to their effect on the location of the *Q* band in the electronic spectrum: $\beta\text{-}Cl_8 < (\beta\text{-}RO)_8 < \alpha\text{-}Cl_8 < \alpha\text{-}Cl_8$, $(\beta\text{-}RO)_8 < Cl_{16} < (\alpha\text{-}RO)_8 \approx (RO)_{16}$.

EXPERIMENTAL

The elemental analysis were performed on a Hewlett–Packard HP-185B C,H,N-analyzer. The IR spectra were recorded on an FSM 1201 Fourier spectrometer from KBr pellets. The mass spectra were obtained on an MKh-1321 mass spectrometer; the ionizing electron energy was 70 eV. The ^1H and ^{13}C NMR spectra were taken on a Bruker AM-300 spectrometer in DMSO-d_6 against internal TMS. The electronic absorption spectra were measured on a Hewlett–Packard HP 8435 spectrophotometer. The compositions of reaction mixtures and purity of the compounds obtained were monitored by TLC on Silufol UV-254 plates.

Reaction of tetrachlorophthalonitrile with phenols *(general procedure).* To a solution of sodium methylate (0.005, 0.010, 0.015, or 0.020 mol) in 30 ml of methanol, and equimolar amount of phenol or 3-hydroxypyridine was added. The solvent was vacuum-evaporated to dryness, and the residue was dissolved in 50 ml of DMF. The solution obtained was added dropwise in the course of 20 min to a solution of 1.33 g of tetrachlorophthalonitrile in 30 ml of DMF at 20°C. The mixture was heated to 50°C and stirred at this temperature for 3 h. Then the mixture was poured in a saturated NaCl solution, and the aqueous layer was extracted with ethyl acetate. The organic layer was washed twice with 5% ammonia and then with water to the neutral reaction and dried over anhydrous sodium sulfate. After that, the solvent was evaporated in a vacuum and the residue was chromatographed on a silica gel column, elution with 2 : 1 benzene-ethyl acetate in the case of 3-hydroxypyridine, and with 1 : 2 benzene–hexane in the case of phenol. The product obtained was recrystallized from ethanol.

General procedure for preparing aryloxy-substituted phthalocyanines. A finely pulverized mixture of substituted phthalonitrile (0.5 mmol), cobalt chloride or zinc acetate (0.12 mmol), and ammonium molybdate (2–3 mg) was placed in a bath preheated to 140°C. The reaction mixture was gradually heated to 210°C and kept at this temperature for 3 h for the cobalt complexes and 6 h for the zinc complexes. After cooling to room temperature, the solidified melt was finely ground and extracted to remove impurities first with boiling ethanol, then with benzene, and finally with distilled water. After that, the precipitates were filtered off, dissolved in DMSO (for the phenoxy derivatives) or in 10% HCl (for the pyridyloxy-substituted complexes), and reprecipitated with water or aqueous ammonia, respectively. The solutions obtained were washed three times on the filter with hot ethanol and distilled water.

Zinc complexes **XIIb**–**XVb** were additionally purified by column chromatography on silica gel (elution with pyridine), and the products were precipitated from pyridine with a benzene–acetic acid mixture, washed on the filter with hot benzene, water, and methanol, and dried.

All the complexes were blue-green powders; yield 35–40%.

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