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Phthalocyanines and Related Compounds: XLIII.[1] Synthesis of Poly[phenyl(alkyl)sulfanyl]-Substituted Phthalonitriles and Some Phthalocyanines Based Thereon

K. A. Volkov[a], G. V. Avramenko[b], V. M. Negrimovskii[a], and E. A. Luk'yanets[a]

[a] *Research Institute of Organic Intermediates and Dyes, ul. Bol'shaya Sadovaya 1/4, Moscow, 123995 Russia*
e-mail: rmeluk@co.ru

[b] *Mendeleev Russian University of Chemical Technology, Moscow, Russia*

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Abstract — Nucleophilic substitution of chlorine atoms in tetrachlorophthalonitrile by benzene- and alkanethiols in the presence of a base was studied at different reactant ratios. The substitution is characterized by complete regioselectivity: the chlorine atom in position 4 of tetrachlorophthalonitrile is replaced first; next follows replacement of the 5-chlorine atom. The reactions of tetrachlorophthalonitrile with nucleophiles at ratios of 1 : 2 and 1 : 4 lead to the formation of the corresponding 3,6-dichloro-4,5-bis[phenyl(alkyl)sulfanyl]- and tetrakis[phenyl(alkyl)sulfanyl]phthalonitriles. The latter were converted into metal complexes of [phenyl-(alkyl)sulfanyl]-substituted phthalocyanines which absorb in the red and near-IR regions of the electronic spectra.

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In the recent years phthalocyanines attract increasing attention as subjects for study due to continuous extension of the scope of their application in various fields of science and engineering. For example, traditional uses of phthalocyanines as dyes and pigments [2–4], catalysts of chemical reactions [5–7], photo- and electrocatalysts [8–10], semiconducting materials [11, 12], heat-resistant polymers [13, 14], laser dyes, and optical filters [15] were supplemented by their application as active media in sensors for various gases [16, 17] and data storage and display devices [18, 19]; studies on liquid crystalline properties of phthalocyanines are in progress [20, 21]. At present, phthalocyanines attract much interest as photosensitizers for photodynamic therapy of cancer [22–24]. Therefore, numerous studies on the synthesis of new phthalocyanine structures have been stimulated.

Most substituted phthalocyanines were synthesized by tetramerization of the corresponding substituted phthalonitriles [2, 3]. The latter are often obtained via aromatic nucleophilic replacement of halogen atoms or nitro group in halo- or nitrophthalonitriles. Following this approach, such substituents as alkoxy [25–28], aryloxy [29–32], alkylsulfanyl [33, 34], arylsulfanyl [35], and amino groups [36, 37] were introduced into the benzene ring of phthalonitrile and, in the next step, into the phthalocyanine macroring. For this purpose, 3-nitrophthalonitrile [38] and especially 4-nitrophthalonitrile [39, 40] are used most frequently; in some cases, monohalo-substituted phthalonitriles, e.g., fairly exotic 3-bromo-5-*tert*-butylphthalonitrile [36], are appropriate; these starting compounds make it possible to obtain unsymmetrical mono- and disubstituted phthalonitrile and finally unsymmetrically substituted phthalocyanines as randomer mixtures.

Phthalonitriles having two replaceable groups possess a great synthetic potential. For example, symmetric 4,5-dichloro- [41, 42] and 3,6-bis(trifluoromethylsulfonyloxy)phthalonitriles [34] make it possible to introduce eight symmetrically arranged substituents into a phthalocyanine macroring. The nitro groups in 3,5-dinitrophthalonitrile can be replaced in succession by two different nucleophiles; however, the regioselectivity of the first replacement is not high [43]. 4-Bromo-5-nitrophthalonitrile [44, 45] is free from this disadvantage: the bromine atom in its molecule is replaced first [46], and the remaining nitro group can also be replaced by the same [47] or different nucleophile [48, 49].

From the viewpoint of synthetic applications, quite interesting substrates are tetrahalo-substituted phth-

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

onitriles, in particular, commercially available tetrachlorophthalonitrile. Theoretically, all four chlorine atoms therein may be replaced by the same or (in succession) by different nucleophiles in various ratios, which could give rise to a diversity of structures. However, it was surprising that, except for several patents [50–55], we found no publications on systematic studies on nucleophilic substitution of halogen atoms in tetrahalophthalonitriles. The above patents described substitution of halogen atoms in perhalogenated phthalonitriles, including tetrachlorophthalonitrile, by sulfur-centered nucleophiles, and the resulting substituted phthalonitriles were then converted into polysubstituted phthalocyanines.

It should be noted that exhaustive replacement of halogen atoms in tetrahalophthalonitrile should give only one product. If only two halogen atoms are replaced, four isomeric products can be obtained via replacement at positions 3,5, 4,5, 3,6, and/or 3,4. Only symmetric disubstituted phthalonitriles and phthalocyanines derived therefrom were described in [50–55], e.g., 3,6-difluoro-4,5-bis(phenylsulfanyl)-phthalonitrile [52, 54] was reported; however, no rigorous proofs for their structure were given.

Taking into account the lack of sufficient information on nucleophilic substitution in tetrahalophthalonitriles, we examined reactions of tetrachlorophthalonitrile with some *S*-nucleophiles. Here, the main goal was to elucidate the possibility for directly synthesizing mono-, di-, tri-, and tetrasulfanyl-substituted phthalonitriles at different reactant ratios. We performed a series of experiments, where tetrachlorophthalonitrile was brought into reactions with thiols (benzenethiol, butane-1-thiol, 2-methylpropane-2-thiol, and decane-1-thiol) whose amount was varied. The reactions were carried oy by gradually adding triethylamine (as a base) to a suspension of tetrachlorophthalonitrile and a required amount of the corresponding thiol in DMF. Nucleophilic replacement occurred even at room temperature, as followed from the brown color of the reaction mixture and heat evolution. The reaction time generally did not exceed 1 h, and it depended on the rate of addition of triethylamine. The progress of reactions was monitored by TLC. After appropriate treatment of the reaction mixture, the products were either purified by crystallization or separated by column chromatography. The results of the reactions of tetrachlorophthalonitrile (**I**) with thiols at different reactant ratios and the yields based on the initial dinitrile **I** are given in Table 1 (Scheme 1).

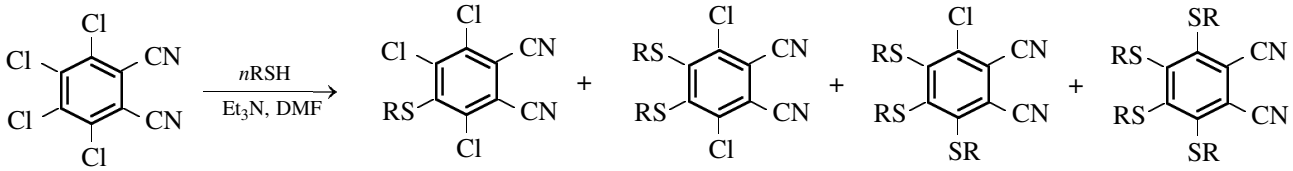
Table 1. Yields of sulfanyl-substituted phthalonitriles (%) at different molar reactant ratios [a]

R in RSH	Product	Molar ratio **I**:RSH			
		1:1	1:2	1:3	1:4
R = Ph	**I**	0.0	–	–	–
	II	28.0	[b]	–	–
	III	20.6	92.0 [c]	25.2	[b]
	IV	–	[b]	26.7	[b]
	V	–	–	36.4	93.0 [d]
R = *t*-Bu	**I**	28.7	–	–	–
	VI	29.1	[b]	–	–
	VII	23.4	91.4 [d]	22.7	[b]
	VIII	–	[b]	26.3	[b]
	IX	–	–	40.0	90.2 [d]
R = *n*-Bu	**X**	[e]	91.0	[e]	[b]
	XI		–		95.0
R = *n*-$C_{10}H_{21}$	**XII**	[e]	87.4	[e]	[b]
	XIII		–		89.3

[a] Unless otherwise stated, the yield refers to the product isolated by preparative column chromatography on silica gel (eluent benzene). [b] Traces according to TLC. [c] After crystallization from benzene–hexane (2:1). [d] After crystallization from ethanol. [e] The products were not isolated.

In the reaction of phthalonitrile **I** with benzenethiol, butane-1-thiol, 2-methylpropane-2-thiol, and decane-1-thiol in a ratio of 1:1, the reaction mixture contained three compounds, one of which was initial

Scheme 1.



I **II, VI** **III, VII, X, XII** **IV, VIII** **V, IX, XI, XIII**

II–**V**, R = Ph; **VI**–**IX**, R = *t*-Bu; **X, XI**, R = *n*-Bu; **XII, XIII**, R = *n*-$C_{10}H_{21}$.

Table 2. Melting points, elemental analyses, and IR and mass spectra of phthalonitriles **II**–**XIII**

Comp. no.	mp, °C	ν_{CN}, cm^{-1}	Found, %					Formula	Calculated, %					M^+
			C	H	Cl	N	S		C	H	Cl	N	S	
II	>232[a]	2239	49.70 49.74	1.50 1.51	31.37 31.43	8.18 8.21	9.18 9.24	$C_{14}H_5Cl_3N_2S$	49.51	1.48	31.32	8.25	9.44	338
III	154–155[b]	2232	58.32 58.38	2.54 2.56	17.07 17.15	6.91 6.99	16.32 16.28	$C_{20}H_{10}Cl_2N_2S_2$	58.11	2.44	17.15	6.78	15.51	412
IV	147–148[c]	2229	64.23 64.29	3.33 3.37	7.15 7.21	5.48 5.54	19.67 19.72	$C_{26}H_{15}ClN_2S_3$	64.12	3.10	7.28	5.75	19.75	486
V	152–153[c]	2218	69.16 69.22	3.62 3.63	–	4.90 4.98	22.54 22.60	$C_{32}H_{20}N_2S_4$	68.54	3.59	–	5.00	22.87	560
VI	210–212[c]	2237	44.94 45.00	2.82 2.88	33.49 33.54	8.93 8.97	9.80 9.85	$C_{12}H_9Cl_3N_2S$	45.09	2.84	33.27	8.76	10.03	318
VII	146–148[c]	2231	51.46 51.53	4.90 4.93	18.72 18.81	7.50 7.58	17.26 17.35	$C_{16}H_{18}Cl_2N_2S_2$	51.47	4.86	18.99	7.50	17.18	372
VIII	159–161[c]	2233	56.32 56.40	6.31 6.37	8.52 8.59	6.47 6.55	22.19 22.26	$C_{20}H_{27}ClN_2S_3$	56.24	6.37	8.30	6.56	22.52	426
IX	141–142[c]	2228	59.80 59.91	7.46 7.57	–	5.89 5.93	26.67 26.74	$C_{24}H_{36}N_2S_4$	59.95	7.55	–	5.83	26.68	480
X	[d]	2234	51.51 51.60	4.84 4.95	18.91 19.02	7.52 7.60	17.03 17.14	$C_{16}H_{18}Cl_2N_2S_2$	51.47	4.86	18.99	7.50	17.18	372
XI	[d]	2228	59.90 60.02	7.50 7.53	–	5.73 5.86	26.65 26.78	$C_{24}H_{36}N_2S_4$	59.95	7.55	–	5.83	26.68	480
XII	[d]	2232	62.15 62.22	7.71 7.78	12.92 13.05	4.92 4.97	12.13 12.22	$C_{28}H_{42}Cl_2N_2S_2$	62.08	7.82	13.09	5.17	11.84	540
XIII	[d]	2225	70.29 70.35	10.29 10.31	–	3.41 3.49	16.01 16.12	$C_{48}H_{84}N_2S_4$	70.53	10.36	–	3.43	15.69	

[a] Sublimation point. [b] From benzene–hexane (2:1). [c] From ethanol. [d] Yellow viscous oil.

dinitrile **I** and the two other were products of replacement of one and two chlorine atoms in molecule **I** by phenylsulfanyl or alkylsulfanyl group. It is notable that each thiol gave rise to only one monosubstituted product (these compounds were isolated and characterized in the reactions with benzenethiol and 2-methylpropane-2-thiol) and one disubstituted product, i.e., the reaction was highly regioselective.

Surprisingly, in the reactions of compound **I** with all the examined thiols in a ratio of 1:2 we isolated in high yields only the corresponding disubstitution products **III**, **VII**, **X**, and **XII**, while only traces of mono- and trisubstituted compounds were detected. Analogous patterns were observed at reactant ratios of 1:3 and 1:4. In the former case, mixtures of three compounds (di-, tri-, and tetrasubstituted) were formed, and in the latter, only tetrasubstituted compounds **V**, **IX**, **XI**, and **XIII** (Table 2).

The number of signals in the ^{13}C NMR spectra of disubstituted compounds **III**, **VII**, **X**, and **XII** was twice as low as the number of carbon atoms in the substituted dinitrile (Table 3), which indicates symmetric replacement of chlorine in molecule **I**. The structure of the disubstituted products was proved by the X-ray diffraction data for compound **III**[2] (Fig. 1, Table 4). It was found that benzenethiol replaces chlorine atoms in positions 4 and 5 of tetrachlorophthalonitrile (**I**). Therefore, we can assume with a high probability that the reactions with the other thiols occur just at the same positions in molecule **I**. On the other hand, these data indicate complete regioselectivity in the replacement of the first chlorine atom at C^4.

Insofar as symmetrically substituted disulfanyldichloro- and tetrasulfanylphthalonitriles turned out to be most accessible from the preparative viewpoint, just these compounds were used to synthesize sulfanyl-

[2] Detailed X-ray diffraction data will be reported elsewhere.

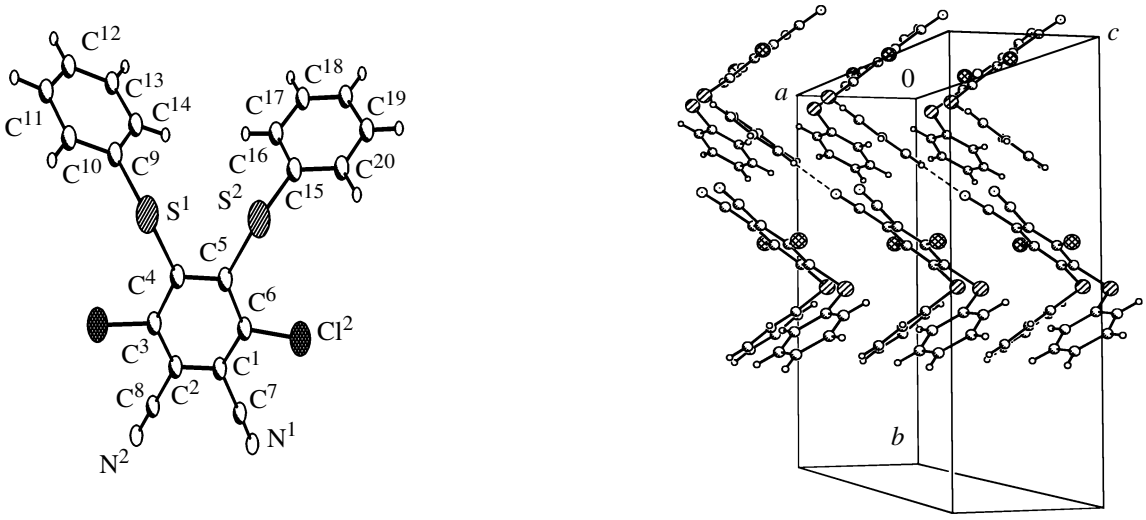


Fig. 1. Structure of the molecule of 3,6-dichloro-4,5-bis(phenylsulfanyl)phthalonitrile (**III**) and its crystal packing according to the X-ray diffraction data.

substituted phthalocyanines (their tetramerization should produce individual compounds rather than mixtures of randomers). Metal phthalocyanines were synthesized under standard conditions of template synthesis, by heating the corresponding substituted phthalonitrile with a metal salt in the presence of ammonium molybdate. The reaction mixtures (in some cases, *o*-dichlorobenzene was added to ensure homogeneous conditions) were gradually heated from 140 to 210°C and were held for about 3 h at that temperature. We thus obtained a series of poly[phenyl(alkyl)sulfanyl]-substituted complexes **XIV**–**XXIII** in 20–40% yield (Scheme 2, Table 5).

The following differences in the reactivity of phenylsulfanyl- and alkylsulfanyl-substituted phthalonitriles should be noted. Both bis(phenylsulfanyl)dichloro and tetrakis(phenylsulfanyl) derivatives **III** and **V** smoothly afforded the corresponding polysubstituted phthalocyanines **XIV**–**XVII** and **XXII**, **XXIII** which were isolated in about 40% yield (after purification). The yields of phthalocyanine metal complexes from bis(alkylsulfanyl)dichloro-substituted phthalonitriles **X** and **XII** having linear alkyl groups were much poorer: they did not exceed 20%. We succeeded in effecting tetramerization of tetrakis(alkylsulfanyl)-phthalonitriles **XI** and **XIII** only in an inert atmos-

Table 3. ^{13}C and ^{1}H NMR spectra of some phenylsulfanyl-substituted phthalonitriles

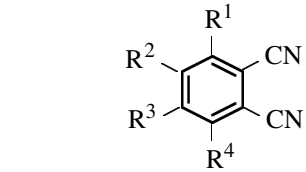
Comp. no.	^{13}C NMR spectrum, δ_C, ppm	^{1}H NMR spectrum, δ, ppm
III[a]	147.9 (C_{Ar}–S), 141.2 (C_{Ar}–Cl), 133.6 (C'_{Ar}–S), 129.8 (C'_{Ar}–H), 129.6 (C'_{Ar}–H), 128.1 (C'_{Ar}–H), 117.8 (C_{Ar}–CN), 112.5 (C≡N)	7.09–7.18 m (4H), 7.22–7.35 m (6H)
V[b]		7.02 d (8H, J_{HH} 8 Hz), 7.18–7.40 m (12H)
VII[b]	150.3 (C_{Ar}–S), 144.4 (C_{Ar}–Cl), 116.0 (C_{Ar}–CN), 114.5 (C≡N), 56.1 (C–CH_3), 55.7 (C–CH_3), 32.2 (CH_3), 32.1 (CH_3), 31.9 (CH_3)	1.27–1.36 m (9H), 1.42–1.38 m (9H)
IX[b]		1.25 s (18H), 1.40 s (18H)
X[b]	149.1 (C_{Ar}–S), 140.8 (C_{Ar}–Cl), 117.3 (C_{Ar}–CN), 114.1 (C≡N), 36.9 (CH_2–S), 32.0 (CH_2), 22.0 (CH_2), 14.1 (CH_3)	0.88 t (6H), 1.30–1.54 m (8H), 3.10 t (4H)
XI[b]		0.80–0.90 m (12H), 1.30–1.52 m (16H), 3.05–3.20 m (8H)
XII[b]	149.2 (C_{Ar}–S), 139.8 (C_{Ar}–Cl), 117.9 (C_{Ar}–CN), 114.1 (C≡N), 37.2 (CH_2–S), 32.0 (CH_2), 29.8 (CH_2), 29.6 (CH_2), 29.4 (CH_2), 29.2 (CH_2), 28.7 (CH_2), 28.5 (CH_2), 22.8 (CH_2), 14.6 (CH_3)	0.86 t (6H), 1.40–1.54 m (32H), 3.10 t (4H)

[a] In $CDCl_3$. [b] In DMSO-d_6.

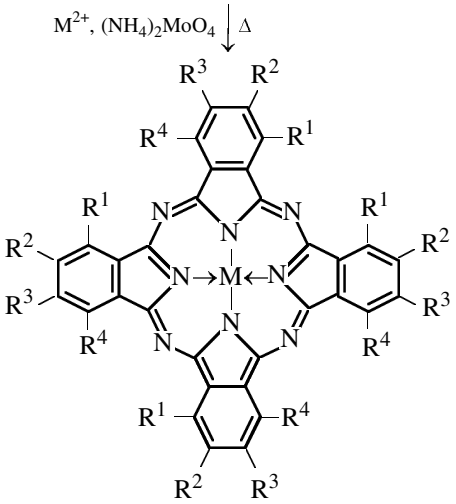
Table 4. Selected bond lengths and bond angles in the molecule of 3,6-dichloro-4,5-bis(phenylsulfanyl)phthalonitrile (**III**) according to the X-ray diffraction data

Bond	*d*, Å	Angle	ω, deg
S^1–C^4	1.775(5)	$C^4S^1C^9$	101.7(2)
S^1–C^9	1.775(5)	$C^3C^2C^1$	118.4(5)
Cl^1–C^3	1.772(4)	$C^1C^2C^8$	120.6(5)
N^1–C^7	1.124(5)	$C^2C^3C^4$	121.7(4)
N^2–C^8	1.149(6)	$C^2C^3Cl^1$	116.6(4)
C^2–C^3	1.374(6)	$C^4C^3Cl^1$	121.7(3)
C^1–C^2	1.397(5)	$C^3C^4C^5$	119.1(5)
C^1–C^7	1.484(7)	$C^3C^4S^1$	120.8(3)
C^2–C^8	1.424(7)	$C^5C^4S^1$	120.0(4)
C^3–C^4	1.402(6)	$N^1C^7C^1$	176.1(5)
C^4–C^5	1.411(4)	$C^{10}C^9C^{14}$	120.3(4)
C^9–C^{10}	1.374(6)	$C^{10}C^9S^1$	118.9(4)
C^9–C^{14}	1.391(6)	$C^9C^{10}C^{11}$	119.9(5)
C^{10}–C^{11}	1.387(6)	$C^{12}C^{11}C^{10}$	120.0(5)
C^{11}–C^{12}	1.375(6)	$C^{11}C^{12}C^{13}$	119.9(5)

Scheme 2.



III, V, X, XII



XIV–XXIII

III, XIV–XVII, $R^1 = R^4$ = Cl, $R^2 = R^3$ = PhS; **X, XVIII, XIX**, $R^1 = R^4$ = Cl, $R^2 = R^3$ = *n*-BuS; **XII, XX, XXI**, $R^1 = R^4$ = Cl, $R^2 = R^3$ = *n*-$C_{10}H_{21}S$; **V, XXII, XXIII**, $R^1 = R^2 = R^3 = R^4$ = PhS; **XIV, XVIII, XX, XXII**, M = Cu; **XV**, M = AlCl; **XVI**, M = $TiCl_2$; **XVII, XIX, XXI, XXIII**, M = Zn.

phere. The zinc complex of hexadecakis(decylsulfanyl)phthalocyanine was isolated in an inert atmosphere only as a crude product (λ_{max} 750 nm; chloroform), for it decomposed during chromatographic purification. Presumably, per(alkylsulfanyl)-substituted phthalocyanines are very sensitive to atmospheric oxygen. Unfortunately, we failed to synthesize the corresponding phthalocyanines from symmetric *tert*-butylsulfanylsubstituted phthalonitriles **VII** and **IX**.

Copper and zinc complexes of phenylsulfanylphthalocyanines (**XIV**, **XVII**, **XXII**, and **XXIII**) and copper complex **XVIII** derived from butylsulfanyl-substituted phthalocyanine are almost insoluble in most organic solvents, except for such dipolar aprotic solvents as DMF and DMSO on heating or at the boiling point. Phenylsulfanyl-substituted chloroaluminum and dichlorotitanium complexes **XV** and **XVI** are readily soluble both in DMSO and DMF and in less polar benzene, chloroform, and methylene chloride due to the presence of axial ligands deviating from the macroring plane. Similar dehavior is shown by decylsulfanyl derivatives **XX** and **XXI** due to the presence of long-chain aliphatic groups. All zinc complexes are also readily soluble in pyridine due to coordination of the latter at the central metal ion.

We have recorded the electronic absorption spectra of phthalocyanine metal complexes **XIV–XXIII** in organic solvents (Figs. 2, 3; Table 5). It is known that

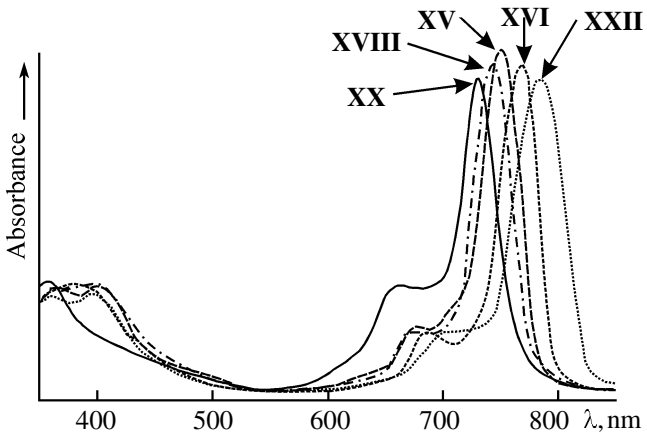


Fig. 2. Electronic absorption spectra of 1,4,8,11,15,18,22,25-octachloro-2,3,9,10,16,17,23,24-octakis(phenylsulfanyl)phthalocyanine complexes with chloroaluminum (**XV**, chloroform) and dichlorotitanium (**XVI**, benzene) and of copper complexes with 2,3,9,10,16,17,23,24-octakis(butylsulfanyl)-1,4,8,11,15,18,22,25-octachloro- (**XVIII**, 1,2-dichlorobenzene), 1,4,8,11,15,18,22,25-octachloro-2,3,9,10,16,17,23,24-octakis(decylsulfanyl)- (**XX**, chloroform), and hexadecakis(phenylsulfanyl)-phthalocyanines (**XXII**, DMSO).

Table 5. Elemental analyses and long-wave absorption maxima in the electronic spectra of phthalocyanine metal complexes **XIV**–**XXIII**

Comp. no.	λ_{max}, nm	Found, %					Formula	Calculated, %				
		C	H	Cl	N	S		C	H	Cl	N	S
XIV	746 [a]	56.04	2.35	16.70	6.57	15.00	$C_{80}H_{40}Cl_8CuN_8S_8$	55.94	2.33	16.55	6.52	14.92
		56.10	2.36	16.76	6.61	15.09						
XV	750 [b]	55.62	2.35	18.71	6.57	14.98	$C_{80}H_{40}AlCl_9N_8S_8$	55.99	2.33	18.63	6.53	14.93
		55.70	2.37	18.79	6.62	15.06						
XVI	768 [c]	54.97	2.33	20.00	6.38	14.58	$C_{80}H_{40}Cl_{10}N_8S_8Ti$	54.45	2.27	20.14	6.35	14.52
		55.04	2.37	20.10	6.42	14.64						
XVII	726 [a]	56.46	2.30	16.69	6.55	14.02	$C_{80}H_{40}Cl_8N_8S_8Zn$	55.92	2.33	16.54	6.52	14.91
		56.53	2.34	16.75	6.58	14.08						
XVIII	741 [d]	49.38	4.70	17.93	7.27	16.54	$C_{64}H_{72}Cl_8CuN_8S_8$	49.48	4.64	18.04	7.22	16.49
		49.42	4.73	17.99	7.34	16.59						
XIX	723 [e]	49.49	4.68	17.91	7.29	16.37	$C_{64}H_{72}Cl_8N_8S_8Zn$	49.45	4.64	18.03	7.21	16.48
		49.53	4.72	17.98	7.35	16.44						
XX	734 [b]	60.34	7.62	12.51	5.07	11.58	$C_{112}H_{168}Cl_8CuN_8S_8$	60.43	7.55	12.59	5.03	11.51
		60.37	7.65	12.55	5.13	11.62						
XXI	722 [e]	60.32	7.65	12.48	5.01	11.40	$C_{112}H_{168}Cl_8N_8S_8Zn$	60.40	7.55	12.58	5.03	11.51
		60.38	7.67	12.53	5.09	11.46						
XXII	783 [a]	66.51	3.37	–	4.88	22.16	$C_{128}H_{80}CuN_8S_{16}$	66.67	3.47	–	4.86	22.23
		66.58	3.42		4.93	22.25						
XXIII	759 [a]	66.49	3.50	–	4.85	22.13	$C_{128}H_{80}N_8S_{16}Zn$	66.60	3.49	–	4.85	22.22
		66.53	3.54		4.94	22.20						

[a] In DMSO. [b] In chloroform. [c] In benzene. [d] In 1,2-dichlorobenzene. [e] In methylene chloride.

introduction of both chlorine atoms [56, 57] and phenylsulfanyl groups [35, 58, 59] into phthalocyanine macroring induces a red shift of the *Q* band. In fact, the *Q* band in the spectra of the obtained complexes was considerably displaced to longer wavelengths. Comparison of the spectral data for the copper and zinc complexes with those reported for octachloro- [56] and octakis(phenylsulfanyl)-substituted phthalocyanines [35, 59] shows that introduction of eight phenylsulfanyl groups into the β-positions of the macroring leads to a ~45–50-nm red shift of the *Q* band and that introduction of eight chlorine atoms into the β-positions induces an analogous shift by about 30 nm. In the spectra of copper complexes **XIV**, **XVIII**, and **XX** and zinc complexes **XVII**, **XIX**, **XXI**, each having eight sulfanyl groups in the β-positions and eight chlorine atoms in the α-positions, the *Q* band is displaced by 60–70 nm toward longer wavelengths; i.e., some additivity of the substituent effects on the position of the *Q* band can be spoken about. On the other hand, comparison of the spectra of the recently reported copper and zinc phthalocyanines having eight hexylsulfanyl groups in the α-positions of the benzene rings [34] (λ_{max} 783 and 781 nm, respectively) with the spectra of hexadecakis(phenyl-

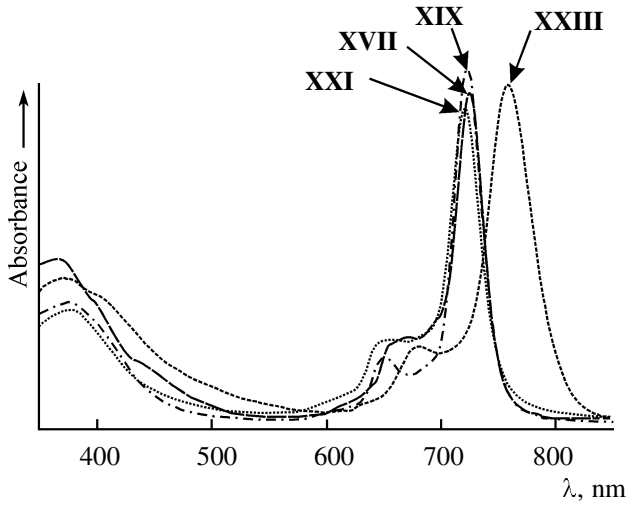


Fig. 3. Electronic absorption spectra of zinc complexes with 1,4,8,11,15,18,22,25-octachloro-2,3,9,10,16,17,23,24-octakis(phenylsulfanyl)- (**XVII**, DMSO), 2,3,9,10,16,17,23,24-octakis(butylsulfanyl)-1,4,8,11,15,18,22,25-octachloro- (**XIX**, methylene chloride), 1,4,8,11,15,18,22,25-octachloro-2,3,9,10,16,17,23,24-octakis(decylsulfanyl)- (**XXI**, methylene chloride), and hexadecakis(phenylsulfanyl)phthalocyanines (**XXIII**, DMSO).

sulfanyl)phthalocyanine complexes **XXII** (Cu) and **XXIII** (Zn) shows the absence of additivity. Thus, on the basis of our results and published data, the examined substituents rank as follows with respect to their effect on the position of the *Q* band in the electronic absorption spectrum: $(\beta\text{-Cl})_8 < (\alpha\text{-Cl})_8 < Cl_{16} < (\beta\text{-RS})_8 < (\alpha\text{-Cl})_8\text{-}(\beta\text{-RS})_8 < (RS)_{16} < (\alpha\text{-RS})_8$. Complexes formed by different metals with phthalocyanines having the same substitution pattern give rise to the series Zn < Cu < AlCl < $TiCl_2$, in keeping with the position of the *Q* band in the electronic spectrum. These results are consistent with the data reported by other authors.

Thus, the results of our study on the reactions of tetrachlorophthalonitrile with benzenethiol and alkanethiols showed that nucleophilic substitution of chlorine atoms in the former is completely regioselective: the 4-chlorine atom is replaced first, and the subsequent replacement occurs at the 5-position. The reactions of tetrachlorophthalonitrile with thiols in ratios of 1 : 2 and 1 : 4 give in high yields the corresponding 4,5-bis[phenyl(alkyl)sulfanyl]-3,6-dichlorophthalonitriles and tetrakis[phenyl(alkyl)sulfanyl]-phthalonitriles which can be converted into a number of substituted phthalocyanine metal complexes.

EXPERIMENTAL

Elemental analysis was performed on a Hewlett–Packard HP-185B C,H,N analyzer. The IR spectra were recorded in KBr on an FSM 1201 spectrometer with Fourier transform. The mass spectra (electron impact, 70 eV) were obtained on an MKh-1321 instrument. The ^1H and ^{13}C NMR spectra were measured on a Bruker AM-300 spectrometer using DMSO-d_6 and $CDCl_3$ as solvents and TMS as internal reference. The electronic absorption spectra were recorded on a Hewlett–Packard HP 8435 spectrophotometer. The compositions of reactions mixtures and the purity of isolated compounds were monitored by TLC on Silufol UV-254 plates.

Reactions of tetrachlorophthalonitrile with thiols *(general procedure).* Tetrachlorophthalonitrile (**I**), 1.33 g, and a required amount (0.005, 0.010, 0.015, or 0.020 mol) of the corresponding thiol were dispersed in 20 ml of DMF, and an equimolar amount of triethylamine (with respect to the thiol) was added dropwise under stirring at room temperature. The mixture gradually turned brown, and a white solid separated. The mixture was stirred for 1 h, poured into 5% hydrochloric acid, and extracted with benzene (or the precipitate was filtered off and dissolved in benzene), and the products were separated by column chromatography on silica gel using benzene as eluent or were purified by recrystallization.

Synthesis of sulfanyl-substituted phthalocyanine metal complexes *(general procedure).* A 10-ml round-bottom flask was charged with a finely ground mixture of substituted phthalonitrile (0.5 mmol), metal salt [0.13 mmol; copper(II) chloride, aluminum(III) chloride, zinc(II) acetate, or titanium(IV) chloride], and ammonium molybdate (2–3 mg). The flask was immersed into a metal bath preliminarily heated to 140°C, and the mixture was gradually heated to 210°C and was kept for 3 h at that temperature. In the synthesis of complexes **XIV**, **XVII**, **XVIII**, **XXII**, and **XXIII**, the resulting melt was cooled, thoroughly ground, and repeatedly extracted with boiling ethanol and hot distilled water to remove impurities; the residue was reprecipitated twice from hot DMF with ethanol. Complexes **XV**, **XVI**, and **XIX**–**XXI** were isolated by column chromatography on silica gel using benzene (**XV**), chloroform–ethanol, 1 : 4 (**XVI**), or methylene chloride (**XIX**–**XXI**) as eluent. The yields were 20–40%.

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REFERENCES

1. Makarova, E.A., Dzyuina, E.V., and Luk'yanets, E.A., *Russ. J. Gen. Chem.,* 2006, vol. 76, no. 7, p. 1165.
2. *Phthalocyanine Compounds,* Moser, F.H. and Thomas, A.L., Eds., New York: Reinhold, 1963.
3. *Phthalocyanines: Properties and Applications,* Leznoff, C.C. and Lever, A.B.P., Eds., New York: VCH, 1989–1996, vols. 1–4.
4. Gregory, P., *J. Porphyrins Phthalocyanines,* 2000, vol. 4, no. 4, p. 432.
5. Ecker, H. and Kiesel, Y., *Angew. Chem., Int. Ed. Engl.,* 1991, vol. 20, no. 5, p. 473.
6. Borisenkova, S., Girenko, E., Mikhalenko, S., Negrimovskii, V., Solov'eva, L., Kaliya, O., and Luk'yanets, E., *Vestn. Mosk. Univ., Ser. 2: Khim.,* 2002, vol. 43, no. 3, p. 192.
7. Kobayashi, N., Sudo, K., and Osa, T., *Bull. Chem. Soc. Jpn.,* 1990, vol. 63, no. 2, p. 317.
8. Goux, A., Bedioui, F., Robbiola, L., and Pontie, M., *Electroanalysis,* 2003, vol. 15, no. 11, p. 969.
9. Shahrokhian, S., Hamzehloei, A., Thaghani, A., and Mousavi, S.R., *Electroanalysis,* 2004, vol. 16, no. 11, p. 915.
10. Wael, K., Westbroek, P., and Temmerman, E., *Electroanalysis,* 2005, vol. 17, no. 3, p. 263.

11. Zhang, P., Wang, H., Yan, X., Wang, J., Shi, J., and Yan, D., *Adv. Mater.,* 2005, vol. 17, no. 9, p. 1191.
12. Simon, J. and Andre, J.-J., *Molecular Semiconductors. Photoelectrical Properties and Solar Cells,* Berlin: Springer, 1985.
13. Achar, B.N., Fohlen, G.M., and Parker, J.A., *J. Polym. Sci.: Polym. Chem.,* 1982, vol. 20, no. 10, p. 2773.
14. Achar, B.N., Fohlen, G.M., and Parker, J.A., *J. Appl. Polym. Sci.,* 1984, vol. 29, p. 353.
15. Casstevens, M.K., Samoc, M., Pfleger, J., and Prasad, P.N., *J. Chem. Phys.,* 1990, vol. 92, p. 2019.
16. Schiebaum, K.D., Zhou, R., Knecht, S., Dieing, R., Hanack, M., and Gopel, W., *Sensors Actuators, B: Chem.,* 1995, vol. 24, nos. 1–3, p. 69.
17. Battenberg, A., Breidt, V.F., and Vahrenkamp, H., *Sensor Actuators, B: Chem.,* 1996, vol. 30, no. 1, p. 29.
18. Kobayashi, S., Iwasaki, K., Sasaki, H., Oh-Hara, S.S., Nishizawa, M., and Katayose, M., *Jpn. J. Appl. Phys.,* 1991, vol. 30, p. 114.
19. Ao, R., Kummert, L., and Haarer, D., *Adv. Mater.,* 1995, vol. 7, no. 5, p. 495.
20. Simon, J. and Sirlin, C., *Pure Appl. Chem.,* 1989, vol. 61, p. 1625.
21. Engel, M.K., Bassoul, P., Bosio, L., Lehmanns, H., Hanacks, M., and Simon, J., *Liq. Cryst.,* 1993, vol. 15, no. 5, p. 709.
22. Wohrle, D., Shopova, M., Muller, S., Milev, A.D., Mantareva, V.N., and Krastev, K.K., *J. Photochem. Photobiol. B,* 1993, vol. 21, p. 155.
23. Luk'yanets, E.A., *Ross. Khim. Zh.,* 1998, vol. 42, no. 5, p. 9.
24. Dysart, J.S., Patterson, M.S., Farelli, T.J., and Singh, G., *J. Photochem. Photobiol.,* 2002, vol. 75, p. 289.
25. Leznoff, C.C., Marcuccio, S.M., Greenberg, S., Lever, A.B.P., and Tomer, K.B., *Can. J. Chem.,* 1985, vol. 63, p. 623.
26. Meier, H., Albrecht, W., Wohrle, D., and Jahn, A., *J. Phys. Chem.,* 1986, vol. 90, p. 6349.
27. Nevin, W.A., Liu, W., and Lever, A.B.P., *Can. J. Chem.,* 1987, vol. 65, p. 855.
28. Cook, M.J., Dunn, A.J., Howe, S.D., Thomson, A.J., and Harrison, K.I., *J. Chem. Soc., Perkin Trans. 1,* 1988, no. 8, p. 2453.
29. Derkacheva, V.M. and Luk'yanets, E.A., *Zh. Obshch. Khim.,* 1980, vol. 50, no. 10, p. 2313.
30. Snow, A.W. and Jarvis, N.L., *J. Am. Chem. Soc.,* 1984, vol. 106, no. 17, p. 4706.
31. Oliver, S.W. and Smith, T.D., *Heterocycles,* 1984, vol. 22, no. 9, p. 2047.
32. Wohrle, D. and Krawczyk, G., *Polym. Bull.,* 1986, vol. 15, p. 193.
33. Lux, A., Rozenberg, G.G., Petritsch, K., Moratti, S.C., Holmes, A.B., and Friend, R.H., *Synth. Met.,* 1999, vol. 102, p. 1527.
34. Burnham, P.M., Cook, M.J., Gerrard, L.A., Heeney, M.J., and Hughes, D.L., *Chem. Commun.,* 2003, p. 2064.
35. Dolotova, O.V., Bundina, N.I., Derkacheva, V.M., Kaliya, O.L., and Luk'yanets, E.A., *Zh. Obshch. Khim.,* 1988, vol. 58, no. 9, p. 2173.
36. Mikhalenko, S.A., Derkacheva, V.M., and Luk'yanets, E.A., *Zh. Obshch. Khim.,* 1981, vol. 51, no. 7, p. 1650.
37. Abramov, I.G., Ivanovskii, S.A., Smirnov, A.V., and Dorogov, M.V., *Izv. Vyssh. Uchebn. Zaved., Ser. Khim. Khim. Tekhnol.,* 2000, vol. 43, no. 1, p. 120.
38. Derkacheva, V.M., Kaliya, O.L., and Luk'yanets, E.A., *Zh. Obshch. Khim.,* 1983, vol. 53, no. 1, p. 188.
39. Hall, T.W., Greenberg, S., McArthur, C.R., Know, B., and Leznoff, C.C., *Nouv. J. Chim.,* 1982, vol. 6, no. 12, p. 653.
40. Ağar, E., Şaşmaz, S., and Ağar, A., *Turk. J. Chem.,* 1999, vol. 23, p. 131.
41. Wohrle, D., Eskes, M., Shigehara, K., and Yamada, A., *Synthesis,* 1993, no. 2, p. 194.
42. Leznoff, C.C., Li, Z., Isago, H., D'ascanio, A.M., and Terekhov, D.S., *J. Porphyrins Phthalocyanines,* 1999, vol. 3, no. 6, p. 406.
43. Negrimovskii, V.M., Derkacheva, V.M., and Luk'yanets, E.A., *Zh. Obshch. Khim.,* 1989, vol. 59, no. 7, p. 1688.
44. Abramov, I.G., Smirnov, A.V., Plakhtinskii, V.V., and Krasovskaya, G.G., *Mendeleev Commun.,* 2002, no. 2, p. 72.
45. Ivanovskii, S.A., Dorogov, M.V., Abramov, I.G., and Smirnov, A.V., Russian Patent no. 2 167 855; *Byull. Izobret.,* 2001, no. 15.
46. Abramov, I.G., Dorogov, M.V., Ivanovskii, S.A., Smirnov, A.V., and Abramova, M.B., *Mendeleev Commun.,* 2000, no. 2, p. 78.
47. Abramov, I.G., Smirnov, A.V., Ivanovskii, S.A., Abramova, M.B., Plakhtinskii, V.V., and Belysheva, M.S., *Mendeleev Commun.,* 2001, no. 2, p. 80.
48. Abramov, I.G., Zhandarev, V.V., Smirnov, A.V., Kalandadze, L.S., Goshin, M.E., and Plakhtinskii, V.V., *Mendeleev Commun.,* 2002, no. 3, p. 120.
49. Abramov, I.G., Smirnov, A.V., Kalandadze, L.S., Plakhtinskii, V.V., and Sakharov, V.N., *Heterocycles,* 2003, vol. 60, no. 7, p. 1611.
50. Masaoka, Y., Matsumoto, M., and Iwasaki, Y., JPN

Patent Appl. no. 02-240167, 1990; *Chem. Abstr.,* 1991, vol. 114, no. 230679.

51. Kaieda, O., Yodoshi, T., Ito, H., and Onaraku, M., EU Patent no. 523959, 1993; *Chem. Abstr.,* 1993, vol. 119, no. 29981.

52. Yoshitoshi, K., Ito, H., and Kaeida, O., JPN Patent Appl. no. 02-283769, 1990; *Chem. Abstr.,* 1991, vol. 114, no. 230682.

53. Takahara, S., Ueno, K., Mirose, S., and Mizogami, K., JPN Patent Appl. no. 02-265788, 1989; *Chem. Abstr.,* 1991, vol. 115, no. 146687.

54. Ito, H., Yoshitoshi, K., and Kaieda, O., JPN Patent Appl. no. 02-175763, 1990; *Chem. Abstr.,* 1990, vol. 113, no. 193454.

55. Yoshitoshi, K. and Onazaki, U., JPN Patent Appl. no. 05-222302, 1993; *Chem. Abstr.,* 1994, vol. 120, no. 109463.

56. Mikhalenko, S.A., Korobkova, E.V., and Luk'yanets, E.A., *Zh. Obshch. Khim.,* 1970, vol. 40, no. 2, p. 400.

57. Golovin, M.N., Seimour, P., Jayaraj, K., Fu, Y.S., and Lever, A.B.P., *Inorg. Chem.,* 1990, vol. 29, no. 9, p. 1719.

58. *Elektronnye spektry ftalotsianinov i rodstvennykh soedinenii. Katalog* (Electronic Spectra of Phthalocyanines and Related Compounds. Catalog), Luk'yanets, E.A., Ed., Cherkassy: NIITEKhim, 1989.

59. Derkacheva, V.M., *Cand. Sci. (Chem.) Dissertation,* Moscow, 1981.