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Synthesis and Properties of Tetra-4-morpholinyl(piperidinyl)-5-R-Substituted Phthalocyanines

A. I. Fedotova, Yu. M. Zhuravleva, V. E. Maizlish, and G. P. Shaposhnikov

Ivanovo State University of Chemical Technology, pr. F. Engel'sa 7, Ivanovo, 153000 Russia
e-mail: ttoc@isuct.ru

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Abstract—Demetallation of magnesium tetra-4-morpholinyl(piperidinyl)-5-R-substituted phthalocyanines was performed to obtain the corresponding metal-free phthalocyanines. Their electronic absorption spectra were shown to depend on the nature of the solvent. It was found that both the saturated heterocycle and the oxyaryl substituent have almost no effect on the position of the absorption maximum.

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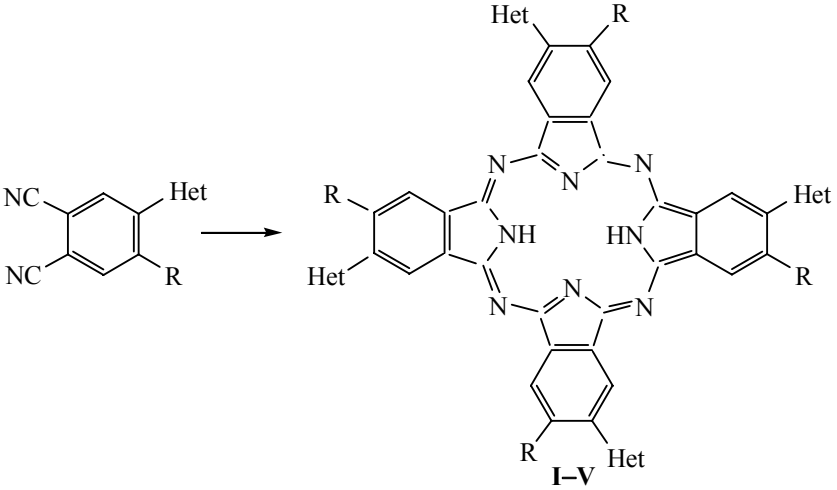
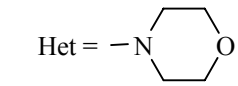
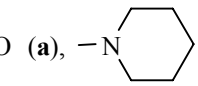
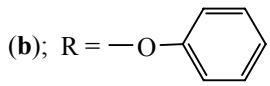
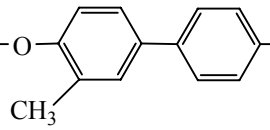
Phthalocyanines (Pc) and related compounds have attracted the attention of researchers for already more than seven decades in view of their unique physicochemical properties which are closely associated with their peculiar molecular structure [1–11].

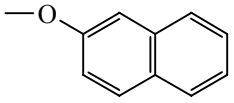
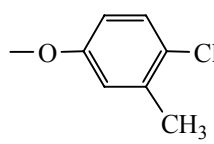
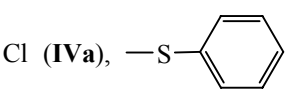
As known, one of the ways of chemical modification of Pc is functional substitution in benzene rings [1–5]. The introduction of substituents in Pc allows wide variation of their physicochemical properties (solubility in various solvents, thermal stability, catalytic, liquid-crystalline, coloristic properties, etc.).

Proceeding with systematic research in the chemistry of phthalocyanines and related compounds [4, 5, 12–20], in the present work we synthesized



I–V

Het =  (**a**),  (**b**); R =  (**Ia, Ib**),  (**IIa, IIb**),

 (**IIIa**),  (**IVa**),  (**Vb**).

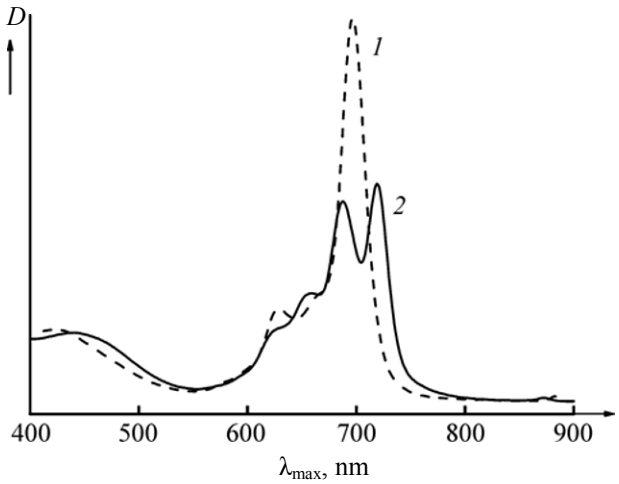


Fig. 1. Electron absorption spectra in chloroform: (*1*) magnesium tetra-4-(morpholin-4-yl)tetra-5-phenoxyphthalocyanine and (*2*) tetra-4-(morpholin-4-yl)tetra-5-phenoxyphthalocyanine (**Ia**).

metal-free morpholine- and piperidine-substituted phthalocyanines and studied some of their physicochemical properties.

There has been some information in the literature on the synthesis of metal-free phthalocyanines with heterocyclic substituents by fusing the corresponding phthalonitriles (method *a*) [20]. It was also experimentally established that some metal-free phthalocyanines [$H_2Pc(4\text{-Het})_4(5\text{-R})_4$] can be prepared by heating the starting phtnalonitriles but in quite low yields which slightly increase in the presence of urea (Table 1, method *b*). Therefore, compounds **I**–**V** were prepared by demetallation of the corresponding magnesium complexes by their reprecipitation from glacial acetic acid solutions (method *c*). The reaction progress was followed by spectrophotometry. The

Table 1. Conditions of synthesis of metal-free phthalocyanines **I**–**V**

Comp. no.	Yield, %		
	method *a*	method *b*	method *c*
Ia	–	22	58
Ib	–	–	47
IIa	9	19	55
IIb	–	–	58
IIIa	9	24	41
IVa	10	15	57
Vb	12	32	48

electronic absorption spectra of the target products no longer contain the *Q* band characteristics of the magnesium complexes and show two bands typical of ligands (Fig. 1). The splitting of the *Q* band of H_2Pc into two components is due to the D_{2h} symmetry of these molecules [3].

The resulting ligands were identified by elemental analysis and electronic, ^{1}H NMR, and IR spectroscopy. The IR spectra showed absorption bands characteristic of phthalocyanine compounds [21, 22]. In the range 2840–2930 cm^{-1} there are absorption bands of methyl and methylene C–H bonds of saturated monoaza cycles and alkyl fragments of phthalocyanines. The spectra of compounds **I**–**IV** containing aryloxy groups show bands at 1210–1220 cm^{-1}, which are assignable to Ar–O–Ar vibrations. The band at 1128 cm^{-1} in the spectrum of compound **Vb** corresponds to Ar–S–Ar vibrations [23]. At 3285–3324 and 1007–1010 cm^{-1} absorption bands characteristic of metal-free phthalocyanines are observed [21, 24]. It was found that the nature of the saturated heterocycle has no effect on the shape and position of bands in the IR spectra.

The ^{1}H NMR spectra of phthalocyanines are similar to the spectra of the corresponding phthalonitriles [25]. Furthermore, in our case an upfield signal from endocyclic NH protons (from –2.00 to –2.02 ppm) is observed which is absent from the spectrum of the parent metal complex (Fig. 2).

The synthesized compounds are soluble in organic solvents (DMF, DMSO, chloroform, etc.) and concentrated sulfuric acid. Moreover, the presence of the morpholine and piperidine fragments endow these compounds with solubility in concentrated hydrochloric acid and glacial acetic acid.

Analysis of the electronic absorption spectra showed that they are solvent dependent (Figs. 3 and 4; Tables 2 and 3). In DMF, the ligands are present as associates. The spectra of these compounds in the visible region (636–709 nm) contain an absorption band which is broadened or split in two components. The shape of the spectrum depends on the concentration of the phthalocyanine. Upon strong dilution (to $<10^{-7}$ M), the spectrum transforms into a one-band spectrum (Fig. 3) which is quite similar to the spectra of metal complexes; the same phenomenon was previously obtained with other substituted metal-free phthalocyanines and was explained by the formation of a dianion with D_{4h} symmetry [22]. In other organic solvents (except for DMSO) the

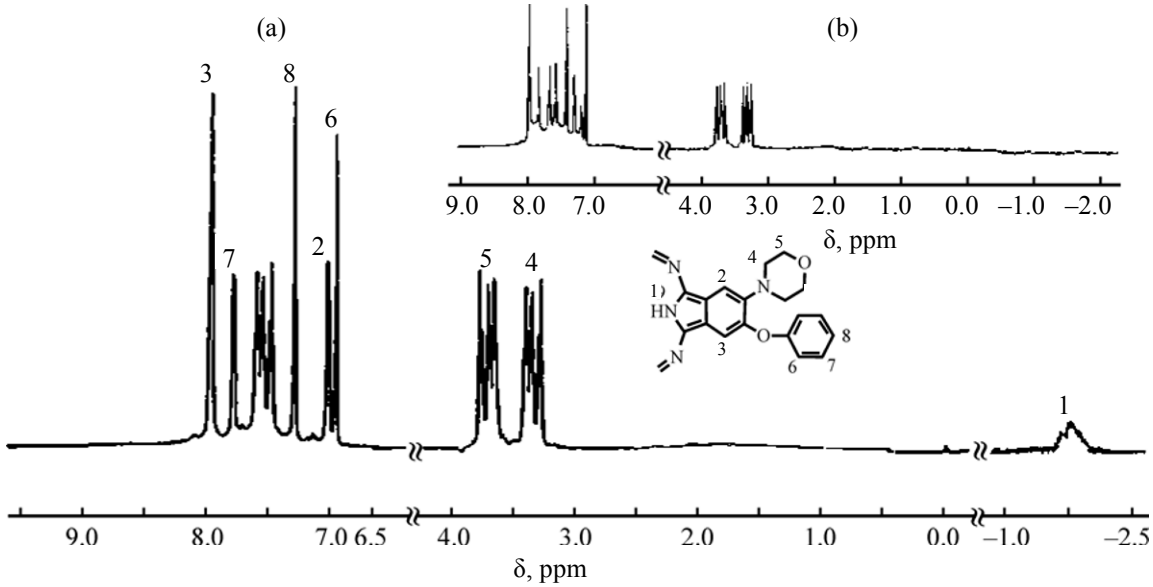


Fig. 2. [1]H NMR spectra of (a) 1-tetra-4-(morpholin-4-yl)tetra-5-phenoxyphthalocyanine (**Ia**) and (b) nickel 2-tetra-4-(morpholin-4-yl)tetra-5-phenoxyphthalocyanine.

spectrum is typical of the ligands. The spectrum of compound **IIIa** in the visible region contains two absorption bands (Q_1 and Q_2) at 714–719 and 684–695 nm (Fig. 4, Tables 2 and 3), and, therewith, the intensity ratio of the Q_1 and Q_2 bands and their positions are solvent-dependent (Fig. 4, Table 3). The electronic absorption spectrum in DMSO contains one absorption band, thus providing evidence showing that, like in DMF, the compound is present in the dianionic form (Table 3). In was found that the nature of both the oxyaryl fragment and the saturated heterocycle scarcely affects the position of the absorption maximum (Table 2).

The replacement of the "bridging" oxygen atoms of the phenoxy groups of tetra-4-(piperidin-1-yl)tetra-5-phenoxyphthalocyanine (**Ib**) by the sulfur atom to obtain tetra-4-(piperidin-1-yl)tetra-5-phenylsulfanylphthalocyanine (**Vb**) leads to a red shift of the long-wave band by 10–11 nm (Table 2), which was previously observed with other substituted phthalocyanines [14].

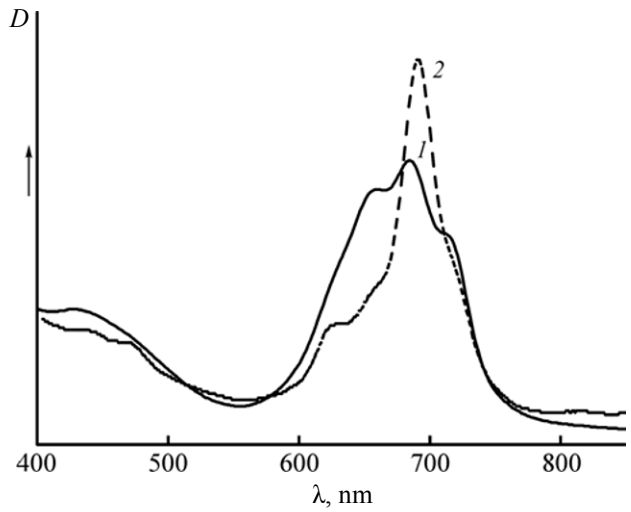


Fig. 3. Electron absorption spectra of tetra-4-(morpholin-4-yl)tetra-5-(2'-naphthyloxy)phthalocyanine (**IIIa**) in DMF: (*1*) c 10^{-5} M and (*2*) c 10^{-7} M.

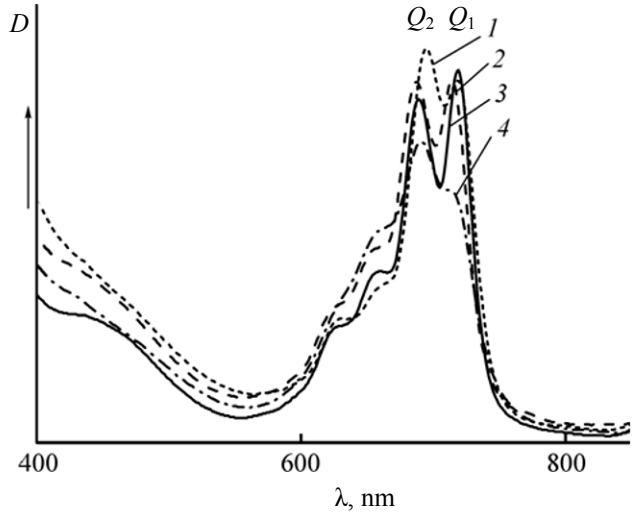


Fig. 4. Electron absorption spectra of tetra-4-(morpholin-4-yl)tetra-5-(2'-naphthyloxy)phthalocyanine (**IIIa**) in (*1*) pyridine, (*2*) dioxane. (*3*) chloroform, and (*4*) DMF (c 10^{-5} M).

Table 2. Long-wave absorption maxima of phthalocyanines **I–V**

Compound	λ_{max}, nm (log ε)	
	$CHCl_3$	DMF
Ia	717 (5.17), 685 (5.14)	693
Ib	717 (5.02), 685 (4.99)	693
IIa	718 (5.02), 687 (4.98)	691
IIb	720 (4.99), 687 (4.96)	691
IIIa	720 (4.98), 688 (4.95)	692
IVa	719 (4.98), 687 (4.93)	694
Vb	727 (5.16), 696 (5.13)	703

Table 3. Intensity ratios of the Q_2 and Q_1 bands in the electron absorption spectra of tetra-4-(morpholin-4-yl)tetra-5-(2'-naphthyloxy)phthalocyanine (**IIIa**)

Solvent	λ_{max}, nm		$D(Q_2)/D(Q_1)$
	Q_1	Q_2	
Chloroform	717	688	0.87
Benzene	719	688	0.91
Toluene	719	688	0.93
Dioxane	714	687	1.00
THF	716	687	0.95
CCl_4	718	684	1.01
Pyridine	719	695	1.10
DMSO	–	686	7.00

EXPERIMENTAL

The electron absorption spectra were registered in organic solvents on a Perkin Elmer Lambda 200 UV/Vis spectrophotometer at room temperature in the range 325–900 nm. The IR spectra were measured on an Avatar 360 ESP FT–IR spectrometer in the range 400–4000 cm^{-1} in thin films (chloroform). The ^1H NMR spectra were obtained on a Bruker DRX-500 spectrometer in 5% solutions in $CDCl_3$ against internal TMS. The elemental analysis was performed on a FlashEA 1112 CHNS/O instrument.

Synthesis of phthalocyanines (*general procedure*)**.** A substituted phthalocyanine, 0.5 mmol, was ground with 63 mg (0.14 mmol) of magnesium acetate tetrahydrate and 60 mg (1 mmol) of urea. The mixture was heated at 180–195°C for 2 h. The reaction mass was repreciptated from a glacial acetic acid solutions. The precipitate was washed with distilled water. The admixtures were extracted with ethanol–water, 1:1 (**Ia**–**IVa**) and acetone–water, 1:2 (**Ib, IIb, Vb**). The targeted phthalocyanines were extracted with chloroform. The final purification was performed by column chromatography (adsorbent Al_2O_3, eluent chloroform). The solvent was removed in a vacuum, and the products were vacuum-dried at 80°C.

The synthesized $H_2Pc(4\text{-Het})_4(5\text{-R})_4$ are dark green powders, they are readily soluble in water, concentrated HCl and H_2SO_4, glacial acetic acid, DMF, chloroform, and some other organic solvents.

Tetra-4-(morpholin-4-yl)tetra-5-phenoxyphthalocyanine (Ia) was obtained by the general procedure from 76 mg of 4-(morpholin-4-yl)tetra-5-phenoxyphthalonitrile. Yield 44 mg (58%). IR spectrum, ν, cm^{-1}: 3285, 1007 (NH), 2869, 2833 (CH_2), 1208 (Ar–O–Ar). ^1H NMR spectrum, δ, ppm: 7.96 s (4H, H^3), 7.55 m (8H, H^7), 7.43 s (4H, H^8), 7.08 s (4H, H^2), 6.92 m (8H, H^6), 3.65 m (16H, H^5), 3.30 m (16H, H^4), –2.00 m (2H, H^1). Found, %: C 70.50; H 5.21; N 13.31. $C_{72}H_{62}N_{12}O_8$. Calculated, %: C 70.69; H 5.11; N 13.74.

Tetra-4-(morpholin-4-yl)tetra-5-{[3,4'-dimethyl-(1,1'-biphenyl)-4-yl]oxy}phthalocyanine (IIa) was obtained by the general procedure from 102 mg of 4-(morpholin-4-yl)tetra-5-{[3,4'-dimethyl(1,1'-biphenyl)-4-yl]oxy}phthalonitrile. Yield 49 mg (48%). IR spectrum, ν, cm^{-1}: 3295, 1005 (NH), 2870, 2832 (CH_2), 1208 (Ar–O–Ar). Found, %: C 76.01; H 5.98; N 10.04. $C_{104}H_{92}N_{12}O_8$. Calculated, %: C 76.17; H 5.78; N 10.25.

Tetra-4-(morpholin-4-yl)tetra-5-(2'-naphthyloxy)phthalocyanine (IIIa) was obtained by the general procedure from 80 mg of 4-(morpholin-4-yl) tetra-5-(2'-naphthyloxy)phthalonitrile. Yield 66 mg (37%). IR spectrum, ν, cm^{-1}: 3299, 1007 (NH), 2868, 2836 (CH_2), 1208 (Ar–O–Ar). Found, %: C 74.02; H 5.08; N 11.97. $C_{88}H_{70}N_{12}O_8$. Calculated, %: C 74.25; H 4.96; N 11.81.

Tetra-4-(morpholin-4-yl)tetra-5-(4'-chloro-3'-methylphenoxy)phthalocyanine (IVa) was obtained by the general procedure from 89 mg of 4-(morpholin-4-yl)tetra-5-(4'-chloro-3'-methylphenoxy)phthalonitrile. Yield 49 mg (55%). IR spectrum, ν, cm^{-1}: 3297, 1007 (NH), 2871, 2835 (CH_2), 1208 (Ar–O–Ar). Found, %: C 64.21; H 4.88; N 11.71. $C_{76}H_{66}N_{12}O_8Cl_4$. Calculated, %: C 64.41; H 4.69; N 11.86.

Tetra-4-(piperidin-1-yl)tetra-5-phenoxyphthalocyanine (Ib) was obtained by the general procedure from 76 mg of 4-(piperidin-1-yl)tetra-5-phenoxyphthalonitrile. Yield 36 mg (47%). IR spectrum, ν, cm^{-1}: 3324, 1007 (NH), 2870, 2834 (CH_2), 1208 (Ar–O–Ar). Found, %: C 76.29; H 7.41; N 11.85. $C_{76}H_{70}N_{12}O_4$. Calculated, %: C 75.10; H 5.80; N 13.83.

Tetra-4-(piperidin-1-yl)tetra-5-{[3,4'-dimethyl-(1,1'-biphenyl)-4-yl]oxy}phthalocyanine (IIb) was obtained by the general procedure from 102 mg of 4-(piperidin-1-yl)tetra-5-{[3,4'-dimethyl (1,1'-biphenyl)-4-yl]oxy}phthalonitrile. Yield 56 mg (55%). IR spectrum, ν, cm^{-1}: 3320, 1006 (NH), 2866, 2832 (CH_2), 1208 (Ar–O–Ar). Found, %: C 79.24; H 6.52; N 10.01. $C_{108}H_{102}N_{12}O_4$. Calculated, %: C 79.48; H 6.30; N 10.30.

Tetra-4-(piperidin-1-yl)tetra-5-(phenylsulfanyl)-phthalocyanine (Vb) was obtained by the general procedure from 90 mg of 4-(piperidin-1-yl)tetra-5-(phenylsulfanyl)phthalonitrile. Yield 35 mg (44%). IR spectrum, ν, cm^{-1}: 3324, 1008 (NH), 2930, 2830 (CH_2), 1128 (Ar–S–Ar). Found, %: C 71.20; H 5.87; N 13.01; S 9.52. $C_{76}H_{70}N_{12}S_4$. Calculated, %: C 71.33; H 5.51; N 13.13; S 9.57.

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