Макрогетероциклы
http://macroheterocycles.isuct.ru

DOI: 10.6060/mhc151192s

Microwave–Assisted Synthesis of Phthalocyanine Zinc Complexes Derived from Aminotricyanobiphenyl–Based Azo Dyes

Galina A. Selivanova,[a@] Evgeny V. Amosov,[a] Vladimir G. Vasilyev,[a] Evgeny A. Lukyanets,[b] Evgeny V. Tretyakov,[a] and Vitalij D. Shteingarts[a†]

[a]*N.N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch of Russian Academy of Sciences, 630090 Novosibirsk, Russia*
[b]*Research Institute of Organic Intermediates and Dyes, 123995 Moscow, Russia*
[@]*Corresponding author E-mail: galseliv@nioch.nsc.ru*

Several new azo compounds were obtained by coupling 2,3',4'-tricyanodiphenyl-4-diazonium bisulfate with β-naphthol, 3-hydroxy-2-naphthoic and salicylic acids, aniline, 2-toluidine, 2,6-xylidine, and N,N-dibutylaniline. New zinc complexes of tetra-4-[2-cyano-4-(2-hydroxy-1-naphthyldiazenyl)phenyl]phthalocyanine and tetra-4-[2-cyano-4-(4-dibutylaminophenyldiazenyl)phenyl]-phthalocyanine were obtained in 84 % and 67 % yields by condensation of the corresponding azo compounds in the presence of zinc acetate under microwave assistance. This method was also succesfully applied for the preparation of known zinc complexes based on 4-substituted 2,3',4'-tricyanodiphenyls with enhanced yields.

Keywords: Azo compounds, zinc complexes of phthalocyanine, microwave assistance.

Синтез с микроволновым содействием цинковых комплексов фталоцианинов из азосоединений на основе аминотрициандифенила

Г. А. Селиванова,[a@] Е. В. Амосов,[a] В. Г. Васильев,[a] Е. А. Лукьянец,[b] Е. В. Третьяков,[a] В. Д. Штейнгарц[a†]

[a]*Новосибирский институт органической химии им. Н.Н. Ворожцова, СО РАН, 630090 Новосибирск, Россия*
[b]*Научно-исследовательский институт органических полупродуктов и красителей, 123995 Москва, Россия*
[@]*E-mail: galseliv@nioch.nsc.ru*

Синтезировано несколько новых азосоединений сочетанием диазотированного 4-амино-2,3',4'-трициандифенила с β-нафтолом, 3-гидрокси-2-нафтойной и салициловой кислотами, анилином, 2-толуидином, 2,6-ксилидином и N,N-дибутиланилином. Новые цинковые комплексы тетра-4-[2-циано-4-(2-гидрокси-1-нафтилдиазенил)фенил]фталоцианина и тетра-4-[2-циано-4-(4-дибутиламинофенилдиазенил)фенил]фталоцианина были получены с выходами 84 % и 67 % конденсацией соответствующих азосоединений в присутствии ацетата цинка при микроволновом содействии. Этот метод также успешно применен для получения уже известных цинковых комплексов на основе 4-производных 2,3',4'-трициандифенила с улучшенными выходами.

Ключевые слова: Азосоединения, цинковые комплексы фталоцианинов, микроволновое содействие.

† Deceased (покойный).

Introduction

Due to the appearance of new applications for compounds from the phthalocyanine (Pc) class in various areas of technology, chemical engineering, medicine, *etc*.[1-4] demanding the development of new materials with different properties on their basis, there is a need in a wide variation of their structure. A peripheral substitution in the Pc nucleus increases their solubility in water[3,4] or organic solvents[4,5] and creates conditions for molecular design of more complex molecular structures including fragments of Pc, and lends useful properties to materials based on them. It could be attained either by the synthesis of "building blocks", or by the chemical transformations of the already assembled Pc. In this connection aryl substituted Pcs are especially interesting as starting compounds for the synthesis of new functionalised species, given the great potential of chemical modification on the aryl moieties, and directly as the component materials for practical use.[2,3,5] New opportunities here open up due to the recent development of the one-step conversion of phthalonitrile into 2,3',4'-tricyanodiphenyl[6]giving rise to 4-amino-2,3',4'-tricyanodiphenyl (**1**)[7,8] – the base compounds with potentially broad application for the synthesis of functionalized Pcs with aryl moiety. The most important spectral feature of such Pcs is the presence of absorption only at the edges of the visible region in the electronic spectra of Pc chromophore, namely *Q*-band in the region of 650–670 nm and *B*-band at around 350 nm. In order to expand the possibilities of using Pcs as photoactive agents, their structural modification would provide, firstly, a red shift of the *Q*-band and, secondly, an additional absorption in the intermediate region of 400–600 nm.

Insertion of the Pc core into a certainly functionalized π-conjugated system is a possible route to varying the photophysical properties of Pcs and materials based on them. In particular, azo compounds provide absorption in the said intermediate region and allow tuning the position of the Pc band by varying the type of substituents present in these fragments. There are only a few examples of Pcs containing arylazo substituents in β-position of the Pc macrocycle. A zinc complex with one arylazo group in nucleus was prepared by transformation of nitro group introduced directly into the Pc.[9] A compound with two Pc macrocycles bound by a bridge from an alternating sequence of two quinoxaline fragments and three azo groups was also prepared from Pc containing nitro group.[10] Syntheses of some tetra-azo substituted Pcs and their complexes[11-13] were carried out by condensation of phthalonitriles containing *N,N*-dialkylaminoarylazo groups. A zinc complex of Pc containing four aryltriazenyl groups was described by Chinese authors.[14]

The aim of our work is to study the possibility of preparation of a broad range of new azo compounds derived from amine **1** and their microwave assisted conversion into polyfunctional phthalocyanine zinc complexes (Scheme 1).

Experimental

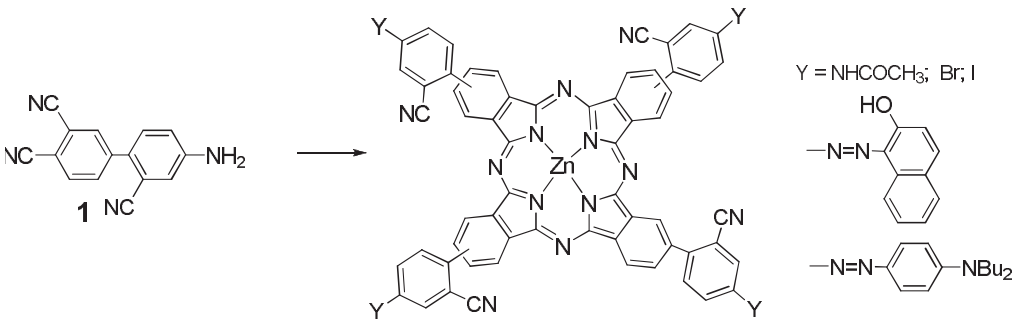
General Procedures

^{1}H NMR spectra of 5–10 % solutions in acetone-d_6 or DMSO-d_6 were recorded on Bruker AC 200 (200.132 MHz) and AV 400 (400.134 MHz) spectrometers using the residual proton-containing solvent as the internal reference. ^{13}C NMR spectra were recorded on Bruker AC-200 (50.323 MHz) and AM-400 (100.614 MHz) spectrometers. IR spectra were registered on a Bruker V-22 spectrophotometer (pellets containing 1 mg of sample in 150 mg KBr); UV-Vis spectra – on Varian Cary-5000 (0.3 mg of sample /150 mg of KBr) and HP Agilent 8453 (10^{-5}–10^{-4} M solutions in DMSO) spectrophotometers.

Thermal analyses were performed on a Netzsch simultaneous heat flux thermal analyzer (STA409PCLuxx) equipped with an S-Type (Pt/RtRh) TG-DSC sample carrier and a PtRh10-Pt thermocouple (Netzsch-Geratebau GmbH, Selb).

For compound **3**, the precise magnitude of the molecular mass was measured on a DFS "Thermo scientific" mass spectrometer; MALDI-TOF mass spectra were recorded on a Bruker Daltonics Autoflex III mass spectrometer in reflection mode with positive ion generation ($[M+H]^+$), a nitrogen laser (λ = 337.1 nm) with frequency of 25 Hz and power of 3–4 mW (150–200 μJ per pulse) was used as ionization source, and a saturated solution of 2,5-dihydroxybenzoic acid in acetonitrile was used as a matrix. For compounds **4**–**10**, the molecular masses were detected on a micrOTOF-Q Bruker hybride quadrupole-time-off light mass spectrometer. The observed relative intensities of the isotope ions and *m/z* values were in good agreement with the calculated values. Ionization methods: for compounds **4**, **5** and **8**–**10** – electrospray (ESI); for compounds **7** and **9** – chemical ionization at atmospheric pressure (APCI); for compounds **6** and **9** – atmosphere pressure photoionization (APPI). Injection methods: for compounds **4**, **5**, **9** and **10**, a solution in DMSO–MeOH fed into the spray chamber of the mass spectrometer with a flow rate 180 μl/h except for APPI where flow rates were 800 and 100 μl/h; for compounds **6**–**8** a solution in DMSO or EtOH fed into the spray chamber of the mass spectrometer by avtosampler of Agilent 1200 chromatograph (5 μl in flows of solvent, 0.1 ml/min).

Composition of the mixtures for compounds **6**, **7**, **9** was revealed using reversed-phase HPLC (ColumnZorbax XDB-C8,



Scheme 1. Target phthalocyanine zinc complexes.

2.1×150 mm, 3.5 μ, eluent H_2O–MeCN, a linear gradient from 10 to 100 % MeCN, a flow rate 0.2 ml/min) with a diode-array and mass selective detectors. The chromatograms were recorded at wavelengths 255/16, 480/32 and 370/60 nm with optical absorption spectra in the range of 230–600 nm at 150 spectra per minute.

Samples of 4-amino- (**1**), 4-acetylamino- (**12**), 4-bromo- (**13**) and 4-iodobiphenyl-2,3',4'-tricarbonitrile (**14**) as well as a solution of 2,3',4'-tricyanobiphenyl-4-diazonium bisulfate (**2**) were prepared as reported previously.[8] 4-((4-(Dibutylamino)phenyl) diazenyl)biphenyl-2,3',4'-tricarbonitrile (**9**) was synthesized according to known procedure.[25,26] Pc syntheses were performed in a Discover SP microwave oven at exposure rate 200 W.

Syntheses

4-(2-Hydroxy-1-naphthyldiazenyl)diphenyl-2,3',4'-tricarbonitrile (3). A cooled solution of *β*-naphthol (118 mg, 0.82 mmol) and NaOH (108 mg, 4.5 mmol) in H_2O (4 ml) was added to a stirred at -5 °C solution of bisulfate **2** prepared from amine **1** (200 mg, 0.82 mmol) in 50 % sulfuric acid (8 ml) and $NaNO_2$ (70 mg, 1.00 mmol) in H_2O (5 ml). The cooling was stopped; the reaction mixture was stirred at room temperature for 2 hrs, then H_2O (60 ml) was added. The precipitate was separated (centrifuging), washed with H_2O (3×10 ml) until neutral and dried in vacuo over P_2O_5. The crude product was recrystallized from ethanol giving 200 mg (62 %) of the title product. Orange crystals, stable up to 300 °C. Found: M^+ 399.1112. $C_{25}H_{13}N_5O$. Calculated 399.1115. Mass spectrum (ESI) *m/z* (%): 399 (69) [M+], 271 (28), 244 (43), 171 (28), 143 (100), 115 (65), 28 (25). IR (KBr) ν cm^{-1}: 1202 (C–OH), 1502 (N=N), 2233 (C≡N), 3437 br. (OH). UV-Vis (C_2H_5OH) λ nm (relative intensity): 220 (1.00), 316 (0.19), 482 (0.20).^{13}C NMR (400 MHz, [D_6]DMSO) δ_C ppm: 111.7, 114.4, 115.1, 115.6, 115.7, 117.4, 122.1, 122.6, 122.8, 124.9, 126.9, 128.2, 128.2, 129.1, 129.6, 130.5, 131.8, 132.5, 134.0, 134.2, 137.9, 142.2, 142.4, 145.0, 174.1.

3-Hydroxy-4-((2,3',4'-tricyanodiphenyl-4-yl)diazenyl)-2-naphthoicacid (4). A cooled solution of bisulfate **2** obtained from amine **1** (20 mg, 0.082 mmol) in 50 % sulfuric acid (1 ml) and $NaNO_2$ (7 mg, 0.10 mmol) in H_2O (0.5 ml) and a cooled solution of NaOH (18 mg, 0.45 mmol) in H_2O (1 ml) were added to a stirred at -5 °C solution of 3-hydroxy-2-naphthoic acid (15 mg, 0.08 mmol) in H_2O (4 ml). The solutions were added portionwise and in such a way to maintain p*H* close to neutral. The mixture was stirred at 5 °C for 3 hrs, the crude product was separated and recrystallized from ethanol to give 22 mg (60 %). Orange crystals, m.p. 292–294 °C. HPLC-MS: (ESI) 442.096 $[M–H]^+$. $C_{26}H_{12}N_5O_3$. Calculated 442.095. MS-spectrum of the anion with the mass 442.1 gives the ions $(M–CO_2)^-$with *m/z* = 398.12 and 370.11 $(398.12–N_2)^-$. IR (KBr) ν cm^{-1}: 1157 (C–OH), 1200 (C–OH), 1500 (N=N), 1606 (C=O), 2233 (C≡N), 3433 br. (OH). UV-Vis (KBr) λ nm (relative intensity): 212 (1.00), 345 (0.37), 502 (0.23).[25]UV-Vis (C_2H_5OH) λ nm (relative intensity): 212 (1.00), 285 (0.30), 417 (0.13), 510 (0.80). ^{13}C NMR (400 MHz, [D_6]DMSO) δ_C ppm:111.4, 114.6, 115.2, 115.8, 115.9, 117.8, 122.6, 123.3, 124.9, 126.3, 126.6, 129.8, 130.0, 131.6, 131.7, 134.2, 134.3, 134.4, 137.2, 140.0, 142.7, 154.0, 161.8, 169.6.

2-Hydroxy-5-((2,3′,4′-tricyanodiphenyl-4-yl)diazenyl) benzoic acid (5). A cooled solution of bisulfate **2** obtained from amine **1** (100 mg, 0.41 mmol) in 50 % sulfuric acid (4 ml) and $NaNO_2$ (34 mg, 0.49 mmol) in H_2O (3 ml) and a cooled solution of NaOH (7 g, 0.45 mmol) in H_2O (15 ml) were added to a stirred at -5 °C solution of salicylic acid (56 mg, 0.41 mmol) in H_2O (4 ml). As in the previous case, the solutions were added portionwise and in such a way to maintain p*H* close to neutral. The mixture was stirred at 5 °C for 3 hrs, the crude product was separated and dried *in vacuo* over P_2O_5 to yield 80 mg (60 %) of the title product. Orange powder, mp>350 °C. HPLC-MS: (ESI) $M–H^+$ 392.08. $C_{22}H_{10}N_5O_3$. Calculated 392.08. MS-spectrum of this anion gives the ions with *m/z* = 348.09 $(392-CO_2)^-$, 320.08 $(348.09-N_2)^-$ and 228.06 $(320.08-C_6H_4O)^-$. IR (KBr) ν cm^{-1}: 1140 (C–OH), 1180 (C–OH), 1486–1430 (N=N), 2231 (C≡N), 1600 (C=O), 3416 br. (OH). UV-Vis (C_2H_5OH) λ nm (relative intensity): 205 (1.00), 220 (0.70), 264 (0.27), 378 (0.39). ^{13}C NMR (400 MHz, [D_6]DMSO) δ_C ppm: 111.5, 114.6, 115.1, 115.5, 115.6, 117.4, 118.5, 119.0, 126.3, 126.9, 127.2, 127.3, 131.7, 134.1, 134.2, 140.7, 141.9, 142.5, 152.4, 170.2, 171.7, 192.1.

4-((4-Aminophenyl)diazenyl)diphenyl-2,3',4'-tricarbonitrile (6), its tautomer (6a) and triazene (11). A cooled solution of bisulfate **2** obtained from amine **1** (200 mg, 0.82 mmol) in 50 % sulfuric acid (8 ml) and $NaNO_2$ (70 mg, 1.00 mmol) in H_2O (5 ml) was added portion wise to a stirred at -5 °C solution of aniline (168 mg, 2.20 mmol) in H_2O (2 ml). The mixture was stirred at 0–5 °C for 2 hrs and at room temperature for 96 hrs. The solid fraction was washed with $NaHCO_3$ water solution (3 × 10 mL), then with H_2O and dried *in vacuo* over P_2O_5 giving a mixture of products which were separated by TLC (silica gel, benzene–ethyl ether, 5:1 v/v, five times elution). The next compounds were identified. Amine **1**, yield 100 mg (50 %). Tricarbonitrile **6**, its tautomer **6a** and triazene **11**, yield 39 mg (35 %). HPLC-MS: (APPI) $M–H^+$ 349.118.$C_{21}H_{13}N_6$. Calculated 349.120. UV-Vis spectra (C_2H_5OH) for **6** and **6a** are equal, λ nm (relative intensity): 210 (1.00), 243 (0.48), 280 (0.25), 368 (0.77), for triazene **11**; UV-Vis (C_2H_5OH) λ nm (relative intensity): 210 (1.00), 276 (0.36), 415 (0.82).

4-((4-Amino-3-methylphenyl)diazenyl)diphenyl-2,3',4'-tricarbonitrile (7). A cooled solution of bisulfate **2** obtained from amine **1** (25 mg, 0.10 mmol) in 50 % sulfuric acid (2 ml) and $NaNO_2$ (9 mg, 0.12 mmol) in H_2O (2 ml) was added portion wise to a stirred at -5 °C solution of *o*-toluidine (11 mg, 0.10 mmol) in H_2O (1 ml). The mixture was stirred at 0–5 °C for 2 hrs and at room temperature for 95 hrs. The solid fraction was treated as described before to produce 22 mg containing according to ^{1}H NMR amine **1** (15 %), compound **7** (58 %) and three non-identified compounds (in equal shares, ∑ 25 %). Found for compound **7**: (APCI) $M–H^+$ 363.136. $C_{22}H_{15}N_6$. Calculated 363.135. Negative ions found M+ē 362.130. $C_{22}H_{14}N_6$. Calculated 362.129. UV-Vis (C_2H_5OH) λ nm (relative intensity): 210 (1.00), 240 (0.45), 344 (0.27).

4-((Amino-3,5-dimethylphenyl)diazenyl)diphenyl-2,3',4'-tricarbonitrile (8). A cooled solution of bisulfate **2** obtained from amine **1** (40 mg, 0.16 mmol) in 50 % sulfuric acid (3 ml) and $NaNO_2$ (14 mg, 0.20 mmol) in H_2O (2 ml) was added portion wise to a stirred at -5 °C solution of 2,6-xylidine (20 mg, 0.16 mmol) in H_2O (2 ml). The mixture was stirred at 0–5 °C for 2 hrs and at room temperature for 96 hrs. The solid fraction was treated as described, and the product was washed with hot ethanol and dried to give **8** in 48 mg yield (77 %). Orange crystals, stable up to 275 °C. HPLC-MS: (ESI) $M–H^+$375.134. $C_{23}H_{15}N_6$. Calculated 375.136. IR (KBr) ν cm^{-1}: 1126 ($C_{Ar.}$–H), 1310 (C–NH_2), 1383 (C–H_3), 1483 (N=N), 1599 (NH_2), 1624 (NH_2), 2231 (C≡N), 2853 (C–H_3), 2916-2966 ($C_{Ar.}$–H), 3071 ($C_{Ar.}$–H), 3395 (NH_2), 3479 (NH_2), 3542. UV-Vis (KBr) λ nm (relative intensity): 224 (0.82), 285 (0.65), 303 (0.66), 432 (1.00), 480 (0.92). UV-Vis (C_2H_5OH) λ nm (relative intensity): 203 (1.00), 211 (0.96), 278 (0.38), 435 (0.61). ^{13}C NMR (400 MHz, [D_6]DMSO) δ_C ppm:17.7, 111.3, 114.4, 115.0, 115.5, 115.6, 117.5, 120.6, 120.6, 124.5, 126.1, 126.6, 131.6, 134.0, 134.2, 140.0, 142.3, 142.4, 150.2, 152.4.

2-(3-(2,3′,4′-Tricyanodiphenyl-4-yl)triazene-2-enyl)benzoic acid (10). A cooled solution of anthranilic acid (22 mg, 0.16 mmol) and NaOH (36 mg, 0.90 mmol) in H_2O (1 ml) was added portionwise to a stirred at -5 °C solution of bisulfate **2** obtained from amine **1** (40 mg, 0.16 mmol) in 40 % hydrochloric acid (1 ml) and $NaNO_2$ (14 mg, 0.20 mmol) in H_2O (0.5 ml). The mixture was stirred at 0–5 °C for 2 hrs and at room temperature for 2 hrs, then it was diluted with H_2O (7 ml), the precipitate was separated (centrifuging), washed with water until neutral and dried *in vacuo* over P_2O_5 to yield a crude product containing the title product **10** (50 % according to ^{1}H NMR). The mother solution was treated

with $NaHCO_3$ solution until neutral that gave additional amount of almost pure **10** (17 mg, 33 %). HPLC-MS: (ESI) $M–H^+$ 391.093. $C_{22}H_{11}N_6O_2$. Calculated 391.095. ^{13}C NMR (400 MHz, [D_6]DMSO) δ_C ppm: 111.6, 113.6, 114.6, 115.4, 116.1, 116.2, 118.2, 122.6, 126.0, 126.2, 131.5, 132.0, 132.1, 133.8, 134.4, 134.5, 134.6, 138.4, 142.0, 143.1, 151.2, 170.4 (COOH).

*Representative procedure for the synthesis of zinc tetra-(2-cyano-4-acetylaminophenyl)phthalocyanine (**15**).*[8] A mixture of compound **12** (40 mg, 0.14 mmol) and $Zn(CH_3COO)_2 \cdot 2H_2O$ (7 mg, 0.03 mmol) in 1-pentanol (0.5 ml) was heated at 155 °C in microwave oven for 10 minutes. After cooling the solvent was evaporated. The residue was washed with diethyl ether (3×7 ml), alcohol (2×2 ml) and H_2O (6 ml), and dried *in vacuo* over P_2O_5 to produce the title product in form of a blue-green powder. Yield 41 mg (97 %).

*Zinc tetra-(2-cyano-4-bromophenyl)phthalocyanine (**16**)*[8] was obtained from phthalonitrile **13** (19 mg) in 88 % yield.

*Zinc tetra-(2-cyano-4-iodophenyl)phthalocyanine (**17**)*[8] was prepared from phthalonitrile **14** (20 mg) in 70 % yield.

*Zinc tetra-4-(2-cyano-4-(2-hydroxy-1-naphthyldiazenyl) phenyl)phthalocyanine (**18**)* was synthesized from phthalonitrile **3** (20 mg) in 84 % yield (brown powder). IR (KBr) ν cm^{-1}: 511, 836, 1096, 1150, 1203, 1254, 1300, 1401, 1452, 1504 (N=N), 1601, 1618, 2228 (C≡N), 2856, 2927, 2956, 3062, 3435 (O–H). UV-Vis (KBr) λ nm (relative intensity): 211 (1.00), 340 (0.35), 393 (0.30), 499 (0.39), 653 (0.06), 717 (0.20). MALDI-TOF: found 1660.23 (M^+), $C_{100}H_{52}N_{20}O_4Zn$. Calculated 1660.37.

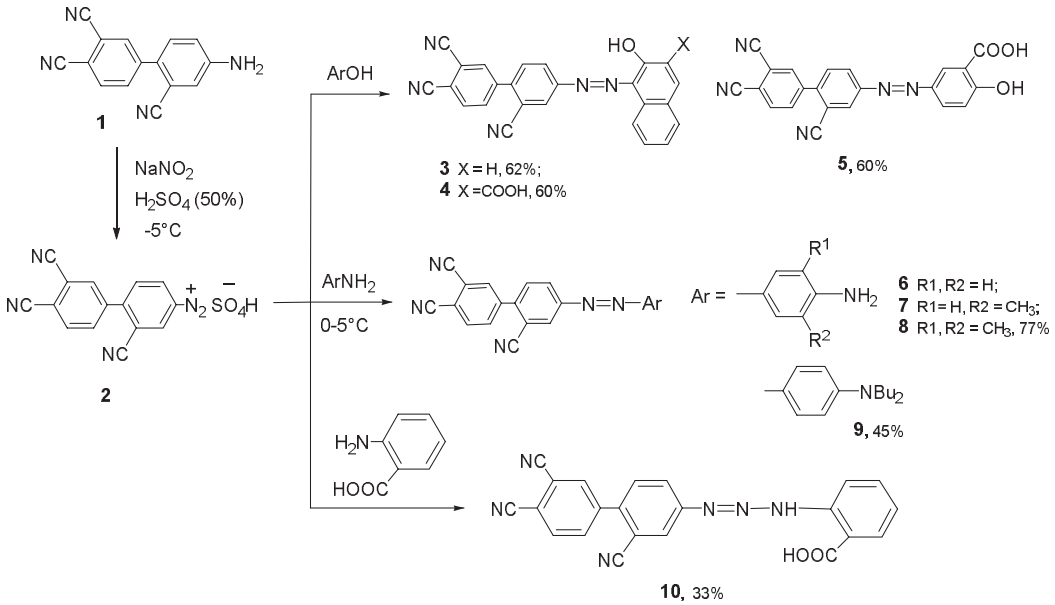
*Zinc tetra-4-(2-cyano-4-(4-dibutylaminophenyldiazenyl) phenyl)phthalocyanine (**19**)* was synthesized from phthalonitrile **9** (20 mg) in 84 % yield (brown powder). IR (KBr) ν cm^{-1}: 524, 823, 1140, 1224, 1309, 1363, 1396, 1513, 1599, 2225 (C≡N), 2868, 2929, 2956, 3432. UV-Vis (DMSO) λ nm (relative intensity): 295 (0.45), 350 (0.38), 483 (1.00), 627 (0.18), 652 (0.23), 693 (0.76). UV-Vis (KBr) λ nm (relative intensity): 208 (1.00), 280 (0.50), 350 (0.42), 479 (0.71), 648 (0.11), 712 (0.46). MALDI-TOF: found 1907.53 (M^+), $C_{116}H_{112}N_{24}Zn$. Calculated 1907.70.

Results and Discussion

Previously amino benzonitriles containing one nitrile group were used as the diazo component in reaction with phenol[15-18] and 2-naphthol.[17,19-20] It is known that under certain conditions (low temperature, diluted acid) the products of reaction of diazotized amino benzonitriles with aniline and phenol are diazo ether[16] and triazenes,[21,22] respectively. Triazenes may be converted into azo compounds by heating in sulfuric acid.[22] To the best of our knowledge, there have been no works on the use of sulfanilic and carboxylic acids, such as salicylic, anthranilic, and 3-hydroxy-2-naphthoic acids in reaction with diazotized aminobenzonitrile.

It is known that 2,3',4'-tricyanodiphenyl-4-diazonium bisulfate **2** could be almost quantitatively obtained by diazotization of amine **1** in dilute sulfuric acid at -10 °C, as indicated by formation of 2,3',4'-tricyanodiphenyl in high yields by treating with ethanol.[8] In light of these data, we have studied the possibility of coupling the diazotized amine **1** with hydroxy-arenes (β-naphthol, 3-hydroxy-2-naphthoic acid, and salicylic acid) and arylamines (aniline, *o*-toluidine, 2,6-xylidine, *N,N*-dibutylaniline, anthranilic acid) to obtain corresponding azo-compounds.

It was shown that the azo coupling of diazonium bisulfate **2** with β-naphthol for 2 hrs[23] has afforded 4-(2-hydroxy-1-naphthyldiazenyl)diphenyl-2,3',4'-tricarbonitrile **3** in 62 % yield[24,25] (Scheme 2). The interaction of salt **2** with 3-hydroxy-2-naphthoic acid by analogy with[27] has led to 3-hydroxy-4-((2,3',4'-tricyanodiphenyl-4-yl) diazenyl)-2-naphthoic acid **4** in 60 % yield. Salt **2** with salicylic acid reacted analogously and after 3 hrs resulted in 2-hydroxy-5-((2,3',4'-tricyanodiphenyl-4-yl)diazenyl) benzoic acid **5** in 60 % yield. In all cases, HPLC-MS data have confirmed the formation of **3**–**5** as virtually the only product. The presence of carboxyl group in compound **5** was also confirmed by its thermal stability: it was found that compound **5** did not melt until decomposition at 265 °C with 11.6 % mass loss corresponding to cleavage of the COOH group. Thus, the azo coupling of salt **2** with hydroxyaryl proceeds smoothly and allows the formation of azocompounds **3**–**5** containing the phthalonitrile fragment.



Scheme 2. Syntheses of azo compounds.

Treating the salt **2** with aniline under similar conditions, but for longer time (96 hrs), according to ^{1}H NMR spectrum, produced the amine **1** (55 %) and a mixture of products having the typical set of signals of the 4-diphenyl-2,3',4'-tricarbonitrile fragment and the same molecular weight of 348 (HPLC-MS). The thorough analysis of ^{1}H NMR data has led to conclusion that the dominant products in the mixture are 4-((4-aminophenyl)diazenyl)diphenyl-2,3',4'-tricarbonitrile **6** (~70 %) and its tautomer **6a** (20 %), and the minor component is triazene **11**(or **11a**) (6 %). Shortening the reaction time to 22 hrs has led to that the amine **1** was isolated even in higher yield (85 %). The reasonable explanation for this, originated from the known reactions of diazonium salts with primary aromatic amines,[28] is that the interaction of aniline with **2** includes a kinetically preferred reversible formation of triazene **11** and a parallel slow thermodynamic irreversible formation of azo compound **6** (Scheme 3). In turn, the triazene **11**, as we believe, is in the equilibrium with its tautomer **11a** that is proved by the analogous formation of 3-(2-methoxy-4-nitrophenyl)-1-*p*-tolyltriaz-1-ene in high yield (70 %) in the 3 hrs reaction of the diazonium salt of 2-methoxy-4-nitrobenzene with 4-toluidine.[29] Thus, appearance of the initial amine **1** may be explained by cleavage of the tautomer triazene **11a** during the working-up procedure.

Similarly the interaction of salt **2** with *o*-toluidine (95 hrs) has led as the main product to 4-((4-amino-3-methylphenyl)diazenyl)diphenyl-2,3',4'-tricarbonitrile **7** (~60 %) and its tautomer (~10 %) according to ^{1}H NMR and HPLC-MS data (Scheme 2). The reaction mixture in addition contained amine **1** (~15 %) and two unknown compounds with total content ~15 % (in equal amounts), the latter had the same molecular weight of 363 as azo compound **7** (HPLC-MS). By analogy with the previous case, these compounds can be assumed to be corresponding triazenes.

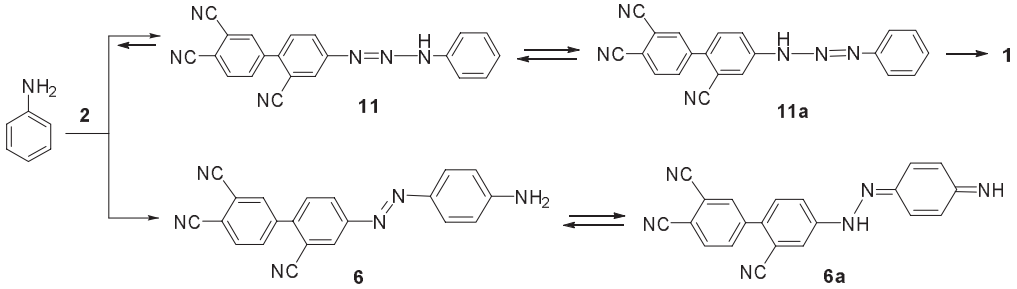
Reacting the salt **2** with anthranilic acid in hydrochloric acid for 3 hrs has given 2-(3-(2,3',4'-tricyanodiphenyl-4-yl)triazene-2-enyl)benzoic acid **10** as the major product, which was isolated in 33 % yield, and two other products. According to ^{1}H NMR data (two broad signals are present in the characteristic region) these are amine **1** (13 %) and an azo compound with a free amino group (12 %), apparently, the latter is an isomer of **10**. In the ^{1}H NMR spectrum of triazene **10** (Table 1) the signals at 7.37 and 7.02 ppm, each containing two splittings ~8.0 Hz, can only be attributed to protons in positions 4 and 5 of the anthranilic acid moiety. The broadened signal at δ 15.82 ppm can belong to the proton of the carboxyl group. According to ^{1}H NMR data, the interaction of salt **2** with anthranilic acid for 96 hrs has given amine **1** (22 %) in addition to several other compounds (~Σ 68 %). Only one broad signal is found in the characteristic region, which corresponds to the amino group of amine **1**. According to HPLC-MS data, in addition to amine **1** four compounds having the same molecular weight corresponding to triazene **10** are found. It is believed that the reaction of salt **2** with anthranilic acid leads to triazenes **10** and tautomers there of like as in the case of aniline.

From the above results of the interaction of salt **2** with primary aromatic amines it follows that conversion of the initially formed triazenes into an azo compound is complicated, and obviously it may be complicated by the cleavage of tautomer to form amine **1**. Increasing duration of coupling of the salt **2** with aniline or *o*-toluidine up to 95–96 hrs allowed us to fix the corresponding azo compounds **6**–**8**, but their isolation from respective tautomers and triazenes failed.

One might expect that the presence of structural factors, such as a spatial blocking of the primary amino group or a substitution at both hydrogen atoms, will prevent the formation of triazenes, it will contribute to formation of the azo product. Indeed, we have found that salt **2** is smoothly reacted with 2,6-xylidine and *N,N*-dibutylaniline to form 4-((amino-3,5-dimethylphenyl)diazenyl)diphenyl-2,3',4'-tricarbonitrile (**8**) and 4-(4-(dibutylaminophenyl)diazenyl) diphenyl-2,3',4'-tricarbonitrile (**9**) with a yield of 77 % and 45 %, respectively (Scheme 2).[25,26]

The obtained azo compounds are refractory colored powders (for **4** mp 292–294 °C; **5** does not melt up to 350 °C and then starts to decompose; **3** and **8** decompose at temperatures above 275–300 °C). An exception is compound **9**,[25] its properties were discussed in a separate article.[26] All compounds are poorly soluble in organic solvents.

IR spectra of the individual azo compounds **3**–**5** and **8** have the characteristic absorption bands corresponding to the stretching vibrations of CN groups (2231–2233 cm^{-1}) and N=N groups for **3** and **4** at 1504–1506 cm^{-1}, for **5** at 1486–1430 cm^{-1}, for **8** at 1430-1483 cm^{-1}, respectively.[30] IR spectra of **3** and **4** have characteristic absorption bands corresponding to C–O stretching vibrations (~1200 cm^{-1}), and the spectra of *o*-hydroxycarboxylic acids **4** and **5** also have bands corresponding to deformation vibrations of the OH group and stretching vibrations of the C–O group: for **4** at 1157 cm^{-1}, for **5** at 1140 cm^{-1}, 1180 cm^{-1} and at 1600–1606 cm^{-1}(C=O).[30] IR spectra of the azo compound **8** containing a free amino group have characteristic absorption



Scheme 3. Formation of **1**, tautomers **6**, **6a**, **11** and **11a** from **2** and aniline.

bands corresponding to the stretching vibrations of C–N (1310 cm^{-1}, 1599–1624 cm^{-1}) and N–H (3395 and 3479 cm^{-1}) groups.

Absorption spectra of **3**–**5** and **8** comprise absorption bands in the ranges 264–294 or 303–316 nm, and 432–494 nm, which is characteristic for azo compounds.[11,31] The spectra of compounds **3** and **4** have an absorption band at 220 nm corresponding to the naphthalene nucleus.[32] As it can be seen in Figure 1, the spectra of azo compound **9** in KBr and ethyl alcohol are rather similar, but the compound is poorly soluble in alcohol, and extinction coefficient is impossible to calculate.

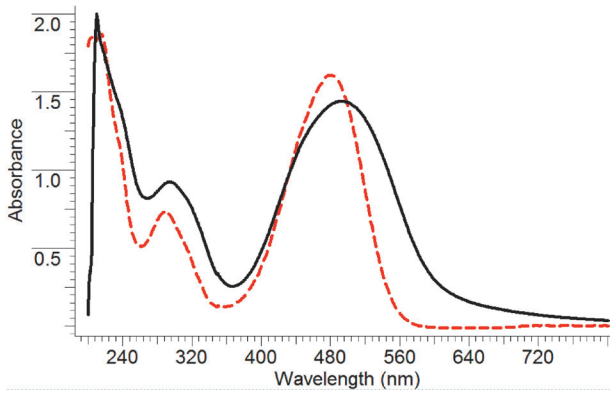


Figure 1. UV-vis spectra of **9** in KBr (solid) and C_2H_5OH (dashed).

^{1}H NMR spectra of azo compounds **3**–**9** (Table 1) contain two characteristic sets of three signals for each tricyanodiphenyl fragment (see data for 4-substituted 2,3',4'-tricyanodiphenyls).[7,8] It is not possible to assign the signals of different diphenyl fragment rings on the basis of the available data. Assignment of signals (Table 1) is made by analogy with the data for 4-iodo-2,3',4'-tricyanodiphenyl.[8] A characteristic feature of ^{1}H NMR spectra of **3** and **4** is the presence of two triplets at δ 7.3–7.7 ppm belonging to the β-proton of unsubstituted naphthalene ring. Proton signals of hydroxyl and carboxyl groups in the spectrum of compound **4** are not detected, presumably due to broadening by exchanging with the environment, just as is the case for 3-hydroxy-2-naphthoic acid. The signal at 15.5 ppm (OH) in the ^{1}H NMR spectrum of compound **3** is broadened. For **5** two of the 11 signals are broad and observed at low field (at 16–18 ppm) allowing to assign them to the proton of the hydroxyl group. The other signals consist of three groups of the same type indicating the presence of three 1,2,4-trisubstituted benzene fragments. The spectra of compounds **6**–**8** contain in the region δ_H 5.9–6.5 ppm a characteristic broad signal with twice the intensity belonging to protons of the amino group.

The obtained new azo compounds based on amine **1** containing the phthalonitrile moiety are potential "building blocks" for Pcs with extended π-electronic system provided due to the presence of arylazo fragments. Previously we have obtained zinc complexes of the corresponding Pcs **15**–**17** in 12–28 % yields by reaction of 4-Y-2,3',4'-tricyanodiphenyls (**12**, Y = $NHCOCH_3$; **13**, Y = Br; **14**, Y = I) with zinc acetate at elevated temperatures (230–260 °C) in the absence of solvent.[7,8] We believe that low yields are due to thermal instability of both the starting materials and the formed Pcs. Recently it was shown that under microwave (MW) radiation Pc synthesis can be carried out at lower temperatures, which allows the use of solvents and increases the yield of the target products.[33,34] Based on these data, we have performed a syntheses of zinc complexes **15**–**17** under MW irradiation in 1-pentanol at 155–170 °C and obtained them in substantially higher yields (70–97 %) (Scheme 4). Their IR and electronic spectra coincide with those described earlier.[7,8]

Similarly, zinc tetra-4-(2-cyano-4-(2-hydroxy-1-naphthyldiazenyl)phenyl)phthalocyanine **18** and zinc tetra-4-(2-cyano-4-(4-dibutylaminophenyldiazenyl)phenyl)phthalocyanine **19** were obtained in 84 % and 67 % yield, respectively, from azo compounds **3** and **9** (Scheme 4). Attempts to obtain zinc complexes from azo compounds **5** and **8** containing *o*-hydroxybenzoic acid and primary amine, respectively, were unsuccessful.

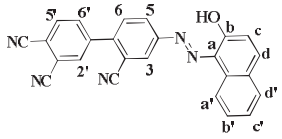
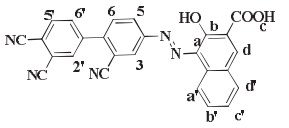
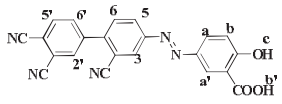
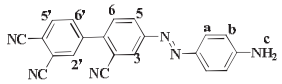
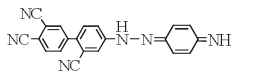
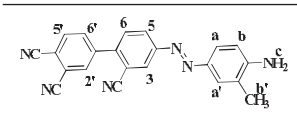
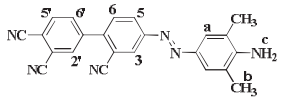
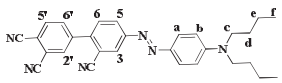
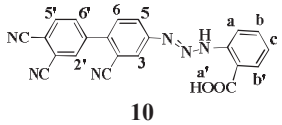
Complexes **18** and **19** were poorly soluble in organic solvents, and they were characterized by IR and electronic spectra, and by MALDI TOF. In IR spectra characteristic absorption bands are presented similar to those mentioned above for the initial diphenyls. The electron absorption spectra of the complexes are typical for Pcs. They contain a longwave *Q*-band with vibronic satellites in the region 648–717 nm and a Soret band in the region 350–355 nm, as well as show the broadening of the bands in the region 393–499 nm, typical for azo compounds (Figure 2).

Pcs **18** and **19** contain the azo groups, and their spectra (Figure 2) have bands with maxima at 480 and 500 nm, the spectrum of compound **17** has no such a band. The longwave *Q*-band of Pc **17** is at 705 nm. In comparison, the *Q*-band of Pcs **18** and **19** is slightly shifted (**18**: 717 nm, **19**: 712 nm). The relatively less bathochromic shift of *Q*-band in Pcs **18** and **19** as compared with unsubstituted Pc (683 nm)[8] can be explained by *o*-located cyano groups, lowering the conjugation between Pc and azo fragments due to steric hindrances.

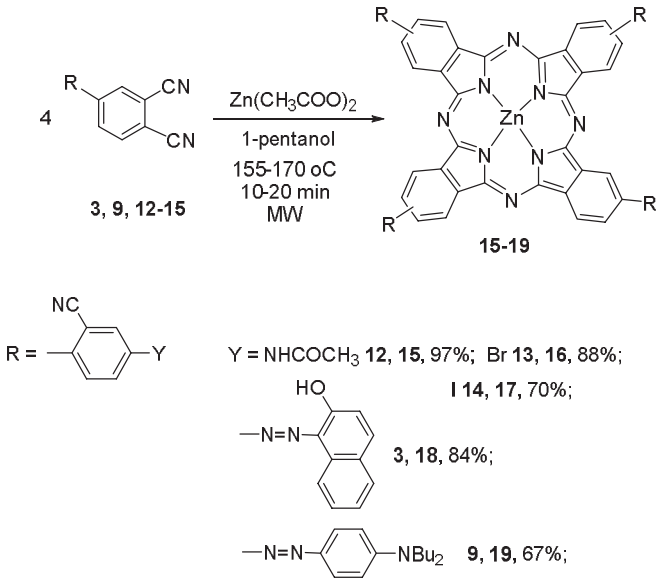
Conclusions

Thus, we have performed the functionalization of 2,3',4'-tricyanodiphenyl in position 4 with arylazo groups by coupling 2,3',4'-tricyanodiphenyl-4-diazonium bisulfate with β-naphthol, 3-hydroxy-2-naphthoic and salicylic acids, aniline, 2-toluidine, 2,6-xylidine, and *N,N*-dibutylaniline, and have demonstrated the possibility to synthesize zinc complexes of phthalocyanines from them. New zinc complexes of tetra-4-[2-cyano-4-(2-hydroxy-1-naphthyldiazenyl)phenyl]phthalocyanine and tetra-4-[2-cyano-4-(4-dibutylaminophenyldiazenyl)phenyl]phthalocyanine were obtained in 84 % and 67 % yields by condensation of the corresponding azo compounds in the presence of zinc acetate under microwave assistance. This method was also applied for the preparation of other known zinc complexes based on 4-substituted 2,3',4'-tricyanodiphenyls with improved yields. The proposed method can be useful for preparation of phthalocyanines and their complexes based on compounds containing thermally unstable fragments.

Table 1.[1]H NMR data recorded in [D_6]DMSO for compounds **3**-**10**.

Compound	δ, ppm; J, Hz								
	2'[a]	5'[a]	6'[a]	3[a]	5[a]	6[a]	a (a')	b (b')	c (c', d, d', e, f,)
 **3**	8.45 d H, ^{4}J 1.5	8.30 d H, ^{3}J 8.0	8.20 dd H, ^{3}J 8.0, ^{4}J 1.5	8.46 d H, ^{4}J 2.0	8.24 dd H, ^{3}J 8.5, ^{4}J 2.0	7.85 d H, ^{3}J 8.5	a' 7.75 br. d H, ^{3}J 7.5	15.50 br. s (H, OH) b' 7.63 td H, 2^3J 7.5, ^{4}J 1	6.83 d H, ^{3}J 9.5 d, 7.96 d H, ^{3}J 9.5 d' 8.56 br.d H, ^{3}J 8.2 c' 7.49 br.td H, ~^{3}J 8.2 ^{3}J 7.5, ^{4}J 1
 **4**	8.36 d H, ^{4}J 1.5	8.36 d H, ^{3}J 8.2	8.27 dd H, ^{3}J 8.2, ^{4}J 1.5	8.54 d H, ^{4}J 1.5	8.22 dd H, ^{3}J 8.4, ^{4}J 1.5	7.90 br.t 2H ~^{3}J 8.4, ^{3}J 7.5	a' 7.90 br.t 2H ~^{3}J 8.4, ^{3}J 7.5	b' 7.32 t H, 2^3J 7.5	d 8.52 s H d' 8.98 d H, ^{3}J 8.0 c' 7.57 br.t H, ~^{3}J 8.0, ^{3}J 7.5
 **5**	8.51 d H, ^{4}J 1.8	8.33 d H, ^{3}J 8.0	8.24 dd H, ^{3}J 8.0, ^{4}J 1.8	8.35 d H, ^{4}J 2.0	8.19 dd H, ^{3}J 8.0, ^{4}J 2.0	7.89 d H, ^{3}J 8.0	7.87 dd H, ^{3}J 9.0, ^{4}J 2.7 a' 8.34 d H, ^{4}J 2.7	6.77 d H, ^{3}J 9.0, b' 18.26 br.s	16.40 br.s
 **6**	8.51 dH, ^{4}J 1.8	8.35 dH, ^{3}J 8.2	8.24 dd H, ^{3}J 8.2, ^{4}J 1.8	8.27 dH, ^{4}J 2.0	8.13 dd H, ^{3}J 8.4, ^{4}J 2.0	7.87 d H, ^{3}J 8.4	7.74 d 2H, ^{3}J 8.8	6.70 d 2H, ^{3}J 8.8	6.46 br.s 2H, NH_2
 **6a**	8.53 d H, ^{3}J 1.8	8.36 d H, ^{3}J 7.8	8.26 dd H, ^{3}J 7.8, ^{4}J 1.8	8.39 dH, ^{4}J 2.1	8.21 dd H, ^{3}J 8.3, ^{4}J 2.1	7.93 d H, ^{3}J 8.3	7.89 d 2H, ^{3}J 8.8	6.99 d 2H, ^{3}J 8.8	10.59 br.s H, NH
 **7**	8.51 d H, ^{4}J 1.5	8.34 d H, ^{3}J 8.2	8.24 dd H, ^{3}J 8.2, ^{4}J 1.5	8.26 d H, ^{4}J 2.0	8.12 dd H, ^{3}J 8.4, ^{4}J 2.0	7.87 d H, ^{3}J8.4	7.64 dd H,^{3}J 8.4, ^{4}J 2.0 a' 7.65 s H	6.74 d H,^{3}J 8.4 b' 2.26[d] s 3H, CH_3	6.22 br.s 2H, NH_2
 **8**	8.24 br.s H	8.32 d H, ^{3}J 8.2	8.22 br.m H	8.48 d H, ^{4}J 1.2	8.11 dd H, ^{3}J 8.4, ^{4}J 1.2	7.85 d H, ^{3}J 8.4	7.55 br.s 2H	2.18 br.s 6H, $2CH_3$	5.86 br.s 2H, NH_2
 **9**	8.51 d H, ^{4}J 1.5	8.34 d H, ^{3}J 8.1	8.23 dd H, ^{3}J 8.3, ^{4}J 1.5	8.28 d H, ^{4}J 2.0	8.13 dd H, ^{3}J 8.5, ^{4}J 2.0	7.87 d H, ^{3}J 8.5	7.82 d 2H, ^{3}J 9.0	6.82 d 2H, ^{3}J 9.0	c 3.42 t 4H, 2 ^{3}J 7.4 d 1.56 quin. 4H, 4 ^{3}J 7.4 e 1.35 m 4H, 5 ^{3}J 7.4 f 0.93 t 6H, $2J_4$ 7.4
 **10**	8.47 d H, ^{4}J 2.0	8.31 d H, ^{3}J 8.0	8.20 dd H, ^{3}J 8.0, ^{4}J 2.0	8.14 d H, ^{4}J 2.0	7.96 d H, ^{3}J 9.0[b]	7.97 d, H, ^{3}J 9.0[b]	7.81 d H, ^{3}J 9.0[b] a' 15.82 br.s H	7.02 t H, 2^3J 9.0 b' 7.77 d H, ^{3}J 9.0[b]	7.37 t H, 2^3J 9.0

[a]signals of one ring can be assigned to another ring; [b]the assignment of signals may change; [c]three signals of one ring may be referred to another ring; [d]in $(CD_3)_2CO$, overlapped signals of water contained in DMSO.



Scheme 4. Syntheses of Pc complexes.

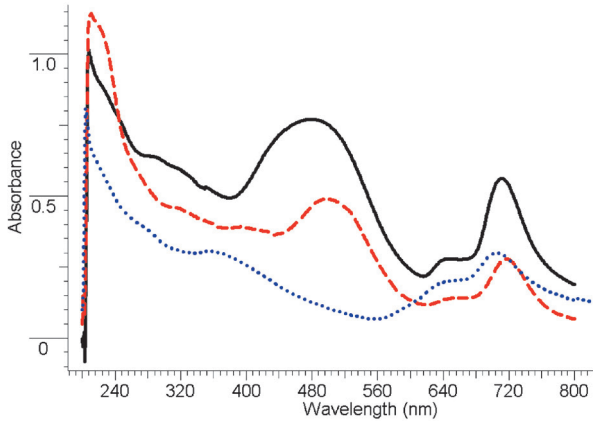


Figure 2. UV-vis spectra of Pcs in KBr: dotted line – zinc Pc complex **17**, dashed line – zinc Pc complex **18**, solid line – zinc Pc complex **19**.

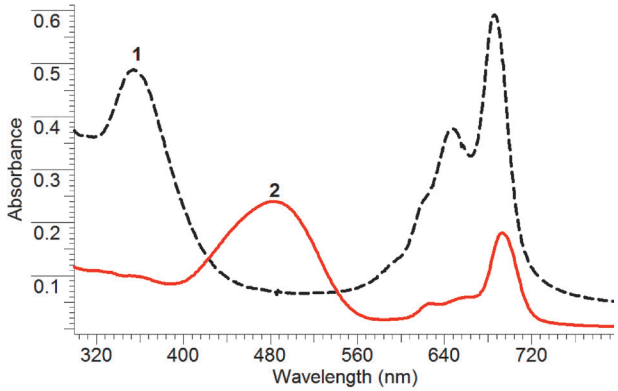


Figure 3. UV-vis spectra of Pcs in DMSO: *1* (dashed line) – zinc Pc complex **17**, *2* (solid line) – zinc Pc complex **19**.

Acknowledgements. The work was supported by the Russian Foundation for Basic Research (grant 14-29-08134). The authors are grateful to the staff of the STN Center and of the Center of Collective Use (CCU) at the Institute of Organic Chemistry of the Siberian Branch of the Russian Academy of Sciences. Molecular weights of zinc complexes **18** and **19** were determined by MALDI TOF by Dr. V.V. Koval' at the Novosibirsk Institute of Chemical Biology and Fundamental Medicine.

References

1. (a) Erk P., Hengelsberg H. Phthalocyanine Dyes and Pigments. In: *The Porphyrin Handbook,* Vol. 19 (Kadish K., Smith K.M., Guilard R., Eds.) N.-Y.: Academic Press, **2003**, 105; (b) Seven O., Dindar B., Aydemir S., Cilli F. *J. Porphyrins Phthalocyanines* **2008**, *12*, 953-963; (c) Armstrong N.R., Wang W., Alloway D.M., Placencia D., Ratcliff E., Brumbach M. *Macromol. Rapid Commun.* **2009**, *30*, 717-731; (d) Torre G., Bottari G., Hahn U., Torres T. Functional Phthalocyanines: Synthesis, Nanostructuration, and Electro-Optical Applications. In: *Functional Phthalocyanine Molecular Materials, Structure and Bonding* (Mingos D.M.P., Ed.) Berlin: Springer Heidelberg **2010**, *135*, 1-44.
2. Vagin S., Hanack M. *Eur. J. Org. Chem*. **2004**, 600-606.
3. Sugimori T., Nojima J., Ozawa T., Handa M., Kasuga K. *Chem. Lett*. **2004**, *33*, 1014-1015.
4. Lee T.-W., Kwon Y., Park J.-J., Pu L., Hayakawa T., Kakimoto M.-A. *Macromol. Rapid Commun*. **2007**, *28,* 1657-1662.
5. Kimura M., Yasuta K., Adachi N., Tatewaki Y., Fukawa T., Shirai H. *Chem. Lett.* **2009**, *38*, 82-83.
6. Panteleeva E.V., Vaganova T.A., Luk´yanets E.A., Shteingarts V.D. *Russ. J. Org. Chem.* **2006**, *42*, 1280-1288.
7. Patent RF2398763 C1. **2010**.
8. Selivanova G.A., Amosov E.V., Goryunov L.I., Balina S.V., Vasil'ev V.G., Sal'nikov G.E., Luk'yanets E.A., Shteingarts V.D. *Russ. J. Org. Chem.* **2011**, *47*, 1240−1246.
9. Yazici A., Ates D., Bekaroglu O., Kobayashi N. *J. Porphyrins Phthalocyanines* **2006**, *10,* 1140-1144.
10. Salan U., Kobayashi N., Bekaroglu O. *Tetrahedron Lett.* **2009**, *50*, 6775-6778.
11. Li Y.-F., Li S. L., Jiang K. J., Yang L.-M. *Chem. Lett.* **2004**, *33*, 1450-1451.
12. Li Y.-F., Jiao T.-F., Liu M.-H., Yang L.-M. *J. Dispersion Sci. Technol.* **2007**, *28*, 603-605.
13. Liu Y., Lin H., Li X., Li J., Nan H. *Inorg. Chem. Commun*. **2010**, *13*, 187-190.
14. Huang X., Li Z.-Y., Bin Y.-J., Huang L., Zhang F.-Sh. *Ganguang Kexue Yu Guang Huaxue* **2007**, *25*, 209-213.
15. Frankovskii Ch., Melamed N., Koval'chuk L. *Zh. Org. Khim.* **1967**, *3,* 1839−1843 (in Russ.).
16. Barltrop J.A., Bunce N.J. *J. Chem. Soc. C* **1968**, 1467-1474.
17. Socha J., Bekárek V., Schreiber J., Večeřa M. *Collect. Czech. Chem. Commun.* **1970**, *35*, 3551-3556.
18. Socha J., Večeřa M. *Collect. Czech. Chem. Commun.* **1970**, *35*, 3072-3078.
19. Berrie A.H., Hampson P., Longworth S.W., Mathias A. *J. Chem. Soc. B* **1968**, 1308-1310.
20. Haessner R., Mustroph H., Borsdorf R. *J. Prakt. Chem.* **1985**, *327*, 555-566.
21. Stevens H.N.E., Stevens M.F.G. *J. Chem. Soc.* C **1970**, 765-771.
22. Stevens M.F.G. *J. Chem. Soc. C.* **1968**, 348-351.
23. Tietse L., Aicher T. *Preparative Organic Chemistry*, Moscow: Mir, **1999**. 704 p. (in Russ.) [Титце Л., Айхер Т.

Препаративная органическая химия (пер. с нем.). М.: Мир, **1999**. 704 с.]
24. Amosov E.V., Selivanova G.A., Polkovnikov N.V., Vasil'ev V.G., Luk'yanets E.A., Shteingarts V.D. Azocompounds on the basis of 4-amino-2,3'4'-tricyanodiphenyl. In: *Current Topics in Organic Chemistry*, June 6-10, **2011**, Novosibirsk, p. 89.
25. Patent RF 2479573 C1. **2013**.
26. Selivanova G.A., Tretyakov E.V., Amosov E.V., Bagryanskaya I.Yu., Vasiliev V.G., Vasiliev E.V., Tikhova V.D., Karpova E.V., Basova T.V., Stass D. V., Shteingarts V.D. *J. Mol. Struc*. **2015**, *1107*, 242-248.
27. Markin S., Kudr'yavtsev G., Udin A., Vertinskaya T., Lisichkin G. *Zh. Obsch. Khim.* **1985**, *55,* 2761-2767 (in Russ.).
28. Zollinger H. *Colour Chemistry: Syntheses, Properties and Applications of Organic Dyes and Pigments,* New-York: VCH Publishing, **1987**. 99–100.
29. Saeki T., Son E.-C., Tamao K. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 1954-1958.
30. Silverstein R., Webster F., Kiemle D. In: *Spectrometric Identification of Organic Cmpounds* (transl. into russ.). Moscow: Binom, **2011**. pp. 107-125 [Сильверстейн Р., Вебстер Ф., Кимл Д. В кн.: *Спектрометрическая идентификация органических соединений* (пер. с англ.). М.: Бином, **2011**, с. 107-125.]
31. Zollinger H. *Colour Chemistry: Syntheses, Properties and Applications of Organic Dyes and Pigments,* New-York: VCH Publishing, **1987**. 25-26.
32. Gordon A., Ford R. *Chemist's Companion* (transl. into russ.). Moscow: Mir, **1976**. 541 p. [Гордон А., Форд Р. *Спутник химика*. М.: Мир, **1976**. 541 с.].
33. *Microwave Heating as a Tool for Sustainable Chemistry* (Leadbeater N.E., Ed.) Boca Ranton, London, NewYork: CRC Press, Taylor and Francis Group, **2010**. 278 p.
34. Chouikrat R., Champion C., Vanderesse R., Frochot C., Moussaron *A. J. Porphyrins Phthalocyanines* **2014**, *18*, 1-6.

Received 07.11.2015
Accepted 25.01.2016