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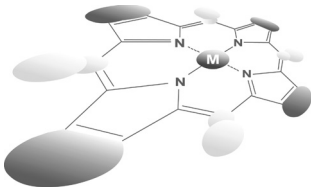

Phthalocyanines with phosphonate moiety *via* C-nucleophilic substitution in phthalonitriles

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Dedicated to Professor Özer Bekaroğlu on the occasion of his 80th birthday

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ABSTRACT: Interaction of isomeric 4-nitro- or 3-nitrophthalonitrile with triethyl phosphonoacetate, diethyl cyanomethylphosphonate or tetraethyl methylenediphosphonate in basic conditions resulted in regioselective C-nucleophilic oxidative substitution of hydrogen *ortho*-located to nitro group, new phthalonitriles with diethoxyphosphorylmethyl or bis(diethoxyphosphoryl)methyl group were isolated in modest yields. In the same conditions one chlorine atom of tetrachlorophthalonitrile was regioselectively substituted with triethyl phosphonoacetate. In basic conditions, both parent phthalonitriles and corresponding zinc phthalocyanines with *ortho*-located nitro and diethoxyphosphoryl substituted methyl groups are involved in reversible acid-base interaction accompanied with large bathochromic shift of their long wavelength absorption maxima in visible or NIR region, correspondingly. Formation of tetraazachlorin- and tetraaza(iso)bacteriochlorin-like anions is proposed for explanation of this unprecedent bathochromic shift for phthalocyanines.

KEYWORDS: phthalonitriles, C-nucleophilic substitution, oxidative nucleophilic substitution, phosphonates, zinc phthalocyanine, synthesis, electronic absorption spectra, NIR absorption.

INTRODUCTION

Due to a number of unique physical and chemical properties phthalocyanines are widely used as dyes [1, 2], catalysts [3], materials for nonlinear optics [4], gas sensors [5], *etc*. Phthalocyanines are effective in light harvesting and in molecular photovoltaics [6–9] and used as photosensitizers for photodynamic therapy of cancer [10, 11]. This variety of applications needs the availability of corresponding starting compounds for their preparation — derivatives of substituted phthalic acids, preferably phthalonitriles [12].

On the other hand, the substances containing phosphonate groups are widely used in various fields: medicine (as antiviral [13, 14], anti-inflammatory [15–17], anticancer drugs [18], inhibitors of bone resorption [19–21], *etc*.), ion exchange resins [22, 23], catalysts [22, 24], memory cells [25] and so on. Therefore, the interest in phthalocyanines stubstituted with phosphonate groups and corresponding phthalonitriles steadily grows [26–41].

In continuation of our work on synthesis and study of phthalogens and phthalocyanines with phosphonate groups [33–38], in this work we have examined the possibility of introduction of substituents with phosphonate group(s) in phthalonitrile molecule *via* aromatic nucleophilic substitution using C-nucleophiles — compounds with a methylene group activated by electron-withdrawing substituents including phosphonic acid derivatives.

◊SPP full member in good standing

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As it was recently published [42], anions of β-dicarbonyl conpounds including β-diketones and β-oxocarboxylates react with 4-bromo-5-nitrophthalonitrile initially as C-nucleophile with substitution of bromine atom and then as O-nucleophile completing formation of benzofuran skeleton.

Malonic ester anion substitutes nitro group and one chlorine atom in 4-nitrophthalonitrile [43–45] and 4,5-dichlorophthalonitrile [46,47], correspondingly, but action of dimedone on 4-nitrophthalonitrile leads to oxidative substitution of hydrogen and further cyclization into corresponding dibenzofuran derivative [43, 44].

In the context of this dual reactivity, it was of interest to study the reactions of the above-mentioned nucleophiles with various phthalonitriles.

EXPERIMENTAL

Equipment and materials

Electronic absorption spectra were recorded on spectrophotometers Cary 50 UV-vis (Varian) in quartz cells of 1.0 cm thickness. For TLC Silufol UV-254 plates used. Elemental analysis of C, H, N were performed on the C,H,N,S-analyzer Vario EL cube (Abacus). Elemental analysis of Cl and P were determined using methods of quantitative microanalysis [48]. IR-spectra were recorded on a FMS-1201 FT spectrometer in KBr pellets. A suitable crystal was selected and mounted on a Bruker SMART-APEX II CCD diffractometer. ^{1}H and ^{13}C NMR spectra were recorded on a Varian INOVA 500 MHz spectrometer using DMSO-d_6 as solvent and TMS as internal reference unless otherwise stated. High-performance liquid chromatography perfomed on Surveyor MSQ (Thermo Fisher Scientific) device with APCI and ELSD detectors and Phenomenex Onyx Monolythic C18 (25 × 4.6 mm) column. 3,5-dinitrophthalonitrile was synthesized by a known procedure [49]; 4-bromo-5-nitrophthalonitrile [50] was a kind gift from Prof. I.G. Abramov (Yaroslavl State Technical University, Russia); 4-bromophthalonitrile was purchased from ABCR GmbH, Germany; all other ragents and solvents were purchased from Sigma-Aldrich Rus. Commercial starting reagents were at least 98% purity and used as received. Solvents were distilled prior use.

Single crystal X-ray diffraction analysis of compound 3aa

Single crystals of **3aa** were obtained after two weeks of slow evaporation from its hexane solution. All data were collected at SMART APEX2 CCD difractometer (λ(Mo-Kα) = 0.71073 Å, graphite monochromator, ω-scans) at 220 K. The analysis of measured intensities was carried out with the SAINT and SADABS programs incorporated in the APEX2 program package [51]. The structure was solved by the direct methods and refined by the full-matrix least-squares procedure against F^2 in anisotropic approximation using SHELXTL program [52].

Crystal data for complex 3aa. $C_{16}H_{18}N_3O_7P$, monoclinic, space group $P2_1/n$: $a = 9.7501(6)$ Å, $b = 9.3349(6)$ Å, $c = 20.8769(14)$ Å, $\beta = 98.5110(10)°$, $V = 1879.2(2)$ Å^3, $Z = 4$, $M = 395.30$, $d_{calc} = 1.397$ g.cm^{-3}, $wR2 = 0.1597$ calculated on F^2_{hkl} for 6541 independent reflections ($R_{int} = 0.0461$) with $2\theta < 64°$, ($GOF = 1.031$, $R = 0.0589$ were calculated on F_{hkl} for 4355 reflections with $I > 2\sigma(I)$).

Synthesis

Triethyl 2-(4,5-dicyano-2-nitrophenyl)-2-phosphonoacetate (3aa). Triethyl phosphonoacetate (**2a**; 1.38 mL, 7 mmol) was added to the suspension of potassium *tert*-butoxide (2.02 g, 18 mmol) in 20 mL of dry THF cooled to -20 °C. Reaction mixture was stirred at the same temperature for 15 min and solution of 4-nitrophthalonitrile (**1a**; 1.0 g, 5.8 mmol) in 8 mL of dry THF was added dropwise under vigorous stirring. Then cooling bath was removed, suspension was allowed to warm to room temperature and stirred for additional one hour. Resulting mixture was poured in water, acidified to pH 5–6 and extracted with ethyl acetate. Evaporated extracts were purified by column chromatography on silica gel using chloroform as eluent. Product was obtained as a yellowish solid (0.73 g, 32.0%). mp 78–81 °C. Anal. calcd. for $C_{16}H_{18}N_3O_7P$: C, 48.61; H, 4.56; N, 10.63; P, 7.85%. Found C, 49.00; H, 4.65; N, 10.66; P, 8.15. IR (KBr): ν, cm^{-1} 2980 (C–H), 2260 (C≡N), 1730 (C=O), 1550 and 1350 (NO_2), 1260 (P=O), 1050 (PO–C), 800 (O–P–O). ^{1}H NMR:δ_H, ppm 8.89 (1H, d, J_{HH} 0.5 Hz, Ar), 8.44 (1H, d, J_{HP} 2 Hz, Ar), 5.24 (1H, d, J_{HP} 26 Hz, C*H*), 4.08–4.24 (4H, m, –OCH_2), 3.97–4.03 (2H, m, –OCH_2), 1.23 (6H, dt, J_{HH} 6.5 Hz, J_{HP} 6.5 Hz, CH_3), 1.11 (3H, t, J_{HH} 6.5 Hz, CH_3). ^{31}P NMR (DMSO; 85% H_3PO_4): δ_P, ppm 15.40–15.60 (m). MS: *m/z* 396 (calcd. for $[M + H]^+$ 396).

Triethyl 2-(3,4-dicyano-2-nitrophenyl)-2-phosphonoacetate (3ba). Compound **3ba** was prepared using the same procedure as for **3aa** except 3-nitrophthalonitrile (**1b**) was used instead of **1a**. Product was obtained as yellow-orange oil (0.57 g, 24.8%). Anal. calcd. for $C_{16}H_{18}N_3O_7P$: C, 48.61; H, 4.56; N, 10.63; P, 7.85%. Found C, 48.95; H, 4.55; N, 10.58; P, 7.80. ^{1}H NMR: δ_H, ppm 8.75 (1H, d, J_{HH} 9 Hz, Ar), 8.42 (1H, dd, J_{HH} 9 Hz, J_{HP} 2 Hz, Ar), 4.94 (1H, d, J_{HH} 25 Hz, C*H*), 4.09–4.29 (4H, m, –OCH_2), 3.92–4.06 (2H, m, –OCH_2), 1.22–1.28 (6H, m, CH_3), 1.15 (3H, t, J_{HH} 7 Hz, CH_3).

Diethyl 4,5,α-tricyano-2-nitrobenzylphosphonate (3ab). Compound **3ab** was prepared using the same procedure as for **3aa** except diethyl cyanomethylphosphonate (**2b**) was used instead of **2a**. Product was obtained as dark red oil (0.20 g, 10.0%). Anal. calcd. for $C_{14}H_{13}N_4O_5P$: C, 48.28; H, 3.74; N, 16.09; P, 8.91%. Found C, 47.86; H, 4.34; N, 15.64; P, 8.45. ^{1}H NMR: δ_H, ppm 14.58 (1H, s, C*H*), 8.23 (1H, d, Ar), 8.13 (1H, d, Ar),

4.05–4.25 (4H, m, OCH_2), 1.23–1.35 (6H, m, CH_3). MS: *m/z* 349 (calcd. for $[M + H]^+$ 349).

Tetraethyl 4,5-dicyano-2-nitrobenzylidenediphosphonate (3ac). To a suspension of NaH (0.24 g, 10 mmol) in dry THF (5 mL) the solution of tetraethyl methylenediphosphonate (**2c**; 2.00 mL, 8 mmol) in dry THF (10 mL) was added dropwise at 0 °C. The mixture was stirred until hydrogen bubbles disappeared and cooled to -20 °C. Solution of **1a** (1.38 g, 8 mmol) in 10 mL of dry THF was added dropwise under vigorous stirring at the same temperature. Then suspension was allowed to warm to room temperature, stirred for 2 h and then for additional 2 h at 40 °C. Resulting mixture was poured in water, acidified to pH 5–6 and extracted with ethyl acetate. Evaporated extracts was purified by column chromatography on silica gel using chloroform as eluent. Product was obtained as orange oil (1.36 g, 37.0%). Anal. calcd. for $C_{17}H_{23}N_3O_8P_2$: C, 44.43; H, 5.01; N, 9.15; P, 13.50%. Found C, 45.60; H, 4.90; N, 9.55; P, 12.90. ^{1}H NMR: δ_H, ppm 8.91 (1H, s, Ar), 8.39 (1H, t, J_{HP} 2 Hz, Ar), 4.60 (1H, t, J_{HP} 24.5 Hz, C*H*), 4.07–4.14 (4H, m, OCH_2), 3.95–4.02 (4H, m, OCH_2), 1.22 (6H, t, J_{HH} 7 Hz, CH_3), 1.11 (6H, t, J_{HP} 7 Hz, CH_3). ^{31}P NMR (DMSO; 85% H_3PO_4): δ_P, ppm 14.70–15.00 (P, m). MS: *m/z* 460 (calcd. for $[M + H]^+$ 460).

Synthesis of diethyl 2-(3,4-dicyano-2-nitrophenyl)-malonate (3bd). Diethyl malonate (**2d**; 9.0 mL, 60 mmol) and **1b** (2.0 g, 12 mmol) were added to the suspension of potassium carbonate (3.0 g, 22 mmol) in 30 mL of dry DMF cooled to -15 °C. Reaction mixture was stirred at the same temperature for 2 h and suspension was allowed to warm to room temperature. Resulting mixture was poured in water, acidified to pH 5–6 and extracted with ethyl acetate. Evaporated extracts was purified by column chromatography on silica gel using chloroform:ethyl acetate of 4:1 as eluent. A mixture of **1b** and **3bd** of 17:1 was obtained as yellow solid after recrystallization from ethanol (0.31 g). mp 140–142 °C. Anal. calcd. for $C_8H_3N_3O_2 \cdot 0.06C_{15}H_{13}N_3O_6$: C, 55.38; H, 1.96; N, 23.08%. Found C, 54.99; H, 1.93; N, 23.04. ^{1}H NMR: δ_H, ppm 8.67 (1H, d, Ar of **1b**), 8.52 (1H, d, Ar of **1b**), 8.47 (0.06H, d, Ar of **3bd**), 8.14 (1H, t, Ar of **1b**), 7.95 (0.06H, d, Ar of **3bd**), 5.37 (0.06H, s, C*H*), 4.15–4.25 (0.24H, m, OCH_2), 1.20 (0.36H, t, CH_3). MS: *m/z* 286 (calcd. for **3bd** $[M + H]^+ - C_2H_5O$ 286). IR (KBr): υ, cm^{-1} 2991 and 2965 (C–H), 2240 (C≡N), 1750 and 1735 (C=O), 1564 and 1540 (NO_2).

Triethyl 2-(2,3,6-trichloro-4,5-dicyanophenyl)-2-phosphonoacetate (3ca). Solution of **2a** (0.38 mL, 1.92 mmol) in DMF (3 mL) was added portionwise to the stirred mixture of tetrachlorophthalonitrile (**1c**; 0.49 g, 1.88 mmol), potassium carbonate (0.55 g, 4 mmol) and 5 mL of DMF. The mixture was stirred at 40 °C for 6 h, then poured in water, acidified to pH 5–6 and extracted with ethyl acetate. Evaporated extracts was purified by column chromatography on silica gel using chloroform as eluent. Product was obtained as orange oily solid (0.23 g, 27.0%). Anal. calcd. for $C_{16}H_{16}Cl_3N_2O_5P$: C, 42.34; H, 3.53; N, 6.17; Cl, 23.48; P, 6.94%. Found C, 42.65; H, 3.76; N, 6.00; Cl, 22.72; P, 7.36. ^{1}H NMR: δ_H, ppm 4.24–4.30 (2H, m, OCH_2), 4.10–4.17 (4H, m, OCH_2), 3.00 (1H, d, J_{HP} 22 Hz, C*H*), 1.27–1.33 (6H, m, CH_3), 1.23–1.27 (3H, m, CH_3). MS: *m/z* 453 (calcd. for $[M + H]^+$ with $^{35}Cl_3$ 453).

4-hydroxy-5-nitrophthalonitrile. 4-hydroxyphthalonitrile was prepared using the same procedure as for **3ca** except 4-bromo-5-nitrophthalonitrile was used instead of **1c** and four drops of water was added to the mixture additionally. Product was obtained as yellow solid after recrystallization from mixture ethanol-water 4:1 (80 mg, 21.2%). mp 210–212 °C (182–184 °C [53]). Anal. calcd. for $C_8H_3N_3O_3$: C, 50.79; H, 1.59; N, 22.22%. Found C, 51.17; H, 1.72; N, 21.90. ^{1}H NMR: δ_H, ppm 8.62 (1H, s, Ar), 7.59 (1H, s, Ar), 4.09 (1H, br, O*H*).

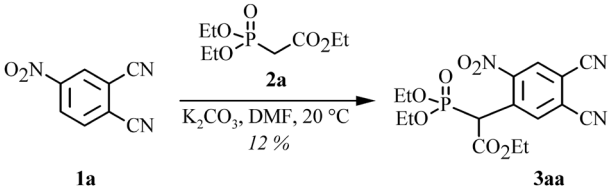
2,9(10),16(17),23(24)-tetrakis[1-diethoxyphosphoryl-1-(ethoxycarbonyl)methyl]-3,10(9),17(16),24(23)-tetranitrophthalocyaninatozinc(II) (4a). Phthalonitrile **3aa** (0.11 g, 0.28 mmol) was mixed with zinc acetate (15 mg, 0.08 mmol), ammonium molybdate (4 mg, 0.02 mmol) and 0.3 mL of 1,3,5-trichlorobenzene. This mixture was heated to 140 °C for 2 h, cooled to room temperature and volatiles were removed in vacuum. Product was purified by column chromatography on silica gel and obtained as green solid (0.05 g, 43.5%). Anal. calcd. for $C_{64}H_{72}N_{12}O_{28}P_4Zn$: C, 46.68; H, 4.38; N, 10.21; P, 7.54%. Found C, 46.90; H, 4.60; N, 10.54; P, 7.15. UV-vis (DMF): λ_{max}, nm (log ε) 343 (3.66), 627 (3.20), 699 (4.35).

2,9(10),16(17),23(24)-tetrakis[bis(diethoxyphosphoryl)methyl]-3,10(9),17(16),24(23)-tetranitrophthalocyaninatozinc(II) (4b). Complex **4b** was prepared using the same procedure as for phthalocyanine **4a** except dinitrile **3ac** was used instead of **3aa**. Product was obtained as green solid (0.035 g, 26.0%). Anal. calcd. for $C_{68}H_{92}N_{12}O_{32}P_8Zn$: C, 42.90; H, 4.84; N, 8.83; P, 13.04%. Found C, 43.29; H, 5.06; N, 8.62; P, 12.66. UV-vis (DMF): λ_{max}, nm (log ε) 355 (4.02), 630 (3.23), 699 (4.26).

RESULTS AND DISCUSSION

As a model of initial study, we chose the reactions of commercially available 4-nitrophthalonitrile (**1a**) and triethyl phosphonoacetate (**2a**). Their reaction in DMF in the presence of potassium carbonate at room temperature under aerobic conditions resulted in complex mixture of mostly unidentified products. After extensive chromatography we separated starting material as well as new compound **3aa** with low yield (Scheme 1).

Structure of phosphonate **3aa** was established as product of hydrogen oxidative substitution by X-ray analysis, as well as by other routine methods (elemental analysis, mass-spectroscopy, IR, ^{1}H and ^{31}P NMR spectroscopy).



Scheme 1. Synthesis of ethyl 2-(4,5-dicyano-2-nitrophenyl)-2-(diethoxyphosphoryl)acetate **3aa**

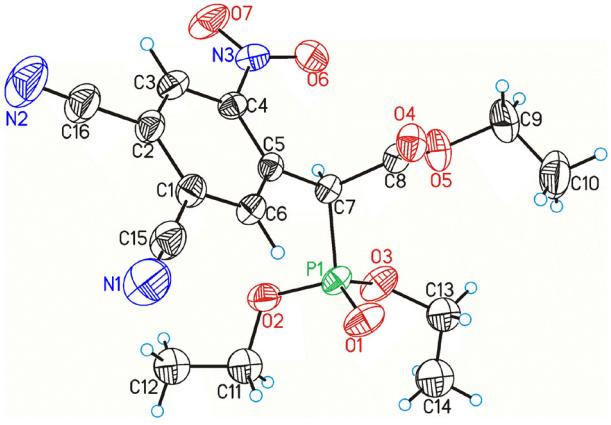


Fig. 1. ORTEP view (50% probability level) of **3aa**

Table 1. Optimization of reaction conditions for synthesis of **3aa**

Entry	Base/oxidant[a]/ solvent	Temperature[b], °C	Yield[c], %
1	K_2CO_3/O_2/DMF	20	12
2	K_2CO_3/O_2/DMF	80	—
3	Et_3N/O_2/DMF	20	—
4	KOH/O_2/DMSO	20	15
5	*t*-BuOK/O_2/THF	20	20
6	*t*-BuOK/O_2/THF	60	12
7	***t*-BuOK/O_2/THF**	**-15**	**32**
8	NaH/O_2/THF	-15	30
9	*t*-BuOK/DDQ/THF	-15	20
10	*t*-BuOK/CAN/THF	-15	—
11	*t*-BuOK/—/THF	-15	25

Notes: [a]air dioxygen used for entry 1-8, Ar atmosphere used for entry 11, DDQ — 2,3-dichloro-5,6-dicyano-benzoquinone, CAN — cerium(IV) ammonium nitrate; [b]temperature of **1a** addition to pre-reacted mixture of triethylphosphonoacetate with base given; [c]isolated yeild after chromatography.

An asymmetric unit cell contains one molecule of **3aa** (Fig. 1). The phosphorous atom adopts usual tetrahedral coordination. The P–O and P–C bond lengths are in the range of normally observed distances for these bonds [54, 55]. The conformation of **3aa** can be described by an orientation of substituents relative to P1–C7 bond: torsion angles O2–P1–C7–C5 and O3–P1–C7–C8 are equal to 56.84(13) and -72.74(13)°, respectively.

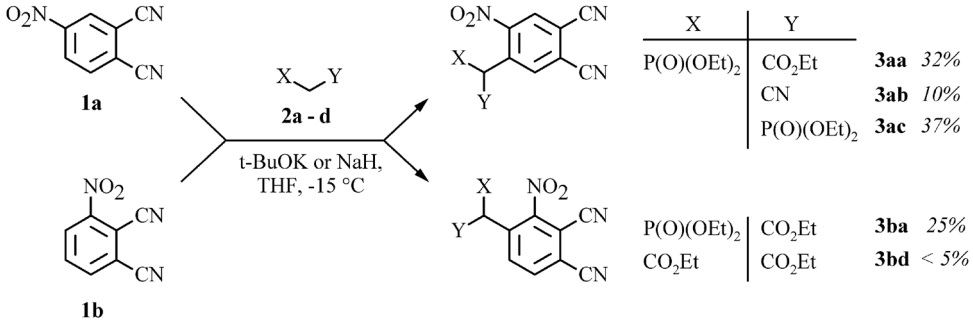
To improve the yield of new phosphonate containing phthalonitrile **3aa**, we have taken some effort to optimize the reaction conditions (Table 1). Increasing the reaction temperature to 80 °C (entry 2) or use of triethylamine instead of potassium carbonate (entry 3) resulted only in traces of the product. The use of potassium hydroxide as a base in DMSO slightly increased the yield up to 15% (entry 4). But the best combination of "base-solvent" was *t*-BuOK in THF at room temperature yielding **3aa** in 20% (entry 5). The increase of the temperature decreased the yield (entry 6). Lowering of the temperature below -15 °C gave the best yield in our hands of 32% for **3aa** (entry 7). The use of NaH instead of *t*-BuOK led to similar result (entry 8). The addition to reaction mixture of strong oxidant DDQ did not improve but even decreased yield of **3aa** (entry 9). In the presence of CAN, we did not detect **3aa** at all (entry 10). To our surprise, the removal of any oxidant including dioxygen from reaction and keeping other conditions optimal still resulted in the product with moderate yield of 25% (entry 11), suggesting 4-nitrophtalonitrile **1a** to be not only the substrate but the oxidant too, by analogy with known data [56–58].

The dinitrile **1a** reacted by oxidative nucleophilic substitution with diethyl cyanomethylphosphonate **2b** and tetraethyl methylenediphosphonate **2c** as well. In first case product **3ab** was isolated as red oil in optimal conditions with yield of only 10%. Diphosphonate **2c** did not form **3ac** in the presence of *t*-BuOK, but with NaH as a more strong base [59, 60] **3ac** was isolated with yield of 37% (Scheme 2).

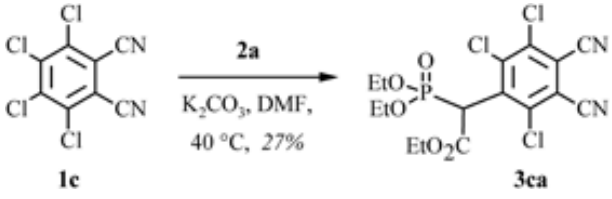
Next we used phosphonoacetate **2a** as pro-nucleophile with other phthalonitriles containing nitro group(s) and/or halogen atoms to study the scope and limitation of this reaction.

Unlike phthalonitrile **1a** its isomer — 3-nitrophthalonitrile (**1b**) — was never used for C-nucleophilic substitution. Reaction of **1b** with phosphonate **2a** in our conditions affords product **3ba** with 25% yield as a result of oxidative nucleophilic substitution (Scheme 3). Its structure was resolved by ^{1}H NMR spectroscopy where spin-spin coupling constant of two remaining aromatic protons (9 Hz) indicates their *ortho* location. In this case substituents in phthalonitrile could be located in positions 3 and 4 or 3 and 6. We deduced that substitution takes place in position 4 on the basis of literature data stating that the nucleophile enters in *ortho* position to nitro group during oxidative nucleophilic substitution [57, 61].

It was interesting that only trace amount of analogous product **3bd** was formed in the reaction of phthalonitrile **1b** with diethyl malonate (**2d**). We managed to isolate it from the reaction as a mixture with starting material 1:17; characterisic vibrations for both nitro and ethoxycarbonyl groups beside cyano groups were present in IR spectrum



Scheme 2. Oxidative substitution of 4-nitrophthalonitrile **1a** with phosphonates **2a–2c**



Scheme 3. Regioselective substitution in tetrachlorophthalonitrile **1c**

of this mixture and all signals in ^{1}H NMR spectrum were found also.

Reaction of phosphonoacetate **2a** with 3,5-dinitrophthalonitrile [49] proceeds even at -78 °C but we failed to identify any products in very complicated reaction mixture. Almost the same result we obtained with 4-bromo-5-nitrophthalonitrile [50] with an exception that 4-hydroxy-5-nitrophthalonitrile [53] was isolated with negligible yield, probably due to the presence of water traces. Indeed, the same reaction in the presence of stoichiometric quantities of water using DMF as solvent and K_2CO_3 as base led to isolation of only 4-hydroxy-5-nitrophthalonitrile with 22% yield.

In analogous conditions, the reaction of tetrachlorophthalonitrile (**1c**) with phosphonoacetate **2a** resulted in isolation of the product of one chlorine atom substitution with 27% yield. This reaction proceeds regioselectively and only one of the two possible isomers was detected in reaction mixture. Analogously to reaction with diethyl malonate [62], isolated product was assumed to be triethyl (2,3,6-trichloro-4,5-dicyanophenyl)phosphonoacetate (**3ca**; Scheme 3).

In contrast, no product was isolated in the reaction of **2a** with 4-bromophthalonitrile, only traces of the product of halogen *ipso*-substitution by phosphonocetate

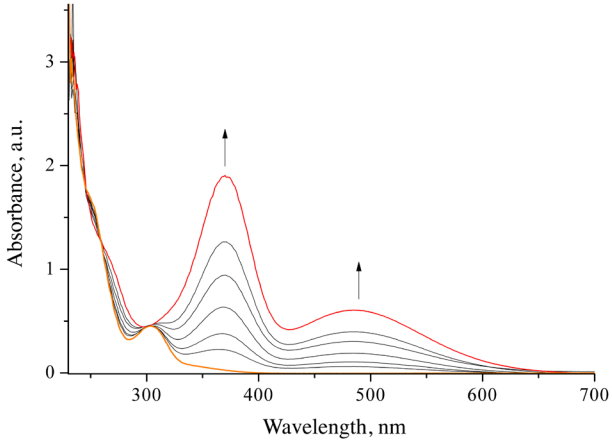
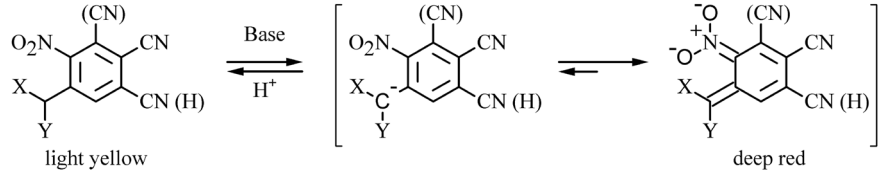


Fig. 2. Evolution of UV-vis spectrum of **3aa** in EtOH under addition of *t*-BuOK

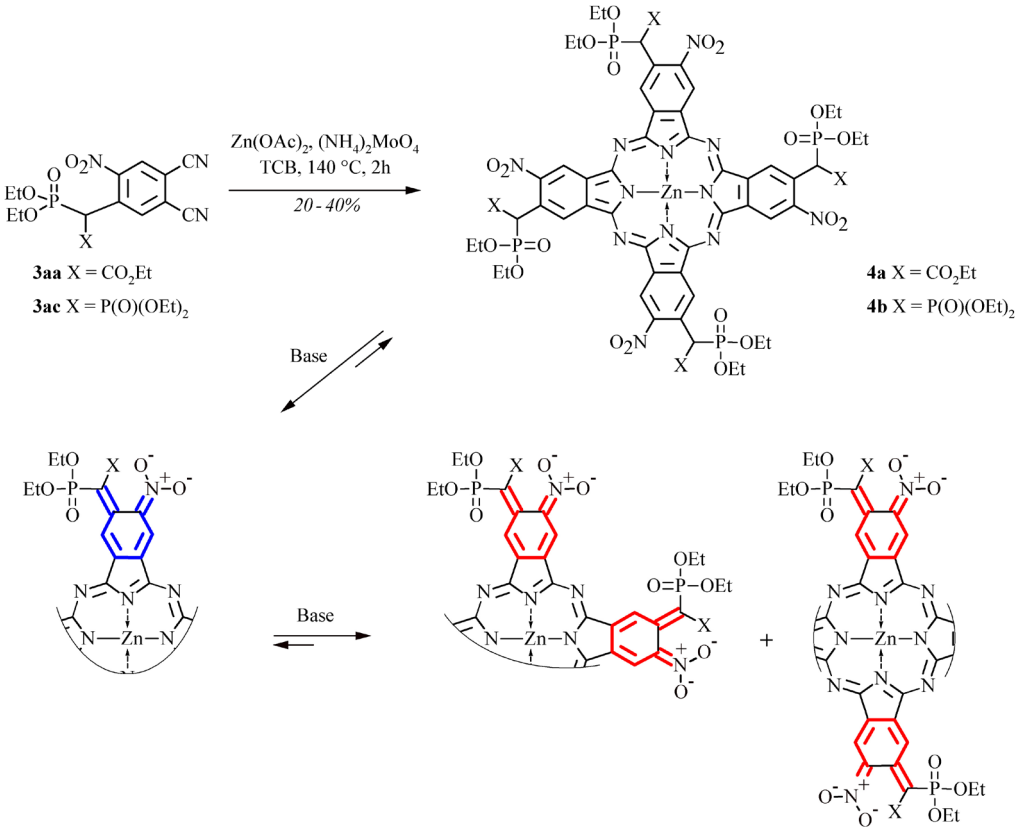
were detected by LC-MS (*m/z* 349; calcd. for $[M - H]^+$ 349).

All phthalonitriles **3aa–3bd** under basic conditions change the color of their solutions from light yellow or orange to deep red or burgundy. In UV-vis spectra intense absorption with the maximum at ~370 nm replaces weak absorption ~300 nm, and new absorption band at ~500 nm appears (an example of this change is shown in the Fig. 2). These changes are reversible, and in acidic medium spectra returned to their initial state.

We suggest that these color changes correspond to acid-base equilibrium of **3aa–3bd** due to the presence of rather acidic methine proton. Its elimination under base conditions leads to formation of carbanion which participates in conjugation with benzene ring, and, as a result, a new chromofore is formed consisting of extended *ortho*-quinoid double bonds system with auxochromic groups at the ends (Scheme 4). Moreover, cyanophosphonate **3ab**



Scheme 4. Acid-base equilibrium of **3aa–3bd**



Scheme 5. Synthesis and acid-base equilibrium of phthalocyanines **4a** and **4b**

have a red color without a base, suggesting this compound to exist as *ortho*-quionoid tautomer even in neutral state.

4-Hydroxy-5-nitrophthalonitrile (X-C-Y = O) also takes part in acid-base interaction but correponding anion maxima in UV-vis spectrum are located much shorter (~340 and ~430 nm) than for **3aa–3bd**.

Having in hand the new phthalonitriles with phosphonate group(s) we used them for synthesis of corresponding phthalocyanines. At first we tried to obtain metal-free phthalocyanines but failed both in classical conditions using DBU or *N*,*N*-dimethylaminoethanol in alcohols or by heating with lithium methoxide [63]. Possibly, this failure is the consequence of acid-base equilibrium discussed elsewhere: non-benzoid anion does not participate in tetramerization with phthalocyanine formation.

Then we tried to synthesize several zinc phthalocyanines avoiding the use of bases or polar solvent to prevent acid-base equilibrium of starting phthalonitriles. The reaction of **3aa** with zinc acetate in the presence of ammonium molybdate without solvent started at ~100 °C; full conversion was achieved at 120 °C in one hour and tetraphosphonate complex **4a** was isolated with yield of 7%. The use of 1,2,4-trichlorobenzene as solvent required temperature ~120 °C for starting the complex formation, and at 140 °C reaction finished in two hours with yield of **4a** higher than 40%, but above 150 °C the product underwent complete decomposition in 10 min. In nitrobenzene as solvent at

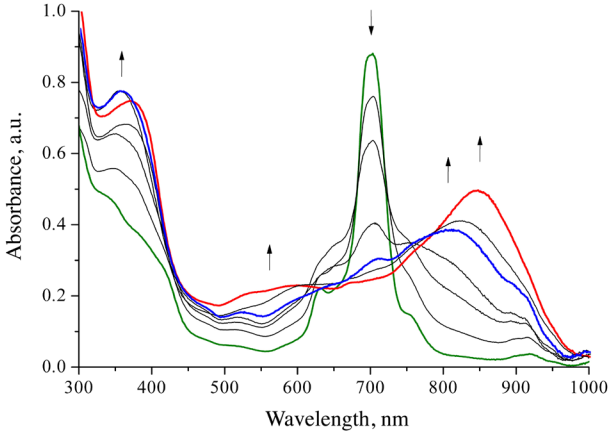


Fig. 3. UV-vis spectra of **4a** in DMF upon the addition of DBU

140 °C reaction proceeds slower and starting material was detected even after 6 h.

In optimal conditions, dinitrile **3ac** led to corresponding octaphosphonate complex **4b** though with lower yield of 20–30%. No conditions were found for synthesis of complex from cyanophosphonate **3ab**, obviously, because of its above-mentioned the *ortho*-quinoid state.

Both obtained complexes are green solids, rather soluble in most organic solvents such as alcohols, dichloromethane, acetone, ethyl acetate, DMF, *etc*. Their UV-vis spectra are

typical for phthalocyanines in non-aggregated state: sharp Q-band (maximum at ~700 nm) and its satellite (maximum ~630 nm) in long wavelength region, and wide splitted band in short wavelength region.

It was intriguing if observed acid-base properties of starting phthalonitriles will affect the properties of corresponding phthalocyanines, particularly absorption spectra. In fact, addition of different bases (K_2CO_3, triethylamine, DBU, *t*-BuOK) to solutions of **4a** or **4b** led to decrease of Q-band intensity and appearance of large diffuse absorption from 500 to 950 nm with a maximum at ~815 nm; simultaneously absorption with a maximum ~370 nm appeared in short wavelength region (Fig. 3). Further addition of bases did not lead to principal changes in character of spectra but maxima of both bands were red shifted to ~870 and ~390 nm, respectively. These spectral changes are reversible, and in acidic medium spectra returned to their initial state as for parent phthalonitriles.

Such large shift of Q-band to near IR region during interaction with a base is unprecedented for phthalocyanines. In order to explain this shift we assume that it is caused by formation of local *ortho*-quinoid chromophores which include benzene ring bearing *ortho*-located methine and nitro groups like in parent phthalonitriles. Deprotonation of one methine group changes the phthalocyanine aromatic system to tetraazachlorine-like one, deprotonation of two groups leads to tetraazabacteriochlorin- and/or tetraazaisobacteriochlorin-like aromatic systems (Scheme 5), which absorb in near IR region [64]. Absence of isosbestic points during an evolution of spectra, possibly, is explained by the presence of all anionic particles due to equilibrium existing in solution till full transformation in dianions only.

CONCLUSION

New way of introduction of dialkoxyphosphorylmethyl groups in phthalonitrile molecule *via* nucleophilic substitution was studied. It was found that interaction of 4-nitro- or 3-phthalonitrile with triethyl phosphonoacetate, diethyl cyanomethylphosphonate or tetraethyl methylenediphosphonate in the presence of base led to regioselective C-nucleophilic oxidative substitution of hydrogen *ortho*-located to nitro group with modest yield.

In basic conditions, both parent phthalonitriles and corresponding zinc phthalocyanines with *ortho*-located nitro and phosphonate(s) substituted methyl group are involved in reversible acid-base interaction accompanied with shift of their long wavelength absorption maxima in visible or NIR region, respectively. Formation of tetraazachlorin- and tetraaza(iso)bacteriochlorin-like anions is assumed as a reason of this unprecedent bathochromic shift in spectra of phthalocyanines.

Acknowledgements

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Supporting information

Crystallographic data (excluding structure factors) and details of the refinement for the structure **3aa** have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under number CCDC-914453. Copies can be obtained on request, free of charge, *via* www.ccdc.cam.ac.uk/data_request/cif or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223-336-033 or email: deposit@ccdc.cam.ac.uk).

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