

Synthesis of 4-(4-Hydrazinylphenoxy)phthalonitrile and Phthalonitriles on Its Basis Containing N-Heterocycles

Andrey V. Ziminov,[@] Dariya I. Pudova, Anna I. Kolganova, Mark A. Stretovich, Marina A. Furman, and Stanislav M. Ramsh

Saint-Petersburg State Institute of Technology (Technical University), 190013 Saint-Petersburg, Russian Federation

[@]Corresponding author E-mail: ziminov@inbox.ru

The synthesis of the novel 4-(4-hydrazinylphenoxy)phthalonitrile was carried out for the first time by nucleophilic aromatic displacement of nitro group in 4-nitrophthalonitrile to aminophenoxy fragment with following diazotization of amino group and reduction of diazo intermediate. The novel phthalonitriles containing substituted pyrazole or pyrazolone fragments were obtained by reaction of 4-(4-hydrazinylphenoxy)phthalonitrile with different 1,3-dicarbonyl compounds. The structures of the compounds obtained were characterized by IR and ¹H NMR spectroscopy.

Keywords: Phthalonitrile, hydrazine, pyrazole, pyrazolone, IR, ¹H NMR spectroscopy.

Синтез 4-(4-гидразинилфенокси)фталонитрила и фталонитрилов на его основе, содержащих N-гетероциклы

А. В. Зиминов,[@] Д. И. Пудова, А. И. Колганова, М. А. Стретович, М. А. Фурман, С. М. Рамш

Санкт-Петербургский государственный технологический институт (технический университет), 190013 Санкт-Петербург, Российская Федерация

[@]E-mail: ziminov@inbox.ru

Впервые осуществлен синтез 4-(4-гидразинилфенокси)фталонитрила путем нуклеофильного ароматического замещения нитрогруппы в 4-нитрофталонитриле на аминифеноксильный фрагмент, диазотирования аминогруппы и восстановления промежуточного диазосоединения. Новые фталонитрилы, содержащие пиразольный или пиразолоновый фрагменты, были получены взаимодействием 4-(4-гидразинилфенокси)фталонитрила с различными 1,3-дикарбонильными соединениями. Структура полученных соединений была подтверждена при помощи ИК и ¹H ЯМР спектроскопии.

Ключевые слова: Фталонитрил, гидразин, пиразол, пиразолон, ИК, ¹H ЯМР спектроскопия.

Introduction

Metallophthalocyanines are used not only as traditional dyes and pigments,^[1,2] but also, thanks to the unique physical and chemical properties, as photocatalysts,^[3] semiconductor materials,^[4,5] photosensitizers for photodynamic therapy of cancer,^[6-10] in optoelectronics.^[11] Introduction of substituents in phthalocyanine enhances solubility of the macroheterocycle in many organic solvents and gives them new functional properties. In the last decade intensive increase of number of the papers devoted to phthalocyanines, containing various nitrogen heterocycles is observed.^[12-15] A number of the works devoted to synthesis of phthalocyanines containing the pyrazole fragments are known. These substituents are attached to a linked phthalocyanine macroheterocycle directly,^[16] through the methoxy spacer moiety^[17] or through oxygen atom spacer moiety.^[18] Interest to such substituents is caused by various biological activity of the pyrazole derivatives (antimicrobial,^[19] antipyretic,^[20] analgesic,^[21] antiinflammatory,^[22] antiviral^[23] properties and others^[24]).

It is known that effective method for synthesis of substituted phthalocyanines is based on the corresponding phthalonitriles.^[25-28] Therefore to obtain the novel phthalocyanines with nitrogen containing heterocyclic substituents it is necessary to receive corresponding phthalonitriles containing pyrazole or pyrazolone derivatives. It is known that arylpyrazoles or arylpyrazolones can be synthesized by the reaction of arylhydrazine with different 1,3-dicarbonyl compounds.^[29,30] Therefore main task is to obtain phthalonitrile containing a hydrazine fragment.

In this paper we report a method for preparation of 4-(4-hydrazinylphenoxy)phthalonitrile hydrochloride in a few simple steps starting from 4-nitrophthalonitrile and 4-aminophenol as well as procedures for synthesis of some phthalonitrile functional derivatives including 4-(4-(3,5-dimethyl-1*H*-pyrazol-1-yl)phenoxy)phthalonitrile and 4-(4-(3-methyl-5-oxo-4,5-dihydro-1*H*-pyrazol-1-yl)phenoxy)phthalonitrile.

Experimental

All the reactions were carried out with dry, freshly distilled solvents. 4-Nitrophthalonitrile was purchased from Acros organics. The melting points were determined in capillaries and were not corrected. The individuality of the products was monitored by thin layer chromatography (TLC) on Silufol UV-254 plates and compounds visualized by exposure to UV light. The ¹H NMR spectra were recorded on a Bruker AVANCE 400 MHz spectrometer using DMSO-*d*₆ as the solvent. The chemical shifts are expressed in δ ppm. The IR spectra were recorded in the range 4000-400 cm⁻¹ as KBr pellets on a Shimadzu FTIR-8400S spectrophotometer. Spectral data of phthalonitriles **3-6** are given in Tables 1 and 2. Elemental analyses were carried out on a Leco CHNS(O) 942 Analyzer.

4-(4-Aminophenoxy)phthalonitrile (3). A mixture of 4-nitrophthalonitrile (**1**) (2.392 g, 10 mmol), 4-aminophenol (**2**) (3.162 g, 29 mmol) and anhydrous DMF (25 ml) was added into a 100 ml single-necked flask and stirred at room temperature. Powdered anhydrous K₂CO₃ (4.01 g, 29 mmol) was added to the reaction mixture in four equal portions at 15 min intervals with efficient stirring and then the reaction mixture was stirred at the same temperature for 3 days. Finish of the reaction was observed by TLC. The reaction mixture was vacuum-filtered from inorganic

impurities and then was poured into 200 ml of water. The dark yellow solid was vacuum-filtered, washed with water (500 ml) and was dried under vacuum. The product was further purified by column chromatography on silicagel L (40-100 mesh), using 50% ethyl acetate in hexane as eluant. The solvents were dried using rotary evaporator to give yellow solid. Yield: 1.519 g, (47 %), mp 126-128 °C, *R*_f = 0.67 (ethyl acetate/hexane 1:1). Anal. calc. for C₁₄H₉N₃O: C, 71.48; H, 3.86; N, 17.86. Found: C, 71.39; H, 4.18; N, 18.08.

4-(4-Hydrazinylphenoxy)phthalonitrile hydrochloride (4). An ice-cold solution of sodium nitrite (1.49 g, 21.6 mmol) in water (7.6 ml) was added dropwise to an ice-cold solution of phthalonitrile **3** (2.54 g, 10.8 mmol) in conc. HCl (22 ml) over 15 min. The reaction mixture was then cooled to 0-5 °C and stirred for 1 h. Urea (0.65 g, 10.8 mmol) was added portion wise to the reaction mixture, over a 10 min period. Then a solution of tin(II) chloride dihydrate (9.78 g, 43.2 mmol) in conc. HCl (8 ml) was added dropwise to the reaction mixture over a 20 min period whilst maintaining the temperature below 0-5 °C. The reaction mixture was stirred at 0 °C for 1 h. The end of the reaction was observed by absence of reaction azocoupling between reaction mixture and 2-naphthol. Then water (25 ml) was added to the reaction mixture. The light yellow precipitate was vacuum-filtered. The product was further purified by recrystallized from hot water with a few drops of conc. HCl to afford pure compound **4** as light yellow solid. Yield: 1.477 g, (58 %), mp 190-192 °C. Anal. calc. for C₁₄H₁₁ClN₄O: C, 58.65; H, 3.87; N, 19.54. Found: C, 58.66; H, 3.58; N, 19.74.

4-(4-(3,5-Dimethyl-1*H*-pyrazol-1-yl)phenoxy)phthalonitrile (5). A mixture of phthalonitrile **4** (0.72 g, 2.51 mmol), ethanol (10 ml) and pentane-2,5-dione (0.264 g, 2.64 mmol) was added into a single-necked flask. The flask was equipped with a calcium chloride guard tube. The reaction mixture was stirred on a magnetic stirrer at reflux for 8 h. Finish of the reaction observed by TLC. After completion of the reaction the solvent was evaporated under reduced pressure and the resulting solid was purified by column chromatography on silicagel L (40-100 mesh) using chloroform as eluent. Light brown solid. Yield: 0.679 g, (86 %), mp 97-98 °C, *R*_f = 0.48 (ethyl acetate/hexane 1:1). Anal. calc. for C₁₉H₁₄N₄O: C, 72.60; H, 4.49; N, 17.82. Found: C, 72.22; H, 3.99; N, 18.03.

4-(4-(3-Methyl-5-oxo-4,5-dihydro-1*H*-pyrazol-1-yl)phenoxy)phthalonitrile (6). A mixture of phthalonitrile **4** (0.6 g, 2.09 mmol), ethanol (10 ml) and ethyl acetoacetate (0.285 g, 2.19 mmol) was added into a single-necked flask. The flask was equipped with a calcium chloride guard tube. The reaction mixture was stirred on a magnetic stirrer at reflux for 12 h. After completion of the reaction mixture was cooled to 0-5 °C. The light yellow precipitate was vacuum-filtered. The resulting solid was purified by column chromatography on silicagel L (40-100 mesh), using chloroform as eluant. Light yellow solid. Yield: 0.25 g, (45.5 %), mp 93-94 °C. Anal. calc. for C₁₈H₁₂N₄O₂: C, 68.35; H, 3.82; N, 17.71. Found: C, 68.02; H, 4.01; N, 17.35.

Results and Discussion

Synthesis

The synthetic pathway to the novel compounds is shown in Scheme 1. The starting compound for synthesis of novel phthalonitrile **4** containing hydrazine group was phthalonitrile **3**. The preparation of phthalonitrile derivative **3** was achieved from the reaction of 4-nitrophthalonitrile **1** and 4-aminophenol **2** in presence of anhydrous K₂CO₃ as a base in DMF at room temperature for 3 days. It presents the base catalyzed nucleophilic aromatic nitro displacement of 4-nitrophthalonitrile with *O*-nucleophile **2**. The phthalonitrile

4 was synthesized from phthalonitrile **3** through two steps: diazotization **3** by NaNO_2 in concentrated HCl and reduction diazo intermediate by SnCl_2 analogous to (4-phenoxyphenyl) hydrazine synthesis as described in.^[31] An order of addition of reagents was very important to high yield of a product. We revealed that it is necessary to add solution of reducing reagent to a reaction mixture. The nature of reducing reagent also plays an important role in the reaction. When the intermediate was reduced by SnCl_2 , an almost quantitative yield of product was obtained. Use of $\text{Na}_2\text{S}_2\text{O}_3$ as reducing reagent led to the lower yields.^[32] It should be noted that 4-(4-hydrazinylphenoxy)phthalonitrile is unstable on air and it needs to be converted *in situ* to its hydrochloride. So after boiling in hot water phthalonitrile **4** was crystallized by addition of several drops of conc. HCl .

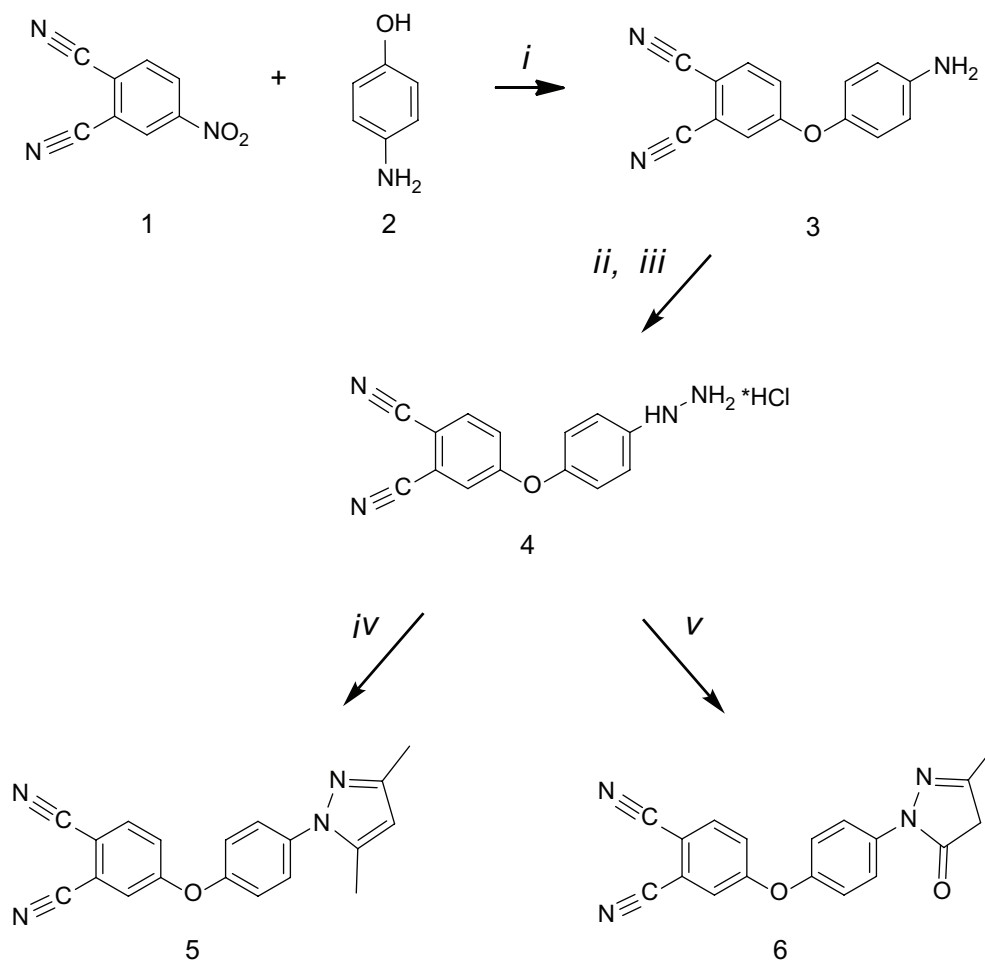
The novel phthalonitriles containing pyrazole **5** or pyrazolone **6** substituents were obtained by reaction of phthalonitrile **4** with different 1,3-dicarbonyl compounds (Scheme 1). The one-pot synthesis of **5** was carried out by the condensation-cyclization reaction between phthalonitrile **4** and pentane-2,5-dione under reflux in ethanol for 8 h. The one-pot synthesis of **6** was carried out by the condensation-cyclization reaction between phthalonitrile **4** and ethyl

acetoacetate under reflux in ethanol for 12 h. This method is easy to perform and requires available β -diketones to give the products in high or moderate yields (86 % for **5** and 45 % for **6**). The structures of novel compounds have been characterized by IR (Table 1) and ^1H NMR (Table 2) spectroscopy.

IR Spectra of the Synthesized Phthalonitriles

The observed IR frequencies and approximate assignments shown in Table 1 have been divided into three main spectral regions: 3600-2000 cm^{-1} , 1700-1000 cm^{-1} , and 1000-700 cm^{-1} .

3600-2000 cm^{-1} region. In the IR spectrum of phthalonitrile **3** disappear the bands of stretching vibrations of $-\text{OH}$ group of 4-aminophenol **2**, as well as characteristic bands stretching/bending vibrations of $-\text{NO}_2$ group of phthalonitrile **1**. At the same time for phthalonitrile **3** the two bands of asymmetric and symmetric stretching vibrations of primary amino group at 3455 and 3376 cm^{-1} appear. For phthalonitrile **4** these bands disappear, but one band of stretching vibration of secondary amino group at 3314 cm^{-1} and the broad bands of stretching vibrations of quaternized amino group at 2809



Reagents and conditions: *i*) K_2CO_3 , DMF, r.t.; *ii*) NaNO_2 , HCl , 0 °C; *iii*) SnCl_2 , HCl , 0 °C; *iv*) 2,4-pentanedione, EtOH, reflux; *v*) Ethyl acetoacetate, EtOH, reflux.

Scheme 1.

Table 1. The infrared spectral data for the synthesised phthalonitriles and their approximate assignments.

Phthalonitrile				Intensity and band assignments*
3	4	5	6	
3455, 3376	–	–	–	m, ν_{as}, ν_s (-NH ₂)
–	3314	–	–	m, ν (-NH-)
–	2809, 2629	–	–	w, ν (-NH ₃ ⁺)
3078, 3046	3058, 3031	3063, 3036	3081	w, ν (C _{Ar} -H)
–	–	2982, 2923	2970, 2878	w, ν_{as}, ν_s (-CH ₃)
–	–	–	2926, 2803	w, ν_{as}, ν_s (-CH ₂ -)
2236	2229	2230	2231	m, ν (-CN)
–	–	–	1631	m, ν (C=O)
1598, 1562,	1589, 1565,	1593, 1559,	1602, 1591,	m, ν (C _{Ar} =C _{Ar})
1510, 1486	1514, 1486	1509, 1488	1503, 1492	
–	–	1421, 1362	1407, 1367	m, ν (C _{Ar} =N)
1283	1307, 1277	1307, 1278	1312, 1276	s, ν (C _{Ar} -N)
1253	1253	1250	1245	s, ν (C _{Ar} -O-C _{Ar})
1205, 1011	1215, 1174,	1213, 1170,	1207, 1135,	m, δ (in plane C _{Ar} -H)
	1114, 1013	1113, 1008	1102, 1009	
1088	1083	1093	1087	m, δ (C _{Ar} -O-C _{Ar})
947	948	951	953	stretching vibrations of benzene fragments
895, 836	909, 838	898, 832	845, 837	m, δ (out of plane C _{Ar} -H)
–	–	795	784, 714	m, δ (C _{Alk} -H)

* w – weak; s – strong, m – medium, ν – stretching vibration, δ – bending vibration

and 2629 cm⁻¹ appear.^[33] In the case of phthalonitriles containing pyrazole derivatives **5** and **6** these bands disappear. For phthalonitrile **5** the bands of asymmetric and symmetric stretching vibrations of -CH₃ groups appear as well as for phthalonitrile **6** appear the bands of asymmetric and symmetric stretching vibrations of -CH₃ and -CH₂- groups. For all phthalonitriles a band of stretching vibrations of nitrile groups appears in the range of 2236-2229 cm⁻¹.

1700-1000 cm⁻¹ region. For all phthalonitriles the characteristic bands of stretching vibrations of double-bond in benzene ring appear in the range of 1600-1480 cm⁻¹ and the bands of stretching and bending vibrations of C-O-C fragment appear at 1253-1245 cm⁻¹ and 1093-1083 cm⁻¹ respectively. The bands of stretching vibrations of double-bond -C=N- in heterocycle appear for both phthalonitriles **5** and **6**. Also for phthalonitrile **6** the characteristic bands of stretching vibrations of C=O bond appear at 1631 cm⁻¹. The bands due to the in plane bending of vibrations of aromatic C-H groups appear in the 1215-1008 cm⁻¹ range.

1000-700 cm⁻¹ region. The very characteristic bands in 909-832 cm⁻¹ range due to the out-of-plane bending vibrations of aromatic C-H in 1,4- and 1,2,4-substituted benzene rings were observed.^[33] For phthalonitriles **5** and **6** the bands of bending vibrations of -CH₃ and -CH₂- groups appear in the range 795-714 cm⁻¹.

¹H NMR Spectra of the Synthesized Phthalonitriles

In the ¹H NMR spectra of all synthesized phthalonitriles the signals of protons of nitrile substituted benzene rings (H¹, H² and H³) possess characteristic AMX spin system and appear at 8.02-8.09, 7.26-7.45 and 7.56-7.77 ppm

respectively. The signal of proton H¹ is split into doublet with spin-spin coupling constant typical to phenyl protons at the ortho position. The signal of proton H³ is split into doublet with spin-spin coupling constant typical to phenyl protons at the meta position. The signal of proton H² is split into double of doublets. Various substituents slightly influence on location of signals of protons H¹, H² and H³ that can be explained to the lack of conjugation between substituents and nitrile substituted benzene rings.

The signals of protons of benzene rings (H⁴, H^{4'} and H⁵, H^{5'}) possess characteristic AA'XX' spin system and split into doublet. Electronic effects of substituents have a large influence on these signals. In the ¹H NMR spectrum of phthalonitrile **4** the proton signals of -NH₃⁺ and -NH- groups appear as broad singlets at 10.33 and 8.43 respectively. The signals of protons of benzene rings are shifted to the low field region and appear as multiplet at 7.11 ppm due to the strong electron-withdrawing effect of -NH-NH₃⁺ group. In the ¹H NMR spectra of phthalonitriles **5** and **6** the signals of protons of -CH₃ and -CH₂- groups appear in high field region at 2.10-2.30 ppm. The signal of protons H⁶ of phthalonitrile **5** appears as singlet at 6.03 ppm.

Conclusions

In this paper, we presented simple method of synthesis of phthalonitriles bearing different nitrogen containing heterocycles based on the reaction of 4-(4-hydrazinylphenoxy)phthalonitrile hydrochloride with some 1,3-dicarbonyl compounds. The novel 4-(4-hydrazinylphenoxy)phthalonitrile and its derivatives 4-(4-(3,5-dimethyl-1H-pyrazol-1-yl)

Table 2. The ¹H NMR spectral data for the synthesized phthalonitriles.

Phthalonitrile	The ¹ H NMR spectral data
	8.02 ppm (d, 1H, H ¹ , <i>J</i> =8.79 Hz); 7.56 ppm (d, 1H, H ³ , <i>J</i> =2.45 Hz); 7.26 ppm (dd, 1H, H ² , <i>J</i> ₁ =8.79 Hz, <i>J</i> ₂ =2.6 Hz); 6.83 ppm (d, 2H, H ⁴ , <i>J</i> =8.71 Hz); 6.65 ppm (d, 2H, H ⁵ , <i>J</i> =8.71 Hz); 5.18 ppm (s, 2H, H ⁶)
	10.33 ppm (bs, 3H, H ⁷); 8.42 ppm (bs, 1H, H ⁶); 8.03 ppm (d, 1H, H ¹ , <i>J</i> =8.78 Hz); 7.55 ppm (d, 1H, H ³ , <i>J</i> =2.4 Hz); 7.30 ppm (dd, 1H, H ² , <i>J</i> ₁ =8.79 Hz, <i>J</i> ₂ =2.39 Hz); 7.11 ppm (m, 4H, H ^{4,5})
	8.09 ppm (d, 1H, H ¹ , <i>J</i> =8.75 Hz); 7.77 ppm (d, 1H, H ³ , <i>J</i> =2.35 Hz); 7.58 ppm (d, 2H, H ⁴ , <i>J</i> =8.76 Hz); 7.45 ppm (dd, 1H, H ² , <i>J</i> ₁ =8.75 Hz, <i>J</i> ₂ =2.36 Hz); 7.27 ppm (d, 2H, H ⁵ , <i>J</i> =8.76 Hz); 6.03 ppm (s, 1H, H ⁶); 2.35 ppm (s, 3H, H ⁷); 2.20 ppm (s, 3H, H ⁸)
	8.07 ppm (d, 1H, H ¹ , <i>J</i> =8.77 Hz); 7.85 ppm (d, 2H, H ³ , <i>J</i> =8.98 Hz); 7.70 ppm (d, 1H, H ² , <i>J</i> =2.52 Hz); 7.38 ppm (dd, 1H, H ² , <i>J</i> ₁ =8.77 Hz, <i>J</i> ₂ =2.54 Hz); 7.22 ppm (d, 2H, H ⁴ , <i>J</i> =8.95 Hz); 2.27 ppm (s, 2H, H ⁶); 2.13 ppm (s, 3H, H ⁷)

phenoxy)phthalonitrile and 4-(4-(3-methyl-5-oxo-4,5-dihydro-1*H*-pyrazol-1-yl)phenoxy)phthalonitrile were synthesized and characterized by IR and ¹H NMR spectroscopy.

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