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The Synthesis and Properties of aza- and oxy-Containing Phthalodinitrile Compounds

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Abstract: **The syntheses of phthalodinitriles containing oxyalkylpyridine or cyclic amine substituents are reported. The phthalodinitriles were prepared from 4-nitrophthalodinitrile in reaction with 3- or 4-piperidinecarboxylic acid ethyl esters, 3- or 4-pyridylmethanol, 3- or 4-pyridylpropanol, 4-piperidine-carboxylic acid in aprotic solvents: *N*,*N*-dimethylformamide (DMF) and *N*-methylpyrrolidone. Influence of nucleophile properties on substitution of nitro group in 4-nitrophthalodinitrile molecule was investigated. Appointed, that 4-nitrophthalodinitrile nitro group was easy replaced with all nucleophiles. Microwave and ultrasonic effects were studied. Found, that both microwave and ultrasonic effects promoted the reaction speed, but did not influence on products yield and composition. The molecular structures of new compounds were characterized by IR, ^{1}H-NMR and mass-spectral data. Obtained products yields were from 18 till 83%.**

Keywords: **4-nitrophthalodinitrile, nucleophilic substitution reaction, nucleophile**

I. Introduction

Phthalodinitriles – phthalic acid dinitriles are a class of chemical compounds, which show thermal and oxidative stability [1]. Phthalodinitriles are commonly used for aerospace, marine, and electronic packaging applications. Phthalodinitriles are the main starting material for phthalocyanine production [1-3].

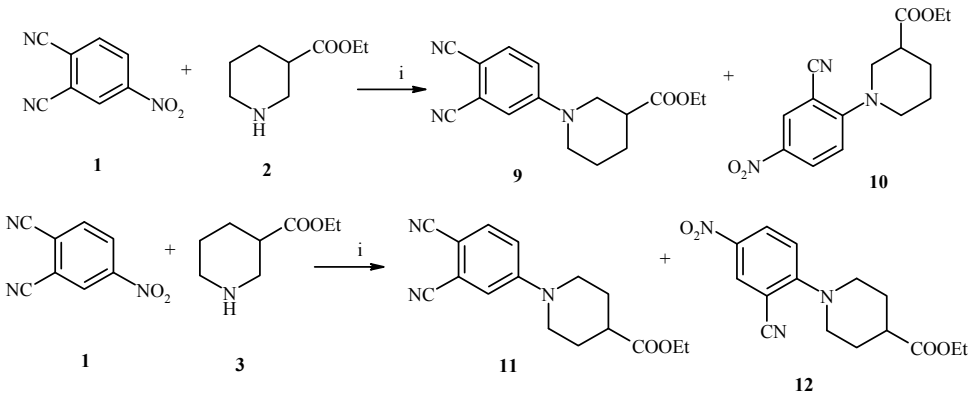
4-Nitrophthalodinitrile is a good starting material for the synthesis of substituted phthalodinitriles, because the nitro group can be replaced by various nucleophiles. Product yield is highly dependent of the nature of the reagent. In some cases products of aromatic proton displacement were found [2-5]. Current research is focused on the development of a new phthalodinitrile derivatives, 1-(3,4-dicyanophenyl)piperidine-3-carboxylic acid ethyl ester and 1-(3,4-dicyanophenyl)-piperidine-4-carboxylic acid ethyl ester, 4-(3-pyridyl-methoxy)phthalodinitrile and 4-(4-pyridylmethoxy)-phthalodinitrile, 4-(3-pyridylpropoxy)phthalodinitrile and 4-(4-pyridylpropoxy)phthalodinitrile (Schemes 1 and 2).

Production of new phthalodinitriles containing cyclic amine or oxyalkylpyridine groups, can be used for new highly soluble phthalocyanine synthesis [6-9]. Phthalocyanines have been studied for diverse applications in molecular electronics, non-linear optics, gas sensors as photosensitizers [10-12] and electrocatalysts [13, 14].

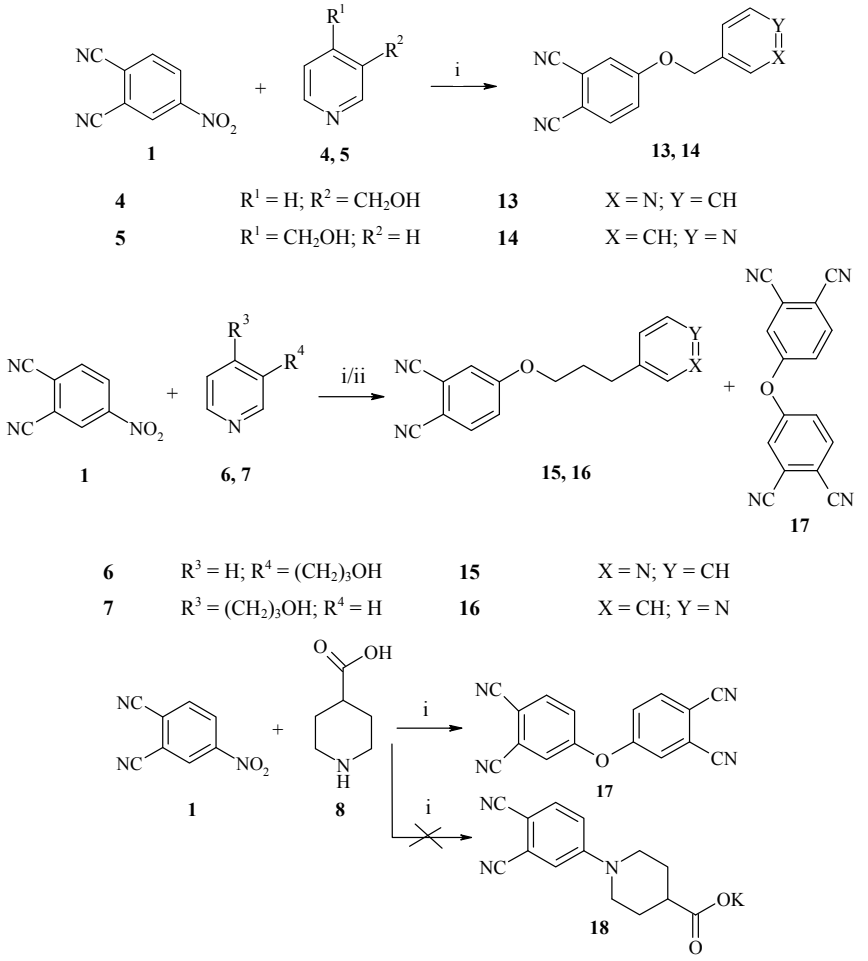
II. Results and discussion

A. Synthesis and characterization

All new phthalodinitriles were prepared from 4-nitro-phthalodinitrile (**1**) by a nucleophilic aromatic substitution of nitro group. As nucleophiles used: 3- or 4-piperidinecarbo-xylic acid ethyl esters (**2**, **3**), 3- or 4-pyridylmethanol (**4**, **5**), 3- or 4-pyridylpropanol (**6**, **7**) and with 4-piperidinecarboxylic acid (**8**) (Schemes 1 and 2).



Scheme 1. Synthesis of substituted phthalodinitriles **9** and **11**. (i) K_2CO_3, DMF, 50 – 55°C.



Scheme 2. Synthesis of substituted phthalodinitriles **13 – 16**. (i) K_2CO_3, DMF, 50 – 55°C, (ii) K_2CO_3, *N*-methylpyrrolidone, 50 – 55°C.

The substituted phthalodinitriles **9**, **11**, **13** – **16** were synthesized according to the route shown in Schemes 1 and 2. 4-Nitrophthalodinitrile (**1**) nucleophilic substitution reactions were carried out in the presence of anhydrous potassium carbonate in dried DMF at 50 – 55°C in an argon atmosphere. Obtained compounds **9**, **11**, **13** – **15** were purified by crystallization from ethanol with activated charcoal; unfortunately, it was not enough to purify phthalodinitriles **9**, **11** and **15**, so these phthalodinitriles were purified by column chromatography on silica gel using toluene/ethyl acetate mixture as eluent. Compound **16** was crystallized from chloroform/heptane mixture.

When of 3-piperidinecarboxylic acid ethyl ester (**2**) was used, a side reaction product in significant amount (15 – 20%) was found. The compounds **9, 10** were separated and purified by column chromatography using toluene/ethyl acetate in ratio 12:1 as eluent. Compound **9** (R_f 0.33) after crystallization from ethanol was obtained in 34% yield. Second product (R_f 0.51) was identified as cyano group substitution product [5] – 1-(2-cyano-4-nitrophenyl)-piperidine-3-carboxylic acid ethyl ester (**10**), which was obtained in 16% yield.

In reaction of 4-piperidinecarboxylic acid ethyl ester (**3**) with 4-nitrophthalodinitrile (**1**) we also observed that the side reaction product was formed. However, after column chromatography we obtained pure 1-(3,4-dicyanophenyl)-piperidine-4-carboxylic acid ethyl ester (**11**) in 74% yield. The smaller part which was a mixture we analyzed by ^{1}H-NMR and found that the aromatic proton spectra structure is similar to compound **10** (doublet at 7.08 ppm, double doublet at 8,2 ppm, and doublet at 8,5 ppm), therefore we suppose that 1-(2-cyano-4-nitrophenyl)piperidine-4-carboxylic acid ethyl ester (**12**) was formed.

TABLE 1.

4-NITROPHTHALODINITRILE (**1**) (0.86 G, 5.0 MMOL) AND 4-PIPERIDINECARBOXYLIC ACID (**8**) NUCLEOPHILE SUBSTITUTION REACTION QUANTITIES AND OBSERVED 3,3',4,4'-TETRACYANODIPHENYLOXIDE (**17**) YIELDS

No	4-Piperidinecarboxylic acid (**8**) quantity		Yield of **17** (g, %)
	g, mmol	eqv	
1	0.65, 5.0	1.1	0.80, 59
2	0.32, 2.5	0.5	0.50, 37
3	0.06, 0.5	0.1	0.34, 25
4	-	-	0.61, 45

In reaction of 4-nitrophthalodinitrile with *O*-nucleophiles **4** – **7** we obtained expected phthalodinitriles **13** – **16** in 18 till 83% yield. But in 4-nitrophthalodinitrile (**1**) reaction with alcohols **6** or **7** along desirable phthalodinitriles **15** or **16**, also 3,3',4,4'-tetracyanodiphenyloxide (**17**) in quantities up to 12% was obtained. Compound **17** also formed if reaction was performed in solution of *N*-methylpyrrolidone. Target products were purified by crystallization and reprecipitation.

Nucleophilic substitution reaction of 4-nitrophthalodinitrile (**1**) with 4-piperidinecarboxylic acid (**8**) did not manage to obtain the salt **18**, but 3,3'4,4'-tetracyanodiphenyloxide (**17**) [15, 16] was formed instead. Further research revealed that 4-piperidinecarboxylic acid (**8**) promotes the formation of compound **17** even when different compound **8** quantities (1.1, 0.5 and 0.1) equivalents were used. The resulting 3,3'4,4'-tetracyanodiphenyloxide (**17**) was formed in all reactions, but the highest yield and purity of compound **17** were observed in reaction when 1.1 equivalent of 4-piperidinecarboxylic acid (**8**) was used. According to literature [16] under these reaction conditions (DMF, 4-nitrophthalodinitrile and potassium carbonate) 3,3',4,4'-tetracyanodiphenyloxide (**17**) in small quantities was formed. If potassium nitrite [15] or potassium fluoride [16] were used 3,3',4,4'-tetracyanodiphenyloxide (**17**) could become a main product. It was found [16] that small amount of water accelerated the formation of compound **17**. There are several attempts [15, 16] to explain the mechanism of reaction but it was not sure proven yet. We supposed that, in our case water, which could formed in 4-piperidinecarboxylic acid (**8**) reaction with potassium carbonate, promotes the formation of 3,3',4,4'-tetracyanodiphenyloxide (**17**). At the same time 4-piperidinecarboxylic acids potassium salt is poorly soluble in DMF and therefore cannot take part in reaction. The structure and purity of synthesized phthalodinitriles were confirmed by IR, 1H-NMR and mass-spectra. In the mass-spectra the expected mass values corresponded with the theoretical values for all compounds. The protonated molecular ion peak [M + H]+, measured in atom units (amu) for compound **11** was observed at 284.3, for compounds **13** and **14** were observed at 236.2 and 236.1, and for compounds **15** and **16** were observed at 264.3 and 264.3, respectively.

B Reaction product yield characterization

1-(3,4-Dicyanophenyl)piperidine-4-carboxylic acid ethyl ester (**11**) and 3-(4-pyridylmethoxy)phthalodinitrile (**13**) product yields are good – 74 and 83%, respectively. Unfortunately, the 4-(4-pyridylmethoxy)phthalodinitrile (**14**) yield is 38%. In 4-nitrophthalodinitrile (1) reactions with 3- or 4-pyridylpropanol as reaction products were observed 3-(4-pyridylpropoxy)phthalodinitrile (**15**) or 4-(4-pyridylpropoxy)-phthalodinitrile (**16**) together with the byproduct 3,3',4,4'-tetracyanodiphenyloxide (**17**). For complete 4-nitrophthalodinitrile (**1**) reaction with 3-pyridylpropanol (**6**) in DMF at 50 – 55°C was necessary 40 hours. Reaction products obtained in 46% yield for compound **15** and 12% yield for compound **17**. To decrease the yield of 3,3',4,4'-tetracyanodiphenyloxide (**17**) the reaction conditions were changed. Microwave or ultrasonics accelerated the reaction, so starting 4-nitrophthalodinitrile was not detected even after 12 – 13 hours. Unfortunately the 3,3',4,4'-tetracyanodiphenyloxide (**17**) yield did not reduced, so 3-(4-pyridylpropoxy)phthalodinitrile (**15**) and 3,3',4,4'-tetracyanodiphenyloxide (**17**) obtained in 51% and 38% yields respectively. When N-methylpyrrolidone was used instead of DMF, 3-(4-pyridylpropoxy)phthalodinitrile (**15**) and 3,3',4,4'-tetracyanodiphenyloxide (**17**) were produced with 3% and 26% yields, respectively. Making 4-(4-pyridylpropoxy)phthalodinitrile (**16**) synthesis in microwave phthalodinitrile **16** yield was low – 18%, but 3,3',4,4'-tetracyanodiphenyloxide (**17**) yield – 19%.

III. Experimental

A. Materials

All reagents and solvents were obtained from commercial suppliers. All solvents were purified as described in literature [17] before use and were used freshly distilled. Silica gel was purchased from Merck. Anhydrous potassium carbonate (K_2CO_3) was dried at 250°C temperature for 16 hours and stored in covered container. 4-Nitrophthalodinitrile (**1**) was synthesized and purified, according to the literature procedure [15]. 3-Piperidinecarboxylic acid ethyl ester (**2**), 4-piperidine-carboxylic acid ethyl ester (**3**), 3-pyridylmethanol (**4**) and 4-pyridylmethanol (**5**) were purchased from Alfa Aesar, 3-pyridylpropanol (**6**) was purchased from Aldrich and 4-pyridylpropanol (**7**) was purchased from TCI, 4-piperidinecarboxylic acid (**8**) was purchased from Aldrich.

B. Measurements

IR spectra (thin films) were recorded on a Thermo-Nicolet 5700 spectrometer. 1H-NMR spectra were obtained using Bruker 300 MHz (J, Hz) spectrometer using as internal standard for CDCl3 – tetramethylsilane and for DMSO-d6 – hexamethyldisiloxane. Mass-spectra were performed on High Performance Liquid Chromatograph (HPLC) with a Waters Alliance 2695 masspectrometer using XTerra® MS C18 5 µm 2.1×100 mm column. Signals were recorded with a Waters 2996 UV-Vis photodiode matrix detector and Waters EMD 1000 masspectrometer, which had ionization electroatomization ESI+. Melting points were recorded using Mel-Temp II apparatus. Ultrasonic and microwave effects were studied using Ultrasonic processor UP200S (Hielscher) and Household Whirlpool microwave oven MWD307 WH

C. Synthesis

1-(3,4-Dicyanophenyl)piperidine-3-carboxylic acid ethyl ester (9) and 1-(2-cyano-4-nitrophenyl)piperidine-3-carboxylic acid ethyl ester (10)

4-Nitrophthalodinitrile (**1**) (0.86 g, 5.0 mmol) was dissolved in 15 mL DMF under argon atmosphere, then 3-piperidinecarboxylic acid ethyl ester (**2**) (0.80 mL, 5.5 mmol) and potassium carbonate (1.38 g, 10.0 mmol) were added. The reaction mixture was stirred at 50 – 55°C temperature for 22 hours, then poured into ice water (~ 50 mL) and extracted twice with 20 mL of ethyl acetate. The solution was washed with water, dried and evaporated. The products were separated and purified by column chromatography on silica gel using toluene/ethyl acetate mixture (6 : 0.5), as eluent. Compound **9**

(R_f 0.33) after crystallization from ethanol gave light yellow crystalline powder. The compound is soluble in $CHCl_3$, CH_3CN, and DMF. Yield: 0.49 g (34%). M.p. 81 – 82°C. IR γ_{max} (cm^{-1}): 2214 (C≡N), 1722 (C=O, ester), 1592 (C=C, Ar). ^{1}H-NMR ($CDCl_3$), δ, ppm: 1.27 (t, *J* = 7.1, 3H), 1.58 - 1.74 (m, 1H), 1.78 - 1.96 (m, 2H), 2.01 - 2.15 (m, 1H), 2.54 - 2.68 (m, 1H), 3.16 (m, 1H), 3.41 (m, 1H), 3.55 - 3.65 (m, 1H), 3.80 (m, 1H), 4.17 (q, *J* =7.1, 2H), 7.05 (dd, *J* = 2.7, *J* = 9.0, 1H), 7.14 (d, *J* = 2.7, 1H), 7.55 (d, *J* = 9.0, 1H). Anal. Calc. for $C_{16}H_{17}N_3O_2$: C 67.83; H 6.05; N 14.83. Found: C 67.69; H 5.89; N 14.69.

Compound **10** (R_f 0.51) gave yellowish oil. The compound is soluble in $CHCl_3$, CH_3CN, and DMF. Yield: 0.24 g (16%). IR γ_{max} (cm^{-1}): 2224 (C≡N), 1725 (C=O, ester), 1601 (C=C, Ar), 1572 (NO_2). ^{1}H-NMR ($CDCl_3$), δ, ppm: 1.24 (t, *J* = 7.1, 3H), 1.72 - 1.81 (m, 2H), 1.90 - 1.95 (m, 1H), 2.11 - 2.22 (m, 1H), 2.69 - 2.80 (m, 1H), 3.10 - 3.20 (m, 1H), 3.31 - 3.39 (m, 1H), 3.81 (m, 1H), 3.93 (m, 1H), 4.15 (q, *J* = 7.1, 2H), 7.02 (d, *J* = 9.4, 1H), 8.24 (dd, *J* = 2.8, *J* = 9.4, 1H), 8.40 (d, *J* = 2.8, 1H). Anal. Calc. for $C_{15}H_{17}N_3O_4$: C 59.40; H 5.65; N 13.85. Found: C 59.75; H 5.78; N 13.76.

1-(3,4-Dicyanophenyl)piperidine-4-carboxylic acid ethyl ester (11)

4-Nitrophthalodinitrile (**1**) (0.86 g, 5.0 mmol) was dissolved in 10 mL DMF under argon atmosphere, then 4-piperidinecarboxylic acid ethyl ester (**3**) (0.80 mL, 5.5 mmol) and potassium carbonate (0.70 g, 5.0 mmol) were added. The reaction mixture was stirred at 50 – 55°C temperature for 25 hours, then poured into ice (~ 50 mL) and the precipitate filtered off and washed with water on the filter. Crude product was crystallized from ethanol with activated charcoal followed by column chromatography on silica gel using toluene/ethyl acetate mixture (6 : 0.5), as eluent. Obtained product was reprecipitated from CH_2Cl_2 with petroleum ether, what gave light yellow crystalline powder. The compound is soluble in $CHCl_3$, CH_3CN, and DMF. Yield: 1.05 g (74%). M.p. 124 – 126 °C. IR γ_{max} (cm^{-1}): 2217 (C≡N), 1712 (C=O, ester), 1592 (C=C, Ar). ^{1}H-NMR ($CDCl_3$), δ, ppm: 1.29 (t, *J* = 7.1, 3H), 1.86 (m, 2H), 2.08 (m, 2H), 2.61 (m, 1H), 3.11 (m, 2H), 3.82 (m, 2H), 4.19 (q, *J* = 7.1, 2H), 7.05 (dd, *J* = 2.6, *J* = 8.9, 1H), 7.13 (d, *J* = 2.6, 1H), 7.58 (d, *J* = 8.9, 1H). MS *m/z*: calculated: $C_{16}H_{17}N_3O_2$, 283.3, found: 284.3 $[M + H]^+$.

3-(4-Pyridylmethoxy)phthalodinitrile (13)

4-Nitrophthalodinitrile (**1**) (0.86 g, 5.0 mmol) was dissolved in 10 mL DMF under argon atmosphere, then 3-pyridylmethanol (**4**) (0.80 mL, 5.5 mmol) and potassium carbonate (0.70 g, 5.0 mmol) were added. The reaction mixture was stirred at 50 – 55°C temperature for 38 hours, then poured into ice (~ 50 mL) and the precipitate filtered off and washed with water on the filter. Crude product was twice crystallized from ethanol with activated charcoal, what gave light yellow crystalline powder. The compound is soluble in $CHCl_3$, CH_3CN, and DMF. Yield: 0.97 g (83%). M.p. 136 – 138°C. IR γ_{max} (cm^{-1}): 2231 (C≡N), 1604 (C=C, Ar). ^{1}H-NMR ($CDCl_3$), δ, ppm: 5.22 (s, 2H), 7.25 (dd, *J* = 2.5, *J* = 8.7, 1H), 7.33 (d, *J* = 2.5, 1H), 7.40 (m, 1H), 7.72 (d, *J* = 8.7, 1H), 7.79 (m 1H), 8.64 (m, 1H), 8.75 (m, 1H). MS *m/z*: calculated: $C_{14}H_9N_3O$, 235.2, found: 236.2 $[M + H]^+$.

4-(4-Pyridylmethoxy)phthalodinitrile (14)

4-Nitrophthalodinitrile (**1**) (0.86 g, 5.0 mmol) was dissolved in 10 mL DMF under argon atmosphere, then 4-pyridylmethanol (**5**) (0.60 g, 5.5 mmol) and potassium carbonate (0.70 g, 5.0 mmol) were added. The reaction mixture was stirred at 50 – 55°C temperature for 20 hours. Subsequent separation and purification of the 4-(4-pyridylmethoxy)phthalodinitrile (**14**) is analogous for the product **13**. Obtained light yellow crystalline powder. The compound is soluble in $CHCl_3$, CH_3CN, and DMF. Yield: 0.45 g (38%). M.p. 135 – 137 °C. IR γ_{max} (cm^{-1}): 2225 (C≡N), 1602 (C=C, Ar). ^{1}H-NMR ($CDCl_3$), δ, ppm: 5.21 (s, 2H), 7.28 (dd, *J* = 2.6, *J* = 8.8, 1H), 7.35 (m, 3H), 7.77 (d, *J* = 8.8, 1H), 8.69 (dd, *J* = 1.6, *J* = 4.4, 2H). MS *m/z*: calculated: $C_{14}H_9N_3O$, 235.2, found: 236.1 $[M + H]^+$.

3-(4-Pyridylpropoxy)phthalodinitrile (15)

4-Nitrophthalodinitrile (**1**) (0.86 g, 5.0 mmol) was dissolved in 10 mL DMF under argon atmosphere, then 3-pyridylpropanol (**6**) (0.80 mL, 5.5 mmol) and potassium carbonate (0.70 g, 5.0 mmol) were added. The reaction mixture was stirred at 50 – 55°C temperature for 40 hours, then poured into ice (~ 50 mL) and the precipitate was filtered off and washed with water on the filter. Then precipitate was stirred with $CHCl_3$ at room temperature for 1 hour and filtered off. 3-(4-Pyridylpropoxy)phthalodinitrile (**15**) is soluble in chloroform. Filtrate evaporated, obtained crude product was crystallized from ethanol with activated charcoal, followed by column chromatography on silica gel using toluene/ethyl acetate mixture (0.5 : 1), as eluent. The product was reprecipitated from CH_2Cl_2 with petroleum ether, what gave white crystalline powder. The compound is soluble in $CHCl_3$, CH_3CN, and DMF. Yield: 0.61 g (46%). M.p. 100 – 102°C. IR γ_{max} (cm^{-1}): 2228 (C≡N), 1596 (C=C, Ar). ^{1}H-NMR ($CDCl_3$), δ, ppm: 2.20 (m, 2H), 2.85 (m, 2H), 4.08 (t, *J* = 6.1, 2H), 7.18 (dd, *J* = 2.6, *J* = 8.8, 1H), 7.26 (m, 2H), 7.54 (m, 1H), 7.73 (d, *J* = 8.8, 1H), 8.50 (m, 2H). MS *m/z*: calculated: $C_{16}H_{13}N_3O$, 263.3, found: 264.3 $[M + H]^+$.

4-(4-Pyridylpropoxy)phthalodinitrile (16)

4-Nitrophthalodinitrile (**1**) (2.60 g, 15.0 mmol) was dissolved in 30 mL DMF under argon atmosphere, then 4-pyridylpropanol (**7**) (2.40 mL, 16.5 mmol) and potassium carbonate (2.07 g, 15.0 mmol) were added. After stirring the reaction mixture at 50 – 55°C temperature for 24 – 25 hours, it was poured into ice (~ 150 mL) and the precipitate was filtered off and washed with water on the filter. Then precipitate was stirred with $CHCl_3$ at room temperature for 1 hour and filtered off. 4-(4-Pyridylpropoxy)phthalodinitrile (**16**) is soluble in chloroform. Filtrate evaporated, obtained crude product was twice crystallized from heptane/chloroform mixture in ratio 5 : 3, what gave white crystalline powder. The compound is soluble in $CHCl_3$, CH_3CN, and DMF. Yield: 0.67 g (18%). M.p. 100 – 102°C. IR γ_{max} (cm^{-1}): 2225 (C≡N), 1595 (C=C, Ar). ^{1}H-NMR ($CDCl_3$), δ, ppm: 2.22 (m, 2H), 2.90 (m, 2H), 4.09 (t, *J* = 6.0, 2H), 7.18 (dd, *J* = 2.6, *J* = 8.8, 1H), 7.25

(m, 3H), 7.73 (d, J = 8.8, 1H), 8.57 (d, J = 6.1, 2H). MS *m/z*: calculated: $C_{16}H_{13}N_3O$, 263.3, found: 264.3 $[M + H]^+$.

3,3',4,4'-Tetracyanodiphenyloxide (17)

4-Nitrophthalodinitrile (**1**) (0.86 g, 5.0 mmol) was dissolved in 10 mL DMF under argon atmosphere, then 4-piperidinecarboxylic acid (**8**) (0.65 g, 5.5 mmol) and potassium carbonate (0.70 g, 5.0 mmol) were added. The reaction mixture was stirred at 50 – 55°C temperature for 30 hours, then poured into ice (~ 50 mL) and the precipitate filtered off and washed with water on the filter. Crude product was twice crystallized from acetic acid. Yield 0.80 g (59%), (see TABLE 1.). M. p. 258 – 260ºC (lit. [15] M. p. 258 – 260°C). IR γ_{max} (cm^{-1}): 2233 (C≡N), 1588, 1569 (C=C, Ar). ^{1}H-NMR ($CDCl_3$), δ, ppm: 7.69 (dd, J = 2.5, J = 8.7, 2H), 8.03 (d, J = 2.5, 2H), 8.22 (d, J = 8.7, 2H).

IV. Conclusion

The synthesis and characterization of substituted phthalodinitriles **9**, **11**, **13** – **16**, 1-(2-cyano-4-nitrophenyl)-piperidine-3-carboxylic acid ethyl ester (**10**) and 3,3'4,4'-tetracyanodiphenyloxide (**17**) are presented. In 4-nitrophthalodinitrile (**1**) nucleophilic substitution reactions with 3- or 4-piperidinecarboxylic acid ethyl esters (**2**, **3**), 3- or 4-pyridylmethanol (**4**, **5**) observed desirable nucleophilic substitution products: 1-(3,4-dicyanophenyl)piperidine-3-carboxylic acid ethyl ester (**9**), 1-(3,4-dicyanophenyl)piperidine-4-carboxylic acid ethyl ester (**11**), 3-(4-pyridylmethoxy)phthalodinitrile (**13**) or 4-(4-pyridylmethoxy)phthalodinitrile (**14**), in 34 – 83% yields. In 4-nitrophthalodinitrile (**1**) reaction with 3- or 4-pyridylpropanol (**6**, **7**) observed desirable products: 3-(4-pyridylpropoxy)phthalodinitrile (**15**) and 4-(4-pyridylpro-poxy)phthalodinitrile (**16**) in 46% and 18% yields, and in small amount side product 3,3',4,4'-tetracyanodiphenyloxide (**17**). In 4-nitrophthalodinitrile reaction with 4-piperidinecarboxylic acid (**8**), as single product observed 3,3',4,4'-tetracyanodiphenyloxide (**17**). Found, that increasing 4-piperidinacarboxylic acid (**8**) equivalent quantity from 0.1 till 1.1, also increased 3,3',4,4'-tetracyanodiphenyloxide (**17**) yield from 25 till 59%. All of obtained derivatived phthalodinitriles can be used for soluble phthalocyanine synthesis.

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Tatjana Kriviča, Modris Roze, Nataļja Kiričenko, Valdis Kampars. Aza- un oksisaturošu ftalodinitrilu sintēze un īpašības

Aizvietoti ftalodinitrili ir izejvielas jaunu ftalocianīnu un citu ciklisku izoindola atvasinājumu iegūšanai. Ftalodinitrili ir arī izejvielas tādu ftalskābju atvasinājumu iegūšanai, kuras ar citām metodēm ir grūti sintezēt.
Nitrogrupa 4-nitroftalodinitrilā viegli stājās nukleofīlās aizvietošanās reakcijās ar skābekļa, oglekļa, slāpekļa vai sēra nukleofīliem, tāpēc šis savienojums ir lieliska izejviela jaunu ftalodinitrila atvasinājumu iegūšanai.
Darba mērķis bija sintezēt ftalodinitrilus, kuri molekulā saturētu vai nu ciklisko amīna vai piridīna fragmentus. 4-Nitroftalodinitrila reakcijā ar 3- vai 4-piperidīnkarbonskābes etilesteriem iegūti 1-(3,4-dicianofenil)piperidīn-3-karbonskābes etilesteris vai 1-(3,4-dicianofenil)piperidīn-4-karbonskābes etilesteris. Kā blakus reakcijas produkts veidojas arī cianogrupas aizvietošanās produkts, kas 3-piperidīnkarbonskābēs etilestera gadījumā tika izdalīts un raksturots, kā 1-(2-ciano-4-nitrofenil)piperidīn-3-karbonskābes etilesteris. 4-Nitroftalodinitrila reakcijā ar 3- vai 4-piridilmetanolu, kā arī 3- vai 4-piridilpropanolu iegūti attiecīgi piridilalkoksiftalodinitrili ar iznākumiem 34 – 83 %, kā blakus produkts veidojas 3,3’,4,4’-tetracianodifeniloksīds.
4-Nitroftalodinitrila reakcijā ar 4-piperidīnkarbonskābi kā vienīgais reakcijas produkts iegūts 3,3’,4,4’-tetracianodifeniloksīds. Konstatēts, ka palielinot 4-piperidīnkarbonskābes daudzumu no 0.1 līdz 1.1 ekvivalentam, palielinās arī 3,3’,4,4’-tetracianodifeniloksīda iznākums no 25 līdz 59 %.
Pētīta mikroviļņu un ultraskaņas ietekme uz reakcijas produktu iznākumiem un sastāvu. Konstatēts, ka gan mikroviļņu, gan ultraskaņas iedarbība palielina reakcijas ātrumu, taču atstāj mazu iespaidu uz galaproduktu iznākumu un produktu sastāvu.
Iegūtie savienojumi raksturoti ar IS, ^{1}H-KMR, masspektru un elementanalīzes palīdzību.

Татьяна Кривич, Модрис Розе, Наталья Кириченко, Валдис Кампарс. Синтез и свойства аза- и оксисодержащих фталодинитрилов

Замещенные фталодинитрилы – основные исходные вещества в производстве новых фталоцианинов и других циклических производных изоиндола. Фталодинитрилы также служат исходными веществами для получения некоторых производных фталевой кислоты, которые сложно получить другими методами.
Нитрогруппа в молекуле 4-нитрофталодинитрила легко вступает в реакции нуклеофильного замещения с кислородными, углеродными, азотными нуклеофилами или нуклеофилами серы, и поэтому такие соединения служат отличными исходными веществами в реакциях получения новых фталодинитрилов.
Цель работы – синтезировать молекулы фталодинитрила, содержащие фрагмент циклического амина или пиридина. В реакциях 4-нитрофталодинитрила с этиловыми эфирами 3- или 4-пиперидинкарбоновых кислот получены этиловые эфиры 1-(3,4-дицианофенил)пиперидин-3-карбоновой или 1-(3,4-дицианофенил)пиперидин-4-карбоновой кислот, а также продукты побочной реакции - замещения цианогруппы. В случае этилового эфира 3-пиперидинкарбоновой кислоты данный продукт – этиловый эфир 1-(2-циано-4-нитрофенил)пиперидин-3-карбоновой кислоты был выделен и охарактеризован. В реакциях 4-нитрофталодинитрила с 3- или 4-пиридилметанолом, а также с 3- или 4-пиридилпропанолом получены соответствующие пиридилалкоксифталодинитрилы с выходами реакций 34 – 83 %, как побочный продукт образуется 3,3’,4,4’-тетрацианодифенилоксид.
В реакции 4-нитрофталодинитрила с 4-пиперидинкарбоновой кислотой получен единственный продукт реакции – 3,3’,4,4’-тетрацианодифенилоксид. В результате проведенных экспериментов констатировано, что увеличивая количество 4-пиперидинкарбоновой кислоты от 0.1 до 1.1 эквивалента, также увеличивается выход 3,3’,4,4’-тетрацианодифенилоксида с 25 до 59%.
Исследовалось влияние микроволнового и ультразвукового излучения на выход и состав продуктов реакции. Констатировано, что использование, как микроволнового, так и ультразвукового излучения увеличивает скорость химической реакции, однако не влияет на выход и состав ожидаемых продуктов.
Полученные соединения охарактеризованы с помощью ИК, ^{1}Н-ЯМР, масс-спектров и элементного анализа.