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New Nitrogen–Containing Five–Membered Heterocyclic *ortho*–Dicarbonitriles for Preparation of Macroheterocycles

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Dedicated to the Corresponding Member of Russian Academy of Sciences, professor Koifman O.I. on the occasion of his 70th birthday

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The reaction of aromatic nucleophilic substitution in 4-methyl-5-nitrophthalonitrile with reagents different structures was used for the synthesis of new substituted 4-azidophthalonitriles. The interaction of the obtained 4-azidophthalonitriles with acetylacetone leads to the formation of substituted (1,2,3-triazol-1-yl)-5-styrylphthalonitriles; the refluxing of 4-azidophthalonitriles in ethyleneglycol results in formation of 2-aryl-1H-indole-5,6-dicarbonitriles. The obtained nitrogen-containing heterocyclic ortho-dicarbonitriles can be used for preparation of macroheterocycles. The structure of all products was established by the data of IR, NMR spectroscopy (including two-dimensional correlation NOESY-spectroscopy) and mass-spectrometry.

Keywords: *ortho*-Dicarbonitriles, phthalocyanines, 4-methyl-5-nitrophthalonitrile (MNPN), 2-aryl-indol-5,6-dicarbonitriles, 4-azido-5-styryl-phthalonitriles.

Новые азот–содержащие пятичленные гетероциклические *орто*–дикарбонитрилы для получения макрогетероциклов

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Посвящается Член-корреспонденту РАН профессору Койфману О. И. по случаю его 70-летнего юбилея

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С использованием реакции ароматического нуклеофильного замещения в 4-метил-5-нитрофталонитриле реагентами различного строения был разработан новый метод синтеза новых замещенных 4-азидофталонитрилов, взаимодействие которых с ацетилацетоном приводит к образованию замещенных (1,2,3-триазол-1-ил)-5-стирилфталонитрилы, а кипячение в этиленгликоле дает 2-арил-1Н-индол-5,6-дикарбонитрилы. Синтезированные N-содержащие. Строение всех синтезированных соединений подтверждено совокупностью данных ИК-, ЯМР-спектроскипии (в том числе двумерной корреляционной NOESY-спектроскопией) и масс-спектрометрией.

Ключевые слова: *орто*-Дикарбонитрилы, фталоцианины, 4-метил-5-нитрофталонитрил, 2-арил-индол-5,6-дикарбонитрилы, 4-азидо-5-стирил-фталонитрилы.

Introduction

Currently, the interest shown by researchers to substituted heterocyclic phthalonitriles and *ortho*-dicarbonitriles is obvious. These compounds are the most commonly used precursors for the preparation of various macroheterocyclic systems including tetrahetarenoporphyrazines,[1] porphyrinoids,[2] triazaporphyrins,[3] crown phthalocyanines,[4,5] azaphthalocyanines,[6] carborane substituted phthalocyanines,[7] phthalocyanine-fullerene conjugates,[8] binuclear phthalocyanines,[9] and a number of other metal-free phthalocyanines and their metal complexes.[10-13] Although they have unique chemical and thermal stabilities, phthalocyanines are practically insoluble in water and most organic solvents. This drawback can be overcome in two ways: by sequentially introducing peripheral substituent's of different chemical nature onto the macroheterocycles, or by synthesizing the desired compound from the precursors already containing appropriate functional groups, *e.g.*, carboxylic acid groups or sulfates imparting water solubility, and a variety of di- and tetraaryl (alkyl) substituted phthalonitriles.[14]

Experimental

IR spectra were measured on a Perkin-Elmer RX-1 spectrometer in the range of 700-4000 cm^{-1} using suspensions of substances in Nujol. The ^{1}H NMR spectra were recorded on a Bruker DRX-500 instrument (500 MHz,) in DMSO-d_6 at 30 °C. The internal standard was the residual signal of the solvent (2.50 ppm for ^{1}H nuclei). Standard Bruker procedures were used for recording the two-dimensional spectra. The mixing time in the NOESY spectra was 0.3 sec. Mass spectra were recorded on a MX-1321 spectrometer with direct insertion of samples at 100-150 °C and with ionizing voltage 70 eV. Elemental analysis was carried out on a Perkin-Elmer 2400 instrument. Melting points were determined on a PTP-M instrument.

The starting material **4** were synthesized using known procedures.[15]

*General method for the synthesis of 4-nitro-5-[(E)-2-arylethenyl]benzene-1,2-dicarbonitriles (**7a-c**)*. A mixture of 2-propanol (10 mL), of MNPN (**4**) (5 mmol), aldehyde **6a-c** (6 mmol) and piperidine (0.6 mL) was heated to 70-80 °C and maintained under these conditions for 2-2.5 hrs. After cooling to room temperature the precipitate was filtered, washed with ethanol and dried at 50 °C.

*4-Nitro-5-[(E)-2-phenylethenyl]benzene-1,2-dicarbonitrile (**7a**)*. Yield: 1.18 g, 4.3 mmol, 86 % based on **4.** M. p. 286-288 °C. Found: C 69.69, H 3.25, N 15.19 %. $C_{16}H_9N_3O_2$ Calculated: C 69.81; H 3.30; N15.27. IR ν_{max} cm^{-1}: 964, 1355, 1522, 1551, 1592, 1629, 2236. ^{1}H NMR δ_H ppm: 6.36 (d, *J*=16.1 Hz ,1H, H-1'), 7.41 (m, 3H, H-3", H-4", H-5"), 7.63 (d, *J*=7.02 Hz, 2H, H-2", H-6"), 7.77 (d, *J*=16.11 Hz, 2H, H-2'), 8.73 (s, 1H, H-3), 8.87 (s, 1H, H-6).

*4-[(E)-2-(4-Methoxyphenyl)ethenyl]-5-nitrobenzene-1,2-dicarbonitrile (**7b**)*: Yield: 1.30 g, 4.2 mmol, 85% based on **4.** M. p. 238-240 °C. Found: C 66.70, H 3.59, N 13.69 %. $C_{17}H_{11}N_3O_3$ Calculated: C 66.88, H 3.63, N 13.76. IR ν_{max} cm^{-1}: 970, 1262, 1344, 1515, 1592, 1627, 2235. ^{1}H NMR δ_H ppm: 3.82 (s, 3H, OMe), 7.00 (d, *J*=8.1 Hz, 2H, H-3", H-5"), 7.21 (d, *J*=15.8Hz, 1H, H-1'), 7.59 (d, *J*=8.1 Hz, 2H, H-2", H-6"), 7.71 (d, *J*=15.8 Hz, 1H, H-2'), 8.69 (s, 1H, H-3), 8.77 (s, 1H, H-6).

4-*[(E)-2-(4-Chlorophenyl)ethenyl]-5-nitrobenzene-1,2-dicarbonitrile (**7c**)*. Yield: 0.69 g, 2.25 mmol, 45 % based on **4**. M. p. 208-210 °C. Found: C 61.87, H 2.53, N 13.45 %. $C_{16}H_8ClN_3O_2$ Calculated: C 62.05, H 2.60, N 13.57. IR ν_{max} cm^{-1}: 970, 1337, 1491, 1523, 1603, 2244. ^{1}H NMR δ_H ppm: 7.42 (d, *J*=16.0 Hz, 1H, H-1'), 7.51 (d, *J*=8.1 Hz, 2H, H-3", H-5"), 7.68 (d, *J*=8.1 Hz, 2H, H-2", H-6"), 7.74 (d, *J*=16.0 Hz, 1H, H-2'), 8.80 (s, 1H, H-3), 8.84 (s, 1H, H-6).

General method for the synthesis of 4-azido-5-[(E)-2-arylethenyl]benzene-1,2-dicarbonitriles (**8a-c**). In a flask equipped with a stirrer, 5 mL of DMF was added to a mixture of compounds **7a-c** (5 mmol) and sodium azide (6 mmol). The reaction mixture was stirred vigorously at room temperature for one hour. Then, the reaction mixture was poured with stirring into 20 mL of water, and the precipitate was filtered, washed with ethanol and dried.

*4-Azido-5-[(E)-2-phenylethenyl]benzene-1,2-dicarbonitrile (**8a**)*. Yield: 1.07 g, 3.94 mmol, 79% based on **7a**. M. p. >300 °C. Found: C 70.68, H 3.25, N 25.69 %. $C_{16}H_9N_5$. Calculated: C 70.84, H 3.34, N 25.82. IR ν_{max} cm^{-1}: 971, 1494, 1590, 1626, 2118, 2233. ^{1}H NMR δ_H ppm: 6.24 (d, *J*=16.5 Hz, 1H, H-1'), 7.38 (m, 3H, H-3", H-4", H-5"), 7.58 (d, *J*=7.0 Hz, 2H, H-2", H-6"), 7.61 (d, *J*=16.5 Hz, 1H, H-2'), 8.12 (s, 1H, H-3), 8.52 (s, 1H, H-6).

*4-Azido-5-[(E)-2-(4-methoxyphenyl)ethenyl]benzene-1,2-dicarbonitrile (**8b**)*. Yield: 1.08 g, 3.6 mmol, 72% based on **7b.** M. p. 292- 293°C (dec.). Found: C 67.58, H 3.61, N 23.12 %. $C_{17}H_{11}N_5O$. Calculated: C 67.77, H 3.68, N 23.24. IR ν_{max} cm^{-1}: 973, 1034, 1170, 1254, 1510, 1584, 1603, 1628, 2109,2230. ^{1}H NMR δ_H ppm:3.81 (s, 3H, OMe), 6.94 (d, *J*=8.7 Hz, 2H, H-3", H-5"), 7.07 (d, *J*=16.4Hz, 1H, H-1'), 7.52 (d, *J*=8.7 Hz, 2H, H-2", H-6"), 7.56 (d, *J*=16.4 Hz, 1H, H-2'), 8.10 (s, 1H, H-3), 8.45 (s, 1H, H-6).

*4-Azido-5-[(E)-2-(4-chlorophenyl)ethenyl]benzene-1,2-dicarbonitrile (**8c**)*. Yield: 1.02 g, 3.5 mmol, 70% based on **7c**. M. p. >300 °C. Found: C 62.68, H 2.61, N 22.80 %. $C_{16}H_8ClN_5$. Calculated: C 62.86, H, 2.64, N 22.91. IR ν_{max} cm^{-1}: 976, 1588, 1630, 2107, 2234. ^{1}H NMR δ_H ppm: 7.23 (d, *J*=16.6 Hz, 1H, H-1'), 7.46 (d, *J*=7.5 Hz, 2H, H-3", H-5"), 7.58 (d, *J*=16.6 Hz, 1H, H-2'), 7.62 (d, *J*=7.5 Hz, 2H, H-2", H-6"), 8.12 (s, 1H, H-3), 8.46 (s, 1H, H-6).

*General method for the synthesis of 4-(4-acetyl-5-methyl-1H-1,2,3-triazol-1-yl)-5-[(E)-2-aryl-ethenyl]benzene-1,2-dicarbonitriles (**9a-c**)*. A flask equipped with a stirrer and a thermometer was charged with 10 mL of dioxane and 2 mmol of compounds **8a-c**. To this solution acetylacetone and Et_3N (2 mmol) were added. The reaction mixture was stirred for 2-3 h at 70-80 °C, diluted with water twice, and the precipitate was filtered, washed with water and dried.

*4-(4-Acetyl-5-methyl-1H-1,2,3-triazol-1-yl)-5-[(E)-2-phenylethenyl]benzene-1,2-dicarbonitrile (**9a**)*. Yield: 0.41 g, 1.16 mmol, 58% based on **8a**. M. p. 240-242 °C. Found: C 71.24, H 4.22, N 19.70 %. $C_{21}H_{15}N_5O$. Calculated: C 71.38, H 4.28, N 19.82. *m/z*, (ESI) (%): 353 [M+] (6), 325 (14), 310 (16), 282 (25), 267 (21), 243 (13), 43 (100). IR ν_{max} cm^{-1}: 968, 1596, 1627, 1678, 2232, 3341. ^{1}H NMR δ_H ppm: 2.42 (s, 3H, Me), 2.69 (s, 3H, Ac), 6.53 (d, *J*=16.3 Hz, 1H, CH-2'), 7.39 (m, 3H, Ph), 7.50 (d, *J*=7.0 Hz, 2H, Ph), 7.77 (d, *J*=16.3 Hz, 1H, CH-1'), 8.42 (s, 1H, H-3), 8.95 (s, 1H, H-6).

*4-(4-Acetyl-5-methyl-1H-1,2,3-triazol-1-yl)-5-[(E)-2-(4-methoxyphenyl)ethenyl]benzene-1,2-dicarbonitrile (**9b**)*. Yield: 0.491 g, 1.28 mmol, 64% based on **8b**. M. p. 245-246 °C. Found: C 68.80, H 4.41, N 18.17 %. $C_{22}H_{17}N_5O_2$. Calculated: C 68.92, H 4.47, N 18.27. IR ν_{max} cm^{-1}: 955, 1174, 1257, 1592,1631, 1672, 1686, 2236, 3352. ^{1}H NMR δ_H ppm: 2.41 (s, 3H, Me), 2.70 (s, 3H, Ac), 3.79 (s, 3H, OMe), 6.29 (d, *J*=16.2 Hz, 1H, CH-2'), 6.91 (d, *J*=8.5 Hz, 2H, H-3", H-5"), 7.42 (d, *J* =8.5Hz, 2H, H-2", H-6"), 7.72 (d, *J*=16.2 Hz, 1H, CH-1'), 8.33 (s, 1H, H-3), 8.89 (s, 1H, H-6).

*4-(4-Acetyl-5-methyl-1H-1,2,3-triazol-1-yl)-5-[(E)-2-(4-chlorophenyl)ethenyl]benzene-1,2-dicarbonitrile (**9c**).* Yield: 0.489 g, 1.26 mmol, 63 % based on **8c**. M. p. 261-262 °C. Found: C 64.8, H 3.58, N 17.97 %. $C_{21}H_{14}ClN_5O$. Calculated: C 65.04, H 3.64, N 18.06. *m/z* (ESI) (%), 388, 386 [M+], 358, 344, 316, 281, 43 (100). IR ν_{max} cm^{-1}: 964, 1590, 1628, 1684, 2236, 3354. ^{1}H NMR δ_H ppm: 2.42 (s, 3H, Me), 2.69 (s, 3H, Ac), 6.58 (d, *J*=16.2 Hz, 1H, CH-2'), 7.46 (d, *J*=8.6 Hz, 2H, H-3", H-5"), 7.54 (d, *J*=8.6 Hz, 2H, H-2", H-6"), 7.75 (d, *J*=16.2 Hz, 1H, CH-1'), 8.43 (s, 1H, H-3), 8.93 (s,1H, H-6).

*General method for the synthesis of 2-aryl-1H-indole-5,6-dicarbonitriles (**10a-c**).* In a flask equipped with a stirrer, reflux condenser and nitrogen bubbler, a solution of compounds **8a-c** (2 mmol) in ethyleneglycol (20 mL) was put. The reaction mixture was stirred at 160-200 °C for 4-6 hrs, and then poured into 20 g of ice, and the precipitate was filtered off and recrystallized from DMF.

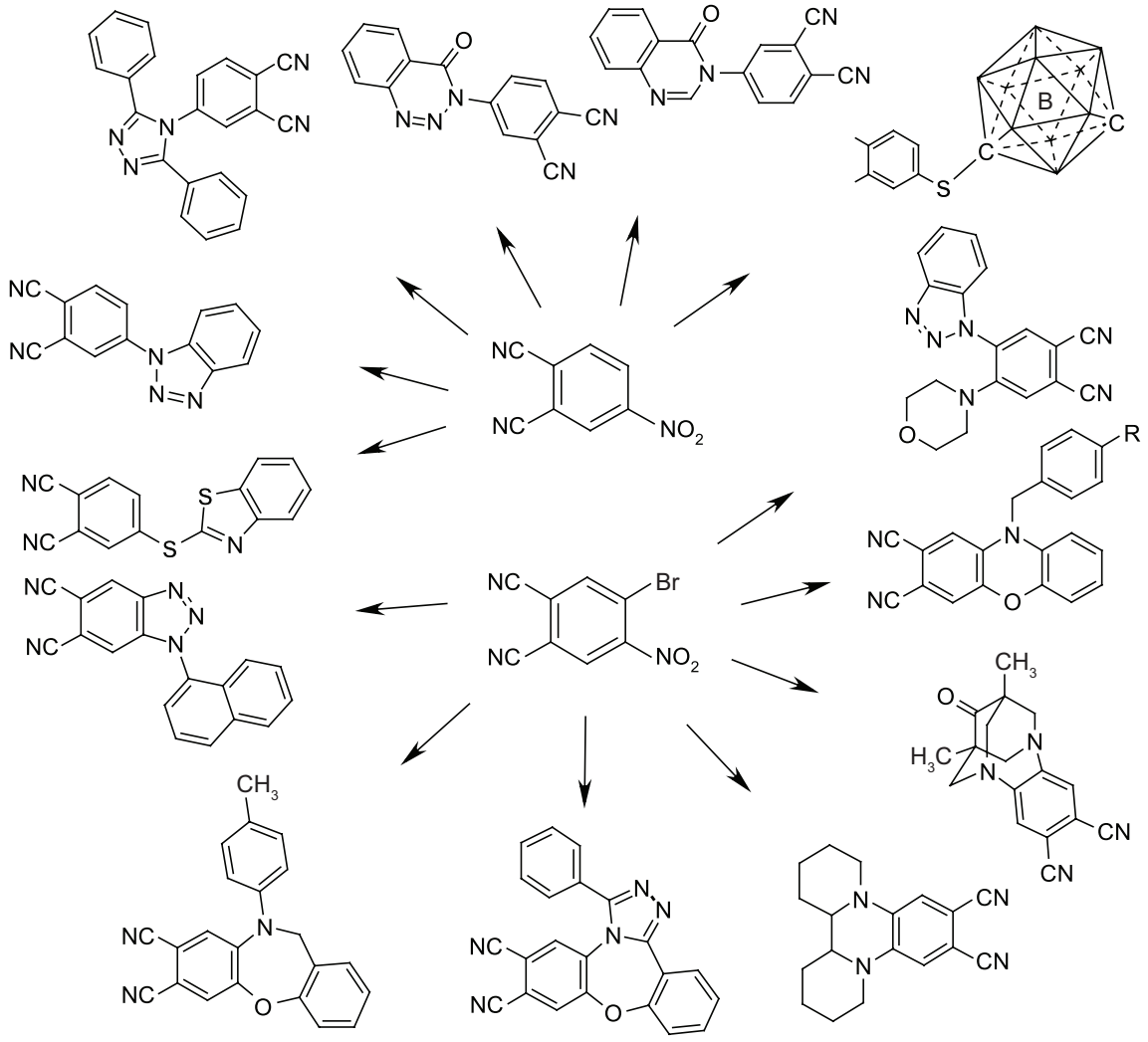
*2-Phenyl-1H-indole-5,6-dicarbonitrile (**10a**)*. Yield: 0.170 g, 0.7 mmol, 35 % based on **8a**. M. p. 288-290 °C. Found: C 78.82, H 3.66, N 17.15 %. $C_{16}H_9N_3$. Calculated: C 79.00, H 3.73, N 17.27. *m*/*z*, (ESI) (%): 243 [M+] (100), 215 (18), 77 (12), 51 (19). IR ν_{max} cm^{-1}: 1584, 2228, 3275. ^{1}H NMR δ_H ppm: 7.24 (s, 1H, H-3), 7.45 (t, *J*=7.4 Hz, 1H, H-4'), 7.54 (t, *J*=7.4 Hz, 2H, H-3', H-5'), 7.96 (d, *J*=7.4 Hz, 2H, H-2', H-6'), 8.10 (s, 1H, H-7), 8.36 (s, 1H, H-4), 12.77 (s, 1H, NH).

*2-(4-Methoxyphenyl)-1H-indole-5,6-dicarbonitrile (**10b**)*. Yield: 0.169 g, 0.6 mmol, 31 % based on **8b.** M. p. 296-298 °C. Found: C 74.55, H 4.00, N 15.27 %. $C_{17}H_{11}N_3O$. Calculated: C 74.71, H 4.06, N 15.38. IR ν_{max} cm^{-1}: 1027, 1188, 1256, 1499, 1609, 2229, 3297. ^{1}H NMR δ_H ppm: 3.83 (s, 3H, OMe), 7.08 (d, *J*=8.2 Hz, 3H, H-3, H-2', H-6'), 7.88 (d, *J*=8.2 Hz, 2H, H-3', H-5'), 8.02 (s, 1H, H-7), 8.26 (s, 1H, H-4), 12.63 (s, 1H, NH).

*2-(4-Chlorophenyl)-1H-indole-5,6-dicarbonitrile (**10c**)*. Yield: 0.183 g, 0.66 mmol, 33 % based on **8c**. M. p. >300 °C. Found: C 69.04, H 2.83, N 15.03 %. $C_{16}H_8ClN_3$. Calculated: C 69.20, H 2.90, N 15.13. *m*/*z*, (ESI) (%):277 [M+] (100), 241 (29), 215 (11), 188 (10), 139 (14), 113 (12), 75 (19), 63 (14). IR ν_{max} cm^{-1}: 779, 828, 1601, 2232, 3265. ^{1}H NMR δ_H ppm: 7.25 (s, 1H, H-3), 7.61 (d, *J*=8.6 Hz, 2H, H-3', H-5'), 7.98 (d, *J*=8.6 Hz, 2H, H-2', H-6'), 8.10 (s, 1H, H-7), 8.35 (s, 1H, H-4), 12.80 (s, 1H, NH).

Results and Discussion

There are various methods used for the synthesis of phthalonitriles. The most famous is the classic Rosenmund-Brown cyanidation reaction. Its modern modification, catalyzed by transition metal complexes,[16] significantly expanded the range of available *ortho*-dicarbonitriles. Despite the progress made recently in this field, alternative methods of synthesizing these compounds continue to be developed. First of all, it should be noted that S_NAr-reactions occurring with the participation of 4-nitro- and 4-bromo-5-nitrophthalonitrile under homo- and hetero-conditions allow the study of the synthesis of a large number of diverse aromatic and heterocyclic compounds,[17-23] and related compounds that are condensed with the phthalonitrile fragment (Scheme1).



Scheme 1

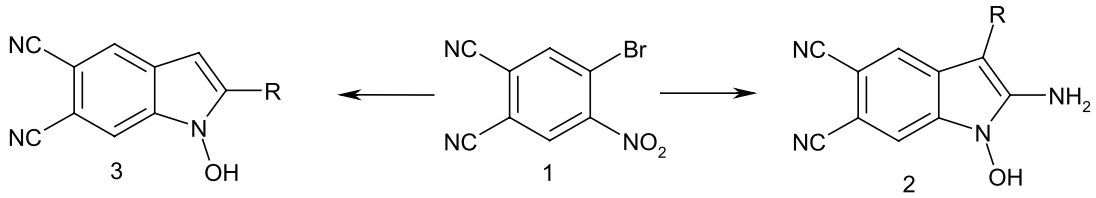
In addition, we have developed methods for the synthesis of 3-substituted 2-amino-1-hydroxy-1*H*-indole-5,6-dicarbonitriles (**2**),[24] and 2-aryl-1-Hydroxy-1*H*-indole-5,6-dicarbonitriles (**3**),[25] based on 4-bromo-5-nitrophthalonitrile (**1**) (Scheme 2). These relatively reactive compounds can be subjected to further functionalization to improve solubility of the target products.

Five-membered nitrogen-containing heterocyclic *ortho*-dicarbonitriles were prepared based on 4-methyl-5-nitrophthalonitrile (MNPN), **4**. The paper describes methods for the synthesis of 2-aryl-1-hydroxy-indole-5,6-dicarbonitriles (**3**)[26] and *N*-substituted 1*H*-indazole-5,6-dicarbonitriles (**5**)[27] (Scheme 3).

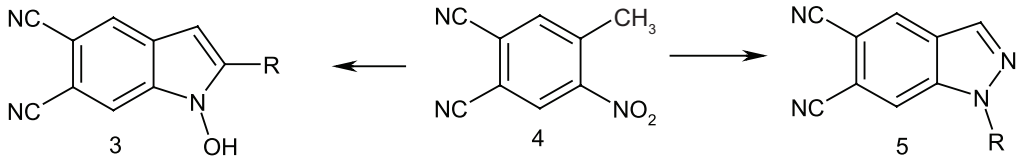
The work on the synthesis of nitrogen-containing heterocyclic compounds based on MNFN, **4**, was continued. The results of these studies – three-step synthetic method, not described in the literature, of 2-aryl-1*H*-indole-5,6-dicarbonitriles and (1,2,3-triazol-1-yl)-5-styrylphthalonitriles.

On the first step, using piperidine as a deprotonation agent, Knoevenagel condensation of activated methyl group of MNPN (**4**) with aromatic and heterocyclic aldehydes **6a-c** leads to the formation of the corresponding 4-nitro-5-styrylphthalonitriles (**7a-c**) with yields of 45-88 % (Scheme 4). We observed the deactivating effect of acceptor substituents in reagents **6a-c** for this reaction. Thus, in the case of *p*-chlorobenzaldehyde, the yield of the desired product drops to 45 %, and in the case of *m*-nitrobenzaldehyde the reaction does not proceed at all. On the second step at ambient temperature in DMF, a S_NAr-substitution reaction of nitro group in the 4-nitro-5-styrylphthalonitriles (**7a-c**) was carried out with sodium azide. The target 4-azido-5-styrylphthalonitriles (**8a-c**) were obtained in the yields of 70-79 % and were used in the subsequent reactions without further purification. On the third step, there are two options for modifying the azido-substrates (**8a-c**), leading to the formation of various nitrogen-containing heterocyclic systems.

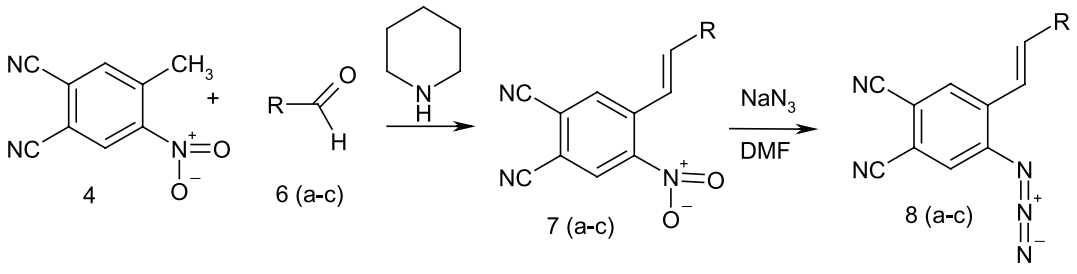
In order to obtain *N*-substituted triazoles, the reaction between 4-azido-5-styrylphthalonitriles (**8a-c**) with acetylacetone was investigated (Scheme 5). This methodology is based on a study of cyclization of azido-group with 1,3-diketones, described in reference [28]. It was established that the maximum yields (58-64 %) of the target 4-acetyl-5-methyl-[1,2,3]triazol-1-yl-5-styrylphthalonitriles (**9a-c**) could be achieved by stirring the starting substrates **8a-c** with acetylacetone in the presence of triethylamine in dioxane at 75-85 °C (Scheme 5). At lower temperatures the reaction is slow and not fully completed, and carrying out synthesis at a higher temperature is associated with a significant increase in the amount of reaction byproducts. Furthermore, it was shown that triazoles are formed selectively. The reaction mixture produces only one isomer. Precise definition of the structure of target compounds was made using NOESY-spectroscopy. For example, in the spectrum of product **9a** (Figure 1), symmetrical cross-peaks were observed for CH_3-group (2.42 ppm) coupled with one of the phthalonitrile protons



Scheme 2.

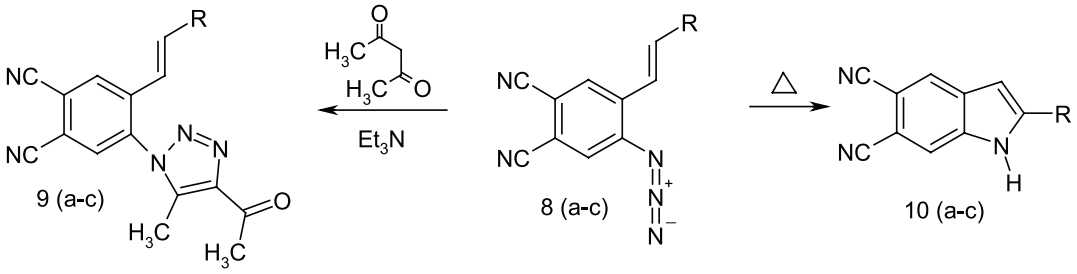


Scheme 3.



6, 7, 8 **a** R=Ph, **b** R=*п*-C_6H_4OMe, **c** R=*п*-C_6H_4Cl

Scheme 4.



8, 9, 10 **a** R=Ph, **b** R=*n*-C_6H_4OMe, **c** R=*n*-C_6H_4Cl

Scheme 5.

(H-3 - 8.42 ppm) and the proton styryl moiety (H-2'- 6.53 ppm). It thus follows that the methyl group is involved in bonding with the phthalonitrile fragment. Along with these fixed cross-peaks of varying intensity, it was observed coupling between styryl protons H-1', H-2' and H-6, H-2'', H-6'', which shows the *trans*-geometry of the styryl unit. These data clearly confirm the structure of compound **9a** and agree with literature[29] on the location of the methyl group in the triazole of acetyl moiety.

For the synthesis of new 2-aryl-1*H*-indole-5,6-dicarbonitriles (**10a-c**), thermal intramolecular cyclization reaction of 4-azido-5-styrylphthalonitriles (**8a-c**) was investigated. Similar reactions to aryl azides are described in references [30,31]. In our case, the best results are achieved by mixing of the starting substrates for 6-8 hours at 180-200 °C in ethylene glycol in atmosphere of nitrogen. Carrying out the reaction in an inert atmosphere and careful protection from oxidation reaction are the decisive factors of increasing yield. The use of other high-temperature solvents (dichlorobenzene, nitrobenzene) was less effective due to the low solubility of the azide. If the photocyclization (UV-irradiation) of the reaction mixture was attempted, yields of the desired products were significantly lower.

In the ^{1}H NMR spectra for compounds **10a-c** the down-field NH-proton signals (about 12.80 ppm) were observed

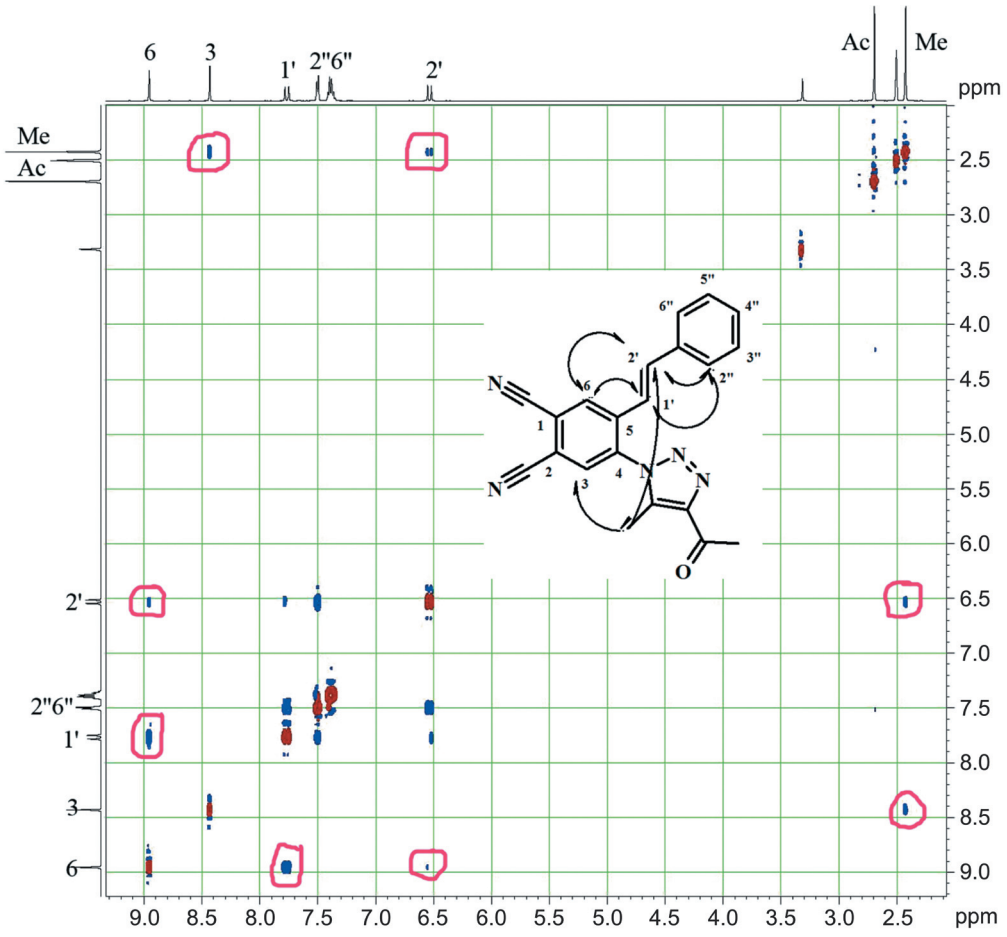


Figure 1. NOESY-spectra of 4-(4-acetyl-5-methyl-1*H*-1,2,3-triazol-1-yl)-5-[(*E*)-2-phenylethenyl]benzene-1,2-dicarbonitrile (**9a**).

along with the characteristic signals of aromatic moieties. These results agree well with the mass-spectrometry where intense signals were observed (100 %) of the molecular ions.

Conclusions

The synthesis based on 4-nitro-5-nitrophthalonitrile provides novel substituted 4-azidophthalonitriles and indole-5,6-dicarbonitrile. The structures of the products obtained were determined using standard spectral analytical methods.

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