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НОВЫЙ ДИНИТРИЛ: СИНТЕЗ, СТРУКТУРА И СПЕКТРЫ

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Катализируемое переходными металлами цианирование по методу Розенмунда-фон Брауна является традиционным способом синтеза замещенных фталонитрилов. Однако невысокие выходы, жесткие условия реакции и ограниченный доступ к галогенсодержащим соединениям делают этот метод ненадежным во многих случаях. В этой работе была проведена направленная С-Н функционализация 5,6-бис(4-бромфенил)пиразин-2,3-дикарбонитрила(4) с бензотиазолом с получением соответствующего 5,6-бис(4-(бензо[d]тиазол-2-ил)фенил)пиразин-2,3-дикарбонитрила(5). Синтез начинается с 4-броманилина, который был подвергнут взаимодействию с формальдоксимом в условиях реакции Меервейна с получением оксима 4-бромбензальдегида. Последующий гидролиз оксима приводит к образованию 4-бромбензальдегида. Для получения 1,2-бис(4-бромфенил)-2-гидроксиэтанона использовали конденсацию бензальдегида, используя NaCN в качестве катализатора. Полученный затем осадок окисляли $CuSO_4$ с получением 1,2-бис(4-бромфенил)этан-1,2-диона. Конденсация диаминомалеодинитрила с полученным 1,2-бис(4-бромфенил)этан-1,2-дионом в ледяной уксусной кислоте привела к образованию 5,6-бис(4-бромфенил)пиразин-2,3-дикарбонитрила с выходом 83%. Реакция С-Н функционализации проводилась с использованием Pd/Cu-каталитической системы в кипящем толуоле в течение 6 ч в присутствии поташа в качестве основания и PPh3 в качестве лиганда для получения 5,6-бис(4-(бензо[d]тиазол-2-ил)фенил)пиразин-2,3-дикарбонитрила с выходом 73%. Структура полученного соединения была установлена с помощью электронной спектроскопии, масс-спектрометрии (MALDI-TOF), ^{1}H и ^{13}C ЯМР-спектроскопии. Согласно расчетам B3LYP/cc-pVTZ выяснено, что соединение 5 характеризуется точечной группой симметрии C2. Проведено описание колебаний соединения 5 на основе анализа распределения потенциальной энергии (РПЭ) форм нормальных колебаний по естественным колебательным координатам. Отмечено, что РПЭ нормальных колебаний по внутренним координатам имеет сложный характер, а ИК-спектры, экспериментальные и смоделированные на основе результатов квантово-химических расчетов, удовлетворительно согласуются друг с другом.

Ключевые слова: С-Н функционализация, дикарбонитрил, бензотиазол

NEW DINITRILE: SYNTHESIS, STRUCTURE, AND SPECTRA

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Transition-metal catalyzed cyanation by Rosenmund-von Braun is conventional approach to substituted phthalonitriles. However, low reaction yields, rough reaction conditions and limited access to halogenated compounds make this technique unreliable in many cases. In this work, we have established the direct C-H functionalization of 5,6-bis(4-bromophenyl)pyrazine-2,3-dicarbonitrile(4) with benzothiazole affording the corresponding 5,6-bis(4-(benzo[d]thiazol-2-yl)phenyl)pyrazine-2,3-dicarbonitrile(5). The reaction pathway starts from the 4-bromoaniline, which was subjected to react with formaldoxime under Meerwein reaction conditions to give the oxime of 4-bromobenzaldehyde. Subsequent hydrolysis of oxime leads to formation of 4-bromobenzaldehyde. To prepare 1,2-bis(4-bromophenyl)-2-hydroxyethanone, benzoin aldehyde condensation was employed using NaCN as a catalyst. The precipitate obtained then was oxidized with $CuSO_4$ to afford 1,2-bis(4-bromophenyl)ethane-1,2-dione. Condensation of diaminomaleodinitrile with 1,2-bis(4-bromophenyl)ethane-1,2-dione in glacial acetic acid led to the formation of 5,6-bis(4-bromophenyl)pyrazine-2,3-dicarbonitrile with 83% yield. Direct C-H functionalization was performed using Pd/Cu-catalytic system in boiling toluene for 6 h in the presence of K_2CO_3 as a base and PPh3 as a ligand to obtain 5 in 73% yield. Structure of 5 was determined by Uv/Vis spectroscopy, mass spectrometry (MALDI-TOF), 1H and 13C NMR spectroscopy. According to B3LYP/cc-pVTZ calculations 5 has the structure of C2 symmetry. Assignment of vibrational modes of 5 was carried out via potential energy distribution analysis among internal coordinates. The complicated composition of vibrational modes was noted. The simulated and experimental IR-spectra were satisfactorily agreed.

Key words: C-H functionalization, dicarbonitrile, benzothiazole

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INTRODUCTION

Nitriles (also called cyano compounds) are the distinct class of organic compounds, which are widespread in nature [1] and utilized as pharmaceuticals [2-4], polymer materials [5] and dyes [6]. They can serve as the starting material for the synthesis of amines, amidines, tetrazoles, aldehydes, amides and carboxylic acids. The synthesis of aromatic 1,2-dicarbon acid dinitriles - phthalonitriles, their modifications, benzo annulated homologs and their derivatives (dinitriles of naphthalene-, anthracene-, pyridine-, pyrazine-, quinoline-, quinoxaline of dicarboxylic acids) have been developed [7-10]. Oxidation reactions of arenes, electrophilic and nucleophilic substitution, Sandmeyer, Rosenmund–von Braun, etc. are employed for the facile introduction of carboxyl or directly nitrile groups as well as other various substituents.

Rosenmund-von Braun reaction, one of the most convenient method for the preparation of dinitriles, involves the transformation of *o*-dihalogenated compounds into the corresponding dinitriles using

CuCN as cyanated agent [8]. Substituted phthalonitriles and their derivatives are required for the development of functional materials based on porphyrazines. Dinitriles can be modified using «*ipso*»-substitution of nitro groups [11], alkylation and arylation of thio-, hydroxy-, and carboxy groups [11-17]; cross-coupling reactions [18-19].

The development of new approaches to the synthesis and modifications of dinitriles is of importance because it opens the gates towards synthesis new symmetrical and unsymmetrical porphyrazines [20]. In this review, we have demonstrated the new synthetic protocol for the synthesis of new undescribed dinitrile using Pd-catalyzed C-H functionalization [21].

EXPERIMENTAL

Paraformaldehyde, hydroxylamine hydrochloride and 4-bromoaniline were purchased from Aldrich, USA. CH_2Cl_2 was distilled from KOH, $CaCl_2$ and Na_2SO_4. A silica gel (from Merck) with 40-60 μm particles was applied in column chromatography. Other chemicals were of reagent grade.

UV/Vis spectra (320-900 nm) of investigated compounds were obtained at ambient temperatures in $CHCl_3$ and CH_2Cl_2 using an UV/VIS Hitachi U2001 spectrometer. NMR spectra (^1H, ^{13}C) were measured on a Bruker Avance-500 spectrometer in standard solutions. The solvent signals were used as the internal standards. IR spectra (3000-300 cm^{-1}) were recorded with an Avatar.360 FT – IR ESP in optically pure KBr. The elemental analysis were performed on a FlashEA 1112 CHNS–O Analyzer apparatus. The MALDI-TOF mass spectra of the positive ions were registered on Shimandzu AXIMA Confidence, a time-of-flight mass spectrometer with matrix-associated laser desorption, and a Bruker Daltonics Ultraflex apparatus.

4-Bromobenzaldehyde (**1**)

Paraformaldehyde (23.0 g, 0.8 mol), hydroxylamine hydrochloride (52.6 g, 0.76 mol) and 340 ml of water were placed in 2 L three-necked round-bottom flask equipped with a reflux condenser and dropping funnel. The reaction mixture was heated to the formation of turbid solution. Then 102.0 g (0.89 mol) of $CH_3COONa·3H_2O$ were added and heating and stirring were continued for 15 min. The mixture was allowed to attain RT and 12.5 g (0.05 mol) of $CuSO_4·5H_2O$, 2.0 g (15.8 mmol) of Na_2SO_3, the solution of $CH_3COONa·3H_2O$ (330 g, 2.89 mol) in 360 ml of water were added to the reaction mixture under stirring.

86.8 g (0.504 mol) of 4-bromoaniline was placed in 1 L beaker and dissolved in mixture of HCl (114 ml) and H_2O (110 ml). The solution was cooled down to 0-5 °C in ice bath and 35.0 g (0.507 mol) of $NaNO_2$ in 50 ml of water was added dropwise keeping the reaction temperature between 0-5 °C. 44.0 g (0.385 mol) of $CH_3COONa·3H_2O$ in 70 ml of water was added to diazo compound salt forming neutral condition (pH = 7). The mixture was cooled down in ice bath and then introduced beneath the surface of formaldoxime solution keeping the reaction temperature less than 15 °C. The stirring was continued for 1 h adding HCl (230 ml, pH = 2) and reaction mixture was refluxed for 2 h.

Crude product was removed by steam distillation collecting of 2 L of residual matter. The distillate was treated by Na_2CO_3, extracted with CH_2Cl_2 and washed with water and an aqueous solution of NaOH (5%). The reaction mixture was dried over Na_2SO_4 and the solvent was removed in vacuo to afford **1** (74.6 g, 80%) m.p. = 55-58 °C. ^1H NMR (500 MHz, $CDCl_3$): δ (ppm): 9.98 (s, 1H), 7.75 m (2H, J = 8.4 Hz, 2,6-Ar), 7.69 m (2H; J = 8.4 Hz, 3,5-Ar).

1,2-bis(4-bromophenyl)-2-hydroxyethanone (**2**)

C_2H_5OH (3.75 ml), H_2O (2.5 ml), **1** (5 g), NaCN (0.25 g) was refluxed for 20 min in a round-bootom flask. After the reaction was completed, the mixture was cooled down and the product was extracted with CH_2Cl_2, washed with water and dried over Na_2SO_4. The solvent was removed in vacuo and the crude precipitate was recrystallized from a C_2H_5OH to afford **2** (4.2 g, 85%). m.p. = 92-93 °C. ^1H NMR (500 MHz, $CDCl_3$): δ (ppm): 7.74 d (2H, J = 8.6, 2.6-Ar), 7.55 d (2H, J = 8.6, 2.6-Ar), 7.46 d (2H, J = 8.4, 3.5-Ar), 7.18 d (2H, J = 8.4 Hz, 3.5-Ar), 5.86 brs (1H, J = 4.6 Hz, α-carbonyl CH), 4.49 brs (1H, J 4.6 Hz, OH).

1,2-bis(4-bromophenyl)ethane-1,2-dione (**3**)

$CuSO_4·5H_2O$ (18 g) and pyridine (17 ml) in water were placed in 250 ml round bottom flask. The mixture was heated and **2** (4 g) was added to solution. The heating and stirring were continued for 2 h (air bath). The mixture was getting dark green. The reaction was cooled and crystalline solid was filtered out, washed with water and dried. The crude product was recrystallized from a CCl_4 to gave **3** (3.6 г, 98%). м.р. = 225-227 °C. ^1H NMR (500 MHz, $CDCl_3$): δ (ppm): 7.83 d (4H, J = 8.5 Hz, 2.6-Ar), 7.67 d (4H, J = 8.5 Hz, 3.5-Ar).

5,6-bis(4-bromophenyl)pyrazine-2,3-dicarbonitrile (**4**)

To a 100 ml round bottom flask charged with **3** (2.5 g) and diaminomaleodinitrile (0.88 g) glacial acetic acid was added. The reaction mixture was refluxed for 4 h, poured down to water and filtered out. The formed precipitate was dried and extracted with dichloromethane. The crude product was purified by silica gel colonel chromatography using dichloro-

methane as an eluent. The first yellow fraction was collected and solvent was removed in vacuo to provide **4** as a yellow solid (2.48 g, 83%). м.р. = 209-211 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm): 7.46 d (4H, J = 8.4 Hz, 2.6-Ar), 7.58 d (4H, J = 8.2 Hz, 3.5-Ar).

5,6-bis(4-(benzo[d]thiazol-2-yl)phenyl)pyrazine-2,3-dicarbonitrile (**5**)

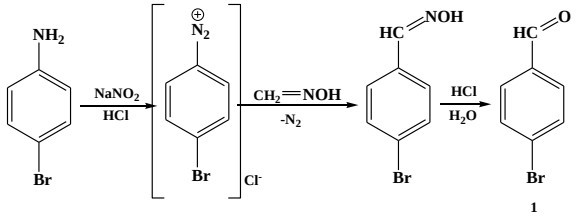
$Pd(OAc)_2$ (0.0509 g, 10 mol%), $Cu(OAc)_2 \cdot 2H_2O$ (0.0906 g, 20 mol%), PPh_3 (0.297 g, 0,5 экв.), toluene (10 ml), benzothiazole (0.988 ml, 9.089 mmol) and 5,6-bis(4'-bromophenyl)pyrazine-2,3-dicarbonitrile (1 g, 2.27 mmol) were placed in a 25 ml one-necked round bottom flask equipped with a reflux condenser and magnetic stirring bar. The reaction mixture was stirring for 1 min and then K_2CO_3 (0.627 g, 2 equiv.) was added. The mixture was refluxed and stirred for 6 h. After the reaction was complete, the mixture was allowed to get cooled to RT and dichloromethane (10 ml) was added washing away the resulted solution. The organic layer was filtered out and washed with CH_2Cl_2 (2·10 ml). The solvent was removed in vacuo. The crude product was purified by silica gel colonel chromatography using CH_2Cl_2 as the eluent and collecting the first yellow fraction to gave 5 (0.9 г, (73%). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm): 7.5m (4H, benzothiazole); 7.73d (4H, J = 8.4 Hz, 3.5-Ar); 7.82d (4H, J = 8.4 Hz, 2.6-Ar); 7.93 m (2H, benzothiazole); 8.03 m (2H, benzothiazole). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm): 113.80br (2C); 118.11br (2C); 121.73 (4C); 124.42br (2C); 126.48d (4C); 130.53br (2C); 132.56br (2C), 136.50br (2C), 140.52br (2C), 142.57br (2C), 148.49br (2C), 153.99br (2C), 164.13br(2C). MALDI-TOFMS: m/z calcd for $[C_{32}H_{16}N_6S_2]$: 548.64; found: 549.48 [M]+.

COMPUTATIONAL DETAILS

Quantum chemical calculations were performed with the Gaussian 09 program package [22] in a framework of DFT approach. Optimized structures were obtained using B3LYP functional with cc-pVTZ basis set [23] for all atoms. Assignment of vibrational modes was carried out by potential energy distribution (PED) analysis along internal coordinates using the VibModule program [24]. Natural bond orbital (NBO) analysis was performed as implemented in the Gaussian 03 package [25]. The ChemCraft program [26] was used for visualization of molecular structure and vibrations.

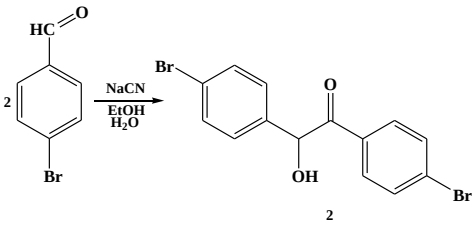
RESULTS AND DISCUSSIONS

The heterocycle-substituted dinitrile **5** was synthesized from the 4-bromobenzaldehyde (**1**) using multistep technique. For the synthesis of **1** we applied Meerwein reaction which involved the attaching of a diazo compound to the heterodual bond of formaldoxime (Scheme **1**) [27]. Formaldoxime was synthesized firstly and then was interacted with the diazo compound salt of 4-bromobenzaldehyde to afford the oxime of 4-bromobenzaldehyde. The subsequent hydrolysis of oxime led to the desired **1** in 80% yield (Scheme **2**).

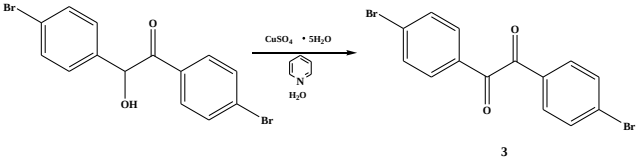


Scheme 1. Synthesis of 1 via the diazonium salt
Схема 1. Синтез соединения 1, используя реакцию циазотирования

Benzoin aldehyde condensation was applied for the preparation of 1,2-bis(4-bromophenyl)-2-hydroxyethanone (**2**) with 85% yield, which then was oxidized with $CuSO_4$ to afford 1,2-bis(4-bromophenyl)ethane-1,2-dione (**3**) in 98% yield (Scheme **3**).



Scheme 2. Benzoin aldehyde condensation of compound 1
Схема 2. Бензоиновая конденсация соединения 1

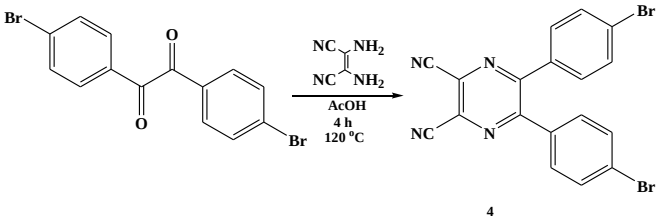


Scheme 3. Oxidation of compound 2 using $CuSO_4$
Схема 3. Окисление соединения 2, используя $CuSO_4$

The subsequent condensation of diaminomaleodinitrile with **3** in glacial acetic acid led to the formation of 5,6-bis(4-bromophenyl)pyrazine-2,3-dicarbonitrile (**4**) with 83% yield (Scheme **4**).

Pd(II)/Cu(II) catalytic system developed by Z.-Z. Huang was chosen for the C-H functionalization of dinitrile due to its efficiency [28, 29]. The reaction was performed in boiling toluene for 6 h in the presence of K_2CO_3 (2 eq.) as a base and PPh_3 (0.5 eq.) as a ligand. The 5,6-bis(4-(benzo[d]thiazol-2-yl)phenyl)pyrazine-2,3-dicarbonitrile (**5**) was obtained as a pale yellow powder (73%).

This approach has paved ways for the facile introduction of variety heterocyclic substituents into dinitrile scaffolds. Diverse porphyrazines and their metallated versions can be prepared according this technique.



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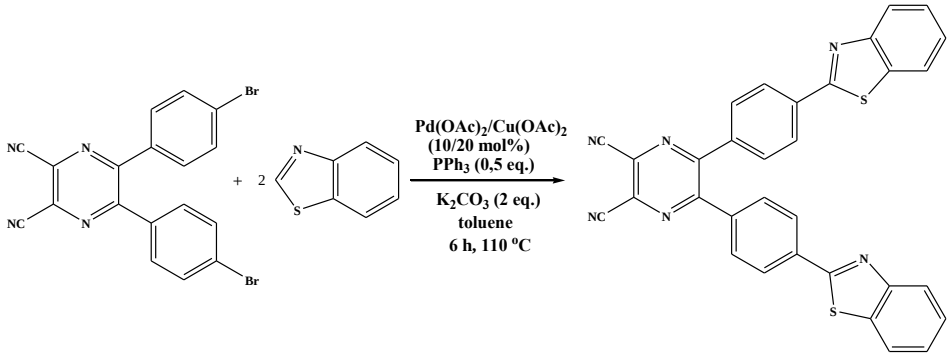
Scheme 4. Condensation of compound 3 with diaminomaleonitrile
Схема 4. Конденсация соединения 3 с диаминомалеонитрилом

According to B3LYP calculations, **5** has three conformers differing in arrangement of sulfur atoms with respect to the center of the molecule: (I) sulfur atoms in cyclic groups are oriented by "outer" direction with respect to center of molecule (Fig. 1); (II) sulfur atoms in cyclic groups are directed by "inner" direction with respect to center of molecule; (III) one sulfur atom in one cyclic group is directed by "inner" direction, another sulfur atom in another group – by "outer". The conformers II and III are higher in energy only by 0.6 and 0.3 kJ·mol^{-1}, respectively. Neighboring phenylene groups are oriented in a "quasi-parallel manner", due to mirrored orientation of neighboring phenylene groups (conformations of C_s symmetry) is energetically unfavorable by at least 23 kJ·mol^{-1} due to induced steric repulsions.

The structural parameters of **5** were compared with the corresponding parameters of "parent" molecules: pyrazine-2,3-dicarbonitrile, benzene and benzothiazole (Table S1-S4). The largest difference in parameters is noted for C_5^{Py}-C_6^{Py}: the neighboring arrangement of two large groups in positions 5 and 6 of the pyrazine cycle leads to an increase in the distance by 0.035 Å. The Wiberg bond index (WI) for this bond decrease from 1.37 in pyrazine-2,3-dicarbonitrile to 1.24 in **5**. It should be noted an increase by 0.02 Å in the S_1^{Bt}-C_2^{Bt} distance in **5** compared to benzothiazole molecule (Table S3). The aromaticity of the pyrazine, phenylene and benzothiazole moieties decreased in **5** with respect to corresponding initial molecules: nucleus-independent chemical shift (NICS) based indexes increase by ~1-2 ppm (Table S4). The natural charges actually change only in the case of atoms involving to bonding of different moieties – C_5^{Py}, C_6^{Py}, C_1^{Ph}, C_4^{Ph}, C_2^{Bt} (Table S3).



5

Scheme 5. Pd/Cu-catalyzed C-H functionalization of compound 4
Схема 5. Pd/Cu-катализируемая реакция С-Н функционализации соединения 4

The highest occupied molecular orbital (HOMO, 70b) and HOMO-1 (71a) of **5** are localized on benzothiazole moieties (55% and 75%, respectively) and phenylene rings (37% and 23%, respectively) (Fig. 2). The lowest unoccupied molecular orbital (LUMO, 72a) is distributed throughout the entire molecule **5** with a dominant contribution of pyrazine unit (52%). Calculations of the electronic absorption spectrum predict the two intensive peaks at λ = 434 and 385 nm (Fig. 3). The first one corresponds to $S_0 \rightarrow S_1$ transition that involves the HOMO → LUMO (70b → 72a) electron transfer. The next intense transition occurs from the ground state to the third excited state originating from HOMO-1 → LUMO (71a → 72a) transition.

Molecule **5** possesses 162 normal modes of vibration. The vibrational representation is Γ = 82A + + 80B. Most of the vibrations are comprised of displacements along several internal coordinates. Assignment of the infrared active modes in **5** is presented in Table 1. Positions of bands in the simulated IR spectrum are in good agreement with appropriate values from the experimental spectrum in a solid phase (Fig. 4). Correlation between relevant bands of the experimental and model spectra is close to linear (Fig. S1). Obtained scaling coefficient 0.970 is consistent with appropriate value 0.976 for theoretical investigation of BODIPY [30] and expected values of 0.967 [31, 32] for the B3LYP/cc-pVTZ calculation. However, there are

some differences in the experimental and theoretical spectra. A strong band at 891 cm^{-1} is observed in the experimental spectrum, but according to calculations there are no vibrations with high IR-intensities in this region. Three signals with similar intensity are observed in the region of 2850-3100 cm^{-1}, while in the model spectrum there is one band at 3196 cm^{-1} corresponding to several CH-stretching vibrations. It should be noted, experimental and theoretical spectra differ in the intensity of the band near 2250 cm^{-1} (Fig. 4) corresponding to the NC-stretching vibrations of cyano-groups.

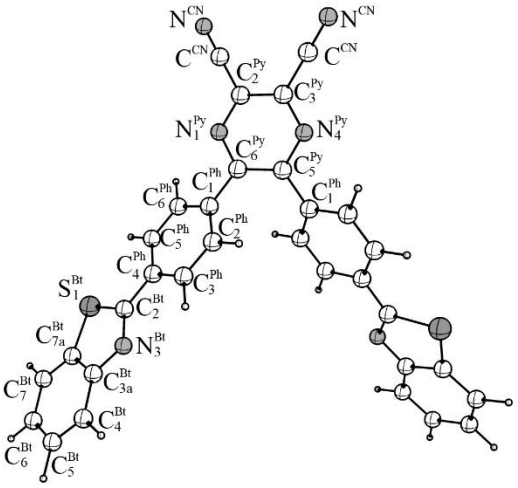


Fig. 1. Geometry model of C_2 symmetry for compound **5**
Рис. 1. Геометрическая модель (симметрии C_2) соединения **5**

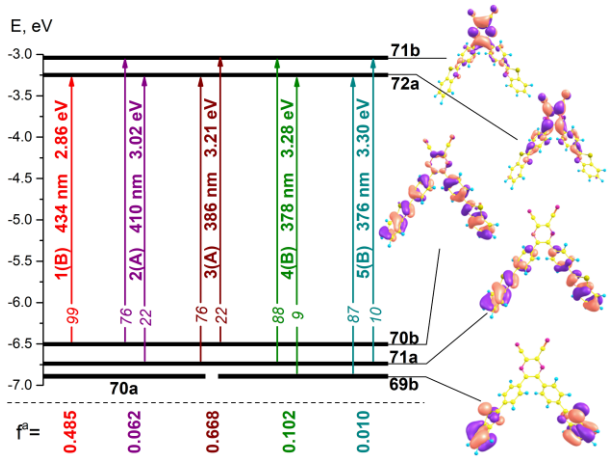


Fig. 2. MO level diagram, composition of canonical MOs and visual representation of the first five transitions (nm, eV) for **5** calculated at B3LYP/cc-pVTZ level. Composition of the lowest excited states is shown in italics. The symmetries of the excited states are indicated in brackets. f_a are oscillator strengths of corresponding transitions
Рис. 2. Диаграммы энергий некоторых МО, состав МО и визуальное представление первых пяти переходов (нм, эВ) для соединения **5** на основе результатов расчетов B3LYP/cc-pVTZ. Состав низших возбужденных состояний выделен курсивом. Симметрии возбужденных состояний указаны в скобках. fa - силы осциллятора соответствующих переходов

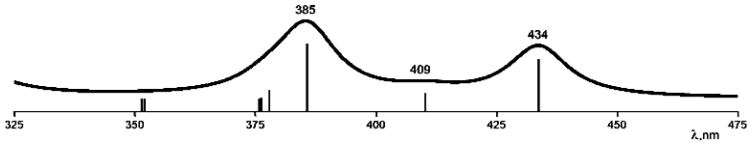


Fig. 3. Calculated electronic spectrum of compound **5**
Рис. 3. Рассчитанный электронный спектр поглощения соединения **5**

Comparison of the simulated spectra of **5**, pyrazine-2,3-dicarbonitrile, benzene and benzothiazole was also carried out (Fig. 5). The vibrational mode ω_{123} of **5** corresponds to the most intense vibrational mode (1412 cm^{-1}, A_1) of pyrazine-2,3-dicarbonitrile. However, ω_{123} is associated not only with motion of pyrazine-dicarbonitrile moiety (~60%, primarily CC stretching), but also with C_6^{Py}-C_1^{Ph} stretching (~30%). This may be the reason for the decrease in frequency by 11 cm^{-1} upon pyrazine-2,3-dicarbonitrile → **5** (Fig. 5). For pyrazine-2,3-dicarbonitrile, the second most intense band at 1140 cm^{-1} is determined by the deformation vibration with the inclusion of C^{Py}-C^{CN} (~18%) and C-N^{Py} (~29%) stretching. In case of corresponding band ω_{99} for **5**, the contributions of these motions (~24%) are inferior to the contributions of motions of phenylene moiety ($\delta(C\text{-}H)^{Ph}$ – ~34%, $\nu(C_5\text{-}C_6)^{Ph}$ – ~16%), which apparently explains low IR intensity of the band ω_{99}. The band at 977 cm^{-1} originates from the vibration ω_{84} in which motion of phenylene moieties (~33%, stretching and deformation) are coupled to motion of thiazole moieties (~58%, stretching and deformation). Analogical complex vibrations leads to appearance of bands at 802 and 883 cm^{-1} in the spectrum of benzothiazole. For ω_{134} mode, the vibration involves motion corresponding to B_2 mode of pyrazine-2,3-dicarbonitrile at 1579 cm^{-1} (~64%) and stretching of N_3^{Bt}-C_2^{Bt} bond (~12%) corresponding to the band at 1525 cm^{-1} in spectrum of benzothiazole (Fig. 5).

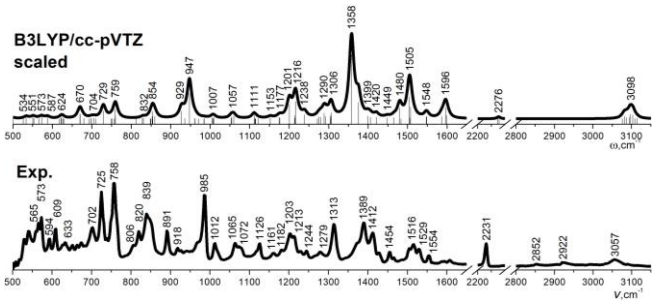


Fig. 4. Simulated and experimental IR spectra for compound **5**. In order to simulate the shape of IR spectrum from results of B3LYP/cc-pVTZ calculations, the individual bands were described by Lorentz curves with a half width of 15 cm^{-1}. A scale coefficient of 0.970 was used (see Figure S1)
Рис. 4. Теоретический и экспериментальный ИК-спектры соединения **5**. Моделирование теоретического ИК-спектра проводилось с использованием функции Лоренца (полуширина 15 $см^{-1}$) на основе результатов B3LYP/cc-pVTZ расчетов (масштабирующий коэффициент 0.970, см. рисунок S1)

Table 1

Descriptions [a] of several [b] vibrational modes for 5

Таблица 1. **Описание [a] некоторых [b] колебаний молекулы 5**

№	Sym	ω_i [c]	$I_{IR\,i}$ [d]	Assignment [a]
1	2	3	4	5
30	B	370.7	10.1	γ(Py); γ(CN)
46	B	550.2	10.0	γ(Py); γ(CN)
50	B	590.7	10.9	γ(molecule): γ(CN); γ(Ph);
54	B	643.0	11.0	$\gamma(C_2)^{Bt}$; γ(C-H);
57	B	690.5	26.5	def(Bt); $\nu(S_1\text{-}C_2)$Bt; def(N_1^{Py}-C_2^{Py}-C^{CN});
58	A	691.2	23.6	def(Bt); $\nu(S_1\text{-}C_2)$Bt;
65	B	751.9	44.3	$\gamma(C\text{-}H)^{Bt}$; γ(Bt);
66	A	752.0	12.8	$\gamma(C\text{-}H)^{Bt}$; γ(Bt);
70	B	783.3	53.1	$\gamma(C\text{-}H)^{Bt}$; γ(Bt);
71	A	783.4	17.2	$\gamma(C\text{-}H)^{Bt}$; γ(Bt);
77	B	879.6	13.5	γ(C-H): $\gamma(C_7\text{-}H_7)^{Bt}$*, $\gamma(C_2\text{-}H_2)^{Ph}$, $\gamma(C_6\text{-}H_6)^{Bt}$*, $\gamma(C_3\text{-}H_3)^{Ph}$;
79	B	880.9	41.6	γ(C-H): $\gamma(C_2\text{-}H_2)^{Ph}$, $\gamma(C_7\text{-}H_7)^{Bt}$*, $\gamma(C_3\text{-}H_3)^{Ph}$;
80	A	886.5	14.9	$\gamma(C\text{-}H)^{Ph}$; γ(Ph, C_6^{Py});
81	B	956.5	44.0	def(Py); ν(C-C): $\nu(C_2^{Py}\text{-}C^{CN})$, $\nu(C_1\text{-}C_6)^{Ph}$*; def(Ph);
84	B	977.1	141.9	def(thiazole)^{Bt}; ν(C-C): $\nu(C_3\text{-}C_4)^{Ph}$; $\nu(S_1\text{-}C_2)^{Bt}$; def(Ph);
85	A	977.4	26.9	def(thiazole)^{Bt}; ν(C-C): $\nu(C_3\text{-}C_4)^{Ph}$; $\nu(S_1\text{-}C_2)$; def(Ph);
97	B	1087.4	10.0	def(Bt); $\nu(S_1\text{-}C_{7a})^{Bt}$; $\nu(C\text{-}C)^{Bt}$;
98	A	1092.8	15.9	ν(C-C): $\nu(C_1\text{-}C_6)^{Ph}$, $\nu(C_5\text{-}C_6)^{Py}$;
99	B	1146.1	22.0	δ(C-H): $\delta(C\text{-}H)^{Ph}$; ν(C-C): $\nu(C_5\text{-}C_6)^{Ph}$*; def(Py)
108	A	1238.2	78.5	$\nu(N\text{-}C)^{Py}$: $\nu(N_1\text{-}C_6)^{Py}$, $\nu(N_1\text{-}C_2)^{Py}$; $\nu(C_2\text{-}C_3)^{Py}$*:
109	B	1252.4	18.0	ν(C-C): $\nu(C_4^{Ph}\text{-}C_2^{Bt})$, $\nu(C_5\text{-}C_6)^{Ph}$*; ν(N-C): $\nu(N_3\text{-}C_{3a})^{Bt}$;
111	B	1254.9	95.5	ν(C-C): $\nu(C_6^{Py}\text{-}C_1^{Ph})$, $\nu(C\text{-}C)^{Ph}$; ν(N-C): $\nu(N_1\text{-}C_6)^{Py}$; $\delta(C\text{-}H)^{Ph}$;
113	B	1278.1	22.5	δ(C-H): $\delta(C_7\text{-}H_7)^{Bt}$*; ν(C-C): $\nu(C_{7a}\text{-}C_7)^{Bt}$*, $\nu(C_4^{Ph}\text{-}C_2^{Bt})$; ν(N-C)^{Bt}: $\nu(N_3\text{-}C_{3a})$;
115	B	1315.1	11.4	ν(C-C): $\nu(C_4\text{-}C_5)^{Ph}$*, $\nu(C_1\text{-}C_6)^{Ph}$*, $\nu(C\text{-}C)^{Bt}$; $\nu(N_3\text{-}C_{3a})^{Bt}$;
117	B	1328.9	31.8	ν(C-C): $\nu(C_1\text{-}C_6)^{Ph}$*, $\nu(C_4\text{-}C_5)^{Ph}$*, $\nu(C_5\text{-}C_6)^{Ph}$*;
118	A	1332.5	13.6	ν(C-C): $\nu(C_1\text{-}C_6)^{Ph}$*, $\nu(C_4\text{-}C_5)^{Ph}$*, $\nu(C_6^{Py}\text{-}C_1^{Ph})$, $\nu(C_5\text{-}C_6)^{Ph}$*; ν(N-C);
120	B	1345.7	17.6	δ(C-H): $\delta(C\text{-}H)^{Ph}$; $\nu(C\text{-}C)^{Bt}$: $\nu(C_{7a}\text{-}C_7)$*;
121	A	1347.1	13.4	$\nu(C\text{-}C)^{Bt}$: $\nu(C_{7a}\text{-}C_7)$*, $\nu(C_{3a}\text{-}C_{7a})$*, $\nu(C_6\text{-}C_7)$*; δ(C-H): $\delta(C\text{-}H)^{Ph}$, $\delta(C_6\text{-}H_6)^{Bt}$*;
122	B	1347.8	34.9	$\nu(C\text{-}C)^{Bt}$: $\nu(C_{7a}\text{-}C_7)$*, $\nu(C_{3a}\text{-}C_{7a})$*, $\nu(C_6\text{-}C_7)$*; $\delta(C\text{-}H)$: $\delta(C\text{-}H)^{Ph}$;
123	A	1400.8	356.3	ν(C-C): $\nu(C_6^{Py}\text{-}C_1^{Ph})$, $\nu(C_6\text{-}C_5)^{Py}$, $\nu(C_2^{Py}\text{-}C^{CN})$; $\nu(N\text{-}C)^{Py}$;
124	B	1418.9	92.1	ν(C-C): $\nu(C_6^{Py}\text{-}C_1^{Ph})$, $\nu(C_5\text{-}C_6)^{Ph}$*, $\nu(C_2^{Py}\text{-}C^{CN})$; $\nu(N\text{-}C)^{Py}$: $\nu(N_1\text{-}C_6)$, $\nu(N_1\text{-}C_2)$; $\delta(C\text{-}H)^{Ph}$;
125	A	1443.4	16.5	$\nu(C_5\text{-}C_6)^{Ph}$*; $\delta(C\text{-}H)^{Ph}$;
128	B	1465.6	10.8	$\delta(C_7\text{-}H_7)^{Bt}$*; $\nu(C\text{-}C)^{Bt}$: $\nu(C_6\text{-}C_7)$*, $\nu(C_{3a}\text{-}C_{7a})$; $\nu(N\text{-}C)^{Bt}$
132	B	1526.5	60.6	ν(N-C): $\nu(N_3\text{-}C_2)^{Bt}$; ν(C-C); $\delta(C\text{-}H)^{Ph}$;
134	B	1551.4	121.8	ν(N-C): $\nu(N_1\text{-}C_6)^{Py}$, $\nu(N_1\text{-}C_2)^{Py}$, $\nu(N_3\text{-}C_2)^{Bt}$; ν(C-C);
136	B	1554.7	65.8	ν(C-C): $\nu(C\text{-}C)^{Ph}$; $\nu(C_4^{Ph}\text{-}C_2^{Bt})$; $\delta(C\text{-}H)^{Ph}$; $\nu(N\text{-}C)^{Py}$;
140	B	1597.0	15.3	$\nu(C\text{-}C)^{Ph}$: $\nu(C_4\text{-}C_5)$*; $\nu(C_1\text{-}C_6)$*; $\delta(C\text{-}H)^{Ph}$;
141	A	1636.4	12.9	$\nu(C\text{-}C)^{Bt}$: $\nu(C_6\text{-}C_7)$*, $\nu(C_7\text{-}C_{7a})$*; $\delta(C\text{-}H)^{Bt}$;
143	A	1646.0	61.8	$\nu(C\text{-}C)^{Ph}$: $\nu(C_5\text{-}C_6)$*, $\nu(C_4\text{-}C_5)$*, $\nu(C_1\text{-}C_6)$*; $\delta(C\text{-}H)^{Ph}$;

1	2	3	4	5
144	B	1649.7	19.6	$\nu(C\text{-}C)^{Ph}$: $\nu(C_5\text{-}C_6)$*,$\nu(C_4\text{-}C_5)$, $\nu(C_1\text{-}C_6)$*; $\delta(C\text{-}H)^{Ph}$;
149	B	3178.1	14.5	$\nu(C\text{-}H)^{Ph}$: $\nu(C_5\text{-}H_5)$;
155	B	3194.3	25.6	$\nu(C\text{-}H)^{Bt}$: $\nu(C_7\text{-}H_7)$, $\nu(C_6\text{-}H_6)$, $\nu(C_4\text{-}H_4)$;
158	A	3200.8	21.7	$\nu(C\text{-}H)^{Bt}$: $\nu(C_4\text{-}H_4)$, $\nu(C_5\text{-}H_5)$, $\nu(C_6\text{-}H_6)$;

Notes: [a] Based on PED. Coordinates are listed if their contributions are greater than ~10%. Coordinates are presented in descending order of their contributions. The designation "Coord-1: Coord-2, Coord-3;" means that the displacement along coordinates Coord-2 and Coord-3 are a parts of the general displacement Coord-1. Given that the molecule have C_2 symmetry, contributions of symmetrically equivalent coordinates (e.g., $N_1^{Py}\text{-}C_2^{Py}$ and $N_4^{Py}\text{-}C_3^{Py}$ and etc.). The symbol * was indicated when contributions of asymmetric coordinates were combined: $(C_7\text{-}H_7)^{Bt}$ and $(C_4\text{-}H_4)^{Bt}$; $(C_6\text{-}H_6)^{Bt}$ and $(C_5\text{-}H_5)^{Bt}$; $(C_{7a}\text{-}C_7)^{Bt}$ and $(C_{3a}\text{-}C_4)^{Bt}$; $(C_{3a}\text{-}C_{7a})^{Bt}$ and $(C_5\text{-}C_6)^{Bt}$; $(C_6\text{-}C_7)^{Bt}$ and $(C_4\text{-}C_5)^{Bt}$; $(C_1\text{-}C_6)^{Ph}$ and $(C_1\text{-}C_2)^{Ph}$; $(C_4\text{-}C_5)^{Ph}$ and $(C_3\text{-}C_4)^{Ph}$; $(C_5\text{-}C_6)^{Ph}$ and $(C_2\text{-}C_3)^{Ph}$; $(C_2\text{-}C_3)^{Py}$ and $(C_5\text{-}C_6)^{Py}$. The following designations are used:
ν(X-Y) – stretching of the X–Y bond; δ – in-plane bending of the fragment indicated in parentheses, including def – deformation of the fragment indicated in parentheses in the molecule plane; γ – out-of-plane bending of the fragment or atom indicated in parentheses; Py – pyrazine moiety; Ph – phenylene moiety; Bt – benzothiazole moiety; CN – cyano substituent; molecule – the whole molecule.
[b] There are normal modes of more than ~10 km·mol^{-1} IR-intensity;
[c] ω_i – calculated frequencies (cm^{-1});
[d] $I_{IR\,i}$ – IR-intensities (km·mol^{-1}).
Примечания: [a] На основе распределения потенциальной энергии. Координаты указаны, если их вклад превышает ~ 10%. Координаты представлены в порядке убывания их вкладов. Обозначение «*Координата-1: Координата-2, Координата-3;*» означает, что смещения по координатам *2* и *3* являются частями общего смещения по *координате-1*. Учитывая, что молекула имеет симметрию C_2, многие пары атомов являются симметрично эквивалентными (например, $N_1^{Py}\text{-}C_2^{Py}$ и $N_4^{Py}\text{-}C_3^{Py}$ и т. д.). Символ * указывался при объединении вкладов несимметричных координат: $(C_7\text{-}H_7)^{Bt}$ и $(C_4\text{-}H_4)^{Bt}$; $(C_6\text{-}H_6)^{Bt}$ и $(C_5\text{-}H_5)^{Bt}$; $(C_{7a}\text{-}C_7)^{Bt}$ и $(C_{3a}\text{-}C_4)^{Bt}$; $(C_{3a}\text{-}C_{7a})^{Bt}$ и $(C_5\text{-}C_6)^{Bt}$; $(C_6\text{-}C_7)^{Bt}$ и $(C_4\text{-}C_5)^{Bt}$; $(C_1\text{-}C_6)^{Ph}$ и $(C_1\text{-}C_2)^{Ph}$; $(C_4\text{-}C_5)^{Ph}$ и $(C_3\text{-}C_4)^{Ph}$; $(C_5\text{-}C_6)^{Ph}$ и $(C_2\text{-}C_3)^{Ph}$; $(C_2\text{-}C_3)^{Py}$ и $(C_5\text{-}C_6)^{Py}$. Используются следующие обозначения: ν (X-Y) - растяжение связи X-Y; δ - изгиб с сохранением плоскостности фрагмента, указанного в скобках, в том числе def - деформация указанного в скобках фрагмента с сохранением плоскостности фрагмента; γ - выход атома или связи, указанных в скобках, из плоскости; P_y - пиразиновый фрагмент; Ph – фениленовый фрагмент;
Bt – бензотиазольный фрагмент; CN – циано-группа; molecule – вся молекула.
[b] представлены колебания с ИК-интенсивностью более ~10 км·моль$^{-1}$;
[c] ω_i – расчитанные значения частот (см$^{-1}$);
[d] $I_{IR\,i}$ – расчитанные значения ИК-интенсивностей (км·моль$^{-1}$).

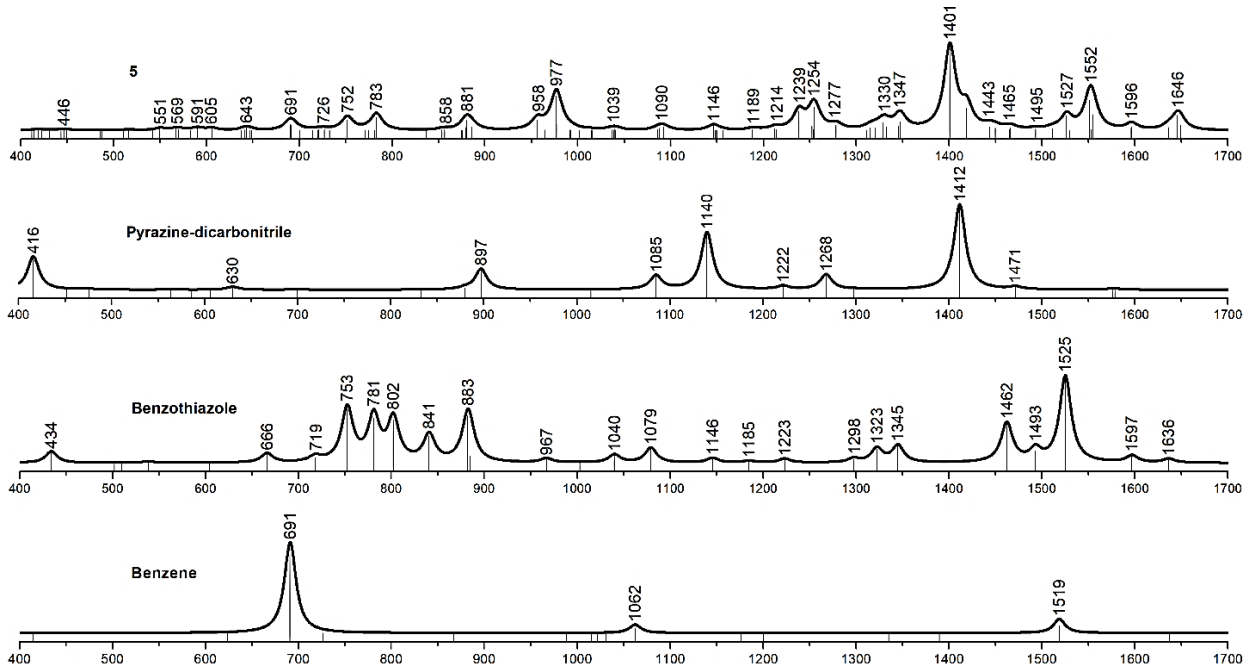


Fig. 5. Simulated IR spectra for compound **5**, pyrazine-2,3-dicarbonitrile, benzothiazole and benzene in the 400–1700 cm^{-1} range. In order to simulate the shape of IR spectrum from results of B3LYP/cc-pVTZ calculations, the individual bands were described by Lorentz curves with a half width of 15 cm^{-1}

Рис. 5. Теоретические ИК-спектры соединений 5, пиразин-2,3-дикарбонитрила, бензотиазола и бензола в диапазоне 400-1700 см$^{-1}$. Моделирование теоретических ИК-спектров проводилось с использованием функции Лоренца (полуширина 15 см$^{-1}$) на основе результатов B3LYP/cc-pVTZ расчетов

CONCLUSION

In conclusion, we have demonstrated new approach to the synthesis of heterocycle-substituted pyrazinedicarbonitriles using Pd-Cu catalyzed C-H functionalization. The presented technique gives easier and safer pathway to dicarbonitriles and allows us to circumvent multistep protocol by Rosenmund-von Braun reaction. Moreover, it also provides the desired product in good yields without using hazardous reagents such as CuCN. Quantum chemical calculation shows that positions of bands of product desired in the simulated IR spectrum are in good agreement with appropriate values from the experimental spectrum in a solid phase.

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SUPPLEMENTARY MATERIALS

The following are available online (http://ctj-isuct.ru/): Table S1. Internuclear distances for **5**, pyrazine-2,3-dicarbonitrile, benzene and benzothiazole optimized at B3LYP/cc-pVTZ level. Table S2. Natural charges at atoms calculated in the framework of natural population analysis for **5**, pyrazine-2,3-dicarbonitrile, benzene and benzothiazole. Table S3. Wiberg bond indexes calculated for 5, pyrazine-2,3-dicarbonitrile, benzene and benzothiazole. Table S4. NICS(0) and NICS(1) values for **5**, pyrazine-2,3-dicarbonitrile, benzene and benzothiazole. Table S5. Cartesian coordinates of **5** according B3LYP/cc-pVTZ calculations. Fig. S1. Correlation dependences $\nu = f(\omega)$: ν and ω – the positions of the band maxima in the experimental and model spectra for **5**, respectively.

CONFLICTS OF INTEREST

Авторы заявляют об отсутствии конфликта интересов, требующего раскрытия в данной статье.

The authors declare the absence a conflict of interest warranting disclosure in this article.

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