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2,4-Diazidopyrrolo[2,3-*d*]pyrimidines: synthesis, ring–chain tautomerism and Cu(I)-catalyzed azide–alkyne cycloaddition reaction

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2,4-Diazidopyrrolo[2,3-*d*]pyrimidines were synthesized by the reaction of the corresponding 2,4-dichloropyrrolo[2,3-*d*]pyrimidines with sodium azide at room temperature. 2,4-Diazidopyrrolo[2,3-*d*]pyrimidines were shown to exist in an equilibrium with the corresponding 5-azidopyrrolo[3,2-*e*]tetrazolo[1,5-*c*]pyrimidine. The proportion of the tetrazole tautomer increases with increasing solvent polarity. The CuAAC reaction of the obtained azides with 3-methylphenyl- and 4-biphenylylethynes afforded the corresponding 2,4-bis(4-aryl-1,2,3-triazol-1-yl)pyrrolo[2,3-*d*]pyrimidines.

Key words: azides, nitrogen heterocycles, tautomerism, 1,2,3-triazoles, cycloaddition reaction

INTRODUCTION

The Huisgen 1,3-dipolar cycloaddition reaction of organic azides and alkynes [1–3] has gained considerable attention in the recent decade after introduction of Cu(I) catalysis in 2001 independently by Meldal [4] and Sharpless [5]. The Cu(I) catalyzed azide–alkyne cycloaddition (CuAAC) reaction showed major improvements in both rate and regioselectivity compared to the 1,3-dipolar Huisgen cycloaddition reaction and provides 1,4-disubstituted 1,2,3-triazoles with such efficiency and scope that transformation is usually referred as "click" chemistry and is one of the most atom-economical transformations [6, 7]. Various 1,4-disubstituted-1,2,3-triazoles have found application in bioconjugation [8–15], material science [16], chemical sensors [17–20] and drug discovery fields [21, 22]. Despite the fact that in most cases products of CuAAC reactions are obtained in very good yields and with low work-up, some cases require search for optimal conditions to obtain satisfactory results [23, 24]. Pyrrolo[2,3-*d*]pyrimidine and its aryl and heteroaryl derivatives were found to display a wide range of biological activities such as antitumor [25], inhibition of protein kinases [26] and dihydrofolate reductase [27], antagonist effects to receptors [28]. In addition to these applications, oligoarylenes with pyrrolo[2,3-*d*]pyrimidine core were shown to exhibit strong UV-blue fluorescence and are promising candidates as fluorescent functional materials [29]. Moreover, pyrrolo[2,3-*d*]pyrimidine-core based derivatives form fluorescent nanoaggregates and show aggregation induced emission enhancement [30]. Continuing our work dedicated to the development of efficient methods for functionalization of pyrimidine [31] and pyrrolo[2,3-*d*]pyrimidine skeletons [32], we became interested in the synthesis of pyrrolopyrimidine derivatives with a 1,2,3-triazole linker between the aromatic side chains and heterocyclic scaffold. However, in the current literature triazolylpyrrolo[2,3-*d*]pyrimidines have received very little attention. To our knowledge, there are only few reports of azide–alkyne ligation reactions wherein 1,2,3-triazole moieties were constructed at position C5 [33] or N7 [22] of the pyrrolopyrimidine ring. None of these reactions were carried out using azidopyrrolo[2,3-*d*]pyrimidines as a reactive partner. The present paper describes the synthesis of 2,4-diazidopyrrolo[2,3-*d*]pyrimidines, their behavior in a solution and ability to couple with alkynes in Cu(I)-catalyzed ligation reactions.

EXPERIMENTAL

Melting points were determined in open capillaries with a digital melting point IA9100 series apparatus (ThermoFischer Scientific). All reactions and purity of the synthesized compounds were monitored by TLC using Silica gel 60 F_{254} aluminium plates (Merck). Visualization was accomplished by UV light. Column chromatography was performed using Silica gel 60 (0.040–0.063 mm) (Merck). Infrared spectra were recorded on an FTIR spectrophotometer Spectrum BX II (Perkin Elmer). NMR spectra were recorded on a Bruker

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Ascend 400 (400 MHz and 100 MHz, respectively). ^{1}H NMR and ^{13}C NMR were referenced to residual solvent peaks. High Resolution Mass Spectrometry (HRMS) analyses were carried out on a quadrupole, time-of-flight mass spectrometer (microTOF-Q II, Bruker Daltonik GmbH, Bremen, Germany) or on a Dual-ESI Q-TOF 6520 (Agilent Technologies) mass spectrometer. All quantum chemical calculations were performed using the Gaussian 09 program package.

2,4-Diazido-7*H*-pyrrolo[2,3-*d*]pyrimidine (2a). A mixture of 2,4-dichloro-7*H*-pyrrolo[2,3-*d*]pyrimidine (**1a**) [42] (500 mg, 2.66 mmol) and NaN_3 (0.44 mg, 6.69 mmol) in DMF (15 mL) was stirred at room temperature for 24 hrs. Then the reaction mixture was poured into ice water (60 mL). The resulting solid was filtered off, washed with MeOH, dried at r. t. and stored in a vessel protected from sunlight. Yield 310 mg (58%), lightly brown solid; m. p. = 120 °C dec. IR (KBr), ν, cm^{-1}: 2175 (N_3), 2131 (N_3). ^{1}H NMR (400 MHz, DMSO-D_6), δ, ppm: 6.42 (d, 1H, *J* = 3.6 Hz, C5-H), 7.42 (d, 1H, *J* = 3.6 Hz, C6-H), 12.28 (s, 1H, N7-H); ^{13}C NMR (100 MHz, DMSO-D_6), δ, ppm: 99.1, 105.7, 126.9, 154.51, 154.55, 154.6; HRMS (ESI): calculated for $C_6H_3N_9Na$ $[M+Na]^+$ = 224.0404; found 224.0400.

2,4-Diazido-7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (2b). Compound **2b** was synthesized from 2,4-dichloro-7-methylpyrrolo[2,3-d]pyrimidine (**1b**) [43] according to the procedure described for **2a**. The reaction time 24 hrs. Yield 78%, white solid, m. p. = 118–119 °C dec. IR (KBr), ν, cm^{-1}: 2152 (N_3), 2115 (N_3); ^{1}H NMR (400 MHz, $CDCl_3$), δ, ppm: 3.80 (s, 3H, CH_3), 6.44 (d, 1H, *J* = 3.6 Hz, C5-H), 7.00 (d, 1H, *J* = 3.6 Hz, C6-H); ^{13}C NMR (100 MHz, $CDCl_3$), δ, ppm: 31.6, 99.0, 105.7, 128.5, 153.6, 155.13, 155.14; HRMS (ESI): calculated for $C_7H_5N_9Na$ $[M+Na]^+$ = 238.0560, found 238.0560.

***tert*-Butyl 2,4-diazido-7*H*-pyrrolo[2,3-*d*]pyrimidine-7-carboxylate (2c).** Compound **2c** was synthesized from 2,4-dichloro-7-(*tert*-butoxycarbonyl)pyrrolo[2,3-*d*]pyrimidine (**1c**) [29a] according to the procedure described for **2a**. The reaction time 2 hrs. Yield 73%, white solid, m. p. = 132 °C dec. IR (KBr), ν, cm^{-1}: 2151 (N_3), 2105 (N_3), 1736 (CO). ^{1}H NMR (400 MHz, $CDCl_3$), δ, ppm: 1.71 (s, 9H, $3CH_3$), 6.49 (d, 1H, *J* = 4.0 Hz, C5-H), 7.54 (d, 1H, *J* = 4.0 Hz, C6-H); ^{13}C NMR (100 MHz, $CDCl_3$), δ, ppm: 28.2, 85.8, 102.2, 107.9, 125.8, 147.9, 154.1, 156.2, 157.5; HRMS (ESI): calculated for $C_{11}H_{11}N_9O_2Na$ $[M+Na]^+$ = 324.0928; found 324.0926.

2,4-Bis[4-(*m*-tolyl)-1,2,3-triazol-1-yl]-7*H*-pyrrolo[2,3-*d*]pyrimidine (3a). A mixture of compound **2a** (100 mg, 0.5 mmol), 3-ethynyltoluene (194 μL, 1,5 mmol), CuI (19 mg, 0.1 mmol) and Et_3N (77 μL, 0.55 mmol) in CH_2Cl_2 (30 mL) was stirred at room temperature for 96 hours. Then precipitate was filtered, washed with CH_2Cl_2 (30 mL) and 5% NH_3 (35 mL) solution and dried to give 106 mg (49%) of compound **3a** as a yellow solid: m. p. = 275–277 °C dec. ^{1}H NMR (400 MHz, $CDCl_3$ + CF_3COOD), δ, ppm: 2.31 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 7.10–7.39 (m, 6H, C5-H, C6-H, ArH), 7.48–7.65 (m, 4H, ArH), 9.14 (s, 1H, N7-H), 9.31–9.83 (overlapped with CF_3COOH, 2H, triazole-H). HRMS (ESI): calculated for $C_{24}H_{19}N_9Na$ $[M+Na]^+$ = 456.1656; found 456.1649.

7-Methyl-2,4-bis[4-(m-tolyl)-1,2,3-triazol-1-yl]-7H-pyrrolo[2,3-d]pyrimidine (3b). A mixture of compound **2b** (100 mg, 0.46 mmol), 3-ethynyltoluene (180 μL, 1,4 mmol), CuI (17 mg, 0.09 mmol), DIPEA (89 μL) and acetic acid (29 μL, 0.51 mmol) in CH_2Cl_2 (5 mL) was stirred at room temperature for 3 days. Then the reaction mixture was poured into water (20 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The extracts were combined, dried over Na_2SO_4 and filtered. After removal of the solvent the residue was purified by column chromatography on a silica gel using hexane: EtOAc (1:1) as an eluent and recrystallized to give 94 mg (46%) of compound **3b** as a white solid: m. p. = 220 °C dec. (from 2-PrOH). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.49 (s, 6H, $2CH_3$), 4.07 (s, 3H, NCH_3), 7.22–7.30 (m, 2H, ArH), 7.40–7.48 (m, 3H, ArH, C5-H), 7.49 (d, 1H, *J* = 3.6 Hz, C6-H), 7.84 (t, 2H, *J* = 8.8 Hz, ArH), 7.90 (s, 2H, ArH), 8.91 (s, 1H, triazole-H), 9.14 (s, 1H, triazole-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.4, 31.9, 103.2, 106.9, 117.5, 118.3, 123.11, 123.16, 126.6, 126.7, 128.7, 128.9, 129.34, 129.36, 129.6, 129.8, 132.3, 138.6, 138.7, 147.1, 147.6, 147.7, 147.9, 154.1. HRMS (ESI): calculated for $C_{25}H_{21}N_9Na$ $[M+Na]^+$ = 470.1812; found: 470.1824.

***tert*-Butyl 2,4-Bis[4-(*m*-tolyl)-1,2,3-triazol-1-yl)-7*H*-pyrrolo[2,3-*d*]pyrimidine-7-carboxylate (3c).** A mixture of compound **2c** (75 mg, 0.25 mmol), 3-ethynyltoluene (97 μL, 0.75 mmol), copper turnings (640 mg, 10 mmol), $CuSO_4$-$5H_2O$ (125 mg, 0.5 mmol) in THF/*t*-BuOH/H_2O (1:1:1) (24 mL) was stirred at room temperature for 72 hours. Then reaction mixture was poured into a mixture of water (40 mL) and CH_2Cl_2 (20 ml), stirred for 30 min., filtered and extracted with CH_2Cl_2 (3 × 15 mL). The extracts were combined, dried over Na_2SO_4 and filtered. After removal of the solvent the residue was purified by column chromatography on a silica gel using hexane : EtOAc (3:1) as an eluent and recrystallized to give 76 mg (57%) of compound **3c** as a white solid. m. p. = 173–174 °C dec. (from 2-PrOH); ^{1}H NMR (400 MHz, $CDCl_3$), δ, ppm: 1.83 (s, 9H, $3CH_3$), 2.48 (s, 6H, $2CH_3$), 7.26 (t, 2H, *J* = 7.2 Hz, ArH), 7.32–7.45 (m, 2H, ArH), 7.59 (d, 1H, *J* = 3.6 Hz, C5-H), 7.75–7.88 (m, 2H, ArH), 7.89 (s, 2H, ArH), 7.93 (d, 1H, *J* = 3.6 Hz, C6-H), 8,91 (s, 1H, triazole-H), 9.17 (s, 1H, triazole-H); ^{13}C NMR (100 MHz, $CDCl_3$), δ, ppm: 21.7, 28.3, 86.6, 106.2, 109.9, 118.0, 118.6, 123.3, 123.4, 126.9, 127.0, 129.1, 129.2, 129.4, 129.6, 129.7, 130.04, 130.05, 138.9, 139.1, 147.3, 148.33, 148.34, 148.38, 149.5, 155.1; HRMS (ESI): calculated for $C_{29}H_{27}N_9O_2Na$ $[M+Na]^+$ 556.2180; found 556.2176.

***tert*-Butyl 2,4-Bis(4-biphenyl-1,2,3-triazol-1-yl)-7*H*-pyrrolo[2,3-*d*]pyrimidine-7-carboxylate (3d).** A mixture of compound **2c** (50 mg, 0.166 mmol), 4-ethynylbiphenyl

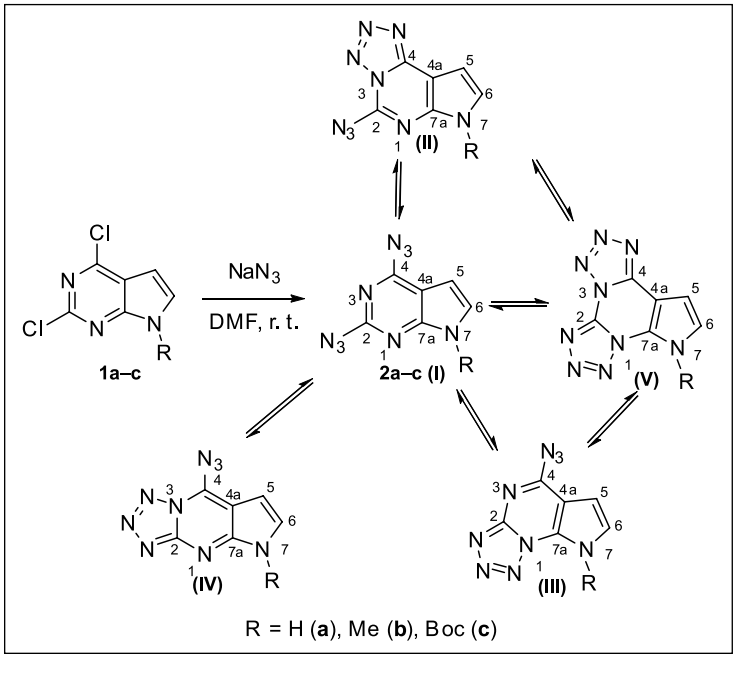
(90 mg, 0.5 mmol), CuI (7 mg, 0.037 mmol) and Et_3N (26 μL, 0.185 mmol) in CH_2Cl_2 (20 mL) was stirred at room temperature for 6 days. Then the reaction mixture was poured into water (20 mL) and extracted with CH_2Cl_2 (2 × 10 mL). The extracts were combined, dried over Na_2SO_4 and filtered. After removal of the solvent the residue was purified by column chromatography on a silica gel using hexane-EtOAc (1:1) as an eluent and recrystallized to give 48 mg (44%) of compound **3d** as a white solid. m. p. = 195–196 °C (from 2-PrOH). ^{1}H NMR (400 MHz, $CDCl_3$), δ, ppm: 1.71 (s, 9H, CH_3), 7.41–7.76 (m, 11H, ArH, C5-H,), 7.95 (m, 8H, ArH), 8.15 (d, 1H, *J* = 3.6 Hz, C6-H), 8.99 (s, 1H, triazole-H), 9.26 (s, 1H, triazole-H); ^{13}C NMR (100 MHz, $CDCl_3$), d, ppm: 28.4, 85.9, 105.8, 110.1, 117.5, 118.3, 122.2, 122.5, 122.9, 123.4, 123.6, 127.12, 127.14, 129.15, 129.17, 129.2, 129.3, 129.65, 129.67, 130.0, 130.1, 137.8, 139.5, 148.33, 148.36, 148.39, 149.5, 149.7, 155.6. HRMS (ESI): calculated for $C_{39}H_{31}N_9NaO_2$ [M+Na]= 680.2493; found 680.2490.

RESULTS AND DISCUSSION

The starting material – 2,4-diazido-7-methylpyrrolo[2,3-*d*]pyrimidines **2a-c** were obtained in 58–78% yield by nucleophilic substitution of the corresponding 2,4-dichloropyrrolo[2,3-*d*] pyrimidines (**1**) with NaN_3 in DMF at ambient temperature (Scheme 1). It should be mentioned that diazides are rather unstable in daylight and at elevated temperatures, but can be stored for a long period of time in the dark below 5 °C. It is known that azides, in which the azido group is adjacent to a nitrogen atom, can undergo spontaneous cyclization to form a tetrazole ring. The azide-tetrazole equilibrium is often observed in π-deficient heterocycles such as azidopyrimidines [34–36] and azidopurines [14, 24]. However, earlier reports on the synthesis of 4-azidopyrrolo[2,3-*d*]pyrimidines indicate that these compounds exist as a tetrazole tautomer [37–40].

Since the subsequent stage of our work entailed the development of azide-alkyne ligation chemistry and in the context of reports that the presence of a tetrazole form can reduce the reactivity of compounds [12, 24], we decided to examine in which tautomeric form compounds **2** exist. Theoretically, 2,4-diazidopyrrolo[2,3-*d*]pyrimidines **2** can exist in five tautomeric forms **I–V** (Scheme 1).

Herein, the analysis of tautomerism is presented on the example of compound **2b**. The presence of two absorption bands of both azido groups at 2 152 cm^{-1} and 2 115 cm^{-1} (KBr), and 2 147 cm^{-1} and 2 132 cm^{-1} (chloroform solution) in the IR spectrum of compound **2b** indicates on diazide tautomer in a solid state and in the chloroform solution. In the ^{1}H NMR spectra recorded in $CDCl_3$, $(CD_3)CO$ and DMSO-D_6 two sets of signals for protons of compound **2b** with varying ratio were observed. This indicates that two tautomeric forms – diazide and another possible tetrazole tautomer exist in solutions. As determined from ^{1}H NMR spectra, a ratio of diazide form (major) and possible tetrazole tautomer (minor) was found to be 99:1 in chloroform, 20:1 in $(CD_3)CO$, and 6.25:1 in DMSO-D_6. In order to determine which tetrazole tautomeric form is observed in solutions experimental values of ^{1}H NMR and ^{13}C NMR were compared with the calculated ones. To identify all ^{1}H and ^{13}C peaks in the NMR spectra of **2b**, HSQC and HMBC NMR experiments were carried out in DMSO-D_6 solution. Density functional theory (DFT) calculations were carried out by using the Gaussian 09[41] program package. Geometry optimizations of tautomers **I–V** were performed using the exchange–correlation hybrid functional B3LYP with the 6–311G** basis set. The *in vacuo* structures were further optimized by applying the self-consistent reaction field (SCRF) under the polarizable continuum model (IEFPCM) incorporating DMSO as a solvent and absolute



Scheme 1. Synthesis of 2,4-diazidopyrrolo[2,3-*d*]pyrimidines (**2a–c**) and structures of possible tautomeric forms

Table. **Experimental and calculated chemical shifts of ^{1}H and ^{13}C NMR spectra for azide and tetrazole tautomers I–V**

Entry	Compound	^{1}H NMR spectra[a], δ, ppm			^{13}C NMR spectra[a], δ, ppm						
		5H	6H	CH_3	CH_3	C_{7a}	C_2	C_4	C_{4a}	C_5	C_6
1	Major (I)b	6.45	7.41	3.75	31.6	153.2	154.3	154.0	105.5	98.3	130.8
2	Minor (II)b	7.01	7.59	3.91	32.5	141.7	137.5	148.0	100.9	99.7	128.9
3	Ic	6.54	7.22	3.72	29.5	156.5	158.3	158.3	109.6	102.5	133.8
4	IIc	7.24	7.49	3.93	30.8	146.1	139.1	152.8	104.8	105.5	133.2
5	IIIc	6.77	7.12	4.17	37.2	136.9	158.0	158.9	109.5	105.0	132.6
6	IVc	6.77	7.54	3.84	29.8	156.4	158.1	134.9	108.3	101.8	140.2
7	Vc	7.33	7.33	4.28	37.9	131.5	147.9	151.7	104.3	107.2	133.4

[a] Atom numbers correspond to the numbering pattern in Scheme 1.

[b] Experimental chemical shifts in DMSO-D_6.

[c] Calculated chemical shifts in DMSO-D_6 by GIAO method.

shielding values were calculated by the GIAO method. TMS was used as a reference in calculating ^{1}H and ^{13}C chemical shifts from absolute shielding values. 5-H and 6-H peaks of the major tautomer are located at 6.45 ppm and 7.41 ppm in DMSO-D_6, respectively (Table). These peaks of the minor tautomeric form are shifted downfield and observed at 7.01 ppm and 7.59 ppm, respectively. Greater downfield shift of the 5-H peak indicates that chain-ring isomerization takes place at position 4 of pyrrolopyrimidine, as the electron-withdrawing tetrazole ring causes the deshielding effect. In addition, experimentally obtained ^{1}H and ^{13}C chemical shifts of the major tautomer (Table, entry 1) showed very good agreement with the calculated chemical shifts for tautomer **I** (Table, entry 3). Comparison of ^{13}C shifts of major and minor forms revealed that peaks of C_{7a} and C_2 of the minor tautomer are up-field shifted (Table, entry 2). Such shift in theoretical values is seen only for tautomeric forms **II** and **V** (Table, entries 4, 7). Nevertheless, experimental chemical shifts of all proton and carbon atoms of the minor tautomer better match with the calculated chemical shifts of tautomer **II** – 5-azidopyrrolo[3,2-*e*]tetrazolo[1,5-*c*]pyrimidine (Table, entry 4).

Moreover, comparison of potential energies of tautomeric forms **I–V** indicates that the smallest difference is between tautomeric forms **I** and **II** (ΔE = 2.9 kcal/mol) what is also consistent with the NMR identification results (Figure).

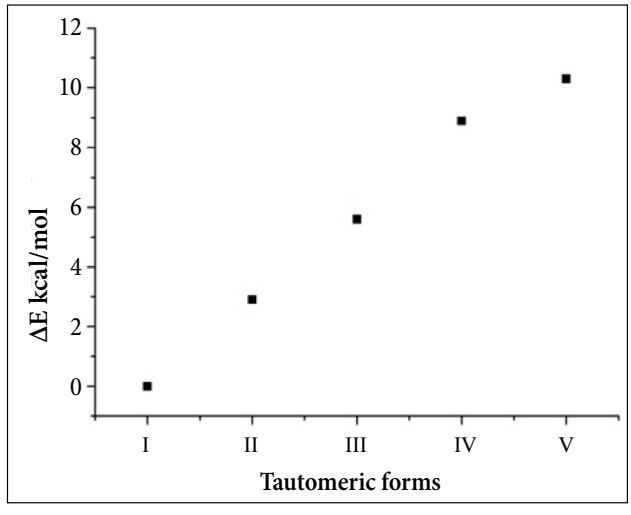
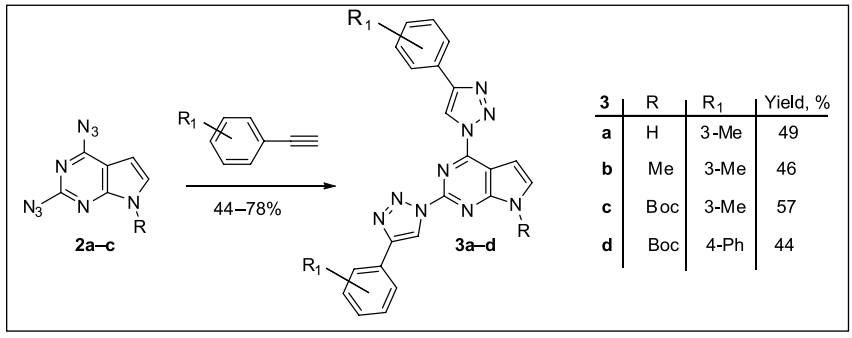


Figure. Potential energy differences of tautomeric forms **I–V** of compound **2b**

Further, the Cu(I)-catalyzed azide-alkyne ligation of azides **2** with 3-ethynyltoluene and 4-ethynylbiphenyl was undertaken. Success of the CuAAC reaction generally depends on selection of a Cu(I) source and a solvent. Therefore, three different Cu(I) sources (CuI; Cu/$CuSO_4$; $CuSO_4$/NaAsc) and various solvents (THF, DMF, DCM, *t*-BuOH, mixture THF/*t*-BuOH/H_2O 1:1:1) have been tested.



3	R	R_1	Yield, %
a	H	3-Me	49
b	Me	3-Me	46
c	Boc	3-Me	57
d	Boc	4-Ph	44

Scheme 2. Synthesis of 2,4-bis(4-aryl-1,2,3-triazol-1-yl)pyrrolo[2,3-*d*]pyrimidines (**3a–d**)

Screening of the conditions for the CuAAC reaction revealed that the reaction is very sensitive not only to the substrate structure and catalyst system but also to the reaction solvent. Diazides **2a–c** do not react with 3-ethynyltoluene in the presence of CuI/Et_3N in DMF or DMSO. However, performing the reaction in dichloromethane using the same catalyst system led to the formation of the corresponding 2,4-bis(triazolyl)pyrrolo[2,3-*d*]pyrimidines **3a–d** in 49, 30, 50 and 44% yields, respectively. Addition of acetic acid to the reaction mixture and switch of triethylamine to di(isopropyl) ethylamine (DIPEA) increased the yield of compound **3b** from 30 to 46%, whereas these changes did not have any reasonable effect on the outcome of the reaction of **2a** with 3-ethynyltoluene. Employing in the reaction the well-established catalyst system – $CuSO_4$/Na ascorbate did not give better results. For example, in the presence of this catalyst system compound **2c** reacted with 4-ethynylbiphenyl in THF/H_2O or *t*-BuOH/THF/H_2O to give **3d** in low 18 and 23% yield. Further optimization of the reaction conditions showed that the best yield of compound **3c** (57%) was achieved when compound **2c** reacted with 3-ethynyltoluene in *t*-BuOH/H_2O/THF (1:1:1) as a solvent system in the presence Cu/$CuSO_4$.

CONCLUSIONS

In summary, 2,4-diazidopyrrolo[2,3-*d*]pyrimidines were synthesized and their ring–chain tautomerism was investigated. The synthesized diazides were shown to exist as diazide (major) and 5-azidopyrrolo[3,2-*e*]tetrazolo[1,5-*c*]pyrimidine (minor) tautomers. Experimental data were supported by DFT/GIAO calculations. In the solution, proportion of the tetrazole tautomer increases with the increase of solvent polarity. Cu(I)-catalyzed azide–alkyne cycloaddition reaction of the synthesized 2,4-diazidopyrrolo[2,3-*d*]pyrimidines with 3-ethynyltoluene and 4-ethynylbiphenyl was investigated. Novel 2,4-bis(4-aryl-1,2,3-triazol-1-yl)pyrrolo[2,3-*d*] pyrimidines were synthesized and characterized. The obtained results can be useful for the development of libraries of novel "push-pull" chromophores, in which electron-donating aryl groups and electron-withdrawing pyrrolo[2,3-*d*] pyrimidine heterocycle are linked with 1,2,3-triazole moiety.

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2,4-DIAZIDOPIROLO[2,3-*D*]PIRIMIDINAI: SINTEZĖ, CIKLO-ATVIROS GRANDINĖS TAUTOMERIJA IR CU(I) KATALIZUOJAMA AZIDO-ALKINO CIKLO JUNGIMO REAKCIJA

S a n t r a u k a

Nukleofilinio pakeitimo reakcija tarp 2,4-dichloro[2,3-*d*]pirimidinų ir natrio azido kambario temperatūroje susintetinti atitinkami 2,4-diazidopirrolo[2,3-*d*]pirimidinai. Nustatyta, kad susintetinti diazidai egzistuoja dinaminėje pusiausvyroje su atitinkamu 5-azidopirolo[3,2-*e*]tetrazolo[1,5-*c*]pirimidinu. Tirpaluose dominuoja azidinė forma, tačiau tetrazolinės formos kiekis didėja, kai auga tirpiklio poliškumas. Ištirta susintetintų diazidopirolopirimidinų Cu(I) katalizuojama ciklo jungimo reakcija su 3-etiniltoluenu ir 4-etinilbifenilu. Susintetinti ir charakterizuoti nauji 2,4-bis(4-aryl-1,2,3-triazol-1-yl)pirolo[2,3-*d*]pirimidinai. Gauti rezultatai gali būti panaudoti naujų multifragmenčių chromoforų sintezėje, kuriuose elektronodonorinės arilgrupės yra sujungtos 1,2-3-triazolo tilteliu su elektronoakceptoriniu pirolo[2,3-*d*]pirimidino heterociklu.