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EDITOR'S CHOICE

REACTION OF 3-ALKYNYLQUINOXALINE-2-CARBONITRILES WITH SODIUM AZIDE: AN EXPERIMENTAL AND THEORETICAL STUDY

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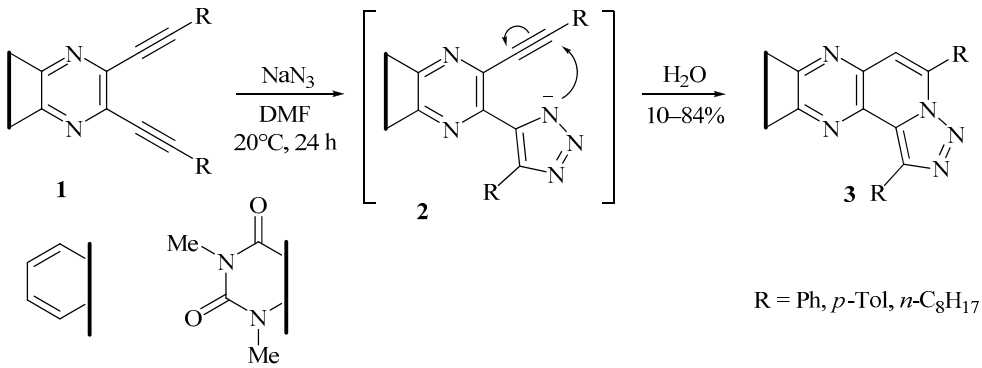
The reaction of 3-alkynylquinoxaline-2-carbonitriles with sodium azide in DMF at 60°C leads to the formation of 4,5-disubstituted 2H-1,2,3-triazoles in 38-82% yields. The analogous reaction in toluene in the presence of $AlCl_3$ takes place as a tandem process involving 1,3-dipolar cycloaddition of the azide ion to the nitrile group followed by 6-endo-digonal cyclization with the formation of 5-aryltetrazolo[1',5':1,3]pyrido[3,4-b]quinoxalines.

Keywords: 3-alkynylquinoxaline-3-carbonitriles, 5-aryltetrazolo[1',5':1,2]pyrido[3,4-*b*]quinoxalines, 2*H*-1,2,3-triazoles, 1,3-dipolar cycloaddition, tandem process.

The quinoxaline ring serves as the structural base of a multitude of biologically active compounds [1-6], including some antibiotics [7]. Quinoxaline derivatives, including condensed derivatives, frequently exhibit photo- and electroluminescent characteristics [8, 9] and are regarded as a promising class of compounds for the creation of organic light-emitting diodes and optoelectronic devises [10, 11]. The development of new methods for the synthesis of quinoxalines is therefore an extremely important task.



In recent years, acetylene derivatives have been used more and more often in the synthesis of heterocycles [12]. However, in spite of the effectiveness of this approach there are few examples of its using in the synthesis of quinoxaline derivatives [13-19]. One of them is found by us tandem cyclization of condenced

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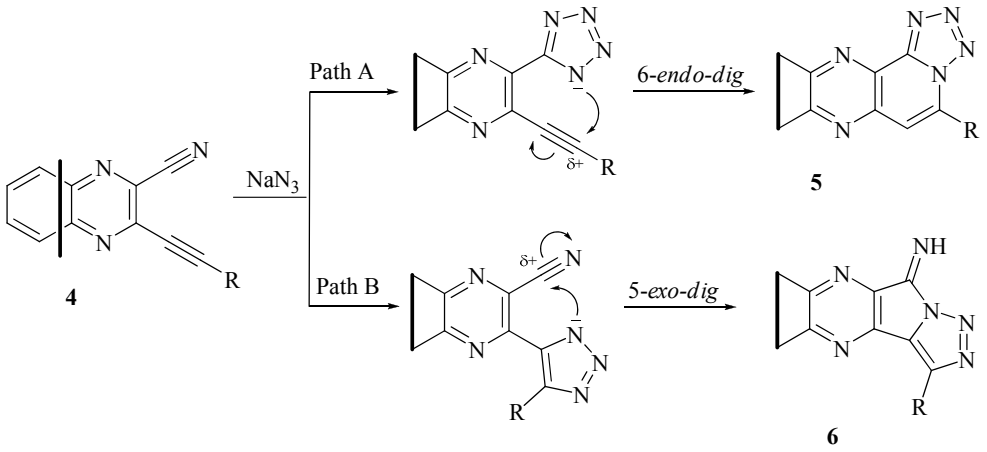
2,3-dialkynylpyrazines (quinoxalines and pteridines) **1** to [1,2,3]triazolo[1',5':1,2]pyrido[3,4-*b*]pyrazines **3** in the presence of sodium azide [20]. The reaction mechanism includes 1,3-dipolar cycloaddition of the azide ion to one of the C≡C bonds and intramolecular *N*-nucleophilic attack by the formed triazolyl anion **2** at the adjacent triple bond, leading to the formation of the pyridine ring. The first stage of this transformation is a quite rare example of cycloaddition of an azide anion with an internal alkyne [21-24]. As a rule such reaction requires prolonged heating and gives moderate yields of the products. However, the cyclization represented in the scheme above takes place under surprisingly mild conditions and give good yields of the products.

The aim of the present work was to investigate the reaction of 3-alkynylquinoxaline-2-carbonitriles **4** with sodium azide. Compounds **4** are unique hetero analogs of 2,3-dialkynylquinoxalines **1**, and their reaction with sodium azide can theoretically proceed through one of the paths indicated in the scheme below and lead to the polynuclear derivatives of quinoxaline **5** or **6**. Path A presupposes initial cycloaddition of the azide anion to the nitrile group followed by 6-*endo*-digonal (6-*endo-dig*) cyclization. Path B involves the intermediate formation of 1,2,3-triazoles and subsequent attack at the nitrile group.

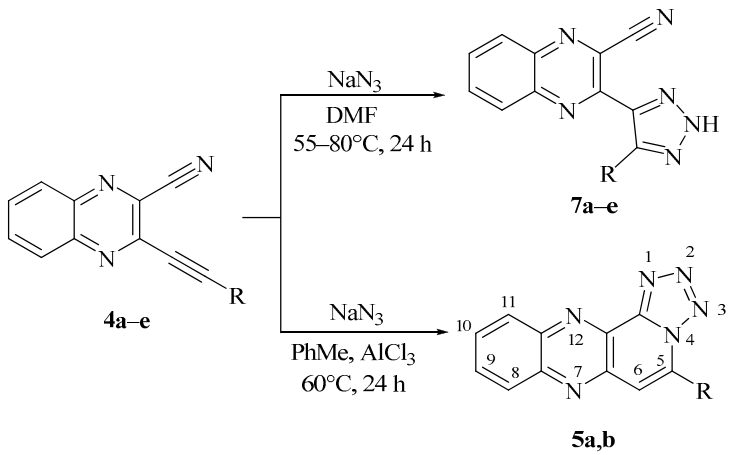


The starting 3-alkynylquinoxaline-3-carbonitriles **4a-e** were obtained through the coupling of 3-chloro-quinoxaline-2-carbonitriles with terminal alkynes by the previously described method [25].

We found that 3-(5-phenyl-2*H*-1,2,3-triazol-4-yl)quinoxaline-2-carbonitrile (**7a**) is formed exclusively in 82% yield when a mixture of 3-(phenylethynyl)quinoxaline-2-carbonitrile (**4a**) is stirred for 24 h with a 1.5-fold excess of sodium azide in DMF at 55-56°C. The reaction of the quinoxalines **4b**,**c** with NaN_3 takes place similarly, i.e., the substituent in the aryl fragment at the C≡C bond does not have an appreciable effect on the cycloaddition. However, the reaction of compounds **4d**,**e** with alkyl or alkenyl substituents at the C≡C bond requires heating up to 80°C and provides the corresponding triazoles **7d**,**e** in 38-50% yields.

The structure of compounds **7** was established on the basis of spectral and mass-spectrometric data. Their IR spectra contain characteristic absorption bands of the C≡N (2235-2250 cm^{-1}) and N–H (3177-3278 cm^{-1}) bonds. In the ^{13}C NMR spectra of the triazoles **7a-e**, the signals typical of the carbon atoms of C≡C bonds at 80-100 ppm are absent. This indicates that the azide is added to the C≡C bond of the initial compound **4**. In the ^{1}H NMR spectra of the triazoles **7** the signal of the N–H proton is observed at 12.1-12.4 ppm ($CDCl_3$) or 15.5-16.0 ppm (DMSO-d_6). In the mass spectra of all the compounds **7** except the triazole **7c** the peak of the molecular ion is the most intense.

Attempts to convert the triazoles **7** into the tetracyclic compounds **6** were unsuccessful; compounds **7a-c** remained unchanged even after prolonged heating with K_2CO_3 in DMF.



a R = Ph, **b** R = *p*-Tol, **c** R = 4-$O_2NC_6H_4$, **d** R = *n*-C_8H_{17}, **e** R = cyclohexenyl

It is known that the 1,3-dipolar cycloaddition of the azide ion at the nitrile group is facilitated by the use of Lewis acids [26]. In order to direct the transformation along path A we performed the reaction of 3-(phenylethynyl)quinoxaline-2-carbonitrile (**4a**) with sodium azide in DMF in the presence of $Zn(OAc)_2$ (5 equiv.). When the reaction mixture was heated to 80°C for 120 h 5-phenyltetrazolo[1',5':1,2]pyrido[3,4-*b*]-quinoxaline (**5a**) was formed in 30% yield. Replacement of the $Zn(OAc)_2$ with zinc bromide led to a slight decrease in the yield of the product, even less effective additive proved to be the NH_4Cl/LiCl (10 equiv.) mixture; it is only provided compound **5a** in 10% yield.

Replacement of the DMF with the low-polarity toluene might accelerate the transformation of the nitrile into the tetrazole [26]. We found that the reaction of 3-(phenylethynyl)quinoxaline-2-carbonitrile (**4a**) with sodium azide (3 equiv.) in toluene in the presence of $AlCl_3$ (1.5 equiv.) at 60°C for 24 h lead to the formation of compound **5a** in 42% yield. The reaction of 3-(*p*-tolylethynyl)quinoxaline-2-carbonitrile (**4b**) with NaN_3 under the same conditions gave the tetrazole **5b** in 40% yield. Compound **4d** did not react with sodium azide under these conditions, and with the carbonitriles **4c**,**e** as starting compounds tarring of the reaction mixture was observed.

The proposed structure **5** is indicated by the following facts. The IR spectra of compounds **5a**,**b** do not contain absorption bands of the triple bonds or the N─H bond. The ^{1}H NMR spectra are characterized by a singlet at 7.8 ppm, corresponding to the H-6 proton. The ^{13}C NMR spectra of the tetrazoles **5a**,**b** do not contain signals in the region of 80-100 ppm typical of the carbon atoms of C≡C bonds. The mass spectra of compounds **5a**,**b** contain molecular-ion peaks with 8-11% intensity, and the strongest in both cases is the $[M\text{-}N_2]^+$ peak. The molecular structure of the tetrazole **5b** was established unambiguously by X-ray structural analysis (Fig. 1).

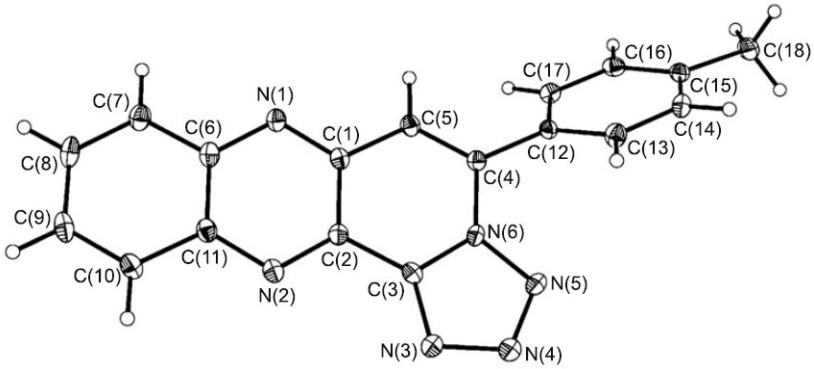


Fig. 1. A general view of the molecule of tetrazole **6b** with the atoms represented by thermal vibration ellipsoids of 50% probability.

TABLE 1. Full and Relative Electronic Energies (E^{zpe} and ΔE) and Gibbs Free Energies ($G^{298.15}$ and $\Delta G^{298.15}$) of the Calculated Structures

Structure	E^{zpe}, au	ΔE, kcal/mol	$G^{298.15}$, au	$\Delta G^{298.15}$, kcal/mol
4a	-817.15553	—	-164.21656	—
N_3^-	-164.20200	—	-817.20056	—
PRC	-981.37978	-14.0	-981.43024	-8.2
TS 1A	-981.34781	6.1	-981.39596	13.3
1A	-981.43779	-50.4	-981.48501	-42.6
TS 2A	-981.41218	-34.3	-981.45700	-25.0
2A	-981.43058	-45.8	-981.47462	-36.1
TS 1B	-981.35655	0.6	-981.40604	7.0
2B	-981.39000	-20.4	-981.43554	-11.6
TS 1C	-981.37256	-9.4	-981.42146	-2.7
1C	-981.39272	-22.1	-981.44182	-15.5
TS 2C	-981.38255	-15.7	-981.43066	-8.5
3C	-981.49150	-84.1	-981.53867	-76.3

For the better understanding of the reaction mechanism between 3-alkynylquinoxaline-2-carbonitriles **4** and sodium azide, DFT calculations were performed with the M05-2X functional [27] in the 6-31+G(d,p) basis set [28-30] using the Gaussian 03 software package [31]. According to the calculations in the gas phase, 3-(phenylethynyl)quinoxaline-2-carbonitrile (**4a**) and the azide ion form a fairly stable pre-reaction π-complex (**PRC**), the stabilization energy of which amounts to ~14.0 kcal/mol (Fig. 2, Table 1). Addition of the azide ion to the C≡N bond takes place as a concerted process with an activation energy of 20.1 kcal/mol. The structure of the transition state **TS 1A** has clearly defined asymmetry (C···N 1.612, N···N 2.385 Å). The transfer of charge from the nucleophile to the electrophile, estimated by NBO analysis [32], amounts to 0.51 e. The energy gain in the transition from the **PRC** to the cyclic adduct **1A** amounts to 36.4 kcal/mol. The subsequent 6-*endo-dig* cyclization (**1A** ⇄ **TS 2A** ⇄ **2A)** requires an activation energy of 16.1 kcal/mol. However, this process is energetically unfavorable (endothermic), and the destabilization energy amounts to 4.6 kcal/mol.

The addition of the azide ion to the C≡C bond can start with attack both at the C(α) atom and at the C(β) atom. In the first case the process is concerted and results in 5-*exo-dig* cyclization with the formation of cyclopentaquinoxaline (**PRC** ⇄ **TS 1B** ⇄ **1B**). The required activation energy amounts to 14.6 kcal/mol. The structure of the transition state **TS 1B** has clearly defined asymmetry (C(α)···N 1.881, C(β)···N 3.145 Å), and the calculated charge transfer is 0.47 e.

The addition of the azide ion at the C(β) atom of the C≡C bond takes place in two kinetic stages with the formation of the metastable intermediate **1C** at the first of them. The activation energy in this case amounts to only 4.6 kcal/mol, and the energy gain is 8.1 kcal/mol. The low kinetic stability of the intermediate **1C** favors its rapid cyclization through the transition state **TS 2C** with a barrier of 6.4 kcal/mol to the corresponding cyclic adduct **2C**. The total energy gain in the transition from the **PRC** to the cyclic adduct **2C** amounts to 70.1 kcal/mol. Thus, the reaction path **PRC** ⇄ **TS 1C** ⇄ **1C** ⇄ **TS 2C** ⇄ **2C** is greatly preferred both kinetically and thermodynamically. Such regioselectivity is also explained well in terms of frontier molecular orbital theory. Thus the HOMO of the nucleophile (the azide ion) and the LUMO of the electrophile (compound **4a**) have close energy values (-1.454 and -2.035 eV, respectively), which in the Pearson classification corresponds to soft base–soft acid interaction. Therefore, the regioselectivity of nucleophilic attack will be determined by the contribution from the atomic orbitals of the electrophile LUMO. Analysis of the contributions from the respective AOs, calculated by the AM1 method, shows that the largest value corresponds to the p_z-orbital of the C(β) atom: 0.005 and 0.011 for the carbon and nitrogen atoms of the C≡N group and 0.169 and 0.290 for the C(α) and C(β) atoms of the C≡C bond. The data from the calculations clearly agree fully with the experimental data.

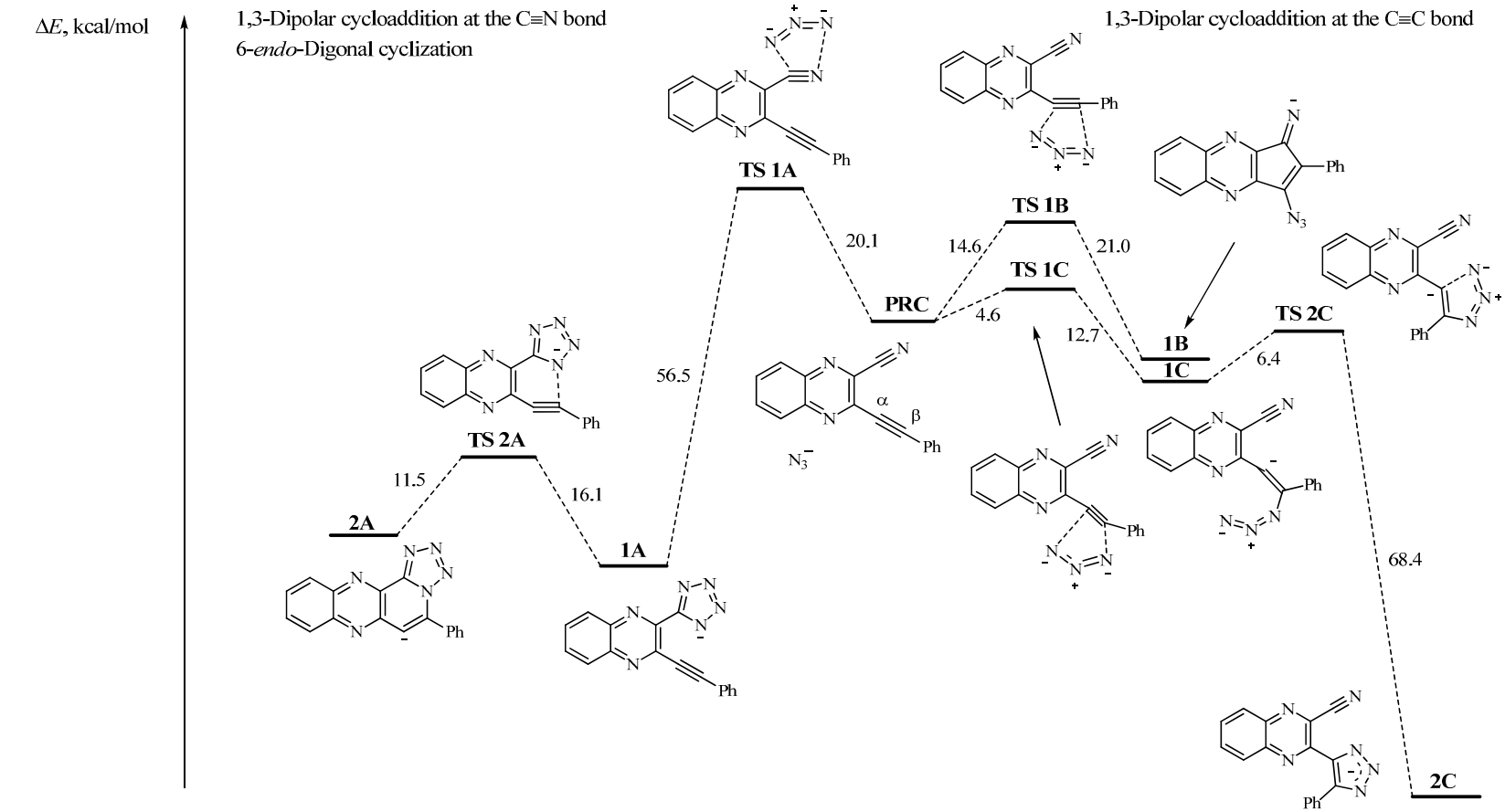


Fig. 2. Energy profile of the reactions of 3-(phenylethynyl)quinoxaline-2-carbonitrile (4a) with sodium azide.

We have thus established that, unlike 2,3-dialkynylquinoxalines, 3-alkynylquinoxaline-2-carbonitriles exhibit dual reactivity toward sodium azide. In the absence of the Lewis acid the reaction develops as 1,3-dipolar cycloaddition of the azide ion at the C≡C bond of the initial molecule, leading to the selective formation of 4,5-disubstituted 2*H*-1,2,3-triazole. The Lewis acid initiates a tandem process involving cycloaddition of the azide ion at the C≡N group and subsequent 6-*endo*-digonal cyclization with the formation of 5-aryl-tetrazolo[1',5':1,2]pyrido[3,4-*b*]quinoxaline.

EXPERIMENTAL

The IR spectra were recorded on a FT FSM-1202 spectrometer in Nujol. The UV spectra were recorded on a Varian Cary 50 Probe spectrometer in MeCN. The ^{1}H and ^{13}C NMR spectra were recored on a Bruker DPX-250 spectrometer (250 и 62.9 MHz, respectively) with TMS as internal standard. The mass spectra were recorded on a Finnigan MAT INCOS 50 mass spectrometer with direct sample introduction and accelerating voltage of 70 eV. Elemental analysis was carried out following the Pregl–Dumas method. The melting points were determined in glass capillaries on a Stuart SMP30 apparatus.

Geometry optimization of the molecular structures corresponding to the stationary points on the PES has been performed by analytical calculation of the gradients according to the Berny algorithm. The nature of the stationary points was established by analysis of the force constant matrix (Hessian). With the presence of one and only one imaginary frequency the structure was referred to the transition state, and with its absence it was assigned to the energy minimum. Zero-point vibration energies and the corresponding thermodynamic corrections were calculated in harmonic approximation. The minimum-energy reaction path connecting the two minima through the corresponding saddle point was calculated by the gradient descent algorithm [33]. The initial direction of the gradient line was set by displacement along the transition vector of the corresponding transition state.

3-(5-Phenyl-2*H*-1,2,3-triazol-4-yl)quinoxaline-2-carbonitrile (**7a**). A mixture of 3-(phenylethynyl)-quinoxaline-2-carbonitrile (**4a**) [25] (0.128 g, 0.50 mmol) and NaN_3 (0.050 g, 0.77 mmol) in DMF (3 ml) was stirred for 24 h at 55-60°C. A saturated NH_4Cl solution (70 ml) was added to the reaction mixture followed by extraction with $CHCl_3$ (3×30 ml). The solvent was removed from the extract on a rotary evaporator, and the residue was separated by chromatography on SiO_2 with $CHCl_3$ as eluent; the fraction with R_f 0.2-0.3 was collected. The product was recrystallized from MeOH. Yield 0.122 g (82%), colorless crystals, mp >180°C (decomp.). IR spectrum, ν, cm^{-1}: 2235 (C≡N), 3202 (N–H). UV spectrum, λ_{max}, nm (log ε): 246 (4.51), 341 (3.65). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.34-7.40 (3H, m, H Ph); 7.67-7.71 (2H, m, H Ph); 7.87-7.97 (2H, m, H-6,7); 8.08-8.12 (1H, m) and 8.19-8.23 (1H, m, H-5,8); 12.28 (1H, br. s, NH). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 116.2; 128.8; 129.0; 129.5; 129.8; 129.9; 130.0; 132.4; 134.1; 139.0; 141.2; 142.2; 145.1; 147.3; 163.5. Mass spectrum, *m*/*z* (I_{rel}, %): 298 $[M]^+$ (100), 272 $[M\text{-}CN]^+$ (96), 243 $[M\text{-}HCN\text{-}N_2]^+$ (39), 217 (34), 190 (18), 115 (16), 102 (17), 89 (17), 77 (29). Found, %: C 68.29; H 3.54; N 28.03. $C_{17}H_{10}N_6$. Calculated, %: C 68.45; H 3.38; N 28.17.

3-[5-(*p*-Tolyl)-2*H*-1,2,3-triazol-4-yl)]quinoxaline-2-carbonitrile (**7b**) was obtained from 3-[(*p*-tolyl)-ethynyl]quinoxaline-2-carbonitrile (**4b**) [25] analogously to compound **7a**. Yield 0.125 g (80%), colorless crystals, mp >172°C (decomp., MeOH). IR spectrum, ν, cm^{-1}: 2249 (C≡N), 3200 (N–H). UV spectrum, λ_{max}, nm (log ε): 247 (4.55), 342 (3.63). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.36 (3H, s, CH_3); 7.18 (2H, d, *J* = 7.9, H Ar); 7.57 (2H, d, *J* = 7.9, H Ar); 7.88-7.98 (2H, m, H-6,7); 8.11-8.23 (2H, m, H-5,8); 12.42 (1H, br. s, NH). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 21.8; 116.2; 126.4; 128.8; 129.8; 130.0; 130.1; 132.4; 134.0; 139.3; 139.8; 141.3; 142.2; 145.3; 147.2; 163.3. Mass spectrum, *m*/*z* (I_{rel}, %): 312 $[M]^+$ (100), 286 $[M\text{-}CN]^+$ (88), 257 $[M\text{-}HCN\text{-}N_2]^+$ (33), 231 (27), 128 (13), 102 (26), 77 (26). Found, %: C 69.06; H 3.98; N 27.09. $C_{18}H_{12}N_6$. Calculated, %: C 69.22; H 3.87; N 26.91.

3-[5-(4-Nitrophenyl)-2*H*-1,2,3-triazol-4-yl)]quinoxaline-2-carbonitrile (**7c**) was obtained from 3-[(4-nitrophenyl)ethynyl]quinoxaline-2-carbonitrile (**4c**) [25] analogously to compound **7a**. Yield 0.130 g (76%), colorless crystals, mp >276°C (decomp., MeOH). IR spectrum, ν, cm^{-1}: 2250 (C≡N), 3177 (N–H). UV spectrum, λ_{max}, nm (log ε): 250 (4.44), 298 (4.06), 347 (sh, 3.71). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 8.04-8.09 (5H, m, H Ar); 8.26-8.29 (3H, m, H Ar); 16.05 (1H, br. s, NH). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 117.2; 124.4; 129.8; 130.0; 130.1; 130.5; 133.4; 135.1; 140.2; 141.1; 141.2; 141.8; 146.6; 146.7; 148.3. Mass spectrum, *m*/*z* (I_{rel}, %): 343 $[M]^+$ (44), 317 $[M\text{-}CN]^+$ (100), 296 $[M\text{-}HNO_2]^+$ (45), 268 (51), 243 (75), 230 (17), 215 (51), 204 (11), 190 (65), 177 (11), 164 (17), 140 (17), 114 (13), 102 (20), 76 (25). Found, %: C 59.33; H 2.47; N 28.66. $C_{17}H_9N_7O_2$. Calculated, %: C 59.48; H 2.64; N 28.56.

3-(5-Octyl-2*H*-1,2,3-triazol-4-yl)quinoxaline-2-carbonitrile (**7d**) was obtained from 3-(dec-1-ynyl)-quinoxaline-2-carbonitrile (**4d**) [25] analogously to compound **7a** at 80°C. Yield 0.084 g (50%), colorless crystals, mp 124-126°C (MeOH). IR spectrum, ν, cm^{-1}: 2249 (C≡N), 3217 (N–H). UV spectrum, λ_{max}, nm (log ε): 246 (4.44), 269 (sh, 4.24), 352 (3.66). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.88 (3H, t, *J* = 7.0, CH_3); 1.23-1.50 (10H, m, $CH_2CH_2(C\underline{H}_2)_5CH_3$); 1.76-1.88 (2H, m, $CH_2C\underline{H}_2(CH_2)_5CH_3$); 3.23 (2H, t, *J* = 7.7, $C\underline{H}_2CH_2(CH_2)_5CH_3$); 7.90-8.03 (2H, m, H-6,7); 8.17-8.25 (2H, m, H-5,8); 12.15 (1H, br. s, NH). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 14.8; 22.9; 28.9; 29.1; 29.4; 29.5; 29.6; 32.0; 117.4; 128.3; 128.4; 129.6; 130.0; 132.6; 134.9; 139.1; 140.4; 142.0; 147.1. Mass spectrum, *m*/*z* (I_{rel}, %): 334 $[M]^+$ (100), 277 $[M\text{-}C_4H_9]^+$ (4), 263 $[M\text{-}C_5H_{11}]^+$ (6), 249 $[M\text{-}C_6H_{13}]^+$ (11), 236 $[M\text{-}C_7H_{14}]^+$ (11), 102 (5). Found, %: C 68.07; H 6.81; N 25.00. $C_{19}H_{22}N_6$. Calculated, %: C 68.24; H 6.63; N 25.13.

3-[5-(Cyclohex-1-enyl)-2*H*-1,2,3-triazol-4-yl)quinoxaline-2-carbonitrile (**7e**) was obtained from 3-[(cyclohex-1-enyl)ethynyl]quinoxaline-2-carbonitrile (**4e**) [25] analogously to compound **7a** at 80°C. Yield 0.057 g (38%), colorless crystals, mp 199-201°C (MeOH). IR spectrum, ν, cm^{-1}: 2242 (C≡N), 3278 (N–H). UV spectrum, λ_{max}, nm (log ε): 247 (4.45), 269 (sh., 4.06), 346 (3.61). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 1.61-1.72 (4H, m, $2CH_2$); 2.08-2.20 (2H, m, CH_2); 2.35-2.45 (2H, m, CH_2); 6.10-6.30 (1H, m, =CH); 8.05-8.17 (2H, m, H-6,7); 8.21-8.31 (2H, m, H-5,8); 15.51 (1H, br. s, NH). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 21.4; 22.2; 25.3; 26.9; 116.4; 129.0; 129.3; 129.5; 131.3; 131.6; 132.6; 134.5; 137.6; 140.1; 141.6; 147.1; 147.2. Mass spectrum, *m*/*z* (I_{rel}, %): 302 $[M]^+$ (100), 273 $[M\text{-}C_2H_5]^+$ (64), 259 $[M\text{-}C_3H_7]^+$ (11), 245 $[M\text{-}C_4H_9]^+$ (30), 232 $[M\text{-}C_5H_{10}]^+$ (10), 219 $[M\text{-}C_6H_{11}]^+$ (15), 129 (9), 102 (26), 77 (17). Found, %: C 67.41; H 4.59; N 27.94. $C_{17}H_{14}N_6$. Calculated, %: C 67.54; H 4.67; N 27.80.

5-Phenyltetrazolo[1',5':1,2]pyrido[3,4-*b*]quinoxaline (**5a**). A mixture of 3-(phenylethynyl)quinoxaline-2-carbonitrile (**4a**) [25] (0.128 g, 0.5 mmol), NaN_3 (0.098 g, 1.5 mmol), and anhydrous $AlCl_3$ (0.100 g, 0.75 mmol) in dry toluene (5 ml) was stirred for 24 h at 60°C. A saturated NH_4Cl solution (70 ml) was added to the reaction mixture followed by extraction with $CHCl_3$ (3×30 ml). The solvent was removed from the extract on a rotary evaporator, and the residue was separated by chromatography on SiO_2 with $CHCl_3$ as eluent; the fraction with R_f 0.3-0.4 was collected. The product was recrystallized from MeOH. Yield 0.062 g (42%), colorless crystals, mp >230°C (decomp.). UV spectrum, λ_{max}, nm (log ε): 265 (4.45), 304 (sh, 3.97), 377 (3.95), 396 (sh, 3.90). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.63-7.66 (3H, m, H Ph); 7.82 (1H, s, H-6); 7.95-8.12 (4H, m, H-9,10, H Ph); 8.29-8.33 (1H, m, H-8); 8.51-8.56 (1H, m, H-11). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 116.9; 129.5; 129.8; 130.0; 130.6; 131.0; 131.9; 132.6; 133.4; 133.6; 140.4; 143.4; 144.4; 145.5; 149.4. Mass spectrum, *m*/*z* (I_{rel}, %): 298 $[M]^+$ (8), 270 $[M–N_2]^+$ (100), 243 (12), 167 (12), 142 (21), 135 (21), 116 (12), 102 (73), 90 (15), 77 (58). Found, %: C 68.61; H 3.49; N 27.99. $C_{17}H_{10}N_6$. Calculated, %: %: C 68.45; H 3.38; N 28.17.

5-(*p*-Tolyl)tetrazolo[1',5':1,2]pyrido[3,4-*b*]quinoxaline (**5b**) was obtained from 3-[(*p*-tolyl)ethynyl]-quinoxaline-2-carbonitrile (**4b**) [25] analogously to compound **5a**. Yield 0.062 g (40%), colorless crystals, mp >250°C (decomp., MeOH). UV spectrum, λ_{max}, nm (log ε): 265 (4.31), 309 (sh, 3.88), 383 (3.83), 402 (sh, 3.80). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.50 (3H, s, CH_3); 7.44 (2H, d, *J* = 7.8, H Ar); 7.78 (1H, s, H-6); 7.95-8.04 (4H, m, H-9,10, H Ar); 8.28-8.32 (1H, m, H-8); 8.51-8.56 (1H, m, H-11). ^{13}C NMR spectrum (CF_3COOD), δ, ppm: 19.1; 105.9; 119.9; 123.6; 129.0; 129.3; 130.5; 131.9; 132.7; 133.9; 134.4; 140.1; 144.0;

145.8; 146.6; 147.1. Mass spectrum, *m*/*z* (I_{rel}, %): 312 $[M]^+$ (11), 284 $[M-N_2]^+$ (100), 142 (17), 115 (23), 102 (17), 91 (10), 76 (9). Found, %: C 69.34; H 4.03; N 26.77. $C_{18}H_{12}N_6$. Calculated, %: C 69.22; H 3.87; N 26.91.

X-ray structure investigation of compound 5b monocrystal was carried out at 100 K on a Bruker APEX II, CCD area detector diffractometer, MoKα radiation, λ 0.71073 Å, ω-scanning. The crystal of compound **5b** ($C_{18}H_{12}N_6$, *M* 312.34) was orthorhombic, space group Aba_2; *a* 18.0728(11), *b* 22.1373(15), *c* 7.1640(4) Å, *V* 2866.2(3) $Å^3$, *Z* 8, d_{calc} 1.448 g/cm^3, μ 0.093 mm^{-1}, *F*(000) 1296. The structure was solved by the direct method and full-matrix least-squares refinement in anisotropic approximation using Bruker SHELXTL software. The complete crystallographic information has been deposited at the Cambridge Crystallographic Data Center (deposit CCDC 955007).

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