Transformations of 8-substituted tetrazolo[1,5-*a*]pyrazines

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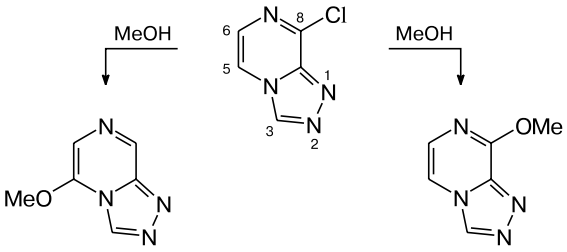
The reactions of 8-chlorotetrazolo[1,5-*a*]pyrazine with N-, O-, and S-nucleophiles involve the *ipso* substitution of the chlorine atom. Heating of this compound with benzotriazole or phenyltetrazole results in elimination of the nitrogen molecule from one of the tetrazole rings to form new annelated azapentalenes.

Key words: 8-substituted tetrazolo[1,5-*a*]pyrazines, nucleophilic substitution.

In spite of extensive progress in the chemistry of azolo[*a*]pyrazines, which have attracted interest because of their numerous useful properties, such as luminescence and complexation properties and bronchospasmolytic, cardiotonic, anti-inflammatory, and antibacterial activities,[1—3] tetrazolo[1,5-*a*]pyrazines are a poorly studied class of heterocycles. The published studies on the chemistry of these compounds were concerned mostly with the azido-tetrazole tautomerism.[4—6] The aim of the present study was to perform the reactions of 8-chlorotetrazolo[1,5-*a*]pyrazine (**1**) with N-, O-, and S-nucleophiles and investigate the properties of 8-substituted tetrazolo[1,5-*a*]pyrazines.

According to the modern concepts of nucleophilic substitution in aromatic moieties, nucleophiles can attack unsubstituted positions of heterocycles even in the presence of good leaving groups.[7] In particular, this is manifested in the competitive *ipso* and *tele* substitution of halogen in triazolo[4,3-*a*]pyrazines, positions 5 and 8 being most prone to the nucleophilic attack (Scheme 1).[8]

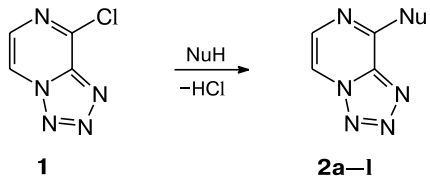
Scheme 1



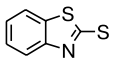
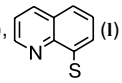
The reactions of 8-chlorotetrazolo[1,5-*a*]pyrazine (**1**) with nucleophiles can involve not only the competitive *ipso* and *tele* substitution but also the azido-tetrazole tautomerism, due to which the course of nucleophilic substitution becomes even less predictable.

In the present study, we investigated the reactions of 8-chlorotetrazolo[1,5-*a*]pyrazine (**1**) with N-, S-, and O-nucleophiles. The reactions were performed at room temperature (with secondary amines, hydrazine, and thiolates) or under reflux in various solvents (with alcohols and aniline). All the reactions under study were demonstrated to involve the *ipso* substitution of the chlorine atom giving rise to the corresponding 8-substituted tetrazolo[1,5-*a*]pyrazines **2a—l** (Scheme 2).

Scheme 2



1 **2a—l**

Nu = H_2C=CHCH_2NH (**a**), PhCH_2NH (**b**), PhNH (**c**), piperidin-1-yl (**d**), morpholin-4-yl (**e**), NH_2NH (**f**), MeO (**g**), Me_2CHO (**h**), PhO (**i**), PhCH_2S (**j**),  (**k**),  (**l**)

The structures of the resulting compounds were established by IR and ^{1}H NMR spectroscopy. The ^{1}H NMR spectra of compounds **2a—l** show signals for the H(5) and H(6) protons of the pyrazine ring as doublets with the spin-spin coupling constants $J_{H(5),H(6)}$ = 4.2—4.6 Hz. In the IR spectra, an N_3 vibration band is absent, which indicates that the products exist in the tetrazole rather than azide form. This approach to the synthesis of 8-substituted tetrazolo[1,5-*a*]pyrazines might be useful taking into account that the synthesis of such compounds by an alternative way, *viz.*, by the reaction of the corresponding 2-substituted 3-chloropyrazine with NaN_3, pre-

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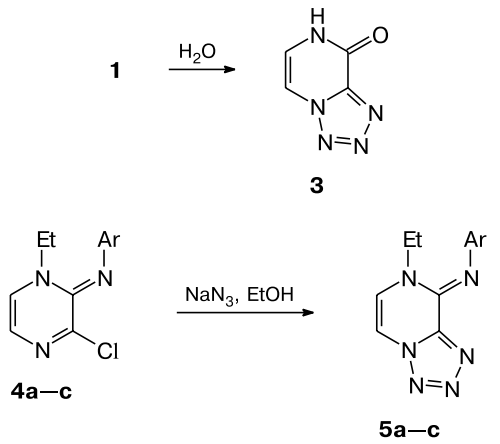
sents difficulties because of low fugacity of the chlorine atom due to the donor effects of the adjacent substituent.

8-Chlorotetrazolo[1,5-*a*]pyrazine (**1**) readily undergoes hydrolysis (samples of compound **1** are gradually hydrolyzed during storage in air) to give 7*H*-tetrazolo[1,5-*a*]pyrazin-8-one (**3**) characterized by $^3J_{H(5),H(6)}$ = 5.6 Hz (Scheme 3).

Scheme 3



Ar = Ph (**a**), 1-naphthyl (**b**), 4-$MeOC_6H_4$ (**c**)

An alternative procedure for the synthesis of 7*H*-tetrazolo[1,5-*a*]pyrazin-8-ylidenes is based on the reaction of 2-arylimino-3-chloro-1-ethyl-1*H*-pyrazines **4a—c** (see Ref. 9) with NaN_3, which can be easily performed under rather mild conditions (see Scheme 3). The resulting 8-arylimino-7-ethyl-7*H*-tetrazolo[1,5-*a*]pyrazines **5a—c** are characterized by the spin constant ^3J = 5.6 Hz. These compounds, unlike compound **3**, cannot undergo prototropic tautomerism, and the ylidene form is strictly fixed. The similarity of the spin-spin coupling constants for compounds **3** and **5a—c** confirms that the former compound exists as pyrazinone rather than as hydroxypyrazine. Taking into account the earlier spectroscopic data,[10] it can be concluded that ^3J = 5.0—5.7 Hz is characteristic of the pyrazin-8-ylidene forms of azolo[*a*]pyrazines.

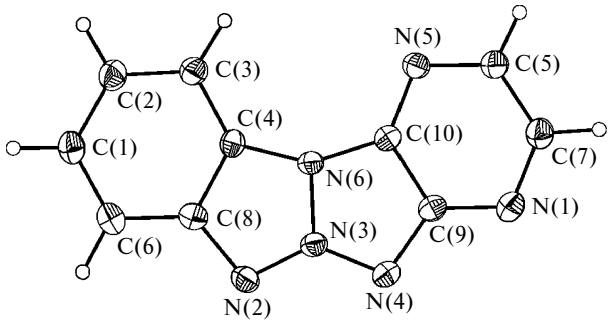


Fig. 1. X-ray diffraction structure of compound **7**.

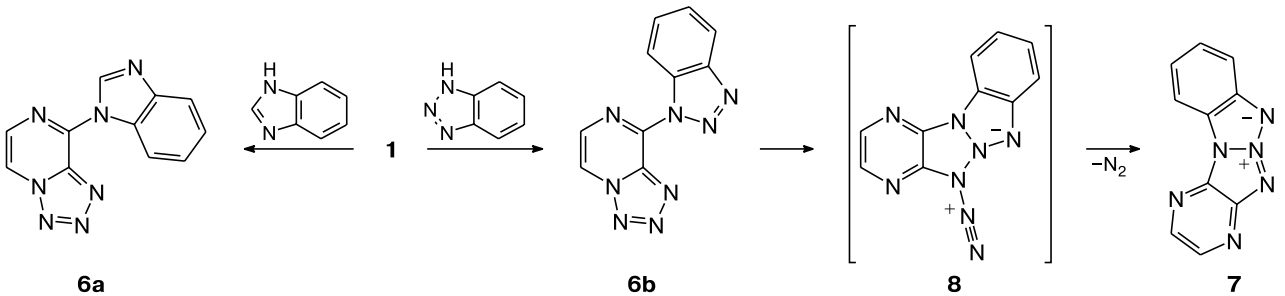
The reactions of compound **1** with such N-nucleophiles as benzazoles (benzimidazole or benzotriazole) proceed under rather mild conditions (MeCN, refluxing for 0.5 h) to give the corresponding 8-substituted tetrazolo[1,5-*a*]pyrazines **6a,b** (Scheme 4). The distinguishing feature of 8-(benzotriazol-1-yl)tetrazolo[1,5-*a*]pyrazine (**6b**) is that refluxing of this compound in DMF is accompanied by elimination of the nitrogen molecule to form azapentalene **7** (see Scheme 4). The same azapentalene was prepared in ~30% yield directly by refluxing compound **1** with benzotriazole in DMF or DMSO. The structure of compound **7** was established by X-ray diffraction (Fig. 1) and is consistent with the elemental analysis data and the results of mass spectrometry and ^{1}H NMR spectroscopy.

It should be noted that the coupling constant (^3J = 2.7 Hz) between the H(2) and H(3) protons of the pyrazine ring in the ^{1}H NMR spectrum of compound **7** is substantially smaller than the corresponding constants in the spectra of 8-substituted tetrazolo[1,5-*a*]pyrazines.

In the crystalline state, compound **7** shows intense yellow-green luminescence (Fig. 2). Product **7** is characterized by a layered crystal structure and the presence of shortened intermolecular C—N and N—N π—π contacts (3.097 and 3.092 Å, respectively) between the azapentalene fragment and the pyrazine ring of the heterocycle.

The proposed mechanism of the formation of azapentalene **7** involves the formation of 8-(benzotriazol-1-

Scheme 4



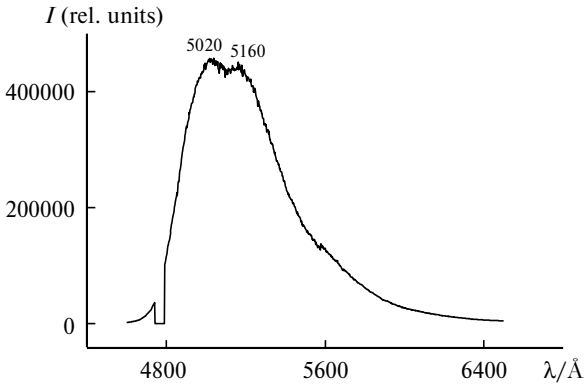


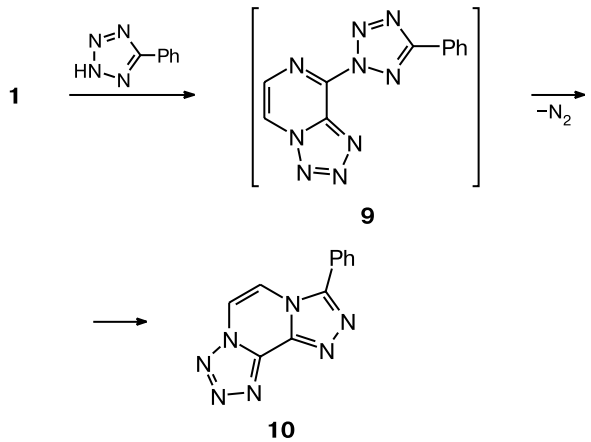
Fig. 2. Luminescence spectrum of compound **7**.

yl)tetrazolo[1,5-*a*]pyrazine (**6b**) followed by intramolecular cyclization and elimination of nitrogen. The question as to whether these processes are concerted or the reaction proceeds through intermediate **8** remains open. The analogous reaction of 8-chlorotetrazolo[1,5-*a*]pyrazine (**1**) with benzimidazole proceeds under reflux in DMF to give the stable *ipso*-substitution product of the chlorine atom **6a** (see Scheme 4).

The formation of azapentalene systems upon thermal decomposition of *o*-azolyl azides was not documented. In a few publications on this problem, azapentalene systems were generally synthesized by reduction of the corresponding *N*-(*o*-nitroaryl)azoles.[11]

Unlike the reaction with benzotriazole, refluxing of compound **1** with 5-phenyltetrazole in DMF leads to elimination of the nitrogen molecule from the tetrazolyl rather than from the tetrazolopyrazine moiety of intermediate 8-azolyltetrazolo[1,5-*a*]pyrazine **9** to give tetrazolo[1,5-*a*]-1,2,4-triazolo[3,4-*c*]pyrazine **10** (Scheme 5).

Scheme 5



The structure of compound **10** was confirmed by X-ray diffraction (Fig. 3).

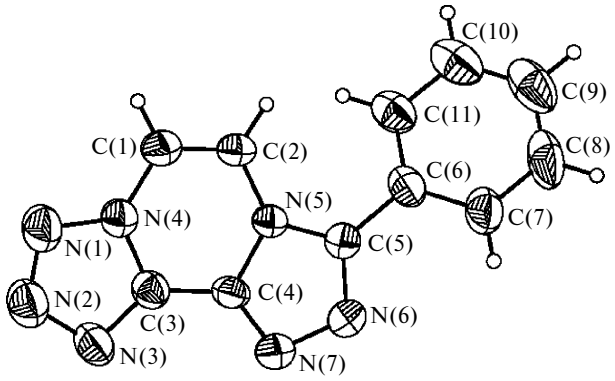


Fig. 3. X-ray diffraction structure of tetrazolo[1,5-*a*]-1,2,4-triazolo[3,4-*c*]pyrazine **10**.

To summarize, we studied the nucleophilic substitution of the chlorine atom in 8-chlorotetrazolo[1,5-*a*]pyrazine and developed a new procedure for the synthesis of azapentalenes.

Experimental

The ^{1}H NMR spectra were recorded on a Bruker DRX-400 spectrometer (400 MHz) in DMSO-d_6, unless otherwise stated, with Me_4Si as the internal standard. The mass spectra were obtained on a Varian MAT-311A spectrometer (the accelerating voltage was 3 kV, the ionizing electron energy was 70 eV, a direct inlet system). The IR spectra were measured on a Specord 75IR spectrometer (Nujol mulls). The luminescence spectrum was recorded on a U-1000 Raman spectrometer at λ_{ex} = 4765 Å. The course of the reactions was monitored and the purity of the products was checked by TLC on Silufol UV-254 plates; spots were visualized with iodine vapor.

Compounds **4a—c** were synthesized according to a known procedure.[9]

8-Allylaminotetrazolo[1,5-*a*]pyrazine (2a). A mixture of compound **1** (156 mg, 1 mmol) and allylamine (0.23 mL, 3 mmol) was refluxed in THF (4 mL) for 2 h, the solvent was evaporated, and the residue was recrystallized from ethanol. Tetrazolopyrazine **2a** was obtained in a yield of 78 mg (44%) as needle-like crystals, m.p. 148—150 °C. Found (%): C, 47.89; H, 4.67; N, 47.77. $C_7H_8N_6$. Calculated (%): C, 47.72; H, 4.58; N, 47.70. ^{1}H NMR, δ: 8.87 (br.s, 1 H, NH); 8.46 and 7.69 (both d, 1 H each, C(6)H, C(5)H, ^3J = 4.65 Hz); 5.96 (m, 1 H, $CH_2C\underline{H}{=}CH_2$); 5.22 and 5.10 (both dm, 1 H each, CH=CH(<u>H</u>), ^2J = 17.2 Hz); 4.15 (br.s, 2 H, $NHC\underline{H}_2CH$).

8-Benzylaminotetrazolo[1,5-*a*]pyrazine (2b). A mixture of compound **1** (260 mg, 1.67 mmol) and benzylamine (0.36 mL, 3.34 mmol) was refluxed in DMF (4 mL) for 6 h. The reaction mixture was cooled and diluted with water. The precipitate that formed was filtered off and recrystallized from ethanol. Tetrazolopyrazine **2b** was obtained in a yield of 213 mg (56%) as colorless crystals, m.p. 178—180 °C. Found (%): C, 58.47; H, 4.57; N, 37.26. $C_{11}H_{10}N_6$. Calculated (%): C, 58.40; H, 4.46; N, 37.15. ^{1}H NMR, δ: 8.06 and 7.69 (both d, 1 H each, C(6)H, C(5)H, ^3J = 4.7 Hz); 7.30—7.50 (m, 5 H, Ph); 6.96 (br.s, 1 H, $N\underline{H}CH_2$); 4.89 (d, 2 H, $NHC\underline{H}_2$, ^3J = 5.8 Hz). IR ($CHCl_3$), ν/cm^{-1}: 3621, 2974, 1611, 1531, 1044.

8-Phenylaminotetrazolo[1,5-*a*]pyrazine (2c) was synthesized analogously in 42% yield as colorless crystals, m.p. 187—189 °C. Found (%): C, 56.70; H, 3.77; N, 39.84. $C_{10}H_8N_6$. Calculated (%): C, 56.60; H, 3.80; N, 39.60. ^{1}H NMR, δ: 10.65 (br.s, 1 H, NH); 8.68 and 7.83 (both d, 1 H each, C(6)H, C(5)H, ^3J = 4.6 Hz); 8.02 (m, 2 H, *m*-H_{Ph}); 7.39 (m, 2 H, *o*-H_{Ph}); 7.12 (m, 1 H, *p*-H_{Ph}).

8-(Piperidin-1-yl)tetrazolo[1,5-*a*]pyrazine (2d). Compound **1** (100 mg, 0.64 mmol) was stirred in piperidine (5 mL) at ~20 °C for 1 h. Then the piperidine was distilled off and the residue was recrystallized from water. Tetrazolopyrazine **2d** was obtained in a yield of 98 mg (75%) as pale-beige crystals, m.p. 162—165 °C. Found (%): C, 52.98; H, 5.90; N, 41.37. $C_9H_{12}N_6$. Calculated (%): C, 52.93; H, 5.92; N, 41.15. ^{1}H NMR, δ: 8.50 and 7.70 (both d, 1 H each, C(6)H, C(5)H, ^3J = 4.5 Hz); 4.20 (s, 4 H, CH_2NCH_2); 1.66 (m, 6 H, $CH_2CH_2CH_2$).

8-Morpholinotetrazolo[1,5-*a*]pyrazine (2e) was synthesized analogously in 44% yield, m.p. 154—156 °C. Found (%): C, 46.80; H, 4.74; N, 40.77. $C_8H_{10}N_6O$. Calculated (%): C, 46.60; H, 4.89; N, 40.76. ^{1}H NMR, δ: 8.59 and 7.78 (both d, 1 H each, C(6)H, C(5)H, ^3J = 4.5 Hz); 4.02 (br.s, 4 H, H_2CNCH_2); 3.78 (m, 4 H, H_2COCH_2).

8-Hydrazinotetrazolo[1,5-*a*]pyrazine (2f). A solution of compound **1** (100 mg, 0.64 mmol) and $N_2H_4 \cdot H_2O$ (0.06 mL, 1.28 mmol) in MeOH (5 mL) was stirred for 0.5 h. The precipitate that formed was filtered off and recrystallized from propanol. Tetrazolopyrazine **2f** was obtained in a yield of 38 mg (39%) as colorless crystals, m.p. 176—178 °C. Found (%): C, 31.78; H, 3.13; N, 64.72. $C_4H_5N_7$. Calculated (%): C, 31.79; H, 3.33; N, 64.88. ^{1}H NMR, δ: 9.96 (br.s, 1 H, NH); 8.40 and 7.69 (both br.d, 1 H each, C(5)H, C(6)H, J = 4.3 Hz); 4.77 (br.s, 2 H, NH_2). IR, ν/cm^{-1}: 3319, 3185, 3089, 2961, 1270, 1044, 983.

8-Methoxytetrazolo[1,5-*a*]pyrazine (2g). Compound **1** (100 mg, 0.64 mmol) was refluxed in MeOH (7 mL) in the presence of Bu^{t}OK (81 mg, 0.71 mmol) for 6 h. Then MeOH was distilled off and the residue was recrystallized from MeCN. Product **2g** was obtained in a yield of 61 mg (64%) as a colorless compound, m.p. 138—141 °C. Found (%): C, 39.35; H, 3.46; N, 46.93. $C_5H_5N_5O$. Calculated (%): C, 39.74; H, 3.33; N, 46.34. ^{1}H NMR, δ: 8.99 and 7.91 (both d, 1 H each, C(6)H, C(5)H, ^3J = 4.7 Hz); 4.19 (s, 3 H, OMe). IR, ν/cm^{-1}: 3192, 1377, 1135, 1055.

8-Isopropoxytetrazolo[1,5-*a*]pyrazine (2h) was synthesized analogously in 20% yield as colorless crystals, m.p. 80—82 °C. Found (%): C, 46.86; H, 5.12; N, 38.93. $C_7H_9N_5O$. Calculated (%): C, 46.92; H, 5.06; N, 39.09. ^{1}H NMR, δ: 8.97 and 7.88 (both d, 1 H each, C(6)H, C(5)H, ^3J = 4.6 Hz); 4.54 (t, 2 H, OCH_2, ^3J = 6.7 Hz); 1.88 (m, 2 H, CH_2); 1.03 (t, 3 H, Me, ^3J = 7.5 Hz).

8-Phenoxytetrazolo[1,5-*a*]pyrazine (2i). A solution of compound **1** (335 mg, 2.15 mmol), phenol (202 mg, 2.15 mmol), and Et_3N (0.3 mL) in DMF (6 mL) was refluxed for 12 h and then diluted with H_2O (7 mL). The precipitate that formed was filtered off, purified on silica gel ($CHCl_3$—AcOEt, 1 : 1, as the eluent), and recrystallized from EtOH. Product **2i** was obtained in a yield of 65 mg (14%) as colorless crystals, m.p. 170—172 °C. Found (%): C, 56.12; H, 3.37; N, 33.03. $C_{10}H_7N_5O$. Calculated (%): C, 56.34; H, 3.31; N, 32.85. ^{1}H NMR ($CDCl_3$), δ: 8.47 and 7.72 (both d, 1 H each, C(6)H, C(5)H, ^3J = 4.7 Hz); 7.52 (m, 2 H, *o*-H_{Ph}); 7.37 (m, 1 H, *p*-H_{Ph}); 7.34 (m, 2 H, *m*-H_{Ph}). IR, ν/cm^{-1}: 3105, 2962, 1190, 997.

8-Benzylthiotetrazolo[1,5-*a*]pyrazine (2j). Compound **1** (156 mg, 1 mmol) was added to a solution of Et_3N (0.14 mL, 1 mmol) and benzylmercaptane (0.12 mL, 1 mmol) in DMF (5 mL). The reaction mixture was stirred for 30 min and diluted with H_2O (7 mL). The precipitate that formed was filtered off and recrystallized from ethanol. Product **2j** was obtained in a yield of 129 mg (53%) as colorless crystals, m.p. 102—103 °C. Found (%): C, 54.17; H, 3.74; N, 28.75. $C_{11}H_9N_5S$. Calculated (%): C, 54.31; H, 3.73; N, 28.79. ^{1}H NMR, δ: 8.45 and 8.07 (both d, 1 H each, C(6)H, C(5)H, ^3J = 4.6 Hz); 7.47 (m, 2 H, Ph); 7.37 (m, 3 H, Ph); 4.64 (s, 2 H, SCH_2).

8-(1,3-Benzothiazol-2-yl)thiotetrazolo[1,5-*a*]pyrazine (2k). A mixture of compound **1** (156 mg, 1 mmol) and 1,3-benzothiazole-2-thiol (167 mg, 1 mmol) was stirred in EtOH (5 mL) in the presence of Et_3N (0.21 mL, 1.5 mmol) for 0.5 h. The precipitate that formed was filtered off and recrystallized from a 4 : 1 EtOH—DMSO mixture. Product **2k** was obtained in a yield of 126 mg (44%) as colorless crystals, m.p. 210—213 °C. Found (%): C, 45.09; H, 2.07; N, 27.93. $C_{11}H_6N_6S_2$. Calculated (%): C, 46.14; H, 2.11; N, 29.35. ^{1}H NMR, δ: 9.36 and 8.34 (both d, 1 H each, C(6)H, C(5)H, ^3J = 4.6 Hz); 8.23 (m, 1 H, C(4′)H in C_6H_4); 8.09 (m, 1 H, C(7′)H in C_6H_4); 7.58 (m, 2 H, C(5′)H, C(6′)H in C_6H_4).

8-(8-Quinolylthio)tetrazolo[1,5-*a*]pyrazine (2l). A mixture of compound **1** (100 mg, 0.64 mmol) and sodium quinoline-8-thiolate dihydrate (131 mg, 0.64 mmol) was refluxed in DMSO (7 mL) for 4.5 h. Then the reaction mixture was cooled and diluted with water (25 mL). The precipitate that formed was filtered off and recrystallized from DMSO. Product **2l** was obtained in a yield of 39 mg (22%) as colorless crystals, m.p. 213—215 °C. Found (%): C, 55.85; H, 2.97; N, 30.26. $C_{13}H_8N_6S$. Calculated (%): C, 55.70; H, 2.88; N, 29.98. ^{1}H NMR, δ: 9.13 and 7.97 (both d, 1 H each, C(6)H, C(5)H, ^3J = 4.6 Hz); 8.89 (dd, 1 H, C(2′)H, ^3J = 4.2 Hz, ^4J = 1.7 Hz); 8.52 (dd, 1 H, C(4′)H, ^3J = 8.3 Hz, ^4J = 1.7 Hz); 8.29 (dd, 1 H, C(5′)H or C(7′)H, ^2J = 7.3 Hz, ^3J = 1.4 Hz); 8.22 (dd, 1 H, C(5′)H or C(7′)H, ^3J = 8.3 Hz, ^4J = 1.4 Hz); 7.75 (dd, 1 H, C(6′)H, ^3J = 8.2 Hz, ^3J = 7.3 Hz); 7.64 (dd, 1 H, C(3′)H, ^3J = 8.3 Hz, ^3J = 4.2 Hz).

7*H*-Tetrazolo[1,5-*a*]pyrazin-8-one (3). 8-Chlorotetrazolo[1,5-*a*]pyrazine (**1**) (156 mg, 1 mmol) was refluxed in H_2O (5 mL) for 3 h. Then the reaction mixture was cooled. The precipitate that formed was filtered off and recrystallized from water. Product **3** was obtained in a yield of 70 mg (51%) as colorless crystals, m.p. 280 °C (with decomp.). Found (%): C, 35.03; H, 2.35; N, 51.52. $C_4H_3N_5O$. Calculated (%): C, 35.04; H, 2.21; N, 51.08. ^{1}H NMR, δ: 8.24 and 7.33 (both d, 1 H each, C(6)H, C(5)H, ^3J = 5.6 Hz); 12.14 (br.s, 1 H, NH). ^{1}H NMR ($(CD_3)_2SO$ + CF_3COOH), δ: 8.22 and 7.32 (both d, 1 H each, C(6)H, C(5)H, ^3J = 5.6 Hz); 12.17 (br.s, 1 H, NH).

7-Ethyl-8-phenylimino-7*H*-tetrazolo[1,5-*a*]pyrazine (5a). A solution of 3-chloro-1-ethyl-2-phenyliminopyrazine (**4a**) (934 mg, 4 mmol) and NaN_3 (260 mg, 4 mmol) in MeOH (13 mL) was refluxed for 10 h. Then the reaction mixture was cooled. The precipitate that formed was filtered off, washed with water, recrystallized from methanol, and dried in air. Product **5a** was obtained in a yield of 724 mg (75%) as yellow flakes, m.p. 132—134 °C. Found (%): C, 59.82; H, 4.82; N, 34.96. $C_{12}H_{12}N_6$.

Calculated (%): C, 59.99; H, 5.03; N, 34.98. ^{1}H NMR, δ: 7.78 and 7.43 (both d, 1 H each, H(5), H(6), ^3J = 5.8 Hz); 7.24 and 6.79 (both m, 2 H each, $H(2)_{Ph}$, $H(3)_{Ph}$); 7.03 (m, 1 H, $H(4)_{Ph}$); 4.11 (q, 2 H, NCH_2, ^3J = 7.0 Hz); 1.37 (t, 3 H, Me, ^3J = 7.0 Hz).

Compounds **5b,c** were synthesized analogously.

7-Ethyl-8-(1-naphthylimino)-7*H*-tetrazolo[1,5-*a*]pyrazine (5b). The yield was 64%, gold-color flakes, m.p. 175—177 °C. Found (%): C, 65.99; H, 4.74; N, 29.08. $C_{16}H_{14}N_6$. Calculated (%): C, 66.19; H, 4.86; N, 28.95. ^{1}H NMR, δ: 7.90—6.80 (m, 9 H, H arom.); 4.27 (q, 2 H, NCH_2, ^3J = 7.0 Hz); 1.49 (t, 3 H, Me, ^3J = 7.0 Hz).

7-Ethyl-8-(4-methoxyphenylimino)-7*H*-tetrazolo[1,5-*a*]pyrazine (5c). The yield was 52%, gold-color flakes, m.p. 111 °C. Found (%): C, 57.76; H, 5.43; N, 31.40. $C_{13}H_{14}N_6O$. Calculated (%): C, 57.78; H, 5.22; N, 31.08. ^{1}H NMR, δ: 7.88 and 7.45 (both d, 1 H each, H(5), H(6), ^3J = 5.8 Hz); 6.80—6.60 (m, 4 H, H arom.); 4.05 (q, 2 H, NCH_2, ^3J = 7.0 Hz); 3.74 (s, 3 H, OMe); 1.30 (t, 3 H, Me, ^3J = 7.0 Hz).

8-(Benzimidazol-1-yl)tetrazolo[1,5-*a*]pyrazine (6a). A mixture of compound **1** (100 mg, 0.64 mmol) and benzimidazole (151 mg, 1.28 mmol) was refluxed in DMF (5 mL) for 0.5 h. Then the reaction mixture was cooled and diluted with water to 15 mL. The precipitate that formed was filtered off and recrystallized from propanol. Product **6a** was obtained in a yield of 64 mg (42%) as colorless crystals, m.p. 272—274 °C. Found (%): C, 55.89; H, 2.89; N, 41.31. $C_{11}H_7N_7$. Calculated (%): C, 55.69; H, 2.97; N, 41.33. ^{1}H NMR, δ: 9.73 (s, 1 H, C(2′)H); 9.38 and 8.40 (both d, 1 H each, C(6)H, C(5)H, ^3J = 4.6 Hz); 8.63 and 7.88 (both m, 1 H each, C(4′)H, C(7′)H); 7.50 (m, 2 H, C(5′)H, C(6′)H). IR, ν/cm^{-1}: 3116, 2957, 2913, 1319, 1064.

8-(Benzotriazol-1-yl)tetrazolo[1,5-*a*]pyrazine (6b). A mixture of compound **1** (156 mg, 1 mmol) and benzotriazole (119 mg, 1 mmol) was refluxed in MeCN (4 mL) in the presence of Na_2CO_3 (106 mg, 1 mmol) for 1 h. Then the reaction mixture was cooled and diluted with water to 40 mL. The precipitate that formed was filtered off and recrystallized from MeCN. Product **6b** was obtained in a yield of 114 mg (48%) as colorless crystals, m.p. 220—222 °C. Found (%): C, 50.20; H, 2.69; N, 46.84. $C_{10}H_6N_8$. Calculated (%): C, 50.42; H, 2.54; N, 47.04. ^{1}H NMR, δ: 9.51 and 8.49 (both d, 1 H each, C(6)H, C(5)H, ^3J = 4.6 Hz); 8.57 and 8.33 (both m, 1 H each, C_6H_4, ^3J = 4.6 Hz); 7.84 and 7.67 (both m, 1 H each, C_6H_4).

Benzotriazolato[1′,2′:1,2]-1,2,3-triazolo[4,5-*b*]pyrazinium (7) (inner salt). Pyrazine **6b** (101 mg, 0.42 mmol) was refluxed in DMF (4 mL) for 3 h. Then DMF was distilled off on a rotary evaporator. The residue was purified by silica gel chromatography using successive elution with $CHCl_3$ and a 1 : 1 acetone—hexane mixture. Compound **7** was obtained in a yield of 44 mg (50%) as yellow crystals, m.p. 219 °C. Found (%): C, 56.99; H, 2.87; N, 40.23. $C_{10}H_6N_6$. Calculated (%): C, 57.14; H, 2.87; N, 39.98. ^{1}H NMR, δ: 8.88 and 8.54 (both d, 1 H each, C(6)H, C(5)H, ^3J = 2.7 Hz); 8.31 and 8.11 (both m, 1 H each, C_6H_4); 7.70 (m, 2 H, C_6H_4). MS, *m/z* (I_{rel} (%)): 210 $[M]^+$ (100); 181 (3.58); 156 (3.95); 128 (63.29); 103 (18.90); 90 (12.96).

8-Phenyltetrazolo[1,5-*a*]-1,2,4-triazolo[3,4-*c*]pyrazine (10). A mixture of compound **1** (100 mg, 0.64 mmol), 5-phenyltetrazole (94 mg, 0.64 mmol), and Na_2CO_3 (41 mg, 0.4 mmol) was refluxed in DMF (5 mL) for 4 h and then diluted with H_2O (10 mL). The precipitate that formed was filtered off and recrystallized from MeCN. Compound **10** was obtained in a yield of 76 mg (50%) as colorless crystals, m.p. 283—285 °C. Found (%): C, 55.48; H, 3.01; N, 41.48. $C_{11}H_7N_7$. Calculated (%): C, 55.70; H, 2.97; N, 41.33. ^{1}H NMR, δ: 8.86 (d, 1 H, H(5), ^3J = 6.1 Hz); 8.42 (d, 1 H, H(6), ^3J = 6.1 Hz); 7.92 (m, 2 H, Ph); 7.70 (m, 3 H, Ph).

X-ray diffraction study of compound 7 was performed on an Xcalibur 3 diffractometer equipped with a CCD detector at 100 K (wavelength of radiation was 0.71073 Å (Mo-K), graphite monochromator). A crystal of dimensions 0.3×0.2×0.1 mm, the monoclinic system, space group $P2(1)/c$, the unit cell parameters a = 9.7794(2) Å, b = 17.1330(3) Å, c = 11.2502(2) Å, α = γ = 90°, β = 103.811(1)°, Z = 8, $F(000)$ = 864. A total of 17515 reflections were collected, of which 5972 reflections were independent (R_{int} = 0.0557). No absorption correction was applied because of the low absorption coefficient (μ = 0.103 mm^{-1}). The structure was solved by direct methods and refined using the SHELXL97 program package[12] by the full-matrix least-squares method with anisotropic (isotropic for H atoms) displacement parameters. The final R factors were as follows: R = 0.0628, wR_2 = 0.1399 ($I > 2\sigma(I)$), GOOF = 1.001.

X-ray diffraction study of compound 10 was performed on an Xcalibur 3 diffractometer equipped with a CCD detector at 295 K (wavelength of radiation was 1.54248 Å (Cu-K), graphite monochromator). A crystal of dimensions 0.3×0.2×0.1 mm, the monoclinic system, space group Cc, the unit cell parameters a = 7.2983(9) Å, b = 13.6873(12) Å, c = 11.1714(16) Å, α = γ = 90°, β = 107.370(13)°, Z = 4, $F(000)$ = 488. A total of 4265 reflections were collected, of which 1347 reflections were independent (R_{int} = 0.0397). No absorption correction was applied because of the low absorption coefficient (μ = 0.101 mm^{-1}). The structure was solved by direct methods and refined using the SHELXL97 program package by the full-matrix least-squares method with anisotropic (isotropic for H atoms) displacement parameters. The final R factors were as follows: R = 0.0396, wR_2 = 0.0978 ($I > 2\sigma(I)$), GOOF = 1.002.

The results of X-ray diffraction studies were deposited with the Cambridge Structural Database with reference codes CCDC 610117 (compound **7**) and CCDC 610118 (compound **10**). These data can be obtained, free of charge, on application to the Cambridge Crystallographic Data Centre, *www.ccdc.cam.ac.uk/data_request/cif*.

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