compound **8**, m.p. 178–180 °C. Found (%): C, 31.39; H, 2.91; F, 50.21; N, 12.52. $C_9H_9F_6N_3 \cdot BF_3$. Calculated (%): C, 31.70; H, 2.66; F, 50.14; N, 12.32. IR, v/cm⁻¹: 3280, 1520 (NH); 1540 sh, 3050 (C=C); 1000–1060 (BF₃). ¹H NMR, δ : 3.10 (t, J = 4.6 Hz, 4 H, CH₂NCH₂); 3.60 (t, J = 4.6 Hz, 4 H, CH₂NCH₂); 3.60 (t, J = 4.6 Hz, 4 H, CH₂—N⁺). ¹⁹F NMR, δ : -60.3 (s, 6 F, 2 CF₃); -158.2 (s, 3 F, BF₃). MS, m/z (I (%)): 273 (100) [M–BF₃]⁺.

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Synthesis and properties of 1,2,4-triazolo[4,3-d]-1,2,4-triazolo-[3,4-f]furazano[3,4-b]pyrazines

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New methods for the synthesis of 1,2,4-triazolo[4,3-d]-1,2,4-triazolo[3,4-f]furazano[3,4-b]pyrazines with functional substituents of various types are proposed and some properties of these compounds are studied.

Key words: 1,2,4-triazolo[4,3-*d*]-1,2,4-triazolo[3,4-*f*]furazano[3,4-*b*]pyrazines; hetero-cyclization reactions; methods of synthesis.

1,2,4-Triazolo[3,4-c]benzopyrazines are of interest as biologically active compounds having diuretic, antiallergic, and antihypertonic action.^{1,2} In order to expand the range of compounds of this type we synthesized fused 1,2,4-triazolo[4,3-d]-1,2,4-triazolo[3,4f]furazano[3,4-b]pyrazines (TTFP) with various functional substituents (Scheme 1).

TTFP are formed by reactions of dihydrazinofurazano[3,4-b]pyrazine derivative (3) with hydrochlorides of carboximidates in glacial AcOH at 60-116 °C. The products of cyclization of compounds 4 and 6 were obtained in 70–80 % yields. Some properties of the synthesized TTFP were studied. It was found that the amino groups in diamine 4 can be transformed into nitro groups upon the action of 30 % H_2O_2 in concentrated H_2SO_4 . Treatment of diester 6 with a mixture of concentrated HNO₃ and H_2SO_4 afforded the tetranitro derivative (7) in 67 % yield. Hydrolysis of compound 7 in aqueous KOH gave the dipotassium salt (8) in 91 % yield. Nitration of salt 8 with concentrated HNO₃ made it possible to synthesize the bis(trinitromethyl) derivative (9). Fluorination of

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salt 8 with XeF_2 gave the respective bis(fluorodinitromethyl) derivative (10).

Experimental

Melting points were determined on a Boetius instrument. Mass spectra were recorded on a Varian MAT CH-6 instrument at 60 eV ionizing energy. ¹H NMR spectra were recorded on a Bruker WM-250 spectrometer; ¹³C and ¹⁴N spectra were obtained on a Bruker AM-300 spectrometer. The ¹³C chemical shifts were measured relative to the solvent, DMSO-d₆ (δ 39.5), and those for ¹⁴N, relative to CH₃NO₂ (δ 0.0) as the external standard. The highfield chemical shifts are given with a minus sign. The ¹H chemical shifts were measured relative to the residual protons of the solvent (DMSO-d₆, δ 2.5). IR spectra were recorded in KBr pellets on a UR-20 spectrophotometer.

4,5-Dichlorofurazano[3,4-b]pyrazine (2). Dry DMF (2.0 mL) was added dropwise at a temperature not exceeding 15–18 °C to a suspension of compound 1 (2.0 g, 13 mmol) in SOCl₂ (15 mL). The mixture was stirred for 0.5 h at 20 °C and for 1 h at 75 °C, cooled to 20 °C, and poured into ice water (100 mL). The precipitate was filtered off, washed with water, and dried to afford 1.23 g (50 %) of compound 2, m.p. 175–177 °C (from Me₂CO). Found (%): C, 24.5; N, 29.1; Cl, 37.3. C₄N₄OCl₂. Calculated (%): C, 24.8; N, 29.3; Cl, 37.1. MS, m/z: 192 [M]⁺. IR, ν/cm^{-1} : 1620, 1575, 1002, 468.

4,5-Dihydrazinofurazano[**3,4-b**]**pyrazine** (**3**). A solution of hydrazine hydrate (4 mL) in MeOH (40 mL) was added dropwise to a solution of compound **2** (2.77 g, 14.5 mmol) in MeOH (110 mL). The mixture was stirred for 3 h at 60 °C and cooled to 20 °C. The precipitate was filtered off, washed with H₂O, MeOH, and Et₂O, and dried to afford 2.54 g (96.5 %) of compound **3**, m.p. 260–262 °C (from H₂O). Found (%): C, 26.0; H, 3.7; N, 61.5. C₄H₆N₈O. Calculated (%): C, 26.37; H, 3.30; N, 61.8. IR, ν/cm^{-1} : 3337, 3248, 3160, 1641, 1620, 1595, 1567, 1541, 1521, 1356, 1316, 1253, 1113, 1031, 948, 821.

4,9-Bis(aminofurazanyl)-1,2,4-triazolo[4,3-d]-1,2,4-triazolo[3,4-f]furazano[3,4-b]pyrazine (4). A mixture of compound 3 (2.25 g, 12 mmol) and ethyl aminofurazanyl-carboximidate hydrochloride in glacial AcOH (60 mL) was stirred for 0.5 h at 50–60 °C and then for 3 h with boiling. The precipitate was filtered off, washed with H₂O, and dried to afford 1.4 g of compound 4. The mother liquor was cooled to 20 °C, diluted with H₂O, and neutralized with NaHCO₃ to pH ~7. The precipitate was filtered off, washed with H₂O, and dried to afford an additional amount of compound 4 (1.13 g). The precipitates were combined to give 2.53 g (55.6 %) of 4, m.p. 210 °C (decomp.) (from EtOH/H₂O, 1:1). Found (%): C, 32.4; H, 1.05; N, 53.45. C₁₀H₄N₁₄O₃. Calculated (%): C, 32.6; H, 1.08; N, 53.26. IR, v/cm⁻¹: 3400, 3300, 1630, 1535, 1360, 1325, 1250, 995, 815.

4,9-Bis(nitrofurazanyl)-1,2,4-triazolo[4,3-d]-1,2,4-triazolo[3,4-f]furazano[3,4-b]pyrazine (5). Compound 4 (0.96 g, 2 mmol) was gradually added at 50-60 °C to a vigorously stirred mixture of 30 % H2O2 (8 mL) and 95 % H2SO4 (10 mL). The mixture was heated to 60-70 °C, stirred for 1 h, cooled to 20 °C, and poured into ice water (50 mL). The precipitate was filtered off, washed with H₂O, and dried to afford 0.08 g of compound 5. The mother liquor was extracted with Et_2O (5 × 50 mL), the extract was dried with MgSO₄, and the solvent was removed in vacuo. Et₂O (30 mL) was added to the oily residue, and the resulting precipitate was filtered off and dried to give an additional amount (0.16 g) of compound 5. The mother liquor was diluted with H_2O ; the precipitate was filtered off, washed with H₂O, and dried to give 0.11 g more of compound 5. In total, 0.35 g (32 %) of compound 5 was obtained, m.p. 242 °C (from HNO₃). Found (%): C, 28.30; N, 45.50. C₁₀N₁₄O₇. Calculated (%): C, 28.04; N, 45.79. MS, m/z: 428 [M]⁺. IR, v/cm⁻¹: 1618, 1560, 1500, 1420, 1360, 1340, 1105, 1000, 960, 815. ¹³C NMR, δ: 137.08 (s); 139.08 (s); 141.30 (s); 143.29 (s, C(3a), C(4), C(6a), <u>C</u>-C-NO₂); 159.98 (C-NO₂). ¹⁴N NMR, δ : -36.70 $(C-NO_2, v_{1/2} = 70 \text{ Hz}).$

4,9-Bis(ethoxycarbonylmethyl)-1,2,4-triazolo[4,3-d]-1,2,4-triazolo[3,4-f]furazano[3,4-b]pyrazine (6). A mixture of compound 3 (1.82 g, 10 mmol) and ethyl ethoxycarbonyl-acetimidate hydrochloride (4.5 g, 23 mmol) in glacial AcOH (40 mL) was stirred for 1 h at 50--60 °C and for 1 h with

boiling, and then cooled to 20 °C. The precipitate was filtered off. The mother liquor was concentrated to 10–15 mL, diluted with H₂O (20 mL), neutralized with NaHCO₃ to pH ~7, and cooled to 5–10 °C. The precipitate was filtered off, washed with H₂O (10 mL), and dried to give 2.6 g (70 %) of compound **6**, m.p. 125 °C (from H₂O). Found (%): C, 45.10; H, 3.70; N, 30.10. C₁₄H₁₄N₈O₅. Calculated (%): C, 44.92; H, 3.74; N, 29.95. MS, *m/z*: 374 [M]⁺. IR, v/cm⁻¹: 2966, 2920, 1730, 1600, 1580, 1527, 1440, 1393, 1360, 1327, 1313, 1300, 1260, 1180, 1140, 1080, 1013, 987, 973, 920, 860, 833. ¹H NMR, δ : 1.22 (t, *J* = 7.1 Hz, 6 H, CH₃); 4.22 (q, *J* = 7.1 Hz, 4 H, OCH₂); 4.60 (s, 4 H, CH₂). ¹³C NMR, δ : 14.08 (qt, ¹*J*_{C-H} = 127.3 Hz, ²*J*_{C-H} = 2.4 Hz, CH₃); 32.16 (t, ¹*J*_{C-H} = 133.5 Hz, CH₂); 62.02 (tq, ¹*J*_{C-H} = 148.5 Hz, ²*J*_{C-H} = 4.6 Hz, OCH₂); 141.80 (s); 141.93 (s, C(3a), C(6a)); 147.34 (t, ²*J*_{C(4)-CH2} = 7.3 Hz, C(4)); 167.04 (tt, ²*J*_{C-H} = 6.6 Hz, ³*J*_{C-H} = 2.6 Hz, COO).

4,9-Bis(ethoxycarbonyldinitromethyl)-1,2,4-triazolo[4,3d]-1,2,4-triazolo[3,4-f]furazano[3,4-b]pyrazine (7). Compound 6 (0.5 g, 1.3 mmol) was dissolved portionwise at 2-8 °C in a mixture of HNO₃ (5 mL, d = 1.5 g cm⁻³) and H₂SO₄ (6 mL, d = 1.84 g cm⁻³), then the temperature was increased to 20 °C. The mixture was stirred for 4 h and poured onto 50 g of crushed ice. The residue was filtered off, washed with H₂O, and dried to give 0.5 g (67 %) of compound 7, m.p. 110-113 °C. Found (%): C, 30.3; H, 1.9; N, 30.6. C₁₄H₁₀N₁₂O₁₃. Calculated (%): C, 30.32; H, 1.81; N, 30.32. IR, v/cm⁻¹: 2970, 2920, 1780, 1613, 1580, 1460, 1366, 1286, 1226, 1200, 1080, 933, 833, 780. ¹H NMR, δ : 1.45 (t, J =7.1 Hz, 6 H, CH₃); 4.77 (q, J = 7.1 Hz, 4 H, OCH₂). ¹³C NMR, δ : 13.76 (qt, ${}^{1}J_{C-H} = 128.3$ Hz, ${}^{2}J_{C-H} = 2.7$ Hz, CH₃); 69.27 (tq, ${}^{1}J_{C-H} = 132.8$ Hz, ${}^{2}J_{C-H} = 4.3$ Hz, OCH₂); 112.51 (s, C(NO₂)₂); 141.61 (s); 142.16 (s, C(3a), C(6a)); 145.68 (s, C(4)); 155.39 (t, ${}^{3}J_{C-H} = 3.9$ Hz, COO). ¹⁴N NMR, δ : -30.91 (s, C(NO₂)₂, $v_{1/2}$ = 34 Hz). Dipotassium 4,9-bis(dinitromethyl)-1,2,4-triazolo[4,3-d]-

Dipotassium 4,9-bis(dinitromethyl)-1,2,4-triazolo[4,3-*d*]-**1,2,4-triazolo**[3,4-*f*]furazano[3,4-*b*]pyrazine (8). 40 % aqueous KOH was added to a solution of compound 7 (0.5 g, 0.9 mmol) in EtOH (10 mL) with stirring at 20 °C until pH 10 was reached. The mixture was kept for 15 min, then AcOH was added to a weakly acid pH. Then the mixture was kept for 15 h at 5–10 °C. The resulting precipitate was filtered off, washed with EtOH (2 × 10 mL) and Et₂O (20 mL), and dried in the air to give 0.4 g (91 %) of compound 8, m.p. 250 °C (decomp.). Found (%): C, 19.8; N, 35.3. C₈N₁₂O₉K₂. Calculated (%): C, 19.75; N, 34.57. IR, v/cm^{-1} : 1607, 1580, 1527, 1466, 1380, 1220, 1127, 1113, 993, 953, 833, 813, 766, 740. UV (H₂O), λ/nm (ε): 347 (32740). ¹³C NMR, δ : 121.19 (s, C(NO₂)₂); 141.61 (s); 142.16 (s, C(3a), C(6a)); 145.07 (s, C(4)). ¹⁴N NMR, δ : -21.30 (c, C(NO₂)₂, $v_{1/2}$ = 500 Hz).

4,9-Bis(trinitromethyl)-1,2,4-triazolo[**4**,**3**-*d*]-**1,2,4-triazolo**[**3,4**-*f*]**furazano**[**3,4**-*b*]**pyrazine (9).** Conc. H₂SO₄ (5 mL) was added at 0–5 °C with stirring to a solution of compound **8** (0.5 g, 1 mmol) in HNO₃ (5 mL, d = 1.50 g cm⁻³). The mixture was heated to 20 °C, kept for 6 h, and poured onto 50 g of crushed ice. The precipitate was filtered off, washed with ice water, and air-dried to give 0.35 g (68 %) of compound **9**, m.p. 128 °C (decomp., from dichloroethane). Found (%): C, 19.0; N, 39.2. C₈N₁₄O₁₃. Calculated (%): C, 19.2; N, 39.2. IR, v/cm⁻¹: 1613, 1600, 1580, 1560, 1513, 1380, 1327, 1266, 1087, 1000, 933, 860, 827, 716. ¹³C NMR, δ : 121.22 (s, C(NO₂)₃); 138.21 (s); 141.80 (s, C(3a), C(6a)); 145.98 (s, C(4)). ¹⁴N NMR, δ : -40.90 (C(NO₂)₃, v_{1/2} = 17 Hz).

4,9-Bis(fluorodinitromethyl)-1,2,4-triazolo[4,3-d]-1,2,4-triazolo[3,4-f]furazano[3,4-b]pyrazine (10). XeF₂ (2 g, 12 mmol) was added with stirring (~20 °C) to a suspension of compound **8** (0.83 g, 2 mmol) in dry MeCN (60 mL). The mixture was stirred for 4 h and left for 48 h. The precipitate was filtered off, and the mother liquor was evaporated in the vacuum of a water-jet pump to give 0.68 g (89.5 %) of compound **10**, m.p. 179–181 °C (from HNO₃). Found (%): C, 21.6; N, 37.4; F, 8.7. C₈N₁₂O₉F₂. Calculated (%): C, 21.52; N, 37.67; F, 8.52. IR, v/cm⁻¹: 1613, 1580, 1566, 1547, 1480, 1400, 1340, 1333, 1307, 1293, 1227, 1213, 1107, 1087, 1073, 947, 873, 833, 800. ¹³C NMR, δ : 115.26 (d, ¹J_{C-F} = 292.5 Hz, C(NO₂)₂F); 139.65 (d, ²J_{C-F} = 26.5 Hz, C(4)); 141.54 (s); 144.84 (s, C(3a), C(6a)). ¹⁴N NMR, δ : -31.45 (s, C(NO₂)₂F, v_{1/2} = 48 Hz).

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