3-Amino-4-(α-nitroalkyl-*ONN*-azoxy)furazans and some of their derivatives

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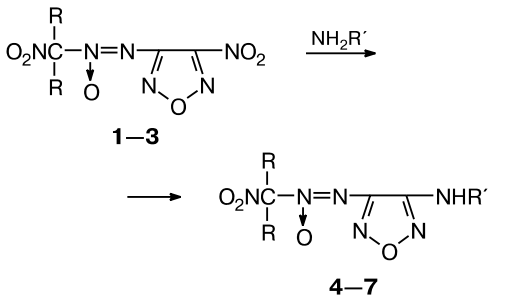
Synthetic procedures towards 3-amino-4-(α-nitroalkyl-*ONN*-azoxy)furazans and their derivatives involving nucleophilic displacement of the nitro group of 3-nitro-4-(α-nitroalkyl-*ONN*-azoxy)furazans on treatment with ammonia, primary and secondary amines, including diamines, were developed.

Key words: furazans, (α-nitroalkyl-*ONN*-azoxy)furazans, 3-amino-4-(α-nitroalkyl-*ONN*-azoxy)furazans, nitrofurazans, aminofurazans, nucleophilic substitution.

Earlier,[1] we have developed method for the synthesis of bis(α-nitroalkyl-*ONN*-azoxy)furazans and their derivatives by the reaction of 3,4-diaminofurazan with geminal nitronitroso compounds in the presence of dibromoisocyanuric acid (DBI). Despite the moderate yields (20—55%) of the aforesaid compounds and stability of the intermediates, 3-amino-4-(α-nitroalkyl-*ONN*-azoxy)furazans, the latter were not obtained in preparative yields even after changing the reaction conditions. Since the compounds of this type are of interest and could be used as half-products towards other energetic compounds, in the present work we suggest another strategy for their synthesis. The approach involved the nucleophilic displacement known for the furazans[2—4], namely, the displacement of the nitro group on the furazan ring by N-nucleophiles. It was found that 3-nitro-4-(α-nitroalkyl-*ONN*-azoxy)furazans and some of their derivatives (compounds **1**—**3**) reacted rather smoothly with ammonia at room temperature in the inert solvents to give target 3-amino-4-(α-nitroalkyl-*ONN*-azoxy)furazans **4**—**7** (Scheme 1).

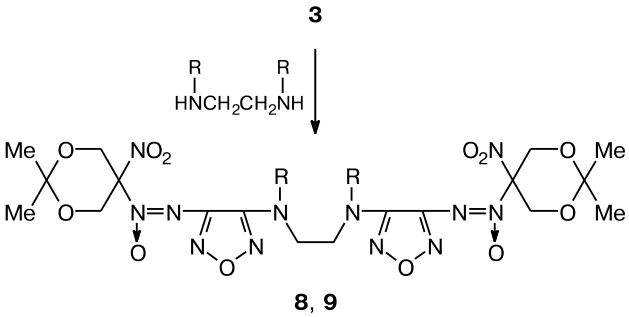
Scheme 1



R = Me (**1**, **4**); R + R = $(CH_2)_5$ (**2**, **5**), $CH_2OCMe_2OCH_2$ (**3**, **6**, **7**); R´ = H (**4**—**6**); Me (**7**)

On going from ammonia to methylamine, the reaction (performed in H_2O—CH_2Cl_2) proceeded more readily. It is of note that disubstitution products **8**—**9** were predominantly formed in the reactions with diamines carried out even with the large excess of the latter (Scheme 2).

Scheme 2



R = H (**8**); R + R = $(CH_2)_2$ (**9**)

However, we were not able to extend this procedure on the aromatic amines (the reactions were carried out on the example of *p*-toluidine); no formation of the substitution product was observed.

In our opinion, these results indicate that electronic effect (electron-withdrawing or electron-releasing) of the α-nitroalkyl substituent at the *ONN*-azoxy group does not affect the nucleophilic substitution of the nitro group on the furazan ring. It is true only when the substituent is stable upon the nucleophilic attack or transforms into stable structural fragment.

Thus, no individual products of the reaction of 3-(dibromonitromethyl-*ONN*-azoxy)-4-nitrofurazan and 3-(2-hydroxy-1-hydroxymethyl-1-nitroethyl-1-*ONN*-azoxy)-4-nitrofurazan with ammonia were isolated, although in

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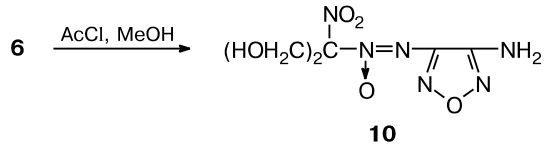
the latter case the target product of the displacement of the nitro group (*i.g.*, compound **10**) is rather stable and was prepared by solvolysis of aminofurazan **6** (Scheme 3).

Scheme 3



10

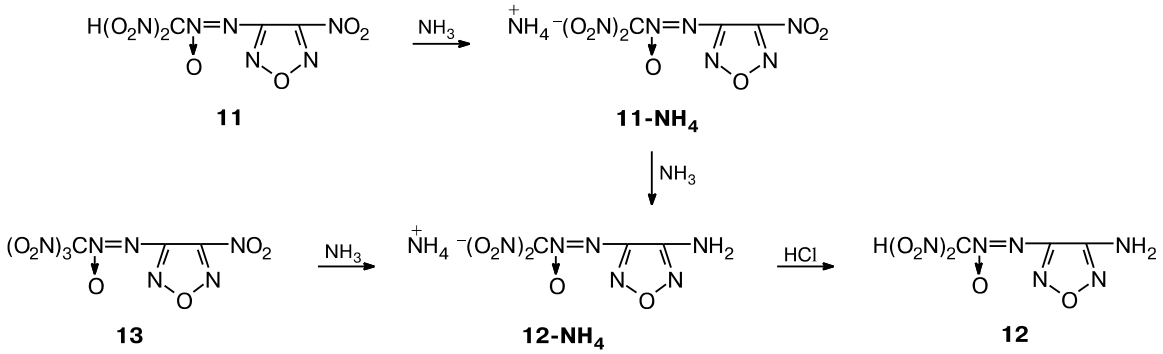
Reaction of 3-(dinitromethyl-*ONN*-azoxy)-4-nitrofurazan (**11**) with ammonia proceeded in two steps. In CH_2Cl_2 after 2 min of the reaction, ammonium salt **11-NH$_4$** was formed in 90% yield. This salt also formed on bubbling of NH_3 through a solution of **11** in MeCN and then within 2.5 h transformed into ammonium salt of 3-amino-4-(dinitromethyl-*ONN*-azoxy)furazan (**12-NH$_4$**) in 95% yield (Scheme 4). Compound **12-NH$_4$** was obtained in a yield of 78% in two steps also (denitration and ammonolysis) by treatment of 3-nitro-4-(trinitromethyl-*ONN*-azoxy)furazan (**13**) with ammonia.

Treatment of salt **12-NH$_4$** with gaseous HCl in MeOH afforded low stable crystalline 3-nitro-4-(dinitromethyl-*ONN*-azoxy)furazan (**12**) with m.p. 85—87.5 °C (decomp.).

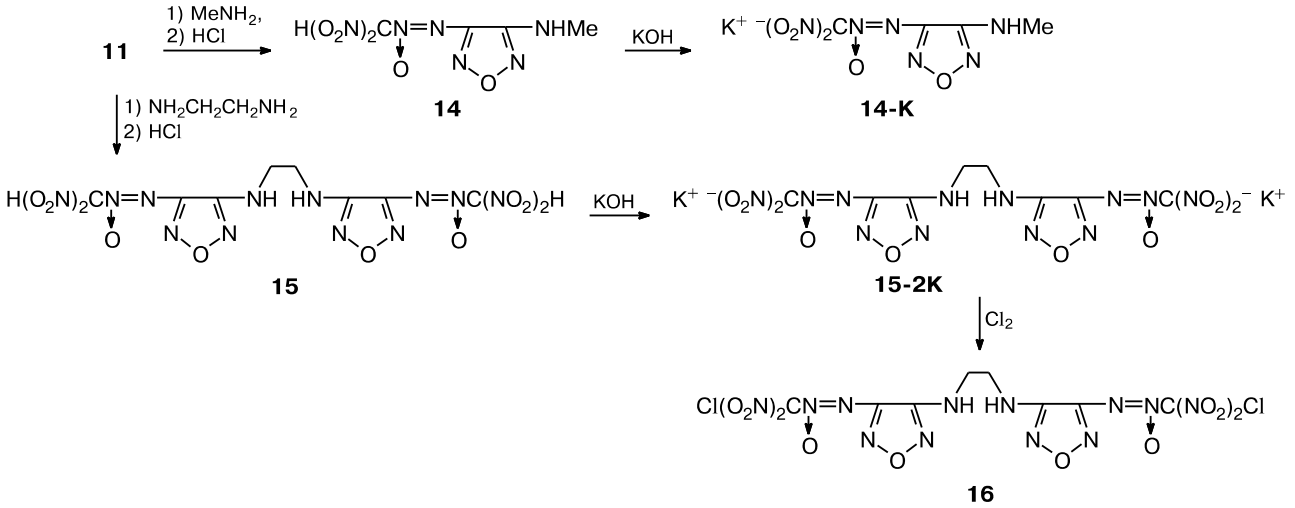
Likewise ammonia, methylamine reacted with **11**. In this reaction due to the higher reactivity of methylamine with respect to ammonia, after methylammonium salt formation bearing the dinitromethyl group, a product of substitution of the methylamino group for the nitro group immediately formed. Treatment of this product with HCl resulted in 3-(*N*-methylamino)-4-(dinitromethyl-*ONN*-azoxy)furazan (**14**). For purification and unambiguous identification, furazan **14** was converted into more stable potassium salt **14-K** by treatment with KOH in MeOH (Scheme 5).

Compound **11** reacted with ethylenediamine similarly but with lower rate to give (after acidification) a product at both the amino group of ethylnediamine, *N*,*N*´-bis-[4-(dinitromethyl-*ONN*-azoxy)furazan-3-yl]ethylenedi-

Scheme 4



Scheme 5



amine (**15**). For identification, diamine **15** as in the case of compound **11** was converted into dipotassium salt **15-2K**, however, the latter turned to be highly hygroscopic and was transformed into dichloro derivative **16** by treatment with gaseous chlorine (see Scheme 5).

In summary, in the present work synthetic procedure towards 3-amino-4-(α-nitroalkyl-*ONN*-azoxy)furazans and some of their derivatives by displacement of the nitro groups of 3-nitro-4-(α-nitroalkyl-*ONN*-azoxy)furazans on treatment with ammonia, primary and secondary amines, and diamines as well, was developed. In the case of (α-nitroalkyl-*ONN*-azoxy)furazans, no nucleofuge activity was observed.

Experimental

The course of the reactions was monitored by TLC on the Silufol UV-254 plates. IR spectra were recorded on a Bruker Alpha instrument. ^{1}H, ^{13}C, and ^{14}N NMR spectra were run on a Bruker AM-300 instrument. High resolution mass spectra with electrospray ionization were obtained on a Bruker micrOTOF II mass spectrometer.[5] Melting points were determined on a Koeffler apparatus. The starting compounds 3-amino-4-nitrofurazan,[6] 1-nitro-1-nitrosocyclohexane,[7] DBI,[8] 3-(dibromonitromethyl-*ONN*-azoxy)-4-nitrofurazan,[9] 3-(2-hydroxy-1-hydroxymethyl-1-nitroethyl-1-*ONN*-azoxy)-4-nitrofurazan,[9] compounds **1**,[9] **3**,[9] **11**,[9] and **13**[9] were synthesized by the known procedures.

3-Nitro-4-(1-nitrocyclohexyl-*ONN*-azoxy)furazan (2). To a stirred solution of 1-nitro-1-nitrosocyclohexane (1.01 g, 6.39 mmol) in anh. CH_2Cl_2 (50.0 mL), DBI (2.20 g, 7.67 mmol) and 3-amino-4-nitrofurazan (0.83 g, 6.39 mmol) were added at 20 °C. The suspension was stirred at 20 °C for 24 h, the precipitate was filtered off, the mother liquor was concentrated *in vacuo*, purification of the residue by column chromatography (silica gel, elution with benzene—hexane, 1 : 4) afforded compound **2** (1.13 g, 62%), yellowish oil. Found (%): C, 33.71; H, 3.71; N, 29.55. $C_8H_{10}N_6O_6$. Calculated (%): C, 33.57; H, 3.50; N, 29.37. IR (KBr), ν/cm^{-1}: 1573 (v.s, C—NO_2); 1542 (s, C—NO_2); 1506 (v.s, N=N→O); 1373 (s, C—NO_2); 1351 (s, C—NO_2); 1306 (m, N=N→O). ^{1}H NMR ($CDCl_3$), δ: 1.65 (m, 2 H, CH_2(CH_2CH_2)$_2$); 1.81 (m, 4 H, CH_2(CH_2CH_2)$_2$); 2.77 (m, 4 H, (CH_2)$_2$$CNO_2$). ^{13}C NMR (75 MHz, acetone-d_6), δ: 22.80 (CH_2(CH_2CH_2)$_2$), 23.71 (CH_2(CH_2CH_2)$_2$), 33.57 ((CH_2)$_2$$CNO_2$), 117.90 (($CH_2$)$_2CNO_2$), 149.91 (C—$NO_2$), 156.47 (C—N=N→O). ^{14}N NMR (22 MHz, acetone-d_6), δ: −35.86 (N→O, NO_2, $\Delta\nu_{0.5}$ = 36 Hz); −2.94 ((CH_2)$_2$$CNO_2$, $\Delta\nu_{0.5}$ = 138 Hz).

3-Amino-4-(1-methyl-1-nitroethyl-1-*ONN*-azoxy)furazan (4). ***A.*** NH_3 was bubbled through a solution of **1** (1.04 g, 4.23 mmol) in CH_2Cl_2 (35.0 mL) for 4 h at 20 °C, the mixture was kept in refrigerator for 24 h, and the solvent was removed *in vacuo*. Purification of the residue by column chromatography (silica gel, elution with benzene) afforded compound **4** (0.800 g, 88%), yellowish crystals, m.p. 89.5—91.0 °C (from $CHCl_3$—hexane). Found (%): C, 27.94; H, 3.86; N, 38.43. $C_5H_8N_6O_4$. Calculated (%): C, 27.78; H, 3.70; N, 38.89. IR (KBr), ν/cm^{-1}: 3464 (s, NH_2); 3328 (s, NH_2); 1624 (v.s, NH_2); 1576 (v.s, C—NO_2); 1504 (v.s, N=N→O); 1380 (s, C—NO_2); 1268 (s, N=N→O). ^{1}H NMR ($CDCl_3$), δ: 2.29 (s, 6 H, 2 Me); 4.53 (s, 2 H, NH_2). ^{13}C NMR (75 MHz, acetone-d_6), δ: 24.69 (Me), 114.56 (C—NO_2), 148.34 (C—NH_2), 154.16 (C—N=N→O). ^{14}N NMR (22 MHz, $CDCl_3$), δ: −45.6 (N→O, $\Delta\nu_{0.5}$ = 97 Hz); −2.6 (NO_2, $\Delta\nu_{0.5}$ = 85 Hz). ^{14}N NMR (22 MHz, acetone-d_6), δ: −43.7 (N→O, $\Delta\nu_{0.5}$ = 83 Hz); 1.2 (NO_2, $\Delta\nu_{0.5}$ = 76 Hz).

B. To a solution of **1** (3.50 g, 14.2 mmol) in MeCN (70 mL), 25% NH_4OH (11 mL) was added at 20 °C. The mixture was kept at 20 °C for 24 h, the solvent was removed *in vacuo*, the residue was washed with water to give compound **4** (2.52 g, 82%). The physicochemical parameters of the sample are in agreement with those of the compound obtained by the method ***A***.

3-Amino-4-(1-nitrocyclohexyl-*ONN*-azoxy)furazan (5). NH_3 was bubbled through a stirred solution of **2** (0.180 g, 0.629 mmol) in CH_2Cl_2 (8.00 mL) for 4 h at 20 °C. The mixture was kept in refrigerator for 24 h, the solvent was removed *in vacuo*. Purification of the residue by preparative TLC (silica gel, elution with benzene—acetone, 5 : 1) afforded compound **5** (0.130 g, 81%), yellowish crystals, m.p. 81.0—83.0 °C (from H_2O—Pr^iOH). MS (ESI), *m/z*: 257.1003 $[M + H]^+$; calculated for $C_8H_{12}N_6O_4$, $[M + H]^+$, *m/z*: 257.0993. IR (KBr), ν/cm^{-1}: 3454 (s, NH_2), 3334 (s, NH_2), 1626 (v.s, NH_2), 1561 (v.s, C—NO_2), 1504 (v.s, N=N→O), 1325 (s, C—NO_2), 1256 (m, N=N→O). ^{1}H NMR ($CDCl_3$), δ: 1.62 (m, 2 H, CH_2(CH_2CH_2)$_2$); 1.77 (m, 4 H, CH_2(CH_2CH_2)$_2$); 2.73 (m, 4 H, (CH_2)$_2$$CNO_2$); 4.53 (s, 2 H, NH_2). ^{13}C NMR (75 MHz, acetone-d_6), δ: 22.92 (CH_2(CH_2CH_2)$_2$), 23.83 (CH_2(CH_2CH_2)$_2$), 33.50 ((CH_2)$_2$$CNO_2$), 116.99 (($CH_2$)$_2CNO_2$), 148.45 (C—$NH_2$), 154.25 (C—N=N→O). ^{14}N NMR (22 MHz, acetone-d_6), δ: −46.41 (N→O, $\Delta\nu_{0.5}$ = = 86 Hz); −0.21 (NO_2, $\Delta\nu_{0.5}$ = 92 Hz).

3-Amino-4-(2,2-dimethyl-5-nitro-1,3-dioxan-5-yl-*ONN*-azoxy)furazan (6). ***A.*** NH_3 was bubbled through a stirred solution of **3** (0.900 g, 2.83 mmol) in CH_2Cl_2 (30.0 mL) for 4 h at 20 °C. The mixture was kept in refrigerator for 24 h, the solvent was removed *in vacuo*. Purification of the residue by column chromatography (silica gel, elution with benzene) afforded compound **6** (0.650 g, 80%), bright yellow crystals, m.p. 150.0—152.0 °C (from $CHCl_3$). Found (%): C, 33.43; H, 4.03; N, 29.18. $C_8H_{12}N_6O_6$. Calculated (%): C, 33.33; H, 4.17; N, 29.17. IR (KBr), ν/cm^{-1}: 3465 (s, NH_2), 3347 (v.s, NH_2), 1629 (v.s, NH_2), 1575 (v.s, C—NO_2), 1506 (v.s, N=N→O), 1385 (s, C—NO_2), 1301 (m, N=N→O). ^{1}H NMR (acetone-d_6), δ: 1.45, 1.53 (both s, 6 H, 2 Me); 4.96 (m, 4 H, CH_2); 6.00 (s, 2 H, NH_2). ^{13}C NMR (75 MHz, acetone-d_6), δ: 21.12 (Me), 25.01 (Me), 62.68 (CH_2), 100.75 (C(Me)$_2$), 107.14 (C—NO_2), 148.04 (C—NH_2), 154.48 (C—N=N→O). ^{14}N NMR (22 MHz, acetone-d_6), δ: −55.87 (N→O, $\Delta\nu_{0.5}$ = 81 Hz); −10.58 (NO_2, $\Delta\nu_{0.5}$ = 86 Hz).

B. To a solution of compound **3** (0.5 g, 1.6 mmol) in CH_2Cl_2 (30 mL), 25% NH_4OH (2 mL) was added at 20 °C. The mixture was stirred at 20 °C for 24 h, the aqueous layer was separated, 25% NH_4OH (2 mL) was added to the organic phase, and the mixture was stirred at 20 °C for 6 days. The organic phase was separated, washed with water (3×5 mL), dried with $MgSO_4$, the solvent was removed *in vacuo*, the residue was washed with hexane—diethyl ether to give compound **6** (0.327 g, 73%). The physicochemical parameters of the sample are in agreement with those of the compound obtained by the method ***A***.

3-(*N*-Methylamino)-4-(2,2-dimethyl-5-nitro-1,3-dioxan-5-yl-*ONN*-azoxy)furazan (7). To a 0 °C solution of $MeNH_2$ (0.1 g, 3.23 mmol) in water (10.0 mL), a solution of compound **3** (0.2 g, 0.629 mmol) in CH_2Cl_2 (10.0 mL) was added with vigorous stirring. Emulsion was stirred at 20 °C for 1.5 h, diluted with water (10 mL), the products were extracted with CH_2Cl_2 (4×10 mL),

the organic layer was separated, washed with water (3×10 mL), 5% aqueous HCl (3×10 mL), 5% aqueous Na_2CO_3 (3×10 mL), and water (3×10 mL), the organic phase was dried with $MgSO_4$. Removal of the solvent *in vacuo* and purification of the residue by preparative TLC (silica gel, elution with benzene—acetone, 5 : 1) afforded compound **7** (0.152 g, 80%), bright yellow crystals, m.p. 50.0—52.0 °C. MS (ESI), *m/z* 303.1048 $[M + H]^+$; calculated for $C_9H_{14}N_6O_6$, $[M + H]^+$, *m/z*: 303.1048. IR (KBr), ν/cm^{-1}: 3432 (m, NH), 1612 (v.s, N—H), 1576 (v.s, C—NO_2), 1508 (v.s, N=N→O), 1380 (s, C—NO_2), 1296 (s, N=N→O). ^{1}H NMR ($CDCl_3$), δ: 1.48, 1.52 (both s, 6 H, Me); 3.05 (s, 3 H, Me); 4.39 (s, 1 H, NH); 4.78 (s, 4 H, CH_2). ^{13}C NMR (75 MHz, acetone-d_6), δ: 21.10 (C—Me), 24.99 (C—Me), 29.32 (NHMe), 62.63 (CH_2), 100.73 (C(Me)$_2$), 107.05 (C—NO_2), 147.45 (C—NHMe), 155.72 (C—N=N→O). ^{14}N NMR (22 MHz, acetone-d_6), δ: −56.69 (N→O, $\Delta\nu_{0.5}$ = 73 Hz); −10.98 (NO_2, $\Delta\nu_{0.5}$ = 86 Hz).

***N,N´*-Bis[4-(2,2-dimethyl-5-nitro-1,3-dioxan-5-yl-*ONN*-azoxy)furazan-3-yl]ethylenediamine (8).** To a 0 °C solution of $H_2NCH_2CH_2NH_2$ (0.04 g, 0.667 mmol) and $NaHCO_3$ (0.05 g, 0.6 mmol) in water (2.0 mL), a solution of compound **3** (0.17 g, 0.535 mmol) in CH_2Cl_2 (2.0 mL) was added with vigorous stirring. The emulsion was stirred at 20 °C for 48 h, the precipitate formed was filtered, washed with water to give 0.07 mg of compound **8**. The mother liquor was diluted with water (10 mL), the product was extracted with CH_2Cl_2 (4×10 mL), the organic layer was separated, washed with water (3×10 mL), 5% aqueous HCl (3×10 mL), 5% aqueous Na_2CO_3 (3×10 mL), and water (3×10 mL), and dried with $MgSO_4$. Removal of the solvent *in vacuo* and purification of the residue by preparative TLC (silica gel, elution with benzene—acetone, 4 : 1) afforded 0.05 g of compound **8**. Total yield was 0.120 g (75%), bright yellow crystals, m.p. 187.0—189.0 °C (from Pr^{i}OH). Found (%): C, 35.92; H, 4.38; N, 27.74. $C_{18}H_{26}N_{12}O_{12}$. Calculated (%): C, 35.88; H, 4.32; N, 27.91. IR (KBr), ν/cm^{-1}: 3400 (s, NH), 1604 (v.s, N—H), 1576 (v.s, C—NO_2), 1504 (v.s, N=N→O), 1380 (s, C—NO_2), 1300 (m, N=N→O). ^{1}H NMR (acetone-d_6), δ: 1.48, 1.53 (both s, 12 H, Me); 3.64 (s, 4 H, CH_2NH); 4.94 (m, 8 H, $(CH_2)_2CNO_2$); 6.35 (s, 2 H, NH). ^{1}H NMR ($CDCl_3$), δ: 1.26 (s, 12 H, Me); 3.70 (s, 4 H, CH_2NH); 4.78 (s, 8 H, $(CH_2)_2CNO_2$); 4.86 (s, 2 H, NH). ^{1}H NMR (DMSO-d_6), δ: 1.48, 1.53 (both s, 12 H, Me); 3.48 (s, 4 H, CH_2NH); 4.86 (m, 8 H, $(CH_2)_2CNO_2$); 7.04 (s, 2 H, NH). ^{13}C NMR (75 MHz, acetone-d_6), δ: 21.31 (C—Me), 24.78 (C—Me), 42.91 (CH_2NH), 62.62 ($(CH_2)_2CNO_2$), 100.78 (C(Me)$_2$), 107.16 (C—NO_2), 147.59 (C—NH), 154.97 (C—N=N→O). ^{14}N NMR (22 MHz, acetone-d_6), δ: −55.8 (N→O, $\Delta\nu_{0.5}$ = 138 Hz), −9.7 (NO_2, $\Delta\nu_{0.5}$ = 158 Hz).

1,4-Bis[4-(2,2-dimethyl-5-nitro-1,3-dioxan-5-yl-*ONN*-azoxy)furazan-3-yl]piperazine (9). To a 0 °C solution of piperazine (0.060 g, 0.698 mmol) and $NaHCO_3$ (0.050 g, 0.595 mmol) in water (2.0 mL), a solution of compound **3** (0.160 g, 0.503 mmol) in CH_2Cl_2 (2.0 mL) was added with vigorous stirring. The emulsion was stirred at 20 °C for 48 h, diluted with water (10 mL), the product was extracted with CH_2Cl_2 (4×10 mL), the organic layer was separated, washed with water (3×10 ml), 5% aqueous HCl (3×10 mL), 5% Na_2CO_3 (3×10 mL), and water (3×10 mL), and dried with $MgSO_4$. Removal of the solvent *in vacuo* and purification of the residue by preparative TLC (silica gel, elution with benzene—acetone, 10 : 1) afforded compound **9** (0.100 g, 63%), yellowish crystals, m.p. 192.0—194.0 °C (from Pr^{i}OH). Found (%): C, 38.35; H, 4.50; N, 26.77. $C_{20}H_{28}N_{12}O_{12}$. Calculated (%): C, 38.22; H, 4.46; N, 26.75. IR (KBr), ν/cm^{-1}: 1571 (v.s, C—NO_2), 1519 (v.s, N=N→O), 1382 (s, C—NO_2), 1279 (m, N=N→O). ^{1}H NMR ($CDCl_3$), δ: 1.50, 1.52 (both s, 12 H, Me); 3.63 (s, 8 H, CH_2N); 4.79 (s, 8 H, $(CH_2)_2CNO_2$). ^{13}C NMR (75 MHz, acetone-d_6), δ: 22.12 (C—Me), 23.94 (C—Me), 47.75 ($(CH_2)_2N$), 62.64 ($(CH_2)_2CNO_2$), 100.95 (C(Me)$_2$), 107.46 (C—NO_2), 148.34 (C—N(CH_2)$_2$), 156.64 (C—N=N→O). ^{14}N NMR (22 MHz, acetone-d_6), δ: −11.5 (N→O, $\Delta\nu_{0.5}$ = = 162 Hz), −55.6 (NO_2, $\Delta\nu_{0.5}$ = 92 Hz).

3-Amino-4-(2-hydroxy-1-hydroxymethyl-1-nitroethyl-1-*ONN*-azoxy)furazan (10). To a suspension of **6** (0.320 g, 1.11 mmol) in MeOH (4.0 mL), AcCl (1.20 mL, 1.26 g, 16.1 mmol) was added dropwise at 20 °C. The mixture was stirred at 20 °C for 0.5 h, the solvent was removed *in vacuo*. Purification of the residue by preparative TLC (silica gel, elution with benzene—acetone, 1.5 : 1) and further trituration of the oily product with diethyl ether—hexane gave compound **10** (0.243 g, 88%), yellowish crystals, m.p. 110.0—112.5 °C. Found (%): C, 24.48; H, 3.38; N, 33.57. $C_5H_8N_6O_6$. Calculated (%): C, 24.19; H, 3.23; N, 33.87. IR (KBr), ν/cm^{-1}: 3480 (v.s, NH_2), 3376 (v.s, NH_2), 1628 (v.s, NH_2), 1588 (v.s, C—NO_2), 1496 (v.s, N=N→O), 1360 (s, C—NO_2), 1264 (m, N=N→O). ^{1}H NMR (acetone-d_6), δ: 4.66 (s, 4 H, CH_2); 5.24 (s, 2 H, OH); 5.88 (s, 2 H, NH_2). ^{13}C NMR (75 MHz, acetone-d_6), δ: 61.18 (CH_2), 115.05 (C—NO_2), 148.20 (C—NH_2), 154.14 (C—N=N→O). ^{14}N NMR (22 MHz, acetone-d_6), δ: −51.8 (N→O, $\Delta\nu_{0.5}$ = 117 Hz), −8.5 (NO_2, $\Delta\nu_{0.5}$ = 114 Hz).

Ammonium salt of 3-(dinitromethyl-*ONN*-azoxy)-4-nitrofurazan (11-NH_4). NH_3 was bubbled through a stirred solution of **11** (0.052 g, 0.198 mmol) in CH_2Cl_2 (3.0 mL) at 20 °C for 2 min. The precipitate formed was filtered, washed with CH_2Cl_2, and vacuum dried. Salt **11-NH_4** was obtained in the yield of 0.050 g (91%), bright yellow crystals, m.p. 129.0 °C (decomp.). Found (%): C, 12.97; H, 1.46; N, 39.43. $C_3H_4N_8O_8$. Calculated (%): C, 12.86; H, 1.44; N, 40.00. IR (KBr), ν/cm^{-1}: 3228 (m, NH_4^+), 1576 (v.s, C—NO_2), 1528 (s, C—NO_2), 1500 (v.s, N=N→O), 1352 (s, C—NO_2), 1288 (m, N=N→O). ^{1}H NMR (acetone-d_6), δ: 7.57 (br.s, 4 H, NH_4^+).

Ammonium salt of 3-amino-4-(dinitromethyl-*ONN*-azoxy)-furazan (12-NH_4). ***A.*** NH_3 was bubbled through a stirred solution of compound **11** (0.100 g, 0.380 mmol) in MeCN (5.0 mL) at 20 °C for 2.5 h. Removal of the solvent *in vacuo* and purification of the residue by preparative TLC (silica gel, elution with benzene—acetone, 1 : 2) afforded salt **12-NH_4** (0.090 g, 95%), yellowish crystals, m.p. 115.0—117.0 °C (decomp.). Found (%): C, 14.39; H, 2.33; N, 44.49. $C_3H_6N_8O_6$. Calculated (%): C, 14.40; H, 2.40; N, 44.80. IR (KBr), ν/cm^{-1}: 3468 (s, NH_2), 3320 (v.s, NH_2), 3245 (m, NH_4^+), 1632 (m, NH_2), 1576 (v.s, C—NO_2), 1484 (v.s, N=N→O), 1368 (s, C—NO_2), 1320 (m, N=N→O). ^{1}H NMR (acetone-d_6), δ: 5.64 (s, 2 H, NH_2); 8.06 (br.s, 4 H, NH_4^+).

B. NH_3 was bubbled through a stirred solution of compound **13** (0.100 g, 0.325 mmol) in MeCN (5.0 mL) at 20 °C for 3 h. Removal of the solvent *in vacuo* and purification of the residue by preparative TLC (silica gel, elution with benzene—acetone, 1 : 2) afforded salt **12-NH_4** (0.063 g, 78%). Physicochemical parameters of the sample are in agreement with those of compound **12-NH_4** obtained by the method ***A***.

3-Amino-4-(dinitromethyl-*ONN*-azoxy)furazan (12). HCl was bubbled through a stirred 0 °C solution of **12-NH_4** (0.090 g, 0.360 mmol) in MeOH (10.0 mL) for 20 min. The solvent was

removed *in vacuo*, the residue was extracted with Et_2O (3×10 mL), and the organic layer was dried with $MgSO_4$. Removal of the solvent *in vacuo* afforded compound **12** (0.065 g, 81%), bright yellow crystals, m.p. 85.0—87.5 °C (decomp.) (from hexane—CH_2Cl_2). ^{1}H NMR ($CDCl_3$), δ: 4.60 (s, 2 H, NH_2); 7.71 (s, 1 H, CH).

Potassium salt of 3-(*N*-methylamino)-4-(dinitromethyl-*ONN*-azoxy)furazan (14-K). To a 0 °C solution of $MeNH_2$ (0.143 g, 4.61 mmol) in water (7.0 mL), a solution of **11** (0.100 g, 0.380 mmol) in CH_2Cl_2 (4.0 mL) was added with vigorous stirring. The emulsion was stirred at 20 °C for 20 min, diluted with water (10 mL), washed with CH_2Cl_2 (3×5 mL), 33% HCl (0.45 mL, 4.74 mmol) was added to the aqueous layer, the product was extracted with CH_2Cl_2 (4×10 mL), the organic phase was dired with $MgSO_4$. Removal of the solvent *in vacuo* afforded compound **14** (0.089 g, 95%), orange oil. ^{1}H NMR ($CDCl_3$), δ: 3.56 (s, 3 H, Me); 4.41 (s, 1 H, NH); 7.71 (s, 1 H, CH). To a solution of compound **14** (0.089 g, 0.360 mmol) in MeOH (2.0 mL), a solution of KOH (0.021 g, 0.375 mmol) in MeOH (2.0 mL) was added, the solvent was removed *in vacuo*. Purification of the residue by preparative TLC (silica gel, elution with benzene—acetone, 1 : 2) and subsequent washing with Et_2O afforded potassium salt **14-K** (0.080 g, 78%), light orange crystals, m.p. 186.0—187.5 °C (decomp.). Found (%): C, 16.61; H, 1.01; N, 34.37. $C_4H_4KN_7O_6$. Calculated (%): C, 16.84; H, 1.40; N, 34.39. IR (KBr), ν/cm^{-1}: 3425 (m, NH), 1614 (m, N—H), 1589 (s, C—NO_2), 1514 (v.s, N=N→O), 1387 (s, C—NO_2), 1294 (s, N=N→O). ^{1}H NMR (acetone-d_6), δ: 2.90 (s, 3 H, Me); 3.53 (s, 1 H, NH).

Dipotassium salt of *N*,*N*′-bis[4-(dinitromethyl-*ONN*-azoxy)-furazan-3-yl]ethylenediamine (15-2K). To a 0 °C solution of $H_2NCH_2CH_2NH_2$ (0.027 g, 0.456 mmol) and $NaHCO_3$ (0.140 g, 1.67 mmol) in water (3.0 mL), a solution of compound **11** (0.200 g, 0.760 mmol) in CH_2Cl_2 (2.0 mL) was added with vigorous stirring. The emulsion was stirred at 20 °C for 7 days, diluted with water (10 mL), washed with CH_2Cl_2 (3×5 mL), 33% HCl (0.17 mL, 1.82 mmol) was added to the aqueous layer, the product was extracted with CH_2Cl_2 (4×10 mL), the organic phase was dried with $MgSO_4$. Removal of the solvent *in vacuo* afforded compound **15** (0.103 g, 55%), light orange crystals, m.p. 131.0—133.0 °C. ^{1}H NMR (acetone-d_6), δ: 3.64 (s, 4 H, CH_2); 6.34 (s, 2 H, NH); 9.20 (s, 2 H, CH). To a solution of compound **15** (0.103 g, 0.209 mmol) in MeOH (2.0 mL), a solution of KOH (0.012 g, 0.214 mmol) in MeOH (2.0 mL) was added, the solvent was removed *in vacuo*. Purification of the residue by preparative TLC (silica gel, elution with benzene—acetone, 1 : 2) afforded salt **15-2K** (0.115 g, 97%), orange crystals (hygroscopic). ^{1}H NMR (acetone-d_6), δ: 3.10 (s, 4 H, CH_2); 3.68 (s, 2 H, NH). The structure of compound **15** was confirmed by the conversion of the latter into dichloride **16**.

***N*,*N*′-Bis[4-(chlorodinitromethyl-*ONN*-azoxy)furazan-3-yl]ethylenediamine (16).** Cl_2 was bubbled through a stirred solution of compound **15-2K** (0.100 g, 0.176 mmol) in MeCN (15.0 mL) at 20 °C for 2 min. The precipitate formed was filtered off, the mother liquor was concentrated *in vacuo*, purification of the residue by preparative TLC (silica gel, elution with benzene—acetone, 5 : 1) afforded compound **16** (0.084 g, 85%), bright orange crystals, m.p. 147.5—149.0 °C (from CCl_4—CH_2Cl_2). MS (ESI), *m*/*z*: 560.9733 $[M + H]^+$; calculated for $C_8H_6Cl_2N_{14}O_{12}$, $[M + H]^+$, *m*/*z*: 560.9739. IR (KBr), ν/cm^{-1}: 3374 (v.s, NH), 1609 (v.s, br, N—H and C—NO_2), 1514 (v.s, N=N→O), 1364 (s, C—NO_2), 1287 (s, N=N→O). ^{1}H NMR ($CDCl_3$), δ: 3.64 (s, 4 H, CH_2); 6.55 (s, 2 H, NH). ^{13}C NMR (75 MHz, acetone-d_6), δ: 42.68 (CH_2NH), 127.05 ($C(NO_2)_2Cl$), 147.37 (C—NH), 155.22 (C—N=N→O). ^{14}N NMR (22 MHz, acetone-d_6), δ: −71.78 (N→O, $\Delta\nu_{0.5}$ = 69 Hz), −31.26 (NO_2, $\Delta\nu_{0.5}$ = 24 Hz).

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