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Reactivity of the low-nucleophilic *N*-dinitromethyl carbanion center in polynitromethylazoles

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Experimental

NMR data were collected on a Bruker AM-300 instrument [working frequencies of 300.13 MHz (^{1}H) and 75.47 (^{13}C)]. IR and UV spectra were obtained using UR-20 and SPECORD UV VIS instruments, respectively.

2-Dinitromethyl-5-nitrotetrazole O*-methyl ester* **2b**. Yield 34%, yellowish crystals, mp 85–90 °C (decomp.). Cooled solution (ice bath) of diazomethane (4.8 mmol, synthesized from 0.5 g nitrozomethylurea) in diethyl ether (5–6 ml) was added to a solution of 0.306 g (1.4 mmol) of 2-dinitromethyl-5-nitrotetrazole **2b**[1] in 5 ml of absolute diethyl ether. Yellow color of diazomethane immediately disappeared during the reaction. Reaction mixture was kept at room temperature for 15 min. The resulting oil after washing with diethyl ether (2–3 ml) was crystallized to afford 0.05 g of compound **2b**. Reaction solution was evaporated and washed with diethyl ether to give additionally 0.06 g of **2b**. Total yield 34%. ^{1}H NMR (CD_3CN) δ: 4.06 (s, OCH_3). UV_{max} (MeOH, λ/nm) 298 (ε = 11.600). IR (KBr, ν/cm^{-1}): 840, 1245 [(O)-OCH_3]; 1302, 1523 [O_2N in fragment O_2N-C=N(O)-OCH_3]; 1626 [C=N in fragment O_2N-C=N(O)-OCH_3]; 1332, 1586 (aromatic NO_2); 1510 (C=N in tetrazole). Found (%): C, 15.41; H, 1.39; N, 42.34. Calc. for $C_3H_3N_7O_6$ (%): C, 15.46; H, 1.30; N, 42.06.

Compound **2b** is soluble in MeOH, MeCN and acetone, and insoluble in H_2O, hexane and CCl_4. Crystals of **2b** are stable at room temperature for 7–8 days, then slowly decompose. In MeCN solution **2b** decomposes during 10–15 h without formation of compounds with $N(CNO_2)_2$ fragment (UV control).

1,1-Dinitro-1-(5-trinitromethyltetrazol-2-yl)pentan-4-one **3a**. Yield 45%, mp 62–63 °C (MeOH–H_2O). Suspension of **1a** (1.28 g, 4 mmol) in water (15 ml) was treated on stirring with solution of N_2CO_3 (0.42 g, 4 mmol) in water (5 ml, pH 3–4), then freshly distilled methyl vinyl ketone (0.35

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g, 5 mmol) was added. The resulting mixture was stirred for 5 h at room temperature, then filtered. The precipitate was washed with water and dried in air. Yield of **3a** 0.88 g (45%). ^{1}H NMR [$(CD_3)_2CO$] δ: 2.17 (s, CH_3), 2.97 (t, *J* = 7.0, CH_2), 3.70 (t, *J* = 7.0, CH_2). IR (KBr, ν/cm^{-1}): 1285, 1600, 1630 [$C(NO_2)_3$, $C(NO_2)_2$]; 1720 (CO). Found (%): C, 21.32; H, 1.90; N, 31.96. Calc. for $C_7H_7N_9O_{11}$ (%): C, 21.38; H, 1.79; N, 32.06.

1,1-Dinitro-1-(5-nitrotetrazol-2-yl)pentan-4-one **3b**. Yield 60%, mp 64.5–65.5 °C. Freshly distilled methyl vinyl ketone (0.7 g, 10 mmol) in water (1 ml) was added (drop by drop) to the stirring solution of **1b** (2.19 g, 10 mmol) in water (10 ml). The resulting mixture was stirred at room temperature for 20 min, then filtered. The precipitate was dried in air. Yield of **3b** 1.72 g (60%). ^{1}H NMR [$(CD_3)_2CO$] δ: 2.27 (s, CH_3), 3.02 (t, *J* = 6.9, CH_2), 3.75 (t, *J* = 6.9, CH_2). IR (KBr, ν/cm^{-1}): 1305, 1598, [$C(NO_2)_2$]; 1360, 1572, 1610 (aromatic NO_2); 1720 (CO). Found (%): C, 25.22; H, 2.29; N, 33.73. Calc. for $C_6H_7N_7O_7$ (%): C, 24.92; H, 2.44; N, 33.91.

2,2-Dinitro-2-(5-trinitromethyltetrazol-2-yl)ethanol **4a**. Yield 30%, mp 65 °C ($CHCl_3$). Suspension of **1a** (1.28 g, 4 mmol) in water (15 ml) was treated on stirring with solution of N_2CO_3 (0.42 g, 4 mmol) in water (5 ml, pH 3–4 in the reaction mixture), then 30% formaldehyde solution (0.75 ml, 7.5 mmol) in water was added. The resulting mixture was stirred at room temperature for 15 h, then filtered. The resulting yellowish precipitate was washed with water and dried in air to afford the target **4a**. ^{1}H NMR ($CDCl_3$) δ: 3.76 (br.s, OH), 5.26 (s, CH_2). IR (KBr, ν/cm^{-1}): 1280, 1585, 1600, 1625 [$C(NO_2)_3$, $C(NO_2)_2$]; 3650 (OH). Found (%): C, 13.72; H, 0.97; N, 35.93. Calc. for $C_4H_3N_9O_{11}$ (%): C, 13.61; H, 0.86; N, 35.70.

2,2-Dinitro-2-(5-nitrotetrazol-2-yl)ethanol **4b**. Yield 75%, mp 91–93 °C ($CHCl_3$). 30% Formaldehyde solution (1.5 ml, 15 mmol) in water was added during 5 min to the stirring solution of **1b** (2.19 g, 10 mmol) and kept for 20 min. The precipitate was filtered off, washed with cold water and dried *in vacuo* over P_2O_5 to afford the target **4b**. ^{1}H NMR (CD_3CN) δ: 4.20 (br. s, OH), 5.38 (s, CH_2). IR (KBr, ν/cm^{-1}): 1300, 1310, 1580, 1610 [$C(NO_2)_2$]; 1344, 1580 (aromatic NO_2); 3440 (OH). Found (%): C, 14.88; H, 1.13; N, 39.47. Calc. for $C_3H_3N_7O_7$ (%): C, 14.47; H, 1.21; N, 39.36.

*2,2΄-Bis(2-hydroxy-1,1-dinitroethyl)-5,5΄-dinitro-2*H,*2΄*H*-3,3΄-bi[1,2,4]triazole* **4f**. Yield 63%, mp 121–122 °C (decomp., $MeNO_2$–$CHCl_3$–CCl_4). 30% Formaldehyde solution (1.2 ml, 12 mmol) was added to the suspension of dipotassium salt **1f** (1 g, 1.96 mmol) in water (11 ml) and H_2SO_4 (0.66 ml, $d = 1.83$) and stirred at room temperature for 5 h. The resulting colorless precipitate was filtered off, washed with 5% H_2SO_4 and dried in air. For the purification it was dissolved in $MeNO_2$ (15 ml) and precipitated by addition of $CHCl_3$ and CCl_4, then filtered off and dried in air to afford the target **4f**. ^{1}H NMR (CD_3CN) δ: 3.07 (br.s, OH), 5.00 (s, CH_2), 8.30 (CH). IR (KBr, ν/cm^{-1}): 1312, 1620 [$C(NO_2)_2$]; 1342, 1582 (aromatic NO_2); 3400 (OH). Found (%): C, 19.49; H, 1.33; N, 4.34. Calc. for $C_8H_6N_{12}O_{14}$ (%): C, 19.44; H, 1.22; N, 34.01.

2,2-Dinitro-2-(4,5-dinitroimidazol-1-yl)ethanol **4g**. Yield 47.5%, mp 124 °C ($CHCl_3$). Prepared analogously to the synthesis of **4a**. ^{1}H NMR (CD_3CN) δ: 3.07 (br.s, OH), 5.00 (s, CH_2), 8.30 (s, CH). IR (KBr, ν/cm^{-1}): 1300, 1616 [$C(NO_2)_2$]; 1370, 1550 (aromatic NO_2); 3410 (OH). Found (%): C, 20.67; H, 1.44; N, 28.95. Calc. for $C_5H_4N_6O_9$ (%): C, 20.56; H, 1.38; N, 28.77.

*5,5′-Dinitro-2,2′-bis(1,1-dinitro-2-nitroxyethyl)-2*H*,2′*H*-3,3′-bi[1,2,4]triazole* **5f**. Yield 47%, mp 125 °C (decomp., $MeNO_2$–$CHCl_3$–CCl_4), $d = 1.96$ g/cm^3. H_2SO_4 (9 ml, $d = 1.83$) was added (drop by drop) to the solution of **4f** (0.9 g, 1.82 mmol) in HNO_3 (4.5 ml, $d = 1.5$) and stirred at room temperature for 4 h. The reaction mixture was poured into *ca.* 75 g of crushed ice. The resulting precipitate was filtered off, dried in air, dissolved in $MeNO_2$ (8 ml) and diluted with $CHCl_3$ and CCl_4, then filtered off and dried in air to afford the target **5f**. ^{1}H NMR (CD_3CN) δ: 5.15 (s, CH_2). IR (KBr, ν/cm^{-1}): 1293, 1310, 1605, 1620 [$C(NO_2)_2$]; 1340, 1579 (aromatic NO_2); 1275, 1683 (ONO_2). Found (%): C, 16.56; H, 0.73; N, 33.69. Calc. for $C_8H_4N_{14}O_{18}$ (%): C, 16.45; H, 0.69; N, 33.57.

N-*[2,2-Dinitro-2-(5-nitrotetrazol-2-yl)ethyl]*-N-*methylnitramine* **7b**. Yield 35%, mp 110–111 °C (decomp., $CHCl_3$). The solution of methylsulfamic acid sodium salt (0.6 g, 4.56 mmol) in water (2 ml) was added to the solution of **4b** (1g, 4.56 mmol) in ethanol (2 ml). The reaction mixture was stirred at 50 °C for 1 h and evaporated to dryness at <50 °C. The nitration mixture [HNO_3(1.5) : H_2SO_4 (1.83) : H_2O, 12:12:1 by volume] was added to the resulting yellow precipitate, then the mixture was stirred at 0–5° for 1 h and poured into crushed ice. The resulting precipitate was filtered off, washed with cold water and dried in air. ^{1}H NMR [$(CD_3)_2CO$] δ: 3.66 (s, CH_3), 6.16 (s CH_2). IR (KBr, ν/cm^{-1}): 1300, 1613 [$C(NO_2)_2$]; 1363, 1582 (aromatic NO_2); 1265, 1552 (N-NO_2). Found (%): C, 15.58; H, 1.70; N, 41.25. Calc. for $C_4H_5N_9O_8$ (%): C, 15.64; H, 1.64; N, 41.04.

N-*[2,2-Dinitro-2-(5-nitrotetrazol-2-yl)ethyl]acetamide* **8b**. Yield 48%, mp 110–112 °C (decomp., 50% EtOH). Solution of **1b** (0.5 g, 2.28 mmol) and *N*-(hydroxymethyl)acetamide[2] (0.203 g, 2.28 mmol) in water (3 ml) was heated at 56° C for 1 h. The resulting precipitate was filtered off, washed with cold water and dried in air. ^{1}H NMR [$(CD_3)_2CO$] δ: 1.97 (s, CH_3), 5.45 (d, $J = 7$ Hz, CH_2), 8.25 (t, $J = 7$, NH). IR (KBr, ν/cm^{-1}): 1310, 1602, 1612 [$C(NO_2)_2$]; 1350, 1577, 1588 (aromatic NO_2); 3270 (NH); 1668, 1689 (CONH). Found (%): C, 20.91; H, 2.17; N, 38.74. Calc. for $C_5H_6N_8O_7$ (%): C, 20.70; H, 2.08; N, 38.62.

General procedure for the synthesis of bis(2-azolyl-2,2-dinitroethyl)amines **9b-e**.
To the vigorously stirred suspension of *N*-dinitromethylazole K-salt (10 mmol) in water (16 ml) and H_2SO_4 (1 ml, $d = 1.83$), a solution of hexamethylenetetramine (0.34 g, 2.4 mmol) in water (2 ml) was added. The heterogeneous reaction mixture was stirred at room temperature for 5 h. The starting yellow salt of **1b-e** disappeared and the resulting colorless precipitate **9b-e** was filtered off, washed with 0.1 N H_2SO_4 and dried in air. Analytically pure samples were obtained by crystallization from $MeNO_2$–$CHCl_3$–CCl_4 as in procedure for **4f**. In some cases methanol (2 ml) was added to reaction mixtures for better filtering the precipitate.

Bis[2-(5-nitrotetrazol-2-yl)-2,2-dinitroethyl]amine **9b**. Yield 86%, mp 94 °C (decomp., $MeNO_2$–$CHCl_3$). IR (KBr, ν/cm^{-1}): 1305, 1593 [$C(NO_2)_2$]; 1362, 1572, 1612 (aromatic NO_2); 3370 (NH).

Bis[2-(3-nitro-1,2,4-triazol-1-yl)-2,2-dinitroethyl]amine **9c**. Yield 100%, mp 137 °C (decomp., $MeNO_2$–$CHCl_3$). IR (KBr, ν/cm^{-1}): 1310, 1592, 1615 [$C(NO_2)_2$]; 1381, 1567 (aromatic NO_2); 3360 (NH).

Bis[2-(4-nitro-1,2,3-triazol-2-yl)-2,2-dinitroethyl]amine **9d**. Yield 88%, mp 134 °C (decomp., $MeNO_2$–$CHCl_3$). IR (KBr, ν/cm^{-1}): 1305, 1585, 1600 [$C(NO_2)_2$]; 1340, 1559 (aromatic NO_2); 3367 (NH).

Bis[2-(3,4-dinitropyrazol-1-yl)-2,2-dinitroethyl]amine **9e**. Yield 100%, mp 100 °C (decomp., $MeNO_2$–$CHCl_3$). IR (KBr, ν/cm^{-1}): 1310 1602 [$C(NO_2)_2$]; 1330, 1361, 1570 (aromatic NO_2); 3368 (NH).

General procedure for the synthesis of bis(2-azolyl-2,2-dinitroethyl)nitramines **10b-e**.
Amine **9b-e** (1.5g, 2.6–3.1 mmol) was added by small portions to the nitration mixture [10 ml, HNO_3 (1.5) : H_2SO_4 (1.83), 1:2 v/v]. The reaction mixture was stirred vigorously at 0–5° for 3 h

and poured into crushed ice. The resulting precipitate was filtered off, washed with cold water and dried in air. Analytically pure samples were obtained by crystallization from $C_2H_4Cl_2$.

Bis[2-(5-nitrotetrazol-2-yl)-2,2-dinitroethyl]nitramine **10b**. Yield 70%, mp 65 ^{o}C (decomp., $MeNO_2$–$CHCl_3$), d = 2.06 g cm^{-3}. ^{1}H NMR (CD_3CN) δ: 6.16 (s, CH_2). ^{13}C NMR [$(CD_3)_2CO$] δ: 56.6 (t, $J_{13C\text{-}1H}$ = 153, CH_2); 114.5 [$C(NO_2)_2$]; 166.8 (C_5). IR (KBr, ν/cm^{-1}): 1292, 1600, 1633 [$C(NO_2)_2$]; 1363, 1373, 1583 (aromatic NO_2); 1280, 1583 (N-NO_2). Found (%): C, 13.61; H, 0.89; N, 42.63. Calc. for $C_6H_4N_{16}O_{14}$ (%): C, 13.75; H, 0.77; N, 42.75.

Bis[2-(3-nitro-1,2,4-triazol-1-yl)-2,2-dinitroethyl]nitramine **10c**. Yield 71%, mp 143 ^{o}C (decomp., $MeNO_2$–$CHCl_3$), d = 1.82 g cm^{-3}. ^{1}H NMR [$(CD_3)_2CO$] δ: 6.32 (s, CH_2); 9.67 (s, CH). ^{13}C NMR [$(CD_3)_2CO$] δ: 56.4 (t, $J_{13C\text{-}1H}$ = 153.5, CH_2); 114.3 [$C(NO_2)_2$]; 151.9 (d, $J_{13C\text{-}1H}$ = 231.2, C_5); 163.5 (d, $J_{13C\text{-}1H}$ = 13.9 C_3). IR (KBr, ν/cm^{-1}): 1306, 1600, 1610 [$C(NO_2)_2$]; 1378, 1575 (aromatic NO_2); 1290, 1575 (N-NO_2). Found (%): C, 18.56; H, 1.22; N, 37.72. Calc. for $C_8H_6N_{14}O_{14}$ (%): C, 18.40; H, 1.16; N, 37.55.

Bis[2-(4-nitro-1,2,3-triazol-2-yl)-2,2-dinitroethyl]nitramine **10d**. Yield 92%, mp 132 ^{o}C (70% HNO_3), d = 1.82 g cm^{-3}. ^{1}H NMR [$(CD_3)_2CO$] δ: 6.28 (s, CH_2); 9.00 (s, CH). ^{13}C NMR [$(CD_3)_2CO$] δ: 56.6 (t, $J_{13C\text{-}1H}$ = 152.6, CH_2); 116.4 [$C(NO_2)_2$]; 136.3 (d, $J_{13C\text{-}1H}$ = 212.7, C_5); 157.0 (d, $J_{13C\text{-}1H}$ = 8.3 C_4). IR (KBr, ν/cm^{-1}): 1305, 1600, 1620 [$C(NO_2)_2$]; 1340, 1560 (aromatic NO_2); 1280, 1570 (N-NO_2). Found (%): C, 18.49; H, 1.28; N, 37.70. Calc. for $C_8H_6N_{14}O_{14}$ (%): C, 18.40; H, 1.16; N, 37.55.

Bis[2-(3,4-dinitropyrazol-1-yl)-2,2-dinitroethyl]nitramine **10e**. Yield 67%, mp 140 ^{o}C (decomp., $C_2H_4Cl_2$), d = 1.89 g cm^{-3}. ^{1}H NMR [$(CD_3)_2CO$] δ: 6.30 (s, CH_2); 9.82 (s, CH). ^{13}C NMR [$(CD_3)_2CO$] δ: 57.7 (t, $J_{13C\text{-}1H}$ = 153.5, CH_2); 115.6 [$C(NO_2)_2$]; 131.2 (d, $J_{13C\text{-}1H}$ = 210.9, C_5); 138.8 (C_3); 150.2 (d, $J_{13C\text{-}1H}$ = 6.5 C_4). IR (KBr, ν/cm^{-1}): 1300, 1610, 1620 [$C(NO_2)_2$]; 1332, 1363, 1570 (aromatic NO_2); 1285, 1570 (N-NO_2). Found (%): C, 19.56; H, 0.88; N, 32.31. Calc. for $C_{10}H_6N_{14}O_{18}$ (%): C, 19.68; H, 0.99; N, 32.13.

N-*[2-(5-nitrotetrazol-2-yl)-2,2-dinitroethyl]*-N-*nitroxymethylnitramine* **12b**. Yield 73%, mp 101 ^{o}C (decomp., $C_2H_4Cl_2$), d = 1.92 g cm^{-3}. Solution of amine **9b** (1 g, 2.09 mmol) in HNO_3 (1.5) (5 ml) was kept at 0–5 ^{o}C for 2.5 h and poured into crushed ice. The resulting precipitate was filtered off, dissolved in minimum quantity of methanol, diluted with water, washed with water and dried *in vacuo* over P_2O_5 to yield the target **12b**. ^{1}H NMR [$(CD_3)_2CO$] δ: 6.07 (s,

CH_2). IR (KBr, ν/cm^{-1}): 1296, 1600, 1622 [$C(NO_2)_2$]; 1368, 1587 (aromatic NO_2); 1278, 1587, 1650 ($N-NO_2$, $O-NO_2$). Found (%): C, 13.21; H, 1.20; N, 38.24. Calc. for $C_4H_4N_{10}O_{11}$ (%): C, 13.05; H, 1.10; N, 38.05.

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