Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Impact insensitive dinitromethanide salts

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Experimental

Caution: *Silver dinitromethanide described in this paper is a powerful and sensitive explosive which should be handled with appropriate precautions. We have not experienced any problems in handling the dinitromethanide salts. However, their friction sensitivities have not been determined. Therefore, they should be handled on a small scale with extreme care using all of the standard safety precautions such as leather gloves, leather coat, face shields and ear plugs.*

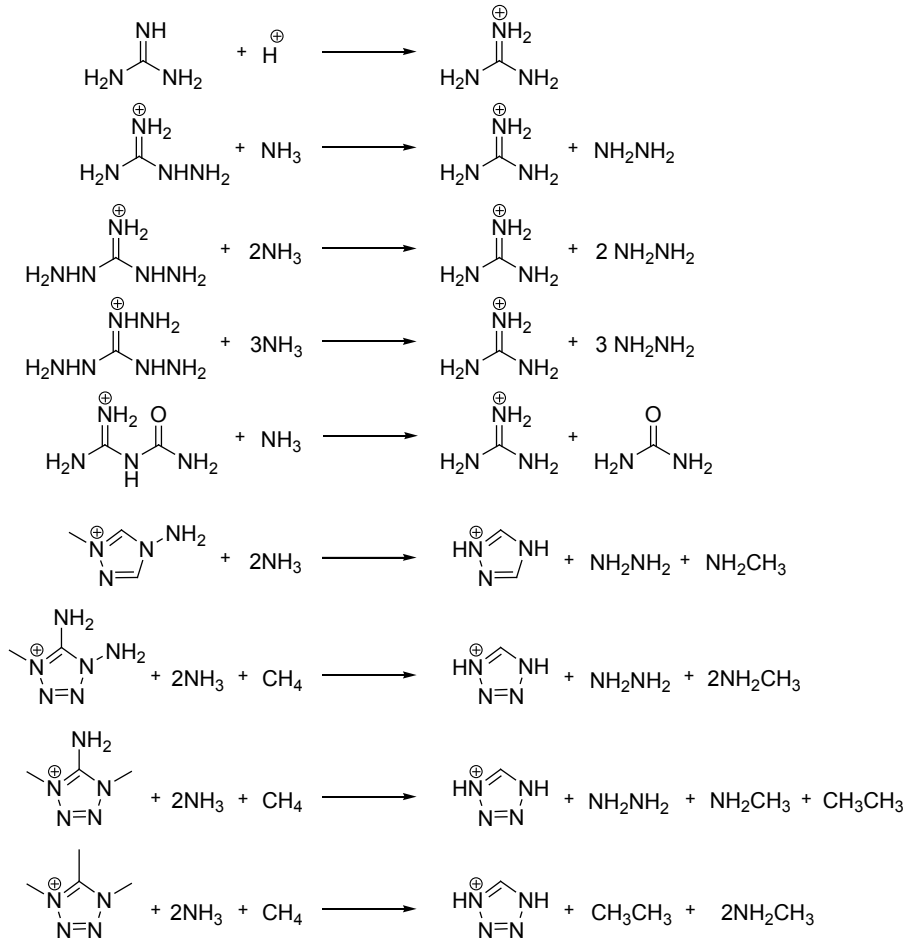
General Methods.

Triaminoguanidium chloride, guanylurea hydrochloride, 4-amino-1-methyl-1,2,4-triazolium iodide, 1,5-diamino-4-methyl-1,2,3,4-tetrazolium iodide, 5-amino-1,4-dimethyl-1,2,3,4-tetrazolium iodide, and 1,4,5-trimethyl-1,2,3,4-tetrazolium iodide were prepared according to the literature procedures.[1] Silver dinitromethanide (AgDNM) was synthesized by the metathesis reaction of KDNM in $AgNO_3$ aqueous solution.[2] All other chemicals were obtained commercially as analytical grade materials and used as received. Solvents were dried by standard procedures. IR spectra were recorded using KBr plates on a Biorad Model 3000 FTS spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz nuclear magnetic resonance spectrometer operating at 300.13 and 75.48 MHz, respectively, with [D_6]DMSO as locking solvent. ^{1}H and ^{13}C chemical shifts are reported in ppm relative to TMS. ^{15}N NMR spectra were recorded on a Brucker 500 MHz nuclear magnetic resonance spectrometer operating at 50.69 MHz with shifts relative to nitromethane. The densities were measured at 25 °C on a Micromeritics Accupyc 1330 gas pycnometer. Differential scanning calorimetry (DSC) measurements were performed on a TA DSC Q10 calorimeter equipped with an auto cool accessory, and calibrated using indium. Elemental analyses (H, C, N) were performed on a CE-440 elemental analyzer.

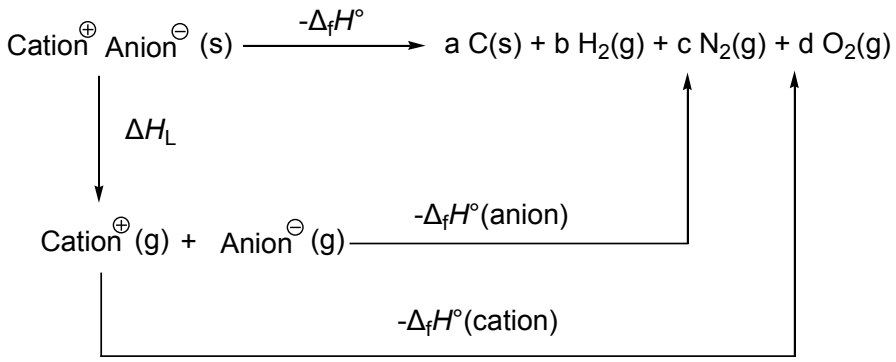
X-ray Crystallography. Crystals of **1** was removed from the flask, a light yellow plate was selected, attached to a glass fiber and data were collected on a Bruker three-circle platform diffractometer equipped with a SMART APEX II CCD detector. The crystals were irradiated using graphite monochromated MoK_α radiation (λ = 0.71073). An Oxford Cobra low temperature device was used to keep the crystals at a constant 100 K during data collection. Data collection was performed and the unit cell

was initially refined using APEX2 [v2009.3-0].[3] Data reduction was performed using SAINT [v7.60A][4] and XPREP [v2008/2].[5] Corrections were applied for Lorentz, polarization, and absorption effects using SADABS [v2008/1].[6] The structure was solved and refined with the aid of the programs in the SHELXTL-plus [v2008/4] system of programs.[7] The full-matrix least-squares refinement on F2 included atomic coordinates and anisotropic thermal parameters for all non-H atoms. The H atoms were included using a riding model. No decomposition was observed during data collection.

Computational methods. Computations were performed by the Gaussian 03 (Revision D.01) suite of programs.[8] The geometric optimization and the frequency analyses were carried out using B3LYP functional analyses with the 6-311+G** basis set.[9] Single-point energies were calculated at the MP2/6-311++G** level.[10] All of the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies.



Scheme S1. The isodesmic reactions of the cations in DNM salts **1**–**9**.



where a, b, c, d are the numbers of moles of the respective products

Scheme S2. Born–Haber cycle for the heats of formation of salts.

The theoretical heats of formation of the cations were computed using the method of isodesmic reactions (Scheme S1). The sources of the energies of the parent ions in the isodesmic reactions were calculated from protonation reactions.[11] The enthalpies of formation of H^+ ($\Delta_f H°(H^+)$ = 1528.085 kJ mol^{-1}), NH_3 ($\Delta_f H°(NH_3, g)$ = –45.9 kJ mol^{-1}) and NH_2NH_2 ($\Delta_f H°(NH_2NH_2, g)$ = 95.4 kJ mol^{-1}) are obtained from the literature.[12]. The enthalpies of reaction ($\Delta_r H°_{298}$) were obtained by combining the MP2/6-311++G** energy differences for the reaction, the scaled zero point energies, and other thermal factors.

Lattice energy can be used for their correction of enthalpies of formation of the DNM salts. The enthalpies of formation can be simply indicated in eq 1. The theoretical heats of formation of the DNM salts at T = 298.15 K were calculated based on a Born-Haber energy cycle (Scheme S2). In a Born-Haber energy cycle, the heat of formation of an ionic liquid can be simplified by the expression:

$$\Delta_f H° \text{ (ionic salts, 298 K)} = \Sigma\Delta_f H° \text{ (cation, 298 K)} + \Sigma\Delta_f H° \text{ (anion, 298 K)} - \Delta H_L \quad (1)$$

where ΔH_L is the lattice energy of the ionic salt. ΔH_L (kJ mol^{-1}) can be predicted by the formula suggested by Jenkins *et al*.[13] as:

$$\Delta H_L = U_{POT} + [p(n_M/2 - 2) + q(n_X/2 - 2)]RT \quad (2)$$

where n_M and n_X depend on the nature of the ions M_p^+ and X_q^-, respectively, and are equal to 6 for polyatomic nonlinear ions in these cases. The equation simply assumes

that the vibrational degrees of freedom are equally excited in both the crystal and the gaseous ions while applying corrections for rotational degrees of freedom possessed by the product gaseous ions. The equation for lattice potential energy U_{POT} has the form:

$$U_{POT}\ (\text{kJ mol}^{-1}) = 1981.2(\rho_m/M_m)^{1/3} + 103.8 \quad (3)$$

where ρ_m is density (g cm^{-3}) and M_m is the chemical formula mass of the ionic material (g).

Guanidium Dinitromethanide (1): Guanidium chloride (96 mg, 1 mmol) was dissolved in methanol (10 mL) in an ice-bath, and then AgDNM (213 mg, 1 mmol) was slowly added. The resulting mixture was stirred in the dark for 24 h. The filtrate was collected and dried to yield **1** as a yellow solid (150 mg, 91%). A light yellow plate crystal was isolated after recrystallization from methanol solution. ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25°C, TMS): δ = 6.92 (s, 6H; NH_2), 8.14 ppm (s, 1H; $CH(NO_2)_2$); ^{13}C NMR (75 MHz, [D$_6$]DMSO, 25°C, TMS): δ = 122.02, 157.91 ppm; ^{15}N NMR (50.69 MHz, [D$_6$]DMSO, 25°C, TMS): δ = –13.37, –297.66 ppm; IR (KBr): ν_{max} = 3402, 3193, 3140, 1659,1465, 1442, 1416, 1322, 1232, 1086, 1001, 779, 702, 570, 514 cm^{-1}; elemental analysis calcd (%) for $C_2H_7N_5O_4$ (165.05): C 14.55, H 4.27, N 42.42; found: C 14.79, H 4.39, N 42.11.

Aminoguanidium Dinitromethanide (2): The same procedure was followed as that described above for **1**. Aminoguanidium chloride (110 mg, 1 mmol) and AgDNM (213 mg, 1 mmol) were reacted in methanol to obtain a yellow solid **2**. Yield 171 mg (91%). ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25°C, TMS): δ = 4.67 (s, 2H; *NH*NH_2), 6.75 (s, 2H; NH_2), 7.18 (s, 2H; NH_2), 8.14 (s, 1H; $CH(NO_2)_2$), 8.53 ppm (s, 1H; NH*NH$_2$*); ^{13}C NMR (75 MHz, [D$_6$]DMSO, 25°C, TMS): δ = 122.13, 158.78 ppm; IR (KBr): ν_{max} = 3459, 3389, 3354, 3287, 3195, 3154, 1671, 1460, 1368, 1230, 1213, 1057, 995, 777, 742, 595 cm^{-1}; elemental analysis calcd (%) for $C_2H_8N_6O_4$ (180.12): C 13.34, H 4.48, N 46.66; found: C 13.37, H 4.28, N 46.70.

Diaminoguanidium Dinitromethanide (3): The same procedure was followed as that described above for **1**. Diaminoguanidium chloride (126 g, 1 mmol) and AgDNM (213 mg, 1 mmol) were reacted in methanol to obtain a yellow solid **3**. Yield 181 mg

(93%). ^{1}H NMR (300 MHz, [D_6]DMSO, 25°C, TMS): δ = 4.58 (s, 4H; *NH*NH_2), 7.15 (s, 2H; NH_2), 8.14 (s, 1H; $CH(NO_2)_2$), 8.58 ppm (s, 2H; NH*NH_2*); ^{13}C NMR (75 MHz, [D_6]DMSO, 25°C, TMS): δ = 122.33, 159.85 ppm; IR (KBr): ν_{max} = 3359, 3253, 3146, 1682, 1625, 1590, 1454, 1398, 1362, 1299, 1224, 1158, 1080, 995, 781, 739, 654, 598 cm^{-1}; elemental analysis calcd (%) for $C_2H_9N_7O_4$ (195.14): C 12.31, H 4.65, N 50.25; found: C 12.36, H 4.63, N 49.84.

Triaminoguanidium Dinitromethanide (4): The same procedure was followed as that described above for **1**. Triaminoguanidium chloride (140 mg, 1 mmol) and AgDNM (213 mg, 1 mmol) were reacted in methanol to obtain a yellow solid **4**. Yield 195 mg (93%). ^{1}H NMR (300 MHz, [D_6]DMSO, 25°C, TMS): δ = 4.50 (s, 6H; *NH*NH_2), 8.14 (s, 1H; $CH(NO_2)_2$), 8.56 ppm (s, 3H; NH*NH_2*); ^{13}C NMR (75 MHz, [D_6]DMSO, 25 °C, TMS): δ = 122.14, 159.10 ppm; ^{15}N NMR (50.69 MHz, [D_6]DMSO, 25 °C, TMS): δ = –13.37, –281.22, –321.76 ppm; IR (KBr): ν_{max} = 3321, 3288, 3212, 3153, 1686, 1479, 1387, 1358, 1301, 1229, 1126, 1081, 988, 777, 740, 674, 613 cm^{-1}; elemental analysis calcd (%) for $C_2H_{10}N_8O_4$ (210.15): C 11.43, H 4.80, N 53.52; found: C 11.61, H 4.80, N 53.01.

Aminocarbonylguanidinium Dinitromethanide (5): The same procedure was followed as that described above for **1**. Guanylurea hydrochloride (138 mg, 1 mmol) and AgDNM (213 mg, 1 mmol) were reacted in methanol to obtain a yellow solid **5**. Yield 200 mg (96%). ^{1}H NMR (300 MHz, [D_6]DMSO, 25 °C, TMS): δ = 6.90 (s, br) , 7.88 (s, br), 8.13 ppm (s, 1H; $CH(NO_2)_2$); ^{13}C NMR (75 MHz, [D_6]DMSO, 25 °C, TMS): δ = 122.24, 155.74, 156.09 ppm; IR (KBr): ν_{max} = 3333, 3207, 3152, 1759, 1709, 1641, 1591, 1466, 1404, 1364, 1311, 1214, 1080, 1001, 924, 783, 743, 692, 606 cm^{-1}; elemental analysis calcd (%) for $C_3H_8N_6O_5$ (208.13): C 17.31, H 3.87, N 40.38; found: C 17.31, H 3.65, N 40.47.

4-Amino-1-methyl-1,2,4-triazolium Dinitromethanide (6): The same procedure was followed as that described above for **1**. 4-Amino-1-methyl-1,2,4-triazolium iodide (226 mg, 1 mmol) and AgDNM (213 mg, 1 mmol) were reacted in methanol to obtain a yellow solid **6**. Yield 188 mg (92%). ^{1}H NMR (300 MHz, [D_6]DMSO, 25 °C, TMS): δ = 4.03 (s, 3H; CH_3) , 7.02 (s, 2H; NH_2), 8.14 (s, 1H; $CH(NO_2)_2$), 9.16 (s, 1H), 10.12 ppm (s, 1H); ^{13}C NMR (75 MHz, [D_6]DMSO, 25°C, TMS): δ = 38.88,

122.22, 142.96, 145.01 ppm; IR (KBr): ν_{max} = 3295, 3144, 1720, 1636, 1572, 1530, 1459, 1361, 1297, 1194, 1123, 1076, 997, 880, 808, 780, 743, 654, 615 cm^{-1}; elemental analysis calcd (%) for $C_4H_8N_6O_4$ (204.14): C 23.53, H 3.95, N 41.17; found: C 23.63, H 3.79, N 41.01.

1,5-Diamino-4-methyl-1,2,3,4-tetrazolium Dinitromethanide (7): The same procedure was followed as that described above for **1**. 1,5-Diamino-4-methyl-1,2,3,4-tetrazolium iodide (242 mg, 1 mmol) and AgDNM (213 mg, 1 mmol) were reacted in methanol to obtain a yellow solid **7**. Yield 191 mg (87%). ^{1}H NMR (300 MHz, [D_6]DMSO, 25 °C, TMS): δ= 3.84 (s, 3H; CH_3) , 6.99 (s, 2H; C-NH_2), 8.14 (s, 1H; $CH(NO_2)_2$), 8.92 ppm (s, 2H; N-NH_2); ^{13}C NMR (75 MHz, [D_6]DMSO, 25°C, TMS): δ = 34.83, 122.73, 147.84 ppm; ^{15}N NMR (50.69 MHz, [D_6]DMSO, 25°C, TMS): δ = –13.31, –16.11, –27.36, –159.67, –178.08, –301.51, –312.01 ppm; IR (KBr): ν_{max} = 3305, 3189, 3148, 1713, 1635, 1462, 1400, 1361, 1297, 1196, 1187, , 1070, 1039, 1000, 940, 782, 743, 643 cm^{-1}; elemental analysis calcd (%) for $C_3H_8N_8O_4$ (220.15): C 16.37, H 3.66, N 50.90; found: C 16.35, H 3.54, N 50.53.

5-Amino-1,4-dimethyl-1,2,3,4-tetrazolium Dinitromethanide (8): The same procedure was followed as that described above for **1**. 5-Amino-1,4-dimethyl-1,2,3,4-tetrazolium iodide (241 mg, 1 mmol) and AgDNM (213 mg, 1 mmol) were reacted in methanol to obtain a yellow solid **8**. Yield 195 mg (89%). ^{1}H NMR (300 MHz, [D_6]DMSO, 25°C, TMS): δ= 3.86 (s, 6H; CH_3) , 8.13 (s, 1H; $CH(NO_2)_2$), 9.07 ppm (s, 2H; NH_2); ^{13}C NMR (75 MHz, [D_6]DMSO, 25 °C, TMS): δ = 34.00, 122.13, 148.54 ppm; IR (KBr): ν_{max} = 3327, 3150, 1666, 1596, 1487, 1466, 1412, 1368, 1315, 1200, 1116, 1087, 1046, 1001, 969, 787, 743, 677 cm^{-1}; elemental analysis calcd (%) for $C_4H_9N_7O_4$ (219.16): C 21.92, H 4.14, N 44.74; found: C 21.73, H 4.08, N 45.79.

1,4,5-Trimethyl-1,2,3,4-tetrazolium Dinitromethanide (9): The same procedure was followed as that described above for **1**. 1,4,5-Trimethyl-1,2,3,4-tetrazolium iodide (240 mg, 1 mmol) and AgDNM (213 mg, 1 mmol) were reacted in methanol to obtain a yellow solid **9**. Yield 196 mg (90%). ^{1}H NMR (300 MHz, [D_6]DMSO, 25°C, TMS): δ = 2.86 (s, 3H) , 4.22 (s, 6H), 8.14 ppm (s, 1H; $CH(NO_2)_2$); ^{13}C NMR (75 MHz,

[D_6]DMSO, 25°C, TMS): δ = 8.16, 36.15, 122.08, 152.69 ppm; IR (KBr): ν_{max} = 3149, 3030, 1638, 1590, 1533, 1456, 1353, 1294, 1200, 1078, 1041, 998, 765, 743, 640 cm^{-1}; elemental analysis calcd (%) for $C_5H_{10}N_6O_4$ (218.17): C 27.53, H 4.62, N 38.52; found: C 27.28, H 4.96, N 37.24.

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