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 AgNO₃ 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. ¹H and ¹³C NMR spectra were recorded on a Bruker 300 MHz nuclear magnetic resonance spectrometer operating at 300.13 and 75.48 MHz, respectively, with [D₆]DMSO as locking solvent. ¹H and ¹³C chemical shifts are reported in ppm relative to TMS. ¹⁵N 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 MoKα 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.

\[
\text{Cation}^+ \text{Anion}^\ominus (s) \xrightarrow{-\Delta_H^\ominus} a \text{C}(s) + b \text{H}_2(g) + c \text{N}_2(g) + d \text{O}_2(g)
\]

\[
\Delta H_L
\]

\[
\text{Cation}^\oplus (g) + \text{Anion}^\ominus (g) \xrightarrow{-\Delta_H^\ominus(\text{cation})} -\Delta_H^\ominus(\text{anion})
\]

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.\textsuperscript{[11]} The enthalpies of formation of \(\text{H}^+ (\Delta_f H_f(\text{H}^+) = 1528.085 \text{ kJ mol}^{-1})\), \(\text{NH}_3 (\Delta_f H_f(\text{NH}_3, \text{ g}) = -45.9 \text{ kJ mol}^{-1})\) and \(\text{NH}_2\text{NH}_2 (\Delta_f H_f(\text{NH}_2\text{NH}_2, \text{ g}) = 95.4 \text{ kJ mol}^{-1})\) are obtained from the literature.\textsuperscript{[12]} The enthalpies of reaction \(\Delta_f H_f^{298}\) 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 \(T = 298.15 \text{ K}\) 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:

\[
\Delta_f H_f^{\text{ionic salts, 298 K}} = \Sigma \Delta_f H_f^{\text{cation, 298 K}} + \Sigma \Delta_f H_f^{\text{anion, 298 K}} - \Delta H_L (1)
\]

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

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

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:

\[
U_{POT} \text{ (kJ mol}^{-1}\text{)} = 1981.2\left(\frac{\rho_m}{M_m}\right)^{1/3} + 103.8 \tag{3}
\]

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

**Guanidinium Dinitromethanide (1):** Guanidinium 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): \( \delta = 6.92 \) (s, 6H; NH\(_2\)), 8.14 ppm (s, 1H;
CH(NO\(_2\))\(_2\)); \(^1\)C NMR (75 MHz, [D\(_6\)]DMSO, 25°C, TMS): \( \delta = 122.02, 157.91
\) ppm; \(^1\)N NMR (50.69 MHz, [D\(_6\)]DMSO, 25°C, TMS): \( \delta = -13.37, -297.66
\) ppm; IR (KBr): \( \nu_{\text{max}} = 3402, 3193, 3140, 1659, 1465, 1442, 1416, 1322, 1232,
1086, 1001, 779, 702, 570, 514 \text{ cm}^{-1} \); elemental analysis calcd (%) for C\(_2\)H\(_7\)N\(_5\)O\(_4\) (165.05): C 14.55, H
4.27, N 42.42; found: C 14.79, H 4.39, N 42.11.

**Aminoguanidinium Dinitromethanide (2):** The same procedure was followed as that
described above for 1. Aminoguanidinium 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): \( \delta = 4.67 \) (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\(_2\)); \(^1\)C NMR (75 MHz, [D\(_6\)]DMSO, 25°C, TMS): \( \delta = 122.13, 158.78 \) ppm; IR
(KBr): \( \nu_{\text{max}} = 3459, 3389, 3354, 3287, 3195, 3154, 1671, 1460, 1368, 1230, 1213,
1057, 995, 777, 742, 595 \text{ cm}^{-1} \); elemental analysis calcd (%) for C\(_2\)H\(_8\)N\(_6\)O\(_4\) (180.12):
C 13.34, H 4.48, N 46.66; found: C 13.37, H 4.28, N 46.70.

**Diaminoguanidinium Dinitromethanide (3):** The same procedure was followed as
that described above for 1. Diaminoguanidinium 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): $\delta$ = 4.58 (s, 4H; NH$_2$NH$_2$), 7.15 (s, 2H; NH$_2$), 8.14 (s, 1H; CH(NO$_2$)$_2$), 8.58 ppm (s, 2H; NHNH$_2$); $^{13}$C NMR (75 MHz, [D$_6$]DMSO, 25°C, TMS): $\delta$ = 122.33, 159.85 ppm; IR (KBr): $\nu_{\text{max}}$ = 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$_2$H$_9$N$_7$O$_4$ (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): $\delta$ = 4.50 (s, 6H; NH$_2$NH$_2$), 8.14 (s, 1H; CH(NO$_2$)$_2$), 8.56 ppm (s, 3H; NHNH$_2$); $^{13}$C NMR (75 MHz, [D$_6$]DMSO, 25°C, TMS): $\delta$ = 122.14, 159.10 ppm; $^{15}$N NMR (50.69 MHz, [D$_6$]DMSO, 25°C, TMS): $\delta$ = -13.37, -281.22, -321.76 ppm; IR (KBr): $\nu_{\text{max}}$ = 3321, 3288, 3212, 3152, 1759, 1709, 1641, 1591, 1466, 1404, 1364, 1311, 1214, 1080, 1001, 924, 783, 743, 692, 606 cm$^{-1}$; elemental analysis calcd (%) for C$_2$H$_{10}$N$_8$O$_4$ (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): $\delta$ = 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): $\delta$ = 122.24, 155.74, 156.09 ppm; IR (KBr): $\nu_{\text{max}}$ = 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$_3$H$_8$N$_6$O$_5$ (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): $\delta$ = 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): $\delta$ = 38.88,
122.22, 142.96, 145.01 ppm; IR (KBr): $\nu_{\text{max}} = 3295, 3144, 1720, 1636, 1572, 1530, 1459, 1361, 1297, 1194, 1123, 1076, 997, 880, 808, 780, 743, 654, 615 \text{ cm}^{-1}$; elemental analysis calcd (%) for $\text{C}_4\text{H}_8\text{N}_6\text{O}_4$ (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): $\delta = 3.84$ (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): $\delta = 34.83, 122.73, 147.84$ ppm; $^{15}$N NMR (50.69 MHz, [D$_6$]DMSO, 25°C, TMS): $\delta = -13.31$, –16.11, –27.36, –159.67, –178.08, –301.51, –312.01 ppm; IR (KBr): $\nu_{\text{max}} = 3305, 3189, 3148, 1713, 1635, 1462, 1400, 1361, 1297, 1196, 1187, \ldots, 1070, 1039, 1000, 940, 782, 743, 643 \text{ cm}^{-1}$; elemental analysis calcd (%) for $\text{C}_3\text{H}_8\text{N}_8\text{O}_4$ (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): $\delta = 3.86$ (s, 6H; CH$_3$), 8.13 (s, 1H; CH(NO$_2$)$_2$), 9.07 ppm (s, 2H; N-NH$_2$); $^{13}$C NMR (75 MHz, [D$_6$]DMSO, 25 °C, TMS): $\delta = 34.00, 122.13, 148.54$ ppm; IR (KBr): $\nu_{\text{max}} = 3327, 3150, 1666, 1596, 1487, 1466, 1412, 1368, 1315, 1200, 1116, 1087, 1046, 1001, 969, 787, 743, 677 \text{ cm}^{-1}$; elemental analysis calcd (%) for $\text{C}_4\text{H}_9\text{N}_7\text{O}_4$ (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): $\delta = 2.86$ (s, 3H), 4.22 (s, 6H), 8.14 ppm (s, 1H; CH(NO$_2$)$_2$); $^{13}$C NMR (75 MHz,

References


