Supporting information for

Nitrogen-rich Nitroguanidyl-functionalized Tetrazolate Energetic Salts

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Table 1

<table>
<thead>
<tr>
<th></th>
<th>ZPE^a</th>
<th>H_T^b</th>
<th>E_0^c</th>
<th>HOF (kJ/mol)</th>
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<tbody>
<tr>
<td>NGT anion</td>
<td>0.092721</td>
<td>0.103327</td>
<td>-664.9351139</td>
<td>165.55</td>
</tr>
<tr>
<td>NAG</td>
<td>0.10347</td>
<td>0.008852</td>
<td>-464.4745091</td>
<td>861.90</td>
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<tr>
<td>INI</td>
<td>0.16066</td>
<td>0.173222</td>
<td>-689.01685</td>
<td>805.32</td>
</tr>
</tbody>
</table>

^a Zero-point correction (Hartree/Particle); ^b Thermal correction to enthalpy (Hartree/Particle); ^c Total energy calculated by B3LYP/6-31+G**//MP2/6-311++G** method (Hartree/Particle).
Geometry coordinates of NGT anion

N  0.00000000  0.00000000  0.00000000
C  1.62048375  0.00000000  0.00000000
N  2.25126045  1.07550303  0.00000000
N  1.55911302  2.39320967 -0.32989734
O  1.35696523  3.14640352  0.49145767
O  1.34433147  2.77653001 -1.74455842
N  2.36618568 -1.32621963  0.35199502
C  -0.78948018  0.07476839  1.42304132
N  -1.01865929  1.19579146  1.94006614
N  -0.65453216  1.19493775  3.45147087
N  -0.26387533  0.15256732  3.83783427
N  -0.26569417 -0.84757164  2.67148261
H  -0.50518548  0.21458716 -0.86935024
H  3.35443422 -1.44101891  0.09322234
H  1.91660188 -2.01280064  0.97101210

Geometry coordinates of NAG Cation

N  0.00000000  0.00000000  0.00000000
C  1.62820290  0.00000000  0.00000000
N  2.35354872  1.37779145  0.00000000
N  2.17913844 -1.02567206  0.46365290
N  -0.59734573  0.52040671  1.10390499
N  3.25785907 -0.80194752  1.47408676
O  3.96692756 -1.65003361  1.72122503
O  2.64525421 -0.06098465  2.53218049
H  -0.51314315 -0.00632962 -0.88549634
H  2.17093724  2.04510483  0.76021812
H  3.16978780  1.51642846 -0.60245462
H  -1.32447560  1.19414799  0.81386184
H  0.11277214  0.99640506  1.67286655
H  -1.02860678 -0.23212065  1.65390970

Geometry coordinates of INI cation

C  0.00000000  0.00000000  0.00000000
C  1.57543915  0.00000000  0.00000000
N  2.02076113  1.38515632  0.00000000
C  0.77990467  2.29675875 -0.03699555
Scheme 1  The isodesmic reactions of NGT anion, NAG and INI cations

Scheme 2. Born-Haber cycle for the formation of energetic salts.
Experimental Section

Caution: Although we experienced no difficulties in handling these energetic materials, small scale and best safety practices (leather gloves, face shield) are strongly encouraged.

General methods: 5-nitroguanidyltetrazole[1] nitroaminoguanidine[2] and 2-iminium-5-nitriminoctahydroimidazo[4,5-d]imidazole chloride [3] were prepared as reported previously. IR spectra were recorded using KBr plate on BIORAD model 3000 FTS spectrometer. 1H and 13C spectra were recorded on spectrometers at 300 and 75 MHz, respectively, by using DMSO-d6 as a locking solvent. Chemical shifts were reported in ppm relative TMS. Densities were measured at 25 °C using a Micromeritics Accupyc 1330 gas pycnometer. Differential scanning calorimetry (DSC) measurements were performed using a calorimeter equipped with an auto-cool accessory and calibrated using indium. The samples were heated from 40 to 300 or 400 °C at 10 °C/min. The transition temperature, Tm, was taken as peak maximum. Thermogravimetric analysis (TGA) measurements were carried out by heating samples at 10 °C/min from 25 to 500 °C in a dynamic nitrogen atmosphere (flow rate = 70 mL/min). Elemental analyses were performed on a CE-440 Elemental Analyzer.

Theoretical study

Calculations were carried out using the Gaussian 03 (Revision D.01) suite of programs.[4] The geometric optimization of the structures and frequency analyses were carried out using B3-LYP functional with the 6-31+G** basis set, single-point energy was calculated at the MP2(full)/6-311++G** level. All of the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies.

Based on a Born-Haber energy cycle (Scheme 2), the heat of formation of a salt can be simplified by the formula:

$$\Delta H_f^o(\text{ionic salt, 298K}) = \Delta H_f^o(\text{cation, 298K}) + \Delta H_f^o(\text{anion, 298 K}) - \Delta H_L$$

where $\Delta H_L$ is the lattice energy of the salt which could be predicted by the formula suggested by Jenkins et al.[5] as:

$$\Delta H_L = U_{\text{POT}} + [p(n_M/2 - 2) + q(n_X/2 - 2)]RT$$  \hspace{1cm} (A)

where $n_M$ and $n_X$ depend on the nature of the ions $M_p^+$ and $Xq^-$, respectively, and are equal to 3 for
monatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions. The equation for lattice potential energy $U_{\text{POT}}$ (eq B) has the form

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

where density ($\rho_m$) g/cm$^3$, $M_m$ is the chemical formula mass of the ionic material, g, and the coefficients $\gamma$ (kJ/mol cm) and $\delta$ (kJ/mol) are assigned literature values.

The heat of formation of the 5-nitroguanidyltetrazolate anion and nitroaminoguanidinium and 2-iminium-5-nitriminooctahydroimidazo[4,5-d]imidazole cations were computed using the method of isodesmic reaction in the Scheme 1. The enthalpy of an isodesmic reaction ($\Delta H_{298}$) is obtained by combining the MP2(full)/6-311++G{*} energy difference for the reaction, the scaled zero point energies (B3LYP/6-31+G{*}), and other thermal factors (B3LYP/6-31+G{*}).[6] The detonation velocity, detonation pressure, and specific impulse were calculated using CHEETAH 5.0.[7]

X-ray Crystallography.

A crystal of compounds 8 and 9 was mounted on a MiteGen MicroMesh using a small amount of Cargille Immersion Oil. Data were collected on a Bruker three-circle platform diffractometer equipped with a SMART CCD detector. The crystals were irradiated using a graphite monochromated MoK$_\alpha$ radiation ($\lambda = 0.71073$). A MSC X-Stream low temperature device was used to keep the crystals at a constant temperature during data collection. Data collection was performed and the unit cell was initially refined using APEX2 [v2.1-0].[8] Data Reduction was performed using SAINT [v7.34A] [9] and XPREP [v6.12] [10]. Corrections were applied for Lorentz, polarization, and absorption effects using SADABS [v2.10].[11] The structure was solved and refined with the aid of the programs in the SHELXTL-plus [v6.12] system of programs.[12] The full-matrix least-squares refinement on $F^2$ included atomic coordinates and anisotropic thermal parameters for all non-H atoms. The H atoms were included using a riding model.

5-Nitroguanidyltetrazole: the compound was prepared according to literature methods.[1] Colorless solid. $^1$H NMR: $\delta$ 9.08 (s); $^{13}$C NMR: $\delta$ 157.4, 154.0. IR: 3384 (w), 3296 (vw), 3192 (vw), 2891 (vw), 2365 (vw), 2149 (vw), 1923 (vw), 1638 (s), 1593 (vw), 1519 (m), 1420 (vw), 1380 (vw), 1255 (s), 1117 (vw), 1065 (w), 1034 (w), 1009 (w), 951 (w), 834 (vw), 785 (w), 734 (vw), 695 (vw), 642 (vw), 597 (w), 529 (vw), 486 (w) cm$^{-1}$.

General procedures for preparation of the energetic compounds 1–10: To a stirring solution of 5-nitroguanidyltetrazole (0.1721 g, 1.0 mmol) in H$_2$O (50 mL) was added barium hydroxide (0.1578 g, 0.5 mmol), the resulting mixture was stirred at 60 °C until all of solids were dissolved. After cooled to 25 °C, sulfate salts (0.5 mmol) or the mixture of halide salts (1.0 mmol) and Ag$_2$SO$_4$ (0.5 mmol) in H$_2$O were added, the resulting mixtures was stirred at 25 °C for additional 1 h. After filtered, the slow evaporation of filtrate gave rise to desirable products, which were washed twice with Et$_2$O.

Guanidinium 5-nitroguanidyltetrazolate (1): Colorless solid, yield: 1.9 g (78%). $^1$H NMR: $\delta$ 10.84 (s, 1H), 9.61 (d, $J = 222.5$ Hz, 2H), 6.95 (s, 6H); $^{13}$C NMR: $\delta$ 158.7, 158.4, 157.8. IR: 3432 (vw), 3385 (w), 3264 (vw), 3180 (w), 2859 (vw), 2765 (vw), 1669 (s), 1616 (s), 1463 (w), 1373 (m), 1271 (s), 1131 (w), 1082 (vw), 1049 (vw), 953 (vw), 841 (w), 775 (w), 751 (vw), 677 (w), 546 (w), 481 (m) cm$^{-1}$. Anal. Calcd for C$_3$H$_9$N$_{11}$O$_2$·0.75H$_2$O (244.60): C, 14.73; H, 4.33; N 62.97. Found: C, 14.87; H, 4.30; N, 62.39.

Aminoguanidinium 5-nitroguanidyltetrazolate (2): Colorless solid, yield: 1.8 g (73%). $^1$H
**NMR:** δ 9.99 (s, 1H), 9.25 (s, 1H), 7.04 (s, 4H), 4.68 (s, 2H); **13C NMR:** δ 159.3, 158.7, 157.8. **IR:** 3385 (w), 3264 (vw), 3177 (w), 2879 (vw), 2765 (vw), 1679 (s), 1667 (s), 1599 (s), 1528 (vw), 1464 (m), 1393 (w), 1265 (s), 1127 (m), 1012 (w), 1074 (m), 1042 (w), 980 (m), 843 (m), 767 (w), 675 (w), 616 (w), 527 (w), 480 (m) cm⁻¹. Anal. Calcd for C₃H₁₀N₁₂O₂ (246.19): C, 14.64; H, 4.09; N 68.27. Found: C, 14.72; H, 4.08; N, 67.77.

**Diaminoguanidinium 5-nitroguanidyltetrazolate (3):** Colorless solid, yield: 2.2 g (84%). **1H NMR:** δ 10.02 (s, 1H), 9.22 (s, 1H), 7.13 (s, 2H), 4.56 (s, 3H); **13C NMR:** δ 160.2, 158.7, 157.8. **IR:** 3430 (w), 3364 (vw), 3304 (m), 3203 (w), 2972 (vw), 2876 (w), 2787 (vw), 1693 (s), 1606 (vs), 1464 (m), 1378 (s), 1346 (w), 1275 (vs), 1212 (w), 1179 (w), 1130 (m), 1018 (w), 1048 (m), 1010 (m), 839 (vw), 779 (w), 717 (vw), 675 (w), 616 (w), 598 (w), 481 (m). Anal. Calcd for C₃H₁₁N₁₃O₂ (261.21): C, 13.79; H, 4.24; N, 69.71. Found: C, 13.77; H, 4.22; N, 69.41.

**Triaminoguanidinium 5-nitroguanidyltetrazolate hemihydrate (4):** Colorless solid, yield: 2.3 g (81%). **1H NMR:** δ 10.02 (s, 1H), 9.22 (s, 1H), 8.58 (s, 2H), 4.46 (s, 5H); **13C NMR:** δ 159.5, 158.7, 157.7. **IR:** 3366 (w), 3264 (s), 3000 (vw), 2850 (vw), 2764 (vw), 1684 (s), 1622 (s), 1529 (vw), 1466 (m), 1368 (s), 1278 (vs), 1144 (w), 1127 (m), 1045 (m), 1018 (w), 953 (w), 878 (vw), 841 (w), 766 (w), 710 (vw), 671 (w), 603 (m), 482 (w) cm⁻¹. Anal. Calcd for C₃H₁₂N₁₄O₂·0.5H₂O (285.23): C, 12.63; H, 4.59; N, 68.75. Found: C, 12.51; H, 4.46; N, 68.29.

**N-carbamoylguanidinium 5-nitroguanidyltetrazolate (5):** Colorless solid, yield: 2.1 g (77%). **1H NMR:** δ 9.95 (s, 1H), 9.23 (s, 1H), 8.04 (s, 4H), 7.09 (s, 2H); **13C NMR:** δ 158.7, 157.7, 155.9, 154.9. **IR:** 3442 (vw), 3380 (w), 3341 (vw), 3198 (vw), 2847 (vw), 2761 (vw), 1740 (s), 1690 (s), 1590 (s), 1528 (vw), 1466 (m), 1339 (w), 1271 (s), 1121 (w), 1072 (w), 1042 (w), 928 (w), 843 (w), 817 (vw), 762 (w), 707 (w), 625 (w), 540 (vw), 483 (m) cm⁻¹. Anal. Calcd for C₄H₁₀N₁₂O₃ (274.20): C, 17.52; H, 3.68; N, 61.30. Found: C, 17.45; H, 3.61; N, 60.70.

**Nitroaminoguanidinium 5-nitroguanidyltetra zolate hydrate (6):** The salt was also synthesized by the following procedure: to a stirring solution of 5-nitroguanidyltetrazole (0.1721 g, 1.0 mmol) in H₂O (30 mL) was added nitroaminoguanidine (0.1191 g, 1.0 mmol), the resulting solution was stirred at 60 °C for 6 h. After cooled to room temperature, the solution was filtered, the slow evaporation of filtrate at room temperature gave rise to colorless solid. Yield: 0.26 g (84%). **1H NMR:** δ 9.11 (s, 2H), 7.82 (s, 2H), 6.88 (s, 2H); **13C NMR:** δ 161.9, 157.4, 154.2. **IR:** 3386 (w), 3308 (w), 3341 (w), 3198 (w), 2847 (w), 2761 (w), 1740 (s), 1690 (s), 1590 (s), 1528 (w), 1466 (m), 1339 (w), 1271 (s), 1121 (w), 1072 (w), 1042 (w), 928 (w), 843 (w), 817 (vw), 762 (w), 707 (w), 673 (w), 625 (w), 540 (w), 483 (m) cm⁻¹. Anal. Calcd for C₃H₉N₁₃O₄·H₂O (309.2): C, 11.65; H, 3.59; N, 58.89. Found: C, 11.52; H, 3.44; N, 58.95.

**1,4,5-Trimethyltetrazolium 5-nitroguanidyltetrazolate (7):** Colorless solid, yield: 2.3 g (81%). **1H NMR:** δ 10.01 (s, 1H), 9.21 (s, 1H), 8.04 (s, 4H), 7.09 (s, 2H); **13C NMR:** δ 158.7, 157.7, 155.9, 154.9. **IR:** 3342 (w), 3380 (w), 3341 (w), 3198 (w), 2847 (w), 2761 (w), 1740 (s), 1690 (s), 1590 (s), 1528 (w), 1466 (m), 1339 (w), 1271 (s), 1121 (w), 1072 (w), 1042 (w), 928 (w), 843 (w), 817 (vw), 762 (w), 707 (w), 673 (w), 625 (w), 540 (w), 483 (m) cm⁻¹. Anal. Calcd for C₆H₁₂N₁₂O₂ (284.24): C, 25.35; H, 4.26; N, 58.95. Found: C, 11.52; H, 3.44; N, 58.95.

**1,4-Dimethyl-5-aminotetrazolium 5-nitroguanidyltetrazolate (8):** Colorless solid, yield: 2.5 g (88%). **1H NMR:** δ 10.01 (s, 1H), 9.21 (s, 1H), 8.04 (s, 4H), 7.09 (s, 2H). **13C NMR:** δ 158.7, 157.8, 149.0, 34.5. **IR:** 3385 (w), 3227 (vw), 3173 (w), 2992 (vw), 2820 (vw), 2670 (vw), 1697 (s), 1607 (s), 1524 (vw), 1462 (w), 1422 (vw), 1371 (m), 1285 (w), 1223 (m), 1097 (w), 1080 (m), 1046 (vw), 996 (vw), 950 (vw), 878 (vw), 778 (m), 710 (vw), 668 (w), 635 (vw), 573 (m), 480 (w) cm⁻¹. Anal. Calcd for C₆H₁₀N₁₂O₂·0.5H₂O (284.24): C, 25.35; H, 4.26; N, 58.95. Found: C, 25.16; H, 4.22; N, 58.03.
Supplementary Material (ESI) for Chemical Communications
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Calcd for C$_5$H$_{11}$N$_{13}$O$_2$ (285.23): C, 21.05; H, 3.89; N, 63.84. Found: C, 21.03; H, 3.84; N, 63.46.

2-Iminium-5-nitriminooctahydroimidazo[4,5-d]imidazole 5-nitroguanidyltetrazolate hydrate (9): Yield: 0.31 g (83 %). $^1$H NMR: δ 9.99 (s, 2H), 9.25 (s, 4H), 8.11 (s, 2H), 5.83 (s, 2H); $^{13}$C NMR: δ 161.7, 159.3, 158.6, 157.7, 70.4. IR: 3358 (s), 3211 (w), 3021 (w), 2864 (w), 2782 (vw), 2225 (vw), 1700 (m), 1628 (vw), 1593 (s), 1502 (vw), 1467 (w), 1360 (s), 1290 (s), 1256 (s), 1136 (w), 1111 (w), 1084 (m), 1043 (w), 972 (w), 894 (w), 846 (w), 777 (w), 741 (w), 675 (w), 637 (m), 546 (w), 482 (vw) cm$^{-1}$. Anal. Calcd for C$_6$H$_{11}$N$_{15}$O$_4$·H$_2$O (375.26): C, 19.20; H, 3.49; N, 55.99. Found: C, 19.25; H, 3.41; N, 55.79.

Carbonic dihydrazidinium bis(5-nitroguanidyltetrazolate) hydrate (10): Colorless solid, yield: 2.0 g (88%). $^1$H NMR: δ 9.96 (s, 2H), 9.22 (s, 2H), δ 4.72 (br, s); $^{13}$C NMR: δ 159.9, 158.3, 157.7. IR: 3380 (w), 3202 (vw), 3015 (vw), 2878 (vw), 2778 (vw), 1630 (s, br), 1464 (w), 1371 (vw), 1273 (s), 1155 (vw), 1137 (vw), 1074 (vw), 1042 (vw), 957 (vw), 841 (w), 777 (vw), 675 (vw), 598 (w), 486 (m) cm$^{-1}$. Anal. Calcd for C$_5$H$_{14}$N$_{20}$O$_5$·H$_2$O (452.31): C, 13.28; H, 3.57; N, 61.93. Found: C, 13.35; H, 3.74; N, 58.77.

References:
[6] Gaussian 03, revision D.01; Gaussian, Inc.: Wallingford CT, 2004