

Supporting information for

Nitrogen-rich Nitroguanidyl-functionalized Tetrazolate Energetic Salts

Ruihu Wang,^[a] Yong Guo,^[b] Zhuo Zeng,^[b] and Jean'ne M. Shreeve^{[b]*}

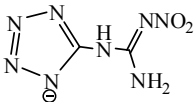
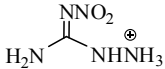
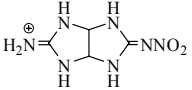
^a *State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China;*

^b *Department of Chemistry, University of Idaho, Moscow, Idaho 83844-2343; E-mail:
jshreeve@uidaho.edu*

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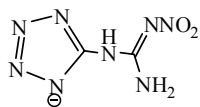
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Table 1 *Ab initio* computational values of NGT anion, nitroaminoguanidinium (NAG) and 2-iminium-5-nitriminoctahydroimidazo[4,5-d]imidazole (INI) cations

	ZPE ^a	H _T ^b	E ₀ ^c	HOF (kJ/mol)
	0.092721	0.103327	-664.9351139	165.55
	0.10347	0.008852	-464.4745091	861.90
	0.16066	0.173222	-689.01685	805.32

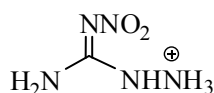
^aZero-point correction (Hartree/Particle); ^b Thermal correction to enthalpy (Hartree/Particle);

^cTotal energy calculated by B3LYP/6-31+G**//MP2/6-311++G** method (Hartree/Particle).



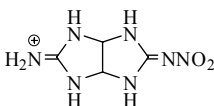
Geometry coordinates of NGT anion

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

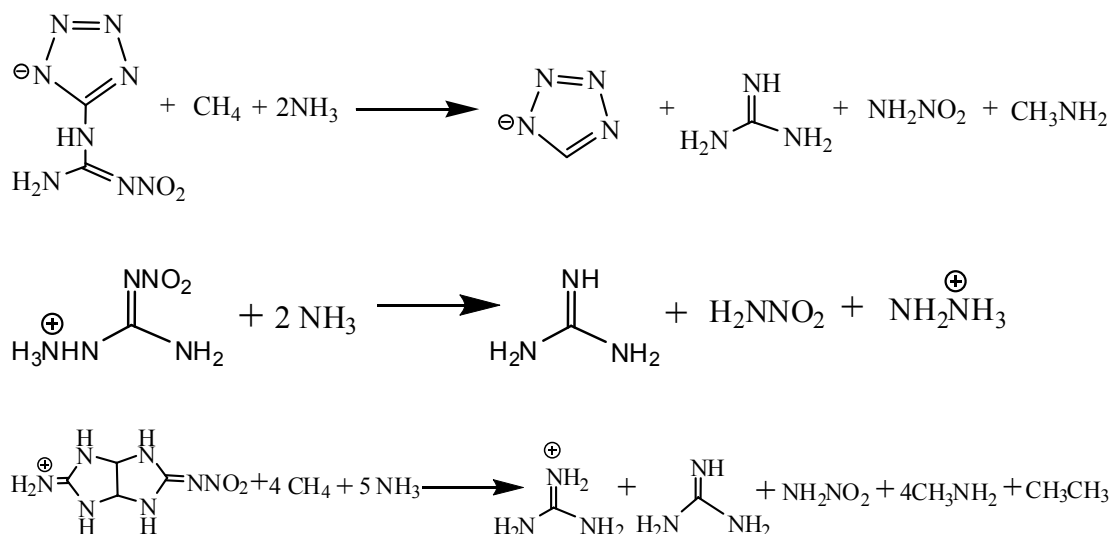
N	0.00000000	0.00000000	0.00000000
C	1.62820290	0.00000000	0.00000000
N	2.35354872	1.37779145	0.00000000
N	2.17913844	-1.02567206	0.46365290
N	-0.59734573	0.52040671	1.10390499
N	3.25785907	-0.80194752	1.47408676
O	3.96692756	-1.65003361	1.72122503
O	2.64525421	-0.06098465	2.53218049
H	-0.51314315	-0.00632962	-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



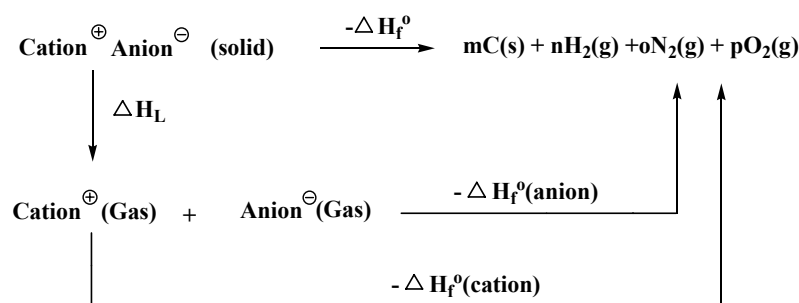
Geometry coordinates of INI cation

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

N	-0.44963782	1.38363280	-0.06461253
N	-0.45817288	-0.61904798	1.23751362
C	0.79799735	-1.07449986	2.05624219
N	2.04644167	-0.65705035	1.21134737
N	0.76914677	3.53802326	0.03440576
N	2.05722015	4.29725752	0.25701896
O	2.24605638	5.26399457	-0.29681996
O	2.81893311	3.92965631	1.36619117
N	0.80739917	-1.65661776	3.15386428
H	-0.40529286	-0.57004108	-0.87827909
H	1.98384429	-0.52768852	-0.90282735
H	2.84655110	1.65591315	0.54903985
H	-1.27080195	1.63906713	-0.62577564
H	-1.28414619	-0.24920747	1.72474433
H	2.87454794	-1.26494352	1.17981700
H	1.69837654	-1.91640066	3.59645484
H	-0.07736791	-1.89350404	3.62139568



Scheme 1 The isodesmic reactions of NGT anion, NAG and INI cations



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

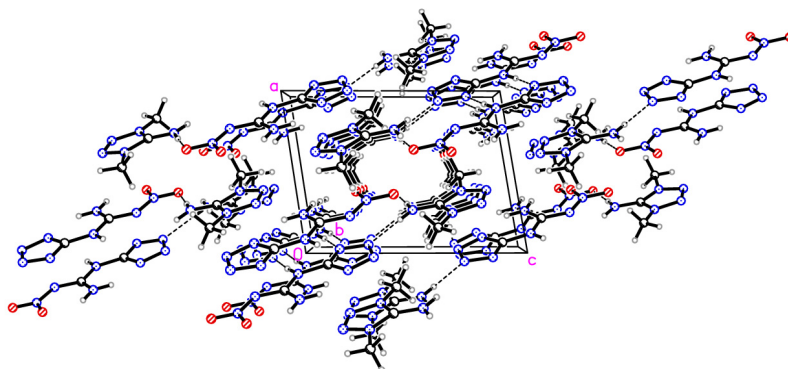


Figure 1 Packing diagram of **8** along the *b*-axis.

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-*d*₆ 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, *T*_m, 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:

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

where ΔH_L is the lattice energy of the salt which could be predicted by the formula suggested by Jenkins *et al.*^[5] as:

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

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_{POT} (eq **B**) has the form

$$U_{\text{POT}}/\text{kJ mol}^{-1} = \gamma (\rho_{\text{m}}/M_{\text{m}})^{1/3} + \delta \quad (\text{B})$$

where density (ρ_{m}) g/cm³, M_{m} is the chemical formula mass of the ionic material, g, and the coefficients γ kJ/mol cm and δ /kJ/mol) are assigned literature values.

The heat of formation of the 5-nitroguanidylnitrazolate anion and nitroaminoguanidinium and 2-iminium-5-nitriminoctahydroimidazo[4,5-d]imidazole cations were computed using the method of isodesmic reaction in the Scheme 1. The enthalpy of an isodesmic reaction ($\Delta H_{r, 298}^{\circ}$) 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 α 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 *SAINTE* [v7.34A]^[9] and *XPREF* [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-Nitroguanidylnitrazole: the compound was prepared according to literature methods.^[1] colorless solid. ¹H NMR: δ 9.08 (s); ¹³C NMR: δ 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-nitroguanidylnitrazole (0.1721 g, 1.0 mmol) in H₂O (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 Ag₂SO₄ (0.5 mmol) in H₂O 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 Et₂O.

Guanidinium 5-nitroguanidylnitrazolate (1) : Colorless solid, yield: 1.9 g (78%). ¹H NMR: δ 10.84 (s, 1H), 9.61 (d, $J = 222.5$ Hz, 2H), 6.95 (s, 6H); ¹³C NMR: δ 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 C₃H₉N₁₁O₂·0.75H₂O (244.60): C, 14.73; H, 4.33; N 62.97. Found: C, 14.87; H, 4.30; N, 62.39.

Aminoguanidinium 5-nitroguanidylnitrazolate (2): Colorless solid, yield: 1.8 g (73%). ¹H

NMR: δ 9.99 (s, 1H), 9.25 (s, 1H), 7.04 (s, 4H), 4.68 (s, 2H); ^{13}C NMR: δ 159.3, 158.7, 157.8. IR: 3385 (w), 3264 (vw), 3177 (w), 3001 (vw), 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 $\text{C}_3\text{H}_{10}\text{N}_{12}\text{O}_2$ (246.19): C, 14.64; H, 4.09; N 68.27. Found: C, 14.72; H, 4.08; N, 67.77.

Diaminoguanidinium 5-nitroguanidyldtetrazolate (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); ^{13}C 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), 1108 (vw), 1048 (m), 1010 (m), 839 (vw), 779 (w), 717 (vw), 675 (w), 616 (w), 598 (w), 481 (m). Anal. Calcd for $\text{C}_3\text{H}_{11}\text{N}_{13}\text{O}_2$ (261.21): C, 13.79; H, 4.24; N 69.71. Found: C, 13.77; H, 4.22; N, 69.41.

Triaminoguanidinium 5-nitroguanidyldtetrazolate 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); ^{13}C 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 (vw), 953 (w), 878 (vw), 841 (w), 766 (w), 710 (vw), 671 (w), 603 (m), 482 (w) cm^{-1} . Anal. Calcd for $\text{C}_3\text{H}_{12}\text{N}_{14}\text{O}_2 \cdot 0.5\text{H}_2\text{O}$ (285.23): C, 12.63; H, 4.59; N, 68.75. Found: C, 12.51; H, 4.46; N, 68.29.

N-carbamoylguanidinium 5-nitroguanidyldtetrazolate (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); ^{13}C 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 (vw), 843 (w), 817 (vw), 762 (w), 707 (w), 673 (w), 625 (w), 540 (vw), 483 (m) cm^{-1} . Anal. Calcd for $\text{C}_4\text{H}_{10}\text{N}_{12}\text{O}_3$ (274.20): C, 17.52; H, 3.68; N, 61.30. Found: C, 17.45; H, 3.61; N, 60.70.

Nitroaminoguanidinium 5-nitroguanidyldtetrazolate hydrate (6): The salt was also synthesized by the following procedure: to a stirring solution of 5-nitroguanidyldtetrazole (0.1721 g, 1.0 mmol) in H_2O (30 mL) was added nitroaminoguanidine (0.1191g, 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); ^{13}C NMR: δ 161.9, 157.4, 154.2. IR: 3386 (w), 3308 (w), 3215 (w), 3154 (vw), 1667 (s), 1620 (s), 1579 (m), 1527 (w), 1592 (w), 1356 (w), 1283 (s), 1181 (w), 1125 (w), 1079 (vw), 1026 (m), 952 (w), 824 (w), 779 (m), 700 (vw), 617 (m), 533 (w), 482 (w) cm^{-1} . Anal. Calcd for $\text{C}_3\text{H}_9\text{N}_{13}\text{O}_4 \cdot \text{H}_2\text{O}$ (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-nitroguanidyldtetrazolate (7): Colorless solid, yield: 2.3 g (81%). ^1H NMR: δ 10.01 (s, 1H), 9.21 (s, 1H), 4.20 (s, 6H), 2.82 (s, 3H); ^{13}C NMR: δ 158.7, 157.7, 153.2, 36.7, 8.6. IR: 3340 (m), 3198 (w), 3004 (w), 2852 (vw), 2771 (vw), 1645 (s), 1608 (m), 1542 (vw), 1491 (vw), 1460 (m), 1376 (s), 1282 (s), 1141 (w), 1124 (w), 1038 (m), 959 (vw), 878 (vw), 843 (w), 760 (m), 710 (w), 699 (m), 567 (vw), 484 (m) cm^{-1} . Anal. Calcd for $\text{C}_6\text{H}_{12}\text{N}_{12}\text{O}_2$ (284.24): C, 25.35; H, 4.26; N, 59.13. Found: C, 25.16; H, 4.22; N, 58.03.

1,4-Dimethyl-5-aminotetrazolium 5-nitroguanidyldtetrazolate (8): Colorless solid, yield: 2.5 g (88%). ^1H NMR: δ 10.01 (s, 1H), 9.21 (s, 1H), 3.83(s, 6H); ^{13}C NMR: δ 158.7, 157.8, 149.0, 34.5. IR: 3385 (w), 3227 (vw), 3173 (vw), 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 C₅H₁₁N₁₃O₂ (285.23): C, 21.05; H, 3.89; N, 63.84. Found: C, 21.03; H, 3.84; N, 63.46.

2-Iminium-5-nitriminoctahydroimidazo[4,5-d]imidazole 5-nitroguanidyltetrazolate hydrate (9): Yield: 0.31 g (83 %). ¹H NMR: δ 9.99 (s, 2H), 9.25 (s, 4H), 8.11 (s, 2H), 5.83 (s, 2H); ¹³C 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 (w), 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 C₆H₁₁N₁₅O₄·H₂O (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%). ¹H NMR: 9.96 (s, 2H), 9.22 (s, 2H), δ 4.72 (br, s); ¹³C 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 C₅H₁₄N₂₀O₅·H₂O (452.31): C, 13.28; H, 3.57; N, 61.93. Found: C, 13.35; H, 3.74; N, 58.77.

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