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Heterocyclic-Based Nitrodicyanomethanide and Dinitrocyanomethanide Salts: A Family of New Energetic Ionic Liquids[†]

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Twelve novel energetic salts **1a**–**f** and **2a**–**f** with nitrodicyanomethanide and dinitrocyanomethanide anions paired with 1,5-diamino-4-methyltetrazolium, 1,4-dimethyl-5-aminotetrazolium 1,4,5-trimethyltetrazolium, 1-methyl-4-amino-1,2,4-triazolium, 1,4-dimethyltriazolium, and 1,3-dimethylimidazolium have been prepared through metathesis reactions of equivalent silver(I) salts with corresponding iodide salts in acetonitrile. Key physical properties, such as melting point, thermal stability and density, were measured. The relationship between their structures and these properties was determined. The structures of 1,5-diamino-4-methyltetrazolium-based salts **1a** and **2a** were further confirmed by single-crystal X-ray analysis. The densities and standard enthalpies of formation for these energetic salts were calculated. All of the salts possess higher enthalpies of formation than the nitrate analogues.

Introduction

Ionic liquids (ILs) have received considerable attention as environmentally benign alternatives in organic synthesis and advanced materials.[1] Recent interest was focused on energetic ILs with the aim to reduce the overall exposure to hazardous and potential toxic materials.[2] Compared with traditional energetic compounds, such as TNT, HMX, and RDX, energetic ILs have several advantages, such as excellent stability and negligible vapor pressure. In addition, their properties are readily tuned through independent modification of both cationic and anionic components. The approach significantly increases the numbers of energetic compounds available.

Five-membered nitrogen-containing heterocycles are traditional sources of energetic materials.[3] They not only are readily quarternized or protonated to form energetic cations,[4−6] but also can be deprotonated to form stable azolate energetic anions.[7−9] Various energetic ILs were prepared through combining heterocycle-based cations with small inorganic anions[4,5] or azolate anions.[8] Their performances are easily optimized and improved through substituting hydrogen atoms in the heterocyclic rings of cations and/or anions with energetic groups, such as nitro, cyano, amino, and azido. Among reported energetic ILs, those possessing lower

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[†] Dedicated to Karl Christe on the occasion of his 70th birthday.

(1) (a) Welton, T. *Chem. Rev.* **1999**, *99*, 2071−2083. (b) Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3773−3789. (c) Dupont, J.; de Souza, R. F.; Suarez, P. A. Z. *Chem. Rev.* **2002**, *102*, 3667−3691.

(2) (a) Singh, R. P.; Verma, R. D.; Meshri, D. T.; Shreeve, J. M. *Angew. Chem., Int. Ed.* **2006**, *45*, 3584−3601. (b) Hammerl, A.; Hiskey, M. A.; Holl, G.; Klapötke T. M.; Polborn, K.; Stierstorfer, J.; Weigand, J. J. *Chem. Mater.* **2005**, *17*, 3784−3793. (c) Oxley, J. C.; Smith, J. L.; Chen, H. *Thermochim. Acta* **2002**, *384*, 91−99. (d) Christe, K. O.; Wilson, W. W.; Sheehy, J. A.; Boatz, J. A. *Angew. Chem., Int. Ed.* **1999**, *38*, 2004−2009.

(3) (a) Sikder, A. K.; Sikder, N. *J. Hazard. Mater.* **2004**, *A112*, 1−15. (b) Pagoria, P. F.; Lee, G. S.; Mitchell, A. R.; Schmidt, R. D. *Thermochim. Acta* **2002**, *384*, 187−204. (c) Fried, L. E.; Manaa, M. R.; Pagoria, P. F.; Simpson, R. L. *Annu. Rev. Mater. Res.* **2001**, *31*, 291−321. (d) Ou, Y.; Chen, B.; Li, J.; Jia, H. *Heterocycles* **1994**, *38*, 1651−1664. (e) Lee, K. Y.; Storm, C. B.; Hiskey, M. A.; Coburn, M. D. *J. Energy Mater.* **1991**, *9*, 415−428.

(4) (a) Drake, G. W.; Hawkins, T. W.; Hall, L. A.; Boatz, J. A.; Brand, A. J. *Propellants, Explos., Pyrotech.* **2005**, *30*, 329−337. (b) Drake, G. W.; Hawkins, T.; Brand, A.; Hall, L.; Mckay, M. *Propellants, Explos., Pyrotech.* **2003**, *28*, 174−180.

(5) (a) Klapötke, T. M.; Mayer, P.; Schulz, A. Weigand, J. J. *J. Am. Chem. Soc.* **2005**, *127*, 2032−2033. (b) Gálvez-Ruiz, J. C.; Holl, G.; Karaghiosoff, K.; Klapötke, T. M.; Löhnwitz, K.; Mayer, P.; Nöth, H.; Polborn, K.; Rohbogner, C. J.; Suter, M.; Weigand, J. J. *Inorg. Chem.* **2005**, *44*, 4237−4253.

(6) (a) Katritzky, A. R.; Yang, H.; Zhang, D.; Kirichenko, K.; Smiglak, M.; Holbrey, J. D.; Reichert, W. M.; Rogers, R. D. *New J. Chem.* **2006**, *30*, 349−358.(b) Gutowski, K. E.; Holbrey, J. D.; Rogers, R. D.; Dixon, D. A. *J. Phys. Chem. B* **2005**, *109*, 23196−23208.(c) Schmidt, M. W.; Gordon, M. S.; Boatz, J. A. *J. Phys. Chem. A* **2005**, *109*, 7285−7295.

(7) (a) Katritzky, A. R.; Singh, S.; Kirichenko, K.; Smiglak, M.; Holbrey, J. D.; Reichert, W. M.; Spear, S. K.; Rogers, R. D. *Chem. Eur. J.* **2006**, *12*, 4630−4641. (b) Katritzky, A. R.; Singh, S.; Kirichenko, K.; Holbrey, J. D.; Smiglak, M.; Reichert, W. M.; Rogers, R. D. *Chem. Commun.* **2005**, 868−870.

(8) Ogihara, W.; Yoshizawa, M.; Ohno, H. *Chem. Lett.* **2004**, *33*, 1022−1023. (b) Xue, H.; Twamley, B.; Shreeve, J. M. *J. Mater. Chem.* **2005**, *15*, 3459−3465.

(9) Hammerl, A.; Klapöetke, T. M.; Nöth, H.; Warchhold, M.; Holl, G.; Kaiser, M.; Ticmanis, U. *Inorg. Chem.* **2001**, *40*, 3570−3575.

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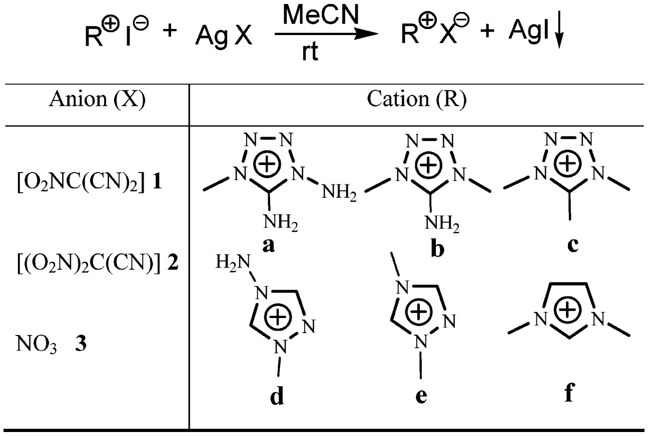
melting points and higher heats of formation appear to be of considerable value. In this context, it seems to be reasonable to develop new anions since the gross characteristics of ILs are controlled by the nature of anionic components.[7b] However, the present search for energetic ILs is mainly directed toward modification of cations or synthesis of organic azolate anions. Further development of energetic materials requires exploring new anions of energetic ILs with high safety, performance, and stability.

The nitrate and dinitramide salts of heterocyclic cations are well investigated owing to easier availability and safety of inorganic starting materials. In general, dinitramide salts exhibit more superior properties than their nitrate analogues owing to the bulky molecular structure and higher energetic content of that anion.[4,5] In our continuing efforts to seek energetic ionic liquids,[10] we became interested in a nitrate pseudochalcogen analogue, nitrodicyanomethanide $[O_2NC(CN)_2]^-$, since theoretical and laboratory investigation revealed significant similarity in their electronic structures, electrochemical, and ligation properties.[11] The electron-withdrawing NO_2 and CN can stabilize the carbanion and deliver their energy characteristics to the resultant salts. In addition, the bulky structure tends to result in salts of lower melting points. Some metal and ammonium salts of the anion have been reported,[11] but the heterocycle-based salts were seldom investigated despite the fact that heterocyclic ring system usually confers a high density, thermal stability, high nitrogen content, high volume of detonation products and insensitivity to impact.[12] Herein, we report synthesis and characterization of a series of heterocycle-based energetic salts from $[O_2NC(CN)_2]^-$ and $[(O_2N)_2C(CN)]^-$. As a comparison, four new nitrate analogues (**3b**, **3c**, **3e**, **3f**) were also reported.

Results and Discussion

The nitrodicyanomethanide (**1a**−**f**) and dinitrocyanomethanide (**2a**−**f**) salts were readily prepared through metathesis reactions between equivalent silver(I) salts and iodide salts in MeCN (Scheme 1). The cation choice was made in order to establish the broad relative potential to form energetic ILs and to comprehensively evaluate their performance.

Scheme 1



Generally, with the increase of the number of nitrogen atoms in heterocycles, the resultant compounds demonstrate considerable gain in standard enthalpy of formation. The enthalpy criteria of energetic chemical systems are governed by their molecular structures. In moving from imidazole ($\Delta H_f^o{}_{(cryst)}$ = 58.5 kJ/mol)[13] to 1,2,4-triazole ($\Delta H_f^o{}_{(cryst)}$ = 109 kJ/mol) to tetrazole ($\Delta H_f^o{}_{(cryst)}$ = 237.2 kJ/mol),[14] the variation in the trend of energetic content is increasingly positive. In this work, 1,5-diamino-4-methyltetrazolium, 1,4-dimethyl-5-aminotetrazolium, 1,4,5-trimethyltetrazolium, 1-methyl-4-amino-1,2,4-triazolium, 1,4-dimethyltriazolium, and 1,3-dimethylimidazolium were chosen as energetic cations to pair with the both anions.

The energetic salts **1a**−**f** and **2a**−**f** are stable in air and moisture. They are soluble in acetone, MeCN, MeOH, H_2O, and DMF, while insoluble in lower polar solvents, such as hexane, diethyl ether, dichloromethane, and ethyl acetate. All of the energetic salts were characterized by ^1H, ^{13}C NMR, IR UV−vis, and elemental analyses. In their ^{13}C NMR spectra, the chemical shifts of cyanide carbon in nitrodicyanomethanide (**1a**−**f**) and dinitrocyanomethanide (**2a**−**f**) salts are in the range of 116.0−116.3 and 114.3−114.4 ppm, respectively. In the IR spectra of the nitrodicyanomethanide and dinitrocyanomethanide salts, strong absorption bands due to cyanide were observed in the 2196−2210 cm^{-1} and 2208−2216 cm^{-1} region, respectively. The UV−vis spectra of nitrodicyanomethanide salts show maximum absorbance around 317 nm, consistent with those of metal nitrodicyanomethanide compounds.[11a] The dinitrocyanomethanide salts show a maximum and an additional absorption with maximum absorbance around 343 and 258 nm, respectively.

Physical Properties of the Energetic Salts. Phase transition temperatures (midpoints of glass transition and/or melting points) were determined by differential scanning calorimetry (DSC) (Table 1). As anticipated, the anion exhibits a major influence on the phase transition temperature. The melting points of dinitrocyanomethanide salts (**2a**−**f**) are higher than those of nitrodicyanomethanide analogues (**1a**−**f**). It should be pointed out that 1,4-dimethyl-5-aminotetrazolium-based salts (**1b**, **2b**) have higher melting points than their analogues, which may be ascribed to their high symmetry and extensive hydrogen bonding interactions

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(10) (a) Xue, H.; Shreeve, J. M. *Adv. Mater.* **2005**, *17*, 2142−2146. (b) Xue, H.; Gao, Y.; Twamley, B.; Shreeve, J. M. *Chem. Mater.* **2005**, *17*, 191−198. (c) Xue, H.; Gao, Y.; Twamley, B.; Shreeve, J. M. *Inorg. Chem.* **2005**, *44*, 5068−5072. (d) Ye, C.; Xiao, J. C.; Twamley, B.; Shreeve, J. M. *Chem. Commun.* **2005**, 2750−2752. (e) Jin, C. M.; Ye, C.; Piekarski, C.; Twamley, B.; Shreeve, J. M. *Eur. J. Inorg. Chem.* **2005**, 3760−3767. (f) Ye, C. University of Idaho, private communication.

(11) (a) Arulsamy, N.; Bohle, D. S.; Doletski, B. G. *Inorg. Chem.* **1999**, *38*, 2709−2715. (b) Bohle, D. S.; Conklin, B. J. Hung, C. H. *Inorg. Chem.* **1995**, *34*, 2569−2581, and references cited therein. (c) Schädler, H. D.; Jäger, L.; Senf, I. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1115−1120.

(12) Sikder, A. K.; Geetha, M.; Sarwade, D. B.; Agrawal, J. P. *J. Hazard. Mater.* **2001**, *A82*, 1−12.

(13) Weast, R. C.; Selby, S. M. *Handbook of Chemistry and Physics*, 48th ed.; 1967−1968; pp D22−D51.

(14) Ostrovskii, V. A.; Pevzner, M. S.; Kofman, T. P.; Tselinskii, I. V. *Targets Heterocycl. Syst.* **1999**, *3*, 467−526.

Table 1. Properties of Energetic Salts

compd	T_{m}[a] (°C)	T_{d}[b] (°C)	d_{exptl}[c] (g/cm^3)	d_{calcd}[d] (g/cm^3)	$\Delta H_{\mathrm{f\ cation}}$ (kJ/mol)	$\Delta H_{\mathrm{f\ anion}}$ (kJ/mol)	$\Delta H_{\mathrm{f\ lat}}$[e] (kJ/mol)	$\Delta H_{\mathrm{f\ m}}$[f] (kJ/mol)	ΔH_{f}[g] (kJ/g)
1a	72	176	1.48	1.52	998.0	32.2	479.9	550.3	2.44
1b	94	260	1.41	1.45	885.5	32.2	474.5	443.2	1.98
1c	50	240	1.38	1.39	844.8	32.2	472.4	404.6	1.81
1d	59[h]	238		1.46	895.6	32.2	487.4[j]	440.4[j]	2.11
1e	61	237	1.39	1.39	756.9	32.2	481.8	307.3	1.48
1f	63	327	1.31	1.36	652.1	32.2	475.1	209.2	1.01
2a	116	182	1.64	1.62	998.0	−127.7	482.1	388.2	1.58
2b	*i*	145	1.56	1.55	885.5	−127.7	476. 4	281.4	1.15
2c	89	215	1.49	1.48	844.8	−127.7	471.3	245.8	1.01
2d	−54	221		1.56	895.6	−127.7	484.2[j]	283.7[j]	1.36
2e	89	206	1.49	1.49	756.9	−127.7	479.1	150.1	0.66
2f	79	267	1.47	1.45	652.1	−127.7	477.9	46.5	0.20
3b	178	206	1.51	1.53	885.5	−307.9	514.2	63.4	0.36
3c	*i*	199	1.38	1.45	844.8	−307.9	503.0	33.9	0.19
3e	63	197	1.38	1.45	756.9	−307.9	515.0	−66.0	−0.41
3f	71	283	1.36	1.40	652.1	−307.9	513.8	−169.6	−1.07

[a] Melting point. [b] Thermal degradation temperature. [c] Experimental density. [d] Calculated density. [e] Calculated molar lattice energy. [f] Calculated molar enthalpy of formation. [g] Calculated enthalpy of formation in kJ/g. [h] Glass transition temperature. [i] Decomposes before melting. [j] Based on calculated density.

Table 2. Crystallographic Data for Compounds **1a** and **2a**

	1a	**2a**
empirical formula	$C_5H_7N_9O_2$	$C_4H_7N_9O_4$
fw	225.20	245.19
crystal size (mm)	0.43 × 0.25 × 0.22	0.45 × 0.40 × 0.26
crystal system	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
a, Å	7.9530(1)	9.5713(1)
b, Å	8.1987(1)	17.0867(2)
c, Å	9.7025(2)	6.4418(1)
α, deg	67.227(1)	
β, deg	111.743(1)	109.094(1)
γ, deg	63.832(1)	
V, Å^3	503.257(14)	995.54(2)
Z	2	4
T [K]	90(2)	90(2)
D_{c}, g cm^{-3}	1.486	1.636
μ, mm^{-1}	0.121	0.143
λ (MoKα) [Å]	0.71073	0.71073
F(000)	232	504
reflections collected	6928	11276
independent reflections	1823	1799
R_{int}	0.0163	0.0192
parameters	163	164
S on F^2	1.078	1.043
R_1 ($I > 2\sigma(I)$)[a]	0.0346	0.0307
$_{\mathrm{w}}R_2$ (all data)[b]	0.0895	0.0801
largest diff peak and hole [e·Å^{-3}]	0.245 and −0.306	0.269 and −0.274

[a] $R = \sum||F_0| - |F_c||/\sum|F_0|$. [b] $_{\mathrm{w}}R = [\sum w(F_0{}^2 - F_c{}^2)^2/\sum w(F_0{}^2)^2]^{1/2}$.

between cation and anion. The melting point of **2a** is above 100 °C which places it outside of the range for an ionic liquid,[15] whereas **2b** decomposed before its phase transition temperature. Interestingly, 1-methyl-4-aminotriazolium-based salts (**1d** and **2d**) are room-temperature ionic liquids. With constant anions, the variation in cations has no obvious effect on melting point. The decomposition temperatures of the salts are in the range of 145−327 °C as determined by thermogravimetric analysis (TGA). The lower thermal stability of **2b** is surprising. The 1,3-dimethylimidazolium-based salts have the higher thermal stabilities than their analogues. Noteworthy, the melting point of the 1,5-diamino-4-methyltetrazolium salt **1a** is lower, but its thermal stability is higher than the nitrate analogue ($T_{\mathrm{m}} = 121$, $T_{\mathrm{d}} = 181$ °C).[5b] Similar results were found for the remainder of salts.

The densities of the dinitrocyanomethanide and nitrodicyanomethanide salts are in the range of 1.31−1.64 g/cm^3. With the presence of a higher concentration of nitro groups, the opportunity for hydrogen bonding is markedly increased; therefore, it is not surprising that the densities of dinitrocyanomethanide salts are higher than those of its nitrodicyanomethanide analogues. With a constant anion, the effect of cation on density is in the following order: 1,5-diamino-4-methyltetrazolium > 1,4-dimethyl-5-aminotetrazolium > 1,4,5-trimethyltetrazolium ∼ 1,4-dimethyltriazolium > 1,3-dimethylimidazolium. Hence, **2a** and **1f** exhibit the highest density (1.64 g/cm^3) and the lowest density (1.31 g/cm^3), respectively. The densities were also estimated according to our newly tabulated volume parameters, which agreed reasonably with the experimental values within 5% deviation.[10f] The measured densities of **1a** and **2a** are consistent with the densities calculated for X-ray crystal structures (vide infra).

The enthalpies of formation for these energetic salts were calculated using Born−Haber energy cycles. Based on the cycle, the heat of formation of an ionic salt can be simplified by the formula

$$\Delta H_{\mathrm{f}}{}^{\mathrm{o}}(\text{ionic salt, 298K}) = \Delta H_{\mathrm{f}}{}^{\mathrm{o}}(\text{cation, 298K}) + \Delta H_{\mathrm{f}}{}^{\mathrm{o}}(\text{anion, 298 K}) - \Delta H_{\mathrm{L}}$$

where ΔH_{L} is the lattice energy of an ionic salt which could be predicted by the formula suggested by Jenkins et al.[16] as

$$\Delta H_{\mathrm{L}} = U_{\mathrm{POT}} + [p(n_{\mathrm{M}}/2 - 2) + q(n_{\mathrm{X}}/2 - 2)]RT \qquad \mathbf{(A)}$$

where n_{M} and n_{X} depend on the nature of the ions $\mathrm{M}_p{}^+$ and $\mathrm{X}q^-$, 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

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

where ρ_{m} is density (g cm^{-3}), M_{m} is the chemical formula mass of the ionic material, (g or Mg), and the coefficients γ (kJ mol^{-1}) and δ (kJ mol^{-1}) take the values from ref 16.

The heat of formation of anions and cations are computed using the method of isodesmic reactions.[6c] The enthalpy of reaction ($\Delta H_{\mathrm{r}}{}^{\mathrm{o}}{}_{298}$) is obtained by combining the MP2(full)/6-311++G** energy difference for the reaction, the scaled zero point energies, and other thermal factors (for higher accuracy, G2MP2 for nitrodicyanomethanide and dinitrocyanomethanide anion, G2 for nitrate anion). Thus, the heat of formation being sought can be readily extracted.

As shown in Table 1, the nitrodicyanomethanide and dinitrocyanomethanide salts exhibit positive enthalpies of formation with the exception of imidazolium-based salt **2f**.

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(15) Seddon, K. R. *J. Chem. Technol. Biotechnol.* **1997**, *68*, 351−356.

(16) Jenkins, H. D. B.; Tudeal, D.; Glasser, L. *Inorg. Chem.* **2002**, *41*, 2364−2367.

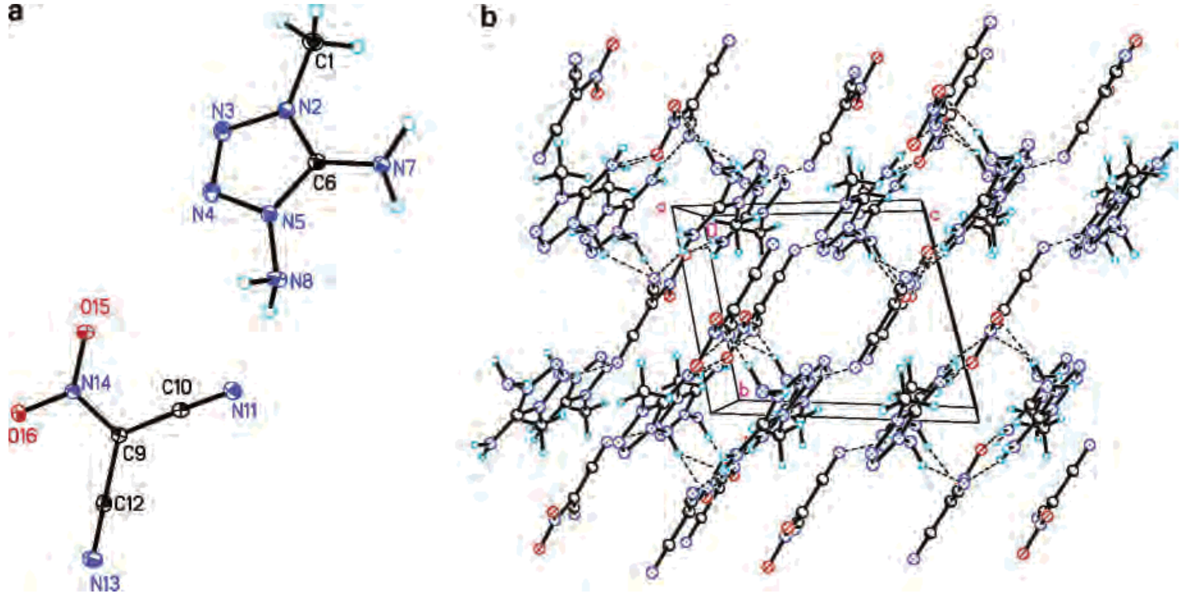

Figure 1. a. Molecular structure of **1a** with thermal ellipsoids at 50% probability. b. Packing diagram of **1a** along the *a*-axis.

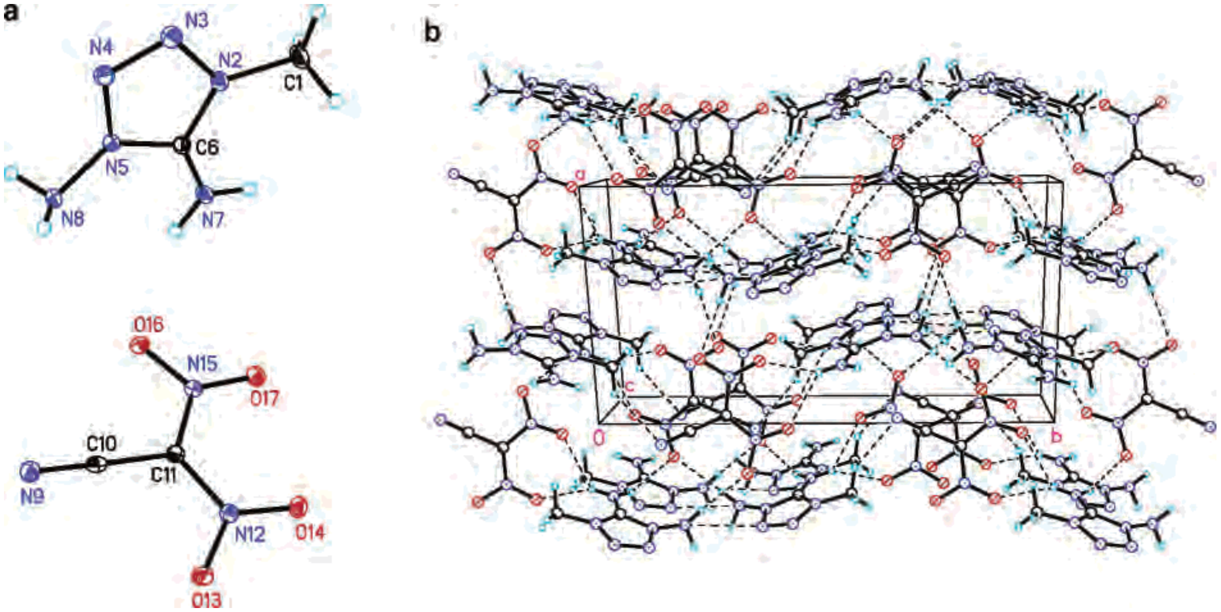

Figure 2. a. Molecular structure of **2a** with thermal ellipsoids at 50% probability. b. Packing diagram of **2a** along the *c*-axis.

Interestingly, the nitrodicyanomethanide anion has a positive calculated heat of formation (32.2 kJ/mol), which is higher than that of dinitrocyanomethanide (−127.7 kJ/mol) and much higher than that of nitrate (−307.9 kJ/mol). Thus, with constant cations, the enthalpies of formation are in the following order: $[O_2NC(CN)_2]^- > [(O_2N)_2C(CN)]^- > NO_3^-$. This suggests $[O_2NC(CN)_2]^-$ is a promising anion in the field of high-energy materials. As anticipated, effect of heterocyclic rings on standard enthalpies of formation of analogous salts is in the following order: 1,5-diamino-4-methyltetrazolium > 1,4-dimethyl-5-aminotetrazolium ∼ 1-methyl-4-amino-1,2,4-triazolium > 1,4,5-trimethyltetrazolium > 1,4-dimethyltriazolium > 1,3-dimethylimidazolium, which is in keeping with the order of calculated heat of formation for those cations. Among them, **1a** has the highest standard molar enthalpy of formation (550.3 kJ/mol).

Crystal Structures of 1a and 2a. **1a** and **2a** crystallize in the triclinic space group *P*-1 and the monoclinic space group $P2_1/c$, respectively (Table 2). The tetrazolium ring in **1a** and **2a** is almost planar with mean deviations from the ring plane are 0.0012 and 0.0027 Å, respectively. The exocyclic nitrogen atoms (N7 and N8) are out of the plane 0.0199 and 0.0933 Å in **1a** and 0.0497 and 0.0225 Å in **2a**, respectively. The bond distances and bond angles of the 1,5-diamino-4-methyltetrazolium cation in **1a** and **2a** are close to each other. The anions dinitrocyanomethanide and nitrodicyanomethanide are also planar with mean deviations from the plane being 0.0139 and 0.0198 Å, respectively. The dihedral angles between cation and anion in **1a** and **2a** are 12.3 and 70.4°, respectively. These differences may be ascribed to different packing effects in the respective crystals. Since the amino groups in the cation are excellent hydrogen bonding formers, the discrete cation and anion in **1a** are linked into a 2D layer by the extensive hydrogen bonding interactions between 1,5-diamino-4-methyltetrazolium and dinitrocyanomethanide [N(8)−H(8B)···N(11), 3.0721(16); N(7)−H(7A)···N(13)^{i}, 3.0165(16); N(7)−H(7B)···O(16)^{ii} 2.9230(14) Å. Symmetry codes: (i) $x + 1, y - 1, z + 1$; (ii) $x, y - 1, z + 1$], the 1D layer is further extended into a double-layer network by the hydrogen bonding interactions between cation and anion [N(8)−H(8A)···O(15)^{iii} 3.0597(14); N(8)−H(8A)···N(13)^{iv} 3.1238(15) Å. Symmetry codes: (iii) $-x + 1, -y + 1, -z + 1$; (iv) $-x, -y + 1, -z + 1$]. The packing diagram of the structure is shown in Figure 1b. There are no significant interactions among adjacent double layers. In **2a**, the discrete 1,5-diamino-4-methyltetrazolium and dinitrocyanomethanide ions are linked into a 3D network by extensive hydrogen bonds [N(7)−H(7B)···2.9521(14); O(16) N(8)−H(8B)···O(16)^{i}; N(8)−H(8A)···O(14)^{ii} 3.2778(15); 3.1962(15); N(8)−H(8A)···O(13)^{ii} 3.0960(15); N(7)−H(7A)···O(14)^{iii} 2.9980(14); N(7)−H(7A)···O(17)^{iii} 3.0246(14) Å. Symmetry codes: (i) $x, -y + 1/2, z - 1/2$; (ii) $x - 1, y, z-1$; (iii) $-x + 2, -y, -z + 2$] (Figure 2b).

Conclusion

A series of nitrodicyanomethanide and dinitrocyanomethanide salts based on nitrogen-containing heterocycle cations was synthesized and characterized. Most of energetic salts show relatively low melting points and good thermal stability. The melting points and densities of dinitrocyanomethanide salts are higher than those of the nitrodicyanomethanide analogues. Effect of cations on the density of analogous energetic salts is in the following order: 1,5-diamino-4-methyltetrazolium > 1,4,5-trimethyltetrazolium ∼ 1,4-dimethyltriazolium > 1,3-dimethylimidazolium. 1,4,5-Trimethyltetrazolium and 1,4-dimethyltriazolium salts show similar physical properties. Nitrodicyanomethanide and dinitrocyanomethanide salts exhibit higher standard enthalpies of formation than their nitrate analogues. In conclusion, this research has demonstrated that nitrodicyanomethanide and dinitrocyanomethanide are promising anions toward design and synthesis of higher energy density materials with lower melting points.

Experimental Section

Caution**:** *Although we have not experienced any problems in handling these compounds, their shock and impact sensitivity have not been determined; they should be synthesized in mmol amounts and handled with extreme care.*

General Methods. IR spectra were recorded using KBr plates for neat liquids and KBr pellets for solids on BIORAD model 3000 FTS spectrometer. UV−vis spectra were measured in acetonitrile on an Ocean Optics USB 2000 UV−vis spectrophotometer in the 250−600 nm region. ^{1}H and ^{13}C spectra were recorded on spectrometers at 300 and 75 MHz, respectively, by using CD_3CN as a locking solvent. Chemical shifts are reported in ppm relative TMS. The densities of the solid salts 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 autocool accessory and calibrated using indium. The following procedure was used in experiments for each sample: cooling from 40 °C to −80 °C and heating to 400 or 500 °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.

Silver(I) nitrodicyanomethanide,[11] silver(I) dinitrocyanomethanide,[17] 1,5-diamino-4-methyltetrazolium iodide,[5b] 1,4-dimethyl-5-aminoterazolium iodide, 1,4,5-trimethyltetrazolium iodide,[8b,10d] 1-methyl-4-amino-1,2,4-triazolium iodide,[10b] 1,4-dimethyltriazolium iodide,[8b] and 1,3-dimethylimidazolium iodide[18] were prepared according to literature methods.

X-ray Crystallography. Crystals of **1a** and **2a** were removed from the flask and covered with a layer of hydrocarbon oil, respectively. A suitable crystal was selected, attached to a glass fiber, and placed in the low-temperature nitrogen stream.[19] Data for **1a** and **2a** were collected at 90(2) K using a Bruker/Siemens SMART APEX instrument (Mo Kα radiation, $\lambda = 0.71073$ Å) equipped with a Cryocool NeverIce low-temperature device. Data were measured using omega scans of 0.3° per frame for 30 s, and a full sphere of data was collected. A total of 1400 (for **1a**) and 1274 (for **2a**) frames were collected with a final resolution of 0.83 Å. Cell parameters were retrieved using SMART[20] software and refined using SAINTPlus[21] on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus software. Absorption corrections were applied using SADABS.[22] The structure was solved by direct methods and refined by least-squares method on F^2 using the SHELXTL program package.[23] The structure of **1a** and **2a** were solved in the space groups *P*-1 (# 2) and *P*2(1)/*c* (# 14), respectively, by analysis of systematic absences. All non-hydrogen atoms were refined anisotropically. No decomposition was observed during data collection. Details of the data collection and refinement for **1a** and **2a** are given in Table 2. Further details are provided in the Supporting Information.

Theoretical Study. Computations were performed with the Gaussian03 (Revision D.01) suite of programs.[24] The geometric optimization of the cation structures and frequency analyses are carried out using B3-LYP functional with 6-31+G** basis set,[25] and single energy points were calculated at the MP_2(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. The anions are calculated at the G2MP2 level (for nitrate anion, G2 level was used). The Cheetah 4.0 program was employed to calculate the detonation properties of **2a** and **2d.**[26]

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(17) (a) Parker, C. O.; Emmons, W. D.; Rolewicz, H. A.; McCallum, K. S. *Tetrahedron* **1962**, *12*, 79−87. (b) Parker, C. O. *Tetrahedron* **1962**, *12*, 109−116.

(18) Bonhöte, P.; Dias, A. P.; Papageorgiou, N.; Kalyanasundaram, K.; Grätzel, M. *Inorg. Chem.* **1996**, *35*, 1168−1178.

(19) Hope, H. *Prog. Inorg. Chem.* **1994**, *41*, 1−19.

(20) *SMART: v.5.626, Bruker Molecular Analysis Research Tool*; Bruker AXS: Madison, WI, 2002.

(21) *SAINTPlus: v. 6.45a, Data Reduction and Correction Program*; Bruker AXS: Madison, WI, 2003.

(22) *SADABS: v.2.01, an empirical absorption correction program*; Bruker AXS Inc.: Madison, WI, 2004.

(23) Sheldrick, G. M. *SHELXTL: v. 6.10, Structure Determination Software Suite*; Bruker AXS Inc.: Madison, WI, 2001.

(24) *Gaussian 03, Revision D.01*; Gaussian, Inc.: Wallingford, CT, 2004.

(25) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.

General Procedures for Preparation of the Energetic Compounds 1a−f, 2a−f, 3b, 3c, 3e, and 3f. To a stirring solution of the iodide salt (1.0 mmol) in MeCN (20 mL) was added dropwise a solution of silver salt (1.0 mmol) in MeCN (5 mL). The resulting solution was stirred at 25 °C for 1 h. After removal of AgI by filtration, the solvent was evaporated in vacuo, and the residue was washed three times with Et_2O (10 mL) and then recrystallized from MeCN/Et_2O.

1,5-Diamino-4-methyltetrazolium nitrodicyanomethanide (1a): Colorless solid, yield: 0.20 g (89%); IR: 3139 (w), 2977 (w), 2871 (vw), 2210 (s), 1713 (s), 1632 (w), 1411 (s), 1346 (s), 1286 (m), 1156 (w), 1074 (vw), 1046 (m), 880 (vw), 775 (vw), 750 (w), 699 (vw), 571 (vw), 528 (w) cm^{-1}; ^1H NMR: δ 7.21 (s, 2H), 6.01 (s, 2H), 3.87 (s, 3H); ^{13}C NMR: δ 148.9, 116.0, 35.8. UV−vis (λ_{max}): 317 nm. Anal. Calcd for $C_5H_7N_9O_2$ (225.17): C, 26.67; H, 3.13; N, 55.98. Found: C, 26.67; H, 3.08; N, 55.18. Colorless crystals suitable for X-ray diffraction were obtained through diffusion of hexane into a CH_2Cl_2 solution of the compound.

1,4-Dimethyl-5-aminotetrazolium nitrodicyanomethanide (1b): Colorless solid, yield: 0.20 g (89%); IR: 3329 (s), 3268 (w), 3148 (s), 2223 (s), 2195 (s), 1693 (s), 1537 (w), 1425 (s), 1402 (w), 1344 (s), 1290 (m), 1180 (w), 1159 (m), 1046 (w), 993 (vw), 776 (w), 743 (w), 708 (vw), 602 (w), 565 (vw), 530 (w) cm^{-1}; ^1H NMR: δ 7.16 (s, 2H), 3.87 (s, 6H); ^{13}C NMR: δ 149.7, 116.0, 35.3. UV−vis (λ_{max}): 317 nm. Anal. Calcd for $C_6H_8N_8O_2$ (224.18): C, 32.15; H, 3.60; N, 49.98. Found: C, 33.12; H, 3.52; N, 50.09.

1,4,5-Trimethyltetrazolium nitrodicyanomethanide (1c): Colorless solid, yield: 0.21 g (94%); IR: 3046 (vw), 3017 (vw), 2209 (s), 2201 (s), 1598 (m), 1539 (w), 1429 (s), 1384 (s), 1358 (s), 1280 (m), 1157 (w), 1042 (w), 762 (m), 742 (m), 714 (vw), 663 (vw), 567 (vw), 523 (m) cm^{-1}; ^1H NMR: δ 4.17 (s, 6H), 2.78 (s, 3H); ^{13}C NMR: δ 116.3, 37.5, 9.02. UV−vis (λ_{max}): 317 nm. Anal. Calcd for $C_7H_9N_7O_2$ (223.19): C, 37.67; H, 4.06; N, 43.93. Found: C, 37.65; H, 3.65; N, 44.01.

1-Methyl-4-amino-1,2,4-triazolium nitrodicyanomethanide (1d): Pale yellow liquid, yield: 0.19 g (89%); IR: 3499 (m), 3327 (s), 3143 (s), 2448 (vw), 2210 (s), 2207 (s), 1631 (m), 1573 (w), 1535 (vw), 1497 (vw), 1414 (s), 1345 (s), 1211 (vw), 1159 (m), 1072 (w), 980 (m), 880 (w), 745 (m), 660 (w), 615 (s), 572 (w) cm^{-1}; ^1H NMR: δ 9.40 (s, 1H), 8.61 (s, 1H), 6.05 (s, 2H), 4.04 (s, 3H); ^{13}C NMR: δ 145.9, 143.8, 116.0, 40.1. UV−vis (λ_{max}): 317 nm. Anal. Calcd for $C_6H_7N_7O_2$ (209.17): C, 34.45; H, 3.37; N, 46.88. Found: C, 34.21; H, 3.20; N, 46.46.

1,4-Dimethyltriazolium nitrodicyanomethanide (1e): Colorless solid, yield: 0.18 g (86%); IR: 3130 (w), 3100 (m), 2974 (vw), 2208 (s), 2197 (s), 1589 (m), 1417 (s), 1412 (s), 1345 (s), 1284 (m), 1159 (m), 1092 (vw), 1067 (w), 985 (vw), 900 (w), 861 (w), 747 (w), 733 (w), 658 (vw), 621 (s), 568 (vw), 530 (w) cm^{-1}; ^1H NMR: δ 9.26 (s, 1H), 8.53 (s, 1H), 4.04 (s, 3H), 3.88 (s, 3H); ^{13}C NMR: δ 146.0, 143.6, 116.3, 39.8, 35.1. UV−vis (λ_{max}): 317 nm. Anal. Calcd for $C_7H_8N_6O_2$ (208.18): C, 40.39; H, 3.87; N, 40.37. Found: C, 40.16; H, 3.84; N, 39.89.

1,3-Dimethylimidazolium nitrodicyanomethanide (1f): Colorless solid, yield: 0.19 g (92%); IR: 3160 (vw), 3128 (vw), 2974 (s), 2208 (s), 2196 (s), 1642 (vw), 1577 (m), 1415 (s), 1339 (s), 1175 (m), 1154 (w), 1083 (s), 1049 (s), 878 (w), 770 (vw), 744 (vw), 711 (vw), 627 (m), 531 (w) cm^{-1}; ^1H NMR: δ 8.42 (s, 1H), 7.32 (d, J = 1.4 Hz, 2H), 3.82 (s, 6H); ^{13}C NMR: δ 137.6, 124.5, 116.3, 36.8. UV−vis (λ_{max}): 317 nm. Anal. Calcd for $C_8H_9N_5O_2$ (207.19): C, 46.38; H, 4.38; N, 33.80. Found: C, 46.17; H, 4.17; N, 33.69.

1,5-Diamino-4-methyltetrazolium dinitrocyanomethanide (2a): Colorless solid, yield: 0.23 g (94%); IR: 3347 (s), 3255 (s), 3170 (m), 2496 (vw), 2214 (s), 1707 (s), 1622 (m), 1595 (w), 1500 (s), 1414 (m), 1369 (w), 1261 (s, br), 1152 (m), 1115 (w), 1044 (w), 1001 (vw), 930 (m), 853 (vw), 773 (m), 745 (m), 704 (w), 669 (vw), 564 (w), 530 (w) cm^{-1}; ^1H NMR: δ 7.20 (s, 2H), 5.98 (s, 2H), 3.87 (s, 3H); ^{13}C NMR: δ 148.9, 114.3, 35.8. UV−vis (λ_{max}): 258, 343 nm. Anal. Calcd for $C_4H_7N_9O_4$ (245.16): C, 19.60; H, 2.88; N, 51.42. Found: C, 19.89; H, 2.60; N, 51.36. Colorless crystals suitable for X-ray diffraction were obtained through diffusion of hexane into a CH_2Cl_2 solution of the compound. Detonation properties include the following: detonation pressure, 23.6 GPa; detonation velocity, 7796 m/s; and specific impulse, 233.4 s.

1,4-Dimethyl-5-aminotetrazolium dinitrocyanomethanide (2b): Colorless solid, yield: 0.21 g (86%); IR: 3335 (s), 3267 (s), 3181 (s), 2505 (vw), 2222 (s), 1686 (s), 1611 (vw), 1513 (s), 1415 (m), 1385 (w), 1365 (w), 1261 (s, br), 1151 (m), 1052 (w), 1025 (w), 853 (vw), 772 (m), 743 (m), 706 (m), 669 (vw), 580 (w), 566 (vw) cm^{-1}; ^1H NMR: δ 7.23 (s, 2H), 3.87 (s, 6H); ^{13}C NMR: δ 149.6, 114.2, 35.3. UV−vis (λ_{max}): 258, 343 nm. Anal. Calcd for $C_5H_8N_8O_4$ (244.17): C, 24.60; H, 3.30; N, 45.89. Found: C, 24.40; H, 3.01; N, 45.27.

1,4,5-Trimethyltetrazolium dinitrocyanomethanide (2c): Colorless solid, yield: 0.23 g (95%); IR: 3034 (w), 2941 (vw), 2502 (vw), 2208 (s), 1710 (vw), 1594 (s), 1504 (s), 1443 (m), 1362 (s), 1331 (m), 1239 (s, br), 1150 (s), 1040 (m), 847 (vw), 762 (s), 743 (s), 714 (vw), 662 (vw), 497 (m) cm^{-1}; ^1H NMR: δ 4.18 (s, 6H), 2.80 (s, 3H); ^{13}C NMR: δ 153.5, 114.4, 37.5, 9.0. UV−vis (λ_{max}): 258, 343 nm. Anal. Calcd for $C_6H_9N_7O_4$ (243.18): C, 29.63; H, 3.73; N, 40.32. Found: C, 29.59; H, 3.54; N, 40.13.

1-Methyl-4-amino-1,2,4-triazolium dinitrocyanomethanide (2d): Pale yellow liquid, yield: 0.17 g (82%); IR: 3584 (m), 3335 (s), 3142 (s), 2493 (w), 2215 (s), 1632 (m), 1572 (w), 1501 (s), 1419 (s), 1362 (m), 1250 (br, s), 1152 (m), 1072 (w), 980 (m), 878 (w), 841 (w), 766 (w), 743 (m), 658 (w), 615 (s), 566 (w) cm^{-1}; ^1H NMR: δ 9.41 (s, 1H), 8.61 (s, 1H), 6.03 (s, 2H), 4.03 (s, 3H); ^{13}C NMR: δ 146.0, 143.9, 114.3, 40.2. UV−vis (λ_{max}): 257, 343 nm. Anal. Calcd for $C_7H_8N_6O_2$ (208.18): C, 26.21; H, 3.08; N, 42.79. Found: C, 25.79; H, 2.96; N, 41.55. Detonation properties include the following: detonation pressure, 21.0 GPa; detonation velocity, 7542 m/s; and specific impulse, 212.6 s.

1,4-Dimethyltriazolium dinitrocyanomethanide (2e): Colorless solid, yield: 0.20 g (88%); IR: 3140 (w), 2488 (vw), 2216 (s), 1588 (m), 1505 (s), 1415 (w), 1360 (w), 1294 (s), 1163 (m), 1145 (m), 1070 (w), 990 (vw), 891 (vw), 847 (w), 760 (w), 739 (m), 660 (vw), 619 (s), 564 (vw) cm^{-1}; ^1H NMR: δ 9.30 (s, 1H), 8.55 (s, 1H), 4.05 (s, 3H), 3.89 (s, 3H); ^{13}C NMR: δ 146.0, 143.7, 114.4, 39.8, 35.1. UV−vis (λ_{max}): 258, 342 nm. Anal. Calcd for $C_6H_8N_6O_4$ (228.17): C, 31.58; H, 3.53; N, 36.83. Found: C, 31.24; H, 3.42; N, 36.90.

1,3-Dimethylimidazolium dinitrocyanomethanide (2f): Colorless solid, yield: 0.21 g (92%); IR: 3157 (w), 3114 (s), 2210 (s), 1741 (s), 1713 (s), 1628 (vw), 1576 (s), 1505 (s), 1421 (s), 1363 (s), 1231 (s), 1167 (s), 1092 (m), 848 (m), 761 (m), 745 (m), 623 (m), 559 (vw), 504 (vw) cm^{-1}; ^1H NMR: δ 8.44 (s, 1H), 7.33 (d, J = 1.5 Hz, 2H), 3.82 (s, 6H); ^{13}C NMR: δ 137.6, 124.5, 114.4,

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(26) (a) Fried, L. E.; Glaesemann, K. R.; Howard, W. M.; Souers, P. C. *CHEETAH 4.0 User's Manual*; Lawrence Livermore National Laboratory: 2004. (b) Lu, J. P. *Evaluation of the Thermochemical Code -CHEETAH 2.0 for Modelling Explosives Performance*; DSTO-TR-1199; DSTO: Edinburgh, 2001.

36.8. UV−vis (λ_{max}): 258, 343 nm. Anal. Calcd for $C_7H_9N_5O_4$ (227.18): C, 37.01; H, 3.99; N, 30.83. Found: C, 36.83; H, 3.69; N, 30.85.

1,4-Dimethyl-5-aminotetrazolium nitrate (3b): Colorless solid, yield: 0.15 g (85%); IR: 3574 (s, br), 3242 (s, br), 2393 (vw), 1760 (w), 1693 (s), 1636 (s), 1536 (w), 1383 (s), 1047 (vw), 826 (m), 777 (vw), 761 (vw), 743 (w), 706 (w), 580 (w) cm^{-1}; ^1H NMR: δ 8.56 (s, 2H), 3.89 (s, 6H); ^{13}C NMR: δ 150.0, 35.0. Anal. Calcd for $C_3H_8N_6O_3$ (176.13): C, 20.46; H, 4.58; N, 47.71. Found: C, 20.70; H, 4.27; N, 47.79.

1,4,5-Trimethyltetrazolium nitrate (3c): Colorless solid, yield: 0.16 g (91%); IR: 3437 (s, br), 2396 (w), 2066 (w), 1763 (m), 1636 (s), 1555 (w), 1539 (vw), 1383 (s), 1174 (vw), 1043 (w), 825 (m), 763 (w), 758 (w), 662 (vw) cm^{-1}; ^1H NMR: δ 4.18 (s, 6H), 2.82 (s, 3H); ^{13}C NMR: δ 153.8, 37.3, 9.0. Anal. Calcd for $C_4H_9N_5O_3$ (175.15): C, 27.43; H, 5.18; N, 39.99. Found: C, 27.16; H, 4.91; N, 39.70.

1,4-Dimethyltriazolium nitrate (3e): Colorless solid, yield: 0.13 g (81%); IR: 3426 (w), 3045 (m), 2396 (w), 1764 (w), 1542 (vw), 1560 (s), 1542 (w), 1384 (s, br), 1171 (m), 1094 (vw), 1070 (w), 988 (w), 922 (vw), 826 (s), 736 (w), 658 (w), 619 (m), cm^{-1}; ^1H NMR: δ 10.04 (s, 1H), 8.86 (s, 1H), 4.03 (s, 3H), 3.91 (s, 3H); ^{13}C NMR: δ 146.3, 144.8, 39.5, 34.9. Anal. Calcd for $C_4H_8N_4O_3$ (160.13): C, 30.00; H, 5.04; N, 34.99. Found: C, 30.26; H, 4.73; N, 35.04.

1,3-Dimethylimidazolium nitrate (3f): Colorless solid, yield: 0.14 g (88%); IR: 3429 (m), 3154 (vw), 3096 (w), 2396 (w), 1763 (m), 1623 (vw), 1576 (s), 1398 (s, br), 1175 (s), 1086 (vw), 826 (s), 758 (w), 710 (vw), 622 (w) cm^{-1}; ^1H NMR: δ 9.02 (s, 1H), 7.44 (s, 2H), 3.83 (s, 6H); ^{13}C NMR: δ 138.6, 124.5, 36.6. Anal. Calcd for $C_5H_9N_3O_3$ (159.14): C, 37.74; H, 5.70; N, 26.40. Found: C, 37.78; H, 5.69; N, 25.70.

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Supporting Information Available: Crystallographic data for **1a and 2a** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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