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Nitrocyanamide-Based Ionic Liquids and Their Potential Applications as Hypergolic Fuels

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Abstract: Nitrocyanamide ionic liquids with substituted imidazolium, guanidinium, and tetrazolium cations have been synthesized and fully characterized. Aminoguanidinium nitrocyanamide (**7**) crystallizes in the triclinic system $P\bar{1}$. The results obtained from theoretical calculations based on **7** are consistent with the single-crystal structure data. These ionic liquids exhibit desirable physicochemical properties, such as low melting points and good thermal stabilities. Furthermore, they are all impact insensitive materials. Their energetic performances, including heats of formation, detonation pressures, and detonation velocities, were studied by a combination of theoretical and empirical calculations. The ionic liquids **1**–**4** have large liquid ranges and low viscosities. They were shown to be promising candidates as hypergolic ionic liquids through the combustion tests with 100% HNO_3.

Keywords: combustion · explosives chemistry · hypergolic fuels · ionic liquids · thermodynamics

Introduction

In recent years, room-temperature ionic liquids have received much attention as interesting modifiable solvents and soft materials.[1] Because of their unique physical properties (e.g., high thermal stability, large liquid range, negligible vapor pressure), these materials are well suited for a wide range of applications, such as solvents,[2] catalysts,[3] electrolytes,[4] lubricants,[5] magnetic,[6] and optical fluids.[7] Energetic ionic liquids do demonstrate some promise in potential applications as propellants, explosives, and pyrotechnics.[8] When compared with traditional energetic compounds, such as 2,4,6-trinitrotoluene (TNT), 1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), and cyclo-1,3,5-trimethylene-2,4,6-trinitramine (RDX), many energetic ionic liquids were reported with several advantages, including enhanced thermal stability, negligible vapor pressure, and little or no vapor toxicity.[9]

The dinitramide (DNA) anion ($N(NO_2)_2^-$) was first reported in 1993[10] and has played a role as an energetic anion in ionic liquids since 2003.[11] DNA^--containing energetic ionic liquids have high oxygen content and high detonation properties necessary to be good candidates as explosives.[12] However, low thermal and impact stabilities limit the applications of DNA^--containing energetic ionic liquids. The dicyanamide (DCA) anion ($N(CN)_2^-$) has been studied as a stable anion for constructing energetic ionic liquids. Compared with other energetic ionic liquids, DCA^- ionic liquids have good fluidity and thermal stability, but much lower detonation properties.[13] Recently DCA^--containing ionic liquids have been shown to behave as hypergolic fuels.[14] The nitrocyanamide (NCA) anion ($N(CN)(NO_2)^-$) is an analogue of the DCA^- and DNA^- anions. Metal NCA^- derivatives, such as potassium nitrocyanamide, have been studied as primary explosives that may play a role in initiating detonation.[15] Most known NCA^- salts were readily eliminated from serious consideration as useful primary explosive compounds because they proved to be too sensitive to impact.[15] It may be that NCA^- may combine the virtues of DCA^- and DNA^- anions with a balance of stability and energy. Little evidence is available, since only a few NCA^- salts, especially ionic liquids, have been reported. Therefore, further study of new NCA^- ionic liquids was undertaken. Now we report novel NCA^- ionic liquids with imidazolium, guanidinium, and tetrazolium cations. Syntheses, full characterization, and theoretical studies of these ionic liquids were in-

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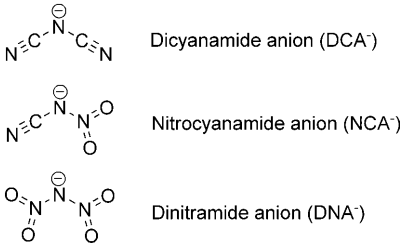
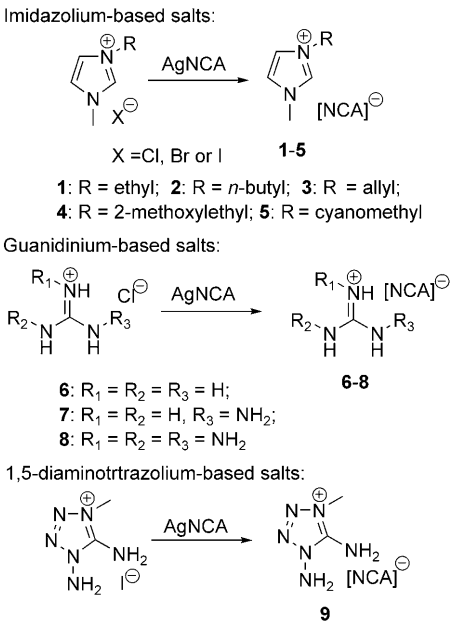
vestigated. The hypergolic properties of ionic liquids **1**–**4** as fuels with 100% HNO_3 as the oxidizer were also examined.



Results and Discussion

Synthesis: The preparative routes to the NCA^- ionic liquids are shown in Scheme 1. The imidazolium-based nitrocyanamides (**1**–**5**) were synthesized by anion exchange between



Scheme 1. Synthesis routes of NCA^- ionic liquids.

imidazolium-based halides and silver nitrocyanamide (AgNCA) in methanol. After separation, the filtrates were dried in vacuo to give light yellow liquids (**1**–**4**) or a light brown solid (**5**). The guanidinium nitrocyanamides (**6**–**8**) were prepared from anion exchange of guanidinium hydrochloride, aminoguanidium hydrochloride, and triaminoguanidium hydrochloride with AgNCA in methanol. The white solid products were washed with ethyl ether, and dried under vacuum. 1,5-Diamino-4-methyl-1,2,3,4-tetrazolium nitrocyanamide (**9**) was obtained from 1,5-diamino-4-methyl-1,2,3,4-tetrazolium iodide and AgNCA in methanol. After evaporation under vacuum, yellow liquid **9** was obtained. These NCA^--containing ionic liquids were characterized by IR and NMR spectroscopies and elemental analysis.

X-ray crystallography: Slow recrystallization of **7** from a solution in acetonitrile/methanol afforded colorless needles suitable for X-ray diffraction analysis. The structure is shown in Figure 1a and the crystallographic data are summarized in the Experimental Section. Selected bond distances and angles are given in Table 1. Compound **7** crystallizes in the triclinic system $P\bar{1}$. Delocalization of the negative charge on the NCA^- anion is evident from several structural features: 1) the $-NO_2$ and $-CN$ groups in the anion are almost coplanar; 2) the N1–C2 bond (1.1494(17) Å) is slightly longer than the normal C≡N bond and the C2–N3 bond (1.3393(17) Å) is much shorter than the normal C–N bond; 3) the N4–O5 bond (1.2395(15) Å) and the N4–O6 bond (1.2473(14) Å) are longer than usual N=O bonds, and the N3–N4 bond (1.3297(16) Å) is shorter than the usual N–N bond. The aminoguanidinium cation also displays delocalization of the positive charge due to bond homogenization. The lengths of the N8–C9 (1.3304(17) Å), C9–N10 (1.3224(16) Å), and C9–N11 bonds (1.3198(17) Å) are all between the lengths of normal C–N and C=N bonds. All of the main atoms (N7, N8, C9, N10, and N11) of the amino-

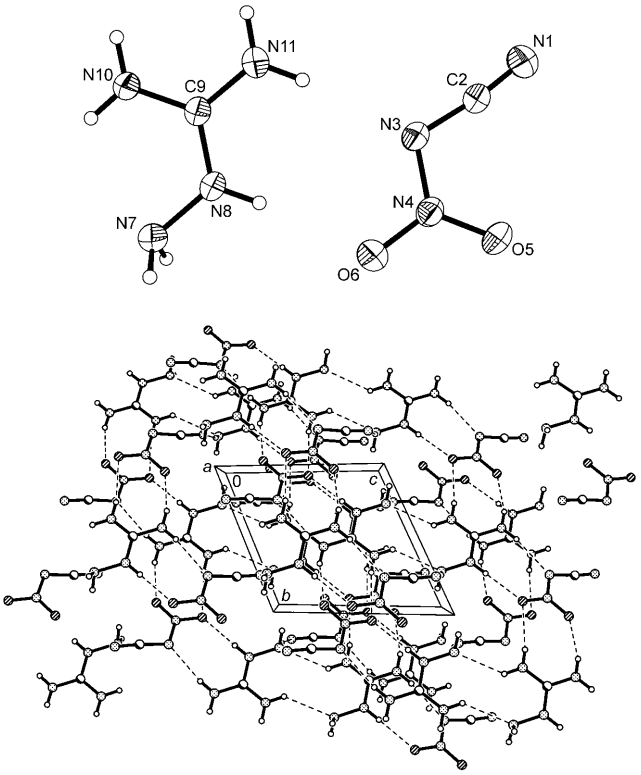


Figure 1. a) Molecular structure of **7** (thermal ellipsoids shown at 30% probability). Hydrogen atoms are shown as open spheres of arbitrary radius and are unlabelled for clarity. b) Packing diagram of **7** viewed down the *a* axis. Unit cell is indicated and dashed lines represent hydrogen bonding.

Table 1. Selected bond lengths [Å] and bond angles [°] in crystal and by calculation (B3LYP/6-311+G(d,p)) for **7**.

	Crystal	Calculated		Crystal	Calculated
N1−C2	1.1494(17)	1.1617	C2−N3	1.3393(17)	1.3338
N3−N4	1.3297(16)	1.3492	N4−O5	1.2395(15)	1.2220
N4−O6	1.2473(14)	1.2654	N7−N8	1.4075(17)	1.4077
N8−C9	1.3304(17)	1.3337	C9−N11	1.3198(17)	1.3300
C9−N10	1.3224(16)	1.3464	N7−H7A	0.905(17)	1.0166
N8−H8	0.8600	1.0110			
N1-C2-N3	173.23(13)	171.58	N4-N3-C2	112.19(10)	115.22
O5-N4-N3	121.11(11)	122.64	O6-N4-N3	116.75(9)	115.16
N8-N7-H7A	108.2(10)	108.78	C9-N8-N7	119.80(9)	118.62
C9-N8-H8	120.1	120.50	N11-C9-N8	118.73(10)	118.82
N10-C9-N8	120.02(11)	119.32	C9-N10-H10A	120.0	120.30

guanidinium cation are coplanar. (Reference bond lengths: C−N, 1.468 Å, C=N, 1.316 Å; C≡N, 1.137 Å; N=N, 1.241 Å and N−N, 1.414 Å, N=O, 1.219 Å and N−O, 1.394 Å)[17]

The packing structure of **7** is built up with hydrogen bonding (Figure 1b). The whole molecular charge delocalization is accomplished by extensive hydrogen bonding in the extended structure. Each NCA^- anion forms moderate hydrogen bonds with the amino groups of two cations *via* the atoms with negative charge (N1, N3, O5, and O6). (donor (D)···acceptor (A) ca. 2.980 to 3.355 Å, Table 2) These

Table 2. Hydrogen bonds for **7** (Å and°).[a]

D−H···A	*d*(D−H)	*d*(H···A)	*d*(D···A)	∠(DHA)
N7−H7A···O5#1	0.905(17)	2.619(17)	3.355(3)	139.0(13)
N7−H7B···N1#2	0.913(18)	2.305(18)	3.206(3)	169.2(15)
N8−H8···O6	0.86	2.16	3.013(2)	170.8
N10−H10A···O6#3	0.86	2.24	3.082(3)	168.1
N10−H10B···N7#4	0.86	2.45	3.147(2)	139.0
N11−H11A···O5#3	0.86	2.15	2.980(3)	162.0
N11−H11B···N3	0.86	2.20	3.043(2)	168.2

[a] Symmetry transformations used to generate equivalent atoms: #1 *x*, *y*, *z*−1 #2 *x*+1, *y*, *z*−1 #3 *x*, *y*−1, *z* #4 −*x*+1, −*y*+1, −*z*.

sheets are also cross-linked by weak hydrogen bonding from the amino group N10 to N7#4 in another cation (N10−H10B··N7#4 = 3.147(2) Å; #4 = −*x*+1, −*y*+1, −*z*). The combination of all these hydrogen bonds forms a complex 3D network.

Theoretical study: To obtain a better understanding of the crystal structure of **7**, the optimized structure of **7** in the gas phase was obtained using B3LYP functional analyses with the 6-311+G** basis set.[18] In Table 1 the calculated bond lengths and angles are listed immediately following the corresponding data obtained for the crystal. The optimized structure is essentially the same as that observed from X-ray data; calculated bond lengths and angles are consistent with the experimental data. In some cases, the calculated bond lengths are a little longer than the crystal bond lengths because there is no molecular packing in the gas phase.

The electronic charge distribution of **7** by natural bond orbital (NBO) analysis[19] based on the optimized structure is shown in Figure 2. The NBO analysis shows that the N1 (−0.389e), N3 (−0.530e), O5 (−0.392e), and O6 (−0.527e) atoms in the NCA^- anion carry negative charges, while C2 (+0.397e) and N4 (+0.605e) atoms carry positive charges. This charge distribution implies that N1, N3, O5, and O6 atoms in the NCA^- anion can form hydrogen bonds with the H atoms in the cation. This weak

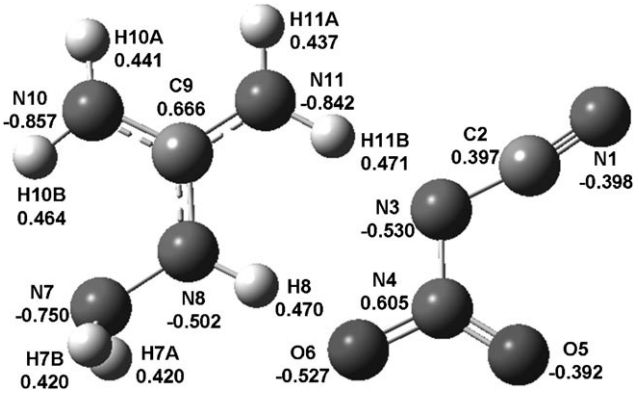


Figure 2. Optimized structure and charge distribution in **7** as found with NBO analysis (B3LYP/6-311+G(d,p)).

hydrogen bonding was found in the crystal as N7−H7A···O5#1 = 3.355(3) Å, #1 = *x*, *y*, *z*−1; N7−H7B···N1#2 = 3.206(3) Å, #2 = *x*+1, *y*, *z*−1; N8−H8···O6 = 3.013(2) Å; N10−H10A···O6#3 = 3.082(3) Å; N11−H11A···O5#3 = 2.980(3) Å, #3 = *x*, *y*−1, *z*; and N11−H11B···N3 = 3.043(2) Å. In the cation, the N7, N8, N10, and N11 atoms carry negative charges (−0.750, −0.502, −0.857, and −0.842 e, respectively). However, only the N7 atom has the steric interspace to form hydrogen bonds with the H atom on another cation. (N10−H10B···N7#4 = 3.147(2) Å; #4 = −*x*+1, −*y*+1, −*z*).

Physicochemical properties: The melting points, viscosities, thermochemical, and energetic data of **1–9** are summarized in Table 3. The melting points of these new compounds (except for **7**, 111 °C) are below 100 °C, the accepted boundary between ionic liquids and melting salts.[16] The ionic liquids **1–5** have similar 1-methylimidazolium cation frameworks with different alkyl-substituted groups. All of the other liquids have glass transition temperatures (T_g) lower than −70 °C, except that **5** has a distinct melting point at 83 °C. The cyanomethyl group helps increase the melting point sharply. The guanidinium-based samples **6–8** melt at 111, 91, and 74 °C, respectively. The relatively high melting points arise from the conjugated structure of the guanidinium framework and the abundant hydrogen bonds in these

Table 3. The physicochemical properties of **1–9** and reference compounds.

Compound	T_m/T_g[a] [°C]	T_d[b] [°C]	d[c] [g cm^{-3}]	η[d] [cP]	ΔH_f[e] [kJ mol^{-1}]	ΔH_f[f] [kJ g^{-1}]	IS[g] [J]	p[h] [GPa]	D[i] [m s^{-1}]	I_{sp}[j] [s]	ID[k] [ms]
1	/−73	253	1.18	23	157.7	0.80	>40	9.2	5807	192.3	78
2	/−90	256	1.13	57	128.5	0.57	>40	8.3	5672	186.4	81
3	/−91	220	1.11	44	274.7	1.31	>40	7.6	5372	196.7	46
4	/−82	266	1.21	54	44.3	0.19	>40	8.7	5582	187.0	65
5	83	203	1.47		368.9	1.77	>40	15.4	6926	203.2	
6	111	219	1.52		28.4	0.19	>40	19.5	7577	200.6	
7	91	223	1.53		138.2	0.86	>40	22.0	7956	212.2	
8	74	209	1.59		322.8	1.69	>40	27.0	8709	227.0	
9	19/−47	188	1.58		409.2	2.03	>40	23.0	8020	225.0	
10[l]	−58	64	0.79	0.56[m]	84.1	1.40		7.8	6280	210.8	
11[n]	−6/−90	240	1.06	33[m]	266.4	1.30	>40	6.6	5294	164.9	47
12[o]	85	150	1.57		184.0	0.87	4	28.6	8730	264.4	
13[p]	85	184	1.72		385.3	1.86	7	33.6	8827		

[a] Melting point/phase transition temperature. [b] Decomposition temperature. [c] Density, gas pycnometer, 25 °C. [d] Viscosity, 25 °C.[e] Molar enthalpy of the formation of ionic liquid. [f] Enthalpy of the formation of ionic liquid in per gram. [g] Impact sensitivity. [h] Detonation pressure. [i] Detonation velocity. [j] The specific impulse. [k] Ignition delay time. [l] 1,1-Dimethylhydrazine, ref. [22]. [m] Viscosity at 20 °C. [n] 1-Butyl-3-methylimidazolium dicyanamide, ref. [23]. [o] Triaminoguanidinium dinitramide, ref. [24]. [p] 1,5-Diamino-4-methyltetrazolium dinitramide, ref. [12a].

salts, which is consistent with the single-crystal structure of **7**. Compound **9**, containing the 1,5-diamino-4-methyl-1,2,3,4-tetrazolium cation, is a viscous liquid at room temperature. Compound **9** has a T_g at −47 °C, and a differential scanning calorimetry (DSC) melting point at 19 °C. This means that **9** has a long-lived supercooled phase like many traditional ionic liquids.[20] For the salts with the same cations, the melting points of NCA^- ionic liquids are generally lower than DNA^- ionic liquids and similar to DCA^- ionic liquids. (compounds **2**, **8**, **9**, **11**, **12**, and **13**; Table 3) The low melting point salts show good liquid-state characteristics.

Melting point and viscosity have positive correlations. Low melting ionic liquids should have lower viscosity and better fluidity.[21] The viscosity of a solid can be thought of as being infinite. Therefore, compounds **5–9** are unsuitable to be good fluid liquids at room temperature. At 25 °C, the viscosity of **1** is only 23 cP, which is lower than that of **11**. The viscosities of ionic liquids **1–4** at 25 °C are less than 60 cP, which puts them in the same class as **11**.

The viscosities of many ionic liquids decrease rapidly as a function of temperature.[16] The temperature dependence of the viscosities for **1–4** are shown in Figure 3. The graph of log(viscosity) plotted versus temperature indicates that these NCA^- ionic liquids do not display Arrhenius temperature behavior. Rather, the significant feature of glassy or supercooled liquids is observed. On approaching the glass transition temperature, there is a rapid increase in the viscosity and a slowing down of the structural relaxation. This temperature dependence of the viscosity, η, for glass-forming liquids is well represented by the VFT empirical equation [Eq. (1)][21]

$$\eta(\mathrm{T}) = \eta_0 \exp\left(\frac{DT_0}{T-T_0}\right) \quad (1)$$

in which η is the viscosity, T is the temperature, T_0 corresponds to the characteristic temperature at which η is infinite, η_0 is a reference viscosity, and D is a constant presenting the structural strength of the system. The VFT fit curves are also shown in Figure 3. The viscosity versus temperature graphs can be fit well to the VFT model ($R^2 > 0.998$). The T_0 of **1–4** were calculated at 168, 186, 184, and 188 K, respectively. The lower T_0 may lead to lower melting points. From the VFT fit curves, the viscosities of ionic liquids at low temperatures can be estimated. The estimated viscosities of **1–4** at 0 °C are only 63, 267, 171, and 229 cP, respectively. These data indicate that NCA^- ionic liquids still have good liquid characteristics at low temperatures.

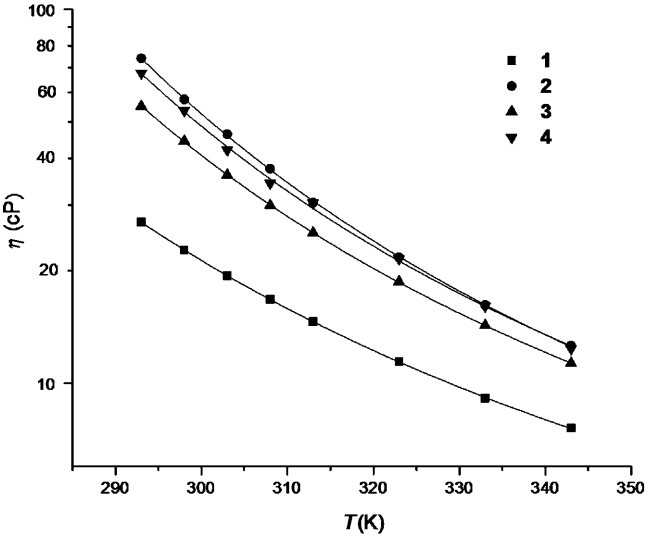


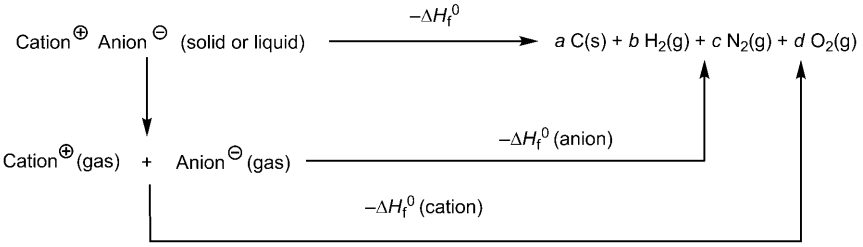
Figure 3. Temperature-dependent viscosities of NCA^- ionic liquids **1** (■), **2** (●), **3** (▲), and **4** (▼), Vogel–Fulcher–Tammann (VFT) fit curves are also shown.

The stabilities toward heat, shock, friction, and electrostatic discharge of energetic materials are as important as their energetic performance.[25] The decomposition temperatures of **1–8** are higher than 200 °C, showing they are thermally stable energetic materials.[26] Compound **9** begins to

decompose at 188 °C. These NCA^- salts are more thermally stable than the corresponding DNA^- salts. For ionic liquids **1–4**, their possible liquid ranges may reach 300 °C. The impact sensitivities of the samples were determined by using the standard BAM Fallhammer method.[27] All of the new NCA^- salts are stable to impact at more than 40 J (10 kg hammer, 40 cm). Based on the classification standard of sensitivities,[28] these compounds are impact insensitive energetic materials. As a comparison, dinitramides **12** and **13** are sensitive to impact at 4 and 7 J respectively. Their nitrocyanamide analogues with the same cations, **8** and **9**, are both impact insensitive. The improved impact stability is because of the NCA^- anion. Friction sensitivity was not determined.

Heat of formation is an important parameter to evaluate the performances of energetic materials. Based on a Born–Haber energy cycle (Scheme 2), heats of formation of ionic salts can be simplified by Equation (2):

$$\Delta H_f^\circ \text{ (ionic salts, 298 K)} = \Sigma\Delta H_f^\circ \text{ (cation, 298 K)} + \Sigma\Delta H_f^\circ \text{ (anion, 298 K)} - \Delta H_L \quad (2)$$



Scheme 2. Born–Haber cycle for the formation of ionic liquids. The number of moles of the respective products are given by *a*, *b*, *c*, and *d*.

in which ΔH_L is the lattice energy of the ionic salts. For 1:1 salts and considering the nonlinear nature of the cations and anion used, ΔH_L (kJ mol^{-1}) can be predicted by Equation (3) suggested by Jenkins et al.[29]:

$$\Delta H_L = U_{POT} + [p(nM/2-2) + q(n_X/2-2)]RT \quad (3)$$

in which nM and n_X depend on the nature of the ions M_p^+ and X_q^-, respectively, and have a value of 6 for nonlinear polyatomic ions. The equation for lattice potential energy U_{POT} (equation 4) has the form shown in Equation (4):

$$U_{POT} \text{ (kJ mol}^{-1}) = 1981.2(\rho_m/M_m)^{1/3} + 103.8 \quad (4)$$

in which ρ_m is density (g cm^{-3}) and M_m is the chemical formula mass of the ionic material (g). The heats of formation of the cations were computed by using isodesmic reactions (See the Supporting Information).[30] The heats of formation of the anion and the parent ions in the isodesmic reactions were calculated from protonation reactions (ΔH_f (H^+) = 1528 kJ mol^{-1}).[30,31] The enthalpies of the isodesmic reactions ($\Delta H_r^\circ{}_{298}$) were obtained by combining the MP2/6-311++G** energy differences for the reactions, the scaled zero-point energies (B3LYP/6-31+G**), and other thermal factors. The calculated heats of formation are summarized in Table 3. All of the salts exhibit positive heats of formation. Salt **9** has the highest value, 409.2 kJ mol^{-1}. For salts with the same cations, the NCA^- salts have higher heats of formation than the DNA^- salts (e.g., **8**, 322.8 kJ mol^{-1} versus **12**, 184 kJ mol^{-1}) and lower heats of formation than the DCA^- salts (e.g., **2**, 128.5 kJ mol^{-1} versus **11**, 266.4 kJ mol^{-1}).

The detonation pressure (P) and velocity (D) were calculated based on traditional Chapman–Jouget thermodynamic detonation theory using CHEETAH 5.0.[32] Compound **8** has the highest calculated detonation pressure (27.0 GPa) and detonation velocity (8709 m s^{-1}). The detonation properties of **5–9** are similar to or better than TNT (P = 19.5 GPa, D = 6881 m s^{-1}); therefore, they can be used as explosives candidates.

Energetic materials detonate more readily when they have higher detonation pressure and velocity values. However, these properties may preclude stable, self-sustained combustion. So the good candidates for fuel applications need a suitable range of detonation pressures and velocities based on consideration of both energy and combustion ability. 1,1-Dimethylhydrazine (**10**, P = 7.8 GPa, D = 6280 m s^{-1}) is the most important practical hypergolic fuel as a bipropellant. 1-Butyl-3-methylimidazolium dicyanamide (**11**, P = 6.6 GPa, D = 5294 m s^{-1}) was shown to be a potential "green" hypergolic fuel.[14b] The detonation properties of imidazolium-based ionic liquids **1–4** (P = 7.6–9.2 GPa, D = 5372-5807 m s^{-1}) are similar to **10** and **11**. The suitable range of detonation pressures and velocities of **1–4** encouraged us to optimize the potential application of these ionic liquids as hypergolic fuels.

Hypergolic properties with 100 % HNO_3: Based on the consideration of environmental friendliness, green chemistry, and low vapor toxicity, energetic ionic liquids are potential replacements for hydrazine and its derivatives for hypergolic fuels in bipropellant applications.[14b,c] However, the number of suitable energetic ionic liquids is very limited. Several minimum criteria should be satisfied for the qualified candidates. 1) The fuel must be liquid. Bipropellant systems mainly use a liquid rocket engine. Solid fuel cannot be easily transported by pumps. 2) The fuel should be hypergolic with a traditional or other oxidizer. 3) The fuel is thermally stable to more than 200 °C, and neither impact nor friction sensitive. 4) The fuel should have as low as possible freezing/melting point and viscosity. Based on these criteria, the NCA^- ionic liquids **1–4**, which have low melting points

and viscosities and high decomposition temperatures, are promising candidates. Moreover, they also have similar detonation properties with 1,1-dimethylhydrazine. The reactivities of **1**–**4** with white fuming nitric acid (WFNA, ≈100% HNO_3) were examined. The test procedures were recorded by using a high-speed camera at 1000 frames s^{-1} to monitor the reactivity and evaluate the performance of the hypergolic ionic liquids. The ignition delay data are listed in Table 3. Some special moments of **4** reacting with WFNA are shown in Figure 4. A droplet of ionic liquid was formed first. (Figure 4a) The droplet fell to the surface of WFNA. The time

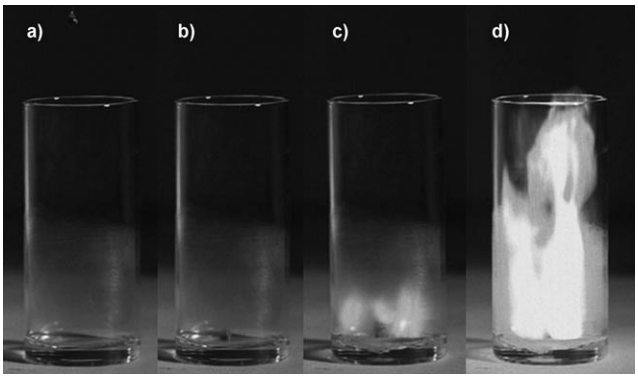


Figure 4. Selected frames from the high-speed video of the hypergolic reaction of compound **4** with WFNA.

between the first hit (Figure 4b) and the sign of the first visible ignition (Figure 4c) is the ignition delay (ID) time. After ignition, self-sustained combustion (Figure 4d) occurred, which indicates the hypergolic compound burned normally. In our tests, all of the ionic liquids **1**–**4** are hypergolic when treated with WFNA. Their ID values are similar to that of $[Bmim]N(CN)_2$ (Bmim = 1-butyl-3-methylimidazolium).[14b]

Conclusion

Nitrocyanamide-containing ionic liquids with substituted imidazolium, guanidinium, and tetrazolium cations were synthesized and fully characterized. They exhibit desirable physicochemical properties, such as low melting points and good thermal stabilities; they are all impact insensitive materials. Their energetic properties, including heats of formation, detonation pressures ,and detonation velocities, were studied by a combination of theoretical and empirical calculations. The ionic liquids **1**–**4** each have a large liquid range and low viscosity at low temperatures. They were shown to be promising candidates as hypergolic ionic liquids through combustion tests with 100% HNO_3.

Experimental Section

Caution! We have not experienced any problems in handling these compounds. Although they are impact insensitive materials, their friction sensitivities have not been determined. Therefore, they should be handled with extreme care using all of the standard safety precautions.

General methods: 1-Ethyl-3-methylimidazolium bromide, 1-butyl-3-methylimidazolium bromide, 1-allyl-3-methylimidazolium iodide, 1-methyl-3-(2′-methoxyl)ethylimidazolium bromide, 1-cyanomethyl-3-methylimidazolium bromide,[16] and 1,5-diamino-4-methyl-1,2,3,4-tetrazolium iodide[9f,g] were prepared by literature methods. All other chemicals were obtained commercially as analytical grade materials and were used as received. IR spectra were recorded by using KBr plates for neat liquids and KBr pellets for solids on a Biorad Model 3000 FTS spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz spectrometer operating at 300 and 75 MHz, respectively, with $[D_6]$DMSO as the locking solvent unless otherwise stated. ^1H and ^{13}C NMR chemical shifts are reported in ppm relative to TMS. The densities were measured at 25 °C on a Micromeritics Accupyc 1330 gas pycnometer. DSC measurements were performed on a TA DSC Q10 calorimeter equipped with an Autocool accessory, and calibrated by using indium. Measurements were carried out by heating from 40 °C (for solids) or −100 (for liquids) to 400 °C at 10 °C min^{-1}. Thermogravimetric analysis (TGA) measurements were accomplished on a TA TGA Q50 instrument by heating samples at 10 °C min^{-1} from 25 to 500 °C in a dynamic nitrogen atmosphere (flow rate 70 mL min^{-1}). Elemental analyses (H, C, N) were performed on a CE-440 Elemental Analyzer. The viscosities were measured with a Grabner MINIVIS II Portable Micro viscometer. Computations were performed by using the Gaussian 03 (Revision D.01) suites of programs[33] and CHEETAH 5.0.[32] The geometric optimization and the frequency analyses were carried out using B3LYP functional analyses with the 6-311++G** basis set.[18] Single energy points were calculated at the MP2/6-311++G** level.[34] All of the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies.

X-ray crystallography: Crystals of **7** were removed from the flask, a suitable crystal 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 by using graphite monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$). formula $C_2H_7N_7O_2$; M_r 161.15 g mol^{-1}; size $0.26 \times 0.25 \times 0.05$ mm^3; triclinic crystal system; $P\bar{1}$ space group; $a = 7.173(5)$, $b = 7.804(6)$, $c = 8.031(6)$ [Å]; $\alpha = 61.488(9)$, $\beta = 71.368(10)$, $\gamma = 64.669(10)$°; $V = 353.3(5)$ $Å^3$; $Z = 2$; $\rho_{calcd} = 1.515$ g cm^{-3}; $T = 293(2)$ K; $\mu = 0.130$ mm^{-1}; $F[000] = 168$; reflections = 3277; $R_{int} = 0.0179$; parameters = 107; S on $F^2 = 1.082$; R_1 $[I > 2\sigma(I)] = 0.0312$; wR_2 $[I > 2\sigma(I)] = 0.0918$; R_1 (all data) = 0.0352; wR_2 (all data) = 0.0954; $\Delta\rho_{min\ and\ max} = 0.148$ and -0.146 e $Å^{-3}$. Data collection was performed and the unit cell was initially refined by using APEX2 [v2.1–0].[35] Data reduction was performed by using SAINT [v7.34A][36] and XPREP [v2005/2].[37] Corrections were applied for Lorentz, polarization, and absorption effects using SADABS [v2004/1].[38] The structure was solved and refined with the aid of the programs in the SHELXTL-plus [v6.12] system of programs.[39] The full-matrix least-squares refinement on F^2 included atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were included by using a riding model. No decomposition was observed during data collection. Further details are provided in the Supporting Information.

CCDC-748744 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Preparation of silver nitrocyanamide (AgNCA):[15] At 0 °C, *N*-methyl-*N*-nitroso-*N*′-nitroguanidine (30.0 mmol, 5.0 g) was added to an aqueous solution of sodium hydroxide (60.0 mL, 40.0 mmol, 1.6 g) in small portions with vigorous stirring. This procedure required more than 10 min. After addition, the mixture was slowly warmed to room temperature with continuous stirring until the mixture became colorless. Then aqueous nitric acid (15.0 mL, 40.0 mmol; 3.6 mL concentrated nitric acid) was added, followed by an aqueous solution of silver nitrate (15 mL, 30.0 mmol,

5.1 g). The precipitate was filtered immediately and washed with water. A white solid was obtained in 88% yield (5.1 g).

Syntheses of nitrocyanamide ionic liquids

*1-Ethyl-3-methylimidazolium nitrocyanamide (**1**)*: 1-Ethyl-3-methylimidazolium bromide (2.0 mmol, 382 mg) was added to a 100 mL flask and dissolved in methanol (10 mL). After silver nitrocyanamide (AgNCA, 2.2 mmol, 426 mg) was added, the mixture was stirred for 24 h at room temperature. The precipitate was filtered and the filtrate was dried under vacuum. A light yellow liquid was obtained (**1**, 367 mg, 93%). ^{1}H NMR: δ = 1.41 (t, J = 7.2 Hz, 3H; CH_2CH_3), 3.84 (s, 3H; CH_3), 4.18 (q, J = 7.2 Hz, 2H; CH_2CH_3), 7.68 (s, 1H), 7.77 (s, 1H), 9.10 ppm (s, 1H); ^{13}C NMR: δ = 15.1, 35.8, 44.4, 116.7, 122.0, 123.6, 136.3 ppm; IR (film): ν_{max} = 3154, 3114, 2988, 2176, 1739, 1630, 1572, 1438, 1274, 1052, 956, 847, 766, 622, 541 cm^{-1}; elemental analysis calcd (%) for $C_7H_{11}N_5O_2$ (197.19): C 42.64, H 5.62, N 35.52; found: C 42.42, H 5.74, N 35.39.

*1-Butyl-3-methylimidazolium nitrocyanamide (**2**)*: The same procedure was followed as that used for **1**. 1-Butyl-3-methylimidazolium bromide (2.0 mmol, 438 mg) and AgNCA (2.2 mmol, 426 mg) were reacted. A light yellow liquid was obtained (**2**, 433 mg, 96%). ^{1}H NMR: δ = 0.90 (t, J = 7.2 Hz, 3H; $CH_2CH_2CH_2CH_3$), 1.25 (m, 2H; $CH_2CH_2CH_2CH_3$), 1.76 (m, 2H; $CH_2CH_2CH_2CH_3$), 3.84 (s, 3H; CH_3), 4.15 (t, J = 7.2 Hz, 2H; $CH_2CH_2CH_2CH_3$), 7.70 (s, 1H), 7.76 (s, 1H), 9.10 ppm (s, 1H); ^{13}C NMR: δ = 13.2, 18.9, 31.4, 35.8, 39.0, 48.6, 116.7, 122.3, 123.6, 136.6 ppm; IR (film): ν_{max} = 3319, 3152, 3113, 2964, 2874, 2176, 1714, 1626, 1572, 1435, 1272, 1152, 1053, 951, 847, 758, 651, 623, 540 cm^{-1}; elemental analysis calcd (%) for $C_9H_{15}N_5O_2$ (225.25): C 47.99, H 6.71, N 31.09; found: C 47.48, H 6.78, N 30.09.

*1-Allyl-3-methylimidazolium nitrocyanamide (**3**)*: The same procedure was followed as that used for **1**. 1-Allyl-3-methylimidazolium iodide (2.0 mmol, 317 mg) and AgNCA (2.2 mmol, 426 mg) were reacted. A light yellow liquid was obtained (**3**, 385 mg, 92%). ^{1}H NMR: δ = 3.86 (s, 3H; CH_3), 4.83 (t, J = 5.7 Hz, 2H; CH_2CHCH_2), 5.34 (t, J = 9.9 Hz, 2H; CH_2CHCH_2), 6.03 (m, 1H; CH_2CHCH_2), 7.70 (s, 1H), 7.72 (s, 1H), 9.10 ppm (s, 1H); ^{13}C NMR: δ = 35.9, 50.9, 116.7, 120.3, 122.4, 123.8, 131.7, 136.7 ppm; IR (film): ν_{max} = 3150, 3111, 2857, 2705, 2173, 1908, 1713, 1645, 1570, 1435, 1269, 1163, 1103, 995, 846, 762, 675, 624, 545 cm^{-1}; elemental analysis calcd (%) for $C_8H_{11}N_5O_2$ (209.20): C 45.93, H 5.30, N 33.48; found: C 45.53, H 5.15, N 33.78.

*1-Methyl-3-(2′-methoxyl)ethylimidazolium nitrocyanamide (**4**)*: The same procedure was followed as that used for **1**. 1-Methyl-3-(2′-methoxyl)ethylimidazolium bromide (2.0 mmol, 442 mg) and AgNCA (2.2 mmol, 426 mg) were reacted. A light yellow liquid was obtained (**4**, 409 mg, 90%). ^{1}H NMR: δ = 3.26 (s, 3H; $CH_2CH_2OCH_3$), 3.67 (t, J = 7.2 Hz, 2H; $CH_2CH_2OCH_3$), 3.86 (s, 3H; CH_3), 4.34 (t, J = 7.2 Hz, 2H; $CH_2CH_2OCH_3$), 7.69 (s, 1H), 7.72 (s, 1H), 9.07 ppm (s, 1H); ^{13}C NMR: δ = 35.8, 48.8, 58.1, 69.7, 116.8, 122.7, 123.5, 136.9 ppm; IR (film): ν_{max} = 3316, 3115, 2940, 2900, 2836, 2174, 1715, 1572, 1435, 1299, 1074, 1038, 952, 835, 756, 705, 652, 623, 542 cm^{-1}; elemental analysis calcd (%) for $C_8H_{13}N_5O_3$ (227.22): C 42.29, H 5.77, N 30.82; found: C 42.68, H 6.00, N 28.23.

*1-Cyanomethyl-3-methylimidazolium nitrocyanamide (**5**)*: The same procedure was followed as that used for **1**. 1-Cyanomethyl-3-methylimidazolium bromide (2.0 mmol, 404 mg) and AgNCA (**5**, 2.2 mmol, 426 mg) were reacted. A light brown solid was obtained (370 mg, 89%). ^{1}H NMR: δ = 3.88 (s, 3H; CH_3), 5.57 (s, 2H; CH_2CN), 7.79 (s, 1H), 7.88 (s, 1H), 9.22 ppm (s, 1H); ^{13}C NMR: δ = 36.2, 36.8, 114.8, 116.8, 122.6, 124.4, 137.8 ppm; IR (KBr): ν_{max} = 3154, 3063, 2993, 2957, 2300, 2176, 1580, 1564, 1446, 1275, 1217, 1175, 1150, 1087, 1018, 935, 882, 749, 665, 621, 544 cm^{-1}; elemental analysis calcd (%) for $C_7H_8N_6O_2$ (208.18): C 40.39, H 3.87, N 40.37; found: C 39.93, H 3.69, N 40.26.

*Guanidinium nitrocyanamide (**6**)*: Guanidinium hydrocholoride (2 mmol, 191 mg) was placed in a 100 mL flask and dissolved in methanol (10 mL). AgNCA (2.2 mmol, 426 mg) was added and stirred at room temperature for 24 h. The precipitate was filtered and the filtrate was dried under vacuum. A white solid was obtained (**6**, 283 mg, 97%). ^{1}H NMR: δ = 6.89 ppm (s, 6H; NH_2); ^{13}C NMR: δ = 117.0, 158.5 ppm; IR (KBr): ν_{max} = 3450, 3354, 3277, 3210, 2199, 1668, 1422, 1291, 1148, 970, 765, 659 cm^{-1}; elemental analysis calcd (%) for $C_2H_6N_6O_2$ (146.11): C 16.44, H 4.14, N 57.52; found: C 16.51, H 4.12, N 57.15.

*Aminoguanidinium nitrocyanamide (**7**)*: The same procedure was followed as that used for **6**. Aminoguanidinium hydrocholoride (2.0 mmol, 221 mg) and AgNCA (2.2 mmol, 426 mg) were reacted. A white solid was obtained (**7**, 303 mg, 94%). ^{1}H NMR: δ = 4.68 (s, 2H; $NHNH_2$), 6.74 (s, 2H; NH_2), 7.25 (s, 2H; NH_2), 8.57 ppm (s, 1H; $NHNH_2$); ^{13}C NMR: δ = 116.7, 158.9 ppm; IR (KBr): ν_{max} = 3431, 3327, 2191, 1679, 1452, 1425, 1297, 1211, 1170, 1086, 988, 762 cm^{-1}; elemental analysis calcd (%) for $C_2H_7N_7O_2$ (161.12): C 14.91, H 4.38, N 60.85; found: C 14.92, H 4.58, N 60.48.

*Triaminoguanidinium nitrocyanamide (**8**)*: The same procedure was followed as that used for **6**. Triaminoguanidinium hydrocholoride (2.0 mmol, 281 mg) and AgNCA (2.2 mmol, 426 mg) were reacted. A white solid was obtained (**8**, 363 mg, 95%). ^{1}H NMR: δ = 4.48 (s, 6H; $NHNH_2$), 8.60 ppm (s, 3H; $NHNH_2$); ^{13}C NMR: δ = 116.6, 159.1 ppm; IR (KBr): ν_{max} = 3364, 3320, 3212, 2193, 1684, 1616, 1439, 1292, 1130, 952, 764, 637, 604, 536 cm^{-1}; elemental analysis calcd (%) for $C_2H_9N_9O_2$ (191.15): C 12.57, H 4.75, N 65.95; found: C 12.78, H 4.95, N 65.48.

*1,5-Diamino-4-methyl-1,2,3,4-tetrazolium nitrocyanamide (**9**)*: The same procedure was followed as that used for **1**. 1,5-Diamino-4-methyl-1,2,3,4-tetrazolium iodide (2.0 mmol, 484 mg) and AgNCA (2.2 mmol, 426 mg) were reacted. A yellow viscous liquid was obtained (**9**, 342 mg, 85%). ^{1}H NMR: δ = 3.84 (s, 3H), 7.03 (s, 2H), 9.00 ppm (s, 2H); ^{13}C NMR: δ = 34.6, 116.6, 147.5 ppm; IR (film): ν_{max} = 3323, 3130, 2184, 1709, 1628, 1436, 1276, 1162, 1117, 1038, 957, 773, 696, 597, 542 cm^{-1}; elemental analysis calcd (%) for $C_3H_7N_9O_2$ (201.15): C 17.91, H 3.51, N 62.67; found: C 17.76, H 3.43, N 62.08.

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