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Liquid Dinitromethanide Salts

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The dinitromethanide (DNM) anion is a useful component of room temperature ionic liquids. Eight DNM ionic liquids with substituted imidazolium cations including 1-butyl-3-methylimidazolium (**1**), 1-allyl-3-methylimidazolium (**2**), 1-allyl-3-butylimidazolium (**3**), 1,3-diallylimidazolium (**4**), 1-(2′-methoxyl)ethyl-3-methylimidazolium (**5**), 1-(ethoxylmethyl)-3-methylimidazolium (**6**), 1-(hydroxyethyl)-3-methylimidazolium (**7**), and 1,3-dimethylimidazolium (**8**) were obtained. DNM ionic liquids **1**−**8** were synthesized by metathesis reactions from the corresponding imidazolium halides with potassium dinitromethanide or silver dinitromethanide. These DNM ionic liquids have been fully characterized by IR, NMR, elemental analysis, thermal stability, phase behavior, and viscosity. The molecular structure of **8** was determined by single-crystal X-ray diffraction. Compound **8** crystallizes in the triclinic space group $P\bar{1}$, with a density of 1.453 g cm^{-3} (a = 7.1402(19) Å, b = 9.376(3) Å, c = 13.793(4) Å, α = 103.759(4)°, β = 90.757(4)°, γ = 96.874(4)°, V = 889.6(4) Å^3, and Z = 4). Delocalization of both the DNM anion and dimethylimidazolium cation was found from the single-crystal structure data of **8**. The heats of formation of **1**−**8** along with their detonation properties were investigated and analyzed. Their sensitivities toward impact were determined by BAM standards and found to be impact-insensitive (>40 J). The DNM-containing ionic liquids **1**−**7** are liquids at room temperature with desirable low viscosities. The temperature dependence of the viscosities for **1**−**7** was studied. These DNM ionic liquids were found to be a significant feature of glass-forming liquids. They also exhibit good liquid characteristics with desirable long liquidus ranges of more than 200 °C.

Introduction

The dinitromethanide [$CH(NO_2)_2^-$, DNM] anion was first reported in 1884.[1] Potassium dinitromethanide (KDNM) was synthesized in low yield via the reduction of bromodinitromethane,[1] which was obtained from the nitration of 2,4,6-tribromoaniline.[2] In 1951, KDNM was obtained in better yield (23%) by the Ter Meer reaction of chloronitromethane.[3] The routes to KDNM based on methyl cyanodinitroacetate or methyl dinitroacetate were reported in 1978.[4] In 2002, a more convenient method to prepare KDNM from barbituric acid was found, resulting in 33% total yield.[5] Other DNM salts, such as ammonium dinitromethanide (NH_4DNM) and sodium dinitromethanide, have also been prepared.[4,6] More recently, some organic DNM salts were reported as potential energetic materials.[7,8] However, the kinds of known DNM salts are still limited. Although the DNM anion has a simple structure, very few properties of its salts have been studied during the past 100 years.

As interesting modifiable solvents and soft materials, room temperature ionic liquids have received much attention.[9] Compared with traditional energetic compounds, such as TNT, HMX, and RDX, many energetic ionic liquids were reported with advantages of enhanced thermal stability,

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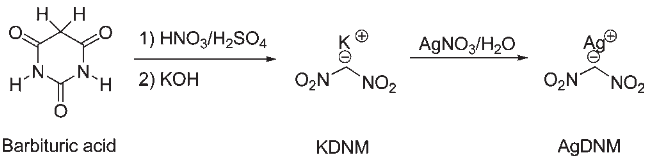
Scheme 1. Preparation of KDNM[5] and AgDNM



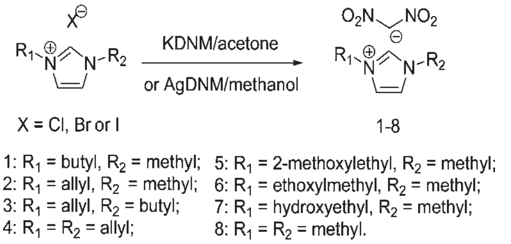
negligible vapor pressure, and little or no vapor toxicity.[10] Their unique properties have promoted them in potential applications such as "green" propellants, explosives, and pyrotechnics.[11] Until now, one known DNM salt, 1-ethyl-3-butylimidazolium dinitromethanide,[7] with a melting point at 48 °C, indicated that DNM salts were good candidates as ionic liquids. Therefore, it is reasonable to believe room temperature liquid DNM salts should surely exist.

We now report eight new ionic liquids based on the DNM anion. To obtain room temperature liquids, 1-butyl-3-methylimidazolium (**1**), 1-allyl-3-methylimidazolium (**2**), 1-allyl-3-butylimidazolium (**3**), 1,3-diallylimidazolium (**4**), 1-(2′-methoxyl)ethyl-3-methylimidazolium (**5**), 1-(ethoxylmethyl)-3-methylimidazolium (**6**), and 1-(hydroxyethyl)-3-methylimidazolium (**7**) cations were employed. Furthermore, to illustrate the structures of these room temperature ionic liquids, 1,3-dimethylimidazolium dinitromethanide (**8**) was prepared and crystallized for single-crystal X-ray analysis.

Results and Discussion

Synthesis. KDNM was prepared from barbituric acid following the literature procedure (Scheme 1).[5] Silver dinitromethanide (AgDNM) was then obtained as a yellow precipitate from the mixture of KDNM and $AgNO_3$ in an aqueous solution. DNM salts were synthesized by the metathesis reactions of the corresponding substituted imidazolium halides[12] with KDNM in acetone or AgDNM in methanol (Scheme 2). The byproduct, potassium halide or silver halide, was removed by filtration. Eight new DNM salts were obtained after the filtrates were collected and dried. DNM salts **1**−**7** are yellow transparent room temperature liquids. DNM salt **8** is a yellow solid and then light-yellow needles after recrystallization from a methanol solution. These DNM salts were characterized by IR, NMR, and elemental analysis.

Scheme 2. Syntheses of DNM Salts **1**−**8**



X-ray Crystallography. Slow recrystallization of **8** from a methanol solution gave light-yellow needles suitable for X-ray diffraction analysis. The structure is shown in Figure 1a, and crystallographic data are summarized in Table S1 (see the Supporting Information). Selected bond distances and angles are given in Table S2 (see the Supporting Information). DNM salt **8** crystallizes in the triclinic space group $P\bar{1}$ with four molecular moieties in the unit cell, a density of 1.453 g cm^{-3}, and a unit cell volume of $V = 889.6(4)$ Å^3. Delocalization of the negative charge on the entire DNM anion is evident from these bond lengths combined with the planarity: (a) the C8−N9 [1.3752(15) Å] and C8−N12 [1.3704(15) Å] bond lengths are much shorter than the average value for a normal C−N single bond but significantly longer than a C=N double bond; (b) a similar trend is observed for the N−O bond of the DNM anion in **8** [N9−O10, 1.2593(13) Å; N9−O11, 1.2516(13) Å; N12−O13, 1.2533(13) Å; N12−O14, (1.2624(13) Å], which are significantly longer than a normal N=O double bond but shorter than a N−O single bond; (c) the $-NO_2$ and −CH groups in the anion are almost coplanar, which is supported by the torsion angles [N9−C8−N12−O13, 4.13(18)°; N9−C8−N12−O14, −175.24(11)°; N12−C8−N9−O11, −4.34(18)°; N12−C8−N9−O10, 175.01(10)°; see Table S3 in the Supporting Information]. These delocalized features are in contrast to nitroformate structures and have some similarities with the tetranitroethanide dianion in some bond distances.[13] The 1,3-dimethylimidazolium cation also displays delocalization of the positive charge due to bond homogenization. The lengths of the N1−C2 [1.3314(15) Å], N1−C5 [1.3805(16) Å], C2−N3 [1.3289(16) Å], N3−C4 [1.3800(15) Å], and C4−C5 [1.3569(17) Å] bonds suggest that some multiple-bond character is present. The two methyl groups and the imidazolium ring are coplanar, which is confirmed by the torsion angles of C6−N1−C2−N3 [177.77(10)°], C6−N1−C5−C4 [−177.85(10)°], N1−C2−N3−C7 [179.51(10)°], and C7−N3−C4−C5 [−179.35(11)°] in Table S3 in the Supporting Information (reference bond lengths: C−N, 1.468 Å, C=N, 1.316 Å; C≡N, 1.137 Å; N=O, 1.219 Å; N−O, 1.394 Å).[14]

No hydrogen bonding is observed in the packing structure of **8** (Figure 1b). Each 1,3-dimethylimidazolium cation is surrounded by six DNM anions. Moreover, the anion and cation are not coplanar. The dimethylimidazolium cations are local in pair with C2 in the opposite view from the *a* axis. The DNM anions are located above or below the cations (Figure 1b).

Physicochemical Properties. The melting points, glass transition temperatures, decomposition temperatures, densities, and viscosities of DNM salts **1**−**8** are summarized

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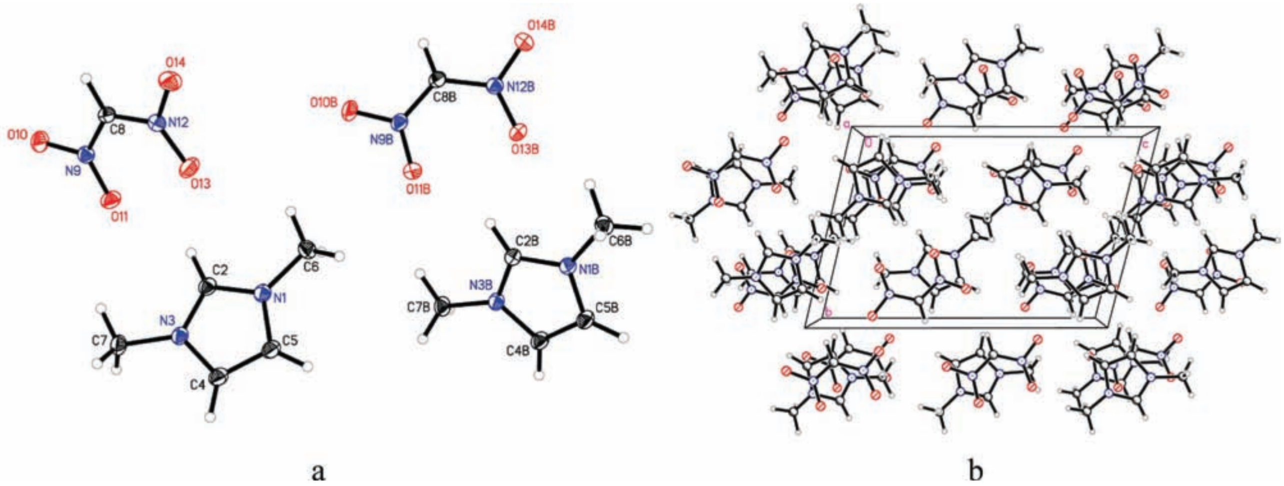

Figure 1. (a) Molecular structure of **8** (thermal ellipsoids shown at 30% probability). Hydrogen atoms are shown as open spheres of arbitrary radius and are unlabeled for clarity. (b) Packing diagram of **8** viewed down the *a* axis.

Table 1. Physicochemical Properties of DNM Salts **1**−**8** and Reference Compounds

compound	$T_g/T_m{}^a$ (°C)	$T_d{}^b$ (°C)	ρ^c (g cm^{-3})	η^d (cP)
1	−83	164	1.21	137
2	−73	162	1.30	90
3	−73	164	1.18	99
4	−79	166	1.23	75
5	−73	162	1.34	254
6	−62	154	1.38	160
7	−67	158	1.38	1441
8	/60	177	1.45	
9 ^{e}	/48	186		
KDNM ^{f}		220		
NH_4DNM ^{g}		110		

[a] Melting point/phase-transition temperature. [b] Thermal degradation. [c] Density, 25 °C. [d] Viscosity, 25 °C. [e] 1-Ethyl-3-methylimidazolium dinitromethanide.[7] [f] Potassium dinitromethanide.[4] [g] Ammonium dinitromethanide.[4]

in Table 1. DNM salts **1**−**8** are thermally stable in the range from 154 to 177 °C. The thermal stabilities of KDNM and NH_4DNM are very different.[4] Combined with the data of DNM salts **1**−**8**, the acidic hydrogen atoms in DNM salts were thought to play the predominant role in determining thermal decomposition temperatures. Free dinitromethane is very unstable[6a] and may be the intermediate of the decomposition of DNM salts. The stronger the acidic hydrogen atoms in the DNM salts, the easier the formation of free dinitromethane. KDNM is thermally stable to 220 °C[4] because there is no acidic hydrogen atom in the salt. NH_4DNM is very unstable thermally (T_d 110 °C)[4] because of its strongly acidic hydrogen atoms. The two hyrogen atoms of the 1,3-dialkylimidazolium ring were found to be weakly acidic.[12] As a result, DNM salts **1**−**8** are more thermally stable than the ammonium salt but less thermally stable than the potassium salt.

The glass transition temperatures (T_g) and melting points (T_m) of **1**−**8** were determined by differential scanning calorimetry (DSC) analysis. No melting point peaks were observed in the DSC curves of **1**−**7**. The T_g values of **1**−**7** are in the range from −80 to −60 °C, which is lower than their corresponding halide precursors.[12] The data are consistent with the phenomenon that these DNM salts are liquids at room temperature. Combined with their decomposition temperatures, the DNM ionic liquids **1**−**7** have a long liquidus range of more than 200 °C.

As confirmed in the crystal structure of **8**, no hydrogen bonding to the terminal oxygen atoms of the DNM anion was found (Figure 1b). Therefore, the liquid feature in relatively low temperature of DNM ionic liquids **1**−**7** was expected. Furthermore, the symmetry and rigidity of the cation can also affect the melting point. The introduction of the differently substituted functional groups in **1**−**3** and **5**−**7**, which give rise to the asymmetric imidazolium cations, significantly facilitates their liquidus characteristics. Although the two allyl substituents on the imidazolium cation are the same, **4** is an exception. Its low melting point is mainly attributed to the flexibility of the two allyl groups and can prevent the regular structure being formed in the salt. On the other hand, the dimethylimidazolium cation in **8** is both symmetric and rigid, resulting in a higher melting point at 60 °C. All of the DNM salts **1**−**8** are liquids, which melt lower than 100 °C and which places them all in the ionic liquid class.[12]

For room temperature ionic liquids, low viscosity is a very attractive key feature. The viscosity and melting point have positive correlations. Low-melting ionic liquids should have lower viscosity and better fluidity.[15] The viscosity of a solid could be thought of as being infinite. Thus, the viscosity of **8** was not determined because it is unsuitable as a good fluid at room temperature. At 25 °C, the viscosities of the DNM ionic liquids **1**−**6** range between 75 and 250 cP. Compound **7** is much more viscous and was found to be 1441 cP, which may be attributed to the rich hydrogen bonding originating from the hydroxyl group.

When the temperature was increased, a rapid decrease of the viscosities was found in many ionic liquids.[12] The temperature dependence of the viscosities for **1**−**7** is also observed (Figure 2). The graph of the log viscosity plotted versus the temperature indicates that the DNM ionic liquids do not display Arrhenius temperature behavior. The significant feature of glassy or supercooled liquids is

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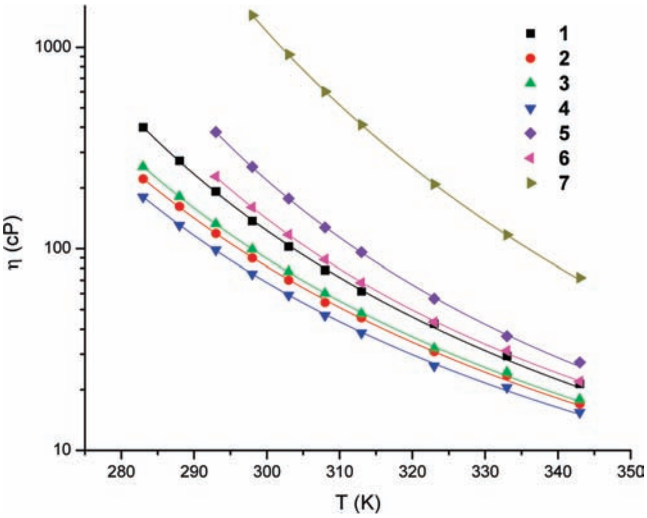

Figure 2. Temperature-dependent viscosities of **1**−**7**. VFT fit curves are also shown.

observed. A rapid increase in the viscosity and a slowing down of the structural relaxation are approached, upon nearing the glass transition temperature. This temperature dependence of the viscosity η for glass-forming liquids is well represented by the Vogel−Fulcher−Tammann (VFT) empirical equation (eq 1)[15,16]

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

where 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 2. The viscosity versus temperature graphs can be fit well to the VFT model ($R^2 > 0.9998$). The T_0 values of DNM ionic liquids **1**−**7** were calculated at 193, 183, 188, 189, 209, 209, and 190 K, i.e., −80, −90, −85, −84, −64, −64, and −83 °C, respectively. The T_0 data are in the same temperature range as the T_g data of **1**−**7**. From the VFT fit curves, the viscosities of these ionic liquids at low temperatures can be estimated. The estimated viscosities of **1**−**7** at 0 °C are 999, 454, 581, 378, 3788, 1557, and 34034 cP, respectively.

Heats of formation are one of the most essential features of the compounds. The gas-phase heats of formation for the separate ions were calculated by the mp2/6-311++G(d,p)//B3LYP/6-31g(d,p) using the *Gaussian 03* program.[17] The isodesmic reactions[18] are listed in Scheme 3. The enthalpy of the isodesmic reaction ($\Delta H_r°_{298}$) was derived from the mp2/6-311++G(d,p) energy difference for the reaction, the scaled zero-point energy (B3LYP/6-31+G**), and other thermal factors. On the basis of a Born−Haber energy cycle (Scheme 4), the heats of formation of ionic salts can then be corrected by the lattice energy of the salt. This can be simply expressed as follows:

$$\Delta H_{f°}(\text{ionic salts, 298 K}) = \sum \Delta H_{f°}(\text{cation, 298 K}) + \sum \Delta H_{f°}(\text{anion, 298 K}) - \Delta H_L \qquad (2)$$

For **1**−**8**, ΔH_L (kJ mol^{-1}) can be predicted by the formula suggested by Jenkins et al.[19]

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

where n_M 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 the lattice potential energy U_{POT} has the form

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

where ρ_m is the density (g cm^{-3}) and M_m is the chemical formula mass of the ionic material (g).[19]

The calculated heats of formation of DNM ionic liquids **1**−**8** are given in Table 2. The heats of formation of **2**−**4** are positive and higher than those of TNT (−67 kJ mol^{-1} and −0.29 kJ g^{-1}).[20] Compound **2** possesses the highest positive values of 64.3 kJ mol^{-1} and 0.28 kJ g^{-1}. The impact sensitivities of **1**−**8** were determined using a standard BAM Fallhammer method.[21] DNM ionic liquids **1**−**8** are stable at 40 J (10 kg hammer, 40 cm). They are impact-insensitive compounds.[22] The improved impact stability may come from the bulky organic cations.

The detonation pressure (P) and velocity (D) were calculated based on traditional Chapman−Jouget thermodynamic detonation theory using *Cheetah 5.0*.[23] Compound **8** has the highest detonation pressure of 15.07 GPa and a detonation velocity of 6873 m s^{-1}. Ionic liquids **1** and **10** have the same 1-butyl-3-methylimidazolium cation but different anions. The detonation pressure and velocity of **1** are higher than those of **10**.[15b] When the cation was 1-allyl-3-methylimidazolium (**2** and **11**), the same trend was also found. Therefore, compared with the nitrocyanamide anion-based ionic liquids, DNM ionic liquids have higher detonation pressures and detonation velocities.

As energetic ionic liquids, **1**−**6** were examined by reactions with white fuming nitric acid (WFNA). When the

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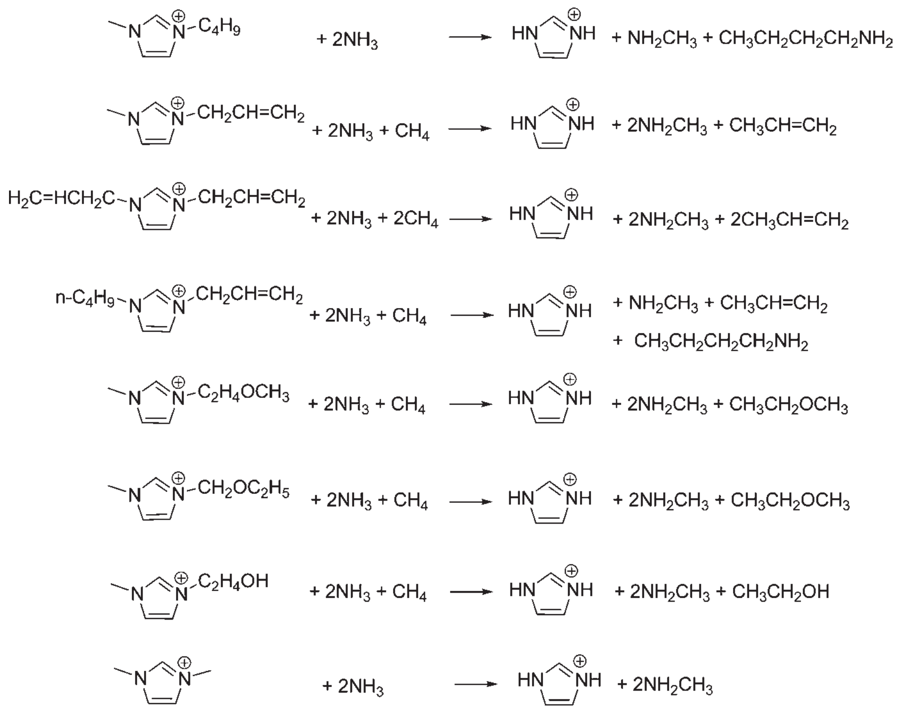
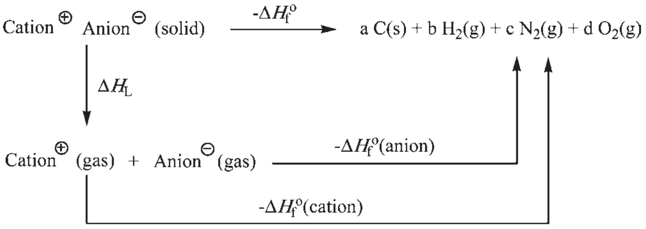
Scheme 3. Isodesmic Reactions of Cations



Scheme 4. Born−Haber Cycle for the Formation of Salts



where a, b, c, d are the number of moles of the respective products

Table 2. Heats of Formation, Detonation, and Impact Sensitivity Properties for **1**−**8** and Reference Compounds

salt	ΔH_f[a] (kJ mol^{-1})	ΔH_f[b] (kJ g^{-1})	P[c] (GPa)	D[d] (m s^{-1})	IS[e] (J)
1	−72.2	−0.30	10.20	6046	>40
2	64.3	0.28	12.01	6281	>40
3	12.2	0.04	9.18	5829	>40
4	7.0	0.03	9.24	5715	>40
5	−160.3	−0.65	13.12	6530	>40
6	−181.9	−0.74	13.94	6695	>40
7	−205.9	−0.89	13.83	6609	>40
8	−166.2	−1.01	15.07	6873	>40
10[f]	128.5	0.57	8.3	5672	>40
11[g]	274.7	1.31	7.6	5372	>40

[a] Molar enthalpy of formation of the ionic liquid. [b] Enthalpy of formation of the ionic liquid. [c] Detonation pressure. [d] Detonation velocity. [e] Impact sensitivity. [f] 1-Butyl-3-methylimidazolium nitrocyanamide.[14] [g] 1-Allyl-3-methylimidazolium nitrocyanamide.[14]

DNM ionic liquids were dropped into WFNA, no flame was observed. Therefore, because DNM ionic liquids cannot be ignited by WFNA as the oxidizer, they are not hypergolic with this oxidizer.

Conclusion

Room temperature liquid DNM salts were prepared for the first time. Eight DNM ionic liquids **1**−**8** combined with 1,3-dialkylimidazolium cations were synthesized by the metathesis reaction of the corresponding halides with KDNM or AgDNM in good yield. These ionic liquids were fully characterized, including the single-crystal X-ray structure determination of **8**. The DNM ionic liquids **1**−**7** are transparent yellow liquids at room temperature. They exhibit desirable long liquidus ranges of more than 200 °C. They have good liquid characteristics with low viscosities. The temperature dependence of the viscosities for **1**−**7** was also studied. These DNM ionic liquids do not display Arrhenius temperature behavior, a significant feature of glass-forming liquids. The energetic properties of DNM ionic liquids **1**−**8**, including heats of formation, detonation pressures, and detonation velocities, were obtained from theoretical calculations. DNM ionic liquids **1**−**8** are impact-insensitive. In summary, this work has demonstrated that the DNM species is a promising anion for the design and synthesis of interesting room temperature ionic liquid materials with desirable properties of low viscosity, long liquidus range, and low impact sensitivity.

Experimental Section

Caution! *Silver dinitromethanide described in this paper is a powerful and very impact-sensitive explosive that should be handled with the appropriate precautions. We have not experienced any problems in handling the DNM ionic liquids. Their friction sensitivities have not been determined. However, they should be handled on a small scale with extreme care using all of the standard safety precautions such as leather gloves, leather coat, face shields, and ear plugs.*

General Methods. 1-Butyl-3-methylimidazolium chloride, 1-allyl-3-methylimidazolium chloride, 1-allyl-3-buthylimidazolium chloride, 1,3-diallylimidazolium chloride, 1-(2′-methoxyl)-ethyl-3-methylimidazolium bromide, 1-(ethoxylmethyl)-3-methylimidazolium bromide, 1-(hydroxyethyl)-3-methylimidazolium chloride, and 1,3-dimethylimidazolium iodide were prepared by literature methods.[12] All other chemicals were obtained commercially as analytical-grade materials and 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 NMR spectrometer operating at 300 and 75 MHz, respectively, with dimethyl-d_6 sulfoxide as a locking solvent unless otherwise stated. ^1H and ^{13}C chemical shifts are reported in ppm relative to tetramethylsilane. Densities were measured at 25 °C on a Micromeritics Accupyc 1330 gas pycnometer. Differential scanning calorimetry (DSC) measurements were performed on a TA DSC Q10 calorimeter equipped with an Autocool accessory and were calibrated using indium. Measurements were carried out by heating from +40 °C (for solids) or −100 °C (for liquids) to 400 °C at 10 °C min^{-1}. Thermogravimetric analysis (TGA) measurements were accomplished on a TA TGA Q50 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) suite of programs.[17] The geometric optimization and frequency analyses were carried out using B3LYP functional analyses with the 6-311+G** basis set.[24] Single-point energies were calculated at the MP2/6-311++G** level.[25] 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 **8** were removed from the flask, a light-yellow crystal was selected and attached to a glass fiber, and data were collected on a Bruker three-circle platform diffractometer equipped with a SMART APEX II CCD detector. The crystals were irradiated using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Formula $C_6H_{10}N_4O_4$: fw 202.18 g mol^{-1}; size 0.42 × 0.28 × 0.25 mm^3; triclinic crystal system; $P\bar{1}$ space group; a = 7.1402(19) Å, b = 9.376(3) Å, c = 13.793(4) Å; α = 103.759(4)°, β = 90.757(4)°, γ = 96.874(4)°; V = 889.6(4) Å^3; Z = 4; ρ = 1.510 g cm^{-3} (−173 °C); ρ = 1.453 g cm^{-3} (20 °C); T = 100(2) K; μ = 0.128 mm^{-1}; $F(000)$ = 424; no. of reflns = 9248; R_{int} = 0.0147; no. of param = 257; S on F^2 = 1.064; R1 [$I > 2\sigma(I)$] = 0.0347; R1 = $\sum||F_o| - |F_c||)/\sum|F_o|$; wR2 [$I > 2\sigma(I)$] = 0.0894; wR2 = $[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; R1 (all data) = 0.0431; wR2 (all data) = 0.0944; $\Delta\rho_{\min}$ and $\Delta\rho_{\max}$ = 0.221 and −0.298 e Å^{-3}. An Oxford Cobra low-temperature device was used to keep the crystals at a constant 100(2) K during data collection. Data collection was performed, and the unit cell was initially refined using *APEX2* [v2009.3-0].[26] Data reduction was performed using *SAINT* [v7.60A],[27] and *XPREP* [v2008/2].[28] Corrections were applied for Lorentz, polarization, and absorption effects using *SADABS* [v2008/1].[29] The structure was solved and refined with the aid of programs in the *SHELXTL-plus* [v2008/4] system of programs.[30] 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 using a riding model. No decomposition was observed during data collection.

Potassium Dinitromethanide (KDNM). KDNM was prepared according to the procedure given in the literature.[5] Fuming nitric acid (0.24 mol, 10 mL) was added into the mixture of barbituric acid (12.8 g, 0.1 mol) dissolved in 95% sulfuric acid (60 mL), while the temperature was kept below 25 °C. The reaction mixture was then heated to 45 °C for 4 h. The resulting precipitate was filtered, washed with trifluoroacetic acid, and dried to yield 5,5-dinitrobarbituric acid (20.8 g, 0.092 mol, 92%). 5,5-Dinitrobarbituric acid (5.0 g, 0.022 mol) was added to water (10 mL) at 10 °C, and then 5 mL of a potassium hydroxide (1.3 g, 0.023 mol) solution was added. The mixture was stirred at 25 °C for 30 min. A yellow precipitate formed. The precipitate was collected, washed by cold water, and dried. The potassium salt of (2,2-dinitroacetyl)urea (yellow crystals, 3.2 g, 0.014 mol) was obtained in 63% yield. Potassium (2,2-dinitroacetyl)urea (10.0 g, 0.052 mol) was added to 100 mL of a KOH (12 g, 0.21 mol) solution. The resulting mixture was held at 80 °C for 2 h and then cooled to room temperature. Yellow crystals of KDNM were filtered, washed with 5−10 mL of cold water, and dried to give pure KDNM (6.2 g, 0.044 mol, 85%).

Silver Dinitromethanide (AgDNM). An aqueous solution of $AgNO_3$ (1.68 g, 5 mL) was added to 20 mL of a KDNM (1.44 g, 10 mmol) aqueous solution. The resulting precipitate was filtered, washed with water, and dried to yield AgDNM (1.87 g, 8.8 mmol, 88%).

1-Butyl-3-methylimidazolium Dinitromethanide (1). 1-Butyl-3-methylimidazolium chloride (0.52 g, 3.00 mmol) was dissolved in acetone (20 mL), and then KDNM (0.43 g, 3.00 mmol) was added. The resulting mixture was stirred for 24 h. The filtrate was collected and dried to yield **1** as a yellow liquid (0.65 g, 91%). ^1H NMR: δ 0.90 (t, 3H, J = 7.2 Hz, $CH_2CH_2CH_2CH_3$), 1.25 (m, 2H, $CH_2CH_2CH_2CH_3$), 1.76 (m, 2H, $CH_2CH_2CH_2CH_3$), 3.84 (s, 3H, CH_3), 4.16 (t, 2H, J = 7.2 Hz, $CH_2CH_2CH_2CH_3$), 7.69 (s, 1H), 7.76 (s, 1H), 8.14 (s, 1H, $CH(NO_2)_2$), 9.10 (s, 1H). ^{13}C NMR: δ 13.17, 18.74, 31.32, 35.68, 48.51, 122.06, 122.22, 123.57, 136.50. IR (film): $\nu_{\max}$ 3148, 3108, 2962, 2938, 2873, 1570, 1463, 1353, 1296, 1200, 1078, 998, 856, 776, 748, 623 cm^{-1}. Anal. Calcd for $C_9H_{16}N_4O_4$ (244.25): C, 44.26; H, 6.60; N, 22.94. Found: C, 43.91; H, 6.81; N, 22.12.

1-Allyl-3-methylimidazolium Dinitromethanide (2). The same procedure as that described for **1** was followed. 1-Allyl-3-methylimidazolium chloride (0.48 g, 3.00 mmol) and KDNM (0.43 g, 3.00 mmol) were reacted in acetone to obtain a yellow liquid **2**. Yield: 0.62 g (91%). ^1H NMR: δ 3.86 (s, 3H, CH_3), 4.83 (d, 2H, J = 6.0 Hz, CH_2CHCH_2), 5.33 (m, 2H, CH_2CHCH_2), 6.05 (m, 1H, CH_2CHCH_2), 7.70 (s, 1H), 7.72 (s, 1H), 8.14 (s, 1H, $CH(NO_2)_2$), 9.09 (s, 1H). ^{13}C NMR: δ 35.74, 50.76, 120.17, 122.10, 122.28, 123.74, 131.65, 136.67. IR (film): $\nu_{\max}$ 3148, 3107, 2992, 2859, 1643, 1570, 1456, 1358, 1298, 1202, 1079, 999, 947, 847, 774, 745, 624 cm^{-1}. Anal. Calcd for $C_8H_{12}N_4O_4$ (228.20): C, 42.10; H, 5.30; N, 24.55. Found: C, 42.09; H, 5.28; N, 23.91.

1-Allyl-3-butylimidazolium Dinitromethanide (3). The same procedure as that described for **1** was followed. 1-Allyl-3-butylimidazolium chloride (0.60 g, 3.00 mmol) and KDNM (0.43 g, 3.00 mmol) were reacted in acetone to obtain a yellow liquid **3**. Yield: 0.71 g (88%). ^1H NMR: δ 0.90 (t, 3H, J = 7.2 Hz, $CH_2CH_2CH_2CH_3$), 1.26 (m, 2H, $CH_2CH_2CH_2CH_3$), 1.78 (m, 2H, $CH_2CH_2CH_2CH_3$), 4.18 (t, 2H, J = 7.2 Hz, $CH_2CH_2CH_2CH_3$), 4.83 (d, 2H, CH_2CHCH_2), 5.32 (m, 2H, CH_2CHCH_2), 6.04 (m, 1H, CH_2CHCH_2), 7.73 (s, 1H), 7.82 (s, 1H), 8.14 (s, 1H, $CH(NO_2)_2$), 9.18 (s, 1H). ^{13}C NMR: δ 13.18, 18.73, 31.23, 48.63, 50.85, 120.14, 121.95, 122.50, 122.54, 131.65, 136.03. IR (film): $\nu_{\max}$ 3142, 3100, 2961, 1643, 1561, 1460, 1353, 1295, 1201, 1078, 998, 945, 851, 772, 745, 625 cm^{-1}. Anal. Calcd for $C_{11}H_{18}N_4O_4$ (270.28): C, 48.88; H, 6.71; N, 20.73. Found: C, 48.82; H, 6.90; N, 19.97.

1,3-Diallylimidazolium Dinitromethanide (4). The same procedure as that described for **1** was followed. 1,3-Diallylimidazolium chloride (0.55 g, 3.00 mmol) and KDNM (0.43 g, 3.00 mmol) were reacted in acetone to obtain a yellow liquid **4**. Yield: 0.66 g (87%). ^1H NMR: δ 4.85 (d, 4H, J = 4.8 Hz, CH_2CHCH_2), 5.33 (m, 4H, CH_2CHCH_2), 6.06 (m, 2H, CH_2CHCH_2),

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(28) *XPREP*, v2008/2. Bruker AXS Inc.: Madison, WI, 2008.

(29) *SADABS*, v2008/1; Bruker AXS Inc.: Madison, WI, 2008.

(30) *SHELXTL*, v2008/4; Bruker AXS Inc.: Madison, WI, 2008.

7.75 (s, 2H), 8.14 (s, 1H, $\mathrm{CH(NO_2)_2}$), 9.17 (s, 1H). ^{13}C NMR: δ 50.91, 120.25, 122.07, 122.63, 131.61, 136.16. IR (film): ν_{max} 3146, 3104, 2988, 1646, 1562, 1464, 1410, 1366, 1299, 1192, 1083,999, 946, 745, 627 cm^{-1}. Anal. Calcd for $C_{10}H_{14}N_4O_4$ (254.24): C, 47.24; H, 5.55; N, 22.04. Found: C, 47.03; H, 5.72; N, 22.41.

1-(2′-Methoxyl)ethyl-3-methylimidazolium Dinitromethanide (5). The same procedure as that described for **1** was followed. 1-(2′-Methoxyl)ethyl-3-methylimidazolium bromide (0.66 g, 3.00 mmol) and KDNM (0.43 g, 3.00 mmol) were reacted in acetone to obtain a yellow liquid **5**. Yield: 0.62 g (84%). ^{1}H NMR: δ 3.27 (s, 3H, $\mathrm{C}H_2\mathrm{C}H_2\mathrm{OCH_3}$), 3.68 (t, 2H, J = 7.2 Hz, $\mathrm{CH_2C}H_2\mathrm{OC}H_3$), 3.86 (s, 3H, $\mathrm{CH_3}$), 4.35 (t, 2H, J = 7.2 Hz, $\mathrm{C}H_2\mathrm{CH_2OC}H_3$), 7.69 (s, 1H), 7.72 (s, 1H), 8.14 (s, 1H, $\mathrm{CH(NO_2)_2}$), 9.08 (s, 1H). ^{13}C NMR: δ 35.69, 48.58, 58.00, 69.53, 122.04, 122.56, 123.39, 136.77 ppm. IR (film): ν_{max} 3149, 3105, 2944, 2900, 1643, 1568, 1456, 1360, 1298, 1198, 1117, 1079, 1003, 833, 745, 624 cm^{-1}. Anal. Calcd for $C_8H_{14}N_4O_5$ (246.22): C, 39.02; H, 5.73; N, 22.75. Found: C, 39.11; H, 5.77; N, 22.24.

1-(Ethoxylmethyl)-3-methylimidazolium Dinitromethanide (6). The same procedure as that described for **1** was followed. 1-(Ethoxylmethyl)-3-methylimidazolium chloride (0.53 g, 3.00 mmol) and KDNM (0.43 g, 3.00 mmol) were reacted in acetone to obtain a yellow liquid **6**. Yield: 0.60 g (86%). ^{1}H NMR: δ 1.13 (t, 3H, J = 7.2 Hz, $\mathrm{C}H_2\mathrm{OC}H_2\mathrm{CH_3}$), 3.54 (q, 2H, J = 7.2 Hz, $\mathrm{C}H_2\mathrm{OCH_2C}H_3$), 3.88 (s, 3H, $\mathrm{CH_3}$), 5.55 (s, 2H, $\mathrm{CH_2OC}H_2\mathrm{C}H_3$), 7.76 (s, 1H), 7.84 (s, 1H), 8.14 (s, 1H, $\mathrm{CH(NO_2)_2}$), 9.28 (s, 1H). ^{13}C NMR: δ 14.51, 35.90, 84.81, 77.94, 121.82, 122.17, 123.99, 137.10. IR (film): ν_{max} 3148, 3112, 2957, 2885, 1635, 1570, 1436, 1366, 1301, 1194, 1080, 999, 842, 781, 745, 624 cm^{-1}. Anal. Calcd for $C_8H_{14}N_4O_5$ (246.22): C, 39.02; H, 5.73; N, 22.75. Found: C, 39.05; H, 5.73; N, 22.71.

1-(Hydroxyethyl)-3-methylimidazolium Dinitromethanide (7). The same procedure as that described for **1** was followed. 1-Ethoxyl-3-methylimidazolium chloride (0.48 g, 3.00 mmol) and KDNM (0.43 g, 3.00 mmol) were reacted in acetone to obtain a yellow liquid **7**. Yield: 0.58 g (83%). ^{1}H NMR: δ 3.72 (t, 2H, J = 4.8 Hz, $\mathrm{CH_2C}H_2\mathrm{O}H$), 3.86 (s, 3H, $\mathrm{CH_3}$), 4.21 (t, 2H, J = 4.8 Hz, $\mathrm{C}H_2\mathrm{CH_2O}H$), 5.20 (s, 1H, $\mathrm{C}H_2\mathrm{C}H_2\mathrm{OH}$), 7.68 (s, 1H), 7.71 (s, 1H), 8.14 (s, 1H, $\mathrm{CH(NO_2)_2}$), 9.08 (s, 1H). ^{13}C NMR: δ 35.62, 51.60, 59.24, 122.08, 122.62, 123.30, 136.79. IR (film): ν_{max} 3149, 3114, 2959, 1636, 1570, 1464, 1410, 1366, 1298, 1194, 1080, 999, 781, 745, 691, 623 cm^{-1}. Anal. Calcd for $C_7H_{12}N_4O_5$ (232.19): C, 36.21; H, 5.21; N, 24.13. Found: C, 36.22; H, 5.58; N, 23.92.

1,3-Dimethylimidazolium Dinitromethanide (8). The similar procedure as that described for **1** was followed. 1,3-Dimethylimidazolium iodide (0.67 g, 3.00 mmol) and AgDNM (0.64 g, 3.00 mmol) were reacted in methanol to obtain a yellow solid **8**. Yield: 0.57 g (95%). Light-yellow needles were obtained after recrystallization from a methanol solution. ^{1}H NMR: δ 3.84 (s, 6H, $\mathrm{CH_3}$), 7.67 (d, 2H), 8.14 (s, 1H, $\mathrm{CH(NO_2)_2}$), 9.02 (s, 1H). ^{13}C NMR: δ 35.63, 122.10, 123.43, 137.09. IR (KBr): ν_{max} 3148, 3092, 1634, 1576, 1465, 1441, 1413, 1368, 1306, 1215, 1176, 1084, 1001, 783, 745, 691, 621 cm^{-1}. Anal. Calcd for $C_6H_{10}N_4O_4$ (202.17): C, 35.65; H, 4.99; N, 27.71. Found: C, 35.60; H, 5.23; N, 26.01.

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Supporting Information Available: X-ray crystallographic data in CIF format, crystal data and structure refinement, selected bond lengths and angles, and torsion angles. This material is available free of charge via the Internet at http://pubs.acs.org.