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Article

Inorganic or Organic Azide-Containing Hypergolic Ionic Liquids[⊥]

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Recently extensive research has focused on replacing toxic hydrazine, monomethylhydrazine, and unsymmetrical dimethylhydrazine as liquid propellant fuels. 2-Azido-*N*,*N*-dimethylethylamine (**1**) is a good candidate to replace hydrazine derivatives in certain hypergolic fuel applications. Energetic ionic liquids that contain the 2-azido-*N*,*N*,*N*-trimethylethylammonium cation with nitrocyanamide, dicyanamide, dinitramide, or azide anion have been successfully synthesized in good yields by metathesis reactions. Ionic liquids have received considerable attention as energetic materials. The replacement of hydrazine with tertiary ammonium salts is especially attractive since many ionic liquids are models for green chemistry. In this work, new azide-functionalized ionic liquids are demonstrated to exhibit hypergolic activity with such oxidizers as 100% nitric acid or nitrogen tetraoxide (NTO).

Introduction

Reports of the development and preparation of many interesting energy-rich compounds which contain organic azide groups[1] and inorganic azides[2] have appeared recently. The chemistry and properties of these energetic materials are discussed in detail. Polyazide compounds have limited use because they tend to be unstable and when decomposition occurs, nitrogen is released giving rise to high pressure and heat.[1a,3a] Previously diverse amine-containing organic azides, for example tris(2-azidoethyl)amine which had low impact sensitivity and were hypergolic, have been reported.[1i] Energetic liquid ionic azides such as urotropinium azide,[2j] methylated hydrazinium azides,[2k] and 1,5-diamino-4-methyl-tetrazolium azide,[2l] have been synthesized and characterized.[3b]

Ionic liquid azides, alkyl-substituted 1,2,4- and 1,2,3-aminotriazole derivatives, were prepared and examined for the first time to investigate their structural and physical properties.[4] Energetic ionic liquids based on the imidazolium cation azides have been reported, and also their physical, structural properties and their reactivity toward strong oxidizers [**I**nhibited **R**ed-**F**uming **N**itric **A**cid (IRFNA) and N_2O_4] were investigated.[5] Although these appear attractive, they did not result in hypergolic ignition under the oxidizing conditions employed.

The toxicological properties of the commonly used hydrazine and its derivatives such as monomethylhydrazine and unsymmetrical dimethyl hydrazine have been extensively studied and are the basis of severe limitations on personnel exposure to these compounds. These substances are highly toxic because of their volatility and carcinogenic properties.

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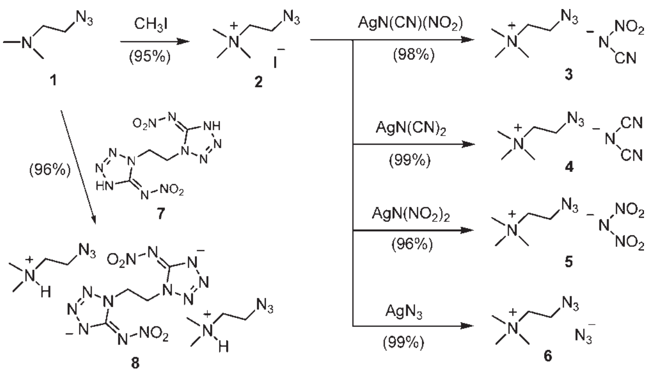
For these reasons, it is desirable to replace hydrazine derivatives with ionic liquids which have become species of green chemistry.[6] Many ionic liquids have unique chemical and physical properties, including high stability, good solvent characteristics, virtually no vapor pressure, and either nontoxic or of relatively low toxicity compared with volatile organic compounds that are traditionally used as "green" alternative solvents.[7] The design and synthesis of ionic liquids based on energetic materials provide a powerful methodology in the development of a new type of hypergolic fuel simply by the combination of different ions for a specific purpose. In addition, their properties are readily varied and tuned through the modification of the cationic and/or anionic components. There is significant interest in the development of new energetic ionic liquids for use as aerospace propellants and fuels for explosives.

In our earlier work, we successfully designed and synthesized hypergolic ionic liquids that contain the 2,2-dialkyltriazanium cation.[8] On the basis of our calculations, we find that the heat of formation is one of important characteristics for energetic salts which is directly related to the number of nitrogen−nitrogen bonds in the ionic species; thus we began to search for new ions with a greater concentration of nitrogen−nitrogen bonds.[9,10] The azido group is highly energetic adding approximately 280 kJ mol^{-1} to the energy content of a molecule. The linear azide anion (N_3^-) is the conjugate base of hydrazoic acid and is isoelectronic with CO_2 and N_2O. On the basis of valence bond theory, the azide anion can be described by several resonance structures, an important one being $N^-{=}N^+{=}N^-$. Our calculations show that the heat of formation of the azide anion in the gas phase is 197.2 kJ mol^{-1}, which is higher than that of the dicyanamide [$^-N(CN)_2$, 113.4 kJ mol^{-1}] and nitrocyanamide [$^-N(CN)(NO_2)$, −27.1 kJ mol^{-1}] anions which have been used in the design of hypergolic ionic liquids.[6,8] Therefore, it is not surprising that azide-containing compounds sometimes are highly endothermic, and that their energy content increases with an increasing number of azido ligands.

Scheme 1. Energetic Ionic Liquids **3**−**6** and Nitroiminotetrazolate Salt **8** Based on 2-azido-*N*,*N*-dimethylethylamine (**1**)



Results and Discussion

Synthesis. In our continuing efforts in this area, we have synthesized new energetic ionic liquids with azide-functionalized groups and studied their hypergolic properties (Scheme 1). 2-Azido-*N*,*N*-dimethylethylamine (DMAZ) (**1**)[11] is a reduced-hazard liquid fuel, which has been developed by the U.S. Army.[12] Many of the physical properties of DMAZ are closely comparable to those of monomethylhydrazine (MMH) fuel, but whereas MMH is highly toxic, the data available to date suggests that DMAZ is relatively less toxic.[13]

The preparation of **1** was accomplished by a literature method where 2-chloro-*N*,*N*-dimethylethylamine hydrochloride was reacted with sodium azide in water, followed by ether extraction to get good yield.[11] After metathesis of the ammonium iodide **2**, which was prepared by methylation of DMAZ with iodomethane, with a slight excess of the corresponding silver salts (silver nitrocyanamide,[14] silver dicyanamide,[15] silver dinitramide,[16] and silver azide), a series of energetic salts (**3**−**6**) were synthesized in excellent yields (96−99%). Compound **4** was reported while our research was underway.[17]

The reaction of DMAZ and ethylene bis(nitroiminotetrazole) (**7**) (I-8) was carried out in water. After evaporation of solvent and washing the residue, ethylene bis(nitroiminotetrazolate) **8** was obtained in pure form and in high yield (96%) (Scheme 1).

The already known bis(2-azidoethyl)dimethylammonium iodide (**9**) was synthesized from iodomethane and bis(azidoethyl)methylamine, which was obtained by

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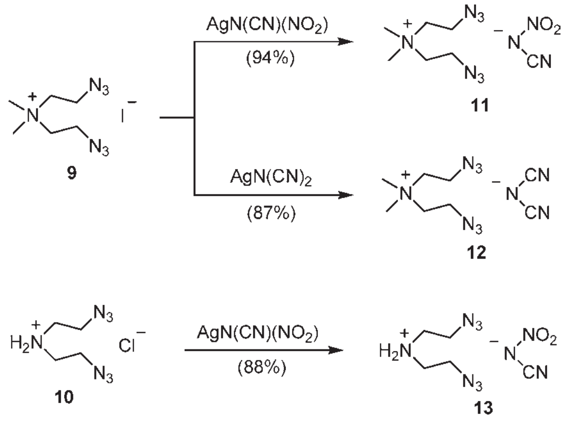
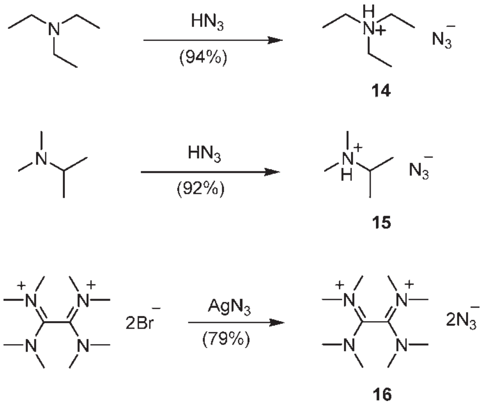
Scheme 2. Synthesis of Hypergolic Ionic Liquids Based on Bis(azidoethyl)ammonium Halide



Scheme 3. Azide Anion Containing Hypergolic Compounds



nucleophilic substitution from the dichloro compound and excess sodium azide (Scheme 2).[18] The different amide salts were readily prepared by exchange of the halide for the amide using silver nitrocyanamide or silver dicyanamide. Insoluble silver amide salts are used in excess assuring complete conversion and were separated together with the silver halide which precipitates during the metathesis procedure. For the preparation of **13**, an analogous route was employed.

All of the energetic salts with azide-containing anion were prepared by metathesis reactions with silver azide[19a] or by direct neutralization with hydrazoic acid (Scheme 3).[19b] Unfortunately these materials (**14** and **15**) are extremely hygroscopic.

^{15}N NMR. In Figure 1, in the ^{15}N NMR spectra of azide-containing ammonium salts **3**, **4**, **6**, and **16**, measured in CD_3CN, [D_6]DMSO, and D_2O solutions, chemical shifts are given with respect to CH_3NO_2 as external standard. The signals of the nitrogen-cation, -anion, and Nα appear at −362.4 and −256.9 in all compounds. The nitrogen signals of the nitrocyanamide anion are observed at relatively lower field at −169.9 (CN), −155.5 (N^-), and 6.3 (NO_2) ppm for compound **3** because of the strong electron withdrawing group NO_2, compared with the dicyanamide anion of compound **4** at −362.4 (N^-) and −207.8 (CN) ppm, respectively. The assignments are made based on the values of the chemical shifts reported for hypergolic ammonium salts in the literature.[4,8,20]

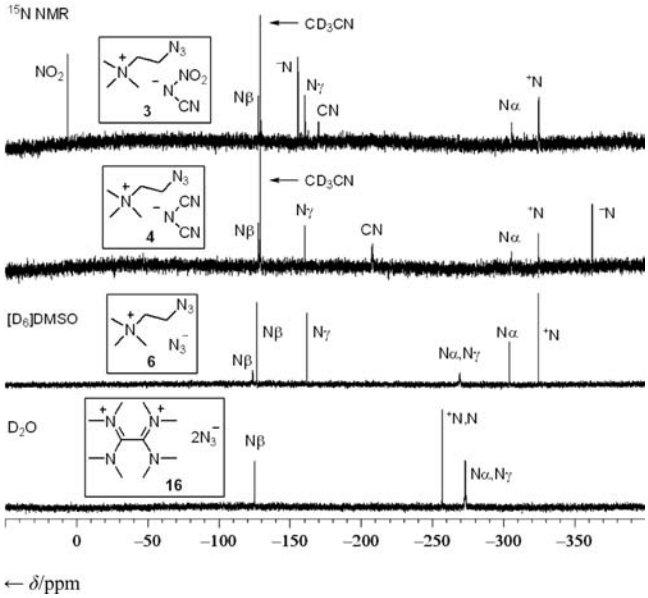


Figure 1. ^{15}N NMR spectra of azide-containing compounds **3**, **4**, **6**, and **16**.

X-ray Diffraction. Figure 2 shows the molecular units of **13** and **16** with the atom labeling and selected bond lengths and angles presented in the legend. Salt **13** crystallizes in the triclinic space group $P\bar{1}$ with two formula units per unit cell. Azide anion salt **16** crystallizes in the monoclinic space group $C2/c$ with four formula units per unit cell (Table 1). Analysis of the crystal packing of **13** shows the existence of two hydrogen bonds, N6−H6A···O17 = 2.9154(14) Å and N6−H6B···N12 = 2.9148(17) Å, respectively.

Properties. Hypergolic ignition delay (ID) for liquids consists of a complex interplay between heat and mass transfer physical factors as well as the kinetics for reactive species production and species identity chemical factors. Therefore, a study of IDs by a modern screening technique allows a better understanding about the mechanism of hypergolic ignition.[22] Our investigation to synthesize azide-containing tertiary amines is based on the following properties that are considered as important factors that influence ignition time: high basicity, high weight percent

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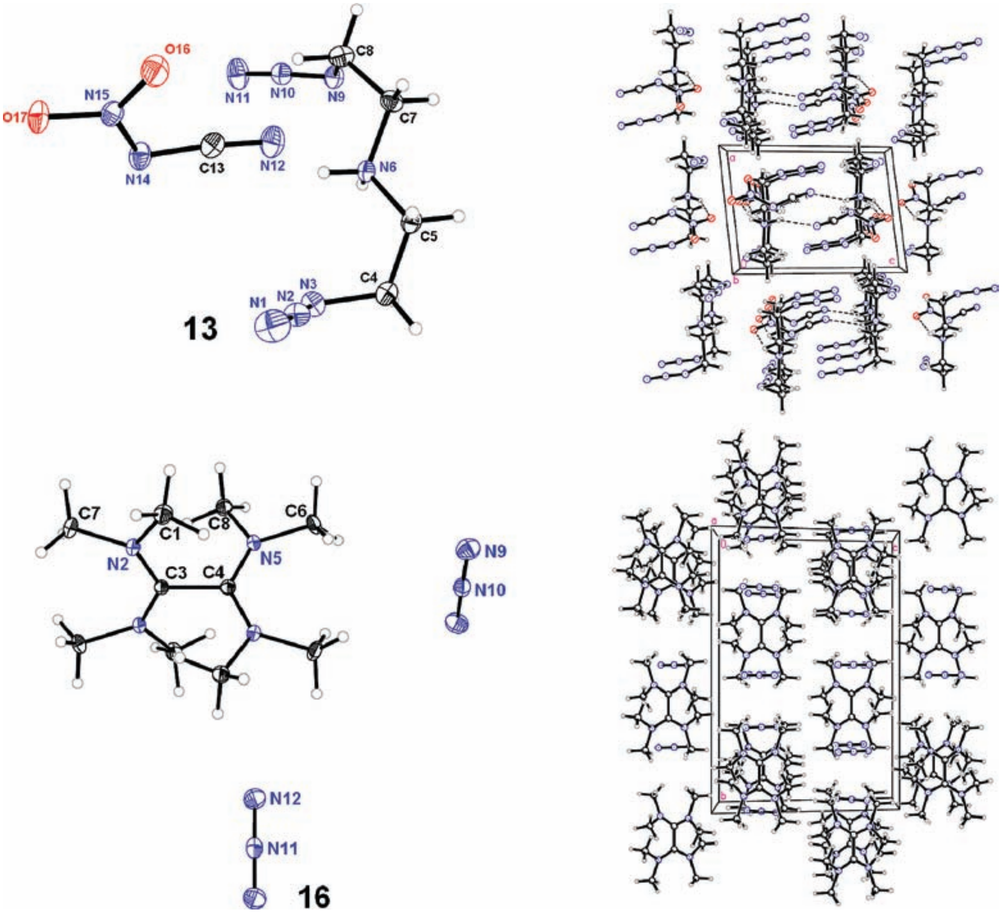

Figure 2. Molecular structures (thermal ellipsoids represent 50% probability) of **13** (top) and **16** (bottom). Selected bond lengths [Å] and angles [deg]: **13**: N1−N2 1.1328(15), N2−N3 1.2367(14), C5−N6 1.4924(14), N12−C13 1.1546(15), C13−N14 1.3385(14), N14−N15 1.3397(13), N1−N2−N3 172.41(12), N12−C13−N14 171.84(12), C13−N14−N15 112.42(9); **16**: C1−N2 1.4734(16), N2−C3 1.3179(12), N2−C7 1.4729(16), N9−N10 1.1835(12), N11−N12 1.1846(12), C1−N2−C3 121.39(11), C3−N2−C7 124.38(11).

Table 1. Crystallographic Data for **13** and **16**

	13	**16**
formula	$C_5H_{10}N_{10}O_2$	$C_{10}H_{24}N_{10}$
fw	242.20	284.39
space group	$P\overline{1}$	$C2/c$
a (Å)	7.296(3)	7.330(2)
b (Å)	7.970(3)	17.421(6)
c (Å)	10.126(4)	11.875(4)
α (deg)	103.976(4)	90
β (deg)	94.637(5)	102.780(5)
γ (deg)	97.667(5)	90
V (Å^3)	562.3(3)	1478.8(8)
Z	2	4
λ (Å)	0.71073	0.71073
T (K)	100(2)	100(2)
D_{calcd} (g cm^{-3})	1.430	1.277
μ (mm^{-1})	0.115	0.088
R_1 [$I > 2\sigma(I)$]^a	0.0301	0.0368
wR_2 [$I > 2\sigma(I)$]^b	0.0757	0.0922
CCDC #	750901	750900

^{a} $\mathrm{R}_1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $\mathrm{wR}_2 = \{\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2\}^{1/2}$.

of nitrogen, and low steric hindrance of substituent at N atoms.[22] The methods employ drop tests with high speed video detection of the ignition event to terminate a measurement period that is initiated upon reagent contact.[23] To observe and measure the actual ID, a drop test was selected. A small fuel sample (ca. 20 mg) was dropped into a beaker which contained an excess (1.5−2.0 mL) of a liquid oxidizer [N_2O_4 or WFNA (White Fuming Nitric Acid)]. A high-speed camera recording 500 frames s^{-1} was used to record the time duration from the moment the fuel contacted the liquid surface of the oxidizer until the first sign of the formation of a visible flame—the ID time (Table 2).

The results show that liquid salts **3**, **4**, **11**, and **12**, and solid salt **14** are hypergolic with WFNA (100% HNO_3), and **14**−**16** with nitrogen tetraoxide (NTO). ID measurements indicate that **3**, **4**, and **12** are hypergolic materials with short ID times (Table 2, Figure 3). Since hypergolic ionic liquid **3** exhibits the same ID (8 ms) as shown by monomethyl-hydrazine (8 ms),[24] it has promise as a hypergolic fuel. Compounds **4** and **12** when being reacted with WFNA show relatively long IDs (16 and 20 ms). ID times depend on many different factors and, especially for solid salts, it is extremely difficult to obtain reproducible values. Therefore, ID numbers are not given for solids. Although the ID times of salts **14** and **15** are not attractive, to the

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Table 2. Properties of Azide-Functionalized Salts

salts	density[a] [g cm^{-3}]	T_m[b] [°C]	T_d[b] [°C]	ID [ms][c]		ΔH_f[e] [kJ mol^{-1}, kJ g^{-1}]	I_{sp}[f] [s]
				N_2O_4	WFNA[d]		
3	1.24	28	245	NH[g]	8	380, 1.9	218
4	1.15	9	235	NH[g]	20	518, 2.4	202
5	1.36		219	NH[g]	NH[g]	251, 1.0	231
6	1.22	92	139	NH[g]	NH[g]	578, 3.4	227
8	1.41	127	182	NH[g]	NH[g]	1577, 3.1	241
11	1.32		222	NH[g]	226	752, 3.2	231
12	1.21		222	NH[g]	16	894, 3.8	221
13	1.41	58	162	NH[g]	NH[g]	777, 3.2	245
14	1.01	80	h	Hypergolic	explodes[i]	457, 3.2	245
15	0.99	75	h	Hypergolic	NH[g]	430, 3.3	249
16	1.24		188	NH[g]	NH[g]	418, 1.5	185

[a] Gas pycnometer (25 °C). [b] Thermal decomposition temperature under nitrogen gas (DSC, 10 °C min^{-1}). [c] High speed camera recording 500 frames s^{-1}. [d] WFNA = white fuming nitric acid. [e] Calculated via Gaussian 03. [f] I_{sp} is the specific impulse (seconds) calculated isobarically at 68 atm using Cheetah 5.0. [g] Not hypergolic. [h] Not obtained because of sublimation. [i] Using 100 mg.

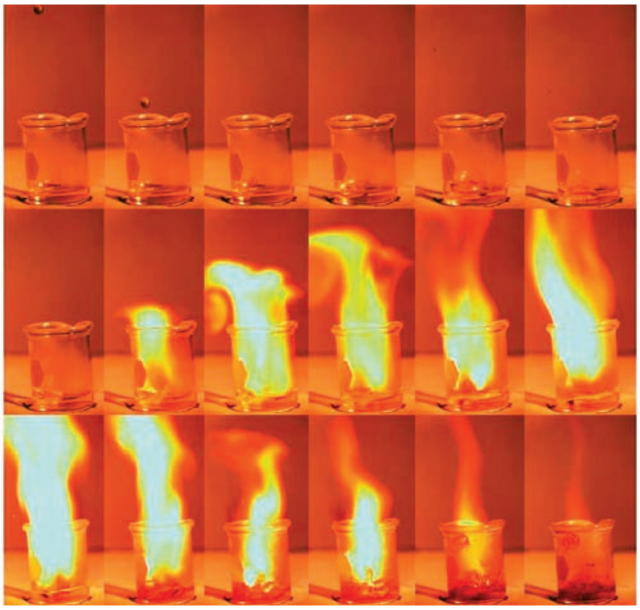
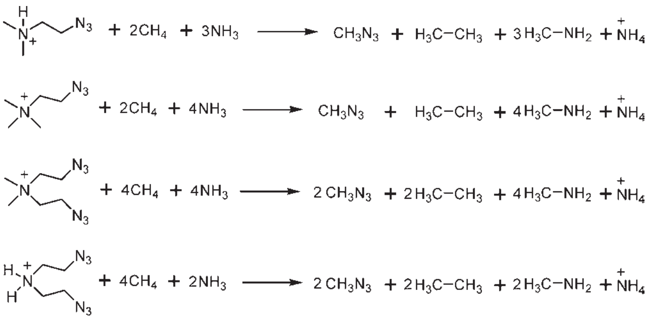


Figure 3. High speed camera photos showing a spatially resolved ignition event for a droplet of salt **12** (21 mg) falling into 100% HNO_3.

Scheme 4. Selected Isodesmic Reactions



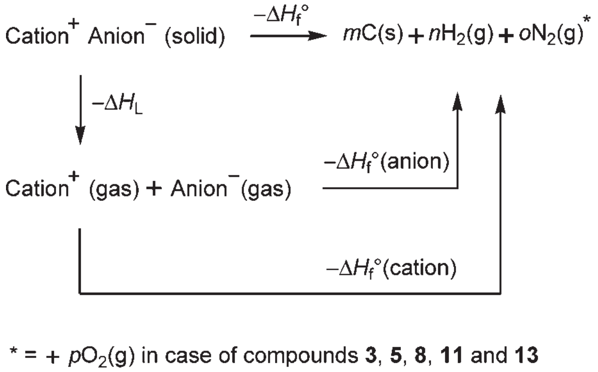


Figure 4. Born–Haber cycle for the formation of ammonium salts.

best of our knowledge, they are the first hypergolic salts with azide anion (Scheme 4).[5]

The geometric optimization of the structures and frequency analyses were carried out by using the B3LYP with the 6-31+G** basis set,[25] and single-point energies were calculated at the MP2/6-311++G** level. Atomization energies were calculated by the G2 method.[26] On the basis of Born–Haber energy cycles (Figure 4), the heats of formation of salts can be simplified by the formula:

$$\Delta H_f°(\text{ionic salt, 298 K}) = \Delta H_f°(\text{cation, 298 K}) + \Delta H_f°(\text{anion, 298 K}) - \Delta H_L \qquad (1)$$

where ΔH_L is the lattice energy of the ionic salt. The ΔH_L value could be predicted by the formula suggested by Jenkins et al. [eq 2],[10] where U_{POT} is the lattice potential energy, n_M and n_X depend on the nature of the ions M_p^+ and X_q^-, respectively, and are equal to three for monatomic ions, five for linear polyatomic ions, and six for nonlinear polyatomic ions.

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

The equation for the lattice potential energy, U_{POT}, takes the form of eq 3,

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

where ρ_m is the density (g cm^{-3}), M_m is the chemical formula mass of the ionic material (g), and the coefficients γ (kJ mol^{-1} cm) and δ (kJ mol^{-1}) are assigned literature values.[10a]

All of the azide-functionalized salts have positive heats of formation with **12** the highest (894 kJ mol^{-1}). With the calculated heats of formation and the experimental densities of salts, the specific impulse I_{sp} were calculated by

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

(26) Suleimenov, O. M.; Ha, T. K. *Chem. Phys. Lett.* **1998**, *290*, 451–457.

means of traditional Chapman−Jouget thermodynamic detonation theory using Cheetah 5.0.[27] Impact sensitivities of the all salts, tested with a BAM Fallhammer, (Table 2) fall into the insensitive region (> 40 J)[28] except for the nitroiminotetrazolate salt **8** which is identified as sensitive (20 J).

Conclusions

A novel approach for the rational design and synthesis of azide-functionalized ionic liquids has been developed. These azide-containing ions are attractive in the development of ionic liquid hypergols. A new pathway for transitioning these ionic liquids into bipropellant applications is provided. The relationship between their structures and melting points, thermal stabilities, densities, standard enthalpies of formation, and specific impulse was determined. The high heat of formation of the azide functional group can be used for fine-tuning the energy content, and thus the performance of the hypergolic ionic liquids. These new azide-functionalized ionic liquids may be good candidates as potential replacements for the highly toxic hydrazine and its derivatives.

Experimental Section

Caution! *While we have experienced no difficulties with shock and friction sensitivity of these salts, the use of appropriate safety precautions where manipulations must be carried out in a hood behind a safety shield and leather gloves must be worn, is essential for work with energetic materials, especially when working on more than millimole scale. Silver azide is a well-known energetic material for primary explosives and can explode violently under certain conditions. Therefore, good safety practices require using it where it is moistened with water. Very toxic hydrazoic acid* (HN_3) *should be handled carefully in the fume hood. Pure* HN_3 *is highly explosive, and, because of its boiling point of 35.7 °C, should be handled in solution.*

General Methods. All the reagents were analytical reagents purchased from commercial sources and used as received. Silver nitrocyanamide,[14] silver dicyanamide,[15] silver azide,[18] and hydrazoic acid[19b] were synthesized by literature methods. ^{1}H, ^{13}C, and ^{15}N NMR spectra were recorded on a 300 MHz nuclear magnetic resonance spectrometer operating at 300.13, 75.48, and 50.7 MHz, respectively. Chemical shifts are reported relative to Me_4Si. The melting and decomposition points were recorded on a differential scanning calorimeter (DSC) at a scan rate of 10 °C min^{-1}. Infrared spectra were recorded using KBr pellets. The densities of energetic salts were measured at room temperature using a Micromeritics Accupyc 1330 gas pycnometer. Elemental analyses were obtained on an Exeter CE-440 Elemental Analyzer.

Crystal Structure Analysis. Data collection was performed and the unit cell was initially refined using APEX2 [v2.1−0].[21a] Data Reduction was performed using SAINT [v7.34A][21b] and XPREP [v2005/2].[21c] Corrections were applied for Lorentz, polarization, and absorption effects using SADABS [v2004/1].[21d] The structure was solved and refined with the aid of the programs in the SHELXTL-plus [v6.12] system of programs.[21e]

To a solution of 5.00 g (43.9 mmol) of 2-azido-*N*,*N*-dimethylethylamine (**1**)[11] in 50 mL of dry acetonitrile was added an excess of 10.5 g (70.0 mmol) of iodomethane at 0 °C, and the resulting mixture was stirred for 24 h at ambient temperature. After removal of the solvent in vacuo, the white solid **2** (10.7 g, 41.6 mol, 95%) was obtained.

2-Azido-*N*,*N*,*N*-trimethylethylammonium Iodide (2). White crystal; mp 89 °C; IR (KBr) $\tilde{\nu}$ 3426, 3007, 2959, 2926, 2877, 2120, 2077, 1273, 1246; ^{1}H NMR ([D_6]DMSO) δ 3.95−3.99 (m, 2H), 3.56−3.60 (m, 2H), 3.15 (s, 9H); ^{13}C NMR ([D_6]DMSO) δ 63.3, 52.8, 44.2; ^{15}N NMR ([D_6]DMSO) δ −126.5 (N_β), −161.7 (N_γ), −304.1 (N_α), −323.8 (N^+); Anal. Calcd for $C_5H_{13}IN_4$: C, 23.45; H, 5.12; N, 21.88; found C, 23.44; H, 5.02; N, 21.93.

To an aqueous solution of 792 mg (3.00 mmol) 2-azido-*N*,*N*,*N*-trimethylethylammonium iodide (**2**) in 35 mL of H_2O was added 600 mg (3.09 mmol) of silver nitrocyanamide.[14] After stirring at ambient temperature for 6 h, silver salts were removed by filtration, and the solvent was removed under reduced pressure. A 632 mg portion (2.94 mmol, 98%) of colorless liquid **3** was obtained.

2-Azido-*N*,*N*,*N*-trimethylethylammonium Nitrocyanamide (3). Colorless liquid; mp 28, 245 °C (dec.); IR (KBr) $\tilde{\nu}$ 3481, 3039, 2967, 2176, 2115, 1632, 1479, 1433, 1274, 1156, 947; ^{1}H NMR (CD_3CN) δ 3.84−3.90 (m, 2H), 3.44−3.48 (m, 2H), 3.10 (s, 9H); ^{13}C NMR (CD_3CN) δ 118.0, 65.4, 54.6, 45.8; ^{15}N NMR (CD_3CN) δ 6.3 (NO_2), −127.6 (N_β), −155.5 (N^-), −160.4 (N_γ), −169.9 (CN),-305.6 (br. s, N^+), −324.6 (N_α); Anal. Calcd for $C_6H_{13}N_7O_2\cdot 1/2H_2O$: C, 32.14; H, 6.29; N, 43.73; found C, 32.00; H, 5.90; N, 44.21.

To an aqueous solution of 792 mg (3.00 mmol) of 2-azido-*N*,*N*,*N*-trimethylethyl-ammonium iodide (**2**) in 50 mL of H_2O was added 550 mg (3.16 mmol) of silver dicyanamide.[15] After stirring at ambient temperature for 6 h, silver salts were removed by filtration, and the solvent was removed under reduced pressure. A 610 mg portion (3.12 mmol, 99%) of colorless liquid **4** was obtained.

2-Azido-*N*,*N*,*N*-trimethylethylammonium Dicyanamide (4). Colorless liquid; m.p.: 9.3, 235 °C (dec.); IR (KBr) $\tilde{\nu}$ 3423, 2252, 2207, 2146, 1634, 1478, 1317 cm^{-1} ; ^{1}H NMR (CD_3CN) δ 3.84−3.89 (m, 2H), 3.44−3.47 (m, 2H), 3.09 (s, 9H); ^{13}C NMR (CD_3CN) δ 120.6, 65.3, 54.5, 45.7; ^{15}N NMR (CD_3CN) δ −127.5 (N_β), −160.4 (N_γ), −207.8 (br. s, CN), −305.5 (br. s, N^+),-324.6 (N_α), −362.4 (N^-); Anal. Calcd for $C_7H_{13}N_7\cdot 1/2H_2O$: C, 41.17; H, 6.91; N, 48.01; found C, 41.24; H, 6.73; N, 48.42.

To an aqueous solution of 1.83 g (6.92 mmol) of 2-azido-*N*,*N*,*N*-trimethylethylammonium iodide (**2**) in 50 mL of H_2O was added 1.48 g (6.92 mmol) of silver dinitramide.[16] After stirring at ambient temperature for 6 h, silver salts were removed by filtration, and water was evaporated under reduced pressure. A 1.56 g portion (6.64 mmol, 96%) of colorless liquid **5** was obtained.

2-Azido-*N*,*N*,*N*-trimethylethylammonium Dinitramide (5). Brown liquid; 219 °C (dec.); IR (KBr) $\tilde{\nu}$ 3439, 3040, 2116, 1633, 1522, 1479, 1434, 1185, 1016, 945, 760; ^{1}H NMR (CD_3CN) δ 3.85−3.90 (m, 2H), 3.46−3.50 (m, 2H), 3.11 (s, 9H); ^{13}C NMR (CD_3CN) δ 65.4, 54.6, 45.8; ^{15}N NMR (CD_3CN) δ −1.3 (NO_2), −46.9 (N^-), −127.6 (N_β), −160.4 (N_γ), −305.5 (br. s, N^+), −324.6 (N_α); Anal. Calcd for $C_5H_{13}N_7O_4\cdot 1/2H_2O$: C, 24.59; H, 5.78; N, 40.15; found C, 24.76; H, 5.49; N, 39.09.

To an aqueous solution of 2.64 g (10.0 mmol) of 2-azido-*N*,*N*,*N*-trimethylethylammonium iodide (**2**) in 50 mL of H_2O was added 2.50 g (16.7 mmol) of silver azide.[19a] After stirring at ambient temperature for 6 h, silver salts were removed by filtration, and the solvent was evaporated under reduced pressure. A 1.65 g portion (9.64 mmol, 96%) of very hygroscopic white solid **6** was obtained.

2-Azido-*N*,*N*,*N*-trimethylethylammonium Azide (6). White solid; m.p.: 92, 139 °C (dec.); IR (KBr): $\tilde{\nu}$ 3428, 3010, 2928, 2137, 2106, 2035, 1485, 1379, 1359, 1289, 1260, 947; ^{1}H NMR (D_2O): $\delta = 4.05$ (br. s, 2H), 3.66−3.69 (s, 2H), 3.29 (s, 9H); ^{13}C NMR (D_2O): $\delta = 64.4$ (t, $^{1}J_{N,C} = 3.2$ Hz), 53.7 (t, $^{1}J_{N,C} = 3.9$ Hz),

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[27] Bastea, S.; Fried, L. E.; Glaesemann, K. R.; Howard, W. M.; Souers, P. C.; Vitello, P. A. *CHEETAH 5.0 User's Manual*; Lawrence Livermore National Laboratory: Livermore, CA, 2007.

[28] (a) www.bam.de. (b) A portion of 20 mg of energetic compounds was subjected to a drop-hammer test using a 5 or 10 kg weight dropped. A range in impact sensitivities according to the U.N. Recommendations (Insensitive > 40 J; less sensitive ≥35 J; sensitive ≥4 J; very sensitive ≤3 J).

44.8; ^{15}N NMR (CD_3CN): $\delta = -123.7$ (N_β), -126.6 (N_β), -161.7 (N_γ), -269.2 (N_α, N_γ), -304.1 (N_α), -324.5 (N^+); Anal. Calcd for $C_5H_{13}N_7 \cdot 1/4H_2O$: C, 34.18; H, 7.74; N, 55.80; C, 34.29; H, 7.71; N, 56.35.

To an aqueous solution of 600 mg (5.26 mmol) of 2-azido-*N*,*N*-dimethylethylamine (**1**)[11] in 40 mL of H_2O was added 633 mg (2.21 mmol) of ethylene bis(5-nitroiminotetrazole).[29] After stirring at ambient temperature for 1 h, the solvent was evaporated under reduced pressure, and the remaining white solid was washed with ether. A 1.12 g portion (2.18 mmol, 99%) of white solid **8** was obtained.

2-Azido-*N*,*N*-dimethylethylammonium Ethylene Bis(5-nitroiminotetrazolate) (8). White solid; mp 127, 182 °C (dec.); IR (KBr): $\tilde{\nu}$ 3426, 2979, 2712, 2639, 2492, 2116, 1512, 1452, 1386, 1324, 1283, 1229, 1096, 1030, 926; ^{1}H NMR ([D_6]DMSO) δ 9.67 (br. s, 2H, NH), 4.47 (s, 4H), 3.79−3.83 (m, 4H), 3.27−3.31 (m, 4H), 2.83 (s, 12H); ^{13}C NMR ([D_6]DMSO) δ 156.9, 55.1, 45.3, 44.0, 42.7; ^{15}N NMR ([D_6]DMSO) δ 12.9, -6.7, -14.0, -67.8, -126.7 (N_β), -150.0, -159.5, -162.5 (N_γ), -305.3 (N_α), -336.3 (N^+); Anal. Calcd for $C_{12}H_{26}N_{20}O_4$: C, 28.02; H, 5.09; N, 54.45; found C, 27.55; H, 4.97; N, 54.04.

To an aqueous solution of 3.40 g (10.9 mmol) of bis(2-azidoethyl)dimethylammonium iodide (**9**)[18] in 50 mL of H_2O was added 2.20 g (11.3 mmol) of silver nitrocyanamide.[14] After stirring at ambient temperature for 6 h, silver salts were removed by filtration, and the solvent was evaporated under reduced pressure. A 2.76 g portion (10.2 mmol, 94%) of colorless liquid **11** was obtained.

Bis(2-azidoethyl)dimethylammonium Nitrocyanamide (11). Colorless liquid; 222 °C (dec.); IR (KBr) $\tilde{\nu}$ 3434, 3040, 2177, 2112, 1633, 1433, 1274; ^{1}H NMR ([D_6]DMSO) δ 3.92 (t, $^3J_{\mathrm{H,H}}$ = 5.6 Hz, 4H), 3.58 (t, $^3J_{\mathrm{H,H}}$ = 5.8 Hz, 4H), 3.13 (s, 6H); ^{13}C NMR ([D_6]DMSO) δ 117.0, 62.5, 51.4, 44.3; ^{15}N NMR ([D_6]DMSO) δ 5.2 (NO_2), -127.2 (N_β), -154.5 ($^-$N), -161.0 (N_γ), -169.0 (CN), -304.5 (N_α), -318.9 (N^+); Anal. Calcd for $C_7H_{14}N_{10} \cdot 1/2H_2O$: C, 30.11; H, 5.41; N, 50.16; found C, 30.33; H, 5.23; N, 48.94.

To an aqueous solution of 3.00 g (9.65 mmol) of bis(2-azidoethyl)dimethylammonium iodide (**9**)[18] in 50 mL of H_2O was added 1.90 g (10.9 mmol) of silver dicyanamide.[15] After stirring at ambient temperature for 6 h, silver salts were removed by filtration, and the solvent was evaporated under reduced pressure. A 2.10 g portion (8.39 mmol, 87%) of colorless liquid **12** was obtained.

Bis(2-azidoethyl)dimethylammonium Dicyanamide (12). Colorless liquid; 222 °C (dec.); IR (KBr) $\tilde{\nu}$ 3433, 3429, 3045, 2247, 2203, 2145, 1633, 1479, 1302; ^{1}H NMR ([D_6]DMSO) δ 3.87 (t, $^3J_{\mathrm{H,H}}$ = 5.5 Hz, 4H), 3.49 (t, $^3J_{\mathrm{H,H}}$ = 5.8 Hz, 4H), 3.10 (s, 6H); ^{13}C NMR ([D_6]DMSO) δ 120.8, 64.2, 53.0 (t, $^1J_{\mathrm{N,C}}$ = 3.6 Hz), 45.6; ^{15}N NMR ([D_6]DMSO) δ -127.0 (N_β), -161.1 (N_γ), -204.9 (CN), -304.4 (N_α), -318.9 (N^+), -360.6 ($^-$N); Anal. Calcd for $C_8H_{14}N_{10} \cdot 1/4H_2O$: C, 37.72; H, 5.74; N, 54.98; found C, 38.18; H, 5.85; N, 53.65.

To an aqueous solution of 1.00 g (5.22 mmol) of bis(2-azidoethyl)ammonium chloride (**10**)[18] in 30 mL of H_2O was added 1.12 g (6.19 mmol) of silver nitrocyanamide.[14] After stirring at ambient temperature for 6 h, silver salts were removed by filtration, and the solvent was evaporated under reduced pressure. A 1.11 g portion (4.59 mmol, 88%) of colorless liquid **13** was obtained.

Bis(2-azidoethyl)ammonium Nitrocyanamide (13). Colorless crystal; mp 58, 162 °C (dec.); IR (KBr) $\tilde{\nu}$ 3414, 3113, 2855, 2189, 2110, 1423, 1279, 1221, 1164, 861, 760; ^{1}H NMR ([D_6]DMSO) δ 8.65 (br. s, 2H), 3.68−3.72 (m, 4H), 3.12−3.16 (m, 4H); ^{13}C NMR ([D_6]DMSO) δ 116.7, 46.8, 45.9; ^{15}N NMR ([D_6]DMSO) δ 5.3 (NO_2), -126.4 (N_β), -153.9 ($^-$N), -162.8 (N_γ), -169.2 (CN), -305.2 (N_α), -333.9 (N^+); Anal. Calcd for $C_5H_{10}N_{10}O_2$: C, 24.80; H, 4.16; N, 57.83; found C, 24.23; H, 4.15; N, 56.67. The structure of **13** is supported by single crystal X-ray analysis.

To a solution of 2.00 g (19.8 mmol) of triethylamine and 30 mL of ether was added a solution of ether and excess hydrazoic acid.[19b] After stirring at 0−10 °C for 6 h, the precipitated white solid was filtered and washed with ether. An extremely hygroscopic product **14** (2.68 g, 18.6 mmol, 94%) was dried under reduced pressure.

Triethylammonium azide (14). Extremely hygroscopic white solid; mp 80 °C; IR (KBr) $\tilde{\nu}$ 3443, 3357, 3286, 3193, 2972, 2937, 2878, 2739, 2679, 2601, 2570, 2528, 2492, 2354, 2049, 1509, 1474, 1433, 1397, 1363, 1331, 1170, 1074, 1036, 849, 804, 758, 642, 456; ^{1}H NMR ([D_6]DMSO) δ 8.52 (br. s, 1H), 3.02 (q, $^3J_{\mathrm{H,H}}$ = 7.3 Hz, 6H), 1.16 (t, $^3J_{\mathrm{H,H}}$ = 7.3 Hz, 9H); ^{13}C NMR ([D_6]DMSO) δ 45.5, 8.6; ^{15}N NMR ([D_6]DMSO) δ -124.9 (N_β), -267.5 (N_α and N_γ), -316.0 ($^+$N); Anal. Calcd for $C_6H_{16}N_4 \cdot H_2O$: C, 44.42; H, 11.18; N, 34.53; found C, 44.20; H, 10.70; N, 33.98.

To a solution of 2.00 g (22.9 mmol) *N*,*N*-dimethylisopropylamine and 30 mL of ether was added a solution of ether and excess hydrazoic acid.[19b] After stirring at 0−10 °C for 6 h, the precipitated white solid was filtered and washed with ether. The extremely hygroscopic product **15** (2.74 g, 21.1 mmol, 92%) was dried under reduced pressure.

***N*,*N*-Dimethylisopropylammonium Azide (15).** Extremely hygroscopic white solid; mp 75 °C; IR (KBr) $\tilde{\nu}$ 3393, 3356, 3285, 2936, 2887, 2776, 2685, 2553, 2478, 2021, 1476, 1439, 1386, 1344, 1223, 1190, 1061,1075, 1014, 940, 882, 765, 642, 445; ^{1}H NMR ([D_6]DMSO) δ 8.33 (br. s, 1H), 3.34 (sept, $^3J_{\mathrm{H,H}}$ = 6.6 Hz, 1H), 2.61 (s, 6H), 1.18 (d, $^3J_{\mathrm{H,H}}$ = 6.7 Hz, 6H); ^{13}C NMR ([D_6]DMSO) δ 56.8, 38.2, 16.2; ^{15}N NMR ([D_6]DMSO) δ -124.8 (N_β), -268.5 (N_α and N_γ), -326.0 ($^+$N); Anal. Calcd for $C_5H_{14}N_4 \cdot H_2O$: C, 40.52; H, 10.88; N, 37.80; found: C, 40.41; H, 10.40; N, 36.90.

To an aqueous solution of 3.00 g (8.33 mmol) of 1,2-bis(dimethylamino)-*N*′,*N*′,*N*″,*N*″-tetramethyl-1,2-ethyldiaminium bromide[30] was added 25% more 1.50 g (10.0 mmol) of silver azide.[19a] After stirring at ambient temperature for 6 h, silver salts were removed by filtration, and the solvent was evaporated under reduced pressure. Yellow crystal **16** (1.87 g, 6.58 mmol, 79%) was obtained.

1,2-Bis(dimethylamino)-*N*′,*N*′,*N*″,*N*″-tetramethyl-1,2-ethyldiaminium Azide (16). Light yellow crystal; mp 188 (dec.); IR (KBr) $\tilde{\nu}$ 3398, 3356, 3292, 3217, 3018, 2549, 2004, 1664, 1518, 1473, 1399, 1264, 1209, 1147, 1111, 1062, 870, 721, 653, 468; ^{1}H NMR (D_2O) δ 3.73 (s, 12H), 3.44 (s, 12H); ^{13}C NMR (D_2O) δ 156.8, 43.1, 41.1; ^{15}N NMR (D_2O) δ -125.0 (N_β), -256.9 (N_α and N_γ), -273.1 ($^+$N); Anal. Calcd for $C_{10}H_{24}N_{10}$: C, 42.24; H, 8.51; N, 49.26; found C, 41.90; H, 8.53; N, 49.38.

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Supporting Information Available: X-ray crystallographic files in CIF format for **13** and **16**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(29) (a) Joo, Y.-H.; Shreeve, J. M. *Angew. Chem., Int. Ed.* **2009**, *48*, 564–567. (b) Joo, Y.-H.; Shreeve, J. M. *Chem.—Eur. J.* **2009**, *15*, 3198–3203.

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