Hypergolic Ionic Liquids

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Hypergolic Ionic Liquids with the 2,2-Dialkyltriazanium Cation**

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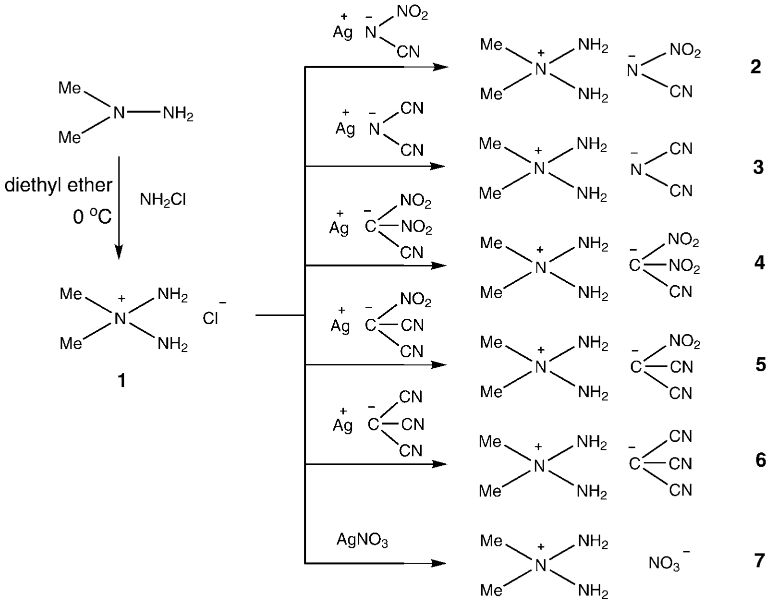
A hypergolic mixture is composed of stable species that readily react on molecular contact and can self-sustain reaction at ambient temperatures.[1] Hypergolic bipropellants are fuel–oxidizer combinations that ignite spontaneously upon mixing at low temperatures and pressures. They facilitate the design of rocket propulsion systems for applications in which variable and/or intermittent thrust capabilities are needed.[2] Among the most commonly fielded bipropellant combinations are hydrazine derivatives/nitrogen tetroxide (N_2O_4) or white fuming nitric acid (WFNA; 100% HNO_3). Hydrazine derivatives are widely used as a component of rocket fuel and are highly toxic owing to their volatility and carcinogenic vapor toxins. For these reasons, it is exceedingly attractive to replace hydrazine with energetic ionic liquids. Ionic liquids are a group of organic salts which are regarded as paragons of environmental friendliness, green chemistry, and low vapor toxicity.[3,4] They have unique chemical and physical properties, including being air and moisture stable, good solvents, have virtually no vapor pressure, and because some ionic liquids are either non-toxic or of relatively low toxicity compared with volatile organic compounds that are traditionally used as "green" alternative solvents. Another advantage is that 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, the properties of ionic liquids 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.[5] Considerable effort has been made in the design and synthesis of high energy-density materials (HEDM) with higher performance and/or enhanced insensitivity to thermal shock, friction, and electrostatic discharge. Based on our calculations,[6] we find that the heat of formation is one of the important characteristics for energetic salts which is directly related to the number of nitrogen–nitrogen bonds in the ionic species. Based on this information, we began to search for new ions with a greater concentration of nitrogen–nitrogen bonds. We synthesized new energetic salts with 2,2-dimethyltriazanium cations (Scheme 1). The 2,2-dimethyltriazanium salts formed by chloramination reactions are the first known stable alkyl compounds which contain a chain of more than two contiguous nitrogen atoms bonded by single bonds.[7] A few salts (halide, nitrate, perchlorate, methanesulfonate) of 2,2-dimethyltriazanium (DMA) have been reported,[7a–c,8] but otherwise this cation with a rather high positive heat of formation (1197 kJ mol^{-1} in gas phase, see below) has been neglected. These compounds are stable in air and in neutral aqueous solutions, and can be recrystallized from boiling solvents, such as acetone, ethanol, and acetonitrile.[9] To take advantage of the energy resulting from two nitrogen–nitrogen bonds, we have synthesized DMA salts with a variety of energetic anions. Their thermal, physical, and energetic properties were



Scheme 1. Synthesis of 2,2-dimethyltriazanium salts.

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studied in detail. We found that some of those energetic salts are potentially hypergolic materials including the chloride salt!

2,2-Dimethyltriazanium chloride (**1**) was prepared and purified by procedures described in the literature.[7b] A chloroamine–diethyl ether solution were prepared by a facile method which avoids the necessity of handling gaseous ammonia and chlorine.[10] After metathesis of **1** with corresponding silver salts, a series of energetic salts (**2**–**7**) were synthesized with good yields (See Supporting Information).

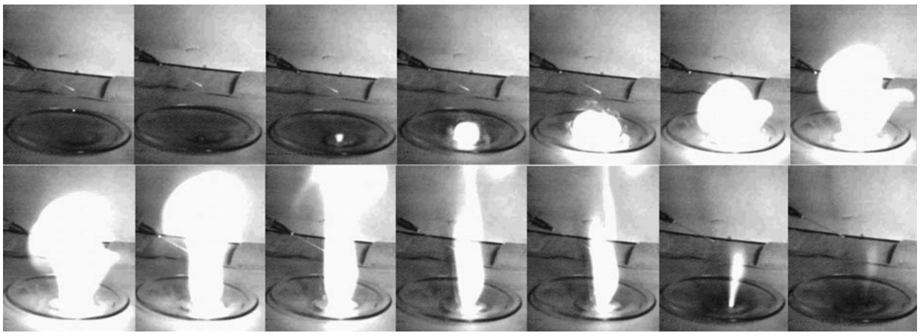

Figure 1. High-speed-camera photos showing a spatially resolved ignition event for a droplet of salt **2** falling into nitrogen tetroxide (the light spot below the needle in the first picture is the droplet of salt **2**).

Since the cation is a derivative of DMH, the structure suggests that its derivatives may have hypergolic properties. Successful ignition of the chloride salt, **1**, with N_2O_4 encouraged us to continue designing salts with hypergolic properties. Hypergolic ignition delay 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). 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.[11]

To observe and measure the actual ignition delay (ID), a droplets test was selected because it is flexible, accurate, simply constructed, and very useful for screening materials and assessing their potential for hypergolic activity.[3] A small fuel sample (10–50 μL) was dropped onto a watch glass containing an excess amount (1.0 mL) of a oxidizer (N_2O_4 or WFNA). 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 when a visible flame is formed—the ignition delay (ID) time (Table 1).

Shown in Figure 1 is a sequence of photos of a falling droplet of salt **2** into a pool of liquid N_2O_4. This sequence demonstrates that after ignition, the hypergolic compounds undergo self-sustained combustion. The results show that salts **1**, **2**, **3**, and **7** are hypergolic with N_2O_4 or WFNA. Chemical-delay measurements show that **2** and **7** are good hypergolic materials with shorter ignition delay (Table 1). In fact, **7** with WFNA exceeds (that is, is shorter than) the ignition delay target of 5 ms.

All of the 2,2-dimethyltriazanium salts were characterized by the usual spectroscopic methods and salts **4** and **7** were characterized by single-crystal X-ray diffraction analyses.[12] Like many of these types of materials, attempts at reducing crystal size or mounting them in a traditional manner leads to loss of crystallinity. Very thin long plates were mounted from the mother liquor directly onto a glass fiber (MiTeGen mounts deform slightly when cooled and this also led to crystallinity loss) and data were collected on a Bruker/Siemens SMART APEX system using $Mo_{K\alpha}$ (0.71073 Å) radiation. The molecular structures of both **4** and **7** are shown in Figure 2. Hydrogen atoms in both structures were located and refined to help identify atom types and define any hydrogen bonding networks.

In **4** there are two sets of crystallographically independent ion pairs and only one in **7**. Each cation has one long N−N bond (N1−N2 1.4561(19) and N15−N17 1.4605(18) Å in **4**; N1−N2 1.4607(12) Å in **7**) and one "shorter" N−N bond (N1−N3 1.4373(19), N15−N16 1.4375(18) in **4** and N1−N3

Table 1: Properties of energetic 2,2-dimethyltriazanium salts.

Salts	d[a]	T_m[b]	T_d[c]	Ignition delay[d] N_2O_4	Ignition delay[d] WFNA	Lattice energy[e]	ΔH_f[e] cation	ΔH_f[e] anion	ΔH_f[e]	P[f]	vD[g]	IS[h]
1	1.47		–	26	nh[i]	576.7	1196.7	−230.3	390	26.8	8474	> 60
2	1.26	−0.19	145.7	8	16	501.2	1196.7	−27.1	668	23.6	7877	> 60
3	1.15	10.7°	134.2	sh[j]	22	506.5	1196.7	113.4	804	16.3	7560	> 60
4	1.48	–	134.2	nh[i]	nh[i]	490.9	1196.7	−127.7	578	25.1	8007	> 60
5	1.35	47.8	142.5	nh[i]	nh[i]	492.2	1196.7	32.2	737	20.0	7755	> 60
6	1.20	74.4	153.3	nh[i]	nh[i]	491.7	1196.7	200.3	905	14.5	7103	> 60
7	1.47	99.0	145.6	10	4	544.5	1196.7	−307.9	344	30.5	8980	> 60
IL A[k]	1.25	−61	–	–	15	481.4	908.0	113.4	540	8.9	5721	–
IL B[l]	1.41[m]	−66	–	–	31	525.8	895.6	113.4	483	16.2	7158	–

[a] Density [g cm^{-3}]. [b] Melting point [°C] (from DSC measurement with $b = 10\,°C\,min^{-1}$). [c] Decomposition temperature [°C], DSC onsets from measurement with $b = 10\,°C\,min^{-1}$). [d] [ms]. [e] Heat of formation [kJ mol^{-1}]. [f] detonation pressure [GPa]. [g] Detonation velocity [m s^{-1}]. [h] impact sensitivity [J] (BAM Fallhammer). [i] nh = not hypergolic. [j] Hypergolic when a second drop of fuel was dropped into N_2O_4. [k] 1-(2-pentynyl)-3-methylimidazolium dicyanamide (ref. [3]). [l] 1-methyl-4-amino-1,2,4-triazolium dicyanamide (ref. [3]). [m] Calculated (ref. [5f]).

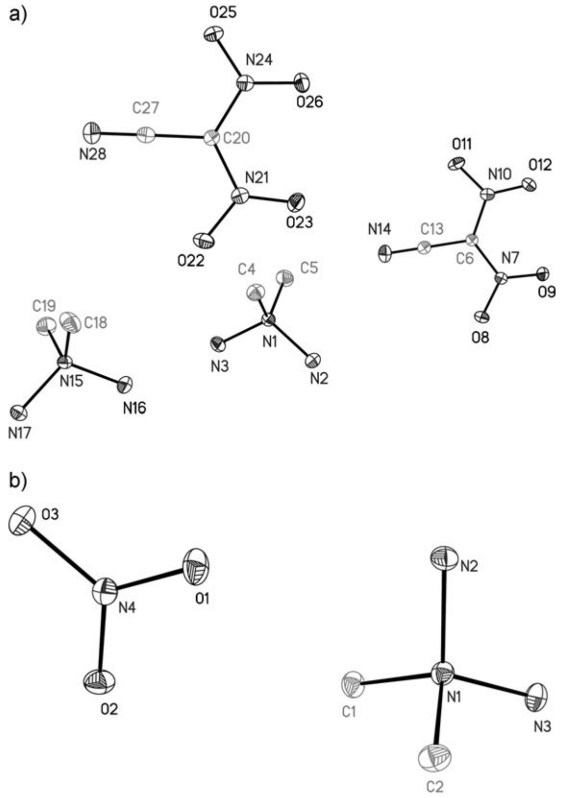

Figure 2. Molecular structures (thermal ellipsoids set at 30% probability) of a) **4** and b) **7**. Hydrogen atoms omitted for clarity.

1.4431(12) Å in **7**), with approximately 0.02 Å difference between them. This phenomenon has been observed in the structure of 2,2-dimethyltriazanium chloride which also has unequal N−N bonds (1.439 and 1.462 Å),[9a] and also in the cyclic structure of *N*,*N*,*N′*,*N′*-tetraaminopiperazinium bis(azide) (1.429 and 1.468 Å).[9b] In both of these structures the N−N bonding pattern (long and short) has been attributed to strong hydrogen bonding elongating one N−N interaction. In both **4** and **7** hydrogen bonding is also the deciding factor (see Supporting Information, Tables S2 and S3, Figure S1, S2) as in $[(CH_3)_2N(NH_2)_2]Cl$,[9a] with one NH group involved in more significant hydrogen-bonding interactions than the other. In the extended structure, **4** and **7** are oriented in planes (the (010) and (040) indexes, respectively) and short contacts and hydrogen bonding ties **4** into a crosslinked three dimensional array of anion–cation, cation–anion pairs and **7** into a crosslinked bilayer.

Density is one of the most important physical properties of energetic materials. The densities of most of the new salts range between 1.15 and 1.47 $g\,cm^{-3}$ (Table 1). The decomposition temperatures lie in the range 193–232 °C; compound **4** explodes at its decomposition temperature (differential scanning calorimetry, DSC). The heats of formation of **1**–**7** were calculated with Gaussian 03[13] (Table 1) by using the method of isodesmic reactions (Supporting Information). The enthalpy of an isodesmic reaction (ΔH_{r298}) is obtained by combining the G2 energy difference for the reaction.

All of the 2,2-dimethyltriazanium salts have positive heats of formation with **6** the highest (905 $kJ\,mol^{-1}$; Table 1). By using the calculated heats of formation and the experimental densities of salts, the detonation pressures *P* and detonation velocities *D* were calculated by means of traditional Chapman–Jouget thermodynamic detonation theory by using Cheetah 5.0.[14] Apparently, to date, only ionic liquids with the dicyanamide anion are found to be hypergolic.[3,4] However, our study shows that nitrocyanamide, and nitrate ions are also possible candidates for designing hypergolic ionic liquids; even salt **1** that contains chloride anion shows hypergolic properties. It seems that not only the anion but also the cation can play an important role in modifying hypergolic properties of ionic liquids thus extending the study area of hypergolic ionic liquids.[3] Impact sensitivities of the 2,2-dimethyltriazanium salts, tested with a BAM Fallhammer (Table 1), are greater than 60 J and thus fall into the insensitive region.[15]

In conclusion, 2,2-dimethyltriazanium is an attractive cation for designing ionic-liquid hypergols. It provides a new path for transferring these ionic liquids into bipropellant applications. The high heat of formation of the cation can be used for fine-tuning the energy content, and thus the performance of the hypergolic ionic liquids. These new 2,2-dimethyltriazanium ionic liquids may provide a potential replacement for the highly toxic hydrazine and its derivatives.

Caution: It must be emphasized that the new ionic liquids reacted with N_2O_4 or WFNA are *violent and hazardous*, and only small quantities should be used under well ventilated conditions with carefully planned safety protocols and protective equipment in place.

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[12] Crystallographic data: **4**: ($C_4H_{10}N_6O_4$): $M_r = 206.18$; crystal size $1.40 \times 0.11 \times 0.06$ mm^3; orthorhombic space group *Pbca*, $a = 9.2209(4)$, $b = 12.6230(5)$, $c = 31.3899(12)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 3653.6(3)$ Å^3, $Z = 16$, $2\theta_{max} = 55°$, 4191 independent reflections, $R_1 = 0.0555$ for 4191 reflections with $I > 2\sigma(I)$ and $wR_2 = 0.1119$, 289 parameters. **7**: ($C_2H_{10}N_4O_3$): $M_r = 138.14$; crystal size $0.59 \times 0.27 \times 0.06$ mm^3; triclinic, space group $P\bar{1}$, $a = 5.3946(9)$, $b = 7.5596(12)$, $c = 7.7299(12)$ Å, $\alpha = 87.609(2)$, $\beta = 88.638(3)$, $\gamma = 82.420(2)°$, $V = 312.15(9)$ Å^3, $Z = 2$, $2\theta_{max} = 55°$, 1416 independent reflections, $R_1 = 0.0155$ for 1416 reflections with $I > 2\sigma(I)$ and $wR_2 = 0.0865$, 122 parameters. CCDC 706856 and CCDC706857 contain 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.

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