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14. ABSTRACT After seminal work presented a decade ago, ionic liquids (IL) have now received a lot of attention as energetic materials for propellant applications. ^[1-3] In bipropellant rocket engines, it is desirable to achieve ignition by means of a hypergolic reaction and so to minimize system complexity. Hypergolic bipropellants are defined as fuel and oxidizer combinations that, upon contact, chemically react and release enough heat to spontaneously ignite, eliminating the need for an additional ignition source. This also makes them highly reliable for spacecraft and satellites which need to fire their rocket engines hundreds, or even thousands, of times during their lifetime. Unfortunately, no reliable <i>a priori</i> method for prediction of hypergolicity for fuel – oxidizer pairs is available today. The initial “hunting for the hypergol”, as John Clark entitled one of the chapters in his book <i>Ignition!</i> , took place mainly during WWII. ^[4] At that time, such toxic systems as “C-Stoff” (a mixture of N ₂ H ₄ ·H ₂ O, methanol and water) and others consisting of triethyl amine, aniline, toluidine, xyldine and N-methyl aniline were developed. Today, environmental and health concerns are becoming more and more pressing in the propellant world. Nevertheless, hydrazine and its methylated derivatives are still the state-of-the-art fuels for bipropellant applications. Most of the problems handling hydrazine and its derivatives are related to their volatility, as they are carcinogenic vapor toxins. For these reasons, it is exceedingly attractive to replace hydrazine with ILs which have become paragons of environmental friendliness, green chemistry and low vapor toxicity.					
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Ionic Liquids as Hypergolic Fuels

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After seminal work presented a decade ago, ionic liquids (IL) have now received a lot of attention as energetic materials for propellant applications.^{1–3} In bipropellant rocket engines, it is desirable to achieve ignition by means of a hypergolic reaction and therefore to minimize system complexity. Hypergolic bipropellants are defined as fuel and oxidizer combinations that, upon contact, chemically react and release enough heat to spontaneously ignite, eliminating the need for an additional ignition source. This also makes them highly reliable for spacecraft and satellites, which need to fire their rocket engines hundreds or even thousands of times during their lifetime. Unfortunately, no reliable *a priori* method for prediction of hypergolicity for fuel–oxidizer pairs is available today. Here, we report the first ILs to manifest hypergolic ignition.

The initial “hunting for the hypergol”, as John Clark entitled one of the chapters in his book, *Ignition!*, took place mainly during World War II.⁴ At that time, such toxic systems as “C-Stoff” (a mixture of N₂H₄·H₂O, methanol, and water) and others consisting of triethyl amine, aniline, toluidine, xylydine, and *N*-methyl aniline were developed. Today, environmental and health concerns are becoming more and more pressing in the propellant world. Nevertheless, hydrazine and its methylated derivatives are still the state-of-the-art fuels for bipropellant applications. Most of the problems handling hydrazine and its derivatives are related to their volatility, because they are carcinogenic vapor toxins. For these reasons, it is exceedingly attractive to replace hydrazine with ILs, which are regarded as paragons of environmental friendliness, green chemistry, and low vapor toxicity.

Most of the focus in energetic ILs research has been on heterocyclic cations in combination with oxygenated anions, which frequently have stability and safety problems.^{5–7} In a

bipropellant system, with ILs used as fuels, it is not necessary to use an oxygen-balanced IL. Furthermore, one can avoid oxygen-carrying anions completely, which, other things being equal, should make handling much safer because fuel and oxidizer are chemically separated. In a salt system, the positive charge of the cation makes it much more resistant toward oxidation. Consequently, electron- and fuel-rich anions are much easier to oxidize and thus would seem to hold the potential to promote hypergolic ignition.

Disappointingly, our first ignition tests carried out with ILs containing fuel-rich azide anions did not reveal any hypergolic properties.⁸ However, the violent nature of their reactions was an encouragement to continue this line of work. In comparison, the same family of cations paired with the nitrate anion showed no noticeable reactivity toward inhibited, red-fuming nitric acid (IRFNA, ~83% HNO₃ plus 14% N₂O₄ plus ~2% H₂O plus 0.6% HF), white fuming nitric acid (WFNA, ~100% HNO₃), or N₂O₄.

Therefore, the aim of this paper is to report on hypergolicity investigations of other fuel-rich anions, especially the dicyanamide anion. Dicyanamide was chosen not only because it is a fuel-rich anion but also because IL dicyanamides have some of the lowest viscosities among known ILs.^{9–11} In bipropellant systems, pumps transport fuel and oxidizer, and therefore, excessive viscosity must be avoided.

Imidazolium-based ILs were first considered because they generally possess greater stability than their triazolium or tetrazolium analogues. Unsaturated sidechains, such as allyl, propargyl, and 2-butenyl were selected because it was hoped that they would initiate or promote hypergolic ignition. It has been demonstrated in the past that unsaturated, especially acetylenic, compounds show a tendency to hypergolicity and can even be used as fuel additives to promote hypergolic ignition.⁴

The starting materials, 1-*R*-3-methylimidazolium bromides (1–5), were prepared by alkylation of methylimidazole followed by metathesis with freshly prepared silver dicyanamide (Scheme 1). Because silver dicyanamide is insoluble in methanol, it can be used in excess, assuring complete conversion (see the Supporting Information).

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Scheme 1

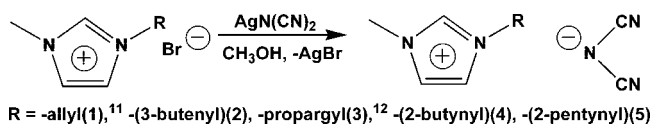


Table 1. Thermal and Physical Data of the Dicyanamide Salts 1–6

compound	T_g (°C) ^a	T_m (°C) ^b	T_d (°C) ^c	η (cP) ^d (25 °C)
1	−85		+207	42
2	−90		+210	27
3	−61	+17 ^e	+144	110
4		+49	+179	
5		+59	+184	
6	−66		+143	92

^a Glass transition. ^b Melting point. ^c Decomposition onset. ^d Viscosity. ^e From ref 12.

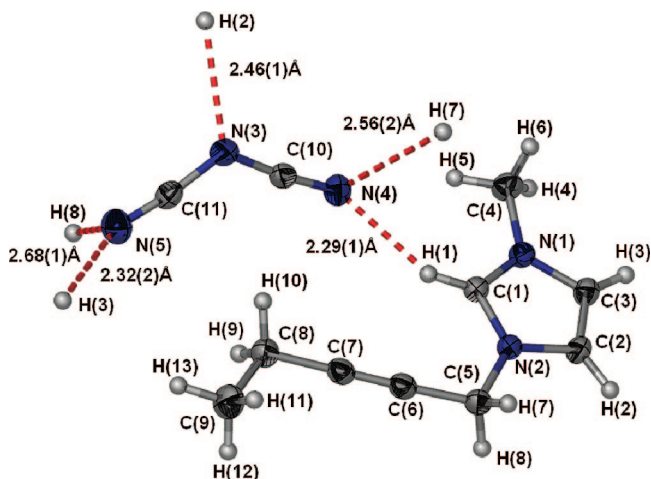


Figure 1. ORTEP diagram showing connectivity, conformation, and the atom-numbering scheme for compound 5.

Physical data for known, 1 and 3, and novel, 2–5, compounds, are shown in Table 1 along with the 1-methyl-4-amino-1,2,4-triazolium analogue, 6, which is discussed later and was prepared by the same method.

Most substituted imidazolium dicyanamides are true room-temperature liquids. Compounds 4 and 5 are solid at ambient conditions, and compound 5 could be recrystallized from methanol layered with diethylether, giving crystals suitable for single-crystal X-ray determination. The structure analysis revealed an extensive hydrogen-bond network involving the dicyanamide anion (Figure 1). Similar to other ILs, solidification can be attributed to extensive hydrogen bonding.

As a simple test for hypergolicity similar to those used historically,⁴ droplet tests were carried out using a glass cuvette, which was filled with ca. 1 mL of IRFNA or WFNA. A syringe generating ca. 10 μL droplets was used to dispense the IL fuel (Figure 2a). A high-speed camera recording 500 frames/s was used to determine the ignition delay (ID) times (Table 2) by counting the frames between the droplet first hitting the surface of the oxidizer (Figure 2b) and the sign of the first visible ignition (Figure 2c). After ignition, the hypergolic compounds undergo self-sustained combustion (Figure 2d).

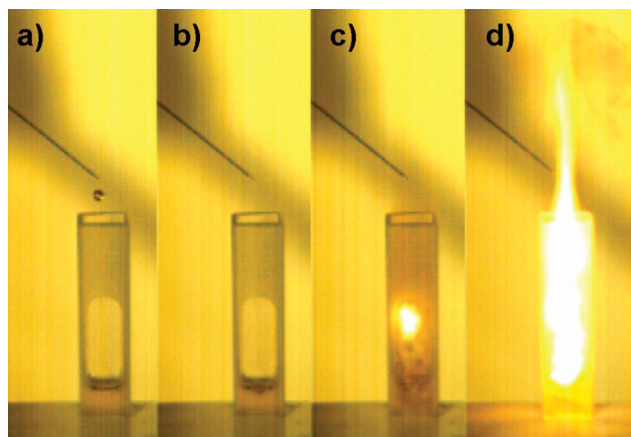


Figure 2. (a–d) Selected frames from the high-speed video of the hypergolic reaction of compound 3 and WFNA.

Table 2. ID Times for Hypergolic ILs with IRFNA and WFNA

compound dicyanamide	IRFNA ID (ms) ^a	WFNA ID (ms)
1	625	43
2	670	^b
3	170	15
6	^b	31
1-butyl-3-methyl-imidazolium ^c	^b	47
1-butyl-1-methyl-pyrrolidinium ^c	^b	44
<i>n</i> -butyl-3-methylpyridinium ^c	^b	37

^a Ignition delay time. ^b Not measured. ^c Purchased from Merck.

By this test, compounds 1–3 were shown to be hypergolic. The solids 4 and 5 were not tested because of their unsuitability as liquid propellants. One example of an IL based on a triazole, compound 6, and three commercially available IL dicyanamides, 1-butyl-3-methyl-imidazolium, 1-butyl-1-methylpyrrolidinium, and *n*-butyl-3-methyl-pyridinium, were also tested with WFNA and found to be hypergolic as well (Table 2).

On the basis of these results and somewhat unexpectedly, unsaturated substituents do not seem to play a determinative role in the ignition process. Rather, it appears that the key to hypergolicity in these systems is the dicyanamide anion.¹³ For a suitable hydrazine replacement, ID times of less than 5 ms are preferred. Aerosol-type fuel and oxidizer sprays are being examined and should lead to shorter ID times as well as better reflecting real-world engine conditions.

With the discovery of these IL hypergols, a new path for transitioning these materials into bipropellant applications seems clear. It is expected that these systems can now be fine-tuned for energy content, performance, and desirable physical properties and that they could replace state-of-the-art, highly toxic hydrazine and its derivatives.

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Supporting Information Available: Crystallographic data for compound 5 in CIF format and further experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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