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# Relationships Between Molecular Structure and Chemical Reactivity in Hypergolic Ionic Liquids: Progress Toward Designing “Green” Fuels for Bipropellant Applications

John P. Maciejewski, Haixiang Gao and Jean’ne M. Shreeve\*

Department of Chemistry, University of Idaho, Moscow, Idaho 83844-2343

## ABSTRACT

Hypergolic ionic liquids have the potential to replace the toxic and volatile hydrazine derivatives currently used as fuels in aerospace and missile propulsion systems. Now we present our results obtained in designing new hypergolic materials, and the impact of the properties of different anions upon the hypergolic reactivity and physical properties of ionic liquids. A new and efficient methodology to prepare hypophosphite (HP, **4**) containing ionic liquids has also been developed. In addition, two anions that emulate the properties of the dicyanamide (DCA, **1**) anion, the vinylogous dicyanamide (vDCA, **5**) and *N,N'*-dicyanoformamidine (DCF, **6**) have been used to prepare ionic liquids for hypergolic studies.

## INTRODUCTION

The ability to design small molecules to perform specific tasks is critical toward advancing fields ranging from pharmaceuticals and therapeutics<sup>1,2</sup> to materials science.<sup>3</sup> In addition to molecular compounds, ionic liquids, which are salts that melt below 100

°C, represent a specific class of compounds that demonstrate low toxicity, low volatility, and broad applicability to the aforementioned fields.<sup>4,5</sup> The emergence of ionic liquids carefully designed for particular roles<sup>6</sup> has demonstrated that these molten salts can be employed over a wide range of applications, which include solvents,<sup>7</sup> electrolytes,<sup>8</sup> pharmaceuticals and therapeutics,<sup>9</sup> and hydrogen storage materials.<sup>10</sup>

One particular aspect of ionic liquid chemistry that remains under-explored is how the molecular structures of the cations and anions influence chemical reactivity in the field of hypergolic ionic liquid fuels.<sup>11</sup> A hypergolic chemical reaction is characterized by the spontaneous combustion reaction between a fuel and an oxidizer.<sup>12</sup> Common hypergolic fuels are hydrazine-based, which are volatile, toxic substances.<sup>13</sup> Hypergolic ionic liquids are considered to be potential surrogates for hydrazine-based fuels in aerospace and missile propulsion applications. Similar to the design of small molecule therapeutics to interact with a specific biological target, we have attempted to design and prepare ionic liquids to react as hypergolic fuels. In terms of ionic liquid fuel design, there exists a multitude of potential cation/anion combinations to prepare new ionic liquids; however, the accurate prediction of hypergolic properties is uncertain. The ability to understand which properties of the ionic liquid partners influence hypergolic reactivity is necessary in order to be able to design new and “green” fuels. Developing the capability to strategically design fuels would be lucrative since it would not only reduce the costs of their research and development, but may result in the production of smart fuels that can be custom tailored to react with an oxidizer of choice for specific bipropellant applications.

Non-corrosive fuels that demonstrate high thermal stability, low viscosity, low toxicity, low volatility, and a wide liquid range are attractive materials for hypergolic applications.<sup>14</sup> When considering ionic liquids as hypergolic fuels, the materials should, in addition, be hydrolytically stable, and undergo a combustion reaction within 10 ms from the time when mixed with oxidizers such as white fuming nitric acid (WFNA, ~100% HNO<sub>3</sub>), inhibited red fuming nitric acid (IRFNA, ~83% HNO<sub>3</sub>, 14% N<sub>2</sub>O<sub>4</sub>, ~2% H<sub>2</sub>O, and 0.6% HF),<sup>15</sup> N<sub>2</sub>O<sub>4</sub>, and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>).<sup>16</sup> Ionic liquids that serve as benchmark fuels often contain the dicyanamide (DCA, **1**), nitrocyanoamide (NCA, **2**), or the dicyanoborohydride (DCB, **3**) anions, where the latter has produced ignition delay (ID) times < 10 ms when paired with various organic cations (Figure 1).<sup>17,18</sup>



**Figure 1.** Common anions used in hypergolic ionic liquids

A comparison of the trends in reactivity of hypergolic ionic liquids shows that the choice of anion (when comparing common cations) can effect the ignition delay (ID) time of the fuel from tens to hundreds of milliseconds. Schneider and coworkers have reported that the anion may be responsible for the hypergolic properties associated with the imidazolium DCA series of ionic liquids, regardless of the substitution on the cation.<sup>13</sup> The variation in ID times as a result of changing the anion supports the observation that the anion may influence the hypergolic reactivity of the ionic liquid.

Our research objective has been to study how the properties of the anions used in hypergolic ionic liquids influence the ID times. This ultimately can lead to the development of new anions for hypergolic applications.

A route to exploit the chemical reactivity of ionic liquids is to understand the mechanism of the hypergolic combustion reaction. It is unknown whether the nonmetal anions **1** and **2** undergo a similar mechanism of hypergolic ignition with WFNA when compared to the metalloid-based dicyanoborohydride **3**. Fortunately, the mechanism of the hypergolic reaction between DCA-based ionic liquids with WFNA continues to be investigated.<sup>19,20,21</sup> Through computational studies and spectroscopic analysis of reaction byproducts,<sup>22</sup> there is evidence for the formation of covalent adducts between the DCA anion and WFNA during the hypergolic reaction. More specifically, the cyanamide moiety appears to undergo a chemoselective reaction with the oxidizer during the hypergolic reaction, and may represent a critical functional group associated with hypergolic combustion.

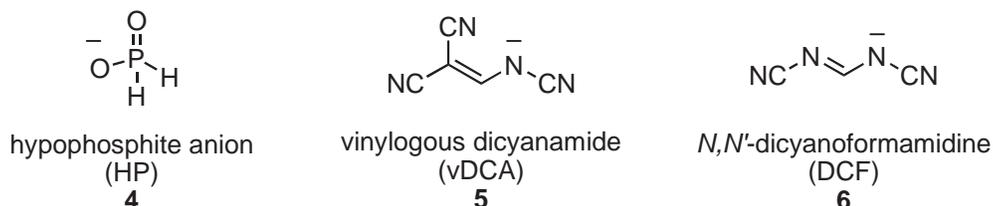
The properties of two fundamentally different classes of anions were investigated. The data from both classes were then compared to the benchmark performance of hypergolic ionic liquids containing the DCA anion. The first class exhibits a stronger reducing ability with respect to the DCA anion, and the second is based upon structural analogs of the DCA anion. In the first class, we hypothesized that if the hypergolic reaction is observed as a result of the oxidation of the anion used in the fuel, then increasing the reduction potential of the anion may increase hypergolic reactivity of the ionic liquid as evidenced by reduction in the ignition delay time. Computational studies involving the relationship between ionization potential of ionic liquids and ID times for

ionic liquids containing the DCA, NCA and nitrate anions have been described.<sup>23</sup> We attempted to put our theory into practice by focusing solely on the properties of the anion, and evaluated candidates that are strong reducing species in an acidic medium. As a result, the conjugate base of phosphinic acid, the hypophosphite ion (HP, **4**) presented itself as a viable anion for investigation and development (Figure 2). Commercially available as sodium hypophosphite monohydrate, the inexpensive phosphorus +1 salt provides a two electron standard reduction potential of  $E^{\circ} = -0.50$  V as phosphinic acid ( $\text{H}_3\text{PO}_2$ , presumably generated when HP is added to WFNA) in acidic medium (eq 1).<sup>24</sup> This anion appeared to be promising since the four electron standard reduction potential of the hydrazinium ion ( $\text{N}_2\text{H}_5^+$ ) in acidic medium is  $E^{\circ} = -0.23$  V (eq 2).<sup>25,26</sup> Since hydrazine is hypergolic when combined with WFNA, we proposed that if a oxidation/reduction process involving the anion governs the hypergolic reaction, then hypophosphite ionic liquids might produce hypergols similar to hydrazine. Qualitatively, the HP anion exhibits a stronger reducing ability than DCA, NCA, and DCB.<sup>27</sup> This is demonstrated by the reduction of silver nitrate with sodium hypophosphite in an aqueous medium to generate silver nanoparticles.<sup>28,29</sup>



The second class of anions proposed emulate the parent DCA anion **1** and include the vinylogous dicyanamide (vDCA, **5**) and *N,N'*-dicyanoformamidine (DCF, **6**) (Figure 2). The DCA anion analogs were selected to probe whether or not anions with similar

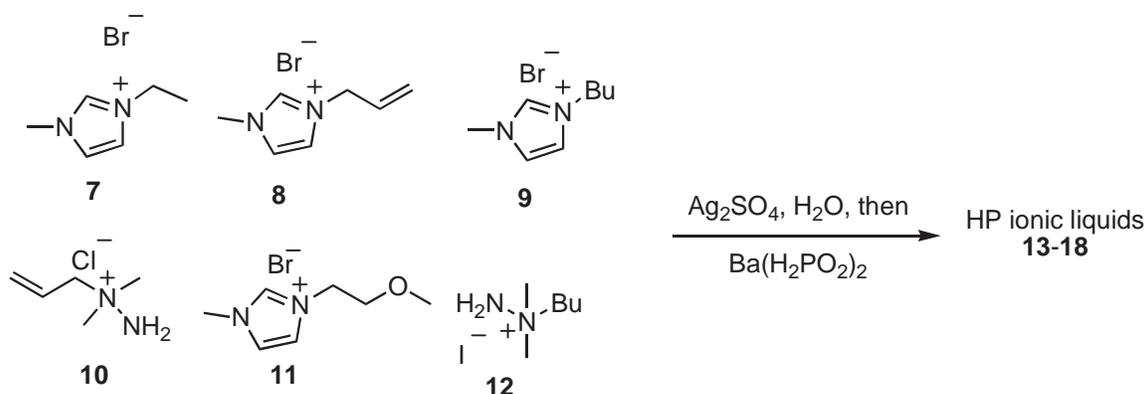
electronic distribution (determined by NBO analysis), and functional groups to DCA could preserve both the hypergolic reactivity, as well as the physical properties associated with DCA-based ionic liquids.



**Figure 2.** Potential anions for hypergolic ionic liquid studies

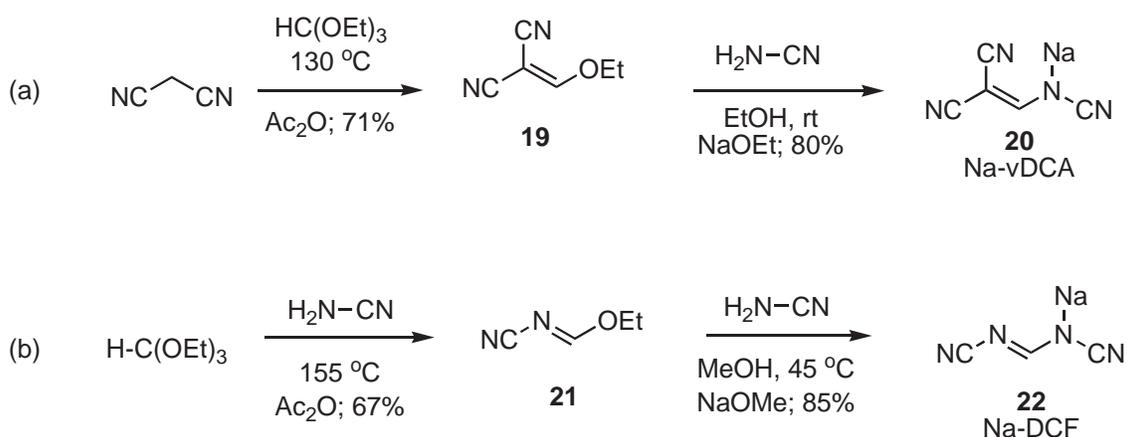
## RESULTS AND DISCUSSION

A new and efficient methodology to prepare hypophosphite-containing ionic liquids was developed. To utilize the efficiency of the silver salt metathesis, we incorporated an intermediate of chemical orthogonality, a bisammonium sulfate, into our general synthetic approach (Scheme 1). These intermediates were prepared by the addition of ammonium halide salts (**7-12**) to an aqueous suspension of silver sulfate. Filtration of the solution containing the organosulfate salt into barium hypophosphite provided water-soluble ammonium hypophosphite ionic liquids, as well as barium sulfate as a precipitate. During this work, an improved synthesis of barium hypophosphite was developed, which involves the reaction of  $\text{BaCO}_3$  and *in situ* generated phosphinic acid. This scalable reaction was used to prepare up to 47 g (75% yield) of  $\text{Ba}(\text{H}_2\text{PO}_2)_2$ , and is less cumbersome than known methods of preparation involving the reaction between white phosphorus and barium hydroxide.<sup>30</sup>



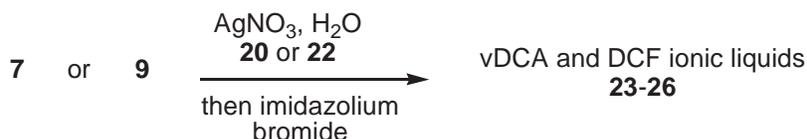
**Scheme 1.** Preparation of HP ionic liquids **13-18**

Scheme 2 outlines the preparation of the DCA anion precursors. The preparation of the *N*-(2,2-dicyanovinyl)cyanamide sodium salt (Na-vDCA) was accomplished in two steps. The condensation of malononitrile with triethylorthoformate provided the vinyl ethyl ether **19**, which was subsequently treated with sodium cyanamide to provide **20** (Scheme 2a). The preparation of the *N,N'*-dicyanoformimidamide sodium salt (Na-DCF) was accomplished through the condensation of cyanamide with triethylorthoformate to provide ethyl *N*-cyanoformimidate **21**, which underwent an analogous addition/elimination reaction with sodium cyanamide to provide **22** (Scheme 2b).



**Scheme 2.** Preparation of the sodium salts of vDCA and DCF

The synthesis of ionic liquids **23-26** containing anions **5** and **6** was accomplished by adding a freshly prepared silver salt of the respective anion to an aqueous solution of the respective cation (Scheme 3).



**Scheme 3.** The preparation of DCF and vDCA ionic liquids

The ionic liquids shown in Table 1 have been characterized by  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  NMR (where appropriate), IR, DSC, elemental analysis, pycnometry and viscometry.

**Table 1.** Physical properties of the HP, vDCA and DCF ionic liquids<sup>a</sup>

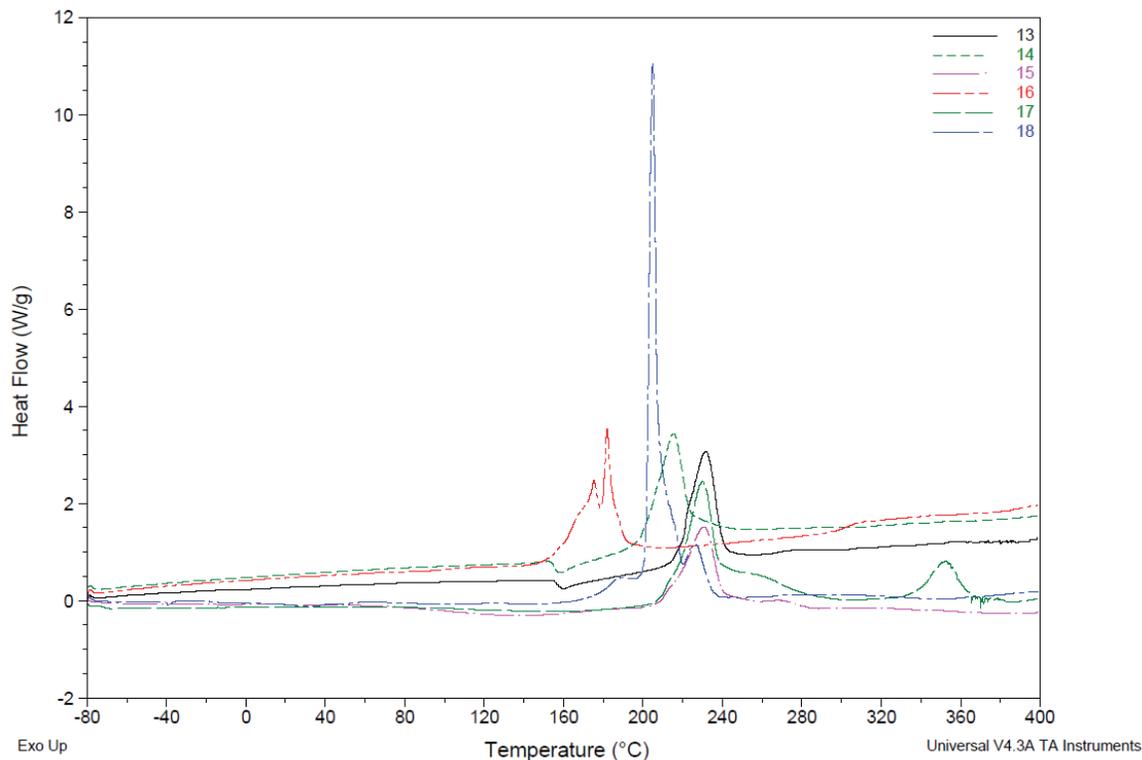
| entry | cation    | anion | product   | yield (%) | $T_m$ (°C) | $T_d$ (°C) | $\eta$ (cP) <sup>b</sup> | $\rho$ (g/cm <sup>3</sup> ) <sup>b</sup> | ID (ms)         |
|-------|-----------|-------|-----------|-----------|------------|------------|--------------------------|--|-----------------|
| 1     | <b>7</b>  | HP    | <b>13</b> | 70        | <-80       | 219        | 56.2                     | 1.180                                    | 203             |
| 2     | <b>8</b>  | HP    | <b>14</b> | 70        | <-80       | 200        | 177.8                    | 1.188                                    | 125             |
| 3     | <b>9</b>  | HP    | <b>15</b> | 80        | <-80       | 214        | 154.1 <sup>c</sup>       | 1.105 <sup>c</sup>                       | 230             |
| 4     | <b>10</b> | HP    | <b>16</b> | 63        | <-80       | 171        | 308.9 <sup>d</sup>       | 1.121 <sup>d</sup>                       | NH              |
| 5     | <b>11</b> | HP    | <b>17</b> | 80        | <-80       | 217        | 251.6                    | 1.254                                    | 241             |
| 6     | <b>12</b> | HP    | <b>18</b> | 80        | <-80       | 202        | -                        | 1.114 <sup>c</sup>                       | -               |
| 7     | <b>7</b>  | vDCA  | <b>23</b> | 87        | <-80       | 205        | 69.40                    | 1.124                                    | NH              |
| 8     | <b>9</b>  | vDCA  | <b>24</b> | 89        | <-80       | 193        | 126.9                    | 1.086                                    | NH              |
| 9     | <b>7</b>  | DCF   | <b>25</b> | 90        | 3          | 197        | 32.76 <sup>c</sup>       | 1.126 <sup>c</sup>                       | 381             |
| 10    | <b>9</b>  | DCF   | <b>26</b> | 86        | <-80       | 186        | 80.19                    | 1.084                                    | NH              |
| 11    | <b>7</b>  | DCA   | <b>27</b> | 72        | -21        | 275        | 21 <sup>f</sup>          | 1.06                                     | 36 <sup>e</sup> |
| 12    | <b>8</b>  | DCA   | <b>28</b> | -         | n/a        | 207        | 42                       | n/a                                      | 43              |
| 13    | <b>9</b>  | DCA   | <b>29</b> | -         | -90        | 240        | 33                       | 1.06                                     | 47              |

<sup>a</sup> $T_m$ : melting temperature,  $T_d$ : decomposition temperature,  $\eta$ : viscosity,  $\rho$ : density, n/a: data not available, ID: ignition delay (average of three measurements using WFNA as oxidizer), NH: not hypergolic. <sup>b</sup>Measurements taken at 25 °C; <sup>c</sup>Measurements taken at 26 °C; <sup>d</sup>measurements taken at 27 °C; <sup>e</sup>ID for ionic liquid not previously reported; <sup>f</sup>measurement taken at 20 °C.

A series of six HP ionic liquids have been prepared in a range of 63-80% yield. The 1-butyl-1,1-dimethylhydrazinium HP salt **18** was isolated as a waxy, hygroscopic solid at room temperature, where the additional products in the HP series exist as liquids at room

temperature. In general, the HP ionic liquids prepared were slightly denser and more viscous materials than the respective DCA compounds. For comparison, entries 11-13 (Table 1) outline the physical properties and ID times of known ethyl-allyl-<sup>13</sup> and butylimidazolium<sup>13</sup> DCA ionic liquids (**27-29**, respectively).

The thermal stability of the HP class was lower than those of the respective DCA ionic liquids, where the onset decomposition temperature ( $T_d$ ) for the HP series was approximately 200 °C (Figure 3). In contrast, the melting points were below -80 °C,



**Figure 3.** DSC of HP ionic liquids **13-18**

which are comparable to those of observed in the DCA, NCA, and DCB ionic liquids. The ID data were recorded in triplicate using WFNA as the oxidizer, and the average ID values are reported in Table 1. In general, the ID times for the room temperature HP ionic liquids are 2-6 times longer (between 125-241 ms) when compared to those

reported for DCA class with the respective cations. In one case, the 1-allyl-1,1-dimethylhydrazinium hypophosphite ionic liquid **16** was not hypergolic. The relatively long ID times recorded for the HP series of ionic liquids indicate that using an anion with a stronger reduction potential than both the DCA anion, and the hydrazinium ion ( $\text{N}_2\text{H}_5^+$ ) does not provide shorter ID times than those observed with DCA-based ionic liquids and hydrazine fuels.

The heat of formation (HoF) and specific impulse (Isp) are key properties of hypergolic ionic liquids. To determine the feasibility for using the HP, vDCA and DCF ionic liquids as fuels, their HoF and Isp values were calculated using our earlier method<sup>31</sup> and computer codes CHEETAH (6.0) and EXPLO5 (5.05) (Table 2). The calculated HoF value for the HP anion is -800.1 kJ/mol, while the HoF values for the vDCA and DCF species were 265.6 kJ/mol and 170.9 kJ/mol, respectively. All ionic liquids prepared have similar heats of formation for the cations and lattice energies, with the exception of the dramatically different HoF values for the ionic liquids containing the HP anion.

Natural bond orbital analysis provides an efficient method for investigating charge distribution in molecular systems.<sup>32</sup> The charge distribution calculated by the NBO method for optimized geometries of HP anion are shown Figure 4. The NBO analysis (DFT (B3LYP)/ 6-31G+(d,p)//mp2(full)/6-311++g(d,p)) shows that the optimized HP anion has a symmetric charge distribution in the whole anion, the electron-withdrawing effect of the oxygen atoms considerably reduces the relative electron density

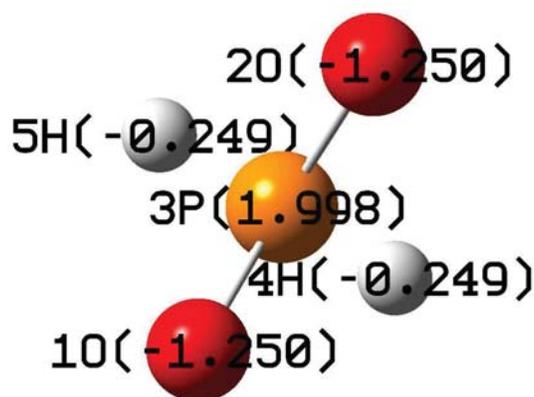
**Table 2.** Calculated heat of formation and specific impulse of ionic liquids

| entry | product   | $\Delta H_f^{\text{Cation}}$ (kJ/mol) <sup>a</sup> | $\Delta H_f^{\text{Anion}}$ (kJ/mol) <sup>a</sup> | $\Delta H_L$ (kJ/mol) <sup>a</sup> | $\Delta H_f^{298}$ (kJ/mol) <sup>a</sup> | Isp (s) <sup>b</sup> |
|-------|-----------|--|---|------------------------------------|--|----------------------|
| 1     | <b>13</b> | 621.5  | -800.4  | 477.3                              | -656.2                                   | 126 <sup>c</sup>     |
| 2     | <b>14</b> | 596.0  | -800.4  | 470.0                              | -674.4                                   | 118 <sup>c</sup>     |
| 3     | <b>15</b> | 569.3  | -800.4  | 451.6                              | -682.7                                   | 128 <sup>c</sup>     |

|    |           |       |        |       |        |                  |
|----|-----------|-------|--------|-------|--------|------------------|
| 4  | <b>16</b> | 814.6 | -800.4 | 478.2 | -464.0 | -                |
| 5  | <b>17</b> | 639.4 | -800.4 | 465.4 | -626.4 | 155 <sup>c</sup> |
| 6  | <b>18</b> | 578.3 | -800.4 | 466.1 | -688.2 | -                |
| 7  | <b>23</b> | 621.5 | 265.6  | 440.9 | 446.3  | -                |
| 8  | <b>24</b> | 569.3 | 265.6  | 424.4 | 410.5  | -                |
| 9  | <b>25</b> | 621.5 | 170.9  | 453.8 | 338.6  | 165 <sup>c</sup> |
| 10 | <b>26</b> | 569.3 | 170.9  | 434.9 | 305.3  | -                |
| 11 | <b>27</b> | 621.5 | 113.4  | 463.4 | 271.5  | 164 <sup>d</sup> |

<sup>a</sup>Heat of formation calculated using Gaussian 3.0 Revision D.01). <sup>b</sup>Specific impulse calculated only for hypergolic, room temperature ionic liquids. <sup>c</sup>Specific impulse calculated using CHEETAH (version 6.0). <sup>d</sup>Specific impulse calculated using EXPLO5 (version 5.05).

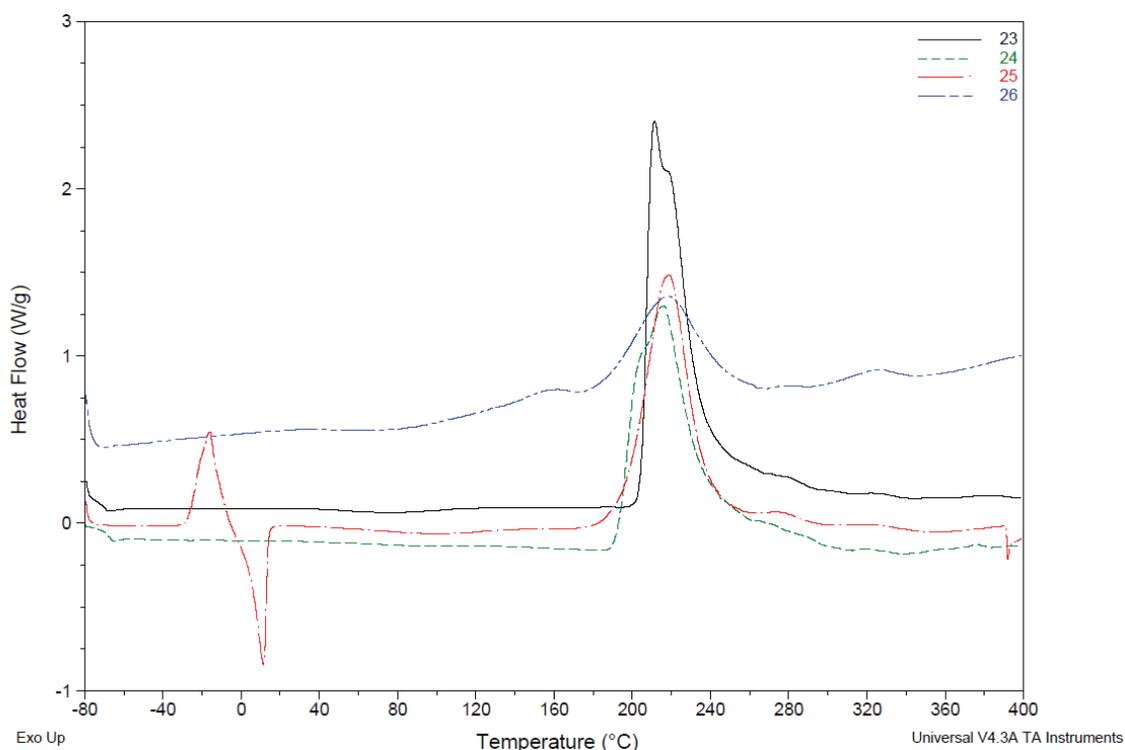
on the central phosphorus atom. Although the phosphorus atom in this anion is assigned a formal oxidation state of +1, the majority of the relative negative charge is mainly delocalized over the oxygen atoms in the anion. Despite the strong reducing ability of the HP anion, only 17% of the charge resides on the hydrogen atoms bonded to phosphorus atom.



**Figure 4.** NBO graphic of HP anion

The vDCA and DCF anions provided ionic liquids with similar density and viscosity to the DCA benchmarks. Figure 5 shows the DSC analyses of the DCF- and

vDCA-based ionic liquids. The decomposition temperatures ( $T_d$ ) for ionic liquids containing the DCF anion were below those of the vDCA analogs. Both classes were less thermally stable



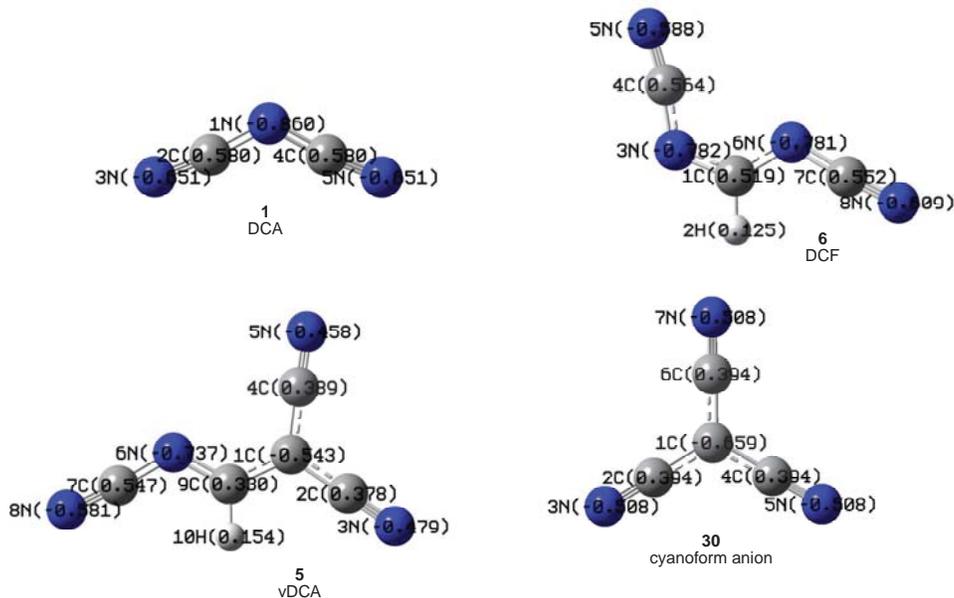
**Figure 5.** DSC of DCF and vDCA ionic liquids **23-26**

than the DCA benchmark ionic liquids (Table 1). Despite the similarities in physical properties to DCA ionic liquids, the hypergolic reactivity for ionic liquids **23-26** was lower than expected. When using the DCF anion, a hypergolic reaction (ID = 381 ms) was observed when paired with the 1-ethyl-3-methylimidazolium cation **7**, but not with the 1-butyl-3-methylimidazolium cation **9**.

Although the viscosity and density of the materials are similar to the analogous DCA ionic liquids, when adding ionic liquids **23** and **24** that contain the vDCA anion to

WFNA, no hypergolic reaction was observed. This was surprising since the anion contains an additional (vinylogous) cyanamide moiety, which is believed to be an important functional group in the chemoselective reaction between WFNA and DCA. The overall hypergolic reactivity trends between DCA ionic liquids and the DCF and vDCA series **23-26** show that increasing the carbon content in the anion leads to non-hypergolic materials. Increasing carbon content in hypergolic ionic liquids over seven carbon atoms is known to decrease hypergolic reactivity.<sup>17</sup>

The NBO analysis of the DCA, DCF and vDCA anions indicate differences in the relative electron density. The parent DCA anion **1** and DCF anion **6** contain no relative negative charge on any carbon in the anion. In contrast, the vDCA anion **5** contains a



**Figure 6.** NBO calculations for DCA, DCF, vDCA and cyanoform anions

localized negative charge on the carbon atom of the malononitrile moiety. This predicted localized negative charge in anion **5** might adversely affect the hypergolic properties of

the ionic liquid. This hypothesis is supported by previous work, which shows ionic liquids that contain the cyanoforn anion **30** are not hypergolic in WFNA.<sup>33</sup> From NBO analysis of the cyanoforn anion, an accumulation of relative negative charge of -0.659 on the central carbon atom is observed. A similar value of -0.543 was calculated for the vDCA anion **5** (Figure 6). Although the NBO analysis indicated no localized negative charge on carbon atoms in the DCF anion **6**, the relatively long ID time for ionic liquid **25**, and lack of ignition with **26** remains difficult to explain.

## CONCLUSIONS

A series of ionic liquids have been designed for hypergolic applications and examined in order to establish trends in how the anion in the ionic liquid influences ID times. When employing a stronger reducing species (HP anion), hypergolic ionic liquids are obtained, but ID times competitive to those observed with the DCA, NCA, DCB anions, as well as molecular hydrazine are not observed. We have also designed ionic liquid analogs that are comparable in physical properties (viscosity, density and thermal stability) to the parent DCA benchmarks. Despite the remarkably similar intrinsic properties when comparing common cations, the performance of these new DCF and vDCA ionic liquids was lower than expected. Our effort to incorporate the (presumably) reactive cyanamide moieties into our DCA anion analogs was successful; however, a rapid hypergolic reaction (ID times between 10-50 ms) similar to DCA ionic liquids was not observed. These results indicate that there may be additional underlying principles that govern and otherwise promote the rapid hypergolic reaction observed in the DCA fuel series. Our efforts to identify and exploit these principles hidden in the DCA analogs

continue, as we work to improve our approach toward the strategic design of “green” ionic liquid fuels for bipropellant applications.

### Supporting Information; Experimental Section

#### **GENERAL EXPERIMENTAL**

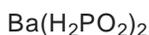
**General methods:**  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  NMR (decoupled) spectra were recorded in DMSO- $d_6$  on a 300 MHz nuclear magnetic resonance spectrometer operating at 300.1, 75.5, and 121.5 MHz, respectively, unless otherwise noted. Chemical shifts were reported relative to the residual solvent peak. Melting and decomposition points for ionic liquids were recorded on a differential scanning calorimeter (DSC) from -80 to 400 °C at a scan rate of 5 °C/min in compressed aluminum pans. Melting and decomposition points for solids were measured by DSC from 40 to 400 °C at a scan rate of 5 °C/min. IR spectra were recorded as thin films using a BIORAD model 3000 FTS spectrometer, unless otherwise noted. Densities were measured using a Micromeritics Accupyc 1330 gas pycnometer. Viscosities were measured with a Grabner MINIVIS II Portable Micro viscometer. Elemental analyses were obtained by using a CE-440 elemental analyzer (EAI Exeter Analytical). Ignition delay (ID) times were measured using the drop test method, where 15-20 mg of sample is dropped into excess white-fuming nitric acid (1.0-1.5 mL). The ignition delay times were recorded in triplicate at 500 frames/s using an Olympus *i*-Speed camera, and the average ID times are reported.

**Reagents:** All solvents were used as received unless otherwise specified. 1-methylimidazole, redistilled 99+% (Acros), 1,1-dimethylhydrazine 98% (Aldrich), 1-butyl bromide 99% (Acros), 1-butyl iodide (Kodak), allyl bromide 99% (Alfa Aesar),

silver nitrate 99.9% (Salt Lake Metals), sodium hypophosphite monohydrate (Alfa Aesar), barium carbonate (General Chemical Company), silver sulfate 99.5% (J.T. Baker), cyanamide 98% (Alfa Aesar), malononitrile 99% (Acros), acetic anhydride 99% (EMD), triethylorthoformate 98% (Acros) were used as received.

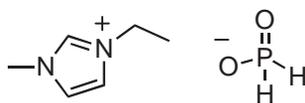
**Ionic liquid precursors:** The preparation of 1-ethyl-3-methylimidazolium bromide,<sup>34</sup> 1-allyl-3-methylimidazolium bromide,<sup>35</sup> 1-butyl-3-methylimidazolium bromide,<sup>36</sup> 1-(ethoxymethyl)-3-methylimidazolium bromide<sup>37</sup> were prepared by the quaternization of 1-methylimidazole. The preparation of 1-butyl-1,1-dimethylhydrazinium iodide,<sup>38</sup> and 1-allyl-1,1-dimethylhydrazinium chloride,<sup>18</sup> resulted from the quaternization of 1,1-dimethylhydrazine. The *N*-(2,2-dicyanovinyl)cyanamide sodium salt (Na-vDCA)<sup>39,40</sup> and *N,N'*-dicyanoformimidamide sodium salt (Na-DCF)<sup>41</sup> were prepared using known protocols.

## EXPERIMENTAL



**Barium hypophosphite:** A beaker was charged with 47.36 g (240.0 mmol) of BaCO<sub>3</sub>. In a separate flask was prepared an aqueous solution of 50.88 g (480.0 mmol) of sodium hypophosphite-monohydrate in 200 mL of 2.4 M HCl. The solution of the *in situ* generated phosphinic acid was slowly added to the flask containing the BaCO<sub>3</sub> under efficient stirring at room temperature. After no further gas evolution, the suspension was slowly heated to 70 °C (internal temperature) over 1 h and then diluted with 200 mL of MeOH where heating was continued. When the internal temperature reached 65 °C the

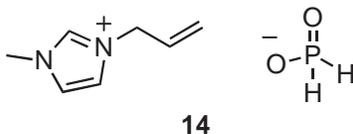
solid was filtered and rinsed with boiling MeOH (2 x 150 mL) to afford 47.33 g (177.1 mmol, 74%) of barium hypophosphite as a white solid;  $T_d = 282\text{ }^\circ\text{C}$  (onset, shoulder),  $T_d = 289\text{ }^\circ\text{C}$  (onset, major); IR (KBr)  $\nu$  2367, 2349, 1151, 1085, 1051, 810, 469  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{D}_2\text{O}$ )  $\delta$  7.11 (d,  $J = 517.7\text{ Hz}$ , 2H,  $\text{H}_2\text{PO}_2$ );  $^{31}\text{P}$  NMR ( $\text{D}_2\text{O}$ )  $\delta$  7.17 (s,  $\text{H}_2\text{PO}_2$ ); elemental analysis calcd (%) for  $\text{BaH}_4\text{O}_4\text{P}_2$  (267.30): C 0.00, H 1.51, N 0.00; found: C 0.08, H 1.31, N 0.03.



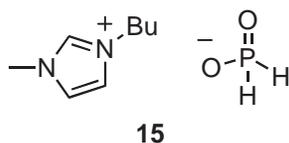
**13**

**3-Ethyl-1-methyl-imidazolium hypophosphite, 13: General protocol A:** To a suspension of 2.083 g (6.681 mmol) of  $\text{Ag}_2\text{SO}_4$  in 4 mL of  $\text{H}_2\text{O}$  cooled in an ice bath and protected from light was added a solution of 2.502 g (13.09 mmol) of **7** in 8 mL of  $\text{H}_2\text{O}$ . The mixture was stirred protected from light for 2 h. The solution was then filtered into a flask containing 3.676 g (13.75 mmol) of  $\text{Ba}(\text{H}_2\text{PO}_2)_2$ , and the solid rinsed with 6 mL of  $\text{H}_2\text{O}$ . The suspension was stirred for 3 h at room temperature, diluted with 10 mL of abs. EtOH and the volatile materials were removed under reduced pressure. The residue was dissolved in EtOH, stirred with activated carbon, filtered, concentrated, and dried *in vacuo* to afford 1.621 g (9.202 mmol, 70%) of **13** as a light yellow oil;  $T_d = 219\text{ }^\circ\text{C}$  (onset); IR  $\nu$  3385, 3083, 2984, 2295, 2258, 1661, 1572, 1455, 1195, 1082, 1050, 807  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  9.29 (brs, 1H, CH), 7.80 (s, 1H, CH), 7.72 (s, 1H, CH), 7.07 (d,  $J = 451.2\text{ Hz}$ , 2H,  $\text{H}_2\text{PO}_2$ ), 4.20 (q,  $J = 7.3\text{ Hz}$ , 2H,  $\text{CH}_2$ ), 3.85 (s, 3H,  $\text{CH}_3$ ), 1.41 (t,  $J = 7.3\text{ Hz}$ , 3H,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR  $\delta$  136.4, 123.5, 121.9, 44.0, 35.6, 15.0;  $^{31}\text{P}$  NMR  $\delta$  -5.61 (s,

H<sub>2</sub>PO<sub>2</sub>); elemental analysis calcd (%) for C<sub>6</sub>H<sub>13</sub>N<sub>2</sub>O<sub>2</sub>P + 1 H<sub>2</sub>O (194.17): C 37.11, H 7.79, N 14.43; found: C 37.44, H 7.63, N 14.15.

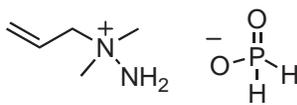


**3-Allyl-1-methylimidazolium hypophosphite, 14.** According to general protocol A, 2.109 g (6.764 mmol) of Ag<sub>2</sub>SO<sub>4</sub>, 2.693 g (13.26 mmol) of **8**, and 3.722 g (13.92 mmol) of Ba(H<sub>2</sub>PO<sub>2</sub>)<sub>2</sub> provided 1.749 g (9.295 mmol, 70%) of **14** as a tan oil; T<sub>d</sub> = 200 °C (onset); IR  $\nu$  3370, 3076, 2859, 2251, 2102, 1646, 1570, 1197, 1050, 805 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  9.29 (brs, 1H, CH), 7.75 (s, 1H, CH), 7.73 (s, 1H, CH), 7.07 (d, *J* = 451.8 Hz, 2H, H<sub>2</sub>PO<sub>2</sub>), 6.11-5.98 (m, 1H, CH), 5.37-5.27 (m, 2H, 2 x CH), 4.85 (d, *J* = 6.0 Hz, 2H, CH<sub>2</sub>), 3.87 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR  $\delta$  136.8, 131.8, 123.7, 122.3, 120.1, 50.7, 35.7; <sup>31</sup>P NMR  $\delta$  -5.52 (s, H<sub>2</sub>PO<sub>2</sub>); elemental analysis calcd (%) for C<sub>7</sub>H<sub>13</sub>N<sub>2</sub>O<sub>2</sub>P + 0.5 H<sub>2</sub>O (197.17): C 42.64, H 7.16, N 14.21; found: C 42.23, H 7.12, N 13.83.



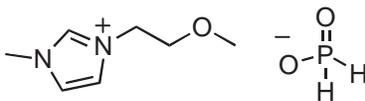
**3-Butyl-1-methylimidazolium hypophosphite, 15.** According to general protocol A, 1.273 g (4.083 mmol) of Ag<sub>2</sub>SO<sub>4</sub>, 1.753 g (8.000 mmol) of **9**, and 2.246 g (8.403 mmol) of Ba(H<sub>2</sub>PO<sub>2</sub>)<sub>2</sub> provided 1.301 g (6.371 mmol, 80%) of **15** as a colorless oil; T<sub>d</sub> = 214 °C (onset); IR  $\nu$  3372, 3065, 2961, 2870, 2247, 1570, 1464, 1200, 1082, 1051, 805 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  9.38 (brs, 1H, CH), 7.82 (s, 1H, CH), 7.74 (s, 1H, CH), 7.07 (d, *J* = 450.0 Hz,

2H, H<sub>2</sub>PO<sub>2</sub>), 4.17 (t, *J* = 7.12 Hz, 2H, CH<sub>2</sub>), 3.86 (s, 3H, CH<sub>3</sub>), 1.81-1.71 (m, 2H, CH<sub>2</sub>), 1.32-1.19 (m, 2H, CH<sub>2</sub>), 0.90 (t, *J* = 7.34 Hz, CH<sub>3</sub>); <sup>13</sup>C NMR δ 136.8, 123.6, 122.3, 48.4, 35.7, 31.3, 18.7, 13.2; <sup>31</sup>P NMR δ -5.48 (s, H<sub>2</sub>PO<sub>2</sub>); elemental analysis calcd (%) for C<sub>8</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub>P + 1 H<sub>2</sub>O (222.22): C 43.24, H 8.62, N 12.61; found: C 43.80, H 8.57, N 12.56.



**16**

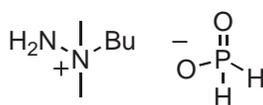
**1-Allyl-1,1-dimethylhydrazinium hypophosphite, 16.** According to general protocol A, 2.018 g (6.472 mmol) of Ag<sub>2</sub>SO<sub>4</sub>, 1.734 g (12.69 mmol) of **10**, and 3.561 g (13.32 mmol) of Ba(H<sub>2</sub>PO<sub>2</sub>)<sub>2</sub> provided 1.336 g (8.040 mmol, 63%) of **16** as a yellow oil; *T<sub>d</sub>* = 171 °C (onset); IR ν 3379, 3237, 3123, 2296, 1646, 1478, 1188, 1083, 1048, 809 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 7.09 (d, *J* = 466.2 Hz, 2H, H<sub>2</sub>PO<sub>2</sub>), 6.14-6.00 (m, 1H, CH), 5.60-5.55 (m, 2H, 2 x CH), 4.14 (d, *J* = 7.2 Hz, 2H, CH<sub>2</sub>), 3.20 (s, 6H, 2 x CH<sub>3</sub>); <sup>13</sup>C NMR δ 126.8, 126.6, 69.5, 54.5; <sup>31</sup>P NMR δ -5.11 (s, H<sub>2</sub>PO<sub>2</sub>); elemental analysis calcd (%) for C<sub>5</sub>H<sub>15</sub>N<sub>2</sub>O<sub>2</sub>P + 0.5 H<sub>2</sub>O (175.17): C 34.28, H 9.21, N 15.99; found: C 34.15, H 9.16, N 15.75.



**17**

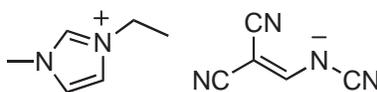
**3-(2-Methoxyethyl)-1-methylimidazolium hypophosphite, 17.** According to general protocol A, 936 mg (3.00 mmol) of Ag<sub>2</sub>SO<sub>4</sub>, 1.30 g (5.88 mmol) of **11**, and 1.65 g (6.17 mmol) of Ba(H<sub>2</sub>PO<sub>2</sub>)<sub>2</sub> provided 968 mg (4.69 mmol, 80%) of **17** as a yellow oil; *T<sub>d</sub>* = 217

$^{\circ}\text{C}$  (onset); IR  $\nu$  3413, 3151, 3096, 2344, 2309, 1644, 1570, 1454, 1191, 1048, 812  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  9.40 (brs, 1H, CH), 7.79-7.76 (m, 2H, 2 x CH), 7.09 (d,  $J = 452.7$  Hz, 2H,  $\text{H}_2\text{PO}_2$ ), 4.38 (t,  $J = 4.8$  Hz, 2H,  $\text{CH}_2$ ), 3.88 (s, 3H,  $\text{CH}_3$ ), 3.69 (t,  $J = 5.0$  Hz, 2H,  $\text{CH}_2$ ), 3.26 (s, 3H,  $\text{OCH}_3$ );  $^{13}\text{C}$  NMR  $\delta$  137.1, 123.4, 122.6, 69.6, 58.0, 48.5, 35.6;  $^{31}\text{P}$  NMR  $\delta$  -5.36 (s,  $\text{H}_2\text{PO}_2$ ); elemental analysis calcd (%) for  $\text{C}_7\text{H}_{15}\text{N}_2\text{O}_3\text{P} + 1 \text{H}_2\text{O}$  (224.19): C 37.50, H 7.64, N 12.50; found: C 37.71, H 7.46, N 12.33.



**18**

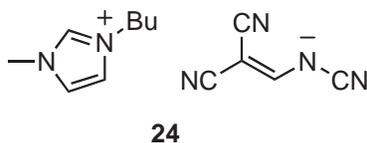
**1-Butyl-1,1-dimethylhydrazinium hypophosphite, 18.** According to general protocol A, 441 mg (1.41 mmol) of  $\text{Ag}_2\text{SO}_4$ , 675 mg (2.77 mmol) of **12**, and 778 mg (2.91 mmol) of  $\text{Ba}(\text{H}_2\text{PO}_2)_2$  provided 405 mg (2.22 mmol, 80%) of **18** as a waxy, hygroscopic solid;  $T_d = 181$   $^{\circ}\text{C}$  (onset, shoulder),  $T_d = 202$   $^{\circ}\text{C}$  (onset, major); IR  $\nu$  3362, 3220, 3096, 2963, 2876, 2255, 1652, 1479, 1193, 1050, 916, 806  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  7.07 (d,  $J = 460.50$  Hz, 2H,  $\text{H}_2\text{PO}_2$ ), 6.36 (brs, 2 H,  $\text{NH}_2$ ), 3.46-3.40 (m, 2H,  $\text{CH}_2$ ), 3.21 (s, 6H, N- $\text{CH}_3$ ), 1.77-1.66 (m, 2H,  $\text{CH}_2$ ), 1.36-1.24 (m, 2H,  $\text{CH}_2$ ), 0.92 (t, 3H,  $J = 7.33$  Hz,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR  $\delta$  67.4, 54.9, 24.1, 19.1, 13.5;  $^{31}\text{P}$  NMR  $\delta$  -4.64 (s,  $\text{H}_2\text{PO}_2$ ); elemental analysis calcd (%) for  $\text{C}_6\text{H}_{19}\text{N}_2\text{O}_2\text{P} + 1 \text{H}_2\text{O}$  (200.22): C 35.99, H 10.57, N 13.99; found: C 36.02, H 10.07, N 13.76.



**23**

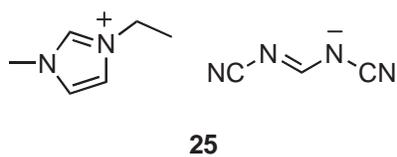
**3-Ethyl-1-methyl-imidazolium N-(2,2-dicyanovinyl)cyanamide, 23: General protocol**

**B:** To a solution of 1.320 g (9.423 mmol) of **20** in 25 mL of H<sub>2</sub>O at room temperature protected from light was added a solution of 1.600 g (9.419 mmol) of AgNO<sub>3</sub> in 15 mL of H<sub>2</sub>O. The resulting suspension was stirred for 1 h, filtered, and rinsed with H<sub>2</sub>O. The silver salt was then suspended in a solution of 1.500 g (7.851 mmol) of **7** in 30 mL of H<sub>2</sub>O. After stirring overnight at room temperature protected from ambient light, the mixture was filtered, rinsed with abs. EtOH, and concentrated under reduced pressure. The residue was dissolved in abs. EtOH, stirred with activated carbon, filtered, concentrated and dried *in vacuo* to afford 1.555 g (6.813 mmol, 87%) of **23** as an amber oil;  $T_d = 205$  °C (onset); IR  $\nu$  3472, 3153, 3111, 2196, 2164, 1549, 1324, 1169 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  9.09 (s, 1H, CH), 8.08 (brs, 1H, CH), 7.75 (s, 1H, CH), 7.67 (s, 1H, CH), 4.19 (q,  $J = 7.3$  Hz, 2H, CH<sub>2</sub>), 3.85 (s, 3H, CH<sub>3</sub>), 1.42 (t,  $J = 7.5$  Hz, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  172.5, 154.5, 136.2, 123.5, 121.9, 120.2, 119.0, 116.2, 44.1, 35.7, 15.0; elemental analysis calcd (%) for C<sub>11</sub>H<sub>12</sub>N<sub>6</sub> (228.25): C 57.88, H 5.30, N 36.82; found: C 57.90, H 5.53, N 36.69.

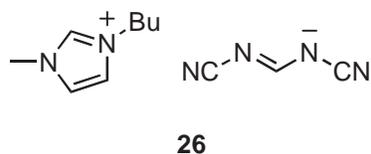


**3-Butyl-1-methyl-imidazolium N-(2,2-dicyanovinyl)cyanamide, 24:** According to general protocol B, 1.967 g (14.04 mmol) of **20**, 2.385 g (14.04 mmol) of AgNO<sub>3</sub>, and 2.564 g (11.70 mmol) of **9** provided 2.667 g (10.41 mmol, 89%) of **24** as an amber oil;  $T_d = 193$  °C (onset); IR  $\nu$  3524, 3151, 3109, 2963, 2193, 2164, 1549, 1323, 1168 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  9.09 (s, 1H, CH), 8.08 (brs, 1H, CH), 7.74 (s, 1H, CH),

7.68 (s, 1H, CH), 4.16 (t, 2H,  $J = 7.2$  Hz, CH<sub>2</sub>), 3.85 (s, 3H, CH<sub>3</sub>), 1.80-1.74 (m, 2H, CH<sub>2</sub>), 1.31-1.23 (m, 2H, CH<sub>2</sub>), 0.91 (t,  $J = 7.4$  Hz, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  172.5, 154.5, 136.4, 123.6, 122.2, 120.2, 119.0, 116.2, 48.5, 35.7, 31.3, 18.7, 13.2; elemental analysis calcd (%) for C<sub>13</sub>H<sub>16</sub>N<sub>6</sub> (256.31): C 60.92, H 6.29, N 32.79; found: C 60.63, H 6.44, N 32.68.

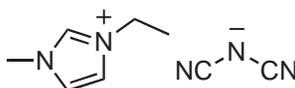


**3-Ethyl-1-methyl-imidazolium *N,N'*-dicyanoformimidamide, 25:** According to general protocol B, 730 mg (6.29 mmol) of **22**, 1.065 g (6.270 mmol) of AgNO<sub>3</sub>, and 1.000 g (5.234 mmol) of **7** provided 966 mg (4.73 mmol, 90%) of **25** as a yellow oil;  $T_m = 3$  °C (onset);  $T_d = 197$  °C (onset); IR  $\nu$  3456, 3151, 3107, 2986, 2159, 1544, 1380, 1341, 1170, 1072 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, external standard)  $\delta$  9.08 (s, 1H, CH), 7.94 (brs, 1H, CH), 7.78 (s, 1H, CH), 7.72 (s, 1H, CH), 4.41 (q,  $J = 7.3$  Hz, 2H, CH<sub>2</sub>), 4.09 (s, 3H, CH<sub>3</sub>), 1.60 (t,  $J = 7.3$  Hz, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>, external standard)  $\delta$  174.0, 136.7, 124.2, 122.5, 121.0, 118.9, 45.4, 36.7, 15.5; elemental analysis calcd (%) for C<sub>9</sub>H<sub>12</sub>N<sub>6</sub> (204.23): C 52.93, H 5.92, N 41.15; found: C 52.70, H 5.92, N 40.86.



**3-Butyl-1-methylimidazolium *N,N'*-dicyanoformimidamide, 26:** According to general protocol B, 755 mg (6.51 mmol) of **22**, 1.105 g (6.505 mmol) of AgNO<sub>3</sub>, and 1.188 g

(5.422 mmol) of **9** provided 1.08 g (4.65 mmol, 86%) of **26** as a yellow oil;  $T_d = 137\text{ }^\circ\text{C}$  (onset, shoulder),  $T_d = 186\text{ }^\circ\text{C}$  (onset, major); IR  $\nu$  3439, 3150, 3108, 2963, 2159, 1544, 1380, 1341, 1169, 1072  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , external standard)  $\delta$  9.21 (brs, 1H, CH), 7.94 (brs, 1H, CH), 7.84 (s, 1H, CH), 7.78 (s, 1H, CH), 4.38 (t,  $J = 6.6$  Hz, 2H,  $\text{CH}_2$ ), 4.11 (s, 3H,  $\text{CH}_3$ ), 1.97-1.93 (m, 2H,  $\text{CH}_2$ ), 1.44-1.37 (m, 2H,  $\text{CH}_2$ ), 0.97 (t,  $J = 7.0$  Hz, 3H,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , external standard)  $\delta$  173.8, 137.2, 124.2, 122.9, 49.8, 36.7, 32.3, 19.7, 13.7; elemental analysis calcd (%) for  $\text{C}_{11}\text{H}_{16}\text{N}_6 + 0.5\text{ H}_2\text{O}$  (241.30): C 54.75, H 7.10, N 34.83; found: C 54.44, H 7.12, N 34.39.



**27**

**3-Ethyl-1-methylimidazolium dicyanamide, 27:**<sup>42</sup> According to general protocol B, 291 mg (3.26 mmol) of sodium dicyanamide, 554 mg (3.26 mmol) of  $\text{AgNO}_3$ , and 565 mg (2.96 mmol) of **7** provided 380 mg (2.14 mmol, 72%) of **27** as a tan oil;  $^1\text{H}$  NMR  $\delta$  9.11 (s, 1H, CH), 7.77 (s, 1H, CH), 7.69 (s, 1H, CH), 4.19 (q,  $J = 7.3$  Hz, 2H,  $\text{CH}_2$ ), 3.85 (s, 3H,  $\text{CH}_3$ ), 1.42 (t,  $J = 7.3$  Hz, 3H,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR  $\delta$  136.2, 123.5, 121.9, 119.1, 44.1, 35.7, 15.0; IR  $\nu$  3484, 3152, 3108, 2240, 2199, 2137, 1638, 1573, 1459, 1314, 1170, 1090, 903, 846, 755, 646, 622, 525  $\text{cm}^{-1}$ .

### Acknowledgment

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