Bicyclic ammonium ionic liquids as dense hypergolic fuels†

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It is critical for hypergolic fuels to be dense so as to enhance the performance of propellants and improve the loading of rockets. Considering that dense elements and bicyclic rings contribute to high density, two series of ionic liquids were prepared with 1-aza-bicyclo[2.2.2]octane-1,4-diazabicyclo[2.2.2]octane-based cations and the dicyanamide anion. Their key properties were measured or calculated as decomposition temperature (208–322 °C), density (1.06–1.31 g cm−3), specific impulse (260.5 to 266.2 s) and ignition delay time (14–1053 ms). Compared with 1-aza-bicyclo[2.2.2]octane-based ionic liquids, the corresponding 1,4-diazabicyclo[2.2.2]octane-based ionic liquids exhibit a lower decomposition temperature, higher density and bigger specific impulse. As expected, 1-methyl-1-azonia-bicyclo[2.2.2]octane and 1-(prop-2-ynyl)-4-aza-1-azonia-bicyclo[2.2.2]octane dicyanamide possess higher densities (1.20 and 1.19 g cm−3) than the corresponding pyrrolidinium and imidazolium-based isomers (1.05 and 1.07 g cm−3), besides hypergolicity with white fuming nitric acid.

Introduction

Hypergolic bipropellants are mainly composed of an energetic fuel and a strong oxidizer. The fuel–oxidizer combinations can simplify engine design and guarantee thousands of ignitions so as to be highly reliable for space crafts during their long lifetime. As to the fuels, hydrazone derivatives with high specific impulse, short ignition delay time and super thrust control, have been widely applied in rockets. Although having high performance, hydrazone derivatives are becoming less and less favorable as propellant fuels because of their high volatility and carcinogenicity. With the enhancement of environmental awareness, it has been an urgent task to develop green alternatives of hydrazone derivatives. Fortunately, energetic ionic liquids (ILs) possess corresponding advantages such as negligible vapor pressure, low toxicity and high thermal/chemical stability, and have potential as candidates of green propellant fuels.

In 2008, the Air Force Research Laboratory reported a series of dicyanamide-based ILs, which first demonstrated that ILs could be spontaneously ignited with white fuming nitric acid (WFNA) and N₂O₄. Since then, hypergolic ILs have gained increasing attention, and become a scientific frontier of propellants. Considering that the anions could play a key role in ignitions, a lot of hypergolic ILs with different anions have been prepared, such as N(CN)₂⁺, BH₄⁻, BH₃CN⁻, BH₂(CN)₂⁻, etc. Most of these studies are focused on shortening the ignition delay times (t الدم) of ILs. However, as hypergolic propellant fuels, it is critical for them to be dense, which not only increases specific impulse (Iₚₛ) values, but also improves efficient fuel loading in rockets. With common cations (imidazolium, pyrrolidinium, pyridinium), densities of BH-based ILs (including BH₄⁻, BH₃CN⁻ and BH₂(CN)₂⁻) are all lower than 1.03 g cm−3 and densities NCN-based ILs (N(CN)₂⁻) are not more than 1.165 g cm−3. Up to now, how to boost the densities of hypergolic ILs is relatively neglected.

In this work, we designed the molecular structures of dense hypergolic ILs following the two basic rules. One is to add the heavy elements to IL molecules. Compared with B atom (diameter, 0.88 Å; relative mass, 10.81; electronegativity, 2.04), N atom is smaller (diameter, 0.74 Å), heavier (relative mass, 14.01) and stronger (electronegativity, 3.04). Thus, the N-based anion (N(CN)₂⁻) was selected rather than B-based anions (BH₄⁻, BH₃CN⁻, BH₂(CN)₂⁻) in targeted ILs. The other is to form polycyclic rings in IL molecules. The tension of polycyclic rings can shorten the bond lengths so as to make the targeted molecules denser. Based on the above two ideas, we synthesized 1-aza-bicyclo[2.2.2]octane-based (ABCO) and 1,4-diazabicyclo[2.2.2]octane-based (DABCO) ILs. The structures of ILs were confirmed by NMR, IR spectroscopies, and electrospray ionization mass spectrometry (ESI-MS). The properties of ILs were fully discussed also. Indeed, these ILs exhibit higher densities...
Yield, 96.6%; colorless liquid: 1H NMR (600 MHz, [D₆]DMSO): δ = 0.88 (t, 3H; CH₃), 1.65 (m, 2H; CH₂), 1.85 (s, 6H; CH₂), 2.06 (t, H; CH), 3.04 (m, 2H; CH₂), 3.35 ppm (t, 6H; CH₃); ¹³C NMR (151 MHz, [D₆]DMSO): δ = 17.84, 23.50, 51.37, 55.92, 119.15 ppm; IR (KBr): ν = 3449, 2961, 2886, 2233, 2238, 2209, 2135, 1648, 1492, 1469, 1383, 1339, 1122, 952, 832, 523 cm⁻¹; HRMS (ESI): m/z calcd for cation C₁₅H₂₀N⁺: 226.1375 [M⁺], found: 226.1370 [M⁺], m/z calcd for C₁₅H₂₀N⁺: 226.1375 [M⁺], found: 226.1370 [M⁺].

1-(Prop-2-ynyl)-azonia-bicyclo[2.2.2]octane dicyanamide (14a). Yield, 94.3%; brown solid: ¹H NMR (600 MHz, [D₆]DMSO): δ = 1.90 (s, 6H; CH₂), 2.08 (t, H; CH), 3.44 (t, 6H; CH₂), 4.05 (s, H; CH), 4.20 ppm (d, 2H; CH); ¹³C NMR (151 MHz, [D₆]DMSO): δ = 19.02, 23.34, 52.83, 54.12, 72.20, 83.40, 119.16 ppm; IR (KBr): ν = 3504, 3233, 3151, 3019, 3002, 2960, 2886, 2240, 2194, 2134, 1496, 1318, 1204, 1121, 923, 892, 833, 714, 663, 521 cm⁻¹; HRMS (ESI): m/z calcd for cation C₁₈H₁₆N⁺: 308.1344 [M⁺], found: 308.1341 [M⁺]; m/z calcd for C₁₈H₁₆N⁺: 308.1344 [M⁺], found: 308.1341 [M⁺].

1-(Cyanoethyl)-azonia-bicyclo[2.2.2]octane dicyanamide (15a). Yield, 97.1%; white solid: ¹H NMR (600 MHz, [D₆]DMSO): δ = 1.92 (d, 6H; CH₂), 2.10 (t, H; CH), 3.54 (t, 6H; CH₂), 4.71 ppm (s, 2H; CH); ¹³C NMR (151 MHz, [D₆]DMSO): δ = 18.54, 23.25, 50.60, 55.54, 111.92, 119.16 ppm; IR (KBr): ν = 3555, 2957, 2885, 2287, 2242, 2199, 2141, 1647, 1492, 1465, 1384, 1322, 1211, 1104, 1086, 1045, 960, 833, 667, 525 cm⁻¹; HRMS (ESI): m/z calcd for cation C₂₀H₁₈N₂⁺: 313.1230 [M⁺], found: 313.1230 [M⁺]; m/z calcd for C₂₀H₁₈N₂⁺: 313.1230 [M⁺], found: 313.1230 [M⁺].

1-(2-Hydroxyethyl)-azonia-bicyclo[2.2.2]octane dicyanamide (16a). Yield, 95.2%; white solid: ¹H NMR (600 MHz, [D₆]DMSO): δ = 1.19 (t, 3H; CH₃), 1.85 (s, 6H; CH₂), 2.06 (m, H; CH), 3.15 (m, 2H; CH₂), 3.33 ppm (t, 6H; CH₃); ¹³C NMR (151 MHz, [D₆]DMSO): δ = 7.43, 19.13, 23.35, 53.23, 58.63, 119.18 ppm; IR (KBr): ν = 3442, 2958, 2886, 2235, 2196, 1364, 1313, 1106, 1094, 961, 523 cm⁻¹; HRMS (ESI): m/z calcd for cation C₂₂H₂₀N⁺: 328.1543 [M⁺], found: 328.1540; m/z calcd for C₂₂H₂₀N⁺: 328.1543 [M⁺], found: 328.1540.
$\delta = 1.85 \text{ (s, 6H; } CH_2)$, 2.05 (t, H; CH), 3.21 (t, 2H; CH$_2$), 3.45 (t, 6H; CH$_2$), 3.80 (d, 2H; CH$_2$), 5.23 ppm (t, H; CH$_2$); $^{13}$C NMR (151 MHz, [D$_6$]DMSO): $\delta = 19.12, 23.45, 54.49, 54.62, 65.23, 119.16$ ppm; IR (KBr): $\nu = 3491, 3014, 2978, 2934, 2888, 2234, 2195, 2131, 1409, 1466, 1425, 1384, 1308, 1254, 1112, 994, 925, 833, 517$ cm$^{-1}$; HRMS (ESI): $m/z$ calcd for cation C$_9$H$_{17}$NO$: 156.1383$ [M]$^+$, found: 156.1412; $m/z$ calcd for C$_{2}N_3$: 66.0096 [M]$^{-}$, found: 66.0058.

1-Methyl-4-aza-1azonia-bicyclo[2.2.2]octane dicyanamide (9b). Yield, 88.5%; white solid; $^1$H NMR (600 MHz, [D$_6$]DMSO): $\delta = 2.95$ (s, 3H; CH$_3$), 3.02 (t, 6H; CH$_2$), 3.25 ppm (t, 6H; CH$_2$); $^{13}$C NMR (600 MHz, [D$_6$]DMSO): $\delta = 44.59, 51.60, 52.68, 71.70, 66.70, 524$ cm$^{-1}$; IR (KBr): $\nu = 2972, 2900, 2890, 2217, 2189, 2133, 1462, 1377, 1309, 1056, 994, 884, 843, 795, 673, 525$ cm$^{-1}$; HRMS (ESI): $m/z$ calcd for cation C$_9$H$_{17}$N$_2$: 141.1386 $[M]^+$, found: 141.1374; $m/z$ calcd for C$_{2}N_3$: 66.0098 [M]$^{-}$, found: 66.0062.

1-Butyl-4-aza-1azonia-bicyclo[2.2.2]octane dicyanamide (12b). Yield, 94.1%; white solid; $^1$H NMR (600 MHz, [D$_6$]DMSO): $\delta = 0.91$ (t, 3H; CH$_3$), 1.67 (m, 2H; CH$_2$), 3.12 (m, 2H; CH$_2$), 3.25 ppm (t, 6H; CH$_2$); $^{13}$C NMR (600 MHz, [D$_6$]DMSO): $\delta = 16.62, 14.63, 44.66, 51.56, 64.66, 119.07$ ppm; IR (KBr): $\nu = 2972, 2900, 2217, 2197, 2137, 1489, 1486, 1190, 1097, 1057, 992, 944, 842, 794, 755, 667, 524$ cm$^{-1}$; HRMS (ESI): $m/z$ calcd for cation C$_{10}$H$_{21}$N$_2$: 152.1183 $[M]^+$, found: 152.1182; $m/z$ calcd for C$_{2}N_3$: 66.0098 [M]$^{-}$, found: 66.0067.

1-(Cyanomethyl)-4-aza-1azonia-bicyclo[2.2.2]octane dicyanamide (15b). Yield, 89.1%; white solid; $^1$H NMR (600 MHz, [D$_6$]DMSO): $\delta = 3.10$ (t, 6H; CH$_2$), 3.45 (t, 6H; CH$_2$), 4.80 ppm (s, 2H; CH$_2$); $^{13}$C NMR (151 MHz, [D$_6$]DMSO): $\delta = 44.47, 50.32, 52.69, 111.51, 119.06$ ppm; IR (KBr): $\nu = 3319, 3021, 2961, 2892, 2239, 2198, 2136, 1463, 1376, 1318, 1103, 1056, 993, 944, 840, 795, 669, 523$ cm$^{-1}$; HRMS (ESI): $m/z$ calcd for cation C$_{8}$H$_{15}$N$_2$: 127.1230 [M]$^+$, found: 127.1245; $m/z$ calcd for C$_{2}N_3$: 66.0098 [M]$^{-}$, found: 66.0063.

1-(2-Hydroxyethyl)-4-aza-1azonia-bicyclo[2.2.2]octane dicyanamide (16b). Yield, 97.6%; white solid; $^1$H NMR (600 MHz, [D$_6$]DMSO): $\delta = 3.03$ (t, 6H; CH$_2$), 3.31 (m, 2H; CH$_2$), 3.37 (t, 6H; CH$_2$), 3.85 (t, 2H; CH$_2$), 5.28 ppm (s, 6H; CH$_2$); $^{13}$C NMR (151 MHz, [D$_6$]DMSO): $\delta = 44.65, 52.41, 54.09, 65.30, 119.06$ ppm; IR (KBr): $\nu = 3489, 3139, 3001, 2966, 2933, 2892, 2232, 2194, 1423, 1459, 1373, 1307, 1103, 1058, 991, 903, 886, 834, 793, 799, 651, 409$ cm$^{-1}$; HRMS (ESI): $m/z$ calcd for cation C$_{9}$H$_{17}$N$_2$O$: 155.1543$ [M]$^+$, found: 155.1540; $m/z$ calcd for C$_{2}N_3$: 66.0098 [M]$^{-}$, found: 66.0065.

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X-ray analysis

The single crystal x-ray diffraction data collections were carried out on a Rigaku AFC-10/Navos 524+ CCD diffractometer with graphite-monochromated Mo K$\alpha$ radiation ($\lambda = 0.71073$ Å) using the multi-scan technique. The structures were determined by direct methods using SHELXS-97 and refined by full-matrix least-squares procedures on $^F$ with SHELXL-97. All non-hydrogen atoms were obtained from the difference Fourier map and subject to anisotropic refinement by full-matrix least squares on $^F$.

A colorless crystal of 15b which suitable for single crystal X-ray diffraction was obtained by slow evaporation of its solutions with the mixture of CH$_3$OH and ethyl acetate. The structure is shown in the Fig. 1. According to the X-ray crystallographic analysis, 15b crystallized in monoclinic space group P2$_1$2$_1$ with a calculated density of 1.36 g cm$^{-3}$ (−120.2 °C). The crystallographic data and refinement details are given in Table 1.

Calculations procedure

Calculations were performed with the Gaussian 09 suite of programs. The geometric optimization of the structures was carried out by using the B3LYP functional with the 6-31+G** basis set, and single energy points were calculated at the MP2/6-311+G** level. For the cations of ILs, their optimized structures were characterized to be true local-energy minima on the potential-energy surface without imaginary frequencies. The molecular volumes were calculated by keyword “volume”. Electron density is 0.001 electrons per bohr$^3$, but the random points were increased to 2000. Heats of formation (HOF) of ILs are calculated based on the Born–Haber energy cycle.
HOF of the cations were obtained by using the method of isodesmic reactions. HOF of the anion (N(CN)₂⁻) is literature values. The enthalpy of reaction $\Delta H_r^\circ$ was obtained by combining the MP2/6-311+G** energy difference for the reaction, the scaled zero-point energies, and other thermal factors. Based on HOF and density values, the specific impulses of ILs were calculated using Explo 5 program.

### Results and discussion

The ABCO and DABCO-based ILs were synthesized by a two-step method including quaternization and metathesis reactions (Scheme 1). The resulting ILs were characterized by $^1$H and $^{13}$C NMR, IR spectroscopies, and ESI-MS, which well support the structures of ILs. The properties of ILs (9–16) were measured or calculated (Table 2), including phase transition temperature ($T_m$ or $T_g$), decomposition temperature ($T_d$), viscosity ($\eta$), density ($\rho$), ignition delay time ($t_{id}$), heat of formation ($\Delta H_f$) and specific impulse ($I_{sp}$).

Thermal properties of ILs mainly include $T_m$ (or $T_g$) and $T_d$, these were determined by differential scanning calorimetric (DSC) measurements with a heating rate of 10 °C min⁻¹. As shown in Table 2, the ABCO-based ILs of 10a, 12a, 13a and 16a melt below room temperature as 2.2, 27.7, 16.5 and 19.7 °C, respectively. For the DABCO-based ILs, 12b, 13b and 16b is liquid at room temperature with $T_m$ (or $T_g$) as 2.0, −80.8 and −71.8 °C. The $T_d$ of ABCO-based ILs range from 230.7 (15a) to 322.0 °C (10a), and DABCO-based ILs from 207.5 (15b) to 281.3 °C (9b). Based on Fig. 2, it is clearly seen that ABCO-based ILs exhibit higher thermal stabilities than DABCO-based ILs. Moreover, the ILs with alkyl substituents (−CH₃, −C₂H₅, −C₃H₇ and −C₄H₉) are thermally stable up to 275.2 °C while the ILs with substituents (−CH₂CCH and −CH₂CN) become much less stable with $T_d$ as 236.0 (14a), 208.2 (14b), 230.7 (15a) and 207.5 °C (15b), respectively.

Density is the key parameter of high-density-energy materials (HDEM) like propellant fuels, which affects $I_{sp}$ values of propellants and fuel loading of rockets. For the resulting N-based ILs, densities are all bigger than 1.00 g cm⁻³ varying from 1.06 to 1.31 g cm⁻³ (Table 2), whereas the densities of BH-anion ILs are all less than 1.03 g cm⁻³ such as [Bmim]BH₄.

### Table 1 Crystallographic data and structure determination parameters for 15b

| Parameter | Value |
|-----------|-------|
| Formula   | C₄₃H₃₇N₆ |
| CCDC number | 1509452 |
| Cristal size | 0.25 × 0.21 × 0.20 |
| Mr        | 219.28 |
| Space group | P2₁/n |
| a [Å]     | 7.008(14) |
| b [Å]     | 14.392(3) |
| c [Å]     | 10.586(2) |
| V [Å³]    | 1071.4(4) |
| Z         | 4 |
| $\rho_{calcd}$ [g cm⁻³] | 1.360 |
| $\mu$ [mm⁻¹] | 0.090 |
| $F$ (000) | 468 |
| $a$ [°]   | 90 |
| $b$ [°]   | 97.40(3) |
| $c$ [°]   | 90 |
| $\omega$ [°] | 2.40 to 27.48 |
| Index range | −8 ≤ h ≤ 9 |
|           | −18 ≤ k ≤ 18 |
|           | −13 ≤ l ≤ 12 |
| Reflections collected | 7726 |
| Independent reflections ($R_{int}$) | 2462/0.0378 |
| Data/restraints/parameters | 2462/0/145 |
| GOF on $F^2$ | 1.197 |
| $R_1$ ($I > 2\sigma(I)$) | 0.0643 |
| $wR_2$ ($I > 2\sigma(I)$) | 0.1476 |
| $R_1$ [all data] | 0.0716 |
| $wR_2$ [all data] | 0.1592 |

$R_1 = \sum |F_o| - |F_c|/\sum |F_o|$, $wR_2 = ([\sum w(F_o^2 - F_c^2)^2]/\sum [w(F_o^2)^2]^{1/2})^{1/2}$.

### Scheme 1 Synthesis of ABCO and DABCO-based ILs

![Scheme 1 Synthesis of ABCO and DABCO-based ILs](image)
| ILs | $T_m$ [°C] | $T_d$ [°C] | $\rho'$ [g cm$^{-3}$] | $\mu'$ [mPa s] | $\Delta H_f^o$ [kJ mol$^{-1}$] | IS$^f$ [J] | FS$^f$ [N] | $t_{sp}^b$ [s] | $t_{id}^i$ [ms] |
|-----|------------|------------|----------------------|----------------|--------------------------|---------|--------|-------------|-------------|
| 9a  | 35.3  | 317.8 | 1.16 | — | 154.4 | >60 | >360 | 262.3 | 34 |
| 10a | 2.7  | 322.0 | 1.09 | 50.1 | 136.9 | >60 | >360 | 260.0 | 63 |
| 11a | 76.0 | 320.7 | 1.14 | — | 123.7 | >60 | >360 | 261.6 | 29 |
| 12a | 22.7 | 318.0 | 1.06 | 74.4 | 116.9 | >60 | >360 | 261.3 | 100 |
| 13a | 16.5 | 303.0 | 1.10 | 44.9 | 254.9 | >60 | >360 | 263.1 | 49 |
| 14a | 64.8 | 236.0 | 1.19 | — | 431.1 | >60 | >360 | 265.2 | 14 |
| 15a | 99.0 | 230.7 | 1.27 | — | 356.7 | >60 | >360 | 263.2 | — |
| 16a | 19.7 | 275.5 | 1.16 | 192.0 | 7.8 | >60 | >360 | 262.0 | 186 |
| 9b  | 50.8 | 281.3 | 1.20 | — | 265.8 | >60 | >360 | 263.8 | 39 |
| 10b | 37.0 | 280.8 | 1.17 | — | 240.6 | >60 | >360 | 264.1 | 82 |
| 11b | 55.3 | 276.8 | 1.17 | — | 232.3 | >60 | >360 | 264.2 | 106 |
| 12b | 2.0  | 275.2 | 1.10 | 195.5 | 223.2 | >60 | >360 | 264.0 | 126 |
| 13b | −0.6 | 264.3 | 1.14 | 141.7 | 366.3 | >60 | >360 | 265.1 | 67 |
| 14b | 105.8 | 208.2 | 1.25 | — | 537.5 | >60 | >360 | 266.2 | 20 |
| 15b | 127.8 | 207.5 | 1.31 | — | 469.0 | >60 | >360 | 261.7 | — |
| 16b | −71.8 | 260.2 | 1.22 | 594.3 | 113.9 | >60 | >360 | 260.5 | 1053 |

* Melting point (peak point).  
* Decomposition temperature (peak point).  
* Density (25 °C).  
* Viscosity (25 °C).  
* Heat of formation.  
* Impact sensitivity.  
* Friction sensitivity.  
* Specific impulse (Explo5 v6.02. IL/WFNA = 24/76, w/w; isobaric conditions, equilibrium expansion, 7.0 MPa chamber pressure).  
* Ignition delay time (WFNA).  
* Glass-transition temperature.

![Fig. 2](image1.png) 

Fig. 2 Variation in decomposition temperatures of ILs with R substituents.

![Fig. 3](image2.png) 

Fig. 3 Variation in densities of ILs with R substituents.

(0.91 g cm$^{-3}$)$^{10}$ [Bmim]BH$_2$(CN) (0.97 g cm$^{-3}$)$^{12}$ and [Bmim]BH$_2$(CN)$_2$ (0.96 g cm$^{-3}$)$^{14}$ respectively. As to cations, bicyclic ammonium cations were chosen rather than the common imidazolium-based cations. Based on Fig. 3, it show that DABCO-based ILs possess higher densities than the corresponding ABCO-based ILs. In other words, ILs become denser by substituting C with N atom in the cations. For the same series, the ILs with function groups (–CH, –CN and –OH) exhibit the higher densities as 1.19 (14a), 1.27 (15a), 1.16 (16a), 1.25 (14b), 1.31 (15b) and 1.22 g cm$^{-3}$ (16b), respectively.

Furthermore, 9a and 14b were targeted for the comparison with their corresponding isomers, shown in Fig. 4. With the same N(CN)$_2$ anion, the two pairs of isomers have the different structures of cations. The results show that 9a (1.20 g cm$^{-3}$) and 14b (1.19 g cm$^{-3}$) possess higher densities than the corresponding pyrrolidinium and imidazolium ILs (1.05 and 1.07 g cm$^{-3}$).$^{30,31}$ It indicates that bicyclic ABCO and DABCO cations contribute to the higher densities of ILs than monocyclic pyrrolidinium and imidazolium. Also, the molecular volumes of four cations were calculated (Fig. 4). The molecular volumes of ABCO (1766.554 bohr$^3$) and DABCO (1953.010 bohr$^3$) are smaller than the corresponding pyrrolidinium (1845.543 bohr$^3$) and imidazolium (2021.264 bohr$^3$) isomers, which are consistent with the experiments.

Heats of formation (HOF) of ILs were calculated based on a Born–Haber energy cycle (Scheme 2). The following equations were used for the HOF calculations.$^{32-34}$

$$\Delta H_f^o (\text{ionic salt}, 298 \text{ K}) = \Delta H_f^o (\text{cation}, 289 \text{ K}) + \Delta H_f^o (\text{anion}, 289 \text{ K}) - \Delta H_L$$  

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

$$U_{POT} = \gamma(p_M/M_m)^{1/3} + \delta$$
where $\Delta H_L$ is the lattice energy of ILs, kJ mol$^{-1}$; $U_{\text{LATT}}$ the lattice potential energy, kJ mol$^{-1}$; $\rho_m$ the density, g cm$^{-3}$; $M_m$ the formula mass of salts; the values for $p$, $q$, $\gamma$, and $\delta$ are taken from the literature.$^{32}$

HOF of cations in the gas phase were calculated by using the Gaussian 09 suite of programs, HOF of N(CN)$_2$ was taken from the literature data,$^{29}$ and lattice energies were calculated with eqn (2). From Table 2, it shows that HOF of the ABCO-based and DABCO-based ILs vary from 7.8 to 431.1 and from 113.9 to 537.5 kJ mol$^{-1}$. Based on Fig. 5, it can be seen that HOF changes of the two series of ILs follow the same trend. ILs with –CH$_2$CCH and –CH$_2$CH$_2$OH substituents have the highest and the lowest HOF.

With HOF and density values in hand, the specific impulses were calculated by using Explo 5 program. The specific impulses of ILs range from 260.5 to 266.2 s, especially 14b possessing the biggest value of 266.2 s.

Ignition delay time ($t_{\text{id}}$) is the critical parameter in determining whether fuels could be suitable for hypergolic bipropellants. Droplet tests with WFNA as the oxidizer were employed to measure the $t_{\text{id}}$ of ILs. The typical test procedure is as follows: (1) a droplet of sample IL (about 50 µL) was dropped into a 10 mL glass breaker containing an excess amount of WFNA (1.5 mL); (2) a high-speed camera operating at 1000 frames per s was used to record the $t_{\text{id}}$ which is measured as the time from initial contact between the sample and WFNA to appearance of a flame. A sequence of pictures of 10a and 13a into WFNA was depicted in Fig. 6, thereby demonstrating that the hypergolic ILs can undergo self-sustained combustion after ignition. The results exhibit that the ILs are hypergolic with WFNA except for 15a and 15b (Table 2). Among these ILs, 11a, 14a, and 14b are excellent hypergolic materials with $t_{\text{id}}$ at 29, 14 and 20 ms, respectively. Compared with DABCO-based ILs, ABCO-based ILs exhibit a shorter $t_{\text{id}}$.

However, in the same
series, the changes of IL’s $t_{\text{id}}$ do not follow a clear trend because of the interactive factors including thermal stability, viscosity, reactivity, and so on.

## Conclusion

Two series of ABCO/DABCO-based ILs were synthesized in good yields through quaternization and metathesis reactions. The resulting bicyclic ammonium ILs were confirmed by $^1$H and $^{13}$C NMR, IR spectroscopies, and ESI-MS. Their key properties such as $T_m$ (or $T_g$), $T_d$, $\rho$, $\eta$, $\Delta H_f$, $I_{sp}$ and $t_{\text{id}}$ were measured or calculated. The results show that DABCO-based ILs possess lower decomposition temperature, higher density and bigger specific impulse than the corresponding ABCO-based ILs. Cations with substituents can tune properties of the resulting ILs as follows: (1) the ILs with alkyl substituents ($-\text{CH}_3$, $-\text{C}_2\text{H}_5$, $-\text{C}_3\text{H}_7$, $-\text{C}_4\text{H}_9$) are thermally stable up to 260 °C while the ILs with substituents ($-\text{CH}_2\text{CH}_3$ and $-\text{CH}_2\text{CN}$) become much less stable with $T_d$ as low as 208.2 and 207.5 °C; (2) ILs with dense function groups ($-\text{CCH}$, $-\text{CN}$, $-\text{OH}$) exhibit higher densities as 1.19 (14a), 1.27 (15a), 1.16 (16a), 1.25 (14b), 1.31 (15b), 1.22 g cm$^{-3}$ (16b), respectively; (3) ILs with $-\text{CH}_2\text{CH}_3$ and $-\text{CH}_2\text{OH}$ substituents have the highest and lowest HOF. Moreover, compared with the corresponding pyrrolidinium- and imidazolium-based isomers (1.05 and 1.07 g cm$^{-3}$), 1-methyl-1-azonia-bicyclo[2.2.2]octane and 1-(prop-2-ynyl)-4-aza-1-azonia-bicyclo[2.2.2]octane dicyanamide possess higher densities as 1.20 (9a) and 1.19 g cm$^{-3}$ (14b), which are consistent with our expectation. With $I_{sp}$ (260.5–266.2 s) and $t_{\text{id}}$ (14–1053 ms), the ABCO/DABCO-based ILs have potential applications as the dense bipropellant fuels.

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