

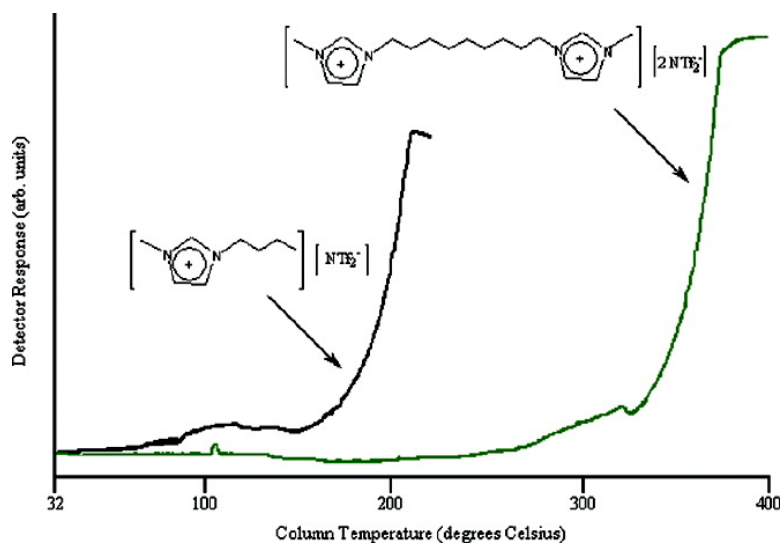
Article

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Structure and Properties of High Stability Geminal Dicationic Ionic Liquids

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Abstract: Thirty-nine geminal dicationic ILs were synthesized and characterized in terms of their surface tensions, densities, melting points, refractive indices, viscosities, and miscibilities with a polar and nonpolar solvent. Two imidazolium or pyrrolidinium cations were joined via different length hydrocarbon linkage chains (from 3 to 12 carbons long). The various geminal dications were paired with up to four different anions. The effect of the dication type, linkage chain, alkyl substituents, and anion type on the physicochemical properties of these compounds was examined. Among the more interesting findings for this class of compounds was that their liquid and thermal stability ranges generally exceeded those of the more conventional, better known ILs. Indeed, this range was from -4 to >400 °C for one of the pyrrolidinium-based geminal dicationic liquids. X-ray crystallography of the smaller solid ionic compounds indicated that there may be a correlation between the configurational degrees of freedom of the ILs and their melting points/glass transition temperatures. In one case, the crystal structure showed that a dicationic moiety had three distinct conformations in an asymmetric unit cell. The solvation properties of the geminal dicationic ILs tend to be similar to those of their monocationic analogues.

Introduction

One of the more rapidly growing areas of chemistry research involves room temperature ionic liquids (RTILs). The wide range of possible cation and anion combinations allows for a large variety of tunable interactions and applications.^{1–18} The uses and applications of RTILs have traversed many areas of chemistry^{1–15} and even areas of biochemistry.^{16–18} Reported thermal stability ranges of 300 °C in some cases,^{19,20} their ability

to solubilize a variety of disparate molecules, and the fact that ionic liquids that are immiscible with both water and nonpolar organic solvents can be synthesized further add to their usefulness.^{21,22} While much work involving RTILs deals with their use as “green” solvents in organic synthesis, their characterization and the understanding of their unique physicochemical and solvation properties are important areas of ongoing investigation. Although the number of ionic liquids described in the literature is growing rapidly, the relationship between their structure/makeup and their physicochemical properties and solvation properties is not well understood. Some research in the field of ionic liquids has explored their fundamental properties in hopes that it would become apparent which cation–anion combinations give rise to specific and/or desired qualities.^{23,24} Thus far, this approach has met with only limited success.

Early work seemed to indicate that the anionic constituents of ionic liquids may have a greater influence on their physical and chemical properties.²⁵ However, this notion may be due, in part, to the fact that the ionic liquids studied contained a variety of different anions, but closely related, structurally similar cations. Indeed, anions, such as halides, possess higher hydrogen bond basicity character ($\text{Cl} > \text{Br} > \text{I}$) and readily hydrogen bond to generally form viscous liquids. This is not to say that only coordinating anions produce viscous liquids; it is well-known that the viscosity of 1-alkyl-3-methylimidazolium

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ionic liquids are found to increase with increasing alkyl chain length even when paired with noncoordinating anions, such as hexafluorophosphate (PF_6^-) and bis(trifluoromethylsulfonyl)imide (NTf_2^-).^{26,27} While the cation and its structure can certainly influence the surface tension, melting point, viscosity, density, and thermal stability as well as interact via dipolar, π - π , and n - π interactions with dissolved molecules, its range of effects has not been studied as extensively as it has for anions.

Despite their touted stability, many of the more common ionic liquids are susceptible to chemical and thermal degradation.^{4,28–30} Recently, it was reported that when 1-butyl-3-methylimidazolium chloride (BMIM-Cl) is exposed to the atmosphere and heated, it begins to turn from a pale yellow to amber color at 120 °C.²⁸ When heated further, the ionic liquid begins to show obvious signs of decomposition at and above 150 °C.²⁸ Most recently, a new class of “high stability ionic liquids” based on bulky cations and triflate anions was introduced, and it was reported that the robustness of some of the more traditional ionic liquids appears to be less than previously thought (in terms of both lower thermal stability and higher volatility).⁴ MacFarlane and co-workers reached similar conclusions via the use of the “step tangent method” for thermogravimetric analysis (TGA) to more accurately determine degradation temperatures of imidazolium-based cations.²⁹ They point out that significant evolution of volatile degradation products takes place well below previously reported degradation temperatures. A maximum operating temperature parameter was proposed to provide a more appropriate estimate of thermal stability using TGA.²⁹

In this work, we present a total of 39 geminal dicationic ionic liquids comprised of both imidazolium- and pyrrolidinium-based dications containing relatively inert anions. They utilize both short and long linkage chains between the cations as well as other substituents on the cationic moieties. The effects of these structural variations on the physicochemical and solvation properties of this unusual class of ionic liquids are examined. X-ray crystal structures could be obtained on the shorter linkage chain geminal dicationic salts, which tend to be solids at room temperature. In addition to their unique and interesting physicochemical properties, it was found that the geminal ionic liquids exhibit superior thermal stabilities compared to the stabilities of traditional ionic liquids (e.g., the 1-butyl-3-methylimidazolium series). We also extend what may be the most sensitive method for accurately determining the thermal stability of ionic liquids, that is, inverse gas chromatography with flame ionization or mass spectrometric detection.

Experimental Section

Materials. 1-Methylimidazole, 1-methylpyrrolidine, 1-butylpyrrolidine, 1,2-dimethylimidazole, 1-butylimidazole, 1-benzylimidazole, 1,3-dibromopropane, 1,6-dibromohexane, 1,9-dibromononane, 1,12-dibromododecane, 1-bromo-3-chloropropane, hexafluorophosphoric acid, sodium tetrafluoroborate, *N*-lithiotrifluoromethylsulfonimide, silver

nitrate, and phosphorus pentoxide were all purchased from Aldrich (Milwaukee, WI). Hexafluorophosphoric acid is toxic and corrosive and must be handled with care. Acetone, ethyl acetate, and 2-propanol were purchased from Fisher Scientific (Fair Lawn, NJ). Untreated fused silica capillary tubing (0.25 mm i.d.) was purchased from Supelco (Bellefonte, PA).

Methods. Figure 1 and Tables 1 and 2 display the ionic liquids synthesized in this study. Complete synthesis procedures for each series of geminal dicationic ionic liquids are described in the Supporting Information. Compounds **1**, **5**, **9**, and **13** were synthesized by reacting 1 molar equiv of 1,3-dibromopropane, 1,6-dibromohexane, 1,9-dibromononane, and 1,12-dibromododecane, respectively, with 2 molar equiv of 1-methylimidazole at room temperature. Compound **17** was synthesized by reacting 1 molar equiv of 1,9-dibromononane with 2 molar equiv of 1-butylimidazole at room temperature. Compounds **21** and **24** were synthesized by refluxing 1 molar equiv of 1,3-dibromopropane and 1,9-dibromononane, respectively, with 1,2-dimethylimidazole dissolved in 125 mL of 2-propanol for 24 h. Compound **28** was synthesized by refluxing 1 molar equiv of 1,12-dibromododecane with 2 molar equiv of 1-benzylimidazole in 100 mL of 2-propanol for 24 h. After complete reaction (as monitored by NMR), the products were all purified by extraction with ethyl acetate and dried under a P_2O_5 vacuum.

Compounds **31** and **34** were produced by refluxing 1 molar equiv of 1,3-dibromopropane and 1,9-dibromononane, respectively, with 2 equiv of 1-methylpyrrolidine in 100 mL of 2-propanol for 24 h. Compound **37** was synthesized by refluxing 2 molar equiv of 1-butylpyrrolidine with 1 equiv of 1,9-dibromononane in 100 mL of 2-propanol for 24 h. These salts were also extracted with ethyl acetate and dried under vacuum. All metathesis reactions involving *N*-lithiotrifluoromethylsulfonimide, hexafluorophosphoric acid, and sodium tetrafluoroborate were performed using previously published procedures, and detailed instructions are listed in the Supporting Information. Ionic liquids formed via metathesis reactions were tested with silver nitrate to ensure no halide impurities remained.

All 39 ionic liquid samples were characterized using ^1H NMR and electrospray ionization (ESI) mass spectrometry. ^1H NMR spectra (400 MHz) were recorded in deuterated DMSO and are included in the Supporting Information.

Surface tension values were measured at room temperature (23 °C) using a Model 20 DuNuoy Tensiometer (Fisher Scientific, Fair Lawn, NJ) equipped with a platinum–iridium ring with a mean circumference of 5.940 cm and a ring/wire radius of 53.21. Viscosities were determined at 30 °C using a falling ball viscometer (Gilmont, Barrington, IL). The densities of the ionic liquids were determined at 23 °C by placing 2.0 mL of the ionic liquid in a 2.0 mL volumetric tube and weighing the difference. The melting points of the ionic liquids were determined using a Perkin-Elmer Pyris 1 Differential Scanning Calorimeter (Boston, MA). Typical methods involved using a 10 °C/min temperature ramp to determine and identify the first- and second-order thermal transitions. Melting points could not be easily determined for all compounds. For solid compounds, the melting points were verified using a capillary melting point apparatus. Refractive index measurements were conducted at 23 °C using a Bausch & Lomb Abbe-3L refractometer.

The preparation of the capillary columns for inverse gas–liquid chromatographic analysis was performed using a previously described procedure.³¹ All capillary columns had efficiencies between 2100 and 2500 plates/meter. Characterization of the capillary columns and probe molecule descriptions are listed in the Supporting Information. Multiple linear regression analysis (MLRA) and statistical calculations were performed using the Analyse-it program (Microsoft, USA).

Three crystals of the geminal dicationic salts were grown and their structures determined. RTILs are good examples of individual substances that undergo liquid–solid transformation congruently; therefore,

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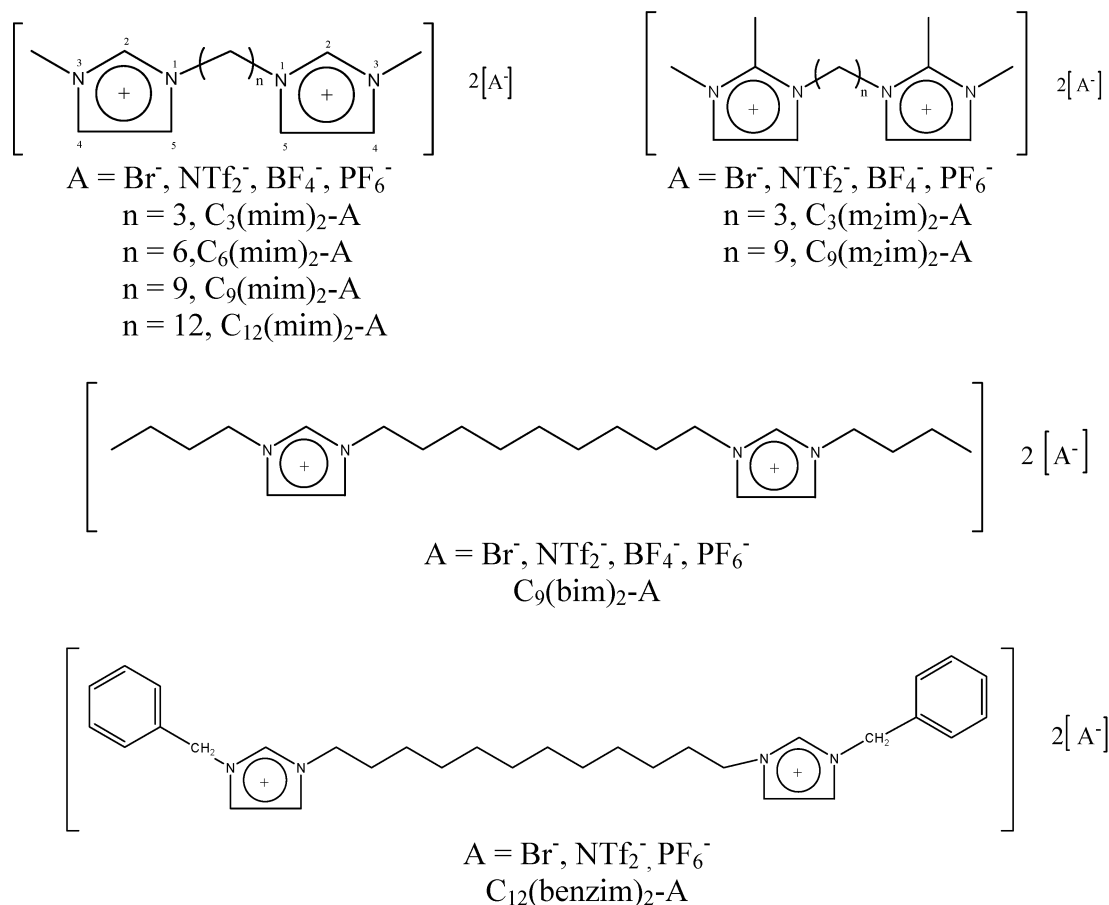
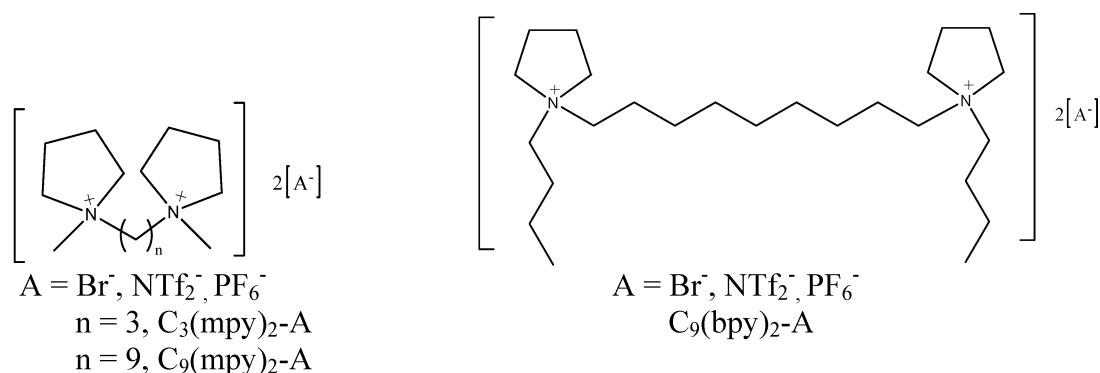
Imidazolium-based Dicationic Ionic LiquidsPyrrolidinium-based Dicationic Ionic Liquids

Figure 1. Structure and abbreviations for 39 imidazolium and pyrrolidinium geminal dicationic ionic liquids evaluated in this study.

traditional crystal growth procedures, such as slow cooling of melt or its zone modification, are preferable. However, these salts have a distinct tendency for supercooling and transforming to plastic modifications or amorphous glasslike states. It was observed that some RTILs slowly transform from solid to liquid at room temperature under the “cold” light (for instance, compound **31**; see Tables 1 and 2 and Figure 1 for numbering system), which brings additional difficulties to crystal growth procedures and handling of the samples. The standard covering of unstable crystal with epoxy glue was successful only for compound **1**. The colorless transparent crystals were found on a surface of glass obtained after slow melting of the liquid. A crystal of **31** was obtained by in situ freezing–melting cycling of the liquid in a 0.5 mm glass

capillary. Initial attempts resulted in transformations to the glass state, however, a good crystal eventually was obtained. X-ray analysis indicated two water solvent molecules per each $\text{C}_3(\text{mpy})_2\text{-Br}$ molecule (this crystal is designated **31h** to indicate the hydrated molecule). The existence of water also was indicated by NMR. To obtain the anhydrous salt, the salt was dried under a high vacuum system containing P_2O_5 . The crystal of **31** was obtained using the procedure described for **31h**.

The crystal evaluations and data collections were performed on a Bruker CCD-1000 diffractometer with $\text{Mo K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation with the detector set to a crystal distance of 5.03 cm. The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 30 frames collected

Table 1. Physicochemical Properties of Imidazolium-Based Dicationic Ionic Liquids^a

| ionic liquid | MW (g/mol) | surface tension (dyn/cm) | D (g/cm ³) | T of solid/liquid transformation (°C) ^b | refractive index | miscibility with heptane ^c | miscibility with water ^c | viscosity (cP) ^d |
|--------------|---|--------------------------|------------------------|--|------------------|---------------------------------------|-------------------------------------|-----------------------------|
| 1 | C ₃ (mim) ₂ -Br | 366.10 | | 162 ^e | | I | M | |
| 2 | C ₃ (mim) ₂ -NTf ₂ | 766.58 | 44.7 | -4 | 1.440 | I | I | 249 |
| 3 | C ₃ (mim) ₂ -BF ₄ | 379.90 | | 117 | | I | M | |
| 4 | C ₃ (mim) ₂ -PF ₆ | 496.22 | | 131 | | I | I | |
| 5 | C ₆ (mim) ₂ -Br | 408.18 | | 155 | | I | M | |
| 6 | C ₆ (mim) ₂ -NTf ₂ | 808.66 | 44.2 | >-14, <-4 | 1.441 | I | I | 362 |
| 7 | C ₆ (mim) ₂ -BF ₄ | 421.98 | | 92 | | I | M | |
| 8 | C ₆ (mim) ₂ -PF ₆ | 538.30 | | 136 | | I | I | |
| 9 | C ₉ (mim) ₂ -Br | 450.26 | 59.6 | 6 | 1.549 | I | M | 1477 |
| 10 | C ₉ (mim) ₂ -NTf ₂ | 850.74 | 43.1 | -14 | 1.442 | I | I | 443 |
| 11 | C ₉ (mim) ₂ -BF ₄ | 464.06 | 61.2 | -4 | 1.469 | I | M | |
| 12 | C ₉ (mim) ₂ -PF ₆ | 580.38 | | 88 | | I | I | |
| 13 | C ₁₂ (mim) ₂ -Br | 492.34 | 57.9 | -17 | 1.540 | I | M | 2008 |
| 14 | C ₁₂ (mim) ₂ -NTf ₂ | 892.82 | 42.3 | -26 | 1.443 | I | I | 606 |
| 15 | C ₁₂ (mim) ₂ -BF ₄ | 506.14 | 55.8 | -19 | 1.503 | I | partially miscible | |
| 16 | C ₁₂ (mim) ₂ -PF ₆ | 622.46 | 53.4 | 9 | 1.436 | I | I | |
| 17 | C ₉ (bim) ₂ -Br | 534.42 | 53.1 | >0, <23 | 1.545 | I | M | >2500 |
| 18 | C ₉ (bim) ₂ -NTf ₂ | 934.90 | 38.0 | >-42, <-8 | 1.446 | I | I | 550 |
| 19 | C ₉ (bim) ₂ -BF ₄ | 548.22 | 50.4 | >-42, <-8 | 1.503 | I | partially miscible | |
| 20 | C ₉ (bim) ₂ -PF ₆ | 664.54 | 48.0 | >0, <23 | 1.439 | I | I | |
| 21 | C ₃ (m ₂ im) ₂ -Br | 394.15 | | 298 | | I | M | |
| 22 | C ₃ (m ₂ im) ₂ -NTf ₂ | 794.63 | | 91 | | I | I | |
| 23 | C ₃ (m ₂ im) ₂ -PF ₆ | 524.27 | | 264 | | I | I | |
| 24 | C ₉ (m ₂ im) ₂ -Br | 478.31 | | 174 | | I | M | |
| 25 | C ₉ (m ₂ im) ₂ -NTf ₂ | 878.79 | 43.5 | >-42, <-8 | 1.448 | I | I | 687 |
| 26 | C ₉ (m ₂ im) ₂ -BF ₄ | 492.11 | 58.1 | >0, <23 | 1.456 | I | M | |
| 27 | C ₉ (m ₂ im) ₂ -PF ₆ | 608.43 | | 130 | | I | I | |
| 28 | C ₁₂ (benzim) ₂ -Br | 644.53 | | 151 | | I | I | |
| 29 | C ₁₂ (benzim) ₂ -NTf ₂ | 1045.01 | 41.5 | >-8, <0 | 1.482 | I | I | |
| 30 | C ₁₂ (benzim) ₂ -PF ₆ | 774.65 | 47.4 | -15 | 1.484 | I | I | |

^a Patents pending. ^b Difficulty arises in determining the melting points of some ionic liquids as they prefer the glass state. Therefore, for some ionic liquids in which the exact melting point/glass transition temperature could not be easily determined, a temperature range is provided. A detailed discussion related to the polymorphic nature of many of these ionic liquids is provided in the section titled "Crystal Structures of Geminal Dicationic Ionic Liquids". ^c M = miscible, I = immiscible. ^d Viscosities measured at 30 °C. ^e This ionic liquid exhibited physicochemical properties very similar to those of the 1-butyl-3-methylimidazolium chloride ionic liquid, making it difficult to fully characterize.

Table 2. Physicochemical Properties of Pyrrolidinium-Based Dicationic Ionic Liquids^a

| ionic liquid | MW (g/mol) | surface tension (dyn/cm) | D (g/cm ³) | T of solid/liquid transformation (°C) ^b | refractive index | miscibility with heptane ^c | miscibility with water ^c | viscosity (cP) ^d |
|--------------|---|--------------------------|------------------------|--|------------------|---------------------------------------|-------------------------------------|-----------------------------|
| 31 | C ₃ (mpy) ₂ -Br | 372.18 | | 51 ^d | | I | M | |
| 32 | C ₃ (mpy) ₂ -NTf ₂ | 772.67 | | 206 | | I | I | |
| 33 | C ₃ (mpy) ₂ -PF ₆ | 502.30 | | 359 | | I | I | |
| 34 | C ₉ (mpy) ₂ -Br | 456.34 | | 257 | | I | M | |
| 35 | C ₉ (mpy) ₂ -NTf ₂ | 856.83 | 42.2 | >-8, <0 | 1.436 | I | I | 502 |
| 36 | C ₉ (mpy) ₂ -PF ₆ | 586.46 | | 223 | | I | I | |
| 37 | C ₉ (bpy) ₂ -Br | 540.50 | | 216 | | I | M | |
| 38 | C ₉ (bpy) ₂ -NTf ₂ | 940.98 | | 84 | | I | I | |
| 39 | C ₉ (bpy) ₂ -PF ₆ | 670.62 | | 249 | | I | I | |

^a Patents pending. ^b Difficulty arises in determining the melting points of some ionic liquids as they prefer the glass state. Therefore, for some ionic liquids in which the exact melting point/glass transition temperature could not be easily determined, a temperature range is provided. A detailed discussion related to the polymorphic nature of many of these ionic liquids is provided in the section titled "Crystal Structures of Geminal Dicationic Ionic Liquids". ^c M = miscible, I = immiscible. ^d Viscosities measured at 30 °C. ^e This ionic liquid exhibited physicochemical properties very similar to those of the 1-butyl-3-methylimidazolium chloride ionic liquid, making it difficult to fully characterize.

at intervals of 0.3° in a 10° range. The final cell constants were calculated from a set of approximately 1000 strong reflections from the actual data collections. The data were obtained using the full sphere routine by collecting four sets of frames with 0.3° scans in ω with an exposure time of 20 s per frame. These data sets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements³² using SADABS software.³³ The structures were solved by direct methods. All atoms were located in

an alternating series of least-squares cycles and difference Fourier maps and were refined in full-matrix anisotropic approximation. All hydrogen atoms were also located objectively and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. A summary of the crystal data for **1**, **31**, and **31h** is given in Table 3. Additional crystallographic data describing hydrogen bonding and other relevant structural data are presented in Tables 4 and 5.

Results and Discussion

Figure 1 gives the structures of the two classes (39 compounds) of geminal dicationic ionic liquids synthesized and characterized in this study. Ionic liquids containing imidazolium-based dications with different alkyl linkage chain lengths

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Table 3. Summary of Crystal Data for **1**, **31h**, and **31**

| | 1 | 31h | 31 |
|---|--|---|--|
| formula | C ₁₁ H ₁₈ Br ₂ N ₄ | C ₁₃ H ₃₂ Br ₂ N ₂ O ₂ | C ₁₃ H ₂₈ Br ₂ N ₂ |
| fw (g) | 366.11 | 408.23 | 372.19 |
| T (K) | 203(2) | 193(2) | 193(2) |
| cryst syst | triclinic | triclinic | orthorhombic |
| space group | <i>P1</i> | <i>P1</i> | <i>Pbca</i> |
| <i>a</i> (Å) | 5.0921(7) | 6.892(1) | 21.367(6) |
| <i>b</i> (Å) | 11.114(1) | 7.024(1) | 19.888(5) |
| <i>c</i> (Å) | 13.560(2) | 10.778(2) | 23.787(6) |
| α (deg) | 76.565(2) | 103.580(3) | 90 |
| β (deg) | 80.455(2) | 93.139(3) | 90 |
| γ (deg) | 84.162(2) | 111.337(3) | 90 |
| <i>V</i> (Å ³) | 734.5(1) | 466.7(1) | 10108(5) |
| <i>Z</i> | 2 | 1 | 24 |
| <i>D</i> (calcd) (Mg/m ³) | 1.655 | 1.452 | 1.467 |
| abs coeff. (mm ⁻¹) | 5.505 | 4.344 | 4.798 |
| <i>F</i> (000) | 364 | 210 | 4560 |
| θ range (deg) | 1.56–28.26 | 1.97–28.30 | 1.64–20.82 |
| reflns collected | 6276 | 4467 | 45036 |
| GOF | 1.056 | 1.006 | 1.067 |
| R1, ^a wR2 ^b [<i>I</i> > 2 σ (<i>I</i>)] | 0.0406, 0.1069 | 0.0295, 0.0722 | 0.0702, 0.1628 |

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$$

Table 4. Relevant Structural Data of Dication [C₃(mpy)₂]²⁺ in **31** and **31h**^a

| | ln 31h | ln 31 , I | ln 31 , II | ln 31 , III |
|---------------------------------------|---------------|------------------|-------------------|--------------------|
| RMS for Plane | | | | |
| mpy(I) | 0.01(1) | 0.01(4) | 0.04(9) | 0.03(9) |
| mpy(II) | 0.03(1) | 0.05(8) | 0.01(8) | 0.01(8) |
| N ₂ C ₃ | 0.03(1) | 0.03(2) | 0.02(8) | 0.1(1) |
| Displacement from the Plane (Å) | | | | |
| N1 from mpy(I) | 0.572(5) | 0.61(2) | 0.44(3) | -0.62(2) |
| N2 from mpy(II) | -0.562(5) | 0.56(2) | -0.63(2) | -0.57(3) |
| C8 from N ₂ C ₃ | 1.152(6) | 1.23(2) | -1.33(2) | -0.98(3) |
| C9 from N ₂ C ₃ | -1.161(6) | 1.17(2) | -1.10(2) | 1.08(3) |
| Interplane Angle (deg) | | | | |
| mpy(I)–N ₂ C ₃ | 37.2(1) | 30.2(6) | 80.0(9) | 43.9(9) |
| mpy(II)–N ₂ C ₃ | 38.1(1) | 38.2(6) | 33.9(9) | 42.1(9) |
| mpy(I)–mpy(II) | 75.2(1) | 8.8(8) | 62.4(9) | 85.9(7) |
| Torsion Angle (deg) | | | | |
| C6C5N1C8 | -61.9(4) | 59.4(9) | -70.1(9) | 59.4(9) |
| C6C7N2C9 | -62.4(4) | -63.3(9) | 62.4(9) | 65.5(9) |

^a The mpy(I)–plane C1C2C3C4, mpy(II)–plane C10C11C12C13, N₂C₃–plane N1C5C6C7N2.

connecting the cations and/or different alkyl substituents on the imidazolium moiety comprise one group of ionic liquids. In most cases, each geminal dicationic entity was paired with four different anions (Br⁻, NTf₂⁻, BF₄⁻, and PF₆⁻) (Figure 1). Pyrrolidinium-based geminal dications with different alkyl linkage chain lengths connecting the cationic and/or different alkyl substituents on the pyrrolidinium group are also shown in Figure 1. For each dication in this class, separate ionic liquids containing three anions (Br⁻, NTf₂⁻, and PF₆⁻) were synthesized. The large number and variety of geminal ionic liquids in this study permitted the evaluation of both cationic and anionic effects.

Tables 1 and 2 give the physicochemical properties for the 39 geminal ionic liquids in this study. Surface tension, density, melting point, and refractive index values were recorded for those samples that were liquids at room temperature. For samples that were solids at room temperature, only the melting point was determined. The miscibility and solubility of all ionic liquids in both heptane and water are indicated as well.

Surface Tension. Plots of surface tension data are shown in Figure 2 for several geminal room temperature ionic liquids.

The length of the alkyl linkage chain separating the dications is observed to have only small effects on the surface tension. Considering ILs **2**, **6**, **10**, and **14** (Table 1) which all contain the bis(trifluoromethylsulfonyl)imide (NTf₂⁻) anion and 3-methylimidazolium cations separated by 3, 6, 9, and 12 carbon linkage chains, respectively, it is apparent that increasing the length of the connecting linkage chain slightly decreases the surface tension (~2.4 dyn/cm). A similar trend is observed for the ionic liquids containing other anions (e.g., BF₄⁻, Br⁻, and PF₆⁻). These results are quite different from those obtained for monocationic ionic liquids by Law et al.³⁴ It was reported that the surface tension for a series of 1-alkyl-3-methylimidazolium-based ionic liquids containing 4, 8, and 12 carbon alkyl groups in the one position of the imidazole ring (refer to Figure 1 for the ring numbering of the imidazolium cation) significantly decreased with increasing alkyl chain length.³⁴ The largest decrease in surface tension was observed between 1-butyl-3-methylimidazolium hexafluorophosphate and 1-dodecyl-3-methylimidazolium hexafluorophosphate in which the total decrease in surface tension was nearly 20 dyn/cm at 330 K. It was also proposed that for a fixed cation at a specific temperature, the compound with the larger anion would possess a higher surface tension. However, our data indicate that this is not true for the geminal dicationic ionic liquids, and if anything, is opposite to what was observed previously for the monocationic-type ionic liquids (Tables 1 and 2).

Ionic liquids **17–20** contain nonpolar butyl groups in the three position of the imidazolium rings. The surface tension values are significantly smaller (11–17%) than those of ILs **9–12** and **13–16** which contain the 3-methylimidazolium dications separated by a nonane and dodecane linkage chain, respectively. These data seem to indicate that the alkyl substituent located on the three position of the imidazolium ring plays a more important role in lowering the surface tension than the alkyl linkage chain that separates the geminal dications.

Replacing hydrogen with a methyl group on the two position of the imidazolium ring (refer to Figure 1 and Table 1) has little effect on the surface tension. In the case of ILs **25** and **26**, containing the 2,3-dimethylimidazolium geminal dications separated by a nonane linkage chain with NTf₂⁻ and BF₄⁻ anions, respectively, the surface tension values are similar to those of the corresponding 3-methylimidazolium dications (ILs **10** and **11**) also containing the nonane connecting chain. Overall, these data indicate that as the alkyl chain in the three position of the imidazolium ring increases in length, the surface tension decreases much more drastically than corresponding increases in the length of the connecting linkage chain.

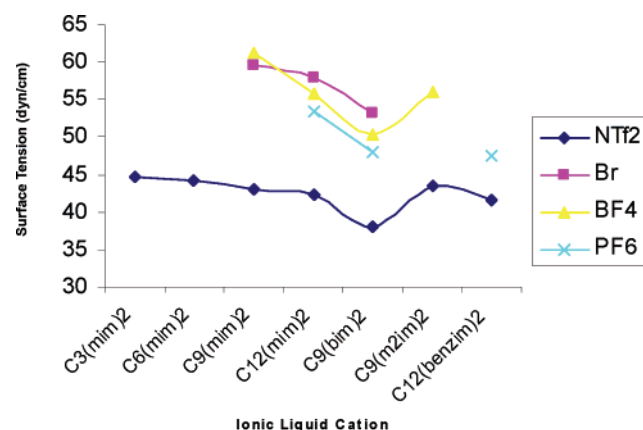
Unfortunately, very little can be said about the effect of the different dications (e.g., imidazolium versus pyrrolidinium) on the overall surface tension due to the fact that most of the pyrrolidinium dications are higher melting salts. However, the 1-methylpyrrolidinium dication (**35**) separated by a nonane linkage chain and with the NTf₂⁻ anion is a room temperature ionic liquid and has a surface tension very similar to that of the corresponding 3-methylimidazolium dications containing the same anion and separated by nonane and dodecane linkage chains (**10** and **14**).

Density. As shown in Figure 3, the densities of the 3-methylimidazolium geminal dicationic ionic liquids were found to

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Table 5. Hydrogen Bonding in Structures **1**, **31h**, and **31** (ESD for All Distances is Better than 0.02 Å)

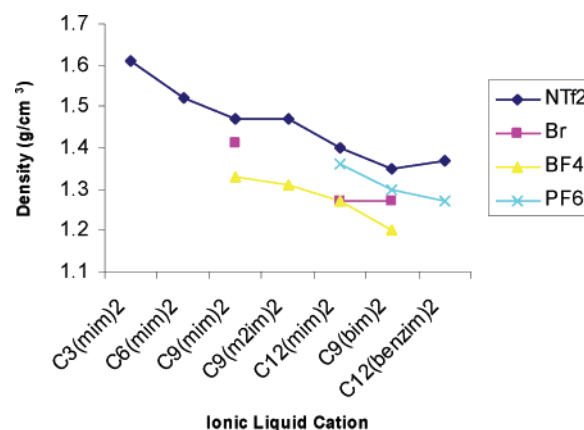
| compound | bond | distance (Å) | symmetry operations | bond | distance (Å) | symmetry operations |
|------------|----------|--------------|---------------------|----------|--------------|---------------------|
| 1 | Br1–H3 | 2.78 | 1–x, 1–y, 2–z | Br1–H5A | 2.85 | –x, 1–y, 2–z |
| | Br1–H7A | 2.99 | x–1, y, z | Br1–H10 | 3.04 | x–1, y, z |
| | Br2–H2 | 2.65 | | Br2–H7B | 2.88 | x–1, y, z |
| | Br2–H9 | 2.93 | –x, 1–y, 1–z | Br2–H11B | 2.90 | –x, 1–y, 1–z |
| 31h | Br1–H4A | 2.86 | x+1, y, z | Br1–H4B | 2.90 | |
| | Br1–H6B | 3.04 | x+1, y, z | Br2–H8C | 2.93 | x, y–1, z–1 |
| | Br2–H9C | 2.98 | x+1, y, z | Br2–H10A | 2.99 | x, y–1, z |
| | Br2–H12B | 3.05 | x+1, y, z | Br1–H2O | 2.45 | |
| | Br1–H3O | 2.46 | | Br2–H4O | 2.41 | |
| | O2–H1O | 1.95 | x–1, y, z | | | |
| 31 | Br1–H5AA | 2.82 | | Br1–H5AB | 2.00 | –x, 1–y, 1–z |
| | Br1–H8AA | 2.98 | –x, 1–y, 1–z | Br1–H5BB | 2.84 | 0.5–x, 0.5+y, z |
| | Br2–H1A | 2.80 | | Br2–H9B | 2.91 | x–0.5, 0.5–y, 1–z |
| | Br2–H11B | 3.03 | x–0.5, 0.5–y, 1–z | Br2–H6AA | 2.94 | |
| | Br2–H8AC | 2.96 | | Br2–H9AB | 2.80 | |
| | Br2–H7BB | 2.73 | | Br3–H6A | 2.97 | |
| | Br3–H8A | 2.80 | | Br3–H7AA | 3.02 | 0.5+x, 0.5–y, 1–z |
| | Br3–H9AA | 2.90 | 0.5+x, 0.5–y, 1–z | Br3–H10C | 2.78 | 0.5+x, 0.5–y, 1–z |
| | Br3–H8BB | 2.82 | x, 0.5–y, 0.5+z | Br3–H9BC | 2.87 | 0.5–x, –y, 0.5+z |
| | Br4–H1B | 3.01 | x, 0.5–y, z–0.5 | Br4–H5A | 2.90 | x, 0.5–y, z–0.5 |
| | Br4–H8AB | 2.89 | x, 0.5–y, z–0.5 | Br4–H12C | 3.02 | |
| | Br4–H13F | 2.87 | | Br5–H7B | 2.98 | 0.5+x, 0.5–y, 1–z |
| | Br5–H13B | 2.86 | 0.5+x, 0.5–y, 1–z | Br5–H2AB | 3.01 | 0.5+x, 0.5–y, 1–z |
| | Br5–H8B | 2.94 | 1–x, –y, 1–z | Br5–H11C | 2.93 | 1–x, y–0.5, 0.5–z |
| | Br5–H4BB | 2.72 | 0.5+x, y, 0.5–z | Br5–H6BB | 2.95 | 0.5+x, y, 0.5–z |
| | Br6–H7A | 2.88 | | Br6–H13A | 2.93 | |
| | Br6–H1AB | 3.00 | | Br6–H6AB | 2.99 | |
| | Br6–H13D | 2.85 | | Br6–H1BA | 2.92 | |
| | Br6–H10E | 2.81 | 0.5–x, 0.5+y, z | | | |

**Figure 2.** Plot illustrating the effect of the cation and anion on the surface tension for dicationic ionic liquids.

be anion dependent and to decrease with increasing length of the hydrocarbon linkage chain. While increases in the linkage chain decrease the density of these ionic liquids, the nature of the anion has a greater influence, with densities in the order of $\text{NTf}_2^- > \text{PF}_6^- > \text{Br}^- > \text{BF}_4^-$ (Tables 1 and 2 and Figure 3). The decrease in density with increasing alkyl chain length has been reported previously for a large series of 1-alkyl-3-methylimidazolium ionic liquids.^{26,27}

When the methyl group on the three position of the imidazolium ring is replaced with a butyl group, the density decreases for all ionic liquids in the series, regardless of the anion (compare **9–12** to **17–20**, Table 1). However, by replacing the hydrogen at the two position of the ring with a methyl group, the density does not appear to change (see **10** and **11** and **25** and **26**, Table 1).

Melting Points. From this study, four main factors were found to affect the melting points of the various geminal

**Figure 3.** Plot illustrating the effect of the cation and anion on the density for dicationic ionic liquids.

dicationic ionic liquids. These factors are (1) the length of the linkage chain separating the geminal dications, (2) the nature of the dication (e.g., imidazolium versus pyrrolidinium), (3) the substituents and their placement on the dication, and (4) the nature of the anion. The effect of each of these factors will be explored in the following discussion.

Considering first the 3-methylimidazolium-based dicationic ionic liquids, longer linkage chains result in a lowering of the melting points. In all cases except for the geminal dications with NTf_2^- anions, which were all liquids regardless of the linkage chain used, compounds containing three and six carbon linkage chains were salts with relatively high melting points. By connecting the 3-methylimidazolium dications with a nonane linkage chain, all samples were room temperature ionic liquids except for the hexafluorophosphate salt, which had a melting point of 88 °C. When the dications were connected by a

dodecane linkage chain, however, all compounds were room temperature ionic liquids.

In addition to the effect of the different length linkage chains connecting the dications, the anion also played a crucial role in determining the melting point. In nearly every case of the imidazolium dications, the melting points increased in the following order: $\text{NTf}_2^- < \text{BF}_4^- < \text{PF}_6^- < \text{Br}^-$ (Tables 1 and 2).

The substituents and their position on the imidazolium ring also affected the melting points of these compounds. Considering **17–20**, which contain the 3-butylimidazolium dications connected by a nonane linkage chain, the melting points were lowered significantly by replacing the methyl group (see **9–12**) with a butyl group. In the case of **12**, which consists of the 3-methylimidazolium dications connected by a nonane linkage chain with the PF_6^- anion, the melting point is decreased by nearly 60 °C by replacing the methyl groups with butyl groups to form **20**. In addition, methylation of the two positions of the imidazolium dications significantly increases the melting point of these compounds (see **21–27**, Table 1). In the case of **21**, which contains the 2,3-dimethylimidazolium dication connected by a propane linkage chain, the melting point is nearly 135 °C higher than that of the corresponding 3-methylimidazolium dication also connected by a propane linkage chain (**1**). Ngo et al. have previously reported the melting points for 1-ethyl-3-methylimidazolium bromide to be 79 °C, whereas the melting point for 1-ethyl-2,3-dimethylimidazolium bromide was found to be 141 °C, a difference of nearly 62 °C.³⁵ While the methyl group on the two position of the imidazolium ring has little effect on the surface tension and density of the geminal dicationic ionic liquids, it is seen to have a profound effect on their melting points, moreso for the dicationic ionic liquids than for the traditional 1-alkyl-3-methylimidazolium ionic liquids.

Finally, by replacing the 3-methylimidazolium dication with the 3-benzylimidazolium dication (**28–30**) and connecting them by a dodecane linkage chain, the melting points appear higher compared to those of the 3-methylimidazolium series, especially in the case of the bromide salt.

In general, the melting points of the pyrrolidinium-based geminal dicationic compounds are significantly higher than those of their corresponding imidazolium analogues. Indeed, only two of their NTf_2^- salts can be considered ionic liquids. However, as will be discussed (vide infra), these particular RTILs may have the greatest thermal stability and other highly useful and interesting properties.

The melting points for the pyrrolidinium-based dication salts show trends similar to those of the imidazolium-based salts. In the two cases involving the propane and nonane linkage chains, the melting point decreases as the linkage chain becomes longer. However, in contrast to the imidazolium-based dications, the pyrrolidinium-based dications are still relatively high melting solids when separated by a nonane alkyl chain. Additionally, substituting a butyl group instead of a methyl group on the quaternary amine of the pyrrolidinium cation causes a decrease in the melting point for the bromide dication but an increase in the melting point for the dications containing bis(trifluoromethylsulfonyl)imide and hexafluorophosphate anions.

From the data in Tables 1 and 2, it appears that longer alkyl linkage chains and long aliphatic substituents on the quaternary amine produce either low melting salts or room temperature ionic liquids. Furthermore, the NTf_2^- salts have melting points

lower than those of corresponding salts with other anions. The contributions of the linkage chain, and other substituents on the geminal dicationic salts, to the number of possible conformational states (and possibly crystal polymorphs) will be considered in the crystal structure section of this paper.

Viscosity. The viscosities of 10 dicationic ionic liquids were measured and are shown in Tables 1 and 2. The dicationic salts with bis(trifluoromethylsulfonyl)imide anions and linear alkyl chains separating the 3-methylimidazolium dications (**2**, **6**, **10**, and **14**) show a nearly linear increase in viscosity with increasing alkyl chain length. This has previously been observed and discussed with traditional monocationic ionic liquids.^{20,27,36,37} As expected, ionic liquids having the NTf_2^- anion were much less viscous than those with bromide anions. Furthermore, it can be observed that the addition of a butyl group on the three position of the imidazolium dication (separated by a nonane linkage chain) increases the viscosity compared to the same ionic liquid with a methyl group at the three position of the imidazolium ring (see **10** and **18**). Due to the fact that most of the pyrrolidinium compounds were high melting salts, IL **35**, consisting of a methyl-substituted pyrrolidinium dication separated by a nonane linkage chain and the NTf_2^- anion, was the only RTIL (of the pyrrolidinium-type) and is observed to possess a viscosity similar to that of the methylimidazolium dication containing a nonane linkage chain (see **10**).

Tables 1 and 2 indicate that the viscosity ranges for the dicationic ionic liquids fall between 240 and 2500 cP at 30 °C. Traditional 1-alkyl-3-methylimidazolium monocationic ionic liquids commonly used in organic synthesis, electrochemical, and analytical studies have reported viscosities ranging from 40 to 11 000 cP, depending on the length of the alkyl chain of the cation.^{27,28} Clearly, the viscosities of the geminal dicationic ionic liquids fall within the same range as most of the traditional, highly useful, monocationic ILs.^{1,27,28} Furthermore, it is known that the viscosities of ionic liquids fall precipitously at the elevated temperatures used in many organic reactions.²⁷ It should be noted that the higher viscosity ionic liquids are preferable for some applications, such as stationary phases for gas–liquid chromatography.^{4,31}

Solubility. The solubility behavior of all 39 geminal dicationic ionic liquids in water and heptane also was explored. None of the dicationic ionic liquids were soluble in heptane. However, most of the ionic liquids containing bromide and tetrafluoroborate anions were soluble in water. Nevertheless, for the tetrafluoroborate ionic liquids, it was found that by using a long linkage chain and a more hydrophobic alkyl substituent on the three position of the imidazole ring (see compounds **15** and **19**), the solubility of the salt in water decreases. In general, the solubility behavior of the geminal dicationic ionic liquids in both water and heptane was quite similar to that of the monocationic ionic liquids, with NTf_2^- and PF_6^- salts being immiscible with water and Br^- and BF_4^- salts being miscible with water.

In the case of the dicationic ionic liquid **28**, which consists of the 3-benzylimidazolium dication separated by a dodecane

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(36) Fannin, A. A.; Floreani, D. A.; King, L. A.; Landers, J. S.; Piersma, B. J.; Stech, D. J.; Vaughn, R. L.; Wilkes, J. S.; Williams, J. L. *J. Phys. Chem.* **1984**, 88, 2614–2621.
(37) Carpio, R. A.; King, L. A.; Lindstrom, R. E.; Nardi, J. C.; Hussey, C. L. *J. Electrochem. Soc.* **1979**, 126, 1644–1650.

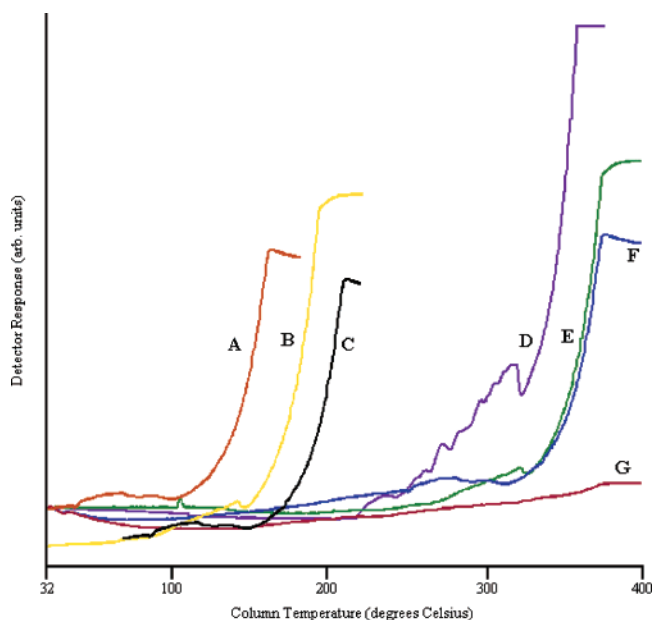


Figure 4. Thermal stability diagram constructed by immobilizing a thin film of the ionic liquid on the wall of fused silica capillary, heating under a constant flow of helium, and detecting volatilization/decomposition products using an ultrasensitive flame ionization detector. The plot illustrates the fact that the geminal dicationic ionic liquids (D–G) have thermal stabilities much higher than those of conventional ionic liquids (A–C). (A) 1-Butyl-3-methylimidazolium chloride (BMIM-Cl); (B) BMIM-PF₆; (C) BMIM-NTf₂; (D) C₉(bpy)₂-NTf₂, **38**; (E) C₉(mim)₂-NTf₂, **10**; (F) C₁₂(benzim)₂-NTf₂, **29**; (G) C₉(mpy)₂-NTf₂, **35**.

linkage chain and bromide anion, the hydrophobicity of the dication evidently overrides the coordinating nature of the bromide anion to make this particular ionic liquid insoluble in water. This is a good example that the properties of the individual cations and anions can be balanced and changed in order to produce ionic liquids (or solids) with the desired properties and characteristics.

Thermal Stability. The thermal stabilities of the geminal dicationic ionic liquids were found to be significantly higher than those that have been observed for many traditional imidazolium-based ionic liquids. Thermal stabilities were measured by immobilizing an approximate 0.15–0.20 μm film of the ionic liquid on the inner wall of a fused silica capillary. The capillary was then heated slowly in an oven, and a very sensitive flame ionization detector (or mass spectrometer) was used to detect any volatilization or decomposition of the ionic liquid. There are several advantages of using this setup to measure the thermal stabilities of ionic liquids. The thermal stability is measured in the absence of oxygen by purging the capillary with a continuous flow of an inert gas, such as helium, hydrogen, or nitrogen. In addition, the detection limit of the detector is very low (~ 10 ppm to 10 ppb, depending on the compound), allowing for very sensitive detection of any thermally induced decomposition/volatilization products from the ionic liquid. Finally, this approach can use mass spectrometry detection to determine the likely volatilization/decomposition products.

Figure 4 shows a thermal stability diagram containing three traditional ionic liquids and four dicationic ionic liquids. The traditional ionic liquids have thermal stabilities ranging from 145 (1-butyl-3-methylimidazolium chloride) to 185 °C (1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide). How-

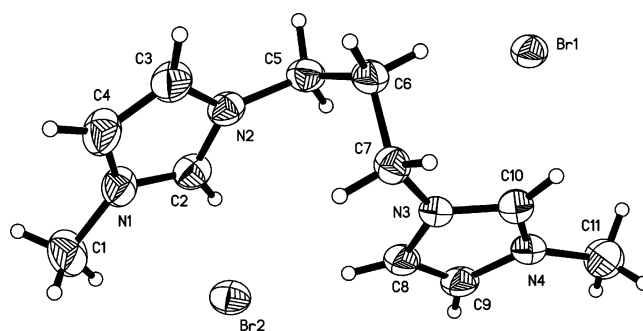


Figure 5. ORTEP diagram of molecule **1** showing the atomic numbering.

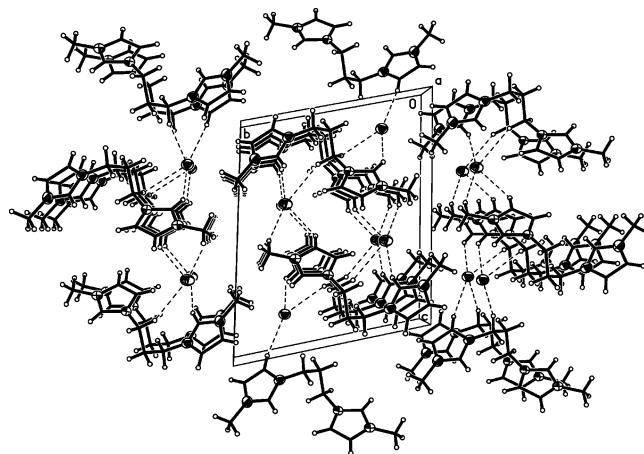


Figure 6. Packing diagram of **1** showing stacks along short *a*-axis and hydrogen bonding.

ever, the thermal stabilities of the geminal dicationic ionic liquids are observed to range from 330 to 400 °C, depending on the cation used. The highest thermal stability (>400 °C) was obtained with the C₉(mpy)₂-NTf₂ (**35**) ionic liquid (1-methylpyrrolidinium dication separated by a nonane linkage chain), while the lowest volatilization/decomposition temperature (330 °C) was observed for the C₉(bpy)₂-NTf₂ (**38**, 1-butylpyrrolidinium dication separated by a nonane linkage chain) ionic liquid. The maximum thermal stabilities of C₉(mim)₂-NTf₂ (**10**, 1-methylimidazolium dication) and C₁₂(benzim)₂-NTf₂ (**29**, 3-benzylimidazolium dication separated by a dodecane linkage chain) were observed to be nearly identical (350–360 °C). In most cases, slight to moderate decomposition/volatilization of the dicationic ionic liquids was observed at these high temperatures. However, due to charring of the polyimide coating on the outside of the fused silica capillary tubing at these high temperatures, the ionic liquids were only tested up to 400 °C.

While the physical and thermal properties of the dicationic ionic liquids are quite impressive, another interesting fact is that some of these compounds possess useful liquid ranges in excess of 400 °C, and one of these (C₉(mpy)₂-NTf₂, **35**) has a stable liquid range of about -4 to >400 °C. This property will undoubtedly ensure their use for a wide variety of applications in which this large liquid range and high thermal stability can be exploited.

Crystal Structures of Geminal Dicationic Ionic Liquids.

Three crystal structures were obtained for two of the geminal dicationic bromide salts. They are C₃(mim)₂-Br (**1**), C₃(mpy)₂-Br (**31**), and a hydrated version of compound **31** containing two water molecules per each dication molecule,

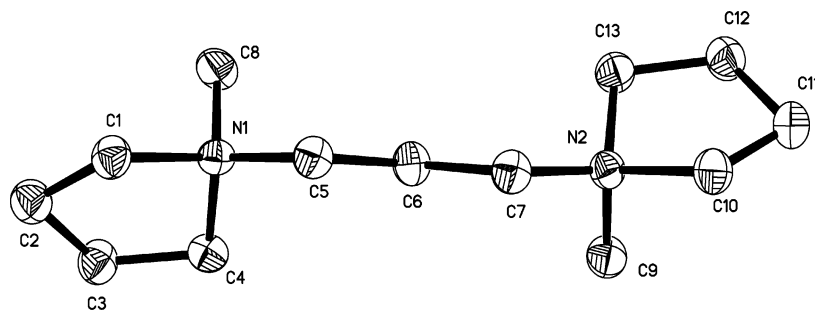


Figure 7. ORTEP diagram of $[\text{C}_3(\text{mpy})_2]^{2+}$ dication in the structure of **31h**, showing the atomic numbering. Hydrogen atoms were omitted for clarity.

referred to as compound **31h**. A summary of the crystal data is given in Table 3 (see Experimental Section).

As shown in Figure 5, the $[\text{C}_3(\text{mim})_2]^{2+}$ dication **1** has a highly twisted configuration with two aromatic rings almost perpendicular to the C_3 plane (angles of C5C6C7-NIC2N2C3C4 and $\text{C5C6C7-C8C9N4C10N3}$ are $92.1(6)$ and $106.8(7)^\circ$, respectively). It should be mentioned that the only other structure found with this configuration is a propeller-like trication of 1,1,1-tris((3-methylimidazolium-1-yl)methyl)ethane tribromide.³⁸ The geometrical parameters of the aromatic rings for both structures are in good accord with each other except that the angle in **1** between the two methylimidazolium rings is much smaller (21.5°). The crystal structure of **1** consists of zigzag bands of molecules along the crystallographic c -axis (see Figure 6). Those bands are formed by separated stacks of isolated dications and bromide anions joined with hydrogen bonds typical for RTILs (this will be discussed further, *vide infra*). It should be mentioned that the stacks are oriented along the short crystallographic a -axis ($5.0921(7)$ Å), which is typical for segregated structures with π -interactions of aromatic rings. Charge-transfer complexes and ion-radical salts of tetrathiafulvalene (TTF) derivatives are very well-known examples of such packing modes.³⁹

The results of the X-ray analysis of compound **31h** (the hydrated version of compound **31**) show the existence of the $[\text{C}_3(\text{mpy})_2]^{2+}$ dication, two bromide counterions, and two solvent water molecules in the asymmetric unit of a noncentrosymmetric triclinic cell. To the best of our knowledge, this is the first structural information on this dication. When the nonaromatic rings are joined to the ends of the C_3 moiety, the resulting molecule (see Figure 7) exhibits an elongated shape with two nitrogen atoms laying almost on the C_3 plane (N1 and N2 are displaced to opposite sides 0.100 and 0.109 Å, respectively, from this plane), contrary to the dication in **1**. In the crystal of **31h** (shown in Figure 8), the dications, bromide counterions, and solvent water molecules participate in a hydrogen-bonding network in which bromide anions are connected with three of four H-atoms of water (strong interaction, $\text{Br}\cdots\text{H}$ distances are in a range of 2.413 – 2.416 Å) and hydrogen atoms of cations (weak interaction, distances 2.901 – 2.992 Å). In addition, two structurally independent water molecules are also bonded. All details of hydrogen bonding are summarized in Table 5.

Most interestingly, there were three structurally independent $\text{C}_3(\text{mpy})_2$ -Br molecules found in an asymmetric unit of the orthorhombic cell for compound **31**. As a matter of fact, all three dications adopt absolutely different conformations, as

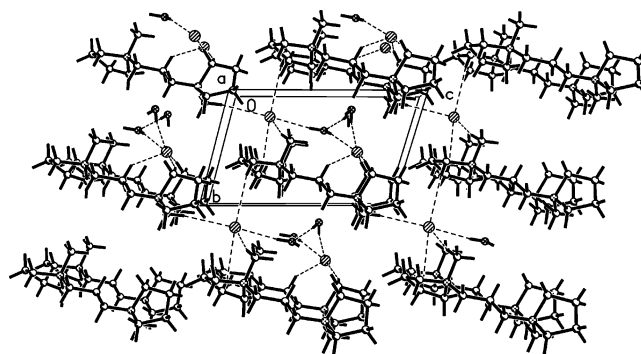


Figure 8. Packing diagram along the a -axis, showing intermolecular interactions in **31h**.

shown in Figure 9 and Table 4. Surprisingly, such diversity in the shapes of the cations together with a complicated hydrogen-bonding network with six structurally independent bromide counterions leads to a very simple packing pattern with a three-dimensional cation–anion alternation, as illustrated in Figure 10.

As mentioned previously, the dicationic class of ionic liquids has an important use because of their stability at wide ranges of temperature and unique liquid properties. Many of these liquids have unpredictably low temperatures of solid–liquid transformation, which from a fundamental standpoint, depends on the energy of their crystal lattice. There are well-known and rather crucial barriers to precisely calculating these energies (i.e., the true determination of atom–atom potentials). On the other hand, the accurate measurement (required for comparison) of solid–liquid transformation temperatures for this family of ionic compounds also has difficulties. The transformation is not sharp in time, and the peaks on DSC curves become very broad. Formally speaking, the temperature of this transformation can be very different from the true melting point, which is the temperature of thermodynamic equilibrium between solid and liquid states. RTILs can be very viscous liquids, which illustrates the high extent of association in the liquid. In this case, some parts of the crystal structure could exist even in liquid as close-ordered moieties. This becomes even more complicated, however, if one considers the formation of different polymorphs with different melting points.⁴⁰

The energy of the crystal lattice mainly depends on interionic forces, molecular symmetry, and the conformational degrees of the freedom of the molecule.⁴¹ As was shown in this paper, $[\text{C}_3(\text{mpy})_2]^{2+}$ can adopt four different conformations in the

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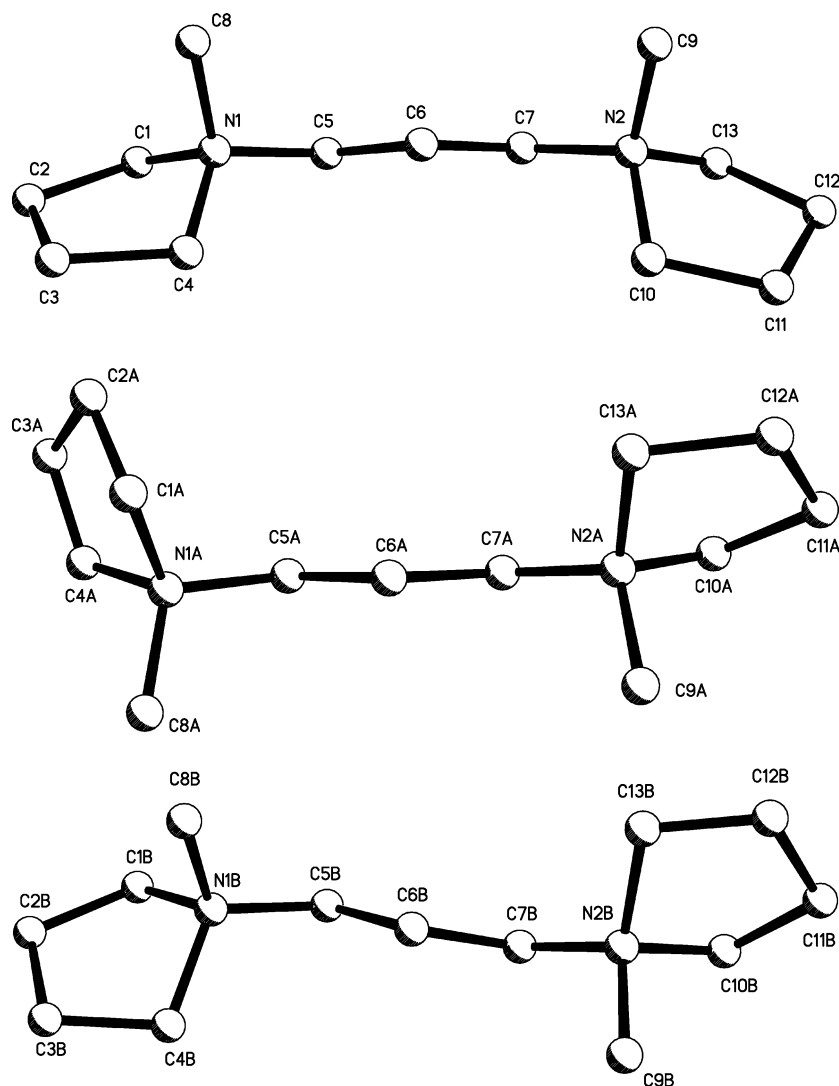


Figure 9. Ball-and-stick representation of three structurally independent $[\text{C}_3(\text{mpy})_2]^{2+}$ dications in the structure of compound **31**, showing atomic numbering. Hydrogen atoms were omitted for clarity. Selected geometrical parameters are summarized in Table 4.

crystal. The reason for this is the extremely high flexibility of the cation because of the rather distant positions of the two charged five-membered rings and a rotation freedom around each of four single bonds in the N_2C_3 moiety in **31h** and **31**. It should be mentioned that all four conformations have almost planar N_2C_3 moiety, leading to an elongated shape of the cation. Generally speaking, the $[\text{C}_3(\text{mim})_2]^{2+}$ cation in **1** is very similar electronically to $[\text{C}_3(\text{mpy})_2]^{2+}$, however, it adopts a space-saving twisted conformation. One of the possible reasons for this difference is the additional intermolecular interactions in the crystal packing of **1**, showing strong intramolecular $\pi-\pi$ stacking between aromatic rings. This interaction can be also responsible for the significant difference in temperature of solid–liquid transformation (51 °C for **31** and 162 °C for **1**).

It was stated that the stability of RTILs depends on the strength and the amount of interionic forces. In our case, the only possible kind of interaction can be $\text{Br}\cdots\text{H}-\text{C}$ weak hydrogen bonding. Usually, the threshold for significance of $\text{Br}\cdots\text{H}$ interaction lays close to 3 Å (van der Waals radius of Br and H are 1.85 and 1.20 Å, respectively).⁴² A summary of the hydrogen bonding is shown in Table 5.

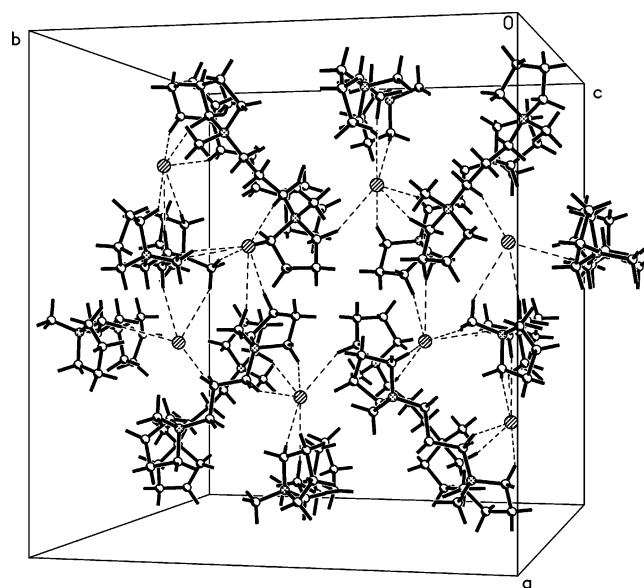


Figure 10. Perspective projection of the structure of **31**, showing 3-D array of cations and anions bounded by hydrogen bonding. The intermolecular contact of $\text{Br}\cdots\text{H}$ with less than 3.05 Å have been shown with dashed lines.

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Table 6. Comparison of Interaction Parameters between Monocationic and Dicationic Ionic Liquids

| T (°C) | Interaction Parameters ^a | | | | | | | | R ² | F |
|--|-------------------------------------|----------------|----------------|----------------|----------------|----------------|----------|----------------|----------------|---|
| | <i>c</i> | <i>r</i> | <i>s</i> | <i>a</i> | <i>b</i> | <i>l</i> | <i>n</i> | | | |
| C ₄ (mim) ₂ -NTf ₂ | | | | | | | | | | |
| 40 | -2.94 (0.13) | 0.25 (0.09) | 2.01 (0.12) | 2.11 (0.11) | 0.50 (0.13) | 0.56 (0.03) | 33 | 0.99 (0.11) | 356.70 | |
| 70 | -2.91 (0.11) | 0.22 (0.10) | 1.78 (0.11) | 1.77 (0.09) | 0.45 (0.14) | 0.44 (0.03) | 32 | 0.99 (0.09) | 370.42 | |
| 100 | -3.06 (0.13) | 0.20 (0.09) | 1.69 (0.10) | 1.57 (0.08) | 0.33 (0.13) | 0.37 (0.03) | 31 | 0.98 (0.09) | 253.79 | |
| C ₉ (mim) ₂ -NTf ₂ (10) | | | | | | | | | | |
| 40 | -2.86 (0.14) | 0.16 (0.11) | 1.81 (0.14) | 1.83 (0.10) | 0.47 (0.17) | 0.62 (0.04) | 32 | 0.98 (0.12) | 257.15 | |
| 70 | -2.95 (0.09) | 0.11 (0.07) | 1.76 (0.08) | 1.75 (0.07) | 0.20 (0.10) | 0.51 (0.02) | 33 | 0.99 (0.07) | 644.20 | |
| 100 | -3.06 (0.08) | 0.11 (0.06) | 1.64 (0.07) | 1.50 (0.06) | 0.15 (0.09) | 0.43 (0.02) | 32 | 0.99 (0.07) | 545.32 | |
| BMIM-NTf ₂ ^b (1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide) | | | | | | | | | | |
| 40 | -2.87 (0.10) | 0 (0.08) | 1.89 (0.10) | 2.02 (0.10) | 0.36 (0.12) | 0.63 (0.03) | 33 | 0.99 (0.09) | 459.64 | |
| 70 | -3.03 (0.09) | 0 (0.08) | 1.67 (0.09) | 1.75 (0.09) | 0.38 (0.11) | 0.56 (0.02) | 35 | 0.99 (0.09) | 413.65 | |
| 100 | -3.13 (0.12) | 0 (0.09) | 1.60 (0.10) | 1.55 (0.10) | 0.24 (0.12) | 0.49 (0.03) | 32 | 0.98 (0.09) | 240.13 | |
| C ₉ (mpy) ₂ -NTf ₂ (35) | | | | | | | | | | |
| 40 | -2.83 (0.12) | 0.27 (0.10) | 1.71 (0.12) | 1.98 (0.10) | 0.32 (0.15) | 0.62 (0.03) | 30 | 0.99 (0.10) | 377.84 | |
| 70 | -2.85 (0.11) | 0.34 (0.09) | 1.52 (0.11) | 1.65 (0.08) | 0.35 (0.13) | 0.48 (0.03) | 32 | 0.99 (0.09) | 419.32 | |
| 100 | -2.99 (0.10) | 0.23 (0.09) | 1.49 (0.10) | 1.48 (0.08) | 0.15 (0.14) | 0.42 (0.03) | 30 | 0.99 (0.08) | 339.79 | |
| BMPY-NTf ₂ ^b (1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide) | | | | | | | | | | |
| 40 | -2.78 (0.11) | 0 (0.09) | 1.69 (0.11) | 2.08 (0.12) | 0.16 (0.14) | 0.68 (0.03) | 34 | 0.98 (0.11) | 321.99 | |
| 70 | -2.80 (0.10) | 0 (0.08) | 1.53 (0.09) | 1.78 (0.08) | 0 (0.11) | 0.56 (0.02) | 34 | 0.99 (0.09) | 393.23 | |
| 100 | -2.92 (0.09) | 0 (0.07) | 1.44 (0.08) | 1.55 (0.07) | 0 (0.09) | 0.48 (0.02) | 32 | 0.99 (0.08) | 358.08 | |
| C ₁₂ (benzim) ₂ -NTf ₂ (29) | | | | | | | | | | |
| 40 | -2.94 (0.11) | 0.11 (0.08) | 1.65 (0.11) | 1.96 (0.08) | 0.84 (0.13) | 0.66 (0.03) | 33 | 0.99 (0.08) | 522.89 | |
| 70 | -3.07 (0.08) | 0.07 (0.05) | 1.62 (0.08) | 1.75 (0.06) | 0.57 (0.09) | 0.56 (0.02) | 30 | 0.99 (0.06) | 888.94 | |
| 100 | -3.12 (0.09) | 0 (0.04) | 1.47 (0.09) | 1.44 (0.06) | 0.52 (0.10) | 0.46 (0.02) | 30 | 0.99 (0.07) | 478.94 | |

^a The *r* = interaction via nonbonding and π -electrons, *s* = dipolarity/polarizability, *a* = hydrogen bond basicity, *b* = hydrogen bond acidity, *l* = dispersion forces, *n* = number of probe molecules subjected to multiple linear regression analysis, R² = statistical correlation coefficient, *F* = Fisher coefficient. Values in parentheses are the standard deviations for each interaction parameter. ^b Values taken from ref 31.

The arrangement of cations–anions in **31** is much more symmetrical, and each anion has more contacts with cations in comparison with the structure of **31h**, where the water solvent molecules are joined with each other and the cations by traditional Br \cdots H–O and O \cdots H–O strong hydrogen bonds. Therefore, the solid–liquid transition point of hydrated modification is lower (\sim 44 °C). No H–O \cdots H–C shortened contacts were observed.

Solvation Characteristics. We have previously reported that the Abraham solvation model, a linear free energy approach that utilizes inverse gas–liquid chromatography to describe the solvation properties of a liquid, can be used to characterize room temperature ionic liquids.³¹ Described by eq 1, the model provides the so-called “interaction parameters” (*r*, *s*, *a*, *b*, *l*) by using multiple linear regression analysis to fit the retention factor (*k*, determined chromatographically) to the solute descriptors (*R*₂, π_2^H , α_2^H , β_2^H , $\log L^{16}$) for a wide variety of probe solute molecules. Complete experimental details and a list of probe

molecules used in the study are presented in the Supporting Information.

$$\log k = c + rR_2 + s\pi_2^H + b\beta_2^H + l \log L^{16} \quad (1)$$

The solvation properties of four dicationic ionic liquids (see Table 6) were evaluated and the interaction parameters compared to those obtained for their traditional monocationic analogues 1-butyl-3-methylimidazolium and 1-butyl-1-methylpyrrolidinium ionic liquids. Nearly all interaction parameters of the dicationic ionic liquids, C₄(mim)₂-NTf₂ and C₉(mim)₂-NTf₂ (**10**), are similar to those of the corresponding monomer-type ionic liquids, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. This is also observed for the pyrrolidinium dication, C₉(mpy)₂-NTf₂ (**35**), as it differs from the monomer-type analogue (1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide). This indicates that the well-known and highly useful solvation properties of traditional RTILs are very similar

to those of the geminal dicationic RTILs. The only interaction parameter that is statistically different between the three ionic liquids is the “ r ” interaction parameter, namely, the ability of the ionic liquid to undergo π - π and n - π interactions with probe solute molecules. Because the pyrrolidinium cation is not aromatic, the higher r values may be due to the anion as each anion contains two sulfone groups that are capable of undergoing such interactions. However, this was not observed for the traditional ionic liquids evaluated previously in our study.³¹

Finally, the interaction parameters for the 3-benzylimidazolium geminal dication separated by a dodecane linkage chain with the NTf₂⁻ anion (**29**) appear similar to those observed previously for 1-benzyl-3-alkylimidazolium ionic liquids. However, the hydrogen bond acidity term, b , is larger for the geminal dicationic ionic liquid. This may be due to the increased acidity of the proton at the two position of the imidazolium ring induced by the electron-withdrawing benzyl group.⁴

Conclusions

Room temperature ionic liquids continue to be an extensively studied group of multipurpose compounds. A new class of 39 ionic liquids were synthesized that employ an alkyl linkage chain separating imidazolium and pyrrolidinium cations with traditional anions (i.e., Br⁻, NTf₂⁻, BF₄⁻, and PF₆⁻). These new geminal dicationic ionic liquids possess many interesting crystalline and physicochemical properties. The thermal stabilities of the geminal dicationic ionic liquids are greater than those of most traditional monocationic ionic liquids. In fact, one ionic liquid was found to possess a liquid/stability range of over 400 °C. This may be one of the most extensive ranges ever reported for organic compounds.

When longer linkage chains are used to separate the dications, a decrease in the melting point was observed for most ionic liquids. This may be related to an increase in the number of closely related configurational states and possibly crystalline polymorphs for these compounds. However, the density of the ionic liquids decreased with increasing linkage chain length. A

small variation in the surface tension was observed when different length linkage chains were used to connect the dications; however, the length of the substituted alkyl group on the imidazolium ring appears to decrease the surface tension with increased length. For the bis(trifluoromethylsulfonyl)imide dicationic salts, the viscosity generally increased when a longer alkyl chain was used to separate the dications. The addition of a longer alkyl group at the three position of the imidazolium ring also provided ionic liquids with higher viscosities. The solubility of the geminal dicationic ionic liquids in water and heptane appears very similar to that of the traditional monocationic ionic liquids, with the exception of one case in which the dication was very hydrophobic, thereby rendering its bromide salt immiscible with water.

Three crystal structures of two dicationic ionic liquids indicate that the [C₃(mpy)₂]²⁺ dication can adopt four different conformations in the crystal, resulting in high flexibility of the cation and the possibility of forming many polymorphs. In the case of the C₃(mpy)₂-Br salt, the three different conformations in the single crystal lead to a very simple packing pattern despite the diversity in the shapes of the cations and the complicated hydrogen-bonding network.

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Supporting Information Available: Complete synthesis procedures for the dicationic ionic liquids, methods used to characterize the ionic liquid using inverse gas chromatography and the solvation parameter model, ¹H NMR spectra of the dicationic salts taken in DMSO-*d*₆, and CIF files of three crystals. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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