

# In situ Formation of Thermally Stable, Room-Temperature Ionic Liquids from CS<sub>2</sub> and Amidine/Amine Mixtures.

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Amidinium dithiocarbamates salts with diverse structures are prepared in situ by adding one equivalent of  $CS_2$  to an equimolar mixture of two nonionic molecules, an amidine and an amine. Many of the salts made in this way are room temperature ionic liquids (RTILs) and the others (ILs) melt well below the decomposition temperature of the salts, ca. 80 °C. Unlike the analogous amidinium carbamate RTILs, which are made by adding  $CO_2$  to amidine/amine mixtures and decompose near 50 °C, the amidinium dithiocarbamates do not revert to their amidine/amine mixtures when they are heated. The thermal, rheological, conductance, and spectroscopic properties of representative examples from a total of 50 of these ILs and RTILs are reported, comparisons between them and their nonionic phases (as well as with their amidinium carbamates analogues) are made, and the thermolysis pathways of the ammonium dithiocarbamates are investigated.

### 1. Introduction

Because they exhibit characteristics of "green solvents"<sup>1</sup> and offer rather unique physicochemical properties,<sup>2</sup> ionic liquids (ILs) and especially room temperature ionic liquids (RTILs)<sup>3</sup> have become increasingly popular

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for diverse applications.<sup>4</sup> A subclass of RTILs can be "switched" reversibly between their ionic and nonionic states.<sup>5,6</sup> This property has been exploited to separate products (or catalysts) in a manner that allows the catalyst<sup>7</sup> to be reused.<sup>8</sup> Previously, we developed a class of thermally reversible ionic liquids by adding CO<sub>2</sub>, a neutral triatomic molecule and a greenhouse gas, to an equimolar mixture of two nonionic molecules, an aliphatic amidine and an amine.<sup>6</sup> The chemistry associated with the formation of the amidinium carbamate RTILs<sup>9</sup> is shown in eq 1 in Scheme 1. The RTILs can be transformed quantitatively back to their nonionic components by passing an unreactive "displacing" gas, such as molecular nitrogen, through the ionic liquid. The nonionic and ionic states can be switched repeatedly in this way without detectable degradation of the system. Although the benign nature of this switching process opens several potential applications for ionic liquids, such as reversible catalyst formation<sup>10</sup> and

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CO<sub>2</sub> gas sequestration,<sup>11</sup> the thermal instability of these ionic liquids above ca. 50 °C (eq 1), even under one atmosphere pressure of CO2, imposes some limitations on their applicability. Thus, RTILs of similar structure but with greater thermal stability would significantly expand their potential uses.

Previously, we observed that the gel networks<sup>12</sup> made when a triatomic molecule is added to a "latent" alkylamine gelator and the ionic cross-links formed similarly within aminopolysiloxanes<sup>13</sup> are thermally more stable with  $CS_2$  (an environmentally harmful liquid  $^{14}$ ) than with CO<sub>2</sub>. In addition, others have investigated the properties of functional materials made by adding  $CS_2$  to liquid-like mixtures.<sup>15–18</sup>

Here, we report the properties of representative examples from a total of 50 ILs and RTILs obtained when CS<sub>2</sub> was added to different combinations of an amidine (D) and an amine (A) (Scheme 1). This approach is amenable to the construction of extensive libraries of ILs whose properties can be tuned for specific tasks. As expected, the amidinium dithiocarbamates (D-A-S) are more stable thermally (to  $\sim 80$  °C under air atmospheres) than the corresponding ammonium carbamates (to ~50 °C under CO<sub>2</sub> atmospheres) and have other attractive features, but they are not thermally reversible. However, loss of CS<sub>2</sub> can be accomplished at room temperature by adding a small amount of a solution of dilute aqueous carboxylic acid. The pathways for reaction of the neat D-A-S above 80 °C have been inferred from their thermolysis products. The thermal, conductive, and spectroscopic properties of these RTILs are compared with those of their nonionic

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phases and of the corresponding amidinium carbamates. The latter comparison addresses the extent to which changing the triatomic molecular adduct influences the properties of the RTILs and demonstrates further that environmentally deleterious triatomic molecules can have beneficial purposes in materials science. Their ease of preparation of these ILs is perhaps their most important and beneficial attribute: they can be made in one pot, in situ, by simply adding the three components—amidine, amine, and CS<sub>2</sub>—together.

## 2. Experimental Section

2.1. Materials. Carbon disulfide (anhydrous, 99.9%) was purchased from Aldrich. t-Butyl amine (99.5%), n-hexylamine (99%), n-octylamine (99%), n-decylamine (99%), cyclohexylamine (99%), dibutylamine (99.5%), and 1,1,3,3-tetramethylguanidine (TMG) (99%) (all from Aldrich) were used as received. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) (98% from Aldrich) was refluxed over CaH<sub>2</sub> (Acros) for 5 h and distilled at 67-68 °C/0.2 Torr onto activated 5 Å molecular sieves (>99.5% by GC).<sup>6a</sup> All organic solvents were HPLC grade (from Aldrich or Fisher). Prolinol (ProOH), leucinol (LeuOH), isoleucine octyl ester (IleC8), **DAPNE** (1-(*p*-dimethylaminophenyl)-2-nitroethylene), and the other aliphatic amidines were available from previous studies.<sup>6</sup> Chloroform-d (99.8% D) and deuterated water (99.9% D) were purchased from Cambridge Isotope Laboratory, Inc.

2.2. Amidinium Dithiocarbamate Sample Preparation. CS<sub>2</sub> liquid (1 mol equivalent) was added slowly to a stirred amidine and amine sample in a glass vial. The vial was placed in an ice-water bath during the CS<sub>2</sub> addition to dissipate the heat from the exothermic reaction. (Warning:  $CS_2$  is a toxic liquid that should be handled carefully.)

2.3. Characterization. NMR spectra were recorded on an Inova 400 MHz Spectrometer operating at 400 MHz (<sup>1</sup>H), or 100.5 MHz (<sup>13</sup>C), respectively. <sup>1</sup>H and <sup>13</sup>C spectra were indirectly referenced to TMS using residual solvent signals as internal standards and CDCl<sub>3</sub> as the solvent. IR spectra were obtained on a Perkin-Elmer Spectrum One FT-IR spectrometer, using an attenuated total reflection accessory or NaCl plates. Gas chromatographic (GC) analyses were performed on a Hewlett-Packard 5890A gas chromatograph equipped with flame ionization detectors and a DB-5 (15 m  $\times$  0.25 mm) column (J & W Scientific). Thermal gravimetric analysis (TGA) measurements were performed under a nitrogen atmosphere at a 5 °C/min heating rate on a TGA Q50 thermogravimetric analyzer (TA Instruments) interfaced to a computer. UV-vis spectra were recorded on a Varian CARY 300 Bio UV-visible spectrophotometer in Hellma

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 Table 1. Phases<sup>a</sup> of Neat 1/1 (mol/mol) Amidine (D)/Amine (A) mixtures before (b) and after (a) adding CS2 at Room Temperature and at -20 °C in Parentheses; Melting Points (°C) of Ammonium Dithiocarbamates that are Solids at Room Temperature Are Presented Numerically

|             | amine (A)                    |             |                     |             |  |             |            |             |            |             |                 |             |              |             |
|-------------|------------------------------|-------------|---------------------|-------------|--|-------------|------------|-------------|------------|-------------|-----------------|-------------|--------------|-------------|
|             | prolinol<br>( <b>ProOH</b> ) |             | leucinol<br>(LeuOH) |             | isoleucine<br>octyl ester ( <b>IleC8</b> ) |             | hexylamine |             | octylamine |             | cyclohexylamine |             | dibutylamine |             |
| amidine (D) | b                            | а           | b                   | а           | b  | а           | b          | а           | b          | а           | b               | а           | b            | а           |
| tC4         | L                            | L(L)        | L                   | L(L)        | L  | L(L)        | L          | L(L)        | L          | L(L)        | L               | L(L)        | L            | L(L)        |
| C4          | L                            | L(L)        | L                   | L(L)        | L  | L(L)        | L          | L(L)        | L          | L(L)        | L               | L(L)        | L            | L(L)        |
| C6          | L                            | L(L)        | L                   | L(L)        | L  | L(L)        | L          | L(S)        | L          | L(S)        | L               | L(S)        | L            | L(S)        |
| C8          | L                            | L(L)        | L                   | L(L)        | L  | L(L)        | L          | L(S)        | L          | S 39.7-41.3 | L               | S 34.5-36.1 | L            | S 38.6-40.1 |
| C16         | S                            | S 48.0-50.2 | S                   | S 49.1-51.7 | S  | S 55.8-58.0 | L          | S 47.5-49.9 | L          | S 55.8-57.1 | L               | S 54.0-55.9 | L            | S 52.8-55.5 |
| DBU         | L                            | L(S)        | L                   | L(S)        | L  | S 59.0-60.3 | L          | S 52.2-53.5 | L          | S 60.5-61.8 | L               | S 50.8-51.8 | L            | S 61.7-63.3 |
| TMG         | L                            | L(S)        | L                   | L(S)        | L  | S 42.9-43.8 | L          | S 38.6-39.6 | L          | S 41.2-42.5 | L               | S 37.3-38.9 | L            | S 42.4-44.0 |
| none        | L                            | S           | L                   | S           | S  | S           | L          | S           | L          | S           | L               | S           | L            | S           |

 $^{a}$ L = liquid, S = solid.

quartz cells with 0.1 cm path lengths. Viscosity measurements were performed on an Anton Paar Physica MCR 301 rheometer (Anton Paar GmbH, Graz, Austria) using a parallel plate (radius 25 mm, gap 0.5 mm) geometry. Conductivities were measured with a Yellow Spring Instrument Co. model 31 conductivity meter using Au electrodes in a cell constructed by Prof. Robert de Levie. GC-MS was performed on a Varian Saturn 2100 instrument in the electron ionization (EI) mode using a DB-5 (15 m  $\times$  0.25 mm) column.

### 3. Results and Discussion

3.1. Preparation and General Properties of the D-A-S. The appearances of the phase of the D/A combinations at room temperature, both before and after adding CS<sub>2</sub>, are collected in Table 1. Primary amines, secondary amines, amino esters and amino alcohols were tested as A components. Aliphatic amidines, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and 1,1,3,3-tetramethylguanidine (TMG) were employed as the D components. A large number of the combinations remain liquids at room temperature after adding  $CS_2$ . However, none of the combinations with the longest-chained linear amidine, C16, produced a liquid dithiocarbamate at room temperature; in general, the shorter chained D appear to favor the formation of liquid D-A-S, probably as a result of less ordering by London dispersion forces. All of the amidinium dithiocarbamates, which are solids at room temperature, have melting points below 65 °C, well below the temperature at which the amidinium dithiocarbamates decompose. Furthermore, many of the RTILs remain noncrystalline and flowing (albeit very viscous fluids) to at least -20 °C; they have a broad and synthetically useful liquid range.

As expected, the **D/A** mixtures were qualitatively less viscous than the corresponding **D-A-S** ionic liquids because of the introduction of strong electrostatic interactions in the latter. The additional hydrogen bonding and dipolar interactions available to the RTILs with an amino alcohols or an amino ester component made them more viscous than the ionic liquids with aliphatic amines. In addition, there was no evidence by polarized optical microscopy for liquid crystallinity in any of the amidinium dithiocarbamates made from hexadecylamidine (C16) and several different aliphatic amines, amino esters and amino alcohols. Unlike the amidinium carbamates (i.e., the RTILs made by adding  $CO_2$  to



Figure 1. FT-IR spectra of (a) C6/cyclohexylamine and (b) C6-cyclohexylamine-CS<sub>2</sub>.

**D**/**A** mixtures), which remain clear and uncolored, the amidinium dithiocarbamates are a yellow or orange color (see Figure S1 in the Supporting Information), which can be attributed to  $n-\pi^*$  electronic transitions of the dithiocarbamate group.<sup>19</sup>

**3.2.** Characterization of the D-A-S. The amidinium dithiocarbamate structures were identified on the basis of analyses of thermal gravimetric analyses (TGA) and <sup>1</sup>H and <sup>13</sup>C NMR and FT-IR spectral data of amidine/amine samples before and after the addition of CS<sub>2</sub>. Figure 1 shows the FT-IR spectra of a representative sample, C6/cyclohex-ylamine, before and after adding CS<sub>2</sub>; spectra for eight additional D-A-S are presented in Figure S2 of the Supporting Information. After addition of CS<sub>2</sub>, the typical N=C stretching band of the amidine at 1629 cm<sup>-1</sup> is replaced by a band at 1645 cm<sup>-1</sup>, which can be assigned to protonated amidine. In addition, the bands at 1088 and 977 cm<sup>-1</sup> are assigned to C=S and C-S stretchings, respectively.<sup>20</sup>

The <sup>1</sup>H NMR spectrum of C6/cyclohexylamine changes markedly upon addition of CS<sub>2</sub> (Figure 2a). Exposing the C6-cyclohexylamine-CS<sub>2</sub> amidinium dithiocarbamate to  $N_2$ 

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Figure 2. NMR spectra: (a) <sup>1</sup>H spectra of C6/cyclohexylamine (black), C6-cyclohexylamine-CS<sub>2</sub> (red), and C6-cyclohexylamine-CS<sub>2</sub>-N<sub>2</sub> (blue) in CDCl<sub>3</sub> with peak assignments in the inset; (b) <sup>13</sup>C spectrum of C6-cyclohexylamine-CS<sub>2</sub> in CDCl<sub>3</sub>.

and gently heating at 50 °C (**C6**-cyclohexylamine-CS<sub>2</sub>-N<sub>2</sub>) for 30 min, conditions that reconvert the analogous amidinium carbamate to its uncharged amidine/amine mixture,<sup>6</sup> results in no discernible changes. Upon addition of CS<sub>2</sub>, the <sup>13</sup>C resonance of the central carbon of the amidine in **C6** shifted downfield from 156 to 162 ppm and the resonance of CS<sub>2</sub> moved from 193<sup>15</sup> to 210 ppm (Figure 2b).

Adding CS<sub>2</sub> to a primary amine is known to yield ammonium dithiocarbamate salts (RNHCS<sub>2</sub><sup>-</sup> H<sub>3</sub>N<sup>+</sup>R).<sup>12b</sup> Given our simple addition method for preparing the D-A-S, some ammonium dithiocarbamate salts could conceivably be present as well.<sup>21</sup> To test this possibility, a sample of hexylammonium dithiocarbamate was made. To it was added 1 equiv. of C6 amidine, and 0.5 equiv. of  $CS_2$  (to obtain the correct stoichiometry for a D-A-S) were added to the hexylammonium dithiocarbamate in a CDCl<sub>3</sub> solution. <sup>1</sup>H and <sup>13</sup>C NMR spectra recorded before and after the addition of the amidine and  $CS_2$  (see Figure S11 in the Supporting Information) show that the ammonium dithiocarbamate was transformed completely (within the limits of detection) to another species. On the basis of the identical nature of the NMR spectra of that species and those of C6-hexylamine-CS<sub>2</sub>, it is the D-A-S.<sup>22</sup> This experiment demonstrates that the thermodynamically less favored ammonium dithiocarbamate (N. B., the amidines are much more basic than the amines employed in this study<sup>23</sup>), if formed kinetically to any extent, equilibrates to D-A-S rapidly when CS<sub>2</sub> is added.

We selected a higher boiling amine, **IleC8**, for TGA studies. On the basis of the data in Figure 3a, the **D-A-S** 

are stable to at least 80 °C under a nitrogen atmosphere and weight losses indicate that decomposition above 150 °C does not involve either CS<sub>2</sub> or H<sub>2</sub>S (Caution:  $H_2S$  is a poisonous gas that should be handled only under well controlled and ventilated conditions) as the exclusive species expelled. The theoretical weight loss from C8-**IleC8-**CS<sub>2</sub> if one molecule of CS<sub>2</sub> or  $H_2S$  (the molecule lost when ammonium dithiocarbamates are heated to their decomposition temperature<sup>12b,24</sup>) is 14.7 or 6.6%, respectively. Nearly 16% more weight was lost when C8/ **IleC8** was heated under the same conditions (Figure 3a). Furthermore, only 0.18% weight was lost from C8-IleC8-CS<sub>2</sub> when it was kept at 25 °C under a dry nitrogen gas flow of 60 cc/min during a 60 min period (Figure 3b), and only 1.7% of the initial weight was lost after heating the sample to ca. 100 °C at a rate of 5 °C/min. As mentioned, the thermal behaviors of this and other D-A-S are in contrast with those of the corresponding ammonium carbamates and amidinium carbamates (which are thermally reversible, losing a molecule of CO<sub>2</sub> when heated to ca. 50 °C).<sup>6,12b</sup> Also, when heated, an amidinium dithiocarbonate has been found to lose a molecule of  $CS_{2}$ ,<sup>15</sup> and we established previously that ammonium dithiocarbamates lose one molecule of H<sub>2</sub>S and become thioureas when heated to ca. 100 °C.12b

**3.3. Thermolysis Pathways.** To the best of our knowledge, the mechanism of thermolysis of amidinium dithiocarbamates has not been investigated.<sup>25</sup> To gain insights into the process, we have isolated and identified the thermolysis products from one amidinium dithiocarbamate, tC4-*t*-butylamine-CS<sub>2</sub>. From them, it is possible to infer a plausible mechanistic pathway for the thermally induced reactions (Scheme 2).<sup>26</sup> Reaction commences with formation of a covalent bond between the amidinium carbon atom and a sulfur from the dithiocarbamate followed by (or synchronous with) addition of a proton from the amine moiety of the

<sup>(21)</sup> In fact, the purity of the **D**-A-S appears to depend upon the purity of the amidine, amine, and CS<sub>2</sub> reagents as well as the accuracy with which each can be weighed. If slightly more or less than the exact molar amount of any of the 3 components is added to the mixture, the IL will contain a small amount of another species. In our experience, making different batches of on **D**-A-S, the very small amounts of the extraneous species (which must be present to some extent), have no discernible influence on the properties of the IL.
(22) In Figure S11a, the 3 protons from RNH<sub>3</sub> at 7.9 ppm and the single

<sup>(22)</sup> In Figure S11a, the 3 protons from  $RNH_3$  at 7.9 ppm and the single proton from  $RNHCO_2$  at 7.75 ppm of the ammonium dithiocarbamate were located by adding a small drop of  $D_2O$  to the sample tube; only those signals disappeared. Thus, the loss of the 7.9 ppm peak and the shift of the 7.75 ppm peak after the addition of amidine and  $CS_2$  have been used as the principal identification tools for the transformation of the ammonium dithiocarbamate to the amidinium dithiocarbamate, given that the eventual spectra matched those of the directly prepared **D-A-S**.

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<sup>(26)</sup> tC4 (which lacks a methyl group at the amidine carbon) and tbutylamine were selected as substrates. These molecules simplify the spectral identification of the thermolysis products. As indicated by the proposed mechanism in Scheme 2, these substrates should react like the others in Scheme 1.



Figure 3. (a) TGA curves of C8/IleC8 (gray) and C8-IleC8-CS<sub>2</sub> (black). (b) Isothermal TGA curve of C8-IleC8-CS<sub>2</sub> at 25 °C for 60 min.

Scheme 2. Thermolysis of tC4-t-Butylamine-CS<sub>2</sub>



dithiocarbamate (blue) to one of the nitrogen atoms of the amidine. Note that two parallel pathways ensue based on which of the amidine nitrogen atoms is the proton acceptor. Some of these steps are reminiscent of the reactions between carbodiimides and carboxylates in Merrifield peptide syntheses.<sup>27</sup> In Scheme 2, cleavage of the original C-S bond of the  $CS_2$  molecule results in an isothiocyanate (V) and a zwitterionic species (III or IV), which cleaves into a thioformamide (VI or VII) and an amine. Cleavage of the original C–S bond of the  $CS_2$  molecule results in V and a zwitterionic species (III or IV), which cleaves into VI or VII and an amine. The resulting amines can then react with V, generating N-tert-butyl-N',N'-dimethylthiourea (VIII) or N, N'-di-*tert*-butylthiourea (IX).<sup>28</sup> The proposed pathways are consistent with the presence of dimethylamine and t-butylamine, which were captured as their hydrochloride salts (see the Supporting Information). Furthermore, the relative yields of VIII and IX suggest that the thermolysis prefers slightly the pathway through intermediate I.

Acid treatment of dithiocarbamates is known to result in formation of ammonium ions and CS<sub>2</sub>.<sup>13</sup> Depending on the  $pK_B$  of the parent amine, acid-derived decomposition of alkyl dithiocarbamates can occur by two different mechanisms.<sup>29</sup> For parent amines with  $pK_B > 10.5$ , the decompositions occur by a concerted intramolecular S-to-N hydrogen transfer with C–N bond cleavage. When  $pK_B < 10.5$ , alkyl dithiocarbamates decompose via zwitterionic intermediates whose N-protonation is slower than the C–N bond breaking (eq 2). The same mechanism should obtain when a **D-A-S** is treated with an acid (such as dilute aqueous acetic acid). Evidence for that chemistry, shown in eq 3, comes from <sup>13</sup>C NMR spectroscopy (see Figure S3 in the Supporting Information).

$$\begin{array}{c} \mathsf{H} \stackrel{\mathsf{S}}{\underset{\mathsf{R}}{\circ}} \stackrel{\Theta}{\underset{\mathsf{C}}{\circ}} \stackrel{\mathsf{H}}{\underset{\mathsf{K}}{\circ}} \stackrel{\mathsf{H}}{\underset{\mathsf{K}}{\circ}} \stackrel{\mathsf{H}}{\underset{\mathsf{K}}{\circ}} \stackrel{\mathsf{C}}{\underset{\mathsf{C}}{\circ}} \stackrel{\mathsf{S}}{\underset{\mathsf{H}}{\circ}} \stackrel{\mathsf{K}_{2}}{\underset{\mathsf{R}}{\circ}} \mathsf{R} \cdot \mathsf{NH}_{2} + \mathsf{CS}_{2} \tag{2}$$

$$\begin{array}{c} \overset{H}{R} \overset{\Theta}{\xrightarrow{}} N(CH_3)_2 \overset{\Theta}{\xrightarrow{}} S \overset{H}{\xrightarrow{}} CH_3COOH \\ \overset{H}{\xrightarrow{}} R' \overset{H}{\xrightarrow{}} H \overset{O}{\xrightarrow{}} O \\ \overset{\Theta}{\xrightarrow{}} N(CH_3)_2 \overset{\Theta}{\xrightarrow{}} O \overset{G}{\xrightarrow{}} C-C-CH_3 + R" \overset{\Theta}{\xrightarrow{}} H_3 \overset{\Theta}{\xrightarrow{}} O \overset{G}{\xrightarrow{}} C-CH_3 + CS_2 \end{array}$$

$$\begin{array}{c} (3) \\ \overset{\Theta}{\xrightarrow{}} N(CH_3)_2 \overset{\Theta}{\xrightarrow{}} O & \overset{G}{\xrightarrow{}} C-C-CH_3 + R" \overset{\Theta}{\xrightarrow{}} H_3 \overset{G}{\xrightarrow{}} O & \overset{G}{\xrightarrow{}} C-C-CH_3 + CS_2 \end{array}$$

**3.4. Conductivity Measurements.** The conductivity ( $\sigma$ ) of some of the **D**-A-S and their mixtures with CHCl<sub>3</sub> was investigated at room temperature. The effect on conductivity of the high ion concentrations upon adding CS<sub>2</sub> to **D**/A combinations were offset to a large extent in the neat RTILs by large viscosity increases (Table 2). However, conductivities increased significantly when CS<sub>2</sub> was added to **D**/A mixtures in 50 wt % CHCl<sub>3</sub> solutions. The increases were slightly smaller than observed when CO<sub>2</sub> was added to either neat or chloroform solutions of a **D**/A.<sup>6c</sup> We attribute these observations to the higher viscosities of the dithiocarbamates (vide infra), and less ion pairing<sup>30</sup> in the carbamates.

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Figure 4. (a) Conductivities of C8/hexylamine mixtures at room temperature as a function of mol % substrate before (A) and after adding 1 equiv. of CO<sub>2</sub> (O) and  $CS_2(\bullet)$ . (b) Conductivities of neat C8-hexylamine-CS<sub>2</sub>( $\bullet$ ) and DBU-LeuOH-CS<sub>2</sub>(O) at various temperatures.

Table 2. Conductivities before (b) and after (a) adding CS<sub>2</sub> to Neat and 50 wt % CHCl<sub>3</sub> Solutions of Neat D/A Combinations at Room Temperature

|                         |                       | с  | onductivi   |                                   |                   |
|-------------------------|-----------------------|----|-------------|-----------------------------------|-------------------|
| $\mathbf{D}/\mathbf{A}$ | triatomic<br>molecule | b  | a<br>(neat) | a (50 wt %<br>CHCl <sub>3</sub> ) | mol % of<br>D-A-S |
| C8/hexylamine           | $CS_2$                | 22 | 39          | 265                               | 24.1              |
| C8/hexylamine           | $CO_2$                | 22 | 58          | 276                               | 25.8              |
| DBU/LeuOH               | $CS_2$                | 31 | 46          | 198                               | 25.7              |
| DBU/LeuOH               | $CO_2$                | 31 | 54          | 214                               | 27.7              |

As shown in Figure 4, for example, the conductivity of neat C8/hexylamine changed very little as it was diluted with CHCl<sub>3</sub>. After adding  $CS_2$ , the conductivity of the C8hexylamine-CS<sub>2</sub> only doubled, but it increased further as small increments of CHCl3 were added as a diluent, reached a maximum at ca. 10 mol  $\%^{31}$  (ca. 20–30 wt % of C8hexylamine-CS<sub>2</sub>), and decreased at still lower concentrations (higher dilutions) in CHCl<sub>3</sub> (Figure 4a). As mentioned, the rise in conductivity upon initial addition of CHCl<sub>3</sub> is attributed to a convolution of decreasing viscosity (i.e., higher ion mobility) and less ion pairing (i.e., leading to an increase in the concentration of free ions).<sup>32</sup> Eventually, the decreased viscosity and ion pairing that accompany the addition of more CHCl<sub>3</sub> are offset by the lower concentration of mobile ions, and the conductivity decreases. Increased conductivity with decreasing viscosity is also seen in neat D-A-S as temperature is raised (Figure 4b).<sup>33</sup>

A Walden plot<sup>34</sup> has been used to evaluate further the ion mobilities of the ionic liquids. It is based on Walden's observation for aqueous solutions of strong electrolytes that the equivalent conductivity of electrolytes (i.e., the conductivity per mole of charge),  $\Lambda = \sigma V_{\rm E}$  (where  $V_{\rm E}$  is the volume containing one Faraday of positive charge) is large, depends inversely on viscosity, and changes with temperature in parallel with the inverse of viscosity. According to Walden's Rule,  $\Lambda \eta = k, \eta$  is the viscosity, and k is a temperaturedependent constant. From the Walden plot in Figure 5, C4hexylamine-CS<sub>2</sub> can be classified as a "good ionic liquid"



**Figure 5.** Log–log plot of equivalent conductivity ( $\Lambda$ ) versus fluidity  $(\eta^{-1})$  for **C4**-hexylamine-CS<sub>2</sub>. The straight line is determined by data for 1 M aqueous KCl.<sup>30</sup>

because it lies very close to the ideal line described by aqueous KCl.33,35 However, because of their relatively high viscosities (vide infra), the ammonium dithiocarbamates exhibit lower conductivities than many other classes of ionic liquids.33

3.5. Miscibility and Polarity. Initially, the miscibilities of the samples in their D/A and D-A-S states were determined empirically as a measure of their polarity.<sup>37</sup> Before adding CS<sub>2</sub>, D/A mixtures with all solvents examined resulted in solutions (Table 3). Similar to many other types of classical RTILs, including amidinium carbamates, 6c our D-A-S phases are miscible with very polar solvents, such as DMSO and ethanol, but not with lower polarity solvents, such as hexane, toluene, and diethyl ether. Furthermore, the length of the Cn amidine alkyl chain appears to influence somewhat the miscibility behavior: C8-hexylamine- $CS_2$  is partially miscible with diethyl ether and C6-hexylamine-CS<sub>2</sub> or C4-hexylamine-CS $_2$  is immiscible with it.

Also, the solvatochromic dye, DAPNE (1-(p-dimethylaminophenyl)-2-nitroethylene),38 was utilized to estimate the polarity of the D/A and D-A-S. For example,  $\lambda_{max} =$ 423 nm for C8-hexylamine and 438 and 440 nm for C8hexylamine-CO<sub>2</sub> and C8-hexylamine-CS<sub>2</sub>, respectively (see Table S1 in the Supporting Information); the  $\lambda_{max}$  of toluene

<sup>(31)</sup> The concentrations are expressed in mol % in order to normalize the concentrations of ionic liquids and amidine/amine.

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| solvent                       | hexane | toluene | diethyl ether | $CH_2Cl_2$ | ethyl acetate | ethanol | DMSO |
|-------------------------------|--------|---------|---------------|------------|---------------|---------|------|
| C4-hexylamine-CS <sub>2</sub> | Ι      | Ι       | Ι             | М          | М             | М       | М    |
| $C6$ -hexylamine- $CS_2$      | Ι      | Ι       | Ι             | М          | М             | М       | М    |
| $C8$ -hexylamine- $CS_2$      | Ι      | Ι       | Р             | М          | М             | М       | М    |
| C4-IleC8-CS <sub>2</sub>      | Ι      | Ι       | Ι             | М          | М             | М       | М    |
| C6-IleC8-CS <sub>2</sub>      | Ι      | Ι       | Р             | М          | М             | М       | М    |
| C8-IleC8-CS <sub>2</sub>      | Ι      | Ι       | Р             | Μ          | М             | Μ       | Μ    |

 ${}^{a}I = \text{immiscible}, M = \text{miscible}, P = \text{partially miscible}.$ 



Figure 6. (a) Viscosities (Pa s) at 25 °C of neat Cn/cyclohexylamine before (white) and after addition of  $CO_2$  (gray) or  $CS_2$  (black). (b) Viscosities (Pa s) of C8-cyclohexylamine- $CS_2$  (white) and C8-IleC8- $CS_2$  (black) at different temperatures.

and *N*,*N*-dimethylformamide are 425 and 446 nm, respectively.<sup>38</sup> According to this probe, the **D**/**A** are much less polar than their **RTILs**, whether they be generated by addition of  $CS_2$  or  $CO_2$ , but are less polar than many imidazolium-based ILs.<sup>39</sup>

3.6. Viscosity Measurements. Consistent with their  $CO_2$  analogues, the D/A and D-A-S exhibit viscosities that are virtually independent of shear rate; they behave like Newtonian liquids (see Figure S4 in the Supporting Information).<sup>40</sup> As shown in Figure 6a, the average viscosity over the range of shear stress values for C6/ cyclohexylamine is 0.010 Pa s at room temperature. After exposure to  $CO_2$ , the viscosities of these samples increase by orders of magnitude to 3.8 Pa s (C6-cyclohexylamine- $CO_2$ ), but the viscosity of the corresponding C6-cyclohexylamine- $CS_2$  is much higher still, ca. 19 Pa s. The higher viscosities of the dithiocarbamates can be explained on the basis of their higher polarizabilities and hard-soft/acid-base<sup>41</sup> (HSAB) theory: dithocarbamate is a softer base than a carbamate and amidinium is a soft acid. Also, the viscosities increase with increasing chain length of the Cn: for example, C4-cyclohexylamine-CS<sub>2</sub>, C6-cyclohexylamine- $CS_2$ , and C8-cyclohexylamine- $CS_2$ have viscosities 8.6, 19, and 69 Pa·s, respectively. As expected, the viscosities of the amidinium dithiocarbamate ionic liquids decrease significantly as temperature is increased within the range below their decomposition temperatures (Figure 6b): the viscosity of C8-IleC8-CS<sub>2</sub> at 45 °C is 1.6 Pa s, almost 25 times lower than that at 25 °C (43 Pa s), which is also lower than the viscosity of **C8-IIeC8-CO**<sub>2</sub> (7.1 Pa s) at 25 °C.

3.7. Comparisons of Phase Types from Dithiocarbamate and Carbamate Analogues. Comparisons of the structural differences between amidinium dithiocarbamates and amidinium carbamates offer a means to gain insights about how they support formation of RTILs. The data in Table 4 demonstrate that the appearances of some of the D/A ionic liquids depend on whether  $CO_2$  or  $CS_2$  is added. For example, **DBU**-hexylamine- $CO_2$  is a liquid, whereas **DBU**-hexylamine- $CS_2$  is a solid. Obviously, these differences are a manifestation of the properties of the carbamate and dithiocarbamate anions. To some extent, those properties can be related to the physical properties of the triatomic molecules from which the anions derive, CO<sub>2</sub> and CS<sub>2</sub>. Both are linear molecules and have zero dipoles.<sup>42</sup> However, they possess large quadrupole moments: for  $CO_2$ ,  $3.00 \times 10^{-26}$  esu cm<sup>2</sup>; for  $CS_2$ ,  $1.84 \times 10^{-26}$  esu cm<sup>2</sup>.<sup>43</sup> In addition, both the bond lengths and kinetic diameter of  $CS_2$  (bond length 1.55 Å and diameter 4.48 Å) are larger than those of  $CO_2$  (1.16 and 3.30 Å).<sup>42</sup>

As mentioned above, whereas the amidinium dithiocarbamates cannot be heated to expel CS<sub>2</sub> and regenerate the nonionic **D**/**A** states, gentle heating or passing nitrogen gas through an amidinium carbamate does result in the loss of CO<sub>2</sub>. This grossly different chemical behavior can be understood from the enthalpies of formation of dithiocarbamates and carbamates. The heats of formation  $\Delta H_{\rm f}$  are -393.5 kJ mol<sup>-142</sup> for CO<sub>2</sub> and 115.7 kJ mol<sup>-1</sup> for CS<sub>2</sub><sup>44</sup> in the gas phase. Thus, it is expected from

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<sup>(44)</sup>  $\Delta H_{\rm f}^{\circ}$  (gas) =  $\Delta H_{\rm f}^{\circ}$  (liquid) +  $\Delta_{\rm vap} H_{\rm f}^{\circ}$  ( $t_{\rm b}$ ) = 89.0 + 26.7 = 115.7 kJ mol<sup>-1</sup>. See ref 42, pp 5–20 and 6–117.

| amidine ( <b>D</b> ) |                               | amine (A)   |                               |                 |                               |                 |                               |             |  |  |  |  |
|----------------------|-------------------------------|-------------|-------------------------------|-----------------|-------------------------------|-----------------|-------------------------------|-------------|--|--|--|--|
|                      | leucinol (                    | LeuOH)      | isoleucine octy               | hexyla          | mine                          | cyclohexylamine |                               |             |  |  |  |  |
|                      | CO <sub>2</sub> <sup>6c</sup> | $CS_2$      | CO <sub>2</sub> <sup>6b</sup> | CS <sub>2</sub> | CO <sub>2</sub> <sup>6a</sup> | $CS_2$          | CO <sub>2</sub> <sup>6a</sup> | $CS_2$      |  |  |  |  |
| C6<br>C8<br>DBU      | L<br>L<br>L                   | L<br>L<br>L | L<br>L<br>L                   | L<br>L<br>S     | L<br>L<br>L                   | L<br>L<br>S     | S<br>S<br>L                   | L<br>L<br>S |  |  |  |  |

Table 4. Phases<sup>a</sup> of Neat 1/1 (mol/mol) D/A Mixtures at Room Temperature after Treating with CO<sub>2</sub> or CS<sub>2</sub>

 $^{a}$ L = liquid, S = solid.

the Hammond Postulate that the enthalpy of formation of a dithiocarbamate will be more favored energetically, although reactions of amines with both  $CO_2$  and  $CS_2$  are exothermic. These results indicate that the addition of  $CO_2$  and  $CS_2$  can tune the physicochemical properties of the ILs and RTILs, although they may do so in subtly different ways.

## 4. Conclusions

Equimolar mixtures of an amidine and an amine can be transformed easily into a new class of room-temperature ionic liquids, amidinium dithiocarbamates, upon addition of one molar equivalent of CS<sub>2</sub>. The amidinium dithiocarbamates are more stable thermally than their amidinium carbamate analogues, made by adding another triatomic molecule, CO<sub>2</sub>, to amidine/amine mixtures. In general, the dithiocarbamates are stable to higher temperatures than their amidine-amine mixtures, even in air. Unlike their amidinium carbamate analogues (which lose a molecule of  $CO_2$  near their decomposition temperatures, ca. 50 °C under an atmosphere of CO<sub>2</sub>), the amidinium dithiocarbamates do not lose a molecule of CS<sub>2</sub> when heated above their decomposition temperatures, ca. 80 °C. Instead, they undergo a series of structural changes that lead to several products, including thioureas and thioformamides, which provide insights into the thermolysis mechanism. However, CS<sub>2</sub> can be expelled from the amidinium dithiocarbamates in the presence of a weak acid.

The thermal, polar, viscous, and conductance properties of the liquid amidinium dithiocarbamates have been characterized and compared with both their amidineamine precursor mixtures and with the analogous amidinium carbamates. The results show that these physical and chemical properties can be tuned by changing the D/A combinations and the nature of the triatomic molecule added. Viscosities of the Cn-amine-CS<sub>2</sub> systems increase as the amidine chain length **n** increases and are more viscous than the corresponding Cn-amine-CO<sub>2</sub> RTILs. Although the C4 amidine provided RTILs when combined with CS<sub>2</sub> and all of the amines examined in this work, only the amidinium dithiocarbamates composed of an amino alcohol were liquids at room temperature when the amidine was the bulky and short-chained guanidine TMG.

According to the spectroscopic probe **DAPNE**, the dithiocarbamates and carbamates have similar polarities and are much more polar than their corresponding

nonionic D/A mixtures. However, as noted by miscibility studies, the polarities of the dithiocarbamates do change subtly when the chain length of the **Cn** amidine or the amine structure is changed. As expected, the conductivities of the structurally analogous neat dithiocarbamates and carbamates are very similar, they remain similar at the same dilution factors in chloroform, and they are significantly higher than the conductivities of their D/Acomponent mixtures.

Attractive attributes of the amidinium dithiocarbamate ILs and RTILs (when compared to many other types of ionic liquids) include their ease of preparation (simple in situ mixing of commercially available or easily synthesized precursors), their diversity of structures, and their broad temperature ranges (commencing at subambient temperatures). This work provides a facile, one-step approach to utilize  $CS_2$ , an environmentally unattractive liquid, to prepare useful and very attractive chemical materials by very simple manipulations and reactions. These ILs and RTILs are expected to find extensive use as media for a broad range of guest molecule reactions, including some that involve the creation of chiral centers or the recuperation of expensive metal catalysts.<sup>45</sup> Future research will focus on such applications.

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Supporting Information Available: Materials, instrumentation, and sample preparation methods, IR spectra, NMR spectra, density investigations, viscosities and conductivities at different temperatures, a Walden plot and photographs of a D/A and D-A-S, UV-vis  $\lambda_{max}$  values of DAPNE in various solvents, and viscosities of some D/A and D-A-S as a function of shear stress, characterizations of thermolysis products, experimental details of transformation from ammonium dithiocarbamates to amidinium dithiocarbamates (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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