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Synthesis and Characterization of Novel Chiral Ionic Liquids and Investigation of their Enantiomeric Recognition Properties

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Abstract

We report the synthesis and characterization of amino acid ester based chiral ionic liquids, derived from L- and D-alanine tert butyl ester chloride. The synthesis was accomplished via an anion metathesis reaction between commercially available L- and D-alanine tert butyl ester chloride using a variety of counterions such as lithium bis (trifluoromethane) sulfonimide, silver nitrate, silver lactate, and silver tetrafluoroborate. Both enantiomeric forms were obtained as confirmed by bands of opposite sign in the circular dichroism spectra. The L- and D-alanine tert butyl ester bis (trifluoromethane) sulfonimide were obtained as liquids at room temperature and intriguingly exhibited the highest thermal stability (up to 263°C). In addition, the ionic liquids demonstrated enantiomeric recognition ability as evidenced by splitting of racemic Mosher's sodium salt signal using a liquid state ¹⁹F nuclear magnetic resonance (NMR) and fluorescence spectroscopy. The L- and D-alanine tert butyl ester chloride resulted in solid salts with nitrate, lactate, and tetrafluoroborate anions. This illustrates the previously observed tunability of ionic liquid synthesis, resulting in ionic liquids of varying properties as a function of varying the anion.

Keywords

chiral ionic liquids; chiral selectors; synthesis; chiral recognition

INTRODUCTION

Ionic liquids (ILs), commonly termed room temperature ionic liquids (RTILs), are a class of organic salts. These molecules typically contain an organic cation with delocalized charge and a bulky inorganic anion. Interest in RTILs continues to grow because of their potential as greener solvent alternatives to conventional environmentally damaging organic solvents.¹ In addition, ILs have unique properties such as lack of measurable vapor pressure, high thermal stability, and recyclability.¹⁻⁵ Such environmental-friendly properties make ILs relatively benign solvents for cleaner processes to minimize toxic chemical wastes which have become a priority for chemical industries.⁶ Room temperature ILs have been used in various applications such as replacing conventional organic solvents in organic synthesis,⁷ solvent extractions,⁸ electrochemical reactions,⁹,¹⁰ liquid-liquid extractions,¹¹ and in enzymatic reactions.¹² In addition, analytical applications of ILs such as their use as buffers in capillary
electrophoresis,\textsuperscript{13} as stationary phases in gas chromatography\textsuperscript{14,15} as well as high performance liquid chromatography,\textsuperscript{16} and enhancement of sensitivity in thermal lens measurement have also been investigated.\textsuperscript{17} A review of several analytical applications of ILs has been reported by Baker et al.\textsuperscript{18} In addition, Baker et al. have developed an optical sensor based on an ionic liquid.\textsuperscript{19}

Analysis of chiral molecules is very important since different enantiomers of a chiral racemic drug may display different properties.\textsuperscript{20} For example, one enantiomer of a chiral drug may have the desired medicinal properties, while the other enantiomer may be harmful. Various chiral selectors, such as cyclodextrins, molecular micelles, antibody, and crown ethers have been widely used because of their chiral recognition abilities.\textsuperscript{21-24} However, the use of many current chiral selectors is often limited because of low solubility, difficult organic syntheses, instability at high temperature, as well as high cost. In addition, many currently available chiral selectors require the use of another solvent and sometimes more than one solvent system if the analyte and the chiral selector are not soluble in the same solvent. Therefore, there is a need for the development of new chiral selectors that can be used simultaneously as solvent and chiral selector. Thus, the use of chiral ILs have gained popularity since they can be used as chiral solvents for asymmetric induction in synthesis.\textsuperscript{25} Chiral ILs can also serve as chiral stationary phases in chromatography as demonstrated by Ding and Armstrong in capillary electrophoresis.\textsuperscript{26} Tran and coworkers have also recently used chiral ILs for determining the enantiomeric composition of pharmaceutical products.\textsuperscript{27,28}

To our knowledge, the first chiral ionic liquid, 1-butyl-3-methyl imidazolium lactate was reported by Seddon and his coworkers in 1999.\textsuperscript{29} This chiral ionic liquid, with a chiral anion, was prepared via anion metathesis using 1-butyl-3-methyl imidazolium chloride and sodium (S)-2-hydroxypropionate. This ionic liquid also afforded good endo/exo selectivity in a Diels-Alder reaction. Recently, ILs with chiral carboxylates have been synthesized by Allen et al.\textsuperscript{30} This synthesis was achieved in water by reacting tetrabutylammonium hydroxide with the corresponding amino acids or chiral carboxylic acids. In 2002, Wasserscheid et al. synthesized chiral ILs from chiral starting materials affording many different chiral ILs in good yields.\textsuperscript{31} A novel imidazolium based chiral ionic liquid with planar chirality was synthesized by Saigo and coworkers in 2002.\textsuperscript{32} However, this ionic liquid could only be obtained as a racemic mixture and required further separation of the enantiomers before investigating its applications. Other chiral ILs based on imidazolium,\textsuperscript{33,34} ephedrinium,\textsuperscript{35} and pyridinium\textsuperscript{36} cations have been synthesized.\textsuperscript{33-36} However, chiral precursors for ILs are often used in a multistep synthesis. A detailed review of chiral ionic liquid synthesis has been reported.\textsuperscript{37} Tao et al. have also successfully prepared chiral ILs from amino acids and their corresponding methyl and ethyl esters.\textsuperscript{38} These chiral ILs from amino acid esters had low melting points compared with those derived from amino acids. Other interesting amino acid derived chiral ILs have also been synthesized recently.\textsuperscript{39-41} Ding et al. have successfully synthesized chiral ILs via a simple anion exchange between a commercially available halide salt with $\text{N}$-lithiotrifluoromethanesulfonimide.\textsuperscript{42} This approach provides an attractive one step synthesis with a chiral precursor, while allowing the product to be easily purified by washing with water. The same approach was employed by Tran and Oliveira to prepare chiral ILs.\textsuperscript{27} The variety and applications of these ILs suggest that other chiral ILs need to be explored in order to obtain ILs for different applications.

Natural materials are often used as precursors for preparing chiral ILs in multiple step synthesis. As an example, the use of amino acids for preparation of imidazolium cations is clear evidence of such use.\textsuperscript{33} Chiral induction in some reactions may be required to afford chiral ILs, mostly in one enantiomeric form. In addition, the few commercially available chiral ILs are often very expensive. The high cost, combined with the difficulty in chiral ionic liquid synthesis, has limited their extensive study and applications.
The primary objective of this study was to synthesize and characterize both enantiomeric forms of new chiral ILs from commercially available amino acid ester chlorides. The presence of a chiral center in the precursor further simplifies the synthesis, alleviating the need for asymmetric induction. In addition, esterification reduces hydrogen bonding of amino acids affording low melting point ILs. By varying the anions, the synthesis of ILs can be tailored, resulting in ILs of different properties that may be used for various applications. In addition, this study reports an investigation of the enantiomeric recognition ability of a variety of chiral amino acid ester based ILs. The synthesis of chiral ILs was accomplished via a simple anion metathesis reaction and characterization was performed using nuclear magnetic resonance (NMR), thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), circular dichroism (CD), and elemental micro-analysis. The relatively simple synthetic procedure and the presence of chiral centers in the precursors is a tremendous advantage for our approach. Finally, the chiral recognition ability of \( \text{L-} \) and \( \text{D-} \) alanine tert-butyl ester bis (trifluoromethane) sulfonimide ionic liquid was evaluated using \(^{19}\text{F NMR}\) with a racemic Mosher's sodium salt substrate and fluorescence spectroscopy with some chiral fluorescent analytes.

**EXPERIMENTAL PROCEDURES**

**Chemicals and Materials**

\( \text{\textit{L-} and \textit{D-}alanine tert butyl ester hydrochloride [\textit{L-} and \textit{D-}AlaC}_4\text{Cl]}\), bis(trifluoromethane) sulfonimide lithium salt (LiNTf\(_2\)), silver tetrafluoroborate (AgBF\(_4\)), silver lactate (AgLac), silver nitrate (AgNO\(_3\)), 2-methoxy-2-(trifluoromethyl) phenylacetic acid (Mosher's acid), and methanol (ACS certified) were purchased from Sigma Aldrich Chemicals (Milwaukee, WI). In addition, enantiomerically pure \( \text{R-} \) and \( \text{S-} \)-enantiomers of warfarin, naproxen and 2,2,2-trifluoroanthylethanol (TFAE) were purchased from Sigma Aldrich Chemicals (Milwaukee, WI). All chemicals were used as received.

**General Instrumental Methods**

The NMR spectra were recorded in \( d_6\)-DMSO on a Bruker-250 MHz instrument with tetramethyl silane (TMS) as an internal standard. Melting point \((T_m)\) was determined by differential scanning calorimetry using a thermal analysis instrument TA SDT2960 at a scanning rate of 5°C min\(^{-1}\). Thermal decomposition temperature \( (T_{dec})\) of ILs was determined with a thermal analysis instrument 2950 TGA HR V6.1A (module TGA 1000°C). The heating rate for TGA was 5°C min\(^{-1}\) under nitrogen from 25 to 300°C. A Jasco-710 spectropolarimeter was used to obtain the CD spectra of our ILs. Steady-state fluorescence measurements were recorded at room temperature by use of a Spex Fluorolog-3 spectrofluorimeter (model FL3-22TAU3; Jobin Yvon, Edison, NJ) equipped with a 450-W xenon lamp and R928P photomultiplier tube (PMT) emission detector. Fluorescence emission spectra were collected in a 4-mm quartz fluorescence cuvet with slit widths set for entrance exit bandwidths of 4 nm on both excitation and emission monochromators for warfarin, 2 nm for TFAE, and 1.5 nm for naproxen, respectively. Fluorescence for warfarin, TFAE, and naproxen were respectively monitored at excitation wavelengths of 306, 365, and 280 nm. In addition, all fluorescence spectra were blank subtracted before data analysis.

**\(^{19}\text{F NMR Experiment}\)**

Racemic Mosher's sodium salt was prepared from Mosher's acid by reacting with an equivalent of sodium hydroxide in water and the salt was dried under vacuum before \(^{19}\text{F NMR}\) measurement. The racemic Mosher's sodium salt (8.38 mg, 0.03 mmol) and 129.07 mg (0.3 mmol) of \( \text{L-} \) or \( \text{D-} \) AlaC\(_4\)NTf\(_2\) were dissolved in 0.75 ml of \( d_6\) DMSO. The mixture was shaken vigorously for 10 min on an orbital shaker before recording \(^{19}\text{F NMR}\) spectra.
Synthesis of \(\alpha\)- and \(\beta\)-Alanine tert Butyl Ester Bis (trifluoromethane) Sulfonimide AlaC\(_4\)NTf\(_2\)

0.5 g (2.75 mmol) of \(\alpha\)-or \(\beta\)-alanine tert butyl ester chloride was dissolved in water. An equimolar amount (0.79 g, 2.75 mmol) of bis (trifluoromethane) sulfonimide lithium salt was dissolved separately in water. The two solutions were mixed and stirred for 2 h at room temperature. The mixture resulted in two layers, of which the lower layer was separated and dried under vacuum overnight. This resulted in 0.94 g (79% yield) of colorless ionic liquid.

The decomposition temperature (\(T_{\text{dec}}\)) of this ionic liquid was found to be 263°C by use of TGA measurements. \(^1\)H NMR (250 MHz, \(d_6\) DMSO) \(\delta\) (ppm) 8.19 (s, 3H), 3.97 (q, 1H), 1.45 (s, 9H), 1.36 (d, \(J = 7.0\) Hz, 3H). \(^1^3\)C NMR \(\delta\) (ppm) 170.12, 83.66, 49.19, 28.32, 16.69. Anal. Calcd. for \(\text{C}_{9}\text{H}_{16}\text{N}_{2}\text{O}_{6}\text{S}_{2}\text{F}_{6}\): C: 35.71; H: 7.38; N: 6.57. Found: C: 35.71; H: 7.38; N: 6.52.

RESULTS AND DISCUSSION

Synthesis and Characterization of a New Amino Acid Ester Chiral Ionic Liquid (\(\alpha\)-or \(\beta\)-AlaC\(_4\)NTf\(_2\))

The synthesis of both enantiomeric forms of alanine tert-butyl ester bis (trifluoromethane) sulfonimide was accomplished via anion metathesis reaction of the corresponding amino acid ester chloride and bis (trifluoromethyl) sulfonylimide lithium salt (Scheme 1). The reaction proceeded well in water with good yield (79%) of \(\alpha\)-or \(\beta\)-alanine tert-butyl ester bis (trifluoromethyl) sulfonylimide (L- or D-AlaC\(_4\)NTf\(_2\)). The \(^1\)H NMR (Fig. 1) and \(^1^3\)C NMR (see Fig. 2) of the ionic liquid was consistent with the chemical structure of AlaC\(_4\)NTf\(_2\). The NMR spectra obtained for other ILs were very similar to that of AlaC\(_4\)NTf\(_2\). The similarity in NMR spectra was expected since only the anions were varied. The alanine tert-butyl ester bis (trifluoromethyl) sulfonylimide ionic liquid was found to be a desirable liquid at room temperature and stable up to 263°C, as indicated by thermal gravimetric analysis (TGA) measurement (Fig. 3A).

The ionic liquid \(\alpha\)-AlaC\(_4\)NTf\(_2\) was also heated at 225°C for 2 h to verify and confirm whether decomposition occurs at a lower temperature. From Figure 3B, it seems that at this isothermal plateau (225°C), there is a constant rate loss of 0.42%/min for the span of 120 min.
constancy of the weight loss rate might be an indication that a physical phenomenon (e.g. evaporation), rather than a chemical decomposition process, is occurring. The rather low decomposition temperature for the BF$_4$ salt (125°C), is still uncertain and may not be solely due to the cation instability upon moderate heating. This is because as much as the cation might not be very stable at moderate heating, the same cation had relatively higher stability (263°C) with the NTf$_2$ anion.

The high thermal stability of alanine tert-butyl ester bis (trifluoromethyl) sulfonylimide makes it a preferred chiral selector and chiral solvent for reactions at high temperature or as a coating in gas chromatography. It is indeed extremely important that the chiral center in the precursor be retained in the final ionic liquid product. According to Jodry and Mikami, some imidazolium based chiral ILs will sometimes undergo racemization after synthesis. The possibility of racemization in the synthesized ILs was investigated by use of circular dichroism (CD) measurements of the ionic liquid products and their precursors. Examples of the CD bands obtained for both enantiomeric forms of the ILs are as shown in Figure 4. As expected, the CD bands of the precursors were in the same direction as those of the ionic liquid products, confirming retention of configuration. In addition, the opposite CD bands confirmed that the $\text{L}$- and $\text{D}$-configurations of the ILs had been retained (see Fig. 4).

**Chiral Recognition Study of ILs Using $^{19}\text{F}$ NMR**

As previously noted, $\text{L}$- and $\text{D}$-alanine tert-butyl ester bis (trifluoromethane) sulfonylimide are liquids at room temperature. It was therefore interesting to investigate their ability to act both as solvent and chiral selector. The chiral recognition ability of $\text{L}$- and $\text{D}$-alanine tert-butyl ester bis (trifluoromethane) sulfonylimide was investigated by use of $^{19}\text{F}$ NMR and racemic Mosher’s sodium salt. In this experiment, various solvents such as methylene chloride, deuterium oxide, dimethyl sulfoxide (DMSO) as well as chloroform were examined. However, $d_6$-DMSO demonstrated good solubility as compared with other solvents investigated. The results of the $^{19}\text{F}$ NMR study for enantiomeric recognition ability of $\text{L}$- and $\text{D}$-alanine tert-butyl ester bis (trifluoromethane) sulfonylimide are shown in Figure 5. The diastereomeric interactions lead to a shift in the $^{19}\text{F}$ NMR signal of the racemic Mosher’s sodium salt. In addition, the $^{19}\text{F}$ NMR signal of the racemic substrate was split by both enantiomeric forms of the ionic liquid demonstrating their enantiomeric recognition (see Fig. 5). This confirms that this ionic liquid can be a suitable chiral selector for various applications such as determination of enantiomeric composition of chiral molecules of pharmaceutical, biomedical, and environmental interest.

**Chiral Recognition of ILs Using Fluorescence Spectroscopy**

Steady-state fluorescence spectroscopy was further used to evaluate the chiral recognition ability and enantio-selectivity of the chiral ILs on 2,2,2-trifluoroanthylethanol (TFAE), warfarin, and naproxen chiral analytes. The choice of these chiral analytes in this study was due to their fluorescence properties; furthermore, they are of environmental and pharmaceutical interest. For instance, warfarin is an anticoagulant drug used for the treatment of thromboembolic diseases and is also generally used as a pesticide, while naproxen is used as an anti-inflammatory drug.

The emission spectra of the 10 μM $R$- and $S$-enantiomers of TFAE, warfarin, and naproxen analytes in the presence of $\text{L}$-AlaC$_4$NTf$_2$ chiral ILs are, respectively, shown in Figures 6A1, B1, and C1. The intensity of emission of the $R$-enantiomers obtained in the presence of ionic liquid solvent and chiral selector is noted to be higher than that of the $S$-enantiomers for all three analytes investigated. A difference in emission intensity of $R$- and $S$-enantiomers in the presence of chiral selectors is due to different diastereomeric interactions between the enantiomers and the IL chiral selectors. Such spectral shifts have been widely reported and
associated with enantioselectivity of chiral selectors as a result of diastereomeric complexes. 43-45

Finally, a mean-centered plot of emission spectra was used to gain better insight into the enantiomeric selectivity and chiral recognition ability of the chiral ILs. The mean centered plot of the emission spectra depicted in Figures 6A1, B1, and C1 are shown in Figure 6A2, B2, and C2, respectively. The spectra were obtained by subtracting the spectrum of R- and S-enantiomer in the presence of chiral selectors from the R- and S-mean spectra. It is of great importance to note that R- and S-enantiomers have opposite mean spectra, further demonstrating the chiral recognition ability and enantio-selectivity of the ionic liquid chiral selector.

Synthesis and Characterization of Novel Amino Acid Ester Chiral ILs (L- or D-AlaC₄NO₃, AlaC₄BF₄, AlaC₄Lac)

A similar anion metathesis reaction used for the synthesis of AlaC₄NTf₂ was employed for the synthesis of AlaC₄NO₃, AlaC₄BF₄, and AlaC₄Lac. However, the reaction was performed in methanol at a shorter time of 5 min (Scheme 2). The silver chloride precipitate was filtered off in each case affording good yields of the respective chiral ILs after removing methanol in vacuo.

Alanine tert-butyl ester nitrate (AlaC₄NO₃) crystallized to form a white solid at room temperature. AlaC₄BF₄ was obtained as a colorless greasy solid, whereas AlaC₄Lac forms clear needle-like crystals at room temperature. The fact that solid ILs were obtained upon changing the anion demonstrates the tunability of the ILs synthesized in this study. By varying the anion or cation, different ILs with different properties is obtained for various applications. These results illustrate that bis (trifluoromethane) sulfonylimide is probably a poorly coordinating anion with an alanine tert-butyl ester cation. The poor crystal packing between the anion and cation results in lower melting point ILs. 46 Their findings are in agreement with our results that bis (trifluoromethane) sulfonylimide being the largest of the anions yielded an ionic liquid product that was liquid at room temperature. The other smaller anions such as nitrate afforded ILs that was solid at room temperature.

CONCLUSION

In summary, we have successfully synthesized a series of new chiral ILs in both enantiomeric forms using a simple metathesis reaction between the chiral chloride ester salt and the corresponding anion sources. Alanine tert-butyl ester bis (trifluoromethane) sulfonylimide is desirably liquid at room temperature and is thermally stable up to 263°C. It can therefore be used in high temperature reactions or as a chiral selector in gas chromatography. Furthermore, the ILs presented here has the same chiral configuration as the chloride salt precursors indicating that enantiomeric salts were obtained upon anion metathesis. Both enantiomeric forms of alanine tert-butyl ester bis (trifluoromethane) sulfonylimide ionic liquid demonstrated enantiomeric recognition of racemic Mosher's sodium salt. This is an advantage since the ionic liquid can serve both as solvent and chiral selector, alleviating the need for use of environmentally damaging solvents to dissolve the analyte. As an example, this compound could probably be used to provide chiral selectivity in the determination of enantiomeric composition of pharmaceutical products and in chiral separations. While the solid ILs could not be used for this purpose, we believe that their synthesis and characterization is a step towards exploring their potential applications.

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Scheme 1.
Synthesis of L-AlaC₄NTf₂.
Fig. 1.
Proton ($^1$H) NMR spectrum of $\alpha$-AlaC$_4$NTf$_2$ in $d_6$ DMSO with tetramethyl silane (TMS) as an internal standard at room temperature.
Fig. 2.
Carbon-13 ($^{13}$C) NMR spectrum of $\psi$-AlaC$_4$NTf$_2$ in $d_6$ DMSO with tetramethyl silane (TMS) as an internal standard at room temperature.
Fig. 3.
Thermal gravimetric analysis of \( \text{L-AlaC}_4\text{NTf}_2 \) with a heating rate of 58°C min\(^{-1}\) under nitrogen (A) from 25 to 3008°C, and (B) from 25 to 2258°C, then isothermally at 2258°C for 2 h.
Fig. 4.
Circular dichroism spectra of \(\text{L}\)-and \(\text{D}\)-\(\text{AlaBuCl}\), \(\text{B}\) \(\text{AlaBuBF}_4\), \(\text{C}\) \(\text{AlaBuNO}_3\), and \(\text{D}\) \(\text{AlaBuNTf}_2\) at room temperature.
Fig. 5. 
$^{19}$F NMR spectra of (A) racemic sodium Mösher's salt; and a mixture of the racemic sodium Mösher's salt with (B) $\alpha$-AlaC$_4$NTf$_2$, and (C) $\beta$-AlaC$_4$NTf$_2$ at room temperature.
Fig. 6.
Fluorescence emission and mean centered spectral plots of 10 μM R- and S- (A) TFAE, (B) warfarin, and (C) naproxen enantiomers in the presence of L-AlaC₄NTf₂ chiral ionic liquid. The emission spectra of TFAE, warfarin, and naproxen were monitored at excitation wavelength of 365, 306, and 280 nm, respectively, at room temperature.
Scheme 2.
Synthesis of AlaC\(_4\)NO\(_3\), AlaC\(_4\)BF\(_4\), AlaC\(_4\)Lac.