



Synthesis of the Novel Compound 1-*tert*-Butyl-3-Propylimidazolium Iodide

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Abstract

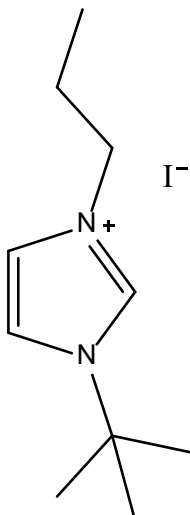
*Research on ionic liquids has been around for several decades. These unique molecules are often used as phase transfer catalysts in chemical reactions that, in contrast to conventional catalysts, can be easily recovered to reduce the environmental impact. Until recently, most ionic liquids have not used 1-*tert*-butylimidazole as a starting material, because it has not been widely commercially available and can be difficult to synthesize. This research focuses on the synthesis of 1-*tert*-butyl-3-propylimidazolium iodide, a molecule not documented in existing literature. This compound was successfully synthesized using an S_N2 reaction with modifications from previously published methods, and was characterized using 1H NMR, ^{13}C NMR, and FT-IR. Unlike many ionic liquids, this molecule is not hygroscopic. Its stability may lead to further research using it as a small, asymmetric ionic catalyst or building block.*

Introduction

Ionic liquids have received a significant amount of attention in the past several decades. Their uses have ranged from biological applications to synthetic processes, and they continue to be utilized in numerous novel applications. Due to the advantageous energy storage and sustainable properties associated with these compounds, interest within the field has greatly expanded. There has been a specific interest in environmental preservation and hazardous solvent replacement (Watanabe et al., 2017).

Imidazolium-based ionic liquids are one of the more promising classes of ionic liquids. They are characterized as a salt composed of an organic cation with an organic or inorganic anion (Fredlake et al., 2004). Imidazolium-based ionic liquids contain an imidazolium ion and various alkyl substituents attached on the 1- and 3-positions of the imidazole ring (Yermalayeu et al., 2020). The weakly bonded ions arranged on the imidazolium ring result in asymmetric structural formations (Figure 1). The large and misshapen nature of the ion structure allows for the ionic bond to be easily broken (Yermalayeu et al., 2020). As a result, imidazolium-based ionic liquids require very little energy to break down, compared to traditional salts, making them a favorable compound for catalysts.

Figure 1: Chemical structure of 1-*tert*-butyl-3-propylimidazolium iodide



Key characteristics of these liquids include: relatively low melting point and vapor pressure, nonflammability, high water solubility, and strong thermal stability and absorption properties (Kitaoka et al., 2022). Furthermore,

their ability to dissolve polar and non-polar organic compounds, inorganic compounds, and polymeric compounds allows for various applications (Kitaoka et al., 2022). The non-toxic properties of imidazolium-based ionic liquids make it a vital candidate as an organic green solvent for potential reduction in toxic waste and byproducts.

Common anions, such as bromide and iodine, are often seen paired with an imidazolium cation (Fredlake et al., 2004). Research on using ionic liquids synthesized from the starting material 1-*tert*-butylimidazole is limited because of the difficulty of synthesizing it and its limited commercial availability. Initial studies have been documented using 1-*tert*-butyl-3-methylimidazolium iodide and 1-*tert*-butyl-3-ethylimidazolium iodide as potential building blocks for various asymmetric molecules and catalysts (Librando et al., 2015). There is no documentation of the synthesis or use of 1-*tert*-butyl-3-propylimidazolium iodide. The purpose of this paper is to document the synthesis of 1-*tert*-butyl-3-propylimidazolium iodide and to describe the variety of uses of an asymmetric ionic liquid.

Results and Discussion

The sample contains an imidazolium structure complete with an aromatic ring containing three hydrogens. The chemical shift values detailed on the ^1H NMR spectra depicted peak values consistent with other known imidazolium structures, such as 1-*tert*-butyl-3-methylimidazolium iodide (Librando and Creencia, 2015; Heckman et al., 2022). In particular, the higher chemical shift value of 10.11 ppm is representative of the single hydrogen attached to the imidazolium ring between the two nitrogen molecules. Similarly, the other two hydrogens on the imidazolium ring are represented as doublets with a chemical shift value of 7.72 ppm.

Furthermore, the various branches attached to the imidazolium should be noted. The propyl branch at the 3-position contains a triplet in the ^1H NMR spectrum at 4.42 ppm, a multiplet near 2.0 ppm, and a triplet at 1.07 ppm. This integration is consistent with what is expected for a propyl branch. The *tert*-butyl at the 1-position contains a singlet at 1.76 ppm with an integration of nine hydrogens. This is also consistent with a *tert*-butyl branch on an imidazolium ionic liquid (Librando and Creencia, 2015; Heckman et al., 2022).

The ^{13}C NMR is also consistent with what we would expect for this compound. The three peaks between 120 and 140 ppm represent the aromatic carbons, while the five other peaks represent the unique carbons within the two alkyl branches. The two peaks above 50 ppm indicate the two carbons directly attached to the aromatic ring. The larger peak at 31.38 ppm clearly shows the three identical carbons in the *tert*-butyl branch. The small triplet near 77 ppm is an artifact of the solvent (CDCl_3) and was expected but is not reflective of any impurities.

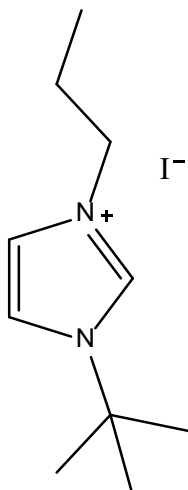
The off-white solid observed and the relatively low melting point

range also aided in the sample's identification. The sample's melting point range of 122–123 °C falls within the previously known thermal ranges of other asymmetric imidazolium-based ionic liquids (Heckman et al., 2022). This data is further supported by the fact that branched ionic liquids often have a higher melting point than those of smaller symmetric ionic liquids (Endo et al., 2019).

The analysis of the FT-IR performed was characteristic of other published imidazolium-based ionic liquids (Roth et al., 2012). The two distinguishing peaks known for imidazolium-based ionic liquids matched the sample's FT-IR analysis, with bands located at 1575 and 3100 cm^{-1} . The peak at 1575 cm^{-1} is due to the carbon nitrogen double bond, and the 3100 peak is due to the protons attached to the sp^2 hybridized carbons in the ring.

Originally when the experiment was performed, the sample was refluxed for 18 hours as documented by Yoshida et al. (2007) for the synthesis of 1-*tert*-butyl-3-methylimidazolium iodide. However, the advised reflux period resulted in a black, tar-like substance and an unclear NMR spectrum with several impurities. Based on visual observations, the reflux period was modified and a three-hour reflux period was instead selected. A visible white solid began to form after an hour. In contrast to one or two hours, three hours provided a good sample yield with minimal impurities.

Figure 2. Characterization of 1-*tert*-butyl-3-propylimidazolium iodide.



Off-white solid, m.p. 122–123 °C, 75% yield, ^1H NMR (60 MHz, CDCl_3) δ : 10.11 (s, 1H), 7.72 (d, 2H), 4.42 (t, 2H), 2.05–1.75 (m, 2H) 1.77 (s, 9H), 1.07 (t, 3H) ^{13}C NMR (15 MHz, CDCl_3) δ : 135.41, 124.00, 121.43, 61.64, 52.11, 31.38, 24.95, 11.80 FT-IR 1575, 3100 cm^{-1}

One extremely useful characteristic of this ionic liquid is that it does not seem to be hygroscopic. Some ionic liquids, such as 1,3-dimethylimidazolium iodide, are extremely hygroscopic, and that makes them difficult to be used either in synthesis or as a catalyst (Gardner et al., 2015). Based on visual observations, it initially appears that this novel compound can be stored under typical atmospheric conditions for long periods of time without much water absorption.

Conclusion

Although imidazolium-based ionic liquid research is quite extensive, little is known about *tert*-butylimidazolium-based ionic liquids. The bulky *tert*-butyl branch may provide a unique property that allows for specific regiochemistry in certain reactions that are unknown at this time.

Investigation of anions with asymmetrical and large chiral imidazolium-based ionic liquids has been documented to revealed dramatically different physical properties of the liquids based on the anion associated with it (Yu et al., 2013). Attempts to synthesize 1-*tert*-butyl-3-propylimidazolium bromide were partially successful using 1-propylbromide instead of 1-propyliodide as a starting material. However, the yields were low, and the samples were not as pure as the compound presented in this paper. Additional research on anion exchange is possible.

The two other general areas for further investigation include using 1-*tert*-butyl-3-propylimidazolium iodide as a building block for other molecules and evaluating it as a catalyst. Using small imidazolium-based ionic liquids as building blocks for thiones has been initially reported, and this compound would be a potential candidate for evaluation in this process (Lu et al., 2013; Sauerbrey et al., 2012; Yoshida et al., 2007). Certainly, there are many reactions that can be evaluated for its use as a catalyst. A natural starting point would be to evaluate its use with reactions that showed a benefit from either the *tert*-butyl branch or the asymmetry of the molecule (Ha et al., 2022; Librando & Creencia, 2015; Ranjan et al., 2018; Yermalayeu et al., 2020).

Although imidazolium-based ionic liquids have been studied for many years, little research has been completed using 1-*tert*-butylimidazole-derived compounds because of its limited commercial availability. This paper documents the synthesis and characterization of the novel compound 1-*tert*-butyl-3-propylimidazolium iodide. The properties of this molecule make it a good candidate for evaluation in future research and could make it a viable alternative to other imidazolium-based ionic liquids that are commonly used.

Materials

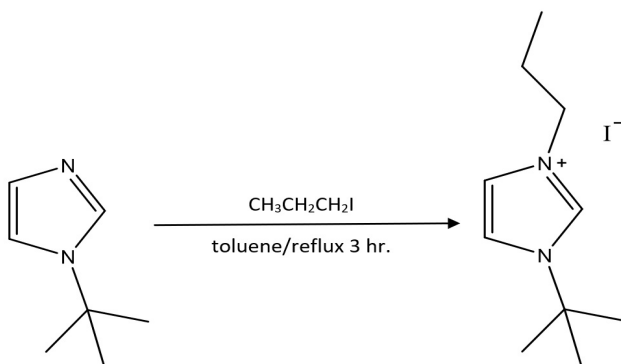
The uncorrected melting point range was determined using a MEL-TEMP II melting point apparatus. The ^1H NMR and ^{13}C NMR spectra were determined in CDCl_3 with TMS as in internal reference using an Anasazi

instrument NMR. The FT-IR spectrum was determined using a Cary 630 from Allegiant Technologies. The 1-*tert*-butyl imidazole was obtained from Ambeed. Toluene, 1-iodopropane, *tert*-butyl methyl ether, and the NMR solvent were obtained from Millipore Sigma. All reagents were commercially available and stored according to the manufacturer's recommendations.

Experimental

A three-neck heat gun dried 300 mL round-bottomed flask with a magnetic stir bar was used as the main apparatus. The center neck of the flask was fitted with a reflux condenser and circulated with cold water. The remaining two necks of the flask were fitted with rubber septa. An oil bath was placed atop a hot plate with a digital thermometer attached to provide a continuous reflux temperature. The bottom of the flask was suspended within an oil bath. Under an atmosphere of nitrogen, 26 mmol of 1-*tert*-butyl imidazole (3.2 g) and toluene (30 mL) were added via syringe, followed by 32 mmol iodopropane (3.1 mL). The solution was stirred continuously and heated at 100°C for three hours (Scheme 1). After three hours, a visible solid formed. Once the reaction was complete, all toluene was removed using vacuum rotary evaporation. The crude product was washed three times with 10 mL *tert*-butyl methyl ether to remove any unreacted starting materials and byproducts. Excess ether was removed using vacuum rotary evaporation. The sample was analyzed using ^1H NMR (60 MHz), ^{13}C NMR (15 MHz), and FT-IR, and the melting point was determined. These procedures were modified from previous published research (Gardner et al., 2015; Rios et al., 2018).

Scheme 1. Synthesis of 1-*tert*-butyl-3-propylimidazolium iodide using a one-step $\text{S}_{\text{N}}2$ reaction.



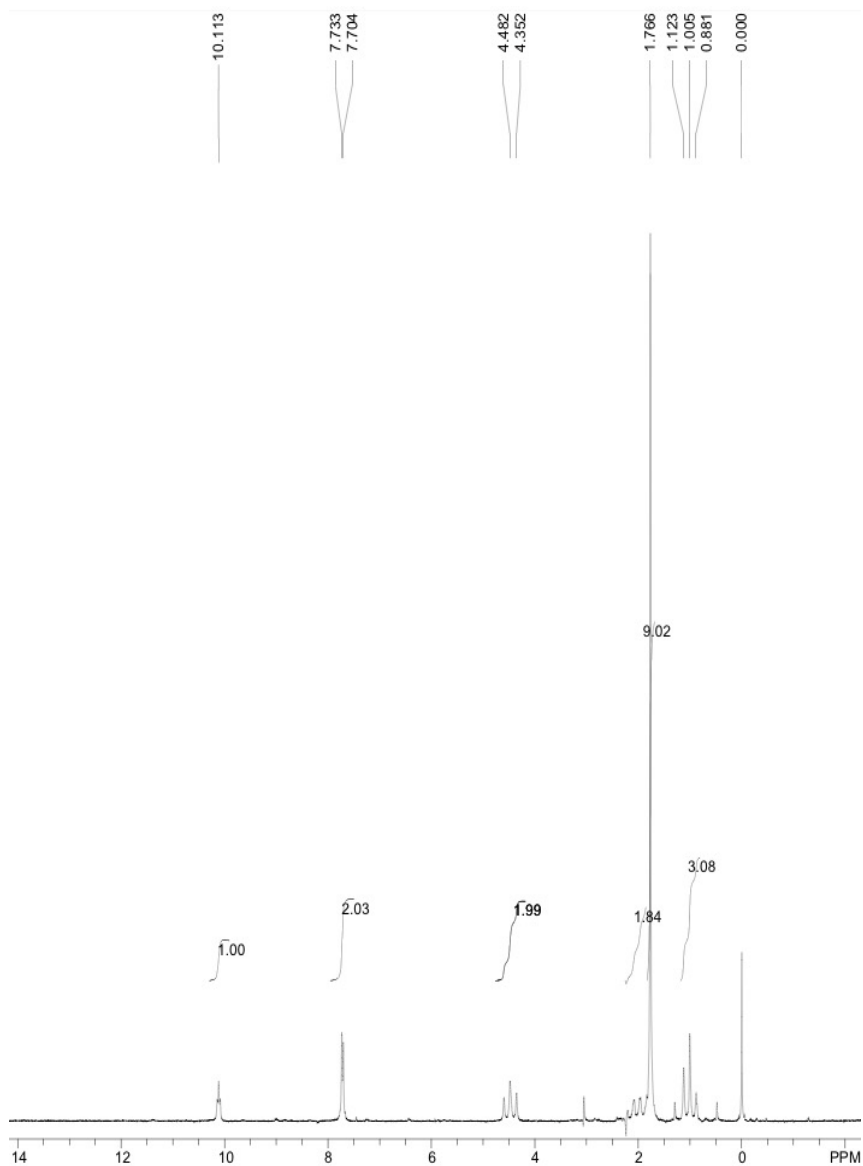
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Supplemental Information

1-*tert*-Butyl-3-Propylimidazolium Iodide | ^{13}C NMR

1-*tert*-Butyl-3-Propylimidazolium Iodide | ^1H NMR

1-*tert*-Butyl-3-Propylimidazolium Iodide | FT-IR

