



2,2,6,6-Tetramethylpiperidine-1-yloxy bound to the imidazolium ion by an acetamido group for investigation of ionic liquids

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ARTICLE INFO

Article history:

Received 5 October 2009

Revised 25 November 2009

Accepted 27 November 2009

Available online 2 December 2009

Keywords:

Spin probes

ESR spectroscopy

Nitroxides

Ionic liquids

ABSTRACT

New spin probes bearing the 2,2,6,6-tetramethylpiperidine-1-yloxy covalently bound to the imidazolium ion via a methylene spacer and an amide group are synthesized. If the anion is bis(trifluoromethylsulfonylimide) instead of iodide, the new spin probe has a similar structure as that of an ionic liquid. Nevertheless, the new spin probes are useful tools to investigate ionic liquids.

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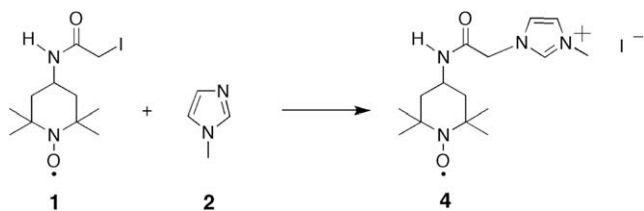
Ionic liquids have received increased attention as solvents in inorganic, organic, and polymer chemistry.^{1–4} Furthermore, they possess a high potential for application in batteries, fuel cells, and solar cells.^{5–7} The mobility of both the individual ions of the ionic liquid and the dissolved species is important in these potential applications. Stable radicals, so called spin probes, have been successfully used as model compounds to describe the mobility of reactive species in the ionic liquids.^{8–20} Furthermore, the isotropic hyperfine coupling constants of the stable radicals give information about micropolarity of the surrounding matrix.^{13,16,20–22} 2,2,6,6-Tetramethylpiperidine-1-yloxy derivatives are examples for spin probes, which have been successfully applied for the investigation of ionic liquids.^{13,14,16–20} Recently, 2,2,6,6-tetramethylpiperidine-1-yloxy derivatives have been modified by various substituents to investigate the interactions between model radicals and ionic liquids.^{17–20} Thus, cationic or anionic substituents are bound at the 4 position with respect to the nitroxyl group resulting in additional ionic interactions with either the anion or the cation of the ionic liquid. They are useful spin probes for the investigation of ionic liquids. It is shown that the ionic substituent at the 4 position with respect to the nitroxyl group significantly reduces the mobility of these spin probes in the ionic liquids caused by the additional ionic interactions between the ionic substituent and the individual ions of the ionic liquids.^{13,14,16,20} Recently, a pyrrolidine-1-yloxy derivative covalently bound via a spacer group to the imidazolium ion was described in the literature as further new spin probe for the investigation of ionic liquids.²¹

In this Letter, we describe the synthesis of a 2,2,6,6-tetramethylpiperidine-1-yloxy derivative that is covalently bound to the imidazolium ion. Covalent bonding of a 2,2,6,6-tetramethylpiperidine-1-yloxy derivative to the imidazolium ion gives more detailed information about the mobility of the cation of the ionic liquid. Furthermore, anion metathesis of the iodide by bis(trifluoromethylsulfonylimide) results in a new spin probe bearing the same anion as the ionic liquid and a radical structure covalently bound to the cation of the ionic liquid. In particular, the new spin probe has a similar structure as 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonylimide).

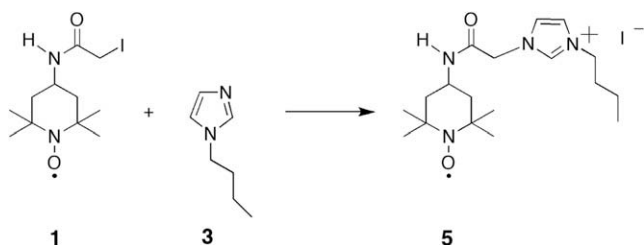
4-(2-Iodacetamido)-2,2,6,6-tetramethylpiperidine-1-yloxy (**1**) was selected for the covalent bonding of 2,2,6,6-tetramethylpiperidine-1-yloxy to the imidazolium ion because this compound reacts with 1-alkylimidazole at room temperature. Reaction of **1** with either 1-methylimidazole (**2**) or 1-butylimidazole (**3**) results in the new spin probe 1-(2-(4-(2,2,6,6-tetramethylpiperidinyl-1-yloxy)amino)-2-oxoethyl)-3-methylimidazolium iodide (**4**) or 1-(2-(4-(2,2,6,6-tetramethylpiperidinyl-1-yloxy)amino)-2-oxoethyl)-3-butylimidazolium iodide (**5**) bearing a radical structure covalently bound to the imidazolium ion as described in the Schemes 1 and 2.^{23,24} Anion metathesis of iodide by bis(trifluoromethylsulfonylimide) using silver bis(trifluoromethylsulfonylimide) results in the new spin probe **6** (Scheme 3), which bears the same anion as the 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonylimide).²⁵ The silver iodide formed in the course of the reaction precipitates from the reaction mixture and can be therefore easily separated from 1-(2-(4-(2,2,6,6-tetramethylpiperidinyl-1-yloxy)amino)-2-oxoethyl)-3-butylimidazolium bis(trifluoromethylsulfonylimide) (**6**), which remains

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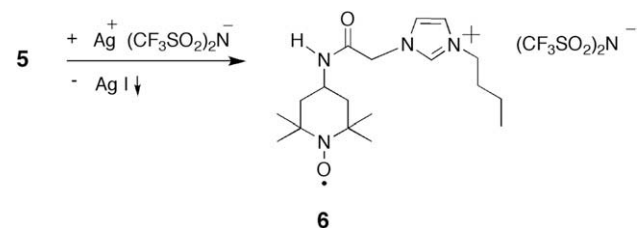
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Scheme 1. Synthesis of 1-(2-(4-(2,2,6,6-tetramethyl-piperidinyl-1-yloxy)amino)-2-oxoethyl)-3-methylimidazolium iodide (**4**).



Scheme 2. Synthesis of 1-(2-(4-(2,2,6,6-tetramethyl-piperidinyl-1-yloxy)amino)-2-oxoethyl)-3-butylimidazolium iodide (**5**).



Scheme 3. Preparation of 1-(2-(4-(2,2,6,6-tetramethyl-piperidinyl-1-yloxy)amino)-2-oxoethyl)-3-butylimidazolium bis(trifluoromethylsulfon)imide (**6**).

dissolved in the organic solvent. The new spin probe **6** remains as orange oil after evaporation of the solvent in vacuo.

The new model radicals **4**, **5**, and **6** contain the 2,2,6,6-tetramethylpiperidine-1-yloxy structure covalently bound to the imidazolium ion via an amide group and a methylene spacer. Therefore, the spin probe mobility is strongly influenced by the mobility of the imidazolium ion of the ionic liquid. Similar ESR spectra are obtained in the case of **1**, **4**, and **5** dissolved in dimethylsulfoxide (Fig. 1). The isotropic hyperfine coupling constants related to nitrogen ($A_{\text{iso}}(^{14}\text{N})$) and the average rotational correlation time (τ) are similar for the three spin probes in dimethylsulfoxide (Fig. 1). The latter were determined by the method of Budil et al.²⁶ This shows that no significant differences exist in the mobility of **1**, **4**, and **5** in dimethylsulfoxide. Furthermore, these spin probes detect the same value for micropolarity, which is similar to the micropolarity of dimethylsulfoxide.

Moreover, the new spin probes were investigated in 1-butyl-3-methylimidazolium tetrafluoroborate (**IL-BF₄**), which is an example for a widely investigated ionic liquid (Scheme 4).²⁷ Although **4** has a methyl substituent at one nitrogen atom of the imidazolium ring, the new spin probe **5** bears a butyl group at this nitrogen atom. Therefore, the structure of **5** is comparable with the cation of **IL-BF₄**.

In contrast to the similar ESR spectra obtained for **1**, **4**, and **5** in dimethylsulfoxide, significant differences are observed in the ESR spectra if these spin probes are dissolved in the ionic liquid **IL-BF₄** (Fig. 2). The three lines of the ESR spectra of **1**, **4**, and **5** show a significant line broadening and differences in the habitus of the spectra in comparison with the ESR spectra of these spin probes

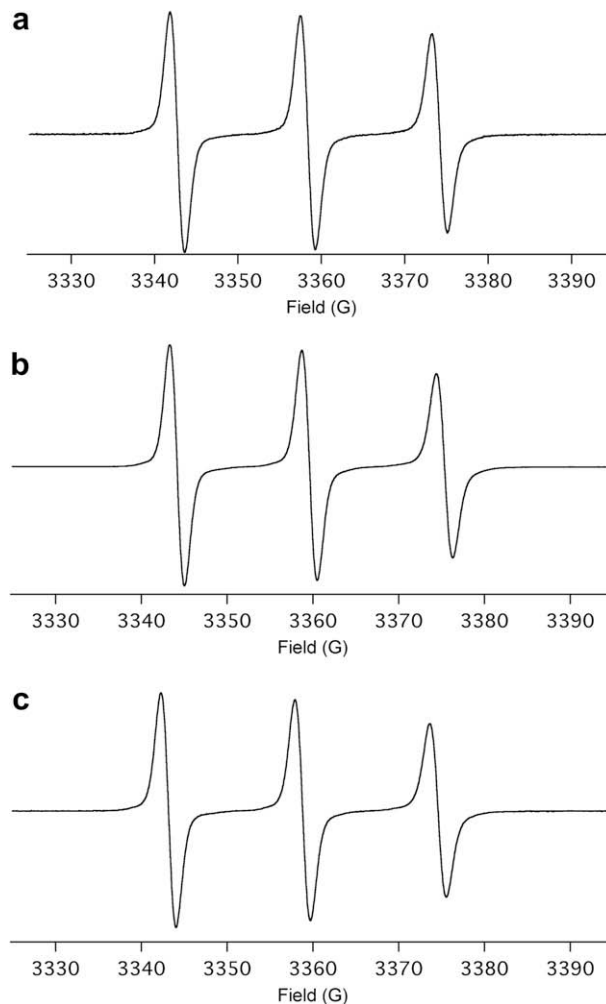
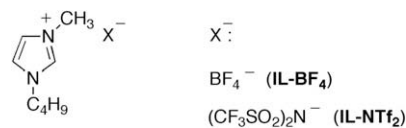


Figure 1. ESR spectra of the new spin probes. (a) **1**: $A_{\text{iso}}(^{14}\text{N}) = 15.7$ G, $\tau = 0.6$ ns; (b) **4**: $A_{\text{iso}}(^{14}\text{N}) = 15.7$ G, $\tau = 0.8$ ns, and (c) **5**: $A_{\text{iso}}(^{14}\text{N}) = 15.7$ G, $\tau = 0.8$ ns dissolved in dimethylsulfoxide at room temperature.



Scheme 4. Chemical structure of 1-butyl-3-methylimidazolium tetrafluoroborate (**IL-BF₄**) and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfon)imide (**IL-NTf₂**).

dissolved in dimethylsulfoxide (Fig. 1). The strong immobilization of the spin probe mobility in **IL-BF₄** is caused by the strong interactions between these spin probes and the ionic liquid. Furthermore, covalent bonding of the spin probe via an amide function and a methylene spacer to the imidazolium ion in the case of **4** and **5** results in a further reduction of the spin probe mobility (Figs. 2b and 2c) in comparison with the spin probe mobility in the case of **1** (Fig. 2a). Although the amide function is also present in **1**, stronger immobilization is found in the case of **4** and **5** in the ionic liquid in comparison with **1**. Covalent binding of the radical structure to the imidazolium ion causes this effect. However, the ESR spectra are similar for the spin probes **4** and **5** although the alkyl substituent at one nitrogen atom of the imidazolium ring is a methyl group in the case of **4** and a butyl group in the case of **5**. The rotational correlation time of the spin probes is significantly increased in **IL-BF₄** in comparison with dimethylsulfoxide (Figure

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