



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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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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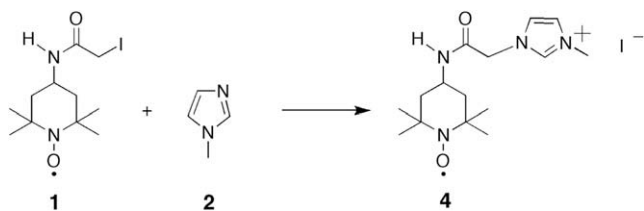
Ionic liquids have received increased attention as solvents in inorganic, organic, and polymer chemistry.^{1–4} Furthermore, they possess a high potential for application in batteries, fuel cells, and solar cells.^{5–7} The mobility of both the individual ions of the ionic liquid and the dissolved species 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).

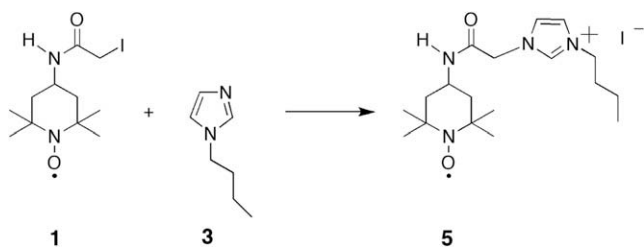
4-(2-Iodacetamido)-2,2,6,6-tetramethylpiperidine-1-yloxy (**1**) was selected for the covalent bonding of 2,2,6,6-tetramethylpiperidine-1-yloxy to the imidazolium ion because this compound reacts with 1-alkylimidazole at room temperature. Reaction of **1** with either 1-methylimidazole (**2**) or 1-butylimidazole (**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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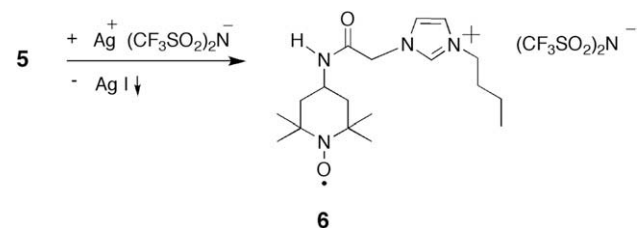
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Scheme 1. Synthesis of 1-(2-(4-(2,2,6,6-tetramethyl-piperidinyl-1-yloxy)amino)-2-oxoethyl)-3-methylimidazolium iodide (**4**).



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(trifluoromethylsulfonate) (**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

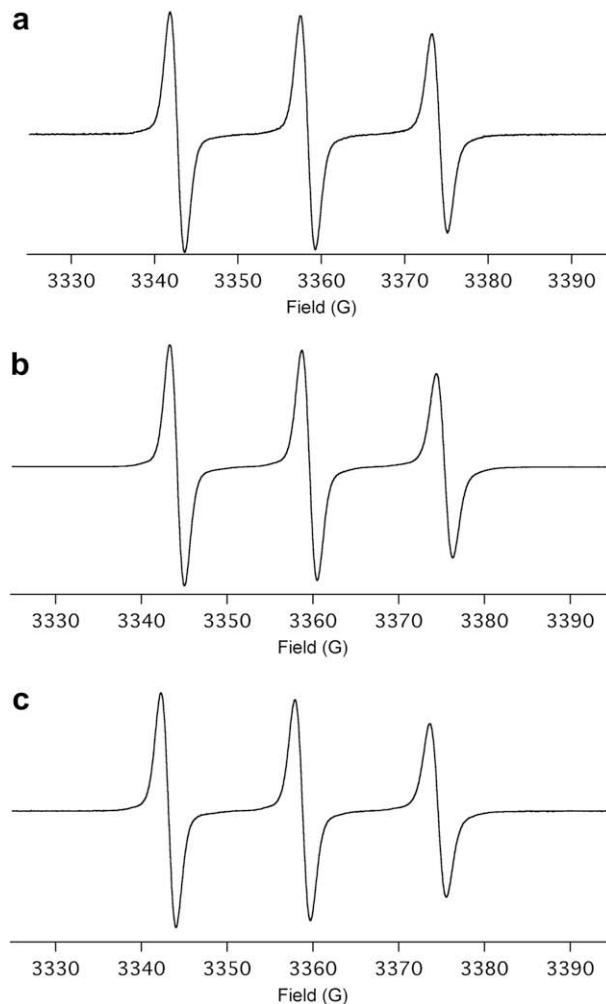
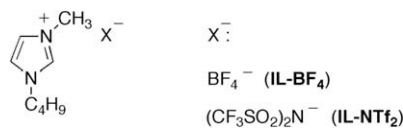


Figure 1. ESR spectra of the new spin probes. (a) **1**: $A_{\text{iso}}(^{14}\text{N}) = 15.7$ G, $\tau = 0.6$ ns; (b) **4**: $A_{\text{iso}}(^{14}\text{N}) = 15.7$ G, $\tau = 0.8$ ns, and (c) **5**: $A_{\text{iso}}(^{14}\text{N}) = 15.7$ G, $\tau = 0.8$ ns dissolved in dimethylsulfoxide at room temperature.



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

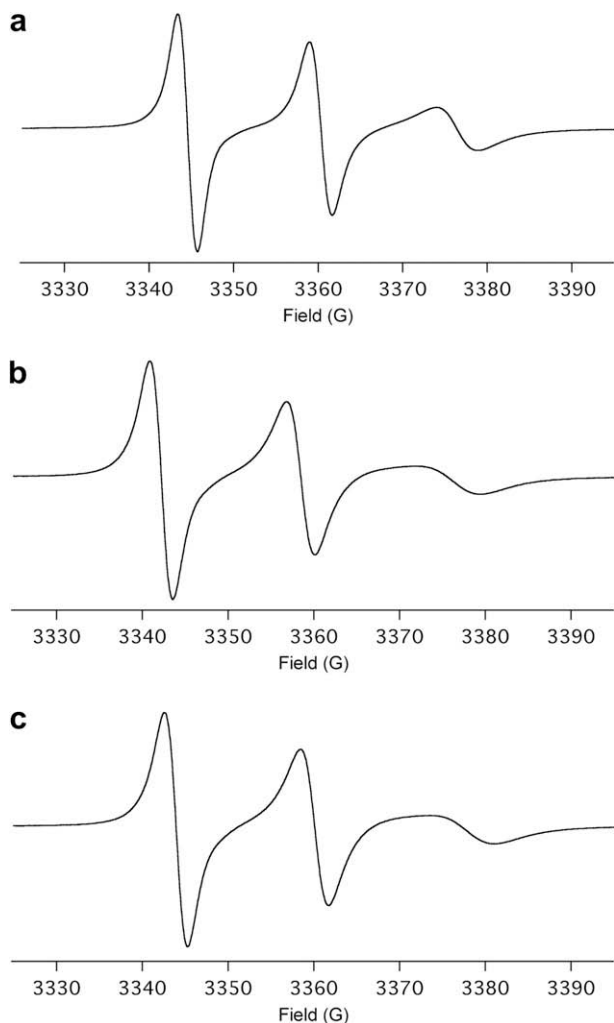


Figure 2. ESR spectra of (a) **1**: ($A_{\text{iso}}(^{14}\text{N}) = 15.9 \text{ G}$, $\tau = 7.1 \text{ ns}$) and of the new spin probes covalently bound at the imidazolium ion; (b) **4**: ($A_{\text{iso}}(^{14}\text{N}) = 16.6 \text{ G}$, $\tau = 9.8 \text{ ns}$), and (c) **5**: ($A_{\text{iso}}(^{14}\text{N}) = 16.5 \text{ G}$, $\tau = 10.2 \text{ ns}$) dissolved in **IL-BF₄** at room temperature.

captions of Figs. 1 and 2). Although the hyperfine coupling constants of **1** are similar in dimethylsulfoxide and **IL-BF₄**, differences exist for the covalently bound spin probes **4** and **5** in these solvents. This may be attributed to the strong immobilization of the spin probe mobility caused by the interactions with the ionic liquid. Therefore, spin probes covalently bound to the imidazolium ion are not useful for the discussion of micropolarity of ionic liquids if their mobility is strongly immobilized.

The new spin probe **6** dissolved in dimethylsulfoxide also shows three narrow lines in the ESR spectrum at room temperature (Fig. 3a). Significant line broadening and differences in the habitus of the ESR spectra are also observed if **6** is dissolved in the ionic liquid **IL-BF₄** or **IL-NTf₂** (Figs. 3b and 3c).²⁷ As discussed for **4** and **5**, the spin probe **6** also shows similar values to **1** for the hyperfine coupling constant and the rotational correlation time if dimethylsulfoxide is used as the solvent although higher values are obtained if an ionic liquid is used as the solvent (Fig. 3). The strong immobilization of the spin probe mobility in the ionic liquid is caused by the strong interactions of **6** with the individual ions of the ionic liquid. Because **6** possesses the same anion as **IL-NTf₂**, this new spin probe is preferred for the investigation of imidazolium bis(trifluoromethylsulfonylimides).

In general, the new spin probes **4**, **5**, and **6** reflect the mobility of reactive species bound to the cation of the ionic liquid in an ionic

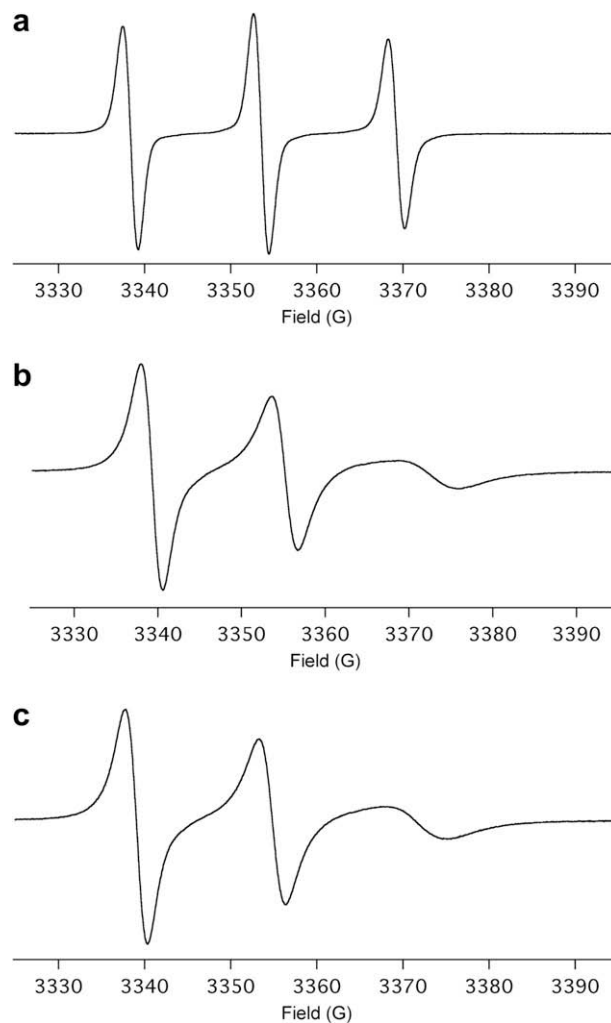


Figure 3. ESR spectra of the new spin probe **6** dissolved in (a) dimethylsulfoxide ($A_{\text{iso}}(^{14}\text{N}) = 15.5 \text{ G}$, $\tau = 1.0 \text{ ns}$), and in the ionic liquids; (b) **IL-BF₄** ($A_{\text{iso}}(^{14}\text{N}) = 16.2 \text{ G}$, $\tau = 10.4 \text{ ns}$), and (c) **IL-NTf₂** ($A_{\text{iso}}(^{14}\text{N}) = 16.0 \text{ G}$, $\tau = 10.0 \text{ ns}$) at room temperature.

liquid. The results show that the mobility of radicals covalently bound to the imidazolium ion is significantly reduced in an ionic liquid compared to the mobility of a radical without additional charged group. Furthermore, these model radicals give information about the mobility of radicals formed in the course of polymerization of ionic liquid monomers.

Acknowledgments

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- Twenty-five milligrams of 4-[(2-iodoacetyl)amino]2,2,6,6-tetramethyl-1-piperidine-1-yloxy (**1**) are dissolved in 5 ml of a *tert*-butyl methyl ether/acetone mixture (Vol:Vol = 1:9). Then, 6 mg of 1-methylimidazole (**2**) dissolved in 1 ml *tert*-butyl methyl ether are added to the solution. The resulting mixture is stirred under nitrogen at room temperature for 7 days resulting in the precipitation of the new spin probe **4** bearing the spin probe covalently bound to the imidazolium ion (50% yield, mp 179–187 °C, decomp.). Mass spectrometric analysis gives 294.2076 Da in the TOF MS ES⁺ mode (Calcd: 294.21 Da) and 127 Da in the TOF MS ES⁻ mode (Calcd: 126.91 Da); IR 1685 cm⁻¹ amido group (shift of the IR vibration from 1643 cm⁻¹ in the case of **1**).
- Twenty milligrams of 4-[(2-iodoacetyl)amino]2,2,6,6-tetramethyl-1-piperidine-1-yloxy (0.059 mmol) (**1**) are dissolved in 5 ml of a *tert*-butyl methyl ether/acetone mixture (Vol:Vol = 2:8). Then, 7.3 mg of 1-butylimidazole (**3**) dissolved in 1 ml *tert*-butyl methyl ether are added to the solution. The resulting mixture is stirred under nitrogen at room temperature for 14 days and kept at room temperature for further 2 days resulting in precipitation of a slightly yellow precipitate. The solution was removed by decanting and the precipitate was washed with 0.2 ml *tert*-butyl methyl ether. After drying the precipitate at room temperature under vacuum (4 mbar) for 24 h, the new spin probe **5** (mp 82–87 °C) is obtained in 74% yield. Mass spectrometric analysis gives 336.2517 Da in the TOF MS ES⁺ mode (Calcd: 336.25 Da) and 127 Da (Calcd: 126.91 Da) in the TOF MS ES⁻ mode; IR 1684 cm⁻¹ amido group (shift of the IR vibration from 1643 cm⁻¹ in the case of **1**).
- Twenty-eight milligrams of 1-(2-(4-(2,2,6,6-tetramethyl-piperidinyl-1-yloxy)amino)-2-oxoethyl)-3-butylimidazolium iodide (**5**) are dissolved in acetone. Then, a solution of 25 mg silver bis(trifluoromethylsulfonilimide) dissolved in 5 ml acetone is added under nitrogen and stirred at room temperature for 30 min. The reaction mixture is kept at room temperature for 1 h, and then at 4 °C for 12 h. The precipitated silver iodide is filtrated using a 0.2 µm polytetrafluoroethylene syringe filter, which results in a clear solution. The solvent is evaporated under vacuo at room temperature. The resulting orange oil-like product **6** is dried at room temperature in vacuo (1–4 mbar) for 4 h. The new spin probe **6** (*T*_g = -10 °C) is obtained in 85% yield. Mass spectrometric analysis gives 336.252 Da in the TOF MS ES⁺ mode (Calcd: 336.25 Da) and 280 Da (Calcd: 279.92 Da) in the TOF MS ES⁻ mode; IR characteristic vibrations for S–N–S (asymmetric vibration) at 1059 cm⁻¹, –SO₂– (symmetric vibration) at 1135 cm⁻¹, CF₃ at 1198 cm⁻¹, –SO₂– (asymmetric vibration) at 1352 cm⁻¹, amido group at 1691 cm⁻¹ (shift of the IR vibration from 1684 cm⁻¹ in the case of **5**). The absence of iodide in the spin probe **6** is checked by washing with water and by adding silver nitrate solution to the washing water. No precipitation is observed.
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- The water content is 0.2% in the case of **IL-BF₄** and 0.03% in the case of **IL-NTF₂**, determined by Karl–Fischer analysis. No halogenide was detected in the ionic liquids using silver nitrate solution.