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Revisiting Ether-Derivatized Imidazolium-Based Ionic Liquids

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A series of ether-derivatized imidazolium halides have been prepared and characterized. Contrary to literature reports, they are all crystalline solids and have melting points well above room temperature (50−100 °C). Single crystals of the imidazolium salts, obtained in situ by slow cooling from their molten state to room temperature, were analyzed by X-ray crystallography, revealing various anion−cation interactions in the solid state. Exchange of the halides with $[Tf_2N]^-$ yielded room temperature ionic liquids with viscosities that are comparable to related 1-alkyl-3-methylimidazolium ionic liquids. Density functional theory combined with IR spectroscopy has been used to analyze the role of functionalization of the imidazolium side chain on the formation of the molecular and supramolecular structure of the compounds and its possible impact on their physical properties.

Introduction

Ionic liquids (ILs) bearing functional groups, the so-called task-specific ionic liquids, are interesting materials that can be designed with specific properties for specific applications.[1,2] For example, ILs with O, N donor centers have been designed for extracting heavy metals.[3] Strongly acidic ILs exhibit excellent properties in acid-catalyzed esterification reactions,[4] whereas weakly acidic ILs can be used as building blocks in coordination polymers.[5] In addition, ionic liquids with certain functional groups can capture CO_2[6] or can reversibly absorb SO_2 from flue gas.[7] Because imidazolium-based ILs are generally not suitable for reactions involving strong bases, phosphonium ILs in which Grignard reactions can be performed[8] have been designed.

In 1996, Grätzel and co-workers first described the synthesis of 1-(2-methoxyethyl)-3-methylimidazolium trifluoromethanesulfonate ([Me-Im-C2OC1][SO₃CF₃],[9] obtained from the reaction of 1-methylimidazole with 2-methoxyethyl trifluoromethanesulfonate. Subsequent exchange of the SO₃CF₃ anion with N(SO₂CF₃)₂ (Tf₂N) afforded the room-temperature ionic liquid ([Me-Im-C2OC1][Tf₂N]). In 2001, 1-methoxymethyl-3-methylimidazolium bromide ([Me-Im-C1OC1]Br) and 1-methoxyethyl-3-methylimidazolium bromide ([Me-Im-C2OC1]Br) were reported and, remarkably, found to be liquids at room temperature (RTILs) that are able to dissolve cellulose (Figure 1).[10]

The synthesis of the polyether functionalized RTIL 1-(1-methoxyethoxyethyl)-3-methylimidazolium chloride, [Me-Im-C1OC2OC2]Cl, was reported (Figure 1),[11] and the thermal analysis of this compound shows a glass transition temperature at −50 °C.[12] The analogous iodide salt [Me-Im-C1OC2OC2]I was also reported and was described as a liquid at room temperature.[13] Other ionic liquids bearing ether groups have also been reported, including methylimidazolium salts with short chain ethers,[14] imidazolium salts with short-chain ether groups attached to both N-centers of the imidazolium ring,[15] as well as ammonium[16] and cyclic quaternary ammonium salts.[17]

In a recent example,[18] the X-ray structures and thermal behavior of the 1-(2-methoxyethyl)-2,3-dimethylimidazolium
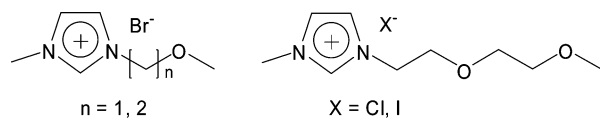
Figure 1. Imidazolium-based ionic liquids with ether groups.
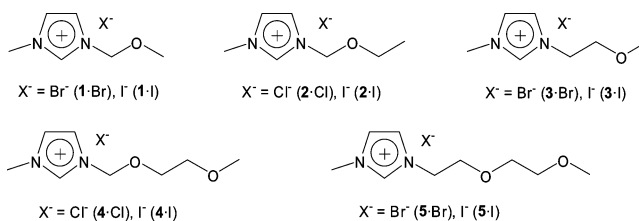
Figure 2. Ether-functionalized imidazolium halides.

chloride and hexafluorophosphate salts were compared with the analogous 1-butyl-2,3-dimethylimidazolium salts. It was found that replacing one CH_2 group in the side chain in the imidazolium salt with an oxygen atom resulted in repulsive interactions between neighboring oxygen atoms or anions, leading to significant ion pairing in the solid phase, resulting in notable differences in the thermal properties of the salts.

During our research involving the design, synthesis, and applications of the functionalized ionic liquids,[19,20] we found all the above-mentioned imidazolium halides have melting points above room temperature. In this paper, we describe the structures of these salts and use density functional theory (DFT) combined with IR spectroscopy to rationalize the role of functionalization of the imidazolium side chain on their structures and their subsequent impact on their physical properties.

Results and Discussion

Our initial interest was to prepare an ether-functionalized imidazolium halide that is a structural analogue of 1-propyl-3-methylimidazolium iodide ([C3C1im]I) for potential applications as an electrolyte in dye-sensitized solar cells (DSCs), and we were encouraged by the report that imidazolium bromides [Me-Im-C1OC1]Br and [Me-Im-C2OC1]Br (Figure 1) are colorless RTILs.[10] In addition, it was reported that [Me-Im-C1OC2OC2]I has a viscosity of 613.4 cp at 20 °C,[13] somewhat lower than ([C3C1im]I), which is a standard IL electrolyte in DSC.[19,21]

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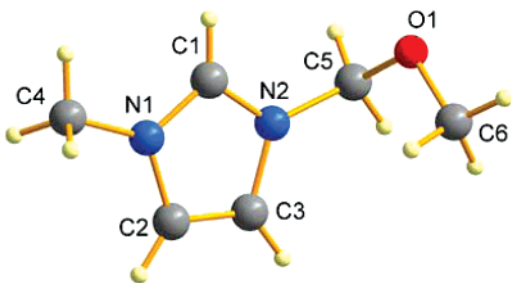
Figure 3. Ball and stick representation of **1**. Atoms are represented by spheres with arbitrary radii.

Since it is believed that the viscosity of the imidazolium iodides is an important factor in determining the efficiency of DSCs,[19,21] we decided to investigate whether the replacement of the propyl group in [C3C1im]I with a methoxymethyl group (C1OC1−) would yield RTILs with lower viscosity. Ether analogues of 1-butyl-3-methylimidazolium salts were also prepared by replacing the *n*-butyl group with ethoxymethyl (C2OC1−) and methoxyethyl groups (C1OC2−). In addition, polyether groups, namely, C1OC2OC1− and C1OC2OC2−, were studied to examine the effect of longer chain polyethers on the physical properties of the resulting ionic liquids (Figure 2).

Reaction of the methoxymethyl bromide (CH3OCH2Br) with 1-methylimidazole gave the desired imidazolium salt **1**·Br as solid at room temperature. The reaction is exothermic and is complete within a few minutes. Metathesis of **1**·Br with sodium iodide gave the imidazolium iodide **1**·I in high yield. Alternatively, since methoxymethyl iodide (CH3OCH2I) is com-

mercially available, **1**·I can also be obtained in a single step from 1-methylimidazole by direct quatinization.[22] The other imidazolium halides shown in Figure 2 were prepared using the same quatinization method, although the iodide salts were prepared by anion exchange of the corresponding chloride or bromide salts. All the halide salts were obtained as solids at room temperature.

It was found that methoxyethyl bromide was necessary for the reaction with 1-methylimidazole since methoxyethyl chloride yielded significant elimination byproducts. Spectroscopic data of all the salts completely corroborate their proposed structures, and the data is listed in the Experimental section. The study of pure imidazolium halides in the solid state is not always possible due to the highly hydrophilic nature of the majority of these salts.[23] In many cases, the halide salts are merely prepared as precursors to other non-halide salts with low melting points. It is therefore perhaps not surprising that investigations of imidazolium salts in the solid state are mostly focused on a few benchmarks; namely, the 1-butyl-3-methylimidazolium halides. In 2003, three papers independently reported the structure of 1-butyl-3-methylimidazolium chloride,[24−26] and four additional papers in the same year reported the structure of 1-butyl-3-methylimidazolium bromide[27,28] and iodide.[29,30]

Single crystals of **1**·I, **2**·I, and **3**·I were obtained by slowly cooling from the liquid state to room temperature.[31] The structures of the cations are shown in Figures 3−5, and selected bond distances and angles for **1**·I, **2**·I, and **3**·I are listed in Table 1. The bond lengths within the imidazolium ring range from 1.312(15) to 1.421(16) Å, with the C1−N1 and C1−N2 bonds significantly shorter than C2−N1 and C3−N2 bonds, which is
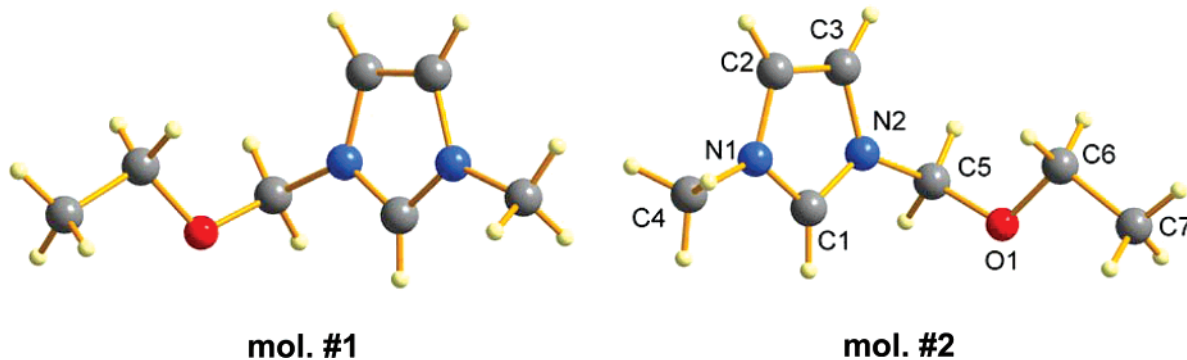
Figure 4. Ball and stick representation of the different cations in the asymmetric cell of **2**. Atoms are represented by spheres with arbitrary radii. Disordered atoms are omitted for clarity.

Figure 5. Ball and stick representation of the different cations in the asymmetric cell of **3**. Atoms are represented by spheres with arbitrary radii.

Ether-Derivatized Imidazolium-Based ILs

J. Phys. Chem. B, Vol. 111, No. 34, 2007 **10097**
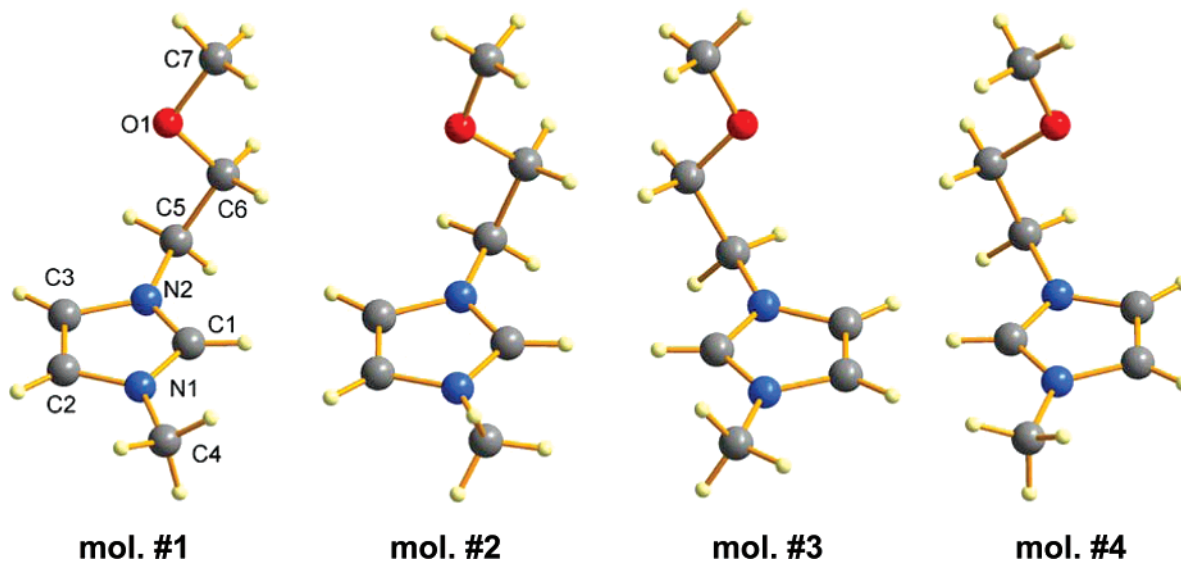
TABLE 1: Selected Bond Lengths (Å) and Angles (degrees) of Imidazolium Halides 1·I, 2·I, and 3·I

	1·I	2·I		3·I			
		molecule no. 1	molecule no. 2	molecule no. 1	molecule no. 2	molecule no. 3	molecule no. 4
N1—C2	1.390 (4)	1.382 (5)	1.375 (5)	1.376 (18)	1.371 (16)	1.375 (17)	1.399 (16)
N1—C4	1.465 (4)	1.478 (5)	1.479 (5)	1.45 (2)	1.409 (18)	1.46 (2)	1.430 (16)
N2—C3	1.389 (4)	1.393 (4)	1.385 (4)	1.419 (16)	1.410 (18)	1.401 (16)	1.375 (16)
N2—C5	1.483 (4)	1.471 (5)	1.480 (5)	1.486 (16)	1.430 (19)	1.481 (18)	1.525 (18)
C1—N1	1.329 (4)	1.326 (5)	1.335 (5)	1.321 (17)	1.373 (16)	1.315 (18)	1.327 (16)
C1—N2	1.341 (4)	1.334 (5)	1.339 (4)	1.337 (16)	1.357 (15)	1.358 (16)	1.310 (16)
C2—C3	1.352 (5)	1.356 (6)	1.355 (5)	1.38 (2)	1.36 (2)	1.34 (2)	1.36 (2)
N1—C1—N2	108.5 (3)	108.5 (3)	108.0 (3)	109.5 (12)	109.2 (11)	109.5 (12)	108.4 (11)
C1—N1—C2	108.9 (3)	109.5 (3)	109.1 (3)	108.8 (13)	108.9 (12)	109.3 (12)	108.6 (12)
C1—N1—C4	125.5 (3)	124.8 (3)	125.2 (3)	124.8 (14)	124.4 (12)	125.2 (13)	125.1 (12)
C1—N2—C3	108.5 (3)	108.5 (3)	108.8 (3)	108.6 (11)	105.5 (12)	105.7 (12)	110.5 (12)
C1—N2—C5	125.2 (3)	124.4 (3)	125.2 (3)	127.5 (12)	126.1 (12)	125.8 (12)	122.9 (11)

TABLE 2: Melting Points (°C) of Ether-Functionalized Imidazolium Halides and Viscosities of Tf₂N RTILs (cP at 21.0 °C)

cation	[Cl]⁻	[Br]⁻	[I]⁻	[Tf₂N]⁻
1		101	75	49.9
2	75		68	42.0
3		80	50	58.5
4	72		63	84.6
5		78	70	70.3

typical for such systems.[21,25−31] The internal bond angles of the ring are also within expected values. Invariably for the three structures, the pendant ether groups are located almost perpendicularly to the plane of the imidazolium ring. In **2·I**, there are two different cation structures in the independent unit, and in **3·I**, four different cation structures are present.

The packing of the imidazolium iodides is characterized by numerous short contacts between the iodide anion and ether O-atoms with the H-atoms on the imidazolium ring/alkyl groups (Figure 6). Interestingly, for **2·I** and **3·I**, each asymmetric unit contains two and four different moieties, respectively, with the key structural difference between the moieties within the asymmetric cell involving the orientation of the pendant ether groups with respect to the imidazolium ring. Unlike **2·I**, the imidazolium rings of the four molecules in the asymmetric cell of **3·I** are π-stacked, with a centroid−centroid distance of 4.06−4.30 Å.

The structure of 1-butyl-3-methylimidazolium iodide ([C4C1im]I) has been studied by X-ray diffraction,[29,30] and compared with the corresponding chloride[24−26] and bromide salts.[27,28] The bonding parameters, including bond lengths and angles in **2·I** and **3·I**, are similar to those in [C4C1im]I.[30] The main differences are the numerous hydrogen-bonding interactions between the H-atoms in the imidazolium ring/alkyl side chain and the oxygen atom, which compete with the iodide counteranion.

Reaction of 1-methylimidazole and 1-methoxyethoxymethyl chloride gave the compound **4·Cl**, a solid with a melting point of 72 °C. Metathesis with sodium iodide gave the solid salt **4·I**. The direct reaction of 2-(methoxyethoxy)ethyl bromide and 1-methylimidazole at room temperature for 24 h in the absence of solvent affords compound **5·Br** as a solid following addition of diethyl ether.[32] The compound is extremely sensitive to moisture and immediately becomes an oil on exposure to air. Reaction of the bromide **5·Br** with sodium iodide gave **5·I** as a solid. This, however, is contrary to previous reports that the chloride and iodide salts, namely, 1-[2-(2-methoxyethoxy)ethyl]-3-methylimidazolium chloride[11] and the corresponding iodide,[13] are RTILs; the iodide salt had a contact angle of 47.2° on a titania/dye surface, with the viscosity being 283.7 cP at 30 °C, 613.4 cP at 20 °C, and 1515.8 cP at 10 °C.[13] The melting points

of the compounds described herein are listed in Table 2. In general, the iodide salts melt at a lower temperature than their corresponding chlorides and bromides.

Compounds **4·I**, **5·Br** and **5·I** were crystallized by slow cooling from the molten state and analyzed by X-ray diffraction. The structures of these salts are shown in Figures 7 and 8, and selected bond distances and angles are given in Table 3. As with **1·I−3·I**, the bond parameters of the polyether−imidazolium compounds **4·I**, **5·Br**, and **5·I** are within the expected values. The pendant ether groups are also oriented almost perpendicularly to the imidazolium rings. In addition, the O-atoms on the polyether groups also participate in intermolecular H-bond interactions, resulting in pseudodimeric units. For **4·I**, the O-atoms interacts with both the imidazolium C1−H atoms and the methyl C4−H atom (Figure 9). For **5·Br** and **5·I**, however, both O-atoms are H-bonded to only the C2-H atoms, and the imidazolium rings are π-stacked (Figure 10). The longer polyether groups in **5·Br** and **5·I** could accommodate the π-stacked imidazolium ring arrangement while maintaining the H-bonding interactions, which is not possible in **4·I**.

All the halide salts have been converted to RTILs by exchange of the halide with the Tf₂N anion (**1·Tf₂N−5·Tf₂N**). The viscosity of **1·Tf₂N** is significantly higher than the structurally related 1-propyl-3-methylimidazolium salt,[33] whereas the viscosities of **2·Tf₂N** and **3·Tf₂N** are comparable to [C4C1im]-[Tf₂N].[34] ILs **4·Tf₂N** and **5·Tf₂N** with the polyether chains have higher viscosities than **1·Tf₂N**, **2·Tf₂N**, and **3·Tf₂N** (Table 2).
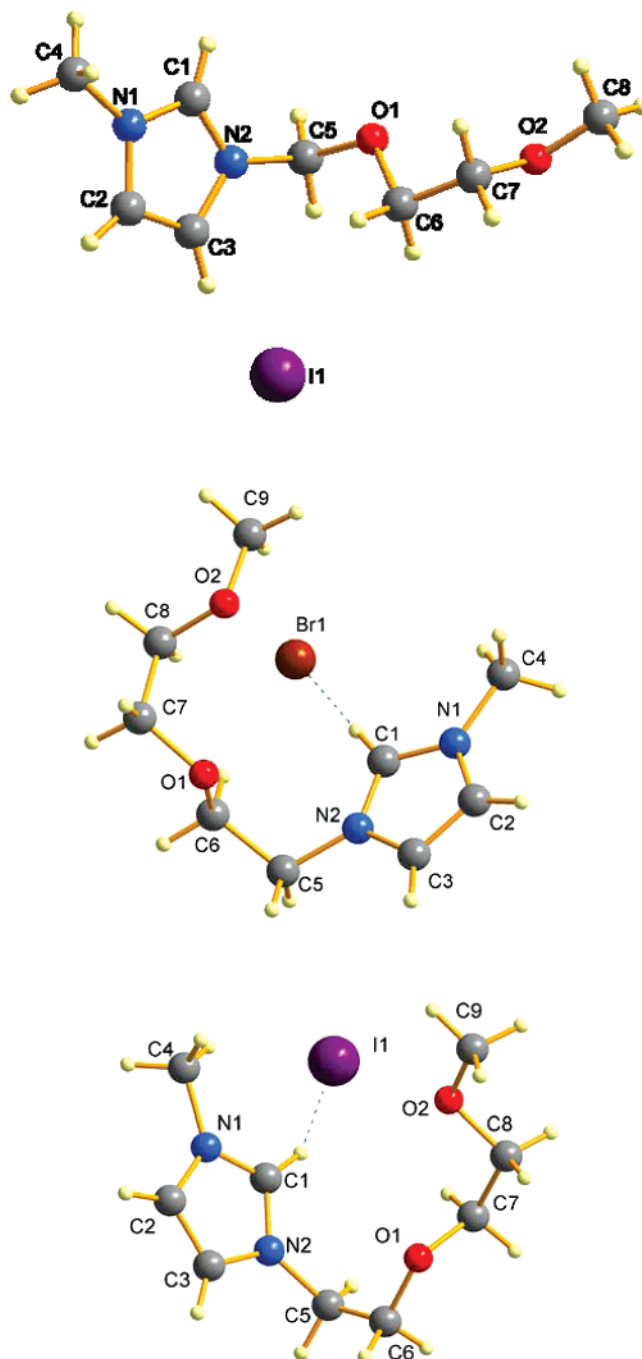
DFT has been used to analyze the role of functionalization of the imidazolium side chain. The conformational behavior of the ether-functionalized compounds **1·I**, **2·I**, and **3·I** was compared with well-documented conformational properties of their structural analogues [C3C1im][BF₄] and [C4C1im]X (X = Cl, Br, I, BF₄).[24−30,35] First, possible conformations of the isolated cations in vacuum were calculated. The conformation of the ether group is determined by the torsion angles: τ_1 = C2−N1−C6−A7, τ_2 = N1−C6−A7−B8, and τ_3 = C6−A7−B8−C9 (A, B = C or O). The torsion angle $\tau_1 \approx 90°$ corresponds to a perpendicular orientation of the ether group relative to the plane of the imidazolium ring. In comparison with the propyl group of [C3C1im] or the butyl group of [C4C1im], which adopt positions almost perpendicular to the plane of the imidazolium ring, the ether groups in vacuum tend to be closer to the plane of the ring ($\tau_1 \leq \sim 60°$). These differences can probably be ascribed to the ability of the oxygen atom of the ether group to form intramolecular hydrogen bonds with the C2−H and C5−H groups of the imidazolium ring. These attractive interactions force the ether groups to deviate from the perpendicular position relative to the plane of the ring. Nevertheless, the geometric conditions are not especially favorable for the formation of hydrogen bonds of type C2−
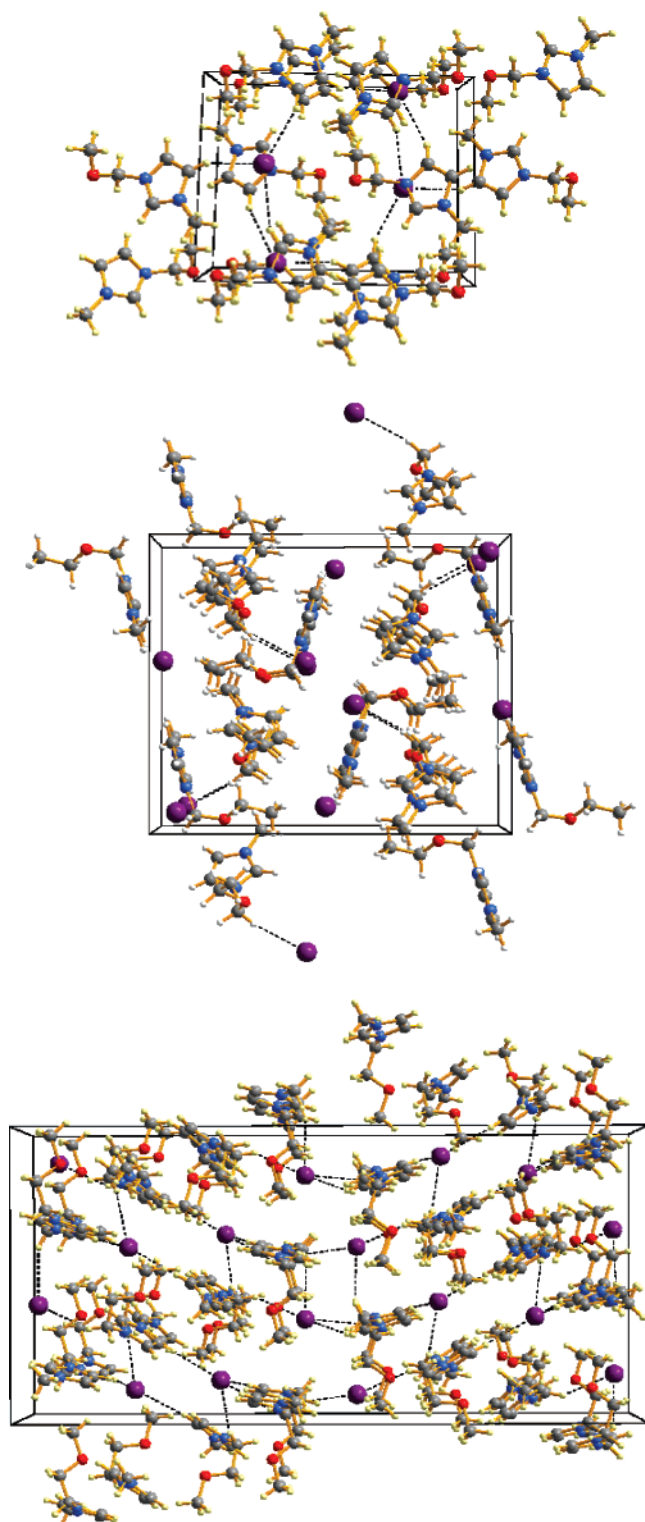
Figure 6. Packing diagrams of **1·I** (top), **2·I** (middle), and **3·I** (bottom). Atoms are represented by spheres with arbitrary radii. Disordered atoms are omitted for clarity.

Figure 7. Ball and stick representations of **4·I** (top), **5·Br** (middle), and **5·I** (bottom). Atoms are represented by spheres with arbitrary radii. Disordered atoms are omitted for clarity.
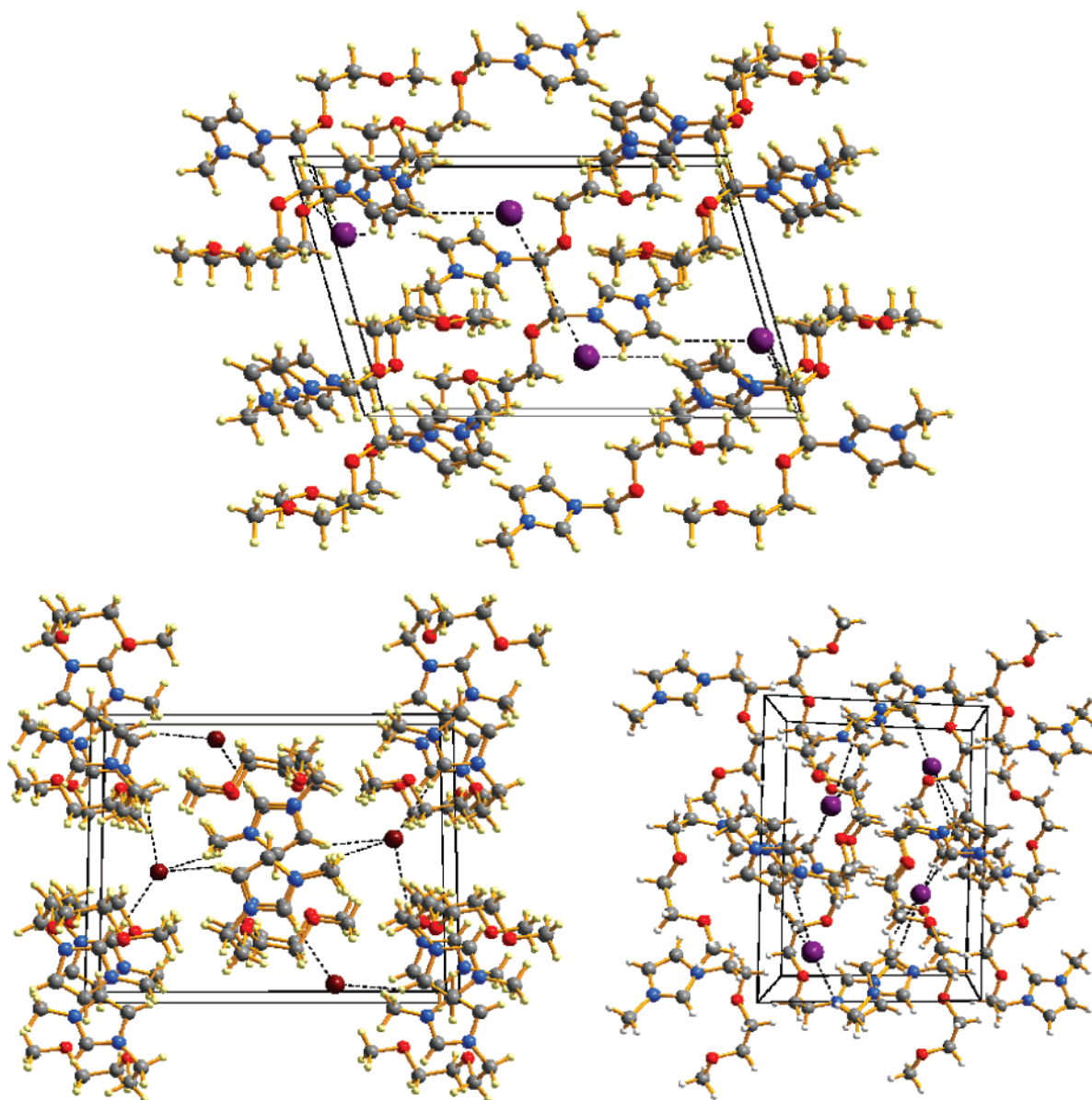
H···O and C5−H···O, and as a result, the H-bonds are rather weak. Consequently, their influence on the geometry of the cations can be easily compensated by the effects of the surrounding medium. To simulate this latter case, the polarized continuum model (PCM) was used.[36] The model employs a self-consistent reaction field methodology for modeling systems in solution. Several parameters of the simulated solution, for example, dielectric constant, are needed for the PCM computations. Since these parameters for the studied compounds are

not available, the isolated cations in diethyl ether were simulated. The PCM computations predict that the ether groups adopt positions almost perpendicular to the plane of the imidazolium ring ($\tau_1 \approx 90°$), similar to the alkyl groups of [C3C1im] and [C4C1im]. These are precisely the conformations found in the crystals of **1·I**, **2·I**, and **3·I**, and our simulations suggest that the ether groups should retain approximately the same value of τ_1 in the liquids **1·Tf₂N**, **2·Tf₂N**, and **3·Tf₂N**.

According to these computations, τ_2 and τ_3 in stable staggered conformations of the ether groups adopt values of ~180° (anti conformation) and ~±70° (±gauche conformation). Gauche conformations ($\tau_2 \approx \pm70°$) of N1−C6−O−C7 and N1−C6−C7−O fragments of the isolated cations of **1**, **2**, and **3** are more energetically stable than the anti conformation ($\tau_2 \approx 180°$) both

Ether-Derivatized Imidazolium-Based ILs

J. Phys. Chem. B, Vol. 111, No. 34, 2007 **10099**

Figure 8. Packing diagrams of **4**·I (top), **5**·Br (bottom, left) and **5**·I (bottom, right). Atoms are represented by spheres with arbitrary radii. Disordered atoms are omitted for clarity.

TABLE 3: Selected Bond Lengths (Å) and Angles (degrees) of Imidazolium Halides 4·I, 5·Br, and 5·I

|	**4**·I	**5**·Br	**5**·I
N1−C2	1.384 (2)	1.372 (9)	1.372 (9)
N1−C4	1.469 (2)	1.460 (9)	1.460 (9)
N2−C3	1.386 (2)	1.393 (9)	1.393 (9)
N2−C5	1.477 (2)	1.481 (9)	1.481 (9)
C1−N1	1.331 (2)	1.335 (9)	1.335 (9)
C1−N2	1.335 (2)	1.327 (9)	1.327 (9)
C2−C3	1.355 (3)	1.365 (10)	1.365 (10)
N1−C1−N2	108.53 (16)	109.3 (6)	109.3 (6)
C1−N1−C2	108.71 (16)	108.3 (6)	108.3 (6)
C1−N1−C4	124.86 (16)	126.2 (6)	126.2 (6)
C1−N2−C3	108.74 (15)	108.4 (6)	108.4 (6)
C1−N2−C5	125.00 (15)	127.9 (6)	127.9 (6)

in vacuum and in diethyl ether. For comparison, the calculated energy of the gauche conformer of the isolated ion pair [C3C1im][BF$_4$] in vacuum is ∼0.5 kcal mol^{-1} higher than the energy of the anti conformer.[355] Nevertheless, in the IL [C3C1im][BF$_4$], the gauche conformer dominates in the liquid state, with the concentration of the anti conformer being too low to be detected in the IR or Raman spectra. In the case of

1·I, **2**·I, and **3**·I, the N1−C6−O−C7 and N1−C6−C7−O fragments in crystals adopt gauche conformations ($\tau_2 \approx \pm 70°$) which, according to the computations, are also the most energetically stable for both the cations and the isolated ion pairs.

For the ether groups of **2** and **3**, nine conformations can be considered: anti, anti; anti, gauche; anti, −gauche; gauche, anti; gauche, gauche; gauche, −gauche; −gauche, anti; -gauche, gauche, and −gauche, −gauche. Similar to the butyl group of the [C4C1im] cation, the N1−C6−O−C7−C8 moiety of the isolated cation **2** is able to adopt all the abovementioned conformations, whereas gauche, −gauche and −gauche, gauche conformations of the N1−C6−C7−O−C8 fragment of **3** do not correspond to minima on a potential energy surface and, hence, cannot be adopted. Computed energies of the possible conformations of the cations **1**, **2**, and **3** are listed in Tables S1−S3 (see Supporting Information). It should be noted that **2**·I and **3**·I adopt gauche, anti and −gauche, anti conformations in the crystal, which have the lowest energy according to the computations for the corresponding isolated cations and isolated ion pairs. This suggests that these conformers should also be present
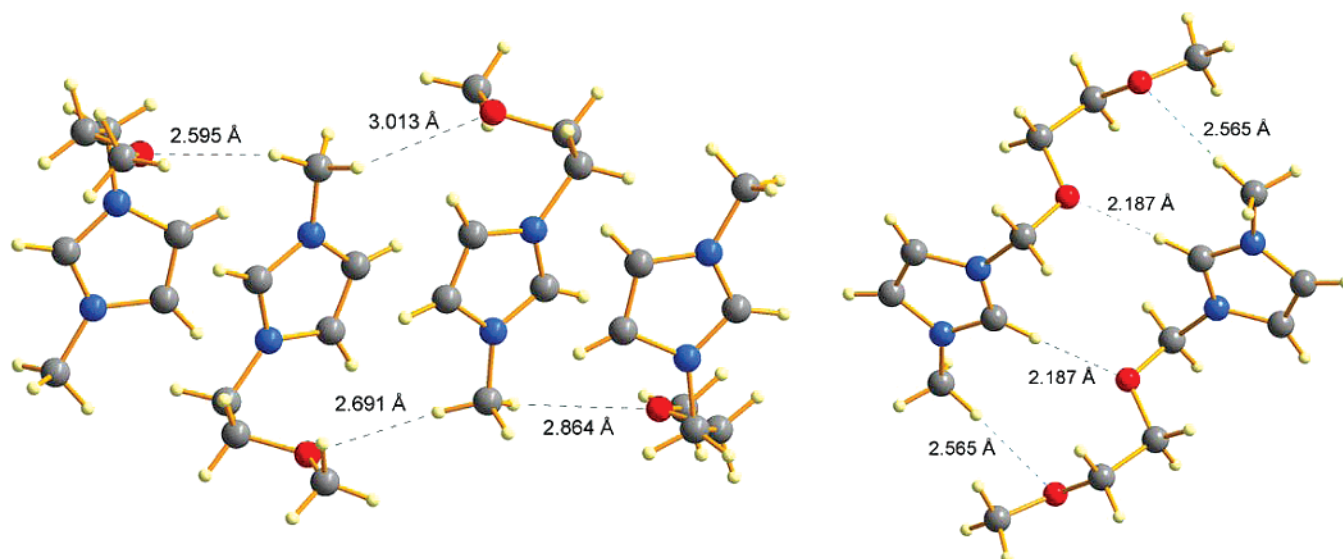
Figure 9. Intermolecular O···H-bonding interactions of **3·I** (left) and **4·I** (right). Atoms are represented by spheres with arbitrary radii. Iodide anions and disordered atoms are omitted for clarity.
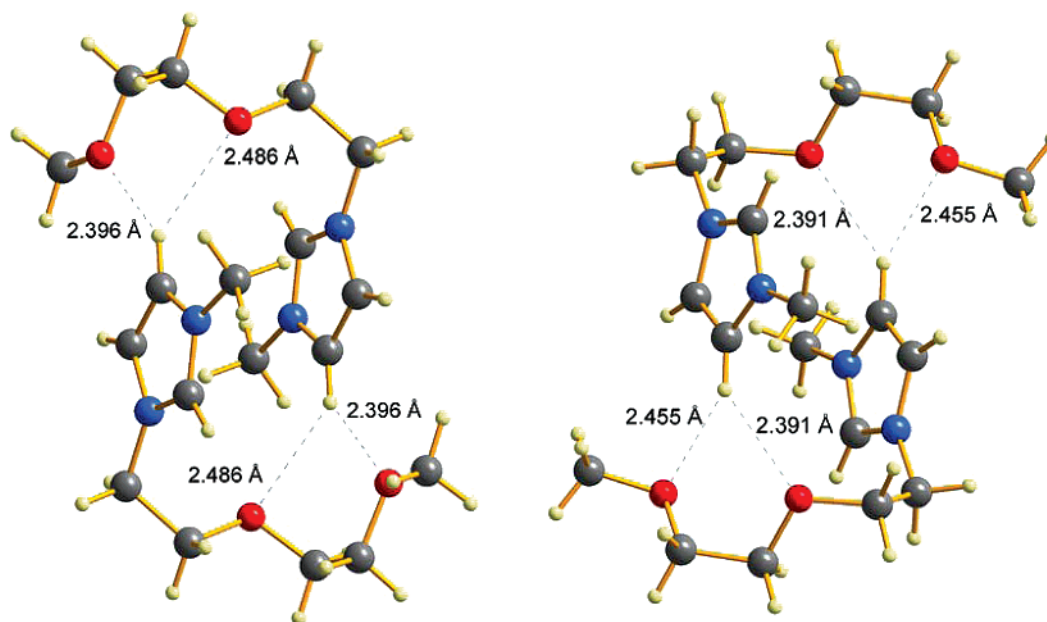
Figure 10. Intermolecular O···H-bonding interactions of **5·Br** (left) and **5·I** (right). Atoms are represented by spheres with arbitrary radii. Halide anions and disordered atoms are omitted for clarity.

in the liquids **2·Tf$_2$N** and **3·Tf$_2$N**. For comparison, only anti, anti− and anti, gauche− conformations were found in the crystals of various [C4C1im] halides,[24−30] and at least one additional conformer, gauche, gauche, most probably participates in the conformational equilibrium in liquid [C4C1im][BF$_4$].[35]

The main difference in the conformational behavior of the ether-functionalized imidazolium cations and their 1-alkyl-3-methylimidazolium analogues is the energetic preference of the gauche conformations ($\tau_2 \approx \pm 70°$) of the N1−C6−O−C7 and N1−C6−C7−O fragments, in contrast to the anti conformations ($\tau_2 \approx 180°$) of the N1−C6−C7−C8 fragment. This difference should be ascribed at least in part to the attraction of the oxygen atoms of the ether groups to the C2−H and C5−H groups of the imidazolium ring. As mentioned above, because of unfavorable geometric conditions, this attraction is too weak to compete with the effects of the surrounding medium; that is, the ether group cannot adopt the plane conformation ($\tau_1 \approx 0°$), even in

the case of the isolated cation immersed in the polarized continuum. Thus, the computations explain why the imidazolium protons do not form intramolecular hydrogen bonds with the ether oxygen atoms, as evidenced from the X-ray structures, and intramolecular H-bonding of type H···O is absent in all the crystals studied.

Nevertheless, the ether groups can compete with the iodide anions for the formation of intermolecular hydrogen bonds because the geometric conditions may be more favorable. This type of H-bonding is found in crystals of **3·I** and **4·I** (Figure 9). According to the computations, both the couples of the cations (Figure 11c) and the dimers (Figure 11b and d) or tetramers (Figure 11e) of the ionic pairs of **1·I**−**4·I** in vacuum are able to form multiple intermolecular O···H−C2 hydrogen bonds (observed in **5·Br** and **5·I**; see Figure 10). Most probably, the C4−H and C5−H groups could also participate in the
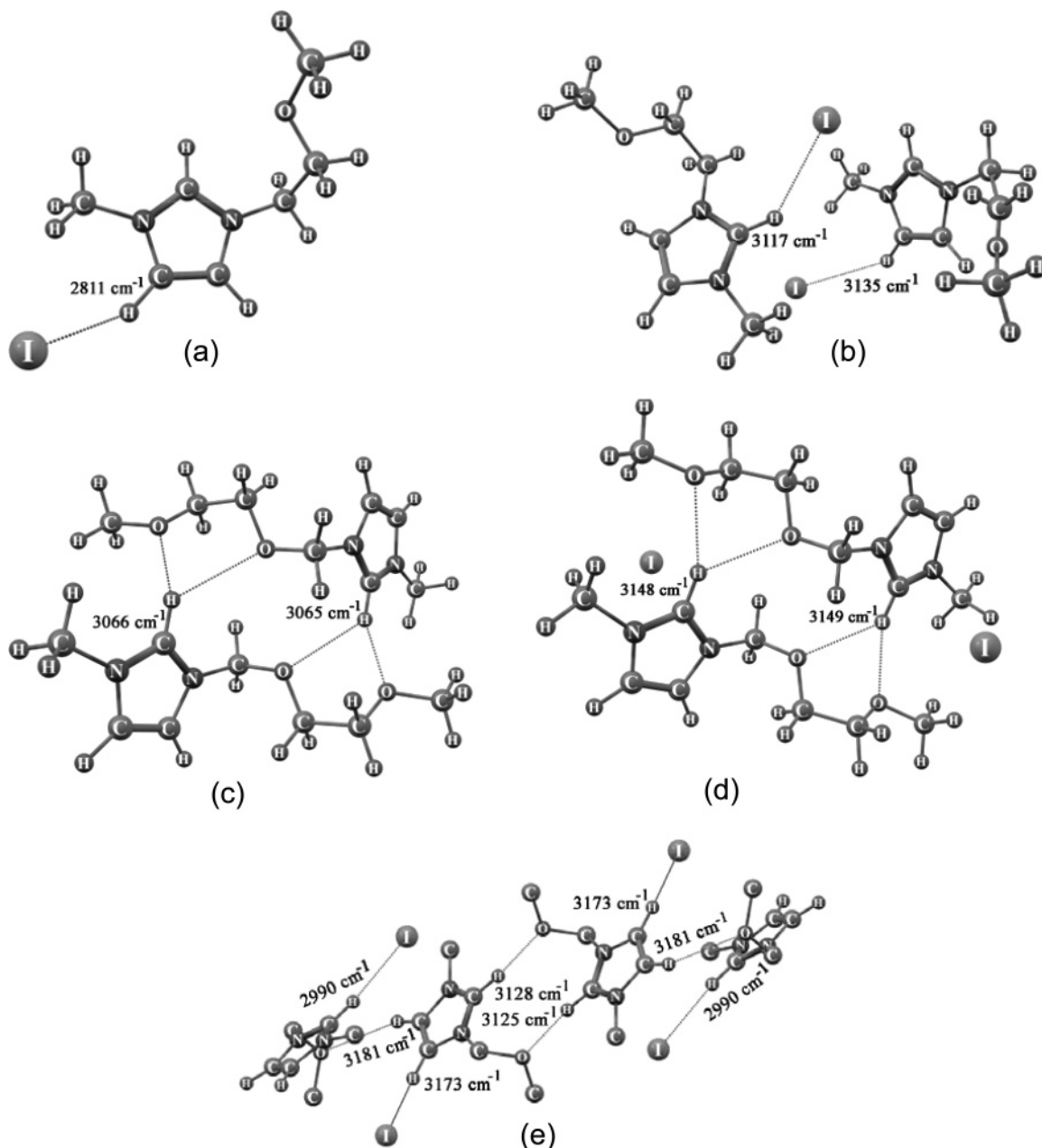
Figure 11. Selected optimized structures and computed frequencies of stretching vibrations of CH aromatic groups. Short contacts between the CH groups and oxygen atoms or anions I⁻ are indicated with dotted lines.

intermolecular H-bonds with ether oxygen atoms, although we have not tried to optimize structures of this type.

The hydrogen bonds between the cations studied and the iodide anions adopt a geometry that is quite different from the 1-alkyl-3-methylimidazolium iodides. As an example, each cation in the X-ray structure of [C2C1im]I is H-bonded via all three aromatic protons to three anions remaining roughly in-plane with the imidazolium ring.[23a] According to the X-ray structures of **1·I**−**5·I**, there are more types of associations. Some of the anions form almost right angles with the aromatic C−H groups. Some of these groups in the crystals of **2·I** and **4·I** have no short contacts at all. It is known[35,37] that the frequency of the stretching vibrations of the imidazolium aromatic CH (νCH) free from H-bonding in ILs is ∼3170 cm⁻¹. IR bands of this kind are observed in the spectra of 1-alkyl-3-methylimidazolium tetrafluoroborates and hexafluorophosphates.[35,37] The absence of these high-frequency bands in the IR spectra of the compounds **1·I**−**5·I** (Tables 4−6) suggests that, in contrast to

the case of perfluorometalates, all the imidazolium protons are involved in rather strong H-bonding, either with counterions or with ether groups. However, as mentioned above, the geometry of some C−H···I⁻ fragments in the crystals of **2·I** and **4·I** does not satisfy formal criteria of hydrogen bonding: either H···I⁻ distances exceed the sums of the corresponding van der Waals radii or the C−H···I⁻ angles are close to 90°. Possibly some of the C−H···I⁻ interactions of this kind, which could be classified as ion−dipole interactions, also cause a red shift of the νCH bands. Another possible explanation for the absence of high-frequency νCH bands in the IR spectra of **1·I**−**5·I** is that they are of low intensity. In any case, these νCH bands are present in the region, ∼3150−3050 cm⁻¹, typical for 1-alkyl-3-methylimidazolium halides (cf., there are three νCH bands at 3133, 3080, and 3052 cm⁻¹ in the IR spectrum of [C2C1im]I).[23a]

To assign the IR bands, the IR spectra of various ion pairs **1·I**−**5·I** and several larger structures, including two and four ion pairs optimized in vacuum, were calculated. Starting

TABLE 4: Vibrational Spectra of 1·I and 1·Tf$_2$N

experiment (IR) ν (cm^{-1}), I[a]		computation[b] ν (cm^{-1})[c]				experiment (IR) ν (cm^{-1}), I[a]		computation[b] ν (cm^{-1})[c]			
1·I (solid)	1·Tf$_2$N (liq)	g	a	−g	assignment[d]	1·I (solid)	1·Tf$_2$N (liq)	g	a	−g	assignment[d]
		3177	3185	3180	νC−H (in phase)	1381 w	1380 w	1375	1384	1378	ν_{as} C2−N3−C4
		3174	3169	3165	νC−H (out of phase)	1358 w		1355	1379	1373	ν_{as} C2−N1−C5, w CH$_2$
		3159	3166	3163	νC4−H, C5−H (out of phase)		1348 s				Tf$_2$N$^-$
3138 m	3154 m					1324 m	1330 s				
3124 sh	3115 m					1302 m	1300 m	1305	1315	1299	ν N−CH$_2$, N−Me, ≪breathing≫, t CH$_2$
3101 sh	3096 m					1289 sh		1284	1277	1289	r CH, ν N−CH$_2$, N−Me, ≪breathing≫, t CH$_2$
3093 m						1266 w	1266 sh				
3065 m	3069 sh					1244 w	1241 sh	1255	1224	1261	r CH
3041 sh							1227 s				Tf$_2$N$^-$
3000 w	2997 sh	3013	3012	3012	ν_{as} CH$_3$ (Me)	1206 m		1197	1200	1196	r CH$_3$ (O)
	2988 m	3008	3006	3008	ν_{as} CH$_3$ (O)		1184 vvs				Tf$_2$N$^-$
2981 m	2971 m	2998	2998	2998	ν_{as} CH$_3$ (Me)	1149 vs	1157 s	1152	1152	1153	ν_{as} C−O−C
	2958 sh	2969		2973	ν_{as} CH$_2$			1136	1142	1136	r CH$_3$ (O)
2952 m	2945 sh							1129	1129	1128	r CH$_3$ (Me)
2938 sh		2938	2923	2931	ν_{as} CH$_3$ (O)		1134 vs				Tf$_2$N$^-$
	2921 sh	2919	2919	2919	ν_s CH$_3$	1114 vs		1114	1119	1122	r C2−H, ν N1−CH$_2$
	2909 sh						1108 sh				
2900 w	2901 m					1091 s		1095	1102	1097	r C4−H, C5−H, ν N1−CH$_2$
	2892 sh	2891		2879	ν_s CH$_2$		1086 sh	1077	1077	1076	r CH$_3$ (Me)
			2882		ν_{as} CH$_2$	1064 vs		1068	1068	1056	r CH$_2$
	2885 sh						1055 vs				Tf$_2$N$^-$
2876 vw	2867 sh	2871	2863	2866	ν_s CH$_3$ (O)	1042 sh					
2841 sh	2843 s		2844		ν_s CH$_2$	1035 sh	1037 sh				
2840 sh						1016 s	1018 sh	1018	1023	1017	δ ring, ν N−CH$_3$
2828 m						1012 sh		1014	1011	1006	δ ring, ν N−CH$_2$
1748 w						985 m	975 vw				
1688 w						958 sh					
1658 w						920 vs	920 m	905	970	907	ν_s C−O−C
1627 w							900 w				
1609 sh						881 m	891 w				
1577 m	1579 m	1579	1586	1580	ν C=C		880 w				
1550 m	1560 m	1565	1573	1562	ν_{as} N1C2N3		867 w				
1535 sh	1540 vw						854 w				
1530 sh	1534 sh					842 vs		850	855	861	γ C4−H, C5−H
1524 sh	1522 sh					825 sh	835 w	832	815	814	γ C2−H
1499 vw	1508 vw					809 sh	791 m				
1470 sh	1467 m br	1476	1487	1480	δ CH$_2$	759 vs	763 m	739	753	741	γ C2−H, C4−H, C5−H
1463 m		1463	1476	1462	δ_{as} CH$_3$ (Me)	733 vs	740 m	728	735	711	ν N−Me, ν N−CH$_2$ (out of phase)
		1461	1462	1460	δ_{as} CH$_3$ (O)		696 w				
1452 m	1451 m br	1452	1459	1450	δ_{as} CH$_3$ (O)	676 s	674 sh				
1437 sh	1433 w	1439	1439	1435	δ_{as} CH$_3$ (Me)	662 sh					
		1435	1434	1434	δ_s CH$_3$ (O)		655 m				
1417 m	1419 w	1425	1424	1423	δ_s CH$_3$ (Me)	621 vs	630 s	638	662	665	ring-puckering
1406 m		1408	1417	1411	w CH$_2$	611 vs	615 sh	624	623	624	γ N−CH$_2$, ring-puckering
1396 sh	1394 w					602 sh		607	615	606	γ N−Me, ring-puckering

[a] w, weak; m, medium; s, strong; v, very; sh, shoulder; br, broad. [b] g, gauche; a, anti. [c] Wavenumbers computed with the use of scaled force constants. [d] ν, stretch; δ, bend; w, wagging; t, twisting; r, rocking; γ, out-of-plane; s, symmetrical; as, antisymmetrical. Assignment of Tf$_2$N$^-$ bands is based on the comparison of the present spectra with the experimental and computed spectra published in ref 54.

geometries in all cases were taken from the X-ray structures. Some of the optimized structures and νCH frequencies computed are shown in Figure 11. It is seen that the aromatic imidazolium protons can be involved in hydrogen bonding either in isolated ion pairs (Figure 11a) or in larger H-bonding networks (Figure 11b−e). In the latter case, H-bonds are weaker than those in isolated ion pairs because of anticooperative charge redistribution. Hence, they cause much smaller red shifts of the νCH frequencies in comparison with a single ionic pair. It should be noted that not only the νCH, but also the frequencies of many other vibrations, depend on the choice of possible structures for computation, although to a much lesser extent. Nevertheless, this hampers spectra interpretation because salts 1·I−5·I should be regarded as polymeric supramolecules, and it is difficult to choose a finite structure of reasonable size for the computations, which would reflect all the effects of the supramolecular structure on the vibrational frequencies. Consequently, we prefer to assign IR bands on the basis of a comparison of the experimental spectra with the computations for isolated cations (Tables 4−6), although these assignments are somewhat tentative.

It should be noted that, according to the computations (Figure 11), red shifts of the C2−H stretching vibrations caused by the H-bonding with either oxygen atoms or anions are of the same order of magnitude. Thus, it is practically impossible to decide which νCH bands in the IR spectra of 1·I−5·I should be assigned to the CH groups H-bonded to the oxygen atoms and which to the CH groups H-bonded to the anions. The same is also true for the spectra of the liquids 1·Tf$_2$N−5·Tf$_2$N. As mentioned above, the ether groups easily compete with the iodide anions for the formation of intermolecular hydrogen bonds. These results imply that at least part of the cations of liquid compounds 1·Tf$_2$N−4·Tf$_2$N are H-bonded intermolecularly via the oxygen atoms of their ether groups. The comparison of the IR spectra of 1·Tf$_2$N−5·Tf$_2$N and [C2C1im][Tf$_2$N][38] gives further support to this idea, because the spectra of the former contain several "extra" νCH bands (Tables 4−6) in

Ether-Derivatized Imidazolium-Based ILs

J. Phys. Chem. B, Vol. 111, No. 34, 2007 **10103**

TABLE 5: Vibrational Spectra of 2·I and 2·Tf₂N

experiment (IR) ν (cm⁻¹), Iᵃ		computations for various conformers of the cationᵇ ν (cm⁻¹)ᶜ								
2·I (solid)	2·Tf₂N (liq)	ga	−ga	−g−g	aa	gg	ag	a−g	−gg	assignmentᵈ
		3178	3182	3183	3187	3181	3188	3196	3183	ν C4−H, C5−H (in phase)
	3175 sh	3174	3165	3165	3169	3174	3168	3176	3165	ν C2−H
	3154 m	3159	3164	3164	3166	3159	3165	3160	3164	ν C4−H, C5−H (out of phase)
	3140 sh									
	3128 sh									
3125 m	3114 m									
	3110 sh									
	3102 sh									
	3095 sh									
3075 s										
3051 s										
3020 s br		3012	3011	3012	3012	3014	3017	3012	3019	νₐₛ CH₃
2990 sh	2986 s	2997	2997	2997	2998	3012	3012	2996	3012	νₐₛ CH₃
		2974	2974	2978	2971	2997	2998	2976	2997	νₐₛ CH₃ (O)
2976 s	2972 s	2965	2968	2968	2967	2970	2963	2963	2961	νₐₛ CH₃ (O)
2967 sh	2961 sh	2964	2967	2966	2920	2964	2946	2945	2958	νₐₛ CH₂
	2954 sh									
2927 m	2944 sh	2931	2931	2945	2919	2948	2919	2918	2945	νₛ CH₃
	2922 sh									
	2909 sh	2918	2918	2918	2896	2918	2892	2912	2918	νₐₛ CH₂
2901 m	2901 s	2896	2897	2914		2901		2898	2884	νₛ CH₃ (O)
2875 br	2885 sh	2889	2878	2892	2879	2887	2883	2885	2882	νₛ CH₂
		2878	2863	2885	2865	2872	2860		2879	νₛ CH₂
					2841		2848	2852		
2811 m										
1779 w										
1744 w										
1673 m										
1642 m										
1567 s	1579 w	1578	1580	1580	1585	1578	1585	1585	1579	ν C=C
1552 s	1561 w	1567	1562	1561	1572	1569	1571	1573	1562	νₐₛ N1C2N3
1483 w	1474 sh	1481	1482	1473	1495	1475	1489	1494	1472	δ CH₂
1466 m	1452 w	1462	1462	1462	1480	1461	1471	1464	1462	δₐₛ CH₃
		1461	1456	1458	1462	1460	1462	1462	1453	δ CH₂
1439 m	1443 vw	1453	1452	1450	1455	1448	1450	1448	1445	δₐₛ CH₃ (O)
		1440	1443	1448	1450	1445	1447	1447	1444	δₐₛ CH₃ (O)
		1435	1440	1437	1441	1435	1444	1441	1441	δₐₛ CH₃
		1432	1435	1434	1435	1432	1434	1435	1435	δₛ CH₃
1425 sh		1416	1421	1421	1423	1414	1424	1418	1421	δₛ CH₃, w CH₂
1401 s	1406 m	1402	1402	1394	1401	1393	1395	1395	1393	w CH₂, δₛ CH₃
1393 s	1393 m	1379	1377	1376	1382	1377	1381	1379	1376	w CH₂, δₛ CH₃
1377 s	1381 m	1376	1377	1375	1379	1373	1378	1376	1375	νₐₛ C2−N3−C4
		1364	1372	1365	1366	1357	1374	1359	1374	νₐₛ C2−N1−C5, w CH₂
	1352 s									Tf₂N⁻
1327 m	1331 s									
1316 s										
1299 m	1297 w	1298	1297	1315	1313	1320	1316	1305	1318	ν N−Et, N−Me, «breathing»
1288 m		1287	1286	1294	1284	1289	1300	1303	1298	t CH₂
		1279	1279	1282	1277	1285	1276	1260	1284	t CH₂
1257 sh	1258 sh									
1249 s		1250	1255	1255		1250		1244	1256	r CH
1232 sh					1228		1229			t CH₂, r CH
	1227 s									Tf₂N⁻
	1193 vs									Tf₂N⁻
1181 w		1158	1163	1186	1162	1186	1182	1183	1183	νₐₛ C−O−C, r CH₂
	1160 sh	1154	1157		1158			1134	1146	r CH₂, CH, νₐₛ C−O−C
1147 vs		1140	1133	1141	1133	1140	1149	1129	1128	r CH₃, νₛ C−O−C
	1136 s									Tf₂N⁻
1108 vs	1101 s	1128	1127	1128	1128	1128	1129	1126	1117	r CH₃
1097 vs	1074 sh	1113	1116	1115	1111	1113	1115	1102	1098	r CH
1088 vs		1094	1096	1097	1101	1096	1100	1094	1082	r CH
				1087		1086	1083			r CH₂, CH₃
1078 vs		1076	1076	1076	1078	1078	1078	1083	1076	r CH₃
	1062 s sh									Tf₂N⁻
1059 vs	1056 vs	1069	1060	1062	1077	1074	1076	1076	1066	r CH₂, CH₃, νₛ C−O−C
1019 vs	1027 sh	1018	1017	1017	1023	1018	1023	1030	1018	δ ring, ν N−CH₃
		1014	1007	1007	1012	1014	1012	1017	1007	δ ring, ν N−CH₂
991 sh		989	989	968	1000	968	984	983	975	νₛ C−C, δ ring
912 w	897 sh									
889 m	891 m									
874 s	879 m									
852 s	868 m	850	861	863	884	849	864	861	861	γ C4−H, C5−H
844 s		835	817	815	856	838	854	848	813	ν C−O, r CH₃
	800 sh	813	811	804	813	806	813	834	795	γ C2−H
786 vs	789 m	806	809	792	812	794	792	793	784	r CH₃
	762 m									
741 vs	740 m	723	705	699	733	720	734	744	740	ν N−Me, ν N−CH₂ (out of phase)
717 w sh	721 w sh									
709 vw sh	714 vw sh	739	741	742	738	739	738	739	698	γ C4−H, C5−H
	692 w									
	673 sh									
661 vs	655 m		666	663	657		658		661	ν N−Me, ν N−CH₂ (in phase)
627 vs	631 vs	637				633		628		
		624	624	624	624	623	624	624	624	γ N−Me, ring-puckering
608 vs	616 sh	607	606	606	615	607	615	616	604	γ N−CH₂, ring-puckering
	603 sh									
567 w										
558 w										

ᵃ⁻ᵈ See the corresponding footnotes to Table 4.

TABLE 6: Vibrational Spectra of 3·I and 3·Tf₂N

experiment (IR) ν (cm⁻¹), Iᵃ		computations for various conformersᵇ ν (cm⁻¹)ᶜ					
3·I (solid)	3·Tf2N (liq)	ga	−ga	aa	gg	−gg	assignmentᵈ
	3191 vw sh	3195	3186	3178	3186	3178	νC4−H, C5−H (in phase)
	3175 sh	3168	3178	3167	3167	3166	νC2−H (in phase)
	3160 w	3167	3162	3162	3166	3162	νC4−H, C5−H (out of phase)
3148 m	3153 w						
	3140 vw sh						
	3127 w						
3135 sh	3119 w						
	3110 sh						
3092 m	3102 sh						
2995 m	2998 sh	3011	3012	3012	3011	3013	νas CH3
	2988 m	2996	2996	2998	2996	2996	νas CH3
2976 m	2972 m	2989	2988	2991	2989	2989	νas CH3 (O)
		2981	2985	2989	2968	2969	νas CH2
2940 sh		2929	2930	2936	2932	2934	νs CH2
2931 m	2921 sh	2918	2918	2919	2918	2918	νs (N)CH3
	2911 sh						
2901 m	2901 m	2911	2915	2902	2916	2918	νas CH3 (O)
2888 m		2861	2870		2912	2915	νas CH2
2868 m		2854	2857	2848	2870	2876	νs CH3 (O)
2865 sh							
2827 m		2826	2833	2830	2849	2853	νs CH2
2804 m				2802			νs CH2
1632 m							
1610 m							
1568 s	1576 vw	1583	1583	1583	1583	1583	ν C=C
1558 s	1567 vw	1571	1562	1571	1568	1562	νas N1C2N3
1544 sh							
1506 vw	1505 vw						
1494 vw	1494 vw						
1472 sh	1475 vw br	1484	1481	1492	1466	1467	δ CH2
1465 m	1462 sh	1463	1461	1462	1463	1462	δas CH3
1451 s	1453 w	1456	1456	1461	1450	1451	δas CH3 (O)
		1443	1444	1451	1449	1448	δas CH3 (O)
		1442	1442	1443	1443	1442	δas CH3
1440 sh	1435 vvw	1442	1441	1441	1435	1436	δ CH2
1425 m		1435	1435	1435	1434	1435	δs CH3 (O)
1415 m	1406 m	1422	1421	1422	1422	1421	δs CH3
1392 sh	1393 m	1405	1409	1406	1398	1404	νas C2N1C5, w CH2
1379 m	1382 m	1399	1399	1400	1387	1387	w CH2
1360 s	1356 m	1379	1376	1378	1378	1376	νas C2N3C4
1341 s	1333 m	1360	1356		1352	1344	w CH2
				1325			
1295 m		1314	1320	1314	1317	1316	ν N−Et, N−Me, «breathing»

experiment (IR) n (cm⁻¹), Iᵃ		computations for various conformersᵇ ν (cm⁻¹)ᶜ					
3·I (solid)	3·Tf2N (liq)	ga	−ga	aa	gg	−gg	assignmentᵈ
1283 m		1284	1283	1285	1290	1298	r C−H, t CH2
1266 m							
1254 m	1257 sh	1251	1251	1265	1275	1272	t CH2
1241 w	1249 w						
	1242 w						Tf2N⁻
1221 m	1230 m	1229	1228		1223	1227	t CH2
	1197 m, br						Tf2N⁻
				1204			t CH2
1196 m		1186	1187	1200	1190	1190	r CH3
1183 m		1158	1157	1157	1155	1154	r CH3 (O), νas N−Me, N−CH2, r CH
1161 vs		1154	1141	1152	1151	1138	r CH3 (O), νas N−Me, N−CH2, r CH
	1136 sh						Tf2N⁻
		1128	1128	1128	1128	1129	r CH3
1113 vs		1119	1113	1128	1111	1110	νas COC
1091 sh		1103	1104	1107	1099	1102	r CH
1083 vs	1074 s	1088	1085	1094	1078	1076	r CH2
1066 sh		1079	1077	1078	1063	1064	r CH3
	1065 s						Tf2N⁻
	1056 s						Tf2N⁻
1050 sh							
1035 sh	1038 sh	1029	1038	1041	1027	1033	δ ring, ν N−CH2, ν C−C, C−O
1020 s	1027 sh	1011	1018	1025	1007	1017	δ ring, ν N−Me
1013 vs	1017 sh	1005	999	1013	972	964	νs C−O−C, ν ring
967 m		947	948	952			ν C−C
943 sh							
929 sh					916	921	ν C−C
	899 w sh						
892 sh	892 m						
879 sh	879 m				878	872	
859 m	869 m	859					γ C−H
839 m			846	852			
818 vs		830	832	816	825	847	ν C−C, O−C
801 sh	800 sh	809	827	793	811	822	γ C−H
762 s	791 vw						
752 vs	763 vw	738	735	738	745	741	γ C−H
732 sh	741 vw				735		
710 s	720 vw	691	696		686	696	ν N−Me, ν N−CH2 (out of phase)
	663 w						
646 vs	631 vs	654	647	654	648	644	γ N−CH2, ring-puckering
641 sh							
617 vs		623	623	623	624	624	γ N−Me, ring-puckering
600 vs		588	585	619	586	584	ν N−Me, ν N−CH2 (in phase)
579 sh							

ᵃ⁻ᵈ See the corresponding footnotes to Table 4.

addition to four νCH bands (3173, 3158, 3125, and 3104 cm⁻¹) assigned to the stretching vibrations of the aromatic CH groups H-bonded to the Tf2N⁻ anion[39] in [C2C1im][Tf2N]. Probably, these C−H···O hydrogen bonds raise the viscosity of 1·Tf2N in comparison to [C3C1im][Tf2N], in which this type of H-bonding is absent. The viscosity of ILs is also dependent on the volume of the cations,[39] which increases when the oxygen atom in the ether group is replaced by a methylene unit. In contrast, the ether groups tend to adopt gauche conformations, which have a larger volume than anti conformations preferentially adopted by alkyl groups. It should be noted, however, that although the free volume of the cations is given by the number of conformations that can be adopted by the side chain, the small energy difference between the various conformations

of both alkyl[35] and ether side chains (Tables S1−S3) makes it is possible for these chains to adopt several conformations in the liquid state at ambient temperature. Complex interplay of all these factors may influence the viscosity in any way: it increases when the propyl group of [C3C1im][Tf2N] is replaced by the C1−O−C1 moiety; it slightly decreases when the butyl group of [C4C1im][Tf2N] is replaced by the C1−O−C2 fragment and slightly increases with the C2−O−C1 moiety. In most cases, it is likely that these factors almost compensate for each other, because in general, the viscosity of the ether-functionalized ILs 1·Tf2N−5·Tf2N practically coincide with the viscosity of related 1-alkyl-3-methylimidazolium based ILs. Thus, contrary to previous reports, the ether group does not reduce the melting points of the imidazolium salt. The ion

Ether-Derivatized Imidazolium-Based ILs

J. Phys. Chem. B, Vol. 111, No. 34, 2007 **10105**

pairings in these salts are different, but there does not appear to be a universal rule.

Experimental

All starting materials were obtained commercially and used as received. The synthesis of the imidazolium salts was performed under an inert atmosphere of dry nitrogen using standard Schlenk techniques in solvents dried using the appropriate reagents and distilled prior to use. IR spectra were recorded on a Perkin-Elmer FT-IR 2000 system. NMR spectra were measured on a Bruker DMX 400 using Me$_4$Si as external standards at 20 °C. Electrospray ionization mass spectra (ESI-MS) were recorded on a ThermoFinnigan LCQ Deca XP Plus quadrupole ion trap instrument on sample diluted in methanol.[40] Samples were infused directly into the source at 5 μL min^{-1} using a syringe pump, and the spray voltage was set at 5 kV, and the capillary temperature, at 50 °C. Elemental analysis was carried out at the Ecole Polytechnique Fédérale de Lausanne. Viscosities were measured with a Brookfield DV-II+ viscometer on 0.50 mL of sample. The temperature of the samples was maintained to 21 ± 1 °C by means of an external temperature controller. The measurements were performed in duplicate.

Synthesis of 1·Br. Methoxymethyl bromide (12 mmol) was added dropwise to a solution of 1-methylimidazole (10 mmol) in diethyl ether (30 mL) at 0 °C while stirring. After the addition was complete, the reaction mixture was stirred at room temperature for 8 h. The excess of methoxymethyl bromide and diethyl ether was then removed in vacuum. The remaining solid was washed with diethyl ether (2 × 5 mL). Yield: 98%; mp 101 °C. ^{1}H NMR (CD$_2$Cl$_2$): 9.90 (s, NCHN, 1H), 7.80 (s, 1H), 7.75 (s, 1H), 5.85 (s, 2H), 4.15 (s, 3H), 3.55 (s, 3H). ^{13}C NMR (CD$_2$Cl$_2$): 133.1, 120.3, 117.9, 76.2, 54.1, 33.1. IR (cm^{-1}): 3135, 3091, 3065, 2981, 2954, 2900, 1580, 1550, 1460, 1450, 1420, 1326, 1205, 1180, 1115, 1065, 920, 844, 761, 732, 678, 623, 611. ESI-MS (CH$_3$OH): positive ion, 127 [cation]. Anal. Calcd. for C$_6$H$_{11}$BrN$_2$O (207.0701): C, 34.80; H, 5.35; N, 13.53%. Found: C, 34.89; H, 5.38; N, 13.52%.

Synthesis of 1·I. Methoxymethyl iodide (12 mmol) was added dropwise to a solution of 1-methylimidazole (10 mmol) in diethyl ether (30 mL) at 0 °C, and the reaction mixture was stirred at room temperature for 2 h. The solid product was collected by filtration and washed with diethyl ether (2 × 5 mL). Yield: 95%; mp 75 °C. ^{1}H NMR (CD$_2$Cl$_2$): 10.10 (s, NCHN, 1H), 7.80 (s, 1H), 7.78 (s, 1H), 5.80 (s, 2H), 4.10 (s, 3H), 3.50 (s, 3H). ^{13}C NMR (CD$_2$Cl$_2$): 133.0, 120.2, 117.8, 76.1, 54.0, 33.2. IR (cm^{-1}): 3138, 3093, 3065, 2981, 2952, 2900, 1577, 1550, 1463, 1452, 1417, 1324, 1206, 1149, 1114, 1064, 920, 842, 759, 733, 676, 621, 611. ESI-MS (CH$_3$OH): positive ion, 127 [cation]. Anal. Calcd. for C$_6$H$_{11}$IN$_2$O (254.0661): C, 28.37; H, 4.36; N, 11.03%. Found: C, 28.39; H, 4.38; N, 11.02%.

Synthesis of 2·Cl. Ethoxymethyl chloride (5.1 mmol) was added to a solution of 1-methylimidazole (5.0 mmol) in diethyl ether (10 mL) at 0 °C while stirring. The reaction mixture was stirred at 30 °C for 8 h. After filtration, the solid was washed with diethyl ether (2 × 5 mL) and dried in vacuum. Yield 90%; mp 75 °C (ref 14, 65−68 °C). ^{1}H NMR (CD$_2$Cl$_2$): 10.00 (s, NCHN, 1H), 7.78 (s, 1H), 7.76 (s, 1H), 5.72 (s, 2H), 4.10 (s, 3H), 3.66 (q, 2H, *J* (HH) = 6.85 Hz), 1.22 (t, 3H, *J* (HH) = 6.85 Hz). ^{13}C NMR (CD$_2$Cl$_2$): 132.8, 120.0, 117.6, 74.6, 62.2, 33.4. IR (cm^{-1}): 3130, 3080, 3055, 2976, 2901, 2860, 1565, 1550, 1465, 1435, 1391, 1315, 1250, 1148, 1090, 1061, 1020, 875, 845, 788, 741, 660, 628, 611. ESI-MS (CH$_3$OH): positive ion, 141 [cation]. Anal. Calcd. for C$_7$H$_{13}$ClN$_2$O (176.6460) C, 47.60; H, 7.42; N, 15.86%. Found: C, 47.66; H, 7.48; N, 15.81%.

Synthesis of 2·I. A mixture of 2·Cl (5.0 mmol) and sodium iodide (5.1mmol) in acetone (50 mmol) was heated to reflux

for 24 h. The reaction mixture was filtered to afford a solid. The solid was dissolved in dichloromethane (30 mL). The solution was stored at −20 °C for 48 h, and then it was filtered. The solvent was removed under vacuum. The solid was recrystallized from dichloromethane and diethyl ether. Yield: 87%; mp 68 °C. ^{1}H NMR (CD$_2$Cl$_2$): 10.05 (s, NCHN, 1H), 7.78 (s, 1H), 7.74 (s, 1H), 5.70 (s, 2H), 4.12 (s, 3H), 3.68 (q, 2H, *J* (HH) = 6.80 Hz), 1.20 (t, 3H, *J* (HH) = 6.80 Hz). ^{13}C NMR (CD$_2$Cl$_2$): 132.8, 120.1, 117.6, 74.8, 62.2, 33.2, 10.8. IR (cm^{-1}): 3125, 3075, 3051, 2976, 2901, 1567, 1552, 1466, 1439, 1401, 1393, 1316, 1249, 1147, 1088, 1059, 1019, 874, 844, 786, 741, 661, 627, 608. ESI-MS (CH$_3$OH): positive ion, 141 [cation]. Anal. Calcd. for C$_7$H$_{13}$IN$_2$O (268.0930): C, 31.36; H, 4.89; N, 10.45%. Found: C, 31.39; H, 4.91; N, 10.42%.

Synthesis of 3·Br. Methoxyethyl bromide (5.1 mmol) was added to 1-methylimidazole (5.0 mmol) (10 mL) at 0 °C while stirring. The reaction mixture was stirred at 30 °C for an additional 8 h. After filtration, the solid was washed with diethyl ether (2 × 5 mL) and dried in vacuum. Yield 92%; mp 80 °C. ^{1}H NMR (CD$_2$Cl$_2$): 10.00 (s, NCHN, 1H), 7.78 (s, 1H), 7.76 (s, 1H), 5.72 (s, 2H), 4.10 (s, 3H), 3.66 (q, 2H, *J* (HH) = 6.86 Hz), 1.22 (t, 3H, *J* (HH) = 6.86 Hz). ^{13}C NMR (CD$_2$Cl$_2$): 132.8, 120.0, 117.6, 74.6, 62.2, 33.4. IR (cm^{-1}): 3120, 3070, 3051, 2978, 2900, 3868, 2855, 1560, 1550, 1470, 1439, 1391, 1316, 1250, 1148, 1091, 1061, 1020, 875, 845, 788, 741, 660, 630, 610. ESI-MS (CH$_3$OH): positive ion, 141 [cation]. Anal. Calcd. for C$_7$H$_{13}$BrN$_2$O (221.0970): C, 38.03; H, 5.93; N, 12.67%. Found: C, 38.19; H, 5.96; N, 12.62%.

Synthesis of 3·I. Prepared using the same procedure from 3·Br as that described for the synthesis of compound 2·I. Yield: 91%; mp 50 °C. ^{1}H NMR (CD$_2$Cl$_2$): 9.80 (s, NCHN, 1H), 7.65 (s, 1H), 7.55 (s, 1H), 4.58 (t, 2H, *J* (HH) = 5.0 Hz), 4.10 (s, 3H), 3.82 (t, 2H, *J* (HH) = 5.0 Hz), 3.40 (s, 3H). ^{13}C NMR (CD$_2$Cl$_2$): 132.8, 119.2, 119.1, 66.0, 54.9, 45.8, 32.8. IR (cm^{-1}): 3148, 3092, 2976, 2931, 2888, 2804, 1568, 1558, 1451, 1360, 1161, 1113, 1083, 1013, 818, 752, 710, 646, 617, 600. ESI-MS (CH$_3$OH): positive ion, 141 [cation]. Anal. Calcd. for C$_7$H$_{13}$IN$_2$O (268.0930): C, 31.36; H, 4.89; N, 10.45%. Found: C, 31.41; H, 4.94; N, 10.46%.

Synthesis of 4·Cl. This compound was obtained in a same manner from 1-methylimidazole (10 mmol) and 1-methoxy-ethoxymethyl chloride (12 mmol), as described for 2·Cl. Yield: 91%; mp 72 °C. ^{1}H NMR (CD$_2$Cl$_2$): 10.10 (s, NCHN, 1H), 7.68 (s, 1H), 7.62 (s, 1H), 4.89 (t, 2H, *J* (HH) = 4.50 Hz), 4.14 (s, 3H), 3.86 (t, 2H, *J* (HH) = 4.50 Hz), 3.57 (t, 2H, *J* (HH) = 4.50 Hz), 3.35 (s, 3H). ^{13}C NMR (CD$_2$Cl$_2$): 132.8, 119.2, 119.1, 66.0, 54.9, 45.8, 32.8. IR (cm^{-1}): 3142, 3072, 2969, 2942, 2922, 2888, 1576, 1560, 1466, 1444, 1405, 1272, 1231, 1200, 1163, 1136, 1109, 1090, 1028, 877, 852, 839, 760, 744, 667, 620, 609. ESI-MS (CH$_3$OH): positive ion, 171 [cation]. Anal. Calcd. for C$_8$H$_{15}$ClN$_2$O$_2$ (206.6723): C, 46.49; H, 7.32; N, 13.55%. Found: C, 46.55; H, 7.38; N, 13.52%.

Synthesis of 4·I. This compound was obtained in the same manner from 4·Cl (5.0 mmol) and sodium iodide (5.5 mmol) as described for the synthesis of compound 2·I. Yield: 85%; mp 63 °C. ^{1}H NMR (CD$_2$Cl$_2$): 10.10 (s, NCHN, 1H), 7.68 (s, 1H), 7.62 (s, 1H), 5.89 (s, 2H), 4.14 (s, 3H), 3.86 (t, 2H, *J* (HH) = 4.50 Hz), 3.57 (t, 2H, *J* (HH) = 4.50 Hz), 3.35 (s, 3H). ^{13}C NMR (CD$_2$Cl$_2$): 132.8, 119.2, 119.1, 66.0, 54.9, 45.8, 32.8. IR (cm^{-1}): 3142, 3072, 2969, 2942, 2922, 2888, 1576, 1560, 1466, 1444, 1405, 1272, 1231, 1200, 1163, 1136, 1109, 1090, 1028, 877, 852, 839, 760, 744, 667, 620, 609. ESI-MS (CH$_3$OH): positive ion, 171 [cation]. Anal. Calcd. for C$_8$H$_{15}$IN$_2$O$_2$ (298.1193): C, 32.23; H, 5.07; N, 9.40%. Found: C, 32.30; H, 5.09; N, 9.42%.

Synthesis of 5·Br. 1-Methoxyethoxyethyl bromide (12 mmol) was added dropwise to a solution of 1-methylimidazole (10

TABLE 7: Crystallographic Data for 1·I, 2·I, 3·I, 4·I, 5·Br, and 5·I

	1·I	**2·I**	**3·I**	**4·I**	**5·Br**	**5·I**
chem formula	$[C_6H_{11}N_2O]I$	$[C_7H_{13}N_2O]I$	$[C_7H_{13}N_2O]I$	$[C_8H_{15}N_2O_2]I$	$[C_9H_{17}N_2O_2]Br$	$[C_9H_{17}N_2O_2]I$
FW	254.07	268.09	268.09	298.12	265.16	312.15
crystal system	monoclinic	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$Pca2_1$	$P2_1/n$	$P2_1/c$	$P2_1/n$
A (Å)	8.3743(6)	9.4059(5)	15.2411(14)	9.5223(5)	7.1550(12)	9.7948(13)
B (Å)	12.0821(8)	16.3399(9)	8.2598(7)	8.0828(4)	14.609(3)	13.0859(12)
C (Å)	9.6014(8)	13.6066(7)	32.681(2)	15.4060(12)	11.880(3)	9.9372(14)
α (°)	90	90	90	90	90	90
β (°)	104.590(7)	91.547(4)	90	106.029(5)	105.698(16)	103.711(12)
γ (°)	90	90	90	90	90	90
vol (Å^3)	940.13(12)	2090.46(19)	4114.2(6)	1139.65(12)	1195.5(4)	1237.4(3)
Z	4	8	16	4	4	4
D_{calc} (g cm^{-3})	1.795	1.704	1.731	1.738	1.473	1.676
$F(000)$	488	1040	2080	584	544	616
μ (mm^{-1})	3.352	3.020	3.069	2.785	3.419	2.569
temp (K)	140(2)	140(2)	140(2)	100(2)	100(2)	140(2)
wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
meas reflxns	5138	12075	25154	12332	7860	8950
unique reflxns	1650	3626	6835	1997	2081	2830
unique reflxns [$I > 2\sigma(I)$]	1496	3215	5139	1843	1464	2370
no. data/restraints/parameters	1650/0/93	3626/21/214	6835/1/406	1997/0/120	2081/0/129	2830/0/185
R^a [$I > 2\sigma(I)$]	0.0249	0.0281	0.0558	0.0134	0.0583	0.0498
$wR2^a$ (all data)	0.0647	0.0735	0.1313	0.0285	0.1378	0.1400
GooF^b	1.049	1.020	1.022	1.135	1.155	1.166

^{a} $R = \Sigma ||F_o| - |F_c||/ \Sigma |F_o|$; $wR2 = \{\Sigma [w(F_o^2 - F_c^2)2]/ \Sigma [w(F_o^2)^2]\}^{1/2}$. ^{b} GooF $= \{\Sigma [w(F_o^2 - F_c^2)2]/(n - p)\}^{1/2}$, where n is the number of data and p is the number of parameters refined.

mmol) at 0 °C while stirring. After the addition was complete, the reaction mixture was stirred at room temperature for 24 h. Diethyl ether (20 mL) was added, and the reaction mixture was stirred for an additional 24 h at room temperature, during which time a solid precipitated. The solid was filtered and washed with diethyl ether (2 × 5 mL). Yield: 81%; mp 78 °C. ^{1}H NMR (CD$_2$Cl$_2$): 10.20 (s, NCHN, 1H), 7.70 (s, 1H), 7.52 (s, 1H), 4.62 (t, 2H, J (HH) = 4.40 Hz), 4.10 (s, 3H), 3.90 (t, 2H, J (HH) = 4.40 Hz), 3.68 (t, 2H, J (HH) = 4.40 Hz), 3.54 (t, 2H, J (HH) = 4.40 Hz), 3.36 (s, 3H). ^{13}C NMR (CD$_2$Cl$_2$): 133.7, 119.2, 119.0, 67.6, 66.0, 64.5, 54.6, 45.7, 32.0. IR (cm^{-1}): 3152, 3058, 2970, 2902, 2808, 2742, 1568, 1449, 1367, 1304, 1177, 1124, 1078, 1043, 1011, 921, 880, 837, 785, 712, 639, 622. Positive ion, 185 [cation]. Anal. Calcd. for C$_9$H$_{17}$BrN$_2$O$_2$ (265.1502): C, 40.77; H, 6.46; N, 10.57%. Found: C, 40.81; H, 6.48; N, 10.55%.

Synthesis of 5·I. This compound was obtained in the same manner from **5·Br** (10 mmol) and sodium iodide (12 mmol) as described for **2·I**. Yield: 86%; mp 70 °C. ^{1}H NMR (CD$_2$Cl$_2$): 9.50 (s, NCHN, 1H), 7.71 (s, 1H), 7.66 (s, 1H), 4.48 (t, 2H, J (HH) = 4.50 Hz), 3.99 (s, 3H), 3.82 (t, 2H, J (HH) = 4.50 Hz), 3.55 (t, 2H, J (HH) = 4.50 Hz), 3.42 (t, 2H, J (HH) = 4.50 Hz), 3.23 (s, 3H). ^{13}C NMR (CD$_2$Cl$_2$): 133.7, 119.2, 119.0, 67.6, 66.0, 64.5, 54.6, 45.7, 32.0. IR (cm^{-1}): 3145, 3064, 3023, 2962, 2902, 2884, 2814, 1572, 1443, 1428, 1336, 1259, 1170, 1133, 1093, 1022, 848, 818, 786, 661, 619. Positive ion, 185 [cation]. Anal. Calcd. for C$_9$H$_{17}$IN$_2$O$_2$ (312.1462): C, 34.63; H, 5.49; N, 8.97%. Found: C, 34.65; H, 5.53; N, 8.96%

Synthesis of 1·Tf$_2$N. A mixture of **1·Br** (5.0 mmol) and Li-[Tf$_2$N] (5.0 mmol) in water (20 mL) was stirred at room temperature for 2 h. The ionic liquid phase (bottom) was separated, it was washed with water (2 × 5 mL), and the product was dried under vacuum at 100 °C for 24 h. Yield: 82%. ^{1}H NMR (CD$_2$Cl$_2$): 8.80 (s, NCHN, 1H), 7.50 (s, 1H), 7.42 (s, 1H), 5.51 (s, 2H), 4.00 (s, 3H), 3.45 (s, 3H). ^{13}C NMR (CD$_2$-Cl$_2$): 132.0, 120.0, 117.6, 76.2, 53.8, 33.2. IR (cm^{-1}): 3154, 3115, 2971, 2901, 1579, 1560, 1348, 1330, 1184, 1134, 1055, 740, 630. ESI-MS (CH$_3$OH): positive ion, 127 [cation]. Anal. Calcd. for C$_8$H$_{11}$F$_6$N$_3$O$_5$S$_2$ (407.3149): C, 23.59; H, 2.72; N, 10.32%. Found: C, 23.69; H, 2.75; N, 10.30%.

Compounds **2·Tf$_2$N**, **3·Tf$_2$N**, **4·Tf$_2$N**, and **5·Tf$_2$N** were prepared in a manner similar to that described above for **1·Tf$_2$N**.

2·Tf$_2$N. Yield 86%. ^{1}H NMR (CD$_2$Cl$_2$): 8.82 (s, NCHN, 1H), 7.52 (s, 1H), 7.42 (s, 1H), 5.55 (s, 2H), 4.02 (s, 3H), 3.65 (q, 2H, J (HH) = 6.80 Hz), 1.27 (t, 3H, J (HH) = 6.80 Hz). ^{13}C NMR (CD$_2$Cl$_2$): 133.1, 120.0, 118.0, 75.1, 62.0, 33.5, 10.2. IR (cm^{-1}): 3154, 2986, 2901, 1579, 1561, 1406, 1352, 1193, 1136, 1056, 891, 740, 631. ESI-MS (CH$_3$OH): positive ion, 141 [cation]. Anal. Calcd. for C$_9$H$_{13}$F$_6$N$_3$O$_5$S$_2$ (421.3417): C, 25.66; H, 3.11; N, 9.97%. Found: C, 25.69; H, 3.15; N, 9.96%.

3·Tf$_2$N. Yield 84%. ^{1}H NMR (CD$_2$Cl$_2$): 9.60 (s, NCHN, 1H), 7.48 (s, 1H), 7.40 (s, 1H), 4.35 (t, 2H, J (HH) = 5.0 Hz), 3.95 (s, 3H), 3.74 (t, 2H, J (HH) = 5.0 Hz), 3.40 (s, 3H). ^{13}C NMR (CD$_2$Cl$_2$): 132.0, 119.2, 119.1, 65.4, 54.6, 45.8, 32.2. IR (cm^{-1}): 3140, 2988, 2901, 1567, 1453, 1406, 1356, 1197, 1065, 1056, 892, 791, 631. ESI-MS (CH$_3$OH): positive ion, 141 [cation]. Anal. Calcd. for C$_9$H$_{13}$F$_6$N$_3$O$_5$S$_2$ (421.3417): C, 25.66; H, 3.11; N, 9.97%. Found: C, 25.68; H, 3.13; N, 9.99%.

4·Tf$_2$N. Yield: 85%. ^{1}H NMR (CD$_2$Cl$_2$): 8.75 (s, NCHN, 1H), 7.54 (s, 1H), 7.42 (s, 1H), 5.61, (s, 2H), 3.98 (s, 3H), 3.74 (t, 2H, J (HH) = 4.30 Hz), 3.56 (t, 2H, J (HH) = 4.30 Hz), 3.36 (s, 3H). ^{13}C NMR (CD$_2$Cl$_2$): 132.0, 120.0, 117.2, 75.4, 67.3, 65.7, 54.6, 32.4. IR (cm^{-1}): 3154, 2988, 2901, 1578, 1560, 1453, 1406, 1394, 1351, 1331, 1190, 1135, 1056, 1028, 892, 790, 740, 631. ESI-MS (CH$_3$OH): positive ion, 171 [cation]. Anal. Calcd. for C$_{10}$H$_{15}$F$_6$N$_3$O$_6$S$_2$ (451.3680): C, 26.61; H, 3.35; N, 9.31%. Found: C, 26.69; H, 3.37; N, 9.32%.

5·Tf$_2$N. Yield 88%. ^{1}H NMR (CD$_2$Cl$_2$): 8.70 (s, NCHN, 1H), 7.50 (s, 1H), 7.32 (s, 1H), 4.36 (t, 2H, J (HH) = 4.50 Hz), 3.95 (s, 3H), 3.85 (t, 2H, J (HH) = 4.50 Hz), 3.66 (t, 2H, J (HH) = 4.50 Hz), 3.55 (t, 2H, J (HH) = 4.50 Hz), 3.37 (s, 3H). ^{13}C NMR (CD$_2$Cl$_2$): 132.2, 119.3, 119.2, 67.4, 66.2, 64.3, 54.4, 45.8, 32.2. IR (cm^{-1}): 3150, 2988, 2901, 1570, 1452, 1406, 1393, 1357, 1229, 1074, 1065, 1056, 892, 792, 632. ESI-MS (CH$_3$OH): positive ion, 185 [cation]. Anal. Calcd. for C$_{11}$H$_{17}$F$_6$N$_3$O$_6$S$_2$ (465.3949): C, 28.39; H, 3.68; N, 9.03%. Found: C, 28.41; H, 3.71; N, 9.01%.

Structure Determinations in the Solid-State. Relevant details about the structural refinements are compiled in Table 7, and selected bond distances and angles are given in Tables 1 and 2. For **1·I**, **2·I**, **3·I**, and **5·I**, data collection was performed on a four-circle Kappa goniometer equipped with an Oxford Diffraction KM4 Sapphire CCD at 140(2) K, and data reduction was performed using CrysAlis RED.[41] For **4·I** and **5·Br**, data

Ether-Derivatized Imidazolium-Based ILs

J. Phys. Chem. B, Vol. 111, No. 34, 2007 **10107**

collection was carried out on a Bruker Nonius APEX II CCD at 100(2) K, and data reduction was performed using Eval-CCD.[42] Structural solution was carried out using SiR92,[43] and structural refinement, using the SHELXTL software package.[44] The structures were solved by direct methods and refined by full-matrix, least-squares refinement (against F^2), with all non-hydrogen atoms refined anisotropically. The hydrogen atoms were placed in their geometrically generated positions using the riding model and refined isotropically. For **5·I**, the twin law ($\bar{1}00/010/00\bar{1}$) was applied using the TWIN command implemented in SHELXTL. Disorder for the pendant alkyl groups was modeled for **2·I** and **5·I**, and restraints were applied using SIMU and DELU commands for **2·I**. Empirical absorption corrections were applied for **1·I**, **2·I**, **3·I**, and **5·I** using DELABS,[45] and for **4·I** and **5·Br**, using SADABS.[46] Graphical representations of the structures were made with Diamond.[47]

Computations. All quantum-chemical calculations were carried out using the Gaussian-03 suite of programs[48] For DFT, Becke's three-parameter exchange functional was used[49] in combination with the Lee−Yang−Parr correlation functional[50] (B3LYP) and standard 6-31G* basis set (B3LYP/6-31G*). All stationary points were characterized as minima by analysis of the Hessian matrices. The B3LYP/6-31G* calculated force fields were transformed to internal coordinates, and the scaling procedure was applied using the program described in ref 51, the reason being that although DFT produces rather accurate vibrational frequencies, even these computations show systematic errors, mainly due to limited basis sets, harmonic approximation, and remaining deficiencies in describing electron correlation. Transferable scaling factors compensate for most of these errors.[52] It has previously been demonstrated that the scaled quantum mechanical (SQM) method allows a priori quantitative prediction of the IR and Raman spectra of various imidazolium-based ILs.[35,37] The transferable scaling factors employed in this work[53] are summarized in the Supporting Information (Table S4).

Supporting Information Available: B3LYP/6-31G* energy of possible conformers of **1**−**3**, scaling factors for the force fields of the compounds studied, crystallographic information files (CIF) of **1·I**, **2·I**, **3·I**, **4·I**, **5·Br**, and **5·I**. This material is available free of charge via the Internet at http://pubs.acs.org.

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