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Infrared Spectroscopy

Strong, Localized, and Directional Hydrogen Bonds Fluidize Ionic Liquids**

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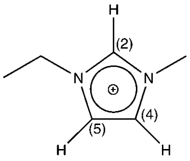
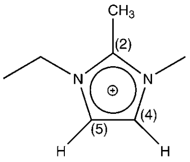
Hydrogen bonds are very important in chemistry and biology.[1–3] The properties of liquids and solutions consisting purely of neutral molecules are characteristically determined by the strength and number of hydrogen bonds. When water freezes to form ice, each water molecule forms four strong hydrogen bonds to its neighbors in tetrahedral fashion giving a periodical H-bond network.[4] In nonpolar solvents peptides retain their helical secondary structure up to very high temperature as a result of intramolecular H bonds.[5] Nucleic acids when neutralized in aqueous electrolyte solutions build the famous double-helical structure on the basis of strong two- and threefold hydrogen bonds between base pairs.[6] What all these important structures have in common is that they are stabilized by hydrogen bonds; they usually become more rigid and less flexible with increasing strength and number of H bonds.

In this study we show that the opposite behavior can be found for ionic liquids (ILs), which are composed solely of ions rather than neutral molecules. ILs constitute a remarkably promising class of technologically useful and fundamentally interesting materials.[7–12] Herein we show that strong and directional H bonds formed between cations and anions destroy the charge symmetry and thus can fluidize ionic liquids. H bonds introduce "defects" into the Coulomb network of ILs and increase the dynamics of the cations and anions, resulting in decreased melting points and reduced viscosities. Thus the properties of ILs can be altered by adjusting the ratio between Coulomb forces and van der Waals interactions represented by H bonds. This possibility is demonstrated by FTIR measurements of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C_2mim][NTf_2] (**1**) and 1-ethyl-2,3-dimethylimidazolium bis(trifluoro methylsulfonyl)imide [C_2C_1mim][NTf_2] (**2**), wherein characteristic H-bond contributions can be switched off by methylation at C(2).



C_2mim^+ in **1**



$C_2C_1mim^+$ in **2**

Recently, we presented low-frequency vibrational spectra of imidazolium-based ionic liquids in the range between 30 and 300 cm^{-1} obtained by far-infrared spectroscopy.[13] We could show that the absorptions at wavenumbers above 150 cm^{-1} can be assigned to intramolecular bending and wagging modes of cations and anions in the ionic liquid. The contributions below 150 cm^{-1} were assigned to the intermolecular interactions between cations and anions that describe the bending and stretching vibrational modes of hydrogen bonds. This assignment was supported by DFT calculations which gave wavenumbers for the bending and stretching modes of ion pairs and ion-pair aggregates in this frequency region. Further proof of the intermolecular interactions came from a nearly linear relation between the average binding energies of calculated IL aggregates and the measured wavenumbers for maxima of the low-frequency vibrational bands for a series of ionic liquids containing the same imidazolium cation but different anions. Although this assignment is supported by recent THz spectroscopy experiments,[14] we could not be completely sure that other motions such as librations and rotations do not contribute significantly to this low-frequency band.

Thus we measured both the mid- and the far-FTIR spectra of **1** and **2** as a function of temperature in order to determine whether the spectra are significantly affected by suppression of the C(2)–H···A^- H bond upon methylation. The FTIR spectra of both ionic liquids in the frequency range between 3000 and 3300 cm^{-1} are shown in Figure 1. The spectral bands between 3070 and 3200 cm^{-1} can be assigned to C–H stretching modes of the imidazolium ring. In a recent study we could show for **1** that the vibrational bands at higher wavenumbers in this region correspond to C(4/5)–H stretching modes whereas those at lower wavenumbers can be assigned to C(2)–H stretching modes.[15] This assignment was supported by DFT calculations as well as temperature- and concentration-dependent measurements. Herein, we can clearly show that this assignment is absolutely correct. When the proton at C(2) is replaced by a methyl group, the cation–anion interaction at this position is switched off. Consequently the stretching modes between 3080 and 3150 cm^{-1} are completely missing in the mid-IR spectra of **2** (shaded region in Figure 1). The remaining C(4/5)–H con-

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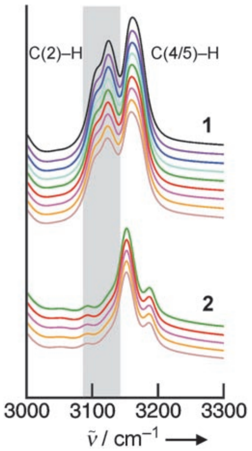

Figure 1. Mid-FTIR spectra of ionic liquids **1** and **2** as a function of temperature recorded in steps of 10 K between 303 K (top) and 343 K (bottom).

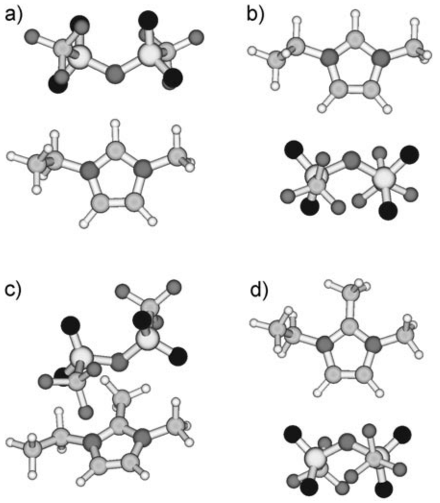

Figure 3. Ion-pair structures obtained by B3LYP/6-31+G* calculations: a) **1** (front structure: C(2)–H···A$^-$), b) **1** (back structure: C(4/5)–H···A$^-$), c) **2** (top structure), and d) **2** (back structure: C(4/5)-H···A$^-$).

Table 1: Total energies E_{B3LYP} and binding energies E_{B3LYP}^{bin} of ion-pair structures of **1** and **2**, along with the calculated energies E_{B3LYP} for the cations and anion obtained from B3LYP/6-31+G* calculations.

IL	Ion-pair structure	E_{B3LYP} [Hartree]	E_{B3LYP}^{bin} [kcal mol^{-1}]
1	C(2)–H···A$^-$(front)	−2171.957744	−74.95
1	C(4/5)–H···A$^-$(back)	−2171.946253	−67.71
2	ring A$^-$(top)	−2211.279200	−71.65
2	C(4/5)–H···A$^-$ (back)	−2211.269692	−65.68
C_2mim^+		−344.5548651	
$C_2C_1mim^+$		−383.8815957	
NTf_2^-		−1827.283431	

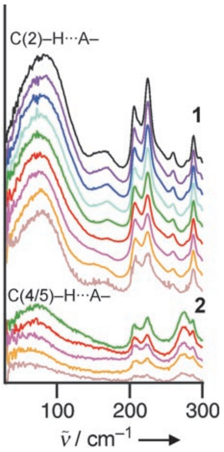

Figure 2. Far-FTIR spectra of ionic liquids **1** and **2** as a function of temperature recorded in steps of 10 K between 303 K (top) and 343 K (bottom).

tributions in **2** are slightly red-shifted compared to those in **1** because intermolecular interaction can take place only through these positions. This finding further underlines that the C(2)–H···A$^-$ hydrogen bonds are significantly stronger than those formed by C(4/5)–H; this finding has already been considered in the development of recent force fields used in molecular dynamics simulations.[16,17]

The low-frequency IR spectra of **1** and **2** also differ (Figure 2). Although IR cells with the same path length were used for the measurements, all bands of **2** are substantially less intense than those of **1** except for contributions of the cation above 250 cm^{-1}. The intramolecular bending and wagging modes of the anion NTf_2^- are affected by the lack of the important H bonds at C(2). But most importantly, the intensities of the vibrational bands which we had assigned to the bending and stretching modes of the C(2)–H···A$^-$ and C(4/5)–H···A$^-$ interactions are now significantly reduced. Additionally, the remaining low-intensity band is red-shifted from 83.5 to 79.0 cm^{-1}. This observation is in agreement with our DFT calculations on the ion-pair structures of **1** and **2** as shown in Figure 3. For both types of ion-pair structures we obtained comparable binding energies for both ILs (Table 1). Switching off the C(2)–H interaction leads to H bonds at positions C(4) and C(5). Those interactions are weaker, leading to a slight redshift of this measured intermolecular vibrational band (Figure 2, Table 2).

In **2** the overall H-bond contributions are significantly suppressed in favor of increasing Coulomb interactions. This can be seen in the far-FTIR spectra by the long tail between 100 and 200 cm^{-1}. The Coulomb interactions are stronger than the H bonds and occur at higher wavenumbers. What we see here is the following: when we replace the proton at C(2) with a methyl group, we replace a strong, localized and highly directional H bond in favor of a nonlocalized and smeared out Coulomb interaction. Thus we could shift the interaction type from short-range H bonds to long-range Coulomb interactions. This balance between hydrogen bonding and electrostatics is also reflected in the macroscopic properties of the

Table 2: Vibrational frequencies of ion-pair structures of **1** and **2** obtained from B3LYP/6-31+G* calculations.

IL	Ion-pair structure	C(*n*)–H···A$^-$)	C(2)–H	C(4)–H/C(5)–H
$[C_2mim][NTf_2]$	a) C(2)–H···A$^-$(front)	120.95	3083.8	3297.4, 3315.3
$[C_2mim][NTf_2]$	b) C(4/5)–H···A$^-$(back)	98.90	3306.4	3249.8, 3228.4
$[C_2C_1mim][NTf_2]$	c) ring···A$^-$(top)			3307.1, 3325.6
$[C_2C_1mim][NTf_2]$	d) C(4/5)–H···A$^-$ (back)	100.63		3233.7, 3252.7
C_2mim^+			3299.8	3304.9, 3316.7
$C_2C_1mim^+$				3300.6, 3317.5

two ionic liquids (Table 3). Suppressing the H bond C(2)−H···A$^-$ leads to a significant increase in the melting point from −3 °C for **1** to 20 °C for **2**.[18–23] At 20 °C **2** is more than twice as viscous as **1**; in other words, against expectation, H-bonding suppression does not reduce the viscosity. In contrast, methylation at C(2) increases the viscosity from 34 to 88 mPa s. Bonhôte et al.[18] already showed that methylation at C(5) keeps the viscosity nearly constant at 37 mPa s. This is further support for our finding that the intensity of the low-frequency vibrational band around 83.5 cm^{-1} is essentially in debt of the C(2)−-H···A$^-$ interaction. Obviously, the introduction of strong and localized directional H bonds (here C(2)−H···A$^-$) in imidazolium-based ionic liquids perturb the Coulomb network because the system then deviates from charge symmetry.[25,26] These "defects" fluidize the IL, resulting in reduced melting points and decreased viscosities. Other "defects" in the Coulomb network of imidazolium-based ILs can be introduced by alkyl chains at the C(1) and C(3) positions of the imidazolium cation (see Figure 4). Replacing the methyl group by an ethyl group at the C(1) position in [C$_1$mim][NTf$_2$] also introduces disorder into the Coulomb field, leading to lower melting points, viscosities, and enthalpies of vaporization.[16–18,20,24,27]

Table 3: Melting points T_m and dynamic viscosities $\eta_{20^\circ C}$ of imidazolium-based ILs from Refs. [18–23].

Ionic liquid	T_m [°C]	$\eta_{20^\circ C}$ [mPa s]
1	−3,[18] −17,[20] −18[19]	34,[18] 36,[22] 39[20]
2	20,[18] 27[21,23]	88[18]
[1-Et-3,5-Me$_2$-Im][NTf$_2$]	−3[18]	37[18]

On going from **2** to **1**, the melting points are reduced and the viscosities are decreased. This has been known for more than ten years from the work of Bonhôte et al.[18] But there was little discussion of the origin of changing macroscopic properties by methylation at the C(2) position. Now we have a reliable explanation for the property changes. We have shown that the properties of imidazolium-based ILs can be tuned by adjusting the ratio between H-bond energies and Coulomb interactions. These interactions are evident in the far-FTIR spectra, which show very pronounced, localized H-bond bands at 83.5 cm^{-1} for **1** and increasing, well-distributed Coulomb interactions from 100 to 200 cm^{-1} for **2**. Tuning thermodynamical and transport properties of ILs is of great importance for their application in science and technology. Suggestions for new synthesis strategies are currently under development in our laboratory.

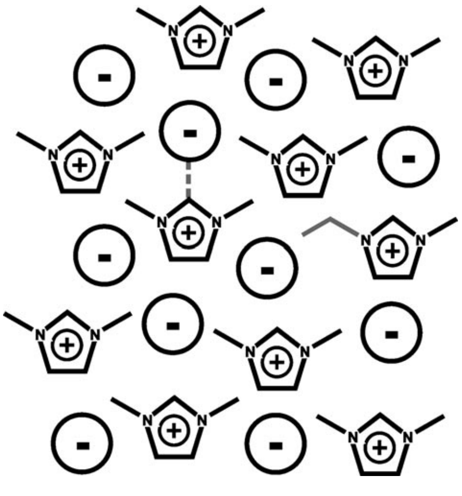

Figure 4. Representation of an imidazolium-based ionic liquid. Replacement of a methyl group at C(1) with an ethyl group (solid gray line) and strong and highly directional H bonds at the C(2) position (dotted gray line) both introduce disorder into the ionic network, leading to reduced melting points and decreased viscosities.[18–23]

Experimental Section

The ionic liquids were purchased from Iolitec GmbH (Denzlingen, Germany) with a stated purity of > 98 %. All substances were dried in vacuum ($p = 8\times10^{-3}$ mbar) for approximately 36 h. The water content was then determined by Karl Fischer titration and was found to be 113 ppm in 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (**1**) and 57 ppm in 1-ethyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide (**2**). Further purification was not carried out.

The FTIR measurements were performed with a Bruker Vertex 70 FTIR spectrometer. The instrument was equipped with an extension for measurements in the far-infrared region. This equipment consisted of a multilayer Mylar beam splitter, a room-temperature DLATGS detector with preamplifier, and polyethylene (PE) windows for the internal optical path. The accessible spectral region for this configuration lies between 30 and 680 cm^{-1}.

Ab initio calculations were performed at the B3LYP level with the Gaussian 98 program.[28] using the 6-31 + G* basis set. The total energies, the binding energies, and important intra- and intermolecular vibrational frequencies of ion-pair structures for **1** and **2** are given in Tables 1 and 2 (see also the Supporting Information).

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