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Structure, Conformations, Vibrations, and Ideal-Gas Properties of 1-Alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide Ionic Pairs and Constituent Ions

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Energies, geometries, and frequencies of normal vibrations have been calculated by quantum-chemical methods for different conformers of a bis(trifluoromethylsulfonyl)imide anion (NTf$_2^-$), 1-alkyl-3-methylimidazolium cations ([C$_n$mim]$^+$, n = 2, 4, 6, 8), and [C$_n$mim]NTf$_2$ ionic pairs. The assignment of frequencies for NTf$_2^-$, [C$_2$mim]$^+$, and [C$_4$mim]$^+$ in the vibrational spectra of ionic liquids have been performed. Thermodynamic properties of [C$_n$mim]NTf$_2$, [C$_n$mim]$^+$, and NTf$_2^-$ in the gas state have been calculated by the statistical thermodynamic methods. The resulting entropies are in satisfactory agreement with the values obtained from the experimental data previously reported in literature.

Introduction

Room-temperature ionic liquids (ILs) attract the interest of researchers because of their possible applications as green solvents in various areas of science and technology (for example, see ref 1). Among the compounds of this class, bis(trifluoromethylsolfonyl)imide (NTf$_2$) ILs possessing high thermal stability should be noted. 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imides ([C$_n$mim]NTf$_2$) are the first compounds of this class for which the saturated vapor pressure has been measured.[2,3] The measurements were performed by the Knudsen method. Later, P_{sat} of [C$_2$mim]NTf$_2$ was determined by the transpiration method.[4] The vaporization enthalpies of these compounds have also been found in a drop calorimeter[5] and by the line-of-sight mass spectrometry.[6]

Thermodynamic properties of [C$_n$mim]NTf$_2$ (n = 2, 4, 6, 8) have been studied by adiabatic calorimetry in refs 7–10 Additivity in their heat capacities and entropies has been reported.[7] If one combines the results of the above-mentioned studies, the entropy in the gas state for [C$_n$mim]NTf$_2$ can be found at T close to 470 K. The entropy calculations from the experimental data are only possible over the temperature range >100 K.

The thermodynamic properties of gaseous [C$_n$mim]NTf$_2$ including the entropy can be found in a much wider range of temperatures by the statistical thermodynamic methods using the molecular and spectral data. These calculations would allow one to check the idea that IL vapor consists of ionic pairs at pressures below 1 Pa, to select the preferable set of the experimental $\Delta_{vap}H$ values[2,5,6] and to develop the procedures for the statistical thermodynamic calculations of such complicated objects as ionic pairs of ILs. Similar calculations have been performed for [C$_4$mim]PF$_6$[11] and [C$_4$mim]N(CN)$_2$.[4]

In this work, the molecular geometries, the frequencies of normal vibrations, and the relative energies of conformers of the [C$_n$mim]NTf$_2$ ionic pairs as well as the [C$_n$mim]$^+$ and NTf$_2^-$ ions have been found. The thermodynamic properties of these compounds in a state of ideal gas have been found using the obtained data. The trends in thermodynamic properties in the [C$_n$mim]NTf$_2$ and [C$_n$mim]$^+$ homologous series have been established. Thermodynamic analysis of the dissociation process for the [C$_n$mim]NTf$_2$ ionic pairs have been performed.

When a thermodynamic property of ideal gas (for example, entropy S_g) is calculated, it is usually represented as a sum of translational $S_{trans}(T, P)$, rotational $S_{rot}(T)$, vibrational $S_{vib}(T)$, and conformational $S_{conf}(T)$ contributions

$$S_g = S_{trans} + S_{rot} + S_{vib} + S_{conf} \tag{1}$$

Normally, the rotational and vibrational contributions are calculated for one or several the most stable conformers (configurations) of the gas species. To calculate the thermodynamic properties, the following procedures have been applied:

(a) identification of possible conformers (configurations) of the species, determination of their geometries, and relative energies;

(b) obtaining the complete set of frequencies of normal modes;

(c) calculation of the thermodynamic properties.

The results reported in this paper are described according to this scheme.

Experimental Section

The samples of [C$_2$mim]NTf$_2$, [C$_4$mim]NTf$_2$, and [C$_4$mim]PF$_6$ used in this study were described earlier.[7,9,11] Purity of the samples was determined by adiabatic calorimetry to be 98.4, 98.5, and 99.5 mol %, respectively. A commercial sample of [BuMe$_3$N]NTf$_2$ was vacuum pumped at $T \leq 393$ K for a few

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TABLE 1: The k' Values for Different Basis Sets Used in the B3LYP Calculations of Vibrational Frequencies

basis set	$[C_2mim]^+$	NTf_2^-
6-31G(d)	1.001 ± 0.014	0.988 ± 0.014
6-31+G(d,p)	0.998 ± 0.010	0.967 ± 0.007
6-31+G(2df,p)	0.999 ± 0.002	0.984 ± 0.004
6-311+G(d,p)	0.996 ± 0.002	0.965 ± 0.009
6-311+G(3df,2p)	1.001 ± 0.002	1.000

days. Its purity was 99.7 mol % as determined in an adiabatic calorimeter. Commercial samples of 1-methylimidazole and 1-ethylimidazole of >98% stated purity were distilled over CaH_2 before use. Since all the studied substances are hygroscopic, special precautions were adopted to avoid absorbance of water by the samples during spectral investigation.

IR spectra of the compounds were recorded by a Bruker Vertex 70 spectrometer at 1 or 2 cm^{-1} resolution and accumulation of 32 spectra. The liquid-state spectra at $T = 290$ K in a wavenumber range of (400 to 4000) cm^{-1} were recorded in KBr pellets. In the (200 to 600) cm^{-1} range, the spectra of the liquid thin films placed between polyethylene windows were recorded. To get the spectrum of the $[C_4mim]NTf_2$ crystal in a wavenumber range of (600 to 4000) cm^{-1}, the liquid thin film between KBr windows was placed into a Specac Variable Temperature Cell equipped by NaCl windows. Liquid nitrogen was used as a cooling agent.

The Raman spectrum of liquid $[C_4mim]PF_6$ in the range of (200 to 4000) cm^{-1} was recorded by a LabRam Raman Microscope (HORIBA Jobin Yvon, Inc.) at $T = 290$ K.

Calculations

Quantum-chemical calculations were performed using Gaussian 2003 software.[12]

The main contribution to the ideal-gas thermodynamic properties of the studied compounds is due to intramolecular vibrations. Therefore, their accurate calculation is very important both for the ions and the ionic pairs. As demonstrated in ref 13, the DFT methods and particularly those with the B3LYP[14−16] functional provide better or similar results in calculation of vibrational spectra of molecules compared to the conventional ab initio methods. Additionally, the DFT methods require significantly less time.

The calculations with the large basis sets for the ionic pairs are very time-consuming, and that is why it is necessary to determine the satisfactory basis. To do that, the vibrational frequencies were calculated with various Pople-type basis sets using the B3LYP functional. The scaling factors are different for various theory levels. However, if the lower basis X makes it possible to reproduce the results obtained with the largest basis (6-311++G(3df,3pd) in this case), then the ratio $k' = w(B3LYP/basis\ X)/w(B3LYP/6-311++G(3df,3pd))$ will be constant. These ratios were found for a series of the basis sets (Table 1). The calculations were performed for the most stable trans-conformer of the anion and the nonplanar conformer of the $[C_2mim]^+$ cation. The uncertainties are the standard deviations of the mean multiplied by a factor of 2.

As follows from Table 1, the least deviation of k' from the constant value for the anion is observed for the B3LYP/6-31+G(2df,p) method. Addition of the polarization and diffusion functions is important for correct calculation of the anion's frequencies, while extension of the double split valence basis to the triple split valence basis is not necessary. The results for the cation using B3LYP/6-31+G(2df,p) and B3LYP/6-311+G(d,p) are comparable. Therefore, the B3LYP/6-

31+G(2df,p) was chosen for the calculation of frequencies of normal modes of the ions and the ionic pairs in this work.

The potential energy curves at the internal rotation of tops were approximated by the functions

$$V(\phi) = V_0 + V_1 \cos \phi + V_2 \cos 2\phi + V_3 \cos 3\phi \quad (2)$$

The reduced moment of inertia of the tops I_r were calculated according to ref 17 in a single-top approximation.

The IUPAC recommended atomic masses were used.[18] The basic procedures of the statistical thermodynamic calculations are described in ref 19.

Results

NTf_2^- Anion. Internal rotation of the CF_3SO_2- and CF_3- tops occurs in the NTf_2 anion. Two conformers are formed in the former case, cis and trans (Figure 1). In the cis conformer, both the CF^{3-} groups lie on the same side with respect to the SNS plane, and in the trans one the groups lie on the opposite sides. The value of $\Delta H_{348}(trans-cis) = 3.5 \pm 0.1$ kJ·mol^{-1} was found from the temperature dependence of Raman spectrum of liquid $[C_2mim]NTf_2$ in the range (380 to 440) cm^{-1},[20] and the value of $\Delta H_{328}(trans-cis) = 4.5 \pm 0.2$ kJ·mol^{-1} from its temperature dependence in a wavenumber range of (260 to 360) cm^{-1}.[21]

The potential energy surface for combined rotation of the tops CF_3SO_2- tops was evaluated.[22,23] According to these papers, coupling of the tops results in rather low (4−8 kJ·mol^{-1}) barriers to their internal rotation. The interconversion between the conformers through the CSSC dihedral value of 0 is not realized due to very high barrier on this way.

High-level quantum-chemical calculations (B3LYP/6-311+G(3df)) gave $\Delta H_0(trans-cis) = 3.2$ kJ·mol^{-1}.[20] The same value $\Delta H_0(trans-cis) = 3.2$ kJ·mol^{-1} was obtained in this work. The value of $\Delta H_{338}(trans-cis) = 4.0$ kJ·mol^{-1} obtained by averaging of the experimental values was accepted in the calculations of the thermodynamic properties. Additionally, chirality of the conformers was taken into account. A contribution to the thermodynamic functions related to the CF_3SO_2- top internal rotation was evaluated as the vibrational one plus the correction for the existence of the equilibrium mixture of the conformers.

According to the quantum-chemical calculations, the height of the barrier to internal rotation of the CF_3- top is $V = 9.4$ kJ·mol^{-1}. The corresponding contributions were found from the energy levels of a hindered rotator with the parameters presented in Table 2. The wavenumbers of the CF_3- top torsional vibrations (46 and 50 cm^{-1} for the trans conformer, 41 and 51 cm^{-1} for the cis conformer) were excluded from the complete set of frequencies of normal vibrations.

The products of principal moments of inertia of the conformers (Table 3) were calculated from the geometries obtained in quantum-chemical calculations.

The vibrational spectra of the NTf_2^- anion in ILs have been studied,[20,21,24−28] and its spectra in various solvents have been analyzed.[29] It was demonstrated that the NTf_2^- conformers can be identified by IR and Raman spectroscopies both in the liquid[20,29] and crystal[21,26−28] states.

The complete set of frequencies of normal vibrations of the conformers (Table 4) was compiled based on the experimental IR spectra of $[C_2mim]NTf_2$, $[BuMe_3N]NTf_2$ obtained in this work (Figures 2 and 3), the results of the DFT calculations, and the literature data mentioned above. A scaling factor k is equal to the ratio of the experimental wavenumber of a vibration
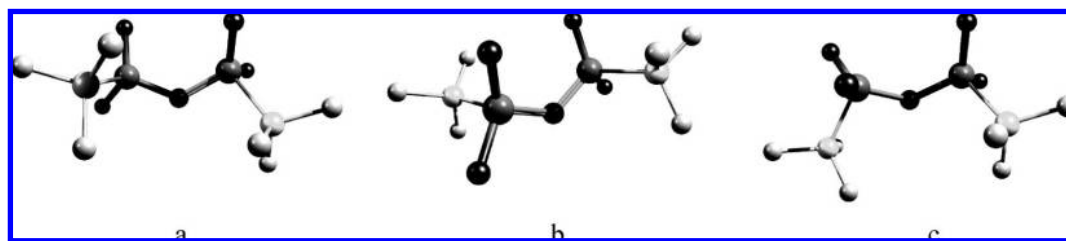
Figure 1. Conformers of the NTf$_2$ anion, (a) cis; (b) trans; (c) cis*.

TABLE 2: Parameters of Internal Rotation for the Studied Species

top	σ_r	$I_r \cdot 10^{47}$ kg$\cdot$m^{2a}	$I_r \cdot 10^{47}$ kg$\cdot$m^{2b}	V_0 kJ$\cdot$mol^{-1}	V_1 kJ$\cdot$mol^{-1}	V_2 kJ$\cdot$mol^{-1}	V_3 kJ$\cdot$mol^{-1}
[C$_2$mim]NTf$_2$							
CF$_3$-	3	129	144	4.70	0	0	4.70
Et-	1	33.0	58.4	2.11	−0.18	1.46	−1.21
Me-(C)	3	5.17	5.26	6.35	0	0	6.35
Me-(N)	3	5.16		0.96	0	0	0.96
Me-(N)	3		5.34	2.2	0	0	2.2
NTf$_2$	2		543	5.5	0	5.5	
[C$_4$mim]NTf$_2$							
CF$_3$-	3	129	145	4.70	0	0	4.70
Bu-	1			2.20	−1.52	2.06	0
Pr-	1			8.76	−3.59	2.02	−7.19
Et-	1			9.39	−4.95	2.22	−6.66
Me-(C)	3	5.16	5.24	5.98	0	0	5.98
Me-(N)	3	5.21		0.95	0	0	0.95
Me-(N)	3		5.34	2.2	0	0	2.2
NTf$_2$	2		1092	5.5	0	5.5	
[C$_6$mim]NTf$_2$							
CF$_3$-	3	129	145	4.70	0	0	4.70
Hex-	1			2.13	−1.51	1.99	0
Pen-	1			8.73	−3.42	1.98	−7.28
Bu-	1			9.02	−4.98	2.36	−6.40
Pr-	1			9.47	−5.08	2.22	−6.61
Et-	1			9.67	−4.92	2.14	−6.89
Me-(C)	3	5.17	5.23	5.98	0	0	5.98
Me-(N)	3	5.24		0.95	0	0	0.95
Me-(N)	3		5.34	2.2	0	0	2.2
NTf$_2$	2		1642	5.5	0	5.5	
[C$_8$mim]NTf$_2$							
CF$_3$-	3	129	145	4.70	0	0	4.70
Me-(C)	3	5.18	5.23	5.98	0	0	5.98
Me-(N)	3	5.25		0.95	0	0	0.95
Me-(N)	3		5.34	2.2	0	0	2.2
NTf$_2$	2		2059	5.5	0	5.5	

^{a} In the most stable conformer of the ion. ^{b} In the ionic pair. $V = V_0 + V_1 \cos \varphi + V_2 \cos 2\varphi + V_3 \cos 3\varphi$.

TABLE 3: Products of Principal Moments of Inertia (B3LYP/6-31+G(2df,p)) for the Species Used in Statistical Thermodynamic Calculations

species	σ	$I_A I_B I_C \times 10^{133}$/kg$^3 \cdot$m^6
cis NTf$_2^-$	1	57.7
trans NTf$_2^-$	2	60.2
[C$_2$mim]$^+$	1	0.793
[C$_4$mim]$^+$	1	5.82
[C$_6$mim]$^+$	1	28.6
[C$_8$mim]$^+$	1	103
[C$_2$mim]NTf$_2$	1	948
[C$_4$mim]NTf$_2$	1	1635
[C$_6$mim]NTf$_2$	1	3319
[C$_8$mim]NTf$_2$	1	7645

w_{exp} to the calculated one w_{calc}. As follows from Figure 4, k depends on w_{calc}. This dependence was approximated by the equations

$$w_{exp} = w_{calc}(1.035 - 1.48 \times 10^{-5} v_{calc}) \text{ above } 400 \text{ cm}^{-1} \quad (3)$$

$$w_{exp} = w_{calc}(1.153 - 3.07 \times 10^{-4} v_{calc}) \text{ below } 400 \text{ cm}^{-1} \quad (4)$$

The equations were obtained by the least-squares method from w_{exp} and w_{calc} presented in Table 4. The wavenumbers of the vibrations not identified in the experimental spectra were calculated from the w_{calc} values using eqs 3 and 4. These values are printed in italics in Table 4.

The thermodynamic properties of the NTf$_2^-$ anion in the ideal-gas state are presented in Table 5.

[C$_n$mim]$^+$ Cations. Internal rotation of the alkyl tops C$_n$H$_{2n+1}$ and the CH$_3$−(N) top is possible in the [C$_n$mim]$^+$ cations.

The barriers to rotation of the methyl tops in [C$_2$mim]$^+$ and [C$_4$mim]$^+$ are little changed when going from [C$_2$mim]$^+$ to [C$_4$mim]$^+$. Similar barriers in [C$_6$mim]$^+$ and [C$_8$mim]$^+$ were assumed to be equal to those in [C$_4$mim]$^+$. The potential functions of the internal rotation of these tops and their reduced moments of inertia are presented in Table 2. The corresponding torsional frequencies specified in Tables 6 and 7 and Supporting Information S4 and S5 were excluded from the complete frequencies' set.

TABLE 4: Vibrational Wavenumbers of the NTf$_2^-$ Anion

$w_{exp}{}^a$/cm^{-1}	w_{calc}/cm^{-1} cis	IR intensity/km·mol^{-1}	w_{calc}/cm^{-1} trans	IR intensity/km·mol^{-1}	selected w/cm^{-1} cis	trans	comment
	12.6	0.3	23.2	1.4	*15*	*27*	torsion CF$_3$SO$_2$-
	36.1	0.0	40.7	0.3	*41*	*46*	torsion CF$_3$-
	44.3	0.1	44.0	1.7	*51*	*50*	torsion CF$_3$-
	65.8	0.1	47.4	0.0	*75*	*54*	torsion CF$_3$SO$_2$-
	110	0.0	106	0.0	122	122	b, c
	151	1.4	151	0.1	170	170	b, c
	174	0.1			*192*		
208 m^f	191	0.9	188	1.7	208	208	this work,b
	193	1.2	194	0.3	208	208	this work,b
225 m^f			214	8.6		225	this work,c
			258	0.1		276	d
	261	0.2			279		d
288 m^f	267	1.2			288		this work,b,d,e
			284	0.5		297	b, d
	295	0.1			310		d
			296	1.2		*314*	
			297	0.0		314	d
	309	0.2			326		b, d, e
	316	1.2			332		d
			326	0.1		341	b, d, e
	336	0.5			352		d, e
362 m^f			340	4.1		362	
396 sh^f			380	4.9		396	this work,c,e
407 m	389	5.6			407		this work,c,e
			395	6.6		413	e
437 w	426	7.1			437		
510 sh	497	97.0			510		
515 s			502	70.2		515	
534 sh	517	7.1	522	0.0	534	534	this work,e
551 sh	536	3.0	538	0.7	551	551	this work,c,e
	547	2.4	546	0.8	560	560	e
571 vs	559	85.6	558	57.7	571	571	
	560	7.8			571		
			576	0.0		592	c
601 s	585	141.1			601		
619 vs			605	349.6		619	
			606	4.8		626	c, e
652 s	637	107.1			652		
741 s	719	33.8	720	16.3	741	741	
762 m	746	3.2	746	5.2	762	762	
791 s	763	33.7	764	12.0	791	791	
1059 vs	1046	235.0	1040	578.9	1059	1059	
1140 s	1116	180.5	1116	1.1	1140	1140	
	1122	53.8	1120	22.5	1140	1140	
	1154	319.8	1151	176.8	*1175*	*1171*	
	1159	119.1	1159	79.9	*1179*	*1180*	
	1165	271.8	1163	164.8	*1186*	*1184*	
1198 vs	1173	864.1	1178	827.5	1198	1198	
1228 sh	1206	291.8	1201	424.1	1228	1228	
	1216	11.3	1216	12.7	1244	1244	c, e
1333 sh	1320	178.0	1322	70.9	1333	1333	
1354 vs	1337	390.9	1343	469.3	1354	1354	

^{a} From IR spectrum of [C$_2$mim]NTf$_2$. ^{b} Reference 22. ^{c} Reference 27. ^{d} Reference 21. ^{e} Reference 20. ^{f} From far IR spectrum of [C$_2$mim]NTf$_2$.

The Et- top rotation in [C$_2$mim]$^+$ results in formation of two chiral nonplanar conformers of C_1 symmetry and one planar conformer of C_s symmetry (Figure 5). The enthalpy difference between these conformers was found from the temperature dependence of Raman spectrum of liquid [C$_2$mim]NTf$_2$ to be ΔH_{338}(npl-pl) = 2.0 ± 0.1 kJ·mol^{-1}.[30]

The potential energy curve for the Et- top was calculated by the quantum-chemical methods.[30] The barriers to internal rotation of the Et- top and the relative energies of the conformers calculated in this work are close to those in ref 30. The parameters of the potential function for the Et-top and its reduced moment of inertia used in the calculation of the

thermodynamic functions are presented in Table 2. The torsional frequency 51.8 cm^{-1} (Table 6) was excluded from the complete set of frequencies.

Unlike [C$_2$mim]$^+$, the planar conformer of [C$_4$mim]$^+$ is a transition state. Therefore, two equal minima corresponding to a chiral pair of conformers (conformer 5) will be observed on the potential energy curve for the Bu- top. Internal rotation of the Pr- and Et- tops results in formation of $3 \times 3 = 9$ conformers are demonstrated in Figure 6, and the relative energies are presented in Supporting Information Table S1. Numbering of the conformers follows.[31] At present, only tt- (conformer 5) and gt- conformers (conformers 1 and 8) of the [C$_4$mim]$^+$ cation
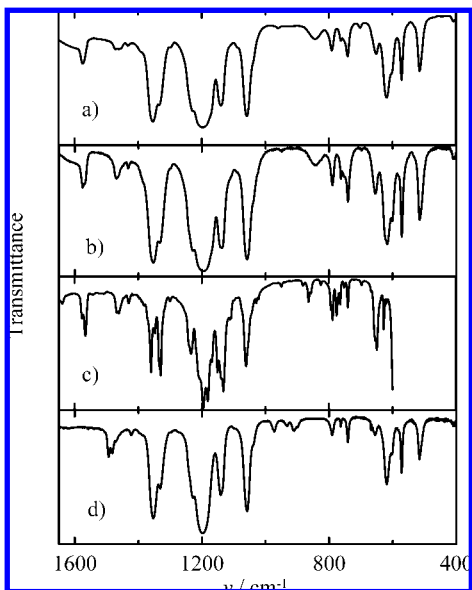
Figure 2. IR spectra of NT_2-containing ionic liquids in the wavenumber range of (1650 to 400) cm^{-1}. (a) liquid $[C_2mim]NTf_2$; (b) liquid $[C_4mim]NTf_2$; (c) crystalline $[C_4mim]NTf_2$ at $T = 243$ K; (d) liquid $[BuMe_3N]NTf_2$.
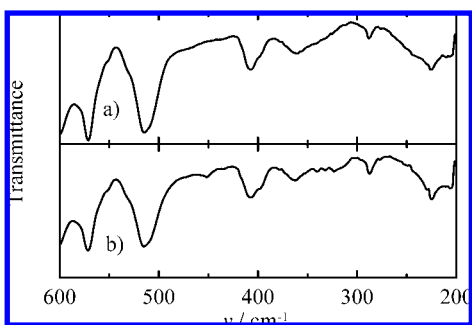
Figure 3. IR spectra of NT_2-containing ionic liquids in the wavenumber range of (600 to 200) cm^{-1}. (a) liquid $[C_2mim]NTf_2$; (b) liquid $[BuMe_3N]NTf_2$.
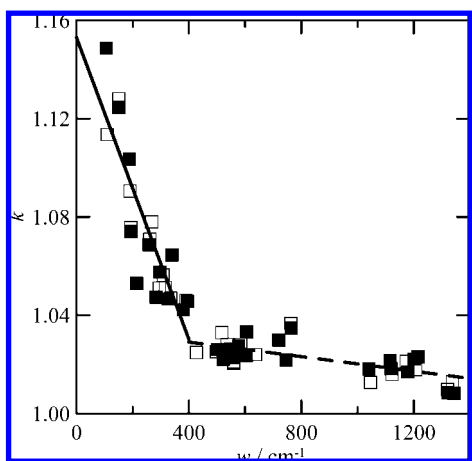

Figure 4. Dependence of a scaling factor on the calculated wavenumbers for the NTf_2^- anion. □, cis conformer; ■, trans conformer; —, eq 3; ---, eq 4.

have been experimentally found.[32−35] The parameters of potential functions (2) and the symmetry numbers for all the tops of $[C_4mim]^+$ are presented in Table 2.

When one calculates the contribution of the internal rotation for the compounds with long alkyl chains, it is unknown how

strong the coupling between the tops will be and how to calculate I_r in this case. Therefore, the procedure is required, which will allow one to calculate these contributions without explicit use of I_r.

The energy levels were calculated for a top with the potential function of internal rotation equal to $V(\varphi)$ of the Et- top in $[C_4mim]^+$ at $I_r = (20$ to $200) \times 10^{-47}$ kg·m². The selected range of I_r is typical for the alkyl tops. From the resulted energy levels, the contribution of internal rotation to the heat capacity for this top C_{top} can be found. On the other hand, if one knows the energy of the lowest vibrational transition for this system, the vibrational contribution to the heat capacity $C_{h.o.}$ can be calculated in an approximation of the harmonic oscillator with $v_0 = \Delta E/h$. It was found that at a given temperature the ($C_{top} - C_{h.o.}$) difference remains stable within ± 0.05 J·K^{-1}·mol^{-1} and does not depend on the reduced moment of inertia of the top. The temperature dependence of ($C_{top} - C_{h.o.}$) in the temperature range of $T = (100$ to $1000)$ K was approximated by the equation

$$(C_{top} - C_{h.o.})/J \cdot K^{-1} \cdot mol^{-1} = a + b(K/T) + c(K/T)^2 + d(K/T)^3 + e(K/T)^4 \quad (5)$$

where $a = -5.87$, $b = 45.19 \times 10^{-2}$, $c = -31.40 \times 10^{-4}$, $d = 27.99 \times 10^{-6}$, and $e = 24.28 \times 10^{-8}$. Similar trends are observed for the other thermodynamic functions: entropy and enthalpy. Taking into account that ($S_{top} - S_{h.o.}$) = 1.3 ± 0.1 J·K^{-1}·mol^{-1} and ($H_{top} - H_{h.o.}$) = 105 ± 4 J·mol^{-1} at $T = 100$ K, the following equations were derived:

$$(S_{top} - S_{h.o.})/J \cdot K^{-1} mol^{-1} = f + a \ln(T/100 \text{ K}) - b(1 \text{ K}/T - 1/100) - 1/2c((1 \text{ K}/T)^2 - (1/100)^2) - 1/3d((1 \text{ K}/T)^3 - (1/100)^3) - 1/4e((1 \text{ K}/T)^4 - (1/100)^4) \quad (6)$$

$$(H_{top} - H_{h.o.})/J \cdot mol^{-1} = g + a((T/K) - 100) + b \ln(T/100 \text{ K}) - c(1 \text{ K}/T - 1/100) - 1/2d((1 \text{ K}/T)^2 - (1/100)^2) - 1/3e((1 \text{ K}/T)^3 - (1/100)^3) \quad (7)$$

where $f = 1.3$, and $g = 105$.

The resulting coefficients of eqs 5−7 for the alkyl tops in $[C_4mim]^+$ and $[C_6mim]^+$ are presented in Table 8.

The contributions of internal rotation of the alkyl tops for the $[C_nmim]^+$ cations ($n = 4, 6, 8$) were found as a sum of the vibrational contributions of the corresponding frequencies of torsional vibrations (Tables 6 and 7 and Supporting Information S4 and S5) and corrections from eqs 5−7. In calculation of the thermodynamic properties for $[C_8mim]^+$, it was assumed that the potential function of the C_nH_{2n+1}- top is equal to that of the $C_{n-2}H_{2(n-2)+1}$- top in $[C_6mim]^+$. The potential functions of the Et- and Pr- tops in $[C_8mim]^+$ were assumed to be equal to the potential function of the Et- top in $[C_6mim]^+$.

The products of principal moments of inertia for the most stable $[C_nmim]^+$ conformers (Table 3) were found from the geometries obtained in quantum-chemical calculations.

The experimental investigation of the vibrational spectra for the $[C_2mim]^+$ containing ILs have been performed.[21,28,30,36−38] The observed bands correspond to the nonplanar conformer. The only frequency assigned to the planar conformer is 448 cm^{-1}.[30]

The vibrational spectra of the $[C_4mim]^+$ containing ILs have been studied.[38−41] In ref 39, it was demonstrated that the gt-

TABLE 5: Thermodynamic Properties of the Studied Species in the Ideal-Gas State[a]

species	$S°/J \cdot K^{-1} \cdot mol^{-1}$	$C_p/J \cdot K^{-1} \cdot mol^{-1}$	$(H°_T - H°_0)/T/J \cdot K^{-1} \cdot mol^{-1}$	$-(G°_T - H°_0)/T/J \cdot K^{-1} \cdot mol^{-1}$
$T = 298$ K				
NTf_2^-	527.8	221.4	139.0	388.8
$[C_2mim]^+$	386.4	131.7	81.8	304.6
$[C_4mim]^+$	465.3	181.5	113.9	67.6
$[C_6mim]^+$	541.5	232.5	146.2	86.3
$[C_8mim]^+$	617.3	284.0	178.7	105.4
$[C_2mim]NTf_2$	777.9	372.7	234.0	543.8
$[C_4mim]NTf_2$	853.8	422.2	266.0	156.2
$[C_6mim]NTf_2$	926.2	472.9	298.0	175.0
$[C_8mim]NTf_2$	1014	524.9	332.0	192.9
$T = 470$ K				
NTf_2^-	639.8	270.1	178.8	461.0
$[C_2mim]^+$	460.8	199.0	112.6	348.2
$[C_4mim]^+$	566.2	266.7	154.5	112.3
$[C_6mim]^+$	669.1	334.9	196.7	138.2
$[C_8mim]^+$	772.0	403.5	239.2	164.3
$[C_2mim]NTf_2$	972.9	487.0	306.7	666.2
$[C_4mim]NTf_2$	1075	554.5	348.4	206.1
$[C_6mim]NTf_2$	1174	622.3	390.3	232.0
$[C_8mim]NTf_2$	1289	691.3	434.0	257.3

[a] Ideal-gas thermodynamic properties in the range $100 - 1000$ K for the studied species are presented in Supporting Information.

and tt-conformers of $[C_4mim]^+$ can be distinguished in the Raman spectra. The characteristic wavenumbers in the Raman spectra were 625 and 730 cm^{-1} for the tt-conformer and 500, 603, and 701 cm^{-1} for the gt-conformer.

The wavenumbers of the C—H stretching vibrations in the imidazolium ring can be significantly changed (up to 100 cm^{-1}) subject to fact whether this hydrogen atom forms an H-bond with the anion or not. On the other hand, it can be expected that the C—H stretching frequencies for the alkyl substituents will not be very different in ILs, 1-methylimidazole, and 1-ethylimidazole.

The calculated and experimental wavenumbers for the C—H stretching vibrations in 1-methylimidazole, 1-ethylimidazole, $[C_2mim]NTf_2$, and $[C_4mim]NTf_2$. From these data, the scaling factor for this type of vibrations $k = 0.957 \pm 0.003$ was found for the imidazols. This factor remains unchanged for the C—H vibrations in the imidazole system and in the alkyl group.

Unlike the corresponding bands observed in the IR spectra, the calculated wavenumbers of the alkyl C—H stretching vibrations are different in alkylimidazoles and $[C_nmim]^+$ (Supporting Information Table S3). It means that the separate scaling factors should be used for the molecules and the ions. The scaling factor of $k = 0.949 \pm 0.001$ was obtained for the alkyl C—H vibrational frequencies in $[C_nmim]^+$. Its application to the imidazolium C—H vibrational frequencies resulted in the wavenumbers of 3115, 3116, and 3132 cm^{-1}, which are close to the observed band at 3124 cm^{-1}. It is important to note that the bands at $w > 3140$ cm^{-1} corresponding to v(C—H) are absent in the IR spectra of imidazoles, but not of $[C_nmim]NTf_2$. These bands are due to vibrations of the H-bonded C—H bonds. The scaling factor with respect to v(C—H) of the imidazolium system was found to be $k = 0.950 \pm 0.001$.

The complete set of the frequencies of normal vibrations for the nonplanar $[C_2mim]^+$ conformer (Table 6) was compiled using the experimental IR spectra of $[C_2mim]NTf_2$ and $[C_2mim]Br$ obtained in this work, vibrational spectra of $[C_2mim]NTf_2$,[21,30] $[C_2mim]Br$,[21] $[C_2mim]AlCl_4$,[36] $[C_2mim]PF_6$,[37,38] and $[C_2mim]BF_4$,[38] and the results of quantum-chemical calculations. In the solution of similar problem for the most stable $[C_4mim]^+$ conformer (Table 7), the experimental IR spectra of $[C_4mim]NTf_2$, IR- and Raman spectra of $[C_4mim]PF_6$ obtained

in this work (Figure 7), and the vibrational spectra of $[C_4mim]BF_4$[38] and $[C_4mim]Cl$[39] were used.

The dependence of the k scaling factor on w_{calc} for $[C_2mim]^+$ and $[C_4mim]^+$ is presented in Figure 8. The k values for the vibrations with the calculated wavenumbers of 637 and 664 cm^{-1} for $[C_2mim]^+$ and 637 and 668 cm^{-1} for $[C_4mim]^+$ are significantly lower than those for the other vibrations with the close wavenumbers. The noted vibrations are out-of-plane vibrations of the imidazolium ring. The cause of this difference is unknown.

The following equations for the scaling factors were obtained $[C_2mim]^+$ and $[C_4mim]^+$:

$$w_{exp} = 0.950w_{calc} \text{ above } 1600 \text{ cm}^{-1} \quad (8)$$

$$w_{exp} = w_{calc}(1.005 - 1.43 \times 10^{-5}w_{calc}) \text{ for } 415 \text{ cm}^{-1} <$$
$$w_{calc} < 1600 \text{ cm}^{-1}(9)$$

$$w_{exp} = w_{calc}(1.089 - 2.17 \times 10^{-4}w_{calc}) \text{ for } w_{calc} <$$
$$415 \text{ cm}^{-1}(10)$$

The wavenumbers w_{exp} of the vibrations not observed in the experimental spectra were calculated from the w_{calc} values using eqs 8–10. These wavenumbers are printed in italics in Tables 6 and 7. Equations 8–10 were used for calculation of the vibrational wavenumbers of $[C_6mim]^+$ (Supporting Information Table S4) and $[C_8mim]^+$ (Supporting Information Table S5).

The thermodynamic properties of the $[C_nmim]^+$ cations in the ideal-gas state are presented in Table 5.

$[C_nmim]NTf_2$ Ionic Pairs. In the most stable configuration of the $[C_nmim]X$ ionic pairs (X is a halide ion, PF_6^-, BF_4^-, $CF_3SO_3^-$), the anion is situated on the side of H—C(2) group above the imidazolium ring.[31,38,40,42] It is also known that the stability of such a structure with respect to other configurations of the ionic pair increases with the anion size.[31] Concerning $[C_nmim]NTf_2$, one may expect that in the most stable configurations, the anion will be near H—C(2) and the total number of

TABLE 6: Vibrational Wavenumbers for the Nonplanar Conformer of the [C₂mim]⁺ Cation

$w_{exp}{}^a$/cm⁻¹	w_{calc}/cm⁻¹	IR intensity/ km·mol⁻¹	selected w/cm⁻¹	comment
	48	0.3	52	tEt
	78.8	0.1	84	tMe(N)
	136	1.2	144	
	208	0.2	217	tMe(C)
	235	1.9	241	b
	291	0.2	297	b
	379	0.3	381	c
	424	0.4	430	b
	593	2.1	600	b
623 d	637	9.7	623	
652 s	664	15.3	652	
702 vw	700	9.3	702	
	760	22.9	748	c
803	799	1.5	803	b, e
843 m	841	42.6	843	
	884	0.0	872	b
961 vw	961	3.1	960	
	1037	0.3	1025	b
	1043	0.9	1033	b
1089 w	1099	4.8	1089	
	1101	1.4	1089	
1109 w	1128	6.8	1109	
	1135	4.3	1122	b
	1153	0.0	1140	
	1180	103.9	1173	b
	1268	0.1	1254	b
1298 sh	1312	0.4	1298	
	1344	10.1	1336	b
1360 d	1382	13.3	1360	
1388 sh	1410	3.6	1388	
	1419	6.2	1388	
	1436	1.0	1411	b
	1458	10.2	1425	b
1460 m	1476	15.1	1460	
	1482	7.4	1460	
	1485	15.6	1460	
1471 m	1500	14.0	1471	
	1503	10.5	1471	
1574 s	1596	37.3	1574	
	1604	42.1	1574	
2889 vw	3049	3.6	2889	
2920 vw	3070	4.4	2920	
	3079	6.0	2920	
2949 vw	3116	1.7	2949	
2968 w	3132	5.2	2968	
	3139	8.1	2968	
2992 w	3154	0.1	2992	
	3171	0.2	3007	c
3124 m	3283	24.8	3124	
	3283	21.6	3124	
	3301	10.4	3124	

a From IR spectrum of [C₂mim]NTf₂. *b* Reference 29. *c* [C₂mim]PF₆.[37] *d* From IR spectrum of [C₂mim]Br. *e* From IR spectrum of crIV [C₂mim]NTf₂.

TABLE 7: Vibrational Wavenumbers for the Nonplanar Conformer of the [C₄mim]⁺ Cation

$w_{exp}{}^a$/cm⁻¹	w_{calc}/cm⁻¹	IR intensity/ km·mol⁻¹	selected w/cm⁻¹	comment
	31.7	0.4	34	torsion Bu
	68.6	0.2	74	
	72.1	0.0	77	torsion Pr
	85.8	0.2	92	torsion Me(N)
	115	0.1	123	torsion Et
	200	2.2	212	b
	240	0.0	249	torsion Me(C)
	248	0.6	257	b
	272	0.3	280	
324 c	317	0.1	324	
	401	0.5	401	
	437	1.0	435	b
624 m	628	3.9	624	
	637	11.2	624	
654 m	668	13.7	654	
	735	11.6	730	d
	739	2.9	730	d
753 m	759	22.3	753	
	799	0.7	790	d
845 wide	839	40.7	845	
884 c	882	0.1	884	
908 c	913	0.2	908	
	941	0.2	933	
	1010	1.7	1000	
1025 c	1037	0.3	1025	
	1042	1.2	1025	
1055 c	1055	0.6	1055	
1094 c	1102	3.1	1094	
1114 c	1124	6.7	1114	
	1129	10.5	1114	
1130 c	1148	2.1	1130	
	1153	0.3	1130	
1170 c	1179	102.2	1170	
1212 c	1232	0.8	1212	
1284 c	1288	2.2	1284	
	1297	0.8	1284	
1303 c	1316	1.2	1303	
1314 c	1327	2.8	1314	
1340 c	1343	5.6	1340	
1363 c	1377	1.3	1363	
1373 c	1389	8.3	1373	
1387 sh	1411	3.7	1387	
	1414	3.9	1387	
1420 c	1435	0.5	1420	
1432 w	1458	12.6	1432	
1448 c	1476	13.7	1448	
	1479	6.4	1448	
	1482	0.6	1448	
1467 m	1493	12.4	1467	
	1493	6.9	1467	
	1502	14.2	1467	
	1505	10.8	1467	
1574 s	1596	40.5	1574	
	1603	44.1	1574	
2878 m	3017	5.8	2878	
	3026	23.3	2878	
	3035	28.4	2878	
	3046	1.4	2878	
2917 m	3070	13.8	2917	
	3070	4.9	2917	
	3071	11.7	2917	
2940 m	3102	34.9	2940	
2967 m	3116	17.8	2967	
	3124	8.1	2967	
	3154	0.1	2993	
	3171	0.3	3009	
3122 m	3283	22.8	3122	
	3284	21.3	3122	
	3302	9.9	3122	

a From IR spectrum of [C₄mim]NTf₂. *b* [C₄mim]BF₄.[37] *c* From IR and/or Raman spectrum of [C₄mim]PF₆. *d* [C₄mim]Cl crystal.[38]

the configurations will be large due to many co-ordinating centers in the anion and its ability to form different conformations.

The exhaustive search of configurations is a very difficult problem even for the [C₂mim]NTf₂ ionic pair. It has been partially solved, as shown in ref 43. In that work, the total number of configurations was found to be 24. Among them, 10 configurations contain the anion in the conformation different from both cis and trans. This conformation (cis*, Figure 1) is a transition state for the isolated NTf₂⁻, but may be stabilized in the ionic pair. It is not clear from the information provided in ref 40 whether all these ionic pair configurations correspond to the minima on the potential energy surface. The relative energy of 5 of the remaining configurations exceeds 35 kJ·mol⁻¹; their contribution to the thermodynamic properties

will be low even at elevated temperatures. Configuration 8e was found to be the most stable configuration at the MP2/6-311G**// HF/6-311G** theory level.[43] In 8e, the trans conformer of the anion is placed under the plane of the imidazolium ring. Most configurations with the lowest energy have the anion in the trans conformation.
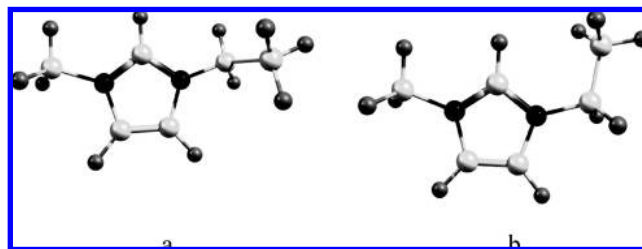
1-Alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide

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Figure 5. Conformers of the [C$_2$mim]$^+$ cation: (a) nonplanar conformer (b) planar conformer.
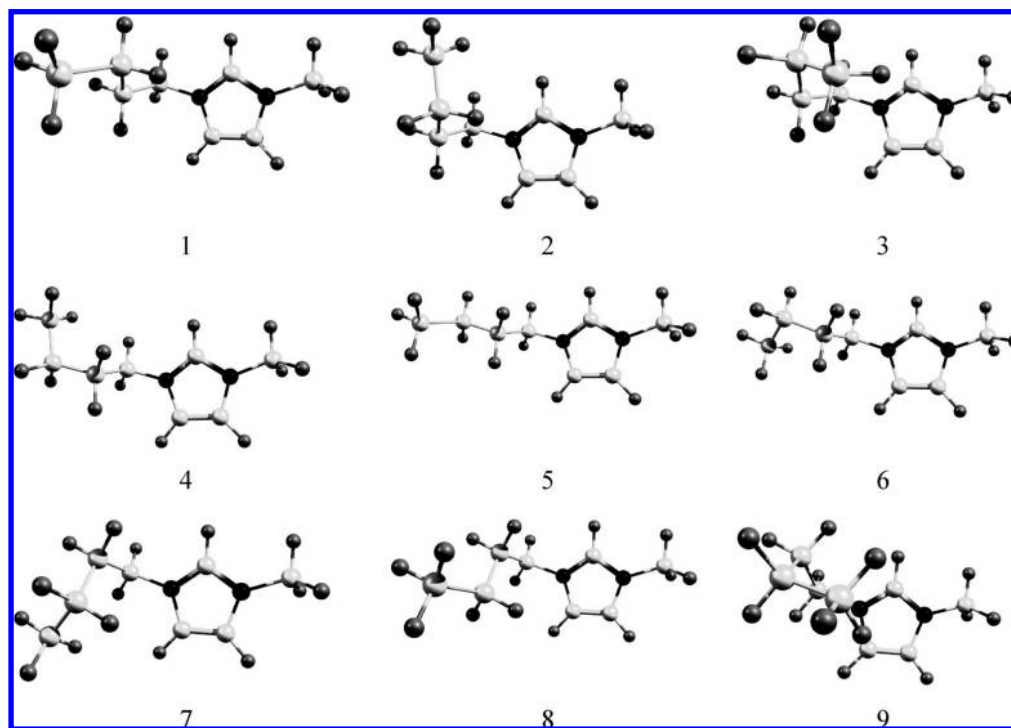

Figure 6. Conformers of the [C$_4$mim]$^+$ cation.

TABLE 8: Coefficients of Equations 5−7 for [C$_4$mim]$^+$ and [C$_6$mim]$^+$

top	a	$b \times 10^2$	$c \times 10^4$	$d \times 10^6$	$e \times 10^8$	f	g
			[C$_4$mim]$^+$				
Et-	−5.87	45.19	−31.40	27.99	24.28	1.3	105
Pr-	−6.08	57.05	−135.9	154.8	−63.58	4.3	300
Bu-	−4.68	7.80	4.51	−9.61	2.96	7.0	69
			[C$_6$mim]$^+$				
Et-	−6.08	49.80	−46.17	−11.72	18.13	1.2	95
Pr-	−5.86	44.11	−18.51	−55.31	39.41	1.2	91
Bu-	−5.59	39.68	−18.33	−36.75	25.71	1.6	124
Pen-	−6.89	69.29	−190.5	236.2	−102.0	4.9	327
Hex-	−4.31	2.64	24.54	−40.09	18.11	7.0	69

Figure 7. Vibrational spectra of liquid [C$_4$mim]PF$_6$: (a) IR; (b) Raman.

In this work, the relative energies of configurations 8a (designated 1 in Figure 9), 8e (2), 8f (3), 8l (4), and 8o (5) in which the anion is in the trans conformation were calculated at the B3LYP/6-31+G(2df,p) theory level. Additionally, the calculations were performed for configuration 6 (not found in ref 43) which is similar to 5, but contains a chiral counterpart conformer of the anion. Configurations 1, 3, 5, and 6 with the anion N atom close to the imidazolium plane were found to be more stable than configurations 2 and 4 with the anion below or above this plane. Configuration 5 appeared to be the global minimum at this theory level. Additional search for conformers was performed at the B3LYP/3-21+G(d) theory level. The found geometries corresponding to the energy minima were optimized at the 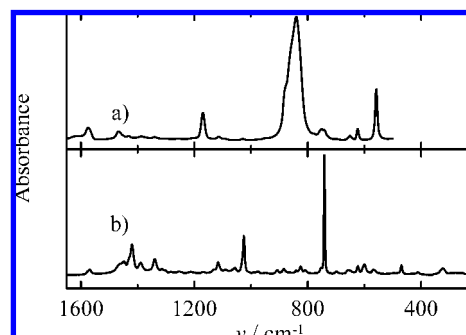B3LYP/6-31+G(d) theory level (see Supporting Information for detail). However, no other low-energy configuration except 1−6 was found at the higher theory level.

In the statistical thermodynamic calculations, the B3LYP/6-31+G(2df,p) relative energies were used. It was assumed that the configurations in all [C$_n$mim]NTf$_2$ are similar to those in [C$_2$mim]NTf$_2$.

The potential barrier to internal rotation of the NTf$_2$ top relative to the cation in configuration 5 was found to be $V = 11.0$ kJ·mol^{-1}. The reduced moment of inertia was calculated assuming that the rotation occurs around the N$_{anion}$ − C(2) axis.

Since in the ionic pair stabilizes the cis* conformer of the anion, it was assumed that in the pair the anion can be in one
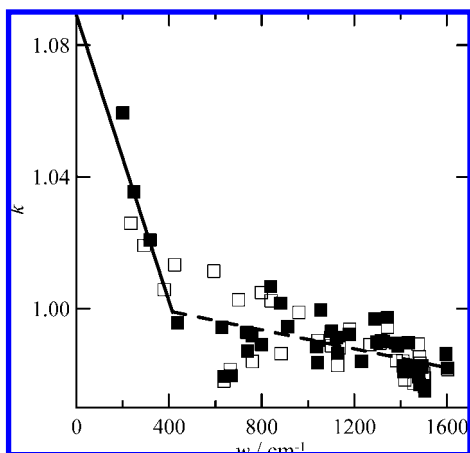
Figure 8. Dependence of a scaling factor on the calculated wavenumbers for the nonplanar conformers of the $[C_2mim]^+$ (□) and $[C_4mim]^+$ (■) cations; —, eq 10; ---, eq 9.

of three conformations (Figure 1) with the energy differences between them equal to ΔE_{tot}. For all the considered compounds, the torsional frequency for the CH_3-(N) top increases by a factor of 1.5 when going from the isolated ion to the ionic pair. Since the reduced moment of inertia is changed insignificantly in this case, the increase of the potential barrier due to interaction with the anion is the main cause of this frequency increase. If one assumes that $w \sim V^{1/2}$, then the considered potential barrier will be close to 4.4 kJ·mol^{-1} in all the ionic pairs. The barrier to internal rotation of the CF_3- top and the other energetic parameters of internal rotation in the cations were assumed to be equal to those in the isolated ions.

The $[C_nmim]NTf_2$ configurations similar to configuration 5 of $[C_2mim]NTf_2$ were chosen as the base structures for the high-level quantum-chemical calculations. The products of principal moments of inertia of the configurations of the ionic pairs are presented in Table 3. The vibrational wavenumbers for $[C_n$-mim]NTf_2$ from the quantum-chemical calculations are presented in Supporting Information Tables S11−S14. The vibrational wavenumbers of the anion were scaled using eqs 3 and 4, those for the cation were scaled using eqs 8−10, and the wavenumbers of the cation−anion vibrations were scaled using eq 4.

The thermodynamic properties of the $[C_nmim]NTf_2$ ionic pairs in the ideal-gas state are presented in Table 5.

Comparison with Experiment

The gas-phase standard entropy $S°_g$ for $[C_nmim]NTf_2$ can be found from the experimental data using the equation

$$S_g^o(T) = S_{liq}^o(T) + \Delta_{vap}H°(T)/T + R \ln(p_{sat}(T)/p°) \quad (11)$$

where $S°_{liq}(T)$ is the standard entropy of liquid; $\Delta_{vap}H°(T)$ is the standard vaporization enthalpy of the compound; $p_{sat}(T)$ is its saturated vapor pressure; and $p° = 10^5$ Pa. The saturated vapor pressure of the considered ILs[2] was measured over the range $T = (410$ to $530)$ K, their vaporization enthalpies are assigned to the average temperatures $<T> = (462−478)$ K. To decrease the error of extrapolation, the $S°_g$ values were found at $T = 470$ K. To adjust $\Delta_{vap}H°$ to this temperature, the values of $\Delta_{liq}^g C_P = C_{p,g} - C_{p,liq}$ were used, where $C_{p,g}$ is the gas heat capacity obtained by the statistical thermodynamic methods; $C_{p,liq}$ is the linearly extrapolated heat capacity of liquid. The latter values correspond to the temperature defined as $(<T> + 470$ K)/2.

The liquid-state entropies of $[C_nmim]NTf_2$ at $T = 370$ K were obtained from the results of adiabatic calorimetry.[7−10] The linear equations for the heat capacity of the liquids obtained from the experimental heat capacities in the temperature range of (300 to 370) K were used to extrapolate C_p to $T = 470$ K at the $S°_{liq}(470$ K) calculation. The $S°_g(470$ K) values found with the use of $\Delta_{vap}H$ from three papers[2,5,6] are presented in Figure 10. The $S°_g(470$ K) values for $[C_nmim]NTf_2$ evaluated using refs 2 and 6 agree within 11 J·K^{-1}·mol^{-1}. The increment per CH_2-group is (51.7 ± 3.5) and (51.9 ± 4.0) J·K^{-1}·mol^{-1}, respectively. The $S°_g$ (470 K) values for $[C_4mim]NTf_2$ and $[C_6mim]NTf_2$ found using calorimetric $\Delta_{vap}H[5]$ are much higher than the former entropies, and the increment per CH_2-group is (66.5 ± 2.8) J·K^{-1}·mol^{-1}.

As follows from the data of Table 9, the dissociation energy of the ionic pairs in a series of $[C_nmim]NTf_2$ changes slightly. On the basis of the temperature dependence of the dissociation constant for $[C_2mim]NTf_2$

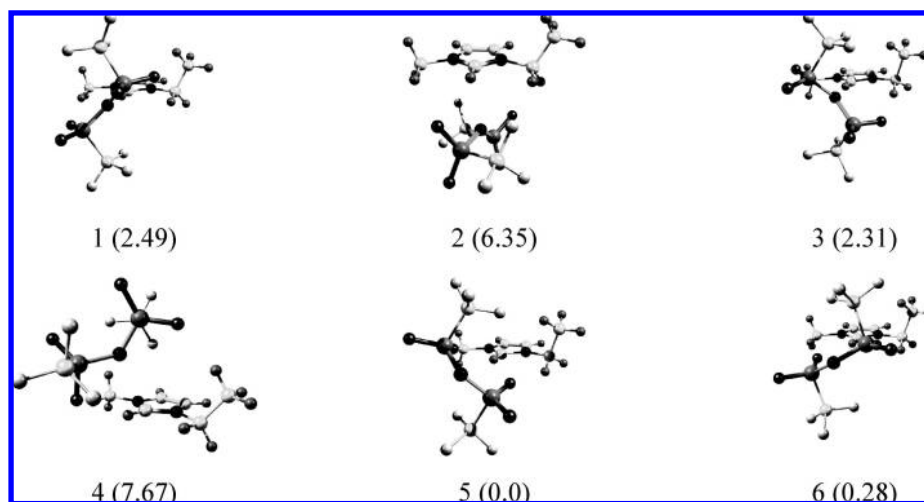$$\ln K = 15.986 - 361.4(100 \text{ K}/T) - 3.935(100 \text{ K}/T)^2 - 0.2022(T/100 \text{ K}) \quad (12)$$

Figure 9. Configurations of the $[C_2mim]NTf_2$ ionic pair. Relative energies ΔE_{tot} (in kJ·mol^{-1}) at the B3LYP/6-31+G(2df,p) theory level are presented in parentheses
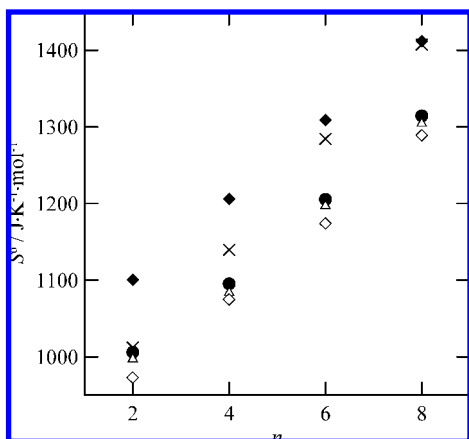
1-Alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide

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Figure 10. Entropy of [$C_n$mim]NTf$_2$ at $T = 470$ K in gas state: Δ, $S°_g$ using $\Delta_{vap}H$ ref 6; ●, $S°_g$ using $\Delta_{vap}H$ from ref 2; ×, $S°_g$ using $\Delta_{vap}H$ from ref 5; ◇, $S°_g$ calculated for ionic pairs; ◆, calculated for the mixture of ions [$C_n$mim]$^+$ + NTf$_2^-$.

TABLE 9: Dissociation Energies of the [$C_n$mim]NTf$_2$ Ionic Pairs at $T = 0$ K

n	$\Delta_{dis}E$/kJ·mol^{-1}	ΔZPVE/kJ·mol^{-1}	$\Delta_{dis}H_0^o$/kJ·mol^{-1}
2	310.3	−4.1	306.2
4	307.5	−4.1	303.4
6	306.7	−4.7	302.0
8	305.9	−3.7	302.2

one may state that the degree of dissociation in the equilibrium state will be negligible even at $T = 1000$ K.

The results[2,6] were obtained assuming the [$C_n$mim]NTf$_2$ vapor consists in ionic pairs. A good agreement between the entropies obtained from the experiment and the calculations confirms the validity of this assumption. If the vapor was a mixture of individual ions, the resulting entropy would be about 130 J·K^{-1}·mol^{-1} higher (Figure 10). On the basis of the Fourier transform ion cyclotron resonance mass spectrometry experiments, Leal et al.[44] concluded that at $T > 474$ K and reduced pressure vapor of ILs consists of ionic pairs. This conclusion is in agreement with the results obtained in the present work.

Supporting Information Available: The results of quantum-mechanical and statistical thermodynamic calculations for all the studied species. This material is available free of charge via the Internet at http://pubs.acs.org.

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