Ionic Liquids. Combination of Combustion Calorimetry with High-Level Quantum Chemical Calculations for Deriving Vaporization Enthalpies

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In this work, the molar enthalpies of formation of the ionic liquids [C$_2$MIM][NO$_3$] and [C$_4$MIM][NO$_3$] were measured by means of combustion calorimetry. The molar enthalpy of fusion of [C$_2$MIM][NO$_3$] was measured using differential scanning calorimetry. Ab initio calculations of the enthalpy of formation in the gaseous phase have been performed for the ionic species using the G3MP2 theory. We have used a combination of traditional combustion calorimertry with modern high-level ab initio calculations in order to obtain the molar enthalpies of vaporization of a series of the ionic liquids under study.

Introduction

Recent studies[1–3] of the ionic liquids (ILs) have shown that nonvolatility is not a property that can be assumed for thermally stable ILs, i.e., vapor pressure of ILs have to be checked experimentally for each new liquid.[4] As a result, the scientific community has been faced with the continuously increasing challenge to measure or to predict the vapor pressure and vaporization enthalpies of ILs. In practice, researchers have to deal with two main problems. At room temperature the low vapor pressures of ILs are practically not measurable, whereas at high temperatures some of them may decompose via processes such as the transfer of an alkyl group or, in the case of protic ILs through deprotonation.[5] To date, there are only a few experimental data sets on vaporization enthalpies of ILs available.[1,6–8] This work continues our study of the thermodynamic properties of pure ILs.[1,6] In our previous study, an excellent thermodynamic consistency of the results from experimental methods (calorimetry, transpiration) and from theoretical ab initio methods was established.[6] In this work we have used a combination of traditional high-precision combustion calorimertry with modern high-level ab initio calculations in order to obtain the molar enthalpies of vaporization of a series of ILs: [C$_2$MIM][NO$_3$] and [C$_4$MIM][NO$_3$].

Experimental Procedure and Methods of Ab Initio Calculations

Materials. The sample of 1-ethyl-3-methyl-imidazolium nitrate [C$_2$MIM][NO$_3$], C$_6$H$_{11}$N$_3$O$_3$ (CAS 143314-14-1) studied was of commercial origin (Aldrich) with a purity of ≥99.0% and containing <0.2% of water according to the specification stated by the supplier. The sample of 1-butyl-3-methyl-imidazolium nitrate [C$_4$MIM][NO$_3$], C$_8$H$_{15}$N$_3$O$_3$ (CAS 179075-88-8) used in this work was the same as those reported in ref 9. This sample was prepared according to the known procedure[10] by means of the reaction between corresponding imidazolium bromide salt and silver nitrate. The mass fraction purity 0.994 of the sample was determined by elemental analysis: 47.45%

C, 7.20% H, 20.91% N. Prior to experiments, all IL samples were subjected to vacuum evaporation at 333 K for more than 24 h to remove possible traces of solvents and moisture. The water concentration in [C$_2$MIM][NO$_3$] was 959.8 ppm and 3287 ppm in [C$_4$MIM][NO$_3$]. It was determined by Karl Fischer titration just before starting the experiments, and appropriate corrections have been made for combustion results. Samples of the ILs were kept and handled under nitrogen stream in a special glass device furnished with a septum for the sample extraction using a syringe.

Thermochemical Measurements: Combustion Calorimetry. An isoperibol bomb calorimeter was used for measuring the energy of combustion of [C$_2$MIM][NO$_3$] and [C$_4$MIM]-[NO$_3$]. The construction of the calorimeter and the detailed experimental procedure has been described previously.[6] A careful encapsulation of the IL sample is required because of its hygroscopic nature. In the present study, we used commercially available polyethylene bulbs (Fa. NeoLab, Heidelberg, Germany) of 1 cm^3 as sample containers. The molten sample was transferred from the stock bottle into the polyethylene bulb with a syringe and sealed according to the procedure described earlier.[6] Seven to nine successful experiments were carried out for each IL. The combustion products were examined for carbon monoxide (Dräger tube) and unburned carbon, but none of these substances was detected. The energy equivalent of the calorimeter ϵ_{calor} was determined with a standard reference sample of benzoic acid (sample SRM 39i, NIST). The calorimeter was specially calibrated for the temperature increase of 2°, which was specific for combustion experiments with the IL enclosed in the polythene bulb (at least half of the temperature increase is due to combustion energy of polyethylene). Correction for nitric acid formation was based on the titration with 0.1 mol·dm^{-3} NaOH (aq). The atomic weights used were those recommended by the IUPAC Commission.[11] The sample masses were reduced to vacuum, taking into consideration the density values (Supporting Information). For converting the energy of the actual combustion process to that of the isothermal process, and reducing to standard states, the conventional procedure[12] was applied. Results for combustion experiments with [C$_2$MIM][NO$_3$] and [C$_4$MIM][NO$_3$] are summarized in the Supporting Information. The total uncertainty of $\Delta_f H_m^\circ$(cr) was calculated according to the guidelines presented by Olofsson.[13]

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TABLE 1: Thermochemical Data at $T = 298$ K ($p^\circ = 0.1$ MPa) for [C₂MIM][NO₃] and [C₄MIM][NO₃]

compounds	$\Delta_c u^\circ$ J·g⁻¹	$\Delta_c H_m^\circ$(cr) kJ·mol⁻¹	$\Delta_f H_m^\circ$(cr) kJ·mol⁻¹	$\Delta_{cr}^l H_m^a$ kJ·mol⁻¹	T_{fus} K	$\Delta_{cr}^l H_m^b$ kJ·mol⁻¹	$\Delta_f H_m^\circ$(l) kJ·mol⁻¹
[C₂MIM][NO₃]	−21355.3 ± 4.6	−3697.5 ± 1.8	−235.7 ± 2.0	19.5 ± 0.2	311.8	18.8	−216.9 ± 2.0
[C₄MIM][NO₃]	−24903.5 ± 6.1	−5013.0 ± 2.7	−278.8 ± 2.9				−261.4 ± 2.9
		−5013.2 ± 2.3ᶜ	−278.6 ± 2.5ᶜ	18.0 ± 0.1ᶜ	309.2	17.4	

ᵃ At the T_{fus}. ᵇ Adjusted to the reference temperature 298 K. ᶜ Results from ref 9.
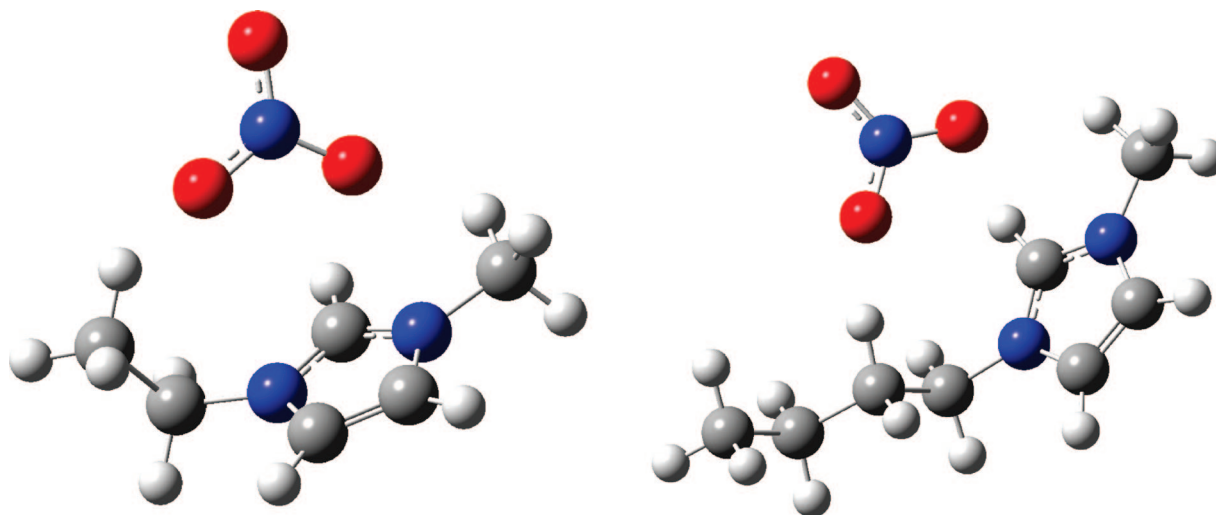
Figure 1. B3LYP/6-311+G(2d,p)-optimized structure of [C₂MIM][NO₃] and [C₄MIM][NO₃].

The uncertainty assigned to $\Delta_f H_m^\circ$(cr) is twice the overall standard deviation and includes the uncertainties from calibration and from the combustion energies of the auxiliary materials, and the uncertainties of the enthalpies of formation of the reaction products H_2O and CO_2.

Phase Transitions in the Solid State. Differential Scanning Calorimetry (DSC) Measurements. The thermal behavior of substituted benzenes including melting temperature and enthalpy of fusion of [C₂MIM][NO₃] were determined with a computer controlled Perkin-Elmer Pyris Diamond DSC. For all measurements, an empty pan was used as the reference. The fusion temperature and enthalpy were determined as the peak onset temperature and by using a straight baseline for integration, respectively. The temperature and heat flow rate scale of the DSC was calibrated by measuring high-purity indium ($T_0 = 429.8$ K and $\Delta H_{ref} = 28.4$ J·g⁻¹). The thermal behavior of the specimen was investigated at a heating rate of 10 K·min⁻¹. The uncertainty for temperature is ±0.5 K and for enthalpy of fusion ±1 J·g⁻¹. The DSC measurements on the sample of [C₂MIM][NO₃] were repeated twice, and the values agreed within the experimental uncertainties of ±0.2 kJ·mol⁻¹ for the enthalpy of fusion and ±0.5 K for the melting temperature. The melting temperature and enthalpy of fusion of the [C₄MIM][NO₃] have been reported recently[9] (see Table 1).

Ab Initio Calculations. Standard ab initio molecular orbital calculations were performed using the Gaussian 03 Rev.04 program package.[14] Rotational conformers of the [CₙMIM] cation were studied at the RHF/3-21G* level at 0 K. Molecular structures and relative energies of all conformations for the cation formed by rotation of alkyl groups around the N−C bond (for C₂MIM) and the N−C and C−C bonds (for C₄MIM) by 360° have been studied with 10° steps starting from the coplanar conformation. It was found that the [C₂MIM] cation has two stable conformations, and the [C₄MIM] cation has seven stable conformations and six of them (conf 1, 2, and 3) formed chiral pairs having identical energies. Energies and frequencies of normal modes were

calculated for all the stable conformers using density functional theory (DFT) methods (see Supporting Information). Corresponding calculations have been performed for the molecular ionic pair [CₙMIM][NO₃] at the HF/3-21G* and HF/6-31G(d,p) levels and fully optimized on the B3LYP/6-311+G(2d,p) level. Starting from 20 to 30 initial geometries, the energy of formation of ion pairs from separated ions was calculated at the B3LYP level. The optimized structures of the [CₙMIM][NO₃] ion pairs are presented in Figure 1. Calculations of energies of the most stable conformers, their enthalpies of formation, Gibbs enthalpies, and equilibrium constants of possible dissociation reactions specific for the ion pairs of [CₙMIM][NO₃] were also performed using the G3MP2[15] method and standard procedures of statistical thermodynamics.[16]

Results and Discussion

Combustion Calorimetry. Results of combustion experiments on [C₂MIM][NO₃] and [C₄MIM][NO₃] are summarized in Table 1 as well as in the Supporting Information. The values of the standard specific energy of combustion, $\Delta_c u^\circ$, the standard molar enthalpy of combustion, $\Delta_c H_m^\circ$, and the standard molar enthalpy of formation in the crystalline state $\Delta_f H_m^\circ$(cr) were based on the following reactions:

$$C_6H_{11}N_3O_3 + 7.25O_2 = 6CO_2 + 5.5H_2O + 1.5N_2 \quad (1)$$

$$C_8H_{15}N_3O_3 + 10.25O_2 = 8CO_2 + 7.5H_2O + 1.5N_2 \quad (2)$$

The values of $\Delta_f H_m^\circ$(cr) for [C₂MIM][NO₃] and [C₄MIM][NO₃] have been obtained from the enthalpic balance according to eq 1 or 2 and Hess's law using the molar enthalpies of formation of H_2O (l) and CO_2 (g) as assigned by CODATA.[17] In the frame of the INTAS cooperation with the working group of Prof. Kabo in Minsk, Belorussia, the enthalpy of combustion of the sample of [C₄MIM][NO₃] from the same batch has been measured independently using an air-bath combustion calorimeter[9] (Table 1). Both results are in the excellent agreement, as can be seen in Table 1.

Vaporization Enthalpies of Ionic Liquids

J. Phys. Chem. B, Vol. 112, No. 27, 2008 **8097**

Determination of the Liquid Phase Enthalpies of Formation of $[C_nMIM][NO_3]$. The enthalpies of formation of both ILs, $\Delta f H_m^\circ(cr)$, derived from the combustion experiments, are referred to the crystalline state. Using the equation

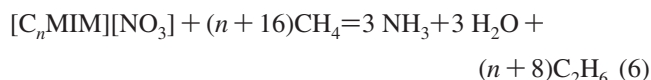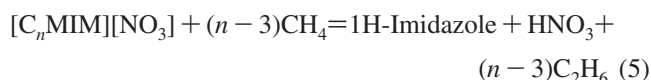$$\Delta_f H_m^\circ(l) = \Delta_f H_m^\circ(cr) + \Delta_{cr}^l H_m \qquad (3)$$

we are able to calculate, $\Delta_f H_m^\circ(l)$, the standard molar enthalpies of formation in the liquid phase, when the enthalpy of fusion, $\Delta_{cr}^l H_m$, is known. As a rule, all three thermodynamic quantities in eq. 3 should be referred to the same temperature, often $T = 298$ K. However, experimental enthalpies of fusion of $[C_n\text{-}MIM][NO_3]$ measured by DSC (see Table 1) are obtained at the melting temperature T_{fus}. Because of the differences in the reference temperatures, the experimental enthalpies of fusion were adjusted to $T = 298$ K. The adjustment was calculated from the equation[18]

$$\{\Delta_{cr}^l H_m(T_{fus}/K) - \Delta_{cr}^l H_m(298\text{ K})\}/(J \cdot mol^{-1}) = \{(0.75 + 0.15 C_p^{cr})[(T_{fus}/K) - 298\text{ K}]\} - \{(10.58 + 0.26 C_p^{cr})[(T_{fus}/K) - 298\text{ K}]\} \quad (4)$$

where the isobaric molar heat capacities, $C_p^{cr} = 305.8$ $J \cdot mol^{-1} \cdot K^{-1}$ and $C_p^l = 353.5$ $J \cdot mol^{-1} \cdot K^{-1}$ of the solid and the liquid $[C_4MIM][NO_3]$ were used from recent work.[9] With this adjustment (the uncertainty of the correlation was not taken into account), the molar enthalpy of fusion, $\Delta_{cr}^l H_m(298\text{ K})$, was calculated (Table 1). Substituting these values into eq 3, the standard molar enthalpies of formation in the undercooled metastable liquid phase, $\Delta_f H_m^\circ(l)$, have been derived (Table 1).

Ab Initio Results and Thermodynamics in the Gaseous Phase. In standard Gaussian-n theories, theoretical enthalpies of formation are calculated through atomization reactions.[19] Raghavachari et al.[20] have proposed using a set of isodesmic reactions, the "bond separation reactions", to derive theoretical enthalpies of formation. Isodesmic reactions conserve the number of types of bonds and should thus be an improvement over simple atomization reactions. Further enhancement in the calculation of enthalpies of formation should be provided by homodesmic reactions, which, in addition to the types of bonds, also conserve the hybridization of the atoms in the bond. We have calculated the enthalpies of formation of $[C_nMIM][NO_3]$ with the help of both standard atomization reactions as well as "bond separation" reactions. For the latter method, we have chosen the following two reactions:

$$[C_nMIM][NO_3] + (n-3)CH_4 = 1H\text{-Imidazole} + HNO_3 + (n-3)C_2H_6 \quad (5)$$

$$[C_nMIM][NO_3] + (n+16)CH_4 = 3\ NH_3 + 3\ H_2O + (n+8)C_2H_6 \quad (6)$$

Using the enthalpies of these reactions calculated by G3MP2 and enthalpies of formation $\Delta_f H_m^\circ(g)$, for the reaction participants in eqs 5 and 6, recommended by Pedley et al.,[21] enthalpies of formation in the gaseous state, $\Delta_f H_m^\circ(g)$, of $[C_nMIM][NO_3]$ have been calculated. As shown in Table 2, these values calculated by G3MP2 using the atomization procedure, as well as eqs 5 and 6, are in acceptable agreement; however, the values obtained by bond separation reactions are somewhat more negative than those from the atomization procedure.

In our recent work[6] we have shown, that one of the aprotic ILs ($[C_4MIM][N(CN)_2]$) exists in the gaseous phase as contact ion pairs and not as a gas of separated ions. In order to justify such an assumption in case of $[C_nMIM][NO_3]$, the following possible

TABLE 2: G3MP2-Calculated Standard Molar Enthalpy of Formation $\Delta_f H_m^\circ(g)$ for $[C_2MIM][NO_3]$ and $[C_4MIM][NO_3]$ in the Gaseous Phase at 298 K in $kJ \cdot mol^{-1}$

compounds	atomization	eq 5	eq 6	average
$[C_2MIM][NO_3]$	−46.6	−58.8	−54.3	−53.2
$[C_4MIM][NO_3]$	−93.0	−104.2	−99.7	−99.0

decomposition reactions have been considered (see Figure 2). In reaction 7 it is assumed that $[C_nMIM][NO_3]$ exists as separated ions in the gaseous phase. Reaction 8 leads to the carbene (the most stable conformer) and the free acid.[22] Using ab initio calculations, it is possible to assess reaction enthalpies and equilibrium constants of reaction pathways 7 and 8. G3MP2 calculations for reactions 7 and 8 have been performed (see Table 3). The purpose of this procedure[23] was to obtain absolute values of the molar standard Gibbs energy of reaction, $\Delta_r G^0$, the standard molar reaction entropy, $\Delta_r S^0$, and the molar reaction enthalpy, $\Delta_r H^0$, for the processes of dissociation (see Figure 2). The chemical equilibrium constants K_p for reactions 7 and 8 in the ideal gaseous state have been calculated at 298 K (see Table 3). For $[C_2MIM][NO_3]$ we have obtained $K_p = 3.2 \times 10^{-61}$ for reaction 7 and $K_p = 1.3 \times 10^{-14}$ for reaction 8. Such low values allow concluding with high reliability that the degree of dissociation of the ion pair is zero for the both ILs under study, i.e. these ILs exist exclusively as ion pairs in the gaseous phase.

Enthalpies of Vaporization $\Delta_l^g H_m$ of $[C_2MIM][NO_3]$ and $[C_4MIM][NO_3]$. Vapor pressures and enthalpy of vaporization, $\Delta_l^g H_m$, of several ILs such as $[BMIM][N(CN)_2]$ and $[EMIM][NTf_2]$ were successfully determined using the method of transference in a saturated stream of helium.[6] In contrast to our previous study,[6] the new ILs $[C_2MIM][NO_3]$ and $[C_4\text{-}MIM][NO_3]$ were not stable enough during the transpiration experiments to obtain reliable results, hence, no experimental enthalpies of vaporization could be determined using this technique. However, in our recent work,[6] we have developed a valuable procedure to obtain vaporization enthalpies of ILs using a combination of traditional combustion calorimetry with high-level ab initio calculations.[6] For that purpose, the following thermodynamic relationship has been used to obtain the molar enthalpy of vaporization of 1-butyl-3-methyl-imidazolium di-cyanamide $[C_4MIM][N(CN)_2]$:
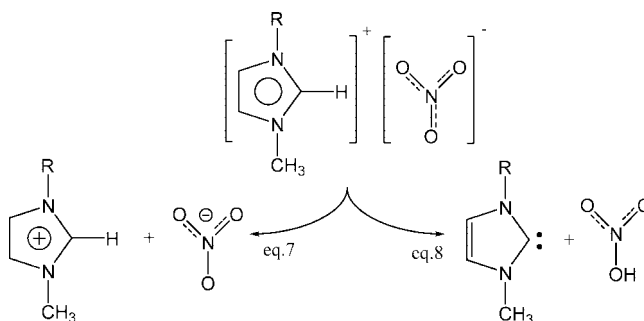
Figure 2. Possible reactions for dissociation of $[C_nMIM][NO_3]$ in the gaseous phase.

TABLE 3: G3MP2 Calculations of the Thermodynamic Properties of Decomposition Reactions of ILs According to Reactions 7 and 8 in Ideal Gas at 298 K ($\Delta_r G^o$ and $\Delta_r H^0$ in $kJ \cdot mol^{-1}$, $\Delta_r S^0$ in $J \cdot mol^{-1} \cdot K^{-1}$)

	$\Delta_r G^0$	$\Delta_r H^0$	$\Delta_r S^0$	K_p
equation 7	345.3	383.8	129.1	3.2×10^{-61}
equation 8	79.4	118.1	129.9	1.3×10^{-14}

$$\Delta_l^g H_m(298 \text{ K}) = \Delta_f H_m^\circ(\text{g}) - \Delta_f H_m^\circ(\text{l}) \qquad (9)$$

where $\Delta_f H_m^\circ(\text{l})$ is the molar enthalpy of formation in the liquid state obtained by high-precision combustion calorimetry, and $\Delta_f H_m^\circ(\text{g})$ is the gaseous enthalpy of formation calculated by one of the suitable ab initio methods (e.g., G3MP2). The quantum chemical calculations of the gaseous enthalpy of formation of $[C_4MIM][N(CN)_2]$ have been performed under the assumption that the gaseous phase of an IL exists entirely of ion pairs. In addition, the enthalpy of vaporization, $\Delta_f^g H_m$, of $[C_4MIM]$-$[N(CN)_2]$ was independently obtained in those work from the temperature dependence of the vapor pressure measured using the transpiration method. Excellent agreement between the value derived from eq 1 with the experimental result for $\Delta_f^g H_m$, has established the thermodynamic consistency. These results have opened a new general way to obtain enthalpies of vaporization of ILs. Therefore, in this work we have used the combination of combustion calorimetry (Table 1) with quantum chemical calculations (Table 2) to derive the vaporization enthalpies for the new series of ILs $[C_nMIM][NO_3]$. Thus, we used the averaged values of $\Delta_f H_m^\circ(\text{g})$ calculated by G3MP2 (Table 2, column 5) and the enthalpies of formation of $[C_2MIM][NO_3]$ and $[C_4MIM][NO_3]$ in the liquid state (Table 1, last column). Using eq 9, the following results have been obtained for enthalpies of vaporization $\Delta_f^g H_m([C_2MIM][NO_3]) = 163.7 \pm 5.3$ kJ·mol^{-1} and $\Delta_f^g H_m([C_4MIM][NO_3]) = 162.4 \pm 5.7$ kJ·mol^{-1}. The uncertainties of vaporization enthalpies, $\Delta_f^g H_m$, result from those of combustion experiments and the uncertainty of (± 4.9 kJ·mol^{-1}) assessed for the G3MP2 calculations.[24] Our results are in close agreement with results from molecular simulations recently obtained by Kelkar and Maginn[25] for $\Delta_f^g H_m([C_4MIM][NO_3]) = 159.0$ kJ·mol^{-1}. At the same time, the united-atom model simulations[26] gave a substantially lower value of $\Delta_f^g H_m([C_4MIM][NO_3]) = 130.2$ kJ·mol^{-1}. Another comparison is useful for validation of the vaporization enthalpies of $[C_nMIM][NO_3]$ derived in this work. Indeed, the experimental vaporization enthalpies of the parent ILs $\Delta_f^g H_m([C_2MIM][NTf_2]) = 135.3 \pm 1.3$ kJ·mol^{-1} and $\Delta_f^g H_m([C_4MIM][NTf_2]) = 136.2 \pm 1.7$ kJ·mol^{-1} have been reported recently.[1] It is clear that these values are indistinguishable within the boundaries of their experimental uncertainties. In spite of the fact that the vaporization enthalpies of the $[C_nMIM][NTf_2]$ family are lower than those for the $[C_nMIM][NO_3]$ family, there is also no difference between ethyl and butyl derivatives in the $[C_nMIM][NO_3]$ family, confirming the consistency of our combustion experiments and ab initio calculations.

Conclusions

A combination of combustion calorimerty (DSC) with the ab initio calculations allows one to obtain the molar enthalpies of vaporization, $\Delta_f^g H_m$, of the ILs $[C_2MIM][NO_3]$ and $[C_4MIM][NO_3]$. Since ab initio results have gained a remarkable reliability in predicting enthalpies of formation in the gaseous phase, the method developed in this work opens a new way to obtain thermodynamic properties of ILs. This procedure provides indispensable data material for testing ab initio procedures and molecular dynamic simulations techniques in order to understand the thermodynamic properties of ILs on a molecular basis.

Supporting Information Available: Results for typical combustion experiments; results from conformational analysis of the cations, optimized structure cations, and relative energies; input data for calculation of enthalpy of formation of the ionic liquid. This material is available free of charge via the Internet at http://pubs.acs.org.

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