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Thermochemistry of Imidazolium-Based Ionic Liquids:

Experiment and First-Principles Calculations

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TABLE S1. Formula, density ρ (T = 293 K), massic heat capacity c_p (T = 298.15 K), and expansion coefficients $(\delta V/\delta T)_p$ of the materials used in the present study.

Compounds	Formula	ρ	c_p	$10^{-6}\cdot(\delta V/\delta T)_p$ [a]
		$g\cdot cm^{-3}$	$J\cdot K^{-1}\ g^{-1}$	$dm^3\cdot K^{-1}$
$[C_2MIM][N(CN)_2]$	$C_8H_{11}N_5$	1.080	1.20	1.0
polyethene [b]	$CH_{1.93}$	0.920	2.53	0.1
Cotton [c]	$CH_{1.774}O_{0.887}$	1.500	1.67	0.1

[a] Estimated. [b] From 10 combustion experiments, $\Delta_c u^\circ$ = -(46354.5.0±4.0) $J\cdot g^{-1}$. [c] From 10 combustion experiments, $\Delta_c u^\circ$ = -(16945.2±4.2) $J\cdot g^{-1}$.

TABLE S2. Results for typical combustion experiments at T = 298.15 K (p° = 0.1 MPa) of the $[C_2MIM][N(CN)_2]$.[a]

m (substance) /g [b]	0.384822	0.425841	0.414895	0.455825	0.438668	0.422283
m'(cotton) /g [b]	0.000778	0.000888	0.000925	0.000988	0.000959	0.001017
m''(polythen) /g [b]	0.326027	0.332255	0.334651	0.323307	0.361073	0.306961
ΔT_c /K[c]	1.75134	1.84943	1.83622	1.8783	1.96348	1.76402
$(\varepsilon_{calor})\cdot(-\Delta T_c)$ /J	-25934.2	-27386.7	-27191.1	-27814.3	-29075.7	-26121.9
$(\varepsilon_{cont})\cdot(-\Delta T_c)$ /J	-32.00	-34.16	-33.88	-34.76	-36.54	-32.28
ΔU_{decomp} HNO_3 /J	82.42	85.41	83.02	82.42	87.2	83.62
ΔU_{corr} /J[d]	10.38	11.23	9.99	10.44	10.78	9.61
$-m'\cdot\Delta_c u'$ /J	13.18	15.05	15.67	16.74	16.25	17.23
$-m''\cdot\Delta_c u''$ /J	15112.82	15401.51	15512.58	14986.73	16737.36	14229.02
$\Delta_c u^\circ$ (liq) /$(J\cdot g^{-1})$	-27928.3	-27962.6	-27967.7	-27977.2	-27949.6	-27978.2

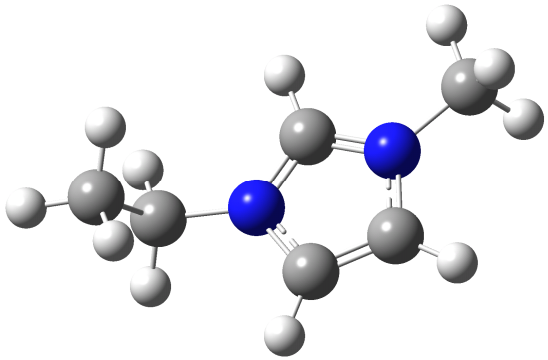
[a] For the definition of the symbols see reference 18, calorimeter: T_h = 298.15 K; V(bomb) = 0.32 dm^3; p^i(gas) = 3.04 MPa; $m^i(H_2O)$ = 1.00 g; [b] Masses obtained from apparent masses. [c] $\Delta T_c = T^f - T^i + \Delta T_{corr}$; $(\varepsilon_{cont})\cdot(-\Delta T_c) = (\varepsilon^i_{cont})\cdot(T^i - 298.15\ K) + (\varepsilon^f_{cont})\cdot(298.15\ K - T^f + \Delta T_{corr.})$. [d] ΔU_{corr}, the correction to standard states, is the sum of items 81 to 85, 87 to 90, 93, and 94 in reference 18. [f] ε = 14808.2 $J\cdot K^{-1}$

TABLE S3. Results for typical combustion experiments at T = 298.15 K (p° = 0.1 MPa) of the $[C_4MIM][N(CN)_2]$[a]

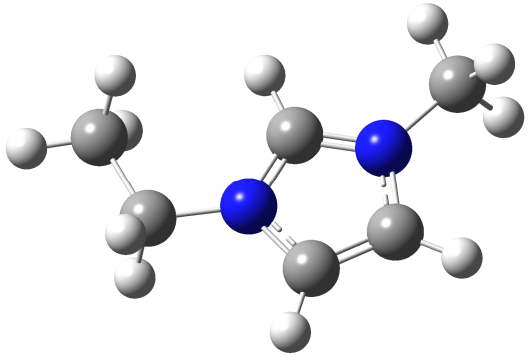
m (substance) /g [b]	0.540534	0.337119	0.329953	0.366428	0.463607	0.415376	0.384793	0.439158	0.442936
m'(cotton) /g [b]	0.004403	0.004	0.003959	0.003931	0.00389	0.003644	0.00362	0.00382	0.004053
m''(polythen) /g [b]	0.296916	0.292229	0.29373	0.306265	0.283129	0.281928	0.28083	0.282947	0.283998
ΔT_c /K[c]	2.05377	1.61783	1.60716	1.72136	1.85038	1.74648	1.67976	1.79964	1.81143
$(\varepsilon_{calor})\cdot(-\Delta T_c)$ /J	-30405.7	-23951.8	-23793.8	-25484.4	-27394.6	-25856.3	-24868.5	-26643.3	-26817.8
$(\varepsilon_{cont})\cdot(-\Delta T_c)$ /J	-38.73	-29.53	-29.32	-31.63	-34.27	-32.17	-30.77	-33.28	-33.53
ΔU_{decomp} HNO_3 /J	75.85	52.86	51.07	54.95	67.19	61.52	57.93	63.91	65.1
ΔU_{corr} /J[d]	11.35	8.32	8.25	8.97	9.95	9.25	8.79	9.61	9.68
$-m'\cdot\Delta_c u'$ /J	74.61	67.78	67.09	66.61	65.92	61.75	61.34	64.73	68.68
$-m''\cdot\Delta_c u''$ /J	13765.32	13548.03	13617.62	14198.75	13126.14	13070.46	13019.56	13117.71	13166.43
$\Delta_c u°$ (liq) /(J·g^{-1})	-30557.3	-30565.8	-30547	-30529.1	-30542.4	-30539.8	-30540.2	-30559.9	-30572.1
$\Delta_c u°$ (liq) /(J·g^{-1})	-30550.4 ± 4.7								
	195.0 ± 2.7								

[a] For the definition of the symbols see reference 13, T_h = 298.15 K; V(bomb) = 0.32 dm^3; p^i(gas) = 3.04 MPa; $m^i(H_2O)$ = 1.00 g; [b] Masses obtained from apparent masses. [c] $\Delta T_c = T^f - T^i + \Delta T_{corr}$; $(\varepsilon_{cont})\cdot(-\Delta T_c) = (\varepsilon^i_{cont})\cdot(T^i - 298.15\ K) + (\varepsilon^f_{cont})\cdot(298.15\ K - T^f + \Delta T_{corr.})$. [d] ΔU_{corr}, the correction to standard states, is the sum of items 81 to 85, 87 to 90, 93, and 94 in reference 13. [f] ε = 14804.82 ± 0.9 J·K^{-1}

TABLE S4. Conformational analysis of the $[C_2MIM]^+$



conf1



conf2

Conformer	Dihedral $C_1N_5C_7C_8$,°	**RHF/6-31G(d)** E_0, Hartree	**RHF/6-31G(d)** TCH, Hartree	Relative energy at 298.15 K, kJ·mol^{-1}
conf1	±105.0	-342.3134241	0.190735	0.00
conf2	0.0	-342.3121849	0.190906	3.70
Conformer	Dihedral $C_1N_5C_7C_8$,°	**RB3LYP/6-31G(d,p)** E_0, Hartree	**RB3LYP/6-31G(d,p)** TCH, Hartree	Relative energy at 298.15 K, kJ·mol^{-1}
conf1	±105.0	-344.5497091	0.179264	0.00
conf2	0.0	-344.5488272	0.179333	2.50

TABLE S5. Calculation G3MP2 Energy and Enthalpies at 298.15 K (in Hartree, ideal gas)

Compounds	G3MP2		$\Delta_f H^\circ_{m\ exp.gas}$
	E_0	H_{298}	
methane	-40.422100	-40.418284	-74.9 ± 0.4 [Pedley]
ethane	-79.651199	-79.646714	-83.8 ± 0.3 [Pedley]
ammonium	-56.470142	-56.466333	-45.94 ± 0.35 [Cox]
methyl-imidazole	-265.097296	-265.090855	125.7
1H-Imidazole	-225.867843	-225.863074	132.9 ± 0.6 [Jimenez]
HCN	-93.298948	-93.295483	135.14 [Chase]
propane	-118.885057	-118.879478	-104.70 [Pedley]
ethene	-78.434778	-78.430777	52.50 [Pedley]
$N(CH_3)_3$	-174.139755	-174.133223	-23.70[Pedley]
$NH_2–(CH_2)_2-NH_2$	-190.194682	-190.188105	-17.00[Pedley]
$[C_2MIM][N(CN)_2]$	-584.263083	-584.247538	---

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TABLE S6. G3MP2 calculations of the process of dissociation of the ion pairs of $[C_nMIM][N(CN)_2]$

$[C_2MIM][N(CN)_2]$			$[C_4MIM][N(CN)_2]$		
Components	Free Energy	Enthalpy	Components	Free Energy	Enthalpy
	Hartree			Hartree	
cation	-343.972545	-343.929305	cation	-422.447867	-265.090845
anion	-240.215284	-240.183854	anion	-240.215284	-319.137933
IL	-584.308419	-584.247537	IL	-662.780247	-584.247537
Δ_rG^o, kJ/mol	316.61		Δ_rG^o, kJ/mol	307.44	
Δ_rH^o, kJ/mol	352.81		Δ_rH^o, kJ/mol	346.69	
Δ_rS^o, J/mol·K	121.42		Δ_rS^o, J/mol·K	131.67	
ln K_p	-127.72		ln K_p	-124.02	
K_p	3.4 E-56		K_p	1.4 E-54	