Supplementary Material (ESI) for PCCP

On the physical origin of the cation-anion intermediate bond in ionic liquids
Part I. Placing a (weak) hydrogen bond between two charges.

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Electronic Supplementary Information

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SI Computational methodologies and systems investigated

Table S1: Ion pairs (IPs) that are studied in this work. Temperature in Kelvin. Data from Ref.[1–4] Viscosity η in cP, conductivity Λ in Sm^{-1}, density ρ in $\mathrm{g/cm}^3$.

IPs	η	T_m	Λ	ρ
[Na][Cl]	–	1074	–	2.17
[Na][NO_3]	–	581	–	2.26
[Na][NTf_2]	–	507-511 (Li)	–	–
[Na][BF_4]	–	657	–	2.47
[NH_4][Cl]	–	608	–	1.52
[NH_4][NO_3]	–	442	–	1.72
[NH_4][NTf_2]	–	–	–	–
[NH_4][BF_4]	–	503	–	1.87
[$EtNH_3$][Cl]	–	378-381	–	–
[$EtNH_3$][NO_3][5]	32(300 K)	288	0.0269	1.216
[$EtNH_3$][NTf_2]	–	–	–	–
[$EtNH_3$][BF_4]	–	–	–	–
[Emim][Cl]	–	358	–	1.186
[Emim][NO_3]	–	311 / 284	–	1.28
[Emim][NTf_2]	32.6	255	0.91	1.53
[Emim][BF_4]	43	288	1.553	1.280

The different ion pairs studied in this work are listed in table S1 together with some of their physical properties.

SII Dependence of intermediate bond on applied methodology

Table S2: Bond length r(XH) in pm and counterpoise-corrected interaction energies ΔE^{cp} for different methods and basis sets. All energies are given in [kJ/mol]. Δr(XH) is the bond elongation taking the difference between complex and isolated cation.

method	basis	r(XH)	Δ r(XH)	ΔE^{cp}	r(XH)	Δ r(XH)	ΔE^{cp}
			$[\mathrm{EtNH_3}][\mathrm{Cl}]$			[Emim][Cl]	
HF	3-21G	108.52	6.74	−456.0	108.26	2.01	−375.8
HF	TZVPP	198.87	98.15	−473.0	108.85	2.24	−374.7
BLYP-D	TZVPP	155.94	52.95	−530.9	113.15	5.22	−407.2
MP2	TZVPP	159.79	57.85	−519.8	111.94	4.79	−400.5
			$[\mathrm{EtNH_3}][\mathrm{NO_3}]$			$[\mathrm{Emim}][\mathrm{NO_3}]$	
HF	3-21G	143.74	41.96	−467.9	108.36	2.11	−375.0
HF	TZVPP	178.22	77.50	−472.1	107.43	0.82	−364.1
BLYP-D	TZVPP	159.28	56.29	−513.7	110.21	2.28	−386.5
MP2	TZVPP	158.20	56.26	−505.0	107.36	0.21	−386.5
			$[\mathrm{EtNH_3}][\mathrm{NTf_2}]$			$[\mathrm{Emim}][\mathrm{NTf_2}]$	
HF	3-21G	104.77	2.99	−403.2	107.53	1.28	−322.9
HF	TZVPP	102.48	1.76	−363.3	107.39	0.76	−302.8
BLYP-D	TZVPP	112.45	9.46	−416.5	110.08	2.15	−339.2
MP2	TZVPP	108.33	6.39	−406.1	108.71	1.56	−331.1
			$[\mathrm{EtNH_3}][\mathrm{BF_4}]$			$[\mathrm{Emim}][\mathrm{BF_4}]$	
HF	3-21G	103.23	1.45	−419.5	106.30	0.05	−337.2
HF	TZVPP	101.72	1.00	−416.1	106.76	0.15	−343.4
BLYP-D	TZVPP	105.88	2.85	−457.5	108.53	0.60	−378.3
MP2	TZVPP	104.11	2.17	−444.4	107.59	0.44	−362.0

In table S2 the binding energies ΔE^{cp} are shown. The applied HF calculations fail in several cases (mostly PILs) to obtain the complex geometry the other methods end up in. In order to verify the failure of the Hartree–Fock results we started these geometry optimizations also from the MP2/TZVPP geometries and obtained the same differing results. Even the cases where a similar geometry of HF compared to the other methods is obtained, the HF bond elongations are different from the other methods. Additionally, the deviation between the MP2 and the HF calculations can be as large as 60 kJ/mol stressing the importance of proper treatment of the dispersion effects in ILs.

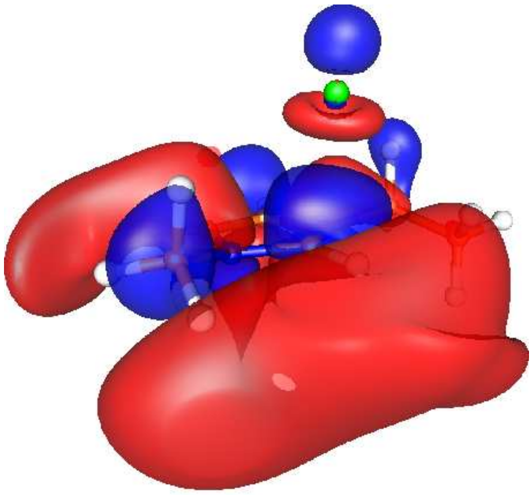
SIII The role of charge transfer

Table S3: Interaction energies ΔE^{cp} and zero-point energy corrected interaction energy $\Delta E^{\mathrm{cp}}_{\mathrm{ZPE}}$ are given in kJ/mol and contact distances of ion pairs (IPs) are given in pm, for definition see section 2. The angle a(XHY) is also given in degrees. Δr(XH) gives the difference for r(XH) of complex minus isolated cation. All data obtained from MP2/TZVPP optimizations.

IPs	ΔE^{cp}	$\Delta E^{\mathrm{cp}}_{\mathrm{ZPE}}$	r(XH)	r(XY)	r(HY)	a(XHY)	Δr(XH)
[NH_3][HCl]	−571.6	−583.8	176.47	308.24	131.78	179.8	74.56
[NH_3][HNO_3]	−469.2	–	166.46	268.07	101.62	179.0	64.51
[NH_3][$HNTf_2$]	−435.3	−472.3	159.64	268.44	108.86	177.5	57.69
[$EtNH_2$][HCl]	−519.8	−533.7	159.79	295.03	135.67	160.6	57.85
[$EtNH_2$][HNO_3]	−505.0	−507.1	158.20	261.92	103.82	176.9	56.23

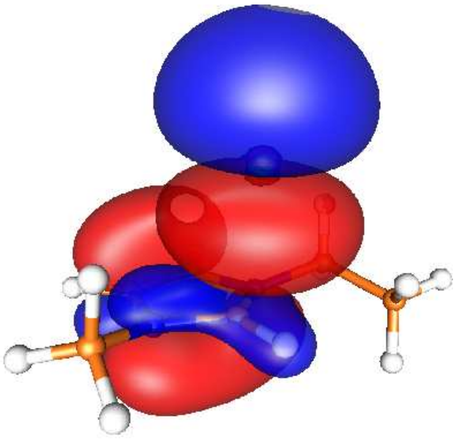
Table S4: NPA charges in a.u. on contact atoms of the hydrogen bond and net charge transferred (NTC) to the hydrogen bond donor. All data obtained from MP2/TZVPP.

IPs	X	H	Y	NCT
[NH_3][HCl]	−1.0244	0.2934	−0.3747	−0.6253
[NH_3][HNO_3]	−1.0417	0.5270	−0.5594	−0.7658
[NH_3][$HNTf_2$]	−1.2623	0.4976	−1.0225	−0.1097
[$EtNH_2$][HCl]	−0.4403	0.3322	−0.8073	−0.1081
[$EtNH_2$][HNO_3]	−0.5674	0.5206	−0.8314	−0.1017



LUMO (+0.121919)

Figure S1: LUMO orbitals of [Emim][Cl] on-top. The numbers in parenthesis are the orbital energies in atomic units.



HOMO (-0.303189)

Figure S2: HOMO orbitals of [Emim][Cl] on-top. The numbers in parenthesis are the orbital energies in atomic units.

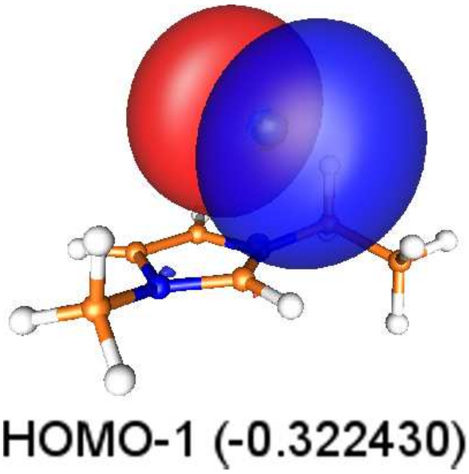


Figure S3: HOMO-1 orbitals of [Emim][Cl] on-top. The numbers in parenthesis are the orbital energies in atomic units.

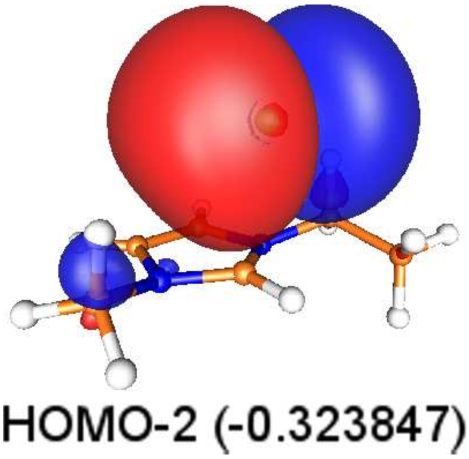


Figure S4: HOMO-2 orbitals of [Emim][Cl] on-top. The numbers in parenthesis are the orbital energies in atomic units.

SIV Potential energy surfaces and forces

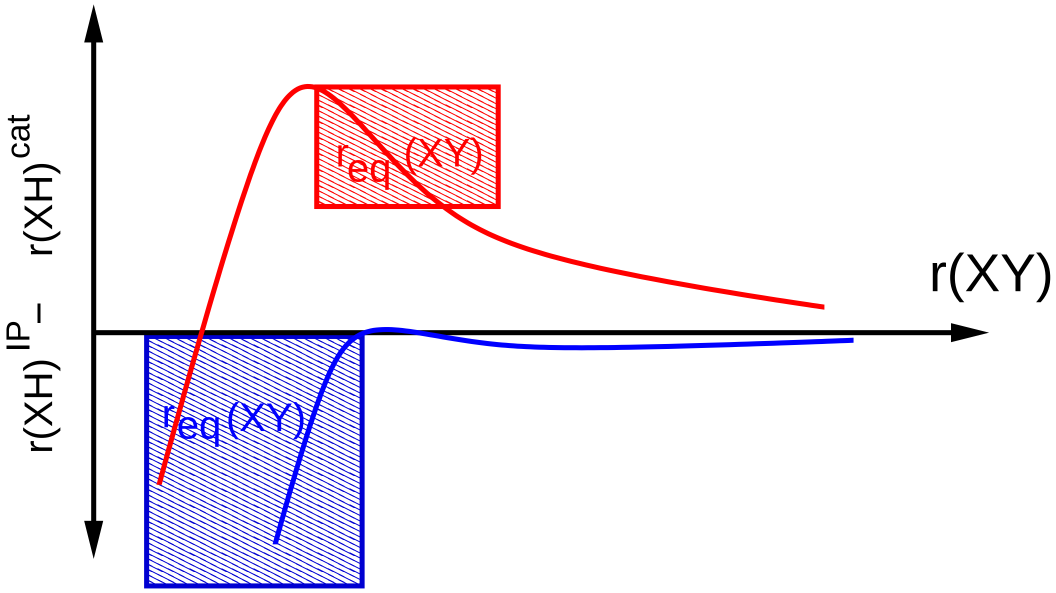


Figure S5: Schematical drawing of r(XH) bond elongation from isolated cation (cat) to ion pair complex (IP) against the r(XY) distance. Red: Traditional hydrogen bond; Blue: Weak hydrogen bond. The squared box indicates at which XY distances the complex can exhibit the equilibrium distance r_{eq}(XY).

References

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