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Hydrogen Bonding in Ionic Liquids

P.A. Hunt, C.R. Ashworth and R. P. Matthews

Computational details

Molecular Dynamics Simulations.
Classical MD simulations for $[C_2C_1im]Cl$ and $[C_4C_1im]Cl$ ILs have been previously reported by us.[1] Simulations were carried out with 128 IPs at 450 K ($[C_2C_1im]Cl$) and 400K ($[C_4C_1im]Cl$) employing the canonical (NVT) ensemble within the DL_POLY simulation package.[2] Equations of motion were integrated using the leapfrog Verlet algorithm with a 1fs time step.[3] A Nose-Hoover thermostat with a temperature relaxation time of 0.2 ps was used.[4] The modified SHAKE[5,6] algorithm was used to constrain bonds terminating in H atoms. Spatial distribution functions (SDFs) have been generated from the last 5ns of a total simulation length of 20ns using the TRAVIS software package[7]

Ab-initio calculations.
DFT calculations using Becke's three-parameter exchange functional [8] in combination with the Lee, Yang and Parr correlation functional[9] (B3LYP) have been carried out with a 6-311+G(d,p) OR aug-cc-pVTZ basis set have been carried out as implemented in the Gaussian 09 suite of programs.[10] To account for dispersion interactions Grimme's -D3[11,12] dispersion correction has been added to the B3LYP functional (referred to as B3LYP-D3).

Optimisation convergence criteria have been tightened from the Gaussian 09 defaults to 10^{-9} on the density matrix and 10^{-7} on the energy matrix. The numerical grid was improved from the default to a pruned (optimised) grid of 99 radial shells and 590 angular points per shell. All structures have been fully optimised under no symmetry constraints and have been confirmed as minima by vibrational analysis. These enhanced criteria have been maintained for the vibrational and counterpoise calculations. Vibrational frequencies and zero-point vibrational energy corrections (ZPE) have been obtained within the harmonic approximation. Basis set superposition error (BSSE) has been determined using the counterpoise method.[13]

Population analysis was carried out using the Natural Bond Orbital (NBO) method (version 5.9)[14,15]. Topological analysis of the electron density, □, within the Quantum Theory of Atoms in Molecules (QTAIM) framework introduced by Bader [16] has been carried out using the AIMALL software [17,18]

Values included in section 4.1 (Rosaz thermodynamic cycles[19] applied to doubly ionic H-bonds) have been computed at the MP2/aug-cc-pVDZ level and are ZPE and BSSE corrected. This level of calculation was chosen for comparison with previous studies.[19] Specifically if the neutral species are AH and B and the ionic species are A^- and BH^+ then

$E_{neutral}=E(AH\cdots B)-[E(AH)+E(B)]$ $E_{anionc}=E(A^-\cdots B)-[E(A^-)+E(B)]$

$E_{cationic}=E(AH\cdots HB^+)-[E(AH)+E(HB^+)]$ $E_{ionic}=E(A^-\cdots HB^+)-[E(A^-)+E(HB^+)]$

The energy difference between the above dissociation energies are:

$\Delta E_{neutral\text{->}anionic}=E_{neutral}-E_{anionic}$ $\Delta E_{neutral\text{->}cationic}=E_{neutral}-E_{cationic}$

$\Delta E_{anionic\text{->}ionic}=E_{anionic}-E_{ionic}$ $\Delta E_{cationic\text{->}ionic}=E_{cationic}-E_{ionic}$

$\Delta E_{neutral\text{->}ionic}=E_{neutral}-E_{ionic}$

These relate to the thermodynamic cycle and determination of the H-bond energy and ionic energy as shown below:

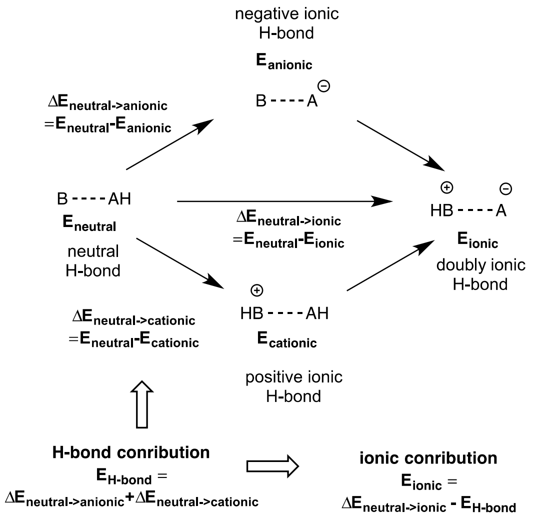
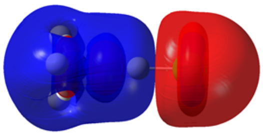
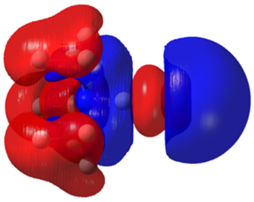
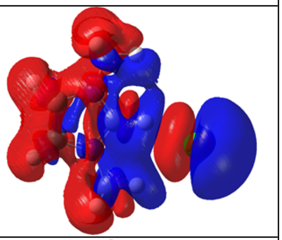
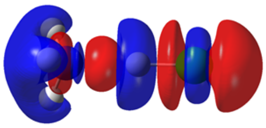
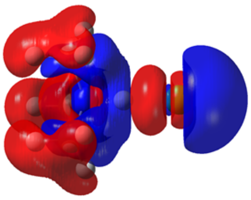
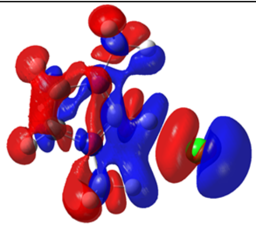
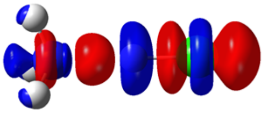
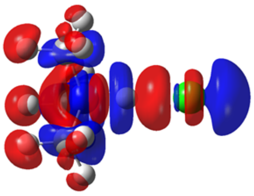
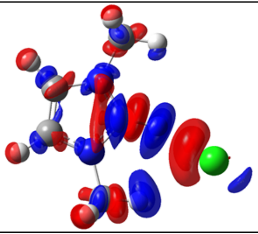
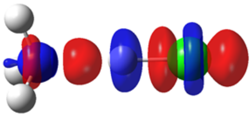
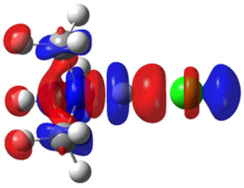
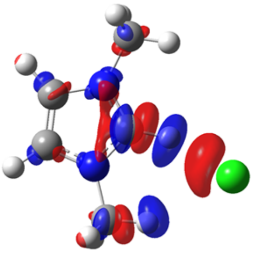
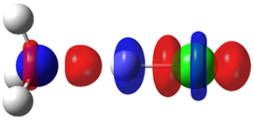
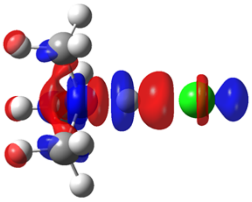
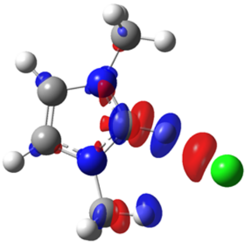


Figure S1.

Isovalue	H_3N---HCl	Me_3NH---Cl	mmim---Cl
0.0004			
0.0008			
0.002			
0.003			
0.004			

3D electron density difference isosuraces for $H_3N\cdots HCl$, $[C_1C_1im]Cl$ and $[Me_3NH]Cl$. Structures and density computed at B3LYP-D3/aug-cc-pVTZ level.

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