Electronic Supplementary Information

Doubly Ionic Hydrogen Bond Interactions Within the Choline Chloride-Urea Deep Eutectic Solvent

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ESI Contents:

1. Introduction

1.1 QTAIM

QTAIM links the topology of the electron density, ρ(r), to concepts of chemical bonding. A chemical bond between two atoms is indicated by the presence of a bond critical point (BCP). A BCP is a saddle point in ρ(r), being a minimum along the atomic interaction line between two bonded atoms and a maximum in the two perpendicular directions. The Laplacian of ρ(r), $\nabla^2\rho$ (r), provides information about the local curvature of ρ (r). The sign of $\nabla^2\rho$ (r) together with the sign of the total energy density, H_c, at the BCP provide further information regarding the nature of the interaction. At the extreme ends of the scale, $\nabla^2\rho$ (r) > 0 and H_c > 0 at the BCP indicates a closed shell interaction, whereas, $\nabla^2\rho$ (r) < 0 and H_c < 0 is indicative of a covalent bond.[1] The magnitude of ρ(r) at a H-bonding BCP has been linked to the strength of the H-bond and together with the sign and magnitude of both $\nabla^2\rho(r)$ and H_c has been related to the covalency of the interaction.[2] ρ_{BCP} and $\nabla^2\rho_{BCP}$ correspond to ρ(r) and $\nabla^2\rho(r)$ at the BCP respectively.

1. R. Parthasarathi and V. Subramanian, in *Hydrogen Bonding—New Insights*, ed. S. Grabowski, Springer Netherlands, 2006, vol. 3, ch. 1, pp. 1-50.
2. S. J. Grabowski, *Chemical Reviews*, 2011, 111, 2597-2625.

1.2 NBO

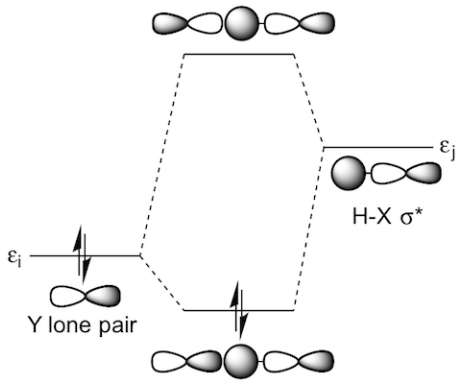

Figure S1. Simplified representation of the donor- acceptor interaction between localised NBO fragment orbitals upon H-bond formation (X-H···Y).

1.3 Correlation between ρ_{BCP} and $\nabla^2\rho_{BCP}$

It was previously suggested that $\nabla^2\rho_{BCP}$ for weak H-bonds should be small and positive, likely < 0.01 au.[1] Upon further review of the values of $\nabla^2\rho_{BCP}$ associated with H-bonds defined as weak (using a cut-off in ρ_{BCP} of 0.02 au), and examination of ρ_{BCP} and associated $\nabla^2\rho_{BCP}$ values for the H-bonds observed here, we have increased the suggested upper bound of $\nabla^2\rho_{BCP}$ to a value 0.07 au for weak H-bonds.

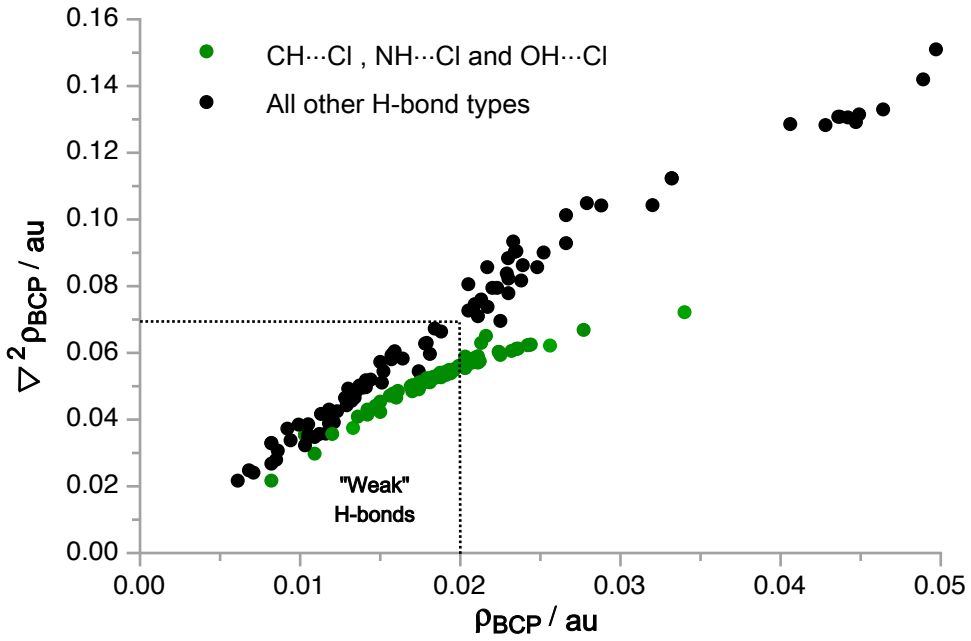

Figure S2. Correlation between ρ_{BCP}/au and $\nabla^2\rho_{BCP}$/au for the H-bonds identified within this work. "Other" H-bond types: NH···O=C, OH···O=C, CH···O=C, intramolecular CH···O(H), NH···N(H) and NH···O(H).

Figure S2 clearly demonstrates that there is a correlation between ρ_{BCP} and $\nabla^2\rho_{BCP}$ for the H-bonds identified within this work. Such correlations have previously been established for other H-bond systems. Based on the above correlation, and assuming a cut-off in ρ_{BCP} of 0.02 au, an upper limit of 0.07 au for $\nabla^2\rho_{BCP}$ is tentatively proposed for weak H-bonds. However, for a given value of ρ_{BCP} there is evidently some variation in $\nabla^2\rho_{BCP}$, or *vice versa*. Additionally, there appears to be two divergent correlations within the data set, becoming more apparent in the moderate to strong H-bond regions. Upon further analysis, it was revealed that the divergent group of data points corresponded solely to H-bonds involving the chloride anion (doubly ionic CH···Cl and OH···Cl, and anionic NH···Cl). This finding could indicate that there is a functional group, and/or charge, dependence in the correlation between ρ_{BCP} and $\nabla^2\rho_{BCP}$ for H-bonds.

1. P. A. Hunt, C. R. Ashworth and R. P. Matthews, *Chemical Society Reviews*, 2015, 44, 1257-1288, DOI: 10.1039/C4CS00278D.

2. The Choline Cation

2.1 Relative Energies

Table S1. Relative electronic energies (with and without ZPE correction) and relative Gibbs free energies of the choline conformers.

Choline Conformer	E /au	ΔE_{rel} /kJ mol^{-1}	E+ZPE /au	ΔE_{rel} (with ZPE correction) /kJ mol^{-1}	G /au	ΔG_{rel} /kJ mol^{-1}
Gauche	-328.819938	0.00	-328.623147	0.00	-328.655286	0.00
Trans	-328.812538	19.43	-328.616231	18.16	-328.649539	15.09
Trans-rotated‡	-328.810428	24.97	-328.614307	23.21	-328.647542	20.33

‡ In order to obtain the trans-rotated conformation, the C-C-O-H torsion angle had to be constrained to 90°, nevertheless vibrational analysis returned no negative frequencies.

2.2. Partial Charge Analysis of Gauche Choline

Both the NBO and CHELPG charge partitioning schemes indicate that the electronegative oxygen atom of the substituent bears a negative partial charge (≈ -0.65 to -0.76 *e*) and that the positive charge is largely distributed over the hydrogen atoms of the alkyl groups.

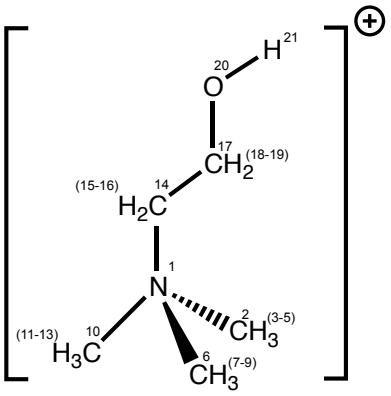

Figure S3. Atomic numbering scheme used for the choline cation

Table S2. Partial charge analysis of gauche choline

	q/e	
	NBO	**CHELPG**
N^{1}	-0.347	0.211
C^{2}	-0.353	-0.250
H^{3}	0.256	0.170
H^{4}	0.218	0.139
H^{5}	0.221	0.147
C^{6}	-0.358	-0.266
H^{7}	0.236	0.164
H^{8}	0.222	0.154
H^{9}	0.228	0.144
C^{10}	-0.347	-0.306
H^{11}	0.227	0.150
H^{12}	0.227	0.165
H^{13}	0.224	0.162
C^{14}	-0.176	-0.161
H^{15}	0.229	0.151
H^{16}	0.228	0.105
C^{17}	-0.053	0.240
H^{18}	0.205	0.065
H^{19}	0.177	0.021
O^{20}	-0.757	-0.654
H^{21}	0.493	0.448

2.3 H-Bond Data

Table S3. H-bond lengths (r), $E^{(2)}$ values and selected topological properties of the ρ(r) at the BCPs for the intramolecular H-bond within choline (cationic) and *N,N*-dimethylethanolamine (neutral)

	Cationic	Neutral
r CH…O / Å	2.21	2.54
$E^{(2)}$/ kJ mol^{-1}	5.23	-
ρ_{BCP}/ au	0.0164	0.0103
$\nabla^2\rho_{BCP}$/au	0.0629	0.0366
H_c /au	0.00237	0.00121

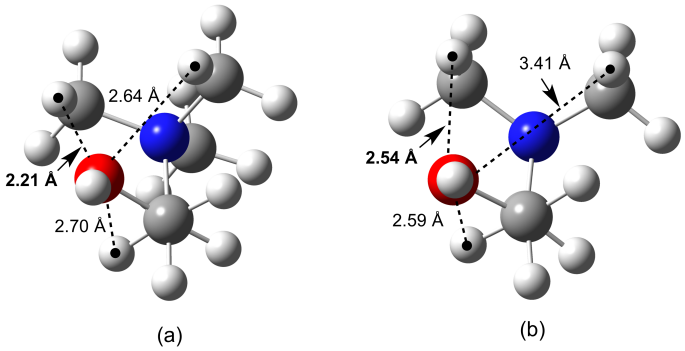

Figure S4. CH…OH interaction distances within (a) gauche choline and (b) gauche *N,N*-dimethylethanolamine

2.4 Discussion: Why is the gauche conformer lower in energy?

β-substituted ethyltrimethylammonium cations either adopt a trans or gauche conformation with respect to the N-C-C-X torsion angle (X = *β* substituent). Choline (X=OH) belongs to a sub-class of this type of cation in which the gauche conformation strongly predominates in both the solid and solution phases.[1-4] Preference for the gauche conformer in the gas phase has also been reported.[5] In the gas phase the gauche conformer is found here to be ≈ 18 kJ mol^{-1} lower in energy than the trans conformer.

Based on steric arguments one would anticipate the trans conformer of choline to predominate. For the related neutral analogue of choline, *N,N*-dimethylethanolamine, the gauche conformer lies ≈ 2 kJ mol^{-1} higher in energy than the comparable lowest energy trans conformation (**Table S4**).

Table S4. Relative energies of *N,N*-dimethylethanolamine conformers.

***N,N*-dimethylethanolamine Conformer**	**E /au**	**ΔE_{rel} /kJ mol^{-1}**	**E+ZPE /au**	**ΔE_{rel} (with ZPE correction) /kJ mol^{-1}**
Gauche	-289.106672	2.22	-288.953931	2.15
Trans-a	-289.107516	0.00	-288.954748	0.00
Trans-b	-289.105777	4.57	-288.953229	3.99

Electronic factors must, therefore, influence the conformation of choline. A favourable, non-specific, electrostatic interaction between the electronegative oxygen and the positive charge distributed over the ammonium head group has

been hypothesised.[2, 3] The computed partial charge distribution of choline (**Table S2**) supports this hypothesis; the negative oxygen atom "sees" the positive charge smeared out over the periphery of the ammonium head group

The possible contribution of an intramolecular H-bond to stabilisation of the gauche conformer has also been explored. One CH···O distance is notably shorter than the others (**Figure S4)** with a BCP identified, ρ_{BCP}=0.016 au (**Table S3)**. $\nabla^2\rho_{BCP}$ and the total energy density are indicative of the formation of a weak, predominantly electrostatic H-bond. *N,N*-dimethylethonolamine exhibits a weaker H-bond, (**Figure S4** and **Table S3**), indicating that the positive charge of choline strengthens the intramolecular H-bond, and thus contributes to the preference for the gauche conformation. Only within gauche choline is a $\sigma_{C\text{-}H} \rightarrow \sigma_{C\text{-}N}^*$ donor-acceptor interaction obtained ($E^{(2)}$ = 26.5 kJ mol^{-1}), indicating that hyperconjugation could also be contributing to the stabilisation of the gauche conformer.

Overall, we conclude that the gauche conformer of choline is stabilised by both a non-specific electrostatic interaction and the formation of an intramolecular H-bond. These results indicate that an anisotropic distribution of the overall +1 charge within the cation facilitates the formation of H-bonds, over and above that of the neutral analogue.

1. J. Hjortas and H. Sorum, *Acta Crystallographica Section B*, 1971, 27, 1320-1323.
2. P. Partington, J. Feeney and A. S. V. Burgen, *Molecular Pharmacology*, 1972, 8, 269-277.
2. Y. Terui, M. Ueyama, S. Satoh and K. Tori, *Tetrahedron*, 1974, 30, 1465-1471.
4. K. M. Harmon, A. C. Akin, G. F. Avci, L. S. Nowos and M. B. Tierney, *Journal of Molecular Structure*, 1991, 244, 223-236.
5. L. Tanzi, P. Benassi, M. Nardone and F. Ramondo, *The Journal of Physical Chemistry A*, 2014, 118, 12229-12240.

3. Choline-Chloride Ion Pairs

3.1 Relative Energies

Table S5. Absolute and relative electronic energies of the choline chloride ion pairs: without any corrections, with ZPE corrections and with both ZPE and CP corrections. Absolute and relative Gibbs free energies of the choline chloride ion pairs.

Ion Pair	E /au	ΔE_{rel} /kJ mol^{-1}	E+ZPE /au	ΔE_{rel} (with ZPE correction) /kJ mol^{-1}	BSSE /kJ mol^{-1}	ΔE_{rel} (with ZPE + CP correction) /kJ mol^{-1}	G /au	ΔG_{rel} /kJ mol^{-1}
A_ChG	-789.281345	0.000	-789.083878	0.000	3.370	0.000	-789.118673	0.00
B_ChG	-789.281068	0.726	-789.083596	0.739	3.444	0.814	-789.118466	0.54
C_ChG	-789.276470	12.799	-789.079141	12.436	3.146	12.213	-789.114741	10.32
A_ChT	-789.273526	20.529	-789.075726	21.403	3.424	21.457	-789.111892	17.80
D_ChG	-789.269489	31.128	-789.072746	29.227	2.883	28.740	-789.108700	26.18
E_ChG	-789.269206	31.870	-789.072290	30.423	2.738	29.792	-789.108726	26.12
B_ChT	-789.267669	35.906	-789.071038	33.711	2.778	33.119	-789.107688	28.84
C_ChT	-789.266262	39.600	-789.069471	37.825	3.045	37.501	-789.105349	34.98

3.2 Estimation of the Coulomb Interaction

Table S6. Estimated Coulomb interaction within each choline chloride ion pair, assuming the ions are point charges with the positive charge centred on the nitrogen of choline and the negative charge on chloride. The Coulomb potential has been estimated using charges of unity and a reduced charge of +/- 0.9e. Δr is the separation between the ions (i.e. the distance between the N centre of choline and Cl), E_a is the total association energy of the ion pair and E_C is the estimated Coulomb potential. ΔE corresponds to the difference between the total association energy and the estimated Coulomb potential.

			|q| = 1 e		|q| = 0.9 e	
Ion Pair	**Δr (N···Cl)/ Å**	E_a /kJ mol^{-1}	E_C / kJ mol^{-1}	ΔE (E_C - E_a) /kJ mol^{-1}	E_C / kJ mol^{-1}	ΔE (E_C - E_a) /kJ mol^{-1}
A_ChG	3.84	-409	-362	+47	-293	+116
B_ChG	3.60	-408	-386	+22	-313	+95
C_ChG	3.55	-397	-391	+6	-317	+80
A_ChT	3.63	-380	-383	+4	-310	+77
D_ChG	3.59	-379	-387	-7	-314	+66
E_ChG	3.60	-387	-386	-7	-313	+66
B_ChT	3.58	-376	-388	-12	-314	+62
C_ChT	3.77	-371	-369	+2	-299	+72

3.3 H-Bond Data

Table S7. H-bond lengths (r), $E^{(2)}$ values and selected topological properties of the ρ(r) at the BCPs for the individual H-bonds within the choline chloride ion pairs

A_ChG					
H-bond	**r/Å**	**$\Sigma E^{(2)}$/ kJ mol^{-1}**	**ρ_{BCP}/au**	**$\nabla^2\rho_{BCP}$ /au**	**H /au**
Intra CH…O(H)	2.519	-	0.0113	0.0417	0.00142
CH…Cl (a)	2.417	30.25	0.0180	0.0514	0.00176
CH…Cl (b)	2.381	38.24	0.0193	0.0540	0.00167
OH…Cl	2.090	89.37	0.0340	0.0722	-0.00315
B_ChG					
H-bond	**r/Å**	**$\Sigma E^{(2)}$/ kJ mol^{-1}**	**ρ_{BCP}/au**	**$\nabla^2\rho_{BCP}$ /au**	**H /au**
Intra CH…O(H)	2.432	-	0.0141	0.0512	0.00157
CH…Cl (a)	2.433	26.82	0.0178	0.0513	0.00178
CH…Cl (b)	2.714	9.92	0.0109	0.0298	0.00123
CH…Cl (c)	2.353	32.47	0.0213	0.0630	0.00170
OH…Cl	2.214	59.79	0.0256	0.0622	-0.00011
C_ChG					
H-bond	**r/Å**	**$\Sigma E^{(2)}$/ kJ mol^{-1}**	**ρ_{BCP}/au**	**$\nabla^2\rho_{BCP}$ /au**	**H /au**
Intra CH…O(H)	2.289	3.77	0.0141	0.0518	0.00190
CH…Cl (a)	2.375	34.85	0.0199	0.0561	0.00164
CH…Cl (b)	2.532	18.90	0.0150	0.0423	0.00163
CH…Cl (c)	2.381	29.54	0.0203	0.0589	0.00173
D_ChG					
H-bond	**r/Å**	**$\Sigma E^{(2)}$/ kJ mol^{-1}**	**ρ_{BCP}/au**	**$\nabla^2\rho_{BCP}$ /au**	**H /au**
Intra CH…O(H)	2.254	4.56	0.0150	0.0573	0.00216
CH…Cl (a)	2.444	27.07	0.0174	0.0492	0.00170
CH…Cl (b)	2.388	34.35	0.0194	0.0539	0.00164
CH…Cl (c)	2.351	37.99	0.0209	0.0584	0.00155
E_ChG					
H-bond	**r/Å**	**$\Sigma E^{(2)}$/ kJ mol^{-1}**	**ρ_{BCP}/au**	**$\nabla^2\rho_{BCP}$ /au**	**H /au**
Intra CH…O(H)	2.319	2.09	0.0141	0.0508	0.00176
CH…Cl (a)	2.443	27.66	0.0174	0.0491	0.00170
CH…Cl (b)	2.350	39.20	0.0208	0.0572	0.00151
CH…Cl (c)	2.356	38.45	0.0206	0.0569	0.00155
A_ChT					
H-bond	**r/Å**	**$\Sigma E^{(2)}$/ kJ mol^{-1}**	**ρ_{BCP}/au**	**$\nabla^2\rho_{BCP}$ /au**	**H /au**
CH…Cl (a)	2.378	35.27	0.0196	0.0551	0.00168
CH…Cl (b)	2.898	4.85	0.0082	0.0217	0.00084
CH…Cl (c)	2.354	30.54	0.0216	0.0651	0.00176
OH…Cl	2.545	16.07	0.0133	0.0375	0.00140
B_ChT					
H-bond	**r/Å**	**$\Sigma E^{(2)}$/ kJ mol^{-1}**	**ρ_{BCP}/au**	**$\nabla^2\rho_{BCP}$ /au**	**H /au**
CH…Cl (a)	2.367	36.53	0.0202	0.0559	0.00157
CH…Cl (b)	2.367	36.53	0.0202	0.0559	0.00157
CH…Cl (c)	2.382	34.60	0.0196	0.0548	0.00163
C_ChT					
H-bond	**r/Å**	**$\Sigma E^{(2)}$/ kJ mol^{-1}**	**ρ_{BCP}/au**	**$\nabla^2\rho_{BCP}$ /au**	**H /au**
CH…Cl (a)	2.312	47.95	0.0224	0.0603	0.00130
CH…Cl (b)	2.312	47.70	0.0224	0.0603	0.00129
CH…Cl (c)	2.835	1.55	0.0103	0.0354	0.00160
CH…Cl (d)	2.835	1.55	0.0103	0.0354	0.00160

3.4 Selected QTAIM Molecular Graphs

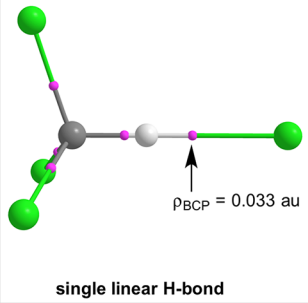

Figure S5. QTAIM molecular graph of chloroform-chloride complex.

4. Urea Monomers and Urea-Urea Dimers

4.1 Conformers and Relative Energies

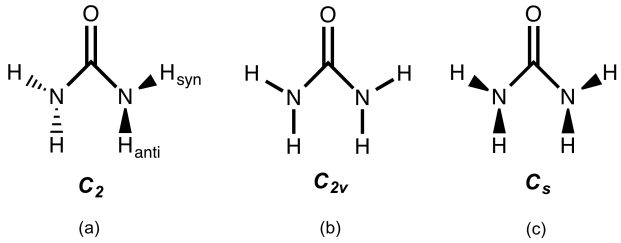

Figure S6. Conformers of urea.

Table S8. Absolute and relative electronic energies of the urea conformers with and without ZPE correction.

Urea Conformer	E /au	ΔE_{rel} /kJ mol^{-1}	E+ZPE /au	ΔE_{rel} (with ZPE correction) /kJ mol^{-1}	G /au	ΔG_{rel} /kJ mol^{-1}
C_2	-225.353480	0.000	-225.289997	1.357	-225.316305	0.84
C_{2v}	-225.351956	4.00	-225.290514	0.000	-225.316624	0.00
C_s	-225.352295	3.11	-225.289862	1.712		

Table S9. Absolute and relative electronic energies of the urea-urea dimers: without any corrections, with ZPE corrections and with both ZPE and CP corrections. Absolute and relative Gibbs free energies of the urea-urea dimers.

Dimer	E /au	ΔE_{rel} /kJ mol^{-1}	E+ZPE /au	ΔE_{rel} (with ZPE correction) /kJ mol^{-1}	BSSE /kJ mol^{-1}	ΔE_{rel} (with ZPE + CP correction) /kJ mol^{-1}	G /au	ΔG_{rel} /kJ mol^{-1}
Ribbon	-450.732052	0.000	-450.603139	0.000	2.193	0.000	-450.639159	0.00
Distorted Chain	-450.728823	8.476	-450.599592	9.314	2.325	9.446	-450.635657	9.19

Comment on urea dimer distorted chain motif: Within the distorted chain a chelating H-bond motif is observed where the oxygen atom of one urea interacts with two different hydrogen atoms of the other urea. Each individual interaction is weaker than the analogous interaction in the ribbon dimer, **Figure 6b**. The sum for the combined H-bonding interactions $\Sigma\rho_{BCP} = 0.058$ au. The contributions from the individual urea fragments to any given MO is very unequal, **Figure 6b**. Moreover, the delocalisation between the urea units $E^{(2)}$ only equates to a total of 63.2 kJ mol^{-1}. Thus, there is a substantially reduced degree of delocalisation within the distorted chain motif.

4.2 H-Bond Data

Table S10. H-bond lengths (r), $E^{(2)}$ values and selected topological properties of the ρ(r) at the BCPs for the individual H-bonds within the urea dimers

Ribbon					
H-bond	**r/Å**	**$\Sigma E^{(2)}$/ kJ mol^{-1}**	**ρ_{BCP}/au**	**$\nabla^2\rho_{BCP}$ /au**	**H /au**
NH…O=C (a)	1.826	68.53	0.0332	0.1123	0.00059
NH…O=C (b)	1.825	68.91	0.0332	0.1124	0.00057
Distorted Chain					
H-bond	**r/Å**	**$\Sigma E^{(2)}$/ kJ mol^{-1}**	**ρ_{BCP}/au**	**$\nabla^2\rho_{BCP}$ /au**	**H /au**
NH…O=C (a)	1.990	26.74	0.0229	0.0838	0.00232
NH…O=C (b)	2.397	4.52	0.0118	0.0389	0.00108
NH…N	2.088	31.97	0.0225	0.0696	0.00167

5. Urea – Chloride Complexed Anions

5.1 Relative Energies

Table S11. Absolute and relative electronic energies of the urea-chloride complexes: without any corrections, with ZPE corrections and with both ZPE and CP corrections. Absolute and relative Gibbs free energies of the urea-chloride complexes.

Complex	E /au	ΔE_{rel} /kJ mol^{-1}	E+ZPE /au	ΔE_{rel} (with ZPE correction) /kJ mol^{-1}	BSSE /kJ mol^{-1}	ΔE_{rel} (with ZPE + CP correction) /kJ mol^{-1}	G /au	ΔG_{rel} /kJ mol^{-1}
1.0.0_A	-685.699365	0.000	-685.634804	0.000	1.428	0.000	-685.665596	0.00
1.0.0_B‡	-685.679640	51.790	-685.615991	49.394	1.360	49.325	-685.649291	42.81
2.0.0_A	-911.087208	0.000	-910.958020	0.000	4.186	0.000	-911.004318	0.00
2.0.0_B	-911.086767	1.158	-910.957573	1.174	4.089	1.077	-911.000890	9.00
1.1.0_A	-911.083968	8.507	-910.954439	9.402	3.772	8.987	-910.998429	15.46
1.1.0_B	-911.074102	34.410	-910.944666	35.062	3.980	34.855	-910.986157	47.68
2.1.0_A	-1136.478947	0.000	-1136.281542	**0.000**	8.642	0.000	-1136.327149	**16.22**
2.1.0_B	-1136.470841	21.282	-1136.276361	**13.602**	6.441	11.401	-1136.332518	**2.12**
2.1.0_C	-1136.469377	25.128	-1136.275091	**16.939**	6.074	14.370	-1136.330801	**6.63**
3.0.0_A	-1136.468913	26.344	-1136.275124	**16.851**	6.486	14.694	-1136.333325	**0.00**
1.1.1_A	-1136.466189	33.496	-1136.271542	26.255	6.070	23.683	-1136.325532	20.46
2.1.0_D	-1136.462255	43.825	-1136.267980	35.607	6.286	33.251	-1136.323846	24.89
1.2.0_A	-1136.465543	35.193	-1136.268539	34.140	8.009	33.507	-1136.315468	46.88
2.1.0_E	-1136.462038	44.394	-1136.267728	36.268	6.363	33.988	-1136.321318	31.52
1.1.1_B	-1136.459629	50.719	-1136.264902	43.688	6.001	41.056	-1136.318422	39.13
1.1.1_C	-1136.454424	64.385	-1136.259575	57.674	6.543	55.575	-1136.310453	60.05
1.2.0_A	-1136.448052	81.116	-1136.253382	73.935	6.436	71.729	-1136.304608	75.40

‡ Structure 1.0.0_B can be obtained at the B3LYP level without constraints. Re-optimisation of B3LYP 1.0.0_B with inclusion of the D2 dispersion correction returned a structure with the chelating H-bond motif (i.e. 1.0.0_A). To isolate 1.0.0_B at the B3LYP-D2 level it was necessary to constrain the NH···Cl distance; vibrational analysis of this structure returned no negative frequencies.

5.2 Structures

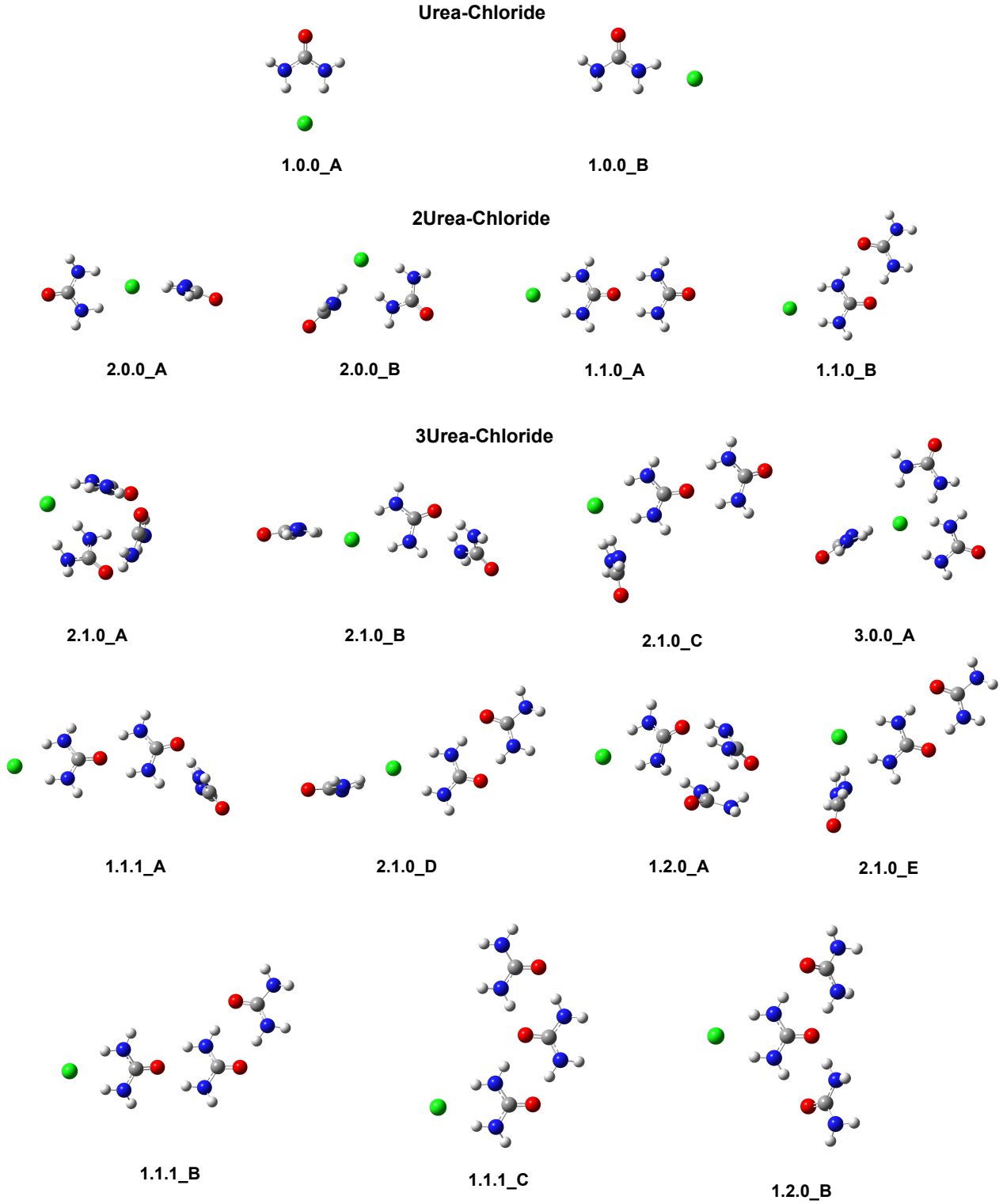

Figure S7. Urea-chloride complexes.

5.3 Geometries of Urea-Chloride Complexes

The simplified representations of the urea-chloride complexes do not illustrate the full complexity of the geometries of these structures. For example, the four NH···Cl H-bonds in structure 2.0.0_A are in a tetrahedral arrangement about the chloride centre, **Figure S8 a**. Within structure 2.0.0_B, the two urea molecules are found to have "slipped" closer together, leaving one side of chloride exposed, **Figure S8 b**. Structure 2.0.0_B therefore appears to be the intermediate between tetrahedral 2.0.0_A and the distorted octahedral structure of 3.0.0, **Figure S8 c**. Furthermore, the geometry of urea shows some variation within the complexes, adopting predominantly either a C_s or C_2 conformation, and almost exclusively the C_s conformation when directly coordinated to chloride.

Cooperative effects are thought to influence the geometry of urea oligomers, stabilising the chain motif for larger aggregates.[1,2] At the Hartree-Fock level it is estimated that for tetramers and above the energy for the successive addition of urea favours the chain motif.[1] Within the *n*.urea-chloride complexes, n=2,3, it is found that the urea-urea chain motif is favoured over the ribbon, despite the latter being energetically favoured when isolated. For example, structure 1.1.0_A (chain) is ≈ 26 kJ mol^{-1} lower in energy than structure 1.1.0_B (ribbon). This would suggest that chloride enhances the cooperative effect in these short urea chains.

Furthermore, the urea-urea interaction within 1.1.0_A (**Figure S9 a)** is a linear, rather than distorted, chain motif, again indicating cooperative effects within the [chloride-urea-urea] unit. However, this effect is short ranged. For example, within structure 1.1.1_A, **Figure S9 b**, the chain interaction between urea in the 2nd and 3rd coordination shells is distorted. The influence of chloride on the urea-urea chain interaction can also be attenuated by complexing chloride to another urea, e.g. 2.1.0_B, **Figure S9 c**. In this case, the chloride can be thought of as effectively being "pulled" in two opposite directions (reducing its long-range effect in one direction).

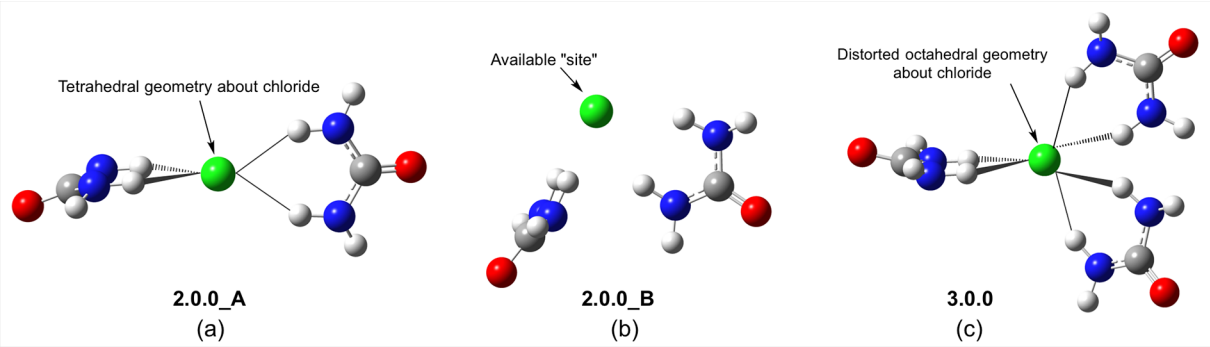

Figure S8. Geometry of selected urea-chloride complexes

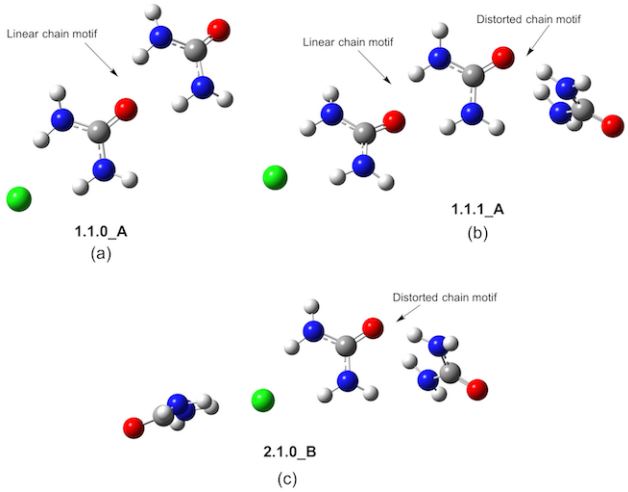

Figure S9. Examples of urea-chloride complexes featuring the linear and distorted chain motifs

1. A. Masunov and J. J. Dannenburg, *The Journal of Physical Chemistry B*, 2001, 104, 806-810
2. J. J. Dannenburg, *Journal of Molecular Structure*, 2002, 615, 219-226

5.4 H-Bond Data

Table S12. H-bond lengths (r), $E^{(2)}$ values and selected topological properties of the ρ(r) at the BCPs for the individual H-bonds within the urea-chloride complexes

1.0.0_A					
H-bond	**r/Å**	**$\Sigma E^{(2)}$/ kJ mol^{-1}**	**ρ_{BCP}/au**	**$\nabla^2\rho_{BCP}$ /au**	**H /au**
NH…Cl (a)	2.321	43.10	0.0203	0.0555	0.00137
NH…Cl (b)	2.322	42.89	0.0203	0.0555	0.00137
1.0.0_B					
H-bond	**r/Å**	**$\Sigma E^{(2)}$/ kJ mol^{-1}**	**ρ_{BCP}/au**	**$\nabla^2\rho_{BCP}$ /au**	**H /au**
NH…Cl (a)	2.320	38.58	0.0203	0.0577	0.00154
2.0.0_A					
H-bond	**r/Å**	**$\Sigma E^{(2)}$/ kJ mol^{-1}**	**ρ_{BCP}/au**	**$\nabla^2\rho_{BCP}$ /au**	**H /au**
NH…Cl (a)	2.382	29.83	0.0174	0.0510	0.00170
NH…Cl (b)	2.379	32.84	0.0175	0.0512	0.00171
NH…Cl (c)	2.381	31.38	0.0174	0.0510	0.00170
NH…Cl (d)	2.380	32.22	0.0175	0.0511	0.00171
2.0.0_B					
H-bond	**r/Å**	**$\Sigma E^{(2)}$/ kJ mol^{-1}**	**ρ_{BCP}/au**	**$\nabla^2\rho_{BCP}$ /au**	**H /au**
NH…Cl (a)	2.34385	37.15	0.0193	0.0549	0.00156
NH…Cl (b)	2.36547	35.31	0.0183	0.0528	0.00168
NH…Cl (c)	2.50221	20.38	0.0142	0.0415	0.00172
NH…Cl (d)	2.36629	34.52	0.0180	0.0521	0.00173
1.1.0_A					
H-bond	**r/Å**	**$\Sigma E^{(2)}$/ kJ mol^{-1}**	**ρ_{BCP}/au**	**$\nabla^2\rho_{BCP}$ /au**	**H /au**
NH…Cl (a)	2.252	55.69	0.0236	0.0613	0.00072
NH…Cl (b)	2.253	55.40	0.0235	0.0612	0.00074
NH…O=C (a)	1.968	31.25	0.0234	0.0903	0.00262
NH…O=C (b)	1.968	31.17	0.0235	0.0905	0.00262
1.1.0_B					
H-bond	**r/Å**	**$\Sigma E^{(2)}$/ kJ mol^{-1}**	**ρ_{BCP}/au**	**$\nabla^2\rho_{BCP}$ /au**	**H /au**
NH…Cl (a)	2.406	40.67	0.0170	0.0485	0.00174
NH…Cl (b)	2.236	59.83	0.0243	0.0624	0.00054
NH…O=C (a)	2.077	26.48	0.0188	0.0664	0.00219
NH…O=C (b)	1.697	118.16	0.0464	0.1330	-0.00047
2.1.0_A					
H-bond	**r/Å**	**$\Sigma E^{(2)}$/ kJ mol^{-1}**	**ρ_{BCP}/au**	**$\nabla^2\rho_{BCP}$ /au**	**H /au**
NH…Cl (a)	2.594	14.77	0.0120	0.0357	0.00096
NH…Cl (b)	2.356	35.61	0.0191	0.0534	0.00154
NH…Cl (c)	2.361	37.11	0.0184	0.0525	0.00165
NH…Cl (d)	2.386	34.02	0.0181	0.0512	0.00160
NH…O=C (a)	1.971	34.52	0.0248	0.0857	0.00183
NH…O=C (b)	2.033	23.97	0.0208	0.0728	0.00213
NH…O=C (c)	2.155	15.36	0.0181	0.0597	0.00149
NH…O=C (d)	2.058	17.95	0.0205	0.0727	0.00203
NH…N (a)	2.646	1.72	0.0085	0.0280	0.00096
NH…N (b)	2.783	0.88	0.0068	0.0248	0.00100
2.1.0_B					
H-bond	**r/Å**	**$\Sigma E^{(2)}$/ kJ mol^{-1}**	**ρ_{BCP}/au**	**$\nabla^2\rho_{BCP}$ /au**	**H /au**
NH…Cl (a)	2.393	30.13	0.0169	0.0500	0.00176
NH…Cl (b)	2.391	30.96	0.0170	0.0503	0.00176
NH…Cl (c)	2.293	45.48	0.0211	0.0590	0.00129
NH…Cl (d)	2.368	32.97	0.0179	0.0524	0.00168
NH…O=C (a)	2.060	23.35	0.0217	0.0738	0.00175
NH…O=C (b)	1.959	32.80	0.0252	0.0901	0.00200
NH…N	2.432	8.08	0.0112	0.0357	0.00143

2.1.0_C					
H-bond	**r/Å**	**$\Sigma E^{(2)}$/ kJ mol^{-1}**	**ρ_{BCP}/au**	**$\nabla^2\rho_{BCP}$ /au**	**H /au**
NH…Cl (a)	2.359	33.68	0.01874	0.054047	0.001643
NH…Cl (b)	2.372	33.60	0.01807	0.0524	0.00172
NH…Cl (c)	2.444	26.19	0.01600	0.0466	0.00172
NH…Cl (d)	2.304	44.89	0.02064	0.0577	0.00140
NH…O=C (a)	1.995	26.95	0.02168	0.0857	0.00281
NH…O=C (b)	1.977	28.58	0.02298	0.0884	0.00262
NH…N	2.672	1.92	0.00708	0.0241	0.00099
3.0.0_A					
H-bond	**r/Å**	**$\Sigma E^{(2)}$/ kJ mol^{-1}**	**ρ_{BCP}/au**	**$\nabla^2\rho_{BCP}$ /au**	**H /au**
NH…Cl (a)	2.415	28.20	0.0161	0.0486	0.00185
NH…Cl (b)	2.471	21.88	0.0147	0.0441	0.00175
NH…Cl (c)	2.468	22.68	0.0149	0.0446	0.00172
NH…Cl (d)	2.453	22.68	0.0150	0.0454	0.00182
NH…Cl (e)	2.431	25.31	0.0156	0.0472	0.00182
NH…Cl (f)	2.423	24.44	0.0158	0.0478	0.00182
NH…N	2.915	0.50	0.0061	0.0217	0.00092
1.1.1_A					
H-bond	**r/Å**	**$\Sigma E^{(2)}$/ kJ mol^{-1}**	**ρ_{BCP}/au**	**$\nabla^2\rho_{BCP}$ /au**	**H /au**
NH…Cl (a)	2.238	58.74	0.0244	0.0625	0.00052
NH…Cl (b)	2.240	58.28	0.0242	0.0623	0.00057
NH…O=C (a)	1.959	30.46	0.0233	0.0934	0.00287
NH…O=C (b)	1.897	41.63	0.0279	0.1049	0.00215
NH…O=C (c)	1.981	28.79	0.0239	0.0863	0.00211
NH…O=C (d)	2.030	26.99	0.0230	0.0779	0.00170
NH…N	2.464	6.61	0.0105	0.0347	0.00147
2.1.0_D					
H-bond	**r/Å**	**$\Sigma E^{(2)}$/ kJ mol^{-1}**	**ρ_{BCP}/au**	**$\nabla^2\rho_{BCP}$ /au**	**H /au**
NH…Cl (a)	2.377	32.93	0.0176	0.0513	0.00170
NH…Cl (b)	2.376	33.47	0.0177	0.0514	0.00170
NH…Cl (c)	2.296	44.64	0.0209	0.0585	0.00133
NH…Cl (d)	2.478	21.59	0.0142	0.0430	0.00180
NH…O=C (a)	2.018	33.43	0.0213	0.0760	0.00227
NH…O=C (b)	1.715	110.21	0.0442	0.1306	-0.00366
1.2.0_A					
H-bond	**r/Å**	**$\Sigma E^{(2)}$/ kJ mol^{-1}**	**ρ_{BCP}/au**	**$\nabla^2\rho_{BCP}$ /au**	**H /au**
NH…Cl (a)	2.305	46.48	0.0211	0.0571	0.00124
NH…Cl (b)	2.179	72.97	0.0277	0.0669	-0.00046
NH…O=C (a)	2.316	8.08	0.0121	0.0392	0.00123
NH…O=C (b)	2.020	21.67	0.0223	0.0795	0.00204
NH…O=C (c)	1.896	46.32	0.0288	0.1042	0.00174
NH…O=C (d)	2.476	2.38	0.0105	0.0354	0.00114
NH…O=C (e)	2.066	22.47	0.0211	0.0710	0.00175
NH…N (a)	2.555	2.97	0.0103	0.0323	0.00110
NH…N (b)	2.211	19.46	0.0174	0.0545	0.00185
2.1.0_E					
H-bond	**r/Å**	**$\Sigma E^{(2)}$/ kJ mol^{-1}**	**ρ_{BCP}/au**	**$\nabla^2\rho_{BCP}$ /au**	**H /au**
NH…Cl (a)	2.352	35.02	0.0190	0.0542	0.00159
NH…Cl (b)	2.362	35.40	0.0185	0.0531	0.00167
NH…Cl (c)	2.342	39.12	0.0195	0.0548	0.00150
NH…Cl (d)	2.504	21.34	0.0136	0.0409	0.00184
NH…O=C (a)	2.027	31.67	0.0209	0.0746	0.00226
NH…O=C (b)	1.709	112.84	0.0449	0.1315	-0.00394
1.1.1_B					
H-bond	**r/Å**	**$\Sigma E^{(2)}$/ kJ mol^{-1}**	**ρ_{BCP}/au**	**$\nabla^2\rho_{BCP}$ /au**	**H /au**
NH…Cl (a)	2.260	54. 10	0.0232	0.0606	0.00083
NH…Cl (b)	2.253	55.44	0.0235	0.0612	0.00074
NH…O=C (a)	2.023	24.60	0.0205	0.0806	0.00275
NH…O=C (b)	1.913	38.58	0.0266	0.1013	0.00236
NH…O=C (c)	1.983	37.49	0.0230	0.0823	0.00223
NH…O=C (d)	1.728	103.70	0.0428	0.1283	-0.00300

1.1.1_C					
H-bond	**r/Å**	**$\Sigma E^{(2)}$/ kJ mol^{-1}**	**ρ_{BCP}/au**	**$\nabla^2\rho_{BCP}$ /au**	**H /au**
NH…Cl (a)	2.357	38.70	0.0188	0.0527	0.00159
NH…Cl (b)	2.272	52.01	0.0225	0.0594	0.00097
NH…O=C (a)	2.008	30.42	0.0220	0.0795	0.00221
NH…O=C (b)	1.713	113.47	0.0447	0.1292	-0.00400
NH…O=C (c)	1.924	47.45	0.0266	0.0929	0.00182
NH…O=C (d)	1.744	92.51	0.0406	0.1286	-0.00192
1.2.0_B					
H-bond	**r/Å**	**$\Sigma E^{(2)}$/ kJ mol^{-1}**	**ρ_{BCP}/au**	**$\nabla^2\rho_{BCP}$ /au**	**H /au**
NH…Cl (a)	2.299	47.95	0.0212	0.0575	0.00124
NH…Cl (b)	2.299	47.95	0.0212	0.0575	0.00124
NH…O=C (a)	2.099	22.93	0.0178	0.0628	0.00211
NH…O=C (b)	2.097	23.01	0.0179	0.0630	0.00211
NH…O=C (c)	1.722	95.90	0.0437	0.1308	-0.00342
NH…O=C (d)	1.722	95.98	0.0436	0.1308	-0.00341

5.5 Selected Molecular Orbitals

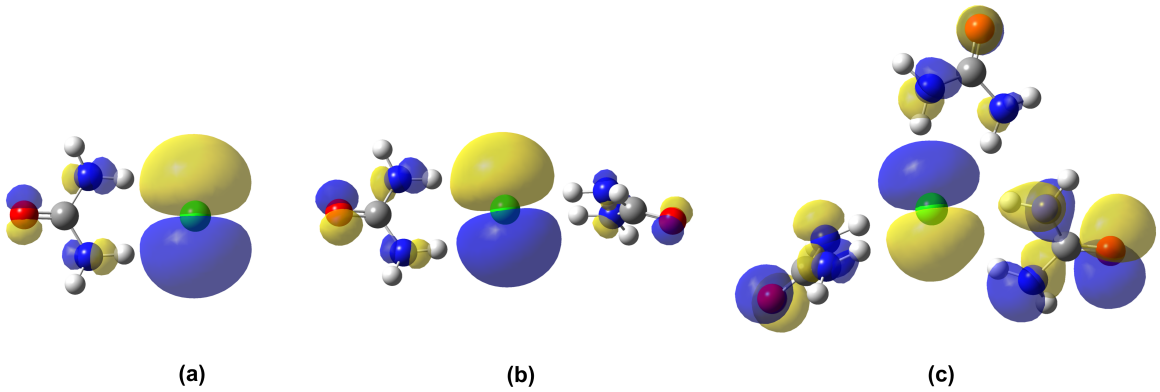

Figure S10. HOMO-1 of (a) [urea.Cl]$^-$ (1.0.0 A), (b) [urea$_2$.Cl]$^-$ (2.0.0 A) and (c) [urea$_3$.Cl]$^-$ (3.0.0 A) generated at the 0.02 au isosurface.

6. Choline –Urea Pairs

6.1 Relative Energies

Table S13. Absolute and relative electronic energies of the choline urea pairs: without any corrections, with ZPE corrections and with both ZPE and CP corrections. Absolute and relative Gibbs free energies of the choline urea pairs.

Ion Pair	E /au	ΔE_{rel} /kJ mol^{-1}	E+ZPE /au	ΔE_{rel} (with ZPE correction) /kJ mol^{-1}	BSSE /kJ mol^{-1}	ΔE_{rel} (with ZPE + CP correction) /kJ mol^{-1}	G /au	ΔG_{rel} /kJ mol^{-1}
A_UChG	-554.207244	0.000	-553.945257	**0.000**	2.674	0.000	-553.988192	**0.85**
B_UChG	-554.204551	7.070	-553.943473	**4.683**	1.489	3.499	-553.988003	**1.35**
C_UChG	-554.204543	7.091	-553.943287	**5.172**	1.769	4.267	-553.988517	**0.00**
D_UChG	-554.203266	10.444	-553.942222	**7.968**	1.258	6.552	-553.987777	**1.94**
E_UChG	-554.203337	10.258	-553.942235	7.935	1.517	6.778	-553.986537	5.20
F_UChG	-554.202443	12.604	-553.940014	13.765	2.921	14.012	-553.981183	19.26
A_UChT	-554.200689	17.209	-553.939064	16.258	2.804	16.389	-553.981385	18.73
B_UChT	-554.197555	25.437	-553.936973	21.748	1.276	20.350	-553.983119	14.17
C_UCht	-554.199468	20.416	-553.936970	21.757	2.807	21.891	-553.979565	23.50
D_UChT	-554.196133	29.172	-553.935585	25.394	1.737	24.458	-553.980414	21.27

6.2 H-Bond Data

Table S14. H-bond lengths (r), $E^{(2)}$ values and selected topological properties of the ρ(r) at the BCPs for the individual H-bonds within the choline-urea pair

A_UChG					
H-bond	**r/Å**	**$\Sigma E^{(2)}$/ kJ mol^{-1}**	**ρ_{BCP}/au**	**$\nabla^2\rho_{BCP}$ /au**	**H /au**
Intra CH…O(H)	2.474	-	0.0118	0.0430	0.00165
CH…O=(a)	2.298	6.15	0.0094	0.0338	0.00132
CH…O=(b)	2.434	3.89	0.0119	0.0426	0.00168
OH…O=	1.683	114.39	0.0489	0.1420	-0.00565
NH…O(H)	2.477	3.72	0.0092	0.0373	0.00162
B_UChG					
H-bond	**r/Å**	**$\Sigma E^{(2)}$/ kJ mol^{-1}**	**ρ_{BCP}/au**	**$\nabla^2\rho_{BCP}$ /au**	**H /au**
Intra CH…O(H)	2.229	4.77	0.0159	0.0605	0.00228
CH…O=(a)	2.279	9.71	0.0134	0.0466	0.00171
CH…O=(b)	2.319	5.73	0.0123	0.0425	0.00154
CH…O=(c)	2.245	9.04	0.0144	0.0520	0.00195
C_UChG					
H-bond	**r/Å**	**$\Sigma E^{(2)}$/ kJ mol^{-1}**	**ρ_{BCP}/au**	**$\nabla^2\rho_{BCP}$ /au**	**H /au**
Intra CH…O(H)	2.179	8.83	0.0184	0.0673	0.00226
OH…O=	1.648	124.81	0.0497	0.1510	-0.00579
D_UChG					
H-bond	**r/Å**	**$\Sigma E^{(2)}$/ kJ mol^{-1}**	**ρ_{BCP}/au**	**$\nabla^2\rho_{BCP}$ /au**	**H /au**
Intra CH…O(H)	2.240	4.44	0.0157	0.0593	0.00221
CH…O=(a)	2.297	8.79	0.0129	0.0443	0.00160
CH…O=(b)	2.241	8.12	0.0137	0.0502	0.00120
CH…O=(c)	2.239	10.38	0.0141	0.0507	0.00194
E_UChG					
H-bond	**r/Å**	**$\Sigma E^{(2)}$/ kJ mol^{-1}**	**ρ_{BCP}/au**	**$\nabla^2\rho_{BCP}$ /au**	**H /au**
Intra CH…O(H)	2.237	4.31	0.0158	0.0598	0.00223
CH…O=(a)	2.286	8.08	0.0132	0.0456	0.00165
CH…O=(b)	2.258	9.83	0.0135	0.0485	0.00188
CH…O=(c)	2.238	9.46	0.0142	0.0513	0.00194

F_UChG					
H-bond	**r/Å**	**$\Sigma E^{(2)}$/ kJ mol^{-1}**	**ρ_{BCP}/au**	**$\nabla^2\rho_{BCP}$ /au**	**H /au**
Intra CH…O(H)	2.458	-	0.0128	0.0465	0.00154
CH…O=(a)	2.384	4.81	0.0109	0.0348	0.00113
CH…O=(b)	2.240	8.91	0.0130	0.0493	0.00210
CH…O=(c)	2.440	4.60	0.0116	0.0358	0.00089
OH…N	2.165	20.08	0.0192	0.0587	0.00152
A_UChT					
H-bond	**r/Å**	**$\Sigma E^{(2)}$/ kJ mol^{-1}**	**ρ_{BCP}/au**	**$\nabla^2\rho_{BCP}$ /au**	**H /au**
CH…O=(a)	2.185	10.33	0.0157	0.0581	0.00222
CH…O=(b)	2.480	2.68	0.0086	0.0307	0.00116
CH…O=(c)	2.041	25.65	0.0238	0.0817	0.00205
NH…O(H)	2.136	19.71	0.0164	0.0583	0.00206
B_UChT					
H-bond	**r/Å**	**$\Sigma E^{(2)}$/ kJ mol^{-1}**	**ρ_{BCP}/au**	**$\nabla^2\rho_{BCP}$ /au**	**H /au**
CH…O=(a)	2.248	10.79	0.0141	0.0497	0.00186
CH…O=(b)	2.249	9.37	0.0139	0.0496	0.00187
CH…O=(c)	2.246	8.45	0.0138	0.0499	0.00191
C_UChT					
H-bond	**r/Å**	**$\Sigma E^{(2)}$/ kJ mol^{-1}**	**ρ_{BCP}/au**	**$\nabla^2\rho_{BCP}$ /au**	**H /au**
CH…O=(a)	2.559	1.76	0.0082	0.0268	0.00089
CH…O=(b)	2.464	1.51	0.0099	0.0385	0.00148
OH…O=	1.879	45.06	0.0320	0.1043	0.00001
NH…O(H)	2.403	5.65	0.0105	0.0386	0.00153
D_UChT					
H-bond	**r/Å**	**$\Sigma E^{(2)}$/ kJ mol^{-1}**	**ρ_{BCP}/au**	**$\nabla^2\rho_{BCP}$ /au**	**H /au**
CH…O=(a)	2.204	13.43	0.0151	0.0511	0.00208
CH…O=(b)	2.204	13.18	0.0152	0.0545	0.00207
CH…O=(c)	2.641	0.50	0.0082	0.0329	0.00137
CH…O=(d)	2.642	0.46	0.0082	0.0330	0.00138

7. Comparison of H-bonding and Pair Interactions

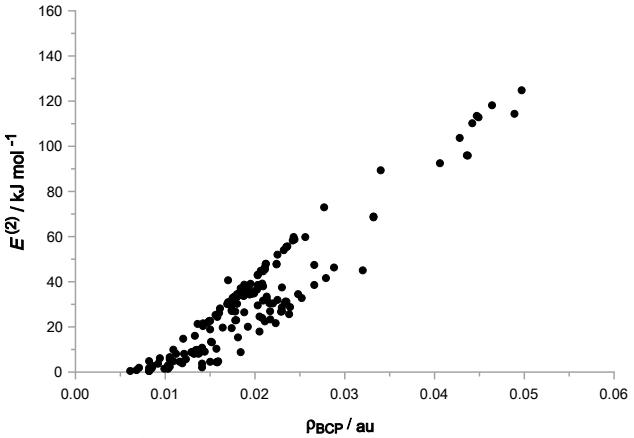

Figure S11. $E^{(2)}$ and ρ_{BCP} values for all H-bonds isolated herein.

8. Validation Calculations

Table S15. Single point energies of selected structures computed at the MP2/aug-cc-pVTZ and CCSD(T)/aug-cc-pVDZ levels of theory (using B3LYP-D2/6-311++G(d,p) geometries).

System	MP2/aug-cc-pVTZ				CCSD(T)/aug-cc-pVDZ	
	E **/au**	**ΔE_{rel} /kJ mol^{-1}**	**BSSE /kJ mol^{-1}**	**ΔE_{rel} (with CP correction) /kJ mol^{-1}**	***E*** **/au**	**ΔE_{rel} /kJ mol^{-1}**
Isolated						
Choline (gauche)	-328.184071	-	-	-	-327.891381	-
Urea (C_2)	-224.977728	-	-	-	-224.771749	-
Choline chloride						
A_ChG	-788.165177	0.00	18.98	0.00	-787.798335	0.00
B_ChG	-788.164503	1.77	18.15	0.94	-787.797810	1.38
C_ChG	-788.158896	16.49	15.62	13.14	-787.792925	14.20
Urea dimer						
ribbon	-449.982105	-	14.00	-	-449.567604	-
Urea chloride clusters						
1.0.0_A	-684.839049	-	-	-	-684.560185	-
2.0.0_A	-909.853979	0.00	20.54	0.00	-909.367242	0.00
1.1.0_A	-909.849938	10.61	22.25	12.32	-909.362771	11.74
3.0.0_A	-1134.863092	-	32.35	-	-	-
Urea choline pairs						
A_UChG	-553.197093	0.00	16.01	0.00	-552.696302	0.00
B_UChG	-553.194651	6.41	11.25	1.65	-552.694269	5.34