Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

What a Difference a Methyl Group Makes – Probing Choline-Urea Molecular Interactions Through Urea Structure Modification

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Table S1. Experimental SLE data (choline chloride mole fraction-x_1, temperature-T) and activity coefficients for cholinium chloride(ChCl)-based eutectic mixtures at atmospheric pressure[a,b].

x_1	T /K	γ_1	x_1	T /K	γ_2
ChCl (1) + Urea (2)					
0.890	539.6[b]	1.03	0.391	294.6[a]	0.313
0.796	475.6[b]	1.01	0.307	321.3[a]	0.451
0.698	438.7[b]	1.05	0.200	355.5[b]	0.660
0.596	380.4[b]	1.03	0.101	381.8[b]	0.826
0.493	331.8[a]	1.02	0	408.2[b]	1
ChCl (1) + Methylurea (2)					
0.893	526.7[b]	0.997	0.329	317.9[a]	0.597
0.797	478.4[b]	1.01	0.298	324.3[a]	0.645
0.700	439.9[b]	1.05	0.200	335.7[a]	0.698
0.589	398.7[b]	1.10	0.100	352.9[b]	0.830
0.499	365.1[b]	1.16	0	372.2[b]	1
0.400	341.4[a]	1.31			
ChCl (1) + 1,1-Dimethylurea (2)					
0.894	552.5[b]	1.04	0.402	392.3[b]	0.509
0.777	521.4[b]	1.14	0.297	408.6[b]	0.619
0.695	488.5[b]	1.19	0.191	416.6[b]	0.634
0.601	467.0[b]	1.31	0.100	434.3[b]	0.803
0.490	434.7[b]	1.48	0	452.5[b]	1
ChCl (1) + 1,3-Dimethylurea (2)					
0.900	560.5[b]	1.05	0.329	336.5[a]	0.884
0.800	528.2[b]	1.12	0.300	343.8[a]	0.935
0.701	480.9[b]	1.16	0.200	354.4[b]	0.935
0.598	429.0[b]	1.19	0.102	367.4[b]	0.971
0.498	395.0[b]	1.29	0	379.8[b]	1
0.402	358.1[b]	1.39			
ChCl (1) + Thiourea (2)					
0.896	529.5[b]	1.00	0.400	324.7[a]	0.440
0.799	474.1[b]	1.00	0.332	342.3[a]	0.503
0.696	419.5[b]	0.995	0.302	348.6[a]	0.521
0.601	368.1[b]	0.971	0.192	380.9[b]	0.650
0.503	313.9[a]	0.910	0.100	410.7[b]	0.778
			0	454.9[b]	1.000

[a] Data obtained using the oil bath method. [b] Data obtained using the melting points device. Standard uncertainties are $u(T) = 1.4$ K, $u_r(p) = 0.05$ and $u_r(x) = 0.002$.

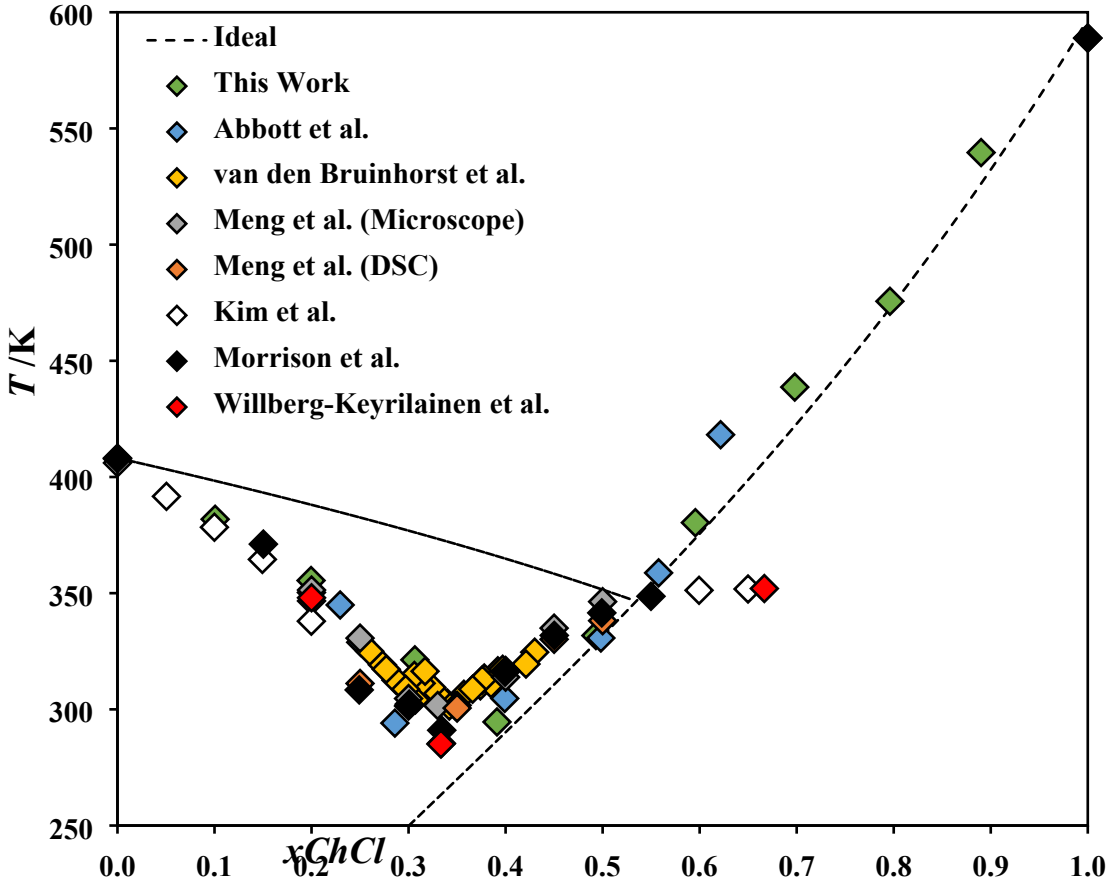

Figure S1. Compendium of solid-liquid equilibrium data for the system choline chloride/urea, measured by several authors[1–6]. The ideal solid-liquid equilibrium lines for both components are also included.

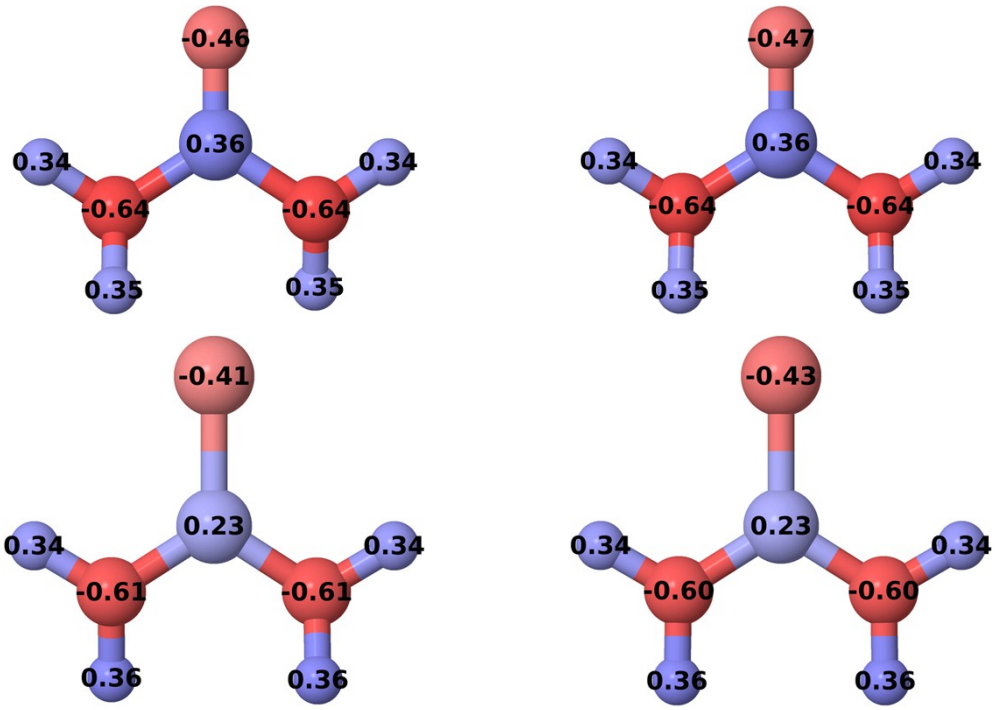

Figure S2. Partial charges at the M06-2X-GIL-6-31+g(d,p)/M06-2X-6-31+g(d,p) level of theory for urea (top) and thiourea (bottom), for the C_2 (left) and D_{2h} (right) conformations**.** Red represents negative charges, blue represents positive charges while white is neutral.

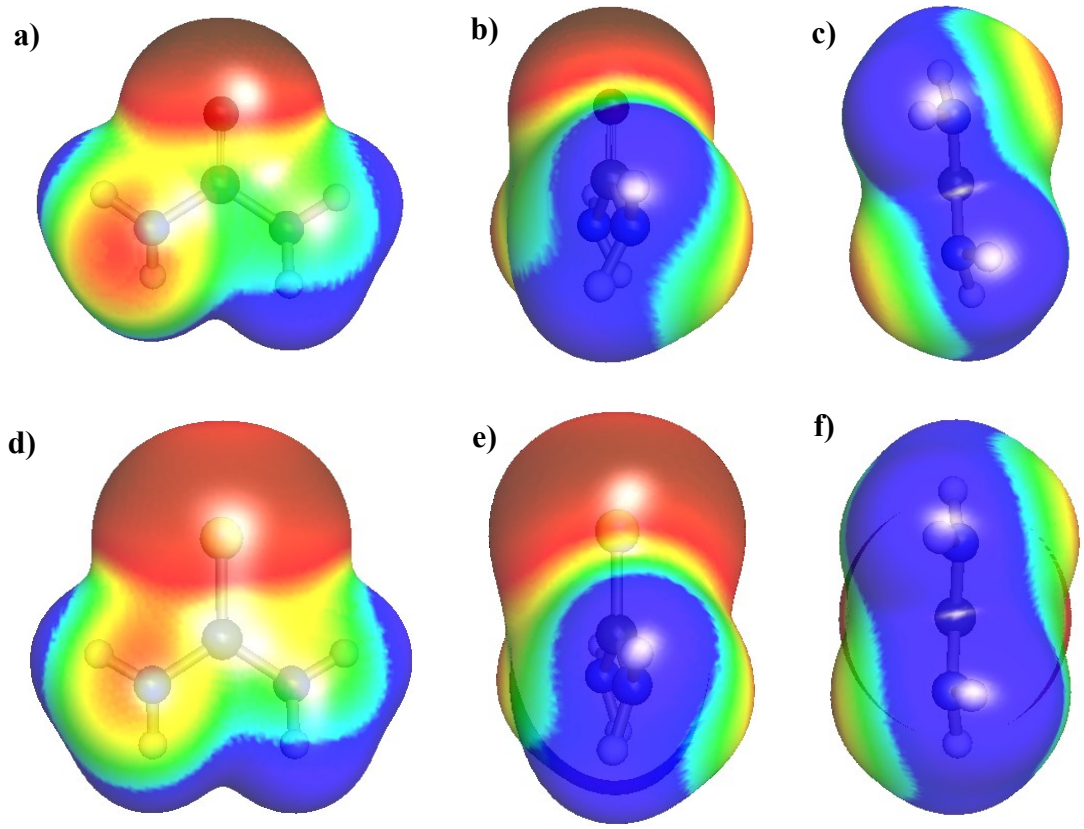

Figure S3. Electrostatic potential color-coded (red = negative, green = neutral and blue = positive) on density isosurface of urea (front view **a**, side view **b** and bottom view **c**) and of thiourea (front view **d**, side view **e** and bottom view **f**), obtained using TURBOMOLE (gas phase, 6-311++G(d,p) basis set, M06-2X DFT and a isovalue of 0.002).

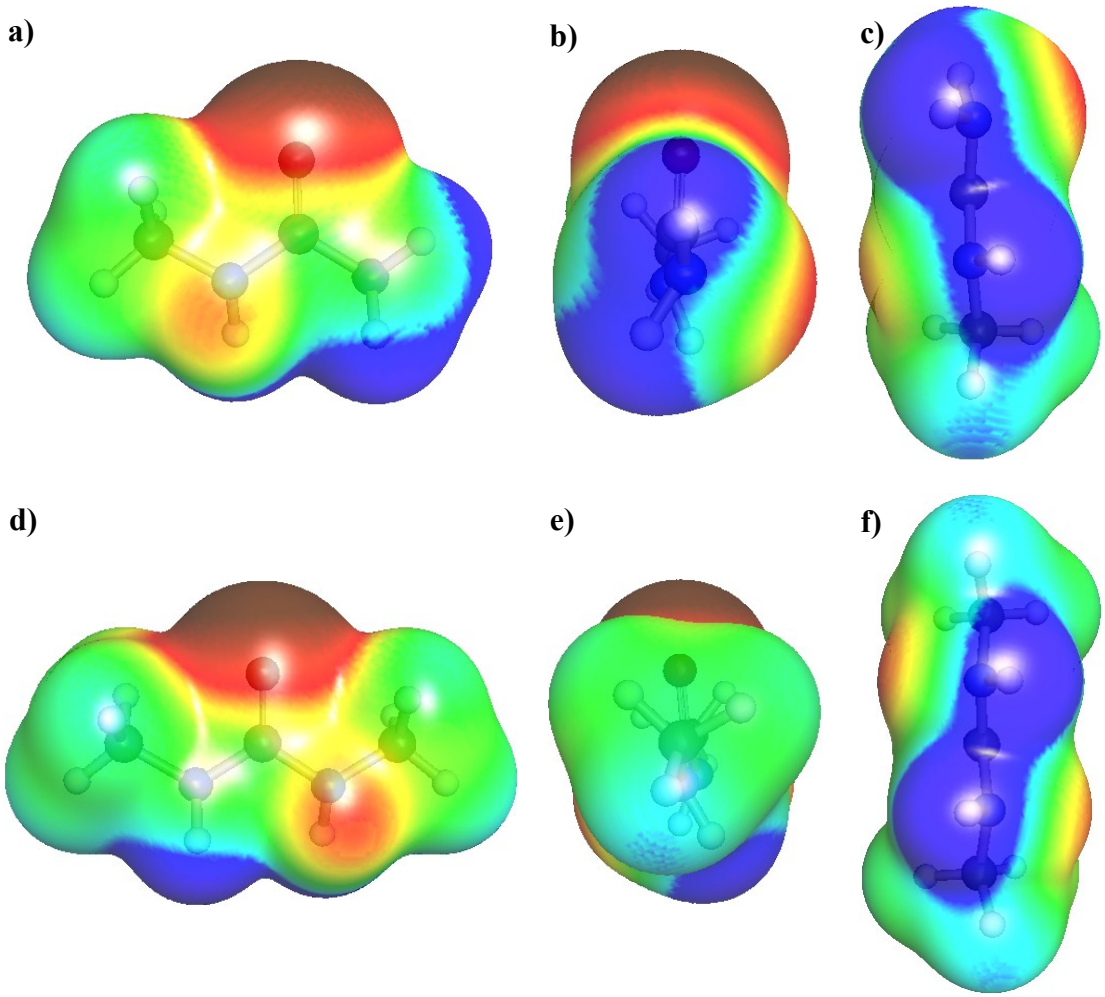

Figure S4. Electrostatic potential color-coded (red = negative, green = neutral and blue = positive) on density isosurface of methylurea (front view **a**, side view **b** and bottom view **c**) and of 1,3-dimethylurea (front view **d**, side view **e** and bottom view **f**), obtained using TURBOMOLE (gas phase, 6-311++G(d,p) basis set, M06-2X DFT and a isovalue of 0.002).

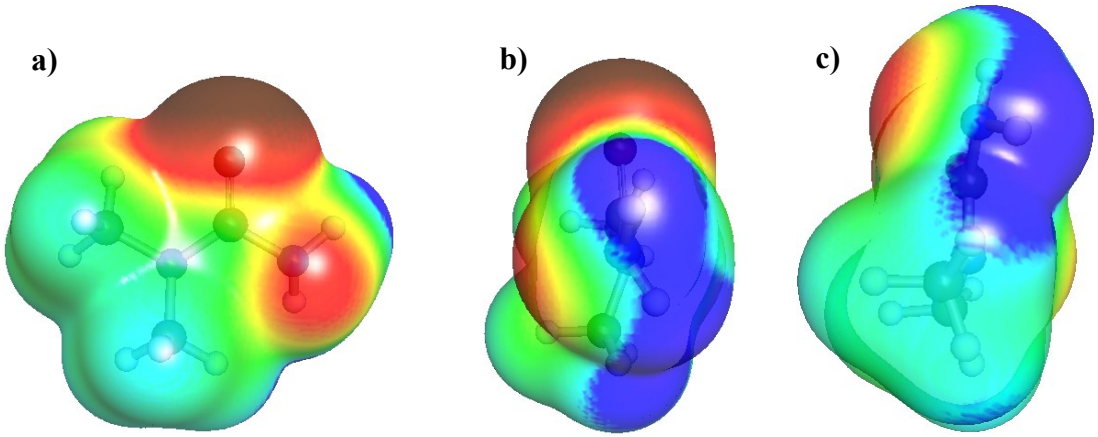

Figure S5. Electrostatic potential color-coded (red = negative, green = neutral and blue = positive) on density isosurface of 1,1-dimethylurea (front view **a**, side view **b** and bottom view **c**), obtained TURBOMOLE (gas phase, 6-311++G(d,p) basis set, M06-2X DFT and a isovalue of 0.002).

References

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