Hydrogen-Bonding Interactions in Pyridinium-Based Ionic Liquids and Dimethyl Sulfoxide Binary Systems: A Combined Experimental and Computational Study

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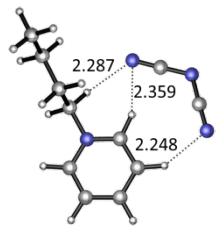
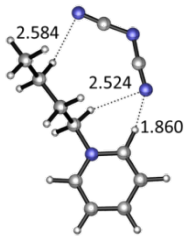
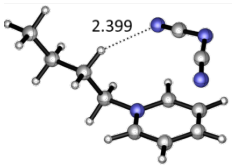


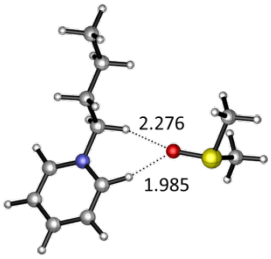
A: -317.87 kJ/mol



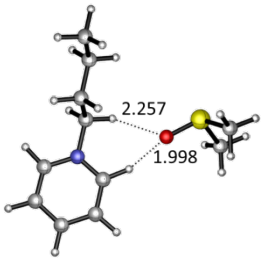
B: -305.89 kJ/mol



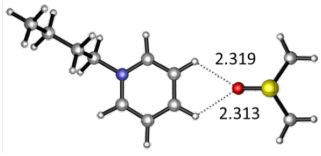
C: -310.10 kJ/mol



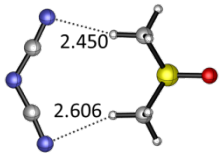
D: -74.25 kJ/mol



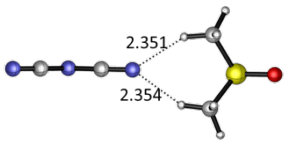
E: -73.20 kJ/mol



F: -59.13 kJ/mol

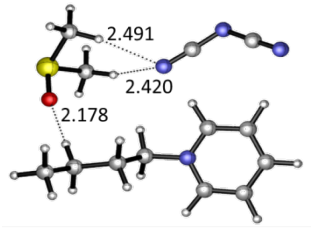


G: -44.64 kJ/mol

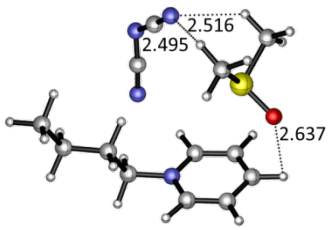


H: -52.59 kJ/mol

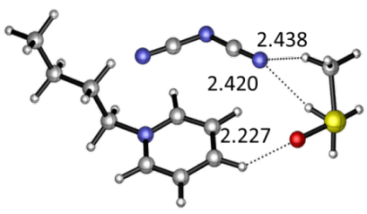
Figure S1. Structures of ion pairs (A, B, C), $[Bpy]^+$-DMSO (D, E, F), and $[DCA]^-$-DMSO (G, H) optimized at the B3LYP/6-31++g(d, p) level. The H-bonds are marked with dashed lines and the corresponding bond lengths are labeled in angstrom.



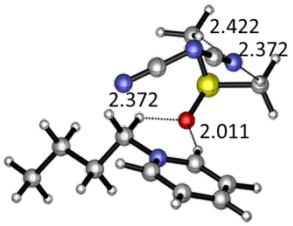
A: -348.05 kJ/mol



B: -358.36 kJ/mol

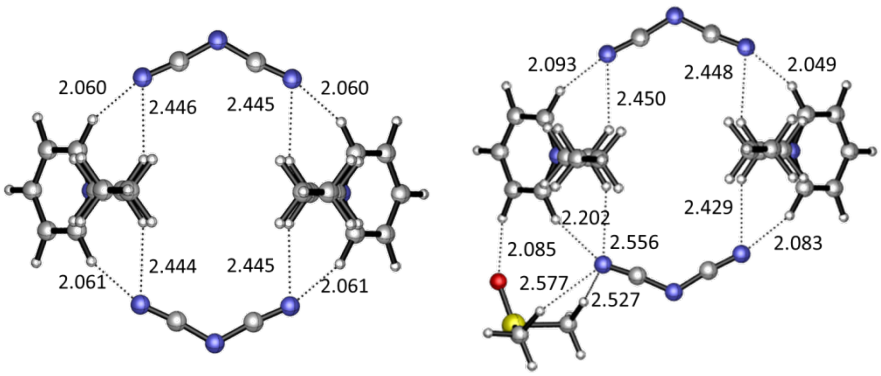


C: -371.96 kJ/mol



D: -381.14 kJ/mol

Figure S2. The possible geometrics and interaction energies of [Bpy][DCA]-DMSO optimized at the level of B3LYP/6-31++g(d, p). The H-bonds are marked with dash lines and the corresponding H⋯N and H⋯O distances are labeled in angstroms.

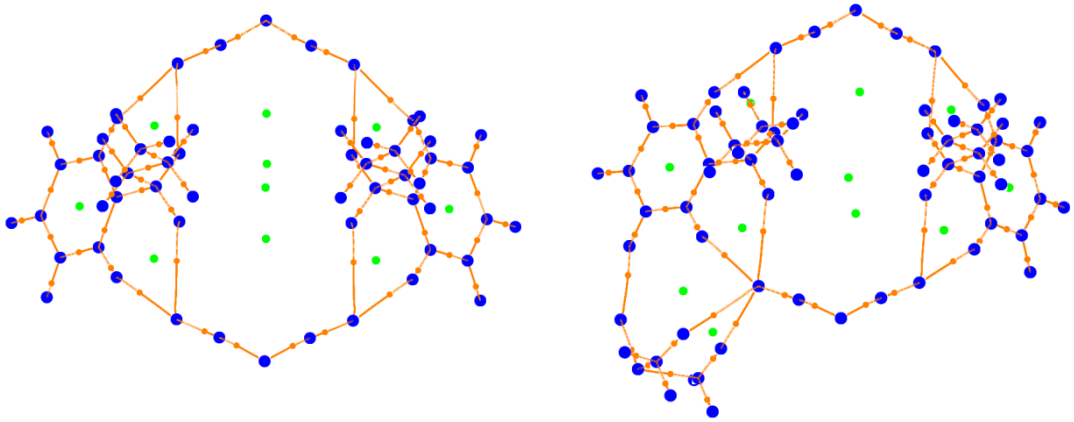


A: -754.44 kJ/mol B: -778.06 kJ/mol

Figure S3. Optimized geometrics for the ion cluster (A, 2[Bpy]$^+$-2[DCA]$^-$) and for one DMSO molecule interacting with the ion cluster (B, 2[Bpy]$^+$-2[DCA]$^-$-DMSO). H-bonds between cations and anions, and between DMSO and ion pairs, are denoted by dash lines, and the corresponding H···N and H···O distances are label in angstrom.

Table S1. Properties of electron density at bond critical point (BCP) for the ion clusters (a.u.).

H-bonds	Figure S3 A: 2[Bpy]$^+$-2[DCA]$^-$			Figure S3 B: 2[Bpy]$^+$-2[DCA]$^-$-DMSO		
	Length	ρ_{BCP}	$\nabla^2\rho_{BCP}$	Length	ρ_{BCP}	$\nabla^2\rho_{BCP}$
C5-H11···N57	2.061	0.023	0.066	2.083	0.022	0.064
C12-H14···N57	2.444	0.011	0.035	2.429	0.012	0.035
C30-H37···N58	2.061	0.023	0.066	2.202	0.017	0.051
C41-H42···N58	2.445	0.011	0.001	2.556	0.009	0.028
C34-H40···N28	2.060	0.023	0.066	2.093	0.021	0.062
C41-H43···N28	2.445	0.011	0.035	2.450	0.011	0.035
C1-H8···N29	2.060	0.023	0.066	2.049	0.023	0.068
C12-H13···N29	2.446	0.011	0.035	2.448	0.011	0.035
C60-H63···N58				2.527	0.009	0.025
C64-H66···N58				2.577	0.281	-1.017
C31-H38···O68				2.085	0.018	0.060



A: 2[Bpy]$^{+}$-2[DCA]$^{-}$ B: 2[Bpy]$^{+}$-2[DCA]$^{-}$-DMSO

Figure S4. Critical points (CPs) for ion clusters. Color legend for the atom nuclear: blue (C, H O, N, S), bond CP: orange and ring CP: green.

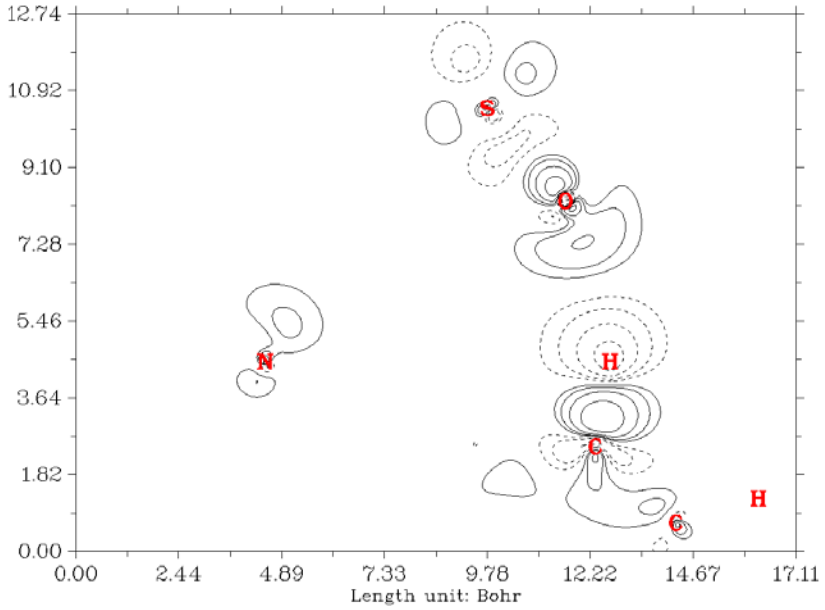


Figure S5. Electron density difference around the H-bond C31-H38···O68. The solid lines represent the accumulation of electrons, and the dotted lines represent the reduction of electrons.

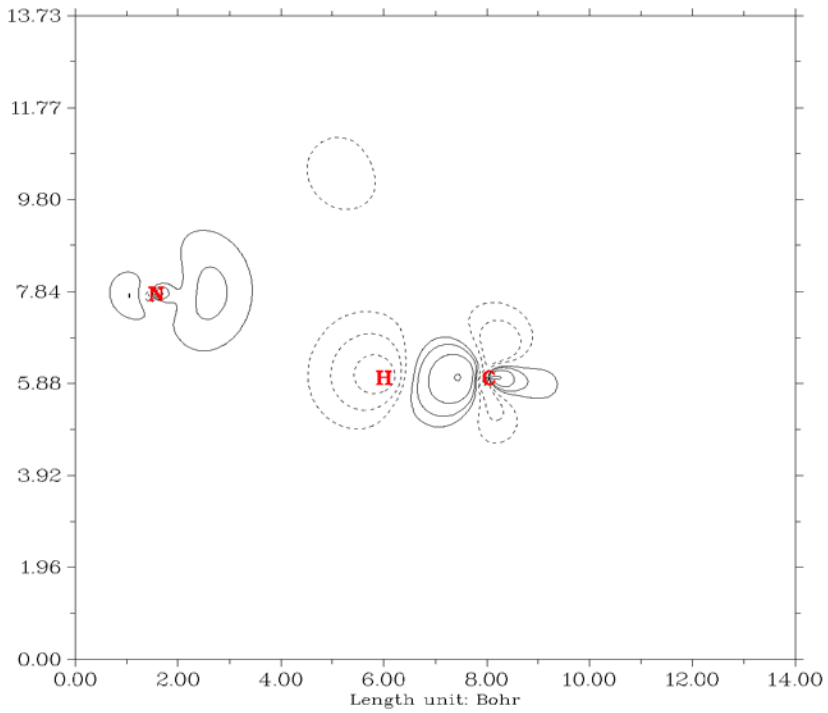


Figure S6. Electron density difference around the H-bond C64-H66⋯N58. The solid lines represent the accumulation of electrons, and the dotted lines represent the reduction of electrons.

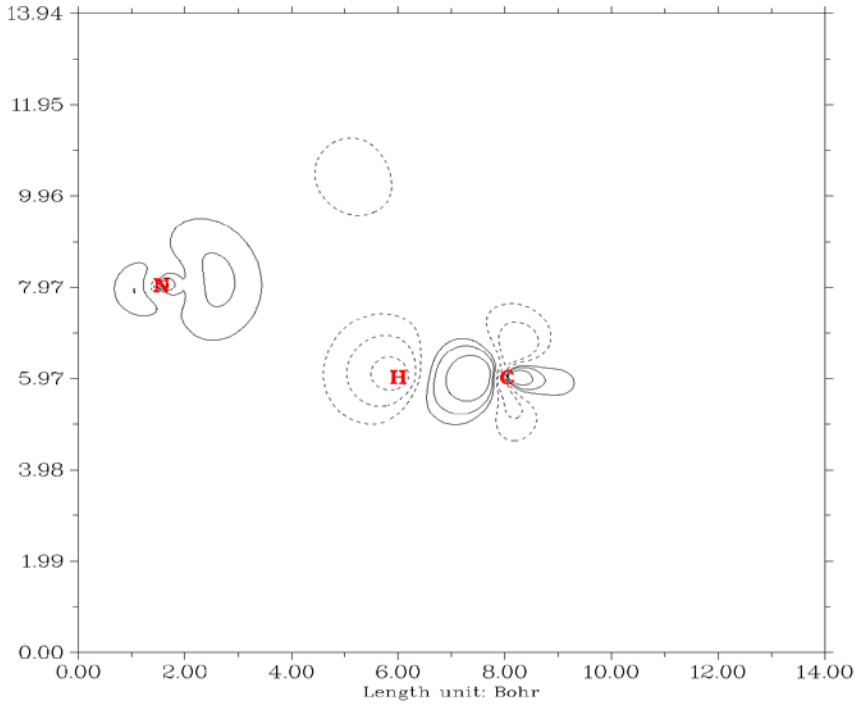


Figure S7. Electron density difference around the H-bond C60-H63⋯N58. The solid lines represent the accumulation of electrons, and the dotted lines represent the reduction of electrons.

Table S2. Chemical shifts of hydrogen atoms of $[Bpy]^+$ and DMSO at different molar concentrations of DMSO in [Bpy][DCA]-DMSO solutions.

x(IL)	x(DMSO)	H(C2,6)	H(C4)	H(C3,5)	H(C7)	DMSO	H(C8)	H(C9)	H(C10)
1.0000	0.0000	8.600	8.095	7.624	4.175		1.426	0.742	0.278
0.9021	0.0979	8.612	8.105	7.637	4.184	2.118	1.438	0.757	0.297
0.7970	0.2030	8.637	8.127	7.662	4.203	2.144	1.462	0.787	0.330
0.6964	0.3036	8.661	8.149	7.687	4.222	2.158	1.485	0.816	0.363
0.5999	0.4001	8.688	8.173	7.714	4.244	2.179	1.509	0.845	0.398
0.4991	0.5009	8.720	8.203	7.747	4.269	2.203	1.537	0.880	0.438
0.4001	0.5999	8.760	8.242	7.790	4.303	2.236	1.575	0.925	0.490
0.2999	0.7001	8.800	8.290	7.839	4.343	2.276	1.619	0.977	0.552
0.2006	0.7994	8.878	8.359	7.913	4.402	2.329	1.682	1.050	0.636
0.1002	0.8998	8.967	8.456	8.011	4.499	2.405	1.766	1.146	0.748
0.0000	1.0000					2.513			

Table S3. Chemical shift changes of hydrogen atoms of $[Bpy]^+$ and DMSO at different molar concentrations of DMSO in [Bpy][DCA]-DMSO solutions.

x(IL)	x(DMSO)	H(C2,6)	H(C4)	H(C3,5)	H(C7)	DMSO	H(C8)	H(C9)	H(C10)
1.0000	0.0000	0.000	0.000	0.000	0.000		0.000	0.000	0.000
0.9021	0.0979	0.011	0.010	0.013	0.009	-0.395	0.012	0.016	0.018
0.7970	0.2030	0.037	0.032	0.038	0.028	-0.369	0.036	0.045	0.052
0.6964	0.3036	0.061	0.054	0.063	0.048	-0.355	0.060	0.074	0.085
0.5999	0.4001	0.088	0.078	0.090	0.069	-0.334	0.083	0.104	0.119
0.4991	0.5009	0.120	0.108	0.123	0.094	-0.310	0.112	0.139	0.160
0.4001	0.5999	0.160	0.147	0.166	0.128	-0.277	0.149	0.183	0.212
0.2999	0.7001	0.200	0.195	0.215	0.168	-0.237	0.193	0.236	0.274
0.2006	0.7994	0.278	0.264	0.289	0.227	-0.184	0.257	0.309	0.357
0.1002	0.8998	0.367	0.361	0.387	0.324	-0.108	0.341	0.404	0.469
0.0000	1.0000					0.000			

A **B**

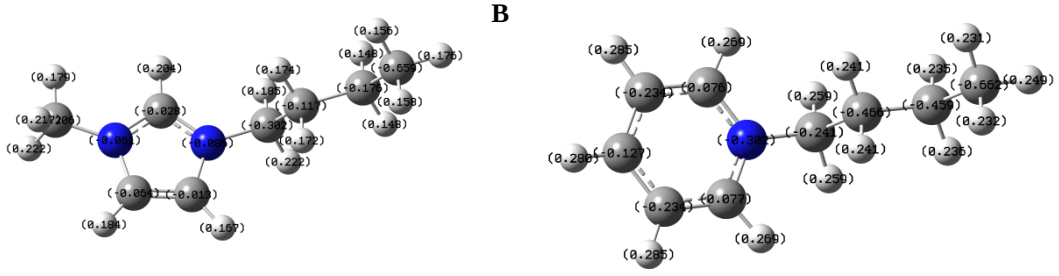


Figure S8. Natural population analysis charges of A: $[Bmim]^+$ and B: $[Bpy]^+$ cations.