Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information
Comparing intermediate range order for alkyl- vs. ether-substituted cations in ionic liquids.

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Quantum calculation results

Geometry optimization was done on B3LYP/6-31+G(d,p) level in both gas phase and polarized continuum solvation model for dielectric constant of 36 for two different conformations: all *trans* and *trans-gauche*. Electrostatic potentials were calculated using pop=chelpg command.

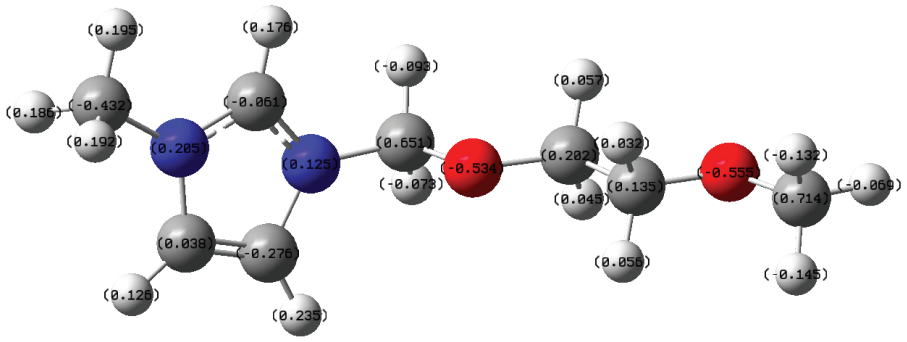

Figure 1: ESP calculation results on *trans*-(COC_2OC)mim^+ cation in gas phase.

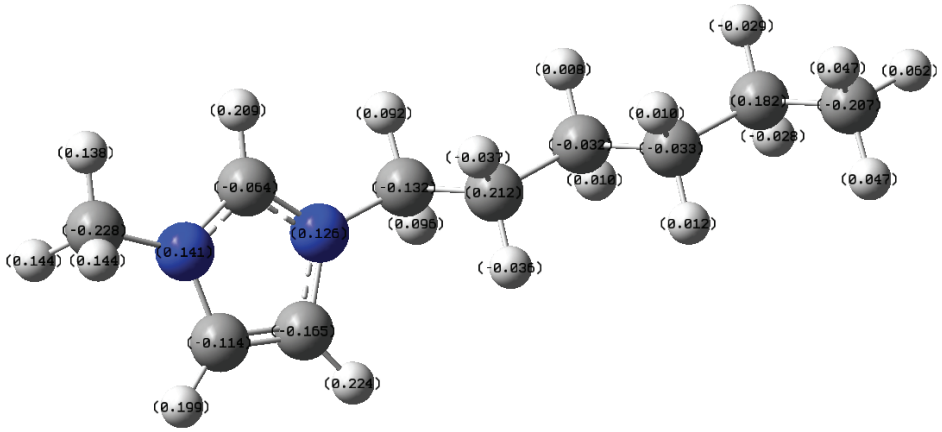

Figure 2: ESP calculation results on *trans*-(C_6mim^+ cation in gas phase.

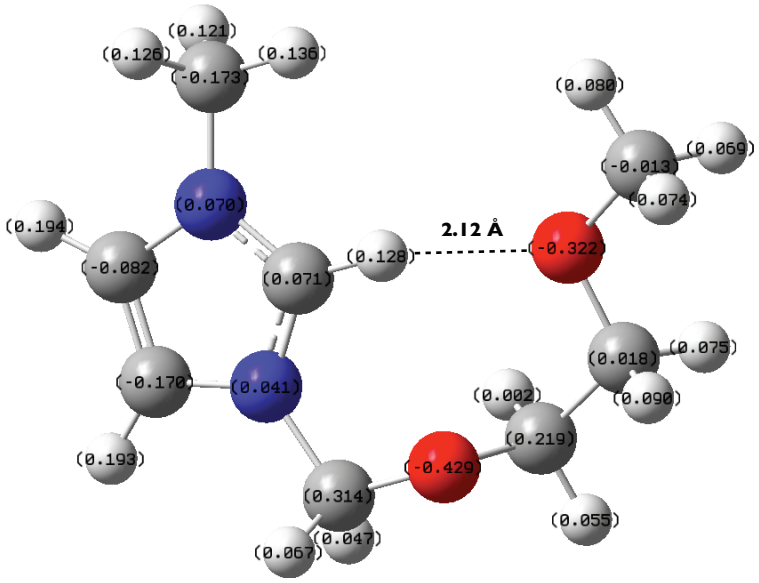

Figure 3: ESP calculation results on *trans-gauche*-$(COC_2OC)mim^+$ cation in gas phase, showing the hydrogen bond.

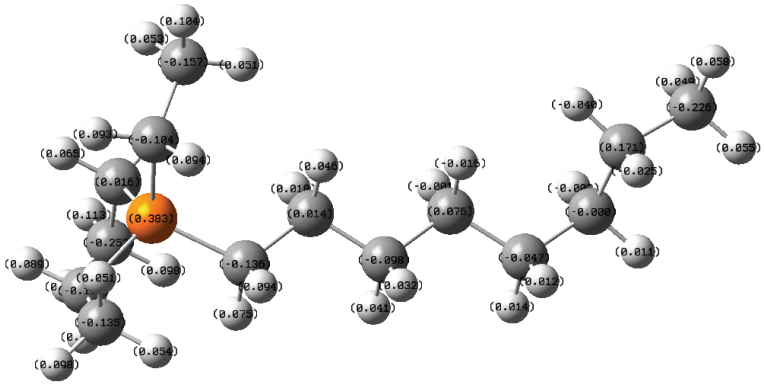

Figure 4: ESP calculation results on *trans-gauche*-$P_{2228}{}^+$ cation in gas phase.

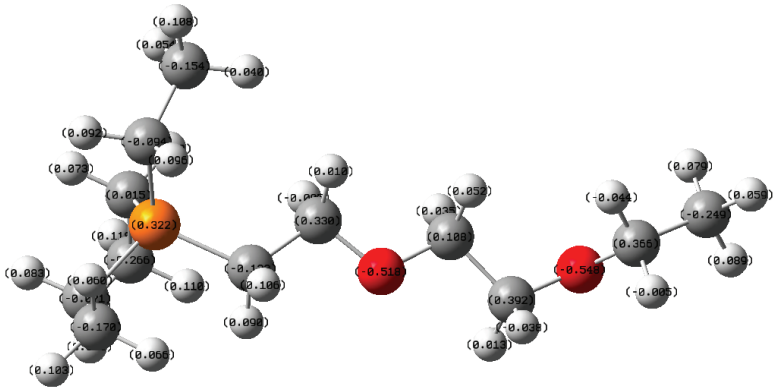

Figure 5: ESP calculation results on *trans-gauche*-$P_{222(2O2O2)}{}^+$ cation in gas phase.

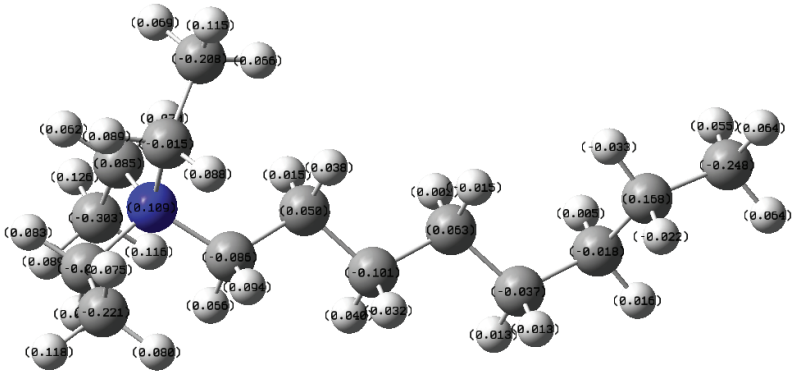

Figure 6: ESP calculation results on *trans-gauche*-N_{2228}^{+} cation in gas phase.

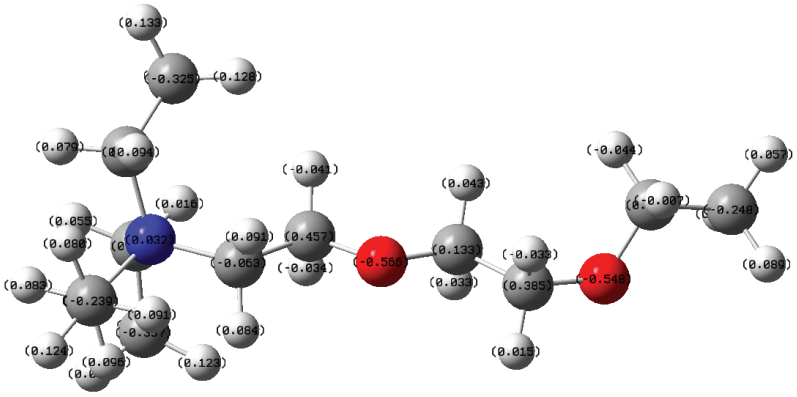

Figure 7: ESP calculation results on *trans-gauche*-$N_{222(2O_2O_2)}^{+}$ cation in gas phase

Table 1: Table summarizing the ESP calculation results on *trans*- and *trans-gauche*-C_6mim^+ and $(COC_2OC)mim^+$ cations in gas phase.

GAS-phase	***trans*-C6mim**	***trans*-C1OC2OC1mim**	***trans-gauche*-C6mim**	***trans-gauche*-C1OC2OC1mim**
N1	0.126	0.125	0.15	0.041
C2	-0.064	-0.061	-0.082	0.071
H2a	0.209	0.176	0.202	0.128
N3	0.141	0.205	0.12	0.07
C4	-0.114	0.038	-0.117	-0.082
H4a	0.199	0.126	0.2	0.194
C5	-0.165	-0.276	-0.138	-0.17
H5a	0.224	0.235	0.198	0.193
SUM(ring)	0.556	0.568	0.533	0.445
C2'	-0.132	0.651	-0.121	0.314
H2'a	0.092	-0.093	0.097	0.047
H2'b	0.096	-0.073	0.103	0.067
C3' / O3'	0.212	-0.534	0.096	-0.429
H3'a	-0.037		-0.001	
H3'b	-0.036		0	
C4'	-0.032	0.202	-0.037	0.219
H4'a	0.008	0.057	0.023	0.002
H4'b	0.01	0.045	0.026	0.055
C5'	-0.033	0.135	-0.037	0.018
H5'a	0.01	0.032	0.031	0.075
H5'b	0.012	0.056	0.011	0.09
C6' / O6'	0.182	-0.555	0.171	-0.322
H6'a	-0.029		-0.027	
H6'b	-0.028		-0.045	
C7'	-0.207	0.714	-0.183	-0.013
H7'a	0.047	-0.132	0.05	0.069
H7'b	0.047	-0.145	0.041	0.074
H7'c	0.062	-0.069	0.052	0.08
SUM(chain)	0.244	0.291	0.25	0.346
C2"	-0.228	-0.432	-0.148	-0.173
H2"a	0.138	0.195	0.121	0.136
H2"b	0.144	0.192	0.12	0.126
H2"c	0.144	0.186	0.122	0.121
SUM(methyl)	0.198	0.141	0.215	0.21
SUM(methyl+ring)	0.754	0.709	0.748	0.655
Sum(total)	0.998	1	0.998	1.001
Energy (HF)	-501.9372273	-573.7369436	-501.8399529	-573.6246271

Table 2: Table summarizing the ESP calculation results on *trans-* and *trans-gauche-*C_6mim^+ and $(COC_2OC)mim^+$ cations in polarized continuum solvation model for dielectric constant of 36.

Acetonitrile	***trans-*C6mim**	***trans-*C1OC2OC1mim**	***trans-gauche-*C6mim**	***trans-gauche-*C1OC2OC1mim**
N1	0.149	0.007	0.169	-0.02
C2	-0.076	-0.056	-0.188	-0.076
H2a	0.231	0.241	0.228	0.209
N3	0.176	0.209	-0.122	-0.183
C4	-0.125	-0.132	0.201	0.21
H4a	0.202	0.201	0.17	0.23
C5	-0.194	-0.127	-0.089	-0.055
H5a	0.233	0.224	0.232	0.217
SUM(ring)	0.596	0.567	0.601	0.532
C2'	-0.112	0.349	-0.144	0.427
H2'a	0.089	0.05	0.096	-0.017
H2'b	0.089	0.051	0.103	0.05
C3' / O3'	0.244	-0.475	0.207	-0.494
H3'a	-0.043		-0.033	
H3'b	-0.046		-0.019	
C4'	-0.03	0.093	-0.082	0.156
H4'a	0.003	0.061	0.028	0.057
H4'b	0.005	0.064	0.029	0.059
C5'	-0.03	0.306	-0.069	0.13
H5'a	0.002	0.013	0.019	0.049
H5'b	0.004	0.013	0.024	0.032
C6' / O6'	0.228	-0.525	0.21	-0.331
H6'a	-0.046		-0.035	
H6'b	-0.048		-0.031	
C7'	-0.214	0.18	-0.237	-0.061
H7'a	0.04	0.014	0.046	0.071
H7'b	0.04	0.015	0.051	0.082
H7'c	0.045	0.043	0.049	0.08
SUM(chain)	0.22	0.252	0.212	0.29
C2"	-0.222	-0.222	-0.188	-0.229
H2"a	0.135	0.131	0.126	0.138
H2"b	0.136	0.14	0.126	0.133
H2"c	0.135	0.134	0.127	0.135
SUM(methyl)	0.184	0.183	0.191	0.177
SUM(methyl+ ring)	0.78	0.75	0.792	0.709
Sum(total)	0.998	1	0.998	1.001
Energy (HF)	-502.0091524	-573.8135974	-502.007896	-573.814263

Table 3: Table summarizing the ESP calculation results on *trans-gauche*-P_{2228}^{+}, $P_{222(2O2O2)}^{+}$, N_{2228}^{+}, and $N_{222(2O2O2)}^{+}$ cations in gas phase.

	***trans-gauche-* P2228**	***trans-gauche-* P222(2O2O2)**	***trans-gauche-* N2228**	***trans-gauche-* N222(2O2O2)**
P1 / N1	0.383	0.322	0.109	0.032
C2	-0.136	-0.132	-0.086	-0.063
H2a	0.075	0.09	0.066	0.084
H2b	0.094	0.106	0.094	0.091
C3	0.014	0.33	0.05	0.457
H3a	0.018	-0.005	0.015	-0.034
H3b	0.046	0.01	0.038	-0.041
C4 / O4	-0.098	-0.518	-0.101	-0.566
H4a	0.041		0.04	
H4b	0.032		0.032	
C5	0.076	0.108	0.063	0.133
H5a	-0.001	0.035	0.002	0.033
H5b	-0.016	0.052	-0.015	0.043
C6	-0.047	0.392	-0.037	0.385
H6a	0.014	0.013	0.013	0.015
H6b	0.012	-0.038	0.013	-0.033
C7 / O7	0	-0.548	-0.018	-0.548
H7a	-0.002		0.005	
H7b	0.011		0.016	
C8	0.171	0.366	0.168	0.367
H8a	-0.04	-0.005	-0.033	-0.007
H8b	-0.025	-0.044	-0.022	-0.044
C9	-0.226	-0.249	-0.248	-0.248
H9a	0.049	0.089	0.055	0.08
H9b	0.058	0.079	0.064	0.089
H9c	0.055	0.059	0.064	0.057
SUM(chain)	0.175	0.19	0.238	0.25
C2'	-0.104	0.015	-0.015	0.034
H2'a	0.094	0.06	0.088	0.094
H2'b	0.093	0.073	0.089	0.079
C3'	-0.157	-0.266	-0.208	-0.325
H3'a	0.051	0.11	0.066	0.128
H3'b	0.053	0.075	0.069	0.102
H3'c	0.104	0.118	0.115	0.133
SUM(ethyl1)	0.134	0.185	0.204	0.245
C2"	0.016	-0.071	0.085	0.161
H2"a	0.063	0.091	0.07	0.016
H2"b	0.065	0.083	0.062	0.055
C3"	-0.252	-0.17	-0.303	-0.337
H3"a	0.098	0.066	0.116	0.123
H3"b	0.113	0.103	0.126	0.136
H3"c	0.072	0.06	0.089	0.094
SUM(ethyl2)	0.175	0.162	0.245	0.248
2C'''	-0.119	-0.094	-0.025	-0.011
H2'''a	0.095	0.096	0.097	0.096
H2'''b	0.089	0.092	0.083	0.083
C3'''	-0.135	-0.154	-0.221	-0.239