Supporting information

"Fluorohydrogenate Cluster Ions in the Gas Phase: Electrospray Ionization Mass Spectrometry of the [ethylmethylimidazolium][$F(HF)_{2.3}$] Ionic Liquid"

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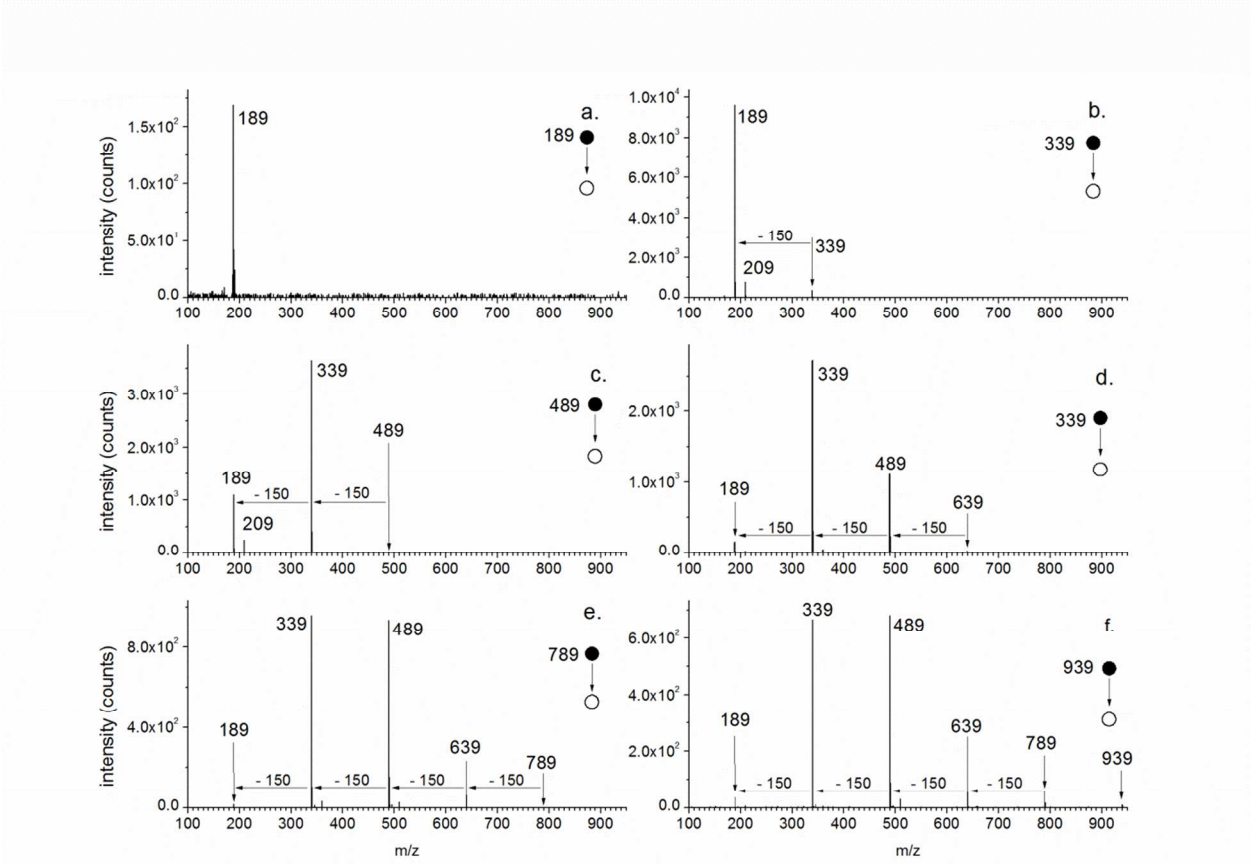


Figure S1. MS^2 collision induced dissociation mass spectra of negative cluster ions with the composition $[EMIm^+]_n[F(HF)^-]_{n+1}$.

Table S1. Source Parameters for the Bruker MicrOTOF-QII, optimized for transmission of low *m/z* ions, negative mode.

Tune low neg					
Parameter	*Value*	*Unit*	*Parameter*	*Value*	*Unit*
Source					
End plate offset	-0.5	V	Capillary	+3500	V
Nebulizer	0.4	Bar	Dry Gas	4.0	l/min
Dry Temp	180	^{o}C			
Transfer					
Funnel 1 RF	200	V_{pp}	Funnel 2 RF	200	V_{pp}
ISCID Energy	0	eV	Hexapole RF	100	V_{pp}
Quadrupole					
Ion energy	5	eV	Low mass	100	m/z
Collision Cell					
Collision energy	10	eV	Collision RF	100	V_{pp}
Transfer time	70	μs	Pre-pulse storage	5	μs

Table S2. Source Parameters for the Bruker MicrOTOF-QII, optimized for transmission of mid *m/z* ions, negative mode.

Tune wide neg					
Parameter	*Value*	*Unit*	*Parameter*	*Value*	*Unit*
Source					
End plate offset	-0.5	V	Capillary	+3000	V
Nebulizer	0.4	Bar	Dry Gas	4.0	l/min
Dry Temp	180	^{o}C			
Transfer					
Funnel 1 RF	300	V_{pp}	Funnel 2 RF	400	V_{pp}
ISCID Energy	0	eV	Hexapole RF	300	V_{pp}
Quadrupole					
Ion energy	5	eV	Low mass	322	m/z
Collision Cell					
Collision energy	10	eV	Collision RF	500	V_{pp}
Transfer time	140	μs	Pre-pulse storage	10	μs

Table S3. Source Parameters for the Bruker MicrOTOF-QII, optimized for transmission of low *m/z* ions, positive mode.

Tune low pos					
Parameter	*Value*	*Unit*	*Parameter*	*Value*	*Unit*
Source					
End plate offset	+0.5	V	Capillary	-4500	V
Nebulizer	0.4	Bar	Dry Gas	4.0	l/min
Dry Temp	180	^{o}C			
Transfer					
Funnel 1 RF	200	V_{pp}	Funnel 2 RF	200	V_{pp}
ISCID Energy	0	eV	Hexapole RF	100	V_{pp}
Quadrupole					
Ion energy	3	eV	Low mass	100	m/z
Collision Cell					
Collision energy	8	eV	Collision RF	100	V_{pp}
Transfer time	70	μs	Pre-pulse storage	5	μs

Table S4. Source Parameters for the Bruker MicrOTOF-QII, optimized for transmission of mid *m/z* ions, positive mode.

Tune low wide					
Parameter	*Value*	*Unit*	*Parameter*	*Value*	*Unit*
Source					
End plate offset	+0.5	V	Capillary	-4500	V
Nebulizer	0.4	Bar	Dry Gas	4.0	l/min
Dry Temp	180	^{o}C			
Transfer					
Funnel 1 RF	300	V_{pp}	Funnel 2 RF	400	V_{pp}
ISCID Energy	0	eV	Hexapole RF	300	V_{pp}
Quadrupole					
Ion energy	5	eV	Low mass	322	m/z
Collision Cell					
Collision energy	10	eV	Collision RF	500	V_{pp}
Transfer time	140	μs	Pre-pulse storage	10	μs

Table S5. Calculated Energetics for structures

Structure	ΔE_0 (Hartrees)a	ΔH (Hartrees, 298.15 K)	ΔG (Hartrees, 298.15 K)	$\Delta\Delta G$ for isomers (kcal/ mol)
[$EMIm^+$]	-344.468806	-344.459437	-344.502456	---
[FHF^-]	-200.434893	-200.431404	-200.456188	---
[F^-]	-99.88869	---	---	---
[$F(HF)_2^-$]	-300.951883	-300.946544	-300.979597	---
1a, [$EMIm^+$][FHF^-]	-545.038298	-545.024981	-545.079934	+10.52
1b, [$EMIm^+$][FHF^-]	-545.056232	-545.043139	-545.096705	0
1c, [$EMIm^+$][FHF^-]	-545.056157	-545.043002	-545.096609	+0.06
2a, [$EMIm^+$][F^-]$_2$	-544.497233	-544.454459	-544.535828	0
2b, [$EMIm^+$][F^-]$_2$	-544.496529	-544.483605	-544.535455	+0.23
3a, [$EMIm^+$][FHF^-][F^-]	-645.004304	-644.989925	-645.047136	+12.71
3b, [$EMIm^+$][FHF^-][F^-]	-645.022094	-645.006663	-645.067391	0
3c, [$EMIm^+$][FHF^-][F^-]	-645.018547	-645.003600	-645.062078	+3.33
4a, [$EMIm^+$][FHF^-]$_2$	-745.538170	-745.521032	-745.586631	+1.51
4b, [$EMIm^+$][FHF^-]$_2$	-745.537954	-745.520753	-745.586101	+1.85
4c, [$EMIm^+$][FHF^-]$_2$	-745.540854	-745.523794	-745.589042	0
5a, [$EMIm^+$][FHF^-][$F(HF)_2^-$]	-846.045845	-846.026327	-846.100766	0
5b, [$EMIm^+$][FHF^-][$F(HF)_2^-$]	-846.047003	-846.027531	-846.100539	+0.14
5c, [$EMIm^+$][FHF^-][$F(HF)_2^-$]	-846.047853	-846.028440	-846.100149	+0.39
5c, [$EMIm^+$][FHF^-][$F(HF)_2^-$]	-846.043629	-846.024165	-846.097652	+1.95
5c, [$EMIm^+$][FHF^-][$F(HF)_2^-$]	-846.044932	-846.025467	-846.097711	+1.92
6, [$EMIm^+$]$_2$[FHF^-]$_3$	-1290.621601	-1290.590187	-1290.695397	---
[a]$\Delta E_0 = \Delta E$ + zero point energy.				

Table S6. Coordinates for HF

F	1	0.000000	0.000000	0.092225
H	2	0.000000	0.000000	-0.830022

Table S7. Coordinates for [FHF^-]

F	1	0.000000	0.000000	-1.146827
F	2	0.000000	0.000000	1.147548
H	3	0.000000	0.000000	-0.006496

Table S8. Coordinates for [$F(HF)_2^-$]

F	1	0.000579	0.571850	0.000000
F	2	2.197174	-0.293078	-0.000008
H	3	1.253448	0.063521	0.000124
H	4	-1.254505	0.063131	-0.000117
F	5	-2.197635	-0.292844	0.000007

Table S9. Coordinates for [$EMIm^+$]

C	1	0.152650	1.311117	-0.136603
C	2	-1.187226	1.225199	0.086766
C	3	-0.411048	-0.817947	-0.205809
N	4	0.620367	0.023989	-0.319282
H	5	0.800202	2.169939	-0.185924
H	6	-1.920574	1.993101	0.266364
H	7	-0.357773	-1.889951	-0.300805
C	8	-2.871776	-0.669670	0.223064
H	9	-3.238090	-0.412238	1.216324
H	10	-3.536934	-0.263894	-0.538469
H	11	-2.825636	-1.752179	0.123312
C	12	2.033195	-0.362715	-0.559311
H	13	2.015463	-1.382860	-0.944357
H	14	2.404600	0.282741	-1.356651
C	15	2.887660	-0.254733	0.699291
H	16	3.910243	-0.552989	0.460076
H	17	2.918799	0.768137	1.079921
H	18	2.518038	-0.911396	1.489485
N	19	-1.521662	-0.114835	0.040188

Table S10. Coordinates for **1a**, [$EMIm^+$][FHF^-]

C	1	-0.327092	-0.091352	-0.185751
C	2	0.528740	-1.136537	-0.007824
C	3	1.741443	0.709961	-0.128578
N	4	0.452312	1.046923	-0.257304
H	5	-1.435475	-0.107869	-0.233963
H	6	0.277750	-2.180199	0.100695
H	7	2.578863	1.386116	-0.147152
C	8	3.039378	-1.396223	0.199845
H	9	3.004570	-1.925834	1.152059
H	10	3.137822	-2.115933	-0.613042
H	11	3.895945	-0.723880	0.192163
C	12	-0.079732	2.410300	-0.443740
H	13	0.776677	3.086705	-0.478795
H	14	-0.568986	2.434928	-1.419530
C	15	-1.057644	2.796431	0.661608
H	16	-1.431100	3.805593	0.473403
H	17	-1.910802	2.115558	0.685148
H	18	-0.571081	2.785221	1.639722
N	19	1.813047	-0.620056	0.024273
H	20	-2.495675	-1.769832	0.000339
F	21	-2.993750	-0.630080	-0.155418
F	22	-1.915868	-2.651489	0.122841

Table S11. Coordinates for **1b**, [$EMIm^+$][FHF^-]

C	1	-1.638497	1.478065	-0.209519
C	2	-0.523082	2.228704	-0.004888
C	3	0.108637	0.105894	-0.139947
N	4	-1.221189	0.160511	-0.292586
H	5	-2.670787	1.767161	-0.305182
H	6	-0.403671	3.292486	0.108044
H	7	0.692951	-0.859292	-0.169125
C	8	1.962763	1.723699	0.231627
H	9	2.069680	2.237965	1.187502
H	10	2.561842	0.808919	0.228686
H	11	2.278681	2.381283	-0.579255
C	12	-2.063108	-1.036021	-0.483436
H	13	-2.704478	-0.852981	-1.348534
H	14	-1.376345	-1.846748	-0.730141
C	15	-2.882831	-1.373981	0.758272
H	16	-3.476335	-2.270605	0.566092
H	17	-2.229306	-1.576043	1.609163
H	18	-3.568942	-0.566318	1.026039
N	19	0.552226	1.356331	0.035864
H	20	2.466635	-1.708374	-0.017970
F	21	1.310260	-2.261522	-0.241801
F	22	3.274132	-1.092201	0.165031

Table S12. Coordinates for **1c**, [$EMIm^+$][FHF^-]

C	1	-1.103887	-1.810128	-0.342794
C	2	-2.216208	-1.051486	-0.150779
C	3	-0.442784	0.285215	-0.035650
N	4	-0.012668	-0.959972	-0.270088
H	5	-0.999506	-2.865203	-0.528057
H	6	-3.258503	-1.320014	-0.139861
H	7	0.155845	1.236733	0.078478
C	8	-2.605824	1.436440	0.274459
H	9	-3.179144	1.313428	1.194095
H	10	-1.937572	2.291897	0.367537
H	11	-3.283245	1.588763	-0.566611
C	12	1.411337	-1.345416	-0.394711
H	13	1.492415	-1.981708	-1.278891
H	14	1.969563	-0.422041	-0.570431
C	15	1.923345	-2.055932	0.854372
H	16	2.975859	-2.310379	0.711981
H	17	1.853469	-1.401455	1.725617
H	18	1.375342	-2.979547	1.061564
N	19	-1.780149	0.248845	0.039379
H	20	1.933576	2.085659	-0.117649
F	21	2.728117	1.489349	-0.387934
F	22	0.789188	2.620606	0.215468

Table S13. Coordinates for **2a**, [$EMIm^+$][F^-]$_2$

C	1	-0.847615	-1.015250	-0.111302
C	2	0.276929	-1.764212	0.065399
C	3	0.942651	0.357037	-0.108544
N	4	-0.394612	0.299458	-0.215616
H	5	-1.964335	-1.224387	-0.155481
H	6	0.393430	-2.827171	0.193508
H	7	1.720521	1.203455	-0.141098
C	8	2.783413	-1.237670	0.220098
H	9	2.946663	-1.717773	1.188572
H	10	3.093361	-1.919040	-0.576609
H	11	3.338107	-0.293298	0.158313
C	12	-1.268275	1.464267	-0.429267
H	13	-0.607914	2.331286	-0.494890
H	14	-1.763980	1.330807	-1.394037
C	15	-2.317659	1.611746	0.669141
H	16	-2.918813	2.505492	0.471235
H	17	-2.973740	0.731231	0.660400
H	18	-1.841638	1.728521	1.647907
N	19	1.370169	-0.901843	0.063786
F	20	3.111266	1.762398	-0.098362
F	21	-3.518734	-1.109946	-0.160322

Table S14. Coordinates for **2b**, $[EMIm^+][F^-]_2$

C	1	0.152304	-1.454905	-0.339553
C	2	1.351840	-0.838826	-0.145118
C	3	-0.264748	0.720438	-0.071385
N	4	-0.834939	-0.474451	-0.290995
H	5	-0.082733	-2.491567	-0.509659
H	6	2.431087	-1.121066	-0.090033
H	7	-0.936020	1.641955	-0.011670
C	8	2.094979	1.523509	0.251172
H	9	3.052825	0.979053	0.261394
H	10	2.068358	2.262759	-0.551667
H	11	1.912102	2.021485	1.205314
C	12	-2.286663	-0.644429	-0.437626
H	13	-2.687967	0.376669	-0.487013
H	14	-2.470886	-1.162854	-1.384282
C	15	-2.899578	-1.412829	0.731813
H	16	-3.978104	-1.512604	0.578011
H	17	-2.476802	-2.416788	0.838071
H	18	-2.740955	-0.868577	1.665641
N	19	1.057279	0.510245	0.019506
F	20	-2.306579	2.328142	-0.064954
F	21	4.024791	-0.696672	0.115009

Table S15. Coordinates for **3a**, [$EMIm^+$][FHF^-][F^-]

C	1	0.767361	0.903608	0.026121
C	2	-0.559033	0.632600	0.232641
C	3	0.462152	-1.278819	-0.213754
N	4	1.380801	-0.307749	-0.251544
H	5	1.424107	1.790394	0.019494
H	6	-1.428816	1.240487	0.465178
H	7	0.640049	-2.325055	-0.392190
C	8	-1.984376	-1.471765	0.228378
H	9	-1.795916	-2.521094	-0.003892
H	10	-2.334495	-1.371881	1.255483
H	11	-2.754589	-1.056880	-0.427689
C	12	2.825920	-0.461699	-0.525125
H	13	2.928667	-1.015041	-1.463516
H	14	3.190916	0.583859	-0.628046
C	15	3.548223	-1.163290	0.621631
H	16	4.612393	-1.238406	0.381167
H	17	3.456375	-0.573876	1.536701
H	18	3.171725	-2.174952	0.813412
N	19	-0.723669	-0.735161	0.077503
F	20	3.112379	2.289265	-0.247314
F	21	-3.386072	1.283547	0.786370
H	22	-3.951105	0.679734	-0.029667
F	23	-4.406386	0.018218	-0.819889

Table S16. Coordinates for **3b**, [$EMIm^+$][FHF^-][F^-]

C	1	-0.739564	0.319635	-0.188130
C	2	-0.745387	-1.018200	0.023392
C	3	1.426908	-0.367739	-0.118251
N	4	0.599279	0.694113	-0.273320
H	5	-1.597062	0.979953	-0.276386
H	6	-1.605210	-1.663087	0.137641
H	7	2.864087	-0.409847	-0.139138
C	8	1.045679	-2.782162	0.264765
H	9	0.700167	-3.160494	1.230300
H	10	0.662680	-3.432414	-0.525918
H	11	2.134376	-2.785104	0.241841
C	12	1.069785	2.063496	-0.467891
H	13	2.127198	1.996552	-0.726716
H	14	0.535500	2.488166	-1.322793
C	15	0.868409	2.935204	0.771968
H	16	1.227629	3.950523	0.577880
H	17	-0.187619	2.991943	1.045793
H	18	1.425290	2.528251	1.619589
N	19	0.588693	-1.416514	0.063076
F	20	3.958427	-0.469242	-0.151907
F	21	-3.595122	1.074324	-0.207761
F	22	-3.746320	-1.188793	0.129603
H	23	-3.710689	-0.075643	-0.034914

Table S17. Coordinates for **3c**, [$EMIm^+$][FHF^-][F^-]

C	1	-1.596985	-1.142683	-0.008971
C	2	-0.583349	-2.038870	0.157186
C	3	0.354269	-0.047282	-0.124525
N	4	-0.977482	0.087630	-0.181838
H	5	-2.724419	-1.136961	-0.046115
H	6	-0.604764	-3.103052	0.318463
H	7	1.110221	0.747988	-0.220802
C	8	1.957195	-1.926415	0.203854
H	9	2.716600	-1.143003	0.119767
H	10	2.048410	-2.419587	1.174227
H	11	2.103916	-2.663872	-0.588667
C	12	-1.726382	1.345676	-0.389542
H	13	-1.383108	1.782995	-1.330523
H	14	-2.774511	1.025248	-0.478590
C	15	-1.528508	2.321169	0.767231
H	16	-2.112272	3.226184	0.576222
H	17	-1.888155	1.881583	1.701105
H	18	-0.480384	2.608963	0.886303
N	19	0.619920	-1.344007	0.082211
F	20	-4.129412	-0.406449	-0.220795
F	21	2.454382	1.862887	-0.301064
H	22	3.363721	1.093070	-0.159028
F	23	4.105057	0.301953	-0.021071

Table S18. Coordinates for **4a**, [$EMIm^+$][FHF^-]$_2$

C	1	-1.269947	0.017770	-0.177212
C	2	-0.810952	-1.249573	-0.003648
C	3	0.960619	0.086733	-0.116762
N	4	-0.147819	0.830343	-0.244864
H	5	-2.303745	0.369437	-0.239360
H	6	-1.386394	-2.155094	0.097732
H	7	1.992773	0.476191	-0.135853
C	8	1.490065	-2.319536	0.202477
H	9	1.282080	-2.807963	1.156244
H	10	1.333108	-3.033481	-0.608157
H	11	2.521279	-1.955832	0.185452
C	12	-0.150543	2.287748	-0.424505
H	13	0.893903	2.591949	-0.507088
H	14	-0.646872	2.504241	-1.373879
C	15	-0.853132	3.006629	0.724643
H	16	-0.838274	4.084769	0.543142
H	17	-1.893836	2.687469	0.812023
H	18	-0.344959	2.810900	1.671922
N	19	0.576544	-1.187139	0.031198
H	20	-3.992762	-0.884246	-0.024706
F	21	-3.770991	-1.939995	0.092418
F	22	-4.117106	0.319210	-0.162330
H	23	4.048552	0.031326	-0.028152
F	24	3.563934	1.147764	-0.181665
F	25	4.339432	-0.993726	0.108954

Table S19. Coordinates for **4b**, [$EMIm^+$][FHF^-]$_2$

C	1	1.081275	-0.559878	-0.179139
C	2	1.425963	0.743426	-0.004349
C	3	-0.800593	0.613330	-0.029061
N	4	-0.306295	-0.619513	-0.193613
H	5	1.752323	-1.400447	-0.289702
H	6	2.429133	1.162474	0.053268
H	7	-1.860557	0.917110	0.005611
C	8	0.101602	2.894589	0.274045
H	9	0.570131	3.191372	1.213713
H	10	0.585513	3.421504	-0.549798
H	11	-0.959661	3.139523	0.296147
C	12	-1.126879	-1.834723	-0.337809
H	13	-2.157811	-1.510951	-0.504044
H	14	-0.772127	-2.357984	-1.229255
C	15	-1.034734	-2.733865	0.892899
H	16	-1.650187	-3.623249	0.734772
H	17	-0.008239	-3.054513	1.087707
H	18	-1.414222	-2.214881	1.776134
N	19	0.237702	1.453810	0.087130
H	20	4.133393	-0.382503	-0.118753
F	21	4.308541	0.767117	0.029833
F	22	3.868446	-1.463411	-0.260438
H	23	-3.862294	0.386586	-0.193418
F	24	-4.078842	-0.635303	-0.413699
F	25	-3.452038	1.525886	0.062470

Table S20. Coordinates for **4c**, [$EMIm^+$][FHF^-]$_2$

C	1	0.317997	-1.644351	-0.283115
C	2	1.377764	-0.833189	-0.014658
C	3	-0.484046	0.396081	0.041880
N	4	-0.829776	-0.865301	-0.248891
H	5	0.285141	-2.695428	-0.511596
H	6	2.456307	-1.027156	0.039459
H	7	-1.196089	1.236483	0.148426
C	8	1.625112	1.629390	0.535523
H	9	2.611233	1.571888	0.064879
H	10	1.076419	2.506847	0.196196
H	11	1.747617	1.674813	1.619457
C	12	-2.209248	-1.341489	-0.450305
H	13	-2.835963	-0.478707	-0.689976
H	14	-2.192175	-2.010128	-1.314960
C	15	-2.758174	-2.053666	0.783979
H	16	-3.780008	-2.383531	0.581285
H	17	-2.158563	-2.926788	1.058201
H	18	-2.792166	-1.368756	1.633789
N	19	0.847771	0.432298	0.184248
H	20	4.445091	0.042955	-0.187084
F	21	4.249164	-1.094808	0.109608
F	22	4.510473	1.108777	-0.448807
H	23	-3.451141	1.687559	-0.170009
F	24	-4.206379	1.039929	-0.581045
F	25	-2.504157	2.311026	0.287423

Table S21. Coordinates for **5a**, [$EMIm^+$][FHF^-][$F(HF)_2^-$]

C	1	-0.879097	-0.211015	-0.166828
C	2	-0.333543	-1.445417	-0.001066
C	3	1.336584	0.013046	-0.125658
N	4	0.178696	0.680702	-0.238589
H	5	-1.927562	0.070030	-0.235774
H	6	-0.833879	-2.393336	0.106071
H	7	2.340520	0.467519	-0.143983
C	8	2.037776	-2.349171	0.189851
H	9	3.039085	-1.910321	0.167112
H	10	1.870897	-2.848467	1.145864
H	11	1.928135	-3.073405	-0.619232
C	12	0.060464	2.134761	-0.456096
H	13	0.320129	2.341549	-1.497764
H	14	-0.995299	2.372682	-0.321771
C	15	0.944403	2.942286	0.490123
H	16	0.806995	4.006799	0.281638
H	17	0.663076	2.759977	1.530547
H	18	2.001607	2.695758	0.359998
N	19	1.044146	-1.284852	0.021801
F	20	3.838392	1.293880	-0.115830
H	21	4.410249	0.200357	0.002981
F	22	4.765327	-0.799423	0.103042
F	23	-5.213397	1.598488	0.305693
H	24	-4.658507	0.816931	0.080076
F	25	-3.792401	-0.249615	-0.258756
H	26	-3.554375	-1.585283	-0.048808
F	27	-3.261309	-2.532072	0.091253

Table S22. Coordinates for **5b**, [$EMIm^+$][FHF^-][$F(HF)_2^-$]

C	1	0.377416	1.381742	0.083955
C	2	-0.762465	2.118338	0.173812
C	3	-1.357603	-0.001774	-0.090473
N	4	-0.019787	0.066102	-0.083259
H	5	1.421110	1.674542	0.114654
H	6	-0.903259	3.178195	0.295984
H	7	-1.980649	-0.912747	-0.202318
C	8	-3.249081	1.616432	0.092216
H	9	-3.873194	0.720886	0.015889
H	10	-3.463416	2.131828	1.030384
H	11	-3.462565	2.283828	-0.745158
C	12	0.895782	-1.092985	-0.182163
H	13	0.368547	-1.857590	-0.753855
H	14	1.773395	-0.758130	-0.737883
C	15	1.310826	-1.612869	1.190681
H	16	2.041405	-2.413164	1.057881
H	17	1.798587	-0.825385	1.769506
H	18	0.452309	-1.994491	1.749971
N	19	-1.831633	1.243031	0.063118
F	20	-3.107682	-2.146361	-0.335091
H	21	-4.164911	-1.546402	-0.229184
F	22	-5.021808	-0.901585	-0.123447
F	23	4.609454	-1.922182	0.004611
H	24	4.287274	-1.056750	-0.339041
F	25	3.722991	0.141625	-0.834852
H	26	3.570894	1.313212	-0.278421
F	27	3.330951	2.211273	0.153713

Table S23. Coordinates for **5c**, [$EMIm^+$][FHF^-][$F(HF)_2^-$]

C	1	-1.005040	-0.383700	-0.162395
C	2	-0.391957	-1.588655	-0.023476
C	3	1.190974	-0.035591	-0.137547
N	4	-0.002553	0.568164	-0.228313
H	5	-2.057289	-0.141447	-0.213794
H	6	-0.829161	-2.566953	0.077376
H	7	2.172366	0.467815	-0.154719
C	8	2.025124	-2.363728	0.129774
H	9	3.003432	-1.874841	0.105793
H	10	1.894770	-2.887268	1.078672
H	11	1.946647	-3.079232	-0.690860
C	12	-0.215740	2.021223	-0.404688
H	13	0.043161	2.269899	-1.437442
H	14	-1.285560	2.187736	-0.268473
C	15	0.614697	2.848222	0.572349
H	16	0.412524	3.908015	0.395562
H	17	0.335201	2.619510	1.604048
H	18	1.686275	2.673435	0.446354
N	19	0.974388	-1.351793	-0.010849
F	20	3.671551	1.288143	-0.123350
H	21	4.288276	0.230107	-0.032114
F	22	4.698394	-0.758424	0.046620
F	23	-3.481721	-2.479002	0.225597
H	24	-3.782578	-1.544170	0.078023
F	25	-4.077101	-0.206558	-0.168095
H	26	-3.804686	1.109332	0.011670
F	27	-3.492742	2.058823	0.111445

Table S24. Coordinates for **5d**, [$EMIm^+$][FHF^-][$F(HF)_2^-$]

C	1	-1.615744	0.383947	-0.163992
C	2	-1.673277	-0.967360	-0.019180
C	3	0.465285	-0.377505	-0.056385
N	4	-0.274385	0.731126	-0.186379
H	5	-2.455689	1.068985	-0.247058
H	6	-2.564353	-1.581572	0.034733
H	7	1.542575	-0.447113	-0.035787
C	8	0.053641	-2.816885	0.196987
H	9	-0.355481	-3.217271	1.125714
H	10	-0.325825	-3.399577	-0.643709
H	11	1.142084	-2.849086	0.219199
C	12	0.259780	2.099355	-0.306238
H	13	1.332388	2.013060	-0.484667
H	14	-0.209703	2.548225	-1.184513
C	15	-0.019845	2.930033	0.943829
H	16	0.383847	3.935901	0.803376
H	17	-1.090718	3.012550	1.143745
H	18	0.468535	2.489645	1.816252
N	19	-0.366643	-1.422624	0.046668
C	20	-4.533140	-0.048943	-0.118345
F	21	-4.560552	-1.177801	-0.007245
F	22	-4.400140	1.095992	-0.231903
F	23	3.386431	1.702911	-0.424094
H	24	3.943716	0.870956	-0.283085
F	25	4.587898	-0.285286	-0.084661
H	26	3.789528	-1.250499	0.083260
F	27	3.053073	-1.981847	0.212207

Table S25. Coordinates for **5e**, [$EMIm^+$][FHF^-][$F(HF)_2^-$]

C	1	-1.589632	0.295820	-0.156696
C	2	-1.512101	-1.053985	-0.011054
C	3	0.558978	-0.252268	0.005783
N	4	-0.288465	0.774198	-0.146210
H	5	-2.491936	0.896544	-0.260681
H	6	-2.333984	-1.756654	0.021951
H	7	1.646425	-0.184642	0.063494
C	8	0.385220	-2.720635	0.257642
H	9	0.085358	-3.116940	1.229300
H	10	-0.003707	-3.367969	-0.529308
H	11	1.473068	-2.679237	0.193082
C	12	0.110900	2.187490	-0.256218
H	13	1.182380	2.211831	-0.462078
H	14	-0.414517	2.600458	-1.120056
C	15	-0.223758	2.974831	1.008510
H	16	0.082297	4.015773	0.876760
H	17	-1.295062	2.953940	1.221185
H	18	0.314069	2.570074	1.869128
N	19	-0.166720	-1.375597	0.087339
H	20	-4.454388	-0.298460	-0.171380
F	21	-4.404005	-1.414841	-0.063537
F	22	-4.400000	0.866110	-0.281954
F	23	3.655420	-2.429148	-0.021689
H	24	3.665742	-1.439070	0.050611
F	25	3.476224	-0.072820	0.182783
H	26	3.532481	1.230996	-0.305986
F	27	3.430186	2.160214	-0.632462

Table S26. Coordinates for **6**, $[EMIm^+]_2[FHF^-]_3$

C	1	4.806137	-0.691947	-0.106993
C	2	4.904744	0.620248	-0.448931
C	3	2.744862	0.136688	-0.278382
N	4	3.452101	-0.969630	-0.007419
H	5	5.618868	-1.402347	0.076377
H	6	5.806895	1.190853	-0.607445
H	7	1.655506	0.213358	-0.276035
C	8	3.254155	2.491971	-0.910236
H	9	3.755411	3.181504	-0.229738
H	10	3.579637	2.695980	-1.931622
H	11	2.173845	2.620078	-0.833252
C	12	2.872023	-2.269958	0.357047
H	13	1.791215	-2.174684	0.244047
H	14	3.226286	-3.003838	-0.370465
C	15	3.248870	-2.689980	1.775340
H	16	2.802965	-3.662876	1.997250
H	17	4.331668	-2.776188	1.885707
H	18	2.879023	-1.966945	2.506206
N	19	3.614166	1.118626	-0.550644
H	20	7.657557	-0.739142	-0.018921
F	21	7.818348	0.303161	-0.309044
F	22	7.348031	-1.863545	0.289906
H	23	-0.064226	1.648156	-0.445282
F	24	-0.164684	0.415794	-0.253105
F	25	0.027424	2.685356	-0.593483
H	26	-1.979469	0.278628	-0.139439
C	27	-3.062196	0.387156	-0.029843
N	28	-3.710036	1.548756	0.131702
N	29	-3.969138	-0.597050	-0.023826
C	30	-5.066165	1.282795	0.250471
C	31	-3.079292	2.876981	0.216106
C	32	-5.236381	-0.064423	0.149965
C	33	-3.664323	-2.030429	-0.153410
H	34	-5.790290	2.068725	0.376750
H	35	-2.089522	2.810679	-0.237426
H	36	-3.685458	3.555658	-0.388753
C	37	-2.971693	3.373830	1.656224
H	38	-6.135415	-0.698653	0.169556
H	39	-4.482368	-2.525091	-0.687879
H	40	-2.723867	-2.134305	-0.692979
H	41	-3.566813	-2.468858	0.841458
H	42	-2.504558	4.361496	1.662345
H	43	-3.951540	3.451938	2.134657
H	44	-2.346235	2.702773	2.248775
F	45	-7.412948	-1.895287	0.089747

H	46	-6.841358	-2.661857	-0.628201
F	47	-6.208600	-3.290763	-1.264969

Table S27. Atomic Charges calculated using Natural Population Analysis

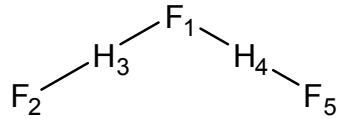
HF

Atom	No	Natural Charge
F1		-0.54803
H2		0.54803

FHF^-

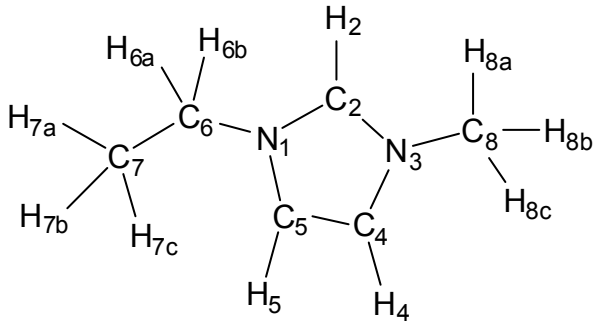
Atom	No	Natural Charge
F1		-0.76306
F2		-0.76998
H3		0.53304

$F(HF)_2^-$



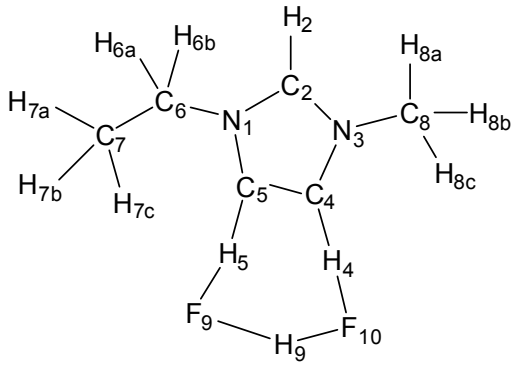
Atom	No	Natural Charge
F1		-0.76530
F2		-0.67481
H3		0.55709
H4		0.55733
F5		-0.67431

$EMIm^+$



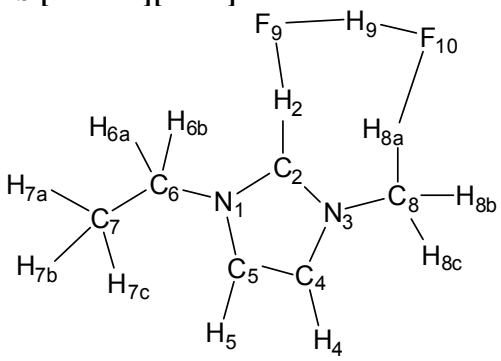
Atom	Natural Charge
N1	-0.34814
C2	0.29611
N3	-0.34641
C4	-0.00564
C5	-0.00372
C6	-0.16693
C7	-0.58885
C8	-0.35327
H2	0.23768
H4	0.24798
H5	0.2477
H6a	0.2165
H6b	0.22211
H7a	0.2356
H7b	0.21335
H7c	0.21404
H8a	0.22873
H8b	0.22892
H8c	0.22424

1a [$EMIm^+$][FHF^-]



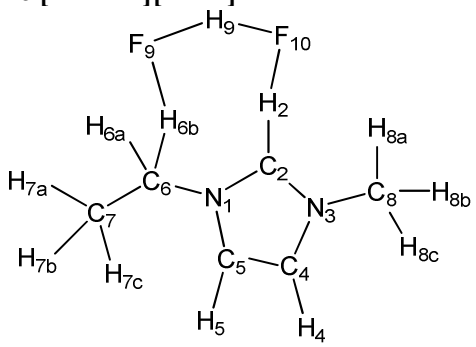
Atom	Natural Charge
N1	-0.35676
C2	0.24884
N3	-0.35948
C4	-0.02273
C5	-0.01183
C6	-0.15967
C7	-0.5918
C8	-0.34836
F9	-0.75742
F10	-0.7012
H2	0.21535
H4	0.277
H5	0.3182
H6a	0.21574
H6b	0.19465
H7a	0.21423
H7b	0.24168
H7c	0.20227
H8a	0.207
H8b	0.21802
H8c	0.2185
H9	0.53778

1b [$EMIm^+$][FHF^-]



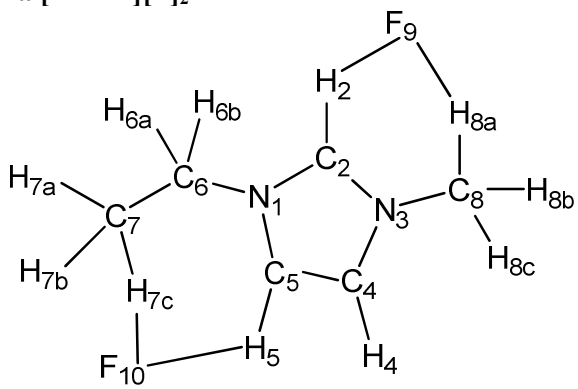
Atom	Natural Charge
N1	-0.37408
C2	0.29501
N3	-0.36332
C4	-0.03085
C5	-0.03527
C6	-0.1726
C7	-0.58364
C8	-0.37366
F9	-0.75678
F10	-0.674
H2	0.31602
H4	0.22602
H5	0.22569
H6a	0.24607
H6b	0.19782
H7a	0.21751
H7b	0.21649
H7c	0.19584
H8a	0.28209
H8b	0.20097
H8c	0.20083
H9	0.54385

1c [$EMIm^+$][FHF^-]



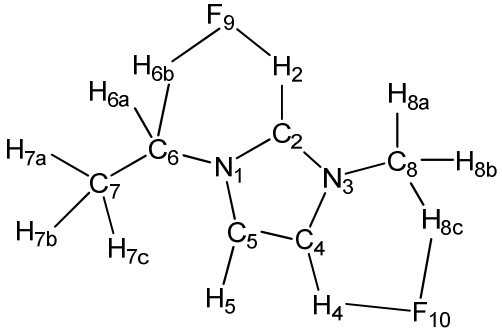
Atom	Natural Charge
N1	-0.36676
C2	0.29473
N3	-0.37121
C4	-0.03746
C5	-0.02867
C6	-0.19118
C7	-0.58198
C8	-0.35639
F9	-0.67407
F10	-0.75759
H2	0.31644
H4	0.22542
H5	0.22641
H6a	0.19322
H6b	0.27794
H7a	0.21989
H7b	0.21437
H7c	0.19055
H8a	0.2525
H8b	0.20517
H8c	0.20457
H9	0.54413

2a [EMIm][$F]_2^-$



Atom	Natural Charge
N1	-0.38959
C2	0.24789
N3	-0.38631
C4	-0.08893
C5	-0.04476
C6	-0.15437
C7	-0.61189
C8	-0.37419
F9	-0.86474
F10	-0.88524
H2	0.32723
H4	0.20321
H5	0.33142
H6a	0.19992
H6b	0.19487
H7a	0.18595
H7b	0.28278
H7c	0.18227
H8a	0.28318
H8b	0.18073
H8c	0.18057

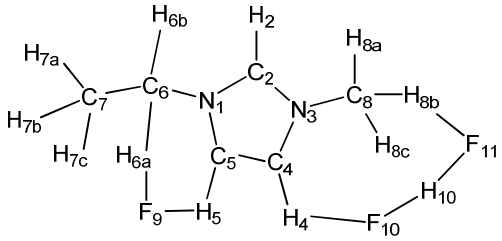
2b [EMIm][F]$_2^-$



N1	-0.38821
C2	0.2536
C4	-0.03504
N3	-0.37857
C5	-0.09333
C6	-0.19667
C7	-0.57821
C8	-0.3824
F9	-0.87228
F10	-0.89726

H2	0.32473
H4	0.32351
H5	0.20358
H6a	0.17422
H6b	0.28815
H7a	0.1971
H7b	0.18409
H7c	0.20927
H8a	0.18498
H8b	0.18541
H8c	0.29331

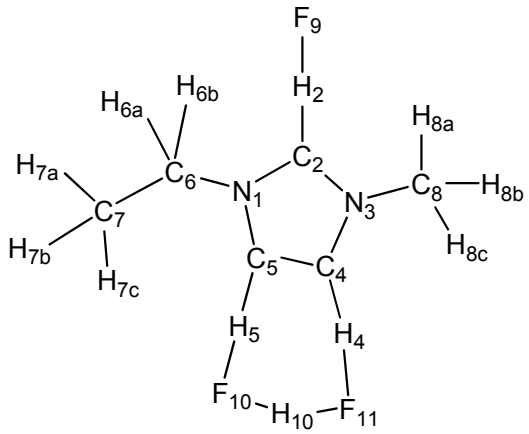
3a [EMIm$^+$][FHF$^-$][F$^-$]



N1	-0.35811
C2	0.2373
N3	-0.34779
C4	-0.04302
C5	-0.02737
C6	-0.22165
C7	-0.57943
C8	-0.36925
F9	-0.89516
F10	-0.75341
F11	-0.73468

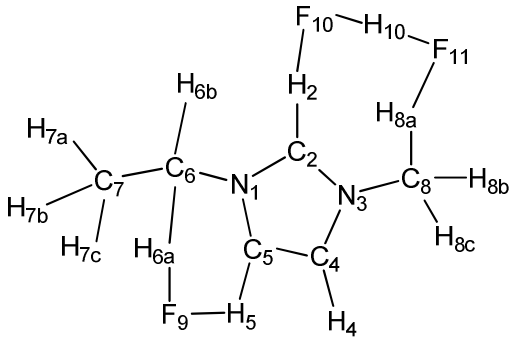
H2	0.20107
H4	0.29027
H5	0.31924
H6a	0.32082
H6b	0.17132
H7a	0.17229
H7b	0.20319
H7c	0.21395
H8a	0.17499
H8b	0.28013
H8c	0.21488
H10	0.53042

3b [$EMIm^+$][FHF^-][F^-]



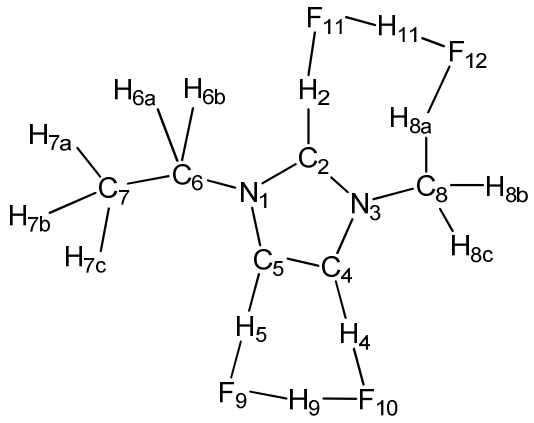
N1	-0.42072
C2	0.14706
N3	-0.41823
C4	-0.05874
C5	-0.0558
C6	-0.15932
C7	-0.58128
C8	-0.34236
F9	-0.71703
F10	-0.75874
F11	-0.74277
H2	0.42103
H4	0.266
H5	0.28097
H6a	0.18915
H6b	0.2126
H7a	0.20205
H7b	0.19244
H7c	0.21012
H8a	0.22146
H8b	0.18971
H8c	0.18971
H10	0.53269

3c [$EMIm^+$][FHF^-][F^-]



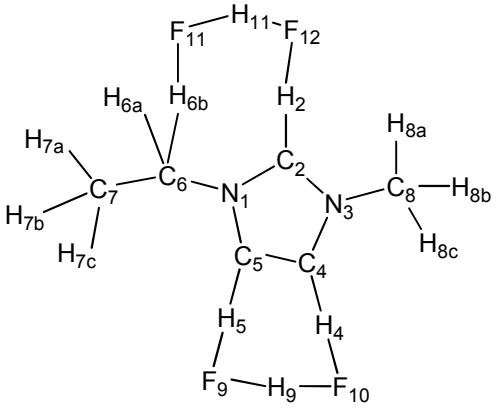
N1	-0.37303
C2	0.26277
N3	-0.36958
C4	-0.08563
C5	-0.02919
C6	-0.19931
C7	-0.5847
C8	-0.37408
F9	-0.88556
F10	-0.75284
F11	-0.71511
H2	0.29398
H4	0.20651
H5	0.33116
H6a	0.29078
H6b	0.18586
H7a	0.20772
H7b	0.20161
H7c	0.19893
H8a	0.27991
H8b	0.18779
H8c	0.18809
H10	0.5339

4a [$EMIm^+$][FHF^-]$_2$



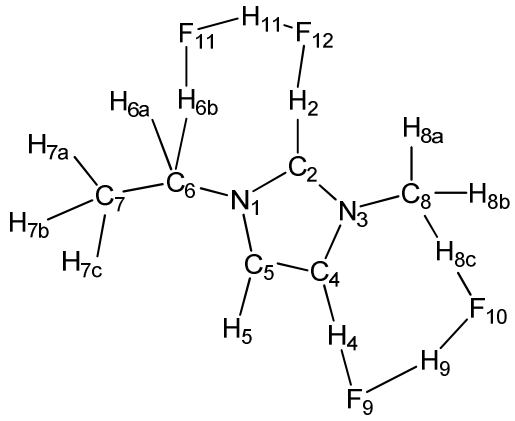
N1	-0.37757
C2	0.26427
N3	-0.36568
C4	-0.03851
C5	-0.03586
C6	-0.16439
C7	-0.58585
C8	-0.37154
F9	-0.76807
F10	-0.72071
F11	-0.76007
F12	-0.70537
H2	0.29558
H4	0.25781
H5	0.29863
H6a	0.19784
H6b	0.22267
H7a	0.20020
H7b	0.22351
H7c	0.20257
H8a	0.27353
H8b	0.19371
H8c	0.19388
H9	0.53392
H11	0.53551

4b [$EMIm^+$][FHF^-]$_2$



N1	-0.36803
C2	0.26301
N3	-0.37250
C4	-0.04100
C5	-0.03819
C6	-0.18912
C7	-0.57952
C8	-0.34960
F9	-0.73740
F10	-0.75479
F11	-0.70317
F12	-0.76476
H2	0.29537
H4	0.29197
H5	0.27715
H6a	0.19013
H6b	0.26778
H7a	0.20445
H7b	0.20090
H7c	0.20537
H8a	0.20104
H8b	0.20138
H8c	0.23090
H9	0.53265
H11	0.53599

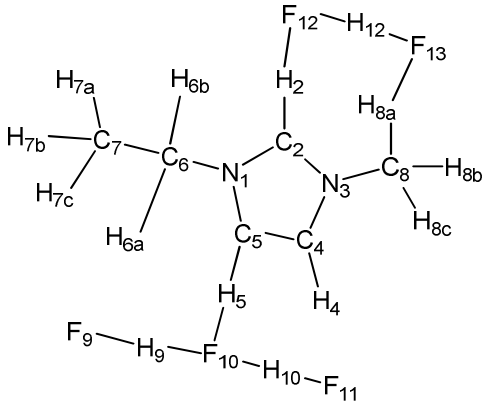
4c [$EMIm^+$][FHF^-]$_2$



N1	-0.37098
C2	0.26955
N3	-0.35982
C4	-0.02314
C5	-0.06312
C6	-0.19183
C7	-0.57771
C8	-0.37313
F9	-0.75468
F10	-0.71977
F11	-0.70682
F12	-0.75799

H2	0.30007
H4	0.30293
H5	0.21345
H6a	0.18396
H6b	0.27638
H7a	0.20898
H7b	0.18637
H7c	0.21205
H8a	0.20520
H8b	0.19505
H8c	0.27657
H9	0.53273
H11	0.53570

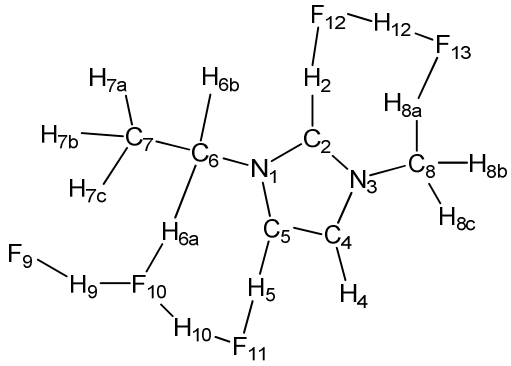
5a [$EMIm^+$][FHF^-][$F(HF)_2^-$]



N1	-0.37185
C2	0.26306
N3	-0.36077
C4	-0.04221
C5	-0.02631
C6	-0.15900
C7	-0.60274
C8	-0.37207
F9	-0.65241
F10	-0.77671
F11	-0.66262
F12	-0.76390
F13	-0.69947

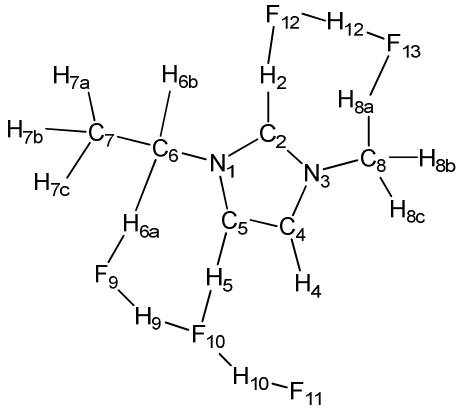
H2	0.29656
H4	0.25240
H5	0.29065
H6a	0.21217
H6b	0.19803
H7a	0.20149
H7b	0.19920
H7c	0.25225
H8a	0.27434
H8b	0.19557
H8c	0.19495
H9	0.56300
H10	0.55869
H12	0.53770

5b [$EMIm^+$][FHF^-][$F(HF)_2^-$]



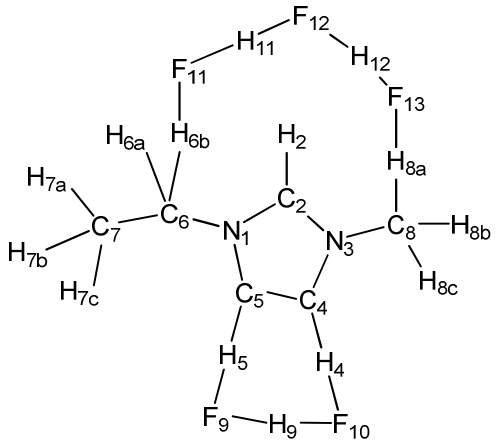
N1	-0.36353
C2	0.27780
N3	-0.36745
C4	-0.05591
C5	-0.02074
C6	-0.18566
C7	-0.58478
C8	-0.37478
F9	-0.65087
F10	-0.75859
F11	-0.66815
F12	-0.75255
F13	-0.70417
H2	0.30358
H4	0.21573
H5	0.28126
H6a	0.26047
H6b	0.20588
H7a	0.19273
H7b	0.20760
H7c	0.23074
H8a	0.28222
H8b	0.19181
H8c	0.19203
H9	0.55919
H10	0.55033
H12	0.53584

5c [$EMIm^+$][FHF^-][$F(HF)_2^-$]



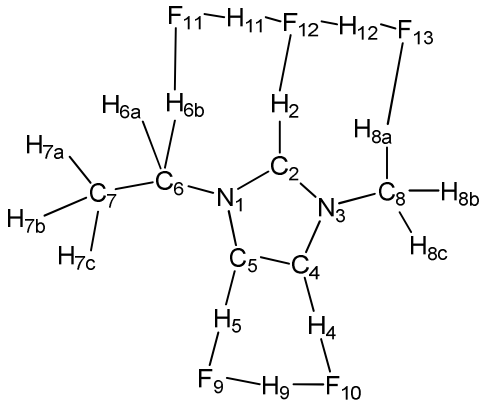
N1	-0.36541
C2	0.26523
N3	-0.36304
C4	-0.04268
C5	-0.01678
C6	-0.17814
C7	-0.59787
C8	-0.37315
F9	-0.66191
F10	-0.76826
F11	-0.65698
F12	-0.75906
F13	-0.70342
H2	0.29722
H4	0.24169
H5	0.27793
H6a	0.25144
H6b	0.19265
H7a	0.24029
H7b	0.19948
H7c	0.20266
H8a	0.27680
H8b	0.19408
H8c	0.19313
H9	0.55683
H10	0.56071
H12	0.53656

5d [$EMIm^+$][FHF^-][$F(HF)_2^-$]



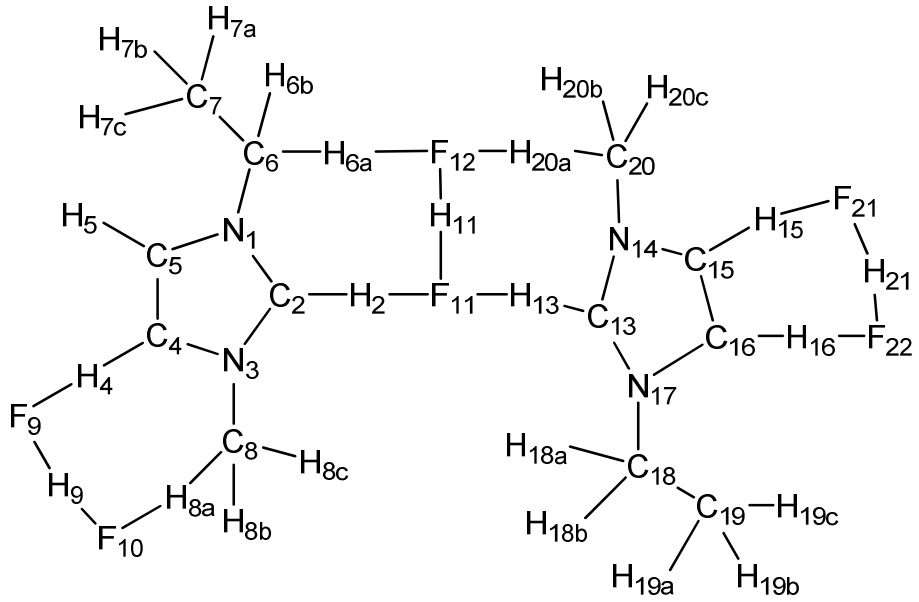
N1	-0.36168
C2	0.27103
N3	-0.36015
C4	-0.03549
C5	-0.03386
C6	-0.18640
C7	-0.58052
C8	-0.36360
F9	-0.74866
F10	-0.74126
F11	-0.66698
F12	-0.71291
F13	-0.68905
H2	0.26844
H4	0.28445
H5	0.29197
H6a	0.19531
H6b	0.26086
H7a	0.20618
H7b	0.20704
H7c	0.20418
H8a	0.26080
H8b	0.19882
H8c	0.19920
H9	0.53246
H11	0.55242
H12	0.54743

5e [$EMIm^+$][FHF^-][$F(HF)_2^-$]



N1	-0.36787
C2	0.26109
N3	-0.36340
C4	-0.03746
C5	-0.03435
C6	-0.18128
C7	-0.58073
C8	-0.36384
F9	-0.75289
F10	-0.73719
F11	-0.65007
F12	-0.77095
F13	-0.65128
H2	0.28067
H4	0.27926
H5	0.29431
H6a	0.19863
H6b	0.25001
H7a	0.20558
H7b	0.20897
H7c	0.20365
H8a	0.25590
H8b	0.20111
H8c	0.19847
H9	0.53260
H11	0.56069
H12	0.56040

6 $[EMIm^+]_2[FHF^-]_3$



N1	-0.36778	H2	0.28550
C2	0.26586	H4	0.30818
N3	-0.35298	H5	0.21764
C4	-0.01587	H6a	0.26034
C5	-0.05860	H6b	0.19153
C6	-0.18569	H7a	0.21102
C7	-0.57853	H7b	0.19363
C8	-0.37536	H7c	0.20999
F9	-0.75087	H8a	0.28320
F10	-0.71460	H8b	0.19781
F11	-0.76521	H8c	0.20089
F12	-0.68571	H9	0.53312
C13	0.25587	H11	0.53344
N14	-0.36163	H13	0.28173
C15	-0.03364	H15	0.27142
C16	-0.03218	H16	0.30241
N17	-0.36893	H18a	0.21301
C18	-0.16314	H18b	0.20388
C19	-0.58589	H19a	0.20554
C20	-0.36613	H19b	0.22393
F21	-0.72291	H19c	0.20258
F22	-0.76032	H20a	0.25773
		H20b	0.20155
		H20c	0.20032
		H21	0.53387
		---	---