Molecular structure and interactions in the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide

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Table S1. Selected vibrational frequencies (in cm^{-1}) of lowest energy conformer of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide in B3LYP B97D and MP2 framework. Intensities (in KM/Mole) are given in parentheses. In the experimental column,R and IR refer to Raman and infrared results.

Vibrations	EMIM	Tf_2N	Experimental	B3LYP		B97D	MP2
				C1	C2	C3	C2
C_4-H_{13}, C_5-H_{12} stretch	3198 (16)		3185 (R), 3165 (IR) 3125 (R), 3126 (IR)	3198 (8)	3200 (6)	3141 (3)	3170 (1)
C_8-H_{22} stretch			3107 (IR)	3073 (21)	3035 (15)		
C_6-H_{17} stretch	3093 (0)			3072 (65)		3045 (17)	3044 (4)
asymm. H_{18}-C_7-H_{19} stretch	3062 (9)			3060 (11)			3079(1)
asymm. H_{20}-C_8-H_{21} stretch	3042 (1)			3040 (24)			
C_7-H_{19} stretch			2991 (IR)	2991 (33)	2989 (19)	2919 (34)	3065 (4)
symm. H_{15}-C_6-H_{17} stretch			2986 (R), 2980 (IR)	2973 (85)	2988 (29)		3028 (11)
asymm. H_{20}-C_8-H_{21} stretch			2970 (R), 2958 (IR)	2968 (20)	2969 (16)	2981 (12)	
C_2-H_{14} stretch	3202 (30)		2948 (R), 2914 (R)	2931 (735)	3155 (254)	3047 (268)	3155 (116)
H_{16}-C_6-H_{17} sym stretch						2914 (20)	2964 (24)
H_{20}-C_8-H_{21} sym stretch						2885 (27)	2958 (19)
N_3-C_4-H_{13} rock	1570 (32)		1575 (R), 1574 (IR)	1571 (22)	1574 (34)	1526 (13)	1550 (71)
N_1-C_2-H_{14} rock	1562 (54)			1562 (50)	1566 (48)	1511 (44)	1524 (9)
H_{18}-C_7-H_{19} scissor	1473 (15)			1480 (9)	1476 (6)	1447 (13)	1453 (7)
H_{15}-C_6-H_{17} scissor	1456 (9)		1471 (IR)	1473 (12)	1474 (17)	1430 (21)	1467 (9)
H_{21}-C_8-H_{22} scissor	1460 (16)		1458 (R), 1464 (IR)	1466 (11)	1464 (14)	1418 (18)	1464 (8)
H_{20}-C_8-H_{22} scissor							

H_{15}-C_6-H_{17} rock	1448 (16)		1426 (R), 1433 (IR)	1435 (11)	1456 (14)	1408 (20)	1446 (21)
					1429 (8)	1392 (7)	1410 (7)
CN stretch	1407 (2)			1412 (18)	1317 (13)	1377 (4)	1399 (2)
H_{21}-C_8-H_{22} rock	1395 (7)		1390 (IR)	1392 (8)	1396 (9)	1357 (8)	1380 (8)
H_{18}-C_7-H_{19} rock	1349 (14)		1340 (R), 1348 (IR)	1350 (8)	1352 (11)	1310 (6)	1332 (12)
N_1-C_2-H_{14} rock	1311 (11)		1330 (R), 1331 (IR)	1300 (13)		1243 (9)	1309 (14)
C_4-C_5-H_{12} rock							
SO stretch		1284 (444)	1244 (R)	1295 (585)	1269 (415)	1219 (410)	1273 (390)
N_1-C_2-H_{14} rock						1207 (23)	1229 (126)
		1261 (71)	1237 (R)				
H_{18}-C_7-H_{19} twist				1270 (38)	1246 (51)		
H_{18}-C_7-H_{19} twist			1244 (R)	1253 (21)			
SO stretch + H_{18}-C_7-H_{19} wag						1195 (182)	
CF Stretch		1197 (396)	1227 (IR), 1200 (IR)	1225 (403)	1233 (299)	1168 (188)	1217 (303)
		1193 (52)	1182 (IR)	1217 (46)	1214 (225)	1164 (102)	1201 (130)
		1186 (92)	1200 (IR), 1182 (IR)	1202 (176)	1211 (179)	1151 (225)	1198 (66)
		1182 (167)	1200 (IR), 1182 (IR)	1195 (103)	1197 (177)	1118 (179)	1192 (106)
		1175 (160)	1141 (R), 1169 (IR) 1132 (IR)	1145 (156)	1187 (83)	1101 (172)	1187 (132)
		1169 (307)			1179 (148)		1174 (226)
SC stretch			1169 (IR)	1175 (156)	1168 (134)		1170 (228)
H_{15}-C_6-H_{17} twist						1094 (114), 1094 (112)	
N_1-C_2-H_{14} rock	1148 (108)		1169 (IR)	1170 (98)	1149 (32)	1114 (54)	
			1141 (R)				
H_{21}-C_8-H_{22} twist			1092 (R), 1088 (IR)	1078 (64)	1077 (76)	1087 (10)	
H_{20}-C_8-H_{21}							
SO* stretch			1051 (IR)	1070 (127)	1070 (346)	1018 (67)	1084 (291)
			1051 (IR) 1038 (IR)	1066 (171)	1038 (237)	1003 (194)	1078 (120)

C_4-C_5-H_{12} scissor						1058 (8)	
C_2-N_3-C_4 bend						976 (44)	1001 (7)
C_7-C_8 stretch			1026 (R), 1022 (R)	1018 (8)	1017 (8)		
C_2-N_3-C_4				1006 (12)	1009 (22)		
N1-C2-H14 wag	805 (38)		963 (R), 960 (IR)	969 (331)		866 (33)	
			954 (R), 843 (IR)	946 (231)	902 (32)		
C_7-C_8 stretch						899 (101)	
H_{18}-C_7-H_{19} wag			793 (R)	792 (14)	789 (7)	771 (5)	
Symm. CF_3 stretch			754 (R), 752 (IR)	753 (31)			754 (23)
C_4-C_5-H_{12} wag	729 (21)			724 (33)	716 (29)	688 (28)	806 (60)
SN stretch		745 (12)	740 (R), 741 (IR) 701 (R), 702 (IR)	700 (90)	972 (500)	904 (479)	990 (416)
S-N-S symm. stretch		695 (23)			700 (16)	657 (38)	674 (14)
C_4-C_5-H_{12} wag							
S-N-S bend						632 (77)	706 (10)
CN bond oscillation	642 (15)		650 (IR)	651 (21)	649 (21)	632 (25)	630 (57)
					617 (23)		621 (91)
SN bond oscillation		584 (343)	592 (R), 569 (R) 569 (IR)	587 (308)	633 (111)		

Table S2. B3LYP results for electron density at BCP of different bonds in free cation[a], anion[b] and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide conformers

	C1	**S1**	**C2**	**S2**	**C3**	**S3**	**C4**	**S4**	**C5**	**S5**
	In gas	In solution	In gas	In solution	In gas	In solution	In gas	In solution	In gas	In solution
C_2-H_{14}	0.28629	0.29647	0.29672	0.29523	0.29359	0.29292	0.28669	0.29716	0.29501	0.29407
C_6-H_{17}	0.28931	0.28717	0.28825	0.28898	0.29025	0.28823	0.28891	0.28852	0.28842	0.28621
C_7-H_{18}	0.29129	0.28921	0.28995	0.28934	0.29219	0.28920	0.29174	0.28762	0.29136	0.28960
C_8-H_{22}	0.28121	0.28017	0.28252	0.27957	0.28106	0.27961	0.28220	0.28032	0.28239	0.27771
N-S	0.24008	0.24490	0.24871	0.24563	0.24791	0.24286	0.24100	0.27789	0.24747	0.24535
N-S	0.23987	0.24318	0.24373	0.24271	0.24386	0.24266	0.23876	0.24457	0.24377	0.24233
S-C	0.19175	0.19234	0.19429	0.19251	0.19274	0.19245	0.19178	0.19400	0.19250	0.19265
S-C	0.19076	0.19196	0.19217	0.19205	0.19071	0.19222	0.19140	0.19201	0.19174	0.18998
S-O	0.28482	0.27736	0.27606	0.28230	0.28707	0.28081	0.28513	0.27781	0.28726	0.28100
S-O	0.27816	0.28240	0.27422	0.27697	0.27328	0.28030	0.27860	0.27697	0.27268	0.27970
S-O	0.28549	0.28216	0.28615	0.28235	0.28651	0.28099	0.28528	0.28134	0.28668	0.28083
S-O	0.27999	0.27828	0.27506	0.27802	0.27255	0.28098	0.27877	0.27877	0.27497	0.27850
C-F	0.28566	0.28465	0.28564	0.28475	0.28470	0.28231	0.28293	0.28415	0.28716	0.28317
C-F	0.28221	0.28224	0.28491	0.27936	0.28056	0.28203	0.28171	0.28394	0.27898	0.28160
C-F	0.26812	0.27512	0.27998	0.27743	0.27932	0.28119	0.28071	0.28121	0.26543	0.27803
C-F	0.28485	0.28356	0.28405	0.28252	0.28704	0.28288	0.28262	0.28192	0.28618	0.28127
C-F	0.28151	0.28077	0.27934	0.28162	0.27320	0.28231	0.28185	0.28056	0.27672	0.28127
C-F	0.27963	0.27918	0.27680	0.28128	0.26928	0.27710	0.27266	0.28045	0.27334	0.28045
H_{14}---O		0.01461	0.02182	0.01142	0.01692			0.01070	0.02597	0.01683
H_{14}---O		0.00984		0.01058	0.1830			0.00958		
H_{14}---N	0.03064					0.01996	0.02908			
H_{14}---F		0.00359								
H_{15}---F					0.00342					
H_{17}---O	0.01882		0.00670	0.01160	0.01762	0.01168	0.01957	0.00755		
H_{17}---F		0.00594		0.00349					0.00895	
H_{18}---O	0.01480	0.00511	0.00842	0.00812	0.01482	0.00863	0.01001	0.00289	0.00864	0.00464
H_{18}---F		0.00477					0.00661		0.00445	0.00746
H_{20}---N										0.00529
H_{22}---O	0.00618	0.00541	0.00163			0.00538	0.00825		0.00727	
H_{22}---F		0.00347	0.00643	0.00316	0.00457			0.00550	0.00480	
H_{21}---F									0.00344	

[a]In free cation: C_2-H_{14} (0.29389), C_4-H_{13} (0.29161), C_5-H_{12} (0.29173), C_6-H_{17} (0.28648), C_7-H_{18} (0.28695), C_8-H_{21} (0.27899); [b]Free anion: S-O (~0.282) S-N (0.24403)