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Fig. S1. Geometric structures of the two methanesulphonate (MS) and trifluoromethanesulfonate (TfO) anions and of the five conformers of the diethylmethylammonium (DEMA) cation, calculated as isolated ions in vacuum at the B3LYP level of theory with the 6-31G** basis set.

Table S1. DEMA cation conformers (calculated as isolated ions at the B3LYP level of theory with the 6-31G** basis set) and their relative energies.

Conformer	ΔE (kJ/mol)	ZPE (kJ/mol)	Entropy	Enthalpy (a.u)	Gibbs Energy
			(J/mol∙K)		(a.u)
C1	0.0	506.54	366.21	-253.307788	-253.349375
C2	0.1	507.29	365.45	-253.307468	-253.348968
C3	3.1	508.83	356.74	-253.305829	-253.346340
C4	3.5	507.35	361.14	-253.306146	-253.347157
C5	16.0	509.40	353.81	-253.300678	-253.340856

Table S2. Infrared vibrational frequencies (ω in cm⁻¹) and intensities (I in km/mol) of the MS and TfO anions and of the five conformers of DEMA calculated at the B3LYP level of theory with the 6-31G** basis set.

ConfC1	DEMA	ConfC2	DEMA	ConfC3	DEMA	ConfC4	DEMA	ConfC5	DEMA	MS		TfO	
ω	I	ω	T	ω	T	ω	I	ω	I	ω	I	ω	1
70	0.16	54	0.55	98	0.75	62	0.63	100	0.06	268	0	62	0
74	1.35	104	0.56	114	0.49	118	0.31	132	0.37	307	0.47	195	1.3
204	0.03	197	0.07	228	0.08	226	0.04	246	0.01	307	0.48	195	1.29
215	0.81	225	0.18	232	0.55	238	0.27	263	0.04	503	15.62	293	0.01
244	0.6	251	0.51	268	0.46	274	0.23	271	0.09	503	15.58	333	0.13
273	0.23	277	1.15	293	0.13	279	0.25	289	0.68	518	21.76	333	0.14
349	0.82	330	0.29	329	0.79	309	0.12	320	0.05	725	118.87	500	14.99
392	0.68	406	0.22	401	0.69	388	0.41	393	1.44	958	0.34	500	14.97
449	0.04	452	0.63	427	1.11	448	1.35	431	0.11	958	0.33	559	7.67
464	1.26	478	1.15	566	0.87	530	1.89	603	1.26	1000	136.1	559	7.68
764	3.93	750	2.49	751	1.64	717	4.06	693	2.24	1221	289.92	623	166.15
798	0.02	806	7.57	816	6.98	788	11.6	805	7.37	1221	290.06	741	7.42
832	7.43	831	4.55	820	8.51	829	2.7	826	7.64	1337	5.81	994	150.78
861	24.58	870	13.32	865	10.55	859	4.36	846	6.49	1485	0.08	1181	132.86
964	1.44	972	9.32	957	1.9	966	9.36	956	1.13	1485	0.08	1181	132.85
1000	46.05	1012	41.1	1013	35.1	1013	18.02	1018	33.88	3050	21.65	1227	91.96
1036	14.62	1024	17.24	1025	16.82	1023	26.79	1030	15.72	3146	32.67	1252	358.43
1060	10.57	1061	3.68	1068	2.63	1058	2.83	1065	1.33	3146	32.52	1252	358.58
1069	0.62	1074	4.96	1071	2.8	1071	1.79	1073	8.67				
1102	0.03	1099	0.18	1105	0.15	1101	1.34	1114	0.24				
1168	10.11	1188	5.22	1179	5.3	1192	4.77	1183	6.24				
1219	0.03	1206	2.56	1219	4.38	1204	5.79	1215	3.42				
1234	0.71	1229	0.79	1230	1.55	1219	1.65	1223	0.15				
1299	2.18	1301	0.97	1317	13.17	1306	4.16	1346	0.44				
1358	4.62	1350	4.13	1341	1.28	1349	0.89	1357	31.53				

1363	0.34	1395	2.07	1375	14.22	1381	11.85	1368	2.57		
1415	50.53	1407	6.06	1402	8.02	1401	2.13	1408	13.73		
1415	0.92	1428	33.48	1436	16.23	1421	15.13	1432	13.42		
1436	8.02	1437	8.89	1442	7.75	1433	30.61	1439	8.49		
1439	12.28	1444	10.39	1446	14.83	1442	5.49	1465	16.11		
1452	3.86	1448	9.08	1468	16.01	1462	10.45	1469	9.84		
1466	12.13	1467	10.66	1473	7.99	1468	6.91	1470	3.5		
1491	0.06	1493	5.96	1499	3.15	1492	18.37	1498	6.88		
1497	27.13	1502	16.84	1502	3.39	1497	5.44	1502	5.49		
1504	2.08	1507	1.23	1509	18.35	1506	5.4	1506	5.89		
1506	3.23	1510	7.91	1513	8.51	1511	10.98	1512	24.62		
1510	23.93	1513	11.02	1517	25.27	1516	7.07	1520	20.39		
1516	7.86	1519	24.46	1522	22.89	1519	26.3	1523	11.79		
1528	42.52	1525	34.03	1529	16.27	1524	36.71	1529	13.74		
1529	7.15	1528	16.01	1532	9.28	1529	2.07	1534	9.98		
3061	0.01	3062	3.29	3062	3.6	3062	2.85	3075	0.83		
3061	6.59	3063	3.73	3074	1.83	3072	1.76	3079	2.03		
3090	1.28	3094	1.37	3091	5.57	3092	0.26	3087	4.08		
3097	7.12	3097	3.14	3099	3.93	3097	7.22	3090	6.7		
3102	0.2	3104	3.15	3103	0.27	3100	1.88	3097	0.52		
3133	0.15	3133	2.07	3134	2.92	3133	2.9	3137	0.34		
3134	5.1	3138	4.57	3139	0.31	3143	1.34	3141	0.5		
3146	0.14	3146	0.97	3147	1.84	3145	0.84	3145	1.5		
3147	2.17	3153	1.96	3151	1.62	3150	3.47	3148	6.06		
3158	0.29	3159	7.63	3161	11.74	3160	7.16	3167	6.17		
3162	14.19	3174	5.88	3166	4.65	3166	8.22	3178	10.29		
3199	0.67	3190	0.36	3198	0.26	3189	0.35	3185	0.43		
3213	0.09	3207	0.62	3212	0.32	3203	0.32	3217	0.23		
3422	29.54	3425	29.22	3435	37.95	3437	38.55	3445	48.63		



Fig. S2. Geometric structures of the six conformers of DEMA-MS, calculated as a ionic couple in a polar medium at the ω B97X-D level of theory with the 6-31G** basis set.

Table S3. Conformers of DEMA-MS (calculated at the ω B97X-D level of theory with the 6-31G^{**} basis set and a polar medium) and their relative energies.

Conformer	∆E (kJ/mol)	ZPE (kJ/mol)	Entropy (J/mol∙K)	Enthalpy (a.u)	Gibbs Energy (a.u)
С	0.0	649.35	519.38	-917.077480	-917.136460
В	0.2	649.22	523.74	-917.077494	-917.136969
А	2.2	649.19	523.67	-917.076765	-917.136232
E	2.8	649.06	502.71	-917.076559	-917.133646
D	5.4	650.53	484.38	-917.075015	-917.130021
F	14.6	650.69	493.52	-917.071553	-917.127596

Table S4. Infrared vibrational frequencies (ω in cm⁻¹) and intensities (I in km/mol) of the six conformers of DEMA-MS calculated at the ω B97X-D level of theory with the 6-31G** basis set and a polar medium.

ConfA	IfA ConfB			ConfC		ConfD		ConfE		ConfF	
ω	1	ω	1	ω	Ι	ω	1	ω	Ι	ω	1
26	9.72	17	9.74	14	10.26	10	1.04	9	1.64	12	1.68
31	11.69	36	8.32	47	10.96	42	6.69	17	1	23	0.58
56	1.2	53	1.04	58	0.88	70	5.54	49	9.77	54	7.51
66	10.02	74	13.51	87	7.1	85	0.43	64	12.26	70	24.36
84	17.01	85	10.09	93	5.47	98	6.75	78	7.22	79	6.94

92	1.23	90	6.49	108	10.51	105	14.58	96	0.32	106	1.55
109	2.63	133	1.98	126	2.75	151	35.94	111	3.85	141	2.63
158	42.21	155	49.44	160	48.29	172	14.59	159	40.83	163	43.35
208	3.65	213	0.58	224	2.03	230	0.09	222	3.07	237	0.99
231	2.32	248	0.31	242	1.99	239	0.03	238	2.38	258	0.01
257	0.06	248	0.04	245	0.64	251	0.14	260	0.01	284	0.13
281	0.82	260	1.48	267	0.86	256	2.53	276	2.41	307	1.62
300	0.89	293	0.15	275	1.28	312	0.22	286	0.06	310	0.47
328	1.73	328	1.44	330	1.43	329	1.41	327	1.34	326	1.39
339	5.08	338	7.68	342	8.77	343	7.78	352	8.49	341	0.28
344	7.05	351	6.13	353	2.82	361	5.61	392	1.22	358	10.55
419	0.6	422	0.91	432	2.5	423	0.73	416	0.53	416	0.86
451	3.79	479	0.69	469	7.65	465	3.66	466	17.37	449	0.24
513	44.36	513	47.01	502	5.59	510	19.04	499	0.08	508	37.95
517	53.13	520	53.73	516	44.61	515	50.49	510	40.14	513	41.25
543	126.63	541	121.26	518	44.77	522	20.75	515	36.66	548	134.68
577	17.42	563	23.25	545	138.87	547	138.33	548	142.59	625	17.51
779	92.18	771	2.47	778	101.07	780	100.59	781	96.59	755	2.39
792	4.58	779	97.32	787	4.41	792	7.36	804	13.53	782	99.2
817	16	812	13.89	815	8.54	804	12.16	811	0.04	809	7.88
834	11.26	841	12.65	850	22.29	848	16.99	851	17.82	826	15.03
913	1.54	914	0.36	924	1.76	922	0.86	920	5.92	902	0.94
999	11.39	996	14.66	995	15.71	995	9.8	1001	14.63	996	22.74
999	7.37	999	6.3	1001	5.23	998	4.34	1004	3.97	1003	9.79
1002	2.33	1014	9.59	1016	10.33	1034	39.84	1011	10.74	1005	2.18
1043	329.3	1040	347.19	1039	349.62	1042	329.71	1039	363.51	1040	384.01
1062	54.45	1060	24.74	1059	55.38	1062	33.59	1048	71.16	1072	40.54
1073	14.36	1075	19.79	1080	16.58	1072	38.75	1086	13.05	1081	17.18
1099	20.75	1095	12.79	1096	6.07	1096	6.88	1092	8.47	1104	15.27
1106	5.97	1107	2.5	1107	3.9	1105	15.56	1116	9.89	1112	5.69
1121	3.89	1120	4.11	1119	2.82	1135	0.63	1126	0.11	1126	0.72
1175	475.59	1175	477.79	1175	507.64	1181	509.61	1176	522.66	1175	483.43
1204	52.88	1217	32.46	1215	14.98	1219	10.07	1215	28.76	1202	50.63
1229	26.49	1222	11.61	1238	15.7	1233	23.36	1241	418.37	1230	23.63
1248	530.49	1253	10.93	1247	156.64	1250	256.39	1242	72.19	1249	474.99
1253	5.5	1255	564.09	1253	376.91	1253	275.57	1249	15.24	1253	8.98
1348	5.3	1336	3.06	1327	0.76	1334	1.97	1319	0.01	1358	1.92
1362	2.72	1366	0.28	1363	0.12	1369	1.21	1378	1.14	1387	23.68
1384	26.05	1382	28.4	1382	25.78	1380	25.48	1385	0.38	1389	4.09
1405	11.44	1400	7.43	1404	5.15	1406	2.04	1386	25.27	1397	17.81
1410	5.59	1413	3.03	1413	3.24	1414	5.09	1418	2.58	1424	6.57
1436	6.85	1436	20.8	1436	6.58	1436	12.63	1435	29.7	1436	25.53
1444	28.63	1440	13.03	1447	18.58	1442	11.17	1455	0.26	1450	13.65
1464	5.51	1463	6.74	1463	7.04	1463	6.57	1466	5.55	1466	6.81
1466	8.8	1467	3.18	1466	4.81	1464	5.06	1469	5.05	1468	5.71
1467	4.76	1470	9.07	1468	7.78	1474	4.13	1470	8.07	1477	8.42
1490	19.59	1489	22.94	1490	2.84	1490	17.54	1485	1.35	1490	5.75
1491	4.86	1492	6.23	1493	9.83	1490	1.49	1492	29.6	1494	0.75
1495	13.84	1498	1.43	1493	2.96	1495	5.55	1495	6.98	1496	4.25
1499	11.74	1502	15.2	1495	25.82	1497	21.69	1496	12.69	1504	23.37
1509	14.43	1505	10.46	1504	21.29	1507	9.43	1498	15.28	1507	27.02
									J		

1514	7.07	1509	13.55	1513	4.73	1509	10.5	1513	2.08	1519	18.42
1516	8.26	1523	20.71	1515	17.1	1519	7.65	1521	24.69	1524	6.37
1532	7.96	1538	7.51	1527	3.85	1532	34.01	1537	2.09	1533	22.64
1557	43.83	1556	39.76	1553	59.57	1540	42.75	1556	65.57	1566	41.29
1582	62	1582	58.67	1589	58.49	1604	74.97	1586	61.69	1590	75.35
2949	1899.74	2940	1965.84	2935	1828.76	2993	1621.75	2950	1885.06	2955	2039.41
3086	12.17	3084	10.06	3084	14.25	3082	12.64	3083	17.15	3085	8.32
3087	13.3	3085	15.16	3085	14.49	3090	24.18	3084	9.47	3093	10.57
3096	1	3099	1.03	3098	1.05	3101	0.93	3096	0.91	3093	0.49
3113	13.19	3105	8.41	3108	9.49	3104	12.55	3109	0.4	3108	9.93
3116	12.2	3119	14.07	3117	7.76	3115	7.64	3113	21.4	3115	7.71
3120	6.32	3128	10.81	3120	4.72	3129	2.16	3116	4.58	3117	28.57
3165	7.43	3164	12.31	3167	5.95	3165	11.71	3164	0.13	3165	1.96
3170	9.62	3167	6.01	3171	20.17	3172	9.65	3166	4.39	3170	9.83
3172	11.51	3175	18.27	3174	13.2	3175	20.57	3173	14.49	3171	17.36
3176	14.16	3180	15.35	3175	8.31	3181	12.52	3175	14.77	3178	22.47
3184	29.92	3184	24.9	3191	13.39	3187	6.94	3182	0.66	3183	20.61
3189	19.47	3189	15.71	3194	18.65	3193	21.52	3184	43.25	3193	26.83
3206	2.83	3210	2.66	3208	2.61	3211	4.03	3205	2.63	3204	2.62
3211	2.6	3210	4.84	3212	2.58	3213	2.8	3212	2.62	3208	2.65
3221	3.42	3214	2.89	3213	3.51	3214	2.64	3221	1.15	3209	3.67
3227	0.5	3216	0.66	3230	1.8	3219	0.83	3225	1.28	3224	0.75

DEMA-TFO



Fig. S3. Geometric structures of the six conformers of DEMA-TfO, calculated as ionic couples in a polar medium at the ω B97X-D level of theory with the 6-31G** basis set.

Conformer	∆E (kJ/mol)	ZPE (kJ/mol)	Entropy	Enthalpy (a.u)	Gibbs Energy					
			(J/mol∙K)		(a.u)					
С	0.00	589.68	570.00	-1214.72686	-1214.79158					
D	0.1	589.06	572.04	-1214.72702	-1214.79198					
В	0.4	590.12	563.90	-1214.72655	-1214.79059					
A	2.5	589.60	570.13	-1214.72598	-1214.79072					
E	6.1	587.97	551.83	-1214.72513	-1214.78779					
F	12.0	590.17	563.90	-1214.72213	-1214.78617					

Table S5. Conformers of DEMA-TfO (calculated at the ω B97X-D level of theory with the 6-31G^{**} basis set and a polar medium) and their relative energies.

Table S6. Infrared vibrational frequencies (ω in cm⁻¹) and intensities (I in km/mol) of the six conformers of DEMA-TfO calculated at the ω B97X-D level of theory with the 6-31G^{**} basis set and a polar medium.

ConfA		ConfB		ConfC		ConfD		ConfE		ConfF	
ω	I	ω	I	ω	I	ω	I	ω	I	ω	I
23	2.48	24	3.46	15	3.72	14	1.61	7	4.59	22	6.92
34	5.39	42	7.99	37	0.37	41	7.08	26	7.71	38	1.96
47	1.03	51	0.96	45	9.01	46	2.37	47	5.36	51	3.26
60	4.3	57	2.9	52	4.67	56	4.71	56	1.66	55	4.72
73	5.49	71	4.96	78	3.08	66	3.67	60	3.76	73	7.73
81	2.92	83	2.29	85	8	86	1.57	75	2.3	82	9.87
91	10.62	97	7.87	103	1.62	92	2.49	91	0.96	119	3.31
111	1.38	142	8.51	136	25.48	125	5.75	95	10.93	134	17.19
146	37.34	148	35.6	146	12.33	147	41.97	132	20.99	150	20.64
201	4.86	201	4.13	205	4.56	202	5.85	196	3.14	204	5.98
204	0.54	205	3.23	210	2.97	203	3.08	208	2.69	206	1.5
205	2.35	225	0.48	218	1.19	234	0.28	222	3.98	238	1
239	3.39	253	0.21	253	1.24	249	0.37	238	4.54	274	0.19
286	0.4	280	1.09	262	3.14	263	2.23	267	2.33	282	0.37
309	0.86	301	0.03	294	0.27	282	0.12	281	0.1	310	0.42
316	2.89	316	2.58	318	3.86	316	2.64	324	7.56	317	2.65
342	0.59	342	0.54	342	0.78	343	0.47	344	0.68	329	0.23
344	1.04	345	0.51	352	6.22	348	2.96	352	1.78	342	0.74
350	5.57	352	6.6	374	1.4	356	3.7	357	8.19	351	6.41
419	0.56	426	0.73	432	1.58	429	1.24	415	0.67	415	1.14
452	3.37	482	1.32	468	2.67	469	4.35	470	13.25	449	0.14
506	40.7	506	41.66	502	11.01	499	5.25	493	0.18	506	41.29
515	54.37	515	53.84	508	33.6	507	34.99	504	43.38	515	56.85
571	12.52	560	12.25	516	55.17	517	58.12	506	35.45	572	11.78
574	18.7	573	17.49	574	14.06	575	12.53	572	10.76	577	23.32
586	21.15	580	22.65	578	19.52	578	25.71	575	9.3	618	240.54
619	261.29	619	260.65	622	275.61	619	267.37	628	304.09	627	34.29
777	5.58	771	3.65	778	6.11	778	6.34	779	7.31	754	1.18
791	2.4	777	4.95	785	6.16	783	4.49	804	10.7	777	5.95
823	17.66	816	14.78	823	11.14	818	10.36	813	0.01	816	7.99
834	7.26	847	9.94	850	19.11	848	17.97	850	16.74	829	17.67
914	2.1	914	0.15	924	3.13	921	2.11	915	8.04	900	1.27
998	6.75	1013	13.61	1019	33.73	1015	9.06	1008	18.09	995	7.56
1032	275.62	1029	265.92	1029	264.12	1030	286.17	1029	338.96	1033	279.81
1060	53.54	1058	42.63	1058	66.42	1057	57.18	1039	72.45	1068	41.85

1074	19.46	1076	27.18	1078	24.89	1076	23.17	1081	17.62	1077	32.7
1100	18.66	1095	14.45	1095	5.34	1094	7.58	1089	9.55	1101	17.8
1106	7.92	1106	6.79	1108	8.43	1105	6.71	1110	7.95	1104	8.48
1122	2.19	1123	3.04	1120	2.48	1118	3.74	1122	0.23	1126	1.3
1205	2.36	1215	57.72	1213	14.88	1212	16.91	1210	12.46	1194	36.28
1226	160.25	1221	23.68	1224	124.96	1226	195.59	1225	111.59	1227	224.24
1228	217.96	1226	299.05	1231	380.28	1229	344.3	1237	281.32	1229	60.56
1232	4.93	1228	81.02	1239	554.51	1238	55.34	1238	689.73	1232	94.51
1240	711.15	1238	631.97	1240	38.82	1240	486.5	1240	3.59	1241	693.11
1254	20.05	1252	25.4	1248	37.27	1247	31.94	1243	29.31	1249	3.7
1265	126.24	1265	127.4	1265	118.44	1267	130.02	1267	132.33	1267	131.03
1296	581.35	1293	588.53	1300	552.68	1300	556.59	1291	503.61	1300	571.78
1348	7.43	1338	6.18	1328	4.09	1327	4.13	1320	0.26	1360	3.62
1364	3.33	1369	0.28	1371	1.65	1370	1.38	1380	1.42	1385	1.04
1409	14.01	1403	8.31	1411	3.48	1407	4.69	1385	0.05	1396	22.65
1410	1.4	1417	1.56	1413	4.8	1411	4.33	1417	2.21	1426	3.96
1438	3.81	1439	25.04	1441	6.08	1438	4.84	1434	27.82	1434	22.94
1446	32.89	1444	13.88	1449	16.69	1444	14.89	1453	1.7	1449	20.36
1467	9.01	1476	5.89	1468	7.67	1470	6.38	1461	10.59	1470	15.33
1489	22.71	1490	28.83	1488	4.52	1488	2.69	1483	5.99	1489	7.03
1490	3.29	1494	8.62	1493	7.74	1490	12.58	1488	30.49	1493	3.37
1495	14.85	1499	0.6	1494	10.03	1492	13.13	1494	8.19	1496	3.4
1502	11.08	1501	12.66	1497	23.84	1497	21.93	1496	8.57	1503	13.03
1509	10.74	1505	8.61	1501	23.45	1502	25.24	1497	18.06	1508	24.76
1515	14.95	1515	6.03	1515	8.15	1511	9.99	1513	5.44	1510	7.15
1517	7.51	1523	28.51	1515	8.08	1515	7.65	1515	10.44	1523	10.99
1533	7.39	1541	6.61	1532	16.21	1527	26.84	1526	5.05	1529	25.47
1544	43.91	1545	48.26	1543	50.68	1534	41.73	1539	65.5	1541	48.42
1570	58.54	1569	55.53	1564	60.57	1568	52.98	1556	69.86	1558	31.88
3088	11.39	3084	11.52	3080	11.57	3082	11.53	3087	12.06	3089	11.64
3089	15.58	3086	16.19	3089	12.16	3084	10.72	3088	6.17	3092	26.47
3116	97.1	3114	70.54	3111	129.95	3111	98.11	3111	210.06	3112	50.64
3120	46.77	3120	76.19	3113	63.9	3117	116.71	3115	38.74	3114	12.54
3125	13.5	3138	8.52	3122	58.26	3122	28.65	3119	50.82	3127	13.62
3163	898.58	3161	729.48	3164	135.03	3167	38.04	3159	892.29	3161	1290.44
3171	245.56	3168	435.17	3165	611.95	3168	865.73	3168	33.57	3167	23.09
3173	47.52	3170	29.2	3173	228.11	3170	27.32	3172	102.44	3172	18.81
3176	11.41	3176	21.53	3177	21.9	3178	33.27	3180	6.6	3174	23.4
3184	14.75	3179	26.33	3178	41.71	3182	48.31	3181	15.28	3182	21.45
3193	28.91	3189	26.24	3190	12.85	3194	14.64	3187	9.27	3187	24.36
3194	14.98	3199	13.48	3199	22.73	3198	25.62	3192	40.08	3199	12.69
3226	3.35	3221	3.7	3221	7.25	3220	7.03	3225	3.02	3216	2.81
3228	4.36	3231	4.16	3230	2.68	3236	2.26	3233	1.3	3232	5.25



Fig. S4. Experimental spectra of the DEMA-TfO sample between 600 and 1100 cm⁻¹ measured on cooling (panel a) and subsequent heating (panel b).



Fig. S5. Temperature dependence of the far infrared spectra of DEMA-MS and DEMA-TfO samples.



Fig. S6. Measured far infrared spectrum of DEMA-TfO at 320 K (black line) and deconvolution by means of a fit to a sum (red line) of individual gaussians (other colors) as described in the text.



Fig. S7. Measured far infrared spectrum of DEMA-TfO sample at 320 K (black line) and deconvolution by means of a fit to a sum (red line) of individual gaussians (other colors) as described in the text.