

# **Understanding the impact of the central atom on the ionic liquid behavior: Phosphonium vs Ammonium cations**

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## Methods

### Activity coefficients at infinite dilution

Inverse chromatography experiments were carried out using a Varian CP-3800 gas chromatograph equipped with a heated on-column injector and a flame ionization detector. The injector and detector temperatures were kept at 523 K during all experiments. The helium flow rate was adjusted to obtain adequate retention times. Methane was used to determine the column hold-up time. Exit gas flow rates were measured with a soap bubble flow meter. The temperature of the oven was determined with a Pt100 probe and controlled to within  $\pm 0.1$  K. A computer directly recorded the detector signals and the corresponding chromatograms were generated using the Galaxie Chromatography Software. Using a rotary evaporation preparatory technique, 1.0 meter length columns were packed with a stationary phase, consisting of 0.20 to 0.35 mass fraction of IL on in Chromosorb WHP (60-80 mesh) sorbent media. After the solvent (chloroform) evaporation, under vacuum, the support was let to equilibrate, at 333 K during 6 h. Prior to the measurements, each packed column was conditioned for 12 h at 363 K with a flow rate of  $20 \text{ cm}^3 \cdot \text{min}^{-1}$ . The packing level was calculated from the masses of the packed and empty columns and was checked throughout experiments. The masses of the stationary phase were determined to a precision of  $\pm 0.0003$  g. A headspace sample volume of (1 to 5)  $\mu\text{L}$  was injected to satisfy infinite dilution conditions and each experiment was repeated at least twice to confirm reproducibility. Retention times were generally rigorously reproducible to within (0.01 to 0.03) min. To verify stability under these experimental conditions, ruling out elution of the stationary phase by the helium stream, measurements of retention time were repeated systematically each day for three selected typical solutes. No changes in the retention times were observed during this study.

The retention data garnered by inverse chromatography experiments were used to calculate partition coefficients of the numerous solutes in the different ILs. The standardized retention volume,  $V_N$ , was calculated following the relationship:<sup>1,2</sup>

$$V_N = J \cdot U_0 t'_R \frac{T_{col}}{T_{rt}} \left( 1 - \frac{P_{ow}}{P_0} \right) \quad (1)$$

The adjusted retention time,  $t'_R$ , was taken as the difference between the retention time of a particular solute and that of methane,  $T_{col}$  is the column temperature,  $U_0$  is the flow rate of the carrier gas measured at room temperature ( $T_{rt}$ ),  $P_{ow}$  is the vapor pressure of water at  $T_{rt}$  and  $P_0$  is the outlet pressures. The factor  $J$  in Eq. 1 corrects for the influence of the pressure drop along the column and is given through the relation:<sup>1,2</sup>

$$J = \frac{3 \left[ \left( \frac{P_i}{P_0} \right)^2 - 1 \right]}{2 \left[ \left( \frac{P_i}{P_0} \right)^3 - 1 \right]} \quad (1)$$

where  $P_i$  is the inlet pressure.

Activity coefficients at infinite dilution for solute  $I$  in each IL,  $\gamma_{i,IL}^\infty$ , were calculated with the following expression<sup>1,2</sup>

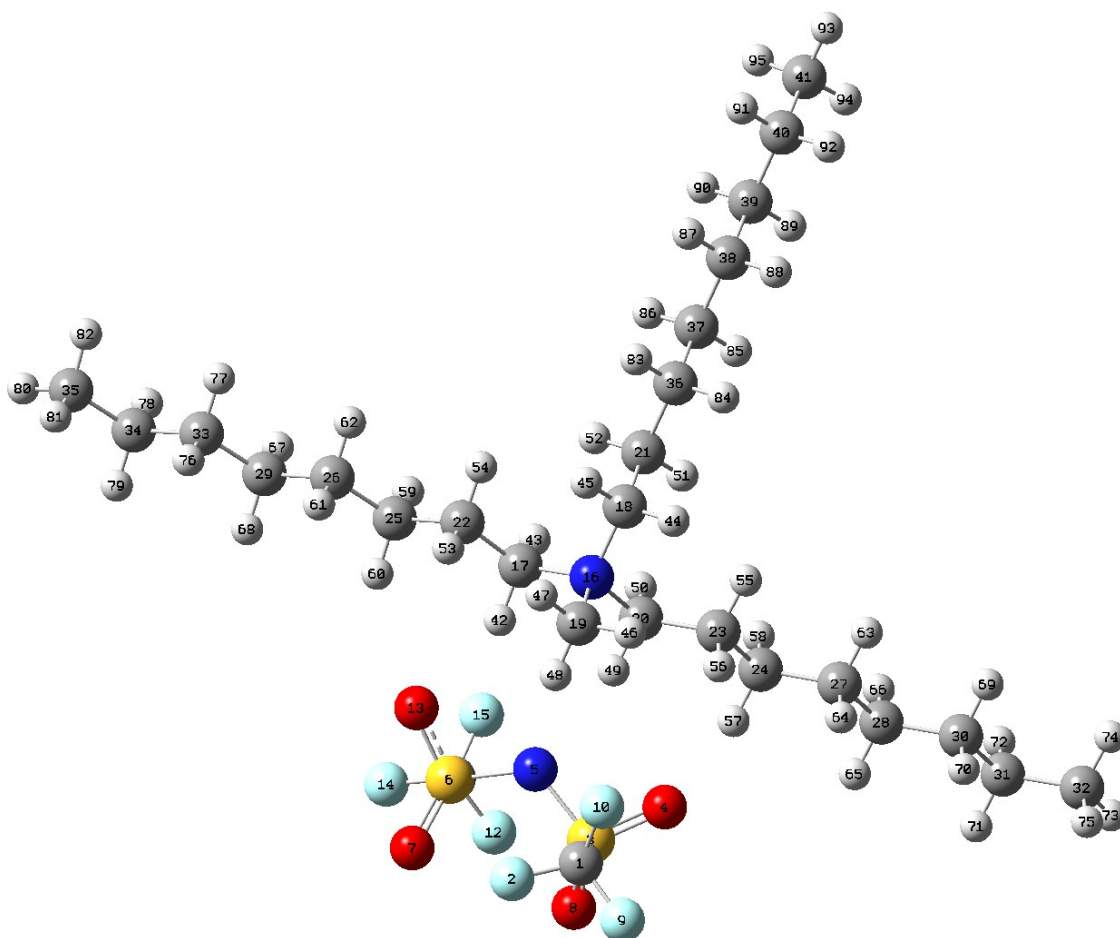
$$\ln \gamma_{i,IL}^\infty = \ln \left( \frac{n_2 R \cdot T}{V_N P_i^0} \right) - P_1^0 \frac{B_{11} - V_1^0}{R \cdot T} + \frac{2 B_{13} - V_i^\infty}{R \cdot T} J \cdot P_0 \quad (1)$$

where  $n_2$  is the number of moles of stationary phase component within the column,  $R$  is the ideal gas constant,  $T$  is the oven temperature,  $B_{11}$  is the second virial coefficient of the solute in the gaseous state at temperature  $T$ ,  $B_{13}$  is the mutual virial coefficient between solute  $I$  and the carrier gas (helium, denoted by “3”), and  $P_i^0$  is the probe’s vapor pressure at temperature  $T$ . The values of  $P_i^0$  result from correlated experimental data. The molar volume of the solute,  $V_1^0$  was determined from experimental densities and the partial molar volumes of the solutes at infinite dilution,  $V_1^\infty$ , were assumed to be equal to  $V_1^0$ . The values required for the calculation of these parameters were taken from previous works.<sup>3</sup>

## References

- <sup>1</sup> A.J.B. Cruickshank, M. L. Windsor, and C. L. Young, Proc. R. Soc. Lond. A 295, 259 (1966).
- <sup>2</sup> A.J.B. Cruickshank, M. L. Windsor, and C. L. Young, Proc. R. Soc. Lond. A 295, 271 (1966).
- <sup>3</sup> A. Revelli, L. M. Sprunger, J. Gibbs, W. E. Acree, G. A. Baker, and F. Mutelet, J. Chem. Eng. Data 54, 977 (2009).

**Table S1.** Atom coordinates and charges from Mulliken population analysis, Natural Population Analysis (NPA) and electrostatic potential-derived (CHelpG) charges, calculated at the BP-TZVP level of theory for the  $[N_{8,8,8,1}][NTf_2]$ .



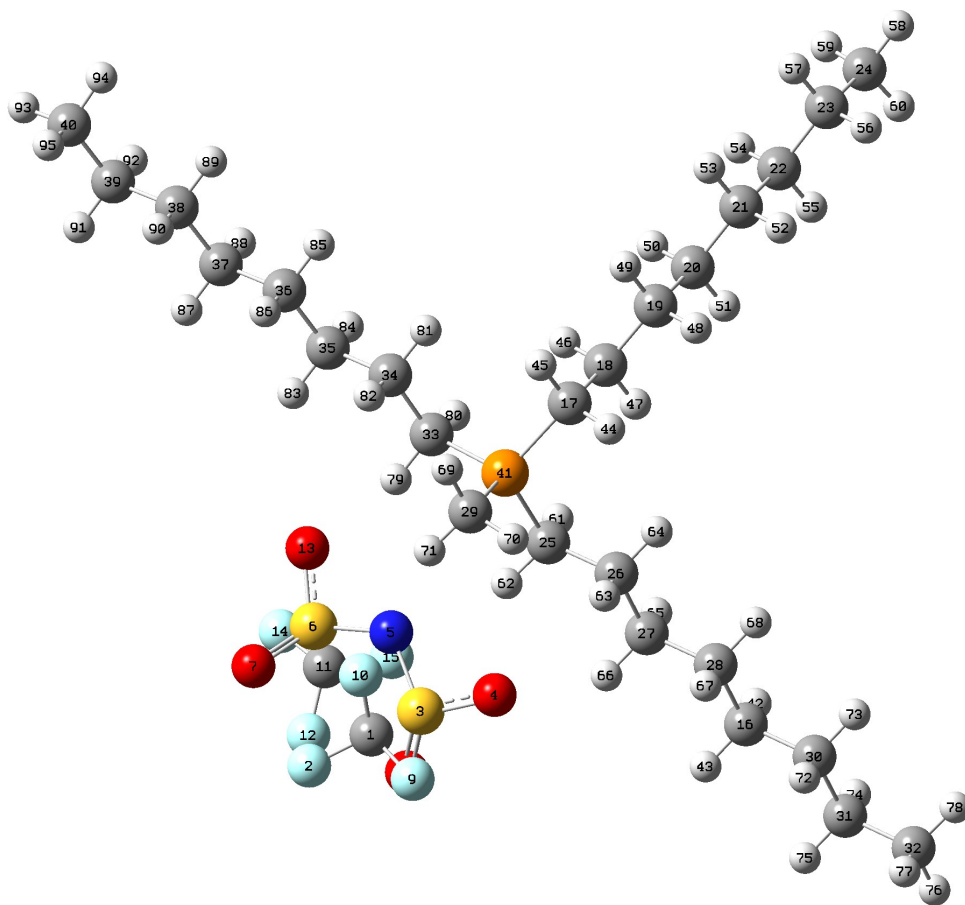
Center Number	Atomic Number	Coordinates/ Å			Atomic charges		
		x	y	z	NPA	Mulliken	CHelpG
1	6	3.304161	-3.10901	2.302932	0.67639	0.222586	0.400551
2	9	2.680008	-4.279725	2.503523	-0.27288	-0.08829	-0.118393
3	16	3.149089	-2.539071	0.451014	1.94714	0.512878	0.726068
4	8	3.590329	-1.104073	0.503425	-0.87201	-0.35766	-0.44355
5	7	1.487734	-2.444077	0.21787	-1.14935	-0.49776	-0.366289
6	16	0.599568	-3.730429	-0.384026	1.9492	0.514215	0.656331
7	8	1.090808	-5.113734	-0.12315	-0.80572	-0.27867	-0.416785
8	8	3.906931	-3.548608	-0.343429	-0.80882	-0.28181	-0.426391
9	9	4.606178	-3.238009	2.614925	-0.27752	-0.09905	-0.144123
10	9	2.754295	-2.178131	3.121318	-0.29683	-0.12021	-0.163661
11	6	0.675711	-3.513615	-2.315491	0.67651	0.22516	0.515548
12	9	1.936638	-3.568254	-2.766162	-0.27061	-0.08517	-0.144053
13	8	-0.821818	-3.34638	-0.066586	-0.88658	-0.36808	-0.423299
14	9	-0.047358	-4.491379	-2.891963	-0.27832	-0.10033	-0.167786
15	9	0.139054	-2.31749	-2.664375	-0.29752	-0.12295	-0.201625
16	7	-0.531946	0.653092	0.874731	-0.15407	-0.0816	-0.077735
17	6	-1.543283	-0.149767	0.040924	-0.24682	-0.25244	0.370661
18	6	-1.131058	1.94095	1.417975	-0.23142	-0.30121	-0.120543
19	6	-0.073456	-0.185653	2.044121	-0.45123	-0.28904	-0.059394
20	6	0.673109	0.910152	-0.050768	-0.24339	-0.29506	0.179516
21	6	-1.639267	2.940318	0.374269	-0.43133	-0.13783	0.089431

22	6	-2.877676	-0.486068	0.714455	-0.42899	-0.15048	-0.200245
23	6	1.787227	1.798795	0.509867	-0.43392	-0.11944	-0.023803
24	6	2.863035	2.008505	-0.57855	-0.39413	-0.27462	-0.015547
25	6	-3.738942	-1.321693	-0.259403	-0.39654	-0.27428	0.083852
26	6	-5.08528	-1.745917	0.354045	-0.38945	-0.18824	0.020711
27	6	4.019232	2.90684	-0.103475	-0.38955	-0.19372	0.074855
28	6	5.096332	3.112108	-1.183362	-0.39397	-0.20786	-0.031868
29	6	-5.944654	-2.584158	-0.609779	-0.3944	-0.20836	-0.001588
30	6	6.25128	4.02398	-0.731438	-0.39292	-0.20367	-0.009014
31	6	7.326728	4.228707	-1.813477	-0.39763	-0.17605	0.174289
32	6	8.47263	5.147223	-1.358218	-0.61012	-0.33544	-0.236377
33	6	-7.290497	-3.021674	-0.005017	-0.39318	-0.20283	-0.008756
34	6	-8.147888	-3.863718	-0.967578	-0.3977	-0.17656	0.161572
35	6	-9.487677	-4.30243	-0.35444	-0.61025	-0.33531	-0.240681
36	6	-2.228854	4.183788	1.07371	-0.38905	-0.26755	-0.047632
37	6	-2.736795	5.243548	0.078571	-0.39101	-0.19684	0.017298
38	6	-3.333278	6.483103	0.768914	-0.39544	-0.19901	-0.006931
39	6	-3.826555	7.554339	-0.220398	-0.39382	-0.20826	0.004361
40	6	-4.42552	8.793189	0.469858	-0.39763	-0.17623	0.145927
41	6	-4.904824	9.863359	-0.524415	-0.61045	-0.33592	-0.224958
42	1	-1.027307	-1.087	-0.227547	0.27709	0.215369	-0.093426
43	1	-1.71329	0.434848	-0.878453	0.21526	0.166108	-0.009735
44	1	-0.347899	2.403086	2.041145	0.22684	0.184134	0.066402
45	1	-1.951145	1.638624	2.090633	0.22544	0.181354	0.062454
46	1	0.673402	0.38286	2.616689	0.22409	0.155862	0.087866
47	1	-0.937815	-0.413057	2.684184	0.21869	0.152269	0.073017
48	1	0.377818	-1.109849	1.645105	0.28503	0.268376	0.045807
49	1	1.069045	-0.094793	-0.284351	0.27818	0.258153	-0.043179
50	1	0.255949	1.351283	-0.971707	0.21373	0.162598	0.013099
51	1	-0.817087	3.253544	-0.295195	0.216	0.142071	0.007599
52	1	-2.416039	2.477897	-0.262128	0.21423	0.138574	0.004109
53	1	-2.709177	-1.077917	1.632356	0.22104	0.134029	0.080122
54	1	-3.431393	0.428173	1.002925	0.19923	0.114698	0.045415
55	1	1.398989	2.784215	0.831796	0.19647	0.115334	0.019389
56	1	2.264392	1.316176	1.381214	0.23263	0.147141	0.026482
57	1	3.261888	1.020315	-0.873003	0.2377	0.158419	0.037393
58	1	2.396024	2.455509	-1.480274	0.19029	0.098707	-0.003682
59	1	-3.923459	-0.736712	-1.183532	0.19435	0.097999	-0.012562
60	1	-3.166422	-2.2191	-0.560945	0.23749	0.163274	0.002853
61	1	-4.896414	-2.330147	1.277265	0.20119	0.109378	-0.000414
62	1	-5.654814	-0.845963	0.667381	0.19159	0.091697	-0.020418
63	1	3.62182	3.893946	0.213628	0.18901	0.087901	-0.034047
64	1	4.48398	2.453792	0.794802	0.20595	0.1163	-0.004035
65	1	5.502053	2.124761	-1.481572	0.2087	0.118812	0.011261
66	1	4.627642	3.5393	-2.094218	0.19266	0.091441	-0.004242
67	1	-6.130317	-2.003752	-1.536999	0.19461	0.095265	-0.009499
68	1	-5.37178	-3.481101	-0.920243	0.20696	0.116083	0.005068
69	1	5.845176	5.01133	-0.427553	0.19178	0.088621	-0.002041
70	1	6.72386	3.595488	0.176235	0.19787	0.100071	0.00091
71	1	7.735778	3.242744	-2.110576	0.20137	0.107186	-0.026805
72	1	6.853142	4.648107	-2.723718	0.19689	0.097142	-0.034523
73	1	9.229714	5.277107	-2.15178	0.21175	0.120774	0.056452
74	1	8.097541	6.151359	-1.08694	0.20182	0.101898	0.046101
75	1	8.987504	4.734788	-0.471112	0.20457	0.107301	0.050998
76	1	-7.104641	-3.602675	0.921737	0.19703	0.098697	0.002007
77	1	-7.864732	-2.124486	0.306742	0.19283	0.09044	-0.0025
78	1	-8.334231	-3.283114	-1.893229	0.19765	0.098688	-0.029448
79	1	-7.571745	-4.757074	-1.280281	0.20109	0.106648	-0.024294
80	1	-10.081613	-4.904602	-1.064558	0.21237	0.121742	0.059335
81	1	-9.330497	-4.915146	0.55214	0.20449	0.107124	0.05189
82	1	-10.100531	-3.429476	-0.063127	0.20234	0.102659	0.049535
83	1	-3.059832	3.873734	1.738761	0.20131	0.112562	0.023833

84	1	-1.459801	4.636873	1.731143	0.20178	0.113523	0.026974
85	1	-1.902318	5.556354	-0.581471	0.20004	0.108085	0.000136
86	1	-3.499858	4.78931	-0.585939	0.19959	0.106443	-0.000614
87	1	-4.173805	6.171188	1.422217	0.20011	0.101813	-0.003206
88	1	-2.573011	6.929587	1.442186	0.20023	0.101795	-0.004213
89	1	-2.98473	7.869669	-0.870574	0.19677	0.098482	0.000553
90	1	-4.584761	7.109807	-0.897586	0.19666	0.097859	-0.001209
91	1	-5.269943	8.478689	1.115125	0.19881	0.102152	-0.024618
92	1	-3.669196	9.23152	1.151243	0.19881	0.101923	-0.02427
93	1	-5.325418	10.741504	-0.003632	0.21371	0.123942	0.05771
94	1	-4.073724	10.219351	-1.160303	0.20464	0.107167	0.049012
95	1	-5.688995	9.466042	-1.194597	0.20455	0.106868	0.049256

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**Table S2.** Atom coordinates and charges from Mulliken population analysis, Natural Population Analysis (NPA) and electrostatic potential-derived (CHelpG) charges, calculated at the BP-TZVP level of theory for the  $[P_{8,8,8,1}][NTf_2]$ .



Center Number	Atomic Number	Coordinates/ Å			Atomic charges		
		x	y	z	NPA	Mulliken	CHelpG
1	6	-3.54168	-3.23385	-2.127027	0.68532	0.229511	0.449987
2	9	-3.79573	-4.49936	-1.784839	-0.26235	-0.07398	-0.129118
3	16	-3.28381	-2.09888	-0.555014	1.92893	0.500139	0.741646
4	8	-3.36849	-0.70885	-1.121358	-0.87706	-0.37125	-0.470494
5	7	-1.67634	-2.21973	-0.090368	-1.1258	-0.44985	-0.369308
6	16	-1.15365	-3.54802	0.79305	1.92936	0.500803	0.693346
7	8	-1.61454	-4.88296	0.303719	-0.82217	-0.29401	-0.440712
8	8	-4.29218	-2.58152	0.438069	-0.82775	-0.29792	-0.451031
9	9	-4.58509	-2.74619	-2.827839	-0.28084	-0.10407	-0.164775
10	9	-2.43868	-3.19217	-2.910109	-0.29235	-0.11611	-0.166669
11	6	-1.8625	-3.40986	2.618009	0.68972	0.231991	0.514805
12	9	-3.03597	-4.03407	2.737663	-0.26137	-0.07354	-0.14129
13	8	0.313821	-3.26807	0.977356	-0.88165	-0.38033	-0.452597
14	9	-0.9699	-3.98595	3.448643	-0.28106	-0.10505	-0.180321
15	9	-2.00072	-2.11141	2.965541	-0.28894	-0.11162	-0.185756
16	6	-5.03849	3.888635	0.77018	-0.3938	-0.19962	0.000844
17	6	1.591298	2.068273	-1.476455	-0.69926	-0.31085	-0.22394
18	6	2.16251	2.989884	-0.377369	-0.40675	-0.26187	0.074646
19	6	2.981029	4.157227	-0.963047	-0.39017	-0.23033	-0.007156
20	6	3.549212	5.103799	0.108864	-0.39344	-0.20565	-0.006512
21	6	4.39902	6.241496	-0.484737	-0.39499	-0.19683	-0.007049
22	6	4.962493	7.203206	0.5776	-0.39404	-0.20971	0.007863
23	6	5.827248	8.329174	-0.017086	-0.39772	-0.17544	0.164463

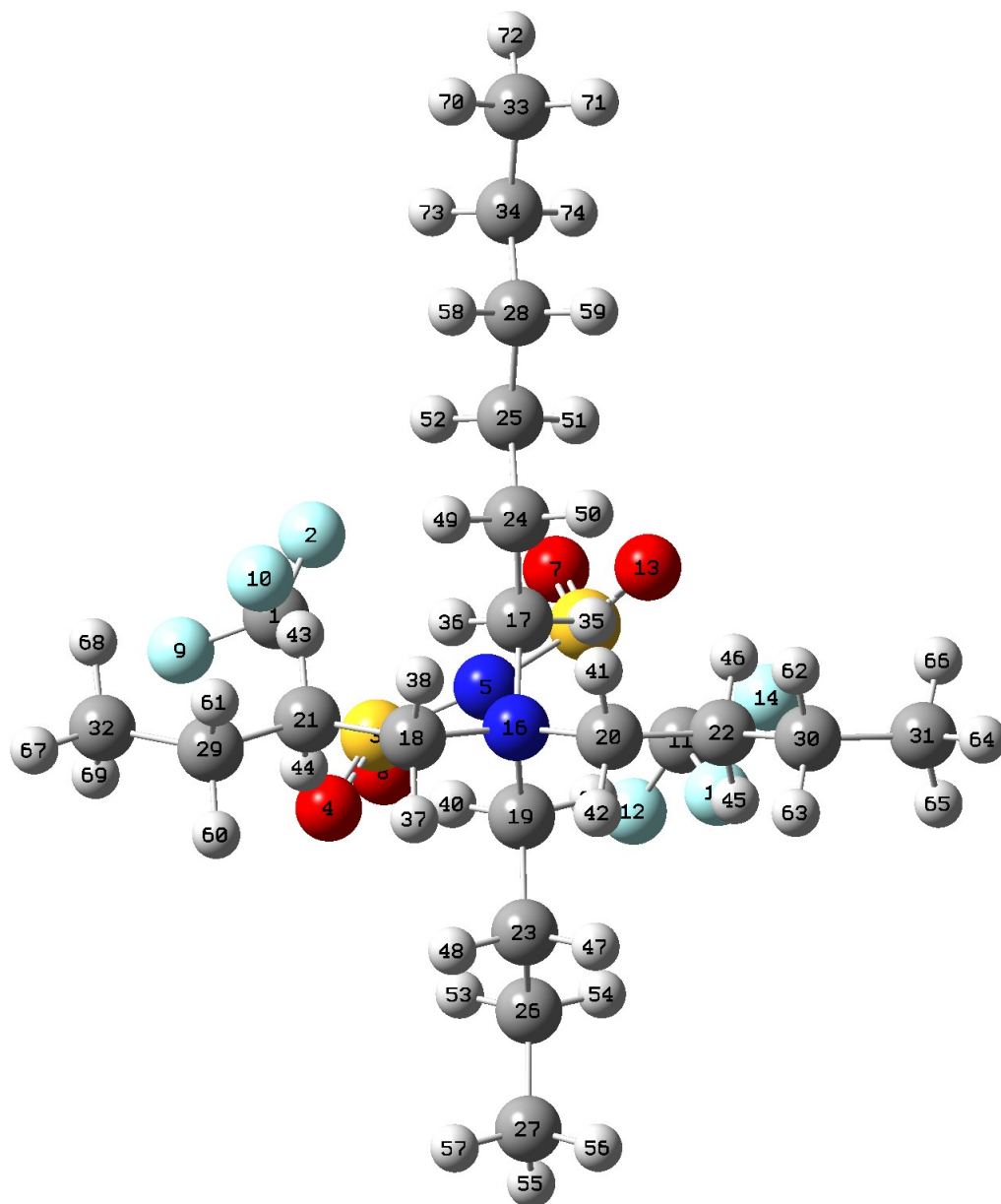
24	6	6.384225	9.288963	1.047088	-0.61065	-0.33637	-0.222533
25	6	-0.78012	1.115766	0.187145	-0.70413	-0.24471	0.040658
26	6	-1.70964	2.16547	-0.457401	-0.40475	-0.20531	-0.007726
27	6	-2.90722	2.495904	0.456213	-0.39406	-0.25619	-0.029955
28	6	-3.84346	3.5586	-0.1429	-0.39189	-0.21001	-0.00059
29	6	0.051079	-0.34575	-2.321843	-0.93604	-0.4409	-0.152272
30	6	-5.9863	4.944925	0.173893	-0.39316	-0.20786	0.006957
31	6	-7.17777	5.283435	1.088665	-0.39763	-0.17428	0.169515
32	6	-8.12172	6.336305	0.485177	-0.61037	-0.3361	-0.248421
33	6	1.757282	-0.4966	0.148455	-0.71685	-0.24396	0.141033
34	6	3.007698	-1.0179	-0.593862	-0.40008	-0.23606	-0.068364
35	6	3.846411	-1.96373	0.288963	-0.3955	-0.24507	0.036137
36	6	5.075768	-2.53089	-0.441464	-0.38983	-0.20374	0.000946
37	6	5.897157	-3.50266	0.424669	-0.39398	-0.19907	-0.010577
38	6	7.119174	-4.08547	-0.308456	-0.39311	-0.20768	0.009482
39	6	7.938573	-5.06527	0.550701	-0.39769	-0.17459	0.160918
40	6	9.154645	-5.64509	-0.190322	-0.61028	-0.3363	-0.213852
41	15	0.651588	0.588925	-0.858571	1.47706	0.413355	0.306154
42	1	-4.66391	4.243996	1.752293	0.19392	0.093763	-0.0081
43	1	-5.60656	2.959433	0.9763	0.20701	0.115252	-0.001352
44	1	0.89998	2.622715	-2.139264	0.24877	0.17986	0.076683
45	1	2.399335	1.677139	-2.124593	0.24616	0.174697	0.077142
46	1	2.805726	2.40549	0.309447	0.20739	0.127714	0.003614
47	1	1.334569	3.393978	0.236478	0.20985	0.129899	0.008994
48	1	2.347083	4.738524	-1.664054	0.20108	0.112472	0.016942
49	1	3.8149	3.749643	-1.570922	0.19989	0.110551	0.016836
50	1	4.164185	4.522866	0.826256	0.19882	0.105496	0.003698
51	1	2.715792	5.536397	0.699146	0.2022	0.107795	0.004463
52	1	3.788686	6.816038	-1.211374	0.20016	0.101322	-0.002928
53	1	5.237092	5.806068	-1.066628	0.19965	0.101051	-0.003598
54	1	5.563617	6.628545	1.311881	0.19644	0.097173	-0.002465
55	1	4.124513	7.64907	1.151749	0.19646	0.098452	-0.001995
56	1	5.227184	8.899839	-0.753886	0.19877	0.101458	-0.031916
57	1	6.664752	7.881667	-0.588822	0.19857	0.101461	-0.031672
58	1	6.999747	10.08495	0.5923	0.21346	0.123469	0.056908
59	1	7.018218	8.753774	1.777463	0.20451	0.106738	0.046557
60	1	5.569451	9.779108	1.610784	0.20461	0.107141	0.046971
61	1	-0.35724	1.47528	1.14578	0.2415	0.157023	0.021337
62	1	-1.31986	0.170088	0.394517	0.30055	0.21999	-0.014987
63	1	-2.10055	1.770855	-1.413742	0.22293	0.134706	0.047984
64	1	-1.14713	3.094534	-0.68162	0.19247	0.10619	0.006959
65	1	-2.53763	2.844685	1.443176	0.19297	0.098202	0.008556
66	1	-3.47633	1.564149	0.63839	0.22791	0.157279	0.066292
67	1	-4.2203	3.201101	-1.12233	0.20612	0.113787	0.003627
68	1	-3.27181	4.487571	-0.349379	0.18995	0.090331	-0.007554
69	1	0.901107	-0.60986	-2.971407	0.24857	0.157216	0.079988
70	1	-0.67815	0.260886	-2.881622	0.2614	0.166673	0.078134
71	1	-0.44803	-1.25388	-1.940371	0.30455	0.226351	0.064715
72	1	-6.36667	4.584997	-0.804031	0.19687	0.099146	-0.000194
73	1	-5.41544	5.871782	-0.042382	0.19221	0.089159	-0.009544
74	1	-6.79666	5.641957	2.065809	0.19725	0.097844	-0.033993
75	1	-7.74492	4.356496	1.305331	0.20103	0.106126	-0.026118
76	1	-8.96354	6.563334	1.163003	0.21181	0.120786	0.061
77	1	-8.54973	5.987551	-0.472546	0.20436	0.107052	0.052341
78	1	-7.58895	7.284265	0.285086	0.202	0.101995	0.050214
79	1	1.12331	-1.34389	0.486673	0.31018	0.236455	-0.046455
80	1	2.034262	0.081126	1.052025	0.24124	0.15107	0.012348
81	1	3.640406	-0.17402	-0.935597	0.19497	0.101901	0.008034
82	1	2.694795	-1.57151	-1.500676	0.20925	0.1181	0.042926
83	1	3.200657	-2.79461	0.634388	0.22727	0.162325	0.036108
84	1	4.17516	-1.42468	1.201366	0.19611	0.099179	-0.004025
85	1	5.728828	-1.699	-0.778982	0.19212	0.094167	-0.007458
86	1	4.744774	-3.05493	-1.361373	0.1991	0.106376	-0.000997



87	1	5.241685	-4.33008	0.763513	0.20601	0.113647	0.003896
88	1	6.233857	-2.98237	1.344802	0.19549	0.096524	-0.003727
89	1	7.776215	-3.25745	-0.646661	0.19309	0.09107	-0.008764
90	1	6.781017	-4.60238	-1.23005	0.19639	0.0976	-0.001538
91	1	7.280578	-5.89055	0.888129	0.20077	0.1058	-0.02727
92	1	8.275394	-4.5493	1.472005	0.19786	0.098978	-0.033244
93	1	9.720737	-6.34821	0.445838	0.21237	0.121813	0.053115
94	1	9.850875	-4.84612	-0.505617	0.20243	0.103057	0.04192
95	1	8.845091	-6.19306	-1.099176	0.20427	0.106716	0.043207

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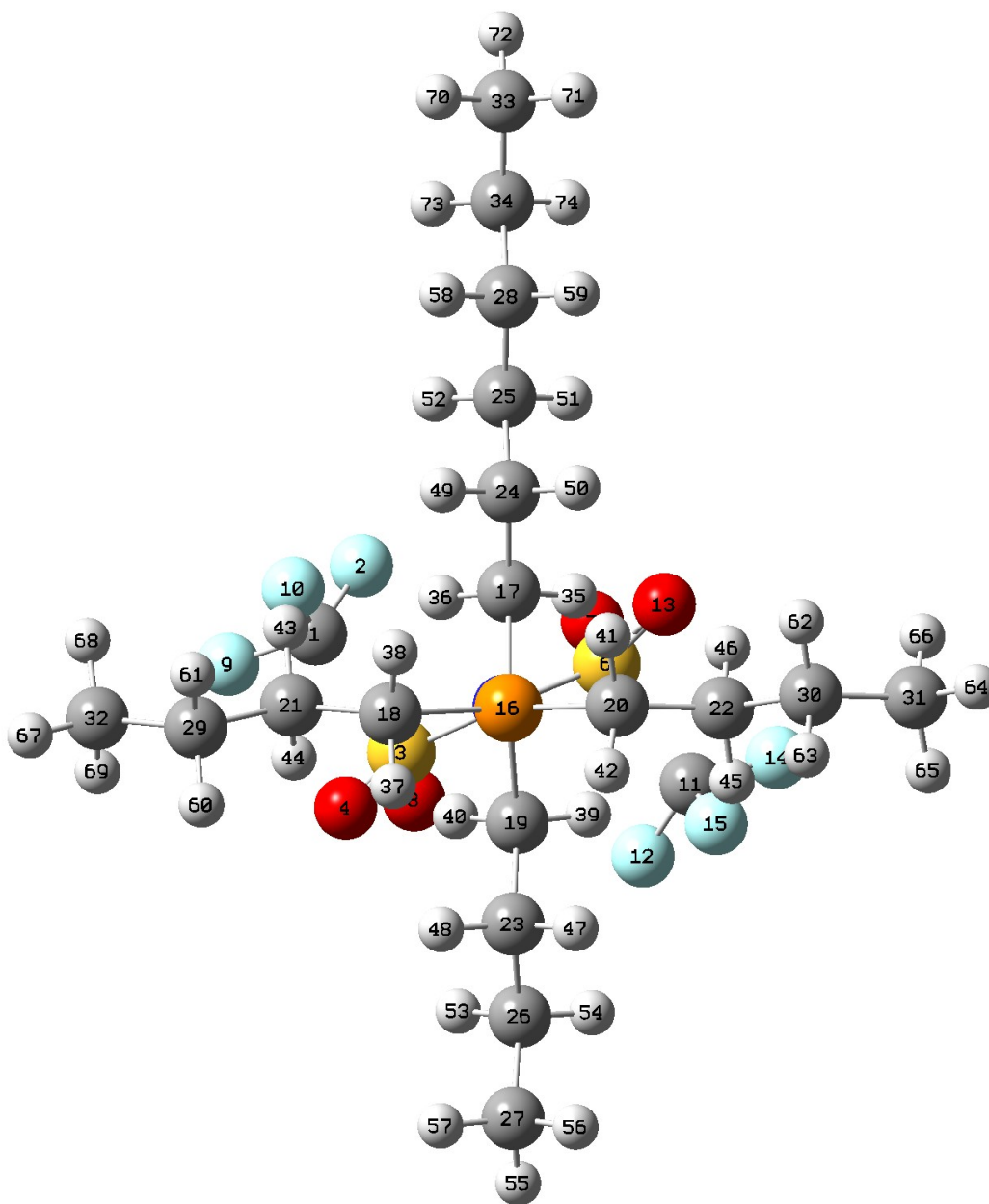
**Table S3.** Atom coordinates and charges from Mulliken population analysis, Natural Population Analysis (NPA) and electrostatic potential-derived (CHelpG) charges, calculated at the BP-TZVP level of theory for the  $[N_{4,4,4,6}][NTf_2]$ .



Center Number	Atomic Number	Coordinates/ Å			Atomic charges		
		x	y	z	NPA	Mulliken	CHelpG
1	6	2.294394	-2.63301	1.212104	0.67582	0.223554	0.453478
2	9	2.43236	-3.46775	0.172767	-0.27055	-0.08502	-0.128754
3	16	2.674999	-0.79439	0.705892	1.94572	0.512126	0.777804
4	8	2.2686	-0.02852	1.939028	-0.88491	-0.38926	-0.487821
5	7	1.487024	-0.39816	-0.399902	-1.12991	-0.44797	-0.545916
6	16	1.644885	-0.69116	-2.039925	1.94692	0.511336	0.809664
7	8	2.529699	-1.81281	-2.471984	-0.81226	-0.28444	-0.440674
8	8	4.09772	-0.80119	0.255431	-0.81106	-0.28211	-0.436961
9	9	3.141019	-2.99905	2.192608	-0.27916	-0.10152	-0.163814
10	9	1.024904	-2.73094	1.682918	-0.29961	-0.12421	-0.175128
11	6	2.483233	0.919764	-2.733979	0.67448	0.222089	0.394912
12	9	3.698033	1.11236	-2.200259	-0.27196	-0.08692	-0.117814
13	8	0.240177	-0.57537	-2.565537	-0.87611	-0.37437	-0.502345
14	9	2.596384	0.813428	-4.070651	-0.27859	-0.10062	-0.145897

15	9	1.710264	2.001534	-2.454011	-0.30137	-0.12676	-0.160965
16	7	-1.73083	1.340245	0.927074	-0.1589	-0.08553	0.110796
17	6	-1.66694	0.038299	0.113596	-0.25886	-0.28801	0.348998
18	6	-2.13669	1.061766	2.377199	-0.22529	-0.27191	-0.205074
19	6	-0.3252	1.960877	0.87053	-0.25951	-0.2502	0.029011
20	6	-2.77714	2.293571	0.356723	-0.22784	-0.25513	-0.196375
21	6	-1.30865	0.008421	3.120945	-0.44494	-0.20572	0.048156
22	6	-2.55344	2.756812	-1.08639	-0.43521	-0.18646	0.00492
23	6	-0.15216	3.316005	1.562818	-0.43126	-0.19402	-0.040779
24	6	-2.97553	-0.74877	0.016155	-0.43007	-0.15711	-0.118639
25	6	-2.73065	-2.08664	-0.718673	-0.39613	-0.27152	-0.134691
26	6	1.314898	3.782954	1.424314	-0.39877	-0.23824	0.072666
27	6	1.567129	5.118791	2.140618	-0.60972	-0.3306	-0.256986
28	6	-4.03348	-2.86833	-0.96157	-0.39174	-0.19538	-0.009858
29	6	-1.69734	-0.00714	4.615351	-0.3915	-0.23026	0.079285
30	6	-3.71634	3.667985	-1.536113	-0.39344	-0.22601	0.099928
31	6	-3.53607	4.172122	-2.977269	-0.61025	-0.33339	-0.27499
32	6	-0.93237	-1.08506	5.400734	-0.61049	-0.33607	-0.251932
33	6	-5.11449	-4.98577	-1.923019	-0.61033	-0.33483	-0.242222
34	6	-3.80799	-4.21593	-1.671738	-0.39849	-0.18703	0.1712
35	1	-1.29222	0.304027	-0.887277	0.26247	0.224207	0.028843
36	1	-0.86034	-0.55965	0.564344	0.26279	0.22745	-0.063788
37	1	-2.08003	2.033162	2.895604	0.2209	0.179322	0.073785
38	1	-3.19881	0.764417	2.351501	0.21943	0.175329	0.081575
39	1	-0.06874	2.026532	-0.197916	0.24217	0.201589	-0.006679
40	1	0.36415	1.213619	1.293099	0.27762	0.227012	0.083521
41	1	-3.7445	1.771937	0.443061	0.22291	0.17714	0.071517
42	1	-2.80845	3.162122	1.036542	0.22236	0.176955	0.081976
43	1	-1.4848	-0.99312	2.688044	0.21765	0.137718	0.043815
44	1	-0.22546	0.201258	3.022276	0.24496	0.184225	0.040286
45	1	-1.60106	3.310175	-1.175454	0.21861	0.143447	0.058087
46	1	-2.48012	1.891446	-1.768882	0.22487	0.151723	0.031031
47	1	-0.81944	4.084556	1.126267	0.20079	0.118604	0.03159
48	1	-0.39899	3.24808	2.639662	0.20447	0.121553	0.040226
49	1	-3.39609	-0.96181	1.017815	0.20291	0.127078	0.039333
50	1	-3.74212	-0.17249	-0.537706	0.2031	0.122139	0.039998
51	1	-2.21789	-1.89047	-1.679557	0.22742	0.153577	0.075739
52	1	-2.02927	-2.70463	-0.125002	0.20828	0.119773	0.051892
53	1	1.982631	2.999769	1.828236	0.22759	0.153878	0.037935
54	1	1.568432	3.877806	0.351516	0.20998	0.120014	0.023718
55	1	2.619078	5.432944	2.030574	0.22289	0.137116	0.081981
56	1	0.93282	5.926489	1.730725	0.20165	0.102013	0.053359
57	1	1.355357	5.041086	3.222699	0.2045	0.107648	0.059944
58	1	-4.54756	-3.04701	0.006265	0.19238	0.090296	0.002545
59	1	-4.727	-2.24865	-1.567118	0.19386	0.095304	0.006927
60	1	-1.49489	0.988467	5.056724	0.201	0.110407	0.009326
61	1	-2.78852	-0.17481	4.716802	0.19827	0.105676	-0.006097
62	1	-4.6717	3.113687	-1.45155	0.20232	0.110675	0.005944
63	1	-3.79783	4.531047	-0.846159	0.20143	0.10967	0.001191
64	1	-4.37695	4.819101	-3.280791	0.21863	0.129775	0.079547
65	1	-2.60618	4.758798	-3.083553	0.21059	0.116702	0.070381
66	1	-3.48344	3.331969	-3.692293	0.21286	0.121808	0.077585
67	1	-1.21337	-1.07474	6.467941	0.21581	0.125336	0.072875
68	1	-1.14559	-2.09444	5.006257	0.20964	0.113658	0.066116
69	1	0.158434	-0.9271	5.335177	0.21877	0.133468	0.071356
70	1	-5.639	-5.2073	-0.975161	0.20228	0.102706	0.048067
71	1	-5.80725	-4.40385	-2.558472	0.203	0.104502	0.049989
72	1	-4.92524	-5.94741	-2.431377	0.21532	0.126692	0.063433
73	1	-3.1194	-4.83692	-1.0656	0.20253	0.108988	-0.021018
74	1	-3.28756	-4.03744	-2.632804	0.20629	0.116332	-0.021035

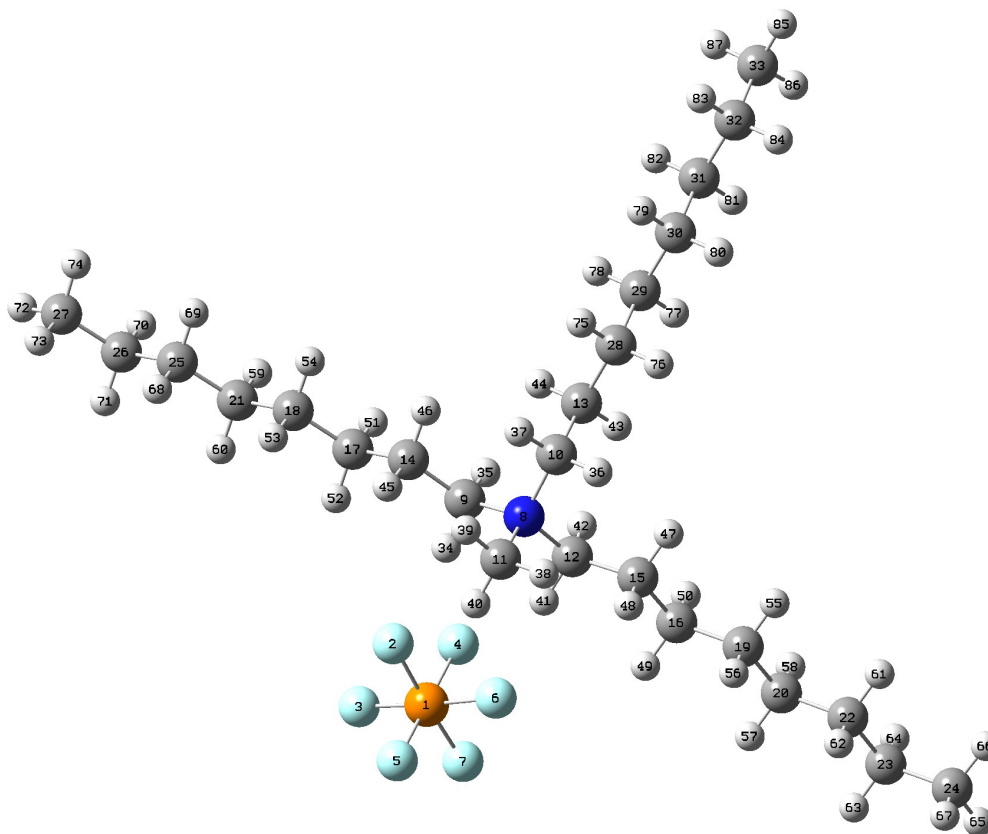
**Table S4.** Atom coordinates and charges from Mulliken population analysis, Natural Population Analysis (NPA) and electrostatic potential-derived (CHelpG) charges, calculated at the BP-TZVP level of theory for the  $[P_{4,4,4,6}][NTf_2]$ .



Center Number	Atomic Number	Coordinates/ Å			Atomic charges		
		x	y	z	NPA	Mulliken	CHelpG
1	6	0.997919	-3.45557	1.054276	0.67555	0.224906	0.421503
2	9	0.815389	-4.18611	-0.054904	-0.27148	-0.08633	-0.121717
3	16	2.135721	-1.91749	0.710042	1.94634	0.517978	0.775203
4	8	1.996017	-1.11466	1.977637	-0.88076	-0.38838	-0.485532
5	7	1.294515	-1.01826	-0.419172	-1.13081	-0.45564	-0.542686
6	16	1.457642	-1.24049	-2.067369	1.94783	0.520998	0.821569
7	8	1.837847	-2.59576	-2.562973	-0.81187	-0.28356	-0.442848
8	8	3.457712	-2.49114	0.321944	-0.81176	-0.28309	-0.434758
9	9	1.5696	-4.22057	2.002336	-0.27851	-0.10062	-0.152059
10	9	-0.21373	-3.04421	1.508087	-0.29956	-0.12557	-0.168529
11	6	2.937831	-0.08347	-2.568753	0.67451	0.222205	0.397869
12	9	4.066208	-0.42518	-1.930517	-0.272	-0.08668	-0.118996
13	8	0.269761	-0.51854	-2.644903	-0.87608	-0.38631	-0.50694

14	9	3.133595	-0.16985	-3.8969	-0.27802	-0.09988	-0.146617
15	9	2.64159	1.207539	-2.262962	-0.30211	-0.1282	-0.162529
16	15	-1.02957	1.816482	0.865533	1.49105	0.379055	0.317914
17	6	-1.62544	0.307959	-0.016882	-0.72578	-0.2163	-0.002825
18	6	-1.70585	1.83495	2.595421	-0.69699	-0.3125	-0.174044
19	6	0.814676	1.858116	0.92353	-0.72858	-0.19691	-0.008427
20	6	-1.6657	3.339745	0.012155	-0.69731	-0.31395	-0.18138
21	6	-1.3938	0.557154	3.407846	-0.4174	-0.27198	-0.007154
22	6	-1.11594	3.531005	-1.419118	-0.41355	-0.26272	-0.004576
23	6	1.39947	3.058135	1.6991	-0.40497	-0.27868	-0.052072
24	6	-3.15865	0.243545	-0.187379	-0.40292	-0.27655	0.015631
25	6	-3.60888	-1.05634	-0.885189	-0.39451	-0.22865	-0.10118
26	6	2.942302	3.02766	1.718546	-0.4005	-0.20598	0.097244
27	6	3.547008	4.194186	2.512798	-0.61033	-0.34249	-0.255308
28	6	-5.1309	-1.12744	-1.093903	-0.39236	-0.21067	-0.037661
29	6	-1.7695	0.703559	4.895777	-0.39406	-0.20646	0.123001
30	6	-1.77033	4.720343	-2.149992	-0.39487	-0.20167	0.110227
31	6	-1.22264	4.908392	-3.572667	-0.61124	-0.34303	-0.256316
32	6	-1.46928	-0.56678	5.705313	-0.61141	-0.34345	-0.254699
33	6	-7.11358	-2.49011	-1.98053	-0.61033	-0.33754	-0.227374
34	6	-5.59029	-2.42527	-1.782667	-0.39825	-0.18358	0.176767
35	1	-1.09223	0.257637	-0.987064	0.3012	0.221143	0.101974
36	1	-1.2328	-0.54975	0.560234	0.2763	0.203949	0.017915
37	1	-1.28496	2.733958	3.085794	0.24438	0.171962	0.056154
38	1	-2.79698	2.003372	2.516163	0.24341	0.172393	0.075083
39	1	1.156058	1.835431	-0.127748	0.27092	0.191811	0.004611
40	1	1.142237	0.888221	1.347352	0.3054	0.203333	0.092896
41	1	-2.77006	3.261079	0.009106	0.2446	0.172552	0.058254
42	1	-1.41258	4.201907	0.658945	0.24433	0.173548	0.075343
43	1	-1.94629	-0.29743	2.973493	0.2126	0.121911	0.050277
44	1	-0.32103	0.295648	3.324254	0.23092	0.165236	0.037367
45	1	-0.02122	3.686383	-1.378088	0.21326	0.125022	0.050782
46	1	-1.26838	2.608521	-2.011714	0.22161	0.146188	0.036104
47	1	1.061419	4.014379	1.251291	0.19616	0.104656	0.025167
48	1	1.032295	3.052428	2.744783	0.19956	0.108913	0.037522
49	1	-3.66246	0.315585	0.797989	0.19709	0.109889	0.009677
50	1	-3.51037	1.108365	-0.784397	0.19967	0.113167	0.019714
51	1	-3.09118	-1.14486	-1.860933	0.2173	0.13904	0.052991
52	1	-3.27678	-1.92801	-0.286007	0.20623	0.118399	0.045215
53	1	3.277908	2.063237	2.145739	0.2221	0.1447	0.021699
54	1	3.320721	3.047183	0.677859	0.2089	0.119576	0.0176
55	1	4.649273	4.146334	2.51062	0.22175	0.135099	0.078683
56	1	3.255773	5.171598	2.08522	0.20194	0.10321	0.05314
57	1	3.216969	4.178317	3.56795	0.20408	0.107442	0.058266
58	1	-5.64501	-1.03417	-0.114215	0.19291	0.09286	0.006188
59	1	-5.46315	-0.2576	-1.698147	0.1944	0.09555	0.009177
60	1	-1.21524	1.560611	5.328269	0.20049	0.11012	-0.00086
61	1	-2.8458	0.956711	4.986677	0.19933	0.107384	-0.016557
62	1	-2.86739	4.56652	-2.190191	0.20107	0.110059	0.002144
63	1	-1.6121	5.648782	-1.564431	0.20075	0.109108	-0.009218
64	1	-1.70959	5.759559	-4.078642	0.21766	0.128202	0.07258
65	1	-0.13497	5.103013	-3.56309	0.20989	0.115923	0.065455
66	1	-1.39265	4.00838	-4.190078	0.2133	0.12355	0.072363
67	1	-1.73318	-0.43379	6.768527	0.21646	0.126075	0.070428
68	1	-2.04191	-1.43171	5.324269	0.20915	0.113953	0.065077
69	1	-0.39814	-0.83069	5.653613	0.21623	0.129606	0.071785
70	1	-7.64619	-2.43846	-1.013148	0.20272	0.103863	0.046966
71	1	-7.47289	-1.65069	-2.603699	0.20332	0.10486	0.046985
72	1	-7.41739	-3.42774	-2.478152	0.21504	0.126655	0.057516
73	1	-5.25459	-3.29447	-1.183299	0.20211	0.10819	-0.024976
74	1	-5.08223	-2.51782	-2.762654	0.20449	0.113126	-0.022191

**Table S5.** Atom coordinates and charges from Mulliken population analysis, Natural Population Analysis (NPA) and electrostatic potential-derived (CHelpG) charges, calculated at the BP-TZVP level of theory for the  $[\text{N}_{8,8,8,1}][\text{PF}_6]$ .

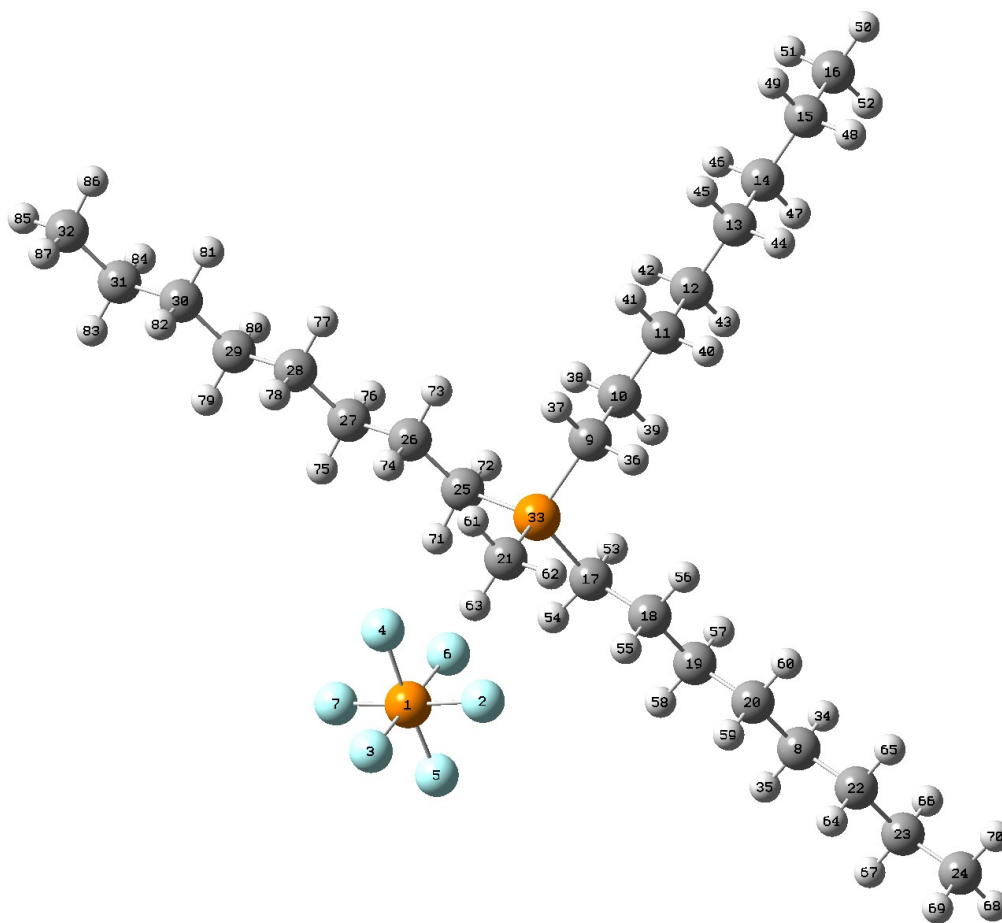


Center Number	Atomic Number	Coordinates/ Å			Atomic charges		
		x	y	z	NPA	Mulliken	CHelpG
1	15	0.123831	-4.34792	-0.16035	2.46265	1.0144	1.189224
2	9	-1.05342	-3.53111	0.744578	-0.5935	-0.35308	-0.356022
3	9	-1.05597	-5.11991	-1.00077	-0.55166	-0.283668	-0.317805
4	9	0.0717	-3.06495	-1.25848	-0.58859	-0.344485	-0.38269
5	9	0.172584	-5.53338	0.973394	-0.55096	-0.28235	-0.332011
6	9	1.29112	-3.47474	0.701872	-0.59279	-0.351909	-0.355188
7	9	1.307096	-5.06294	-1.0446	-0.55146	-0.283341	-0.318269
8	7	0.004455	0.019627	0.951433	-0.15268	-0.08237	-0.042139
9	6	-1.21641	-0.34027	0.086432	-0.24942	-0.265267	0.125026
10	6	-0.02743	1.468991	1.416903	-0.23071	-0.276843	-0.007272
11	6	0.029553	-0.86351	2.177835	-0.44905	-0.273505	-0.108182
12	6	1.236325	-0.28203	0.078291	-0.25026	-0.262378	0.153772
13	6	-0.10672	2.528249	0.313888	-0.43076	-0.14324	0.005141
14	6	-2.59097	-0.14154	0.731421	-0.43006	-0.141594	-0.112227
15	6	2.602159	0.048232	0.686587	-0.42926	-0.150963	-0.115505
16	6	3.714752	-0.44231	-0.26658	-0.3918	-0.283395	-0.038564
17	6	-3.68611	-0.58949	-0.26202	-0.39107	-0.28872	-0.023623
18	6	-5.10619	-0.45033	0.315979	-0.38962	-0.185626	0.030569
19	6	5.127748	-0.16261	0.276125	-0.38954	-0.186029	0.04037
20	6	6.241067	-0.67583	-0.65466	-0.39457	-0.209075	-0.014263
21	6	-6.20119	-0.90286	-0.66655	-0.39433	-0.208988	0.003637
22	6	7.658064	-0.40616	-0.11803	-0.39308	-0.201507	-0.014566
23	6	8.771612	-0.93081	-1.04264	-0.3979	-0.177293	0.165307
24	6	10.18403	-0.65413	-0.50243	-0.61035	-0.335391	-0.226894
25	6	-7.62446	-0.77785	-0.094	-0.39308	-0.202049	-0.015571

26	6	-8.71979	-1.23434	-1.07478	-0.39774	-0.176998	0.166516
27	6	-10.1381	-1.1107	-0.49434	-0.61024	-0.335428	-0.226358
28	6	-0.06336	3.944736	0.926944	-0.38882	-0.269296	-0.055906
29	6	-0.18674	5.053198	-0.13476	-0.39091	-0.197974	0.018094
30	6	-0.12523	6.472124	0.458471	-0.39359	-0.197192	-0.003423
31	6	-0.26081	7.580442	-0.60095	-0.39378	-0.209013	0.000436
32	6	-0.19545	9.001629	-0.01218	-0.39738	-0.175995	0.147644
33	6	-0.34377	10.10233	-1.07541	-0.61057	-0.336107	-0.240324
34	1	-1.0734	-1.39787	-0.19006	0.2879	0.237933	0.054908
35	1	-1.12662	0.268278	-0.82881	0.21508	0.160608	0.016321
36	1	0.880442	1.615704	2.02594	0.22546	0.181122	0.030046
37	1	-0.89456	1.556614	2.092805	0.2244	0.178849	0.046449
38	1	0.938221	-0.64271	2.7557	0.21854	0.148462	0.081764
39	1	-0.85598	-0.64115	2.790174	0.21759	0.148331	0.077003
40	1	0.02145	-1.91677	1.860769	0.28937	0.237413	0.127821
41	1	1.168386	-1.35759	-0.15342	0.28838	0.23439	0.038348
42	1	1.086902	0.278268	-0.85984	0.21565	0.160917	0.023768
43	1	0.731504	2.415684	-0.39825	0.21479	0.139538	0.033136
44	1	-1.04012	2.41103	-0.26684	0.215	0.139015	0.037474
45	1	-2.67923	-0.75068	1.649026	0.22191	0.140953	0.070463
46	1	-2.76126	0.915105	1.015587	0.19813	0.112677	0.041688
47	1	2.718113	1.135524	0.861543	0.19886	0.11512	0.044868
48	1	2.729636	-0.45739	1.66085	0.2183	0.131213	0.069921
49	1	3.586818	-1.52849	-0.43435	0.22686	0.162612	0.057803
50	1	3.596492	0.042606	-1.25678	0.19787	0.101871	0.019194
51	1	-3.60753	0.005526	-1.1945	0.19636	0.100011	0.015081
52	1	-3.5018	-1.64293	-0.54643	0.22551	0.159622	0.053312
53	1	-5.18054	-1.04793	1.247043	0.20113	0.109533	-0.002702
54	1	-5.28811	0.604563	0.609874	0.19194	0.093077	-0.016178
55	1	5.256671	0.927852	0.438849	0.19211	0.093583	-0.016633
56	1	5.237088	-0.63825	1.272067	0.19986	0.106743	-0.005032
57	1	6.108692	-1.76491	-0.81347	0.20741	0.117681	0.009042
58	1	6.130947	-0.2065	-1.65393	0.19576	0.097015	-0.002526
59	1	-6.1272	-0.30763	-1.5999	0.19507	0.096081	-0.008618
60	1	-6.01447	-1.95541	-0.96028	0.20708	0.1168	0.003613
61	1	7.793875	0.684701	0.035825	0.19276	0.090321	-0.001216
62	1	7.766472	-0.87138	0.883471	0.19658	0.097637	0.003914
63	1	8.636903	-2.02048	-1.19157	0.20157	0.107784	-0.024742
64	1	8.659786	-0.47146	-2.04517	0.19809	0.099335	-0.031114
65	1	10.96227	-1.04208	-1.18319	0.21255	0.122106	0.055872
66	1	10.36041	0.430211	-0.37762	0.20221	0.102545	0.044913
67	1	10.33627	-1.13071	0.483432	0.2043	0.106579	0.047552
68	1	-7.69803	-1.37403	0.838763	0.19703	0.098782	0.003196
69	1	-7.81325	0.275506	0.200844	0.19276	0.090156	-0.001585
70	1	-8.64565	-0.63948	-2.00705	0.19774	0.098908	-0.032417
71	1	-8.52905	-2.28537	-1.36931	0.20143	0.107409	-0.025674
72	1	-10.9032	-1.44474	-1.21729	0.21245	0.121938	0.05536
73	1	-10.2513	-1.72444	0.418079	0.20449	0.107186	0.048101
74	1	-10.3705	-0.06459	-0.22203	0.20222	0.102434	0.044773
75	1	-0.87981	4.053649	1.668986	0.20152	0.112724	0.02861
76	1	0.883665	4.075157	1.487993	0.20142	0.113306	0.031682
77	1	0.620984	4.934206	-0.88547	0.19985	0.10698	-0.000907
78	1	-1.13977	4.926164	-0.68745	0.19982	0.107628	-0.001088
79	1	-0.92672	6.589821	1.216364	0.19742	0.101104	-0.004431
80	1	0.832086	6.601165	1.003932	0.20004	0.101961	-0.004311
81	1	0.536027	7.461352	-1.36373	0.19691	0.098395	0.001071
82	1	-1.22155	7.455434	-1.14156	0.1966	0.098177	0.003229
83	1	-0.9892	9.115645	0.75285	0.19889	0.101499	-0.024284
84	1	0.765306	9.131276	0.525049	0.19886	0.102333	-0.024078
85	1	-0.31512	11.10865	-0.6218	0.21369	0.1239	0.062718
86	1	0.468253	10.05035	-1.82343	0.20482	0.10754	0.053292
87	1	-1.30199	10.00837	-1.61836	0.20457	0.106832	0.052293

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**Table S6.** Atom coordinates and charges from Mulliken population analysis, Natural Population Analysis (NPA) and electrostatic potential-derived (CHelpG) charges, calculated at the BP-TZVP level of theory for the  $[P_{8,8,8,1}][PF_6]$ .



Center Number	Atomic Number	Coordinates/ Å			Atomic charges		
		x	y	z	NPA	Mulliken	CHelpG
1	15	0.393926	-4.34868	-0.37188	2.46352	1.013235	1.18683
2	9	1.482501	-3.44073	0.55329	-0.59405	-0.352213	-0.353048
3	9	0.455717	-5.55576	0.73891	-0.55161	-0.28442	-0.334565
4	9	-0.85751	-3.61194	0.498775	-0.59397	-0.354097	-0.354806
5	9	1.645344	-4.98631	-1.2209	-0.55127	-0.282615	-0.318247
6	9	0.324362	-3.04614	-1.44973	-0.59088	-0.345423	-0.377673
7	9	-0.71049	-5.1578	-1.27697	-0.55119	-0.283144	-0.318444
8	6	6.658532	-0.22109	-0.59601	-0.39356	-0.199173	-0.024507
9	6	-0.09948	1.660297	1.478935	-0.69719	-0.296003	-0.219417
10	6	-0.24214	2.725881	0.372669	-0.40645	-0.267579	0.04232
11	6	-0.35566	4.156526	0.936087	-0.39008	-0.226145	-0.040399
12	6	-0.52085	5.22235	-0.16102	-0.39139	-0.211574	0.025879
13	6	-0.64165	6.653149	0.394162	-0.3952	-0.193428	-0.002931
14	6	-0.81856	7.716144	-0.70527	-0.39361	-0.212044	0.008086
15	6	-0.9419	9.149952	-0.15795	-0.39743	-0.174432	0.150102
16	6	-1.12148	10.20235	-1.26427	-0.61042	-0.336581	-0.226185
17	6	1.552458	-0.28217	-0.18	-0.70759	-0.226895	-0.064574
18	6	2.891304	-0.15484	0.575636	-0.40454	-0.250218	-0.011549
19	6	4.099911	-0.24536	-0.37745	-0.39126	-0.248476	-0.019264
20	6	5.449601	-0.1536	0.354575	-0.39235	-0.205483	0.033607
21	6	0.141483	-1.17171	2.357214	-0.93877	-0.438977	-0.234044
22	6	8.011275	-0.14129	0.134495	-0.39323	-0.208136	0.01011
23	6	9.222769	-0.19554	-0.81403	-0.39736	-0.174574	0.15835

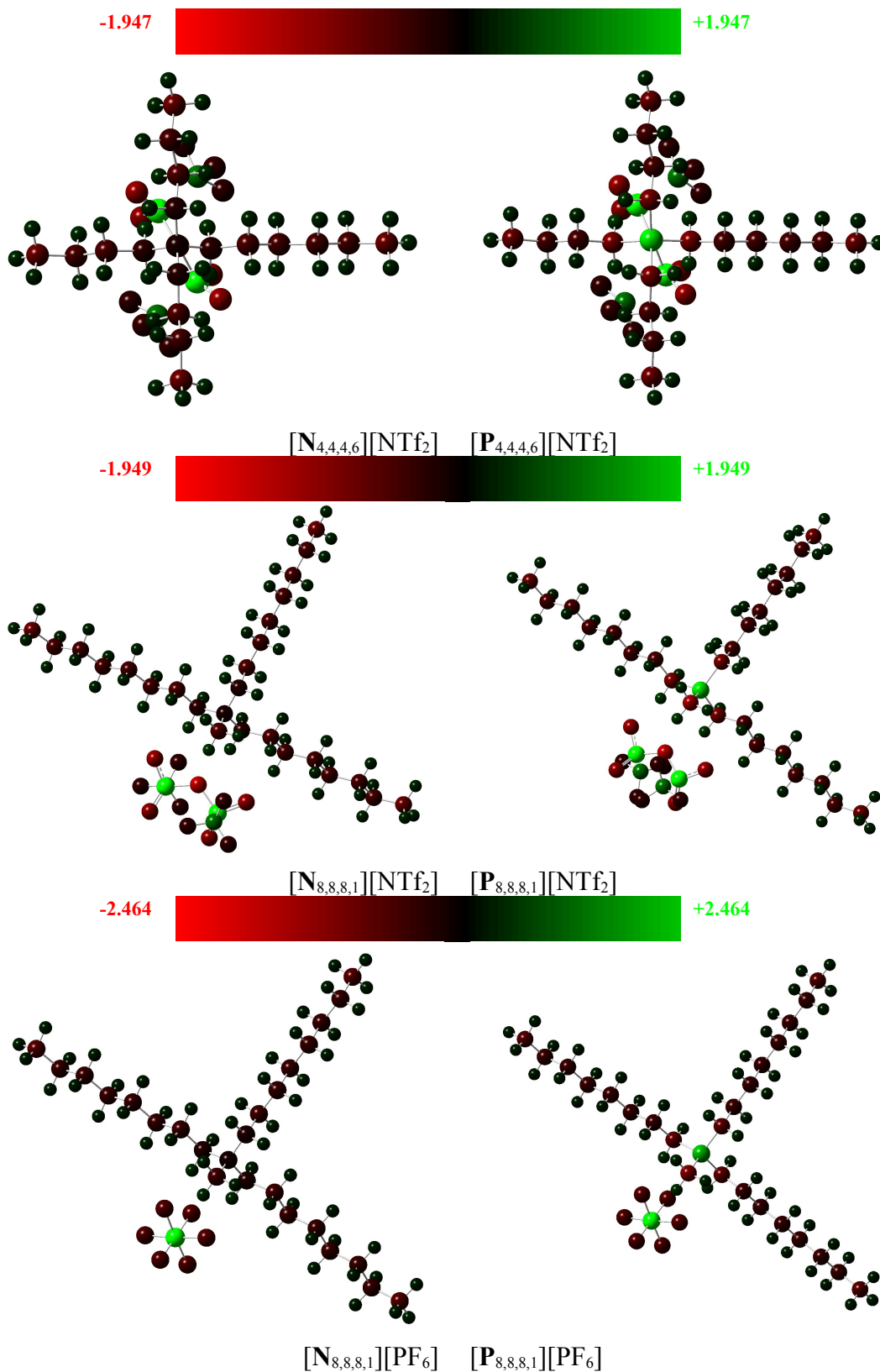


24	6	10.56986	-0.11729	-0.07718	-0.61026	-0.336299	-0.218065
25	6	-1.42575	-0.52588	-0.1663	-0.70903	-0.231892	-0.021891
26	6	-2.7811	-0.47893	0.568145	-0.40321	-0.245464	-0.047378
27	6	-3.94837	-0.88447	-0.35403	-0.39209	-0.24841	-0.017698
28	6	-5.31461	-0.84265	0.351033	-0.39189	-0.202946	0.035893
29	6	-6.48033	-1.25712	-0.56494	-0.39377	-0.200448	-0.001069
30	6	-7.85132	-1.20013	0.132723	-0.39302	-0.207506	-0.00554
31	6	-9.01975	-1.61883	-0.77812	-0.39746	-0.174895	0.164759
32	6	-10.3858	-1.55212	-0.07596	-0.61012	-0.336217	-0.220832
33	15	0.042419	-0.09363	0.872268	1.4766	0.391694	0.404179
34	1	6.591083	0.603171	-1.33564	0.19417	0.094892	-0.004406
35	1	6.611727	-1.16184	-1.18088	0.20518	0.112134	0.007764
36	1	0.796385	1.849856	2.102205	0.24577	0.168767	0.087824
37	1	-0.96736	1.684078	2.166523	0.2458	0.170929	0.072174
38	1	-1.13745	2.508568	-0.24157	0.20837	0.12619	0.025937
39	1	0.625961	2.674496	-0.31293	0.2078	0.124204	0.02451
40	1	0.544157	4.388621	1.541997	0.20065	0.11208	0.022591
41	1	-1.21763	4.211806	1.632642	0.20021	0.111368	0.026073
42	1	-1.41925	4.988389	-0.76798	0.19897	0.106658	-0.006294
43	1	0.340658	5.171132	-0.85774	0.19924	0.107085	-0.004154
44	1	0.259338	6.892439	0.995257	0.20001	0.101271	-0.00465
45	1	-1.49978	6.704177	1.095261	0.19974	0.100864	-0.006897
46	1	-1.71904	7.475147	-1.30669	0.19645	0.097823	-0.000821
47	1	0.039072	7.664868	-1.4071	0.19654	0.09797	-0.003051
48	1	-0.04133	9.390223	0.441702	0.19858	0.101549	-0.026951
49	1	-1.79744	9.199727	0.544839	0.1985	0.101396	-0.026474
50	1	-1.20587	11.22066	-0.84579	0.21337	0.123519	0.057856
51	1	-2.03431	10.00831	-1.85663	0.20451	0.106993	0.048188
52	1	-0.26513	10.19876	-1.96322	0.20452	0.106955	0.04944
53	1	1.462485	0.471901	-0.98679	0.23874	0.15639	0.034068
54	1	1.451749	-1.27949	-0.64997	0.30909	0.237427	0.08968
55	1	2.964025	-0.97103	1.318377	0.22237	0.143631	0.043674
56	1	2.940294	0.802567	1.133993	0.19107	0.097255	0.006405
57	1	4.035477	0.562653	-1.13549	0.19389	0.098407	0.01163
58	1	4.047595	-1.20135	-0.93531	0.21878	0.14811	0.037748
59	1	5.520428	-0.97595	1.095079	0.20565	0.114434	0.00145
60	1	5.494416	0.790654	0.936503	0.19172	0.09255	-0.015972
61	1	-0.77737	-1.05697	2.954289	0.25109	0.157195	0.089951
62	1	1.015465	-0.87856	2.961158	0.25122	0.158614	0.082892
63	1	0.247788	-2.21628	2.018296	0.31717	0.232203	0.1442
64	1	8.08193	-0.97177	0.866471	0.19732	0.100549	-0.000799
65	1	8.054051	0.794524	0.729564	0.19285	0.090186	-0.007721
66	1	9.150138	0.634057	-1.54556	0.19714	0.097992	-0.031113
67	1	9.177947	-1.12959	-1.40855	0.2006	0.105553	-0.027159
68	1	11.42039	-0.1576	-0.78045	0.21201	0.121235	0.053322
69	1	10.68608	-0.95515	0.634491	0.20474	0.107837	0.046318
70	1	10.65771	0.822164	0.499137	0.20231	0.10267	0.042091
71	1	-1.21073	-1.54158	-0.55063	0.31033	0.234434	0.077449
72	1	-1.4044	0.162637	-1.03369	0.24091	0.160451	0.024848
73	1	-2.97097	0.535954	0.973258	0.19319	0.101733	0.020416
74	1	-2.75503	-1.17187	1.430592	0.21536	0.129574	0.045947
75	1	-3.76108	-1.90534	-0.7413	0.22004	0.151291	0.039484
76	1	-3.97187	-0.21552	-1.23945	0.19563	0.100023	0.014342
77	1	-5.50096	0.179956	0.740846	0.1919	0.093524	-0.018521
78	1	-5.29135	-1.5102	1.236451	0.20356	0.109727	-0.002968
79	1	-6.30113	-2.28414	-0.94205	0.20564	0.113539	0.002618
80	1	-6.49657	-0.60124	-1.45969	0.19497	0.096096	-0.010315
81	1	-8.03052	-0.1713	0.508317	0.19279	0.090653	-0.004192
82	1	-7.83439	-1.85341	1.029256	0.19651	0.098521	-0.001245
83	1	-8.84173	-2.6479	-1.14836	0.20079	0.106235	-0.026742
84	1	-9.03189	-0.97057	-1.67724	0.19756	0.098568	-0.03207
85	1	-11.2047	-1.85607	-0.75163	0.21221	0.121694	0.05373

86	1	-10.6063	-0.52727	0.275507	0.20227	0.102802	0.043293
87	1	-10.4162	-2.21884	0.805325	0.20436	0.10703	0.046612

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**Table S7.** Natural Population Analysis charge distribution details for the studied ILs, at the BP-TZVP level of theory.



**Table S8.** Atom coordinates and charges from Mulliken population analysis, Natural Population Analysis (NPA) and electrostatic potential-derived (CHelpG) charges, calculated at the BP-TZVP level of theory for the 1-octane.

Center Number	Atomic Number	Coordinates/ Å			Atomic charges		
		x	y	z	NPA	Mulliken	CHelpG
1	6	4.384848	0.255397	0.00081	-0.60841	-0.323606	-0.24382
2	6	3.106904	-0.542924	0.00081	-0.39947	-0.16708	0.189317
3	6	1.889196	0.356738	0.00081	-0.3982	-0.202916	0.005858
4	6	0.608376	-0.44967	0.000645	-0.39548	-0.187718	0.015131
5	6	-0.608502	0.450536	0.000097	-0.3955	-0.187513	0.010359
6	6	-1.889122	-0.356187	-0.000254	-0.39819	-0.203097	0.004543
7	6	-3.107291	0.542851	-0.001342	-0.3995	-0.166968	0.185898
8	6	-4.3846	-0.25646	-0.001721	-0.60841	-0.323596	-0.24232
9	1	5.269066	-0.42658	0.000605	0.2097	0.114354	0.052065
10	1	4.442549	0.907206	0.905957	0.20269	0.101107	0.046975
11	1	4.44241	0.907871	-0.903872	0.20269	0.101102	0.046968
12	1	3.078841	-1.20915	0.903367	0.19748	0.096535	-0.03717
13	1	3.078807	-1.209462	-0.901527	0.19747	0.096536	-0.03724
14	1	1.91488	1.023046	-0.901473	0.19766	0.091862	-0.00366
15	1	1.914656	1.022379	0.903587	0.19766	0.091868	-0.00353
16	1	0.583209	-1.115404	0.903402	0.19812	0.093939	-0.01514
17	1	0.583638	-1.116054	-0.901659	0.19811	0.093933	-0.01482
18	1	-0.583066	1.116677	-0.902359	0.19812	0.093944	-0.0138
19	1	-0.583794	1.116414	0.902763	0.19812	0.093935	-0.01373
20	1	-1.914721	-1.021696	0.902613	0.19766	0.091879	-0.00251
21	1	-1.91378	-1.022743	-0.902391	0.19765	0.09186	-0.00271
22	1	-3.078929	1.209066	-0.903911	0.19748	0.096547	-0.03602
23	1	-3.080019	1.209383	0.901026	0.19748	0.096536	-0.03599
24	1	-5.269463	0.424732	-0.002943	0.2097	0.114347	0.051794
25	1	-4.442232	-0.907853	0.903727	0.2027	0.101114	0.046719
26	1	-4.440899	-0.909518	-0.906067	0.20269	0.101097	0.046832