Supplementary Material for PCCP

Electronic supporting information for

"Ionic liquids through the looking glass: theory mirrors experiment and provides further insight in aromatic substitution processes"

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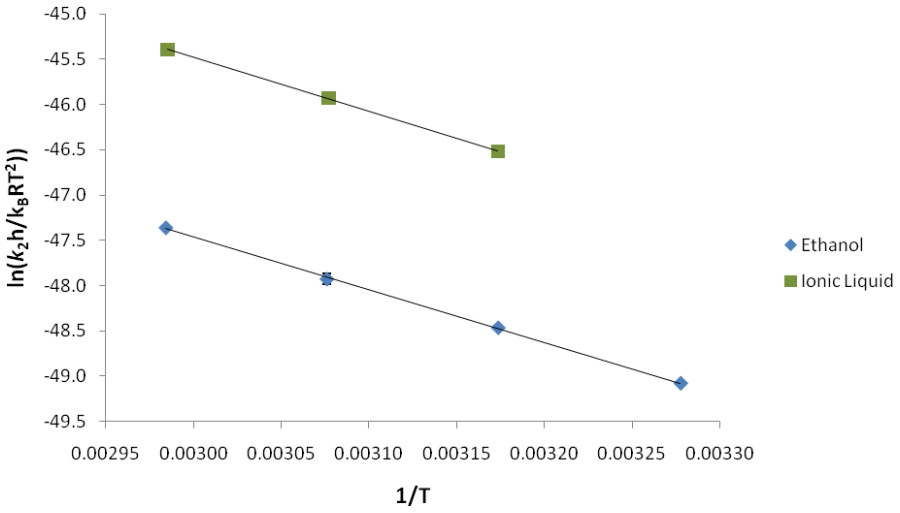
Experimental – Sample preparation

Preparation of the reaction mixtures for the S_NAr reaction of 2,4-dinitrofluorobenzene

For the solvolysis reactions of 2,4-dinitrofluorobenzene carried out in ethanol where ethanol is the nucleophile, a solution containing triethylamine (2.18 g, 21.5 mmol) and acetonitrile-d_3 (3.11 g, 7.06 mmol) was mixed with ethanol (14.5 g, 315 mmol, 12.6 M) in a 25 mL volumetric flask and used as the reaction mixture.

Where [BMIM][$N(SO_2CF_3)_2$] was the reaction medium, the reaction mixture was prepared by mixing triethylamine (395 mg, 3.90 mmol) and ethanol (944 mg, 20.5 mmol, 2.05 M) with [BMIM][$N(SO_2CF_3)_2$] (11.9 g, 28.37 mmol) in a 10 mL volumetric flask.

Eyring plot showing the data from which activation parameters shown in Table 2 are derived



The temperature-dependent kinetic data shown in Table 1 were fitted to the Eyring equation for the S_NAr reaction of 2,4-dinitrofluorobenzene shown in Scheme 1. Each of the data points is the average of three kinetic experiments and the errors are reported as the standard deviation of the mean. The enthalpies ($\Delta H^{\ddagger}$) and entropies of activation ($\Delta S^{\ddagger}$) for the reaction were derived from the slope and intercept of the curves.

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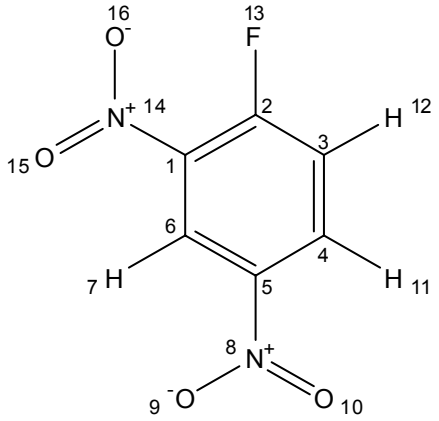
RESP charges and OPLS force field parameters

1-fluoro-2,4-dinitrobenzene



Atom	Element	RESP	Type	ε / kcal.mol^{-1}	σ / Å
1	C	-0.0269	CA	0.070	3.550
2	C	0.3938	CA	0.070	3.550
3	C	-0.3075	CA	0.070	3.550
4	C	-0.1253	CA	0.070	3.550
5	C	0.0554	CA	0.070	3.550
6	C	-0.2392	CA	0.070	3.550
7	H	0.2577	HA	0.030	2.420
8	N	0.7709	NO	0.120	3.250
9	O	-0.4503	ON	0.170	2.960
10	O	-0.4694	ON	0.170	2.960
11	H	0.2230	HA	0.030	2.420
12	H	0.2218	HA	0.030	2.420
13	F	-0.1849	F	0.061	2.850
14	N	0.7748	NO	0.120	3.250
15	O	-0.4587	ON	0.170	2.960
16	O	-0.4353	ON	0.170	2.960

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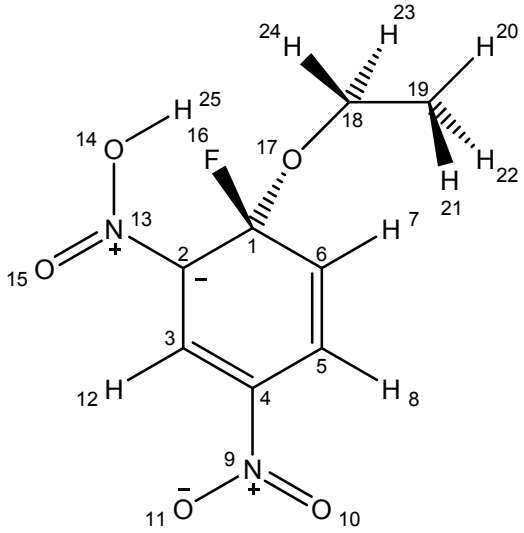
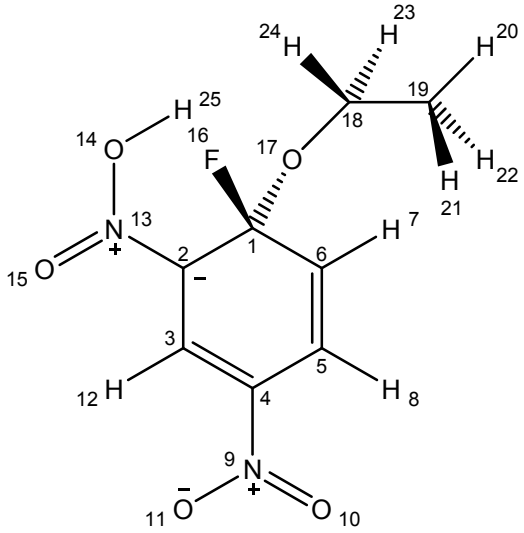
Intermediate calculated using alkene OPLS parameters for the cyclic carbons



Atom	Element	RESP	Type	ε / kcal.mol^{-1}	σ / Å
1	C	0.9708	CT	0.066	3.500
2	C	-0.2329	CM	0.076	3.550
3	C	-0.1445	CM	0.076	3.550
4	C	0.0769	CM	0.076	3.550
5	C	-0.1900	CM	0.076	3.550
6	C	-0.4242	CM	0.076	3.550
7	H	0.2206	HC	0.030	2.420
8	H	0.2141	HC	0.030	2.420
9	N	0.7197	NO	0.120	3.250
10	O	-0.4601	ON	0.170	2.960
11	O	-0.4704	ON	0.170	2.960
12	H	0.2184	HC	0.030	2.420
13	N	0.6053	NO	0.120	3.250
14	O	-0.5020	OH	0.170	3.000
15	O	-0.3831	ON	0.170	2.960
16	F	-0.3881	F	0.053	2.950
17	O	-0.6836	OS	0.140	2.900
18	C	0.3686	CT	0.066	3.500
19	C	-0.2904	CT	0.066	3.500
20	H	0.0715	HC	0.030	2.500
21	H	0.0775	HC	0.030	2.500
22	H	0.1073	HC	0.030	2.500
23	H	0.0329	HC	0.030	2.500
24	H	-0.0025	HC	0.030	2.500
25	H	0.4882	HO	0	0

Supplementary Material for PCCP

Intermediate calculated using aromatic OPLS parameters for the cyclic carbons



Atom	Element	RESP	Type	ε / kcal.mol^{-1}	σ / Å
1	C	0.9708	CT	0.066	3.500
2	C	-0.2329	CA	0.070	3.550
3	C	-0.1445	CA	0.070	3.550
4	C	0.0769	CA	0.070	3.550
5	C	-0.1900	CA	0.070	3.550
6	C	-0.4242	CA	0.070	3.550
7	H	0.2206	HA	0.030	2.420
8	H	0.2141	HA	0.030	2.420
9	N	0.7197	NO	0.120	3.250
10	O	-0.4601	ON	0.170	2.960
11	O	-0.4704	ON	0.170	2.960
12	H	0.2184	HA	0.030	2.420
13	N	0.6053	NO	0.120	3.250
14	O	-0.5020	OH	0.170	3.000
15	O	-0.3831	ON	0.170	2.960
16	F	-0.3881	F	0.053	2.950
17	O	-0.6836	OS	0.140	2.900
18	C	0.3686	CT	0.066	3.500
19	C	-0.2904	CT	0.066	3.500
20	H	0.0715	HC	0.030	2.500
21	H	0.0775	HC	0.030	2.500
22	H	0.1073	HC	0.030	2.500
23	H	0.0329	HC	0.030	2.500
24	H	-0.0025	HC	0.030	2.500
25	H	0.4882	HO	0	0

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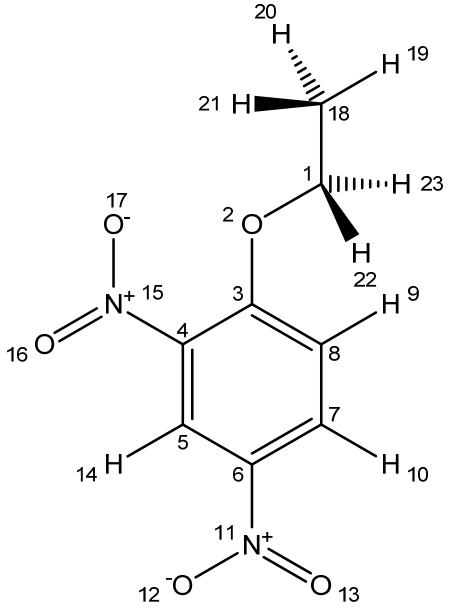
1-ethoxy-2,4-dinitrobenzene



Atom	Element	RESP	Type	ε / kcal.mol^{-1}	σ / Å
1	C	0.2940	CT	0.066	3.500
2	O	-0.2972	OS	0.140	2.900
3	C	0.3312	CA	0.070	3.550
4	C	-0.1050	CA	0.070	3.550
5	C	-0.1803	CA	0.070	3.550
6	C	0.0360	CA	0.070	3.550
7	C	-0.1579	CA	0.070	3.550
8	C	-0.2512	CA	0.070	3.550
9	H	0.1496	HA	0.030	2.420
10	H	0.2257	HA	0.030	2.420
11	N	0.7633	NO	0.120	3.250
12	O	-0.4690	ON	0.170	2.960
13	O	-0.4690	ON	0.170	2.960
14	H	0.2451	HA	0.030	2.420
15	N	0.8015	NO	0.120	3.250
16	O	-0.4657	ON	0.170	2.960
17	O	-0.4657	ON	0.170	2.960
18	C	-0.4395	CT	0.066	3.500
19	H	0.1318	HC	0.030	2.500
20	H	0.1318	HC	0.030	2.500
21	H	0.1318	HC	0.030	2.500
22	H	0.0278	HC	0.030	2.500
23	H	0.0316	HC	0.030	2.500

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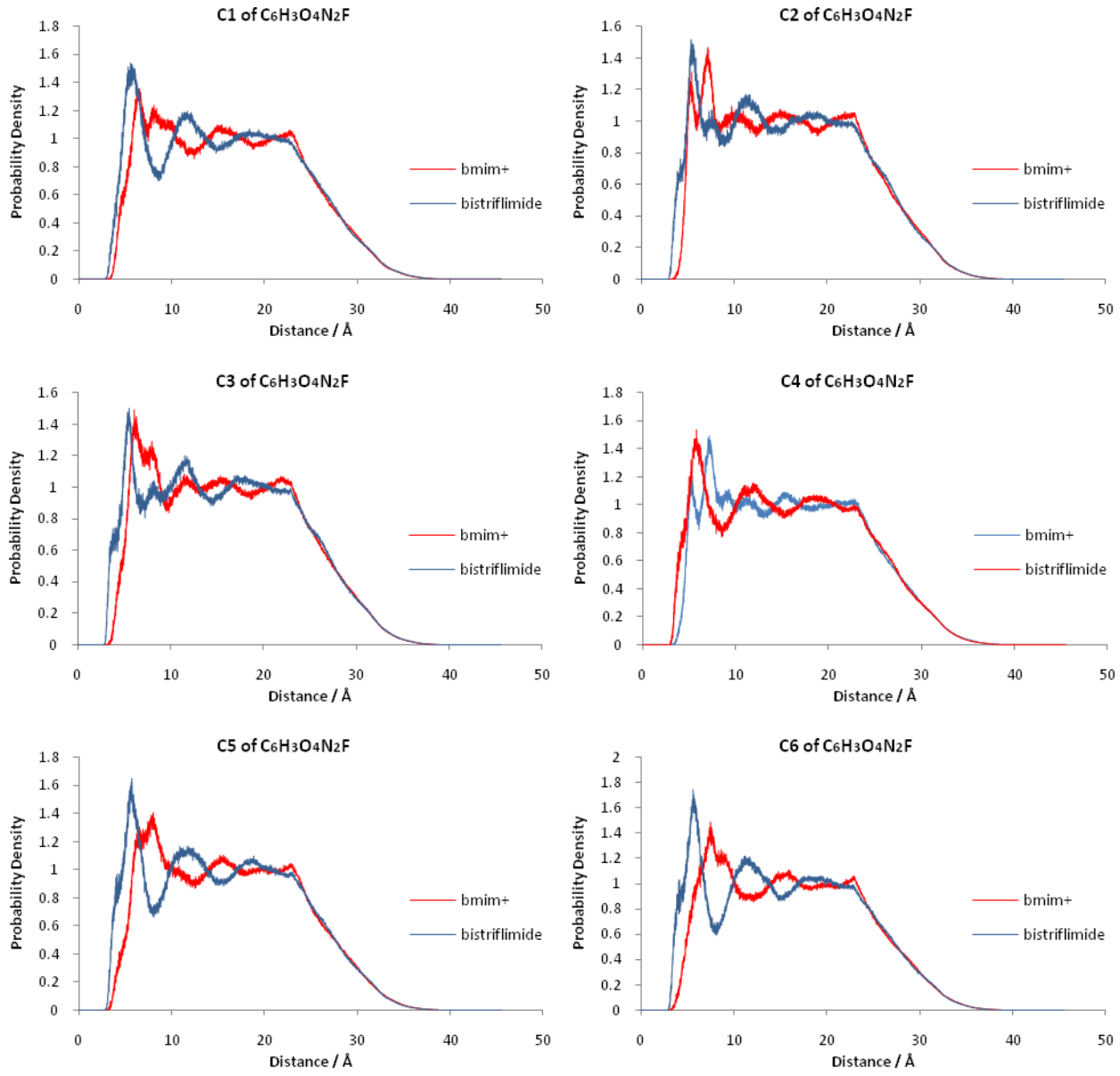
Equilibrated box sizes for simulations (single side dimension of cube)

	Starting material		Intermediate		Product	
Solvent	**EtOH**	**IL**	**EtOH**	**IL**	**EtOH**	**IL**
Size (Å)	27.4	45.9	30.5	46.0	29.7	45.9

Selected radial distribution functions for 1-fluoro-2,4-dinitrobenzene in the ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide



Radial distribution functions showing the degree of ordering of the components of the ionic liquid around the ring carbon of the fluoride starting material. The distribution functions were generated by counting the probability of the corresponding ion over 4 ns.

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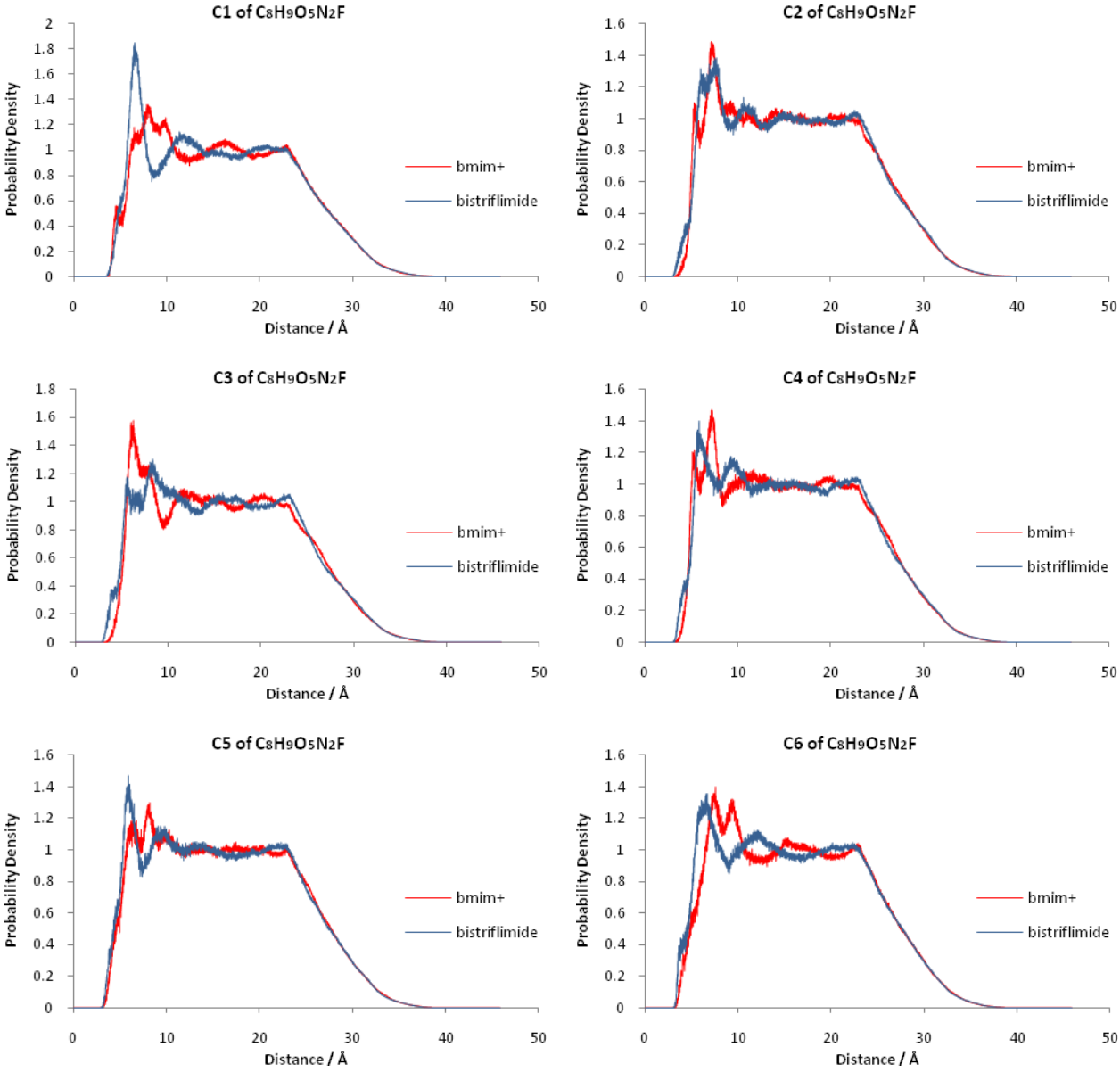
Selected radial distribution functions for 1-fluoro-2,4-dinitrobenzene – ethanol adduct in the ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide



Radial distribution functions showing the organisation of the components of the ionic liquid around the intermediate. The distribution functions were generated by counting the probability of corresponding ion over 4 ns. It is worth noting that on average components of the ionic liquids are further away from the intermediate than the starting material, and particularly so for the imidazolium cation, which suggests that the ionic liquid is becoming more disordered on going from the starting material to the intermediate.

Note that the interaction with other parts of the starting material and with the intermediate have also been considered. However, in all cases the distances for the first maxima are similar and fluctuate without bias for either the starting the material or the intermediate, indicating that the interactions are likely to be hydrogen-bonding limited. The probability densities are also generally higher for the starting material than the corresponding densities for the intermediate.

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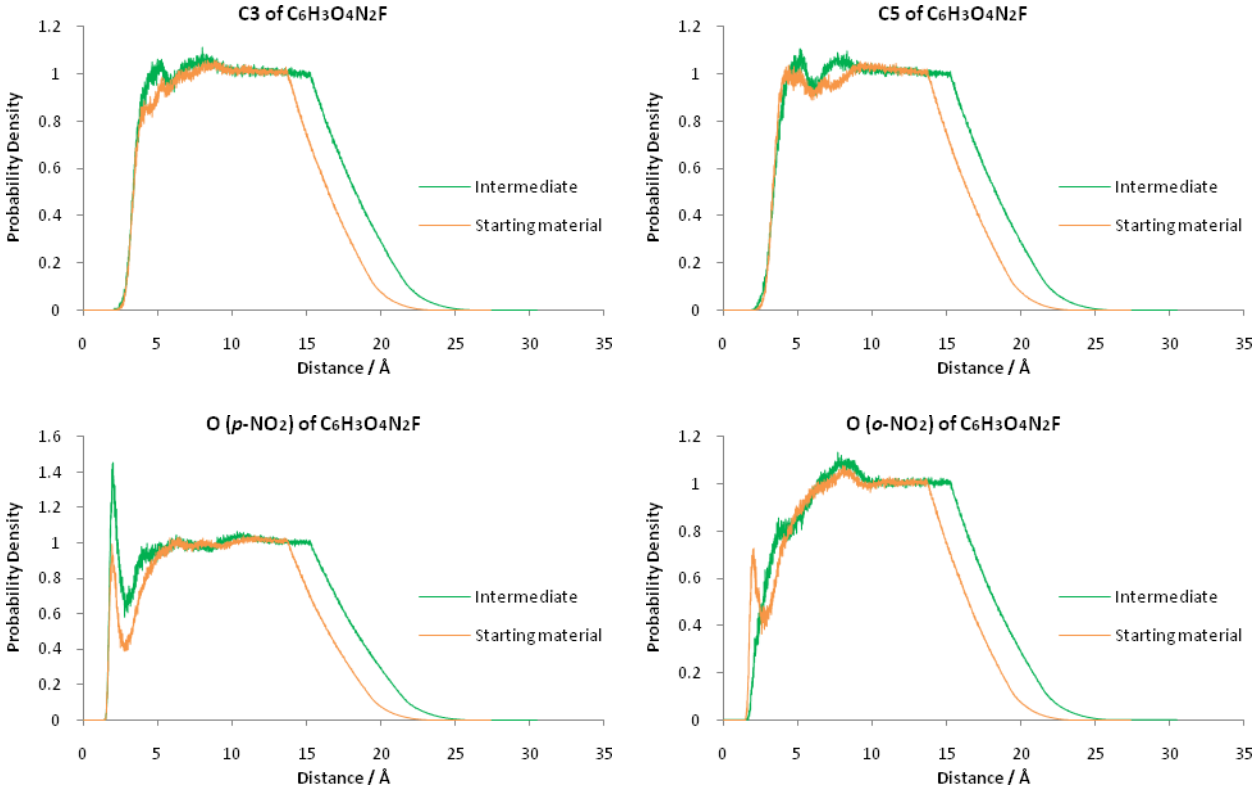
Typical radial distribution functions for 1-fluoro-2,4-dinitrobenzene or 1-fluoro-2,4-dinitrobenzene adduct in ethanol



There is no significant change in ordering of ethanol around the ring carbon of both the starting material and the intermediate as indicated by the radial distribution function. Also shown in the plots above is the effect of hydrogen boding around the *p*-NO_2 and *o*-NO_2 functional groups. Of particular interest is that the radial distribution function for the oxygen of the *o*-NO_2 in the intermediate indicates diminished hydrogen bonding, which is most likely due to the intramolecular hydrogen bonding between the *o*-NO_2 functional group and the hydrogen of the part of the molecule relating to the ethanol nucleophile.

Distance and probability densities of the first local maxima of the radial distribution functions shown above

	Distance (Å)				Probability Density			
	Starting material		Intermediate		Starting material		Intermediate	
	Tf_2N^-	$bmim^+$	Tf_2N^-	$bmim^+$	Tf_2N^-	$bmim^+$	Tf_2N^-	$bmim^+$
C1	5.565	6.385	6.535	6.465	1.315	1.517	1.854	1.179
C2	5.375	5.345	5.985	5.295	1.538	1.347	1.316	1.099
C3	5.515	6.065	5.555	5.995	1.750	1.492	1.174	1.563
C4	5.775	5.355	5.825	5.325	1.651	1.302	1.403	1.212
C5	5.695	6.505	5.895	6.425	1.530	1.203	1.472	1.186
C6	5.585	7.455	6.555	7.565	1.500	1.490	1.354	1.400

Average	5.585	6.185	6.058	6.178	1.547	1.392	1.429	1.273

The data in the table above shows that, on average, cationic shell maintains roughly the same distance on going from the starting material to the intermediate; whereas the anion shell 'expands'. Together with the probability density, the data suggests that there is more ordering of the ionic liquid around the starting material than the intermediate.