Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Nature of the C2-methylation effect on the properties of imidazolium ionic liquids

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Supporting information

Theoretical calculation

Table S1. Results of the anion rotation around cation of [$^1C_1{}^3C_1$im][NTf_2] IL.

C1C1im Ntf2 (around rotation)		
CHN angle / º	**E_{el} / Hartree**	**ΔE_{rel} / kJ.mol^{-1}**
0.0		
10.0	-2132.071663	81.0
20.0	-2132.091425	29.1
30.0	-2132.094264	21.6
40.0	-2132.097351	13.5
50.0	-2132.101476	2.7
60.0	-2132.102498	0.0
70.0	-2132.101479	2.7
80.0	-2132.101486	2.7
90.0	-2132.101008	3.9
100.0	-2132.099166	8.7
110.0	-2132.096956	14.6
120.0	-2132.095798	17.6
130.0	-2132.094654	20.6
140.0	-2132.093935	22.5
150.0	-2132.093514	23.6
160.0	-2132.093081	24.7
170.0	-2132.092622	25.9
176.0	-2132.091899	27.8
184.0	-2132.091899	27.8
190.0	-2132.092622	25.9
200.0	-2132.093081	24.7
210.0	-2132.093514	23.6
220.0	-2132.093935	22.5
230.0	-2132.094654	20.6
240.0	-2132.095798	17.6
250.0	-2132.096956	14.6
260.0	-2132.099166	8.7
270.0	-2132.101008	3.9
280.0	-2132.101486	2.7
290.0	-2132.101479	2.7
300.0	-2132.102498	0.0
310.0	-2132.101476	2.7
320.0	-2132.097351	13.5
330.0	-2132.094264	21.6
340.0	-2132.091425	29.1
350.0	-2132.071663	81.0
360.0		

Table S.2 Results of the anion rotation around cation of [$^1C_1{}^2C_1{}^3C_1$im][NTf_2].

C1C1C1im Ntf2 (around rotation)		
CHN angle / º	**E_{el} / Hartree**	**ΔE_{rel} / kJ.mol^{-1}**
6.0	-2171.387001	65.1
16.0	-2171.395865	41.8
26.0	-2171.399101	33.3
36.0	-2171.407841	10.4
46.0	-2171.411794	0.0
56.0	-2171.409541	5.9
66.0	-2171.403721	21.2
76.0	-2171.404508	19.1
86.0	-2171.405733	15.9
96.0	-2171.401947	25.9
106.0	-2171.405727	15.9
116.0	-2171.400732	29.0
126.0	-2171.392669	50.2
136.0	-2171.39381	47.2
146.0	-2171.391344	53.7
156.0	-2171.388701	60.6
166.0	-2171.385311	69.5
176.0	-2171.382784	76.2
184.0	-2171.382784	76.2
194.0	-2171.385311	69.5
204.0	-2171.388701	60.6
214.0	-2171.391344	53.7
224.0	-2171.39381	47.2
234.0	-2171.392669	50.2
244.0	-2171.400732	29.0
254.0	-2171.405727	15.9
264.0	-2171.401947	25.9
274.0	-2171.405733	15.9
284.0	-2171.404508	19.1
294.0	-2171.403721	21.2
304.0	-2171.409541	5.9
314.0	-2171.411794	0.0
324.0	-2171.407841	10.4
334.0	-2171.399101	33.3
344.0	-2171.395865	41.8
354.0	-2171.387001	65.1

Table S.3. $\Delta_{int}E_m$, were calculated for $[^1C_1{}^3C_1im][NTf_2]$ using M06-2X/6-31+G(d,p) and corrected for BSSE by the counterpoise method

C1C1im		
optimization	M06-2X/6-31+G(d,p)	
energy	M06-2X/6-31+G(d,p)	
Species	*Eel(DFT)*	*BSSE corrected*
C1C1 (BSSE)	-305.10090	
C1C1	-305.09994	
NTf2 (BSSE)	-1826.86299	
NTf2	-1826.86010	
Ion pair	-2132.10250	-2132.098653
ΔEint / kJ·mol^{-1}	-371.5	(no BSSE)
	-361.4	(BSSE)

Table S.4. $\Delta_{int}E_m$, were calculated for $[^1C_1{}^2C_1{}^3C_1im][NTf_2]$ using M06-2X/6-31+G(d,p) and corrected for BSSE by the counterpoise method.

C1C1C1im		
optimization	M06-2X/6-31+G(d,p)	
energy	M06-2X/6-31+G(d,p)	
Species	*Eel(DFT)*	*BSSE corrected*
C1C1C1 (BSSE)	-344.41082	
C1C1C1	-344.40980	
NTf2 (BSSE)	-1826.86357	
NTf2	-1826.860202	
Ion pair	-2171.41179	-2171.407409
ΔEint / kJ.mol-1	-372.3	(no BSSE)
	-360.8	(BSSE)