Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting information

to

"Free volume in ionic liquids: A connection of experimentally accessible observables from PALS and PVT experiments with the molecular structure from XRD data"

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1. Van der Waals volume calculations

The van der Waals volumes were calculated from the crystal structures of the investigated salts via a radii based approach. In radii based approaches, atoms are assumed as fused spheres with van der Waals radii and the space occupied by the hard spheres is calculated. As a first attempt to estimate V_{vdw} of crystalline ILs, the *calc void* option of the Platon program package[1] was chosen. Information about the crystal structure in the CIF format – available free of charge from the Cambridge Structural Database (CSD)[2]– is required as input. The *calc void* option employs a grid technique to calculate and detect voids in a crystal structure.[3] The packing index (*P*), given in %, is calculated additionally. Here, the packing index *P* was used to calculate the van der Waals volume of a given molecule (ion pair) via

$$V_{vdw,r} = \frac{V_{cell} \cdot P}{Z \cdot 100}.$$

Default parameter (1.2 Å probe radius and 0.2 Å grid spacing) were used. The suitability of radii based techniques to calculate van der Waals volume of organic salts will be presented in a forthcoming paper. Table S.1 summarizes all the used data for $V_{vdw,r}$ determinations.

Table S.1: Packing index *P*, molecular volume V_m and the Platon van der Waals volume $V_{vdw,r}$ of all the compounds considered for this work along with their CSD Refcodes and the temperature at which the crystal structure was measured.

Compound	CSD Refcode	*T* / K	V_m / Å^3	*P* / %	$V_{vdw,r}$ / Å^3
[C_4MIM][Cl]	TAJCUD	173	242	67.8	164
[C_4MIM][Cl]	TAJCUD01	173	240	68.0	163
[C_4MIM][Cl]	TAJCUD02	293	248	65.8	163
[C_4MIM][Cl]	TAJCUD03	150	240	68.6	165
[C_4MIM][Cl]	TAJCUD04	150	236	69.7	165
[C_4MIM][Cl]				**mean value**	**164**
[C_4MIM][PF_6]	MAZXOB	173	302	69.8	211
[C_4MIM][PF_6]	MAZXOB01	183	305	68.9	210
[C_4MIM][PF_6]				**mean value**	**211**
[C_4MIM][OTf]	LAZRUA	200	360	61.6	222
[C_4MIM][NTf_2]	IGUPUW[a]	120	438	65.9	288
[C_4MIM][B(hfip)$_4$]	this work	115	759	68.1	517
[C_4MIM][Al(hfip)$_4$]	SIWSOH	173	807	64.2	518
[C_4MIM][BPh_4]	WITJUE	173	671	67.2	451
[C_4MIM][C_1SO_4]	VIGMAA	173	328	66.2	217
[C_4C_1MIM][Cl]	AYIBOZ01	150	259	68.7	178
[C_4C_1MIM][Cl]	AYIBOZ02	233	264	67.9	180
[C_4C_1MIM][Cl]	AYIBOZ03	233	276	65.0	179
[C_4C_1MIM][Cl]				**mean value**	**179**
[C_4MIM][Br]	TAJDAK	173	251.6	66.7	168
[C_4MIM][Br]	TAJDAK01	RT[b]	256.4	65.8	169
Compound	CSD Refcode	*T* / K	V_m / Å^3	*P* / %	$V_{vdw,r}$ / Å^3

[C_4MIM][Br]	TAJDAK02	110	247.9	67.7	168
[C_4MIM][Br]				**mean value**	**168**
[C_4C_1MIM][Br]	EDOTEX	120	272	68.0	185
[C_4C_1MIM][Br]	920920[c]	100	269.2	68.5	184
[C_4C_1MIM][Br]	920921[c]	125	270.0	68.3	184
[C_4C_1MIM][Br]	920922[c]	150	271.0	68.0	184
[C_4C_1MIM][Br]	920923[c]	175	271.5	67.9	184
[C_4C_1MIM][Br]	920924[c]	200	273.4	67.5	185
[C_4C_1MIM][Br]	920925[c]	225	274.6	66.9	184
[C_4C_1MIM][Br]	920926[c]	250	276.5	66.4	184
[C_4C_1MIM][Br]	920927[c]	275	278.0	65.8	183
[C_4C_1MIM][Br]				**mean value**	**184**
[C_4C_1MIM][BF_4]	EZILII01[a]	150	307	67.4	207
[C_4C_1MIM][PF_6]	EZILOO	293	328	68.5	224
[C_4C_1MIM][PF_6]	EZILOO01	150	326	69.5	226
[C_4C_1MIM][PF_6]				**mean value**	**225**
[C_2MIM][NTf_2]	RENSEJ	230	384	66.6	256
[C_2MIM][NTf_2]	RENSEJ01	100	385	66.6	256
[C_2MIM][NTf_2]				**mean value**	**256**
[C_2MIM][NO_3]	KUCPED	RT[b]	225	67.7	152
[C_2MIM][NO_3]	920928[c]	100	209.5	72.0	151
[C_2MIM][NO_3]	920929[c]	120	209.7	71.8	151
[C_2MIM][NO_3]	920930[c]	140	210.5	71.5	151
[C_2MIM][NO_3]	920931[c]	160	211.3	71.2	150
[C_2MIM][NO_3]	920932[c]	180	212.4	70.8	150
[C_2MIM][NO_3]	920933[c]	200	213.4	70.5	150
[C_2MIM][NO_3]	920934[c]	220	214.5	69.9	150
[C_2MIM][NO_3]	920935[c]	240	215.4	69.6	150
[C_2MIM][NO_3]	920936[c]	260	216.6	69.0	149
[C_2MIM][NO_3]	920937[c]	280	217.8	68.5	149
[C_2MIM][NO_3]				**mean value**	**150**
[C_2MIM][OTs]	920939[c]	100	350	69.6	243
[C_2MIM][OTs]	920940[c]	120	350.7	69.7	244
[C_2MIM][OTs]	920941[c]	140	351.5	69.6	245
[C_2MIM][OTs]	920942[c]	160	352.7	69.3	244
[C_2MIM][OTs]	920943[c]	180	354.4	68.9	244
[C_2MIM][OTs]	920944[c]	200	355.2	68.6	244
[C_2MIM][OTs]				**mean value**	**244**
[C_2C_1Pyr][NTf_2]	KEKVEC	153	399	68.2	272
[C_1MIM][C_1SO_4]	912923[c]	110	240.8	69.6	168
[C_1MIM][C_1SO_4]	912924[c]	150	241.9	69.2	167
[C_1MIM][C_1SO_4]	912925[c]	200	244.0	68.6	167
[C_1MIM][C_1SO_4]	912926[c]	250	246.9	67.6	167
[C_1MIM][C_1SO_4]	912929[c]	298	248.4	66.7	166
[C_1MIM][C_1SO_4]	UJOSER	173	242.6	67.9	165
[C_1MIM][C_1SO_4]				**mean value**	**167**

a) Disorder was removed manually; b) RT = room temperature; c) CCDC number. These data will be published in a separate study.

1.1 Comparison with volume increment schemes

For further comparisons with the Platon results, the van der Waals volumes calculated by the volume increment scheme[4] ($V_{vdw,inc}$) were investigated. The volumes are quite similar apart from that for [C_4MIM][B(hfip)$_4$]. Here, $V_{vdw,inc}$ is much higher than $V_{vdw,r}$. Similar observations were made with further [C_4MIM]$^+$ based borate and aluminate salts (Table S.2). Even in the more simple salt [C_4MIM][C_1SO_4] considerable deviations are observed. This finding indicates that these deviations are not systematic for a certain class of compounds and that volume increment schemes are not suitable for determining the volume of organic salts in the crystalline state.

Table S.2: Comparison of the van der Waals volumes calculated by a volume increment scheme ($V_{vdw,inc}$) and by Platon ($V_{vdw,r}$) for selected [C_4MIM]$^+$ salts. The absolute (Δ_{abs}) and relative (Δ_{rel}) deviations are given additionally.

	CSD Refcode	T / K	$V_{vdw,r}$ / Å^3	$V_{vdw,inc}$ / Å^3	$\lvert\Delta_{abs}\rvert$ / Å^3	$\lvert\Delta_{rel}\rvert$ / %
[C_4MIM][Cl]	mean value (S.1)		164	158	6	4
[C_4MIM][BF_4]	estimated (S.3)		192 ± 1	195	3	2
[C_4MIM][PF_6]	mean value (S.1)		211	205	6	3
[C_4MIM][OTf]	LAZRUA	200	222	223	1	0
[C_4MIM][NTf_2]	IGUPUW[a]	120	288	297	9	3
[C_4MIM][B(hfip)$_4$]	this work	115	517	559	42	8
[C_4MIM][Al(hfip)$_4$]	SIWSOH	173	518	571	53	10
[C_4MIM][BPh_4]	WITJUE	173	451	555	104	23
[C_4MIM][C_1SO_4]	VIGMAA	173	217	235	18	8

a) Disorder was removed manually.

1.2 Estimation of $V_{vdw,r}$ of [C_4MIM][BF_4] and [C_3MIM][NTf_2]

[C_4MIM][BF_4]: $V_{vdw,r}$ was estimated by subtraction of $V_{vdw,r}(CH_2)$ from $V_{vdw,r}$([C_4C_1MIM][BF_4]). The former was calculated as ($V_{vdw,r}$([C_4C_1MIM][X])–$V_{vdw,r}$([C_4MIM][X])) for a series of [C_4C_1MIM][X] and [C_4MIM][X] salts with [X] = [Br]$^-$, [Cl]$^-$ and [PF_6]$^-$ as counter ions. If the same difference holds true for the [BF_4]$^-$ salts, the value $V_{vdw,r}$ = 192 ± 1 Å^3 can be assigned to [C_4MIM][BF_4].

[C_3MIM][NTf_2]: $V_{vdw,r}$([C_3MIM][NTf_2]) was estimated by subtracting $V_{vdw,r}(CH_2)$ = 15 Å^3 from $V_{vdw,r}$([C_4MIM][NTf_2]) or adding $V_{vdw,r}(CH_2)$ to $V_{vdw,r}$([C_2MIM][NTf_2]). Alternatively, the arithmetic mean value of $V_{vdw,r}$([C_2MIM][NTf_2]) and $V_{vdw,r}$([C_4MIM][NTf_2]) can be taken. These estimates are consistent among each other leading to $V_{vdw,r}$([C_3MIM][NTf_2]) = 273 Å^3.

Table S.3: Data for the estimation of $V_{vdw,r}$([C_4MIM][BF_4]/[C_3MIM][NTf_2]).

[C_4MIM][BF_4]	[C_3MIM][NTf_2]

Compound	$V_{vdw,r}$ / Å^3	Compound	$V_{vdw,r}$ / Å^3
[C_4C_1MIM][Cl][a]	179	[C_2MIM][NTf_2]+[CH_2]	273
[C_4MIM][Cl][a]	164	[C_4MIM][NTf_2]–[CH_2]	274
Difference	**15**	**[C_3MIM][NTf_2]**	**273**
[C_4C_1MIM][Br][a]	184 ± 1	[C_2MIM][NTf_2][a]	256
[C_4MIM][Br][a]	168	[C_4MIM][NTf_2][b]	289
Difference	**16 ± 1**	**Arithmetic mean**	**273**
[C_4C_1MIM][PF_6][a]	225		
[C_4MIM][PF_6][a]	211		
Difference	**15**		
mean value CH_2	**15 ± 1**		
[C_4C_1MIM][BF_4]	207[b]		
[C_4MIM][BF_4]	**192 ± 1**		

a) Multiple crystal structures available. The mean value was taken. See Table S.1 for all data; b) disorder from the used structures (CSD refcodes EZILII01 and IGUPUW) was removed manually.

2. Crystal structure of [C_4MIM][B(hfip)$_4$]

The compound [C_4MIM][B(hfip)$_4$] crystallizes in the monoclinic space group $P2_1$ with four molecules in the unit cell. Two ion pairs form the asymmetric unit. Bond lengths and angles in the borate anion are similar to the published values for [Na][B(hfip)$_4$]·$(THF)_2$ and [Na][B(hfip)$_4$]·DME.[5] The butyl group is nearly perpendicular to the ring moiety with torsion angles between 78.2(12)° and 110.4(8)° for the two cations in the asymmetric unit (see Figure S.1 and Table S.4). Furthermore, the butyl chain adopts a gauche, anti conformation in both independent cations. There are several short contacts between the hydrogens of the imidazolium cations and the fluorine atoms of the anion in the distance range 2.33–2.60 Å. These contacts are shorter than in [C_4MIM][Al(hfip)$_4$][6] but agree well with similar compounds based on the [Al(hfip)$_4$]$^-$[7] anion. However, additional H···O contacts exist in the latter compounds[6,7] which are absent in [C_4MIM][B(hfip)$_4$]. Furthermore, short F···F and H···H contacts are observed with distances around 2.66–2.93 Å and 2.37 Å correspondingly. The distances of the F···F contacts are comparable to the published values for [Al(hfip)$_4$]$^-$ based ILs.[6,7]

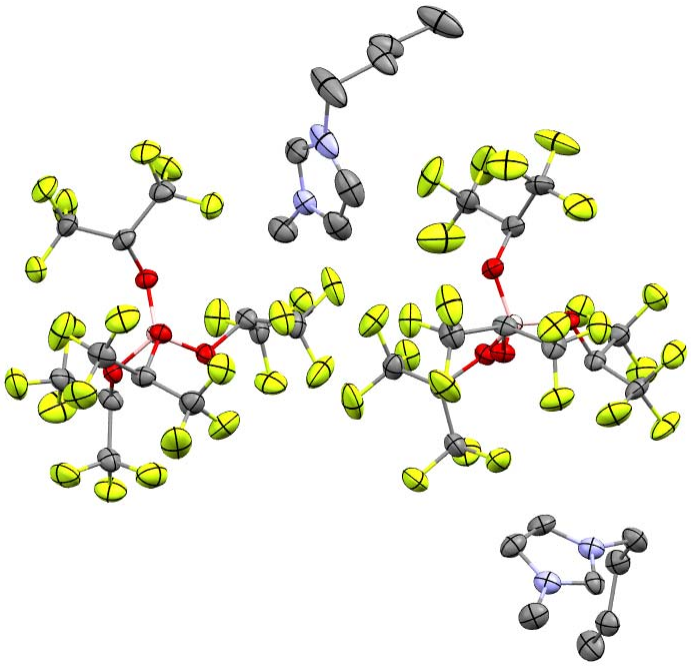


Figure S.1: Asymmetric unit of $[C_4MIM][B(hfip)_4]$. Thermal ellipsoids are drawn with 50% probability. Hydrogen atoms were omitted for clarity.

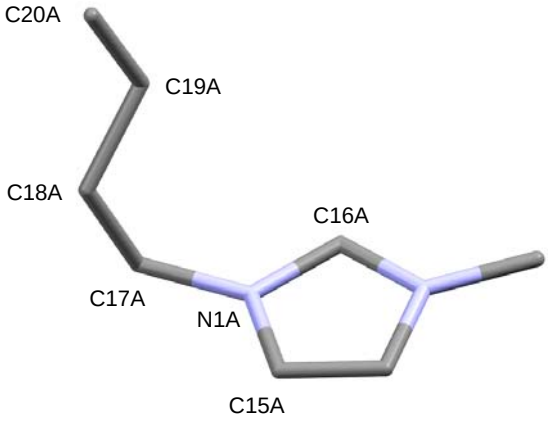


Figure S.2: Labeling scheme for the illustration of the torsion angles for the $[C_4MIM]^+$ cations in $[C_4MIM][B(hfip)_4]$. The same labeling with an appended "B" instead of "A" is used for the second cation in the asymmetric unit.

Table S.4: Torsion angles for the butyl chain in the $[C_4MIM]^+$ cations in the asymmetric unit of $[C_4MIM][B(hfip)_4]$. Labeling as shown in Figure S.2.

	torsion angle / °
C15A N1A C17A C18A	78.2(12)
C16A N1A C17A C18A	–96.8(12)
N1A C17A C18A C19A	64.6(14)
C17A C18A C19A C20A	–177.0(9)
C15B N1B C17B C18B	–73.9(6)
C16B N1B C17B C18B	110.4(8)
N1B C17B C18B C19B	–49.2(7)
C17B C18B C19B C20B	–179.9(6)

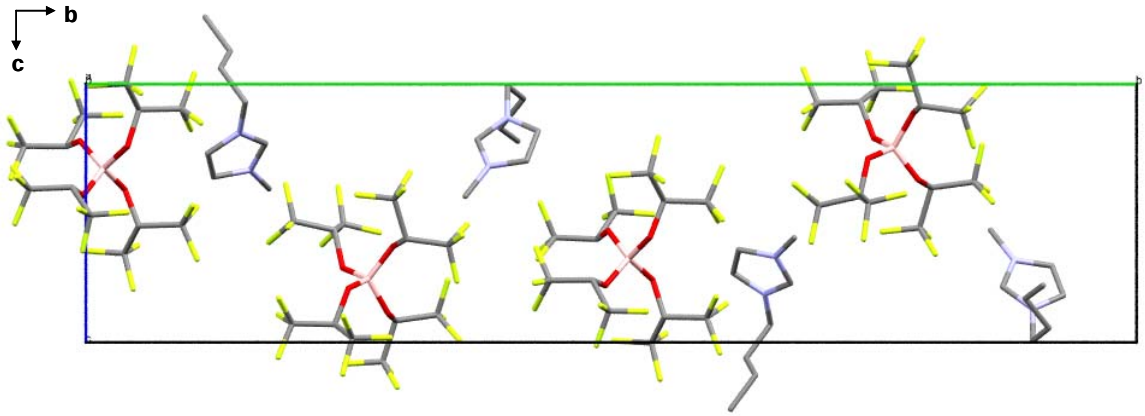


Figure S.3: Packing diagram of $[C_4MIM][B(hfip)_4]$ along the crystallographic a axis.

3. Scaled molecular volumes for compounds not mentioned in Table 1

Table S.5: Scaled molecular volumes ($V_{m,scaled}$, $V_{m,scaked}^{+/-}$) for compounds not mentioned in Table 1.

Compound	$V_{m,scaled}$ / Å^3	$V_{m,scaled}^-$ / Å^3	$V_{m,scaled}^+$ / Å^3
$[C_2MIM][NO_3]$	211	62	149
$[C_2MIM][OTs]$	345	196	149
$[C_4C_1MIM][Br]$	265	47	218
$[C_3MIM][NTf_2]$	406	233	173

4. PALS mean hole volumes at different temperatures for the investigated salts

For further insight, the hole volumes in the glassy $< v_{h,glass} >$ and the supercooled state $< v_{h,supercooled} >$ were compared with $V_{m,scaled}$. Here, the available data were collected at arbitrarily chosen temperatures of 160 K ($< v_{h,glass} >$) and 240 K ($< v_{h,supercooled} >$) (Table S.6). At T = 160 K $< v_{h,glass} >$ is much smaller than almost all ionic volumes, supporting the fact that the dynamics are frozen in a glass. The hole volume in $[C_4MIM][Cl]$ ($< v_{h,glass} >$ = 41±5 Å^3) is equal to $V_{m,scaled}^-([Cl]^-)$, indicating that anion diffusion might still occur in the glassy state. The hole sizes in the supercooled state at 240 K are still large enough to accommodate single ions with the exception of $[C_4MIM][NTf_2]$ and $[C_2MIM][OTs]$. In the latter compound, the reference temperature is close to the glass temperature (T_g(PALS) = 225 K), where $< v_{h,supercooled} >$ is highly reduced. However, even at T_k, the mean hole volume does not exceed $V_{m,scaled}^{+/-}$, indicating a different diffusion mechanism for this compound. To allow better comparisons in a well-defined state, the temperature $T = T_g$ + 70 K was arbitrarily chosen. Here, $< v_{h,supercooled} >$ exceeds the size of all ions, still with the exception of

[C_2MIM][OTs]. From this comparison, it can be concluded that the hole volume behaviour in the supercooled state is closely related to the situation in the liquid state at T_m.

Table S.6: PALS mean hole volumes at the "knee" temperature T_k and at arbitrarily chosen temperatures in the glassy state at 140 K and in the supercooled state at 260 K as well as at $T = T_g$ (PALS) +70 K for the investigated salts.

Compound	$< v_h > (T_k)$ / Å^3	$< v_{h,glass} >$ (T = 160 K) / Å^3	$< v_{h,supercooled} >$ (T = 240 K) / Å^3	$< v_{h,supercooled} >$ ($T = T_g$ (PALS) +70 K) / Å^3
[C_4MIM][Cl][a]	115±5	41±5	52±5	52±5
[C_4MIM][BF_4][a]	150±5	55±5	100±5	100±5
[C_4MIM][PF_6][a]	180±5	63±5	115±5	115±5
[C_4MIM][OTf][a]	215±5			
[C_4MIM][NTf_2][a]	240±5	60±5	173±5	173±5
[C_4MIM][FAP]	295±5	82±5	201±5	201±5
[C_4MIM][FPI]	350±5	93±5	232±5	232±5
[C_4MIM][B(hfip)$_4$][a]	340±5			
[C_2MIM][NO_3]	58±5			
[C_2MIM][OTs]	110±5	45±5	47±5	47±5
[C_4C_1MIM][Br]	96±5			
[C_3MIM][NTf_2][b]	245±5	73±5	187±5	187±5

a) See also ref. [8]; b) see also ref. [9].

5. Fits of the mean hole volume at T_k against volumes from XRD data

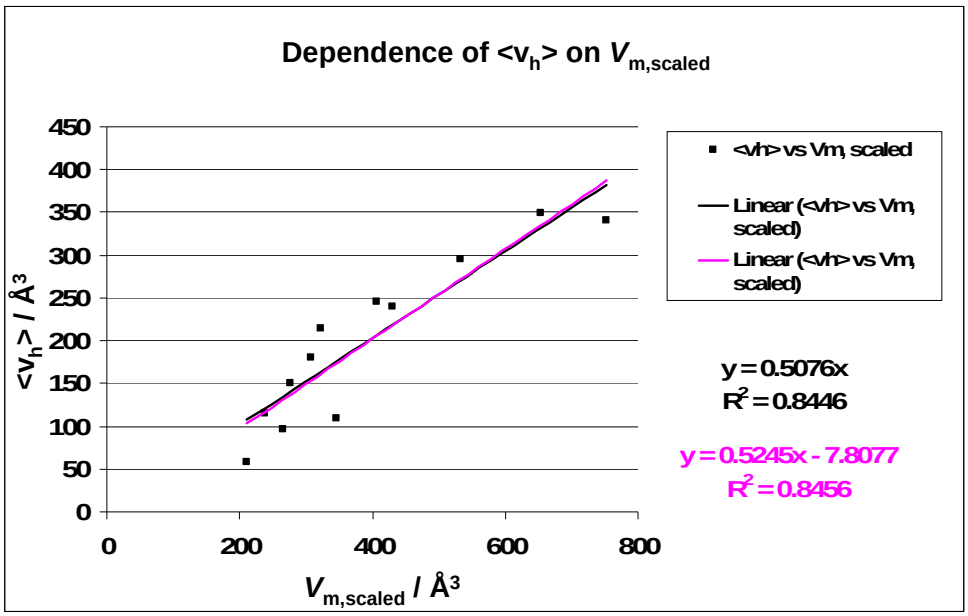


Figure S.4: Plots of the mean hole volume $< v_h > (T_k)$ against the scaled molecular volume $V_{m,scaled}$.

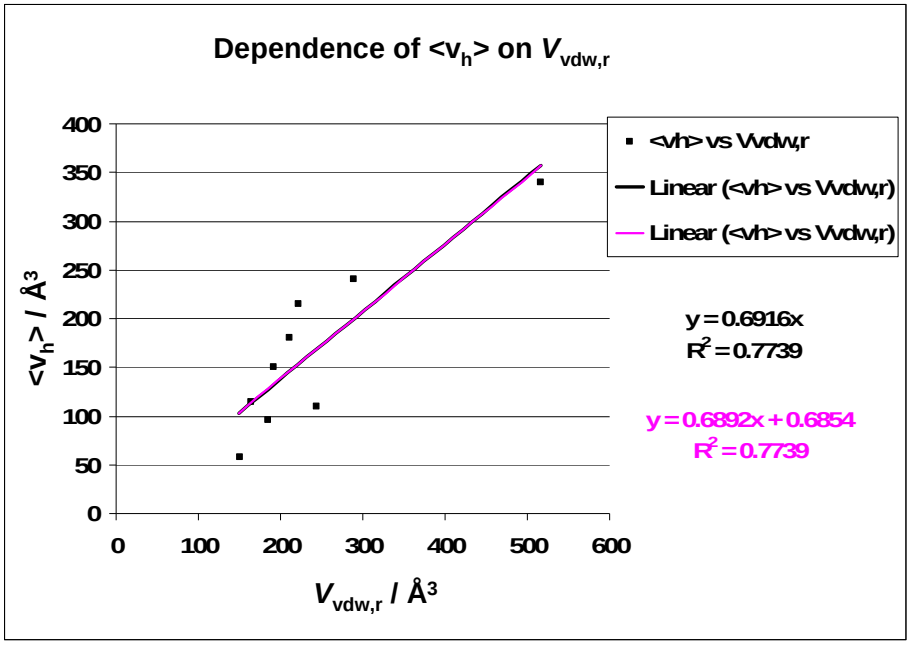


Figure S.5: Plots of the mean hole volume $< v_h > (T_k)$ against the van der Waals volume calculated by Platon $V_{vdw,r}$.

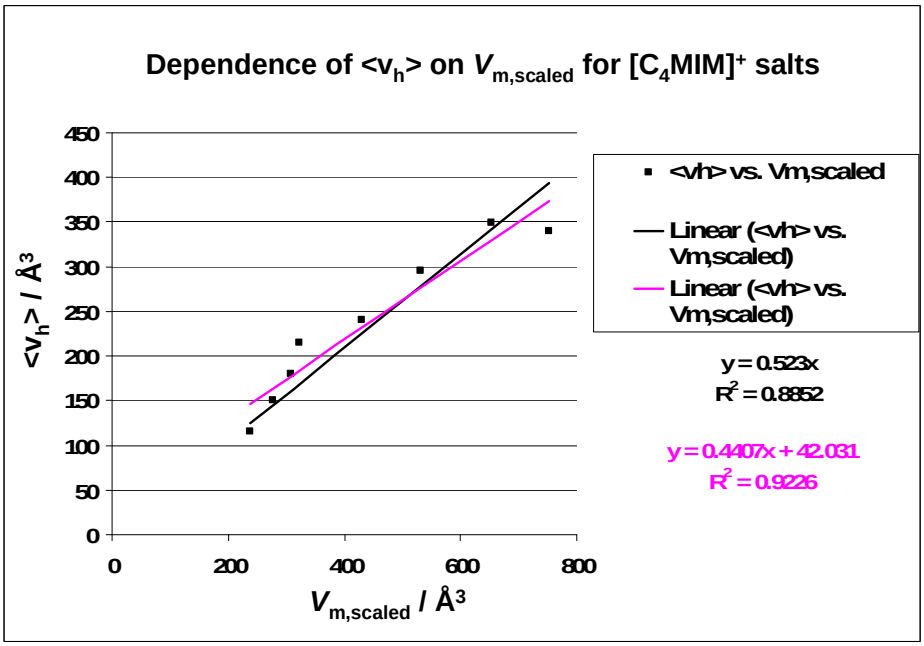


Figure S.6: Plots of the mean hole volume $< v_h > (T_k)$ against the scaled molecular volume $V_{m,scaled}$ for the $[C_4MIM]^+$ series.

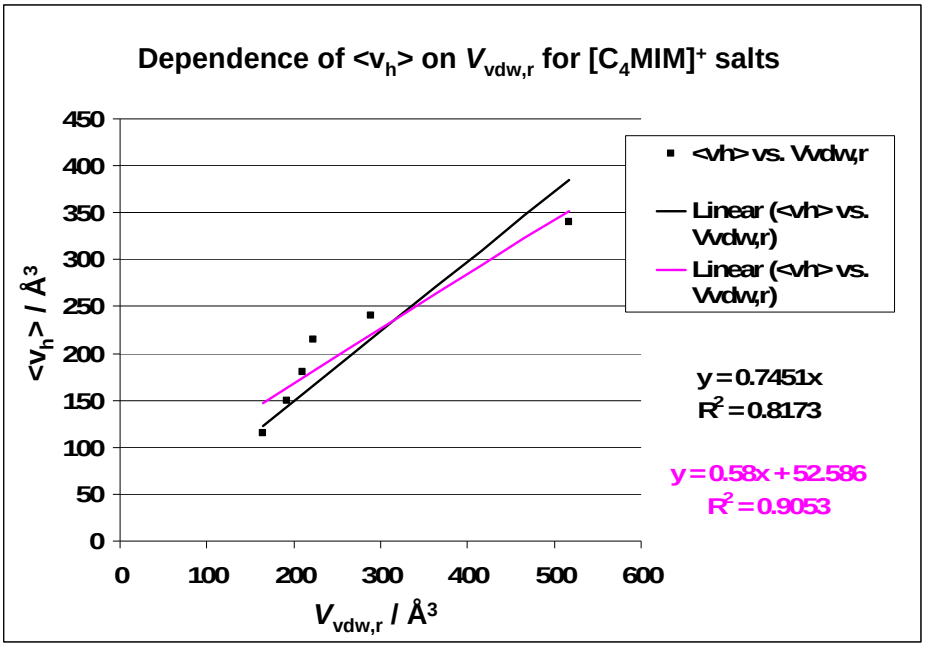


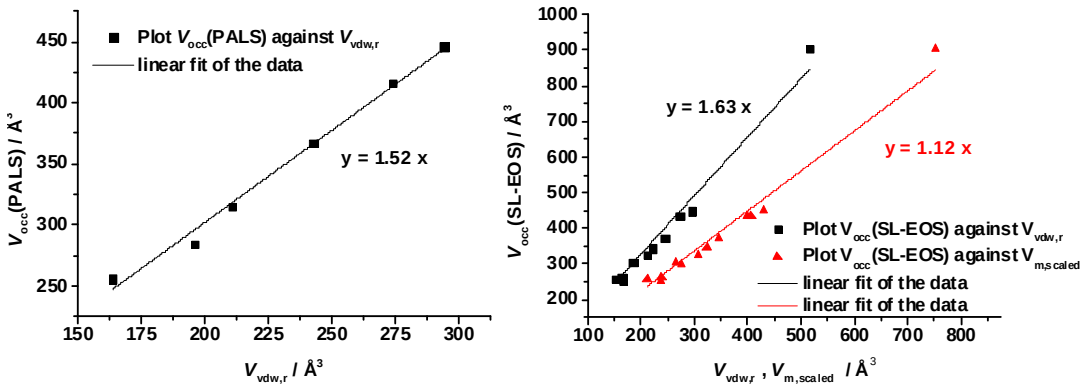
Figure S.7: Plots of the mean hole volume $< v_h > (T_k)$ against the van der Waals volume calculated by Platon $V_{vdw,r}$ for the $[C_4MIM]^+$ series.

6. Occupied volume from the SL-EOS fits

Table S.7: Occupied volumes for compounds where volumes from XRD data existed.

Compound	V_{occ}(SL-EOS) / Å^3	fitting range T / K	fitting range P / MPa	source of the PVT data
$[C_4MIM][Cl]$	263	348-478	0-50	[a]
$[C_4MIM][BF_4]$	299	298-473	0-50	[a]
$[C_4MIM][PF_6]$	325	293-428	0-200	[a]
$[C_4MIM][OTf]$	345	291-424	10-200	[b]
$[C_4MIM][NTf_2]$	448	292-424	10-200	[a]
$[C_4MIM][B(hfip)_4]$	905	398-358	10-200	[b]
$[C_2MIM][NO_3]$	257	329-418	10-200	[b]
$[C_2MIM][OTs]$	373	318–428	0.1–60	[c]
$[C_4C_1MIM][Br]$	305	393-473	0-50	[b]
$[C_3MIM][NTf_2]$	435	303-473	0-50	[d]
$[C_1MIM][C_1SO_4]$	254	318–428	0.1–60	[c]
$[C_2C_1Pyr][NTf_2]$	437	403-473	0-50	[b]

a) Ref. [8]; b) this work; c) ref. [10]; d) ref. [9].



(a) (b)

Figure S.8: (a) Plot of the occupied volume from PALS/PVT against $V_{vdw,r}$; (b) plot of the occupied volume from SL-EOS against $V_{vdw,r}$ and $V_{m,scaled}$. The experimental values are represented by data points, whereas the fits are denoted by lines.

7. Viscosity and conductivity data

7.1 References for the used experimental data

Table S.8: References for the used viscosity and conductivity data.

Compound	viscosity	conductivity
[C_4MIM][Cl]	this work (see below)	this work (see below)
[C_4MIM][BF_4]	[11]	[12]
[C_4MIM][PF_6]	mean value from [13] and [14]	[15]
[C_4MIM][OTf]	[16]	[15]
[C_4MIM][NTf_2]	[17]	[16]
[C_4MIM][B(hfip)$_4$]	[5]	[5]
[C_2MIM][NO_3]	[18]	this work (see below)
[C_2MIM][OTs]	[19]	[10]
[C_3MIM][NTf_2]	[17]	[17]

See also our recent compilation of viscosity and conductivity data.[19]

7.2 Temperature-dependent viscosity and conductivity measurements of [C_4MIM][Cl] and [C_2MIM][NO_3]

(a) (b)

Figure S.9: Pictures of the used equipments for (a) viscosity and (b) conductivity measurements.

Table S.9: Temperature dependent viscosity η and conductivity σ data of [C_4MIM][Cl] and [C_2MIM][NO_3].

[C_4MIM][Cl]				[C_2MIM][NO_3]	
T / K	η / Pa s	T / K	σ / mS cm^{-1}	T / K	σ / mS cm^{-1}
363.15	0.0862	353.15	2.7345	318.15	21.1
353.15	0.1531	348.15	2.1075	323.15	24.43
343.15	0.2929	343.15	1.592	328.15	27.83
333.15	0.6081	338.15	1.175	333.15	31.16
323.15	1.424	333.15	0.828	338.15	34.72
318.15	2.285	328.15	0.5789	343.15	38.66
313.15	3.873	323.15	0.3953	348.15	42.22
308.15	6.919	318.15	0.2396	353.15	46.54
		313.15	0.1633		

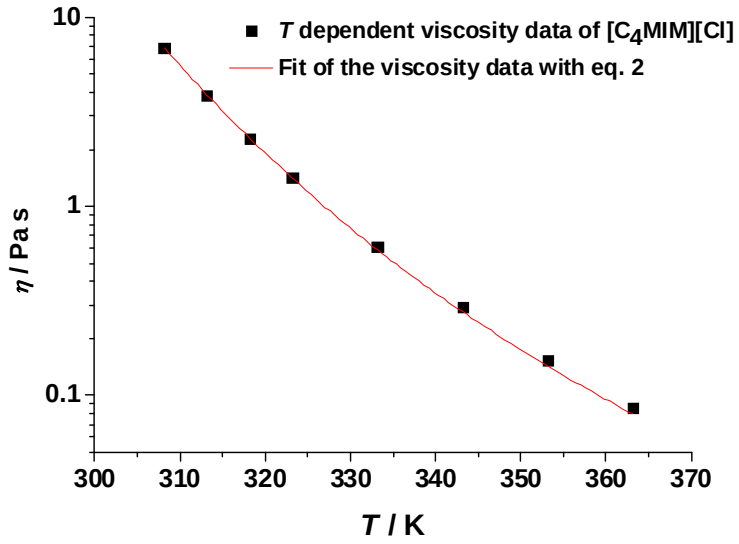


Figure S.10: Fit of the viscosity data of [C_4MIM][Cl] with eq. 2.

8. Linear fits of the used density data

The volume of the liquid phase V_{liquid} at ambient pressure of each compound obtained from PVT analysis were fitted to the linear equation: $V_{\text{liquid}} = aT + b$. The coefficients a is the thermal expansivity, whereas b is the zero Kelvin volume of the liquid phase. The same source of PVT data as given in Table S.7 was used.

Table S.10: Thermal expansivity a and the zero Kelvin volume b of the liquid phase together with their standard deviations σ(a) and σ(b) from the linear plot of PVT data at ambient pressure.

Compound	a / Å^3 K^{-1}	σ(a) / Å^3 K^{-1}	b / Å^3	σ(b) / K
[C_4MIM][Cl]	0.15082	0.00102	224.52968	0.40653
[C_4MIM][BF_4]	0.20386	0.00046	252.75925	0.17734
[C_4MIM][PF_6]	0.21325	0.00017	284.64114	0.06169
[C_4MIM][OTf]	0.22088	0.00048	304.30342	0.17327
[C_4MIM][NTf_2]	0.31491	0.00056	390.54630	0.20052
[C_4MIM][B(hfip)$_4$]	0.72593	0.00390	765.34529	1.46509
[C_2MIM][NO_3]	0.11854	0.00045	233.16878	0.16355
[C_2MIM][OTs]	0.18678	0.00126	328.75733	0.47265
[C_3MIM][NTf_2]	0.32212	0.00088	361.81889	0.34170

9. Fit parameters of the Cohen-Turnbull plots

Table S.11: Fit parameters of the plots via eqn. 2 and 3 for $[C_3MIM][NTf_2]$, $[C_2MIM][NO_3]$ and $[C_2MIM][OTs]$.

	$[C_3MIM][NTf_2]$	$[C_2MIM][NO_3]$	$[C_2MIM][OTs]$
A_{visc} / 10^{-7} Pa·s·$K^{-0.5}$	10.33	5.02	0.33
V^*_{visc} / Å^3	406	241	361
A_{cond} / 10^4 mS·cm^{-1}·$K^{0.5}$	5.7	56.7	24.5
V^*_{cond} / Å^3	398	238	348

Table S.12: Fit parameters of the plots via eqn. 2 and 3 by replacing $\exp\left(\frac{V^*_{visc/cond}}{(V_{liquid}-V^*_{visc/cond})}\right)$ with $\exp\left(\frac{\gamma V_{m,scaled}}{(V_{liquid}-V_{m,scaled})}\right)$.

Compound	viscosity		electrical conductivity	
	A_{visc}	γ	A_{cond}	γ
$[C_4MIM][Cl]$	6.76E-12	3.44	1.86E+08	2.52
$[C_4MIM][BF_4]$	1.76E-07	1.43	8.48E+04	0.93
$[C_4MIM][PF_6]$	1.28E-07	1.55	9.80E+04	1.01
$[C_4MIM][OTf]$	5.00E-08	1.68	8.48E+04	1.03
$[C_4MIM][NTf_2]$	3.91E-07	1.13	3.54E+04	0.79
$[C_4MIM][B(hfip)_4]$	1.90E-09	4.58	7.35E+04	2.45
$[C_2MIM][OTs]$	3.65E-12	2.81	3.87E+05	1.13
$[C_2MIM][NO_3]$	3.24E-10	4.40	1.13E+08	3.57
$[C_3MIM][NTf_2]$	1.04E-06	1.00	2.81E+04	0.76

10. Crystallographic tables for the compound $[C_4MIM][B(hfip)_4]$

Table S.13: Crystal data and structure refinement for 1-butyl-3-methylimidazolium tetrakis(hexafluoroisopropoxy)borate.

Identification code	shelx_structure	
Empirical formula	C20 H19 B F24 N2 O4	
Formula weight	818.18	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 8.9539(2) Å	α = 90°
	b = 37.2276(6) Å	β = 90.1219(16)°
	c = 9.1021(2) Å	γ = 90°
Volume	3034.02(11) Å^3	
Z	2	
Density (calculated)	1.791 Mg/m^3	

Absorption coefficient	0.218 mm^{-1}
F(000)	1624
Crystal size	0.3 x 0.3 x 0.3 mm
θ range for data collection	2.19 to 23.25°
Index ranges	-9<=h<=9, -41<=k<=41, -10<=l<=10
Reflections collected	36211
Independent reflections	4396 [R_{int} = 0.0686]
Completeness to θ = 23.25°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.865
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4396 / 61 / 923
Goodness-of-fit on F^2	S = 1.142
R indices [for 4022 reflections with I>2σ(I)]	R_1 = 0.0468, wR_2 = 0.1146
R indices (for all 4396 data)	R_1 = 0.0671, wR_2 = 0.1294
Weighting scheme	$w^{-1} = \sigma^2(F_o^2) + (aP)^2 + (bP)$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$ a = **0.0527**, b = **1.2958**
Largest diff. peak and hole	0.436 and -0.390 $eÅ^{-3}$

Table S.14: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for 1-butyl-3-methylimidazolium tetrakis(hexafluoroisopropoxy)borate. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x / a	y / b	z / c	U(eq)
F(1A)	5661(5)	2465(1)	10828(5)	55(1)
F(1B)	6946(5)	5998(1)	8247(5)	55(1)
F(2A)	4862(4)	2963(1)	11725(4)	51(1)
F(2B)	9292(5)	6094(1)	8503(5)	52(1)
F(3A)	7172(4)	2905(1)	11172(4)	45(1)
F(3B)	7905(6)	6033(1)	10401(4)	53(1)
F(4A)	7283(5)	3404(2)	9057(5)	61(1)
F(4B)	9391(5)	5465(1)	11418(4)	54(1)
F(5A)	5147(7)	3555(1)	9911(5)	67(1)
F(5B)	10952(4)	5521(1)	9654(5)	53(1)
F(6A)	5400(5)	3446(1)	7601(4)	51(1)
F(6B)	9788(5)	5025(1)	9934(4)	50(1)
F(7A)	425(5)	2895(1)	9811(5)	57(1)
F(7B)	6015(6)	4286(1)	6360(5)	63(1)

F(8A)	-827(4)	2449(2)	9005(5)	56(1)
F(8B)	6229(4)	4273(1)	8689(4)	43(1)
F(9A)	8(5)	2445(1)	11217(4)	49(1)
F(9B)	4063(5)	4273(1)	7698(6)	63(1)
F(10A)	1372(6)	1830(1)	10574(5)	72(2)
F(10B)	4807(5)	4859(1)	10116(4)	49(1)
F(11A)	783(5)	1835(1)	8294(6)	60(1)
F(11B)	3000(4)	4898(1)	8568(5)	55(1)
F(12A)	3081(4)	1832(1)	8932(5)	52(1)
F(12B)	4558(5)	5333(1)	8803(5)	48(1)
F(13A)	1442(6)	2582(1)	4286(5)	65(1)
F(13B)	8118(5)	6015(1)	5288(4)	50(1)
F(14A)	-79(5)	3025(2)	4078(5)	63(1)
F(14B)	5732(5)	6057(1)	5238(4)	49(1)
F(15A)	2205(5)	3084(1)	3427(4)	59(1)
F(15B)	6965(5)	6057(1)	3223(4)	52(1)
F(16A)	334(5)	3582(1)	5862(6)	67(1)
F(16B)	4298(5)	5492(2)	3758(6)	65(1)
F(17A)	2676(5)	3629(1)	5442(5)	52(1)
F(17B)	5956(6)	5450(2)	2073(4)	67(2)
F(18A)	1911(6)	3531(1)	7624(5)	57(1)
F(18B)	5564(5)	5006(1)	3541(4)	50(1)
F(19A)	3163(4)	1924(1)	5539(4)	47(1)
F(19B)	10996(7)	5394(2)	5038(8)	92(2)
F(20A)	5356(5)	1742(1)	6123(6)	58(1)
F(20B)	12471(5)	4934(2)	5156(6)	80(2)
F(21A)	4872(5)	1904(1)	3893(5)	62(1)
F(21B)	10784(6)	4970(2)	3547(5)	68(2)
F(22A)	7571(4)	2247(1)	6210(5)	49(1)
F(22B)	11410(6)	4336(2)	6399(7)	89(2)
F(23A)	7049(5)	2403(1)	3994(4)	50(1)
F(23B)	9920(7)	4325(1)	4608(5)	73(2)
F(24A)	6958(5)	2792(1)	5744(5)	51(1)
F(24B)	9098(7)	4304(2)	6765(8)	96(2)
O(1A)	4694(4)	2445(1)	7123(4)	27(1)
O(1B)	8689(4)	5396(1)	7586(4)	25(1)
O(2A)	2089(4)	2500(1)	7904(4)	27(1)
O(2B)	6880(4)	4943(1)	7802(4)	27(1)
O(3A)	3168(4)	2922(1)	6294(4)	28(1)

O(3B)	6533(4)	5371(1)	5920(4)	28(1)
O(4A)	3967(4)	2877(1)	8879(4)	29(1)
O(4B)	8562(4)	4972(1)	5673(4)	27(1)
N(1A)	8574(7)	4013(3)	1303(6)	59(2)
N(1B)	1231(6)	6565(2)	6668(5)	35(1)
N(2A)	7337(6)	3835(2)	3182(5)	34(1)
N(2B)	3105(6)	6463(2)	8122(5)	34(1)
C(1A)	5454(7)	2947(2)	9159(6)	29(1)
C(1B)	8375(7)	5506(2)	9014(6)	27(1)
C(2A)	5774(7)	2825(2)	10745(7)	32(2)
C(2B)	8143(8)	5907(2)	9042(7)	34(2)
C(3A)	5801(8)	3343(2)	8931(7)	36(2)
C(3B)	9631(7)	5382(2)	10014(7)	36(2)
C(4A)	1793(7)	2369(2)	9304(6)	32(2)
C(4B)	5434(6)	4820(2)	7585(6)	26(1)
C(5A)	346(7)	2537(2)	9829(7)	34(2)
C(5B)	4449(7)	4978(2)	8783(7)	36(2)
C(6A)	1735(7)	1964(2)	9270(8)	39(2)
C(6B)	5426(7)	4416(2)	7597(7)	37(2)
C(7A)	1738(7)	3048(2)	5991(6)	31(1)
C(7B)	6833(7)	5503(2)	4516(6)	29(1)
C(8A)	1677(8)	3451(2)	6214(7)	40(2)
C(8B)	5648(8)	5364(2)	3449(7)	40(2)
C(9A)	1329(8)	2935(2)	4436(7)	40(2)
C(9B)	6895(8)	5913(2)	4564(6)	35(2)
C(10A)	5018(7)	2367(2)	5657(6)	31(1)
C(10B)	10008(7)	4866(2)	6007(6)	31(1)
C(11A)	4622(7)	1979(2)	5305(7)	37(2)
C(11B)	11077(7)	5043(2)	4937(8)	44(2)
C(12A)	6651(8)	2451(2)	5412(7)	38(2)
C(12B)	10123(7)	4462(2)	5941(8)	38(2)
C(13A)	6724(9)	3612(2)	4339(8)	48(2)
C(13B)	-34(8)	6743(2)	5951(7)	43(2)
C(14A)	7028(8)	4194(2)	2964(9)	48(2)
C(14B)	1731(8)	6215(2)	6408(7)	37(2)
C(15A)	7800(9)	4302(3)	1817(10)	59(2)
C(15B)	2883(8)	6161(2)	7316(7)	39(2)
C(16A)	8287(8)	3725(2)	2157(7)	44(2)
C(16B)	2097(7)	6709(2)	7702(6)	30(1)

C(17A)	9666(11)	4013(4)	66(10)	99(5)
C(17B)	4206(7)	6517(2)	9307(7)	40(2)
C(18A)	11172(8)	4165(3)	563(8)	54(2)
C(18B)	3825(7)	6283(2)	10611(7)	38(2)
C(19A)	11932(9)	3941(3)	1698(10)	57(2)
C(19B)	2305(7)	6373(2)	11272(7)	38(2)
C(20A)	13362(9)	4110(4)	2205(10)	84(4)
C(20B)	1928(9)	6137(3)	12584(7)	51(2)
B(1A)	3482(7)	2687(2)	7538(7)	26(2)
B(1B)	7654(7)	5169(2)	6739(7)	26(2)

Table S.15: Bond lengths [Å] and angles [°] for 1-butyl-3-methylimidazolium tetrakis(hexafluoroisopropoxy)borate.

F(1A)-C(2A)	1.346(8)
F(1B)-C(2B)	1.336(8)
F(2A)-C(2A)	1.316(8)
F(2B)-C(2B)	1.336(8)
F(3A)-C(2A)	1.343(8)
F(3B)-C(2B)	1.340(7)
F(4A)-C(3A)	1.351(8)
F(4B)-C(3B)	1.333(8)
F(5A)-C(3A)	1.328(9)
F(5B)-C(3B)	1.333(8)
F(6A)-C(3A)	1.318(8)
F(6B)-C(3B)	1.338(8)
F(7A)-C(5A)	1.333(8)
F(7B)-C(6B)	1.335(8)
F(8A)-C(5A)	1.330(8)
F(8B)-C(6B)	1.337(8)
F(9A)-C(5A)	1.344(7)
F(9B)-C(6B)	1.335(8)
F(10A)-C(6A)	1.328(8)
F(10B)-C(5B)	1.331(8)
F(11A)-C(6A)	1.320(9)
F(11B)-C(5B)	1.346(8)
F(12A)-C(6A)	1.337(8)
F(12B)-C(5B)	1.324(8)
F(13A)-C(9A)	1.327(9)

F(13B)-C(9B)	1.332(8)
F(14A)-C(9A)	1.343(8)
F(14B)-C(9B)	1.322(8)
F(15A)-C(9A)	1.331(9)
F(15B)-C(9B)	1.336(7)
F(16A)-C(8A)	1.336(8)
F(16B)-C(8B)	1.330(9)
F(17A)-C(8A)	1.317(9)
F(17B)-C(8B)	1.322(8)
F(18A)-C(8A)	1.333(8)
F(18B)-C(8B)	1.335(9)
F(19A)-C(11A)	1.340(8)
F(19B)-C(11B)	1.311(9)
F(20A)-C(11A)	1.328(8)
F(20B)-C(11B)	1.328(8)
F(21A)-C(11A)	1.335(8)
F(21B)-C(11B)	1.320(9)
F(22A)-C(12A)	1.334(8)
F(22B)-C(12B)	1.312(8)
F(23A)-C(12A)	1.352(7)
F(23B)-C(12B)	1.329(8)
F(24A)-C(12A)	1.333(9)
F(24B)-C(12B)	1.324(9)
O(1A)-C(10A)	1.397(7)
O(1A)-B(1A)	1.463(8)
O(1B)-C(1B)	1.391(7)
O(1B)-B(1B)	1.472(8)
O(2A)-C(4A)	1.390(7)
O(2A)-B(1A)	1.469(8)
O(2B)-C(4B)	1.387(7)
O(2B)-B(1B)	1.458(8)
O(3A)-C(7A)	1.391(7)
O(3A)-B(1A)	1.457(8)
O(3B)-C(7B)	1.396(7)
O(3B)-B(1B)	1.458(8)
O(4A)-C(1A)	1.381(7)
O(4A)-B(1A)	1.473(8)
O(4B)-C(10B)	1.387(7)
O(4B)-B(1B)	1.464(8)

N(1A)-C(15A)	1.363(13)
N(1A)-C(16A)	1.351(11)
N(1A)-C(17A)	1.493(11)
N(1B)-C(13B)	1.466(9)
N(1B)-C(14B)	1.396(9)
N(1B)-C(16B)	1.330(9)
N(2A)-C(13A)	1.451(9)
N(2A)-C(14A)	1.380(10)
N(2A)-C(16A)	1.329(9)
N(2B)-C(15B)	1.355(9)
N(2B)-C(16B)	1.339(9)
N(2B)-C(17B)	1.474(9)
C(1A)-C(2A)	1.540(8)
C(1A)-C(3A)	1.520(10)
C(1B)-C(2B)	1.508(9)
C(1B)-C(3B)	1.517(9)
C(4A)-C(5A)	1.517(9)
C(4A)-C(6A)	1.510(10)
C(4B)-C(5B)	1.522(9)
C(4B)-C(6B)	1.505(9)
C(7A)-C(8A)	1.515(10)
C(7A)-C(9A)	1.521(9)
C(7B)-C(8B)	1.528(9)
C(7B)-C(9B)	1.527(10)
C(10A)-C(11A)	1.518(10)
C(10A)-C(12A)	1.513(9)
C(10B)-C(11B)	1.517(10)
C(10B)-C(12B)	1.510(10)
C(14A)-C(15A)	1.316(12)
C(14B)-C(15B)	1.336(10)
C(17A)-C(18A)	1.530(11)
C(17B)-C(18B)	1.512(10)
C(18A)-C(19A)	1.489(12)
C(18B)-C(19B)	1.527(9)
C(19A)-C(20A)	1.499(13)
C(19B)-C(20B)	1.521(10)

C(10A)-O(1A)-B(1A)	122.1(5)
C(1B)-O(1B)-B(1B)	122.0(4)

C(4A)-O(2A)-B(1A)	122.6(5)
C(4B)-O(2B)-B(1B)	122.7(4)
C(7A)-O(3A)-B(1A)	122.2(5)
C(7B)-O(3B)-B(1B)	121.1(4)
C(1A)-O(4A)-B(1A)	121.8(5)
C(10B)-O(4B)-B(1B)	121.1(4)
C(15A)-N(1A)-C(17A)	126.3(9)
C(16A)-N(1A)-C(15A)	109.5(7)
C(16A)-N(1A)-C(17A)	124.1(10)
C(14B)-N(1B)-C(13B)	126.5(6)
C(16B)-N(1B)-C(13B)	125.6(6)
C(16B)-N(1B)-C(14B)	108.0(6)
C(14A)-N(2A)-C(13A)	125.7(6)
C(16A)-N(2A)-C(13A)	125.1(7)
C(16A)-N(2A)-C(14A)	109.1(6)
C(15B)-N(2B)-C(17B)	127.3(6)
C(16B)-N(2B)-C(15B)	108.2(5)
C(16B)-N(2B)-C(17B)	124.4(6)
O(4A)-C(1A)-C(2A)	107.1(5)
O(4A)-C(1A)-C(3A)	110.9(5)
C(3A)-C(1A)-C(2A)	112.2(5)
O(1B)-C(1B)-C(2B)	109.5(5)
O(1B)-C(1B)-C(3B)	108.7(5)
C(2B)-C(1B)-C(3B)	113.2(5)
F(1A)-C(2A)-C(1A)	109.5(5)
F(2A)-C(2A)-F(1A)	107.7(5)
F(2A)-C(2A)-F(3A)	107.2(5)
F(2A)-C(2A)-C(1A)	113.9(6)
F(3A)-C(2A)-F(1A)	106.0(5)
F(3A)-C(2A)-C(1A)	112.1(5)
F(1B)-C(2B)-F(2B)	106.6(5)
F(1B)-C(2B)-F(3B)	106.4(5)
F(1B)-C(2B)-C(1B)	110.7(6)
F(2B)-C(2B)-F(3B)	106.3(6)
F(2B)-C(2B)-C(1B)	113.8(5)
F(3B)-C(2B)-C(1B)	112.5(5)
F(4A)-C(3A)-C(1A)	110.6(6)
F(5A)-C(3A)-F(4A)	106.1(6)
F(5A)-C(3A)-C(1A)	113.2(5)

F(6A)-C(3A)-F(4A)	107.1(5)
F(6A)-C(3A)-F(5A)	109.0(6)
F(6A)-C(3A)-C(1A)	110.5(5)
F(4B)-C(3B)-F(5B)	106.9(5)
F(4B)-C(3B)-F(6B)	107.5(6)
F(4B)-C(3B)-C(1B)	112.6(5)
F(5B)-C(3B)-F(6B)	106.2(6)
F(5B)-C(3B)-C(1B)	113.0(6)
F(6B)-C(3B)-C(1B)	110.3(5)
O(2A)-C(4A)-C(5A)	108.0(5)
O(2A)-C(4A)-C(6A)	109.7(5)
C(6A)-C(4A)-C(5A)	113.0(5)
O(2B)-C(4B)-C(5B)	108.2(5)
O(2B)-C(4B)-C(6B)	109.5(5)
C(6B)-C(4B)-C(5B)	112.3(5)
F(7A)-C(5A)-F(9A)	106.2(5)
F(7A)-C(5A)-C(4A)	111.3(5)
F(8A)-C(5A)-F(7A)	106.3(6)
F(8A)-C(5A)-F(9A)	106.7(5)
F(8A)-C(5A)-C(4A)	113.2(6)
F(9A)-C(5A)-C(4A)	112.6(5)
F(10B)-C(5B)-F(11B)	106.7(5)
F(10B)-C(5B)-C(4B)	112.6(6)
F(11B)-C(5B)-C(4B)	111.6(5)
F(12B)-C(5B)-F(10B)	107.7(6)
F(12B)-C(5B)-F(11B)	107.2(6)
F(12B)-C(5B)-C(4B)	110.7(5)
F(10A)-C(6A)-F(12A)	106.9(6)
F(10A)-C(6A)-C(4A)	111.3(6)
F(11A)-C(6A)-F(10A)	107.9(6)
F(11A)-C(6A)-F(12A)	107.1(6)
F(11A)-C(6A)-C(4A)	113.5(6)
F(12A)-C(6A)-C(4A)	109.9(5)
F(7B)-C(6B)-F(8B)	105.6(6)
F(7B)-C(6B)-F(9B)	106.1(6)
F(7B)-C(6B)-C(4B)	110.8(6)
F(8B)-C(6B)-C(4B)	113.7(5)
F(9B)-C(6B)-F(8B)	106.3(6)
F(9B)-C(6B)-C(4B)	113.8(6)

O(3A)-C(7A)-C(8A)	110.0(5)
O(3A)-C(7A)-C(9A)	108.1(5)
C(8A)-C(7A)-C(9A)	112.9(6)
O(3B)-C(7B)-C(8B)	109.1(5)
O(3B)-C(7B)-C(9B)	109.5(5)
C(9B)-C(7B)-C(8B)	112.5(5)
F(16A)-C(8A)-C(7A)	111.3(6)
F(17A)-C(8A)-F(16A)	107.5(6)
F(17A)-C(8A)-F(18A)	107.2(6)
F(17A)-C(8A)-C(7A)	113.6(6)
F(18A)-C(8A)-F(16A)	106.8(6)
F(18A)-C(8A)-C(7A)	110.0(6)
F(16B)-C(8B)-F(18B)	107.0(6)
F(16B)-C(8B)-C(7B)	112.0(6)
F(17B)-C(8B)-F(16B)	107.8(6)
F(17B)-C(8B)-F(18B)	108.2(6)
F(17B)-C(8B)-C(7B)	112.0(6)
F(18B)-C(8B)-C(7B)	109.8(5)
F(13A)-C(9A)-F(14A)	107.0(6)
F(13A)-C(9A)-F(15A)	107.3(6)
F(13A)-C(9A)-C(7A)	110.6(6)
F(14A)-C(9A)-C(7A)	112.4(6)
F(15A)-C(9A)-F(14A)	106.5(6)
F(15A)-C(9A)-C(7A)	112.7(6)
F(13B)-C(9B)-F(15B)	107.3(5)
F(13B)-C(9B)-C(7B)	109.2(5)
F(14B)-C(9B)-F(13B)	107.6(5)
F(14B)-C(9B)-F(15B)	107.4(6)
F(14B)-C(9B)-C(7B)	112.9(5)
F(15B)-C(9B)-C(7B)	112.2(5)
O(1A)-C(10A)-C(11A)	110.5(5)
O(1A)-C(10A)-C(12A)	107.4(5)
C(12A)-C(10A)-C(11A)	113.1(6)
O(4B)-C(10B)-C(11B)	109.0(5)
O(4B)-C(10B)-C(12B)	109.7(5)
C(12B)-C(10B)-C(11B)	111.4(6)
F(19A)-C(11A)-C(10A)	109.9(5)
F(20A)-C(11A)-F(19A)	106.9(6)
F(20A)-C(11A)-F(21A)	108.4(6)

F(20A)-C(11A)-C(10A)	113.4(5)
F(21A)-C(11A)-F(19A)	106.6(5)
F(21A)-C(11A)-C(10A)	111.3(6)
F(19B)-C(11B)-F(20B)	110.3(7)
F(19B)-C(11B)-F(21B)	105.3(7)
F(19B)-C(11B)-C(10B)	110.7(6)
F(20B)-C(11B)-C(10B)	111.3(6)
F(21B)-C(11B)-F(20B)	105.4(6)
F(21B)-C(11B)-C(10B)	113.6(6)
F(22A)-C(12A)-F(23A)	106.3(6)
F(22A)-C(12A)-C(10A)	113.4(6)
F(23A)-C(12A)-C(10A)	111.7(5)
F(24A)-C(12A)-F(22A)	107.0(6)
F(24A)-C(12A)-F(23A)	106.7(6)
F(24A)-C(12A)-C(10A)	111.3(6)
F(22B)-C(12B)-F(23B)	105.7(6)
F(22B)-C(12B)-F(24B)	105.6(7)
F(22B)-C(12B)-C(10B)	113.9(6)
F(23B)-C(12B)-C(10B)	114.2(6)
F(24B)-C(12B)-F(23B)	104.6(7)
F(24B)-C(12B)-C(10B)	112.0(6)
C(15A)-C(14A)-N(2A)	107.7(8)
C(15B)-C(14B)-N(1B)	106.4(6)
C(14A)-C(15A)-N(1A)	107.4(8)
C(14B)-C(15B)-N(2B)	108.8(6)
N(2A)-C(16A)-N(1A)	106.3(8)
N(1B)-C(16B)-N(2B)	108.6(6)
N(1A)-C(17A)-C(18A)	110.8(7)
N(2B)-C(17B)-C(18B)	110.1(6)
C(19A)-C(18A)-C(17A)	113.6(8)
C(17B)-C(18B)-C(19B)	112.7(6)
C(18A)-C(19A)-C(20A)	111.6(7)
C(20B)-C(19B)-C(18B)	112.5(6)
O(1A)-B(1A)-O(2A)	113.3(6)
O(1A)-B(1A)-O(4A)	107.0(5)
O(2A)-B(1A)-O(4A)	106.8(5)
O(3A)-B(1A)-O(1A)	108.1(5)
O(3A)-B(1A)-O(2A)	107.4(5)
O(3A)-B(1A)-O(4A)	114.5(6)

O(2B)-B(1B)-O(1B)	106.5(4)
O(2B)-B(1B)-O(4B)	114.6(6)
O(3B)-B(1B)-O(1B)	113.8(6)
O(3B)-B(1B)-O(2B)	108.0(5)
O(3B)-B(1B)-O(4B)	107.6(4)
O(4B)-B(1B)-O(1B)	106.6(5)

Table S.16: Anisotropic displacement parameters ($Å^2$ x 10^3) for 1-butyl-3-methylimidazolium tetrakis(hexafluoroisopropoxy)borate. The anisotropic displacement factor exponent takes the form:

$-2\pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F(1A)	79(3)	41(3)	46(2)	9(2)	-20(2)	-12(2)
F(1B)	67(3)	50(3)	47(2)	3(2)	1(2)	31(2)
F(2A)	44(2)	85(4)	25(2)	-2(2)	6(2)	2(2)
F(2B)	72(3)	32(3)	51(2)	-1(2)	22(2)	-12(2)
F(3A)	40(2)	57(3)	39(2)	0(2)	-14(2)	-3(2)
F(3B)	92(3)	39(3)	27(2)	-8(2)	20(2)	3(2)
F(4A)	53(3)	67(4)	62(3)	12(2)	-17(2)	-36(2)
F(4B)	58(3)	75(3)	29(2)	-7(2)	-9(2)	11(2)
F(5A)	105(4)	37(3)	59(3)	-17(2)	20(3)	-8(3)
F(5B)	33(2)	70(3)	57(2)	-11(2)	-7(2)	-3(2)
F(6A)	58(3)	52(3)	43(2)	16(2)	-10(2)	-18(2)
F(6B)	63(3)	41(3)	46(2)	7(2)	-16(2)	10(2)
F(7A)	57(3)	42(3)	71(3)	5(2)	20(2)	7(2)
F(7B)	92(3)	48(3)	49(2)	-18(2)	1(2)	6(3)
F(8A)	29(2)	87(4)	51(2)	-12(2)	-7(2)	6(2)
F(8B)	42(2)	36(2)	52(2)	14(2)	-18(2)	-1(2)
F(9A)	49(2)	63(3)	34(2)	8(2)	13(2)	2(2)
F(9B)	39(2)	44(3)	105(4)	5(3)	-31(2)	-9(2)
F(10A)	103(4)	50(3)	62(3)	28(2)	36(3)	4(3)
F(10B)	61(3)	60(3)	25(2)	0(2)	6(2)	-6(2)
F(11A)	46(2)	47(3)	86(3)	-7(2)	-5(2)	-15(2)
F(11B)	31(2)	70(3)	63(3)	-12(2)	9(2)	-11(2)
F(12A)	42(2)	49(3)	64(3)	17(2)	7(2)	12(2)
F(12B)	46(2)	35(3)	63(3)	-8(2)	9(2)	4(2)
F(13A)	90(4)	40(3)	63(3)	-14(2)	-36(3)	8(3)
F(13B)	63(3)	48(3)	40(2)	1(2)	-6(2)	-13(2)

F(14A)	43(2)	91(4)	54(3)	-8(2)	-19(2)	20(2)
F(14B)	66(3)	42(3)	39(2)	8(2)	11(2)	22(2)
F(15A)	74(3)	71(4)	31(2)	2(2)	5(2)	10(3)
F(15B)	83(3)	45(3)	27(2)	14(2)	7(2)	8(2)
F(16A)	51(3)	42(3)	108(4)	-3(3)	-19(3)	19(2)
F(16B)	30(2)	76(4)	88(3)	21(3)	-15(2)	-1(2)
F(17A)	61(3)	32(3)	63(3)	15(2)	5(2)	-3(2)
F(17B)	82(3)	86(4)	31(2)	15(2)	-20(2)	-35(3)
F(18A)	73(3)	49(3)	50(3)	-14(2)	4(2)	13(2)
F(18B)	62(3)	41(3)	47(2)	1(2)	-13(2)	-14(2)
F(19A)	34(2)	57(3)	51(2)	-19(2)	-4(2)	-9(2)
F(19B)	83(4)	61(4)	132(5)	-9(3)	65(4)	-23(3)
F(20A)	59(3)	27(3)	87(3)	-1(2)	-22(2)	3(2)
F(20B)	31(2)	142(6)	67(3)	24(3)	13(2)	16(3)
F(21A)	70(3)	66(3)	49(2)	-34(2)	14(2)	-11(3)
F(21B)	77(3)	95(4)	33(2)	21(2)	11(2)	16(3)
F(22A)	31(2)	62(3)	53(2)	5(2)	-7(2)	4(2)
F(22B)	62(3)	63(4)	141(5)	-40(3)	-67(3)	32(3)
F(23A)	58(2)	60(3)	32(2)	-8(2)	19(2)	-2(2)
F(23B)	110(4)	53(3)	56(3)	-26(2)	-37(3)	5(3)
F(24A)	60(3)	38(3)	55(2)	-13(2)	18(2)	-16(2)
F(24B)	112(4)	54(4)	122(5)	44(3)	62(4)	29(3)
O(1A)	30(2)	32(3)	20(2)	0(2)	1(2)	2(2)
O(1B)	27(2)	29(3)	21(2)	-1(2)	4(2)	-3(2)
O(2A)	26(2)	28(3)	27(2)	3(2)	0(2)	-4(2)
O(2B)	24(2)	35(3)	24(2)	2(2)	-3(2)	-1(2)
O(3A)	24(2)	31(3)	27(2)	3(2)	0(2)	2(2)
O(3B)	26(2)	28(3)	28(2)	9(2)	4(2)	6(2)
O(4A)	25(2)	37(3)	24(2)	-3(2)	0(2)	-4(2)
O(4B)	29(2)	32(3)	22(2)	-1(2)	-5(2)	7(2)
N(1A)	43(4)	111(7)	23(3)	9(4)	-10(3)	-30(4)
N(1B)	34(3)	44(4)	26(3)	8(2)	1(2)	2(3)
N(2A)	32(3)	37(4)	32(3)	7(2)	-6(2)	-2(2)
N(2B)	33(3)	40(4)	28(3)	6(2)	2(2)	3(3)
C(1A)	29(3)	40(4)	19(3)	0(3)	-1(2)	-2(3)
C(1B)	33(3)	29(4)	19(3)	1(2)	4(2)	-3(3)
C(2A)	36(4)	30(4)	31(3)	1(3)	-3(3)	-8(3)
C(2B)	52(4)	24(4)	26(3)	-3(3)	10(3)	5(3)
C(3A)	45(4)	32(4)	32(3)	4(3)	-2(3)	-9(3)

C(3B)	35(4)	38(4)	33(3)	-4(3)	0(3)	2(3)
C(4A)	29(3)	44(4)	25(3)	5(3)	0(2)	-4(3)
C(4B)	29(3)	31(4)	20(3)	5(2)	-5(2)	-4(3)
C(5A)	36(4)	38(5)	29(3)	6(3)	3(3)	-6(3)
C(5B)	28(3)	41(5)	38(4)	2(3)	-1(3)	-7(3)
C(6A)	36(4)	28(4)	54(4)	11(3)	12(3)	-2(3)
C(6B)	37(4)	34(4)	39(4)	-2(3)	-9(3)	1(3)
C(7A)	30(3)	39(4)	26(3)	1(3)	2(2)	4(3)
C(7B)	28(3)	41(4)	17(3)	6(3)	1(2)	2(3)
C(8A)	39(4)	41(5)	41(4)	-3(3)	-5(3)	6(3)
C(8B)	43(4)	45(5)	33(3)	10(3)	-7(3)	-5(3)
C(9A)	35(4)	52(5)	33(3)	8(3)	-8(3)	7(3)
C(9B)	51(4)	31(4)	23(3)	11(3)	3(3)	-5(3)
C(10A)	38(3)	35(4)	20(3)	-4(3)	-2(2)	5(3)
C(10B)	26(3)	43(4)	23(3)	-4(3)	-9(2)	8(3)
C(11A)	38(4)	40(5)	34(3)	-15(3)	-3(3)	2(3)
C(11B)	30(4)	50(5)	51(4)	-3(4)	7(3)	12(3)
C(12A)	41(4)	46(5)	27(3)	-4(3)	7(3)	2(3)
C(12B)	32(4)	37(4)	45(4)	-3(3)	-11(3)	6(3)
C(13A)	46(4)	59(6)	38(4)	8(4)	2(3)	-3(4)
C(13B)	50(4)	43(5)	35(4)	7(3)	-4(3)	12(3)
C(14A)	36(4)	46(5)	63(5)	14(4)	-10(3)	3(3)
C(14B)	51(4)	32(4)	29(3)	1(3)	4(3)	6(3)
C(15A)	53(5)	61(6)	63(5)	31(5)	-20(4)	-17(5)
C(15B)	44(4)	39(4)	34(3)	-4(3)	8(3)	11(3)
C(16A)	44(4)	62(6)	27(3)	-11(3)	-2(3)	-9(4)
C(16B)	31(3)	29(4)	30(3)	4(3)	3(3)	-8(3)
C(17A)	59(6)	197(14)	42(5)	3(6)	1(4)	-60(7)
C(17B)	29(3)	45(5)	47(4)	6(3)	-5(3)	1(3)
C(18A)	41(4)	89(7)	31(4)	18(4)	2(3)	-23(4)
C(18B)	35(3)	44(4)	35(3)	0(3)	-7(3)	4(3)
C(19A)	42(4)	59(6)	69(5)	22(4)	18(3)	3(4)
C(19B)	35(3)	47(5)	32(3)	-1(3)	-8(3)	0(3)
C(20A)	37(4)	155(12)	60(5)	46(6)	-2(4)	5(5)
C(20B)	53(4)	71(6)	27(3)	2(3)	-6(3)	-9(4)
B(1A)	21(3)	28(4)	28(3)	-1(3)	4(3)	-3(3)
B(1B)	25(3)	34(4)	19(3)	-1(3)	-1(2)	3(3)

Table S.17: Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for 1-butyl-3-methylimidazolium tetrakis(hexafluoroisopropoxy)borate.

	x / a	y / b	z / c	U(eq)
H(1A)	6068	2805	8485	35
H(1B)	7448	5389	9330	32
H(4A)	2602	2443	9964	39
H(4B)	5076	4904	6627	32
H(7A)	1037	2935	6675	38
H(7B)	7810	5413	4204	34
H(10A)	4418	2524	5028	37
H(10)	10253	4946	7005	37
H(13D)	7123	3373	4259	71
H(13E)	5656	3603	4246	71
H(13F)	6986	3711	5278	71
H(13A)	-948	6630	6248	64
H(13B)	70	6725	4904	64
H(13C)	-53	6992	6230	64
H(14A)	6389	4335	3526	58
H(14)	1339	6052	5735	45
H(15A)	7815	4533	1428	71
H(15)	3442	5951	7384	46
H(16A)	8677	3495	2050	53
H(16)	2016	6941	8071	36
H(17C)	9277	4158	-736	119
H(17D)	9799	3770	-291	119
H(17A)	4208	6767	9604	48
H(17B)	5196	6457	8953	48
H(18C)	11821	4185	-285	64
H(18D)	11020	4404	955	64
H(18A)	4589	6312	11358	46
H(18B)	3828	6033	10304	46
H(19C)	12142	3706	1293	68
H(19D)	11272	3910	2532	68
H(19A)	2301	6622	11578	46
H(19B)	1540	6343	10526	46
H(20D)	13974	4165	1370	126
H(20E)	13885	3947	2839	126

H(20F)	13145	4327	2733	126
H(20A)	1920	5890	12286	76
H(20B)	962	6202	12956	76
H(20C)	2665	6171	13340	76

11. References

1. A.L.Spek, (2005.), PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands.
2. www.ccdc.cam.ac.uk/data_request/cif, Cambridge Crystallographic Data Centre.
3. P. van der Sluis and A. L. Spek, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1990, **46**, 194-201.
4. Y. H. Zhao, M. H. Abraham and A. M. Zissimos, *J. Org. Chem.*, 2003, **68**, 7368-7373.
5. S. Bulut, P. Klose and I. Krossing, *Dalton T.*, 2011, **40**, 8114-8124.
6. T. Timofte, S. Pitula and A. V. Mudring, *Inorg. Chem.*, 2007, **46**, 10938-10940.
7. S. Bulut, P. Klose, M. M. Huang, H. Weingärtner, P. J. Dyson, G. Laurenczy, C. Friedrich, J. Menz, K. Kummerer and I. Krossing, *Chem. Eur. J.*, 2010, **16**, 13139-13154.
8. Y. Yu, W. Beichel, G. Dlubek, R. Krause-Rehberg, M. Paluch, J. Pionteck, D. Pfefferkorn, S. Bulut, C. Friedrich, N. Pogodina and I. Krossing, *PCCP*, 2012, **14**, 6856-6868.
9. G. Dlubek, Y. Yu, R. Krause-Rehberg, W. Beichel, S. Bulut, N. Pogodina, I. Krossing and C. Friedrich, *J. Chem. Phys.*, 2010, **133**, 124502.
10. S. Aparicio, R. Alcalde, B. Garcia and J. M. Leal, *J. Phys. Chem. B*, 2009, **113**, 5593-5606.
11. K. R. Harris, M. Kanakubo and L. A. Woolf, *J. Chem. Eng. Data*, 2007, **52**, 2425-2430.
12. A. Stoppa, O. Zech, W. Kunz and R. Buchner, *J. Chem. Eng. Data*, 2009, **55**, 1768-1773.
13. Z. Jiqin, C. Jian, L. Chengyue and F. Weiyang, *J. Chem. Eng. Data*, 2007, **52**, 812-816.
14. A. B. Pereiro, J. L. Legido and A. Rodriguez, *J. Chem. Thermodyn.*, 2007, **39**, 1168-1175.
15. O. Zech, A. Stoppa, R. Buchner and W. Kunz, *J. Chem. Eng. Data*, 2010, **55**, 1774-1778.
16. H. Tokuda, S. Tsuzuki, M. A. B. H. Susan, K. Hayamizu and M. Watanabe, *J. Phys. Chem. B*, 2006, **110**, 19593-19600.
17. S. Bulut, P. Eiden, W. Beichel, J. M. Slattery, T. F. Beyersdorff, T. J. S. Schubert and I. Krossing, *ChemPhysChem*, 2011, **12**, 2296-2310.
18. R. Seddon Kenneth, A. Stark and M.-J. Torres, in *Clean Solvents*, American Chemical Society, 2002, vol. 819, pp. 34-49.
19. P. Eiden, S. Bulut, T. Köchner, C. Friedrich, T. Schubert and I. Krossing, *J. Phys. Chem. B*, 2011, **115**, 300-309.