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**The crystal structures of 1-(polyfluorophenylmethyl)-3-methylimidazolium bromide salts**

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*Abstract* -

The crystal structures of 1-(2,3,5,6-tetrafluorophenylmethyl)-3-methylimidazolium bromide (**2**), 1-(2,3,4,5-tetrafluorophenylmethyl)-3-methylimidazolium bromide (**3**), 1-(2,4,6-trifluorophenylmethyl)-3-methylimidazolium bromide (**4**) and 1-(2,3,6-trifluorophenylmethyl)-3-methylimidazolium bromide (**5**) have been determined. The structures contain non-covalent interactions: hydrogen bonding, anion- $\pi$  and  $\pi$ - $\pi$  stacking interactions. The strengths of these interactions have been calculated using DFT. The structures and interactions are compared with those of 1-(2,3,4,5,6-pentafluorophenylmethyl)-3-methylimidazolium bromide (**1**) and 1-(2,6-difluorophenylmethyl)-3-methylimidazolium bromide (**6**).

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*Keywords*

Imidazolium salt, anion- $\pi$  interaction,  $\pi$ - $\pi$  stacking, hydrogen bonding, crystal structure, DFT calculation

## 1. Introduction

The crystal structures of fluoroaryl-substituted imidazolium salts have provided information on a range of relatively weak non-covalent interactions, in particular  $\pi$ - $\pi$  stacking [1–5] and anion- $\pi$  interactions [2,3,5–8], in the presence of much stronger charge-assisted hydrogen bonding. The dependence of the structural motifs on the combination of interactions is of importance in crystal engineering. Ultimately, the prediction and the control of crystal structures of this class of salts may be realized by the judicious choice of fluoroaryl substituents.

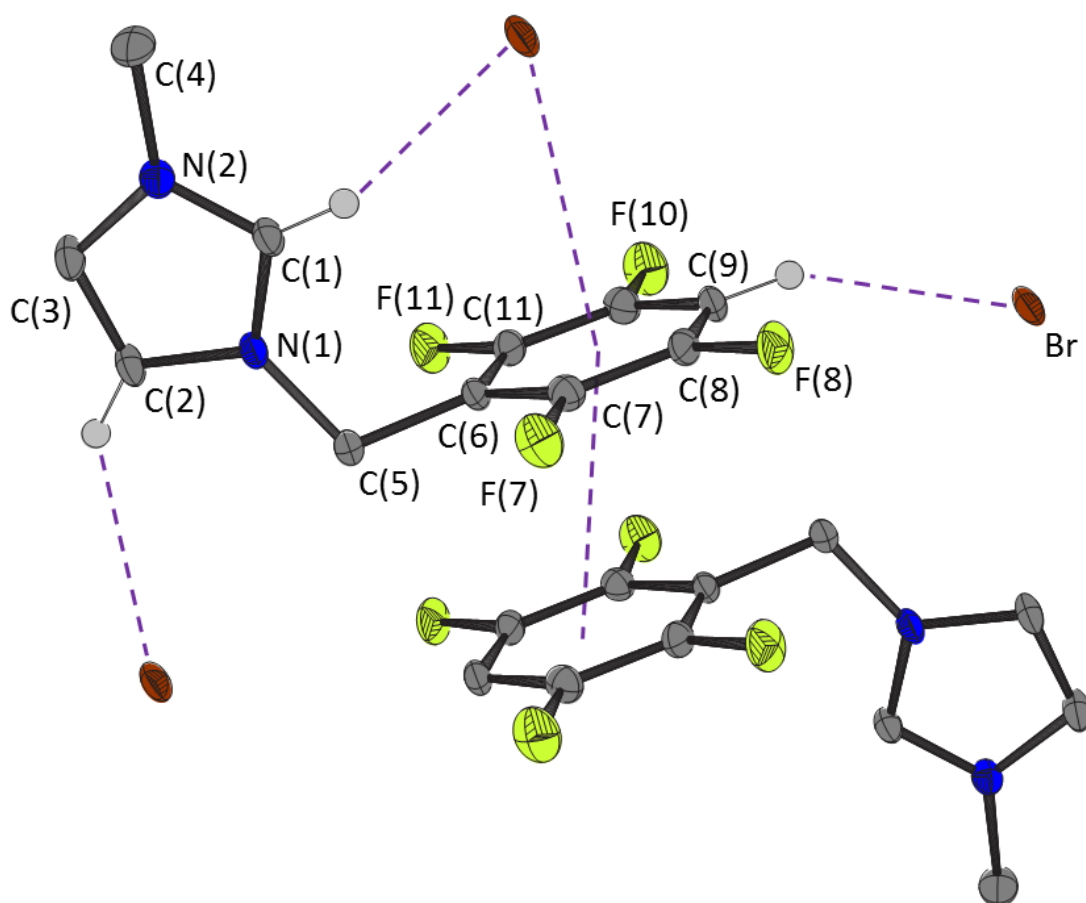
The majority of crystal structures of fluoroaryl-substituted imidazolium bromide salts possess a  $N_2C-H\cdots Br^-$  hydrogen bond [2,3,9-11], unless this position is blocked, as is the case for 2-methyl substituted imidazolium cations [12]. Typically this charge-assisted hydrogen bonding is the strongest inter-ion interaction [3,8,11-13]. Most structures also possess weaker  $C-H\cdots Br^-$  hydrogen bonding involving one or both of the other hydrogen atoms of the imidazolium ring. For structures of hydrates there may also be  $C-H\cdots O$  hydrogen bonding [3,11,14]. In a number of structures the interactions are augmented by anion- $\pi$  interactions, as occurs for 1-pentafluorophenylmethylimidazolium bromides [7,10].

Here we report the crystal structures and inter-ion interactions of two isomers of 1-(tetrafluorophenylmethyl)-3-methylimidazolium bromide and two isomers of 1-(trifluorophenylmethyl)-3-methylimidazolium bromide, and compare these with those of 1-(pentafluorophenylmethyl)-3-methylimidazolium bromide, **1** (CCDC code: ROTMEU) [7], and 1-(2,6-difluorophenylmethyl)-3-methylimidazolium bromide, **6** (CCDC code: GEWWIR) [11].

## 2. Results and discussion

1-(2,3,5,6-Tetrafluorophenylmethyl)-3-methylimidazolium bromide (**2**), 1-(2,3,4,5-tetrafluorophenylmethyl)-3-methylimidazolium bromide (**3**), 1-(2,4,6-trifluorophenylmethyl)-3-methylimidazolium bromide (**4**) and 1-(2,3,6-trifluorophenylmethyl)-3-methylimidazolium

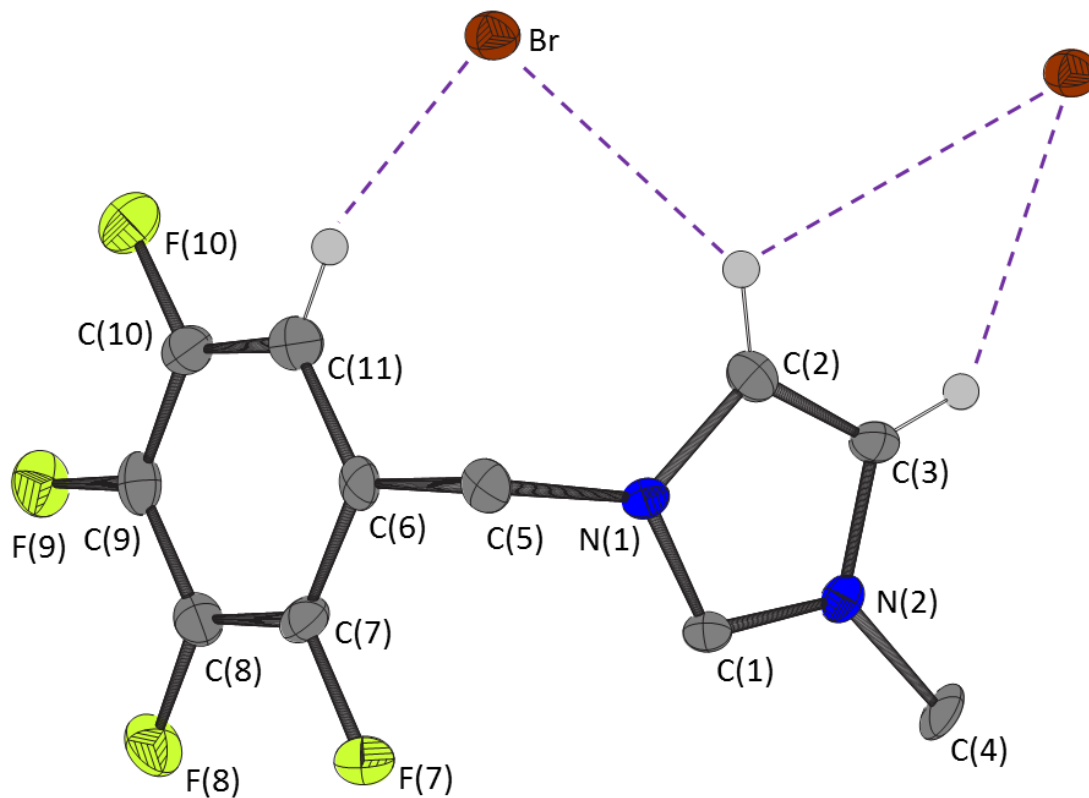
bromide (**5**) were prepared from 1-methylimidazole by treatment with the appropriate benzyl bromide, and crystals suitable for single crystal X-ray diffraction were grown from dichloromethane. Salts **4** and **5** crystallized as monohydrates in which pairs of water molecules form hydrogen-bonded rhomboids with pairs of bromide anions, as occurs in the crystal structure of the monohydrate of 1-(2,6-difluorophenylmethyl)-3-methylimidazolium bromide (**6**) [11]. Crystal data are given in Table 1, selected bond distances and angles are given in Table 2, and selected inter-ion distances, angles and energies are given in Table 3 together with those of **1** and **6**. The structures of the cations with the positions of ions with which they interact are shown in Figures 1 – 4.



**Fig. 1.** The structure of the cation of 1-(2,3,5,6-tetrafluorophenylmethyl)-3-methylimidazolium bromide (**2**) indicating the interactions with bromide anions close to C(1), C(2) and C(9) and the

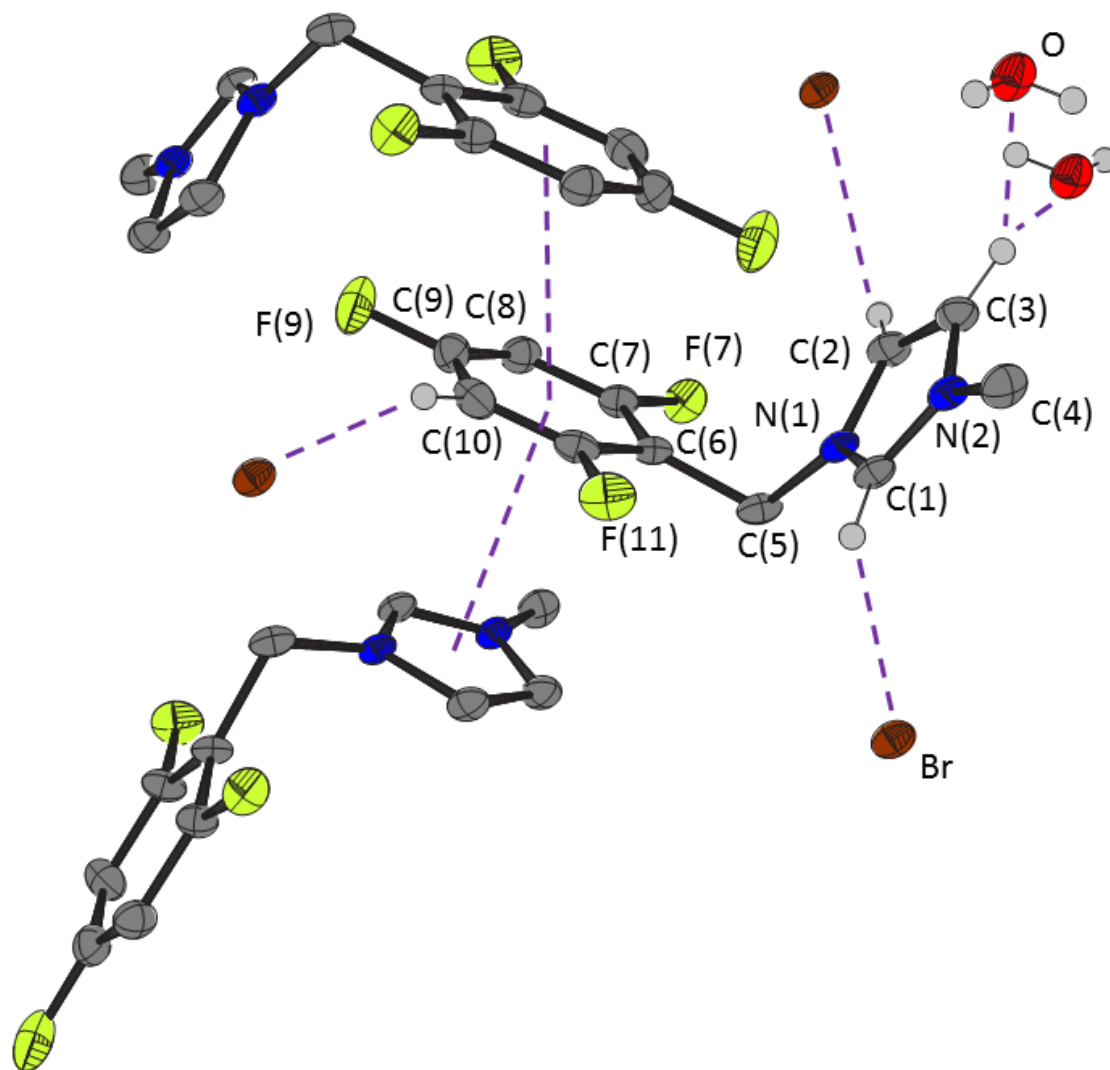
cation with which there is a stacking interaction. Thermal ellipsoids are at the 50% level.

Hydrogen atoms not involved in the interactions are omitted for clarity.

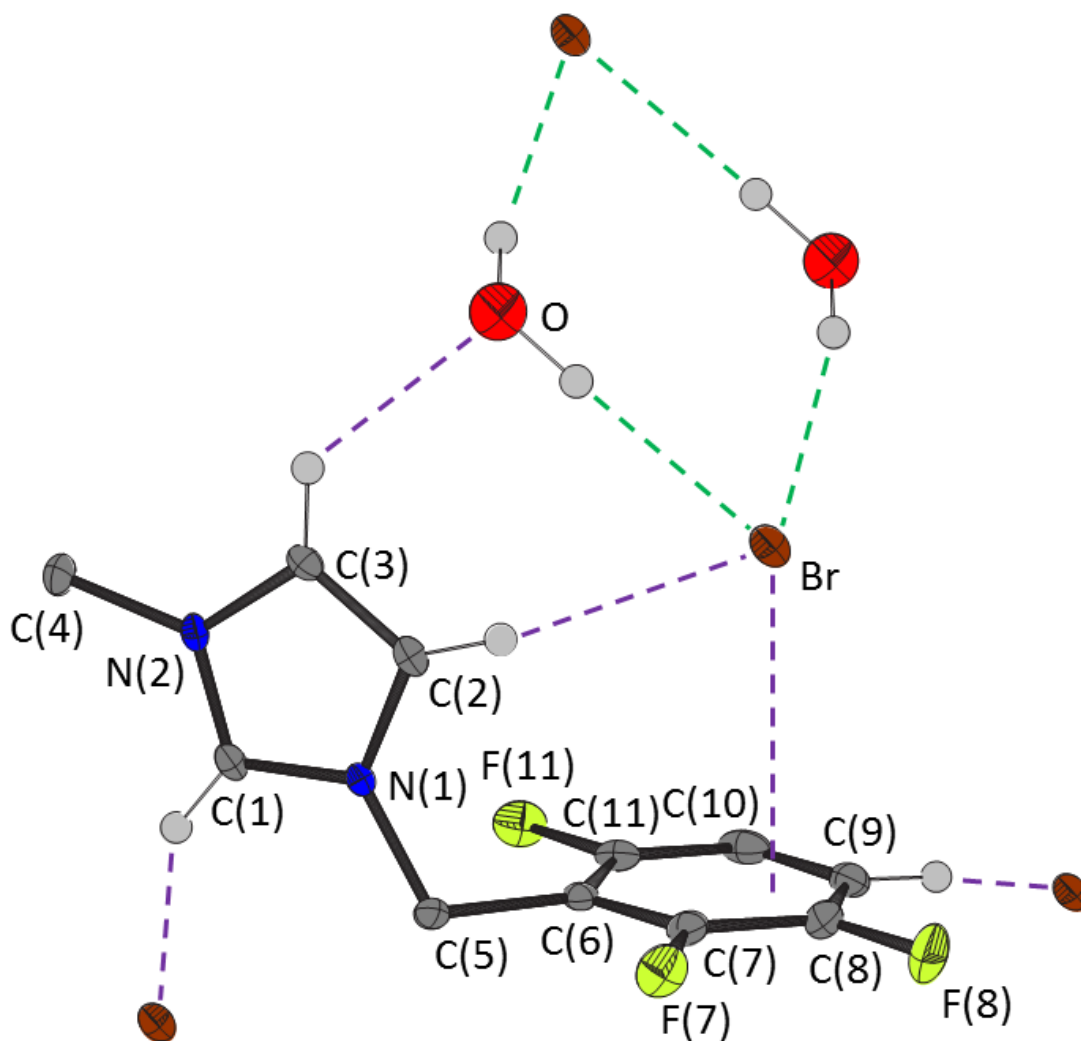


**Fig. 2.** The structure of the cation of 1-(2,3,4,5-tetrafluorophenylmethyl)-3-methylimidazolium bromide (**3**) indicating the interactions with bromide anions close to C(2), C(3) and C(11).

Thermal ellipsoids are at the 50% level. Hydrogen atoms not involved in the interactions are omitted for clarity.



**Fig. 3.** The structure of the cation of 1-(2,4,6-trifluorophenylmethyl)-3-methylimidazolium bromide (**4**) indicating the interactions with bromide anions and water molecules close to C(1), C(2), C(3) and C(10) and the cations with which there are stacking interactions. Thermal ellipsoids are at the 50% level. Hydrogen atoms not involved in the interactions are omitted for clarity.



**Fig. 4.** The structure of the cation of 1-(2,3,6-trifluorophenylmethyl)-3-methylimidazolium bromide (**5**) indicating the interactions with bromide anions and water molecules close to C(1), C(2), C(3) and C(9). Thermal ellipsoids are at the 50% level. Hydrogen atoms not involved in the interactions are omitted for clarity.

The structures of the imidazolium rings of the cations of **2** - **5** are similar, with bond distances and angles close to those calculated using the  $\omega$ B97xD functional [15] with the 6-311G++(2d,2p) basis set for the isolated cations in the gas phase (Table 2). The planes defined by the atoms of the imidazolium and aryl rings are approximately orthogonal for the cations of **2** and **5**, whereas those of **3** and **4** are 67.5 and 75.0° respectively. The calculated angles between



the planes lie between 71.8 and 79.0°, indicating that inter-ion interactions have a significant impact upon the structures of **2** and **5**.

Consistent with other imidazolium bromide salts, including **1** and **6**, there are bromide anions close to C(1) of cations of **2**, **4** and **5** with geometric parameters (Table 3) indicative of hydrogen bonding. In particular, the C(1)⋯Br<sup>-</sup> distances are less than 4.05 Å, the sum of the van der Waals radius of carbon (1.70 Å) [16] and the corrected value of the van der Waals' radius of the bromide anion (2.35 Å) [17]. The energies of the interactions, calculated for ion pairs in the gas phase using the ωB97xD functional [15] with the 6-311G++(2d,2p) basis set, for **1**, **2** and **4** – **6** are consistent with those of other salts. The energies show a correlation with the C(1)⋯Br<sup>-</sup> distance, except for that of salt **2** for which the interaction is augmented by an anion–π interaction. Surprisingly there is no bromide anion close to C(1) in the crystal structure of **3** (*vide infra*).

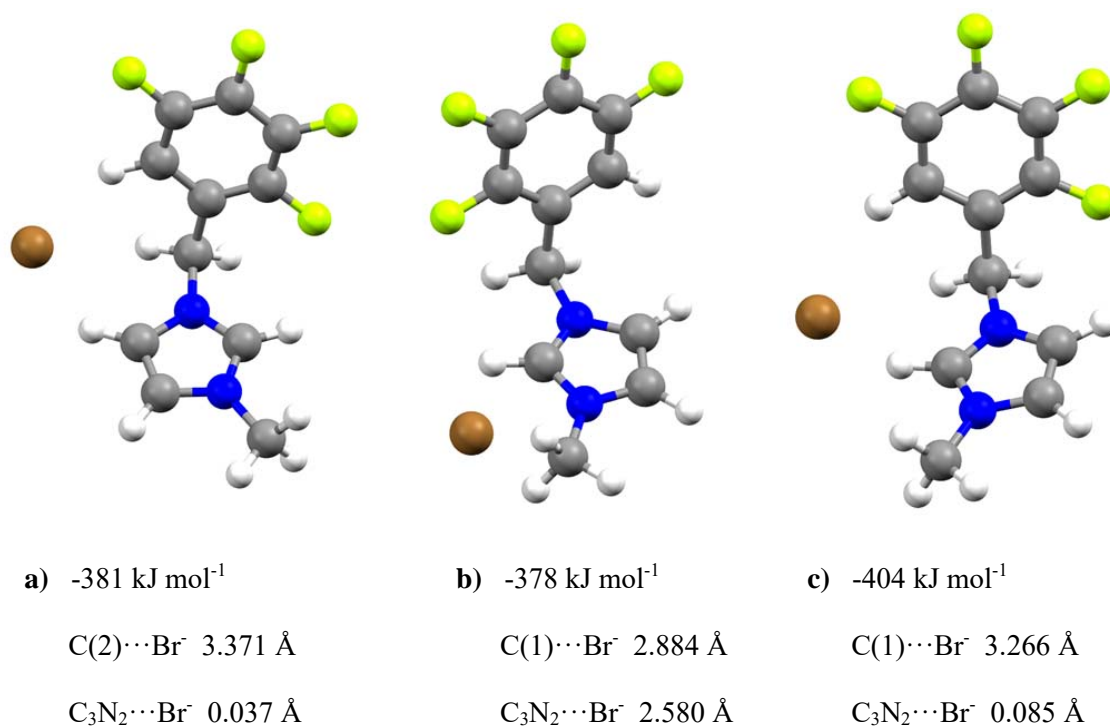
For all the salts a bromide anion is also close to C(2) with geometric parameters indicative of C(2)–H⋯Br<sup>-</sup> hydrogen bonding (Table 3). For **1**, **4**, **5** and **6** this bromide anion is also positioned close to a face of the polyfluoroaryl ring suggesting an anion–π interaction. Calculations of the interaction energies between a bromide anion and polyfluorotoluene using the atom positions of the salts indicate that this interaction is significant for **1** and **5**, less so for **4** and negligible for **6** (Table 3).

The crystal structure of **3** contains two bromide anions close to C(2). The closer one is also close to C(3) indicating bifurcated hydrogen bonding. The more distant one is involved in hydrogen bonding with the tetrafluorophenyl ring (Figure 2): the C(11)⋯Br<sup>-</sup> distance is ca. 0.35 Å less than the sum of the van der Waal's radii of carbon and bromide and the C–C(11)⋯Br<sup>-</sup> angles are ca. 100° and 140° (Table 3). The energy of the analogous interaction between bromide and tetrafluorotoluene using the positions of the atoms of **3** was calculated to be -65 kJ mol<sup>-1</sup>, 26 kJ mol<sup>-1</sup> stronger than the anion–π interaction of **1**. As a consequence the energy of interaction between the cation and the bromide anion close to C(2) is stronger for **3** than those

for the other salts, which are dependent on the geometric parameters and the strength of the anion– $\pi$  interactions (Table 3). DFT calculations reveal that optimization of the bromide close to C(2) leads to an increase in stabilization of 19 kJ mol<sup>-1</sup> resulting from the anion moving ca. 0.5 Å closer to C(2) and ca. 0.1 Å closer to C(11) (Figure 5a).

The structure of **3** cannot accommodate both an anion– $\pi$  interaction and a C(11)–H $\cdots$ Br<sup>-</sup> interaction because the C(1)–N(1)–C(5)–C(6) angle needs to be close to 0 or 180° for the former but close to 90° for the latter. As a consequence of the conformation of the cation, if there were a bromide anion close to C(1) it would also be close to F(7) and a presumably repulsive F $\cdots$ Br<sup>-</sup> interaction would arise. This would decrease the attraction between the cation and an anion in this position. Indeed the energy of interaction between the bromide anion and cation in the same relative positions, but with the tetrafluorophenyl rotated by 180° (N(1)–C(5)–C(6)–C(11) 82.4°) was calculated to be -252 kJ mol<sup>-1</sup>. Optimization of the position of the bromide anion gave an interaction that is ca. 20 kJ mol<sup>-1</sup> more favourable than that found for **3**, but with the anion displaced from the plane of the imidazolium ring and the tetrafluorophenyl group (Figure 5b). The more favourable interaction in this conformation is presumably a consequence of the anion being ca. 1.8 Å closer to the midpoint of the N $\cdots$ N axis (3.28 Å *cf.* 5.05 Å), which is considered to be the centre of positive charge [13]: the Coulombic attraction between the anion and a positive charge at this point is considerably stronger (423 *cf.* 275 kJ mol<sup>-1</sup>).

An alternative conformation with both C(1)–H $\cdots$ Br<sup>-</sup> and C(11)–H $\cdots$ Br<sup>-</sup> interactions is possible (N(1)–C(5)–C(6)–C(11) -97.5°) (Figure 5c). Optimization of the position of the bromide anion for this conformation gave an interaction that is 42 kJ mol<sup>-1</sup> more favourable than that found for **3**, but the anion is ca. 1 Å closer to the midpoint of the N $\cdots$ N axis giving a stronger Coulombic interaction (347 *cf.* 275 kJ mol<sup>-1</sup>). It is presumed that this conformation is not adopted because of the interactions with surrounding ions.



**Fig. 5.** Comparison of conformations and their energies of 1-(2,3,4,5-tetrafluorophenylmethyl)-3-methylimidazolium bromide (**3**): **a**) the experimental structure with the bromide anion position optimized close to C(2), **b**) the bromide anion position optimized close to C(1) and **c**) the bromide anion position optimized close to C(1) with the tetrafluorophenyl ring orientated to provide C(11)—H $\cdots$ Br $^-$  hydrogen bonding.

The crystal structure of **3** is the only other one to possess a short C(3) $\cdots$ Br $^-$  distance. Consistent with other studies [8,11,13] the interaction energies follow the order C(1)—H $\cdots$ Br $^-$  > C(2)—H $\cdots$ Br $^-$  > C(3)—H $\cdots$ Br $^-$  for each salt. The crystal structures of **4** and **6** contain two water molecules close to C(3) with geometric parameters that suggest hydrogen bonding. The energies of these interactions are attractive by ca.  $10 \text{ kJ mol}^{-1}$ . The structure of **5** contains one water

molecule close to C(3), but the geometry around C(3) and the energy indicate that there is little or no hydrogen bonding.

All the crystal structures, except that of **1**, possess short aryl C $\cdots$ Br $^-$  distances suggestive of hydrogen bonding. The energies of interaction between the respective polyfluorotoluene and bromide using the positions of the atoms of the salts follows the order **3** > **5** > **4**  $\approx$  **6** > **2** (Table 3). This order results from a combination of the C $\cdots$ Br $^-$  distance, the displacement of the bromide anion from the plane of the aryl ring, and the degree of fluorination, which affects the acidity of the hydrogen atoms [18]. The hydrogen atoms of the tetrafluorophenyl rings are expected to be the most acidic, and this is reflected in the strongest interaction being C(11)–H $\cdots$ Br $^-$  for **3**. However, since the bromide anion for interaction in **2** is a considerable distance out of the plane of the aryl ring, and thus the C(9)–H $\cdots$ Br $^-$  angle is far from linear, this interaction is the weakest, despite the C $\cdots$ Br $^-$  distance being the shortest. The interaction for **5** is stronger than that for the other trifluorinated salt, **4**, because the bromide anion is closer.

The crystal structures of **2**, **4** and **6** possess  $\pi$ – $\pi$  stacking between parallel polyfluoroaryl rings separated by ca. 3.5 Å. The energies of these interactions calculated for appropriate toluene rings correlate with the centroid to plane distance (Table 3) being similar for **4** and **6** and larger for **2**. Similar energies were calculated for the interaction between the imidazole molecules, except for **6** [11] for which there is a close contact between C(10) and the imidazole ring of the adjacent molecule, and evidently a significant C–H $\cdots$  $\pi$  interaction. Additionally the crystal structures of **4** and **6** contain  $\pi$ – $\pi$  stacking between the polyfluoroaryl and imidazolium rings. The interactions between the appropriate polyfluorotoluenes and 1,3-dimethylimidazolium were calculated to be ca. -40 kJ mol $^{-1}$ .

### 3. Conclusions

A number of interactions occur in the crystal structures of 1-polyfluorophenylmethyl-3-imidazolium bromide salts **1** - **6**. Hydrogen bonding involving the imidazolium ring occurs with all the salts. C(1)—H $\cdots$ Br $^-$  interactions occur with all the salts except for **3** and is the strongest interaction. C(2)—H $\cdots$ Br $^-$  interactions occur for all the salts and are typically *ca.* 40 kJ mol $^{-1}$  weaker than the respective C(1)—H $\cdots$ Br $^-$  interaction. That for salt **3** is augmented by a phenyl C—H $\cdots$ Br $^-$  interaction, which results in a combined strength similar to that of the C(1)—H $\cdots$ Br $^-$  interaction of salt **1**. C(3)—H $\cdots$ Br $^-$  interactions are evident in the structures of **1** and **3** and C(3)—H $\cdots$ OH $_2$  interactions occur in the hydrates **4**, **5** and **6**. All the salts except **3** and **6** possess anion $\cdots\pi$  interactions, which is strongest for **1** and **2** which have a greater degree of fluorination than **4** and **5**. These interactions support the C(2)—H $\cdots$ Br $^-$  interactions of **1**, **4** and **5**, and the C(1)—H $\cdots$ Br $^-$  interaction of **2**. There is also hydrogen bonding involving the phenyl group, except for **1** which possesses no phenyl hydrogen atoms.

## 4. Experimental

### 4.1 Instrumentation

The  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  and  $^{19}\text{F}$  NMR spectra were recorded in  $\text{CDCl}_3$  using Bruker DRX300 or DPX400 spectrometers.  $^1\text{H}$  (300.13 or 400.14 MHz) were referenced internally using the residual protio solvent resonance relative to  $\text{SiMe}_4$  ( $\delta$  0),  $^{13}\text{C}$  (100.61 MHz) externally to  $\text{SiMe}_4$  ( $\delta$  0), and  $^{19}\text{F}$  (282.40 MHz) externally to  $\text{CFCl}_3$  ( $\delta$  0). All chemical shifts are quoted in  $\delta$  (ppm), using the high frequency positive convention, and coupling constants in Hz. Elemental analyses were carried out by the Campbell Microanalytical Laboratory, The University of Otago. The mass spectra were recorded on a Bruker Daltonics micrOTOF spectrometer.

### 4.2 Materials

1-Methylimidazole (Aldrich) and 2,3,5,6-tetrafluorobenzyl bromide, 2,3,4,5-tetrafluorobenzyl bromide, 2,4,6-trifluorobenzyl bromide and 2,3,6-trifluorobenzyl bromide (Apollo Scientific) were used as supplied.

#### 4.3 Preparation of 1-(2,3,5,6-tetrafluorophenylmethyl)-3-methylimidazolium bromide (2)

1-Methylimidazole (0.17 g, 2.1 mmol) was added to 2,3,5,6-tetrafluorobenzyl bromide (0.50 g, 2.1 mmol) in dichloromethane (30 cm<sup>3</sup>). The mixture was maintained at ambient temperature for 4 days. The solvent was removed by rotary evaporation affording the product as a white powder. Yield 0.643 g (97%). MS: C<sub>11</sub>H<sub>9</sub>F<sub>4</sub>N<sub>2</sub> requires 245.0702; found [M - Br]<sup>+</sup> 245.0939. <sup>1</sup>H ((CD<sub>3</sub>)<sub>2</sub>SO): δ = 9.22 (1H, br s, N<sub>2</sub>CH), 8.05 (1H, m, C<sub>6</sub>H), 7.79 (1H, br s, HCCH), 7.74 (1H, br s, HCCH), 5.63 (2H, s, CH<sub>2</sub>), 3.84 (3H, s, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR ((CD<sub>3</sub>)<sub>2</sub>SO): δ = 145.9 (dm, <sup>1</sup>J<sub>CF</sub> = 246 Hz, CF), 145.2 (dm, <sup>1</sup>J<sub>CF</sub> = 249 Hz, CF), 137.6 (s, N<sub>2</sub>CH), 124.4 (s, CHCH), 123.1 (s, CHCH), 113.8 (t, <sup>2</sup>J<sub>CF</sub> = 17 Hz, C<sub>para</sub> or C<sub>ipso</sub>), 108.8 (t, <sup>2</sup>J<sub>CF</sub> = 24 Hz, C<sub>para</sub> or C<sub>ipso</sub>), 36.4 (s, NCH<sub>3</sub>). The NCH<sub>2</sub> resonance is obscured by that of (CD<sub>3</sub>)<sub>2</sub>SO. <sup>19</sup>F ((CD<sub>3</sub>)<sub>2</sub>SO): δ = -138.63 (2F, AA'BB'X spin system), -142.09 (2F, AA'BB'X spin system).

#### 4.4 Preparation of 1-(2,3,4,5-tetrafluorophenylmethyl)-3-methylimidazolium bromide (3)

1-Methylimidazole (0.51 g, 1.3 mmol) and 2,3,4,5-tetrafluorobenzyl bromide (1.51 g, 6.2 mmol) were treated as in 4.3. Yield 1.78 g (88%). MS: C<sub>11</sub>H<sub>9</sub>F<sub>4</sub>N<sub>2</sub> requires 245.0702; found [M - Br]<sup>+</sup> 245.0708. <sup>1</sup>H ((CD<sub>3</sub>)<sub>2</sub>SO): δ = 9.33 (1H, s, N<sub>2</sub>CH), 7.85 (1H, m, HCCH), 7.79 (1H, m, HCCH), 7.74 (1H, m, C<sub>6</sub>H), 5.61 (2H, s, CH<sub>2</sub>), 3.88 (3H, s, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR ((CD<sub>3</sub>)<sub>2</sub>SO): δ = 146.9 (dm, <sup>1</sup>J<sub>CF</sub> = 247 Hz, CF), 146.1 (dm, <sup>1</sup>J<sub>CF</sub> = 247 Hz, CF), 140.7 (m, CF), 140.5 (m, CF), 137.5 (s, N<sub>2</sub>CH), 124.4 (s, CHCH), 122.8 (s, CHCH), 118.7 (m, CH<sub>ortho</sub> or C<sub>ipso</sub>), 113.5 (dm, <sup>2</sup>J<sub>CF</sub> = 20 Hz, CH<sub>ortho</sub> or C<sub>ipso</sub>), 45.5 (s, CH<sub>2</sub>), 36.4 (s, NCH<sub>3</sub>). <sup>19</sup>F ((CD<sub>3</sub>)<sub>2</sub>SO): δ = -139.07 (1F, m), -141.46 (1F, m), -155.10 (1F, m), -155.68 (1F, m).

#### 4.5 Preparation of 1-(2,4,6-trifluorophenylmethyl)-3-methylimidazolium bromide (4)

1-Methylimidazole (0.10 g, 1.3 mmol) and 2,4,6-trifluorobenzyl bromide (0.31 g, 1.4 mmol) were treated as in 4.3. Yield 1.81 g (92%). Anal. Calc. for  $C_{11}H_{10}BrF_3N_2$ : C, 43.0; H, 3.3; N, 9.1. Found: C, 43.2; H, 3.2; N, 9.3%.  $^1H$  ( $CDCl_3/(CD_3)_2SO$ ):  $\delta$  = 9.72 (1H, s,  $N_2CH$ ), 7.62 (1H, m, HCCH), 7.41 (1H, m, HCCH), 6.80 (2H, tm,  $^3J_{FH}$  = 8.0 Hz,  $H_{meta}$ ), 5.48 (2H, s,  $CH_2$ ), 3.95 (3H, s,  $CH_3$ ).  $^{19}F$  ( $CDCl_3/(CD_3)_2SO$ ):  $\delta$  = -102.85 (1F, quint,  $^3J_{FH}$  = 8.0 Hz,  $^4J_{FF}$  = 8.0 Hz,  $F_{para}$ ), -110.51 (2F, t,  $^3J_{FH}$  = 8.0 Hz,  $^4J_{FF}$  = 8.0 Hz,  $F_{ortho}$ ).

#### 4.6 Preparation of 1-(2,3,6-trifluorophenylmethyl)-3-methylimidazolium bromide (**5**)

1-Methylimidazole (0.51 g, 6.2 mmol) and 2,3,6-trifluorobenzyl bromide (1.41 g, 6.3 mmol) were treated as in 4.3. Yield 0.56 g (30%). Anal. Calc. for  $C_{11}H_{10}BrF_3N_2$ : C, 43.0; H, 3.3; N, 9.1. Found: C, 42.5; H, 3.4; N, 9.0%.  $^1H$  ( $CDCl_3/(CD_3)_2SO$ ):  $\delta$  = 9.50 (1H, s,  $N_2CH$ ), 7.69 (1H, m, HCCH), 7.58 (1H, m, HCCH), 7.37 (1H, ddd,  $J$  = 18.7, 9.2, 5.1 Hz,  $C_6H_2$ ), 7.04 (1H, ddd,  $J$  = 8.8, 3.6, 2.2 Hz,  $C_6H_2$ ), 5.46 (2H, s,  $CH_2$ ), 3.91 (3H, s,  $CH_3$ ).  $^{19}F$  ( $CDCl_3/(CD_3)_2SO$ ):  $\delta$  = -118.64 (1F, m), -136.49 (1F, dd,  $J$  = 21.0, 8.7 Hz), -140.58 (1F, m).

#### 4.7 X-ray crystallography

Crystals of **2** - **5** were obtained by slow evaporation of solvent from solutions in dichloromethane. Crystal data are listed in Table 1. Diffraction data were collected on an Agilent SuperNova, single source at offset, Atlas diffractometer with graphite-monochromated Cu— $K_\alpha$  radiation. The structures were solved using Olex2 [19] structure solution programme using Charge Flipping and refined with the olex2.refine [20] refinement package using Gauss-Newton minimization. The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atom positions were added in idealized positions and a riding model with fixed thermal parameters ( $U_{ij}$  = 1.2 $U_{eq}$  for the atom to which they are bonded (1.5 for  $CH_3$ )) was used for subsequent refinements. The function minimized was  $\Sigma[w(|F_o|^2 - |F_c|^2)]$  with reflection weights  $w^{-1} = [\sigma^2 |F_o|^2 + (g1P)^2 + (g2P)]$  where  $P = [\max |F_o|^2 + 2|F_c|^2]/3$ .

CCDC 1959896 (2), 1959897 (3), 1026822 (4) and 1959898 (5) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

#### 4.8 DFT calculations

DFT calculations were performed using Gaussian09 [21] with the long range corrected functional  $\omega$ B97XD [15] method and the 6-311G++(2d,2p) basis set. The energies of interaction were calculated as the difference between the difference between the energy of the species and the sum of those of its components. The C–H bond lengths were adjusted to 1.083 Å before calculation of their energies [22].

## 5. Acknowledgement

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**Table 1**

Crystallographic data for 1-(2,3,5,6-tetrafluorophenylmethyl)-3-methylimidazolium bromide **2**, 1-(2,3,4,5-tetrafluorophenylmethyl)-3-methylimidazolium bromide **3**, 1-(2,4,6-trifluorophenylmethyl)-3-methylimidazolium bromide **4** and 1-(2,3,6-trifluorophenylmethyl)-3-methylimidazolium bromide **5**.<sup>a</sup>

	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>
Formula	C <sub>12</sub> H <sub>11</sub> BrF <sub>4</sub> N <sub>2</sub>	C <sub>12</sub> H <sub>11</sub> BrF <sub>4</sub> N <sub>2</sub>	C <sub>11</sub> H <sub>12</sub> BrF <sub>3</sub> N <sub>2</sub> .H <sub>2</sub> O	C <sub>11</sub> H <sub>12</sub> BrF <sub>3</sub> N <sub>2</sub> .H <sub>2</sub> O
Formula weight	325.10	325.10	325.13	325.13
Crystal system	triclinic	monoclinic	monoclinic	triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> , Å	7.3179(4)	8.6892(3)	7.40688(9)	7.3004(3)
<i>b</i> , Å	8.5467(3)	5.9475(2)	12.32937(15)	8.6741(4)
<i>c</i> , Å	10.3401(4)	23.3257(9)	14.00431(18)	10.7786(4)
$\alpha$ , °	101.841(4)	—	—	75.745(3)

$\beta$ , °	108.511(4)	97.663(4)	98.9093(11)	88.621(3)
$\gamma$ , °	93.629(4)	—	—	70.611(4)
$V$ , Å <sup>3</sup>	594.42(5)	1194.69(8)	1263.47(3)	622.77(4)
$Z$	2	4	4	2
$D_c$ (g cm <sup>-3</sup> )	1.816	1.807	1.709	1.734
Crystal size (mm <sup>3</sup> )	0.029 × 0.077 × 0.651	0.200 × 0.076 × 0.120	0.112 × 0.211 × 0.305	0.217 × 0.395 × 0.575
$T$ (K)	100.0(1)	100.0(1)	100.4(6)	104(6)
$\lambda$ (Å)	1.54184	1.54184	1.54184	1.54184
$\mu$ (mm <sup>-1</sup> )	5.091	5.066	4.730	4.798
$\theta$ range (°)	4.64 → 73.70	3.82 → 74.08	4.80 → 73.46	4.24 → 73.47
Total reflections	6,668	7,023	11,752	6,001
Unique reflections ( $R_{int}$ )	2,315 (0.0309)	2,375 (0.0310)	2,480 (0.0344)	2,409 (0.0248)

Observed reflections [ $I > 2\sigma(I)$ ]	2,212	2,217	2,413	2,394
Parameters	164	164	171	161
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0230$ $wR_2 = 0.0600$	$R_1 = 0.0672$ $wR_2 = 0.1708$	$R_1 = 0.0247$ $wR_2 = 0.0696$	$R_1 = 0.0361$ $wR_2 = 0.0917$
$R$ indices (all data)	$R_1 = 0.0246$ $wR_2 = 0.0618$	$R_1 = 0.0704$ $wR_2 = 0.1730$	$R_1 = 0.0252$ $wR_2 = 0.0701$	$R_1 = 0.0366$ $wR_2 = 0.0921$
Weighting scheme	$w = 1/[\sigma^2(F_o)^2 + \{0.330 (F_o^2 + 2F_c^2)/3\}^2 + 0.4580 (F_o^2 + 2F_c^2)/3]$	$w = 1/[\sigma^2(F_o)^2 + 38.8989 (F_o^2 + 2F_c^2)/3]$	$w = 1/[\sigma^2(F_o)^2 + \{0.0460 (F_o^2 + 2F_c^2)/3\}^2 + 0.6170 (F_o^2 + 2F_c^2)/3]$	$w = 1/[\sigma^2(F_o)^2 + \{0.0510 (F_o^2 + 2F_c^2)/3\}^2 + 1.6820 (F_o^2 + 2F_c^2)/3]$
Max., min. $\Delta\rho$ ( $e\text{\AA}^{-3}$ )	0.317, -0.428	1.76, -1.26	0.258, -0.694	0.993, -0.804
Goodness of fit on $F^2$	1.046	1.009	1.044	1.039

<sup>a</sup> Estimated standard deviations are given in parentheses.

**Table 2**

Selected bond distances (Å) and angles (°) for 1-(2,3,5,6-tetrafluorophenylmethyl)-3-methylimidazolium bromide **2**, 1-(2,3,4,5-tetrafluorophenylmethyl)-3-methylimidazolium bromide **3**, 1-(2,4,6-trifluorophenylmethyl)-3-methylimidazolium bromide **4** and 1-(2,3,6-trifluorophenylmethyl)-3-methylimidazolium bromide **5**.

	<b>2</b>		<b>3</b>		<b>4</b>		<b>5</b>	
	exptl	calc	exptl	calc	exptl	calc	exptl	calc
N(1)—C(1)	1.336(2)	1.329	1.334(9)	1.328	1.334(2)	1.328	1.334(4)	1.328
N(2)—C(1)	1.322(3)	1.327	1.323(10)	1.327	1.322(2)	1.327	1.325(4)	1.327
N(1)—C(2)	1.384(2)	1.374	1.390(10)	1.375	1.377(2)	1.374	1.325(4)	1.374
N(2)—C(3)	1.376(3)	1.376	1.380(10)	1.376	1.380(2)	1.375	1.382(4)	1.375
C(2)—C(3)	1.349(3)	1.354	1.360(11)	1.353	1.349(3)	1.354	1.357(4)	1.353
N(1)—C(5)	1.471(2)	1.471	1.482(9)	1.472	1.471(2)	1.474	1.476(3)	1.472
N(2)—C(4)	1.464(2)	1.461	1.473(9)	1.461	1.467(2)	1.460	1.463(3)	1.461
C(5)—C(6)	1.504(3)	1.501	1.506(10)	1.503	1.505(2)	1.498	1.507(4)	1.500
N(1)—C(1)—N(2)	108.17(17)	108.8	108.8(7)	108.9	108.53(14)	108.8	108.5(2)	108.8
C(1)—N(1)—C(2)	108.74(16)	108.7	108.6(6)	108.5	108.61(14)	108.6	108.9(2)	108.7



C(1)—N(1)—C(5)	126.58(16)	125.5	124.8(6)	125.6	125.26(14)	125.4	123.6(2)	125.6
C(1)—N(2)—C(3)	109.21(16)	108.5	109.0(6)	108.5	108.81(14)	108.5	108.9(2)	108.5
C(1)—N(2)—C(4)	124.66(17)	125.8	124.6(7)	125.9	124.89(14)	125.9	125.0(2)	126.0
N(1)—C(5)—C(6)	111.97(15)	111.6	110.6(6)	111.8	111.10(13)	112.0	111.7(2)	111.7
C(1)—N(1)—C(5)—C(6)	-31.5(3)	-81.4	-80.3(9)	104.5	106.0(2)	95.7	146.5(3)	99.2
C(2)—N(1)—C(5)—C(6)	153.9(2)	93.9	101.8(8)	-71.5	-71.2(2)	-79.5	-39.5(4)	-76.8
N(1)—C(5)—C(6)—C(7)	103.2(2)	97.3	83.7(9)	-69.0	108.0(2)	99.3	111.8(3)	96.2
N(1)—C(5)—C(6)—C(11)	-78.8(2)	-82.4	-97.8(5)	110.9	-74.7(2)	-80.9	-70.8(4)	-83.7
$\angle$ C <sub>3</sub> N <sub>2</sub> C <sub>6</sub> <sup>b</sup>	86.9	72.1	67.5	79.0	75.0	72.2	89.3	71.8

<sup>a</sup> Estimated standard deviations are given in parentheses. <sup>b</sup> The angle subtended by the planes of the aryl and imidazolium rings

**Table 3**

Selected interionic bond distances (Å), angles (°) and energies of interaction for 1-(2,3,4,5,6-pentafluorophenylmethyl)-3-methylimidazolium bromide **1**, 1-(2,3,5,6-tetrafluorophenylmethyl)-3-methylimidazolium bromide **2**, 1-(2,3,4,5-tetrafluorophenylmethyl)-3-methylimidazolium bromide **3**, 1-(2,4,6-trifluorophenylmethyl)-3-methylimidazolium bromide **4**, 1-(2,3,6-trifluorophenylmethyl)-3-methylimidazolium bromide **5** and 1-(2,6-difluorophenylmethyl)-3-methylimidazolium bromide **6**.<sup>a</sup>

	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>
C(1)⋯Br <sup>-</sup>	3.479(2)	3.524(2)	—	3.660(1)	3.561(3)	3.648(1)
N(1)—C(1)⋯Br <sup>-</sup>	108.5(1)	138.6(1)	—	136.9(1)	140.2(2)	139.0(1)
N(2)—C(1)⋯Br <sup>-</sup>	143.2(1)	112.9(1)	—	111.7(1)	107.3(2)	110.5(1)
C <sub>3</sub> N <sub>2</sub> ⋯Br <sup>-</sup>	0.144(3)	0.240	—	0.904	1.017	0.769(2)
C <sub>6</sub> ⋯Br <sup>-</sup>	—	3.799	—	—	—	—
C <sub>6</sub> <sup>†</sup> ⋯Br <sup>-</sup>	—	4.002	—	—	—	—
E, kJ mol <sup>-1</sup>	-372	-376	—	-341	-352	-338
E [C <sub>6</sub> ⋯Br <sup>-</sup> ], kJ mol <sup>-1 b</sup>	—	-39	—	—	—	—

C(2)⋯Br <sup>-</sup>	3.667(2)	3.695(2)	3.666(7)	3.828(8)	3.794(2)	3.684(3)	3.760(2)		
N(1)—C(2)⋯Br <sup>-</sup>	130.6(1)	96.9(1)	163.2(5)	95.3(4)	139.9(1)	132.1(2)	145.1(1)		
C(3)—C(2)⋯Br <sup>-</sup>	119.6(1)	156.0(1)	76.7(4)	158.3(5)	102.4(1)	121.1(2)	103.0(1)		
C <sub>3</sub> N <sub>2</sub> ⋯Br <sup>-</sup>	0.978(3)	0.316	1.089	0.053	1.736	0.262	1.144(2)		
C <sub>6</sub> ⋯Br <sup>-</sup>	3.412(3)	—	—	—	4.410	3.795	4.382(4)		
C <sub>6</sub> <sup>†</sup> ⋯Br <sup>-</sup>	3.497(2)	—	—	—	5.258	4.041	5.487(2)		
E, kJ mol <sup>-1</sup>	-338	-330	-31	-362	-290	-313	-285		
E [C <sub>6</sub> ⋯Br <sup>-</sup> ], kJ mol <sup>-1 b</sup>	-39	—	—	—	-9	-17	-2		
C(3)⋯Br <sup>-</sup>	3.624(2)	—	3.606(8)		—	—	—		
N(2)—C(3)⋯Br <sup>-</sup>	99.0(1)	—	161.0(5)		—	—	—		
C(2)—C(3)⋯Br <sup>-</sup>	148.4(1)	—	81.7(5)		—	—	—		
C <sub>3</sub> N <sub>2</sub> ⋯Br <sup>-</sup>	1.116(3)	—	1.089		—	—	—		
E, kJ mol <sup>-1</sup>	-325	—	-313		—	—	—		
C(3)⋯O	—	—	—		3.298(3)	3.286(3)	3.194(4)	3.213(3)	3.413(3)

N(2)—C(3)⋯O	—	—	—	99.6(1)	158.3(1)	161.5(2)	104.6(1)	151.3(1)
C(2)—C(3)⋯O	—	—	—	139.5(1)	83.5(1)	91.5(2)	139.6(1)	86.0(1)
C <sub>3</sub> N <sub>2</sub> ⋯O	—	—	—	1.655	1.090	0.001	1.317(3)	1.503(3)
E [H(3)...OH <sub>2</sub> ], kJ mol <sup>-1</sup>	—	—	—	-7	-19	0	-14	-13
		x = 9	x = 11	x = 10		x = 9	x = 10	
C(x)⋯Br <sup>-</sup>	—	3.631(2)	3.706(7)	3.826(2)		3.743(3)	3.847(2)	
C(x-1)—C(x)⋯Br <sup>-</sup>	—	114.9(1)	139.7(5)	126.5(1)		123.8(1)	128.3(1)	
C(x+1)—C(x)⋯Br <sup>-</sup>	—	123.8(1)	100.4(5)	115.9(1)		91.4(2)	112.8(1)	
C <sub>6</sub> ⋯Br <sup>-</sup>	—	1.254	0.347	0.893		0.881	0.656	
E, kJ mol <sup>-1</sup>	—	-222	-362	-224		-224	-213	
E [C <sub>6</sub> ⋯Br <sup>-</sup> ], kJ mol <sup>-1 b</sup>	—	-26	-65	-30		-46	-29	
C <sub>6</sub> <sup>†</sup> ⋯C <sub>6</sub> <sup>†</sup>	—	3.603	—	4.180		—	4.196	
C <sub>6</sub> ⋯C <sub>6</sub> planes	—	3.397	—	3.516		—	3.726	
E(imidazole), kJ mol <sup>-1 c</sup>	—	-36	—	-20		—	-55	

E(toluene), kJ mol <sup>-1</sup> <sup>d</sup>	—	-37	—	-24	—	-19
C <sub>6</sub> <sup>†</sup> ...C <sub>3</sub> N <sub>2</sub> <sup>†</sup>	—	—	—	3.485	—	3.562
C <sub>6</sub> <sup>†</sup> ...C <sub>3</sub> N <sub>2</sub> plane	—	—	—	3.427	—	3.431
∠ C <sub>6</sub> ·C <sub>3</sub> N <sub>2</sub> <sup>f</sup>	—	—	—	4.4	—	6.4
E(C <sub>6</sub> ...C <sub>3</sub> N <sub>2</sub> ), kJ mol <sup>-1</sup> <sup>f</sup>	—	—	—	-41	—	-37

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<sup>a</sup> Estimated standard deviations are given in parentheses. Energies calculated using the functional ωB97XD [15] method and the 6-311G++(2d,2p) basis set. C<sub>3</sub>N<sub>2</sub> and C<sub>6</sub> indicate the planes of the imidazolium and polyfluorophenyl rings respectively. C<sub>3</sub>N<sub>2</sub><sup>†</sup> and C<sub>6</sub><sup>†</sup> indicate the centroids of the imidazolium and polyfluorophenyl rings respectively. <sup>b</sup> The energy of interaction between bromide and the appropriate polyfluorotoluene using the positions of the atoms determined experimentally for the imidazolium salt. <sup>c</sup> The energy of interaction two imidazole molecules using the positions of the atoms determined experimentally for the imidazolium salt. <sup>d</sup> The energy of interaction two polyfluorotoluene molecules using the positions of the atoms determined experimentally for the imidazolium salt. <sup>e</sup> The angle subtended by the planes of the aryl and imidazolium rings of adjacent cations. <sup>f</sup> The energy of interaction between 1,3-dimethylimidazolium and the appropriate polyfluorotoluene using the positions of the atoms determined experimentally for the imidazolium salt.