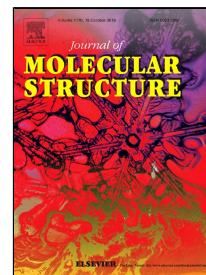# Accepted Manuscript

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The crystal structures of 1-(4-bromo-2,3,5,6-tetrafluorophenyl)-3-benzyl-methylimidazolium bromides

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Abstract -

The crystal structures of 1-(4-bromo-2,3,5,6-tetrafluorophenyl)-2-methyl-3-benzylimidazolium bromide (**8**) and 1-(4-bromo-2,3,5,6-tetrafluorophenyl)-3-benzyl-4-methylimidazolium bromide (**9**) have been determined by single crystal X-ray diffraction. Both crystal structures possess C(2)─H···Br⁻ hydrogen bonding and C─Br···Br⁻ halogen bonding. That of **8** also contains π–π stacking between bromotetrafluorophenyl and phenyl rings, and that of **9** also contains C(1)─H···Br⁻ hydrogen bonding and anion–π interactions. The crystal structure of **9** is similar to that of the non-methylated salt, 1-(4-bromo-2,3,5,6-tetrafluorophenyl)-3-benzylimidazolium bromide (**4**), with columns of alternating parallel bromotetrafluorophenyl rings and bromide.

2

1. Introduction

The crystal structures of 1-polyfluoroaryl-3-benzylimidazolium bromide salts display a range of interactions which are dependent on the nature of the polyfluoroaryl substituent (Figure 1) [1-6]. Charge-assisted hydrogen bonding [7,8] can occur between all of the hydrogen atoms of the imidazolium ring and three bromide anions, and this is evident in the crystal structures of 1-(2,3,5,6-tetrafluoro-4-pyridyl)-3-benzylimidazolium bromide (**1**) (CCDC reference: AMOCOV) [1,2], 1-(4-chloro-2,3,5,6-tetrafluorophenyl)-3-benzylimidazolium bromide (**2**) (CCDC reference: UQEHOP) [3,4] and 1-(4-iodo-2,3,5,6-tetrafluorophenyl)-3-benzylimidazolium bromide (**3**) (CCDC reference: TEMWIU) [3]. In the crystal structure of 1-(4-bromo-2,3,5,6-tetrafluorophenyl)-3-benzylimidazolium bromide (**4**) (CCDC reference: LIJPUR) only C(1)─H⋯Br⁻ and C(2)─H⋯Br⁻ hydrogen bonding is present [3,5], whilst the crystal structure of 1-(4-trifluoromethyl-2,3,5,6-tetrafluorophenyl)-3-benzylimidazolium bromide (**5**) (CCDC reference: GEFYUO) [6] possesses only C(1)─H⋯Br⁻ and C(3)─H⋯Br⁻ hydrogen bonding. π–π Stacking between the polyfluoroaryl and aryl rings [9] is evident in salts **1** and **2**, anion–π interactions [10] are evident in salts **1**, **4** and **5**, and an iodine lone pair–π interaction [11] is evident in salt **2**. Salts **3** and **4** also possess X⋯Br⁻ halogen bonding [12]. Since the hydrogen bonding is the strongest interaction [3], the bromide anions are expected to be positioned close to the three hydrogen atoms of the imidazolium ring, as observed for **1**, **2** and **3**. However, in cases where different interactions involve the same bromide anion, there is competition and the bromide is not located in an optimum position for the hydrogen bond. For example, in the crystal structure of **4** the bromide anions close to C(1) and C(2) are also involved in anion–π interactions with the ring. Consequently they are shifted away from the imidazolium ring and towards the bromotetrafluorophenyl ring (Figure 1d). For **5** the competing interactions appear sufficiently strong to move the bromide anion away from C(2) and to the normal to the centroid of the trifluoromethyltetrafluorophenyl ring (Figure 1e), the optimum position for an anion–π interaction.

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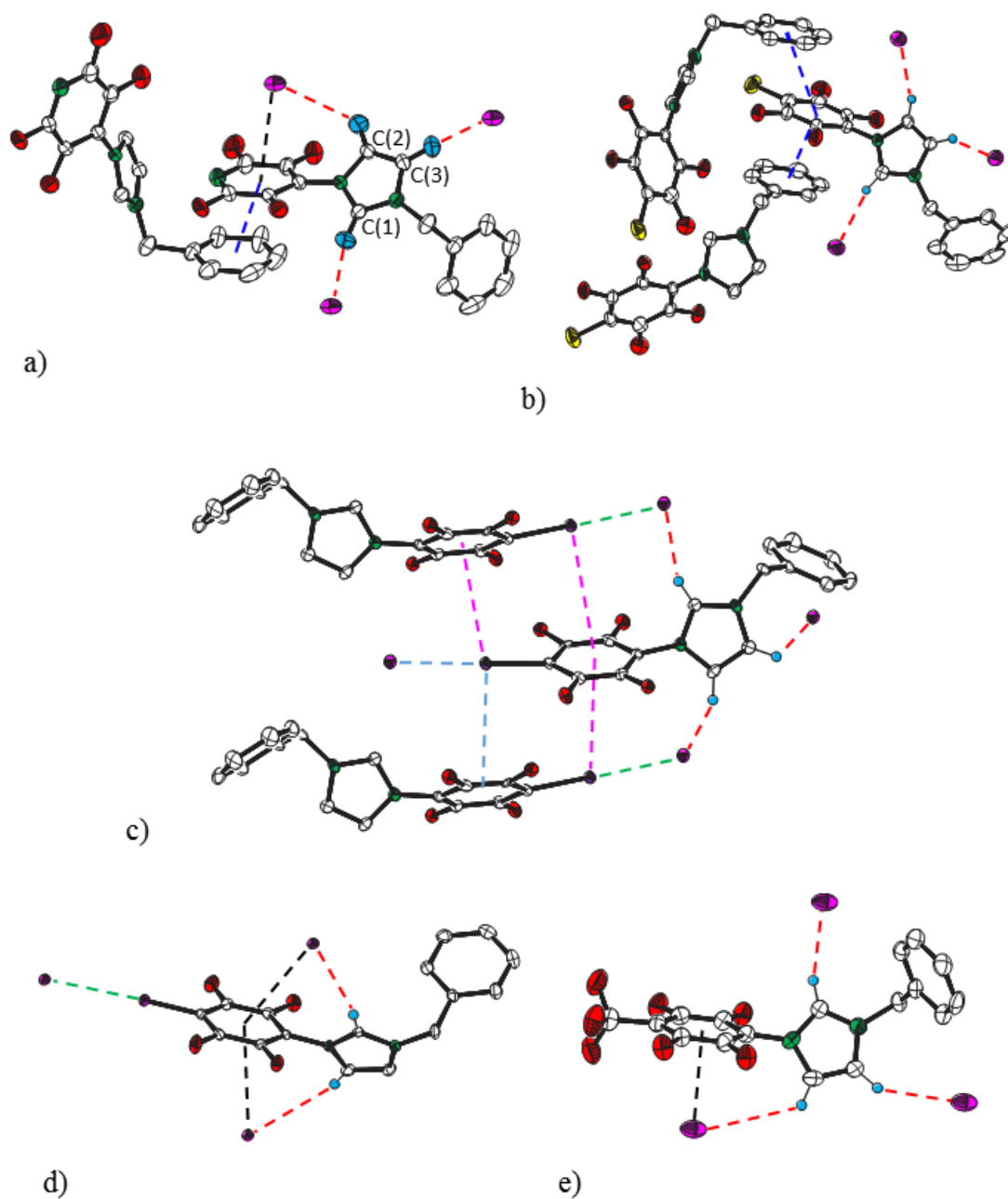
Figure 1. The structures of (a) 1-(2,3,5,6-tetrafluoro-4-pyridyl)-3-benzylimidazolium bromide (**1**), indicating the labelling of the imidazolium carbon atoms, (b) 1-(4-chloro-2,3,5,6-tetrafluorophenyl)-3-benzylimidazolium bromide (**2**), (c) 1-(4-iodo-2,3,5,6-tetrafluorophenyl)-3-benzylimidazolium bromide (**3**), (d) 1-(4-bromo-2,3,5,6-tetrafluorophenyl)-3-benzylimidazolium bromide (**4**) and (e) 1-(4-trifluoromethyl-2,3,5,6-tetrafluorophenyl)-3-benzylimidazolium bromide (**5**) showing the interactions (red C─H⋯Br⁻ hydrogen bonding,

blue π–π stacking, black anion–π, pink lone pair–π, green halogen bonding). Thermal ellipsoids are at the 50% level. Only hydrogen atoms involved in the interactions are included. The positions for those of **1** were determined by neutron diffraction, the positions for those of the other salts were calculated.

The hydrogen bonding interactions can be prevented by substitution of the relevant hydrogen atom by a methyl group. In this way, the C(1)─H···Br‾ and C(3)─H···Br‾ hydrogen bonding of **1** are precluded in the crystal structures of 1-(2,3,5,6-tetrafluoro-4-pyridyl)-2-methyl-3-benzylimidazolium bromide (**6**) (CCDC reference: JAFLIO) and 1-(2,3,5,6-tetrafluoro-4-pyridyl)-3-benzyl-4-methylimidazolium bromide (**7**) (CCDC reference: JAFXUM) respectively [2]. In both cases the C_6H_5···C_5F_4N···Br‾ motif and the C(2)─H···Br‾ hydrogen bonding are maintained, but the crystal structure of **6** differs significantly from that of **1**, whilst that of **7** is similar to that of **1** (Figure 2).

a)   b)
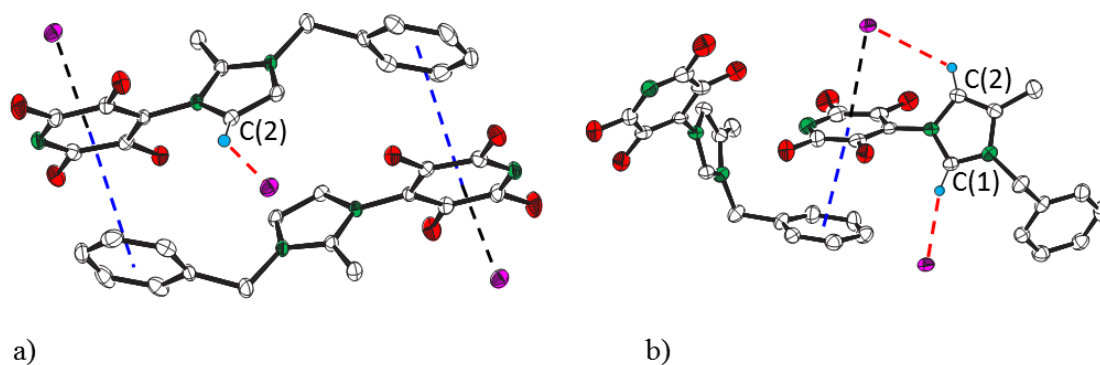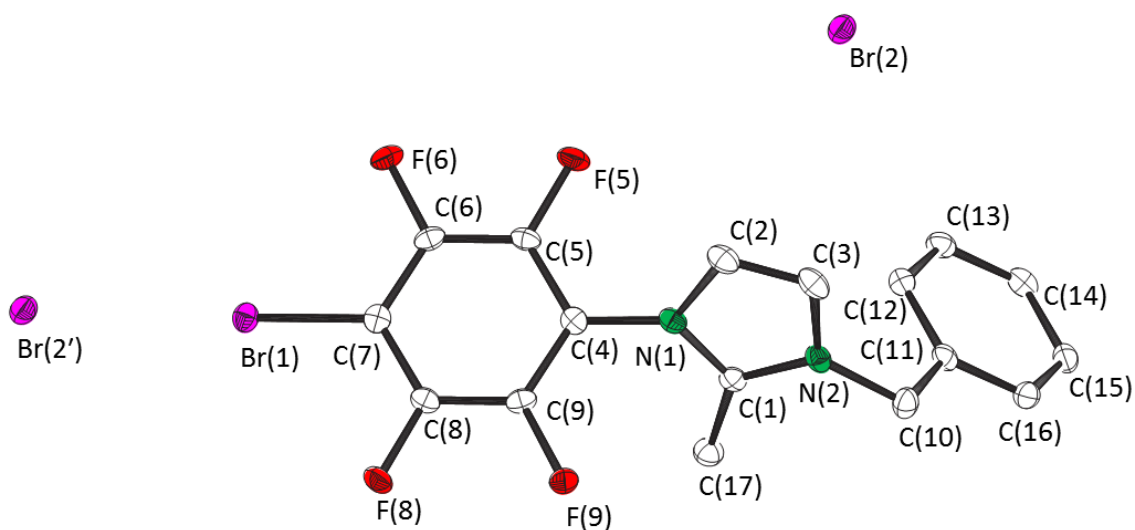
Figure 2. The structures of (a) 1-(2,3,5,6-tetrafluoro-4-pyridyl)-2-methyl-3-benzylimidazolium bromide (**6**), and (b) 1-(2,3,5,6-tetrafluoro-4-pyridyl)-3-benzyl-4-methylimidazolium bromide (**7**) showing the interactions (red C─H···Br‾ hydrogen bonding, blue π–π stacking, black anion–π). Thermal ellipsoids are at the 50% level. Hydrogen atoms are omitted for clarity.

The data for **1**, **6** and **7** indicate that preventing the C(1)─H···Br⁻ hydrogen bonding has a large impact on the crystal structure of the imidazolium salt, whilst preventing the C(3)─H···Br⁻ hydrogen bonding has a less pronounced effect. We wished to investigate whether the same is true for other 1-polyfluoroaryl-3-benzylimidazolium bromide salts, and chose to examine the effect of methyl groups in these positions on the crystal structure of 1-(4-bromo-2,3,5,6-tetrafluorophenyl)-3-benzylimidazolium bromide (**4**). Here we report the crystal structures of 1-(4-bromo-2,3,5,6-tetrafluorophenyl)-2-methyl-3-benzylimidazolium bromide (**8**) and 1-(4-bromo-2,3,5,6-tetrafluorophenyl)-3-benzyl-4-methylimidazolium bromide (**9**), and the results of a DFT study.

2. Results and discussion

1-(4-Bromo-2,3,5,6-tetrafluorophenyl)-2-methyl-3-benzylimidazolium bromide (**8**) and 1-(4-bromo-2,3,5,6-tetrafluorophenyl)-3-benzyl-4-methylimidazolium bromide (**9**) were prepared by treatment of the respective 1-(4-bromo-2,3,5,6-tetrafluorophenyl)methylimidazole with benzyl bromide. Salts **8** and **9** crystallized from methanol in the monoclinic space groups *P*2₁/c and *I*2/a, an alternative setting of *C*2/c, respectively, with one ion pair in the asymmetric unit. Crystal data are given in Table 1 and selected distances and angles are given in Table 2. The structures the cations of **8** and **9**, together with the positions of the closest bromide anions, are shown in Figures 3 and 4 respectively.

6

Figure 3. The structure of one of the cations of 1-(4-bromo-2,3,5,6-tetrafluorophenyl)-2-methyl-3-benzylimidazolium bromide (**8**) indicating the positions of the bromide anions close to C(2) and Br(1). Thermal ellipsoids are at the 50% level. Hydrogen atoms are omitted for clarity.
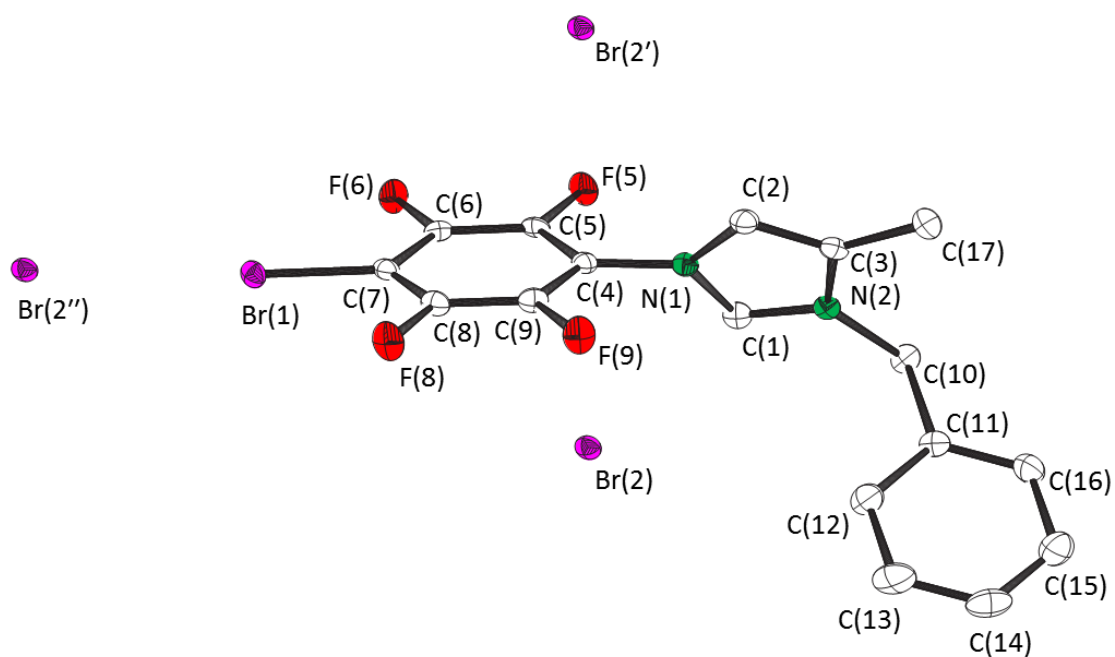
Figure 4. The structure of one of the cations of 1-(4-bromo-2,3,5,6-tetrafluorophenyl)-3-benzyl-4-methylimidazolium bromide (**9**) indicating the positions of the bromide anions close to C(1), C(2) and Br(1). Thermal ellipsoids are at the 50% level. Hydrogen atoms are omitted for clarity.

The bond distances and angles of the cations of **8** and **9** are similar to those calculated using the ωB97X-D [13] functional with the 6-311++G(2d,2p) basis set for the isolated cations in the gas phase (Table 2). The experimentally determined angle subtended by the planes of the halotetrafluorophenyl and imidazolium rings is ca. 20° larger than the calculated value for **8**, but similar for **9**. That between the planes of the halotetrafluorophenyl and phenyl rings is ca. 30° larger than the calculated value for **8**, and ca. 10° smaller for **9**. That between the planes of the phenyl and imidazolium rings is similar to the calculated value for both structures. The data indicate that although the crystal packing has a small effect on the bond distances and angles, it does effect the conformations of the cations.

The crystal structures of both salts show the presence of halogen bonding, similar in both geometry (Table 3) and energy (Table 4) to that found in salt **4**. The Br···Br⁻ distances are ca. 1 Å less than the sum of the van der Waals' radius of bromine (1.85 Å [14]) and the corrected value of the van der Waals' radius for bromide (2.35 Å [15]).

Consistent with replacing the C(1) hydrogen atom with a methyl group in **1**, salt **8** possesses a very different crystal structure to **4** (Figure 5). A bromide anion is close to both C(2) and C(3) with C···Br⁻ distances that are ca. 0.3 Å less than the sum of the van der Waals' radius of carbon (1.70 Å [14]) and the corrected value of the van der Waals' radius for bromide (2.35 Å [15]). The distances and geometry (Table 3) are consistent with bifurcated hydrogen bonding. The energy of interaction between the cation and this bromide anion was calculated to be similar to the analogous interaction for **4** (Table 4), and ca. 30 kJ mol⁻¹ greater than for a purely electrostatic interaction between the anion and the centre of the positive charge of the cation, which is considered to be the midpoint of the two nitrogen atoms [16]. This anion is too far
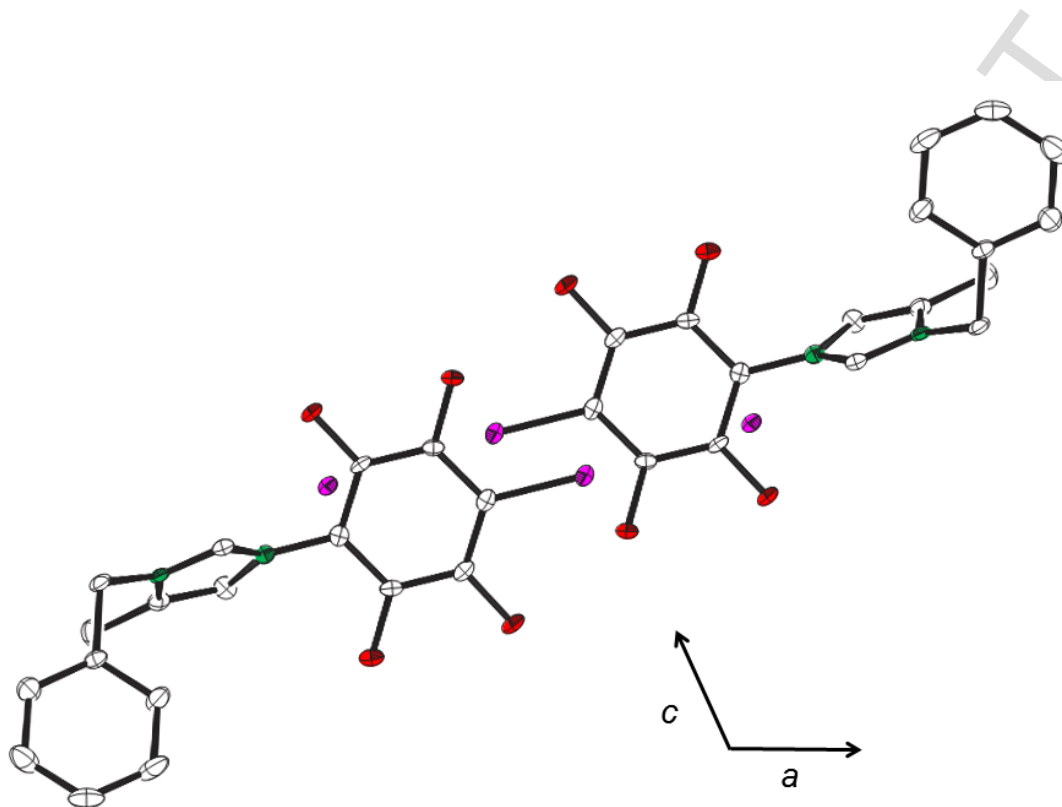
from the bromotetrafluorophenyl ring (Table 3) for there to be an anion–π interaction, as shown by the very low energy of interaction between a bromide anion and bromopentafluorobenzene calculated using the positions of the analogous atoms of **8** (Table 4). The bromotetrafluorophenyl ring of one cation is close to and almost parallel with the phenyl ring of another (Figure 5), with parameters (Table 3) that suggest a π–π stacking interaction. The energies of interaction between molecules of bromotetrafluorophenyl- and benzyl-imidazole and between molecules of bromopentafluorobenzene and toluene derived from the cations of **8** (using the positions of the relevant atoms) were calculated to be attractive by 44 and 38 kJ mol^{-1} respectively. These values are consistent with those obtained for similar model interactions for **2** [3], and with those calculated for interactions between toluene and hexafluorobenzene at a separation of 3.4 Å (-33.6 and -36.0 kJ mol^{-1} depending on the orientation) [17]. The interactions are ca. 50% stronger than that between indole and hexafluorobenzene at a separation of 3.26 Å (ca. -28 kJ mol^{-1}) [18]. There is no interaction involving the opposite face of the bromotetrafluorophenyl ring (Figure 5); the closest bromide anion and covalently bonded bromine atom are 4.5 Å and 4.0 Å from the ring's centroid, and displaced 3.0 and 2.2 Å respectively from the normal to the centroid.
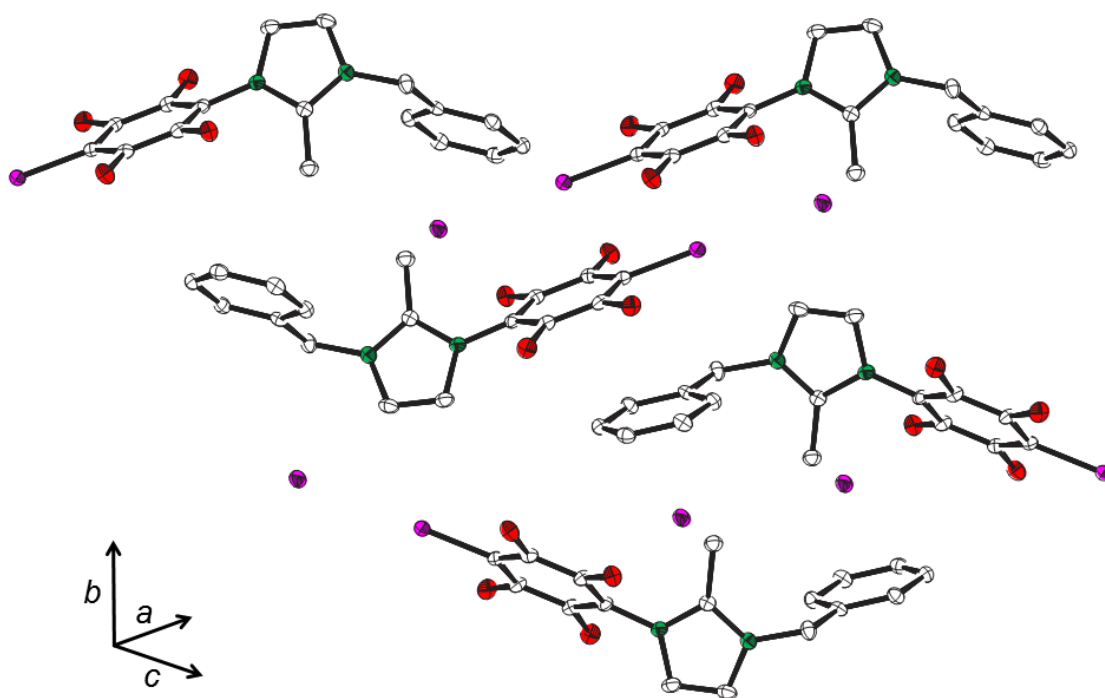
Figure 5. The crystal structure of 1-(4-bromo-2,3,5,6-tetrafluorophenyl)-2-methyl-3-benzylimidazolium bromide (**8**) viewed perpendicular to the b axis. Thermal ellipsoids are at the 50% level. Hydrogen atoms are omitted for clarity.

The crystal structure of **9** is similar to that of **4**, but this is not unexpected since there is no C(3)─H···Br⁻ hydrogen bonding with **4**. Both structures have columns of alternating parallel bromotetrafluorophenyl rings and bromide anions with similar geometric parameters (Table 3). The bromide anions close to C(1) and C(2) are involved in anion–π interactions with the bromotetrafluorophenyl ring. This is apparent from the energies of interaction between the bromide anions and cation compared to those calculated for purely electrostatic interactions between the anion and the centre of the positive charge of the cation, and the energies of interaction between the bromide anion and bromotetrafluorophenylimidazole and bromopentafluorobenzene calculated using the positions of the relevant atoms of salts **4** and **9** (Table 4). The bromide anion close to C(1) is closer to the imidazolium ring, whilst that close to C(2) is closer to the bromotetrafluorophenyl ring. The differences in the distances between the

10

two bromide positions are mirrored in the energies of the interactions. The bromide anions lie

ca. 0.5 Å outside the hexagonal prism defined by the carbon atoms for the

bromotetrafluorophenyl rings within a column (Figure 6), ca. 0.3 Å further than for salt **4**.

Figure 6. The arrangement of bromotetrafluorophenyl rings and bromide anions of 1-(4-bromo-2,3,5,6-tetrafluorophenyl)-3-benzyl-4-methylimidazolium bromide (**9**) viewed parallel to the *b* axis. Thermal ellipsoids are at the 50% level. Hydrogen atoms are omitted for clarity.

3. Conclusions

Preventing the C(1)─H···Br⁻ hydrogen bond of salt **4** by substitution of the hydrogen

atom by a methyl group, has a profound influence on the crystal structure. The Br···Br⁻ halogen

bonding persists, but the hydrogen bonding between the cation and anion becomes bifurcated,

rather than being restricted to just the C(2)─H moiety. There is no anion–π interaction, but π–π

stacking between the bromotetrafluorophenyl ring of one cation and the phenyl ring of another

11

occurs. In contrast, placing a methyl group on C(3) has a much smaller effect on the crystal structure, and that of **9** possesses similar features to that of **4**, in particular columns of alternating parallel bromotetrafluorophenyl rings and bromide anions. The impact of placing methyl groups in these positions on the crystal structure of **4** is consistent with that on the crystal structure of **1** [2].

4. Experimental

4.1 Instrumentation

The ^{1}H, ^{13}C{^{1}H} and ^{19}F NMR spectra were recorded in CDCl$_3$ using Bruker DRX300 or DPX400 spectrometers. ^{1}H (300.13 or 400.14 MHz) were referenced internally using the residual protio solvent resonance relative to SiMe$_4$ (δ 0) and ^{19}F (282.40 MHz) externally to CFCl$_3$ (δ 0). All chemical shifts are quoted in δ (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

Pentafluorobenzene (Apollo Scientific), 2-methylimidazole, 4-methylimidazole and benzyl bromide (Aldrich) was used as supplied.

4.3 Preparation of 1-(4-bromo-2,3,5,6-tetrafluorophenyl)-2-methylimidazole

1-(4-Bromo-2,3,5,6-tetrafluorophenyl)-2-methylimidazole was prepared by a modfication of the preparation of 1-(4-bromo-2,3,5,6-tetrafluorophenyl)imidazole [19] from 2-methylimidazole (1.65 g, 20 mmol) and bromopentafluorobenzene (4.95 g, 20 mmol) in dimethylsulphoxide (20 cm^3) and tetrahydrofuran (10 cm^3) by heating at 80ºC with stirring for 8 days. Yield 1.86 g (30%). MS: C$_{10}$H$_6$F$_4$N$_2$^{79}Br requires 308.9650; found [M +

12

H]$^+$ 308.9621. ^{1}H NMR (CDCl$_3$): δ = 7.13 (1H, d, J = 1.5 Hz), (1H, q, J = 0.9 Hz), 2.62 (3H, s, CH$_3$). ^{19}F NMR (CDCl$_3$): δ = -130.70 (2F), -144.58 (2F) (A and B components of an AA'BB' spin pattern).

*4.4 Preparation of 1-(4-bromo-2,3,5,6-tetrafluorophenyl)-3-benzyl-2methylimidazolium bromide (**8**)*

Benzyl bromide (0.221 g, 1.29 mmol) was added to 1-(4-bromo-2,3,5,6-tetrafluorobenzene)-2-methylimidazole (0.353 g, 1.14 mmol) in dichloromethane, and the mixture maintained at ambient temperature for 48 hr. The solvent was removed by rotary evaporation to yield the product as a colourless crystalline solid. Yield ca. 0.57 g (ca. 100%). MS: C$_{17}$H$_{11}$F$_4$N$_2$^{81}Br requires 400.138; found [M − Br]$^+$ 400.0144. ^{1}H NMR (CDCl$_3$/(CD$_3$)$_2$SO): δ = 8.07 (2H, s, N$_2$CH and NCH), 7.45 (5H, m, C$_6$H$_5$), 5.58 (2H, s, CH$_2$), 3.44 (3H, s, CH$_3$). ^{19}F NMR (CDCl$_3$/(CD$_3$)$_2$SO): δ = -132.39 (2F), -145.25 (2F) (A and B components of an AA'BB' spin pattern).

4.5 Preparation of 1-(4-bromo-2,3,5,6-tetrafluorophenyl)-4-methylimidazole

1-(4-Bromo-2,3,5,6-tetrafluorophenyl)-4-methylimidazole was prepared by a modficication of the preparation of 1-(4-bromo-2,3,5,6-tetrafluorophenyl)imidazole [19] from 4-methylimidazole (1.65 g, 20.0 mmol) and bromopentafluorobenzene (4.95 g, 20.0 mmol) in dimethylsulphoxide (20 cm^3) and tetrahydrofuran (10 cm^3) by heating at 80ºC with stirring for 4 days. Yield 2.60 g (ca. 42%). MS: C$_{10}$H$_6$F$_4$N$_2$^{79}Br requires 308.9650; found [M + H]$^+$ 308.9555. ^{1}H NMR (CDCl$_3$): δ = 7.72 (1H), 6.94 (1H, m), 2.63 (3H, d, $^3J_{HH}$ = 3.2 Hz, CH$_3$). ^{19}F NMR (CDCl$_3$): δ = -130.84 (2F), -146.94 (2F) (A and B components of an AA'BB' spin pattern).

13

4.6 Preparation of 1-(4-bromo-2,3,5,6-tetrafluorophenyl)-3-benzyl-4-methylimidazolium

bromide (**9**)

Benzyl bromide (0.322 g, 1.88 mmol) was added to 1-(4-bromo-2,3,5,6-

tetrafluorobenzene)-4-methylimidazole (0.545 g, 1.83 mmol) in dichloromethane, and

the mixture maintained at ambient temperature for 48 hr. The solvent was removed by

rotary evaporation to yield the product as a colourless crystalline solid. Yield 0.68 g (ca.

93%). MS: $C_{17}H_{11}F_4N_2{}^{81}Br$ requires 400.138; found $[M - Br]^+$ 400.0157. ^1H NMR

$(CDCl_3/(CD_3)_2SO)$: δ = 9.77 (1H, s, N_2CH), 7.97 (1H, m, NCH), 7.43 (5H, m, C_6H_5), 5.61 (2H,

s, CH_2), 3.35 (3H, s, CH_3). ^{19}F NMR $(CDCl_3/(CD_3)_2SO)$: δ = -132.39 (2F), -145.25 (2F) (A and

B components of an AA'BB' spin pattern).

4.5 X-ray crystallography

Crystals of **8** and **9** were obtained by slow evaporation of solvent from solutions in

methanol. 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—$K_α$

radiation. The structures of **8** and **9** were solved using Olex2 [20] and refined with the

olex2.refine [21] 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 (Uij = 1.2Ueq 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 1837171 (**8**) and 1837172 (**9**) 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.

14

4.6 Density functional theory calculations

DFT calculations were performed using Gaussian09 [22] with the long-range corrected functional ωB97X-D [13] method and the 6-311++G(2d,2p) basis set. The energies of interaction were calculated as the difference between the energy of the species and the sum of those of its components. A neutron diffraction study has revealed that all the C─H bond distances of the cation of 1-(2,3,5,6-tetrafluoropyridyl)-3-benzylimidazolium bromide are 1.08 Å within experimental error [2]. Consequently C─H bonds of the experimental structures were fixed at 1.080 Å before calculation of their energies and optimization of the positions of the bromide anions. Calculations performed on model systems involving halotetrafluorophenylimidazoles and halopentafluorobenzenes used the positions of the relevant atoms of the experimentally determined salts. The fluorine atoms in the 4-position of halopentafluorobenzenes were positioned to give a C─F bond distance of 1.350 Å with C─C─F angles identical to the C─C─N angles of the cation.

5. Acknowledgement

15

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Table 1

Crystallographic data for 1-(4-bromo-2,3,5,6-tetrafluorophenyl)-2-methyl-3-benzylimidazolium bromide **8**, and 1-(4-bromo-2,3,5,6-tetrafluorophenyl)-3-benzyl-4-methylimidazolium bromide **9**.[a]

	8	9
Formula	$C_{15}H_{13}F_4Br_2N_2$	$C_{15}H_{13}F_4Br_2N_2$
Formula weight	480.10	480.10
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$I2/a$
a, Å	10.46398(15)	23.6805(3)
b, Å	13.31629(15)	7.13235(7)
c, Å	12.60995(16)	21.0790(2)
β, °	110.7404(15)	103.6307(11)
V, Å^3	1643.22(4)	3459.92(6)
Z	4	8
D_c (g cm^{-3})	1.941	1.843
Crystal size (mm^3)	0.15 × 0.10 × 0.07	0.25 × 0.24 × 0.11
μ (mm^{-1})	6.687	6.352
θ range (°)	4.52 → 73.81	3.84 → 73.57

Total reflections	9,410	17,663
Unique reflections (R_{int})	3,246 (0.0161)	3,447 (0.0515)
Observed reflections [$I > 2\sigma(I)$]	3,059	3,419
Parameters	227	226
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0213$, $wR_2 = 0.0536$	$R_1 = 0.0321$, $wR_2 = 0.0852$
R indices (all data)	$R_1 = 0.0244$, $wR_2 = 0.0547$	$R_1 = 0.0325$, $wR_2 = 0.0856$
Weighting scheme	$w = 1/[\sigma^2(F_o)^2 + \{0.0330 (F_o^2 + 2F_c^2)/3\}^2 + 0.9640 (F_o^2 + 2F_c^2)/3]$	$w = 1/[\sigma^2(F_o)^2 + \{0.0467 (F_o^2 + 2F_c^2)/3\}^2 + 15.1382 (F_o^2 + 2F_c^2)/3]$
Max., min. $\Delta\rho$ (eÅ^{-3})	0.362, -0.760	0.812, -0.798
Goodness of fit on F^2	1.046	1.049

[a] Estimated standard deviations are given in parentheses. Data were collected at 100(2) K with graphite monochromated radiation ($\lambda = 1.54184$ Å).

Table 2

Selected experimental and calculated bond distances (Å) and angles (°) for 1-(4-bromo-2,3,5,6-tetrafluorophenyl)-2-methyl-3-benzylimidazolium bromide **8**, and 1-(4-bromo-2,3,5,6-tetrafluorophenyl)-3-benzyl-4-methylimidazolium bromide **9**.[a]

	8		**9**	
	Expt	Calc [b]	Expt	Calc [b]
C(1)─N(1)	1.352(2)	1.343	1.331(3)	1.331
C(1)─N(2)	1.329(2)	1.332	1.320(3)	1.323
N(1)─C(2)	1.401(2)	1.383	1.389(3)	1.381
N(1)─C(4)	1.419(2)	1.420	1.421(3)	1.420
N(2)─C(3)	1.391(2)	1.379	1.389(3)	1.387
N(2)─C(10)	1.470(2)	1.470	1.468(3)	1.469
C(2)─C(3)	1.336(3)	1.347	1.353(4)	1.355
C(7)─Br	1.8870(19)	1.865	1.880(3)	1.865
C(10)─C(11)	1.516(3)	1.509	1.517(3)	1.508
C─C(17)	1.470(3)	1.479	1.488(4)	1.484
N(1)─C(1)─N(2)	107.06(16)	107.09	107.9(2)	108.6
C(1)─N(1)─C(2)	108.96(16)	109.49	109.2(2)	108.4
N(1)─C(2)─C(3)	106.76(17)	106.54	106.8(2)	107.6

N(2)─C(3)─C(2)	107.41(17)	107.35	106.2(2)	106.1
C(1)─N(2)─C(3)	109.79(16)	109.53	109.9(2)	109.3
C(1)─N(1)─C(4)	125.36(16)	125.71	123.6(2)	125.4
C(1)─N(2)─C(10)	125.70(16)	125.32	124.2(2)	124.8
N(2)─C(10)─C(11)	112.10(15)	112.76	111.2(2)	112.4
$\angle$ C$_6$F$_4$Br^{plane} C$_3$N$_2$$^{plane\ c}$	53.4(4)	71.6	63.0(4)	68.5
$\angle$ C$_6$H$_5$^{plane} C$_3$N$_2$$^{plane\ c}$	87.1(3)	85.1	88.1(6)	88.5
$\angle$ C$_6$F$_4$Br^{plane} C$_6$H$_5$$^{plane\ c}$	50.3(3)	77.7	30.9(4)	20.7
C(1)─N(1)─C(4)─C(5)	-128.3(2)	-108.7	-63.8(4)	-68.3
C(1)─N(1)─C(4)─C(9)	55.5(3)	72.3	113.5(3)	112.7
C(1)─N(2)─C(10)─C(11)	86.0(2)	61.9	-100.4(3)	-114.1
C(3)─N(2)─C(10)─C(11)	-90.4(2)	-96.7	75.0(3)	64.2
N(2)─C(10)─C(11)─C(12)	-0.2(3)	45.3	38.6(3)	48.2
N(2)─C(10)─C(11)─C(16)	-178.4(2)	-135.6	-143.2(3)	-133

[a] Estimated standard deviations are given in parentheses.

[b] Data for the cation are for its optimized structure. Calculations were performed using the ωB97X-D method and the 6-311++G(2d,2p) basis set.

[c] $C_6F_4Br^{plane}$ and $C_6H_5^{plane}$ represent the planes defined by the six carbon atoms of the bromotetrafluorophenyl and phenyl rings respectively. $C_3N_2^{plane}$ represents the plane defined by the three carbon and two nitrogen atoms of the imidazolium ring.

Table 3

Selected experimental and calculated interionic distances (Å) and angles (°) for 1-(4-bromo-2,3,5,6-tetrafluorophenyl)-3-benzylimidazolium bromide, **4**, 1-(4-bromo-2,3,5,6-tetrafluorophenyl)-2-methyl-3-benzylimidazolium bromide, **8**, and 1-(4-bromo-2,3,5,6-tetrafluorophenyl)-3-benzyl-4-methylimidazolium bromide, **9**.[a]

	4		**8**		**9**	
	Expt	Calc [b]	Expt	Calc [b]	Expt	Calc [b]
C(1)···Br⁻	3.350(4)	3.076	—	—	3.485(3)	3.076
N(1)—C(1)···Br⁻	100.5(3)	96.8	—	—	109.2(2)	98.6
N(2)—C(1)···Br⁻	140.3(3)	132.3	—	—	142.0(2)	129.1
C₃N₂^{plane}···Br⁻ [c]	1.564(5)	2.028	—	—	0.452(3)	2.088
C₆F₄Br^{plane}···Br⁻ [c]	3.534(5)	3.293	—	—	3.602(3)	3.371
C₆F₄Br†···Br⁻ [d]	3.888(5)	3.769	—	—	4.093(3)	3.790
C(2)···Br⁻	3.846(5)	3.271	3.755(2)	3.247	3.581(3)	3.280
N(1)—C(2)···Br⁻	88.3(3)	93.5	152.0(1)	174.1	88.4(1)	91.4
C(3)—C(2)···Br⁻	144.0(3)	152.3	79.0(1)	79.1	145.7(2)	153.2
C(3)···Br⁻	—	—	3.373(2)	3.270	—	—
N(2)—C(3)···Br⁻	—	—	150.9(1)	175.4	—	—

24

C(2)─C(3)···Br⁻	—	—	80.5(1)	77.2	—	—
C₃N₂ᵖˡᵃⁿᵉ···Br⁻ ᶜ	2.256(6)	1.164	1.785(2)	0.000	1.870(3)	1.130
C₆F₄Br ᵖˡᵃⁿᵉ···Br⁻ ᶜ	3.402(5)	3.289	2.283(2)	3.341	3.453(3)	3.254
C₆F₄Br†···Br⁻ ᵈ	3.626(5)	3.534	6.940(2)	6.549	3.788(3)	3.600
Br···Br⁻	3.2670(6)	2.875	3.1829(2)	2.869	3.2360(4)	2.879
C(7)─Br···Br⁻	177.4(1)	179.8	178.59(6)	179.68	176.27(8)	179.38
∠ C₆H₅ᵖˡᵃⁿᵉ C₆F₄Brᵖˡᵃⁿᵉ ᶜ	—	—	6.7(1)	—	—	—
C₆H₅†···C₆F₄Brᵖˡᵃⁿᵉ ᶜ	—	—	3.330(3)	—	—	—
C₆H₅ᵖˡᵃⁿᵉ···C₆F₄Br† ᶜ,ᵈ	—	—	3.466(3)	—	—	—
C₆H₅†···C₆F₄Br† ᵈ	—	—	3.601(3)	—	—	—
C₆F₄Brᵖˡᵃⁿᵉ···C₆F₄Brᵖˡᵃⁿᵉ ᶜ,ᵉ	6.936(1)	—	—	—	7.132(3)	—
Br···Br⁻ ᶠ	6.9774(7)	—	—	—	7.1323(4)	—
Br···C₆F₄Br†···Br⁻ ᵍ	136.4(1)	—	—	—	129.6(1)	—
∠ column C₆F₄Brᵖˡᵃⁿᵉ ʰ	83.8(3)	—	—	—	81.5(3)	—
∠ C₆F₄Br ᵖˡᵃⁿᵉ C₆F₄Brᵖˡᵃⁿᵉ ⁱ	0	—	—	—	16.9(3)	—

25

a Estimated standard deviations are given in parentheses.

b Data for the optimized positions of the bromide anion relative to the experimentally determined structure of the cation with C─H bond distances of 1.080 Å. Calculations were performed using the ωB97X-D method and the 6-311G++(2d,2p) basis set.

c $C_6F_4Br^{plane}$ and $C_6H_5^{plane}$ represent the planes defined by the six carbon atoms of the bromotetrafluorophenyl and phenyl rings respectively. $C_3N_2^{plane}$ represents the plane defined by the three carbon and two nitrogen atoms of the imidazolium ring.

d $C_6F_4Br^{\dagger}$ and $C_6H_5^{\dagger}$ represent the centroids of the rings defined by the six carbon atoms of the bromotetrafluorophenyl and phenyl rings respectively.

e The separation between the planes of the rings within a column.

f The separation between the bromide anions within a column.

g $C_6F_4Br^{\dagger}\cdots Br^-\cdots C_6F_4Br^{\dagger}$ has the same value as $Br^-\cdots C_6F_4Br^{\dagger}\cdots Br^-$.

h The angle subtended by the column and the plane defined by the six carbon atoms of the bromotetrafluorophenyl ring.

i The angle subtended by the planes defined by the six carbon atoms of bromotetrafluorophenyl rings of adjacent columns.

26

Table 4

Calculated energies of interaction (kJ mol^{-1}) between the bromide anion at different positions and the cation of 1-(4-bromo-2,3,5,6-tetrafluorophenyl)-3-benzylimidazolium bromide, **4**, 1-(4-bromo-2,3,5,6-tetrafluorophenyl) -2-methyl-3-benzylimidazolium bromide, **8**, 1-(4-bromo-2,3,5,6-tetrafluorophenyl)-3-benzyl-4-imidazolium bromide, **9**, and related model systems.[a]

Bromide close to:	Compound	Experimental Structure	Optimized bromide position [b]	Electrostatic (r, Å) [c]	Bromotetrafluoro-phenylimidazole [d]	Bromopenta-fluorobenzene [d,e]
C(1)	**4**	-371	-379	-346 (4.010)	-70	-44
	9	-357	-374	-328 (4.232)	-67	-40
C(2)	**4**	-321	-331	-293 (4.733)	-70	-47
	8	-292	-315	-283 (4.900)	-29	-2
	9	-323	-331	-302 (4.593)	-69	-47
Br(1)	**4**	-222	-240	-136 (10.218)	-60	-52
	8	-230	-240	-134 (10.344)	-61	-55

	9	-219	-228	-135 (10.323)	-59	-54

[a] Calculations were performed using the ωB97X-D method and the 6-311++G(2d,2p) basis set. C─H bond distances were adjusted to 1.080 Å.

[b] Data for the optimized positions of the bromide anion relative to the experimentally determined structure of the cation.

[c] The energy of interaction ($e^2/4\pi\varepsilon_0 r$) between point charges located at the centre of the anion and at the midpoint of the two nitrogen atoms of the imidazolium ring. The distance between the two points is given in parentheses.

[d] Using the experimentally determined positions of the relevant atoms.

[e] The fluorine atoms in the 4-position of halopentafluorobenzenes positioned to give a C─F bond distance of 1.350 Å with C─C─F angles identical to the C─C─N angles of the cation.

28

- Crystal structures of 1-(4-bromo-2,3,5,6-tetrafluorophenyl)-2-methyl-3-benzylimidazolium bromide and 1-(4-bromo-2,3,5,6-tetrafluorophenyl)-3-benzyl-4-methylimidazolium bromide have been determined by single crystal X-ray diffraction.

- Both crystal structures possess C(2)─H⋯Br⁻ hydrogen bonding and C─Br⋯Br⁻ halogen bonding.

- The crystal structure of **8** contains π–π stacking between bromotetrafluorophenyl and phenyl rings,

- The crystal structure of **9** contains C(1)─H⋯Br⁻ hydrogen bonding and anion–π interactions.

- The crystal structure of **9** comprises columns of alternating bromide anions and parallel bromotetrafluorophenyl rings.