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Arene-Perfluoroarene-Anion Stacking and Hydrogen Bonding Interactions in Imidazolium Salts for the Crystal Engineering of Polarity

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ABSTRACT

The crystal structure of 1-(2,3,5,6-tetrafluoropyridyl)-3-benzylimidazolium bromide possesses $C_6H_5\cdots C_5F_4N\cdots Br^-$ interactions that link the cations into chains, $N(C)C—H\cdots Br^-$ interactions that link the chains into sheets, and $N_2C—H\cdots Br^-$ interactions that link the sheets to one another. As a consequence of these it is polar (*Pna*2$_1$). DFT calculations indicate that the strength of the interaction between a cation and a bromide anion lies in the order $N_2C—H\cdots Br^- > N(C)C—H\cdots Br^- > C_6H_5\cdots C_5F_4N\cdots Br^-$. Prevention of the $N_2C—H\cdots Br^-$ interaction by substitution of the hydrogen atom with a methyl group leads to dimers linked by two $C_6H_5\cdots C_5F_4N\cdots Br^-$ interactions. Prevention of the $N(C)C—H\cdots Br^-$ interaction by substitution of the hydrogen with a methyl group permits chains of cations, but because the $N_2C—H\cdots Br^-$ interactions link the chains there are no strong interactions between the sheets. Chains of cations linked by $Ar\cdots C_5F_4N\cdots Br^-$ interactions also arise when the benzyl group is replaced by 3-phenylbenzyl and 2-naphthylmethyl groups. The former also contains $N_2C—H\cdots Br^-$ and $N(C)C—H\cdots Br^-$ interactions and is centrosymmetric. The latter does not contain $N(C)C—H\cdots Br^-$ interactions and is chiral and polar (*P*2$_1$). Exchanging the positions of the aryl and polyfluoroaryl groups results in a crystal structure with no π–π stacking between the aryl and polyfluoroaryl groups although $N_2C—H\cdots Br^-$ and $N(C)C—H\cdots Br^-$ interactions persist.

INTRODUCTION

The offset parallel stacking of polyfluoroarenes with arenes, termed 'π–π stacking', has been identified as a useful interaction for crystal engineering.[1] The attraction between arenes and polyfluoroarenes arises in part from interactions between the ring quadrupoles which are of opposite sign.[2,3] For example, the quadrupole moments of benzene and hexafluorobenzene are $-33.3 \pm 2.1 \times 10^{-40}$ and $31.7 \pm 1.7 \times 10^{-40}$ C m^2 respectively,[4] and their interaction, calculated to be -5.38 kcal mol^{-1},[5] results in π–π stacking to give the archetypal structure (Cambridge Structural Database entry code: BICVUE01): alternating parallel benzene and hexafluorobenzene molecules arranged in columns inclined at *ca.* 63° to the planes of the rings, with a separation of *ca.* 3.35 Å and an offset of *ca.* 1.7 Å.[6-8] The structures of co-crystals of other arenes and fluoroarenes show similar features.[9-16] π–π Stacking also occurs between complementary compounds with two or more rings,[17-22] and compounds containing both an aryl and a polyfluoroaryl group.[21-27] In most of the structures of the latter, the rings of each molecule are co-planar, but this is not necessary for π–π stacking. In the crystal structures of 2,3,4,5,6-pentafluorobiphenyl (CSD entry code: PFBIPH)[26] and both polymorphs of 2-(pentafluorophenylimino)methylphenol (CSD entry codes: BANGOM, BANGOM02),[27] the plane of the polyfluoroaryl ring is twisted by *ca.* 53º and *ca.* 40° respectivley relative to the plane of the aryl ring of the same molecule. π–π Stacking is also tolerant of some functional groups,[27-29] and this has allowed the use of these interactions to control the stereochemistry of the [2+2] photodimerization of stilbenes in the solid state.[30]

If compounds bearing both aryl and polyfluoroaryl rings undergo 'bifurcated stacking', in which each molecule stacks with four others (Figure 1a), sheets with polarity in one dimension result. If the sheets pack in a parallel manner then this provides the basis for the generation of crystal polarity, which is a requirement for pyroelectric and ferroelectric properties, and also gives rise to piezoelectric and second-order non-linear optical properties.[31] For molecules in which the complementary rings can be co-planar, structures containing 'columnar stacking', in which each molecule stacks with only two others (Figure 1b), dominate. Exceptions include 2-(4-nitrilotetrafluorophenyl)benzo[d][1,2,3]triazole (CSD entry code: OKAJAM), which adopts bifurcated stacking, possibly because of its multicomponent nature ($NC-C_6F_4-N_3-C_6H_4$) and those components' dimensions,[32] and 4-methoxytetrafluorophenyl-2-phenylacetylene (CSD entry code: ASIJOB) which adopts a structure with bifurcated stacking to accommodate the methoxy groups.[22] The alternating direction of the polarity of the molecules arising from columnar stacking does not give rise to net polarity. Molecules bearing both aryl and polyfluoroaryl rings tend, in consequence, not to crystallize in one of the polar crystal classes (1, 2, *m*, *mm*2, 4, 4*mm*, 3, 3*m*, 6 and 6*mm*); however, other factors may lead to crystallization in polar space groups. 2-(Pentafluorophenylimino)methylphenol crystallizes with columnar stacking in both the centrosymmetric space group $P2_1/c$ (the α2 polymorph, CSD entry code: BANGOM) and the polar space group $P2_1$ (the α1 polymorph, CSD entry code: BANGOM02).[27]

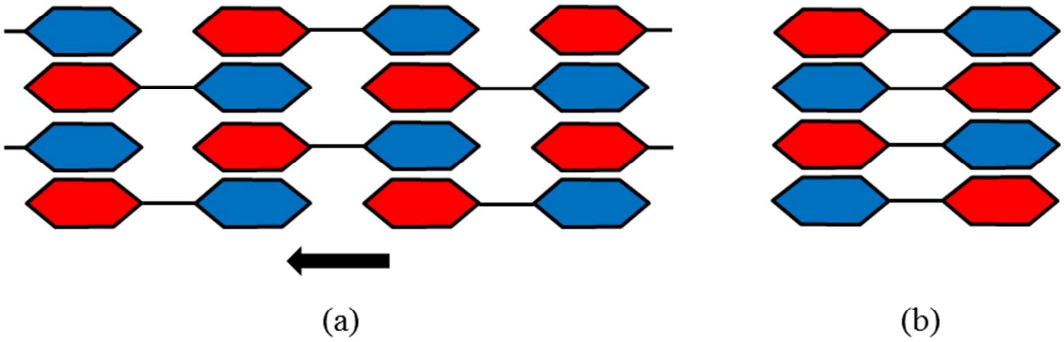


Figure 1. (**a**) Bifurcated and (**b**) columnar stacking of molecules containing complementary polyfluoroaryl and aryl rings. The arrow indicates the direction of polarity.

The design and construction of a polar network incorporating π–π stacking interactions between benzyl and pentafluorobenzyl substituents of an imidazolium cation was recently reported (CSD entry code: BONKUL).[33] It was argued that preventing columnar stacking, and thereby facilitating the bifurcated stacking of the rings, would generate non-centrosymmetry. It was reasoned that columnar stacking could be prevented by the use of imidazolium cations in which the planes of the complementary rings could be parallel but not co-planar, and in which the 'step' is more than 4 Å. The cation of 1-(2,3,4,5,6-pentafluorobenzyl)-3-benzyl-imidazolium bromide satisfies the criteria, and the salt was indeed found to crystallize in the polar (and chiral) space group *P*1.[33] The cations undergo bifurcated π–π stacking to produce sheets with polarity in two directions: parallel to the *b* and *c* axes. It is the packing of the sheets that determines the non-centrosymmetry, and this is determined by interactions between the bromide anions and cations of adjacent sheets: the N_2CH hydrogen atom and one other hydrogen atom of each imidazolium ring interact with bromide anions to orientate the rings, and sheets, parallel, generating polarity parallel to the *a* axis.

We hypothesize that prevention of columnar stacking can also be achieved by using check mark shaped (tick shaped) molecules or ions. Angular, chevron shaped molecules bearing both polyfluoroaryl and aryl groups have been reported to undergo columnar stacking.[28,29] For 1,2,3,4-tetrafluorodibenzo[*b*,*f*][1,4]-oxazepine (CSD entry code: HUTYAW)[28] the planes of the phenylene and tetrafluorophenylene rings subtend an angle of *ca.* 144° at the hinge, and together with the equidistance of the rings from the fold, this allows the sufficiently close approach of the molecules to give rise to π–π stacking interactions and resultant columnar stacking (Figure 2a). If the complementary rings are not equidistant from the hinge then columnar stacking does not maximize the π–π stacking interactions (Figure 2b), but bifurcated stacking may do so (Figure 2c). The validity of this hypothesis was demonstrated recently for 1-(4-nitrilo-2,3,5,6-tetrafluorophenyl)benzimidazole which crystallized in the polar space group *C*c (CSD entry code: PEYDEE).[34,35] Since this compound is neutral and contains no groups capable of hydrogen bonding, the π–π stacking interactions determine the crystal structure.

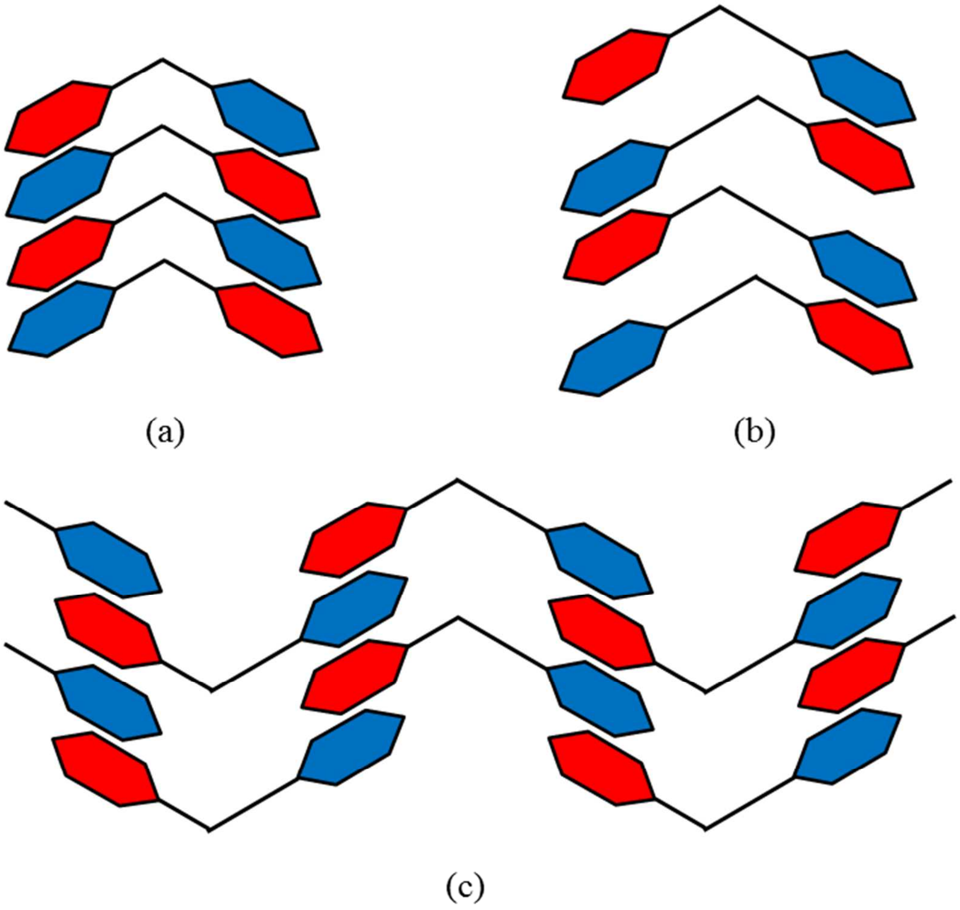


Figure 2. Columnar stacking of (**a**) chevron shaped and (**b**) check mark shaped molecules, and (**c**) bifurcated stacking of check mark shaped molecules.

We wished to test this hypothesis for salts; *i.e.* can crystal polarity be engineered by π–π stacking between check mark shaped ions? The polar crystal structure of 1-(2,3,4,5,6-pentafluorobenzyl)-3-benzyl-imidazolium bromide[33] prompted us to start an investigation of 1-polyfluoroaryl-3-benzylimidazolium salts. In addition to the desired π–π stacking interactions, other interactions are expected. Short distances between carbon atoms of the imidazolium ring and anions lying in, or close to, the plane of the imidazolium ring have been observed for other salts.[33,36-43] The distances and geometries are indicative of hydrogen bonding,[44-46] the importance of which in determining crystal structures is well established.[47-49] Calculations performed on 1-ethyl-3-methylimidazolium salts suggest that the interactions are not conventional hydrogen bonds, and are dominated by an isotropic charge–charge term that is nearly inversely proportional to the distance of the anion from the center of the positive charge, which is close to the midpoint between the two nitrogen atoms.[46] These interactions were calculated to be attractive by 68 to 82 kcal mol^{-1}. Crystal structures of the 1-polyfluoroaryl-3- benzylimidazolium salts may also contain anion–π interactions,[50] which have been observed in a number of crystal structures of ammonium,[51-56] phosphonium,[55,57] imidazolium[58.59] and other[56,60] salts in which the cation bears a polyfluoroaryl group. Chloride, bromide and iodide typically lie *ca.* 3.2, 3.4 and 3.7 Å from the plane of the polyfluroaryl ring and are displaced from the normal to its centroid towards an atom bearing the positive charge. Theoretical studies have shown that the interactions between hexafluorobenzene and halide anions are attractive by 10.6 to 20.9 kcal mol^{-1},[50,61-64] and that the energy decreases by only a small extent as the anion is diplaced from the normal to the centroid of the ring towards an edge. For chloride at 3.05 Å from the plane of the hexafluorobenzene ring energies of interaction were calculated by the RI-MP2(full) method using the aug-cc-pVDZ basis set to be -14.05, -13.12 and -13.43 kcal mol^{-1} when it lies on the normals to the centroid, a carbon atom and the midpoint of a

C–C bond respectively.[61] The interactions are expected to be stronger for polyfluoroaryl groups that are part of a cation.

Here we report the results of a structural study of six imidazolium bromide salts with check mark shaped cations bearing both aryl and fluoroaryl substituents. The crystal structure of one, 1-(2,3,5,6-tetrafluoropyridyl)-3-benzylimidazolium bromide (**1**), has been communicated.[65]

EXPERIMENTAL SECTION

Pentafluoropyridine, 1,2,3,4,5-pentafluorobenzyl bromide (Apollo Scientific), benzyl bromide, 3-phenylbenzyl bromide, 2-bromomethylnaphthalene, imidazole, 2-methylimidazole, 4-methylimidazole and 1-phenylimidazole (Aldrich) were used as supplied. NMR spectra were recorded on Bruker DRX300 or DPX400 spectrometers. ^{1}H NMR spectra (300.13 or 400.14 MHz) were referenced internally using the residual protio solvent resonance relative to tetramethylsilane (δ 0), ^{13}C NMR spectra (100.61 MHz) were referenced externally to tetramethylsilane (δ 0), and ^{19}F NMR spectra (282.40 or 376.47 MHz) externally to trichlorofluoromethane (δ 0). All chemical shifts are quoted in δ (ppm) using the high frequency positive convention, and coupling constants in Hz. Elemental analyses were performed by the Campbell Microanalytical Laboratory, The University of Otago. The electron impact mass spectrum of 1-(2,3,5,6-tetrafluoropyridyl)imidazole was recorded on a VG Autospec X series and the electrospray ionization mass spectra on a Bruker Daltonics MicrOTOF spectrometer.

Synthesis of 1-(2,3,5,6-Tetrafluoropyridyl)imidazole. A solution of imidazole (0.30 g, 4.4 mmol) and pentafluoropyridine (0.74 g, 4.4 mmol) in THF (50 cm^3) was left at ambient temperature for 20 hours, during which time a small number of colourless crystals were deposited. The solvent was removed by rotary evaporation affording a pale yellow oil and colourless solid, which is presumed to be salts formed by the reaction of hydrogen fluoride, the by-product of the reaction, with borosilicate glass. The product was extracted into dichloromethane (2 × 50 cm^3), and the solution filtered. Concentration by rotary evaporation afforded the product as a pale yellow oil. Yield 2.38 g (62%). ^{1}H NMR ($CDCl_3$): δ = 7.99 (1H, s, N_2CH), 7.41 (1H, m, HC=CH),7.32 (1H, m, HC=CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 144.7 (dddd, $^1J_{CF}$ = 246 Hz, J_{CF} = 15, 15, 4 Hz, CF), 137.5 (t, J_{CF} = 6 Hz), 135.6 (dm, $^1J_{CF}$ = 264 Hz, CF), 131.2 (s), 128.1 (m), 119.4 {t, J_{CF} = 4 Hz, $NC(C_5F_4N)$}. ^{19}F NMR ($CDCl_3$): δ = -86.81 (2F), -149.07 (2F) A and B parts of an AA'BB' spin system. EI MS: $C_8H_3N_3F_4$ requires 217.0263; found 217.0242.

Synthesis of 1-(2,3,5,6-Tetrafluoropyridyl)-3-benzylimidazolium bromide (1). Benzyl bromide (0.56 g, 2.6 mmol) was added to 1-(2,3,5,6-tetrafluoropyridyl)imidazole (0.45 g, 2.6 mmol) in dichloromethane (50 cm^3) and the solution left at ambient temperature for 24 h. The solvent was removed by rotary evaporation to afford the product as a white powder, which was recrystallized from methanol. Yield 0.88 g (87%). Found: C 46.55, H 2.61, N 10.81. Calc. for $C_{15}H_{10}BrN_3F_4$: C, 46.41, H 2.60, N 10.83%. ^{1}H NMR {$(CD_3)_2SO$}: δ = 10.09 (1H, s, N_2CH), 8.27 (2H, m, HC=CH), 7.55 (2H, m, C_6H_5), 7.46 (3H, m, C_6H_5), 5.67 (2H, s, CH_2). $^{13}C\{^1H\}$ {$(CD_3)_2SO$}: δ = 143.3 (dddd, $^1J_{CF}$ = 242, J_{CF} = 15, 15, 4 Hz, CF), 139.1 (s), 137.3 (dm, $^1J_{CF}$ = 266 Hz, CF), 134.4 (s), 129.6 (m), 129.2 (s), 126.3 (s), 124.4 (s), 121.0 (m), 53.4 (s, CH_2). ^{19}F NMR {$(CD_3)_2SO$}: δ = -88.74 (2F), -146.69 (2F) A and B parts of an AA'BB' spin system. ESI MS: $C_{15}H_{10}F_4N_3$ requires 308.081; found: $[M - Br]^+$ 308.084.

Synthesis of 1-(2,3,5,6-Tetrafluoropyridyl)-2-methylimidazole. Pentafluoropyridine (0.85 g, 5.0 mmol) and 2-methylimidazole (0.39 g, 4.7 mmol) were treated as for the preparation of 1-(2,3,5,6-tetrafluoropyridyl)imidazole. The product was obtained as a viscous yellow oil. Yield 0.99 g (91%). ^{1}H NMR (CDCl$_3$): δ = 7.19 (1H, s, HC=CH), 7.03 (1H, s, HC=CH), 2.40 (3H, m, CH$_3$). ^{19}F NMR (CDCl$_3$): δ = -86.10 (2F), -146.09 (2F) A and B parts of an AA'BB' spin system. ESI MS: $C_8H_3N_3F_4$ requires 232.050; found [*M* + H]$^+$ 232.050.

Synthesis of 1-(2,3,5,6-Tetrafluoropyridyl)-2-methyl-3-benzylimidazolium bromide (2). 1-(2,3,5,6-tetrafluoropyridyl)-2-methylimidazole (0.42 g, 1.8 mmol) and benzyl bromide (0.28 g, 1.6 mmol) were treated as for **1**. The product was obtained as a white powder. Yield 0.49 g (76%). Found: C 47.86, H 2.89, N 10.51. Calc. for $C_{16}H_{12}BrN_3F_4$: C, 47.78, H 3.01, N 10.45%. ^{1}H NMR {CDCl$_3$/(CD$_3$)$_2$SO}: δ = 8.06 (2H, s, HC=CH), 7.47 (5H, m, C$_6$H$_5$), 5.55 (2H, s, CH$_2$), 2.72 (s, CH$_3$). ^{13}C {(CD$_3$)$_2$SO}: δ = 147.9 (s), 143.4 (dm, $^{1}J_{CF}$ = 243, CF), 138.4 (dm, $^{1}J_{CF}$ = 267 Hz, CF), 133.7 (s), 129.7 (dd, $^{1}J_{CH}$ = 161, $^{2}J_{CH}$ = 5 Hz), 129.5 (dm, $^{1}J_{CH}$ = 159 Hz), 128.9 (dm, $^{1}J_{CH}$ = 160 Hz), 124.9 {m, NC(C$_5$F$_4$N)}, 124.7 (dd, $^{1}J_{CH}$ = 207, $^{2}J_{CH}$ = 10 Hz, HC=CH), 123.2 (dd, $^{1}J_{CH}$ = 211, $^{2}J_{CH}$ = 12 Hz, HC=CH), 52.3 (t, $^{1}J_{CH}$ = 146 Hz, CH$_2$), 11.0 (quart, $^{1}J_{CH}$ = 135 Hz, CH$_2$). ^{19}F NMR {CDCl$_3$/(CD$_3$)$_2$SO}: δ = -88.14 (2F), -144.19 (2F) A and B parts of an AA'BB' spin system. ESI MS: $C_{16}H_{12}F_4N_3$ requires 322.097; found: [*M* - Br]$^+$ 322.095.

Synthesis of 1-(2,3,5,6-Tetrafluoropyridyl)-4-methylimidazole. Pentafluoropyridine (0.576 g, 3.4 mmol) and 4-methylimidazole (0.307 g, 3.7 mmol) were treated as for the preparation of 1-(2,3,5,6-tetrafluoropyridyl)imidazole. The product was obtained as a viscous pale yellow oil. Yield 0.78 g (100%). ^{1}H NMR (CDCl$_3$): δ = 7.15 (1H, s, HC=CH), 7.03 (1H, m, HC=CH), 2.37 (3H, m, CH$_3$). ^{19}F NMR (CDCl$_3$): δ = -87.06 (2F), -149.30 (2F) A and B parts of an AA'BB' spin system. ESI MS: $C_9H_6N_3F_4$ requires 232.050; found [*M* + H]$^+$ 232.049.

Synthesis of 1-(2,3,5,6-Tetrafluoropyridyl)-3-benzyl-4-methylimidazolium bromide (3). 1-(2,3,5,6-tetrafluoropyridyl)-4-methylimidazole (0.78 g, 3.4 mmol) and benzyl bromide (0.64 g, 3.7 mmol) were treated as for **1**. The product was obtained as a white powder. Yield 0.66 g (49%). Found: C 48.14, H 3.14, N 10.56. Calc. for $C_{16}H_{12}BrN_3F_4$: C, 47.78, H 3.01, N 10.45%. ^1H NMR {$CDCl_3/(CD_3)_2SO$}: δ = 9.99 (1H, s, N_2CH), 8.08 (1H, m, HC=C), 7.45 (5H, m, C_6H_5), 5.68 (2H, s, CH_2), 3.35 (s, CH_3). ^{13}C {$(CD_3)_2SO$}: δ =143.4 (dm, $^1J_{CF}$ = 241, CF), 139.1 (dm, $^1J_{CH}$ = 229 Hz), 137.3 (dm, $^1J_{CF}$ = 265 Hz, CF), 133.5 (m), 133.1 (m), 129.7 (dd, $^1J_{CH}$ = 162 Hz), 129.4 (dm, $^1J_{CH}$ = 162 Hz), 128.7 (dm, $^1J_{CH}$ = 159 Hz), 126.4 {m, $NC(C_5F_4N)$}, 120.9 (dm, $^1J_{CH}$ = 210 Hz, HC=C), 51.0 (t, $^1J_{CH}$ = 145 Hz, CH_2), 9.9 (quart, $^1J_{CH}$ = 130 Hz, CH_2). ^{19}F NMR {$CDCl_3/(CD_3)_2SO$}: δ = -88.79 (2F), -146.87 (2F) A and B parts of an AA'BB' spin system. ESI MS: $C_{16}H_{12}F_4N_3$ requires 322.097; found: $[M - Br]^+$ 322.105.

Synthesis of 1-(2,3,5,6-Tetrafluoropyridyl)-3-(3-phenylbenzyl)imidazolium bromide (4). 3-Phenylbenzyl bromide (0.558 g, 2.26 mmol) was added to 1-(2,3,4,5-tetrafluoropyridyl)imidazole (0.488 g, 2.25 mmol) in dichloromethane (30 cm^3) and the solution left at ambient temperature for 24 h. The solvent was removed by rotary evaporation to give a white powder. Recrystallization from methanol afforded the product as the monohydrate. Yield 0.394 g (36.5%). Found: C, 52.46; H, 3.25; N, 8.75. Calc. for $C_{21}H_{12}BrF_4N_3.H_2O$: C, 52.52; H, 2.94; N, 8.75%. ^1H NMR {$(CD_3)_2SO$}: δ = 10.15 (1H, br s, N_2CH), 8.36 (1H, m), 8.29 (1H, m), 7.93 (1H, m), 7.74 (1H, m), 7.71 (2H, dm, J = 8.2 Hz), 7.57 (2H, m), 7.50 (2H, tm, J = 7.7 Hz), 7.41 (1H, m), 5.75 (2H, s, CH_2). ^{19}F NMR{$(CD_3)_2SO$}: δ = -88.86 (2F), -146.62 (2F) A and B parts of an AA'BB' spin system. ESI MS: $C_{21}H_{14}F_4N_3$ requires 384.112; found: $[M - Br]^+$ 384.118.

Synthesis of 1-(2,3,5,6-Tetrafluoropyridyl)-3-(2-naphthylmethyl)imidazolium bromide (5). 2-Bromomethylnaphthalene (0.424 g, 1.92 mmol) was added to 1-(2,3,5,6-tetrafluoropyridyl)imidazole (0.415 g, 1.91 mmol) in dichloromethane (50 cm^3) and the solution left at ambient temperature for 24 h. The solvent was removed by rotary evaporation to give a yellow oil. Recrystallization from methanol afforded yellow crystals of the product as the monohydrate. Yield 0.762g (87.4%). Found: C 49.35, H 3.01, N 9.13. Calc. for $C_{19}H_{12}BrF_4N_3.H_2O$: C, 50.02, H 3.09, N 9.21%. ^{1}H NMR (CD_3Cl): δ = 11.69 (1H, s, N_2CH), 8.13 (1H, s, HC=CH), 7.90 (3H, m), 7.65 (3H, m), 7.59 (2H, m), 6.13 (2H, s, CH_2). ^{19}F NMR (CD_3Cl): δ = -83.05 (2F, m), -145.97 (2F, m) ppm A and B parts of an AA'BB' spin system. ESI MS: $C_{19}H_{12}F_4N_3$ requires 358.097; found: $[M - Br]^+$ 358.104.

Synthesis of 1-(2,3,4,5,6-Pentafluorobenzyl)-3-phenylimidazolium bromide (6).[66] 2,3,4,5,6-Pentafluorobenzyl bromide (0.67 g, 2.57 mmol) was added to 1-phenylimidazole (0.31 g, 2.15 mol) in dichloromethane (20 cm^3) and the solution left at ambient temperature for 24 h. The solvent was removed by rotary evaporation to afford the product as a white powder. Yield 0.88 g (*ca.* 100%). ^{1}H {$(CD_3)_2SO$}: δ = 9.91 (1H, s, N_2CH), 8.40 (1H, t, J = 1.9 Hz, HC=CH), 8.10 (1H, t, J = 1.9 Hz, HC=CH), 7.81 (2H, m, C_6H_5), 7.64 (3H, m, C_6H_5), 5.72 (2H, s, CH_2). ^{19}F {$(CD_3)_2SO$}: δ = -140.38 (2F, m, F_{ortho}), -153.05 (1F, t, ^3J = 22.3 Hz, F_{para}), -161.84 (2F, m, F_{meta}). ESI MS: $C_{16}H_{10}F_5N_2$ requires 325.076; found: $[M - Br]^+$ 325.074.

Single-crystal X-ray Diffraction Structure Determination. Crystals of **1, 3**, **4** and **5** were grown from methanol, and crystals of **2** and **6** were grown from dichloromethane. Unit cell dimensions and reflection data for **1** and **3** - **6** were recorded on a Bruker Nonius Apex II CCD diffractometer at 89(2) or 90(2) K using Mo K*a* radiation. Absorption corrections to the data were made by SADABS.[67] Crystal and refinement data are presented in Table 1. The structures were solved by direct methods using SHELXS-97.[68] The structures of **1**, **3**, **4** and **6** were refined using SHELXL-97[69] and that of **5** using CRYSTALS[70] with non-hydrogen atoms anisotropic. All hydrogen atoms were included in calculated positions. For **5** initial refinement reached only $R_1 = 0.14$ with several large, obviously spurious, peaks in difference maps. Since the angle β was close to 90°, twinning by pseudo-merohedry was suspected and treatment of the data using the ROTAX[71] procedure incorporated in

CRYSTALS revealed the twin operator {100/0-10/-0.0080-1}.[72] Data were re-indexed to assign reflections either to the sum of the components or to the dominant component and refinement of the model with suitable distance restraints was successful converging at a 76:24 twin ratio. Hydrogen atoms were included in the refinement for water of solvation. The final model gave R_1 of 0.040, with no significant residual electron density.

Unit cell dimensions and reflection data for **2** were recorded on an Agilent SuperNova, single source at offset, Atlas diffractometer at 101.3(5) K using Cu Kα radiation. Using Olex2[73] the structure was solved with the olex2.solve[74] structure solution program using Charge Flipping and refined with the olex2.refine[74] refinement package using Gauss-Newton minimization. Structure and packing diagrams were generated using ORTEP3v2[75] and Mercury[76] respectively and are shown with displacement ellipsoids at the 50% level.

CIF files have been deposited with the Cambridge Structural Database (CCDC reference numbers 806231 (**1**), 1024878 (**2**), 976401 (**3**) and 934194–934196 (**4** - **6**)) and can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223−336−033; or deposit@ccdc.cam.ac.uk).

Single-crystal Neutron Diffraction Structure Determination. Laue neutron diffraction data were collected for **1** using the KOALA instrument[77] on a thermal neutron guide at the OPAL reactor source, ANSTO, Australia. After screening, a suitable single crystal (0.30 × 0.60 × 0.67 mm) was mounted on a thin aluminium support using perfluorinated silicon oil. The temperature was maintained at 90 K using an Oxford Cryosystems Cobra^{TM} device. Twenty static images were collected at 17° intervals (rotation perpendicular to the incident beam) with exposure times of one hour. Diffraction images were indexed to the unit cell obtained from X-ray data and data reduction was performed using the Laue1234 software suite.[78] Structure refinement commenced from the non-hydrogen atom positions determined from X-ray diffraction data. All hydrogen atom positions were located as large negative peaks in the Fourier difference map and were freely refined using anisotropic models. Final refinement cycles of 298 parameters against 1211 reflections ($I > 2\sigma I$) with no restraints converged at $R_1 = 0.0398$ and wR_2 (all reflections) = 0.0528. TLS analysis was conducted using the program CRYSTALS.[70]

Quantum Mechanical Calculations. All calculations were performed using Gaussian 09 programs.[79] Initially calculations were performed using the B3LYP method[80,81] with the 6-311G++(2d,2p) basis set. In order to confirm that the level of theory was sufficient selected calculations were repeated using the M062x method[82] and aug-cc-pVTZ basis set. Differences between the calculated energies determined by the two methods of the experimental structure and those with different C1—H1 lengths agreed to within 0.1 kcal mol^{-1}.

RESULTS AND DISCUSSION

1-(2,3,5,6-Tetrafluoropyridyl)-3-benzylimidazolium bromide **1** crystallized from methanol in the polar space group $Pna2_1$ of the orthorhombic crystal system with one cation-anion pair in the asymmetric unit. The structure was determined by a single crystal X-ray diffraction study augmented by a Laue neutron diffraction study to determine the positions of the hydrogen atoms. Selected distances and angles are given in Table 2. Those involving hydrogen atoms are given in Table 3. As expected the cation adopts a check mark shape (Figure 3) with an angle at the methylene carbon atom of 107.68(15)° with the aryl and fluoroaryl rings non-equidistant. The cation adopts a conformation in which the imidazolium and phenyl rings are almost perpendicular to the plane defined by N2, C10 and C11 (*ca.* 91° and 82° respectively). The cation is chiral, and both enantiomers are present in the crystal structure. The tetrafluoropyridyl ring is twisted by *ca.* 40° from co-planarity with the imidazolium ring, and is perpendicular to the plane of the phenyl ring. The phenyl ring of one cation stacks with the tetrafluoropyridyl ring of a cation of opposite configuration. The planes of these complementary rings are almost parallel, deviating by only *ca.* 4.8°, with a separation ranging from 3.26(3) (N3···Ar′*) to 3.38(5) Å (ArF*···C15′),[†] and an offset of *ca.* 1.4 Å, which is consistent with π–π stacking between arenes and fluoroarenes.[6-29] As predicted, the check-mark shape prevents columnar π–π stacking of the cations. Unlike the structure of 1-(2,3,4,5,6-pentafluorobenzyl)-3-benzyl-imidazolium bromide,[33] however, the complementary rings do not form infinite stacks. Instead a bromide anion is positioned close to the face of the tetrafluoropyridyl ring opposite to the phenyl ring such that C14′···ArF···Br^- is almost linear (171.8(3)°) (Figure 4). The only short distance to the face of the phenyl ring opposite to the tetrafluoropyridyl ring is with one carbon atom of an imidazolium ring (C13···C3′ 3.358(3) Å), which is non-parallel. The complementary rings and anion are therefore arranged in $C_6H_5\cdots C_5F_4N\cdots Br^-$ triad stacks. The length of the normal to the plane of the tetrafluoropyridyl ring to the bromide anion is 3.32(3) Å and the bromide is offset by *ca.* 0.8 Å towards C5. Similar positions of a bromide anion relative to a polyfluorophenyl rings have been observed in the crystal structures of pentafluorobenzylammonium and pyridinium bromide salts,[51-56] and other salts.[57,60] Theoretical calculations using the RI-MP2 method and 6-31++G** basis set, with BSSE correction, have shown that the optimized three-component $C_6H_6\cdots C_6F_6\cdots Br^-$ interaction, for the system with C_{6v} symmetry, is attractive by -16.1 kcal mol^{-1}, but that this is 0.4 kcal mol^{-1} less stable than the sum of separate $C_6H_6\cdots C_6F_6$ and $C_6F_6\cdots Br^-$ interactions.[83]

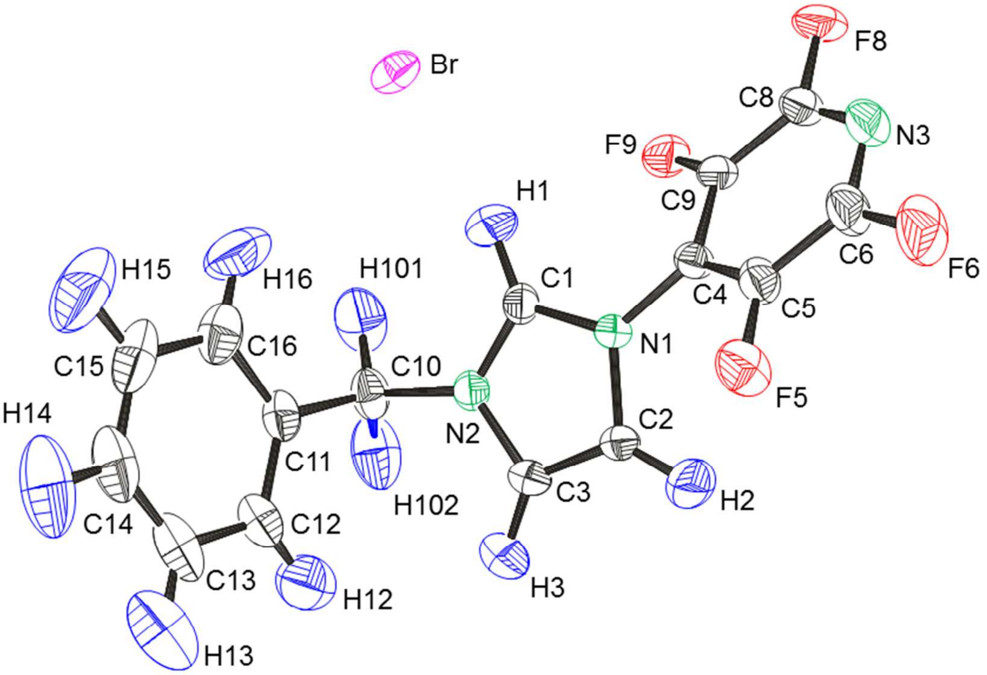


Figure 3. A representative ion pair of 1-(2,3,5,6-tetrafluoropyridyl)-3-benzylimidazolium bromide (**1**) from the neutron Laue diffraction structure determination.

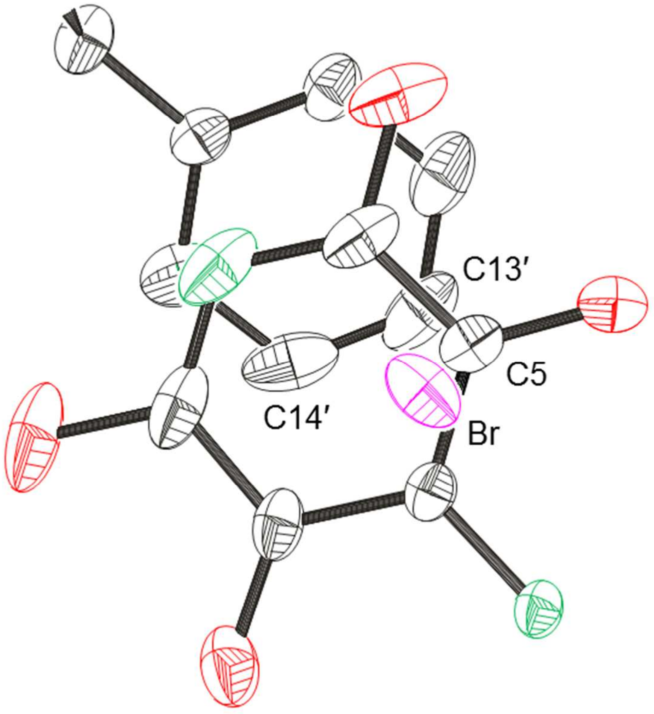
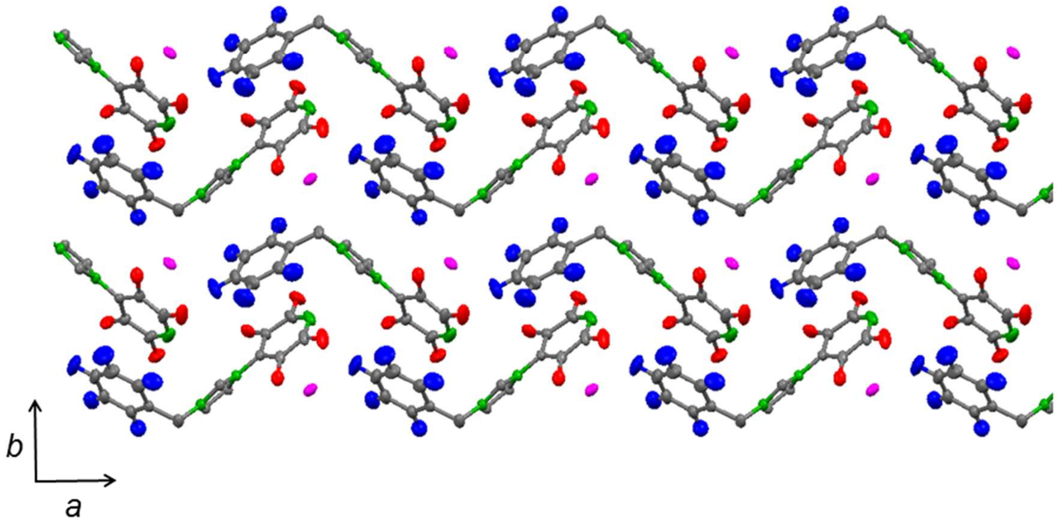
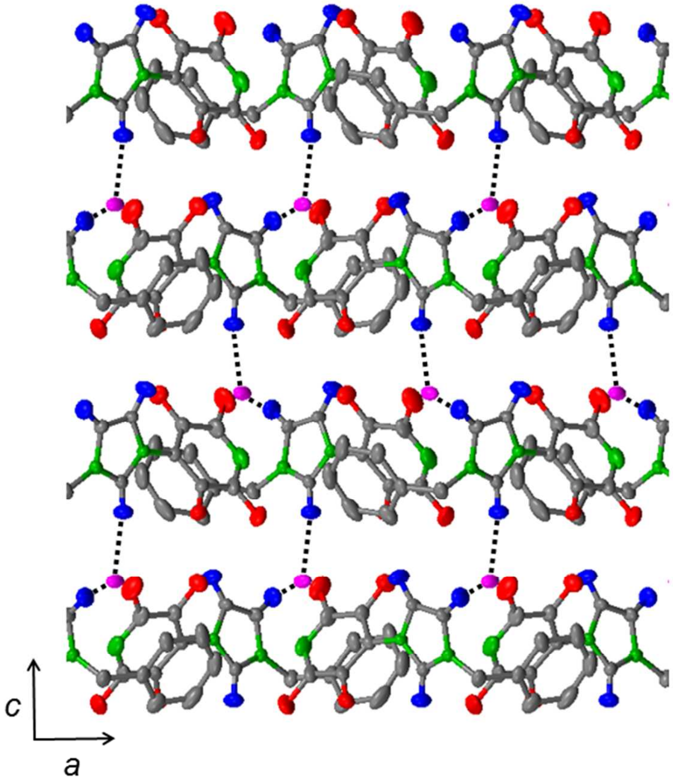


Figure 4. The $C_6H_5\cdots C_5F_4N\cdots Br^-$ motif of 1-(2,3,5,6-tetrafluoropyridyl)-3-benzylimidazolium bromide (**1**) viewed perpendicular to the plane of the tetrafluoropyridyl ring. The hydrogen atoms are omitted for clarity.

The $C_6H_5\cdots C_5F_4N\cdots Br^-$ interactions hold the cations in polar chains (Figure 5a). The bromide anion has a close contact with the H3 hydrogen atom of the imidazolium ring in an adjacent chain. The H3···Br and C3···Br distances, the latter of which is significantly less than the sum of the van der Waals radius of carbon (1.70 Å)[84,85] and the corrected van der Waals radius of the bromide anion (2.35 Å),[61] and the C3—H3···Br angle are indicative of hydrogen bonding.[44,45] The chains are linked by these interactions into sheets parallel to the *a* and *b* axes with polarity parallel to the *a* axis. The bromide anion also possesses a close contact with the H1 hydrogen atom of the imidazolium ring of an adjacent sheet. The H1···Br and C1···Br distances and the C1—H1···Br angle are also characteristic of hydrogen bonding.[44,45] The sheets are thus linked by interactions between hydrogen atoms of imidazolium rings and bromide anions, which are in an approximately trigonal planar environment ($C1\cdots Br\cdots C_6F_4N'$ 116.0(2)°, $C3\cdots Br\cdots C_5F_4N'$ 122.7(2)°, C1···Br···C3′ 121.1(2)°) (Figure 6). Although the sheets have polarity parallel to the *a* axis, adjacent sheets are arranged antiparallel resulting in no net polarity parallel to the *a* and *b* axes. There is, however, polarity parallel to the *c* axis arising from the four orientations of the imidazolium rings. The C_3N_2(centroid)—C1 axes of the four different orientations subtend angles with the *a* and *b* axes of 85.5 and 73.7°, 85.5 and 106.3°, 95.5 and 73.7°, and 95.5 and 106.3° respectively, and hence any polarity cancels in these directions, but all subtend an angle of 163.1° with the *c* axis (Figure 5b).



(a)



(b)

Figure 5. The packing of 1-(2,3,5,6-tetrafluoropyridyl)-3-benzylimidazolium bromide (**1**) viewed (**a**) parallel to the *c* axis showing chains parallel to the *a* axis held together by Ar···ArF···Br$^-$ interactions (the hydrogen atoms of the imidazolium ring are omitted for clarity) and (**b**) parallel to the *b* axis showing interactions between the bromide anion and the imidazolium rings (the hydrogen atoms of the benzyl group are omitted for clarity).

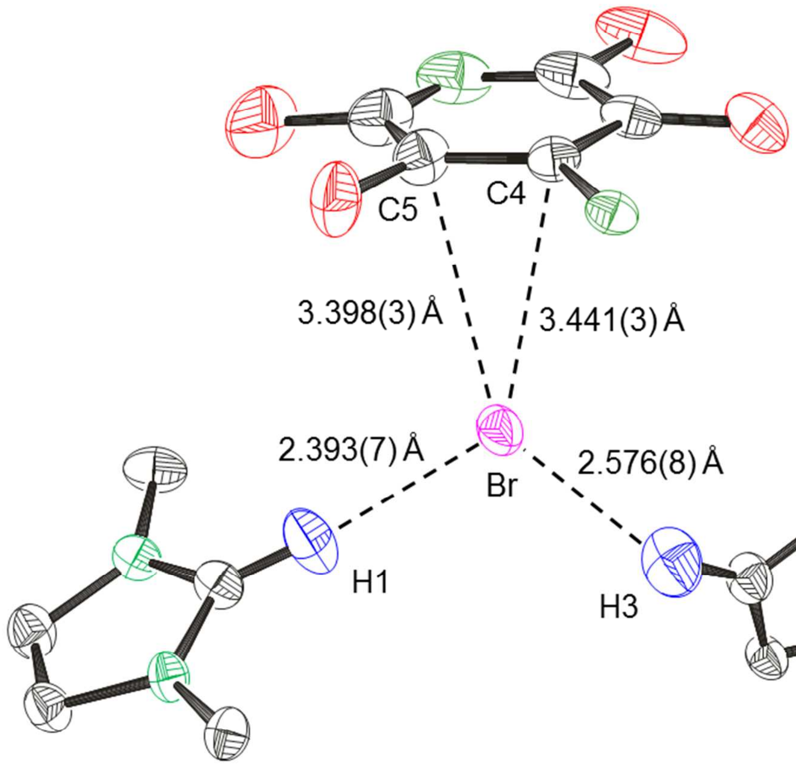


Figure 6. The environment about bromide in the crystal structure of 1-(2,3,5,6-tetrafluoropyridyl)-3-benzylimidazolium bromide (**1**) showing short interionic distances. The hydrogen atoms are omitted for clarity.

The C—H bond lengths for all the hydrogen atoms are surprisingly invariant within experimental error (Table 3). It might be expected that the hydrogen atoms of the imidazolium ring, especially H1, which is the most acidic and readily removed by base,[86] would be drawn towards the bromide anions, lengthening the respective C—H bonds, as usually occurs with hydrogen bonding.[44,45] In order to investigate this, the change in energy of an ion pair with C1—H1 distance was calculated using the B3LYP method[80,81] and 6-311G++(2d,2p) basis set. The calculations (Figure 7) reveal that there is a minimum at 1.105 Å, with a H···Br distance of 2.383 Å, which is only 0.1 kcal mol^{-1} lower than that of the actual structure. The C1—H1 and H1···Br distances and C1—H1···Br angle of this calculated minimum are within 3σ of those experimentally determined. The results also reveal that variation of C1—H1 between 1.05 and 1.16 Å produces only a small change in energy (< 1 kcal mol^{-1}). The calculation was also performed to optimize the position of H1, which resulted in a structure with C1—H1 and H1···Br distances of 1.115 Å and 2.360 Å, a C1—H1···Br angle of 169.16° and an energy 0.3 kcal mol^{-1} lower than that of the experimentally determined structure. Evidently the interaction has only a small effect on the C—H bond distance in the crystals studied.

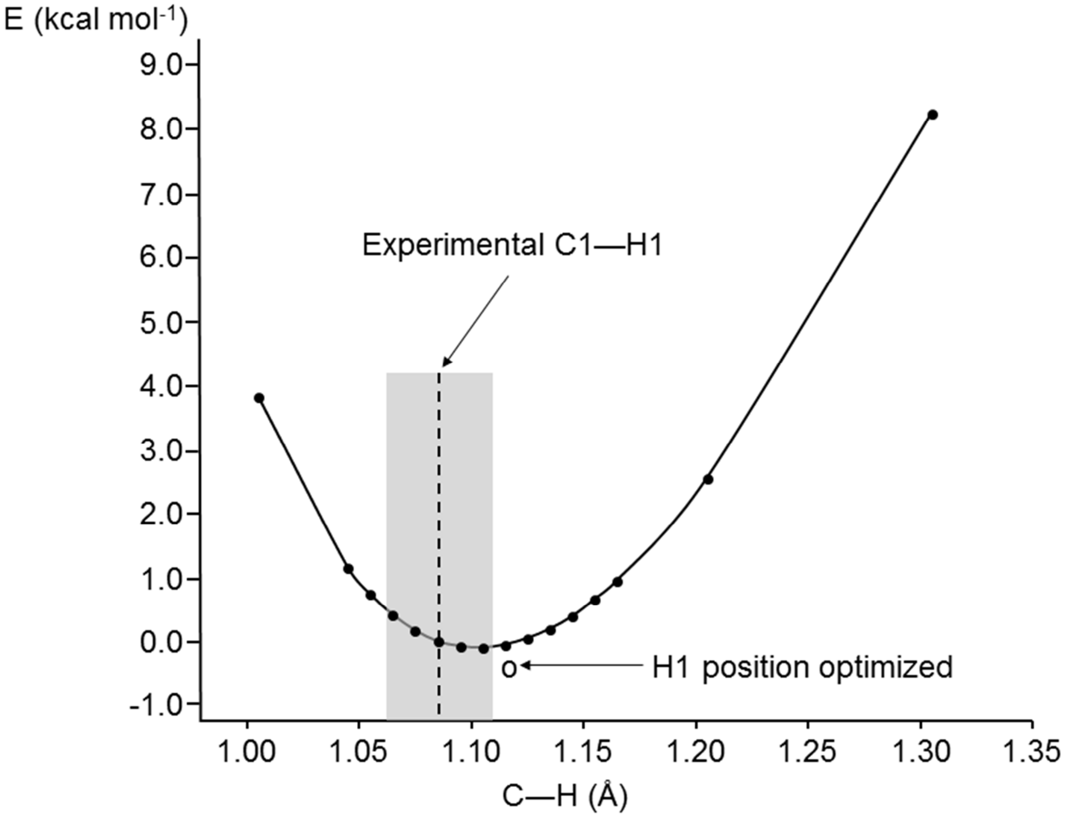


Figure 7. Variation of energy, relative to the experimental structure, with C1—H1 distance calculated by the B3LYP method using the 6-311G++(2d,2p) basis set. The shaded area represents 3σ of the experimental value.

The energies of interaction between the cation and bromide were calculated by the B3LYP method[80,81] and 6-311G++(2d,2p) basis set to be -87.5, -81.2 and -76.2 kcal mol^{-1} for the experimentally determined structures of the ion pairs with the bromide anion close to H1, H3 and the tetrafluoropyridyl ring respectively. The first two values are *ca.* 7 kcal mol^{-1} more attractive than those calculated using the MP2 method and the 6-311G** basis set for similar positions of the bromide in the 1-ethyl-3-methylimidazolium salt (*vide supra*),[46] but the difference between the two energies for the two different systems is similar: 6.3 *cf.* 6.7 kcal mol^{-1}. For 1-ethyl-3-methylimidazolium bromide the energies of interaction were found to be almost inversely proportional to the distance from the midpoint of the two nitrogen atoms, which is close to the center of positive charge.[46] Such a relationship is not evident from the calculations performed on **1**: the bromide anion close to H3 is further from the midpoint of the two nitrogen atoms of the imidazolium ring than that close to the tetrafluoropyridyl ring (4.93 *cf.* 4.71 Å) and yet has an interaction that is calculated to be 5 kcal mol^{-1} stronger. Since the $C_5F_4N\cdots Br^-$ is not expected to be repulsive,[50,61-64] we conclude that the interactions cannot be considered exclusively electrostatic interactions between the anion and the center of charge of the cation. A calculation was also performed to optimize the position of the bromide anion close to H1. This resulted in a structure in which the bromide anion is still in the plane of the imidazolium ring, but shifted towards C10 to give an H1···Br distance of 2.230 Å and a C1—H1···Br angle of 154.69°. This structure was calculated to be 2.2 kcal mol^{-1} lower in energy than that of the structure determined experimentally. As a result it is tentatively suggested that, although the $H1\cdots Br^-$ and $H3\cdots Br^-$ interactions may not be conventional hydrogen bonds, the orientation dependence of the interaction may be greater than previous calculations suggest.[46]

In summary in the crystal structure of **1** the $C_6H_5\cdots C_5F_4N\cdots Br^-$ stacking involving the complementary rings of adjacent cations generates polar chains which arrange in sheets which are connected by interactions between acidic hydrogen atoms of imidazolium rings and bromide anions. The sheets are antiparallel, but the orientation of the imidazolium rings gives rise to polarity parallel to the *c* axis and hence the polar space group.

In order to examine further the importance of the interactions between the imidazolium hydrogen atoms and the bromide anions the crystal structures of the salts in which the hydrogen atoms H1 and H3 had been replaced by methyl groups were investigated. 1-(2,3,5,6-Tetrafluoropyridyl)-2-methyl-3-benzylimidazolium bromide (**2**) crystallized in the space group $P\bar{1}$ of the triclinic crystal system and 1-(2,3,5,6-tetrafluoropyridyl)-3-benzyl-4-

methylimidazolium bromide (**3**) crystallized of the space group $P2_1/c$ of the monoclinic crystal system. The cations of **2** (Figure 8) and **3** (Figure 9) possess very similar geometric parameters to **1** (Table 2), with the exceptions that the tetrafluoropyridyl rings of **2** and **3** are twisted *ca.* 20° more from co-planarity with the imidazolium ring than for **1**, and the phenyl ring of **2** is positioned such that the plane of the imidazolium ring and that defined by N2, C10 and C11 are close to co-planar; they are close to parallel for **1** and **3**. Whilst the planes of the phenyl and tetrafluoropyridyl rings of **1** are approximately orthogonal, those of **2** are close to parallel and those of **3** lie at *ca.* 60° to each other.

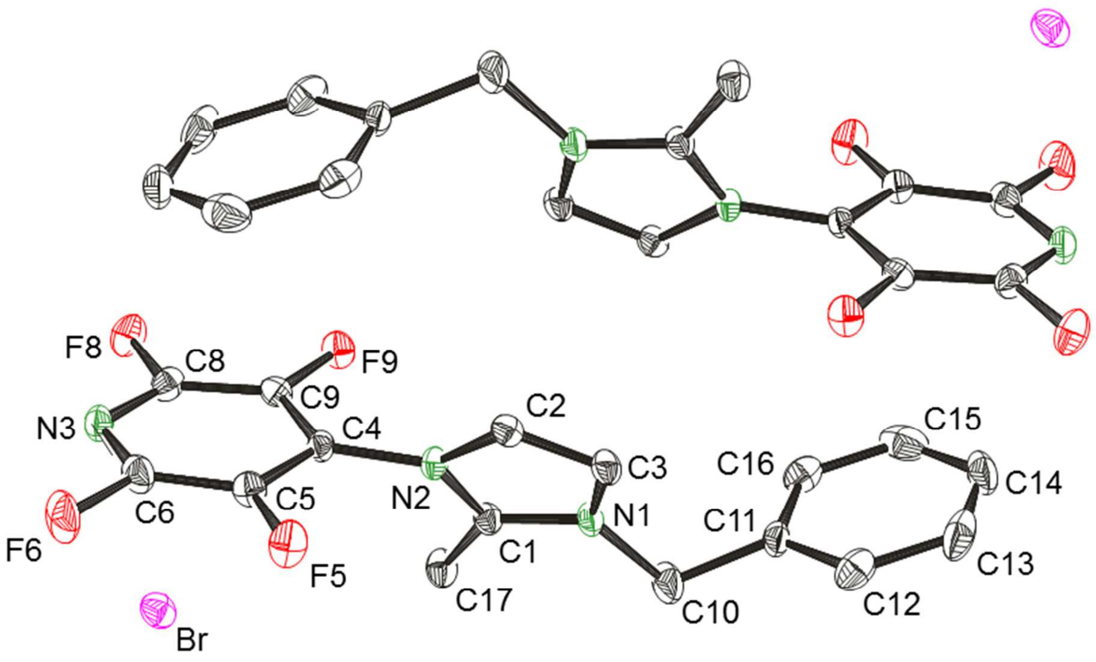


Figure 8. Two stacked ion pairs of 1-(2,3,5,6-tetrafluoropyridyl)-3-benzyl-2-methylimidazolium bromide (**2**). The hydrogen atoms are omitted for clarity.

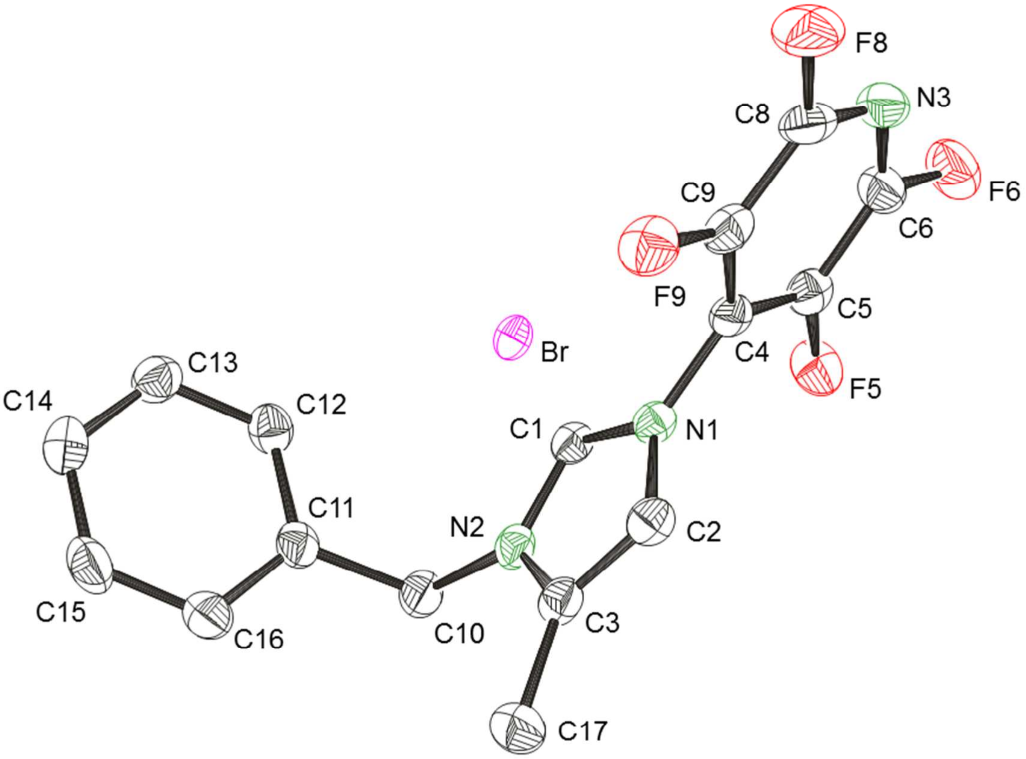


Figure 9. Structure of 1-(2,3,5,6-tetrafluoropyridyl)-3-benzyl-5-methylimidazolium bromide (**3**). The hydrogen atoms are omitted for clarity.

The crystal structure of **2** comprises pairs of cations, related by a centre of inversion, held together by two $C_6H_5\cdots C_5F_4N\cdots Br^-$ interactions. The bromide and the midpoint of C13′—C14′ lie on opposite faces of the tetrafluoropyridyl ring on the normal from C8 ($C13'—C14'_{midpoint}\cdots C8\cdots Br^-$ 177.1(3)°) (Figure 10). The planes of the two interacting rings subtend an angle of 17.3(3)°. In addition to that interacting with the tetrafluoropyridyl ring, two other bromide anions are close to the cation. One is positioned close to C2, in the plane of the imidazolium ring, with the geometric parameters (Table 2) suggesting hydrogen bonding. The other is positioned on one face of the imidazolium ring, 3.36 Å along the normal to the midpoint of C1—N2. Although the planes of adjacent imidazolium rings are parallel and separated by just 3.44(3) Å, the rings are displaced by *ca.* 1.9 Å which prevents a π–π stacking interaction, or avoids repulsion, between them.

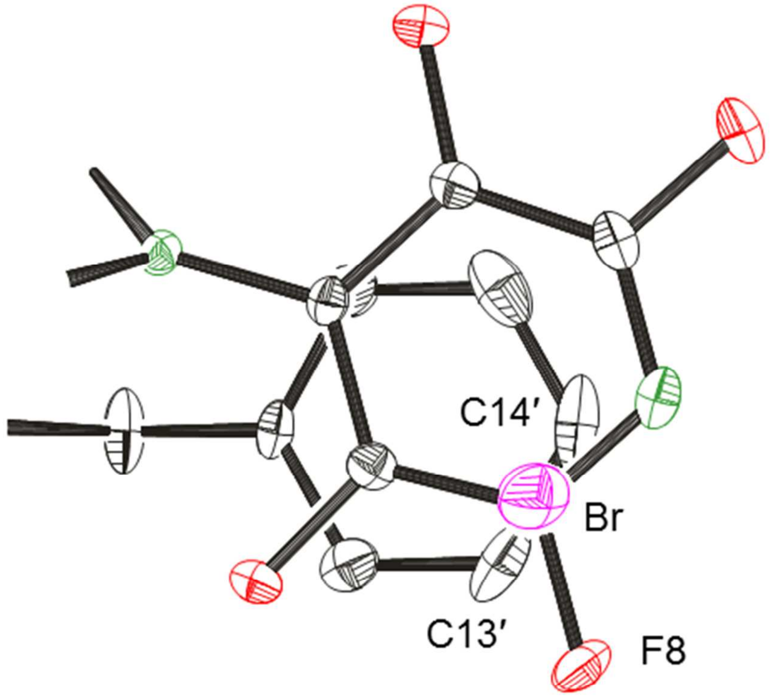


Figure 10. The C_6H_5···C_5F_4N···Br^- motif of 1-(2,3,5,6-tetrafluoropyridyl)-3-benzyl-2-methylimidazolium bromide (**2**) viewed perpendicular to the plane of the tetrafluoropyridyl ring. The hydrogen atoms are omitted for clarity.

The cations of **3** are arranged in polar chains connected by C_6H_5···C_5F_4N···Br^- stacks involving cations of opposite configuration similar to the crystal structure of **1**. The planes of the complementary rings deviate from parallel by *ca.* 9.4° with a separation ranging from 3.386(4) Å (N3···Ar′) to 3.669(4) Å (ArF···C14′). The length of the normal from the plane of the tetrafluoropyridyl ring to the bromide anion is 3.32(3) Å and the bromide is offset by 0.96

Å towards the midpoint of C4—C9 (Figure 11). The Ar···ArF···Br$^-$ angle is almost linear (173.2(3)°). The bromide anion also possesses a close contact with the H1 hydrogen atom of the imidazolium ring of an adjacent chain. The C1···Br distance and the N—C1···Br angles (Table 2) are suggestive of hydrogen bonding.[44,45] The interaction forms sheets parallel to the *a* and *c* axes with polarity parallel to the *c* axis (Figure 12). The other imidazolium hydrogen atom, H2, is positioned close to the bromide anion adjacent to the tetrafluoropyridyl ring (C2···Br 3.683(3) Å). The lack of a hydrogen atom in the 4 position prevents further hydrogen···bromide interactions, and consequently there is no strong interaction between the sheets, which align anti-parallel and so with no net polarity.

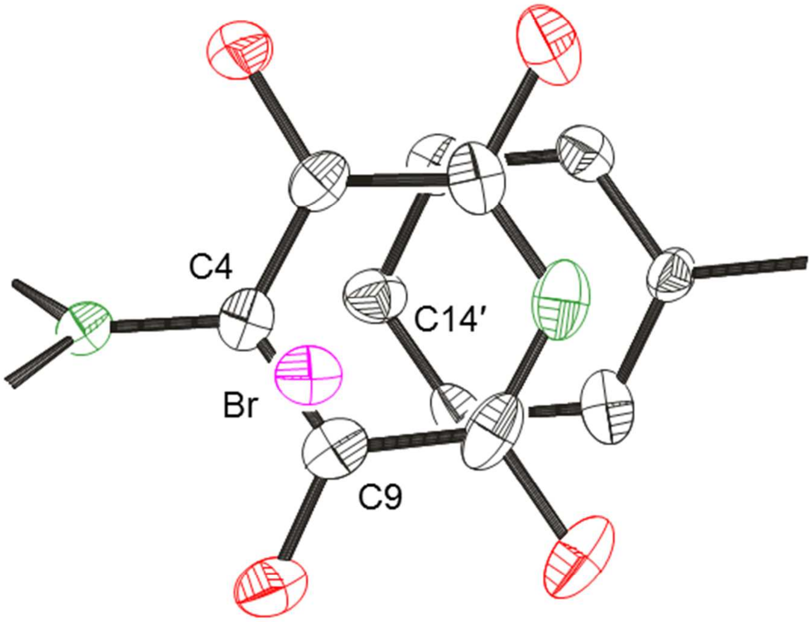


Figure 11. The C_6H_5···C_5F_4N···Br$^-$ motif of 1-(2,3,5,6-tetrafluoropyridyl)-3-benzyl-4-methylimidazolium bromide (**3**) viewed perpendicular to the plane of the tetrafluoropyridyl ring. The hydrogen atoms are omitted for clarity.

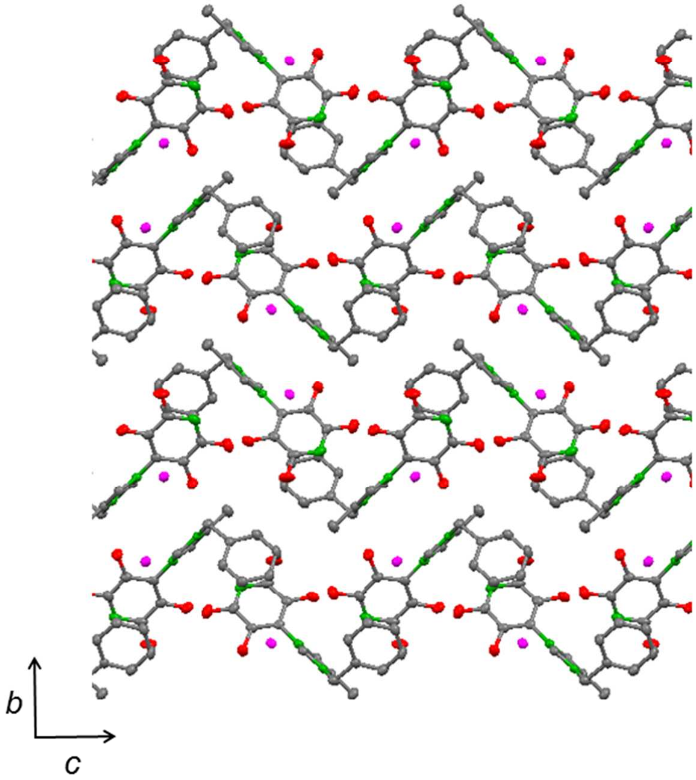


Figure 12. The packing of 1-(2,3,5,6-tetrafluoropyridyl)-3-benzyl-4-methylimidazolium bromide (**3**) viewed parallel to the *a* axis showing chains parallel to the *c* axis held together by Ar···ArF···Br$^-$ interactions. The hydrogen atoms are omitted for clarity.

Since the structures of **1**, **2** and **3** all contain $C_6H_5\cdots C_5F_4N\cdots Br^-$ motifs we were prompted to investigate whether this interaction occurs for other polyfluoroaryl- and aryl-substituted imidazolium salts. The structures of 1-(2,3,5,6-tetrafluoropyridyl)-3-(3-phenylbenzyl)imidazolium bromide (**4**) and 1-(2,3,5,6-tetrafluoropyridyl)-3-(2-naphthylmethyl)imidazolium bromide (**5**), which bear the same polyfluoroaryl substituent as **1**, but a more elaborate benzyl substituent, and 1-(2,3,4,5,6-pentafluorobenzyl)-3-phenylimidazolium bromide (**6**),[65] in which the positions of the aryl and polyfluoroaryl substituents are switched, were then determined. Salt **4** crystallized as the monohydrate from methanol in the centrosymmetric space group $P2_1/c$ with one cation-anion pair and one water molecule in the asymmetric unit. Salt **5** crystallized also as the monohydrate from methanol in the polar space group $P2_1$ with four cation-anion pairs and four water molecules in the asymmetric unit. The crystal from which the structure was determined was pseudo-merohedrally twinned with additional racemic twinning. Salt **6** crystallized from dichloromethane in the centrosymmetric space group *Pbca* in the orthorhombic crystal system with one cation-anion pair in the asymmetric unit.

The cations of **4**, **5** and **6** exhibit a similar check mark shaped geometry to **1** (Figures 13 – 15), with similar bond distances and angles for the imidazolium ring and methylene group (Table 2). As in the structure of **1** there is a close contact between a bromide anion and H1 of the cations, with C1···Br distances significantly less than the sum of the van der Waals radius of carbon and the corrected van der Waals radius of bromide (4.05 Å[61,84,85]) and an approximately trigonal planar arrangement of N1, N2 and the anion about C1 (Table 2), indicating a hydrogen···bromide interaction.

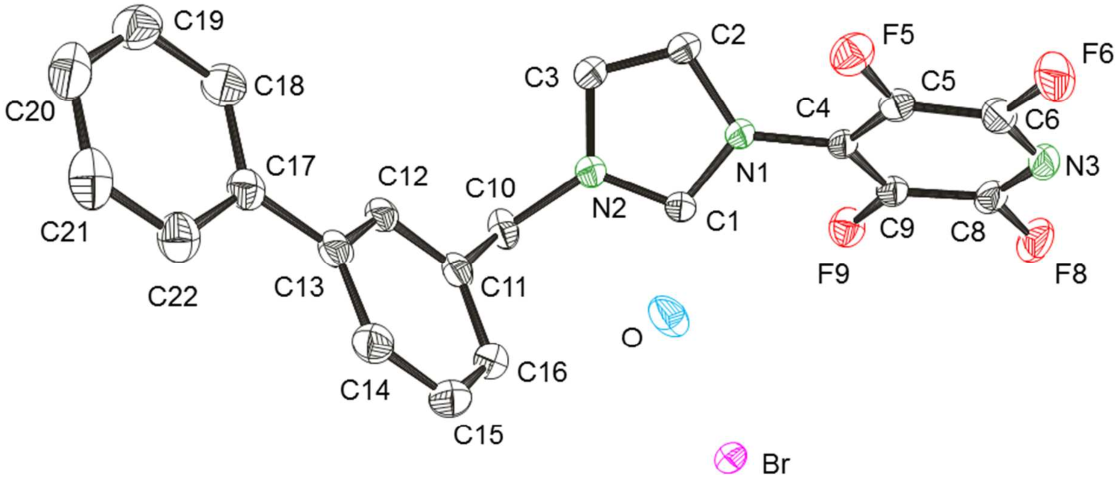


Figure 13. Structure of 1-(2,3,5,6-tetrafluoropyridyl)-3-(3-phenylbenzyl)imidazolium bromide monohydrate (**4**). The hydrogen atoms are omitted for clarity.

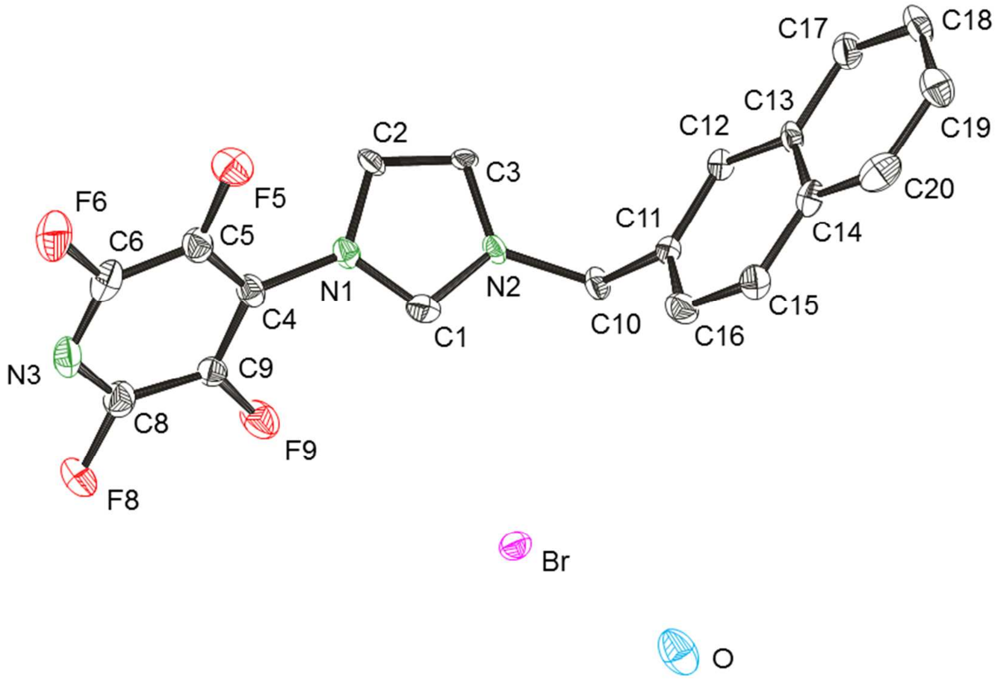


Figure 14. Structure of one of the ion pairs of 1-(2,3,5,6-tetrafluoropyridyl)-3-(2-naphthylmethyl)imidazolium bromide monohydrate (**5**). The hydrogen atoms are omitted for clarity.

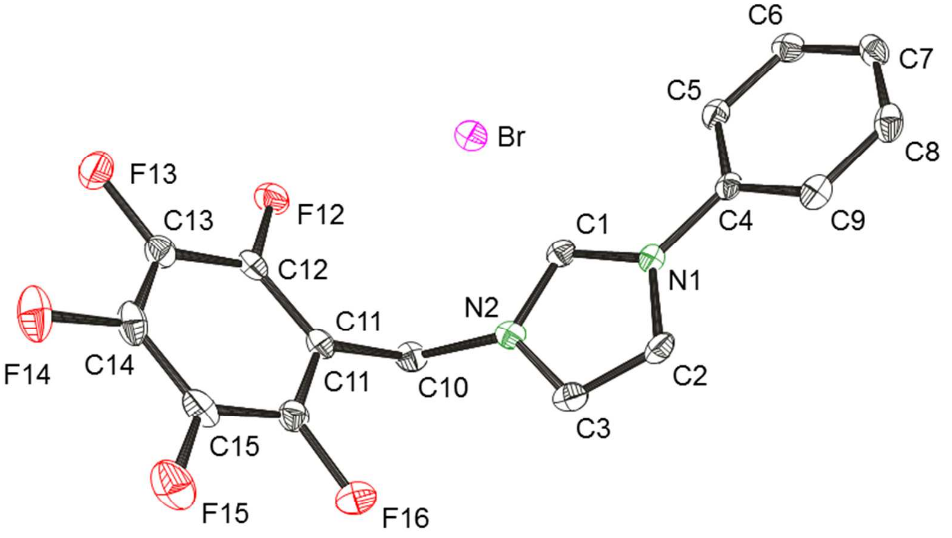


Figure 15. Structure of 1-(2,3,4,5,6-pentafluorobenzyl)-3-phenylimidazolium bromide (**6**). The hydrogen atoms are omitted for clarity.

The conformation of the cation of **4** is similar to that of **1** with the imidazolium and methylene-bonded phenyl rings almost perpendicular to the plane defined by N2, C10 and C11 (*ca.* 86 and 88° respectively) and the tetrafluoropyridyl ring twisted by *ca.* 41° relative to the imidazolium ring. The two phenyl rings are twisted relative to each other by *ca.* 15°. The cation is chiral, and the structure contains both enantiomers. The distances of the tetrafluoropyridyl and closer phenyl rings to the methylene carbon atom are similar to those of **1**. The plane of the tetrafluorophenyl ring subtends an angle of 74.2° with the plane of the nearer phenyl ring (C11-C16) and an angle of 89.1° with the plane of the further phenyl ring (C17-C22). The structure possesses $C_6H_4\cdots C_5F_4N\cdots Br^-$ stacking involving the tetrafluoropyridyl ring of one cation with the biphenyl group of a cation of opposite configuration (Figure 16) which forms chains that are parallel to the *c* axis. The planes of the tetrafluoropyridyl ring and that of the closer phenylene ring, C11-C16, deviate from parallel by *ca.* 4.0° with a separation of *ca.* 3.3 Å (C8···C12′ 3.283(2) Å, C8···C11′ 3.283(2) Å, C6···C13′ 3.390(2) Å, N3···Ar′ 3.332(2) Å). The length of the normal to the plane of the tetrafluoropyridyl ring to the bromide anion is 3.33(1) Å and the bromide is offset by 1.65 Å towards the midpoint of C6—N3, such that the $C13'\cdots C6\cdots Br^-$ angle is 166.86(6)°. The stacking interaction is augmented by the interactions of H1 of one cation and H3 of another cation with the same bromide anion. These interactions assemble the chains into sheets parallel to the *bc* plane with polarity parallel to the *c* axis (Figure 17). Pairs of sheets of opposite polarity are linked by short CH···arene distances (C14···C19′ 3.614(3) Å, C14···C20′ 3.702(2) Å, C22···C18′ 3.829(2) Å, C22···C17′ 4.101(2) Å) between cations of the same stereoconfiguration to form bilayers with hydrophobic (biphenyl) cores and hydrophilic (imidazolium, bromide) exteriors. The bilayers are bridged by water molecules, pairs of which interact with bromide anions to form $2Br^-.2H_2O$ rhomboids centered on crystallographic inversion centers. The Br···O distances of 3.320(1) and 3.323(1) Å are significantly shorter than the sum of the van der Waals radius of oxygen and the corrected van der Waals radius of bromide (3.87 Å[61,84,85]). The O···Br···O and Br···O···Br angles are 71.75(4) and 108.25(4)° respectively. Similar $2Br^-.2H_2O$ rhomboids are present in crystal structures of several other hydrated bromide salts,[87-100] and a similar arrangement of bilayers in the crystal structure of 4-trifluoromethyl-2,3,5,6-tetrafluorobenzyl-2-phenylpyridium cations separated by $2Br^-.2H_2O$ rhomboids has been reported.[101]

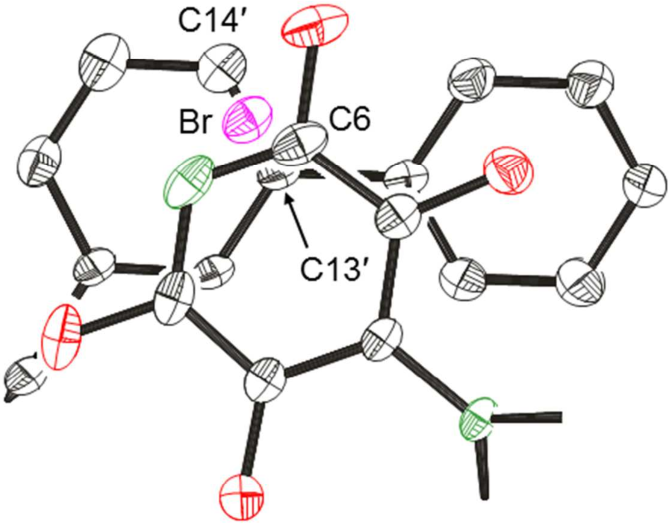
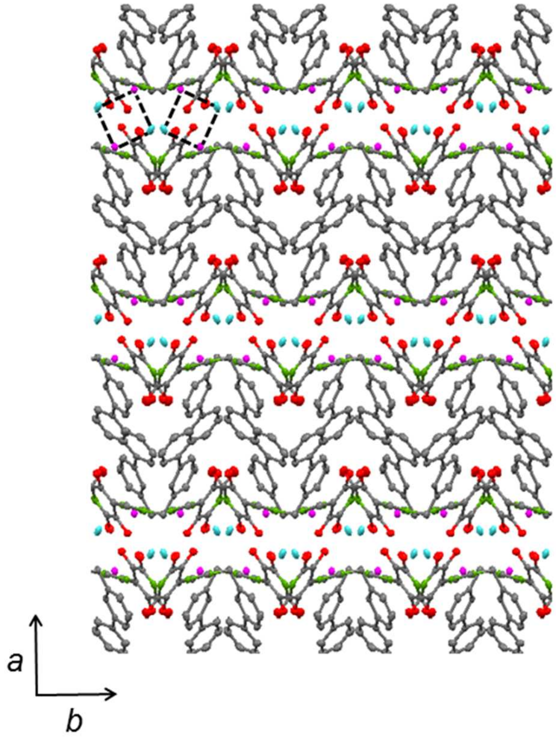
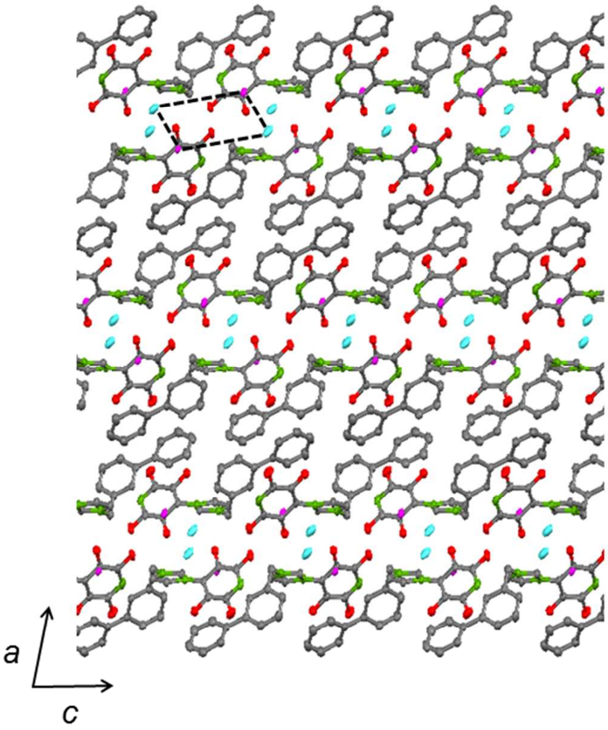


Figure 16. The $C_6H_4 \cdots C_5F_4N \cdots Br^-$ motif of 1-(2,3,5,6-tetrafluoropyridyl)-3-(3-phenylbenzyl)imidazolium bromide (**4**) viewed perpendicular to the plane of the tetrafluoropyridyl ring. The hydrogen atoms are omitted for clarity.



(a)



(b)

Figure 17. The packing of 1-(2,3,5,6-tetrafluoropyridyl)-3-(3-phenylbenzyl)imidazolium bromide monohydrate (**4**) viewed (**a**) parallel to the *c* axis and (**b**) parallel to the *b* axis showing bilayers separated by $[2Br.2H_2O]^{2-}$ anions (indicated top left). The hydrogen atoms are omitted for clarity.

The conformation of the cations of **5** are similar to those of **1** and **4** with the imidazolium and naphthyl rings almost perpendicular to the plane defined by N2, C10 and C11 (**A** *ca.* 79 and 90°; **B** *ca.* 72 and 83°; **C** *ca.* 75 and 90°; **D** *ca.* 67 and 88° respectively) and the tetrafluoropyridyl ring twisted relative to the imidazolium ring by *ca.* 54°, 44°, 50° and 44° for cations **A**, **B**, **C** and **D** respectively. The cations are chiral with cations **A** and **D** having the same configuration. Cation **C** is approximately the mirror image of **A**, and cation **D** is approximately the mirror image of **B**. The cations are linked by $C_{10}H_7\cdots C_5F_4N\cdots Br^-$ interactions (Figure 18) to form two independent chains, one comprising cations **A** and **B**, and the other cations **C** and **D**, parallel to the *c* axis. The four different stacks have similar parameters (Table 2) with the centroid of the tetrafluoropyridyl ring lying approximately on the normal to the plane of the naphthyl ring from the bridgehead carbon atom *meta* to the methylene group (C13), and the angle formed by the centroid of the unsubstituted ring of the naphthyl group, the carbon atom of the pyridyl ring *meta* to the ring nitrogen atom (C5), and the bromide anion being almost linear: $C_6H_4(B)_{centroid}\cdots C5A\cdots Br1$ 175.8°, $C_6H_4(A)_{centroid}\cdots C5B\cdots Br2$ 174.1°, $C_6H_4(D)_{centroid}\cdots C5C\cdots Br3$ 174.1°, $C_6H_4(C)\cdots C5D\cdots Br4$ 173.8° (Figure 18).

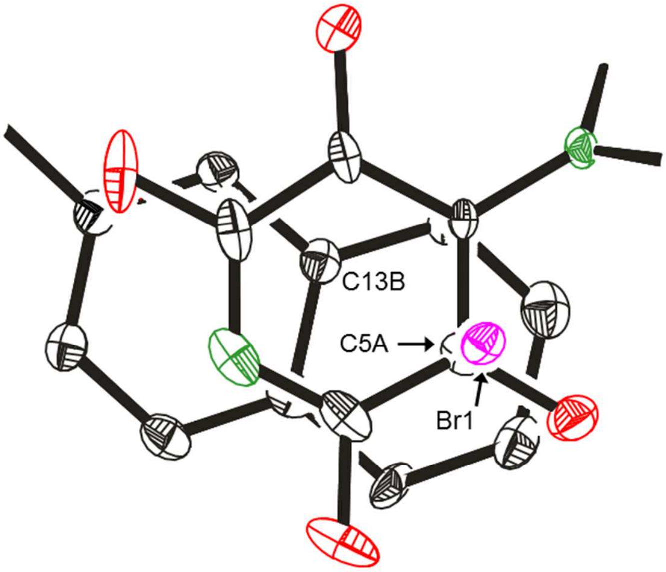
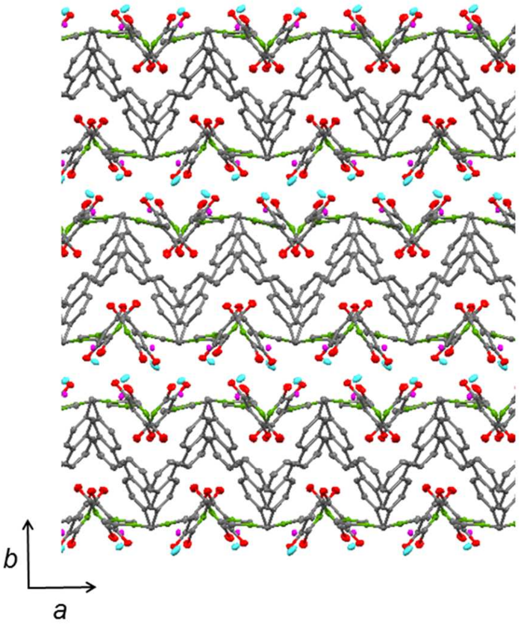
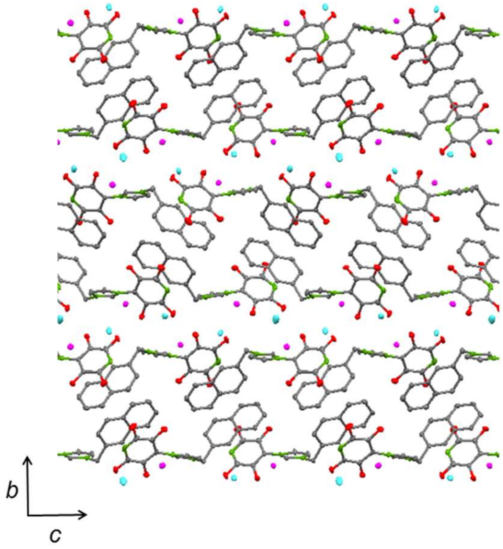


Figure 18. One of the $C_{10}H_7\cdots C_5F_4N\cdots Br^-$ motifs of 1-(2,3,5,6-tetrafluoropyridyl)-3-(2-naphthylmethyl)imidazolium bromide (**5**) viewed perpendicular to the plane of the tetrafluoropyridyl ring. The hydrogen atoms are omitted for clarity.

Equivalent chains are connected by the interactions between H1 and the bromide anion into sheets parallel to the *ac* plane (Figure 19). The sheets alternate along the *b* axis giving polarity in that direction. As with the crystal structure of **4** pairs of sheets are linked by short CH···arene distances (C15A···C17D 4.09(1) Å, C15A···C18B 4.11(1) Å, C20A···C12D 4.069(9) Å, C20A···C13D 4.027(9) Å, C15B···C17C 4.09(1) Å, C15B···C18C 4.10(1) Å, C20B···C12C 4.03(1) Å, C20B···C13C 3.967(9) Å, C15C···C17B 4.07(1) Å, C15C···C18B 4.12(1) Å, C20C···C12B 4.11(1) Å, C20C···C13B 4.06(1) Å, C15D···C17A 4.057(9) Å, C15D···C18A 4.07(1) Å, C20D···C12A 4.06(1) Å, C20D···C13A 3.98(1) Å) between cations of the same stereoconfiguration to form bilayers with hydrophobic (biphenyl) cores and hydrophilic (imidazolium, bromide) exteriors. Water molecules are positioned between the bilayers and interact with the bromide anions forming ribbons which run perpendicular to the *b* axis and parallel to the diagonal bisecting the *a* and *c* axes. The Br···O distances of 3.334(5), 3.393(6), 3.378(5), 3.379(6), 3.396(7), 3.355(8), 3.373(5) and 3.418(6) Å are significantly shorter than the sum of the van der Waals radius of oxygen and the corrected van der Waals radius of bromide (3.87 Å[61,84,85]). The O···Br···O and Br···O···Br angles are 98.8(1), 94.6(2), 86.4(2) and 99.2(1)°, and 121.9(2), 124.4(2), 116.8(2) and 123.5(2)° respectively. Similar ribbons of bromide anions and water molecules are present in crystal structures of several other hydrated bromide salts.[102-114]



(a)



(b)

Figure 19. The packing of 1-(2,3,5,6-tetrafluoropyridyl)-3-(2-naphthylmethyl)imidazolium bromide monohydrate (**5**) viewed (**a**) parallel to the *c* axis and (**b**) parallel to the *a* axis showing bilayers separated by $(Br^{-}.H_2O)_n$ chains. The hydrogen atoms are omitted for clarity.

The conformation of the cation of **6** is similar to those of **1**, **4** and **5** with the imidazolium ring almost perpendicular to the plane defined by N2, C10 and C11 (*ca.* 80°). The pentafluorophenyl ring is, however, twisted slightly more relative to the plane defined by N2, C10 and C11 (*ca.* 75°) than the phenyl rings of **1**, **4** and **5**, and the phenyl ring is almost co-planar with the imidazolium ring (twisted by *ca.* 12°). In contrast to the crystal structures of **1**–**5** that of **6** does not possess π–π stacking interactions between the aryl and polyfluoroaryl rings, but rather has offset face-to-face stacking of the phenyl rings to give columns parallel to the *b* axis (Figure 20). The planes of adjacent phenyl rings are separated by *ca.* 3.44 Å, subtend an angle of *ca.* 6.0°, and are offset by *ca.* 1.51 Å so that the columns are at *ca.* 66° to the planes of the rings. These parameters are consistent with π–π stacking of other arenes.[2,3,115] There is polarity parallel to the column by virtue of the hinges being unidirectional. The hinge carbon atoms of a column define a plane on one side of which lies the imidazolium and phenyl rings and on the other side are positioned the pentafluorophenyl rings, which gives polarity perpendicular to the column, parallel to the *c* axis. The columns possess no net polarity parallel to *a* axis because the cations are related by a glide plane. Although each column possesses polarity in two directions, the columns are arranged such that the polarity parallel to the *b* and *c* axes cancels. As with **1** and **4** there are short contacts between the bromide anion and two of the carbon atoms of the imidazolium ring. In addition a bromide anion is positioned in the cleft between the imidazolium and pentafluorophenyl rings. It lies at 3.585(4) Å from the plane of the former, almost on the normal to the centroid, and at 3.813(4) Å from the plane of the latter, almost on the normal to C11, suggesting anion–π interactions.[50]

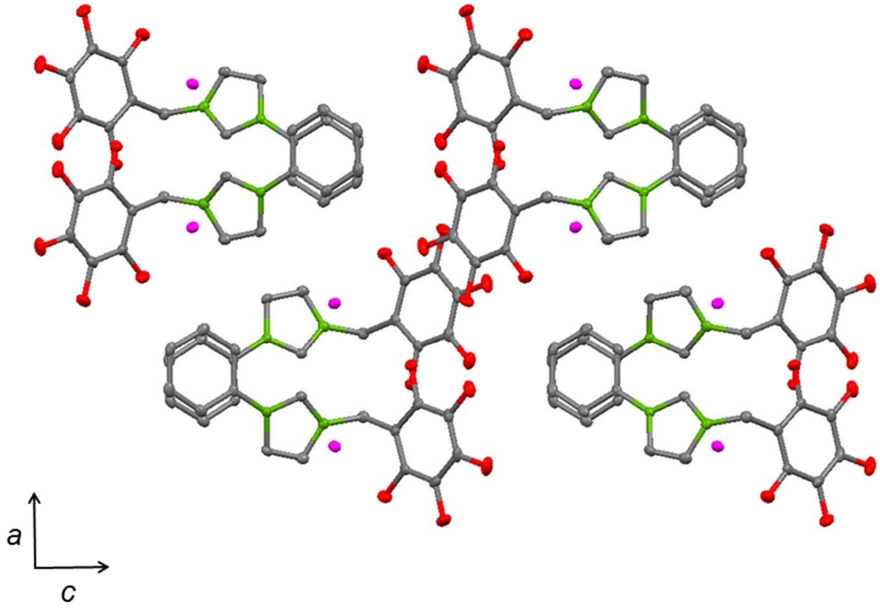


Figure 20. The packing of 1-(2,3,4,5,6-pentafluorobenzyl)-3-phenylimidazolium bromide (**6**) viewed parallel to the *b* axis. The hydrogen atoms are omitted for clarity.

Although the cation of **6** adopts a similar conformation to that of **1**, **6** cannot adopt a similar crystal structure containing $C_6H_5\cdots C_6F_5\cdots Br^-$ interactions and allow sufficient space for the bromide anions to lie close to the faces of pentafluorophenyl rings. To accommodate the bromide anions in such a manner the separation between the chains of cations would need to increase, but even then the anions would be positioned close to one another; the consequent repulsion is likely to destabilize the model structure sufficiently that another is preferred. Although the crystal structure of **6** does not contain $C_6H_5\cdots C_6F_5\cdots Br^-$ interactions there are still C1—H1···Br$^-$ and C2—H2···Br$^-$ interactions, which supports the conclusions of the theoretical study into the strength and orientation dependence of stacking and C—H···Br$^-$ interactions of **1**.

CONCLUSIONS

The crystal structures of **1** – **5** demonstrate that π–π stacking occurs between the tetrafluoropyridyl and arylmethyl substitutents of enantiomeric pairs of imidazolium cations. Each tetrafluoropyridyl ring also has a close contact to a bromide anion on the opposite face to the π–π stacking interaction, forming Ar···ArF···Br$^-$ triad stacks. The check mark geometry of the cations prevents columnar stacking and in consequence polar chains are generated in the crystal structures of **1** and **3** – **5**. The chains are linked by C—H···Br$^-$ interactions into sheets which possess polarity along both axes. The sheets are aligned antiparallel thereby cancelling polarity parallel to the axes of the sheet. For **1** the sheets are linked by C—H···Br$^-$ interactions, which align the imidazolium rings with polarity perpendicular to the sheets. For **4** and **5** the sheets form bilayers linked by C─H···arene interactions. The bilayers are separated by $[2Br.2H_2O]^{2-}$ rhomboids and $(Br^{-}.H_2O)_n$ chains in the crystal structures of **4** and **5** respectively. Although the structure of **4** is centrosymmetric, that of **5** is non-centrosymmetric with polarity perpendicular to the bilayers by virtue of slight differences between the cations of adjacent sheets.

ASSOCIATED CONTENT

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Footnote

[†] Ar′* indicates the centroid of the phenyl ring, ArF* indicates the centroid of the fluoroaryl ring.

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Table 1. Crystal and Refinement Data for 1− 6

	1	**2**	**3**	**4**	**5**	**6**
formula	$C_{15}H_{10}BrF_4N_3$ [a]	$C_{16}H_{12}BrF_4N_3$	$C_{16}H_{12}BrF_4N_3$	$C_{21}H_{14}BrF_4N_3.H_2O$	$C_{19}H_{12}N_3F_4Br.H_2O$	$C_{16}H_{10}N_2F_5Br$
M	388.17	402.20	402.20	482.28	456.24	405.17
crystal system	orthorhombic	triclinic	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$Pna2_1$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1$	$Pbca$
a/Å	12.7109(3)	7.1399(3)	7.9987(4)	14.4532(4)	8.1985(2)	15.0112(8)
b/Å	9.5071(3)	9.6073(4)	16.4596(9)	8.9340(2)	26.1678(7)	7.5164(4)
c/Å	12.7444(4)	11.6962(4)	12.9003(7)	15.9537(4)	17.5064(4)	26.1872(14)
$\alpha/^\circ$	—	95.074(3)	—	—	—	—
$\beta/^\circ$	—	99.929(3)	106.104(2)	100.663(1)	90.106(1)	—
$\gamma/^\circ$	—	98.871(3)	—	—	—	—
V/Å^3	1540.08(8)	775.36(5)	1631.75(15)	2024.45(9)	3755.76(9)	2954.7(3)
D_c/g cm^{-3}	1.674	1.723	1.637	1.582	1.614	1.822
Z, Z'	4, 1	2, 1	4, 1	4, 1	8, 4	8, 1

dimensions/mm^3	0.67 × 0.60 × 0.37	0.29 × 0.17 × 0.12	0.25 × 0.12 × 0.12	0.30 × 0.30 × 0.20	0.40 × 0.32 × 0.12	0.47 × 0.19 × 0.03
μ (Mo Kα)/mm^{-1}	2.712	4.064 [b]	2.563	2.084	2.242	2.839
$T_{\mathrm{min,max}}$	0.6110, 0.7458	0.680, 0.847	0.5667, 0.7484	0.5736, 0.6806	0.4675, 0.7747	0.3488, 0.9197
N_{ind} (R_{int})	4090 (0.0367)	2974 (0.0211)	3936 (0.0590)	4868 (0.0313)	18233 (0.0430)	3515 (0.0468)
N_{obs} ($I > 2\sigma(I)$)	3706	2853	2957	4240	16274	2807
N_{var}	208	217	217	335	1010	217
R_1, wR_2 [$I > 2\sigma(I)$] [c]	0.0214, 0.0511	0.0293, 0.0786	0.0363, 0.0847	0.0242, 0.305	0.0399, 0.0447	0.0448, 0.0576
R_1, wR_2 (all data) [c]	0.0261, 0.0528	0.0303, 0.0794	0.0576, 0.0918	0.0597, 0.0626	0.0454, 0.0477	0.0988, 0.1039
GOF	1.047	1.051	1.029	1.030	1.158	1.012
$\Delta\rho_{\mathrm{min,max}}$/e$^-$ Å^{-3}	-0.201, 0.311	-0.418, 0.742	-0.593, 0.631	-0.0206, 0.378	-0.81, 2.25	-0.491, 0.768

[a] Flack parameter 0.008(6). [b] μ (Cu Kα)/mm^{-1}. [c] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for $F_o > 2\sigma(F_o)$ and $wR_{2(\mathrm{all})} = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_c^2)^2]\}^{1/2}$ where $w = 1/[\sigma 2(F_o^2) + (\mathrm{A}P)^2 + \mathrm{B}P]$, $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Selected Distances and Angles for 1 − 6

	1	**2**	**3**	**4**	**5**				**6**
					A	**B**	**C**	**D**	
C1—N1	1.342(2)	1.349(3)	1.336(3)	1.346(2)	1.327(9)	1.336(9)	1.336(8)	1.326(8)	1.335(5)
C1—N2	1.313(2)	1.331(3)	1.320(3)	1.321(2)	1.333(7)	1.302(7)	1.294(7)	1.315(7)	1.325(5)
N1—C2	1.393(2)	1.398(3)	1.386(3)	1.397(2)	1.374(9)	1.590(8)	1.352(9)	1.313(7)	1.386(5)
N2—C3	1.385(2)	1.385(3)	1.390(4)	1.389(2)	1.372(8)	1.585(8)	1.378(8)	1.302(8)	1.387(5)
C2—C3	1.348(3)	1.346(3)	1.348(4)	1.339(2)	1.304(9)	1.294(9)	1.281(9)	1.313(8)	1.342(5)
N1—C4	1.416(2)	1.419(3)	1.420(3)	1.419(2)	1.435(7)	1.364(8)	1.433(7)	1.453(7)	1.443(5)
N2—C10	1.485(2)	1.481(3)	1.483(3)	1.486(2)	1.497(8)	1.457(8)	1.505(8)	1.509(8)	1.472(5)
C10—C11	1.511(3)	1.501(3)	1.517(4)	1.511(2)	1.506(8)	1.499(8)	1.497(7)	1.509(7)	1.505(5)
C10—ArF* [a]	6.249(3)	6.171(3)	6.192(4)	6.235(2)	6.234(8)	6.272(8)	6.244(8)	6.242(8)	2.925(5)
C10—Ar*	2.898(3)	2.891(3)	2.917(4)	2.899(2)	2.916(8) [b]	2.905(8) [b]	2.912(8) [b]	2.916(8) [b]	6.223(5)
N1—C1—N2	107.68(15)	107.03(19)	107.8(2)	107.67(13)	105.1(5)	113.1(6)	108.9(5)	106.2(6)	108.6(3)

C1—N1—C2	109.14(14)	109.57(18)	109.1(2)	108.85(13)	110.2(5)	106.9(5)	106.1(5)	108.2(5)	108.5(3)
C1—N1—C4	125.63(15)	123.54(18)	124.1(2)	124.28(13)	122.6(5)	130.3(6)	125.1(5)	123.6(5)	124.9(3)
C1—N2—C3	109.89(15)	109.55(19)	109.6(2)	109.50(13)	110.4(5)	106.8(5)	108.3(5)	110.0(5)	108.5(3)
C1—N2—C10	125.45(17)	122.2(2)	122.7(2)	124.79(13)	123.9(5)	130.5(5)	124.3(5)	123.6(5)	124.0(3)
N2—C10—C11	110.68(15)	114.4(2)	111.6(2)	110.12(12)	112.1(4)	111.9(5)	112.2(4)	111.9(4)	113.5(3)
C1—N1—C4—C5	-144.27(17)	-116.0(2)	61.5(4)	-136.42(15)	129.8(6)	-139.3(7)	-129.9(6)	137.0(6)	10.3(5)
C1—N1—C4—C9	39.7(2)	61.6(3)	-119.0(3)	44.7(2)	-55.6(8)	41.3(9)	52.6(8)	-43.7(9)	-170.8(3)
C1—N2—C10—C11	98.1(2)	-151.7(2)	87.1(3)	91.23(17)	-103.3(6)	107.0(7)	104.0(6)	-112.2(6)	101.8(4)
N2—C10—C11—C12	81.7(2)	-92.3(3)	-76.9(3)	91.30(17)	-93.3(7)	99.9(6)	91.4(6)	-94.5(6)	-107.1(4)
N2—C10—C11—C16	-96.1(2)	93.2(3)	103.0(3)	-86.69(18)	91.2(6)	-85.0(7)	-91.7(6)	86.5(6)	76.3(4)
ArF*···Ar(plane) [a]	3.37(1)	3.24(1)	3.59(1)	3.31(1)	3.41(1)	3.37(1)	3.41(1)	3.41(1)	—
Ar*···ArF(plane) [a]	3.27(1)	3.59(1)	3.46(1)	3.29(1)	3.40(1)	3.37(1)	3.40(1)	3.39(1)	—
ArF*···Ar* [a]	3.61(1)	3.70(1)	3.64(1)	3.78(1)	3.44(1)	3.38(1)	3.42(1)	3.44(1)	—

∠ ArF(plane) Ar(plane) [c]	4.8(1)	17.3(3)	9.4(1)	4.0(1)	7.4(2)	4.7(2)	8.0(2)	4.9(2)	—
ArF(plane)···Br [d]	3.32(3)	3.39(1)	3.33(1)	3.47(1)	3.33(1)	3.32(1)	3.31(1)	3.36(1)	3.81(1)
C1···Br	3.467(2)	—	3.453(3)	3.581(2)	3.437(6)	3.422(7)	3.469(6)	3.483(7)	3.450(3)
N1—C1···Br	135.0(1)	—	137.6(2)	129.5(1)	142.8(4)	141.6(4)	141.2(4)	145.4(4)	134.9(2)
N2—C1···Br	117.3(1)	—	113.7(2)	122.1(1)	109.9(4)	105.3(4)	107.5(4)	108.0(4)	112.2(2)
C_3N_2···Br [e]	0.15(1)	—	0.52(1)	0.50(1)	0.81(3)	0.00(4)	0.69(3)	0.16(3)	1.04(1)
C3/2···Br [f]	3.593(2)	3.601(2)	—	3.709(2)	—	—	—	—	3.592(3)
C2/3—C3/2···Br [f]	139.6(1)	98.7(1)	—	142.9(1)	—	—	—	—	116.3(2)
N2/1—C3/2···Br [f]	109.7(1)	155.4(1)	—	109.03(9)	—	—	—	—	134.3(2)
C_3N_2···Br [e]	0.97(1)	0.07(1)	—	0.40(1)	—	—	—	—	0.82(1)

[a] ArF* and Ar* indicate the centroids of the fluoroarene and arene rings respectively. For **4** Ar* is the centroid of the ring C11 – C16. For **5** Ar* is the centroid of the naphthyl group. ArF(plane) and Ar(plane) indicate the planes of the fluoroarene and arene rings respectively. For **5** the values of

interionic distances refer to those for which the tetrafluoropyridyl group is a component of the title cation. [b] The centroid of the ring C11 – C16. [c] The angle subtended by the planes of the fluoroarene and arene rings. [d] ArF(plane)···Br is the length of the normal from the plane of the polyfluoroaryl ring to the bromide anion. [e] C_3N_2···Br is the length of the normal from the plane of the imidazolium ring to the bromide anion.[f] For **1** and **3** the bromide anion interacts with C3—H3; the distance and angles refer to C3···Br, C2—C3···Br and N2—C3···Br. For **2** and **6** the bromide anion interacts with C2—H2; the distance and angles refer to C2···Br, C3—C2···Br and N1—C2···Br.

Table 3. Selected Distances and Angles about Hydrogen Atoms from the Neutron Diffraction Study of 1

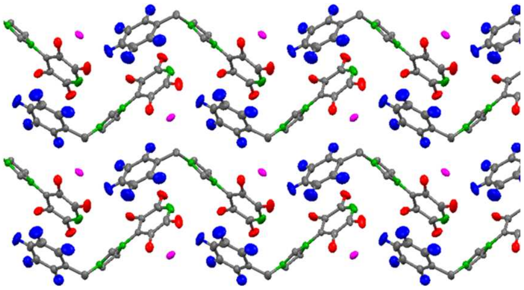
C1—H1	1.086(6)	H1···Br	2.393(7)
C2—H2	1.075(7)	C3—H3	1.093(7)
H3···Br	2.576(8)	C10—H101	1.089(8)
C10—H102	1.091(9)	C12—H12	1.084(10)
C13—H13	1.066(13)	C14—H14	1.087(7)
C15—H15	1.101(10)	C16—H16	1.091(11)
N1—C1—H1	127.1(4)	N2—C1—H1	125.2(4)
C1—H1···Br	168.0(5)	C2—C3—H3	131.3(5)
N2—C3—H3	121.5(5)	C3—H3···Br	155.1(5)

For Table of Contents Use Only

Arene-Perfluoroarene-Anion Stacking and Hydrogen Bonding Interactions in Imidazolium Salts for the Crystal Engineering of Polarity

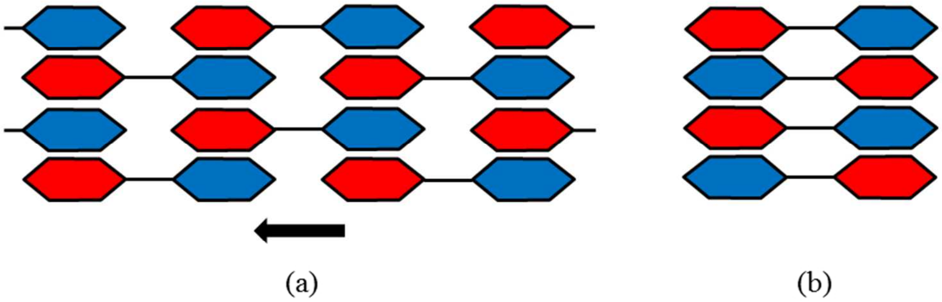
Hanan I. Althagbi, Alison J. Edwards, Brian K. Nicholson, Daniel A. Reason, Graham C. Saunders, Sophie A. Sim, and Danielle A. van der Heijden

Table of contents graphic



Synopsis

The structures of four tetrafluoropyridyl-imidazolium bromide salts comprise chains linked by aryl-tetrafluoropyridyl-anion interactions. The chains are linked by hydrogen bonding between the imidazolium ring and bromide anions. Two of the structures are polar. Prevention of hydrogen bonding at the 2-position resulted in dimers linked by aryl-perfluoroaryl-anion interactions.



(**a**) Bifurcated and (**b**) columnar stacking of molecules containing complementary polyfluoroaryl and aryl rings. The arrow indicates the direction of polarity.
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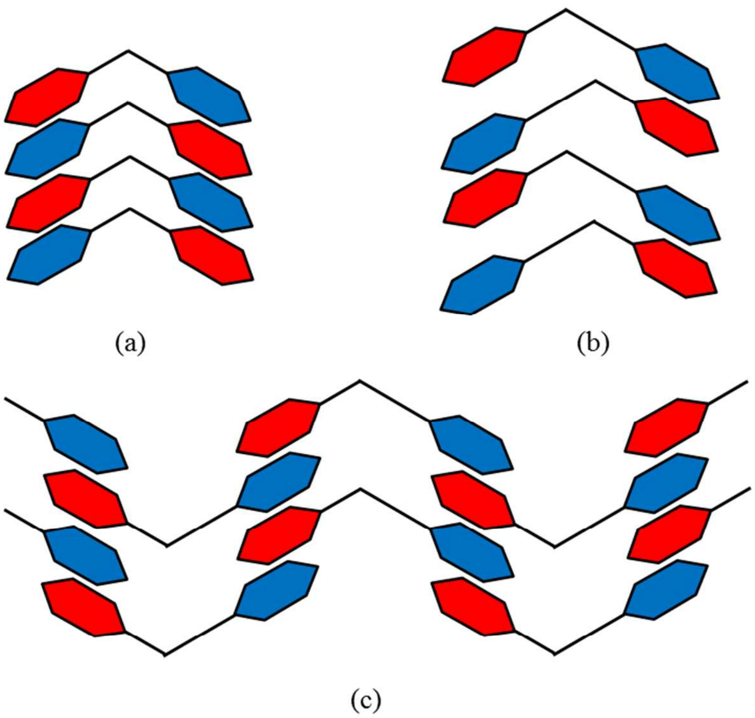
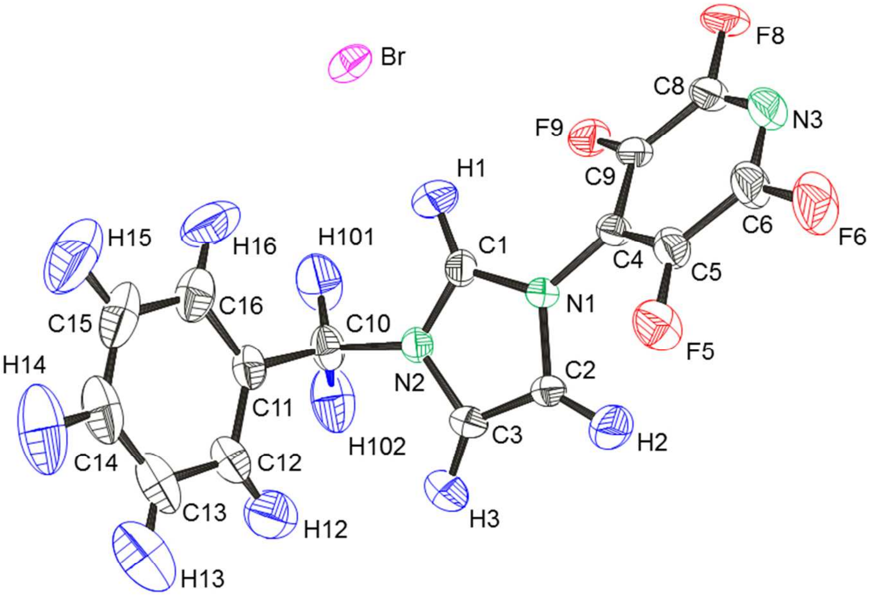
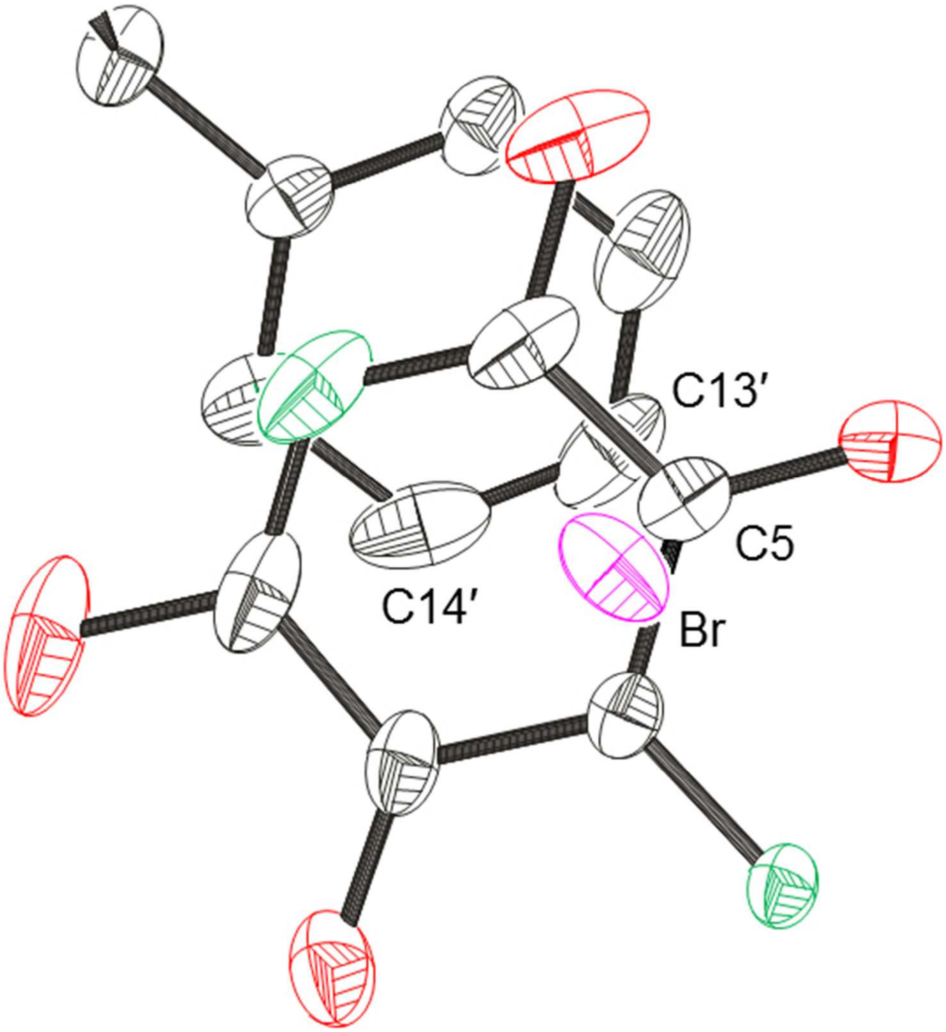


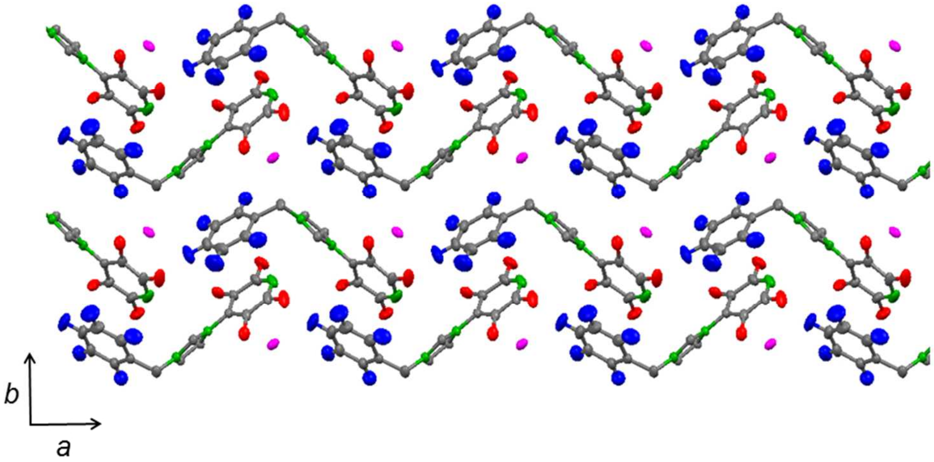
Columnar stacking of (**a**) chevron shaped and (**b**) check mark shaped molecules, and (**c**) bifurcated stacking of check mark shaped molecules.
254x190mm (96 x 96 DPI)



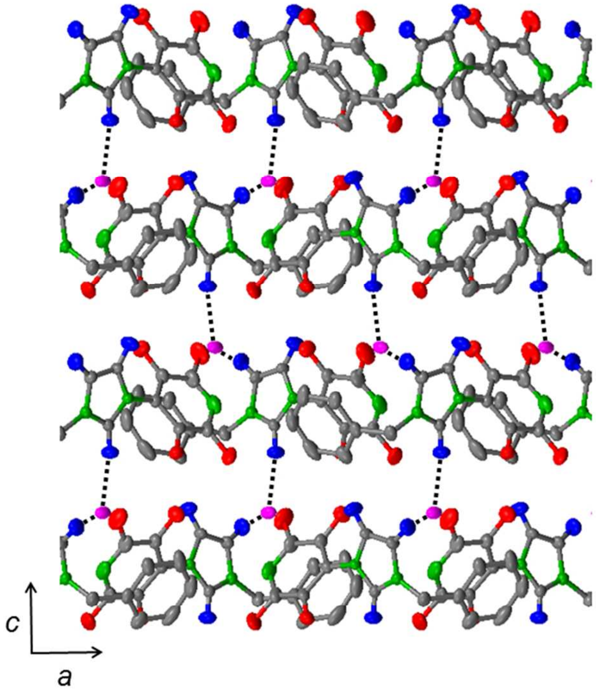
A representative ion pair of 1-(2,3,5,6-tetrafluoropyridyl)-3-benzylimidazolium bromide (**1**) from the neutron Laue diffraction structure determination.
254x190mm (96 x 96 DPI)



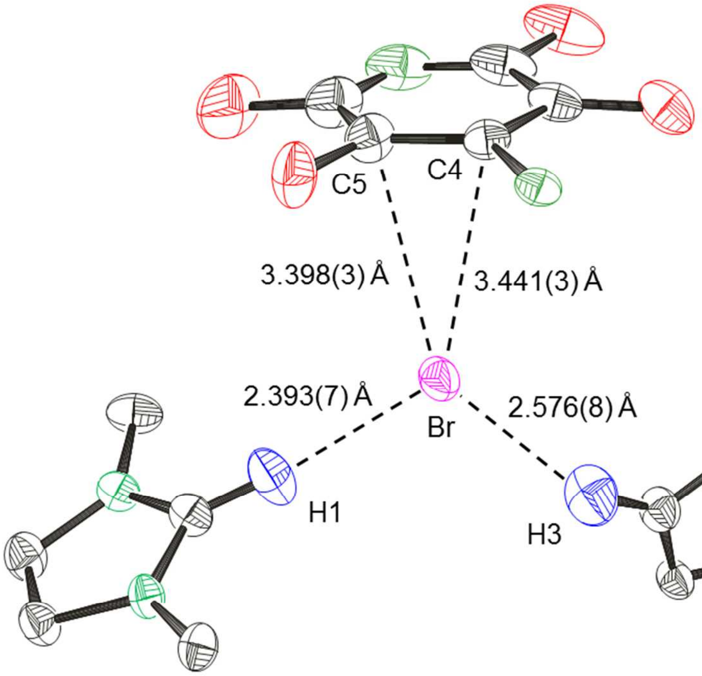
The $C_6H_5\cdots CF_4N\cdots Br^-$ motif of 1-(2,3,5,6-tetrafluoropyridyl)-3-benzylimidazolium bromide (**1**) viewed perpendicular to the plane of the tetrafluoropyridyl ring. The hydrogen atoms are omitted for clarity.
150x161mm (96 x 96 DPI)



The packing of 1-(2,3,5,6-tetrafluoropyridyl)-3-benzylimidazolium bromide (**1**) viewed (**a**) parallel to the *c* axis showing chains parallel to the *a* axis held together by Ar···ArF···Br- interactions (the hydrogen atoms of the imidazolium ring are omitted for clarity) and (**b**) parallel to the *b* axis showing interactions between the bromide anion and the imidazolium rings (the hydrogen atoms of the benzyl group are omitted for clarity).
254x190mm (96 x 96 DPI)



The packing of 1-(2,3,5,6-tetrafluoropyridyl)-3-benzylimidazolium bromide (**1**) viewed (**a**) parallel to the *c* axis showing chains parallel to the *a* axis held together by Ar···ArF···Br- interactions (the hydrogen atoms of the imidazolium ring are omitted for clarity) and (**b**) parallel to the *b* axis showing interactions between the bromide anion and the imidazolium rings (the hydrogen atoms of the benzyl group are omitted for clarity). 254x190mm (96 x 96 DPI)



The environment about bromide in the crystal structure of 1-(2,3,5,6-tetrafluoropyridyl)-3-benzylimidazolium bromide (**1**) showing short interionic distances. The hydrogen atoms are omitted for clarity.
254x190mm (96 x 96 DPI)