Short Note

1-(4-Bromo-2,3,5,6-tetrafluoropheyl)-3-(3-phenylbenzyl)-4-methylimidazolium Bromide

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Abstract: In this paper, we report on the crystal structure of salt 1-(4-bromo-2,3,5,6-tetrafluorophenyl)-3-(3-phenylbenzyl)-4-methylimidazolium bromide, **3**, synthesized by the sequential nucleophilic attack of 4-methylimidazole on bromopentafluorobenzene and then 3-phenylbenzyl bromide. The salt was characterized by ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy and mass spectrometry.

Keywords: imidazolium; halogen bonding; hydrogen bonding; X-ray structure; DFT

1. Introduction

The crystal structures of 1-polyfluoroarylimidazolium salts have proven useful for studying a number of non-covalent interactions: charge-assisted hydrogen bonding [1–7], π–π stacking between polyfluoroaryl and aryl rings [2,4], lone pair–π and anion–π interactions [3–7], and halogen bonding [6,7]. These interactions, and the interplay between them, have importance in crystal engineering: the goal of which is the predictable and reproducible control packing of component molecules or ions. Combinations of these interactions can direct the packing of the components. Conversely, interactions may be prevented by the use of substituents that cannot take part in these interactions. Hydrogen bonding is the strongest interaction, and commonly, all three hydrogen atoms of the imidazolium ring are involved (Figure 1). However, this is not always the case, and in the crystal structure of 1-(4-bromo-2,3,5,6-tetrafluorophenyl)-3-benzylimidazolium bromide (**1**), only C(1)—H and C(2)—H are involved in hydrogen bonding (Figure 2) [8]. The combination of hydrogen bonding, anion–π interactions, and halogen bonding determines the crystal structure, which contains columns of alternating bromotetrafluorophenyl rings and bromide anions. A similar crystal structure arises when hydrogen bonding to the third hydrogen atom is precluded by its substitution with a methyl group **2** (Figure 3) [7]. In order to further investigate the importance of the inter–ion interactions, we wished to study the effect of the further elaboration of the cation whilst still allowing C(1)—H···Br⁻ and C(2)—H···Br⁻ interactions and C—Br···Br⁻ halogen bonding. Consequently, a study of the crystal structure of 1-(4-bromo-2,3,5,6-tetrafluorophenyl)-3-(3-phenylbenzyl)-4-methylimidazolium bromide (**3**) and a DFT study of the inter–ion interactions were undertaken. Here, we report the results.
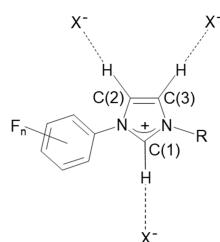

Figure 1. Hydrogen bond donor sites of the 1,3-disubstituted imidazolium cation showing the labeling scheme.
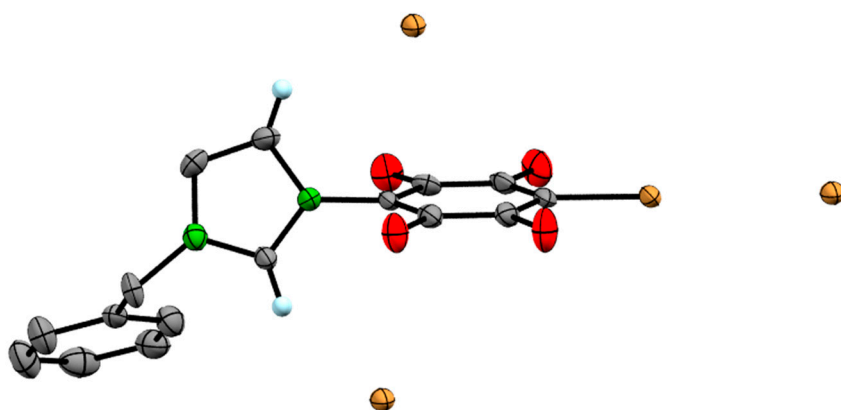
Figure 2. Structure of the cation of **1** indicating the positions of the closest bromide anions. Thermal ellipsoids are at the 50% level. Hydrogen atoms, except those involved in hydrogen bonding, are omitted for clarity.

Figure 3. Structure of cation **2** indicating the positions of the closest bromide anions. Thermal ellipsoids are at the 50% level. Hydrogen atoms, except those involved in hydrogen bonding, are omitted for clarity.
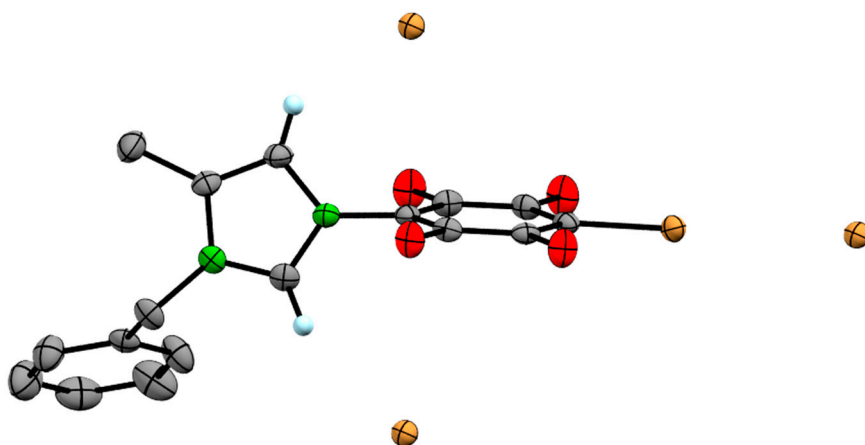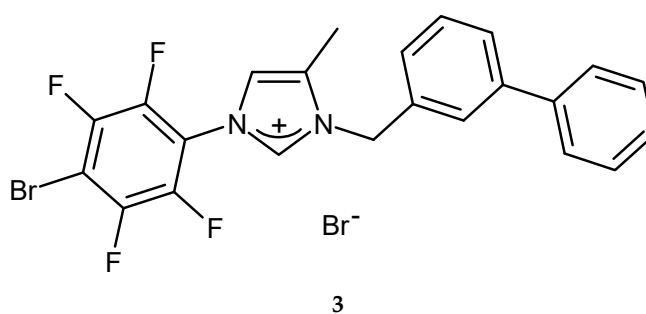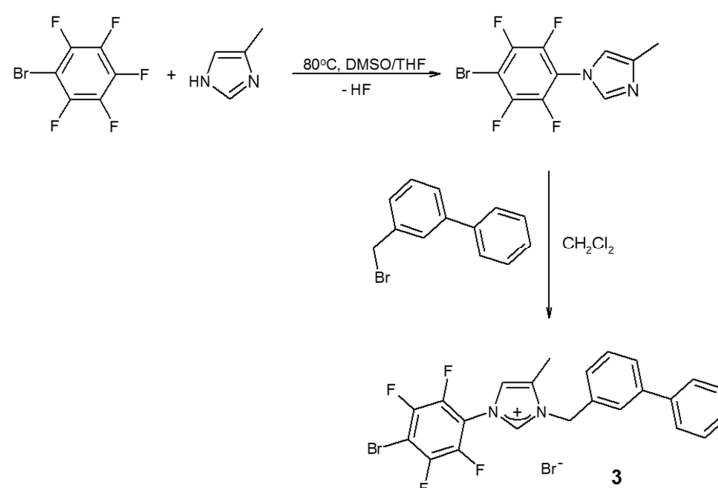

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2. Results

The title compound (**3**) was synthesized in two steps from 4-methylimidazole (Scheme 1). The treatment of bromopentafluorobenzene with 4-methylimidazole in dimethylsulphoxide and tetrahydrofuran at 80 °C for 4 days afforded 1-(4-bromo-2,3,5,6-tetrafluorophenyl)-4-methylimidazole in ca. A total 40% yield [7], which on treatment with 3-phenylbenzyl bromide in dichloromethane at an ambient temperature gave the title compound in ca. a 75% yield. The ^{1}H NMR spectrum displayed the characteristic acidic N$_2$CH hydrogen atom resonance at δ 9.79, and, as expected, the ^{19}F NMR spectrum possessed two resonances that were characteristic of an AA'BB' spin system. Further, the cation peak was evident in the mass spectrum. (See Supplementary Materials.)

Scheme 1. Synthesis of 1-(4-bromo-2,3,5,6-tetrafluorophenyl)-3-(3-phenylbenzyl)-4-methylimidazolium bromide (**3**).

Salt **3** was crystallized from methanol in the centrosymmetric space group $P2_1/c$. There are four anions in close proximity to each cation (Figure 4). The geometric parameters and energies of the interactions are given in Table 1. As expected, both hydrogen atoms of the imidazolium ring were involved in charge-assisted hydrogen bonding to the anions. Consistent with other imidazolium bromide salts [5–7], the C(1)—H···Br⁻ interaction is stronger, despite C(2)—H···Br⁻ being augmented by an anion-π interaction. The anion lies 3.518(2) Å from the plane of the C_6F_4Br ring on the normal to approximately the midpoint of C(4), F(9), and 4.112(2) Å from the centroid (Figure 5). The energy of the interaction between a bromide anion and the neutral bromotetrafluorophenylimidazole fragment was calculated to be -71 kJ mol^{-1}. That C(1)—H···Br⁻ produced a stronger interaction was a consequence of the anion being closer to the center of positive charge, which is considered to be the mid-point of the two nitrogen atoms of the imidazolium ring [1]. The C(1)—H···Br⁻ interaction is 39 kJ mol^{-1} stronger than a purely electrostatic interaction, whilst the C(2)—H···Br⁻ interaction is 24 kJ mol^{-1} stronger.
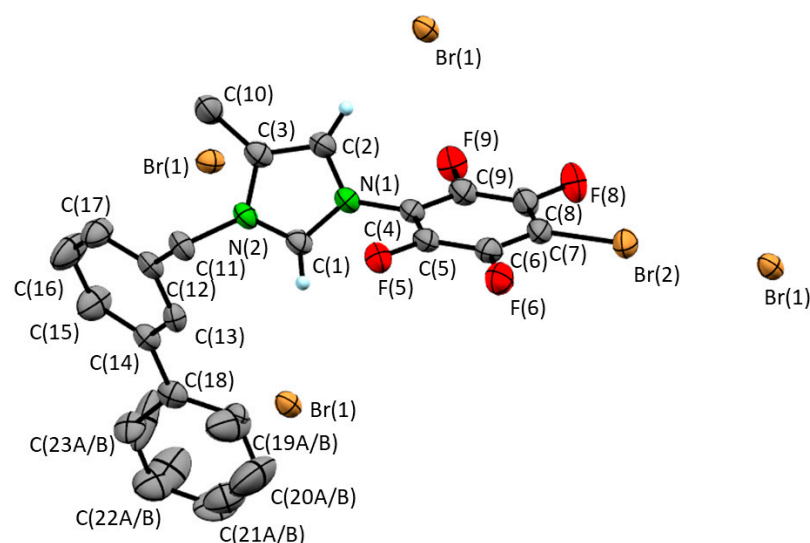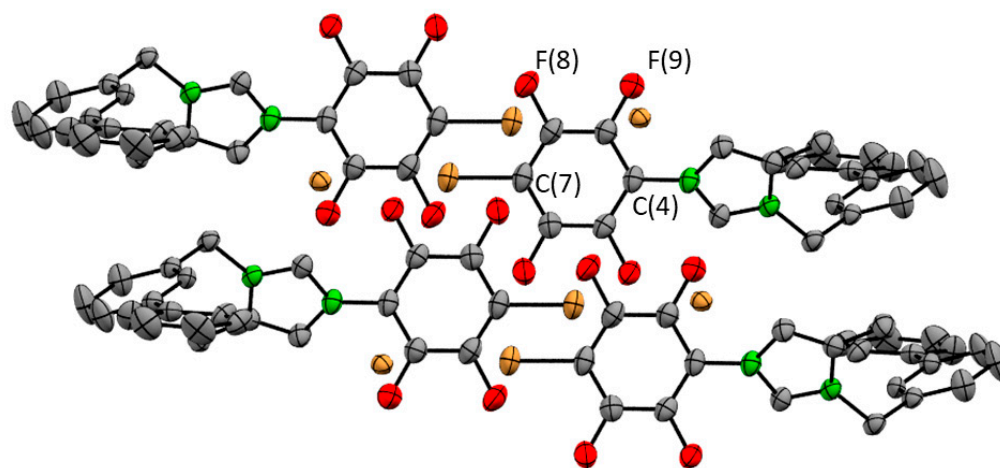

Figure 4. Structure of the cation of salt **3** indicating the positions of the four closest bromide anions. Thermal ellipsoids are at the 50% level. Hydrogen atoms, except those involved in hydrogen bonding, are omitted for clarity.

Table 1. Cation-anion interactions in the crystal structure of salt **3**.

	d(X···Br$^-$), Å	$\angle$(Y—X···Br$^-$), °	(C$_3$N$_2$···Br$^-$), Å	Energy, kJ mol^{-1} [a]
C(1)—H···Br$^-$	3.429(2)	135.6(1), Y = N(1) 114.5(1), Y = N(2)	0.693	−371 (−332)
C(2)—H···Br$^-$	3.473(2)	100.3(1), Y = N(1) 138.3(2), Y = C(3)	1.773	−323 (−299)
N(2)···Br$^-$	3.365(2)	90.3(1), Y = C(1) 93.5(1), Y = C(3) 80.4(1), Y = C(11)	3.351	−345 (−391)
Br(2)···Br$^-$	3.2387(3)	178.27(7), Y = C(7)	-	−207 (−134)

[a] Energy calculated using the wB97xV method and 6-311++G(2d, 2p) basis set. That in parentheses is the purely electrostatic 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.

Figure 5. Packing of salt **3** viewed perpendicular to the planes of bromotetrafluorophenyl rings. Thermal ellipsoids were at the 50% level. Hydrogen atoms are omitted for clarity.

A bromide anion lies close to the face of the imidazolium ring 3.365(2) Å along the normal plane of the ring at N(2). The energy of interaction lies between the two hydrogen bonding interactions. The position of the anion suggests an anion–π interaction, but it is 46 kJ mol^{-1} weaker than a purely electrostatic interaction indicating that other contributions to the interaction are repulsive.

The weakest of the four cation–anion interactions involves Br···Br$^-$ halogen bonding. As was found for 1-(4-bromo-2,3,5,6-tetrafluorophenyl)-3-benzylimidazolium bromide (**1**) [6] and 1-(4-bromo-2,3,5,6-tetrafluorophenyl)-3-benzyl-4-methylimidazolium bromide (**2**) [7], the strength of the Br···Br$^-$ halogen bond was ca. 55% that of the hydrogen bonds. However, because of the distance from the imidazolium ring, the interaction was 73 kJ mol^{-1}, stronger than a purely electrostatic interaction.

In addition, the bromine of one cation lies 3.589(2) Å from the plane of the bromotetrafluorophenyl ring of another cation on the normal at approximately the midpoint of C(7), F(8), and 4.138(2) Å from the centroid, hinting at a lone pair–π interaction. However, the interaction between two bromotetrafluorophenylimidazole fragments, which involves two such interactions, was calculated to be only −19 kJ mol^{-1}. This suggests that the interaction was too weak to be described other than as a van der Waals interaction.

In contrast to the crystal structures of **1** [8] and **2** [7], that of **3** does not contain columns of alternating bromide anions and parallel bromotetrafluorophenyl rings. Instead, only one face of the bromotetrafluorophenyl ring is shown to interact with a bromide anion. The confirmation of the cation of **3** is similar to that of **2**: the angle subtended by the planes of the imidazolium and bromotetrafluorophenyl rings is 41° for **3** and 63° for **2**, and that

subtended by the imidazolium and benzyl rings is 88° for both **3** and **2**. The considerable difference between the crystal structures arises from the additional phenyl ring of **2**, which is approximately co-planar with the phenylene ring, deviating by 16°. The extra bulk prevents the sufficiently close approach of cations and leads to the bromide anion involved in the C(1)—H···Br⁻ interaction being displaced from above the bromotetrafluorophenyl ring (Figure 5). The distance of the anion from the centroid of the ring is 5.441(2) Å, although the distance of the anion to the plane of the ring is only 3.395(2) Å.

3. Materials and Methods

3-Phenylbenzyl bromide (Aldrich, Milwaukee, WI, USA) was used as supplied. 1-(4-Bromo-2,3,5,6-tetrafluorophenyl)-4-methylimidazole was prepared as previously described [7]. The mass spectrum was recorded on a Bruker Daltonics micrOTOF spectrometer (Billerica, MA, USA). The ^{1}H and ^{19}F NMR spectra were recorded using a JEOL ECZ600R spectrometer (Tokyo, Japan). ^{1}H was referenced internally using the residual protio solvent resonance relative to SiMe4 (δ 0) and ^{19}F 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.

3.1. Synthesis of 1-(4-Bromo-2,3,5,6-tetrafluoropheyl)-3-(3-phenylbenzyl)-4-methylimidazolium Bromide (3)

3-Phenylbenzyl bromide (0.84 g, 3.4 mmol) was added to 1-(4-bromo-2,3,5,6-tetrafluorophenyl)-4-methylimidazole (0.96 g, 3.1 mmol) in dichloromethane (60 cm^3). After 7 days, the solvent was removed by rotary evaporation to afford a brown oil. Recrystallization from methanol gave crystals of 1-(4-bromo-2,3,5,6-tetrafluorophenyl)-3-(3-phenylbenzyl)-4-methylimidazolium bromide, **3**. Yield: 1.33 g (77.1%). MS(ESI): [M − Br]$^+$ found m/z = 477.0505; C$_{23}$H$_{16}$N$_2$^{81}BrF$_4$ requires m/z = 477.0529. ^{1}H NMR (600.17 MHz, (CD$_3$)$_2$SO): δ 9.79 (1H, s, N$_2$CH), 7.96 (1H, s, NCHC), 7.75 (1H, s, C$_6$H$_4$C$_6$H$_5$), 7.69 (1H, d, J = 7.3 Hz, C$_6$H$_4$C$_6$H$_5$), 7.64 (2H, d, J = 7.8 Hz, C$_6$H$_4$C$_6$H$_5$), 7.53 (1H, t, J = 7.7 Hz, C$_6$H$_5$ H$_{para}$), 7.45 (2H, t, J = 7.3 Hz, C$_6$H$_4$C$_6$H$_5$), 7.39 (1H, d, J = 7.2 Hz, C$_6$H$_4$C$_6$H$_5$), 7.36 (1H, t, J = 7.3 Hz, C$_6$H$_4$C$_6$H$_5$), 5.63 (2H, s, CH$_2$), 2.33 (3H, s, CH$_3$). ^{13}C{^{1}H} NMR (150.91 MHz, (CD$_3$)$_2$SO): δ 145.09 (dd, $^1J_{C–F}$ = 244 Hz, $J_{C–F}$ = 12 Hz, CF), 143.18 (dd, $^1J_{C–F}$ = 233 Hz, $J_{C–F}$ = 15 Hz, CF), 141.59 (s), 139.90 (s,), 139.09 (s, N$_2$CH), 134.36 (s), 132.97 (s), 130.41 (s, CH), 129.56 (s, CH), 128.43 (s, CH), 127.93 (s, CH), 127.80 (s, CH), 127.43 (s, CH), 127.32 (s, CH), 121.53 (s, NCH), 114.78 (t, $J_{C–F}$ = 13 Hz, C$_6$F$_4$Br$_{ipso}$ or CBr), 103.14 (t, $J_{C–F}$ = 24 Hz, C$_6$F$_4$Br$_{ipso}$ or CBr) 51.05 (s, CH$_2$), 9.46 (s, CH$_3$). ^{19}F NMR (564.73 MHz, (CD$_3$)$_2$SO): δ −132.52 (2F, A component of AA'BB' spin system), −145.62 (2F, B component of AA'BB' spin system).

3.2. Single Crystal XRD Determination

Diffraction data of a single crystal with dimensions 0.11 mm × 0.06 mm × 0.04 mm were collected at 100.1(1) K on an Agilent SuperNova (Santa Clara, CA, USA), a single source at the offset, and an Atlas diffractometer using graphite-monochromated Cu—Kα radiation (λ = 1.54184 Å). Using Olex2 [9], the structure was solved with Olex2.solve [10] structure program using charge flipping refined with the Olex2.refine [10] refinement package and Gauss–Newton minimization. The phenyl ring is disordered consistent with a slight rotation about the (C$_6$H$_4$)C—C(C$_6$H$_5$) bond. This was modeled by 50% occupancy over two sites for five atoms of the phenyl ring: C(19A/B) to C(23A/B). The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atom positions were added in idealized positions, and a riding model with fixed thermal parameters (U$_{ij}$ = 1.2 U$_{eq}$ for the atom to which they were bonded (1.5 for CH$_3$)) was used for subsequent refinements. The function minimized was $\Sigma[w(|F_o|^2 - |F_c|^2)]$.

Crystal Data for C$_{23}$H$_{16}$Br$_2$F$_4$N$_2$ (M = 556.20 g/mol): monoclinic, space group P2$_1$/c (no. 14), a = 11.9324(3) Å, b = 8.27895(12) Å, c = 27.3704(8) Å, β = 126.320(4)°, V = 2178.57(15) Å^3, Z = 4, T = 100.0(1) K, μ(CuKα) = 5.144 mm^{-1}, D$_{calc}$ = 1.696 g/cm^3, 12,705 reflections measured (7.8° ≤ 2Θ ≤ 147.6°), 4303 unique (R$_{int}$ = 0.0194, R$_{sigma}$ = 0.0192) which were used in all calculations. The final R1 was 0.0214 (I > 2σ(I)), and wR2 was 00555 (all data).

3.3. DFT Calculations

DFT calculations were performed using Q-CHEM [11] with the long-range corrected functional ωB97X-V [12] method and the basis set 6-311++G(2d,2p). The energies of interaction were calculated as the difference between the energy of the species and the sum of those of the component ions and molecules.

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 were 1.083 Å within experimental error [4]. Consequently, the C—H bonds of the experimental structures were normalized to 1.083 Å before the calculation of their energies and optimization of the positions of the halide ions. Calculations performed on model systems involving 1-(4-bromo-2,3,5,6-tetrafluorophenyl)imidazole used the positions of the relevant atoms of the experimentally determined crystal structure of the salt.

4. Conclusions

The substitution of the phenyl ring of **2** for a biphenyl ring had an impact on the cation–anion interactions. Although the charge-assisted hydrogen bonding and halogen bonding interactions were maintained, the weaker anion–π interactions were disrupted such that there were no infinite columns of alternating bromotetrafluorophenyl rings and bromide anions in the crystal structure of **3**.

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