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# CRYSTAL STRUCTURE AND THEORETICAL CALCULATIONS OF 1-(4-TRIFLUOROMETHYL-2,3,5,6-TETRAFLUOROPHENYL)-3-BENZYLIMIDAZOLIUM BROMIDE

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The salt 1-(4-trifluoromethyl-2,3,5,6-tetrafluorophenyl)-3-benzylimidazolium bromide $[(CF_3C_6F_4)NC_3H_3N(CH_2Ph)]^+\cdot Br^-$ is crystallized from methanol in the space group $P$-$42_1c$ of the tetragonal crystal system with unit cell parameters $a = b = 21.6531(3)$ Å, $c = 8.1968(2)$ Å, $V = 3843.13(13)$ Å$^3$, $Z = 8$, $d_{calc} = 1.5732$ g/cm$^{-3}$. The structure possesses square channels with a width of *ca.* 5.2 Å, which accounts for 14 % of the volume, and contains one methanol molecule per ion pair. The cation interacts with three bromide ions through an anion—π interaction and two C—H···Br$^-$ interactions. These interactions are investigated by DFT calculations.

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Weak non-covalent interactions, such as π—π stacking [1] and $n \rightarrow \pi$ interactions [2, 3], are becoming increasingly recognised as important in crystal engineering. These interactions in imidazolium salts, in combination with charge-assisted hydrogen bonding [4, 5], have proved to be useful in engineering polar crystal structures, for example those of 1-(2,3,4,5,6-pentafluorobenzyl)-3-benzylimidazolium bromide ($P1$) [6] and 1-(2,3,5,6-tetrafluoropyridyl)-3-benzylimidazolium bromide **1** ($Pna2_1$) [7]. The former possesses columns of π—π stacked pentafluorophenyl and phenyl rings and hydrogen bonding interactions orthogonal to them. The latter possesses an interaction in which the tetrafluoropyridyl ring is sandwiched between a parallel phenyl ring (π—π stacking) and a bromide anion (anion—π interaction) in addition to two charge-assisted hydrogen bonding C—H···Br$^-$ interactions involving the imidazolium ring. The structure of the similar salt 1-(4-bromo-2,3,5,6-tetrafluorophenyl)-3-benzylimidazolium bromide **2** possesses anion—π interactions in columns of alternating bromofluorophenyl rings and bromide anions with Br···Br$^-$ halogen bonding and C—H···Br$^-$ interactions [8]. In order to further investigate the interplay between interactions in polyfluoroaryl-imidazolium bromide salts a study of the structure of 1-(trifluoromethyl-2,3,5,6-tetrafluorophenyl)-3-benzylimidazolium bromide **3** augmented by DFT calculations was undertaken.

**Experimental.** Crystals of salt **3** were grown from methanol. Diffraction data of a single crystal (0.18×0.13×0.05 mm$^3$) were collected at 108(0.5) K on an Agilent SuperNova, single source at offset, Atlas diffractometer in the θ range 2.89—73.59°. 18716 reflections were collected. Crystallographic data: space group $P$-$42_1c$, $a = b = 21.6531(3)$ Å, $c = 8.1968(2)$ Å, $V = 3843.13(13)$ Å$^3$, $Z = 8$, $d_{calc} = 1.573$ g/cm$^{-3}$. Using Olex2 [9], the structure was solved with the Olex2.solve [10] structure program using Charge Flipping and refined with the Olex2.refine [10] refinement package using the Gauss-Newton minimization. In addition to eight ion pairs of **3**, the unit cell contained 147 electrons in a void of 528 Å$^3$, which is consistent with *ca.* 8 molecules of methanol. Attempts to model these data were unsuccessful. Consequently, this electron density was removed from the diffraction data. Final refinement on 3682 independent reflections gave $R1 = 0.0786$ ($wR2 = 0.1157$). For 2994 reflections with $I > 2\sigma(I)$ $R1 = 0.0584$ ($wR2 = 0.1076$). The goodness of fit on $F^2$, $S = 1.047$ and the Flack parameter [ 11 ] is –0.02(5). CCDC 1413722 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Energy and optimization calculations were performed using Gaussian09 [ 12 ] with the wB97XD [ 13 ] functional, which includes empirical dispersion, and the 6-311G++(2*d*,2*p*) basis set. The optimized structure of the cation was calculated and confirmed to be a minimum by frequency calculations. From this the structure with the C(11)—C(12) bond perpendicular to the plane of the imidazolium ring was also optimized and found to be a minimum. Single point calculations were performed using the experimentally determined coordinates of the ions, but with the C—H bonds set to 1.08 Å, the distance of the C—H bonds of **1** determined by neutron diffraction [ 14 ]. The three positions of the bromide ion relative to the experimentally determined cation, with C—H bonds set to 1.08 Å, were also optimized and single point calculations performed. Interaction energies were calculated by the difference between the energy of the appropriate pair of species and the sum of the energies of the isolated components.

**Results and discussion.** 1-(Trifluoromethyl-2,3,5,6-tetrafluorophenyl)-3-benzyl-imidazolium bromide **3** crystallized from methanol in the non-centrosymmetric space group $P\text{-}42_1c$. The cations are arranged in columns parallel to the *c* axis held by C(1)—H(1)$\cdots$$Br^-$$\cdots$$C_6F_4$ linkages. The bromide anions link adjacent columns into squares by C(3)—H(3)$\cdots$$Br^-$ interactions. As a consequence, the structure contains square channels with a width of *ca.* 5.2 Å (Fig. 1). Not unexpectedly, the channels that

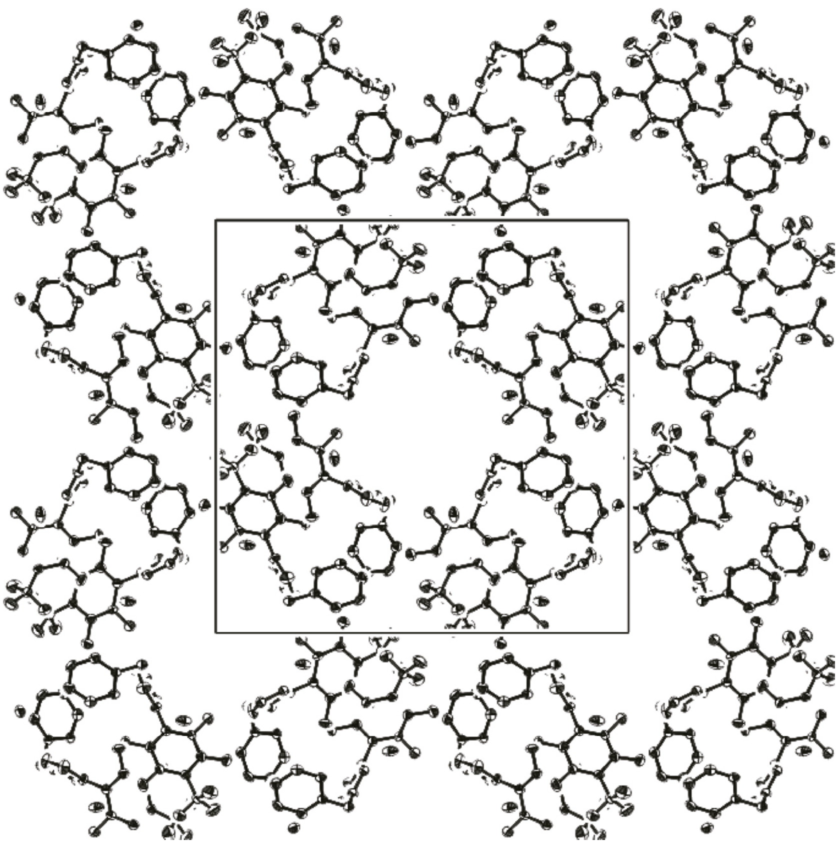

*Fig. 1.* Crystal structure of **1** viewed parallel to the *c* axis showing the square channels.
The perimeter of a unit cell is shown

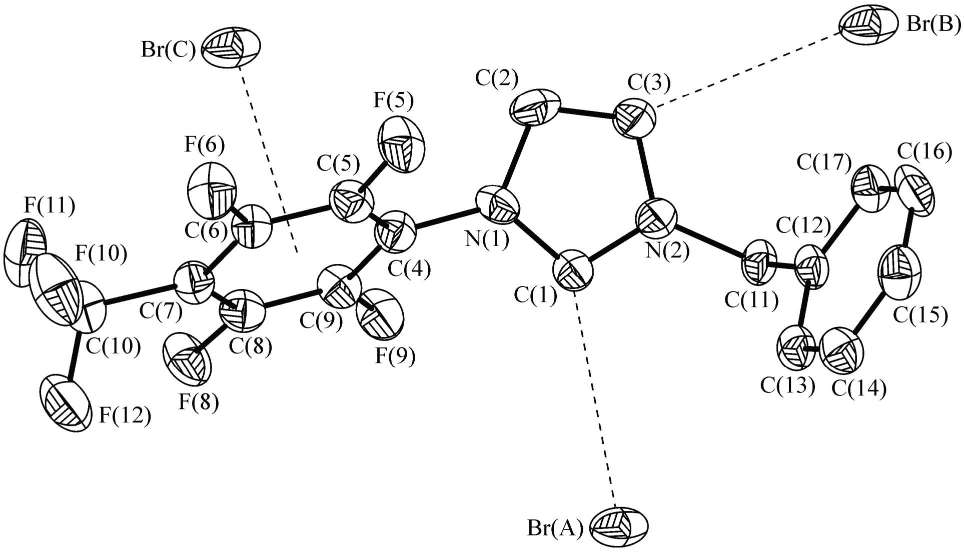


*Fig. 2.* Molecular structure of the cation of salt **1**, showing the positions of the three bromide anions with which it interacts

account for 14 % of the volume contain the electron density (147 electrons per unit cell) which could not be modelled, but is consistent with 8 methanol molecules.

The conformation of the cation (Fig. 2) is very similar to those of **1** [ 7 ] and **2** [ 8 ]. The optimized structure of an isolated cation in the gas phase was found to be very similar to that determined experimentally (Table 1) with the exception of the position of the phenyl ring relative to the imidazolium ring. For the calculated structure of the cation the C(11)—C(12) bond lies in the plane of the imidazolium ring, whereas it is perpendicular in the experimentally determined structure, allowing space for a bromide anion to approach C(1). The conformation of the calculated structure of the cation with the C(11)—C(12) bond perpendicular to the plane of the imidazolium ring is 10 kJ/mol$^{-1}$ higher and is also a minimum.

Three bromide anions are close to each cation (Fig. 2). The geometric parameters (Table 1) strongly suggest the charge-assisted hydrogen bonding [ 4, 5 ] between the cation and the anions in positions A (close to C(1)) and B (close to C(3)): the C···Br$^-$ distances are considerably less than the sum of the van der Waals radius of carbon (1.70 Å) [ 15 ] and the corrected van der Waals radius of the bromide anion (2.35 Å) [ 16 ]. These two bromide ions are also close to the methylene carbon atom C(11) and *ortho* carbon atoms of the phenyl ring C(13) and C(17) (Table 1). The position of the third bromide anion is approximately on the normal to the centroid of the tetrafluorophenyl ring. The position and distance from the centroid (3.301(6) Å) are consistent with an anion—π interaction [ 16—19 ]. The distance is slightly shorter than those of **1** (3.419(2) Å) and **2** (3.626(5) and 3.888(5) Å). The polyfluoroaryl ring of another cation occupies space over the opposite face of the polyfluoroaryl ring, with a C—F···π interaction [ 20 ] involving F(6′) (F(6′)···$C_6F_4$(plane) 2.975(7) Å, F(6′)···$C_6F_4$(centroid) 3.082(7) Å, C(6′)—F(6′)···$C_6F_4$(centroid) 137.2(3)°). The structure is in contrast to those of **1** and **2** for which there is π—π stacking and an anion—π interaction respectively on the face opposite an anion—π interaction.

DFT calculations were undertaken to investigate the interionic interactions in the structure of **3**. Values of –379 kJ/mol$^{-1}$, –339 kJ/mol$^{-1}$, and –319 kJ/mol$^{-1}$ were calculated for anions in positions A, B, and C respectively (Fig. 2), clearly indicating that all the interactions are strongly attractive. The values are similar to the energies for analogous interactions in **1** (–366 kJ/mol$^{-1}$, –340 kJ/mol$^{-1}$, and –318 kJ/mol$^{-1}$) [ 14 ]. It has been noted that the energy of the interionic interactions between 1-alkyl-3-methylimidazolium cations and various anions are inversely proportional to the distance between the anion and the midpoint of the two nitrogen atoms of the imidazolium ring, which is considered to be

Table 1

*Selected experimental and calculated distances* (Å) *and angles* (°) *for salt* **1**

| Parameter | Crystal data | DFT data[a] | Parameter | Crystal data | DFT data[a] |
|---|---|---|---|---|---|
| N(1)—C(1) | 1.336(7) | 1.336 | N(1)—C(1)—N(2) | 107.9(5) | 108.5 |
| N(2)—C(1) | 1.321(7) | 1.320 | C(1)—N(1)—C(4) | 124.7(5) | 125.0 |
| N(1)—C(2) | 1.384(7) | 1.381 | C(1)—N(2)—C(11) | 124.8(5) | 126.0 |
| C(2)—C(3) | 1.344(8) | 1.350 | N(2)—C(11)—C(12) | 110.0(4) | 111.7 |
| N(2)—C(3) | 1.350(7) | 1.378 | C(1)—N(1)—C(4)—C(5) | –117.9(6) | –120.6 |
| N(1)—C(4) | 1.432(7) | 1.420 | C(1)—N(2)—C(11)—C(12) | 90.2(6) | –0.3 |
| N(2)—C(11) | 1.495(7) | 1.485 | N(2)—C(11)—C(12)—C(13) | –86.4(6) | –86.2 |
| C(1)···$Br^-$(A) | 3.462(5) | 3.216 | C(3)···$Br^-$(B) | 3.763(5) | 3.322 |
| N(1)—C(1)···$Br^-$(A) | 141.1(3) | 137.7 | C(2)—C(3)···$Br^-$(B) | 148.4(4) | 147.5 |
| N(2)—C(1)···$Br^-$(A) | 110.9(3) | 114.6 | N(2)—C(3)···$Br^-$(B) | 98.0(3) | 100.7 |
| $C_3N_2$(plane)···$Br^-$(A) | 0.233(6) | 0.050 | $C_3N_2$(plane)···$Br^-$(B) | 1.071(5) | 0.816 |
| C(11)···$Br^-$(A) | 3.965(6) | 3.901 | C(11)···$Br^-$(B) | 3.807(6) | 3.562 |
| C(13)···$Br^-$(A) | 3.904(6) | 3.801 | C(17)···$Br^-$(B) | 3.973(6) | 3.722 |
| $C_6F_4$(centroid)···$Br^-$(C) | 3.301(6) | 3.492 | N(1)—C(2)···$Br^-$(C) | 81.4(3) | 91.6 |
| $C_6F_4$(plane)···$Br^-$(C) | 3.296(6) | 3.251 | C(2)—C(3)···$Br^-$(C) | 157.6(4) | 150.8 |
| C(2)···$Br^-$(C) | 4.197(7) | 3.268 | $C_3N_2$(plane)···$Br^-$(C) | 1.577(7) | 1.334 |

[a] DFT data (wB97XD/6-311G++(2*d*,2*p*)) for the cation refer to the optimized structure of the cation, and for the data involving bromide anions refer to the optimized positions of the bromide anion relative to the experimentally determined structure of the cation (with C—H bond distances fixed at 1.08 Å).

the centre of the positive charge [ 21 ], suggesting that electrostatic forces dominate. Such a relationship is not evident in the energies of **1** and **3**, demonstrating that the hydrogen bonding and the anion—π interaction are important in determining the arrangement of the ions.

The positions of the bromide anions were also optimized relative to the experimentally determined cation structure. The optimized positions A and B are close to those found experimentally but closer to C(1) and C(3) respectively (Table 1), and are –7 $kJ/mol^{-1}$ and –12 $kJ/mol^{-1}$ lower respectively than the experimentally determined ion pairs. That of C is close to a face of the tetrafluorophenyl ring, but shifted *ca.* 1 Å towards C(2) so as to lie approximately on the normal to C(4), and is 28 $kJ/mol^{-1}$ lower. Evidently interactions with other cations have a significant impact on the position of this bromide anion.

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