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The structures of 1-(2-halo-6-fluorophenylmethyl)-1-methylimidazolium bromide salts

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Abstract -

The crystal structures of 1-(2-halo-6-fluorophenylmethyl)-1-methylimidazolium bromide salts and 1-(2-trifluoromethyl-6-fluorophenylmethyl)-1-methylimidazolium bromide $[MeNC_3H_3NCH_2C_6H_3X\text{-}2\text{-}F\text{-}6]^+.Br^-$ [X = F (**1**), Cl (**2**), Br (**3**), I (**4**), CF_3 (**5**)] have been determined. The crystal structure of the hydrate of salt **1** contains π–π stacked imidazolium···difluorophenyl···difluorophenyl···imidazolium units. Those of salts **2**, **4** and **5** possess bromide···halofluorophenyl···halofluorophenyl···bromide motifs comprising anion–π and π–π stacking interactions. That of salt **4** also contains bromide···iodide halogen bonding. The crystal structure of the sesquihydrate of salt **3** possesses bromine···halofluorophenyl···halofluorophenyl···bromine motifs.

Keywords

Imidazolium salt; hydrogen bonding; anion–π interaction; π–π stacking; halogen bonding; crystal structure; DFT calculations

1. Introduction

The crystal structures of fluoroaryl-substituted imidazolium salts are a valuable source of information on a range of non-covalent interactions, in particular, π–π stacking [1-5] and anion–π interactions [2,3,5-8], arising from the presence of fluorine atoms, along with charge-assisted hydrogen bonding [3,9]. These interactions have importance in crystal engineering and through the judicious choice of fluoroaryl substituents polar crystal structures can be realized [1-5]. Furthermore, the incorporation of other halogen atoms into the polyfluoroaryl group provides the opportunity for halogen bonding when the anion is a halide [5,6].

Control of interionic and intermolecular interactions is fundamental to crystal engineering [10]. It is expected that non-covalent interactions can be turned on or off for imidazolium halide salts by variation of the substituent aryl group. As an example, although the structures of the related cations of 1-pentafluorophenylmethyl-3-methylimidazolium bromide (ROTMEU) [7] and 1-(2-bromophenylmethyl)-3-methylimidazolium bromide (EVACIO) [11] adopt similar conformations, because of the difference in the electronic nature of the phenyl ring the crystal structure of the former possesses an anion–π interaction [2,3,5-8,12], whereas that of the latter does not (Figure 1). In order to further probe these structural features and non-covalent interactions we are investigating fluoroaryl-substituted imidazolium salts. Here we report the results of our structural study, supported by density functional theory calculations, into 1-phenylmethyl-3-methylimidazolium bromide salts with a fluorine atom and a halogen atom or a trifluoromethyl group occupying the *ortho* positions of the phenyl ring.

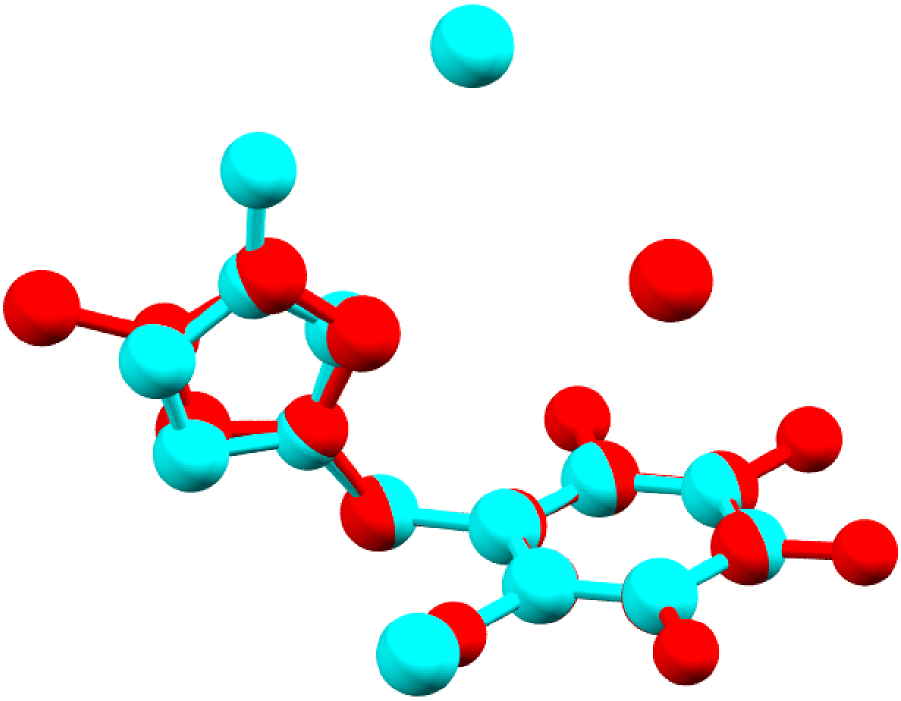

Figure 1. Overlay of the structures of the cations of 1-(pentafluorophenylmethyl)-3-methylimidazolium bromide (red) and 1-(2-bromophenylmethyl)-3-methylimidazolium bromide (cyan) with the bromide anion closest to the face of the phenyl ring.

2. Results and discussion

The 2,6-disubstituted phenylmethylimidazolium bromide salts $[MeNC_3H_3NCH_2C_6H_3X\text{-}2\text{-}F\text{-}6]^+.Br^-$ [X = F (**1**), Cl (**2**), Br (**3**), I (**4**), CF_3 (**5**)] were prepared by treatment of 1-methylimidazole with the appropriate benzyl bromide. The salts were characterized by mass spectrometry and ^{1}H, ^{13}C and ^{19}F NMR spectroscopy. The salts crystallized with one ion pair in the asymmetric unit, with that of **1** also containing one molecule of water, and that of **3** also containing one and a half molecules of water (the oxygen atom of the half water molecule lies on a crystallographic two-fold rotation axis). Crystal data are given in Table 1 and selected distances and angles are given in Table 2. The structures of the cations and positions of the nearest bromide anions and water molecules are shown in Figures 2–6. The bond distances and angles are similar to those calculated using the ωB97X-D functional [13] with the 6-311++G(2d,2p) basis set for the isolated cations in the gas phase.

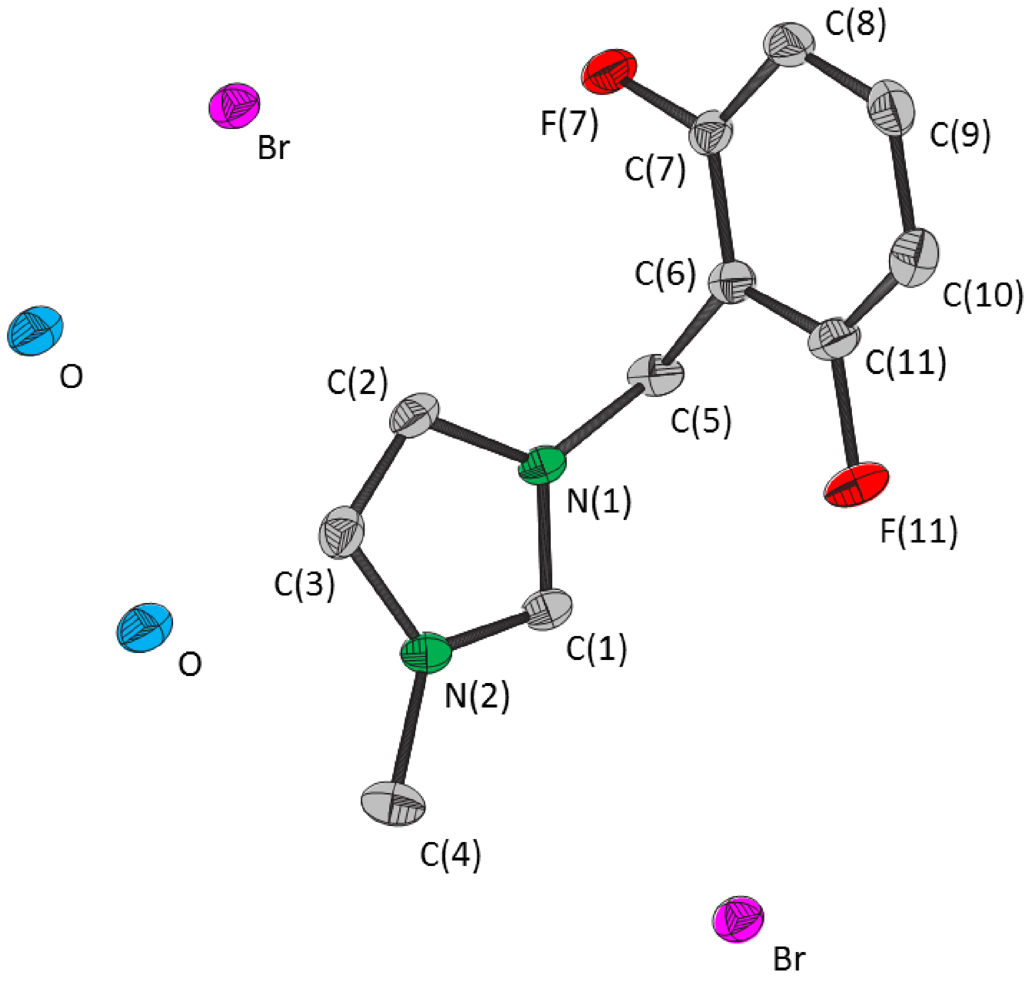

Figure **2**. The structure of the cation of 1-(2,6-difluorophenylmethyl)-3-methylimidazolium bromide (**1**) indicating the positions of the bromide anions and water molecules close to C(1), C(2) and C(3). Thermal ellipsoids are at the 50% level. Hydrogen atoms are omitted for clarity.

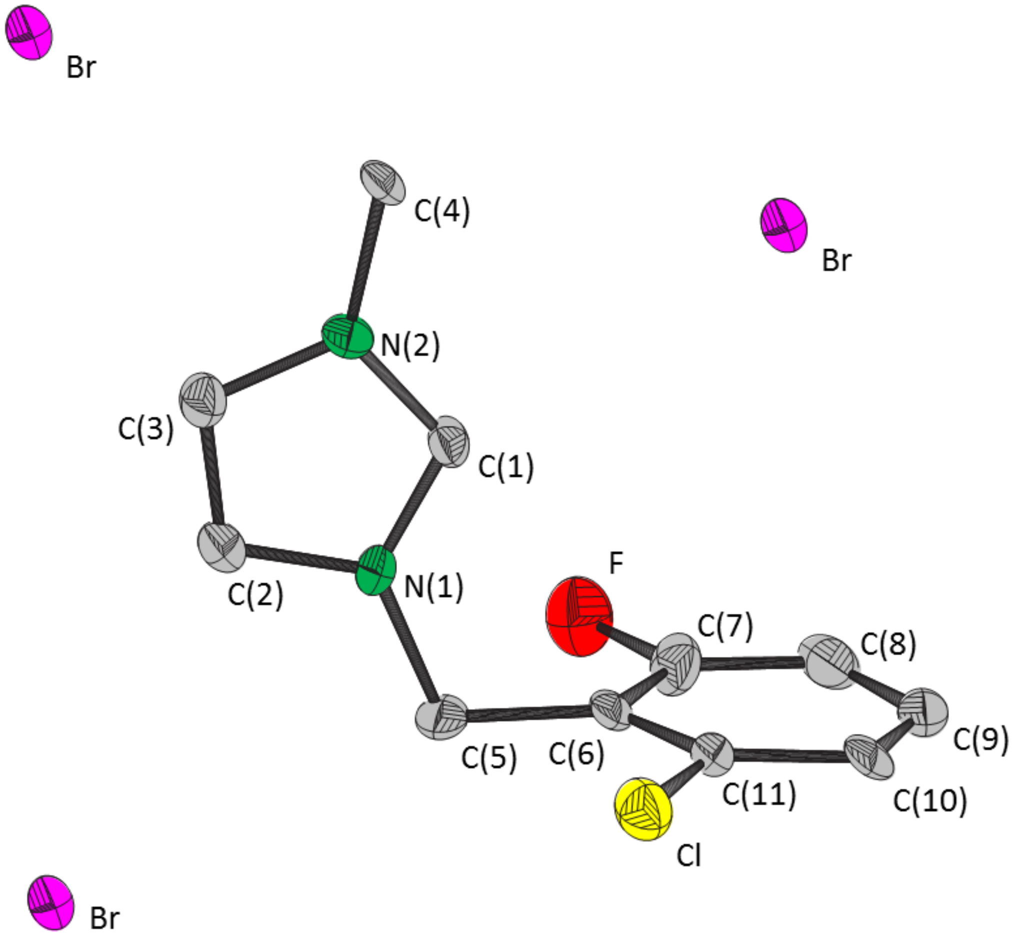

Figure **3**. The structure of the cation of 1-(2-chloro-6-fluorophenylmethyl)-3-methylimidazolium bromide (**2**) indicating the positions of the bromide anions close to C(1), C(2) and C(3). Thermal ellipsoids are at the 50% level. Hydrogen atoms are omitted for clarity.

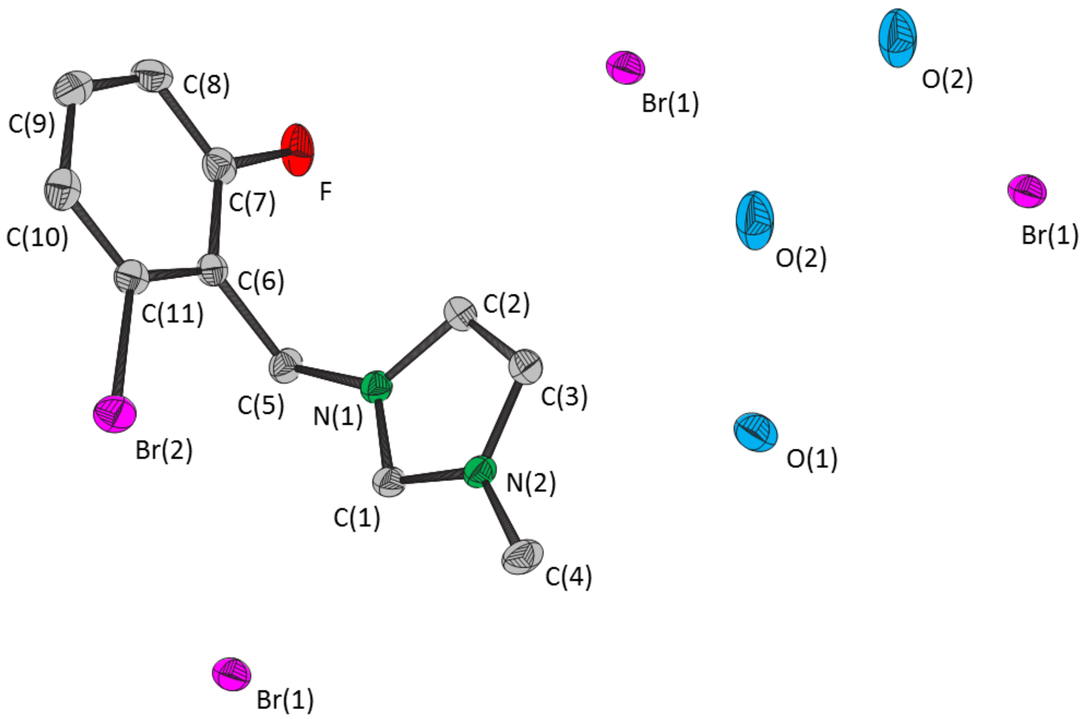

Figure **4**. The structure of the cation of 1-(2-bromo-6-fluorophenylmethyl)-3-methylimidazolium bromide (**3**) indicating the positions of the bromide anions and water molecules close to C(1), C(2) and C(3), and a $[(Br^-)_2.2H_2O]$ rhomboid. Thermal ellipsoids are at the 50% level. Hydrogen atoms are omitted for clarity.

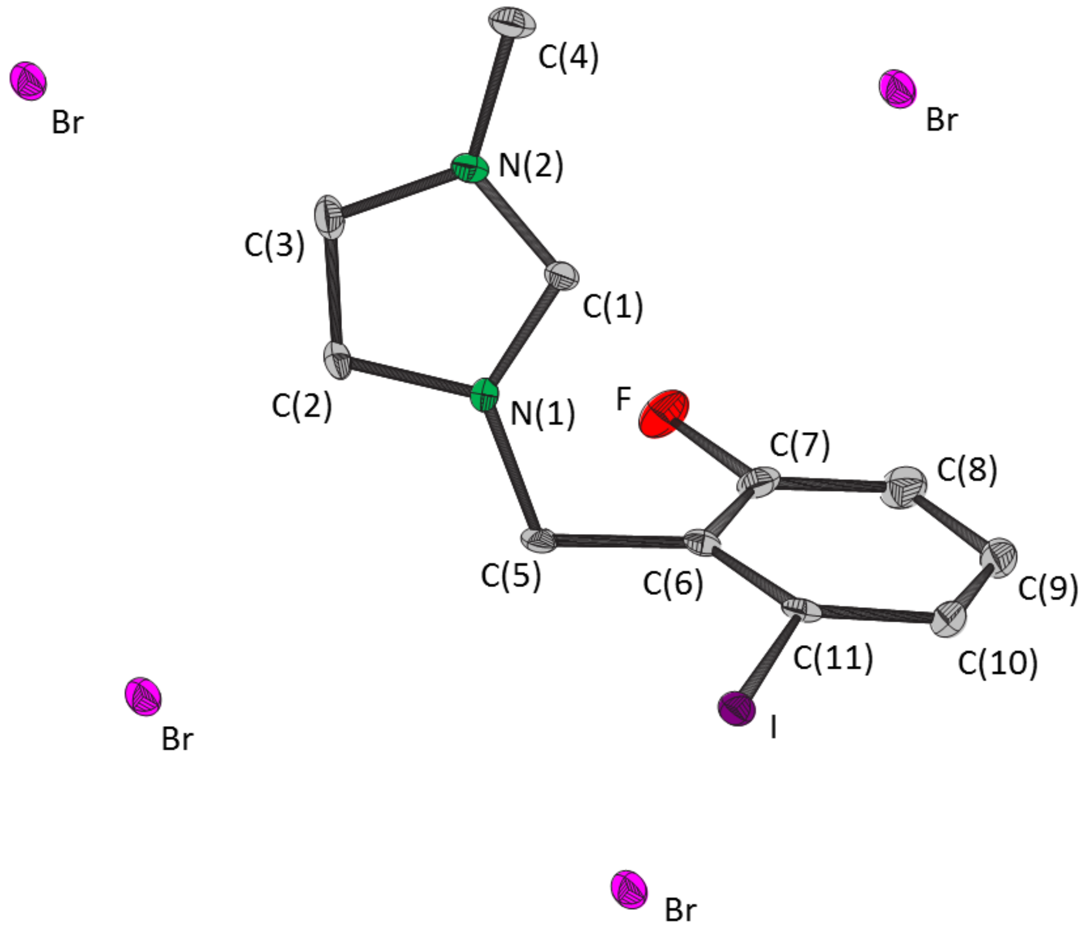

Figure **5**. The structure of the cation of 1-(2-iodo-6-fluorophenylmethyl)-3-methylimidazolium bromide (**4**) indicating the positions of the bromide anions close to C(1), C(2), C(3) and I. Thermal ellipsoids are at the 50% level. Hydrogen atoms are omitted for clarity.

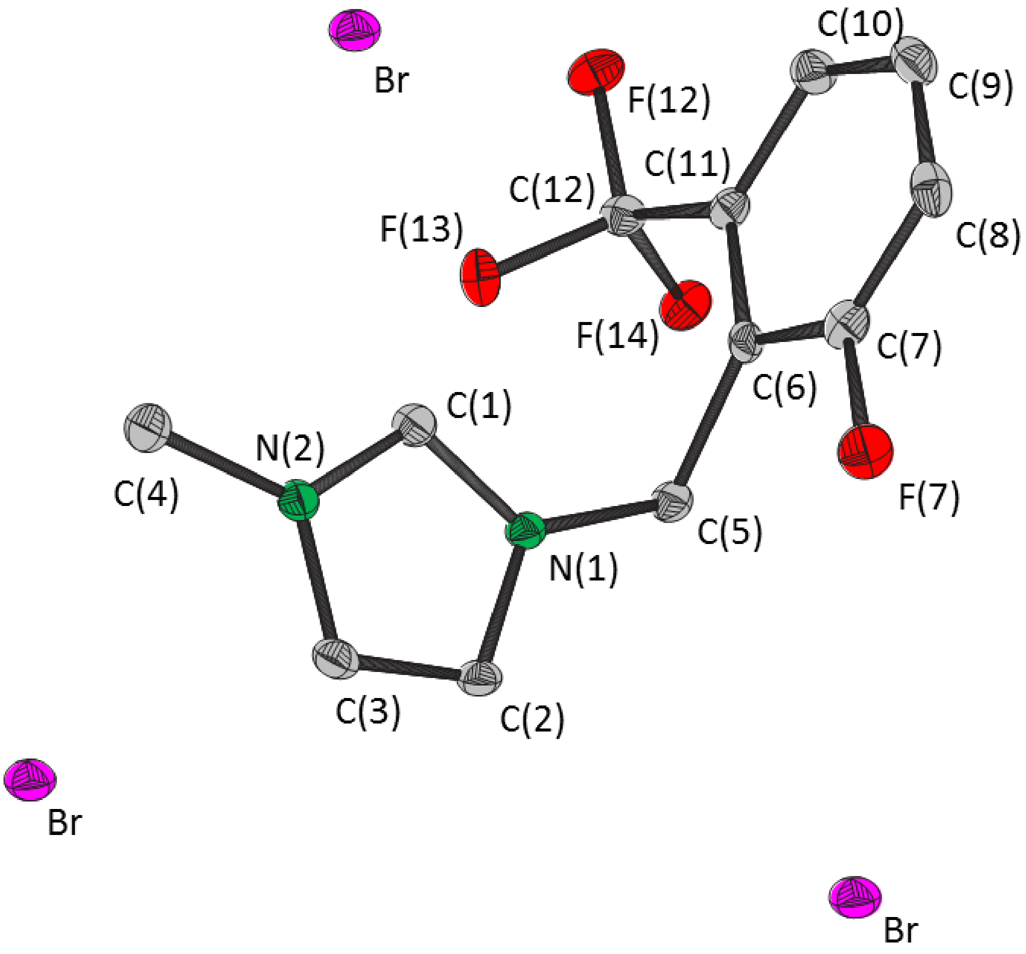

Figure **6**. The structure of the cation of 1-(2-trifluoromethyl-6-fluorophenylmethyl)-3-methylimidazolium bromide (**5**) indicating the positions of the bromide anions close to C(1), C(2) and C(3). Thermal ellipsoids are at the 50% level. Hydrogen atoms are omitted for clarity.

The cations of **1** and **3** adopt almost identical conformations (Figure 7a) in which the plane of the imidazolium ring is perpendicular to the C(5)─C(6) bond. This conformation is calculated to be the most favoured (Table 2). The positions of the closest bromide anions and water molecules are similar for the two salts. In contrast, the planes of the of the imidazolium rings of **2**, **4** and **5**, which adopt almost identical conformations (Figure 7b), are parallel to the C(5)─C(6) bond with the N_2C─H bond *syn* to the phenyl ring. This conformation is similar to that of 1-pentafluorophenylmethyl-3-methylimidazolium bromide [7], with the exception that in this salt the N_2C─H bond is *anti* to the phenyl ring.

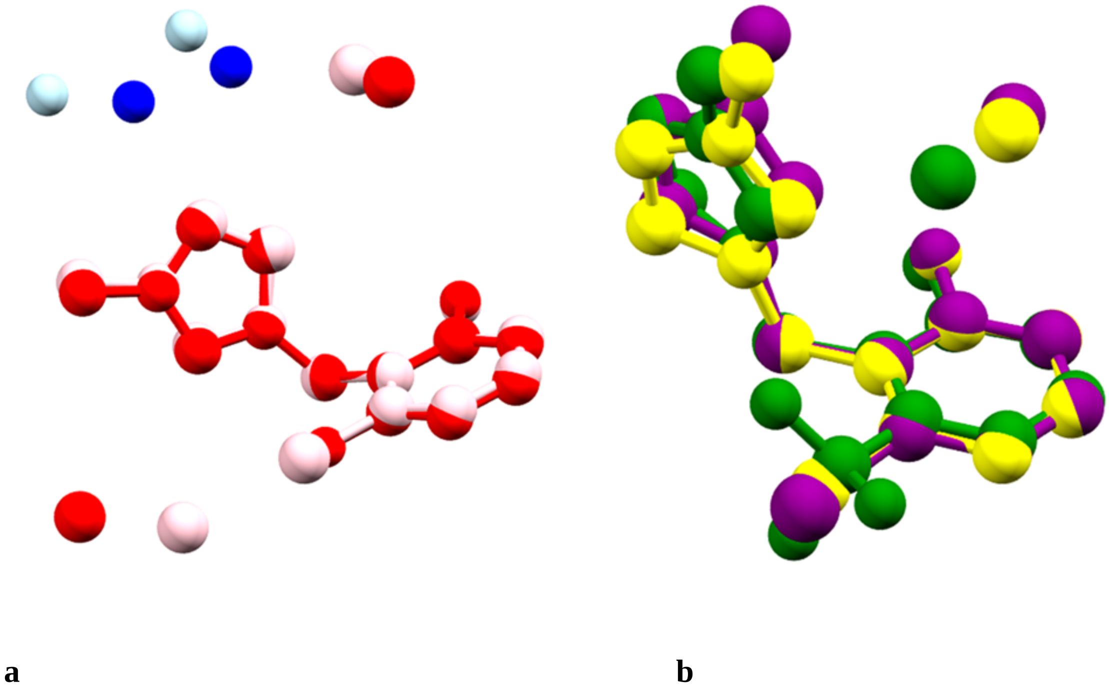

Figure **7**. Overlay of the structures of the cations of (**a**) 1-(2,6-difluorophenylmethyl)-3-methylimidazolium bromide (**1**) (red) and of 1-(2-bromo-6-fluorophenylmethyl)-3-methylimidazolium bromide (**3**) (pink) indicating the positions of the closest bromide anions and the oxygen atoms of the water molecules (dark blue for **1**, light blue for **3**), and (**b**) 1-(2,6-chlorofluorophenylmethyl)-3-methylimidazolium bromide (**2**) (yellow), 1-(2,6-iodofluorophenylmethyl)-3-methylimidazolium bromide (**4**) (purple) and of

1-(2-trifluoromethyl-6-fluorophenylmethyl)-3-methylimidazolium bromide (**5**) (green) indicating the positions of the bromide anions closest to C(1).

Consistent with other imidazolium bromide salts [3,9] all five crystal structures possess bromide anions lying close to both the plane of the imidazolium ring and C(1) (Table 3). The $C(1)\cdots Br^-$ distances are considerably less than the sum of the van der Waals' radius of carbon (1.70 Å [14]) and the corrected value of the van der Waals radius for bromide (2.35 Å [15]), and the $N{-}C(1)\cdots Br^-$ angles are between 100 and 150° suggestive of charge-assisted hydrogen-bonding [16,17] between H(1) and the bromide anion. The interactions between the cations and this bromide anion were calculated to be attractive by 338 to 372 kJ mol^{-1} (Table 3), which is consistent with other imidazolium bromide salts [3,9]. The magnitudes of the interactions for **2**, **4** and **5** in which the bromide anion lies above one face of the fluorophenyl ring, suggestive of an anion–π interaction [18,19], are more than 10 kJ mol^{-1} higher than those of **1** and **3**. Consistent with this observation, the interactions between bromide anion and 2-chloro-6-fluorotoluene, 2-iodo-6-fluorotoluene and 2-trifluoromethyl-6-fluorotoluene in the same relative positions as the respective imidazolium salts were calculated to be attractive by 11, 21 and 12 kJ mol^{-1} respectively. The anion–π interaction between bromide and hexafluorobenzene has been calculated to be -38 kJ mol^{-1} when the bromide anion is 3.37 Å along the normal to the ring's centroid [19]. The lower values for **2**, **4** and **5** are presumably a consequence of the less electron poor character of the arene and the non-optimal position of the bromide anion (Table 2); it is further from the ring's plane and situated on the normal to the ring carbon attached to the most electron-withdrawing substituent, C(7) for **2** and **4**, and C(11) for **5**.

All the crystal structures also possess bromide anions lying close to the plane of the imidazolium ring and close to C(2) with geometric parameters (Table 3) that also suggest charge-assisted hydrogen-bonding [16,17] between H(2) and the bromide anion. Although the C(2)···Br^- distances are similar for all the salts, the bromide anion is displaced away from N(1) in **1** and **3** because of an interaction with a water molecule which is close to C(3) (Figures 1 and 3). The N(1)─C(1)···Br^- angles are ca. 40° greater and the N(2)─C(1)···Br^- angles are ca. 50° smaller respectively for **1** and **3** compared to **2**, **4** and **5**. The interactions between the cations and this bromide anion were calculated to be attractive by ca. 300 kJ mol^{-1} (Table 3), which is consistent with other imidazolium bromide salts [3,5,9]. The magnitude of the interactions is smaller for **1** and **3**, which is presumed to be a consequence of the positions of the bromide anions being less favourable for hydrogen bonding. In both these structures this bromide anion lies approximately on the normal to F(7), ca. 4.5 Å from the plane the halophenyl ring, and over 5 Å from the centroid, and consequently there is no significant anion–π interaction (Table 3).

The crystal structures of **2**, **4** and **5** also possesses bromide anions close to C(3) with geometric parameters (Table 3) that also suggest charge-assisted hydrogen-bonding [16,17]. The interactions between the cations and the anion in this position were calculated to be attractive by ca. 300 kJ mol (Table 3), which is ca. 10% lower than the values calculated for 1-(4-chloro-2,3,5,6-tetrafluorophenylmethyl)-3-benzylimidazolium bromide [5]. In contrast, there are two molecules of water close to C(3) in the structures of **1** and **3**. The

C(3)···O distances, which are close to the sum of the van der Waals radii of carbon and oxygen (3.22 Å [14]), and the N(2)─C(3)···O and C(2)─C(3)···O angles suggest hydrogen bonding between H(3) and the water molecules. The interactions were calculated to be attractive by ca. 15 kJ mol^{-1} (Table 3). Pairs of water molecules are linked by hydrogen bonding to two bromide anions forming $[(Br^-)_2.(H_2O)_2]$ rhomboids, which are a common motif in bromide hydrates [3,20]. For each structure the centre of the rhomboid lies on a crystallographic inversion centre. In the structure of **3** the rhombi are linked into chains parallel to the *a* axis by hydrogen bonding to other water molecules, the oxygen atoms of which lie on crystallographic two-fold rotation axes (O···O 2.815(4) Å, O···O···O 97.2(1)°).

The structure of **4** possesses a bromide anion close to the iodine atom. The I···Br$^-$ distance, which is ca. 1 Å less than the sum of van der Waals' radius of iodine (1.98 Å [14]) and the corrected value of the van der Waals radius for bromide (2.35 Å [15]), and almost linear C─I···Br$^-$ angle (Table 3) are indicative of halogen bonding [21]. The I···Br$^-$ distance is consistent with those between bromide anions and polyfluoroiodobenzenes (3.02 to 3.64 Å) [22]. The energy of this interaction is similar to that for 1-(4-iodo-2,3,5,6-tetrafluorobenzyl)-3-benzylimidazolium bromide [5]. This is most likely a coincidence, since the electrostatic interaction between the ions is likely to be stronger for **4**, for which the distance between the anion and the centre of positive charge, the midpoint of N(1) and N(2), is 7.317 Å compared to 10.399 Å for 1-(4-iodo-2,3,5,6-tetrafluorobenzyl)-3-benzylimidazolium bromide, whilst the interaction between the bromide anion and iodoarene is expected to be weaker for the less electron poor arene of **4**.

In all the crystal structures there are pairs of adjacent cations related by a centre of inversion and with their halofluorophenyl rings parallel and in close proximity. For **1** each difluorophenyl ring lies close to and almost parallel to an imidazolium ring of another adjacent cation forming motifs of apparently π–π stacked imidazolium···difluorophenyl···difluorophenyl···imidazolium units (Figure 8). To investigate the interaction between two the difluorophenyl groups a study DFT of a pair of 1-(2,6-difluorophenylmethyl)imidazole molecules and a pair of 2,6-difluorotoluene molecules using the experimentally determined positions of the relevant atoms of **1** were undertaken. The interactions between the two 1-(2,6-difluorophenylmethyl)imidazole molecules and the two 2,6-difluorotoluene molecules were calculated to be attractive by 55 and 19 kJ mol^{-1} respectively. The difference indicates a significant interaction between the imidazole and the phenyl rings. For **2**, **4** and **5** there are bromide···halofluorophenyl···halofluorophenyl···bromide motifs comprising anion–π and π–π stacking interactions (that of **2** is shown in Figure 9). Similar arrangements involving metal complexes have been reported previously [23]. The interactions between the two 1-(2-halo-6-fluorophenylmethyl)imidazole molecules and the two 2-halo-6-fluorotoluene molecules using experimentally determined positions of the relevant atoms were calculated to be attractive by ca. 35 kJ mol^{-1} (Table 3). There is little difference between the values calculated for the two different molecules because, unlike for **1**, the imidazole rings are orientated away from the other molecule (Figure 9). The larger magnitude of the interactions between the 2-halo-6-fluorotoluene molecules compared to that of **1** is consistent with the shorter distance between the planes and centroids of the aryl rings. For **3** there are bromine···halofluorophenyl···halofluorophenyl···bromine motifs with the covalently bonded bromine atoms directed at, and close to, the centroids of the bromofluorophenyl rings of the central cations, suggesting lone pair–π interactions (Figure 10). The π–π stacking interactions between 1-(2-bromo-6-fluorophenylmethyl)imidazole molecules and 2-bromo-6-fluorotoluene molecules with parallel aryl rings using experimentally determined positions of the relevant atoms were calculated to be attractive by ca. 40 kJ mol^{-1} (Table 3). The larger magnitude is consistent with the aryl rings of **3** being closer than those of the other salts. The Br···C_6(plane) distance and C─Br···C_6(centroid) angle (Table 3) are consistent with a lone pair–π interaction in which the bromine atom acts as the acceptor [24]. This interaction between two 2-bromo-6-fluorotoluene molecules using experimentally determined positions of the relevant atoms was calculated to be attractive by 12 kJ mol^{-1}.

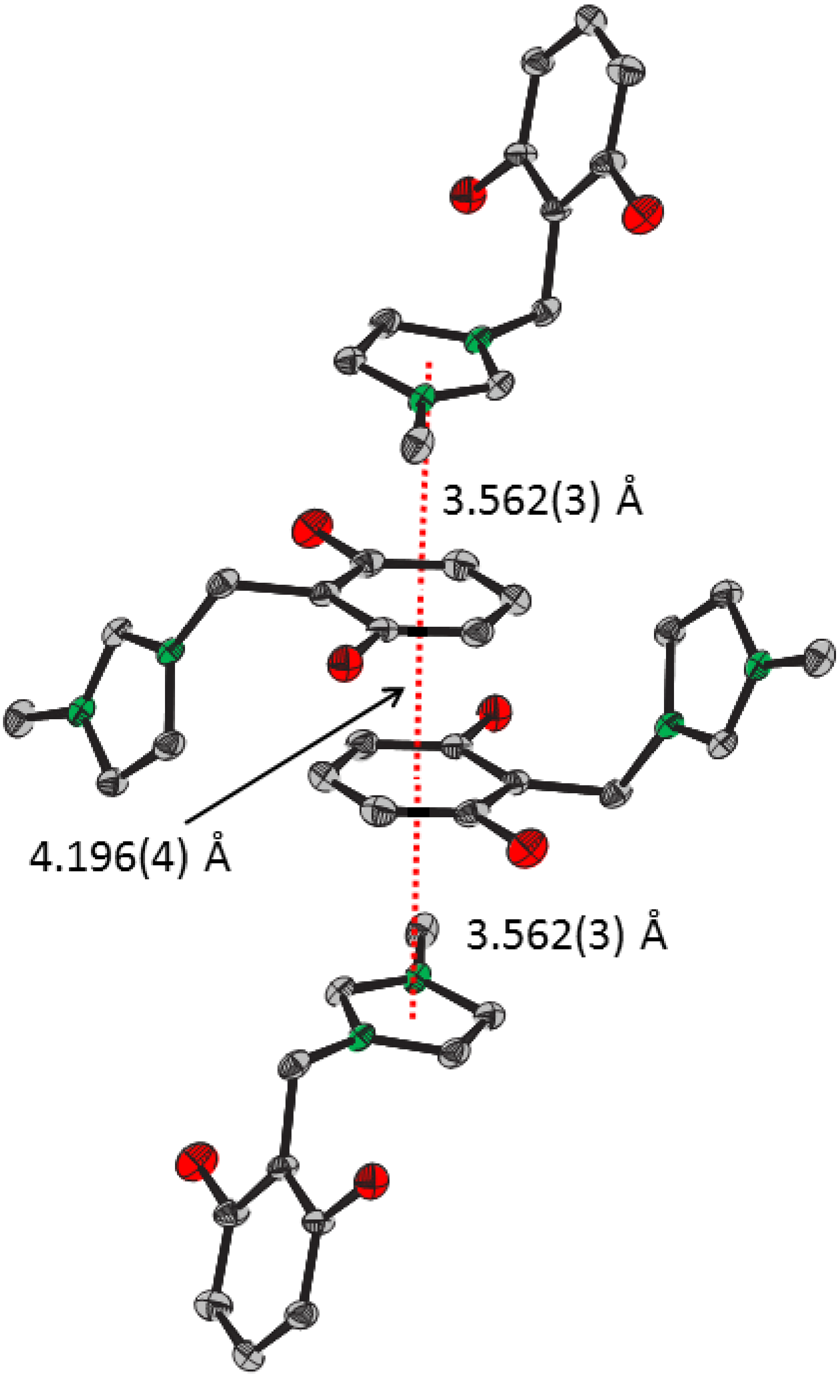

Figure **8**. The stacking of the cations of 1-(2,6-difluorophenylmethyl)-3-methylimidazolium bromide (**1**). Thermal ellipsoids are at the 50% level. Hydrogen atoms are omitted for clarity.

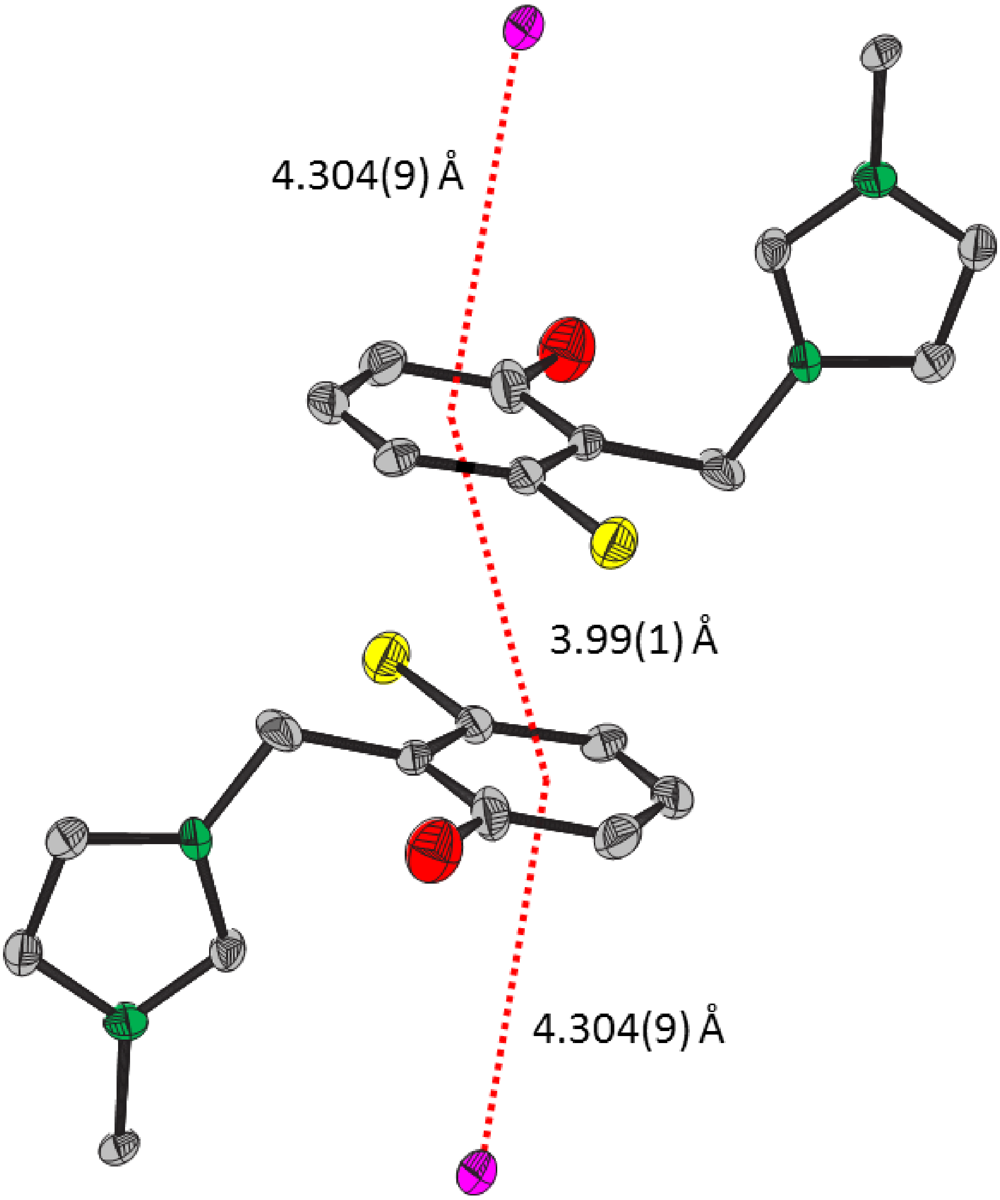

Figure **9**. The stacking of the cations of 1-(2-chloro-6-fluorophenylmethyl)-3-methylimidazolium bromide (**2**). Thermal ellipsoids are at the 50% level. Hydrogen atoms are omitted for clarity.

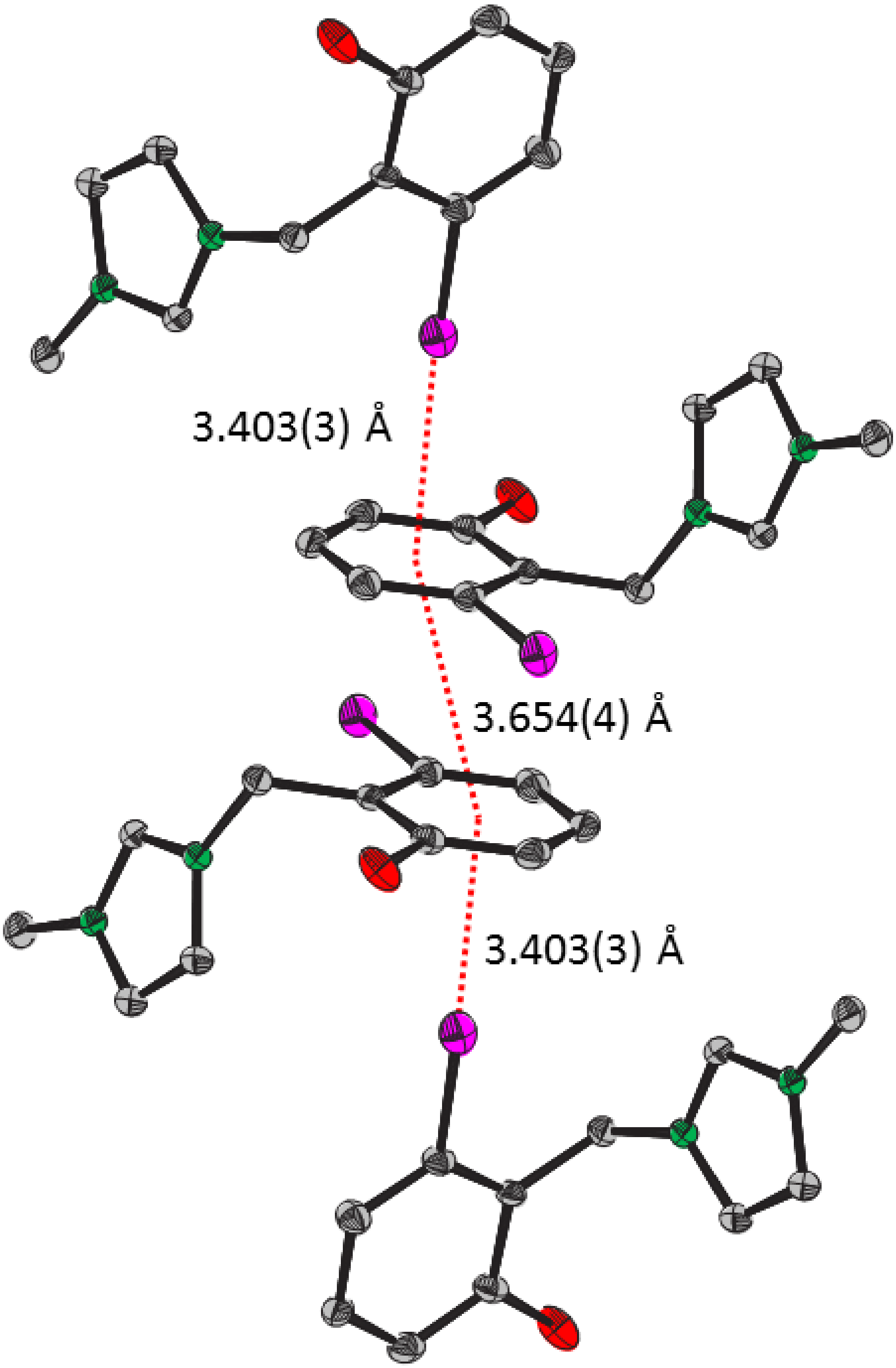

Figure **10**. The stacking of the cations of 1-(2-bromo-6-fluorophenylmethyl)-3-methylimidazolium bromide (**3**). Thermal ellipsoids are at the 50% level. Hydrogen atoms are omitted for clarity.

3. Conclusions

The crystal structures of 1-(2-halo-6-fluorophenylmethyl)-1-methylimidazolium bromide salts possess common features: charge-assisted hydrogen bonding between bromide anions and H(1) and H(2), and π–π stacking between phenyl rings, which are related by a centre of inversion. The presence of water molecules in the crystals structures of **1** and **3** does not affect these similarities, but it does lead to significant differences between the conformations of the cations, the absence of anion–π interactions, and hydrogen bonding between H(3) and water molecules instead of bromide anions. Only the crystal structure of **4** possesses halogen bonding, which is presumably a consequence of the interaction between the iodine atom and the bromide anion being stronger than that between the other halogen atoms and a bromide anion. The relative strengths of the interactions are consistent with those observed previously for imidazolium salts [3,5,9]: $H(1)\cdots Br^{-} > H(2)\cdots Br^{-} \approx H(3)\cdots Br^{-} > I\cdots Br^{-} > \pi\cdots Br^{-} > \pi\cdots\pi$.

4. Experimental

4.1 Instrumentation

The ^{1}H, $^{13}C\{^{1}H\}$ and ^{19}F NMR spectra were recorded in $CDCl_3$ using Bruker DRX300 or DPX400 spectrometers. ^{1}H (300.13 or 400.14 MHz) were referenced internally using the residual protio solvent resonance relative to $SiMe_4$ (δ 0), ^{13}C (75.48

or 100.61 MHz) externally to $SiMe_4$ (δ 0), and ^{19}F (282.40 or 376.47 MHz) externally to $CFCl_3$ (δ 0). All chemical shifts are quoted in δ (ppm), using the high frequency positive convention, and coupling constants in Hz. Electrospray mass spectra were recorded on a Bruker Daltonics micrOTOF spectrometer.

4.2 Materials

1-Methylimidazole (Aldrich), and 2-halo-6-fluorobenzyl bromides and 2-trifluoromethyl-6-fluorobenzyl bromide (Apollo Scientific) were used as supplied.

4.3 Preparation of 1-(2,6-difluorophenylmethyl)-3-methylimidazolium bromide (**1**)

1-Methylimidazole (0.57 g, 6.93 mmol) was added to 2,6-difluorophenylmethyl bromide (1.45 g, 6.99 mmol) in dichloromethane (30 cm^3). The mixture was left at ambient temperature for 96 h. The solvent was removed by rotary evaporation affording the product as a white powder. Yield 1.89 g (94%). MS: $C_{11}H_{11}F_2N_2$ requires 209.0890; found $[M - Br]^+$ 209.0913. ^1H ($CDCl_3/(CD_3)_2SO$): δ = 10.07 (1H, s, N_2CH), 7.43 (1H, t, $^3J_{HH}$ = 1.8 Hz, *H*CCH), 7.34 (1H, m, H_{para}), 7.18 (1H, t, $^3J_{HH}$ = 1.8 Hz, HCC*H*), 6.29 (2H, m, H_{meta}), 5.50 (2H, s, CH_2), 3.98 (3H, s, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3/(CD_3)_2SO$): δ = 162.8 (dd, $^1J_{CF}$ = 252 Hz, $^3J_{CF}$ = 6 Hz, CF), 137.7 (s, N_2CH), 132.5 (t, $^2J_{CF}$ = 10 Hz, C_{para}), 124.1 (s, *C*HCH), 121.6 (s, CH*C*H), 112.3 (dm, $^2J_{CF}$ = 24 Hz, C_{meta}), 109.2 (t, $^2J_{CF}$ = 18 Hz, C_{ipso}), 41.0 (t, $^3J_{CF}$, NCH_2), 36.7 (NCH_3). ^{19}F ($CDCl_3/(CD_3)_2SO$): δ = -113.80 (2F, m).

4.4 Preparation of 1-(2-chloro-6-fluorophenylmethyl)-3-methylimidazolium bromide (**2**)

1-Methylimidazole (0.58 g, 7.00 mmol) and 2-chloro-6-fluorophenylmethyl bromide (1.54 g, 6.87 mmol) were treated as in *4.3*. Yield 1.81 g (86%). MS: $C_{11}H_{11}{}^{35}ClFN_2$ and $C_{11}H_{11}{}^{37}ClFN_2$ require 225.0595 and 227.0595; found $[M - Br]^+$ 225.0630 and 227.0691. ^1H ($(CD_3)_2SO$): δ = 9.18 (1H, s, N_2CH), 7.72 (1H, s, $\mathit{H}CCH$), 7.71 (1H, s, $HCC\mathit{H}$), 7.58 (1H, td, $^3J_{HH}$ = 8.2, $^3J_{HF}$ = 6.3 Hz, C_6H_3), 7.49 (1H, dt, J_{HH} = 8.2 Hz, J_{HH} = 1.1 Hz, C_6H_3), 7.40 (1H, ddd, J_{HF} = 9.5 Hz, J_{HH} = 8.2, J_{HH} = 1.3 Hz, C_6H_3), 5.56 (2H, d, J = 1.6 Hz, NCH_2), 3.84 (3H, s, NCH_3). $^{13}C\{^1H\}$ NMR ($(CD_3)_2SO$): δ = 163.4 (d, $^1J_{CF}$ = 251 Hz, CF), 137.3 (N_2CH), 135.4 (d, J_{CF} = 5 Hz, C_6), 133.1 (d, J_{CF} = 10 Hz, C_6), 126.6 (d, J_{CF} = 3 Hz, C_6) 124.4 (s, $H\mathit{C}CH$), 122.9 (s, $H\mathit{C}CH$), 120.3 (d, J_{CF} = 17 Hz, C_6), 115.9 (d, $^2J_{CF}$ = 22 Hz, C_{ipso}), 44.2 (d, $^3J_{CF}$ = 4 Hz, NCH_2), 36.4 (s, NCH_3). ^{19}F (d_6-DMSO): δ = -111.89 (1F, m).

4.5 Preparation of 1-(2-bromo-6-fluorophenylmethyl)-3-methylimidazolium bromide (**3**)

1-Methylimidazole (0.155g, 1.88 mmol) and 2-bromo-6-fluorophenylmethyl bromide (0.505 g, 1.88 mmol) were treated as in *4.3*. Yield 0.635 g (96%). MS: $C_{11}H_{11}{}^{79}BrFN_2$ and $C_{11}H_{11}{}^{81}BrFN_2$ require 269.0090 and 271.0186; found $[M - Br]^+$ 269.0087 and 271.0068. ^1H ($(CD_3)_2SO$): δ = 9.22 (1H, s, N_2CHN), 7.76 (1H, s, $\mathit{H}CCH$), 7.73 (1H, s, $HCC\mathit{H}$), 7.64 (1H, d, $^3J_{HH}$ = 7.9 Hz, C_6H_3), 7.51 (1H, td, $^3J_{HH}$ = 8.4 Hz, J_{HF} = 6.2 Hz, C_6H_3), 7.46 (1H, ddd, $^3J_{HF}$ = 9.6 Hz, J_{HH} = 8.4 Hz, J_{HH} = 1.2 Hz, C_6H_3), 5.56 (2H, d, $^3J_{HF}$ = 1.5 Hz, NCH_2), 3.86 (3H, s, NCH_3). $^{13}C\{^1H\}$ NMR ($(CD_3)_2SO$): δ = 163.4 (d, $^1J_{CF}$ = 251 Hz, CF), 137.2 (N2CH), 133.5 (d, J_{CF} = 10 Hz, C_6), 129.9 (d, J_{CF} = 3 Hz, C_6), 125.6 (d, J_{CF} = 4 Hz, C_6), 124.5 (s, $H\mathit{C}CH$), 122.9 (s, $HC\mathit{C}H$), 121.6 (d, J_{CF} = 17 Hz, C_6), 116.4 (d, $^2J_{CF}$ = 22 Hz, C_{ipso}), 46.7 (d, $^3J_{CF}$ = 3 Hz, NCH_2), 36.4 (s, NCH_3). ^{19}F ($(CD_3)_2SO$): δ = -110.71 (m).

4.6 Preparation of 1-(2-iodo-6-fluorophenylmethyl)-3-methylimidazolium bromide (**4**)

1-Methylimidazole (0.135g, 1.65 mmol) and 2-iodo-6-fluorophenylmethyl bromide (0.505 g, 1.60 mmol) were treated as in *4.3*. Yield 0.595 g (93%). MS: $C_{11}H_{11}FIN_2$ requires 316.9951; found $[M - Br]^+$ 316.9960. ^1H ($(CD_3)_2SO$): δ = 9.16 (1H, s, N_2CH), 7.86 (1H, d, J_{HH} = 7.7 Hz, C_6H_3), 7.76 (1H, m, *H*CCH), 7.72 (1H, m, HCC*H*), 7.41 (1H, ddd, J_{HF} = 9.6 Hz, J_{HH} = 8.4, 1.1 Hz, C_6H_3), 7.32 (1H, td, J_{HH} = 8.0 Hz, J_{HF} = 6.1 Hz, C_6H_3), 5.52 (2H, d, J_{HF} = 1.8 Hz, NCH_2), 3.86 (3H, s, NCH_3). $^{13}C\{^1H\}$ NMR ($(CD_3)_2SO$): δ = 162.7 (d, $^1J_{CF}$ = 252 Hz, CF), 137.1 (s, N_2CH), 136.4 (d, J_{CF} = 3 Hz, C_6), 134.0 (d, J_{CF} = 9 Hz, C_6), 124.5 (s, H*C*CH), 124.3 (d, J_{CF} = 16, C_6), 122.9 (s, HC*C*H), 116.9 (d, $^2J_{CF}$ = 22 Hz, C_{ipso}), 103.9 (s, C_6), 51.2 (d, $^3J_{CF}$ = 4, NCH_2), 36.4 (s, NCH_3). ^{19}F ($(CD_3)_2SO$): δ = -109.88 (m)

4.7 Preparation of 1-(2-trifluoromethyl-6-fluorophenylmethyl)-3-methylimidazolium bromide (**5**)

1-Methylimidazole (ca. 0.1 g, 1.3 mmol) and 2-bromo-6-fluorophenylmethyl bromide (0.478 g, 1.86 mmol) were treated as in *4.3*. Yield 0.36 g (82%). MS: $C_{12}H_{11}F_4N_2$ requires 259.0858; found $[M - Br]^+$ 259.1499. ^1H ($CDCl_3/(CD_3)_2SO$): 9.52 (s, 1H, N_2CH), 7.64 (s, 1H, *H*CCH), 7.63 (1H, m, C_6H_3), 7.59 m (1H, m, C_6H_3), 7.43 (1H, dd, *J* = 9.3 Hz, *J* = 9.3 Hz, C_6H_3), 7.31 (s, 1H, HCC*H*), 5.85 (2H, s, CH_2), 3.94 (3H, s, CH_3). $^{13}C\{^1H\}$ ($CDCl_3/(CD_3)_2SO$): δ = 162.2 (d, $^1J_{CF}$ = 250 Hz, CF), 137.4 (s, N_2CH), 132.8 (d, J_{CF} = 10 Hz, C_6), 130.8 (q, $^2J_{CF}$ = 31 Hz, *C*CF_3), 124.4 (s, H*C*CH), 123.2 (qd, $^1J_{CF}$ = 275 Hz, $^4J_{CF}$ = 4 Hz, CF_3), 122.8 (dq, J_{CF} = 6 Hz, J_{CF} = 5 Hz, C_6), 122.0 (s, HC*C*H), 120.8 (d, J_{CF} = 22 Hz, C_6), 118.2 (d, $^2J_{CF}$ = 17 Hz, C_{ipso}), 43.6 (s, CH_2), 36.7 (s, CH_3). ^{19}F ($CDCl_3/(CD_3)_2SO$): δ = -57.84 (3F, s, CF_3), -111.16 (1F, m, C_6F).

4.8 X-ray crystallography

Crystals of **1** and **5** were grown from dichloromethane. Crystals of **2** were grown from diffusion of pentane into a solution in dichloromethane. Crystals of **3** and **4** were grown from a mixture of dichloromethane, tetrahydrofuran and methanol. Crystal data are listed in Table 1. Diffraction data were collected on an Agilent SuperNova, single source at offset, Atlas diffractometer with graphite-monochromated Cu—K_α radiation. The structures of **1 – 5** were solved using Olex2 [25] structure solution programme using Charge Flipping and refined with the olex2.refine [26] refinement package using Gauss-Newton minimization. The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atom positions were added in idealized positions and a riding model with fixed thermal parameters (Uij = 1.2Ueq for the atom to which they are bonded (1.5 for CH_3)) was used for subsequent refinements. The function minimized was $\Sigma[w(|F_o|^2 - |F_c|^2)]$ with reflection weights $w^{-1} = [\sigma^2 |Fo|^2 + (g1P)^2 + (g2P)]$ where $P = [\max |F_o|^2 + 2|F_c|^2]/3$. CCDC 1583317 - 1583321 (**1** – **5** respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4.9 DFT calculations

DFT calculations were performed using Gaussian09 [27] with the long range corrected functional ωB97X-D [13] method with the 6-311++G(2d,2p) basis set, except for iodine for which the 6-311G(d) basis set was used. The energies of interaction were calculated as the difference between the difference between the energy of the species and the sum of those of its components. The C─H and O─H bond distances of the experimental were changed to 1.083 and 0.960 Å before calculation of their energies [28].

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Table 1

Crystallographic data for 1-(2,6-difluorophenylmethyl)-3-methylimidazolium bromide **1**, 1-(2-chloro-6-fluorophenylmethyl)-3-methylimidazolium bromide **2**, 1-(2-bromo-6-fluorophenylmethyl)-3-methylimidazolium bromide **3**, 1-(2-iodo-6-difluorophenylmethyl)-3-methylimidazolium bromide **4**, and 1-(2-trifluoromethyl-6-fluorophenylmethyl)-3-methylimidazolium bromide **5**.[a]

	1	**2**	**3**	**4**	**5**
Formula	$C_{11}H_{11}BrF_2N_2.H_2O$	$C_{11}H_{11}BrClFN_2$	$C_{11}H_{11}Br_2FN_2.1½H_2O$	$C_{11}H_{11}BrFIN_2$	$C_{12}H_9BrF_4N_2$
Formula weight	307.14	305.58	377.05	397.03	339.13
Crystal system	monoclinic	triclinic	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$I2/c$	$P\bar{1}$	$P2_1/c$
a, Å	7.32808(12)	6.9865(11)	13.8188(4)	7.4492(4)	8.59143(17)
b, Å	12.4953(2)	8.8271(7)	8.7968(2)	8.9471(5)	10.82231(17)
c, Å	13.7069(2)	10.1670(13)	22.6679(8)	10.3194(5)	14.1621(3)

α, °	—	76.806(9)	—	76.142(5)	—
β, °	97.1464(15)	75.514(13)	92.576(3)	81.048(4)	104.443(2)
γ, °	—	85.464(10)	—	67.455(5)	—
V, Å^3	1245.34(4)	590.88(14)	2752.74(14)	615.17(6)	1275.17(4)
Z	4	2	8	2	4
D_c (g cm^{-3})	1.638	1.717	1.820	2.143	1.766
Crystal size (mm^3)	0.033 × 0.105 × 0.146	0.075 × 0.169 × 0.440	0.141 × 0.151 × 0.216	0.057 × 0.068 × 0.306	0.232 × 0.302 × 0.540
μ (mm^{-1})	4.639	6.729	7.526	24.173	4.775
θ range (°)	4.81 → 74.00	4.60 → 74.51	3.90 → 74.05	4.42 → 73.97	5.21 → 73.75
Total reflections	7,147	5,733	7,667	6,540	12,304
Unique reflections (R_{int})	2,443 (0.0173)	2,312 (0.0645)	2,716 (0.212)	2,410 (0.0416)	2,530 (0.0506)

Observed reflections [$I > 2\sigma(I)$]	2,226	1927	2,610	2,316	2,104
Parameters	163	146	167	146	172
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0213$ $wR_2 = 0.0541$	$R_1 = 0.0723$ $wR_2 = 0.1732$	$R_1 = 0.0283$ $wR_2 = 0.0744$	$R_1 = 0.0309$ $wR_2 = 0.0792$	$R_1 = 0.0312$ $wR_2 = 0.0708$
R indices (all data)	$R_1 = 0.0255$ $wR_2 = 0.0557$	$R_1 = 0.0909$ $wR_2 = 0.1848$	$R_1 = 0.0311$ $wR_2 = 0.0753$	$R_1 = 0.0345$ $wR_2 = 0.0825$	$R_1 = 0.0428$ $wR_2 = 0.0775$
Weighting scheme	$w = 1/[\sigma^2(F_o)^2 + \{0.0270\ (F_o^2 + 2F_c^2)/3\}^2 + 0.8870\ (F_o^2 + 2F_c^2)/3]$	$w = 1/[\sigma^2(F_o)^2 + \{0.0330\ (F_o^2 + 2F_c^2)/3\}^2 + 12.4940\ (F_o^2 + 2F_c^2)/3]$	$w = 1/[\sigma^2(F_o)^2 + \{0.0450\ (F_o^2 + 2F_c^2)/3\}^2 + 9.2540\ (F_o^2 + 2F_c^2)/3]$	$w = 1/[\sigma^2(F_o)^2 + \{0.0550\ (F_o^2 + 2F_c^2)/3\}^2 + 0.6490\ (F_o^2 + 2F_c^2)/3]$	$w = 1/[\sigma^2(F_o)^2 + \{0.0350\ (F_o^2 + 2F_c^2)/3\}^2 + 1.0700\ (F_o^2 + 2F_c^2)/3]$
Max., min. $\Delta\rho$ (eÅ^{-3})	0.402, -0.405	1.988, -1.918	0.700, -0.885	1.510, -1.272,	0.496, -0.636
Goodness of fit on F^2	1.052	1.048	1.021	1.041	1.054

[a] Estimated standard deviations are given in parentheses. The data were collected at 100.0(1) K using Cu Kα radiation (λ = 1.54184 Å).

Table 2

Selected bond distances (Å) and angles (°) for 1-(2,6-difluorophenylmethyl)-3-methylimidazolium bromide **1**, 1-(2-chloro-6-fluorophenylmethyl)-3-methylimidazolium bromide **2**, 1-(2-bromo-6-fluorophenylmethyl)-3-methylimidazolium bromide **3**, 1-(2-iodo-6-difluorophenylmethyl)-3-methylimidazolium bromide **4**, and 1-(2-trifluoromethyl-6-fluorophenylmethyl)-3-methylimidazolium bromide **5**.[a]

	1		**2**		**3**		**4**		**5**	
	exptl	calc [b]	exptl	calc [b]	exptl	calc [b]	exptl	calc [b]	exptl	calc [b]
N(1)─C(1)	1.335(2)	1.328	1.333(10)	1.327	1.332(3)	1.327	1.342(5)	1.327	1.333(3)	1.328
N(2)─C(1)	1.329(2)	1.328	1.322(10)	1.328	1.332(3)	1.328	1.322(5)	1.328	1.326(3)	1.327
N(1)─C(2)	1.378(2)	1.374	1.379(10)	1.374	1.376(3)	1.373	1.388(5)	1.373	1.378(3)	1.375
N(2)─C(3)	1.380(2)	1.375	1.399(10)	1.376	1.382(3)	1.374	1.377(5)	1.374	1.381(4)	1.376
C(2)─C(3)	1.349(3)	1.354	1.349(11)	1.353	1.356(4)	1.354	1.355(6)	1.354	1.357(4)	1.353
N(1)─C(5)	1.474(2)	1.473	1.491(9)	1.472	1.473(3)	1.476	1.474(5)	1.477	1.482(3)	1.472

N(2)─C(4)	1.466(2)	1.460	1.474(9)	1.460	1.467(3)	1.460	1.469(5)	1.460	1.470(3)	1.460
C(5)─C(6)	1.501(3)	1.498	1.498(11)	1.501	1.508(3)	1.498	1.513(6)	1.499	1.512(4)	1.508
C(7)─F	1.356(2)	1.347	1.362(10)	1.347	1.368(3)	1.340	1.363(3)	1.341	1.358(3)	1.347
C(11)─X [c]	1.357(2)	1.342	1.748(9)	1.744	1.891(3)	1.898	2.114(4)	2.111	1.510(3)	1.510
N(1)─C(1)─N(2)	108.47(16)	108.8	108.7(6)	108.8	108.4(2)	108.8	108.2(3)	108.8	108.4(2)	108.9
C(1)─N(1)─C(2)	108.57(15)	108.7	109.0(6)	108.6	109.1(2)	108.7	108.6(3)	108.6	108.9(2)	108.6
C(1)─N(1)─C(5)	125.32(15)	125.5	123.1(7)	125.6	124.9(2)	126.4	127.9(3)	126.4	127.0(2)	125.5
C(1)─N(2)─C(3)	108.68(15)	108.5	108.4(6)	108.5	108.5(2)	108.5	109.5(3)	108.5	109.0(2)	108.4
C(1)─N(2)─C(4)	124.68(16)	125.8	125.4(6)	125.8	125.6(2)	125.7	124.5(3)	125.7	125.2(2)	126.0
N(1)─C(5)─C(6)	111.57(14)	111.9	112.0(6)	111.9	112.0(2)	112.4	113.0(3)	112.3	113.7(2)	111.7

C(1)─N(1)─C(5)─C(6)	-111.3(2)	94.7	1(1)	102.1	118.1(3)	21.0	-9.2(6)	17.1	36.8(4)	110.9
C(2)─N(1)─C(5)─C(6)	68.5(2)	-80.9	178.0(7)	-74.7	-62.4(3)	159.8	169.7(4)	-162.9	-148.1(2)	-67.1
N(1)─C(5)─C(6)─C(7)	-109.6(2)	97.1	-89.8(9)	-81.8	105.3(3)	-105.1	-74.6(5)	78.4	84.4(3)	-70.1
N(1)─C(5)─C(6)─C(11)	76.0(2)	-83.1	95(1)	98.7	-75.8(3)	76.0	109.7(5)	-102.1	-100.3(3)	110.6
∠ C_3N_2 C_6 [d]	73.0(4)	71.1	85(2)	71.9	76.7(4)	84.9	76.2(7)	85.3	77.9(7)	79.4

[a] Estimated standard deviations are given in parentheses.

[b] The calculations were performed using the ωB97X-D functional and 6-311++G(2d,2p) basis set, except for the iodine atom, for which the 6-311G(d) basis set was used.

[c] **1** X = F, **2** X = Cl, **3** X = Br, **4** X = I, **5** X = CF_3

[d] The angle between the planes defined by the non-hydrogen atoms of the imidazolium and phenyl rings.

Table 3

Selected interionic bond distances (Å), angles (°) and energies of interaction (kJ mol^{-1}) for 1-(2,6-difluorophenylmethyl)-3-methylimidazolium bromide **1**, 1-(2-chloro-6-fluorophenylmethyl)-3-methylimidazolium bromide **2**, 1-(2-bromo-6-fluorophenylmethyl)-3-methylimidazolium bromide **3**, 1-(2-iodo-6-difluorophenylmethyl)-3-methylimidazolium bromide **4**, and 1-(2-trifluoromethyl-6-fluorophenylmethyl)-3-methylimidazolium bromide **5**.[a]

	1	**2**	**3**	**4**	**5**
C(1)···Br$^-$	3.648(1)	3.568(3)	3.612(3)	3.562(5)	3.486(3)
N(1)─C(1)···Br$^-$	139.0(1)	145.0(5)	101.0(1)	102.2(3)	143.2(2)
N(2)─C(1)···Br$^-$	110.5(1)	102.6(5)	144.1(2)	145.5(3)	103.4(2)
C_3N_2···Br$^-$ [b]	0.769(2)	0.922(9)	1.282(3)	0.942(6)	1.115(3)
C_6···Br$^-$ [c]	─	4.190(9)	─	4.108(4)	4.334(3)
$C_6^{\dagger}$···Br$^-$ [d]	─	4.304(9)	─	4.334(4)	4.511(3)

E [H(1)···Br^{-}] ^{e}	-338	-354	-343	-372	-357
E [C$_{6}$···Br^{-}] ^{e}	─	-11	─	-21	-12
C(2)···Br^{-}	3.760(2)	3.660(7)	3.547(3)	3.709(4)	3.758(3)
N(1)─C(2)···Br^{-}	145.1(1)	104.2(5)	158.0(2)	105.5(3)	97.9(2)
C(3)─C(2)···Br^{-}	103.0(1)	148.3(6)	95.2(2)	147.8(3)	154.4(2)
C$_{3}$N$_{2}$···Br^{-b}	1.144(2)	0.328(8)	0.120(3)	0.118(5)	0.443(3)
C$_{6}$···Br^{-} ^{c}	4.382(2)	─	4.563(3)	─	─
C$_{6}^{\dagger}$···Br^{-} ^{d}	5.487(2)	─	5.941(3)	─	─
E [H(2)···Br^{-}] ^{e}	-285	-310	-296	-323	-314
E [C$_{6}$···Br^{-}] ^{e}	-2	─	-2	─	─

C(3)···Br$^-$	—	3.841(9)	—	3.769(5)	3.900(3)
N(2)—C(3)···Br$^-$	—	92.6(4)	—	129.9(3)	53.9(1)
C(2)—C(3)···Br$^-$	—	139.5(6)	—	102.5(3)	104.4(2)
C_3N_2···Br$^-$ [b]	—	2.256(9)	—	2.385(5)	1.059(3)
E [H(3)···Br$^-$] [e]	—	-300	—	-290	-302
C(3)···O	3.213(3), 3.413(3)	—	3.474(4), 3.768(4)	—	—
N(2)—C(3)···O	104.6(1), 151.3(1)	—	135.8(2), 90.3(2)	—	—
C(2)—C(3)···O	139.6(1), 86.0(1)	—	117.0(2), 162.50(2)	—	—
C_3N_2···O	1.317(3), 1.503(3)	—	0.013(4), 0.039(4)	—	—

E [H(3)···OH$_2$] [e]	-14, -13	—	-18, -14	—	—
I···Br$^-$	—	—	—	3.3095(5)	—
C(11)─I···Br$^-$	—	—	—	174.9(1)	—
C$_6$F$_4$I···Br$^-$	—	—	—	0.344(4)	—
E [I···Br$^-$] [e]	—	—	—	-269	—
E [C$_6$···Br$^-$] [e,f]	—	—	—	-54	—
O···Br$^-$	3.314(2), 3.342(2)	—	3.286(2), 3.314(3)	—	—
Br$^-$···O···Br$^-$	106.27(4)	—	106.89(7)	—	—
O···Br$^-$···O	73.73(4)	—	73.11(6)	—	—

$C_6\cdots C_6$ [c]	3.726(4)	3.54(1)	3.410(4)	3.590(6)	3.751(4)
$C_6^{\dagger}\cdots C_6^{\dagger}$ [d]	4.196(4)	3.99(1)	3.654(4)	4.087(6)	3.901(4)
E $[C_6\cdots C_6]$ [e,g]	-55	-37	-42	-37	-37
E $[C_6\cdots C_6]$ [e,h]	-19	-37	-37	-33	-32
$C_3N_2\cdots C_6^{\dagger}$ [b,d]	3.431(3)	—	—	—	—
$\angle C_3N_2\ C_6$ [b,c]	6.4(1)	—	—	—	—
$Br\cdots C_6$ [c]	—	—	3.345(3)	—	—
$Br\cdots C_6^{\dagger}$ [d]	—	—	3.403(3)	—	—
C(11)—$Br\cdots C_6^{\dagger}$ [d]	—	—	174.4(1)	—	—

E $[Br\cdots C_6]$ [e,i]	—	—	-12	—	—

[a] Estimated standard deviations are given in parentheses.

[b] C_3N_2 represents the plane defined by the non-hydrogen atoms of the imidazolium ring.

[c] C_6 represents the plane defined by the six carbon atoms of the halotetrafluorophenyl ring.

[d] $C_6^{\dagger}$ represents the centroid of the six carbon atoms of the halotetrafluorophenyl ring.

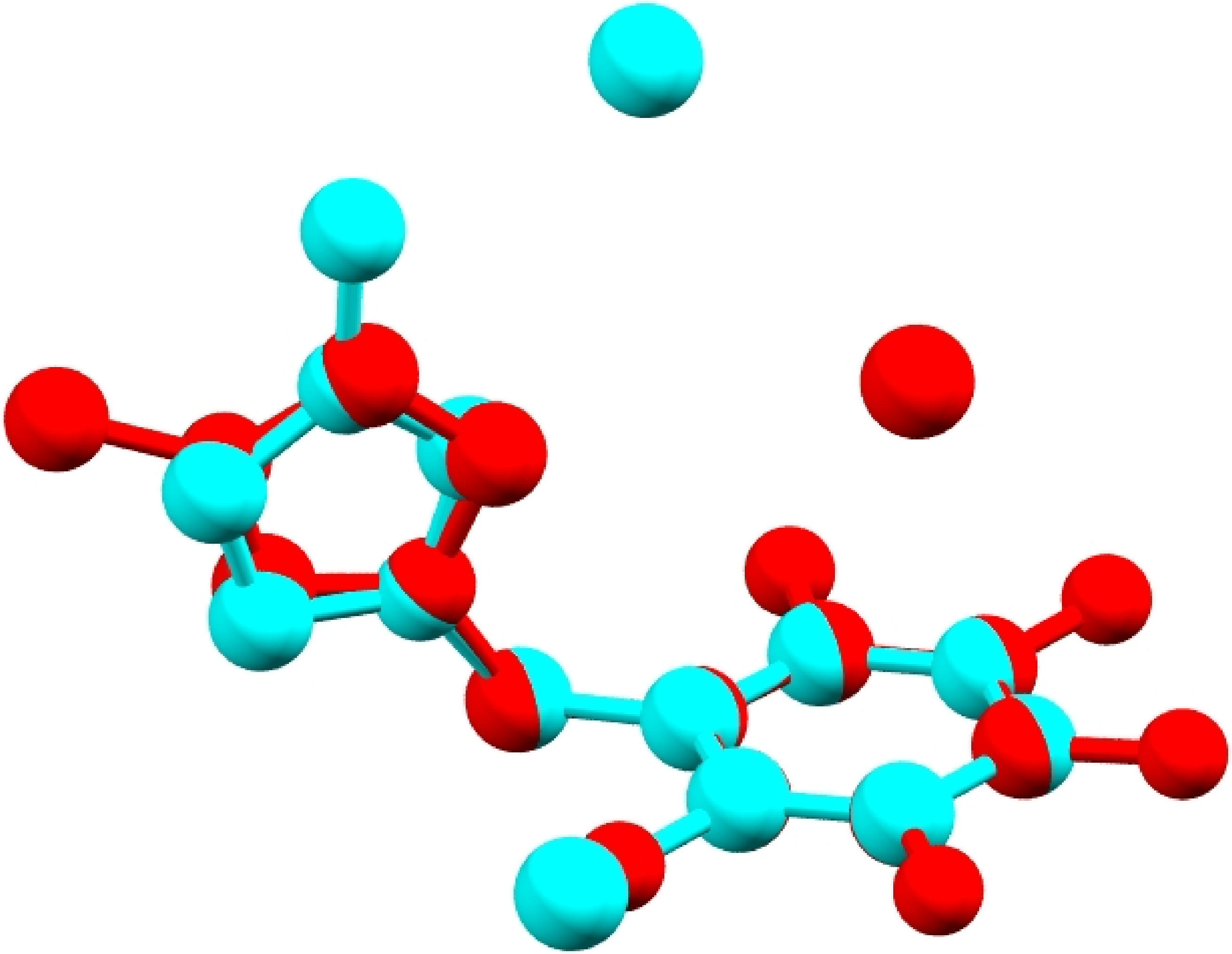
[e] The calculations were performed using the ωB97X-D functional and 6-311++G(2d,2p) basis set, except for the iodine atom, for which the 6-311G(d) basis set was used.

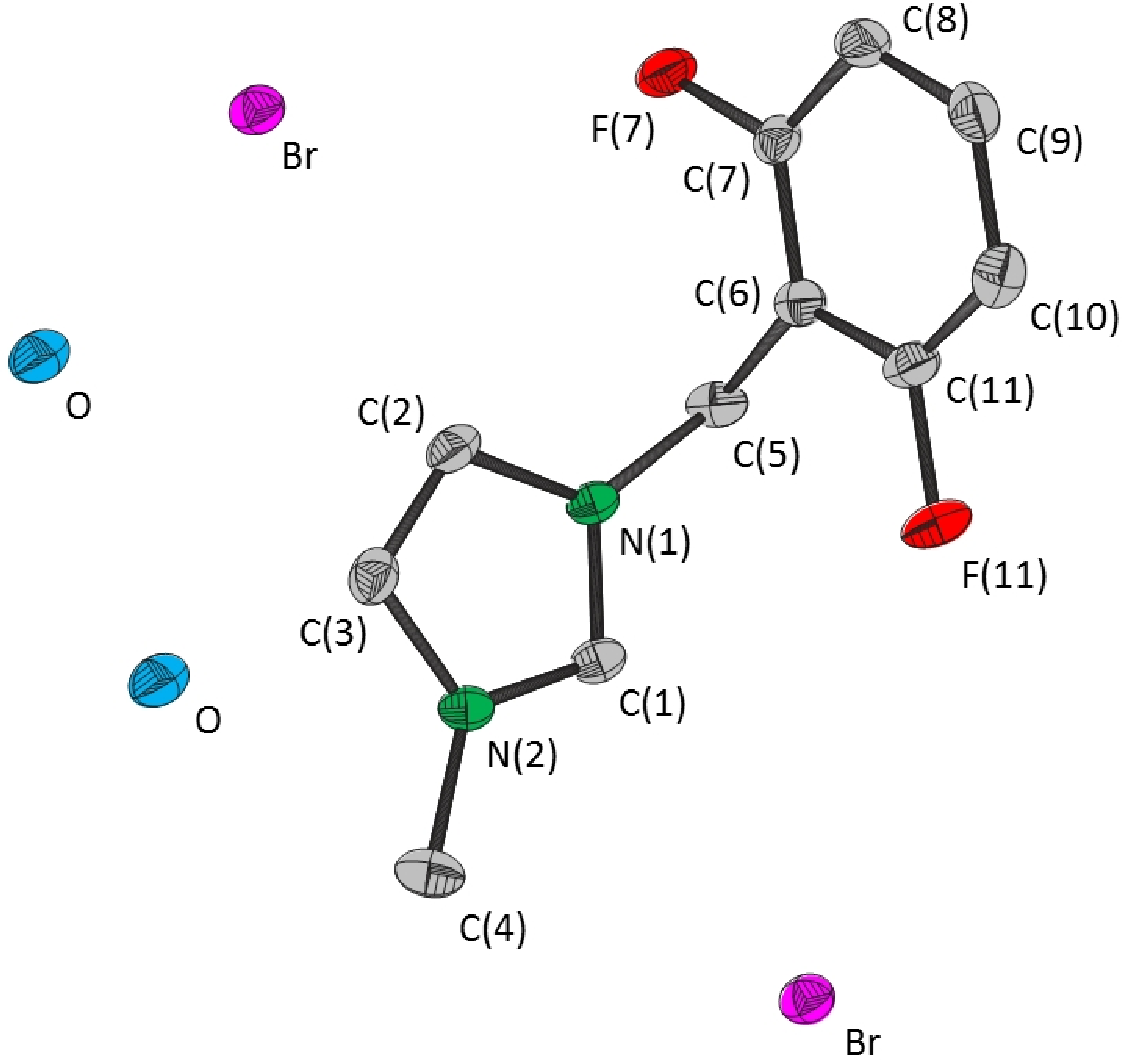
[f] The anion–π interaction between bromide anion and 2-iodo-6-fluorotoluene based on the atom positions of **4**.

[g] The π–π stacking interaction between adjacent imidazole molecules based on the atom positions of the salts.

[h] The π–π stacking interaction between adjacent 2-halo-6-fluorotoluene molecules based on the atom positions of the salts.

[i] The lone pair–π interaction between two molecules of 2-bromo-6-fluorotoluene based on the atom positions of **3**.

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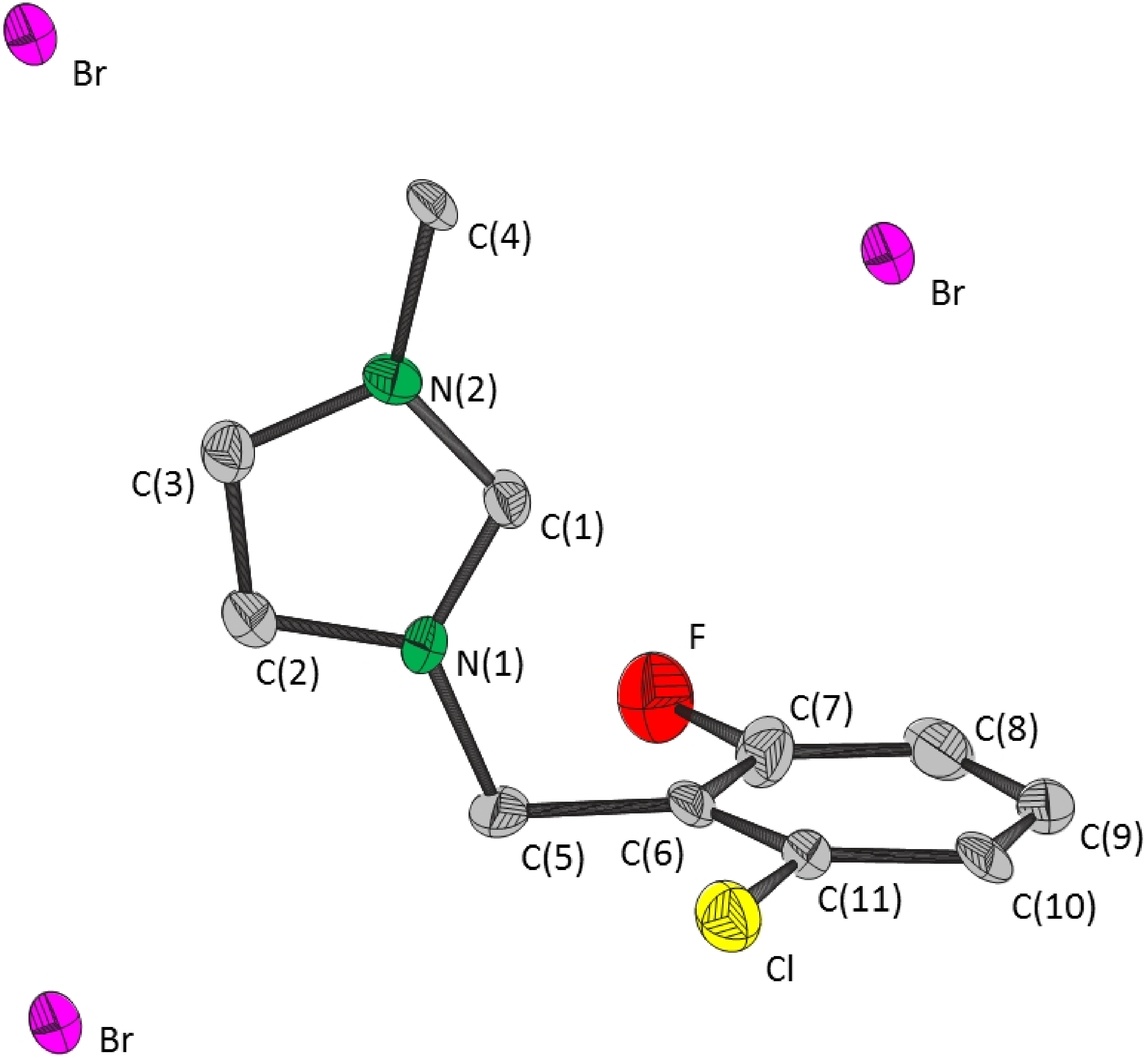
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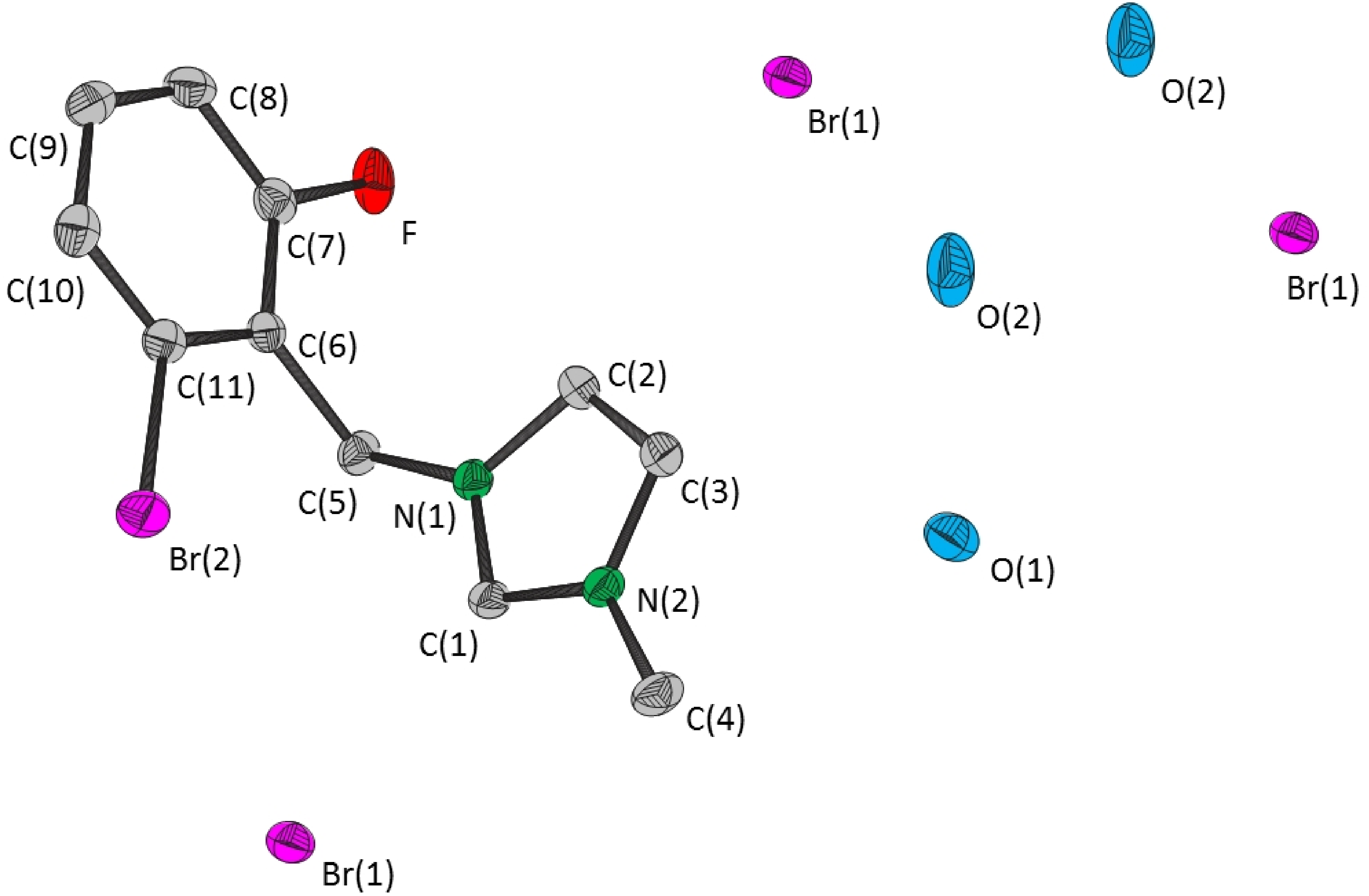
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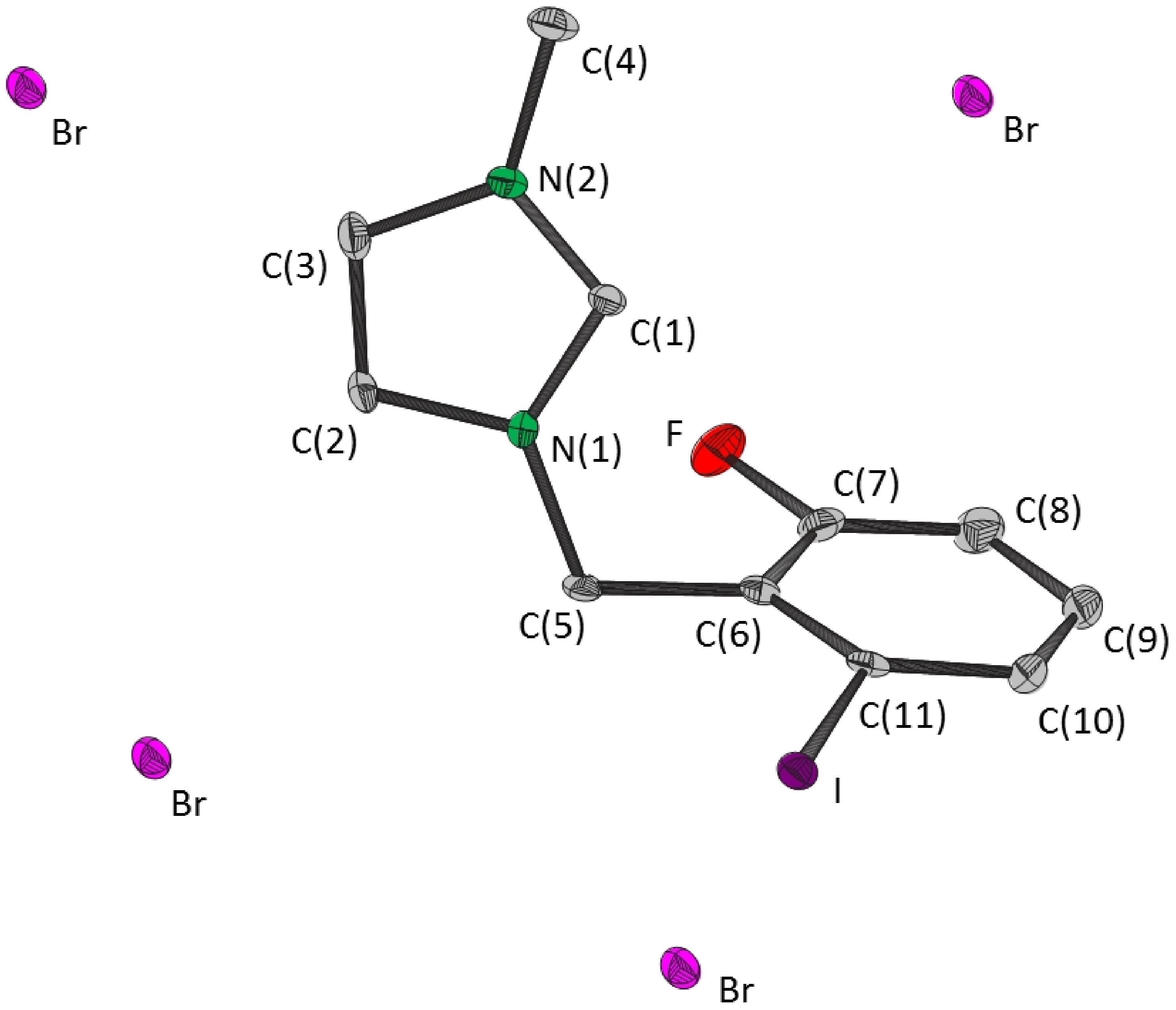
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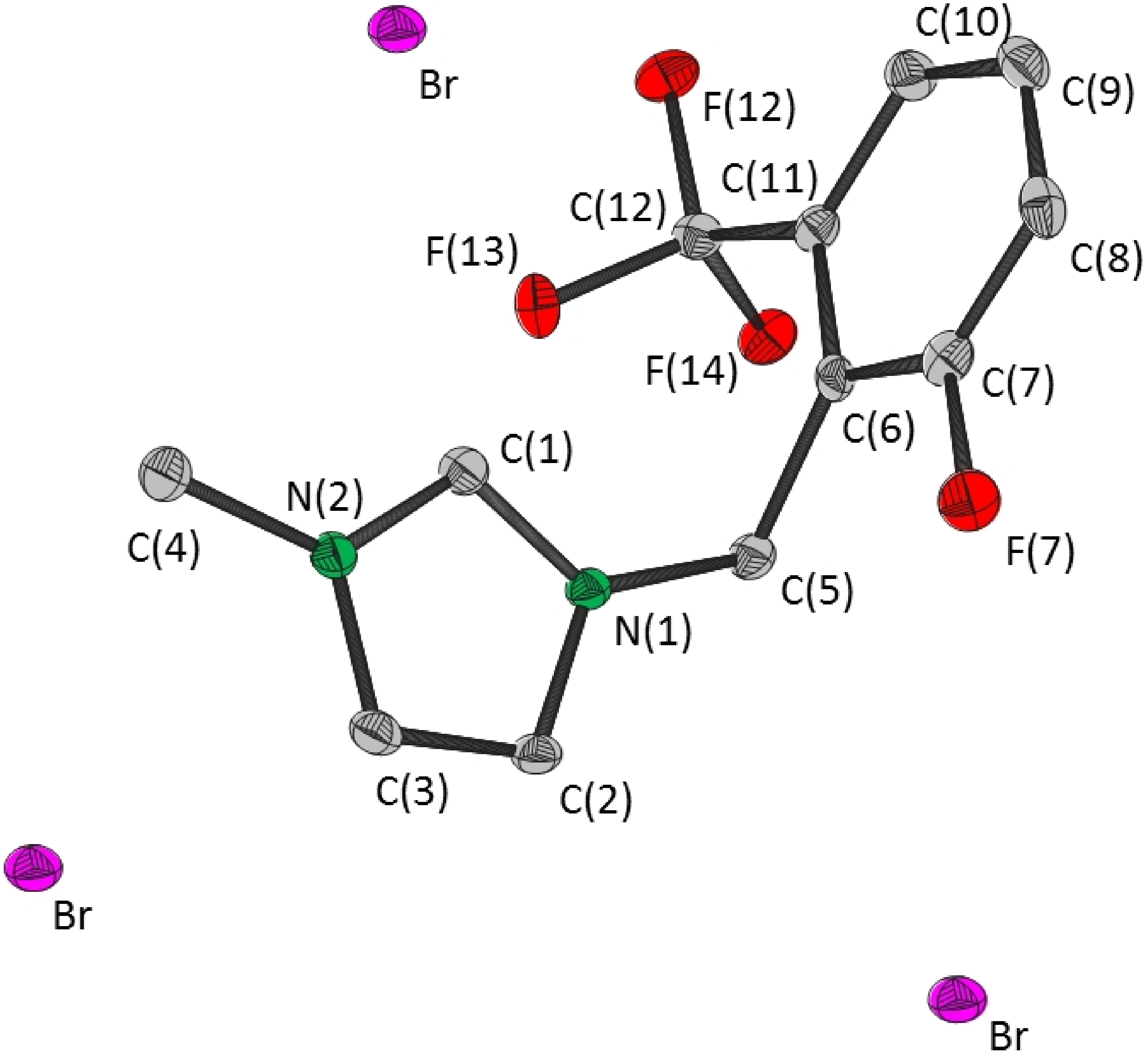
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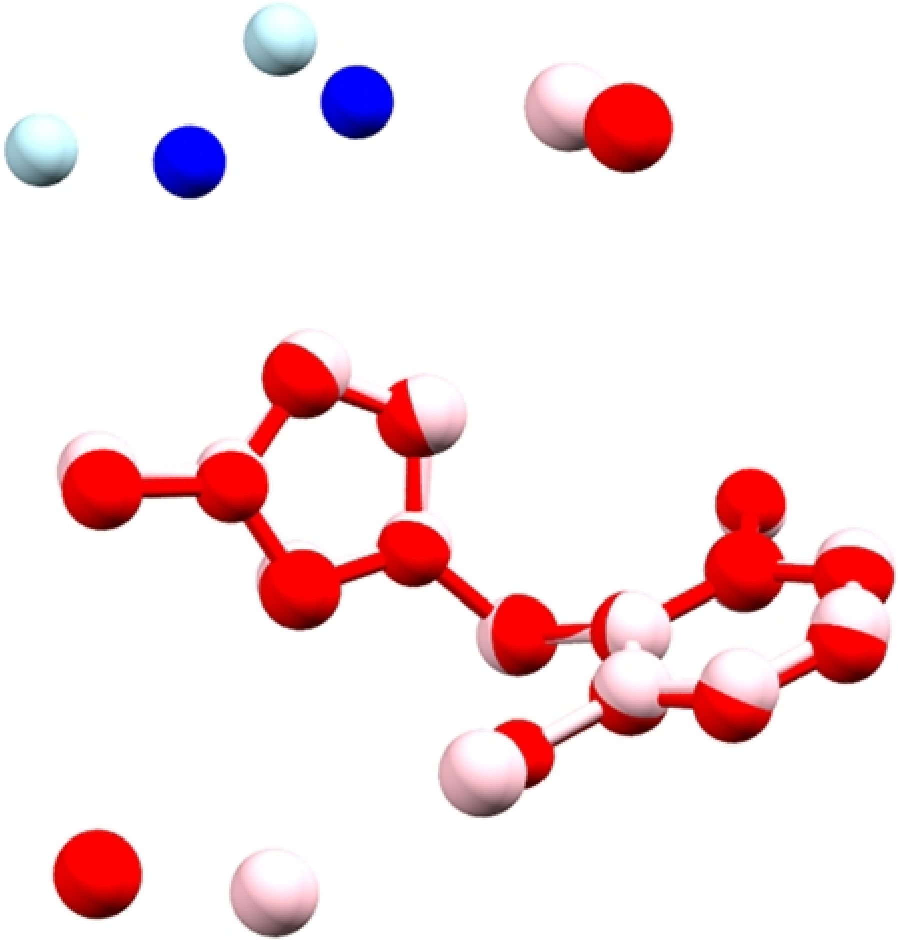

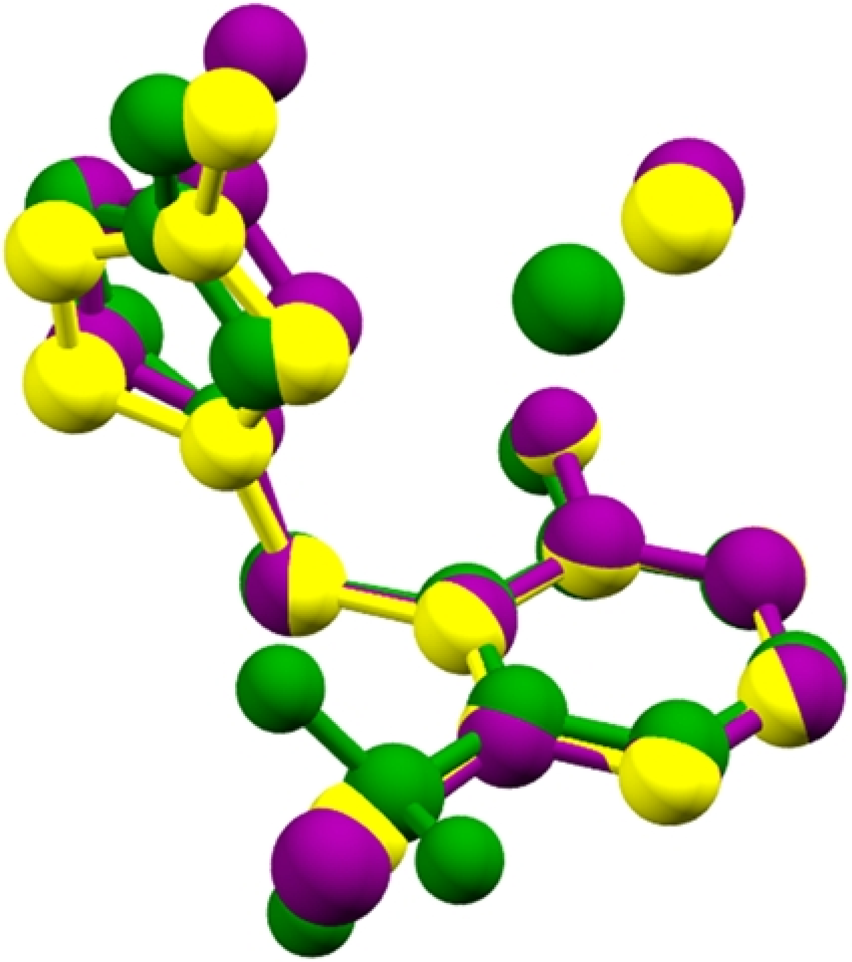

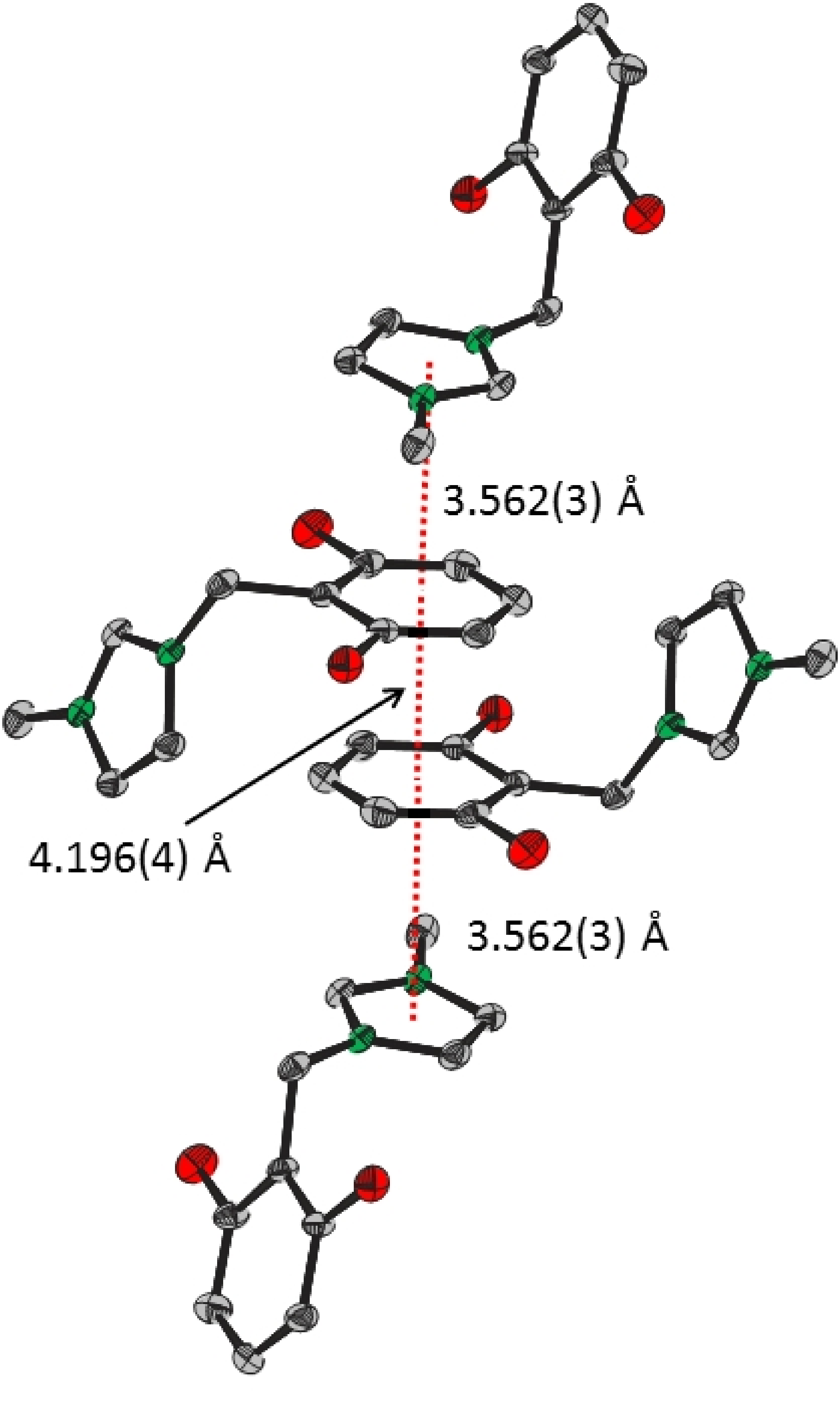
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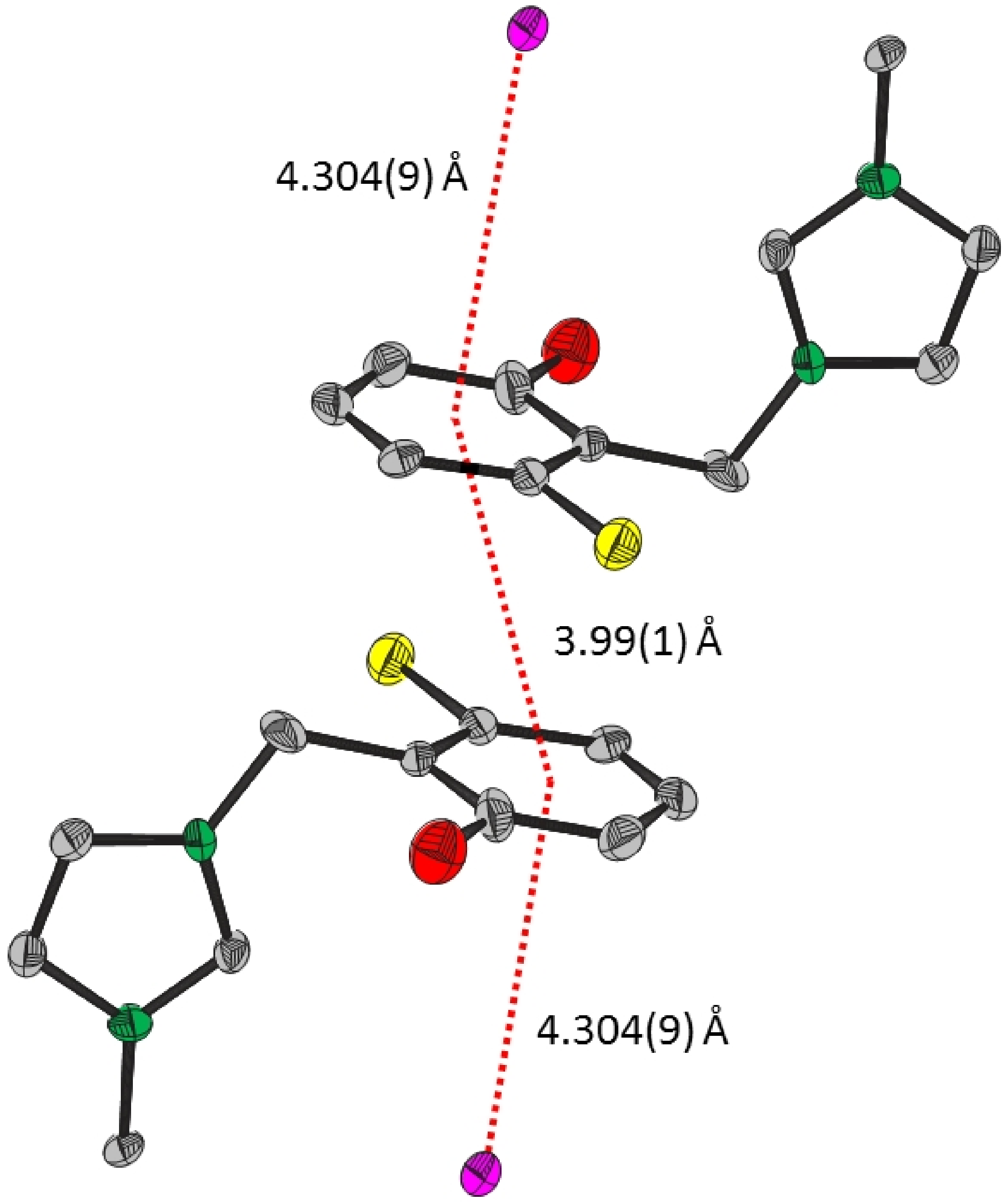
4.196(4) Å
3.562(3) Å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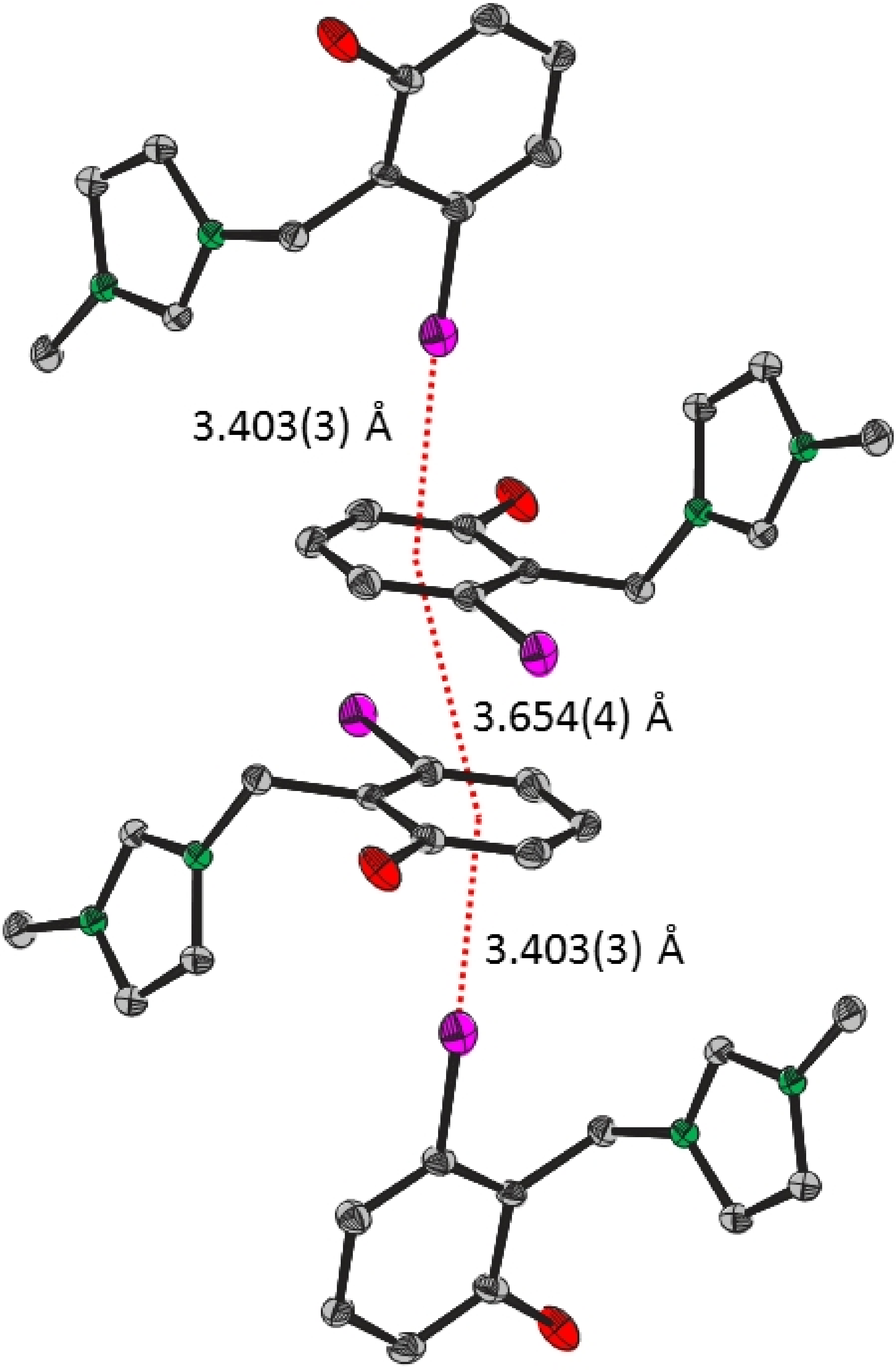
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