



## Short communication

Polyfluoroarene–arene  $\pi$ – $\pi$  stacking in three directions to provide crystal polarity

Melissa A. Oosterwijk, Graham C. Saunders\*, Wenji Zou

School of Science, University of Waikato, Hamilton 3240, New Zealand

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## ABSTRACT

1-(4-Chloro-2,3,5,6-tetrafluorophenyl)-3-benzylimidazolium bromide crystallized from chloroform in the polar space group Cc. The geometry of the cation and the presence of a chloroform molecule, which interacts with the cations and anions through hydrogen- and halogen-bonding, leads to  $\pi$ – $\pi$  stacked columns in three, approximately orthogonal, directions. The crystal polarity arises from the orientation of the cations which is determined by the stacking.

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## 1. Introduction

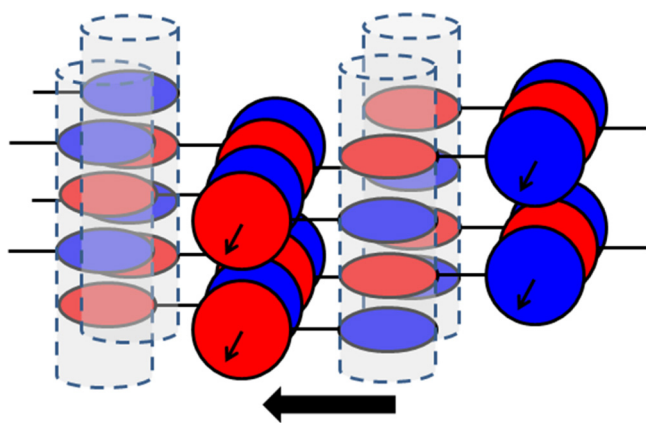
The  $\pi$ – $\pi$  stacking of complementary arenes and polyfluoroarenes in columns has been reported for many molecules bearing both polyfluoroaryl and aryl substituents [1]. In most cases, because these substituents can be co-planar, ‘columnar stacking’ results [2]. Consequently the crystal structures comprise parallel columns of molecules and are centrosymmetric. A necessary condition for generating a non-centrosymmetric crystal structure for these compounds is the prevention of columnar stacking [2]. To achieve this a number of strategies have been suggested. Incorporating a sufficiently large step between the complementary rings of the cations of 1-(2,3,4,5,6-pentafluorobenzyl)-3-benzylimidazolium bromide prevented columnar stacking, but ultimately hydrogen-bonding interactions determined the non-centrosymmetry (CSD code number: BONKUL) [3]. The angularity of the cations prevented columnar stacking in the structures of 1-(2,3,5,6-tetrafluoropyridyl)-3-benzylimidazolium bromide (AMOCOV) and related salts [2], but the  $\pi$ – $\pi$  stacking was disrupted by anion– $\pi$  interactions and three component Ar···ArF···Br<sup>−</sup> motifs resulted. Substitution of the tetrafluoropyridyl group by 4-bromo-2,3,5,6-tetrafluorophenyl frustrated the  $\pi$ – $\pi$  stacking completely and columns of alternating fluoroaryl rings and anions resulted (LIJPUR) [4]. It has been postulated that  $\pi$ – $\pi$  stacking in two orthogonal directions can provide polarity, and therefore, non-centrosymmetry (Fig. 1), and a number of criteria were proposed

for generating the appropriate stacking. These were satisfied by 1-(4-cyano-2,3,5,6-tetrafluorophenyl)benzimidazole, which crystallized in the polar space group Cc (PEYDEE) [5]. It was found subsequently that these criteria, although sufficient conditions for preventing columnar stacking, were only necessary conditions for generating non-centrosymmetry [6].

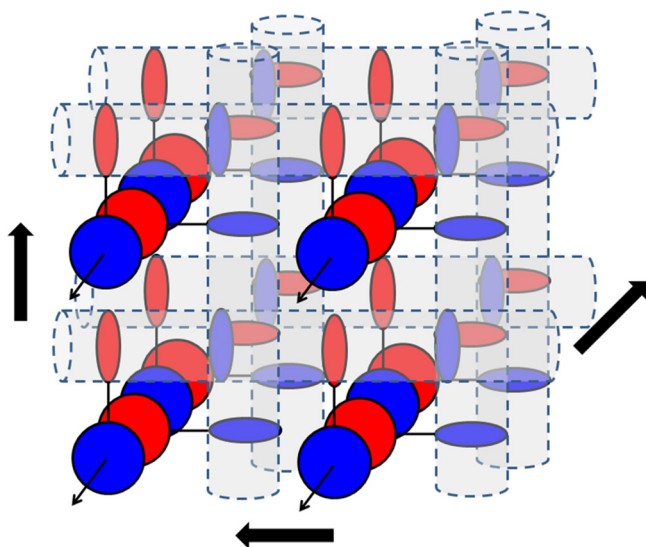
Since  $\pi$ – $\pi$  stacking in two directions in the crystal structure of 1-(4-cyano-2,3,5,6-tetrafluorophenyl)benzimidazole provided a lattice on which non-centrosymmetry could be generated, we wished to explore the possibility of  $\pi$ – $\pi$  stacked columns in three orthogonal directions. A centrosymmetric and a non-centrosymmetric arrangement are readily envisaged. The non-centrosymmetric structure is shown in Fig. 2; for the centrosymmetric structure the direction of the molecules alternate along each column. To realize these structures it is necessary for the components to possess the correct geometric parameters to allow the  $\pi$ – $\pi$  stacking, and for there to be no strong interactions that militate against the stacking. To obtain these structures it is also necessary that within a component the planes of the arene and polyfluoroarene rings are perpendicular. This has rarely been observed, but it is present in the crystal structures of 1-(2,3,5,6-tetrafluoropyridyl)-3-benzylimidazolium bromide and related salts that also possess Ar···ArF···Br<sup>−</sup> motifs [2]. This observation hints that similar imidazolium salts may generate the desired  $\pi$ – $\pi$  stacking if the anion– $\pi$  bonding can be overcome. Consequently we were prompted to investigate other 1-polyfluoroaryl-3-benzylimidazolium bromide salts. Here we report the crystal structure of 1-(4-chloro-2,3,5,6-tetrafluorophenyl)-3-benzylimidazolium bromide, **1**, which is the first example of a structure with

\* Corresponding author.

E-mail address: [g.saunders@waikato.ac.nz](mailto:g.saunders@waikato.ac.nz) (G.C. Saunders).



**Fig. 1.** Control of structure by  $\pi$ - $\pi$  stacking in two orthogonal directions with the stacking and polarity indicated.

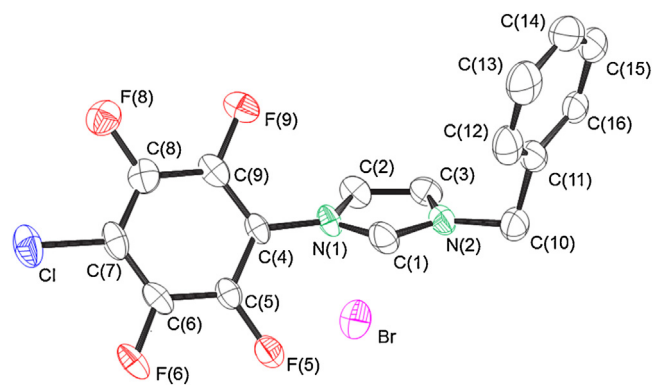


**Fig. 2.**  $\pi$ - $\pi$  stacking in three orthogonal directions to generate a non-centrosymmetric structure. The stacking and polarity are indicated.

$\pi$ - $\pi$  stacked columns of aryl and polyfluoroaryl rings in three orthogonal directions.

## 2. Results and discussion

Salt **1** crystallized from chloroform in the polar space group  $Cc$  with three ion pairs and two solvent molecules (*vide infra*) in the asymmetric unit. The three unique cations (cation **A** is shown in Fig. 3) have similar structural parameters and are chiral, with their enantiomers generated by the symmetry of the space group. The bond distances and angles are close to those calculated for an isolated cation in the gas phase using the  $\omega B97X-D$  [7] and the 6-311G++(2d,2p) basis set (Table 1), as are the angles subtended by the planes of the polyfluoroaryl and imidazolium rings: **A** 56.7(8)°, **B** 62.3(8)°, **C** 58.8(8)°, calculated 62.8°. However, the angles subtended by the planes of the phenyl and imidazolium rings (**A** 73.3(7)°, **B** 70.5(7)°, **C** 71.3(7)°) are ca. 20° more acute, and those subtended by the planes of the polyfluoroaryl and phenyl rings (**A** 62.1(8)°, **B** 63.7(8)°, **C** 69.0(8)°) are 25–30° more obtuse than those of the calculated structure (89.9° and 37.4° respectively). The data indicate the interionic interactions have a significant impact on the



**Fig. 3.** The structure of cation **A** of salt **1** showing the atomic labelling. Displacements ellipsoids are at the 50% level. Hydrogen atoms are omitted for clarity.

conformations of the cations, but not on the bond distances and angles.

Despite the planes of the aryl and polyfluoroaryl rings not being perpendicular the crystal structure contains  $\pi$ - $\pi$  stacked columns in three approximately orthogonal directions. The columns are of two types:  $C_6H_5^A \cdots C_6F_4Cl^B \cdots C_6H_5^A \cdots C_6F_4Cl^B$  (the superscripts indicate the cation label) parallel to the  $c$  axis and  $C_6F_4Cl^A \cdots C_6H_5^B \cdots C_6F_4Cl^C \cdots C_6H_5^C$  parallel to the lines bisecting the  $a$  and  $b$  axes in planes of alternating column direction (Fig. 4). The former column lies at 87.6(2)° to both of the latter, which subtend an angle of 80.9(2)°. Polarity is evident within each column: the phenyl and chlorotetrafluorophenyl components not involved in stacking in that column are positioned on the same side of the plane of the respective chlorotetrafluorophenyl or phenyl ring of the cation (Fig. 5). The  $\pi$ - $\pi$  stacking in the other two directions fixes each crystallographically identical column to be parallel, rather than adjacent columns being antiparallel, thus engendering the crystal structure with polarity.

The columns are inclined by ca. 70° to the planes of their constituent rings, which are approximately parallel, deviating by

**Table 1**

Selected bond, intramolecular and intermolecular distances (Å) and angles (°) for 1-(4-chloro-2,3,5,6-tetrafluorophenyl)-3-benzylimidazolium bromide **1**.<sup>a</sup>

	Cation <b>A</b>	Cation <b>B</b>	Cation <b>C</b>	Calculated <sup>b</sup>
C(1)–N(1)	1.347(7)	1.340(7)	1.324(7)	1.336
C(1)–N(2)	1.328(7)	1.326(7)	1.327(7)	1.321
N(1)–C(4)	1.413(6)	1.426(6)	1.428(6)	1.421
N(2)–C(10)	1.496(6)	1.496(6)	1.480(8)	1.482
C(10)–C(11)	1.519(8)	1.505(7)	1.522(8)	1.502
C(7)–Cl	1.707(5)	1.714(6)	1.710(5)	1.707
C–F (mean)	1.345(6)	1.342(7)	1.343(6)	1.321
N(1)–C(1)–N(2)	106.8(5)	107.9(4)	107.6(5)	108.6
C(1)–N(1)–C(2)	109.6(4)	108.9(4)	109.7(5)	108.5
C(1)–N(2)–C(3)	109.9(4)	108.9(4)	109.8(5)	108.8
C(1)–N(1)–C(4)	124.9(4)	125.9(4)	125.4(4)	125.3
C(1)–N(2)–C(10)	124.7(5)	124.3(4)	124.9(5)	125.4
N(2)–C(10)–C(11)	110.7(4)	111.2(4)	112.2(4)	111.5
C(1)–N(1)–C(4)–C(5)	–57.9(7)	63.7(8)	–59.1(7)	–62.5
C(1)–N(2)–C(10)–C(11)	–88.3(6)	99.5(6)	–95.3(6)	143.7
C(1)···Br <sup>–</sup>	3.415(6)	3.447(6)	3.468(6)	
C(2)···Br <sup>–</sup>	3.605(6)	3.746(6)	3.653(6)	
C(3)···Br <sup>–</sup>	3.547(6)	3.619(6)	3.573(6)	

<sup>a</sup> Estimated standard deviations are given in parentheses.

<sup>b</sup> Calculated using the  $\omega B97X-D$  functional [7] and the 6-311G++(2d,2p) basis set.

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