

# Crystal structures of potassium trifluorido(4-methoxyphenyl)borate and potassium trifluorido-(4-fluorophenyl)borate

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**Keywords:** crystal structure; boron; Lewis acid; layered structure

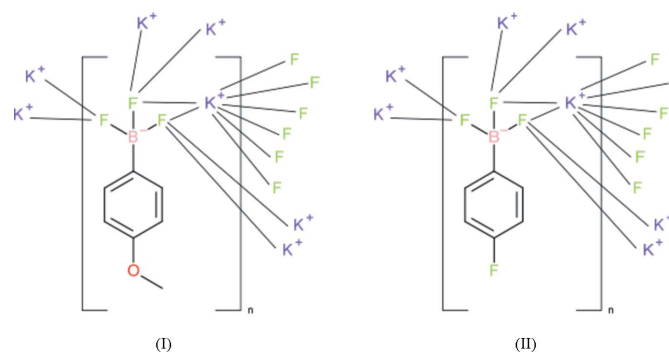
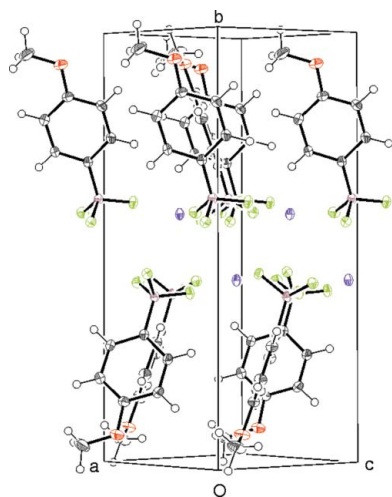
**CCDC references:** 1004280; 1004281

**Supporting information:** this article has  
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The title compounds,  $\text{K}^+\cdot\text{C}_7\text{H}_7\text{BF}_3\text{O}^-$ , (I), and  $\text{K}^+\cdot\text{C}_6\text{H}_4\text{BF}_4^-$ , (II), are molecular salts containing *para*-substituted phenyltrifluoridoborate anions. In each compound, the B atom adopts a distorted tetrahedral  $\text{BCF}_3$  geometry. Despite their different compositions and space groups, the irregular  $\text{KF}_8$  coordination polyhedra of the potassium cations in the structures are almost identical. These polyhedra share faces and edges, generating infinite (010) layers in (I) and infinite (001) layers in (II). In (I), adjacent layers are stacked in an *AAA*... fashion, whereas in (II), they are stacked in an *ABAB*... sequence.

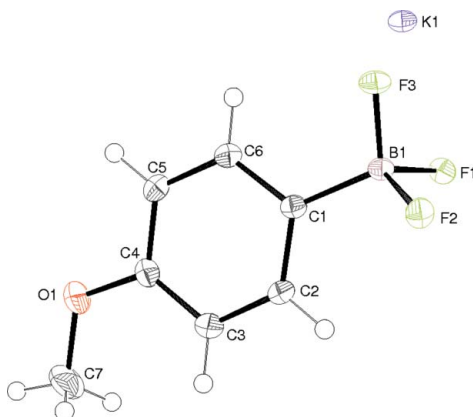
## 1. Chemical context

The phenyltrifluoridoborate anion is an interesting intermediate species between the well-known tetrafluoridoborate ( $\text{BF}_4^-$ ) and tetraphenylborate [ $\text{B}(\text{C}_6\text{H}_5)_4^-$ ] ions (Conole *et al.*, 1995) and may serve as a bulky charge-balancing anion (Quach *et al.*, 2001; Fei *et al.*, 2010). As part of our studies in this area, we now describe the syntheses and structures of the *para*-substituted phenyltrifluoridoborate salts  $\text{K}^+\text{C}_7\text{H}_7\text{BF}_3\text{O}^-$  (I) and  $\text{K}^+\text{C}_6\text{H}_4\text{BF}_4^-$  (II).



## 2. Structural commentary

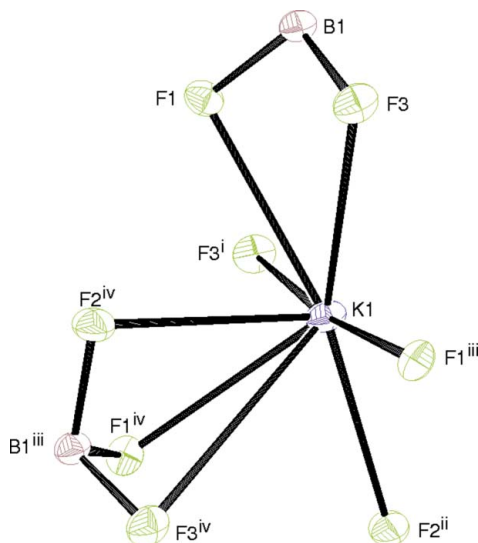
Compound (I) comprises one cation and one anion in the asymmetric unit (Fig. 1). In the anion, the C7 atom of the methoxy group is close to coplanar with the benzene ring [displacement = 0.048 (2) Å]. The B atom adopts its expected tetrahedral  $\text{BF}_3\text{C}$  geometry (Conole *et al.*, 1995) and the C1–B1 bond length of 1.5987 (18) Å is consistent with previous data (Quach *et al.*, 2001). One of the B–F bonds (to F1) in (I) is notably longer than the other two, which might reflect the different modes of coordination of the fluorine atoms to the potassium ions. The F–B–F bond angles (mean = 105.7°) are



**Figure 1**  
The asymmetric unit of (I) showing 50% displacement ellipsoids.

significantly smaller than the C–B–F angles (mean =  $113.0^\circ$ ). F1 is displaced by  $-1.427(2)$  Å from the plane of the benzene ring and F2 and F3 are displaced in the opposite sense, by  $0.715(2)$  and  $0.252(2)$  Å, respectively.

The potassium ion in (I) is coordinated by eight fluorine atoms, with one of the K–F bonds substantially longer than the others (Table 1): the next-nearest F atom is over 4 Å distant. The coordination geometry of the  $K^+$  ion, which arises from one tridentate, one bidentate and three monodentate  $BF_3^-$  groups, is irregular and highly asymmetric (Fig. 2), with five of the F atoms forming an approximate plane and the other three (arising from one  $BF_3$  group) lying to one side. The metal ion is displaced by  $1.00$  Å from the geometric centroid of the eight F atoms. In terms of the F atoms in (I), F1 bonds to three different metal ions (mean K–F =  $2.734$  Å), generating a distorted  $FBK_3$  tetrahedron, whereas F2 bonds to two  $K^+$  ions (mean K–F =  $2.755$  Å) in an  $FBK_2$  distorted T-shape. If the geometry around F3 is not merely deemed to be irregular, it could be described as an  $FBK_3$  trigonal-based pyramid, with the long K–F bond (Table 1) as the apex (mean K–F =



**Figure 2**  
The coordination of the potassium ion in (I). See Table 1 for symmetry codes.

**Table 1**  
Selected bond lengths (Å) for (I).

K1–F3 <sup>i</sup>	2.6156 (10)	K1–F2 <sup>iv</sup>	2.8885 (8)
K1–F2 <sup>ii</sup>	2.6211 (7)	K1–F3 <sup>iv</sup>	3.4886 (9)
K1–F1 <sup>iii</sup>	2.6550 (10)	B1–F3	1.4162 (19)
K1–F1 <sup>iv</sup>	2.7568 (10)	B1–F2	1.4196 (14)
K1–F3	2.7836 (8)	B1–F1	1.4403 (17)
K1–F1	2.7887 (8)		

Symmetry codes: (i)  $-x + \frac{3}{2}, y, z - \frac{1}{2}$ ; (ii)  $x + 1, y, z$ ; (iii)  $-x + \frac{3}{2}, y, z + \frac{1}{2}$ ; (iv)  $x + \frac{1}{2}, -y + 1, z$ .

**Table 2**  
Selected bond lengths (Å) for (II).

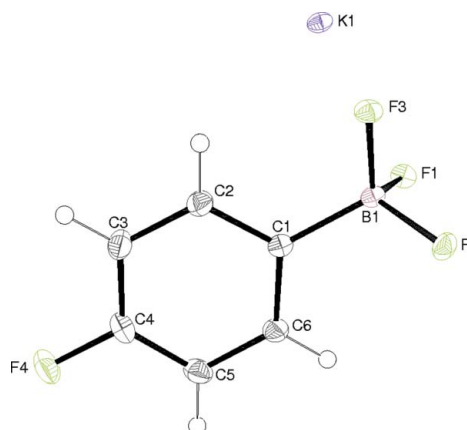
K1–F3 <sup>i</sup>	2.6116 (10)	K1–F2 <sup>iv</sup>	2.8853 (10)
K1–F2 <sup>ii</sup>	2.6159 (9)	K1–F3 <sup>iv</sup>	3.3927 (10)
K1–F1 <sup>iii</sup>	2.6527 (9)	B1–F2	1.4166 (17)
K1–F1 <sup>iv</sup>	2.7612 (10)	B1–F3	1.4182 (19)
K1–F3	2.7732 (9)	B1–F1	1.4393 (18)
K1–F1	2.8050 (9)		

Symmetry codes: (i)  $-x + \frac{1}{2}, y + \frac{1}{2}, z$ ; (ii)  $x - 1, y, z$ ; (iii)  $-x + \frac{1}{2}, y - \frac{1}{2}, z$ ; (iv)  $x - \frac{1}{2}, y, -z + \frac{1}{2}$ .

$2.963$  Å). The extended structure in (I) consists of (010) sheets in which the  $KF_8$  polyhedra share faces in the [100] direction and edges in [001]: the shortest  $K \cdots K$  separation is  $4.4523(4)$  Å.

The asymmetric unit of compound (II) also consists of an ion-pair (Fig. 3). The geometry of the anion in (II) is very similar to that of the equivalent species in (I): the C1–B1 bond length is  $1.590(2)$  Å and the mean F–B–F and C–B–F bond angles are  $105.5$  and  $113.2^\circ$ , respectively. The displacements of F1, F2 and F3 from the benzene-ring plane are  $-1.386(2)$ ,  $0.813(3)$  and  $0.131(3)$  Å, respectively. As seen for (I), the B1–F1 bond in (II) is noticeably longer than the B1–F2 and B1–F3 bonds.

It is notable that the  $K^+$  ion in (II) adopts a very similar coordination geometry (Table 2) to the equivalent species in (I), despite the different space groups. Again, a very asymmetric  $KF_8$  coordination polyhedron (Fig. 4) arises from one tridentate, one bidentate and three monodentate anions; one K–F bond is much longer than the others and the potassium



**Figure 3**  
The asymmetric unit of (II) showing 50% displacement ellipsoids.

**Table 3**

Hydrogen-bond geometry (Å, °) for (I).

Cg1 is the centroid of the C1–C6 benzene ring.

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
C2–H2...F2 <sup>v</sup>	0.95	2.50	3.3359 (17)	147
C7–H7a...O1 <sup>vi</sup>	0.98	2.72	3.496 (1)	137
C3–H3...Cg1 <sup>v</sup>	0.95	2.85	3.7171 (15)	152

Symmetry codes: (v)  $-x + \frac{1}{2}, y, z - \frac{1}{2}$ ; (vi)  $-x + 1, -y + 2, z - \frac{1}{2}$ .

**Table 4**

Hydrogen-bond geometry (Å, °) for (II).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
C6–H6...F2 <sup>v</sup>	0.95	2.53	3.4099 (19)	154

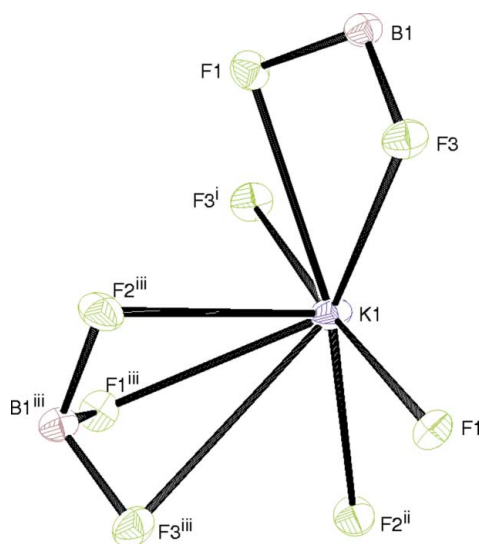
Symmetry code: (v)  $-x + \frac{3}{2}, y + \frac{1}{2}, z$ .

ion is displaced by 0.98 Å from the geometric centroid of the fluorine atoms.

The extended structure of (II) consists of (001) sheets [rather than (010) sheets, as seen in (I)] of face- and edge-sharing  $\text{KF}_8$  groups with the same topology as in (I): the shortest  $\text{K}\cdots\text{K}$  separation is 4.4255 (5) Å.

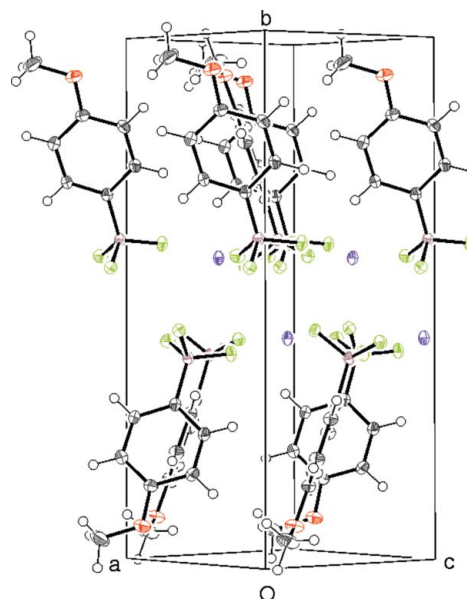
### 3. Supramolecular features

In (I) the methoxyphenyl groups lie roughly normal to (010). When the packing is viewed along [101] (Fig. 5), it may be seen that adjacent benzene ring planes are rotated by 90°, which facilitates the formation of a weak edge-to-face intra-sheet  $\text{C}-\text{H}\cdots\pi$  interaction (Table 3). An intra-sheet  $\text{C2}-\text{H2}\cdots\text{F2}$  hydrogen bond also occurs. The only possible inter-sheet interaction in (I) is an extremely weak  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bond with an  $\text{H}\cdots\text{O}$  separation essentially the same as the van der Waals separation of these species. The layer-stacking sequence for (I) is *AAA*....



**Figure 4**

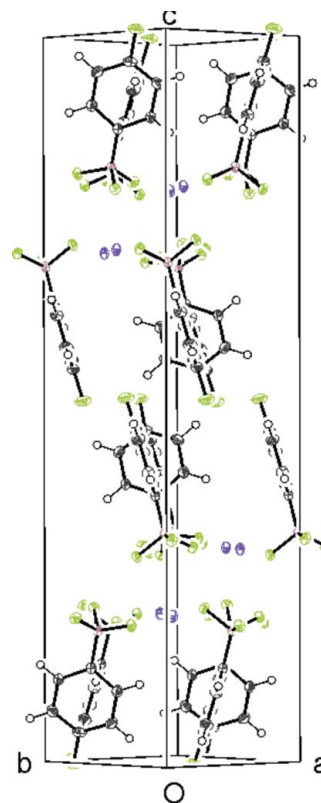
The coordination of the potassium ion in (II). See Table 2 for symmetry codes.



**Figure 5**

The unit-cell packing in (I) viewed approximately down [101].

When the crystal structure of (II) is viewed down [110] (Fig. 6), adjacent aromatic rings show the same 90° rotation as they do in (I), but the only directional interaction identified is an intralayer weak  $\text{C}-\text{H}\cdots\text{F}$  hydrogen bond (Table 4) and there are no  $\text{C}-\text{H}\cdots\pi$  interactions. There are no identified inter-layer interactions and the stacking sequence is *ABAB*....



**Figure 6**

The unit-cell packing in (II) viewed approximately down [110].

**Table 5**  
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	$\text{K}^+\cdot\text{C}_7\text{H}_7\text{BF}_3\text{O}^-$	$\text{K}^+\cdot\text{C}_6\text{H}_4\text{BF}_4^-$
$M_r$	214.04	202.00
Crystal system, space group	Orthorhombic, $Pca2_1$	Orthorhombic, $Pbca$
Temperature (K)	120	100
$a, b, c$ (Å)	7.1347 (2), 17.2819 (7), 7.3289 (3)	7.1317 (5), 7.3757 (5), 29.129 (2)
$V$ (Å <sup>3</sup> )	903.66 (6)	1532.22 (18)
$Z$	4	8
Radiation type	Mo $K\alpha$	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	0.59	0.70
Crystal size (mm)	0.52 × 0.15 × 0.15	0.07 × 0.05 × 0.01
Data collection		
Diffractometer	Rigaku CCD	Rigaku CCD
Absorption correction	Multi-scan ( <i>SADABS</i> ; Bruker, 2012)	Multi-scan ( <i>SADABS</i> ; Bruker, 2012)
$T_{\text{min}}, T_{\text{max}}$	0.750, 0.917	0.953, 0.993
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	5789, 1833, 1822	9537, 1726, 1435
$R_{\text{int}}$	0.026	0.037
$(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )	0.649	0.649
Refinement		
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.021, 0.059, 1.10	0.027, 0.065, 1.06
No. of reflections	1833	1726
No. of parameters	120	109
No. of restraints	1	0
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.24, -0.20	0.27, -0.23
Absolute structure	Flack (1983), 712 Friedel pairs	—
Absolute structure parameter	0.02 (3)	—

Computer programs: *CrystalClear* (Rigaku, 2010), *SHELXS97* and *SHELXL97* (Sheldrick, 2008), *ORTEP-3 for Windows* (Farrugia, 2012) and *pubCIF* (Westrip, 2010).

#### 4. Database survey

Compound (I) is closely related to  $\text{K}^+\cdot\text{C}_6\text{H}_5\text{BF}_3^-$  (Conole *et al.*, 1995), (III). Compounds (I) and (III) have the same space group and a similar unit cell, extended in the  $b$ -axis direction for (I) to accommodate the methoxy group. The potassium ion in (III) has almost the same  $\text{KF}_8$  coordination geometry as the equivalent species in (I) and (II) described above. In (III), weak edge-to-face  $\text{C}-\text{H}\cdots\pi$  interactions occur between approximately perpendicular aromatic rings, as they do in (I). As already noted, the  $\text{C}_6\text{H}_5\text{BF}_3^-$  anion has found use as a bulky charge-balancing species (Quach *et al.*, 2001; Fei *et al.*, 2010).

#### 5. Synthesis and crystallization

(I) and (II) were received as commercial samples from Aldrich and recrystallized from ethanol solution, yielding colourless blocks.

#### 6. Refinement

The H atoms were placed in idealized positions ( $\text{C}-\text{H} = 0.95\text{--}0.98$  Å) and refined as riding atoms with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$

or  $1.5U_{\text{eq}}$  (methyl C). The methyl group in (I) was allowed to rotate, but not to tip, to best fit the electron density. Experimental details are given in Table 5.

#### Acknowledgements

We thank the National Crystallography Service (University of Southampton) for the data collections.

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## supporting information

*Acta Cryst.* (2014). E70, 68-71 [doi:10.1107/S1600536814009684]

## Crystal structures of potassium trifluorido(4-methoxyphenyl)borate and potassium trifluorido(4-fluorophenyl)borate

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### Computing details

For both compounds, data collection: *CrystalClear* (Rigaku, 2010); cell refinement: *CrystalClear* (Rigaku, 2010); data reduction: *CrystalClear* (Rigaku, 2010); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *publCIF* (Westrip, 2010).

### (I) Potassium trifluorido(4-methoxyphenyl)borate

#### Crystal data

$\text{K}^+\cdot\text{C}_7\text{H}_7\text{BF}_3\text{O}^-$

$M_r = 214.04$

Orthorhombic, *Pca*2<sub>1</sub>

$a = 7.1347$  (2) Å

$b = 17.2819$  (7) Å

$c = 7.3289$  (3) Å

$V = 903.66$  (6) Å<sup>3</sup>

$Z = 4$

$F(000) = 432$

$D_x = 1.573$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71075$  Å

Cell parameters from 4830 reflections

$\theta = 1.2\text{--}27.5^\circ$

$\mu = 0.59$  mm<sup>-1</sup>

$T = 120$  K

Block, colourless

0.52 × 0.15 × 0.15 mm

#### Data collection

Rigaku CCD  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\omega$  scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2012)

$T_{\min} = 0.750$ ,  $T_{\max} = 0.917$

5789 measured reflections

1833 independent reflections

1822 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.026$

$\theta_{\max} = 27.5^\circ$ ,  $\theta_{\min} = 1.2^\circ$

$h = -9\text{--}9$

$k = -22\text{--}20$

$l = -8\text{--}9$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.021$

$wR(F^2) = 0.059$

$S = 1.10$

1833 reflections

120 parameters

1 restraint

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier  
map

Hydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.035P)^2 + 0.1245P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.24$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.20$  e Å<sup>-3</sup>

Extinction correction: *SHELXL97* (Sheldrick, 2008),  $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$   
 Extinction coefficient: 0.0115 (14)

Absolute structure: Flack (1983), 712 Friedel pairs  
 Absolute structure parameter: 0.02 (3)

*Special details*

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
K1	0.93636 (3)	0.577078 (16)	0.49116 (4)	0.01659 (9)
C1	0.48663 (17)	0.69908 (7)	0.3989 (2)	0.0159 (3)
C2	0.36313 (18)	0.72309 (8)	0.2628 (2)	0.0195 (3)
H2	0.2718	0.6875	0.2199	0.023*
C3	0.36757 (18)	0.79722 (8)	0.1867 (2)	0.0223 (3)
H3	0.2813	0.8114	0.0938	0.027*
C4	0.5004 (2)	0.84983 (8)	0.2493 (2)	0.0208 (3)
C5	0.62439 (19)	0.82828 (8)	0.3880 (2)	0.0233 (3)
H5	0.7139	0.8643	0.4324	0.028*
C6	0.61673 (19)	0.75407 (8)	0.4608 (2)	0.0206 (3)
H6	0.7018	0.7402	0.5549	0.025*
C7	0.3970 (3)	0.94712 (11)	0.0422 (3)	0.0393 (5)
H7A	0.4278	1.0000	0.0044	0.059*
H7B	0.2674	0.9454	0.0865	0.059*
H7C	0.4105	0.9121	-0.0622	0.059*
B1	0.48502 (18)	0.61227 (8)	0.4743 (2)	0.0153 (3)
F1	0.57562 (10)	0.55930 (5)	0.35081 (13)	0.01754 (18)
F2	0.30347 (10)	0.58074 (4)	0.50165 (17)	0.02096 (19)
F3	0.58402 (11)	0.60460 (5)	0.64078 (13)	0.02023 (19)
O1	0.52053 (18)	0.92364 (6)	0.1842 (2)	0.0297 (3)

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
K1	0.01225 (13)	0.02391 (15)	0.01361 (16)	0.00081 (8)	0.00031 (12)	0.00042 (12)
C1	0.0132 (5)	0.0193 (6)	0.0152 (6)	0.0009 (5)	0.0007 (5)	-0.0009 (5)
C2	0.0199 (6)	0.0204 (6)	0.0183 (7)	-0.0015 (5)	-0.0044 (5)	-0.0014 (6)
C3	0.0233 (6)	0.0229 (6)	0.0206 (7)	0.0011 (5)	-0.0043 (5)	0.0017 (6)
C4	0.0234 (6)	0.0167 (6)	0.0222 (7)	0.0007 (5)	0.0007 (6)	0.0011 (6)
C5	0.0223 (6)	0.0200 (6)	0.0277 (8)	-0.0036 (5)	-0.0054 (5)	-0.0028 (6)
C6	0.0181 (5)	0.0211 (6)	0.0226 (8)	0.0002 (5)	-0.0046 (5)	-0.0010 (6)
C7	0.0421 (9)	0.0273 (7)	0.0484 (13)	0.0011 (7)	-0.0085 (8)	0.0167 (9)

B1	0.0121 (5)	0.0185 (6)	0.0153 (7)	0.0000 (4)	0.0002 (6)	0.0008 (6)
F1	0.0182 (4)	0.0196 (4)	0.0148 (5)	0.0031 (3)	0.0025 (3)	-0.0007 (4)
F2	0.0129 (3)	0.0209 (3)	0.0291 (5)	-0.0015 (2)	0.0028 (4)	-0.0004 (3)
F3	0.0204 (3)	0.0271 (4)	0.0132 (5)	-0.0004 (3)	-0.0022 (3)	0.0025 (4)
O1	0.0352 (5)	0.0176 (5)	0.0362 (8)	-0.0009 (4)	-0.0037 (6)	0.0052 (5)

*Geometric parameters (Å, °)*

K1—F3 <sup>i</sup>	2.6156 (10)	C4—C5	1.398 (2)
K1—F2 <sup>ii</sup>	2.6211 (7)	C5—C6	1.390 (2)
K1—F1 <sup>iii</sup>	2.6550 (10)	C5—H5	0.9500
K1—F1 <sup>iv</sup>	2.7568 (10)	C6—H6	0.9500
K1—F3	2.7836 (8)	C7—O1	1.423 (2)
K1—F1	2.7887 (8)	C7—H7A	0.9800
K1—F2 <sup>iv</sup>	2.8885 (8)	C7—H7B	0.9800
K1—F3 <sup>iv</sup>	3.4886 (9)	C7—H7C	0.9800
C1—C2	1.3940 (19)	B1—F3	1.4162 (19)
C1—C6	1.4036 (18)	B1—F2	1.4196 (14)
C1—B1	1.5987 (18)	B1—F1	1.4403 (17)
C2—C3	1.398 (2)	B1—K1 <sup>v</sup>	3.2930 (14)
C2—K1 <sup>i</sup>	3.5183 (15)	F1—K1 <sup>i</sup>	2.6550 (10)
C2—H2	0.9500	F1—K1 <sup>v</sup>	2.7568 (10)
C3—C4	1.3910 (19)	F2—K1 <sup>vi</sup>	2.6211 (7)
C3—H3	0.9500	F2—K1 <sup>v</sup>	2.8885 (8)
C4—O1	1.3696 (17)	F3—K1 <sup>iii</sup>	2.6157 (10)
F3 <sup>i</sup> —K1—F2 <sup>ii</sup>	94.59 (3)	O1—C4—C5	115.78 (13)
F3 <sup>i</sup> —K1—F1 <sup>iii</sup>	173.67 (3)	C3—C4—C5	119.79 (13)
F2 <sup>ii</sup> —K1—F1 <sup>iii</sup>	90.34 (3)	C6—C5—C4	119.99 (13)
F3 <sup>i</sup> —K1—F1 <sup>iv</sup>	79.00 (3)	C6—C5—H5	120.0
F2 <sup>ii</sup> —K1—F1 <sup>iv</sup>	70.82 (2)	C4—C5—H5	120.0
F1 <sup>iii</sup> —K1—F1 <sup>iv</sup>	106.45 (2)	C5—C6—C1	121.78 (14)
F3 <sup>i</sup> —K1—F3	107.78 (2)	C5—C6—H6	119.1
F2 <sup>ii</sup> —K1—F3	152.47 (3)	C1—C6—H6	119.1
F1 <sup>iii</sup> —K1—F3	66.40 (3)	O1—C7—H7A	109.5
F1 <sup>iv</sup> —K1—F3	128.21 (2)	O1—C7—H7B	109.5
F3 <sup>i</sup> —K1—F1	66.83 (3)	H7A—C7—H7B	109.5
F2 <sup>ii</sup> —K1—F1	159.35 (3)	O1—C7—H7C	109.5
F1 <sup>iii</sup> —K1—F1	108.89 (2)	H7A—C7—H7C	109.5
F1 <sup>iv</sup> —K1—F1	95.79 (2)	H7B—C7—H7C	109.5
F3—K1—F1	47.98 (3)	F3—B1—F2	107.30 (13)
F3 <sup>i</sup> —K1—F2 <sup>iv</sup>	100.35 (3)	F3—B1—F1	104.95 (10)
F2 <sup>ii</sup> —K1—F2 <sup>iv</sup>	110.489 (19)	F2—B1—F1	104.73 (10)
F1 <sup>iii</sup> —K1—F2 <sup>iv</sup>	81.59 (3)	F3—B1—C1	112.45 (11)
F1 <sup>iv</sup> —K1—F2 <sup>iv</sup>	47.24 (3)	F2—B1—C1	114.56 (11)
F3—K1—F2 <sup>iv</sup>	81.63 (2)	F1—B1—C1	112.10 (12)
F1—K1—F2 <sup>iv</sup>	66.60 (3)	B1—F1—K1 <sup>i</sup>	122.39 (8)
C2—C1—C6	116.59 (12)	B1—F1—K1 <sup>v</sup>	98.47 (7)

C2—C1—B1	121.46 (12)	K1 <sup>i</sup> —F1—K1 <sup>v</sup>	117.24 (3)
C6—C1—B1	121.90 (12)	B1—F1—K1	96.46 (7)
C1—C2—C3	122.95 (12)	K1 <sup>i</sup> —F1—K1	112.53 (3)
C1—C2—K1 <sup>i</sup>	86.24 (8)	K1 <sup>v</sup> —F1—K1	106.81 (3)
C3—C2—K1 <sup>i</sup>	114.99 (10)	B1—F2—K1 <sup>vi</sup>	156.48 (8)
C1—C2—H2	118.5	B1—F2—K1 <sup>v</sup>	93.39 (6)
C3—C2—H2	118.5	K1 <sup>vi</sup> —F2—K1 <sup>v</sup>	107.73 (2)
K1 <sup>i</sup> —C2—H2	68.1	B1—F3—K1 <sup>iii</sup>	146.64 (8)
C4—C3—C2	118.88 (13)	B1—F3—K1	97.29 (7)
C4—C3—H3	120.6	K1 <sup>iii</sup> —F3—K1	113.95 (3)
C2—C3—H3	120.6	C4—O1—C7	117.09 (13)
O1—C4—C3	124.43 (14)		
C6—C1—C2—C3	1.2 (2)	C2—C1—C6—C5	-1.1 (2)
B1—C1—C2—C3	-176.35 (14)	B1—C1—C6—C5	176.46 (14)
C6—C1—C2—K1 <sup>i</sup>	118.72 (12)	C2—C1—B1—F3	-164.66 (12)
B1—C1—C2—K1 <sup>i</sup>	-58.84 (12)	C6—C1—B1—F3	17.90 (18)
C1—C2—C3—C4	-0.2 (2)	C2—C1—B1—F2	-41.81 (19)
K1 <sup>i</sup> —C2—C3—C4	-102.69 (14)	C6—C1—B1—F2	140.76 (15)
C2—C3—C4—O1	179.10 (14)	C2—C1—B1—F1	77.36 (16)
C2—C3—C4—C5	-0.9 (2)	C6—C1—B1—F1	-100.07 (15)
O1—C4—C5—C6	-178.99 (14)	C3—C4—O1—C7	-0.4 (2)
C3—C4—C5—C6	1.0 (2)	C5—C4—O1—C7	179.62 (15)
C4—C5—C6—C1	0.0 (2)		

Symmetry codes: (i)  $-x+3/2, y, z-1/2$ ; (ii)  $x+1, y, z$ ; (iii)  $-x+3/2, y, z+1/2$ ; (iv)  $x+1/2, -y+1, z$ ; (v)  $x-1/2, -y+1, z$ ; (vi)  $x-1, y, z$ .

### Hydrogen-bond geometry ( $\text{\AA}, ^\circ$ )

Cg1 is the centroid of the C1—C6 benzene ring.

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
C2—H2 $\cdots$ F2 <sup>vii</sup>	0.95	2.50	3.3359 (17)	147
C7—H7a $\cdots$ O1 <sup>viii</sup>	0.98	2.72	3.496 (1)	137
C3—H3 $\cdots$ Cg1 <sup>vii</sup>	0.95	2.85	3.7171 (15)	152

Symmetry codes: (vii)  $-x+1/2, y, z-1/2$ ; (viii)  $-x+1, -y+2, z-1/2$ .

## (II) Potassium trifluorido(4-fluorophenyl)borate

### Crystal data

$\text{K}^+\cdot\text{C}_6\text{H}_4\text{BF}_4^-$

$M_r = 202.00$

Orthorhombic, *Pbca*

Hall symbol: -P 2ac 2ab

$a = 7.1317 (5) \text{\AA}$

$b = 7.3757 (5) \text{\AA}$

$c = 29.129 (2) \text{\AA}$

$V = 1532.22 (18) \text{\AA}^3$

$Z = 8$

$F(000) = 800$

$D_x = 1.751 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71075 \text{\AA}$

Cell parameters from 8210 reflections

$\theta = 3.2\text{--}27.5^\circ$

$\mu = 0.70 \text{ mm}^{-1}$

$T = 100 \text{ K}$

Block, colourless

$0.07 \times 0.05 \times 0.01 \text{ mm}$



*Data collection*

Rigaku CCD diffractometer	9537 measured reflections
Radiation source: fine-focus sealed tube	1726 independent reflections
Graphite monochromator	1435 reflections with $I > 2\sigma(I)$
$\omega$ scans	$R_{\text{int}} = 0.037$
Absorption correction: multi-scan (SADABS; Bruker, 2012)	$\theta_{\text{max}} = 27.5^\circ$ , $\theta_{\text{min}} = 3.2^\circ$
$T_{\text{min}} = 0.953$ , $T_{\text{max}} = 0.993$	$h = -9 \rightarrow 8$
	$k = -9 \rightarrow 7$
	$l = -32 \rightarrow 37$

*Refinement*

Refinement on $F^2$	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.027$	H-atom parameters constrained
$wR(F^2) = 0.065$	$w = 1/[\sigma^2(F_o^2) + (0.0274P)^2 + 0.6658P]$
$S = 1.06$	where $P = (F_o^2 + 2F_c^2)/3$
1726 reflections	$(\Delta/\sigma)_{\text{max}} = 0.001$
109 parameters	$\Delta\rho_{\text{max}} = 0.27 \text{ e } \text{\AA}^{-3}$
0 restraints	$\Delta\rho_{\text{min}} = -0.23 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	

*Special details*

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) etc. and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
K1	0.06924 (4)	0.02356 (5)	0.205013 (12)	0.01668 (10)
C1	0.5118 (2)	0.1023 (2)	0.13156 (5)	0.0161 (3)
C2	0.3892 (2)	0.0245 (2)	0.09978 (6)	0.0213 (3)
H2	0.3130	-0.0745	0.1091	0.026*
C3	0.3750 (2)	0.0869 (2)	0.05506 (6)	0.0245 (4)
H3	0.2905	0.0324	0.0339	0.029*
C4	0.4867 (2)	0.2301 (2)	0.04213 (5)	0.0236 (4)
C5	0.6112 (2)	0.3121 (2)	0.07145 (6)	0.0250 (4)
H5	0.6871	0.4105	0.0616	0.030*
C6	0.6226 (2)	0.2463 (2)	0.11604 (6)	0.0207 (3)
H6	0.7085	0.3011	0.1367	0.025*
B1	0.5200 (2)	0.0373 (2)	0.18355 (6)	0.0147 (3)
F1	0.43225 (11)	0.16564 (12)	0.21396 (3)	0.0178 (2)
F2	0.70288 (11)	0.01321 (13)	0.20154 (3)	0.0210 (2)
F3	0.42107 (11)	-0.12680 (12)	0.19106 (3)	0.0193 (2)
F4	0.47218 (15)	0.29343 (14)	-0.00157 (3)	0.0327 (3)

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
K1	0.01228 (15)	0.01386 (17)	0.02390 (18)	0.00022 (12)	0.00079 (12)	0.00020 (13)
C1	0.0143 (6)	0.0139 (7)	0.0200 (8)	0.0019 (6)	0.0007 (6)	-0.0006 (6)
C2	0.0214 (7)	0.0201 (8)	0.0225 (8)	-0.0029 (7)	-0.0016 (6)	0.0002 (7)
C3	0.0268 (8)	0.0256 (9)	0.0211 (9)	-0.0019 (7)	-0.0056 (7)	-0.0016 (7)
C4	0.0306 (9)	0.0243 (9)	0.0160 (8)	0.0046 (7)	0.0013 (6)	0.0020 (7)
C5	0.0296 (9)	0.0221 (9)	0.0234 (9)	-0.0056 (7)	0.0052 (6)	0.0014 (7)
C6	0.0222 (7)	0.0189 (8)	0.0211 (8)	-0.0050 (7)	0.0007 (6)	-0.0014 (7)
B1	0.0116 (7)	0.0130 (8)	0.0194 (8)	0.0014 (6)	0.0006 (6)	-0.0008 (6)
F1	0.0184 (4)	0.0152 (5)	0.0198 (5)	0.0027 (4)	0.0027 (3)	-0.0012 (4)
F2	0.0125 (4)	0.0295 (5)	0.0209 (5)	0.0032 (4)	-0.0024 (3)	-0.0012 (4)
F3	0.0205 (4)	0.0125 (5)	0.0247 (5)	-0.0017 (4)	0.0003 (4)	0.0026 (4)
F4	0.0474 (6)	0.0332 (6)	0.0174 (5)	-0.0013 (5)	-0.0007 (5)	0.0061 (4)

*Geometric parameters (Å, °)*

K1—F3 <sup>i</sup>	2.6116 (10)	C4—F4	1.3597 (18)
K1—F2 <sup>ii</sup>	2.6159 (9)	C4—C5	1.373 (2)
K1—F1 <sup>iii</sup>	2.6527 (9)	C5—C6	1.389 (2)
K1—F1 <sup>iv</sup>	2.7612 (10)	C5—H5	0.9500
K1—F3	2.7732 (9)	C6—H6	0.9500
K1—F1	2.8050 (9)	B1—F2	1.4166 (17)
K1—F2 <sup>iv</sup>	2.8853 (10)	B1—F3	1.4182 (19)
K1—F3 <sup>iv</sup>	3.3927 (10)	B1—F1	1.4393 (18)
C1—C2	1.397 (2)	B1—K1 <sup>v</sup>	3.2665 (18)
C1—C6	1.399 (2)	F1—K1 <sup>i</sup>	2.6527 (9)
C1—B1	1.590 (2)	F1—K1 <sup>v</sup>	2.7612 (9)
C2—C3	1.385 (2)	F2—K1 <sup>vi</sup>	2.6159 (9)
C2—H2	0.9500	F2—K1 <sup>v</sup>	2.8852 (10)
C3—C4	1.375 (2)	F3—K1 <sup>iii</sup>	2.6116 (10)
C3—H3	0.9500	F3—K1 <sup>v</sup>	3.3928 (10)
F3 <sup>i</sup> —K1—F2 <sup>ii</sup>	92.82 (3)	F4—C4—C3	118.44 (15)
F3 <sup>i</sup> —K1—F1 <sup>iii</sup>	176.44 (3)	C5—C4—C3	122.87 (16)
F2 <sup>ii</sup> —K1—F1 <sup>iii</sup>	88.32 (3)	C4—C5—C6	117.74 (16)
F3 <sup>i</sup> —K1—F1 <sup>iv</sup>	76.56 (3)	C4—C5—H5	121.1
F2 <sup>ii</sup> —K1—F1 <sup>iv</sup>	71.99 (3)	C6—C5—H5	121.1
F1 <sup>iii</sup> —K1—F1 <sup>iv</sup>	107.00 (2)	C5—C6—C1	122.34 (15)
F3 <sup>i</sup> —K1—F3	110.37 (2)	C5—C6—H6	118.8
F2 <sup>ii</sup> —K1—F3	152.42 (3)	C1—C6—H6	118.8
F1 <sup>iii</sup> —K1—F3	67.67 (3)	F2—B1—F3	107.08 (12)
F1 <sup>iv</sup> —K1—F3	126.67 (3)	F2—B1—F1	104.80 (12)
F3 <sup>i</sup> —K1—F1	67.74 (3)	F3—B1—F1	104.48 (11)
F2 <sup>ii</sup> —K1—F1	159.45 (3)	F2—B1—C1	115.08 (12)
F1 <sup>iii</sup> —K1—F1	111.49 (2)	F3—B1—C1	112.70 (13)
F1 <sup>iv</sup> —K1—F1	96.05 (2)	F1—B1—C1	111.86 (12)

F3—K1—F1	47.78 (3)	F2—B1—K1 <sup>v</sup>	61.95 (7)
F3 <sup>i</sup> —K1—F2 <sup>iv</sup>	99.45 (3)	F3—B1—K1 <sup>v</sup>	82.74 (8)
F2 <sup>ii</sup> —K1—F2 <sup>iv</sup>	111.45 (2)	F1—B1—K1 <sup>v</sup>	57.03 (7)
F1 <sup>iii</sup> —K1—F2 <sup>iv</sup>	83.24 (3)	C1—B1—K1 <sup>v</sup>	163.77 (11)
F1 <sup>iv</sup> —K1—F2 <sup>iv</sup>	47.18 (2)	F2—B1—K1	145.97 (10)
F3—K1—F2 <sup>iv</sup>	80.14 (3)	F3—B1—K1	57.04 (6)
F1—K1—F2 <sup>iv</sup>	67.51 (3)	F1—B1—K1	58.42 (6)
F3 <sup>i</sup> —K1—F3 <sup>iv</sup>	118.03 (3)	C1—B1—K1	98.93 (9)
F2 <sup>ii</sup> —K1—F3 <sup>iv</sup>	73.38 (3)	K1 <sup>v</sup> —B1—K1	85.12 (4)
F1 <sup>iii</sup> —K1—F3 <sup>iv</sup>	65.53 (2)	B1—F1—K1 <sup>i</sup>	126.56 (8)
F1 <sup>iv</sup> —K1—F3 <sup>iv</sup>	41.51 (2)	B1—F1—K1 <sup>v</sup>	97.04 (8)
F3—K1—F3 <sup>iv</sup>	106.37 (3)	K1 <sup>i</sup> —F1—K1 <sup>v</sup>	117.58 (3)
F1—K1—F3 <sup>iv</sup>	109.07 (3)	B1—F1—K1	95.66 (8)
F2 <sup>iv</sup> —K1—F3 <sup>iv</sup>	41.62 (2)	K1 <sup>i</sup> —F1—K1	111.04 (3)
C2—C1—C6	116.82 (15)	K1 <sup>v</sup> —F1—K1	105.32 (3)
C2—C1—B1	122.05 (14)	B1—F2—K1 <sup>vi</sup>	158.46 (9)
C6—C1—B1	121.08 (14)	B1—F2—K1 <sup>v</sup>	92.38 (8)
C3—C2—C1	122.18 (15)	K1 <sup>vi</sup> —F2—K1 <sup>v</sup>	107.01 (3)
C3—C2—H2	118.9	B1—F3—K1 <sup>iii</sup>	148.62 (8)
C1—C2—H2	118.9	B1—F3—K1	97.55 (8)
C4—C3—C2	118.06 (15)	K1 <sup>iii</sup> —F3—K1	113.33 (3)
C4—C3—H3	121.0	B1—F3—K1 <sup>v</sup>	72.76 (8)
C2—C3—H3	121.0	K1 <sup>iii</sup> —F3—K1 <sup>v</sup>	100.12 (3)
F4—C4—C5	118.69 (15)	K1—F3—K1 <sup>v</sup>	91.16 (3)
C6—C1—C2—C3	-0.7 (2)	C2—C1—C6—C5	0.8 (2)
B1—C1—C2—C3	176.65 (15)	B1—C1—C6—C5	-176.56 (15)
C1—C2—C3—C4	0.1 (3)	C2—C1—B1—F2	135.24 (15)
C2—C3—C4—F4	-179.32 (15)	C6—C1—B1—F2	-47.6 (2)
C2—C3—C4—C5	0.4 (3)	C2—C1—B1—F3	12.0 (2)
F4—C4—C5—C6	179.43 (15)	C6—C1—B1—F3	-170.75 (13)
C3—C4—C5—C6	-0.3 (3)	C2—C1—B1—F1	-105.32 (17)
C4—C5—C6—C1	-0.3 (3)	C6—C1—B1—F1	71.88 (18)

Symmetry codes: (i)  $-x+1/2, y+1/2, z$ ; (ii)  $x-1, y, z$ ; (iii)  $-x+1/2, y-1/2, z$ ; (iv)  $x-1/2, y, -z+1/2$ ; (v)  $x+1/2, y, -z+1/2$ ; (vi)  $x+1, y, z$ .

*Hydrogen-bond geometry* ( $\text{\AA}, ^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C6—H6 <sup>iii</sup> —F2 <sup>vii</sup>	0.95	2.53	3.4099 (19)	154

Symmetry code: (vii)  $-x+3/2, y+1/2, z$ .