



## Crystal structure of 4'-bromo-2,3,5,6-tetrafluorobiphenyl-4-carbonitrile

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The title compound, C<sub>13</sub>H<sub>4</sub>BrF<sub>4</sub>N, synthesized from 1,4'-bromiodobenzene and 4-bromo-2,3,5,6-tetrafluorobenzonitrile in a coupling reaction was found to crystallize in the orthorhombic space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>. The two phenyl rings are rotated with respect to each other by 40.6 (6)°. The molecules interact *via* aryl–perfluoroaryl stacking [3.796 (2) and 3.773 (2) Å], resulting in intermolecular chains along the *a*-axis direction. C–H···F contacts of about 2.45 Å connect these chains. In contrast to the structure of the parent compound 4'-bromobiphenyl-4-carbonitrile, CN···Br contacts that could have given rise to a linear arrangement of the biphenyl molecules desirable for non-linear optical (NLO) materials are not observed in the packing. Instead, several Br···F [3.2405 (17) and 3.2777 (18) Å] and F···F [2.894 (2) Å] contacts of side-on type II form an intermolecular network of zigzag chains. The crystal studied was refined as an inversion twin.

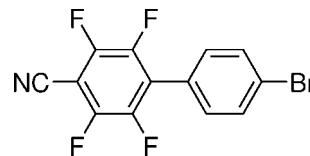
**Keywords:** crystal structure; biphenyl; tetrafluoro substitution; bromo–cyano substitution;  $\pi$ – $\pi$  stacking; halogen interactions.

**CCDC reference:** 1060721

### 1. Related literature

For crystal structures of 4-cyano-4'-halogene substituted biphenyls, see: Gleason *et al.* (1991) for fluorine, Kronebusch *et al.* (1976) for bromine, Britton & Gleason (1991) for iodine. For halogen interactions in molecular crystal structures, see: Ramasubbu *et al.* (1986), Awwadi *et al.* (2006), Brammer *et al.* (2001) and Metrangolo *et al.* (2008). For interactions of halogens with cyano groups, see: Desiraju & Harlow (1989), Süß *et al.* (2005) and Mukherjee *et al.* (2014). For fluorine involved into these interactions, see: Schwarzer *et al.* (2010),

Merz & Vasylyeva (2010), Schwarzer & Weber (2008) and Reichenbacher *et al.* (2005).



### 2. Experimental

#### 2.1. Crystal data

C <sub>13</sub> H <sub>4</sub> BrF <sub>4</sub> N	<i>V</i> = 1133.1 (4) Å <sup>3</sup>
<i>M<sub>r</sub></i> = 330.08	<i>Z</i> = 4
Orthorhombic, <i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	Mo <i>K</i> α radiation
<i>a</i> = 7.3560 (15) Å	$\mu$ = 3.66 mm <sup>-1</sup>
<i>b</i> = 12.107 (2) Å	<i>T</i> = 93 K
<i>c</i> = 12.723 (3) Å	0.49 × 0.13 × 0.10 mm

#### 2.2. Data collection

Bruker SMART CCD area-detector diffractometer	18347 measured reflections
Absorption correction: multi-scan ( <i>SADABS</i> ; Bruker, 2012)	3234 independent reflections
<i>T</i> <sub>min</sub> = 0.486, <i>T</i> <sub>max</sub> = 0.718	2930 reflections with <i>I</i> > 2σ( <i>I</i> )
	<i>R</i> <sub>int</sub> = 0.053

#### 2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$	$\Delta\rho_{\max} = 0.46 \text{ e } \text{Å}^{-3}$
$wR(F^2) = 0.052$	$\Delta\rho_{\min} = -0.31 \text{ e } \text{Å}^{-3}$
<i>S</i> = 0.99	Absolute structure: refined as an inversion twin.
3234 reflections	Absolute structure parameter: 0.011 (9)
173 parameters	
H-atom parameters constrained	

**Table 1**

Hydrogen-bond geometry (Å, °).

<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>
C9–H9···F2	0.95	2.47	2.882 (4)	106
C13–H13···F3	0.95	2.45	2.865 (3)	107

Data collection: *SMART* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2012* (Sheldrick, 2015); molecular graphics: *XP* (Sheldrick, 2008); software used to prepare material for publication: *WinGX* (Farrugia, 2012), *publCIF* (Westrip, 2010) and *SHELXLE* (Hübschle *et al.*, 2011).

Supporting information for this paper is available from the IUCr electronic archives (Reference: IM2464).

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## supporting information

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## Crystal structure of 4'-bromo-2,3,5,6-tetrafluorobiphenyl-4-carbonitrile

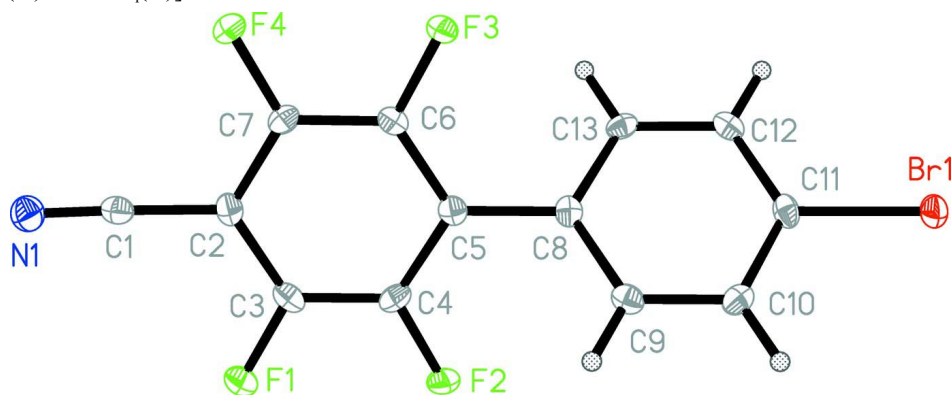
Ricarda Heckel, Jürg Hulliger, Anke Schwarzer and Edwin Weber

### S1. Synthesis and crystallization

Under inert conditions, 1-bromo-4-iodobenzene (22.6 g, 80 mmol) in THF (90 mL) was added dropwise to magnesium shaving (1.8 g, 75 mmol). The reaction mixture was refluxed for 90 min. After cooling to room temperature, CuBr (25.8 g, 180 mmol) was added and the mixture was stirred for 1 h at this temperature. Then 15 ml of 1,4-dioxane was added and the mixture was stirred for an hour followed by dropwise addition of a solution of 4-bromo-2,3,5,6-tetrafluorobenzonitrile (6.4 g, 25 mmol) in toluene (50 ml). After refluxing for 2 d, the mixture was cooled to room temperature, filtered over Celite and freed from solvents removed under reduced pressure. The residue was dissolved in toluene and washed with 3M HCl followed by aqueous NaOH solution. The organic phases were collected, dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated. The raw product was purified by column chromatography (SiO<sub>2</sub>; eluent: CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane, 2/1 v/v to yield 1.00 g (12 %) of the title compound. Single crystals suitable for X-ray diffraction were obtained from acetone solution at room temperature. Data for (I): M.p. 133–134 °C. <sup>1</sup>H NMR(400 MHz; acetone-d<sub>6</sub>): δ<sub>H</sub> = 7.57 (d, <sup>3</sup>J<sub>HH</sub> = 8.9, 2H, H-9, H-13), 7.82 (d, <sup>3</sup>J<sub>HH</sub> = 8.9, 2H, H-10, H12) ppm. <sup>13</sup>C NMR (100 MHz; acetone-d<sub>6</sub>): δ<sub>C</sub> = 94.30 (d, <sup>2</sup>J<sub>CF</sub> = 17.4, C-2), 108.62 (t, <sup>3</sup>J<sub>CF</sub> = -3.7, C-1), 125.52, 126.32 (s, C-8, C11), 127.04 (t, <sup>2</sup>J<sub>CF</sub> = 17.4, C-5), 133.05 (t, <sup>4</sup>J<sub>CF</sub> = 2.5, C-9), 133.32 (s, C-10), 143.39, 146.69 (d, <sup>1</sup>J<sub>CF</sub> = -147.2, C-4), 147.01, 150.43 (d, <sup>1</sup>J<sub>CF</sub> = -265.5, C-3) ppm. <sup>19</sup>F NMR(376 MHz; acetone-d<sub>6</sub>): δ<sub>F</sub> = -136.15 (F-1, d, <sup>3</sup>J<sub>FF</sub> = 9.3 ), -142.53 (F-2, d, <sup>3</sup>J<sub>FF</sub> = 9.3) ppm. GC—MS (m/z) 329 [M]<sup>+</sup>, 250 [M—Br]<sup>+</sup>, 231 [-F]<sup>+</sup>, 200 [-CF]<sup>+</sup>, 125, 99, 74, 50.

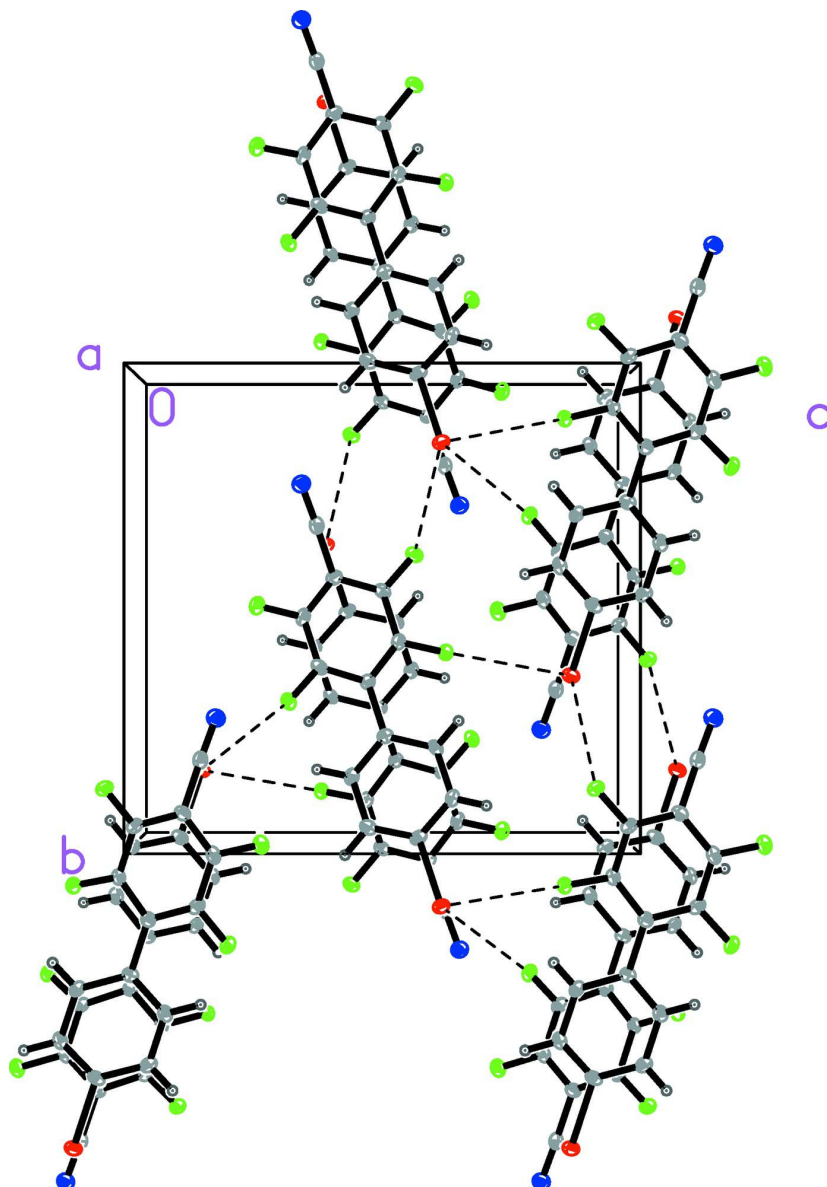
### S2. Refinement details

The C-bound H atoms were positioned geometrically and allowed to ride on their parent atoms: C—H = 0.95 Å for aryl H atoms, with [*U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C)].



**Figure 1**

The molecular structure of the title molecule including atom labelling. Displacement ellipsoids drawn at the 50% probability level.



**Figure 2**

The crystal packing of the title compound showing the stacking interactions along [100].

**4'-Bromo-2,3,5,6-tetrafluorobiphenyl-4-carbonitrile**

*Crystal data*

$C_{13}H_4BrF_4N$

$M_r = 330.08$

Orthorhombic,  $P2_12_12_1$

$a = 7.3560$  (15) Å

$b = 12.107$  (2) Å

$c = 12.723$  (3) Å

$V = 1133.1$  (4) Å<sup>3</sup>

$Z = 4$

$F(000) = 640$

$D_x = 1.935$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 4750 reflections

$\theta = 3.2$ – $28.4^\circ$

$\mu = 3.66$  mm<sup>-1</sup>

$T = 93$  K

Splitter, colorless

$0.49 \times 0.13 \times 0.10$  mm

*Data collection*

Bruker SMART CCD area-detector  
diffractometer  
Radiation source: fine-focus sealed tube  
phi and  $\omega$  scans  
Absorption correction: multi-scan  
(*SADABS*; Bruker, 2012)  
 $T_{\min} = 0.486$ ,  $T_{\max} = 0.718$   
18347 measured reflections

3234 independent reflections  
2930 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.053$   
 $\theta_{\max} = 29.8^\circ$ ,  $\theta_{\min} = 2.3^\circ$   
 $h = -10 \rightarrow 10$   
 $k = -16 \rightarrow 16$   
 $l = -17 \rightarrow 17$

*Refinement*

Refinement on  $F^2$   
Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.028$   
 $wR(F^2) = 0.052$   
 $S = 0.99$   
3234 reflections  
173 parameters  
0 restraints  
Hydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0144P)^2]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.46 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.31 \text{ e } \text{\AA}^{-3}$   
Absolute structure: Refined as an inversion  
twin.  
Absolute structure parameter: 0.011 (9)

*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.** Refined as a 2-component inversion twin.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.89811 (4)	0.35795 (3)	0.37922 (2)	0.01853 (8)
F1	0.7744 (2)	1.00596 (16)	0.75920 (12)	0.0196 (4)
F2	0.7639 (2)	0.79698 (15)	0.69387 (12)	0.0179 (4)
F3	1.0359 (2)	0.90632 (14)	0.37137 (13)	0.0163 (4)
F4	1.0323 (2)	1.11450 (14)	0.43493 (13)	0.0196 (4)
N1	0.9005 (4)	1.2681 (2)	0.66563 (19)	0.0208 (6)
C1	0.9026 (4)	1.1790 (2)	0.6343 (2)	0.0161 (6)
C2	0.9029 (5)	1.0664 (2)	0.5984 (2)	0.0153 (6)
C3	0.8371 (4)	0.9812 (3)	0.6627 (2)	0.0154 (7)
C4	0.8354 (4)	0.8729 (3)	0.6295 (2)	0.0147 (6)
C5	0.9004 (4)	0.8418 (2)	0.5296 (2)	0.0131 (6)
C6	0.9650 (4)	0.9283 (3)	0.4667 (2)	0.0129 (6)
C7	0.9665 (4)	1.0369 (3)	0.4992 (2)	0.0144 (6)
C8	0.8998 (5)	0.7249 (2)	0.4938 (2)	0.0133 (6)
C9	0.9476 (4)	0.6389 (3)	0.5620 (2)	0.0145 (6)
H9	0.9807	0.6555	0.6324	0.017*
C10	0.9474 (4)	0.5302 (3)	0.5286 (2)	0.0161 (7)
H10	0.9795	0.4725	0.5756	0.019*
C11	0.8997 (5)	0.5065 (2)	0.4254 (2)	0.0148 (6)

C12	0.8517 (4)	0.5894 (3)	0.3554 (2)	0.0153 (7)
H12	0.8191	0.5720	0.2851	0.018*
C13	0.8520 (4)	0.6986 (3)	0.3898 (2)	0.0142 (6)
H13	0.8196	0.7560	0.3424	0.017*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Br1	0.02368 (15)	0.01300 (14)	0.01890 (13)	-0.00129 (14)	0.00259 (14)	-0.00242 (13)
F1	0.0229 (10)	0.0218 (10)	0.0141 (8)	0.0003 (8)	0.0031 (7)	-0.0022 (7)
F2	0.0213 (10)	0.0185 (10)	0.0138 (8)	-0.0028 (8)	0.0029 (7)	0.0034 (7)
F3	0.0201 (9)	0.0163 (9)	0.0125 (7)	0.0014 (7)	0.0034 (7)	-0.0004 (8)
F4	0.0265 (10)	0.0143 (10)	0.0179 (8)	-0.0015 (7)	0.0042 (7)	0.0030 (7)
N1	0.0216 (14)	0.0193 (15)	0.0215 (12)	0.0015 (14)	0.0011 (13)	-0.0013 (11)
C1	0.0153 (14)	0.0200 (15)	0.0130 (13)	-0.0011 (13)	0.0005 (14)	0.0010 (11)
C2	0.0156 (13)	0.0137 (14)	0.0165 (13)	0.0012 (14)	-0.0020 (13)	-0.0026 (11)
C3	0.0133 (15)	0.0204 (18)	0.0125 (13)	0.0020 (13)	-0.0003 (11)	-0.0034 (12)
C4	0.0121 (13)	0.0149 (16)	0.0169 (13)	-0.0017 (11)	-0.0013 (12)	0.0049 (14)
C5	0.0112 (12)	0.0144 (15)	0.0136 (11)	0.0014 (14)	-0.0040 (12)	-0.0006 (11)
C6	0.0110 (14)	0.0162 (16)	0.0116 (13)	0.0024 (12)	-0.0007 (11)	-0.0012 (12)
C7	0.0136 (14)	0.0138 (16)	0.0160 (14)	0.0003 (12)	-0.0008 (11)	0.0035 (12)
C8	0.0101 (13)	0.0134 (15)	0.0164 (12)	-0.0001 (13)	0.0009 (13)	-0.0013 (11)
C9	0.0117 (14)	0.0187 (16)	0.0133 (12)	-0.0030 (13)	-0.0021 (10)	-0.0017 (14)
C10	0.0155 (17)	0.0149 (16)	0.0178 (14)	0.0010 (12)	0.0008 (12)	0.0033 (13)
C11	0.0125 (13)	0.0136 (15)	0.0183 (13)	-0.0029 (14)	0.0017 (14)	-0.0048 (11)
C12	0.0147 (16)	0.0191 (17)	0.0120 (14)	-0.0006 (12)	0.0002 (10)	-0.0025 (12)
C13	0.0136 (15)	0.0151 (15)	0.0137 (13)	0.0018 (11)	-0.0005 (11)	0.0045 (12)

*Geometric parameters (Å, °)*

Br1—C11	1.892 (3)	C5—C8	1.487 (4)
F1—C3	1.346 (3)	C6—C7	1.379 (4)
F2—C4	1.339 (3)	C8—C9	1.400 (4)
F3—C6	1.347 (3)	C8—C13	1.406 (4)
F4—C7	1.336 (3)	C9—C10	1.383 (4)
N1—C1	1.150 (4)	C9—H9	0.9500
C1—C2	1.438 (4)	C10—C11	1.389 (4)
C2—C7	1.393 (4)	C10—H10	0.9500
C2—C3	1.402 (4)	C11—C12	1.388 (4)
C3—C4	1.377 (4)	C12—C13	1.392 (4)
C4—C5	1.409 (4)	C12—H12	0.9500
C5—C6	1.401 (4)	C13—H13	0.9500
N1—C1—C2	178.1 (3)	C9—C8—C13	118.6 (3)
C7—C2—C3	117.1 (3)	C9—C8—C5	121.2 (2)
C7—C2—C1	122.1 (3)	C13—C8—C5	120.3 (3)
C3—C2—C1	120.8 (2)	C10—C9—C8	121.1 (3)
F1—C3—C4	119.3 (3)	C10—C9—H9	119.4

F1—C3—C2	119.1 (3)	C8—C9—H9	119.4
C4—C3—C2	121.6 (3)	C9—C10—C11	119.2 (3)
F2—C4—C3	118.0 (3)	C9—C10—H10	120.4
F2—C4—C5	120.1 (3)	C11—C10—H10	120.4
C3—C4—C5	121.9 (3)	C12—C11—C10	121.4 (3)
C6—C5—C4	115.5 (3)	C12—C11—Br1	119.1 (2)
C6—C5—C8	122.5 (2)	C10—C11—Br1	119.5 (2)
C4—C5—C8	122.0 (3)	C11—C12—C13	119.0 (3)
F3—C6—C7	117.1 (3)	C11—C12—H12	120.5
F3—C6—C5	119.8 (3)	C13—C12—H12	120.5
C7—C6—C5	123.0 (3)	C12—C13—C8	120.7 (3)
F4—C7—C6	119.3 (3)	C12—C13—H13	119.6
F4—C7—C2	119.8 (3)	C8—C13—H13	119.6
C6—C7—C2	120.9 (3)		
C7—C2—C3—F1	179.9 (3)	C5—C6—C7—C2	0.2 (5)
C1—C2—C3—F1	-0.5 (4)	C3—C2—C7—F4	-179.4 (3)
C7—C2—C3—C4	0.1 (5)	C1—C2—C7—F4	1.0 (5)
C1—C2—C3—C4	179.7 (3)	C3—C2—C7—C6	-0.3 (4)
F1—C3—C4—F2	2.6 (4)	C1—C2—C7—C6	-179.9 (3)
C2—C3—C4—F2	-177.5 (3)	C6—C5—C8—C9	139.2 (3)
F1—C3—C4—C5	-179.5 (3)	C4—C5—C8—C9	-40.8 (4)
C2—C3—C4—C5	0.3 (5)	C6—C5—C8—C13	-40.4 (5)
F2—C4—C5—C6	177.3 (3)	C4—C5—C8—C13	139.6 (3)
C3—C4—C5—C6	-0.5 (4)	C13—C8—C9—C10	-0.3 (4)
F2—C4—C5—C8	-2.6 (4)	C5—C8—C9—C10	-179.9 (3)
C3—C4—C5—C8	179.6 (3)	C8—C9—C10—C11	0.3 (4)
C4—C5—C6—F3	177.6 (2)	C9—C10—C11—C12	-0.2 (5)
C8—C5—C6—F3	-2.4 (4)	C9—C10—C11—Br1	-179.8 (2)
C4—C5—C6—C7	0.2 (4)	C10—C11—C12—C13	0.1 (5)
C8—C5—C6—C7	-179.8 (3)	Br1—C11—C12—C13	179.7 (2)
F3—C6—C7—F4	1.8 (4)	C11—C12—C13—C8	-0.1 (4)
C5—C6—C7—F4	179.3 (3)	C9—C8—C13—C12	0.2 (4)
F3—C6—C7—C2	-177.3 (3)	C5—C8—C13—C12	179.8 (3)

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

<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>
C9—H9 $\cdots$ F2	0.95	2.47	2.882 (4)	106
C13—H13 $\cdots$ F3	0.95	2.45	2.865 (3)	107