

# Crystal structure of tetraethylammonium chloride 3,4,5,6-tetrafluoro-1,2-diiodobenzene

Jasmine Viger-Gravel, Ilia Korobkov and David L. Bryce\*

Department of Chemistry, University of Ottawa, D'lorio Hall, 10 Marie Curie Private, Ottawa, Ontario, K1N 6N5, Canada. \*Correspondence e-mail: dbryce@uottawa.ca

Received 12 March 2015; accepted 13 April 2015

Edited by T. N. Guru Row, Indian Institute of Science, India

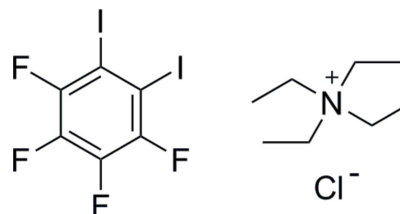
Equimolar quantities of tetraethylammonium chloride ( $\text{Et}_4\text{NCl}$ ) and 3,4,5,6-tetrafluoro-1,2-diiodobenzene (*o*-DITFB or *o*- $\text{C}_6\text{F}_4\text{I}_2$ ) have been co-crystallized in a solution of dichloromethane yielding a pure halogen-bonded compound, 3,4,5,6-tetrafluoro-1,2-diiodobenzene–tetraethyl ammonium chloride (2/1),  $\text{Et}_4\text{N}^+\cdot\text{Cl}^- \cdot 2\text{C}_6\text{F}_4\text{I}_2$ , in the form of translucent needles.  $[(\text{Et}_4\text{NCl})(\text{o}-\text{C}_6\text{F}_4\text{I}_2)_2]$  packs in the  $C2/c$  space group. The asymmetric unit includes one molecule of DITFB, one  $\text{Et}_4\text{N}^+$  cation located on a twofold rotation axis, and one chloride anion also located on a twofold rotation symmetry axis. This compound has an interesting halogen-bonding environment surrounding the halide. Here, the chloride anion acts as a tetradentate halogen bond acceptor and forms a distorted square-pyramidal geometry, with  $\text{I} \cdots \text{Cl}^- \cdots \text{I}$  angles of  $80.891(6)$  and  $78.811(11)^\circ$ , where two crystallographically distinct iodine atoms form halogen bonds with the chloride anion. Resulting from that square-pyramidal geometry are short contacts between some of the adjacent F atoms. Along the *b* axis, the halogen-bonding interaction results in a polymeric network, producing a sheet in which the two closest chloride ions are  $7.8931(6)$  Å apart. The  $\text{Et}_4\text{N}^+$  cation alternates in columns with the halide ion. The expected short contacts (shorter than the sum of their van der Waals radii) are observed for the halogen bonds [ $3.2191(2)$  and  $3.2968(2)$  Å], as well as almost linear angles [ $170.953(6)$  and  $173.529(6)^\circ$ ].

**Keywords:** crystal structure; halogen bond; non-covalent interactions; short contacts.

**CCDC reference:** 1059313

## 1. Related literature

The crystal structure of 3,4,5,6-tetrafluoro-1,2-diiodobenzene has been recently published by our group (Viger-Gravel, Leclerc *et al.*, 2014) and the crystal structure of  $\text{Et}_4\text{NCl}$  was reported by Staples (1999). Reports by Abate *et al.* (2009), and our previous work (Viger-Gravel, Leclerc *et al.*, 2014; Viger-Gravel, Meyer *et al.*, 2014; Viger-Gravel *et al.*, 2015) may be consulted for other similar halogen-bonded compounds containing *o*- or *p*-DITFB and ammonium halide salts. In these reports, halogen-bonding interactions are observed. Abate *et al.* discuss applications in crystal engineering. The latter reports describe the usefulness of solid-state nuclear magnetic resonance to characterize these types of halogen-bonding environments (Viger-Gravel, Leclerc *et al.*, 2014; Viger-Gravel, Meyer *et al.*, 2014).



## 2. Experimental

### 2.1. Crystal data

$\text{C}_8\text{H}_{20}\text{N}^+\cdot\text{Cl}^- \cdot 2\text{C}_6\text{F}_4\text{I}_2$   
 $M_r = 969.42$   
 Monoclinic,  $C2/c$   
 $a = 7.8930(6)$  Å  
 $b = 16.8088(13)$  Å  
 $c = 20.9962(16)$  Å  
 $\beta = 97.803(3)^\circ$

$V = 2759.8(4)$  Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 4.68$  mm<sup>-1</sup>  
 $T = 200$  K  
 $0.23 \times 0.18 \times 0.08$  mm

### 2.2. Data collection

Bruker APEXII CCD  
 diffractometer  
 Absorption correction: multi-scan  
 (SADABS; Bruker, 2009)  
 $T_{\min} = 0.555$ ,  $T_{\max} = 0.746$

19329 measured reflections  
 3445 independent reflections  
 3260 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.019$

### 2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.023$   
 $wR(F^2) = 0.070$   
 $S = 1.02$   
 3445 reflections

155 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\max} = 0.31$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -1.75$  e Å<sup>-3</sup>

**Table 1**

Halogen-bonded geometry (Å, °).

C—X···Y	X···Y	C—X···Y	Y···X···Y	Y···X···Y
C1—I1···Cl3 <sup>i</sup>	3.2968 (2)	173.529 (6)	I1 <sup>ii</sup> ···Cl3···I2	80.891 (6)
C2—I2···Cl3	3.2191 (2)	170.953 (6)	I2···Cl3···I1 <sup>iii</sup>	78.811 (11)

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

**Table 2**

Short contacts between hydrogen, DITFB or chloride (Å, °).

C—X···Z	F···Z	C—F···Z
C3—F1···F4	2.532 (2)	166.944 (15)
C3—F1···F2	2.663 (3)	62.0647 (13)
C4—F2···F3	2.713 (2)	59.936 (12)
C5—F3···F4	2.671 (2)	60.201 (13)
C3—F1···C2	2.364 (3)	30.165 (12)
C3—F1···H8B <sup>i</sup>	2.614 (2)	100.233 (14)
C4—F2···H10B <sup>ii</sup>	2.570 (2)	165.27 (2)
C10—H10C···Cl3 <sup>iii</sup>	2.936 (2)	148.5 (2)

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

Data collection: *APEX2* (Bruker, 2009); cell refinement: *APEX2* and *SAINT* (Bruker, 2009); data reduction: *SAINT* and *XPREP* (Bruker, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick,

2015); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

## Acknowledgements

DLB thanks the Natural Sciences and Engineering Research Council (NSERC) of Canada for funding and JVG thanks the Fonds de Recherche du Québec – Nature et Technologies (FRQNT) for a scholarship.

Supporting information for this paper is available from the IUCr electronic archives (Reference: GW2151).

## References

- Abate, A., Biella, S., Cavallo, G., Meyer, F., Neukirch, H., Metrangolo, P., Pilati, T., Resnati, G. & Terraneo, G. (2009). *J. Fluor. Chem.* **130**, 1171–1177.
- Bruker (2009). *APEX2*, *SAINT* and *XPREP*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sheldrick, G. M. (2015). *Acta Cryst.* **C71**, 3–8.
- Staples, R. J. (1999). *Z. Kristallogr. New Cryst. Struct.* **214**, 231–232.
- Viger-Gravel, J., Korobkov, I. & Bryce, D. L. (2015). *Acta Cryst.* **E71**, o286–o287.
- Viger-Gravel, J., Leclerc, S., Korobkov, I. & Bryce, D. L. (2014). *J. Am. Chem. Soc.* **136**, 6929–6942.
- Viger-Gravel, J., Meyer, J. E., Korobkov, I. & Bryce, D. L. (2014). *CrystEngComm*, **16**, 7285–7297.

## supporting information

*Acta Cryst.* (2015). E71, o319–o320 [doi:10.1107/S205698901500732X]

## Crystal structure of tetraethylammonium chloride 3,4,5,6-tetrafluoro-1,2-diiodobenzene

Jasmine Viger-Gravel, Ilia Korobkov and David L. Bryce

### S1. Experimental

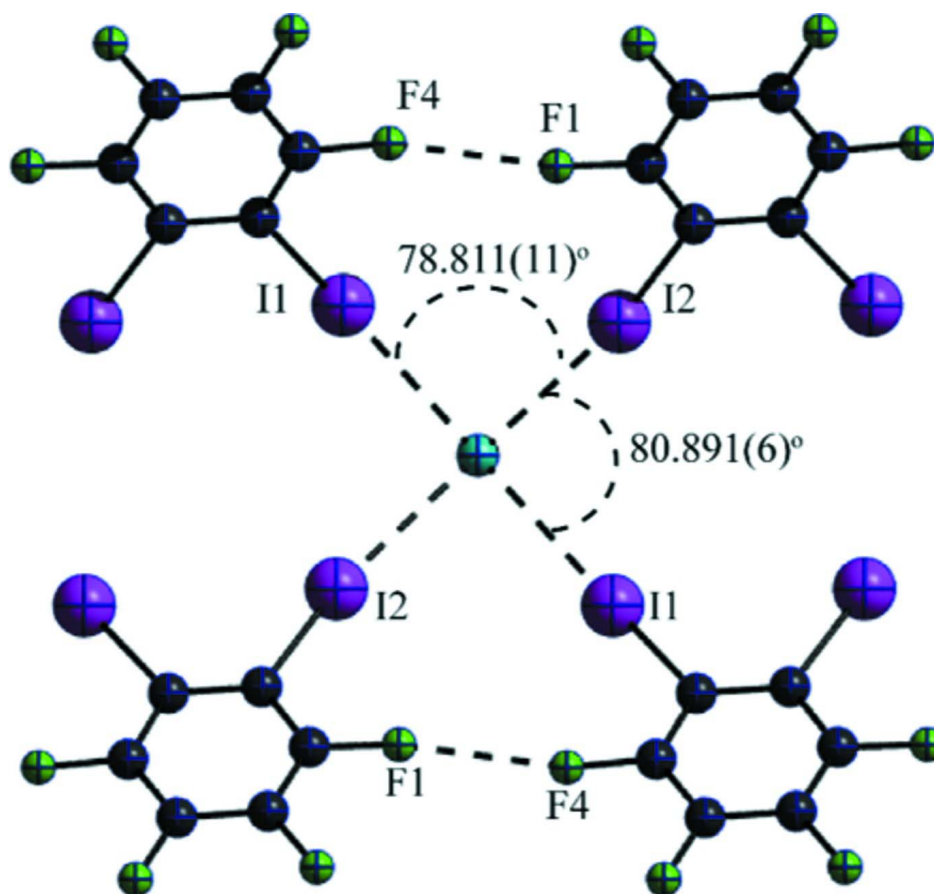
Data collection results for [(Et<sub>4</sub>NCl)(*o*-C<sub>6</sub>F<sub>4</sub>I<sub>2</sub>)] represent the best data set obtained in several trials. The crystal was mounted on a thin glass fiber using paraffin oil. Prior to data collection, crystals were cooled to 200.15 °K. Data were collected on a Bruker AXS SMART single crystal diffractometer equipped with a sealed Mo tube source (wavelength 0.71073 Å) APEX II CCD detector. Raw data collection and processing were performed with the APEX II software package (Bruker, 2009). Diffraction data were collected with a sequence of 0.3°  $\omega$  scans at 0, 120, and 240° in  $\varphi$ . Due to lower symmetry in order to ensure adequate data completeness and redundancy the initial unit cell parameters were determined from 60 data frames with 0.3°  $\omega$  scan each collected at the different sections of the Ewald sphere. Semi-empirical absorption corrections based on equivalent reflections were applied.

### S2. Refinement details

Systematic absences in the diffraction data set and unit cell parameters were consistent with the monoclinic C2/*c* (No.15) space group for [(Et<sub>4</sub>NCl)(*o*-C<sub>6</sub>F<sub>4</sub>I<sub>2</sub>)]. The solution in the centrosymmetric space group yielded chemically reasonable and computationally stable results of refinement. The structure was solved by direct methods, completed with difference Fourier synthesis, and refined with full-matrix least-squares procedures based on  $F^2$ .

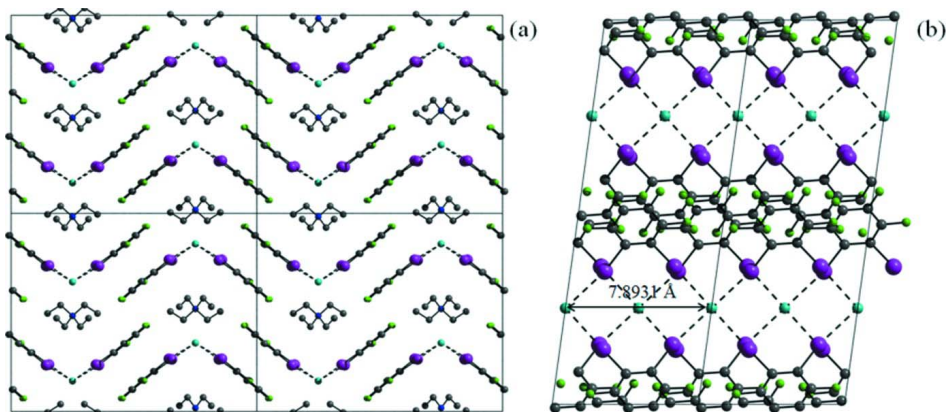
The structural model for [(Et<sub>4</sub>NCl)(*o*-C<sub>6</sub>F<sub>4</sub>I<sub>2</sub>)] contains one ammonium cation and one chlorine atom located on two different two-fold axis symmetry elements of the space group while aromatic molecules are located in general positions.

In this structural model, the hydrogen atom positions were located from the differences in Fourier maps. However, after initial positioning, all hydrogen atomic positions were constrained to suitable geometries and subsequently treated as idealized contributions. All scattering factors are contained in several versions of the SHELXTL program library, with the latest version used being v.6.12 (Sheldrick, 2008).



**Figure 1**

Halogen-bonding interactions in  $[(\text{Et}_4\text{NCl})(o\text{-C}_6\text{F}_4\text{I}_2)]$ , where iodine is in purple, carbon in black, fluorine in green, and chloride in blue. Short type I fluorine–fluorine contacts are also shown.



**Figure 2**

$2 \times 2 \times 2$  supercell of  $[(\text{Et}_4\text{NCl})(o\text{-DITFB})]$  along the  $a$  axis in (a). Along the  $a$  axis, rows of alternating halogen-bonded complexes and cations are easily observed. In (b) is presented the network formed in the  $ac$  plane where the closest anions are 7.8931 Å apart. The color legend used is: iodine in purple, carbon in black, fluorine in green, and chloride in blue.

## 3,4,5,6-Tetrafluoro-1,2-diiodobenzene-tetraethyl ammonium chloride (2/1)

## Crystal data

 $C_8H_{20}N^+ \cdot Cl^- \cdot 2C_6F_4I_2$  $M_r = 969.42$ Monoclinic,  $C2/c$  $a = 7.8930$  (6) Å $b = 16.8088$  (13) Å $c = 20.9962$  (16) Å $\beta = 97.803$  (3)° $V = 2759.8$  (4) Å<sup>3</sup> $Z = 4$  $F(000) = 1792$  $D_x = 2.333$  Mg m<sup>-3</sup>Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 9886 reflections

 $\theta = 2.4$ – $28.3$ ° $\mu = 4.68$  mm<sup>-1</sup> $T = 200$  K

Plate, colourless

 $0.23 \times 0.18 \times 0.08$  mm

## Data collection

Bruker APEXII CCD

diffractometer

 $\varphi$  and  $\omega$  scans

Absorption correction: multi-scan

(SADABS; Bruker, 2009)

 $T_{\min} = 0.555$ ,  $T_{\max} = 0.746$ 

19329 measured reflections

3445 independent reflections

3260 reflections with  $I > 2\sigma(I)$  $R_{\text{int}} = 0.019$  $\theta_{\max} = 28.3$ °,  $\theta_{\min} = 2.4$ ° $h = -10 \rightarrow 10$  $k = -21 \rightarrow 22$  $l = -27 \rightarrow 27$ 

## Refinement

Refinement on  $F^2$ 

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.023$  $wR(F^2) = 0.070$  $S = 1.02$ 

3445 reflections

155 parameters

0 restraints

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0482P)^2 + 4.146P]$ where  $P = (F_o^2 + 2F_c^2)/3$  $(\Delta/\sigma)_{\max} = 0.004$  $\Delta\rho_{\max} = 0.31$  e Å<sup>-3</sup> $\Delta\rho_{\min} = -1.74$  e Å<sup>-3</sup>

## Special details

**Experimental.** Data collection is performed with three batch runs at  $\phi = 0.00$  ° (650 frames), at  $\phi = 120.00$  ° (650 frames), and at  $\phi = 240.00$  ° (650 frames). Frame width =  $0.30$  ° in omega. Data is merged, corrected for decay (if any), and treated with multi-scan absorption corrections (if required). All symmetry-equivalent reflections are merged for centrosymmetric data. Friedel pairs are not merged for noncentrosymmetric data.

**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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
I1	1.20603 (2)	0.23394 (2)	0.64245 (2)	0.03195 (7)
I2	0.73344 (2)	0.23667 (2)	0.65441 (2)	0.03262 (7)
Cl3	0.5000	0.15395 (5)	0.7500	0.03270 (17)
F1	0.57429 (19)	0.34488 (13)	0.54284 (9)	0.0488 (4)
F2	0.6984 (2)	0.43431 (12)	0.45505 (9)	0.0548 (5)
F3	1.0382 (2)	0.43372 (12)	0.44632 (9)	0.0552 (5)
F4	1.2508 (2)	0.34428 (14)	0.52645 (10)	0.0551 (5)

N1	1.0000	0.98253 (15)	0.7500	0.0303 (6)
C1	1.0245 (3)	0.29692 (14)	0.57959 (11)	0.0285 (4)
C2	0.8494 (3)	0.29779 (14)	0.58425 (11)	0.0281 (4)
C3	0.7436 (3)	0.34314 (17)	0.54106 (12)	0.0325 (5)
C4	0.8050 (3)	0.38943 (16)	0.49509 (12)	0.0363 (5)
C5	0.9761 (3)	0.38863 (16)	0.49051 (13)	0.0372 (5)
C6	1.0838 (3)	0.34232 (17)	0.53238 (13)	0.0347 (5)
C7	1.0674 (4)	1.03725 (15)	0.70149 (13)	0.0378 (5)
H7A	0.9725	1.0715	0.6818	0.045*
H7B	1.1558	1.0723	0.7247	0.045*
C8	1.1435 (5)	0.9949 (2)	0.64821 (18)	0.0577 (9)
H8A	1.1831	1.0343	0.6192	0.087*
H8B	1.0564	0.9609	0.6241	0.087*
H8C	1.2403	0.9621	0.6669	0.087*
C9	0.8599 (4)	0.92855 (16)	0.71801 (15)	0.0401 (6)
H9A	0.9077	0.8954	0.6858	0.048*
H9B	0.8246	0.8922	0.7510	0.048*
C10	0.7022 (4)	0.9708 (2)	0.68505 (18)	0.0525 (8)
H10A	0.6191	0.9313	0.6658	0.079*
H10B	0.7344	1.0058	0.6514	0.079*
H10C	0.6511	1.0025	0.7167	0.079*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
I1	0.02594 (10)	0.03161 (11)	0.03700 (11)	0.00044 (5)	−0.00040 (7)	0.00317 (6)
I2	0.02988 (10)	0.03613 (12)	0.03308 (11)	−0.00047 (6)	0.00879 (7)	−0.00037 (6)
Cl3	0.0309 (4)	0.0339 (4)	0.0335 (4)	0.000	0.0050 (3)	0.000
F1	0.0244 (7)	0.0691 (12)	0.0524 (10)	0.0085 (7)	0.0034 (7)	0.0081 (9)
F2	0.0482 (10)	0.0664 (12)	0.0472 (10)	0.0187 (9)	−0.0025 (8)	0.0198 (9)
F3	0.0542 (11)	0.0637 (11)	0.0490 (10)	−0.0016 (9)	0.0122 (8)	0.0254 (9)
F4	0.0261 (8)	0.0771 (13)	0.0631 (12)	−0.0022 (8)	0.0100 (7)	0.0259 (10)
N1	0.0397 (15)	0.0185 (12)	0.0328 (15)	0.000	0.0047 (12)	0.000
C1	0.0250 (10)	0.0298 (11)	0.0297 (11)	−0.0006 (8)	0.0001 (8)	−0.0006 (9)
C2	0.0260 (10)	0.0312 (11)	0.0270 (11)	−0.0016 (9)	0.0033 (8)	−0.0041 (9)
C3	0.0246 (10)	0.0398 (13)	0.0325 (12)	0.0029 (9)	0.0014 (9)	−0.0021 (10)
C4	0.0347 (12)	0.0411 (13)	0.0309 (12)	0.0066 (10)	−0.0030 (9)	0.0037 (11)
C5	0.0383 (13)	0.0404 (13)	0.0330 (13)	−0.0019 (11)	0.0053 (10)	0.0081 (11)
C6	0.0257 (11)	0.0416 (14)	0.0370 (13)	−0.0016 (10)	0.0047 (9)	0.0038 (11)
C7	0.0503 (15)	0.0278 (11)	0.0364 (13)	0.0003 (11)	0.0104 (11)	0.0044 (10)
C8	0.077 (2)	0.0514 (18)	0.0494 (19)	0.0087 (17)	0.0271 (17)	−0.0018 (15)
C9	0.0433 (14)	0.0279 (12)	0.0472 (15)	−0.0045 (10)	−0.0004 (11)	−0.0066 (11)
C10	0.0464 (16)	0.0472 (16)	0.060 (2)	0.0030 (14)	−0.0062 (14)	−0.0076 (15)

*Geometric parameters (Å, °)*

I1—C1	2.098 (2)	N1—C7 <sup>i</sup>	1.521 (3)
I2—C2	2.105 (2)	C1—C6	1.382 (3)

F1—C3	1.342 (3)	C1—C2	1.398 (3)
F2—C4	1.339 (3)	C2—C3	1.377 (3)
F3—C5	1.341 (3)	C3—C4	1.378 (4)
F4—C6	1.341 (3)	C4—C5	1.367 (4)
N1—C9 <sup>i</sup>	1.515 (3)	C5—C6	1.378 (4)
N1—C9	1.515 (3)	C7—C8	1.517 (4)
N1—C7	1.521 (3)	C9—C10	1.516 (4)
C9 <sup>i</sup> —N1—C9	106.4 (3)	F1—C3—C4	117.0 (2)
C9 <sup>i</sup> —N1—C7	111.01 (16)	C2—C3—C4	122.3 (2)
C9—N1—C7	111.46 (16)	F2—C4—C5	120.3 (2)
C9 <sup>i</sup> —N1—C7 <sup>i</sup>	111.45 (16)	F2—C4—C3	120.5 (2)
C9—N1—C7 <sup>i</sup>	111.01 (16)	C5—C4—C3	119.2 (2)
C7—N1—C7 <sup>i</sup>	105.6 (3)	F3—C5—C4	120.0 (2)
C6—C1—C2	118.6 (2)	F3—C5—C6	120.6 (2)
C6—C1—I1	117.43 (17)	C4—C5—C6	119.4 (2)
C2—C1—I1	123.94 (18)	F4—C6—C5	117.1 (2)
C3—C2—C1	118.5 (2)	F4—C6—C1	120.9 (2)
C3—C2—I2	116.65 (17)	C5—C6—C1	122.0 (2)
C1—C2—I2	124.86 (18)	C8—C7—N1	114.8 (2)
F1—C3—C2	120.7 (2)	C10—C9—N1	115.3 (2)
C6—C1—C2—C3	0.8 (4)	C3—C4—C5—C6	-0.7 (4)
I1—C1—C2—C3	178.32 (18)	F3—C5—C6—F4	-0.4 (4)
C6—C1—C2—I2	-177.65 (19)	C4—C5—C6—F4	-179.2 (3)
I1—C1—C2—I2	-0.1 (3)	F3—C5—C6—C1	178.2 (3)
C1—C2—C3—F1	178.8 (2)	C4—C5—C6—C1	-0.7 (4)
I2—C2—C3—F1	-2.6 (3)	C2—C1—C6—F4	179.2 (2)
C1—C2—C3—C4	-2.2 (4)	I1—C1—C6—F4	1.4 (4)
I2—C2—C3—C4	176.4 (2)	C2—C1—C6—C5	0.6 (4)
F1—C3—C4—F2	0.8 (4)	I1—C1—C6—C5	-177.1 (2)
C2—C3—C4—F2	-178.2 (2)	C9 <sup>i</sup> —N1—C7—C8	58.5 (3)
F1—C3—C4—C5	-178.8 (3)	C9—N1—C7—C8	-60.0 (3)
C2—C3—C4—C5	2.2 (4)	C7 <sup>i</sup> —N1—C7—C8	179.4 (3)
F2—C4—C5—F3	0.9 (4)	C9 <sup>i</sup> —N1—C9—C10	177.6 (3)
C3—C4—C5—F3	-179.6 (3)	C7—N1—C9—C10	-61.2 (3)
F2—C4—C5—C6	179.7 (3)	C7 <sup>i</sup> —N1—C9—C10	56.2 (3)

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