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Crystal structure of 1-benzyl-3-methyl-1*H*-imidazolium hexafluoridophosphate

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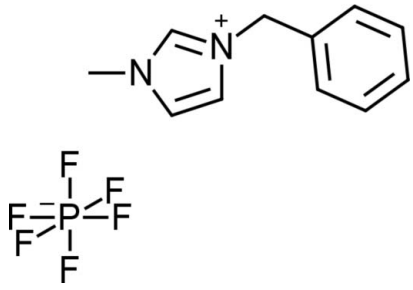
In the title salt, $C_{11}H_{13}N_2^+\cdot PF_6^-$, the dihedral angle between the planes of the imidazole and benzene rings is 84.72 (4)°. In the crystal, C—H···F interactions connect the cation and anion pairs into a three-dimensional network. Weak π–π interactions are observed between the imidazolium ring and the aromatic benzene ring of an adjacent molecule with C···C and C···N distances ranging from 3.3714 (16) to 3.4389 (15) Å.

Keywords: crystal structure; imidazolium; hexafluoridophosphate; hydrogen bonding; π–π interactions.

CCDC reference: 1032692

1. Related literature

For related structures containing imidazolium rings bearing *N*-benzyl groups, see: Haque *et al.* (2012); Jiang (2009); Lu *et al.* (2010); Pi *et al.* (2009). For an overview of applications for ionic liquids, see: Plechkova & Seddon (2008). For applications of benzyl-containing ionic liquids, see: Mahurin *et al.* (2011). For the synthesis of the title compound, see: Shkrob *et al.* (2013). For use of imidazolium compounds as carbene precursors, see: Scholl *et al.* (1999).



2. Experimental

2.1. Crystal data

$C_{11}H_{13}N_2^+\cdot F_6P^-$
M_r = 318.20
Monoclinic, $P2_1/c$
a = 10.4989 (3) Å
b = 11.2755 (3) Å
c = 11.9769 (3) Å
β = 109.926 (1)°
V = 1332.95 (6) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.27 mm^{-1}
T = 100 K
0.45 × 0.27 × 0.12 mm

2.2. Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2014)
T_{min} = 0.906, T_{max} = 0.991
42589 measured reflections
3188 independent reflections
2746 reflections with $I > 2\sigma(I)$
R_{int} = 0.055

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.083
S = 1.07
3188 reflections
182 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.42 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1···F3^{i}	0.95	2.23	3.1503 (14)	164
C1—H1···F4^{i}	0.95	2.61	3.2860 (14)	129
C3—H3···F5^{ii}	0.95	2.30	3.1456 (15)	148
C9—H9···F2^{iii}	0.95	2.60	3.2680 (16)	128

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

Data collection: *APEX2* (Bruker, 2014); cell refinement: *SAINT* (Bruker, 2013); data reduction: *SAINT*; program(s) used to solve structure: *SHELXT* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL* (Sheldrick, 2008); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2*.

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: ZL2605).

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supporting information

Acta Cryst. (2014). E**70**, o1248–o1249 [doi:10.1107/S1600536814024301]

Crystal structure of 1-benzyl-3-methyl-1*H*-imidazolium hexafluoridophosphate

Patrick C. Hillesheim and Kent A. Scipione

S1. Structural commentary

Ionic liquids are a class of materials which have found a wide range of applications in recent years (Plechkova & Seddon, 2008). In addition to their applications involving ionic liquids, imidazolium based salts are also commonly employed as starting materials for carbene ligands, perhaps most famously for their use in the so called Grubbs catalyst (Scholl *et al.*, 1999). For both ionic liquids and carbene ligands, cationic nitrogen containing heterocycles are the dominant structural motif, providing an ideal combination of chemical and physical properties useful in both instances. Electronic and structural factors play a large role in the fine tuning of both ionic liquids and carbenes, thus the structure reported herein will provide a useful analysis of this common, yet unreported structure.

The asymmetric unit of the title compound contains one cation-anion pair (Fig. 1). The dihedral angle of the benzene ring and the imidazolium ring is 84.72° (4), see table 1. Crystal packing appears to be stabilized by the presence of several C—H···F interactions summarized in table 2 and shown in Figure 2. There are several close contacts between C7 and C8 of the benzene ring and the symmetry generated imidazole ring (symmetry operator 1-x,1/2+y,1.5-z) with C···C and C···N distances ranging from 3.3714 (16) to 3.4389 (15) (for C7···C2 and C8···N1 respectively). These interactions likely point towards the presence of a weak, highly slipped and tilted π-π interaction. No classical centroid-centroid π stacking was observed in the lattice.

S2. Synthesis and crystallization

The title compound was synthesized according to established literature procedures (Shkrob *et al.*, 2013). Single crystals suitable for diffraction were grown by slow solvent evaporation from an ethanolic solution of the title compound.

S3. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. H atoms were included at calculated positions using a riding model, with aromatic, methylene, and methyl C—H bond lengths of 0.95, 0.99 and 0.98Å, respectively. The U_{iso}(H) values were fixed at 1.5U_{eq}(C) for methyl H atoms, and 1.2U_{eq}(C) for all other C atoms.

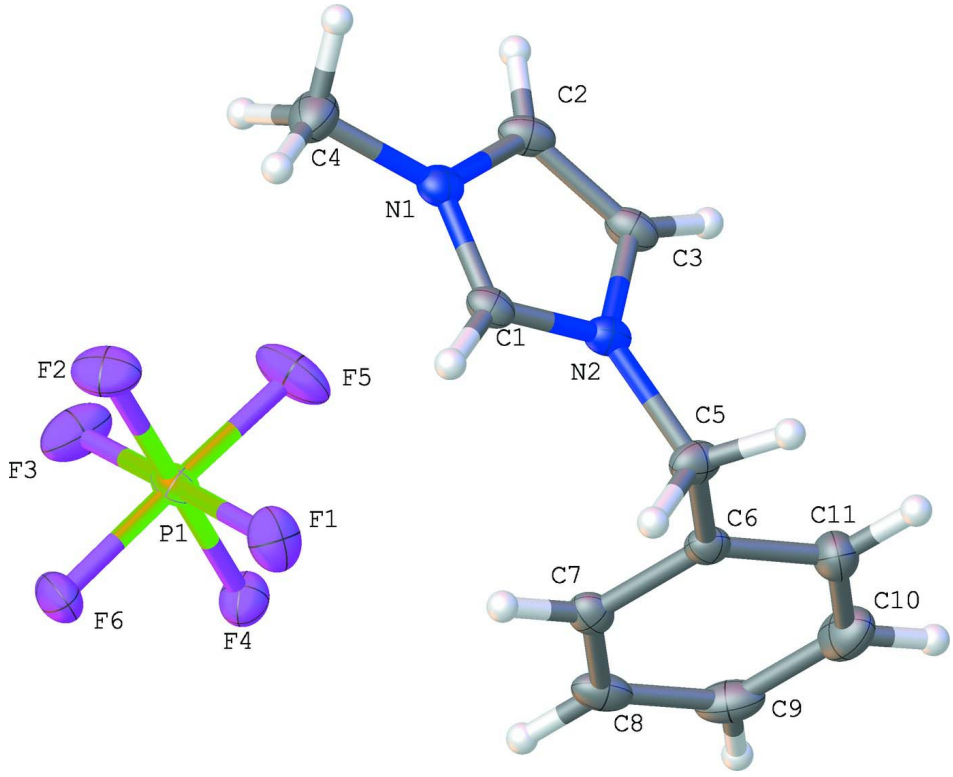

Figure 1

The molecular structure of the title compound with 50% probability ellipsoids. Nitrogen atoms shown in blue, carbon in grey, fluorine in pink, and phosphorous in green.

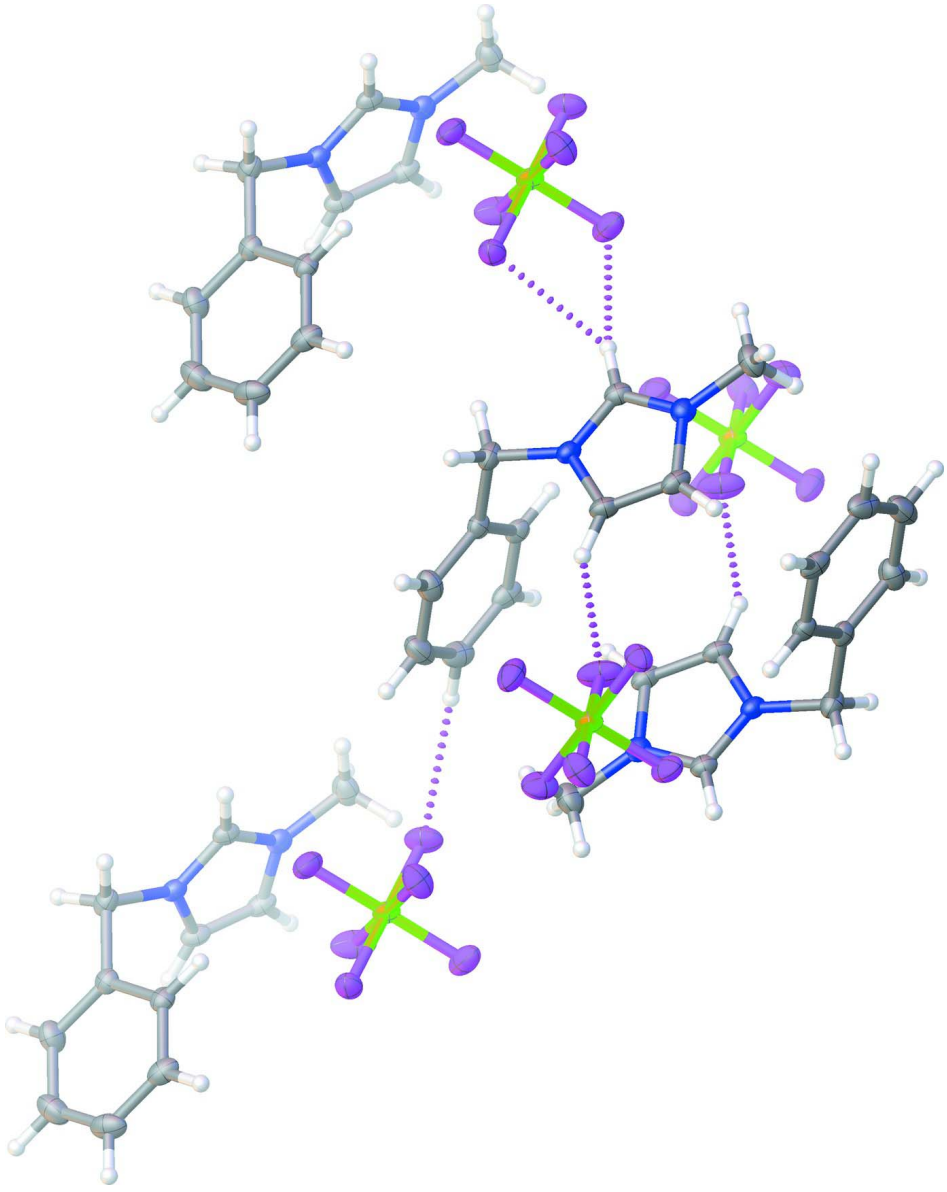

Figure 2

Diagram of the hydrogen bonding observed in the title compound shown as pink dotted lines.

1-Benzyl-3-methyl-1*H*-imidazolium hexafluoridophosphate

Crystal data

$C_{11}H_{13}N_2^+ \cdot F_6P^-$
$M_r = 318.20$
Monoclinic, $P2_1/c$
$a = 10.4989$ (3) Å
$b = 11.2755$ (3) Å
$c = 11.9769$ (3) Å
$\beta = 109.926$ (1)°
$V = 1332.95$ (6) Å^3
$Z = 4$
$F(000) = 648$
$D_x = 1.586$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9735 reflections
$\theta = 2.6$–27.9°
$\mu = 0.27$ mm^{-1}
$T = 100$ K
Plates, colourless
0.45 × 0.27 × 0.12 mm

Data collection

Bruker APEXII CCD diffractometer
Detector resolution: 8.33 pixels mm^{-1}
combination of ω and φ–scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2014)
T_{min} = 0.906, T_{max} = 0.991
42589 measured reflections
3188 independent reflections
2746 reflections with $I > 2\sigma(I)$
R_{int} = 0.055
θ_{max} = 27.9°, θ_{min} = 2.1°
h = −13→13
k = −14→14
l = −15→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.083
S = 1.07
3188 reflections
182 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0416P)^2 + 0.409P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.42 e Å^{-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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.71519 (10)	0.47646 (9)	0.73967 (9)	0.0195 (2)
N2	0.51532 (10)	0.53231 (9)	0.72989 (9)	0.0177 (2)
C1	0.64714 (12)	0.54719 (10)	0.78756 (10)	0.0188 (2)
H1	0.6860	0.5997	0.8523	0.023*
C2	0.62396 (13)	0.41476 (11)	0.64770 (11)	0.0219 (3)
H2	0.6453	0.3583	0.5979	0.026*
C3	0.49888 (13)	0.44926 (10)	0.64138 (11)	0.0210 (2)
H3	0.4154	0.4217	0.5866	0.025*
C4	0.86303 (13)	0.46510 (13)	0.77897 (13)	0.0296 (3)
H4A	0.8957	0.4942	0.7165	0.044*
H4B	0.8883	0.3816	0.7954	0.044*
H4C	0.9039	0.5119	0.8513	0.044*
C5	0.40534 (13)	0.59543 (11)	0.75594 (11)	0.0226 (3)
H5A	0.4451	0.6509	0.8229	0.027*
H5B	0.3491	0.5373	0.7803	0.027*
C6	0.31700 (12)	0.66383 (11)	0.64927 (11)	0.0190 (2)
C7	0.36887 (12)	0.76192 (10)	0.60829 (10)	0.0196 (2)
H7	0.4604	0.7850	0.6469	0.023*
C8	0.28734 (14)	0.82614 (11)	0.51126 (11)	0.0244 (3)
H8	0.3230	0.8933	0.4841	0.029*

C9	0.15414 (15)	0.79246 (13)	0.45415 (12)	0.0303 (3)
H9	0.0986	0.8364	0.3877	0.036*
C10	0.10175 (14)	0.69493 (14)	0.49367 (14)	0.0334 (3)
H10	0.0105	0.6716	0.4540	0.040*
C11	0.18284 (13)	0.63074 (12)	0.59182 (13)	0.0276 (3)
H11	0.1464	0.5644	0.6194	0.033*
P1	0.76866 (3)	0.81119 (3)	0.62758 (3)	0.01967 (10)
F1	0.71267 (8)	0.80793 (7)	0.73665 (7)	0.0306 (2)
F2	0.90222 (8)	0.74247 (7)	0.70492 (7)	0.0333 (2)
F3	0.82307 (9)	0.81640 (8)	0.51809 (7)	0.0363 (2)
F4	0.63354 (7)	0.88092 (7)	0.54915 (7)	0.02663 (18)
F5	0.69426 (10)	0.68792 (7)	0.58054 (8)	0.0392 (2)
F6	0.84023 (8)	0.93566 (7)	0.67485 (8)	0.0310 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0232 (5)	0.0161 (5)	0.0195 (5)	0.0017 (4)	0.0076 (4)	0.0036 (4)
N2	0.0232 (5)	0.0154 (4)	0.0148 (5)	0.0016 (4)	0.0069 (4)	0.0008 (4)
C1	0.0253 (6)	0.0146 (5)	0.0157 (5)	−0.0003 (4)	0.0061 (5)	0.0018 (4)
C2	0.0336 (7)	0.0163 (5)	0.0161 (6)	0.0028 (5)	0.0089 (5)	0.0001 (4)
C3	0.0293 (6)	0.0163 (5)	0.0155 (6)	−0.0010 (5)	0.0051 (5)	−0.0014 (4)
C4	0.0227 (6)	0.0292 (7)	0.0372 (8)	0.0041 (5)	0.0106 (6)	0.0070 (6)
C5	0.0271 (6)	0.0219 (6)	0.0224 (6)	0.0049 (5)	0.0132 (5)	0.0034 (5)
C6	0.0215 (6)	0.0171 (5)	0.0203 (6)	0.0023 (4)	0.0095 (5)	−0.0015 (4)
C7	0.0239 (6)	0.0183 (5)	0.0178 (6)	−0.0010 (5)	0.0088 (5)	−0.0033 (5)
C8	0.0387 (7)	0.0165 (6)	0.0200 (6)	0.0050 (5)	0.0127 (6)	−0.0005 (5)
C9	0.0345 (7)	0.0288 (7)	0.0235 (7)	0.0145 (6)	0.0043 (6)	−0.0007 (5)
C10	0.0206 (6)	0.0375 (8)	0.0368 (8)	0.0035 (5)	0.0030 (6)	−0.0075 (6)
C11	0.0236 (6)	0.0239 (6)	0.0364 (8)	−0.0024 (5)	0.0115 (6)	−0.0017 (6)
P1	0.02424 (17)	0.01596 (16)	0.01680 (17)	−0.00009 (11)	0.00438 (13)	0.00205 (11)
F1	0.0351 (4)	0.0369 (5)	0.0204 (4)	−0.0067 (3)	0.0103 (3)	0.0022 (3)
F2	0.0365 (5)	0.0288 (4)	0.0271 (4)	0.0110 (3)	0.0013 (3)	0.0054 (3)
F3	0.0406 (5)	0.0465 (5)	0.0264 (4)	0.0185 (4)	0.0175 (4)	0.0112 (4)
F4	0.0224 (4)	0.0296 (4)	0.0265 (4)	0.0025 (3)	0.0065 (3)	0.0077 (3)
F5	0.0572 (6)	0.0205 (4)	0.0282 (5)	−0.0093 (4)	−0.0007 (4)	−0.0038 (3)
F6	0.0262 (4)	0.0201 (4)	0.0450 (5)	−0.0052 (3)	0.0099 (4)	−0.0014 (3)

Geometric parameters (Å, º)

N1—C1	1.3247 (16)	C6—C11	1.3914 (18)
N1—C2	1.3768 (16)	C7—H7	0.9500
N1—C4	1.4660 (16)	C7—C8	1.3891 (17)
N2—C1	1.3301 (16)	C8—H8	0.9500
N2—C3	1.3805 (15)	C8—C9	1.384 (2)
N2—C5	1.4774 (15)	C9—H9	0.9500
C1—H1	0.9500	C9—C10	1.383 (2)
C2—H2	0.9500	C10—H10	0.9500

C2—C3	1.3468 (18)	C10—C11	1.396 (2)
C3—H3	0.9500	C11—H11	0.9500
C4—H4A	0.9800	P1—F1	1.6053 (8)
C4—H4B	0.9800	P1—F2	1.5935 (8)
C4—H4C	0.9800	P1—F3	1.6000 (8)
C5—H5A	0.9900	P1—F4	1.6139 (8)
C5—H5B	0.9900	P1—F5	1.5999 (8)
C5—C6	1.5098 (17)	P1—F6	1.6016 (8)
C6—C7	1.3939 (17)		

C1—N1—C2	108.65 (10)	C6—C7—H7	119.8
C1—N1—C4	125.58 (11)	C8—C7—C6	120.33 (12)
C2—N1—C4	125.77 (11)	C8—C7—H7	119.8
C1—N2—C3	108.67 (10)	C7—C8—H8	120.0
C1—N2—C5	125.40 (10)	C9—C8—C7	120.08 (12)
C3—N2—C5	125.93 (11)	C9—C8—H8	120.0
N1—C1—N2	108.57 (10)	C8—C9—H9	119.9
N1—C1—H1	125.7	C10—C9—C8	120.11 (13)
N2—C1—H1	125.7	C10—C9—H9	119.9
N1—C2—H2	126.3	C9—C10—H10	120.0
C3—C2—N1	107.35 (11)	C9—C10—C11	120.05 (13)
C3—C2—H2	126.3	C11—C10—H10	120.0
N2—C3—H3	126.6	C6—C11—C10	120.10 (13)
C2—C3—N2	106.76 (11)	C6—C11—H11	119.9
C2—C3—H3	126.6	C10—C11—H11	119.9
N1—C4—H4A	109.5	F1—P1—F4	89.53 (4)
N1—C4—H4B	109.5	F2—P1—F1	90.55 (5)
N1—C4—H4C	109.5	F2—P1—F3	90.29 (5)
H4A—C4—H4B	109.5	F2—P1—F4	179.90 (5)
H4A—C4—H4C	109.5	F2—P1—F5	90.55 (5)
H4B—C4—H4C	109.5	F2—P1—F6	90.39 (4)
N2—C5—H5A	109.3	F3—P1—F1	179.05 (5)
N2—C5—H5B	109.3	F3—P1—F4	89.63 (4)
N2—C5—C6	111.49 (10)	F3—P1—F6	90.11 (5)
H5A—C5—H5B	108.0	F5—P1—F1	89.80 (5)
C6—C5—H5A	109.3	F5—P1—F3	90.64 (5)
C6—C5—H5B	109.3	F5—P1—F4	89.51 (5)
C7—C6—C5	120.15 (11)	F5—P1—F6	178.80 (5)
C11—C6—C5	120.52 (11)	F6—P1—F1	89.44 (4)
C11—C6—C7	119.32 (12)	F6—P1—F4	89.56 (4)

N1—C2—C3—N2	0.15 (13)	C5—N2—C1—N1	−179.75 (10)
N2—C5—C6—C7	−67.85 (14)	C5—N2—C3—C2	179.52 (11)
N2—C5—C6—C11	112.96 (13)	C5—C6—C7—C8	−179.04 (11)
C1—N1—C2—C3	−0.35 (13)	C5—C6—C11—C10	179.65 (12)
C1—N2—C3—C2	0.11 (13)	C6—C7—C8—C9	−0.45 (18)
C1—N2—C5—C6	121.23 (12)	C7—C6—C11—C10	0.45 (19)
C2—N1—C1—N2	0.42 (13)	C7—C8—C9—C10	0.14 (19)

C3—N2—C1—N1	−0.33 (13)	C8—C9—C10—C11	0.5 (2)
C3—N2—C5—C6	−58.10 (15)	C9—C10—C11—C6	−0.8 (2)
C4—N1—C1—N2	−179.05 (11)	C11—C6—C7—C8	0.16 (18)
C4—N1—C2—C3	179.12 (11)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1···F3^{i}	0.95	2.23	3.1503 (14)	164
C1—H1···F4^{i}	0.95	2.61	3.2860 (14)	129
C3—H3···F5^{ii}	0.95	2.30	3.1456 (15)	148
C9—H9···F2^{iii}	0.95	2.60	3.2680 (16)	128

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