Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

1-Chloromethyl-1,4-diazoniabicyclo-[2.2.2]octane bis(hexafluorophosphate)

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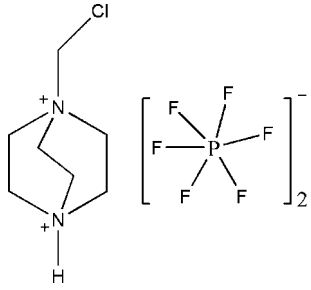
Received 13 December 2010; accepted 5 January 2011

Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.004 Å; R factor = 0.056; wR factor = 0.146; data-to-parameter ratio = 15.9.

In the crystal structure of the title compound, $C_7H_{15}ClN_2^{2+}\cdot 2PF_6^-$, the cations and anions are linked by intermolecular N—H···F hydrogen bonds.

Related literature

For general background to ferroelectric metal-organic frameworks, see: Fu *et al.* (2009); Ye *et al.* (2006); Zhang *et al.* (2008, 2010).



Experimental

Crystal data

$C_7H_{15}ClN_2^{2+}\cdot 2PF_6^-$
M_r = 452.6
Orthorhombic, *Pbca*
a = 14.414 (8) Å
b = 12.976 (7) Å
c = 16.115 (9) Å
V = 3014 (3) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.60 mm^{-1}
T = 293 K
0.30 × 0.25 × 0.20 mm

Data collection

Rigaku SCXmini diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
T_{min} = 0.836, T_{max} = 0.888
30798 measured reflections
3447 independent reflections
3197 reflections with $I > 2\sigma(I)$
R_{int} = 0.050

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.056
$wR(F^2)$ = 0.146
S = 1.24
3447 reflections
217 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.58 e Å^{-3}
$\Delta\rho_{min}$ = −0.46 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2*C*···F3^{i}	0.91	2.26	2.924 (3)	130
N2—H2*C*···F4^{i}	0.91	2.40	3.073 (3)	131
N2—H2*C*···F9^{i}	0.91	2.43	3.055 (3)	126

Symmetry code: (i) $x, y-1, z$.

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

This work was supported by Southeast University.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2377).

References

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Ye, Q., Song, Y.-M., Wang, G.-X., Chen, K. & Fu, D.-W. (2006). *J. Am. Chem. Soc.* **128**, 6554–6555.
Zhang, W., Xiong, R.-G. & Huang, S.-P. D. (2008). *J. Am. Chem. Soc.* **130**, 10468–10469.
Zhang, W., Ye, H.-Y., Cai, H.-L., Ge, J.-Z. & Xiong, R.-G. (2010). *J. Am. Chem. Soc.* **132**, 7300–7302.

supporting information

Acta Cryst. (2011). E**67**, o346 [doi:10.1107/S1600536811000390]

1-Chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(hexafluorophosphate)

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S1. Comment

We synthesized the title compound to find ferroelectric material by dielectric measurements of compound as a function of temperature(Fu *et al.* 2009;Ye *et al.*2006; Zhang *et al.*2008; Zhang *et al.*2010). In the range from 190 K to near its melting point(m.p. >452 K), no dielectric anomaly was observed.

Single crystal of the title compound suitable for X-ray diffraction analysis were obtained by evaporating an water solution in 123.5 K. As Fig.1, the compound consists of one 1-(chloromethyl)-1,4- diazabicyclo[2.2.2]octane-1,4-diium cations and two hexafluorophosphate anions. The hydrogen bonds linked one 1-(chloromethyl)-1,4- diazabicyclo-[2.2.2]octane-1,4-diium cations and two hexafluorophosphate anions of the another cell as showed in the Fig.2.

S2. Experimental

1,4-Diazabicyclo[2.2.2]octane(5.6 g,0.05 mol)was dissolved in 20 ml of dichloromethane and the mixture solution was refluxed for 8 h. A white precipitate of 1-(chloromethyl)-1,4-diazabicyclo[2.2.2]octan-1-ium chloride were obtained. The title compound was synthesized by the mixed solution of 1-(chloromethyl)-1,4-diazabicyclo[2.2.2]octan-1-ium chloride(1.97 g, 10 mmol) and hexafluorophosphoric acid(20 mmol). After a few days, colorless block crystals of the title compound were obtained on slow evaporation of the solvent.

S3. Refinement

Positional parameter of all the H atoms except for H2 were calculated geometrically and the H atoms were set to ride on the C atoms to which they are bonded, with U_{iso}(H) =1.2Ueq(C). The position of the H atom on N2 was determined from a difference Fourier map and was not refined.

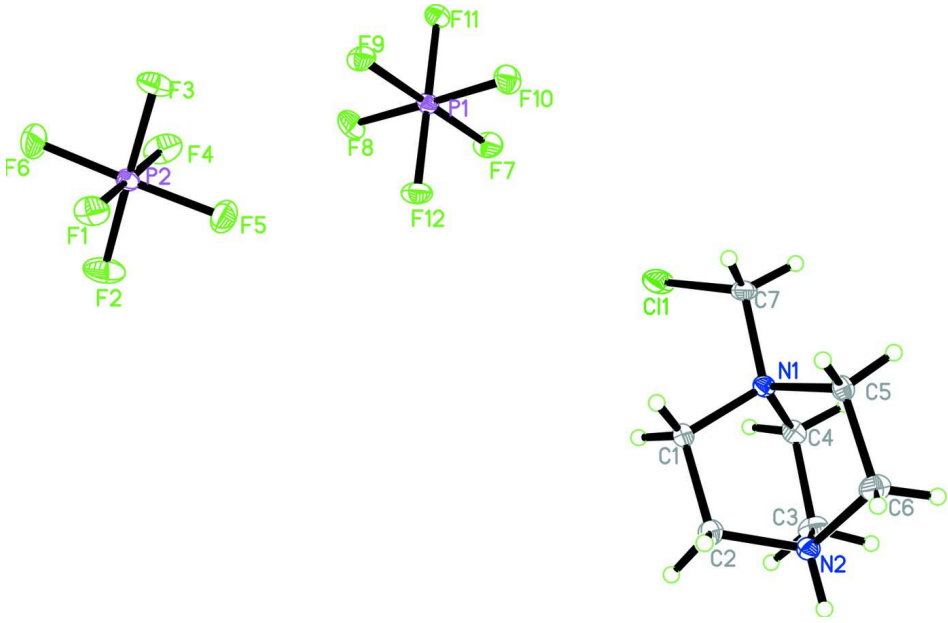

Figure 1

A partial packing diagram of the title compound, with displacement ellipsoids drawn at the 30% probability level.

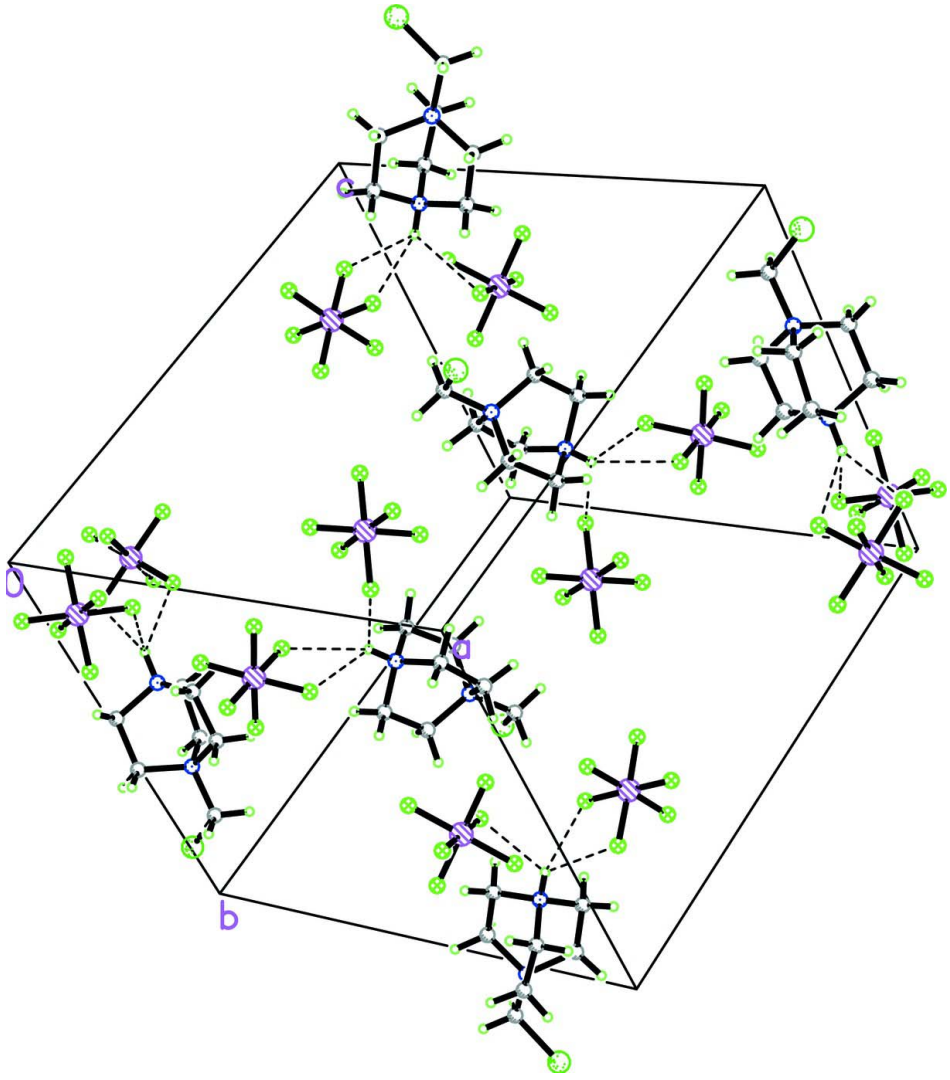

Figure 2

Packing diagram of the title compound, hydrogen bonds are shown as dashed lines.

1-Chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(hexafluorophosphate)

Crystal data

$C_7H_{15}ClN_2^{2+}\cdot 2PF_6^-$
$M_r = 452.6$
Orthorhombic, *Pbca*
Hall symbol: -P 2ac 2ab
$a = 14.414\ (8)$ Å
$b = 12.976\ (7)$ Å
$c = 16.115\ (9)$ Å
$V = 3014\ (3)$ Å^3
$Z = 8$
$F(000) = 1808$
$D_x = 1.995$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 6697 reflections
$\theta = 2.5–27.5°$
$\mu = 0.60$ mm^{-1}
$T = 293$ K
Prism, colorless
0.30 × 0.25 × 0.20 mm

Data collection

Rigaku SCXmini diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
CCD Profile fitting scans
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
T_{min} = 0.836, T_{max} = 0.888
30798 measured reflections
3447 independent reflections
3197 reflections with $I > 2\sigma(I)$
R_{int} = 0.050
θ_{max} = 27.5°, θ_{min} = 2.5°
h = −18→18
k = −16→16
l = −20→20

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.056
$wR(F^2)$ = 0.146
S = 1.24
3447 reflections
217 parameters
0 restraints
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
$w = 1/[\sigma^2(F_o^2) + (0.0625P)^2 + 3.8206P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.58 e Å^{-3}
$\Delta\rho_{min}$ = −0.46 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008)
Extinction coefficient: 0.0014 (1)

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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
P1	0.10243 (5)	0.80778 (6)	0.38500 (5)	0.01982 (19)
P2	0.25717 (5)	0.96221 (6)	0.14312 (5)	0.01997 (19)
F8	0.19471 (13)	0.87588 (16)	0.38218 (13)	0.0359 (5)
F9	0.06202 (13)	0.87478 (14)	0.30870 (11)	0.0293 (4)
F11	0.05718 (12)	0.88833 (14)	0.44911 (11)	0.0268 (4)
F10	0.00885 (13)	0.74127 (15)	0.38738 (13)	0.0331 (4)
F7	0.14303 (13)	0.74224 (16)	0.46061 (11)	0.0343 (5)
F12	0.14650 (13)	0.72793 (15)	0.32030 (12)	0.0322 (4)
F3	0.15177 (12)	1.00058 (16)	0.15861 (13)	0.0347 (5)
F1	0.23000 (15)	0.92628 (16)	0.05253 (11)	0.0363 (5)
F4	0.28151 (16)	0.99851 (17)	0.23639 (13)	0.0430 (6)
F2	0.36096 (14)	0.92349 (19)	0.13078 (16)	0.0479 (6)
F5	0.22953 (16)	0.85130 (15)	0.17743 (14)	0.0421 (5)
F6	0.28287 (17)	1.07397 (16)	0.11115 (15)	0.0465 (6)
Cl1	0.09951 (6)	0.45726 (7)	0.44115 (7)	0.0419 (3)

N1	0.05494 (16)	0.26975 (18)	0.37949 (15)	0.0189 (5)
N2	0.11243 (16)	0.10322 (19)	0.31629 (15)	0.0206 (5)
H2C	0.1332	0.0434	0.2933	0.025*
C5	−0.02655 (19)	0.2006 (2)	0.35656 (18)	0.0207 (6)
H5A	−0.0654	0.1896	0.4049	0.025*
H5B	−0.0638	0.2336	0.3141	0.025*
C1	0.1107 (2)	0.2924 (2)	0.30230 (19)	0.0224 (6)
H1A	0.1657	0.3316	0.3168	0.027*
H1B	0.0740	0.3333	0.2641	0.027*
C3	0.1568 (2)	0.1167 (2)	0.39967 (18)	0.0278 (7)
H3A	0.2234	0.1239	0.3935	0.033*
H3B	0.1446	0.0569	0.4341	0.033*
C7	0.0138 (2)	0.3663 (2)	0.4162 (2)	0.0266 (6)
H7A	−0.0207	0.3486	0.4660	0.032*
H7B	−0.0293	0.3964	0.3769	0.032*
C2	0.1390 (2)	0.1914 (2)	0.2609 (2)	0.0280 (7)
H2A	0.1080	0.1847	0.2077	0.034*
H2B	0.2054	0.1908	0.2513	0.034*
C4	0.1162 (2)	0.2138 (2)	0.44068 (18)	0.0232 (6)
H4A	0.0804	0.1946	0.4892	0.028*
H4B	0.1662	0.2588	0.4584	0.028*
C6	0.0090 (2)	0.0978 (3)	0.3247 (3)	0.0364 (8)
H6A	−0.0078	0.0434	0.3631	0.044*
H6B	−0.0188	0.0825	0.2713	0.044*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P1	0.0173 (4)	0.0238 (4)	0.0184 (4)	0.0025 (3)	0.0000 (3)	0.0006 (3)
P2	0.0181 (4)	0.0220 (4)	0.0198 (4)	−0.0001 (3)	0.0000 (3)	−0.0018 (3)
F8	0.0217 (9)	0.0451 (12)	0.0410 (11)	−0.0067 (8)	0.0054 (8)	−0.0014 (9)
F9	0.0340 (10)	0.0322 (10)	0.0218 (9)	0.0108 (8)	−0.0020 (7)	0.0035 (7)
F11	0.0282 (9)	0.0286 (9)	0.0235 (9)	0.0024 (7)	0.0050 (7)	−0.0028 (7)
F10	0.0264 (9)	0.0311 (10)	0.0419 (11)	−0.0074 (8)	0.0020 (8)	−0.0041 (9)
F7	0.0372 (10)	0.0422 (11)	0.0235 (9)	0.0133 (9)	−0.0027 (8)	0.0073 (8)
F12	0.0367 (10)	0.0335 (10)	0.0265 (10)	0.0142 (8)	0.0038 (8)	−0.0031 (8)
F3	0.0199 (9)	0.0403 (11)	0.0440 (11)	0.0016 (8)	0.0030 (8)	−0.0162 (9)
F1	0.0466 (12)	0.0429 (11)	0.0195 (9)	0.0112 (10)	−0.0053 (8)	−0.0082 (8)
F4	0.0560 (14)	0.0420 (12)	0.0310 (11)	0.0127 (10)	−0.0191 (10)	−0.0121 (9)
F2	0.0208 (10)	0.0539 (14)	0.0690 (16)	0.0064 (9)	−0.0004 (10)	−0.0187 (12)
F5	0.0614 (14)	0.0256 (10)	0.0392 (11)	−0.0020 (10)	0.0077 (10)	0.0035 (9)
F6	0.0572 (14)	0.0280 (10)	0.0544 (14)	−0.0099 (10)	0.0148 (11)	0.0055 (10)
Cl1	0.0285 (4)	0.0331 (4)	0.0641 (6)	−0.0071 (3)	0.0121 (4)	−0.0250 (4)
N1	0.0164 (11)	0.0205 (11)	0.0199 (11)	−0.0001 (9)	0.0005 (9)	−0.0011 (9)
N2	0.0191 (12)	0.0200 (11)	0.0227 (12)	0.0001 (9)	0.0003 (9)	−0.0010 (10)
C5	0.0159 (13)	0.0237 (14)	0.0225 (14)	−0.0027 (10)	−0.0020 (10)	−0.0003 (11)
C1	0.0218 (14)	0.0202 (13)	0.0252 (14)	−0.0011 (11)	0.0051 (11)	0.0007 (11)
C3	0.0348 (17)	0.0266 (15)	0.0220 (14)	0.0078 (13)	−0.0052 (12)	0.0007 (12)

C7	0.0204 (14)	0.0213 (14)	0.0382 (17)	0.0025 (11)	0.0046 (12)	−0.0076 (13)
C2	0.0377 (17)	0.0239 (15)	0.0223 (15)	0.0035 (13)	0.0074 (13)	0.0043 (12)
C4	0.0200 (13)	0.0294 (15)	0.0201 (13)	0.0005 (12)	−0.0014 (11)	−0.0014 (11)
C6	0.0190 (15)	0.0282 (16)	0.062 (2)	−0.0040 (13)	−0.0030 (15)	−0.0145 (16)

Geometric parameters (Å, º)

P1—F7	1.597 (2)	N2—C2	1.501 (4)
P1—F8	1.598 (2)	N2—H2C	0.9100
P1—F12	1.601 (2)	C5—C6	1.518 (4)
P1—F10	1.602 (2)	C5—H5A	0.9700
P1—F11	1.6079 (19)	C5—H5B	0.9700
P1—F9	1.6147 (19)	C1—C2	1.527 (4)
P2—F1	1.582 (2)	C1—H1A	0.9700
P2—F6	1.583 (2)	C1—H1B	0.9700
P2—F2	1.591 (2)	C3—C4	1.538 (4)
P2—F5	1.592 (2)	C3—H3A	0.9700
P2—F4	1.614 (2)	C3—H3B	0.9700
P2—F3	1.618 (2)	C7—H7A	0.9700
Cl1—C7	1.756 (3)	C7—H7B	0.9700
N1—C7	1.507 (4)	C2—H2A	0.9700
N1—C4	1.510 (4)	C2—H2B	0.9700
N1—C1	1.510 (4)	C4—H4A	0.9700
N1—C5	1.524 (3)	C4—H4B	0.9700
N2—C6	1.498 (4)	C6—H6A	0.9700
N2—C3	1.498 (4)	C6—H6B	0.9700
F7—P1—F8	90.65 (12)	C6—C5—N1	109.8 (2)
F7—P1—F12	90.40 (11)	C6—C5—H5A	109.7
F8—P1—F12	90.53 (12)	N1—C5—H5A	109.7
F7—P1—F10	90.19 (12)	C6—C5—H5B	109.7
F8—P1—F10	178.98 (12)	N1—C5—H5B	109.7
F12—P1—F10	90.06 (11)	H5A—C5—H5B	108.2
F7—P1—F11	90.26 (11)	N1—C1—C2	109.6 (2)
F8—P1—F11	89.79 (11)	N1—C1—H1A	109.8
F12—P1—F11	179.26 (11)	C2—C1—H1A	109.8
F10—P1—F11	89.62 (11)	N1—C1—H1B	109.8
F7—P1—F9	179.52 (13)	C2—C1—H1B	109.8
F8—P1—F9	88.90 (11)	H1A—C1—H1B	108.2
F12—P1—F9	89.75 (11)	N2—C3—C4	108.6 (2)
F10—P1—F9	90.26 (11)	N2—C3—H3A	110.0
F11—P1—F9	89.59 (10)	C4—C3—H3A	110.0
F1—P2—F6	91.58 (13)	N2—C3—H3B	110.0
F1—P2—F2	91.39 (12)	C4—C3—H3B	110.0
F6—P2—F2	91.64 (14)	H3A—C3—H3B	108.3
F1—P2—F5	89.54 (12)	N1—C7—Cl1	111.8 (2)
F6—P2—F5	178.30 (13)	N1—C7—H7A	109.3
F2—P2—F5	89.61 (13)	Cl1—C7—H7A	109.3

F1—P2—F4	178.20 (13)	N1—C7—H7B	109.3
F6—P2—F4	89.13 (13)	Cl1—C7—H7B	109.3
F2—P2—F4	90.24 (13)	H7A—C7—H7B	107.9
F5—P2—F4	89.71 (13)	N2—C2—C1	109.1 (2)
F1—P2—F3	90.03 (11)	N2—C2—H2A	109.9
F6—P2—F3	89.32 (13)	C1—C2—H2A	109.9
F2—P2—F3	178.26 (14)	N2—C2—H2B	109.9
F5—P2—F3	89.40 (12)	C1—C2—H2B	109.9
F4—P2—F3	88.32 (11)	H2A—C2—H2B	108.3
C7—N1—C4	111.9 (2)	N1—C4—C3	109.6 (2)
C7—N1—C1	111.8 (2)	N1—C4—H4A	109.8
C4—N1—C1	108.7 (2)	C3—C4—H4A	109.8
C7—N1—C5	106.3 (2)	N1—C4—H4B	109.8
C4—N1—C5	109.0 (2)	C3—C4—H4B	109.8
C1—N1—C5	109.0 (2)	H4A—C4—H4B	108.2
C6—N2—C3	110.4 (3)	N2—C6—C5	109.0 (2)
C6—N2—C2	110.1 (3)	N2—C6—H6A	109.9
C3—N2—C2	109.6 (2)	C5—C6—H6A	109.9
C6—N2—H2C	108.9	N2—C6—H6B	109.9
C3—N2—H2C	108.9	C5—C6—H6B	109.9
C2—N2—H2C	108.9	H6A—C6—H6B	108.3

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*C*···F3^{i}	0.91	2.26	2.924 (3)	130
N2—H2*C*···F4^{i}	0.91	2.40	3.073 (3)	131
N2—H2*C*···F9^{i}	0.91	2.43	3.055 (3)	126

Symmetry code: (i) $x, y-1, z$.