

[μ -Bis(5,7-dimethyl-1,8-naphthyridin-2-yl)diazene]bis[difluoridoboron(III)]

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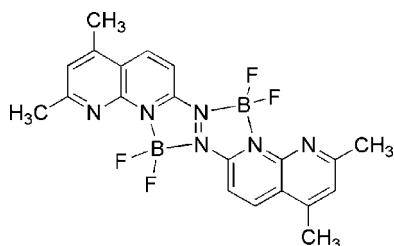
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Key indicators: single-crystal X-ray study; $T = 272$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.045; wR factor = 0.127; data-to-parameter ratio = 15.0.

In the title compound, $\text{C}_{20}\text{H}_{18}\text{B}_2\text{F}_4\text{N}_6$, the bis(5,7-dimethyl-1,8-naphthyridin-2-yl)diazene molecule is bisected by a symmetry centre midway between the central N atoms of the diazene group. Each of the symmetry-related halves of the molecule binds to a B atom through an N,N' -bite. Two terminal F ions complete the distorted BN_2F_2 tetrahedral geometry around each B atom. The BF_2 plane is almost perpendicular to the boron–naphthyridine ring plane, with a dihedral angle of $87.8(2)^\circ$. The main interactions in the crystal structure are some $\text{C}-\text{H}\cdots\text{F}$ hydrogen bonds and $\pi-\pi$ contacts between 1,8-naphthyridine rings [centroid–centroid distance = $4.005(1)$ Å].

Related literature

For 1,8-naphthyridine derivatives, see: Gavrilova & Bosnich (2004); Goswami & Mukherjee (1997); Nakatani *et al.* (2000).



Experimental

Crystal data

$\text{C}_{20}\text{H}_{18}\text{B}_2\text{F}_4\text{N}_6$	$V = 1940.6(7)$ Å ³
$M_r = 440.02$	$Z = 4$
Orthorhombic, $Pbca$	Mo $K\alpha$ radiation
$a = 8.5379(17)$ Å	$\mu = 0.12$ mm ⁻¹
$b = 14.696(3)$ Å	$T = 272$ K
$c = 15.467(3)$ Å	$0.10 \times 0.08 \times 0.06$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	14645 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	2221 independent reflections
$T_{\min} = 0.985$, $T_{\max} = 0.994$	1714 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.058$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$	148 parameters
$wR(F^2) = 0.127$	H-atom parameters constrained
$S = 1.07$	$\Delta\rho_{\text{max}} = 0.32$ e Å ⁻³
2221 reflections	$\Delta\rho_{\text{min}} = -0.24$ e Å ⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{C}1-\text{H}1\text{C}\cdots\text{F}1^{\text{i}}$	0.96	2.54	3.291 (2)	135
$\text{C}8-\text{H}8\cdots\text{F}1^{\text{ii}}$	0.93	2.48	3.2434 (19)	140

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

Data collection: SMART (Bruker, 2000); cell refinement: SAINT (Bruker, 2000); data reduction: SAINT; 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: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BG2262).

References

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supporting information

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[μ -Bis(5,7-dimethyl-1,8-naphthyridin-2-yl)diazene]bis[difluoridoboron(III)]

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S1. Comment

The derivatives of 1,8-naphthyridine have been widely utilized as mono-nucleating and dinucleating ligands in coordination chemistry or as antimycobacterial and antimicrobial agents (Gavrilova & Bosnich, 2004; Goswami *et al.*, 1997; Nakatani *et al.*, 2000). Here, we report the crystal structure of the centrosymmetric dinuclear title compound, $C_{20}H_{18}B_2F_4N_6$, where the di-5,7-dimethyl-1,8-naphthyl-2,2'-diazene (ddnd) ligand is halved by a symmetry centre midway the central nitrogens in the diazene group, and where each boron atom is coordinated by a N,N' bite of the ddnd ligand and two terminal F ions. The result is a distorted BN_2F_2 tetrahedral geometry, with a N—B—N bite angle of $94.35(11)^\circ$. The compound skeleton is formed by four conjugated heterocyclic rings which are nearly coplanar; the least-squares plane through B1,N1,N2,C2- \rightarrow C10 has a mean deviation of 0.02 \AA . The BF_2 plane is almost perpendicular to the boron-naphthyridine ring plane, with a dihedral angle of $92.2(2)^\circ$.

There are two main C—H \cdots F hydrogen bonding interactions involving F1 as an acceptor and two C—H donor sets, C1—H1C, C8—H8. There is also a π - π stacking interaction between adjacent parallel naphthyridyl rings: with a closest C—C distance of $3.499(1) \text{ \AA}$ and a centroid to centroid distance of $4.005(1) \text{ \AA}$. Via these interactions (with H-bonding mainly in the (100) plane and π - π stacking along the [100] direction) the compound forms a three-dimensional network structure as shown in Fig. 2.

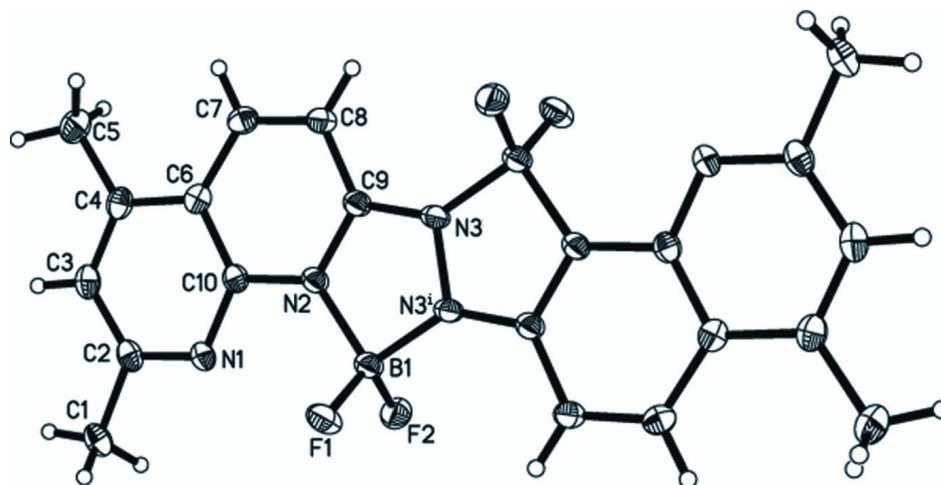
S2. Experimental

A cold solution of 7-amino-2,4-dimethyl-1,8-naphthyridine (2 g) in water (100 mL) was added dropwise to 150 ml of a 10% NaOCl solution. The mixture was stirred at 0 degree and a dark green precipitate formed. Filtration was performed a few minutes after the end of addition, and the aqueous phase and the precipitate were extracted with diethyl ether. The ether phases were gathered, dried on $MgSO_4$, and evaporated. The crude product was purified by chromatography on Al_2O_3 (eluent: acetone/hexane 1/10). Recrystallization in water yielded ddnd as green product. Yield: 70%.

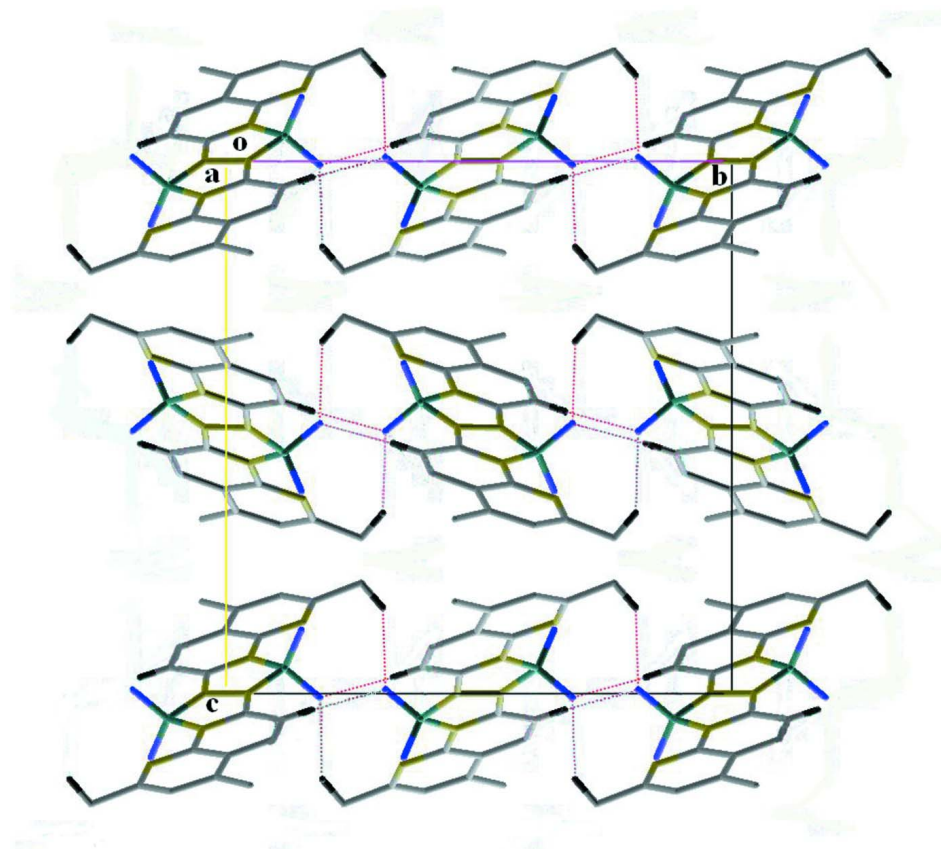
The ddnd (0.34 g, 1 mmol) ligand was dissolved in 50 ml newly dry dichloromethane and then treated with triethylamine (3 ml) and boron trifluoride etherate (3 ml). After stirring for 30 min, the solution was washed with water, dried over Na_2SO_4 , and concentrated at reduced pressure. Single crystals of (I) suitable for an X-ray study were obtained by slow evaporation of an $CHCl_3$ /hexane solution (50% v/v) over a period of one month.

S3. Refinement

All hydrogen atoms were generated geometrically (C—H bond lengths of methyl group fixed at 0.96 \AA , C—H bond lengths of naphthyridine fixed at 0.93 \AA), assigned appropriated isotropic thermal parameters, $U_{iso}(H) = 1.2U_{eq}(C)$.

**Figure 1**

Molecular structure of the title compound showing the atom-numbering scheme and displacement ellipsoids drawn at the 40% probability level. (Symmetry code: $-x, -y, 2 - z$).

**Figure 2**

The crystal packing of the title compound, viewed along the a axis. Hydrogen bonds are shown as dashed lines.

[μ -Bis(5,7-dimethyl-1,8-naphthyridin-2-yl)diazene]bis[difluoridoboron(III)]*Crystal data*C₂₀H₁₈B₂F₄N₆ $M_r = 440.02$ Orthorhombic, *Pbca*

Hall symbol: -P 2ac 2ab

 $a = 8.5379 (17) \text{ \AA}$ $b = 14.696 (3) \text{ \AA}$ $c = 15.467 (3) \text{ \AA}$ $V = 1940.6 (7) \text{ \AA}^3$ $Z = 4$ $F(000) = 904$ $D_x = 1.506 \text{ Mg m}^{-3}$ Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 3723 reflections

 $\theta = 3.1\text{--}27.5^\circ$ $\mu = 0.12 \text{ mm}^{-1}$ $T = 272 \text{ K}$

Block, brown

 $0.10 \times 0.08 \times 0.06 \text{ mm}$ *Data collection*Bruker SMART CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

 φ and ω scansAbsorption correction: multi-scan
(*SADABS*; Sheldrick, 2003) $T_{\min} = 0.985$, $T_{\max} = 0.994$

14645 measured reflections

2221 independent reflections

1714 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.058$ $\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 3.1^\circ$ $h = -9 \rightarrow 11$ $k = -19 \rightarrow 15$ $l = -20 \rightarrow 19$ *Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.045$ $wR(F^2) = 0.127$ $S = 1.07$

2221 reflections

148 parameters

0 restraints

Primary atom site location: structure-invariant
direct methodsSecondary atom site location: difference Fourier
mapHydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0655P)^2 + 0.3984P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.002$ $\Delta\rho_{\max} = 0.32 \text{ e \AA}^{-3}$ $\Delta\rho_{\min} = -0.24 \text{ e \AA}^{-3}$ Extinction correction: *SHELXL*, $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.012 (2)

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
F1	0.11305 (12)	0.18492 (6)	1.00731 (7)	0.0319 (3)
F2	-0.00219 (12)	0.14892 (7)	0.87999 (7)	0.0323 (3)
N1	0.36490 (16)	0.15195 (8)	0.86608 (9)	0.0227 (3)

N2	0.20684 (15)	0.04677 (8)	0.93336 (9)	0.0221 (3)
N3	0.03539 (17)	-0.04321 (8)	1.00022 (10)	0.0260 (4)
B1	0.0693 (2)	0.11566 (11)	0.95247 (13)	0.0243 (4)
C1	0.5141 (2)	0.26721 (11)	0.79215 (12)	0.0319 (4)
H1A	0.4310	0.2784	0.7517	0.048*
H1B	0.6132	0.2741	0.7635	0.048*
H1C	0.5071	0.3099	0.8390	0.048*
C2	0.50004 (19)	0.17214 (10)	0.82689 (11)	0.0254 (4)
C3	0.6203 (2)	0.10902 (11)	0.81609 (12)	0.0279 (4)
H3	0.7136	0.1272	0.7903	0.033*
C4	0.60339 (19)	0.02021 (11)	0.84293 (11)	0.0264 (4)
C5	0.7318 (2)	-0.04743 (12)	0.82761 (13)	0.0345 (4)
H5A	0.7073	-0.0835	0.7776	0.052*
H5B	0.7418	-0.0863	0.8772	0.052*
H5C	0.8287	-0.0158	0.8182	0.052*
C6	0.46063 (19)	-0.00410 (10)	0.88339 (11)	0.0235 (4)
C7	0.4213 (2)	-0.09362 (10)	0.91393 (11)	0.0252 (4)
H7	0.4938	-0.1404	0.9078	0.030*
C8	0.2814 (2)	-0.11140 (10)	0.95139 (11)	0.0245 (4)
H8	0.2559	-0.1699	0.9696	0.029*
C9	0.17464 (19)	-0.03837 (10)	0.96207 (11)	0.0226 (4)
C10	0.34843 (19)	0.06558 (10)	0.89359 (11)	0.0217 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
F1	0.0394 (6)	0.0203 (5)	0.0361 (7)	-0.0040 (4)	0.0109 (5)	-0.0022 (4)
F2	0.0286 (6)	0.0336 (5)	0.0347 (7)	0.0027 (4)	0.0020 (5)	0.0125 (4)
N1	0.0224 (7)	0.0230 (6)	0.0227 (8)	-0.0048 (5)	0.0010 (6)	0.0018 (5)
N2	0.0233 (7)	0.0184 (6)	0.0245 (8)	-0.0016 (5)	0.0034 (6)	0.0027 (5)
N3	0.0261 (7)	0.0154 (6)	0.0366 (9)	0.0022 (5)	0.0087 (6)	0.0039 (5)
B1	0.0260 (10)	0.0187 (8)	0.0283 (11)	-0.0004 (6)	0.0047 (8)	0.0029 (7)
C1	0.0326 (10)	0.0296 (8)	0.0335 (10)	-0.0099 (7)	0.0043 (8)	0.0039 (7)
C2	0.0269 (9)	0.0285 (8)	0.0207 (9)	-0.0076 (6)	-0.0011 (7)	0.0000 (6)
C3	0.0224 (9)	0.0368 (9)	0.0245 (9)	-0.0059 (7)	0.0019 (7)	0.0007 (7)
C4	0.0224 (8)	0.0345 (8)	0.0223 (9)	-0.0009 (6)	-0.0015 (7)	-0.0018 (7)
C5	0.0274 (9)	0.0419 (10)	0.0341 (11)	0.0045 (7)	0.0049 (8)	-0.0006 (8)
C6	0.0224 (8)	0.0282 (8)	0.0198 (9)	0.0010 (6)	0.0001 (7)	-0.0007 (6)
C7	0.0272 (9)	0.0251 (7)	0.0234 (9)	0.0044 (6)	0.0000 (7)	-0.0013 (6)
C8	0.0279 (9)	0.0193 (7)	0.0262 (9)	0.0017 (6)	0.0012 (7)	0.0009 (6)
C9	0.0245 (8)	0.0190 (7)	0.0244 (9)	-0.0005 (6)	0.0027 (7)	0.0023 (6)
C10	0.0221 (8)	0.0232 (7)	0.0197 (8)	-0.0028 (6)	0.0008 (7)	0.0001 (6)

Geometric parameters (Å, °)

F1—B1	1.377 (2)	C2—C3	1.394 (2)
F2—B1	1.367 (2)	C3—C4	1.377 (2)
N1—C2	1.337 (2)	C3—H3	0.9300

N1—C10	1.3461 (19)	C4—C6	1.416 (2)
N2—C9	1.3559 (18)	C4—C5	1.499 (2)
N2—C10	1.384 (2)	C5—H5A	0.9600
N2—B1	1.579 (2)	C5—H5B	0.9600
N3—C9	1.329 (2)	C5—H5C	0.9600
N3—N3 ⁱ	1.407 (2)	C6—C10	1.411 (2)
N3—B1 ⁱ	1.571 (2)	C6—C7	1.438 (2)
B1—N3 ⁱ	1.571 (2)	C7—C8	1.353 (2)
C1—C2	1.502 (2)	C7—H7	0.9300
C1—H1A	0.9600	C8—C9	1.417 (2)
C1—H1B	0.9600	C8—H8	0.9300
C1—H1C	0.9600		
C2—N1—C10	116.28 (14)	C3—C4—C6	117.55 (15)
C9—N2—C10	120.45 (13)	C3—C4—C5	120.28 (16)
C9—N2—B1	112.31 (13)	C6—C4—C5	122.16 (15)
C10—N2—B1	127.23 (12)	C4—C5—H5A	109.5
C9—N3—N3 ⁱ	109.50 (15)	C4—C5—H5B	109.5
C9—N3—B1 ⁱ	138.76 (12)	H5A—C5—H5B	109.5
N3 ⁱ —N3—B1 ⁱ	111.70 (16)	C4—C5—H5C	109.5
F2—B1—F1	111.22 (13)	H5A—C5—H5C	109.5
F2—B1—N3 ⁱ	111.75 (14)	H5B—C5—H5C	109.5
F1—B1—N3 ⁱ	111.63 (14)	C10—C6—C4	116.79 (14)
F2—B1—N2	114.07 (15)	C10—C6—C7	117.96 (15)
F1—B1—N2	112.80 (14)	C4—C6—C7	125.25 (15)
N3 ⁱ —B1—N2	94.35 (11)	C8—C7—C6	121.57 (14)
C2—C1—H1A	109.5	C8—C7—H7	119.2
C2—C1—H1B	109.5	C6—C7—H7	119.2
H1A—C1—H1B	109.5	C7—C8—C9	118.11 (14)
C2—C1—H1C	109.5	C7—C8—H8	120.9
H1A—C1—H1C	109.5	C9—C8—H8	120.9
H1B—C1—H1C	109.5	N3—C9—N2	112.09 (13)
N1—C2—C3	122.85 (14)	N3—C9—C8	125.89 (13)
N1—C2—C1	115.96 (15)	N2—C9—C8	122.02 (15)
C3—C2—C1	121.16 (15)	N1—C10—N2	114.83 (13)
C4—C3—C2	121.17 (16)	N1—C10—C6	125.31 (15)
C4—C3—H3	119.4	N2—C10—C6	119.85 (13)
C2—C3—H3	119.4		
C9—N2—B1—F2	-114.73 (16)	B1 ⁱ —N3—C9—N2	-178.24 (19)
C10—N2—B1—F2	66.2 (2)	N3 ⁱ —N3—C9—C8	179.03 (18)
C9—N2—B1—F1	117.11 (15)	B1 ⁱ —N3—C9—C8	1.5 (3)
C10—N2—B1—F1	-61.9 (2)	C10—N2—C9—N3	178.49 (15)
C9—N2—B1—N3 ⁱ	1.44 (17)	B1—N2—C9—N3	-0.6 (2)
C10—N2—B1—N3 ⁱ	-177.59 (15)	C10—N2—C9—C8	-1.3 (2)
C10—N1—C2—C3	-1.4 (2)	B1—N2—C9—C8	179.64 (15)
C10—N1—C2—C1	176.83 (15)	C7—C8—C9—N3	-177.38 (17)
N1—C2—C3—C4	2.4 (3)	C7—C8—C9—N2	2.3 (3)

C1—C2—C3—C4	-175.71 (16)	C2—N1—C10—N2	-179.60 (14)
C2—C3—C4—C6	-1.2 (3)	C2—N1—C10—C6	-0.7 (2)
C2—C3—C4—C5	177.65 (17)	C9—N2—C10—N1	178.44 (15)
C3—C4—C6—C10	-0.7 (2)	B1—N2—C10—N1	-2.6 (2)
C5—C4—C6—C10	-179.57 (16)	C9—N2—C10—C6	-0.5 (2)
C3—C4—C6—C7	178.76 (16)	B1—N2—C10—C6	178.48 (16)
C5—C4—C6—C7	-0.1 (3)	C4—C6—C10—N1	1.8 (3)
C10—C6—C7—C8	0.0 (2)	C7—C6—C10—N1	-177.73 (16)
C4—C6—C7—C8	-179.45 (17)	C4—C6—C10—N2	-179.38 (15)
C6—C7—C8—C9	-1.7 (2)	C7—C6—C10—N2	1.1 (2)
N3 ⁱ —N3—C9—N2	-0.7 (2)		

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C1—H1C \cdots F1 ⁱⁱ	0.96	2.54	3.291 (2)	135
C8—H8 \cdots F1 ⁱⁱⁱ	0.93	2.48	3.2434 (19)	140

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