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2-(Pyridin-2-yl)pyridinium trifluoromethanesulfonate

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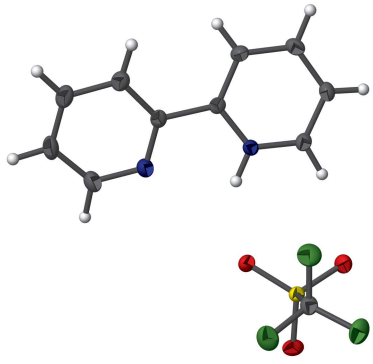
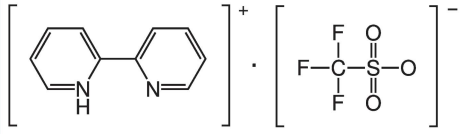
Although in the title salt, $C_{10}H_9N_2^+\cdot CF_3SO_3^-$, the C—C and C—N bond lengths within the aromatic rings are normal, there is a considerable difference in the C—N—C angles at the protonated and unprotonated N atoms, *viz*. 123.42 (10) and 117.10 (11)°, respectively. Bifurcated N—H···*X* (*X* = N or O) hydrogen bonds form within the cation and between cation and anion. As a result, the cation exists in a *cis* conformation in the solid state. An obvious π–π contact is also present between the non-protonated pyridyl rings of neighbouring cations.

3D view



Chemical scheme



Structure description

2,2'-Bipyridine (bpy) and its derivatives not only play important roles in the formation of numerous metal complexes but are also useful model compounds for dinitrogen proton sponges such as 1,8-bis(dimethylamino)naphthalene (DMAN) (Howard, 1996). Since the first report of the monoprotonated bipyridinium cation ($bpyH^+$) by Lipkowski *et al.* (1976), several crystal structures of $bpyH^+$ compounds having simple counter-anions such as ClO_4^- (Kavitha *et al.*, 2005), PF_6^- (Kraus & Breu, 2002) and BPh_4^- (Bakshi *et al.*, 1996) have been described. To the best of our knowledge, however, no structural characterization of the $bpyH^+$ cation with a trifluoromethanesulfonate (OTf^-) counter-anion has been reported.

The cation in the title salt, $(C_{10}H_9N_2^+)(CF_3SO_3^-)$, comprises the protonated ring 1 (N1/C1–C5) and the non-protonated ring 2 (N2/C6–C10) (Fig. 1). These rings are approximately parallel to each other, making a dihedral angle of 15.967 (4)°, similar to previous reports (Milani *et al.*, 1997; Kraus & Breu, 2002; Kavitha *et al.*, 2005). The deviation from planarity is considered to be caused by intramolecular (N1—H1···N2) and intermolecular hydrogen-bonding interactions (N1—H1···O1, C1—H2···O2;

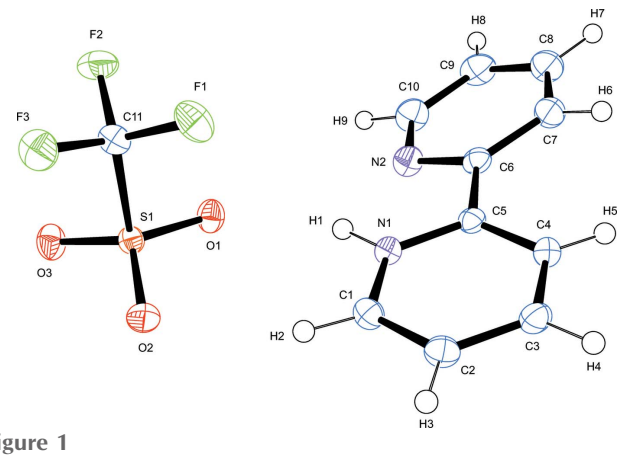


Figure 1
The structures of the molecular components in the title salt, with atom labels and displacement ellipsoids for non-H atoms drawn at the 50% probability level. H atoms are shown as small spheres of arbitrary radius.

Table 1). The hydrogen bond involving the protonated nitrogen atom N1 is bifurcated. It is connected with both intra- and intermolecular N—H···*X* (*X* = N or O) interactions and leads to a *cis* conformation in the cation. Although the C—C and C—N bond lengths within the aromatic rings are normal, bond angles around the two N atoms are different. The C—N—C angle in ring 1 is 123.42 (10)°, whereas in ring 2 it is 117.10 (11)°, in agreement with structural data for other monovalent bipyridinium cations reported so far. The protonation is associated with an increase in the C—N—C angle as the result of the strong *s*-electron-withdrawing effect of the proton. The N1—H1 bond length [0.906 (15) Å] is somewhat longer than the previously reported value [0.827 (18) Å; Kraus & Breu, 2002]. This may be due to the difference of the counter-anions. In addition, the distance between two N atoms (N1···N2) in the bpyH$^+$ cation is 2.6556 (15) Å, which is shorter than the corresponding N···N distance in protonated 1,10-phenanthroline (phen) in the structure of (phenH$^+$)(BPh_4^-), 2.709 (6) Å (Bakshi *et al.*, 1996). Although the N1—H1···N2 angle of 105.0 (11)° looks unfavourable even for a branched hydrogen bond, this interaction must be important. As a result, the intramolecular interaction may be strong enough to bend and thus reduce the N···N distance.

An obvious π–π contact is also revealed [*Cg*2···*Cg*2^{ii} = 3.7416 (8) Å; *Cg*2 is the centroid of ring 2; symmetry code: (ii) $-x+\frac{1}{2}, -y, z+\frac{1}{2}$]. This contact clearly stacks molecules along the *a*-axis direction (Fig. 2).

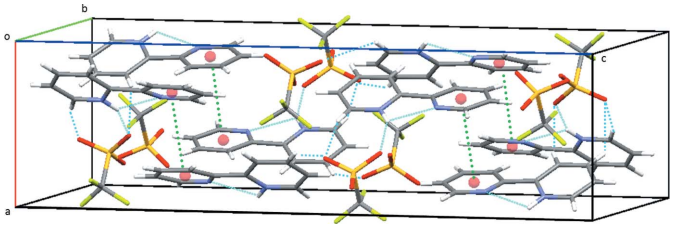


Figure 2
Overall packing of the compound viewed along *b*. Hydrogen bonds are drawn as blue dashed lines, representative π–π contacts as green dotted lines (for numerical values see Table 1). Ring centroids are shown as coloured spheres.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1	0.906 (15)	2.054 (15)	2.8705 (13)	149.3 (13)
N1—H1···N2	0.906 (15)	2.273 (15)	2.6556 (15)	105.0 (11)
C1—H2···O2	0.954 (15)	2.299 (15)	3.2072 (14)	159.0 (13)
C4—H5···O1^{i}	0.910 (15)	2.561 (15)	3.3822 (14)	150.3 (13)

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{10}H_9N_2^+\cdot CF_3O_3S^-$
M_r	306.26
Crystal system, space group	Orthorhombic, *Pbca*
Temperature (K)	93
a, *b*, *c* (Å)	7.37174 (13), 12.5726 (3), 26.4454 (5)
V (Å^3)	2451.02 (8)
Z	8
Radiation type	Mo *Kα*
μ (mm^{-1})	0.31
Crystal size (mm)	0.22 × 0.20 × 0.10
Data collection	
Diffractometer	Rigaku Saturn70
Absorption correction	Multi-scan (*REQAB*; Rigaku, 1998)
T_{min}, T_{max}	0.892, 0.969
No. of measured, independent and observed [$F^2 > 2.0\sigma(F^2)$] reflections	23637, 2792, 2645
R_{int}	0.017
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.028, 0.077, 1.04
No. of reflections	2792
No. of parameters	208
H-atom treatment	Only H-atom coordinates refined
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.55, −0.27

Computer programs: *CrystalClear* (Rigaku, 2008), *SIR92* (Altomare *et al.*, 1993), *SHELXL97* (Sheldrick, 2008), *Mercury* (Macrae *et al.*, 2008), *ORTEP-3 for Windows* (Farrugia, 2012), *CrystalStructure* (Rigaku, 2010), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

Synthesis and crystallization

The title compound was synthesized according to the method of Milani *et al.* (1997). Single crystals suitable for X-ray analysis were obtained directly from reaction mixture.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

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full crystallographic data

IUCrData (2017). **2**, x170689 [https://doi.org/10.1107/S2414314617006897]

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2-(Pyridin-2-yl)pyridinium trifluoromethanesulfonate

Crystal data

$C_{10}H_9N_2^+·CF_3O_3S^-$
M_r = 306.26
Orthorhombic, *Pbca*
Hall symbol: -P 2ac 2ab
a = 7.37174 (13) Å
b = 12.5726 (3) Å
c = 26.4454 (5) Å
V = 2451.02 (8) Å^3
Z = 8
F(000) = 1248.00
D_x = 1.660 Mg m^{-3}
Mo *Kα* radiation, λ = 0.71075 Å
Cell parameters from 22516 reflections
θ = 3.2–27.5°
μ = 0.31 mm^{-1}
T = 93 K
Prism, yellow
0.22 × 0.20 × 0.10 mm

Data collection

Rigaku Saturn70 diffractometer
Detector resolution: 7.143 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*REQAB*; Rigaku, 1998)
T_{min} = 0.892, T_{max} = 0.969
23637 measured reflections
2792 independent reflections
2645 reflections with $F^2 > 2.0\sigma(F^2)$
R_{int} = 0.017
θ_{max} = 27.5°
h = −9→9
k = −16→16
l = −33→34

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.077
S = 1.04
2792 reflections
208 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
Only H-atom coordinates refined
$w = 1/[\sigma^2(F_o^2) + (0.0413P)^2 + 1.2577P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.55 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}

Special details

Refinement. Refinement was performed using all reflections. The weighted *R*-factor (*wR*) and goodness of fit (*S*) are based on F^2. *R*-factor (gt) are based on *F*. The threshold expression of $F^2 > 2.0$ sigma(F^2) is used only for calculating *R*-factor (gt).
All H atoms were identified in a difference Fourier map and their positions refined freely with U_{iso}(H) = 1.2U_{eq}(C,N).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.73669 (4)	−0.04002 (2)	0.591120 (10)	0.01655 (10)
F1	0.87891 (12)	0.14988 (6)	0.58423 (3)	0.03090 (19)
F2	1.02567 (11)	0.04361 (6)	0.63335 (3)	0.02992 (19)
F3	1.04474 (11)	0.02562 (6)	0.55249 (3)	0.02982 (19)
O1	0.62575 (11)	0.00477 (7)	0.63122 (3)	0.02162 (19)
O2	0.66074 (12)	−0.02773 (7)	0.54113 (3)	0.0240 (2)
O3	0.81362 (12)	−0.14243 (7)	0.60200 (3)	0.0244 (2)
N1	0.38986 (13)	0.17987 (8)	0.60824 (4)	0.0168 (2)
N2	0.36613 (15)	0.16588 (8)	0.70822 (4)	0.0233 (3)
C1	0.38861 (16)	0.16817 (9)	0.55786 (4)	0.0198 (3)
C2	0.30132 (17)	0.24209 (10)	0.52815 (4)	0.0215 (3)
C3	0.21711 (17)	0.32785 (10)	0.55133 (5)	0.0222 (3)
C4	0.21855 (16)	0.33665 (9)	0.60371 (5)	0.0201 (3)
C5	0.30751 (14)	0.26105 (9)	0.63239 (4)	0.0169 (3)
C6	0.31646 (15)	0.25954 (10)	0.68827 (4)	0.0192 (3)
C7	0.27456 (18)	0.34882 (11)	0.71704 (5)	0.0253 (3)
C8	0.2822 (2)	0.33986 (12)	0.76928 (5)	0.0300 (3)
C9	0.32996 (19)	0.24359 (12)	0.79048 (5)	0.0300 (3)
C10	0.3724 (2)	0.15936 (11)	0.75864 (5)	0.0286 (3)
C11	0.93188 (17)	0.04896 (9)	0.59007 (4)	0.0202 (3)
H1	0.450 (2)	0.1312 (12)	0.6272 (6)	0.0202*
H2	0.451 (2)	0.1073 (12)	0.5452 (6)	0.0238*
H3	0.302 (2)	0.2305 (12)	0.4933 (6)	0.0258*
H4	0.156 (2)	0.3816 (13)	0.5318 (6)	0.0266*
H5	0.159 (2)	0.3907 (12)	0.6195 (6)	0.0241*
H6	0.243 (3)	0.4154 (14)	0.7015 (6)	0.0303*
H7	0.259 (3)	0.4006 (14)	0.7890 (7)	0.0359*
H8	0.337 (3)	0.2359 (13)	0.8263 (7)	0.0360*
H9	0.405 (3)	0.0867 (14)	0.7717 (6)	0.0343*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.01725 (15)	0.01533 (15)	0.01708 (15)	0.00033 (10)	0.00052 (10)	0.00012 (9)
F1	0.0425 (5)	0.0156 (4)	0.0346 (5)	−0.0025 (4)	0.0017 (4)	0.0019 (3)
F2	0.0273 (4)	0.0362 (5)	0.0262 (4)	−0.0049 (4)	−0.0077 (3)	−0.0036 (3)
F3	0.0272 (4)	0.0338 (4)	0.0285 (4)	−0.0052 (3)	0.0110 (3)	−0.0019 (3)
O1	0.0217 (4)	0.0236 (5)	0.0196 (4)	0.0039 (4)	0.0040 (4)	0.0014 (4)
O2	0.0241 (5)	0.0279 (5)	0.0199 (5)	0.0020 (4)	−0.0043 (4)	−0.0039 (4)
O3	0.0257 (5)	0.0157 (4)	0.0317 (5)	0.0023 (4)	0.0031 (4)	0.0029 (4)
N1	0.0166 (5)	0.0174 (5)	0.0165 (5)	0.0004 (4)	0.0005 (4)	0.0013 (4)
N2	0.0241 (5)	0.0272 (6)	0.0187 (5)	0.0023 (5)	0.0006 (4)	0.0016 (4)
C1	0.0210 (6)	0.0198 (6)	0.0186 (6)	−0.0008 (5)	0.0027 (5)	−0.0007 (5)
C2	0.0246 (6)	0.0240 (6)	0.0159 (6)	−0.0015 (5)	−0.0006 (5)	0.0006 (5)
C3	0.0221 (6)	0.0220 (6)	0.0225 (6)	0.0010 (5)	−0.0054 (5)	0.0021 (5)

C4	0.0191 (6)	0.0195 (6)	0.0217 (6)	0.0029 (5)	−0.0014 (5)	−0.0024 (5)
C5	0.0135 (5)	0.0189 (5)	0.0182 (5)	−0.0011 (4)	0.0003 (4)	−0.0011 (4)
C6	0.0151 (5)	0.0248 (6)	0.0178 (6)	−0.0002 (5)	0.0005 (4)	−0.0010 (5)
C7	0.0262 (7)	0.0277 (7)	0.0219 (6)	0.0028 (5)	−0.0006 (5)	−0.0035 (5)
C8	0.0317 (8)	0.0368 (8)	0.0213 (6)	0.0036 (6)	−0.0004 (5)	−0.0084 (6)
C9	0.0303 (7)	0.0438 (8)	0.0161 (6)	0.0004 (6)	−0.0000 (5)	−0.0010 (6)
C10	0.0316 (7)	0.0343 (7)	0.0199 (6)	0.0023 (6)	−0.0009 (5)	0.0040 (5)
C11	0.0228 (6)	0.0190 (6)	0.0189 (6)	−0.0018 (5)	0.0007 (5)	−0.0006 (4)

Geometric parameters (Å, º)

S1—O1	1.4528 (9)	C5—C6	1.4794 (15)
S1—O2	1.4440 (9)	C6—C7	1.3908 (19)
S1—O3	1.4360 (10)	C7—C8	1.3872 (19)
S1—C11	1.8228 (13)	C8—C9	1.380 (2)
F1—C11	1.3365 (14)	C9—C10	1.389 (2)
F2—C11	1.3389 (14)	N1—H1	0.906 (15)
F3—C11	1.3289 (14)	C1—H2	0.954 (15)
N1—C1	1.3404 (15)	C2—H3	0.934 (16)
N1—C5	1.3484 (15)	C3—H4	0.962 (16)
N2—C6	1.3413 (16)	C4—H5	0.911 (15)
N2—C10	1.3367 (17)	C7—H6	0.961 (17)
C1—C2	1.3766 (17)	C8—H7	0.940 (17)
C2—C3	1.3870 (18)	C9—H8	0.953 (19)
C3—C4	1.3897 (19)	C10—H9	1.006 (17)
C4—C5	1.3816 (17)		
F1···O1	2.8906 (12)	F1···H3^{ii}	2.605 (16)
F1···O2	2.9786 (12)	F1···H4^{ii}	3.503 (16)
F2···O1	2.9888 (12)	F1···H8^{iv}	2.620 (18)
F2···O3	2.9329 (12)	F2···H1^{iii}	3.318 (15)
F3···O2	2.9246 (12)	F2···H5^{v}	3.040 (15)
F3···O3	3.0135 (12)	F2···H6^{v}	2.956 (17)
N1···N2	2.6556 (15)	F2···H7^{viii}	3.443 (17)
N1···C3	2.7108 (17)	F2···H8^{iv}	2.986 (17)
N2···C8	2.7883 (18)	F2···H9^{iv}	2.719 (17)
C1···C4	2.7439 (17)	F3···H2^{iii}	3.173 (16)
C2···C5	2.7673 (15)	F3···H3^{iii}	3.561 (16)
C4···C7	3.0292 (19)	F3···H4^{v}	2.905 (16)
C6···C9	2.7122 (17)	F3···H5^{v}	3.286 (15)
C7···C10	2.721 (2)	O1···H1	2.054 (15)
F1···O3^{i}	3.0089 (12)	O1···H2	2.914 (15)
F1···C2^{ii}	3.3173 (14)	O1···H5^{vii}	2.560 (15)
F1···C3^{iii}	3.4611 (15)	O1···H6^{vii}	3.481 (17)
F1···C4^{iii}	3.4710 (15)	O1···H7^{viii}	2.626 (17)
F1···C9^{iv}	3.5351 (16)	O1···H8^{viii}	3.572 (17)
F2···N1^{iii}	3.2532 (13)	O1···H8^{iv}	3.485 (17)
F2···N2^{iii}	3.5472 (14)	O1···H9^{iv}	3.448 (17)

F2···C4^{v}	3.3076 (14)	O2···H1	3.404 (15)
F2···C5^{iii}	3.4338 (14)	O2···H2	2.298 (16)
F2···C9^{iv}	3.5300 (17)	O2···H2^{ix}	2.626 (15)
F2···C10^{iv}	3.3991 (16)	O2···H3^{ix}	2.721 (16)
F3···F3^{vi}	2.9253 (12)	O2···H4^{vii}	2.611 (16)
F3···O2^{vi}	3.2931 (12)	O2···H4^{ii}	2.664 (16)
F3···N1^{iii}	3.5224 (13)	O2···H5^{vii}	3.301 (15)
F3···C1^{iii}	3.1077 (14)	O3···H1^{v}	3.404 (15)
F3···C2^{iii}	3.3762 (15)	O3···H3^{ix}	2.881 (16)
F3···C3^{v}	3.0439 (15)	O3···H5^{vii}	3.538 (15)
F3···C4^{v}	3.2441 (15)	O3···H7^{viii}	2.982 (17)
O1···N1	2.8705 (13)	O3···H8^{viii}	2.678 (18)
O1···N2	3.4514 (14)	N2···H6^{vii}	3.255 (17)
O1···C1	3.3227 (14)	N2···H9^{xiii}	3.583 (17)
O1···C4^{vii}	3.3821 (15)	C1···H3^{ii}	3.568 (16)
O1···C8^{viii}	3.4180 (17)	C1···H4^{ii}	3.147 (16)
O2···F3^{vi}	3.2931 (12)	C2···H4^{ii}	3.431 (16)
O2···O2^{ix}	3.2916 (12)	C3···H2^{xi}	3.320 (15)
O2···C1	3.2072 (15)	C3···H3^{xi}	3.362 (16)
O2···C1^{ix}	3.1785 (14)	C4···H8^{xiii}	3.596 (18)
O2···C2^{ix}	3.2708 (15)	C6···H8^{xiii}	3.565 (18)
O2···C3^{vii}	3.3359 (16)	C7···H9^{xii}	3.575 (17)
O2···C3^{ii}	3.5308 (16)	C8···H9^{xii}	3.396 (17)
O3···F1^{v}	3.0089 (12)	C10···H6^{vii}	3.524 (17)
O3···N1^{v}	3.1300 (14)	C10···H7^{vii}	3.487 (18)
O3···C1^{v}	3.4426 (15)	C11···H8^{iv}	3.302 (18)
O3···C4^{v}	3.4590 (15)	H1···S1	3.165 (15)
O3···C5^{v}	3.1494 (14)	H1···F1	3.370 (15)
O3···C8^{viii}	3.4837 (16)	H1···F2^{x}	3.318 (15)
O3···C9^{viii}	3.3554 (16)	H1···O1	2.054 (15)
N1···F2^{x}	3.2532 (13)	H1···O2	3.404 (15)
N1···F3^{x}	3.5224 (13)	H1···O3^{i}	3.404 (15)
N1···O1	2.8705 (13)	H1···H5^{vii}	3.13 (2)
N1···O3^{i}	3.1300 (14)	H1···H8^{iv}	3.38 (3)
N2···F2^{x}	3.5472 (14)	H2···S1	3.055 (15)
N2···O1	3.4514 (14)	H2···F1	3.361 (16)
N2···C9^{iv}	3.5562 (18)	H2···F3^{x}	3.173 (16)
C1···F3^{x}	3.1077 (14)	H2···O1	2.914 (15)
C1···O1	3.3227 (14)	H2···O2	2.298 (16)
C1···O2	3.2072 (15)	H2···O2^{ix}	2.626 (15)
C1···O2^{ix}	3.1785 (14)	H2···C3^{ii}	3.320 (15)
C1···O3^{i}	3.4426 (15)	H2···H3^{ii}	3.45 (3)
C2···F1^{xi}	3.3173 (14)	H2···H4^{vii}	2.97 (3)
C2···F3^{x}	3.3762 (15)	H2···H4^{ii}	2.54 (3)
C2···O2^{ix}	3.2708 (15)	H2···H5^{vii}	3.45 (3)
C3···F1^{x}	3.4611 (15)	H3···S1^{ix}	3.286 (16)
C3···F3^{i}	3.0439 (15)	H3···F1^{xi}	2.605 (16)
C3···O2^{xii}	3.3359 (16)	H3···F3^{x}	3.561 (16)

C3···O2^{xi}	3.5308 (16)	H3···O2^{ix}	2.721 (16)
C4···F1^{x}	3.4710 (15)	H3···O3^{ix}	2.881 (16)
C4···F2^{i}	3.3076 (14)	H3···C1^{xi}	3.568 (16)
C4···F3^{i}	3.2441 (15)	H3···C3^{ii}	3.362 (16)
C4···O1^{xii}	3.3822 (15)	H3···H2^{xi}	3.45 (3)
C4···O3^{i}	3.4590 (15)	H3···H4^{ii}	3.04 (3)
C5···F2^{x}	3.4338 (14)	H4···S1^{xii}	3.438 (16)
C5···O3^{i}	3.1494 (14)	H4···F1^{xi}	3.503 (16)
C7···C9^{xiii}	3.540 (2)	H4···F3^{i}	2.905 (16)
C8···O1^{xiv}	3.4180 (17)	H4···O2^{xii}	2.611 (16)
C8···O3^{xiv}	3.4837 (16)	H4···O2^{xi}	2.664 (16)
C9···F1^{xiii}	3.5351 (16)	H4···C1^{xi}	3.147 (16)
C9···F2^{xiii}	3.5300 (17)	H4···C2^{xi}	3.431 (16)
C9···O3^{xiv}	3.3554 (16)	H4···H2^{xii}	2.97 (3)
C9···N2^{xiii}	3.5562 (18)	H4···H2^{xi}	2.54 (3)
C9···C7^{iv}	3.540 (2)	H4···H3^{xi}	3.04 (3)
C10···F2^{xiii}	3.3991 (16)	H5···S1^{xii}	3.134 (15)
N1···H3	3.173 (16)	H5···F2^{i}	3.040 (15)
N1···H5	3.165 (15)	H5···F3^{i}	3.286 (15)
N2···H1	2.273 (15)	H5···O1^{xii}	2.560 (15)
N2···H6	3.271 (17)	H5···O2^{xii}	3.301 (15)
N2···H8	3.251 (19)	H5···O3^{xii}	3.538 (15)
C1···H4	3.257 (16)	H5···H1^{xii}	3.13 (2)
C2···H1	3.162 (15)	H5···H2^{xii}	3.45 (3)
C2···H5	3.230 (16)	H5···H8^{xiii}	3.38 (3)
C3···H2	3.270 (16)	H6···F2^{i}	2.956 (17)
C4···H1	3.157 (15)	H6···O1^{xii}	3.481 (17)
C4···H3	3.269 (16)	H6···N2^{xii}	3.255 (17)
C4···H6	2.774 (16)	H6···C10^{xii}	3.524 (17)
C5···H2	3.189 (15)	H6···H7^{xiii}	3.59 (3)
C5···H4	3.259 (16)	H6···H9^{xii}	3.05 (3)
C5···H6	2.707 (17)	H6···H9^{xiv}	3.44 (3)
C6···H1	2.486 (15)	H7···S1^{xiv}	3.258 (17)
C6···H5	2.716 (15)	H7···F2^{xiv}	3.443 (17)
C6···H7	3.227 (17)	H7···O1^{xiv}	2.626 (17)
C6···H9	3.165 (17)	H7···O3^{xiv}	2.982 (17)
C7···H5	2.767 (16)	H7···C10^{xii}	3.487 (18)
C7···H8	3.252 (18)	H7···H6^{iv}	3.59 (3)
C8···H9	3.310 (17)	H7···H9^{xii}	2.67 (3)
C9···H6	3.259 (17)	H8···F1^{xiii}	2.620 (18)
C10···H1	3.541 (15)	H8···F2^{xiii}	2.986 (17)
C10···H7	3.247 (18)	H8···O1^{xiv}	3.572 (17)
H1···H2	2.19 (2)	H8···O1^{xiii}	3.485 (17)
H2···H3	2.34 (3)	H8···O3^{xiv}	2.678 (18)
H3···H4	2.41 (3)	H8···C4^{iv}	3.596 (18)
H4···H5	2.32 (3)	H8···C6^{iv}	3.565 (18)
H5···H6	2.28 (3)	H8···C11^{xiii}	3.302 (18)
H6···H7	2.32 (3)	H8···H1^{xiii}	3.38 (3)

H7···H8	2.37 (3)	H8···H5^{iv}	3.38 (3)
H8···H9	2.42 (3)	H9···F2^{xiii}	2.719 (17)
S1···H1	3.165 (15)	H9···O1^{xiii}	3.448 (17)
S1···H2	3.055 (15)	H9···N2^{iv}	3.583 (17)
S1···H3^{ix}	3.286 (16)	H9···C7^{vii}	3.575 (17)
S1···H4^{vii}	3.438 (16)	H9···C8^{vii}	3.396 (17)
S1···H5^{vii}	3.134 (15)	H9···H6^{vii}	3.05 (3)
S1···H7^{viii}	3.258 (17)	H9···H6^{viii}	3.44 (3)
F1···H1	3.370 (15)	H9···H7^{vii}	2.67 (3)
F1···H2	3.361 (16)		

O1—S1—O2	114.11 (5)	S1—C11—F2	111.33 (8)
O1—S1—O3	115.06 (5)	S1—C11—F3	111.72 (8)
O1—S1—C11	102.57 (5)	F1—C11—F2	107.30 (9)
O2—S1—O3	115.63 (5)	F1—C11—F3	107.83 (9)
O2—S1—C11	103.09 (5)	F2—C11—F3	107.75 (10)
O3—S1—C11	103.98 (6)	C1—N1—H1	118.6 (10)
C1—N1—C5	123.42 (10)	C5—N1—H1	118.0 (10)
C6—N2—C10	117.10 (11)	N1—C1—H2	115.7 (9)
N1—C1—C2	119.76 (11)	C2—C1—H2	124.6 (9)
C1—C2—C3	118.80 (11)	C1—C2—H3	117.2 (10)
C2—C3—C4	119.94 (12)	C3—C2—H3	124.0 (10)
C3—C4—C5	119.74 (11)	C2—C3—H4	121.2 (10)
N1—C5—C4	118.32 (11)	C4—C3—H4	118.9 (10)
N1—C5—C6	116.32 (10)	C3—C4—H5	120.9 (10)
C4—C5—C6	125.34 (11)	C5—C4—H5	119.4 (10)
N2—C6—C5	114.61 (11)	C6—C7—H6	121.5 (10)
N2—C6—C7	123.64 (11)	C8—C7—H6	120.5 (10)
C5—C6—C7	121.75 (11)	C7—C8—H7	118.5 (11)
C6—C7—C8	118.05 (13)	C9—C8—H7	122.3 (11)
C7—C8—C9	119.10 (13)	C8—C9—H8	120.4 (10)
C8—C9—C10	118.69 (13)	C10—C9—H8	120.8 (10)
N2—C10—C9	123.39 (13)	N2—C10—H9	114.0 (10)
S1—C11—F1	110.72 (9)	C9—C10—H9	122.6 (10)

O1—S1—C11—F1	−54.89 (8)	N1—C1—C2—C3	0.38 (17)
O1—S1—C11—F2	64.39 (8)	C1—C2—C3—C4	−1.40 (18)
O1—S1—C11—F3	−175.08 (7)	C2—C3—C4—C5	1.45 (18)
O2—S1—C11—F1	63.90 (8)	C3—C4—C5—N1	−0.46 (16)
O2—S1—C11—F2	−176.82 (7)	C3—C4—C5—C6	−178.67 (10)
O2—S1—C11—F3	−56.30 (9)	N1—C5—C6—N2	−15.39 (14)
O3—S1—C11—F1	−175.07 (7)	N1—C5—C6—C7	165.14 (9)
O3—S1—C11—F2	−55.79 (8)	C4—C5—C6—N2	162.84 (10)
O3—S1—C11—F3	64.73 (8)	C4—C5—C6—C7	−16.62 (17)
C1—N1—C5—C4	−0.60 (16)	N2—C6—C7—C8	−0.93 (18)
C1—N1—C5—C6	177.77 (9)	C5—C6—C7—C8	178.48 (10)
C5—N1—C1—C2	0.64 (17)	C6—C7—C8—C9	−0.25 (19)
C6—N2—C10—C9	0.20 (19)	C7—C8—C9—C10	1.3 (2)

C10—N2—C6—C5	−178.50 (10)	C8—C9—C10—N2	−1.3 (3)
C10—N2—C6—C7	0.95 (17)		

Symmetry codes: (i) −*x*+3/2, *y*+1/2, *z*; (ii) *x*+1/2, −*y*+1/2, −*z*+1; (iii) *x*+1, *y*, *z*; (iv) *x*+1/2, *y*, −*z*+3/2; (v) −*x*+3/2, *y*−1/2, *z*; (vi) −*x*+2, −*y*, −*z*+1; (vii) −*x*+1/2, *y*−1/2, *z*; (viii) −*x*+1, *y*−1/2, −*z*+3/2; (ix) −*x*+1, −*y*, −*z*+1; (x) *x*−1, *y*, *z*; (xi) *x*−1/2, −*y*+1/2, −*z*+1; (xii) −*x*+1/2, *y*+1/2, *z*; (xiii) *x*−1/2, *y*, −*z*+3/2; (xiv) −*x*+1, *y*+1/2, −*z*+3/2.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1	0.906 (15)	2.054 (15)	2.8705 (13)	149.3 (13)
N1—H1···N2	0.906 (15)	2.273 (15)	2.6556 (15)	105.0 (11)
C1—H2···O2	0.954 (15)	2.299 (15)	3.2072 (14)	159.0 (13)
C4—H5···O1^{xii}	0.910 (15)	2.561 (15)	3.3822 (14)	150.3 (13)

Symmetry code: (xii) −*x*+1/2, *y*+1/2, *z*.