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Crystal structure of fipronil

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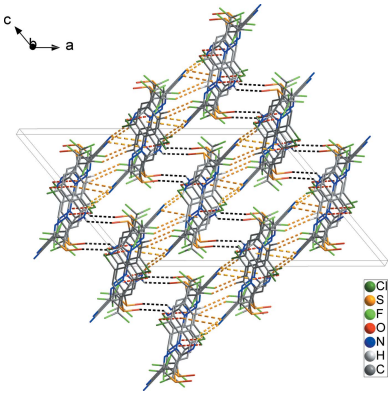
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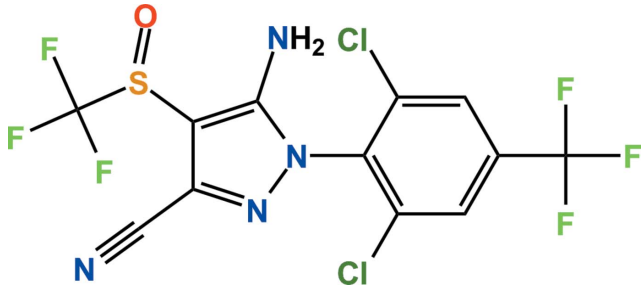
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The title compound, $C_{12}H_4Cl_2F_6N_4OS$ {systematic name: 5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-[(trifluoromethane)sulfinyl]-1*H*-pyrazole-3-carbonitrile}, is a member of the phenylpyrazole group of acaricides, and one of the phenylpyrazole group of insecticides. The dihedral angle between the planes of the pyrazole and benzene rings is 89.03 (9)°. The fluorine atoms of the trifluoromethyl substituent on the benzene ring are disordered over two sets of sites, with occupancy ratios 0.620 (15):0.380 (15). In the crystal, C—N···π interactions [N···ring centroid = 3.607 (4) Å] together with N—H···N and C—H···F hydrogen bonds form a looped chain structure along [10$\bar{1}$]. Finally, N—H···O hydrogen bonds and C—Cl···π interactions [Cl···ring centroid = 3.5159 (16) Å] generate a three-dimensional structure. Additionally, there are a short intermolecular F··· F contacts present.

1. Chemical context

Fipronil is an insecticide that belongs to the phenylpyrazole group. It is an insecticide with extended use in the control of many agricultural vermin. Fipronil contains a trifluoromethylsulfinyl substituent that is not present in any other agrochemicals and this is thought to contribute to its remarkable potency in the field (Hainzl & Casida, 1996). In addition, it is a highly effective and broad-spectrum insecticide against piercing–sucking, contact and chewing pests and is widely used to control many species of soil and foliar insects on various crops including rice, vegetables and fruits (Kaur *et al.*, 2015). The toxicity of fipronil is attributed to its ability to act at the GABA receptor as a non-competitive inhibitor of the GABA-gated chloride channels of neurons in the central nervous system. Impediments to the influx of the chloride ions affect the transmission of nervous impulses, causing insect death by neuronal hyperexcitation and paralysis (Medeiros *et al.*, 2015). Recently, eggs contaminated with fipronil have been found in Europe, Hong Kong and the Republic of Korea. We report here the crystal structure of fipronil, 5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-(trifluoromethanesulfinyl)-1*H*-pyrazole-3-carbonitrile.





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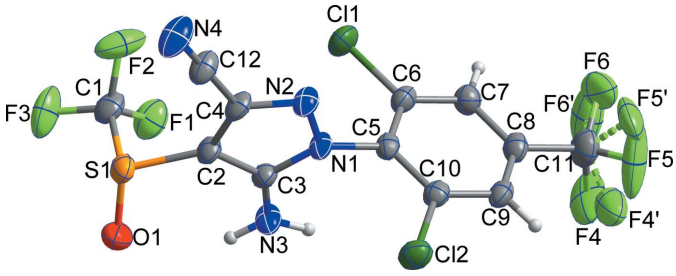


Figure 1
The structure of the title compound, with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as small spheres of arbitrary radius.

2. Structural commentary

The molecular structure of the title compound is shown in Fig. 1. The dihedral angle between the planes of the pyrazole and benzene rings is 89.03 (9)°. All bond lengths and bond angles are normal and comparable to those observed in similar crystal structures (Kang *et al.*, 2015; Jiang & Xu, 2009).

3. Supramolecular features

In the crystal, molecules are linked by C12—N4···*Cg*1^{iii} interactions [N···*Cg*1 = 3.607 (4) Å; *Cg*1 is the centroid of the C5–C10 ring; symmetry code: (iii) $-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$], together with N3—H3*A*···N4^{i} and C9—H9···F2^{i} hydrogen bonds, forming looped chains along [10$\bar{1}$] (Fig. 2). Inversion-related C10—Cl2···*Cg*1^{iv} interactions [Cl···*Cg*1 = 3.5159 (16)Å; symmetry code: (iv) $2-x, -y, 2-z$] (red dashed lines), link adjacent chains, resulting in a two-dimensional network parallel to the (10$\bar{1}$) plane (Fig. 3). Finally, classical N3—H3*B*···O1^{ii} hydrogen bonds (black dashed lines) combine with these contacts to generate a three-dimensional network structure (Fig. 4 and Table 1). Short F2···F4′^{v} [2.762 (14) Å] and F3···F6′^{vi} [2.855 (12) Å] interactions are also present [symmetry codes: (v) $-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$; (vi) $-\frac{1}{2}+x, \frac{1}{2}+y, -1+z$].

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3*A*···N4^{i}	0.88	2.39	3.183 (3)	151
N3—H3*B*···O1^{ii}	0.88	2.28	2.896 (3)	127
C9—H9···F2^{i}	0.95	2.42	3.222 (3)	143

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

4. Database survey

The title compound has been used as a starting material for the synthesis of other materials (Tang *et al.*, 2005; Liu *et al.*, 2013). Moreover, the structures of Cu^{II}, Cd^{II}, Zn^{II} and Mn^{II} complexes using fipronil as a ligand are known (Tang *et al.*, 2009, 2010). The crystal structures of other phenylpyrazole compounds such as ethyl 7-methyl-2-phenylpyrazolo[1,5-*a*]-pyrimidine-5-carboxylate (Bassoude *et al.*, 2013) and 4-{[(*E*)-(3,5-dimethyl-1-phenyl-1*H*-pyrazol-4-yl)methylidene]amino}-1,5-dimethyl-2-phenyl-1*H*-pyrazol-3(2*H*)-one (Fun *et al.*, 2010) have also been reported.

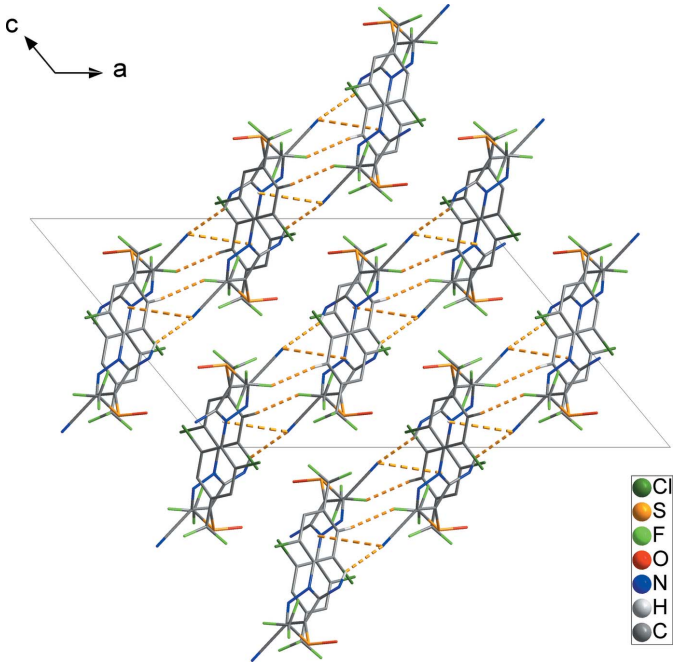


Figure 2
A view along the *b* axis of the crystal packing of the title compound. Looped chains are formed through intermolecular C—N···π interactions together with N—H···N and C—H···F hydrogen bonds (yellow dashed lines). H atoms not involved in intermolecular interactions have been omitted for clarity.

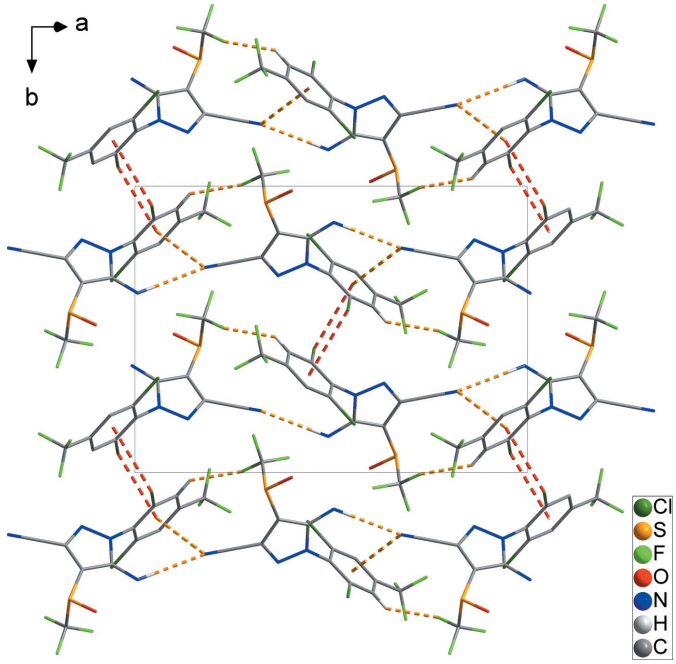


Figure 3
The two-dimensional network formed through intermolecular C—Cl···π interactions (red dashed lines). H atoms not involved in intermolecular interactions have been omitted for clarity.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{12}H_4Cl_2F_6N_4OS$
M_r	437.15
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	173
a, *b*, *c* (Å)	22.5649 (16), 12.6823 (9), 14.9051 (11)
β (°)	129.699 (3)
V (Å^3)	3281.9 (4)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.60
Crystal size (mm)	0.15 × 0.13 × 0.04
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2014)
T_{min}, T_{max}	0.587, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	14125, 3731, 2506
R_{int}	0.066
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.648
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.048, 0.120, 1.03
No. of reflections	3731
No. of parameters	263
No. of restraints	36
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.38, −0.32

Computer programs: *APEX2* and *SAINT* (Bruker, 2014), *SHELXS97* and *SHELXTL* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *DIAMOND* (Brandenburg, 2010) and *publCIF* (Westrip, 2010).

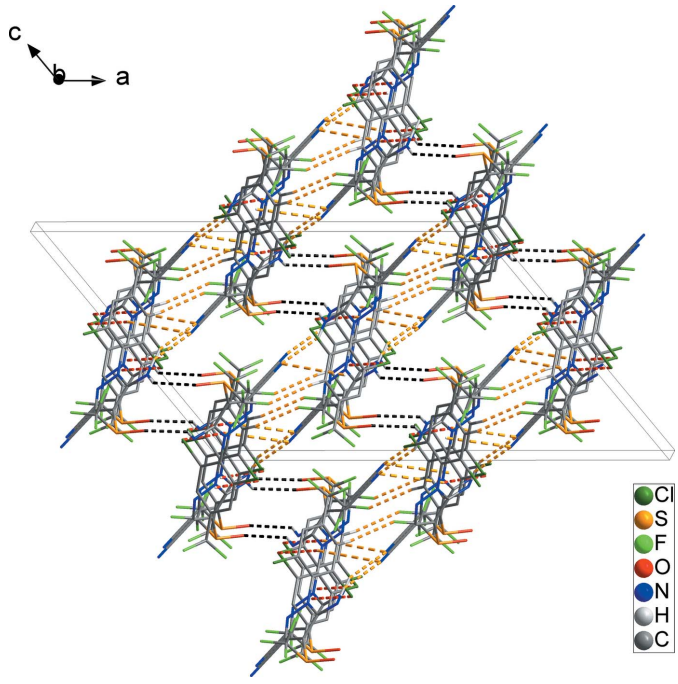


Figure 4
The overall packing of the title compound, showing the three-dimensional network formed through N—H···O hydrogen bonds (black dashed lines). H atoms not involved in intermolecular interactions have been omitted for clarity.

5. Synthesis and crystallization

The title compound was purchased from Dr. Ehrenstorfer GmbH. Colourless single crystals suitable for X-ray diffraction were obtained from a CH_3CN solution by slow evaporation at room temperature.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms were positioned geometrically and refined using a riding model with d(N—H) = 0.88 Å, U_{iso} = 1.2U_{eq}(C) for the N—H group, d(C—H) = 0.95 Å, U_{iso} = 1.2U_{eq}(C) for aromatic C—H. Atoms F4–F6 of the CF_3 substituent are disordered over two sets of sites. Their occupancies refined to 0.620 (15) and 0.380 (15).

Funding information

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Computing details

Data collection: *APEX2* (Bruker, 2014); cell refinement: *SAINT* (Bruker, 2014); data reduction: *SAINT* (Bruker, 2014); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *DIAMOND* (Brandenburg, 2010); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008) and *publCIF* (Westrip, 2010).

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-[(trifluoromethanesulfinyl])-1*H*-pyrazole-3-carbonitrile

Crystal data

$C_{12}H_4Cl_2F_6N_4OS$
$M_r = 437.15$
Monoclinic, $C2/c$
$a = 22.5649$ (16) Å
$b = 12.6823$ (9) Å
$c = 14.9051$ (11) Å
$\beta = 129.699$ (3)°
$V = 3281.9$ (4) Å^3
$Z = 8$
$F(000) = 1728$
$D_x = 1.769$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2101 reflections
$\theta = 2.4$–$21.6°$
$\mu = 0.60$ mm^{-1}
$T = 173$ K
Plate, colourless
0.15 × 0.13 × 0.04 mm

Data collection

Bruker APEXII CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2014)
$T_{min} = 0.587$, $T_{max} = 0.746$
14125 measured reflections
3731 independent reflections
2506 reflections with $I > 2\sigma(I)$
$R_{int} = 0.066$
$\theta_{max} = 27.4°$, $\theta_{min} = 2.0°$
$h = -28 \rightarrow 29$
$k = -16 \rightarrow 16$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.120$
$S = 1.03$
3731 reflections
263 parameters
36 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0463P)^2 + 0.8977P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.38$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Cl1	0.94088 (4)	0.32995 (6)	1.06637 (7)	0.0429 (2)	
Cl2	1.04310 (4)	0.06765 (6)	0.90739 (7)	0.0417 (2)	
S1	0.83382 (4)	0.44166 (6)	0.63886 (6)	0.0337 (2)	
F1	0.89072 (10)	0.55280 (14)	0.83001 (16)	0.0516 (5)	
F2	0.77293 (11)	0.50457 (17)	0.7312 (2)	0.0695 (7)	
F3	0.80245 (12)	0.62984 (14)	0.66925 (18)	0.0673 (6)	
F4	1.2426 (3)	0.1359 (8)	1.3877 (5)	0.084 (2)	0.620 (15)
F5	1.1906 (7)	−0.0112 (5)	1.3561 (5)	0.110 (4)	0.620 (15)
F6	1.1641 (4)	0.1123 (8)	1.4199 (6)	0.075 (2)	0.620 (15)
F4′	1.2399 (5)	0.0680 (16)	1.3697 (9)	0.081 (4)	0.380 (15)
F5′	1.1577 (6)	−0.0083 (10)	1.3614 (9)	0.075 (3)	0.380 (15)
F6′	1.1875 (10)	0.1483 (11)	1.4220 (10)	0.092 (5)	0.380 (15)
O1	0.89951 (12)	0.48383 (17)	0.6504 (2)	0.0470 (6)	
N1	0.93791 (12)	0.22985 (17)	0.88474 (19)	0.0279 (5)	
N2	0.86486 (12)	0.18765 (17)	0.8196 (2)	0.0321 (6)	
N3	1.00700 (13)	0.37326 (19)	0.8898 (2)	0.0376 (6)	
H3A	1.0499	0.3510	0.9563	0.045*	
H3B	1.0072	0.4310	0.8572	0.045*	
N4	0.67806 (14)	0.2159 (2)	0.5679 (3)	0.0525 (8)	
C1	0.82489 (17)	0.5375 (2)	0.7227 (3)	0.0398 (8)	
C2	0.86620 (15)	0.3372 (2)	0.7357 (2)	0.0291 (6)	
C3	0.94140 (15)	0.3194 (2)	0.8382 (2)	0.0278 (6)	
C4	0.82316 (15)	0.2528 (2)	0.7293 (2)	0.0304 (6)	
C5	0.99688 (14)	0.1918 (2)	0.9991 (2)	0.0268 (6)	
C6	1.00414 (16)	0.2340 (2)	1.0918 (3)	0.0302 (6)	
C7	1.06225 (16)	0.2006 (2)	1.2042 (2)	0.0325 (7)	
H7	1.0673	0.2297	1.2676	0.039*	
C8	1.11308 (15)	0.1241 (2)	1.2236 (2)	0.0319 (7)	
C9	1.10661 (15)	0.0802 (2)	1.1335 (2)	0.0307 (7)	
H9	1.1411	0.0264	1.1480	0.037*	
C10	1.04895 (15)	0.1158 (2)	1.0209 (2)	0.0287 (6)	
C11	1.1763 (2)	0.0878 (3)	1.3460 (3)	0.0481 (9)	
C12	0.74238 (17)	0.2320 (2)	0.6396 (3)	0.0364 (7)	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0409 (5)	0.0398 (4)	0.0512 (5)	0.0144 (3)	0.0308 (4)	0.0070 (3)
Cl2	0.0381 (4)	0.0498 (5)	0.0383 (5)	0.0030 (3)	0.0249 (4)	−0.0050 (3)

S1	0.0242 (4)	0.0383 (4)	0.0292 (4)	0.0042 (3)	0.0127 (4)	0.0077 (3)
F1	0.0376 (11)	0.0530 (12)	0.0410 (12)	0.0005 (9)	0.0143 (10)	−0.0068 (8)
F2	0.0514 (13)	0.0723 (15)	0.1067 (19)	−0.0067 (11)	0.0606 (14)	−0.0199 (13)
F3	0.0577 (13)	0.0370 (11)	0.0654 (14)	0.0157 (9)	0.0200 (12)	0.0090 (9)
F4	0.026 (2)	0.100 (5)	0.060 (3)	−0.007 (3)	−0.003 (2)	0.023 (3)
F5	0.138 (7)	0.048 (3)	0.041 (3)	0.043 (4)	0.010 (3)	0.010 (2)
F6	0.059 (3)	0.125 (6)	0.037 (3)	0.020 (3)	0.030 (3)	0.022 (3)
F4′	0.039 (4)	0.128 (9)	0.063 (5)	0.019 (5)	0.026 (4)	0.048 (5)
F5′	0.062 (5)	0.087 (6)	0.058 (4)	0.006 (4)	0.031 (4)	0.046 (4)
F6′	0.103 (8)	0.081 (6)	0.030 (4)	0.037 (6)	0.013 (5)	−0.001 (4)
O1	0.0429 (13)	0.0494 (14)	0.0594 (15)	0.0056 (11)	0.0376 (13)	0.0151 (11)
N1	0.0143 (11)	0.0307 (12)	0.0257 (13)	−0.0012 (9)	0.0067 (11)	0.0049 (9)
N2	0.0178 (11)	0.0313 (13)	0.0332 (14)	−0.0032 (10)	0.0098 (11)	0.0022 (10)
N3	0.0169 (12)	0.0442 (15)	0.0356 (15)	−0.0038 (10)	0.0093 (12)	0.0110 (11)
N4	0.0248 (15)	0.0419 (16)	0.0570 (19)	−0.0042 (12)	0.0104 (15)	−0.0070 (13)
C1	0.0229 (15)	0.0400 (18)	0.045 (2)	0.0010 (13)	0.0164 (16)	0.0011 (14)
C2	0.0166 (13)	0.0316 (15)	0.0286 (16)	0.0007 (11)	0.0096 (13)	0.0033 (11)
C3	0.0210 (14)	0.0306 (15)	0.0285 (16)	0.0021 (11)	0.0144 (13)	0.0035 (12)
C4	0.0165 (13)	0.0294 (15)	0.0325 (16)	0.0005 (11)	0.0097 (13)	−0.0011 (12)
C5	0.0189 (13)	0.0267 (14)	0.0264 (15)	−0.0023 (11)	0.0106 (13)	0.0033 (11)
C6	0.0248 (15)	0.0264 (14)	0.0361 (17)	0.0032 (11)	0.0178 (14)	0.0025 (12)
C7	0.0316 (16)	0.0332 (15)	0.0286 (16)	−0.0008 (13)	0.0173 (15)	−0.0011 (12)
C8	0.0226 (15)	0.0326 (16)	0.0288 (16)	−0.0006 (12)	0.0110 (14)	0.0045 (12)
C9	0.0221 (14)	0.0280 (15)	0.0364 (17)	0.0031 (11)	0.0161 (14)	0.0044 (12)
C10	0.0232 (14)	0.0282 (15)	0.0302 (16)	−0.0013 (11)	0.0150 (14)	−0.0004 (11)
C11	0.040 (2)	0.055 (2)	0.0331 (19)	0.0070 (17)	0.0153 (18)	0.0064 (16)
C12	0.0237 (16)	0.0269 (15)	0.0414 (19)	−0.0029 (12)	0.0128 (15)	−0.0019 (13)

Geometric parameters (Å, º)

Cl1—C6	1.724 (3)	N2—C4	1.327 (3)
Cl2—C10	1.723 (3)	N3—C3	1.340 (3)
S1—O1	1.479 (2)	N3—H3A	0.8800
S1—C2	1.739 (3)	N3—H3B	0.8800
S1—C1	1.844 (3)	N4—C12	1.144 (4)
F1—C1	1.329 (3)	C2—C3	1.398 (4)
F2—C1	1.325 (3)	C2—C4	1.408 (4)
F3—C1	1.321 (4)	C4—C12	1.437 (4)
F4—C11	1.344 (7)	C5—C10	1.388 (4)
F5—C11	1.281 (7)	C5—C6	1.389 (4)
F6—C11	1.331 (8)	C6—C7	1.379 (4)
F4′—C11	1.265 (9)	C7—C8	1.384 (4)
F5′—C11	1.357 (11)	C7—H7	0.9500
F6′—C11	1.253 (13)	C8—C9	1.373 (4)
N1—C3	1.359 (3)	C8—C11	1.500 (4)
N1—N2	1.379 (3)	C9—C10	1.387 (4)
N1—C5	1.418 (3)	C9—H9	0.9500

O1—S1—C2	108.69 (13)	C7—C6—C5	120.5 (3)
O1—S1—C1	102.58 (14)	C7—C6—Cl1	119.7 (2)
C2—S1—C1	96.30 (14)	C5—C6—Cl1	119.9 (2)
C3—N1—N2	113.4 (2)	C6—C7—C8	119.1 (3)
C3—N1—C5	125.6 (2)	C6—C7—H7	120.4
N2—N1—C5	119.7 (2)	C8—C7—H7	120.4
C4—N2—N1	103.1 (2)	C9—C8—C7	121.6 (3)
C3—N3—H3A	120.0	C9—C8—C11	119.3 (3)
C3—N3—H3B	120.0	C7—C8—C11	119.1 (3)
H3A—N3—H3B	120.0	C8—C9—C10	118.9 (3)
F3—C1—F2	108.4 (3)	C8—C9—H9	120.6
F3—C1—F1	107.4 (3)	C10—C9—H9	120.6
F2—C1—F1	107.9 (3)	C9—C10—C5	120.6 (3)
F3—C1—S1	110.0 (2)	C9—C10—Cl2	119.8 (2)
F2—C1—S1	110.0 (2)	C5—C10—Cl2	119.6 (2)
F1—C1—S1	112.9 (2)	F6′—C11—F4′	109.4 (8)
C3—C2—C4	104.7 (2)	F5—C11—F6	107.4 (6)
C3—C2—S1	127.2 (2)	F5—C11—F4	105.6 (5)
C4—C2—S1	128.1 (2)	F6—C11—F4	105.6 (5)
N3—C3—N1	122.4 (2)	F6′—C11—F5′	107.5 (9)
N3—C3—C2	132.0 (3)	F4′—C11—F5′	101.2 (7)
N1—C3—C2	105.5 (2)	F6′—C11—C8	113.4 (6)
N2—C4—C2	113.2 (2)	F4′—C11—C8	115.4 (5)
N2—C4—C12	119.1 (3)	F5—C11—C8	114.6 (4)
C2—C4—C12	127.8 (3)	F6—C11—C8	113.3 (4)
C10—C5—C6	119.3 (3)	F4—C11—C8	109.7 (4)
C10—C5—N1	121.4 (3)	F5′—C11—C8	108.9 (5)
C6—C5—N1	119.2 (2)	N4—C12—C4	179.7 (4)

C3—N1—N2—C4	1.3 (3)	N2—N1—C5—C6	−85.1 (3)
C5—N1—N2—C4	169.4 (2)	C10—C5—C6—C7	−0.2 (4)
O1—S1—C1—F3	67.2 (2)	N1—C5—C6—C7	−178.2 (2)
C2—S1—C1—F3	178.0 (2)	C10—C5—C6—Cl1	179.0 (2)
O1—S1—C1—F2	−173.4 (2)	N1—C5—C6—Cl1	1.0 (4)
C2—S1—C1—F2	−62.6 (2)	C5—C6—C7—C8	−0.3 (4)
O1—S1—C1—F1	−52.8 (2)	Cl1—C6—C7—C8	−179.5 (2)
C2—S1—C1—F1	58.0 (2)	C6—C7—C8—C9	−0.5 (4)
O1—S1—C2—C3	24.2 (3)	C6—C7—C8—C11	179.9 (3)
C1—S1—C2—C3	−81.4 (3)	C7—C8—C9—C10	1.8 (4)
O1—S1—C2—C4	−156.3 (3)	C11—C8—C9—C10	−178.7 (3)
C1—S1—C2—C4	98.1 (3)	C8—C9—C10—C5	−2.3 (4)
N2—N1—C3—N3	178.6 (3)	C8—C9—C10—Cl2	176.2 (2)
C5—N1—C3—N3	11.4 (4)	C6—C5—C10—C9	1.5 (4)
N2—N1—C3—C2	−0.3 (3)	N1—C5—C10—C9	179.5 (2)
C5—N1—C3—C2	−167.6 (3)	C6—C5—C10—Cl2	−177.0 (2)
C4—C2—C3—N3	−179.6 (3)	N1—C5—C10—Cl2	1.0 (4)
S1—C2—C3—N3	0.0 (5)	C9—C8—C11—F6′	164.8 (12)
C4—C2—C3—N1	−0.8 (3)	C7—C8—C11—F6′	−15.6 (12)

S1—C2—C3—N1	178.9 (2)	C9—C8—C11—F4′	37.5 (12)
N1—N2—C4—C2	−1.8 (3)	C7—C8—C11—F4′	−142.9 (11)
N1—N2—C4—C12	178.8 (3)	C9—C8—C11—F5	−38.1 (10)
C3—C2—C4—N2	1.7 (3)	C7—C8—C11—F5	141.4 (9)
S1—C2—C4—N2	−177.9 (2)	C9—C8—C11—F6	−161.9 (6)
C3—C2—C4—C12	−179.0 (3)	C7—C8—C11—F6	17.6 (6)
S1—C2—C4—C12	1.4 (5)	C9—C8—C11—F4	80.4 (6)
C3—N1—C5—C10	−96.6 (3)	C7—C8—C11—F4	−100.0 (6)
N2—N1—C5—C10	96.9 (3)	C9—C8—C11—F5′	−75.4 (7)
C3—N1—C5—C6	81.4 (3)	C7—C8—C11—F5′	104.1 (7)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3*A*···N4^{i}	0.88	2.39	3.183 (3)	151
N3—H3*B*···O1^{ii}	0.88	2.28	2.896 (3)	127
C9—H9···F2^{i}	0.95	2.42	3.222 (3)	143

Symmetry codes: (i) *x*+1/2, −*y*+1/2, *z*+1/2; (ii) −*x*+2, *y*, −*z*+3/2.