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

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Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.003 Å
Disorder in main residue
R factor = 0.047
wR factor = 0.113
Data-to-parameter ratio = 10.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The molecule of the title compound, $C_{12}H_4Cl_2F_6N_4S$, exhibits disorder of both trifluoromethyl groups. Crystal packing is realised by N—H···N hydrogen bonds.

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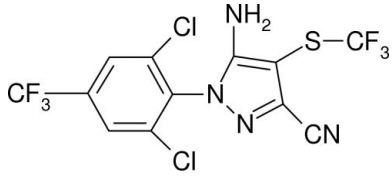
Comment

The title compound, (I) (Fig. 1), is an important starting material for the synthesis of fipronil, a very useful insecticide (Clavel *et al.*, 2003; Hatton *et al.*, 1993).



(I)

One of the two trifluoromethyl groups occurs in two equally populated orientations, whereas the other oscillates about the C1—F1 bond, having two equally populated positions for atoms F2 and F3. The pyrazole ring and benzene ring make a dihedral angle of 83.15 (12)°.

The regular self-assembly of the title compound (Fig. 2) is realised by intermolecular hydrogen bonds: an amino group forms a hydrogen bond with the cyano N atom of another molecule (Table 2).

Experimental

According to the method of Wakselman *et al.* (1992), the following procedure was employed. Into a 100 ml Teflon-coated autoclave, a dimethylformamide solution (48 ml) of 5-amino-3-cyano-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-pyrazolyl disulfide (0.8 g) was placed, followed by an aqueous solution (24 ml) of sodium hydrogen phosphate (1.2 g). Sodium dithionate (0.6 g) was then added with

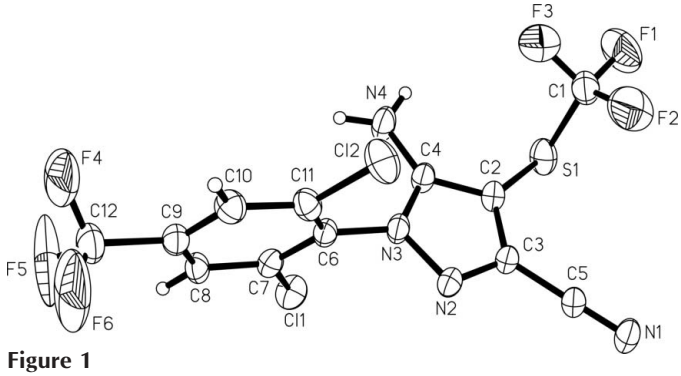


Figure 1
The structure of (I), showing the atom-numbering scheme and with displacement ellipsoids at the 50% probability level.

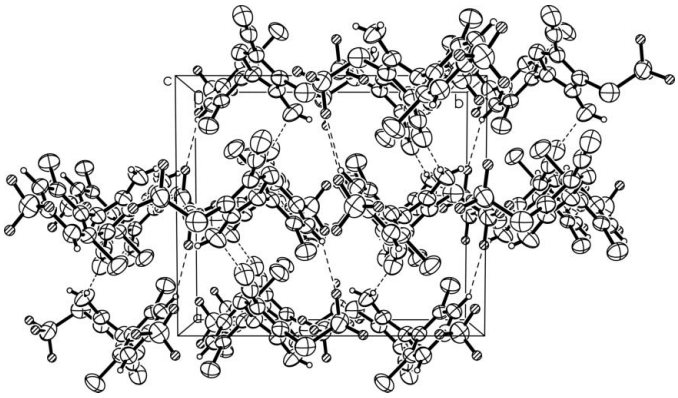


Figure 2
The crystal packing of (I), with N—H···N hydrogen bonds shown as dashed lines.

stirring. The preparation of the disulfide was carried out according to Clavel *et al.* (2003) and Tang *et al.* (2005). Next, CF_3Br was introduced at a pressure of 5–6 bar (autogenous pressure; 1 bar = 100 000 Pa) and, after 5 h of vigorous stirring at room temperature, the title compound was obtained in 51% yield. Single crystals of (I) suitable for X-ray analysis were obtained by slow evaporation of a toluene solution (m.p. 434–436 K). Spectroscopic analysis: IR (KBr, ν, cm^{-1}): 3475, 3331, 3233, 2258, 1631, 1561, 1513, 1463, 1399, 1318, 1153, 1109, 886, 812, 635; ^{1}H NMR (C_3D_6O, δ, p.p.m.): 8.11 (*s*, 2H), 6.64 (*s*, 2H); ^{13}C NMR (C_3D_6O, δ, p.p.m.): 153.4 (1C), 136.3 (1C), 135.4 (1C), 133.9 (1C), 132.4 (1C), 128.9 (1C), 126.5 (2C), 126.3 (2C), 122.2 (1C), 111.6 (1C); ^{19}F NMR (C_3D_6O, δ, p.p.m.): −46.25 (3F), −63.63 (3F).

Crystal data

$C_{12}H_4Cl_2F_6N_4S$
M_r = 421.16
Monoclinic, $P2_1/n$
a = 10.7801 (8) Å
b = 12.7006 (9) Å
c = 12.1039 (9) Å
β = 96.973 (1)°
V = 1644.9 (2) Å^3
Z = 4
D_x = 1.701 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3781 reflections
θ = 2.3–25.0°
μ = 0.59 mm^{-1}
T = 298 (2) K
Prism, colourless
0.42 × 0.29 × 0.21 mm

Data collection

Bruker APEX area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
T_{min} = 0.791, T_{max} = 0.887
8518 measured reflections
2953 independent reflections
2636 reflections with $I > 2\sigma(I)$
R_{int} = 0.018
θ_{max} = 25.2°
$h = -12 \rightarrow 12$
$k = -12 \rightarrow 15$
$l = -14 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.114
S = 1.10
2953 reflections
277 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.059P)^2 + 0.9497P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cl1—C7	1.726 (2)	N3—C4	1.349 (3)
Cl2—C11	1.727 (3)	N3—C6	1.420 (3)
S1—C2	1.735 (3)	N4—C4	1.340 (3)
S1—C1	1.783 (4)	C3—C5	1.438 (3)
F3—C1	1.266 (11)	C6—C11	1.383 (4)
F4—C12	1.321 (8)	C6—C7	1.384 (3)
N1—C5	1.135 (3)	C8—C9	1.377 (4)
N2—C3	1.323 (3)	C8—H8	0.9300
N2—N3	1.374 (3)	C9—C12	1.503 (4)
C2—S1—C1	100.16 (15)	N1—C5—C3	179.0 (3)
C3—N2—N3	102.7 (2)	C11—C6—C7	119.0 (2)
C4—N3—N2	113.58 (19)	C11—C6—N3	120.4 (2)
C4—N3—C6	126.99 (19)	C7—C6—N3	120.6 (2)
N2—N3—C6	119.44 (19)	C8—C7—C6	121.1 (2)
H4*A*—N4—H4*B*	123 (3)	C8—C7—Cl1	119.27 (19)
F3—C1—F2	111.0 (13)	C9—C8—H8	120.7
F3—C1—F1	110.7 (7)	C10—C9—C8	121.6 (2)
F2—C1—F1	100.7 (13)	C10—C9—C12	119.1 (3)
C4—C2—C3	104.4 (2)	C10—C11—C6	120.7 (2)
C4—C2—S1	125.86 (19)	F5—C12—F4	71.4 (7)
C3—C2—S1	129.47 (18)	F6′—C12—F6	48.2 (6)
N4—C4—N3	123.2 (2)	F5—C12—C9	112.3 (6)
N4—C4—C2	130.9 (2)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4*A*···N1^{i}	0.85 (2)	2.27 (2)	3.099 (3)	164 (3)

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

All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with N—H = 0.83–0.85 Å and C—H = 0.93 Å, and with U_{iso}(H) = 1.2U_{eq}(C,N). The two CF_3 groups were treated as disordered over two positions using free variables.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2002); software used to prepare material for publication: *SHELXL97*.

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