Lianqing Chen*, Gengtao Yang and Zhongda Wu

The synthesis and crystal structure of 5-amino-1-(2,6-dichloro-4-(trifluoromethyl)phenyl)-4-((trifluoromethyl)sulfinyl)-1*H*-pyrazole-3-carboxamide–tetrahydrofuran (1/1), C₁₆H₁₄N₄Cl₂F₆O₃S

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.15 × 0.11 × 0.10 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.46 mm ^{−1}
Diffractometer, scan mode:	Bruker D8 Venture, ω
$\theta_{\max}$, completeness:	27.6°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	12895, 5026, 0.038
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3492
$N(\text{param})_{\text{refined}}$:	317
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], Diamond [4]

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Abstract

C₁₆H₁₄N₄Cl₂F₆O₃S, monoclinic, $P2_1/c$ (no. 14), $a = 10.927(3)$ Å, $b = 13.542(3)$ Å, $c = 15.744(4)$ Å, $\beta = 107.360(4)^\circ$, $V = 2223.6(10)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0480$, $wR_{\text{ref}}(F^2) = 0.1471$, $T = 294.15$ K.

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The asymmetric unit of the title molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

All chemical solvents and reagents were of analytical grade quality, which were obtained from commercial suppliers and

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.50585(7)	0.32342(6)	0.55174(5)	0.0577(2)
Cl2	0.05544(8)	0.37360(6)	0.62024(5)	0.0684(3)
S1	0.38652(6)	0.68735(4)	0.72851(4)	0.03707(17)
F1	0.13390(19)	0.69871(17)	0.66620(16)	0.0887(7)
F2	0.2007(2)	0.6642(2)	0.80521(17)	0.1012(8)
F3	0.2222(2)	0.81018(16)	0.7601(2)	0.1106(9)
F4 ^a	−0.0032(5)	0.0826(5)	0.3972(5)	0.115(3)
F5 ^a	0.1628(6)	0.0058(2)	0.4617(3)	0.103(2)
F6 ^a	0.1581(9)	0.0838(5)	0.3467(3)	0.125(3)
O1	0.3760(2)	0.73393(14)	0.64091(12)	0.0587(6)
O2	0.4544(2)	0.57390(12)	0.90067(11)	0.0491(5)
N1	0.3298(2)	0.41718(14)	0.64094(12)	0.0385(5)
N2	0.3887(2)	0.39540(14)	0.72956(12)	0.0381(5)
N3	0.2587(2)	0.55420(16)	0.54353(13)	0.0504(6)
H3A	0.231256	0.515518	0.498519	0.060*
H3B	0.250661	0.617096	0.536484	0.060*
N4	0.5326(2)	0.41757(15)	0.91040(13)	0.0436(5)
H4A	0.567109	0.420808	0.967075	0.052*
H4B	0.539100	0.364404	0.882197	0.052*
C1	0.3509(2)	0.28631(18)	0.53890(16)	0.0381(5)
C2	0.2764(2)	0.33866(16)	0.58181(14)	0.0352(5)
C3	0.4100(2)	0.48269(16)	0.76859(14)	0.0321(5)
C4	0.3641(2)	0.56130(16)	0.70806(14)	0.0331(5)
C5	0.2254(3)	0.7154(2)	0.7426(2)	0.0615(8)
C6	0.3141(2)	0.51630(17)	0.62500(15)	0.0353(5)
C7	0.4691(2)	0.49472(17)	0.86641(15)	0.0354(5)
C8	0.1495(3)	0.30932(18)	0.56821(17)	0.0415(6)
C9	0.0982(3)	0.2292(2)	0.51533(17)	0.0450(6)

*Corresponding author: Lianqing Chen, Key Laboratory of Catalysis and Energy Materials Chemistry of Ministry of Education and Hubei Key Laboratory of Catalysis and Materials Science, South-Central University for Nationalities, Wuhan 430074, P.R. China, e-mail: lqchen@mail.scuec.edu.cn, chen_lianqing@163.com. <https://orcid.org/0000-0003-3706-0683>

Gengtao Yang and Zhongda Wu: Key Laboratory of Catalysis and Energy Materials Chemistry of Ministry of Education & Hubei Key Laboratory of Catalysis and Materials Science, South-Central University for Nationalities, Wuhan 430074, P.R. China

Table 2 (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
H9	0.013784	0.209963	0.507119	0.054*
C10	0.1753(3)	0.17809(18)	0.47480(17)	0.0432(6)
C11	0.1228(4)	0.0885(2)	0.4184(2)	0.0629(8)
C12	0.3005(3)	0.20609(19)	0.48558(17)	0.0444(6)
H12	0.350485	0.171312	0.457232	0.053*
O3	0.2421(2)	0.45878(19)	0.37493(14)	0.0708(7)
C13	0.1216(3)	0.4301(3)	0.3185(2)	0.0772(11)
H13A	0.071067	0.487927	0.293874	0.093*
H13B	0.075646	0.392347	0.351586	0.093*
C14	0.1424(4)	0.3693(3)	0.2463(3)	0.0838(12)
H14A	0.131768	0.299738	0.257097	0.101*
H14B	0.082278	0.387275	0.189460	0.101*
C15	0.2733(4)	0.3899(5)	0.2471(3)	0.128(2)
H15A	0.273596	0.428678	0.195388	0.153*
H15B	0.319005	0.328692	0.246067	0.153*
C16	0.3346(3)	0.4449(3)	0.3288(2)	0.0746(10)
H16A	0.407461	0.408257	0.365633	0.090*
H16B	0.364720	0.508266	0.314452	0.090*
F6A ^b	0.2059(10)	0.0334(10)	0.4032(14)	0.112(7)
F5A ^b	0.040(2)	0.0428(13)	0.4388(14)	0.144(9)
F4A ^b	0.0557(16)	0.1239(8)	0.3351(7)	0.103(5)

^aOccupancy: 0.715(11), ^bOccupancy: 0.285(11).

used directly without further purification (Shanghai Guoyao Chemical Reagent Co., Ltd.). Doubly distilled water was used throughout all experiments.

4.55 g (98%, 0.01 mol) of fipronil and 3.24 g (97%, 0.02 mol) of FeCl₃ were dissolved in 30 mL of tetrahydrofuran to obtain a solution. Thereafter, the solution was ultrasonically stirred for 10 min, and then transferred the reaction mixture into a dried 100 mL Teflon-lined autoclave and heated with the heating rate of 5 °C/min to the reaction temperature in the electric oven and kept for a few hours. After the reaction was over, the resulting solution was cooled to room temperature, all the excess solvent was removed to give a brown oil. To this brown oil was added 100 mL of distilled water and 50 mL of ethyl acetate, extracted three times, and the organic phase was dried over MgSO₄, then the filtrate was adsorbed on activated silica gel to dry the sample. The crude product was obtained by column chromatography on silica gel with $V_{ethyl\ acetate}/V_{petroleum\ ether}$ (1:6) as the eluent, which was dried under vacuum to obtain the purified product.

¹H NMR (CDCl₃, 400 MHz, ppm) δ 8.26 (s, 2H, Ar—H), 7.86 (s, 1H, N—H), 7.62 (s, 1H, N—H), 6.75 (s, 2H, NH₂). IR (KBr, v/cm⁻¹): 3449, 3301 (N—H), 2252, 1668 (C=N), 1633, 1500, 818. Anal. calcd for C₁₂H₆Cl₂F₆N₄O₂S: C, 31.67; H, 1.33; N, 12.31. Found: C, 31.60; H, 1.37; N, 12.35%. MS (FAB): *m/e*, 454 (*M*⁺).

After allowing the $V_{ethyl\ acetate}/V_{petroleum\ ether}$ (1:6) to stand in air for 12 days, transparent colorless cubic crystals were formed by slow evaporation of the solvent. The crystals of the title compound were isolated, washed with light petroleum (yield 78.4%).

Experimental details

All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with C—H distances in the range 0.93–0.98 Å, and with $U_{iso}(H) = 1.2 U_{eq}$ for aryl H atoms. The CF₃ group was refined with a disorder model. Atom F4, F5 and F6 of the CF₃ moiety were found to be disordered (F4/F4A, F5/F5A and F6/F6A).

Comment

As a lead compound is an efficient, broad-spectrum and low-resistance insecticide, and shortcoming is slow degradation and high toxicity to non-target organisms [5]. Only a limited number of its derivatives have been characterized structurally [6–9]. Recently, we have studied the crystal structure of an amidation derivative. These studies help us to understand the hydrogen bonding between fipronil derivatives and tetrahydrofuran and its functional toxicity.

The crystal structure of the title compound belongs to the monoclinic system, the space group is *P*₂₁/*c*. The title compound 5-amino-1-(2,6-dichloro-4-(trifluoromethyl)phenyl)-4-((trifluoromethyl)sulfonyl)pyrazole-3-carboxamide fragment, and is bridged with a C—C bond 1.491(3) Å formed by C3—C7. The bridge angle N2—C3—C7 is 122.7(2)°. The C3—N2 and C6—N1 (pyrazole) bond distance were 1.320(3) Å and 1.367(3) Å respectively, which were smaller than the value of 1.419(3) Å in the C2—N1 bond connecting the pyrazole ring and 2,6-dichloro-4-trifluoromethyl-phenyl moiety. The single bond C6—N3 connecting the pyrazole ring to the primary amino group bond distance was 1.346(3) Å and single bond C7—N4 in the amido group was 1.329(3) Å. The S1—C4 bond distance was 1.741(2) Å, connecting 4-trifluoromethyl-sulfonyl and pyrazolyl.

The compound forms intermolecular hydrogen bonds with a tetrahydrofuran molecule. Specifically, the hydrogen bond formed by H3a on the primary amino group O3 of a tetrahydrofuran molecule. The zigzag chain was partially facilitated by the title molecule and the tetrahydrofuran molecule by intermolecular H-bond interactions O3···H3a—N3 of two adjacent molecules with a distance of 2.90 Å.

The bioactivities of compound 4-((trifluoromethyl)sulfonyl)-1*H*-pyrazole-3-carboxamide tetrahydrofuran disolvate phenylpyrazole insecticide took the big ternary variety of tussah silkworm. Take 20 as a group, dilute the drug to 200, 320, 520 mg·L⁻¹ with distilled water, observe the poisoning situation within 96 h. Five repetitive experiments were performed. Then, ethylene glycol monomethyl ether and distilled water were used as blank control experiments, respectively, and other conditions remained unchanged. The death rate of each treatment group was confirmed. LC₅₀ value was calculated by the DPS. Bioactivity results showed

that the activity of compound 5-amino-1-(2,6-dichloro-4-(trifluoromethyl) phenyl)-4-((trifluoromethyl)sulfinyl)-1*H*-pyrazole-3-carboxamide after 96 h is $993.5 \text{ mg}\cdot\text{L}^{-1}$ and it is about nine times than fibronil $182.2 \text{ mg}\cdot\text{L}^{-1}$. Through the toxicity results, it is shown that compound 5-amino-1-(2,6-dichloro-4-(trifluoromethyl)phenyl)-4-((trifluoromethyl)sulfinyl)-1*H*-pyrazole-3-carboxamide tetrahydrofurandisolvate has little toxicity to tussah silkworm and has considerable application prospect in the protection of tussah silkworm.

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