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The crystal structure of 5-amino-1-(2,6-dichloro-4-(trifluoromethyl)phenyl)-4-(trifluoromethylsulfonyl)-1H-pyrazole-3-carboxamide, $C_{12}H_6N_4Cl_2F_6O_3S$

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Abstract

$C_{12}H_6N_4Cl_2F_6O_3S$, orthorhombic, $Pna2_1$ (no. 33), $a = 18.7340(10)$ Å, $b = 9.4010(10)$ Å, $c = 19.2330(10)$ Å, $V = 3387.3(4)$ Å³, $Z = 8$, $R_{gt}(F) = 0.0449$, $wR_{ref}(F^2) = 0.1074$, $T = 100.15$ K.

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The crystal 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 materials

All chemical solvents and reagents were of analytical grade quality, which were obtained from commercial suppliers and used directly without further purification (Shanghai Guoyao

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	$0.15 \times 0.12 \times 0.1$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.59 mm ⁻¹
Diffractometer, scan mode:	Bruker D8 Venture, φ and ω -scans
θ_{max} , completeness:	27.7° , >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	19660, 6747, 0.056
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 5379
$N(param)_{refined}$:	534
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], DIAMOND [4]

Chemical Reagent Co., Ltd.). Doubly distilled water was used throughout all experiments.

To a 100 mL flask, 9.10 g (96%, 0.02 mol) of fipronil and 30 mL of DMSO were added, and 2.76 g of potassium carbonate was added to the reaction mixture and stirred well. 15 mL of H₂O₂ (30%) was slowly added to the flask under ice-water bath, and a dry tube containing calcium chloride was attached to the top of the flask. Stirred until no significant bubbles were formed and reacted overnight at room temperature. After the reaction was completed, the reaction solution was cooled, and transferred to a 250 mL separatory funnel. After extracting with 100 mL of distilled water and 30 mL of ethyl acetate, the organic phase was dried over MgSO₄ and filtered, and the filtrate was evaporated by rotary evaporation, and then adsorbed on activated silica gel (10 g). The crude product was obtained by column chromatography, which was washed several times with petroleum ether, filtered and dried under vacuum. The compound 5-amino-1-(2,6-dichloro-4-(trifluoromethyl)phenyl)-4-(trifluoromethylsulfonyl)-1H-pyrazole-3-carboxamide was obtained. Yield: 8.22 g (87.5%), ¹H NMR (CDCl₃, 400MHz, ppm) 8.28 (s, 2H, Ar-H), 7.80 (s, 1H, N-H), 7.60 (s, 1H, N-H), 7.40 (s, 2H, C-NH₂). IR (KBr, I/cm^{-1}): 3390, 3293 (N-H), 3120 (benzene C-H), 1681 (C=O), 1645 (C=N), 1567, 1467, 1354 (benzene skeleton), 1312 (C-F), 882, 819 (aromatic ring C-H). Calcd for $C_{12}H_6N_4Cl_2F_6O_3S$: C, 30.59; H, 1.28; N, 11.89%, found C, 30.51; H, 1.24; N, 11.86%. MS (FAB): m/e , 469.94 (M^+).

After allowing the $V_{ethyl\ acetate}/V_{petroleum\ ether}$ (1:4) to stand in air for 10 days, colorless block crystals were formed by slow evaporation of the solvent. The single crystals were isolated,

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
Cl1	0.77185(7)	0.90346(17)	0.43825(8)	0.0287(3)
Cl2	0.61800(8)	0.59394(17)	0.61913(8)	0.0293(3)
Cl3	0.47759(8)	0.40557(17)	0.55889(8)	0.0288(3)
Cl4	0.63223(8)	0.08968(17)	0.38111(8)	0.0319(4)
S1	0.51646(7)	0.62475(15)	0.34512(7)	0.0192(3)
S2	0.73035(7)	0.13112(15)	0.65853(7)	0.0192(3)
F1	0.4945(2)	0.8637(4)	0.2803(2)	0.0373(9)
F2	0.5986(3)	0.7760(5)	0.2649(3)	0.0478(13)
F3	0.5083(2)	0.6836(5)	0.21449(19)	0.0464(11)
F4	0.8556(3)	0.8044(7)	0.7357(3)	0.0693(16)
F5	0.8949(3)	0.6210(5)	0.6908(3)	0.0675(17)
F6	0.9302(3)	0.8211(7)	0.6519(3)	0.0680(16)
F7	0.7493(2)	0.3761(4)	0.7188(2)	0.0436(10)
F8	0.6460(3)	0.2873(6)	0.7328(3)	0.0507(13)
F9	0.7348(3)	0.2006(6)	0.7881(2)	0.0575(13)
F10 ^a	0.3505(8)	0.0920(15)	0.3202(8)	0.044(3)
F10A ^b	0.3338(6)	0.1228(13)	0.3388(6)	0.052(3)
F11 ^a	0.3831(7)	0.290(2)	0.2730(8)	0.061(4)
F11A ^b	0.3951(5)	0.2088(12)	0.2597(4)	0.050(2)
F12 ^a	0.3129(6)	0.2889(15)	0.3575(7)	0.046(3)
F12A ^b	0.3376(6)	0.3503(11)	0.3229(6)	0.066(3)
O1	0.5552(2)	0.5006(4)	0.3269(2)	0.0280(10)
O2	0.4409(2)	0.6187(4)	0.3534(2)	0.0259(9)
O3	0.46079(19)	0.9778(4)	0.5207(2)	0.0218(9)
O4	0.80578(19)	0.1257(4)	0.6527(2)	0.0258(9)
O5	0.6913(2)	0.0076(5)	0.6775(2)	0.0305(11)
O6	0.78642(19)	0.4813(4)	0.4827(2)	0.0225(9)
N1	0.6395(4)	0.7557(5)	0.4884(4)	0.0189(16)
N2	0.5808(2)	0.8340(5)	0.5089(3)	0.0202(10)
N3	0.6761(2)	0.5941(5)	0.4029(2)	0.0191(10)
H3A	0.719532	0.591108	0.420379	0.023*
H3B	0.665501	0.543101	0.365973	0.023*
N4	0.4077(2)	0.8576(5)	0.4358(3)	0.0221(10)
H4A	0.367454	0.904195	0.441811	0.026*
H4B	0.410778	0.791699	0.403392	0.026*
N5	0.6096(3)	0.2523(5)	0.5100(4)	0.0163(15)
N6	0.6676(2)	0.3314(5)	0.4908(2)	0.0182(10)
N7	0.5716(2)	0.0957(5)	0.5987(2)	0.0192(10)
H7A	0.529028	0.088369	0.579778	0.023*
H7B	0.581569	0.048923	0.637131	0.023*
N8	0.8405(2)	0.3569(5)	0.5657(3)	0.0243(11)
H8A	0.880559	0.404517	0.560011	0.029*
H8B	0.837953	0.289101	0.597099	0.029*
C1	0.7624(3)	0.8194(6)	0.5164(3)	0.0199(12)
C2	0.6985(4)	0.7525(6)	0.5345(5)	0.0175(19)
C3	0.5315(3)	0.8069(6)	0.4633(3)	0.0164(11)
C4	0.5560(3)	0.7070(7)	0.4126(3)	0.0162(11)
C5	0.5312(5)	0.7447(7)	0.2705(5)	0.031(2)
C6	0.6271(3)	0.6750(6)	0.4320(3)	0.0154(11)
C7	0.4631(3)	0.8863(6)	0.4749(3)	0.0177(11)
C8	0.6945(3)	0.6836(6)	0.5977(3)	0.0189(12)
C9	0.7504(3)	0.6837(6)	0.6440(3)	0.0227(12)
H9	0.746315	0.637894	0.687848	0.027*
C10	0.8122(4)	0.7518(6)	0.6252(5)	0.0232(19)
C11	0.8737(5)	0.7501(7)	0.6748(5)	0.033(2)

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
C12	0.8200(3)	0.8194(6)	0.5614(3)	0.0210(12)
H12	0.863664	0.864315	0.549038	0.025*
C13	0.4862(3)	0.3155(6)	0.4818(3)	0.0184(12)
C14	0.5495(4)	0.2477(5)	0.4657(5)	0.0171(19)
C15	0.7168(3)	0.3062(6)	0.5373(3)	0.0156(11)
C16	0.6917(3)	0.2080(7)	0.5881(3)	0.0161(11)
C17	0.7145(5)	0.2557(7)	0.7275(5)	0.031(2)
C18	0.6212(3)	0.1776(6)	0.5691(3)	0.0147(11)
C19	0.7848(3)	0.3870(6)	0.5273(3)	0.0177(11)
C20	0.5551(3)	0.1765(6)	0.4025(3)	0.0216(13)
C21	0.4983(3)	0.1723(6)	0.3573(3)	0.0250(13)
H21	0.502398	0.124655	0.313970	0.030*
C22	0.4343(4)	0.2392(7)	0.3760(5)	0.026(2)
C23	0.3729(5)	0.2293(10)	0.3264(6)	0.041(2)
C24	0.4289(3)	0.3098(6)	0.4371(3)	0.0245(13)
H24	0.385364	0.355470	0.449231	0.029*

Occupancy: ^a = 0.406(15), ^b = 406(15)

washed with light petroleum and dried under vacuum (yield 88.2%).

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 and 1.5 *U*_{eq} for the methyl H atoms. Methyl H atoms were allowed to rotate to best fit the experimental electron density. The CF₃ group was refined with a disorder model. Atom F10, F11 and F12 of the CF₃ moiety were found to be disordered over three positions (F10/F10A, F11/F11A and F12/F12A) and split into two positions with occupancies of 0.53323 and 0.46677 and refined anisotropically.

Comment

As a typical representative of phenylpyrazole pesticides, fipronil is the first commercial phenylpyrazole insecticide for pest control [5], which is highly effective against soil insects, such as wireworms and aquatic insects, with extended use in the control of many agricultural vermin on various crops, such as water rice weevil and locust [6]. The molecular structure of fipronil contains a trifluoromethylsulfinyl substituent that is not present in any other agrochemicals, which is thought to contribute to its remarkable potency in the insecticidal field [7]. However, Fipronil is not easy to be degraded under the natural light irradiation [8]. Sulfone compounds are a class of compounds with high biological activity and have a broad spectrum of biological activities [9, 10]. They are widely used as fungicides, herbicides and antitumor drugs in the fields of medicine and pesticides [11]. To ensure the safe

use of fipronil, prevent ecological pollution and ensure the safety of humans and animals, we have employed a facile one-pot method to prepare fipronil sulfone hydrolysate by using fipronil as a lead compound.

The structure of title compound consisted of a benzene moiety and a pyrazole ring. The benzene ring and pyrazole ring in the same phenylpyrazole moiety (molecule 1; see the figure) made a dihedral angle of $51.34(3)^\circ$, which was similar to the molecular structure of Fipronil [12]. In each phenylpyrazole moiety, 1,3-dichloro-5-(trifluoro-methyl)phenyl ring was almost perpendicular to the plane of pyrazole ring. Each free trifluoromethyl group was twisted out of the pyrazole plane by rotation of the C-S single bond. The C(3)-N(2) and C(6)-N(1) (pyrazole) bond distance were $1.299(7)$ Å and $1.343(8)$ Å, respectively, which were smaller than the value of $1.417(10)$ Å observed in the C(2)-N(1) bond. The bond of C(11)-F(4), C(11)-F(5) and C(11)-F(6) (CF₃ group connecting with phenyl unit) were $1.321(10)$ Å, $1.314(8)$ Å and $1.326(9)$ Å, respectively, which were longer than the average value of $1.308(10)$ Å observed in the trifluoromethyl sulfonyl group. The C(4)-S(1) (sulfonyl) bond distance was $1.683(6)$ Å, which was smaller than the value of $1.845(9)$ Å observed in the C(5)-S(1) bond. The S(1)-O(2) (sulfonyl) bond distance was $1.425(4)$ Å, which was longer than the value of $1.419(4)$ Å observed in the S(1)-O(1) bond.

The packing of the title compound was partially facilitated by intramolecular and intermolecular H-bonds [13]. The intramolecular H-bonds of the title compound were O(2)—H(4b), O(4)—H(8b) and O(6)—H(3a), respectively. These H-bond lengths were $2.8173(3)^\circ$, $2.8149(3)^\circ$ and $2.7831(3)^\circ$, respectively [14].

The bioactivities of the title compound and phenylpyrazole insecticide (fipronil) against the 3rd instar larvae of *Plutella xylostella* were tested by the leaf disc-dipping assay. The compound was dissolved in acetone and suspended in distilled water containing Triton X-100. Distilled water containing acetone-Triton X-100 solution was used as the control. Leaves of Chinese cabbage grown in the greenhouse were collected and discs (5 cm in diameter) were punched from each leaf. The leaf discs were dipped into each test solution for 40 seconds and allowed to dry for 2.0 hours. The treated leaf discs were placed in a Petri dish (10 cm in diameter). Then, fifteen *Plutella xylostella* larvae were introduced into each dish. Petri dishes were kept in incubator at 27 °C and 86% relative humidity under a photoperiod of 15:9 h light: dark. All treatments were replicated five times. Mortalities were determined 24 h after treatment. The death rate of each treatment group was confirmed. LC₅₀ value was calculated by the SPSS. The insecticidal bioactivities result displayed that the activities of title compounds against *Plutella xylostella* after 24 h was $16.23 \text{ mg} \cdot \text{L}^{-1}$ better than that of fipronil $26.41 \text{ mg} \cdot \text{L}^{-1}$.

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