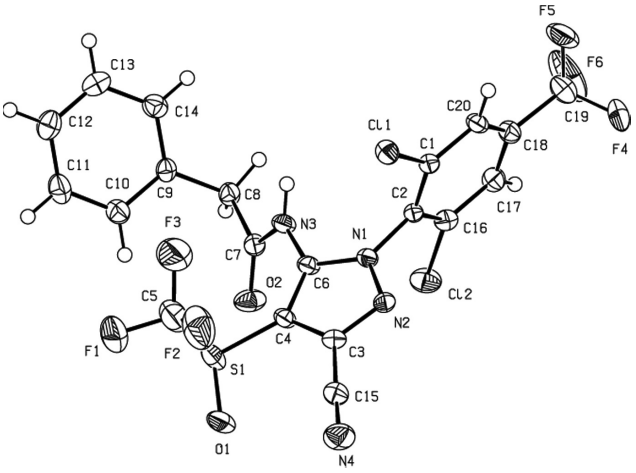
Lianqing Chen*, Chenglong Tang, Zhang Long and Zhongda Wu

The synthesis and crystal structure of *N*-(3-cyano-1-(2,6-dichloro-4-(trifluoromethyl)phenyl)-4-(trifluoromethylsulfinyl)-1*H*-pyrazol-5-yl)-2-phenylacetamide, $C_{20}H_{10}N_4Cl_2F_6O_2S$



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Abstract

$C_{20}H_{10}N_4Cl_2F_6O_2S$, monoclinic, $P2_1/n$ (no. 14), $a = 11.5523(17)$ Å, $b = 16.120(2)$ Å, $c = 13.0228(18)$ Å, $\beta = 114.297(2)°$, $V = 2210.3(5)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0578$, $wR_{ref}(F^2) = 0.1699$, $T = 173$ K.

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The 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.

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.20 × 0.20 × 0.20 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.46 mm^{-1}
Diffractometer, scan mode:	Bruker P4, φ and ω
θ_{max}, completeness:	27.6°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	13018, 4977, 0.037
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3585
$N(param)_{refined}$:	344
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], Diamond [4]

Source of material

All chemical solvents and reagents were of analytical grade quality, which were obtained from commercial suppliers and used directly without further purification (Wu Han Chemical Reagent Co., Ltd.).

Firstly, to a 10.0 mL toluene solution of fipronil (4.37 g, 10 mmol), we added a certain amount of phenylacetyl (12 mmol) in toluene (35.0 mL) and 4 Å molecular sieves (2.0 g). After that *p*-TSA (0.2 g) was added as a catalyst with ultrasonic stirring for 0.5 h. This reaction mixture was reacted at about 120 °C for 8 h. The resulting solution was then cooled to room temperature and purified by filtration. The filtrate was washed with saturated sodium carbonate solution (30.0 mL), water and brine, respectively, and then dried over $MgSO_4$. The filtrate was concentrated by rotary evaporation, and adsorbed on activated silica gel. The crude product was obtained by column chromatography on silica gel with $V_{\text{ethyl acetate}}/V_{\text{petroleum ether}}$ (1:8) as the eluent.

Secondly, $NaBH_4$ in CH_2Cl_2 (25.0 mL) was added to the reaction mixture and stirred for 4 h. Finally, the filtrate was concentrated by rotary evaporation, and adsorbed on activated silica gel (2.0 g), the crude product was obtained by column chromatography on silica gel with ethyl acetate, which was dried under vacuum to give the compound *N*-(3-cyano-1-(2,6-dichloro-4-(trifluoromethyl)phenyl)-4-(trifluoromethylsulfinyl)-1*H*-pyrazol-5-yl)-2-phenylacetamide. Yield: 1.22 g (74.1%), **^{1}H NMR** ($CDCl_3$, 400 MHz, ppm) 8.11 (s, 1H, N—H), 7.72 (s, 1H, Ar—H), 7.59 (s, 1H, Ar—H), 7.32 (s, 1H, Ar—H), 7.26 (s, 1H, Ar—H), 7.11 (s, 1H, Ar—H), 2.59 (t,

***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
Chenglong Tang, Zhang Long and Zhongda Wu: 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

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.33212(8)	0.84882(5)	0.53960(7)	0.0261(2)
Cl2	0.67489(9)	0.60655(6)	0.72792(8)	0.0347(2)
S1	0.54653(10)	0.76081(6)	1.03711(7)	0.0327(2)
F1	0.3820(3)	0.8346(2)	1.0956(2)	0.0659(8)
F2	0.4350(3)	0.9073(2)	0.9861(3)	0.0706(8)
F3	0.3107(3)	0.8035(3)	0.9199(3)	0.0911(10)
O1	0.6575(3)	0.8061(2)	1.1182(2)	0.0445(7)
O2	0.5355(2)	0.59016(16)	0.9433(2)	0.0363(6)
N1	0.5287(3)	0.75773(16)	0.7310(2)	0.0206(6)
N2	0.6054(3)	0.82512(16)	0.7684(2)	0.0212(6)
N3	0.4123(3)	0.65703(17)	0.7837(2)	0.0248(6)
H3	0.3445	0.6559	0.7221	0.030*
N4	0.7608(3)	0.9520(2)	0.9934(3)	0.0409(8)
C1	0.4207(3)	0.76711(19)	0.5259(3)	0.0202(6)
C2	0.5052(3)	0.72647(19)	0.6214(3)	0.0191(6)
C3	0.6170(3)	0.83447(19)	0.8737(3)	0.0217(7)
C4	0.5470(3)	0.7739(2)	0.9034(3)	0.0223(7)
C5	0.4117(5)	0.8307(4)	1.0070(4)	0.0555(9)
C6	0.4910(3)	0.7259(2)	0.8083(3)	0.0214(7)
C7	0.4406(3)	0.59026(19)	0.8562(3)	0.0225(7)
H8A	0.3860	0.4695	0.8553	0.029*
H8B	0.3157	0.5129	0.7380	0.029*
C8	0.3451(3)	0.5205(2)	0.8187(3)	0.0238(7)
C9	0.2320(3)	0.53733(19)	0.8462(3)	0.0216(7)
H10	0.3306	0.5713	1.0092	0.035*
C10	0.2491(4)	0.5628(2)	0.9540(3)	0.0290(8)
C11	0.1447(4)	0.5752(2)	0.9787(3)	0.0353(9)
H11	0.1563	0.5929	1.0503	0.042*
C12	0.0236(4)	0.5617(2)	0.8979(3)	0.0332(8)
H12	−0.0462	0.5698	0.9151	0.040*
C13	0.0063(3)	0.5359(2)	0.7917(3)	0.0336(8)
H13	−0.0753	0.5259	0.7375	0.040*
C14	0.1098(3)	0.5249(2)	0.7654(3)	0.0284(7)
H14	0.0972	0.5090	0.6929	0.034*
C15	0.6963(3)	0.8998(2)	0.9416(3)	0.0268(7)
C16	0.5723(3)	0.6579(2)	0.6093(3)	0.0234(7)
C17	0.5568(3)	0.6308(2)	0.5040(3)	0.0264(7)
H17	0.6006	0.5846	0.4962	0.032*
C18	0.4750(3)	0.6737(2)	0.4102(3)	0.0259(7)
C19	0.4619(4)	0.6472(3)	0.2952(3)	0.0397(9)
C20	0.4056(3)	0.7413(2)	0.4200(3)	0.0227(7)
H20	0.3498	0.7688	0.3560	0.027*
F4[a]	0.5559(3)	0.6769(3)	0.2713(3)	0.0638(14)
F4A[b]	0.550(2)	0.6088(17)	0.2976(14)	0.074(6)
F5[a]	0.3566(4)	0.6746(4)	0.2125(4)	0.0696(18)
F5A[b]	0.403(2)	0.6989(14)	0.217(2)	0.058(5)
F6[a]	0.4668(7)	0.5666(2)	0.2842(4)	0.084(2)
F6A[b]	0.361(2)	0.5871(12)	0.2615(13)	0.066(5)

[a]Occupancy: 0.811(8), [b]Occupancy: 0.189(8).

2H, CH—H). **IR**(KBr, υ/*cm-1*) : 3417 (N—H), 1718 (—C=O), 1528 (pyrazole ring skeleton vibration), 1508 (benzene ring skeleton vibration), 1314 (C—F), 609 (aromatic ring C—H). **MS** (FAB): *m*/*e*, 556 (M^+).

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 $U_{iso}(H) = 1.2\ U_{eq}$. The CF_3 group was refined with a disorder model. Atom F4, F5 and F6 of the CF_3 moiety were found to be disordered over two positions (F4/F4A, F5/F5A and F6/F6A).

Comment

Amides [5] have attracted much attention because of their strong physiological activity [6] in the fields of insecticide, weed control, and antiviral, especially in the field of pesticides [7, 8]. For the characterization of similar compounds, we found that these compounds have good fluorescence and hydrophobic properties [9], which greatly helped to detect the molecular orientation and insecticidal activity of pesticides [10]. Fipronil is also used in pesticides [11]. Its mechanism of action is to inhibit the GABA-gated chloride channels [12], so it has high insecticidal activity, thus has a high level of emulation to Plutella xylostella and other insects and has a long duration. However, fipronil is extremely unfriendly to the environment and can have harmful effects on various types of mammals around it [13], so it must be optimized.

In this experiment, we also collected the NMR and IR spectra of the synthesized product [14] to verify the structure of the product, and the results proved that the obtained product was the expected target product. The crystal structure of the title compound consists of a fipronil structure and phenylacetyl moiety, and is bridged with C—N bond 1.379(4) Å formed by N(3)—C(7) [15]. The bridge angle C(7)—N(3)—C(6) is 121.2(3)°. In the crystal structure the 1,3-dichloro-5-(trifluoromethyl)benzene ring is not coplanar with the plane of the pyrazole ring. Two of the heterocyclic rings make a dihedral angle of C(6)—N(1)—C(2) 128.5(3)°. The N(1)—C(2) bond distance is 1.430(4) Å. The mean plane of C(4)-S(1)-C(5) is slightly twisted out of the pyrazole ring with a dihedral angle of 93.65(18)°. The C(4)-S(1), S(1)-O(1) and C(7)-O(2) bond distance are 1.756(3) Å, 1.476(3) Å and 1.211(4) Å. The N4—C15 bond distance is 1.142(5) Å. The spatial angle between the benzene ring and the pyrazole ring in fipronil is 90°.

The packing of the title compound is partially facilitated by Y—X$\cdots\pi$ interactions between aromatic rings in neighboring molecules. The two most prominent such interactions are given in the Y-X$\cdots$Cg(π-Ring) interactions table (*Cg*1 represents the centroid of ring N1/N2/C4/C2/C3, *Cg*2 that of C7/C12/C11/C10/C9/C8). There is no classical intermolecular H-bonds in the title structure. And the first of these interactions, C9—Cl(2)$\cdots$*C(g)*1π which acts in centrosymmetric pairs, connects the molecules to infinite chains along the *c*-axis of the unit cell. The second slightly weaker type of

C19—F6A$\cdots$*C(g)*2π interaction connects these chains with each other.

The bioactivities of *N*-(3-cyano-1-(2,6-dichloro-4-(trifluoromethyl)phenyl)-4-(trifluoromethylsulfinyl)-1*H*-pyrazol-5-yl)-2-phenylacetamide phenylpyrazole insecticide (fipronil) against the 3rd instar larvae of *Plutella xylostella* were determined by the leaf disc-dipping assay. Leaves of Chinese cabbage grown in the greenhouse were collected, and discs (5 cm diameter) were punched from each leaf. The compounds were dissolved in acetone and suspended in distilled water containing Triton X-100. Leaf discs were dipped in each test solution for 30 s and allowed to dry for 2 h. The treated leaf discs were placed into Petri dishes (10 cm diameter). Then, ten *Plutella xylostella* larvae were introduced into each dish. Doubly distilled water containing acetone-Triton X-100 solution was used as the control. Petri dishes were kept in incubator at 25 °C and 85% relative humidity under a photoperiod of 16:8 h light: dark. All treatments were replicated three times. Mortalities were determined 24 h after treatment. The death rate of each treatment group was confirmed. LC_{50} value was calculated by the SPSS. Bioactivity result showed that the activities of compounds *N*-(3-cyano-1-(2,6-dichloro-4-(trifluoromethyl)phenyl)-4-(trifluoromethylsulfinyl)-1*H*-pyrazol-5-yl)-2-phenylacetamide against *Plutella xylostella* after 24 h is 14.67 $mg{\cdot}L^{-1}$ better than that of fipronil 27.24 $mg{\cdot}L^{-1}$. This approach proposes a novel insight to provide a great number of novel phenylpyrazole fluorescent insecticide by a general green method.

The absorption and photoluminescence spectra of the title compound in CH_2Cl_2 solution were investigated. In the absorption spectrum, intense absorptions are observed in the ultraviolet region of the spectrum. Strong absorption peak near 210 nm and 275 nm, belonging to the conjugated absorption peak of benzene ring and pyrazole ring, in the title compound. The benzene ring forms a larger conjugated structure with the pyrazole ring, resulting in a red shift in the UV absorption and a medium-intensity absorption peak at 320–387 nm. Its UV absorption is mainly attributed to the p-π* transition of the compound conjugated system. The fluorescene spectrum of the title compound shows a major strong peak at 445 nm. Phenylpyrazole heterocycle compounds are good candidates to design and develop new fluorescent pesticides, which lays a foundation for the natural degradation and fluorescence detection of pesticide residues.

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