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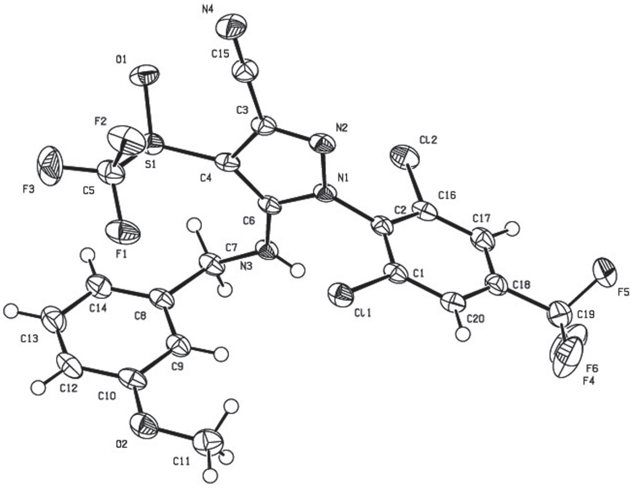
Synthesis and crystal structure of 1-(2,6-dichloro-4-trifluoromethyl-phenyl)-5-(3-methoxy-benzylamino)-4-trifluoromethanesulfinyl-1*H*-pyrazole-3-carbonitrile, $C_{20}H_{12}N_4Cl_2F_6O_2S$



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Abstract

$C_{20}H_{12}N_4Cl_2F_6O_2S$, triclinic, $P\bar{1}$ (no. 2), $a = 8.581(3)$ Å, $b = 10.967(4)$ Å, $c = 13.802(5)$ Å, $\alpha = 106.287(4)°$, $\beta = 105.505(4)°$, $\gamma = 101.592(4)°$, $V = 1146.7(7)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0500$, $wR_{ref}(F^2) = 0.1426$, $T = 173$ K.

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The asymmetric unit of the title crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

All chemicals were of analytical grade, which were obtained from commercial suppliers and used directly without further purification (Shanghai Guoyao Chemical Reagent Co., Ltd.). Doubly distilled water was used throughout all experiments. The synthesis of the target product involves two steps. Firstly, to a 10 mL toluene solution of fipronil (4.37 g, 10 mmol), we added a 12 mmol *m*-methoxybenzaldehyde in toluene (35 mL) and 4 Å molecular sieves (2.0 g). Furthermore *p*-toluene sulfonic acid (0.2 g) was added as a catalyst followed by ultrasonic stirring for 0.5 h, the reaction mixture was reacted at about 120 °C for 8 h. The resulting solution was cooled to room temperature, and the filtrate was washed with saturated sodium carbonate solution (30 mL), water and saturated 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, which was dried under vacuum to give the compound (1) 1-(2,6-dichloro-4-trifluoromethyl-phenyl)-5-[(3-methoxy-benzylidene)-amino]-4-trifluoromethanesulfinyl-1*H*-pyrazole-3-carbonitrile. Yield: 2.90 g (66.4%), ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 3.79(s, 3H), 7.14(s, 1H), 7.27 (s, 1H), 7.37 (s, 2H), 7.75 (s, 1H), 7.83 (s, 1H), 8.85 (s, 1H). IR (KBr, ν, cm^{-1}) : 3075 (Ar-H), 2251 (−C≡N), 1599 (—C≡N), 1575, 1545, 1507 (benzene ring skeleton vibration), 1315 (C—F), 789, 685 (C—H). MS (FAB): m/e, 553 (M^+).

In the second step, to a solution of 1-(2,6-dichloro-4-trifluoromethyl-phenyl)-5-[(3-methoxy-benzylidene)-amino]-4-trifluoromethanesulfinyl-1*H*-pyrazole-3-carbonitrile (1.65 g, 3 mmol), $NaBH_4$ in CH_2Cl_2 (25 mL) was added an stirred for 4 h. 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

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	$0.20 \times 0.20 \times 0.20$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.45 mm^{-1}
Diffractometer, scan mode:	CCD, φ and ω
θ_{max}, completeness:	27.5°, 99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	8996, 4840, 0.047
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3883
$N(param)_{refined}$:	348
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], Diamond [4]

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

Atom	x	y	z	$U_{\mathrm{iso}}*/U_{\mathrm{eq}}$
Cl1	0.42976(7)	0.64428(6)	0.46938(5)	0.02837(17)
Cl2	0.12755(8)	0.22127(6)	0.10049(5)	0.03224(18)
S1	0.58199(7)	0.67201(6)	0.09013(5)	0.02390(17)
F1	0.6659(2)	0.88764(15)	0.26399(13)	0.0397(4)
F2	0.86959(19)	0.80324(16)	0.25479(15)	0.0467(5)
F3	0.7904(2)	0.90945(17)	0.15035(16)	0.0573(5)
O1	0.6947(2)	0.60694(18)	0.04333(14)	0.0314(4)
O2	0.3537(2)	1.07381(17)	0.40044(15)	0.0345(4)
N1	0.3930(2)	0.47616(18)	0.25036(16)	0.0212(4)
N2	0.5489(2)	0.4542(2)	0.27234(17)	0.0253(5)
N3	0.2240(2)	0.57975(19)	0.15852(17)	0.0219(4)
H3	0.146(4)	0.549(3)	0.177(2)	0.026*
N4	0.9221(3)	0.5047(3)	0.2248(2)	0.0387(6)
C1	0.2862(3)	0.4873(2)	0.3982(2)	0.0228(5)
C2	0.2757(3)	0.4200(2)	0.29383(19)	0.0212(5)
C3	0.6278(3)	0.5235(2)	0.2263(2)	0.0231(5)
C4	0.5278(3)	0.5920(2)	0.17467(19)	0.0220(5)
C5	0.7361(3)	0.8270(2)	0.1972(2)	0.0317(6)
C6	0.3725(3)	0.5558(2)	0.18978(18)	0.0200(5)
C7	0.1827(3)	0.6551(2)	0.0879(2)	0.0250(5)
H7A	0.0581	0.6362	0.0597	0.030*
H7B	0.2202	0.6240	0.0259	0.030*
C8	0.2637(3)	0.8046(2)	0.1430(2)	0.0236(5)
C9	0.2717(3)	0.8661(2)	0.2480(2)	0.0252(5)
H9	0.2302	0.8143	0.2857	0.030*
C10	0.3409(3)	1.0042(2)	0.2981(2)	0.0278(5)
C11	0.2849(4)	1.0000(3)	0.4585(2)	0.0374(6)
H11A	0.1631	0.9574	0.4201	0.056*
H11B	0.3036	1.0605	0.5307	0.056*
H11C	0.3413	0.9316	0.4642	0.056*
C12	0.4030(3)	1.0798(2)	0.2425(2)	0.0327(6)
H12	0.4516	1.1735	0.2764	0.039*
C13	0.3935(4)	1.0181(3)	0.1386(2)	0.0348(6)
H13	0.4351	1.0699	0.1010	0.042*
C14	0.3236(3)	0.8806(3)	0.0878(2)	0.0297(6)
H14	0.3169	0.8391	0.0158	0.036*
C15	0.7929(3)	0.5144(3)	0.2259(2)	0.0285(5)
C16	0.1529(3)	0.2977(2)	0.2339(2)	0.0241(5)
C17	0.0494(3)	0.2382(2)	0.2801(2)	0.0274(5)
H17	−0.0324	0.1536	0.2400	0.033*
C18	0.0677(3)	0.3046(2)	0.3860(2)	0.0266(5)
C19	−0.0419(4)	0.2381(3)	0.4364(3)	0.0392(7)
C20	0.1832(3)	0.4296(2)	0.4452(2)	0.0251(5)
H20	0.1915	0.4749	0.5169	0.030*
F4[a]	−0.0202(4)	0.3086(3)	0.5348(2)	0.0628(11)
F5[a]	−0.0321(5)	0.1164(3)	0.4271(3)	0.0682(10)
F6[a]	−0.2091(3)	0.2166(3)	0.3821(3)	0.0687(10)
F4A[b]	−0.135(2)	0.2866(16)	0.4619(16)	0.073(4)
F5A[b]	−0.1058(18)	0.1210(16)	0.3930(11)	0.058(4)
F6A[b]	0.0812(14)	0.2373(13)	0.5368(9)	0.060(4)

[a]Occupancy: 0.826(5), [b]Occupancy: 0.174(5).

ethyl acetate, which was dried under vacuum to give the title compound. Yield: 1.22 g (74.1%), ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 3.75 (s, 3H), 4.11 (d, $J = 8.4$ Hz, 2H), 6.44 (s, 1H), 6.51 (s, 2H), 6.76 (d, $J = 8.7$ Hz, 1H), 7.12 (s, 1H), 7.55 (s, 1H), 7.61 (s, 1H). IR(KBr, v, cm^{-1}) : 3321 (Ar—H), 3045 (Ar—H), 2256 (—C≡N), 1586, 1545, 1496 (benzene ring skeleton vibration), 1316 (C—F), 769, 655 (aromatic ring C—H). MS (FAB): *m/e*, 556 (M^+).

After allowing the $V_{\text{ethyl acetate}}/V_{\text{petroleum ether}}$ (1:4) solution to stand in air for 15 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 and dried in vacuum (yield 70.4%).

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 $U_{\mathrm{iso}}(\mathrm{H}) = 1.2\,U_{\mathrm{eq}}$ for aryl H atoms and 1.5 U_{eq} for the methyl H atoms. All H atoms in the methyl group were allowed to rotate to best fit the experimental electron density. 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 three positions (F4/F4A, F5/F5A and F6/F6A) and split into two positions with occupancies of 0.604 and 0.396 and refined anisotropically.

Comment

Schiff base reduction derivatives are important chemical reagents, which act as a foundational role of antibacterial, anti-oxidation, anti-tumor and have a wide range of applications in the fields of catalysis, biochemistry, functional materials, medicine and other research areas [5]. Some Schiff base reduction derivatives have a strong coordination effect [6]. Recently, such compounds are identified as potential components in the luminescent materials. Phenylpyrazole derivatives are a class of nitrogen-containing heterocyclic compounds with broad biological activity [7]. In the field of medicine, such compounds can reduce inflammation and analgesia [8] and in the field of pesticides, they can be used as herbicides and pesticides [9]. Furthermore, from the perspective of the molecular structure, the phenylpyrazole heterocycle can form a conjugated system with high fluorescence quantum yield and intramolecular charge transfer characteristics.

The crystal structure of the title compound consists of a fipronil sub structure and a *m*-methoxybenzaldehyde moiety, and is bridged with C—N bond 1.464(3) Å formed by N3—C7. The bridge angle C7—N3—C6 is 124.9(2)°. In the crystal structure the 1,3-dichloro-5-(trifluoromethyl)benzene rings are not coplanar to the plane of the pyrazole ring [10]. The two heterocyclic rings make a dihedral angle of C6—N1—C2 127.65(18)°. The N1—C2 bond distance is 1.425(3) Å, which is the single bond connecting pyrazole ring to 2,6-dichloro-4-trifluoromethylphenyl. The mean plane of C4-S1-C5 is slightly twisted out of pyrazole ring with a dihedral angle of 97.29(12)°.

The aryl moieties of 1,3-dichloro-5-(trifluoromethyl)benzene, pyrazole and *m*-methoxybenzene are not in the same plane [11]. The C4—S1, S1—O1 and C10—O2 bond distance are 1.746(2) Å, 1.4879(18) Å and 1.368(3) Å respectively. The N4—C15 bond distance is 1.139(3) Å.

The packing of the title compound is partially facilitated by Y—X$\cdots\pi$ interactions. The two most prominent such interactions are given in the Y-X$\cdots$Cg (Pi-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). The first of these interactions, C8—Cl(2)$\cdots$*C(g)*1π which acts in centrosymmetric pairs between two molecules, 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. There are no classical intermolecular hydrogen bonds.

The bioactivities of the title compound and 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 results showed that the activities of the title compounds against *Plutella xylostella* after 24 h is 14.34 $mg\cdot L^{-1}$ 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 near 210 nm and 275 nm, belonging to the conjugated absorption peak of benzene ring and pyrazole ring. The conjugated structure with the pyrazole ring, results in a red shift in 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 conjugated system. The fluorescence spectrum of the title compound shows a strong peak at 445 nm. Finally it should be mentioned that 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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