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Crystal structure of the fluorescent fipronil derivative 5,5'-(methylenebis(azanediyl))bis(1-(2,6-dichloro-4-(trifluoromethyl)phenyl)-4-((trifluoromethyl)sulfinyl)-1H-pyrazole-3-carbonitrile), C₂₅H₆N₈O₂Cl₄F₁₂S₂

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.08 × 0.07 × 0.07 mm
Wavelength:	Cu K α radiation (1.54184 Å)
μ :	5.26 mm ⁻¹
Diffractometer, scan mode:	Xcalibur, ω
$\theta_{\max}$, completeness:	71.3°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	11572, 3311, 0.069
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1912
$N(\text{param})_{\text{refined}}$:	269
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], Diamond [4]

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

Source of material

A solution of fipronil (4.37 g, 10 mmol), paraformaldehyde (0.32 g, 10.5 mmol) in toluene (20 mL), was stirred with gentle refluxing for 2 h. The resulting solution was cooled to room temperature, and filtered to remove the excess of paraformaldehyde. The filtrate was evaporated, and adsorbed on activated silica gel. The crude product was obtained by column chromatography on silica gel with $V_{\text{ethyl acetate}}/V_{\text{petroleum ether}}$ (1:4) as eluent. The residue was dried under vacuum, yield: 3.64 g (78.1%). After allowing the ethyl acetate solution to stand in air for 8 d, light yellow block crystals were formed by slow evaporation of the solvent. The crystals were isolated, washed with light petroleum and dried in vacuum (yield 85.8%). **IR(KBr):** ν (cm⁻¹): 3231, 3064, 2252 (cyano group), 1727 (S=O), 1509 (phenyl ring), 1396, 1375, 1312, 1279, 955, 820, 752. **¹H NMR** (CDCl₃, 400 MHz, δ [ppm]) 7.90 (s, 1H), 7.85 (s, 1H), 7.02 (t, J = 8.0 Hz, 2H), 4.85 (t, J = 7.6 Hz, 2H). Calcd for C₂₅H₆Cl₄F₁₂N₈O₂S₂: C, 33.88; H, 0.91; N, 12.64%; Found: C, 33.76; H, 0.89; N, 12.48%. MS (FAB): m/e , 886.29 (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 $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}$.

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Abstract

C₂₅H₆N₈O₂Cl₄F₁₂S₂, monoclinic, $C2/c$ (no. 15), $a = 20.0584(9)$ Å, $b = 16.1373(7)$ Å, $c = 10.6232(5)$ Å, $\beta = 93.238(4)^\circ$, $V = 3433.1(3)$ Å³, $Z = 8$, $R_{\text{gt}}(F) = 0.0543$, $wR_{\text{ref}}(F^2) = 0.1427$, $T = 293(2)$ K.

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

Atom	x	y	z	<i>U</i> _{iso} ^a / <i>U</i> _{eq}
S1	0.50139(6)	0.22249(7)	0.57566(10)	0.0583(3)
Cl1	0.23676(8)	0.27271(10)	0.33585(15)	0.0990(5)
Cl2	0.44287(6)	0.42750(8)	0.13244(13)	0.0783(4)
F1	0.42648(17)	0.09930(18)	0.4679(3)	0.0933(10)
F2	0.41030(18)	0.12763(19)	0.6605(3)	0.1022(12)
F3	0.4977(2)	0.06252(18)	0.6121(3)	0.1104(12)
F4 ^a	0.1493(4)	0.4534(7)	−0.0544(7)	0.125(4)
F5 ^a	0.2337(6)	0.4769(7)	−0.1652(13)	0.143(5)
F6 ^a	0.1872(5)	0.3578(6)	−0.1579(12)	0.121(4)
N1	0.3629(2)	0.3761(2)	0.4465(4)	0.0673(11)
N2	0.37535(18)	0.3355(2)	0.3361(3)	0.0580(9)
N3	0.43951(17)	0.22822(19)	0.2541(3)	0.0518(9)
H3	0.412399	0.227477	0.188444	0.062 [*]
N4	0.4080(3)	0.3814(3)	0.7651(4)	0.1018(17)
O1	0.56337(15)	0.2060(2)	0.5107(3)	0.0677(9)
C1	0.4550(3)	0.1215(3)	0.5762(5)	0.0707(14)
C2	0.4429(2)	0.2762(2)	0.4793(4)	0.0491(10)
C3	0.4041(2)	0.3404(3)	0.5304(4)	0.0580(11)
C4	0.4224(2)	0.2744(2)	0.3520(4)	0.0477(9)
C5	0.4054(3)	0.3654(3)	0.6616(5)	0.0696(14)
C6	0.500000	0.1794(3)	0.250000	0.0481(13)
H6A ^b	0.496393	0.143953	0.176236	0.058 [*]
H6B ^b	0.503606	0.143955	0.323765	0.058 [*]
C7	0.3347(2)	0.3543(3)	0.2261(4)	0.0561(11)
C8	0.3599(2)	0.3987(3)	0.1275(4)	0.0570(11)
C9	0.3194(2)	0.4216(3)	0.0232(4)	0.0594(11)
H9	0.336789	0.451445	−0.042224	0.071 [*]
C10	0.2534(2)	0.3996(3)	0.0182(5)	0.0622(12)
C11	0.2270(2)	0.3536(3)	0.1130(5)	0.0677(13)
H11	0.182324	0.337714	0.107266	0.081 [*]
C12	0.2683(2)	0.3314(3)	0.2172(4)	0.0624(12)
C13	0.2084(3)	0.4262(4)	−0.0925(6)	0.0861(16)
F5A ^c	0.2422(17)	0.433(2)	−0.197(3)	0.156(13)
F4A ^c	0.1953(13)	0.5088(12)	−0.084(2)	0.131(9)
F6A ^c	0.1627(14)	0.393(2)	−0.125(3)	0.172(14)

^aOccupancy: 0.701(15), ^bOccupancy: 0.5, ^cOccupancy: 0.299(15).

Atom F4, F5 and F6 of the CF₃ moiety were found to be disordered over two positions (F4/F4A, F5/F5A, F6/F6A) and split into two positions with occupancies of 0.70 and 0.30 and refined anisotropically.

Comment

Phenylpyrazole derivatives play an important role in the development of pesticides. For example fipronil is the first phenylpyrazole insecticide introduced for pest control [5]. It acts on the GABA receptor, interfering with the nerve system of insect by blocking the chloride channel led to insect death in acertain dose [6]. Generally, fipronil is considered as the new generation high-tech pesticide for its novel structure, unique action mechanism and high activity [7]. In order

to further study the fluorescent phenylpyrazole derivatives, a derivative of fipronil was prepared. Its insecticidal bioactivities against the 3rd instar larvae of *Plutella xylostella* were determined. The result suggested that bioactivity of the title compound is higher than that of fipronil.

Phenylpyrazole are of interest as potential components in the electroactive and photoactive materials. In organic light-emitting diodes, phenylpyrazole-based compounds are usually used as host materials for both small molecule OLEDs due to their high triplet energy and good hole-transporting and electron-blocking capability [8]. The title compound emits blue green luminescence in both solid state and organic solution upon by UV-light at ambient temperature.

The title compound has a C₂ symmetry. In the title compound two fipronil moieties are bridged by one methylene group with C—N bond 1.449(4) Å (cf. the figure). The bridge angle C4—N3—C6 is 125.2(3)°. In each fipronil part, the 1,3-dichloro-5-(trifluoromethyl)benzene rings are not coplanar to the plane of pyrazole ring [9]. The two heterocyclic rings make a dihedral angle of 73.2(3)°. The C4—N2 and C3—N1 (pyrazole) bond distance are 1.370(5) Å and 1.314(6) Å, respectively, which are smaller than the value of 1.449(4) Å observed in the C6—N3 bond. The C4—N3 bond distance 1.339(5) Å is shorter than the C6—N3 bond due to π-π conjugation between N and the pyrazole ring. The N atom in the cyano group gives a short distance from C5 (1.128(6) Å) as expected. The C1—F1, C1—F2 and C1—F3 (CF₃ group connecting with pyrazole moiety) bond distance are 1.306(6) Å, 1.306(5) Å and 1.322(6) Å, respectively, which are shorter than the average value of 1.321(10) Å observed in the other trifluoromethyl-sulfinyl group connecting with phenyl moiety.

The packing of the title structure is partially facilitated by Y—X...π interactions between aromatic rings in neighboring molecules, the two most prominent interactions are given in the Y—X...C_g (π-Ring) interactions table (C_g1 represents the centroid of ring N1/N2/C4 /C2/C3, C_g2 that of C7/C12/C11/C10/C9/C8). The first of these interactions, C8—Cl(2)...C(*g*)1π acts between centrosymmetric pairs connecting the molecules to infinite chains along the *c*-axis of the unit cell. The second slightly weaker type of C13—F5...C(*g*)2π interaction connects these chains with each other. There is no classical intermolecular H-bond.

The **bioactivities** of the title compound and 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 35 s and allowed to dry for 3 h. The treated leaf discs were placed into Petri dishes (10 cm diameter).

Then, ten *Plutella xylostella* larvae were introduced into each dish. 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 the title each treatment group was confirmed. LC_{50} value was calculated by the SPSS program system. Bioactivity result showed that the activities of the title compounds against *Plutella xylostella* after 24 h is $12.41 \text{ mg}\cdot\text{L}^{-1}$ better than that of fipronil $25.36 \text{ mg}\cdot\text{L}^{-1}$.

In order to find a new type of fluorescent pesticide, 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. The strong absorption peak at 230 nm can be assigned to benzene ring with benzenoid bands, and the weaker absorption peak at 270 nm can be assigned to pyrazole ring with its $\pi-\pi^*$ conjugation. The fluorescence spectrum of the title compound shows a strong peak at 392 nm, which was due to two fipronil groups formed a large conjugated system and more easily from the domain of electronic excitation. The vibronic fine structures in the photoluminescence spectrum imply that the emission predominantly results from a ligand-based $3\pi-\pi^*$ transition. So it is a good candidate to design and develop a new type of fluorescent pesticide.

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