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The synthesis and crystal structure of ethyl (E)-1-(2,6-dichloro-4-(trifluoromethyl)phenyl)-5-((2-methoxybenzylidene)amino)-4-((trifluoromethyl)sulfinyl)-1H-pyrazole-3-carboxylate, C_{22}H_{15}N_{3}Cl_{2}F_{6}O_{4}S

Table 1: Data collection and handling.

| Crystal: | Colourless block |
| Size: | 0.11 × 0.10 × 0.08 mm |
| Wavelength: | Mo Kα radiation (0.71073 Å) |
| μ: | 0.43 mm⁻¹ |
| Diffractometer, scan mode: | Bruker APEX-II, φ and ω |
| R_{max} completeness: | 26.4°, >99% |
| N(hkl)measured, N(hkl)unique, R_{int}: | 32747, 5048, 0.065 |
| Criterion for I_{obs}, N(hkl)gt: | I_{obs} > 2σ(I_{obs}), 3776 |
| N(param)refined: | 365 |
| Programs: | CrysAlisPRO [1], SHELX [2, 3], Diamond [4] |

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

| Atom | x | y | z | U_{eq} |
|------|---|---|---|-------|
| Cl1  | 0.64428(5) | 0.40984(5) | 0.32028(4) | 0.03194(16) |
| Cl2  | 0.95717(5) | 0.60071(5) | 0.59897(4) | 0.02916(16) |
| S1   | 0.66553(5) | 0.32083(5) | 0.67938(4) | 0.02626(16) |
| F1   | 0.73916(14) | 0.34879(15) | 0.85167(11) | 0.0457(4) |
| F2   | 0.85658(13) | 0.28402(16) | 0.80652(12) | 0.0503(5) |
| F3   | 0.71822(15) | 0.45606(14) | 0.78981(11) | 0.0504(5) |
| F4   | 0.98300(11) | 0.68408(15) | 0.27405(11) | 0.0405(4) |
| F5   | 0.81942(12) | 0.70765(14) | 0.18918(10) | 0.0382(4) |
| Cl6  | 0.89606(15) | 0.82160(13) | 0.29631(12) | 0.0483(5) |
| O1   | 0.58367(13) | 0.40576(16) | 0.67148(12) | 0.0318(4) |
| O2   | 0.63617(14) | 0.69185(16) | 0.76076(11) | 0.0329(4) |
| O3   | 0.87976(17) | 0.12062(15) | 0.56810(13) | 0.0404(5) |
| O4   | 0.78788(18) | 0.12097(16) | 0.65830(12) | 0.0469(5) |
| N1   | 0.78450(15) | 0.43550(16) | 0.51083(13) | 0.0205(4) |
| N2   | 0.82589(15) | 0.33133(16) | 0.52604(13) | 0.0223(4) |
| N3   | 0.67546(15) | 0.55701(16) | 0.55107(13) | 0.0219(4) |
| C1   | 0.74978(18) | 0.50129(18) | 0.36041(16) | 0.0207(5) |
| C2   | 0.80615(18) | 0.50982(18) | 0.45202(15) | 0.0191(5) |
| C3   | 0.79293(18) | 0.28412(19) | 0.57945(15) | 0.0224(5) |
| C4   | 0.73337(18) | 0.3582(2) | 0.61005(15) | 0.0218(5) |
| C5   | 0.7774(2) | 0.3549(2) | 0.78808(17) | 0.0303(6) |
| C6   | 0.72765(18) | 0.45682(19) | 0.56288(15) | 0.0204(5) |
| C7   | 0.65873(18) | 0.5996(2) | 0.61674(16) | 0.0227(5) |
| H7   | 0.689666 | 0.565645 | 0.673842 | 0.027* |
| C8   | 0.59356(18) | 0.6986(2) | 0.60634(16) | 0.0219(5) |
| C9   | 0.58016(19) | 0.7411(2) | 0.68174(16) | 0.0250(5) |
| C10  | 0.6125(2) | 0.7209(2) | 0.83648(17) | 0.0335(6) |
| H10A | 0.536661 | 0.708144 | 0.822756 | 0.050* |

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Abstract

C_{22}H_{15}N_{3}Cl_{2}F_{6}O_{4}S, monoclinic, P_{1} (no. 14), a = 13.6099(10) Å, b = 12.0571(9) Å, c = 16.2351(13) Å, α = 90°, β = 112.714(2)°, γ = 90°, V = 1146.7(7) Å³, Z = 4, R_{gt}(F) = 0.0419, wR_{ref}(F^2) = 0.1087, 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.

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In the second step, 5.0 mmol of ethyl 5-amino-1-(2,6-dichloro-4-(trifluoromethylsulfinyl)-1H-pyrazole-3-carboxylate were added to 5.0 mmol of an aromatic aldehyde, and 1.0 g of 4 Å molecular sieve. Finally, 0.1 g of methylbenzenesulfonic acid was used as a catalyst, which was dissolved in 20.0 mL of toluene and heated under reflux at 120 °C for 20 h. After the reaction was completed, the reaction solution was cooled to 70 °C with suction filtration, and the filtrate was collected in a rotary flask, and 2.0 g of silica gel was added. Finally, different proportions of ethyl acetate and petroleum ether were used as developing agents. Dry loading and chromatography were performed to obtain the title compound. Yield: 1.25 g (76.0%).

\[ \text{H NMR (CDCl}_3, 400 MHz, ppm) \delta 3.75 (s, J = 7.2 Hz, 3H), 4.11 (d, J = 8.4 Hz, 2H), 6.44 (s, J = 6.8 Hz, 1H), 6.51 (s, J = 7.2 Hz, 2H), 6.76 (s, J = 7.2 Hz, 2H), 7.12 (s, J = 8.4 Hz, 1H), 7.55 (s, J = 7.2 Hz, 1H), 7.61 (s, J = 6.4 Hz, 1H). \]

IR (KBr, cm⁻¹): 3063 (bezene ring (C–H), 1729 (C=O), 1570–1394 (benzene ring skeleton vibration), 1311 (C–F), 815 (aromatic ring C–H).

MS (FAB): m/z, 602 (M⁺).

After allowing the \( V_{\text{ethyl acetate}}/V_{\text{petroleum ether}} \) (1:4) to stand in air for 14 days, transparent colorless 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 82.4%).

**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 and 1.5 \( U_{eq} \) for the methyl H atoms. All H atoms were allowed to rotate to best fit the experimental electron density. The ethyl group was refined with a disorder model. Atom C16 and C17 of the ethyl moiety were found to be disordered over two positions (C16/C16A and C17/C17A).

**Comment**

Schiff base compounds are carbon-nitrogen double bond imine compounds, which are widely used in the fields of...
medicine and biology, and have antiviral, bactericidal and antibacterial activities. They also play a huge role in the field of fluorescent probes and organic optoelectronics [5, 6]. Some new fipronil Schiff base derivatives have been synthesized in the early stage of this experiment and achieved good insecticidal effects. Because the ester group occupies an important position in the fields of pesticides and medicines, such as pyrethroid pesticides and pre-ester compounds, it proves that the ester compounds have good activity. Phenylpyrazoles are widely used in pesticides, such as fipronil and acetonitrile. The toxicity of phenylpyrazoles to insects and mammals can be attributed to their role as non-competitive blockers on GABA receptors, affecting the structure of GABA-gated chloride channels [7–10]. Many useful organic reactions are often used in pesticide synthesis, and reasonable and innovative methods are hoped for in the “acetation, phthalamidation, and sulfophthalation” [11]. In this experiment, esterification was used to synthesize ethyl 5-amino-1-(2,6-dichloro-4-(trifluoromethyl)phenyl)-4-(trifluoromethylsulfinyl)-1H-pyrazole-3-carboxylate with high yield, which is beneficial to the synthesis of title product.

The crystal structure of the title compound belongs to the space group $P\bar{1}$, each unit cell is composed of 4 molecules. According to the data, in the ester group of the pyridine ring, the O(4)·C(15) bond length is with 1.210(3) Å shorter than the O(2)·C(9) bond length of 1.367(3) Å. This is because O(4)·C(15) is a carbon-oxygen double bond. N(3)·C(7) bond length is 1.280(3) Å, which is typical for a double bond. From the crystal structure, it is seen that the aryl and pyrazolyl moieties are not coplanar.

The packing of the title structure is partially facilitated by $Y\cdots\pi$ interactions between aromatic rings in neighboring molecules. The two most prominent interactions are given in the $YX\cdots CG(\pi$-ring) interactions table ($CG1$ represents the centroid of ring N1/N2/C4/C2/C3, $CG2$ that of C7/C12/C11/C10/C9/C8). The first of these interactions, C8·Cl(2)·Cl(1)·π which acts in centrosymmetric pairs as well as two molecules, connects the molecules to infinite chains along the c axis of the unit cell. The second slightly weaker type of C19·F6A·C(g)2π interaction connects these chains with each other.

The bioactivities of the title compound 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 60 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. Dually distilled water containing acetone-Triton X-100 solution was used as the control. Petri dishes were kept in incubator at 20 °C and 80% relative humidity under a photoperiod of 18:10 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 the title compound against Plutella xylostella after 24 h is 13.86 mg·L$^{-1}$ better than that of fipronil 26.97 mg·L$^{-1}$. This approach proposes a novel insight to provide a great number of novel phenylpyrazole Schiff base fluorescent insecticide by a general green method.

It is noted that the absorption and photoluminescence spectra of the title compound in CH$_2$Cl$_2$ solution were investigated. In the absorption spectrum, intense absorptions are observed in the ultraviolet region of the spectrum. Strong absorption peak near 221 nm and 286 nm, belonging to the conjugated absorption peak of benzene ring and pyrazole ring, in the title compound. The aryl moiety C8·C13 forms a larger conjugated structure with the pyrazolyl moiety, resulting in a red shift in UV absorption and a medium-intensity absorption peak at 332–398 nm. Its UV absorption is mainly attributed to the p-$\pi^*$ transition of the compound conjugated system. The fluorescent spectrum of the title compound shows a strong peak at 456 nm. Thus phenylpyrazole heterocycle are good candidates to design and develop new fluorescent pesticides, which lays a foundation for the natural degradation and fluorescence detection of pesticide residues based on the phenylpyrazole Schiff base structure.

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