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1-[2,6-Dichloro-4-(trifluoromethyl)phenyl]-5-[(3,4-methylenedioxyphenyl)methyleneimino]-1*H*-pyrazole-3-carbonitrile

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Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.008 Å
Disorder in main residue
R factor = 0.065
wR factor = 0.154
Data-to-parameter ratio = 10.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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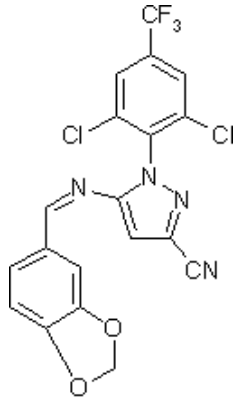
In the title molecule, $C_{19}H_9Cl_2F_3N_4O_2$, all bond lengths and angles are normal. The dihedral angle between the pyrazole and attached benzene rings is 77.5 (2)°. The crystal packing is mainly stabilized by van der Waals forces.

Comment

The title compound, (I), is an intermediate for the synthesis of 5-amino-3-cyano-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-[(trifluoromethyl)thio]pyrazole, 5-amino-3-cyano-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-[(trifluoromethyl)-sulfenyl]pyrazole and 5-amino-3-cyano-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-[(trifluoromethyl)sulfonyl]-pyrazole, which are known insecticides (Hatton *et al.*, 1993).



(I)

The molecule of (I) (Fig. 1) contains three essentially planar groups, which form an overall U-shape. All bond lengths and angles in (I) are normal (Table 1). The dihedral angles between the pyrazole ring and the C13–C18 and C2–C7 benzene rings are 21.1 (4) and 77.5 (2)°, respectively.

In the crystal structure, there are no obvious π–π interactions between the pyrazole and benzene rings, although such interactions were found in 1-[2,6-dichloro-4-(trifluoromethyl)-phenyl]-5-[(4-methoxyphenyl)methyleneimino]-1*H*-pyrazole-3-carbonitrile (Zhang *et al.*, 2005).

Experimental

Following the method of Hatton *et al.* (1993), reaction of 2,6-dichloro-4-trifluoromethylamine with a suspension of nitrosylsulfuric acid, followed by reaction with a solution of ethyl 2,3-dicyanopropionate in acetic acid, gave 5-amino-3-cyano-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]pyrazole. This compound was then reacted with 3,4-methylenedioxybenzaldehyde to give the title compound, (I). Single

crystals of (I) suitable for X-ray analysis were obtained by slow evaporation of an acetone solution (m.p. 446–447 K). Spectroscopic analysis: IR (KBr, ν, cm^{-1}): 3080, 2900, 2359, 2236, 1586, 1493, 1444, 1355, 1256, 1131, 816; ^{1}H NMR ($CDCl_3$, δ, p.p.m.): 8.55 (*s*, 1H), 7.76 (*s*, 2H), 7.24 (*d*, 2H), 6.86 (*d*, 2H), 6.73 (*s*, 1H), 6.04 (*s*, 1H); ^{13}C NMR ($CDCl_3$, δ, p.p.m.): 162.2 (1C), 152.4 (1C), 148.4 (1C), 135.8 (1C), 133.5 (1C), 129.3 (1C), 127.4 (1C), 126.6 (1C), 124.4 (1C), 113.4 (1C), 109.4 (1C), 107.7 (1C), 107.1 (1C), 101.8 (1C), 99.5 (1C), 97.9 (1C), 95.3 (1C), 76.8 (1C).

Crystal data

$C_{19}H_9Cl_2F_3N_4O_2$
M_r = 453.20
Monoclinic, $P2_1$
a = 6.4308 (11) Å
b = 9.8948 (17) Å
c = 15.356 (3) Å
β = 99.179 (4)°
V = 964.6 (3) Å^3
Z = 2
D_x = 1.547 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1189 reflections
θ = 2.5–24.2°
μ = 0.38 mm^{-1}
T = 298 (2) K
Block, colourless
0.21 × 0.19 × 0.13 mm

Data collection

Bruker APEX CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
T_{min} = 0.924, T_{max} = 0.952
5177 measured reflections
3274 independent reflections
2530 reflections with $I > 2\sigma(I)$
R_{int} = 0.036
θ_{max} = 25.6°
$h = -7 \rightarrow 7$
$k = -12 \rightarrow 11$
$l = -18 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.065
$wR(F^2)$ = 0.154
S = 1.07
3274 reflections
308 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0709P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}
Absolute structure: Flack (1983), with 3573 Friedel pairs
Flack parameter: 0.15 (11)

Table 1
Selected geometric parameters (Å, °).

C1—F2	1.275 (6)	O2—C19	1.444 (7)
C1—F23	1.279 (6)	N1—N2	1.354 (6)
C1—C2	1.512 (8)	N1—C5	1.421 (7)
F1—F21	0.968 (18)	N4—C12	1.279 (6)
F3—F21	1.373 (13)	C8—C9	1.368 (7)
O1—C19	1.391 (8)	C10—C11	1.451 (7)
F1—C1—F21	44.6 (8)	C8—N1—N2	113.5 (4)
F2—C1—F22	64.9 (9)	C8—N1—C5	125.7 (4)
F21—C1—F22	106.3 (5)	C12—N4—C8	118.1 (4)
F3—C1—F22	45.2 (7)	C6—C5—N1	122.4 (5)
F21—C1—F23	106.3 (5)	N1—C8—N4	117.1 (4)
F2—C1—C2	113.0 (9)	N2—C10—C9	114.0 (5)
F22—C1—C2	114.1 (7)	N3—C11—C10	176.1 (7)
C1—F2—F22	57.7 (5)	C14—C13—C12	119.0 (5)
F1—F21—F3	120.5 (8)	C15—C16—O1	128.1 (5)
C1—F21—F3	57.5 (4)	O2—C17—C16	110.6 (5)
F2—F23—F1	119.7 (8)	O1—C19—O2	108.9 (5)
C16—O1—C19	106.2 (5)		

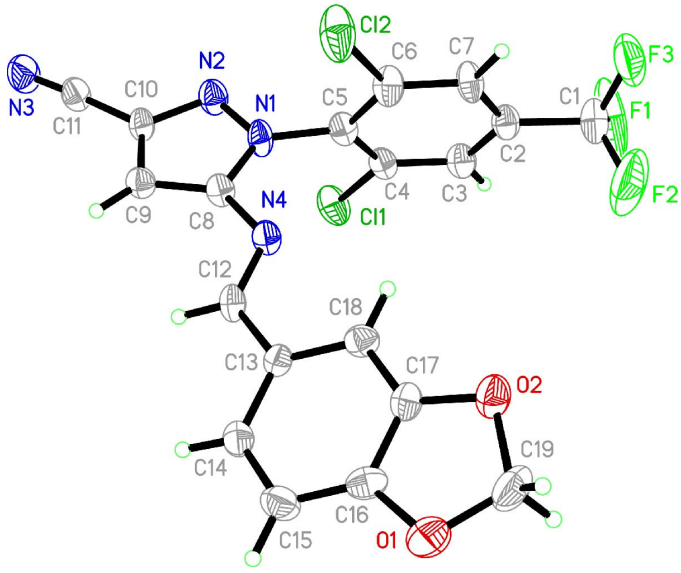


Figure 1
A view of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. For the disordered CF_3 group, only the major component is shown.

All H atoms were initially located in a difference Fourier map. They were then placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances in the range 0.93–0.97 Å and with U_{iso}(H) = 1.2$_{eq}$(C). The CF_3 group is disordered between two sites, with refined occupancies of 0.45 (3) and 0.55 (3). The F atoms were restrained, with all C—F distances equal and all F···F distances also equal.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2002); software used to prepare material for publication: *SHELXL97*.

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