organic papers

5-(2,4-Dichlorobenzamido)-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-1H-pyrazole-3-carbonitrile

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The title compound, $C_{18}H_7Cl_4F_3N_4O$, is a tricyclic amide with an overall U shape, each of the three rings being planar. The dihedral angle between the pyrazole and attached benzene ring is 90.1 (1)°. Intermolecular N—H···N hydrogen bonds, with an N(amide)···N(cyano) separation of 3.068 (6) Å, link the molecules.

Comment

The title compound, (I), is an intermediate for the synthesis of 5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-trifluoromethyl-thiopyrazole, 5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-trifluoromethylsulphenyl-pyrazole and 5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-trifluoromethylsulfonyl pyrazole, which are all good insecticides (Hatton *et al.*, 1993). The structure of (I) is shown in Fig. 1. The molecule contains three planar groups, forming an overall U shape. All bond lengths and angles are in agreement with those observed in similar compounds (Zhang *et al.*, 2005; Zhong *et al.*, 2005) The dihedral angles between the pyrazole and the C2–C7 and C13–C18 benzene rings are 90.1 (1) and 112.8 (1)°, respectively.

(I)
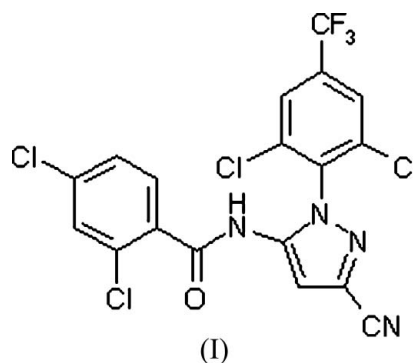
Experimental

Following the method of Hatton *et al.* (1993), the reaction of 2,6-dichloro-4-(trifluoromethyl)aniline (0.01 mol) with a suspension of nitrosylsulfuric acid (0.01 mol), followed by reaction with a solution of ethyl 2,3-dicyanopropionate (0.01 mol) in acetic acid, gave 5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)pyrazole (about 0.005 mol), which was then refluxed with 2,4-dichlorobenzoyl chloride (0.005 mol) and pyridine in chloroform (10 ml) overnight to give the title compound, (I). Single crystals suitable for X-ray analysis were obtained by slow evaporation of an acetone solution (m.p. 505–506 K). IR (KBr, cm^{-1}): ν 3420, 2252, 1705, 1627, 1554, 1380, 1307, 1191, 881; ^{1}H NMR (CDCl$_3$, p.p.m.): δ 10.22 (s,1H), 8.10 (*s*, 2H), 7.55 (*d*, 2H), 7.50 (*d*, 1H), 7.40 (*s*, 1H); ^{13}C NMR (CDCl$_3$, p.p.m.): δ 163.9 (1C), 140.7 (1C), 137.5 (1C), 137.4 (1C), 136.7 (1C), 135.3 (1C), 134.8

(1C), 134.7 (1C), 132.7 (1C), 131.4 (1C), 130.4 (1C), 128.4 (1C), 128.3 (1C), 127.5 (1C), 127.4 (2C), 127.3 (1C), 125.1 (1C).

Crystal data

$C_{18}H_7Cl_4F_3N_4O$	$D_x = 1.564$ Mg m^{-3}
$M_r = 494.08$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 1812
$a = 7.776$ (1) Å	reflections
$b = 16.453$ (2) Å	$\theta = 2.8–24.3°$
$c = 16.622$ (2) Å	$\mu = 0.61$ mm^{-1}
$\beta = 99.31$ (3)°	$T = 298$ (2) K
$V = 2098.6$ (5) Å^3	Block, colorless
$Z = 4$	$0.35 \times 0.27 \times 0.17$ mm

Data collection

Bruker APEX area-detector diffractometer	3779 independent reflections
	3196 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.023$
Absorption correction: multi-scan (SADABS; Bruker, 2002)	$\theta_{max} = 25.2°$
$T_{min} = 0.815$, $T_{max} = 0.904$	$h = -9 \rightarrow 8$
	$k = -17 \rightarrow 19$
10608 measured reflections	$l = -18 \rightarrow 19$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1073P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.093$	$+ 5.2953P]$
$wR(F^2) = 0.244$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{max} < 0.001$
3779 reflections	$\Delta\rho_{max} = 1.02$ e Å^{-3}
271 parameters	$\Delta\rho_{min} = -0.69$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

O1—C12	1.197 (6)	N4—C10	1.377 (6)
F1—C1	1.235 (10)	C1—C2	1.473 (7)
N1—C10	1.349 (6)	C5—C6	1.381 (7)
N1—N2	1.352 (5)	C8—C9	1.385 (7)
N1—C5	1.425 (5)	C13—C18	1.361 (8)
N2—C8	1.330 (6)	C13—C14	1.377 (8)
N4—C12	1.366 (6)		
C10—N1—N2	113.1 (4)	N2—C8—C9	113.4 (4)
C10—N1—C5	127.4 (4)	C10—C9—C8	104.2 (4)
N2—N1—C5	119.2 (4)	N1—C10—N4	120.5 (4)
C8—N2—N1	102.9 (4)	C9—C10—N4	133.1 (4)
F3—C1—F2	105.4 (11)	O1—C12—N4	121.8 (5)
C7—C2—C3	121.6 (5)	N4—C12—C13	115.5 (4)
C7—C2—C1	119.2 (6)	C18—C13—C14	117.3 (5)
C3—C4—C5	120.7 (5)	C15—C14—C13	117.1 (5)
C6—C5—N1	119.7 (4)	C16—C17—C18	118.9 (6)
C2—C7—C6	118.9 (5)	C13—C18—C17	122.2 (6)
C10—N1—N2—C8	−1.4 (5)	N1—C5—C6—C7	179.8 (4)
C5—N1—N2—C8	−175.3 (4)	C3—C2—C7—C6	0.0 (8)
F1—C1—C2—C7	162.4 (9)	N2—N1—C10—N4	−177.7 (4)
C7—C2—C3—C4	−0.3 (8)	C12—N4—C10—N1	−179.5 (5)
C3—C4—C5—N1	179.9 (4)	N4—C12—C13—C14	61.2 (7)
N2—N1—C5—C4	−93.5 (5)	Cl3—C14—C15—C16	−179.7 (5)
C10—N1—C5—C6	−86.3 (6)	C16—C17—C18—C13	0.7 (11)
N2—N1—C5—C6	86.6 (5)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D \cdots A$	D—H$\cdots A$
N4—H4$\cdots$N3^i	0.86	2.23	3.068 (6)	166

Symmetry codes: (i) $x - \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$.
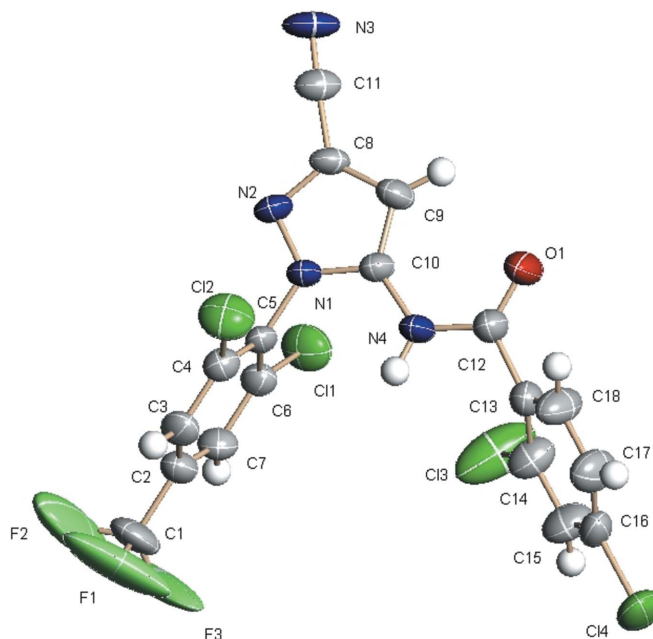

Figure 1
The structure of (I), showing the atom-numbering scheme and with displacement ellipsoids for non-H atoms at the 50% probability level.

The H atoms were positioned geometrically and allowed to ride on their parent atoms at distances of C—H = 0.93 Å and N—H = 0.86 Å with U_{iso}(H) = 1.2U_{eq}(parent atom). The low U_{eq} of C1 as compared to its neighbours may be attributed to the high displacement parameters for atoms F1, F2 and F3, indicating either large thermal motion or rotational disorder of the trifluoromethyl group. However, attempts to represent the CF$_3$ group using a disorder model were unsuccessful. The inability to account for the electron-density distribution in the vicinity of the CF$_3$ group is the most likely reason for the limited overall precision of the structure and the high R value.

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.

References

Bruker (2002). SMART, SAINT, SADABS and SHELXTL. Bruker AXS Inc., Madison, Wisconsin, USA.
Hatton, L. R., Buntain, I. G., Hawkins, D. W., Parnell, E. W., Pearson, C. J. & Roberts, D. A. (1993). US Patent No. 5 2329 40.
Sheldrick, G. M. (1997). SHELXL97 and SHELXS97. University of Göttingen, Germany.
Zhang, X., Zhong, P., Xiao, H. & Hu, M. (2005). Acta Cryst. E61, o806–o807.
Zhong, P., Yang, Z. & Shi, Q. (2005). Acta Cryst. E61, o841–o842.