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4-Bromo-5-[(4-chlorobenzylidene)-amino]-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-1*H*-pyrazole-3-carbonitrile

Xiao-Chun Yu, Shu-Yan Li and Ping Zhong*

Department of Chemistry, Wenzhou University, 325027 Wenzhou, People's Republic of China
Correspondence e-mail: zhongp0512@163.com

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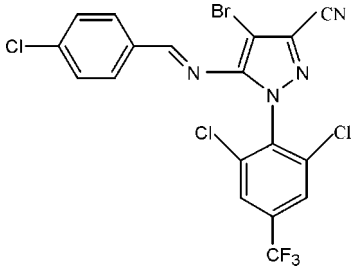
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.006 Å; R factor = 0.058; wR factor = 0.186; data-to-parameter ratio = 18.1.

The title compound, $C_{18}H_7BrCl_3F_3N_4$, is an imine relevant to insecticides. The dihedral angles between the central pyrazole ring and the benzene ring planes are 84.3 (2) and 68.5 (2)°.

Related literature

For related literature, see: Philippe (1997, 2000); Zhong *et al.* (2005).



Experimental

Crystal data

$C_{18}H_7BrCl_3F_3N_4$
M_r = 522.54
Orthorhombic, *Pbca*
a = 10.0338 (7) Å
b = 11.5819 (8) Å
c = 34.499 (3) Å
V = 4009.1 (5) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 2.49 mm^{-1}
T = 298 (2) K
0.39 × 0.17 × 0.16 mm

Data collection

Bruker APEX area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
T_{min} = 0.444, T_{max} = 0.691
23679 measured reflections
4736 independent reflections
3014 reflections with $I > 2\sigma(I)$
R_{int} = 0.036

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.058
$wR(F^2)$ = 0.186
S = 1.04
4736 reflections
262 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.84 e Å^{-3}

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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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK2157).

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supplementary materials

Acta Cryst. (2007). E**63**, o3098 [**doi:10.1107/S1600536807026256**]

4-Bromo-5-[(4-chlorobenzylidene)amino]-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-1*H*-pyrazole-3-carbonitrile

X.-C. Yu, S.-Y. Li and P. Zhong

Comment

The title compound, (I), (Fig. 1) is similar to the very effective insecticides used to treat animals such as cows and sheep (Philippe, 1997, 2000) and its structure is reported here. The molecule of (I) contains three essentially planar rings. The dihedral angles between the central pyrazole ring (C9—C11, N1, N2) and the benzene (C2—C7) and (C13—C16) ring planes are 84.3 (2)° and 68.5 (2)°, respectively.

Experimental

According to the method of Zhong *et al.* (2005), using 5-amino- 3-cyano-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]pyrazole (2.5 mmol), followed by reaction with 4-chlorobenzaldehyde (2.5 mmol) and HCl (2 ml) in anhydrous ethanol (5 ml), we obtained 1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-3-cyano- 5-[(4-chlorobenzylidene)amino]-1*H*-pyrazole, which was then reacted with *N*-bromosuccinimide (1.5 mmol) (Philippe, 2000) in acetonitrile (6 ml) at room temperature. After being stirred a few minutes, the reaction was monitored by TLC until the starting materials were consumed. Finally, the reaction mixture was evaporated under reduced pressure to provide the required crude product, which was then partitioned between dichloromethane and water, separating and drying the organic phase and evaporating it under reduced pressure gave the title compound in 90.8% yield. Colorless single crystals suitable for X-ray analysis were obtained by slow evaporation of an anhydrous ethanol-acetone (2:1) solution of (I), m.p. 488–489 K. IR (KBr, ν cm^{-1}): 3047, 2202, 1618, 1387, 1313, 1179, 1136, 825; ^{1}H NMR (C_3D_6O, δ, p.p.m.): 9.39 (s, 1H), 8.14 (s, 2H), 7.90 (d, J = 8.52 Hz, 2H), 7.55 (d, J = 8.52 Hz, 2H); ^{13}C NMR (C_3D_6O, δ, p.p.m.): 167.4, 148.4, 140.2, 137.6, 136.4, 134.5 (q, J = 34.1 Hz), 134.3, 131.9, 130.2 (2 C), 130.1 (2 C), 127.2 (2 C), 127.1 (2 C), 121.5 (q, J = 271.1 Hz), 112.4.

Refinement

All H atoms were constrained to ride on their parent atoms, with C—H = 0.93 Å, and with U_{iso}(H) = 1.2$_{eq}$(C). 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 CF3 group using a disorder model were unsuccessful. The maximum residual electron density peak was located 1.27 Å from the C1 and F1 atoms.

Figures

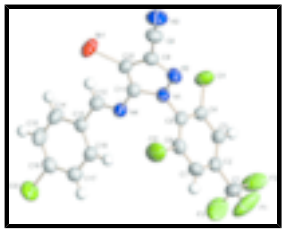


Fig. 1. The molecular structure of (I) showing the atom numbering scheme and displacement ellipsoids at 50% probability level.

4-Bromo-5-[(4-chlorobenzylidene)amino]-1-[2,6-dichloro-4- (trifluoromethyl)phenyl]-1*H*-pyrazole-3-carbonitrile

Crystal data

$C_{18}H_7BrCl_3F_3N_4$	D_x = 1.731 Mg m^{-3}
M_r = 522.54	Melting point: 488-489 K
Orthorhombic, *Pbca*	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: -P 2ac 2ab	Cell parameters from 4261 reflections
a = 10.0338 (7) Å	θ = 2.4–21.3º
b = 11.5819 (8) Å	μ = 2.49 mm^{-1}
c = 34.499 (3) Å	*T* = 298 (2) K
V = 4009.1 (5) Å^3	Block, colorless
Z = 8	0.39 × 0.17 × 0.16 mm
F_{000} = 2048	

Data collection

Bruker APEX area-detector diffractometer	4736 independent reflections
Radiation source: fine-focus sealed tube	3014 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.036
T = 298(2) K	θ_{max} = 28.3º
φ and ω scans	θ_{min} = 1.2º
Absorption correction: multi-scan (SADABS; Bruker, 2002)	*h* = −13→9
T_{min} = 0.444, T_{max} = 0.691	*k* = −15→14
23679 measured reflections	*l* = −45→45

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.058	H-atom parameters constrained
$wR(F^2)$ = 0.186	$w = 1/[\sigma^2(F_o^2) + (0.0966P)^2 + 3.5182P]$ where $P = (F_o^2 + 2F_c^2)/3$

S = 1.04	$(\Delta/\sigma)_{max}$ = 0.001
4736 reflections	$\Delta\rho_{max}$ = 1.20 e Å^{-3}
262 parameters	$\Delta\rho_{min}$ = −0.84 e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	1.01932 (6)	0.22489 (5)	0.020072 (16)	0.0781 (2)
Cl1	0.50245 (14)	0.43701 (13)	0.08080 (3)	0.0729 (4)
Cl2	0.81344 (15)	0.17122 (15)	0.17059 (4)	0.0894 (5)
Cl3	1.32776 (14)	0.77979 (12)	0.17945 (4)	0.0804 (4)
F1	0.4269 (6)	0.3602 (5)	0.25418 (13)	0.150 (2)
F2	0.3552 (4)	0.4993 (4)	0.22440 (9)	0.1293 (18)
F3	0.5420 (6)	0.5033 (7)	0.25062 (15)	0.200 (4)
N1	0.7224 (3)	0.2693 (3)	0.09621 (9)	0.0474 (8)
N2	0.6684 (3)	0.1819 (3)	0.07601 (10)	0.0530 (8)
N3	0.7249 (5)	−0.0086 (4)	0.00155 (12)	0.0825 (14)
N4	0.9101 (3)	0.3884 (3)	0.10357 (9)	0.0471 (8)
C1	0.4628 (5)	0.4421 (5)	0.23040 (13)	0.0639 (13)
C2	0.5282 (4)	0.3954 (4)	0.19469 (12)	0.0484 (9)
C3	0.4871 (4)	0.4337 (4)	0.15874 (12)	0.0474 (9)
H3	0.4178	0.4867	0.1564	0.057*
C4	0.5516 (4)	0.3913 (3)	0.12611 (11)	0.0443 (9)
C5	0.6547 (4)	0.3127 (3)	0.12953 (11)	0.0438 (9)
C6	0.6911 (4)	0.2741 (4)	0.16625 (13)	0.0527 (10)
C7	0.6291 (4)	0.3172 (4)	0.19877 (12)	0.0552 (10)
H7	0.6557	0.2934	0.2233	0.066*
C8	0.7399 (5)	0.0671 (4)	0.02214 (12)	0.0581 (11)
C9	0.7597 (4)	0.1600 (3)	0.04885 (11)	0.0474 (9)
C10	0.8695 (4)	0.2339 (3)	0.05139 (11)	0.0475 (9)
C11	0.8445 (4)	0.3047 (3)	0.08248 (11)	0.0446 (9)
C12	0.9998 (4)	0.4510 (4)	0.08793 (12)	0.0483 (9)
H12	1.0163	0.4440	0.0615	0.058*
C13	1.0769 (4)	0.5334 (3)	0.11074 (11)	0.0425 (8)

C14	1.1751 (5)	0.5990 (4)	0.09282 (13)	0.0585 (11)
H14	1.1897	0.5908	0.0663	0.070*
C15	1.2515 (5)	0.6764 (4)	0.11383 (14)	0.0642 (12)
H15	1.3170	0.7203	0.1017	0.077*
C16	1.2289 (4)	0.6867 (3)	0.15246 (12)	0.0501 (9)
C17	1.1317 (4)	0.6240 (3)	0.17108 (12)	0.0503 (9)
H17	1.1176	0.6331	0.1975	0.060*
C18	1.0557 (4)	0.5480 (3)	0.15006 (11)	0.0468 (9)
H18	0.9892	0.5058	0.1624	0.056*

Atomic displacement parameters (Å^2)

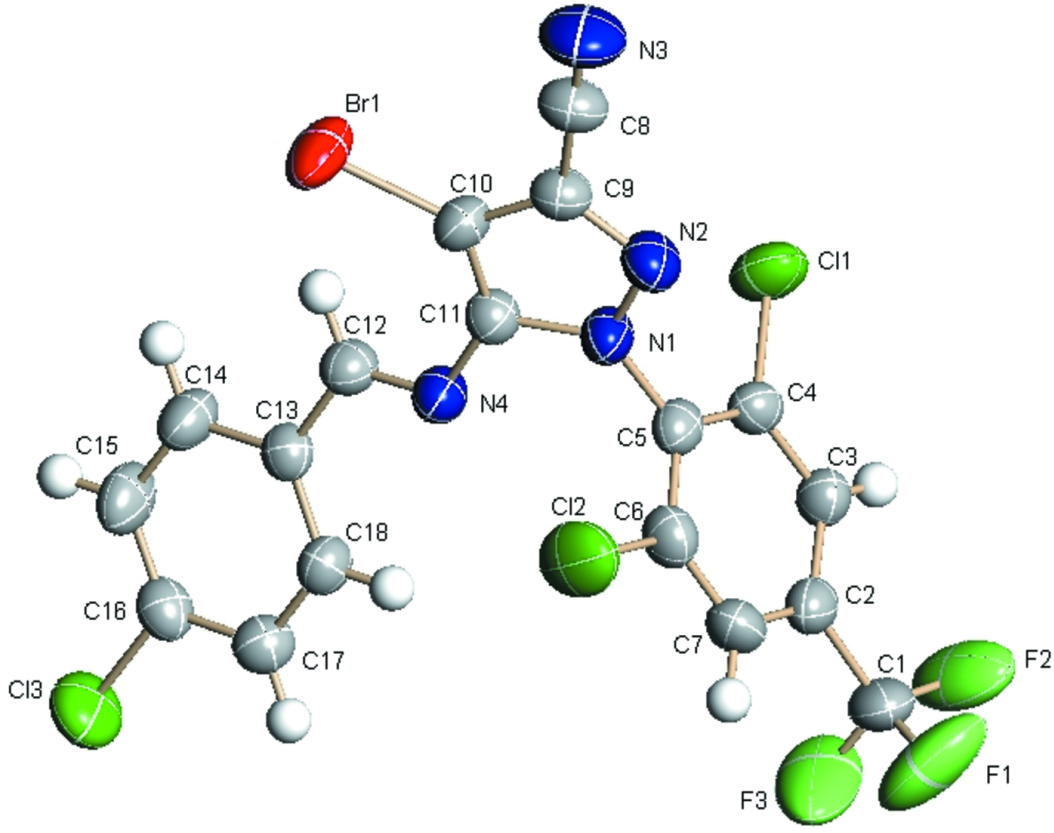
	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0779 (4)	0.0866 (4)	0.0696 (4)	−0.0145 (3)	0.0327 (3)	−0.0231 (3)
Cl1	0.0865 (9)	0.0873 (9)	0.0450 (6)	0.0215 (7)	0.0038 (5)	0.0120 (6)
Cl2	0.0807 (9)	0.1045 (11)	0.0831 (9)	0.0444 (9)	−0.0068 (7)	0.0048 (8)
Cl3	0.0756 (9)	0.0734 (9)	0.0922 (10)	−0.0251 (7)	−0.0067 (7)	−0.0206 (7)
F1	0.191 (5)	0.163 (4)	0.097 (3)	0.050 (4)	0.084 (3)	0.037 (3)
F2	0.137 (4)	0.185 (4)	0.066 (2)	0.092 (3)	0.009 (2)	−0.021 (2)
F3	0.128 (4)	0.342 (9)	0.130 (4)	−0.077 (4)	0.041 (3)	−0.163 (6)
N1	0.0422 (18)	0.0493 (19)	0.0507 (19)	−0.0050 (15)	0.0045 (14)	−0.0097 (15)
N2	0.050 (2)	0.0506 (19)	0.058 (2)	−0.0075 (16)	−0.0029 (16)	−0.0093 (17)
N3	0.107 (4)	0.076 (3)	0.065 (3)	−0.003 (3)	−0.011 (2)	−0.028 (2)
N4	0.0471 (19)	0.0453 (18)	0.0487 (18)	−0.0064 (15)	0.0043 (14)	−0.0071 (15)
C1	0.063 (3)	0.087 (4)	0.041 (2)	0.003 (3)	0.003 (2)	−0.011 (2)
C2	0.043 (2)	0.056 (2)	0.047 (2)	−0.0071 (18)	0.0034 (16)	−0.0035 (18)
C3	0.043 (2)	0.051 (2)	0.049 (2)	0.0034 (18)	0.0023 (16)	0.0014 (18)
C4	0.046 (2)	0.048 (2)	0.0394 (19)	−0.0045 (17)	−0.0002 (16)	0.0034 (16)
C5	0.040 (2)	0.044 (2)	0.046 (2)	−0.0082 (17)	0.0037 (16)	−0.0053 (17)
C6	0.043 (2)	0.056 (3)	0.059 (2)	0.0049 (19)	−0.0029 (18)	−0.001 (2)
C7	0.050 (2)	0.071 (3)	0.045 (2)	−0.001 (2)	−0.0079 (18)	0.004 (2)
C8	0.068 (3)	0.058 (3)	0.048 (2)	0.000 (2)	−0.009 (2)	−0.006 (2)
C9	0.054 (2)	0.046 (2)	0.043 (2)	0.0008 (18)	−0.0038 (18)	−0.0032 (17)
C10	0.051 (2)	0.050 (2)	0.042 (2)	−0.0013 (18)	0.0088 (17)	0.0000 (17)
C11	0.044 (2)	0.044 (2)	0.046 (2)	−0.0024 (17)	0.0006 (16)	−0.0012 (17)
C12	0.051 (2)	0.049 (2)	0.045 (2)	−0.0043 (18)	0.0032 (17)	−0.0042 (18)
C13	0.039 (2)	0.0398 (19)	0.049 (2)	0.0019 (16)	0.0013 (16)	−0.0016 (16)
C14	0.062 (3)	0.063 (3)	0.051 (2)	−0.013 (2)	0.016 (2)	−0.008 (2)
C15	0.061 (3)	0.059 (3)	0.072 (3)	−0.022 (2)	0.018 (2)	−0.006 (2)
C16	0.046 (2)	0.043 (2)	0.061 (2)	−0.0036 (18)	−0.0032 (18)	−0.0066 (19)
C17	0.057 (2)	0.044 (2)	0.049 (2)	−0.0011 (19)	0.0013 (18)	−0.0017 (18)
C18	0.046 (2)	0.045 (2)	0.049 (2)	−0.0031 (17)	0.0067 (17)	0.0029 (17)

Geometric parameters (Å, °)

Br1—C10	1.854 (4)	C4—C5	1.383 (6)
Cl1—C4	1.722 (4)	C5—C6	1.392 (6)
Cl2—C6	1.717 (4)	C6—C7	1.377 (6)
Cl3—C16	1.735 (4)	C7—H7	0.9300

F1—C1	1.305 (7)	C8—C9	1.431 (6)
F2—C1	1.283 (6)	C9—C10	1.398 (6)
F3—C1	1.273 (6)	C10—C11	1.373 (5)
N1—N2	1.343 (5)	C12—C13	1.459 (5)
N1—C11	1.376 (5)	C12—H12	0.9300
N1—C5	1.427 (5)	C13—C18	1.383 (5)
N2—C9	1.335 (5)	C13—C14	1.390 (6)
N3—C8	1.138 (5)	C14—C15	1.384 (6)
N4—C12	1.276 (5)	C14—H14	0.9300
N4—C11	1.380 (5)	C15—C16	1.357 (6)
C1—C2	1.498 (6)	C15—H15	0.9300
C2—C7	1.365 (6)	C16—C17	1.376 (6)
C2—C3	1.380 (6)	C17—C18	1.372 (6)
C3—C4	1.388 (6)	C17—H17	0.9300
C3—H3	0.9300	C18—H18	0.9300
N2—N1—C11	113.9 (3)	N2—C9—C10	112.4 (3)
N2—N1—C5	119.5 (3)	N2—C9—C8	120.0 (4)
C11—N1—C5	126.6 (3)	C10—C9—C8	127.6 (4)
C9—N2—N1	103.3 (3)	C11—C10—C9	105.7 (3)
C12—N4—C11	120.9 (3)	C11—C10—Br1	129.6 (3)
F3—C1—F2	109.1 (6)	C9—C10—Br1	124.6 (3)
F3—C1—F1	103.4 (6)	C10—C11—N1	104.7 (3)
F2—C1—F1	104.2 (5)	C10—C11—N4	138.1 (4)
F3—C1—C2	112.2 (4)	N1—C11—N4	116.9 (3)
F2—C1—C2	115.0 (4)	N4—C12—C13	121.2 (4)
F1—C1—C2	112.0 (5)	N4—C12—H12	119.4
C7—C2—C3	121.9 (4)	C13—C12—H12	119.4
C7—C2—C1	118.7 (4)	C18—C13—C14	118.6 (4)
C3—C2—C1	119.4 (4)	C18—C13—C12	121.8 (4)
C2—C3—C4	118.4 (4)	C14—C13—C12	119.6 (4)
C2—C3—H3	120.8	C15—C14—C13	120.9 (4)
C4—C3—H3	120.8	C15—C14—H14	119.5
C5—C4—C3	120.8 (4)	C13—C14—H14	119.5
C5—C4—Cl1	119.6 (3)	C16—C15—C14	118.6 (4)
C3—C4—Cl1	119.6 (3)	C16—C15—H15	120.7
C4—C5—C6	119.0 (4)	C14—C15—H15	120.7
C4—C5—N1	121.3 (4)	C15—C16—C17	122.0 (4)
C6—C5—N1	119.7 (4)	C15—C16—Cl3	119.1 (3)
C7—C6—C5	120.4 (4)	C17—C16—Cl3	118.9 (3)
C7—C6—Cl2	120.3 (3)	C18—C17—C16	119.1 (4)
C5—C6—Cl2	119.3 (3)	C18—C17—H17	120.5
C2—C7—C6	119.5 (4)	C16—C17—H17	120.5
C2—C7—H7	120.3	C17—C18—C13	120.8 (4)
C6—C7—H7	120.3	C17—C18—H18	119.6
N3—C8—C9	178.4 (5)	C13—C18—H18	119.6

Fig. 1


N3
Br1
C8
C10
C9
N2
Cl1
C12
C11
N1
C14
C13
N4
C4
C5
C15
C3
Cl2
C6
C18
C2
C16
C7
C1
F2
C17
Cl3
F1
F3