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Ethyl 1-(4-chlorobenzyl)-3-(4-fluorophenyl)-1*H*-pyrazole-5-carboxylate

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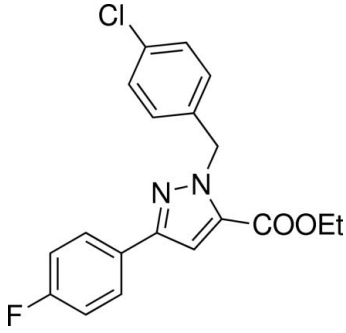
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.003 Å; R factor = 0.042; wR factor = 0.117; data-to-parameter ratio = 13.6.

In the title compound, $C_{19}H_{16}ClFN_2O_2$, the pyrazole ring makes dihedral angles of 5.15 (6) and 77.72 (6)°, with the fluorophenyl and chlorophenyl rings, respectively.

Related literature

For the pharmacological activity of pyrazole compounds, see: Ge *et al.* (2007). For the synthesis of the title compound, see: Li *et al.* (2011). For the structure of ethyl 1-benzyl-3-(4-fluorophenyl)-1*H*-pyrazole-5-carboxylate, see: Han *et al.* (2011). For applications of nitrogen-containing heterocyclic compounds, see: Ge *et al.* (2009, 2011).



Experimental

Crystal data

$C_{19}H_{16}ClFN_2O_2$
M_r = 358.79
Triclinic, $P\overline{1}$
a = 8.267 (4) Å
b = 10.375 (5) Å
c = 11.368 (5) Å
α = 109.128 (7)°
β = 93.269 (7)°
γ = 104.842 (7)°
V = 879.8 (7) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.24 mm^{-1}
T = 298 K
0.22 × 0.14 × 0.11 mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.949, T_{max} = 0.974
4589 measured reflections
3091 independent reflections
2570 reflections with $I > 2\sigma(I)$
R_{int} = 0.017

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.117
S = 1.05
3091 reflections
227 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}

Data collection: *SMART* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008); 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: FY2010).

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supplementary materials

Acta Cryst. (2011). E**67**, o1387 [**doi:10.1107/S1600536811017156**]

Ethyl 1-(4-chlorobenzyl)-3-(4-fluorophenyl)-1*H*-pyrazole-5-carboxylate

Y. Q. Ge, J. M. Zhang, G. L. Wang, H. Xu and B. Shi

Comment

Synthesis of nitrogen-containing heterocyclic compounds has been a subject of great interest due to their applications in the agrochemical and pharmaceutical fields (Ge *et al.*, 2009, 2011). Some pyrazole derivatives which belong to this category have been of interest for their biological activities. Considerable effort has been devoted to the development of novel pyrazole compounds. We report here the crystal structure of the title compound, (I) (Fig. 1)

Experimental

A mixture of ethyl 3-(4-fluorophenyl)-1*H*-pyrazole-5-carboxylate (0.02 mol), 1-chloro-4-(chloromethyl)benzene (0.0024 mol) and potassium carbonate (0.02 mol) in acetonitrile (100 ml) was heated to reflux for 3 h. The solvent was removed under reduced pressure and the product was isolated by column chromatography on silica gel (yield 88%). Crystals of (I) suitable for X-ray diffraction were obtained by allowing a refluxed solution of the product in ethyl acetate to cool slowly to room temperature and allowing the solvent to evaporate for 1 d.

Refinement

All H atoms were placed in geometrically calculated positions and refined using a riding model with C—H = 0.97 Å (for CH_2 groups) and 0.96 Å (for CH_3 groups), their isotropic displacement parameters were set to 1.2 times (1.5 times for CH_3 groups) the equivalent displacement parameter of their parent atoms.

Figures

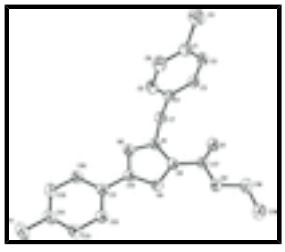


Fig. 1. The molecular structure of (I), showing displacement ellipsoids drawn at the 50% probability level.

Ethyl 1-(4-chlorobenzyl)-3-(4-fluorophenyl)-1*H*-pyrazole-5-carboxylate

Crystal data

$C_{19}H_{16}ClFN_2O_2$	$Z = 2$
$M_r = 358.79$	$F(000) = 372$
Triclinic, $P\overline{1}$	$D_x = 1.354$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

a = 8.267 (4) Å	Cell parameters from 2637 reflections
b = 10.375 (5) Å	θ = 2.3–28.0°
c = 11.368 (5) Å	μ = 0.24 mm^{-1}
α = 109.128 (7)°	T = 298 K
β = 93.269 (7)°	Block, colourless
γ = 104.842 (7)°	0.22 × 0.14 × 0.11 mm
V = 879.8 (7) $Å^3$	

Data collection

Bruker SMART APEX CCD diffractometer	3091 independent reflections
Radiation source: fine-focus sealed tube	2570 reflections with $I > 2\sigma(I)$
graphite	R_{int} = 0.017
φ and ω scans	θ_{max} = 25.1°, θ_{min} = 2.2°
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)	$h = -9 \rightarrow 9$
T_{min} = 0.949, T_{max} = 0.974	$k = -7 \rightarrow 12$
4589 measured reflections	$l = -13 \rightarrow 13$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.042	H-atom parameters constrained
$wR(F^2)$ = 0.117	$w = 1/[\sigma^2(F_o^2) + (0.0578P)^2 + 0.1997P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.05	$(\Delta/\sigma)_{max} < 0.001$
3091 reflections	$\Delta\rho_{max}$ = 0.20 e $Å^{-3}$
227 parameters	$\Delta\rho_{min}$ = −0.32 e $Å^{-3}$
0 restraints	Extinction correction: *SHELXL*, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.377 (15)

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 $F^2 > \sigma(F^2)$ 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}
Cl1	1.50553 (8)	0.97753 (7)	0.28534 (7)	0.0902 (3)
F1	0.58679 (18)	0.70217 (16)	1.03659 (11)	0.0901 (4)
O1	0.8333 (2)	0.38223 (15)	0.13974 (12)	0.0730 (4)
O2	0.85036 (17)	0.24464 (14)	0.25387 (12)	0.0635 (4)
N1	0.76250 (18)	0.58191 (16)	0.36486 (13)	0.0520 (4)
N2	0.72669 (19)	0.64677 (16)	0.47978 (13)	0.0538 (4)
C1	1.2960 (3)	0.8828 (2)	0.28289 (19)	0.0623 (5)
C2	1.2032 (3)	0.7838 (2)	0.17127 (17)	0.0613 (5)
H2	1.2510	0.7663	0.0976	0.074*
C3	1.0381 (3)	0.7106 (2)	0.17021 (16)	0.0581 (5)
H3	0.9750	0.6430	0.0949	0.070*
C4	0.9639 (2)	0.73540 (19)	0.27895 (15)	0.0530 (4)
C5	1.0613 (3)	0.8359 (2)	0.39014 (17)	0.0665 (5)
H5	1.0142	0.8537	0.4641	0.080*
C6	1.2269 (3)	0.9101 (2)	0.39306 (19)	0.0735 (6)
H6	1.2910	0.9774	0.4681	0.088*
C7	0.7810 (2)	0.6583 (2)	0.27612 (17)	0.0589 (5)
H7A	0.7168	0.7269	0.2968	0.071*
H7B	0.7342	0.5910	0.1916	0.071*
C8	0.7893 (2)	0.45469 (18)	0.35425 (15)	0.0489 (4)
C9	0.7673 (2)	0.43606 (18)	0.46724 (15)	0.0502 (4)
H9	0.7764	0.3590	0.4890	0.060*
C10	0.7285 (2)	0.55756 (18)	0.54247 (15)	0.0480 (4)
C11	0.6912 (2)	0.59545 (18)	0.67292 (15)	0.0490 (4)
C12	0.7055 (2)	0.5107 (2)	0.74363 (17)	0.0599 (5)
H12	0.7390	0.4291	0.7082	0.072*
C13	0.6705 (3)	0.5465 (2)	0.86630 (18)	0.0663 (5)
H13	0.6798	0.4896	0.9133	0.080*
C14	0.6221 (2)	0.6670 (2)	0.91642 (17)	0.0633 (5)
C15	0.6065 (3)	0.7534 (2)	0.85037 (18)	0.0642 (5)
H15	0.5733	0.8349	0.8870	0.077*
C16	0.6412 (2)	0.7171 (2)	0.72777 (17)	0.0564 (4)
H16	0.6309	0.7747	0.6817	0.068*
C17	0.8260 (2)	0.35999 (19)	0.23761 (16)	0.0535 (4)
C18	0.8920 (3)	0.1438 (2)	0.1458 (2)	0.0723 (6)
H18A	0.9889	0.1920	0.1161	0.087*
H18B	0.7970	0.1014	0.0776	0.087*
C19	0.9320 (3)	0.0317 (3)	0.1868 (3)	0.0882 (7)
H19A	1.0243	0.0751	0.2555	0.132*
H19B	0.9631	−0.0351	0.1177	0.132*
H19C	0.8343	−0.0171	0.2136	0.132*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0733 (4)	0.0979 (5)	0.1037 (5)	0.0228 (3)	0.0231 (3)	0.0415 (4)
F1	0.1132 (10)	0.1118 (10)	0.0493 (7)	0.0361 (8)	0.0303 (6)	0.0283 (7)
O1	0.1059 (11)	0.0717 (9)	0.0482 (8)	0.0343 (8)	0.0217 (7)	0.0219 (7)
O2	0.0808 (9)	0.0592 (8)	0.0567 (8)	0.0294 (7)	0.0222 (6)	0.0198 (6)
N1	0.0610 (9)	0.0581 (9)	0.0442 (8)	0.0220 (7)	0.0137 (6)	0.0229 (7)
N2	0.0632 (9)	0.0583 (9)	0.0459 (8)	0.0234 (7)	0.0151 (6)	0.0206 (7)
C1	0.0701 (12)	0.0634 (11)	0.0642 (12)	0.0276 (9)	0.0183 (9)	0.0292 (10)
C2	0.0821 (13)	0.0669 (12)	0.0503 (10)	0.0354 (10)	0.0256 (9)	0.0277 (9)
C3	0.0814 (13)	0.0575 (10)	0.0414 (9)	0.0275 (9)	0.0134 (8)	0.0192 (8)
C4	0.0727 (11)	0.0539 (10)	0.0438 (9)	0.0274 (9)	0.0146 (8)	0.0240 (8)
C5	0.0851 (14)	0.0716 (13)	0.0418 (10)	0.0225 (11)	0.0198 (9)	0.0173 (9)
C6	0.0840 (15)	0.0748 (14)	0.0507 (11)	0.0163 (11)	0.0079 (10)	0.0139 (10)
C7	0.0733 (12)	0.0672 (11)	0.0492 (10)	0.0293 (9)	0.0124 (8)	0.0300 (9)
C8	0.0494 (9)	0.0522 (9)	0.0449 (9)	0.0146 (7)	0.0074 (7)	0.0171 (7)
C9	0.0546 (10)	0.0512 (9)	0.0475 (9)	0.0162 (8)	0.0088 (7)	0.0202 (8)
C10	0.0473 (9)	0.0538 (10)	0.0433 (9)	0.0134 (7)	0.0071 (7)	0.0188 (7)
C11	0.0463 (9)	0.0546 (10)	0.0445 (9)	0.0117 (7)	0.0068 (7)	0.0180 (8)
C12	0.0726 (12)	0.0609 (11)	0.0502 (10)	0.0217 (9)	0.0130 (8)	0.0225 (9)
C13	0.0807 (13)	0.0731 (13)	0.0521 (11)	0.0215 (11)	0.0138 (9)	0.0315 (10)
C14	0.0646 (11)	0.0799 (13)	0.0419 (9)	0.0145 (10)	0.0134 (8)	0.0212 (9)
C15	0.0692 (12)	0.0685 (12)	0.0543 (11)	0.0262 (10)	0.0157 (9)	0.0152 (9)
C16	0.0624 (11)	0.0623 (11)	0.0501 (10)	0.0222 (9)	0.0123 (8)	0.0236 (8)
C17	0.0549 (10)	0.0546 (10)	0.0478 (10)	0.0135 (8)	0.0097 (7)	0.0157 (8)
C18	0.0880 (14)	0.0623 (12)	0.0657 (12)	0.0312 (11)	0.0238 (10)	0.0125 (10)
C19	0.0947 (17)	0.0722 (14)	0.112 (2)	0.0396 (13)	0.0408 (14)	0.0357 (14)

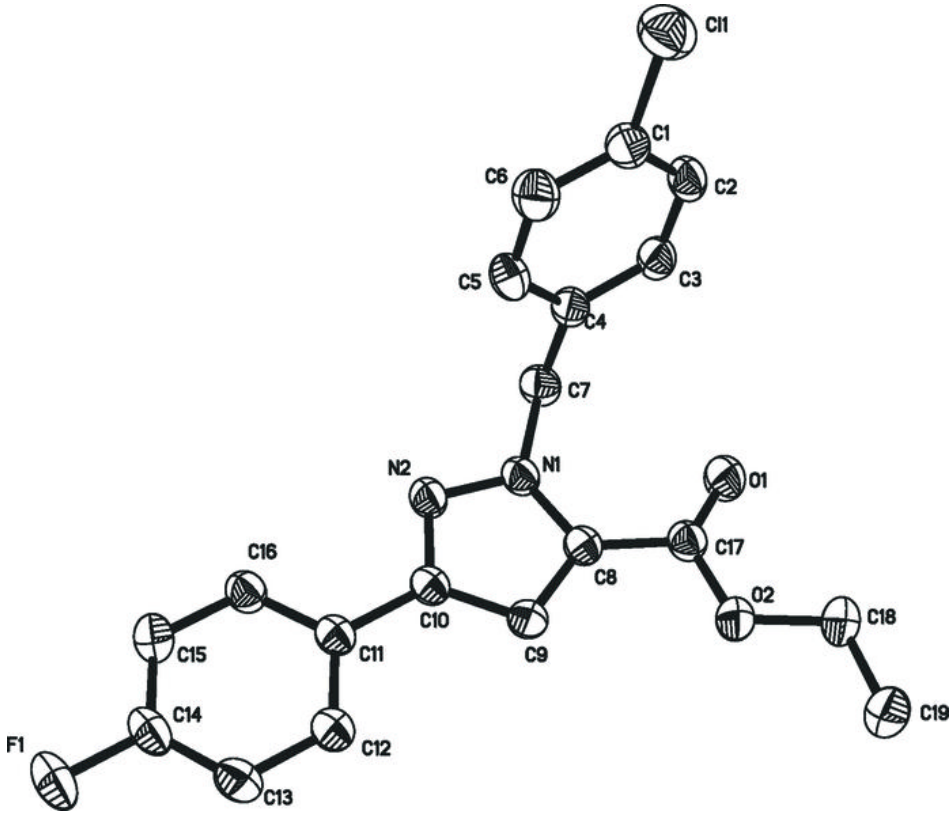
Geometric parameters (Å, °)

Cl1—C1	1.753 (2)	C8—C9	1.375 (2)
F1—C14	1.363 (2)	C8—C17	1.470 (2)
O1—C17	1.210 (2)	C9—C10	1.398 (2)
O2—C17	1.331 (2)	C9—H9	0.9300
O2—C18	1.454 (2)	C10—C11	1.477 (2)
N1—N2	1.348 (2)	C11—C16	1.390 (3)
N1—C8	1.362 (2)	C11—C12	1.392 (2)
N1—C7	1.466 (2)	C12—C13	1.388 (3)
N2—C10	1.343 (2)	C12—H12	0.9300
C1—C2	1.373 (3)	C13—C14	1.366 (3)
C1—C6	1.381 (3)	C13—H13	0.9300
C2—C3	1.379 (3)	C14—C15	1.368 (3)
C2—H2	0.9300	C15—C16	1.387 (3)
C3—C4	1.389 (2)	C15—H15	0.9300
C3—H3	0.9300	C16—H16	0.9300
C4—C5	1.387 (3)	C18—C19	1.488 (3)
C4—C7	1.512 (3)	C18—H18A	0.9700

C5—C6	1.380 (3)	C18—H18B	0.9700
C5—H5	0.9300	C19—H19A	0.9600
C6—H6	0.9300	C19—H19B	0.9600
C7—H7A	0.9700	C19—H19C	0.9600
C7—H7B	0.9700		
C17—O2—C18	115.92 (15)	N2—C10—C11	119.71 (15)
N2—N1—C8	111.63 (13)	C9—C10—C11	129.52 (15)
N2—N1—C7	118.43 (15)	C16—C11—C12	118.60 (17)
C8—N1—C7	129.72 (15)	C16—C11—C10	120.50 (16)
C10—N2—N1	105.41 (14)	C12—C11—C10	120.90 (16)
C2—C1—C6	121.27 (19)	C13—C12—C11	120.85 (19)
C2—C1—Cl1	119.37 (15)	C13—C12—H12	119.6
C6—C1—Cl1	119.37 (17)	C11—C12—H12	119.6
C1—C2—C3	118.90 (17)	C14—C13—C12	118.54 (18)
C1—C2—H2	120.6	C14—C13—H13	120.7
C3—C2—H2	120.6	C12—C13—H13	120.7
C2—C3—C4	121.55 (17)	F1—C14—C13	118.73 (19)
C2—C3—H3	119.2	F1—C14—C15	118.72 (19)
C4—C3—H3	119.2	C13—C14—C15	122.55 (18)
C5—C4—C3	118.05 (18)	C14—C15—C16	118.70 (19)
C5—C4—C7	120.71 (16)	C14—C15—H15	120.6
C3—C4—C7	121.22 (16)	C16—C15—H15	120.6
C6—C5—C4	121.21 (18)	C15—C16—C11	120.75 (18)
C6—C5—H5	119.4	C15—C16—H16	119.6
C4—C5—H5	119.4	C11—C16—H16	119.6
C5—C6—C1	119.02 (19)	O1—C17—O2	124.03 (17)
C5—C6—H6	120.5	O1—C17—C8	125.40 (18)
C1—C6—H6	120.5	O2—C17—C8	110.57 (15)
N1—C7—C4	112.17 (14)	O2—C18—C19	107.60 (18)
N1—C7—H7A	109.2	O2—C18—H18A	110.2
C4—C7—H7A	109.2	C19—C18—H18A	110.2
N1—C7—H7B	109.2	O2—C18—H18B	110.2
C4—C7—H7B	109.2	C19—C18—H18B	110.2
H7A—C7—H7B	107.9	H18A—C18—H18B	108.5
N1—C8—C9	106.76 (15)	C18—C19—H19A	109.5
N1—C8—C17	122.96 (15)	C18—C19—H19B	109.5
C9—C8—C17	130.22 (17)	H19A—C19—H19B	109.5
C8—C9—C10	105.43 (15)	C18—C19—H19C	109.5
C8—C9—H9	127.3	H19A—C19—H19C	109.5
C10—C9—H9	127.3	H19B—C19—H19C	109.5
N2—C10—C9	110.77 (15)		
C8—N1—N2—C10	−0.88 (18)	C8—C9—C10—N2	−0.08 (19)
C7—N1—N2—C10	−175.99 (14)	C8—C9—C10—C11	179.54 (16)
C6—C1—C2—C3	−0.1 (3)	N2—C10—C11—C16	5.1 (2)
Cl1—C1—C2—C3	−179.55 (14)	C9—C10—C11—C16	−174.51 (17)
C1—C2—C3—C4	0.3 (3)	N2—C10—C11—C12	−174.77 (16)
C2—C3—C4—C5	−0.5 (3)	C9—C10—C11—C12	5.6 (3)
C2—C3—C4—C7	177.88 (16)	C16—C11—C12—C13	0.1 (3)

C3—C4—C5—C6	0.4 (3)	C10—C11—C12—C13	179.94 (17)
C7—C4—C5—C6	−177.99 (18)	C11—C12—C13—C14	−0.2 (3)
C4—C5—C6—C1	−0.1 (3)	C12—C13—C14—F1	179.67 (17)
C2—C1—C6—C5	0.0 (3)	C12—C13—C14—C15	0.2 (3)
Cl1—C1—C6—C5	179.45 (16)	F1—C14—C15—C16	−179.51 (17)
N2—N1—C7—C4	95.64 (18)	C13—C14—C15—C16	0.0 (3)
C8—N1—C7—C4	−78.4 (2)	C14—C15—C16—C11	−0.1 (3)
C5—C4—C7—N1	−57.5 (2)	C12—C11—C16—C15	0.1 (3)
C3—C4—C7—N1	124.17 (18)	C10—C11—C16—C15	−179.79 (16)
N2—N1—C8—C9	0.85 (19)	C18—O2—C17—O1	1.5 (3)
C7—N1—C8—C9	175.25 (16)	C18—O2—C17—C8	−178.52 (16)
N2—N1—C8—C17	178.25 (15)	N1—C8—C17—O1	−1.4 (3)
C7—N1—C8—C17	−7.3 (3)	C9—C8—C17—O1	175.33 (19)
N1—C8—C9—C10	−0.45 (18)	N1—C8—C17—O2	178.63 (15)
C17—C8—C9—C10	−177.60 (17)	C9—C8—C17—O2	−4.6 (3)
N1—N2—C10—C9	0.57 (18)	C17—O2—C18—C19	174.11 (17)
N1—N2—C10—C11	−179.09 (14)		

Fig. 1


Cl1
C1
C6
C2
C5
C3
C4
C7
N2
N1
O1
C16
C17
C8
O2
C18
C10
C15
C11
C9
C14
C19
F1
C12
C13