Ethyl 1-(2,4-dichlorophenyl)-5-phenyl-1*H*-pyrazole-3-carboxylate

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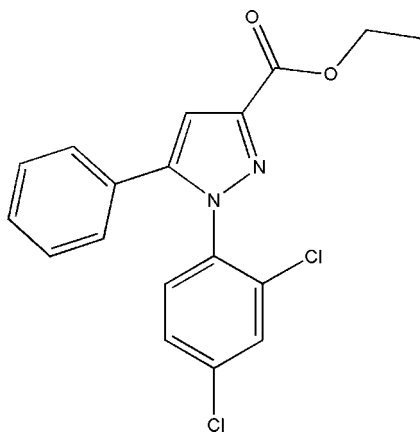Correspondence e-mail: mmartins@base.ufsm.br

In the title compound, $C_{18}H_{14}Cl_2N_2O_2$, the 2,4-dichlorophenyl and phenyl rings form dihedral angles with the pyrazole system of 77.6 (3) and 32.8 (4)°, respectively. The crystal packing is stabilized mainly by van der Waals forces.

Related literature

For related pyrazole compounds, see: Xia *et al.* (2007); Luo *et al.* (2007); Dinçer *et al.* (2004). For related literature, see: Katritzky *et al.* (2001) and references therein; Martins *et al.* (2004) and references therein. For pharmacological activities, see: Lan *et al.* (1999).

Experimental

Crystal data

$C_{18}H_{14}Cl_2N_2O_2$	V = 1765.53 (7) Å^3
M_r = 361.21	Z = 4
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
a = 11.2424 (2) Å	μ = 0.38 mm^{-1}
b = 15.3773 (4) Å	T = 294 (2) K
c = 10.9320 (2) Å	$0.55 \times 0.32 \times 0.21$ mm
β = 110.902 (1)°	

Data collection

Bruker X8 APEX II diffractometer	21369 measured reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2006)	4400 independent reflections
	3151 reflections with $I > 2\sigma(I)$
T_{min} = 0.834, T_{max} = 0.920	R_{int} = 0.025

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.055	217 parameters
$wR(F^2)$ = 0.203	H-atom parameters constrained
S = 1.10	$\Delta\rho_{max}$ = 0.65 e Å^{-3}
4400 reflections	$\Delta\rho_{min}$ = −0.68 e Å^{-3}

Data collection: *APEX2*, *COSMO* and *BIS* (Bruker, 2006); cell refinement: *SAINT* (Bruker, 2006); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RZ2172).

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supplementary materials

Ethyl 1-(2,4-dichlorophenyl)-5-phenyl-1*H*-pyrazole-3-carboxylate

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Comment

The synthesis of pyrazole and its analogues has been a subject of consistent interest because of the wide applications of such heterocycles in the pharmaceutical and agrochemical industries (Katritzky *et al.*, 2001; Martins *et al.*, 2004). In addition, the title compound is a precursor of potent cannabinoid CB_1 receptor antagonists, analogues of the Rimonabant (Sanofi-Aventis *inc*) (Lan *et al.*, 1999). In this context, we are interested in detailed knowledge of the molecular structure of the above derivatives. In this communication we reported the crystal structure of the title compound, Ethyl 1-(2,4-dichlorophenyl)-5-phenyl-1*H*-pyrazole-3-carboxylate. The analysis showed that the pyrazole ring is essentially planar with maximum deviation from mean plane of 0.003 (2) Å. The 2,4-dichlorophenyl and phenyl rings form dihedral angles with the pyrazole system of 77.6 (3)° and 32.8 (4)°, respectively. The crystal packing is stabilized mainly by van der Waals forces.

Experimental

To a stirred solution of 1-(2,4-dichlorophenyl)hydrazine (0.212 g, 1.2 mmol) in dry EtOH (15 ml) at −78°C, a solution containing the (*E*)-4-methoxy-2-oxo-4-phenyl-but-3-enoic acid ethyl ester (0.234 g, 1 mmol), EtOH (15 ml) was added dropwise. The mixture was left to cool for at least 1 h, then was allowed to warm to room temperature and stirred for 16 h. After this time, the ethanol was removed by rotatory evaporation and the crude product was extracted with CH_2Cl_2 (15 ml). The organic layer were washed with distilled water (2 × 10 ml). Finally, the solution was dried with magnesium sulfate, the solvent removed by rotatory evaporation and a solid was obtained in good yield (80%). The crystal used for the data collection was obtained by recrystallization from hexane followed by slow evaporation at room temperature.

Refinement

All H atoms were refined using a riding model, with C—H distances set to 0.93 (aromatic CH), 0.97 (methylene CH_2) and 0.98 Å (methine CH). In all cases, isotropic displacement parameters for H atoms were set to $U_{iso}(H) = xU_{eq}$ (carrier C atom), with $x = 1.5$ for methyl groups and $x = 1.2$ otherwise.
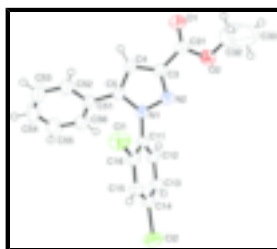
Figures

Fig. 1. View of the asymmetric unit of the title compound, showing the atom labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by circles of arbitrary radii.

Ethyl 1-(2,4-dichlorophenyl)-5-phenyl-1*H*-pyrazole-3-carboxylate

Crystal data

$C_{18}H_{14}Cl_2N_2O_2$	$F_{000} = 744$
$M_r = 361.21$	$D_x = 1.359$ Mg m^{-3}
Monoclinic, $P2_1/c$	Melting point: 123–125 C K
Hall symbol: -P 2ybc	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 11.2424$ (2) Å	Cell parameters from 150 reflections
$b = 15.3773$ (4) Å	$\theta = 2.4$–$24.4°$
$c = 10.9320$ (2) Å	$\mu = 0.38$ mm^{-1}
$\beta = 110.9020$ (10)°	$T = 294$ (2) K
$V = 1765.53$ (7) Å^3	Block, colorless
$Z = 4$	$0.55 \times 0.32 \times 0.21$ mm

Data collection

Bruker X8 APEX II diffractometer	3151 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.025$
$T = 294(2)$ K	$\theta_{max} = 28.3°$
φ and ω scans	$\theta_{min} = 1.9°$
Absorption correction: multi-scan (SADABS; Bruker, 2006)	$h = -14 \rightarrow 15$
$T_{min} = 0.834$, $T_{max} = 0.920$	$k = -20 \rightarrow 17$
21369 measured reflections	$l = -13 \rightarrow 14$
4400 independent reflections	Standard reflections: none

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.055$	H-atom parameters constrained
$wR(F^2) = 0.203$	$w = 1/[\sigma^2(F_o^2) + (0.107P)^2 + 0.6763P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.10$	$(\Delta/\sigma)_{max} = 0.001$
4400 reflections	$\Delta\rho_{max} = 0.65$ e Å^{-3}
217 parameters	$\Delta\rho_{min} = -0.68$ 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 $F^2 > 2sigma(F^2)$ 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}
O2	0.7249 (3)	0.7009 (3)	1.0257 (2)	0.1275 (15)
C32	0.8251 (6)	0.6266 (5)	1.1019 (6)	0.148 (2)
H32A	0.7996	0.5944	1.1647	0.177*
H32B	0.8476	0.5875	1.044	0.177*
C33	0.9135 (7)	0.6875 (5)	1.1566 (7)	0.161 (3)
H33A	0.9904	0.66	1.2126	0.242*
H33B	0.883	0.7266	1.2072	0.242*
H33C	0.9306	0.7194	1.0892	0.242*
Cl1	0.46219 (8)	1.03338 (5)	0.76742 (8)	0.0677 (3)
Cl2	0.13704 (7)	1.07676 (6)	1.02116 (8)	0.0716 (3)
N2	0.53242 (18)	0.80598 (13)	0.90129 (18)	0.0421 (4)
N1	0.43224 (17)	0.84323 (12)	0.80693 (17)	0.0384 (4)
C3	0.5958 (2)	0.76637 (16)	0.8352 (2)	0.0426 (5)
C5	0.4317 (2)	0.82734 (15)	0.6836 (2)	0.0401 (5)
C4	0.5379 (2)	0.77786 (16)	0.7001 (2)	0.0446 (5)
H4	0.5655	0.7565	0.6352	0.053*
C51	0.3311 (2)	0.85510 (16)	0.5614 (2)	0.0436 (5)
C56	0.2037 (2)	0.8516 (2)	0.5449 (3)	0.0583 (7)
H56	0.1796	0.8365	0.6152	0.07*
C52	0.3650 (3)	0.8777 (2)	0.4554 (3)	0.0595 (7)
H52	0.4504	0.8802	0.4646	0.071*
C55	0.1114 (3)	0.8706 (3)	0.4247 (3)	0.0761 (10)
H55	0.0257	0.868	0.4144	0.091*
C54	0.1460 (3)	0.8930 (3)	0.3215 (3)	0.0837 (11)
H54	0.084	0.9059	0.2408	0.1*
C53	0.2718 (3)	0.8965 (3)	0.3363 (3)	0.0791 (10)
H53	0.2949	0.9117	0.2655	0.095*
C16	0.3610 (2)	0.98943 (16)	0.8376 (2)	0.0425 (5)
C14	0.2174 (2)	1.00804 (17)	0.9505 (2)	0.0463 (6)
C11	0.3539 (2)	0.90014 (15)	0.8495 (2)	0.0373 (5)
C15	0.2916 (2)	1.04442 (16)	0.8873 (2)	0.0485 (6)
H15	0.2951	1.1044	0.8783	0.058*
C13	0.2074 (2)	0.91953 (18)	0.9627 (3)	0.0504 (6)

H13	0.1557	0.8965	1.0047	0.06*
C12	0.2762 (2)	0.86547 (17)	0.9110 (2)	0.0472 (6)
H12	0.2701	0.8055	0.9176	0.057*
C31	0.7121 (3)	0.7164 (2)	0.9032 (3)	0.0574 (7)
O1	0.78556 (18)	0.69195 (15)	0.8532 (2)	0.0670 (6)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O2	0.118 (2)	0.219 (4)	0.0577 (14)	0.116 (2)	0.0463 (14)	0.0580 (18)
C32	0.160 (6)	0.188 (7)	0.116 (4)	0.002 (5)	0.075 (4)	0.009 (4)
C33	0.140 (5)	0.195 (7)	0.174 (6)	0.007 (5)	0.087 (5)	−0.037 (6)
Cl1	0.0749 (5)	0.0564 (5)	0.0915 (6)	−0.0096 (3)	0.0538 (4)	0.0028 (3)
Cl2	0.0649 (5)	0.0826 (6)	0.0757 (5)	0.0131 (4)	0.0354 (4)	−0.0203 (4)
N2	0.0432 (10)	0.0509 (11)	0.0340 (9)	0.0068 (8)	0.0159 (8)	0.0034 (8)
N1	0.0389 (9)	0.0467 (11)	0.0312 (9)	0.0046 (7)	0.0147 (7)	0.0026 (7)
C3	0.0423 (11)	0.0517 (13)	0.0362 (11)	0.0025 (10)	0.0168 (9)	0.0025 (9)
C5	0.0428 (11)	0.0470 (12)	0.0325 (11)	−0.0024 (9)	0.0159 (9)	−0.0029 (9)
C4	0.0474 (12)	0.0546 (14)	0.0354 (11)	0.0028 (10)	0.0193 (9)	−0.0028 (10)
C51	0.0446 (12)	0.0511 (13)	0.0335 (11)	0.0006 (10)	0.0120 (9)	−0.0017 (9)
C56	0.0487 (14)	0.082 (2)	0.0457 (14)	−0.0036 (13)	0.0184 (11)	−0.0028 (13)
C52	0.0527 (14)	0.084 (2)	0.0420 (14)	−0.0010 (13)	0.0172 (11)	0.0074 (13)
C55	0.0440 (14)	0.117 (3)	0.0578 (18)	0.0006 (16)	0.0070 (13)	0.0014 (18)
C54	0.0616 (18)	0.129 (3)	0.0454 (16)	0.0010 (19)	0.0009 (14)	0.0157 (18)
C53	0.070 (2)	0.121 (3)	0.0415 (15)	−0.0059 (19)	0.0138 (14)	0.0188 (17)
C16	0.0411 (11)	0.0477 (13)	0.0398 (12)	−0.0022 (9)	0.0159 (9)	−0.0001 (9)
C14	0.0402 (11)	0.0582 (15)	0.0400 (12)	0.0078 (10)	0.0138 (9)	−0.0068 (10)
C11	0.0371 (10)	0.0447 (12)	0.0302 (10)	0.0025 (9)	0.0121 (8)	−0.0006 (8)
C15	0.0516 (13)	0.0452 (13)	0.0495 (14)	0.0035 (10)	0.0191 (11)	−0.0037 (10)
C13	0.0497 (13)	0.0628 (16)	0.0470 (14)	0.0011 (11)	0.0274 (11)	0.0014 (11)
C12	0.0532 (13)	0.0488 (13)	0.0459 (13)	0.0022 (10)	0.0253 (11)	0.0041 (10)
C31	0.0557 (14)	0.0770 (19)	0.0425 (13)	0.0199 (13)	0.0212 (11)	0.0039 (12)
O1	0.0563 (11)	0.0938 (16)	0.0553 (11)	0.0250 (11)	0.0252 (9)	−0.0008 (10)

Geometric parameters (Å, °)

O2—C31	1.316 (3)	C51—C52	1.387 (4)
O2—C32	1.612 (8)	C56—C55	1.384 (4)
C32—C33	1.340 (9)	C56—H56	0.93
C32—H32A	0.97	C52—C53	1.379 (4)
C32—H32B	0.97	C52—H52	0.93
C33—H33A	0.96	C55—C54	1.364 (5)
C33—H33B	0.96	C55—H55	0.93
C33—H33C	0.96	C54—C53	1.366 (5)
Cl1—C16	1.722 (2)	C54—H54	0.93
Cl2—C14	1.740 (2)	C53—H53	0.93
N2—C3	1.329 (3)	C16—C11	1.384 (3)
N2—N1	1.353 (3)	C16—C15	1.386 (3)
N1—C5	1.368 (3)	C14—C13	1.376 (4)

N1—C11	1.432 (3)	C14—C15	1.378 (3)
C3—C4	1.397 (3)	C11—C12	1.385 (3)
C3—C31	1.469 (3)	C15—H15	0.93
C5—C4	1.372 (3)	C13—C12	1.386 (3)
C5—C51	1.473 (3)	C13—H13	0.93
C4—H4	0.93	C12—H12	0.93
C51—C56	1.380 (4)	C31—O1	1.202 (3)
C31—O2—C32	117.1 (3)	C53—C52—H52	120.1
C33—C32—O2	90.4 (6)	C51—C52—H52	120.1
C33—C32—H32A	113.6	C54—C55—C56	120.0 (3)
O2—C32—H32A	113.6	C54—C55—H55	120
C33—C32—H32B	113.6	C56—C55—H55	120
O2—C32—H32B	113.6	C55—C54—C53	120.1 (3)
H32A—C32—H32B	110.9	C55—C54—H54	120
C32—C33—H33A	109.5	C53—C54—H54	120
C32—C33—H33B	109.5	C54—C53—C52	120.6 (3)
H33A—C33—H33B	109.5	C54—C53—H53	119.7
C32—C33—H33C	109.5	C52—C53—H53	119.7
H33A—C33—H33C	109.5	C11—C16—C15	120.6 (2)
H33B—C33—H33C	109.5	C11—C16—Cl1	120.05 (18)
C3—N2—N1	103.97 (17)	C15—C16—Cl1	119.28 (19)
N2—N1—C5	112.66 (18)	C13—C14—C15	122.3 (2)
N2—N1—C11	116.86 (17)	C13—C14—Cl2	118.99 (19)
C5—N1—C11	130.00 (18)	C15—C14—Cl2	118.6 (2)
N2—C3—C4	112.3 (2)	C16—C11—C12	119.7 (2)
N2—C3—C31	121.2 (2)	C16—C11—N1	120.9 (2)
C4—C3—C31	126.6 (2)	C12—C11—N1	119.3 (2)
N1—C5—C4	105.78 (19)	C14—C15—C16	118.4 (2)
N1—C5—C51	125.1 (2)	C14—C15—H15	120.8
C4—C5—C51	129.1 (2)	C16—C15—H15	120.8
C5—C4—C3	105.3 (2)	C14—C13—C12	118.5 (2)
C5—C4—H4	127.3	C14—C13—H13	120.7
C3—C4—H4	127.3	C12—C13—H13	120.7
C56—C51—C52	118.9 (2)	C11—C12—C13	120.5 (2)
C56—C51—C5	122.2 (2)	C11—C12—H12	119.8
C52—C51—C5	118.7 (2)	C13—C12—H12	119.8
C51—C56—C55	120.5 (3)	O1—C31—O2	124.3 (3)
C51—C56—H56	119.8	O1—C31—C3	124.4 (2)
C55—C56—H56	119.8	O2—C31—C3	111.3 (2)
C53—C52—C51	119.9 (3)		
N2—N1—C11—C12	−70.7 (3)	C3—C4—C31—O1	−168.1 (4)
C5—C4—C51—C52	147.2 (4)	O2—C32—C31—O1	167.6 (5)
N1—C5—C51—C11	5.25 (17)	O2—N2—C3—C31	−7.5 (2)

Fig. 1