organic compounds

Methyl 5-phenyl-1H-pyrazole-3-carboxylate

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The title compound, $C_{11}H_{10}N_2O_2$, was prepared by the esterfication of 5-phenyl-1H-pyrazole-3-carboxylic acid with methanol. The phenyl ring is rotated out of the pyrazole plane, forming a dihedral angle of 6.4 (1)°. The crystal structure is stabilized by intermolecular aromatic π–π interactions [with a centroid–centroid distance of 3.862 (3) Å between the pyrazole ring and the benzene ring of a neighboring molecule], and by three different types of hydrogen bond (N—H···N, N—H···O and C—H···O).

Related literature

For the coordination chemistry of similar pyrazole derivatives, see: Trofimenko (1972); Xing *et al.* (2007); Infantes *et al.* (1999). For related literature, see: Otieno *et al.* (2002); Roussel *et al.* (2006).
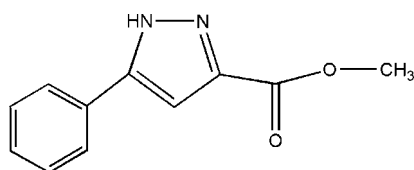
Experimental

Crystal data

$C_{11}H_{10}N_2O_2$	$b = 5.980$ (1) Å
$M_r = 202.21$	$c = 16.387$ (4) Å
Monoclinic, $C2/c$	$\beta = 122.933$ (2)°
$a = 24.540$ (6) Å	$V = 2018.3$ (8) Å³
$Z = 8$	$T = 293$ (2) K
Mo $K\alpha$ radiation	$0.20 \times 0.15 \times 0.05$ mm
$\mu = 0.09$ mm⁻¹	

Data collection

Bruker APEXII diffractometer	2185 independent reflections
Absorption correction: none	1612 reflections with $I > 2\sigma(I)$
5591 measured reflections	$R_{int} = 0.022$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.044$	136 parameters
$wR(F^2) = 0.120$	H-atom parameters constrained
$S = 1.05$	$\Delta\rho_{max} = 0.21$ e Å⁻³
2185 reflections	$\Delta\rho_{min} = -0.22$ e Å⁻³

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1N···N2^i	0.86	2.20	2.998 (2)	153
N1—H1N···O2^i	0.86	2.52	3.134 (2)	130
C5—H5···O1^{ii}	0.93	2.52	3.372 (2)	153

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

Data collection: *APEXII* (Bruker, 2005); cell refinement: *APEXII*; data reduction: *SAINT* (Bruker, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997b); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997b); molecular graphics: *SHELXTL* (Sheldrick, 1997a) and *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LX2019).

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supplementary materials

Methyl 5-phenyl-1*H*-pyrazole-3-carboxylate

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Comment

The coordination chemistry of pyrazole and its derivatives has been received great attention since poly(pyrazolyl)borate was found (Trofimenko, 1972). The electron donor (nitrogen) of non-substituted pyrazole unit can coordinate to many metal ions such as copper and vanadium, *etc*. (Otieno *et al.*, 2002; Xing *et al.*, 2007). When the carboxyl group as the substitutent at three or five position on the pyrazole ring is present, this will enhance the coordination capability of the pyrazole ring, and the substituted carboxyl group and the pyrazole ring with the metal ion can form a steady five-member cycle (Roussel *et al.*, 2006). Herein we report the molecular and crystal structure of the title compound, methyl 5-phenyl-1*H*-pyrazole-3-carboxylic acid (Fig. 1).

The crystal structure of the title compound (Fig. 1) indicates that the phenyl plane was not coplanar with the pyrazole plane, with their dihedron angle of 6.4 (1)°. All the bond lengths of the pyrazole ring are close to the corresponding bond lengths of ethyl 5-phenyl-1*H*-pyrazole-3-carboxylate as reported previously (Infantes *et al.*, 1999). The molecular packing (Fig. 2) is stabilized by π···π stacking interactions between the pyrazole ring and the benzene ring of adjacent molecule, with the *Cg*1···*Cg*2 distance of 3.862 (3) Å (*Cg*1 and *Cg*2 are the centorids of the C7—C9/N2—N1 pyrazole ring and the C1—C6 benzene ring, respectively; symmetry code as in Fig. 2). The molecular packing is further stabilized by three different hydrogen bonds (Fig. 2 and Table 1).

Experimental

CuCl$_2$ (40.0 mg, 0.21 mmol) was added into the methanol (10 ml) gently, the suspension was kept stirring at room temperature until the solution turned clear green, after which, 5-phenyl-1*H*-pyrazole-3-carboxylic acid (36.3 mg, 0.21 mmol) was added, then HCl (6.0*M*, 1.0 ml) was dropped in and stirred for 7 h continuously. Precipitate was filtered off and the filtrate was kept in conical flask for about one month and some pretty colorless rhombic crystals were obtained from the solution, dried in vacuum. Yield: 31.2%. Crystal of the title compound suitable for single-crystal X-ray diffraction was selected directly from the sample as prepared.

Refinement

All H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93 Å for aromatic H atoms, 0.96 Å for methyl H atoms and 0.86 Å for Nitrogen H atoms, respectively, and with $U_{iso}(H) = 1.2U_{eq}(C)$ for aromatic and methylene H atoms, $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H atoms and $U_{iso}(H) = 1.2U_{eq}(N)$ for Nitrogen H atoms.

Figures
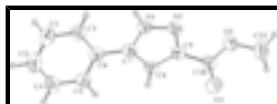

Fig. 1. The molecular structure of the title compound, showing displacement ellipsoides drawn at the 50% probability level.
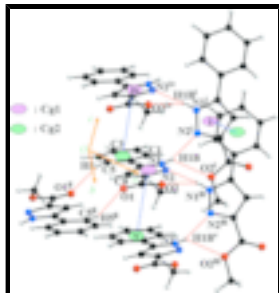
supplementary materials

Fig. 2. Packing arrangement of the title compound along *b* axis. *Cg* denotes the ring centroids. [Symmetry code: (i) −*x* + 1/2, *y* − 1/2, −*z* + 1/2; (ii) −*x*, −*y* + 1,-*z*; (iii) −*x* + 1/2, *y* + 1/2, −*z* + 1/2; (iv) *x*, *y* − 1, *z*; (v) *x*, *y* + 1, *z*.]

Methyl 5-phenyl-1*H*-pyrazole-3-carboxylate

Crystal data

$C_{11}H_{10}N_2O_2$	$F_{000} = 848$
$M_r = 202.21$	$D_x = 1.331$ Mg m^{-3}
Monoclinic, *C*2/*c*	Melting point: 185.5-185.9 K
Hall symbol: -c 2yc	Mo *K*α radiation λ = 0.71073 Å
$a = 24.540$ (6) Å	Cell parameters from 2416 reflections
$b = 5.980$ (1) Å	θ = 2.5–29.0º
$c = 16.387$ (4) Å	μ = 0.09 mm^{-1}
β = 122.933 (2)º	$T = 293$ (2) K
$V = 2018.3$ (8) Å^3	Rhombic, colorless
$Z = 8$	0.20 × 0.15 × 0.05 mm

Data collection

Bruker P4 diffractometer	1612 reflections with $I > 2σ(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.022$
Monochromator: graphite	$θ_{max} = 27.0º$
$T = 293(2)$ K	$θ_{min} = 2.5º$
ω scans	$h = −31→31$
Absorption correction: none	$k = −7→5$
5591 measured reflections	$l = −20→20$
2185 independent reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2σ(F^2)] = 0.044$	H-atom parameters constrained
$wR(F^2) = 0.120$	$w = 1/[σ^2(F_o^2) + (0.0548P)^2 + 0.752P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(Δ/σ)_{max} < 0.001$
2185 reflections	$Δρ_{max} = 0.21$ e Å^{-3}

136 parameters	$\Delta\rho_{min} = -0.22$ 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$^2 > 2$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}
C1	0.17604 (8)	−0.1789 (3)	0.03661 (12)	0.0476 (4)
H1	0.2185	−0.1488	0.0870	0.057*
C2	0.16326 (10)	−0.3570 (3)	−0.02517 (13)	0.0580 (5)
H2	0.1973	−0.4456	−0.0162	0.070*
C3	0.10077 (10)	−0.4042 (3)	−0.09971 (14)	0.0594 (5)
H3	0.0924	−0.5242	−0.1410	0.071*
C4	0.05089 (9)	−0.2733 (3)	−0.11276 (13)	0.0563 (5)
H4	0.0085	−0.3054	−0.1631	0.068*
C5	0.06269 (8)	−0.0947 (3)	−0.05225 (11)	0.0471 (4)
H5	0.0283	−0.0069	−0.0623	0.057*
C6	0.12571 (7)	−0.0444 (3)	0.02380 (10)	0.0365 (4)
C7	0.13661 (7)	0.1465 (3)	0.08722 (10)	0.0349 (3)
C8	0.09485 (7)	0.3081 (3)	0.08165 (10)	0.0373 (4)
H8	0.0508	0.3221	0.0345	0.045*
C9	0.13253 (7)	0.4464 (3)	0.16157 (10)	0.0358 (4)
C10	0.11091 (8)	0.6429 (3)	0.19061 (11)	0.0398 (4)
C11	0.14358 (11)	0.9382 (3)	0.30373 (15)	0.0663 (6)
H11A	0.1821	0.9962	0.3604	0.099*
H11B	0.1126	0.8983	0.3198	0.099*
H11C	0.1252	1.0502	0.2537	0.099*
N1	0.19519 (6)	0.1955 (2)	0.16806 (9)	0.0405 (3)
H1N	0.2296	0.1177	0.1872	0.049*
N2	0.19433 (6)	0.3774 (2)	0.21536 (9)	0.0413 (3)
O1	0.05575 (6)	0.7053 (2)	0.14871 (10)	0.0640 (4)
O2	0.15988 (6)	0.7429 (2)	0.26949 (8)	0.0522 (3)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}

C1	0.0431 (9)	0.0528 (11)	0.0442 (9)	0.0067 (8)	0.0219 (8)	−0.0001 (8)
C2	0.0669 (13)	0.0531 (11)	0.0609 (11)	0.0143 (9)	0.0392 (10)	0.0002 (9)
C3	0.0805 (14)	0.0510 (11)	0.0535 (11)	−0.0026 (10)	0.0409 (11)	−0.0100 (9)
C4	0.0554 (11)	0.0605 (12)	0.0454 (9)	−0.0107 (9)	0.0225 (8)	−0.0135 (9)
C5	0.0383 (9)	0.0530 (10)	0.0430 (9)	−0.0004 (8)	0.0176 (7)	−0.0066 (8)
C6	0.0374 (8)	0.0391 (8)	0.0326 (7)	0.0008 (6)	0.0188 (7)	0.0036 (6)
C7	0.0292 (7)	0.0378 (8)	0.0328 (7)	−0.0017 (6)	0.0138 (6)	0.0023 (6)
C8	0.0254 (7)	0.0401 (9)	0.0361 (8)	0.0004 (6)	0.0100 (6)	0.0011 (6)
C9	0.0296 (8)	0.0363 (8)	0.0371 (8)	−0.0011 (6)	0.0152 (6)	0.0030 (6)
C10	0.0383 (9)	0.0364 (9)	0.0426 (8)	−0.0022 (7)	0.0207 (7)	0.0010 (7)
C11	0.0917 (16)	0.0487 (12)	0.0713 (13)	−0.0093 (10)	0.0526 (12)	−0.0182 (10)
N1	0.0269 (7)	0.0431 (8)	0.0414 (7)	0.0048 (5)	0.0121 (6)	−0.0022 (6)
N2	0.0322 (7)	0.0402 (7)	0.0412 (7)	0.0002 (6)	0.0132 (6)	−0.0041 (6)
O1	0.0428 (7)	0.0590 (8)	0.0755 (9)	0.0109 (6)	0.0227 (7)	−0.0104 (7)
O2	0.0491 (7)	0.0479 (7)	0.0538 (7)	−0.0055 (5)	0.0242 (6)	−0.0153 (6)

Geometric parameters (Å, °)

C1—C2	1.383 (2)	C7—C8	1.375 (2)
C1—C6	1.391 (2)	C8—C9	1.392 (2)
C1—H1	0.9300	C8—H8	0.9300
C2—C3	1.374 (3)	C9—N2	1.339 (2)
C2—H2	0.9300	C9—C10	1.471 (2)
C3—C4	1.368 (3)	C10—O1	1.197 (2)
C3—H3	0.9300	C10—O2	1.336 (2)
C4—C5	1.377 (2)	C11—O2	1.443 (2)
C4—H4	0.9300	C11—H11A	0.9600
C5—C6	1.393 (2)	C11—H11B	0.9600
C5—H5	0.9300	C11—H11C	0.9600
C6—C7	1.467 (2)	N1—N2	1.342 (2)
C7—N1	1.355 (2)	N1—H1N	0.8600
C2—C1—C6	120.36 (16)	C7—C8—C9	105.38 (13)
C2—C1—H1	119.8	C7—C8—H8	127.3
C6—C1—H1	119.8	C9—C8—H8	127.3
C3—C2—C1	120.56 (17)	N2—C9—C8	111.80 (13)
C3—C2—H2	119.7	N2—C9—C10	120.80 (13)
C1—C2—H2	119.7	C8—C9—C10	127.38 (14)
C4—C3—C2	119.54 (17)	O1—C10—O2	123.87 (15)
C4—C3—H3	120.2	O1—C10—C9	123.93 (14)
C2—C3—H3	120.2	O2—C10—C9	112.21 (13)
C3—C4—C5	120.74 (17)	O2—C11—H11A	109.5
C3—C4—H4	119.6	O2—C11—H11B	109.5
C5—C4—H4	119.6	H11A—C11—H11B	109.5
C4—C5—C6	120.56 (16)	O2—C11—H11C	109.5
C4—C5—H5	119.7	H11A—C11—H11C	109.5
C6—C5—H5	119.7	H11B—C11—H11C	109.5
C1—C6—C5	118.25 (15)	N2—N1—C7	113.48 (12)
C1—C6—C7	122.54 (14)	N2—N1—H1N	123.3
C5—C6—C7	119.21 (14)	C7—N1—H1N	123.3

N1—C7—C8	105.59 (13)	C9—N2—N1	103.74 (12)
N1—C7—C6	123.29 (13)	C10—O2—C11	116.42 (14)
C8—C7—C6	131.11 (13)		
C6—C1—C2—C3	−0.3 (3)	C7—C8—C9—N2	−0.41 (18)
C1—C2—C3—C4	0.1 (3)	C7—C8—C9—C10	−178.60 (15)
C2—C3—C4—C5	0.2 (3)	N2—C9—C10—O1	−175.69 (16)
C3—C4—C5—C6	−0.3 (3)	C8—C9—C10—O1	2.4 (3)
C2—C1—C6—C5	0.2 (2)	N2—C9—C10—O2	4.0 (2)
C2—C1—C6—C7	−179.99 (15)	C8—C9—C10—O2	−178.00 (14)
C4—C5—C6—C1	0.1 (2)	C8—C7—N1—N2	0.08 (17)
C4—C5—C6—C7	−179.73 (15)	C6—C7—N1—N2	179.93 (13)
C1—C6—C7—N1	−6.1 (2)	C8—C9—N2—N1	0.45 (17)
C5—C6—C7—N1	173.74 (14)	C10—C9—N2—N1	178.78 (13)
C1—C6—C7—C8	173.71 (16)	C7—N1—N2—C9	−0.33 (17)
C5—C6—C7—C8	−6.5 (2)	O1—C10—O2—C11	−0.4 (2)
N1—C7—C8—C9	0.19 (16)	C9—C10—O2—C11	179.90 (14)
C6—C7—C8—C9	−179.64 (15)		

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1N···N2[i]	0.86	2.20	2.998 (2)	153
N1—H1N···O2[i]	0.86	2.52	3.134 (2)	130
C5—H5···O1[ii]	0.93	2.52	3.372 (2)	153

Symmetry codes: (i) −x+1/2, y−1/2, −z+1/2; (ii) −x, −y+1, −z.

Fig. 1

Fig. 2