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4-Acetyl-5-methyl-1-phenyl-1*H*-pyrazole-3-carboxylic acid

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.040
wR factor = 0.109
Data-to-parameter ratio = 12.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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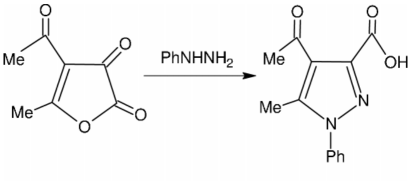
In the title compound, $C_{13}H_{12}N_2O_3$, the phenyl ring is nearly planar, with a maximum deviation of 0.012 (1) Å. The pyrazole ring is planar and forms a 48.45 (5)° dihedral angle with the phenyl ring. There is an intramolecular O—H···O hydrogen bond between the hydroxy group and the ketone group. The packing is governed by weak C—H···N,O interactions.

Comment

Some pyrazoles are known to possess considerable antimicrobial, antiviral, antitumor, anti-inflammatory, antihistaminic and phytotoxic activities (Mahajan *et al.*, 1991; Janus *et al.*, 1999; Katayama & Oshiyama, 1997; Badawey & El-Ashmawey, 1998; Mishra *et al.*, 1998; Bernard *et al.*, 1985). As part of our current interest in such compounds, we synthesized and studied the X-ray structure of the title compound, (I).



(I)

The phenyl ring is nearly planar, with a maximum deviation of 0.012 (1) Å for atom C9. The pyrazole ring is planar and forms a 48.45 (5)° dihedral angle with the phenyl ring. The carboxylic moiety is slightly twisted by 3.9 (1)° with respect to the pyrazole ring, whereas the ketone group makes a 2.9 (1)° angle with the pyrazole ring. The N1—C4 bond length of 1.442 (2) Å corresponds to a C—N single bond.

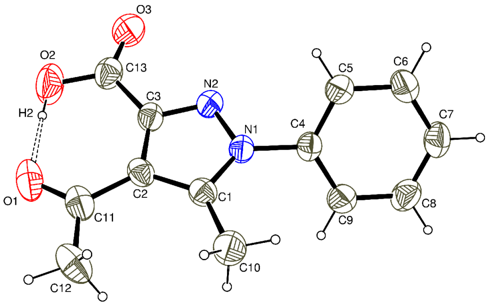


Figure 1
*ORTEP*III (Burnett & Johnson, 1996) view of the title compound, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as small circles of arbitrary radii. The hydrogen bond is shown dashed.

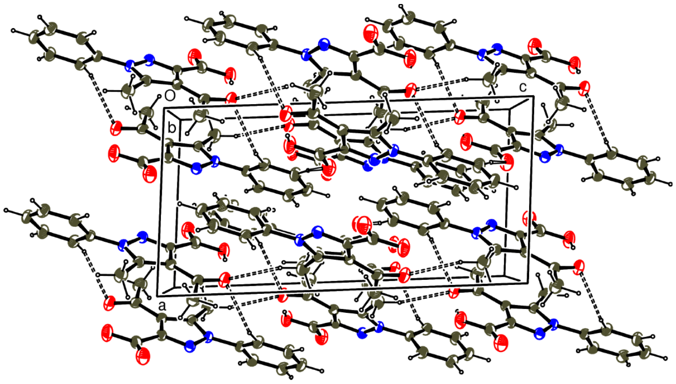


Figure 2
Packing in the unit cell, showing the C—H···O hydrogen-bond interactions. Displacement ellipsoids are drawn at the 30% probability level.

The N—N distance in the pyrazole ring [1.357 (2) Å] is slightly shorter than reported values observed in other pyrazole ring-based organic compounds (Hökelek, Kılıç & Hayvalı, 2002; Hökelek, Kılıç, Işıkalan & Hayvalı, 2002). The C3—N2—N1—C4 torsion angle is 179.2 (2)°.

There is an intramolecular O—H···O hydrogen bond between the hydroxy group of the carboxylic moiety and the O atom of the ketone group (Table 2). The packing, as shown in Fig. 2, is governed by weak intermolecular C—H···O(N) hydrogen bonds between some C atoms of the phenyl ring and O or N atoms of symmetry-related molecules.

Experimental

Solvents were dried by refluxing with the appropriate drying agent and distilled before use. The melting point was determined on an Electrothermal 9200 apparatus. Elemental analysis was performed with a Carlo Erba 1108 Elemental Analyzer. The FT–IR spectrum was measured on a Jasco Plus Model 460 spectrometer using a potassium bromide pellet. The ^{1}H and ^{13}C NMR spectra were obtained on a Gemn–Varian 200 MHz instrument. The chemical shifts were reported in p.p.m. from tetramethylsilsane.

To a mixture of 4-acetyl-5-methyl-2,3-dioxo-2,3-dihydrofuran (1.54 g, 10 mmol) and dry ether (30 ml), phenylhydrazine (1.08 g, 10 mmol) in dry ether (10 ml) were added dropwise, and the reaction mixture was stirred at room temperature for 1 h. The precipitate was filtered off and crystallized from toluene; yield: 1.66 g (68%), m.p: 456 K. IR (KBr, cm^{-1}): ν = 1727 (C═O), 3434 (broad, OH). ^{1}H NMR (CDCl$_3$, p.p.m.): δ = 2.575 (*s*, 3 H, CH$_3$), 2.683 (*s*, 3H, COCH$_3$), 7.407–7.468 (*m*, 5H, C$_6$H$_5$). ^{13}C NMR (CDCl$_3$, p.p.m.): δ = 200.064 (Me-C═O), 162.508 (COOH), 148.441 (C1), 145.713 (C3), 139.488, 131.880, 131.414, 128.414 (C═C, arom.), 121.982 (C2), 32.345 (C12), 18.366 (C10). Analysis calculated for $C_{13}H_{12}N_2O_3$: C 63.93, H 4.95, N 11.47 %; found: C 63.86,H 4.93, N 11.54%.

Crystal data

$C_{13}H_{12}N_2O_3$
M_r = 244.25
Monoclinic, $P2_1/c$
a = 7.5389 (12) Å
b = 10.3932 (13) Å
c = 14.8992 (13) Å
β = 93.881 (6)°
V = 1164.7 (3) Å^3
Z = 4

D_x = 1.393 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 2.4–25.7°
μ = 0.10 mm^{-1}
T = 293 (2) K
Prism, colorless
0.25 × 0.20 × 0.15 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (*MolEN*; Fair, 1990)
$T_{\min}$ = 0.976, $T_{\max}$ = 0.985
2277 measured reflections
2221 independent reflections
1356 reflections with $I > 2\sigma(I)$

$R_{\rm int}$ = 0.024
$\theta_{\max}$ = 25.7°
$h = 0 \rightarrow 9$
$k = -12 \rightarrow 0$
$l = -18 \rightarrow 17$
3 standard reflections
frequency: 120 min
intensity decay: 0.7%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.109
S = 1.00
2221 reflections
166 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0505P)^2 + 0.1554P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 0.19 e Å^{-3}
$\Delta\rho_{\min}$ = −0.17 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—C1	1.355 (2)	O1—C11	1.237 (2)
N1—N2	1.358 (2)	O2—C13	1.308 (2)
N1—C4	1.442 (2)	O3—C13	1.204 (2)
N2—C3	1.320 (2)		
C1—N1—N2	112.95 (14)	N2—N1—C4	117.41 (14)
C1—N1—C4	129.64 (15)	C3—N2—N1	105.32 (15)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O1	0.82	1.70	2.521 (2)	174
C5—H5···O1$^{\rm i}$	0.93	2.56	3.325 (2)	140
C6—H6···O3$^{\rm ii}$	0.93	2.59	3.486 (3)	161
C10—H10*C*···O1$^{\rm iii}$	0.96	2.48	3.381 (2)	156

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

All H atoms were positioned geometrically and treated as riding, with C—H = 0.93 (aromatic) and 0.96 Å (methyl), O—H = 0.82 Å, and $U_{\rm eq}$(H) = 1.2$U_{\rm eq}$(C$_{\rm aromatic}$) and 1.5$U_{\rm eq}$(C$_{\rm methyl}$, O).

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1993); cell refinement: *CAD-4 EXPRESS*; data reduction: *CAD-4 EXPRESS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996) and *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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o866 Cengiz Arıcı *et al.* • $C_{13}H_{12}N_2O_3$ *Acta Cryst.* (2004). E**60**, o865–o867

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Acta Cryst. (2004). E**60**, o865–o867 Cengiz Arıcı *et al.* • $C_{13}H_{12}N_2O_3$ **o867**