

1-(2,4-Dinitrophenyl)-3-(2-hydroxy-5-methylphenyl)-
pyrazole-4-carboxaldehydeJ. Jeyakanthan,^a
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Key indicators

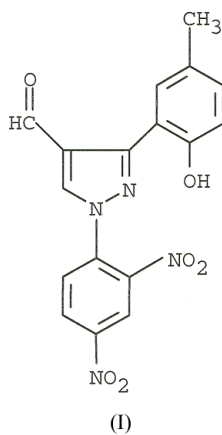
Single-crystal X-ray study
T = 293 K
Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$
R factor = 0.050
wR factor = 0.176
Data-to-parameter ratio = 12.0For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

In the title compound, $\text{C}_{17}\text{H}_{12}\text{N}_4\text{O}_6$, the dinitrophenyl and 2-hydroxy-5-methylphenyl groups are oriented with dihedral angles of $23.9 (1)$ and $13.1 (1)^\circ$, respectively, with respect to the pyrazole ring. The internal C—C—C ring angles at the *ortho* and *para* positions where NO_2 is bonded are $121.7 (2)$ and $121.9 (2)^\circ$. The dihedral angle between the phenyl rings is $11.2 (1)^\circ$. The crystal structure is stabilized by O—H...N intramolecular and by C—H...O intermolecular hydrogen bonds.

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Comment

Pyrazole derivatives are principally used in medicine; many alkyl pyrazoles have shown quite significant bacteriostatic, bacteriocidal and fungicidal, analgesic and antipyretic activity (Malhotra *et al.*, 1997; Potts, 1986). Nitrogen heterocycles, such as pyrazoles, imidazoles and triazoles, either in isolation or in a fused system, are well documented for their antifertility



activity (Omodei-Sale *et al.*, 1976). Pyrazole derivatives have been found to have moderate antimalarial activity (Garg *et al.*, 1973) and are also used as anti-inflammatory (Mani Naidu *et al.*, 1996; Lesyk *et al.*, 1998), antihyperglycaemic (Kees *et al.*, 1996), multidrug resistance (MDR) modulating (Chiba *et al.*, 1998) agents and analgesics (Sobczak & Pawlaczyk, 1998), and they have many important applications in the areas of medicine, agriculture, and also in synthetic organic chemistry (Weily & Wiley, 1964; Taki *et al.*, 1992). Pyrazole compounds are widely used as extractants in the separation of trace metals (Akama *et al.*, 1995). In view of the wide biological applications of the pyrazole derivatives, the crystal structure of the title compound, (I), has been determined.

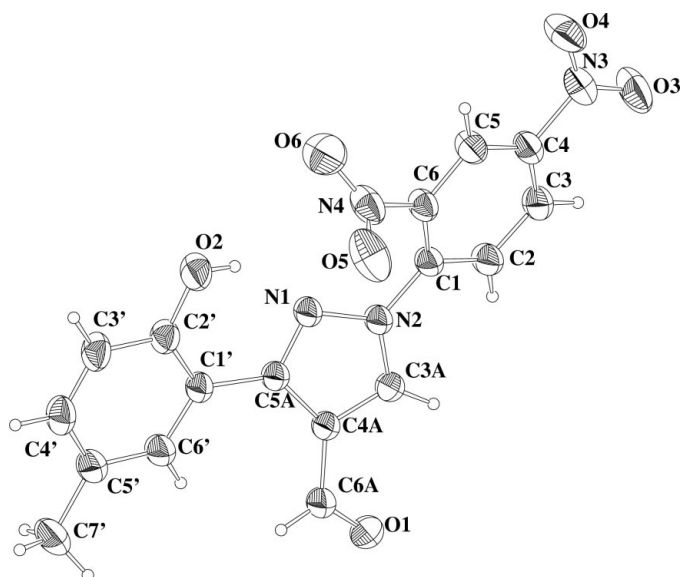


Figure 1
A ZORTEP diagram of (I) drawn with 30% probability displacement ellipsoids. H atoms have been omitted.

The bond lengths in the five-membered ring [N1—N2 1.370 (3), N2—C3A 1.341 (3), C3A—C4A 1.371 (3), C4A—C5A 1.433 (3) and C5A—N1 1.329 (3) Å] agree well with several related pyrazole derivatives (Bonati & Bovio, 1990; Allen *et al.*, 1987; Fronczek *et al.*, 1989; Panneerselvam *et al.*, 1996; Mani Naidu *et al.*, 1996; Malhotra *et al.*, 1997). The C—O [1.359 (3) Å] and C=O [1.201 (3) Å] distances compare well with those found in related pyrazole derivatives (Allen *et al.*, 1987; Malhotra *et al.*, 1997). The Csp^2 —N bonds associated with the nitro groups are clearly single bonds, while the C1—N2 [1.409 (3) Å] bond shows partial double-bond character (Jeyakanthan *et al.*, 1999) which is also evidence for conjugation. The experimental values of the internal C—C—C ring angles [121.7 (2)° and 121.9 (2)°] of the phenyl ring to which NO₂ is bonded at *ortho* and *para* positions agree with the value of 122.3 (1)° from MO calculations and 122.7 (1)° for nitrobenzene in a crystalline environment (Domenicano *et al.*, 1990). Also, absence of π — π -stacking interactions indicates that the electronic interaction of the nitro group with the ring occurs primarily at the σ level, with limited transfer of π electrons from the ring to the substituent.

The carboxaldehyde group is twisted by 13.5 (2)° from the best plane of the pyrazole ring; the C5A—C4A—C6A—O1 [169.9 (3)°] and C5A—C1'—C2'—O2 [5.6 (4)°] torsion angles give the orientations of the carboxaldehyde group and the primed phenyl group with respect to the pyrazole ring. The interplanar angle between the phenyl rings is 11.2 (1)°. The dihedral angles between the phenyl and pyrazole rings are 23.9 (1) (dinitrophenyl) and 13.1 (1)° (2-hydroxy-5-methylphenyl). There is conjugation between the phenyl and pyrazole rings.

The bond lengths and bond angles in the NO₂ groups [N3—O3 1.209 (3), N3—O4 1.220 (4), N4—O5 1.214 (4) and N4—O6 1.209 (4) Å; O3—N3—O4 124.4 (3) and O5—N4—O6 125.7 (3)°] are comparable to those found in several related pyrazole derivatives (Fronczek *et al.*, 1989; Aygün *et al.*, 1998). The nitro group in the *ortho* position is twisted 62.1 (1)° from the plane of the phenyl ring, whereas the nitro group in the *para* position is almost coplanar [dihedral angle 9.1 (2)° with the ring].

Apart from normal van der Waals interactions, the molecular structure is stabilized by O—H...N-type intramolecular hydrogen bonds, while the molecular packing in the solid state is stabilized by four C—H...O intermolecular hydrogen bonds (Table 2).

Experimental

The title compound was synthesized as follows: 1.65 g (0.005 mol) of 2-hydroxy-5-methylacetophenone 2,4-dinitrophenylhydrazone was dissolved in *N,N*-dimethylformamide (5 ml) and kept under ice-cold conditions. To this, (1.4 ml) POCl₃ was added dropwise with stirring over a period of 15 min. The reaction was stirred at room temperature for about 3–4 h, after which time the contents were poured on to crushed ice (100 g). The yellow precipitate obtained was filtered off, washed and dried. The product was purified by column chromatography using 60–120 mesh and 20% ethyl acetate–petroleum ether (yield 1.50 g) and recrystallized from ethyl acetate by slow evaporation.

Crystal data

C₁₇H₁₂N₄O₆
M_r = 368.31
 Triclinic, *P* $\bar{1}$
a = 8.411 (2) Å
b = 9.617 (3) Å
c = 10.538 (3) Å
 α = 102.62 (2)°
 β = 91.23 (2)°
 γ = 102.94 (2)°
V = 808.5 (4) Å³

Z = 2
D_x = 1.513 Mg m⁻³
 Cu K α radiation
 Cell parameters from 25 reflections
 θ = 15–25°
 μ = 1.00 mm⁻¹
T = 293 (2) K
 Block, orange
 0.25 × 0.18 × 0.15 mm

Data collection

Enraf-Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 3140 measured reflections
 2960 independent reflections
 1897 reflections with $I > 2\sigma(I)$
R_{int} = 0.016

θ_{\max} = 69.9°
 h = -10 → 10
 k = -11 → 11
 l = 0 → 12
 3 standard reflections
 frequency: 60 min
 intensity decay: 1%

Refinement

Refinement on *F*²
R[*F*² > 2 σ (*F*²)] = 0.050
 wR (*F*²) = 0.176
S = 1.17
 2960 reflections
 247 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.005$
 $\Delta\rho_{\max} = 0.23 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.28 \text{ e \AA}^{-3}$
 Extinction correction: SHELXL97
 Extinction coefficient: 0.011 (2)

Table 1

Selected geometric parameters (Å, °).

| | | | |
|-----------|-----------|-------------|-----------|
| N3—C4 | 1.470 (3) | N4—C6 | 1.473 (3) |
| C5A—N1—N2 | 105.8 (2) | C5—C6—N4 | 115.4 (2) |
| C3A—N2—N1 | 111.6 (2) | C1—C6—N4 | 122.8 (2) |
| C3A—N2—C1 | 127.5 (2) | O2—C2'—C3' | 116.6 (2) |
| N1—N2—C1 | 120.9 (2) | O2—C2'—C1' | 123.2 (2) |
| O3—N3—C4 | 117.6 (3) | N2—C3A—C4A | 107.7 (2) |
| O4—N3—C4 | 118.0 (3) | C3A—C4A—C5A | 105.0 (2) |
| O6—N4—C6 | 117.8 (3) | C3A—C4A—C6A | 121.5 (2) |
| O5—N4—C6 | 116.4 (3) | C5A—C4A—C6A | 133.4 (2) |
| C6—C1—N2 | 123.3 (2) | N1—C5A—C4A | 109.9 (2) |
| C2—C1—N2 | 118.7 (2) | N1—C5A—C1' | 119.4 (2) |
| C3—C4—N3 | 119.8 (2) | C4A—C5A—C1' | 130.6 (2) |
| C5—C4—N3 | 118.3 (3) | O1—C6A—C4A | 122.6 (3) |

Table 2

Hydrogen-bonding geometry (Å, °).

| <i>D</i> —H... <i>A</i> | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|---------------------------|-------------|---------------|-----------------------|-------------------------|
| O2—H2...N1 | 0.82 | 1.89 | 2.610 (3) | 146 |
| C2—H2A...O1 ⁱ | 0.93 | 2.43 | 3.202 (3) | 141 |
| C3A—H3A...O1 ⁱ | 0.93 | 2.34 | 3.244 (3) | 165 |

Symmetry code: (i) 1 - x, 2 - y, 2 - z.

All H atoms are included at calculated positions and refined using a riding model. The U_{iso} values for H atoms were taken as 1.2 (1.5 for methyl groups) times U_{eq} of the carrier atom.

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *SDP* (Frenz, 1978); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ZORTEP* (Zsolnai, 1997); software used to prepare material for publication: *SHELXL97* and *PARST* (Nardelli, 1983; 1995).

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