Refinement

Refinement on F^2
$R(F) = 0.045$
$wR(F^2) = 0.077$
$S = 1.51$
2666 reflections
210 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o) + 0.00027|F_o|^2]$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.33$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ e Å^{-3}
Extinction correction: Zachariasen (1967)
Extinction coefficient: 7.3 (5) $\times 10^{-6}$
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Selected geometric parameters (Å, °) for (2)*

Cl1—C2	1.730 (2)	C4—C5	1.444 (2)
Cl2—C5	1.726 (2)	C4—C6^{ii}	1.522 (2)
O1—C1	1.222 (2)	C5—C6	1.355 (2)
O2—C3	1.295 (2)	O5—C8	1.420 (2)
O3—C4	1.216 (2)	O5—C9	1.424 (2)
O4—C6	1.299 (2)	N—C7	1.489 (2)
C1—C2	1.439 (2)	N—C10	1.492 (2)
C1—C3^{i}	1.527 (2)	C7—C8	1.507 (2)
C2—C3	1.357 (2)	C9—C10	1.504 (2)
O5—C8—C7	110.5 (1)	N—C10—C9	109.3 (1)
O5—C9—C10	111.6 (2)	C7—N—C10	111.1 (1)
N—C7—C8	109.2 (1)	C8—O5—C9	110.1 (1)

Symmetry codes: (i) $2 - x, 2 - y, 2 - z$; (ii) $1 - x, 1 - y, -z$.

Table 4. *Hydrogen-bonding geometry (Å, °) for (2)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H1*A*···O4	0.90 (4)	1.72 (5)	2.512 (2)	145 (4)
O2—H1*A*···O3^{i}	0.90 (4)	2.45 (5)	3.067 (2)	126 (3)
O4—H1*B*···O2	0.70 (5)	1.92 (5)	2.512 (2)	142 (5)
O4—H1*B*···O3^{i}	0.70 (5)	2.25 (5)	2.686 (2)	122 (4)
N—H2···O4	0.91 (2)	1.99 (2)	2.851 (2)	157 (2)
N—H3···O1^{ii}	0.93 (2)	2.07 (2)	2.928 (2)	153 (2)
N—H3···O2^{iii}	0.93 (2)	2.27 (2)	2.963 (2)	131 (2)

Symmetry codes: (i) $1 - x, 1 - y, -z$; (ii) $x, y - 1, z - 1$; (iii) $2 - x, 1 - y, 1 - z$.

H atoms were located on difference syntheses and all H atoms except H1*A* and H1*B* in (2) were refined isotropically. The coordinates of H1*A* and H1*B* were refined with an occupancy factor of 0.5; the values of U_{iso} were assumed to be equal to 1.5 times the average value of U_{eq} of O2 and O4 in (2).

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1990); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1997). Program(s) used to solve structures: *PATTY* in *DIRDIF*92 (Beurskens *et al.*, 1992) for (1); *SIR*92 (Altomare *et al.*, 1993) for (2). For both compounds, program(s) used to refine structures: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

This work was supported by a Grant-in-Aid for Scientific Research (B) No. 10440208 from the Ministry of Education, Science, Sports and Culture, Japan.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1016). Services for accessing these data are described at the back of the journal.

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1-(2,4-Dinitrophenyl)-3-(2-hydroxyphenyl)-4-methyl-1*H*-pyrazole

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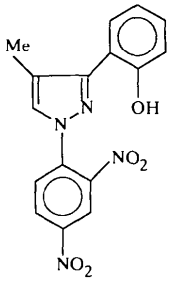
(*Received 6 May 1999; accepted 18 June 1999*)

Abstract

The molecular structure of the title compound, 2-[1-(2,4-dinitrophenyl)-4-methyl-1*H*-pyrazol-3-yl]phenol, $C_{16}H_{12}N_4O_5$, containing a dinitrophenyl and a hydroxyphenyl ring substituted to the pyrazole moiety is one of the products obtained from the reaction of *o*-hydroxy propiophenone 2,4-dinitrophenylhydrazone. The phenyl and pyrazole rings are quite planar. The dihedral angles between the pyrazole and the two phenyl rings are 23.5 (1) and 15.3 (1)°. The interplanar angle between the phenyl ring is 32.6 (1)°. The crystal structure is stabilized by O—H···N-, and O—H···O-type intramolecular hydrogen bonds and the packing of the molecules are stacked by C—H···O-type intermolecular hydrogen bonds.

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) and analgesic (Sobczak & Pawlaczyk, 1998) agents. Pyrazole compounds are widely used as an extraction reagent in the separation of trace metals (Akama *et al.*, 1995). In view of wide biological applications of the pyrazole compounds, the crystal structure of 1-(2,4-dinitrophenyl)-3-(2-hydroxyphenyl)-4-methyl-1*H*-pyrazole, (I), has been determined.



(I)

The *ORTEP* (Zsolnai, 1997) diagram of the molecule with numbering scheme is shown in Fig. 1. The bond lengths in the five-membered ring (see Table 1) all agree well with several related pyrazole derivatives (Bonati & Bovio, 1990; Allen *et al.*, 1987; Fronczek *et al.*, 1989; Panneerselvam *et al.*, 1996). The dihedral angles between phenyl rings *A* and *C* with the pyrazole ring *B* are 23.5 (1) and 15.3 (1)°, respectively, showing the conjugation between the phenyl rings and the pyrazole moiety. The Csp^2—N bonds associated with the nitro groups are clearly single bonds, while the C1—N2 [1.402 (2) Å] bond shows a partial double-bond character (Mani Naidu *et al.*, 1996) which is also evidence for the conjugation. The pyrazole ring is quite planar [maximum deviation from the least-squares plane is 0.001 (2) Å for C3*A*]. The average C—C bond distance of ring *A* is 1.383 (3) Å and ring *C* is 1.381 (3) Å and the angles are normal (Allen *et al.*, 1987). The C—O distance [1.366 (3) Å] also agrees well with those found in related pyrazole derivatives (Malhotra *et al.*, 1997; Allen *et al.*, 1987). The phenyl rings are nearly planar and the maximum deviations from the plane are 0.023 (2) Å for ring *A* and 0.011 (1) Å for ring *C*. The interplanar angle between the phenyl rings (*A* and *C*) is 32.6 (1)°.

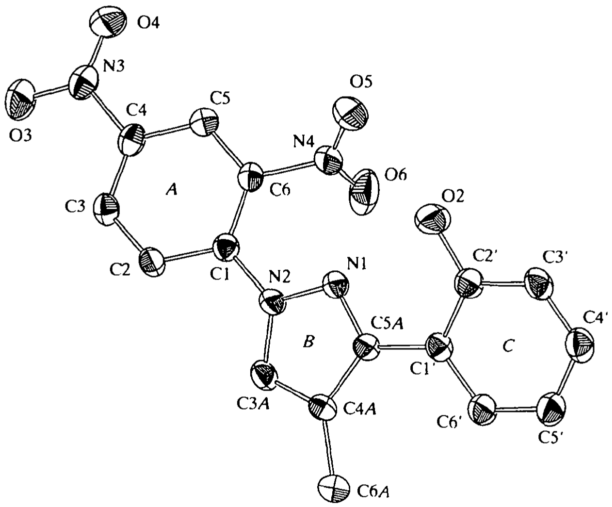


Fig. 1. An *ORTEP* (Zsolnai, 1997) displacement ellipsoid plot of (I) at the 30% probability level.

The bond lengths and bond angles in the NO_2 groups (see Table 1) are comparable to those found in several related pyrazole derivatives (Fronczek *et al.*, 1989; Mani Naidu *et al.*, 1996; Aygün *et al.*, 1998). The nitro group in the *ortho* position is twisted 67.3 (2)° from the plane of the phenyl ring (*A*), whereas the *para* position of the nitro group is almost coplanar with the ring. This tilting of the nitro group avoids unfavourable steric contacts of O6 with N1. This phenomenon may be related to the electron-withdrawing character of the nitro group.

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

Experimental

o-Hydroxypropiophenone 2,4-dinitrophenylhydrazone (1.68 g, 0.005 mol) was dissolved in *N*,*N*-dimethylformamide (5 ml) and kept in an ice-cold condition. To this, $POCl_3$ (1.4 ml) was added dropwise with stirring for 15 min. The reaction was stirred at room temperature for about 3–4 h then the contents poured into crushed ice (100 g). The yellow precipitate obtained was filtered, washed and dried. The product was purified by column chromatography using 60–120 mesh and 20% ethyl acetate–petroleum ether (yield 1.45 g) and recrystallized from ethyl acetate by slow evaporation.

Crystal data

$C_{16}H_{12}N_4O_5$
M_r = 340.30
Cu $K\alpha$ radiation
λ = 1.54180 Å

Monoclinic
$P2_1/c$
$a = 7.5598\,(1)$ Å
$b = 15.5263\,(2)$ Å
$c = 13.0732\,(2)$ Å
$\beta = 98.1394\,(10)°$
$V = 1519.02\,(4)$ Å^3
$Z = 4$
$D_x = 1.488$ Mg m^{-3}
D_m not measured

Cell parameters from 25 reflections
$\theta = 20–30°$
$\mu = 0.963$ mm^{-1}
$T = 293\,(2)$ K
Needle
0.3 × 0.1 × 0.1 mm
Orange

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.761$, $T_{\max} = 0.910$
2868 measured reflections
2654 independent reflections

1912 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.016$
$\theta_{\max} = 66.27°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 18$
$l = -15 \rightarrow 15$
2 standard reflections frequency: 60 min intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.240$
$S = 1.094$
2654 reflections
229 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.18P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.27$ e Å^{-3}
$\Delta\rho_{\min} = -0.31$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0018 (7)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

N1—C5*A*	1.327 (2)	N4—O5	1.216 (3)
N1—N2	1.355 (2)	N4—O6	1.224 (3)
N2—C3*A*	1.363 (3)	N4—C6	1.471 (3)
N2—C1	1.402 (2)	O2—C2′	1.366 (3)
N3—O4	1.216 (3)	C3*A*—C4*A*	1.355 (3)
N3—O3	1.221 (2)	C4*A*—C5*A*	1.437 (3)
N3—C4	1.463 (3)		
C5*A*—N1—N2	105.77 (14)	C3—C4—N3	120.83 (18)
N1—N2—C3*A*	111.04 (15)	C5—C4—N3	117.89 (19)
N1—N2—C1	120.45 (14)	C5—C6—N4	116.84 (17)
C3*A*—N2—C1	128.50 (15)	C1—C6—N4	121.01 (17)
O4—N3—O3	123.77 (19)	C4*A*—C3*A*—N2	108.23 (16)
O4—N3—C4	118.69 (18)	C3*A*—C4*A*—C5*A*	104.34 (16)
O3—N3—C4	117.54 (19)	C3*A*—C4*A*—C6*A*	124.71 (18)
O5—N4—O6	126.9 (2)	C5*A*—C4*A*—C6*A*	130.96 (17)
O5—N4—C6	116.5 (2)	N1—C5*A*—C4*A*	110.62 (15)
O6—N4—C6	116.5 (2)	N1—C5*A*—C1′	119.26 (16)
C6—C1—N2	122.48 (16)	O2—C2′—C3′	117.1 (2)
C2—C1—N2	119.52 (16)	O2—C2′—C1′	122.89 (18)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···N1	0.82	1.94	2.646 (2)	144
C3*A*—H3···O4$^{\rm i}$	0.93	2.51	3.439 (3)	175
C3—H3···O6$^{\rm ii}$	0.93	2.68	3.356 (3)	131
C5′—H5′···O5$^{\rm iii}$	0.93	2.49	3.219 (3)	135
C4′—H4′···O3$^{\rm iv}$	0.93	2.64	3.314 (3)	130

Symmetry codes: (i) $-x, \frac{1}{2} + y, -\frac{1}{2} - z$; (ii) $x, \frac{3}{2} - y, z - \frac{1}{2}$; (iii) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iv) $1 + x, y, 1 + z$.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *SDP* (Frenz, 1978). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ZORTEP* (Zsolnai, 1997). Software used to prepare material for publication: *SHELXL*97 and *PARST* (Nardelli, 1983, 1995).

JJ thanks CSIR, India, for providing a Senior Research Fellowship.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1331). Services for accessing these data are described at the back of the journal.

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