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2-[3-(4-Chlorophenyl)pyrazol-5-yl]-1-(2-hydroxy-4-methoxyphenyl)ethanone

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Key indicators

Single-crystal X-ray study
T = 200 K
Mean σ(C–C) = 0.002 Å
R factor = 0.042
wR factor = 0.105
Data-to-parameter ratio = 15.2

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

In the title compound, $C_{18}H_{15}ClN_2O_3$, the planes of the chlorophenyl and hydroxymethoxyphenyl groups are inclined at angles of 3.13 (8) and 38.80 (4)° with respect to the plane of the pyrazole ring. Intra- and intermolecular hydrogen bonding results in the formation of dimeric units; further interactions produce short Cl···Cl intermolecular separations.

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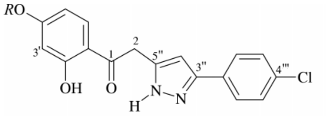
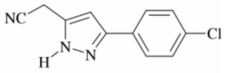
Comment

Pyrazole derivatives are used in various forms in medicines as they have shown quite significant bacteriostatic, anti-inflammatory, anticonvulsive and antihypertensive activities (Mahajan *et al.*, 1991; Biere *et al.*, 1982; Lepage & Hublot, 1992; Nakamura *et al.*, 1993). We have synthesized a series of pyrazoles to study structure–activity relationships. In the process of their derivatization, we condensed (II) (Ram *et al.*, 1991) with resorcinol in the presence of dry HCl gas and anhydrous zinc chloride to obtain the corresponding ketone (III); methylation of (III) gave the title compound, (I).



(I) $R = CH_3$
(III) $R = H$



(II)

The structure of (I) is illustrated in Fig. 1. The planes of the chlorophenyl and hydroxymethoxyphenyl groups are inclined at angles of 3.13 (8) and 38.80 (4)° with respect to the plane of the pyrazole ring. The bond lengths and angles are largely unremarkable. The H atoms with a high potential to hydrogen bond (*i.e.* those bonded to N1 and O2) were located from electron-density maps and allowed to refine freely. The O1···O2 separation of 2.5040 (18) Å (*cf.* sum of van der Waals radii = 3.04 Å) is indicative of hydrogen bonding, which restrains the atoms O1, C1, C1′, C2′, O2 and H2 to form an essentially planar unit (r.m.s. deviation = 0.0034 Å). The H atom directly bonded to N1 is involved in bifurcated hydrogen bonding intramolecularly to O1 and intermolecularly to O2 ($-x$+0.5, $-y$+0.5, $-z$+2); the sum of the angles about this H atom is 360° as required in the ideal situation. The overall effect of the hydrogen bonding in this system is to produce dimeric units as illustrated in Fig. 2. There are also significant intermolecular interactions which result in Cl···Cl separations of 3.224 (1) Å (*cf.* sum of van der Waals radii = 3.50 Å) and a C—Cl···Cl($-x$, y, 0.5$-z$) angle of 170.6 (1)°.

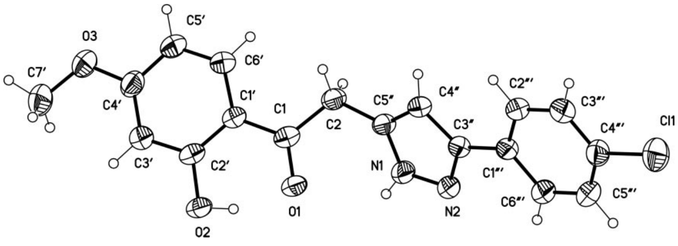


Figure 1
View of the molecule showing the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level for non-H atoms. H atoms are shown as spheres of arbitrary radii.

Experimental

Compound (III) was prepared by passing a rapid stream of dry HCl gas through a solution of (II) (2 g, 9.0 mmol), fused zinc chloride (10 g) and resorcinol (1.01 g, 9.0 mmol) in dry ether (25 ml). The mixture was stored in an ice-chest for 2 d and the supernatant ethereal layer was decanted. The dark-brown sticky mass was washed twice with dry ether and refluxed with water (20 ml) for 2 h, when a light-brown solid precipitated out. It was filtered off, washed with water and crystallized from acetone to get a white solid (1.4 g, 46.6%), m.p. 553–555 K. Compound (I) was prepared by adding dimethyl sulfate (0.315 g) to a mixture of (III) (0.82 g) and fused potassium carbonate (4 g) in anhydrous acetone (60 ml) and refluxing for 5 h. The potassium carbonate was filtered off and the filtrate was evaporated to dryness, the residue was macerated with ice and the mixture extracted with ethyl acetate. The organic layer was dried over anhydrous sodium sulfate, the solid obtained on evaporation of the solvent was purified by column chromatography using ethyl acetate/petrol (333–353 K, 1:4) as eluent to obtain (I). The title compound crystallized from acetone as yellow needles (0.59, 70% yield), m.p. 426–427 K. Physical properties of (I): IR ν_{max} (KBr): 3331, 2925, 2854, 2364, 1628, 1507, 1443, 1358, 1221 and 781 cm^{-1}; UV λ_{max} (MeOH): 202 and 238 nm; ^{1}H NMR (300 MHz, acetone-d_6) δ: 3.88 (3H, *s*, OCH$_3$), 4.45 (2H, *s*, C2—H), 6.46 (1H, *d*, J = 1.3 Hz, C3′—H), 6.53 (1H, *dd*, J = 1.3 and 9 Hz each, C5′—H), 6.64 (1H, *s*, C4″—H), 7.57 (2H, *d*, J = 8.4 Hz, C2‴—H and C6‴—H), 7.76 (2H, *d*, J = 8.4 Hz, C3‴—H and C5‴—H) and 8.03 (1H, *d*, J = 9 Hz, C6′—H). EIMS, *m*/*z* (% relative intensity): 345 [*M*+2] (35), 343 [M^+] (100), 179 (23), 167 (20), 151 (18), 91 (20), 74 (30).

Crystal data

$C_{18}H_{15}ClN_2O_3$
M_r = 342.77
Monoclinic, $C2/c$
a = 30.1055 (18) Å
b = 7.5383 (11) Å
c = 13.8612 (14) Å
β = 90.338 (4)°
V = 3145.7 (6) Å^3
Z = 8
D_x = 1.448 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3596 reflections
θ = 2.7–27.0°
μ = 0.26 mm^{-1}
T = 200 (2) K
Plate, yellow
0.40 × 0.40 × 0.08 mm

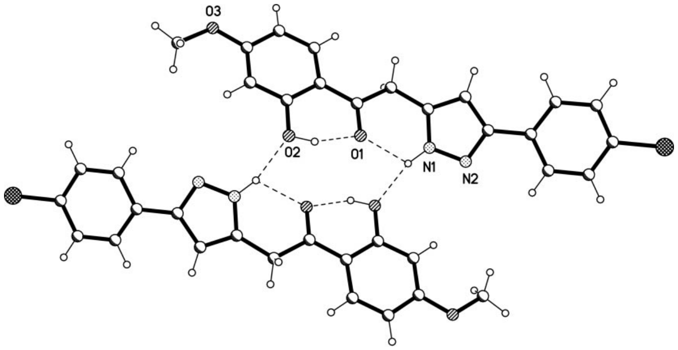


Figure 2
The hydrogen-bonded units in (I).

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.902, T_{max} = 0.979
8778 measured reflections
3425 independent reflections
2145 reflections with $I > 2\sigma(I)$
R_{int} = 0.037
θ_{max} = 27.0°
$h = -38 \rightarrow 34$
$k = -9 \rightarrow 9$
$l = -17 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.105
S = 0.91
3425 reflections
226 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0562P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}

Table 1
Selected torsion angles (°).

O1—C1—C2—C5″	−8.3 (2)	O1—C1—C1′—C2′	−1.1 (2)
C1′—C1—C2—C5″	174.18 (14)	C1—C1′—C2′—O2	0.7 (2)

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···O1	0.89 (2)	1.66 (2)	2.5040 (18)	157 (2)
N1—H1···O1	0.94 (2)	2.347 (19)	2.7311 (19)	104.0 (14)
N1—H1···O2^i	0.94 (2)	1.99 (2)	2.902 (2)	162.0 (17)

Symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} - y, 2 - z$.

Most of the H atoms were added at calculated positions and refined using a riding model; however, those bonded to N1 and O1 were located from electron-density maps and allowed to refine freely. H atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl–H atoms) times the equivalent isotropic displacement parameter of their parent atoms.

Data collection: *SMART* (Siemens, 1994); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Siemens, 1994);

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software used to prepare material for publication: *SHELXTL*/*PC*.

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