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3-(3-Chloro-2-hydroxyphenyl)-1-phenyl-1*H*-pyrazole-4-carbaldehyde

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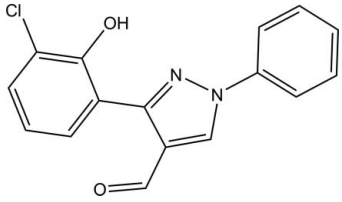
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.003 Å; R factor = 0.038; wR factor = 0.075; data-to-parameter ratio = 11.5.

In the title compound, $C_{16}H_{11}ClN_2O_2$, the pyrazole ring makes dihedral angles of 11.88 (13) and 22.33 (13)° with the 3-chloro-2-hydroxybenzene group and phenyl rings, respectively. The phenolic hydroxy group forms an intramolecular O—H···N hydrogen bond with the imine N atom of the pyrazole unit. The formyl group is virtually coplanar with the pyrazole ring [dihedral angle = 4.5 (19)°] and acts as an acceptor in an intramolecular C—H···O hydrogen bond closing seven-membered ring. In the crystal, adjacent molecules are linked through C—H···O hydrogen bonds into infinite chains along the *b* axis.

Related literature

For structures of similar compounds, see: Jeyakanthan *et al.* (2001); Shanmuga Sundara Raj *et al.* (1999).



Experimental

Crystal data

$C_{16}H_{11}ClN_2O_2$ M_r = 298.72
Orthorhombic, $P2_12_12_1$
a = 3.8142 (1) Å
b = 15.9367 (3) Å
c = 21.4121 (5) Å
V = 1301.55 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.30 mm^{-1}
T = 100 K
0.11 × 0.06 × 0.04 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.968, T_{max} = 0.988
11133 measured reflections
2563 independent reflections
2195 reflections with $I > 2\sigma(I)$
R_{int} = 0.061

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.075
S = 1.04
2563 reflections
223 parameters
Only H-atom coordinates refined
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}
Absolute structure: Flack (1983), 1005 Friedel pairs
Flack parameter: −0.03 (7)

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···N2	0.79 (3)	1.89 (3)	2.585 (2)	147 (3)
C5—H5···O2	0.95 (2)	2.18 (2)	3.024 (3)	148 (2)
C10—H10···O1^{i}	1.00 (3)	2.58 (3)	3.568 (3)	171 (2)

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

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: '*SHELXL97* and *publCIF* (Westrip, 2010)'.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: GK2410).

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supplementary materials

Acta Cryst. (2011). E**67**, o2736 [**doi:10.1107/S1600536811038025**]

3-(3-Chloro-2-hydroxyphenyl)-1-phenyl-1*H*-pyrazole-4-carbaldehyde

P. Lokhande, K. Hasanzadeh, H. Khaledi and H. Mohd Ali

Comment

The title compound was synthesized through the action of Vilsmeier–Haack reagent (DMF/$POCl_3$) on 3-chloro-2-hydroxy-acetophenone phenylhydrazone. The compound contains three aromatic rings, the dihedral angles between them being 11.88 (13)° (pyrazole and phenol), 22.33 (13)° (pyrazole and phenyl) and 31.29 (12)° (phenyl and phenol). The phenol hydroxyl is hydrogen bonded to the pyrazole nitrogen, N2, and the formyl oxygen atom is directed towards the phenol ring to make an intramolecular C—H···O hydrogen bond with C5—H5. In contrary, in the crystal structures of the related compounds (Jeyakanthan *et al.*, 2001; Shanmuga Sundara Raj *et al.*, 1999) the formyl oxygen atoms are directed away from the phenol rings, being involved in intermolecular C—H···O hydrogen bonding. The crystal packing of the present compound exhibits infinite chains along the *b* axis formed by intermoleculoar C—H···O hydrogen bonds (Table 1).

Experimental

A mixture of equivalent amounts (24 mmol) of 3-chloro-2-hydroxyacetophenone and phenyl hydrazine in methanol (40 ml) was refluxed for 2 h. The reaction mixture was then cooled to room temperature whereupon the condensation product, 3-chloro-2-hydroxy acetophenone phenylhydrazone, was seperated out with 92% yield. The hydrazone (2.6 g, 0.01 mol) was dissolved in DMF (15 ml) and then $POCl_3$ (0.03 mol) was added dropwise at 0 ^{o}C. After the addition was complete, the reaction mixture was warmed to 60–70 ^{o}C and stirred for 2.5 h. The mixture was then poured onto crushed ice and neutralized by aqueous NaOH solution (10%). The precipitate was filtered, strongly washed with water and recrystallized from ethanol, yielding 85% of the pyrazole product (m.p. = 422-423 K). The needle shaped crystals of the compound were grown in a DMF solution at room temperature.

Refinement

Hydrogen atoms were all located in a difference Fourier map and their positions refined with U_{iso}(H) set to 1.2U_{eq}(C) or 1.2U_{eq}(O).

Figures

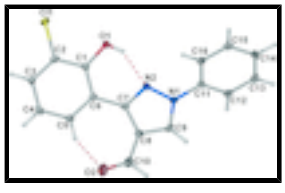

Fig. 1. Molecular structure of the title compound with displacement ellipsoids at the 50% probability level. Hydrogen atoms are drawn as spheres of arbitrary radius. Intramolecular H-bonds are depicted as red dashed lines.

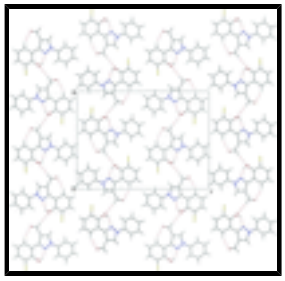

Fig. 2. Packing view along the *a* axis showing hydrogen-bonded chains along the *b* axis. Hydrogen bonds are depicted as red dashed lines

3-(3-Chloro-2-hydroxyphenyl)-1-phenyl-1*H*-pyrazole-4-carbaldehyde

Crystal data

$C_{16}H_{11}ClN_2O_2$	$F(000) = 616$
$M_r = 298.72$	$D_x = 1.524$ Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: P 2ac 2ab	Cell parameters from 1835 reflections
$a = 3.8142$ (1) Å	$\theta = 2.3$–$27.7°$
$b = 15.9367$ (3) Å	$\mu = 0.30$ mm^{-1}
$c = 21.4121$ (5) Å	$T = 100$ K
$V = 1301.55$ (5) Å^3	Needle, colorless
$Z = 4$	0.11 × 0.06 × 0.04 mm

Data collection

Bruker APEXII CCD diffractometer	2563 independent reflections
Radiation source: fine-focus sealed tube	2195 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.061$
φ and ω scans	$\theta_{max} = 26.0°$, $\theta_{min} = 2.3°$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$h = -4\rightarrow4$
$T_{min} = 0.968$, $T_{max} = 0.988$	$k = -19\rightarrow19$
11133 measured reflections	$l = -26\rightarrow26$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.038$	Only H-atom coordinates refined
$wR(F^2) = 0.075$	$w = 1/[\sigma^2(F_o^2) + (0.0338P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} < 0.001$
2563 reflections	$\Delta\rho_{max} = 0.20$ e Å^{-3}
223 parameters	$\Delta\rho_{min} = -0.23$ e Å^{-3}
0 restraints	Absolute structure: Flack (1983), 1005 Friedel pairs

Primary atom site location: structure-invariant direct methods

Flack parameter: −0.03 (7)

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 $F^2 > \sigma(F^2)$ 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}
Cl1	−0.15696 (17)	0.83249 (4)	0.11291 (3)	0.02120 (16)
O1	0.1795 (5)	0.74015 (10)	0.21221 (7)	0.0193 (4)
H1	0.288 (8)	0.7150 (17)	0.2372 (12)	0.029*
O2	0.2257 (7)	0.38231 (11)	0.14904 (10)	0.0523 (8)
N1	0.6317 (6)	0.55861 (11)	0.30360 (8)	0.0146 (4)
N2	0.4904 (5)	0.61122 (12)	0.26021 (8)	0.0152 (5)
C1	0.1243 (7)	0.69086 (14)	0.16139 (10)	0.0146 (5)
C2	−0.0338 (6)	0.72717 (14)	0.10952 (12)	0.0166 (5)
C3	−0.0909 (6)	0.68296 (14)	0.05499 (11)	0.0170 (6)
H3	−0.205 (7)	0.7091 (14)	0.0212 (11)	0.020*
C4	0.0085 (7)	0.59966 (16)	0.05228 (11)	0.0189 (6)
H4	−0.027 (6)	0.5695 (15)	0.0148 (11)	0.023*
C5	0.1558 (7)	0.56110 (14)	0.10338 (10)	0.0169 (5)
H5	0.217 (7)	0.5034 (14)	0.1021 (11)	0.020*
C6	0.2166 (6)	0.60481 (14)	0.15903 (10)	0.0136 (5)
C7	0.3790 (7)	0.56342 (13)	0.21291 (11)	0.0145 (5)
C8	0.4516 (7)	0.47684 (15)	0.22672 (11)	0.0193 (6)
C9	0.6108 (7)	0.47880 (15)	0.28431 (11)	0.0185 (6)
H9	0.705 (7)	0.4337 (15)	0.3073 (11)	0.022*
C10	0.3808 (9)	0.39580 (16)	0.19719 (13)	0.0340 (8)
H10	0.478 (7)	0.3494 (17)	0.2230 (13)	0.041*
C11	0.7764 (6)	0.59165 (14)	0.36014 (10)	0.0148 (6)
C12	0.8074 (7)	0.54004 (15)	0.41212 (11)	0.0177 (5)
H12	0.726 (7)	0.4860 (15)	0.4085 (10)	0.021*
C13	0.9498 (7)	0.57231 (16)	0.46616 (12)	0.0205 (6)
H13	0.959 (7)	0.5372 (16)	0.5017 (11)	0.025*
C14	1.0616 (6)	0.65466 (16)	0.46938 (12)	0.0194 (6)
H14	1.158 (7)	0.6750 (14)	0.5087 (11)	0.023*
C15	1.0272 (7)	0.70584 (16)	0.41707 (11)	0.0192 (6)
H15	1.114 (7)	0.7627 (15)	0.4189 (10)	0.023*
C16	0.8840 (6)	0.67472 (15)	0.36244 (11)	0.0161 (5)

H16	0.865 (7)	0.7101 (14)	0.3265 (11)	0.019*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0235 (3)	0.0144 (3)	0.0257 (3)	0.0028 (3)	−0.0039 (3)	0.0023 (3)
O1	0.0271 (10)	0.0136 (9)	0.0173 (9)	0.0022 (8)	−0.0054 (8)	−0.0012 (7)
O2	0.090 (2)	0.0165 (10)	0.0498 (13)	−0.0030 (11)	−0.0428 (14)	−0.0012 (9)
N1	0.0162 (11)	0.0122 (10)	0.0155 (10)	0.0009 (9)	0.0023 (10)	0.0013 (8)
N2	0.0157 (11)	0.0160 (11)	0.0138 (10)	0.0010 (9)	0.0018 (9)	0.0010 (8)
C1	0.0146 (13)	0.0148 (12)	0.0145 (12)	−0.0027 (10)	0.0019 (11)	−0.0013 (9)
C2	0.0133 (13)	0.0138 (12)	0.0226 (12)	−0.0001 (10)	0.0022 (11)	0.0026 (12)
C3	0.0168 (14)	0.0189 (14)	0.0153 (12)	−0.0024 (10)	−0.0030 (10)	0.0032 (10)
C4	0.0205 (15)	0.0216 (14)	0.0145 (12)	−0.0030 (11)	0.0004 (11)	−0.0029 (11)
C5	0.0187 (13)	0.0144 (12)	0.0177 (13)	0.0014 (12)	0.0039 (12)	−0.0032 (10)
C6	0.0116 (14)	0.0132 (12)	0.0159 (12)	−0.0020 (9)	0.0043 (10)	0.0023 (10)
C7	0.0122 (13)	0.0124 (12)	0.0188 (12)	−0.0005 (11)	0.0014 (11)	−0.0009 (9)
C8	0.0228 (16)	0.0160 (13)	0.0192 (13)	0.0003 (11)	−0.0040 (11)	−0.0013 (10)
C9	0.0187 (15)	0.0130 (12)	0.0238 (13)	0.0024 (11)	−0.0002 (12)	0.0034 (10)
C10	0.050 (2)	0.0159 (14)	0.0359 (17)	0.0009 (15)	−0.0215 (17)	−0.0009 (12)
C11	0.0114 (15)	0.0172 (13)	0.0159 (12)	0.0004 (10)	0.0021 (10)	−0.0019 (10)
C12	0.0168 (14)	0.0139 (12)	0.0224 (13)	0.0001 (11)	−0.0008 (11)	0.0002 (10)
C13	0.0211 (16)	0.0197 (14)	0.0208 (13)	0.0007 (11)	−0.0016 (11)	0.0046 (11)
C14	0.0170 (15)	0.0238 (15)	0.0174 (12)	0.0009 (11)	−0.0026 (11)	−0.0041 (11)
C15	0.0158 (14)	0.0153 (13)	0.0264 (14)	0.0006 (10)	0.0020 (11)	−0.0016 (11)
C16	0.0149 (13)	0.0177 (13)	0.0158 (11)	0.0031 (12)	0.0026 (11)	0.0011 (10)

Geometric parameters (Å, °)

Cl1—C2	1.745 (2)	C6—C7	1.466 (3)
O1—C1	1.358 (3)	C7—C8	1.438 (3)
O1—H1	0.79 (3)	C8—C9	1.375 (3)
O2—C10	1.208 (3)	C8—C10	1.463 (3)
N1—C9	1.340 (3)	C9—H9	0.94 (2)
N1—N2	1.363 (3)	C10—H10	1.00 (3)
N1—C11	1.431 (3)	C11—C16	1.387 (3)
N2—C7	1.337 (3)	C11—C12	1.389 (3)
C1—C2	1.390 (3)	C12—C13	1.378 (3)
C1—C6	1.417 (3)	C12—H12	0.92 (2)
C2—C3	1.381 (3)	C13—C14	1.382 (3)
C3—C4	1.382 (3)	C13—H13	0.95 (2)
C3—H3	0.94 (2)	C14—C15	1.392 (3)
C4—C5	1.375 (3)	C14—H14	0.98 (2)
C4—H4	0.94 (2)	C15—C16	1.383 (3)
C5—C6	1.400 (3)	C15—H15	0.97 (2)
C5—H5	0.95 (2)	C16—H16	0.96 (2)
C1—O1—H1	109 (2)	C9—C8—C10	119.3 (2)
C9—N1—N2	110.51 (19)	C7—C8—C10	136.3 (2)

C9—N1—C11	129.3 (2)	N1—C9—C8	108.9 (2)
N2—N1—C11	120.21 (17)	N1—C9—H9	122.7 (15)
C7—N2—N1	106.97 (18)	C8—C9—H9	128.2 (15)
O1—C1—C2	117.8 (2)	O2—C10—C8	128.1 (3)
O1—C1—C6	123.4 (2)	O2—C10—H10	121.6 (16)
C2—C1—C6	118.8 (2)	C8—C10—H10	110.3 (16)
C3—C2—C1	122.1 (2)	C16—C11—C12	120.8 (2)
C3—C2—Cl1	118.92 (19)	C16—C11—N1	119.7 (2)
C1—C2—Cl1	118.95 (18)	C12—C11—N1	119.5 (2)
C2—C3—C4	118.8 (2)	C13—C12—C11	119.0 (2)
C2—C3—H3	119.8 (14)	C13—C12—H12	123.6 (15)
C4—C3—H3	121.3 (14)	C11—C12—H12	117.3 (15)
C5—C4—C3	120.5 (2)	C12—C13—C14	121.2 (2)
C5—C4—H4	120.4 (15)	C12—C13—H13	118.1 (15)
C3—C4—H4	119.1 (15)	C14—C13—H13	120.6 (15)
C4—C5—C6	121.5 (2)	C13—C14—C15	119.2 (2)
C4—C5—H5	120.7 (14)	C13—C14—H14	118.4 (14)
C6—C5—H5	117.8 (14)	C15—C14—H14	122.4 (14)
C5—C6—C1	118.1 (2)	C16—C15—C14	120.5 (2)
C5—C6—C7	121.1 (2)	C16—C15—H15	120.4 (14)
C1—C6—C7	120.8 (2)	C14—C15—H15	119.0 (14)
N2—C7—C8	109.3 (2)	C15—C16—C11	119.3 (2)
N2—C7—C6	118.3 (2)	C15—C16—H16	120.0 (14)
C8—C7—C6	132.4 (2)	C11—C16—H16	120.7 (14)
C9—C8—C7	104.3 (2)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···N2	0.79 (3)	1.89 (3)	2.585 (2)	147 (3)
C5—H5···O2	0.95 (2)	2.18 (2)	3.024 (3)	148 (2)
C10—H10···O1^{i}	1.00 (3)	2.58 (3)	3.568 (3)	171 (2)

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

Fig. 1

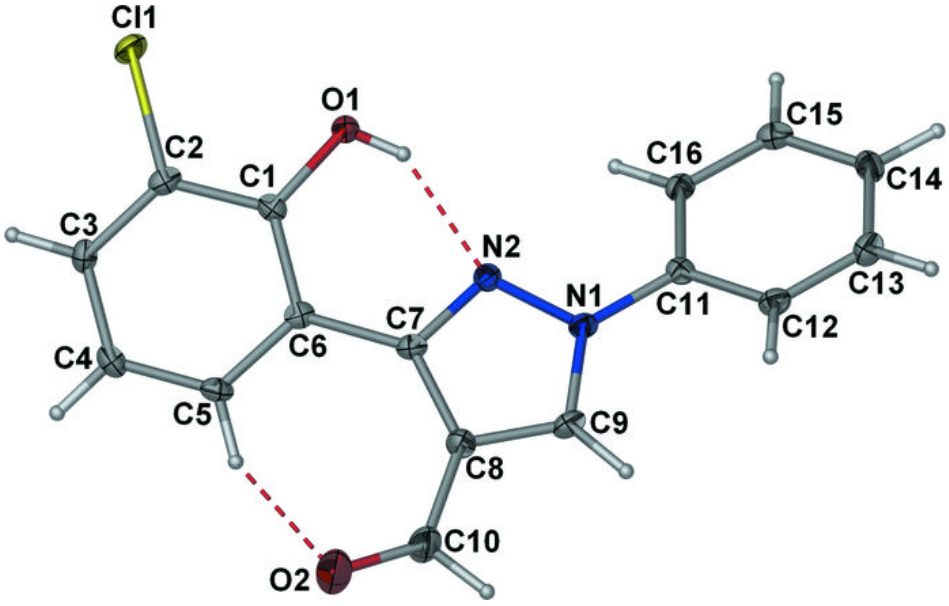
Cl1
O1
C2
C1
C3
N2
N1
C11
C15
C16
C14
C13
C12
C7
C6
C4
C5
C9
C8
C10
O2

Fig. 2