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

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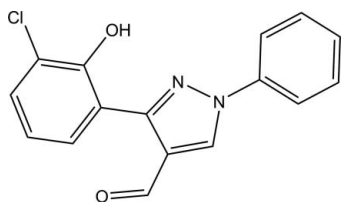
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.038; wR factor = 0.075; data-to-parameter ratio = 11.5.

In the title compound, $\text{C}_{16}\text{H}_{11}\text{ClN}_2\text{O}_2$, 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 $\text{O}-\text{H}\cdots\text{N}$ 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 $\text{C}-\text{H}\cdots\text{O}$ hydrogen bond closing seven-membered ring. In the crystal, adjacent molecules are linked through $\text{C}-\text{H}\cdots\text{O}$ 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

 $\text{C}_{16}\text{H}_{11}\text{ClN}_2\text{O}_2$ $M_r = 298.72$

Orthorhombic, $P2_12_12_1$
 $a = 3.8142$ (1) Å
 $b = 15.9367$ (3) Å
 $c = 21.4121$ (5) Å
 $V = 1301.55$ (5) Å³

$Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.30$ mm⁻¹
 $T = 100$ K
 $0.11 \times 0.06 \times 0.04$ 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 $I > 2\sigma(I)$
 $R_{\text{int}} = 0.061$

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, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O1}-\text{H1}\cdots\text{N2}$	0.79 (3)	1.89 (3)	2.585 (2)	147 (3)
$\text{C5}-\text{H5}\cdots\text{O2}$	0.95 (2)	2.18 (2)	3.024 (3)	148 (2)
$\text{C10}-\text{H10}\cdots\text{O1}^i$	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).

References

- Barbour, L. J. (2001). *J. Supramol. Chem.* **1**, 189–191.
 Bruker (2007). APEX2 and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.
 Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
 Jeyakanthan, J., Velmurugan, D., Selvi, S. & Perumal, P. T. (2001). *Acta Cryst.* **E57**, o474–o476.
 Shanmuga Sundara Raj, S., Jeyakanthan, J., Selvi, S., Velmurugan, D., Fun, H.-K. & Perumal, P. T. (1999). *Acta Cryst.* **C55**, 1667–1669.
 Sheldrick, G. M. (1996). SADABS. University of Göttingen, Germany.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
 Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

supporting information

Acta Cryst. (2011). E67, o2736 [https://doi.org/10.1107/S1600536811038025]

3-(3-Chloro-2-hydroxyphenyl)-1-phenyl-1*H*-pyrazole-4-carbaldehyde**Pradeep Lokhande, Kamal Hasanzadeh, Hamid Khaledi and Hapipah Mohd Ali****S1. Comment**

The title compound was synthesized through the action of Vilsmeier–Haack reagent (DMF/POCl₃) on 3-chloro-2-hydroxyacetophenone 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 intermolecular C—H···O hydrogen bonds (Table 1).

S2. 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 separated out with 92% yield. The hydrazone (2.6 g, 0.01 mol) was dissolved in DMF (15 ml) and then POCl₃ (0.03 mol) was added dropwise at 0 °C. After the addition was complete, the reaction mixture was warmed to 60–70 °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.

S3. Refinement

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

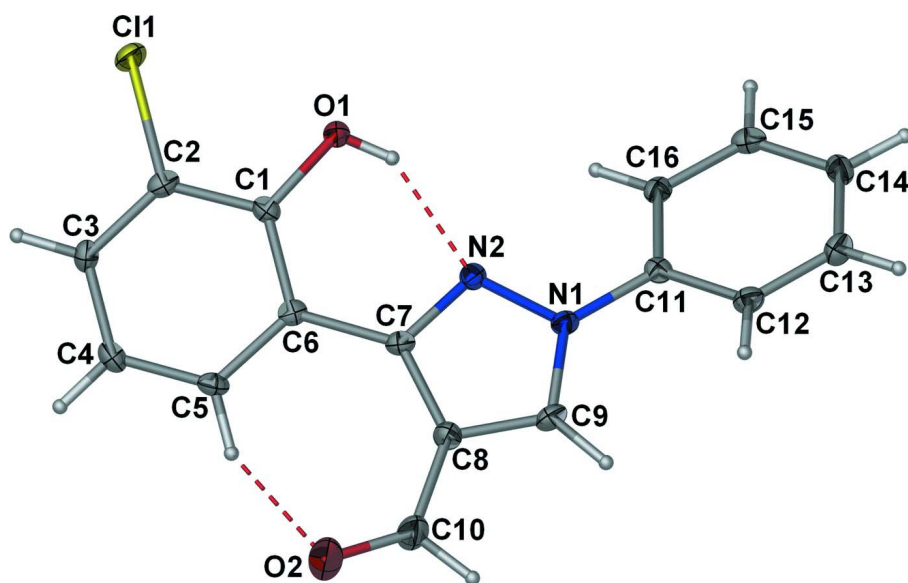


Figure 1

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.

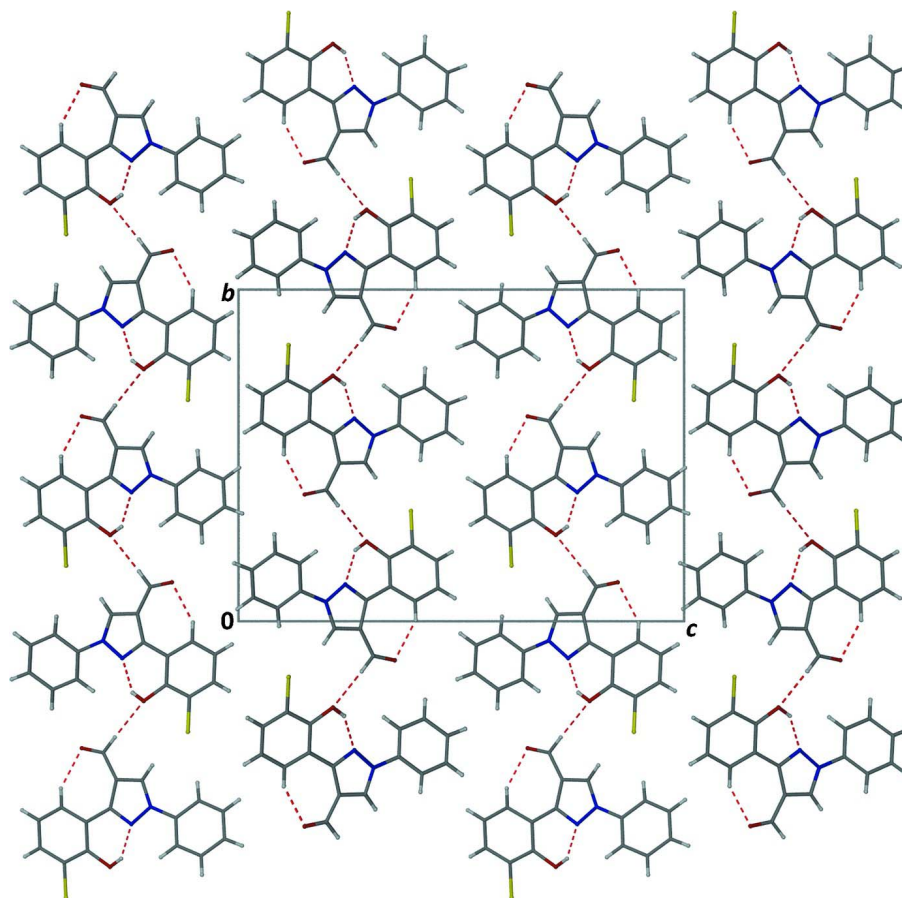


Figure 2

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-1H-pyrazole-4-carbaldehyde

Crystal data

$C_{16}H_{11}ClN_2O_2$

$M_r = 298.72$

Orthorhombic, $P2_12_12_1$

Hall symbol: P 2ac 2ab

$a = 3.8142$ (1) Å

$b = 15.9367$ (3) Å

$c = 21.4121$ (5) Å

$V = 1301.55$ (5) Å³

$Z = 4$

$F(000) = 616$

$D_x = 1.524$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 1835 reflections

$\theta = 2.3$ – 27.7°

$\mu = 0.30$ mm⁻¹

$T = 100$ K

Needle, colorless

$0.11 \times 0.06 \times 0.04$ mm

Data collection

Bruker APEXII CCD
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan
(*SADABS*; Sheldrick, 1996)

$T_{\min} = 0.968$, $T_{\max} = 0.988$

11133 measured reflections

2563 independent reflections

2195 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.061$
 $\theta_{\text{max}} = 26.0^\circ$, $\theta_{\text{min}} = 2.3^\circ$
 $h = -4 \rightarrow 4$

$k = -19 \rightarrow 19$
 $l = -26 \rightarrow 26$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.075$
 $S = 1.04$
 2563 reflections
 223 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods
 Secondary atom site location: difference Fourier
 map

Hydrogen site location: inferred from
 neighbouring sites
 Only H-atom coordinates refined
 $w = 1/[\sigma^2(F_o^2) + (0.0338P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.20 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.23 \text{ e } \text{\AA}^{-3}$
 Absolute structure: Flack (1983), 1005 Friedel
 pairs
 Absolute structure 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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
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 (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	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, °)

C11—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—C11	118.92 (19)	C16—C11—N1	119.7 (2)
C1—C2—C11	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 (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1 \cdots N2	0.79 (3)	1.89 (3)	2.585 (2)	147 (3)
C5—H5 \cdots O2	0.95 (2)	2.18 (2)	3.024 (3)	148 (2)
C10—H10 \cdots O1 ⁱ	1.00 (3)	2.58 (3)	3.568 (3)	171 (2)

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