



Crystal structure, DFT and Hirshfeld surface analysis of 2-amino-4-(2-chlorophenyl)-7-hydroxy-4*H*-benzo[1,2-*b*]pyran-3-carbonitrile

M. Beemaroo,^a S. Silambarasan,^b A. Jamal Abd Nasser,^b M. Purushothaman^b and K. Ravichandran^{a*}

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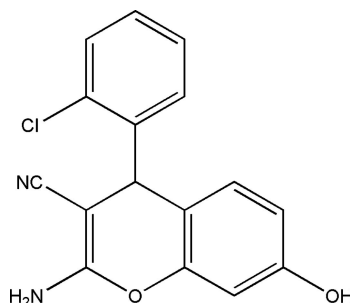
Supporting information: this article has supporting information at journals.iucr.org/e

^aDepartment of Physics, Kandaswami Kandari's College, Velur, Namakkal 638 182, India, and ^bDepartment of Chemistry, Jamal Mohamed College, Tiruchirappalli 620 020, India. *Correspondence e-mail: kravichandran05@gmail.com

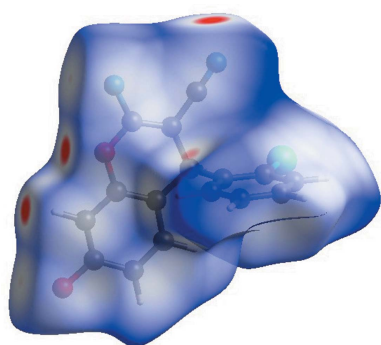
The benzopyran ring of the title compound, C₁₆H₁₁ClN₂O₂, is planar [maximum deviation = 0.079 (2) Å] and is almost perpendicular to the chlorophenyl ring [dihedral angle = 86.85 (6)°]. In the crystal, N—H···O, O—H···N, C—H···O and C—H···Cl hydrogen bonds form inter- and intramolecular interactions. The DFT/B3LYP/6-311G(d,p) method was used to determine the HOMO–LUMO energy levels. The molecular electrostatic potential surfaces were investigated by Hirshfeld surface analysis and two-dimensional fingerprint plots were used to analyse the intermolecular interactions in the molecule.

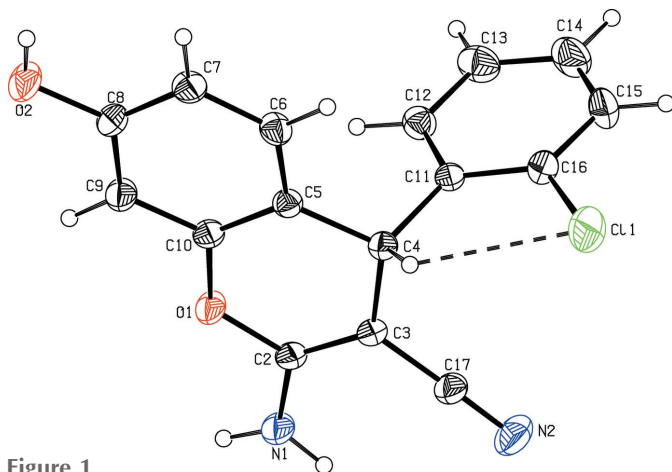
1. Chemical context

Pyran is an oxygen-containing heterocyclic group that exhibits various pharmacological activities. The pyran ring is a core unit in benzopyrans, chromones, flavanoids and coumarins. Numerous naturally-occurring compounds containing pyrans and benzopyrans show fascinating therapeutic activities, which include their use as antimicrobial (Khafagy *et al.*, 2002), antiviral (Smith *et al.*, 1998; Martínez-Grau & Marco, 1997), mutagenicity (Hiramoto *et al.*, 1997), antiproliferative (Dell & Smith, 1993), antitumour (Mohr *et al.*, 1975), antituberculosis (Ferreira *et al.*, 2010), anti-HIV (He *et al.*, 2011), antifungal (Schiller *et al.*, 2010), antidiabetic (Bisht *et al.*, 2011) and anti-inflammatory agents (Wang *et al.*, 1996, 2005). They are also used in cancer chemotherapy (Anderson *et al.*, 2005), in sex pheromone therapy (Bianchi & Tava, 1987) to control central nervous system activities (Eiden & Denk, 1991) and as calcium-channel antagonists (Shahrissa *et al.*, 2011),

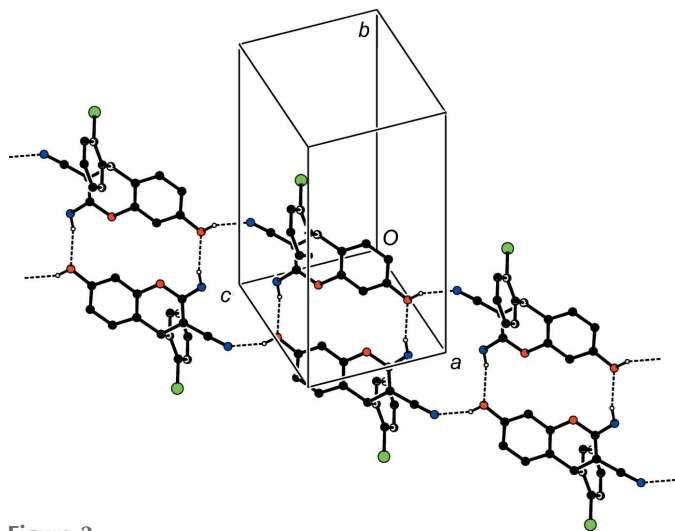


These attributes have prompted considerable research work in the synthetic field and interest in their structures, reactivities and biological properties. Against this background and to ascertain the structure of the title compound, namely 2-amino-4-(2-chlorophenyl)-7-hydroxy-4*H*-benzo[1,2-*b*]pyran-3-carbonitrile, crystallographic studies have been carried out and are here reported.




Figure 1

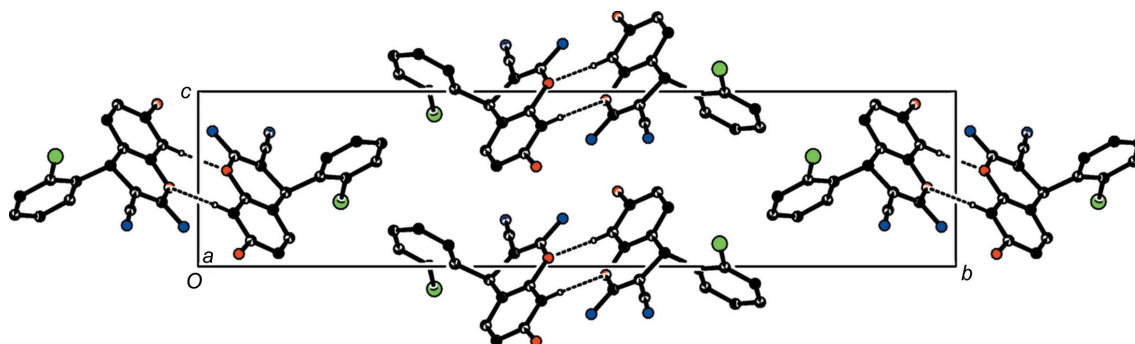
The molecular structure of the title compound, showing the atom-numbering scheme and displacement ellipsoids drawn at the 30% probability level. The intramolecular C4—H4···Cl1 hydrogen bond is drawn as a dashed line.


Figure 2

The crystal packing of the title compound, showing an $R_2^2(16)$ motif and the $C(8)$ chain formed *via* a pair of O—H···N and N—H···O hydrogen bonds.

2. Structural commentary

Fig. 1 shows the molecular structure of the title molecule and the intramolecular C4—H4···Cl1 hydrogen bond. The


Figure 3

Part of the crystal structure showing the $R_2^2(8)$ dimers. H atoms not involved in hydrogen bonding (dashed lines) have been omitted for clarity.

Table 1

Hydrogen-bond geometry (Å, °).

$Cg1$, $Cg3$ and $Cg4$ are the centroids of the O1/C2—C5/C10 ring, the C11—C16 ring and the benzopyran system, respectively.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A···O2 ⁱ	0.86	2.19	3.037 (2)	167
C9—H9···O1 ⁱ	0.93	2.50	3.416 (2)	168
O2—H2···N2 ⁱⁱ	0.82	1.99	2.773 (2)	160
C4—H4···Cl1	0.98	2.58	3.102 (2)	113
C12—H12···Cg1	0.93	2.74	3.085 (2)	103
C12—H12···Cg4	0.93	2.83	3.291 (2)	112
C14—H14···Cg3 ⁱⁱⁱ	0.93	2.85	3.494 (2)	127

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

chlorophenyl-substituted benzopyran compound crystallizes in the monoclinic space group $P2_1/c$. The benzopyran and chlorophenyl rings in the molecule are planar, as confirmed by the puckering parameters (Cremer & Pople, 1975) and asymmetry parameters $Q = 0.101$ (2) Å, $\theta = 105.6$ (11)° and $\varphi = 349.9$ (14)° (Nardelli, 1983).

The bond lengths and angles are well within the expected limits and comparable with literature values (Allen *et al.*, 1998). The plane of the benzopyran ring forms a dihedral angle of 86.85 (6)° with that of the chlorophenyl ring and confirms the fact that the two moieties are in an axial orientation. The chlorophenyl group is also planar, with a maximum deviation for atom C12 of -0.040 (1) Å. The orientation of the benzopyran and chlorophenyl rings is also confirmed by the torsion angles $C3-C4-C11-C12 = 76.5$ (2)° and $C3-C4-C11-C16 = -100.4$ (2)°.

In the benzopyran system, the attached carbonitrile, amino and hydroxy groups lie in the same plane, with a maximum deviation for atom N2 of -0.053 (2) Å. The sum of the bond angles around atom N1 of the pyran ring is in accordance with the sp^2 -hybridization state (360°; Beddoes *et al.*, 1986).

3. Supramolecular features

The packing of the molecules in the unit cell is stabilized by strong intermolecular C—H···O, O—H···N and N—H···O hydrogen bonds (Table 1). The O2—H2···N2ⁱⁱ interaction leads to the formation of a $C(10)$ chain running along the a axis. The molecules are also linked by pairs of intermolecular

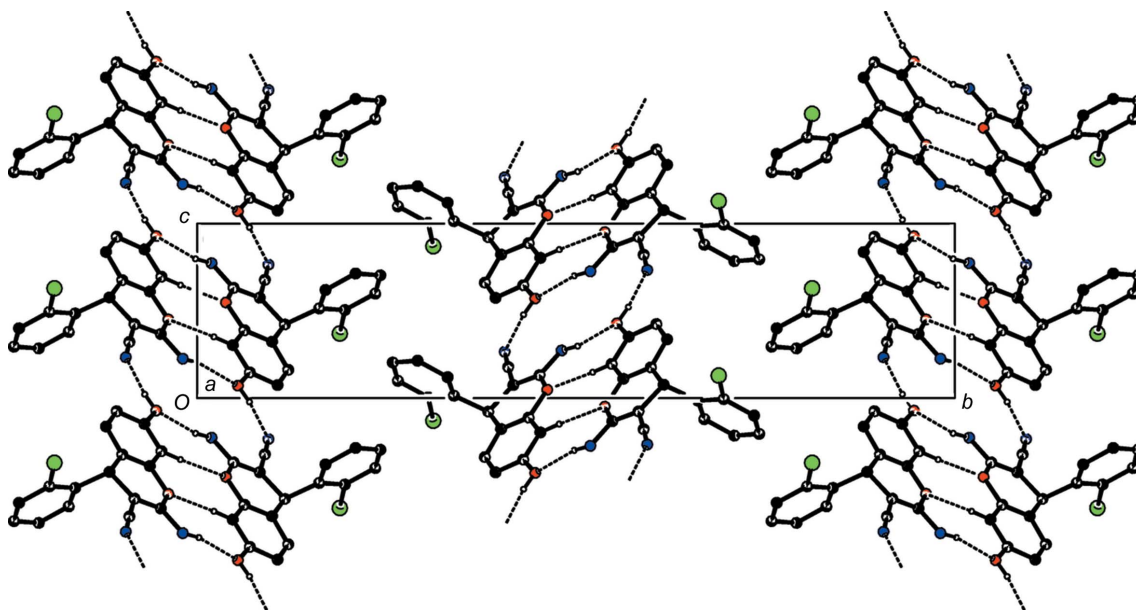


Figure 4
The overall crystal packing of the title compound, viewed along the *a*-axis direction.

$\text{N1-H1A}\cdots\text{O2}^i$ and $\text{O2-H2}\cdots\text{N2}^{ii}$ hydrogen bonds, forming inversion dimers with $R_2^2(16)$ ring motifs (Fig. 2) (Bernstein *et al.*, 1995), and the dimers are further connected by $\text{C9-H9}\cdots\text{O1}^i$ hydrogen bonds, forming a $R_2^2(8)$ rings along the *b*-axis direction, as shown in Fig. 3. Three $\text{C-H}\cdots\pi$ (Table 1) interactions complete the packing, forming a three-dimensional (3D) supramolecular structure. The overall crystal packing of the title compound is shown in Fig. 4.

4. Density functional theory (DFT) study

The optimized molecular structure and frontier molecular orbitals (FMOs) were calculated using the DFT/B3LYP/6-311G(d,p) basis set implemented in the *GAUSSIAN09* program package (Frisch *et al.*, 2009). The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are called FMOs as they lie at the outermost boundaries of the electrons of the molecules. The frontier orbital gap helps to characterize the chemical reactivity and the kinetic stability of the molecule. A molecule with a small frontier orbital gap is generally associated with a high chemical reactivity and a low kinetic stability, and is also termed a soft molecule. The electron distribution of the HOMO-1, HOMO, LUMO and LUMO+1 energy levels and the energy values are shown in Fig. 5. The positive and negative phases are represented in green and red, respectively.

The HOMO of the title molecule is localized on the entire molecule except for the chlorobenzene ring, while the LUMO is located on the whole molecule. However, the HOMO-1 is localized on the entire molecule, with the LUMO+1 confined to the chlorobenzene and benzopyran rings, except for the amino substituent. The DFT study shows that the FMO energies, *i.e.* E_{HOMO} and E_{LUMO} , are -6.354 and -2.712 eV, respectively, and the HOMO–LUMO energy gap is 3.642 eV.

The title compound has a small frontier orbital gap, hence the molecule has high chemical reactivity and low kinetic stability.

5. Hirshfeld surface analysis

Hirshfeld surface analysis (Spackman & Jayatilaka, 2009) and two-dimensional (2D) fingerprint plots (McKinnon *et al.*,

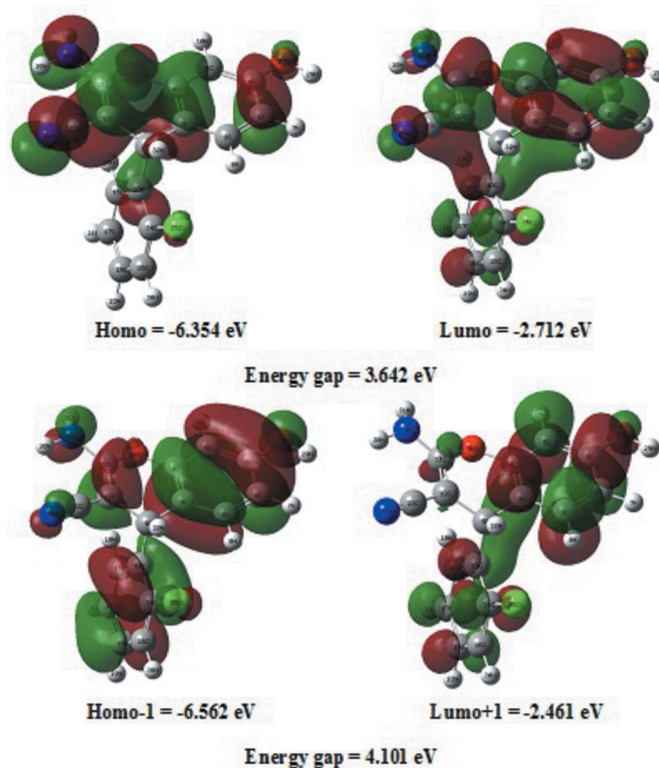


Figure 5
The frontier molecular orbitals (FMOs) of the title compound.

Table 2

Experimental details.

Crystal data	
Chemical formula	C ₁₆ H ₁₁ ClN ₂ O ₂
<i>M_r</i>	298.72
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>
Temperature (K)	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	6.6658 (3), 30.1600 (16), 7.2193 (4)
β (°)	106.088 (2)
<i>V</i> (Å ³)	1394.53 (12)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.28
Crystal size (mm)	0.15 × 0.10 × 0.10
Data collection	
Diffractometer	Bruker SMART APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2008)
<i>T</i> _{min} , <i>T</i> _{max}	0.959, 0.973
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	21888, 2941, 2115
<i>R</i> _{int}	0.034
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.632
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.037, 0.103, 1.05
No. of reflections	2941
No. of parameters	191
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.19, -0.29

Computer programs: *APEX2* (Bruker, 2008), *SAINT* (Bruker, 2008), *SHELXS97* (Sheldrick, 2008), *SHELXL2018* (Sheldrick, 2015), *ORTEP-3* (Farrugia, 2012), *SHELXL97* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

2007) were performed and created with *CrystalExplorer17* (Turner *et al.*, 2017) for the identification of the intermolecular interactions in the title compound. The Hirshfeld surface diagram mapped over *d*_{norm} is shown in Fig. 6. The 3D *d*_{norm} surfaces were plotted with a standard (high) surface resolution and are shown as blue and red regions around the atoms

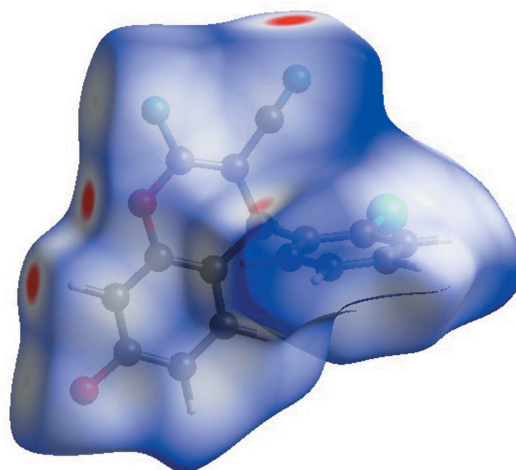


Figure 6
Hirshfeld surface mapped over *d*_{norm} in the range -0.6146 to 1.6047 a.u.

related with positive (hydrogen-bond donors) and negative (hydrogen-bond acceptors) electrostatic potentials, respectively.

The 2D fingerprint plots of the *d_i* and *d_e* points for the contacts contributing to the Hirshfeld surface analysis are shown in Fig. 7. They indicate that intermolecular H...H contacts provide the largest contribution (29.2%) to the Hirshfeld surface and the percentage contributions of the other interactions are C...H/H...C = 24.6%, N...H/H...N = 13.6%, Cl...H/H...Cl = 12.9% and O...H/H...O = 10.6%.

6. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.40, update of November 2018; Groom *et al.*, 2016) for the 4*H*-benzopyran fragment revealed 10 hits where the

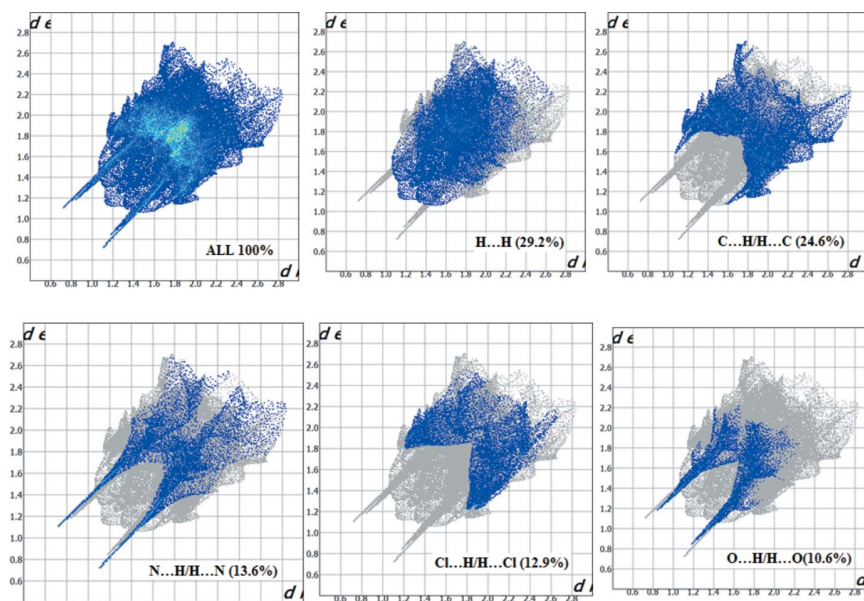


Figure 7
The 2D fingerprint plots for the title compound.

fragment adopts a planar conformation. Nearly all the bond lengths in the title structure are the same within standard uncertainties as the corresponding values in the structure of 2-amino-4-(2-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile hemihydrate (CSD refcode LAPZIN; Hu *et al.*, 2012).

7. Synthesis and crystallization

A mixture of 2-chlorobenzaldehyde (6.2 g, 0.05 mol), malononitrile (3.3 ml, 0.05 mol) and resorcinol (5.5 g, 0.05 mol) in water (150 ml) was added to a 10% aqueous K₂CO₃ solution (10 ml) in a 250 ml round-bottomed flask. The resulting solution was refluxed for about 2 h. The progress of the reaction was monitored by thin-layer chromatography using silica gel-G plates. After product formation, the reaction mixture was kept in a refrigerator overnight. The solid mass that settled was filtered off by suction and washed well with a mixture of methanol and water, and finally dried in air. The resulting crude solid was recrystallized from methanol giving a white solid. The purified sample was recrystallized from 1,4-dioxane using the slow-evaporation method (m.p. 250–255 °C).

8. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms were positioned geometrically (N–H = 0.88–0.90 Å and C–H = 0.93–0.98 Å) and allowed to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl H atoms and $1.2U_{\text{eq}}(\text{C})$ otherwise.

Acknowledgements

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supporting information

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Crystal structure, DFT and Hirshfeld surface analysis of 2-amino-4-(2-chlorophenyl)-7-hydroxy-4*H*-benzo[1,2-*b*]pyran-3-carbonitrile

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Computing details

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINTE* (Bruker, 2008); data reduction: *SAINTE* (Bruker, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015); molecular graphics: *ORTEP-3* (Farrugia, 2012); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

2-Amino-4-(2-chlorophenyl)-7-hydroxy-4*H*-benzo[1,2-*b*]pyran-3-carbonitrile

Crystal data

$C_{16}H_{11}ClN_2O_2$
 $M_r = 298.72$
 Monoclinic, $P2_1/c$
 $a = 6.6658$ (3) Å
 $b = 30.1600$ (16) Å
 $c = 7.2193$ (4) Å
 $\beta = 106.088$ (2)°
 $V = 1394.53$ (12) Å³
 $Z = 4$

$F(000) = 616$
 $D_x = 1.423$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 2115 reflections
 $\theta = 2.7$ – 26.7 °
 $\mu = 0.28$ mm⁻¹
 $T = 296$ K
 Block, white crystalline
 $0.15 \times 0.10 \times 0.10$ mm

Data collection

Bruker SMART APEXII CCD
 diffractometer
 Radiation source: fine-focus sealed tube
 ω and ϕ scans
 Absorption correction: multi-scan
 (*SADABS*; Bruker, 2008)
 $T_{\min} = 0.959$, $T_{\max} = 0.973$
 21888 measured reflections

2941 independent reflections
 2115 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.034$
 $\theta_{\text{max}} = 26.7$ °, $\theta_{\text{min}} = 2.7$ °
 $h = -6 \rightarrow 8$
 $k = -38 \rightarrow 38$
 $l = -9 \rightarrow 8$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.103$
 $S = 1.05$
 2941 reflections
 191 parameters
 0 restraints
 Hydrogen site location: inferred from
 neighbouring sites

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0392P)^2 + 0.5426P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.19$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.28$ e Å⁻³
 Extinction correction: *SHELXL2018*
 (Sheldrick, 2015),
 $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.0061 (13)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 $F^2 > 2\sigma(F^2)$ 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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C2	0.9057 (3)	0.54802 (6)	-0.1320 (2)	0.0342 (4)
C3	1.0377 (3)	0.58264 (5)	-0.0758 (2)	0.0334 (4)
C4	1.0200 (3)	0.61567 (5)	0.0772 (2)	0.0314 (4)
H4	1.156330	0.618094	0.172872	0.038*
C5	0.8634 (3)	0.59885 (5)	0.1766 (2)	0.0314 (4)
C6	0.8329 (3)	0.62022 (6)	0.3376 (3)	0.0379 (4)
H6	0.915142	0.644648	0.387878	0.045*
C7	0.6839 (3)	0.60615 (6)	0.4248 (3)	0.0408 (4)
H7	0.665264	0.621197	0.531266	0.049*
C8	0.5627 (3)	0.56954 (6)	0.3525 (3)	0.0379 (4)
C9	0.5916 (3)	0.54711 (6)	0.1960 (3)	0.0398 (4)
H9	0.512626	0.522076	0.148322	0.048*
C10	0.7398 (3)	0.56246 (6)	0.1111 (2)	0.0335 (4)
C11	0.9601 (3)	0.66108 (5)	-0.0142 (2)	0.0322 (4)
C12	0.7556 (3)	0.66946 (6)	-0.1204 (3)	0.0400 (4)
H12	0.654979	0.647668	-0.127966	0.048*
C13	0.6976 (4)	0.70909 (7)	-0.2149 (3)	0.0539 (5)
H13	0.559727	0.713738	-0.285481	0.065*
C14	0.8442 (4)	0.74176 (7)	-0.2045 (4)	0.0621 (6)
H14	0.805563	0.768466	-0.268905	0.075*
C15	1.0465 (4)	0.73504 (7)	-0.0995 (4)	0.0600 (6)
H15	1.145714	0.757164	-0.091365	0.072*
C16	1.1027 (3)	0.69495 (6)	-0.0052 (3)	0.0446 (5)
C17	1.1869 (3)	0.58941 (6)	-0.1782 (3)	0.0402 (4)
O1	0.7539 (2)	0.53801 (4)	-0.04856 (18)	0.0420 (3)
O2	0.4103 (2)	0.55394 (5)	0.4287 (2)	0.0552 (4)
H2	0.406537	0.569128	0.521925	0.083*
Cl1	1.36070 (9)	0.68831 (2)	0.12960 (12)	0.0757 (2)
N1	0.9057 (3)	0.51897 (5)	-0.2734 (2)	0.0455 (4)
H1A	0.816166	0.497735	-0.298713	0.055*
H1B	0.995343	0.521634	-0.338516	0.055*
N2	1.3050 (3)	0.59408 (7)	-0.2655 (3)	0.0608 (5)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C2	0.0376 (10)	0.0333 (9)	0.0359 (9)	0.0032 (7)	0.0174 (8)	-0.0023 (7)
C3	0.0336 (9)	0.0322 (9)	0.0385 (10)	0.0028 (7)	0.0169 (8)	-0.0012 (7)
C4	0.0314 (9)	0.0305 (9)	0.0334 (9)	-0.0007 (7)	0.0110 (7)	-0.0026 (7)
C5	0.0339 (9)	0.0306 (9)	0.0310 (9)	0.0025 (7)	0.0113 (7)	0.0014 (7)
C6	0.0474 (11)	0.0339 (9)	0.0335 (9)	-0.0043 (8)	0.0132 (8)	-0.0054 (7)
C7	0.0556 (12)	0.0392 (10)	0.0332 (10)	0.0003 (9)	0.0215 (9)	-0.0050 (8)
C8	0.0423 (10)	0.0419 (10)	0.0349 (10)	-0.0008 (8)	0.0198 (8)	0.0007 (8)
C9	0.0442 (11)	0.0394 (10)	0.0403 (10)	-0.0071 (8)	0.0192 (9)	-0.0085 (8)
C10	0.0391 (10)	0.0340 (9)	0.0308 (9)	0.0008 (7)	0.0155 (8)	-0.0042 (7)
C11	0.0384 (10)	0.0298 (8)	0.0329 (9)	-0.0008 (7)	0.0172 (8)	-0.0043 (7)
C12	0.0434 (11)	0.0373 (10)	0.0395 (10)	-0.0014 (8)	0.0117 (9)	-0.0021 (8)
C13	0.0610 (14)	0.0490 (12)	0.0493 (12)	0.0128 (10)	0.0113 (10)	0.0079 (10)
C14	0.0862 (18)	0.0437 (12)	0.0623 (15)	0.0089 (12)	0.0303 (13)	0.0165 (11)
C15	0.0759 (16)	0.0375 (11)	0.0783 (16)	-0.0104 (11)	0.0407 (14)	0.0059 (11)
C16	0.0445 (11)	0.0405 (10)	0.0554 (12)	-0.0057 (8)	0.0248 (10)	-0.0037 (9)
C17	0.0408 (11)	0.0408 (10)	0.0433 (11)	-0.0024 (8)	0.0188 (9)	-0.0082 (8)
O1	0.0484 (8)	0.0419 (7)	0.0444 (7)	-0.0136 (6)	0.0274 (6)	-0.0159 (6)
O2	0.0659 (10)	0.0596 (9)	0.0547 (9)	-0.0182 (7)	0.0409 (8)	-0.0158 (7)
C11	0.0392 (3)	0.0653 (4)	0.1207 (6)	-0.0156 (3)	0.0190 (3)	-0.0037 (4)
N1	0.0532 (10)	0.0422 (9)	0.0511 (10)	-0.0077 (8)	0.0309 (8)	-0.0147 (7)
N2	0.0571 (12)	0.0748 (13)	0.0627 (12)	-0.0146 (10)	0.0368 (10)	-0.0200 (10)

Geometric parameters (\AA , $^\circ$)

C2—N1	1.345 (2)	C9—H9	0.9300
C2—O1	1.347 (2)	C10—O1	1.3932 (19)
C2—C3	1.353 (2)	C11—C16	1.385 (2)
C3—C17	1.408 (2)	C11—C12	1.389 (2)
C3—C4	1.516 (2)	C12—C13	1.377 (3)
C4—C5	1.509 (2)	C12—H12	0.9300
C4—C11	1.525 (2)	C13—C14	1.375 (3)
C4—H4	0.9800	C13—H13	0.9300
C5—C10	1.375 (2)	C14—C15	1.367 (3)
C5—C6	1.393 (2)	C14—H14	0.9300
C6—C7	1.382 (3)	C15—C16	1.387 (3)
C6—H6	0.9300	C15—H15	0.9300
C7—C8	1.382 (3)	C16—C11	1.737 (2)
C7—H7	0.9300	C17—N2	1.146 (2)
C8—O2	1.366 (2)	O2—H2	0.8200
C8—C9	1.376 (2)	N1—H1A	0.8600
C9—C10	1.379 (2)	N1—H1B	0.8600
N1—C2—O1	110.58 (15)	C5—C10—C9	123.36 (16)
N1—C2—C3	126.39 (16)	C5—C10—O1	122.36 (15)
O1—C2—C3	123.03 (15)	C9—C10—O1	114.28 (15)

C2—C3—C17	116.70 (15)	C16—C11—C12	116.58 (17)
C2—C3—C4	123.38 (15)	C16—C11—C4	123.24 (16)
C17—C3—C4	119.72 (15)	C12—C11—C4	120.11 (15)
C5—C4—C3	109.23 (13)	C13—C12—C11	121.94 (18)
C5—C4—C11	112.01 (13)	C13—C12—H12	119.0
C3—C4—C11	109.81 (13)	C11—C12—H12	119.0
C5—C4—H4	108.6	C14—C13—C12	119.8 (2)
C3—C4—H4	108.6	C14—C13—H13	120.1
C11—C4—H4	108.6	C12—C13—H13	120.1
C10—C5—C6	116.37 (15)	C15—C14—C13	120.1 (2)
C10—C5—C4	122.16 (15)	C15—C14—H14	120.0
C6—C5—C4	121.44 (15)	C13—C14—H14	120.0
C7—C6—C5	121.86 (17)	C14—C15—C16	119.5 (2)
C7—C6—H6	119.1	C14—C15—H15	120.3
C5—C6—H6	119.1	C16—C15—H15	120.3
C6—C7—C8	119.46 (16)	C11—C16—C15	122.1 (2)
C6—C7—H7	120.3	C11—C16—C11	120.11 (15)
C8—C7—H7	120.3	C15—C16—C11	117.79 (16)
O2—C8—C9	116.76 (16)	N2—C17—C3	178.0 (2)
O2—C8—C7	123.03 (16)	C2—O1—C10	118.87 (13)
C9—C8—C7	120.21 (16)	C8—O2—H2	109.5
C8—C9—C10	118.71 (17)	C2—N1—H1A	120.0
C8—C9—H9	120.6	C2—N1—H1B	120.0
C10—C9—H9	120.6	H1A—N1—H1B	120.0
N1—C2—C3—C17	1.4 (3)	C4—C5—C10—O1	1.5 (3)
O1—C2—C3—C17	-179.18 (17)	C8—C9—C10—C5	1.0 (3)
N1—C2—C3—C4	176.25 (17)	C8—C9—C10—O1	-178.75 (16)
O1—C2—C3—C4	-4.3 (3)	C5—C4—C11—C16	138.04 (17)
C2—C3—C4—C5	10.3 (2)	C3—C4—C11—C16	-100.42 (19)
C17—C3—C4—C5	-175.06 (16)	C5—C4—C11—C12	-45.1 (2)
C2—C3—C4—C11	-112.94 (19)	C3—C4—C11—C12	76.49 (19)
C17—C3—C4—C11	61.7 (2)	C16—C11—C12—C13	1.1 (3)
C3—C4—C5—C10	-8.7 (2)	C4—C11—C12—C13	-176.05 (17)
C11—C4—C5—C10	113.14 (18)	C11—C12—C13—C14	-0.3 (3)
C3—C4—C5—C6	172.89 (16)	C12—C13—C14—C15	-0.5 (3)
C11—C4—C5—C6	-65.2 (2)	C13—C14—C15—C16	0.5 (3)
C10—C5—C6—C7	-1.2 (3)	C12—C11—C16—C15	-1.0 (3)
C4—C5—C6—C7	177.30 (17)	C4—C11—C16—C15	175.98 (18)
C5—C6—C7—C8	0.8 (3)	C12—C11—C16—C11	178.20 (13)
C6—C7—C8—O2	-179.04 (18)	C4—C11—C16—C11	-4.8 (2)
C6—C7—C8—C9	0.5 (3)	C14—C15—C16—C11	0.3 (3)
O2—C8—C9—C10	178.20 (17)	C14—C15—C16—C11	-178.97 (18)
C7—C8—C9—C10	-1.4 (3)	N1—C2—O1—C10	175.17 (15)
C6—C5—C10—C9	0.3 (3)	C3—C2—O1—C10	-4.3 (3)
C4—C5—C10—C9	-178.19 (17)	C5—C10—O1—C2	5.7 (3)
C6—C5—C10—O1	179.99 (16)	C9—C10—O1—C2	-174.53 (16)

Hydrogen-bond geometry (Å, °)

*Cg*1, *Cg*3 and *Cg*4 are the centroids of the O1/C2–C5/C10 and C11–C16 rings, and the benzopyran system, respectively.

<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>
N1—H1 <i>A</i> ···O2 ⁱ	0.86	2.19	3.037 (2)	167
C9—H9···O1 ⁱ	0.93	2.50	3.416 (2)	168
O2—H2···N2 ⁱⁱ	0.82	1.99	2.773 (2)	160
C4—H4···C11	0.98	2.58	3.102 (2)	113
C12—H12··· <i>Cg</i> 1	0.93	2.74	3.085 (2)	103
C12—H12··· <i>Cg</i> 4	0.93	2.83	3.291 (2)	112
C14—H14··· <i>Cg</i> 3 ⁱⁱⁱ	0.93	2.85	3.494 (2)	127

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