



Crystal structures of two 4*H*-chromene derivatives: 2-amino-3-cyano-4-(3,4-dichlorophenyl)-7-hydroxy-4*H*-benzo[1,2-*b*]pyran 1,4-dioxane monosolvate and 2-amino-3-cyano-4-(2,6-dichlorophenyl)-7-hydroxy-4*H*-benzo[1,2-*b*]pyran

S. Silambarasan,^{a*} A. Jamal Abdul Nasser^a and T. Mohandas^b^aDepartment of Chemistry, Jamal Mohamed College, Tiruchirappalli 620 020, India, and ^bDepartment of Physics, K. Ramakrishnan College of Engineering, Samayapuram, Tiruchirappalli 621 115, India. *Correspondence e-mail: ssilambu2012@gmail.com

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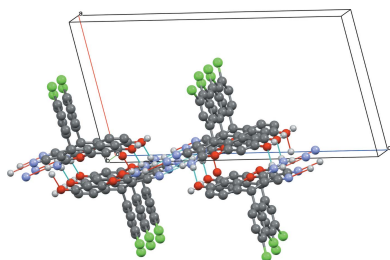
In the title compounds, C₁₆H₉Cl₂N₂O₂·C₄H₈O₂ and C₁₆H₉Cl₂N₂O₂, the bicyclic 4*H*-chromene cores are nearly planar with maximum deviations of 0.081 (2) and 0.087 (2) Å. In both structures, the chromene derivative molecules are linked into centrosymmetric dimers by pairs of N—H···O hydrogen bonds, forming *R*²₂(16) motifs. These dimers are further linked in the 3,4-dichlorophenyl derivative by N—H···N hydrogen bonds into double layers parallel to (100) and in the 2,6-dichlorophenyl derivative by O—H···N hydrogen bonds into ribbons along the [1 $\bar{1}$ 0] direction. In the 3,4-dichlorophenyl derivative, the 1,4-dioxane solvent molecules are connected to the chromene molecules *via* O—H···O hydrogen bonds.

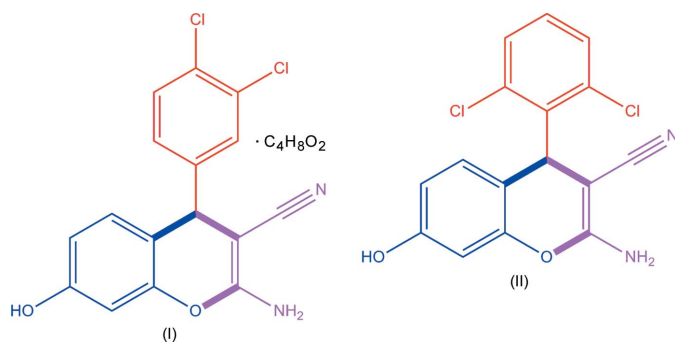
1. Chemical context

Many compounds containing the heterocyclic pyran moiety exhibit diverse pharmacological activities. The pyran ring is a core unit found in benzopyrans, chromones, coumarins and flavanoids. Numerous naturally occurring compounds containing a pyran ring show therapeutic activities such as antiviral (Martínez-Grau & Marco, 1997), antimicrobial (Khafagy *et al.*, 2002), mutagenicity (Hiramoto *et al.*, 1997), sex pheromone (Bianchi & Tava, 1987), antitumor (Mohr *et al.*, 1975), cancer therapy (Anderson *et al.*, 2005), central nervous system activity (Eiden & Denk, 1991), antifungal (Schiller *et al.*, 2010), antiproliferative (Osman *et al.*, 2011), antidiabetic (Bisht *et al.*, 2011), anti-inflammatory (Wang *et al.*, 1996; Wang *et al.*, 2005) and calcium channel antagonist activity (Shahrissa *et al.*, 2011).

2-Amino-4*H*-benzo[1,2-*b*]pyrans (2-amino-4*H*-chromenes) act as synthetic building blocks for the design of various pyran-containing bio-active molecules (Kale *et al.*, 2013; Sabry *et al.*, 2011; Kidwai *et al.*, 2010); among them are cytotoxic and anti-HIV preparations (Patil *et al.*, 1993; Emmadi *et al.*, 2012) and anticancer (Wu *et al.*, 2003; Perrella *et al.*, 1994), antimicrobial (Mungra *et al.*, 2011) and anticoagulant agents (Cingolani *et al.*, 1969).

Against this background we carried out the crystallographic studies of the title 4*H*-chromenes 2-amino-3-cyano-4-(3,4-dichlorophenyl)-7-hydroxy-4*H*-benzo[1,2-*b*]pyran 1,4-dioxane mono solvate (I) and 2-amino-3-cyano-4-(2,6-dichlorophenyl)-7-hydroxy-4*H*-benzo[1,2-*b*]pyran (II).





2. Structural commentary

The asymmetric units of the title compounds are illustrated in Figs. 1 and 2. The molecules of the two 4*H*-chromene derivatives differ only in the positions of the chlorine atoms attached to the phenyl ring, and the key bond dimensions in (I) and (II) essentially coincide. The bicyclic chromene cores in the two structures are nearly planar, with the largest deviation from the mean plane being observed for the sp^3 -hybridized C7 atom in both cases [0.081 (2) and 0.087 (2) Å in (I) and (II), respectively]. The interatomic distances in the pyran rings indicate a strong π -conjugation of the electron-donating atoms O2 and N2 with the cyano acceptor groups. As a result of this conjugation, the C8=C9 bonds [1.349 (3) Å in (I) and 1.354 (2) Å in (II)] are longer than the typical double bonds (Allen *et al.*, 1987), whereas the C9–N2 bonds are shortened [1.335 (3) and 1.342 (2) Å for (I) and (II), respectively], thus the amino groups in the studied structures were assumed to be planar and treated with the AFIX 43 instruction. Besides this, the O–C distances in the pyran rings are asymmetric [1.393 (2) and 1.393 (2) Å for

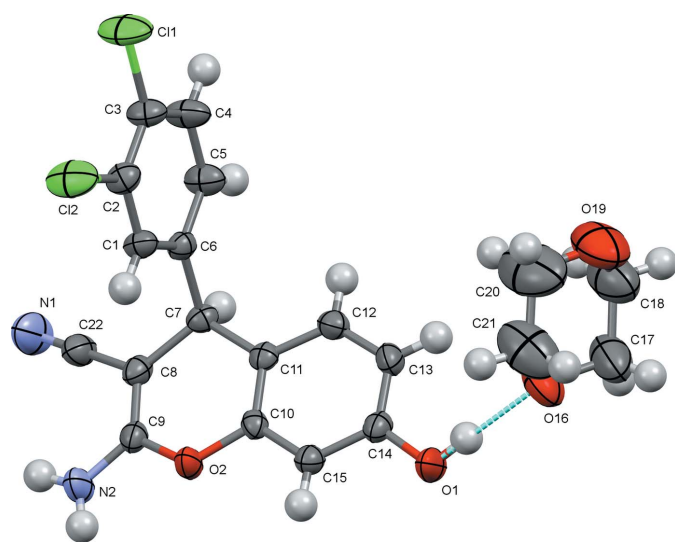


Figure 1
The asymmetric unit of (I), with atom labelling and 50% probability displacement ellipsoids. The hydrogen bond is represented by a dashed line.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1–H01 \cdots O16	0.82	1.85	2.658 (3)	167
N2–HNB \cdots O1 ⁱ	0.86	2.19	2.978 (3)	153
N2–HNA \cdots N1 ⁱⁱ	0.86	2.22	2.989 (3)	149
C4–H4 \cdots Cl2 ⁱⁱⁱ	0.93	2.87	3.692 (3)	148

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

Table 2
Hydrogen-bond geometry (Å, °) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C7–H7 \cdots Cl2	0.98	2.50	3.078 (3)	117
N2–HNB \cdots O1 ⁱ	0.86	2.19	3.048 (2)	173
O1–H01 \cdots N1 ⁱⁱ	0.85 (3)	1.95 (3)	2.762 (2)	160 (3)

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

O2–C10 vs. 1.357 (3) and 1.353 (2) Å for O2–C9 in (I) and (II), respectively]. The observed planarity of the bicyclic chromene units is also a consequence of π -conjugation. The dihedral angle between the mean planes of the 4*H*-chromene ring system and the phenyl ring attached to C7 is 80.82 (9)° in (I) and 85.36 (8)° in (II). In (II), the *o*-chlorine atom Cl1 forms short intramolecular contacts with atoms C8 and C9 of the pyran ring of 3.111 (2) and 3.193 (2) Å, respectively.

3. Supramolecular features

As shown in Figs. 3 and 4, in both of the title structures the 4*H*-chromene derivative molecules are linked by pairs of N–H \cdots O hydrogen bonds (Tables 1 and 2) into centrosymmetric dimers, thus forming $R^2_2(16)$ motifs. In (I), these dimers are further connected by N–H \cdots N hydrogen bonds into double

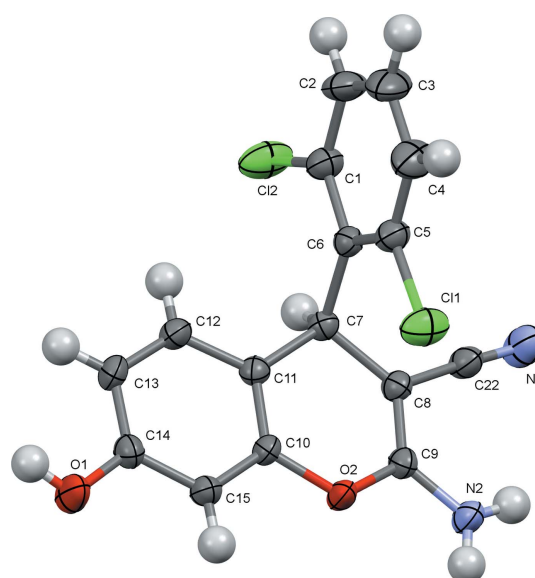
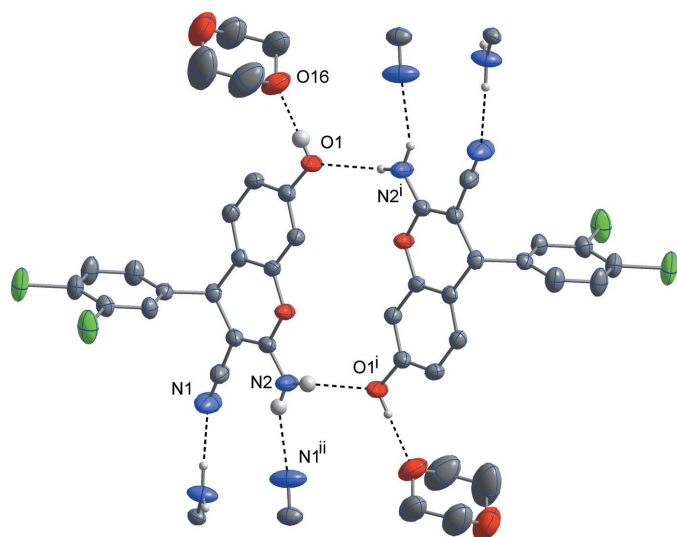


Figure 2
The molecular structure of (II), with atom labelling and 50% probability displacement ellipsoids.

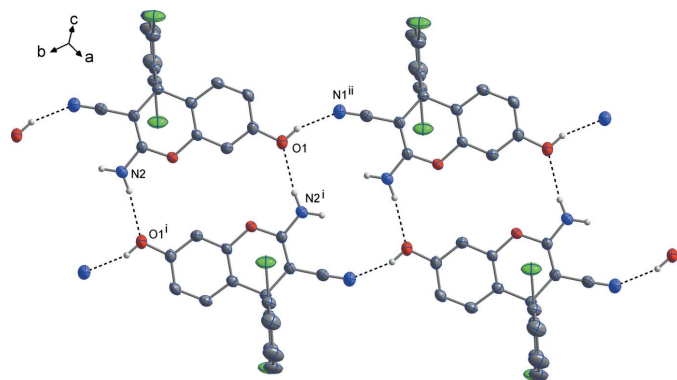

Figure 3

A view of the hydrogen-bonding interactions in (I), showing the formation of centrosymmetric dimers. The C-bound hydrogen atoms are omitted for clarity. [Symmetry codes: (i) $-x, 2 - y, 1 - z$; (ii) $-x, \frac{1}{2} + y, \frac{1}{2} - z$.]

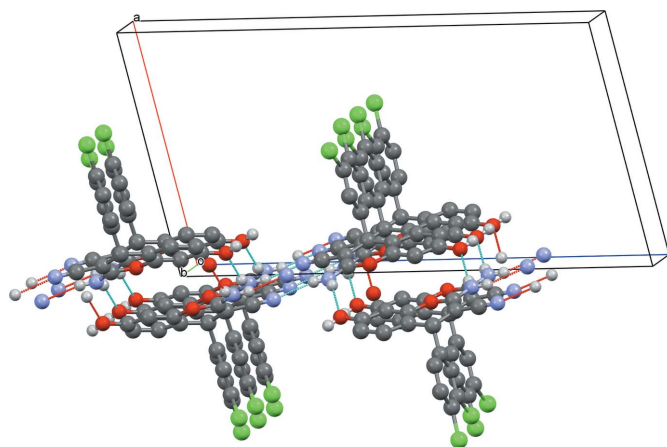
layers parallel to the (100) plane (Fig. 5). In (II), the dimers are linked by $O-H \cdots N$ hydrogen bonds into ribbons along the $[1\bar{1}0]$ direction. In (I), the 1,4-dioxane solvent molecules are linked to the chromene molecules *via* $O-H \cdots O$ hydrogen bonds. In this compound, the $C-H \cdots Cl$ contacts (Table 2) also contribute to the stability of crystal structure.

4. Database survey

A search in the Cambridge Structural Database (CSD version 5.40, last update August 2019; Groom *et al.*, 2016), revealed 107 structures of 4*H*-chromene derivatives, among them 25 containing the 2-amino-3-cyano-4*H*-chromene moiety. Of these, two structures, *viz.* 2-amino-7-hydroxy-4-(4-hydroxyphenyl)-4*H*-chromene-3-carbonitrile (HUPCEC; Horton *et al.*, 2015) and 2-amino-4-(4-bromophenyl)-7-hydroxy-4*H*-


Figure 4

A view of the hydrogen-bonding interactions in (II), showing the formation of centrosymmetric dimers and ribbons. The C-bound hydrogen atoms are omitted for clarity. [Symmetry codes: (i) $2 - x, 1 - y, -z$; (ii) $1 + x, y - 1, z$.]


Figure 5

Double layers of hydrogen-bonded molecules in (I). The 1,4-dioxane molecules are omitted for clarity.

chromene-3-carbonitrile (UFEKOI; Bi *et al.*, 2017) are closely related to compounds (I) and (II). In the structures of both HUPCEC and UFEKOI, the molecules adopt the same conformation as in (I) and (II) and also form centrosymmetric dimers by pairs of $N-H \cdots O$ hydrogen bonds as in the title structures.

5. Synthesis and crystallization

Both studied compounds were prepared by the same procedure. Mixtures of 3,4-chlorobenzaldehyde (8.75 g, 0.05 mol) [for (I)] or 2,4-dichlorobenzaldehyde (8.75 g, 0.05 mol) [for (II)], malononitrile (3.3 ml, 0.05 mol) and resorcinol (5.5 g, 0.05 mol) in 150 ml of water were refluxed for about 10-20 minutes in 250 ml round-bottom flasks. The progress of the reaction was monitored by thin layer chromatography using silica gel-G plates. After the product had formed, the reaction mixtures were kept in the refrigerator overnight. The solid mass that settled was filtered using a suction pump, washed well with a mixture of methanol and water and dried in air. The crude products were recrystallized from methanol giving white powders. Single crystals were grown by slow evaporation of solutions in 1,4-dioxane (I) or acetonitrile (II). The melting points are 518-523 K for (I) and 513-515 K for (II).

6. Refinement

Crystal data, diffraction data and structure refinement details for (I) and (II) are summarized in Table 3. All hydrogen atoms bound to C and N were located from the difference-Fourier maps and refined isotropically using a riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N})$ and $C-H = 0.98 \text{ \AA}$ for methine, 0.97 \AA for methylene and 0.93 \AA for aromatic C atoms, and $N-H = 0.86 \text{ \AA}$. In (I), the hydroxy H atom was constrained with AFIX 147, but its U_{iso} value was allowed to refine freely. In (II), the OH hydrogen atom was freely refined.

Table 3
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	C ₁₆ H ₉ Cl ₂ N ₂ O ₂ ·C ₄ H ₈ O ₂	C ₁₆ H ₉ Cl ₂ N ₂ O ₂
<i>M_r</i>	420.25	332.15
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	294	294
<i>a</i> , <i>b</i> , <i>c</i> (Å)	12.753 (9), 6.665 (4), 24.050 (14)	6.271 (3), 8.697 (5), 13.794 (7)
α , β , γ (°)	90, 102.95 (3), 90	107.06 (2), 94.269 (17), 95.00 (3)
<i>V</i> (Å ³)	1992 (2)	712.5 (7)
<i>Z</i>	4	2
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm ⁻¹)	0.36	0.46
Crystal size (mm)	0.15 × 0.15 × 0.10	0.15 × 0.15 × 0.10
Data collection		
Diffractometer	Bruker Kappa APEX3 CMOS	Bruker Kappa APEX3 CMOS
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2018)	Multi-scan (<i>SADABS</i> ; Bruker, 2018)
<i>T</i> _{min} , <i>T</i> _{max}	0.704, 0.745	0.704, 0.746
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	34682, 3492, 2885	22289, 2499, 2239
<i>R</i> _{int}	0.033	0.023
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.595	0.595
Refinement		
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.044, 0.121, 1.11	0.033, 0.081, 1.11
No. of reflections	3492	2499
No. of parameters	256	204
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.26, -0.24	0.23, -0.25

Computer programs: *APEX3*, *SAINT* and *XPREP* (Bruker, 2018), *SHELXT2014/5* (Sheldrick, 2015a), *SHELXL2014/6* (Sheldrick, 2015b), *DIAMOND* (Brandenburg, 2007), *Mercury* (Macrae *et al.*, 2008) and *PLATON* (Spek, 2009).

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supporting information

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S. Silambarasan, A. Jamal Abdul Nasser and T. Mohandas

Computing details

For both structures, data collection: *APEX3* (Bruker, 2018); cell refinement: *APEX3* and *SAINT* (Bruker, 2018); data reduction: *SAINT* and *XPREP* (Bruker, 2018); program(s) used to solve structure: *SHELXT2014/5* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014/6* (Sheldrick, 2015b); molecular graphics: *DIAMOND* (Brandenburg, 2007) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *PLATON* (Spek, 2009).

2-Amino-3-cyano-4-(3,4-dichlorophenyl)-7-hydroxy-4*H*-benzo[1,2-*b*]pyran 1,4-dioxane monosolvate (I)

Crystal data

$C_{16}H_9Cl_2N_2O_2 \cdot C_4H_8O_2$

$M_r = 420.25$

Monoclinic, $P2_1/c$

$a = 12.753$ (9) Å

$b = 6.665$ (4) Å

$c = 24.050$ (14) Å

$\beta = 102.95$ (3)°

$V = 1992$ (2) Å³

$Z = 4$

$F(000) = 868$

$D_x = 1.401$ Mg m⁻³

Melting point: 520 K

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

Cell parameters from 9965 reflections

$\theta = 3.2$ – 26.7 °

$\mu = 0.36$ mm⁻¹

$T = 294$ K

Block, colourless

$0.15 \times 0.15 \times 0.10$ mm

Data collection

Bruker Kappa APEX3 CMOS
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω and φ scan

Absorption correction: multi-scan
(SADABS; Bruker, 2018)

$T_{\min} = 0.704$, $T_{\max} = 0.745$

34682 measured reflections

3492 independent reflections

2885 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.033$

$\theta_{\max} = 25.0$ °, $\theta_{\min} = 3.2$ °

$h = -15 \rightarrow 15$

$k = -7 \rightarrow 7$

$l = -28 \rightarrow 26$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.044$

$wR(F^2) = 0.121$

$S = 1.11$

3492 reflections

256 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: difference Fourier map

H atoms treated by a mixture of independent
and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0541P)^2 + 1.1852P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 0.26 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.24 \text{ e } \text{\AA}^{-3}$$

Extinction correction: SHELXL,

$$F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$$

Extinction coefficient: 0.0174 (18)

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 $F^2 > 2\text{sigma}(F^2)$ 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	0.60648 (5)	0.18411 (11)	0.42962 (4)	0.0702 (3)
Cl2	0.52933 (5)	0.63066 (11)	0.40894 (4)	0.0679 (3)
O1	0.12386 (15)	0.8018 (3)	0.63654 (6)	0.0519 (5)
HO1	0.1545	0.7386	0.6648	0.074 (10)*
O2	0.07140 (12)	0.8197 (2)	0.43851 (6)	0.0379 (4)
N2	0.01565 (18)	0.8571 (3)	0.34552 (8)	0.0530 (6)
HNA	0.0051	0.8207	0.3104	0.064*
HNB	-0.0032	0.9750	0.3540	0.064*
N1	0.0608 (2)	0.3924 (4)	0.28098 (9)	0.0748 (8)
C3	0.47549 (17)	0.2502 (4)	0.42953 (10)	0.0424 (6)
C4	0.40418 (19)	0.1065 (4)	0.43879 (12)	0.0512 (6)
H4	0.4266	-0.0260	0.4452	0.061*
C5	0.29931 (18)	0.1579 (3)	0.43861 (11)	0.0439 (6)
H5	0.2516	0.0592	0.4448	0.053*
C6	0.26401 (16)	0.3532 (3)	0.42946 (8)	0.0303 (5)
C7	0.14837 (15)	0.4087 (3)	0.43059 (8)	0.0305 (5)
H7	0.1068	0.2841	0.4279	0.037*
C11	0.14231 (15)	0.5105 (3)	0.48595 (8)	0.0292 (4)
C12	0.17291 (16)	0.4127 (3)	0.53832 (9)	0.0358 (5)
H12	0.1980	0.2815	0.5391	0.043*
C13	0.16731 (17)	0.5037 (4)	0.58889 (9)	0.0382 (5)
H13	0.1868	0.4337	0.6231	0.046*
C14	0.13242 (16)	0.7003 (3)	0.58846 (8)	0.0354 (5)
C10	0.10667 (15)	0.7052 (3)	0.48756 (8)	0.0291 (4)
C15	0.10195 (16)	0.8023 (3)	0.53756 (8)	0.0337 (5)
H15	0.0786	0.9346	0.5369	0.040*
C9	0.06130 (16)	0.7304 (3)	0.38688 (8)	0.0342 (5)
C8	0.09544 (16)	0.5416 (3)	0.38111 (8)	0.0347 (5)
C22	0.07678 (19)	0.4596 (4)	0.32560 (10)	0.0459 (6)
C1	0.33627 (17)	0.4972 (3)	0.42043 (9)	0.0361 (5)

H1	0.3140	0.6298	0.4143	0.043*
C2	0.44144 (17)	0.4463 (3)	0.42042 (9)	0.0380 (5)
O16	0.24114 (17)	0.6481 (4)	0.73252 (9)	0.0769 (6)
C17	0.2288 (3)	0.5035 (7)	0.77295 (16)	0.0937 (12)
H171	0.1565	0.4491	0.7630	0.112*
H172	0.2389	0.5659	0.8102	0.112*
C18	0.3066 (3)	0.3413 (7)	0.7754 (2)	0.1008 (13)
H181	0.2976	0.2450	0.8042	0.121*
H182	0.2930	0.2727	0.7389	0.121*
O19	0.4122 (2)	0.4128 (5)	0.78824 (13)	0.1129 (10)
C20	0.4249 (4)	0.5602 (9)	0.7484 (3)	0.140 (2)
H201	0.4159	0.4986	0.7111	0.169*
H202	0.4974	0.6137	0.7590	0.169*
C21	0.3484 (3)	0.7239 (7)	0.7450 (2)	0.1147 (16)
H211	0.3622	0.7957	0.7810	0.138*
H212	0.3573	0.8171	0.7154	0.138*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.0349 (3)	0.0613 (5)	0.1189 (7)	0.0130 (3)	0.0268 (4)	0.0064 (4)
C12	0.0449 (4)	0.0492 (4)	0.1188 (7)	-0.0051 (3)	0.0379 (4)	0.0059 (4)
O1	0.0682 (12)	0.0615 (11)	0.0250 (8)	0.0233 (9)	0.0080 (8)	-0.0009 (8)
O2	0.0528 (9)	0.0356 (8)	0.0245 (7)	0.0081 (7)	0.0070 (6)	0.0006 (6)
N2	0.0766 (15)	0.0540 (13)	0.0266 (10)	0.0236 (11)	0.0079 (9)	0.0035 (9)
N1	0.100 (2)	0.0820 (18)	0.0351 (13)	0.0287 (16)	-0.0006 (12)	-0.0151 (12)
C3	0.0294 (11)	0.0424 (13)	0.0557 (14)	0.0061 (10)	0.0105 (10)	-0.0031 (11)
C4	0.0408 (13)	0.0324 (12)	0.0819 (18)	0.0077 (10)	0.0171 (12)	0.0016 (12)
C5	0.0362 (12)	0.0333 (12)	0.0634 (15)	-0.0015 (10)	0.0138 (11)	-0.0009 (11)
C6	0.0300 (10)	0.0334 (11)	0.0273 (10)	0.0020 (9)	0.0059 (8)	-0.0045 (9)
C7	0.0258 (10)	0.0325 (11)	0.0328 (11)	-0.0011 (8)	0.0062 (8)	-0.0046 (9)
C11	0.0220 (9)	0.0354 (11)	0.0305 (10)	-0.0020 (8)	0.0062 (8)	-0.0008 (9)
C12	0.0333 (11)	0.0346 (12)	0.0394 (12)	0.0048 (9)	0.0082 (9)	0.0041 (9)
C13	0.0374 (12)	0.0481 (14)	0.0285 (11)	0.0053 (10)	0.0060 (9)	0.0080 (10)
C14	0.0305 (11)	0.0481 (13)	0.0275 (11)	0.0035 (9)	0.0065 (8)	-0.0018 (9)
C10	0.0244 (9)	0.0370 (11)	0.0253 (10)	-0.0007 (8)	0.0042 (8)	0.0035 (9)
C15	0.0323 (11)	0.0377 (12)	0.0306 (11)	0.0046 (9)	0.0061 (8)	-0.0010 (9)
C9	0.0317 (11)	0.0455 (13)	0.0261 (10)	0.0020 (9)	0.0079 (8)	0.0005 (9)
C8	0.0284 (10)	0.0474 (13)	0.0274 (10)	0.0041 (9)	0.0043 (8)	-0.0054 (9)
C22	0.0459 (13)	0.0541 (15)	0.0347 (13)	0.0145 (11)	0.0028 (10)	-0.0041 (11)
C1	0.0344 (11)	0.0306 (11)	0.0450 (12)	0.0042 (9)	0.0126 (9)	-0.0021 (9)
C2	0.0320 (11)	0.0395 (12)	0.0439 (12)	-0.0026 (9)	0.0115 (9)	-0.0032 (10)
O16	0.0632 (13)	0.0935 (16)	0.0644 (13)	0.0044 (12)	-0.0062 (10)	0.0279 (12)
C17	0.067 (2)	0.126 (3)	0.091 (2)	0.018 (2)	0.0234 (18)	0.049 (2)
C18	0.082 (3)	0.096 (3)	0.126 (3)	0.008 (2)	0.027 (2)	0.042 (2)
O19	0.0663 (16)	0.131 (3)	0.137 (2)	0.0268 (17)	0.0141 (15)	0.043 (2)
C20	0.075 (3)	0.139 (4)	0.219 (6)	0.007 (3)	0.056 (3)	0.052 (5)
C21	0.079 (3)	0.108 (3)	0.141 (4)	-0.018 (3)	-0.008 (2)	0.034 (3)

Geometric parameters (Å, °)

C11—C3	1.727 (2)	C12—H12	0.9300
C12—C2	1.727 (2)	C13—C14	1.383 (3)
O1—C14	1.365 (3)	C13—H13	0.9300
O1—HO1	0.8200	C14—C15	1.378 (3)
O2—C9	1.357 (3)	C10—C15	1.379 (3)
O2—C10	1.393 (2)	C15—H15	0.9300
N2—C9	1.335 (3)	C9—C8	1.349 (3)
N2—HNA	0.8600	C8—C22	1.413 (3)
N2—HNB	0.8600	C1—C2	1.384 (3)
N1—C22	1.138 (3)	C1—H1	0.9300
C3—C4	1.373 (3)	O16—C17	1.403 (4)
C3—C2	1.379 (3)	O16—C21	1.426 (5)
C4—C5	1.380 (3)	C17—C18	1.459 (5)
C4—H4	0.9300	C17—H171	0.9700
C5—C6	1.379 (3)	C17—H172	0.9700
C5—H5	0.9300	C18—O19	1.396 (5)
C6—C1	1.381 (3)	C18—H181	0.9700
C6—C7	1.527 (3)	C18—H182	0.9700
C7—C11	1.512 (3)	O19—C20	1.406 (5)
C7—C8	1.515 (3)	C20—C21	1.453 (7)
C7—H7	0.9800	C20—H201	0.9700
C11—C10	1.378 (3)	C20—H202	0.9700
C11—C12	1.394 (3)	C21—H211	0.9700
C12—C13	1.375 (3)	C21—H212	0.9700
C14—O1—HO1	109.5	C10—C15—H15	120.5
C9—O2—C10	118.75 (17)	N2—C9—C8	127.6 (2)
C9—N2—HNA	120.0	N2—C9—O2	109.9 (2)
C9—N2—HNB	120.0	C8—C9—O2	122.48 (19)
HNA—N2—HNB	120.0	C9—C8—C22	117.9 (2)
C4—C3—C2	119.4 (2)	C9—C8—C7	124.17 (18)
C4—C3—C11	119.81 (19)	C22—C8—C7	117.8 (2)
C2—C3—C11	120.80 (18)	N1—C22—C8	179.3 (3)
C3—C4—C5	120.2 (2)	C6—C1—C2	120.7 (2)
C3—C4—H4	119.9	C6—C1—H1	119.6
C5—C4—H4	119.9	C2—C1—H1	119.6
C6—C5—C4	121.1 (2)	C3—C2—C1	120.2 (2)
C6—C5—H5	119.4	C3—C2—C12	120.48 (17)
C4—C5—H5	119.4	C1—C2—C12	119.31 (18)
C5—C6—C1	118.41 (19)	C17—O16—C21	110.4 (3)
C5—C6—C7	120.53 (19)	O16—C17—C18	110.9 (3)
C1—C6—C7	121.05 (19)	O16—C17—H171	109.5
C11—C7—C8	109.13 (17)	C18—C17—H171	109.5
C11—C7—C6	111.39 (16)	O16—C17—H172	109.5
C8—C7—C6	112.94 (16)	C18—C17—H172	109.5
C11—C7—H7	107.7	H171—C17—H172	108.1

C8—C7—H7	107.7	O19—C18—C17	111.6 (4)
C6—C7—H7	107.7	O19—C18—H181	109.3
C10—C11—C12	116.24 (18)	C17—C18—H181	109.3
C10—C11—C7	121.97 (18)	O19—C18—H182	109.3
C12—C11—C7	121.79 (19)	C17—C18—H182	109.3
C13—C12—C11	122.2 (2)	H181—C18—H182	108.0
C13—C12—H12	118.9	C18—O19—C20	109.9 (3)
C11—C12—H12	118.9	O19—C20—C21	112.6 (4)
C12—C13—C14	119.5 (2)	O19—C20—H201	109.1
C12—C13—H13	120.3	C21—C20—H201	109.1
C14—C13—H13	120.3	O19—C20—H202	109.1
O1—C14—C15	116.6 (2)	C21—C20—H202	109.1
O1—C14—C13	123.34 (19)	H201—C20—H202	107.8
C15—C14—C13	120.01 (19)	O16—C21—C20	110.2 (4)
C11—C10—C15	123.07 (18)	O16—C21—H211	109.6
C11—C10—O2	122.57 (17)	C20—C21—H211	109.6
C15—C10—O2	114.36 (18)	O16—C21—H212	109.6
C14—C15—C10	119.0 (2)	C20—C21—H212	109.6
C14—C15—H15	120.5	H211—C21—H212	108.1
C2—C3—C4—C5	0.4 (4)	C11—C10—C15—C14	-1.1 (3)
C11—C3—C4—C5	-179.8 (2)	O2—C10—C15—C14	178.35 (18)
C3—C4—C5—C6	-0.3 (4)	C10—O2—C9—N2	173.17 (18)
C4—C5—C6—C1	0.0 (3)	C10—O2—C9—C8	-7.7 (3)
C4—C5—C6—C7	-178.7 (2)	N2—C9—C8—C22	-3.7 (3)
C5—C6—C7—C11	102.8 (2)	O2—C9—C8—C22	177.2 (2)
C1—C6—C7—C11	-75.9 (2)	N2—C9—C8—C7	178.9 (2)
C5—C6—C7—C8	-134.0 (2)	O2—C9—C8—C7	-0.1 (3)
C1—C6—C7—C8	47.3 (3)	C11—C7—C8—C9	7.6 (3)
C8—C7—C11—C10	-8.1 (2)	C6—C7—C8—C9	-116.9 (2)
C6—C7—C11—C10	117.2 (2)	C11—C7—C8—C22	-169.73 (19)
C8—C7—C11—C12	172.12 (18)	C6—C7—C8—C22	65.8 (2)
C6—C7—C11—C12	-62.5 (2)	C5—C6—C1—C2	0.2 (3)
C10—C11—C12—C13	0.5 (3)	C7—C6—C1—C2	178.92 (19)
C7—C11—C12—C13	-179.75 (19)	C4—C3—C2—C1	-0.2 (4)
C11—C12—C13—C14	-1.4 (3)	C11—C3—C2—C1	179.98 (18)
C12—C13—C14—O1	179.6 (2)	C4—C3—C2—C12	179.7 (2)
C12—C13—C14—C15	1.1 (3)	C11—C3—C2—C12	-0.1 (3)
C12—C11—C10—C15	0.8 (3)	C6—C1—C2—C3	-0.1 (3)
C7—C11—C10—C15	-178.98 (18)	C6—C1—C2—C12	179.97 (16)
C12—C11—C10—O2	-178.63 (18)	C21—O16—C17—C18	-56.6 (5)
C7—C11—C10—O2	1.6 (3)	O16—C17—C18—O19	57.7 (5)
C9—O2—C10—C11	6.9 (3)	C17—C18—O19—C20	-56.0 (5)
C9—O2—C10—C15	-172.56 (18)	C18—O19—C20—C21	55.8 (6)
O1—C14—C15—C10	-178.52 (19)	C17—O16—C21—C20	55.5 (5)
C13—C14—C15—C10	0.1 (3)	O19—C20—C21—O16	-55.7 (6)

Hydrogen-bond geometry (Å, °)

<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>
O1—HO1···O16	0.82	1.85	2.658 (3)	167
N2—HNB···O1 ⁱ	0.86	2.19	2.978 (3)	153
N2—HNA···N1 ⁱⁱ	0.86	2.22	2.989 (3)	149
C4—H4···Cl2 ⁱⁱⁱ	0.93	2.87	3.692 (3)	148

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

2-Amino-3-cyano-4-(2,6-dichlorophenyl)-7-hydroxy-4H-\ benzo[1,2-*b*]pyran (II)

Crystal data

$C_{16}H_9Cl_2N_2O_2$

$M_r = 332.15$

Triclinic, $P\bar{1}$

$a = 6.271$ (3) Å

$b = 8.697$ (5) Å

$c = 13.794$ (7) Å

$\alpha = 107.06$ (2)°

$\beta = 94.269$ (17)°

$\gamma = 95.00$ (3)°

$V = 712.5$ (7) Å³

$Z = 2$

$F(000) = 338$

$D_x = 1.548$ Mg m⁻³

Melting point: 514 K

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

Cell parameters from 8750 reflections

$\theta = 3.1$ – 30.4 °

$\mu = 0.46$ mm⁻¹

$T = 294$ K

Block, colourless

$0.15 \times 0.15 \times 0.10$ mm

Data collection

Bruker Kappa APEX3 CMOS
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω and ϕ scan

Absorption correction: multi-scan
(SADABS; Bruker, 2018)

$T_{\min} = 0.704$, $T_{\max} = 0.746$

22289 measured reflections

2499 independent reflections

2239 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.023$

$\theta_{\max} = 25.0$ °, $\theta_{\min} = 3.9$ °

$h = -7 \rightarrow 7$

$k = -10 \rightarrow 10$

$l = -16 \rightarrow 16$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.033$

$wR(F^2) = 0.081$

$S = 1.11$

2499 reflections

204 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0263P)^2 + 0.4717P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.23$ e Å⁻³

$\Delta\rho_{\min} = -0.25$ e Å⁻³

Extinction correction: SHELXL,

$F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.080 (10)

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>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.84692 (8)	0.84534 (6)	0.32241 (4)	0.04703 (19)
Cl2	0.10752 (8)	0.50064 (7)	0.36100 (4)	0.0536 (2)
O1	1.0482 (2)	0.15972 (18)	0.09764 (12)	0.0484 (4)
HO1	1.058 (5)	0.092 (4)	0.130 (2)	0.084 (10)*
O2	0.7394 (2)	0.62001 (14)	0.07971 (9)	0.0331 (3)
N1	0.1786 (3)	0.9314 (2)	0.18547 (15)	0.0538 (5)
N2	0.6119 (3)	0.83118 (18)	0.04811 (12)	0.0372 (4)
HNB	0.7128	0.8266	0.0087	0.045*
HNA	0.5262	0.9046	0.0540	0.045*
C14	0.8930 (3)	0.2578 (2)	0.12922 (13)	0.0314 (4)
C13	0.7476 (3)	0.2339 (2)	0.19616 (13)	0.0327 (4)
H13	0.7498	0.1452	0.2207	0.039*
C12	0.6001 (3)	0.3428 (2)	0.22588 (13)	0.0303 (4)
H12	0.5033	0.3258	0.2706	0.036*
C11	0.5912 (3)	0.47743 (19)	0.19116 (12)	0.0252 (4)
C7	0.4337 (3)	0.59914 (19)	0.22777 (12)	0.0244 (3)
H7	0.2892	0.5394	0.2131	0.029*
C6	0.4733 (3)	0.67923 (19)	0.34378 (12)	0.0256 (4)
C1	0.3324 (3)	0.6415 (2)	0.40945 (13)	0.0340 (4)
C2	0.3630 (4)	0.7086 (3)	0.51432 (15)	0.0489 (5)
H2	0.2637	0.6808	0.5549	0.059*
C3	0.5406 (4)	0.8159 (3)	0.55754 (15)	0.0545 (6)
H3	0.5623	0.8621	0.6280	0.065*
C8	0.4401 (3)	0.7173 (2)	0.16603 (12)	0.0272 (4)
C22	0.2927 (3)	0.8338 (2)	0.17803 (13)	0.0333 (4)
C9	0.5883 (3)	0.72374 (19)	0.10034 (12)	0.0270 (4)
C10	0.7341 (3)	0.49354 (19)	0.12257 (12)	0.0258 (4)
C15	0.8841 (3)	0.3873 (2)	0.09093 (13)	0.0306 (4)
H15	0.9778	0.4028	0.0446	0.037*
C4	0.6873 (4)	0.8561 (3)	0.49742 (15)	0.0482 (5)
H4	0.8094	0.9282	0.5269	0.058*
C5	0.6524 (3)	0.7886 (2)	0.39261 (13)	0.0333 (4)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0390 (3)	0.0566 (3)	0.0404 (3)	-0.0157 (2)	0.0042 (2)	0.0129 (2)
Cl2	0.0435 (3)	0.0712 (4)	0.0448 (3)	-0.0174 (2)	0.0084 (2)	0.0216 (3)
O1	0.0615 (10)	0.0440 (8)	0.0580 (9)	0.0319 (7)	0.0295 (7)	0.0303 (7)
O2	0.0421 (7)	0.0305 (6)	0.0376 (7)	0.0150 (5)	0.0189 (5)	0.0204 (5)

N1	0.0546 (11)	0.0603 (12)	0.0685 (12)	0.0324 (10)	0.0294 (9)	0.0405 (10)
N2	0.0469 (9)	0.0356 (8)	0.0409 (9)	0.0166 (7)	0.0178 (7)	0.0231 (7)
C14	0.0388 (10)	0.0269 (8)	0.0303 (9)	0.0110 (7)	0.0057 (7)	0.0088 (7)
C13	0.0433 (10)	0.0254 (8)	0.0340 (9)	0.0057 (7)	0.0052 (8)	0.0154 (7)
C12	0.0362 (9)	0.0298 (9)	0.0276 (8)	0.0013 (7)	0.0063 (7)	0.0128 (7)
C11	0.0289 (8)	0.0243 (8)	0.0222 (8)	0.0023 (6)	0.0012 (6)	0.0071 (6)
C7	0.0235 (8)	0.0264 (8)	0.0242 (8)	0.0026 (6)	0.0033 (6)	0.0090 (6)
C6	0.0285 (8)	0.0259 (8)	0.0247 (8)	0.0063 (7)	0.0043 (6)	0.0098 (7)
C1	0.0354 (10)	0.0376 (10)	0.0314 (9)	0.0017 (8)	0.0065 (7)	0.0139 (8)
C2	0.0648 (14)	0.0541 (12)	0.0293 (10)	-0.0009 (11)	0.0165 (9)	0.0143 (9)
C3	0.0846 (17)	0.0510 (13)	0.0232 (9)	-0.0059 (12)	0.0054 (10)	0.0076 (9)
C8	0.0309 (9)	0.0284 (8)	0.0249 (8)	0.0082 (7)	0.0036 (7)	0.0107 (7)
C22	0.0358 (9)	0.0374 (10)	0.0341 (9)	0.0099 (8)	0.0097 (7)	0.0191 (8)
C9	0.0325 (9)	0.0252 (8)	0.0255 (8)	0.0085 (7)	0.0032 (7)	0.0094 (7)
C10	0.0328 (9)	0.0232 (8)	0.0248 (8)	0.0055 (7)	0.0043 (7)	0.0113 (6)
C15	0.0362 (9)	0.0304 (9)	0.0299 (9)	0.0092 (7)	0.0109 (7)	0.0130 (7)
C4	0.0604 (13)	0.0444 (11)	0.0323 (10)	-0.0108 (10)	-0.0050 (9)	0.0073 (9)
C5	0.0375 (10)	0.0336 (9)	0.0298 (9)	0.0002 (7)	0.0057 (7)	0.0118 (7)

Geometric parameters (Å, °)

C11—C5	1.7383 (19)	C11—C7	1.515 (2)
C12—C1	1.736 (2)	C7—C8	1.515 (2)
O1—C14	1.362 (2)	C7—C6	1.538 (2)
O1—HO1	0.85 (3)	C7—H7	0.9800
O2—C9	1.353 (2)	C6—C5	1.394 (3)
O2—C10	1.392 (2)	C6—C1	1.397 (2)
N1—C22	1.144 (2)	C1—C2	1.383 (3)
N2—C9	1.342 (2)	C2—C3	1.364 (3)
N2—HNB	0.8600	C2—H2	0.9300
N2—HNA	0.8600	C3—C4	1.373 (3)
C14—C15	1.381 (2)	C3—H3	0.9300
C14—C13	1.390 (3)	C8—C9	1.354 (2)
C13—C12	1.380 (3)	C8—C22	1.413 (2)
C13—H13	0.9300	C10—C15	1.380 (2)
C12—C11	1.392 (2)	C15—H15	0.9300
C12—H12	0.9300	C4—C5	1.384 (3)
C11—C10	1.378 (2)	C4—H4	0.9300
C14—O1—HO1	112 (2)	C2—C1—C12	116.30 (15)
C9—O2—C10	118.64 (13)	C6—C1—C12	120.20 (14)
C9—N2—HNB	120.0	C3—C2—C1	119.25 (19)
C9—N2—HNA	120.0	C3—C2—H2	120.4
HNB—N2—HNA	120.0	C1—C2—H2	120.4
O1—C14—C15	116.39 (16)	C2—C3—C4	120.18 (19)
O1—C14—C13	123.88 (16)	C2—C3—H3	119.9
C15—C14—C13	119.73 (16)	C4—C3—H3	119.9
C12—C13—C14	119.48 (15)	C9—C8—C22	115.95 (15)

C12—C13—H13	120.3	C9—C8—C7	123.49 (14)
C14—C13—H13	120.3	C22—C8—C7	120.51 (15)
C13—C12—C11	122.22 (16)	N1—C22—C8	177.10 (19)
C13—C12—H12	118.9	N2—C9—O2	110.03 (14)
C11—C12—H12	118.9	N2—C9—C8	126.71 (15)
C10—C11—C12	116.26 (15)	O2—C9—C8	123.25 (15)
C10—C11—C7	122.30 (14)	C11—C10—C15	123.29 (15)
C12—C11—C7	121.44 (15)	C11—C10—O2	122.40 (14)
C11—C7—C8	109.10 (13)	C15—C10—O2	114.31 (14)
C11—C7—C6	111.28 (13)	C10—C15—C14	118.96 (16)
C8—C7—C6	114.32 (14)	C10—C15—H15	120.5
C11—C7—H7	107.3	C14—C15—H15	120.5
C8—C7—H7	107.3	C3—C4—C5	119.6 (2)
C6—C7—H7	107.3	C3—C4—H4	120.2
C5—C6—C1	114.50 (15)	C5—C4—H4	120.2
C5—C6—C7	124.05 (14)	C4—C5—C6	123.02 (17)
C1—C6—C7	121.41 (15)	C4—C5—C11	116.49 (15)
C2—C1—C6	123.48 (18)	C6—C5—C11	120.49 (13)
O1—C14—C13—C12	178.13 (17)	C10—O2—C9—N2	-176.56 (14)
C15—C14—C13—C12	-1.9 (3)	C10—O2—C9—C8	4.5 (2)
C14—C13—C12—C11	-0.1 (3)	C22—C8—C9—N2	1.8 (3)
C13—C12—C11—C10	2.0 (2)	C7—C8—C9—N2	-175.57 (16)
C13—C12—C11—C7	-177.63 (15)	C22—C8—C9—O2	-179.42 (15)
C10—C11—C7—C8	8.4 (2)	C7—C8—C9—O2	3.2 (3)
C12—C11—C7—C8	-172.08 (15)	C12—C11—C10—C15	-2.0 (2)
C10—C11—C7—C6	-118.71 (17)	C7—C11—C10—C15	177.61 (15)
C12—C11—C7—C6	60.9 (2)	C12—C11—C10—O2	178.39 (15)
C11—C7—C6—C5	70.1 (2)	C7—C11—C10—O2	-2.0 (2)
C8—C7—C6—C5	-54.1 (2)	C9—O2—C10—C11	-5.0 (2)
C11—C7—C6—C1	-107.41 (18)	C9—O2—C10—C15	175.30 (15)
C8—C7—C6—C1	128.44 (17)	C11—C10—C15—C14	0.1 (3)
C5—C6—C1—C2	1.3 (3)	O2—C10—C15—C14	179.77 (15)
C7—C6—C1—C2	179.01 (18)	O1—C14—C15—C10	-178.14 (16)
C5—C6—C1—C12	-177.27 (13)	C13—C14—C15—C10	1.9 (3)
C7—C6—C1—C12	0.4 (2)	C2—C3—C4—C5	0.9 (4)
C6—C1—C2—C3	-0.9 (3)	C3—C4—C5—C6	-0.3 (3)
C12—C1—C2—C3	177.78 (18)	C3—C4—C5—C11	-179.69 (18)
C1—C2—C3—C4	-0.3 (4)	C1—C6—C5—C4	-0.7 (3)
C11—C7—C8—C9	-9.1 (2)	C7—C6—C5—C4	-178.35 (17)
C6—C7—C8—C9	116.24 (18)	C1—C6—C5—C11	178.63 (13)
C11—C7—C8—C22	173.69 (15)	C7—C6—C5—C11	1.0 (2)
C6—C7—C8—C22	-61.0 (2)		

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C7—H7 \cdots C12	0.98	2.50	3.078 (3)	117

N2—HNB···O1 ⁱ	0.86	2.19	3.048 (2)	173
O1—HO1···N1 ⁱⁱ	0.85 (3)	1.95 (3)	2.762 (2)	160 (3)

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