



Crystal structure of 4-chloro-2-nitrobenzoic acid with 4-hydroxyquinoline: a disordered structure over two states of 4-chloro-2-nitrobenzoic acid–quinolin-4(1*H*)-one (1/1) and 4-hydroxyquinolinium 4-chloro-2-nitrobenzoate

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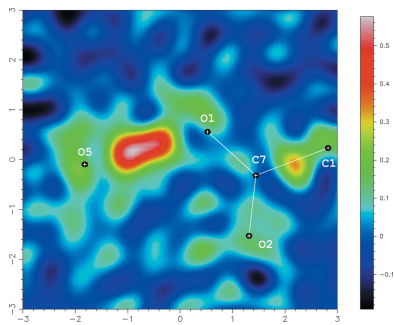
Keywords: crystal structure; 4-chloro-2-nitrobenzoic acid; 4(1*H*)-quinolinone; 4-hydroxyquinoline; hydrogen bond; keto–enol tautomerization; Hirshfeld surface.

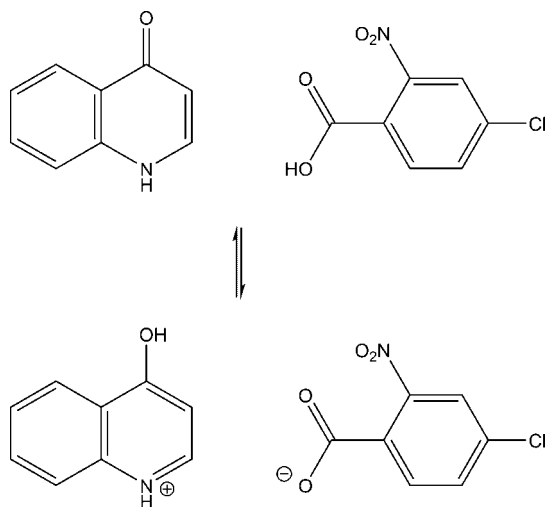
CCDC reference: 1963942**Supporting information:** this article has supporting information at journals.iucr.org/e

The title compound, $C_9H_{7.5}NO \cdot C_7H_{3.5}ClNO_4$, was analysed as a disordered structure over two states, *viz.* co-crystal and salt, accompanied by a keto–enol tautomerization in the base molecule. The co-crystal is 4-chloro-2-nitrobenzoic acid–quinolin-4(1*H*)-one (1/1), $C_7H_4ClNO_4 \cdot C_9H_7NO$, and the salt is 4-hydroxyquinolinium 4-chloro-2-nitrobenzoate, $C_9H_8NO^+ \cdot C_7H_3ClNO_4^-$. In the compound, the acid and base molecules are held together by a short hydrogen bond [$O \cdots O = 2.4393(15) \text{ \AA}$], in which the H atom is disordered over two positions with equal occupancies. In the crystal, the hydrogen-bonded acid–base units are linked by $N-H \cdots O$ and $C-H \cdots O$ hydrogen bonds, forming a tape structure along the *a*-axis direction. The tapes are stacked into a layer parallel to the *ab* plane *via* π – π interactions [centroid–centroid distances = $3.5504(8)$ – $3.9010(11) \text{ \AA}$]. The layers are further linked by another $C-H \cdots O$ hydrogen bond, forming a three-dimensional network. Hirshfeld surfaces for the title compound mapped over shape-index and d_{norm} were generated to visualize the intermolecular interactions.

1. Chemical context

In our previous study on $D-H \cdots A$ hydrogen bonding ($D = N, O, \text{ or } C, A = N, O \text{ or } Cl$) in chloro- and nitro-substituted benzoic acid–pyridine derivative systems, we have shown that several compounds, namely, three compounds of quinoline with 3-chloro-2-nitrobenzoic acid, 4-chloro-2-nitrobenzoic acid and 5-chloro-2-nitrobenzoic acid (Gotoh & Ishida, 2009), two compounds of phthalazine with 3-chloro-2-nitrobenzoic acid and 4-chloro-2-nitrobenzoic acid (Gotoh & Ishida, 2011), and 3-chloro-2-nitrobenzoic acid–isoquinoline (Gotoh & Ishida, 2015), have a short double-well $O \cdots H \cdots N$ hydrogen bond between the carboxy O atom and the aromatic N atom. Hydroxyquinolines, which have hydrogen-bond acceptor as well as donor groups, appear attractive as a base molecule in the above systems for investigating the hydrogen bonds (Babu & Chandrasekaran, 2014; Gotoh & Ishida, 2019). We report here the crystal structure of the title compound, in which there exists another type of short double-well hydrogen bond, namely, an $O \cdots H \cdots O$ hydrogen bond between the acid and base molecules, accompanied by a keto–enol tautomerization of the base molecule.





2. Structural commentary

The molecular structure of the title compound is shown in Fig. 1. The acid and base molecules are held together by a short hydrogen bond between atom O1 of the acid molecule and atom O5 of the base [O1...O5 = 2.4393 (15) Å; Table 1]. In the hydrogen bond, the H atom is disordered as indicated in the difference-Fourier map (Fig. 2), in which a broad peak along the line connecting the two O atoms is observed. Although two distinct peaks were not clearly observed in the map, the H atom was successfully analysed as being disordered over two positions of the O1 and O5 sites with equal occupancies. The title compound is, thus, interpreted as a disordered structure over two states, *viz.* the co-crystal, 4-chloro-2-nitrobenzoic acid-4(1*H*)-quinolinone (1/1), and the salt, 4-hydroxyquinolinium 4-chloro-2-nitrobenzoate, accompanied by a keto-enol tautomerization in the base molecule. The C10–O5 bond length [1.2956 (18) Å] is intermediate between a C–O single bond [1.36 Å in phenol] and a C=O double bond [1.23 Å in ketones of the (C_{ar})₂–C=O type] (Allen *et al.*, 1987), supporting that hypothesis that the base molecule has an intermediate state between the keto and enol forms.

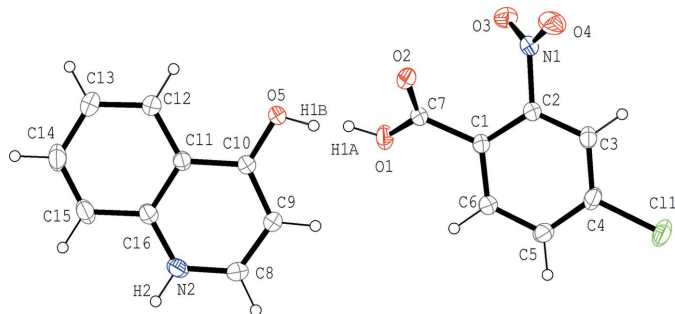


Figure 1

The molecular structure of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

Table 1

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–H1A...O5	0.84 (3)	1.61 (2)	2.4393 (15)	172 (5)
O5–H1B...O1	0.84 (2)	1.60 (2)	2.4393 (15)	173 (4)
N2–H2...O2 ⁱ	0.89 (2)	1.86 (2)	2.7475 (18)	176 (2)
C3–H3...O4 ⁱⁱ	0.95	2.53	3.469 (2)	170
C8–H8...O5 ⁱ	0.95	2.45	3.208 (2)	137
C9–H9...O1	0.95	2.51	3.121 (2)	123

Symmetry codes: (i) $x - \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (ii) $-x + 1, y, -z + \frac{3}{2}$.

In the hydrogen-bonded acid–base unit, the benzene ring (C1–C6) of the acid molecule and the quinoline ring system (N2/C8–C16) of the base are slightly inclined to each other by a dihedral angle of 10.27 (6)°, while the carboxy group (O1/C7/O2) is twisted by 38.66 (18) and 45.93 (18)°, respectively, with respect to the C1–C6 ring and the N2/C8–C16 ring system. The dihedral angle between the C1–C6 ring and the nitro group (O3/N1/O4) is 50.33 (19)°.

3. Supramolecular features

In the crystal of the title compound, the hydrogen-bonded acid–base units are linked by N–H...O and C–H...O hydrogen bonds (N2–H2...O2ⁱ, C8–H8...O5ⁱ and C9–H9...O1ⁱ; symmetry code as in Table 1), forming a tape structure along the *a* axis (Fig. 3). The tapes are stacked into a layer parallel to the *ab* plane *via* π – π interactions formed between the acid molecules and between the base molecules (Fig. 4); the centroid–centroid distances are 3.5504 (8), 3.7141 (9), 3.7382 (10) and 3.9010 (11) Å, respectively, for Cg1...Cg1^{iv}, Cg2...Cg2^{iv}, Cg3...Cg2^{iv} and Cg3...Cg3^{iv}, where Cg1, Cg2 and Cg3 are the centroids of the C1–C6 ring of the

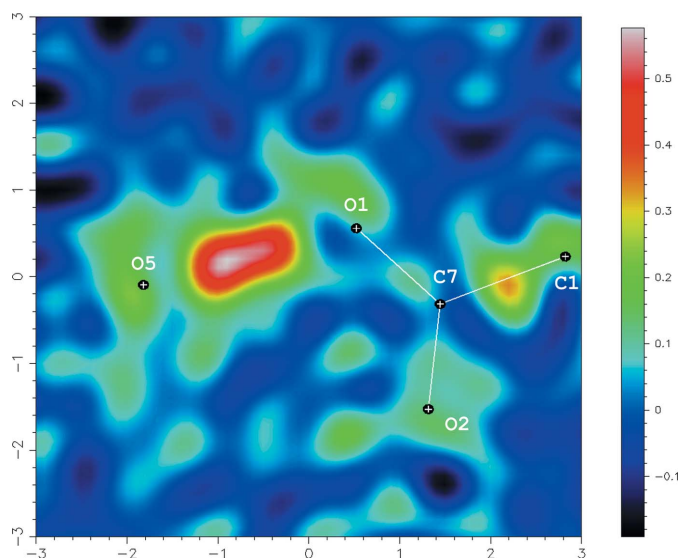
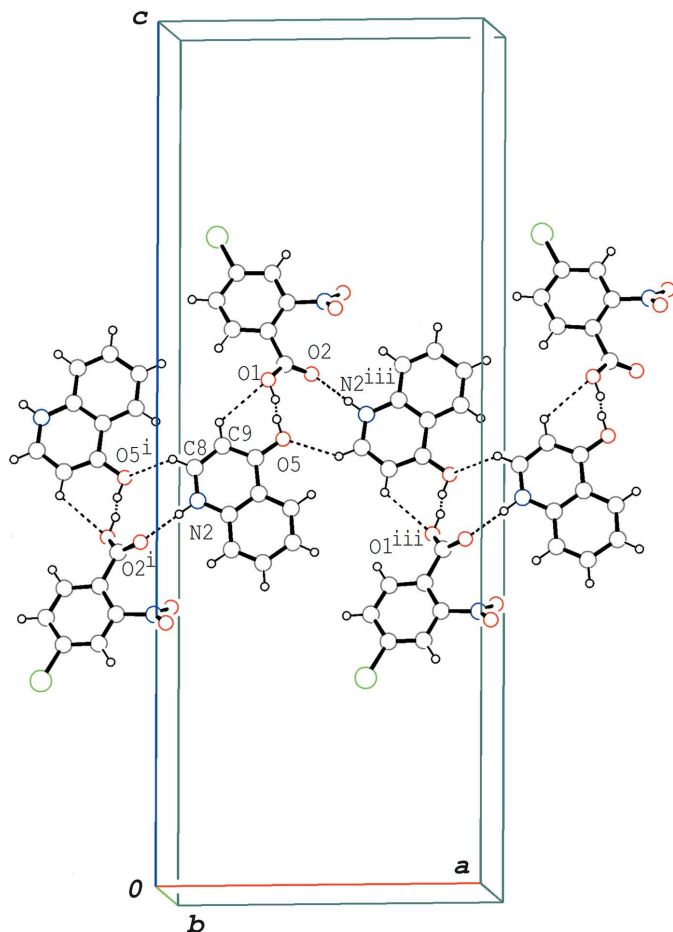


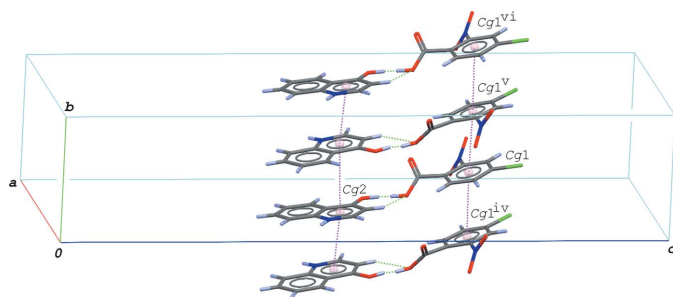
Figure 2

A difference-Fourier map of the title compound associated with the O...H...O hydrogen bond between the acid and the base. The map was calculated on the plane of atoms O1, C7 and O5 from a model containing all atoms apart from the H atom in the hydrogen bond.

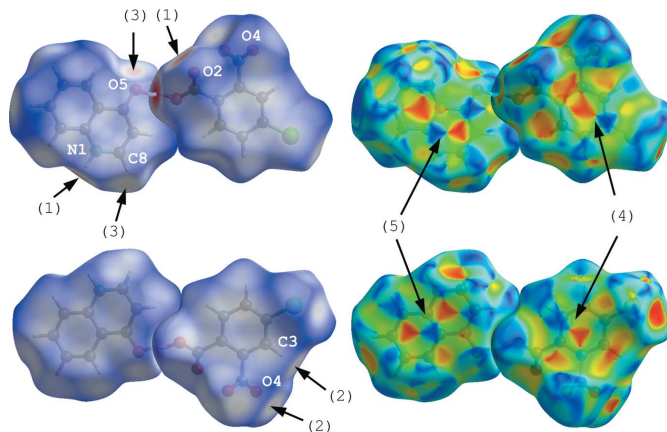

Figure 3

A packing diagram of the title compound, showing the hydrogen-bonded tape structure formed *via* the O \cdots H \cdots O, N–H \cdots O and C–H \cdots O hydrogen bonds (dashed lines). [Symmetry codes: (i) $x - \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (iii) $x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$.]

acid molecule, and the N2/C8–C11/C16 and C11–C16 rings of the base molecule, respectively [symmetry code: (iv) $-x + \frac{1}{2}, y - \frac{1}{2}, z$]. The layers are further linked by another C–H \cdots O hydrogen bond (C3–H3 \cdots O4^{iv}; Table 1), forming a three-dimensional network.


Figure 4

A packing diagram of the title compound, showing hydrogen-bonded acid-base units stacked along the *b* axis *via* the π – π interactions (magenta dashed lines). The π – π interactions including the centroid of the C11–C16 ring of the base (Cg3) are omitted for clarity. The O \cdots H \cdots O and C–H \cdots O hydrogen bonds are indicated by green dashed lines. [Symmetry codes: (iv) $-x + \frac{1}{2}, y - \frac{1}{2}, z$; (v) $-x + \frac{1}{2}, y + \frac{1}{2}, z$; (vi) $x, y + 1, z$.]


Figure 5

Hirshfeld surfaces (front and back views) for the title compound mapped over d_{norm} and shape-index, indicating the N–H \cdots O [arrows (1)], C–H \cdots O [arrows (2) and (3)] and π – π [arrows (4) and (5)] interactions.

In order to visualize the intermolecular interactions, Hirshfeld surfaces for the acid and base molecules of the title compound, mapped over shape-index and d_{norm} (Turner *et al.*, 2017; McKinnon *et al.*, 2004, 2007), were generated (Fig. 5). Intermolecular hydrogen bonds of N2–H2 \cdots O2ⁱ, C3–H3 \cdots O4ⁱⁱ and C8–H8 \cdots O5ⁱ (Table 1) are represented as faint-red spots on the d_{norm} surfaces [arrows (1)–(3)]. The π – π interactions between the benzene rings of the acid molecules [Cg1 \cdots Cg1^{iv}] and between the quinoline ring systems of the base molecules [Cg2 \cdots Cg2^{iv}, Cg3 \cdots Cg2^{iv} and Cg3 \cdots Cg3^{iv}; symmetry code: (iv) $-x + \frac{1}{2}, y - \frac{1}{2}, z$] are indicated by blue and red triangles on the shape-index surfaces [arrows (4) and (5)].

4. Database survey

A search of the Cambridge Structural Database (Version 5.40, last update August 2019; Groom *et al.*, 2016) for organic co-crystals/salts of 4(1*H*)-quinolinone (keto tautomer) showed one structure, namely, 4-amino-1-(2-(hydroxymethyl)-1,3-oxathiolan-5-yl)-2(1*H*)-pyrimidinone 4(1*H*)-quinolinone (refcode COWTAK; Bhatt *et al.*, 2009). The structure of the 4(1*H*)-quinolinone itself was reported by Nasiri *et al.* (2006; NICIOZ). The C=O bond length in COWTAK is 1.265 (7) Å and those in NICIOZ are 1.2686 (16) and 1.2742 (15) Å, which are shorter than the C10–O5 bond length of 1.2956 (18) Å in the title compound. No structure was found in the CSD for organic co-crystals/salts of 4-hydroxyquinoline (enol tautomer). A search for organic co-crystals/salts of 4-chloro-2-nitrobenzoic acid with base molecules gave eight compounds. Of these compounds, disorder of H atom between the acid O atom and the base N atom was observed in two compounds of 4-chloro-2-nitrobenzoic acid with quinoline (AJIWUM; Gotoh & Ishida, 2009) and phthalazine (CALKAD; Gotoh & Ishida, 2011).

5. Synthesis and crystallization

Single crystals of the title compound suitable for X-ray diffraction analysis were obtained by slow evaporation from

Table 2
Experimental details.

Crystal data	
Chemical formula	C ₇ H _{3.5} ClNO ₄ ·C ₉ H _{7.5} NO
<i>M</i> _r	346.73
Crystal system, space group	Orthorhombic, <i>Pbcn</i>
Temperature (K)	190
<i>a</i> , <i>b</i> , <i>c</i> (Å)	12.6336 (8), 7.0701 (3), 33.5956 (15)
<i>V</i> (Å ³)	3000.8 (3)
<i>Z</i>	8
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.29
Crystal size (mm)	0.35 × 0.28 × 0.09
Data collection	
Diffractometer	Rigaku R-Axis RAPIDII
Absorption correction	Numerical (NUMABS; Higashi, 1999)
<i>T</i> _{min} – <i>T</i> _{max}	0.939, 0.975
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	36709, 4380, 3235
<i>R</i> _{int}	0.052
(sin θ/λ) _{max} (Å ⁻¹)	0.704
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.046, 0.136, 1.13
No. of reflections	4380
No. of parameters	227
No. of restraints	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.39, -0.42

Computer programs: *PROCESS-AUTO* (Rigaku, 2006), *SHELXT2018* (Sheldrick, 2015a), *SHELXL2018* (Sheldrick, 2015b), *ORTEP-3 for Windows* and *WinGX* (Farrugia, 2012); *Mercury* (Macrae *et al.*, 2008), *CrystalStructure* (Rigaku, 2018) and *PLATON* (Spek, 2015).

an acetonitrile solution (130 ml) of 4-hydroxyquinoline (0.075 g) with 4-chloro-2-nitrobenzoic acid (0.106 g) in a 1:1 molar ratio at room temperature.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms except one H atom between the two O atoms (O1 and O5) of the acid and base molecules were found in a difference-Fourier map. A broad peak in a difference-Fourier map between atoms O1 and O5

was observed (Fig. 2). Although two distinct peaks were not observed in the map, the H atom between the O atoms was analysed using a model of an H atom disordered over two positions. The occupancies of the two sites were refined to 0.47 (4) and 0.53 (4) for H1A (O1 site) and H1B (O5 site), respectively, with bond restraints of O–H = 0.84 (1) Å and with *U*_{iso}(H) = 1.5*U*_{eq}(O). In the final refinement, the occupancies were fixed at 0.5, and one outlier (6,8,13) was omitted. The N-bound H atom was refined freely [refined distance: N2–H2 = 0.89 (2) Å]. Other H atoms were positioned geometrically (C–H = 0.95 Å) and treated as riding, with *U*_{iso}(H) = 1.2*U*_{eq}(C).

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supporting information

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Crystal structure of 4-chloro-2-nitrobenzoic acid with 4-hydroxyquinoline: a disordered structure over two states of 4-chloro-2-nitrobenzoic acid–quinolin-4(1*H*)-one (1/1) and 4-hydroxyquinolinium 4-chloro-2-nitrobenzoate

Kazuma Gotoh and Hiroyuki Ishida

Computing details

Data collection: *PROCESS-AUTO* (Rigaku, 2006); cell refinement: *PROCESS-AUTO* (Rigaku, 2006); data reduction: *PROCESS-AUTO* (Rigaku, 2006); program(s) used to solve structure: *SHELXT2018* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015b); molecular graphics: *ORTEP-3 for Windows* and *WinGX* (Farrugia, 2012); *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *CrystalStructure* (Rigaku, 2018) and *PLATON* (Spek, 2015).

4-Chloro-2-nitrobenzoic acid–quinolin-4(1*H*)-one (1/1)–4-hydroxyquinolinium 4-chloro-2-nitrobenzoate

Crystal data

$C_7H_{3.5}ClNO_4 \cdot C_9H_{7.5}NO$

$M_r = 346.73$

Orthorhombic, *Pbcn*

$a = 12.6336$ (8) Å

$b = 7.0701$ (3) Å

$c = 33.5956$ (15) Å

$V = 3000.8$ (3) Å³

$Z = 8$

$F(000) = 1424.00$

$D_x = 1.535$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71075$ Å

Cell parameters from 23445 reflections

$\theta = 3.0$ – 30.2°

$\mu = 0.28$ mm⁻¹

$T = 190$ K

Platelet, colorless

$0.35 \times 0.28 \times 0.09$ mm

Data collection

Rigaku R-AXIS RAPIDII
diffractometer

Detector resolution: 10.000 pixels mm⁻¹

ω scans

Absorption correction: numerical
(*NUMABS*; Higashi, 1999)

$T_{\min} = 0.939$, $T_{\max} = 0.975$

36709 measured reflections

4380 independent reflections

3235 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.052$

$\theta_{\max} = 30.0^\circ$, $\theta_{\min} = 3.2^\circ$

$h = -17 \rightarrow 17$

$k = -9 \rightarrow 9$

$l = -47 \rightarrow 47$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.046$

$wR(F^2) = 0.136$

$S = 1.13$

4380 reflections

227 parameters

2 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
 $w = 1/[\sigma^2(F_o^2) + (0.0641P)^2 + 0.6358P]$
where $P = (F_o^2 + 2F_c^2)/3$

$$\begin{aligned}(\Delta/\sigma)_{\max} &= 0.002 \\ \Delta\rho_{\max} &= 0.39 \text{ e } \text{\AA}^{-3} \\ \Delta\rho_{\min} &= -0.42 \text{ e } \text{\AA}^{-3}\end{aligned}$$

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
C11	0.14687 (4)	0.53104 (8)	0.76188 (2)	0.05607 (17)	
O1	0.32791 (10)	0.20128 (19)	0.58896 (3)	0.0439 (3)	
H1A	0.351 (4)	0.185 (8)	0.5658 (6)	0.066*	0.5
O2	0.44512 (9)	0.43255 (18)	0.60030 (3)	0.0423 (3)	
O3	0.52878 (10)	0.26978 (19)	0.67248 (4)	0.0497 (3)	
O4	0.53263 (11)	0.5533 (2)	0.69656 (5)	0.0636 (4)	
O5	0.37717 (9)	0.15689 (18)	0.51938 (3)	0.0376 (3)	
H1B	0.356 (3)	0.177 (7)	0.5427 (6)	0.056*	0.5
N1	0.48587 (11)	0.4153 (2)	0.68364 (4)	0.0404 (3)	
N2	0.11801 (11)	0.1179 (2)	0.44816 (4)	0.0379 (3)	
C1	0.31559 (12)	0.3666 (2)	0.64897 (4)	0.0318 (3)	
C2	0.37014 (12)	0.4213 (2)	0.68293 (4)	0.0333 (3)	
C3	0.32058 (13)	0.4729 (2)	0.71785 (5)	0.0373 (3)	
H3	0.360145	0.511101	0.740510	0.045*	
C4	0.21176 (14)	0.4671 (2)	0.71868 (5)	0.0377 (4)	
C5	0.15375 (13)	0.4103 (2)	0.68590 (5)	0.0389 (4)	
H5	0.078678	0.405323	0.687096	0.047*	
C6	0.20643 (12)	0.3610 (2)	0.65135 (4)	0.0345 (3)	
H6	0.166717	0.322352	0.628754	0.041*	
C7	0.36954 (12)	0.3319 (2)	0.60966 (4)	0.0334 (3)	
C8	0.10616 (13)	0.1492 (2)	0.48692 (5)	0.0381 (3)	
H8	0.036732	0.163593	0.497354	0.046*	
C9	0.19038 (13)	0.1612 (2)	0.51224 (5)	0.0357 (3)	
H9	0.179065	0.181221	0.539873	0.043*	
C10	0.29314 (11)	0.1441 (2)	0.49744 (4)	0.0306 (3)	
C11	0.30605 (12)	0.1122 (2)	0.45544 (4)	0.0306 (3)	
C12	0.40628 (13)	0.0928 (2)	0.43769 (5)	0.0385 (4)	
H12	0.468363	0.099954	0.453575	0.046*	
C13	0.41438 (16)	0.0636 (3)	0.39760 (5)	0.0492 (4)	
H13	0.482176	0.050157	0.385705	0.059*	
C14	0.32353 (17)	0.0534 (3)	0.37403 (5)	0.0533 (5)	
H14	0.330455	0.035088	0.346139	0.064*	
C15	0.22572 (16)	0.0693 (3)	0.39020 (5)	0.0459 (4)	
H15	0.164531	0.059820	0.373885	0.055*	
C16	0.21571 (12)	0.0997 (2)	0.43129 (4)	0.0331 (3)	

H2 0.0611 (18) 0.107 (3) 0.4325 (6) 0.052 (6)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.0601 (3)	0.0749 (3)	0.0332 (2)	0.0104 (2)	0.01812 (19)	0.00122 (19)
O1	0.0488 (7)	0.0572 (7)	0.0257 (5)	-0.0068 (6)	0.0010 (5)	-0.0078 (5)
O2	0.0363 (6)	0.0585 (7)	0.0321 (5)	-0.0033 (5)	0.0060 (5)	-0.0043 (5)
O3	0.0385 (7)	0.0637 (8)	0.0468 (7)	0.0164 (6)	0.0004 (5)	0.0024 (6)
O4	0.0434 (8)	0.0792 (10)	0.0681 (9)	-0.0088 (7)	-0.0108 (7)	-0.0217 (8)
O5	0.0290 (5)	0.0565 (7)	0.0273 (5)	0.0005 (5)	-0.0025 (4)	-0.0066 (5)
N1	0.0338 (7)	0.0594 (8)	0.0282 (6)	0.0038 (6)	-0.0041 (5)	-0.0013 (6)
N2	0.0314 (7)	0.0430 (7)	0.0391 (7)	0.0016 (6)	-0.0090 (6)	-0.0023 (6)
C1	0.0325 (7)	0.0384 (8)	0.0245 (6)	0.0037 (6)	-0.0003 (5)	0.0010 (6)
C2	0.0313 (7)	0.0415 (8)	0.0271 (7)	0.0038 (6)	-0.0007 (5)	0.0011 (6)
C3	0.0424 (9)	0.0437 (8)	0.0257 (7)	0.0029 (7)	0.0007 (6)	-0.0008 (6)
C4	0.0429 (9)	0.0421 (8)	0.0281 (7)	0.0061 (7)	0.0093 (6)	0.0020 (6)
C5	0.0317 (8)	0.0484 (9)	0.0366 (8)	0.0036 (7)	0.0045 (6)	0.0062 (7)
C6	0.0315 (8)	0.0424 (8)	0.0297 (7)	0.0019 (6)	-0.0004 (6)	0.0028 (6)
C7	0.0307 (7)	0.0447 (8)	0.0247 (6)	0.0055 (6)	-0.0020 (5)	0.0011 (6)
C8	0.0294 (8)	0.0433 (8)	0.0417 (8)	0.0011 (6)	0.0014 (6)	0.0002 (7)
C9	0.0323 (8)	0.0443 (8)	0.0305 (7)	0.0008 (6)	0.0027 (6)	-0.0010 (6)
C10	0.0298 (7)	0.0337 (7)	0.0282 (7)	-0.0004 (6)	-0.0010 (5)	-0.0004 (6)
C11	0.0321 (7)	0.0320 (7)	0.0277 (7)	0.0004 (6)	-0.0008 (5)	-0.0002 (6)
C12	0.0345 (8)	0.0485 (9)	0.0326 (7)	0.0000 (7)	0.0011 (6)	-0.0042 (7)
C13	0.0492 (10)	0.0633 (11)	0.0350 (8)	0.0040 (9)	0.0094 (7)	-0.0065 (8)
C14	0.0653 (13)	0.0669 (13)	0.0279 (8)	0.0087 (10)	0.0002 (8)	-0.0072 (8)
C15	0.0550 (11)	0.0523 (10)	0.0304 (7)	0.0077 (8)	-0.0124 (7)	-0.0048 (7)
C16	0.0365 (8)	0.0318 (7)	0.0311 (7)	0.0018 (6)	-0.0042 (6)	-0.0016 (6)

Geometric parameters (Å, °)

C11—C4	1.7271 (16)	C5—C6	1.383 (2)
O1—C7	1.270 (2)	C5—H5	0.9500
O1—H1A	0.841 (10)	C6—H6	0.9500
O2—C7	1.2317 (19)	C8—C9	1.365 (2)
O3—N1	1.2218 (19)	C8—H8	0.9500
O4—N1	1.220 (2)	C9—C10	1.395 (2)
O5—C10	1.2956 (18)	C9—H9	0.9500
O5—H1B	0.841 (10)	C10—C11	1.438 (2)
N1—C2	1.463 (2)	C11—C16	1.403 (2)
N2—C8	1.329 (2)	C11—C12	1.406 (2)
N2—C16	1.364 (2)	C12—C13	1.366 (2)
N2—H2	0.90 (2)	C12—H12	0.9500
C1—C6	1.382 (2)	C13—C14	1.396 (3)
C1—C2	1.388 (2)	C13—H13	0.9500
C1—C7	1.506 (2)	C14—C15	1.355 (3)
C2—C3	1.379 (2)	C14—H14	0.9500

C3—C4	1.376 (2)	C15—C16	1.403 (2)
C3—H3	0.9500	C15—H15	0.9500
C4—C5	1.382 (2)		
C7—O1—H1A	117 (4)	O1—C7—C1	114.27 (14)
C10—O5—H1B	106 (3)	N2—C8—C9	122.21 (15)
O4—N1—O3	124.57 (15)	N2—C8—H8	118.9
O4—N1—C2	117.80 (14)	C9—C8—H8	118.9
O3—N1—C2	117.58 (14)	C8—C9—C10	119.87 (14)
C8—N2—C16	121.64 (14)	C8—C9—H9	120.1
C8—N2—H2	120.1 (14)	C10—C9—H9	120.1
C16—N2—H2	118.3 (14)	O5—C10—C9	123.62 (14)
C6—C1—C2	117.13 (14)	O5—C10—C11	118.44 (13)
C6—C1—C7	119.84 (13)	C9—C10—C11	117.94 (13)
C2—C1—C7	122.78 (14)	C16—C11—C12	118.77 (14)
C3—C2—C1	123.20 (15)	C16—C11—C10	119.00 (13)
C3—C2—N1	116.59 (14)	C12—C11—C10	122.23 (13)
C1—C2—N1	120.11 (13)	C13—C12—C11	120.00 (16)
C4—C3—C2	117.59 (15)	C13—C12—H12	120.0
C4—C3—H3	121.2	C11—C12—H12	120.0
C2—C3—H3	121.2	C12—C13—C14	120.35 (17)
C3—C4—C5	121.49 (15)	C12—C13—H13	119.8
C3—C4—C11	118.92 (13)	C14—C13—H13	119.8
C5—C4—C11	119.59 (13)	C15—C14—C13	121.21 (16)
C4—C5—C6	119.13 (15)	C15—C14—H14	119.4
C4—C5—H5	120.4	C13—C14—H14	119.4
C6—C5—H5	120.4	C14—C15—C16	119.31 (16)
C1—C6—C5	121.44 (15)	C14—C15—H15	120.3
C1—C6—H6	119.3	C16—C15—H15	120.3
C5—C6—H6	119.3	N2—C16—C15	120.32 (15)
O2—C7—O1	126.98 (14)	N2—C16—C11	119.34 (14)
O2—C7—C1	118.71 (14)	C15—C16—C11	120.34 (15)
C6—C1—C2—C3	-1.4 (2)	C16—N2—C8—C9	-1.3 (3)
C7—C1—C2—C3	172.84 (15)	N2—C8—C9—C10	1.2 (3)
C6—C1—C2—N1	174.88 (14)	C8—C9—C10—O5	178.85 (15)
C7—C1—C2—N1	-10.9 (2)	C8—C9—C10—C11	-0.5 (2)
O4—N1—C2—C3	-50.5 (2)	O5—C10—C11—C16	-179.45 (14)
O3—N1—C2—C3	127.10 (16)	C9—C10—C11—C16	0.0 (2)
O4—N1—C2—C1	132.98 (17)	O5—C10—C11—C12	0.7 (2)
O3—N1—C2—C1	-49.4 (2)	C9—C10—C11—C12	-179.91 (15)
C1—C2—C3—C4	0.7 (2)	C16—C11—C12—C13	0.4 (2)
N1—C2—C3—C4	-175.67 (14)	C10—C11—C12—C13	-179.68 (16)
C2—C3—C4—C5	0.5 (2)	C11—C12—C13—C14	0.2 (3)
C2—C3—C4—C11	-179.91 (13)	C12—C13—C14—C15	-1.0 (3)
C3—C4—C5—C6	-0.9 (3)	C13—C14—C15—C16	1.1 (3)
C11—C4—C5—C6	179.46 (13)	C8—N2—C16—C15	-179.16 (16)
C2—C1—C6—C5	0.9 (2)	C8—N2—C16—C11	0.7 (2)

C7—C1—C6—C5	-173.51 (15)	C14—C15—C16—N2	179.37 (17)
C4—C5—C6—C1	0.2 (3)	C14—C15—C16—C11	-0.5 (3)
C6—C1—C7—O2	138.07 (16)	C12—C11—C16—N2	179.85 (14)
C2—C1—C7—O2	-36.0 (2)	C10—C11—C16—N2	0.0 (2)
C6—C1—C7—O1	-39.9 (2)	C12—C11—C16—C15	-0.3 (2)
C2—C1—C7—O1	146.07 (15)	C10—C11—C16—C15	179.82 (15)

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
O1—H1A...O5	0.84 (3)	1.61 (2)	2.4393 (15)	172 (5)
O5—H1B...O1	0.84 (2)	1.60 (2)	2.4393 (15)	173 (4)
N2—H2...O2 ⁱ	0.89 (2)	1.86 (2)	2.7475 (18)	176 (2)
C3—H3...O4 ⁱⁱ	0.95	2.53	3.469 (2)	170
C8—H8...O5 ⁱ	0.95	2.45	3.208 (2)	137
C9—H9...O1	0.95	2.51	3.121 (2)	123

Symmetry codes: (i) $x-1/2, -y+1/2, -z+1$; (ii) $-x+1, y, -z+3/2$.