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(Pyridin-2-yl)methyl 2-oxo-1-[(pyridin-2-yl)methyl]-1,2-dihydroquinoline-4-carboxylate hemihydrate

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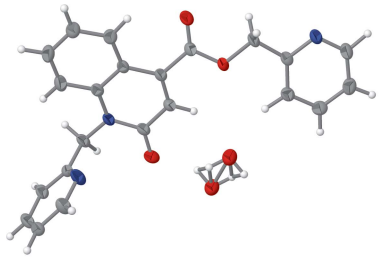
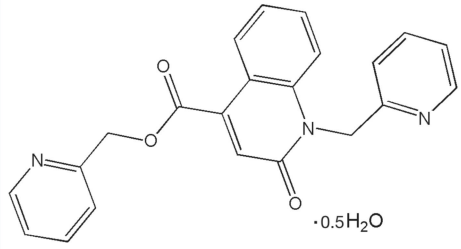
In the title compound, $C_{22}H_{17}N_3O_3\cdot0.5H_2O$, the heterocyclic portion of the dihydroquinoline moiety is distinctly nonplanar. Two quinolinecarboxylate molecules are associated through hydrogen bonding to a disordered lattice water molecule. These units stack along the *a*-axis direction assisted by C—H···O and C—H···N hydrogen bonds, as well as C—H···π(ring) interactions.

3D view



Chemical scheme



Structure description

Quinoline and its derivatives have aroused great attention in recent years due to the wide variety of their biological activities, relevant to applications as anticancer agents (Elderfield & Le Von, 1960), HIV protease inhibitors (Garrouste *et al.*, 1998) and antileishmanial agents (Desrivot *et al.*, 2007). As a continuation of our research work devoted to the development of substituted quinoline derivatives (Filali Baba *et al.*, 2016), we report here the synthesis of (pyridin-2-yl)methyl 2-oxo-1-[(pyridin-2-yl)methyl]-1,2-dihydroquinoline-4-carboxylate hemihydrate by the reaction of 2-oxo-1,2-dihydroquinoline-4-carboxylic acid with 2-(bromomethyl)pyridine hydrobromide under phase-transfer catalysis conditions using tetra-*n*-butylammonium bromide (TBAB) as catalyst and potassium carbonate as base.

In the title molecule (Fig. 1), the N1/C1/C6–C9 ring deviates from planarity by between 0.0464 (13) (for atom C9) and −0.0498 (12) Å (N1), with an r.m.s. deviation from the mean plane of 0.0329 Å. The dihedral angles between this plane and those of the C1–C6 and N3/C18–C22 rings are 3.2 (1) and 88.54 (4)°, respectively. The C7/C10/O1/O2 unit is twisted out of the mean plane of the N1/C1/C6–C9 ring by 11.8 (1)°, while the dihedral angle between this plane and the N2/C12–C16 ring is 18.1 (1)°. In the crystal, two molecules are connected by a disordered lattice water molecule through O4—H4*A*···O3 and O4—H4*B*···O3^{ii} hydrogen bonds, as well as by weaker C—H···O interactions (Table 1

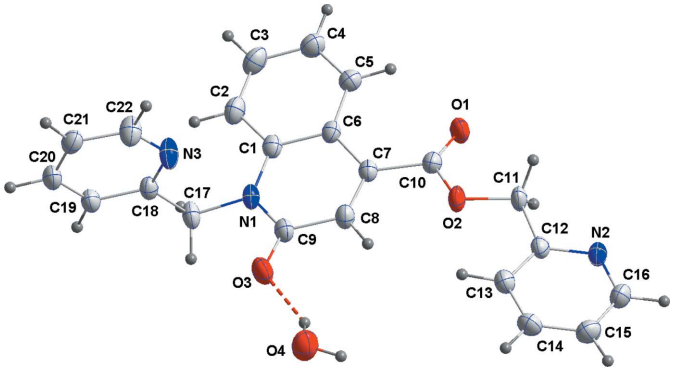


Figure 1
The title molecule, showing the atom-labelling scheme and 50% probability displacement ellipsoids. Only one orientation of the disordered water molecule is shown and its hydrogen bonding to the main molcule is designated by a dashed line.

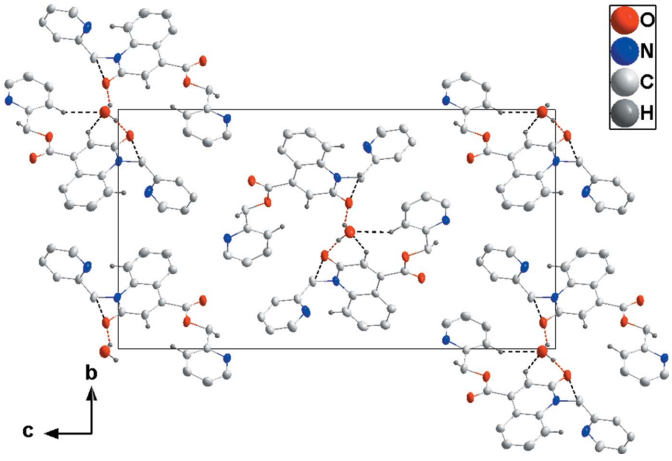


Figure 3
The packing of the title compound, viewed along the *a*-axis direction, with hydrogen bonds depicted as in Fig. 2.

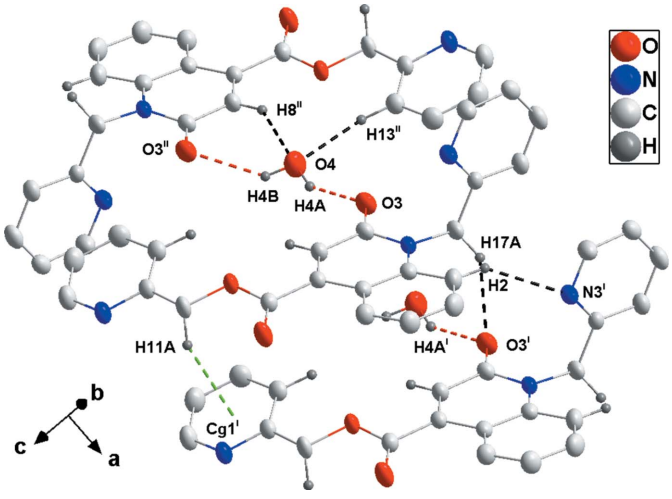


Figure 2
Detail of the intermolecular interactions projected onto (011). O—H···O hydrogen bonds are indicated by red dashed lines, C—H···O and C—H···N hydrogen bonds by black dashed lines, and the C—H···π(ring) interaction by a green dashed line. [Symmetry codes: (i) $x+1, y, z$; (ii) $-x, -y+1, -z+1$.]

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

*Cg*1 is the centroid of the C12–C16/N2 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···N3^{i}	0.98 (3)	2.50 (3)	3.344 (3)	145 (2)
O4—H4*A*···O3	0.87	1.87	2.647 (4)	147
O4—H4*B*···O3^{ii}	0.87	2.26	2.989 (4)	141
C8—H8···O4^{ii}	0.97 (2)	2.28 (2)	3.113 (4)	143.7 (17)
C13—H13···O4^{ii}	1.00 (2)	2.44 (2)	3.345 (4)	149.3 (19)
C17—H17*A*···O3^{i}	1.00 (2)	2.57 (2)	3.307 (3)	130.4 (16)
C11—H11*A*···*Cg*1^{i}	1.02 (2)	2.85 (2)	3.673 (2)	137.9 (15)

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

and Fig. 2). These units stack along the *a*-axis direction assisted by C17—H17*A*···O3^{i} and C2—H2···N3^{i} hydrogen bonds, and C11—H11*A*···*Cg*1^{i} interactions (*Cg*1 is the centroid of the C12–C16/N2 ring) (Table 1 and Figs. 2 and 3).

Synthesis and crystallization

A solution of 0.5 g (2.64 mmol) of 2-oxo-1,2-dihydroquinoline-4-carboxylic acid in 10 ml dimethylformamide (DMF) was mixed with 1.47 g (5.82 mmol) of 2-(bromomethyl)pyridine hydrobromide, 1.09 g (7.92 mmol) of K_2CO_3 and 0.17 g (0.52 mmol) of TBAB. The reaction mixture was stirred at room temperature in DMF for 6 h. After removal of the

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{22}H_{17}N_3O_3{\cdot}0.5H_2O$
M_r	380.40
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	150
a, *b*, *c* (Å)	4.9634 (1), 14.0708 (3), 25.7168 (6)
β (°)	90.602 (1)
V (Å^3)	1795.94 (7)
Z	4
Radiation type	Cu $K\alpha$
μ (mm^{-1})	0.80
Crystal size (mm)	0.16 × 0.10 × 0.01
Data collection	
Diffractometer	Bruker D8 VENTURE PHOTON 100 CMOS
Absorption correction	Multi-scan (*SADABS*; Bruker, 2016)
T_{min}, T_{max}	0.86, 0.99
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	13518, 3502, 2673
R_{int}	0.052
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.618
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.047, 0.106, 1.04
No. of reflections	3502
No. of parameters	330
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.18, −0.21

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *DIAMOND* (Brandenburg & Putz, 2012) and *SHELXTL* (Sheldrick, 2008).

salts by filtration, the DMF was evaporated under reduced pressure and the residue obtained was dissolved in dichloromethane. The organic phase was dried over Na_2SO_4 and then concentrated *in vacuo*. The resulting mixture was chromatographed on a silica-gel column (eluent: ethyl acetate–hexane 1:3 *v*/*v*). The product was obtained in 85% yield and was crystallized by slow evaporation from an ethanol solution.

Refinement

Crystal and refinement details are presented in Table 2. The lattice water molecule is disordered about the centre of symmetry at $(0, \frac{1}{2}, \frac{1}{2})$.

Acknowledgements

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full crystallographic data

IUCrData (2017). **2**, x171038 [https://doi.org/10.1107/S2414314617010380]

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Crystal data

$C_{22}H_{17}N_3O_3·0.5H_2O$
M_r = 380.40
Monoclinic, $P2_1/c$
a = 4.9634 (1) Å
b = 14.0708 (3) Å
c = 25.7168 (6) Å
β = 90.602 (1)°
V = 1795.94 (7) Å^3
Z = 4
$F(000)$ = 796
D_x = 1.407 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54178 Å
Cell parameters from 7827 reflections
θ = 3.4–72.4°
μ = 0.80 mm^{-1}
T = 150 K
Plate, colourless
0.16 × 0.10 × 0.01 mm

Data collection

Bruker D8 VENTURE PHOTON 100 CMOS diffractometer
Radiation source: INCOATEC IμS micro-focus source
Mirror monochromator
Detector resolution: 10.4167 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2016)
T_{min} = 0.86, T_{max} = 0.99
13518 measured reflections
3502 independent reflections
2673 reflections with $I > 2\sigma(I)$
R_{int} = 0.052
θ_{max} = 72.4°, θ_{min} = 3.4°
h = −6→5
k = −15→17
l = −31→30

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.106
S = 1.04
3502 reflections
330 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
$w = 1/[\sigma^2(F_o^2) + (0.031P)^2 + 0.9731P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

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. The lattice water molecule is disordered about the centre of symmetry at 0,1/2,1/2. The associated hydrogen atoms were included as riding contributions with idealized geometry.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
O1	0.6090 (3)	0.70283 (11)	0.69423 (5)	0.0385 (4)	
O2	0.2853 (3)	0.61435 (10)	0.65746 (5)	0.0306 (3)	
O3	0.4227 (3)	0.61004 (11)	0.47233 (5)	0.0378 (4)	
N1	0.7442 (3)	0.71558 (11)	0.49832 (6)	0.0268 (3)	
N2	−0.0427 (3)	0.46214 (12)	0.74963 (6)	0.0317 (4)	
N3	0.5118 (3)	0.84261 (13)	0.42986 (6)	0.0376 (4)	
C1	0.8541 (4)	0.77580 (13)	0.53640 (7)	0.0262 (4)	
C2	1.0459 (4)	0.84395 (15)	0.52284 (8)	0.0355 (5)	
H2	1.108 (5)	0.8472 (18)	0.4868 (10)	0.054 (7)*	
C3	1.1542 (4)	0.90375 (16)	0.55987 (9)	0.0399 (5)	
H3	1.288 (5)	0.9520 (18)	0.5494 (9)	0.050 (7)*	
C4	1.0711 (4)	0.89791 (15)	0.61121 (9)	0.0368 (5)	
H4	1.143 (5)	0.9417 (17)	0.6375 (9)	0.046 (7)*	
C5	0.8819 (4)	0.83122 (14)	0.62528 (8)	0.0310 (4)	
H5	0.833 (5)	0.8278 (16)	0.6618 (9)	0.039 (6)*	
C6	0.7705 (4)	0.76796 (13)	0.58865 (7)	0.0244 (4)	
C7	0.5721 (4)	0.69590 (13)	0.60066 (7)	0.0242 (4)	
C8	0.4610 (4)	0.64377 (14)	0.56205 (7)	0.0285 (4)	
H8	0.328 (4)	0.5950 (15)	0.5682 (8)	0.035 (6)*	
C9	0.5352 (4)	0.65462 (14)	0.50801 (7)	0.0279 (4)	
C10	0.4961 (4)	0.67449 (13)	0.65563 (7)	0.0259 (4)	
C11	0.2171 (4)	0.58148 (15)	0.70873 (7)	0.0307 (4)	
H11A	0.387 (5)	0.5565 (15)	0.7270 (8)	0.036 (6)*	
H11B	0.142 (4)	0.6371 (16)	0.7294 (8)	0.037 (6)*	
C12	0.0124 (4)	0.50362 (13)	0.70393 (7)	0.0263 (4)	
C13	−0.1113 (4)	0.47750 (14)	0.65748 (7)	0.0302 (4)	
H13	−0.060 (5)	0.5114 (17)	0.6247 (9)	0.047 (7)*	
C14	−0.3031 (4)	0.40591 (15)	0.65822 (8)	0.0358 (5)	
H14	−0.389 (5)	0.3878 (18)	0.6266 (10)	0.057 (8)*	
C15	−0.3632 (5)	0.36315 (16)	0.70488 (9)	0.0389 (5)	
H15	−0.496 (5)	0.3130 (19)	0.7073 (10)	0.057 (8)*	
C16	−0.2284 (4)	0.39295 (15)	0.74904 (8)	0.0361 (5)	
H16	−0.259 (5)	0.3606 (17)	0.7842 (9)	0.046 (7)*	
C17	0.8454 (4)	0.71720 (16)	0.44491 (7)	0.0313 (4)	

H17A	1.045 (5)	0.7265 (16)	0.4468 (8)	0.041 (6)*	
H17B	0.804 (4)	0.6514 (16)	0.4298 (8)	0.033 (6)*	
C18	0.7117 (4)	0.79080 (13)	0.41056 (7)	0.0252 (4)	
C19	0.7988 (4)	0.80085 (14)	0.35978 (7)	0.0304 (4)	
H19	0.951 (5)	0.7607 (17)	0.3464 (9)	0.045 (7)*	
C20	0.6714 (5)	0.86600 (15)	0.32762 (8)	0.0355 (5)	
H20	0.728 (5)	0.8726 (17)	0.2904 (10)	0.050 (7)*	
C21	0.4628 (4)	0.92012 (14)	0.34694 (8)	0.0317 (4)	
H21	0.365 (5)	0.9702 (17)	0.3254 (9)	0.045 (6)*	
C22	0.3924 (4)	0.90607 (17)	0.39807 (8)	0.0387 (5)	
H22	0.246 (5)	0.9434 (18)	0.4128 (10)	0.056 (7)*	
O4	0.0130 (7)	0.4897 (2)	0.46975 (12)	0.0499 (8)	0.5
H4A	0.1557	0.5180	0.4821	0.060*	0.5
H4B	−0.0416	0.4545	0.4954	0.060*	0.5

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0519 (9)	0.0436 (9)	0.0201 (7)	−0.0178 (7)	0.0006 (6)	−0.0004 (6)
O2	0.0314 (7)	0.0403 (8)	0.0200 (6)	−0.0096 (6)	0.0027 (5)	0.0058 (5)
O3	0.0441 (9)	0.0476 (9)	0.0217 (7)	−0.0048 (7)	−0.0019 (6)	−0.0015 (6)
N1	0.0263 (8)	0.0349 (9)	0.0194 (7)	0.0016 (6)	0.0035 (6)	0.0056 (6)
N2	0.0383 (10)	0.0337 (9)	0.0232 (8)	−0.0068 (7)	0.0044 (7)	0.0033 (7)
N3	0.0335 (9)	0.0522 (11)	0.0274 (9)	0.0121 (8)	0.0095 (7)	0.0120 (8)
C1	0.0251 (9)	0.0290 (10)	0.0245 (9)	0.0037 (7)	0.0018 (7)	0.0043 (7)
C2	0.0334 (11)	0.0394 (12)	0.0338 (11)	−0.0026 (9)	0.0078 (8)	0.0079 (9)
C3	0.0364 (12)	0.0376 (12)	0.0459 (13)	−0.0099 (9)	0.0035 (9)	0.0098 (10)
C4	0.0395 (12)	0.0330 (11)	0.0378 (11)	−0.0087 (9)	0.0000 (9)	0.0017 (9)
C5	0.0343 (11)	0.0284 (10)	0.0303 (10)	−0.0034 (8)	0.0016 (8)	0.0002 (8)
C6	0.0248 (10)	0.0246 (9)	0.0239 (9)	0.0019 (7)	0.0016 (7)	0.0049 (7)
C7	0.0247 (9)	0.0269 (9)	0.0211 (9)	0.0019 (7)	0.0022 (7)	0.0028 (7)
C8	0.0288 (10)	0.0344 (11)	0.0222 (9)	−0.0031 (8)	0.0012 (7)	0.0041 (8)
C9	0.0311 (10)	0.0319 (10)	0.0208 (9)	0.0011 (8)	−0.0001 (7)	0.0029 (8)
C10	0.0289 (10)	0.0252 (9)	0.0237 (9)	−0.0018 (7)	0.0031 (7)	0.0015 (7)
C11	0.0377 (12)	0.0364 (11)	0.0180 (9)	−0.0070 (9)	0.0058 (8)	0.0039 (8)
C12	0.0294 (10)	0.0286 (10)	0.0210 (9)	0.0011 (7)	0.0055 (7)	0.0010 (7)
C13	0.0332 (11)	0.0330 (11)	0.0245 (10)	−0.0002 (8)	0.0035 (8)	−0.0008 (8)
C14	0.0415 (12)	0.0362 (12)	0.0296 (11)	−0.0047 (9)	−0.0021 (9)	−0.0059 (9)
C15	0.0428 (13)	0.0331 (12)	0.0410 (12)	−0.0107 (9)	0.0045 (9)	−0.0018 (9)
C16	0.0444 (12)	0.0332 (11)	0.0309 (11)	−0.0086 (9)	0.0066 (9)	0.0039 (9)
C17	0.0323 (11)	0.0425 (12)	0.0194 (9)	0.0044 (9)	0.0050 (8)	0.0056 (8)
C18	0.0232 (9)	0.0315 (10)	0.0210 (9)	−0.0044 (7)	0.0011 (7)	0.0027 (7)
C19	0.0357 (11)	0.0334 (11)	0.0224 (9)	−0.0029 (8)	0.0054 (8)	0.0001 (8)
C20	0.0495 (13)	0.0355 (11)	0.0215 (9)	−0.0054 (9)	0.0040 (8)	0.0029 (8)
C21	0.0353 (11)	0.0309 (11)	0.0288 (10)	−0.0049 (8)	−0.0026 (8)	0.0057 (8)
C22	0.0348 (12)	0.0475 (13)	0.0339 (11)	0.0085 (10)	0.0054 (9)	0.0108 (10)
O4	0.050 (2)	0.057 (2)	0.0420 (18)	−0.0207 (16)	−0.0022 (15)	0.0030 (15)

Geometric parameters (Å, º)

O1—C10	1.203 (2)	C11—C12	1.498 (3)
O2—C10	1.347 (2)	C11—H11A	1.02 (2)
O2—C11	1.441 (2)	C11—H11B	1.02 (2)
O3—C9	1.240 (2)	C12—C13	1.387 (3)
N1—C9	1.371 (2)	C13—C14	1.386 (3)
N1—C1	1.401 (2)	C13—H13	1.01 (2)
N1—C17	1.468 (2)	C14—C15	1.378 (3)
N2—C16	1.341 (3)	C14—H14	0.95 (3)
N2—C12	1.343 (2)	C15—C16	1.377 (3)
N3—C18	1.331 (2)	C15—H15	0.97 (3)
N3—C22	1.344 (3)	C16—H16	1.03 (2)
C1—C2	1.398 (3)	C17—C18	1.510 (3)
C1—C6	1.415 (2)	C17—H17A	1.00 (2)
C2—C3	1.376 (3)	C17—H17B	1.02 (2)
C2—H2	0.98 (3)	C18—C19	1.387 (2)
C3—C4	1.390 (3)	C19—C20	1.383 (3)
C3—H3	0.99 (3)	C19—H19	1.01 (2)
C4—C5	1.379 (3)	C20—C21	1.382 (3)
C4—H4	0.98 (2)	C20—H20	1.00 (2)
C5—C6	1.405 (3)	C21—C22	1.378 (3)
C5—H5	0.97 (2)	C21—H21	1.02 (2)
C6—C7	1.449 (2)	C22—H22	0.98 (3)
C7—C8	1.348 (3)	O4—O4^{i}	1.589 (6)
C7—C10	1.498 (2)	O4—H4A	0.8701
C8—C9	1.450 (2)	O4—H4B	0.8700
C8—H8	0.97 (2)		
C10—O2—C11	115.06 (14)	H11A—C11—H11B	109.2 (17)
C9—N1—C1	122.76 (15)	N2—C12—C13	123.09 (18)
C9—N1—C17	116.55 (16)	N2—C12—C11	112.95 (16)
C1—N1—C17	120.67 (16)	C13—C12—C11	123.96 (16)
C16—N2—C12	116.89 (17)	C14—C13—C12	118.61 (18)
C18—N3—C22	117.55 (17)	C14—C13—H13	122.5 (14)
C2—C1—N1	120.11 (17)	C12—C13—H13	118.8 (14)
C2—C1—C6	119.83 (18)	C15—C14—C13	118.95 (19)
N1—C1—C6	120.06 (16)	C15—C14—H14	122.0 (16)
C3—C2—C1	120.60 (19)	C13—C14—H14	119.1 (16)
C3—C2—H2	120.1 (15)	C16—C15—C14	118.5 (2)
C1—C2—H2	119.2 (15)	C16—C15—H15	119.6 (15)
C2—C3—C4	120.2 (2)	C14—C15—H15	121.8 (15)
C2—C3—H3	119.4 (14)	N2—C16—C15	123.93 (19)
C4—C3—H3	120.4 (14)	N2—C16—H16	114.8 (13)
C5—C4—C3	120.0 (2)	C15—C16—H16	121.2 (14)
C5—C4—H4	119.4 (15)	N1—C17—C18	113.91 (16)
C3—C4—H4	120.7 (15)	N1—C17—H17A	107.7 (13)
C4—C5—C6	121.29 (19)	C18—C17—H17A	111.6 (13)

C4—C5—H5	117.7 (14)	N1—C17—H17B	105.7 (12)
C6—C5—H5	121.0 (14)	C18—C17—H17B	108.3 (12)
C5—C6—C1	118.06 (17)	H17A—C17—H17B	109.3 (18)
C5—C6—C7	124.32 (17)	N3—C18—C19	122.41 (18)
C1—C6—C7	117.62 (16)	N3—C18—C17	118.83 (16)
C8—C7—C6	119.84 (17)	C19—C18—C17	118.76 (17)
C8—C7—C10	118.73 (17)	C20—C19—C18	119.05 (19)
C6—C7—C10	121.36 (16)	C20—C19—H19	120.5 (13)
C7—C8—C9	122.87 (18)	C18—C19—H19	120.4 (13)
C7—C8—H8	122.7 (13)	C21—C20—C19	119.32 (18)
C9—C8—H8	114.4 (13)	C21—C20—H20	120.6 (14)
O3—C9—N1	121.20 (17)	C19—C20—H20	120.0 (14)
O3—C9—C8	122.63 (18)	C22—C21—C20	117.54 (19)
N1—C9—C8	116.14 (16)	C22—C21—H21	119.6 (13)
O1—C10—O2	122.33 (16)	C20—C21—H21	122.8 (13)
O1—C10—C7	126.34 (17)	N3—C22—C21	124.1 (2)
O2—C10—C7	111.27 (15)	N3—C22—H22	116.5 (15)
O2—C11—C12	108.95 (15)	C21—C22—H22	119.4 (15)
O2—C11—H11A	109.3 (13)	O4^{i}—O4—H4A	68.4
C12—C11—H11A	109.9 (12)	O4^{i}—O4—H4B	48.2
O2—C11—H11B	108.8 (13)	H4A—O4—H4B	104.0
C12—C11—H11B	110.6 (13)		

C9—N1—C1—C2	−172.75 (18)	C11—O2—C10—C7	173.42 (16)
C17—N1—C1—C2	5.5 (3)	C8—C7—C10—O1	166.6 (2)
C9—N1—C1—C6	7.1 (3)	C6—C7—C10—O1	−10.5 (3)
C17—N1—C1—C6	−174.69 (17)	C8—C7—C10—O2	−10.8 (2)
N1—C1—C2—C3	179.69 (19)	C6—C7—C10—O2	172.11 (16)
C6—C1—C2—C3	−0.1 (3)	C10—O2—C11—C12	−170.60 (16)
C1—C2—C3—C4	−0.9 (3)	C16—N2—C12—C13	−0.5 (3)
C2—C3—C4—C5	0.8 (3)	C16—N2—C12—C11	178.63 (18)
C3—C4—C5—C6	0.3 (3)	O2—C11—C12—N2	173.67 (16)
C4—C5—C6—C1	−1.3 (3)	O2—C11—C12—C13	−7.2 (3)
C4—C5—C6—C7	179.69 (19)	N2—C12—C13—C14	0.7 (3)
C2—C1—C6—C5	1.2 (3)	C11—C12—C13—C14	−178.30 (19)
N1—C1—C6—C5	−178.64 (17)	C12—C13—C14—C15	−0.2 (3)
C2—C1—C6—C7	−179.73 (17)	C13—C14—C15—C16	−0.4 (3)
N1—C1—C6—C7	0.4 (3)	C12—N2—C16—C15	−0.2 (3)
C5—C6—C7—C8	174.55 (19)	C14—C15—C16—N2	0.7 (4)
C1—C6—C7—C8	−4.5 (3)	C9—N1—C17—C18	91.8 (2)
C5—C6—C7—C10	−8.4 (3)	C1—N1—C17—C18	−86.6 (2)
C1—C6—C7—C10	172.59 (16)	C22—N3—C18—C19	0.4 (3)
C6—C7—C8—C9	1.5 (3)	C22—N3—C18—C17	−178.54 (19)
C10—C7—C8—C9	−175.68 (17)	N1—C17—C18—N3	−3.3 (3)
C1—N1—C9—O3	171.88 (18)	N1—C17—C18—C19	177.71 (18)
C17—N1—C9—O3	−6.4 (3)	N3—C18—C19—C20	−1.0 (3)
C1—N1—C9—C8	−9.9 (3)	C17—C18—C19—C20	177.95 (18)
C17—N1—C9—C8	171.83 (17)	C18—C19—C20—C21	0.7 (3)

C7—C8—C9—O3	−176.17 (19)	C19—C20—C21—C22	0.1 (3)
C7—C8—C9—N1	5.6 (3)	C18—N3—C22—C21	0.5 (3)
C11—O2—C10—O1	−4.1 (3)	C20—C21—C22—N3	−0.8 (3)

Symmetry code: (i) −*x*, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···N3^{ii}	0.98 (3)	2.50 (3)	3.344 (3)	145 (2)
O4—H4*A*···O3	0.87	1.87	2.647 (4)	147
O4—H4*B*···O3^{i}	0.87	2.26	2.989 (4)	141
C8—H8···O4^{i}	0.97 (2)	2.28 (2)	3.113 (4)	143.7 (17)
C13—H13···O4^{i}	1.00 (2)	2.44 (2)	3.345 (4)	149.3 (19)
C17—H17*A*···O3^{ii}	1.00 (2)	2.57 (2)	3.307 (3)	130.4 (16)
C11—H11*A*···*Cg*1^{ii}	1.02 (2)	2.85 (2)	3.673 (2)	137.9 (15)

Symmetry codes: (i) −*x*, −*y*+1, −*z*+1; (ii) *x*+1, *y*, *z*.