# organic compounds

# 3-Acetyl-4-hydroxyquinolin-2(1*H*)-one: resonance-assisted O—H···O hydrogen bonding

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The molecule of the title compound, $C_{11}H_9NO_3$, a pharmacologically important quinoline derivative, adopts an overall planar shape. The structure is stabilized by an intramolecular O—H···O=C hydrogen bond, forming an $S(6)$ hydrogen-bonded ring pattern. The O—H···O interaction results in delocalization of the electron density within the dihydropyridine ring, as observed for resonance-assisted hydrogen bonds, leading to lengthening of the carbonyl O=C and pyridyl C=C bonds, and shortening of the C—OH bond in this hydrogen-bonded $S(6)$ ring structure. The cooperative intermolecular N—H···O hydrogen bonds cluster molecules into closed dimers, characterized by an $R_2^2(8)$ ring pattern. Aromatic–aromatic stacking interactions are also observed in the packing, with an interplanar distance of 3.352 Å and a slippage of 1.855 Å

## Related literature

Quinoline-2,4-dione derivatives are useful molecules for the synthesis of many pharmacologically active compounds (Detsi *et al.*, 1996; Lange *et al.*, 2001; Sarveswari & Raja, 2006). 18 analogous structures have been reported in the Cambridge Structural Database (Version 5.28; Allen, 2002). For relevent literature for resonance-assisted hydrogen bonds, see Gilli *et al.* (1989), Jeffrey (1997) and Shishkina *et al.* (2005). Molecular bond distances are reported by Bürgi & Dunitz (1994).
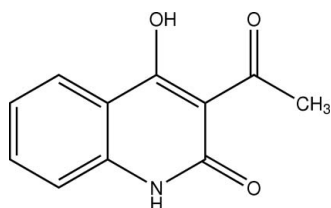


## Experimental

### Crystal data

| | |
|---|---|
| $C_{11}H_9NO_3$ | $V$ = 920.9 (4) Å$^3$ |
| $M_r$ = 203.19 | $Z$ = 4 |
| Monoclinic, $P2_1/n$ | Mo $K\alpha$ radiation |
| $a$ = 11.914 (3) Å | $\mu$ = 0.11 mm$^{-1}$ |
| $b$ = 5.2297 (12) Å | $T$ = 295 (2) K |
| $c$ = 14.946 (3) Å | 0.3 × 0.25 × 0.10 mm |
| $\beta$ = 98.555 (4)° | |

### Data collection

| | |
|---|---|
| Bruker SMART CCD area-detector diffractometer | 6736 measured reflections |
| Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996) | 1812 independent reflections |
| | 1209 reflections with $I > 2\sigma(I)$ |
| $T_{min}$ = 0.95, $T_{max}$ = 0.98 | $R_{int}$ = 0.032 |

### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)]$ = 0.048 | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2)$ = 0.124 | |
| $S$ = 1.02 | |
| 1812 reflections | $\Delta\rho_{max}$ = 0.18 e Å$^{-3}$ |
| 144 parameters | $\Delta\rho_{min}$ = −0.12 e Å$^{-3}$ |
| 1 restraint | |

**Table 1**
Selected bond lengths (Å).

| N1—C1 | 1.368 (2) | C1—C2 | 1.458 (3) |
|---|---|---|---|
| N1—C9 | 1.371 (2) | C2—C3 | 1.402 (3) |
| O1—C1 | 1.240 (2) | C2—C10 | 1.453 (3) |
| O2—C3 | 1.321 (2) | C3—C4 | 1.432 (3) |
| O3—C10 | 1.255 (2) | | |

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O2—H2···O3 | 0.86 (2) | 1.64 (2) | 2.459 (2) | 158 (3) |
| N1—H1···O1$^i$ | 0.92 (2) | 1.91 (2) | 2.831 (2) | 177 (2) |

Symmetry code: (i) −x, −y, −z.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT-Plus* (Bruker, 2003); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Bruker, 2003); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PLATON*.

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**supplementary materials**

## 3-Acetyl-4-hydroxyquinolin-2(1*H*)-one: resonance-assisted O-H···O hydrogen bonding

## S. Sarveswari, T. K. Raja, R. Vijayaraghavan, T. Narasimhamurthy and R. S. Rathore

### Comment

Quinoline-2,4-dione derivatives are useful molecules for the synthesis of many pharmacologically active compounds including glycine NMDA and serotonin (5-HT$_3$) receptor antagonists (Detsi *et al.*, 1996; Lange *et al.*, 2001; Sarveswari & Raja, 2006). The title compound, 3-acetyl-4-hydroxyquinolin-2(1*H*)-one, (I), is one such derivative having antimalarial and antimicrobial properties, where acetyl group is substituted at the position-3. A search of quinoline-2,4-dione derivatives, substituted at the position-3 in Cambridge Structural Database (CSD, Version 5.28; Allen, 2002) reveled following 18 similar compounds (the CSD entry numbers are provided within the braces): *N*-methyl-*N*-phenyl-1,2-dihydro-4-hydroxy-1-methyl-2-oxoquinoline- 3-carboxamide (BEHDUO), 3-(1,2-dimethyl-2-hydroxypropyl)-4-hydroxy-1-methylquinolin-2(1*H*)-one (CEPTAS), ethyl-1-phenyl-2-oxo-4-hydroxyquinoline-3-carboxylate (EYOTUH), 1-ethyl-4-hydroxy-2-oxo-1,2-dihydroquinoline-3-carboxylic acid (FACVUB) 1-Propyl-2-oxo-3-ethoxycarbonyl-4-hydroxyquinoline (FOWKIL), *N*-(6-hydroxybenzothiazol-2-yl)-1-ethyl-4-hydroxy-2-oxo-1,2- dihydroquinolinyl-3-carboxamide (IBEGAY), 4-hydroxy-1-methyl-2-oxo-*N*-(4-oxo-2-propyl-3,4-dihydroquinazolin-3-yl)-1, 2-dihydroquinoline-3-carboxamide (KOBZOQ), 6-bromo-1-isopentyl-2-oxo-3-(*N*-(1-phenylethyl)carboxamido)-4- hydroxyquinoline (LOHFOD), 2-oxo-4-hydroxy-3-(1-phenylethylaminocarbonyl)-1-pentylquinoline (LOHNIF), 1-ethyl-4-hydroxy-2-oxo-1,2-dihydroquinoline-3-carboxylic acid 3-chloro-benzylidenehydrazide (NAMYIK), 6-bromo-4-hydroxy-2-oxo-1-phenyl-3-ethoxycarbonyl-1,2-dihydroquinoline (NANFIS), *N*-(2-diethylaminoethyl) 1-allyl–4-hydroxy-2-oxo-1,2-dihydroquinoline-3-carbox amide hydrochloride (NANFOY), 3-ethoxycarbonyl-4-hydroxy-6-(methoxymethoxy)-1-methyl-2-quinolone (OJILIC), 3-(1-hydroxyiminoethyl)-4-hydroxyquinolin-2(1*H*)-one (QONPOY), *N*-(1-adamantyl)-4-hydroxy-1-(2-methylpropyl)-2-oxo-1,2-dihydroquinoline- 3-carboxamide 2-propanol solvate (QOQQUI), 3-benzoyl-1-ethyl-4-hydroxy-2-quinolone (TEZHAH), 3-(*N,N*-dibutylaminocarbonylmethyl)-2-oxo-1,2-dihydro-4- hydroxyquinoline (XEPPEN), 1,1,3,6-tetramethyl-1,2,4a,11,12,12*a*-hexahydro-12-(4-hydroxy-1- methylquinolin-2-one-3-yl)-2-benzopyrano(3,4 − c)quinolin-5-one chloroform (YIVMIZ).

The crystal structure of (I) is discussed in this report. The molecular structure with atom numbering scheme is shown in Fig 1. A l l the non-hydrogen atoms in (I) are coplanar with maximum deviation of −0.07 (1)Å for C11. The acetyl group is slighly tilted with respect to the quinoline ring with the torsion angle C3—C2—C10—C11 of −177.4 (2)°. An intra-molecular O2—H2···O3 hydrogen bond stabilize the structure, which form a hydrogen-bonded S(6) closed-ring structure. Hydrogen bond parameters are provided in Table 2. The intramolecular hydrogen bond leads to delocalization of the electron density within the dihydropyridine ring thereby affecting bond distances in S(6) ring-pattern as also observed in an analogus structure of methyl 1-acetonyl-4-hydroxy-2-oxo-1,2-dihydro-quinoline-3-carboxylate (Shishkina *et al.*, 2005). Such hydrogen bonds, observed first by Gilli *et al.* (1989) are referred to as resonance-assisted hydrogen bond (RAHB), which are formed betweeen conjugated multiple π-bonds (Jeffrey, 1997). The relevent bond distances are listed in Table 1. A s a result of RAHB in (I), the carbonyl O3═C10 and C2═C3 bonds are longer than standard values for O═C (1.210 Å) and C═C (1.334 Å), respectively (Bürgi & Dunitz, 1994). On the other hand, hydroxyl O2—C3, and C3—C4 bonds in the pyridine ring are shorter than their respective standard values ($C_{sp}{}^2$—O = 1.362 Å; $C_{sp}{}^2$—$C_{sp}{}^2$ = 1.455 Å). There is no significant change observed in the bond length C2—C10 as compared to the standard value.

Crystal packing diagram is shown in Fig. 2. In the crystal, the molecules cluster into closed dimers *via* cooperative intermolecular N1—H1···O1[i] hydrogen bonds [symmetry code (i): −*x*, −*y*, −*z*]. The dimeric assembly is characterized by $R_2^2(8)$ ring pattern. Significant π···π interactions were also observed in the packing. *Cg*1 (centeroid of C4—C9 ring) makes a parallel stacking interaction with *Cg*1 of the molecule, related by a center of inversion with *Cg*1···*Cg*1[ii] [symmetry code (ii): −*x*, 1 − *y*, −*z*] 3.352Å apart and a slippage of 1.855 Å. The center-to-center distance is 3.831 (1) Å.

## Experimental

A mixture of methylanthranilate(3.85 ml, 25 mmol), ethylacetoacetate (4 ml, 5 mmol) and a catalytic amount of sodium ethoxide was irradiated under microwave at 360 W for 3 minutes. The solid obtained, following the cooling was then dissolved in water and acidified with dilute acetic acid. The product was filtered, dried and recrystallized from acetic acid [melting point 261–263°C].

## Refinement

All the parameters of heavy atoms and polar H atoms (NH and OH) were freely refined except that the O–H distance, in the final cycle of refinement was restrained to 0.86 (2) Å. Rest of the H atoms were positioned geometrically and refined as riding on their carrier atoms. The distances with hydrogen atoms were $C_{ar}$—H = 0.93 Å, methyl C—H = 0.96Å with $U_{iso}$ (H) = 1.2 $U_{eq}$(C) [= 1.5 $U_{eq}$(C) for methyl H atoms], N—H = 0.92 (2) Å.
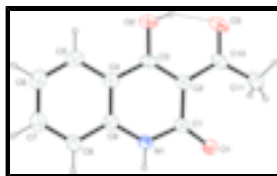
## Figures



Fig. 1. A view of (I). Displacement ellipsoids are drawn at the 30% probability level.
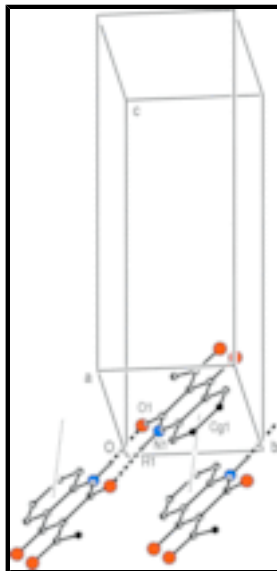


Fig. 2. The crystal packing, showing the cooperative N—H···O hydrogen bonds forming molecular dimers and aromatic–aromatic stacking interactions. For clarity, only selected molecules and H atoms involved in the interactions are shown.

**3-Acetyl-4-hydroxyquinolin-2(1*H*)-one**

*Crystal data*

| | |
|---|---|
| $C_{11}H_9NO_3$ | $F_{000} = 424$ |
| $M_r = 203.19$ | $D_x = 1.466$ Mg m$^{-3}$ |
| Monoclinic, $P2_1/n$ | Melting point: 261(2) K |
| Hall symbol: -P 2yn | Mo $K\alpha$ radiation<br>$\lambda = 0.71073$ Å |
| $a = 11.914$ (3) Å | Cell parameters from 1119 reflections |
| $b = 5.2297$ (12) Å | $\theta = 3.5–24.5º$ |
| $c = 14.946$ (3) Å | $\mu = 0.11$ mm$^{-1}$ |
| $\beta = 98.555$ (4)º | $T = 295$ (2) K |
| $V = 920.9$ (4) Å$^3$ | Needle, colorless |
| $Z = 4$ | $0.3 \times 0.25 \times 0.10$ mm |

*Data collection*

| | |
|---|---|
| Bruker SMART CCD area-detector diffractometer | 1812 independent reflections |
| Radiation source: fine-focus sealed tube | 1209 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite | $R_{int} = 0.032$ |
| $T = 295(2)$ K | $\theta_{max} = 26.0º$ |
| φ and ω–scans | $\theta_{min} = 2.0º$ |
| Absorption correction: multi-scan (SADABS; Sheldrick, 1996) | $h = -14 \rightarrow 14$ |
| $T_{min} = 0.95$, $T_{max} = 0.98$ | $k = -6 \rightarrow 6$ |
| 6736 measured reflections | $l = -18 \rightarrow 18$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.048$ | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2) = 0.124$ | $w = 1/[\sigma^2(F_o^2) + (0.0575P)^2 + 0.1258P]$<br>where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.02$ | $(\Delta/\sigma)_{max} < 0.001$ |
| 1812 reflections | $\Delta\rho_{max} = 0.18$ e Å$^{-3}$ |
| 144 parameters | $\Delta\rho_{min} = -0.12$ e Å$^{-3}$ |
| 1 restraint | Extinction correction: none |
| Primary atom site location: structure-invariant direct methods | |

*Special details*

**Geometry**. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Weighted least-squares planes through the starred atoms (Nardelli, Musatti, Domiano & Andreetti Ric·Sci.(1965),15(II—A),807). Equation of the plane: $m1*X+m2*Y+m3*Z=d$

Plane 1 m1 = −0.50700(0.00021) m2 = 0.60194(0.00025) m3 = −0.61695(0.00021) D = −0.10597(0.00110) Atom d s d/s (d/s)**2 N1 * 0.0083 0.0016 5.067 25.673 O1 * 0.0131 0.0014 9.641 92.953 O2 * 0.0038 0.0015 2.461 6.055 O3 * 0.0102 0.0016 6.322 39.968 C1 * 0.0062 0.0019 3.297 10.873 C2 * 0.0048 0.0018 2.638 6.959 C3 * 0.0101 0.0019 5.207 27.112 C4 * 0.0108 0.0019 5.612 31.497 C5 * 0.0034 0.0022 1.524 2.323 C6 * −0.0105 0.0025 − 4.150 17.226 C7 * −0.0224 0.0024 − 9.321 86.872 C8 * −0.0161 0.0022 − 7.329 53.707 C9 * −0.0049 0.0019 − 2.549 6.497 C10 * −0.0117 0.0021 − 5.673 32.181 C11 * −0.0747 0.0025 − 30.230 913.870 =========== Sum((d/s)**2) for starred atoms 1353.766 Chi-squared at 95% for 12 degrees of freedom: 21.00 The group of atoms deviates significantly from planarity

Plane 2 m1 = −0.50314(0.00026) m2 = 0.60226(0.00028) m3 = −0.61979(0.00030) D = −0.10111(0.00121) Atom d s d/s (d/s)**2 N1 * 0.0060 0.0016 3.654 13.355 O1 * 0.0008 0.0014 0.587 0.344 O2 * −0.0046 0.0015 − 2.940 8.646 C1 * −0.0026 0.0019 − 1.362 1.854 C2 * −0.0063 0.0018 − 3.419 11.690 C3 * 0.0035 0.0019 1.805 3.259 C4 * 0.0110 0.0019 5.697 32.456 C5 * 0.0081 0.0022 3.691 13.624 C6 * 0.0007 0.0025 0.266 0.071 C7 * −0.0092 0.0024 − 3.846 14.794 C8 * −0.0074 0.0022 − 3.347 11.202 C9 * −0.0027 0.0019 − 1.416 2.006 C10 − 0.0296 0.0021 − 14.379 206.766 O3 − 0.0094 0.0016 − 5.870 34.458 C11 − 0.0978 0.0025 − 39.563 1565.243 =========== Sum((d/s)**2) for starred atoms 113.302 Chi-squared at 95% for 9 degrees of freedom: 16.90 The group of atoms deviates significantly from planarity

Plane 3 m1 = −0.53467(0.00105) m2 = 0.57611(0.00100) m3 = −0.61824(0.00080) D = −0.16756(0.00482) Atom d s d/s (d/s)**2 O3 * −0.0011 0.0016 − 0.688 0.473 C2 * −0.0013 0.0018 − 0.714 0.510 C10 * 0.0050 0.0021 2.444 5.975 C11 * −0.0023 0.0025 − 0.922 0.849 C1 0.0302 0.0019 15.947 254.299 C3 − 0.0490 0.0019 − 25.144 632.222 O1 0.0840 0.0014 61.747 3812.751 O2 − 0.0847 0.0016 − 54.488 2968.986 =========== Sum((d/s)**2) for starred atoms 7.807 Chi-squared at 95% for 1 degrees of freedom: 3.84 The group of atoms deviates significantly from planarity

Dihedral angles formed by LSQ-planes Plane - plane angle (s.u.) angle (s.u.) 1 2 0.28 (0.02) 179.72 (0.02) 1 3 2.17 (0.06) 177.83 (0.06) 2 3 2.35 (0.06) 177.65 (0.06)

**Refinement**. Refinement of $F^2$ against ALL reflections. The weighted $R$-factor $wR$ and goodness of fit $S$ are based on $F^2$, conventional $R$-factors $R$ are based on $F$, with $F$ set to zero for negative $F^2$. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating $R$-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. $R$-factors based on $F^2$ are statistically about twice as large as those based on $F$, and $R$- factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\mathring{A}^2$)*

|  | $x$ | $y$ | $z$ | $U_{iso}*/U_{eq}$ |
|---|---|---|---|---|
| N1 | 0.09377 (13) | 0.2592 (3) | 0.04347 (11) | 0.0403 (4) |
| H1 | 0.0852 (16) | 0.139 (4) | −0.0022 (14) | 0.048* |
| O1 | −0.05886 (11) | 0.1058 (3) | 0.09779 (9) | 0.0491 (4) |
| O2 | 0.14531 (14) | 0.8292 (3) | 0.22959 (10) | 0.0552 (5) |
| H2 | 0.0905 (16) | 0.813 (5) | 0.2603 (15) | 0.078 (9)* |
| O3 | −0.02021 (14) | 0.6819 (3) | 0.29588 (10) | 0.0628 (5) |

| | | | |
|---|---|---|---|
| C1 | 0.01820 (16) | 0.2671 (4) | 0.10394 (12) | 0.0385 (5) |
| C2 | 0.03497 (16) | 0.4702 (4) | 0.17146 (12) | 0.0394 (5) |
| C3 | 0.12517 (17) | 0.6416 (4) | 0.17013 (13) | 0.0408 (5) |
| C4 | 0.20119 (16) | 0.6217 (4) | 0.10472 (13) | 0.0404 (5) |
| C5 | 0.29257 (18) | 0.7891 (4) | 0.10253 (15) | 0.0514 (6) |
| H5 | 0.3054 | 0.9213 | 0.1444 | 0.062* |
| C6 | 0.3628 (2) | 0.7584 (5) | 0.03905 (17) | 0.0622 (7) |
| H6 | 0.4232 | 0.8703 | 0.0377 | 0.075* |
| C7 | 0.34452 (19) | 0.5602 (5) | −0.02366 (16) | 0.0598 (7) |
| H7 | 0.3931 | 0.5408 | −0.0665 | 0.072* |
| C8 | 0.25622 (18) | 0.3942 (4) | −0.02310 (14) | 0.0506 (6) |
| H8 | 0.2444 | 0.2631 | −0.0655 | 0.061* |
| C9 | 0.18338 (16) | 0.4227 (4) | 0.04178 (13) | 0.0395 (5) |
| C10 | −0.03790 (17) | 0.5005 (4) | 0.24056 (13) | 0.0459 (5) |
| C11 | −0.1327 (2) | 0.3222 (5) | 0.24988 (16) | 0.0624 (7) |
| H11A | −0.1715 | 0.3790 | 0.2982 | 0.094* |
| H11B | −0.1030 | 0.1536 | 0.2631 | 0.094* |
| H11C | −0.1849 | 0.3190 | 0.1944 | 0.094* |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| N1 | 0.0464 (10) | 0.0384 (10) | 0.0377 (9) | −0.0026 (8) | 0.0115 (8) | −0.0061 (8) |
| O1 | 0.0508 (8) | 0.0500 (9) | 0.0489 (9) | −0.0089 (7) | 0.0147 (7) | −0.0074 (7) |
| O2 | 0.0673 (11) | 0.0479 (9) | 0.0499 (9) | −0.0026 (8) | 0.0065 (8) | −0.0147 (8) |
| O3 | 0.0813 (12) | 0.0613 (11) | 0.0490 (9) | 0.0115 (9) | 0.0202 (8) | −0.0135 (8) |
| C1 | 0.0413 (11) | 0.0379 (11) | 0.0359 (11) | 0.0055 (9) | 0.0044 (8) | 0.0038 (9) |
| C2 | 0.0474 (12) | 0.0367 (11) | 0.0342 (11) | 0.0070 (9) | 0.0060 (9) | 0.0031 (9) |
| C3 | 0.0529 (12) | 0.0330 (11) | 0.0344 (11) | 0.0076 (9) | −0.0001 (9) | −0.0017 (9) |
| C4 | 0.0446 (11) | 0.0382 (11) | 0.0374 (11) | 0.0029 (9) | 0.0024 (9) | 0.0037 (9) |
| C5 | 0.0538 (13) | 0.0451 (13) | 0.0531 (13) | −0.0067 (10) | 0.0012 (10) | −0.0004 (11) |
| C6 | 0.0533 (14) | 0.0644 (16) | 0.0698 (16) | −0.0137 (12) | 0.0121 (12) | 0.0082 (13) |
| C7 | 0.0547 (14) | 0.0711 (18) | 0.0573 (15) | −0.0015 (12) | 0.0203 (11) | 0.0056 (13) |
| C8 | 0.0538 (13) | 0.0551 (14) | 0.0454 (12) | 0.0019 (11) | 0.0160 (10) | −0.0001 (11) |
| C9 | 0.0432 (11) | 0.0396 (12) | 0.0352 (11) | 0.0030 (9) | 0.0047 (9) | 0.0065 (9) |
| C10 | 0.0542 (13) | 0.0474 (13) | 0.0373 (11) | 0.0149 (10) | 0.0107 (10) | 0.0040 (10) |
| C11 | 0.0682 (15) | 0.0688 (17) | 0.0566 (15) | 0.0083 (13) | 0.0301 (12) | 0.0044 (12) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| N1—C1 | 1.368 (2) | C5—C6 | 1.365 (3) |
| N1—C9 | 1.371 (2) | C5—H5 | 0.9300 |
| N1—H1 | 0.92 (2) | C6—C7 | 1.393 (3) |
| O1—C1 | 1.240 (2) | C6—H6 | 0.9300 |
| O2—C3 | 1.321 (2) | C7—C8 | 1.365 (3) |
| O2—H2 | 0.856 (10) | C7—H7 | 0.9300 |
| O3—C10 | 1.255 (2) | C8—C9 | 1.402 (3) |
| C1—C2 | 1.458 (3) | C8—H8 | 0.9300 |
| C2—C3 | 1.402 (3) | C10—C11 | 1.487 (3) |

| | | | |
|---|---|---|---|
| C2—C10 | 1.453 (3) | C11—H11A | 0.9600 |
| C3—C4 | 1.432 (3) | C11—H11B | 0.9600 |
| C4—C9 | 1.398 (3) | C11—H11C | 0.9600 |
| C4—C5 | 1.401 (3) | | |
| C1—N1—C9 | 125.76 (17) | C5—C6—H6 | 119.9 |
| C1—N1—H1 | 119.9 (12) | C7—C6—H6 | 119.9 |
| C9—N1—H1 | 114.4 (12) | C8—C7—C6 | 120.9 (2) |
| C3—O2—H2 | 102.3 (18) | C8—C7—H7 | 119.6 |
| O1—C1—N1 | 118.91 (17) | C6—C7—H7 | 119.6 |
| O1—C1—C2 | 124.79 (17) | C7—C8—C9 | 119.6 (2) |
| N1—C1—C2 | 116.30 (17) | C7—C8—H8 | 120.2 |
| C3—C2—C10 | 118.73 (18) | C9—C8—H8 | 120.2 |
| C3—C2—C1 | 118.84 (17) | N1—C9—C4 | 119.51 (17) |
| C10—C2—C1 | 122.44 (18) | N1—C9—C8 | 120.69 (19) |
| O2—C3—C2 | 121.87 (18) | C4—C9—C8 | 119.80 (18) |
| O2—C3—C4 | 116.31 (19) | O3—C10—C2 | 119.4 (2) |
| C2—C3—C4 | 121.82 (17) | O3—C10—C11 | 117.86 (18) |
| C9—C4—C5 | 119.35 (19) | C2—C10—C11 | 122.72 (19) |
| C9—C4—C3 | 117.75 (18) | C10—C11—H11A | 109.5 |
| C5—C4—C3 | 122.89 (19) | C10—C11—H11B | 109.5 |
| C6—C5—C4 | 120.1 (2) | H11A—C11—H11B | 109.5 |
| C6—C5—H5 | 119.9 | C10—C11—H11C | 109.5 |
| C4—C5—H5 | 119.9 | H11A—C11—H11C | 109.5 |
| C5—C6—C7 | 120.3 (2) | H11B—C11—H11C | 109.5 |
| C9—N1—C1—O1 | −179.67 (18) | C4—C5—C6—C7 | −0.2 (3) |
| C9—N1—C1—C2 | 0.7 (3) | C5—C6—C7—C8 | 0.2 (4) |
| O1—C1—C2—C3 | −179.37 (18) | C6—C7—C8—C9 | −0.3 (3) |
| N1—C1—C2—C3 | 0.2 (2) | C1—N1—C9—C4 | −1.6 (3) |
| O1—C1—C2—C10 | 1.1 (3) | C1—N1—C9—C8 | 179.29 (18) |
| N1—C1—C2—C10 | −179.33 (17) | C5—C4—C9—N1 | −179.71 (18) |
| C10—C2—C3—O2 | −0.2 (3) | C3—C4—C9—N1 | 1.4 (3) |
| C1—C2—C3—O2 | −179.73 (17) | C5—C4—C9—C8 | −0.6 (3) |
| C10—C2—C3—C4 | 179.27 (18) | C3—C4—C9—C8 | −179.47 (19) |
| C1—C2—C3—C4 | −0.3 (3) | C7—C8—C9—N1 | 179.67 (19) |
| O2—C3—C4—C9 | 178.97 (17) | C7—C8—C9—C4 | 0.5 (3) |
| C2—C3—C4—C9 | −0.5 (3) | C3—C2—C10—O3 | 1.6 (3) |
| O2—C3—C4—C5 | 0.1 (3) | C1—C2—C10—O3 | −178.83 (18) |
| C2—C3—C4—C5 | −179.38 (18) | C3—C2—C10—C11 | −177.42 (18) |
| C9—C4—C5—C6 | 0.4 (3) | C1—C2—C10—C11 | 2.1 (3) |
| C3—C4—C5—C6 | 179.3 (2) | | |

*Hydrogen-bond geometry (Å, °)*

| D—H···A | D—H | H···A | D···A | D—H···A |
|---|---|---|---|---|
| O2—H2···O3 | 0.86 (2) | 1.64 (2) | 2.459 (2) | 158 (3) |
| N1—H1···O1[i] | 0.92 (2) | 1.91 (2) | 2.831 (2) | 177 (2) |

Symmetry codes: (i) −*x*, −*y*, −*z*.

**Fig. 1**

**Fig. 2**