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Methyl 2-(4-hydroxy-1-methyl-2-oxo-1,2-dihydroquinolin-3-yl)acetate

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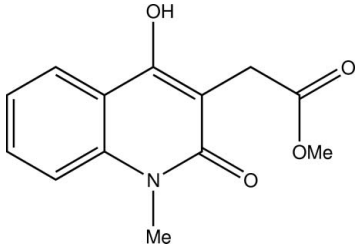
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.002 Å; R factor = 0.035; wR factor = 0.082; data-to-parameter ratio = 19.5.

In the title compound, $C_{13}H_{13}NO_4$, the bicyclic quinolone fragment and the ester group are approximately orthogonal, making a dihedral angle of 83.3 (2)° and an intramolecular C—H···O interaction occurs. In the crystal, intermolecular O—H···O hydrogen bonding generates a zigzag chain along the c axis.

Related literature

Esters of 4-hydroxy-2-oxo-1,2-dihydroquinolin-3-acetic acids reveal appreciable biological activity, see: Ukrainets *et al.* (2010). For a related structure, see: Ukrainets *et al.* (2009). For van der Waals radii, see: Zefirov (1997). For reference bond lengths, see: Bürgi & Dunitz (1994).



Experimental

Crystal data

$C_{13}H_{13}NO_4$ M_r = 247.24
Monoclinic, $P2_1/c$
a = 9.0792 (6) Å
b = 11.4904 (6) Å
c = 11.4071 (7) Å
β = 105.272 (7)°
V = 1148.00 (12) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 293 K
0.20 × 0.10 × 0.10 mm

Data collection

Oxford Xcalibur3 diffractometer
11774 measured reflections
3295 independent reflections
1454 reflections with $I > 2\sigma(I)$
R_{int} = 0.031

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.082
S = 0.72
3295 reflections
169 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.14 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2O···O1^{i}	0.921 (17)	1.760 (17)	2.6456 (12)	160.2 (15)
C10—H10A···O1^{i}	0.97	2.48	3.3335 (16)	147

Symmetry code: (i) $x, -y+\frac{1}{2}, z+\frac{1}{2}$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2005); cell refinement: *CrysAlis RED*; data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *XP* (Siemens, 1998); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: KP2282).

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supporting information

Acta Cryst. (2010). E**66**, o3195 [https://doi.org/10.1107/S1600536810046453]

Methyl 2-(4-hydroxy-1-methyl-2-oxo-1,2-dihydroquinolin-3-yl)acetate

Svitlana V. Shishkina, Oleg V. Shishkin, Igor V. Ukrainets and Elena V. Mospanova

S1. Comment

Esters of 4-hydroxy-2-oxo-1,2-dihydroquinolin-3-acetic acids reveal appreciable biological activity (Ukrainets *et al.*, 2010). It is interesting that the ethyl ester possesses stronger anti-inflammory activity than methyl ester. On the contrary, the methyl ester has pronounced analgetic activity. In this paper we report the molecular and crystal structure of the (4-hydroxy-1-methyl-2-oxo-1,2- dihydroquinolin-3-yl)-acetic acid methyl ester (I) (Fig. 1) with a comparative analysis with previously studied ethyl analogue (II) (Ukrainets *et al.*, 2009). In contrast to II the bicyclic fragment of I is not strictly planar (the C1—N1—C9—C8 torsion angle is -5.8 (2) °). The planar ester group at the C10 atom is orthogonal to the plane of quinoline ring (the C7—C8—C10—C11 torsion angle is 93.9 (1) °) and the C8—C10—C11—O3 torsion angle is -19.7 (2) °. The C9—O1 bond (1.251 (1) Å) is elongated comparing with its mean value (1.210 Å; Bürgi & Dunitz, 1994) owing to the formation of the intermolecular hydrogen bond O2—H2O···O1 (Table 1). The presence of this hydrogen bond determines the orientation of the hydrogen atom of hydroxy group despite of repulsion with one of hydrogen atoms of neighbouring methylene group: the H10*a*···H2O distance is 2.09 Å [the van der Waals radii sum is 2.34 Å (Zefirov, 1997)]. In the crystal packing the molecules are connected by the O2—H2O···O1 intermolecular hydrogen bond into a zigzag chain along the [0 0 1] direction (Table 1, Fig. 2). Neighbouring chains are connected by the C-H···π interactions between the methyl group at N1-pyridyl atom and C1···C6 aromatic ring [-x, 1-y, 1-z; H···Cg distance (Cg is centre of aromatic ring) is 3.28 Å, C-H···Cg bond angle is 125 °].

S2. Experimental

(4-hydroxy-1-methyl-2-oxo-1,2-dihydroquinolin-3-yl)-acetic acid is synthesised using the published method (Ukrainets *et al.*, 2010). Yield 96%; m.p. 452-454 K.

S3. Refinement

All hydrogen atoms were located from electron density difference maps and were refined in the riding mode approximation with U_{iso} constrained to be 1.5 times U_{eq} of the carrier atom for the methyl group and 1.2 times U_{eq} of the carrier atom for the other atoms. The hydrogen atom of the hydroxyl group was refined in an isotropic mode.

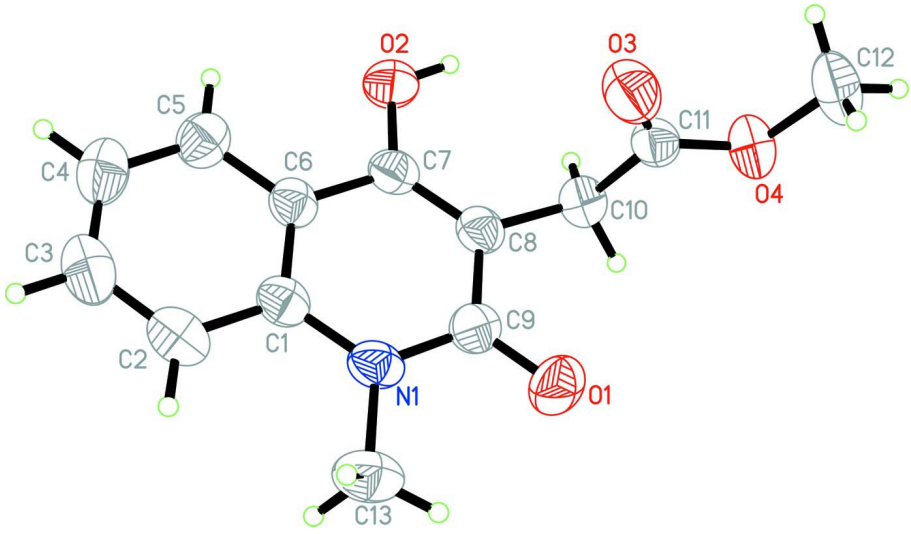

Figure 1

View of the title compound with atomic membering. All atoms are shown with displacement ellipsoids drawn at the 50% probability level.

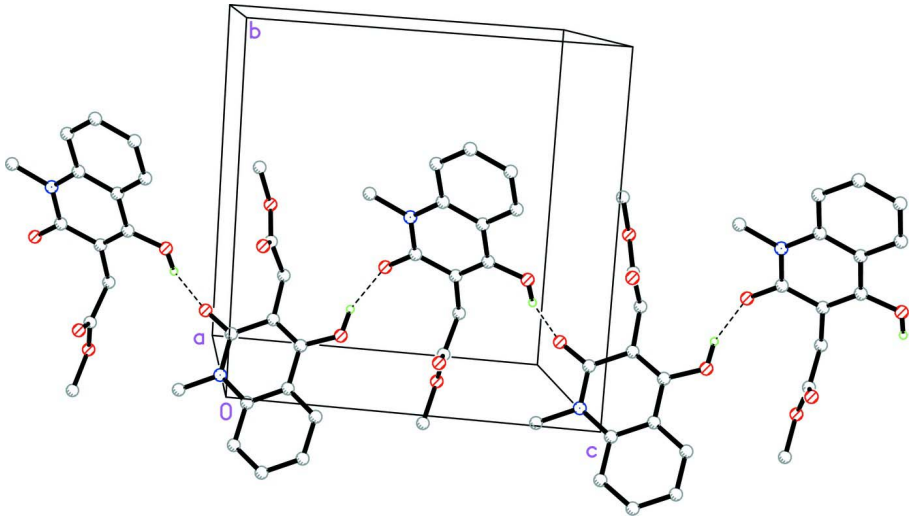

Figure 2

Crystal packing of the title molecules. The hydrogen bonds are shown by dashed lines.

Methyl 2-(4-hydroxy-1-methyl-2-oxo-1,2-dihydroquinolin-3-yl)acetate

Crystal data

$C_{13}H_{13}NO_4$
$M_r = 247.24$
Monoclinic, $P2_1/c$
$a = 9.0792\ (6)$ Å
$b = 11.4904\ (6)$ Å
$c = 11.4071\ (7)$ Å
$\beta = 105.272\ (7)°$
$V = 1148.00\ (12)$ Å^3
$Z = 4$

$F(000) = 520$
$D_x = 1.431$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3049 reflections
$\theta = 2.9–32.1°$
$\mu = 0.11$ mm^{-1}
$T = 293$ K
Block, colourless
0.20 × 0.10 × 0.10 mm

Data collection

Oxford Xcalibur3 diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 16.1827 pixels mm^{-1}
ω scans
11774 measured reflections
3295 independent reflections
1454 reflections with $I > 2\sigma(I)$
$R_{int} = 0.031$
$\theta_{max} = 30.0°$, $\theta_{min} = 2.9°$
$h = -12 \rightarrow 12$
$k = -15 \rightarrow 16$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.082$
$S = 0.72$
3295 reflections
169 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
$w = 1/[\sigma^2(F_o^2) + (0.044P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.14$ e Å^{-3}
$\Delta\rho_{min} = -0.14$ e Å^{-3}

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.

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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
N1	0.27207 (11)	0.49052 (8)	0.49471 (8)	0.0442 (3)
O1	0.39749 (11)	0.33292 (7)	0.44953 (8)	0.0582 (3)
O2	0.26304 (11)	0.34913 (8)	0.82386 (8)	0.0565 (3)
H2O	0.3143 (18)	0.2811 (15)	0.8511 (15)	0.100 (6)*
O3	0.19057 (12)	0.11214 (7)	0.58965 (9)	0.0613 (3)
O4	0.41580 (10)	0.02233 (7)	0.61834 (8)	0.0576 (3)
C1	0.19562 (14)	0.54717 (10)	0.56935 (11)	0.0412 (3)
C2	0.11931 (15)	0.65295 (10)	0.53520 (13)	0.0538 (4)
H2	0.1204	0.6877	0.4618	0.065*
C3	0.04276 (16)	0.70527 (12)	0.61044 (14)	0.0615 (4)
H3	−0.0073	0.7755	0.5873	0.074*
C4	0.03911 (16)	0.65520 (11)	0.71953 (14)	0.0591 (4)
H4	−0.0132	0.6916	0.7693	0.071*
C5	0.11239 (14)	0.55205 (11)	0.75432 (12)	0.0500 (3)
H5	0.1093	0.5183	0.8277	0.060*
C6	0.19244 (13)	0.49640 (9)	0.68027 (10)	0.0404 (3)
C7	0.27042 (13)	0.38819 (10)	0.71437 (10)	0.0411 (3)

C8	0.34114 (14)	0.33278 (9)	0.63922 (11)	0.0416 (3)
C9	0.33855 (14)	0.38309 (10)	0.52337 (11)	0.0433 (3)
C10	0.42339 (14)	0.21863 (10)	0.66808 (12)	0.0487 (3)
H10B	0.5113	0.2192	0.6348	0.058*
H10A	0.4607	0.2112	0.7556	0.058*
C11	0.32703 (16)	0.11471 (10)	0.61955 (11)	0.0439 (3)
C12	0.33896 (18)	−0.08538 (12)	0.57708 (14)	0.0681 (4)
H12C	0.2641	−0.1004	0.6209	0.102*
H12B	0.4120	−0.1477	0.5910	0.102*
H12A	0.2895	−0.0800	0.4918	0.102*
C13	0.27996 (17)	0.54417 (12)	0.38000 (11)	0.0600 (4)
H13C	0.3199	0.6217	0.3953	0.090*
H13B	0.1795	0.5472	0.3254	0.090*
H13A	0.3456	0.4988	0.3442	0.090*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0566 (7)	0.0417 (6)	0.0338 (6)	−0.0103 (5)	0.0112 (5)	−0.0002 (4)
O1	0.0705 (6)	0.0588 (6)	0.0493 (6)	−0.0083 (5)	0.0230 (5)	−0.0177 (4)
O2	0.0725 (7)	0.0558 (6)	0.0474 (6)	0.0058 (5)	0.0269 (5)	0.0123 (5)
O3	0.0581 (6)	0.0474 (6)	0.0775 (7)	−0.0025 (5)	0.0159 (5)	−0.0014 (4)
O4	0.0650 (6)	0.0387 (5)	0.0674 (6)	0.0057 (4)	0.0144 (5)	−0.0046 (4)
C1	0.0428 (7)	0.0371 (7)	0.0410 (7)	−0.0088 (5)	0.0064 (5)	−0.0028 (5)
C2	0.0580 (9)	0.0469 (8)	0.0511 (9)	−0.0068 (7)	0.0049 (7)	0.0062 (6)
C3	0.0560 (9)	0.0444 (8)	0.0781 (11)	0.0047 (7)	0.0071 (8)	−0.0007 (7)
C4	0.0554 (9)	0.0539 (9)	0.0672 (10)	0.0045 (7)	0.0150 (7)	−0.0136 (7)
C5	0.0506 (8)	0.0524 (8)	0.0467 (8)	−0.0019 (6)	0.0125 (6)	−0.0069 (6)
C6	0.0444 (7)	0.0354 (6)	0.0403 (7)	−0.0057 (5)	0.0090 (5)	−0.0048 (5)
C7	0.0478 (7)	0.0382 (7)	0.0375 (7)	−0.0080 (6)	0.0117 (6)	−0.0002 (5)
C8	0.0464 (7)	0.0355 (6)	0.0435 (7)	−0.0070 (5)	0.0127 (6)	−0.0027 (5)
C9	0.0468 (7)	0.0417 (7)	0.0423 (8)	−0.0117 (6)	0.0131 (6)	−0.0099 (5)
C10	0.0529 (8)	0.0414 (7)	0.0537 (8)	0.0001 (6)	0.0174 (6)	−0.0016 (6)
C11	0.0577 (9)	0.0385 (7)	0.0377 (7)	0.0003 (7)	0.0164 (6)	0.0019 (5)
C12	0.0916 (11)	0.0384 (8)	0.0681 (10)	0.0022 (7)	0.0100 (8)	−0.0086 (6)
C13	0.0731 (10)	0.0644 (9)	0.0426 (8)	−0.0146 (7)	0.0152 (7)	0.0062 (6)

Geometric parameters (Å, º)

N1—C9	1.3751 (15)	C4—H4	0.9300
N1—C1	1.3936 (15)	C5—C6	1.4049 (16)
N1—C13	1.4652 (15)	C5—H5	0.9300
O1—C9	1.2512 (14)	C6—C7	1.4330 (16)
O2—C7	1.3454 (14)	C7—C8	1.3574 (16)
O2—H2O	0.921 (17)	C8—C9	1.4370 (17)
O3—C11	1.1957 (14)	C8—C10	1.5023 (15)
O4—C11	1.3351 (14)	C10—C11	1.4975 (17)
O4—C12	1.4378 (15)	C10—H10B	0.9700

C1—C6	1.4005 (16)	C10—H10A	0.9700
C1—C2	1.4025 (17)	C12—H12C	0.9600
C2—C3	1.3766 (19)	C12—H12B	0.9600
C2—H2	0.9300	C12—H12A	0.9600
C3—C4	1.379 (2)	C13—H13C	0.9600
C3—H3	0.9300	C13—H13B	0.9600
C4—C5	1.3660 (17)	C13—H13A	0.9600

C9—N1—C1	122.15 (10)	C7—C8—C10	124.17 (11)
C9—N1—C13	117.93 (11)	C9—C8—C10	116.07 (11)
C1—N1—C13	119.90 (11)	O1—C9—N1	119.49 (11)
C7—O2—H2O	116.9 (10)	O1—C9—C8	121.83 (12)
C11—O4—C12	116.46 (10)	N1—C9—C8	118.66 (11)
N1—C1—C6	119.31 (11)	C11—C10—C8	114.01 (10)
N1—C1—C2	121.62 (11)	C11—C10—H10B	108.8
C6—C1—C2	119.06 (12)	C8—C10—H10B	108.8
C3—C2—C1	119.92 (13)	C11—C10—H10A	108.8
C3—C2—H2	120.0	C8—C10—H10A	108.8
C1—C2—H2	120.0	H10B—C10—H10A	107.6
C2—C3—C4	121.09 (13)	O3—C11—O4	124.09 (11)
C2—C3—H3	119.5	O3—C11—C10	125.86 (11)
C4—C3—H3	119.5	O4—C11—C10	110.01 (11)
C5—C4—C3	119.90 (13)	O4—C12—H12C	109.5
C5—C4—H4	120.1	O4—C12—H12B	109.5
C3—C4—H4	120.1	H12C—C12—H12B	109.5
C4—C5—C6	120.65 (13)	O4—C12—H12A	109.5
C4—C5—H5	119.7	H12C—C12—H12A	109.5
C6—C5—H5	119.7	H12B—C12—H12A	109.5
C1—C6—C5	119.38 (11)	N1—C13—H13C	109.5
C1—C6—C7	118.71 (11)	N1—C13—H13B	109.5
C5—C6—C7	121.91 (11)	H13C—C13—H13B	109.5
O2—C7—C8	125.26 (11)	N1—C13—H13A	109.5
O2—C7—C6	113.55 (10)	H13C—C13—H13A	109.5
C8—C7—C6	121.18 (11)	H13B—C13—H13A	109.5
C7—C8—C9	119.75 (11)		

C9—N1—C1—C6	3.30 (16)	O2—C7—C8—C9	178.97 (10)
C13—N1—C1—C6	−178.30 (10)	C6—C7—C8—C9	0.14 (17)
C9—N1—C1—C2	−175.55 (11)	O2—C7—C8—C10	−0.41 (19)
C13—N1—C1—C2	2.85 (17)	C6—C7—C8—C10	−179.24 (10)
N1—C1—C2—C3	178.85 (11)	C1—N1—C9—O1	175.57 (11)
C6—C1—C2—C3	−0.01 (17)	C13—N1—C9—O1	−2.86 (16)
C1—C2—C3—C4	−0.2 (2)	C1—N1—C9—C8	−5.80 (16)
C2—C3—C4—C5	0.0 (2)	C13—N1—C9—C8	175.77 (11)
C3—C4—C5—C6	0.3 (2)	C7—C8—C9—O1	−177.38 (11)
N1—C1—C6—C5	−178.52 (11)	C10—C8—C9—O1	2.05 (17)
C2—C1—C6—C5	0.36 (16)	C7—C8—C9—N1	4.03 (17)
N1—C1—C6—C7	0.99 (15)	C10—C8—C9—N1	−176.54 (10)

C2—C1—C6—C7	179.87 (11)	C7—C8—C10—C11	93.90 (14)
C4—C5—C6—C1	−0.53 (18)	C9—C8—C10—C11	−85.50 (13)
C4—C5—C6—C7	179.98 (11)	C12—O4—C11—O3	0.54 (18)
C1—C6—C7—O2	178.39 (10)	C12—O4—C11—C10	178.27 (11)
C5—C6—C7—O2	−2.12 (16)	C8—C10—C11—O3	−19.67 (18)
C1—C6—C7—C8	−2.65 (16)	C8—C10—C11—O4	162.65 (10)
C5—C6—C7—C8	176.84 (12)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2*O*···O1^{i}	0.921 (17)	1.760 (17)	2.6456 (12)	160.2 (15)
C10—H10*A*···O1^{i}	0.97	2.48	3.3335 (16)	147
C5—H5···O2	0.93	2.40	2.7138 (16)	100

Symmetry code: (i) *x*, −*y*+1/2, *z*+1/2.