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1-Ethyl-4-hydroxy-2-oxo-1,2-dihydroquinoline-3-carboxylic acid

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An X-ray diffraction study of the title compound, $C_{12}H_{11}NO_4$, has shown that this compound exists in the crystal as the 2-oxo-4-hydroxy tautomer. The formation of two O—H···O═C-type intramolecular hydrogen bonds leads to the elongation of both exocyclic and carboxylic C═O double bonds involved in the hydrogen bonding, causes shortening of the exocyclic C—O single bond, and also affects the C—C bond lengths in the dihydropyridine ring.

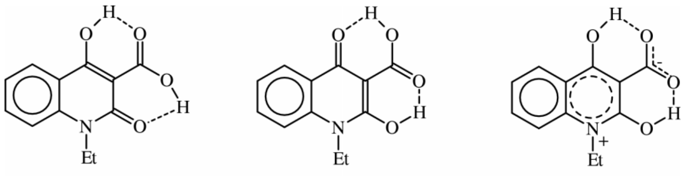
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.002 Å
R factor = 0.038
wR factor = 0.116
Data-to-parameter ratio = 11.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The derivatives of 4-hydroxyquinol-2-one can exist in different tautomeric forms depending on the substituent in the 3-position. They provide a relatively rare example of systems where more than two tautomeric forms are conceivable. These forms differ from each other in the H-atom positions and the location of hydroxy and carbonyl groups. Therefore, these compounds have been the focus of several structural investigations (Ukrainets *et al.*, 1992, 1996; Garsia Ruano *et al.*, 1991). In the present paper, we report the crystal and molecular structure of 1-ethyl-4-hydroxy-2-oxo-1,2-dihydroquinoline-3-carboxylic acid, (I) (Fig. 1).



2-oxo-4-hydroxy 2-hydroxy-4-oxo 2,4-dihydroxy

(I)

The C2—O13, C4—O17, C14—O16 and C3—C4 bond lengths [1.266 (2), 1.333 (2), 1.239 (3) and 1.381 (2) Å, respectively] indicate that the title compound exists in the crystal as the 2-oxo-4-hydroxy tautomer. This conclusion is also confirmed by the positions of the H atoms of the hydroxy and carboxy groups, which were located in a difference map.

All non-H atoms of this molecule with the exception of the atom C12 lie in one plane. The formation of the O15—H15O···O13 and O17—H17O···O16 hydrogen bonds [H15O···O13 1.67 (3), O15···O13 2.505 (2) Å, O15—H15O···O13 147 (3)°; H17O···O16 1.66 (3), O17···O16 2.548 (2) Å, O17—H17O···O16 151 (3)°] leads to a significant change in the bond lengths of the hydroxy, carboxy and carbonyl groups: the O13—C2 and O16—C14 bonds are longer than the standard value for the C═O bond of 1.210 Å (Bürgi & Dunitz, 1994) and the O17—C4 bond is shorter than the standard value for Csp^2—O (1.362 Å). The presence of intramolecular hydrogen bonds causes a noticeable redis-

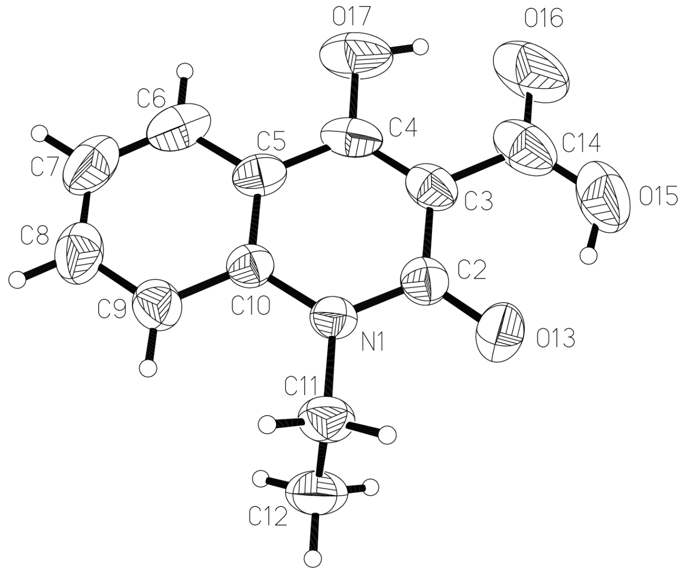


Figure 1
View of the title compound. The non-H atoms are shown with displacement ellipsoids drawn at the 50% probability level.

tribution of the electron density within the dihydropyridine ring. As a result, the C3—C4 and C5—C10 bonds are longer and the C2—C3 and C4—C5 bonds are shorter than the standard values for C═C (1.334 Å) and Csp^2—Csp^2 (1.455 Å) bonds (Bürgi & Dunitz, 1994).

The repulsion between the substituent at the N1 atom, the carbonyl group and the H atom in the *peri*-position of the aromatic ring {the shortened intramolecular contacts O13···H11*b* 2.33 Å [van der Waals radii sum is 2.45 Å according to Zefirov & Zorky (1995)], H9···C11 2.55 Å (2.87 Å), H9···H11*a* 2.06 Å (2.32 Å)} causes an elongation of the N1—C2, N1—C10 and N1—C11 bonds to 1.371 (2), 1.403 (2) and 1.488 (2) Å, respectively [standard values for the N—Csp^2 and N—Csp^3 bonds are 1.355 and 1.464%A (Bürgi & Dunitz, 1994)]. The C12 atom of the substituent at atom N1 is oriented orthogonally with respect to the plane of the dihydrocycle [the C2—N1—C11—C12 torsion angle is −94.2 (2)°].

Molecules of the title compound are linked into infinite chains along the *a* axis of the crystal, as a result of the C9—H9···O16^{i} intermolecular hydrogen bond [H···O^{i} 2.36 Å and C—H···O^{i} 154°; symmetry code: (i) $1 + x, y, z$].

Experimental

The title compound was prepared according to the procedure of Ukrainets *et al.* (1996).

Crystal data

$C_{12}H_{11}NO_4$
$M_r = 233.22$
Monoclinic, $P2_1/c$
$a = 9.278$ (2) Å
$b = 14.050$ (4) Å
$c = 8.938$ (2) Å
$\beta = 111.21$ (3)°
$V = 1086.2$ (5) Å^3
$Z = 4$

$D_x = 1.426$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24 reflections
$\theta = 10$–11°
$\mu = 0.11$ mm^{-1}
$T = 293$ (2) K
Needle, colorless
0.40 × 0.20 × 0.20 mm

Data collection

Siemens *P*3/*PC* diffractometer
θ–2θ scans
Absorption correction: none
2133 measured reflections
1885 independent reflections
1153 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.012$

$\theta_{\rm max} = 25.0$°
$h = -11 \rightarrow 10$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 10$
2 standard reflections every 98 reflections intensity decay: 5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.116$
$S = 0.97$
1885 reflections
162 parameters

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0812P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.085$
$\Delta\rho_{\rm max} = 0.15$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.14$ e Å^{-3}

Table 1
Selected interatomic distances (Å).

N1—C2	1.3712 (19)	C3—C14	1.473 (3)
N1—C10	1.4026 (18)	C4—O17	1.333 (2)
N1—C11	1.4885 (19)	C4—C5	1.435 (2)
C2—O13	1.2660 (18)	C5—C10	1.416 (2)
C2—C3	1.442 (2)	C14—O16	1.239 (3)
C3—C4	1.381 (2)	C14—O15	1.320 (3)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O17—H17O···O16	0.96 (3)	1.66 (3)	2.548 (2)	151 (3)
O15—H15O···O13	0.93 (3)	1.67 (3)	2.505 (2)	147 (3)
C9—H9···O16^{i}	0.93	2.36	3.227 (2)	154

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

All H atoms, except the H atoms of the hydroxy groups, were placed in calculated positions and included in the refinement as riding, with $U_{\rm iso}$ constrained to be $1.2U_{\rm eq}$ of the carrier atom ($1.5U_{\rm eq}$ for methyl H atoms). Hydroxy H atoms were located in a difference maps and refined isotropically.

Data collection: *P*3 (Siemens, 1989); cell refinement: *P*3; data reduction: *XDISK* (Siemens, 1991); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1991); software used to prepare material for publication: *SHELXL*97.

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