Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

1-Allyl-4-hydroxy-2-oxo-1,2,5,6,7,8-hexahydroquinoline-3-carboxylic acid

Svetlana V. Shishkina,[a]* Oleg V. Shishkin,[a] Igor V. Ukrainets[b] and Elena V. Kolesnik[b]

[a]Institute for Scintillation Materials, NTC 'Institute for Single Crystals', National Academy of Sciences of Ukraine, 60 Lenina Ave., Kharkiv 61001, Ukraine, and [b]Department of Pharmaceutical Chemistry, National University of Pharmacy, 4 Blyukhera Ave., Kharkiv 61002, Ukraine

Correspondence e-mail: sveta@xray.isc.kharkov.com

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.047
wR factor = 0.132
Data-to-parameter ratio = 12.6

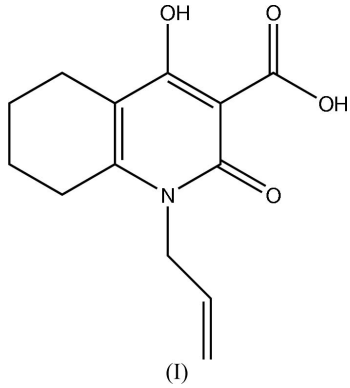
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 16 March 2005
Accepted 12 May 2005
Online 21 May 2005

An X-ray diffraction study of the title compound, $C_{13}H_{15}NO_4$, has demonstrated that the formation of intramolecular O—H···O=C hydrogen bonds leads to the lengthening of the carbonyl C=O bonds, shortening of the (C=)C—O(—H) bond and delocalization of the electron density within the dihydropyridine ring.

Comment

N-substituted 4-hydroxy-2-oxo-1,2-dihydroquinoline-3-carboxylic acids possess interesting pharmacological properties (Rowley *et al.*, 1993; Ukrainets *et al.*, 1994). These compounds are also used for the synthesis of different drugs, for example, the synthetic immunomodulator Roquinimex (trademark name for 4-hydroxy-1-methyl-2-oxo-1,2-dihydroquinoline-3-carboxylic acid methyl-phenyl amide; Jönsson *et al.*, 2004) and the injectable anesthetic Chinoxicaine (trademark name for 4-hydroxy-2-oxo-1-propyl-1,2-dihydroquinoline-3-carboxylic acid diethylaminoethyl amide hydrochloride; Ukrayinecz & Bezuhliy, 2002). Structures of *N*-substituted 4-hydroxy-2-oxo-1,2,5,6,7,8-hexahydroquinoline-3-carboxylic acids should be similar to their 1,2-dihydro analogues but remain almost unexplored. In the present paper, we report the crystal structure of the title *N*-allyl derivative, (I) (Table 1).



(I)

The cyclohexene ring of (I) has a half-chair conformation, with atoms C6 and C7 displaced from the plane of the remaining ring atoms by −0.382 (6) and 0.360 (6) Å, respectively. All non-H atoms of the pyridine ring, the carboxy, hydroxy and carbonyl groups, and atom C10 are almost coplanar (Fig. 1). The formation of the O4—H4O···O2 and O3—H3O···O1 intramolecular hydrogen bonds (Table 2) leads to a significant change of bond lengths in the hydroxy, carboxy and carbonyl groups; the O1—C1 and O2—C13 bonds are long compared with standard value for a C=O bond (1.210 Å; Bürgi & Dunitz, 1994), and the O4—C3 bond

is shorter than the standard value for the Csp^2—O bond length (1.362 Å). The presence of the hydrogen bonds results in the delocalization of the electron density within the dihydropyridine ring; the C2═C3 and C4═C9 bonds are longer and the C1—C2 and C3—C4 bonds are shorter than standard values for C═C (1.334 Å) and Csp^2—Csp^2 (1.455 Å) bond lengths, respectively (Bürgi & Dunitz, 1994). The structure of this fragment is very similar to that observed for 1-ethyl-4-hydroxy-2-oxo-1,2-dihydroquinoline-3-carboxylic acid (Shishkina *et al.*, 2002).

The repulsion between the substituent at atom N1 and the methylene and carbonyl groups is reflected in short intramolecular contacts O1···H10*A* = 2.39 Å [van der Waals radii sum is 2.72 Å (Bondi, 1964)], H8*A*···C10 = 2.66 Å (van der Waals sum 2.90 Å), H8*A*···H10*B* = 2.22 Å (van der Waals sum 2.40 Å) and H8*B*···H10*B* = 2.27 Å (van der Waals sum 2.40 Å). This hindered arrangement causes a lengthening of the N1—C1, N1—C9 and N1—C10 bonds [standard values for N—Csp^2 and N—Csp^3 bonds lengths are 1.355 and 1.464 Å, respectively (Bürgi & Dunitz, 1994)]. The double bond of the allyl group is situated almost orthogonal to the plane of the pyridine ring; the C1—N1—C10—C11 torsion angle is 81.7 (3)° and has +*ac* orientation with respect to the N1—C10 bond, while the N1—C10—C11—C12 torsion angle is 120.3 (3)°.

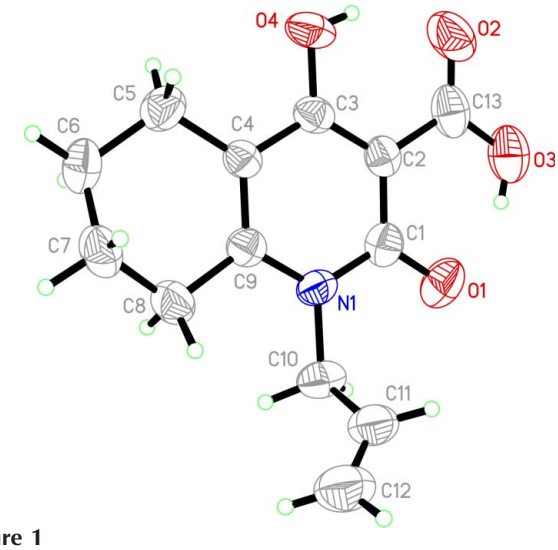


Figure 1
View of the title compound. Non-H atoms are shown with displacement ellipsoids drawn at the 50% probability level.

Table 1
Selected interatomic distances (Å).

N1—C1	1.381 (3)	O4—C3	1.339 (3)
N1—C9	1.397 (3)	C1—C2	1.436 (4)
N1—C10	1.485 (3)	C2—C3	1.395 (4)
O1—C1	1.268 (3)	C2—C13	1.468 (4)
O2—C13	1.236 (4)	C3—C4	1.421 (4)
O3—C13	1.320 (4)	C4—C9	1.384 (4)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3O···O1	0.82	1.73	2.485 (3)	153
O4—H4O···O2	0.82	1.85	2.576 (3)	147

Experimental

The title compound was prepared by hydrolysis of 1-allyl-4-hydroxy-2-oxo-1,2,5,6,7,8-hexahydroquinoline-3-carboxylic acid ethyl ester, following a published procedure (Ukrainets *et al.*, 2004; Jönsson *et al.*, 2004).

Crystal data

$C_{13}H_{15}NO_4$
M_r = 249.26
Orthorhombic, *Pbca*
a = 16.823 (4) Å
b = 7.179 (2) Å
c = 19.847 (5) Å
V = 2397.0 (11) Å^3
Z = 8
D_x = 1.381 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 24 reflections
θ = 10–11°
μ = 0.10 mm^{-1}
T = 293 (2) K
Needle, colourless
0.30 × 0.10 × 0.10 mm

Data collection

Siemens P3/PC diffractometer
ω–2θ scans
2087 measured reflections
2086 independent reflections
935 reflections with $I > 2\sigma(I)$
R_{int} = 0.030
θ_{max} = 25.1°
$h = 0 \rightarrow 20$
$k = 0 \rightarrow 8$
$l = -23 \rightarrow 0$
2 standard reflections
every 98 reflections
intensity decay: 5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.132
S = 0.85
2086 reflections
165 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0714P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}

H atoms bonded to C atoms were placed in calculated positions, while H atoms of the hydroxy groups were located in difference maps. All H atoms were refined in the riding model approximation, with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(O); constrained distances: 0.97 Å for methylene CH_2 groups, 0.93 Å for C(allyl)H groups and 0.82 Å for hydroxy OH groups.

Data collection: *P3* (Siemens, 1989); cell refinement: *P3*; data reduction: *XDISK* (Siemens, 1991); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1991); software used to prepare material for publication: *SHELXL97*.

References

Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
Bürgi, H.-B. & Dunitz, J. D. (1994). *Structure Correlation*, Vol. 2, pp. 767–784. Weinheim: VCH.
Jönsson, S., Andersson, G., Fex, T., Fristedt, T., Hedlund, G., Jansson, K., Abramo, L., Fritzson, I., Pekarski, O., Runström, A., Sandin, H., Thuvesson, I. & Björk, A. (2004). *J. Med. Chem.* **47**, 2075–2088.

Rowley, M., Leeson, P. D., Stevenson, G. I., Moseley, A. M., Stansfield, I., Sanderson, I., Robinson, L., Baker, R., Kemp, J. A., Marshall, G. R., Foster, A. C., Grimwood, S., Tricklebank, M. D. & Saywell, K. L. (1993). *J. Med. Chem.* **36**, 3386–3396.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Shishkina, S. V., Shishkin, O. V., Ukrainets, I. V., Dakhah, A. N. & Sidorenko, L. V. (2002). *Acta Cryst.* E**58**, o254–o256.
Siemens (1989). *P3*. Siemens Analytical X-ray Instruments Inc., Karlsruhe, Germany.
Siemens (1991). *XDISK* and *XP*. Siemens Analytical X-ray Instruments Inc., Karlsruhe, Germany.
Ukrainets, I. V., Gorokhova, O. V., Taran, S. G., Bezuglyi, P. A., Turov, A. V., Marusenko, N. A. & Evtifeeva, O. V. (1994). *Khim. Geterotsikl. Soedin.* pp. 958–966.
Ukrainets, I. V., Sidorenko, L. V., Gorokhova, O. V., Rybakov, V. B., Chernyshev, V. V. & Kolesnik, E. V. (2004). *News Pharmacy* (*Visnyk Pharmatsii*), **2**, 7–12.
Ukrayinecz, I. V. & Bezuhliy, P. A. (2002). US Patent No. 6 3406 92.