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Key indicators

Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
 R factor = 0.056
 wR factor = 0.164
Data-to-parameter ratio = 13.7For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Ethyl 4-(2-amino-1-cyano-2-oxoethyl)-2-oxo-1-propyl-1,2-dihydroquinoline-3-carboxylate

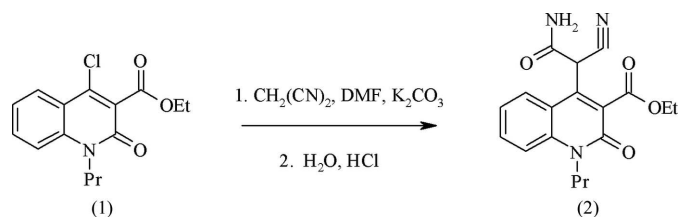
The mean planes of the propyl chain and carboxylate group of the ethoxycarbonyl substituent are almost orthogonal to the virtually planar dihydroquinoline bicyclic framework of the title compound, $\text{C}_{18}\text{H}_{19}\text{N}_3\text{O}_4$ [dihedral angles 89.6 (2) and 79.5 (1)°, respectively]. The nitrile group bond vector forms an angle of 59.4 (1)° with the dihydroquinoline plane. Both H atoms of the amide group participate in intermolecular hydrogen bonds which link molecules into infinite chains running along the a axis of the crystal structure.

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Comment

Ethyl esters of 1- R -4-chloro-2-oxo-1,2-dihydroquinoline-3-carboxylic acids ($R = \text{H}, \text{Me}, \text{Et}, {}^i\text{Pr}$) react readily with ethyl cyanoacetate in the presence of dimethylformamide and K_2CO_3 . The alkaline hydrolysis of the resulting compounds leads to the formation of 4-methyl-substituted 1- R -2-oxo-1,2-dihydroquinoline-3-carboxylic acids (Ukrainets *et al.*, 2006). However, when malononitrile was used instead of cyanoacetate, the reaction took a different course. Thus, reaction of the 4-chloroquinoline (1) ($R = n\text{-Pr}$) with malononitrile results in the formation of the cyanoacetamide (2), the structure of which is reported in the present paper.



The bicyclic fragment of the molecule of (2) (Fig. 1) is planar to within 0.06 Å. The mean planes of the propyl substituent and carboxylate group of the ethylcarboxylate substituent are almost orthogonal to the mean plane of the dihydroquinoline bicyclic system [the corresponding dihedral angles are 89.6 (2) and 79.5 (1)°, respectively]. The $\text{O}3-\text{C}10$ bond of the ethylcarboxylate group has an antiperiplanar orientation with respect to the $\text{C}9-\text{C}3$ bond [torsion angle $\text{C}3-\text{C}9-\text{O}3-\text{C}10 = 175.0$ (2)°]; the $\text{C}10-\text{C}11$ bond is in a (-)-anticlinal conformation relative to $\text{C}9-\text{O}3$ [$\text{C}9-\text{O}3-\text{C}10-\text{C}11 = -93.1$ (4)°]. The vector of the nitrile group $\text{C}14\equiv\text{N}2$ is inclined by 59.4 (1)° with respect to the mean plane of the ring system, and both $\text{C}12-\text{C}13$ and $\text{C}13-\text{O}4$ bonds of the acetamide group are in (+)-anticlinal conformations with respect to the $\text{C}3-\text{C}4$ and $\text{C}4-\text{C}12$ bonds, respectively [the $\text{C}3-\text{C}4-\text{C}12-\text{C}13$ and $\text{C}4-\text{C}12-\text{C}13-\text{O}4$ torsion angles are 127.0 (2) and 123.9 (2)°, respectively]. The $\text{C}2-\text{O}1$, $\text{C}4-\text{C}12$, $\text{C}3-\text{C}9$ and $\text{C}12-\text{C}13$ bonds (Table 1) are slightly longer than corresponding standard bonds for

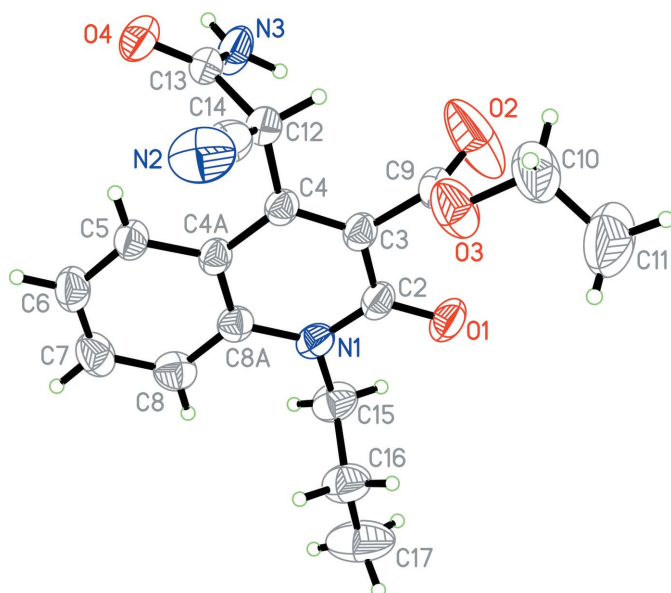


Figure 1
The molecular structure of the title compound with atomic labelling and displacement ellipsoids drawn at the 50% probability level.

C=O (1.210 Å), Csp^2-Csp^3 (1.510 Å), Csp^2-Csp^2 (1.478 Å) and Csp^3-Csp^2 for acyclic amides (1.514 Å; all standard values according to Bürgi & Dunitz, 1994).

Owing to the formation of N—H...O intermolecular hydrogen bonds (Table 2), molecules of the title compound are linked into infinite chains running along the *a* axis of the crystal structure.

Experimental

To a solution of ethyl 4-chloro-2-oxo-1-propyl-1,2-dihydroquinoline-3-carboxylate (2.93 g, 0.01 mol) in dimethylformamide (15 ml) were added K_2CO_3 (2 g, 0.014 mol) and malononitrile (0.72 g, 0.011 mol). After a few minutes the reaction mixture began to warm up. The temperature was maintained at 323 K while mixture was stirred until the reaction was completed (3–4 h). The completion of the process was established by the absence of the starting Cl-substituted derivative, as determined by liquid chromatography/mass spectroscopy. The reaction mixture was then diluted with water and acidified with HCl to give a pH of 4. The isolated cyanoacetamide was filtered off, washed with water and dried [yield 2.63 g, 77%; m.p. 466 K (decomposition)]. Crystals suitable for X-ray analysis were obtained by recrystallization from ethanol.

Crystal data

$C_{18}H_{19}N_3O_4$
 $M_r = 341.36$
Triclinic, $P\bar{1}$
 $a = 8.2279$ (15) Å
 $b = 10.555$ (2) Å
 $c = 11.701$ (3) Å
 $\alpha = 116.092$ (15)°
 $\beta = 94.213$ (16)°
 $\gamma = 104.475$ (15)°

$V = 863.8$ (4) Å³
 $Z = 2$
 $D_x = 1.312$ Mg m⁻³
Mo $K\alpha$ radiation
 $\mu = 0.09$ mm⁻¹
 $T = 293$ (2) K
Block, colourless
0.40 × 0.20 × 0.20 mm

Data collection

Siemens P3/PC diffractometer
 $\omega/2\theta$ scans
Absorption correction: none
3365 measured reflections
3132 independent reflections
2139 reflections with $I > 2\sigma(I)$

$R_{int} = 0.037$
 $\theta_{max} = 25.5^\circ$
2 standard reflections
every 98 reflections
intensity decay: 5%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.056$
 $wR(F^2) = 0.164$
 $S = 1.02$
3132 reflections
228 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.094P)^2 + 0.213P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.52$ e Å⁻³
 $\Delta\rho_{min} = -0.26$ e Å⁻³

Table 1

Selected bond lengths (Å).

N1—C2	1.363 (3)	C3—C4	1.344 (3)
N1—C8A	1.402 (3)	C3—C9	1.496 (3)
N1—C15	1.475 (3)	C4—C4A	1.444 (3)
O1—C2	1.239 (3)	C4—C12	1.525 (3)
C2—C3	1.451 (3)	C12—C13	1.547 (3)

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N3—H3NA...O1 ⁱ	0.86	2.30	2.904 (3)	128
N3—H3NB...O1 ⁱⁱ	0.86	2.05	2.908 (3)	178

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

All H atoms were located in difference maps. They were then placed in idealized positions (C—H = 0.93–0.97 and N—H = 0.86 Å) and included in the refinement in the riding model approximation with $U_{iso}(H)$ set at $1.2U_{eq}$ of the carrier atom ($1.5U_{eq}$ for the methyl H atoms).

Data collection: P3 (Siemens, 1989); cell refinement: P3; data reduction: XDISK (Siemens, 1991); program(s) used to solve structure: SHELXTL (Sheldrick, 1998); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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