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Methyl 4-amino-2-oxo-1,2-dihydroquinoline-3-carboxylate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
R factor = 0.045
wR factor = 0.119
Data-to-parameter ratio = 12.3

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

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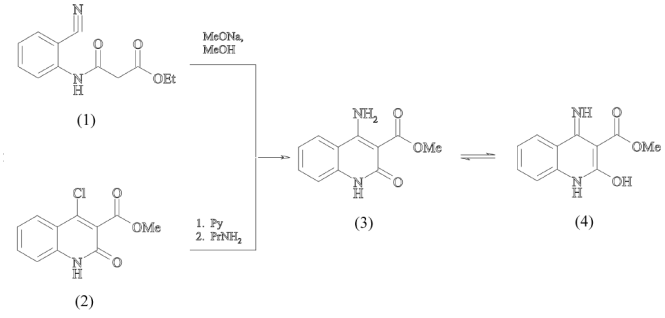
In the structure of the title compound, $C_{11}H_{10}N_2O_3$, pairs of molecules are linked into centrosymmetric dimers by N—H···O hydrogen bonds, which involve the cycloamino N—H and the keto C=O groups. In addition, the 4-amino group is involved in both intramolecular and intermolecular hydrogen bonds.

Comment

An initial investigation of the structure of the title compound, (3), by ^{1}H NMR spectroscopy suggested that this quinolone, in DMSO-d_6 solution, was represented by two tautomers, namely the 4-amino-2-oxo, (3), and 4-imino-2-hydroxy, (4), forms in a 4:1 ratio. However, ethyl 4-amino-2-oxo-1,2-dihydroquinoline-3-carboxylate has been shown to have only the 1,2-dihydro-form, analogous to (3) (Veronese *et al.*, 1995).



We synthesized the title compound in two ways: by intramolecular cyclization with the simultaneous re-esterification of 2-cyanomalonanilic acid ethyl ester, (1), as well as the reaction of methyl 4-chloro-2-oxo-1,2-dihydroquinoline-3-carboxylate, (2), with pyridine and the subsequent degradation of the pyridinium group under the action of propylamine by the known method (Esteve & Gaozza, 1981; Gewald *et al.*, 1991). According to our data, only the amidic tautomer, (3), is registered in the ^{1}H NMR spectrum of the resulting product. The X-ray structure of the enolic form, (4), of the ester, (3), has not been determined.

The results of this present X-ray analysis show that the 10-membered heterocycle (N1/C2–C10) is planar within 0.077 (1) Å and atoms O21 and N41 show small displacements from this plane [0.218 (2) and −0.110 (3) Å, respectively]. The N1—H1···O21 intermolecular hydrogen bond (Table 2) links the molecules into centrosymmetric dimers. The previously investigated (Rybakov *et al.*, 2001) crystal structure of 4-(4-ethoxyphenylamino)-2-oxo-1,2-dihydroquinoline forms the same type of hydrogen-bonded dimers. In addition, the 4-

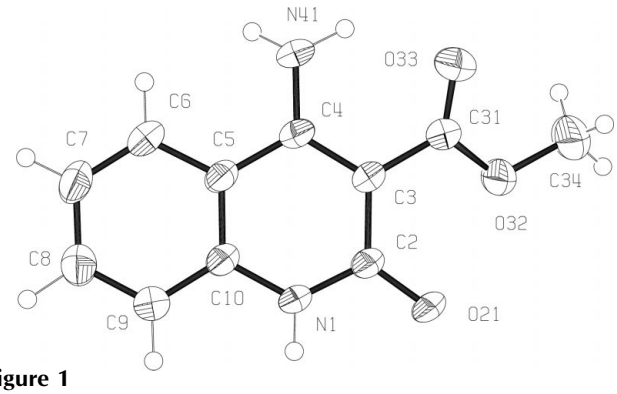


Figure 1
ORTEP-3 (Farrugia, 1998) plot of the molecule of the title compound. Displacement ellipsoids are shown at the 50% probability level.

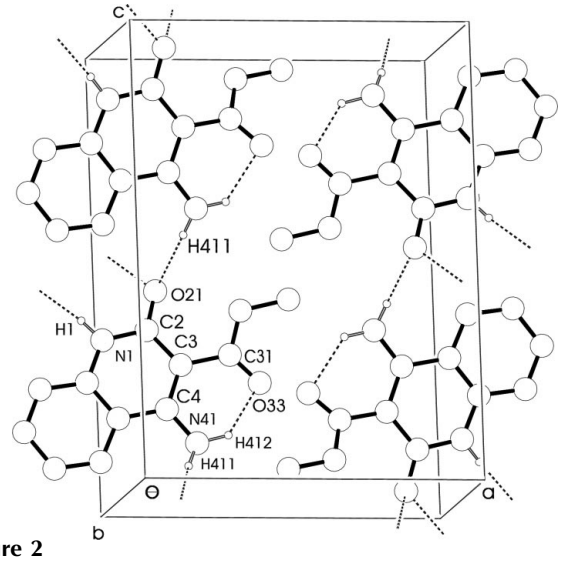


Figure 2
*PLUTON*97 (Spek, 1997) packing diagram, showing the hydrogen bonds as dashed lines.

amino group is involved in intra- and intermolecular hydrogen bonding (see Table 2 and Fig. 2).

Experimental

Preparation from (1): 2.32 g (0.01 mol) of (1) was refluxed for 1 h in 20 ml of methanol with 1.08 g (0.02 mol) sodium methylate. The reaction mixture was cooled to room temperature, 50 ml water was added and was acidified with acetic acid to pH 4. The precipitate was filtered, washed with water and dried. Methyl 4-amino-2-oxo-1,2-dihydroquinoline-3-carboxylate, (3), was obtained (yield 2.03 g, 93%). Recrystallization from dimethylformamide gave colourless crystals (m.p. 554–556 K). ^{1}H NMR (200 MHz, DMSO-d_6): 3.72 (3H, *s*, Me), 7.04–7.23 (2H, *m*, 6,8–H), 7.53 (1H, *t*, 7H), 8.07 (1H, *d*, 5–H), 8.37 (2H, *s*, NH_2), 10.84 (1H, *s*, NH). Preparation from (2): a mixture of 2.37 g (0.01 mol) of (2) and 10 ml pyridine was heated under reflux for 30 min. Then 4.13 ml (0.05 mol) propylamine and 15 ml water were added and the resulting solution boiled for 4 h. Then propylamine and most of the pyridine were removed *in vacuo*. The residue was worked up as in the previous experiment. The yield was 1.81 g (83%). A mixture of the ester (3) samples obtained by the two methods did not give a depression of the melting point. Their ^{1}H NMR spectra are identical.

Crystal data

$C_{11}H_{10}N_2O_3$
M_r = 218.21
Monoclinic, $P2_1/c$
a = 10.033 (2) Å
b = 7.27 (2) Å
c = 13.538 (3) Å
β = 90.64 (2)°
V = 987 (3) Å^3
Z = 4
D_x = 1.468 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 14–15°
μ = 0.11 mm^{-1}
T = 293 (2) K
Prism, colourless
0.40 × 0.30 × 0.20 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Non-profiled ω scans
Absorption correction: none none
1939 measured reflections
1939 independent reflections
1414 reflections with $I > 2\sigma(I)$
R_{int} = 0.010
θ_{max} = 26.0°
$h = -12 \rightarrow 12$
$k = 0 \rightarrow 8$
$l = 0 \rightarrow 16$
3 standard reflections
every 200 reflections
frequency: 133 min

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.119
S = 1.03
1939 reflections
158 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0622P)^2 + 0.1214P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.13 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.030 (4)

Table 1
Selected geometric parameters (Å, °).

N1—C2	1.358 (2)	C5—C6	1.403 (2)
N1—C10	1.379 (2)	C6—C7	1.375 (3)
C2—O21	1.2509 (19)	C7—C8	1.386 (3)
C2—C3	1.445 (2)	C8—C9	1.366 (2)
C3—C4	1.398 (2)	C9—C10	1.395 (2)
C3—C31	1.470 (2)	C31—O33	1.207 (2)
C4—N41	1.343 (2)	C31—O32	1.332 (2)
C4—C5	1.457 (2)	O32—C34	1.443 (2)
C5—C10	1.393 (2)		
C2—N1—C10	124.81 (15)	C6—C5—C4	123.93 (15)
O21—C2—N1	117.97 (14)	C7—C6—C5	121.41 (17)
O21—C2—C3	125.10 (15)	C6—C7—C8	119.66 (17)
N1—C2—C3	116.93 (14)	C9—C8—C7	120.40 (17)
C4—C3—C2	120.37 (15)	C8—C9—C10	120.10 (17)
C4—C3—C31	119.19 (15)	N1—C10—C5	119.63 (15)
C2—C3—C31	120.41 (14)	N1—C10—C9	119.64 (15)
N41—C4—C3	122.46 (16)	C5—C10—C9	120.72 (15)
N41—C4—C5	118.15 (15)	O33—C31—O32	120.92 (16)
C3—C4—C5	119.39 (14)	O33—C31—C3	124.72 (17)
C10—C5—C6	117.63 (16)	O32—C31—C3	114.30 (15)
C10—C5—C4	118.43 (14)	C31—O32—C34	115.89 (15)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O21^{i}	0.91 (2)	1.96 (2)	2.848 (8)	166 (2)
N41—H411···O21^{ii}	0.88 (2)	2.20 (2)	3.015 (9)	154 (2)
N41—H412···O33	0.97 (2)	1.90 (2)	2.677 (8)	136 (2)

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

H atoms bonded to N atoms were refined freely with isotropic displacement parameters; N—H bond lengths are in the range 0.88 (2)–0.97 (2) Å. H atoms bonded to C atoms were included in

calculated positions and refined as riding atoms. Calculated C—H bond lengths are in the range 0.93–0.96 Å.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *Software*; data reduction: *WinGX* (Farrugia, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 for Windows (Farrugia, 1998) and *PLUTON*97 (Spek, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1998).

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