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3-Ethoxycarbonyl-4-hydroxy-6-(methoxymethoxy)-1-methyl-2-quinolone

C. Gustavo Pozzi,[a]* Andrés E. Goeta,[b] Juan C. Autino[c] and Graciela Punte[a]

[a]IFLP and LANADI, Departamento de Física, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, La Plata, CC 67, Argentina, [b]Department of Chemistry, University of Durham, Durham DH1 3LE, England, and [c]LADECOR, Departamento de Química, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, 47 y 115, B1900AJL La Plata, Argentina

Correspondence e-mail:
pozzi@fisica.unlp.edu.ar

Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.002 Å
R factor = 0.041
wR factor = 0.116
Data-to-parameter ratio = 14.9

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

In the title compound, $C_{15}H_{17}NO_6$, the formation of an intramolecular O—H···O resonance-assisted hydrogen bond extends the delocalization of the electronic system beyond the two quinoline fused rings.

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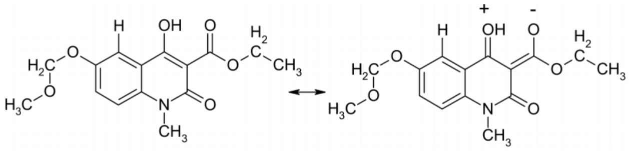
Comment

N-Alkyl-4-hydroxy-3-ethoxycarbonyl-2-quinolones having substitution at the carbocyclic ring – as well as related derivatives prepared from the 3-ethoxycarbonyl compounds, such as *N*-alkyl-4-hydroxy-3-carboxamido-2-quinolones (Ukrainets, Gorokhova, Taram, Filimonova & Turov, 1994; Fujisawa, 1995) – have shown diverse biological activities (Ukrainets, Gorokhova, Taram, Bezugly *et al.*, 1994). Moreover, 2-quinolones are valuable synthetic intermediates for other heterocyclic bioactive compounds; in particular, the title compound, (I), was employed in the synthesis of ribaline, an alkaloid of the *Rutaceae* family (Corral *et al.*, 1983). From the structural chemistry point of view, and after Gilli *et al.* (1989, 1993), these kinds of molecules are interesting due to their ability to build inter- or intramolecular hydrogen bonds assisted by resonance (RAHB). The examination of (I) by NMR in solution showed that the H5 proton exhibits a downfield shift with respect to related 2-quinolones, suggesting some double-bond character of the C—OH bond. This would indicate the presence of an intramolecular hydrogen bond involving some degree of resonance. The present low-temperature single-crystal study confirms that an intramolecular RAHB is also present in the crystalline state. This can be seen from the position of H14 (Fig. 1), the shortening of the formally single bonds O14—C4 and C3—C9 and the lengthening of the formally double bonds C4═C3 and C9═O13 (Table 2). The molecules of (I) can be considered planar, with a 0.05 Å r.m.s. deviation if C12, O19 and C20 and non-aromatic H atoms are excluded. The heterocyclic ring is less planar than the carbocyclic one, with r.m.s. deviations of 0.014 and 0.005 Å, respectively. The distortion from planarity of the former is related to a slight pyramidalization of the N atom, as measured by its departure of 0.022 (1) Å from the plane of its three bonded neighbours.



(I)

In the crystal structure, molecules are stacked in the form of centrosymmetric dimers, with a distance between ring system

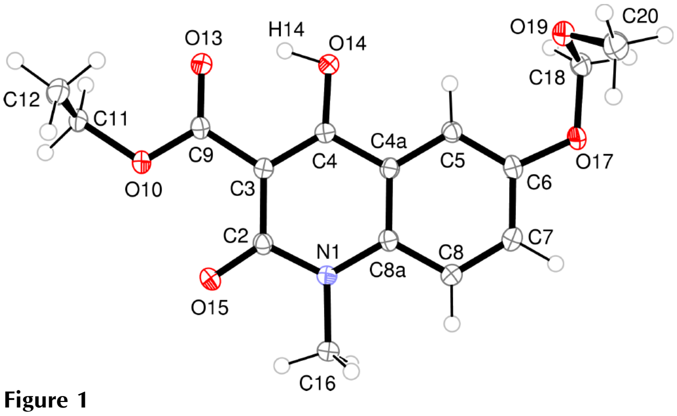


Figure 1
View of (I), showing the labelling of the non-H atoms and the hydroxyl hydrogen. Displacement ellipsoids are shown at the 50% probability level and H atoms are drawn as small circles of arbitrary radius.

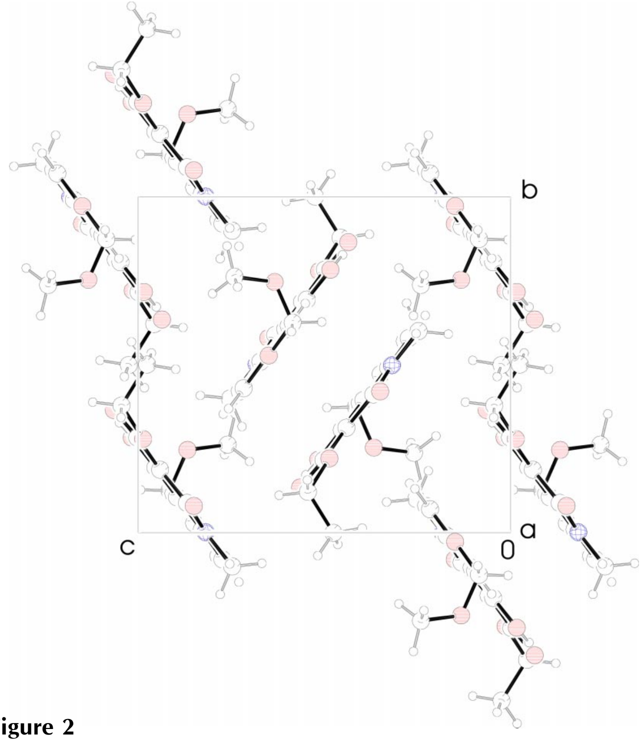


Figure 2
View down the *a* axis, showing the molecular herring-bone packing.

mean planes of 3.370 (2) Å. The dimers are arranged in a herringbone fashion (Fig. 2). The bulky substituent at C6 seems to exclude the possibility of an infinite stacking arrangement, as observed in related compounds, for example 3-benzoyl-1-ethyl-4-hydroxy-2-quinolone (Borowiec *et al.*, 1996) and 2-oxo-4-hydroxy-3-(1-phenylethylaminocarbonyl)-1-pentylquinoline (Ukrainets *et al.*, 2000).

Experimental

The title compound was prepared by thermal condensation of 4-methoxymethyleneoxy-*N*-methylaniline and tricarbethoxymethane, as described by Corral *et al.* (1983). Pale yellow crystals suitable for X-ray diffraction were obtained by slow cooling of a saturated solution in anhydrous methanol.

Crystal data

$C_{15}H_{17}NO_6$
$M_r = 307.30$
Monoclinic, $P2_1/c$
$a = 11.558$ (3) Å
$b = 10.476$ (2) Å
$c = 11.750$ (2) Å
$\beta = 98.823$ (3)°
$V = 1405.9$ (5) Å^3
$Z = 4$
$D_x = 1.445$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 755 reflections
$\theta = 13.7$–24.3°
$\mu = 0.11$ mm^{-1}
$T = 100$ (2) K
Irregular shape, colourless
0.36 × 0.26 × 0.18 mm

Data collection

Bruker SMART 1K CCD diffractometer
ω scans
Absorption correction: none
16953 measured reflections
3978 independent reflections
2908 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.037$
$\theta_{\rm max} = 30.4°$
$h = -16 \rightarrow 15$
$k = -14 \rightarrow 14$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.116$
$S = 1.01$
3978 reflections
267 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0632P)^2 + 0.3584P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.36$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.29$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O14—H14···O13	0.90 (2)	1.65 (2)	2.4844 (14)	153 (2)

Table 2
Bond distances (Å) within the RAHB fragment and their expected values (Bürgi & Dunitz, 1994).

Bond	This work	Expected
O13—C9^a	1.2392 (16)	1.199 (9)
C9—C3^a	1.4721 (17)	1.488 (14)
C3—C4^b	1.3899 (17)	1.340 (13)
C4—O14^c	1.3312 (15)	1.362 (15)

Expected values in the fragments: (*a*) C═C—C(═O)—O—C*; (*b*) C═C—C═O; (*c*) $C_{\rm ar}$—OH.

The H atoms were located from difference Fourier syntheses and refined as free isotropic atoms.

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SMART-NT*; data reduction: *SAINT-NT* (Bruker, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997) and *PLATON* (Spek, 1998); software used to prepare material for publication: *PLATON* (Spek, 1998) and *SHELXTL-NT* (Bruker, 1998).

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