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7-Chloro-1-cyclopropyl-6-fluoro-1,4-dihydro-4-oxoquinoline-3-carboxylic acid

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.040
wR factor = 0.094
Data-to-parameter ratio = 13.6

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

The title compound, $C_{13}H_9ClFNO_3$, was synthesized from ethyl 2,4-dichloro-5-fluorobenzoylacetate.

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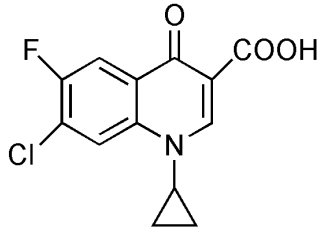
Comment

Ciprofloxacin [1-cyclopropyl-6-fluoro-1,4-dihydro-4-oxo-7-(1-piperazinyl)-3-quinolinecarboxylic acid] is one of the fluorinated quinolone antibacterial agents (Koga *et al.*, 1980), which are among the most attractive drugs in the field of anti-infective chemotherapy. These fluorinated quinolone compounds are characterized by having an F atom at the 6-position and a substituted amino group at the 7-position. The title compound, (I), is an intermediate in the synthesis of ciprofloxacin, and the molecular structure is illustrated in Fig. 1.



(I)

Experimental

The title compound was prepared according to the literature method of Grohe *et al.* (1983) from ethyl 2,4-dichloro-5-fluorobenzoylacetate. Condensation of ethyl 2,4-dichloro-5-fluorobenzoylacetate with triethyl orthoformate by refluxing in acetic anhydride produced ethyl 2-(2,4-dichloro-5-fluorobenzoyl)-3-ethoxyacrylate. This intermediate

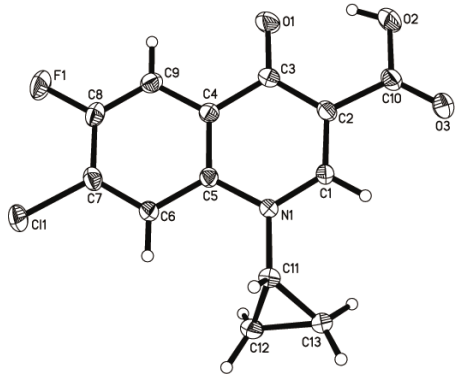


Figure 1
The molecular structure of (I), drawn with 30% probability displacement ellipsoids.

was reacted without further purification with cyclopropanamine in dichloromethane to afford ethyl 2-(2,4-dichloro-5-fluorobenzoyl)-3-cyclopropanaminoacrylate. This was cyclized by heating with sodium hydride to give 7-chloro-1-cyclopropyl-6-fluoro-1,4-dihydro-3-ethoxycarbonyl-4-oxoquinoline. The ester (50 mmol) was hydrolyzed by heating with aqueous KOH (150 mmol) in tetrahydrofuran at 353 K to give 7-chloro-1-cyclopropyl-6-fluoro-1,4-dihydro-4-oxoquinoline-3-carboxylic acid. This crude product, (I), was purified by recrystallization from *N*,*N*-dimethylformamide. Compound (I) (50 mg) was dissolved in dichloromethane (20 ml) and the solution was kept at room temperature for 10 d, whereby slow evaporation gave colourless single crystals of (I), suitable for X-ray analysis.

Crystal data

$C_{13}H_9ClFNO_3$
$M_r = 281.66$
Monoclinic, $P2_1/n$
$a = 9.194$ (4) Å
$b = 7.515$ (4) Å
$c = 16.635$ (8) Å
$\beta = 93.784$ (7)°
$V = 1146.9$ (9) Å^3
$Z = 4$
$D_x = 1.631$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 821 reflections
$\theta = 2.6$–25.9°
$\mu = 0.35$ mm^{-1}
$T = 293$ (2) K
Block, colourless
0.20 × 0.20 × 0.18 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
$T_{min} = 0.791$, $T_{max} = 0.939$
6311 measured reflections
2345 independent reflections
1753 reflections with $I > 2\sigma(I)$
$R_{int} = 0.027$
$\theta_{max} = 26.4°$
$h = -11 \rightarrow 11$
$k = -9 \rightarrow 7$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.094$
$S = 1.04$
2345 reflections
173 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0523P)^2 + 0.214P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.19$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···O1	0.82	1.80	2.559 (2)	154
O2—H2···Cl1^{i}	0.82	2.87	3.348 (2)	119

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

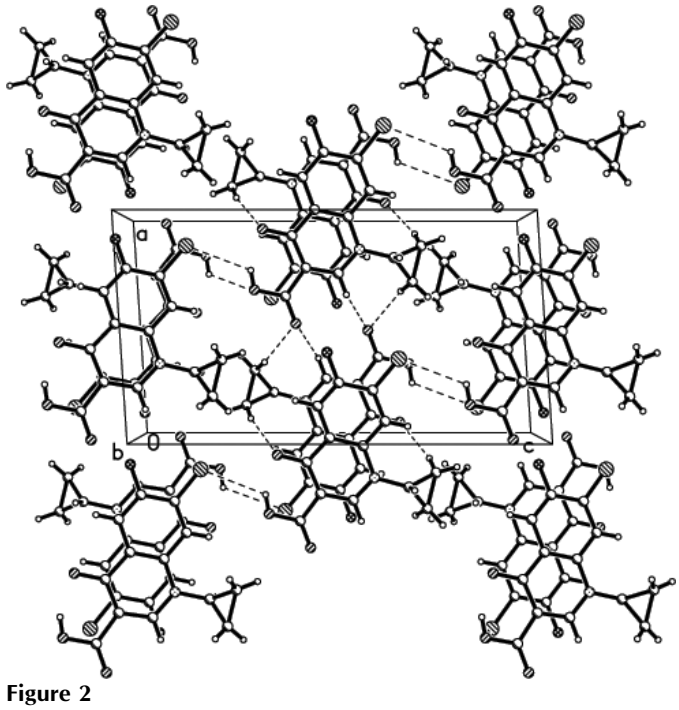


Figure 2
The crystal structure of (I), viewed along the *a* axis. Dashed lines indicate hydrogen bonds.

H atoms were positioned geometrically, with C—H = 0.93–0.98 Å, and were refined in a riding model, with $U_{iso}(H) = 1.2U_{eq}$(carrier).

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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