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1-Ethyl-6-fluoro-7-(4-formylpiperazin-1-yl)-4-oxo-1,4-dihydroquinoline-3-carboxylic acid

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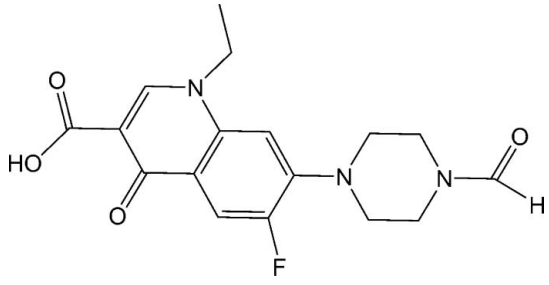
Key indicators: single-crystal X-ray study; T = 150 K; mean σ(C–C) = 0.002 Å; R factor = 0.043; wR factor = 0.123; data-to-parameter ratio = 16.0.

The formylation reaction of norfloxacin with *N*,*N*-dimethylformamide (DMF) gives the title compound, $C_{17}H_{18}FN_3O_4$. In the structure, molecules are connected *via* weak C—H···O, C—H···π and π–π interactions [perpendicular distance 3.423 Å and centroid–centroid distance 3.8141 Å].

Related literature

For related literature, see: Barbas *et al.* (2006); Basavoju *et al.* (2006); Holmes *et al.* (1985); Li *et al.* (2005).



Experimental

Crystal data

$C_{17}H_{18}FN_3O_4$
M_r = 347.34
Triclinic, $P\overline{1}$
a = 8.6689 (17) Å
b = 9.6727 (19) Å
c = 10.142 (2) Å
α = 73.41 (3)°
β = 81.41 (3)°
γ = 86.48 (3)°
V = 805.8 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 150 (2) K
0.24 × 0.20 × 0.16 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: none
6043 measured reflections
3635 independent reflections
2913 reflections with $I > 2\sigma(I)$
R_{int} = 0.020

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.123
S = 1.05
3635 reflections
227 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}

Table 1
Geometry (Å, °) of hydrogen bonds.

*Cg*1 is the centroid of the N3/C2–C6 ring.

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···O3	0.84	1.75	2.5315 (16)	154.5
C4—H4···O1^{i}	0.95	2.36	3.1872	145
C10—H10···O4^{ii}	0.95	2.58	3.4323	149
C11—H11*A*···O4^{ii}	0.99	2.42	3.3413	155
C14—H14*B*···O3^{iii}	0.99	2.46	3.2465	136
C15—H15*B*···*Cg*1^{iv}	0.99	2.64	3.3749	131

Symmetry codes: (i) $2-x, 2-y, 2-z$; (ii) $1-x, 1-y, 1-z$; (iii) $x, y, z-1$; (iv) $1-x, 1-y, 2-z$.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK*/*DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NC2060).

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supplementary materials

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1-Ethyl-6-fluoro-7-(4-formylpiperazin-1-yl)-4-oxo-1,4-dihydroquinoline-3-carboxylic acid

B. Lou, D. Boström and S. P. Velaga

Comment

Norfloxacin (1-ethyl-6-fluoro-1,4-dihydro-4-oxo-7-(1-piperazinyl)-3- quinolinecarboxylic acid) is a widely used fluoroquinolone antibacterial compound (Holmes *et al.*, 1985). For this compound, polymorphs, salts and cocrystals have been widely studied (Barbas *et al.*, 2006; Basavoju *et al.*, 2006). In this paper, we report the title compound (I), a derivative of norfloxacin.

The molecular structure of compound (I) (Fig.1) is similar with that of formylated ciprofloxacin reported previously (Li *et al.*, 2005). The piperazinyl ring adopts a chair conformation and the carboxylic group is involved in intramolecular hydrogen bonding with the quinolone oxygen atom (O2—H2···O3, see Table. 1).

In the crystal structure the molecules are connected *via* weak C—H···O interactions (Fig.2 and Table. 2). Additionally weak π-π interactions between quinolone rings and C—H···π interactions between piperazinyl ring and quinolone ring might exist (Table. 2).

Experimental

A mixture of norfloxacin (0.032 g, 0.1 mmol) and phosphoric acid (0.020 g, 0.2 mmol) was dissolved in DMF (10 ml) by heating. Afterwards, the solution was kept in air and after several days yellow crystals were obtained. The DSC showed one sharp endothermic peak at 562 K attributed to the melting transition.

Refinement

H atoms were calculated in geometrically idealized positions (OH allowed to rotate but not to tip)with C—H = 0.95–0.99 Å and O—H = 0.84 Å and were refined isotropic with U_{iso}(H) = 1.2Ueq(C,*O*) or 1.5Ueq(C) for methyl C atom using a riding model.

Figures

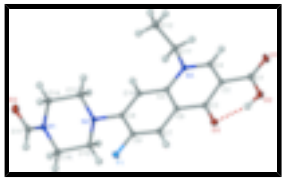

Fig. 1. *ORTEP* plot of compound (I) with 30% thermal ellipsoids. The dashed line indicate hydrogen bonding.

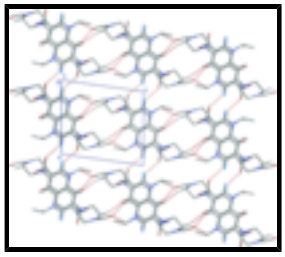

Fig. 2. Packing diagram of compound (I) viewed along *b* axis. The dashed lines indicate C—H···O interactions.

1-Ethyl-6-fluoro-7-(4-formylpiperazin-1-yl)-4-oxo-1,4-dihydroquinoline- 3-carboxylic acid

Crystal data

$C_{17}H_{18}FN_3O_4$	$Z = 2$
$M_r = 347.34$	$F_{000} = 364$
Triclinic, $P\overline{1}$	$D_x = 1.432$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 8.6689$ (17) Å	Cell parameters from 7249 reflections
$b = 9.6727$ (19) Å	$\theta = 2.6$–27.5°
$c = 10.142$ (2) Å	$\mu = 0.11$ mm^{-1}
$\alpha = 73.41$ (3)°	$T = 150$ (2) K
$\beta = 81.41$ (3)°	Block, yellow
$\gamma = 86.48$ (3)°	0.24 × 0.20 × 0.16 mm
$V = 805.8$ (3) Å^3	

Data collection

Nonius KappaCCD diffractometer	3635 independent reflections
Radiation source: fine-focus sealed tube	2913 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.020$
Detector resolution: 9 pixels mm^{-1}	$\theta_{max} = 27.4^\circ$
$T = 150(2)$ K	$\theta_{min} = 3.2^\circ$
CCD scans	$h = -11 \rightarrow 11$
Absorption correction: none	$k = -11 \rightarrow 12$
6043 measured reflections	$l = -13 \rightarrow 13$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.043$	H-atom parameters constrained
$wR(F^2) = 0.123$	$w = 1/[\sigma^2(F_o^2) + (0.0613P)^2 + 0.2204P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} < 0.001$
3635 reflections	$\Delta\rho_{max} = 0.21$ e Å^{-3}

227 parameters	$\Delta\rho_{min} = -0.25$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
F1	0.10241 (9)	0.66737 (10)	1.00486 (9)	0.0311 (2)
O3	0.45388 (12)	0.85673 (12)	1.26189 (11)	0.0311 (3)
O1	0.91842 (14)	0.96327 (14)	1.19206 (12)	0.0404 (3)
N3	0.72533 (13)	0.81858 (12)	0.90353 (12)	0.0212 (2)
C2	0.69908 (16)	0.88460 (14)	1.11704 (14)	0.0216 (3)
O2	0.68961 (14)	0.94959 (13)	1.32791 (11)	0.0342 (3)
H2	0.5985	0.9248	1.3277	0.041*
C10	0.50281 (15)	0.72728 (15)	0.83179 (14)	0.0215 (3)
H10	0.5663	0.7181	0.7498	0.026*
C6	0.47421 (15)	0.79129 (14)	1.05125 (13)	0.0204 (3)
C5	0.56759 (15)	0.77973 (14)	0.92778 (13)	0.0199 (3)
C7	0.31595 (16)	0.75016 (15)	1.07694 (14)	0.0233 (3)
H7	0.2517	0.7564	1.1596	0.028*
N2	0.27120 (13)	0.64380 (13)	0.76203 (11)	0.0220 (3)
C3	0.53768 (16)	0.84585 (14)	1.15125 (14)	0.0220 (3)
C9	0.34614 (15)	0.68881 (14)	0.85666 (14)	0.0208 (3)
C8	0.25720 (15)	0.70150 (15)	0.98143 (14)	0.0229 (3)
C1	0.77959 (18)	0.93698 (16)	1.21315 (15)	0.0272 (3)
C16	0.10726 (16)	0.46445 (15)	0.72264 (14)	0.0238 (3)
H16A	0.0806	0.3610	0.7525	0.029*
H16B	0.0098	0.5216	0.7329	0.029*
C4	0.78423 (16)	0.86968 (14)	0.99515 (14)	0.0226 (3)
H4	0.8904	0.8971	0.9750	0.027*
C13	0.35023 (17)	0.67645 (17)	0.61811 (14)	0.0274 (3)
H13A	0.4439	0.6133	0.6131	0.033*
H13B	0.3839	0.7780	0.5861	0.033*
C11	0.83052 (15)	0.80245 (16)	0.77815 (15)	0.0259 (3)
H11A	0.8088	0.7100	0.7615	0.031*
H11B	0.9401	0.7982	0.7962	0.031*
C14	0.23709 (18)	0.65157 (17)	0.52533 (15)	0.0296 (3)

H14A	0.1485	0.7214	0.5236	0.036*
H14B	0.2911	0.6673	0.4292	0.036*
C15	0.22025 (16)	0.49259 (15)	0.81329 (14)	0.0243 (3)
H15A	0.1685	0.4732	0.9105	0.029*
H15B	0.3122	0.4268	0.8117	0.029*
C12	0.81170 (18)	0.92472 (19)	0.64838 (15)	0.0330 (4)
H12A	0.7042	0.9279	0.6282	0.050*
H12B	0.8838	0.9087	0.5698	0.050*
H12C	0.8349	1.0165	0.6634	0.050*
O4	0.25308 (14)	0.44029 (14)	0.37679 (12)	0.0406 (3)
N1	0.17883 (14)	0.50451 (13)	0.57763 (12)	0.0256 (3)
C17	0.19313 (17)	0.41258 (17)	0.49896 (16)	0.0294 (3)
H17	0.1537	0.3184	0.5412	0.035*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
F1	0.0184 (4)	0.0461 (5)	0.0299 (5)	−0.0092 (4)	0.0009 (3)	−0.0130 (4)
O3	0.0297 (5)	0.0413 (6)	0.0251 (5)	−0.0075 (5)	0.0026 (4)	−0.0155 (5)
O1	0.0342 (6)	0.0570 (8)	0.0371 (6)	−0.0161 (5)	−0.0073 (5)	−0.0199 (6)
N3	0.0181 (5)	0.0254 (6)	0.0211 (5)	−0.0023 (4)	−0.0024 (4)	−0.0077 (4)
C2	0.0241 (7)	0.0191 (6)	0.0222 (6)	−0.0022 (5)	−0.0058 (5)	−0.0052 (5)
O2	0.0379 (6)	0.0423 (6)	0.0280 (6)	−0.0089 (5)	−0.0049 (5)	−0.0168 (5)
C10	0.0196 (6)	0.0243 (7)	0.0204 (6)	−0.0029 (5)	−0.0016 (5)	−0.0061 (5)
C6	0.0211 (6)	0.0190 (6)	0.0204 (6)	−0.0008 (5)	−0.0037 (5)	−0.0042 (5)
C5	0.0179 (6)	0.0199 (6)	0.0211 (6)	−0.0009 (5)	−0.0032 (5)	−0.0040 (5)
C7	0.0221 (7)	0.0264 (7)	0.0200 (6)	−0.0027 (5)	−0.0005 (5)	−0.0051 (5)
N2	0.0221 (5)	0.0240 (6)	0.0194 (5)	−0.0062 (4)	−0.0034 (4)	−0.0041 (4)
C3	0.0262 (7)	0.0182 (6)	0.0210 (6)	−0.0008 (5)	−0.0036 (5)	−0.0042 (5)
C9	0.0212 (6)	0.0205 (6)	0.0204 (6)	−0.0019 (5)	−0.0051 (5)	−0.0039 (5)
C8	0.0165 (6)	0.0259 (7)	0.0244 (7)	−0.0042 (5)	−0.0017 (5)	−0.0040 (5)
C1	0.0318 (7)	0.0265 (7)	0.0246 (7)	−0.0047 (6)	−0.0067 (6)	−0.0069 (6)
C16	0.0226 (6)	0.0245 (7)	0.0243 (7)	−0.0050 (5)	−0.0030 (5)	−0.0062 (5)
C4	0.0214 (6)	0.0209 (6)	0.0260 (7)	−0.0029 (5)	−0.0056 (5)	−0.0057 (5)
C13	0.0270 (7)	0.0334 (8)	0.0218 (7)	−0.0117 (6)	−0.0007 (6)	−0.0070 (6)
C11	0.0172 (6)	0.0354 (8)	0.0292 (7)	−0.0026 (5)	−0.0005 (5)	−0.0168 (6)
C14	0.0345 (8)	0.0324 (8)	0.0223 (7)	−0.0110 (6)	−0.0059 (6)	−0.0050 (6)
C15	0.0254 (7)	0.0218 (7)	0.0254 (7)	−0.0044 (5)	−0.0059 (5)	−0.0041 (5)
C12	0.0295 (7)	0.0458 (9)	0.0241 (7)	−0.0067 (7)	0.0020 (6)	−0.0120 (6)
O4	0.0386 (6)	0.0569 (8)	0.0344 (6)	−0.0012 (6)	−0.0048 (5)	−0.0258 (6)
N1	0.0249 (6)	0.0290 (6)	0.0251 (6)	−0.0057 (5)	−0.0037 (5)	−0.0098 (5)
C17	0.0244 (7)	0.0363 (8)	0.0328 (8)	0.0005 (6)	−0.0095 (6)	−0.0155 (6)

Geometric parameters (Å, °)

F1—C8	1.3713 (15)	C16—N1	1.4594 (18)
O3—C3	1.2699 (17)	C16—C15	1.5243 (19)
O1—C1	1.2201 (19)	C16—H16A	0.9900
N3—C4	1.3428 (17)	C16—H16B	0.9900

N3—C5	1.4076 (17)	C4—H4	0.9500
N3—C11	1.4909 (17)	C13—C14	1.529 (2)
C2—C4	1.3822 (19)	C13—H13A	0.9900
C2—C3	1.4365 (19)	C13—H13B	0.9900
C2—C1	1.4908 (19)	C11—C12	1.520 (2)
O2—C1	1.3328 (18)	C11—H11A	0.9900
O2—H2	0.8400	C11—H11B	0.9900
C10—C9	1.3974 (18)	C14—N1	1.4619 (19)
C10—C5	1.4146 (19)	C14—H14A	0.9900
C10—H10	0.9500	C14—H14B	0.9900
C6—C5	1.4150 (18)	C15—H15A	0.9900
C6—C7	1.4175 (19)	C15—H15B	0.9900
C6—C3	1.4553 (19)	C12—H12A	0.9800
C7—C8	1.363 (2)	C12—H12B	0.9800
C7—H7	0.9500	C12—H12C	0.9800
N2—C9	1.4116 (17)	O4—C17	1.2298 (19)
N2—C13	1.4712 (17)	N1—C17	1.3435 (19)
N2—C15	1.4768 (17)	C17—H17	0.9500
C9—C8	1.4130 (19)		
C4—N3—C5	119.98 (11)	N3—C4—C2	123.71 (12)
C4—N3—C11	118.71 (11)	N3—C4—H4	118.1
C5—N3—C11	121.30 (11)	C2—C4—H4	118.1
C4—C2—C3	120.16 (12)	N2—C13—C14	108.92 (11)
C4—C2—C1	118.61 (12)	N2—C13—H13A	109.9
C3—C2—C1	121.20 (12)	C14—C13—H13A	109.9
C1—O2—H2	109.5	N2—C13—H13B	109.9
C9—C10—C5	120.53 (12)	C14—C13—H13B	109.9
C9—C10—H10	119.7	H13A—C13—H13B	108.3
C5—C10—H10	119.7	N3—C11—C12	113.11 (12)
C5—C6—C7	119.28 (12)	N3—C11—H11A	109.0
C5—C6—C3	121.07 (12)	C12—C11—H11A	109.0
C7—C6—C3	119.66 (12)	N3—C11—H11B	109.0
N3—C5—C10	120.87 (12)	C12—C11—H11B	109.0
N3—C5—C6	119.15 (12)	H11A—C11—H11B	107.8
C10—C5—C6	119.97 (12)	N1—C14—C13	110.16 (12)
C8—C7—C6	119.10 (12)	N1—C14—H14A	109.6
C8—C7—H7	120.5	C13—C14—H14A	109.6
C6—C7—H7	120.5	N1—C14—H14B	109.6
C9—N2—C13	116.48 (11)	C13—C14—H14B	109.6
C9—N2—C15	113.88 (11)	H14A—C14—H14B	108.1
C13—N2—C15	111.25 (11)	N2—C15—C16	110.17 (11)
O3—C3—C2	122.95 (12)	N2—C15—H15A	109.6
O3—C3—C6	121.14 (12)	C16—C15—H15A	109.6
C2—C3—C6	115.91 (12)	N2—C15—H15B	109.6
C10—C9—N2	123.69 (12)	C16—C15—H15B	109.6
C10—C9—C8	117.67 (12)	H15A—C15—H15B	108.1
N2—C9—C8	118.60 (12)	C11—C12—H12A	109.5
C7—C8—F1	118.55 (12)	C11—C12—H12B	109.5
C7—C8—C9	123.45 (12)	H12A—C12—H12B	109.5

F1—C8—C9	117.96 (12)	C11—C12—H12C	109.5
O1—C1—O2	121.46 (13)	H12A—C12—H12C	109.5
O1—C1—C2	123.40 (13)	H12B—C12—H12C	109.5
O2—C1—C2	115.11 (12)	C17—N1—C16	122.70 (12)
N1—C16—C15	109.65 (11)	C17—N1—C14	122.50 (13)
N1—C16—H16A	109.7	C16—N1—C14	114.79 (11)
C15—C16—H16A	109.7	O4—C17—N1	125.40 (15)
N1—C16—H16B	109.7	O4—C17—H17	117.3
C15—C16—H16B	109.7	N1—C17—H17	117.3
H16A—C16—H16B	108.2		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O3	0.84	1.75	2.5315 (16)	155

Geometry (Å, °) of hydrogen bonds and π–π interactions

*Cg*1 is the centroid of the N3/C2–C6 ring.

D-H···A	D-H(Å)	H···A(Å)	D···A(Å)	D-H···A(°)
O2—H2···O3	0.84	1.75	2.5315 (16)	154.5
C4-H4···O1^{i}	0.95	2.36	3.1872	145
C10-H10···O4^{ii}	0.95	2.58	3.4323	149
C11-H11A···O4^{ii}	0.99	2.42	3.3413	155
C14-H14B···O3^{iii}	0.99	2.46	3.2465	136
C15-H15B···*Cg*1^{iv}	0.99	2.64	3.3749	131
*Cg*1···*Cg*1^{v}		3.423[a]	3.8141[b]	26[c]

Notes: (*a*) Perpendicular distance of rings. (*b*) Distance between ring centroids. (*c*) Angle between the *Cg*1→*Cg*1^{v} vector and the normal to the plane of *Cg*1^{v}.
Symmetry codes: (i) 2 − *x*,2 − *y*,2 − *z*; (ii)1 − *x*,1 − *y*,1 − *z*; (iii) *x*,*y*,*z* − 1; (iv)1 − *x*,1 − *y*,2 − *z*; (v) 1 − *x*,2 − *y*,2 − *z*

Fig. 1

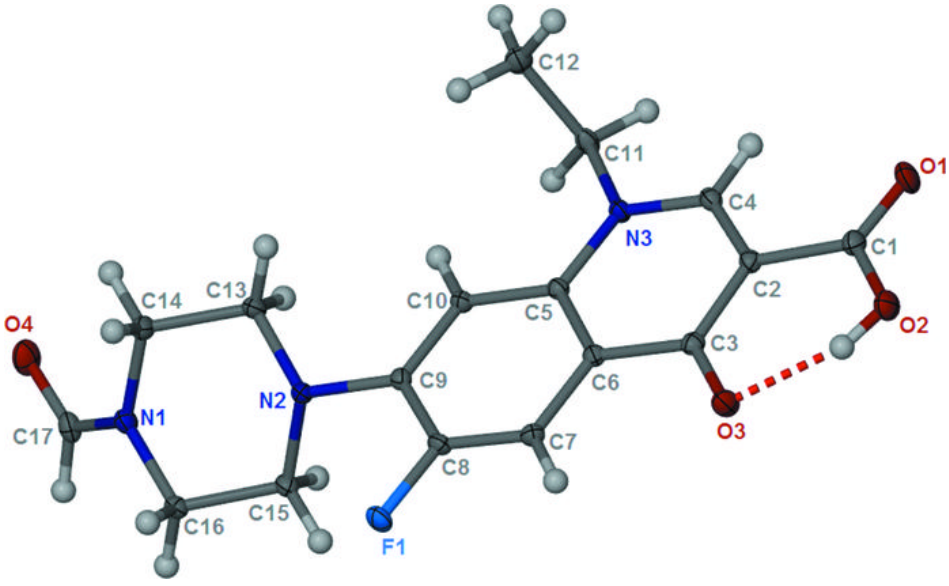
C12
C11
O1
C4
N3
C1
C14
C13
C10
C5
C2
O2
O4
C3
N2
C9
C6
N1
O3
C17
C7
C8
C16
C15
F1

Fig. 2