Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

1-Cyclopropyl-6-fluoro-7-(4-nitroso-piperazin-1-yl)-4-oxo-1,4-dihydro-quinoline-3-carboxylic acid

Tao Li,[a] Li-Rong Tang,[b] Qiao-Ling Zeng,[b] Wei-Jin Chen[a] and Biao Huang[b]*

[a]School of Life Sciences, Fujian Agriculture and Forestry University, Fuzhou, Fujian 350002, People's Republic of China, and [b]Material Engineering College, Fujian Agriculture and Forestry University, Fuzhou, Fujian 350002, People's Republic of China
Correspondence e-mail: ltdl@sina.com

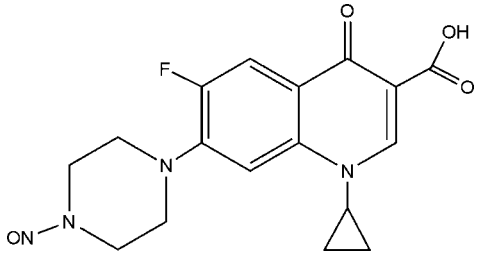
Received 20 June 2009; accepted 27 July 2009

Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.003 Å; R factor = 0.067; wR factor = 0.207; data-to-parameter ratio = 15.4.

The title compound, $C_{17}H_{17}FN_4O_4$, is a derivative of ciprofloxacin [1-cyclopropyl-6-fluoro-4-oxo-7-(1-piperazinyl)-1,4-dihydroquinoline-3-carboxylic acid]. The crystal packing is stabilized by intermolecular C—H···O hydrogen bonds together with π–π electron ring interactions [centroid–centroid separations between quinoline rings of 3.5864 (11) and 3.9339 (13) Å]. A strong intramolecular O—H···O hydrogen bonds is present as well as an intramolecular C—H···F interaction.

Related literature

For the biological activity of ciprofloxacin compounds, see: Neu (1987). For related structures, see: Turel *et al.* (1996); Drevenšek *et al.* (2003); Li *et al.* (2005); Lou *et al.* (2007). The nitroso-group geometry is similar to that observed in 1,4-dinitrosopiperazine, see: Sekido *et al.* (1985).



Experimental

Crystal data

$C_{17}H_{17}FN_4O_4$
M_r = 360.35
Triclinic, $P\overline{1}$
a = 8.378 (3) Å
b = 9.625 (4) Å
c = 10.328 (4) Å
α = 102.99 (2)°
β = 96.089 (14)°
γ = 97.392 (16)°
V = 797.0 (6) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.12 mm^{-1}
T = 293 K
0.2 × 0.2 × 0.2 mm

Data collection

Rigaku Mercury CCD/AFC diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2007)
T_{min} = 0.976, T_{max} = 0.977
6267 measured reflections
3631 independent reflections
2568 reflections with $I > 2\sigma(I)$
R_{int} = 0.031

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.067
$wR(F^2)$ = 0.207
S = 1.06
3631 reflections
236 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.52 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H18···O3	0.84	1.78	2.562 (2)	153
C15—H15A···O2^{i}	0.99	2.50	3.405 (3)	151
C15—H15B···O3^{ii}	0.99	2.51	3.385 (3)	147
C16—H16A···O1^{iii}	0.99	2.60	3.264 (3)	125
C16—H16B···F1	0.99	2.14	2.852 (3)	128

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

Data collection: *CrystalClear* (Rigaku, 2007); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXL97* and *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

The work was supported by a grant from the National Science Foundation of China (30771682).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FB2160).

References

Brandenburg, K. (2005). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Drevenšek, P., Leban, I., Turel, I., Giester, G. & Tillmanns, E. (2003). *Acta Cryst.* C**59**, m376–m378.
Li, X.-W., Zhi, F., Shen, J.-H. & Hu, Y.-Q. (2005). *Acta Cryst.* E**61**, o2235–o2236.
Lou, B., Boström, D. & Velaga, S. P. (2007). *Acta Cryst.* C**63**, o731–o733.
Neu, H. C. (1987). *Am. J. Med.* **82**, 395-404.
Rigaku (2007). *CrystalClear*. Rigaku Corporation, Tokyo, Japan.
Sekido, K., Okamoto, K. & Hirokawa, S. (1985). *Acta Cryst.* C**41**, 741–743.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Turel, I., Leban, I., Zupancic, M., Bukovec, P. & Gruber, K. (1996). *Acta Cryst.* C**52**, 2443–2445.

supplementary materials

Acta Cryst. (2009). E**65**, o2053 [**doi:10.1107/S1600536809029729**]

1-Cyclopropyl-6-fluoro-7-(4-nitrosopiperazin-1-yl)-4-oxo-1,4-dihydroquinoline-3-carboxylic acid

T. Li, L.-R. Tang, Q.-L. Zeng, W.-J. Chen and B. Huang

Comment

Ciprofloxacin (1-cyclopropyl-6-fluoro -1,4-dihydro-4-oxo-7-(1-piperazinyl)-3-quinoline carboxylic acid) is used as an antibacterial agent. Ciprofloxacin is widely used in clinical practice for the treatment of certain diseases caused by some Gram negative and as well as Gram positive microorganisms (Neu, 1987). Recently, several structures containing ciprofloxacin have been reported (Turel *et al.*, 1996; Drevenšek *et al.*, 2003; Lou *et al.*, 2007).

Nitrosation of amines by nitrites takes place in acid medium. The nature of the product depends on the nature of the initial amine. Commonly the secondary alkyl amines yield *N*-nitrosoamines. In our case, the *N*-nitrosation of ciprofloxacin occurs by ytterbium nitrate in nitric acid and results in the formation of ON-ciprofloxacin under hydrothermal reaction.

The title compound is composed of an essentially planar quinoline ring system [the mean deviation from best plane is 0.0274 (2) Å] which is substituted with cyclopropyl, fluoro, oxo, carboxyl and nitrosopiperazinium groups (Fig. 1). The bond distances and angles are in agreement with those in 1-cyclopropyl-6-fluoro-7- (4-formylpiperazin-1-yl)-4-oxo-1,4-dihydroquinoline-3-carboxylic acid (Li *et al.*, 2005).

In the title structure, the six-membered piperazinyl ring adopts a chair conformation. The nitroso-group geometry with the NO distance equal to 1.2382 (31) Å and O—N—N bond angle of 115.583 (20)° is similar to that observed in 1,4-dinitrosopiperazine (Sekido *et al.*, 1985).

For the hydrogen bonding, please see Tab. 1 that comprises intramolecular and intermolecular hydrogen bonds in the structure (Fig. 2). As shown in Fig. 3, the crystal packing is stabilized by π-π stacking interactions of the quinoline rings, in which the N1 ring (N1/C4—C6/C7—C13) stacks with the inversion-related N1 rings, with the centroid-centroid separations of 3.5864 (11) and 3.9339 (13) Å.

Experimental

The title compound was hydrothermally synthesized under autogenous pressure. A mixture of $C_{17}H_{18}FN_3O_3$.HCl (ciprofloxacin hydrochloride) (50 mg, 0.14 mmol), $Yb(NO_3)_3$ (72 mg, 0.2 mmol), HNO_3 (1 ml of 0.5 M), C_2H_5OH (4 ml) and H_2O (8 ml) was sealed in a stainless reactor with a Teflon liner. The mixture was heated to 393 K for one day. After cooling at a rate of 10 K h^{-1} to room temperature, yellow needle crystals (average 4 mm long by 0.6 mm diameter) were separated by filtration, washed with distilled water and finally dried in air. Yield 75%, Anal. calc. for $C_{17}H_{17}FN_4O_4$: C, 56.66; H, 4.76; N, 15.55%; Found: C, 56.82; H, 4.75; N, 15.63%. IR (KBr pellet): 1719(*s*), 1627(*s*), 1489(*m*), 1454(*m*), 1334(*m*), 1339(*m*), 1257(*s*), 1152(*m*), 994(*m*), 896(*m*), 798(*m*), 743(*m*).

Refinement

All the hydrogen atoms were discernible in the difference electron density maps. However, the hydrogens were situated into idealized positions and constrained by the riding model approximation: O—$H_{carboxyl}$ = 0.84 [the command AFIX 147 of SHELXL-97 has been applied (Sheldrick, 2008)], C_{aryl}—H_{aryl} = 0.95, $C_{methylene}$—$H_{methylene}$ = 0.99 and $C_{methine}$—$H_{methine}$ = 1.00 Å; $U_{iso}H = 1.2U_{eq}(C)$; $U_{iso}H_{carboxyl} = 1.5U_{eq}(O)$. The highest electron-density peak is situated 1.12 Å from H16A and the deepest hole 0.54 Å from C17.

Figures

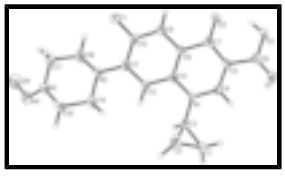


Fig. 1. View of the title molecule. The displacement ellipsoids are drawn at the 30% propability level

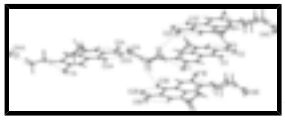


Fig. 2. The intramolecular and intermoleclar hydrogen bonds or interactions (the dashed lines) in title compound (see Table 1). Symmetry codes: (A) *x*+1, *y*+1, *z*+1; (B) *x*+1, *y*+1, *z*; (C) *x*, *y*+1, *z*

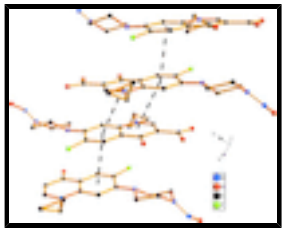


Fig. 3. The packing of title molecules, showing the π-π-electron ring interactions. The H atoms have been omitted for clarity

1-Cyclopropyl-6-fluoro-7-(4-nitrosopiperazin-1-yl)-4-oxo- 1,4-dihydroquinoline-3-carboxylic acid

Crystal data

$C_{17}H_{17}FN_4O_4$	$Z = 2$
$M_r = 360.35$	$F_{000} = 376$
Triclinic, $P\overline{1}$	$D_x = 1.502$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, λ = 0.71073 Å
$a = 8.378$ (3) Å	Cell parameters from 771 reflections
$b = 9.625$ (4) Å	θ = 2.0–27.4º
$c = 10.328$ (4) Å	μ = 0.12 mm^{-1}
α = 102.99 (2)º	$T = 293$ K
β = 96.089 (14)º	Block, yellow
γ = 97.392 (16)º	0.2 × 0.2 × 0.2 mm
$V = 797.0$ (6) Å^3	

Data collection

Rigaku Mercury CCD/AFC	3631 independent reflections

diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

T = 293 K

φ and ω scans

Absorption correction: multi-scan (CrystalClear; Rigaku, 2007)

T_{min} = 0.976, T_{max} = 0.977

6267 measured reflections

2568 reflections with $I > 2\sigma(I)$

R_{int} = 0.031

θ_{max} = 27.4º

θ_{min} = 2.5º

$h = -10 \rightarrow 10$

$k = -12 \rightarrow 12$

$l = -13 \rightarrow 11$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)]$ = 0.067

$wR(F^2)$ = 0.207

S = 1.06

3631 reflections

236 parameters

67 constraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: difference Fourier map

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1165P)^2 + 0.047P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max}$ = 0.52 e Å^{-3}

$\Delta\rho_{min}$ = −0.35 e Å^{-3}

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 $F^2 > \sigma(F^2)$ 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}
N1	0.14474 (19)	0.38921 (17)	0.16119 (15)	0.0330 (4)
O2	−0.1340 (2)	0.09746 (18)	−0.25939 (15)	0.0561 (5)
H18	−0.0827	0.1674	−0.2814	0.084*
O3	0.0676 (2)	0.32428 (17)	−0.25086 (13)	0.0472 (4)
C8	0.2117 (2)	0.4611 (2)	−0.03990 (18)	0.0331 (4)
F1	0.51960 (16)	0.74426 (14)	−0.07933 (12)	0.0505 (4)
C13	0.2335 (2)	0.48548 (19)	0.10118 (18)	0.0318 (4)
C11	0.4372 (2)	0.6987 (2)	0.1245 (2)	0.0342 (4)
C5	0.0120 (2)	0.2477 (2)	−0.05450 (19)	0.0356 (5)

O1	−0.1742 (2)	0.03235 (18)	−0.07173 (17)	0.0580 (5)
C12	0.3415 (2)	0.6063 (2)	0.18211 (19)	0.0344 (4)
H12A	0.3488	0.6247	0.2770	0.041*
C9	0.3081 (3)	0.5551 (2)	−0.0978 (2)	0.0372 (5)
H9A	0.2962	0.5415	−0.1925	0.045*
N2	0.5528 (2)	0.81427 (18)	0.20147 (16)	0.0380 (4)
C7	0.0944 (2)	0.3414 (2)	−0.1242 (2)	0.0361 (5)
C10	0.4184 (3)	0.6654 (2)	−0.0179 (2)	0.0361 (5)
C4	0.0408 (2)	0.2758 (2)	0.0830 (2)	0.0359 (5)
H4A	−0.0163	0.2111	0.1257	0.043*
C6	−0.1066 (3)	0.1168 (2)	−0.1269 (2)	0.0428 (5)
N3	0.7368 (3)	1.0685 (2)	0.37104 (18)	0.0492 (5)
C3	0.1612 (3)	0.4155 (2)	0.30774 (19)	0.0373 (5)
H3A	0.1132	0.4997	0.3544	0.045*
C14	0.5794 (3)	0.8301 (2)	0.3473 (2)	0.0473 (6)
H14A	0.5869	0.7346	0.3663	0.057*
H14B	0.4859	0.8666	0.3870	0.057*
C2	0.3112 (3)	0.3878 (3)	0.3816 (2)	0.0512 (6)
H2A	0.3549	0.4545	0.4696	0.061*
H2B	0.3943	0.3493	0.3283	0.061*
C15	0.7354 (3)	0.9344 (2)	0.4114 (2)	0.0487 (6)
H15A	0.7434	0.9535	0.5103	0.058*
H15B	0.8306	0.8901	0.3840	0.058*
C16	0.5548 (3)	0.9558 (3)	0.1687 (2)	0.0570 (7)
H16A	0.4633	1.0008	0.2039	0.068*
H16B	0.5390	0.9417	0.0700	0.068*
C17	0.7110 (3)	1.0550 (3)	0.2268 (2)	0.0574 (7)
H17A	0.8022	1.0156	0.1856	0.069*
H17B	0.7058	1.1509	0.2082	0.069*
C1	0.1525 (3)	0.2910 (3)	0.3709 (2)	0.0551 (7)
H1A	0.1379	0.1929	0.3111	0.066*
H1B	0.0986	0.2981	0.4524	0.066*
N4	0.7544 (3)	1.1903 (2)	0.4635 (2)	0.0654 (7)
O4	0.7463 (3)	1.3001 (2)	0.4211 (2)	0.0895 (7)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0369 (9)	0.0264 (8)	0.0303 (8)	−0.0042 (6)	−0.0015 (7)	0.0040 (6)
O2	0.0664 (11)	0.0464 (10)	0.0397 (9)	−0.0092 (8)	−0.0087 (8)	−0.0047 (7)
O3	0.0588 (10)	0.0433 (9)	0.0306 (8)	−0.0015 (7)	−0.0052 (7)	0.0012 (6)
C8	0.0372 (10)	0.0277 (9)	0.0302 (10)	0.0036 (8)	−0.0017 (8)	0.0023 (7)
F1	0.0587 (8)	0.0475 (8)	0.0438 (7)	−0.0084 (6)	0.0111 (6)	0.0155 (6)
C13	0.0359 (10)	0.0249 (9)	0.0310 (10)	0.0015 (8)	0.0008 (8)	0.0029 (7)
C11	0.0373 (10)	0.0278 (9)	0.0340 (10)	0.0004 (8)	−0.0015 (8)	0.0061 (8)
C5	0.0382 (10)	0.0268 (10)	0.0348 (11)	0.0003 (8)	−0.0037 (8)	−0.0008 (8)
O1	0.0590 (11)	0.0456 (10)	0.0569 (10)	−0.0192 (8)	−0.0103 (8)	0.0103 (8)
C12	0.0416 (11)	0.0270 (9)	0.0295 (10)	−0.0019 (8)	0.0003 (8)	0.0025 (7)

C9	0.0455 (11)	0.0354 (10)	0.0293 (10)	0.0065 (9)	0.0029 (8)	0.0057 (8)
N2	0.0446 (10)	0.0308 (9)	0.0329 (9)	−0.0071 (7)	−0.0044 (7)	0.0074 (7)
C7	0.0390 (11)	0.0306 (10)	0.0336 (10)	0.0058 (8)	−0.0010 (8)	−0.0002 (8)
C10	0.0395 (10)	0.0312 (10)	0.0375 (11)	0.0008 (8)	0.0039 (8)	0.0115 (8)
C4	0.0361 (10)	0.0284 (10)	0.0380 (11)	−0.0023 (8)	−0.0013 (8)	0.0043 (8)
C6	0.0426 (11)	0.0340 (11)	0.0436 (12)	0.0024 (9)	−0.0064 (9)	0.0002 (9)
N3	0.0662 (13)	0.0354 (10)	0.0359 (9)	−0.0088 (9)	−0.0016 (9)	0.0013 (7)
C3	0.0473 (12)	0.0311 (10)	0.0294 (10)	−0.0022 (8)	0.0031 (8)	0.0045 (8)
C14	0.0608 (14)	0.0394 (12)	0.0337 (11)	−0.0112 (10)	−0.0030 (10)	0.0075 (9)
C2	0.0527 (14)	0.0551 (14)	0.0393 (12)	−0.0017 (11)	−0.0041 (10)	0.0086 (10)
C15	0.0607 (15)	0.0401 (12)	0.0364 (11)	−0.0056 (10)	−0.0068 (10)	0.0051 (9)
C16	0.0679 (16)	0.0395 (13)	0.0546 (14)	−0.0137 (11)	−0.0191 (12)	0.0179 (11)
C17	0.0767 (18)	0.0424 (13)	0.0451 (13)	−0.0128 (12)	−0.0004 (12)	0.0104 (10)
C1	0.0709 (16)	0.0458 (13)	0.0420 (12)	−0.0121 (12)	−0.0059 (11)	0.0150 (10)
N4	0.0859 (17)	0.0430 (12)	0.0536 (13)	−0.0081 (11)	0.0084 (12)	−0.0059 (10)
O4	0.132 (2)	0.0383 (11)	0.0856 (16)	0.0046 (12)	0.0002 (14)	0.0002 (10)

Geometric parameters (Å, °)

N1—C4	1.346 (2)	C4—H4A	0.9500
N1—C13	1.405 (2)	N3—N4	1.315 (3)
N1—C3	1.466 (2)	N3—C15	1.442 (3)
O2—C6	1.330 (3)	N3—C17	1.456 (3)
O2—H18	0.8400	C3—C1	1.485 (3)
O3—C7	1.273 (2)	C3—C2	1.485 (3)
C8—C9	1.410 (3)	C3—H3A	1.0000
C8—C13	1.411 (3)	C14—C15	1.528 (3)
C8—C7	1.458 (3)	C14—H14A	0.9900
F1—C10	1.365 (2)	C14—H14B	0.9900
C13—C12	1.414 (3)	C2—C1	1.501 (3)
C11—C12	1.394 (3)	C2—H2A	0.9900
C11—N2	1.404 (2)	C2—H2B	0.9900
C11—C10	1.420 (3)	C15—H15A	0.9900
C5—C4	1.373 (3)	C15—H15B	0.9900
C5—C7	1.431 (3)	C16—C17	1.496 (3)
C5—C6	1.493 (3)	C16—H16A	0.9900
O1—C6	1.210 (3)	C16—H16B	0.9900
C12—H12A	0.9500	C17—H17A	0.9900
C9—C10	1.361 (3)	C17—H17B	0.9900
C9—H9A	0.9500	C1—H1A	0.9900
N2—C14	1.469 (3)	C1—H1B	0.9900
N2—C16	1.474 (3)	N4—O4	1.238 (3)
C4—N1—C13	119.38 (16)	C1—C3—C2	60.70 (16)
C4—N1—C3	120.52 (15)	N1—C3—H3A	115.5
C13—N1—C3	120.07 (15)	C1—C3—H3A	115.5
C6—O2—H18	109.5	C2—C3—H3A	115.5
C9—C8—C13	118.03 (17)	N2—C14—C15	110.91 (17)
C9—C8—C7	120.60 (17)	N2—C14—H14A	109.5
C13—C8—C7	121.36 (18)	C15—C14—H14A	109.5

N1—C13—C8	119.20 (16)	N2—C14—H14B	109.5
N1—C13—C12	120.02 (17)	C15—C14—H14B	109.5
C8—C13—C12	120.77 (17)	H14A—C14—H14B	108.0
C12—C11—N2	122.48 (18)	C3—C2—C1	59.64 (15)
C12—C11—C10	116.46 (17)	C3—C2—H2A	117.8
N2—C11—C10	120.98 (17)	C1—C2—H2A	117.8
C4—C5—C7	120.37 (17)	C3—C2—H2B	117.8
C4—C5—C6	117.68 (18)	C1—C2—H2B	117.8
C7—C5—C6	121.95 (18)	H2A—C2—H2B	114.9
C11—C12—C13	120.90 (18)	N3—C15—C14	110.6 (2)
C11—C12—H12A	119.6	N3—C15—H15A	109.5
C13—C12—H12A	119.6	C14—C15—H15A	109.5
C10—C9—C8	119.97 (18)	N3—C15—H15B	109.5
C10—C9—H9A	120.0	C14—C15—H15B	109.5
C8—C9—H9A	120.0	H15A—C15—H15B	108.1
C11—N2—C14	117.59 (15)	N2—C16—C17	111.9 (2)
C11—N2—C16	117.81 (17)	N2—C16—H16A	109.2
C14—N2—C16	111.17 (17)	C17—C16—H16A	109.2
O3—C7—C5	123.16 (18)	N2—C16—H16B	109.2
O3—C7—C8	121.43 (18)	C17—C16—H16B	109.2
C5—C7—C8	115.41 (17)	H16A—C16—H16B	107.9
C9—C10—F1	117.51 (17)	N3—C17—C16	108.62 (19)
C9—C10—C11	123.63 (18)	N3—C17—H17A	110.0
F1—C10—C11	118.81 (17)	C16—C17—H17A	110.0
N1—C4—C5	124.20 (18)	N3—C17—H17B	110.0
N1—C4—H4A	117.9	C16—C17—H17B	110.0
C5—C4—H4A	117.9	H17A—C17—H17B	108.3
O1—C6—O2	121.06 (19)	C3—C1—C2	59.66 (15)
O1—C6—C5	123.8 (2)	C3—C1—H1A	117.8
O2—C6—C5	115.15 (19)	C2—C1—H1A	117.8
N4—N3—C15	119.31 (19)	C3—C1—H1B	117.8
N4—N3—C17	125.3 (2)	C2—C1—H1B	117.8
C15—N3—C17	115.35 (18)	H1A—C1—H1B	114.9
N1—C3—C1	119.44 (18)	O4—N4—N3	115.6 (2)
N1—C3—C2	119.07 (18)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H18···O3	0.84	1.78	2.562 (2)	153
C4—H4A···O1	0.95	2.48	2.812 (3)	101
C15—H15A···O2^{i}	0.99	2.50	3.405 (3)	151
C15—H15B···O3^{ii}	0.99	2.51	3.385 (3)	147
C16—H16A···O1^{iii}	0.99	2.60	3.264 (3)	125
C16—H16B···F1	0.99	2.14	2.852 (3)	128
C17—H17B···O4	0.99	2.30	2.692 (3)	102

Symmetry codes: (i) *x*+1, *y*+1, *z*+1; (ii) −*x*+1, −*y*+1, −*z*; (iii) −*x*, −*y*+1, −*z*.

Fig. 1

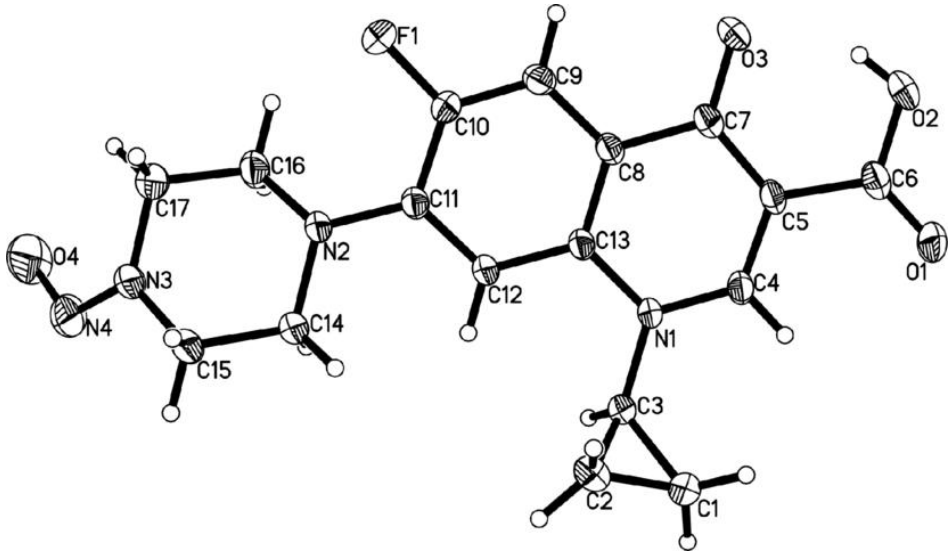

F1
C9
O3
C10
C7
O2
C16
C8
C6
C17
C11
C5
O4
N2
C13
O1
N3
C12
C4
N4
C14
N1
C15
C3
C2
C1

Fig. 2

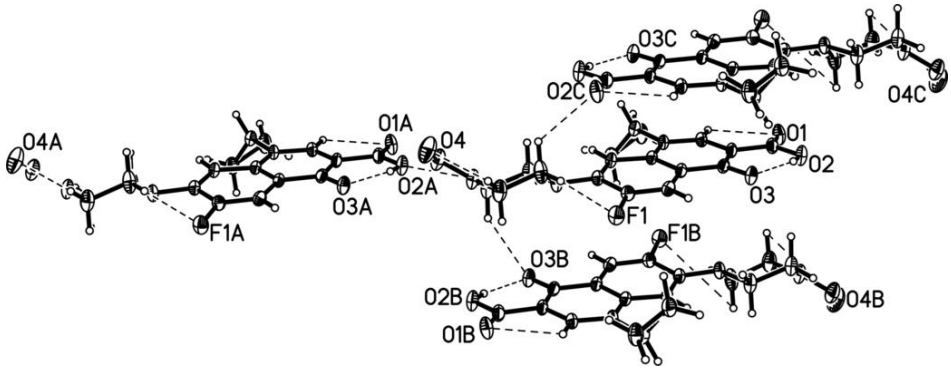


Fig. 3