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Enoxacin hydroiodide

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Key indicators

Single-crystal X-ray study
T = 193 K
Mean σ(C–C) = 0.005 Å
R factor = 0.042
wR factor = 0.078
Data-to-parameter ratio = 16.5

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

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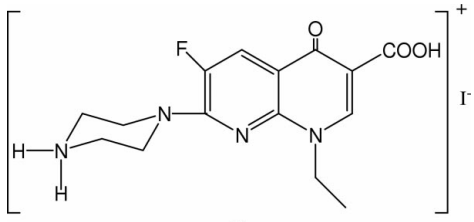
The title compound, $C_{15}H_{18}FN_4O_3^+\cdot I^-$, forms ionic crystals consisting of protonated enoxacin cations, $C_{15}H_{18}FN_4O_3^+$, and I^- anions. The naphthyridine system of the cation is essentially planar, whereas the piperazine ring has a chair conformation; the enoxacin is protonated at the unsubstituted N atom of the piperazine ring. The carboxyl OH group forms an intramolecular hydrogen bond with the carbonyl O atom of the naphthyridine system, thus forming a six-membered pseudo-ring. The crystal packing is stabilized by π–π stacking of the naphthyridine rings and intermolecular hydrogen bonding involving the piperazine N—H group, the carboxyl group of the cation and the I^- anion, linking the residues of the structure into infinite chains running along the diagonal of the *ac* plane.

Comment

Enoxacin, 1-ethyl-6-fluoro-1,4-dihydro-4-oxo-7-(1-piperazinyl)-1,8-naphthyridine-3-carboxylic acid, is a synthetic antibacterial drug of the fluoroquinolone class, and is rapidly bactericidal against Gram-positive and -negative organisms including *Pseudomonas aeruginosa* and *Enterobacteriaceae* (Siporin & Towse, 1984). A number of such naphthyridine derivatives have been crystallographically characterized (Datta *et al.*, 1995); one of them, *viz*. nalidixic acid, has been studied several times (Achari & Neidle, 1976; Huber *et al.*, 1980; Oh *et al.*, 1986). However, as far as we are aware, the crystal structure of enoxacin has not been reported.



(I)

The ionic crystals of enoxacin of the title salt, (I), of enoxacin are composed of cations involving protonated quinolone groups and iodide anions (Fig. 1). Similar to what is observed in the structure of 6-chloro-1-ethyl-1,4-dihydro-4-oxo-7-(4-methyl-1-piperazinyl)-1,8-naphthyridine-3-carboxylic acid (Datta *et al.*, 1995), the bicyclic naphthyridine system is essentially planar, whereas the piperazine ring has a chair conformation. The unsubstituted N atom of the piperazine ring (N4) is protonated, while the carboxyl group is not dissociated. The ethyl group plane (N1, C10 and C11) is almost orthogonal to the mean plane of the naphthyridine system; the corresponding dihedral angle is 80.57 (19)°. All the

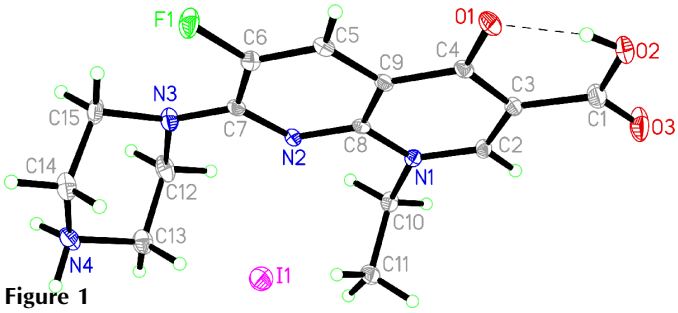


Figure 1
The structure of compound (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme. The dashed line indicates the intramolecular hydrogen bond.

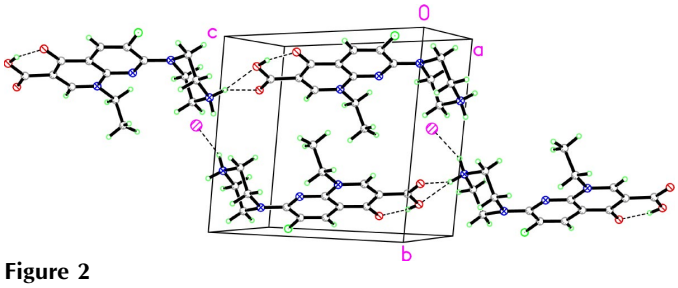


Figure 2
A packing diagram for compound (I). Dashed lines indicate hydrogen bonds.

distances and angles within the rigid quinolone ring system and in the piperazine ring are similar to those found previously in related compounds (*e.g.* nalidixic acid and its derivatives; Achari & Neidle, 1976; Datta *et al.*, 1995; Huber *et al.*, 1980; Oh *et al.*, 1986).

The hydrogen bond O2—H2···O1, involving the carboxyl OH group and the naphthyridine oxo atom, forms a six-membered pseudo-ring within the cation. The piperazine NH groups function as the donors of hydrogen bonds involving caboxyl O atoms and link neighbouring cations in the crystal structure; they also participate in hydrogen bonds with the I^- anions (Table 2). Interionic hydrogen bonds link the residues in the structure of (I) into infinite chains extending along the diagonal of the *ac* plane of the unit cell (Fig. 2). The crystal packing of (I) is also stabilized by π–π stacking of the napthhyridine rings.

Experimental

Samples of 1.5 mmol of enoxacin (purchased from Fluka) and 1 mmol of PbI_2 were thoroughly mixed and placed in an autoclave. After addition of 4 ml of EtOH and 12 ml of H_2O (pH = 5.0), the autoclave was heated at 373 K for 3 d to give light-yellow crystals of compound (I) in a 40% yield.

Crystal data

$C_{15}H_{18}FN_4O_3^+\cdot I^-$
M_r = 448.23
Triclinic, $P\overline{1}$
a = 6.9831 (17) Å
b = 10.235 (3) Å
c = 11.931 (3) Å
α = 82.783 (11)°
β = 79.961 (11)°
γ = 85.934 (12)°
V = 832.0 (4) Å^3
Z = 2
D_x = 1.789 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3760 reflections
θ = 3.2–27.5°
μ = 1.96 mm^{-1}
T = 193 (2) K
Irregular, light yellow
0.20 × 0.11 × 0.07 mm

Data collection

Rigaku Mercury CCD diffractometer
ω scans
Absorption correction: multi-scan (Jacobson, 1998)
T_{min} = 0.696, T_{max} = 0.875
9442 measured reflections
3753 independent reflections
3401 reflections with $I > 2\sigma(I)$
R_{int} = 0.037
θ_{max} = 27.5°
$h = -7 \rightarrow 9$
$k = -13 \rightarrow 13$
$l = -15 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.078
S = 1.18
3753 reflections
227 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0167P)^2 + 1.7702P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.55 e Å^{-3}
$\Delta\rho_{min}$ = −0.64 e Å^{-3}

Table 1
Selected bond distances (Å).

C1—C3	1.480 (5)	O2—C1	1.326 (5)
C2—C3	1.376 (5)	O3—C1	1.214 (5)
C3—C4	1.432 (5)	N1—C2	1.340 (5)
C4—C9	1.432 (5)	N1—C8	1.398 (5)
C5—C6	1.351 (5)	N1—C10	1.488 (5)
C5—C9	1.411 (5)	N2—C8	1.331 (5)
C6—C7	1.420 (5)	N2—C7	1.339 (5)
C8—C9	1.395 (5)	N3—C7	1.365 (5)
C10—C11	1.509 (5)	N3—C12	1.466 (5)
C12—C13	1.507 (6)	N3—C15	1.467 (5)
C14—C15	1.510 (6)	N4—C13	1.490 (5)
F1—C6	1.369 (4)	N4—C14	1.491 (6)
O1—C4	1.275 (4)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···O1	0.84	1.65	2.442 (4)	156
N4—H4B···I1^{i}	0.84 (5)	2.61 (5)	3.421 (4)	163 (4)
N4—H4A···O2^{ii}	0.91 (6)	2.02 (6)	2.880 (5)	156 (5)
N4—H4A···O3^{ii}	0.91 (6)	2.39 (6)	3.182 (5)	145 (5)

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

H atoms bonded to C and O atoms were positioned geometrically; they were treated as riding, with C—H = 0.93 Å, O—H = 0.84 Å and U_{iso}(H) = 1.2$_{eq}$(C) or 1.5$_{eq}$(O). H atoms bound to atom N4 were located in a difference map and refined isotropically; N—H = 0.84 (5) and 0.91 (6) Å.

Data collection: *CrystalClear* (Rigaku, 1999); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku and Rigaku/MSC, 2000); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Siemens, 1994); software used to prepare material for publication: *SHELXTL*.

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References

Achari, A. & Neidle, S. (1976). *Acta Cryst.* B**32**, 600–602.
Datta, M., Hannan, S. S. & Talukdar, A. N. (1995). *Acta Cryst.* C**51**, 978–980.
Huber, C. P., Gowda, D. S. S. & Acharya, K. R. (1980). *Acta Cryst.* B**36**, 497–499.
Jacobson, R. (1998). Private communication to Rigaku. Rigaku Corporation, Tokyo, Japan.
Oh, I.-K., Ko, T.-S., Lee, C.-B., Suh, J.-I. & Suh, I.-H. (1986). *Chung. J. Sci.* **13**, 51–58.
Rigaku & Rigaku/MSC (2000). *CrystalStructure*. Rigaku/MSC, 9009 New Trails Drive, The Woodlands, TX 77381, USA, and Rigaku Corporation, Tokyo, Japan.
Rigaku (1999). *CrystalClear*. Rigaku Corporation, Tokyo, Japan.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Siemens (1994). *XSCANS* (Version 2.10b) and *SHELXTL*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siporin, C. & Towse, G. (1984). *J. Antimicrob. Chemother.* **14**, Suppl. C, 47–55.