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4-(3-Carboxy-1-ethyl-6-fluoro-4-oxo-1,4-dihydro-7-quinolyl)-1-methylpiperazin-ium picrate

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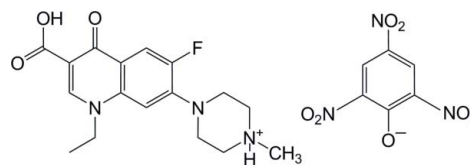
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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; disorder in main residue; R factor = 0.047; wR factor = 0.123; data-to-parameter ratio = 11.7.

The pefloxacinium cation of the title salt, $\text{C}_{17}\text{H}_{21}\text{FN}_3\text{O}_3^+$ · $\text{C}_6\text{H}_2\text{N}_3\text{O}_7^-$, is composed of an essentially planar quinoline ring system [maximum deviation = 0.021 (2) Å] and a piperazine ring, which adopts a chair conformation. In the picrate anion, the two O atoms of one of the *o*-NO₂ groups are disordered over two positions, with an occupancy ratio of 0.56 (4):0.44 (4). In the crystal structure, cations and anions are connected by intermolecular N—H···O, O—H···O, C—H···O and C—H···F hydrogen bonds, forming a three-dimensional network. In addition, π – π interactions between the pyridine rings and between the benzene rings of the anions, with centroid–centroid distances of 3.6103 (12) and 3.5298 (11) Å, respectively, are observed.

Related literature

For background to the biological activity, pharmacokinetic properties and therapeutic use of pefloxacin, a synthetic chemotherapeutic agent used to treat severe bacterial infections, see: Mizuki *et al.* (1996); Gonzalez & Henwood (1989); Tripathi (1995); Ross & Riley (1990); Burkhardt *et al.* (1997). For the silver(I), manganese(II) and cobalt(II) derivatives of the pefloxacin anion, see: Baenziger *et al.* (1986); An, Huang & Qi (2007); An, Qi & Huang (2007). For related structures, see: An & Liang (2008); Florence *et al.* (2000); Hu & Yu (2005); Parvez *et al.* (2000). For hydrogen-bonding motifs see: Bernstein *et al.* (1995). For ring conformations, see: Cremer & Pople (1975).



Experimental

Crystal data

$\text{C}_{17}\text{H}_{21}\text{FN}_3\text{O}_3^+ \cdot \text{C}_6\text{H}_2\text{N}_3\text{O}_7^-$
 $M_r = 562.47$
Triclinic, $P\bar{1}$
 $a = 7.2645$ (1) Å
 $b = 9.1987$ (2) Å
 $c = 20.2253$ (4) Å
 $\alpha = 77.116$ (1)°
 $\beta = 81.315$ (1)°

$\gamma = 67.124$ (1)°
 $V = 1210.77$ (4) Å³
 $Z = 2$
Mo $K\alpha$ radiation
 $\mu = 0.13$ mm⁻¹
 $T = 296$ K
 $0.36 \times 0.13 \times 0.13$ mm

Data collection

Bruker SMART APEXII CCD
area-detector diffractometer
Absorption correction: multi-scan
(SADABS; Bruker, 2009)
 $T_{\min} = 0.955$, $T_{\max} = 0.984$

23708 measured reflections
5523 independent reflections
3682 reflections with $I > 2s(I)$
 $R_{\text{int}} = 0.039$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.047$
 $wR(F^2) = 0.123$
 $S = 1.03$
5523 reflections

472 parameters
All H-atom parameters refined
 $\Delta\rho_{\text{max}} = 0.21$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.22$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| <i>D</i> —H··· <i>A</i> | <i>D</i> —H | H··· <i>A</i> | <i>D</i> ··· <i>A</i> | <i>D</i> —H··· <i>A</i> |
|------------------------------|-------------|---------------|-----------------------|-------------------------|
| O9—H1O9···O10 | 0.96 (3) | 1.62 (3) | 2.519 (2) | 155 (3) |
| N6—H1N6···O1 ⁱ | 0.91 (2) | 1.84 (2) | 2.701 (2) | 159 (2) |
| N6—H1N6···O7 ⁱ | 0.91 (2) | 2.422 (19) | 2.987 (2) | 120.6 (15) |
| C6—H6···O3 | 0.878 (19) | 2.38 (2) | 2.706 (16) | 102.3 (14) |
| C11—H11···F1 ⁱⁱ | 0.933 (19) | 2.46 (2) | 3.209 (2) | 137.3 (18) |
| C16—H16A···F1 | 0.97 (2) | 2.18 (2) | 2.846 (2) | 124.6 (15) |
| C17—H17A···O8 ⁱⁱⁱ | 0.928 (19) | 2.582 (19) | 3.430 (3) | 152.2 (14) |
| C17—H17B···O4 ^{iv} | 1.02 (2) | 2.55 (2) | 3.407 (3) | 141.2 (16) |
| C18—H18A···O3 ^v | 0.940 (19) | 2.47 (2) | 3.241 (16) | 139.2 (18) |
| C19—H19B···O5 ^{vi} | 0.990 (17) | 2.566 (17) | 3.300 (2) | 131.0 (13) |
| C20—H20A···O7 ⁱ | 0.97 (2) | 2.51 (2) | 3.079 (3) | 118.0 (18) |
| C20—H20C···O4 ^{iv} | 1.01 (3) | 2.39 (3) | 3.245 (3) | 141.8 (19) |
| C21—H21B···O8 ^{vii} | 0.90 (3) | 2.53 (3) | 3.415 (3) | 169 (2) |

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

Data collection: APEX2 (Bruker, 2009); cell refinement: SAINT (Bruker, 2009); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL and PLATON (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK2633).

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supporting information

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4-(3-Carboxy-1-ethyl-6-fluoro-4-oxo-1,4-dihydro-7-quinolyl)-1-methyl-piperazinium picrate

Hoong-Kun Fun, Madhukar Hemamalini, Divya N. Shetty, B. Narayana and H. S. Yathirajan

S1. Comment

Pefloxacin is a synthetic chemotherapeutic agent used to treat severe and life-threatening bacterial infections (Mizuki *et al.*, 1996). A review of its anti-bacterial activity, pharmacokinetic properties and therapeutic use is available (Gonzalez & Henwood, 1989). Pefloxacin is commonly referred to as a fluoroquinolone (or quinolone) drug and is a member of the fluoroquinolone class of anti-bacterials. It is an analog of norfloxacin and is a synthetic fluoroquinolone, belonging to the third generation of quinolones. As an antibacterial drug, it is highly effective against both Gram-negative and Gram-positive pathogens that are resistant to other anti-bacterials (Tripathi, 1995; Ross *et al.*, 1990). Pefloxacin is well known to be associated with high incidence of arthropathy in humans because the drug affects articular cartilage and the epiphyseal growth plate (Burkhardt *et al.*, 1997). The silver(I), manganese(II) and cobalt(II) derivatives of the pefloxacin anion have been reported (Baenziger *et al.*, 1986; An, Huang, & Qi, 2007; An, Qi & Huang, 2007). The crystal structures of silver pefloxacin (Baenziger *et al.*, 1986), pefloxacinium methane sulfonate 0.10-hydrate (Parvez *et al.*, 2000), norfloxacin dihydrate (Florence *et al.*, 2000), norfloxacin picrate (Hu & Yu, 2005), 1-ethyl-6-fluoro-7-(4-methyl-piperazin-4-ium-1-yl)-4-oxo-1,4-dihydroquinoline-3-carboxylate hexahydrate (An & Liang, 2008) have been reported. In view of the importance of pefloxacin, this paper reports the crystal structure of the title compound.

The asymmetric unit of the title compound (Fig. 1), contains a protonated pefloxacinium cation and a picrate anion. The cation is composed of an essentially planar quinoline ring system [maximum deviation 0.021 (2) Å]. The six-membered piperazinyl ring adopts a chair conformation with puckering parameters (Cremer & Pople, 1975) $Q = 0.5621$ (2) Å, $\Theta = 174.05$ (18)° and $\varphi = 169$ (2)°. In the picrate anion, atoms O2 and O3 are disordered over two positions, with occupancy ratio of 0.56 (4):0.44 (4). The phenolate oxygen atoms are bent slightly away from the mean plane of the benzene ring (torsion angle O1—C2—C3—C4 = -177.76 (18)°).

In the crystal structure (Fig. 2), the picrate anion interacts with the cations through bifurcated N6—H1N6···O1 and N6—H1N6···O7 hydrogen bonds, forming an $R_1^2(6)$ (Bernstein *et al.*, 1995) ring motif. There is an intramolecular O9—H1O9···O10 hydrogen bond between the carbonyl and carboxyl groups in the cation, which generates an $S(6)$ ring motif. The crystal structure is further stabilized by several weak C—H···O and C—H···F interactions (Table 1), forming a three-dimensional network. Also, π - π interactions between pyridine rings, and between benzene rings of anions/anions, with centroid-to-centroid distances = 3.6103 (12) Å and 3.5298 (11) Å, respectively, are observed.

S2. Experimental

Each of the pefloxacin (3.33 g, 0.01 mol) and picric acid (2.29 g, 0.01 mol) were individually dissolved in water (60 ml). The solutions were mixed and 5 M HCl (2 ml) was added with stirring for a few minutes. The product formed was filtered and dried. Yellow crystals of pefloxacinium picrate were obtained by slow evaporation in DMF (m.p.: 515 K).

S3. Refinement

All the H atoms were located in a difference Fourier map and allowed to refine freely [N—H = 0.905 (19) Å, O—H = 0.96 (3) Å, C—H = 0.88 (19)–1.01 (3) Å]. In the picrate anion, atoms O2 and O3 are disordered over two positions, with an occupancy ratio of 0.56 (4):0.44 (4).

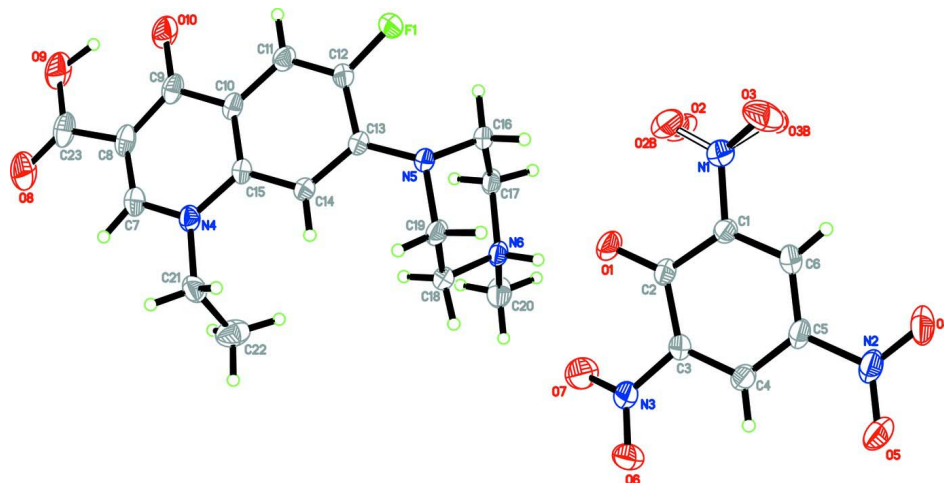


Figure 1

The asymmetric unit of the title compound, showing 50% probability displacement ellipsoids and the atom-numbering scheme.

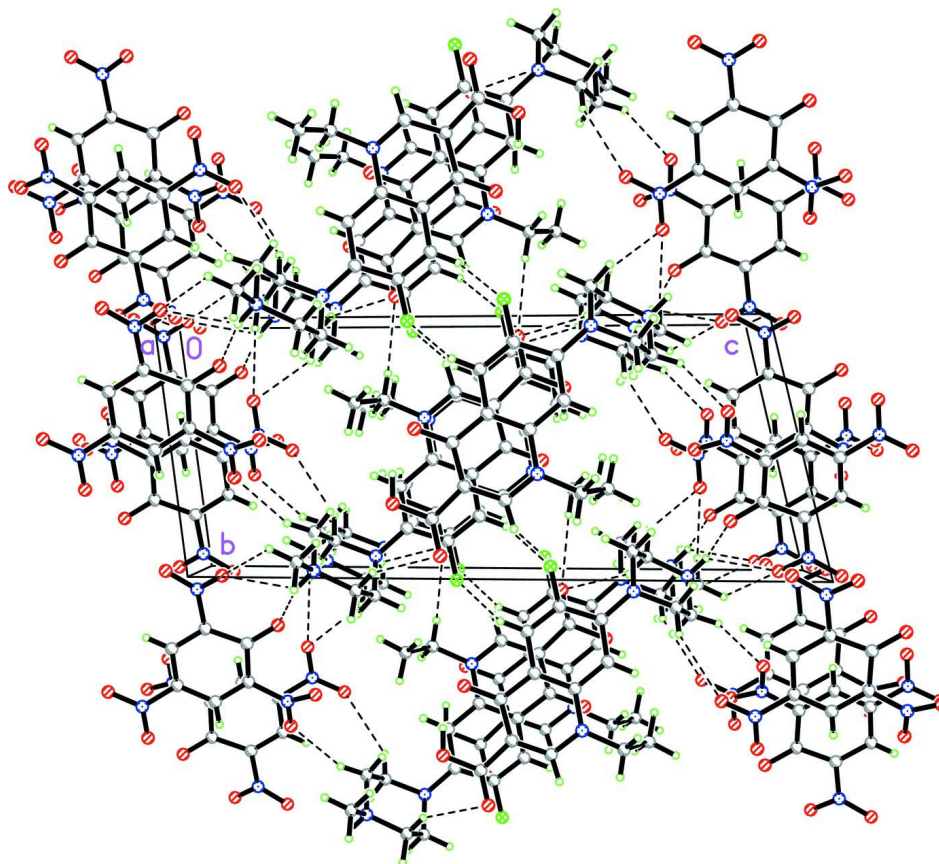


Figure 2

The crystal packing of the title compound, showing hydrogen-bonded (dashed lines) network.

4-(3-Carboxy-1-ethyl-6-fluoro-4-oxo-1,4-dihydro-7-quinoly)-1-methylpiperazinium picrate

Crystal data

$C_{17}H_{21}FN_3O_3^+ \cdot C_6H_2N_3O_7^-$

$M_r = 562.47$

Triclinic, $P\bar{1}$

Hall symbol: -P 1

$a = 7.2645$ (1) Å

$b = 9.1987$ (2) Å

$c = 20.2253$ (4) Å

$\alpha = 77.116$ (1)°

$\beta = 81.315$ (1)°

$\gamma = 67.124$ (1)°

$V = 1210.77$ (4) Å³

$Z = 2$

$F(000) = 584$

$D_x = 1.543$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 4949 reflections

$\theta = 2.5$ – 31.8 °

$\mu = 0.13$ mm⁻¹

$T = 296$ K

Block, yellow

$0.36 \times 0.13 \times 0.13$ mm

Data collection

Bruker SMART APEXII CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan
(*SADABS*; Bruker, 2009)

$T_{\min} = 0.955$, $T_{\max} = 0.984$

23708 measured reflections

5523 independent reflections

3682 reflections with $I > 2s(I)$

$R_{\text{int}} = 0.039$
 $\theta_{\text{max}} = 27.5^\circ$, $\theta_{\text{min}} = 2.1^\circ$
 $h = -9 \rightarrow 9$

$k = -11 \rightarrow 11$
 $l = -26 \rightarrow 26$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.047$
 $wR(F^2) = 0.123$
 $S = 1.03$
 5523 reflections
 472 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: inferred from
 neighbouring sites
 All H-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.0539P)^2 + 0.1877P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.21 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.22 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 $F^2 > 2\sigma(F^2)$ 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 (\AA^2)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ | Occ. (<1) |
|-----|--------------|---------------|--------------|----------------------------------|-----------|
| O1 | 0.4979 (2) | 0.79508 (17) | 0.88294 (6) | 0.0614 (4) | |
| O2 | 0.7151 (13) | 0.5178 (13) | 0.8445 (5) | 0.067 (2) | 0.56 (4) |
| O3 | 0.9703 (16) | 0.3754 (18) | 0.9011 (8) | 0.075 (3) | 0.56 (4) |
| O2B | 0.768 (5) | 0.546 (3) | 0.8376 (7) | 0.120 (6) | 0.44 (4) |
| O3B | 0.934 (4) | 0.357 (3) | 0.9074 (10) | 0.103 (5) | 0.44 (4) |
| O4 | 0.8735 (3) | 0.32881 (19) | 1.14260 (8) | 0.0788 (5) | |
| O5 | 0.6553 (3) | 0.5215 (2) | 1.18879 (7) | 0.0730 (5) | |
| O6 | 0.2844 (2) | 1.00907 (18) | 1.04797 (8) | 0.0663 (4) | |
| O7 | 0.2049 (3) | 0.9961 (2) | 0.95255 (9) | 0.0994 (7) | |
| N1 | 0.8047 (2) | 0.4832 (2) | 0.89513 (8) | 0.0473 (4) | |
| N2 | 0.7383 (3) | 0.4603 (2) | 1.13878 (9) | 0.0543 (4) | |
| N3 | 0.3077 (3) | 0.9389 (2) | 1.00085 (9) | 0.0531 (4) | |
| C1 | 0.7049 (2) | 0.5634 (2) | 0.95257 (8) | 0.0367 (4) | |
| C2 | 0.5487 (2) | 0.7206 (2) | 0.94034 (8) | 0.0388 (4) | |
| C3 | 0.4645 (3) | 0.7803 (2) | 1.00324 (9) | 0.0391 (4) | |
| C4 | 0.5270 (3) | 0.6985 (2) | 1.06618 (10) | 0.0422 (4) | |
| C5 | 0.6760 (3) | 0.5484 (2) | 1.07199 (9) | 0.0425 (4) | |
| C6 | 0.7669 (3) | 0.4806 (2) | 1.01542 (9) | 0.0404 (4) | |
| F1 | 0.63677 (18) | -0.03326 (12) | 0.57808 (5) | 0.0561 (3) | |
| O8 | -0.0325 (3) | 0.9171 (2) | 0.40639 (8) | 0.0782 (5) | |
| O9 | 0.0924 (3) | 0.7207 (2) | 0.34701 (8) | 0.0711 (5) | |
| O10 | 0.2917 (2) | 0.43985 (18) | 0.40332 (7) | 0.0611 (4) | |

| | | | | |
|------|-------------|--------------|--------------|-------------|
| N4 | 0.2108 (2) | 0.60713 (17) | 0.58140 (7) | 0.0395 (3) |
| N5 | 0.5335 (2) | 0.06173 (16) | 0.70402 (7) | 0.0355 (3) |
| N6 | 0.2153 (2) | 0.01715 (17) | 0.80261 (7) | 0.0381 (3) |
| C7 | 0.1335 (3) | 0.7054 (2) | 0.52424 (10) | 0.0452 (5) |
| C8 | 0.1526 (3) | 0.6553 (2) | 0.46406 (9) | 0.0456 (5) |
| C9 | 0.2625 (3) | 0.4915 (2) | 0.45840 (9) | 0.0440 (5) |
| C10 | 0.3409 (3) | 0.3855 (2) | 0.52080 (8) | 0.0375 (4) |
| C11 | 0.4521 (3) | 0.2212 (2) | 0.52173 (9) | 0.0419 (4) |
| C12 | 0.5179 (3) | 0.1222 (2) | 0.58059 (9) | 0.0386 (4) |
| C13 | 0.4736 (2) | 0.1723 (2) | 0.64432 (8) | 0.0329 (4) |
| C14 | 0.3771 (2) | 0.3363 (2) | 0.64216 (9) | 0.0341 (4) |
| C15 | 0.3112 (2) | 0.4432 (2) | 0.58177 (8) | 0.0343 (4) |
| C16 | 0.4921 (3) | -0.0875 (2) | 0.71661 (10) | 0.0403 (4) |
| C17 | 0.2763 (3) | -0.0593 (2) | 0.74081 (9) | 0.0403 (4) |
| C18 | 0.2690 (3) | 0.1625 (2) | 0.79291 (10) | 0.0409 (4) |
| C19 | 0.4868 (3) | 0.1236 (2) | 0.76759 (9) | 0.0386 (4) |
| C20 | -0.0031 (3) | 0.0581 (3) | 0.82167 (14) | 0.0571 (6) |
| C21 | 0.1823 (3) | 0.6765 (3) | 0.64328 (11) | 0.0493 (5) |
| C22 | 0.0028 (4) | 0.6633 (4) | 0.68827 (13) | 0.0664 (7) |
| C23 | 0.0618 (3) | 0.7773 (3) | 0.40435 (11) | 0.0563 (6) |
| H4 | 0.468 (3) | 0.743 (2) | 1.1031 (11) | 0.055 (6)* |
| H6 | 0.864 (3) | 0.386 (2) | 1.0177 (9) | 0.046 (5)* |
| H7 | 0.066 (3) | 0.813 (3) | 0.5297 (10) | 0.055 (6)* |
| H11 | 0.485 (3) | 0.181 (2) | 0.4813 (10) | 0.047 (5)* |
| H14 | 0.349 (2) | 0.379 (2) | 0.6821 (9) | 0.036 (5)* |
| H16A | 0.526 (3) | -0.136 (2) | 0.6761 (11) | 0.057 (6)* |
| H16B | 0.583 (3) | -0.163 (2) | 0.7505 (10) | 0.053 (5)* |
| H17A | 0.193 (3) | 0.012 (2) | 0.7078 (9) | 0.044 (5)* |
| H17B | 0.251 (3) | -0.164 (3) | 0.7550 (10) | 0.059 (6)* |
| H18A | 0.245 (3) | 0.196 (2) | 0.8351 (10) | 0.043 (5)* |
| H18B | 0.182 (3) | 0.241 (2) | 0.7603 (10) | 0.045 (5)* |
| H19A | 0.569 (3) | 0.039 (2) | 0.8001 (9) | 0.040 (5)* |
| H19B | 0.521 (2) | 0.220 (2) | 0.7621 (9) | 0.040 (5)* |
| H20A | -0.038 (3) | 0.107 (3) | 0.8617 (12) | 0.072 (7)* |
| H20B | -0.079 (4) | 0.131 (3) | 0.7848 (13) | 0.081 (8)* |
| H20C | -0.033 (3) | -0.043 (3) | 0.8318 (12) | 0.080 (8)* |
| H21A | 0.303 (3) | 0.623 (2) | 0.6670 (9) | 0.046 (5)* |
| H21B | 0.161 (3) | 0.781 (3) | 0.6285 (10) | 0.055 (6)* |
| H22A | -0.106 (4) | 0.710 (3) | 0.6634 (14) | 0.096 (9)* |
| H22B | 0.022 (4) | 0.552 (4) | 0.7065 (13) | 0.092 (9)* |
| H22C | -0.013 (4) | 0.715 (3) | 0.7274 (15) | 0.103 (9)* |
| H1O9 | 0.179 (4) | 0.610 (4) | 0.3556 (15) | 0.110 (11)* |
| H1N6 | 0.284 (3) | -0.055 (2) | 0.8372 (10) | 0.044 (5)* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|----|------------|------------|------------|-------------|-------------|------------|
| O1 | 0.0640 (9) | 0.0613 (9) | 0.0329 (7) | -0.0004 (7) | -0.0099 (6) | 0.0052 (6) |

| | | | | | | |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| O2 | 0.075 (3) | 0.091 (4) | 0.032 (3) | -0.022 (3) | -0.008 (2) | -0.019 (3) |
| O3 | 0.046 (3) | 0.075 (4) | 0.094 (7) | -0.001 (3) | -0.005 (3) | -0.037 (4) |
| O2B | 0.146 (11) | 0.093 (7) | 0.041 (3) | 0.026 (7) | 0.016 (6) | 0.001 (4) |
| O3B | 0.114 (10) | 0.072 (7) | 0.058 (5) | 0.034 (7) | 0.006 (7) | -0.015 (4) |
| O4 | 0.1096 (14) | 0.0488 (10) | 0.0600 (10) | -0.0117 (9) | -0.0349 (9) | 0.0128 (8) |
| O5 | 0.1082 (13) | 0.0755 (11) | 0.0342 (8) | -0.0327 (10) | -0.0172 (8) | -0.0017 (8) |
| O6 | 0.0818 (10) | 0.0514 (9) | 0.0601 (10) | -0.0210 (8) | 0.0176 (8) | -0.0208 (8) |
| O7 | 0.0998 (13) | 0.0821 (13) | 0.0596 (11) | 0.0313 (10) | -0.0219 (10) | -0.0093 (9) |
| N1 | 0.0471 (9) | 0.0478 (11) | 0.0434 (10) | -0.0148 (8) | 0.0000 (8) | -0.0083 (8) |
| N2 | 0.0789 (12) | 0.0483 (11) | 0.0388 (10) | -0.0286 (9) | -0.0205 (9) | 0.0067 (8) |
| N3 | 0.0613 (10) | 0.0434 (10) | 0.0418 (10) | -0.0125 (8) | 0.0051 (8) | -0.0009 (8) |
| C1 | 0.0402 (9) | 0.0377 (10) | 0.0325 (9) | -0.0152 (7) | -0.0031 (7) | -0.0047 (8) |
| C2 | 0.0416 (9) | 0.0395 (10) | 0.0310 (9) | -0.0138 (8) | -0.0066 (7) | 0.0024 (8) |
| C3 | 0.0439 (9) | 0.0336 (10) | 0.0362 (10) | -0.0135 (7) | -0.0027 (7) | -0.0010 (8) |
| C4 | 0.0556 (11) | 0.0425 (11) | 0.0330 (10) | -0.0240 (9) | -0.0026 (8) | -0.0049 (8) |
| C5 | 0.0565 (11) | 0.0398 (11) | 0.0333 (10) | -0.0226 (9) | -0.0138 (8) | 0.0050 (8) |
| C6 | 0.0438 (10) | 0.0316 (10) | 0.0443 (11) | -0.0131 (8) | -0.0118 (8) | 0.0006 (8) |
| F1 | 0.0842 (8) | 0.0348 (6) | 0.0393 (6) | -0.0115 (5) | -0.0012 (5) | -0.0083 (5) |
| O8 | 0.0905 (12) | 0.0572 (11) | 0.0693 (11) | -0.0164 (9) | -0.0349 (9) | 0.0226 (8) |
| O9 | 0.0922 (12) | 0.0720 (12) | 0.0470 (9) | -0.0327 (10) | -0.0345 (8) | 0.0176 (8) |
| O10 | 0.0940 (11) | 0.0621 (10) | 0.0345 (8) | -0.0367 (8) | -0.0223 (7) | 0.0031 (7) |
| N4 | 0.0437 (8) | 0.0334 (8) | 0.0361 (8) | -0.0114 (6) | -0.0087 (6) | 0.0029 (6) |
| N5 | 0.0403 (7) | 0.0311 (8) | 0.0285 (7) | -0.0093 (6) | -0.0023 (6) | 0.0002 (6) |
| N6 | 0.0377 (7) | 0.0351 (8) | 0.0320 (8) | -0.0092 (6) | -0.0041 (6) | 0.0057 (7) |
| C7 | 0.0468 (10) | 0.0387 (11) | 0.0453 (11) | -0.0154 (9) | -0.0107 (8) | 0.0066 (9) |
| C8 | 0.0454 (10) | 0.0489 (12) | 0.0415 (11) | -0.0233 (9) | -0.0161 (8) | 0.0133 (9) |
| C9 | 0.0529 (11) | 0.0516 (12) | 0.0352 (10) | -0.0310 (9) | -0.0149 (8) | 0.0066 (9) |
| C10 | 0.0455 (9) | 0.0406 (10) | 0.0299 (9) | -0.0230 (8) | -0.0085 (7) | 0.0038 (7) |
| C11 | 0.0595 (11) | 0.0435 (11) | 0.0293 (9) | -0.0265 (9) | -0.0054 (8) | -0.0045 (8) |
| C12 | 0.0490 (10) | 0.0306 (10) | 0.0352 (10) | -0.0154 (8) | -0.0019 (8) | -0.0033 (7) |
| C13 | 0.0350 (8) | 0.0342 (9) | 0.0281 (9) | -0.0141 (7) | -0.0029 (7) | 0.0002 (7) |
| C14 | 0.0387 (9) | 0.0334 (10) | 0.0287 (9) | -0.0129 (7) | -0.0033 (7) | -0.0030 (7) |
| C15 | 0.0360 (8) | 0.0324 (9) | 0.0332 (9) | -0.0144 (7) | -0.0063 (7) | 0.0025 (7) |
| C16 | 0.0508 (10) | 0.0286 (10) | 0.0322 (10) | -0.0089 (8) | -0.0008 (8) | 0.0012 (8) |
| C17 | 0.0506 (10) | 0.0344 (10) | 0.0328 (10) | -0.0154 (8) | -0.0088 (8) | 0.0035 (8) |
| C18 | 0.0506 (10) | 0.0355 (10) | 0.0314 (10) | -0.0132 (8) | 0.0014 (8) | -0.0033 (8) |
| C19 | 0.0456 (10) | 0.0404 (11) | 0.0277 (9) | -0.0156 (8) | -0.0083 (7) | 0.0013 (8) |
| C20 | 0.0404 (10) | 0.0558 (14) | 0.0611 (15) | -0.0133 (10) | 0.0024 (10) | 0.0048 (12) |
| C21 | 0.0618 (13) | 0.0315 (11) | 0.0475 (12) | -0.0074 (9) | -0.0142 (10) | -0.0037 (9) |
| C22 | 0.0521 (13) | 0.080 (2) | 0.0512 (14) | -0.0029 (12) | -0.0062 (11) | -0.0177 (14) |
| C23 | 0.0603 (12) | 0.0582 (14) | 0.0483 (13) | -0.0283 (11) | -0.0245 (10) | 0.0201 (11) |

Geometric parameters (Å, °)

| | | | |
|--------|-------------|---------|------------|
| O1—C2 | 1.2375 (19) | N6—H1N6 | 0.905 (19) |
| O2—N1 | 1.212 (8) | C7—C8 | 1.365 (3) |
| O3—N1 | 1.228 (13) | C7—H7 | 0.94 (2) |
| O2B—N1 | 1.196 (13) | C8—C9 | 1.426 (3) |

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|------------|-------------|--------------|-------------|
| O3B—N1 | 1.177 (17) | C8—C23 | 1.488 (3) |
| O4—N2 | 1.221 (2) | C9—C10 | 1.451 (2) |
| O5—N2 | 1.229 (2) | C10—C15 | 1.404 (2) |
| O6—N3 | 1.222 (2) | C10—C11 | 1.407 (3) |
| O7—N3 | 1.214 (2) | C11—C12 | 1.351 (2) |
| N1—C1 | 1.460 (2) | C11—H11 | 0.932 (19) |
| N2—C5 | 1.448 (2) | C12—C13 | 1.415 (2) |
| N3—C3 | 1.457 (2) | C13—C14 | 1.388 (2) |
| C1—C6 | 1.368 (2) | C14—C15 | 1.401 (2) |
| C1—C2 | 1.446 (2) | C14—H14 | 0.936 (17) |
| C2—C3 | 1.452 (2) | C16—C17 | 1.508 (3) |
| C3—C4 | 1.369 (2) | C16—H16A | 0.97 (2) |
| C4—C5 | 1.377 (3) | C16—H16B | 0.98 (2) |
| C4—H4 | 0.90 (2) | C17—H17A | 0.929 (19) |
| C5—C6 | 1.380 (3) | C17—H17B | 1.02 (2) |
| C6—H6 | 0.882 (19) | C18—C19 | 1.514 (3) |
| F1—C12 | 1.3609 (19) | C18—H18A | 0.942 (19) |
| O8—C23 | 1.206 (3) | C18—H18B | 0.956 (19) |
| O9—C23 | 1.329 (3) | C19—H19A | 0.959 (18) |
| O9—H109 | 0.96 (3) | C19—H19B | 0.994 (18) |
| O10—C9 | 1.264 (2) | C20—H20A | 0.97 (2) |
| N4—C7 | 1.343 (2) | C20—H20B | 0.96 (3) |
| N4—C15 | 1.396 (2) | C20—H20C | 1.01 (3) |
| N4—C21 | 1.480 (2) | C21—C22 | 1.502 (3) |
| N5—C13 | 1.396 (2) | C21—H21A | 0.964 (19) |
| N5—C19 | 1.462 (2) | C21—H21B | 0.90 (2) |
| N5—C16 | 1.477 (2) | C22—H22A | 0.91 (3) |
| N6—C20 | 1.491 (2) | C22—H22B | 0.97 (3) |
| N6—C17 | 1.496 (2) | C22—H22C | 0.98 (3) |
| N6—C18 | 1.498 (2) | | |
| O3B—N1—O2B | 120.7 (12) | C12—C11—H11 | 119.8 (12) |
| O3B—N1—O2 | 119.9 (11) | C10—C11—H11 | 119.8 (12) |
| O2B—N1—O2 | 25.4 (19) | C11—C12—F1 | 118.09 (16) |
| O3B—N1—O3 | 17.2 (18) | C11—C12—C13 | 123.53 (16) |
| O2B—N1—O3 | 114.2 (11) | F1—C12—C13 | 118.36 (14) |
| O2—N1—O3 | 121.9 (8) | C14—C13—N5 | 123.69 (15) |
| O3B—N1—C1 | 116.8 (10) | C14—C13—C12 | 115.50 (15) |
| O2B—N1—C1 | 122.4 (7) | N5—C13—C12 | 120.75 (15) |
| O2—N1—C1 | 118.6 (5) | C13—C14—C15 | 122.18 (16) |
| O3—N1—C1 | 119.3 (7) | C13—C14—H14 | 120.3 (11) |
| O4—N2—O5 | 122.98 (17) | C15—C14—H14 | 117.5 (11) |
| O4—N2—C5 | 118.14 (18) | N4—C15—C14 | 120.91 (15) |
| O5—N2—C5 | 118.87 (17) | N4—C15—C10 | 118.98 (14) |
| O7—N3—O6 | 122.52 (18) | C14—C15—C10 | 120.08 (16) |
| O7—N3—C3 | 119.07 (17) | N5—C16—C17 | 111.86 (15) |
| O6—N3—C3 | 118.41 (17) | N5—C16—H16A | 111.3 (12) |
| C6—C1—C2 | 124.48 (16) | C17—C16—H16A | 109.6 (12) |

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|--------------|-------------|-----------------|--------------|
| C6—C1—N1 | 116.28 (16) | N5—C16—H16B | 106.4 (11) |
| C2—C1—N1 | 119.24 (15) | C17—C16—H16B | 111.3 (11) |
| O1—C2—C1 | 123.51 (16) | H16A—C16—H16B | 106.2 (16) |
| O1—C2—C3 | 124.90 (16) | N6—C17—C16 | 111.76 (15) |
| C1—C2—C3 | 111.58 (14) | N6—C17—H17A | 105.8 (11) |
| C4—C3—C2 | 124.16 (16) | C16—C17—H17A | 110.2 (11) |
| C4—C3—N3 | 116.38 (16) | N6—C17—H17B | 105.1 (11) |
| C2—C3—N3 | 119.44 (15) | C16—C17—H17B | 112.0 (11) |
| C3—C4—C5 | 119.36 (18) | H17A—C17—H17B | 111.7 (16) |
| C3—C4—H4 | 119.3 (13) | N6—C18—C19 | 110.49 (15) |
| C5—C4—H4 | 121.4 (13) | N6—C18—H18A | 107.9 (11) |
| C4—C5—C6 | 121.23 (16) | C19—C18—H18A | 110.3 (11) |
| C4—C5—N2 | 119.28 (18) | N6—C18—H18B | 105.3 (11) |
| C6—C5—N2 | 119.49 (17) | C19—C18—H18B | 111.5 (11) |
| C1—C6—C5 | 119.18 (17) | H18A—C18—H18B | 111.3 (16) |
| C1—C6—H6 | 117.8 (12) | N5—C19—C18 | 112.19 (14) |
| C5—C6—H6 | 123.0 (12) | N5—C19—H19A | 105.6 (10) |
| C23—O9—H109 | 108.0 (18) | C18—C19—H19A | 108.9 (10) |
| C7—N4—C15 | 119.85 (16) | N5—C19—H19B | 110.7 (10) |
| C7—N4—C21 | 118.47 (16) | C18—C19—H19B | 109.8 (10) |
| C15—N4—C21 | 121.66 (14) | H19A—C19—H19B | 109.6 (14) |
| C13—N5—C19 | 117.44 (14) | N6—C20—H20A | 108.9 (14) |
| C13—N5—C16 | 118.83 (14) | N6—C20—H20B | 109.9 (14) |
| C19—N5—C16 | 108.08 (14) | H20A—C20—H20B | 110 (2) |
| C20—N6—C17 | 110.80 (17) | N6—C20—H20C | 109.0 (14) |
| C20—N6—C18 | 110.72 (16) | H20A—C20—H20C | 110 (2) |
| C17—N6—C18 | 111.68 (14) | H20B—C20—H20C | 109.3 (19) |
| C20—N6—H1N6 | 108.7 (11) | N4—C21—C22 | 112.15 (19) |
| C17—N6—H1N6 | 107.7 (11) | N4—C21—H21A | 108.2 (11) |
| C18—N6—H1N6 | 107.1 (12) | C22—C21—H21A | 111.4 (11) |
| N4—C7—C8 | 123.61 (19) | N4—C21—H21B | 105.7 (13) |
| N4—C7—H7 | 113.1 (12) | C22—C21—H21B | 108.4 (13) |
| C8—C7—H7 | 123.3 (12) | H21A—C21—H21B | 110.9 (17) |
| C7—C8—C9 | 120.63 (16) | C21—C22—H22A | 108.4 (17) |
| C7—C8—C23 | 118.05 (19) | C21—C22—H22B | 110.9 (15) |
| C9—C8—C23 | 121.28 (19) | H22A—C22—H22B | 110 (2) |
| O10—C9—C8 | 123.29 (16) | C21—C22—H22C | 109.2 (17) |
| O10—C9—C10 | 121.36 (18) | H22A—C22—H22C | 112 (2) |
| C8—C9—C10 | 115.36 (17) | H22B—C22—H22C | 107 (2) |
| C15—C10—C11 | 117.85 (15) | O8—C23—O9 | 121.43 (19) |
| C15—C10—C9 | 121.42 (17) | O8—C23—C8 | 123.9 (2) |
| C11—C10—C9 | 120.73 (16) | O9—C23—C8 | 114.6 (2) |
| C12—C11—C10 | 120.33 (17) | | |
| O3B—N1—C1—C6 | -2.1 (18) | O10—C9—C10—C11 | -0.1 (3) |
| O2B—N1—C1—C6 | -177 (2) | C8—C9—C10—C11 | -179.94 (16) |
| O2—N1—C1—C6 | 153.5 (6) | C15—C10—C11—C12 | 3.5 (3) |
| O3—N1—C1—C6 | -21.4 (8) | C9—C10—C11—C12 | -177.41 (16) |

| | | | |
|----------------|--------------|-----------------|--------------|
| O3B—N1—C1—C2 | 178.6 (18) | C10—C11—C12—F1 | -175.41 (15) |
| O2B—N1—C1—C2 | 3 (2) | C10—C11—C12—C13 | 3.1 (3) |
| O2—N1—C1—C2 | -25.9 (6) | C19—N5—C13—C14 | 1.4 (2) |
| O3—N1—C1—C2 | 159.2 (7) | C16—N5—C13—C14 | 134.68 (17) |
| C6—C1—C2—O1 | 178.26 (18) | C19—N5—C13—C12 | 178.36 (15) |
| N1—C1—C2—O1 | -2.5 (3) | C16—N5—C13—C12 | -48.4 (2) |
| C6—C1—C2—C3 | -0.2 (2) | C11—C12—C13—C14 | -7.6 (2) |
| N1—C1—C2—C3 | 179.05 (15) | F1—C12—C13—C14 | 170.87 (14) |
| O1—C2—C3—C4 | -177.76 (18) | C11—C12—C13—N5 | 175.20 (16) |
| C1—C2—C3—C4 | 0.7 (2) | F1—C12—C13—N5 | -6.3 (2) |
| O1—C2—C3—N3 | 0.3 (3) | N5—C13—C14—C15 | -177.14 (15) |
| C1—C2—C3—N3 | 178.69 (15) | C12—C13—C14—C15 | 5.8 (2) |
| O7—N3—C3—C4 | -157.8 (2) | C7—N4—C15—C14 | -174.14 (15) |
| O6—N3—C3—C4 | 21.9 (2) | C21—N4—C15—C14 | 4.4 (2) |
| O7—N3—C3—C2 | 24.0 (3) | C7—N4—C15—C10 | 4.2 (2) |
| O6—N3—C3—C2 | -156.28 (17) | C21—N4—C15—C10 | -177.34 (16) |
| C2—C3—C4—C5 | -1.4 (3) | C13—C14—C15—N4 | 178.65 (15) |
| N3—C3—C4—C5 | -179.47 (16) | C13—C14—C15—C10 | 0.4 (2) |
| C3—C4—C5—C6 | 1.6 (3) | C11—C10—C15—N4 | 176.55 (15) |
| C3—C4—C5—N2 | -178.45 (16) | C9—C10—C15—N4 | -2.6 (2) |
| O4—N2—C5—C4 | -178.56 (18) | C11—C10—C15—C14 | -5.1 (2) |
| O5—N2—C5—C4 | 0.5 (3) | C9—C10—C15—C14 | 175.75 (15) |
| O4—N2—C5—C6 | 1.4 (3) | C13—N5—C16—C17 | -77.71 (19) |
| O5—N2—C5—C6 | -179.54 (17) | C19—N5—C16—C17 | 59.43 (18) |
| C2—C1—C6—C5 | 0.5 (3) | C20—N6—C17—C16 | 174.57 (16) |
| N1—C1—C6—C5 | -178.80 (15) | C18—N6—C17—C16 | 50.64 (19) |
| C4—C5—C6—C1 | -1.2 (3) | N5—C16—C17—N6 | -55.40 (19) |
| N2—C5—C6—C1 | 178.90 (16) | C20—N6—C18—C19 | -175.03 (17) |
| C15—N4—C7—C8 | -2.3 (3) | C17—N6—C18—C19 | -51.05 (19) |
| C21—N4—C7—C8 | 179.16 (17) | C13—N5—C19—C18 | 77.00 (19) |
| N4—C7—C8—C9 | -1.3 (3) | C16—N5—C19—C18 | -60.83 (18) |
| N4—C7—C8—C23 | -179.19 (17) | N6—C18—C19—N5 | 57.51 (19) |
| C7—C8—C9—O10 | -177.07 (17) | C7—N4—C21—C22 | 94.7 (2) |
| C23—C8—C9—O10 | 0.7 (3) | C15—N4—C21—C22 | -83.8 (2) |
| C7—C8—C9—C10 | 2.8 (2) | C7—C8—C23—O8 | -2.2 (3) |
| C23—C8—C9—C10 | -179.41 (16) | C9—C8—C23—O8 | 179.97 (19) |
| O10—C9—C10—C15 | 179.02 (15) | C7—C8—C23—O9 | 177.75 (17) |
| C8—C9—C10—C15 | -0.8 (2) | C9—C8—C23—O9 | -0.1 (3) |

Hydrogen-bond geometry (Å, °)

| <i>D</i> —H... <i>A</i> | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|----------------------------|-------------|---------------|-----------------------|-------------------------|
| O9—H1O9...O10 | 0.96 (3) | 1.62 (3) | 2.519 (2) | 155 (3) |
| N6—H1N6...O1 ⁱ | 0.91 (2) | 1.84 (2) | 2.701 (2) | 159 (2) |
| N6—H1N6...O7 ⁱ | 0.91 (2) | 2.422 (19) | 2.987 (2) | 120.6 (15) |
| C6—H6...O3 | 0.878 (19) | 2.38 (2) | 2.706 (16) | 102.3 (14) |
| C11—H11...F1 ⁱⁱ | 0.933 (19) | 2.46 (2) | 3.209 (2) | 137.3 (18) |
| C16—H16A...F1 | 0.97 (2) | 2.18 (2) | 2.846 (2) | 124.6 (15) |

| | | | | |
|------------------------------|------------|------------|------------|------------|
| C17—H17A···O8 ⁱⁱⁱ | 0.928 (19) | 2.582 (19) | 3.430 (3) | 152.2 (14) |
| C17—H17B···O4 ^{iv} | 1.02 (2) | 2.55 (2) | 3.407 (3) | 141.2 (16) |
| C18—H18A···O3 ^v | 0.940 (19) | 2.47 (2) | 3.241 (16) | 139.2 (18) |
| C19—H19B···O5 ^{vi} | 0.990 (17) | 2.566 (17) | 3.300 (2) | 131.0 (13) |
| C20—H20A···O7 ⁱ | 0.97 (2) | 2.51 (2) | 3.079 (3) | 118.0 (18) |
| C20—H20C···O4 ^{iv} | 1.01 (3) | 2.39 (3) | 3.245 (3) | 141.8 (19) |
| C21—H21B···O8 ^{vii} | 0.90 (3) | 2.53 (3) | 3.415 (3) | 169 (2) |

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