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Syntheses and crystal structures of three salts of sparfloxacin, one incorporating extended tapes of fused pentagonal water assemblies

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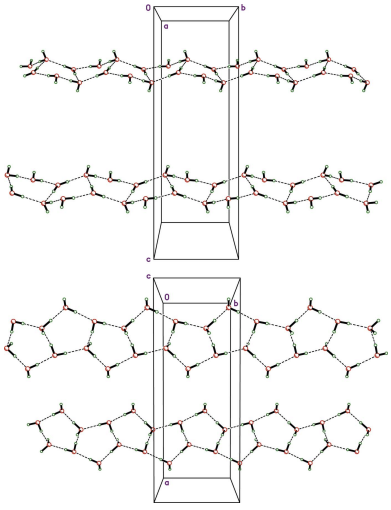
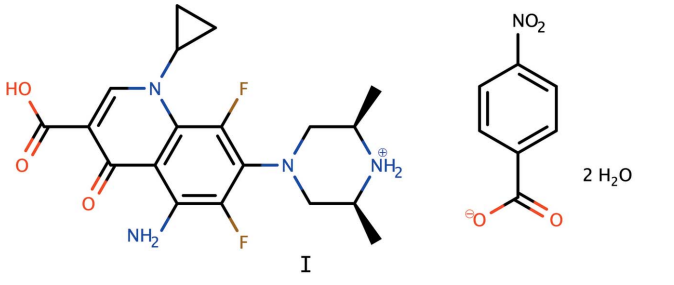
Three organic salts of sparfloxacin, a difluorinated third-generation fluoroquinolone antibiotic, have been synthesized and their crystal structures determined. The salts, sparfloxacinium 4-nitrobenzoate dihydrate, $C_{19}H_{23}F_2N_4O_3^+\cdot C_7H_4NO_4^-\cdot 2H_2O$ (**I**), sparfloxacinium 2-phenylacetate, $C_{19}H_{23}F_2N_4O_3^+\cdot C_8H_7O_2^-$ (**II**), and sparfloxacinium 4-methylbenzoate trihydrate, $C_{19}H_{23}F_2N_4O_3^+\cdot C_8H_7O_2^-\cdot 3H_2O$ (**III**), exhibit similar inter-species packing interactions. The overall crystal structures each, however, have their own distinct characteristics, which are described here along with a Hirshfeld surface analysis of the various atom–atom contacts involving the sparfloxacinium cations. In the crystal structure of **III**, an extended supramolecular tape of edge-fused hydrogen-bonded water pentagons was found. These pentagonal water and tape motifs are compared to related constructs in a broad selection of structure types, ranging from macromolecules to small molecules, clathrates, and exotic 'ice' formations on clean metal surfaces.

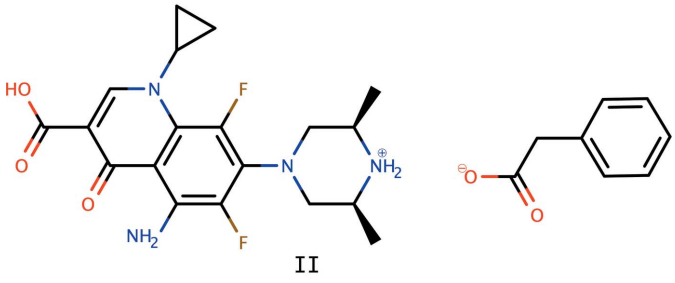
1. Chemical context

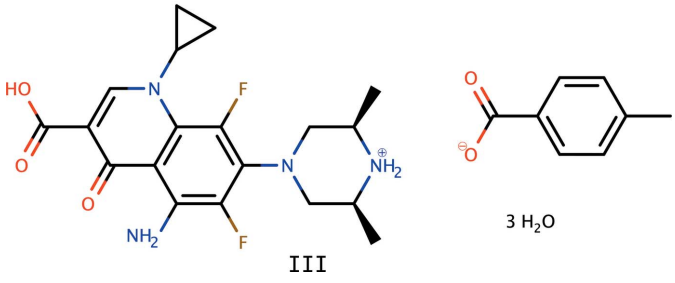
Fluoroquinolones are highly effective antibiotics that have many advantageous pharmacokinetic properties, including high oral bioavailability, large volume of distribution, and broad-spectrum antimicrobial activity (Jain *et al.*, 2002; Marona *et al.*, 2001; Faria *et al.*, 2006). A critical review of fluoroquinolones was given by Zhanel *et al.*, 2002. Sparfloxacin, systematic name: 5-amino-1-cyclopropyl-7-(*cis*-3,5-dimethyl-1-piperazinyl)-6,8-difluoro-1,4-dihydro-4-oxo-3-quinoline carboxylic acid, $C_{19}H_{22}F_2N_4O_3$, is a difluorinated third-generation fluoroquinolone antibiotic and is one of the most important and successful classes of man-made antibacterials used in the treatment of lung infections, urinary tract infections, and cutaneous allergy. A structural investigation of sparfloxacin using mass spectrometry and MNDO semi-empirical molecular orbital calculations was published by Abd El-Kareem *et al.* (2018). The photodegradation of sparfloxacin and isolation of its degradation products by preparative HPLC was published by Salgado *et al.* (2005). Nanoparticles of Ag–TiO_2 for photocatalytic degradation of sparfloxacin was reported by Kulkarni *et al.* (2018). Newly validated UV spectrophotometric methods for the determination of sparfloxacin in tablets was described by Sowjanya *et al.* (2020). The electrostatic properties of nine fluoroquinolone



antibiotics derived directly from their crystal structures was given by Holstein *et al.* (2012). Reviews of sparfloxacin (Schentag, 2000), its antibacterial activity, pharmacokinetic properties, clinical efficacy, and tolerability in lower respiratory tract infections (Goa *et al.*, 1997), as well as a review of its penetration into the lower respiratory tract and sinuses (Wise & Honeybourne, 1996) have also been published.







In view of the importance of floxacin drugs, particularly sparfloxacin, the present paper reports the crystal structures of three sparfloxacin salts with organic anions: sparfloxacinium 4-nitrobenzoate dihydrate (**I**), sparfloxacinium 2-phenylacetate (**II**) and sparfloxacinium 4-methylbenzoate trihydrate (**III**). A serendipitous extended tape of fused water pentagons in **III** is also described.

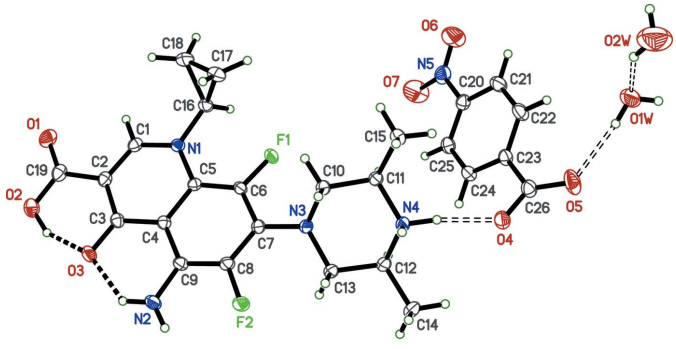


Figure 2
An ellipsoid (50% probability) plot of **II**. Intramolecular hydrogen bonds are drawn as thick dashed lines while intermolecular hydrogen bonds are drawn as open dashed lines.

2. Structural commentary

Reactions between sparfloxacin and 4-nitrobenzoic acid, phenylacetic acid, and 4-methylbenzoic acid yielded the three salts sparfloxacinium 4-nitrobenzoate (**I**), sparfloxacinium 2-phenylacetate (**II**), and sparfloxacinium 4-methylbenzoate (**III**) (see Scheme). Crystals of **I** (Fig. 1) form as a dihydrate, with a chain of disordered water molecules occupying channels parallel to the *a*-axis. In **II** (Fig. 2), the crystals are solvent free. Compound **III** (Fig. 3) crystallizes as a trihydrate, with the water molecules in channels parallel to the *b*-axis (section 3, *Supramolecular details*). Within each salt, the sparfloxacinium cations are structurally similar and have no unusual bond lengths or angles. The dihydroquinoline ring system plus the attached amino, carboxyl, and fluorine atoms are essentially planar (r.m.s. deviations are: **I** = 0.0744 Å, **II** = 0.0505 Å and **III** = 0.0496 Å), with the largest deviations being 0.1901 (8) Å for F1 in **I**, 0.1392 (8) Å for O2 in **II**, and 0.1343 (8) for F1 in **III**. A pair of intramolecular hydrogen bonds (Tables 1–3), O2—H2*O*···O3 and N2—H2*NB*···O3, each form *S*(6) ring motifs that are preserved in all three

Figure 1
An ellipsoid (30% probability) plot of **I**. Intramolecular hydrogen bonds are drawn as thick dashed lines while intermolecular hydrogen bonds are drawn as open dashed lines. Minor disorder components of water molecules are omitted to enhance clarity.

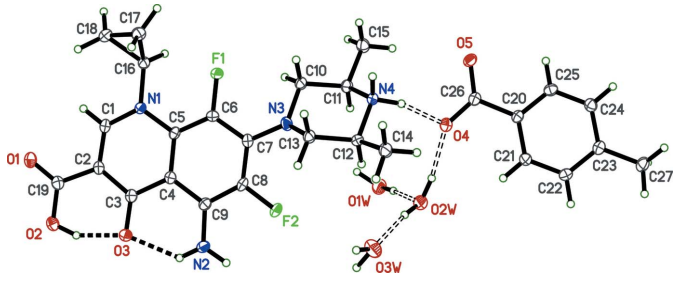


Figure 3
An ellipsoid (50% probability) plot of **III**. Intramolecular hydrogen bonds are drawn as thick dashed lines while intermolecular hydrogen bonds are drawn as open dashed lines.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2*O*···O3	0.97 (3)	1.60 (3)	2.5257 (15)	157 (2)
N2—H2*NB*···O3	0.92 (2)	1.901 (19)	2.6343 (17)	135.0 (16)
N4—H4*NA*···O4	0.960 (18)	1.824 (18)	2.7666 (15)	166.4 (15)
O1*W*—H1*W*1···O5	0.81	2.00	2.806 (2)	173
O2*W*—H1*W*2···O1*W*	0.82	2.12	2.811 (5)	141
O1*W*—H2*W*1···O2*W*^{i}	0.80	2.01	2.803 (5)	172
O2*W*—H2*W*2···O1^{ii}	0.82	2.02	2.807 (3)	161
N2—H2*NA*···O1*W*^{iii}	0.89 (2)	2.07 (2)	2.947 (2)	167.8 (19)
N4—H4*NB*···O4^{iv}	0.913 (18)	1.957 (18)	2.8405 (16)	162.5 (15)

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

Table 2
Hydrogen-bond geometry (Å, °) for **II**.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2*O*···O3	0.95 (2)	1.61 (2)	2.5162 (12)	157.3 (18)
N2—H2*NB*···O3	0.900 (17)	1.917 (16)	2.6200 (13)	133.6 (14)
N4—H4*NB*···O4	0.949 (16)	1.781 (16)	2.7122 (12)	166.3 (13)
N2—H2*NA*···O5^{i}	0.869 (17)	2.232 (17)	2.9958 (13)	146.5 (14)
N4—H4*NA*···O4^{ii}	0.956 (16)	1.834 (16)	2.7580 (12)	161.8 (14)

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

structures. The main differences in the cations result from variations in the orientation of the dimethyl piperazine rings, the C6—C7—N3—C10 torsion angles being 60.12 (16)° in **I**, 39.09 (16)° in **II**, and −30.9 (2)° in **III**. By contrast, there is much less variation of the cyclopropyl orientations: C1—N1—C16—C17 torsion angles are 105.99 (15)°, 103.20 (12)°, and 102.71 (15)° for **I**, **II**, and **III**, respectively. The similarities and differences are highlighted in a least-squares-fit overlay of the three cations (Fig. 4).

In the chosen asymmetric units for each structure, anion placement was selected (amongst symmetry equivalents) so as to form the shortest hydrogen bond between the cationic N4 and the carboxylate O4 of their respective anions (Tables 1–3). In **I** and **III**, these involve the equatorial hydrogen (H4*NA*), *i.e.*, N4—H4*NA*···O4, having donor—acceptor distances of 2.7666 (15) Å in **I** and 2.6722 (16) Å in **III**. By contrast, in **II**, the shortest hydrogen bond for N4 involves the axial hydrogen (H4*NB*), *i.e.*, N4—H4*NB*···O4 at 2.7122 (12) Å.

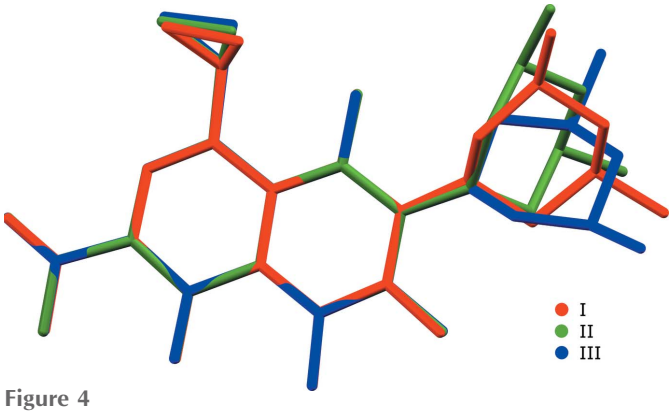


Figure 4
A least-squares-fit overlay of the sparfloxacinium cations in **I** (red), **II** (green), and **III** (blue).

Table 3
Hydrogen-bond geometry (Å, °) for **III**.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2*O*···O3	0.92 (2)	1.64 (2)	2.5014 (14)	155 (2)
N2—H2*NB*···O3	0.91 (2)	1.93 (2)	2.6367 (17)	133.4 (18)
N4—H4*NA*···O4	0.967 (19)	1.73 (2)	2.6722 (16)	164.1 (17)
N4—H4*NB*···O5^{i}	0.91 (2)	1.86 (2)	2.7473 (16)	163.0 (18)
N2—H2*NA*···O2*W*^{ii}	0.91 (2)	2.12 (2)	2.9664 (17)	153.9 (17)
O2*W*—H2*W*2···O4	0.94 (3)	1.80 (3)	2.7371 (16)	171 (2)
O1*W*—H1*W*1···O2*W*	1.04 (3)	1.71 (3)	2.7503 (17)	175 (2)
O2*W*—H1*W*2···O3*W*	0.93 (3)	1.83 (3)	2.7546 (18)	171 (2)
O1*W*—H2*W*1···O1^{iii}	0.96 (3)	1.89 (3)	2.8434 (16)	171 (2)
O3*W*—H1*W*3···O1*W*^{ii}	1.02 (3)	1.82 (3)	2.8362 (17)	173 (2)
O3*W*—H2*W*3···O1*W*^{iv}	1.00 (4)	1.88 (4)	2.8798 (18)	178 (3)

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$; (iii) $-x, -y+1, -z+1$; (iv) $x, y+1, z$.

3. Supramolecular features

The crystal packing in **I**, **II**, and **III** share a few of types of supramolecular features, including extensive hydrogen bonding and π–π stacking of their quinoline ring systems. Nevertheless, within each structure, the specific interactions lead to distinct structural motifs.

In **I**, pairs of N4—H4*NA*···O4 and N4—H4*NB*···O4^{inv} (inv = $-x+1, -y+1, -z+1$) hydrogen bonds (Table 1) form $R_4^2(8)$ ring motifs (Fig. 5) with their inversion-related counterparts, in which the anion O4 atom is a bifurcated acceptor. Hydrogen bonding to the water channel is complicated by the inherent disorder within the water chains, but there is clear evidence of an O1*W*—H1*W*1···O5 hydrogen bond to the 4-nitrobenzoate anion (Table 1, Fig. 5). In **II**, a similar $R_4^2(8)$ ring motif (Fig. 6), to that in **I**, with bifurcated acceptor O4, is built from N4—H4*NB*···O4 and N4—H4*NA*···O4^{inv} hydrogen bonds (Table 2). Structure **III** features a hydrogen-bonded $R_4^4(12)$ ring motif formed from N4—H4*NA*···O4 and N4—

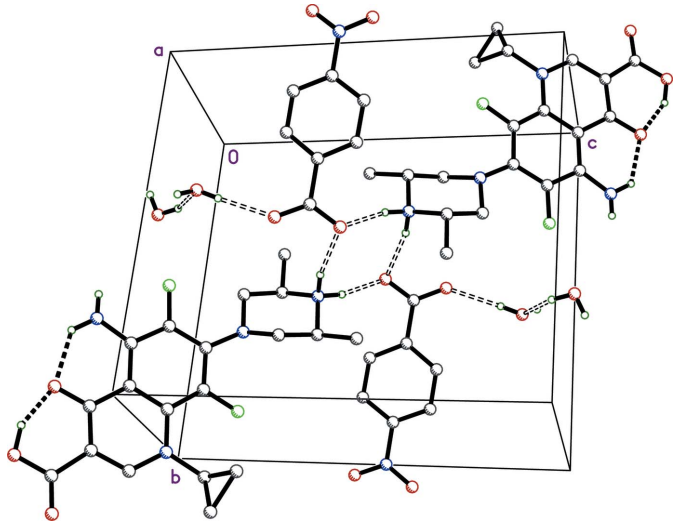


Figure 5
A partial packing plot of **I** viewed approximately down the *a*-axis. Intramolecular hydrogen bonds are drawn as thick dashed lines while intermolecular hydrogen bonds are drawn as open dashed lines. Minor disorder components of water molecules and H atoms on groups not involved in hydrogen bonding are omitted.

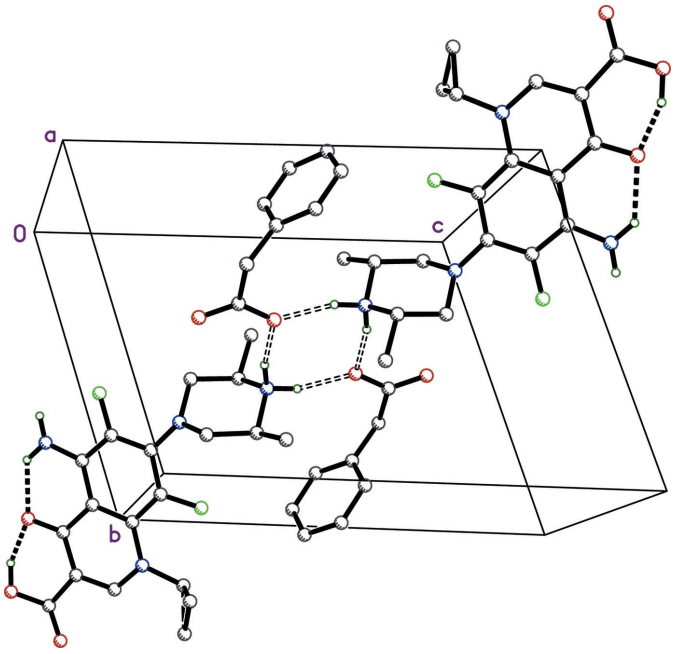


Figure 6
A partial packing plot of **II** viewed down the *a*-axis. Intramolecular hydrogen bonds are drawn as thick dashed lines and intermolecular hydrogen bonds are drawn as open dashed lines. H atoms on groups not involved in hydrogen bonding are omitted.

H4*NB*···O5^{inv} hydrogen bonds of cation/anion pairs (Table 3, Fig. 7). For each structure, additional strong intermolecular N—H···O hydrogen bonds connect the NH_2 amine group to a water molecule (in **I** and **III**) or to an anion (in **II**) (Tables 1–3). The hydrogen-bonded water structure in **III** is especially intricate, and will be described separately (*vide infra*).

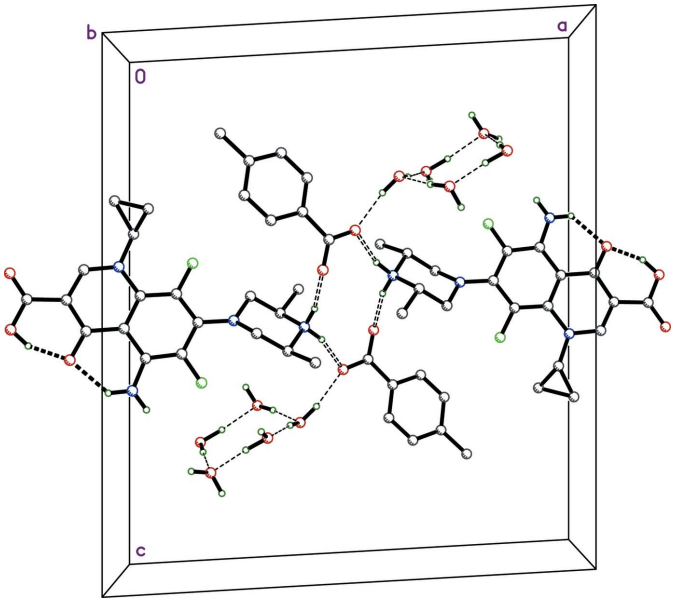


Figure 7
A partial packing plot of **III** viewed down the *b*-axis. Intramolecular hydrogen bonds are drawn as thick dashed lines, intermolecular hydrogen bonds are drawn as open dashed lines, and hydrogen bonds to and between water molecules are drawn as thin dashed lines. The water molecules form hydrogen-bonded pentagons (see also Fig. 11). H atoms on groups not involved in hydrogen bonding are omitted.

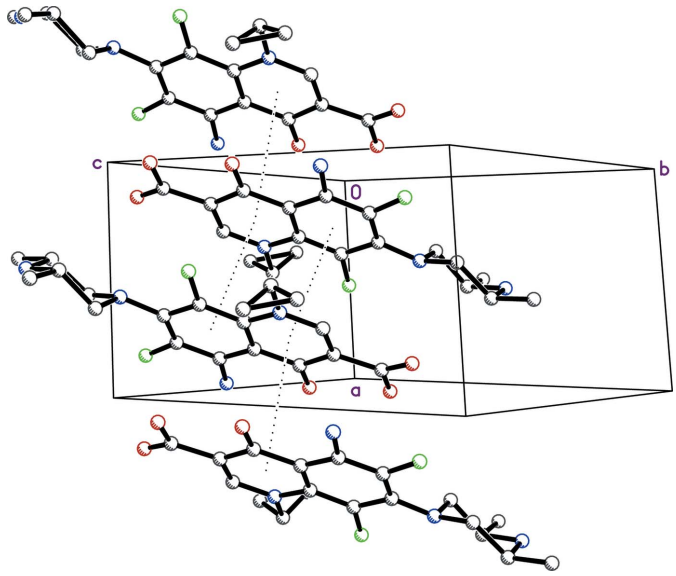


Figure 8
A partial packing plot of **I** viewed approximately along [0$\overline{1}\overline{1}$] showing π–π stacking of inversion-related sparfloxacinium cations into columns that extend parallel to the *a*-axis. Dotted lines connect the centroids of overlapping rings.

Inversion-related quinoline ring systems in **I** π–π stack to give two different interplanar spacings: 3.3789 (14) Å (*via* $-x$, $-y$, $-z+2$) and 3.3901 (14) Å (*via* $-x+1$, $-y$, $-z+2$) for the mean planes through N1,C1–C9,O3, leading to columns of cations along the *a*-axis (Fig. 8). In **II**, stacking of inversion-related ($-x+2$, $-y$, $-z+2$) cations gives an interplanar

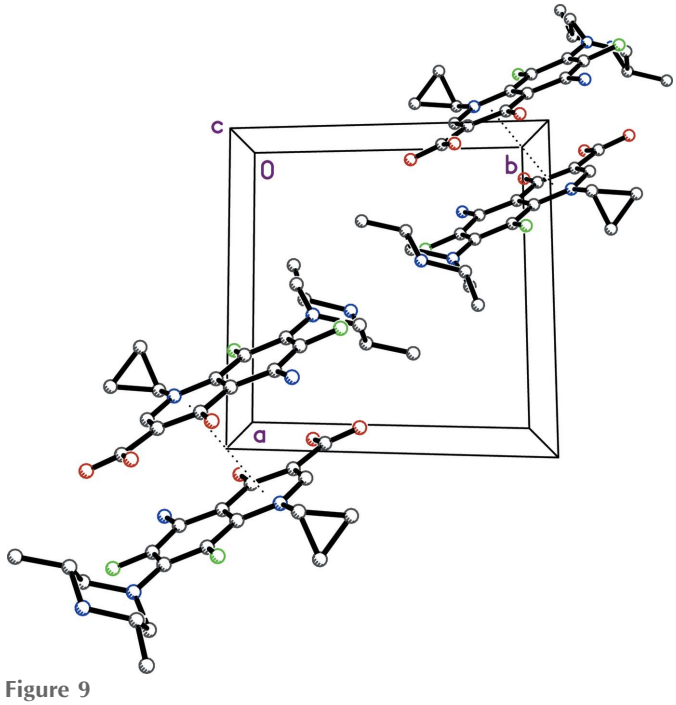


Figure 9
A partial packing plot of **II** viewed down the *c*-axis. Pairs of inversion-related sparfloxacinium cations form π–π-stacked dimers. Dotted lines connect the centroids of overlapping rings.

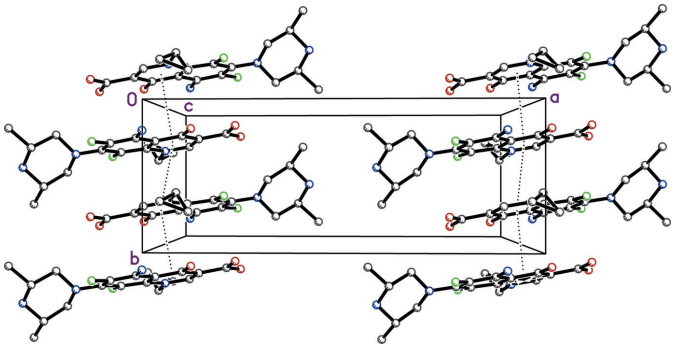


Figure 10
A partial packing plot of **III** viewed down the *c*-axis showing π–π stacking of inversion-related sparfloxacinium cations into columns that extend parallel to the *b*-axis. Dotted lines connect the centroids of overlapping rings.

spacing of 3.3413 (11) Å, but does not lead to extended columns because the offset to adjacent pairs is too great (Fig. 9). In **III**, π–π stacking again leads to extended columns, this time parallel to the *b*-axis (Fig. 10), with interplanar spacings of 3.3452 (15) Å (*via* $-x$, $-y+2$, $-z+1$) and 3.4677 (14) Å (*via* $-x$, $-y+1$, $-z+1$).

Atom–atom contact coverages obtained from Hirshfeld surface 2D fingerprint plots calculated using *CrystalExplorer* (Spackman *et al.*, 2021) for the sparfloxacinium cations in **I**, **II**, and **III** are given in the supporting information (Figs. S1–S3) and summarized in Table 4. In all three salts, the predominant contacts are between H···H, H···O/O···H, and H···C/C···H.

Table 4
Atom-atom contact coverages (%) in **I**, **II**, and **III**.

Atom contacts	I	II	III
H···H	41.2	40.3	48.0
H···O	28.8	25.5	23.4
H···C	10.0	15.5	7.9
C···C	6.0	4.6	7.7
H···F	3.5	7.7	5.7
O···F	2.6	0.2	1.3
C···O	2.3	1.4	2.5
H···N	1.6	3.0	1.5

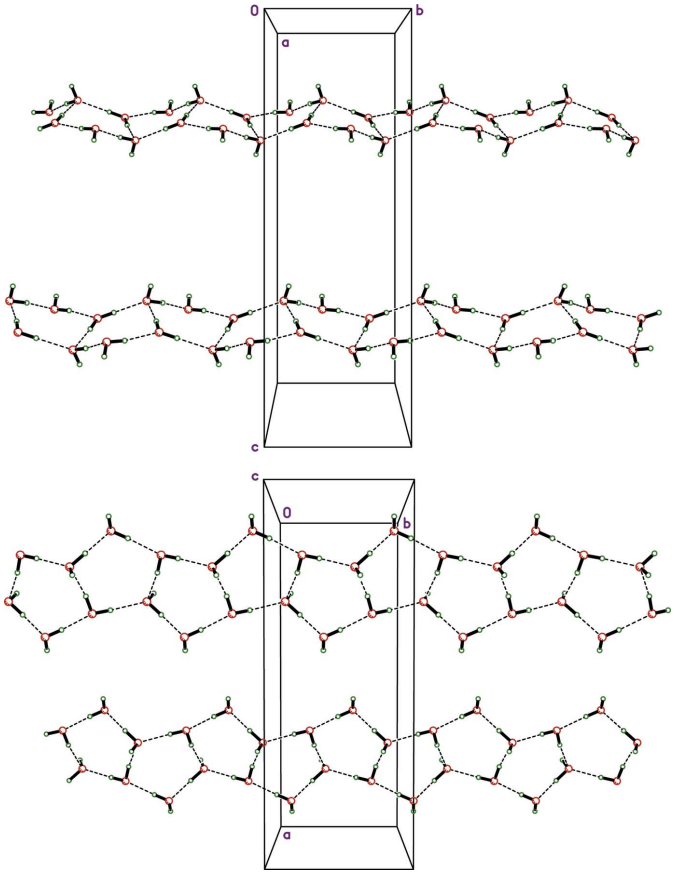


Figure 11
Two views of the extended chains of water-molecule pentagons observed in the crystal packing of **III**. Hydrogen bonds are depicted as dashed lines. For the sake of clarity, the cations and anions are omitted.

In the structure of **III**, the three water molecules hydrogen bond to *n*-glide-related copies (Table 3) to form cyclic five-membered slightly puckered pentagonal ring structures. These water pentagons are edge-fused to form extended ribbon- or tape-like chains that propagate parallel to the *b*-axis by further hydrogen bonding to *n*-glide- and translation-related water molecules. The tapes hydrogen bond to the sparfloxacinium cation as both donor (O1*W*—H2*W*1···O1^{iii}) and acceptor (N2—H2*NA*···O2*W*^{ii}) and to the anion as a donor (O2*W*—H2*W*2···O4) (symmetry codes as per Table 3). Two views of these supramolecular water-tape structures are shown in Fig. 11. A few other instances of similar pentagonal water assemblies are known. These are compared to those of **III**, along with some additional background information, in section 4 (*Database survey and related literature*).

4. Database survey and related literature

A search of the Cambridge Structure Database (CSD version 5.43 with all updates through September 2022; Groom *et al.*, 2016) for the keyword 'sparfloxacin' returned (ignoring duplicates) 29 records. Of these, 11 are complexes with metals and have few structural characteristics in common with **I**, **II**, or **III** other than the presence of ligated sparfloxacin molecules. Of the remaining 18 entries, 12 are salts and all but one are co-crystals, hydrates and/or solvates. CSD entry JEKMOB (Miyamoto *et al.*, 1990) corresponds to pure sparfloxacin, while COQWOU (Sivalakshmidevi *et al.*, 2000) is a trihydrate of sparfloxacin. Four entries, UXEPUK, UXEQEV, UXEQAR, and UXEQIZ (Gunnam *et al.*, 2016) are sparfloxacin co-crystallized with methyl, ethyl, propyl, and isobutyl *para*-hydroxybenzoic acids, respectively. The remaining 12 structures are sparfloxacinium salts, five of which have inorganic counter-anions [CIBYIW (BF_4^-; Shingnapurkar *et al.*, 2007), GALFEH (Br^-; Golovnev & Vasil'ev, 2016), JADGON and JADGUT ($CdBr_4^{2-}$ and $ZnBr_4^{2-}$; Vasil'ev & Golovnev, 2015), and YOBCUP ($CuBr_4^-$; Vasil'ev & Golovnev, 2014)]. Of the seven entries with organic counter-anions, GAPCUZ and GAPDAG (Zhang *et al.*, 2022) are salts with pyrocatechuic acid that differ in their occluded solvent, while

Table 5
Experimental details.

	I	II	III
Crystal data			
Chemical formula	$C_{19}H_{23}F_2N_4O_3^+\cdot C_7H_4NO_4^-\cdot 2H_2O$	$C_{19}H_{23}F_2N_4O_3^+\cdot C_8H_7O_2^-$	$C_{19}H_{23}F_2N_4O_3^+\cdot C_8H_7O_2^-\cdot 3H_2O$
M_r	595.56	528.55	582.60
Crystal system, space group	Triclinic, $P\overline{1}$	Triclinic, $P\overline{1}$	Monoclinic, $P2_1/n$
Temperature (K)	250	90	90
a, b, c (Å)	7.5736 (4), 13.1809 (9), 13.8947 (9)	10.0222 (4), 10.1145 (4), 13.5255 (5)	18.4423 (9), 7.0694 (3), 21.0669 (10)
α, β, γ (°)	85.658 (2), 82.316 (2), 81.108 (2)	69.606 (2), 73.032 (2), 83.747 (2)	90, 93.252 (2), 90
V (Å^3)	1355.94 (15)	1229.15 (9)	2742.2 (2)
Z	2	2	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.12	0.11	0.11
Crystal size (mm)	0.33 × 0.31 × 0.27	0.34 × 0.28 × 0.26	0.19 × 0.15 × 0.04
Data collection			
Diffractometer	Bruker D8 Venture dual source	Bruker D8 Venture dual source	Bruker D8 Venture dual source
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)	Multi-scan (*SADABS*; Krause *et al.*, 2015)	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.930, 0.971	0.914, 0.959	0.894, 0.959
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	45287, 6210, 4944	41293, 5639, 5029	44990, 6296, 5086
R_{int}	0.033	0.038	0.043
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.653	0.650	0.650
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.039, 0.107, 1.04	0.034, 0.092, 1.02	0.040, 0.100, 1.04
No. of reflections	6210	5639	6296
No. of parameters	443	365	418
No. of restraints	46	0	0
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.27, −0.22	0.37, −0.20	0.31, −0.23

Computer programs: *APEX3* (Bruker, 2016), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2019/2* (Sheldrick, 2015*b*), *SHELXTL* and *XP* in *SHELXTL* (Sheldrick, 2008), and *publCIF* (Westrip, 2010).

IJEBIL, IJEBOR, IJEBUX, IJECAE, and IJEDIN (Djalò *et al.*, 2021) have 2-(carboxymethyl)-2-hydroxybutanedioate, pyridine-3-carboxylate, 3-carboxybenzoate, 3-carboxyprop-2-enoate, and 2-aminobenzoate anions respectively. The crystal structures of some closely related compounds, *viz.*, bis(-lomefloxacin) 1,4-benzenedicarboxylate dihydrate (XEWSOI; Zhou *et al.*, 2006), gatifloxacin hydrochloride (HOTTOA; Yu *et al.*, 2009), lomefloxacinium picrate (IKAPIU; Jasinski *et al.*, 2011) and lomefloxacin chloride dihydrate (LATPON; Holstein *et al.*, 2012) have also been reported.

Assemblies of water having pentagonal structural units are not uncommon. They are ubiquitous in the clathrate hydrates (see *e.g.*, Englezos, 1993), but are far less common in other structure types. They have been reported in studies of small proteins [*e.g.*, crambin (refcode 1CRN in PDB; Teeter, 1984), BPTI (refcode 1BPI; Parkin *et al.*, 1996); PDB = Protein Data Bank (Berman *et al.*, 2000)] and collagen peptides (Bella *et al.*, 1995), and in small molecules, including a hexahydrate of pinacol (CSD code PINOLH01; Hao *et al.*, 2005), amongst others. A few extended linear water–pentagon tapes similar to those in **III** have also been reported, *e.g.*, L-leucyl-L-alanine tetrahydrate (CSD code RAVMOQ; Görbitz, 1997); *trans*-4,4′-azopyridine dioxide tetrahydrate (WAGMOH; Ma *et al.*, 2004), a Cu^{II}-based MOF (OFUYOE02; Mukherjee *et al.*, 2011), and a Co(cyclam)Cl_2 complex (REFDUD; Jana *et al.*, 2012). In RAVMOQ, the pentagons have similar regularity to those in **III** but the tapes are considerably more buckled, while in WAGMOH and OFUYOE02 the pentagons/tapes are both severely distorted/buckled relative to those in **III**. In REFDUD, the tapes of pentagons are further linked into extended layers. Water pentagons are also believed to play a role in ice nucleation (see *e.g.* Pirzadeh *et al.*, 2011 and references therein). Indeed, an exotic mono-periodic form of 'ice' consisting of a linear array of fused water pentagons, reported to nucleate on the (110) surface of copper at temperatures between 100 and 140 K (Carrasco *et al.*, 2009), bears a *striking* resemblance to the water-pentagon tape in **III**.

5. Synthesis and crystallization

Sparfloxacin (a gift from Recon Healthcare, Bengaluru) (100 mg, 0.255 mmol) was dissolved in methanol (10 ml) and water (1 ml) under constant stirring at 333 K for 30 min. Equimolar solutions of either 4-nitrobenzoic acid (43 mg, 0.255 mmol), phenylacetic acid (35 mg, 0.255 mmol), or 4-methylbenzoic acid (35 mg, 0.255 mmol) in methanol (10 ml) and acetonitrile (10 ml) were added separately to the solutions of sparfloxacin and stirring was continued for 60 min at 333 K. The mixtures were then cooled to room temperature. X-ray quality crystals were formed by slow evaporation over

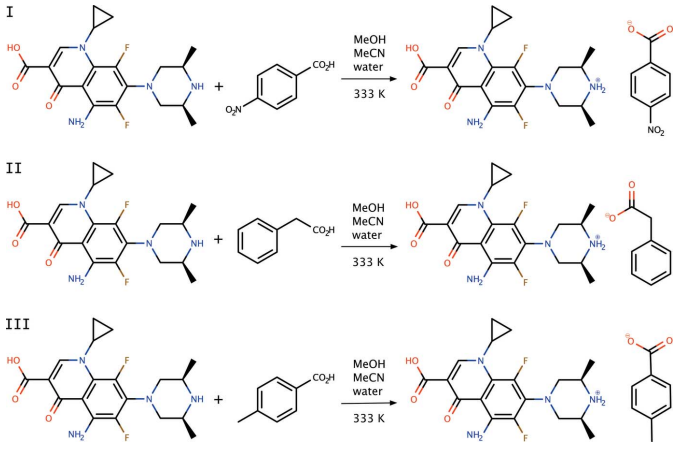


Figure 12
Synthetic routes to the formation of **I**, **II**, and **III**.

fifteen days. The melting points were 511–514 K (**I**), 485–488 K (**II**) and 498–503 K (**III**). A generalized reaction scheme for the three salts of sparfloxacin is given in Fig. 12.

6. Data collection and structure refinement

Crystal data, data collection, and structure refinement details are given in Table 5. At 90 K, crystals of **I** gave diffraction with satellite reflections, suggesting modulation of the structure. On warming, the satellites diminished, and were absent at the data collection temperature of 250 (1) K. The water molecules in **I** were extensively disordered. The *SQUEEZE* routine in *PLATON* (Spek, 2015) suggested the presence of ∼40e$^-$ in the cell 'voids', corresponding to two water molecules per asymmetric unit. Thus, a hydrate model consisting of two major components [occupancies 0.688 (3) for O1*W* and 0.608 (3) for O2*W*] and two minor parts for each major [occupancies 0.185 (3), 0.127 (3), 0.265 (3), and 0.128 (3) for O1*W*′, O1*W*", O2*W*′, and O2*W*", respectively] was built from difference-map peaks. Hydrogen atoms on these partial-occupancy fragments were placed so as to make reasonable hydrogen bonds, but other than H1*W*1 and H1*W*2, their presence is solely to ensure a correct atom count. Occupancies for these disordered waters were restrained using SUMP and their U^{ij} restrained with SIMU in *SHELXL* (Sheldrick, 2015*b*). Crystals of **II** and **III** presented no such problems. All non-disordered hydrogen atoms were found in difference-Fourier maps, but those bound to carbon were subsequently included in the refinement using riding models, with constrained distances set to *SHELXL* defaults [0.99 Å (R_3CH), 0.94 Å (Csp^2H), 0.98 Å (R_2CH$_2$), 0.97 Å (RCH$_3$) in **I** and 1.00 Å (R_3CH), 0.95 Å (Csp^2H), 0.99 Å (R_2CH$_2$), 0.98 Å (RCH$_3$) in **II** and **III**]. U_{iso}(H) values for carbon-bound hydrogens were set to 1.2U_{eq} or 1.5U_{eq} (CH$_3$) of the parent atom. The OH and NH hydrogen atoms were refined freely (as per Fábry, 2018), aside from the minor-component water hydrogens of **I**, which were fixed and had U_{iso}(H) set to 1.5U_{eq} of their water oxygen.

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supporting information

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Syntheses and crystal structures of three salts of sparfloxacin, one incorporating extended tapes of fused pentagonal water assemblies

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Computing details

For all structures, data collection: *APEX3* (Bruker, 2016); cell refinement: *APEX3* (Bruker, 2016); data reduction: *APEX3* (Bruker, 2016); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2019/2* (Sheldrick, 2015b); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008) and *publCIF* (Westrip, 2010).

4-(5-Amino-3-carboxy-1-cyclopropyl-6,8-difluoro-4-oxo-1,4-dihydroquinolin-7-yl)-2,6-dimethylpiperazin-1-ium 4-nitrobenzoate dihydrate (I)

Crystal data

$C_{19}H_{23}F_2N_4O_3^+ \cdot C_7H_4NO_4^- \cdot 2H_2O$
M_r = 595.56
Triclinic, $P\overline{1}$
a = 7.5736 (4) Å
b = 13.1809 (9) Å
c = 13.8947 (9) Å
α = 85.658 (2)°
β = 82.316 (2)°
γ = 81.108 (2)°
V = 1355.94 (15) Å^3
Z = 2
$F(000)$ = 624
D_x = 1.459 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9803 reflections
θ = 2.8–27.5°
μ = 0.12 mm^{-1}
T = 250 K
Cut block, yellow
0.33 × 0.31 × 0.27 mm

Data collection

Bruker D8 Venture dual source diffractometer
Radiation source: microsource
Detector resolution: 7.41 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min} = 0.930, T_{max} = 0.971
45287 measured reflections
6210 independent reflections
4944 reflections with $I > 2\sigma(I)$
R_{int} = 0.033
θ_{max} = 27.6°, θ_{min} = 2.2°
h = −9→9
k = −17→17
l = −17→18

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.107
S = 1.04
6210 reflections
443 parameters
46 restraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map	$w = 1/[\sigma^2(F_o^2) + (0.0419P)^2 + 0.4829P]$ where $P = (F_o^2 + 2F_c^2)/3$
Hydrogen site location: mixed	$(\Delta/\sigma)_{max} = 0.001$
H atoms treated by a mixture of independent and constrained refinement	$\Delta\rho_{max} = 0.27$ e Å^{-3}
	$\Delta\rho_{min} = -0.22$ e Å^{-3}

Special details

Experimental. The crystal was mounted using polyisobutene oil on the tip of a fine glass fibre, which was fastened in a copper mounting pin with electrical solder. It was placed directly into the cold gas stream of a liquid-nitrogen based cryostat (Hope, 1994; Parkin & Hope, 1998).
The crystals appeared to become modulated (doubled cell, some satellite reflections) when cooled to 90K. Visual inspection of crystal integrity and diffraction quality vs temperature established a safe temperature for data collection of -23° C.

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 progress was checked using *Platon* (Spek, 2020) and by an *R*-tensor (Parkin, 2000). The final model was further checked with the IUCr utility *checkCIF*.

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
O1W	1.0080 (5)	0.43691 (14)	0.13115 (13)	0.0767 (9)	0.688 (3)
H1W1	0.989672	0.457266	0.185755	0.115*	0.688 (3)
H2W1	1.079647	0.467749	0.098119	0.115*	0.688 (3)
O1W′	0.8676 (14)	0.4128 (5)	0.1178 (6)	0.070 (3)	0.185 (3)
H5W1	0.868139	0.425647	0.174506	0.105*	0.185 (3)
H6W1	0.860698	0.433812	0.056840	0.105*	0.185 (3)
O2W	0.7704 (6)	0.4430 (2)	−0.0090 (2)	0.0987 (12)	0.607 (3)
H1W2	0.795334	0.431906	0.047015	0.148*	0.607 (3)
H2W2	0.794277	0.387475	−0.034142	0.148*	0.607 (3)
O2W′	0.6241 (18)	0.4587 (10)	0.0029 (7)	0.148 (4)	0.265 (3)
H3W2	0.591257	0.540477	−0.008066	0.222*	0.265 (3)
H4W2	0.611625	0.429007	0.056105	0.222*	0.265 (3)
O1W"	1.1155 (10)	0.5163 (6)	0.1538 (6)	0.035 (2)	0.127 (2)
H3W1	1.079941	0.501309	0.210951	0.053*	0.127 (2)
H4W1	1.058065	0.486154	0.122076	0.053*	0.127 (2)
O2W"	0.4728 (18)	0.3998 (9)	0.0386 (7)	0.071 (4)	0.128 (3)
H5W2	0.458449	0.355478	0.002884	0.107*	0.128 (3)
H6W2	0.421442	0.383063	0.092059	0.107*	0.128 (3)
F1	0.52757 (11)	0.05643 (6)	0.77813 (6)	0.0371 (2)	
F2	0.18695 (13)	0.33665 (6)	0.93914 (6)	0.0439 (2)	
O1	0.17039 (17)	−0.28135 (8)	1.13520 (8)	0.0491 (3)	
O2	0.04706 (18)	−0.15414 (10)	1.22784 (8)	0.0531 (3)	
H2O	0.038 (3)	−0.080 (2)	1.2189 (18)	0.092 (8)*	
O3	0.05728 (15)	0.02882 (8)	1.16122 (7)	0.0410 (2)	
N1	0.36989 (15)	−0.08370 (8)	0.91686 (8)	0.0278 (2)	
N2	0.06988 (19)	0.21803 (10)	1.08748 (9)	0.0408 (3)	
H2NA	0.054 (3)	0.2860 (17)	1.0912 (15)	0.068 (6)*	

H2NB	0.028 (3)	0.1740 (15)	1.1371 (14)	0.056 (5)*
N3	0.42835 (16)	0.25859 (8)	0.77468 (8)	0.0312 (2)
N4	0.53893 (17)	0.38569 (8)	0.61030 (8)	0.0302 (2)
H4NA	0.627 (2)	0.4111 (13)	0.5620 (13)	0.047 (5)*
H4NB	0.433 (2)	0.4245 (13)	0.5980 (12)	0.045 (5)*
C1	0.30722 (18)	−0.14548 (10)	0.99045 (9)	0.0299 (3)
H1	0.337777	−0.216882	0.985064	0.036*
C2	0.20213 (18)	−0.11166 (10)	1.07257 (9)	0.0304 (3)
C3	0.15347 (17)	−0.00419 (10)	1.08473 (9)	0.0292 (3)
C4	0.22010 (17)	0.06439 (10)	1.00629 (9)	0.0266 (3)
C5	0.33138 (16)	0.02359 (9)	0.92265 (9)	0.0250 (2)
C6	0.40038 (17)	0.0912 (1)	0.85124 (9)	0.0269 (3)
C7	0.35467 (17)	0.1980 (1)	0.85219 (9)	0.0275 (3)
C8	0.24335 (18)	0.23468 (10)	0.93348 (10)	0.0305 (3)
C9	0.17783 (18)	0.17274 (10)	1.01162 (9)	0.0292 (3)
C10	0.38665 (19)	0.24164 (10)	0.67695 (9)	0.0313 (3)
H10A	0.270121	0.281690	0.666003	0.038*
H10B	0.378584	0.168737	0.672166	0.038*
C11	0.53265 (18)	0.27401 (9)	0.60029 (9)	0.0297 (3)
H11	0.649781	0.234195	0.613369	0.036*
C12	0.5777 (2)	0.40582 (10)	0.71004 (10)	0.0333 (3)
H12	0.697490	0.367927	0.720892	0.040*
C13	0.4360 (2)	0.36726 (10)	0.78632 (10)	0.0336 (3)
H13A	0.465625	0.375773	0.851484	0.040*
H13B	0.318020	0.407835	0.779453	0.040*
C14	0.5807 (3)	0.51991 (11)	0.71586 (12)	0.0502 (4)
H14A	0.608301	0.532920	0.779579	0.075*
H14B	0.463712	0.557707	0.705381	0.075*
H14C	0.671827	0.542109	0.666327	0.075*
C15	0.5023 (2)	0.25721 (12)	0.49722 (10)	0.0389 (3)
H15A	0.498785	0.184777	0.490906	0.058*
H15B	0.599751	0.279189	0.451824	0.058*
H15C	0.388849	0.296912	0.483088	0.058*
C16	0.4737 (2)	−0.12999 (10)	0.83077 (10)	0.0334 (3)
H16	0.603900	−0.124621	0.821780	0.040*
C17	0.3878 (2)	−0.12486 (13)	0.73970 (11)	0.0475 (4)
H17A	0.262288	−0.091945	0.741442	0.057*
H17B	0.463252	−0.114810	0.677711	0.057*
C18	0.4245 (3)	−0.22495 (13)	0.79618 (13)	0.0575 (5)
H18A	0.321508	−0.253376	0.832512	0.069*
H18B	0.522463	−0.276239	0.768785	0.069*
C19	0.1399 (2)	−0.18977 (11)	1.14682 (10)	0.0378 (3)
O4	0.75064 (14)	0.48408 (8)	0.46618 (8)	0.0416 (3)
O5	0.9197 (2)	0.49587 (10)	0.32356 (9)	0.0704 (4)
O6	1.2405 (3)	−0.02164 (11)	0.40432 (12)	0.0886 (5)
O7	1.2235 (3)	0.00344 (12)	0.55450 (12)	0.0933 (6)
N5	1.20030 (19)	0.03305 (10)	0.47204 (11)	0.0486 (3)
C20	1.11515 (19)	0.13962 (10)	0.45442 (11)	0.0349 (3)

C21	1.1012 (2)	0.17648 (12)	0.35967 (11)	0.0441 (4)
H21	1.140867	0.133723	0.307551	0.053*
C22	1.0273 (2)	0.27779 (12)	0.34355 (11)	0.0431 (4)
H22	1.018655	0.304761	0.279485	0.052*
C23	0.96571 (18)	0.34046 (11)	0.42053 (10)	0.0328 (3)
C24	0.98225 (19)	0.30048 (11)	0.51504 (10)	0.0338 (3)
H24	0.942055	0.342696	0.567518	0.041*
C25	1.05718 (19)	0.19935 (11)	0.53262 (10)	0.0355 (3)
H25	1.068158	0.172163	0.596423	0.043*
C26	0.8742 (2)	0.44884 (11)	0.40125 (11)	0.0384 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1W	0.150 (3)	0.0352 (10)	0.035 (1)	0.0000 (13)	0.0110 (12)	−0.0034 (7)
O1W′	0.089 (6)	0.032 (4)	0.074 (5)	0.014 (4)	0.023 (5)	−0.007 (3)
O2W	0.138 (3)	0.0614 (17)	0.093 (2)	0.0114 (19)	−0.015 (2)	−0.0300 (15)
O2W′	0.152 (9)	0.198 (11)	0.103 (6)	−0.014 (9)	−0.021 (7)	−0.076 (7)
O1W"	0.035 (4)	0.035 (4)	0.034 (4)	−0.003 (3)	−0.005 (3)	0.009 (3)
O2W"	0.107 (10)	0.067 (7)	0.043 (6)	−0.021 (7)	−0.003 (6)	−0.022 (5)
F1	0.0448 (5)	0.0298 (4)	0.0315 (4)	−0.0027 (3)	0.0113 (3)	−0.0035 (3)
F2	0.0602 (6)	0.0226 (4)	0.0418 (5)	0.0027 (4)	0.0092 (4)	−0.0022 (3)
O1	0.0692 (8)	0.0342 (6)	0.0456 (6)	−0.0145 (5)	−0.0130 (6)	0.0113 (5)
O2	0.0740 (8)	0.0489 (7)	0.0341 (6)	−0.0190 (6)	0.0073 (5)	0.0082 (5)
O3	0.0515 (6)	0.0395 (6)	0.0280 (5)	−0.0064 (5)	0.0082 (4)	−0.0004 (4)
N1	0.0335 (6)	0.0228 (5)	0.0262 (5)	−0.0020 (4)	−0.0033 (4)	−0.0010 (4)
N2	0.0544 (8)	0.0304 (7)	0.0321 (6)	−0.0001 (6)	0.0092 (6)	−0.0048 (5)
N3	0.0459 (7)	0.0243 (5)	0.0237 (5)	−0.0093 (5)	−0.0011 (5)	0.0003 (4)
N4	0.0354 (6)	0.0231 (5)	0.0296 (6)	−0.0018 (5)	0.0000 (5)	0.0031 (4)
C1	0.0362 (7)	0.0242 (6)	0.0301 (7)	−0.0048 (5)	−0.0095 (5)	0.0028 (5)
C2	0.0346 (7)	0.0310 (7)	0.0271 (6)	−0.0078 (5)	−0.0085 (5)	0.0046 (5)
C3	0.0298 (6)	0.0341 (7)	0.0241 (6)	−0.0052 (5)	−0.0050 (5)	0.0006 (5)
C4	0.0286 (6)	0.0270 (6)	0.0240 (6)	−0.0032 (5)	−0.0048 (5)	−0.0003 (5)
C5	0.0272 (6)	0.0227 (6)	0.0252 (6)	−0.0024 (5)	−0.0056 (5)	−0.0009 (5)
C6	0.0299 (6)	0.0271 (6)	0.0225 (6)	−0.0023 (5)	0.0001 (5)	−0.0034 (5)
C7	0.0323 (6)	0.0259 (6)	0.0241 (6)	−0.0049 (5)	−0.0037 (5)	0.0008 (5)
C8	0.0373 (7)	0.0215 (6)	0.0311 (7)	−0.0002 (5)	−0.0023 (5)	−0.0018 (5)
C9	0.0329 (7)	0.0292 (6)	0.0244 (6)	−0.0012 (5)	−0.0028 (5)	−0.0027 (5)
C10	0.0409 (7)	0.0279 (6)	0.0252 (6)	−0.0075 (5)	−0.0032 (5)	0.0005 (5)
C11	0.0369 (7)	0.0224 (6)	0.0278 (6)	−0.0015 (5)	−0.0011 (5)	0.0003 (5)
C12	0.0443 (8)	0.0249 (6)	0.0306 (7)	−0.0076 (6)	−0.0030 (6)	0.0001 (5)
C13	0.0468 (8)	0.0234 (6)	0.0298 (7)	−0.0060 (6)	−0.0001 (6)	−0.0013 (5)
C14	0.0772 (12)	0.0299 (8)	0.0452 (9)	−0.0202 (8)	0.0012 (8)	−0.0020 (6)
C15	0.0495 (9)	0.0399 (8)	0.0272 (7)	−0.0107 (7)	0.0000 (6)	−0.0014 (6)
C16	0.0397 (7)	0.0263 (6)	0.0318 (7)	−0.0006 (5)	0.0011 (6)	−0.0050 (5)
C17	0.0602 (10)	0.0509 (9)	0.0329 (8)	−0.0105 (8)	−0.0027 (7)	−0.0126 (7)
C18	0.0856 (13)	0.0344 (8)	0.0513 (10)	−0.0160 (8)	0.0122 (9)	−0.0163 (7)
C19	0.0442 (8)	0.0379 (8)	0.0332 (7)	−0.0117 (6)	−0.0110 (6)	0.0085 (6)

O4	0.0427 (6)	0.0327 (5)	0.0423 (6)	0.0030 (4)	0.0069 (5)	0.0031 (4)
O5	0.0889 (10)	0.0538 (8)	0.0475 (7)	0.0188 (7)	0.0197 (7)	0.0213 (6)
O6	0.1316 (15)	0.0443 (8)	0.0737 (10)	0.0239 (8)	0.0071 (10)	−0.0100 (7)
O7	0.1428 (16)	0.0572 (9)	0.0674 (10)	0.0305 (9)	−0.0285 (10)	0.0123 (7)
N5	0.0492 (8)	0.0353 (7)	0.0557 (9)	0.0007 (6)	0.0019 (6)	0.0043 (6)
C20	0.0325 (7)	0.0303 (7)	0.0399 (8)	−0.0023 (5)	−0.0014 (6)	0.0016 (6)
C21	0.0546 (9)	0.0396 (8)	0.0343 (8)	0.0008 (7)	0.0020 (7)	−0.0066 (6)
C22	0.0552 (9)	0.0434 (8)	0.0261 (7)	0.0026 (7)	−0.0018 (6)	0.0017 (6)
C23	0.0307 (7)	0.0337 (7)	0.0315 (7)	−0.0016 (5)	0.0001 (5)	0.0017 (5)
C24	0.0347 (7)	0.0374 (7)	0.0274 (7)	−0.0014 (6)	−0.0011 (5)	−0.0030 (5)
C25	0.0352 (7)	0.0390 (8)	0.0308 (7)	−0.0037 (6)	−0.0045 (6)	0.0042 (6)
C26	0.0412 (8)	0.0357 (8)	0.0342 (7)	0.0012 (6)	−0.0004 (6)	0.0036 (6)

Geometric parameters (Å, º)

O1W—O1W′	1.196 (10)	C6—C7	1.3973 (18)
O1W—H1W1	0.8112	C7—C8	1.3865 (18)
O1W—H2W1	0.8024	C8—C9	1.3923 (18)
O1W—H5W1	1.1709	C10—C11	1.5170 (18)
O1W′—H5W1	0.8189	C10—H10A	0.9800
O1W′—H6W1	0.8767	C10—H10B	0.9800
O1W′—H1W2	1.1808	C11—C15	1.5182 (19)
O2W—H6W1	1.2013	C11—H11	0.9900
O2W—H1W2	0.8218	C12—C14	1.5157 (19)
O2W—H2W2	0.8195	C12—C13	1.5223 (19)
O2W′—H3W2	1.0717	C12—H12	0.9900
O2W′—H4W2	0.8116	C13—H13A	0.9800
O1W"—H3W1	0.8237	C13—H13B	0.9800
O1W"—H4W1	0.8198	C14—H14A	0.9700
O2W"—H5W2	0.8223	C14—H14B	0.9700
O2W"—H6W2	0.8224	C14—H14C	0.9700
F1—C6	1.3573 (14)	C15—H15A	0.9700
F2—C8	1.3508 (14)	C15—H15B	0.9700
O1—C19	1.2124 (18)	C15—H15C	0.9700
O2—C19	1.3224 (19)	C16—C18	1.490 (2)
O2—H2O	0.97 (3)	C16—C17	1.491 (2)
O3—C3	1.2705 (16)	C16—H16	0.9900
N1—C1	1.3408 (16)	C17—C18	1.491 (2)
N1—C5	1.4053 (16)	C17—H17A	0.9800
N1—C16	1.4601 (16)	C17—H17B	0.9800
N2—C9	1.3601 (17)	C18—H18A	0.9800
N2—H2NA	0.89 (2)	C18—H18B	0.9800
N2—H2NB	0.92 (2)	O4—C26	1.2682 (17)
N3—C7	1.3986 (16)	O5—C26	1.2384 (18)
N3—C13	1.4644 (16)	O6—N5	1.207 (2)
N3—C10	1.4751 (17)	O7—N5	1.209 (2)
N4—C11	1.4975 (16)	N5—C20	1.4694 (18)
N4—C12	1.5053 (18)	C20—C25	1.374 (2)

N4—H4NA	0.960 (18)	C20—C21	1.380 (2)
N4—H4NB	0.913 (18)	C21—C22	1.380 (2)
C1—C2	1.3633 (19)	C21—H21	0.9400
C1—H1	0.9400	C22—C23	1.388 (2)
C2—C3	1.4245 (19)	C22—H22	0.9400
C2—C19	1.4852 (18)	C23—C24	1.3916 (19)
C3—C4	1.4506 (17)	C23—C26	1.5095 (19)
C4—C9	1.4199 (18)	C24—C25	1.383 (2)
C4—C5	1.4292 (17)	C24—H24	0.9400
C5—C6	1.3867 (17)	C25—H25	0.9400

O1W′—O1W—H1W1	104.5	C10—C11—H11	108.7
O1W′—O1W—H2W1	133.2	C15—C11—H11	108.7
H1W1—O1W—H2W1	110.0	N4—C12—C14	109.29 (11)
O1W′—O1W—H5W1	40.5	N4—C12—C13	109.42 (11)
H1W1—O1W—H5W1	64.5	C14—C12—C13	111.47 (12)
H2W1—O1W—H5W1	156.0	N4—C12—H12	108.9
O1W—O1W′—H5W1	68.1	C14—C12—H12	108.9
O1W—O1W′—H6W1	102.1	C13—C12—H12	108.9
H5W1—O1W′—H6W1	150.1	N3—C13—C12	110.13 (11)
O1W—O1W′—H1W2	126.7	N3—C13—H13A	109.6
H5W1—O1W′—H1W2	146.3	C12—C13—H13A	109.6
H6W1—O1W′—H1W2	25.0	N3—C13—H13B	109.6
H6W1—O2W—H1W2	21.9	C12—C13—H13B	109.6
H6W1—O2W—H2W2	104.5	H13A—C13—H13B	108.1
H1W2—O2W—H2W2	106.0	C12—C14—H14A	109.5
H3W2—O2W′—H4W2	122.7	C12—C14—H14B	109.5
H3W1—O1W"—H4W1	104.8	H14A—C14—H14B	109.5
H5W2—O2W"—H6W2	104.4	C12—C14—H14C	109.5
C19—O2—H2O	105.3 (14)	H14A—C14—H14C	109.5
C1—N1—C5	119.87 (11)	H14B—C14—H14C	109.5
C1—N1—C16	118.82 (11)	C11—C15—H15A	109.5
C5—N1—C16	121.29 (10)	C11—C15—H15B	109.5
C9—N2—H2NA	120.4 (14)	H15A—C15—H15B	109.5
C9—N2—H2NB	115.8 (12)	C11—C15—H15C	109.5
H2NA—N2—H2NB	123.3 (18)	H15A—C15—H15C	109.5
C7—N3—C13	120.17 (11)	H15B—C15—H15C	109.5
C7—N3—C10	116.79 (11)	N1—C16—C18	119.56 (13)
C13—N3—C10	111.65 (10)	N1—C16—C17	118.95 (12)
C11—N4—C12	111.82 (10)	C18—C16—C17	60.01 (11)
C11—N4—H4NA	111.3 (10)	N1—C16—H16	115.6
C12—N4—H4NA	109.6 (11)	C18—C16—H16	115.6
C11—N4—H4NB	110.7 (11)	C17—C16—H16	115.6
C12—N4—H4NB	109.2 (11)	C18—C17—C16	59.96 (11)
H4NA—N4—H4NB	104.0 (14)	C18—C17—H17A	117.8
N1—C1—C2	124.37 (12)	C16—C17—H17A	117.8
N1—C1—H1	117.8	C18—C17—H17B	117.8
C2—C1—H1	117.8	C16—C17—H17B	117.8

C1—C2—C3	120.03 (12)	H17A—C17—H17B	114.9
C1—C2—C19	118.03 (12)	C16—C18—C17	60.03 (10)
C3—C2—C19	121.93 (12)	C16—C18—H18A	117.8
O3—C3—C2	120.95 (12)	C17—C18—H18A	117.8
O3—C3—C4	122.34 (12)	C16—C18—H18B	117.8
C2—C3—C4	116.71 (11)	C17—C18—H18B	117.8
C9—C4—C5	118.93 (11)	H18A—C18—H18B	114.9
C9—C4—C3	120.79 (11)	O1—C19—O2	120.84 (13)
C5—C4—C3	120.28 (11)	O1—C19—C2	122.93 (14)
C6—C5—N1	122.45 (11)	O2—C19—C2	116.23 (13)
C6—C5—C4	118.84 (11)	O6—N5—O7	122.86 (15)
N1—C5—C4	118.70 (11)	O6—N5—C20	118.87 (15)
F1—C6—C5	120.87 (11)	O7—N5—C20	118.25 (14)
F1—C6—C7	115.55 (11)	C25—C20—C21	122.68 (13)
C5—C6—C7	123.46 (11)	C25—C20—N5	118.74 (13)
C8—C7—C6	115.87 (11)	C21—C20—N5	118.56 (13)
C8—C7—N3	125.60 (12)	C22—C21—C20	118.18 (14)
C6—C7—N3	118.49 (11)	C22—C21—H21	120.9
F2—C8—C7	119.99 (11)	C20—C21—H21	120.9
F2—C8—C9	115.54 (11)	C21—C22—C23	120.96 (14)
C7—C8—C9	124.44 (12)	C21—C22—H22	119.5
N2—C9—C8	118.91 (12)	C23—C22—H22	119.5
N2—C9—C4	122.81 (12)	C22—C23—C24	119.14 (13)
C8—C9—C4	118.21 (11)	C22—C23—C26	119.83 (13)
N3—C10—C11	109.88 (11)	C24—C23—C26	120.96 (13)
N3—C10—H10A	109.7	C25—C24—C23	120.74 (13)
C11—C10—H10A	109.7	C25—C24—H24	119.6
N3—C10—H10B	109.7	C23—C24—H24	119.6
C11—C10—H10B	109.7	C20—C25—C24	118.29 (13)
H10A—C10—H10B	108.2	C20—C25—H25	120.9
N4—C11—C10	107.6 (1)	C24—C25—H25	120.9
N4—C11—C15	109.68 (11)	O5—C26—O4	124.62 (14)
C10—C11—C15	113.43 (12)	O5—C26—C23	118.92 (13)
N4—C11—H11	108.7	O4—C26—C23	116.44 (12)

C5—N1—C1—C2	1.5 (2)	C5—C4—C9—C8	1.62 (18)
C16—N1—C1—C2	−176.94 (13)	C3—C4—C9—C8	−179.06 (12)
N1—C1—C2—C3	−0.6 (2)	C7—N3—C10—C11	−155.08 (11)
N1—C1—C2—C19	178.70 (12)	C13—N3—C10—C11	61.19 (14)
C1—C2—C3—O3	−179.23 (13)	C12—N4—C11—C10	58.92 (14)
C19—C2—C3—O3	1.5 (2)	C12—N4—C11—C15	−177.27 (11)
C1—C2—C3—C4	0.35 (18)	N3—C10—C11—N4	−59.62 (14)
C19—C2—C3—C4	−178.93 (12)	N3—C10—C11—C15	178.88 (11)
O3—C3—C4—C9	−0.8 (2)	C11—N4—C12—C14	−179.49 (12)
C2—C3—C4—C9	179.66 (12)	C11—N4—C12—C13	−57.18 (14)
O3—C3—C4—C5	178.54 (12)	C7—N3—C13—C12	159.20 (12)
C2—C3—C4—C5	−1.03 (18)	C10—N3—C13—C12	−58.45 (15)
C1—N1—C5—C6	176.48 (12)	N4—C12—C13—N3	55.29 (15)

C16—N1—C5—C6	−5.09 (19)	C14—C12—C13—N3	176.29 (13)
C1—N1—C5—C4	−2.13 (17)	C1—N1—C16—C18	36.0 (2)
C16—N1—C5—C4	176.30 (12)	C5—N1—C16—C18	−142.40 (14)
C9—C4—C5—C6	2.57 (18)	C1—N1—C16—C17	105.99 (15)
C3—C4—C5—C6	−176.75 (12)	C5—N1—C16—C17	−72.46 (17)
C9—C4—C5—N1	−178.76 (11)	N1—C16—C17—C18	−109.38 (15)
C3—C4—C5—N1	1.92 (18)	N1—C16—C18—C17	108.37 (15)
N1—C5—C6—F1	−8.58 (19)	C1—C2—C19—O1	−4.0 (2)
C4—C5—C6—F1	170.03 (11)	C3—C2—C19—O1	175.27 (14)
N1—C5—C6—C7	175.64 (12)	C1—C2—C19—O2	176.23 (13)
C4—C5—C6—C7	−5.75 (19)	C3—C2—C19—O2	−4.5 (2)
F1—C6—C7—C8	−171.68 (11)	O6—N5—C20—C25	175.16 (17)
C5—C6—C7—C8	4.30 (19)	O7—N5—C20—C25	−3.3 (2)
F1—C6—C7—N3	5.98 (18)	O6—N5—C20—C21	−6.6 (2)
C5—C6—C7—N3	−178.03 (12)	O7—N5—C20—C21	174.94 (18)
C13—N3—C7—C8	18.0 (2)	C25—C20—C21—C22	0.6 (2)
C10—N3—C7—C8	−122.47 (14)	N5—C20—C21—C22	−177.55 (15)
C13—N3—C7—C6	−159.38 (12)	C20—C21—C22—C23	−1.2 (3)
C10—N3—C7—C6	60.12 (16)	C21—C22—C23—C24	1.2 (2)
C6—C7—C8—F2	−177.64 (12)	C21—C22—C23—C26	−175.88 (15)
N3—C7—C8—F2	4.9 (2)	C22—C23—C24—C25	−0.7 (2)
C6—C7—C8—C9	0.3 (2)	C26—C23—C24—C25	176.36 (13)
N3—C7—C8—C9	−177.18 (13)	C21—C20—C25—C24	−0.1 (2)
F2—C8—C9—N2	−2.18 (19)	N5—C20—C25—C24	178.04 (13)
C7—C8—C9—N2	179.79 (13)	C23—C24—C25—C20	0.2 (2)
F2—C8—C9—C4	174.87 (11)	C22—C23—C26—O5	−31.0 (2)
C7—C8—C9—C4	−3.2 (2)	C24—C23—C26—O5	151.92 (17)
C5—C4—C9—N2	178.55 (13)	C22—C23—C26—O4	147.01 (15)
C3—C4—C9—N2	−2.1 (2)	C24—C23—C26—O4	−30.0 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2*O*···O3	0.97 (3)	1.60 (3)	2.5257 (15)	157 (2)
N2—H2*NB*···O3	0.92 (2)	1.901 (19)	2.6343 (17)	135.0 (16)
N4—H4*NA*···O4	0.960 (18)	1.824 (18)	2.7666 (15)	166.4 (15)
O1*W*—H1*W*1···O5	0.81	2.00	2.806 (2)	173
O2*W*—H1*W*2···O1*W*	0.82	2.12	2.811 (5)	141
O1*W*—H2*W*1···O2*W*^{i}	0.80	2.01	2.803 (5)	172
O2*W*—H2*W*2···O1^{ii}	0.82	2.02	2.807 (3)	161
N2—H2*NA*···O1*W*^{iii}	0.89 (2)	2.07 (2)	2.947 (2)	167.8 (19)
N4—H4*NB*···O4^{iv}	0.913 (18)	1.957 (18)	2.8405 (16)	162.5 (15)

Symmetry codes: (i) −*x*+2, −*y*+1, −*z*; (ii) −*x*+1, −*y*, −*z*+1; (iii) *x*−1, *y*, *z*+1; (iv) −*x*+1, −*y*+1, −*z*+1.

4-(5-Amino-3-carboxy-1-cyclopropyl-6,8-difluoro-4-oxo-1,4-dihydroquinolin-7-yl)-2,6-dimethylpiperazin-1-ium 2-phenylacetate (II)

Crystal data

$C_{19}H_{23}F_2N_4O_3^+ \cdot C_8H_7O_2^-$
$M_r = 528.55$
Triclinic, $P\overline{1}$
$a = 10.0222$ (4) Å
$b = 10.1145$ (4) Å
$c = 13.5255$ (5) Å
$\alpha = 69.606$ (2)°
$\beta = 73.032$ (2)°
$\gamma = 83.747$ (2)°
$V = 1229.15$ (9) Å^3
$Z = 2$
$F(000) = 556$
$D_x = 1.428$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9186 reflections
$\theta = 3.0$–27.5°
$\mu = 0.11$ mm^{-1}
$T = 90$ K
Irregular block, pale yellow
0.34 × 0.28 × 0.26 mm

Data collection

Bruker D8 Venture dual source diffractometer
Radiation source: microsource
Detector resolution: 7.41 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Krause *et al.*, 2015)
$T_{min} = 0.914$, $T_{max} = 0.959$
41293 measured reflections
5639 independent reflections
5029 reflections with $I > 2\sigma(I)$
$R_{int} = 0.038$
$\theta_{max} = 27.5°$, $\theta_{min} = 2.1°$
$h = -12 \rightarrow 12$
$k = -12 \rightarrow 13$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.092$
$S = 1.02$
5639 reflections
365 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0413P)^2 + 0.5792P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.37$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}

Special details

Experimental. The crystal was mounted using polyisobutene oil on the tip of a fine glass fibre, which was fastened in a copper mounting pin with electrical solder. It was placed directly into the cold gas stream of a liquid-nitrogen based cryostat (Hope, 1994; Parkin & Hope, 1998).
Diffraction data were collected with the crystal at 90K, which is standard practice in this laboratory for the majority of flash-cooled crystals.

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 progress was checked using *Platon* (Spek, 2020) and by an *R*-tensor (Parkin, 2000). The final model was further checked with the IUCr utility *checkCIF*.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
F1	0.70792 (7)	0.00637 (7)	0.83721 (5)	0.01777 (15)
F2	0.63127 (7)	0.35650 (7)	1.00282 (5)	0.01665 (14)
O1	1.05409 (8)	−0.41085 (8)	1.22035 (7)	0.01857 (17)
O2	1.00723 (10)	−0.25755 (9)	1.31012 (7)	0.02240 (19)
H2O	0.970 (2)	−0.164 (2)	1.2943 (16)	0.051 (5)*
O3	0.89918 (9)	−0.02316 (8)	1.22819 (6)	0.01721 (17)
N1	0.84402 (9)	−0.17056 (9)	0.99535 (7)	0.01228 (18)
N2	0.77272 (12)	0.21351 (11)	1.14682 (8)	0.0201 (2)
H2NA	0.7380 (17)	0.2964 (18)	1.1458 (13)	0.029 (4)*
H2NB	0.8144 (17)	0.1606 (17)	1.1985 (13)	0.027 (4)*
N3	0.59393 (10)	0.26309 (10)	0.84423 (7)	0.01448 (19)
N4	0.58386 (10)	0.38019 (10)	0.62261 (7)	0.01321 (18)
H4NA	0.6191 (17)	0.3897 (17)	0.5467 (13)	0.029 (4)*
H4NB	0.5030 (16)	0.4386 (16)	0.6268 (12)	0.023 (4)*
C1	0.91214 (11)	−0.24536 (11)	1.06947 (9)	0.0133 (2)
H1	0.950209	−0.334367	1.065994	0.016*
C2	0.93024 (11)	−0.20187 (11)	1.14943 (8)	0.0134 (2)
C3	0.88013 (11)	−0.06613 (11)	1.15534 (8)	0.0129 (2)
C4	0.80895 (11)	0.01794 (11)	1.07502 (8)	0.0123 (2)
C5	0.78917 (11)	−0.03613 (11)	0.99549 (8)	0.0119 (2)
C6	0.71912 (11)	0.04728 (11)	0.91986 (8)	0.0131 (2)
C7	0.66418 (11)	0.18133 (11)	0.91898 (8)	0.0128 (2)
C8	0.68554 (11)	0.22948 (11)	0.99773 (9)	0.0135 (2)
C9	0.75685 (11)	0.15531 (11)	1.07451 (8)	0.0131 (2)
C10	0.49686 (11)	0.20780 (11)	0.80689 (8)	0.0137 (2)
H10A	0.405327	0.255422	0.822658	0.016*
H10B	0.483568	0.105862	0.848679	0.016*
C11	0.54638 (11)	0.22823 (11)	0.68460 (8)	0.0132 (2)
H11	0.630826	0.167958	0.670230	0.016*
C12	0.68765 (11)	0.43180 (11)	0.66142 (9)	0.0149 (2)
H12	0.775319	0.374507	0.651603	0.018*
C13	0.62643 (12)	0.41177 (11)	0.78307 (9)	0.0145 (2)
H13A	0.694316	0.443183	0.810613	0.017*
H13B	0.540560	0.469619	0.793619	0.017*
C14	0.72062 (14)	0.58531 (13)	0.59395 (10)	0.0242 (3)
H14A	0.755513	0.594990	0.516135	0.036*
H14B	0.791838	0.617518	0.616781	0.036*
H14C	0.635807	0.642584	0.605345	0.036*
C15	0.43375 (12)	0.18919 (12)	0.64521 (9)	0.0176 (2)
H15A	0.466770	0.208543	0.565850	0.026*
H15B	0.349399	0.245187	0.662023	0.026*
H15C	0.412447	0.088674	0.682358	0.026*
C16	0.83214 (11)	−0.23184 (11)	0.91487 (8)	0.0139 (2)
H16	0.885555	−0.182759	0.837347	0.017*
C17	0.69701 (12)	−0.29534 (12)	0.92921 (9)	0.0190 (2)

H17A	0.668119	−0.282994	0.862478	0.023*
H17B	0.619520	−0.295690	0.994438	0.023*
C18	0.82133 (13)	−0.38861 (12)	0.94729 (9)	0.0189 (2)
H18A	0.820179	−0.446110	1.023612	0.023*
H18B	0.868786	−0.433412	0.891632	0.023*
C19	1.00275 (11)	−0.29946 (12)	1.22819 (9)	0.0153 (2)
O4	0.35788 (9)	0.55031 (9)	0.60167 (6)	0.01934 (18)
O5	0.29414 (9)	0.53584 (9)	0.77723 (7)	0.02231 (19)
C20	0.18020 (11)	0.80365 (11)	0.56629 (9)	0.0143 (2)
C21	0.27729 (12)	0.89939 (12)	0.55673 (9)	0.0183 (2)
H21	0.327649	0.877691	0.610123	0.022*
C22	0.30119 (13)	1.02595 (13)	0.47016 (10)	0.0221 (2)
H22	0.367933	1.090038	0.464389	0.026*
C23	0.22759 (13)	1.05909 (12)	0.39183 (9)	0.0213 (2)
H23	0.243173	1.146127	0.332936	0.026*
C24	0.13151 (12)	0.96463 (12)	0.40009 (9)	0.0194 (2)
H24	0.081044	0.986744	0.346737	0.023*
C25	0.10881 (12)	0.83743 (12)	0.48642 (9)	0.0164 (2)
H25	0.043610	0.772607	0.490962	0.020*
C26	0.14869 (11)	0.66952 (12)	0.66354 (9)	0.0157 (2)
H26A	0.083521	0.612589	0.652443	0.019*
H26B	0.100571	0.694457	0.729885	0.019*
C27	0.27658 (11)	0.57882 (11)	0.68409 (9)	0.0142 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
F1	0.0263 (4)	0.0183 (3)	0.0142 (3)	0.0045 (3)	−0.0104 (3)	−0.0093 (3)
F2	0.0211 (3)	0.0131 (3)	0.0188 (3)	0.0042 (2)	−0.0083 (3)	−0.0079 (3)
O1	0.0188 (4)	0.0148 (4)	0.0223 (4)	0.0014 (3)	−0.0083 (3)	−0.0047 (3)
O2	0.0312 (5)	0.0204 (4)	0.0215 (4)	0.0064 (4)	−0.0166 (4)	−0.0083 (3)
O3	0.0221 (4)	0.0179 (4)	0.0160 (4)	0.0021 (3)	−0.0099 (3)	−0.0077 (3)
N1	0.0138 (4)	0.0119 (4)	0.0115 (4)	−0.0007 (3)	−0.0029 (3)	−0.0045 (3)
N2	0.0308 (6)	0.0160 (5)	0.0210 (5)	0.0070 (4)	−0.0152 (4)	−0.0106 (4)
N3	0.0179 (5)	0.0123 (4)	0.0139 (4)	−0.0017 (3)	−0.0078 (4)	−0.0020 (3)
N4	0.0144 (4)	0.0134 (4)	0.0109 (4)	0.0004 (3)	−0.0036 (3)	−0.0031 (3)
C1	0.0114 (5)	0.0126 (5)	0.0139 (5)	−0.0008 (4)	−0.0016 (4)	−0.0032 (4)
C2	0.0127 (5)	0.0135 (5)	0.0127 (5)	−0.0013 (4)	−0.0031 (4)	−0.0027 (4)
C3	0.0116 (5)	0.0147 (5)	0.0117 (5)	−0.0026 (4)	−0.0016 (4)	−0.0038 (4)
C4	0.0123 (5)	0.0134 (5)	0.0107 (5)	−0.0015 (4)	−0.0023 (4)	−0.0038 (4)
C5	0.0120 (5)	0.0115 (5)	0.0109 (5)	−0.0014 (4)	−0.0011 (4)	−0.0036 (4)
C6	0.0151 (5)	0.0157 (5)	0.0100 (5)	−0.0015 (4)	−0.0031 (4)	−0.0059 (4)
C7	0.0117 (5)	0.0141 (5)	0.0108 (5)	−0.0018 (4)	−0.0020 (4)	−0.0025 (4)
C8	0.0146 (5)	0.0112 (5)	0.0142 (5)	0.0008 (4)	−0.0026 (4)	−0.0048 (4)
C9	0.0140 (5)	0.0141 (5)	0.0113 (5)	−0.0013 (4)	−0.0026 (4)	−0.0047 (4)
C10	0.0132 (5)	0.0157 (5)	0.0125 (5)	−0.0012 (4)	−0.0038 (4)	−0.0042 (4)
C11	0.0142 (5)	0.0124 (5)	0.0126 (5)	0.0002 (4)	−0.0035 (4)	−0.0040 (4)
C12	0.0147 (5)	0.0151 (5)	0.0145 (5)	−0.0014 (4)	−0.0056 (4)	−0.0028 (4)

C13	0.0173 (5)	0.0120 (5)	0.0145 (5)	0.0002 (4)	−0.0063 (4)	−0.0033 (4)
C14	0.0316 (7)	0.0180 (6)	0.0206 (6)	−0.0087 (5)	−0.0097 (5)	0.0011 (5)
C15	0.0189 (5)	0.0206 (6)	0.0152 (5)	−0.0025 (4)	−0.0057 (4)	−0.0068 (4)
C16	0.0179 (5)	0.0135 (5)	0.0114 (5)	−0.0007 (4)	−0.0032 (4)	−0.0058 (4)
C17	0.0203 (6)	0.0218 (6)	0.0178 (5)	−0.0047 (4)	−0.0043 (4)	−0.0093 (4)
C18	0.0276 (6)	0.0138 (5)	0.0169 (5)	−0.0023 (4)	−0.0063 (4)	−0.0062 (4)
C19	0.0133 (5)	0.0157 (5)	0.0156 (5)	−0.0021 (4)	−0.0047 (4)	−0.0026 (4)
O4	0.0206 (4)	0.0220 (4)	0.0134 (4)	0.0070 (3)	−0.0039 (3)	−0.0063 (3)
O5	0.0283 (5)	0.0249 (4)	0.0148 (4)	0.0089 (4)	−0.0089 (3)	−0.0082 (3)
C20	0.0147 (5)	0.0138 (5)	0.0140 (5)	0.0033 (4)	−0.0021 (4)	−0.0065 (4)
C21	0.0213 (6)	0.0183 (5)	0.0170 (5)	−0.0004 (4)	−0.0063 (4)	−0.0070 (4)
C22	0.0279 (6)	0.0171 (5)	0.0217 (6)	−0.0041 (5)	−0.0044 (5)	−0.0078 (5)
C23	0.0303 (6)	0.0140 (5)	0.0159 (5)	0.0031 (5)	−0.0031 (5)	−0.0038 (4)
C24	0.0217 (6)	0.0215 (6)	0.0149 (5)	0.0076 (4)	−0.0064 (4)	−0.0071 (4)
C25	0.0149 (5)	0.0186 (5)	0.0166 (5)	0.0023 (4)	−0.0033 (4)	−0.0085 (4)
C26	0.0144 (5)	0.0163 (5)	0.0147 (5)	0.0009 (4)	−0.0030 (4)	−0.0041 (4)
C27	0.0158 (5)	0.0117 (5)	0.0144 (5)	−0.0006 (4)	−0.0033 (4)	−0.0041 (4)

Geometric parameters (Å, º)

F1—C6	1.3562 (11)	C12—C13	1.5266 (15)
F2—C8	1.3560 (12)	C12—H12	1.0000
O1—C19	1.2126 (14)	C13—H13A	0.9900
O2—C19	1.3304 (14)	C13—H13B	0.9900
O2—H2O	0.95 (2)	C14—H14A	0.9800
O3—C3	1.2738 (13)	C14—H14B	0.9800
N1—C1	1.3423 (14)	C14—H14C	0.9800
N1—C5	1.4104 (13)	C15—H15A	0.9800
N1—C16	1.4646 (13)	C15—H15B	0.9800
N2—C9	1.3567 (14)	C15—H15C	0.9800
N2—H2NA	0.869 (17)	C16—C17	1.4945 (15)
N2—H2NB	0.900 (17)	C16—C18	1.4978 (15)
N3—C7	1.3812 (14)	C16—H16	1.0000
N3—C10	1.4548 (13)	C17—C18	1.5044 (17)
N3—C13	1.4609 (13)	C17—H17A	0.9900
N4—C11	1.5000 (13)	C17—H17B	0.9900
N4—C12	1.5026 (13)	C18—H18A	0.9900
N4—H4NA	0.956 (16)	C18—H18B	0.9900
N4—H4NB	0.949 (16)	O4—C27	1.2777 (13)
C1—C2	1.3636 (15)	O5—C27	1.2401 (13)
C1—H1	0.9500	C20—C25	1.3916 (15)
C2—C3	1.4305 (15)	C20—C21	1.3949 (16)
C2—C19	1.4833 (15)	C20—C26	1.5091 (15)
C3—C4	1.4452 (14)	C21—C22	1.3876 (17)
C4—C9	1.4285 (15)	C21—H21	0.9500
C4—C5	1.4329 (14)	C22—C23	1.3906 (18)
C5—C6	1.3927 (15)	C22—H22	0.9500
C6—C7	1.4041 (15)	C23—C24	1.3841 (18)

C7—C8	1.3910 (14)	C23—H23	0.9500
C8—C9	1.3877 (15)	C24—C25	1.3900 (16)
C10—C11	1.5264 (14)	C24—H24	0.9500
C10—H10A	0.9900	C25—H25	0.9500
C10—H10B	0.9900	C26—C27	1.5283 (15)
C11—C15	1.5194 (15)	C26—H26A	0.9900
C11—H11	1.0000	C26—H26B	0.9900
C12—C14	1.5169 (15)		

C19—O2—H2O	105.6 (12)	N3—C13—H13B	109.8
C1—N1—C5	119.83 (9)	C12—C13—H13B	109.8
C1—N1—C16	117.94 (9)	H13A—C13—H13B	108.2
C5—N1—C16	122.22 (9)	C12—C14—H14A	109.5
C9—N2—H2NA	120.6 (11)	C12—C14—H14B	109.5
C9—N2—H2NB	117.6 (10)	H14A—C14—H14B	109.5
H2NA—N2—H2NB	121.7 (14)	C12—C14—H14C	109.5
C7—N3—C10	124.24 (9)	H14A—C14—H14C	109.5
C7—N3—C13	122.03 (9)	H14B—C14—H14C	109.5
C10—N3—C13	113.16 (8)	C11—C15—H15A	109.5
C11—N4—C12	112.99 (8)	C11—C15—H15B	109.5
C11—N4—H4NA	107.3 (10)	H15A—C15—H15B	109.5
C12—N4—H4NA	111.1 (10)	C11—C15—H15C	109.5
C11—N4—H4NB	110.9 (9)	H15A—C15—H15C	109.5
C12—N4—H4NB	109.4 (9)	H15B—C15—H15C	109.5
H4NA—N4—H4NB	104.9 (13)	N1—C16—C17	119.36 (9)
N1—C1—C2	124.25 (10)	N1—C16—C18	119.26 (9)
N1—C1—H1	117.9	C17—C16—C18	60.36 (8)
C2—C1—H1	117.9	N1—C16—H16	115.6
C1—C2—C3	120.08 (10)	C17—C16—H16	115.6
C1—C2—C19	117.76 (10)	C18—C16—H16	115.6
C3—C2—C19	122.16 (10)	C16—C17—C18	59.93 (7)
O3—C3—C2	120.62 (10)	C16—C17—H17A	117.8
O3—C3—C4	122.58 (10)	C18—C17—H17A	117.8
C2—C3—C4	116.80 (9)	C16—C17—H17B	117.8
C9—C4—C5	119.35 (9)	C18—C17—H17B	117.8
C9—C4—C3	120.38 (9)	H17A—C17—H17B	114.9
C5—C4—C3	120.28 (9)	C16—C18—C17	59.71 (7)
C6—C5—N1	122.53 (9)	C16—C18—H18A	117.8
C6—C5—C4	118.75 (9)	C17—C18—H18A	117.8
N1—C5—C4	118.71 (9)	C16—C18—H18B	117.8
F1—C6—C5	121.11 (9)	C17—C18—H18B	117.8
F1—C6—C7	115.64 (9)	H18A—C18—H18B	114.9
C5—C6—C7	123.12 (9)	O1—C19—O2	121.36 (10)
N3—C7—C8	121.0 (1)	O1—C19—C2	123.17 (10)
N3—C7—C6	122.83 (9)	O2—C19—C2	115.47 (10)
C8—C7—C6	116.17 (9)	C25—C20—C21	118.45 (10)
F2—C8—C9	116.52 (9)	C25—C20—C26	120.7 (1)
F2—C8—C7	118.76 (9)	C21—C20—C26	120.8 (1)

C9—C8—C7	124.71 (10)	C22—C21—C20	120.78 (11)
N2—C9—C8	119.61 (10)	C22—C21—H21	119.6
N2—C9—C4	122.51 (10)	C20—C21—H21	119.6
C8—C9—C4	117.87 (9)	C21—C22—C23	120.09 (11)
N3—C10—C11	112.99 (9)	C21—C22—H22	120.0
N3—C10—H10A	109.0	C23—C22—H22	120.0
C11—C10—H10A	109.0	C24—C23—C22	119.67 (11)
N3—C10—H10B	109.0	C24—C23—H23	120.2
C11—C10—H10B	109.0	C22—C23—H23	120.2
H10A—C10—H10B	107.8	C23—C24—C25	120.03 (11)
N4—C11—C15	108.99 (9)	C23—C24—H24	120.0
N4—C11—C10	108.68 (8)	C25—C24—H24	120.0
C15—C11—C10	111.49 (9)	C24—C25—C20	120.96 (11)
N4—C11—H11	109.2	C24—C25—H25	119.5
C15—C11—H11	109.2	C20—C25—H25	119.5
C10—C11—H11	109.2	C20—C26—C27	114.65 (9)
N4—C12—C14	109.52 (9)	C20—C26—H26A	108.6
N4—C12—C13	108.54 (9)	C27—C26—H26A	108.6
C14—C12—C13	111.62 (9)	C20—C26—H26B	108.6
N4—C12—H12	109.0	C27—C26—H26B	108.6
C14—C12—H12	109.0	H26A—C26—H26B	107.6
C13—C12—H12	109.0	O5—C27—O4	124.4 (1)
N3—C13—C12	109.59 (9)	O5—C27—C26	119.62 (10)
N3—C13—H13A	109.8	O4—C27—C26	115.97 (9)
C12—C13—H13A	109.8		

C5—N1—C1—C2	1.77 (16)	C7—C8—C9—C4	−1.82 (16)
C16—N1—C1—C2	−179.51 (10)	C5—C4—C9—N2	−179.51 (10)
N1—C1—C2—C3	−2.65 (17)	C3—C4—C9—N2	0.89 (16)
N1—C1—C2—C19	177.40 (9)	C5—C4—C9—C8	1.59 (15)
C1—C2—C3—O3	−178.44 (10)	C3—C4—C9—C8	−178.01 (9)
C19—C2—C3—O3	1.50 (16)	C7—N3—C10—C11	−116.00 (11)
C1—C2—C3—C4	1.16 (15)	C13—N3—C10—C11	55.53 (12)
C19—C2—C3—C4	−178.89 (9)	C12—N4—C11—C15	175.95 (9)
O3—C3—C4—C9	0.20 (16)	C12—N4—C11—C10	54.26 (11)
C2—C3—C4—C9	−179.39 (9)	N3—C10—C11—N4	−51.50 (11)
O3—C3—C4—C5	−179.40 (9)	N3—C10—C11—C15	−171.65 (9)
C2—C3—C4—C5	1.01 (15)	C11—N4—C12—C14	179.47 (9)
C1—N1—C5—C6	179.14 (10)	C11—N4—C12—C13	−58.45 (11)
C16—N1—C5—C6	0.48 (15)	C7—N3—C13—C12	113.64 (11)
C1—N1—C5—C4	0.54 (14)	C10—N3—C13—C12	−58.10 (12)
C16—N1—C5—C4	−178.13 (9)	N4—C12—C13—N3	58.10 (11)
C9—C4—C5—C6	−0.12 (15)	C14—C12—C13—N3	178.90 (9)
C3—C4—C5—C6	179.48 (9)	C1—N1—C16—C17	103.20 (12)
C9—C4—C5—N1	178.54 (9)	C5—N1—C16—C17	−78.11 (13)
C3—C4—C5—N1	−1.86 (15)	C1—N1—C16—C18	32.78 (14)
N1—C5—C6—F1	−4.25 (16)	C5—N1—C16—C18	−148.53 (10)
C4—C5—C6—F1	174.35 (9)	N1—C16—C17—C18	−108.97 (11)

N1—C5—C6—C7	−179.91 (9)	N1—C16—C18—C17	109.14 (11)
C4—C5—C6—C7	−1.31 (16)	C1—C2—C19—O1	4.97 (16)
C10—N3—C7—C8	−141.61 (11)	C3—C2—C19—O1	−174.97 (10)
C13—N3—C7—C8	47.59 (15)	C1—C2—C19—O2	−174.44 (10)
C10—N3—C7—C6	39.09 (16)	C3—C2—C19—O2	5.62 (15)
C13—N3—C7—C6	−131.71 (11)	C25—C20—C21—C22	0.59 (17)
F1—C6—C7—N3	4.61 (15)	C26—C20—C21—C22	−176.77 (10)
C5—C6—C7—N3	−179.52 (10)	C20—C21—C22—C23	0.31 (18)
F1—C6—C7—C8	−174.73 (9)	C21—C22—C23—C24	−0.65 (18)
C5—C6—C7—C8	1.15 (16)	C22—C23—C24—C25	0.07 (17)
N3—C7—C8—F2	2.55 (15)	C23—C24—C25—C20	0.85 (17)
C6—C7—C8—F2	−178.11 (9)	C21—C20—C25—C24	−1.17 (16)
N3—C7—C8—C9	−178.87 (10)	C26—C20—C25—C24	176.2 (1)
C6—C7—C8—C9	0.47 (16)	C25—C20—C26—C27	128.84 (11)
F2—C8—C9—N2	−2.14 (15)	C21—C20—C26—C27	−53.85 (14)
C7—C8—C9—N2	179.25 (10)	C20—C26—C27—O5	130.02 (11)
F2—C8—C9—C4	176.79 (9)	C20—C26—C27—O4	−51.32 (13)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2*O*···O3	0.95 (2)	1.61 (2)	2.5162 (12)	157.3 (18)
N2—H2*NB*···O3	0.900 (17)	1.917 (16)	2.6200 (13)	133.6 (14)
N4—H4*NB*···O4	0.949 (16)	1.781 (16)	2.7122 (12)	166.3 (13)
N2—H2*NA*···O5^{i}	0.869 (17)	2.232 (17)	2.9958 (13)	146.5 (14)
N4—H4*NA*···O4^{ii}	0.956 (16)	1.834 (16)	2.7580 (12)	161.8 (14)

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

4-(5-Amino-3-carboxy-1-cyclopropyl-6,8-difluoro-4-oxo-1,4-dihydroquinolin-7-yl)-2,6-dimethylpiperazin-1-ium 4-methylbenzoate trihydrate (III)

Crystal data

$C_{19}H_{23}F_2N_4O_3^+ \cdot C_8H_7O_2^- \cdot 3H_2O$
M_r = 582.60
Monoclinic, $P2_1/n$
a = 18.4423 (9) Å
b = 7.0694 (3) Å
c = 21.0669 (10) Å
β = 93.252 (2)°
V = 2742.2 (2) Å^3
Z = 4
$F(000)$ = 1232
D_x = 1.411 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9800 reflections
θ = 2.9–27.5°
μ = 0.11 mm^{-1}
T = 90 K
Tablet, pale yellow
0.19 × 0.15 × 0.04 mm

Data collection

Bruker D8 Venture dual source diffractometer
Radiation source: microsource
Detector resolution: 7.41 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min} = 0.894, T_{max} = 0.959
44990 measured reflections
6296 independent reflections
5086 reflections with $I > 2\sigma(I)$

R_{int} = 0.043
θ_{max} = 27.5°, θ_{min} = 2.2°
h = −23→23
k = −9→9
l = −27→27

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.100
S = 1.04
6296 reflections
418 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.040P)^2 + 1.6577P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}
Extinction correction: SHELXL-2019/2 (Sheldrick, 2015b), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0021 (5)

Special details

Experimental. The crystal was mounted using polyisobutene oil on the tip of a fine glass fibre, which was fastened in a copper mounting pin with electrical solder. It was placed directly into the cold gas stream of a liquid-nitrogen based cryostat (Hope, 1994; Parkin & Hope, 1998).
Diffraction data were collected with the crystal at 90K, which is standard practice in this laboratory for the majority of flash-cooled crystals.
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 progress was checked using *Platon* (Spek, 2020) and by an *R*-tensor (Parkin, 2000). The final model was further checked with the IUCr utility *checkCIF*.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
F1	0.16930 (4)	0.64545 (14)	0.41384 (4)	0.0232 (2)
F2	0.19188 (4)	0.74700 (13)	0.63429 (4)	0.0213 (2)
O1	−0.20441 (5)	0.79723 (16)	0.41468 (5)	0.0235 (2)
O2	−0.19618 (5)	0.87221 (15)	0.51703 (5)	0.0202 (2)
H2O	−0.1594 (12)	0.877 (3)	0.5482 (10)	0.044 (6)*
O3	−0.07638 (5)	0.84435 (15)	0.57818 (5)	0.0189 (2)
N1	0.01575 (6)	0.68755 (17)	0.41300 (5)	0.0142 (2)
N2	0.05167 (7)	0.8265 (2)	0.64025 (6)	0.0213 (3)
H2NA	0.0811 (11)	0.828 (3)	0.6762 (10)	0.034 (5)*
H2NB	0.0031 (12)	0.843 (3)	0.6419 (10)	0.042 (6)*
N3	0.25676 (6)	0.66015 (18)	0.52407 (6)	0.0177 (3)
N4	0.40460 (6)	0.56168 (18)	0.54358 (6)	0.0147 (2)
H4NA	0.4412 (10)	0.495 (3)	0.5696 (9)	0.029 (5)*
H4NB	0.4268 (10)	0.618 (3)	0.5108 (10)	0.034 (5)*
C1	−0.05565 (7)	0.7201 (2)	0.41541 (7)	0.0152 (3)
H1	−0.085398	0.704074	0.377484	0.018*
C2	−0.08820 (7)	0.7749 (2)	0.46899 (7)	0.0151 (3)

C3	−0.04622 (7)	0.79463 (19)	0.52777 (7)	0.0147 (3)
C4	0.03060 (7)	0.75619 (19)	0.52685 (7)	0.0140 (3)
C5	0.06170 (7)	0.70427 (19)	0.46870 (6)	0.0138 (3)
C6	0.13643 (7)	0.6767 (2)	0.46875 (7)	0.0152 (3)
C7	0.18246 (7)	0.6910 (2)	0.52359 (7)	0.0152 (3)
C8	0.15010 (7)	0.7376 (2)	0.57941 (7)	0.0161 (3)
C9	0.07665 (7)	0.7750 (2)	0.58355 (7)	0.0151 (3)
C10	0.28872 (7)	0.5277 (2)	0.48072 (7)	0.0161 (3)
H10A	0.307178	0.597178	0.444152	0.019*
H10B	0.251383	0.436797	0.464287	0.019*
C11	0.35064 (7)	0.4220 (2)	0.51562 (7)	0.0155 (3)
H11	0.330677	0.346821	0.550866	0.019*
C12	0.37170 (7)	0.7063 (2)	0.58566 (7)	0.0156 (3)
H12	0.353367	0.640709	0.623632	0.019*
C13	0.30834 (7)	0.8012 (2)	0.54943 (7)	0.0160 (3)
H13A	0.283667	0.887997	0.578133	0.019*
H13B	0.326437	0.876885	0.514093	0.019*
C14	0.43038 (8)	0.8463 (2)	0.60792 (7)	0.0209 (3)
H14A	0.449360	0.909818	0.570983	0.031*
H14B	0.469877	0.778736	0.631283	0.031*
H14C	0.409720	0.940576	0.635826	0.031*
C15	0.38846 (8)	0.2884 (2)	0.47176 (7)	0.0206 (3)
H15A	0.353957	0.192234	0.455446	0.031*
H15B	0.429211	0.226688	0.495390	0.031*
H15C	0.406627	0.360047	0.436145	0.031*
C16	0.04298 (7)	0.6192 (2)	0.35325 (7)	0.0163 (3)
H16	0.062144	0.486827	0.354403	0.020*
C17	0.08061 (8)	0.7518 (2)	0.31081 (7)	0.0218 (3)
H17A	0.122153	0.702225	0.288103	0.026*
H17B	0.085039	0.885832	0.324048	0.026*
C18	0.00625 (8)	0.6788 (3)	0.29126 (7)	0.0264 (4)
H18A	−0.035058	0.767882	0.292530	0.032*
H18B	0.002063	0.584243	0.256578	0.032*
C19	−0.16741 (7)	0.8147 (2)	0.46384 (7)	0.0173 (3)
O4	0.48721 (6)	0.37218 (16)	0.63034 (5)	0.0225 (2)
O5	0.55454 (5)	0.23301 (15)	0.55920 (5)	0.0191 (2)
C20	0.59698 (7)	0.2240 (2)	0.66740 (7)	0.0146 (3)
C21	0.58790 (8)	0.2764 (2)	0.73007 (7)	0.0169 (3)
H21	0.544617	0.338837	0.740721	0.020*
C22	0.64159 (8)	0.2383 (2)	0.77720 (7)	0.0171 (3)
H22	0.634344	0.274197	0.819832	0.021*
C23	0.70593 (8)	0.1483 (2)	0.76303 (7)	0.0166 (3)
C24	0.71450 (8)	0.0948 (2)	0.70020 (7)	0.0173 (3)
H24	0.757892	0.033059	0.689484	0.021*
C25	0.66076 (8)	0.1303 (2)	0.65326 (7)	0.0172 (3)
H25	0.667292	0.090469	0.610891	0.021*
C26	0.54199 (7)	0.2778 (2)	0.61474 (7)	0.0159 (3)
C27	0.76456 (8)	0.1112 (2)	0.81411 (7)	0.0209 (3)

H27A	0.765320	−0.023819	0.824717	0.031*
H27B	0.754839	0.184994	0.852067	0.031*
H27C	0.811717	0.148138	0.798799	0.031*
O1W	0.29379 (6)	0.11084 (17)	0.69541 (6)	0.0268 (3)
H1W1	0.3314 (14)	0.219 (4)	0.7047 (12)	0.064 (7)*
H2W1	0.2678 (15)	0.150 (4)	0.6565 (14)	0.077 (9)*
O2W	0.39349 (6)	0.39000 (18)	0.72635 (5)	0.0236 (2)
H1W2	0.3732 (13)	0.510 (4)	0.7276 (11)	0.060 (7)*
H2W2	0.4297 (13)	0.386 (4)	0.6967 (12)	0.058 (7)*
O3W	0.32955 (6)	0.73767 (19)	0.74222 (6)	0.0302 (3)
H1W3	0.2830 (13)	0.702 (4)	0.7636 (11)	0.057 (7)*
H2W3	0.3180 (17)	0.868 (5)	0.7265 (15)	0.100 (11)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
F1	0.0146 (4)	0.0418 (6)	0.0133 (4)	0.0048 (4)	0.0013 (3)	−0.0019 (4)
F2	0.0176 (4)	0.0310 (5)	0.0147 (4)	0.0010 (4)	−0.0054 (3)	−0.0021 (4)
O1	0.0155 (5)	0.0304 (6)	0.0241 (6)	0.0022 (5)	−0.0036 (4)	−0.0007 (5)
O2	0.0143 (5)	0.0240 (6)	0.0224 (6)	0.0014 (4)	0.0015 (4)	0.0000 (4)
O3	0.0168 (5)	0.0245 (6)	0.0157 (5)	0.0019 (4)	0.0030 (4)	0.0003 (4)
N1	0.0139 (5)	0.0158 (6)	0.0127 (6)	0.0002 (5)	−0.0002 (4)	0.0003 (5)
N2	0.0174 (6)	0.0331 (8)	0.0132 (6)	0.0015 (6)	0.0001 (5)	−0.0029 (5)
N3	0.0124 (5)	0.0200 (6)	0.0204 (6)	0.0009 (5)	−0.0019 (5)	−0.0050 (5)
N4	0.0131 (5)	0.0173 (6)	0.0136 (6)	0.0009 (5)	−0.0008 (5)	−0.0009 (5)
C1	0.0140 (6)	0.0134 (6)	0.0176 (7)	−0.0004 (5)	−0.0028 (5)	0.0021 (5)
C2	0.0130 (6)	0.0147 (7)	0.0174 (7)	0.0001 (5)	−0.0002 (5)	0.0024 (5)
C3	0.0160 (6)	0.0111 (6)	0.0171 (7)	−0.0008 (5)	0.0006 (5)	0.0031 (5)
C4	0.0145 (6)	0.0122 (6)	0.0152 (7)	−0.0007 (5)	0.0001 (5)	0.0012 (5)
C5	0.0144 (6)	0.0127 (6)	0.0139 (7)	−0.0013 (5)	−0.0015 (5)	0.0016 (5)
C6	0.0158 (6)	0.0172 (7)	0.0127 (6)	0.0003 (5)	0.0024 (5)	0.0001 (5)
C7	0.0130 (6)	0.0141 (7)	0.0182 (7)	0.0004 (5)	−0.0010 (5)	0.0010 (5)
C8	0.0166 (7)	0.0180 (7)	0.0132 (7)	−0.0010 (5)	−0.0047 (5)	0.0011 (5)
C9	0.0168 (7)	0.0143 (7)	0.0142 (7)	−0.0012 (5)	0.0003 (5)	0.0012 (5)
C10	0.0147 (6)	0.0175 (7)	0.0160 (7)	−0.0004 (5)	−0.0013 (5)	−0.0029 (6)
C11	0.0143 (6)	0.0149 (7)	0.0171 (7)	−0.0013 (5)	−0.0007 (5)	−0.0003 (5)
C12	0.0148 (6)	0.0191 (7)	0.0127 (6)	0.0007 (6)	0.0003 (5)	−0.0021 (6)
C13	0.0143 (6)	0.0164 (7)	0.0171 (7)	−0.0002 (5)	−0.0009 (5)	−0.0022 (6)
C14	0.0158 (7)	0.0251 (8)	0.0215 (8)	−0.0008 (6)	−0.0019 (6)	−0.0067 (6)
C15	0.0199 (7)	0.0189 (7)	0.0229 (8)	0.0025 (6)	−0.0007 (6)	−0.0042 (6)
C16	0.0163 (6)	0.0177 (7)	0.0147 (7)	0.0017 (5)	−0.0008 (5)	−0.0020 (5)
C17	0.0234 (7)	0.0245 (8)	0.0180 (7)	0.0036 (6)	0.0040 (6)	0.0041 (6)
C18	0.0223 (7)	0.0419 (10)	0.0148 (7)	0.0071 (7)	−0.0009 (6)	0.0002 (7)
C19	0.0154 (7)	0.0166 (7)	0.0200 (7)	−0.0004 (6)	0.0015 (5)	0.0021 (6)
O4	0.0197 (5)	0.0300 (6)	0.0174 (5)	0.0076 (5)	−0.0009 (4)	0.0015 (5)
O5	0.0201 (5)	0.0236 (6)	0.0135 (5)	−0.0011 (4)	−0.0011 (4)	0.0008 (4)
C20	0.0158 (6)	0.0138 (6)	0.0139 (7)	−0.0016 (5)	−0.0008 (5)	0.0012 (5)
C21	0.0153 (6)	0.0191 (7)	0.0164 (7)	0.0003 (6)	0.0013 (5)	0.0005 (6)

C22	0.0199 (7)	0.0180 (7)	0.0135 (7)	−0.0009 (6)	0.0010 (5)	0.0003 (6)
C23	0.0185 (7)	0.0137 (7)	0.0172 (7)	−0.0014 (5)	−0.0015 (5)	0.0032 (5)
C24	0.0176 (7)	0.0149 (7)	0.0194 (7)	0.0030 (6)	0.0007 (6)	0.0010 (6)
C25	0.0211 (7)	0.0151 (7)	0.0152 (7)	−0.0003 (6)	0.0012 (5)	−0.0004 (6)
C26	0.0160 (6)	0.0158 (7)	0.0159 (7)	−0.0024 (5)	−0.0002 (5)	0.0027 (5)
C27	0.0225 (7)	0.0212 (7)	0.0184 (7)	0.0025 (6)	−0.0041 (6)	0.0018 (6)
O1W	0.0254 (6)	0.0285 (6)	0.0262 (6)	0.0007 (5)	−0.0017 (5)	−0.0008 (5)
O2W	0.0219 (5)	0.0287 (6)	0.0201 (6)	0.0018 (5)	0.0008 (4)	0.0019 (5)
O3W	0.0257 (6)	0.0307 (7)	0.0349 (7)	0.0040 (5)	0.0072 (5)	0.0039 (5)

Geometric parameters (Å, º)

F1—C6	1.3541 (16)	C13—H13B	0.9900
F2—C8	1.3540 (15)	C14—H14A	0.9800
O1—C19	1.2138 (18)	C14—H14B	0.9800
O2—C19	1.3305 (18)	C14—H14C	0.9800
O2—H2O	0.92 (2)	C15—H15A	0.9800
O3—C3	1.2758 (17)	C15—H15B	0.9800
N1—C1	1.3404 (17)	C15—H15C	0.9800
N1—C5	1.4129 (17)	C16—C17	1.493 (2)
N1—C16	1.4636 (18)	C16—C18	1.497 (2)
N2—C9	1.3542 (19)	C16—H16	1.0000
N2—H2NA	0.91 (2)	C17—C18	1.501 (2)
N2—H2NB	0.91 (2)	C17—H17A	0.9900
N3—C7	1.3870 (17)	C17—H17B	0.9900
N3—C10	1.4558 (18)	C18—H18A	0.9900
N3—C13	1.4585 (18)	C18—H18B	0.9900
N4—C11	1.4987 (18)	O4—C26	1.2692 (18)
N4—C12	1.5036 (18)	O5—C26	1.2465 (17)
N4—H4NA	0.967 (19)	C20—C21	1.391 (2)
N4—H4NB	0.91 (2)	C20—C25	1.397 (2)
C1—C2	1.364 (2)	C20—C26	1.5089 (19)
C1—H1	0.9500	C21—C22	1.388 (2)
C2—C3	1.4296 (19)	C21—H21	0.9500
C2—C19	1.4855 (19)	C22—C23	1.394 (2)
C3—C4	1.4438 (19)	C22—H22	0.9500
C4—C5	1.4298 (19)	C23—C24	1.394 (2)
C4—C9	1.4321 (19)	C23—C27	1.5045 (19)
C5—C6	1.3920 (19)	C24—C25	1.383 (2)
C6—C7	1.3980 (19)	C24—H24	0.9500
C7—C8	1.388 (2)	C25—H25	0.9500
C8—C9	1.3877 (19)	C27—H27A	0.9800
C10—C11	1.5193 (19)	C27—H27B	0.9800
C10—H10A	0.9900	C27—H27C	0.9800
C10—H10B	0.9900	O1W—H1W1	1.04 (3)
C11—C15	1.518 (2)	O1W—H2W1	0.96 (3)
C11—H11	1.0000	O2W—H1W2	0.93 (3)
C12—C13	1.5155 (19)	O2W—H2W2	0.94 (3)

C12—C14	1.521 (2)	O3W—H1W3	1.02 (3)
C12—H12	1.0000	O3W—H2W3	1.00 (4)
C13—H13A	0.9900		

C19—O2—H2O	107.5 (14)	C12—C13—H13B	109.6
C1—N1—C5	119.89 (12)	H13A—C13—H13B	108.1
C1—N1—C16	118.36 (11)	C12—C14—H14A	109.5
C5—N1—C16	121.53 (11)	C12—C14—H14B	109.5
C9—N2—H2NA	121.5 (12)	H14A—C14—H14B	109.5
C9—N2—H2NB	117.1 (13)	C12—C14—H14C	109.5
H2NA—N2—H2NB	120.8 (18)	H14A—C14—H14C	109.5
C7—N3—C10	122.11 (12)	H14B—C14—H14C	109.5
C7—N3—C13	121.25 (12)	C11—C15—H15A	109.5
C10—N3—C13	113.00 (11)	C11—C15—H15B	109.5
C11—N4—C12	113.50 (11)	H15A—C15—H15B	109.5
C11—N4—H4NA	109.2 (11)	C11—C15—H15C	109.5
C12—N4—H4NA	106.8 (11)	H15A—C15—H15C	109.5
C11—N4—H4NB	107.8 (12)	H15B—C15—H15C	109.5
C12—N4—H4NB	111.4 (13)	N1—C16—C17	120.10 (13)
H4NA—N4—H4NB	108.1 (16)	N1—C16—C18	119.79 (12)
N1—C1—C2	124.01 (13)	C17—C16—C18	60.25 (10)
N1—C1—H1	118.0	N1—C16—H16	115.2
C2—C1—H1	118.0	C17—C16—H16	115.2
C1—C2—C3	120.15 (12)	C18—C16—H16	115.2
C1—C2—C19	118.06 (13)	C16—C17—C18	60.0 (1)
C3—C2—C19	121.78 (13)	C16—C17—H17A	117.8
O3—C3—C2	120.51 (12)	C18—C17—H17A	117.8
O3—C3—C4	122.51 (13)	C16—C17—H17B	117.8
C2—C3—C4	116.98 (12)	C18—C17—H17B	117.8
C5—C4—C9	119.40 (12)	H17A—C17—H17B	114.9
C5—C4—C3	120.09 (12)	C16—C18—C17	59.75 (10)
C9—C4—C3	120.49 (13)	C16—C18—H18A	117.8
C6—C5—N1	122.42 (12)	C17—C18—H18A	117.8
C6—C5—C4	118.73 (12)	C16—C18—H18B	117.8
N1—C5—C4	118.83 (12)	C17—C18—H18B	117.8
F1—C6—C5	120.90 (12)	H18A—C18—H18B	114.9
F1—C6—C7	115.95 (12)	O1—C19—O2	121.19 (13)
C5—C6—C7	123.03 (13)	O1—C19—C2	123.08 (13)
N3—C7—C8	120.21 (12)	O2—C19—C2	115.72 (12)
N3—C7—C6	123.22 (13)	C21—C20—C25	118.51 (13)
C8—C7—C6	116.57 (12)	C21—C20—C26	121.24 (13)
F2—C8—C9	116.56 (12)	C25—C20—C26	120.12 (13)
F2—C8—C7	118.93 (12)	C22—C21—C20	120.52 (13)
C9—C8—C7	124.51 (13)	C22—C21—H21	119.7
N2—C9—C8	119.27 (13)	C20—C21—H21	119.7
N2—C9—C4	123.04 (13)	C21—C22—C23	121.13 (13)
C8—C9—C4	117.69 (13)	C21—C22—H22	119.4
N3—C10—C11	109.43 (11)	C23—C22—H22	119.4

N3—C10—H10A	109.8	C22—C23—C24	118.09 (13)
C11—C10—H10A	109.8	C22—C23—C27	120.84 (13)
N3—C10—H10B	109.8	C24—C23—C27	121.07 (13)
C11—C10—H10B	109.8	C25—C24—C23	120.97 (13)
H10A—C10—H10B	108.2	C25—C24—H24	119.5
N4—C11—C15	109.35 (11)	C23—C24—H24	119.5
N4—C11—C10	109.27 (11)	C24—C25—C20	120.76 (13)
C15—C11—C10	111.72 (12)	C24—C25—H25	119.6
N4—C11—H11	108.8	C20—C25—H25	119.6
C15—C11—H11	108.8	O5—C26—O4	124.71 (13)
C10—C11—H11	108.8	O5—C26—C20	118.24 (13)
N4—C12—C13	109.24 (11)	O4—C26—C20	117.00 (12)
N4—C12—C14	108.69 (11)	C23—C27—H27A	109.5
C13—C12—C14	112.46 (12)	C23—C27—H27B	109.5
N4—C12—H12	108.8	H27A—C27—H27B	109.5
C13—C12—H12	108.8	C23—C27—H27C	109.5
C14—C12—H12	108.8	H27A—C27—H27C	109.5
N3—C13—C12	110.49 (12)	H27B—C27—H27C	109.5
N3—C13—H13A	109.6	H1W1—O1W—H2W1	104 (2)
C12—C13—H13A	109.6	H1W2—O2W—H2W2	110 (2)
N3—C13—H13B	109.6	H1W3—O3W—H2W3	102 (2)

C5—N1—C1—C2	1.9 (2)	C5—C4—C9—N2	178.94 (13)
C16—N1—C1—C2	176.62 (13)	C3—C4—C9—N2	0.8 (2)
N1—C1—C2—C3	−2.2 (2)	C5—C4—C9—C8	−1.3 (2)
N1—C1—C2—C19	177.15 (13)	C3—C4—C9—C8	−179.45 (13)
C1—C2—C3—O3	−179.45 (13)	C7—N3—C10—C11	−140.81 (13)
C19—C2—C3—O3	1.3 (2)	C13—N3—C10—C11	60.49 (15)
C1—C2—C3—C4	0.6 (2)	C12—N4—C11—C15	177.44 (12)
C19—C2—C3—C4	−178.66 (12)	C12—N4—C11—C10	54.87 (15)
O3—C3—C4—C5	−178.86 (13)	N3—C10—C11—N4	−56.09 (15)
C2—C3—C4—C5	1.06 (19)	N3—C10—C11—C15	−177.22 (12)
O3—C3—C4—C9	−0.7 (2)	C11—N4—C12—C13	−53.64 (15)
C2—C3—C4—C9	179.20 (13)	C11—N4—C12—C14	−176.68 (12)
C1—N1—C5—C6	−178.40 (13)	C7—N3—C13—C12	141.28 (13)
C16—N1—C5—C6	7.0 (2)	C10—N3—C13—C12	−59.81 (16)
C1—N1—C5—C4	−0.05 (19)	N4—C12—C13—N3	54.01 (15)
C16—N1—C5—C4	−174.64 (12)	C14—C12—C13—N3	174.77 (12)
C9—C4—C5—C6	−1.1 (2)	C1—N1—C16—C17	102.71 (15)
C3—C4—C5—C6	177.05 (13)	C5—N1—C16—C17	−82.62 (17)
C9—C4—C5—N1	−179.52 (12)	C1—N1—C16—C18	31.9 (2)
C3—C4—C5—N1	−1.36 (19)	C5—N1—C16—C18	−153.41 (14)
N1—C5—C6—F1	4.8 (2)	N1—C16—C17—C18	−109.28 (15)
C4—C5—C6—F1	−173.55 (12)	N1—C16—C18—C17	109.78 (15)
N1—C5—C6—C7	−179.38 (13)	C1—C2—C19—O1	1.4 (2)
C4—C5—C6—C7	2.3 (2)	C3—C2—C19—O1	−179.26 (14)
C10—N3—C7—C8	148.72 (14)	C1—C2—C19—O2	−178.35 (13)
C13—N3—C7—C8	−54.31 (19)	C3—C2—C19—O2	1.0 (2)

C10—N3—C7—C6	−30.9 (2)	C25—C20—C21—C22	0.8 (2)
C13—N3—C7—C6	126.05 (15)	C26—C20—C21—C22	−175.08 (13)
F1—C6—C7—N3	−5.2 (2)	C20—C21—C22—C23	0.5 (2)
C5—C6—C7—N3	178.76 (13)	C21—C22—C23—C24	−1.0 (2)
F1—C6—C7—C8	175.12 (12)	C21—C22—C23—C27	178.68 (14)
C5—C6—C7—C8	−0.9 (2)	C22—C23—C24—C25	0.1 (2)
N3—C7—C8—F2	−1.9 (2)	C27—C23—C24—C25	−179.53 (14)
C6—C7—C8—F2	177.78 (12)	C23—C24—C25—C20	1.2 (2)
N3—C7—C8—C9	178.56 (13)	C21—C20—C25—C24	−1.6 (2)
C6—C7—C8—C9	−1.8 (2)	C26—C20—C25—C24	174.28 (13)
F2—C8—C9—N2	3.0 (2)	C21—C20—C26—O5	177.27 (13)
C7—C8—C9—N2	−177.39 (14)	C25—C20—C26—O5	1.5 (2)
F2—C8—C9—C4	−176.72 (12)	C21—C20—C26—O4	−0.3 (2)
C7—C8—C9—C4	2.8 (2)	C25—C20—C26—O4	−176.07 (13)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2*O*···O3	0.92 (2)	1.64 (2)	2.5014 (14)	155 (2)
N2—H2*NB*···O3	0.91 (2)	1.93 (2)	2.6367 (17)	133.4 (18)
N4—H4*NA*···O4	0.967 (19)	1.73 (2)	2.6722 (16)	164.1 (17)
N4—H4*NB*···O5^{i}	0.91 (2)	1.86 (2)	2.7473 (16)	163.0 (18)
N2—H2*NA*···O2*W*^{ii}	0.91 (2)	2.12 (2)	2.9664 (17)	153.9 (17)
O2*W*—H2*W*2···O4	0.94 (3)	1.80 (3)	2.7371 (16)	171 (2)
O1*W*—H1*W*1···O2*W*	1.04 (3)	1.71 (3)	2.7503 (17)	175 (2)
O2*W*—H1*W*2···O3*W*	0.93 (3)	1.83 (3)	2.7546 (18)	171 (2)
O1*W*—H2*W*1···O1^{iii}	0.96 (3)	1.89 (3)	2.8434 (16)	171 (2)
O3*W*—H1*W*3···O1*W*^{ii}	1.02 (3)	1.82 (3)	2.8362 (17)	173 (2)
O3*W*—H2*W*3···O1*W*^{iv}	1.00 (4)	1.88 (4)	2.8798 (18)	178 (3)

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) −*x*+1/2, *y*+1/2, −*z*+3/2; (iii) −*x*, −*y*+1, −*z*+1; (iv) *x*, *y*+1, *z*.