research communications

Crystal structure of the co-crystal salt 2-amino-6-bromopyridinium 2,3,5,6-tetrafluorobenzoate

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The asymmetric unit of the co-crystal salt 2-amino-6-bromopyridinium 2,3,5,6-tetrafluorobenzoate, $C_5H_6BrN_2^+ \cdot C_7HF_4O_2^-$, contains one pyridinium cation and one benzoate anion. In the crystal, the aminopyridinium cationic unit forms two hydrogen bonds to the benzoate oxygen atoms in an $R_2^2(8)$ motif. Two pyridinium benzoate units are hydrogen bonded through self-complementary hydrogen bonds between the second amine hydrogen and a carboxylate O with a second $R_2^2(8)$ motif to form a discrete hydrogen-bonded complex containing two 2-amino-6-bromopyridinium moieties and two 2,3,5,6-tetrafluorobenzoate moieties. The 2-amino-6-bromopyridinium moieties π-stack in a head-to-tail mode with a centroid–centroid separation of 3.7227 (12) Å and adjacent tetrafluorobenzoates also π-stack in a head-to-tail mode with a centroid–centroid separation of 3.6537 (13) Å.

1. Chemical context

The fields of crystal engineering and supramolecular chemistry rely on the identification and application of versatile synthons to guide the construction of molecular solids (Desiraju, 1995, 2013). For example carboxylic acids are known to form a centrosymmetric dimer through self-complementary O—H⋯O hydrogen bonds (Fig. 1a) in addition to hydrogen-bonded catemer chains and rings. It has been shown that these hydrogen bonds can be diverted by O—H⋯N hydrogen bonding to pyridines, often supported by a non-conventional pyridine C—H⋯O hydrogen bond (Fig. 1b). The interaction of the more basic pyridines, for example 4-(N,N-dimethyl-amino)pyridine, with carboxylic acids most often yields charge-assisted hydrogen-bonded salts (Fig. 1c). Similarly, the combination of 2-aminopyridines and benzoic acids has been
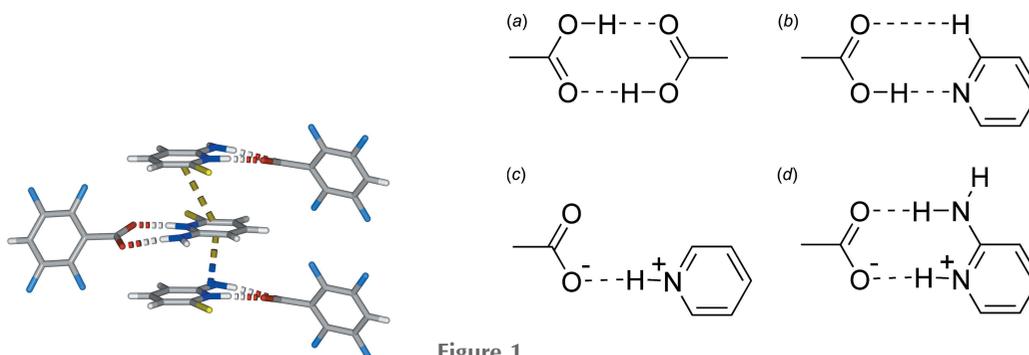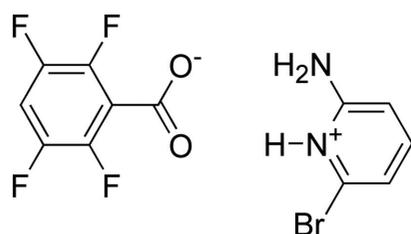

Figure 1
Potential hydrogen-bonding motifs for (a) carboxylic acid dimers, (b) neutral hydrogen-bonded pyridine carboxylic acid co-crystals, (c) charge-assisted pyridinium carboxylate hydrogen-bonded complexes, and (d) charge-assisted 2-aminopyridinium carboxylate hydrogen-bonded complexes.

demonstrated to be a reliable supramolecular synthon resulting in the formation of charge-assisted hydrogen-bonded complexes shown in Fig. 1d (Bis & Zaworotko, 2005). The formation of hydrogen-bonded co-crystals or salts of amines and acids has potential in the pharmaceutical field where the physicochemical properties of active pharmaceuticals, including aqueous solubility and physical and chemical stability, may be modulated and tailored by co-crystal or salt formation (Schultheiss & Newman, 2009). For example a study involving the non-steroidal anti-inflammatory drug piroxicam reported the formation of 19 pyridine based co-crystals (Wales *et al.*, 2012). The present study presents the first co-crystal/salt formed between a substituted pyridine and 2,3,5,6-tetra-fluorobenzoic acid.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1···O1	0.91 (2)	1.68 (2)	2.585 (2)	177 (2)
N2—H2A···O2	0.87 (2)	1.98 (2)	2.845 (2)	175 (2)
N2—H2B···O2[i]	0.87 (2)	2.02 (2)	2.854 (2)	162 (2)
C9—H9···Br1[ii]	0.95	2.94	3.867 (2)	166

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

3. Supramolecular features

In the co-crystal salt (I), adjacent amino pyridinium benzoate salt units are linked into dimeric salt complexes with self-complementary hydrogen bonds (Table 1, entry 3) from the second amine hydrogen atom and carboxylate oxygen atom O2 in a second $R_4^2(8)$ motif (Fig. 3). The two components are relatively well separated within the crystal structure into zones parallel to the *c* axis.

There are two interactions that involve the tetrafluoro-benzoate (Fig. 4). Adjacent tetrafluorobenzoates π-stack in a head-to-tail mode with a $Cg1\cdots Cg1^i$ distance of 3.6537 (13) Å

2. Structural commentary

The asymmetric unit of the co-crystal salt 2-amino-6-bromo-pyridinium 2,3,5,6-tetrafluorobenzoate (I), contains one pyridinium cation and one benzoate anion that are held together by two charge-assisted hydrogen bonds (Table 1, first two entries) to form an $R_2^2(8)$ motif (Fig. 2). The bond distance C12—O2 is slightly shorter than C12—O1, with distances of 1.236 (2) and 1.267 (2) Å respectively. The atoms that form this $R_2^2(8)$ motif (Fig. 1) are almost coplanar, with the maximum deviation above and below the least-squares plane calculated through all of these atoms being 0.169 (7) and −0.147 (8) Å, respectively, for O2 and O1. The angle between the planes defined by the benzene and pyridine rings is 67.04 (7)° and the carboxylate anion is twisted out of the plane of the benzene ring, with C12 0.103 (3) Å above the plane of the benzene ring and O1 1.043 (3) Å above, and O2 0.713 (4) Å below the plane defined by the benzene ring.
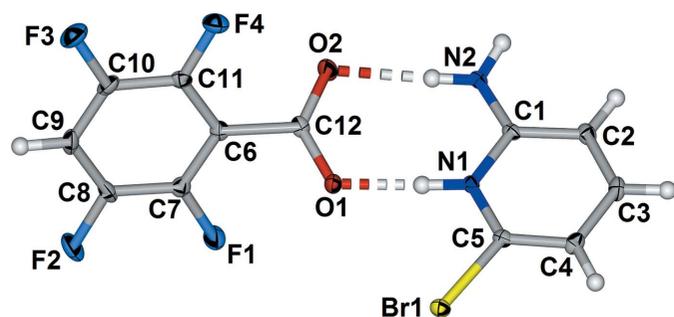

Figure 3
Part of the crystal structure of (I) viewed along *b*, highlighting the hydrogen-bonded dimeric salt unit.

Figure 2
The molecular structure of the co-crystal salt (I) showing the atom-labeling scheme. Displacement ellipsoids drawn at the 50% probability level and hydrogen bonds (Table 1) are shown as dotted lines.

Figure 4
Partial view of the packing in the crystal structure of (I) highlighting the head-to-tail π-stacking of the tetrafluorobenzoate molecules and the C—F···π interaction.

Figure 5
Partial view of the packing in the crystal structure of (I) highlighting the head-to-tail π-stacking of the 2-amino-6-bromopyridinium cations.

[symmetry code: (i) $-x$, $1 - y$, z; $Cg1$ is the centroid of the benzene ring C6–C11] and there is a close C—F···π interaction with a $Cg1 \cdots F3^{ii}$ distance of 3.1640 (17) Å [symmetry code: (ii) $-x$, $y - \frac{1}{2}$, $\frac{1}{2} - z$].

The 2-aminopyridinium groups form offset alternating head-to-tail π-stacks parallel to the b axis (Fig. 5) with a $Cg2 \cdots Cg2^{iii}$ distance of 3.7227 (12) Å and a shortest perpendicular interplanar distance of 3.2547 (8) Å [symmetry code: (iii) $1 - x$, $y - \frac{1}{2}$, $\fr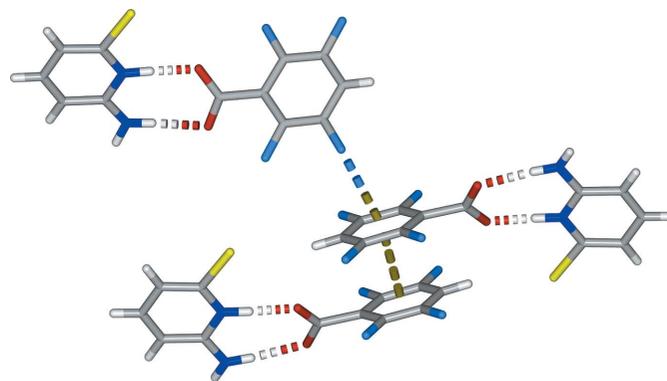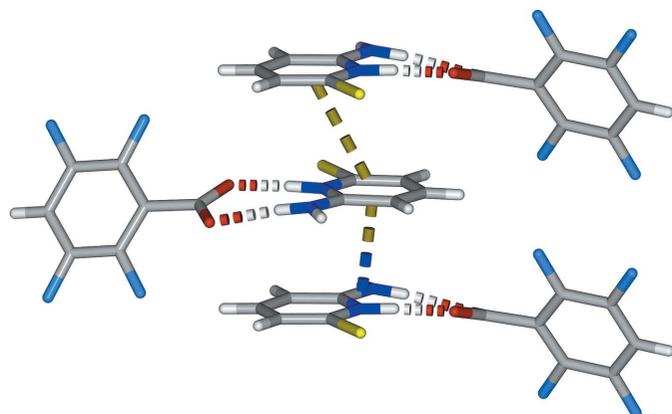ac{3}{2} - z$; $Cg2$ is the centroid of the pyridine ring]. There is one short contact to the bromine with a $C9 \cdots Br1^{iv}$ distance of 3.867 (2) Å [symmetry code: (iv) $1 - x$, $1 - y$, $2 - z$].

4. Database survey

A search of the Cambridge Crystallographic Database (Version 5.39, update of August 2018; Groom *et al.*, 2016) using *Conquest* (Bruno *et al.*, 2002) for structures including the neutral carboxylic acid dimer synthon as shown in Fig. 1*a* revealed 6,016 hits, while a search for neutral pyridine carboxylic acid interactions where the distance between the acid proton and the pyridine N is equal to or less than the sum of the van der Waals radii revealed 2189 hits. In 966 of the 2189 structures the distance between the carbonyl O and the pyridine H is also equal to or less than the sum of the van der Waals radii, corresponding to the synthon shown in Fig. 1*b*. A related search of the Cambridge Crystallographic Database for co-crystals with 4-(*N*,*N*-dimethylamino)pyridine and carboxylic acids revealed only four neutral co-crystals and 54 structures corresponding to the pyridinium carboxylate as shown in Fig. 1*c*. A similar search for co-crystals formed between 2-aminopyridines with benzoic acids yielded 41 hits, of which 40 feature charge-assisted aminopyridinium carboxylate hydrogen-bonded co-crystals as the result of proton transfer shown in Fig. 1*d*. The structure that is reported to form a neutral hydrogen-bonded complex corresponds to the co-crystal formed between 2-aminopyridine and 4-aminobenzoic acid [refcode WOPCOV; Chandrasekaran & Babu, 2014]. Finally there is only one reported co-crystal of 2,3,5,6-tetrafluorobenzoic acid, or the corresponding 2,3,5,6-

tetrafluorobenzoate, with an organic base. In that example theophylline forms a neutral hydrogen-bonded complex (Corpinot *et al.*, 2016).

5. Synthesis and crystallization

2-Amino-6-bromopyridine and 2,3,5,6-tetrafluorobenzoic acid were used as supplied. An equimolar amount (0.1 mmol) of each component were added to a screw-capped vial and 3 mL of ethanol added to effect a clear colorless solution that was allowed to slowly concentrate over two weeks. A homogeneous mass of crystals was obtained.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All hydrogen atoms were located in Fourier-difference maps. Hydrogen atoms involved in hydrogen-bonding interactions were restrained in the refinement with N—H = 0.87 (2) Å and with $U_{iso}(H) = 1.2U_{eq}(N)$. The aromatic H atoms were included in the refinement at calculated positions with C—H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_5H_6BrN_2^+ \cdot C_7HF_4O_2^-$
M_r	367.11
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a, b, c (Å)	13.7230 (9), 6.5757 (4), 15.3224 (10)
β (°)	111.841 (1)
V (Å^3)	1283.42 (14)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	3.26
Crystal size (mm)	0.25 × 0.20 × 0.03
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2014)
T_{min}, T_{max}	0.788, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	16099, 2847, 2395
R_{int}	0.045
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.641
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.026, 0.059, 1.04
No. of reflections	2847
No. of parameters	199
No. of restraints	3
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.41, −0.32

Computer programs: *SMART* and *SAINT* (Bruker, 2014), *SHELXT2018/2* (Sheldrick, 2015*a*), *SHELXL2018/3* (Sheldrick, 2015*b*) and *X-SEED* (Barbour, 2001).

Acknowledgements

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supporting information

Crystal structure of the co-crystal salt 2-amino-6-bromopyridinium 2,3,5,6-tetrafluorobenzoate

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Computing details

Data collection: *SMART* (Bruker, 2014); cell refinement: *SMART* (Bruker, 2014); data reduction: *SAINT* (Bruker, 2014); program(s) used to solve structure: *SHELXT2018/2* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *X-SEED* (Barbour, 2001).

2-Amino-6-bromopyridinium 2,3,5,6-tetrafluorobenzoate

Crystal data

$C_5H_6BrN_2^+ \cdot C_7HF_4O_2^-$	$F(000) = 720$
$M_r = 367.11$	$D_x = 1.900$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 13.7230$ (9) Å	Cell parameters from 3850 reflections
$b = 6.5757$ (4) Å	$\theta = 2.7–25.7°$
$c = 15.3224$ (10) Å	$\mu = 3.26$ mm^{-1}
$\beta = 111.841$ (1)°	$T = 100$ K
$V = 1283.42$ (14) Å^3	Cut block, colourless
$Z = 4$	$0.25 \times 0.20 \times 0.03$ mm

Data collection

Bruker APEXII CCD diffractometer	16099 measured reflections
Radiation source: fine-focus sealed tube	2847 independent reflections
Graphite monochromator	2395 reflections with $I > 2\sigma(I)$
Detector resolution: 8.3660 pixels mm^{-1}	$R_{int} = 0.045$
phi and ω scans	$\theta_{max} = 27.1°$, $\theta_{min} = 1.6°$
Absorption correction: multi-scan (SADABS; Bruker, 2014)	$h = -17 \rightarrow 17$
	$k = -8 \rightarrow 8$
$T_{min} = 0.788$, $T_{max} = 1.000$	$l = -19 \rightarrow 19$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent
$R[F^2 > 2\sigma(F^2)] = 0.026$	and constrained refinement
$wR(F^2) = 0.059$	$w = 1/[\sigma^2(F_o^2) + (0.0271P)^2 + 0.3891P]$
$S = 1.04$	where $P = (F_o^2 + 2F_c^2)/3$
2847 reflections	$(\Delta/\sigma)_{max} = 0.002$
199 parameters	$\Delta\rho_{max} = 0.41$ e Å^{-3}
3 restraints	$\Delta\rho_{min} = -0.32$ e Å^{-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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.35106 (2)	0.41134 (3)	0.84202 (2)	0.01733 (7)
F1	0.10223 (10)	0.15160 (19)	0.49369 (9)	0.0248 (3)
F4	0.17441 (10)	0.8060 (2)	0.40322 (9)	0.0275 (3)
F2	−0.10146 (10)	0.2028 (2)	0.38905 (10)	0.0321 (3)
F3	−0.03037 (12)	0.8562 (2)	0.30158 (10)	0.0365 (4)
O1	0.27555 (11)	0.4079 (2)	0.59997 (10)	0.0188 (3)
O2	0.32636 (12)	0.4894 (3)	0.48172 (11)	0.0238 (4)
N1	0.46382 (13)	0.4100 (3)	0.72562 (12)	0.0130 (4)
H1	0.3977 (13)	0.404 (3)	0.6815 (14)	0.016*
N2	0.53368 (14)	0.4068 (3)	0.61009 (13)	0.0171 (4)
H2A	0.4701 (14)	0.424 (3)	0.5700 (14)	0.020*
H2B	0.5859 (15)	0.422 (3)	0.5919 (16)	0.020*
C4	0.57133 (17)	0.4158 (3)	0.88912 (15)	0.0170 (4)
H4	0.577544	0.416389	0.952978	0.020*
C2	0.65046 (17)	0.4148 (3)	0.77289 (15)	0.0172 (4)
H2	0.711166	0.414715	0.757094	0.021*
C12	0.25906 (16)	0.4564 (3)	0.51564 (15)	0.0155 (5)
C5	0.47591 (16)	0.4124 (3)	0.81748 (14)	0.0147 (4)
C1	0.54936 (16)	0.4114 (3)	0.70135 (15)	0.0136 (4)
C7	0.07144 (17)	0.3268 (3)	0.44649 (15)	0.0173 (5)
C3	0.66028 (17)	0.4183 (3)	0.86458 (15)	0.0182 (5)
H3	0.728259	0.422448	0.912677	0.022*
C11	0.10738 (17)	0.6527 (3)	0.40039 (15)	0.0183 (5)
C10	0.00175 (18)	0.6802 (4)	0.34810 (15)	0.0228 (5)
C8	−0.03368 (17)	0.3535 (4)	0.39179 (16)	0.0206 (5)
C6	0.14445 (16)	0.4777 (3)	0.45227 (14)	0.0157 (5)
C9	−0.06994 (18)	0.5308 (4)	0.34355 (15)	0.0241 (5)
H9	−0.142601	0.549773	0.307970	0.029*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.01626 (12)	0.02221 (12)	0.01623 (12)	−0.00014 (9)	0.00917 (8)	0.00008 (9)
F1	0.0203 (7)	0.0188 (7)	0.0320 (8)	−0.0013 (5)	0.0061 (6)	0.0036 (6)
F4	0.0277 (8)	0.0257 (8)	0.0320 (8)	−0.0027 (6)	0.0144 (6)	0.0081 (6)
F2	0.0175 (7)	0.0384 (9)	0.0383 (9)	−0.0100 (6)	0.0081 (6)	−0.0041 (7)
F3	0.0341 (8)	0.0443 (9)	0.0320 (9)	0.0155 (7)	0.0133 (7)	0.0215 (7)
O1	0.0134 (7)	0.0282 (9)	0.0142 (8)	0.0001 (7)	0.0045 (6)	0.0028 (7)
O2	0.0150 (8)	0.0418 (10)	0.0171 (8)	−0.0004 (7)	0.0089 (7)	0.0003 (7)

N1	0.0101 (8)	0.0137 (9)	0.0154 (9)	0.0021 (7)	0.0051 (7)	0.0015 (7)
N2	0.0115 (9)	0.0234 (10)	0.0184 (10)	0.0008 (8)	0.0079 (8)	0.0027 (8)
C4	0.0196 (11)	0.0169 (11)	0.0134 (10)	0.0032 (9)	0.0049 (9)	−0.0012 (9)
C2	0.0135 (10)	0.0150 (11)	0.0231 (12)	0.0021 (9)	0.0070 (9)	0.0004 (9)
C12	0.0145 (11)	0.0167 (11)	0.0159 (11)	−0.0007 (8)	0.0062 (9)	−0.0057 (8)
C5	0.0153 (10)	0.0129 (10)	0.0173 (11)	0.0005 (9)	0.0077 (9)	0.0003 (9)
C1	0.0137 (10)	0.0093 (10)	0.0195 (11)	0.0009 (8)	0.0083 (8)	0.0018 (8)
C7	0.0174 (11)	0.0193 (11)	0.0154 (11)	0.0014 (9)	0.0062 (9)	−0.0003 (9)
C3	0.0143 (11)	0.0169 (11)	0.0191 (11)	0.0022 (9)	0.0011 (9)	−0.0012 (9)
C11	0.0192 (11)	0.0240 (12)	0.0152 (11)	−0.0010 (9)	0.0103 (9)	0.0006 (9)
C10	0.0226 (12)	0.0313 (14)	0.0159 (11)	0.0111 (11)	0.0088 (10)	0.0098 (10)
C8	0.0132 (11)	0.0312 (13)	0.0191 (12)	−0.0056 (10)	0.0080 (9)	−0.0057 (10)
C6	0.0150 (11)	0.0225 (12)	0.0118 (10)	0.0018 (9)	0.0075 (9)	−0.0036 (9)
C9	0.0129 (11)	0.0439 (16)	0.0144 (12)	0.0052 (10)	0.0037 (9)	0.0002 (10)

Geometric parameters (Å, º)

Br1—C5	1.886 (2)	C4—C3	1.405 (3)
F1—C7	1.342 (2)	C4—H4	0.9500
F4—C11	1.355 (3)	C2—C3	1.361 (3)
F2—C8	1.349 (3)	C2—C1	1.413 (3)
F3—C10	1.345 (3)	C2—H2	0.9500
O1—C12	1.267 (2)	C12—C6	1.517 (3)
O2—C12	1.236 (2)	C7—C8	1.384 (3)
N1—C5	1.355 (3)	C7—C6	1.389 (3)
N1—C1	1.357 (3)	C3—H3	0.9500
N1—H1	0.909 (16)	C11—C10	1.383 (3)
N2—C1	1.334 (3)	C11—C6	1.383 (3)
N2—H2A	0.868 (16)	C10—C9	1.374 (3)
N2—H2B	0.866 (16)	C8—C9	1.371 (3)
C4—C5	1.360 (3)	C9—H9	0.9500
C5—N1—C1	120.04 (18)	F1—C7—C8	118.9 (2)
C5—N1—H1	118.4 (15)	F1—C7—C6	120.24 (19)
C1—N1—H1	121.5 (15)	C8—C7—C6	120.8 (2)
C1—N2—H2A	117.8 (16)	C2—C3—C4	120.9 (2)
C1—N2—H2B	120.3 (16)	C2—C3—H3	119.5
H2A—N2—H2B	119 (2)	C4—C3—H3	119.5
C5—C4—C3	117.10 (19)	F4—C11—C10	118.3 (2)
C5—C4—H4	121.4	F4—C11—C6	120.04 (19)
C3—C4—H4	121.4	C10—C11—C6	121.6 (2)
C3—C2—C1	119.5 (2)	F3—C10—C9	120.1 (2)
C3—C2—H2	120.2	F3—C10—C11	119.1 (2)
C1—C2—H2	120.2	C9—C10—C11	120.8 (2)
O2—C12—O1	126.5 (2)	F2—C8—C9	120.0 (2)
O2—C12—C6	118.28 (19)	F2—C8—C7	118.5 (2)
O1—C12—C6	115.18 (18)	C9—C8—C7	121.5 (2)
N1—C5—C4	123.21 (19)	C11—C6—C7	117.1 (2)

N1—C5—Br1	115.97 (15)	C11—C6—C12	121.12 (19)
C4—C5—Br1	120.82 (16)	C7—C6—C12	121.8 (2)
N2—C1—N1	117.94 (19)	C8—C9—C10	118.1 (2)
N2—C1—C2	122.87 (19)	C8—C9—H9	120.9
N1—C1—C2	119.18 (19)	C10—C9—H9	120.9

Hydrogen-bond geometry (Å, º)

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
N1—H1⋯O1	0.91 (2)	1.68 (2)	2.585 (2)	177 (2)
N2—H2*A*⋯O2	0.87 (2)	1.98 (2)	2.845 (2)	175 (2)
N2—H2*B*⋯O2[i]	0.87 (2)	2.02 (2)	2.854 (2)	162 (2)
C4—H4⋯Br1[ii]	0.95	3.13	4.017 (2)	155
C9—H9⋯Br1[iii]	0.95	2.94	3.867 (2)	166

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