



Crystal and molecular structure of 4-fluoro-1*H*-pyrazole at 150 K

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Only two 4-halo-1*H*-pyrazole crystal structures are known to date (chloro and bromo, the structure of 4-iodo-1*H*-pyrazole has not been reported yet). The triclinic structure of 4-fluoro-1*H*-pyrazole, C₃H₃FN₂ (*P* $\bar{1}$), reported here is not isomorphous with those of the chloro and bromo analogues (which are isomorphous, orthorhombic *Pnma*). To avoid sublimation during the measurement, diffraction data were collected at 150 K. Two crystallographically unique 4-fluoro-1*H*-pyrazole moieties linked by an N—H...N hydrogen bond are found in the asymmetric unit. Unlike the trimeric supramolecular motifs found in the structures of the chloro and bromo analogues, 4-fluoro-1*H*-pyrazole forms one-dimensional chains by intermolecular hydrogen bonding in the crystal.

1. Chemical context

1*H*-Pyrazole (pzH) is both a hydrogen-bond donor and acceptor molecule, owing to its NH and N centers. Consequently, pyrazole moieties of the parent compound or C-substituted analogues form hydrogen bonds to each other in the corresponding crystal structures, and similarly to imidazole, have higher melting and boiling points than other five-membered cyclic aromatic molecules lacking either the hydrogen-bond acceptor (pyrrole), the hydrogen-bond donor (*N*-methyl derivatives, furan, isoxazole, oxazole, thiophene, isothiazole, thiazole) or both centers (cyclopentadiene) (Fig. 1). The proximity of the hydrogen-bond donor and acceptor centers in pz allows for the formation of either

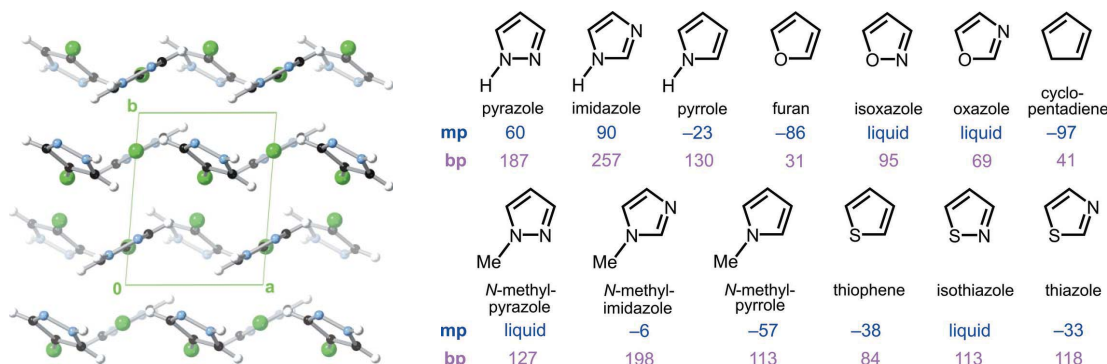


Figure 1

Comparison of the structures of five-membered aromatic heterocycles and their corresponding melting and boiling points (°C) according to the *CRC Handbook of Chemistry and Physics* (Rumble, 2022) or the literature. Those with no melting points reported are liquids at room temperature.



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Table 1

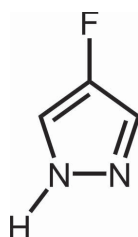
Comparison of N—N, C—N and C—C bond lengths determined by X-ray diffraction in 4-*R*pzH (*R* = H, F, Cl and Br).

Numbers marked with an asterisk indicate average values in the case of pyrazoles with disordered NH/N centers.

	N—N	C—N (NH)	C—N (N)	C—C (NH)	C—C (N)
pzH ^a	1.354 (2) 1.351 (2)	1.337 (3) 1.344 (3)	1.330 (3) 1.326 (3)	1.368 (3) 1.366 (3)	1.389 (3) 1.389 (3)
4-FpzH ^b	1.3484 (9) 1.3513 (10)	1.3473 (10) 1.3476 (10)	1.3391 (10) 1.3375 (10)	1.3729 (11) 1.3742 (10)	1.3922 (11) 1.3924 (10)
4-ClpzH ^c	1.346 (2) 1.345 (3)	1.335 (2)* 1.334 (2)*	1.334 (2)* 1.334 (2)*	1.380 (2)* 1.377 (2)*	1.374 (2)* 1.377 (2)*
4-BrpzH ^d	1.335 (9) 1.335 (9)	1.327 (10)* 1.343 (10)*	1.331 (10)* 1.343 (10)*	1.391 (11)* 1.371 (9)*	1.338 (10)* 1.371 (9)*

Notes: (a) Sikora & Katrusiak (2013); (b) this work; (c) Rue & Raptis (2021); (d) Foces-Foces *et al.* (1999).

discreet hydrogen-bonded motifs, such as dimers, trimers, tetramers and hexamers, or polymeric catemers depending on the substituents (Bertolasi *et al.*, 1999; Foces-Foces *et al.*, 2000; Claramunt *et al.*, 2006; Alkorta *et al.*, 2006), whereas imidazole only forms catemers (Cammers & Parkin, 2004).



2. Structural commentary

As shown in Fig. 2, the asymmetric unit contains two symmetry-independent 4-fluoro-1*H*-pyrazole moieties ($Z' = 2$; $P\bar{1}$), similarly to 1*H*-pyrazole ($Z' = 2$; $P2_1cn/Pna2_1$; La Cour & Rasmussen, 1973; Sikora & Katrusiak, 2013) but unlike the chloro and bromo analogues ($Z' = 1.5$; $Pnma$) (Rue & Raptis, 2021; Foces-Foces *et al.*, 1999). Structures with $Z' > 1$ result when two or more intermolecular interactions, such as optimal shape packing, optimization of hydrogen bonds and aromatic interactions, are in conflict (Steed & Steed, 2015). Therefore, the Z' value larger than 1 observed in these pyrazole structures emphasizes the importance of hydrogen bonding in their solid-state structures.

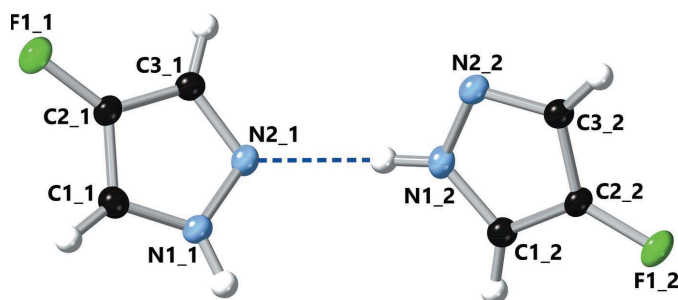


Figure 2

Displacement ellipsoid plot (50% probability) of the crystal structure of 4-fluoro-1*H*-pyrazole, showing the contents of the asymmetric unit.

The two crystallographically independent 4-Fpz moieties, which are identical within experimental error, are planar with deviations from the C_3FN_2 mean-plane of less than 0.004 and 0.008 Å, respectively. Table 1 presents a comparison of bond lengths determined by X-ray diffraction for the parent pzH at 150 K (Sikora & Katrusiak, 2013), 4-FpzH at 150 K, 4-ClpzH at 150 K (Rue & Raptis, 2021) and 4-BrpzH at room temperature (Foces-Foces *et al.*, 1999). All structures contain two symmetry-independent moieties. In the case of pzH and 4-FpzH, the NH and N centers of the pz rings are distinct, unlike in the case of 4-Cl/BrpzH. Therefore, in the former case two distinct sets of C—N and C—C bond distances are observed. Similarly to pzH, in 4-FpzH the C—N bond adjacent to N is shorter than the one adjacent to NH [by 0.008 (1)/0.010 (1) Å], whereas the C—C bond adjacent to N is longer than the one adjacent to NH [by 0.019 (1)/0.018 (1) Å]. In general, the N—N, C—N and C—C bond distances in 4-*R*pH are consistent across the *R* = H, F, Cl and Br series.

3. Supramolecular features

The pz N—H proton donates an N—H...N hydrogen bond to a neighbouring pz unit on one side, while the pz N atom accepts an N—H...N hydrogen bond from another pz unit on the opposite side (Table 2, Fig. 3). Thus, pz units in the resulting 4-FpzH catemer form dihedral angles of 59.74 (3)° with each other, with centroid-centroid distances of

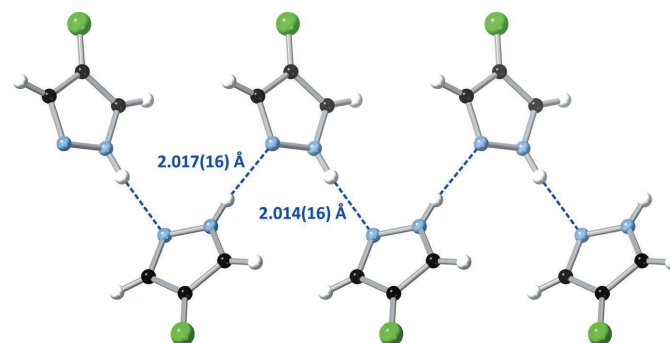


Figure 3

View (along the *b* axis) of one of the hydrogen-bonded chains in the crystal of 4-fluoro-1*H*-pyrazole.

Table 2

Hydrogen-bond geometry (Å, °) for 4-*R*pzH (*R* = H, F, Cl and Br).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
pzH				
N1—H1...N3	0.860 (2)	2.038 (2)	2.885 (3)	167.73 (10)
N4—H5...N2 ⁱ	0.861 (2)	2.083 (2)	2.881 (3)	153.87 (13)
4-FpzH				
N1_2—H1N_2...N2_1	0.878 (14)	2.014 (16)	2.8764 (10)	166.6 (13)
N1_1—H1N_1...N2_2 ⁱⁱ	0.892 (14)	2.017 (16)	2.9024 (10)	172.4 (15)
4-ClpzH				
N1—H1A...N1 ⁱⁱⁱ	0.88	2.03	2.885 (3)	165
N2—H2...N3 ^{iv}	0.88	1.99	2.8582 (19)	169
N3—H3A...N2 ^{iv}	0.88	1.99	2.8582 (19)	169
4-BrpzH				
N12—H12...N21	1.02	1.87	2.871 (9)	169
N21—H21...N12	1.01	1.87	2.871 (9)	171
N22—H22...N22 ^v	1.02	1.93	2.922 (9)	164

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

4.9487 (5) Å. Adjacent catemers interact with each other by π – π stacking [distance between pz mean-planes = 3.4911 (8) Å; dihedral angle between pz mean planes = 0°, crystallographically imposed; centroid–centroid distance = 3.7034 (6) Å] and C–H... π interactions [dihedral angle between pz mean planes = 59.74 (3)°; centroid–centroid distance = 4.3794 (5)/4.4791 (5) Å, H...centroid distance = 2.8030 (3)/2.9007 (4) Å], on alternate sides (Fig. 4). As a result, the pz units are arranged in a herringbone pattern within the crystal (Fig. 5).

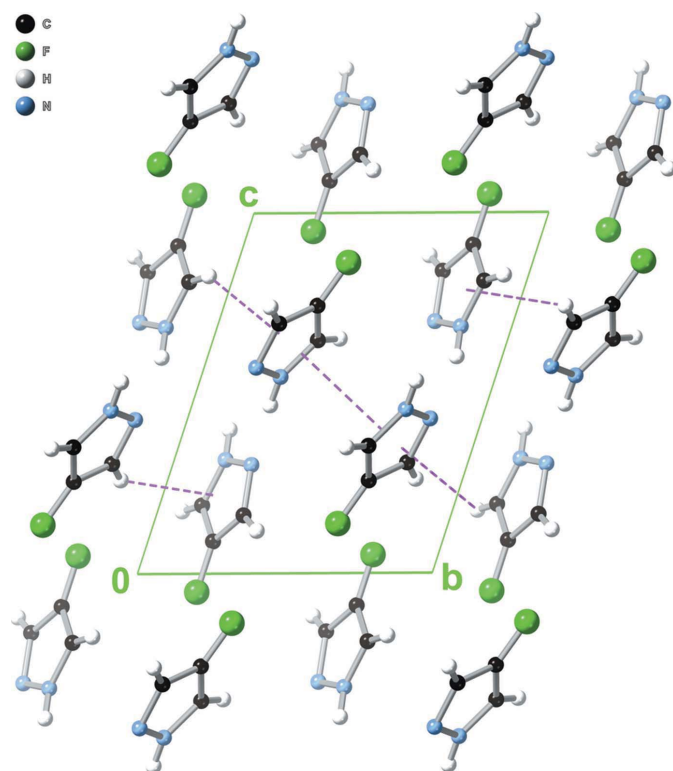


Figure 4

Packing diagram (along the *a* axis) of 4-fluoro-1*H*-pyrazole, showing both π – π and C–H... π interactions.

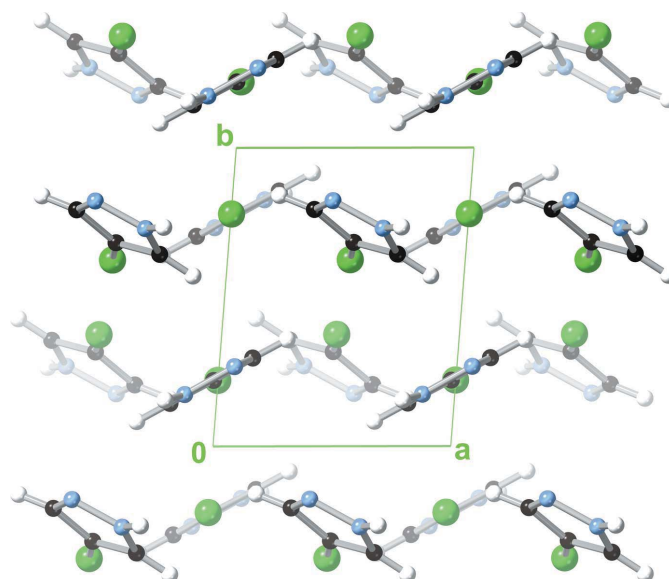


Figure 5

Packing diagram (along the *c* axis) of 4-fluoro-1*H*-pyrazole, showing the herringbone-type packing of the pyrazole moieties.

4. Database survey

Although the parent pyrazole (pzH) also forms a hydrogen-bonded catemer in the crystal packing, its structure is quite different from the one formed by 4-FpzH. As illustrated in Fig. 6, pairs of pz units are found in two different geometries in the catemer of pzH: one in which they form dihedral angles of 5.45 (9)° with centroid–centroid distances of 5.1659 (15) Å, and another with dihedral angles of 74.64 (9)° and centroid–centroid distances of 5.0504 (15) Å. In contrast, pz units in 4-Cl/BrpzH form discrete hydrogen-bonded trimers. While the presence/nature of the 4-halo substituent leads to very different outcomes in terms of the overall packing and hydrogen-bonded motifs in 4-*R*pzH (*R* = H, F, Cl/Br), it has little effect on the corresponding hydrogen bonding parameters (Table 2). Interestingly, the structure of the catemer in 4-FpzH is essentially identical to the one found in the lattice of 4-acetyl-1*H*-pyrazole (monoclinic *P*2₁/*n*; Frey *et al.*, 2014), with dihedral angles of 57.28 (7)° and centroid–centroid distances of 4.9501 (13) Å between adjacent pz units. The structure of

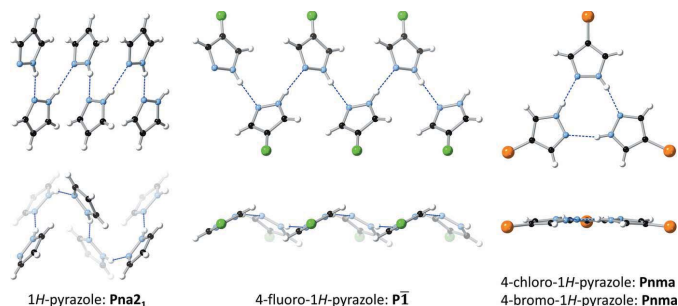


Figure 6

Comparison of the hydrogen-bonded motifs (two different views for each) in the crystal packing of 4-*R*pzH (*R* = H, F, Cl and Br).

the different catemer of pzH is also found in the crystal lattices of 4-phenyl-1*H*-pyrazole (orthorhombic, *Pbcn*; Reger *et al.*, 2003) and 4-adamantyl-1*H*-pyrazole (triclinic, *P1̄*; Cabildo *et al.*, 1994), despite the large substituents. 4-Methyl-1*H*-pyrazole (orthorhombic, *Pca2₁*; Goddard *et al.*, 1999) and 4-nitro-1*H*-pyrazole (triclinic, *P1̄*; Llamas-Saiz *et al.*, 1994), on the other hand, form trimers, similarly to 4-Cl/BrpzH.

5. Synthesis and crystallization

4-Fluoro-1*H*-pyrazole was synthesized according to a published procedure, from sodium fluoroacetate (**WARNING: highly toxic!**) by reaction with oxalyl chloride and dimethylformamide, followed by treatment with base and then hydrazine (England *et al.*, 2010). Single crystals were obtained from the powder by slow isothermal sublimation inside a sealed vial under ambient conditions.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. C—H bond distances were constrained to 0.95 Å and these H atoms were refined as riding. Positions of N-bound H atoms were freely refined. $U_{\text{iso}}(\text{H})$ values were set to 1.2 times $U_{\text{eq}}(\text{C/N})$ for all H atoms.

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Table 3

Experimental details.

Crystal data	
Chemical formula	C ₃ H ₃ FN ₂
M_r	86.07
Crystal system, space group	Triclinic, <i>P1̄</i>
Temperature (K)	150
a, b, c (Å)	5.6045 (2), 7.4315 (3), 9.5396 (4)
α, β, γ (°)	71.689 (2), 87.731 (2), 84.968 (2)
V (Å ³)	375.72 (3)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ^{−1})	0.14
Crystal size (mm)	0.45 × 0.43 × 0.38
Data collection	
Diffractometer	Bruker AXS D8 Quest
Absorption correction	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)
$T_{\text{min}}, T_{\text{max}}$	0.678, 0.747
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	15049, 2875, 2635
R_{int}	0.024
$(\sin \theta/\lambda)_{\text{max}}$ (Å ^{−1})	0.770
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.036, 0.108, 1.06
No. of reflections	2875
No. of parameters	116
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ^{−3})	0.47, −0.26

Computer programs: *APEX4* and *SAINT* (Bruker, 2022), *SHELXT* (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick, 2015b) and *ShelXle* Rev1460 (Hübschle *et al.*, 2011).

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supporting information

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Computing details

Data collection: *APEX4* v2022.1-1 (Bruker, 2022); cell refinement: *SAINT* V8.40B (Bruker, 2022); data reduction: *SAINT* V8.40B (Bruker, 2022); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b), *ShelXle* Rev1460 (Hübschle *et al.*, 2011).

4-Fluoro-1*H*-pyrazole

Crystal data

$\text{C}_3\text{H}_3\text{FN}_2$	$Z = 4$
$M_r = 86.07$	$F(000) = 176$
Triclinic, $P\bar{1}$	$D_x = 1.522 \text{ Mg m}^{-3}$
$a = 5.6045 (2) \text{ \AA}$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$b = 7.4315 (3) \text{ \AA}$	Cell parameters from 9943 reflections
$c = 9.5396 (4) \text{ \AA}$	$\theta = 2.3\text{--}33.1^\circ$
$\alpha = 71.689 (2)^\circ$	$\mu = 0.14 \text{ mm}^{-1}$
$\beta = 87.731 (2)^\circ$	$T = 150 \text{ K}$
$\gamma = 84.968 (2)^\circ$	Block, colourless
$V = 375.72 (3) \text{ \AA}^3$	$0.45 \times 0.43 \times 0.38 \text{ mm}$

Data collection

Bruker AXS D8 Quest	$T_{\min} = 0.678, T_{\max} = 0.747$
diffractometer	15049 measured reflections
Radiation source: fine focus sealed tube X-ray	2875 independent reflections
source	2635 reflections with $I > 2\sigma(I)$
Triumph curved graphite crystal	$R_{\text{int}} = 0.024$
monochromator	$\theta_{\max} = 33.2^\circ, \theta_{\min} = 2.3^\circ$
Detector resolution: $7.4074 \text{ pixels mm}^{-1}$	$h = -8 \rightarrow 8$
ω and ϕ scans	$k = -11 \rightarrow 11$
Absorption correction: multi-scan	$l = -14 \rightarrow 14$
(SADABS; Krause <i>et al.</i> , 2015)	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier
Least-squares matrix: full	map
$R[F^2 > 2\sigma(F^2)] = 0.036$	Hydrogen site location: mixed
$wR(F^2) = 0.108$	H atoms treated by a mixture of independent
$S = 1.06$	and constrained refinement
2875 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0579P)^2 + 0.0788P]$
116 parameters	where $P = (F_o^2 + 2F_c^2)/3$
0 restraints	$(\Delta/\sigma)_{\max} < 0.001$
Primary atom site location: dual	$\Delta\rho_{\max} = 0.47 \text{ e \AA}^{-3}$
	$\Delta\rho_{\min} = -0.26 \text{ e \AA}^{-3}$

Extinction correction: *SHELXL2018/3*
 (Sheldrick 2015b),
 $F_c^* = k F_c [1 + 0.001 x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.040 (10)

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 ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
F1_1	0.51610 (12)	0.62514 (11)	0.13759 (7)	0.03931 (17)
N1_1	0.64380 (12)	0.73038 (10)	0.45438 (7)	0.02162 (13)
H1N_1	0.721 (3)	0.7343 (19)	0.5331 (15)	0.032*
N2_1	0.42422 (12)	0.82300 (10)	0.42828 (7)	0.02262 (14)
C1_1	0.71303 (14)	0.64372 (11)	0.35314 (9)	0.02302 (15)
H1_1	0.859931	0.571209	0.349074	0.028*
C2_1	0.52537 (14)	0.68285 (11)	0.25714 (8)	0.02251 (15)
C3_1	0.34891 (13)	0.79346 (11)	0.30642 (8)	0.02192 (15)
H3_1	0.198692	0.840571	0.260776	0.026*
F1_2	0.00161 (11)	0.77865 (9)	1.05091 (6)	0.03386 (15)
N1_2	0.13614 (12)	0.82593 (10)	0.68400 (7)	0.02239 (14)
H1N_2	0.217 (3)	0.845 (2)	0.6004 (16)	0.034*
N2_2	−0.06438 (12)	0.73275 (10)	0.69835 (7)	0.02286 (14)
C1_2	0.19488 (14)	0.85549 (11)	0.81020 (8)	0.02229 (15)
H1_2	0.328762	0.916175	0.826384	0.027*
C2_2	0.01926 (14)	0.77888 (11)	0.91040 (8)	0.02065 (14)
C3_2	−0.13824 (14)	0.70401 (11)	0.83817 (8)	0.02168 (14)
H3_2	−0.276718	0.642113	0.881490	0.026*

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
F1_1	0.0372 (3)	0.0597 (4)	0.0370 (3)	−0.0145 (3)	0.0046 (2)	−0.0357 (3)
N1_1	0.0213 (3)	0.0267 (3)	0.0166 (3)	−0.0024 (2)	−0.0017 (2)	−0.0061 (2)
N2_1	0.0220 (3)	0.0284 (3)	0.0182 (3)	−0.0005 (2)	0.0008 (2)	−0.0090 (2)
C1_1	0.0207 (3)	0.0237 (3)	0.0261 (3)	−0.0022 (2)	0.0014 (2)	−0.0098 (3)
C2_1	0.0232 (3)	0.0278 (3)	0.0213 (3)	−0.0083 (3)	0.0027 (2)	−0.0131 (3)
C3_1	0.0197 (3)	0.0276 (3)	0.0190 (3)	−0.0036 (2)	−0.0007 (2)	−0.0075 (2)
F1_2	0.0395 (3)	0.0492 (3)	0.0174 (2)	−0.0117 (2)	0.00202 (19)	−0.0149 (2)
N1_2	0.0231 (3)	0.0266 (3)	0.0183 (3)	−0.0023 (2)	0.0033 (2)	−0.0085 (2)
N2_2	0.0236 (3)	0.0275 (3)	0.0196 (3)	−0.0021 (2)	−0.0016 (2)	−0.0102 (2)
C1_2	0.0210 (3)	0.0261 (3)	0.0216 (3)	−0.0044 (2)	0.0006 (2)	−0.0094 (3)
C2_2	0.0228 (3)	0.0248 (3)	0.0156 (3)	−0.0029 (2)	−0.0004 (2)	−0.0078 (2)
C3_2	0.0208 (3)	0.0256 (3)	0.0200 (3)	−0.0044 (2)	0.0002 (2)	−0.0082 (2)

Geometric parameters (Å, °)

F1_1—C2_1	1.3428 (8)	F1_2—C2_2	1.3396 (8)
N1_1—C1_1	1.3473 (10)	N1_2—C1_2	1.3476 (10)
N1_1—N2_1	1.3484 (9)	N1_2—N2_2	1.3513 (10)
N1_1—H1N_1	0.892 (14)	N1_2—H1N_2	0.878 (14)
N2_1—C3_1	1.3391 (10)	N2_2—C3_2	1.3375 (10)
C1_1—C2_1	1.3729 (11)	C1_2—C2_2	1.3742 (10)
C1_1—H1_1	0.9500	C1_2—H1_2	0.9500
C2_1—C3_1	1.3922 (11)	C2_2—C3_2	1.3924 (10)
C3_1—H3_1	0.9500	C3_2—H3_2	0.9500
C1_1—N1_1—N2_1	112.75 (6)	C1_2—N1_2—N2_2	112.72 (6)
C1_1—N1_1—H1N_1	129.5 (9)	C1_2—N1_2—H1N_2	129.9 (9)
N2_1—N1_1—H1N_1	117.7 (9)	N2_2—N1_2—H1N_2	116.9 (9)
C3_1—N2_1—N1_1	105.50 (6)	C3_2—N2_2—N1_2	105.43 (6)
N1_1—C1_1—C2_1	105.09 (7)	N1_2—C1_2—C2_2	105.10 (7)
N1_1—C1_1—H1_1	127.5	N1_2—C1_2—H1_2	127.5
C2_1—C1_1—H1_1	127.5	C2_2—C1_2—H1_2	127.5
F1_1—C2_1—C1_1	125.91 (7)	F1_2—C2_2—C1_2	126.25 (7)
F1_1—C2_1—C3_1	126.73 (7)	F1_2—C2_2—C3_2	126.46 (7)
C1_1—C2_1—C3_1	107.36 (7)	C1_2—C2_2—C3_2	107.29 (6)
N2_1—C3_1—C2_1	109.29 (7)	N2_2—C3_2—C2_2	109.46 (7)
N2_1—C3_1—H3_1	125.4	N2_2—C3_2—H3_2	125.3
C2_1—C3_1—H3_1	125.4	C2_2—C3_2—H3_2	125.3
C1_1—N1_1—N2_1—C3_1	0.49 (9)	C1_2—N1_2—N2_2—C3_2	0.85 (9)
N2_1—N1_1—C1_1—C2_1	−0.31 (9)	N2_2—N1_2—C1_2—C2_2	−0.88 (9)
N1_1—C1_1—C2_1—F1_1	179.71 (7)	N1_2—C1_2—C2_2—F1_2	−178.67 (7)
N1_1—C1_1—C2_1—C3_1	0.01 (9)	N1_2—C1_2—C2_2—C3_2	0.55 (9)
N1_1—N2_1—C3_1—C2_1	−0.46 (9)	N1_2—N2_2—C3_2—C2_2	−0.46 (9)
F1_1—C2_1—C3_1—N2_1	−179.41 (7)	F1_2—C2_2—C3_2—N2_2	179.16 (7)
C1_1—C2_1—C3_1—N2_1	0.29 (9)	C1_2—C2_2—C3_2—N2_2	−0.06 (9)