

Acta Crystallographica Section E

## Structure Reports

Online

ISSN 1600-5368

## 2-Amino-5-bromopyridinium trifluoroacetate

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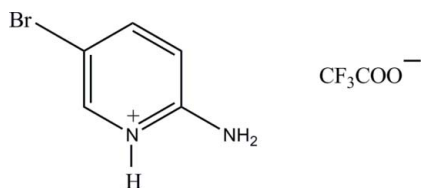
Received 22 February 2010; accepted 3 March 2010

 Key indicators: single-crystal X-ray study;  $T = 296$  K; mean  $\sigma(\text{C}-\text{C}) = 0.006$  Å; disorder in main residue;  $R$  factor = 0.039;  $wR$  factor = 0.099; data-to-parameter ratio = 16.5.

In the title compound,  $\text{C}_5\text{H}_6\text{BrN}_2^+\cdot\text{C}_2\text{F}_3\text{O}_2^-$ , the F atoms of the anion are disordered over two sets of sites, with occupancies of 0.59 (2):0.41 (2). In the crystal structure, the anions and cations are linked into a two-dimensional network parallel to (100) by  $\text{N}-\text{H}\cdots\text{O}$  and  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds. Within this network, the  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds generate  $R_2^2(8)$  ring motifs.

### Related literature

For background to the chemistry of substituted pyridines, see: Pozharski *et al.* (1997); Katritzky *et al.* (1996). For related structures, see: Goubitz *et al.* (2001); Vaday & Foxman (1999). For details of hydrogen bonding, see: Jeffrey & Saenger (1991); Jeffrey (1997); Scheiner (1997). For hydrogen-bond motifs, see: Bernstein *et al.* (1995). For bond-length data, see: Allen *et al.* (1987).



### Experimental

#### Crystal data

$\text{C}_5\text{H}_6\text{BrN}_2^+\cdot\text{C}_2\text{F}_3\text{O}_2^-$   
 $M_r = 287.05$   
 Orthorhombic,  $Pna2_1$   
 $a = 17.5852$  (13) Å  
 $b = 11.3010$  (9) Å  
 $c = 5.1264$  (4) Å

$V = 1018.77$  (14) Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 4.06$  mm<sup>-1</sup>  
 $T = 296$  K  
 $0.73 \times 0.41 \times 0.09$  mm

#### Data collection

Bruker SMART APEXII CCD  
 area-detector diffractometer  
 Absorption correction: multi-scan  
 (SADABS; Bruker, 2009)  
 $T_{\min} = 0.156$ ,  $T_{\max} = 0.709$

8343 measured reflections  
 2899 independent reflections  
 1547 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.056$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$   
 $wR(F^2) = 0.099$   
 $S = 0.93$   
 2899 reflections  
 176 parameters  
 56 restraints

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\max} = 0.46$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.28$  e Å<sup>-3</sup>  
 Absolute structure: Flack (1983),  
 1254 Friedel pairs  
 Flack parameter: 0.024 (12)

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1N1}\cdots\text{O1}^i$	0.93 (3)	1.80 (3)	2.720 (5)	171 (3)
$\text{N2}-\text{H1N2}\cdots\text{O1}^{ii}$	0.83 (4)	2.05 (4)	2.870 (4)	176 (5)
$\text{N2}-\text{H2N2}\cdots\text{O2}^i$	0.83 (4)	2.03 (4)	2.849 (5)	170 (4)
$\text{C1}-\text{H1A}\cdots\text{O2}^{iii}$	0.93	2.34	3.245 (4)	164

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

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

MH and HKF thank the Malaysian Government and Universiti Sains Malaysia (USM) for the Research University Golden Goose grant No. 1001/PFIZIK/811012. MH thanks USM for a post-doctoral research fellowship.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI5042).

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‡ Thomson Reuters ResearcherID: A-3561-2009.

## supporting information

*Acta Cryst.* (2010). E66, o775 [doi:10.1107/S1600536810008184]

## 2-Amino-5-bromopyridinium trifluoroacetate

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### S1. Comment

Pyridine and its derivatives play an important role in heterocyclic chemistry (Pozharski *et al.*, 1997; Katritzky *et al.*, 1996). They are often involved in hydrogen-bond interactions (Jeffrey & Saenger, 1991; Jeffrey, 1997; Scheiner, 1997). The crystal structures of 2-amino-5-bromopyridine (Goubitz *et al.*, 2001) and 2-amino-5-bromopyridinium propynoate (Vaday & Foxman, 1999) have been reported. In order to study hydrogen bonding interactions, the title salt was prepared and its crystal structure is reported here.

The asymmetric unit of (I) (Fig. 1) contains one 2-amino-5-bromopyridinium cation and one trifluoroacetate anion, indicating that proton transfer has occurred during the co-crystallisation. The 2-amino-5-methylpyridinium cation is essentially planar, with a maximum deviation of 0.016 (4) Å for atom C1; As a result of protonation, the C1—N1—C5 angle is widened to 122.5 (4)°. The bond lengths and angles are normal (Allen *et al.*, 1987).

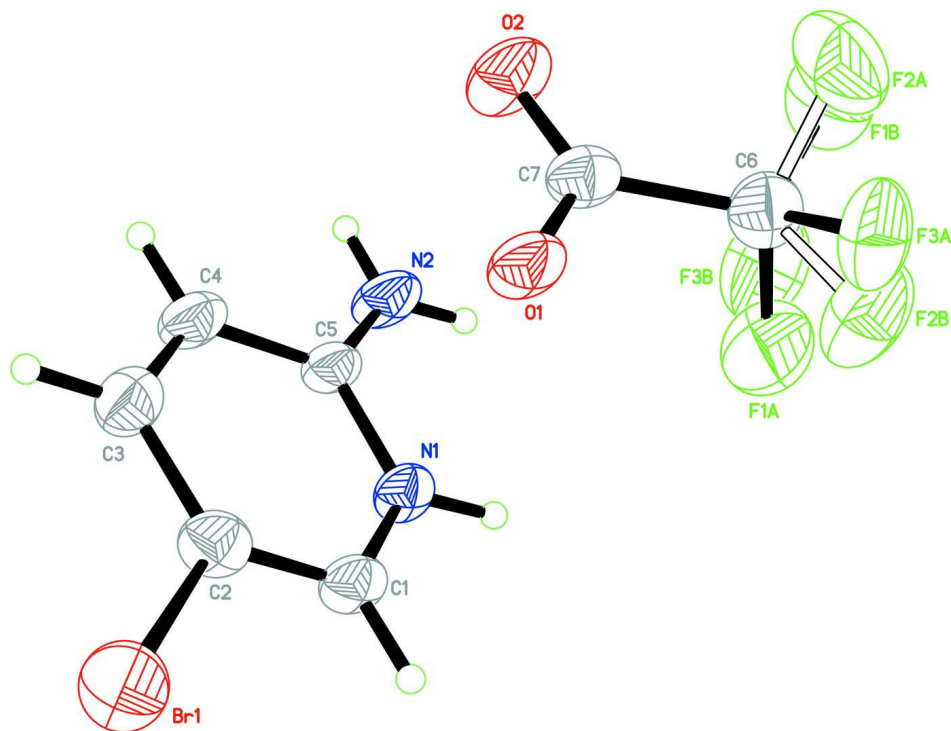
In the crystal packing (Fig. 2), the cations and anions are linked via N—H···O hydrogen bonds to form  $R_2^2(8)$  ring motifs (Bernstein *et al.*, 1995). The ionic units are linked into a two-dimensional network parallel to the (100) by N—H···O and C—H···O hydrogen bonds (Table 1).

### S2. Experimental

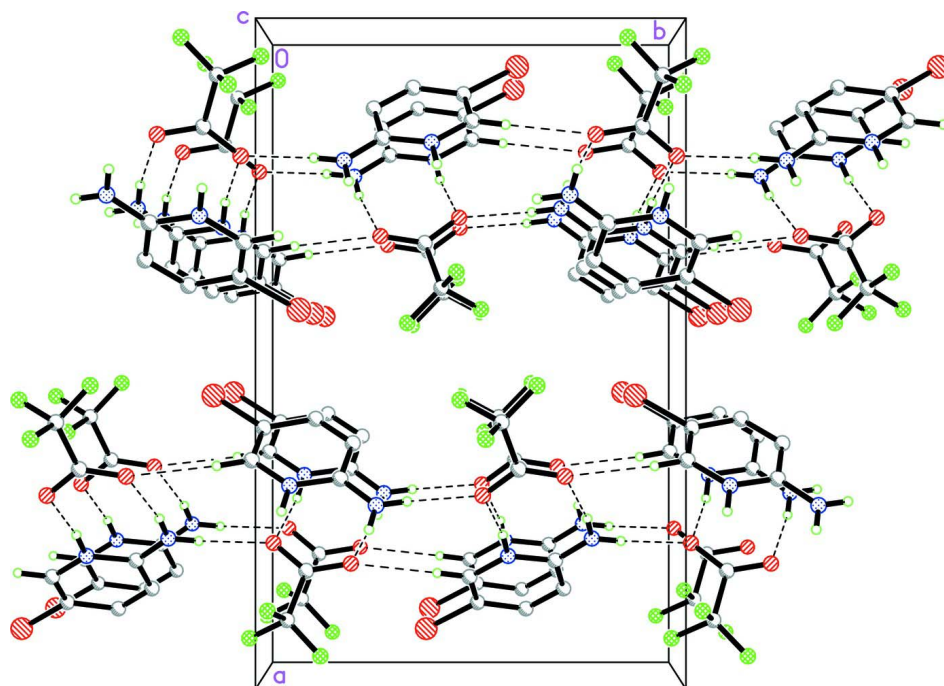
To a hot methanol solution (20 ml) of 2-amino-5-bromopyridine (44 mg, Aldrich) was added a few drops of trifluoroacetic acid. The solution was warmed over a water bath for a few minutes. The resulting solution was allowed to cool slowly to room temperature. Crystals of the title compound appeared after a few days.

### S3. Refinement

Atoms H1N1, H1N2 and H2N2 were located in a difference Fourier map and refined; the N—H distances of the NH<sub>2</sub> group were restrained to be equal. The remaining H atoms were positioned geometrically [C—H = 0.93 Å] and were refined using a riding model, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . The F atoms of the anion are disordered over two positions with occupancies of 0.59 (2):0.41 (2). The C—F distances were restrained to be equal and the  $U^{\text{ij}}$  components of F atoms were restrained to an approximate isotropic behaviour.

**Figure 1**

The asymmetric unit of the title compound. Displacement ellipsoids are drawn at the 30% probability level. Both disorder components are shown.

**Figure 2**

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

## 2-Amino-5-bromopyridinium trifluoroacetate

## Crystal data

C<sub>5</sub>H<sub>6</sub>BrN<sub>2</sub><sup>+</sup>·C<sub>2</sub>F<sub>3</sub>O<sub>2</sub><sup>-</sup> $M_r = 287.05$ Orthorhombic, *Pna2*<sub>1</sub>

Hall symbol: P 2c -2n

 $a = 17.5852 (13) \text{ \AA}$  $b = 11.3010 (9) \text{ \AA}$  $c = 5.1264 (4) \text{ \AA}$  $V = 1018.77 (14) \text{ \AA}^3$  $Z = 4$  $F(000) = 560$  $D_x = 1.871 \text{ Mg m}^{-3}$ Mo *K* $\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$ 

Cell parameters from 1994 reflections

 $\theta = 2.9\text{--}22.5^\circ$  $\mu = 4.06 \text{ mm}^{-1}$  $T = 296 \text{ K}$ 

Plate, colourless

 $0.73 \times 0.41 \times 0.09 \text{ mm}$ 

## Data collection

Bruker SMART APEXII CCD area-detector  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

 $\varphi$  and  $\omega$  scans

Absorption correction: multi-scan

(SADABS; Bruker, 2009)

 $T_{\min} = 0.156$ ,  $T_{\max} = 0.709$ 

8343 measured reflections

2899 independent reflections

1547 reflections with  $I > 2\sigma(I)$  $R_{\text{int}} = 0.056$  $\theta_{\max} = 30.1^\circ$ ,  $\theta_{\min} = 2.1^\circ$  $h = -24 \rightarrow 24$  $k = -14 \rightarrow 15$  $l = -7 \rightarrow 7$ 

## Refinement

Refinement on  $F^2$ 

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.039$  $wR(F^2) = 0.099$  $S = 0.93$ 

2899 reflections

176 parameters

56 restraints

Primary atom site location: structure-invariant  
direct methodsSecondary atom site location: difference Fourier  
mapHydrogen site location: inferred from  
neighbouring sitesH atoms treated by a mixture of independent  
and constrained refinement $w = 1/[\sigma^2(F_o^2) + (0.0247P)^2]$ where  $P = (F_o^2 + 2F_c^2)/3$  $(\Delta/\sigma)_{\max} = 0.001$  $\Delta\rho_{\max} = 0.46 \text{ e \AA}^{-3}$  $\Delta\rho_{\min} = -0.28 \text{ e \AA}^{-3}$ Absolute structure: Flack (1983), 1254 Friedel  
pairs

Absolute structure parameter: 0.024 (12)

## Special details

**Geometry.** All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted R-factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional R-factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > 2\sigma(F^2)$  is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and R-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Br1	0.93625 (2)	0.38997 (4)	0.26064 (12)	0.0770 (2)	
N1	0.80785 (16)	0.5888 (2)	0.7575 (9)	0.0462 (6)	
N2	0.7800 (2)	0.7862 (3)	0.8112 (8)	0.0631 (11)	

C1	0.8432 (2)	0.4973 (3)	0.6357 (8)	0.0489 (8)	
H1A	0.8355	0.4204	0.6947	0.059*	
C2	0.8889 (2)	0.5166 (4)	0.4322 (8)	0.0540 (9)	
C3	0.9016 (2)	0.6353 (4)	0.3492 (8)	0.0585 (11)	
H3A	0.9342	0.6507	0.2106	0.070*	
C4	0.8661 (2)	0.7253 (4)	0.4722 (8)	0.0563 (10)	
H4A	0.8743	0.8029	0.4183	0.068*	
C5	0.81681 (19)	0.7018 (3)	0.6821 (7)	0.0474 (9)	
O1	0.70895 (14)	0.5277 (2)	0.1425 (6)	0.0589 (7)	
O2	0.67948 (17)	0.7148 (2)	0.2175 (8)	0.0751 (9)	
F1A	0.6204 (5)	0.5331 (17)	0.6225 (16)	0.120 (4)	0.59 (2)
F2A	0.5460 (5)	0.6483 (7)	0.419 (3)	0.104 (3)	0.59 (2)
F3A	0.5673 (5)	0.4758 (8)	0.273 (3)	0.095 (3)	0.59 (2)
F1B	0.5407 (6)	0.6290 (16)	0.294 (4)	0.115 (5)	0.41 (2)
F2B	0.5819 (10)	0.4561 (7)	0.392 (4)	0.105 (5)	0.41 (2)
F3B	0.6028 (10)	0.6030 (19)	0.6312 (19)	0.113 (5)	0.41 (2)
C6	0.5992 (2)	0.5688 (3)	0.3866 (8)	0.0636 (11)	
C7	0.66887 (19)	0.6091 (3)	0.2336 (9)	0.0510 (9)	
H1N1	0.7730 (19)	0.576 (3)	0.891 (7)	0.041 (9)*	
H1N2	0.785 (2)	0.856 (3)	0.767 (11)	0.060 (11)*	
H2N2	0.748 (2)	0.773 (4)	0.927 (7)	0.067 (14)*	

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Br1	0.0861 (3)	0.0606 (3)	0.0842 (3)	0.0050 (2)	0.0152 (3)	-0.0136 (3)
N1	0.0546 (15)	0.0281 (14)	0.0561 (15)	-0.0047 (11)	0.002 (2)	-0.004 (2)
N2	0.085 (2)	0.0291 (17)	0.075 (3)	0.0045 (18)	0.014 (2)	0.0079 (18)
C1	0.058 (2)	0.0280 (18)	0.061 (2)	-0.0045 (16)	-0.0053 (18)	-0.0018 (17)
C2	0.059 (2)	0.040 (2)	0.063 (2)	0.0022 (17)	-0.0031 (18)	-0.0071 (18)
C3	0.061 (2)	0.054 (3)	0.061 (3)	-0.007 (2)	0.0016 (18)	0.0057 (19)
C4	0.067 (2)	0.037 (2)	0.064 (2)	-0.0068 (19)	-0.004 (2)	0.013 (2)
C5	0.0519 (18)	0.0322 (19)	0.058 (2)	-0.0045 (16)	-0.0059 (16)	0.0088 (16)
O1	0.0679 (15)	0.0319 (14)	0.0768 (16)	0.0077 (12)	0.0135 (14)	0.0109 (13)
O2	0.0987 (19)	0.0303 (14)	0.096 (3)	0.0012 (13)	0.0185 (18)	0.0044 (18)
F1A	0.115 (5)	0.166 (9)	0.078 (4)	-0.013 (5)	0.011 (3)	0.046 (5)
F2A	0.093 (4)	0.080 (4)	0.139 (8)	0.018 (3)	0.040 (4)	-0.019 (4)
F3A	0.083 (3)	0.082 (4)	0.119 (6)	-0.036 (3)	0.008 (4)	-0.011 (5)
F1B	0.069 (5)	0.143 (8)	0.132 (9)	0.030 (5)	0.009 (6)	-0.004 (7)
F2B	0.119 (7)	0.062 (6)	0.133 (9)	-0.011 (5)	0.047 (7)	-0.001 (5)
F3B	0.130 (8)	0.121 (9)	0.088 (6)	-0.024 (6)	0.036 (5)	-0.009 (6)
C6	0.065 (3)	0.045 (2)	0.080 (3)	0.002 (2)	0.005 (2)	-0.007 (2)
C7	0.062 (2)	0.037 (2)	0.054 (2)	0.0022 (16)	-0.005 (2)	0.001 (2)

*Geometric parameters (Å, °)*

Br1—C2	1.875 (4)	C4—C5	1.407 (5)
N1—C5	1.344 (4)	C4—H4A	0.93

N1—C1	1.358 (5)	O1—C7	1.250 (4)
N1—H1N1	0.93 (4)	O2—C7	1.212 (4)
N2—C5	1.330 (5)	F1A—C6	1.329 (6)
N2—H1N2	0.82 (3)	F2A—C6	1.307 (6)
N2—H2N2	0.84 (3)	F3A—C6	1.327 (6)
C1—C2	1.334 (5)	F1B—C6	1.321 (7)
C1—H1A	0.93	F2B—C6	1.310 (7)
C2—C3	1.425 (6)	F3B—C6	1.314 (7)
C3—C4	1.349 (6)	C6—C7	1.524 (6)
C3—H3A	0.93		
C5—N1—C1	122.5 (4)	N2—C5—N1	118.8 (3)
C5—N1—H1N1	116 (2)	N2—C5—C4	123.0 (4)
C1—N1—H1N1	121 (2)	N1—C5—C4	118.1 (4)
C5—N2—H1N2	120 (4)	F2B—C6—F3B	106.2 (8)
C5—N2—H2N2	124 (3)	F2B—C6—F1B	109.0 (10)
H1N2—N2—H2N2	116 (5)	F3B—C6—F1B	103.2 (9)
C2—C1—N1	120.7 (4)	F2A—C6—F3A	107.3 (7)
C2—C1—H1A	119.6	F2A—C6—F1A	107.2 (6)
N1—C1—H1A	119.6	F3A—C6—F1A	106.1 (6)
C1—C2—C3	118.8 (4)	F2A—C6—C7	115.8 (6)
C1—C2—Br1	120.6 (3)	F2B—C6—C7	119.1 (7)
C3—C2—Br1	120.6 (3)	F3B—C6—C7	111.4 (7)
C4—C3—C2	119.8 (4)	F1B—C6—C7	106.8 (8)
C4—C3—H3A	120.1	F3A—C6—C7	110.4 (6)
C2—C3—H3A	120.1	F1A—C6—C7	109.5 (5)
C3—C4—C5	120.0 (4)	O2—C7—O1	127.8 (4)
C3—C4—H4A	120.0	O2—C7—C6	116.9 (4)
C5—C4—H4A	120.0	O1—C7—C6	115.2 (3)
C5—N1—C1—C2	-0.2 (6)	F2B—C6—C7—O2	174.5 (14)
N1—C1—C2—C3	1.7 (5)	F3B—C6—C7—O2	-61.4 (13)
N1—C1—C2—Br1	-178.9 (3)	F1B—C6—C7—O2	50.6 (12)
C1—C2—C3—C4	-1.6 (6)	F3A—C6—C7—O2	142.0 (8)
Br1—C2—C3—C4	179.0 (3)	F1A—C6—C7—O2	-101.5 (10)
C2—C3—C4—C5	0.1 (6)	F2A—C6—C7—O1	-161.2 (9)
C1—N1—C5—N2	179.8 (3)	F2B—C6—C7—O1	-6.5 (14)
C1—N1—C5—C4	-1.4 (6)	F3B—C6—C7—O1	117.6 (12)
C3—C4—C5—N2	-179.8 (4)	F1B—C6—C7—O1	-130.4 (12)
C3—C4—C5—N1	1.4 (5)	F3A—C6—C7—O1	-39.0 (8)
F2A—C6—C7—O2	19.8 (10)	F1A—C6—C7—O1	77.5 (10)

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1N1 $\cdots$ O1 <sup>i</sup>	0.93 (3)	1.80 (3)	2.720 (5)	171 (3)
N2—H1N2 $\cdots$ O1 <sup>ii</sup>	0.83 (4)	2.05 (4)	2.870 (4)	176 (5)

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N2—H2N2···O2 <sup>i</sup>	0.83 (4)	2.03 (4)	2.849 (5)	170 (4)
C1—H1A···O2 <sup>iii</sup>	0.93	2.34	3.245 (4)	164

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Symmetry codes: (i)  $x, y, z+1$ ; (ii)  $-x+3/2, y+1/2, z+1/2$ ; (iii)  $-x+3/2, y-1/2, z+1/2$ .