

2-Amino-4-methylpyrimidinium dihydrogen phosphate

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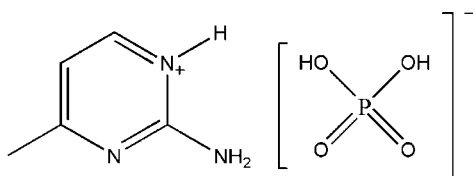
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 Key indicators: single-crystal X-ray study; $T = 295$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.031; wR factor = 0.088; data-to-parameter ratio = 13.7.

A charge-assisted hydrogen-bonding network involving $\text{N}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds stabilizes the crystal of the title salt, $\text{C}_5\text{H}_8\text{N}_3^+\cdot\text{H}_2\text{PO}_4^-$. The dihydrogen phosphate anions form one-dimensional chains along $[100]$, via $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds. The 2-amino-4-methylpyrimidinium cations are linked to these chains by means of two different kinds of $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds. Neighbouring chains are linked via $\text{C}-\text{H}\cdots\text{N}$ and $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds forming two-dimensional slab-like networks lying parallel to $(01\bar{1})$.

Related literature

Intriguing anion clusters formed by the supramolecular assembly of dihydrogen phosphates have been investigated recently (see: Hossain *et al.*, 2012). Methylpyrimidine derivatives are known to be synthetic precursors to many bioactive pyrimidine derivatives (see: Xue *et al.*, 1993). Metal complexes of pyrimidines (see: Zhu *et al.*, 2008) and their proton transfer complexes with mineral acids are reported (see: Aakeroy *et al.*, 2003). The infinite $\text{O}-\text{H}\cdots\text{O}$ hydrogen-bond chain present in this material is a structural feature suggestive of possible proton conducting behaviour (see: Haile *et al.*, 2001).



Experimental

Crystal data

 $\text{C}_5\text{H}_8\text{N}_3^+\cdot\text{H}_2\text{PO}_4^-$
 $M_r = 207.13$
 Triclinic, $P\bar{1}$
 $a = 6.1720$ (2) Å
 $b = 7.5616$ (3) Å

 $c = 9.9216$ (4) Å
 $\alpha = 100.562$ (3)°
 $\beta = 99.821$ (3)°
 $\gamma = 102.279$ (4)°
 $V = 434.07$ (3) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.31$ mm⁻¹
 $T = 295$ K
 $0.25 \times 0.20 \times 0.18$ mm

Data collection

 Oxford Xcalibur Eos (Nova) CCD detector diffractometer
 Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2006)
 $T_{\min} = 0.928$, $T_{\max} = 0.947$
 9718 measured reflections
 1717 independent reflections
 1546 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.027$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.031$
 $wR(F^2) = 0.088$
 $S = 1.08$
 1717 reflections
 125 parameters

 H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.21$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.34$ e Å⁻³

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O1}-\text{H1}\cdots\text{O4}^{\text{i}}$	0.82	1.80	2.6100 (18)	168
$\text{N1}-\text{H1N}\cdots\text{O2}^{\text{ii}}$	0.86	2.14	3.000 (2)	177
$\text{O2}-\text{H2}\cdots\text{O4}^{\text{iii}}$	0.82	1.80	2.5843 (17)	161
$\text{N1}-\text{H2N}\cdots\text{O3}^{\text{iv}}$	0.86	2.01	2.845 (2)	163
$\text{N3}-\text{H3N}\cdots\text{O3}^{\text{ii}}$	0.90 (2)	1.73 (2)	2.6276 (19)	173 (2)
$\text{C4}-\text{H4}\cdots\text{N2}^{\text{v}}$	0.93	2.55	3.463 (2)	166
$\text{C5}-\text{H5B}\cdots\text{O1}^{\text{vi}}$	0.96	2.58	3.531 (3)	171

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis PRO* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED* (Oxford Diffraction, 2006); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008) and *WinGX* (Farrugia, 2012); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DS2227).

References

- Aakeroy, C. B., Beffert, K., Desper, J. & Elisabeth, E. (2003). *Cryst. Growth Des.* **3**, 837–846.
 Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
 Haile, S. M., Boysen, D. A., Chisholm, C. R. I. & Merle, R. B. (2001). *Nature*, **410**, 910–913.
 Hossain, M. A., Muhammet, I. K., Avijit, P., Musabbir, A. S. & Frank, R. F. (2012). *Cryst. Growth Des.* **12**, 567–571.
 Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
 Oxford Diffraction (2006). *CrysAlis CCD*, *CrysAlis PRO* and *CrysAlis RED*. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
 Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
 Xue, S. J., Zhang, A. D. & Wang, H. T. (1993). *Chem. Reagents*, **15**, 181–182.
 Zhu, W., Liu, X. & Wang, H. (2008). *Acta Opt. Sin.* **28**, 1155–1160.

supporting information

Acta Cryst. (2013). E69, o529 [doi:10.1107/S160053681300648X]

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S1. Comment

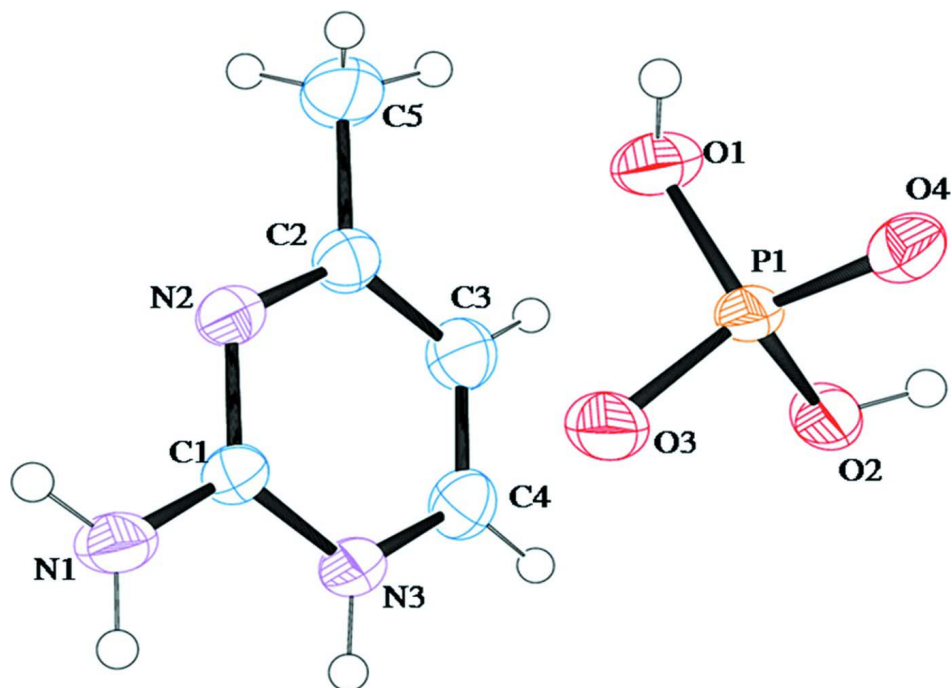
The title compound, a multicomponent crystal, AMHP, crystallizes in triclinic P-1, with a protonated 2-amino-4-methylpyrimidine molecule and a dihydrogenphosphate moiety in the asymmetric unit (Fig. 1). The dihydrogenphosphate residue forms a chain *via* O—H···O hydrogen bonds. 2-Amino-4-methylpyrimidinium cations are linked to these chains by means of two different kinds of N—H···O hydrogen bonds. The crystal packing is stabilized by N—H···O and O—H···O hydrogen bonds and the resulting supramolecular assembly is shown in Figure 2. The infinite hydrogen bond chains present in this structure are of special interest due to the anticipated proton conductivity of the material (see: Haile *et al.* 2001).

S2. Experimental

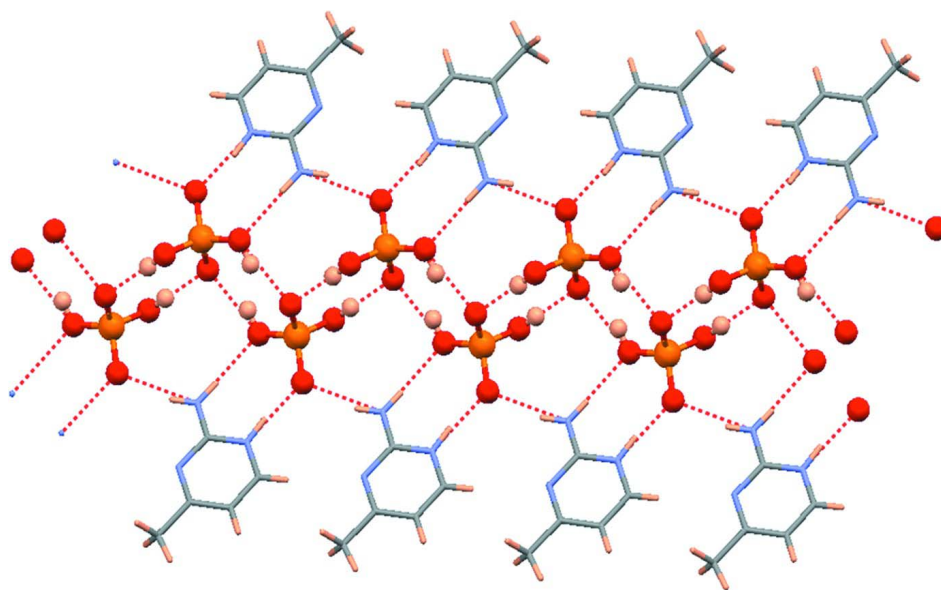
The title compound was prepared by treating 2-amino 4-methyl pyrimidine with phosphoric acid (H₃PO₄) in aqueous solution (Scheme 1) in 1:1 molar ratio. The crystals were harvested from the solution after 10 days and suitable crystal for single-crystal X-ray diffraction study were chosen using a polarizing microscope.

S3. Refinement

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis PRO* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED* (Oxford Diffraction, 2006); program(s) used to solve structure: *SHELXL97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008), *WinGX* (Farrugia, 2012); molecular graphics: Mercury 2.3 (Macrae *et al.* 2008); software used to prepare material for publication: *PLATON* (Spek, 2009).

**Figure 1**

ORTEP view of the title compound with the atom numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level.

**Figure 2**

A view of supramolecular chain showing the hydrogen bonding between dihydrogen phosphate residues and the interlinked 2-amino-4-methylpyrimidine molecules.

2-Amino-4-methylpyrimidinium dihydrogen phosphate

Crystal data

$C_5H_8N_3^+ \cdot H_2PO_4^-$
 $M_r = 207.13$
 Triclinic, $P\bar{1}$
 Hall symbol: -P 1
 $a = 6.1720$ (2) Å
 $b = 7.5616$ (3) Å
 $c = 9.9216$ (4) Å
 $\alpha = 100.562$ (3)°
 $\beta = 99.821$ (3)°
 $\gamma = 102.279$ (4)°
 $V = 434.07$ (3) Å³
 $Z = 2$

$F(000) = 216$
 Least Squares Treatment of 25 SET4 setting angles.
 $D_x = 1.585$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 326 reflections
 $\theta = 2.8$ – 26.0 °
 $\mu = 0.31$ mm⁻¹
 $T = 295$ K
 Block, colourless
 $0.25 \times 0.20 \times 0.18$ mm

Data collection

Oxford Xcalibur Eos (Nova) CCD detector diffractometer
 Radiation source: Enhance (Mo) X-ray Source
 Graphite monochromator
 ω scans
 Absorption correction: multi-scan
 (CrysAlis RED; Oxford Diffraction, 2006)
 $T_{\min} = 0.928$, $T_{\max} = 0.947$

9718 measured reflections
 1717 independent reflections
 1546 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.027$
 $\theta_{\max} = 26.0$ °, $\theta_{\min} = 2.8$ °
 $h = -7 \rightarrow 7$
 $k = -9 \rightarrow 9$
 $l = -12 \rightarrow 12$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.031$
 $wR(F^2) = 0.088$
 $S = 1.08$
 1717 reflections
 125 parameters
 0 restraints
 Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
 Hydrogen site location: inferred from neighbouring sites
 H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0449P)^2 + 0.1805P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.21$ e Å⁻³
 $\Delta\rho_{\min} = -0.34$ e Å⁻³

Special details

Geometry. Bond distances, angles *etc.* have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement on F^2 for ALL reflections except those flagged by the user for potential systematic errors. Weighted R -factors wR and all goodnesses 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 observed criterion of $F^2 > \sigma(F^2)$ is used only for calculating $-R$ -factor-obs *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 (Å²)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.1136 (3)	0.3869 (2)	1.11795 (16)	0.0405 (5)

N2	-0.0464 (2)	0.1740 (2)	0.90738 (15)	0.0332 (4)
N3	0.3480 (2)	0.2530 (2)	0.99937 (15)	0.0326 (4)
C1	0.1379 (3)	0.2712 (2)	1.00803 (17)	0.0293 (5)
C2	-0.0146 (3)	0.0613 (2)	0.79698 (18)	0.0341 (5)
C3	0.2007 (3)	0.0371 (3)	0.7852 (2)	0.0407 (6)
C4	0.3796 (3)	0.1362 (3)	0.88869 (19)	0.0386 (6)
C5	-0.2202 (4)	-0.0381 (3)	0.6843 (2)	0.0507 (7)
P1	0.28422 (7)	0.48498 (6)	0.64883 (4)	0.0283 (1)
O1	0.0685 (2)	0.31898 (17)	0.59152 (14)	0.0418 (4)
O2	0.4901 (2)	0.39299 (18)	0.64980 (12)	0.0365 (4)
O3	0.2949 (2)	0.5709 (2)	0.79898 (13)	0.0439 (4)
O4	0.29115 (19)	0.61556 (16)	0.55043 (13)	0.0336 (4)
H1N	0.23060	0.44920	1.18240	0.0490*
H2N	-0.01930	0.40020	1.12510	0.0490*
H3	0.21960	-0.04470	0.70830	0.0490*
H3N	0.464 (4)	0.319 (3)	1.071 (2)	0.048 (6)*
H4	0.52500	0.12390	0.88380	0.0460*
H5A	-0.31890	-0.12620	0.71950	0.0760*
H5B	-0.17500	-0.10210	0.60520	0.0760*
H5C	-0.29890	0.05020	0.65580	0.0760*
H1	-0.03370	0.35420	0.54850	0.0630*
H2	0.53240	0.39280	0.57580	0.0550*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0258 (7)	0.0530 (9)	0.0348 (8)	0.0121 (7)	0.0011 (6)	-0.0069 (7)
N2	0.0252 (7)	0.0384 (8)	0.0319 (7)	0.0049 (6)	0.0049 (6)	0.0030 (6)
N3	0.0238 (7)	0.0423 (8)	0.0309 (7)	0.0087 (6)	0.0047 (6)	0.0069 (6)
C1	0.0241 (8)	0.0338 (8)	0.0303 (8)	0.0081 (6)	0.0052 (6)	0.0081 (7)
C2	0.0327 (9)	0.0334 (8)	0.0331 (9)	0.0033 (7)	0.0079 (7)	0.0048 (7)
C3	0.0410 (10)	0.0435 (10)	0.0373 (10)	0.0132 (8)	0.0140 (8)	0.0003 (8)
C4	0.0315 (9)	0.0494 (10)	0.0403 (10)	0.0173 (8)	0.0134 (8)	0.0103 (8)
C5	0.0393 (11)	0.0546 (12)	0.0424 (11)	-0.0023 (9)	0.0047 (8)	-0.0077 (9)
P1	0.0201 (2)	0.0388 (3)	0.0242 (2)	0.0076 (2)	0.0030 (2)	0.0046 (2)
O1	0.0294 (7)	0.0421 (7)	0.0492 (8)	0.0029 (5)	-0.0041 (6)	0.0177 (6)
O2	0.0300 (6)	0.0563 (8)	0.0293 (6)	0.0201 (6)	0.0081 (5)	0.0126 (6)
O3	0.0298 (7)	0.0705 (9)	0.0280 (7)	0.0165 (6)	0.0057 (5)	-0.0015 (6)
O4	0.0238 (6)	0.0396 (6)	0.0379 (7)	0.0078 (5)	0.0066 (5)	0.0106 (5)

Geometric parameters (Å, °)

P1—O3	1.4964 (13)	N1—H2N	0.8600
P1—O1	1.5623 (14)	N1—H1N	0.8600
P1—O2	1.5725 (14)	N3—H3N	0.90 (2)
P1—O4	1.5098 (13)	C2—C5	1.492 (3)
O1—H1	0.8200	C2—C3	1.401 (3)
O2—H2	0.8200	C3—C4	1.347 (3)

N1—C1	1.319 (2)	C3—H3	0.9300
N2—C2	1.329 (2)	C4—H4	0.9300
N2—C1	1.349 (2)	C5—H5C	0.9600
N3—C1	1.348 (2)	C5—H5A	0.9600
N3—C4	1.347 (2)	C5—H5B	0.9600
P1…H3N ⁱ	2.89 (2)	C2…C1 ^{ix}	3.481 (2)
P1…H2N ⁱⁱ	3.1000	C2…O1	3.099 (2)
P1…H1 ⁱⁱⁱ	2.8900	C3…O1	3.257 (2)
P1…H1N ⁱ	3.0600	C4…O2	3.395 (2)
P1…H2 ^{iv}	2.8800	C5…O1	3.277 (3)
O1…C3	3.257 (2)	C5…H4 ^{viii}	2.9800
O1…C5	3.277 (3)	H1…P1 ⁱⁱⁱ	2.8900
O1…O4 ⁱⁱⁱ	2.6100 (18)	H1…O4 ⁱⁱⁱ	1.8000
O1…C2	3.099 (2)	H1…H1 ⁱⁱⁱ	2.5500
O2…N1 ⁱ	3.000 (2)	H1N…H2 ⁱ	2.5200
O2…C4	3.395 (2)	H1N…H3N	2.2400
O2…O4 ^{iv}	2.5843 (17)	H1N…P1 ⁱ	3.0600
O3…N1 ⁱⁱ	2.845 (2)	H1N…O2 ⁱ	2.1400
O3…N3 ⁱ	2.6276 (19)	H2…O4 ^{iv}	1.8000
O4…O1 ⁱⁱⁱ	2.6100 (18)	H2…H1N ⁱ	2.5200
O4…O2 ^{iv}	2.5843 (17)	H2…H2 ^{iv}	2.4500
O1…H5B ^v	2.5800	H2…P1 ^{iv}	2.8800
O2…H1N ⁱ	2.1400	H2N…P1 ⁱⁱ	3.1000
O3…H3N ⁱ	1.73 (2)	H2N…O3 ⁱⁱ	2.0100
O3…H2N ⁱⁱ	2.0100	H3…O4 ^x	2.9100
O4…H2 ^{iv}	1.8000	H3…H5B	2.3900
O4…H1 ⁱⁱⁱ	1.8000	H3N…H1N	2.2400
O4…H3 ^{vi}	2.9100	H3N…P1 ⁱ	2.89 (2)
O4…H5A ^{vii}	2.8000	H3N…O3 ⁱ	1.73 (2)
N1…O2 ⁱ	3.000 (2)	H4…N2 ^{xi}	2.5500
N1…O3 ⁱⁱ	2.845 (2)	H4…C5 ^{xi}	2.9800
N3…O3 ⁱ	2.6276 (19)	H5A…O4 ^{xiii}	2.8000
N2…H4 ^{viii}	2.5500	H5B…H3	2.3900
C1…C2 ^{ix}	3.481 (2)	H5B…O1 ^v	2.5800
O3—P1—O4	115.79 (8)	N2—C1—N3	121.54 (15)
O1—P1—O3	109.84 (8)	N2—C2—C3	122.14 (16)
O1—P1—O4	109.55 (7)	N2—C2—C5	116.73 (17)
O1—P1—O2	104.78 (7)	C3—C2—C5	121.13 (17)
O2—P1—O4	110.13 (7)	C2—C3—C4	117.84 (18)
O2—P1—O3	106.13 (7)	N3—C4—C3	120.03 (18)
P1—O1—H1	109.00	C2—C3—H3	121.00
P1—O2—H2	109.00	C4—C3—H3	121.00
C1—N2—C2	117.90 (15)	C3—C4—H4	120.00
C1—N3—C4	120.52 (15)	N3—C4—H4	120.00
H1N—N1—H2N	120.00	C2—C5—H5B	109.00
C1—N1—H1N	120.00	C2—C5—H5C	109.00

C1—N1—H2N	120.00	C2—C5—H5A	109.00
C1—N3—H3N	117.5 (15)	H5A—C5—H5C	109.00
C4—N3—H3N	121.9 (15)	H5B—C5—H5C	109.00
N1—C1—N3	118.80 (16)	H5A—C5—H5B	110.00
N1—C1—N2	119.66 (17)		
C2—N2—C1—N1	178.81 (15)	C4—N3—C1—N2	0.1 (2)
C2—N2—C1—N3	-1.3 (2)	C1—N3—C4—C3	0.3 (3)
C1—N2—C2—C3	2.1 (2)	N2—C2—C3—C4	-1.7 (3)
C1—N2—C2—C5	-177.38 (16)	C5—C2—C3—C4	177.75 (19)
C4—N3—C1—N1	-179.98 (18)	C2—C3—C4—N3	0.4 (3)

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

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1...O4 ⁱⁱⁱ	0.82	1.80	2.6100 (18)	168
N1—H1N...O2 ⁱ	0.86	2.14	3.000 (2)	177
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N1—H2N...O3 ⁱⁱ	0.86	2.01	2.845 (2)	163
N3—H3N...O3 ⁱ	0.90 (2)	1.73 (2)	2.6276 (19)	173 (2)
C4—H4...N2 ^{xi}	0.93	2.55	3.463 (2)	166
C5—H5B...O1 ^v	0.96	2.58	3.531 (3)	171

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