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3,4-Diaminopyridinium hydrogen malonate

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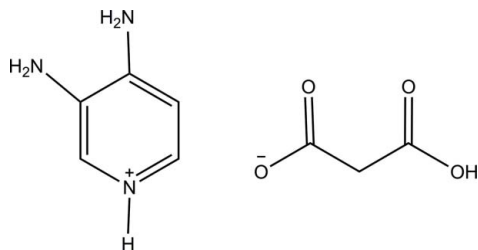
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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.040; wR factor = 0.102; data-to-parameter ratio = 8.9.

In the title salt, $\text{C}_5\text{H}_8\text{N}_3^+\cdot\text{C}_3\text{H}_3\text{O}_4^-$, the 3,4-diaminopyridinium cation is almost planar, with an r.m.s. deviation of 0.02 Å. The conformation of the hydrogen malonate anion is stabilized by an intramolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bond, which generates an $S(6)$ ring. In the crystal, $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds link cations and anions into layers parallel to the ab plane.

Related literature

For applications of 3,4-diaminopyridine, see: Maddison *et al.* (2001); Argov (2009). For related structures, see: De Cires-Mejias *et al.* (2004); Koleva *et al.* (2007, 2008); Fun & Balasubramani (2009). For graph-set notation, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$\text{C}_5\text{H}_8\text{N}_3^+\cdot\text{C}_3\text{H}_3\text{O}_4^-$
 $M_r = 213.20$
 Monoclinic, $P2_1$
 $a = 8.7761$ (18) Å
 $b = 5.088$ (1) Å

$c = 10.636$ (2) Å
 $\beta = 101.381$ (4)°
 $V = 465.58$ (17) Å³
 $Z = 2$
 Mo $K\alpha$ radiation

$\mu = 0.12$ mm⁻¹
 $T = 296$ K

0.30 × 0.20 × 0.20 mm

Data collection

Bruker APEXII CCD diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.964$, $T_{\max} = 0.976$

3498 measured reflections
 1248 independent reflections
 1066 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.026$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.102$
 $S = 1.18$
 1248 reflections
 140 parameters
 1 restraint

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.19$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.15$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-\text{H}\cdots A$ | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|--|--------------|--------------------|-------------|----------------------|
| $\text{N1}-\text{H1A}\cdots\text{O3}$ | 0.86 | 1.93 | 2.784 (3) | 175 |
| $\text{N2}-\text{H2A}\cdots\text{O1}^{\text{i}}$ | 0.86 | 2.28 | 3.132 (3) | 174 |
| $\text{N2}-\text{H2B}\cdots\text{O1}^{\text{ii}}$ | 0.86 | 2.15 | 3.005 (3) | 176 |
| $\text{N3}-\text{H3A}\cdots\text{O2}^{\text{iii}}$ | 0.86 | 2.28 | 3.048 (3) | 149 |
| $\text{N3}-\text{H3B}\cdots\text{O1}^{\text{ii}}$ | 0.86 | 2.10 | 2.960 (3) | 177 |
| $\text{O4}-\text{H4}\cdots\text{O2}$ | 0.91 (3) | 1.55 (3) | 2.442 (3) | 164 (3) |

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

Data collection: APEX2 (Bruker, 2005); cell refinement: SAINT (Bruker, 2001); 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.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV5392).

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3,4-Diaminopyridinium hydrogen malonate

Surendra Thapa, Sergiu Draguta, Bhupinder Sandhu, Mikhail Yu. Antipin and Tatiana V. Timofeeva

S1. Comment

3,4-Diaminopyridine is used for the treatment of Lambert-Eaton myasthenic syndrome (LEMS) which significantly improve the primary endpoint of muscle strength score, or myometric limb measurement following treatment (Maddison *et al.* 2001). It is also used to treat many of the congenital myasthenic syndromes (Argov, 2009). The crystal structures of adducts of 3,4-diaminopyridine with different acids such as succinic (Fun *et al.*, 2009), tartaric (Koleva *et al.*, 2008) and squaric acid (Koleva *et al.*, 2007) have been reported in the literature. Herewith we present the crystal structure of the title compound (I).

In (I) (Fig 1), the asymmetric unit consists of a 3,4-diaminopyridinium cation and a hydrogen malonate anion. In the 3,4-diaminopyridinium cation, endocyclic angles cover the range 117.98 (18)–121.95 (18)°. Protonation at atom N1 has led to slight increase in the C2—N1—C6 angle to 121.32 (2)° compared to that in unprotonated structure (De Cires-Mejias *et al.*, 2004). All non-hydrogen atoms lie within the same plane (r.m.s. deviation is 0.02 Å). The dihedral angle between the pyridine ring and the plane formed by the malonic acid molecule is 5.08 (6)°. Hydrogen malonate anion is stabilized by intramolecular O4—H···O2 hydrogen bond.

In the crystal, the protonated N1 atom is bonded to the carboxylate oxygen atom O3 through N—H···O hydrogen bond. The two amino groups (N2 and N3) are involved in the hydrogen bonding *via* N—H···O H-bonds with hydrogen malonate oxygen atom (O1) to form an $R^1_2(7)$ ring motif (Bernstein *et al.*, 1995). The N3 amino group is hydrogen-bonded to the carboxylate oxygen atom (O3). The N—H···O hydrogen bonds (Table 1) link cations and anions into layers parallel to *ab* plane (Fig. 2).

S2. Experimental

The initial compounds were obtained commercially (Aldrich) as fine-crystalline powders and purified additionally by filtration. 0.003 g (0.028 mmol) of malonic acid and 0.0035 (0.032 mmol) of 3,4 diaminopyridine were dissolved in hot ethanol. Crystals suitable for the X-ray diffraction study were obtained after couple of days by slow evaporation (m.p.:130–135°C).

S3. Refinement

The hydrogen atom of hydroxyl group was localized in the difference-Fourier map and refined isotropically. The other hydrogen atoms were placed in the calculated positions with N—H = 0.86 Å, C—H = 0.93 Å (aromatic) and C—H = 0.97 Å (methylene) and refined in the riding model with fixed isotropic displacement parameters [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$, $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$]. In the absence of any significant anomalous scatterers, the 369 Friedel pairs were merged before the final refinement.

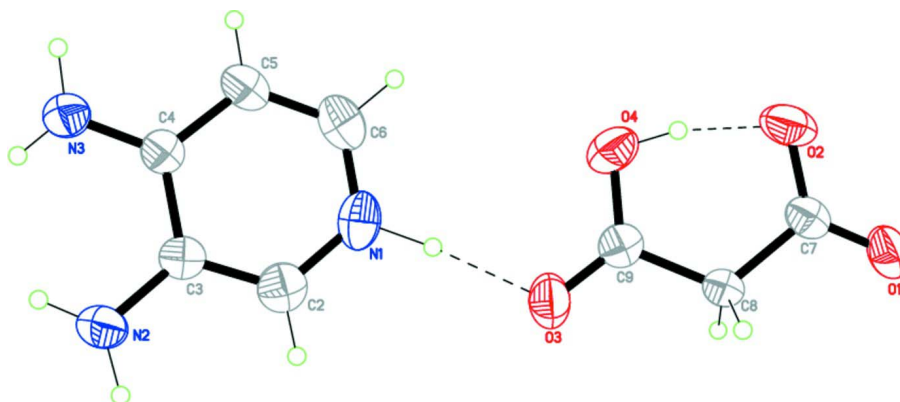


Figure 1

The content of asymmetric unit of **I** showing the atomic numbering and hydrogen bonds as dashed lines. Displacement ellipsoids are drawn at the 50% probability level. H atoms are presented as small spheres of arbitrary radius.

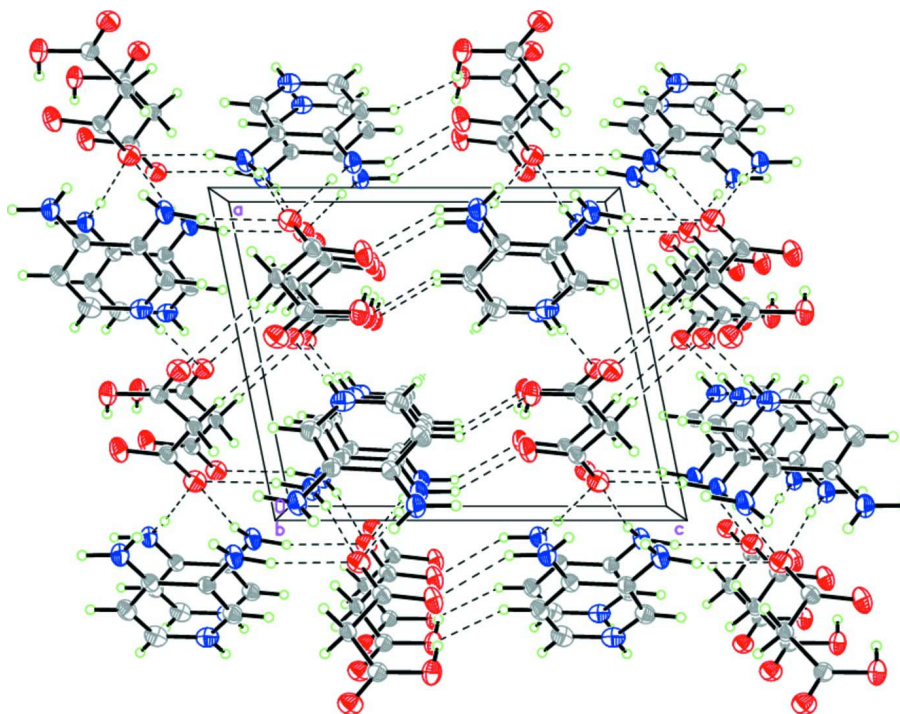


Figure 2

A portion of the crystal packing viewed approximately down the *b* axis and showing intermolecular N—H...O hydrogen bonds as dashed lines.

3,4-Diaminopyridinium 2-carboxyethanoate

Crystal data

$C_5H_8N_3^+ \cdot C_3H_3O_4^-$

$M_r = 213.20$

Monoclinic, $P2_1$

Hall symbol: P 2yb

$a = 8.7761(18) \text{ \AA}$

$b = 5.088(1) \text{ \AA}$

$c = 10.636(2) \text{ \AA}$

$\beta = 101.381(4)^\circ$

$V = 465.58(17) \text{ \AA}^3$

$Z = 2$

$F(000) = 224$

$D_x = 1.521 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 1070 reflections
 $\theta = 2.8\text{--}27.0^\circ$
 $\mu = 0.12 \text{ mm}^{-1}$

$T = 296 \text{ K}$
 Prism, colourless
 $0.30 \times 0.20 \times 0.20 \text{ mm}$

Data collection

Bruker APEXII CCD
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.964$, $T_{\max} = 0.976$

3498 measured reflections
 1248 independent reflections
 1066 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.026$
 $\theta_{\max} = 28.0^\circ$, $\theta_{\min} = 2.0^\circ$
 $h = -11 \rightarrow 11$
 $k = -6 \rightarrow 6$
 $l = -14 \rightarrow 14$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.102$
 $S = 1.18$
 1248 reflections
 140 parameters
 1 restraint
 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
 $w = 1/[\sigma^2(F_o^2) + (0.0456P)^2 + 0.0455P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.19 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.15 \text{ e \AA}^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'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 $F^2 > \sigma(F^2)$ 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 (\AA^2)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|------------|------------|--------------|----------------------------------|
| N1 | 0.3630 (3) | 0.6491 (5) | 0.2325 (2) | 0.0467 (6) |
| H1A | 0.4198 | 0.5329 | 0.2052 | 0.056* |
| N2 | 0.0891 (3) | 1.1609 (5) | 0.09714 (19) | 0.0461 (6) |
| H2A | 0.0922 | 1.1490 | 0.0170 | 0.055* |
| H2B | 0.0283 | 1.2730 | 0.1225 | 0.055* |
| N3 | 0.0818 (3) | 1.1851 (5) | 0.3616 (2) | 0.0428 (5) |
| H3A | 0.0792 | 1.1894 | 0.4420 | 0.051* |
| H3B | 0.0253 | 1.2917 | 0.3094 | 0.051* |
| C2 | 0.2794 (3) | 0.8205 (5) | 0.1477 (3) | 0.0422 (6) |
| H2 | 0.2893 | 0.8147 | 0.0623 | 0.051* |
| C3 | 0.1811 (3) | 1.0013 (5) | 0.1844 (2) | 0.0333 (5) |
| C4 | 0.1737 (3) | 1.0129 (5) | 0.3178 (2) | 0.0335 (5) |

| | | | | |
|-----|------------|-------------|--------------|------------|
| C5 | 0.2662 (3) | 0.8383 (6) | 0.4014 (3) | 0.0423 (6) |
| H5 | 0.2649 | 0.8450 | 0.4886 | 0.051* |
| C6 | 0.3587 (3) | 0.6579 (6) | 0.3574 (3) | 0.0485 (7) |
| H6 | 0.4184 | 0.5416 | 0.4142 | 0.058* |
| O1 | 0.8907 (2) | -0.4299 (4) | 0.19036 (19) | 0.0501 (5) |
| O2 | 0.7898 (2) | -0.2740 (5) | 0.35111 (17) | 0.0536 (6) |
| O3 | 0.5470 (2) | 0.2937 (4) | 0.13031 (19) | 0.0483 (5) |
| O4 | 0.6154 (3) | 0.1047 (4) | 0.32045 (18) | 0.0494 (5) |
| H4 | 0.674 (4) | -0.042 (7) | 0.345 (3) | 0.044 (9)* |
| C7 | 0.8059 (3) | -0.2775 (5) | 0.2335 (2) | 0.0356 (6) |
| C8 | 0.7139 (3) | -0.0761 (5) | 0.1443 (2) | 0.0340 (5) |
| H8A | 0.7865 | 0.0192 | 0.1034 | 0.041* |
| H8B | 0.6444 | -0.1711 | 0.0774 | 0.041* |
| C9 | 0.6182 (3) | 0.1235 (5) | 0.1993 (2) | 0.0348 (5) |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|----|-------------|-------------|-------------|--------------|-------------|--------------|
| N1 | 0.0438 (12) | 0.0339 (12) | 0.0626 (14) | 0.0032 (11) | 0.0108 (10) | -0.0094 (12) |
| N2 | 0.0563 (13) | 0.0490 (14) | 0.0309 (10) | 0.0087 (12) | 0.0035 (9) | 0.0022 (10) |
| N3 | 0.0515 (12) | 0.0438 (13) | 0.0325 (10) | 0.0068 (11) | 0.0071 (9) | -0.0015 (10) |
| C2 | 0.0424 (14) | 0.0394 (15) | 0.0431 (13) | -0.0060 (13) | 0.0043 (11) | -0.0061 (12) |
| C3 | 0.0334 (12) | 0.0334 (13) | 0.0324 (11) | -0.0062 (11) | 0.0043 (9) | -0.0017 (10) |
| C4 | 0.0359 (12) | 0.0296 (12) | 0.0337 (11) | -0.0025 (11) | 0.0039 (9) | -0.0014 (10) |
| C5 | 0.0464 (14) | 0.0396 (15) | 0.0374 (12) | 0.0013 (13) | 0.0002 (11) | 0.0068 (11) |
| C6 | 0.0493 (16) | 0.0365 (14) | 0.0565 (16) | 0.0019 (13) | 0.0027 (12) | 0.0082 (14) |
| O1 | 0.0502 (11) | 0.0430 (12) | 0.0555 (11) | 0.0150 (10) | 0.0066 (9) | 0.0097 (10) |
| O2 | 0.0702 (14) | 0.0551 (13) | 0.0323 (9) | -0.0030 (11) | 0.0025 (8) | 0.0095 (9) |
| O3 | 0.0470 (11) | 0.0402 (11) | 0.0558 (11) | 0.0132 (9) | 0.0055 (8) | -0.0025 (9) |
| O4 | 0.0606 (12) | 0.0508 (13) | 0.0380 (10) | 0.0003 (12) | 0.0129 (9) | -0.0113 (10) |
| C7 | 0.0361 (13) | 0.0345 (13) | 0.0340 (12) | -0.0029 (11) | 0.0014 (9) | 0.0048 (11) |
| C8 | 0.0381 (12) | 0.0363 (13) | 0.0268 (10) | 0.0051 (11) | 0.0044 (9) | 0.0028 (10) |
| C9 | 0.0328 (12) | 0.0346 (13) | 0.0363 (11) | -0.0054 (11) | 0.0053 (9) | -0.0038 (11) |

Geometric parameters (Å, °)

| | | | |
|--------|-----------|--------|-----------|
| N1—C6 | 1.337 (4) | C5—C6 | 1.368 (4) |
| N1—C2 | 1.360 (4) | C5—H5 | 0.9300 |
| N1—H1A | 0.8600 | C6—H6 | 0.9300 |
| N2—C3 | 1.370 (3) | O1—C7 | 1.225 (3) |
| N2—H2A | 0.8600 | O2—C7 | 1.286 (3) |
| N2—H2B | 0.8600 | O3—C9 | 1.224 (3) |
| N3—C4 | 1.335 (3) | O4—C9 | 1.298 (3) |
| N3—H3A | 0.8600 | O4—H4 | 0.91 (3) |
| N3—H3B | 0.8600 | C7—C8 | 1.517 (3) |
| C2—C3 | 1.369 (4) | C8—C9 | 1.507 (3) |
| C2—H2 | 0.9300 | C8—H8A | 0.9700 |
| C3—C4 | 1.435 (3) | C8—H8B | 0.9700 |

| | | | |
|-------------|------------|-------------|-------------|
| C4—C5 | 1.398 (3) | | |
| C6—N1—C2 | 121.3 (3) | C6—C5—H5 | 119.4 |
| C6—N1—H1A | 119.4 | C4—C5—H5 | 119.4 |
| C2—N1—H1A | 119.4 | N1—C6—C5 | 119.9 (3) |
| C3—N2—H2A | 120.0 | N1—C6—H6 | 120.1 |
| C3—N2—H2B | 120.0 | C5—C6—H6 | 120.1 |
| H2A—N2—H2B | 120.0 | C9—O4—H4 | 102.8 (19) |
| C4—N3—H3A | 120.0 | O1—C7—O2 | 124.4 (2) |
| C4—N3—H3B | 120.0 | O1—C7—C8 | 118.7 (2) |
| H3A—N3—H3B | 120.0 | O2—C7—C8 | 116.9 (2) |
| N1—C2—C3 | 122.0 (2) | C9—C8—C7 | 118.75 (19) |
| N1—C2—H2 | 119.0 | C9—C8—H8A | 107.6 |
| C3—C2—H2 | 119.0 | C7—C8—H8A | 107.6 |
| C2—C3—N2 | 121.7 (2) | C9—C8—H8B | 107.6 |
| C2—C3—C4 | 117.6 (2) | C7—C8—H8B | 107.6 |
| N2—C3—C4 | 120.7 (2) | H8A—C8—H8B | 107.1 |
| N3—C4—C5 | 120.7 (2) | O3—C9—O4 | 122.7 (2) |
| N3—C4—C3 | 121.4 (2) | O3—C9—C8 | 120.1 (2) |
| C5—C4—C3 | 118.0 (2) | O4—C9—C8 | 117.2 (2) |
| C6—C5—C4 | 121.2 (2) | | |
| C6—N1—C2—C3 | -3.3 (4) | C3—C4—C5—C6 | -1.4 (4) |
| N1—C2—C3—N2 | -175.4 (3) | C2—N1—C6—C5 | 1.4 (4) |
| N1—C2—C3—C4 | 2.7 (4) | C4—C5—C6—N1 | 0.9 (4) |
| C2—C3—C4—N3 | 179.4 (3) | O1—C7—C8—C9 | -175.8 (2) |
| N2—C3—C4—N3 | -2.5 (4) | O2—C7—C8—C9 | 3.6 (4) |
| C2—C3—C4—C5 | -0.4 (3) | C7—C8—C9—O3 | 177.5 (2) |
| N2—C3—C4—C5 | 177.7 (2) | C7—C8—C9—O4 | -2.7 (3) |
| N3—C4—C5—C6 | 178.8 (3) | | |

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

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-----------------------------------|----------|-------------|-------------|---------------|
| N1—H1A \cdots O3 | 0.86 | 1.93 | 2.784 (3) | 175 |
| N2—H2A \cdots O1 ⁱ | 0.86 | 2.28 | 3.132 (3) | 174 |
| N2—H2B \cdots O1 ⁱⁱ | 0.86 | 2.15 | 3.005 (3) | 176 |
| N3—H3A \cdots O2 ⁱⁱⁱ | 0.86 | 2.28 | 3.048 (3) | 149 |
| N3—H3B \cdots O1 ⁱⁱ | 0.86 | 2.10 | 2.960 (3) | 177 |
| O4—H4 \cdots O2 | 0.91 (3) | 1.55 (3) | 2.442 (3) | 164 (3) |

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