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2,3-Diaminopyridinium 4-carboxybutanoate

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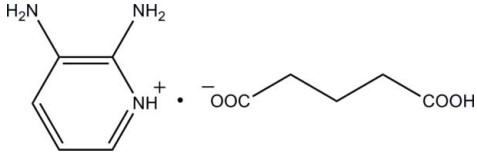
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; R factor = 0.050; wR factor = 0.123; data-to-parameter ratio = 17.2.

In the title molecular salt, $C_5H_8N_3^+\cdot C_5H_7O_4^-$, the 2,3-diaminopyridine molecule is protonated at the pyridine N atom. The cation is essentially planar, with a maximum deviation of 0.015 (2) Å, and the anion adopts an extended conformation. In the crystal, the hydrogen glutarate (4-carboxybutanoate) anions are self-assembled through O—H···O hydrogen bonds, forming chains. The cations are connected to the anion chains *via* N—H···O hydrogen bonds, forming a three-dimensional network. The crystal structure also features aromatic π–π interactions between the pyridinium cations, with a centroid–centroid distance of 3.4464 (10) Å.

Related literature

For applications of 2-aminopyridine derivatives, see: Bis *et al.* (2006); Gellert & Hsu (1988). For glutaric acid conformations, see: Saraswathi *et al.* (2001). For hydrogen-bond motifs, see: Bernstein *et al.* (1995). For bond-length data, see: Allen *et al.* (1987). For the stability of the temperature controller used in the data collection, see: Cosier & Glazer (1986).



Experimental

Crystal data

$C_5H_8N_3^+\cdot C_5H_7O_4^-$
M_r = 241.25
Monoclinic, $P2_1/c$
a = 7.7052 (1) Å
b = 21.4626 (4) Å
c = 7.8450 (1) Å
β = 119.473 (1)°
V = 1129.46 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 100 K
0.35 × 0.18 × 0.05 mm

Data collection

Bruker APEXII DUO CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.962, T_{max} = 0.994
9826 measured reflections
3281 independent reflections
2475 reflections with $I > 2\sigma(I)$
R_{int} = 0.030

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.123
S = 1.04
3281 reflections
191 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.43 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1*N*1···O2^{i}	0.86	1.94	2.7571 (18)	159
N2—H2*N*1···O1^{i}	0.86	2.13	2.9077 (19)	151
N2—H2*N*2···O1^{ii}	0.86	2.04	2.8766 (18)	164
N3—H3*N*1···O4^{iii}	0.86	2.16	3.0054 (18)	168
N3—H3*N*2···O1^{ii}	0.86	2.17	3.0194 (18)	167
O3—H1*O*1···O2^{iv}	0.82	1.74	2.5546 (18)	171

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

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).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB6458).

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§ Thomson Reuters ResearcherID: A-3561-2009.

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2,3-Diaminopyridinium 4-carboxybutanoate

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S1. Comment

2-Aminopyridine and its derivatives are some of the most frequently-used synthons in supramolecular chemistry based on hydrogen bonds (Bis *et al.*, 2006; Gellert & Hsu, 1988). Glutaric acid is found in the blood and urine. It is used in the synthesis of pharmaceuticals, surfactants and metal finishing compounds. Herein, we report the crystal structure determination of the title compound, (I).

The asymmetric unit (Fig. 1) contains a 2,3-diaminopyridinium cation and hydrogenglutarate anion. The cation is essentially planar, with a maximum deviation of 0.015 (2) Å for atom C1. In the 2,3-diaminopyridinium cation, a wide angle [123.94 (14)°] is subtended at the protonated N1 atom. The conformation of the hydrogenglutarate anion can be described by the two torsion angles C6-C7-C8-C9 of 58.61 (16)° and C7-C8-C9-C10 of 175.91 (13)°. As evident from the torsion angles, the hydrogenglutarate anion is in a fully extended conformation (Saraswathi *et al.*, 2001). Of the two carboxyl groups, one is deprotonated while the other is not. The bond lengths (Allen *et al.*, 1987) and angles are within normal ranges.

In the crystal (Fig. 2), the protonated N1 atom and the 2-amino group (N2) are hydrogen-bonded to the carboxylate oxygen atoms (O1 and O2) *via* a pair of intermolecular N—H···O hydrogen bonds, forming a ring motif $R^2_2(8)$ (Bernstein *et al.*, 1995). The hydrogen glutarate anions self-assemble through O—H···O hydrogen bonds, forming chains. Furthermore, the cations are connected via N—H···O hydrogen bonds (Table 1) to these anoinic chains to form a three-dimensional network. The crystal structure is further stabilized by weak π–π interactions between the pyridinium (Cg1 = N1/C1–C5) cations [Cg1···Cg1 = 3.4464 (10) Å; -x, 2-y, 2-z].

S2. Experimental

Hot methanol solution (20 ml) of 2,3-diaminopyridine (52 mg, Aldrich) and glutaric acid (66 mg, Merck) were mixed and warmed over a heating magnetic stirrer hotplate for a few minutes. The resulting solution was allowed to cool slowly at room temperature and brown plates of the title compound appeared after a few days.

S3. Refinement

The C-bonded hydrogen atoms were located from a difference Fourier maps and refined freely [C–H = 0.96 (2)–1.00 (2) Å] and C–H = 0.93 (2)–1.01 (2) Å]. The O- and N- bonded hydrogen atoms can also be located but in the final refinement, these hydrogen were positioned geometrically [N–H = 0.86 Å and O–H = 0.82°] and were refined using a riding model, with U_{iso}(H) = 1.2 or 1.5 U_{eq}(C).

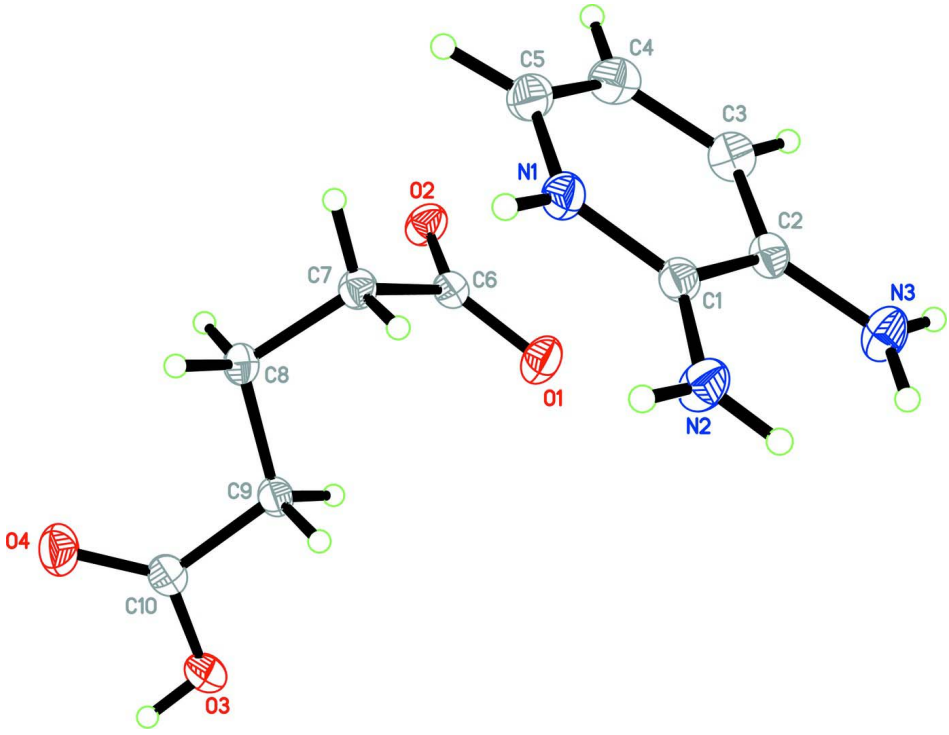

Figure 1

The asymmetric unit of the title compound, showing 50% probability displacement ellipsoids.

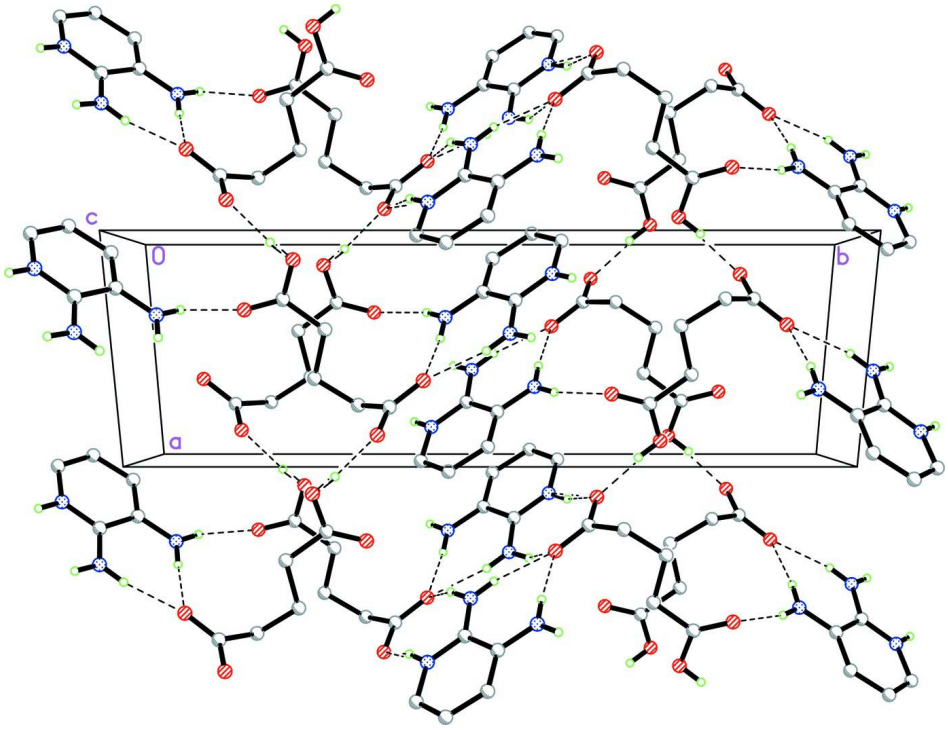

Figure 2

The crystal packing of title compound (I).

2,3-Diaminopyridinium 4-carboxybutanoate

Crystal data

$C_5H_8N_3^+ \cdot C_5H_7O_4^-$
$M_r = 241.25$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 7.7052$ (1) Å
$b = 21.4626$ (4) Å
$c = 7.8450$ (1) Å
$\beta = 119.473$ (1)°
$V = 1129.46$ (3) Å^3
$Z = 4$
$F(000) = 512$
$D_x = 1.419$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3028 reflections
$\theta = 3.1$–$30.0°$
$\mu = 0.11$ mm^{-1}
$T = 100$ K
Plate, brown
0.35 × 0.18 × 0.05 mm

Data collection

Bruker APEXII DUO CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
$T_{min} = 0.962$, $T_{max} = 0.994$
9826 measured reflections
3281 independent reflections
2475 reflections with $I > 2\sigma(I)$
$R_{int} = 0.030$
$\theta_{max} = 30.1°$, $\theta_{min} = 3.0°$
$h = -10 \rightarrow 9$
$k = -30 \rightarrow 16$
$l = -11 \rightarrow 10$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.123$
$S = 1.04$
3281 reflections
191 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
$w = 1/[\sigma^2(F_o^2) + (0.0439P)^2 + 0.6889P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.43$ e Å^{-3}
$\Delta\rho_{min} = -0.35$ e Å^{-3}

Special details

Experimental. The crystal was placed in the cold stream of an Oxford Cryosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1) K.

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.1547 (2)	0.91493 (6)	1.0497 (2)	0.0199 (3)
H1N1	0.1763	0.8895	1.1428	0.024*

N2	0.4178 (2)	0.97294 (6)	1.27871 (19)	0.0227 (3)
H2N1	0.4358	0.9454	1.3657	0.027*
H2N2	0.4941	1.0051	1.3105	0.027*
N3	0.3437 (2)	1.06274 (6)	0.9866 (2)	0.0236 (3)
H3N1	0.3206	1.0897	0.8967	0.028*
H3N2	0.4382	1.0690	1.1044	0.028*
C1	0.2710 (2)	0.96571 (7)	1.0940 (2)	0.0174 (3)
C2	0.2301 (2)	1.00984 (7)	0.9422 (2)	0.0179 (3)
C3	0.0765 (3)	0.99662 (8)	0.7572 (2)	0.0218 (3)
C4	−0.0356 (3)	0.94140 (8)	0.7180 (2)	0.0243 (3)
C5	0.0045 (2)	0.90133 (8)	0.8661 (2)	0.0230 (3)
O1	0.37775 (18)	0.91001 (5)	0.58579 (17)	0.0259 (3)
O2	0.14921 (17)	0.85057 (5)	0.35117 (16)	0.0231 (3)
O3	0.89545 (17)	0.73680 (5)	0.77123 (18)	0.0250 (3)
H1O1	0.9696	0.7065	0.8003	0.037*
O4	0.68383 (19)	0.66708 (5)	0.78111 (19)	0.0286 (3)
C6	0.2633 (2)	0.86410 (7)	0.5313 (2)	0.0184 (3)
C7	0.2679 (2)	0.81908 (7)	0.6837 (2)	0.0180 (3)
C8	0.3856 (2)	0.76040 (7)	0.6920 (2)	0.0177 (3)
C9	0.5983 (2)	0.77618 (7)	0.7421 (2)	0.0181 (3)
C10	0.7278 (2)	0.72033 (7)	0.7669 (2)	0.0190 (3)
H3A	0.044 (3)	1.0263 (9)	0.654 (3)	0.031 (5)*
H4A	−0.143 (3)	0.9321 (9)	0.589 (3)	0.031 (5)*
H5A	−0.066 (3)	0.8624 (9)	0.854 (3)	0.026 (5)*
H7A	0.331 (3)	0.8398 (8)	0.812 (3)	0.019 (4)*
H7B	0.131 (3)	0.8081 (9)	0.649 (3)	0.025 (5)*
H8A	0.317 (3)	0.7388 (8)	0.562 (3)	0.019 (4)*
H8B	0.389 (3)	0.7319 (8)	0.792 (3)	0.018 (4)*
H9A	0.601 (3)	0.8033 (9)	0.642 (3)	0.025 (5)*
H9B	0.664 (3)	0.8000 (9)	0.867 (3)	0.028 (5)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0211 (6)	0.0171 (6)	0.0228 (7)	−0.0007 (5)	0.0118 (5)	0.0011 (5)
N2	0.0241 (7)	0.0215 (6)	0.0182 (7)	−0.0050 (5)	0.0071 (6)	0.0039 (5)
N3	0.0300 (7)	0.0199 (6)	0.0181 (6)	−0.0049 (5)	0.0097 (6)	0.0028 (5)
C1	0.0182 (7)	0.0157 (7)	0.0196 (7)	0.0011 (5)	0.0102 (6)	0.0001 (5)
C2	0.0208 (7)	0.0160 (6)	0.0192 (7)	0.0014 (5)	0.0117 (6)	0.0006 (5)
C3	0.0251 (8)	0.0238 (8)	0.0168 (7)	0.0010 (6)	0.0105 (6)	0.0009 (6)
C4	0.0223 (8)	0.0294 (8)	0.0189 (8)	−0.0003 (6)	0.0085 (7)	−0.0058 (6)
C5	0.0218 (8)	0.0218 (8)	0.0272 (8)	−0.0022 (6)	0.0134 (7)	−0.0072 (6)
O1	0.0285 (6)	0.0209 (6)	0.0233 (6)	−0.0069 (5)	0.0091 (5)	0.0011 (4)
O2	0.0226 (6)	0.0232 (6)	0.0196 (6)	−0.0046 (4)	0.0073 (5)	0.0025 (4)
O3	0.0194 (6)	0.0228 (6)	0.0316 (7)	0.0047 (4)	0.0117 (5)	0.0022 (5)
O4	0.0326 (7)	0.0179 (6)	0.0386 (7)	0.0018 (5)	0.0200 (6)	−0.0013 (5)
C6	0.0172 (7)	0.0160 (7)	0.0214 (8)	0.0018 (5)	0.0090 (6)	0.0020 (5)
C7	0.0191 (7)	0.0174 (7)	0.0190 (7)	−0.0002 (6)	0.0105 (6)	0.0006 (5)

C8	0.0208 (7)	0.0154 (6)	0.0180 (7)	0.0004 (5)	0.0104 (6)	0.0016 (5)
C9	0.0192 (7)	0.0155 (7)	0.0189 (7)	0.0015 (5)	0.0088 (6)	0.0005 (5)
C10	0.0219 (7)	0.0187 (7)	0.0147 (7)	0.0020 (6)	0.0076 (6)	−0.0013 (5)

Geometric parameters (Å, º)

N1—C1	1.3435 (19)	O1—C6	1.2491 (18)
N1—C5	1.364 (2)	O2—C6	1.2774 (19)
N1—H1N1	0.8600	O3—C10	1.3235 (19)
N2—C1	1.338 (2)	O3—H1O1	0.8200
N2—H2N1	0.8600	O4—C10	1.2125 (19)
N2—H2N2	0.8600	C6—C7	1.524 (2)
N3—C2	1.3698 (19)	C7—C8	1.535 (2)
N3—H3N1	0.8600	C7—H7A	0.981 (18)
N3—H3N2	0.8600	C7—H7B	0.98 (2)
C1—C2	1.430 (2)	C8—C9	1.523 (2)
C2—C3	1.378 (2)	C8—H8A	0.999 (18)
C3—C4	1.408 (2)	C8—H8B	0.987 (18)
C3—H3A	0.96 (2)	C9—C10	1.510 (2)
C4—C5	1.353 (2)	C9—H9A	0.98 (2)
C4—H4A	0.96 (2)	C9—H9B	1.00 (2)
C5—H5A	0.97 (2)		
C1—N1—C5	123.94 (14)	O1—C6—O2	122.93 (14)
C1—N1—H1N1	118.0	O1—C6—C7	119.46 (14)
C5—N1—H1N1	118.0	O2—C6—C7	117.48 (13)
C1—N2—H2N1	120.0	C6—C7—C8	109.78 (12)
C1—N2—H2N2	120.0	C6—C7—H7A	108.9 (11)
H2N1—N2—H2N2	120.0	C8—C7—H7A	110.1 (11)
C2—N3—H3N1	120.0	C6—C7—H7B	109.2 (11)
C2—N3—H3N2	120.0	C8—C7—H7B	110.4 (11)
H3N1—N3—H3N2	120.0	H7A—C7—H7B	108.4 (16)
N2—C1—N1	118.36 (13)	C9—C8—C7	111.52 (12)
N2—C1—C2	123.19 (14)	C9—C8—H8A	109.1 (10)
N1—C1—C2	118.44 (14)	C7—C8—H8A	109.5 (10)
N3—C2—C3	123.32 (14)	C9—C8—H8B	109.2 (10)
N3—C2—C1	119.05 (14)	C7—C8—H8B	109.0 (10)
C3—C2—C1	117.63 (14)	H8A—C8—H8B	108.5 (14)
C2—C3—C4	121.33 (15)	C10—C9—C8	114.57 (13)
C2—C3—H3A	118.8 (13)	C10—C9—H9A	107.5 (12)
C4—C3—H3A	119.9 (12)	C8—C9—H9A	111.5 (12)
C5—C4—C3	119.41 (15)	C10—C9—H9B	107.4 (11)
C5—C4—H4A	119.1 (12)	C8—C9—H9B	109.1 (12)
C3—C4—H4A	121.5 (12)	H9A—C9—H9B	106.4 (16)
C4—C5—N1	119.17 (15)	O4—C10—O3	124.24 (14)
C4—C5—H5A	125.4 (12)	O4—C10—C9	124.27 (15)
N1—C5—H5A	115.4 (11)	O3—C10—C9	111.48 (13)
C10—O3—H1O1	109.5		

C5—N1—C1—N2	−177.92 (14)	C3—C4—C5—N1	−0.9 (2)
C5—N1—C1—C2	3.0 (2)	C1—N1—C5—C4	−1.6 (2)
N2—C1—C2—N3	−1.0 (2)	O1—C6—C7—C8	−101.51 (16)
N1—C1—C2—N3	178.07 (14)	O2—C6—C7—C8	74.36 (17)
N2—C1—C2—C3	179.09 (15)	C6—C7—C8—C9	58.61 (16)
N1—C1—C2—C3	−1.8 (2)	C7—C8—C9—C10	175.91 (13)
N3—C2—C3—C4	179.59 (15)	C8—C9—C10—O4	−12.6 (2)
C1—C2—C3—C4	−0.5 (2)	C8—C9—C10—O3	167.48 (13)
C2—C3—C4—C5	1.9 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*1···O2^{i}	0.86	1.94	2.7571 (18)	159
N2—H2*N*1···O1^{i}	0.86	2.13	2.9077 (19)	151
N2—H2*N*2···O1^{ii}	0.86	2.04	2.8766 (18)	164
N3—H3*N*1···O4^{iii}	0.86	2.16	3.0054 (18)	168
N3—H3*N*2···O1^{ii}	0.86	2.17	3.0194 (18)	167
O3—H1*O*1···O2^{iv}	0.82	1.74	2.5546 (18)	171

Symmetry codes: (i) *x*, *y*, *z*+1; (ii) −*x*+1, −*y*+2, −*z*+2; (iii) −*x*+1, *y*+1/2, −*z*+3/2; (iv) *x*+1, −*y*+3/2, *z*+1/2.