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Hexane-1,6-diammonium dinitrate

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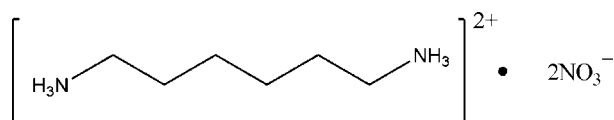
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Key indicators: single-crystal X-ray study; $T = 295$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.045; wR factor = 0.147; data-to-parameter ratio = 23.2.

The hexane-1,6-diammonium cation of the title compound, $\text{C}_6\text{H}_{18}\text{N}_2^{2+} \cdot 2\text{NO}_3^-$, lies across a crystallographic inversion centre and shows significant deviation from planarity in the hydrocarbon chain. This is evident from the torsion angle of $-64.0^\circ(2)$ along the $\text{N}-\text{C}-\text{C}$ bond and the torsion angle of $-67.1^\circ(2)$ along the $\text{C}-\text{C}-\text{C}$ bonds. An intricate three-dimensional hydrogen-bonding network exists in the crystal structure, with each H atom on the ammonium group exhibiting bifurcated interactions to the nitrate anion. Complex hydrogen-bonded ring and chain motifs are also evident, in particular a 26-membered ring with graph-set notation $R_4^4(26)$ is observed.

Related literature

For related structural studies of hexane-1,6-diammonium salts, see: van Blerk & Kruger (2008). For hydrogen-bond motifs, see: Bernstein *et al.* (1995). For a description of the Cambridge Structural Database, see: Allen (2002).



Experimental

Crystal data

$\text{C}_6\text{H}_{18}\text{N}_2^{2+} \cdot 2\text{NO}_3^-$
 $M_r = 242.24$
 Monoclinic, $P2_1/n$
 $a = 6.2947(1)$ Å
 $b = 11.6783(3)$ Å
 $c = 8.1211(2)$ Å
 $\beta = 92.840(1)^\circ$

$V = 596.26(2)$ Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.12$ mm⁻¹
 $T = 295$ K
 $0.46 \times 0.20 \times 0.16$ mm

Data collection

Bruker SMART CCD diffractometer
 Absorption correction: multi-scan (AX-Scan; Bruker, 2008)
 $T_{\min} = 0.948$, $T_{\max} = 0.981$

14665 measured reflections
 1718 independent reflections
 1107 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.026$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$
 $wR(F^2) = 0.147$
 $S = 1.02$
 1718 reflections

74 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.37$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.19$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{N1}-\text{H1C} \cdots \text{O2}$	0.89	2.53	3.1760 (19)	130
$\text{N1}-\text{H1C} \cdots \text{O3}$	0.89	2.04	2.9184 (19)	171
$\text{N1}-\text{H1D} \cdots \text{O1}^{\text{ii}}$	0.89	2.13	2.9692 (18)	158
$\text{N1}-\text{H1D} \cdots \text{O2}^{\text{ii}}$	0.89	2.36	3.1374 (19)	146
$\text{N1}-\text{H1E} \cdots \text{O1}^{\text{iii}}$	0.89	2.26	3.0561 (18)	149
$\text{N1}-\text{H1E} \cdots \text{O3}^{\text{iii}}$	0.89	2.23	3.0110 (18)	146

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

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *pubCIF* (Westrip, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2206).

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supporting information

Acta Cryst. (2009). E65, o1008 [doi:10.1107/S1600536809012963]

Hexane-1,6-diammonium dinitrate

Charmaine van Blerk and Gert J. Kruger

S1. Comment

The crystal structure of the title compound (I) adds to our current ongoing studies of long-chained diammonium salts. Colourless needle-like rectangular crystals of hexane-1,6-diammonium dinitrate were synthesized and formed as part of our structural chemistry study of the inorganic mineral acid salts of hexane-1,6-diamine. A search of the Cambridge Structural Database (Version 5.30, February 2009 release; Allen, 2002) revealed that this compound had not previously been determined.

The diammonium hexane chain lies across a crystallographic inversion centre and hence the asymmetric unit contains one nitrate anion and one-half of the hexane diammonium cation. The hydrocarbon chain is also not extended as is common in long chained hydrocarbons but shows significant folding and deviation from planarity. This is clearly evident from the torsion angle along the N1—C1—C2—C3 bond ($-64.0^\circ(2)$) and along the C1—C2—C3—C3ⁱ bond ($-67.1^\circ(2)$). Selected torsion angles can be found in Table 1. The molecular structure of (I) is shown in Figure 1.

Figure 2 illustrates the layered packing arrangement of the title compound (I). Single stacked layers of folded cations pack in between layers of nitrate anions showing a distinct inorganic - organic layering effect that is a common feature of these long-chained diammonium salts. The diammonium cations form bridges between the nitrate anion layers and an extensive three-dimensional hydrogen-bonding network is formed.

A close-up view of the hydrogen bonding interactions can be viewed in Figure 3 where very clear evidence of bifurcated interactions can be seen on each hydrogen atom of both ammonium groups. The hydrogen bond distances and angles for (I) can be found in Table 2. Since the hydrogen bonding network is complex, we focus on one particularly interesting hydrogen-bonding ring motif in the structure. Figure 4 shows a view of two diammonium cations and two nitrate anions (viewed down the *c* axis) that are hydrogen bonded together to form a large, 26-membered ring motif with graph set notation $R_4^4(26)$. Another smaller ring motif is evident as a result of the bifurcated hydrogen-bond interaction with the nitrate anion and this ring has the graph-set notation $R_2^1(4)$ but is not depicted graphically. Chain motifs also exist and were identified with *Mercury* (Macrae *et al.*), but again, these are not shown graphically.

S2. Experimental

Compound (I) was prepared by adding 1,6-diamino-hexane (0.50 g, 4.30 mmol) to 55% nitric acid (2 ml, 42.5 mmol) in a sample vial. The mixture was then refluxed at 363 K for 2 h. The solution was cooled at 2 K h⁻¹ to room temperature. Colourless rectangular needles of hexane-1,6-diammonium dinitrate were collected and a suitable single-crystal was selected for the X-ray diffraction study.

S3. Refinement

H atoms were geometrically positioned and refined in the riding-model approximation, with C—H = 0.97 Å, N—H = 0.89 Å, and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{N})$. For (I), the highest peak in the final difference map is 0.99 Å from C3 and

the deepest hole is 0.63 Å from N2.

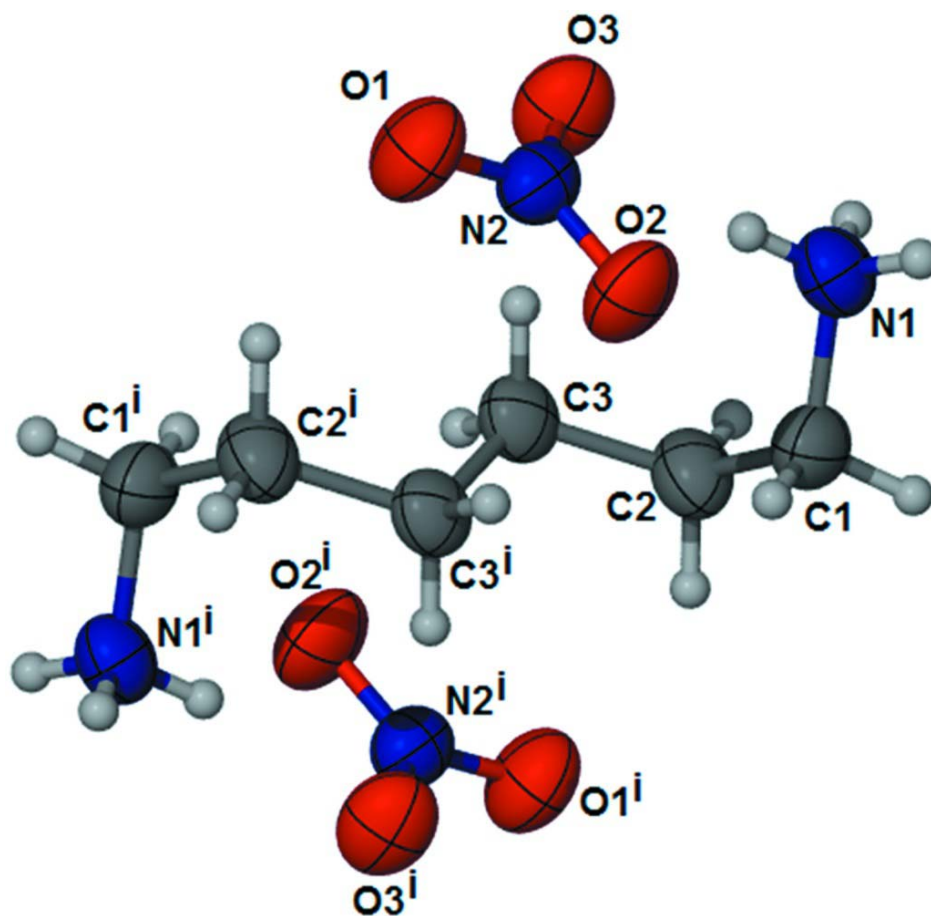


Figure 1

Molecular structure of (I), with atomic numbering scheme and displacement ellipsoids drawn at the 50% probability level. Atoms labelled with (i) are at the symmetry position ($1 - x, -y, -z$)

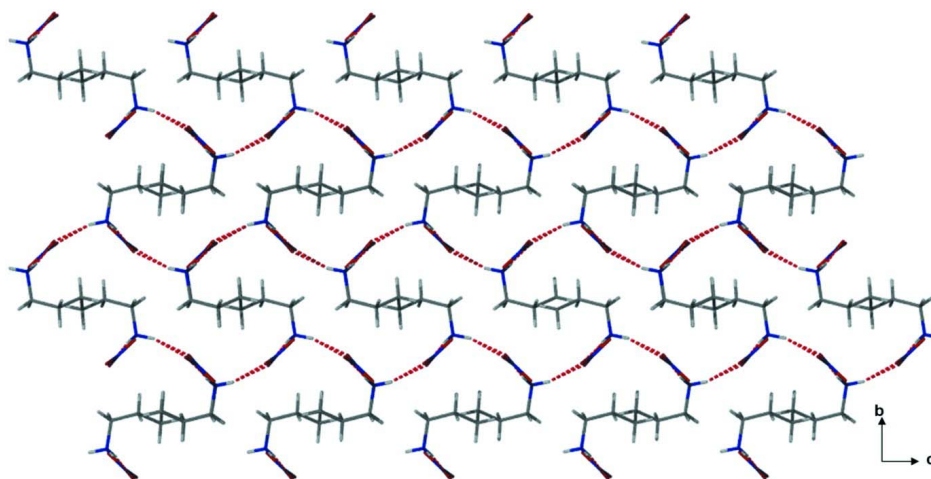


Figure 2

Packing arrangement of (I) viewed down the *a* axis. Hydrogen bonds are indicated by dashed lines.

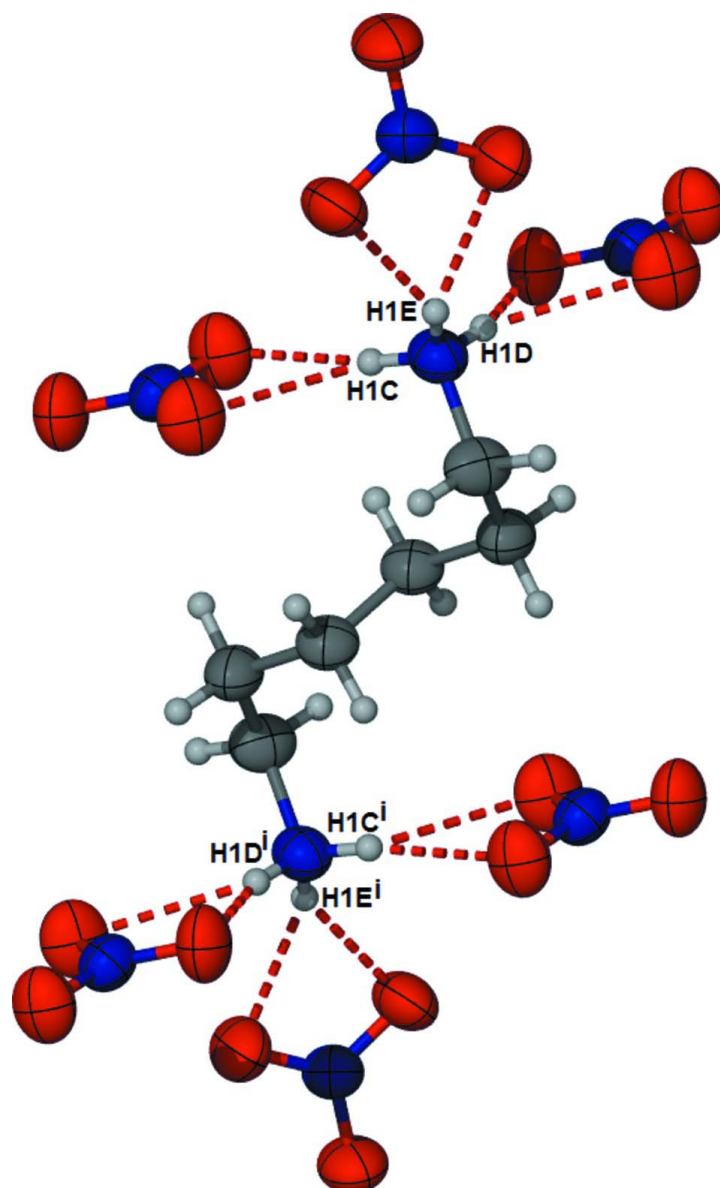


Figure 3

Close-up view of (I) viewed down the *a* axis clearly showing the bifurcated hydrogen-bonding interactions. Hydrogen bonds are indicated by dashed lines.

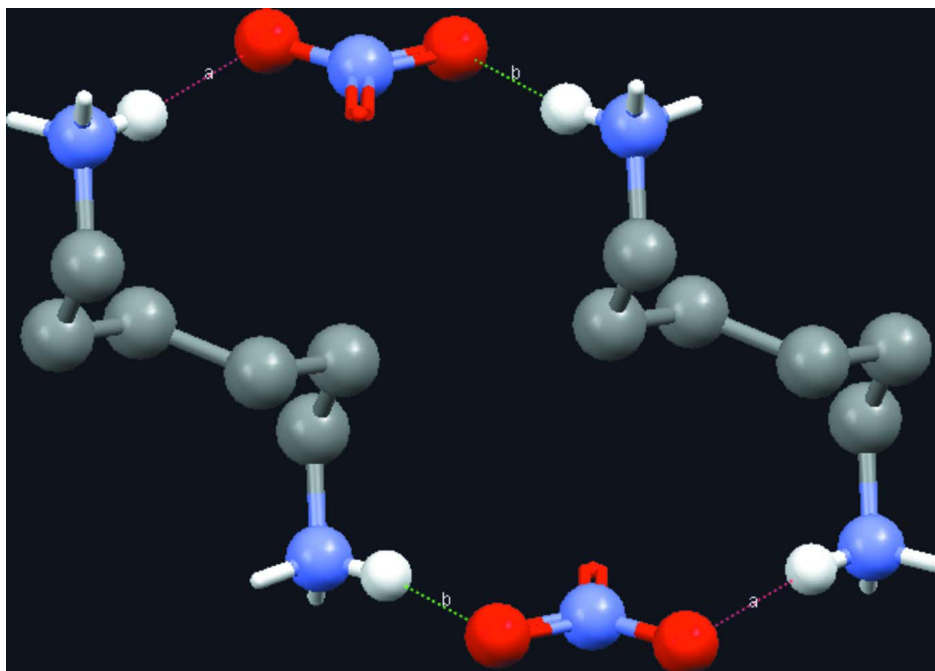


Figure 4

Close up view of (I) viewed down the c axis showing the ring motif involving two diammonium cations and two nitrate anions. Hydrogen atoms on the hydrocarbon chain are omitted for clarity.

Hexane-1,6-diammonium dinitrate

Crystal data

$C_6H_{18}N_2^{2+} \cdot 2NO_3^-$

$M_r = 242.24$

Monoclinic, $P2_1/n$

Hall symbol: $-P\ 2_1n$

$a = 6.2947$ (1) Å

$b = 11.6783$ (3) Å

$c = 8.1211$ (2) Å

$\beta = 92.840$ (1)°

$V = 596.26$ (2) Å³

$Z = 2$

$F(000) = 260$

$D_x = 1.349$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 5933 reflections

$\theta = 2.5$ – 25.2 °

$\mu = 0.12$ mm⁻¹

$T = 295$ K

Rectangular, colourless

$0.46 \times 0.20 \times 0.16$ mm

Data collection

Bruker SMART CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan
(*AX-Scan*; Bruker, 2008)

$T_{\min} = 0.948$, $T_{\max} = 0.981$

14665 measured reflections

1718 independent reflections

1107 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.026$

$\theta_{\max} = 30.0$ °, $\theta_{\min} = 3.1$ °

$h = -8 \rightarrow 8$

$k = -16 \rightarrow 16$

$l = -11 \rightarrow 11$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.045$

$wR(F^2) = 0.147$

$S = 1.02$

1718 reflections

74 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-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0674P)^2 + 0.1254P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.37 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.19 \text{ e } \text{\AA}^{-3}$

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)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.7036 (3)	0.01369 (13)	0.31554 (19)	0.0599 (4)
H1A	0.5614	-0.0134	0.3351	0.072*
H1B	0.8020	-0.0243	0.3934	0.072*
C2	0.7584 (3)	-0.01708 (14)	0.1427 (2)	0.0593 (4)
H2A	0.7644	-0.0999	0.1351	0.071*
H2B	0.9000	0.0117	0.1251	0.071*
C3	0.6095 (2)	0.02648 (14)	0.00229 (18)	0.0540 (4)
H3A	0.5955	0.1088	0.0126	0.065*
H3B	0.6737	0.0110	-0.1016	0.065*
N1	0.7138 (2)	0.13945 (11)	0.34353 (15)	0.0544 (4)
H1C	0.6044	0.1730	0.2893	0.082*
H1D	0.8350	0.1667	0.3072	0.082*
H1E	0.7082	0.1539	0.4508	0.082*
N2	0.2075 (2)	0.23209 (11)	0.22415 (16)	0.0510 (3)
O1	0.03639 (19)	0.26482 (12)	0.15889 (16)	0.0710 (4)
O2	0.2102 (2)	0.15918 (11)	0.33405 (15)	0.0732 (4)
O3	0.3767 (2)	0.27276 (12)	0.17480 (16)	0.0714 (4)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0791 (11)	0.0552 (9)	0.0448 (8)	0.0006 (8)	-0.0042 (7)	0.0031 (6)
C2	0.0622 (9)	0.0591 (9)	0.0559 (9)	0.0067 (7)	-0.0052 (7)	-0.0109 (7)
C3	0.0632 (9)	0.0583 (9)	0.0407 (7)	-0.0024 (7)	0.0046 (6)	-0.0062 (6)
N1	0.0544 (8)	0.0610 (8)	0.0479 (7)	-0.0035 (6)	0.0033 (6)	-0.0087 (5)

N2	0.0584 (8)	0.0501 (7)	0.0451 (7)	0.0059 (6)	0.0070 (6)	-0.0002 (5)
O1	0.0567 (7)	0.0808 (9)	0.0755 (9)	0.0130 (6)	0.0018 (6)	0.0188 (6)
O2	0.0782 (9)	0.0798 (8)	0.0615 (7)	0.0012 (7)	0.0045 (6)	0.0279 (6)
O3	0.0576 (8)	0.0846 (9)	0.0731 (8)	-0.0041 (6)	0.0131 (6)	0.0188 (6)

Geometric parameters (Å, °)

C1—N1	1.487 (2)	C3—H3A	0.9700
C1—C2	1.505 (2)	C3—H3B	0.9700
C1—H1A	0.9700	N1—H1C	0.8900
C1—H1B	0.9700	N1—H1D	0.8900
C2—C3	1.527 (2)	N1—H1E	0.8900
C2—H2A	0.9700	N2—O2	1.2330 (16)
C2—H2B	0.9700	N2—O1	1.2369 (17)
C3—C3 ⁱ	1.510 (3)	N2—O3	1.2504 (17)
N1—C1—C2	111.60 (13)	C2—C3—H3A	108.7
N1—C1—H1A	109.3	C3 ⁱ —C3—H3B	108.7
C2—C1—H1A	109.3	C2—C3—H3B	108.7
N1—C1—H1B	109.3	H3A—C3—H3B	107.6
C2—C1—H1B	109.3	C1—N1—H1C	109.5
H1A—C1—H1B	108.0	C1—N1—H1D	109.5
C1—C2—C3	117.17 (14)	H1C—N1—H1D	109.5
C1—C2—H2A	108.0	C1—N1—H1E	109.5
C3—C2—H2A	108.0	H1C—N1—H1E	109.5
C1—C2—H2B	108.0	H1D—N1—H1E	109.5
C3—C2—H2B	108.0	O2—N2—O1	120.27 (14)
H2A—C2—H2B	107.2	O2—N2—O3	120.85 (14)
C3 ⁱ —C3—C2	114.07 (17)	O1—N2—O3	118.86 (13)
C3 ⁱ —C3—H3A	108.7		
N1—C1—C2—C3	-64.0 (2)	C1—C2—C3—C3 ⁱ	-67.1 (2)

Symmetry code: (i) $-x+1, -y, -z$.*Hydrogen-bond geometry (Å, °)*

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1C \cdots O2	0.89	2.53	3.1760 (19)	130
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