

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

N-Carbamothioylamino-7-oxabicyclo-[2.2.1]hept-5-ene-2,3-dicarboximide

Jian Li

 Department of Chemistry and Chemical Engineering, Weifang University, Weifang 261061, People's Republic of China
 Correspondence e-mail: ljwfu@163.com

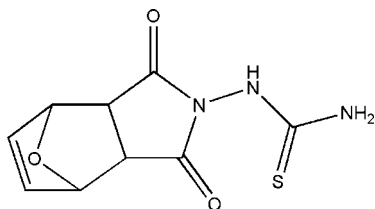
Received 11 November 2010; accepted 19 November 2010

 Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.029; wR factor = 0.071; data-to-parameter ratio = 12.4.

The title compound, $\text{C}_9\text{H}_9\text{N}_3\text{O}_3\text{S}$, comprises a racemic mixture of chiral molecules containing four stereogenic centres. The cyclohexane ring tends towards a boat conformation, while the tetrahydrofuran ring and the dihydrofuran ring adopt envelope conformations. The dihedral angle between the thiosemicarbazide fragment and the fused-ring system is 77.20 (10)°. The crystal structure is stabilized by two intermolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds.

Related literature

For the use of 7-oxa-bicyclo[2,2,1]hept-5-ene-2,3-dicarboxylic anhydride in clinical practice, see: Deng & Hu (2007). For the pharmacological activity of its derivatives, see: Hart *et al.* (2004). For bond lengths and angles in related structures, see: Goh *et al.* (2008).



Experimental

Crystal data

 $\text{C}_9\text{H}_9\text{N}_3\text{O}_3\text{S}$
 $M_r = 239.25$

 Orthorhombic, $P2_12_12_1$
 $a = 8.3978$ (8) Å
 $b = 8.9032$ (9) Å
 $c = 13.5930$ (14) Å
 $V = 1016.31$ (18) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.31$ mm⁻¹
 $T = 298$ K
 $0.45 \times 0.43 \times 0.40$ mm

Data collection

 Bruker SMART CCD area-detector diffractometer
 Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
 $T_{\min} = 0.872$, $T_{\max} = 0.885$

 5015 measured reflections
 1791 independent reflections
 1632 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.023$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.029$
 $wR(F^2) = 0.071$
 $S = 1.07$
 1791 reflections
 145 parameters
 H-atom parameters constrained

 $\Delta\rho_{\max} = 0.14$ e Å⁻³
 $\Delta\rho_{\min} = -0.16$ e Å⁻³
 Absolute structure: Flack (1983),
 728 Friedel pairs
 Flack parameter: 0.01 (9)

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N2}-\text{H2}\cdots\text{O3}^{\text{i}}$	0.86	1.96	2.809 (2)	167
$\text{N3}-\text{H3B}\cdots\text{O1}^{\text{ii}}$	0.86	2.14	2.958 (2)	160

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

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Shandong Provincial Natural Science Foundation, China, is thanked for support (ZR2009BL027).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BX2331).

References

- Bruker (1997). *SADABS*, *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Deng, L. P. & Hu, Y. Z. (2007). *J. Heterocycl. Chem.* **44**, 597–601.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Goh, Y. W., Pool, B. R. & White, J. M. (2008). *J. Org. Chem.* **73**, 151–156.
- Hart, M. E., Chamberlin, A. R., Walkom, C., Sakoff, J. A. & McCluskey, A. (2004). *Bioorg. Med. Chem. Lett.* **14**, 1969–1973.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

supporting information

Acta Cryst. (2010). E66, o3327 [https://doi.org/10.1107/S160053681004835X]

N*-Carbamothioylamino-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide*Jian Li****S1. Comment**

7-Oxa-bicyclo[2,2,1]hept-5-ene-2,3-dicarboxylic anhydride has been widely employed in clinical practice, as it is less toxic and much easier to be synthesized [Deng *et al.*, 2007]. Its derivatives are also pharmacologically active [Hart *et al.*, 2004]. We report here the crystal structure of the title compound, (I) which comprises a racemic mixture of chiral molecules containing four stereogenic centres. The cyclohexane ring tends towards a boat conformation, the tetrahydrofuran ring and the dihydrofuran ring adopt envelope conformations (Fig. 1). The bond lengths and bond angles are normal range and comparable to those in the similar compound [Goh, *et al.*, 2008] as representative example. The dihedral angle between the thiosemicarbazide fragment and fused-ring system is $77.20(10)^\circ$. The crystal structure is stabilized by two intermolecular N—H \cdots O and one intramolecular N—H \cdots N hydrogen bonds (Table 1, Fig. 2).

S2. Experimental

A mixture of *exo*-7-oxa-bicyclo[2,2,1]hept-5-ene-2,3-dicarboxylic anhydride (0.332 g, 2 mmol) and thiocarbanide (0.182 g, 2 mmol) in methanol (5 ml) was stirred for 5 h at room temperature, and then refluxed for 1 h. After cooling the precipitate was filtered and dried, the title compound was obtained. The crude product of 20 mg was dissolved in methanol of 10 ml. The solution was filtered to remove impurities, and then the filtrate was left for crystallization at room temperature. The single-crystal suitable for X-ray determination was obtained by evaporation from the methanol solution after 5 d.

S3. Refinement

H atoms were initially located from difference maps and then refined in a riding model with C—H = 0.93–0.96 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{methyl C})$.

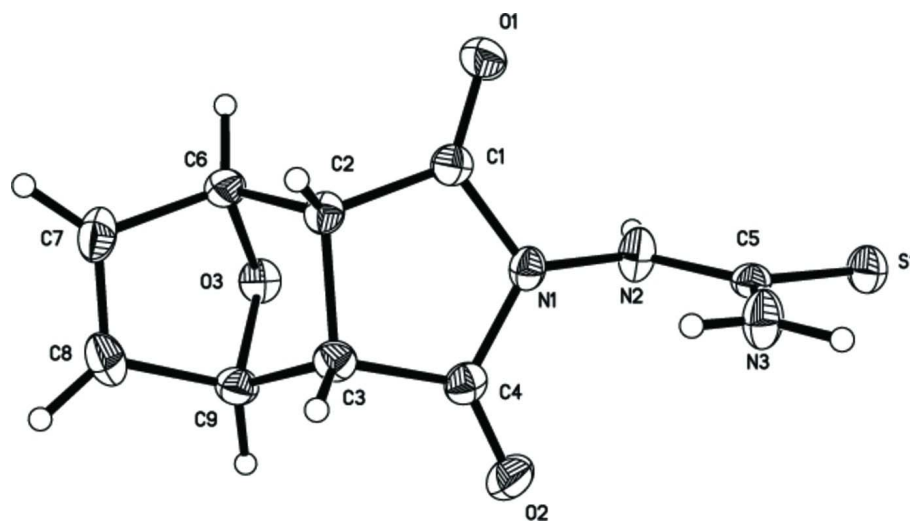


Figure 1

The molecular structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at 30% probability level.

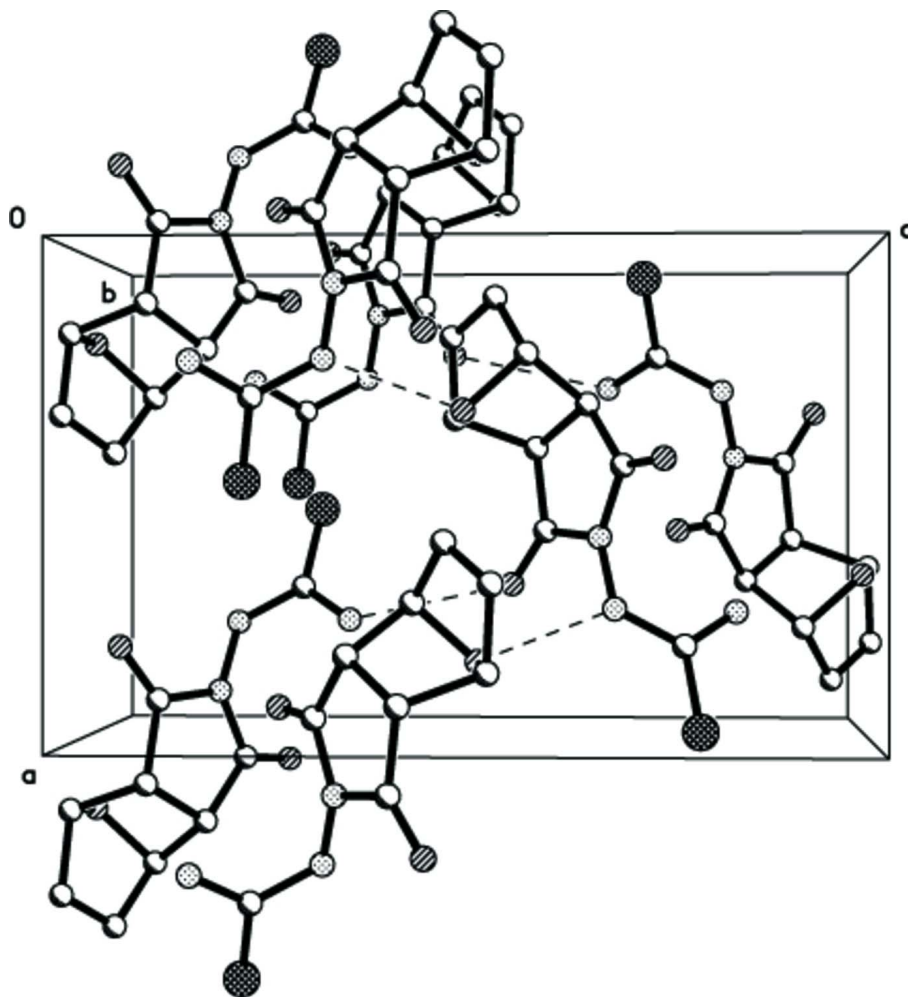


Figure 2

The crystal packing of (I), viewed along *b* axis. Dashed lines indicate hydrogen bonds.

***N*-Carbamthioylamino-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide**

Crystal data

$C_9H_9N_3O_3S$

$M_r = 239.25$

Orthorhombic, $P2_12_12_1$

Hall symbol: P 2ac 2ab

$a = 8.3978$ (8) Å

$b = 8.9032$ (9) Å

$c = 13.5930$ (14) Å

$V = 1016.31$ (18) Å³

$Z = 4$

$F(000) = 496$

$D_x = 1.564$ Mg m⁻³

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

Cell parameters from 2624 reflections

$\theta = 2.7$ – 26.3°

$\mu = 0.31$ mm⁻¹

$T = 298$ K

Block, light yellow

$0.45 \times 0.43 \times 0.40$ mm

Data collection

Bruker SMART CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

phi and ω scans

Absorption correction: multi-scan
(*SADABS*; Bruker, 1997)

$T_{\min} = 0.872$, $T_{\max} = 0.885$

5015 measured reflections

1791 independent reflections

1632 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.023$
 $\theta_{\text{max}} = 25.0^\circ$, $\theta_{\text{min}} = 2.7^\circ$

$h = -9 \rightarrow 9$
 $k = -10 \rightarrow 10$
 $l = -16 \rightarrow 11$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.029$
 $wR(F^2) = 0.071$
 $S = 1.07$
 1791 reflections
 145 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
 $w = 1/[\sigma^2(F_o^2) + (0.0346P)^2 + 0.1693P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.14 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.16 \text{ e } \text{\AA}^{-3}$
 Absolute structure: Flack (1983), 728 Friedel
 pairs
 Absolute structure parameter: 0.01 (9)

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	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.97059 (7)	0.24096 (7)	0.78384 (4)	0.04347 (17)
N1	0.5849 (2)	0.39754 (19)	0.65892 (11)	0.0314 (4)
N2	0.7287 (2)	0.3264 (2)	0.67804 (13)	0.0407 (5)
H2	0.7712	0.2722	0.6327	0.049*
N3	0.7384 (2)	0.4298 (2)	0.83195 (13)	0.0447 (5)
H3A	0.6516	0.4766	0.8184	0.054*
H3B	0.7826	0.4413	0.8885	0.054*
O1	0.68615 (19)	0.5596 (2)	0.54443 (11)	0.0466 (4)
O2	0.4254 (2)	0.22814 (19)	0.73858 (12)	0.0529 (5)
O3	0.32651 (18)	0.33700 (17)	0.48808 (10)	0.0362 (4)
C1	0.5731 (3)	0.5099 (2)	0.58861 (14)	0.0321 (5)
C2	0.4001 (2)	0.5466 (2)	0.57606 (14)	0.0306 (5)
H2A	0.3754	0.6517	0.5911	0.037*
C3	0.3110 (2)	0.4351 (2)	0.64312 (15)	0.0322 (5)
H3	0.2452	0.4855	0.6927	0.039*
C4	0.4385 (3)	0.3383 (2)	0.68800 (14)	0.0334 (5)
C5	0.8043 (3)	0.3395 (2)	0.76542 (14)	0.0298 (5)
C6	0.3396 (3)	0.4970 (3)	0.47264 (15)	0.0357 (5)
H6	0.4065	0.5276	0.4171	0.043*
C7	0.1677 (3)	0.5434 (3)	0.46640 (18)	0.0457 (6)

H7	0.1252	0.6207	0.4287	0.055*
C8	0.0896 (3)	0.4521 (3)	0.52523 (17)	0.0450 (6)
H8	-0.0191	0.4531	0.5382	0.054*
C9	0.2106 (3)	0.3459 (3)	0.56743 (15)	0.0368 (5)
H9	0.1687	0.2495	0.5906	0.044*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0357 (3)	0.0469 (3)	0.0479 (3)	0.0058 (3)	-0.0064 (3)	0.0046 (3)
N1	0.0315 (9)	0.0367 (10)	0.0261 (8)	0.0045 (8)	-0.0032 (8)	-0.0030 (8)
N2	0.0382 (10)	0.0540 (12)	0.0299 (10)	0.0176 (9)	-0.0048 (8)	-0.0105 (8)
N3	0.0447 (11)	0.0553 (12)	0.0342 (10)	0.0059 (10)	-0.0116 (9)	-0.0121 (9)
O1	0.0357 (9)	0.0642 (12)	0.0399 (9)	-0.0093 (8)	0.0035 (8)	0.0077 (8)
O2	0.0607 (10)	0.0508 (10)	0.0472 (9)	-0.0104 (9)	-0.0100 (8)	0.0191 (9)
O3	0.0405 (8)	0.0351 (8)	0.0330 (8)	0.0003 (7)	-0.0017 (7)	-0.0079 (7)
C1	0.0368 (12)	0.0350 (11)	0.0245 (10)	-0.0046 (10)	-0.0007 (9)	-0.0048 (9)
C2	0.0333 (11)	0.0257 (11)	0.0329 (11)	0.0010 (9)	-0.0030 (10)	-0.0008 (9)
C3	0.0324 (11)	0.0354 (12)	0.0287 (10)	0.0009 (9)	0.0042 (9)	-0.0030 (9)
C4	0.0411 (13)	0.0348 (12)	0.0243 (10)	-0.0023 (10)	-0.0010 (9)	-0.0046 (9)
C5	0.0330 (11)	0.0283 (10)	0.0282 (11)	-0.0068 (9)	0.0014 (9)	0.0015 (9)
C6	0.0360 (11)	0.0411 (13)	0.0300 (11)	-0.0061 (11)	-0.0019 (9)	0.0050 (10)
C7	0.0449 (14)	0.0464 (15)	0.0459 (13)	0.0038 (12)	-0.0185 (12)	0.0023 (11)
C8	0.0292 (11)	0.0590 (17)	0.0469 (13)	-0.0001 (11)	-0.0064 (11)	-0.0078 (12)
C9	0.0352 (12)	0.0405 (12)	0.0345 (12)	-0.0095 (10)	0.0001 (10)	0.0027 (10)

Geometric parameters (Å, °)

S1—C5	1.668 (2)	C2—C3	1.542 (3)
N1—C1	1.387 (3)	C2—C6	1.558 (3)
N1—N2	1.388 (2)	C2—H2A	0.9800
N1—C4	1.395 (3)	C3—C4	1.504 (3)
N2—C5	1.352 (3)	C3—C9	1.549 (3)
N2—H2	0.8600	C3—H3	0.9800
N3—C5	1.331 (3)	C6—C7	1.505 (3)
N3—H3A	0.8600	C6—H6	0.9800
N3—H3B	0.8600	C7—C8	1.315 (3)
O1—C1	1.207 (2)	C7—H7	0.9300
O2—C4	1.203 (2)	C8—C9	1.502 (3)
O3—C6	1.444 (3)	C8—H8	0.9300
O3—C9	1.455 (3)	C9—H9	0.9800
C1—C2	1.499 (3)		
C1—N1—N2	121.34 (18)	O2—C4—N1	123.4 (2)
C1—N1—C4	113.89 (17)	O2—C4—C3	129.3 (2)
N2—N1—C4	122.77 (17)	N1—C4—C3	107.21 (16)
C5—N2—N1	122.28 (18)	N3—C5—N2	116.96 (19)
C5—N2—H2	118.9	N3—C5—S1	124.34 (16)

N1—N2—H2	118.9	N2—C5—S1	118.69 (16)
C5—N3—H3A	120.0	O3—C6—C7	101.85 (18)
C5—N3—H3B	120.0	O3—C6—C2	99.98 (16)
H3A—N3—H3B	120.0	C7—C6—C2	106.61 (17)
C6—O3—C9	96.03 (15)	O3—C6—H6	115.5
O1—C1—N1	123.4 (2)	C7—C6—H6	115.5
O1—C1—C2	128.8 (2)	C2—C6—H6	115.5
N1—C1—C2	107.75 (17)	C8—C7—C6	105.9 (2)
C1—C2—C3	105.23 (17)	C8—C7—H7	127.0
C1—C2—C6	110.89 (17)	C6—C7—H7	127.0
C3—C2—C6	101.12 (16)	C7—C8—C9	106.5 (2)
C1—C2—H2A	112.9	C7—C8—H8	126.7
C3—C2—H2A	112.9	C9—C8—H8	126.7
C6—C2—H2A	112.9	O3—C9—C8	101.75 (17)
C4—C3—C2	105.28 (17)	O3—C9—C3	99.01 (15)
C4—C3—C9	111.29 (18)	C8—C9—C3	107.42 (18)
C2—C3—C9	101.62 (16)	O3—C9—H9	115.5
C4—C3—H3	112.6	C8—C9—H9	115.5
C2—C3—H3	112.6	C3—C9—H9	115.5
C9—C3—H3	112.6		
C1—N1—N2—C5	114.5 (2)	C9—C3—C4—N1	115.12 (18)
C4—N1—N2—C5	-82.6 (3)	N1—N2—C5—N3	-3.0 (3)
N2—N1—C1—O1	-4.8 (3)	N1—N2—C5—S1	176.11 (16)
C4—N1—C1—O1	-169.10 (19)	C9—O3—C6—C7	-49.14 (18)
N2—N1—C1—C2	171.97 (16)	C9—O3—C6—C2	60.34 (17)
C4—N1—C1—C2	7.6 (2)	C1—C2—C6—O3	76.2 (2)
O1—C1—C2—C3	173.2 (2)	C3—C2—C6—O3	-34.98 (19)
N1—C1—C2—C3	-3.4 (2)	C1—C2—C6—C7	-178.11 (19)
O1—C1—C2—C6	64.6 (3)	C3—C2—C6—C7	70.7 (2)
N1—C1—C2—C6	-111.89 (18)	O3—C6—C7—C8	32.6 (2)
C1—C2—C3—C4	-1.5 (2)	C2—C6—C7—C8	-71.7 (2)
C6—C2—C3—C4	113.97 (17)	C6—C7—C8—C9	-1.1 (2)
C1—C2—C3—C9	-117.64 (18)	C6—O3—C9—C8	48.43 (18)
C6—C2—C3—C9	-2.2 (2)	C6—O3—C9—C3	-61.60 (17)
C1—N1—C4—O2	170.38 (19)	C7—C8—C9—O3	-30.6 (2)
N2—N1—C4—O2	6.3 (3)	C7—C8—C9—C3	72.9 (2)
C1—N1—C4—C3	-8.6 (2)	C4—C3—C9—O3	-73.4 (2)
N2—N1—C4—C3	-172.69 (17)	C2—C3—C9—O3	38.29 (19)
C2—C3—C4—O2	-173.1 (2)	C4—C3—C9—C8	-178.77 (18)
C9—C3—C4—O2	-63.8 (3)	C2—C3—C9—C8	-67.1 (2)
C2—C3—C4—N1	5.8 (2)		

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

<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>
N2—H2 \cdots O3 ⁱ	0.86	1.96	2.809 (2)	167

N3—H3B···O1 ⁱⁱ	0.86	2.14	2.958 (2)	160
N3—H3A···N1	0.86	2.35	2.697 (2)	105

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