

tert-Butyl (3-oxocyclopentyl)carbamate

Alan J. Lough,^{a*} Katrina Tait^b and William Tam^b^aDepartment of Chemistry, University of Toronto, Toronto, Ontario, M5S 3H6, Canada, and ^bDepartment of Chemistry, University of Guelph, Guelph, Ontario, N1G 2W1, Canada. *Correspondence e-mail: alough@chem.utoronto.ca

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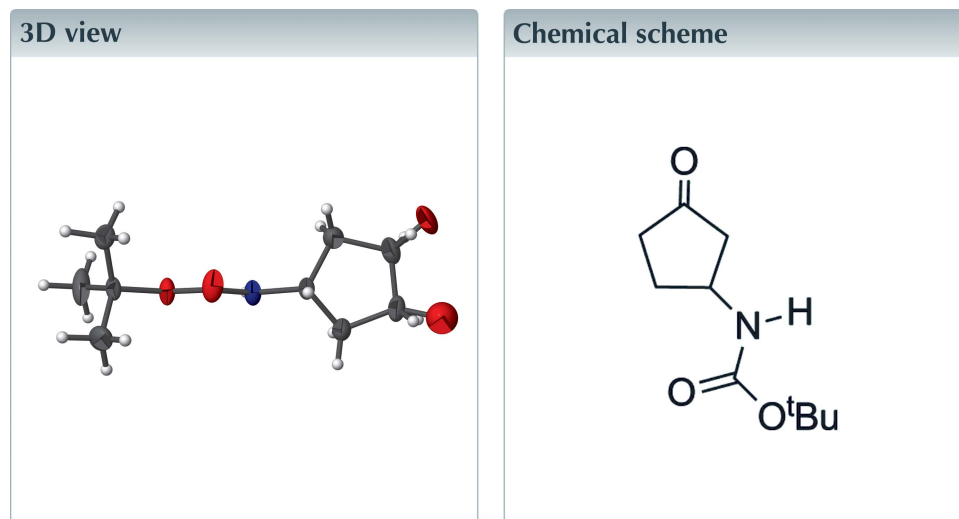
Edited by W. T. A. Harrison, University of Aberdeen, Scotland

Keywords: crystal structure; acid-catalysed ring-opening; stereoisomer; hydrogen bonds.

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Structural data: full structural data are available from iucrdata.iucr.org

In the title compound, C₁₀H₁₇NO₃, the five-membered ring is in a slightly twisted envelope conformation. The carbonyl group is disordered over two sites on the five-membered ring, with refined occupancies of 0.906 (4) and 0.094 (4). In the crystal, molecules are linked *via* N–H···O hydrogen bonds forming C(4) chains along [001].



Structure description

Recently, Tam and coworkers investigated the ruthenium-catalysed nucleophilic ring-opening of 3-aza-2-oxabicyclic alkenes with alcohols, which produced either a *cis*- or *trans*-1,2-cyclopentene depending on the catalyst used (Fig. 1) (Machin *et al.*, 2009). The aim was to expand the scope of the reaction to include amine nucleophiles, though the expected nucleophilic addition product was not formed. When 3-aza-2-oxabicyclic alkene **I** was subjected to the same conditions as previously except using an amine instead of an alcohol, an unexpected product, **II**, was formed (Fig. 2) with the crystal structure reported here. The investigation into the mechanism of this reaction is ongoing.

The molecular structure of **II** is shown in Fig. 3. The five-membered ring is in a slightly-twisted envelope conformation with atom C1 forming the flap. The carbonyl group is disordered over two sites on the five-membered ring with refined occupancies of 0.906 (4) and 0.094 (4). In the crystal, molecules are linked *via* N–H···O hydrogen bonds forming C(4) chains along [001] (Fig. 4, Table 1) with adjacent molecules related by *c*-glide symmetry.

Synthesis and crystallization

In a small screw-cap vial containing a stir bar, 3-aza-2-oxabicyclic alkene **I** (91.1 mg, 0.462 mmol, 1.0 equiv.) was added and transferred into a glove box. The catalyst Cp**Ru*Cl(COD) (17.5 mg, 0.046 mmol, 0.10 equiv.) was added into the same vial and

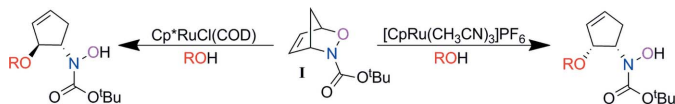


Figure 1
Previously reported ruthenium-catalysed nucleophilic ring opening of 3-aza-2-oxabicyclic alkene **I** with alcohols.

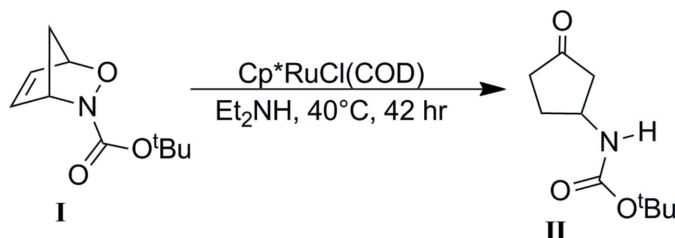


Figure 2
Ruthenium-catalysed ring-opening reaction of 3-aza-2-oxabicyclic alkene **I** with diethylamine.

reagents were dissolved in diethylamine (1.8 ml). The vial was sealed, transferred out of the glove box, and heated to 313 K with continuous stirring for 42 h. The crude product was purified by column chromatography using a gradient (EtOAc:hexanes = 1:9 to 1:1), followed by static vacuum sublimation for two weeks by gradually heating to 363 K to give clear, colourless crystals of **II**.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The carbonyl group is disordered over two sites on the five-membered ring with refined occupancies of 0.906 (4) and 0.094 (4). The C=O distance in the minor component was constrained to be the same as that in the major component.

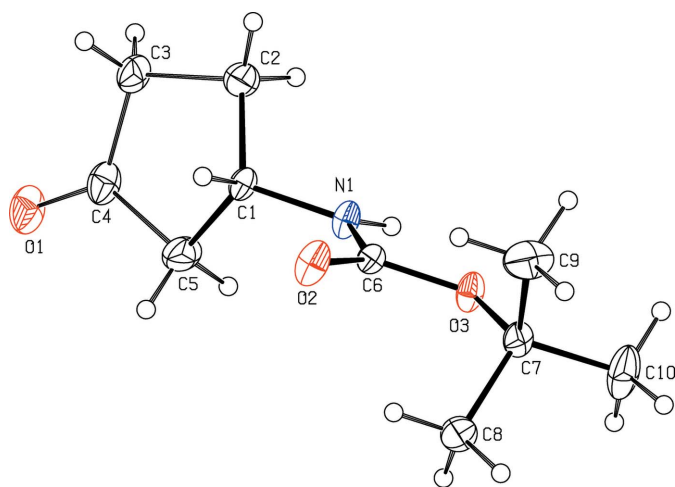


Figure 3
The molecule structure of **II**, with displacement ellipsoids drawn at the 30% probability level. The minor component of disorder is not shown.

Table 1
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>
N1—H1N···O2 ⁱ	0.84 (2)	2.05 (2)	2.8684 (17)	164.4 (19)

Symmetry code: (i) *x*, $-y + 1$, $z - \frac{1}{2}$.

Table 2
Experimental details.

Crystal data	
Chemical formula	C ₁₀ H ₁₇ NO ₃
<i>M_r</i>	199.24
Crystal system, space group	Monoclinic, <i>C2/c</i>
Temperature (K)	147
<i>a</i> , <i>b</i> , <i>c</i> (Å)	20.6617 (14), 11.6924 (9), 9.9566 (7)
β (°)	111.295 (4)
<i>V</i> (Å ³)	2241.1 (3)
<i>Z</i>	8
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.09
Crystal size (mm)	0.25 × 0.18 × 0.03
Data collection	
Diffractometer	Bruker Kappa APEX DUO CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2014)
<i>T_{min}</i> , <i>T_{max}</i>	0.707, 0.746
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	8250, 2586, 1695
<i>R_{int}</i>	0.039
(sin θ/λ) _{max} (Å ⁻¹)	0.652
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.050, 0.130, 1.05
No. of reflections	2586
No. of parameters	139
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.25, -0.19

Computer programs: *APEX2* and *SAINT* (Bruker, 2014), *SHELXT* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

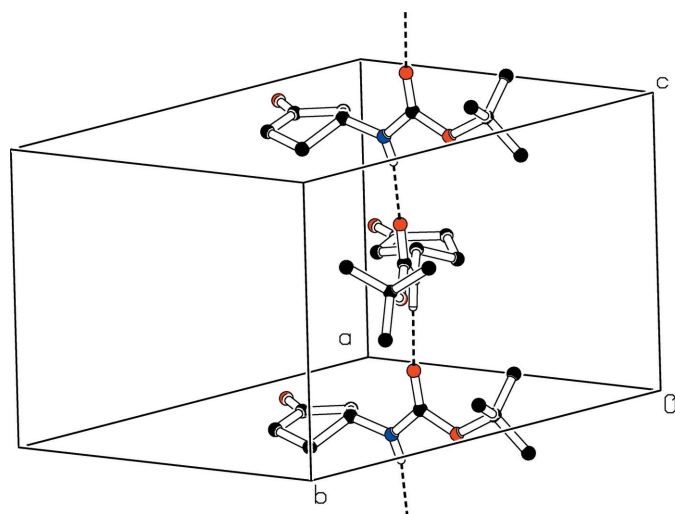


Figure 4
Part of the crystal structure of **II**, with hydrogen bonds shown as dashed lines. The disorder is not shown.

Funding information

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full crystallographic data

IUCrData (2017). 2, x171418 [https://doi.org/10.1107/S2414314617014183]

tert-Butyl (3-oxocyclopentyl)carbamate

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tert-Butyl (3-oxocyclopentyl)carbamate*Crystal data*

$C_{10}H_{17}NO_3$	$F(000) = 864$
$M_r = 199.24$	$D_x = 1.181 \text{ Mg m}^{-3}$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$a = 20.6617 (14) \text{ \AA}$	Cell parameters from 1745 reflections
$b = 11.6924 (9) \text{ \AA}$	$\theta = 2.7\text{--}23.5^\circ$
$c = 9.9566 (7) \text{ \AA}$	$\mu = 0.09 \text{ mm}^{-1}$
$\beta = 111.295 (4)^\circ$	$T = 147 \text{ K}$
$V = 2241.1 (3) \text{ \AA}^3$	Plate, colourless
$Z = 8$	$0.25 \times 0.18 \times 0.03 \text{ mm}$

Data collection

Bruker Kappa APEX DUO CCD diffractometer	8250 measured reflections
Radiation source: sealed tube with Bruker Triumph monochromator	2586 independent reflections
φ and ω scans	1695 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 2014)	$R_{\text{int}} = 0.039$
$T_{\text{min}} = 0.707$, $T_{\text{max}} = 0.746$	$\theta_{\text{max}} = 27.6^\circ$, $\theta_{\text{min}} = 2.0^\circ$
	$h = -25 \rightarrow 26$
	$k = -12 \rightarrow 15$
	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.050$	$w = 1/[\sigma^2(F_o^2) + (0.0552P)^2 + 1.179P]$
$wR(F^2) = 0.130$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{\text{max}} < 0.001$
2586 reflections	$\Delta\rho_{\text{max}} = 0.25 \text{ e \AA}^{-3}$
139 parameters	$\Delta\rho_{\text{min}} = -0.19 \text{ e \AA}^{-3}$
1 restraint	

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. H atoms were placed in calculated positions with C–H = 0.98–1.00 Å and included in the refinement with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$. The H atom bonded to N was refined independently with an isotropic displacement parameter.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
O1	0.52124 (7)	0.36776 (15)	0.60633 (18)	0.0513 (6)	0.906 (4)
C3	0.41982 (10)	0.25014 (18)	0.5483 (2)	0.0392 (5)	0.906 (4)
H3A	0.4309	0.2073	0.6397	0.047*	0.906 (4)
H3B	0.4315	0.2019	0.4785	0.047*	0.906 (4)
C4	0.45871 (10)	0.35970 (18)	0.5731 (2)	0.0401 (5)	0.906 (4)
O1A	0.4615 (8)	0.1760 (13)	0.6013 (19)	0.070 (7)*	0.094 (4)
C3A	0.41982 (10)	0.25014 (18)	0.5483 (2)	0.0392 (5)	0.094 (4)
C4A	0.45871 (10)	0.35970 (18)	0.5731 (2)	0.0401 (5)	0.094 (4)
H4A1	0.4820	0.3682	0.5025	0.048*	0.094 (4)
H4A2	0.4947	0.3607	0.6713	0.048*	0.094 (4)
O2	0.25826 (7)	0.51394 (12)	0.68422 (12)	0.0382 (4)	
O3	0.18971 (6)	0.57509 (11)	0.46075 (12)	0.0313 (3)	
N1	0.27867 (7)	0.46337 (13)	0.48373 (15)	0.0267 (3)	
C1	0.34193 (8)	0.39996 (15)	0.55617 (17)	0.0243 (4)	
H1A	0.3463	0.3875	0.6585	0.029*	
C2	0.34363 (10)	0.28369 (17)	0.4884 (2)	0.0430 (5)	
H2A	0.3150	0.2273	0.5163	0.052*	
H2B	0.3263	0.2893	0.3819	0.052*	
C5	0.40809 (10)	0.45669 (18)	0.5565 (3)	0.0470 (6)	
H5A	0.3996	0.4983	0.4651	0.056*	
H5B	0.4261	0.5112	0.6377	0.056*	
C6	0.24354 (8)	0.51738 (14)	0.55445 (16)	0.0227 (4)	
C7	0.14221 (9)	0.64310 (16)	0.50923 (18)	0.0293 (4)	
C8	0.18093 (10)	0.73408 (17)	0.6154 (2)	0.0385 (5)	
H8A	0.1477	0.7890	0.6279	0.058*	
H8B	0.2129	0.7739	0.5789	0.058*	
H8C	0.2073	0.6985	0.7083	0.058*	
C9	0.10128 (12)	0.56591 (19)	0.5703 (3)	0.0579 (7)	
H9A	0.0678	0.6116	0.5962	0.087*	
H9B	0.1330	0.5273	0.6564	0.087*	
H9C	0.0765	0.5087	0.4981	0.087*	
C10	0.09596 (12)	0.6992 (2)	0.3699 (2)	0.0571 (7)	
H10A	0.0612	0.7470	0.3888	0.086*	
H10B	0.0724	0.6400	0.2994	0.086*	
H10C	0.1243	0.7468	0.3317	0.086*	
H1N	0.2658 (10)	0.4773 (17)	0.395 (2)	0.034 (5)*	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0249 (9)	0.0658 (12)	0.0656 (11)	0.0069 (8)	0.0195 (7)	0.0193 (9)
C3	0.0333 (11)	0.0373 (12)	0.0456 (11)	0.0133 (9)	0.0125 (9)	-0.0024 (9)
C4	0.0285 (10)	0.0502 (13)	0.0451 (11)	0.0095 (9)	0.0174 (8)	0.0094 (10)
C3A	0.0333 (11)	0.0373 (12)	0.0456 (11)	0.0133 (9)	0.0125 (9)	-0.0024 (9)
C4A	0.0285 (10)	0.0502 (13)	0.0451 (11)	0.0095 (9)	0.0174 (8)	0.0094 (10)

O2	0.0476 (8)	0.0512 (9)	0.0206 (6)	0.0204 (7)	0.0183 (5)	0.0060 (6)
O3	0.0293 (7)	0.0413 (8)	0.0226 (6)	0.0156 (6)	0.0086 (5)	-0.0021 (5)
N1	0.0281 (7)	0.0372 (9)	0.0167 (6)	0.0114 (7)	0.0105 (6)	0.0039 (6)
C1	0.0238 (8)	0.0283 (9)	0.0234 (8)	0.0074 (7)	0.0116 (6)	0.0041 (7)
C2	0.0302 (10)	0.0325 (11)	0.0626 (13)	0.0048 (9)	0.0124 (10)	-0.0066 (10)
C5	0.0332 (11)	0.0328 (11)	0.0752 (15)	0.0024 (9)	0.0201 (11)	0.0059 (11)
C6	0.0230 (8)	0.0242 (9)	0.0232 (8)	0.0030 (7)	0.0109 (6)	0.0012 (7)
C7	0.0227 (8)	0.0340 (10)	0.0329 (9)	0.0082 (8)	0.0122 (7)	-0.0047 (8)
C8	0.0363 (10)	0.0341 (11)	0.0453 (11)	0.0060 (9)	0.0150 (9)	-0.0077 (9)
C9	0.0421 (12)	0.0432 (13)	0.104 (2)	-0.0013 (11)	0.0458 (13)	0.0002 (13)
C10	0.0492 (13)	0.0732 (17)	0.0403 (11)	0.0360 (13)	0.0060 (10)	-0.0055 (11)

Geometric parameters (Å, °)

O1—C4	1.215 (2)	C1—C2	1.524 (3)
C3—C4	1.484 (3)	C1—H1A	1.0000
C3—C2	1.518 (3)	C2—H2A	0.9900
C3—H3A	0.9900	C2—H2B	0.9900
C3—H3B	0.9900	C5—H5A	0.9900
C4—C5	1.510 (3)	C5—H5B	0.9900
O1A—C3A	1.201 (9)	C7—C9	1.508 (3)
C3A—C4A	1.484 (3)	C7—C8	1.508 (3)
C3A—C2	1.518 (3)	C7—C10	1.518 (3)
C4A—C5	1.510 (3)	C8—H8A	0.9800
C4A—H4A1	0.9900	C8—H8B	0.9800
C4A—H4A2	0.9900	C8—H8C	0.9800
O2—C6	1.2158 (18)	C9—H9A	0.9800
O3—C6	1.3451 (19)	C9—H9B	0.9800
O3—C7	1.4739 (19)	C9—H9C	0.9800
N1—C6	1.339 (2)	C10—H10A	0.9800
N1—C1	1.447 (2)	C10—H10B	0.9800
N1—H1N	0.84 (2)	C10—H10C	0.9800
C1—C5	1.518 (3)		
C4—C3—C2	105.30 (16)	C4A—C5—C1	105.03 (16)
C4—C3—H3A	110.7	C4—C5—C1	105.03 (16)
C2—C3—H3A	110.7	C4—C5—H5A	110.7
C4—C3—H3B	110.7	C1—C5—H5A	110.7
C2—C3—H3B	110.7	C4—C5—H5B	110.7
H3A—C3—H3B	108.8	C1—C5—H5B	110.7
O1—C4—C3	124.75 (19)	H5A—C5—H5B	108.8
O1—C4—C5	126.7 (2)	O2—C6—N1	124.69 (15)
C3—C4—C5	108.55 (16)	O2—C6—O3	125.33 (14)
O1A—C3A—C4A	106.9 (10)	N1—C6—O3	109.98 (13)
O1A—C3A—C2	146.6 (10)	O3—C7—C9	110.30 (15)
C4A—C3A—C2	105.30 (16)	O3—C7—C8	111.30 (14)
C3A—C4A—C5	108.55 (16)	C9—C7—C8	111.84 (17)
C3A—C4A—H4A1	110.0	O3—C7—C10	101.94 (14)

C5—C4A—H4A1	110.0	C9—C7—C10	111.60 (18)
C3A—C4A—H4A2	110.0	C8—C7—C10	109.46 (17)
C5—C4A—H4A2	110.0	C7—C8—H8A	109.5
H4A1—C4A—H4A2	108.4	C7—C8—H8B	109.5
C6—O3—C7	121.65 (12)	H8A—C8—H8B	109.5
C6—N1—C1	122.93 (14)	C7—C8—H8C	109.5
C6—N1—H1N	115.9 (14)	H8A—C8—H8C	109.5
C1—N1—H1N	120.4 (13)	H8B—C8—H8C	109.5
N1—C1—C5	115.27 (15)	C7—C9—H9A	109.5
N1—C1—C2	113.47 (14)	C7—C9—H9B	109.5
C5—C1—C2	103.01 (14)	H9A—C9—H9B	109.5
N1—C1—H1A	108.3	C7—C9—H9C	109.5
C5—C1—H1A	108.3	H9A—C9—H9C	109.5
C2—C1—H1A	108.3	H9B—C9—H9C	109.5
C3A—C2—C1	104.11 (15)	C7—C10—H10A	109.5
C3—C2—C1	104.11 (15)	C7—C10—H10B	109.5
C3—C2—H2A	110.9	H10A—C10—H10B	109.5
C1—C2—H2A	110.9	C7—C10—H10C	109.5
C3—C2—H2B	110.9	H10A—C10—H10C	109.5
C1—C2—H2B	110.9	H10B—C10—H10C	109.5
H2A—C2—H2B	109.0		
C2—C3—C4—O1	-171.8 (2)	O1—C4—C5—C1	-164.6 (2)
C2—C3—C4—C5	10.6 (2)	C3—C4—C5—C1	12.9 (2)
O1A—C3A—C4A—C5	-160.6 (10)	N1—C1—C5—C4A	-155.20 (15)
C2—C3A—C4A—C5	10.6 (2)	C2—C1—C5—C4A	-31.1 (2)
C6—N1—C1—C5	-106.9 (2)	N1—C1—C5—C4	-155.20 (15)
C6—N1—C1—C2	134.68 (18)	C2—C1—C5—C4	-31.1 (2)
O1A—C3A—C2—C1	134.5 (17)	C1—N1—C6—O2	-4.3 (3)
C4A—C3A—C2—C1	-30.1 (2)	C1—N1—C6—O3	175.97 (15)
C4—C3—C2—C1	-30.1 (2)	C7—O3—C6—O2	0.7 (3)
N1—C1—C2—C3A	163.07 (15)	C7—O3—C6—N1	-179.64 (15)
C5—C1—C2—C3A	37.8 (2)	C6—O3—C7—C9	-66.5 (2)
N1—C1—C2—C3	163.07 (15)	C6—O3—C7—C8	58.3 (2)
C5—C1—C2—C3	37.8 (2)	C6—O3—C7—C10	174.87 (17)
C3A—C4A—C5—C1	12.9 (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>
N1—H1N \cdots O2 ⁱ	0.84 (2)	2.05 (2)	2.8684 (17)	164.4 (19)

Symmetry code: (i) $x, -y+1, z-1/2$.