Powder study of 3-azabicyclo[3.3.1]nonane-2,4-dione form 2

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A polycrystalline sample of a new polymorph of the title compound, $C_8H_{11}NO_2$, was produced during a variable-temperature X-ray powder diffraction study. The crystal structure was solved at 1.67 Å resolution by simulated annealing from laboratory powder data collected at 250 K. Subsequent Rietveld refinement yielded an R_{wp} of 0.070 to 1.54 Å resolution. The structure contains two molecules in the asymmetric unit, which form a $C_2^2(8)$ chain motif *via* N—H···O hydrogen bonds.

Comment

The crystal structure of the title compound, (I), was solved by simulated annealing using laboratory capillary X-ray powder diffraction data. The compound crystallizes in space group $P2_1/c$ with two independent molecules of 3-azabicyclononane-2,4-dione in the asymmetric unit (Fig. 1).

(I)
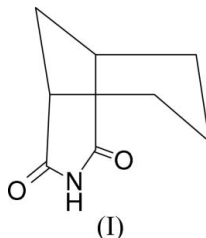
The crystal structure of this polymorph (form 2) is approximately a cell-doubled modification of the stable room-temperature form of 3-azabicyclononane-2,4-dione (form 1) (Howie & Skakle, 2001), with the cell doubling in the *c* direction [18.8867 (4) *versus* 9.3384 (6) Å]. Form 2 is meta-stable with respect to form 1 at room temperature, with full conversion taking less than 1 h. However, with rapid cooling to 250 K (the data collection temperature), form 2 is kinetically trapped and stable for over 10 h.

The basic hydrogen-bond motif in (I) is a chain [graph set $C_2^2(8)$; Etter, 1990] running parallel to the *a* axis. Each chain contains alternating independent molecules linked by N—H···O hydrogen bonds (Table 1). Form 2 packs the chains in a manner similar to form 1, with the chains lying side by side to form layers (Fig. 2) parallel to the *ab* plane. The layers are related by the 2_1 screw axis and the stacking of the layers differs between the two forms, with form 1 showing an *AB* repeat packing and form 2 an *ABCD* repeat packing (Fig. 3). This stacking difference can be attributed to form 2 having two symmetry-independent molecules. The stacking in form 2 can be envisaged as related to that of form 1 by a translation of approximately half a unit cell parallel to the *b* axis of the *C* and

D layers. With no strong interactions between the layers, the conversion from form 2 to form 1 would be facile and may account for the rapid conversion at room temperature.

Experimental

A polycrystalline sample of (I) was prepared by heating a sample of the raw material (form 1) to 420 K and subsequently quenching *in situ* to 250 K. The sample was held in a rotating 0.7 mm borosilicate glass capillary and the temperature controlled using an Oxford Cryosystems Cryostream Plus 700 series device. Data were collected over a period of 7.5 h using a variable-counting-time scheme (Shankland *et al.*, 1997; Hill & Madsen, 2002) in the range 7–60° 2θ. The final data set showed no evidence of diffraction associated with the form 1 structure.

Crystal data

$C_8H_{11}NO_2$
$M_r = 153.18$
Monoclinic, $P2_1/c$
$a = 7.67102 (18)$ Å
$b = 10.5483 (2)$ Å
$c = 18.8867 (4)$ Å
$\beta = 95.5800 (12)°$
$V = 1521.00 (6)$ Å^3
$Z = 8$

$D_x = 1.338$ Mg m^{-3}
Cu $K\alpha_1$ radiation
$\mu = 0.79$ mm^{-1}
$T = 250$ K
Specimen shape: cylinder
$12 \times 0.7 \times 0.7$ mm
Specimen prepared at 420 K
Particle morphology: polycrystalline mass, white

Data collection

Bruker AXS D8 Advance diffractometer
Specimen mounting: 0.7 mm borosilicate capillary
Specimen mounted in transmission mode

Scan method: step
Absorption correction: none
$2\theta_{min} = 7.0$, $2\theta_{max} = 60.0°$
Increment in $2\theta = 0.017°$

Refinement

$R_p = 0.054$
$R_{wp} = 0.070$
$R_{exp} = 0.016$
$R_B = 3.058$
$S = 4.31$
Profile function: Fundamental parameters with axial divergence correction.
142 parameters

H atoms treated by a mixture of independent and constrained refinement
$w = 1/\sigma(Y_{obs})^2$
$(\Delta/\sigma)_{max} = 0.111$
Preferred orientation correction: a spherical harmonics-based preferred orientation correction (Järvinen, 1993) was applied with *TOPAS* (Coelho, 2003) during the Rietveld refinement.

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

| $D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1···O1w^i	0.90 (1)	2.11 (1)	3.006 (4)	172 (1)
N1w—H1w···O1^{ii}	0.91 (1)	2.03 (1)	2.931 (4)	172 (1)

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

The diffraction pattern indexed to a monoclinic cell [$M(18) = 28.0$, $F(18) = 65.9$; *DICVOL91*; Boultif & Louër, 1991] and space group $P2_1/c$ was assigned from volume considerations and a statistical consideration of the systematic absences (Markvardsen *et al.*, 2001). $P2_1/a$ and $P2_1/n$ were discounted as they did not account for the peak attributable to form 2 at 15.63° 2θ.
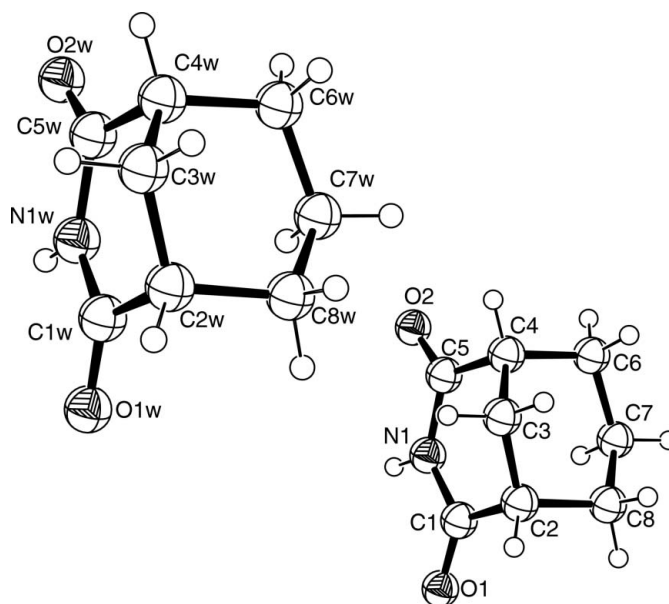
Figure 1
The asymmetric unit of (I) with the atom-numbering scheme. Displacement spheres are shown at the 50% probability level.
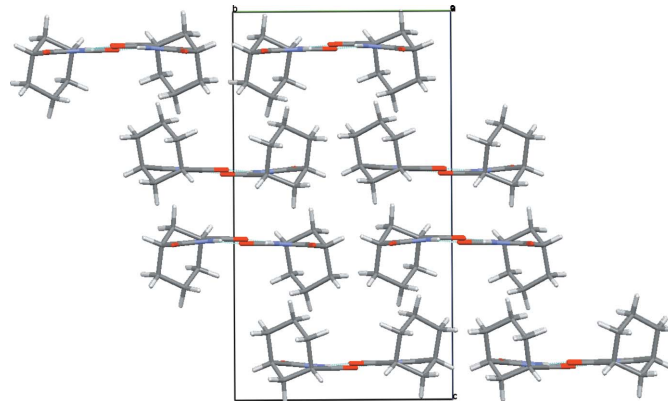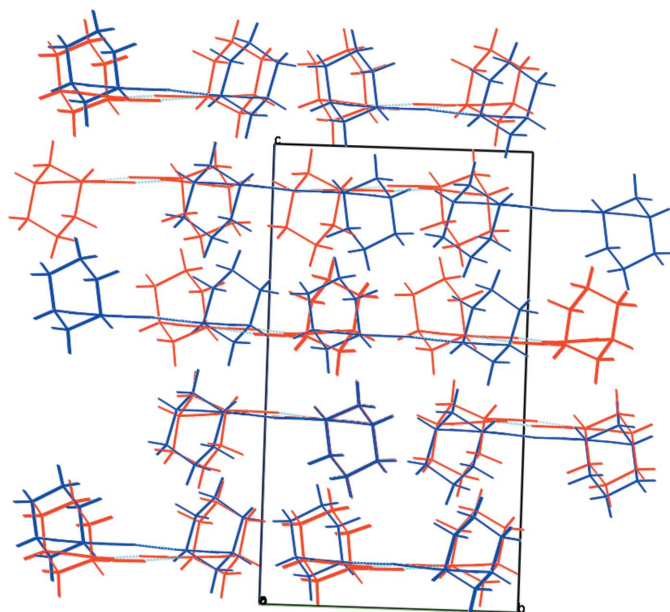

Figure 2
Four layers, each containing two ribbons, stacking in an *ABCD* repeat pattern. The view is parallel to the axis of propagation of the ribbons and the *a* axis.

The data were background subtracted and truncated to 54.8° 2θ for Pawley fitting (Pawley, 1981; $\chi^2_{Pawley} = 18.50$) and the structure solved using the simulated annealing (SA) global optimization procedure, described previously (David *et al.*, 1998), that is now implemented in the *DASH* computer program (David *et al.*, 2001). The internal coordinate description (including H atoms) of the molecules was constructed from standard bond lengths, bond angles and bond torsions where appropriate. The structure was solved using data to 54.8° 2θ, comprising 402 reflections. The structure was refined against data in the range 7.0–60.0° 2θ (448 reflections). The restraints were set such that bonds and angles did not deviate more than 0.01 Å and 1°, respectively, from their initial values during the refinement. Atoms C1, C5, C4, C2, O1, N1, O2 and H1 (first molecule) and atoms C1*w*, C5*w*, C4*w*, C1*w*, O1*w*, N1*w*, O2*w* and H1*w* (second molecule) of 3-azabicyclo[3.3.1]nonane-2,4-dione were restrained to be coplanar.

The SA structure solution involved the optimization of two independent molecules totaling 12 degrees of freedom (positional and

organic papers

Figure 3
Overlay of the layer stacking of form 1 (blue) and form 2 (red). The members of the uppermost layer and two bottom layers coincide, while the remaining two layers do not. Hydrogen bonds are shown as dashed lines.

orientational). All degrees of freedom were assigned random values at the start of the simulated annealing run. The best SA solution had a favourable $\chi^2_{SA}/\chi^2_{Pawley}$ ratio of 4.5, had a chemically reasonable packing arrangement and exhibited no significant misfit to the data.

The solved structure was subsequently refined against data in the range 7.0–60.0° 2θ using a restrained Rietveld (1969) method as implemented in *TOPAS* (Coelho, 2003), with R_{wp} falling to 0.0698 during the refinement. All atomic positions (including H atoms) for the structure of (I) were refined, subject to a series of restraints on bond lengths, bond angles and planarity. A spherical harmonics (8th order) correction of intensities for preferred orientation was applied in the final refinement (Järvinen, 1993). An 8th order correction yielded a significant improvement in R_{wp} compared with lower orders. The need for such a high level of correction is most likely due to the effect of the *in situ* method of sample preparation on particle morphology. The observed and calculated diffraction patterns for the refined crystal structure are shown in Fig. 4.

Data collection: *DIFFRAC plus XRD Commander* (Kienle & Jacob, 2003); cell refinement: *TOPAS* (Coelho, 2003); data reduction: *DASH* (David *et al.*, 2001); program(s) used to solve structure: *DASH*; program(s) used to refine structure: *TOPAS*; molecular graphics: *MERCURY* (Macrae *et al.*, 2006) and *PLATON* (Spek, 2003); software used to prepare material for publication: *enCIFer* (Version 1.1; Allen *et al.*, 2004).
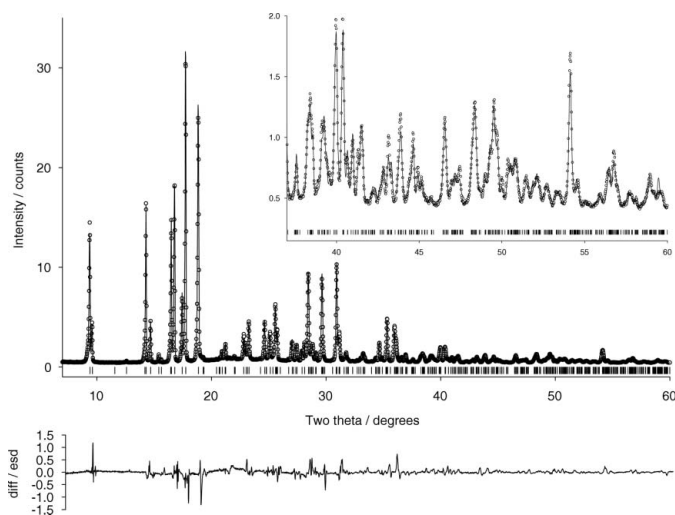
Figure 4
Final observed (points), calculated (line) and difference $[(y_{obs} - y_{calc})/\sigma(y_{obs})]$ profiles for the Rietveld refinement of the title compound.

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supporting information

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Crystal data

$C_8H_{11}NO_2$	$Z = 8$
$M_r = 153.18$	$F(000) = 656.0$
Monoclinic, $P2_1/c$	$D_x = 1.338$ Mg m^{-3}
Hall symbol: -P 2ybc	Cu $K\alpha_1$ radiation, $\lambda = 1.54056$ Å
$a = 7.67102$ (18) Å	$\mu = 0.79$ mm^{-1}
$b = 10.5483$ (2) Å	$T = 250$ K
$c = 18.8867$ (4) Å	white
$\beta = 95.5800$ (12)°	cylinder, 12×0.7 mm
$V = 1521.00$ (6) Å^3	Specimen preparation: Prepared at 420 K

Data collection

Bruker AXS D8 Advance diffractometer	Specimen mounting: 0.7 mm borosilicate capillary
Radiation source: sealed X-ray tube, Bruker-AXS D8	Data collection mode: transmission
Primary focussing, Ge 111 monochromator	Scan method: step
	$2\theta_{min} = 7.0°$, $2\theta_{max} = 60.0°$, $2\theta_{step} = 0.017°$

Refinement

Least-squares matrix: selected elements only	H atoms treated by a mixture of independent and constrained refinement
$R_p = 0.054$	Weighting scheme based on measured s.u.'s $1/\sigma(Y_{obs})^2$
$R_{wp} = 0.070$	
$R_{exp} = 0.016$	$(\Delta/\sigma)_{max} = 0.111$
$R_{Bragg} = 3.058$	Background function: Chebyshev polynomial
3070 data points	Preferred orientation correction: A spherical harmonics-based preferred orientation correction (Järvinen, 1993) was applied with Topas during the Rietveld refinement.
Profile function: Fundamental parameters with axial divergence correction.	
142 parameters	
92 restraints	
2 constraints	

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

	x	y	z	$U_{iso}*/U_{eq}$
N1	0.7188 (2)	0.20485 (14)	0.59572 (18)	0.0380*
H1	0.8105 (12)	0.1517 (6)	0.5942 (4)	0.0760*
C1	0.5536 (2)	0.14964 (16)	0.5933 (2)	0.0380*
O1	0.5397 (5)	0.0342 (2)	0.5915 (3)	0.0380*
C2	0.3992 (2)	0.23660 (16)	0.59562 (9)	0.0380*

H2	0.3033 (12)	0.1955 (6)	0.5695 (4)	0.0760*
C3	0.4373 (2)	0.36391 (16)	0.56342 (9)	0.0380*
H3A	0.3414 (11)	0.4204 (6)	0.5661 (4)	0.0760*
H3B	0.4527 (10)	0.3553 (6)	0.5143 (5)	0.0760*
C4	0.6000 (2)	0.41980 (16)	0.60445 (9)	0.0380*
H4	0.6326 (12)	0.4984 (6)	0.5846 (4)	0.0760*
C5	0.7548 (2)	0.33355 (17)	0.5989 (2)	0.0380*
O2	0.9060 (3)	0.3689 (3)	0.6007 (3)	0.0380*
C6	0.5709 (2)	0.43895 (15)	0.68362 (8)	0.0380*
H6A	0.4815 (11)	0.5017 (6)	0.6831 (4)	0.0760*
H6B	0.6770 (13)	0.4725 (6)	0.7066 (4)	0.0760*
C7	0.5134 (2)	0.31638 (15)	0.71761 (9)	0.0380*
H7A	0.6069 (11)	0.2563 (6)	0.7206 (5)	0.0760*
H7B	0.4810 (10)	0.3317 (7)	0.7643 (4)	0.0760*
C8	0.3599 (2)	0.25471 (16)	0.67356 (9)	0.0380*
H8A	0.3286 (11)	0.1746 (7)	0.6922 (4)	0.0760*
H8B	0.2564 (12)	0.3047 (6)	0.6726 (4)	0.0760*
N1w	0.2227 (2)	0.62126 (15)	0.0902 (3)	0.0380*
H1w	0.3151 (11)	0.5676 (6)	0.0925 (6)	0.0760*
C1w	0.0572 (2)	0.56668 (17)	0.0834 (3)	0.0380*
O1w	0.0443 (5)	0.4507 (3)	0.0867 (4)	0.0380*
C2w	−0.0968 (2)	0.65429 (15)	0.08651 (9)	0.0380*
H2w	−0.1932 (11)	0.6143 (6)	0.0598 (4)	0.0760*
C3w	−0.0589 (2)	0.78378 (15)	0.05587 (9)	0.0380*
H3Aw	−0.1535 (11)	0.8405 (6)	0.0603 (4)	0.0760*
H3Bw	−0.0449 (10)	0.7782 (6)	0.0064 (4)	0.0760*
C4w	0.1043 (2)	0.83674 (16)	0.09717 (9)	0.0380*
H4w	0.1381 (12)	0.9151 (7)	0.0777 (4)	0.0760*
C5w	0.2583 (2)	0.75006 (17)	0.0912 (2)	0.0380*
O2w	0.4093 (3)	0.7853 (3)	0.0928 (4)	0.0380*
C6w	0.0742 (2)	0.85581 (15)	0.17599 (8)	0.0380*
H6Aw	−0.0119 (11)	0.9206 (7)	0.1752 (4)	0.0760*
H6Bw	0.1815 (12)	0.8864 (7)	0.1993 (4)	0.0760*
C7w	0.0097 (2)	0.73736 (16)	0.21080 (9)	0.0380*
H7Aw	0.1038 (12)	0.6790 (6)	0.2192 (5)	0.0760*
H7Bw	−0.0318 (10)	0.7583 (7)	0.2553 (4)	0.0760*
C8w	−0.1364 (2)	0.66815 (17)	0.16490 (9)	0.0380*
H8Aw	−0.1579 (11)	0.5853 (7)	0.1828 (4)	0.0760*
H8Bw	−0.2463 (12)	0.7112 (6)	0.1643 (4)	0.0760*

Geometric parameters (Å, º)

O1—C1	1.223 (3)	C6—H6B	0.953 (9)
O2—C5	1.216 (3)	C7—H7B	0.953 (8)
O1W—C1W	1.230 (4)	C7—H7A	0.955 (8)
O2W—C5W	1.214 (3)	C8—H8B	0.952 (9)
N1—C5	1.386 (2)	C8—H8A	0.955 (8)
N1—C1	1.391 (2)	C1W—C2W	1.506 (2)

N1—H1	0.902 (8)	C2W—C8W	1.547 (2)
N1W—C5W	1.386 (2)	C2W—C3W	1.523 (2)
N1W—C1W	1.389 (2)	C3W—C4W	1.516 (2)
N1W—H1W	0.905 (8)	C4W—C5W	1.507 (2)
C1—C2	1.502 (2)	C4W—C6W	1.542 (2)
C2—C3	1.514 (2)	C6W—C7W	1.517 (2)
C2—C8	1.543 (2)	C7W—C8W	1.534 (2)
C3—C4	1.522 (2)	C2W—H2W	0.952 (8)
C4—C6	1.546 (2)	C3W—H3AW	0.951 (8)
C4—C5	1.508 (2)	C3W—H3BW	0.953 (8)
C6—C7	1.528 (2)	C4W—H4W	0.951 (8)
C7—C8	1.520 (2)	C6W—H6AW	0.950 (8)
C2—H2	0.950 (8)	C6W—H6BW	0.951 (9)
C3—H3B	0.951 (8)	C7W—H7AW	0.950 (8)
C3—H3A	0.952 (8)	C7W—H7BW	0.953 (8)
C4—H4	0.953 (7)	C8W—H8AW	0.957 (8)
C6—H6A	0.953 (8)	C8W—H8BW	0.957 (9)
C1—N1—C5	126.06 (15)	C7—C8—H8A	112.7 (5)
C1—N1—H1	116.7 (5)	C2—C8—H8A	108.8 (5)
C5—N1—H1	117.2 (5)	C2—C8—H8B	106.9 (5)
C1W—N1W—C5W	125.81 (16)	O1W—C1W—N1W	119.0 (2)
C5W—N1W—H1W	117.4 (5)	N1W—C1W—C2W	117.11 (16)
C1W—N1W—H1W	116.7 (5)	O1W—C1W—C2W	122.8 (2)
O1—C1—N1	119.6 (2)	C1W—C2W—C8W	108.9 (2)
N1—C1—C2	117.50 (14)	C3W—C2W—C8W	109.98 (14)
O1—C1—C2	122.8 (2)	C1W—C2W—C3W	110.87 (16)
C1—C2—C8	109.34 (19)	C2W—C3W—C4W	108.28 (14)
C3—C2—C8	109.67 (14)	C3W—C4W—C6W	110.56 (13)
C1—C2—C3	110.26 (14)	C3W—C4W—C5W	110.62 (16)
C2—C3—C4	108.64 (13)	C5W—C4W—C6W	110.10 (18)
C3—C4—C6	110.76 (13)	O2W—C5W—C4W	124.4 (2)
C3—C4—C5	110.07 (16)	N1W—C5W—C4W	116.18 (14)
C5—C4—C6	109.56 (18)	O2W—C5W—N1W	119.1 (2)
O2—C5—C4	124.7 (2)	C4W—C6W—C7W	113.38 (13)
N1—C5—C4	116.06 (14)	C6W—C7W—C8W	113.47 (14)
O2—C5—N1	119.2 (2)	C2W—C8W—C7W	112.66 (13)
C4—C6—C7	111.75 (13)	C1W—C2W—H2W	106.2 (5)
C6—C7—C8	111.85 (13)	C3W—C2W—H2W	111.3 (4)
C2—C8—C7	111.24 (13)	C8W—C2W—H2W	109.5 (5)
C1—C2—H2	106.2 (5)	C2W—C3W—H3AW	110.8 (5)
C3—C2—H2	111.5 (4)	C2W—C3W—H3BW	111.2 (4)
C8—C2—H2	109.8 (5)	C4W—C3W—H3AW	108.8 (5)
C2—C3—H3A	110.7 (5)	C4W—C3W—H3BW	111.2 (5)
H3A—C3—H3B	106.4 (6)	H3AW—C3W—H3BW	106.6 (6)
C2—C3—H3B	110.8 (4)	C3W—C4W—H4W	111.3 (5)
C4—C3—H3A	109.3 (5)	C5W—C4W—H4W	104.7 (6)
C4—C3—H3B	111.1 (5)	C6W—C4W—H4W	109.4 (5)

C3—C4—H4	111.7 (5)	C4W—C6W—H6AW	104.4 (5)
C5—C4—H4	105.0 (5)	C4W—C6W—H6BW	106.7 (5)
C6—C4—H4	109.6 (5)	C7W—C6W—H6AW	110.1 (5)
C7—C6—H6B	113.1 (4)	C7W—C6W—H6BW	112.5 (5)
H6A—C6—H6B	109.2 (6)	H6AW—C6W—H6BW	109.4 (7)
C4—C6—H6A	104.6 (5)	C6W—C7W—H7AW	109.4 (5)
C4—C6—H6B	107.0 (5)	C6W—C7W—H7BW	110.0 (5)
C7—C6—H6A	110.8 (5)	C8W—C7W—H7AW	106.7 (5)
C6—C7—H7B	110.9 (5)	C8W—C7W—H7BW	108.7 (5)
H7A—C7—H7B	108.7 (7)	H7AW—C7W—H7BW	108.4 (7)
C8—C7—H7A	106.6 (5)	C2W—C8W—H8AW	108.0 (5)
C6—C7—H7A	109.9 (5)	C2W—C8W—H8BW	106.8 (5)
C8—C7—H7B	108.7 (5)	C7W—C8W—H8AW	112.1 (5)
C7—C8—H8B	111.9 (5)	C7W—C8W—H8BW	112.1 (5)
H8A—C8—H8B	105.0 (7)	H8AW—C8W—H8BW	104.8 (7)

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1W[i]	0.90 (1)	2.11 (1)	3.006 (4)	172 (1)
N1W—H1W···O1[ii]	0.91 (1)	2.03 (1)	2.931 (4)	172 (1)
C2—H2···O1W[iii]	0.95 (1)	2.56 (1)	3.355 (4)	141 (1)
C3W—H3BW···O2[iv]	0.95 (1)	2.56 (1)	3.406 (5)	148 (1)
C3—H3*B*···O2W[v]	0.95 (1)	2.49 (1)	3.384 (7)	158 (1)

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