

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

(E)-1-(4-Bromophenyl)ethan-1-one semicarbazone

 Hoong-Kun Fun,^{a,*} Jia Hao Goh,^a Mahesh Padaki,^b
 Shridhar Malladi^b and Arun M. Isloor^b
^aX-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, and ^bDepartment of Chemistry, National Institute of Technology-Karnataka, Surathkal, Mangalore 575 025, India
 Correspondence e-mail: hkfun@usm.my

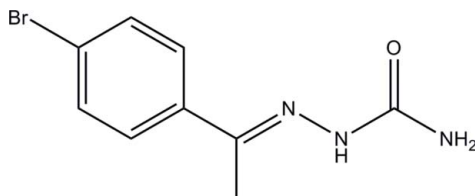
Received 10 June 2009; accepted 11 June 2009

 Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.016$ Å; R factor = 0.080; wR factor = 0.249; data-to-parameter ratio = 22.8.

In the title compound, $\text{C}_9\text{H}_{10}\text{BrN}_3\text{O}$, the hydrazone portion and aliphatic chain are essentially coplanar [maximum deviation 0.057 (15) Å] and the mean plane makes a dihedral angle of 70.9 (6)° with the benzene ring. The main feature of the crystal structure is the intermolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bond, which links molecules into zigzag chains along the a axis. These chains are further stacked along the b axis. The crystal structure features non-classical intermolecular $\text{C}-\text{H}\cdots\text{O}$ interactions. The crystal studied was a nonmerohedral twin, with a twin ratio of 0.505 (1):0.495 (1).

Related literature

For general background and applications of semicarbazone derivatives, see: Chandra & Gupta (2005); Jain *et al.* (2002); Pilgram (1978); Warren *et al.* (1977); Yogeewari *et al.* (2004). For the preparation, see: Furniss *et al.* (1978). For bond-length data, see: Allen *et al.* (1987). For a related structure, see: Fun *et al.* (2009). For the stability of the temperature controller used for the data collection, see: Cosier & Glazer (1986).



Experimental

Crystal data

 $\text{C}_9\text{H}_{10}\text{BrN}_3\text{O}$
 $M_r = 256.11$
 Monoclinic, $P2_1/c$
 $a = 17.6700$ (8) Å
 $b = 7.3426$ (4) Å
 $c = 7.9082$ (4) Å

^{*} Thomson Reuters ResearcherID: A-3561-2009.

 $\beta = 102.953$ (3)°
 $V = 999.93$ (9) Å³
 $Z = 4$
 Mo $K\alpha$ radiation

 $\mu = 4.08$ mm⁻¹
 $T = 100$ K
 $0.22 \times 0.12 \times 0.08$ mm

Data collection

 Bruker SMART APEXII CCD
 area-detector diffractometer
 Absorption correction: multi-scan
 (SADABS; Bruker, 2005)
 $T_{\min} = 0.466$, $T_{\max} = 0.733$

 12017 measured reflections
 2945 independent reflections
 2105 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.053$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.080$
 $wR(F^2) = 0.249$
 $S = 1.16$
 2945 reflections
 129 parameters

 1 restraint
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 3.03$ e Å⁻³
 $\Delta\rho_{\text{min}} = -1.11$ e Å⁻³
Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N}2-\text{H}2\text{B}\cdots\text{O}1^{\text{i}}$	0.86	2.21	3.052 (12)	168
$\text{N}3-\text{H}3\text{A}\cdots\text{O}1^{\text{ii}}$	0.86	2.03	2.885 (13)	171
$\text{C}9-\text{H}9\text{A}\cdots\text{O}1^{\text{iii}}$	0.96	2.51	3.34 (2)	144

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

Data collection: APEX2 (Bruker, 2005); cell refinement: SAINT (Bruker, 2005); 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).

HKF and JHG thank Universiti Sains Malaysia for the Research University Golden Goose Grant (No. 1001/PFIZIK/811012). JHG thanks the Malaysia Government and Universiti Sains Malaysia for a student assistantship under the Science Fund (Grant No. 305/PFIZIK/613312). AMI is grateful to the Head of the Department of Chemistry and the Director, NITK, Surathkal, India, for providing research facilities.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG2596).

References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
 Bruker (2005). APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
 Chandra, S. & Gupta, L. K. (2005). *Spectrochim Acta*, **A62**, 1089–1094.
 Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.
 Fun, H.-K., Quah, C. K., Sujith, K. V. & Kalluraya, B. (2009). *Acta Cryst.* **E65**, o1184–o1185.
 Furniss, B. S., Hannaford, A. J., Rogers, V., Smith, P. W. G. & Tatchell, A. R. (1978). *Vogel's Textbook of Practical Organic Chemistry*, 4th ed., p. 1112. London: ELBS.

- Jain, V. K., Handa, A., Pandya, R., Shrivastav, P. & Agrawal, Y. K. (2002). *React. Funct. Polym.* **51**, 101–110.
- Pilgram, K. H. G. (1978). US Patent No. 4 108 399.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Warren, J. D., Woodward, D. L. & Hargreaves, R. T. (1977). *J. Med. Chem.* **20**, 1520–1521.
- Yogeeswari, P., Sriram, D., Pandeya, S. N. & Stables, J. P. (2004). *Farmaco*, **59**, 609–613.

supporting information

Acta Cryst. (2009). E65, o1591–o1592 [doi:10.1107/S1600536809022284]

(E)-1-(4-Bromophenyl)ethan-1-one semicarbazone

Hoong-Kun Fun, Jia Hao Goh, Mahesh Padaki, Shridhar Malladi and Arun M. Isloor

S1. Comment

In organic chemistry, a semicarbazone is a derivative of an aldehyde or ketone formed by a condensation between a ketone or aldehyde and semicarbazide. Semicarbazones find immense applications in the field of synthetic chemistry, such as in medicinal chemistry (Warren *et al.*, 1977), organometallics (Chandra & Gupta, 2005), polymers (Jain *et al.*, 2002) and herbicides (Pilgram, 1978). 4-Sulphamoylphenyl semicarbazones were synthesized and were found to possess anticonvulsant activity (Yogeeswari *et al.*, 2004). We hereby report the crystal structure of the semicarbazone of commercial importance keeping in view of their synthetic importance.

The bond lengths (Allen *et al.*, 1987) and angles in the molecule (Fig. 1) are within normal ranges and are comparable to a closely related structure (Fun *et al.*, 2009). Atoms C7, C8, N1, N2, N3 and O1 lie on the same plane with a maximum deviation of 0.057 (15) Å for atom N1. This plane makes dihedral angle of 70.9 (6)° with the C1–C6 benzene ring.

In the crystal packing (Fig. 2), N3—H3A···O1 hydrogen bonds link the molecules into one-dimensional zig-zag extended chains along the *a* axis. These chains are further stacked along the *b* axis and thus forming two-dimensional extended networks parallel to the *ab* plane. The crystal structure is further stabilized by intermolecular C9—H9A···O1 interactions.

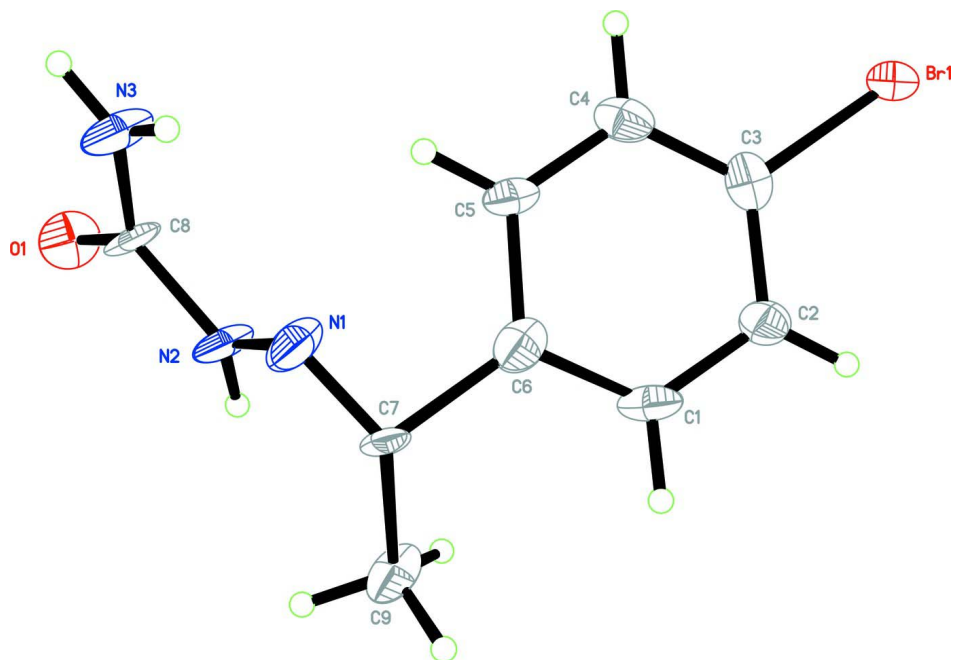
S2. Experimental

0.57 g (5.11 mmol) of semicarbazide hydrochloride and 0.54 g (6.60 mmol) of crystallized sodium acetate was dissolved in 10 ml of water (Furniss *et al.*, 1978). The reaction mixture was stirred at room temperature for 10 minutes. 1 g (5.02 mmol) 4-Bromoacetophenone was added to this and shaken well. A little alcohol was added to dissolve the turbidity. It was shaken for 10 more minutes and allowed to stand. The semicarbazone crystallizes on standing for 6 h. The separated crystals were filtered, washed with cold water and recrystallized from alcohol. Yield was found to be 1.158 g, 90.05 %. *M.p.* 479–481 K.

S3. Refinement

The H-atoms bound to N2 and N3 was located from the difference Fourier map and refined freely. The rest of the hydrogen atoms were placed in calculated positions, with C—H = 0.93 Å, $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C})$ for aromatic, and C—H = 0.96 Å, $U_{\text{iso}} = 1.5U_{\text{eq}}(\text{C})$ for CH₃ atom. A rotating group model was used for the methyl group. The N1—N2 bond was restrained with a N—N bond distance of 1.37 (1) Å. The crystal studied was a twin with the refined BASF parameter of 0.495 (1).

The final difference Fourier map had a peak/hole in the vicinity of Br1.

**Figure 1**

The molecular structure of the title compound, showing 50% probability displacement ellipsoids and the atom-numbering scheme.

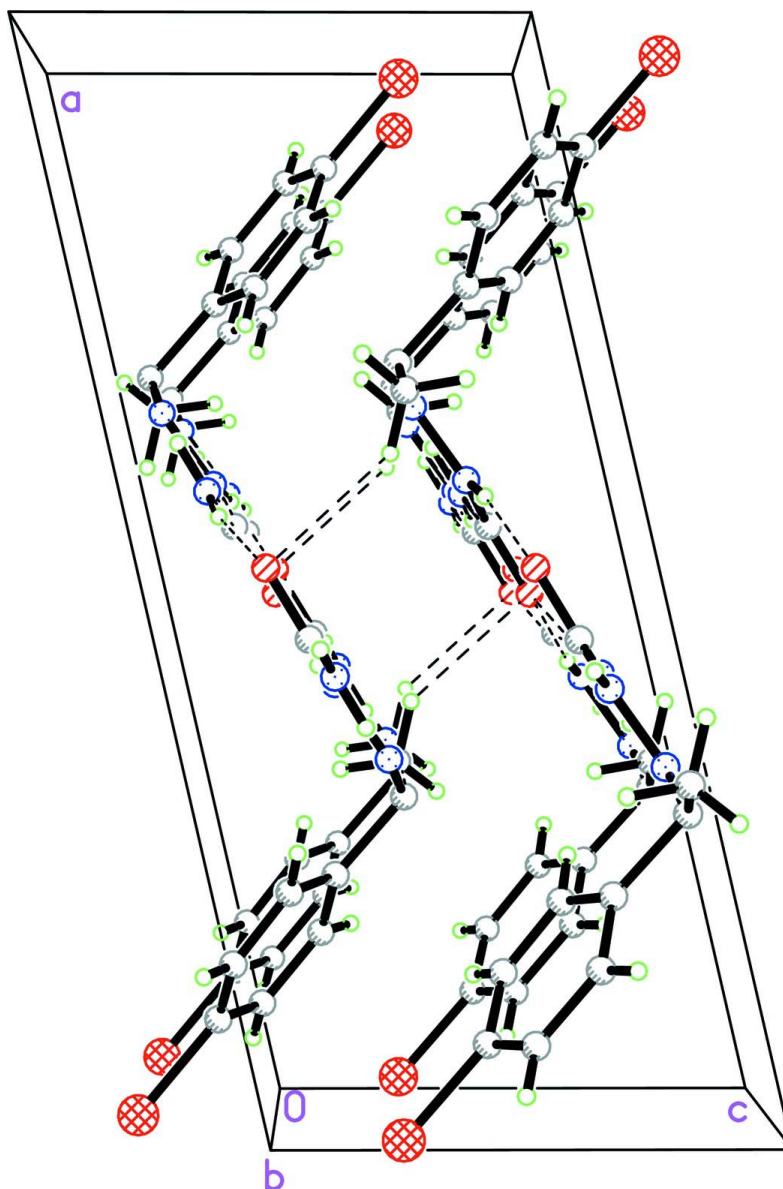


Figure 2

The crystal packing of the title compound, viewed along the *b* axis. Intermolecular interactions are shown as dashed lines.

(*E*)-1-(4-Bromophenyl)ethan-1-one semicarbazone

Crystal data

$C_9H_{10}BrN_3O$

$M_r = 256.11$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2_1/c$

$a = 17.6700\ (8)\ \text{\AA}$

$b = 7.3426\ (4)\ \text{\AA}$

$c = 7.9082\ (4)\ \text{\AA}$

$\beta = 102.953\ (3)^\circ$

$V = 999.93\ (9)\ \text{\AA}^3$

$Z = 4$

$F(000) = 512$

$D_x = 1.701\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 3514 reflections

$\theta = 3.0\text{--}28.2^\circ$

$\mu = 4.08\ \text{mm}^{-1}$

$T = 100\ \text{K}$

Block, colourless

$0.22 \times 0.12 \times 0.08\ \text{mm}$

Data collection

Bruker SMART APEXII CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan
(*SADABS*; Bruker, 2005)

$T_{\min} = 0.466$, $T_{\max} = 0.733$

12017 measured reflections

2945 independent reflections

2105 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.053$

$\theta_{\max} = 30.2^\circ$, $\theta_{\min} = 1.2^\circ$

$h = -24 \rightarrow 24$

$k = -10 \rightarrow 10$

$l = -11 \rightarrow 11$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.080$

$wR(F^2) = 0.249$

$S = 1.16$

2945 reflections

129 parameters

1 restraint

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

$w = 1/[\sigma^2(F_o^2) + (0.1217P)^2 + 9.4338P]$

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

$(\Delta/\sigma)_{\max} < 0.000$

$\Delta\rho_{\max} = 3.03 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -1.11 \text{ e } \text{\AA}^{-3}$

Special details

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

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. 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.03467 (5)	0.43707 (10)	0.2675 (2)	0.0212 (2)
N3	0.4198 (6)	0.1238 (13)	0.8352 (16)	0.034 (2)
H3A	0.4430	0.0237	0.8214	0.041*
H3B	0.3772	0.1214	0.8704	0.041*
N1	0.3450 (5)	0.4205 (11)	0.899 (2)	0.039 (3)
N2	0.4105 (5)	0.4401 (11)	0.8290 (14)	0.027 (2)
H2B	0.4257	0.5459	0.8038	0.032*
O1	0.5113 (4)	0.2902 (11)	0.7512 (13)	0.032 (2)
C1	0.1856 (7)	0.6630 (14)	0.6881 (14)	0.026 (2)
H1A	0.1894	0.7729	0.7479	0.032*
C2	0.1231 (6)	0.6387 (14)	0.5429 (16)	0.027 (2)
H2A	0.0876	0.7317	0.5050	0.032*
C3	0.1165 (6)	0.4722 (15)	0.4594 (13)	0.023 (2)
C4	0.1698 (7)	0.3367 (14)	0.5184 (14)	0.025 (2)

H4A	0.1638	0.2236	0.4642	0.030*
C5	0.2310 (7)	0.3651 (14)	0.6544 (16)	0.028 (2)
H5A	0.2671	0.2725	0.6885	0.033*
C6	0.2409 (6)	0.5321 (14)	0.7448 (17)	0.027 (2)
C7	0.3094 (5)	0.5625 (12)	0.911 (3)	0.0244 (19)
C8	0.4503 (7)	0.2840 (13)	0.8017 (14)	0.025 (2)
C9	0.3368 (5)	0.7556 (12)	0.914 (3)	0.030 (2)
H9A	0.3911	0.7610	0.9682	0.045*
H9B	0.3081	0.8292	0.9779	0.045*
H9C	0.3288	0.8004	0.7971	0.045*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0269 (4)	0.0173 (4)	0.0201 (8)	-0.0037 (3)	0.0067 (17)	-0.0023 (5)
N3	0.039 (5)	0.013 (4)	0.057 (7)	0.000 (4)	0.026 (5)	-0.004 (5)
N1	0.019 (3)	0.015 (4)	0.083 (11)	0.001 (3)	0.011 (6)	-0.004 (6)
N2	0.033 (5)	0.009 (4)	0.043 (6)	0.001 (3)	0.018 (4)	-0.004 (4)
O1	0.029 (3)	0.037 (5)	0.038 (4)	-0.003 (3)	0.021 (4)	-0.001 (5)
C1	0.043 (6)	0.013 (4)	0.023 (5)	-0.003 (4)	0.008 (5)	-0.004 (4)
C2	0.023 (5)	0.019 (4)	0.039 (6)	-0.005 (4)	0.008 (5)	-0.003 (5)
C3	0.020 (4)	0.034 (6)	0.016 (4)	-0.001 (4)	0.008 (4)	0.005 (4)
C4	0.035 (5)	0.019 (5)	0.019 (5)	-0.008 (4)	0.002 (4)	0.004 (4)
C5	0.033 (5)	0.013 (4)	0.034 (6)	0.000 (4)	0.004 (5)	-0.005 (4)
C6	0.024 (5)	0.020 (5)	0.040 (6)	0.000 (4)	0.014 (5)	0.004 (4)
C7	0.021 (3)	0.016 (3)	0.036 (6)	0.003 (3)	0.005 (8)	-0.016 (6)
C8	0.046 (6)	0.007 (4)	0.024 (5)	0.007 (4)	0.009 (5)	-0.002 (4)
C9	0.022 (4)	0.011 (3)	0.060 (8)	-0.003 (3)	0.018 (8)	0.009 (8)

Geometric parameters (Å, °)

Br1—C3	1.865 (10)	C2—C3	1.382 (16)
N3—C8	1.344 (14)	C2—H2A	0.9300
N3—H3A	0.8600	C3—C4	1.378 (15)
N3—H3B	0.8600	C4—C5	1.359 (15)
N1—C7	1.233 (11)	C4—H4A	0.9300
N1—N2	1.397 (9)	C5—C6	1.410 (15)
N2—C8	1.387 (12)	C5—H5A	0.9300
N2—H2B	0.8600	C6—C7	1.59 (2)
O1—C8	1.232 (13)	C7—C9	1.496 (12)
C1—C6	1.373 (15)	C9—H9A	0.9600
C1—C2	1.415 (16)	C9—H9B	0.9600
C1—H1A	0.9300	C9—H9C	0.9600
C8—N3—H3A	120.0	C4—C5—C6	121.4 (11)
C8—N3—H3B	120.0	C4—C5—H5A	119.3
H3A—N3—H3B	120.0	C6—C5—H5A	119.3
C7—N1—N2	115.2 (10)	C1—C6—C5	116.4 (11)

C8—N2—N1	118.1 (8)	C1—C6—C7	121.7 (9)
C8—N2—H2B	121.0	C5—C6—C7	121.8 (9)
N1—N2—H2B	121.0	N1—C7—C9	129.3 (10)
C6—C1—C2	123.1 (10)	N1—C7—C6	97.0 (12)
C6—C1—H1A	118.5	C9—C7—C6	109.2 (13)
C2—C1—H1A	118.5	O1—C8—N3	121.0 (9)
C3—C2—C1	117.8 (10)	O1—C8—N2	122.1 (9)
C3—C2—H2A	121.1	N3—C8—N2	116.9 (10)
C1—C2—H2A	121.1	C7—C9—H9A	109.5
C4—C3—C2	119.9 (10)	C7—C9—H9B	109.5
C4—C3—Br1	121.5 (8)	H9A—C9—H9B	109.5
C2—C3—Br1	118.6 (8)	C7—C9—H9C	109.5
C5—C4—C3	121.3 (10)	H9A—C9—H9C	109.5
C5—C4—H4A	119.4	H9B—C9—H9C	109.5
C3—C4—H4A	119.4		
C7—N1—N2—C8	-176.1 (14)	C4—C5—C6—C7	176.3 (13)
C6—C1—C2—C3	2.4 (17)	N2—N1—C7—C9	-20 (3)
C1—C2—C3—C4	0.1 (15)	N2—N1—C7—C6	101.6 (13)
C1—C2—C3—Br1	-179.9 (8)	C1—C6—C7—N1	-174.6 (12)
C2—C3—C4—C5	-2.4 (16)	C5—C6—C7—N1	9.4 (17)
Br1—C3—C4—C5	177.5 (9)	C1—C6—C7—C9	-38.6 (17)
C3—C4—C5—C6	2.4 (18)	C5—C6—C7—C9	145.3 (12)
C2—C1—C6—C5	-2.4 (17)	N1—N2—C8—O1	-175.3 (12)
C2—C1—C6—C7	-178.7 (12)	N1—N2—C8—N3	3.9 (16)
C4—C5—C6—C1	0.0 (17)		

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>
N2—H2B...O1 ⁱ	0.86	2.21	3.052 (12)	168
N3—H3A...O1 ⁱⁱ	0.86	2.03	2.885 (13)	171
C9—H9A...O1 ⁱⁱⁱ	0.96	2.51	3.34 (2)	144

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