

(E)-1-(4-Chlorophenyl)ethanone semicarbazoneHoong-Kun Fun,^{a*} Ching Kheng Quah,^{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
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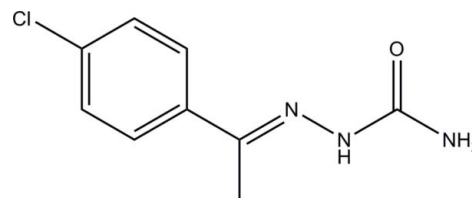
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.039; wR factor = 0.101; data-to-parameter ratio = 21.2.

In the title compound, $\text{C}_9\text{H}_{10}\text{ClN}_3\text{O}$, the semicarbazone group is approximately planar, with an r.m.s. deviation from the mean plane of 0.054 (1) Å. The dihedral angle between the least-squares planes through the semicarbazone group and the benzene ring is 30.46 (5)°. In the solid state, molecules are linked *via* intermolecular $\text{N}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds, generating $R_2^2(9)$ ring motifs which, together with $R_2^2(8)$ ring motifs formed by pairs of intermolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds, lead to the formation of a seldom-observed molecular trimer. Furthermore, $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds form $R_2^1(7)$ ring motifs with $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds, further consolidating the crystal structure. Molecules are linked by these intermolecular interactions, forming two-dimensional networks parallel to (100).

Related literature

For the synthetic utility and applications of semicarbazone derivatives, see: Warren *et al.* (1977); Chandra & Gupta (2005); Jain *et al.* (2002); Pilgram (1978); Yogeewari *et al.* (2004). For a related structure, see: Fun *et al.* (2009). For the preparation, see: Furniss *et al.* (1978). For hydrogen-bond motifs, see: Bernstein *et al.* (1995). For bond-length data, see: Allen *et al.* (1987). For the stability of the temperature controller used for the data collection, see: Cosier & Glazer (1986).

**Experimental***Crystal data*

$\text{C}_9\text{H}_{10}\text{ClN}_3\text{O}$
 $M_r = 211.65$
 Monoclinic, $C2/c$
 $a = 21.8191$ (4) Å
 $b = 7.0484$ (1) Å
 $c = 13.7249$ (2) Å
 $\beta = 109.633$ (1)°

$V = 1988.04$ (6) Å³
 $Z = 8$
 Mo $K\alpha$ radiation
 $\mu = 0.35$ mm⁻¹
 $T = 100$ K
 $0.41 \times 0.20 \times 0.03$ mm

Data collection

Bruker SMART APEXII CCD
 area-detector diffractometer
 Absorption correction: multi-scan
 (SADABS; Bruker, 2005)
 $T_{\min} = 0.867$, $T_{\max} = 0.991$

28636 measured reflections
 3539 independent reflections
 2912 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.052$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.101$
 $S = 1.04$
 3539 reflections
 167 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.45$ e Å⁻³
 $\Delta\rho_{\min} = -0.27$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N}2-\text{H}1\text{N}2\cdots\text{O}1^{\text{i}}$	0.884 (19)	2.007 (19)	2.8866 (12)	173.3 (19)
$\text{N}3-\text{H}1\text{N}3\cdots\text{N}1^{\text{ii}}$	0.835 (18)	2.264 (18)	3.0904 (14)	170.5 (16)
$\text{N}3-\text{H}2\text{N}3\cdots\text{O}1^{\text{iii}}$	0.826 (17)	2.316 (17)	3.0499 (13)	148.4 (15)
$\text{C}9-\text{H}9\text{C}\cdots\text{O}1^{\text{i}}$	0.94 (2)	2.55 (2)	3.2162 (16)	128.1 (16)

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

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).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2631).

* Thomson Reuters ResearcherID: A-3561-2009.

§ Thomson Reuters ResearcherID: A-5525-2009.

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supporting information

Acta Cryst. (2009). E65, o1634–o1635 [doi:10.1107/S160053680902279X]

(E)-1-(4-Chlorophenyl)ethanone semicarbazone**Hoong-Kun Fun, Ching Kheng Quah, 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 numerous applications in the field of synthetic chemistry, such as medicinal chemistry (Warren *et al.*, 1977), organometalics (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). Herein we report the crystal structure of the title semicarbazone which may have commercial and synthetic importance.

The bond lengths (Allen *et al.*, 1987) and angles in the molecule (Fig. 1) are within normal ranges, and are comparable to those observed in a closely related structure (Fun *et al.*, 2009). The semicarbazone group (C9/C6/C7/N1/N2/C8/O1/N3) is approximately planar, with an r.m.s. deviation of 0.054 (1) Å for atom N2 while the dihedral angle between the least-squares planes through the semicarbazone group and the benzene ring is 30.46 (5)°.

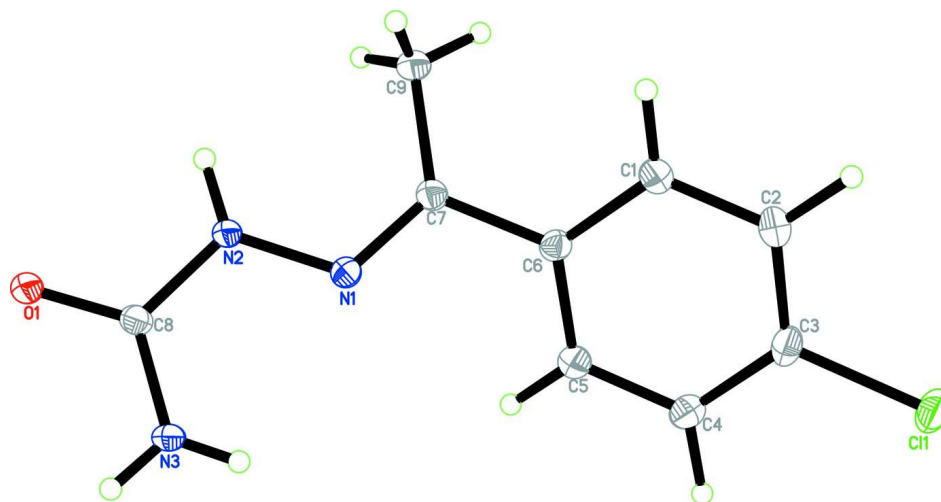
In the solid state, the molecules are linked *via* intermolecular N3—H2N3···O1 and N3—H1N3···N1 hydrogen bonds to generate $R_2^2(9)$ ring motifs which, together with the $R_2^2(8)$ ring motifs formed by pairs of intermolecular N2—H1N2···O1 hydrogen bonds, lead to the formation of a seldom-observed molecular trimer (Fig. 2). Furthermore, N2—H1N2···O1 hydrogen bonds form $R_2^1(7)$ ring motifs (Fig. 2) with C9—H9C···O1 hydrogen bonds to further consolidated the crystal structure. The molecules are linked by these intermolecular interactions to form two-dimensional networks parallel to the (1 0 0) plane.

S2. Experimental

0.780 g (7.0 mmol) of semicarbazide hydrochloride and 0.698 g (8.5 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. To this (1 g, 6.5 mmol) of 4-chloroacetophenone was added 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 1.1 g, 80.35%. *M.p.* 478–479 K.

S3. Refinement

All hydrogen atoms were located from the difference Fourier map and refined freely.

**Figure 1**

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

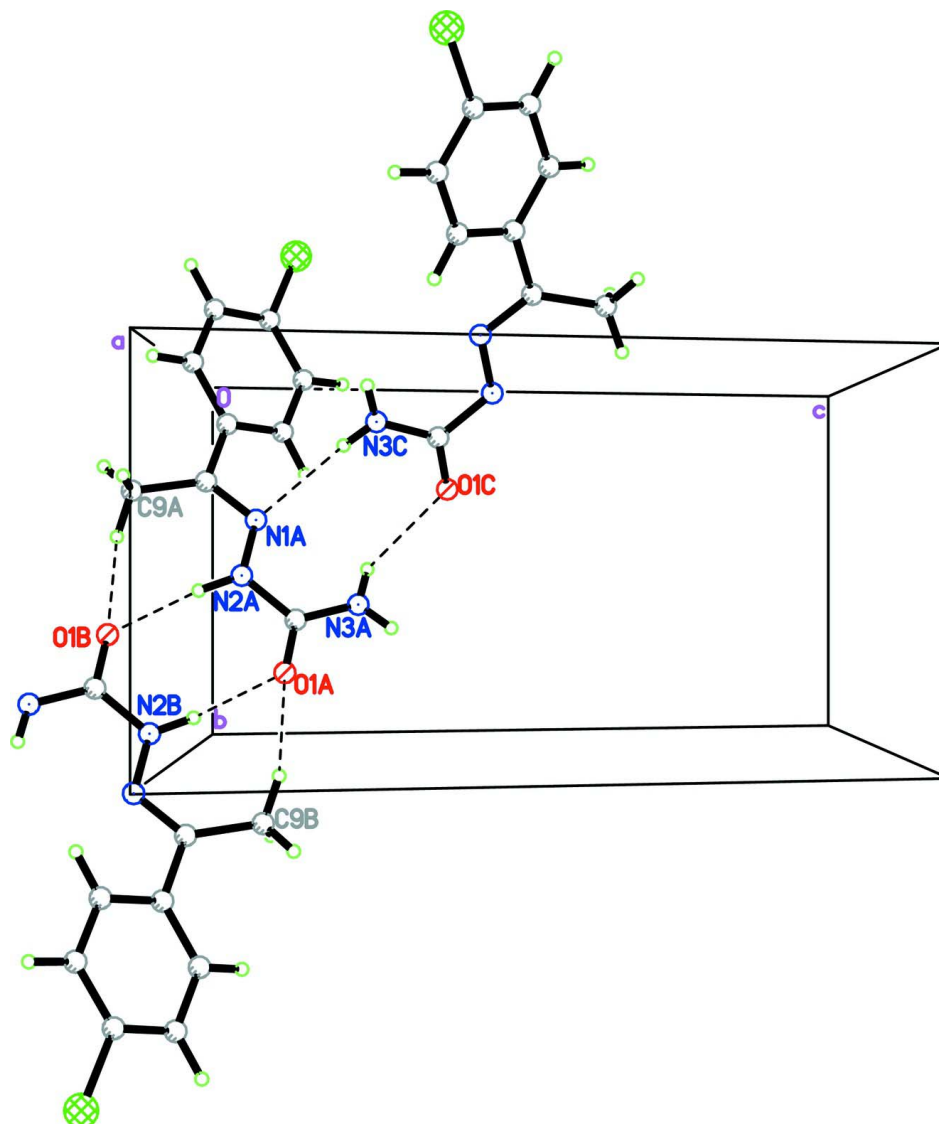


Figure 2

Part of the crystal packing of the title compound, viewed along the *a* axis, showing the formation of a molecular trimer. Atom-numbering is shown for those non-H atoms involved in hydrogen bonds and intermolecular interactions are shown as dashed lines. Molecule A is related to molecules B and C via symmetry codes of $-x + 1/2, -y + 1/2, -z$ and $-x + 1/2, y + 1/2, -z + 1/2$, respectively.

(*E*)-1-(4-Chlorophenyl)ethanone semicarbazone

Crystal data

$C_9H_{10}ClN_3O$

$M_r = 211.65$

Monoclinic, $C2/c$

Hall symbol: $-C 2yc$

$a = 21.8191(4) \text{ \AA}$

$b = 7.0484(1) \text{ \AA}$

$c = 13.7249(2) \text{ \AA}$

$\beta = 109.633(1)^\circ$

$V = 1988.04(6) \text{ \AA}^3$

$Z = 8$

$F(000) = 880$

$D_x = 1.414 \text{ Mg m}^{-3}$

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

Cell parameters from 6351 reflections

$\theta = 3.1\text{--}32.1^\circ$

$\mu = 0.35 \text{ mm}^{-1}$

$T = 100$ K $0.41 \times 0.20 \times 0.03$ mm
 Plate, colourless

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) $T_{\min} = 0.867$, $T_{\max} = 0.991$	28636 measured reflections 3539 independent reflections 2912 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.052$ $\theta_{\text{max}} = 32.3^\circ$, $\theta_{\text{min}} = 3.1^\circ$ $h = -32 \rightarrow 32$ $k = -10 \rightarrow 10$ $l = -20 \rightarrow 20$
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Refinement

Refinement on F^2 Least-squares matrix: full $R[F^2 > 2\sigma(F^2)] = 0.039$ $wR(F^2) = 0.101$ $S = 1.04$ 3539 reflections 167 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 atoms treated by a mixture of independent and constrained refinement $w = 1/[\sigma^2(F_o^2) + (0.049P)^2 + 1.2937P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\text{max}} = 0.001$ $\Delta\rho_{\text{max}} = 0.45 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\text{min}} = -0.27 \text{ e } \text{\AA}^{-3}$
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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 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	$U_{\text{iso}}^*/U_{\text{eq}}$
C11	0.023375 (16)	-0.37949 (4)	0.13113 (2)	0.02330 (9)
O1	0.28038 (4)	0.80096 (12)	0.13075 (6)	0.01675 (17)
N1	0.18652 (5)	0.38677 (13)	0.08164 (7)	0.01332 (18)
N2	0.22047 (5)	0.53956 (13)	0.06342 (7)	0.01416 (18)
N3	0.24395 (6)	0.61942 (14)	0.23627 (8)	0.0176 (2)
C1	0.11370 (6)	-0.05633 (16)	-0.01844 (9)	0.0167 (2)
C2	0.08397 (6)	-0.21004 (16)	0.01146 (10)	0.0178 (2)
C3	0.06045 (6)	-0.18847 (16)	0.09274 (9)	0.0172 (2)
C4	0.06590 (6)	-0.01713 (17)	0.14505 (9)	0.0184 (2)
C5	0.09612 (6)	0.13476 (16)	0.11541 (9)	0.0167 (2)
C6	0.12052 (6)	0.11705 (15)	0.03359 (9)	0.0136 (2)

C7	0.15469 (6)	0.27915 (15)	0.00516 (9)	0.0137 (2)
C8	0.24965 (6)	0.65995 (15)	0.14448 (8)	0.0136 (2)
C9	0.15172 (7)	0.30648 (18)	-0.10430 (9)	0.0189 (2)
H1	0.1299 (8)	-0.071 (2)	-0.0751 (13)	0.022 (4)*
H2	0.0807 (8)	-0.332 (3)	-0.0235 (13)	0.029 (4)*
H4	0.0472 (8)	-0.007 (2)	0.2047 (13)	0.026 (4)*
H5	0.0998 (8)	0.254 (2)	0.1502 (13)	0.024 (4)*
H9A	0.1211 (11)	0.237 (3)	-0.1478 (18)	0.053 (6)*
H9B	0.1901 (12)	0.271 (3)	-0.1107 (18)	0.064 (7)*
H9C	0.1416 (9)	0.433 (3)	-0.1261 (15)	0.036 (5)*
H1N2	0.2197 (8)	0.579 (3)	0.0019 (14)	0.028 (4)*
H1N3	0.2668 (8)	0.684 (2)	0.2863 (13)	0.022 (4)*
H2N3	0.2271 (8)	0.522 (2)	0.2487 (12)	0.020 (4)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.02608 (17)	0.01993 (15)	0.02367 (16)	-0.00699 (11)	0.00806 (12)	0.00422 (10)
O1	0.0227 (4)	0.0154 (4)	0.0128 (4)	-0.0054 (3)	0.0067 (3)	-0.0010 (3)
N1	0.0157 (4)	0.0121 (4)	0.0120 (4)	-0.0013 (3)	0.0044 (3)	0.0007 (3)
N2	0.0202 (5)	0.0127 (4)	0.0100 (4)	-0.0042 (3)	0.0056 (4)	-0.0007 (3)
N3	0.0272 (6)	0.0163 (4)	0.0102 (4)	-0.0065 (4)	0.0076 (4)	-0.0015 (3)
C1	0.0176 (5)	0.0165 (5)	0.0163 (5)	-0.0024 (4)	0.0064 (4)	-0.0024 (4)
C2	0.0183 (6)	0.0141 (5)	0.0204 (6)	-0.0024 (4)	0.0055 (4)	-0.0019 (4)
C3	0.0165 (5)	0.0148 (5)	0.0188 (5)	-0.0024 (4)	0.0039 (4)	0.0037 (4)
C4	0.0200 (6)	0.0194 (5)	0.0166 (5)	-0.0019 (4)	0.0074 (4)	0.0013 (4)
C5	0.0200 (6)	0.0151 (5)	0.0158 (5)	-0.0013 (4)	0.0073 (4)	-0.0010 (4)
C6	0.0138 (5)	0.0142 (5)	0.0121 (5)	-0.0004 (4)	0.0034 (4)	0.0013 (4)
C7	0.0158 (5)	0.0127 (4)	0.0121 (5)	-0.0006 (4)	0.0040 (4)	0.0003 (4)
C8	0.0164 (5)	0.0129 (4)	0.0109 (5)	-0.0002 (4)	0.0040 (4)	-0.0005 (4)
C9	0.0266 (7)	0.0185 (5)	0.0124 (5)	-0.0052 (5)	0.0077 (5)	-0.0008 (4)

Geometric parameters (Å, °)

C11—C3	1.7410 (12)	C2—C3	1.3842 (18)
O1—C8	1.2481 (13)	C2—H2	0.977 (18)
N1—C7	1.2922 (14)	C3—C4	1.3895 (17)
N1—N2	1.3768 (13)	C4—C5	1.3882 (16)
N2—C8	1.3737 (14)	C4—H4	1.033 (17)
N2—H1N2	0.883 (18)	C5—C6	1.4006 (16)
N3—C8	1.3378 (14)	C5—H5	0.958 (17)
N3—H1N3	0.835 (18)	C6—C7	1.4863 (15)
N3—H2N3	0.826 (17)	C7—C9	1.4943 (16)
C1—C2	1.3935 (16)	C9—H9A	0.88 (2)
C1—C6	1.3979 (15)	C9—H9B	0.91 (2)
C1—H1	0.963 (16)	C9—H9C	0.94 (2)
C7—N1—N2	119.12 (9)	C4—C5—C6	120.81 (11)

C8—N2—N1	117.86 (9)	C4—C5—H5	120.0 (10)
C8—N2—H1N2	115.9 (12)	C6—C5—H5	119.1 (10)
N1—N2—H1N2	125.4 (12)	C1—C6—C5	118.92 (10)
C8—N3—H1N3	116.1 (12)	C1—C6—C7	120.97 (10)
C8—N3—H2N3	124.2 (11)	C5—C6—C7	120.08 (10)
H1N3—N3—H2N3	118.0 (16)	N1—C7—C6	114.71 (10)
C2—C1—C6	120.63 (11)	N1—C7—C9	124.82 (10)
C2—C1—H1	119.1 (10)	C6—C7—C9	120.46 (10)
C6—C1—H1	120.3 (10)	O1—C8—N3	122.47 (10)
C3—C2—C1	119.16 (11)	O1—C8—N2	119.73 (10)
C3—C2—H2	120.4 (10)	N3—C8—N2	117.80 (10)
C1—C2—H2	120.4 (10)	C7—C9—H9A	112.1 (14)
C2—C3—C4	121.43 (11)	C7—C9—H9B	109.4 (15)
C2—C3—C11	119.65 (9)	H9A—C9—H9B	107 (2)
C4—C3—C11	118.92 (9)	C7—C9—H9C	111.6 (11)
C5—C4—C3	119.04 (11)	H9A—C9—H9C	105.6 (19)
C5—C4—H4	122.2 (10)	H9B—C9—H9C	110.9 (19)
C3—C4—H4	118.7 (10)		
C7—N1—N2—C8	175.03 (10)	C4—C5—C6—C7	-177.97 (11)
C6—C1—C2—C3	0.79 (18)	N2—N1—C7—C6	179.22 (9)
C1—C2—C3—C4	-0.05 (18)	N2—N1—C7—C9	0.30 (17)
C1—C2—C3—C11	-179.84 (9)	C1—C6—C7—N1	-146.43 (11)
C2—C3—C4—C5	-0.55 (19)	C5—C6—C7—N1	31.82 (15)
C11—C3—C4—C5	179.24 (9)	C1—C6—C7—C9	32.55 (16)
C3—C4—C5—C6	0.41 (18)	C5—C6—C7—C9	-149.20 (12)
C2—C1—C6—C5	-0.92 (18)	N1—N2—C8—O1	-179.37 (10)
C2—C1—C6—C7	177.35 (11)	N1—N2—C8—N3	0.92 (16)
C4—C5—C6—C1	0.32 (17)		

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H1N2 \cdots O1 ⁱ	0.884 (19)	2.007 (19)	2.8866 (12)	173.3 (19)
N3—H1N3 \cdots N1 ⁱⁱ	0.835 (18)	2.264 (18)	3.0904 (14)	170.5 (16)
N3—H2N3 \cdots O1 ⁱⁱⁱ	0.826 (17)	2.316 (17)	3.0499 (13)	148.4 (15)
C9—H9C \cdots O1 ⁱ	0.94 (2)	2.55 (2)	3.2162 (16)	128.1 (16)

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