IUCrData

(4Z)-4-(2-Oxopropylidene)-2,3,4,5-tetrahydro-1H-1,5-benzodiazepin-2-one

Jihad Sebhaoui,[a]* Youness El Bakri,[a] El Mokhtar Essassi[a] and Joel T. Mague[b]

[a]Laboratoire de Chimie Organique Hétérocyclique, Centre de Recherche des Sciences des Médicaments, URAC 21, Pôle de Compétence Pharmacochimie, Av Ibn Battouta, BP 1014, Faculté des Sciences, Université Mohammed V, Rabat, Morocco, and [b]Department of Chemistry, Tulane University, New Orleans, LA 70118, USA. *Correspondence e-mail: jihadita.chimiste@gmail.com

In the title compound, $C_{12}H_{12}N_2O_2$, the seven-membered ring adopts a boat conformation. The orientation of the acetyl substituent on this ring is partly determined by an intramolecular N—H···O hydrogen bond. In the crystal, wrinkled sheets stacked along the *a*-axis direction are formed by pairwise N—H···O and C—H···O hydrogen bonds. The sheets are connected through additional N—H···O and C—H···O hydrogen bonds stacking the molecules along the *a*-axis direction. The structure was refined as a three-component twin.

3D view
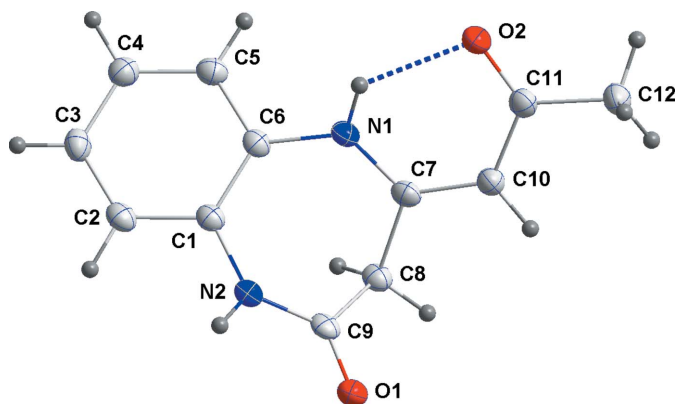

Chemical scheme
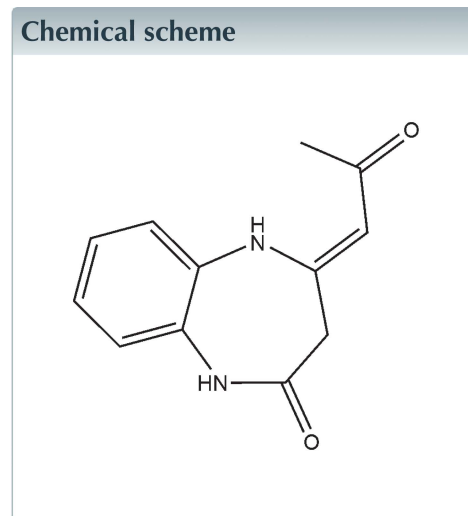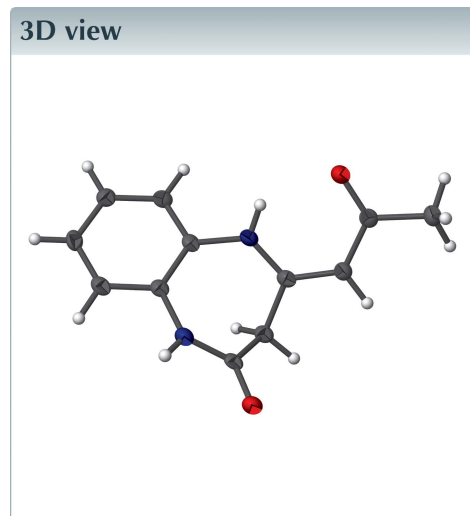
Structure description

1,5-Benzodiazepine derivatives are very useful as they are found in many biologically active compounds. Applications of these derivatives include use as anti-inflammatory (Romal *et al.*, 1991), anticonvulsant, antianxiety, and hypnotic agents (Randall *et al.*, 1973; Smiley *et al.*, 1979). As a continuation of our studies on benzodiazepine derivatives (Sebhaoui *et al.*, 2017), we report here the synthesis and the crystal structure of the title compound that was synthesized by condensation of *o*-phenylenediamine with dehydroacetic acid (3-acetyl-6-methyl-2H-pyran-2,4(3H)-dione) in refluxing xylene.

In the title molecule, the seven-membered heterocyclic ring adopts a boat conformation. A puckering analysis of this conformation gave the parameters $Q(2) = 0.777 (4)$ Å, $Q(3) = 0.257 (4)$ Å, $\varphi(2) = 209.0 (3)°$ and $\varphi(3) = 307.6 (9)°$. The dihedral angle between the C1—C6 plane and that defined by C1/C6/N1/N2 is 6.0 (2)°. The rotational orientation of the acyl substituent on this ring is partially determined by an intramolecular N1—H1A···O2 hydrogen bond (Table 1 and Fig. 1). Pairwise N2—H2A···O1 and C12—H12A···O1 hydrogen bonds (Table 1 and Fig. 2) form zigzag chains along the *b*-axis direction that are elaborated into wrinkled sheets stacked in the *a*-axis

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

| D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$A\cdots$O2	0.85 (6)	2.06 (6)	2.693 (5)	131 (5)
N1—H1$A\cdots$O2^{i}	0.85 (6)	2.55 (5)	3.291 (5)	146 (5)
N2—H2$A\cdots$O1^{ii}	0.89 (6)	2.02 (6)	2.876 (4)	161 (6)
C8—H8$B\cdots$O1^{iii}	1.00 (5)	2.58 (5)	3.469 (5)	149 (4)
C12—H12$A\cdots$O1^{iv}	0.97 (6)	2.57 (6)	3.483 (5)	157 (5)

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

Figure 1
The title molecule with labeling scheme and 50% probability ellipsoids. The intramolecular hydrogen bond is shown by a dashed line.
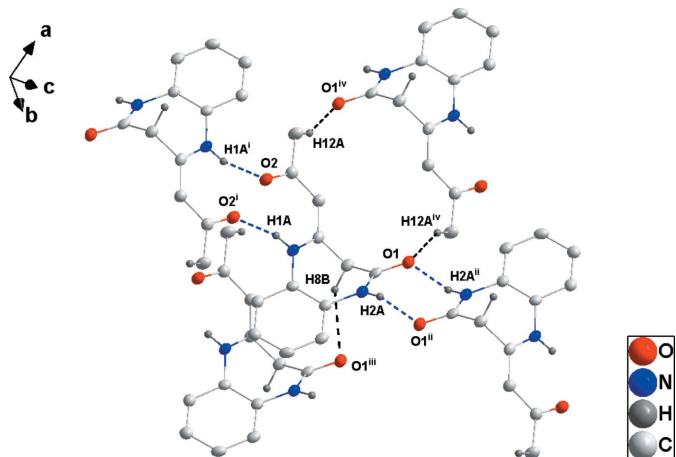
Figure 2
Detail of the intermolecular N—H$\cdots$O and C—H$\cdots$O hydrogen bonding (blue and black dashed lines, respectively). [Symmetry codes: (i) $-x+1$, $-y+1$, $-z$; (ii) $-x+2$, $-y+2$, $-z+1$; (iii) $-x, y, z$; (iv) $-x+2$, $-y+1$, $-z$.]
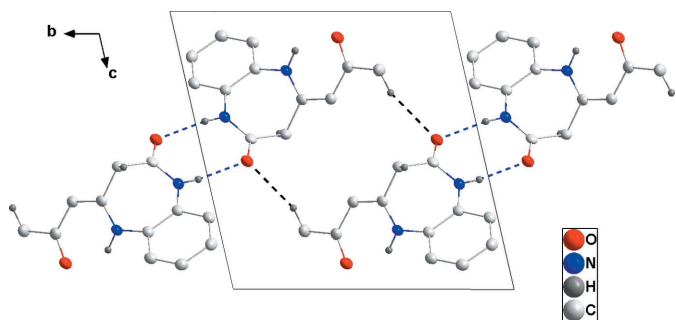
Figure 3
Packing viewed along the a-axis direction, showing the wrinkled sheets of molecules in the bc plane.

Table 2
Experimental details.

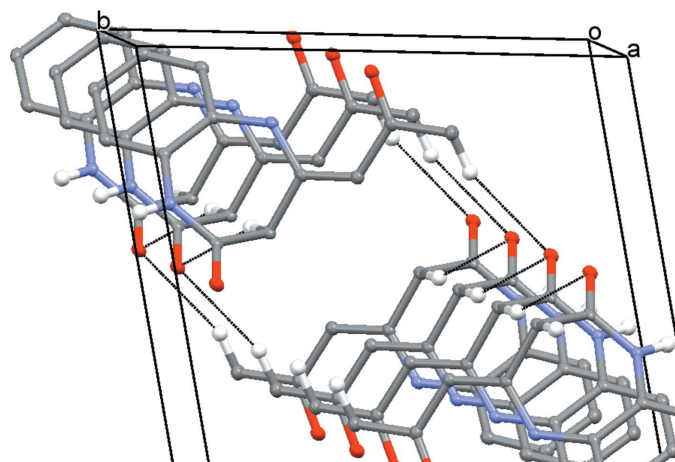| Crystal data	
Chemical formula	$C_{12}H_{12}N_2O_2$
M_r	216.24
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	100
a, b, c (Å)	4.5801 (9), 10.870 (2), 10.971 (2)
α, β, γ (°)	101.043 (3), 98.854 (3), 99.868 (3)
V (Å^3)	518.20 (18)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.10
Crystal size (mm)	0.44 × 0.26 × 0.11
Data collection	
Diffractometer	Bruker SMART APEX CCD
Absorption correction	Multi-scan (*TWINABS*; Sheldrick, 2009)
T_{min}, T_{max}	0.96, 0.99
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	26238, 26238, 19750
R_{int}	0.041
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.676
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.090, 0.281, 1.03
No. of reflections	26238
No. of parameters	195
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.34, −0.36

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *CELL_NOW* (Sheldrick, 2008a), *SHELXT* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b), *DIAMOND* (Brandenburg & Putz, 2012) and *SHELXTL* (Sheldrick, 2008b).

direction through N2—H2$A\cdots$O1 and C8—H8$B\cdots$O1 hydrogen bonds (Table 1 and Figs. 3 and 4).

Synthesis and crystallization

A mixture of *o*-phenylendiamine (80 mmol) and dehydroacetic acid (40 mmol) in 40 ml of xylene was heated under reflux for 2 h and the water was removed with a Dean–Stark trap by azeotropic distillation. After cooling, the residue obtained was washed with ethanol. The solid isolated was

Figure 4
Overall packing viewed along a.

recrystallized from *N*,*N*-dimethylformamide solution to give colourless crystals of the title compound.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The structure was refined as a three-component twin.

Acknowledgements

References

Brandenburg, K. & Putz, H. (2012). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.

Bruker (2016). *APEX3*, *SADABS* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Randall, L. O. & Kappel, B. (1973). *Benzodiazepines*, edited by S. Garattini, E. Mussini & L. O. Randall, p. 27. New York: Raven Press.

Roma, G., Grossi, G., Di Braccio, M., Ghia, M. & Mattioli, F. (1991). *Eur. J. Med. Chem.* **26**, 489–496.

Sebhaoui, J., El Bakri, Y., Rayni, I., El Bourakadi, K., Essassi, E. M. & Mague, J. T. (2017). *IUCrData*, **2**, x170493.

Sheldrick, G. M. (2008*a*). *CELL_NOW*. University of Göttingen, Göttingen, Germany.

Sheldrick, G. M. (2008*b*). *Acta Cryst.* A**64**, 112–122.

Sheldrick, G. M. (2009). *TWINABS*. University of Göttingen, Göttingen, Germany.

Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.

Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.

Smiley, R. K. (1979). *Comprehensive Organic Chemistry*, edited by D. Barton & W. D. Ollis, Vol. 4, p. 600. Oxford: Pergamon.

full crystallographic data

(4*Z*)-4-(2-Oxopropylidene)-2,3,4,5-tetrahydro-1*H*-1,5-benzodiazepin-2-one

Jihad Sebhaoui, Youness El Bakri, El Mokhtar Essassi and Joel T. Mague

(4*Z*)-4-(2-Oxopropylidene)-2,3,4,5-tetrahydro-1*H*-1,5-benzodiazepin-2-one

Crystal data

$C_{12}H_{12}N_2O_2$
$M_r = 216.24$
Triclinic, $P\bar{1}$
$a = 4.5801$ (9) Å
$b = 10.870$ (2) Å
$c = 10.971$ (2) Å
$\alpha = 101.043$ (3)°
$\beta = 98.854$ (3)°
$\gamma = 99.868$ (3)°
$V = 518.20$ (18) Å^3

$Z = 2$
$F(000) = 228$
$D_x = 1.386$ Mg m^{-3}
Mo *Kα* radiation, $\lambda = 0.71073$ Å
Cell parameters from 8186 reflections
$\theta = 2.4$–28.6°
$\mu = 0.10$ mm^{-1}
$T = 100$ K
Thick plate, colourless
$0.44 \times 0.26 \times 0.11$ mm

Data collection

Bruker SMART APEX CCD
  diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 8.3333 pixels mm^{-1}
φ and *ω* scans
Absorption correction: multi-scan
  (*TWINABS*; Sheldrick, 2009)
$T_{min} = 0.96$, $T_{max} = 0.99$

26238 measured reflections
26238 independent reflections
19750 reflections with $I > 2\sigma(I)$
$R_{int} = 0.041$
$\theta_{max} = 28.7°$, $\theta_{min} = 1.9°$
$h = -6 \rightarrow 6$
$k = -14 \rightarrow 14$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.090$
$wR(F^2) = 0.281$
$S = 1.03$
26238 reflections
195 parameters
0 restraints
Primary atom site location: structure-invariant
  direct methods

Secondary atom site location: difference Fourier
  map
Hydrogen site location: difference Fourier map
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0477P)^2 + 1.0312P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.34$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ e Å^{-3}

Special details

Experimental. The diffraction data were obtained from 3 sets of 400 frames, each of width 0.5° in ω, colllected at φ = 0.00, 90.00 and 180.00° and 2 sets of 800 frames, each of width 0.45° in φ, collected at ω = –30.00 and 210.00°. The scan time was 20 sec/frame. Analysis of 1142 reflections having $I/\sigma(I) > 12$ and chosen from the full data set with *CELL_NOW* (Sheldrick, 2008) showed the crystal to belong to the triclinic system and to be consist of three components. The raw data were processed using the multi-component version of *SAINT* under control of the 3-component orientation file generated by *CELL_NOW*.

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 $F^2 > 2\text{sigma}(F^2)$ 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. Refined as a 3-component twin.

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

	x	y	z	$U_{iso}*/U_{eq}$
O1	0.9985 (6)	0.8467 (3)	0.5387 (3)	0.0245 (7)
O2	0.5860 (6)	0.4238 (3)	0.0933 (3)	0.0260 (7)
N1	0.4186 (7)	0.6333 (3)	0.2127 (3)	0.0211 (7)
H1A	0.412 (12)	0.586 (5)	0.141 (5)	0.042 (15)*
N2	0.6861 (7)	0.8902 (3)	0.3797 (3)	0.0208 (7)
H2A	0.816 (13)	0.965 (6)	0.395 (5)	0.053 (17)*
C1	0.4276 (8)	0.8655 (4)	0.2830 (4)	0.0196 (8)
C2	0.3141 (9)	0.9716 (4)	0.2584 (4)	0.0228 (8)
H2	0.412 (10)	1.056 (5)	0.312 (4)	0.024 (11)*
C3	0.0710 (9)	0.9579 (4)	0.1619 (4)	0.0243 (9)
H3	0.002 (11)	1.031 (5)	0.145 (5)	0.035 (13)*
C4	−0.0668 (9)	0.8358 (4)	0.0887 (4)	0.0240 (9)
H4	−0.251 (10)	0.824 (5)	0.021 (4)	0.031 (12)*
C5	0.0461 (9)	0.7304 (4)	0.1113 (4)	0.0222 (8)
H5	−0.044 (11)	0.646 (5)	0.060 (5)	0.034 (13)*
C6	0.2965 (8)	0.7433 (4)	0.2065 (4)	0.0195 (8)
C7	0.5517 (8)	0.6022 (4)	0.3171 (4)	0.0200 (8)
C8	0.5476 (9)	0.6884 (4)	0.4413 (4)	0.0216 (8)
H8A	0.609 (9)	0.648 (4)	0.513 (4)	0.022 (11)*
H8B	0.343 (11)	0.708 (5)	0.439 (4)	0.029 (12)*
C9	0.7631 (9)	0.8150 (4)	0.4580 (4)	0.0204 (8)
C10	0.6880 (9)	0.4980 (4)	0.3145 (4)	0.0214 (8)
H10	0.784 (9)	0.483 (4)	0.394 (4)	0.022 (11)*
C11	0.7009 (9)	0.4115 (4)	0.1992 (4)	0.0219 (8)
C12	0.8585 (11)	0.3019 (4)	0.2103 (4)	0.0275 (9)
H12A	0.871 (13)	0.280 (6)	0.292 (6)	0.055 (17)*
H12B	0.759 (13)	0.228 (6)	0.140 (6)	0.059 (18)*
H12C	1.061 (14)	0.326 (6)	0.200 (6)	0.061 (18)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0277 (15)	0.0222 (14)	0.0211 (15)	0.0053 (12)	0.0020 (11)	0.0007 (11)
O2	0.0316 (16)	0.0233 (15)	0.0218 (15)	0.0096 (12)	0.0024 (12)	0.0010 (12)
N1	0.0251 (17)	0.0188 (16)	0.0183 (17)	0.0053 (13)	0.0046 (13)	0.0006 (13)
N2	0.0224 (17)	0.0182 (16)	0.0207 (17)	0.0035 (13)	0.0047 (13)	0.0015 (13)
C1	0.0212 (18)	0.0203 (18)	0.0179 (18)	0.0049 (15)	0.0074 (14)	0.0025 (14)
C2	0.027 (2)	0.0208 (19)	0.022 (2)	0.0058 (16)	0.0095 (16)	0.0015 (16)
C3	0.030 (2)	0.023 (2)	0.025 (2)	0.0127 (17)	0.0105 (16)	0.0066 (16)
C4	0.024 (2)	0.027 (2)	0.021 (2)	0.0081 (16)	0.0056 (16)	0.0042 (16)
C5	0.0218 (19)	0.023 (2)	0.020 (2)	0.0041 (16)	0.0058 (15)	0.0020 (16)
C6	0.0201 (18)	0.0198 (18)	0.0197 (19)	0.0062 (14)	0.0077 (14)	0.0022 (15)
C7	0.0202 (18)	0.0178 (18)	0.0200 (19)	0.0002 (14)	0.0052 (15)	0.0018 (15)
C8	0.026 (2)	0.0214 (19)	0.0184 (19)	0.0051 (16)	0.0080 (15)	0.0028 (15)
C9	0.0251 (19)	0.0197 (18)	0.0166 (18)	0.0067 (15)	0.0089 (15)	−0.0009 (14)
C10	0.0235 (19)	0.0197 (18)	0.021 (2)	0.0049 (15)	0.0043 (15)	0.0040 (15)
C11	0.0222 (19)	0.0191 (18)	0.023 (2)	0.0029 (15)	0.0040 (15)	0.0039 (15)
C12	0.036 (2)	0.023 (2)	0.026 (2)	0.0123 (18)	0.0059 (18)	0.0049 (17)

Geometric parameters (Å, º)

O1—C9	1.236 (5)	C4—H4	1.01 (5)
O2—C11	1.242 (4)	C5—C6	1.395 (5)
N1—C7	1.343 (5)	C5—H5	0.96 (5)
N1—C6	1.412 (5)	C7—C10	1.382 (6)
N1—H1A	0.85 (6)	C7—C8	1.503 (5)
N2—C9	1.344 (5)	C8—C9	1.511 (5)
N2—C1	1.412 (5)	C8—H8A	1.00 (4)
N2—H2A	0.89 (6)	C8—H8B	1.00 (5)
C1—C2	1.399 (5)	C10—C11	1.440 (6)
C1—C6	1.405 (5)	C10—H10	0.97 (4)
C2—C3	1.379 (6)	C11—C12	1.509 (6)
C2—H2	0.98 (5)	C12—H12A	0.97 (6)
C3—C4	1.397 (6)	C12—H12B	0.98 (6)
C3—H3	0.95 (5)	C12—H12C	0.95 (6)
C4—C5	1.383 (6)		
C7—N1—C6	127.0 (3)	N1—C7—C10	123.5 (4)
C7—N1—H1A	119 (4)	N1—C7—C8	116.2 (4)
C6—N1—H1A	114 (4)	C10—C7—C8	120.3 (4)
C9—N2—C1	127.9 (3)	C7—C8—C9	109.8 (3)
C9—N2—H2A	113 (4)	C7—C8—H8A	111 (3)
C1—N2—H2A	119 (4)	C9—C8—H8A	109 (2)
C2—C1—C6	119.5 (4)	C7—C8—H8B	109 (3)
C2—C1—N2	116.7 (3)	C9—C8—H8B	106 (3)
C6—C1—N2	123.6 (3)	H8A—C8—H8B	112 (4)
C3—C2—C1	121.0 (4)	O1—C9—N2	122.0 (4)

C3—C2—H2	121 (3)	O1—C9—C8	121.6 (4)
C1—C2—H2	118 (3)	N2—C9—C8	116.4 (3)
C2—C3—C4	119.5 (4)	C7—C10—C11	123.3 (4)
C2—C3—H3	120 (3)	C7—C10—H10	119 (3)
C4—C3—H3	121 (3)	C11—C10—H10	118 (3)
C5—C4—C3	119.9 (4)	O2—C11—C10	122.4 (4)
C5—C4—H4	120 (3)	O2—C11—C12	119.9 (4)
C3—C4—H4	120 (3)	C10—C11—C12	117.7 (4)
C4—C5—C6	121.2 (4)	C11—C12—H12A	114 (4)
C4—C5—H5	121 (3)	C11—C12—H12B	109 (4)
C6—C5—H5	118 (3)	H12A—C12—H12B	112 (5)
C5—C6—C1	118.7 (4)	C11—C12—H12C	109 (4)
C5—C6—N1	117.3 (3)	H12A—C12—H12C	106 (5)
C1—C6—N1	123.8 (3)	H12B—C12—H12C	107 (5)
C9—N2—C1—C2	148.6 (4)	C7—N1—C6—C1	38.2 (6)
C9—N2—C1—C6	−36.0 (6)	C6—N1—C7—C10	−174.5 (4)
C6—C1—C2—C3	1.4 (6)	C6—N1—C7—C8	5.3 (5)
N2—C1—C2—C3	177.0 (3)	N1—C7—C8—C9	−72.2 (4)
C1—C2—C3—C4	0.9 (6)	C10—C7—C8—C9	107.6 (4)
C2—C3—C4—C5	−1.7 (6)	C1—N2—C9—O1	179.2 (4)
C3—C4—C5—C6	0.1 (6)	C1—N2—C9—C8	−0.1 (6)
C4—C5—C6—C1	2.2 (6)	C7—C8—C9—O1	−111.1 (4)
C4—C5—C6—N1	−172.4 (3)	C7—C8—C9—N2	68.3 (5)
C2—C1—C6—C5	−3.0 (5)	N1—C7—C10—C11	−0.2 (6)
N2—C1—C6—C5	−178.2 (3)	C8—C7—C10—C11	−179.9 (3)
C2—C1—C6—N1	171.3 (3)	C7—C10—C11—O2	−0.9 (6)
N2—C1—C6—N1	−4.0 (6)	C7—C10—C11—C12	179.7 (4)
C7—N1—C6—C5	−147.5 (4)		

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O2	0.85 (6)	2.06 (6)	2.693 (5)	131 (5)
N1—H1A···O2[i]	0.85 (6)	2.55 (5)	3.291 (5)	146 (5)
N2—H2A···O1[ii]	0.89 (6)	2.02 (6)	2.876 (4)	161 (6)
C8—H8B···O1[iii]	1.00 (5)	2.58 (5)	3.469 (5)	149 (4)
C12—H12A···O1[iv]	0.97 (6)	2.57 (6)	3.483 (5)	157 (5)

Symmetry codes: (i) −x+1, −y+1, −z; (ii) −x+2, −y+2, −z+1; (iii) x−1, y, z; (iv) −x+2, −y+1, −z+1.