

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

N-(3,4-Dichlorophenyl)-3-oxobutanamide

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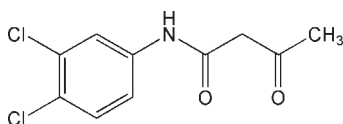
Received 21 November 2009; accepted 28 November 2009

Key indicators: single-crystal X-ray study; $T = 200$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.048; wR factor = 0.123; data-to-parameter ratio = 27.3.

In the title compound, $\text{C}_{10}\text{H}_9\text{Cl}_2\text{NO}_2$, the acetamide residue is twisted out of the phenyl ring plane by 25.40 (9°). An intramolecular $\text{C}-\text{H}\cdots\text{O}$ close contact is observed. The N atom of the butanamide unit forms an intermolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bond with the symmetry-related carbonyl O atom, interlinking molecules into a $C(4)$ chain along [100]. Additional $\text{C}-\text{H}\cdots\text{O}$ intermolecular interactions and $\text{Cl}\cdots\text{Cl}$ contacts [3.4364 (8) Å] contribute to the stability of the crystal packing.

Related literature

For the synthesis and biological activity of the title compound, see: Lliopoulos *et al.* (1986); Grissar *et al.* (1982). For related structures, see: Whitaker (1986, 1987, 1988); Whitaker & Walker (1987); Brown & Yadav (1984); Tai *et al.* (2005); Sundar *et al.* (2005); Guo (2004); Robin *et al.* (2002). For hydrogen-bond motifs, see: Bernstein *et al.* (1995). For density functional theory (DFT), see: Becke (1988, 1993); Hehre *et al.* (1986); Lee *et al.* (1988); Schmidt & Polik (2007). For the GAUSSIAN03 program package, see: Frisch *et al.* (2004).



Experimental

Crystal data

$\text{C}_{10}\text{H}_9\text{Cl}_2\text{NO}_2$
 $M_r = 246.08$
Orthorhombic, $Pbca$
 $a = 9.7171$ (4) Å

$b = 8.2834$ (5) Å
 $c = 27.4857$ (16) Å
 $V = 2212.3$ (2) Å³
 $Z = 8$

Mo $K\alpha$ radiation
 $\mu = 0.57$ mm⁻¹

$T = 200$ K
 $0.56 \times 0.35 \times 0.14$ mm

Data collection

Oxford Diffraction Gemini diffractometer
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2007)
 $T_{\min} = 0.725$, $T_{\max} = 0.924$

16980 measured reflections
3745 independent reflections
1910 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.045$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.048$
 $wR(F^2) = 0.123$
 $S = 1.04$
3745 reflections

137 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.21$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.27$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N}-\text{H}0\text{A}\cdots\text{O}1^i$	0.88	1.95	2.824 (2)	172
$\text{C}6-\text{H}6\text{A}\cdots\text{O}1$	0.95	2.35	2.865 (2)	113
$\text{C}2-\text{H}2\text{A}\cdots\text{O}2^{ii}$	0.95	2.58	3.345 (2)	138
$\text{C}8-\text{H}8\text{A}\cdots\text{O}2^{iii}$	0.99	2.45	3.327 (2)	147

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

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2007); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2007); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

RJB acknowledges the NSF MRI program (grant No. CHE-0619278) for funds to purchase an X-ray diffractometer.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI2974).

References

- Becke, A. D. (1988). *Phys. Rev.* **A38**, 3098–100.
Becke, A. D. (1993). *J. Chem. Phys.* **98**, 5648–5652.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N. L. (1995). *Angew. Chem. Int. Ed. Eng.* **34**, 1555–1573.
Brown, C. J. & Yadav, H. R. (1984). *Acta Cryst.* **C40**, 564–566.
Frisch, M. J., *et al.* (2004). *GAUSSIAN03*. Gaussian Inc., Wallingford, CT, USA.
Grissar, J. M., Schnettler, R. A. & Dage, R. C. (1982). US Patent 4329470.
Guo, M.-L. (2004). *Acta Cryst.* **E60**, o736–o737.
Hehre, W. J., Random, L., Schleyer, P. & Pople, J. A. (1986). *Ab Initio Molecular Orbital Theory*. New York: Wiley.
Lee, C., Yang, W. & Parr, R. G. (1988). *Phys. Rev.* **B37**, 785–789.
Lliopoulos, P., Fallon, G. D. & Murray, S. (1986). *J. Chem. Soc. Dalton Trans.* pp. 437–443.
Oxford Diffraction (2007). *CrysAlis PRO* and *CrysAlis RED*. Oxford Diffraction Ltd, Abingdon, England.
Robin, M., Galy, J.-P., Kenz, A. & Pierrot, M. (2002). *Acta Cryst.* **E58**, o644–o645.
Schmidt, J. R. & Polik, W. F. (2007). *WebMO Pro*. WebMO, LLC: Holland, MI, USA; available from <http://www.webmo.net>.

- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Sundar, T. V., Parthasarathi, V., Walfort, B., Lang, H., Piplani, P. & Malik, R. (2005). *Acta Cryst.* **E61**, o2868–o2870.
Tai, X.-S., Liu, W.-Y., Liu, Y.-Z. & Li, Y.-Z. (2005). *Acta Cryst.* **E61**, o389–o390.
Whitaker, A. (1986). *Acta Cryst.* **C42**, 1566–1569.
Whitaker, A. (1987). *Acta Cryst.* **C43**, 2141–2144.
Whitaker, A. (1988). *Acta Cryst.* **C44**, 1587–1590.
Whitaker, A. & Walker, N. P. C. (1987). *Acta Cryst.* **C43**, 2137–2141.

supporting information

Acta Cryst. (2010). E66, o58–o59 [doi:10.1107/S1600536809051307]

***N*-(3,4-Dichlorophenyl)-3-oxobutanamide**

Mukesh M. Jotani, Jerry P. Jasinski, Bharat B. Baldaniya and Ray J. Butcher

S1. Comment

Acetoacetanilide, a very useful chemical intermediate in the production of pigments (Whitaker, 1986, 1987, 1988; Whitaker & Walker, 1987; Brown & Yadav, 1984) possesses cardiogenic, antihypertensive and anti-thrombotic properties (Grissar *et al.*, 1982). The title compound, (I), is used as an intermediate in the synthesis of acetoacetanilide and a variety of other biologically important heterocyclic compounds containing pyridine, pyrimidine and imidazole. In the view of the importance of (I), its crystal structure is determined.

In (I), the C=O bond lengths are 1.2292 (18) Å and 1.207 (2) Å which confirms that the compound is in the keto form (Fig. 1). The phenyl ring (C1–C6) is planar with a maximum deviation of 0.007 (1) Å for the C1 atom, from the least-squares plane of the ring. The short C–N distances of 1.407 (2) and 1.346 (2) Å and C1–N–C7 larger bond angle of 126.9 (13)° may be attributed to the involvement of the butanamide N atom in the intermolecular N–H···O interaction and a short intramolecular contact (1.95 Å) between O1 and H0A which is less than their van der Waals radii (2.72 Å). Similar short contacts are also observed in other related structures containing the acetamide residue (Sundar *et al.*, 2005; Guo, 2004; Robin *et al.*, 2002). Atoms N, C7, O1 and C8 forming the acetamide residue are coplanar with a maximum deviation of -0.005 (2) Å for the C7 atom. The acetamide residue is twisted considerably from the least-squares plane of phenyl ring having a dihedral angle of 25.40 (9)°. Atoms C8, C9, O2 and C10 from the *O*-acetyl group are also coplanar displaying a dihedral angle of 49.21 (10)° with the mean plane of the phenyl ring (C1–C6) and 73.78 (11)° with the least-squares plane of the acetamide residue.

The N atom in the butanamide moiety forms an intermolecular hydrogen bond (N–H0A···O1) with the symmetry related carbonyl oxygen atom interlinking molecules into an one-dimensional chain along the [100] (Fig. 2 and Table 1) forming a C(4) graph-set motif (Bernstein *et al.*, 1995). Torsional angles C7–C8–C9–O2 (15.9 (2)°) and O1–C7–C8–C9 (67.3 (2)°) about C8–C9 and C7–C8, respectively, suggest the involvement of O1 and O2 atoms in a weak C–H···O1 intermolecular hydrogen bonding interaction. Atoms C2 from the phenyl ring (C1–C6) and C8 from the butanamide group form weak, bifurcated intermolecular hydrogen bonds with nearby symmetry related O2 atoms (Table 2). In addition, a short intramolecular C–H···O contact (Table 2) and a weak intermolecular C1···C1 contact (3.4364 (8) Å) exists which influences crystal packing.

Following a density functional theory calculation (Schmidt & Polik 2007) at the B3LYP 6–31-G(*d*) level (Becke, 1988, 1993; Lee *et al.* 1988; Hehre *et al.* 1986) with the GAUSSIAN03 program package (Frisch *et al.* 2004) the angle between the mean planes of the C8/C9/O2/C10 and N/C7/O1/C8 groups change from 73.7 (8)° to 33.0 (2)°. The angle between the least-squares plane of the benzene ring and the mean planes of the C8/C9/O2/C10 and N/C7/O1/C8 groups change from 49.2 (1)° and 25.4 (1)° to 30.1 (5)° and 3.6 (5)°, respectively. This results in twisting the C8=O2 keto group to be in the proximity of the butanamide N atom forming a pseudo intramolecular N–H···O hydrogen bond interaction (D–H = 1.02 (0) Å; H···A = 1.92 (0) Å; D···A = 2.76 (1) Å; D–H···A = 137.6 (9)°). These results support the collective effects of the intra and intermolecular hydrogen bonding described above influencing crystal packing.

S2. Experimental

The title compound was prepared by a method similar to that of Lliopoulos *et al.* (1986). A solution of 3,4-dichloroaniline (10 mmol) in benzene (30 ml) was added to a solution of ethyl acetoacetate (10 mmol) and the reaction mixture was refluxed for 2 h with stirring. The resulting precipitate was collected by filtration, washed several times with benzene and dried *in vacuo* (yield 86%). An ethanol solution of the title compound was allowed to evaporate slowly and colorless crystals of (I) were obtained after a week.

S3. Refinement

All of the H atoms were placed in their calculated positions and then refined using the riding model with C–H = 0.95–0.99 Å, N–H = 0.88 Å and with $U_{\text{iso}}(\text{H}) = 1.19\text{--}1.50U_{\text{eq}}(\text{C})$ and $1.18U_{\text{eq}}(\text{N})$.

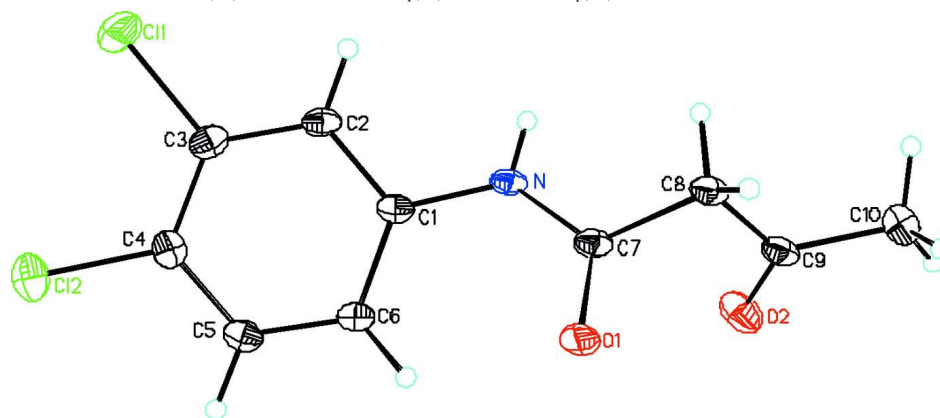


Figure 1

The molecular structure of $\text{C}_{10}\text{H}_9\text{NO}_2\text{Cl}_2$, (I), showing the atom-numbering scheme and 50% probability displacement ellipsoids.

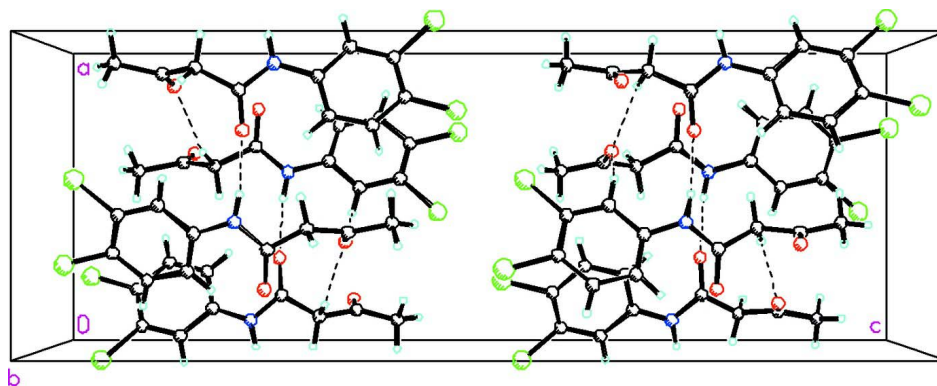


Figure 2

Molecular packing for (I) viewed down the *b* axis. Dashed lines indicate N—H \cdots O and C—H \cdots O intermolecular hydrogen bonds.

N-(3,4-Dichlorophenyl)-3-oxobutanamide

Crystal data

$\text{C}_{10}\text{H}_9\text{Cl}_2\text{NO}_2$
 $M_r = 246.08$

Orthorhombic, *Pbca*
Hall symbol: -P 2ac 2ab

$a = 9.7171$ (4) Å
 $b = 8.2834$ (5) Å
 $c = 27.4857$ (16) Å
 $V = 2212.3$ (2) Å³
 $Z = 8$
 $F(000) = 1008$
 $D_x = 1.478$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 4228 reflections
 $\theta = 4.9\text{--}32.4^\circ$
 $\mu = 0.57$ mm⁻¹
 $T = 200$ K
 Plate, colorless
 $0.56 \times 0.35 \times 0.14$ mm

Data collection

Oxford Diffraction Gemini
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 Detector resolution: 10.5081 pixels mm⁻¹
 φ and ω scans
 Absorption correction: multi-scan
 (*CrysAlis RED*; Oxford Diffraction, 2007)
 $T_{\min} = 0.725$, $T_{\max} = 0.924$

16980 measured reflections
 3745 independent reflections
 1910 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.045$
 $\theta_{\max} = 32.5^\circ$, $\theta_{\min} = 4.9^\circ$
 $h = -14 \rightarrow 14$
 $k = -11 \rightarrow 12$
 $l = -39 \rightarrow 39$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.048$
 $wR(F^2) = 0.123$
 $S = 1.04$
 3745 reflections
 137 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-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0532P)^2 + 0.0634P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.21$ e Å⁻³
 $\Delta\rho_{\min} = -0.27$ e Å⁻³

Special details

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 (Å²)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.44746 (6)	0.24662 (8)	0.45002 (2)	0.0723 (2)
Cl2	0.72279 (6)	0.05651 (7)	0.47381 (2)	0.0685 (2)
O1	0.79285 (11)	0.25949 (19)	0.23755 (5)	0.0569 (4)
O2	0.64604 (16)	0.07935 (16)	0.15306 (6)	0.0661 (4)
N	0.58187 (12)	0.24207 (16)	0.27204 (5)	0.0362 (3)
H0A	0.4932	0.2505	0.2661	0.043*
C1	0.61935 (15)	0.19559 (18)	0.31946 (6)	0.0335 (4)
C2	0.52923 (16)	0.2333 (2)	0.35679 (7)	0.0390 (4)
H2A	0.4453	0.2872	0.3496	0.047*

C3	0.56032 (17)	0.1931 (2)	0.40451 (7)	0.0429 (4)
C4	0.68175 (19)	0.1122 (2)	0.41514 (7)	0.0431 (4)
C5	0.77092 (18)	0.0733 (2)	0.37786 (7)	0.0444 (4)
H5A	0.8543	0.0185	0.3851	0.053*
C6	0.74098 (17)	0.1129 (2)	0.33015 (7)	0.0401 (4)
H6A	0.8027	0.0840	0.3048	0.048*
C7	0.66728 (16)	0.2750 (2)	0.23478 (7)	0.0382 (4)
C8	0.60112 (17)	0.3356 (2)	0.18869 (7)	0.0420 (4)
H8A	0.6441	0.4395	0.1795	0.050*
H8B	0.5023	0.3560	0.1949	0.050*
C9	0.61455 (17)	0.2188 (2)	0.14672 (7)	0.0434 (4)
C10	0.5849 (2)	0.2844 (3)	0.09710 (8)	0.0644 (6)
H10A	0.5898	0.1969	0.0732	0.097*
H10B	0.6529	0.3675	0.0890	0.097*
H10C	0.4925	0.3319	0.0967	0.097*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.0658 (4)	0.0910 (5)	0.0601 (3)	0.0116 (3)	0.0270 (3)	0.0049 (3)
C12	0.0810 (4)	0.0739 (4)	0.0507 (3)	-0.0003 (3)	-0.0064 (3)	0.0127 (3)
O1	0.0190 (6)	0.0920 (11)	0.0598 (8)	0.0011 (6)	0.0034 (5)	0.0184 (8)
O2	0.0785 (10)	0.0437 (8)	0.0759 (11)	0.0137 (7)	-0.0205 (8)	0.0024 (7)
N	0.0162 (5)	0.0413 (8)	0.0510 (8)	0.0006 (6)	0.0005 (6)	0.0015 (7)
C1	0.0230 (7)	0.0275 (8)	0.0500 (10)	-0.0048 (6)	-0.0003 (7)	-0.0027 (7)
C2	0.0258 (8)	0.0354 (9)	0.0557 (11)	-0.0007 (7)	0.0047 (7)	-0.0004 (8)
C3	0.0395 (10)	0.0379 (9)	0.0514 (11)	-0.0054 (8)	0.0113 (8)	0.0002 (8)
C4	0.0477 (10)	0.0373 (9)	0.0443 (11)	-0.0068 (8)	-0.0028 (8)	0.0046 (8)
C5	0.0388 (9)	0.0372 (10)	0.0572 (12)	0.0056 (8)	-0.0034 (9)	0.0019 (9)
C6	0.0314 (8)	0.0382 (10)	0.0508 (10)	0.0051 (7)	0.0012 (8)	-0.0022 (8)
C7	0.0232 (7)	0.0385 (9)	0.0530 (10)	-0.0001 (7)	0.0013 (7)	0.0031 (8)
C8	0.0285 (8)	0.0382 (10)	0.0593 (12)	0.0045 (8)	0.0020 (8)	0.0094 (8)
C9	0.0276 (8)	0.0425 (11)	0.0601 (12)	0.0027 (8)	-0.0050 (8)	0.0089 (9)
C10	0.0637 (13)	0.0739 (15)	0.0558 (13)	0.0119 (11)	-0.0047 (11)	0.0150 (11)

Geometric parameters (Å, °)

C11—C3	1.7215 (18)	C4—C5	1.380 (3)
C12—C4	1.7241 (19)	C5—C6	1.383 (3)
O1—C7	1.2292 (18)	C5—H5A	0.95
O2—C9	1.207 (2)	C6—H6A	0.95
N—C7	1.346 (2)	C7—C8	1.507 (2)
N—C1	1.407 (2)	C8—C9	1.511 (3)
N—H0A	0.88	C8—H8A	0.99
C1—C2	1.385 (2)	C8—H8B	0.99
C1—C6	1.397 (2)	C9—C10	1.496 (3)
C2—C3	1.387 (3)	C10—H10A	0.98
C2—H2A	0.95	C10—H10B	0.98

C3—C4	1.388 (3)	C10—H10C	0.98
C7—N—C1	126.91 (13)	C1—C6—H6A	120.2
C7—N—H0A	116.5	O1—C7—N	122.94 (16)
C1—N—H0A	116.5	O1—C7—C8	120.69 (16)
C2—C1—C6	119.32 (16)	N—C7—C8	116.37 (13)
C2—C1—N	117.45 (14)	C7—C8—C9	113.05 (15)
C6—C1—N	123.22 (15)	C7—C8—H8A	109.0
C1—C2—C3	120.60 (15)	C9—C8—H8A	109.0
C1—C2—H2A	119.7	C7—C8—H8B	109.0
C3—C2—H2A	119.7	C9—C8—H8B	109.0
C2—C3—C4	120.01 (16)	H8A—C8—H8B	107.8
C2—C3—C11	119.13 (13)	O2—C9—C10	121.89 (19)
C4—C3—C11	120.86 (15)	O2—C9—C8	121.61 (18)
C5—C4—C3	119.36 (17)	C10—C9—C8	116.50 (17)
C5—C4—C12	119.13 (14)	C9—C10—H10A	109.5
C3—C4—C12	121.51 (15)	C9—C10—H10B	109.5
C4—C5—C6	121.12 (16)	H10A—C10—H10B	109.5
C4—C5—H5A	119.4	C9—C10—H10C	109.5
C6—C5—H5A	119.4	H10A—C10—H10C	109.5
C5—C6—C1	119.57 (16)	H10B—C10—H10C	109.5
C5—C6—H6A	120.2		
C7—N—C1—C2	152.83 (15)	C12—C4—C5—C6	178.76 (14)
C7—N—C1—C6	-27.9 (2)	C4—C5—C6—C1	0.9 (3)
C6—C1—C2—C3	1.5 (2)	C2—C1—C6—C5	-1.5 (2)
N—C1—C2—C3	-179.14 (15)	N—C1—C6—C5	179.22 (15)
C1—C2—C3—C4	-1.0 (3)	C1—N—C7—O1	3.9 (3)
C1—C2—C3—C11	178.40 (13)	C1—N—C7—C8	-175.10 (15)
C2—C3—C4—C5	0.3 (3)	O1—C7—C8—C9	67.3 (2)
C11—C3—C4—C5	-179.00 (14)	N—C7—C8—C9	-113.63 (17)
C2—C3—C4—C12	-178.72 (14)	C7—C8—C9—O2	15.9 (2)
C11—C3—C4—C12	1.9 (2)	C7—C8—C9—C10	-164.88 (15)
C3—C4—C5—C6	-0.3 (3)		

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>
N—H0A...O1 ⁱ	0.88	1.95	2.824 (2)	172
C6—H6A...O1	0.95	2.35	2.865 (2)	113
C2—H2A...O2 ⁱⁱ	0.95	2.58	3.345 (2)	138
C8—H8A...O2 ⁱⁱⁱ	0.99	2.45	3.327 (2)	147

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