

Acta Crystallographica Section E

## Structure Reports

Online

ISSN 1600-5368

## N-(3-Chlorophenyl)maleamic acid

 B. Thimme Gowda,<sup>a\*</sup> Miroslav Tokarčík,<sup>b</sup> K. Shakuntala,<sup>a</sup> Jozef Kožíšek<sup>b</sup> and Hartmut Fuess<sup>c</sup>

<sup>a</sup>Department of Chemistry, Mangalore University, Mangalagangothri 574 199, Mangalore, India, <sup>b</sup>Faculty of Chemical and Food Technology, Slovak Technical University, Radlinského 9, SK-812 37 Bratislava, Slovak Republic, and <sup>c</sup>Institute of Materials Science, Darmstadt University of Technology, Petersenstrasse 23, D-64287 Darmstadt, Germany

Correspondence e-mail: gowdabt@yahoo.com

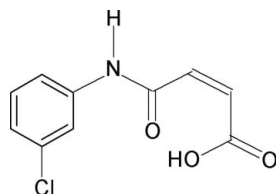
Received 1 June 2010; accepted 4 June 2010

Key indicators: single-crystal X-ray study;  $T = 295$  K; mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å;  $R$  factor = 0.028;  $wR$  factor = 0.081; data-to-parameter ratio = 13.4.

In the title compound,  $\text{C}_{10}\text{H}_8\text{ClNO}_3$ , the molecular conformation is stabilized by two intramolecular hydrogen bonds. The first is a short  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bond within the maleamic acid unit and the second is a  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bond which connects the amide group with the phenyl ring. The maleamic acid unit is essentially planar, with an r.m.s. deviation of 0.044 Å, and makes a dihedral angle of 15.2 (1)° with the phenyl ring. In the crystal, intermolecular  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds link the molecules into  $C(7)$  chains running [010].

## Related literature

For studies on the effect of ring- and side-chain substitutions on the crystal structures of amides, see: Gowda *et al.* (2010*a,b*); Prasad *et al.* (2002); Shakuntala *et al.* (2009). For hydrogen-bond motifs, see: Bernstein *et al.* (1995).



## Experimental

## Crystal data

$\text{C}_{10}\text{H}_8\text{ClNO}_3$   $V = 981.69$  (5) Å<sup>3</sup>  
 $M_r = 225.62$   $Z = 4$   
 Monoclinic,  $P2_1/c$   $\text{Mo } K\alpha$  radiation  
 $a = 10.7779$  (3) Å  $\mu = 0.37$  mm<sup>-1</sup>  
 $b = 13.2103$  (4) Å  $T = 295$  K  
 $c = 7.1372$  (2) Å  $0.55 \times 0.09 \times 0.06$  mm  
 $\beta = 104.976$  (3)°

## Data collection

Oxford Diffraction Gemini R, CCD diffractometer 15632 measured reflections  
 Absorption correction: analytical (CrysAlis PRO; Oxford Diffraction, 2009) 1829 independent reflections  
 $R_{\text{int}} = 0.027$   
 $T_{\text{min}} = 0.852$ ,  $T_{\text{max}} = 0.982$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$  136 parameters  
 $wR(F^2) = 0.081$  H-atom parameters constrained  
 $S = 1.08$   $\Delta\rho_{\text{max}} = 0.16$  e Å<sup>-3</sup>  
 1829 reflections  $\Delta\rho_{\text{min}} = -0.16$  e Å<sup>-3</sup>

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O2}-\text{H2A}\cdots\text{O1}$	0.90	1.60	2.4992 (14)	176
$\text{N1}-\text{H1N}\cdots\text{O3}^i$	0.86	1.99	2.8403 (15)	172
$\text{C6}-\text{H6}\cdots\text{O1}$	0.93	2.31	2.8658 (16)	118

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

Data collection: CrysAlis PRO (Oxford Diffraction, 2009); cell refinement: CrysAlis PRO; data reduction: CrysAlis PRO; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 (Farrugia, 1997) and DIAMOND (Brandenburg, 2002); software used to prepare material for publication: SHELXL97, PLATON (Spek, 2009) and WinGX (Farrugia, 1999).

MT and JK thank the Grant Agency of the Slovak Republic (VEGA 1/0817/08) and the Structural Funds, Interreg IIIA, for financial support in purchasing the diffractometer. KS thanks the University Grants Commission, Government of India, New Delhi, for the award of a research fellowship under its faculty improvement program.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BX2280).

## References

- Bernstein, J., Davis, R. E., Shimon, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.  
 Brandenburg, K. (2002). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.  
 Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.  
 Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.  
 Gowda, B. T., Tokarčík, M., Kožíšek, J., Shakuntala, K. & Fuess, H. (2010*a*). *Acta Cryst.* **E66**, o51.  
 Gowda, B. T., Tokarčík, M., Shakuntala, K., Kožíšek, J. & Fuess, H. (2010*b*). *Acta Cryst.* **E66**, o1554.  
 Oxford Diffraction (2009). *CrysAlis PRO*. Oxford Diffraction Ltd, Yarnton, England.  
 Prasad, S. M., Sinha, R. B. P., Mandal, D. K. & Rani, A. (2002). *Acta Cryst.* **E58**, o1296–o1297.  
 Shakuntala, K., Gowda, B. T., Tokarčík, M. & Kožíšek, J. (2009). *Acta Cryst.* **E65**, o3119.  
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.  
 Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.

## supporting information

*Acta Cryst.* (2010). E66, o1643 [doi:10.1107/S1600536810021446]

## ***N*-(3-Chlorophenyl)maleamic acid**

**B. Thimme Gowda, Miroslav Tokarčík, K. Shakuntala, Jozef Kožíšek and Hartmut Fuess**

### **S1. Comment**

As a part of studying the effect of ring and side chain substitutions on the crystal structures of biologically significant amides (Gowda *et al.*, 2010*a,b*; Prasad *et al.*, 2002; Shakuntala *et al.*, 2009), the crystal structure of *N*-(3-chlorophenyl)-maleamic acid (I) has been determined (Fig. 1). The conformations of the N—H and the C=O bonds in the amide segment are *anti* to each other. The conformation of the N—H bond is also *anti* to the *meta*-C1 group in the phenyl ring. In the maleamic acid moiety, the amide C=O bond is *anti* to the adjacent C—H bond, while the carboxyl C=O bond is *syn* to the adjacent C—H bond. The observed rare *anti* conformation of the C=O and O—H bonds of the acid group is similar to that observed in *N*-(2-methylphenyl)-maleamic acid (Gowda *et al.*, 2010*b*), *N*-(2,5-dichlorophenyl)-maleamic acid (Shakuntala *et al.*, 2009) and *N*-(3,5-dichlorophenyl)-maleamic acid (Gowda *et al.*, 2010*a*).

The molecular structure of (I) is stabilized by two intramolecular hydrogen bonds (Figure 1): the first is a short O—H $\cdots$ O hydrogen bond within maleamic acid unit and the second is a C—H $\cdots$ O hydrogen bond which connects the amide group with the phenyl ring. Amidic O1 atom acts as bifurcated acceptor of O2—H2A $\cdots$ O1 and C6—H6 $\cdots$ O1 intramolecular hydrogen bonds (Table 1). The maleamic acid unit is essentially planar, with r.m.s. deviation of 0.044 Å and makes dihedral angle of 15.2 (1)° with the phenyl ring. The torsion angle C1—N1—C5—C6 = -17.6 (2)° defines the orientation of the phenyl ring towards the central amide group —NHCO. The molecular structure is stabilized by two types intramolecular C—H $\cdots$ O and O—H $\cdots$ O interactions with H $\cdots$ O distances of 1.60 and 2.31 Å respectively and one intermolecular N—H $\cdots$ O hydrogen bonds link the molecules into chains with graph-set notation C(7) (Bernstein *et al.*, 1995) running along the [0 1 0] direction, Table 1, Figure 2.

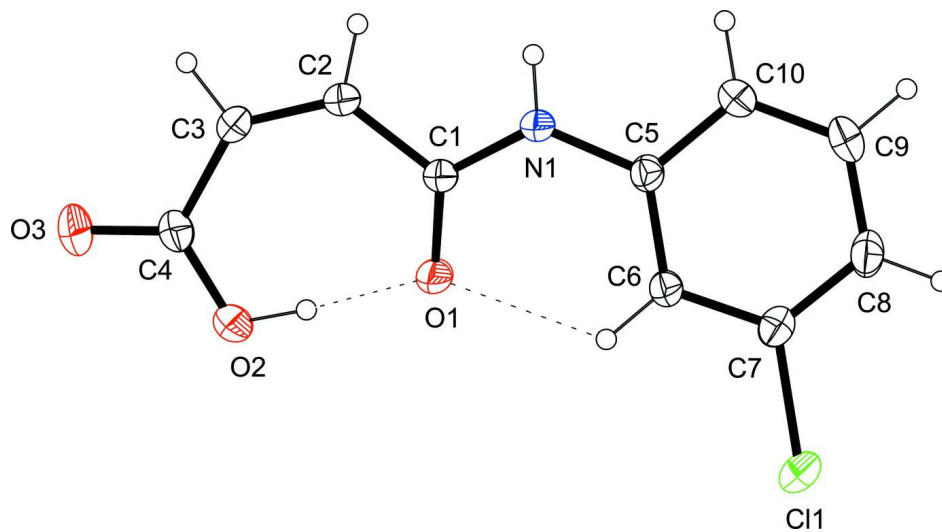
### **S2. Experimental**

The solution of maleic anhydride (0.025 mol) in toluene (25 ml) was treated dropwise with the solution of 3-chloroaniline (0.025 mol) also in toluene (20 ml) with constant stirring. The resulting mixture was warmed with stirring for over 30 min and set aside for an additional 30 min at room temperature for completion of the reaction. The mixture was then treated with dilute hydrochloric acid to remove the unreacted 3-chloroaniline. The resultant solid *N*-(3-chlorophenyl)-maleamic acid was filtered under suction and washed thoroughly with water to remove the unreacted maleic anhydride and maleic acid. It was recrystallized to constant melting point from ethanol. The purity of the compound was checked by elemental analysis and characterized by its infrared spectra.

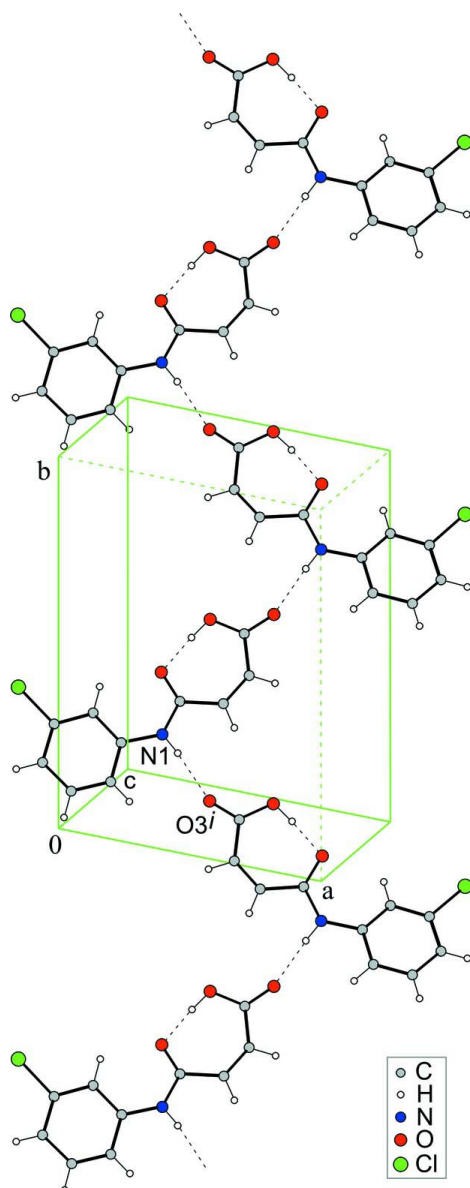
Rod like colourless single crystals used in X-ray diffraction studies were grown in an ethanol solution by slow evaporation at room temperature.

### **S3. Refinement**

All H atoms were found in difference maps and further treated as riding atoms with C—H = 0.93 Å, N—H = 0.86 Å and O—H = 0.90 Å. The  $U_{\text{iso}}(\text{H})$  values were set at  $1.2U_{\text{eq}}(\text{C aromatic, N})$  and  $1.5U_{\text{eq}}(\text{O})$ .

**Figure 1**

Molecular structure of (I) showing the atom labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are represented as small spheres of arbitrary radii and a short intramolecular O—H···O bond as dashed line.



**Figure 2**

Part of crystal structure of (I) showing one-dimensional chain of molecules extending along the [0 1 0] direction and linked by intermolecular N–H···O hydrogen bonds. Hydrogen bonds are shown as dashed lines. Symmetry code (i):  $-x + 1, y - 1/2, -z + 3/2$ .

### ***N*-(3-Chlorophenyl)maleamic acid**

#### *Crystal data*

$C_{10}H_8ClNO_3$

$M_r = 225.62$

Monoclinic,  $P2_1/c$

Hall symbol:  $-P 2_1/c$

$a = 10.7779 (3) \text{ \AA}$

$b = 13.2103 (4) \text{ \AA}$

$c = 7.1372 (2) \text{ \AA}$

$\beta = 104.976 (3)^\circ$

$V = 981.69 (5) \text{ \AA}^3$

$Z = 4$

$F(000) = 464$

$D_x = 1.527 \text{ Mg m}^{-3}$

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

Cell parameters from 8764 reflections

$\theta = 2.0\text{--}29.5^\circ$   
 $\mu = 0.37\text{ mm}^{-1}$   
 $T = 295\text{ K}$

Rod, colourless  
 $0.55 \times 0.09 \times 0.06\text{ mm}$

*Data collection*

Oxford Diffraction Gemini R, CCD diffractometer  
 Graphite monochromator  
 Detector resolution:  $10.434\text{ pixels mm}^{-1}$   
 $\omega$  scans  
 Absorption correction: analytical  
 (*CrysAlis PRO*; Oxford Diffraction, 2009)  
 $T_{\min} = 0.852, T_{\max} = 0.982$

15632 measured reflections  
 1829 independent reflections  
 1533 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.027$   
 $\theta_{\max} = 25.5^\circ, \theta_{\min} = 2.0^\circ$   
 $h = -13 \rightarrow 13$   
 $k = -16 \rightarrow 16$   
 $l = -8 \rightarrow 8$

*Refinement*

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.028$   
 $wR(F^2) = 0.081$   
 $S = 1.08$   
 1829 reflections  
 136 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  
 $w = 1/[\sigma^2(F_o^2) + (0.0488P)^2 + 0.0776P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.16\text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.16\text{ e \AA}^{-3}$

*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 ( $\text{\AA}^2$ )*

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.31064 (12)	0.29347 (9)	0.57205 (19)	0.0320 (3)
C2	0.44462 (13)	0.28772 (10)	0.6940 (2)	0.0372 (3)
H2	0.4774	0.2228	0.7228	0.045*
C3	0.52416 (13)	0.36307 (11)	0.7676 (2)	0.0401 (3)
H3	0.6043	0.3415	0.8403	0.048*
C4	0.50988 (14)	0.47472 (11)	0.7564 (2)	0.0426 (4)
C5	0.12674 (13)	0.18104 (10)	0.42427 (19)	0.0319 (3)
C6	0.03012 (12)	0.25287 (10)	0.38134 (18)	0.0328 (3)
H6	0.0463	0.3197	0.4214	0.039*
C7	-0.09097 (13)	0.22302 (11)	0.27750 (19)	0.0367 (3)
C8	-0.11862 (14)	0.12464 (12)	0.2179 (2)	0.0444 (4)
H8	-0.201	0.1061	0.149	0.053*
C9	-0.02125 (16)	0.05452 (12)	0.2627 (2)	0.0509 (4)

H9	-0.0383	-0.0123	0.2236	0.061*
C10	0.10121 (14)	0.08138 (11)	0.3646 (2)	0.0432 (4)
H10	0.1662	0.0331	0.3932	0.052*
N1	0.25350 (10)	0.20331 (8)	0.53348 (16)	0.0346 (3)
H1N	0.2998	0.1519	0.5813	0.042*
O1	0.25666 (9)	0.37411 (7)	0.51038 (16)	0.0479 (3)
O2	0.40462 (10)	0.51612 (8)	0.65145 (18)	0.0565 (3)
H2A	0.3485	0.4673	0.5973	0.085*
O3	0.59801 (11)	0.52618 (9)	0.84566 (19)	0.0666 (4)
Cl1	-0.21185 (3)	0.31393 (3)	0.22262 (6)	0.05280 (16)

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0286 (7)	0.0273 (7)	0.0383 (7)	0.0013 (5)	0.0054 (6)	0.0006 (6)
C2	0.0316 (7)	0.0292 (7)	0.0465 (8)	0.0040 (6)	0.0023 (6)	0.0016 (6)
C3	0.0284 (7)	0.0370 (8)	0.0484 (8)	0.0011 (6)	-0.0016 (6)	0.0001 (6)
C4	0.0387 (8)	0.0345 (8)	0.0524 (9)	-0.0072 (6)	0.0080 (7)	-0.0053 (6)
C5	0.0306 (7)	0.0300 (7)	0.0336 (7)	-0.0038 (5)	0.0054 (6)	0.0015 (5)
C6	0.0314 (7)	0.0286 (7)	0.0358 (7)	-0.0026 (6)	0.0042 (6)	0.0003 (5)
C7	0.0307 (7)	0.0427 (8)	0.0344 (7)	-0.0021 (6)	0.0045 (6)	0.0031 (6)
C8	0.0362 (8)	0.0462 (9)	0.0461 (8)	-0.0128 (7)	0.0019 (6)	-0.0033 (7)
C9	0.0523 (10)	0.0333 (8)	0.0626 (10)	-0.0119 (7)	0.0069 (8)	-0.0096 (7)
C10	0.0411 (8)	0.0294 (7)	0.0560 (9)	-0.0008 (6)	0.0070 (7)	-0.0021 (6)
N1	0.0293 (6)	0.0257 (6)	0.0444 (7)	0.0022 (5)	0.0014 (5)	0.0023 (5)
O1	0.0340 (5)	0.0281 (5)	0.0707 (7)	0.0001 (4)	-0.0058 (5)	0.0070 (5)
O2	0.0445 (6)	0.0282 (6)	0.0871 (9)	-0.0008 (5)	-0.0004 (6)	-0.0016 (5)
O3	0.0538 (7)	0.0450 (7)	0.0886 (9)	-0.0191 (6)	-0.0038 (6)	-0.0113 (6)
Cl1	0.0326 (2)	0.0540 (3)	0.0625 (3)	0.00544 (16)	-0.00438 (17)	0.00293 (18)

*Geometric parameters (Å, °)*

C1—O1	1.2389 (16)	C6—C7	1.3813 (18)
C1—N1	1.3364 (17)	C6—H6	0.93
C1—C2	1.4828 (19)	C7—C8	1.376 (2)
C2—C3	1.330 (2)	C7—Cl1	1.7404 (15)
C2—H2	0.93	C8—C9	1.374 (2)
C3—C4	1.483 (2)	C8—H8	0.93
C3—H3	0.93	C9—C10	1.379 (2)
C4—O3	1.2073 (18)	C9—H9	0.93
C4—O2	1.3069 (18)	C10—H10	0.93
C5—C6	1.3834 (19)	N1—H1N	0.86
C5—C10	1.3891 (19)	O2—H2A	0.90
C5—N1	1.4178 (17)		
O1—C1—N1	122.96 (12)	C5—C6—H6	120.8
O1—C1—C2	123.32 (12)	C8—C7—C6	122.32 (13)
N1—C1—C2	113.72 (11)	C8—C7—Cl1	119.50 (11)

C3—C2—C1	128.61 (13)	C6—C7—C11	118.19 (11)
C3—C2—H2	115.7	C9—C8—C7	118.25 (13)
C1—C2—H2	115.7	C9—C8—H8	120.9
C2—C3—C4	132.50 (13)	C7—C8—H8	120.9
C2—C3—H3	113.7	C8—C9—C10	121.25 (14)
C4—C3—H3	113.7	C8—C9—H9	119.4
O3—C4—O2	120.99 (14)	C10—C9—H9	119.4
O3—C4—C3	118.36 (14)	C9—C10—C5	119.50 (14)
O2—C4—C3	120.65 (13)	C9—C10—H10	120.2
C6—C5—C10	120.27 (12)	C5—C10—H10	120.2
C6—C5—N1	122.87 (11)	C1—N1—C5	128.71 (11)
C10—C5—N1	116.85 (12)	C1—N1—H1N	115.6
C7—C6—C5	118.41 (12)	C5—N1—H1N	115.6
C7—C6—H6	120.8	C4—O2—H2A	109.5
O1—C1—C2—C3	5.1 (2)	C11—C7—C8—C9	179.82 (12)
N1—C1—C2—C3	-175.30 (14)	C7—C8—C9—C10	0.0 (2)
C1—C2—C3—C4	0.0 (3)	C8—C9—C10—C5	0.4 (2)
C2—C3—C4—O3	177.02 (16)	C6—C5—C10—C9	-0.2 (2)
C2—C3—C4—O2	-3.3 (3)	N1—C5—C10—C9	178.16 (13)
C10—C5—C6—C7	-0.4 (2)	O1—C1—N1—C5	-1.2 (2)
N1—C5—C6—C7	-178.62 (12)	C2—C1—N1—C5	179.26 (12)
C5—C6—C7—C8	0.8 (2)	C6—C5—N1—C1	-17.6 (2)
C5—C6—C7—C11	-179.60 (10)	C10—C5—N1—C1	164.11 (13)
C6—C7—C8—C9	-0.5 (2)		

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>
O2—H2A...O1	0.90	1.60	2.4992 (14)	176
N1—H1N...O3 <sup>i</sup>	0.86	1.99	2.8403 (15)	172
C6—H6...O1	0.93	2.31	2.8658 (16)	118

Symmetry code: (i)  $-x+1, y-1/2, -z+3/2$ .