organic compounds

Ethyl N-(2-acetyl-3-oxo-1-phenylbutyl)carbamate

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In the title compound, $C_{15}H_{19}NO_4$, all three carbonyl groups are *syn*-oriented with respect to the methine group attached to the phenyl ring. The mean planes of the phenyl ring and ethyl carbamate moiety form a dihedral angle of 65.2 (1)°. In the crystal, molecules related by translation in [100] are linked into chains *via* N—H⋯O hydrogen bonds.

Related literature

For details of the synthesis, see: Kuzmina *et al.* (2013). For the crystal structures of related compounds, see: Hatano *et al.* (2008).
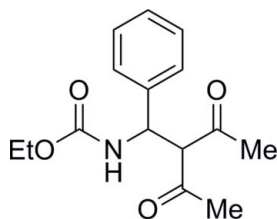
Experimental

Crystal data

C$_{15}$H$_{19}$NO$_4$
M_r = 277.31
Triclinic, $P\bar{1}$
a = 5.392 (2) Å
b = 9.204 (2) Å
c = 15.841 (6) Å

α = 81.58 (2)°
β = 81.98 (2)°
γ = 89.13 (3)°
V = 770.1 (4) Å^3
Z = 2
Cu $K\alpha$ radiation

μ = 0.71 mm^{-1}
T = 295 K

0.50 × 0.21 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.76, T_{max} = 0.92
4976 measured reflections

3176 independent reflections
2057 reflections with $I > 2\sigma(I)$
R_{int} = 0.022
2 standard reflections every 150 reflections
intensity decay: 3%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.068
$wR(F^2)$ = 0.231
S = 1.04
3176 reflections
189 parameters
15 restraints

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1⋯O2^i	0.97 (3)	2.26 (3)	3.180 (4)	158 (2)

Symmetry code: (i) $x + 1, y, z$.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

References

Enraf–Nonius (1994). *CAD-4 EXPRESS*. Enraf–Nonius, Delft, The Netherlands.
Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg, Germany.
Hatano, M., Maki, T., Moriyama, M., Arinobe, M. & Ishihara, K. (2008). *J. Am. Chem. Soc.* **130**, 16858–16860.
Kuzmina, O. M., Volov, A. N., Albov, D. V., Fitch, A. N., Chernyshev, V. V., Shutalev, A. D., Tsivadze, A. Yu., Savinkina, E. V. & Zamilatskov, I. A. (2013). *Tetrahedron Lett.* Submitted.
Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

supporting information

Ethyl *N*-(2-acetyl-3-oxo-1-phenylbutyl)carbamate

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S1. Comment

Recently, we have developed a simple general five-step approach for the synthesis of macrocycles containing semicarbazide moieties *via* heterocyclization of semicarbazides with oxo group in 3 position (Kuzmina *et al.*, 2013). The title compound, **I**, has been obtained as an intermediate product. Herewith we present its molecular and crystal structure.

In **I** (Fig. 1), all bond lengths and angles are normal and correspond well to those observed in the related (1*R*,2*R*)-benzyl (3-oxo-2-((2-oxo-1,3-oxazolidin-3-yl)carbonyl)-1-phenylbutyl)carbamate and (*S*)-benzyl (2-acetyl-1-(4-bromophenyl)-2-hydroxy-3-oxobutyl)carbamate (Hatano *et al.*, 2008). In the molecule, all three carbonyl groups are *syn* oriented with respect to the methine group attached to the phenyl ring.

In the crystal, the molecules related by translation in [1 0 0] are linked into chains *via* intermolecular classical N–H···O hydrogen bonds (Table 1, Fig. 2).

S2. Experimental

To a solution of KOH (0.277 g, 0.0049 mol) in 30 ml ethanol was added acetylacetone (0.495 g, 0.0049 mol) and stirred vigorously for 10 minutes. Ethyl *N*-[(tosyl)(phenyl)methyl]carbamate (1.5 g, 0.0045 mol) was added and reaction mixture stirred for 6.5 h. After completion of reaction, solution was evaporated to dryness and residue washed with saturated solution of NaHCO$_3$, hexane and dried to give 1.1 g (88%) of ethyl *N*-[(2-acetyl-3-oxo-1-phenyl)butyl]carbamate as white powder. An analytically pure sample was obtained by recrystallization from *Me*OH-H$_2$O (2:3). M.p. 421-422 K (*Me*OH-H$_2$O (2:3)).

^{1}H NMR (600 MHz; DMSO-d6): δ_H, p.p.m. 7.76(1*H*, d, J = 9.16 Hz, NH), 7.21-7.30 (5*H*, m, H in *Ph*), 5.15 (1*H*, t, J = 9.78 Hz, CH), 4.47(1*H*, d, J = 11.12 Hz, CH), 3.87-3.93 (2*H*, m, CH$_2$ in COO*Et*), 2.22 (3*H*, s, CH$_3$ in acetyl), 1.87 (3*H*, s, CH$_3$ in acetyl), 1.08 (3*H*, t, J = 7.04 Hz, CH$_3$ in COO*Et*). ^{13}C NMR (150 MHz; DMSO-d6): δ_H, p.p.m. 14.4, 30.1, 30.7, 54.1, 59.9, 71.7, 127.3, 127.5, 128.4, 140.6, 155.3, 201.3, 201.5 Anal. Calcd for C$_{15}$H$_{19}$NO$_4$: C, 64.97; H, 6.91; N 5.05. Found: C, 65.09; H, 6.98; N, 5.12.

S3. Refinement

Atom H1 was located on a difference map and isotropically refined. C-bound H atoms were positioned geometrically (C–H = 0.93Å-0.98Å) and refined as riding, with U_{iso}(H) = 1.2-1.5U_{eq}(C).
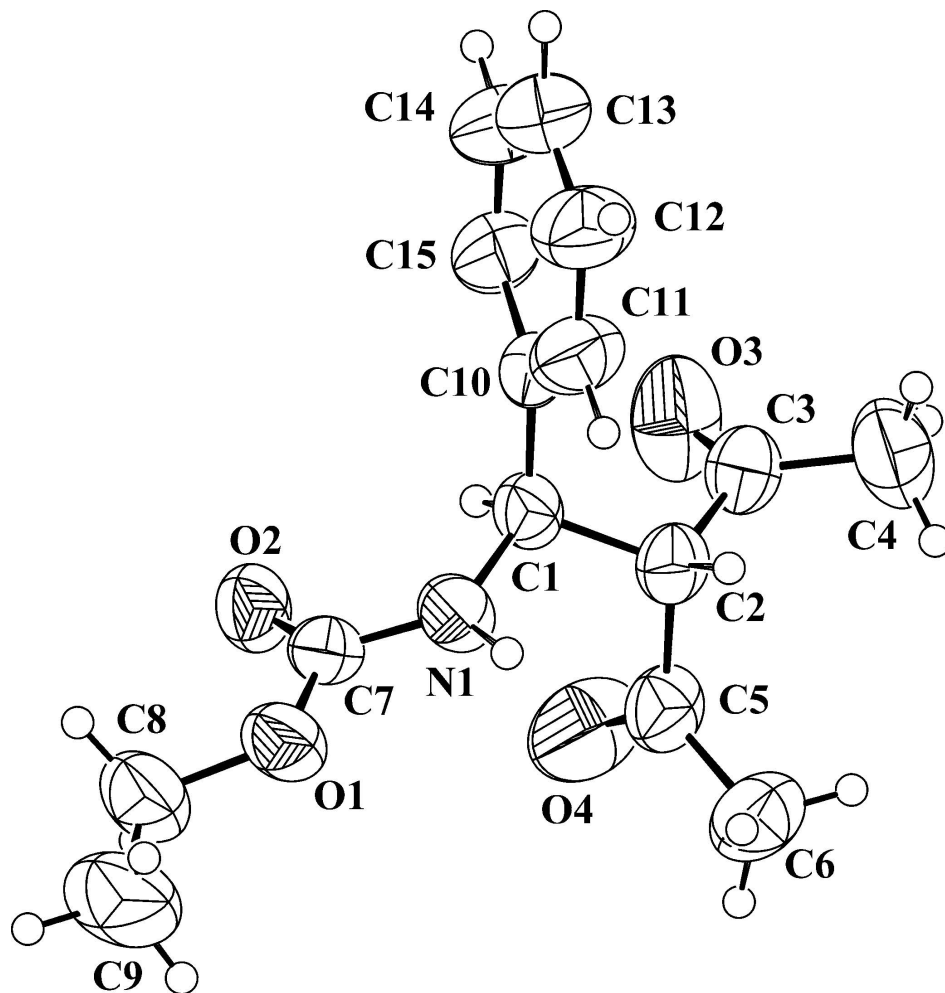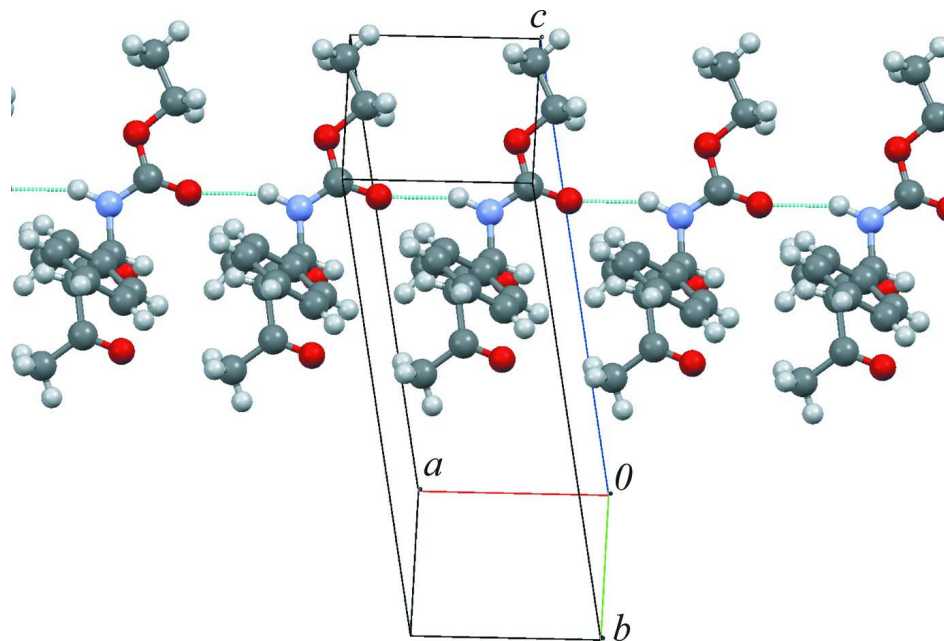
Figure 1

Molecular structure of **I** whith the atom numbering scheme. Displacement ellipsoids are drawn at 50% probability level. H atoms are presented as a small spheres of arbitrary radius.

Figure 2

Portion of the crystal packing in **I**. Dotted blue lines denote hydrogen bonds.

Ethyl *N*-(2-acetyl-3-oxo-1-phenylbutyl)carbamate

Crystal data

$C_{15}H_{19}NO_4$	$F(000) = 296$
$M_r = 277.31$	$D_x = 1.196$ Mg m^{-3}
Triclinic, $P\bar{1}$	Melting point = 421–422 K
$a = 5.392$ (2) Å	Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å
$b = 9.204$ (2) Å	Cell parameters from 25 reflections
$c = 15.841$ (6) Å	$\theta = 31.6$–34.9°
$\alpha = 81.58$ (2)°	$\mu = 0.71$ mm^{-1}
$\beta = 81.98$ (2)°	$T = 295$ K
$\gamma = 89.13$ (3)°	Prism, colourless
$V = 770.1$ (4) Å^3	$0.50 \times 0.21 \times 0.10$ mm
$Z = 2$	

Data collection

Enraf–Nonius CAD-4 diffractometer	3176 independent reflections
Radiation source: fine-focus sealed tube	2057 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{int} = 0.022$
non–profiled ω–scans	$\theta_{max} = 74.9°$, $\theta_{min} = 2.9°$
Absorption correction: ψ scan (North *et al.*, 1968)	$h = -3 \rightarrow 6$
	$k = -11 \rightarrow 11$
	$l = -19 \rightarrow 19$
$T_{min} = 0.76$, $T_{max} = 0.92$	2 standard reflections every 150 reflections
4976 measured reflections	intensity decay: 3%

Refinement

Refinement on F^2	Hydrogen site location: inferred from
Least-squares matrix: full	neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.068$	H atoms treated by a mixture of independent
$wR(F^2) = 0.231$	and constrained refinement
$S = 1.04$	$w = 1/[\sigma^2(F_o^2) + (0.11P)^2 + 0.24P]$
3176 reflections	where $P = (F_o^2 + 2F_c^2)/3$
189 parameters	$(\Delta/\sigma)_{max} < 0.001$
15 restraints	$\Delta\rho_{max} = 0.30$ e Å^{-3}
Primary atom site location: structure-invariant	$\Delta\rho_{min} = -0.19$ e Å^{-3}
direct methods	Extinction correction: *SHELXL97* (Sheldrick,
Secondary atom site location: difference Fourier	2008), Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
map	Extinction coefficient: 0.009 (2)

Special details

Geometry. All s.u.'s (except the s.u. 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 s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 ($Å^2$)

	x	y	z	U_{iso}*/U_{eq}
O1	0.1419 (4)	0.4031 (2)	0.90111 (13)	0.0701 (6)
O2	−0.1063 (4)	0.5365 (2)	0.81579 (14)	0.0702 (6)
O3	0.3293 (5)	0.8086 (4)	0.55078 (16)	0.1061 (10)
O4	0.3031 (5)	0.4665 (3)	0.6140 (3)	0.1242 (12)
N1	0.3154 (5)	0.5683 (3)	0.79670 (16)	0.0609 (6)
H1	0.473 (6)	0.541 (3)	0.8167 (19)	0.064 (8)*
C1	0.3263 (5)	0.6871 (3)	0.72419 (17)	0.0553 (6)
H1A	0.1667	0.6874	0.7012	0.066*
C2	0.5335 (5)	0.6570 (3)	0.65270 (18)	0.0581 (7)
H2	0.6965	0.6633	0.6726	0.070*
C3	0.5268 (6)	0.7669 (4)	0.57095 (19)	0.0649 (7)
C4	0.7610 (7)	0.8120 (5)	0.5160 (3)	0.1017 (13)
H4A	0.7268	0.8494	0.4589	0.153*
H4B	0.8706	0.7291	0.5137	0.153*
H4C	0.8396	0.8873	0.5391	0.153*
C5	0.5017 (6)	0.5036 (4)	0.6283 (2)	0.0691 (8)
C6	0.7211 (7)	0.4071 (4)	0.6219 (3)	0.0900 (11)
H6A	0.6725	0.3140	0.6088	0.135*
H6B	0.7871	0.3930	0.6758	0.135*
H6C	0.8470	0.4515	0.5770	0.135*
C7	0.1002 (5)	0.5061 (3)	0.83558 (17)	0.0548 (6)
C8	−0.0754 (8)	0.3217 (4)	0.9476 (2)	0.0914 (12)
H8A	−0.1578	0.2732	0.9086	0.110*

H8B	−0.1940	0.3873	0.9743	0.110*
C9	0.0159 (12)	0.2109 (5)	1.0147 (3)	0.1292 (19)
H9A	0.1200	0.1409	0.9873	0.194*
H9B	−0.1247	0.1611	1.0506	0.194*
H9C	0.1111	0.2595	1.0493	0.194*
C10	0.3566 (5)	0.8362 (3)	0.75167 (17)	0.0588 (7)
C11	0.5396 (6)	0.8614 (3)	0.8002 (2)	0.0796 (9)
H11	0.6451	0.7851	0.8171	0.096*
C12	0.5704 (8)	0.9968 (3)	0.8243 (3)	0.0980 (12)
H12	0.6966	1.0120	0.8566	0.118*
C13	0.4143 (8)	1.1085 (4)	0.8004 (3)	0.1067 (15)
H13	0.4308	1.1995	0.8181	0.128*
C14	0.2344 (9)	1.0878 (4)	0.7509 (3)	0.1055 (14)
H14	0.1319	1.1652	0.7331	0.127*
C15	0.2056 (7)	0.9521 (3)	0.7275 (2)	0.0822 (10)
H15	0.0808	0.9382	0.6944	0.099*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0820 (15)	0.0563 (11)	0.0669 (12)	−0.0039 (10)	−0.0069 (10)	0.0051 (9)
O2	0.0492 (11)	0.0760 (13)	0.0806 (13)	−0.0023 (9)	−0.0063 (10)	0.0021 (10)
O3	0.0653 (15)	0.159 (3)	0.0856 (17)	0.0111 (16)	−0.0218 (13)	0.0192 (17)
O4	0.0603 (15)	0.115 (2)	0.220 (4)	−0.0017 (14)	−0.0398 (19)	−0.079 (2)
N1	0.0470 (13)	0.0575 (13)	0.0750 (15)	−0.0004 (10)	−0.0148 (11)	0.0071 (11)
C1	0.0428 (13)	0.0567 (14)	0.0633 (15)	0.0001 (11)	−0.0069 (11)	0.0010 (12)
C2	0.0391 (13)	0.0660 (16)	0.0710 (16)	0.0013 (11)	−0.0118 (12)	−0.0116 (13)
C3	0.0503 (16)	0.0802 (19)	0.0655 (16)	0.0004 (14)	−0.0103 (13)	−0.0128 (14)
C4	0.071 (2)	0.113 (3)	0.108 (3)	−0.014 (2)	0.003 (2)	0.016 (2)
C5	0.0503 (16)	0.0778 (19)	0.083 (2)	−0.0032 (14)	−0.0095 (14)	−0.0224 (16)
C6	0.067 (2)	0.086 (2)	0.125 (3)	0.0126 (18)	−0.016 (2)	−0.039 (2)
C7	0.0602 (17)	0.0465 (13)	0.0571 (14)	−0.0002 (11)	−0.0058 (12)	−0.0076 (11)
C8	0.108 (3)	0.076 (2)	0.080 (2)	−0.017 (2)	0.008 (2)	0.0016 (18)
C9	0.195 (6)	0.083 (3)	0.092 (3)	−0.001 (3)	0.011 (3)	0.017 (2)
C10	0.0480 (14)	0.0566 (15)	0.0660 (16)	0.0041 (11)	0.0049 (12)	−0.0026 (12)
C11	0.070 (2)	0.0651 (18)	0.109 (3)	0.0108 (15)	−0.0193 (18)	−0.0244 (18)
C12	0.091 (3)	0.074 (2)	0.136 (3)	0.002 (2)	−0.016 (2)	−0.039 (2)
C13	0.106 (3)	0.064 (2)	0.142 (4)	0.003 (2)	0.020 (3)	−0.028 (2)
C14	0.107 (3)	0.068 (2)	0.134 (4)	0.028 (2)	−0.002 (3)	−0.006 (2)
C15	0.073 (2)	0.071 (2)	0.097 (2)	0.0179 (17)	−0.0054 (18)	−0.0011 (17)

Geometric parameters (Å, º)

O1—C7	1.341 (3)	C6—H6B	0.9600
O1—C8	1.450 (4)	C6—H6C	0.9600
O2—C7	1.216 (3)	C8—C9	1.491 (6)
O3—C3	1.196 (4)	C8—H8A	0.9700
O4—C5	1.190 (4)	C8—H8B	0.9700

N1—C7	1.331 (4)	C9—H9A	0.9600
N1—C1	1.461 (3)	C9—H9B	0.9600
N1—H1	0.97 (3)	C9—H9C	0.9600
C1—C10	1.516 (4)	C10—C11	1.374 (3)
C1—C2	1.529 (4)	C10—C15	1.375 (3)
C1—H1A	0.9800	C11—C12	1.375 (3)
C2—C3	1.526 (4)	C11—H11	0.9300
C2—C5	1.536 (4)	C12—C13	1.363 (3)
C2—H2	0.9800	C12—H12	0.9300
C3—C4	1.459 (5)	C13—C14	1.362 (3)
C4—H4A	0.9600	C13—H13	0.9300
C4—H4B	0.9600	C14—C15	1.371 (3)
C4—H4C	0.9600	C14—H14	0.9300
C5—C6	1.469 (5)	C15—H15	0.9300
C6—H6A	0.9600		
C7—O1—C8	116.4 (3)	O2—C7—N1	126.0 (3)
C7—N1—C1	122.2 (2)	O2—C7—O1	123.9 (3)
C7—N1—H1	121.8 (18)	N1—C7—O1	110.1 (2)
C1—N1—H1	116.0 (18)	O1—C8—C9	107.0 (4)
N1—C1—C10	112.0 (2)	O1—C8—H8A	110.3
N1—C1—C2	109.9 (2)	C9—C8—H8A	110.3
C10—C1—C2	112.1 (2)	O1—C8—H8B	110.3
N1—C1—H1A	107.6	C9—C8—H8B	110.3
C10—C1—H1A	107.6	H8A—C8—H8B	108.6
C2—C1—H1A	107.6	C8—C9—H9A	109.5
C3—C2—C1	111.4 (2)	C8—C9—H9B	109.5
C3—C2—C5	106.9 (2)	H9A—C9—H9B	109.5
C1—C2—C5	110.7 (2)	C8—C9—H9C	109.5
C3—C2—H2	109.3	H9A—C9—H9C	109.5
C1—C2—H2	109.3	H9B—C9—H9C	109.5
C5—C2—H2	109.3	C11—C10—C15	117.4 (3)
O3—C3—C4	121.1 (3)	C11—C10—C1	121.3 (2)
O3—C3—C2	119.5 (3)	C15—C10—C1	121.3 (3)
C4—C3—C2	119.3 (3)	C10—C11—C12	121.6 (3)
C3—C4—H4A	109.5	C10—C11—H11	119.2
C3—C4—H4B	109.5	C12—C11—H11	119.2
H4A—C4—H4B	109.5	C13—C12—C11	119.4 (4)
C3—C4—H4C	109.5	C13—C12—H12	120.3
H4A—C4—H4C	109.5	C11—C12—H12	120.3
H4B—C4—H4C	109.5	C14—C13—C12	120.4 (4)
O4—C5—C6	121.7 (3)	C14—C13—H13	119.8
O4—C5—C2	119.8 (3)	C12—C13—H13	119.8
C6—C5—C2	118.5 (3)	C13—C14—C15	119.5 (4)
C5—C6—H6A	109.5	C13—C14—H14	120.2
C5—C6—H6B	109.5	C15—C14—H14	120.2
H6A—C6—H6B	109.5	C14—C15—C10	121.6 (3)
C5—C6—H6C	109.5	C14—C15—H15	119.2

H6A—C6—H6C	109.5		C10—C15—H15	119.2
H6B—C6—H6C	109.5			

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O2ⁱ	0.97 (3)	2.26 (3)	3.180 (4)	158 (2)

Symmetry code: (i) *x*+1, *y*, *z*.