organic compounds

Methyl 5-hydroxy-3-phenyl-1,2-oxazolidine-5-carboxylate

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In the title compound, $C_{11}H_{13}NO_4$, the isoxazolidine ring has an envelope conformation with the O atom as the flap. In the crystal, molecules are liked *via* N—H···O and bifurcated O—H···(O,N) hydrogen bonds forming chains propagating along [010]. There are also C—H···O interactions present.

Related literature

For the use of isoxazolidine-containing compounds as building blocks in synthesis, see: Carrillo *et al.* (2006); Lv *et al.* (2010); Ibrahem *et al.* (2007); Sharma *et al.* (1999). For information on conjugation additions to α,β-unsaturated ketones, see: Wu *et al.* (2006). For standard bond-lengths see: Allen *et al.* (1987).
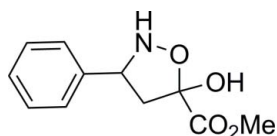
Experimental

Crystal data

$C_{11}H_{13}NO_4$	V = 1117.35 (4) Å^3
M_r = 223.22	Z = 4
Monoclinic, $P2_1/n$	Cu $K\alpha$ radiation
a = 11.8322 (3) Å	μ = 0.85 mm^{-1}
b = 6.0853 (1) Å	T = 291 K
c = 15.8570 (3) Å	0.40 × 0.36 × 0.30 mm
β = 101.864 (2)°	

Data collection

Oxford Gemini S Ultra diffractometer	10901 measured reflections
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)	2165 independent reflections
	1921 reflections with $I > 2\sigma(I)$
T_{min} = 0.726, T_{max} = 0.784	R_{int} = 0.034

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.097	
S = 1.05	
2165 reflections	$\Delta\rho_{max}$ = 0.20 e Å^{-3}
151 parameters	$\Delta\rho_{min}$ = −0.12 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H4···O1^i	0.907 (18)	2.315 (18)	3.1158 (15)	147.0 (13)
O2—H9···O1^i	0.82	2.51	3.0673 (13)	127
O2—H9···N1^i	0.82	1.99	2.7826 (16)	162
C11—H11A···O3^{ii}	0.96	2.54	3.480 (2)	166
C11—H11C···O2^{iii}	0.96	2.53	3.419 (2)	154

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

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); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SU2406).

References

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supplementary materials

Methyl 5-hydroxy-3-phenyl-1,2-oxazolidine-5-carboxylate

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Comment

Isoxazolidines are interesting heterocyclic compounds that may be regarded as unusual constrained β-amino acids or as furanose mimetics, and have been exploited as analogues of natural products (Lv et al., 2010). Isoxazolidines are also applied in the synthesis of oligopeptides in the absence of coupling reagents (Carrillo et al., 2006) and used as building blocks in organic synthesis (Ibrahem et al., 2007; Sharma et al., 1999).

Nitrogen containing nucleophiles such as hydroxylamines and hydrazoic acid are widely employed in conjugation additions to α,β-unsaturated ketones (Wu et al., 2006). The title compound is a Michael addition product from the transformation of hydroxylamine to an α,β-unsaturated ketone ester. We report herein on the crystal structure of the title compound.

The molecular structure of the title molecule is shown in Fig. 1. The bond lengths (Allen et al., 1987) and angles are normal. The isoxazolidine ring possesses an envelope conformation with atom O1 as the flap.

In the crystal, molecules are linked via N—H···O and bifurcated O—H···O,N hydrogen bonds to form chains along the b axis (Table 1). These chains are linked via C-H···O interactions (Table 1).

Experimental

To the solution of (*E*)-methyl 2-oxo-4-phenylbut-3-enoate (0.019 g, 0.1 mmol) and hydroxylamine hydrochloride (0.07 g, 0.1 mmol) in dichloromethane (1 mL) was added triethylamine (0.012 g, 0.12mmol) at room temperature. The reaction mixture was stirred for 24 h at 273 K. The solvent was then removed under reduced pressure, and the residue was purified through column chromatography (petroleum ether: ethyl acetate = 3:1(V/V)). Single crystals, suitable for X-ray diffraction, were obtained by slow evaporation of an ethyl acetate solution at room temperature for 2 d.

Refinement

The NH H atom was located in a difference Fourier map and freely refined. The OH and C-bound H-atoms were included in calculated positions and treated as riding atoms: O-H = 0.82 Å, C-H = 0.93, 0.96, 0.97 and 0.98 Å for CH(aromatic), CH$_3$, CH$_2$ and CH(methine) H-atoms, respectively, with $U_{iso}(H) = k \times U_{eq}(O,C)$, where k = 1.5 for OH and CH$_3$ H-atoms and = 1.2 for other H-atoms.

Computing details

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO* (Oxford Diffraction, 2009); data reduction: *CrysAlis PRO* (Oxford Diffraction, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008).
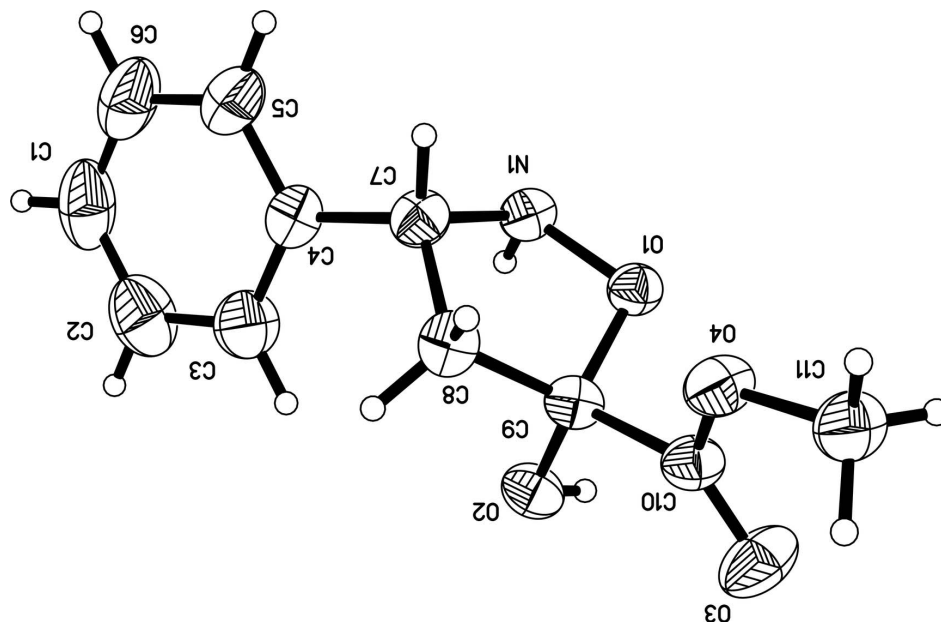
Figure 1

The molecular structure of the title molecule, with the atom numbering. Displacement ellipsoids are drawn at the 30% probability level.

Methyl 5-hydroxy-3-phenyl-1,2-oxazolidine-5-carboxylate

Crystal data

$C_{11}H_{13}NO_4$	$F(000) = 472$
$M_r = 223.22$	$D_x = 1.327$ Mg m^{-3}
Monoclinic, $P2_1/n$	Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å
Hall symbol: -P 2yn	Cell parameters from 7888 reflections
$a = 11.8322$ (3) Å	$\theta = 3.8–71.9°$
$b = 6.0853$ (1) Å	$\mu = 0.85$ mm^{-1}
$c = 15.8570$ (3) Å	$T = 291$ K
$\beta = 101.864$ (2)°	Block, colourless
$V = 1117.35$ (4) Å^3	$0.40 \times 0.36 \times 0.30$ mm
$Z = 4$	

Data collection

Oxford Gemini S Ultra diffractometer	$T_{min} = 0.726$, $T_{max} = 0.784$
Radiation source: Enhance Ultra (Cu) X-ray Source	10901 measured reflections
	2165 independent reflections
Mirror monochromator	1921 reflections with $I > 2\sigma(I)$
Detector resolution: 15.9149 pixels mm^{-1}	$R_{int} = 0.034$
ω scans	$\theta_{max} = 72.1°$, $\theta_{min} = 5.7°$
Absorption correction: multi-scan	$h = -14 \rightarrow 13$
(*CrysAlis PRO*; Oxford Diffraction, 2009)	$k = -6 \rightarrow 7$
	$l = -19 \rightarrow 18$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.042$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.097$	
$S = 1.05$	H atoms treated by a mixture of independent and constrained refinement
2165 reflections	
151 parameters	$w = 1/[\sigma^2(F_o^2) + (0.0323P)^2 + 0.2933P]$ where $P = (F_o^2 + 2F_c^2)/3$
0 restraints	
Primary atom site location: structure-invariant direct methods	$(\Delta/\sigma)_{max} < 0.001$
	$\Delta\rho_{max} = 0.20$ e Å^{-3}
	$\Delta\rho_{min} = -0.12$ e Å^{-3}

Special details

Experimental. Absorption correction: (CrysAlisPro; Oxford Diffraction, 2009) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

Geometry. Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles

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	0.79693 (8)	0.06822 (15)	0.78232 (6)	0.0518 (3)
O2	0.82481 (9)	−0.20986 (16)	0.88556 (6)	0.0604 (4)
O3	1.04065 (10)	−0.0305 (2)	0.89858 (10)	0.0901 (5)
O4	0.96722 (8)	0.30583 (16)	0.89779 (7)	0.0641 (4)
N1	0.67179 (10)	0.0582 (2)	0.76513 (8)	0.0535 (4)
C1	0.3265 (2)	−0.1664 (6)	0.87113 (15)	0.1076 (12)
C2	0.4303 (2)	−0.2651 (4)	0.90278 (16)	0.1061 (10)
C3	0.53265 (17)	−0.1617 (3)	0.89530 (14)	0.0857 (7)
C4	0.53083 (13)	0.0405 (3)	0.85666 (10)	0.0629 (5)
C5	0.42474 (15)	0.1361 (4)	0.82446 (13)	0.0843 (7)
C6	0.32309 (17)	0.0312 (5)	0.83205 (16)	0.1066 (10)
C7	0.63963 (12)	0.1531 (2)	0.84333 (10)	0.0577 (5)
C8	0.74876 (13)	0.1335 (3)	0.91548 (10)	0.0613 (5)
C9	0.83371 (12)	0.0138 (2)	0.87205 (9)	0.0522 (4)
C10	0.96003 (12)	0.0898 (2)	0.89183 (9)	0.0553 (5)
C11	1.08082 (14)	0.4029 (3)	0.90958 (12)	0.0719 (6)
H1	0.25820	−0.23540	0.87650	0.1290*
H2	0.43250	−0.40170	0.92940	0.1270*
H3	0.60300	−0.23020	0.91670	0.1030*
H4	0.6564 (13)	−0.088 (3)	0.7630 (10)	0.062 (4)*
H5	0.42140	0.27220	0.79740	0.1010*
H6	0.25230	0.09750	0.81010	0.1280*
H7	0.62260	0.30950	0.83270	0.0690*
H8A	0.77780	0.27740	0.93560	0.0740*

H8B	0.73310	0.04990	0.96390	0.0740*
H9	0.84150	−0.27740	0.84510	0.0900*
H11A	1.07520	0.55870	0.91730	0.1080*
H11B	1.11280	0.37440	0.85970	0.1080*
H11C	1.12990	0.34020	0.95950	0.1080*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0502 (5)	0.0495 (6)	0.0538 (5)	−0.0012 (4)	0.0064 (4)	0.0012 (4)
O2	0.0731 (7)	0.0478 (6)	0.0577 (6)	−0.0060 (5)	0.0076 (5)	0.0027 (4)
O3	0.0607 (7)	0.0555 (7)	0.1493 (12)	0.0081 (6)	0.0105 (7)	−0.0051 (7)
O4	0.0539 (6)	0.0465 (6)	0.0867 (8)	−0.0031 (4)	0.0023 (5)	0.0018 (5)
N1	0.0496 (6)	0.0472 (7)	0.0608 (7)	−0.0018 (5)	0.0049 (5)	−0.0032 (5)
C1	0.0765 (14)	0.163 (3)	0.0888 (15)	−0.0423 (16)	0.0295 (11)	−0.0271 (16)
C2	0.1073 (18)	0.1077 (18)	0.1067 (16)	−0.0414 (14)	0.0303 (13)	0.0013 (13)
C3	0.0734 (11)	0.0809 (13)	0.1028 (14)	−0.0142 (10)	0.0179 (10)	0.0070 (11)
C4	0.0565 (8)	0.0657 (10)	0.0669 (9)	−0.0030 (7)	0.0136 (7)	−0.0112 (8)
C5	0.0627 (10)	0.0975 (14)	0.0922 (13)	0.0080 (10)	0.0149 (9)	−0.0081 (11)
C6	0.0572 (11)	0.153 (2)	0.1111 (18)	−0.0031 (13)	0.0211 (11)	−0.0198 (17)
C7	0.0593 (8)	0.0481 (8)	0.0653 (9)	0.0006 (6)	0.0120 (7)	−0.0059 (6)
C8	0.0593 (8)	0.0635 (9)	0.0605 (8)	−0.0063 (7)	0.0110 (7)	−0.0115 (7)
C9	0.0564 (8)	0.0463 (7)	0.0511 (7)	−0.0023 (6)	0.0046 (6)	−0.0007 (6)
C10	0.0566 (8)	0.0474 (8)	0.0588 (8)	0.0015 (6)	0.0044 (6)	0.0008 (6)
C11	0.0593 (9)	0.0615 (10)	0.0893 (12)	−0.0118 (8)	0.0026 (8)	0.0030 (8)

Geometric parameters (Å, º)

O1—N1	1.4507 (16)	C5—C6	1.389 (3)
O1—C9	1.4384 (17)	C7—C8	1.544 (2)
O2—C9	1.3852 (16)	C8—C9	1.517 (2)
O3—C10	1.1897 (18)	C9—C10	1.534 (2)
O4—C10	1.3195 (16)	C1—H1	0.9300
O4—C11	1.445 (2)	C2—H2	0.9300
O2—H9	0.8200	C3—H3	0.9300
N1—C7	1.4866 (19)	C5—H5	0.9300
N1—H4	0.907 (18)	C6—H6	0.9300
C1—C2	1.367 (4)	C7—H7	0.9800
C1—C6	1.350 (5)	C8—H8A	0.9700
C2—C3	1.391 (3)	C8—H8B	0.9700
C3—C4	1.373 (3)	C11—H11A	0.9600
C4—C7	1.511 (2)	C11—H11B	0.9600
C4—C5	1.383 (3)	C11—H11C	0.9600
N1—O1—C9	105.41 (10)	O4—C10—C9	111.15 (11)
C10—O4—C11	117.46 (12)	C2—C1—H1	120.00
C9—O2—H9	109.00	C6—C1—H1	120.00
O1—N1—C7	104.68 (10)	C1—C2—H2	120.00
C7—N1—H4	109.2 (10)	C3—C2—H2	120.00
O1—N1—H4	103.7 (10)	C2—C3—H3	120.00

C2—C1—C6	120.0 (2)	C4—C3—H3	120.00
C1—C2—C3	120.2 (2)	C4—C5—H5	120.00
C2—C3—C4	120.62 (19)	C6—C5—H5	120.00
C3—C4—C5	118.15 (17)	C1—C6—H6	120.00
C3—C4—C7	122.23 (15)	C5—C6—H6	120.00
C5—C4—C7	119.50 (16)	N1—C7—H7	108.00
C4—C5—C6	120.8 (2)	C4—C7—H7	108.00
C1—C6—C5	120.3 (2)	C8—C7—H7	108.00
C4—C7—C8	117.92 (13)	C7—C8—H8A	111.00
N1—C7—C8	105.64 (11)	C7—C8—H8B	111.00
N1—C7—C4	108.18 (12)	C9—C8—H8A	111.00
C7—C8—C9	103.42 (12)	C9—C8—H8B	111.00
O1—C9—O2	111.23 (10)	H8A—C8—H8B	109.00
O1—C9—C8	104.16 (11)	O4—C11—H11A	109.00
C8—C9—C10	118.11 (12)	O4—C11—H11B	109.00
O1—C9—C10	102.52 (11)	O4—C11—H11C	109.00
O2—C9—C8	108.85 (12)	H11A—C11—H11B	109.00
O2—C9—C10	111.50 (11)	H11A—C11—H11C	109.00
O3—C10—O4	124.61 (14)	H11B—C11—H11C	109.00
O3—C10—C9	124.22 (12)		
C9—O1—N1—C7	38.90 (12)	C3—C4—C7—C8	−38.7 (2)
N1—O1—C9—O2	76.12 (13)	C5—C4—C7—N1	−94.88 (18)
N1—O1—C9—C8	−40.98 (12)	C5—C4—C7—C8	145.43 (16)
N1—O1—C9—C10	−164.61 (9)	C4—C5—C6—C1	0.0 (4)
C11—O4—C10—O3	2.8 (2)	N1—C7—C8—C9	−3.24 (15)
C11—O4—C10—C9	−175.29 (12)	C4—C7—C8—C9	117.76 (14)
O1—N1—C7—C4	−148.04 (11)	C7—C8—C9—O1	26.43 (14)
O1—N1—C7—C8	−20.90 (13)	C7—C8—C9—O2	−92.30 (13)
C6—C1—C2—C3	0.4 (4)	C7—C8—C9—C10	139.28 (12)
C2—C1—C6—C5	−0.6 (4)	O1—C9—C10—O3	−103.08 (16)
C1—C2—C3—C4	0.4 (3)	O1—C9—C10—O4	75.06 (13)
C2—C3—C4—C5	−1.0 (3)	O2—C9—C10—O3	16.0 (2)
C2—C3—C4—C7	−176.90 (18)	O2—C9—C10—O4	−165.86 (11)
C3—C4—C5—C6	0.8 (3)	C8—C9—C10—O3	143.17 (16)
C7—C4—C5—C6	176.83 (19)	C8—C9—C10—O4	−38.69 (17)
C3—C4—C7—N1	81.02 (19)		

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
N1—H4···O1[i]	0.907 (18)	2.315 (18)	3.1158 (15)	147.0 (13)
O2—H9···O1[i]	0.82	2.51	3.0673 (13)	127
O2—H9···N1[i]	0.82	1.99	2.7826 (16)	162
C11—H11*A*···O3[ii]	0.96	2.54	3.480 (2)	166
C11—H11*C*···O2[iii]	0.96	2.53	3.419 (2)	154

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