Bruceolline J: 2-hydroxy-3,3-dimethyl-2,3-dihydrocyclopenta[*b*]indol-1(4*H*)-one

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The 12-membered cyclopenta[*b*]indole ring system in the title compound, $C_{13}H_{13}NO_2$, deviates only slightly from planarity (r.m.s. deviation = 0.051 Å). In the crystal, N—H⋯O and O—H⋯O hydrogen bonds link the molecules into sheets parallel to (100). The five-membered cyclopentanone ring is in slightly distorted envelope conformation with the C atom bearing the hydroxy substituent as the flap.

Related literature

For a review of compounds isolated from *Brucea sp.* plants, see: Liu *et al.* (2009). For the first isolation of bruceolline J, see: Chen *et al.* (2011). For the DDQ-mediated selective oxidation of indole side chains, see: Oikawa & Yonemitsu (1977). For examples of the reduction of α-keto esters with sodium borohydride, see Dalla *et al.* (1999). For the enantioselective reduction of related sterically hindered ketones with β-chlorodiisopinocampheylborane, see: Brown *et al.* (1986). For the isolation of related bruceollines, see: Ouyang *et al.* (1994*a*,*b*, 1995). For the crystal structure of bruceolline D, see: Lopchuk *et al.* (2013). For the total synthesis and crystal structure of bruceolline E, see: Jordan *et al.* (2011, 2012). For bond-length data, see: Allen *et al.* (1987).
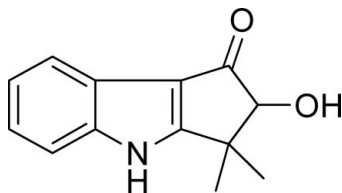
Experimental

Crystal data

$C_{13}H_{13}NO_2$	$V = 1087.15$ (7) Å^3
$M_r = 215.24$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 8.2951$ (3) Å	$\mu = 0.09$ mm^{-1}
$b = 12.3070$ (4) Å	$T = 173$ K
$c = 10.7340$ (4) Å	$0.44 \times 0.38 \times 0.34$ mm
$\beta = 97.207$ (3)°	

Data collection

Agilent Xcalibur (Eos, Gemini) diffractometer	13545 measured reflections
Absorption correction: multi-scan (*CrysAlis PRO* and *CrysAlis RED*; Agilent, 2012)	3753 independent reflections
	2888 reflections with $I > 2\sigma(I)$
$T_{min} = 0.782$, $T_{max} = 1.000$	$R_{int} = 0.035$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.048$	148 parameters
$wR(F^2) = 0.134$	H-atom parameters constrained
$S = 1.04$	$\Delta\rho_{max} = 0.40$ e Å^{-3}
3753 reflections	$\Delta\rho_{min} = -0.25$ e Å^{-3}

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O2—H2⋯O1^i	0.84	1.90	2.7245 (12)	168
N1—H1⋯O2^{ii}	0.88	1.91	2.7500 (12)	158

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

Data collection: *CrysAlis PRO* (Agilent, 2012); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SUPERFLIP* (Palatinus & Chapuis, 2007); program(s) used to refine structure: *SHELXL2012* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *XP* in *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT6922).

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supporting information

Bruceolline J: 2-hydroxy-3,3-dimethyl-2,3-dihydrocyclopenta[*b*]indol-1(4*H*)-one

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S1. Comment

Bruceolline J is a cyclopenta[*b*]indole alkaloid which has been recently isolated from the stems of *Brucea mollis* Wall (Chen *et al.*, 2011). Our total synthesis of racemic bruceolline J was achieved by the oxidation of bruceolline D to bruceolline E with DDQ followed by the selective reduction of bruceolline E with sodium borohydride in 98% yield. Enantioselective reductions with *β*-chlorodiisopinocampheylborane gave both the natural and unnatural enantiomers in excellent yields and enantioselectivites. Further isolation studies of the *Brucea mollis* shrubs have resulted in the discovery of a myriad of other bruceollines and cathan-6-one alkaloids (Ouyang *et al.*, 1994*a*; Ouyang *et al.*, 1994*b*; Ouyang *et al.*, 1995). Although there has been limited attention from the synthetic community given to these compounds, a previous synthesis of bruceolline E has been reported (Jordan *et al.*, 2011). The crystal structures of bruceolline D (Lopchuk *et al.*, 2013) and bruceolline E (Jordon *et al.*, 2012) have been disclosed. In view of the importance of cyclopenta[*b*]indole alkaloids, we report here the crystal structure of the title compound, $C_{13}H_{13}NO_2$, (I).

The title compound, crystallizes with one molecule in the asymmetric unit. The 12-membered cyclopenta[*b*]indole ring system deviates only slightly from planarity (r.m.s. deviation 0.051Å) (Fig. 1). The 5-membered cyclopentanone ring is in slightly distorted envelope configuration (Q= 0.1012 (12)Å, φ = 66.4 (7)°) with C3 as the flap Bond lengths are in normal ranges (Allen *et al.*, 1987). In the crystal N—H···O and O—H···O hydrogen bonds (Table 1) link the molecules into sheets parallel to (1 0 0) and contribute to crystal packing stability (Fig. 2).

S2. Experimental

To an ice-cold solution of bruceolline E (50 mg, 0.234 mmol, 1.0 equiv.) in dry THF (10 mL) was added sodium borohydride (5 mg, 0.117 mmol, 0.5 equiv.) in one portion (Fig. 3). After stirring at 0°C for 5 minutes, the reaction was quenched with water (5 mL) and concentrated to half the original volume. The mixture was extracted with ethyl acetate (3 x 40 mL). The organic extracts were combined, dried over Na_2SO_4, and concentrated *in vacuo* to an off-white solid. The residue was purified by flash chromatography (50% ethyl acetate in pentane) to afford the desired product (I) as a white solid (50 mg, 98% yield). Single crystals suitable for diffraction were grown from ethyl acetate (slow evaporation) at ambient temperature [m.p. 466-467 K (dec); no literature value available].

S3. Refinement

All H atoms were found in a difference map. Nevertheless, they were placed in their calculated positions and then refined using the riding model with Atom—H lengths of 0.95Å, 1.000Å (CH), 0.98Å (CH_3), 0.88Å (NH) or 0.84Å (OH). Isotropic displacement parameters for these atoms were set to 1.2 (CH, NH) or 1.5 (CH_3, OH) times U_{eq} of the parent atom. The methyl groups and the hydroxyl group were refined as rotating groups allowed to rotate but not to tip.
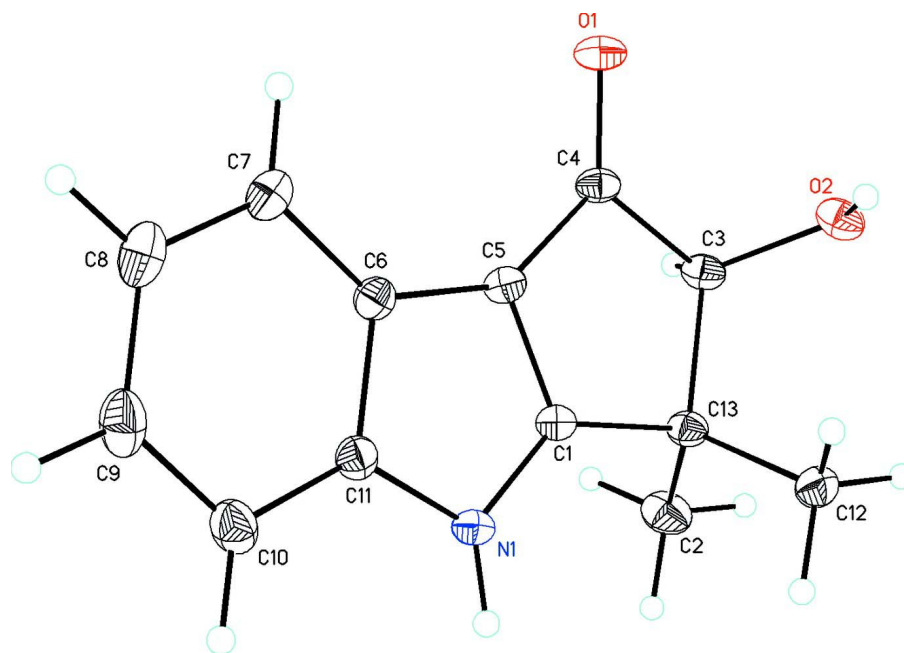
Figure 1

Molecular structure of the title compound showing the atom labeling scheme and 30% probability displacement ellipsoids.
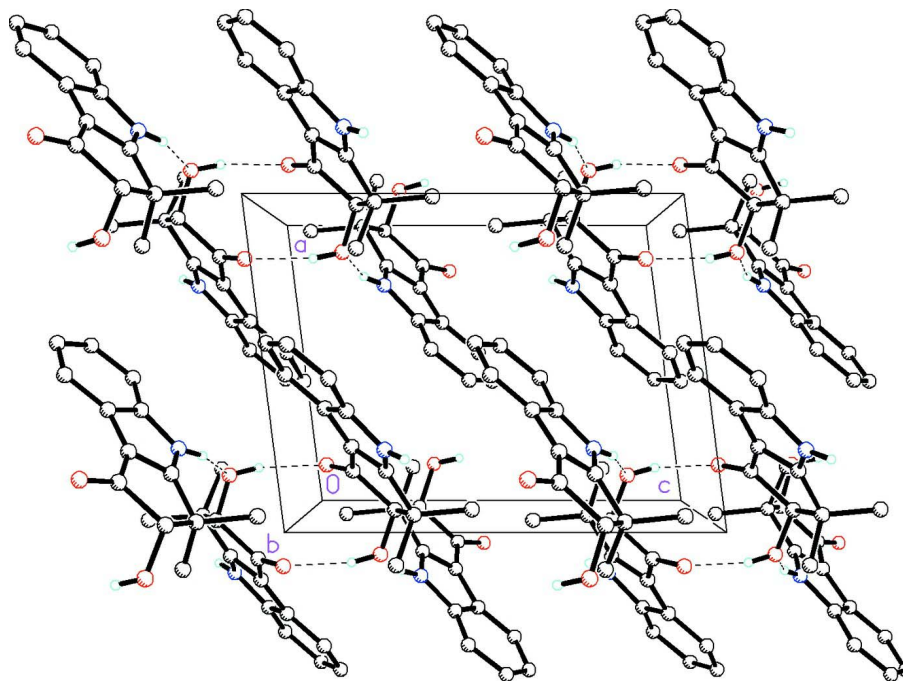
Figure 2

Packing diagram of the title compound viewed along the *b* axis. Dashed lines indicate N—H···O and O—H···O hydrogen bonds forming sheets parallel to (1 0 0). H atoms not involved hydrogen bonding have been deleted for clarity.
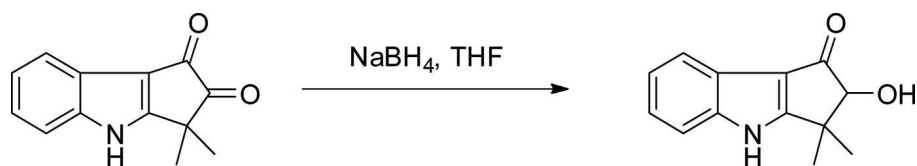
Figure 3

Synthesis of (I).

2-Hydroxy-3,3-dimethyl-2,3-dihydrocyclopenta[*b*]indol-1(4*H*)-one

Crystal data

$C_{13}H_{13}NO_2$	$F(000) = 456$
$M_r = 215.24$	$D_x = 1.315$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.7107$ Å
$a = 8.2951$ (3) Å	Cell parameters from 3528 reflections
$b = 12.3070$ (4) Å	$\theta = 3.3$–32.9°
$c = 10.7340$ (4) Å	$\mu = 0.09$ mm^{-1}
$\beta = 97.207$ (3)°	$T = 173$ K
$V = 1087.15$ (7) Å^3	Irregular, colourless
$Z = 4$	$0.44 \times 0.38 \times 0.34$ mm

Data collection

Agilent Xcalibur (Eos, Gemini) diffractometer	$T_{min} = 0.782$, $T_{max} = 1.000$
	13545 measured reflections
Radiation source: Enhance (Mo) X-ray Source	3753 independent reflections
Graphite monochromator	2888 reflections with $I > 2\sigma(I)$
Detector resolution: 16.0416 pixels mm^{-1}	$R_{int} = 0.035$
ω scans	$\theta_{max} = 33.0°$, $\theta_{min} = 3.4°$
Absorption correction: multi-scan (*CrysAlis PRO* and *CrysAlis RED*; Agilent, 2012)	$h = -12 \rightarrow 12$
	$k = -17 \rightarrow 18$
	$l = -16 \rightarrow 15$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.048$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.134$	
$S = 1.04$	H-atom parameters constrained
3753 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0662P)^2 + 0.2062P]$ where $P = (F_o^2 + 2F_c^2)/3$
148 parameters	
0 restraints	$(\Delta/\sigma)_{max} < 0.001$
	$\Delta\rho_{max} = 0.40$ e Å^{-3}
	$\Delta\rho_{min} = -0.25$ e Å^{-3}

Special details

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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.83909 (11)	0.55666 (6)	0.93513 (8)	0.03008 (19)
O2	1.13253 (11)	0.51818 (7)	0.82424 (8)	0.0297 (2)
H2	1.1552	0.4933	0.8972	0.045*
N1	0.76891 (11)	0.21451 (7)	0.76238 (9)	0.0246 (2)
H1	0.7945	0.1602	0.7152	0.030*
C1	0.83979 (13)	0.31258 (8)	0.77083 (10)	0.0221 (2)
C2	0.98429 (13)	0.35821 (9)	0.71904 (10)	0.0233 (2)
C3	0.98044 (14)	0.47719 (8)	0.77069 (10)	0.0242 (2)
H3	0.9398	0.5254	0.6986	0.029*
C4	0.85291 (13)	0.47926 (8)	0.86414 (9)	0.0230 (2)
C5	0.76844 (13)	0.37877 (9)	0.85201 (10)	0.0233 (2)
C6	0.64335 (13)	0.31588 (9)	0.90039 (10)	0.0239 (2)
C7	0.53565 (14)	0.33227 (11)	0.98851 (11)	0.0301 (2)
H7	0.5298	0.4006	1.0290	0.036*
C8	0.43771 (15)	0.24690 (12)	1.01561 (13)	0.0365 (3)
H8	0.3650	0.2567	1.0764	0.044*
C9	0.44313 (15)	0.14681 (12)	0.95594 (14)	0.0383 (3)
H9	0.3739	0.0899	0.9768	0.046*
C10	0.54722 (15)	0.12837 (10)	0.86689 (13)	0.0333 (3)
H10	0.5498	0.0604	0.8252	0.040*
C11	0.64742 (13)	0.21344 (9)	0.84131 (10)	0.0249 (2)
C12	1.13707 (14)	0.29740 (10)	0.77445 (12)	0.0309 (2)
H12A	1.2332	0.3343	0.7503	0.046*
H12B	1.1332	0.2228	0.7424	0.046*
H12C	1.1429	0.2961	0.8662	0.046*
C13	0.96704 (18)	0.35481 (12)	0.57537 (11)	0.0364 (3)
H13A	0.8664	0.3917	0.5411	0.055*
H13B	0.9636	0.2790	0.5471	0.055*
H13C	1.0601	0.3916	0.5460	0.055*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0424 (5)	0.0199 (4)	0.0285 (4)	0.0036 (3)	0.0066 (3)	−0.0047 (3)
O2	0.0386 (5)	0.0241 (4)	0.0273 (4)	−0.0099 (3)	0.0075 (3)	0.0006 (3)
N1	0.0267 (4)	0.0190 (4)	0.0284 (4)	0.0002 (3)	0.0046 (3)	−0.0042 (3)
C1	0.0248 (5)	0.0199 (4)	0.0216 (4)	0.0009 (4)	0.0033 (3)	−0.0015 (4)
C2	0.0279 (5)	0.0229 (5)	0.0197 (4)	−0.0015 (4)	0.0056 (4)	−0.0019 (4)
C3	0.0332 (6)	0.0189 (4)	0.0210 (5)	−0.0019 (4)	0.0051 (4)	0.0009 (4)
C4	0.0303 (5)	0.0184 (4)	0.0201 (4)	0.0036 (4)	0.0023 (4)	0.0001 (3)
C5	0.0266 (5)	0.0210 (5)	0.0228 (5)	0.0021 (4)	0.0056 (4)	−0.0008 (4)
C6	0.0233 (5)	0.0238 (5)	0.0245 (5)	0.0022 (4)	0.0027 (4)	0.0020 (4)
C7	0.0265 (5)	0.0358 (6)	0.0289 (5)	0.0046 (4)	0.0064 (4)	0.0019 (5)
C8	0.0271 (6)	0.0474 (7)	0.0364 (6)	0.0022 (5)	0.0090 (5)	0.0099 (6)
C9	0.0282 (6)	0.0386 (7)	0.0485 (8)	−0.0043 (5)	0.0068 (5)	0.0136 (6)

C10	0.0293 (6)	0.0262 (6)	0.0436 (7)	−0.0029 (4)	0.0022 (5)	0.0052 (5)
C11	0.0232 (5)	0.0227 (5)	0.0283 (5)	0.0013 (4)	0.0017 (4)	0.0023 (4)
C12	0.0276 (6)	0.0250 (5)	0.0405 (6)	0.0014 (4)	0.0062 (4)	−0.0033 (5)
C13	0.0477 (7)	0.0408 (7)	0.0217 (5)	−0.0070 (6)	0.0080 (5)	−0.0050 (5)

Geometric parameters (Å, º)

O1—C4	1.2341 (13)	C6—C11	1.4136 (15)
O2—H2	0.8400	C7—H7	0.9500
O2—C3	1.4122 (14)	C7—C8	1.3812 (19)
N1—H1	0.8800	C8—H8	0.9500
N1—C1	1.3406 (13)	C8—C9	1.392 (2)
N1—C11	1.3956 (14)	C9—H9	0.9500
C1—C2	1.4928 (15)	C9—C10	1.3849 (19)
C1—C5	1.3793 (14)	C10—H10	0.9500
C2—C3	1.5675 (15)	C10—C11	1.3854 (16)
C2—C12	1.5267 (16)	C12—H12A	0.9800
C2—C13	1.5313 (15)	C12—H12B	0.9800
C3—H3	1.0000	C12—H12C	0.9800
C3—C4	1.5467 (15)	C13—H13A	0.9800
C4—C5	1.4194 (15)	C13—H13B	0.9800
C5—C6	1.4425 (15)	C13—H13C	0.9800
C6—C7	1.3948 (15)		
C3—O2—H2	109.5	C6—C7—H7	120.8
C1—N1—H1	125.9	C8—C7—C6	118.46 (12)
C1—N1—C11	108.15 (9)	C8—C7—H7	120.8
C11—N1—H1	125.9	C7—C8—H8	119.2
N1—C1—C2	132.79 (9)	C7—C8—C9	121.50 (12)
N1—C1—C5	110.80 (10)	C9—C8—H8	119.2
C5—C1—C2	116.19 (9)	C8—C9—H9	119.3
C1—C2—C3	99.60 (8)	C10—C9—C8	121.45 (11)
C1—C2—C12	109.66 (9)	C10—C9—H9	119.3
C1—C2—C13	112.76 (9)	C9—C10—H10	121.5
C12—C2—C3	111.89 (9)	C9—C10—C11	117.03 (12)
C12—C2—C13	110.31 (10)	C11—C10—H10	121.5
C13—C2—C3	112.23 (9)	N1—C11—C6	108.88 (9)
O2—C3—C2	114.89 (9)	C10—C11—N1	128.63 (11)
O2—C3—H3	107.5	C10—C11—C6	122.44 (11)
O2—C3—C4	112.27 (8)	C2—C12—H12A	109.5
C2—C3—H3	107.5	C2—C12—H12B	109.5
C4—C3—C2	106.90 (8)	C2—C12—H12C	109.5
C4—C3—H3	107.5	H12A—C12—H12B	109.5
O1—C4—C3	122.49 (10)	H12A—C12—H12C	109.5
O1—C4—C5	130.25 (10)	H12B—C12—H12C	109.5
C5—C4—C3	107.22 (8)	C2—C13—H13A	109.5
C1—C5—C4	109.06 (9)	C2—C13—H13B	109.5
C1—C5—C6	107.19 (10)	C2—C13—H13C	109.5

C4—C5—C6	143.48 (10)	H13A—C13—H13B	109.5
C7—C6—C5	135.84 (11)	H13A—C13—H13C	109.5
C7—C6—C11	119.12 (10)	H13B—C13—H13C	109.5
C11—C6—C5	104.97 (9)		
O1—C4—C5—C1	−172.60 (11)	C4—C5—C6—C11	−173.69 (15)
O1—C4—C5—C6	0.2 (2)	C5—C1—C2—C3	−7.02 (12)
O2—C3—C4—O1	41.66 (14)	C5—C1—C2—C12	110.49 (11)
O2—C3—C4—C5	−136.56 (9)	C5—C1—C2—C13	−126.17 (11)
N1—C1—C2—C3	178.95 (11)	C5—C6—C7—C8	−175.79 (12)
N1—C1—C2—C12	−63.53 (15)	C5—C6—C11—N1	0.33 (12)
N1—C1—C2—C13	59.81 (16)	C5—C6—C11—C10	177.91 (11)
N1—C1—C5—C4	176.56 (9)	C6—C7—C8—C9	−0.91 (19)
N1—C1—C5—C6	1.03 (13)	C7—C6—C11—N1	−177.07 (10)
C1—N1—C11—C6	0.28 (12)	C7—C6—C11—C10	0.51 (17)
C1—N1—C11—C10	−177.10 (12)	C7—C8—C9—C10	0.1 (2)
C1—C2—C3—O2	134.83 (9)	C8—C9—C10—C11	0.97 (19)
C1—C2—C3—C4	9.56 (10)	C9—C10—C11—N1	175.78 (11)
C1—C5—C6—C7	175.93 (13)	C9—C10—C11—C6	−1.28 (18)
C1—C5—C6—C11	−0.81 (12)	C11—N1—C1—C2	173.45 (11)
C2—C1—C5—C4	1.24 (13)	C11—N1—C1—C5	−0.82 (12)
C2—C1—C5—C6	−174.29 (9)	C11—C6—C7—C8	0.61 (17)
C2—C3—C4—O1	168.51 (10)	C12—C2—C3—O2	19.00 (12)
C2—C3—C4—C5	−9.72 (11)	C12—C2—C3—C4	−106.28 (10)
C3—C4—C5—C1	5.44 (12)	C13—C2—C3—O2	−105.63 (11)
C3—C4—C5—C6	178.25 (14)	C13—C2—C3—C4	129.09 (10)
C4—C5—C6—C7	3.0 (3)		

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···O1[i]	0.84	1.90	2.7245 (12)	168
N1—H1···O2[ii]	0.88	1.91	2.7500 (12)	158

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