

tert-Butyl 2,3-dihydro-1*H*-cyclopenta[*b*]indole-4-carboxylate

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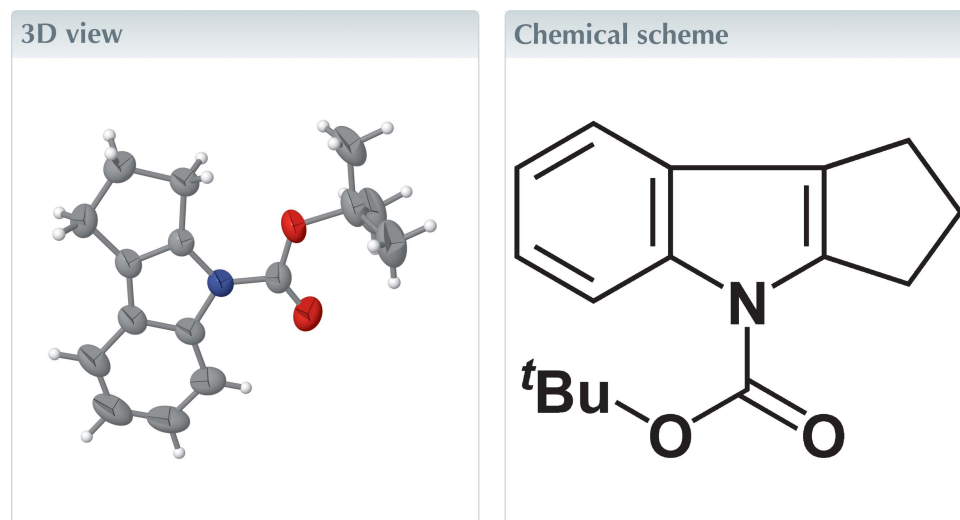
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Structural data: full structural data are available from iucrdata.iucr.org

In the title molecule, C₁₆H₁₉NO₂, all the non-hydrogen atoms except two of the C atoms of the *tert*-butyl group lie on a crystallographic mirror plane. No classical hydrogen bonds are observed. The crystal packing is influenced by weak π - π and C—H... π interactions.



Structure description

We report herein the crystal structure of the title compound, which confirms the previously assigned structure in which it was envisioned that the coupling of an indole with a protected hydroxyl benzaldehyde appendage would install the required vinyl group found in the target molecules Prenostodione, Scytonemin and Nostodione (Macor *et al.*, 1989; Badenock *et al.*, 2013). As such, and in preparation for the coupling, commercially available 1,2,3,4-tetrahydrocyclopenta[*b*]indole was converted to the *N*-BOC derivative using a standard protection protocol in 87% yield. All the atoms except C15 (see Fig. 1) lie on a crystallographic mirror plane: the second methyl group outside the mirror plane is symmetry related and generates the third methyl group in the *tert*-butyl group.

In the crystal, the molecules are in parallel layers alternately inverted along the *c* axis, parallel to the *ac* plane (Fig. 2 and 3). The crystal packing is influenced by weak π - π [Cg1—Cg1 and Cg1—Cg2; Cg1—Cg1 = 3.8718 (5) Å and Cg1—Cg2 = 3.7142 (4) Å, where Cg1 is the centroid of the N1/C1/C5/C6/C11 ring and Cg2 is the centroid of the C1—C5 ring] stacking interactions involving the pyrrole and cyclopentyl moieties and C2—H2(A/B)...Cg3(π) [C—H... π distance = 2.8 (8) Å; symmetry code: $-x + 1, y + \frac{1}{2}$ (H2A) or $y - \frac{1}{2}$ (H2B), $-z + 2$; where Cg3 is the centroid of the C6—C11 ring] interactions involving the benzene ring.

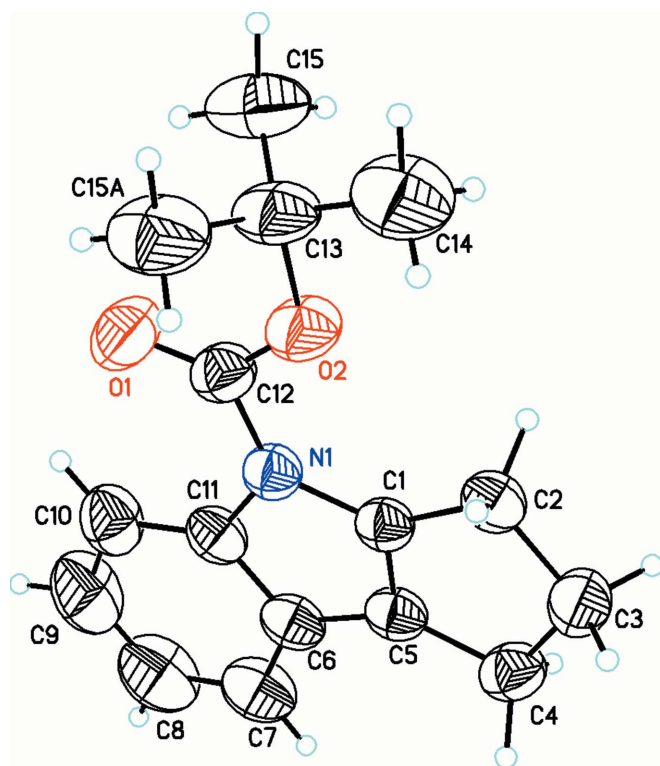


Figure 1
The molecular structure of the title compound, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.

Synthesis and crystallization

To a stirred solution of 1,2,3,4-tetrahydrocyclopenta[*b*]indole (2.48 g, 15.7 mmol, 1.0 equivalent) in freshly distilled THF

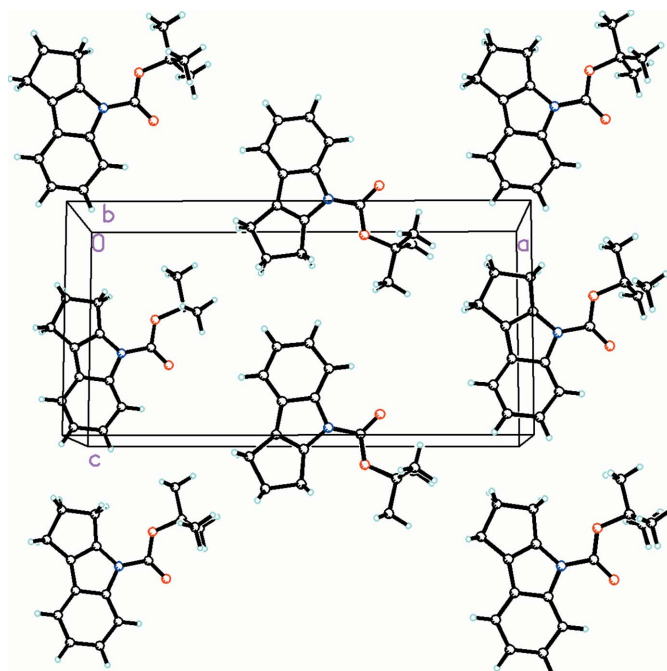


Figure 2
The packing of the title compound, viewed along the *b* axis.

Table 1
Experimental details.

Crystal data	
Chemical formula	C ₁₆ H ₁₉ NO ₂
<i>M</i> _r	257.32
Crystal system, space group	Orthorhombic, <i>Pnma</i>
Temperature (K)	173
<i>a</i> , <i>b</i> , <i>c</i> (Å)	19.6761 (11), 7.2330 (4), 9.9258 (7)
<i>V</i> (Å ³)	1412.61 (15)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.08
Crystal size (mm)	0.38 × 0.26 × 0.15
Data collection	
Diffractometer	Rigaku-Oxford Diffraction
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> & <i>CrysAlis RED</i> ; Rigaku-Oxford Diffraction, 2012)
<i>T</i> _{min} , <i>T</i> _{max}	0.970, 0.988
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	12388, 1808, 1486
<i>R</i> _{int}	0.029
(sin θ/λ) _{max} (Å ⁻¹)	0.658
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.056, 0.147, 1.11
No. of reflections	1808
No. of parameters	113
H-atom treatment	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.16, -0.18

Computer programs: *CrysAlis PRO* (Rigaku-Oxford Diffraction, 2012), *CrysAlis RED* (Rigaku-Oxford Diffraction, 2012), *SHELXL2014* (Sheldrick, 2015b), *SHELXT* (Sheldrick, 2015a) and *OLEX2* (Dolomanov *et al.*, 2009).

(75 ml) was added DMAP (0.10 g, 0.79 mmol, 0.05 equivalents) and di-*tert*-butyl dicarbonate (5.31 g, 24.3 mmol, 1.5 equivalents), and the resulting mixture allowed to stir at room temperature overnight (Grehn & Ragnarsson, 1984). The solvent was removed *via* rotary evaporation and the subsequent brown residue was absorbed directly onto silica and purified using flash column chromatography (9:1 hexanes-ethyl acetate). *tert*-Butyl 2,3-dihydro-1*H*-cyclopenta[*b*]indole-4-carboxylate was obtained as a pale-yellow solid (yield 3.53 g, 87%). Crystals suitable for X-ray diffraction were recrystallized from methanol solution (m.p. 389.0–389.4 K). ¹H NMR (CDCl₃): δ 8.15–8.17 (*d*, *J* = 7.5 Hz, 1H), 7.33–7.35 (*m*, 1H), 7.16–7.23 (*m*, 2H), 3.04–3.07 (*m*, 2H), 2.72–2.76 (*m*, 2H), 2.42–2.49 (*m*, 2H), 1.63 (*s*, 9H); ¹³C NMR (CDCl₃): δ 150.1,

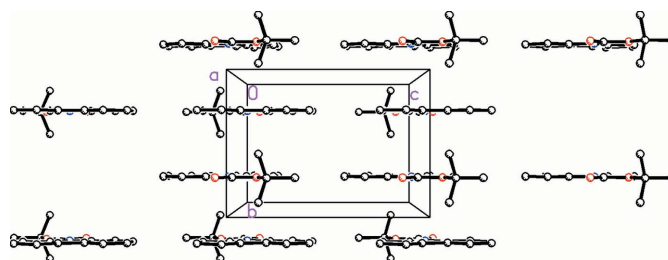


Figure 3
Part of the crystal structure of the title compound, showing the planes of molecules arranged in parallel layers alternately inverted along the *c* axis, parallel to the *ac* plane.

144.1, 140.2, 126.9, 124.5, 122.9, 122.6, 118.6, 115.8, 83.0, 29.2, 28.3, 27.5, 24.1; IR ν (film) 3315, 3053, 2980, 2860, 1727, 1611, 1476, 1453 cm^{-1} ; UV λ_{max} (95% EtOH) 204, 230, 272 nm. Analysis calculated for $\text{C}_{16}\text{H}_{19}\text{NO}_2$: C 74.68, H 7.44, N 5.44%; found: C 74.63, H 7.33, N 5.50.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1.

Acknowledgements

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full crystallographic data

IUCrData (2016). **1**, x161468 [doi:10.1107/S2414314616014681]

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tert-Butyl 2,3-dihydro-1*H*-cyclopenta[*b*]indole-4-carboxylate*Crystal data*

$C_{16}H_{19}NO_2$	$D_x = 1.210 \text{ Mg m}^{-3}$
$M_r = 257.32$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Orthorhombic, <i>Pnma</i>	Cell parameters from 4596 reflections
$a = 19.6761 (11) \text{ \AA}$	$\theta = 3.5\text{--}32.3^\circ$
$b = 7.2330 (4) \text{ \AA}$	$\mu = 0.08 \text{ mm}^{-1}$
$c = 9.9258 (7) \text{ \AA}$	$T = 173 \text{ K}$
$V = 1412.61 (15) \text{ \AA}^3$	Block, colourless
$Z = 4$	$0.38 \times 0.26 \times 0.15 \text{ mm}$
$F(000) = 552$	

Data collection

Rigaku-Oxford Diffraction diffractometer	12388 measured reflections
Detector resolution: 16.1500 pixels mm^{-1}	1808 independent reflections
ω scans	1486 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (CrysAlis PRO & CrysAlis RED; Rigaku- Oxford Diffraction, 2012)	$R_{\text{int}} = 0.029$
$T_{\text{min}} = 0.970$, $T_{\text{max}} = 0.988$	$\theta_{\text{max}} = 27.9^\circ$, $\theta_{\text{min}} = 3.5^\circ$
	$h = -25 \rightarrow 24$
	$k = -9 \rightarrow 8$
	$l = -12 \rightarrow 13$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.056$	H-atom parameters constrained
$wR(F^2) = 0.147$	$w = 1/[\sigma^2(F_o^2) + (0.0562P)^2 + 0.394P]$
$S = 1.11$	where $P = (F_o^2 + 2F_c^2)/3$
1808 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
113 parameters	$\Delta\rho_{\text{max}} = 0.16 \text{ e \AA}^{-3}$
0 restraints	$\Delta\rho_{\text{min}} = -0.18 \text{ e \AA}^{-3}$

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
O1	0.32442 (9)	0.2500	1.10343 (19)	0.0736 (6)	
O2	0.35771 (8)	0.2500	0.88593 (17)	0.0631 (5)	
N1	0.43643 (8)	0.2500	1.04482 (17)	0.0438 (4)	
C1	0.49003 (10)	0.2500	0.9521 (2)	0.0408 (4)	
C2	0.49512 (11)	0.2500	0.8034 (2)	0.0484 (5)	
H2A	0.4739	0.3616	0.7640	0.058*	0.5
H2B	0.4739	0.1384	0.7640	0.058*	0.5
C3	0.57309 (12)	0.2500	0.7828 (2)	0.0586 (6)	
H3A	0.5869	0.1391	0.7311	0.070*	0.5
H3B	0.5869	0.3609	0.7311	0.070*	0.5
C4	0.60802 (11)	0.2500	0.9211 (2)	0.0547 (6)	
H4A	0.6366	0.1385	0.9331	0.066*	0.5
H4B	0.6366	0.3615	0.9331	0.066*	0.5
C5	0.54989 (10)	0.2500	1.0164 (2)	0.0442 (5)	
C6	0.53714 (12)	0.2500	1.1579 (2)	0.0490 (5)	
C7	0.57817 (15)	0.2500	1.2717 (3)	0.0674 (7)	
H7	0.6263	0.2500	1.2632	0.081*	
C8	0.5485 (2)	0.2500	1.3961 (3)	0.0874 (10)	
H8	0.5765	0.2500	1.4741	0.105*	
C9	0.4784 (2)	0.2500	1.4109 (3)	0.0863 (10)	
H9	0.4594	0.2500	1.4989	0.104*	
C10	0.43543 (15)	0.2500	1.3003 (2)	0.0652 (7)	
H10	0.3874	0.2500	1.3104	0.078*	
C11	0.46572 (12)	0.2500	1.1746 (2)	0.0471 (5)	
C12	0.36713 (10)	0.2500	1.0180 (2)	0.0513 (5)	
C13	0.28904 (12)	0.2500	0.8262 (3)	0.0673 (7)	
C14	0.30593 (17)	0.2500	0.6773 (3)	0.0996 (12)	
H14A	0.2638	0.2500	0.6248	0.149*	
H14B	0.3325	0.3606	0.6554	0.149*	0.5
H14C	0.3325	0.1394	0.6554	0.149*	0.5
C15	0.25196 (10)	0.0761 (3)	0.8664 (2)	0.0919 (8)	
H15A	0.2814	-0.0311	0.8514	0.138*	
H15B	0.2106	0.0635	0.8121	0.138*	
H15C	0.2397	0.0830	0.9620	0.138*	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0494 (9)	0.0972 (14)	0.0743 (12)	0.000	0.0089 (8)	0.000
O2	0.0406 (8)	0.0872 (12)	0.0614 (10)	0.000	-0.0137 (7)	0.000
N1	0.0427 (9)	0.0436 (9)	0.0450 (9)	0.000	-0.0029 (7)	0.000
C1	0.0421 (10)	0.0340 (9)	0.0463 (11)	0.000	-0.0026 (8)	0.000
C2	0.0525 (12)	0.0462 (11)	0.0466 (11)	0.000	-0.0054 (9)	0.000
C3	0.0579 (13)	0.0584 (13)	0.0596 (14)	0.000	0.0092 (11)	0.000
C4	0.0433 (11)	0.0507 (12)	0.0701 (15)	0.000	-0.0006 (10)	0.000

C5	0.0453 (10)	0.0363 (9)	0.0511 (11)	0.000	-0.0081 (9)	0.000
C6	0.0559 (12)	0.0384 (10)	0.0526 (12)	0.000	-0.0109 (10)	0.000
C7	0.0740 (17)	0.0687 (15)	0.0596 (15)	0.000	-0.0255 (13)	0.000
C8	0.111 (3)	0.097 (2)	0.0548 (16)	0.000	-0.0305 (17)	0.000
C9	0.122 (3)	0.095 (2)	0.0414 (13)	0.000	-0.0040 (15)	0.000
C10	0.0810 (17)	0.0641 (15)	0.0506 (13)	0.000	0.0058 (12)	0.000
C11	0.0584 (13)	0.0382 (10)	0.0447 (11)	0.000	-0.0059 (9)	0.000
C12	0.0426 (11)	0.0509 (12)	0.0603 (13)	0.000	-0.0022 (10)	0.000
C13	0.0450 (12)	0.0737 (16)	0.0832 (18)	0.000	-0.0249 (12)	0.000
C14	0.079 (2)	0.140 (3)	0.081 (2)	0.000	-0.0380 (17)	0.000
C15	0.0649 (12)	0.0779 (14)	0.133 (2)	-0.0129 (10)	-0.0315 (12)	0.0047 (13)

Geometric parameters (Å, °)

O1—C12	1.194 (3)	C6—C11	1.415 (3)
O2—C12	1.324 (3)	C7—H7	0.9500
O2—C13	1.476 (3)	C7—C8	1.365 (4)
N1—C1	1.400 (3)	C8—H8	0.9500
N1—C11	1.411 (3)	C8—C9	1.388 (5)
N1—C12	1.389 (3)	C9—H9	0.9500
C1—C2	1.479 (3)	C9—C10	1.385 (4)
C1—C5	1.340 (3)	C10—H10	0.9500
C2—H2A	0.9900	C10—C11	1.383 (3)
C2—H2B	0.9900	C13—C14	1.515 (4)
C2—C3	1.548 (3)	C13—C15 ⁱ	1.508 (3)
C3—H3A	0.9900	C13—C15	1.508 (3)
C3—H3B	0.9900	C14—H14A	0.9800
C3—C4	1.536 (3)	C14—H14B	0.9800
C4—H4A	0.9900	C14—H14C	0.9800
C4—H4B	0.9900	C15—H15A	0.9800
C4—C5	1.484 (3)	C15—H15B	0.9800
C5—C6	1.427 (3)	C15—H15C	0.9800
C6—C7	1.388 (3)		
C12—O2—C13	121.74 (19)	C7—C8—H8	119.3
C1—N1—C11	107.02 (16)	C7—C8—C9	121.4 (3)
C12—N1—C1	127.82 (18)	C9—C8—H8	119.3
C12—N1—C11	125.16 (18)	C8—C9—H9	119.3
N1—C1—C2	135.00 (17)	C10—C9—C8	121.5 (3)
C5—C1—N1	110.42 (18)	C10—C9—H9	119.3
C5—C1—C2	114.58 (19)	C9—C10—H10	121.5
C1—C2—H2A	111.5	C11—C10—C9	116.9 (3)
C1—C2—H2B	111.5	C11—C10—H10	121.5
C1—C2—C3	101.51 (17)	N1—C11—C6	107.37 (18)
H2A—C2—H2B	109.3	C10—C11—N1	130.4 (2)
C3—C2—H2A	111.5	C10—C11—C6	122.2 (2)
C3—C2—H2B	111.5	O1—C12—O2	127.2 (2)
C2—C3—H3A	109.9	O1—C12—N1	123.7 (2)

C2—C3—H3B	109.9	O2—C12—N1	109.11 (19)
H3A—C3—H3B	108.3	O2—C13—C14	101.0 (2)
C4—C3—C2	108.96 (19)	O2—C13—C15	109.67 (14)
C4—C3—H3A	109.9	O2—C13—C15 ⁱ	109.67 (14)
C4—C3—H3B	109.9	C15 ⁱ —C13—C14	111.38 (16)
C3—C4—H4A	111.2	C15—C13—C14	111.38 (16)
C3—C4—H4B	111.2	C15 ⁱ —C13—C15	113.0 (2)
H4A—C4—H4B	109.1	C13—C14—H14A	109.5
C5—C4—C3	103.01 (17)	C13—C14—H14B	109.5
C5—C4—H4A	111.2	C13—C14—H14C	109.5
C5—C4—H4B	111.2	H14A—C14—H14B	109.5
C1—C5—C4	111.95 (19)	H14A—C14—H14C	109.5
C1—C5—C6	108.33 (19)	H14B—C14—H14C	109.5
C6—C5—C4	139.71 (19)	C13—C15—H15A	109.5
C7—C6—C5	134.3 (2)	C13—C15—H15B	109.5
C7—C6—C11	118.8 (2)	C13—C15—H15C	109.5
C11—C6—C5	106.85 (18)	H15A—C15—H15B	109.5
C6—C7—H7	120.4	H15A—C15—H15C	109.5
C8—C7—C6	119.1 (3)	H15B—C15—H15C	109.5
C8—C7—H7	120.4		
N1—C1—C2—C3	180.000 (1)	C6—C7—C8—C9	0.000 (1)
N1—C1—C5—C4	180.000 (1)	C7—C6—C11—N1	180.000 (1)
N1—C1—C5—C6	0.000 (1)	C7—C6—C11—C10	0.000 (1)
C1—N1—C11—C6	0.000 (1)	C7—C8—C9—C10	0.000 (1)
C1—N1—C11—C10	180.000 (1)	C8—C9—C10—C11	0.000 (1)
C1—N1—C12—O1	180.000 (1)	C9—C10—C11—N1	180.000 (1)
C1—N1—C12—O2	0.000 (1)	C9—C10—C11—C6	0.000 (1)
C1—C2—C3—C4	0.000 (1)	C11—N1—C1—C2	180.000 (1)
C1—C5—C6—C7	180.000 (1)	C11—N1—C1—C5	0.000 (1)
C1—C5—C6—C11	0.000 (1)	C11—N1—C12—O1	0.000 (1)
C2—C1—C5—C4	0.000 (1)	C11—N1—C12—O2	180.000 (1)
C2—C1—C5—C6	180.000 (1)	C11—C6—C7—C8	0.000 (1)
C2—C3—C4—C5	0.000 (1)	C12—O2—C13—C14	180.000 (1)
C3—C4—C5—C1	0.000 (1)	C12—O2—C13—C15 ⁱ	62.35 (18)
C3—C4—C5—C6	180.000 (1)	C12—O2—C13—C15	-62.35 (18)
C4—C5—C6—C7	0.000 (1)	C12—N1—C1—C2	0.000 (1)
C4—C5—C6—C11	180.000 (1)	C12—N1—C1—C5	180.000 (1)
C5—C1—C2—C3	0.000 (1)	C12—N1—C11—C6	180.000 (1)
C5—C6—C7—C8	180.000 (1)	C12—N1—C11—C10	0.000 (1)
C5—C6—C11—N1	0.000 (1)	C13—O2—C12—O1	0.000 (1)
C5—C6—C11—C10	180.000 (1)	C13—O2—C12—N1	180.000 (1)

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

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C10—H10 \cdots O1	0.95	2.40	2.931 (3)	115

C15—H15C···O1	0.98	2.49	3.025 (3)	114
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