Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Methyl 1′-(3-hydroxy-2-oxo-2,3-dihydro-1*H*-indol-3-yl)-2-oxo-2,3-dihydro-1*H*-indole-3-spiro-3′-pyrrolizidine-1′-carboxylate

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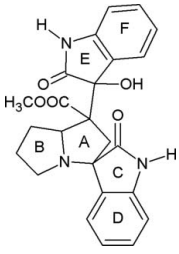
Received 21 July 2007; accepted 24 July 2007

Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.003 Å; R factor = 0.042; wR factor = 0.158; data-to-parameter ratio = 13.0.

In the title compound, $C_{24}H_{23}N_3O_5$, one of the pyrrolidine rings in the pyrrolizine ring system adopts an envelope conformation, whereas the other ring adopts an envelope conformation. Both indol-2-one ring systems are essentially planar. The molecule is stabilized by an intramolecular O—H···O hydrogen bond which generates an S(8) motif. The molecules are linked into a two-dimensional network parallel to the (10$\bar{1}$) plane by intermolecular N—H···O and C—H···O hydrogen bonds.

Related literature

For general background, see: Amalraj *et al.* (2003); Cordell (1981); Rajeswaran *et al.* (1999); Suzuki *et al.* (1994); Usha *et al.* (2005). For ring motifs, see: Bernstein *et al.* (1995). For ring conformations, see: Cremer & Pople (1975); Nardelli (1983). For a related structure, see: Murugavel *et al.* (2007). For related literature, see: Jeyabharathi (2001); Seshadri (2003).



Experimental

Crystal data

$C_{24}H_{23}N_3O_5$
M_r = 433.45
Monoclinic, $P2_1/n$
a = 13.0337 (11) Å
b = 7.9573 (6) Å
c = 19.9303 (17) Å
β = 93.184 (3)°
V = 2063.8 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 293 (2) K
0.25 × 0.21 × 0.18 mm

Data collection

Bruker APEX2 CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
T_{min} = 0.976, T_{max} = 0.982
19499 measured reflections
3783 independent reflections
2567 reflections with $I > 2\sigma(I)$
R_{int} = 0.045

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.158
S = 1.06
3783 reflections
291 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.35 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4···O1	0.82	2.02	2.819 (2)	163
N3—H3···O5^{i}	0.86	2.04	2.894 (3)	175
N19—H19···O5^{ii}	0.86	2.09	2.917 (2)	161
C14—H14···O1	0.98	2.45	3.091 (3)	122
C16—H16*B*···O2	0.97	2.34	2.800 (3)	108
C12—H12*B*···O1^{iii}	0.97	2.50	3.225 (3)	131

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

Data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ZORTEP* (Zsolnai, 1997); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

PR thanks Dr Babu Varghese, SAIF, IIT, Chennai, India, for the X-ray data collection.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI2425).

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supplementary materials

Acta Cryst. (2007). E**63**, o3625-o3626 [**doi:10.1107/S160053680703629X**]

Methyl 1'-(3-hydroxy-2-oxo-2,3-dihydro-1*H*-indol-3-yl)-2-oxo-2,3-dihydro-1*H*-indole-3-spiro-3'-pyrrolizidine-1'-carboxylate

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Comment

Pyrrolizidine alkaloids represent a group of compounds present in a variety of plants throughout the world. Oxindole derivatives are found to be potent aldose reductase inhibitors (ARIs), which helps to treat and prevent diabetic complications arising from elevated levels of sorbitol (Rajeswaran *et al.*, 1999). The pyrrolizidine alkaloids are well documented for their mutagenic, antineoplastic, carcinogenic, hepatoxic and many pharmacological activities (Usha *et al.*, 2005). Substituted pyrrolidine compounds have been found to have antimicrobial and antifungal activity against various pathogens (Amalraj *et al.*, 2003). Several optically active pyrrolidine compounds have been used as intermediates in controlled asymmetric synthesis (Suzuki *et al.*, 1994). The spiro-indole-pyrrolidine ring system is a frquently encountered structural motif in many biologically important and pharmacologically relevant alkaloids, *e.g.* vincrinstine and vinblastine (Cordell *et al.*, 1981). In view of this biological importance, the crystal structure of the title compound has been determined and the results are presented here.

The title compound (Fig. 1) consists of a pyrrolizine ring system (rings A and B) connected to a oxindole ring system (rings C and D) at C1, and a hydroxy oxindole unit (rings E and F) and methoxycarbonyl group at C15. The bond lengths in the pyrrolizine ring system are slightly longer than the values reported for similar structures (Jeyabharathi *et al.*, 2001; Seshadri *et al.*, 2003). This may be due to steric forces caused by the bulky substituents on the pyrrolizine ring system. The sum of angles at N3 (359.9°) and N19 (360°) of the oxindole units are in accordance with sp^2 hybridization, whereas the sum of angles at N10 (337.3°) of the pyrrolizine ring is in accordance with sp^3 hybridization.

In the pyrrolizine ring system, the pyrrolidine ring A adopts an envelope conformation whereas the ring B adopts a twisted conformation. The puckering parameters (q_2 and φ; Cremer & Pople, 1975) and the smallest displacement asymmetric parameter (Δ; Nardelli, 1983) are, for the ring A, q_2 = 0.416 (2) Å, φ = 174.5 (3)° and Δ_s(N10) = 4.8 (2)°; for the ring B q_2 = 0.444 (2) Å, φ = 341.2 (3)° and Δ_2(C12) = 1.3 (2)°. Both indole-2-one ring systems are essentially planar, with atoms O1 and O5 displaced by −0.205 (2) Å and 0.198 (2) Å.

The molecule is stabilized by an intramolecular O—H···O hydrogen bond which generates an S(8) motif (Bernstein *et al.*, 1995), as observed in a similar structure (Murugavel *et al.*, 2007). The crystal packing is stabilized by intermolecular C—H···O and N—H···O hydrogen bonds. Atoms N3 and C12 of the molecule at (*x*, *y*, *z*) donate one proton each to atoms O5 and O1 of moecules at (3/2 − *x*, *y* − 1/2, 1/2 − *z*) and (3/2 − *x*, *y* + 1/2, 1/2 − *z*), respectively, forming a chain along the *b* axis with $R_2^2(12)$ ring motifs. The molecules at (*x*, *y*, *z*) and (2 − *x*, 1 − *y*, 1 − *z*) are linked by N19—H19···O5 hydrogen bonds into cyclic centrosymmetric $R_2^2(8)$ dimers, thus linking the adjacent chains into a two-dimensional network parallel to the (1 0 $\bar{1}$) plane.

Experimental

A solution of Baylis Hillman adduct of isatin (1 mmol), proline (1 mmol) and isatin (1 mmol) in ethanol was refluxed. After completion of the reaction, as monitored by thin-layer chromatographic analysis, the solvent was removed under vacuum, and the crude product was subjected to column chromatography on silica gel (100–200 mesh) using petroleum ether/ethyl acetate (7:3) as eluent. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of an ethyl acetate solution.

Refinement

H atoms were positioned geometrically (O—H = 0.82 Å, N—H = 0.86 Å and C—H = 0.93–0.98 Å) and allowed to ride on their parent atoms, with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(C,*O*) for the methyl and OH groups.

Figures

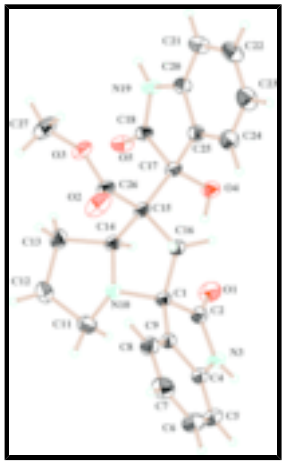


Fig. 1. The molecular structure of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

Methyl 1'-(3-hydroxy-2-oxo-2,3-dihydro-1*H*-indol-3-yl)-2-oxo-2,3-dihydro- 1*H*-indole-3-spiro-3'-pyrrolizidine-1'-carboxylate

Crystal data

$C_{24}H_{23}N_3O_5$	F_{000} = 912
M_r = 433.45	D_x = 1.395 Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2yn	Cell parameters from 6845 reflections
a = 13.0337 (11) Å	θ = 2.8–25.4º
b = 7.9573 (6) Å	μ = 0.10 mm^{-1}
c = 19.9303 (17) Å	T = 293 (2) K
β = 93.184 (3)º	Block, colourless
V = 2063.8 (3) Å^3	0.25 × 0.21 × 0.18 mm
Z = 4	

Data collection

Bruker APEX2 CCD area-detector diffractometer	3783 independent reflections
Radiation source: fine-focus sealed tube	2567 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.045$
$T = 293(2)$ K	$\theta_{max} = 25.4°$
ω scans	$\theta_{min} = 1.8°$
Absorption correction: multi-scan (SADABS; Sheldrick, 2001)	$h = -15\rightarrow15$
$T_{min} = 0.976$, $T_{max} = 0.982$	$k = -9\rightarrow9$
19499 measured reflections	$l = -24\rightarrow23$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.042$	H-atom parameters constrained
$wR(F^2) = 0.158$	$w = 1/[\sigma^2(F_o^2) + (0.0957P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} = 0.016$
3783 reflections	$\Delta\rho_{max} = 0.35$ e Å^{-3}
291 parameters	$\Delta\rho_{min} = -0.26$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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 $F^2 > 2$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	0.72215 (13)	0.1955 (3)	0.25051 (9)	0.0572 (5)
O2	0.56320 (15)	0.2516 (3)	0.50386 (10)	0.0679 (6)
O3	0.70217 (12)	0.4091 (2)	0.52414 (8)	0.0430 (4)
O4	0.84860 (12)	0.1711 (2)	0.36953 (8)	0.0468 (5)
H4	0.8095	0.1980	0.3377	0.070*

O5	0.89232 (12)	0.5038 (2)	0.42579 (8)	0.0421 (4)
C1	0.57372 (16)	0.1871 (3)	0.32218 (11)	0.0343 (5)
C2	0.63301 (19)	0.1579 (3)	0.25855 (12)	0.0413 (6)
N3	0.56772 (16)	0.0858 (3)	0.21180 (10)	0.0501 (6)
H3	0.5825	0.0665	0.1710	0.060*
C4	0.47306 (19)	0.0466 (3)	0.23802 (12)	0.0432 (6)
C5	0.3906 (2)	−0.0395 (4)	0.20867 (15)	0.0644 (9)
H5	0.3908	−0.0752	0.1642	0.077*
C6	0.3081 (2)	−0.0711 (4)	0.24668 (18)	0.0685 (9)
H6	0.2522	−0.1302	0.2278	0.082*
C7	0.3066 (2)	−0.0175 (4)	0.31189 (16)	0.0620 (8)
H7	0.2500	−0.0413	0.3367	0.074*
C8	0.38911 (18)	0.0723 (3)	0.34157 (13)	0.0465 (6)
H8	0.3879	0.1101	0.3857	0.056*
C9	0.47192 (17)	0.1034 (3)	0.30395 (11)	0.0364 (6)
N10	0.56661 (13)	0.3632 (2)	0.34024 (9)	0.0334 (5)
C11	0.53680 (19)	0.4958 (3)	0.29247 (13)	0.0461 (6)
H11A	0.4631	0.4965	0.2824	0.055*
H11B	0.5717	0.4837	0.2510	0.055*
C12	0.57209 (19)	0.6552 (3)	0.33081 (13)	0.0468 (6)
H12A	0.5135	0.7152	0.3469	0.056*
H12B	0.6089	0.7294	0.3019	0.056*
C13	0.64313 (19)	0.5947 (3)	0.39015 (13)	0.0463 (6)
H13A	0.7056	0.6612	0.3943	0.056*
H13B	0.6088	0.6001	0.4320	0.056*
C14	0.66601 (16)	0.4143 (3)	0.37126 (11)	0.0330 (5)
H14	0.7167	0.4148	0.3367	0.040*
C15	0.69104 (16)	0.2662 (3)	0.42044 (11)	0.0322 (5)
C16	0.63300 (17)	0.1148 (3)	0.38523 (11)	0.0349 (5)
H16A	0.6815	0.0297	0.3724	0.042*
H16B	0.5857	0.0644	0.4153	0.042*
C17	0.80709 (16)	0.2245 (3)	0.43055 (10)	0.0320 (5)
C18	0.87766 (16)	0.3723 (3)	0.45599 (11)	0.0316 (5)
N19	0.92764 (14)	0.3246 (2)	0.51369 (9)	0.0368 (5)
H19	0.9698	0.3879	0.5368	0.044*
C20	0.90328 (16)	0.1608 (3)	0.53177 (11)	0.0345 (5)
C21	0.94465 (19)	0.0707 (3)	0.58528 (13)	0.0457 (6)
H21	0.9922	0.1186	0.6161	0.055*
C22	0.9130 (2)	−0.0942 (3)	0.59170 (14)	0.0528 (7)
H22	0.9401	−0.1591	0.6272	0.063*
C23	0.8419 (2)	−0.1631 (3)	0.54602 (15)	0.0566 (7)
H23	0.8212	−0.2740	0.5512	0.068*
C24	0.80034 (19)	−0.0695 (3)	0.49222 (14)	0.0497 (7)
H24	0.7523	−0.1170	0.4616	0.060*
C25	0.83173 (17)	0.0955 (3)	0.48490 (12)	0.0358 (5)
C26	0.64407 (18)	0.3038 (3)	0.48693 (11)	0.0369 (6)
C27	0.6626 (2)	0.4599 (4)	0.58721 (13)	0.0652 (9)
H27A	0.5976	0.5152	0.5789	0.098*
H27B	0.7101	0.5357	0.6099	0.098*

H27C	0.6536	0.3626	0.6148	0.098*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0383 (11)	0.0890 (15)	0.0451 (11)	0.0000 (9)	0.0090 (8)	−0.0160 (9)
O2	0.0514 (12)	0.0914 (16)	0.0631 (13)	−0.0340 (11)	0.0235 (10)	−0.0280 (11)
O3	0.0388 (10)	0.0575 (11)	0.0330 (9)	−0.0114 (7)	0.0057 (7)	−0.0154 (8)
O4	0.0351 (9)	0.0688 (12)	0.0361 (9)	0.0088 (8)	−0.0011 (7)	−0.0137 (9)
O5	0.0415 (10)	0.0482 (11)	0.0360 (9)	−0.0150 (7)	−0.0053 (7)	0.0124 (8)
C1	0.0283 (12)	0.0407 (14)	0.0335 (12)	0.0013 (9)	−0.0016 (9)	−0.0087 (10)
C2	0.0383 (15)	0.0494 (15)	0.0358 (13)	0.0088 (11)	−0.0008 (11)	−0.0101 (11)
N3	0.0508 (14)	0.0674 (16)	0.0312 (11)	0.0092 (10)	−0.0048 (10)	−0.0181 (10)
C4	0.0397 (14)	0.0447 (15)	0.0437 (15)	0.0071 (11)	−0.0095 (12)	−0.0126 (11)
C5	0.062 (2)	0.068 (2)	0.0600 (19)	0.0036 (15)	−0.0238 (16)	−0.0279 (15)
C6	0.0507 (19)	0.066 (2)	0.086 (2)	−0.0103 (14)	−0.0229 (17)	−0.0225 (17)
C7	0.0368 (15)	0.0615 (19)	0.087 (2)	−0.0092 (13)	−0.0016 (15)	−0.0046 (16)
C8	0.0383 (15)	0.0478 (16)	0.0532 (16)	−0.0038 (11)	−0.0002 (12)	−0.0093 (12)
C9	0.0314 (13)	0.0351 (13)	0.0415 (13)	0.0030 (9)	−0.0073 (10)	−0.0110 (10)
N10	0.0297 (10)	0.0348 (11)	0.0352 (10)	0.0001 (8)	−0.0013 (8)	−0.0045 (8)
C11	0.0417 (15)	0.0511 (16)	0.0451 (15)	0.0043 (11)	−0.0024 (12)	0.0029 (12)
C12	0.0414 (14)	0.0388 (15)	0.0608 (17)	0.0039 (11)	0.0073 (12)	0.0030 (12)
C13	0.0447 (15)	0.0360 (14)	0.0578 (16)	−0.0039 (10)	0.0003 (13)	−0.0092 (11)
C14	0.0302 (12)	0.0350 (13)	0.0337 (12)	−0.0033 (9)	0.0002 (9)	−0.0059 (10)
C15	0.0292 (12)	0.0356 (13)	0.0314 (12)	−0.0040 (9)	−0.0013 (9)	−0.0068 (9)
C16	0.0322 (12)	0.0343 (13)	0.0376 (13)	−0.0029 (9)	−0.0036 (10)	−0.0077 (10)
C17	0.0300 (12)	0.0378 (13)	0.0280 (12)	−0.0040 (9)	0.0000 (9)	−0.0048 (9)
C18	0.0253 (11)	0.0408 (14)	0.0286 (11)	−0.0045 (9)	0.0011 (9)	−0.0004 (10)
N19	0.0358 (11)	0.0400 (12)	0.0335 (10)	−0.0121 (8)	−0.0080 (8)	0.0033 (9)
C20	0.0301 (12)	0.0372 (14)	0.0361 (13)	−0.0041 (9)	0.0013 (10)	0.0038 (10)
C21	0.0381 (14)	0.0518 (17)	0.0465 (15)	−0.0031 (11)	−0.0051 (11)	0.0104 (12)
C22	0.0482 (16)	0.0478 (17)	0.0622 (18)	0.0009 (12)	0.0001 (13)	0.0201 (13)
C23	0.0548 (17)	0.0370 (16)	0.078 (2)	−0.0050 (12)	0.0028 (15)	0.0130 (14)
C24	0.0459 (16)	0.0388 (15)	0.0635 (18)	−0.0062 (11)	−0.0045 (13)	−0.0018 (12)
C25	0.0299 (12)	0.0357 (13)	0.0415 (13)	−0.0007 (9)	−0.0001 (10)	−0.0025 (10)
C26	0.0324 (13)	0.0425 (14)	0.0356 (13)	−0.0063 (10)	0.0011 (10)	−0.0050 (10)
C27	0.067 (2)	0.089 (2)	0.0418 (16)	−0.0185 (16)	0.0166 (14)	−0.0283 (15)

Geometric parameters (Å, °)

O1—C2	1.219 (3)	C12—H12A	0.97
O2—C26	1.198 (3)	C12—H12B	0.97
O3—C26	1.328 (3)	C13—C14	1.518 (3)
O3—C27	1.443 (3)	C13—H13A	0.97
O4—C17	1.423 (3)	C13—H13B	0.97
O4—H4	0.82	C14—C15	1.556 (3)
O5—C18	1.227 (3)	C14—H14	0.98
C1—N10	1.451 (3)	C15—C26	1.520 (3)
C1—C9	1.511 (3)	C15—C17	1.551 (3)

C1—C2	1.539 (3)	C15—C16	1.568 (3)
C1—C16	1.549 (3)	C16—H16A	0.97
C2—O1	1.219 (3)	C16—H16B	0.97
C2—O1	1.219 (3)	C17—C25	1.514 (3)
C2—N3	1.354 (3)	C17—C18	1.560 (3)
N3—C4	1.401 (3)	C18—N19	1.344 (3)
N3—H3	0.86	N19—C20	1.394 (3)
C4—C5	1.377 (4)	N19—H19	0.86
C4—C9	1.390 (3)	C20—C21	1.371 (3)
C5—C6	1.372 (4)	C20—C25	1.384 (3)
C5—H5	0.93	C21—C22	1.383 (3)
C6—C7	1.369 (4)	C21—H21	0.93
C6—H6	0.93	C22—C23	1.377 (4)
C7—C8	1.395 (3)	C22—H22	0.93
C7—H7	0.93	C23—C24	1.390 (3)
C8—C9	1.370 (3)	C23—H23	0.93
C8—H8	0.93	C24—C25	1.386 (3)
N10—C11	1.460 (3)	C24—H24	0.93
N10—C14	1.462 (3)	C26—O2	1.198 (3)
C11—C12	1.538 (3)	C27—H27A	0.96
C11—H11A	0.97	C27—H27B	0.96
C11—H11B	0.97	C27—H27C	0.96
C12—C13	1.538 (3)		
C26—O3—C27	116.28 (19)	N10—C14—C15	101.87 (16)
C17—O4—H4	109.5	C13—C14—C15	126.69 (19)
N10—C1—C9	114.72 (18)	N10—C14—H14	108.6
N10—C1—C2	113.10 (19)	C13—C14—H14	108.6
C9—C1—C2	102.10 (18)	C15—C14—H14	108.6
N10—C1—C16	101.15 (16)	C26—C15—C17	111.47 (18)
C9—C1—C16	115.02 (19)	C26—C15—C14	108.65 (18)
C2—C1—C16	111.21 (17)	C17—C15—C14	114.38 (18)
O1—C2—N3	125.5 (2)	C26—C15—C16	109.49 (17)
O1—C2—N3	125.5 (2)	C17—C15—C16	109.68 (17)
O1—C2—N3	125.5 (2)	C14—C15—C16	102.77 (17)
O1—C2—C1	126.7 (2)	C1—C16—C15	106.50 (18)
O1—C2—C1	126.7 (2)	C1—C16—H16A	110.4
O1—C2—C1	126.7 (2)	C15—C16—H16A	110.4
N3—C2—C1	107.8 (2)	C1—C16—H16B	110.4
C2—N3—C4	111.7 (2)	C15—C16—H16B	110.4
C2—N3—H3	124.1	H16A—C16—H16B	108.6
C4—N3—H3	124.1	O4—C17—C25	109.47 (18)
C5—C4—C9	120.9 (3)	O4—C17—C15	111.55 (17)
C5—C4—N3	129.4 (2)	C25—C17—C15	113.87 (18)
C9—C4—N3	109.6 (2)	O4—C17—C18	104.93 (17)
C4—C5—C6	118.3 (3)	C25—C17—C18	100.41 (17)
C4—C5—H5	120.9	C15—C17—C18	115.73 (18)
C6—C5—H5	120.9	O5—C18—N19	125.36 (19)
C7—C6—C5	121.3 (3)	O5—C18—C17	126.03 (19)
C7—C6—H6	119.3	N19—C18—C17	108.32 (18)

C5—C6—H6	119.3	C18—N19—C20	112.2 (2)
C6—C7—C8	120.7 (3)	C18—N19—H19	123.9
C6—C7—H7	119.7	C20—N19—H19	123.9
C8—C7—H7	119.7	C21—C20—C25	123.4 (2)
C9—C8—C7	118.2 (3)	C21—C20—N19	127.2 (2)
C9—C8—H8	120.9	C25—C20—N19	109.34 (18)
C7—C8—H8	120.9	C20—C21—C22	117.5 (2)
C8—C9—C4	120.6 (2)	C20—C21—H21	121.3
C8—C9—C1	131.0 (2)	C22—C21—H21	121.3
C4—C9—C1	108.4 (2)	C23—C22—C21	120.6 (2)
C1—N10—C11	123.7 (2)	C23—C22—H22	119.7
C1—N10—C14	107.8 (2)	C21—C22—H22	119.7
C11—N10—C14	105.8 (2)	C22—C23—C24	121.1 (3)
N10—C11—C12	102.17 (19)	C22—C23—H23	119.5
N10—C11—H11A	111.3	C24—C23—H23	119.5
C12—C11—H11A	111.3	C25—C24—C23	119.0 (2)
N10—C11—H11B	111.3	C25—C24—H24	120.5
C12—C11—H11B	111.3	C23—C24—H24	120.5
H11A—C11—H11B	109.2	C20—C25—C24	118.5 (2)
C11—C12—C13	105.94 (19)	C20—C25—C17	109.68 (19)
C11—C12—H12A	110.5	C24—C25—C17	131.7 (2)
C13—C12—H12A	110.5	O2—C26—O3	123.0 (2)
C11—C12—H12B	110.5	O2—C26—O3	123.0 (2)
C13—C12—H12B	110.5	O2—C26—C15	125.5 (2)
H12A—C12—H12B	108.7	O2—C26—C15	125.5 (2)
C14—C13—C12	102.92 (18)	O3—C26—C15	111.48 (18)
C14—C13—H13A	111.2	O3—C27—H27A	109.5
C12—C13—H13A	111.2	O3—C27—H27B	109.5
C14—C13—H13B	111.2	H27A—C27—H27B	109.5
C12—C13—H13B	111.2	O3—C27—H27C	109.5
H13A—C13—H13B	109.1	H27A—C27—H27C	109.5
N10—C14—C13	100.73 (18)	H27B—C27—H27C	109.5
O1—O1—C2—O1	0.00 (8)	C13—C14—C15—C17	−100.0 (3)
O1—O1—C2—O1	0.00 (8)	N10—C14—C15—C16	28.0 (2)
O1—O1—C2—N3	0.00 (7)	C13—C14—C15—C16	141.2 (2)
O1—O1—C2—N3	0.00 (7)	N10—C1—C16—C15	−22.0 (2)
O1—O1—C2—C1	0.00 (13)	C9—C1—C16—C15	−146.19 (19)
O1—O1—C2—C1	0.00 (13)	C2—C1—C16—C15	98.4 (2)
N10—C1—C2—O1	60.4 (3)	C26—C15—C16—C1	111.6 (2)
C9—C1—C2—O1	−175.7 (2)	C17—C15—C16—C1	−125.80 (19)
C16—C1—C2—O1	−52.6 (3)	C14—C15—C16—C1	−3.8 (2)
N10—C1—C2—O1	60.4 (3)	C26—C15—C17—O4	173.46 (18)
C9—C1—C2—O1	−175.7 (2)	C14—C15—C17—O4	−62.8 (2)
C16—C1—C2—O1	−52.6 (3)	C16—C15—C17—O4	52.0 (2)
N10—C1—C2—O1	60.4 (3)	C26—C15—C17—C25	48.9 (2)
C9—C1—C2—O1	−175.7 (2)	C14—C15—C17—C25	172.69 (18)
C16—C1—C2—O1	−52.6 (3)	C16—C15—C17—C25	−72.5 (2)
N10—C1—C2—N3	−118.2 (2)	C26—C15—C17—C18	−66.7 (2)
C9—C1—C2—N3	5.6 (2)	C14—C15—C17—C18	57.1 (2)

C16—C1—C2—N3	128.8 (2)	C16—C15—C17—C18	171.89 (17)
O1—C2—N3—C4	175.5 (2)	O4—C17—C18—O5	59.8 (3)
O1—C2—N3—C4	175.5 (2)	C25—C17—C18—O5	173.4 (2)
O1—C2—N3—C4	175.5 (2)	C15—C17—C18—O5	−63.6 (3)
C1—C2—N3—C4	−5.9 (3)	O4—C17—C18—N19	−114.24 (19)
C2—N3—C4—C5	−173.9 (3)	C25—C17—C18—N19	−0.7 (2)
C2—N3—C4—C9	3.7 (3)	C15—C17—C18—N19	122.4 (2)
C9—C4—C5—C6	−1.5 (4)	O5—C18—N19—C20	−172.9 (2)
N3—C4—C5—C6	175.9 (3)	C17—C18—N19—C20	1.2 (2)
C4—C5—C6—C7	0.7 (5)	C18—N19—C20—C21	176.0 (2)
C5—C6—C7—C8	0.4 (5)	C18—N19—C20—C25	−1.3 (3)
C6—C7—C8—C9	−0.8 (4)	C25—C20—C21—C22	0.5 (4)
C7—C8—C9—C4	0.0 (4)	N19—C20—C21—C22	−176.5 (2)
C7—C8—C9—C1	−176.2 (2)	C20—C21—C22—C23	−0.6 (4)
C5—C4—C9—C8	1.1 (4)	C21—C22—C23—C24	0.3 (4)
N3—C4—C9—C8	−176.7 (2)	C22—C23—C24—C25	0.1 (4)
C5—C4—C9—C1	178.1 (2)	C21—C20—C25—C24	−0.2 (4)
N3—C4—C9—C1	0.3 (3)	N19—C20—C25—C24	177.3 (2)
N10—C1—C9—C8	−64.2 (3)	C21—C20—C25—C17	−176.7 (2)
C2—C1—C9—C8	173.1 (2)	N19—C20—C25—C17	0.8 (3)
C16—C1—C9—C8	52.6 (3)	C23—C24—C25—C20	−0.2 (4)
N10—C1—C9—C4	119.2 (2)	C23—C24—C25—C17	175.5 (2)
C2—C1—C9—C4	−3.5 (2)	O4—C17—C25—C20	109.9 (2)
C16—C1—C9—C4	−124.1 (2)	C15—C17—C25—C20	−124.4 (2)
C9—C1—N10—C11	−69.2 (3)	C18—C17—C25—C20	−0.1 (2)
C2—C1—N10—C11	47.4 (3)	O4—C17—C25—C24	−66.0 (3)
C16—C1—N10—C11	166.4 (2)	C15—C17—C25—C24	59.7 (3)
C9—C1—N10—C14	166.86 (19)	C18—C17—C25—C24	−176.0 (3)
C2—C1—N10—C14	−76.6 (2)	O2—O2—C26—O3	0.0 (3)
C16—C1—N10—C14	42.4 (2)	O2—O2—C26—C15	0.00 (13)
C1—N10—C11—C12	−163.88 (19)	C27—O3—C26—O2	−0.3 (4)
C14—N10—C11—C12	−39.0 (2)	C27—O3—C26—O2	−0.3 (4)
N10—C11—C12—C13	13.8 (2)	C27—O3—C26—C15	177.2 (2)
C11—C12—C13—C14	14.6 (3)	C17—C15—C26—O2	−135.8 (3)
C1—N10—C14—C13	−176.96 (18)	C14—C15—C26—O2	97.2 (3)
C11—N10—C14—C13	48.9 (2)	C16—C15—C26—O2	−14.3 (3)
C1—N10—C14—C15	−45.6 (2)	C17—C15—C26—O2	−135.8 (3)
C11—N10—C14—C15	−179.73 (17)	C14—C15—C26—O2	97.2 (3)
C12—C13—C14—N10	−37.4 (2)	C16—C15—C26—O2	−14.3 (3)
C12—C13—C14—C15	−151.1 (2)	C17—C15—C26—O3	46.7 (3)
N10—C14—C15—C26	−87.98 (19)	C14—C15—C26—O3	−80.2 (2)
C13—C14—C15—C26	25.2 (3)	C16—C15—C26—O3	168.28 (19)
N10—C14—C15—C17	146.78 (17)		

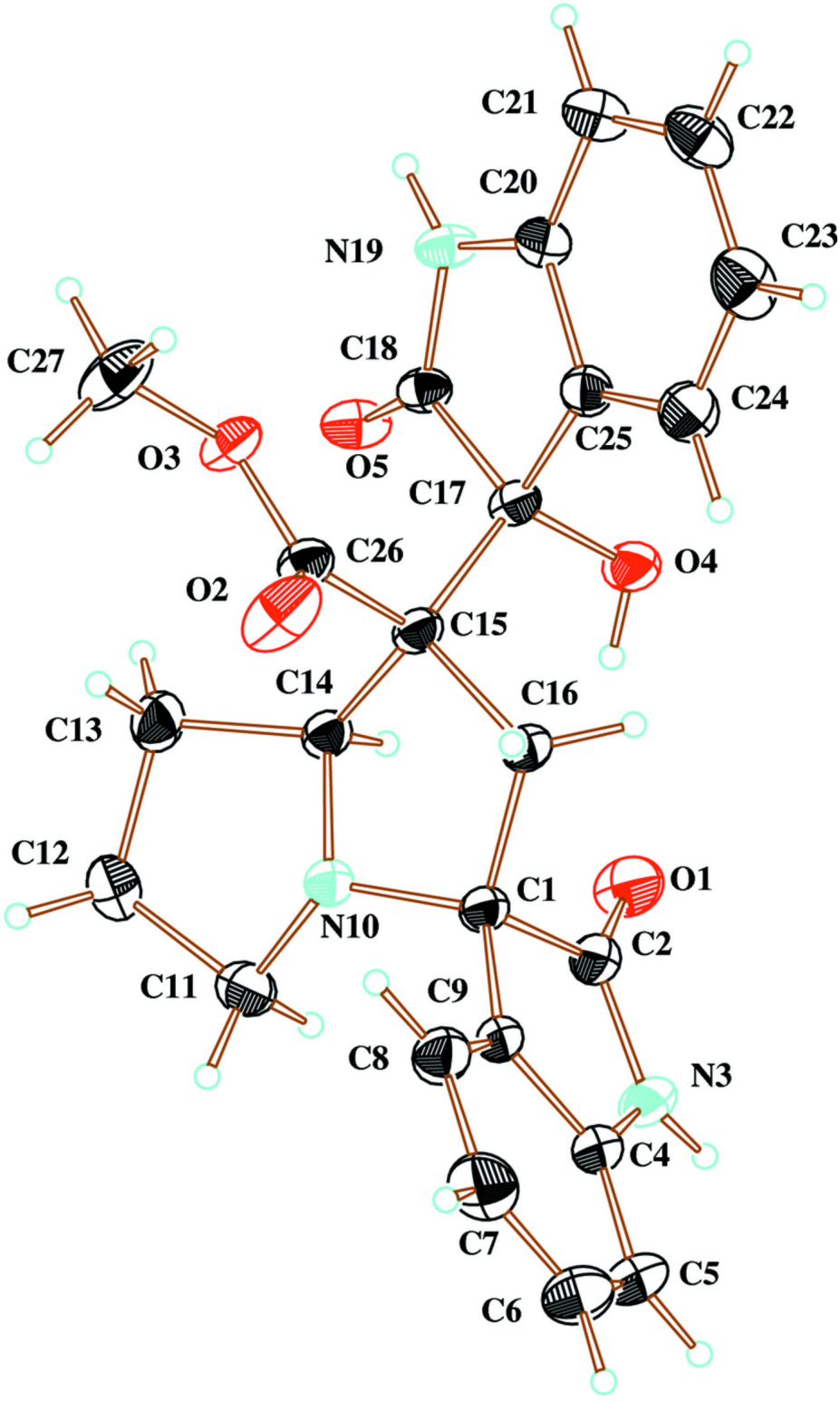
Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4···O1	0.82	2.02	2.819 (2)	163
N3—H3···O5^{i}	0.86	2.04	2.894 (3)	175

N19—H19···O5^{ii}	0.86	2.09	2.917 (2)	161
C14—H14···O1	0.98	2.45	3.091 (3)	122
C16—H16B···O2	0.97	2.34	2.800 (3)	108
C12—H12B···O1^{iii}	0.97	2.50	3.225 (3)	131

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

Fig. 1


C21
C22
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O1
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C11
C9
C8
N3
C4
C7
C5
C6