Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

cis-(9*S*,10*S*)-Methyl 1-propyl-1,2,3,4-tetrahydro-β-carboline-3-carboxylate

Samina Alam,[a] Mashooda Hasan,[a] Sadaf Saeed,[a]* Andreas Fischer[b] and Naeema Khan[a]

[a]Department of Chemistry, Quaid-i-Azam University, Islamabad, Pakistan, and [b]Inorganic Chemistry, School of Chemical Science and Engineering, Royal Institute of Technology (KTH), 10044 Stockholm, Sweden
Correspondence e-mail: sadaf03_2000@yahoo.com

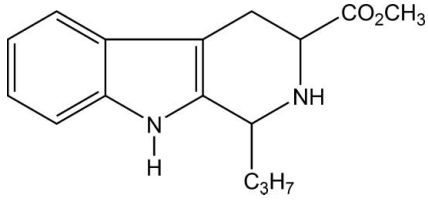
Received 26 October 2007; accepted 6 December 2007

Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.005 Å; R factor = 0.048; wR factor = 0.116; data-to-parameter ratio = 9.4.

The title compound, $C_{16}H_{20}N_2O_2$, was synthesized from (*S*)-tryptophan methyl ester hydrochloride and butyraldehyde. The absolute configuration 9*S*,10*S* was assigned on the basis of the unchanging chirality of the C9 centre. The NH group of the indole ring is involved in intermolecular N—H···O hydrogen bonding, while the NH group of the six-membered ring is not. This latter ring has a half-chair conformation.

Related literature

For related literature, see: Agurell *et al.* (1969); Bein (1953); Herraiz (2000); Johnson *et al.* (1963); Petter & Engelmann (1974). For synthetic details, see: Greenstein & Winiz (1961); Snyder *et al.* (1948).



Experimental

Crystal data

$C_{16}H_{20}N_2O_2$
M_r = 272.34
Tetragonal, $P4_32_12$
a = 9.3410 (11) Å
c = 36.125 (5) Å
V = 3152.1 (7) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 298 K
0.30 × 0.30 × 0.30 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Absorption correction: none
10764 measured reflections
1778 independent reflections
1285 reflections with $I > 2\sigma(I)$
R_{int} = 0.043

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.116
S = 1.08
1778 reflections
189 parameters
2 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1N···O1^{i}	0.84 (3)	2.20 (3)	3.037 (3)	177 (3)

Symmetry code: (i) $x+\frac{1}{2}, -y+\frac{3}{2}, -z+\frac{1}{4}$.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DIRAX* (Duisenberg, 1992); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2007); software used to prepare material for publication: *publCIF* (Westrip, 2008).

MH is grateful to the Alexander von Humboldt Foundation, Germany, and AF thanks the Swedish Research Council for financial assistance.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BI2260).

References

Agurell, S., Holmstedt, B., Lindgren, J. E. & Schultes, R. E. (1969). *Acta Chem. Scand.* **23**, 903–916.
Bein, H. J. (1953). *Experientia*, **9**, 107–110.
Brandenburg, K. (2007). *DIAMOND*. Release 3.1e. Crystal Impact GbR, Bonn, Germany.
Duisenberg, A. J. M. (1992). *J. Appl. Cryst.* **25**, 92–96.
Duisenberg, A. J. M., Kroon-Batenburg, L. M. J. & Schreurs, A. M. M. (2003). *J. Appl. Cryst.* **36**, 220–229.
Greenstein, J. P. & Winiz, M. (1961). *Chemistry of Amino Acids*, Vol. II, p. 926. Weinheim: John Wiley and Sons Inc.
Herraiz, T. (2000). *J. Agric. Food Chem.* **48**, 4900–4904.
Johnson, I. S., Armstrong, J. G., Gorman, M. & Burnett, J. P. (1963). *Cancer Res.* **23**, 1390–1427.
Nonius (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.
Petter, A. & Engelmann, K. (1974). *Arzneim.-Forsch.* **24**, 876–880.
Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
Snyder, H. R., Corwin, H. H., Katz, L., Parmerter, S. M. & Spaeth, E. (1948). *J. Chem. Soc.* pp. 219–221.
Westrip, S. (2008). *publCIF*. In preparation.

supporting information

Acta Cryst. (2008). E**64**, o361 [doi:10.1107/S1600536807066020]

cis-(9*S*,10*S*)-Methyl 1-propyl-1,2,3,4-tetrahydro-*β*-carboline-3-carboxylate

Samina Alam, Mashooda Hasan, Sadaf Saeed, Andreas Fischer and Naeema Khan

S1. Comment

Keeping in mind the diverse biological activities of alkaloids containing an indole or indoline nucleus (Agurell *et al.*, 1969; Bein, 1953; Johnson *et al.*, 1963; Herraiz, 2000), we have designed and synthesized some optically active compounds containing the tetrahydro-*β*-carboline nucleus. We report here the crystal structure of the title compound.

S2. Experimental

The title compound was prepared by condensation of (*S*)-tryptophan methyl ester hydrochloride with an aldehyde under polar protic conditions (Greenstein & Winiz, 1961; Snyder *et al.*, 1948). (*S*)-tryptophan methyl ester hydrochloride (1.5 g, 0.0059 mol) and butyraldehyde (1.50 ml, 0.0059 mol) were dissolved in methanol/water solution (50 ml, 75/25%, *v*/*v*). The mixture was refluxed for 48 h, cooled and the solvent evaporated under vacuum. The residue was dissolved in 14% ammonium hydroxide, extracted with chloroform and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure to yield an oily residue which was subjected to column chromatography. The purified oil was crystallized from benzene/pet. ether (b.p. 373–393 K) to give the title compound: yield 1.2 g, 74.8%, m.p. 413 K, R_f 0.84 methanol / chloroform (3:7). $[a]_D^{28}$-132.8 (c = 0.00348, acetonitrile). The product after purification was subjected to different spectroscopic techniques. This data together with the result of elemental analysis confirmed the formation of a pure stereoisomer.

S3. Refinement

In the absence of significant anomalous scattering effects, Friedel pairs were merged prior to refinement. All C-bonded H atoms were placed at calculated positions. The two N-bonded H atoms were located from the Fourier map and were refined with the restraint N—H = 0.89 (1) Å. The isotropic displacement parameters of the H atoms were fixed at U_{iso}(H) = 1.2U_{eq}(C/N) (1.5U_{eq}(C) for the methyl groups).

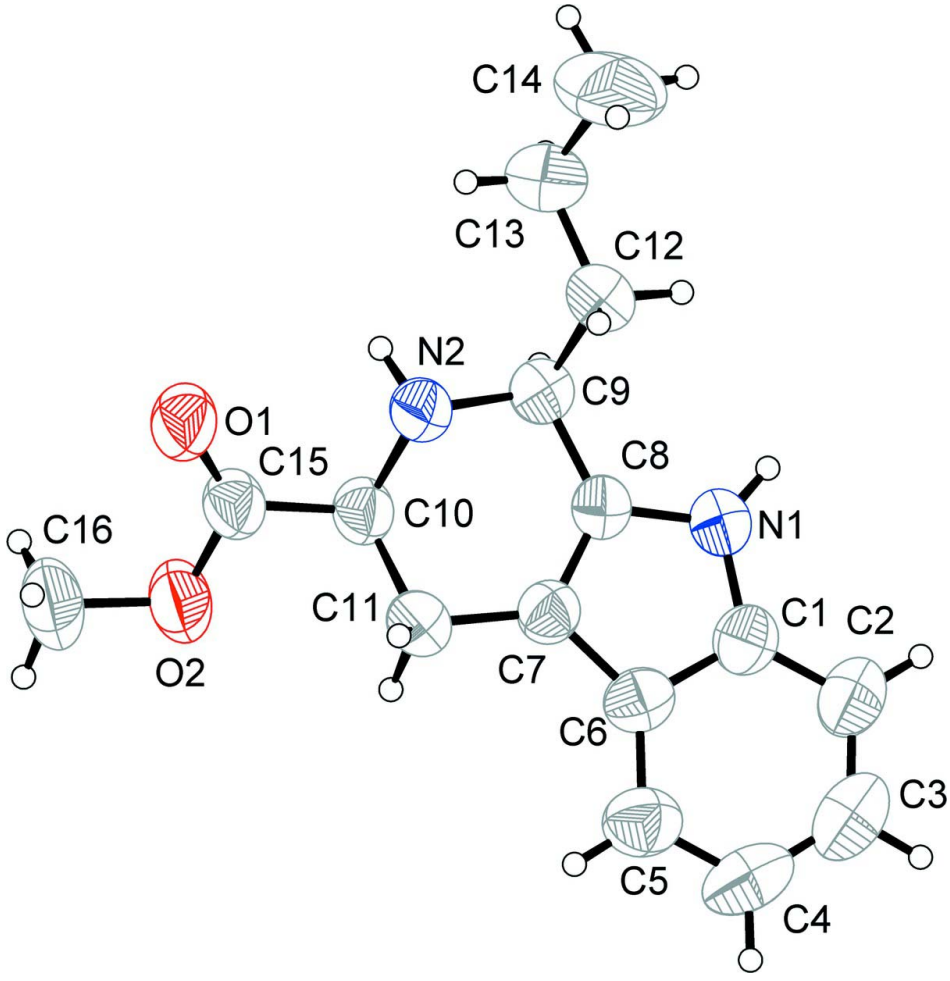


Figure 1

The molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level for non-H atoms.

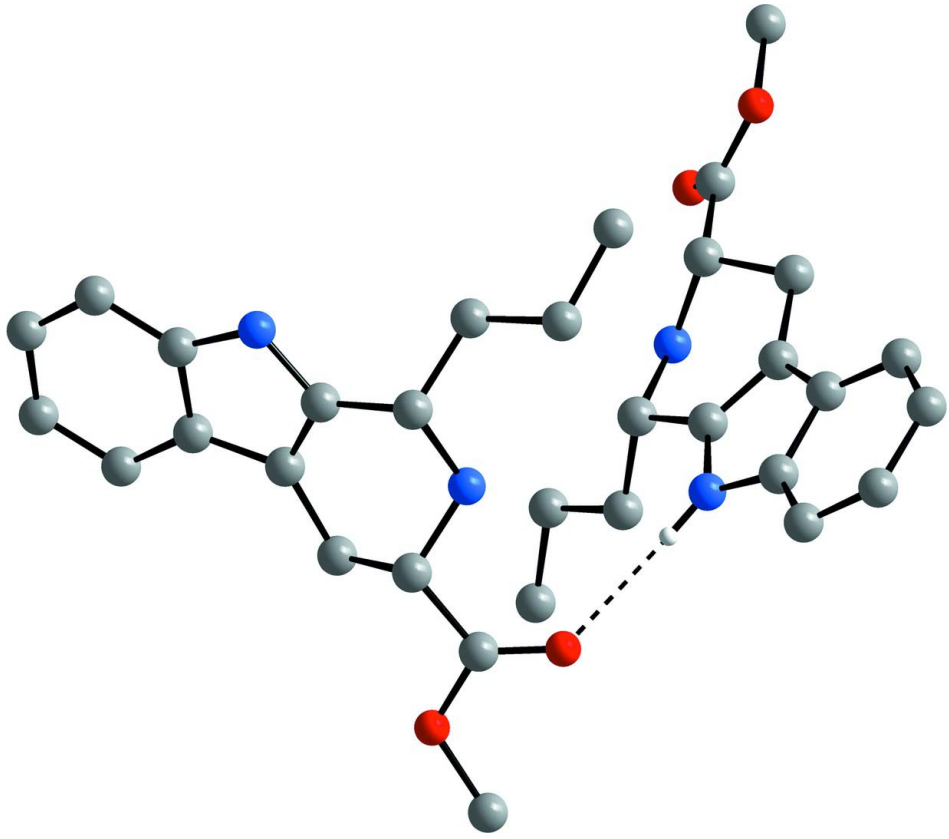


Figure 2

The intermolecular N—H···O hydrogen bond (dashed line). H atoms not involved in hydrogen bonding are omitted.

cis-(9*S*,10*S*)-Methyl 1-propyl-1,2,3,4-tetrahydro-*β*-carboline-3-carboxylate

Crystal data

$C_{16}H_{20}N_2O_2$
$M_r = 272.34$
Tetragonal, $P4_32_12$
Hall symbol: P 4nw 2abw
$a = 9.3410\ (11)$ Å
$c = 36.125\ (5)$ Å
$V = 3152.1\ (7)$ Å^3
$Z = 8$
$F(000) = 1168$
$D_x = 1.148$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 87 reflections
$\theta = 3.8$–$15.5°$
$\mu = 0.08$ mm^{-1}
$T = 298$ K
Block, colourless
0.30 × 0.30 × 0.30 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Radiation source: fine-focus sealed tube
φ & ω scans
10764 measured reflections
1778 independent reflections
1285 reflections with $I > 2\sigma(I)$
$R_{int} = 0.043$
$\theta_{max} = 25.5°$, $\theta_{min} = 4.5°$
$h = -10 \rightarrow 11$
$k = -10 \rightarrow 11$
$l = -42 \rightarrow 43$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.116$
$S = 1.08$
1778 reflections
189 parameters
2 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0441P)^2 + 0.674P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.18$ e Å^{-3}
$\Delta\rho_{min} = -0.14$ e Å^{-3}

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 $F^2 > \sigma(F^2)$ 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}
C1	1.0247 (3)	1.1462 (3)	0.13466 (8)	0.0614 (8)
C2	1.0963 (4)	1.2716 (4)	0.12461 (10)	0.0795 (10)
C3	1.0883 (4)	1.3850 (4)	0.14882 (13)	0.0947 (12)
C4	1.0138 (5)	1.3760 (4)	0.18233 (12)	0.0943 (12)
C5	0.9434 (4)	1.2512 (4)	0.19235 (10)	0.0787 (10)
C6	0.9480 (3)	1.1324 (3)	0.16848 (8)	0.0600 (8)
C7	0.8933 (3)	0.9871 (3)	0.16950 (7)	0.0570 (7)
C8	0.9361 (3)	0.9219 (3)	0.13770 (7)	0.0559 (7)
C9	0.9096 (3)	0.7685 (3)	0.12739 (8)	0.0618 (8)
C10	0.8291 (3)	0.7477 (3)	0.19244 (7)	0.0607 (8)
C11	0.8098 (4)	0.9089 (3)	0.19896 (7)	0.0654 (8)
C12	0.8563 (4)	0.7499 (3)	0.08743 (7)	0.0733 (9)
C13	0.8352 (5)	0.5956 (4)	0.07535 (9)	0.0947 (12)
C14	0.7879 (7)	0.5844 (6)	0.03549 (11)	0.156 (2)
C15	0.7327 (3)	0.6573 (4)	0.21666 (7)	0.0668 (8)
C16	0.6592 (6)	0.6136 (5)	0.27900 (9)	0.140 (2)
O1	0.6595 (3)	0.5587 (3)	0.20643 (5)	0.0843 (7)
O2	0.7402 (3)	0.6986 (3)	0.25177 (6)	0.1103 (10)
N1	1.0152 (3)	1.0167 (3)	0.11634 (7)	0.0639 (7)
N2	0.7998 (3)	0.7132 (3)	0.15343 (7)	0.0660 (7)
H2	1.1472	1.2781	0.1025	0.095*
H3	1.1339	1.4703	0.1427	0.114*
H4	1.0114	1.4547	0.1981	0.113*
H5	0.8936	1.2461	0.2146	0.094*
H9	0.9983	0.7139	0.1306	0.074*

H10	0.9288	0.7226	0.1979	0.073*
H11A	0.7093	0.9342	0.1975	0.078*
H11B	0.8449	0.9349	0.2233	0.078*
H12A	0.7660	0.8001	0.0848	0.088*
H12B	0.9245	0.7949	0.0709	0.088*
H13A	0.9244	0.5438	0.0785	0.114*
H13B	0.7640	0.5509	0.0911	0.114*
H14A	0.7047	0.6429	0.0317	0.235*
H14B	0.7653	0.4866	0.0298	0.235*
H14C	0.8637	0.6166	0.0196	0.235*
H16A	0.5589	0.6186	0.2734	0.211*
H16B	0.6757	0.6511	0.3034	0.211*
H16C	0.6903	0.5157	0.2780	0.211*
H1N	1.052 (3)	0.996 (3)	0.0958 (9)	0.077*
H2N	0.799 (3)	0.620 (4)	0.1515 (9)	0.079*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0602 (19)	0.0582 (19)	0.0658 (18)	0.0029 (14)	−0.0028 (15)	0.0070 (15)
C2	0.084 (2)	0.067 (2)	0.087 (2)	−0.0118 (18)	−0.0036 (18)	0.0132 (19)
C3	0.094 (3)	0.068 (2)	0.121 (3)	−0.015 (2)	−0.010 (3)	0.017 (2)
C4	0.105 (3)	0.055 (2)	0.123 (3)	−0.001 (2)	−0.019 (3)	−0.012 (2)
C5	0.087 (3)	0.068 (2)	0.081 (2)	0.0092 (19)	−0.0023 (19)	−0.0071 (19)
C6	0.0579 (18)	0.0541 (17)	0.0679 (18)	0.0069 (14)	−0.0079 (15)	−0.0013 (15)
C7	0.0585 (18)	0.0534 (17)	0.0590 (16)	0.0006 (13)	0.0017 (13)	0.0011 (14)
C8	0.0575 (17)	0.0558 (17)	0.0542 (15)	−0.0043 (14)	0.0037 (14)	0.0027 (14)
C9	0.0640 (19)	0.0601 (18)	0.0614 (16)	−0.0018 (15)	0.0041 (14)	−0.0013 (14)
C10	0.0611 (19)	0.068 (2)	0.0535 (15)	−0.0128 (15)	−0.0004 (14)	0.0025 (14)
C11	0.072 (2)	0.069 (2)	0.0553 (16)	−0.0053 (16)	0.0071 (15)	−0.0030 (15)
C12	0.086 (2)	0.076 (2)	0.0581 (17)	−0.0049 (18)	0.0105 (17)	−0.0059 (16)
C13	0.122 (3)	0.084 (3)	0.078 (2)	−0.008 (2)	0.005 (2)	−0.018 (2)
C14	0.239 (7)	0.143 (5)	0.087 (3)	−0.011 (5)	−0.025 (4)	−0.042 (3)
C15	0.070 (2)	0.079 (2)	0.0511 (17)	−0.0185 (17)	−0.0037 (15)	0.0033 (16)
C16	0.208 (6)	0.148 (4)	0.065 (2)	−0.090 (4)	0.027 (3)	0.006 (2)
O1	0.0951 (17)	0.0920 (17)	0.0658 (13)	−0.0389 (15)	−0.0028 (12)	0.0037 (12)
O2	0.150 (2)	0.127 (2)	0.0542 (12)	−0.0739 (18)	0.0075 (14)	0.0014 (14)
N1	0.0699 (17)	0.0634 (16)	0.0583 (14)	−0.0033 (13)	0.0096 (13)	0.0024 (13)
N2	0.0749 (17)	0.0676 (17)	0.0555 (14)	−0.0187 (14)	0.0069 (12)	−0.0051 (13)

Geometric parameters (Å, º)

C1—N1	1.382 (4)	C16—O2	1.473 (4)
C1—C2	1.397 (4)	C2—H2	0.930
C1—C6	1.422 (4)	C3—H3	0.930
C2—C3	1.376 (5)	C4—H4	0.930
C3—C4	1.399 (5)	C5—H5	0.930
C4—C5	1.386 (5)	C9—H9	0.980

C5—C6	1.406 (4)	C10—H10	0.980
C6—C7	1.452 (4)	C11—H11A	0.970
C7—C8	1.360 (4)	C11—H11B	0.970
C7—C11	1.508 (4)	C12—H12A	0.970
C8—N1	1.388 (3)	C12—H12B	0.970
C8—C9	1.501 (4)	C13—H13A	0.970
C9—N2	1.484 (4)	C13—H13B	0.970
C9—C12	1.537 (4)	C14—H14A	0.960
C10—N2	1.471 (4)	C14—H14B	0.960
C10—C15	1.513 (4)	C14—H14C	0.960
C10—C11	1.535 (4)	C16—H16A	0.960
C12—C13	1.519 (5)	C16—H16B	0.960
C13—C14	1.510 (5)	C16—H16C	0.960
C15—O1	1.206 (3)	N1—H1N	0.84 (3)
C15—O2	1.327 (3)	N2—H2N	0.87 (3)

N1—C1—C2	129.8 (3)	C6—C5—H5	120.4
N1—C1—C6	107.5 (3)	N2—C9—H9	109.1
C2—C1—C6	122.7 (3)	C8—C9—H9	109.1
C3—C2—C1	117.0 (3)	C12—C9—H9	109.1
C2—C3—C4	122.0 (3)	N2—C10—H10	108.4
C5—C4—C3	120.9 (4)	C15—C10—H10	108.4
C4—C5—C6	119.2 (3)	C11—C10—H10	108.4
C5—C6—C1	118.1 (3)	C7—C11—H11A	110.1
C5—C6—C7	135.4 (3)	C10—C11—H11A	110.1
C1—C6—C7	106.5 (2)	C7—C11—H11B	110.1
C8—C7—C6	107.1 (2)	C10—C11—H11B	110.1
C8—C7—C11	122.1 (3)	H11A—C11—H11B	108.5
C6—C7—C11	130.8 (3)	C13—C12—H12A	108.6
C7—C8—N1	109.9 (3)	C9—C12—H12A	108.6
C7—C8—C9	126.0 (3)	C13—C12—H12B	108.6
N1—C8—C9	124.0 (2)	C9—C12—H12B	108.6
N2—C9—C8	106.8 (2)	H12A—C12—H12B	107.5
N2—C9—C12	109.4 (2)	C14—C13—H13A	109.2
C8—C9—C12	113.2 (3)	C12—C13—H13A	109.2
N2—C10—C15	108.7 (2)	C14—C13—H13B	109.2
N2—C10—C11	109.9 (2)	C12—C13—H13B	109.2
C15—C10—C11	112.9 (3)	H13A—C13—H13B	107.9
C7—C11—C10	107.8 (2)	C13—C14—H14A	109.5
C13—C12—C9	114.8 (3)	C13—C14—H14B	109.5
C14—C13—C12	112.2 (3)	H14A—C14—H14B	109.5
O1—C15—O2	123.0 (3)	C13—C14—H14C	109.5
O1—C15—C10	125.9 (3)	H14A—C14—H14C	109.5
O2—C15—C10	111.0 (3)	H14B—C14—H14C	109.5
C15—O2—C16	117.0 (3)	O2—C16—H16A	109.5
C1—N1—C8	109.1 (2)	O2—C16—H16B	109.5
C10—N2—C9	113.7 (2)	H16A—C16—H16B	109.5
C3—C2—H2	121.5	O2—C16—H16C	109.5

C1—C2—H2	121.5	H16A—C16—H16C	109.5
C2—C3—H3	119.0	H16B—C16—H16C	109.5
C4—C3—H3	119.0	C1—N1—H1N	127 (2)
C5—C4—H4	119.6	C8—N1—H1N	124 (2)
C3—C4—H4	119.6	C10—N2—H2N	107 (2)
C4—C5—H5	120.4	C9—N2—H2N	108 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*···O1^{i}	0.84 (3)	2.20 (3)	3.037 (3)	177 (3)

Symmetry code: (i) $x+1/2, -y+3/2, -z+1/4$.