

5-Methyl-5b β ,6,7,8,9,11a α -hexahydro-5H-indolizino-[1,2-*b*]indol-11(5a α H)-oneJeanese C. Badenock,^a Heidi L. Fraser,^a Gordon W. Gribble^a and Jerry P. Jasinski^{b*}^aDepartment of Chemistry, Dartmouth College, Hanover, NH 03755-3564, USA, and^bDepartment of Chemistry, Keene State College, NH 03435-2001, USA

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Key indicators

Single-crystal X-ray study

T = 296 K

Mean $\sigma(C-C)$ = 0.007 Å

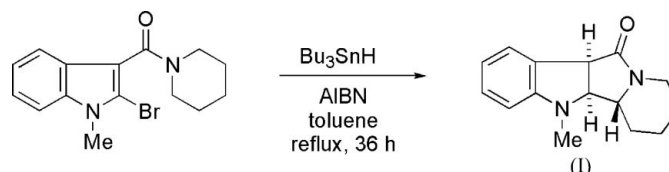
R factor = 0.056

wR factor = 0.239

Data-to-parameter ratio = 17.6

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.The title compound, C₅H₁₈N₂O, reveals a *cis-trans* stereochemistry for this rare example of the 5H-indolizino[1,2-*b*]indole ring system.

Comment

Whereas the indolo[2,3-*a*]quinolizidine ring system is found in plant alkaloids (Gribble, 1997) and in pharmaceutical intermediates and agents (Boido-Canu *et al.*, 1988), the related 5H-indolo[1,2-*b*]indolizidine ring system is virtually unknown. We recently reported a synthesis of this ring system that involves the generation of an indole C-2 radical from the corresponding 2-bromoindole, followed by a 1,5-radical translocation process and subsequent 5-*endo-trig* cyclization to the indole C-2 position to afford (I) (Gribble *et al.*, 2001).

The crystal structure determination of (I) (Fig. 1) supports the stereochemistry suggested by NMR coupling constants (Gribble *et al.*, 2001). The O1–C5 and N2–C5 bond lengths of 1.222 (5) Å and 1.346 (6) Å, respectively, agree with literature values for simple amides (Brown & Corbridge, 1954; Pedersen, 1967). The sum of the angles surrounding N1 is 351.4°, indicating a degree of pyramidalization, as expected for an indoline N atom. The C5–C6–C13–C14 and C7–C6–C13–N1 torsion angles of –9.4 (4) and –12.3 (4)°, respectively, reveal the strong *cis* relationship between C6–H and C13–H, and the C1–C14–C13–N1 torsion angle of 140.7 (3)° supports the *trans* arrangement of C13–H and C14–H. The dihedral angle between the least-squares planes of the *N*-methylindoline ring and the lactam ring is 59.8 (2)°. The piperidine ring defined by C1–C2–C3–C4–N2–C14 has a typical cyclohexane chair conformation with one *sp*² atom (N2), as indicated by the torsion angles C1–C2–C3–C4 [53.4 (5)°] and C14–C1–C2–C3 [–55.3 (5)°].

Experimental

To a refluxing solution of 1-(2-bromo-1-methylindol-3-ylcarbonyl)piperidine (281 mg, 0.875 mmol) in degassed toluene (19 ml) under argon was added a solution of *n*-Bu₃SnH (0.30 ml, 1.05 mmol) and AIBN (azobisisobutyronitrile) (15.9 mg, 0.097 mmol) in degassed toluene (6 ml) dropwise over 8 h *via* a constant-additional funnel. The solution was heated at reflux for a total of 16 h before

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cooling it to room temperature. The solvent was removed under reduced pressure and the residue was dissolved in diethyl ether (35 ml). Aqueous saturated KF (35 ml) was added and the solution was stirred at room temperature for 5 h. The ether layer was dried (MgSO₄) and concentrated under reduced pressure. The resulting yellow solid was purified by silica gel flash chromatography with ethyl acetate–hexane (3:1) as eluant to give 71.1 mg (34%) of (I) as a pale-yellow solid. An analytical sample was obtained by several recrystallizations from diethyl ether (m.p. 393–394 K). Analysis calculated for C₁₅H₁₈N₂O: C 74.34, H 7.49, N 11.57%; found: C 74.12, H 7.41, N 11.54%.

Crystal data

C ₁₅ H ₁₈ N ₂ O	Z = 4
M _r = 242.31	D _x = 1.270 Mg m ⁻³
Monoclinic, P2 ₁ /c	Mo Kα radiation
a = 8.008 (2) Å	μ = 0.08 mm ⁻¹
b = 17.862 (4) Å	T = 296 K
c = 8.888 (3) Å	Prism, yellow
β = 94.53 (3)°	0.50 × 0.40 × 0.30 mm
V = 1267.4 (6) Å ³	

Data collection

Rigaku AFC-6S diffractometer	2912 independent reflections
ω/2θ scans	877 reflections with I > 2σ(I)
Absorption correction: ψ scan	θ _{max} = 27.5°
(North <i>et al.</i> , 1968)	3 standard reflections
T _{min} = 0.961, T _{max} = 0.976	every 150 reflections
2912 measured reflections	intensity decay: 0.6%

Refinement

Refinement on F ²	w = 1/[σ ² (F _o ²) + (0.1076P) ²
R[F ² > 2σ(F ²)] = 0.056	+ 0.3217P]
wR(F ²) = 0.239	where P = (F _o ² + 2F _c ²)/3
S = 1.03	(Δ/σ) _{max} < 0.001
2912 reflections	Δρ _{max} = 0.30 e Å ⁻³
165 parameters	Δρ _{min} = -0.23 e Å ⁻³
H-atom parameters constrained	Extinction correction: SHELXL97
	Extinction coefficient: 0.007 (2)

The H atoms were included in the riding model approximation with C–H = 0.93–0.98 Å, and with U_{iso}(H) = 1.18–1.33U_{eq}(C).

Data collection: MSC/AFC Diffractometer Control Software (Molecular Structure Corporation, 1994); cell refinement: MSC/AFC Diffractometer Control Software; data reduction: CrystalStructure (Rigaku/MSC, 2005; program(s) used to solve structure: SIR92 (Altomare *et al.*, 1994); program(s) used to refine structure:

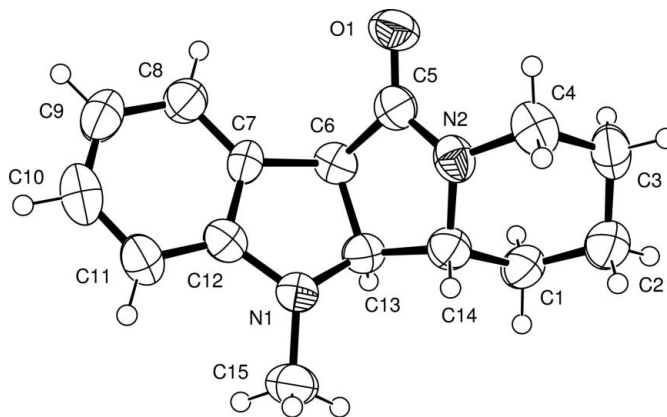


Figure 1 Molecular structure of (I) showing atom labeling and 50% probability displacement ellipsoids.

SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: CrystalStructure.

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References

Altomare, A., Cascarano, G., Giacovazzo, G., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435–435.
 Boido-Canu, C., Boido, V., Sparatore, F., Sparatore, A., Susanna, V., Russo, S., Cenicola, M. L. & Marmo, E. (1988). *Farmaco*, **43**, 819–837.
 Brown, C. J. & Corbridge, D. E. C. (1954). *Acta Cryst.* **7**, 711–715.
 Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
 Gribble, G. W. (1997). *Rodd's Chemistry of Carbon Compounds*, 2nd Supplement to the 2nd ed., Vol. IV, *Heterocyclic Compounds*, ch. 9. Amsterdam: Elsevier.
 Gribble, G. W., Fraser, H. L. & Badenock, J. C. (2001). *Chem. Commun.* pp. 805–806.
 Molecular Structure Corporation. (1994). *MSC/AFC Diffractometer Control Software*. MSC, The Woodlands, Texas, USA.
 North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
 Pedersen, B. F. (1967). *Acta Chem. Scand.* **21**, 1415–1424.
 Rigaku/MSC (2005). *CrystalStructure*. Version 3.5.1. Rigaku/MSC, The Woodlands, Texas, USA.
 Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.