

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1158). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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5,6,7,8,9,10-Hexahydro-10-hydroxy-5,9-methano-4H-thieno[3,2-c]azonine

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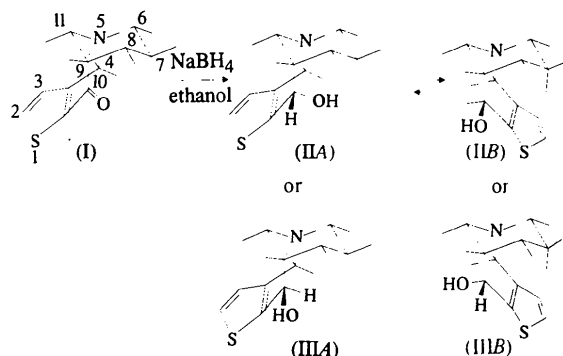
Abstract

The title molecule, C₁₁H₁₅NOS, consists of a seven-membered azepine ring fused to both a five-membered thiophene ring and a six-membered piperidine ring so that a methylene bridge links positions 5 and 9. The thiophene ring is planar, while the azepine ring adopts a pseudo-chair conformation with a pseudo-equatorial hydroxy group at C10. The 1,3-fused piperidine ring also possesses a chair conformation.

Comment

The observation that bridged benzo-fused azocines were obtained in the course of the synthesis of novel non-competitive antagonists of *N*-methyl-D-aspartic acid (NMDA) (Blough, Mascarella, Rothman & Carroll, 1993) stimulated us to search for thieno analogues of this system together with its homologues (Berkeš &

Decroix, 1994; Berkeš, Bar & Decroix, 1995). The stereoselective reduction of 5,6,7,8,9,10-hexahydro-5,9-methano-4H-thieno[3,2-c]azonin-10-one, (I), with NaBH₄ in ethanol at 298 K led to the title compound (II) (Berkeš, Bar & Decroix, 1995). Only one diastereomer was isolated and its structure was inferred from exhaustive ¹H and ¹³C NMR studies.



The X-ray analysis was undertaken in order to distinguish between the diastereomer (II) and possible diastereomer (III), which differ in their relative configurations at the second newly formed asymmetric C10 centres. The other reason was to distinguish between the relative configurations *R**,*R** and *R**,*S**; the *R**,*R** relative configuration is associated with the pseudo-chair conformation of the seven-membered ring found in structure (IIA), whereas a twisted conformation of the seven-membered ring occurs in the *R**,*S** structure (IIIA). The piperidine ring in all cases has a chair conformation. The results establish that diastereomer (II) is formed in preference to (III) and that the conformation is that of (IIB) in which the seven-membered azepine ring is in the chair form (Fig. 1).

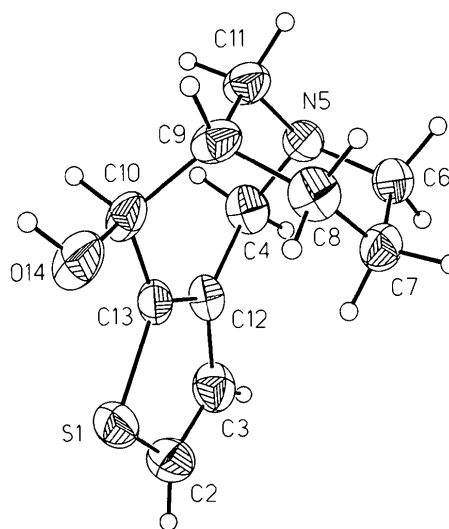


Fig. 1. The molecular structure of the title compound, with displacement ellipsoids given at 50% probability and H atoms shown as spheres of arbitrary radii.

The structural results are in good agreement with the ¹H NMR spectra when allowance is made for the shielding effect on the C7 protons [1.2 p.p.m. for the ketone (I), 0.9 p.p.m. for the aminoalcohol (IIB)] of the thiophene ring in the chair–chair conformation *B*, where the H7B atom is displaced by 2.484 (2) Å from the plane of the thiophene ring. The crystal structure consists of discrete molecules linked by hydrogen bonds [O14—HO14 0.79 (3), HO14···N5¹ 2.02 (3), N5¹···O14 2.800 (2) Å and N5¹···HO14—O14 172 (3)°; symmetry code: (i) $x, \frac{3}{2} - y, \frac{1}{2} + z$].

Experimental

Crystal data

C₁₁H₁₅NOSM_r = 209.30

Monoclinic

P2₁/c

a = 14.150 (3) Å

b = 6.257 (2) Å

c = 12.433 (2) Å

β = 109.400 (10)°

V = 1038.3 (4) Å³

Z = 4

D_x = 1.339 Mg m⁻³D_m not measured

Mo Kα radiation

λ = 0.71069 Å

Cell parameters from 25 reflections

θ = 4.4–14.6°

μ = 0.277 mm⁻¹

T = 299 (2) K

Plate

0.60 × 0.40 × 0.20 mm

Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer

ω/2θ scans

Absorption correction: none

2880 measured reflections

1442 independent reflections

1351 observed reflections

[I > 2σ(I)]

R_{int} = 0.0287θ_{max} = 22.98°

h = -15 → 15

k = 0 → 6

l = -13 → 13

3 standard reflections

frequency: 120 min

intensity decay: none

Refinement

Refinement on F²

R(F) = 0.0305

wR(F²) = 0.0831

S = 1.082

1442 reflections

132 parameters

H14 refined freely, other H atoms refined as riding on their associated C atoms

w = 1/[σ²(F_o²) + (0.0358P)² + 0.4479P]where P = (F_o² + 2F_c²)/3(Δ/σ)_{max} = -0.090Δρ_{max} = 0.19 e Å⁻³Δρ_{min} = -0.16 e Å⁻³

Extinction correction:

SHELXL93

Extinction coefficient:

0.020 (2)

Atomic scattering factors

from *International Tables*for *Crystallography* (1992),

Vol. C, Tables 4.2.6.8 and

6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^*$$

	x	y	z	U _{eq}
S1	0.13093 (4)	0.22722 (8)	0.34767 (4)	0.0471 (2)
C2	0.06005 (15)	0.1754 (3)	0.2103 (2)	0.0514 (5)

C3	0.07713 (14)	0.3194 (3)	0.1377 (2)	0.0461 (5)
C4	0.17881 (13)	0.6575 (3)	0.13004 (14)	0.0412 (5)
N5	0.28536 (11)	0.7072 (2)	0.15870 (11)	0.0341 (4)
C6	0.34676 (14)	0.5322 (3)	0.13942 (14)	0.0387 (4)
C7	0.37088 (14)	0.3565 (3)	0.22891 (15)	0.0391 (4)
C8	0.41137 (14)	0.4451 (3)	0.34997 (15)	0.0421 (5)
C9	0.35230 (14)	0.6368 (3)	0.37100 (14)	0.0373 (4)
C10	0.25797 (14)	0.5792 (3)	0.39861 (13)	0.0372 (4)
C11	0.33126 (15)	0.7962 (3)	0.27302 (14)	0.0395 (5)
C12	0.14811 (12)	0.4784 (3)	0.19344 (14)	0.0347 (4)
C13	0.18389 (13)	0.4493 (3)	0.30872 (14)	0.0338 (4)
O14	0.28275 (12)	0.4666 (2)	0.50346 (10)	0.0506 (4)

Table 2. Selected geometric parameters (Å, °)

S1—C2	1.700 (2)	C6—C7	1.520 (2)
S1—C13	1.723 (2)	C7—C8	1.526 (2)
C2—C3	1.353 (3)	C8—C9	1.533 (3)
C3—C12	1.420 (3)	C9—C11	1.525 (2)
C4—N5	1.463 (2)	C9—C10	1.527 (3)
C4—C12	1.515 (2)	C10—O14	1.419 (2)
N5—C11	1.462 (2)	C10—C13	1.493 (3)
N5—C6	1.466 (2)	C12—C13	1.364 (2)
C2—S1—C13	92.17 (9)	C4—N5—C6	114.84 (14)
C11—N5—C4	114.00 (14)	O14—C10—C13	108.36 (15)
C11—N5—C6	110.32 (14)	O14—C10—C9	110.84 (15)
C12—C4—N5—C11	-67.4 (2)	C6—N5—C11—C9	-55.6 (2)
C11—N5—C6—C7	53.8 (2)	C10—C9—C11—N5	-77.9 (2)
N5—C6—C7—C8	-49.6 (2)	C8—C9—C11—N5	51.8 (2)
C6—C7—C8—C9	45.2 (2)	N5—C4—C12—C13	46.2 (2)
C7—C8—C9—C11	-45.5 (2)	C4—C12—C13—C10	0.5 (3)
C11—C9—C10—C13	69.2 (2)	C9—C10—C13—C12	-46.9 (2)
C4—N5—C11—C9	75.3 (2)		

Data collection: *SDP-Plus* (Frenz, 1985). Cell refinement: *SDP-Plus*. Data reduction: *REDU4* (Stoe & Cie, 1988). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1971). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

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