References

Enraf-Nonius (1992). *CAD-4 Express*. Version 5.1. Enraf-Nonius, Delft, The Netherlands.

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf-Nonius, Delft, The Netherlands.

Kotov, A. I., Faulmann, C., Cassoux, P. & Yagubskii, E. B. (1994). *J. Org. Chem.* **59**, 2626–2629.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Neiland, O. Y., Kacens, Y. Y. & Kreicberga, Y. N. (1989*a*). *Zh. Org. Khim.* **25**, 658–661.

Neiland, O. Y., Kacens, Y. Y. & Kreicberga, Y. N. (1989*b*). *Chem. Abstr.* **111**, 194689 K.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.

Wallis, J. D. & Dunitz, J. D. (1988). *Acta Cryst.* C**44**, 1037–1039.

Williams, J. M., Schultz, A. J., Geiser, U., Carlson, K. D., Kini, A. M., Wang, H. H., Kwok, W.-K., Whangbo, M.-H. & Schirber, J. E. (1991). *Science*, **252**, 1501–1508.

Acta Cryst. (1995). C**51**, 151–152

4,6,7,8,9,9a-Hexahydro-11*H*-pyrido[1,2-*a*]thieno[2,3-*e*][1,3]diazepin-11(10*H*)-one

Josef Kožíšek,[†] Ladislav Ulický[‡] and
Štefan Marchalín[§]

Faculty of Chemical Technology, Radlinského 9,
Slovak Technical University, CS-812 37 Bratislava,
Slovakia

Zdirad Žák

Department of Inorganic Chemistry,
Masaryk University, Kotlářská 2, 611 37 Brno,
Czech Republic

Bernard Decroix

Laboratoire de Chimie, Université de Havre,
30 rue Gabriel Péri, 76600 Le Havre, France

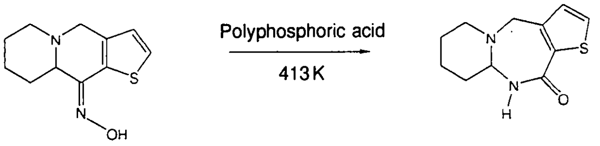
(*Received* 10 *May* 1993; *accepted* 8 *February* 1994)

Abstract

The title molecule ($C_{11}H_{14}N_2OS$) consists of a seven-membered diazepine ring fused to a five-membered thiophene ring and a six-membered piperidine ring. The thiophene ring is planar while the diazepine moiety adopts a half-chair conformation; the *cis*-fused piperidine ring possesses a chair conformation. The least-squares plane of the thiophene and the diazepine rings makes an angle of about 102° with the best plane of the piperidine moiety.

Comment

The reported anticonvulsant, anxiolytic, muscle-relaxant and central nervous system activity of fused tricyclic thienodiazepines (Bauer, Langbein & Weber, 1975; Weber, Bauer, Dannenberg & Kuhn, 1974; Hunkeler & Kyburz, 1981) stimulated the search in our laboratory for other heterocycles incorporating this ring system. The Beckmann rearrangement of 10-(hydroxyimino)-6,7,8,9,9a,10-hexahydro-4*H*-thieno[2,3-*b*]quinolizine (I) with polyphosphoric acid at 413 K led to the title compound (II) (Marchalín & Decroix, 1994).



(I) (II)

The structure of (II) was inferred from exhaustive ^1H and ^{13}C NMR studies. To confirm that the *E* configuration of the starting oxime (I) was retained and to obtain detailed stereochemistry of the new tricyclic heterocycle, the X-ray diffraction study of (II) was undertaken.

The X-ray analysis shows that the molecule consists of a seven-membered diazepine ring fused to a five-membered thiophene ring and a six-membered piperidine ring. The thiophene ring is planar, while the

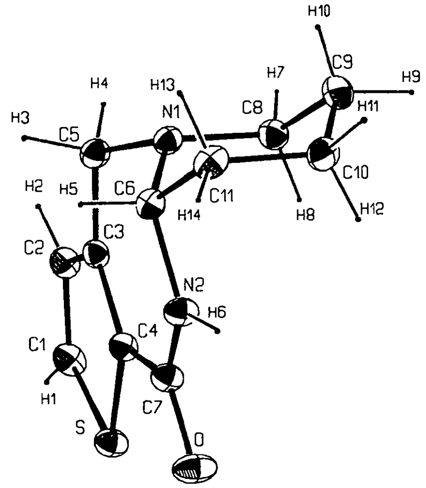


Fig. 1. The molecular structure of the title compound, with displacement ellipsoids given at 30% probability for non-H atoms.

[†] Department of Chemistry.

[‡] Department of Physical Chemistry.

[§] Department of Organic Chemistry.

diazepine ring adopts a half-chair conformation. The piperidine ring, *via* a *cis* junction, has a chair conformation. The thiophene ring and the main part of the diazepine moiety are coplanar and make an angle of about 102° with the best plane of the piperidine ring.

Experimental

Crystals of the title compound were obtained *via* a Beckmann rearrangement of 10-(hydroxyimino)-6,7,8,9,9a,10-hexahydro-4*H*-thieno[2,3-*b*]quinolizine with polyphosphoric acid at 413 K. D_m was measured by flotation in Toullet solution.

Crystal data

$C_{11}H_{14}N_2OS$
$M_r = 222.30$
Monoclinic
$P2_1/n$
$a = 9.028$ (7) Å
$b = 5.256$ (2) Å
$c = 23.022$ (16) Å
$\beta = 92.78$ (6)°
$V = 1091.2$ (6) Å^3
$Z = 4$
$D_x = 1.353$ Mg m^{-3}
$D_m = 1.31$ (2) Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 17$–31°
$\mu = 0.23$ mm^{-1}
$T = 293$ (2) K
Rod
0.70 × 0.25 × 0.20 mm
Colourless

Data collection

Kuma KM4 diffractometer
θ–2θ scans
Absorption correction: none
3204 measured reflections
2352 independent reflections
2147 observed reflections [$F > 4\sigma(F_o)$]
$R_{\rm int} = 0.0628$

$\theta_{\rm max} = 54°$
$h = -11 \rightarrow 11$
$k = 0 \rightarrow 6$
$l = 0 \rightarrow 29$
3 standard reflections monitored every 50 reflections intensity variation: 0.03%

Refinement

Refinement on F
$R = 0.0477$
$wR = 0.0560$
$S = 6.2$
2147 reflections
193 parameters
All H-atom parameters refined
Unit weights applied

$(\Delta/\sigma)_{\rm max} = 0.033$
$\Delta\rho_{\rm max} = 0.52$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.32$ e Å^{-3}
Extinction correction: $F^* = [F_c(1 - xF_c^2]/\sin\theta$
Extinction coefficient: $x = 6.75\ (13) \times 10^{-6}$
Atomic scattering factors from *SHELX*76

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	*y*	*z*	$U_{\rm eq}$
S	0.3284 (1)	0.1707 (1)	0.1759 (1)	0.420 (2)
O	0.3961 (2)	0.1071 (4)	0.0587 (1)	0.569 (7)
N(1)	0.7462 (2)	−0.3434 (3)	0.1434 (1)	0.352 (6)
N(2)	0.5702 (3)	−0.1981 (5)	0.0643 (1)	0.429 (7)
C(1)	0.3758 (3)	0.1027 (5)	0.2471 (1)	0.432 (7)
C(2)	0.4864 (3)	−0.0702 (5)	0.2525 (1)	0.398 (7)
C(3)	0.5366 (2)	−0.1560 (4)	0.1980 (1)	0.342 (7)
C(4)	0.4599 (2)	−0.0391 (4)	0.1523 (1)	0.347 (6)
C(5)	0.6561 (3)	−0.3535 (5)	0.1940 (1)	0.397 (8)
C(6)	0.6682 (3)	−0.4033 (5)	0.0889 (1)	0.382 (8)
C(7)	0.4745 (2)	−0.0454 (5)	0.0885 (1)	0.394 (7)
C(8)	0.8448 (3)	−0.1250 (5)	0.1408 (1)	0.424 (8)
C(9)	0.9607 (3)	−0.1713 (6)	0.0967 (1)	0.536 (10)
C(10)	0.8875 (3)	−0.2417 (6)	0.0375 (1)	0.504 (9)
C(11)	0.7798 (3)	−0.4598 (5)	0.0431 (1)	0.474 (9)

Table 2. *Selected geometric parameters* (Å, °)

S—C(1)	1.712 (3)	C(2)—C(3)	1.428 (4)
S—C(4)	1.727 (2)	C(3)—C(4)	1.376 (3)
O—C(7)	1.252 (3)	C(3)—C(5)	1.503 (4)
N(1)—C(5)	1.454 (4)	C(4)—C(7)	1.481 (3)
N(1)—C(6)	1.444 (3)	C(6)—C(11)	1.523 (4)
N(1)—C(8)	1.456 (3)	C(8)—C(9)	1.513 (4)
N(2)—C(6)	1.489 (4)	C(9)—C(10)	1.531 (4)
N(2)—C(7)	1.322 (4)	C(10)—C(11)	1.513 (4)
C(1)—C(2)	1.351 (4)		
C(1)—S—C(4)	91.4 (2)	S—C(4)—C(7)	114.9 (2)
C(6)—N(1)—C(8)	114.2 (2)	N(1)—C(5)—C(3)	117.1 (2)
C(5)—N(1)—C(8)	115.4 (2)	N(1)—C(6)—N(2)	115.4 (2)
C(5)—N(1)—C(6)	114.9 (3)	N(2)—C(6)—C(11)	106.2 (2)
C(6)—N(2)—C(7)	131.9 (3)	N(1)—C(6)—C(11)	109.5 (3)
S—C(1)—C(2)	112.2 (2)	N(2)—C(7)—C(4)	121.5 (3)
C(1)—C(2)—C(3)	113.3 (3)	O—C(7)—C(4)	117.0 (3)
C(2)—C(3)—C(5)	122.1 (2)	O—C(7)—N(2)	121.4 (3)
C(2)—C(3)—C(4)	111.2 (3)	N(1)—C(8)—C(9)	110.2 (3)
C(4)—C(3)—C(5)	126.7 (2)	C(8)—C(9)—C(10)	110.7 (3)
S—C(4)—C(3)	111.9 (2)	C(9)—C(10)—C(11)	111.0 (2)
C(3)—C(4)—C(7)	133.0 (3)	C(6)—C(11)—C(10)	111.2 (3)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N(2)—H(6)···O$^{\rm i}$	0.65 (3)	2.27 (3)	2.902 (4)	167 (4)

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

The structure was solved by Patterson methods using *SHELXS*86 (Sheldrick, 1990) and refined with *SHELX*76 (Sheldrick, 1976). H atoms were placed in idealized positions (C—H = 1.08 Å) with isotropic displacement parameters ($U_{\rm iso}$ = 0.060 Å^2) and refined. Fig. 1 was drawn using *ORTEP*II (Johnson, 1971). Program used for geometry calculations: *PARST* (Nardelli, 1983). All calculations were carried out on a CDC-4680 computer system.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1048KA1048). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Bauer, A., Langbein, A. & Weber, K. H. (1975). US Patent 4 201 712; *Chem. Abstr.* (1980) 93, 168319.
Hunkeler, W. & Kyburz, E. (1981). Eur. Patent Appl. 59 390; *Chem. Abstr.* (1983) 98, 53949.
Johnson, C. K. (1971). *ORTEP*II. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee, USA.
Marchalín, Š. & Decroix, B. (1994). *J. Heterocycl. Chem.* **31**, 495–499.
Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination.* Univ. of Cambridge, England.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Weber, K. H., Bauer, A., Dannenberg, P. & Kuhn, F. J. (1974). US Patent 4 263 310; *Chem. Abstr.* (1981) 95, 81036.