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8-Methyl-3-methylsulfanyl-8a,8b-dihydro-5*H*-1-oxa-2,4-diazaacenaphthylene

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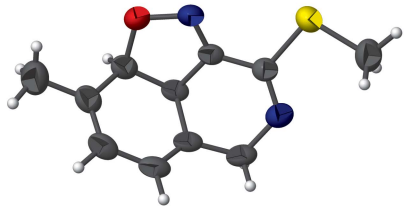
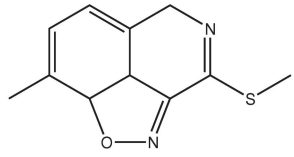
Structural data: full structural data are available from iucrdata.iucr.org

In the tricyclic title compound, $C_{11}H_{12}N_2OS$, the 2,3,4,5-tetrahydropyridine ring adopts a half-chair conformation. This ring makes dihedral angles of 27.72 (7) and 45.17 (7)°, respectively, with the isoxazole and the cyclohexa-1,3-diene rings while the isoxazole ring is oriented at an acute angle of 63.46 (7)° with respect to the cyclohexa-1,3-diene ring. In the crystal, molecules associate *via* C—H···N hydrogen bonds and C—H···π interactions, forming a three-dimensional network.

3D view



Chemical scheme



Structure description

Diazadihydroacenaphthylene derivatives contain an isoxazoline scaffold and constitute an important class of heterocyclic compounds whose chemical properties have been investigated over the years (Jäger & Buss, 1980; Jäger *et al.*, 1980). This scaffold is used in the synthesis of several complex natural products (Saha & Bhattacharjya, 1997; Copp *et al.*,1992) and is a pharmacophore of numerous medicinal chemistry compounds (Brandi *et al.*, 2003; King *et al.*, 1982; Bacher *et al.*, 1997; You *et al.*, 1995). It has also been reported that this scaffold has a multiple range of biological activities, covering the agricultural field (Liu & Howe, 1983), medicinal properties such as anticancer, antibiotic (Habeeb *et al.*, 2001; Mallesha *et al.*, 2001), antiviral and anti-HIV (Ichiba *et al.*, 1993) agents.

We report herein the synthesis and crystal structure of the title compound (Fig. 1). The 2,3,4,5-tetrahydro-pyridine ring adopts a half-chair conformation with puckering para-

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

Cg is the centroid of the cyclohexa-1,3-diene ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1···N12^{i}	0.98	2.64	3.4173 (16)	136
C5—H5*B*···*Cg*3^{ii}	0.97	2.80	3.6158 (17)	142

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

meters (Cremer & Pople, 1975) Q_T = 0.4779 (15) Å, θ = 129.65 (18)°, φ = 29.0 (2)° and is oriented at dihedral angles of 27.72 (7) and 45.17 (7)°, respectively, with the isoxazole and the cyclohexa-1,3-diene rings while the isoxazole ring makes an acute angle of 63.46 (7)° with respect to the cyclohexa-1,3-diene ring. These dihedral angles show that this tricycle compound is not planar, as confirmed by the total puckering amplitude Q_T of 1.4727 (15) Å.

In the crystal, C1—H1···N12($x-\frac{1}{2}, -y+\frac{1}{2}, -z+2$) hydrogen bonds (Table 1) link the molecules along the [010] direction (Fig. 2) and C5—H5*B*···*Cg*3($-x, -y+1, -z$) interactions, where *Cg*3 is the centroid of the cyclohexa-1,3-diene ring (Fig. 3) are observed.

Synthesis and crystallization

1-[(4-Methylbenzyl)amino]-1-methylthio-2-nitroethylene (236 mg; 1 mmol) was dissolved in 4.4 ml (50 mmol) of triflic acid at a temperature within the range −26 to −15°C under a nitrogen atmosphere. The reaction was monitored as follows: one or two drops of the reacting medium were quenched over ice (about 1 g) and extracted with CH_2Cl_2 (0.5 ml). The organic extract was dried over Na_2CO_3 and was purified by flash chromatography on a silica column (eluent: petroleum ether/ethyl acetate: (85:15, *v*/*v*) to afford the title compound (97 mg; 0.441 mmol) as a colourless powder. The powder was dissolved in a minimum of dichloromethane by heating under agitation. To this hot mixture, petroleum ether was added until the formation of a new precipitate started, which dissolved in the resulting mixture upon heating. Upon cooling, colourless

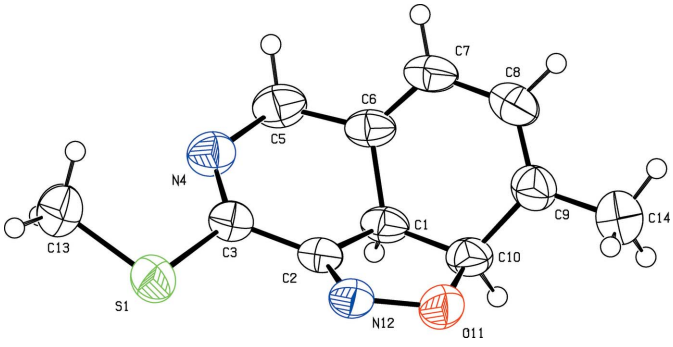


Figure 1
The molecular structure of the title compound and the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radius.

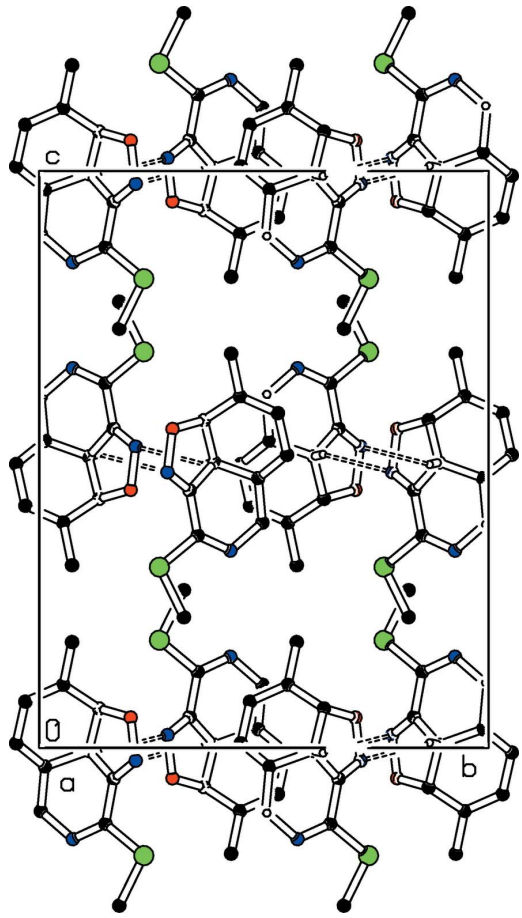


Figure 2
Part of the crystal packing of the title compound showing the formation of intermolecular C1—H1···N12 hydrogen bonds along the **b** axis. Dashed lines indicate hydrogen bond contacts. H atoms not involved in hydrogen bond interactions have been omitted for clarity.

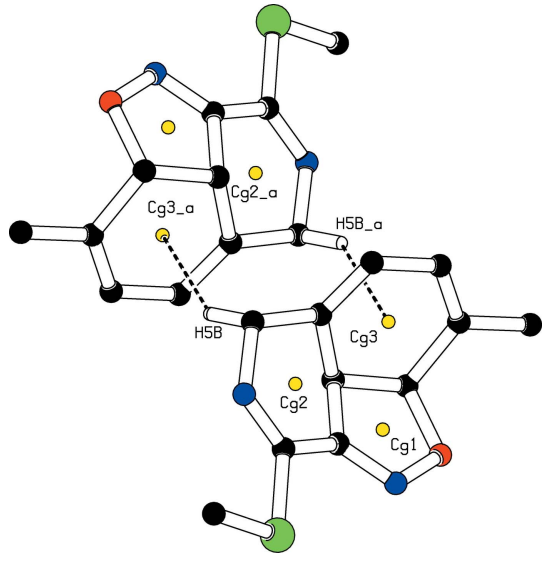


Figure 3
A view of the crystal packing, showing the π–ring interactions (dashed lines). The yellow dots are centroids of rings. H atoms not involved in these interactions have been omitted for clarity.

crystals suitable for single-crystal X-ray diffraction analysis were obtained, m.p. 120.1°C.

^{1}H NMR ($CDCl_3$): δ (p.p.m.) = 2.01 (*s*, 3 H, CH_3); 2.39 (s, 3H, SCH_3); 4.23 (*d*, *J* = 14.94 Hz, 1 H, H-8 b); 4.47 (*s*, 2 H, CH_2); 5.46 (*d*, *J* = 14.9 Hz, 1 H, H-8a); 5.81 (*d*, J = 7.1 Hz, 1 H, vinylic H); 5.84 (*d*, *J* = 7.1 Hz, 1 H, vinylic H).

^{13}C NMR ($CDCl_3$): δ (p.p.m.) = 12.0 (SCH_3); 21.1 (CH_3); 48.0 (C-8a); 58.4 (CH_2); 82.0 (C-8 b); 117.8 (CH); 121.7 (CH); 124.8 (quaternary carbon); 130.4 (C-8); 152.6 (>C═N—O–); 155.4 (–S—C═N–).

MS (mass spectrometer, 70 eV); *m/z* (%): 220 [M^+]. **MS–HR(IE)** *m/z* ([M^+]) $C_{11}H_{12}N_2OS$: 220.0680.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

We thank the laboratory ILV-UVSQ-UMR 8180 CNRS, 45 Avenue des Etats Unis, 78035 Versailles Cedex, France, for the use of the spectrometer and for the spectroscopic analysis.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{11}H_{12}N_2OS$
M_r	220.29
Crystal system, space group	Orthorhombic, *Pbca*
Temperature (K)	293
a, *b*, *c* (Å)	8.0175 (2), 14.4611 (3), 18.5612 (4)
V (Å^3)	2152.02 (8)
Z	8
Radiation type	Mo *Kα*
μ (mm^{-1})	0.27
Crystal size (mm)	0.30 × 0.10 × 0.06
Data collection	
Diffractometer	Bruker CCD area detector
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.922, 0.984
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	67637, 3155, 2560
R_{int}	0.032
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.705
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.041, 0.129, 1.08
No. of reflections	3155
No. of parameters	138
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.32, −0.19

Computer programs: *APEX3* (Bruker, 2018), *SAINT* (Bruker, 2016), *SIR2019* (Burla *et al.*, 2015), *PLATON* (Spek, 2020), *WinGX* (Farrugia, 2012), *SHELXL2018/3* (Sheldrick, 2015) and *publCIF* (Westrip, 2010).

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full crystallographic data

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8-Methyl-3-methylsulfanyl-8a,8b-dihydro-5*H*-1-oxa-2,4-diazaacenaphthylene

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8-Methyl-3-methylsulfanyl-8a,8b-dihydro-5*H*-1-oxa-2,4-diazaacenaphthylene

Crystal data

$C_{11}H_{12}N_2OS$
M_r = 220.29
Orthorhombic, *Pbca*
Hall symbol: -P 2ac 2ab
a = 8.0175 (2) Å
b = 14.4611 (3) Å
c = 18.5612 (4) Å
V = 2152.02 (8) Å^3
Z = 8
$F(000)$ = 928
D_x = 1.360 Mg m^{-3}
Melting point: 393.1 K
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 8401 reflections
θ = 2.2–29.8°
μ = 0.27 mm^{-1}
T = 293 K
Parallelepiped, colorless
0.30 × 0.10 × 0.06 mm

Data collection

Bruker CCD area detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 512 pixels mm^{-1}
phi and ω scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
T_{min} = 0.922, T_{max} = 0.984
67637 measured reflections
3155 independent reflections
2560 reflections with $I > 2\sigma(I)$
R_{int} = 0.032
θ_{max} = 30.1°, θ_{min} = 2.8°
h = −11→11
k = −20→20
l = −26→26

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.129
S = 1.08
3155 reflections
138 parameters
0 restraints
0 constraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0606P)^2 + 0.5724P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.87930 (6)	0.23268 (3)	0.81332 (2)	0.05945 (15)
C1	0.68279 (16)	0.11024 (8)	0.99475 (8)	0.0430 (3)
H1	0.567035	0.131511	0.991152	0.052*
C2	0.79398 (16)	0.16562 (8)	0.94630 (7)	0.0411 (3)
C3	0.78747 (16)	0.14749 (9)	0.86830 (8)	0.0441 (3)
N4	0.72257 (16)	0.07471 (9)	0.84198 (7)	0.0527 (3)
C5	0.6511 (2)	0.00367 (11)	0.89045 (9)	0.0581 (4)
H5A	0.685682	−0.056803	0.873466	0.070*
H5B	0.530492	0.006443	0.887046	0.070*
C6	0.69925 (16)	0.01268 (9)	0.96758 (8)	0.0458 (3)
C7	0.77226 (18)	−0.05134 (9)	1.00803 (9)	0.0512 (3)
H7	0.786148	−0.110657	0.989631	0.061*
C8	0.8308 (2)	−0.03094 (10)	1.08014 (9)	0.0543 (4)
H8	0.871921	−0.079538	1.107742	0.065*
C9	0.8293 (2)	0.05336 (11)	1.10934 (9)	0.0544 (3)
C10	0.7554 (2)	0.13333 (9)	1.06827 (8)	0.0492 (3)
H10	0.668392	0.162125	1.097811	0.059*
O11	0.88721 (16)	0.20355 (7)	1.05266 (6)	0.0584 (3)
N12	0.90369 (16)	0.21466 (8)	0.97783 (7)	0.0486 (3)
C13	0.8627 (3)	0.17816 (14)	0.72661 (9)	0.0685 (5)
H13A	0.748115	0.177828	0.711577	0.103*
H13B	0.902781	0.115738	0.729744	0.103*
H13C	0.928286	0.211794	0.692175	0.103*
C14	0.8944 (4)	0.07297 (16)	1.18338 (10)	0.0846 (7)
H14A	0.928090	0.016115	1.205768	0.127*
H14B	0.808424	0.101512	1.211680	0.127*
H14C	0.988454	0.113844	1.180153	0.127*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0740 (3)	0.0518 (2)	0.0525 (2)	−0.00919 (18)	0.00304 (17)	0.00618 (15)
C1	0.0366 (6)	0.0335 (5)	0.0588 (7)	0.0038 (4)	0.0087 (5)	0.0000 (5)
C2	0.0417 (6)	0.0302 (5)	0.0513 (7)	0.0016 (4)	0.0033 (5)	−0.0005 (5)
C3	0.0415 (6)	0.0407 (6)	0.0502 (7)	0.0004 (5)	−0.0010 (5)	0.0000 (5)
N4	0.0512 (6)	0.0494 (6)	0.0576 (7)	−0.0054 (5)	−0.0049 (5)	−0.0056 (5)
C5	0.0584 (8)	0.0449 (7)	0.0710 (10)	−0.0145 (7)	−0.0018 (7)	−0.0085 (7)
C6	0.0394 (6)	0.0339 (6)	0.0641 (8)	−0.0058 (5)	0.0093 (6)	−0.0037 (5)
C7	0.0477 (7)	0.0319 (5)	0.0739 (9)	−0.0012 (5)	0.0151 (7)	−0.0008 (6)
C8	0.0523 (8)	0.0436 (7)	0.0669 (9)	0.0072 (6)	0.0129 (7)	0.0123 (6)
C9	0.0590 (8)	0.0511 (8)	0.0530 (8)	0.0045 (7)	0.0112 (6)	0.0062 (6)
C10	0.0542 (7)	0.0393 (6)	0.0540 (7)	0.0051 (6)	0.0137 (6)	−0.0016 (5)
O11	0.0802 (8)	0.0458 (5)	0.0493 (6)	−0.0139 (5)	−0.0003 (5)	−0.0045 (4)
N12	0.0596 (7)	0.0358 (5)	0.0504 (6)	−0.0081 (5)	0.0009 (5)	−0.0014 (4)
C13	0.0823 (12)	0.0727 (11)	0.0507 (8)	0.0071 (9)	0.0068 (8)	−0.0005 (8)

C14	0.123 (2)	0.0730 (12)	0.0575 (10)	0.0118 (12)	−0.0060 (11)	0.0052 (9)

Geometric parameters (Å, º)

S1—C3	1.7610 (14)	C7—H7	0.9300
S1—C13	1.7972 (18)	C8—C9	1.334 (2)
C1—C2	1.4984 (18)	C8—H8	0.9300
C1—C6	1.5039 (17)	C9—C14	1.497 (3)
C1—C10	1.521 (2)	C9—C10	1.506 (2)
C1—H1	0.9800	C10—O11	1.4942 (18)
C2—N12	1.2724 (17)	C10—H10	0.9800
C2—C3	1.4723 (19)	O11—N12	1.4045 (16)
C3—N4	1.2717 (17)	C13—H13A	0.9600
N4—C5	1.481 (2)	C13—H13B	0.9600
C5—C6	1.489 (2)	C13—H13C	0.9600
C5—H5A	0.9700	C14—H14A	0.9600
C5—H5B	0.9700	C14—H14B	0.9600
C6—C7	1.328 (2)	C14—H14C	0.9600
C7—C8	1.449 (2)		
C3—S1—C13	100.43 (8)	C9—C8—C7	123.94 (14)
C2—C1—C6	104.35 (10)	C9—C8—H8	118.0
C2—C1—C10	101.16 (11)	C7—C8—H8	118.0
C6—C1—C10	118.25 (12)	C8—C9—C14	122.87 (16)
C2—C1—H1	110.8	C8—C9—C10	119.97 (15)
C6—C1—H1	110.8	C14—C9—C10	117.15 (15)
C10—C1—H1	110.8	O11—C10—C9	109.97 (13)
N12—C2—C3	125.17 (12)	O11—C10—C1	104.24 (10)
N12—C2—C1	115.67 (12)	C9—C10—C1	115.85 (12)
C3—C2—C1	118.29 (11)	O11—C10—H10	108.8
N4—C3—C2	122.66 (13)	C9—C10—H10	108.8
N4—C3—S1	121.83 (12)	C1—C10—H10	108.8
C2—C3—S1	115.49 (9)	N12—O11—C10	109.64 (10)
C3—N4—C5	119.94 (13)	C2—N12—O11	109.03 (11)
N4—C5—C6	115.04 (12)	S1—C13—H13A	109.5
N4—C5—H5A	108.5	S1—C13—H13B	109.5
C6—C5—H5A	108.5	H13A—C13—H13B	109.5
N4—C5—H5B	108.5	S1—C13—H13C	109.5
C6—C5—H5B	108.5	H13A—C13—H13C	109.5
H5A—C5—H5B	107.5	H13B—C13—H13C	109.5
C7—C6—C5	126.65 (14)	C9—C14—H14A	109.5
C7—C6—C1	120.20 (14)	C9—C14—H14B	109.5
C5—C6—C1	112.45 (13)	H14A—C14—H14B	109.5
C6—C7—C8	121.55 (13)	C9—C14—H14C	109.5
C6—C7—H7	119.2	H14A—C14—H14C	109.5
C8—C7—H7	119.2	H14B—C14—H14C	109.5

Hydrogen-bond geometry (Å, º)

Cg is the centroid of the cyclohexa-1,3-diene ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1···N12^{i}	0.98	2.64	3.4173 (16)	136
C5—H5*B*···*Cg*3^{ii}	0.97	2.80	3.6158 (17)	142

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