

(rac-5*RS*,7*RS*,8*SR*)-Spiro[7-methoxy-carbonyl-1-aza-3-thiabicyclo[3.3.0]-octane-8,1'-acenaphthylen]-2'-one

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Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$

R factor = 0.038

wR factor = 0.104

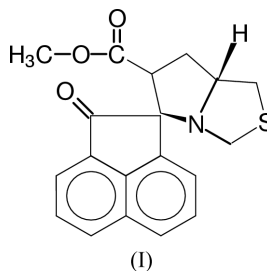
Data-to-parameter ratio = 13.4

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, $\text{C}_{19}\text{H}_{17}\text{NO}_3\text{S}$, crystallizes in the monoclinic space group $P2_1/c$, with four molecules in the unit cell. The structure contains a spiro-carbon connecting a bicyclo-octane group, consisting of two fused five-membered rings, to an acenaphthylene moiety. The five-membered ring containing the S atom is in an envelope conformation. The conformation of the other five-membered ring of the bicyclo-octane moiety is close to a half-chair. The methoxycarbonyl group is equatorially substituted.

Comment

We are interested in the X-ray structure determination of some novel polycyclic spiro-heterocyclic compounds, as they can be used as precursors for the total synthesis of naturally occurring alkaloids (Grundon, 1988). The bicyclo-octane ring system has three chiral atoms, *viz.* C5, C7 and C8 (Fig. 1), and the coordinates of these atoms correspond to 5*R*, 7*R* and 8*S*. However, the compound crystallizes as a racemic mixture in the space group $P2_1/c$. The angles around the spiro atom C8 are $\text{C7}-\text{C8}-\text{N1} = 103.34(12)^\circ$, $\text{C9}-\text{C8}-\text{C18} = 102.40(12)^\circ$, $\text{N1}-\text{C8}-\text{C18} = 116.20(13)^\circ$, $\text{C7}-\text{C8}-\text{C9} = 111.24(13)^\circ$, $\text{C18}-\text{C8}-\text{C7} = 116.12(12)^\circ$ and $\text{N1}-\text{C8}-\text{C9} = 107.46(12)^\circ$. The methoxycarbonyl group is equatorially substituted at C7. The acenaphthylene moiety occupies two substituent positions at C8.



The Csp^2 to Csp^2 distances in the acenaphthylene group range from 1.366 (3) (C15–C16) to 1.570 (2) \AA (C8–C9) and the C–C–C bond angles range from 102.40 (12) ($\text{C9}-\text{C8}-\text{C18}$) to 123.78 (15) ($\text{C14}-\text{C19}-\text{C18}$). These values compare well with those of previously reported related structures (Hazell, 1976; Hazell & Hazell, 1977; Hazell & Weigelt, 1976; Jones *et al.* 1992).

Both the fused five-membered rings of the bicyclo-octane moiety are puckered. The N1/C2/S3/C4/C5 five-membered ring of the bicyclo-octane group is in an envelope conformation [puckering parameters $Q = 0.498(2)\text{ \AA}$ and $\varphi = 176.2(2)^\circ$ for the atom sequence S3–C2–N1–C5–C4; Cremer & Pople, 1975], with atom S3 in the flap position. The torsion

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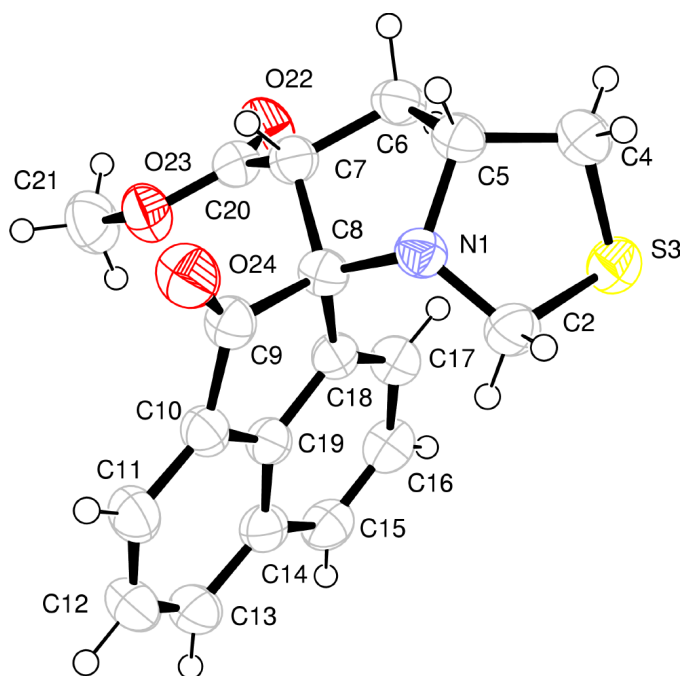


Figure 1
The molecular structure of the title compound, showing 50% probability displacement ellipsoids and the atom-numbering scheme.

angle C2–S3–C4–C5 is $-39.58(12)^\circ$, while the angle C4–S3–C2–N1 is $38.80(12)^\circ$. The conformation of the other five-membered ring (N1/C5/C6/C7/C8) of the bicyclo-octane group is close to a half-chair [puckering parameters $Q = 0.384(2) \text{ \AA}$ and $\varphi = 86.4(3)^\circ$ for the atom sequence N1–C5–C6–C7–C8]. The dihedral angle between the least-squares planes of the above two rings is $51.96(10)^\circ$.

The C5–N1 bond distance is $1.488(2) \text{ \AA}$. This is comparable to the Csp^3-Nsp^3 distances found in similar structures (Sussman & Wodak, 1973; Wodak, 1975). The geometry around the N atom is pyramidal. The bond distance C2–S3 is $1.8323(18) \text{ \AA}$ and S3–C4 is $1.8044(18) \text{ \AA}$. The angle C2–S3–C4 is $86.99(8)^\circ$. The structure is stabilized mainly by van der Waals interactions.

Experimental

A mixture of acenaphthylene-1,2-dione (0.364 g, 2 mmol), (*R*)-(-)-thiazolidine-4-carboxylic acid (0.27 g, 2 mmol) and methyl acrylate (0.172 g, 2 mmol), in an equimolar ratio, was refluxed for 22 h in acetonitrile under a nitrogen atmosphere. After completion of the reaction, monitored by the disappearance of the acenaphthylene-1,2-dione spot in TLC analysis, the reaction mixture was filtered to remove the unreacted acid. The filtrate was concentrated *in vacuo* and kept at 273 K. A yellow crystalline solid was obtained and recrystallized from chloroform/*n*-hexane as yellow cuboidal crystals (0.604 g, 75%; m.p. 445 K). A small amount of the compound (0.2 g) was dissolved in chloroform (2 ml). *N*-Hexane (8 ml) was layered carefully down the side of the test tube on to the solution. The volume ratio of solvent to precipitant was 1:4. The test tube was plugged with cotton wool and left to stand undisturbed for 24 h. As the precipitant (*n*-hexane) diffused into the solution, crystals were formed at the interface.

Crystal data

$C_{19}H_{17}NO_3S$
 $M_r = 339.40$
Monoclinic, $P2_1/c$
 $a = 9.3597(1) \text{ \AA}$
 $b = 14.7896(2) \text{ \AA}$
 $c = 14.9199(1) \text{ \AA}$
 $\beta = 128.660(5)^\circ$
 $V = 1612.73(3) \text{ \AA}^3$
 $Z = 4$

$D_x = 1.398 \text{ Mg m}^{-3}$
Cu $K\alpha$ radiation
Cell parameters from 9012 reflections
 $\theta = 2.2\text{--}68.3^\circ$
 $\mu = 1.93 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
Rectangular block, yellow
 $0.32 \times 0.20 \times 0.18 \text{ mm}$

Data collection

Nonius KappaCCD diffractometer
 φ scans with κ offsets
Absorption correction: multi-scan (SORTAV; Blessing, 1995)
 $T_{\min} = 0.583$, $T_{\max} = 0.707$
21 038 measured reflections
2926 independent reflections

2567 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.051$
 $\theta_{\max} = 68.2^\circ$
 $h = -11 \rightarrow 11$
 $k = -17 \rightarrow 17$
 $l = -16 \rightarrow 17$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.104$
 $S = 1.04$
2926 reflections
218 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0531P)^2 + 0.4649P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.19 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.34 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

C6–C7	1.517 (2)		
C2–N1–C8	119.47 (13)	C8–N1–C5	110.46 (12)
C2–N1–C5	111.25 (13)	C7–C6–C5	102.89 (13)
N1–C5–C6–C7	33.55 (16)	C5–C6–C7–C20	$-163.65(14)$
C4–C5–C6–C7	152.37 (14)	C6–C7–C8–N1	30.13 (15)

All H atoms were treated as riding; C–H = $0.93\text{--}0.98 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl H and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for all others.

Data collection: *COLLECT* (Nonius, 1997–2000); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *WinGX* (Version 1.64.02; Farrugia, 1999) and *PLATON* (Spek, 2002); software used to prepare material for publication: *SHELXL97*.

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