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# (*rac*-2*SR*,3*RS*,5*SR*)-Spiro[3-methoxycarbonyl-1-azabicyclo[3.3.0]octane-2,1′-acenaphthylen]-2′-one

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**Key indicators**

Single-crystal X-ray study
$T$ = 293 K
Mean $\sigma$(C–C) = 0.003 Å
$R$ factor = 0.047
$wR$ factor = 0.137
Data-to-parameter ratio = 13.7

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

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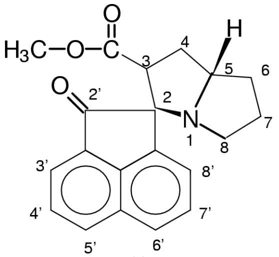
The molecular structure of the title compound, $C_{20}H_{19}NO_3$, contains a spiro-C atom connecting a bicyclooctane group, consisting of two fused five-membered rings, to an acenaphthylene moiety. One of the five-membered rings of the bicyclooctane moiety is in an envelope conformation, while the conformation of the other five-membered ring is close to a half-chair. The methoxycarbonyl substituent is equatorial.

## 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 structure determination of the title compound, (I), is the second in our series of spiro heterocyclic compounds. Compound (I), in which the S atom has been replaced by a $CH_2$ group, is isostructural with the first compound, *viz*. (*rac*-5*RS*,7*RS*,8*SR*)-spiro[7-methoxycarbonyl-1-aza-3-thiabicyclo[3.3.0]octane-8,1′-acenaphthylen]-2′-one (Sundar *et al.*, 2002). Hence, the structure was refined with the coordinates of the non-H atoms, except S, of the first compound as input. The structure has been refined to an $R$ value of 0.047, confirming the isostructural nature of these two compounds.



(I)

The bicyclooctane ring system has three chiral atoms, *viz*. C2, C3 and C5 (Fig. 1). The compound crystallizes as a racemic mixture in the space group $P2_1/c$. The spiro atom C2 is essentially $sp^3$-hybridized, with bond angles in the range 102.05 (12)–116.28 (13)° (Table 1). The acenaphthylene moiety occupies two substituent positions at C2. The methoxycarbonyl substituent at C3 is equatorial.

The bond distances in the acenaphthylene moiety are similar to those in previously reported related structures (Gupta & Gupta, 1975; Mak & Trotter, 1963). In the aliphatic planar five-membered ring of the acenaphthylene moiety, the C2—C2′ bond distance, 1.569 (2) Å, is exceptionally long; this may be attributed to the steric strain caused by the planarity of

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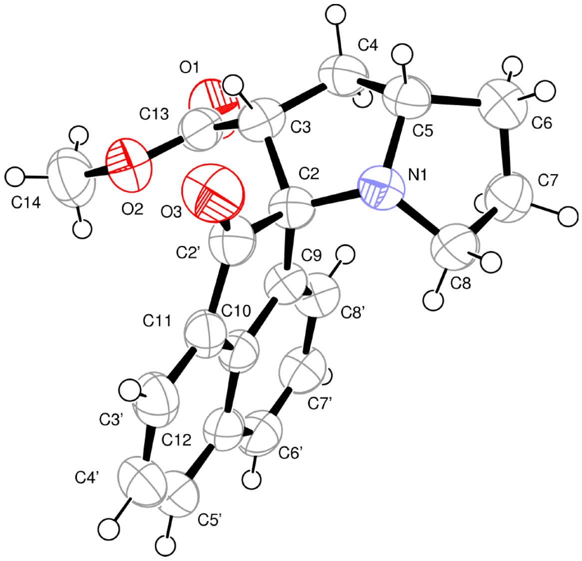

**Figure 1**
The molecular structure of the title compound, showing 50% probability displacement ellipsoids and the atom-numbering scheme.

the aliphatic five-membered ring and also by the bulky bicyclooctane moiety connected to spiro atom C2 (Trotter & Mak, 1963). The C—C—C bond angles range from 102.05 (12) (C9—C2—C2′) to 123.91 (15)° (C12—C10—C9). These values compare well with those of the first compound (Sundar *et al.*, 2002).

Both the five-membered rings of the fused bicyclooctane moiety are puckered. One of the five-membered rings of the bicyclooctane group is in an envelope conformation [puckering parameters $Q$ = 0.377 (3) Å and $\varphi$ = 99.3 (3)°, for the atom sequence N1—C5—C6—C7—C8; Cremer & Pople, 1975], with atom C7 in the flap position. The torsion angle C5—C6—C7—C8 is −38.10 (19) Å, while C6—C7—C8—N1 is 35.63 (19)°. The conformation of the other five-membered ring of the bicyclooctane group is close to a half-chair [puckering parameters $Q$ = 0.374 (2) Å and $\varphi$ = 96.2 (3)°, for the atom sequence N1—C2—C3—C4—C5].

The C5—N1 bond distance is 1.484 (2) Å. This is comparable to the C$sp^3$—N$sp^3$ distances found in similar structures (Sundar *et al.*, 2002; Sussman & Wodak, 1973; Wodak, 1975). The geometry around the N atom is pyramidal and the pyramidality of atom N1 is evident from the fact that it is 0.392 (2) Å out of the plane through atoms C2, C5 and C8. When compared with our first compound (Sundar *et al.*, 2002; values in square brackets), the angles C8—N1—C5 of 108.04 (13)° [C2—N1—C5 = 111.25 (13)°] and C5—C6—C7 of 103.35 (14)° [C5—C4—S3 = 105.92 (11)°] are found to be smaller. The structure is stabilized mainly by van der Waals interactions.

## Experimental

A mixture of acenaphthylene-1,2-dione (0.364 g, 2 mmol), L-proline (0.23 g, 2 mmol) and methyl acrylate (0.172 g, 2 mmol) was refluxed for 20 h in acetonitrile under a nitrogen atmosphere. Unreacted proline was removed by filtration and the filtrate was evaporated *in vacuo* and the crude product subjected to column chromatography, giving the title compound as a yellow powder (0.592 g, 77.28%; m.p. 418 K) from the fraction of 30% petroleum ether and 70% chloroform. A diffusion method was adopted for the crystallization. A small quantity (0.29 g) of the cycloadduct was dissolved in chloroform (2 ml). $n$-Hexane (8 ml) was then layered carefully down the side of the test tube on to the solution. The volume ratio of solvent/precipitant taken was 1:4. The test tube was then corked with cotton and left to stand undisturbed for 48 h. As the precipitant ($n$-hexane) diffused into the solution, crystals formed at the interface.

### *Crystal data*

$C_{20}H_{19}NO_3$
$M_r$ = 321.36
Monoclinic, $P2_1/c$
$a$ = 9.5206 (1) Å
$b$ = 14.7738 (2) Å
$c$ = 14.6958 (2) Å
$\beta$ = 129.182 (1)°
$V$ = 1602.25 (4) Å$^3$
$Z$ = 4

$D_x$ = 1.332 Mg m$^{-3}$
Cu $K\alpha$ radiation
Cell parameters from 18832 reflections
$\theta$ = 4.9–69.9°
$\mu$ = 0.72 mm$^{-1}$
$T$ = 293 (2) K
Rectangular block, yellow
0.30 × 0.20 × 0.10 mm

### *Data collection*

Nonius KappaCCD diffractometer
$\varphi$ scans with $\kappa$ offset
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{min}$ = 0.812, $T_{max}$ = 0.931
35 501 measured reflections
2994 independent reflections

2476 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.051
$\theta_{max}$ = 69.9°
$h$ = −11 → 11
$k$ = −17 → 17
$l$ = −16 → 17

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.137
$S$ = 1.07
2994 reflections
218 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0711P)^2 + 0.3621P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.37 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.16 e Å$^{-3}$

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| C2—C3 | 1.554 (2) | C6—C7 | 1.505 (3) |
| C3—C4 | 1.516 (3) | C7—C8 | 1.517 (3) |
| | | | |
| C8—N1—C2 | 120.69 (13) | N1—C2—C2′ | 107.20 (12) |
| C8—N1—C5 | 108.04 (13) | C9—C2—C2′ | 102.05 (12) |
| C2—N1—C5 | 110.67 (12) | C3—C2—C2′ | 112.02 (13) |
| N1—C2—C9 | 116.28 (13) | C5—C4—C3 | 102.92 (14) |
| N1—C2—C3 | 103.18 (12) | C6—C7—C8 | 102.36 (15) |
| C9—C2—C3 | 116.06 (13) | | |
| N1—C2—C3—C4 | 28.17 (16) | C3—C4—C5—N1 | 33.70 (17) |
| C13—C3—C4—C5 | −163.23 (14) | C3—C4—C5—C6 | 149.53 (15) |

The structure was refined with the coordinates of the non-H atoms, except sulfur, of the first compound as starting parameters (Sundar *et al.*, 2002). Atom C7 was located from a difference Fourier map. All H atoms of the compound were treated as riding, with C—H = 0.93–0.98 Å and $U_{iso}$(H) = 1.5$U_{eq}$(C) for methyl H and 1.2$U_{eq}$(C) for all other H atoms.

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: isomorphous method; program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2002); software used to prepare material for publication: *SHELXL*97 and *PARST* (Nardelli, 1995).

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