# (2E,4E)-8-Methyl-2,4-bis(3-thienylmethylene)-8-azabicyclo[3.2.1]octan-3-one

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The title compound, $C_{18}H_{17}NOS_2$, was prepared by the base-catalyzed Aldol condensation of tropinone with thiophene-3-carboxaldehyde. It crystallizes with the molecule on a mirror plane. Both double bonds linking the tropinone and thiophene rings adopt the $E$ configuration, with the thienyl-ring flip and the H atoms of the $N$-methyl group disordered.

## Comment

Tropane alkaloids comprise a large group of bases occurring predominantly in the family *Solanaceae*. Many of these compounds have interesting biological properties. A series of tropanes have shown anticonvulsant activity against pentylenetetrazol-induced convulsions in mice and anti-arrhythmic activity in rabbits previously treated with ouabain (Trigo *et al.*, 1981). The title compound, (I), is a synthetic precursor of a drug candidate with defined double-bond geometry and was prepared by the base-catalyzed Aldol condensation of tropinone with thiophene-3-carboxaldehyde to afford a single geometric isomer. The product, the title compound, (I), was identified by NMR spectroscopy. In order to confirm the double-bond geometries and to study the structural conformation of the molecule in the solid state, its X-ray crystal structure determination has been carried out and the results are presented here.
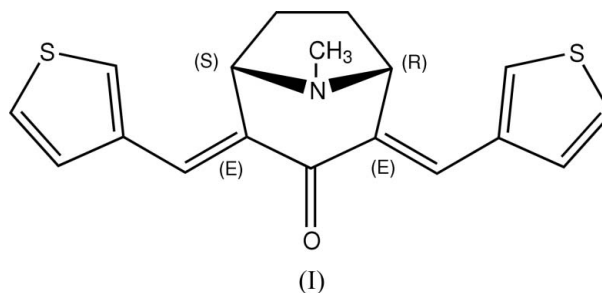


(I)

Fig. 1 illustrates a displacement ellipsoid plot of (I), and selected geometric parameters are presented in Table 1. The molecule has mirror symmetry, with both C=C double-bonds adopting the $E$ configuration. Deviations from the ideal bond-angle geometry around the $sp^2$ C atoms of the double bonds are observed. The angles C6=C2—C1, C2=C6—C7 and C8=C7—C6 are distorted because of steric hindrance, due to the double bonds linking the thiophene rings on both sides of the tropinone group. These angles have values of 116.60 (15), 130.07 (14) and 128.6 (5)° respectively. The C2=C6—C7=C8 torsion angle [−21.6 (12)°] indicates a deviation of the plane of the thiophene rings from the plane of the double bonds
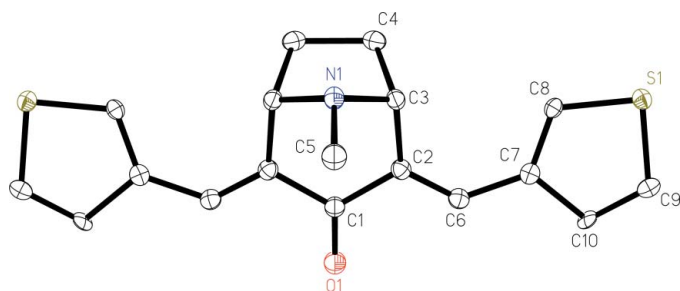
**Figure 1**
A view of (I), after application of the mirror symmetry operation $(2 - x, y, z)$ to the asymmetric unit to generate the full molecule. H atoms and the disorder of the thienyl rings have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

connecting the rings. The C6—C7 bond length [1.458 (2) Å] is slightly shorter than typical C—C single bonds, suggesting extended conjugation of the thiophene ring $\pi$-electron systems with the C2=C6 double bond (Wilson & Prince, 1992). The molecule has thienyl-ring flip disorder, the thiophene rings being disordered over two conformations about the C6–C7 bond. The H atoms of the *N*-methyl group are also disordered.

## Experimental

Potassium hydroxide (1.25 g) dissolved in water (5 ml) was added to tropinone (0.418 g, 3 mmol) and thiophene-3-carboxaldehyde (0.673 g, 6 mmol) dissolved in ethanol (20 ml), and the solution was then boiled under reflux for 1 h. After cooling the reaction mixture to room temperature, crystals separated and were collected by filtration and washed with water. Recrystallization from ethyl acetate afforded (I) as brown needles which were suitable for X-ray analysis. Spectroscopic analysis: $^1$H NMR (CDCl$_3$, $\delta$, p.p.m.): 1.94 (*m*, 2H), 2.38 (*s*, 3H), 2.61 (*m*, 2H), 4.48 (*m*, 2H), 7.23 (*dd*, 2H), 7.39 (*q*, 2H), 7.45 (*m*, 2H), 7.77 (*s*, 2H); $^{13}$C NMR (CDCl$_3$, $\delta$, p.p.m.): 30.3, 36.4, 61.5, 126.3, 128.3, 129.2, 130.1, 136.9, 137.1, 187.5.

### Crystal data

| | |
|---|---|
| C$_{18}$H$_{17}$NOS$_2$ | Mo $K\alpha$ radiation |
| $M_r = 327.45$ | Cell parameters from 994 |
| Orthorhombic, $Cmc2_1$ | reflections |
| $a = 19.3783$ (4) Å | $\theta = 1.0$–$27.5°$ |
| $b = 10.5680$ (6) Å | $\mu = 0.36$ mm$^{-1}$ |
| $c = 7.3257$ (3) Å | $T = 90.0$ (2) K |
| $V = 1500.23$ (11) Å$^3$ | Irregular fragment, brown |
| $Z = 4$ | $0.25 \times 0.20 \times 0.15$ mm |
| $D_x = 1.450$ Mg m$^{-3}$ | |

### Data collection

| | |
|---|---|
| Nonius KappaCCD area-detector diffractometer | 1668 independent reflections |
| | 1551 reflections with $I > 2\sigma(I)$ |
| $\omega$ scans | $R_{int} = 0.036$ |
| Absorption correction: multi-scan (*SCALEPACK*; Version 0.95.373; Otwinowski & Minor, 1997) | $\theta_{max} = 27.5°$ |
| | $h = -24 \rightarrow 25$ |
| | $k = -13 \rightarrow 13$ |
| $T_{min} = 0.916$, $T_{max} = 0.949$ | $l = -9 \rightarrow 9$ |
| 6649 measured reflections | |

### Refinement

| | |
|---|---|
| Refinement on $F^2$ | $w = 1/[\sigma^2(F_o^2) + (0.0376P)^2$ |
| $R[F^2 > 2\sigma(F^2)] = 0.031$ | $+ 0.3768P]$ |
| $wR(F^2) = 0.074$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.08$ | $(\Delta/\sigma)_{max} = 0.001$ |
| 1668 reflections | $\Delta\rho_{max} = 0.23$ e Å$^{-3}$ |
| 144 parameters | $\Delta\rho_{min} = -0.20$ e Å$^{-3}$ |
| H-atom parameters constrained | Absolute structure: Flack (1983), with 710 Friedel pairs |
| | Flack parameter: 0.47 (9) |

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

| | | | |
|---|---|---|---|
| O1—C1 | 1.221 (3) | C2—C3 | 1.513 (2) |
| N1—C5 | 1.469 (3) | C3—C4 | 1.543 (3) |
| N1—C3 | 1.470 (2) | C6—C7 | 1.458 (2) |
| C1—C2 | 1.4952 (19) | C8—S1 | 1.716 (11) |
| C2—C6 | 1.347 (2) | S1—C9 | 1.733 (9) |
| | | | |
| O1—C1—C2 | 121.62 (9) | C8—C7—C6 | 128.6 (5) |
| C6—C2—C1 | 116.60 (15) | C7—C8—S1 | 114.6 (7) |
| C2—C6—C7 | 130.07 (14) | C8—S1—C9 | 90.0 (4) |
| | | | |
| O1—C1—C2—C6 | 6.6 (3) | C2—C6—C7—C8 | −21.6 (12) |
| O1—C1—C2—C3 | −173.9 (2) | C2—C6—C7—C10 | 162.7 (7) |

H atoms were placed in idealized positions and were constrained, with C—H distances of 0.99, 0.98 and 0.95 Å for methyl, *sp* and *sp*$^2$ C atoms, respectively, and with $U_{iso}$(H) = 1.2$U_{eq}$(C), or 1.5$U_{eq}$(C) for methyl H atoms. The Flack (1983) parameter refined to 0.47 (9) and was subsequently fixed at 0.5 in the final rounds of refinement so as to make the structure a 50:50 inversion twin. The crystals are inversion twins. Disorder of the thiophene ring is common in this type of molecule. The geometries of the two disorder components were subject to geometrical similarity and anisotropic displacement parameter restraints, and atoms occupying approximately the same sites were assigned equal displacement parameters.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 1995); software used to prepare material for publication: *SHELXL97* and local procedures.

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