**Vijayakumar N. Sonar,[a] M. Venkataraj,[a] Sean Parkin[b] and Peter A. Crooks[a]***

[a]Department of Pharmaceutical Sciences, College of Pharmacy, University of Kentucky, Lexington, KY 40536, USA, and [b]Department of Chemistry, University of Kentucky, Lexington, KY 40506, USA

Correspondence e-mail: pcrooks@uky.edu

Key indicators

Single-crystal X-ray study
T = 90 K
Mean σ(C–C) = 0.002 Å
R factor = 0.036
wR factor = 0.091
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.

(Z)-2-(Thiophen-2-ylmethylene)-1-azabicyclo[2.2.2]octan-3-one

Crystals of the title compound, $C_{12}H_{13}NOS$, were prepared by base-catalyzed reaction of thiophene-2-carboxaldehyde with 1-azabicyclo[2.2.2]octan-3-one and subsequent crystallization of the product from ethyl acetate. The olefinic bond connecting the 2-thienyl and 1-azabicyclo[2.2.2]octan-3-one moieties has Z geometry. No thienyl ring flip is observed.

Comment

In view of the biological activity associated with 1-azabicyclo[2.2.2]octan-3-ones, we have undertaken the synthesis and structural analysis of a series of 2-(substituted benzylidene/heteroaryl-3-ylmethylene)-1-azabicylo[2.2.2]octan-3-ones (Sonar *et al.*, 2003). The title compound, (I), was prepared by base-catalyzed condensation of thiophene-2-carboxaldehyde with 1-azabicyclo[2.2.2]octan-3-one as a single geometrical isomer. In order to confirm the double-bond geometry and to determine the molecular conformation in the crystal structure, the X-ray analysis of the title compound, (I), has been carried out, and the results are presented here.

(I)
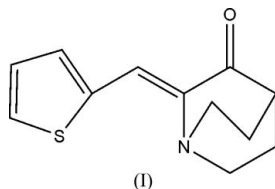
The molecular structure and atom-numbering scheme of (I) are shown in Fig. 1, and selected bond lengths and angles are listed in Table 1. The molecule consists of the 1-azabicyclo[2.2.2]octan-3-one system substituted at position 2 with a 2-thienyl ring. These moieties are linked by an olefinic bond that has the Z geometry. The double bond has a nearly planar atomic arrangement, since the r.m.s. deviation from the mean plane passing through atoms N1, C6, C10, C5 and C1 is 0.027 (8) Å. The bond angles around the atoms C1, C5, C6 and C10 deviate from the ideal value (120°); the angles for N1—C6—C10, C6=C5—C1, C4=C1—C5, and C6—C10—C9 are distorted (Table 1), as a consequence of the strain induced by the double bond linkage at C5=C6. These deviations contribute to the release of the intramolecular non-bonded interactions. The azabicyclic system presents small distortions in its geometry with respect to literature data on the 1-azabicyclo[2.2.2]octane system. The C4=C1—C5=C6 torsion angle indicates a deviation of the 2-thienyl ring from the plane of the double bond connected to the azabicyclic ring. However, the bond length C1—C5, in comparison with the standard value for a C_{ar}—Csp^2 single bond [1.470 (15) Å; Wilson, 1992], suggests weak conjugation to the 2-thienyl ring.

Experimental

The title compound was prepared according to the previously reported procedure of Sonar *et al.* (2003). Crystallization from ethyl acetate afforded yellow crystals.

Crystal data

$C_{12}H_{13}NOS$
$M_r = 219.29$
Monoclinic, $P2_1/n$
$a = 11.0171$ (2) Å
$b = 5.9253$ (1) Å
$c = 16.1888$ (2) Å
$\beta = 94.640$ (1)°
$V = 1053.34$ (3) Å^3

$Z = 4$
$D_x = 1.383$ Mg m^{-3}
Cu $K\alpha$ radiation
$\mu = 2.48$ mm^{-1}
$T = 90.0$ (2) K
Block, yellow
$0.15 \times 0.08 \times 0.08$ mm

Data collection

Bruker–Nonius X8 Proteum diffractometer
ω scans
Absorption correction: multi-scan (*SADABS* in *APEX2*; Bruker–Nonius, 2004)
$T_{min} = 0.657$, $T_{max} = 0.836$

11773 measured reflections
1880 independent reflections
1845 reflections with $I > 2\sigma(I)$
$R_{int} = 0.031$
$\theta_{max} = 68.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.091$
$S = 1.09$
1880 reflections
137 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0559P)^2 + 0.4238P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.29$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0209 (12)

Table 1
Selected geometric parameters (Å, °).

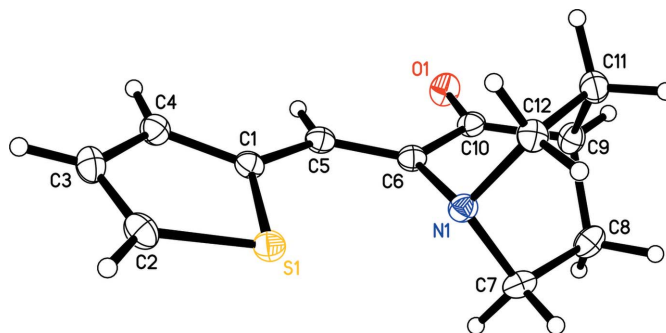|			
S1—C2	1.7178 (13)	C1—C5	1.4429 (18)
S1—C1	1.7342 (13)	C5—C6	1.3394 (19)
N1—C6	1.4417 (16)	C6—C10	1.4838 (17)
O1—C10	1.2219 (16)	C9—C10	1.5169 (18)
C2—S1—C1	91.29 (6)	C5—C6—N1	122.60 (12)
C6—N1—C7	108.69 (10)	C5—C6—C10	123.15 (12)
C4—C1—C5	124.55 (12)	N1—C6—C10	113.97 (11)
C6—C5—C1	127.29 (12)	C6—C10—C9	109.87 (11)
C4—C1—C5—C6	168.73 (13)	C5—C6—C10—O1	−9.2 (2)
C1—C5—C6—N1	−1.0 (2)	N1—C6—C10—O1	176.83 (12)

Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

H atoms were found in difference Fourier maps and subsequently placed in idealized positions with constrained C—H distances of 1.00 (R_3CH), 0.99 (R_2CH$_2$) and 0.95 Å (Csp^2). U_{iso}(H) values were set at $1.2U_{eq}$ of the attached C atom.

Data collection: *APEX2* (Bruker–Nonius, 2004); cell refinement: *SAINT* (Bruker–Nonius, 2004); data reduction: *SAINT*; 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.

References

Bruker–Nonius (2004). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Sheldrick (1995). *XP* in *SHELXTL/PC*. Siemens Analytical Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Sonar, V. N., Parkin, S. & Crooks, P. A. (2003). *Acta Cryst.* E**59**, o1464–o1466.
Wilson, A. J. C. (1992). Editor. *International Tables for Crystallography*, Vol. C., Table 9.5.1.1. Dordrecht: Kluwer Academic Publishers.