Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

(*Z*)-2-(2-Methoxybenzylidene)-1-azabicyclo[2.2.2]-octan-3-one

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Received 15 December 2005
Accepted 20 December 2005
Online 7 January 2006

Key indicators

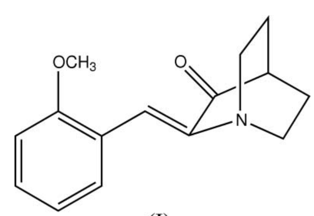
Single-crystal X-ray study
T = 90 K
Mean σ(C–C) = 0.004 Å
R factor = 0.045
wR factor = 0.098
Data-to-parameter ratio = 9.5

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

The title compound, $C_{15}H_{17}NO_2$, was prepared by base-catalyzed reaction of 2-methoxybenzaldehyde with 1-aza-bicyclo[2.2.2]octan-3-one. The configuration about the olefinic bond connecting the methoxyphenyl and 1-azabicylo[2.2.2]-octan-3-one moieties is *Z*.

Comment

In view of the biological activity associated with 1-aza-bicyclo[2.2.2]octan-3-ones, we have undertaken the synthesis and structural analysis of a series of 2-(substituted benzyl-idene/heteroaryl-3-ylmethylene)-1-azabicyclo[2.2.2]octan-3-ones (Sonar *et al.*, 2004). The title compound, (I), was prepared by base-catalyzed condensation of 2-methoxy-benzaldehyde with 1-azabicyclo[2.2.2]octan-3-one, to afford (*Z*)-2-(2-methoxybenzylidene)-1-azabicyclo[2.2.2]octan-3-one as a single geometrical isomer. In order to confirm the double-bond geometry, and determine how the molecular conformation in the crystal structure is affected by the position of the *ortho*-methoxy group, the X-ray analysis of this isomer has been carried out, and the results are presented here.



(I)

Fig. 1 illustrates an ellipsoid plot of (I), with the atom-numbering scheme, and selected geometrical parameters are listed in Table 1. The configuration about the olefinic bond connecting the methoxyphenyl and 1-azabicylo[2.2.2]octan-3-one groups is *Z*. The double bond has a nearly planar atomic arrangement, since the r.m.s. deviation from the mean plane passing through atoms N1, C8, C9, C7 and C1 is 0.0182 (19) Å. The bond angles C8═C7—C1, N1—C8—C9, O1—C9—C8 and C8—C9—C10 (Table 1) deviate from the ideal bond angle (120°). These deviations are caused by strain induced by the double bond linking the methoxyphenyl ring with the aza-bicyclic system. Within the azabicyclic group, the bond angles at atoms C10, C11 and C13 are, on average, smaller than the ideal tetrahedral value of 109.5°, while those at atoms C12 and C14 are, on average, slightly larger than the tetrahedral value.

The C2═C1—C7═C8 torsion angle [−24.2 (5)°] indicates a deviation of the methoxyphenyl ring from the plane of the double bond connected to the azabicyclic system. The C1—C7 bond length, in comparison with the standard value for a C_{ar}—

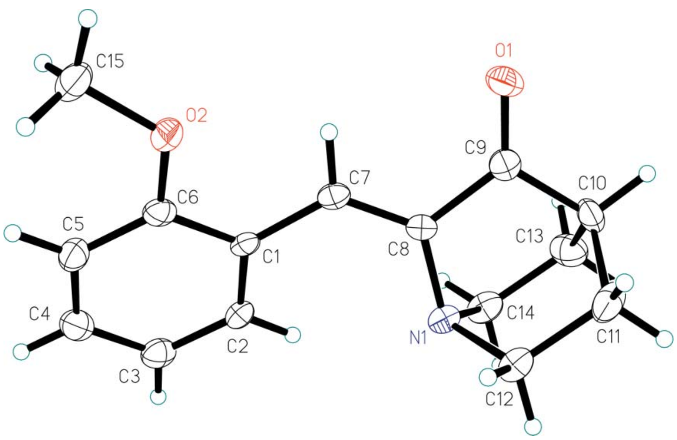


Figure 1
A view of the molecule of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

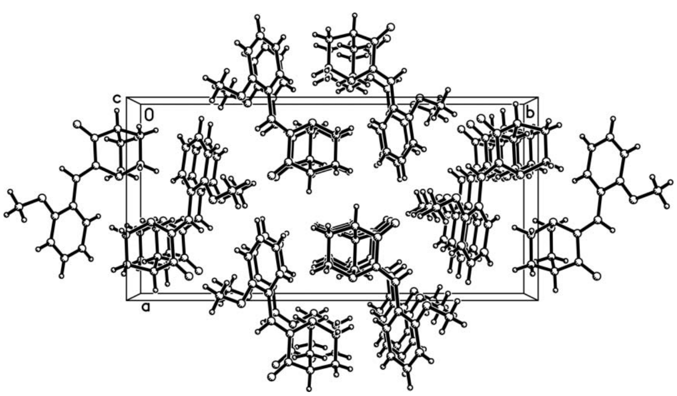


Figure 2
The crystal structure of (I), viewed along the *a* axis.

Csp^2 single bond [1.470 (15) Å; Allen *et al.*, 1987], suggests weak conjugation with the methoxyphenyl ring. The observed O2—C6 and O2—C15 bond lengths are comparable to values found for aromatic methoxy bonds. There is an asymmetry of the exocyclic angles at C6. This situation is typical of that found in anisoles and is caused by the tendency of the methoxy group to be coplanar with the phenyl ring through the conjugation of the O atom with the phenyl ring (Domiano *et al.*, 1979).

The mode of packing of (I) along the *a* direction is illustrated in Fig. 2. In addition to non-bonded interactions, van der Waals forces contribute to the stabilization of the crystal structure.

Experimental

A mixture of 2-methoxybenzaldehyde (0.408 g, 3 mmol) and 1-azabicyclo[2.2.2]octane hydrochloride (0.483 g, 3 mmol) was dissolved in 10% methanolic KOH (10 ml) and the solution refluxed for 5 h. The cooled reaction mixture was poured on to crushed ice (100 g) and the yellow crystalline solid (I) that separated was collected by filtration and air-dried. Crystallization from methanol afforded yellow needles, which were suitable for X-ray analysis. ^{1}H NMR ($CDCl_3$, p.p.m.): δ 1.98–2.04 (*td*, 4H), 2.60–2.64 (*p*, 1H), 2.94–3.04 (*m*, 2H), 3.10–3.19 (*m*, 2H), 3.85 (*s*, 3H), 6.87 (*d*, 1H), 6.96 (*t*, 1H), 7.30 (*td*, 1H), 7.57 (*s*, 1H), 8.50 (*dd*, 1H). ^{13}C NMR ($CDCl_3$, p.p.m.): δ 26.2, 40.6, 47.9, 55.7, 110.6, 119.3, 120.5, 122.8, 131.0, 132.7, 144.4, 159.1, 206.2.

Crystal data

$C_{15}H_{17}NO_2$
M_r = 243.30
Orthorhombic, $Pna2_1$
a = 10.3050 (3) Å
b = 20.9052 (6) Å
c = 5.7182 (13) Å
V = 1231.9 (3) Å^3
Z = 4
D_x = 1.312 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3925 reflections
θ = 1.0–27.5°
μ = 0.09 mm^{-1}
T = 90.0 (2) K
Irregular, yellow
0.35 × 0.20 × 0.12 mm

Data collection

Nonius KappaCCD diffractometer
ω scans
Absorption correction: multi-scan (*SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.970, T_{max} = 0.990
7940 measured reflections
1558 independent reflections
973 reflections with $I > 2\sigma(I)$
R_{int} = 0.114
θ_{max} = 27.5°
$h = -12 \rightarrow 13$
$k = -27 \rightarrow 27$
$l = -7 \rightarrow 6$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.098
S = 1.00
1558 reflections
164 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0438P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C9	1.223 (3)	O2—C15	1.437 (4)
N1—C8	1.445 (4)	C7—C8	1.342 (4)
C1—C7	1.459 (4)	C8—C9	1.487 (4)
O2—C6	1.375 (4)	C9—C10	1.505 (4)
C2—C1—C7	122.4 (3)	C7—C8—C9	121.2 (3)
C6—C1—C7	119.7 (3)	N1—C8—C9	113.6 (3)
C6—O2—C15	117.2 (2)	O1—C9—C8	125.3 (3)
C8—C7—C1	129.3 (3)	C8—C9—C10	110.2 (3)
C15—O2—C6—C5	−13.4 (4)	C6—C1—C7—C8	159.4 (3)
C2—C1—C7—C8	−24.2 (5)	C7—C8—C9—O1	4.6 (5)

H atoms were treated as riding (C—H = 0.95–1.00 Å), with U_{iso}(H) values set at 1.2 or 1.5 times U_{eq}(C). In the absence of significant anomalous dispersion effects, Friedel pairs were averaged.

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: *SHELX97*-2 (Sheldrick, 1997) and local procedures.

This investigation was supported by the National Institute of Alcohol Abuse and Alcoholism Grant AA12600.

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