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(*Z*)-2-(1,3-Benzodioxol-5-ylmethylene)-1-azabicyclo[2.2.2]octan-3-one

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Key indicators

Single-crystal X-ray study
T = 90 K
Mean σ(C–C) = 0.002 Å
R factor = 0.048
wR factor = 0.131
Data-to-parameter ratio = 16.2

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

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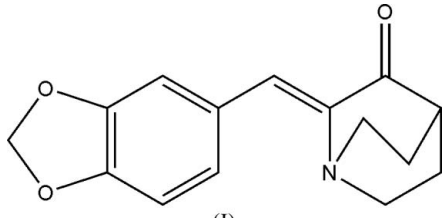
Crystals of the title compound, $C_{15}H_{15}NO_3$, were obtained from a condensation reaction of piperonal with 1-azabicyclo[2.2.2]octan-3-one and subsequent crystallization of the product from ethyl acetate. The geometry about the C=C double bond connecting the 1,3-benzodioxole moiety to the azabicylic ring system is *Z*.

Comment

The title compound is a synthetic intermediate in our ongoing synthesis of 2-(substituted benzylidene/heteroaryl-3-yl-methylene)-1-azabicylo[2.2.2]octan-3-ones (Sonar *et al.*, 2003). The title compound, (I), was prepared by base-catalyzed condensation of piperonal with 1-azabicyclo[2.2.2]octan-3-one, and the resultant product was crystallized from ethyl acetate to afford a single geometric isomer. The present X-ray crystallographic determination was carried out in order to confirm the double-bond geometry and to obtain more detailed information on the conformation of the molecule.



(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. In the title compound, the olefinic bond connecting the 1,3-benzodioxole moiety with the azabicyclic ring system has *Z* geometry. The double bond has a nearly planar atomic arrangement, since the r.m.s. deviation from the mean plane passing through atoms N9/C8/C13/C7/C1 is 0.0076 (9) Å. Deviations from ideal geometry are observed in the bond angles around atoms C1 and C8.

The C7—C8—C13 angle is close to the ideal value of 120°. The angles N9—C8—C13, C7—C8—N9 and C8—C7—C1 are more distorted (Table 1), as a consequence of the strain induced by the double-bond linkage at C7=C8. The latter two angles contribute to the relief of the intramolecular nonbonded interactions. The azabicyclic system presents small distortions in its geometry with respect to literature data on the 1-azabicyclo[2.2.2]octane system, which is caused by the effect of the double bonds connecting C7=C8 and C13=O13 on the azabicyclic system. In both cases, Csp^2 atoms replace Csp^3 atoms and, as a result, atoms N9, C8, C13 and C12

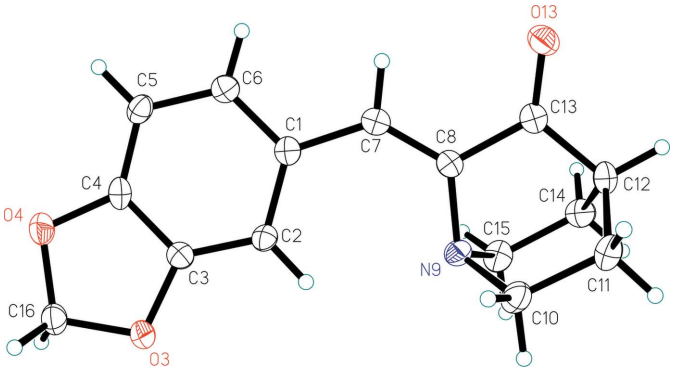


Figure 1
The molecular structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

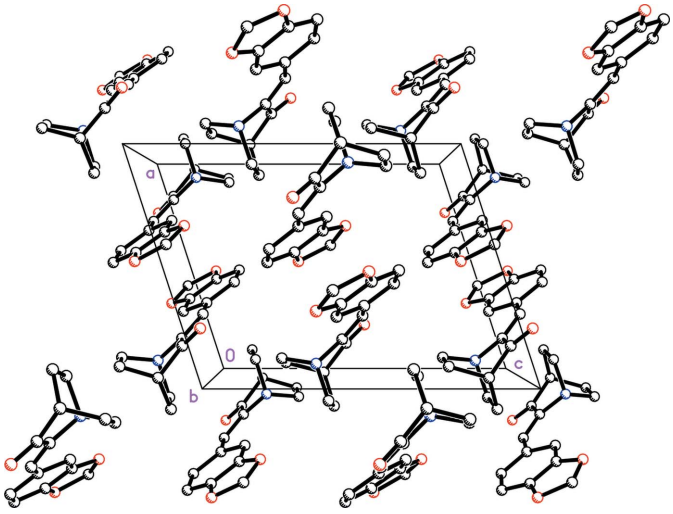


Figure 2
A packing diagram of (I), viewed down the *a* axis. H atoms have been omitted for clarity.

assume a planar arrangement with partial conjugation between the double bond and the 1,3-benzodioxole moiety, as indicated by the shortening of the C1—C7 single bond in comparison with the standard value for a C_{ar}—Csp^2 single bond [1.470 (15) Å; Wilson, 1992].

The observed bond lengths, C3—O3/C4—O4 and C16—O3/C16—O4, are comparable with the values for aromatic methoxy bonds (Domiano *et al.*, 1979), and there is an asymmetry of the angles around atoms C3 and C4.

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

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

$C_{15}H_{15}NO_3$
M_r = 257.28
Monoclinic, $P2_1/c$
a = 9.2694 (2) Å
b = 11.3621 (3) Å
c = 12.1721 (3) Å
β = 108.0245 (10)°
V = 1219.05 (5) Å^3
Z = 4
D_x = 1.402 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 90.0 (2) K
Slab, yellow
0.30 × 0.22 × 0.10 mm

Data collection

Nonius KappaCCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.971, T_{max} = 0.990
5401 measured reflections
2785 independent reflections
1795 reflections with $I > 2\sigma(I)$
R_{int} = 0.041
θ_{max} = 27.5°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.131
S = 0.99
2785 reflections
172 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0738P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—C7	1.461 (2)	C8—C13	1.484 (2)
C3—O3	1.3793 (19)	O13—C13	1.2320 (19)
C4—O4	1.373 (2)	O3—C16	1.4353 (19)
C7—C8	1.338 (2)	O4—C16	1.442 (2)
C8—N9	1.4465 (19)		
C2—C1—C7	122.87 (15)	C7—C8—C13	120.93 (15)
C2—C3—O3	127.18 (15)	N9—C8—C13	113.40 (13)
O3—C3—C4	109.92 (15)	O13—C13—C8	124.63 (15)
C5—C4—O4	127.83 (15)	O13—C13—C12	124.49 (16)
O4—C4—C3	110.31 (14)	C8—C13—C12	110.88 (14)
C8—C7—C1	131.45 (15)	O3—C16—O4	107.95 (13)
C7—C8—N9	125.62 (15)		
C2—C1—C7—C8	12.7 (3)	N9—C8—C13—C12	3.23 (18)
C1—C7—C8—C13	−179.54 (15)	C2—C3—O3—C16	179.01 (16)
C7—C8—C13—O13	6.1 (3)		

H atoms were found in difference Fourier maps and subsequently placed in idealized positions, with constrained C—H distances of 1.00 Å (R_3CH), 0.99 Å (R_2CH_2), and 0.95 Å (Csp^2). U_{iso}(H) values were set to 1.2U_{eq} of the attached C atom.

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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