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

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Key indicators

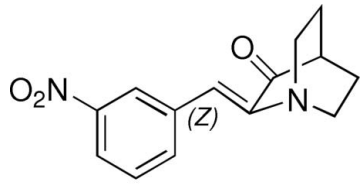
Single-crystal X-ray study
T = 90 K
Mean σ(C–C) = 0.002 Å
R factor = 0.037
wR factor = 0.098
Data-to-parameter ratio = 15.9

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

The title compound, $C_{14}H_{14}N_2O_3$, was prepared by the base-catalyzed condensation reaction of 3-nitrobenzaldehyde with 1-azabicyclo[2.2.2]octan-3-one. The 3-nitrophenyl ring is twisted by 27.29 (19)° with respect to the plane of the C=C double bond connected to the azabicyclic ring. The molecule adopts the *Z* configuration.

Comment

In continuation of our work with 2-(substituted benzylidene/heteroaryl-3-ylmethylene)-1-azabicyclo[2.2.2]octan-3-ones (Sonar *et al.*, 2004), as precursors of medicinal agents, we synthesized the title compound, (I). The compound was prepared by base-catalyzed condensation of 3-nitrobenzaldehyde with 1-azabicyclo[2.2.2]octan-3-one, to afford a single geometrical isomer. To study the structural conformation of the molecule, its X-ray crystal structure determination has been carried out.



(I)

In the title compound, the C1—C7 bond is in a *trans* disposition with respect to the C8—C9 bond and the molecule adopts the *Z* configuration. The C7=C8 double bond is nearly planar, as indicated by the value of 0.0091 (7) Å for the r.m.s. deviation of atoms N1, C8, C9, C7 and C1 from the mean plane passing through them. The Csp^2—N bond associated with the nitro group attached to the benzene ring is clearly of single-bond character [1.4739 (16) Å]. Deviations from the ideal

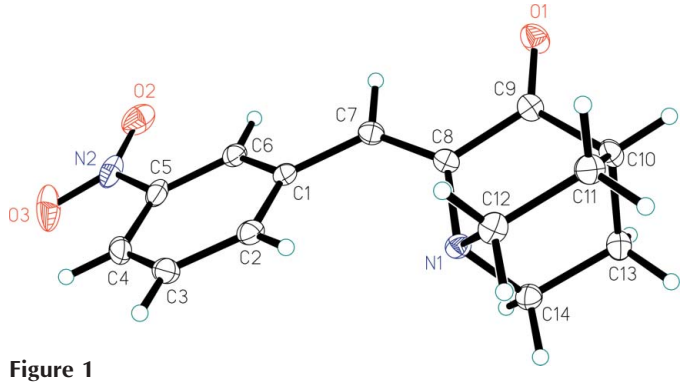


Figure 1
A view of the molecule of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

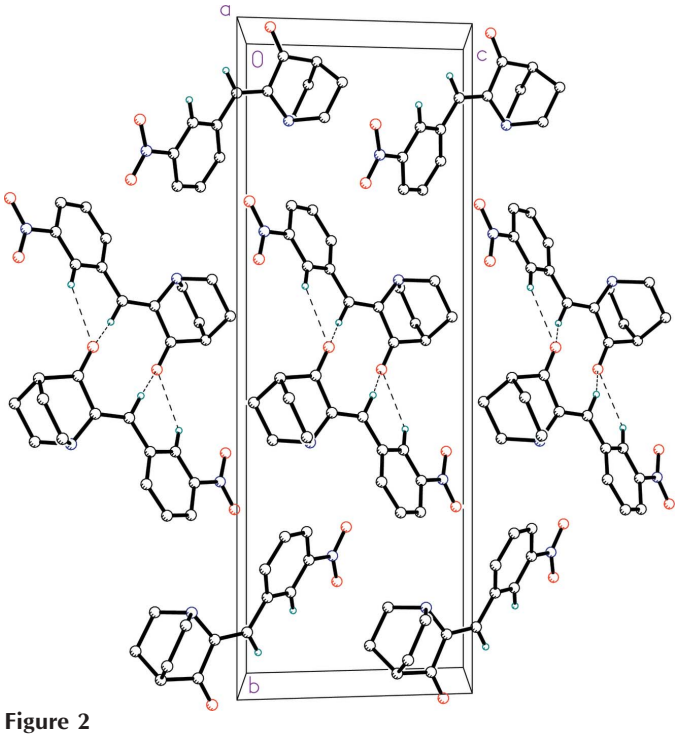


Figure 2
A packing diagram of (I), viewed down the a axis, showing hydrogen-bonding interactions (dashed lines). H atoms, except those involved in hydrogen bonding have been omitted for clarity.

bond-angle geometry around the sp^2 C atoms of the double bonds are observed. While the N2—C5—C6, C6—C1—C7, C2—C1—C7 and C7—C8—C9 angles show values of 118.24 (11), 117.87 (11), 123.18 (11) and 121.26 (11)°, respectively, which are close to ideal geometry (120°), the C1—C7—C8, C7—C8—N1, N1—C8—C9, C8—C9—O1 and C8—C9—C10 angles are distorted because of steric hindrance of the double bond linking the two ring systems. They assume values of 128.62 (11), 125.40 (11), 113.33 (10), 124.75 (11) and 110.76 (10)°, respectively. These deviations contribute significantly to the release of the intramolecular non-bonded interactions present in this portion of the molecule. The C2—C1—C7—C8 torsion angle [27.29 (19)°] indicates a deviation of the 3-nitrophenyl ring from the plane of the double bond connected to the azabicyclic ring. However, the C4—C7 bond length [1.4660 (16) Å] suggests conjugation of the C7—C8 π electrons with those of the 3-nitrophenyl ring (Wilson & Prince, 1999).

The crystal packing of (I) (Fig. 2) shows that the molecules exist as hydrogen-bonded dimers, connected through weak C—H···O hydrogen bonds.

Experimental

A mixture of 3-nitrobenzaldehyde (0.499 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 into crushed ice (100 g) and the yellow crystalline solid that separated was collected by filtration, washed with water and air dried. Recrystallization from methanol afforded yellow needles of (I), which were suitable for X-ray analysis. Spectroscopic analysis: ^{1}H NMR ($CDCl_3$, δ, p.p.m.): 2.04–2.09 (*td*, 4H), 2.66–2.7 (*p*, 1H), 2.95–3.06 (*m*, 2H), 3.18–3.28 (*m*, 2H), 7.03 (*s*, 1H), 7.51–7.57 (*t*, 1H), 8.15–8.24 (*m*, 2H), 9.02–9.03 (*t*, 1H); ^{13}C NMR ($CDCl_3$, δ, p.p.m.): 25.9, 40.4, 47.6, 122.3, 123.9, 126.6, 129.4, 135.6, 137.7, 146.9, 148.5, 205.7.

Crystal data

$C_{14}H_{14}N_2O_3$
M_r = 258.27
Monoclinic, $P2_1/c$
a = 5.8095 (1) Å
b = 24.2920 (4) Å
c = 8.5473 (2) Å
β = 99.2211 (8)°
V = 1190.64 (4) Å^3
Z = 4
D_x = 1.441 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4654 reflections
θ = 1–27.5°
μ = 0.10 mm^{-1}
T = 90.0 (2) K
Block, yellow
0.30 × 0.25 × 0.20 mm

Data collection

Nonius KappaCCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.970, T_{max} = 0.980
9090 measured reflections
2739 independent reflections
2275 reflections with $I > 2\sigma(I)$
R_{int} = 0.027
θ_{max} = 27.5°
$h = -7 \rightarrow 7$
$k = -29 \rightarrow 31$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.099
S = 1.04
2739 reflections
172 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0463P)^2 + 0.444P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—C8	1.4448 (15)	N2—O3	1.2303 (15)
N1—C12	1.4846 (15)	N2—C5	1.4739 (16)
O1—C9	1.2223 (14)	C7—C8	1.3376 (17)
C1—C7	1.4660 (16)	C8—C9	1.4937 (16)
C2—C1—C7	123.18 (11)	C8—C7—C1	128.62 (11)
O2—N2—O3	123.65 (11)	C7—C8—N1	125.40 (11)
O2—N2—C5	118.19 (11)	N1—C8—C9	113.33 (10)
C6—C5—N2	118.24 (11)	C8—C9—C10	110.76 (10)
C6—C1—C7—C8	−154.52 (12)	C1—C7—C8—N1	2.5 (2)
C2—C1—C7—C8	27.29 (19)	C7—C8—C9—O1	−0.98 (19)

H atoms were positioned geometrically and refined as riding, with C—H distances in the range 0.95–0.99 Å and with U_{iso}(H) = 1.2U_{eq}(C).

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/PC* (Sheldrick, 1995); software used to prepare material for publication: *SHELXL97* and local procedures.

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