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N-{3-(4-Methylphenyl)-6-[(*Z*)-(4-methylphenyl)-methylidene]-2-phenyl-2-azabicyclo[2.2.2]oct-5-ylidene}aniline

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The title compound, $C_{34}H_{32}N_2$, is formed as a result of the Diels–Alder reaction of *N*-benzylideneaniline and cyclohexen-2-one, catalyzed by zirconium tetrachloride. The molecule exists as the *Z* isomer. All three rings in the azabicyclo[2.2.2]octane system adopt boat conformations. The crystal packing is stabilized by van der Waals forces.

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Imino Diels–Alder adducts. VII

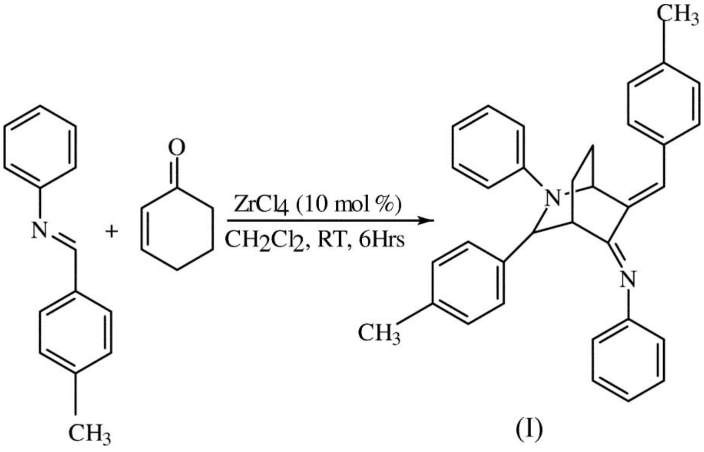
Key indicators

Single-crystal X-ray study
T = 273 K
Mean σ(C–C) = 0.003 Å
R factor = 0.043
wR factor = 0.127
Data-to-parameter ratio = 13.1

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

Comment

The azabicyclo[2.2.2] (isoquinuclidine) ring system has received an increasing amount of attention, mainly due to its occurrence in the natural products dioscorine and ibogaine. In addition, azabicyclo[2.2.2]octanone may serve as a precursor for the synthesis of naturally occurring piperidine alkaloids of the prosopis family (Birkinshaw & Holmes, 1987; Birkinshaw *et al.*, 1988). We have recently synthesized and purified azabicyclo[2.2.2]octane derivatives using an imino Diels–Alder reaction with $ZrCl_4$ as a 'green' catalyst (Mahesh, 2005). *N*-Benzylideneaniline was reacted with cyclohexen-2-one in the presence of zirconium tetrachloride in dichloromethane at ambient temperature, to afford the title 2-azabicyclo[2,2,2]-octane derivative, (I). The present X-ray structure determination was carried out in order to confirm the identity of (I) and to obtain more detailed information on the conformation of the molecule.



(I)

In the molecule of (I), two benzene rings are directly connected to the azabicyclic system and the other two are connected through a double-bond linkage as an extended 'arm' (Fig. 1). In all essential details, the molecular geometry

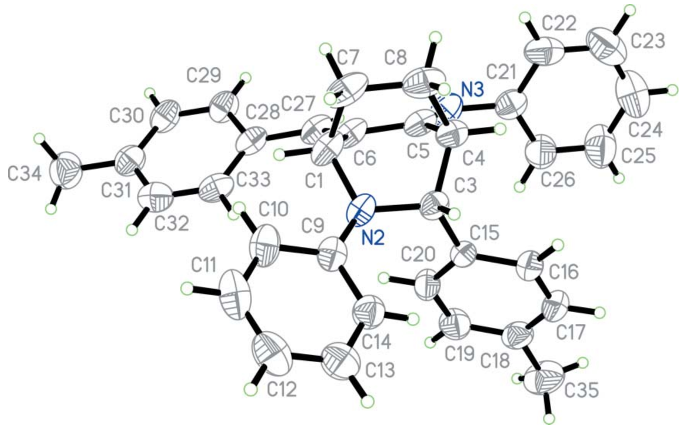


Figure 1
A view of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

of (I) is not very different from the values found in the literature for other azabicyclo[2.2.2] systems (Sonar *et al.*, 2003, 2004). The disposition of the double bonds C6═C27 and C5═N3 (Table 1) with respect to the azabicyclo[2.2.2] ring system affords the possibility of *E* and *Z* isomers. In the structure of (I), the C27—C28 bond is in a *trans* configuration with respect to the C5—C6 bond [C5—C6—C27—C28 = 175.9 (1)°]. Similarly, the N3—C21 bond is also in a *trans* configuration with respect to the C5—C6 bond [C5—C6—N3—C21 = 175.4 (1)°]. As observed in similar azabicyclo structures, deviations from the ideal bond-angle geometry around the Csp^2 atoms of the double bonds are also found in (I). The C27—C28—C29 [118.8 (2)°], C27—C28—C33 [124.3 (1)°], C5—C6—C27 [121.7 (2)°], N3—C21—C22 [122.9 (2)°], N3—C21—C26 [118.1 (2)°] and N3—C5—C6 [121.1 (1)°] bond angles are close to the ideal value of 120°, while the C1—C6—C27 [127.5 (2)°] and N3—C5—C4 [128.3 (2)°] angles are more distorted, as a consequence of the strain induced by the C6═C27 and C5═N3 double-bond linkages. The sum of the angles around atom N2 is 351.2° and the deviation of atom N2 from the C1/C3/C9 plane is 0.234 (1) Å, indicating its pyramidal nature.

In the azabicyclo[2.2.2] system, all three six-membered rings adopt boat conformations, with asymmetry parameters (Nardelli, 1983) ΔC_s(C1) of 0.019 (1), 0.023 (1) and 0.040 (1) for the rings C3/N2/C1/C7/C8/C4, C1/C4–C8 and C1/N1/C3–C6, respectively. The torsion angles C6—C27—C28—C33 and C5—N3—C21—C22 are −37.1 (2) and −80.8 (2)°, respectively. The benzene ring substituted at N2 is almost coplanar with the nearest arm of the azabicyclo[2.2.2] ring system, with a C1—N2—C9—C10 torsion angle of 7.6 (2)°, while the benzene ring attached at atom C3 is twisted, with a C4—C3—C15—C16 torsion angle of 72.2 (2)°.

In the absence of H-donating groups, the crystal packing (Fig. 2) is stabilized by van der Waals forces.

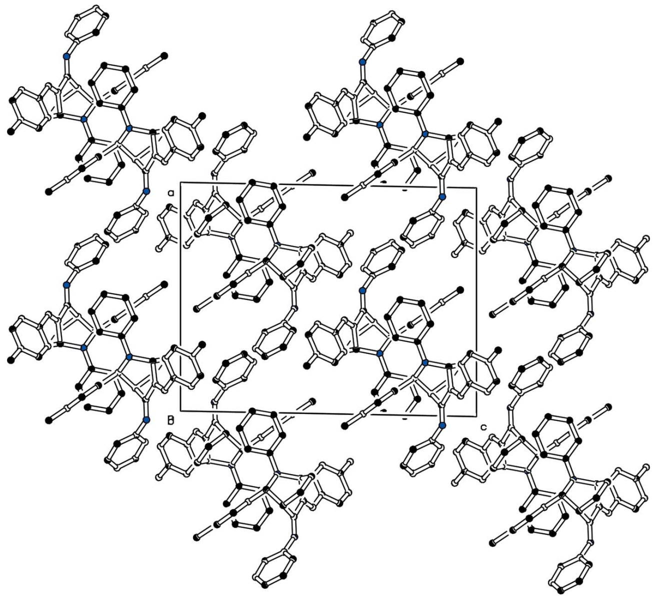


Figure 2
A packing diagram for (I), viewed down the *c* axis. H atoms have been omitted.

Experimental

To a solution of *N*-benzylideneaniline (5.5 mmol) in CH_2Cl_2 (5 ml) at room temperature, $ZrCl_4$ (10 mol%) and cyclohexen-2-one (5.5 mmol) were added sequentially and the mixture was stirred for 6 h. After completion of the reaction, as indicated by thin-layer chromatography, the reaction was quenched with water, diluted with CH_2Cl_2 (20 ml) and washed with water (10 ml). The aqueous layer was extracted with CH_2Cl_2 (2 × 10 ml). The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo* to yield a dark-brown residue, which was purified by column chromatography using 2–10% ethyl acetate in hexane as eluent, to obtain the pure product.

Crystal data

$C_{34}H_{32}N_2$
M_r = 468.62
Monoclinic, $P2_1/n$
a = 14.1805 (8) Å
b = 10.1822 (5) Å
c = 18.3636 (10) Å
β = 91.080 (1)°
V = 2651.0 (2) Å^3
Z = 4
D_x = 1.174 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6129 reflections
θ = 2.2–24.2°
μ = 0.07 mm^{-1}
T = 273 (2) K
Block, colourless
0.20 × 0.15 × 0.10 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
ω scans
Absorption correction: none
18613 measured reflections
4659 independent reflections
3617 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.019
$\theta_{\rm max}$ = 25.0°
$h = -16 \rightarrow 16$
$k = -12 \rightarrow 12$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.127$
S = 1.03
4659 reflections
357 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0649P)^2 + 0.3061P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max}$ = 0.15 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.14 e Å^{-3}

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Table 1

Selected bond lengths (Å).

C1—N2	1.4770 (19)	C6—C27	1.337 (2)
C5—N3	1.272 (2)	C29—C30	1.373 (2)

H atoms were included in calculated positions and refined as riding, with C—H distances in the range 0.93–0.98 Å and with $U_{\rm iso}$(H) = 1.2–1.5$U_{\rm eq}$ of the parent atom.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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