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

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The title compound, $C_{32}H_{26}N_2Cl_2$, exists as the Z isomer. All three rings in the azabicylo[2.2.2]octane system adopt a boat conformation. Intermolecular C—H···Cl interactions form a dimer in the crystal structure.

Key indicators

Comment

In continuation of our ongoing structural elucidation of aza-bicyclo[2.2.2]octane derivatives obtained from the Diels–Alder reaction, we report here the crystal structure of the title compound, (I).

(I)
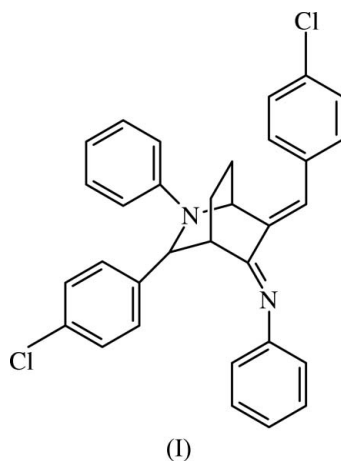
The molecular geometry of (I) (Fig. 1), in terms of bond distances and angles, is in good agreement with that of similar structures (Sonar *et al.*, 2004; Ravikumar *et al.*, 2005a,b). The torsion angles C5—C6—C27—C28 = −176.2 (2)° and C5—C6—N2—C21 = 176.4 (2)° indicate a *trans* configuration, and hence the Z isomer. Due to the double-bond strain, the bond angles C4—C5—N2, C6—C27—C28 and C1—C6—C27 deviate from ideal values (Table 1).

All three six-membered rings of the azabicyclo[2.2.2]octane system adopt the expected boat conformation, with asymmetry parameters (Nardelli, 1983) ΔC_s(C1) = 0.009 (2), 0.017 (2), 0.027 (1) for the rings C1/C4–C8, N1/C1/C3/C4/C7/C8 and N1/C1/C3–C6, respectively. The C9–C14 phenyl ring and C15–C20 chlorophenyl ring make dihedral angles with the mean plane of atoms C1/C3/C4/N1 of the azabicyclo[2.2.2]-octane cage of 30.7 (1) and 66.7 (1)°, respectively. Similarly, the dihedral angles are 77.9 (1) and 35.1 (1)°, respectively, for the C21–C26 phenyl ring and C28–C33 chlorophenyl ring with respect to the C1/C4/C5/C6 mean plane of the cage. The torsion angle C9—N1—C3—C15 is −90.2 (2)°, but N2—C5—C6—C27 is only 2.8 (4)°, as a consequence of the double bonds.
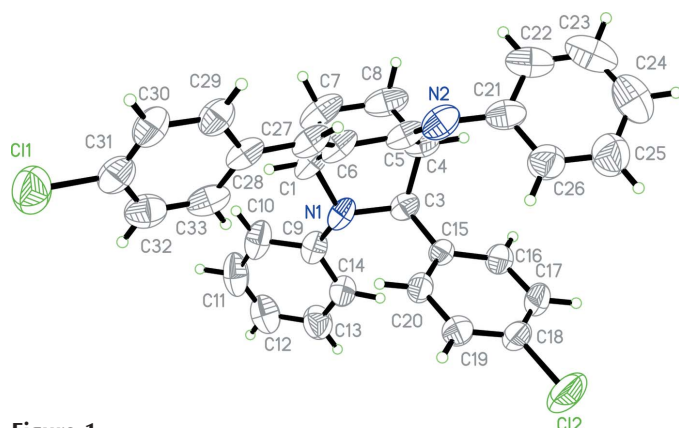
Figure 1
A view of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

The crystal structure is stabilized by weak intermolecular C—H···Cl interactions (You *et al.*, 2004) (Table 2). One of them leads to formation of a centrosymmetric dimer with a characteristic $R_2^2(26)$ motif (Bernstein *et al.*, 1995) in the crystal packing (Fig. 2).

Experimental

To a solution of *N*-benzylideneaniline (5.5 mmol) in CH_2Cl_2 (5 ml) at room temperature were sequentially added $ZrCl_4$ (10 mol%) and cyclohexen-2-one (5.5 mmol). The mixture was stirred for 6 h. After completion of the reaction as indicated by thin-layer chromatography, the reaction was quenched with water, and the mixture 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

$C_{32}H_{26}Cl_2N_2$	$D_x = 1.274$ Mg m^{-3}
$M_r = 509.45$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 5389
$a = 14.3560$ (6) Å	reflections
$b = 10.0621$ (4) Å	$\theta = 2.2–23.0°$
$c = 18.3872$ (8) Å	$\mu = 0.27$ mm^{-1}
$\beta = 91.427$ (1)°	$T = 273$ (2) K
$V = 2655.24$ (19) Å^3	Block, colorless
$Z = 4$	$0.20 \times 0.12 \times 0.07$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer	3312 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.021$
ω scans	$\theta_{max} = 25.0°$
Absorption correction: none	$h = -17 \rightarrow 17$
18622 measured reflections	$k = -11 \rightarrow 11$
4657 independent reflections	$l = -21 \rightarrow 21$

Refinement

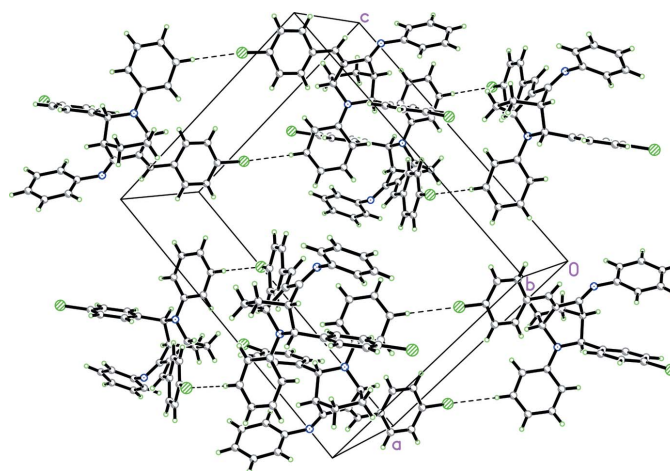|	
Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0676P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.055$	$+ 0.9266P]$
$wR(F^2) = 0.163$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} = 0.001$
4657 reflections	$\Delta\rho_{max} = 0.37$ e Å^{-3}
325 parameters	$\Delta\rho_{min} = -0.36$ e Å^{-3}
H-atom parameters constrained	

Figure 2
A view of the packing, showing the dimers. Dashed lines indicate C—H···Cl interactions.

Table 1
Selected geometric parameters (Å, °).

Cl1—C31	1.737 (4)	N2—C5	1.267 (4)
Cl2—C18	1.745 (3)	C6—C27	1.333 (4)
N2—C5—C4	128.3 (3)	C6—C27—C28	131.1 (3)
C27—C6—C1	128.5 (3)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C11—H11···Cl1^i	0.93	2.78	3.706 (3)	177
C10—H10···Cl2^{ii}	0.93	3.06	3.974 (3)	167

Symmetry codes: (i) $-x + 1, -y + 1, -z + 2$; (ii) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$.

H atoms were included in calculated positions (C—H = 0.93–0.98 Å) and refined as riding, with U_{iso}(H) values set at 1.2 or 1.5 (CH$_3$) times U_{eq}(C).

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: *SHELXTL/PC* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL97*.

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