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2,3a-*trans*-1,3a-*cis*-1,2-Bis(4-chlorophenyl)-1′,2′,3′-trihydro-3a-hydroxybenzo[e]bicyclo[3.3]octane-3-spiro-2′-indene-1′-one acetone solvate

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Key indicators

Single-crystal X-ray study
T = 193 K
Mean σ(C–C) = 0.003 Å
R factor = 0.047
wR factor = 0.115
Data-to-parameter ratio = 14.2

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

The title compound, $C_{32}H_{24}Cl_2O_2\cdot C_3H_6O$, was synthesized by the dimerization of 2-(4-chlorobenzal)inden-1-one, induced by a low-valent titanium reagent ($TiCl_4$/Zn). X-ray analysis reveals that the cyclopentane ring spiro-fused to the five-membered ring adopts an envelope conformation, while the other cyclopentane ring adopts an envelope conformation.

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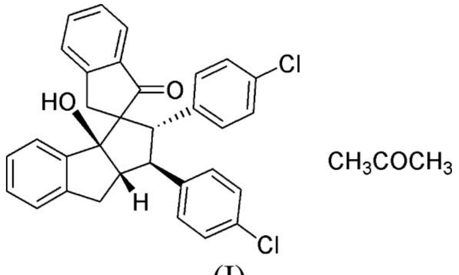
Comment

The spiro[4.4]nonane skeleton has been found in many compoundss for highly enantioselective hydrogenation (Lin *et al.*, 2004). Compounds containing the spiro[4.4]nonane skeleton show the following biological activities: anticonvulsant (Obniska & Zagorska, 2003) and potent platelet-activating factor (PAF) antagonist (Obitsu *et al.*, 2003). Low-valent titanium reagents have an exceedingly high ability to promote the reductive coupling of carbonyl compounds and are attracting increasing interest in organic synthesis (McMurry, 1983; Shi *et al.*, 1993, 1997, 1998, 2003). We report here the synthesis and the crystal structure of the title compound, (I).



(I)

In the title molecule, the cyclopentane ring (C1–C5) is the new ring formed by dimerization of 2-(4-chlorobenzal)inden-1-one, induced by the low-valent titanium reagent. This ring adopts an envelope conformation; atoms C1, C2, C4 and C5 are coplanar, while atom C3 deviates from this plane by 0.705 (1) Å. There are two cyclopentane rings in the molecule; one (C5–C8/C1) adopts an envelope conformation, with atom C6 deviating from the plane defined by C7/C8/C5/C1 by 0.065 (3) Å, and the other (C2/C9–C12) adopts an envelope conformation, with C2 deviating from the plane defined by C9/C10/C11/C12 by 0.337 (3) Å. The dihedral angle between the two 4-chlorophenyl rings is 83.1 (1)°.

In the crystal structure, the classical intermolecular hydrogen bond O1—H1···O2($-x+2, -y+1, -z+1$) and the weak interactions C3—H3···O1 and C4—H4···O3 connect adjacent molecules (Fig. 2 and Table 2).

Experimental

The title compound was prepared by the reaction of 2-(4-chlorobenzal)inden-1-one (1.28 g, 5 mmol) induced by a low-valent titanium reagent ($TiCl_4$/Zn) (yield 46%, m.p. 462–463 K). IR: 3375 (OH), 1692 (CO), 1605, 1493, 1465, 850, 829, 763, 750 (phenyl ring); ^1H NMR: δ 2.17 (6H, *s*, 2CH_3), 2.23 (1H, *d*, J = 16.8 Hz, $C^{3'}$—H), 2.68 (1H, *d*, J = 16.8 Hz, $C^{3'}$—H), 2.77–2.84 (1H, *m*, C^6—H), 2.98–3.03 (1H, *m*, C^6—H), 3.26–3.32 (1H, *m*, C^5—H), 3.68 (1H, *dd*, J_1 = 12.8 Hz, J_2 = 8.4 Hz, C^4—H), 4.73 (1H, *d*, J = 12.8 Hz, C^3—H), 5.85 (1H, *s*, OH), 6.10 (1H, *d*, J = 8.4 Hz, ArH), 6.75 (1H, *t*, J = 7.2 Hz, ArH), 6.98 (1H, *d*, J = 7.6 Hz, ArH), 7.14–7.24 (4H, *m*, ArH), 7.29–7.38 (5H, *m*, ArH), 7.46 (1H, *t*, J = 7.2 Hz, ArH), 7.53 (2H, *d*, J = 8.0 Hz, ArH), 7.67 (1H, *d*, J = 7.2 Hz, ArH). Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a petroleum ether/acetone solution (5:1 *v*/*v*).

Crystal data

$C_{32}H_{24}Cl_2O_2 \cdot C_3H_6O$
M_r = 569.49
Triclinic, $P\overline{1}$
a = 10.1669 (16) Å
b = 10.9425 (16) Å
c = 13.6510 (12) Å
α = 74.001 (10)°
β = 77.008 (11)°
γ = 88.039 (13)°
V = 1421.9 (3) Å^3
Z = 2
D_x = 1.330 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5464 reflections
θ = 3.2–25.3°
μ = 0.26 mm^{-1}
T = 193 (2) K
Block, colorless
0.30 × 0.25 × 0.11 mm

Data collection

Rigaku Mercury CCD diffractometer
ω scans
Absorption correction: multi-scan (Jacobson, 1998)
T_{min} = 0.925, T_{max} = 0.972
14209 measured reflections
5185 independent reflections
4293 reflections with $I > 2\sigma(I)$
R_{int} = 0.027
θ_{max} = 25.4°
$h = -12 \rightarrow 10$
$k = -13 \rightarrow 13$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.115
S = 1.08
5185 reflections
365 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0499P)^2 + 0.4952P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.34 e Å^{-3}
$\Delta\rho_{min}$ = −0.43 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.424 (2)	C2—C3	1.545 (3)
O2—C9	1.221 (2)	C3—C4	1.540 (2)
C1—C5	1.557 (3)	C4—C23	1.503 (3)
C1—C2	1.592 (3)	C4—C5	1.544 (3)
C2—C9	1.527 (2)	C5—C6	1.542 (3)
O1—C1—C8	108.60 (15)	C3—C4—C5	103.04 (14)
O1—C1—C2	110.31 (14)	C6—C5—C4	115.13 (15)
C5—C1—C2	103.78 (14)	C4—C5—C1	107.08 (14)
C3—C2—C1	101.42 (14)	C11—C12—C2	103.96 (14)
C17—C3—C4	117.06 (15)		
O1—C1—C2—C9	−32.57 (19)	O1—C1—C5—C4	−114.72 (16)
C5—C1—C2—C3	−31.62 (16)	C8—C1—C5—C4	126.95 (15)
O1—C1—C2—C12	−146.72 (15)	C2—C1—C5—C4	4.94 (18)
C2—C3—C4—C5	−44.07 (16)	C4—C5—C6—C7	−122.99 (17)
C23—C4—C5—C6	−90.6 (2)	C1—C5—C6—C7	−4.1 (2)
C3—C4—C5—C6	142.73 (16)	O1—C1—C8—C32	55.5 (2)
C3—C4—C5—C1	23.83 (18)		

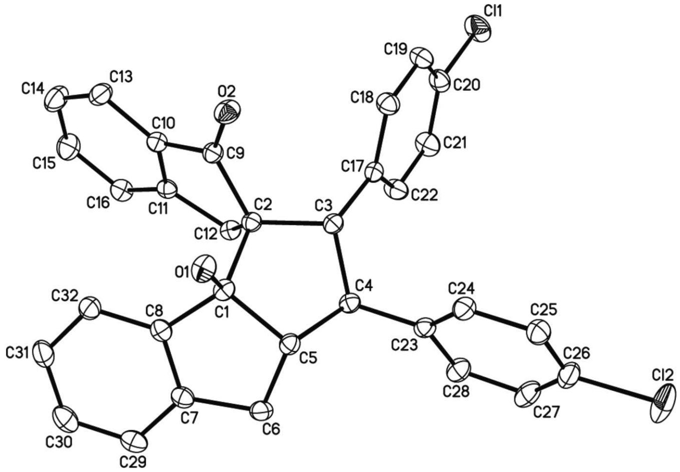


Figure 1
The molecular structure of (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity.

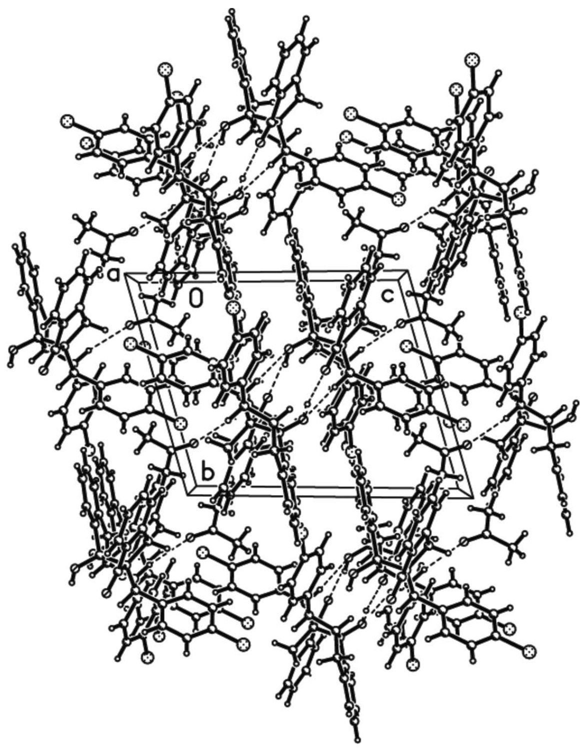


Figure 2
A molecular packing diagram of (I). Hydrogen-bonding interactions are shown as dashed lines.

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

D—H···A	D—H	H···A	D···A	D—H···A
C4—H4···O3^i	1.00	2.51	3.495 (3)	167
C3—H3···O1^{ii}	1.00	2.50	3.445 (2)	158
O1—H1···O2^{ii}	0.84	1.99	2.8213 (19)	168

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

H atoms were positioned geometrically and refined as riding, with C—H = 0.95–1.00 Å and O—H = 0.84 Å, and $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(O)$.

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Data collection: *CrystalClear* (Rigaku, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku/MSC, 2003); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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