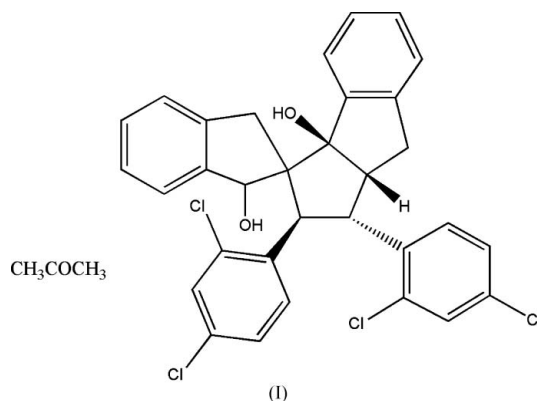


1,3-*trans*-1,4-*cis*-1,2-Bis(2,4-dichlorophenyl)-1,2,3,3a,8,8a-hexahydrobenzo[e]pentalene-3-spiro-2'-indan-3a,1'-diol acetone solvateDa-Qing Shi,^{a,b*} Zheng-Yi Li,^a
Chun-Ling Shi^a and Guo-Lan
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Key indicatorsSingle-crystal X-ray study
T = 293 K
Mean $\sigma(\text{C}-\text{C}) = 0.007 \text{ \AA}$
R factor = 0.056
wR factor = 0.170
Data-to-parameter ratio = 14.1For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.The title compound, $\text{C}_{32}\text{H}_{24}\text{Cl}_4\text{O}_2 \cdot \text{C}_3\text{H}_6\text{O}$, was obtained as a by-product of the reaction of 2-(2',4'-dichlorobenzal)-1-indenone induced by a low-valent titanium reagent (TiCl_4/Zn). Each of the fused cyclopentane rings adopts an envelope conformation.Received 22 July 2005
Accepted 7 September 2005
Online 14 September 2005**Comment**The spiro[4.4]nonane skeleton has been found in many ligands for highly enantioselective hydrogenation (Lin *et al.*, 2004). Compounds containing the spiro[4.4]nonane skeleton show biological activities such as anticonvulsant (Obniska *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).

In (I), the C1/C9/C10–C12 cyclopentane ring is the new ring formed by dimerization of 2-(2',4'-chlorobenzal)-1-indenone induced by a low-valent titanium reagent. This ring adopts an envelope conformation; atoms C1, C9, C10 and C11 are coplanar, while atom C12 deviates from this plane by 0.672 (2) Å. The C1/C2/C7–C9 cyclopentane ring also adopts an envelope conformation, atom C9 deviating from the C1/C2/C7/C8 plane by 0.440 (3) Å. The third five-membered ring is an envelope conformation; atoms C12, C13, C14 and C19 are coplanar, while atom C20 deviates from this plane by –0.534 (2) Å. The dihedral angle between the two 2,4-dichlorophenyl rings is 78.4 (5)°. In the crystal structure, classical O–H...O hydrogen bonds (Table 2) connect adjacent molecules into centrosymmetric dimers (Fig. 2).

Experimental

Compound (I), as a by-product, was prepared by the dimerization of 2-(2',4'-dichlorobenzal)-1-indenone (1.45 g, 5 mmol) induced by a

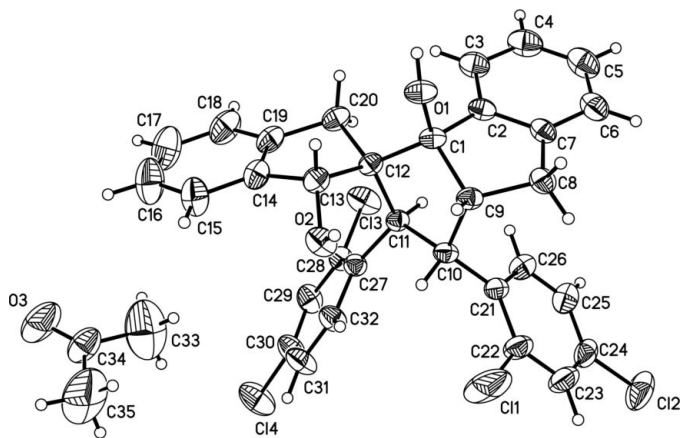


Figure 1
The molecular structure of (I), showing 40% probability displacement ellipsoids and the atom-numbering scheme.

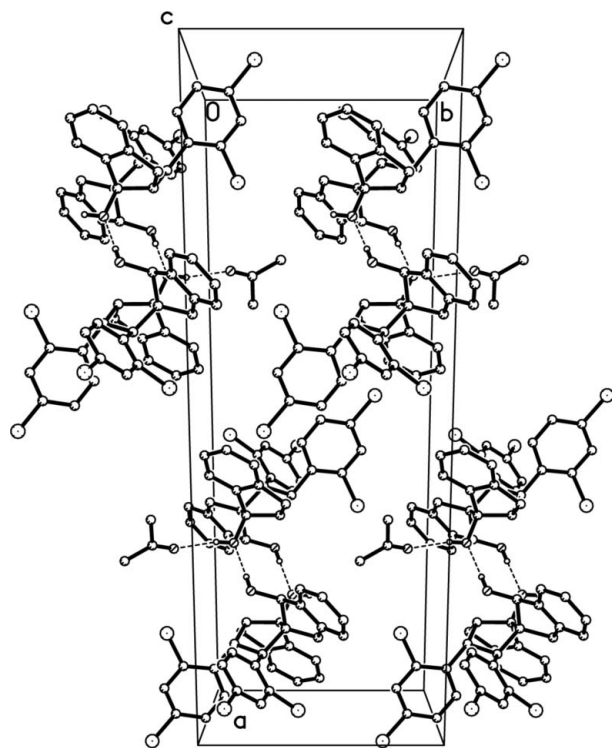


Figure 2
The packing of (I). Dashed lines indicated hydrogen bonds. H atoms have been omitted unless they are involved in hydrogen bonding.

low-valent titanium reagent (TiCl₄/Zn). Yield of (I) 16%, m.p. 516–518 K. The main product was 2,2'-[1,2-bis(2,4-dichlorophenyl)ethane-1,2-diyl] bis(1-tetralone). Single crystals of (I) suitable for X-ray diffraction were obtained by slow evaporation of a petroleum ether/acetone solution. ¹H NMR: 2.09 (2H, s, C^{3'}–H), 2.51–2.57 (1H, m, C⁶–H), 2.89–2.96 (2H, m, C⁶–H, C⁵–H), 3.03 (1H, dd, J₁ = 16.8 Hz, J₂ = 8.4 Hz, C⁴–H), 3.17 (1H, d, J = 16.8 Hz, C³–H), 4.09–4.12 (1H, m, C^{1'}–H), 5.31 (1H, d, J = 12.4 Hz, OH), 6.09 (1H, s, OH), 6.43 (1H, d, J = 8.0 Hz, ArH), 6.88 (1H, t, J = 7.2 Hz, ArH), 7.08 (1H, d, J = 7.6 Hz, ArH), 7.21–7.27 (3H, m, ArH), 7.33–7.37 (2H, m, ArH), 7.46–7.52 (3H, m, ArH), 7.58–7.64 (2H, m, ArH), 7.86 (1H, d, J = 8.4 Hz, ArH).

Crystal data

C₃₂H₂₄Cl₄O₂·C₃H₆O
M_r = 640.39
Monoclinic, C2/c
a = 31.620 (8) Å
b = 10.443 (3) Å
c = 20.993 (5) Å
β = 116.931 (4)°
V = 6180 (3) Å³
Z = 8

D_x = 1.376 Mg m⁻³
Mo Kα radiation
Cell parameters from 2726 reflections
θ = 2.5–20.6°
μ = 0.42 mm⁻¹
T = 293 (2) K
Block, colorless
0.39 × 0.37 × 0.15 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
T_{min} = 0.854, T_{max} = 0.940
15854 measured reflections

5442 independent reflections
2710 reflections with I > 2σ(I)
R_{int} = 0.047
θ_{max} = 25.0°
h = -23 → 37
k = -12 → 12
l = -24 → 24

Refinement

Refinement on F²
R[F² > 2σ(F²)] = 0.056
wR(F²) = 0.170
S = 1.00
5442 reflections
387 parameters
H atoms treated by a mixture of independent and constrained refinement

w = 1/[σ²(F_o²) + (0.0568P)² + 14.254P]
where P = (F_o² + 2F_c²)/3
(Δ/σ)_{max} < 0.001
Δρ_{max} = 0.68 e Å⁻³
Δρ_{min} = -0.53 e Å⁻³

Table 1
Selected geometric parameters (Å, °).

O1–C1	1.439 (4)	C8–C9	1.524 (5)
O2–C13	1.423 (5)	C9–C10	1.578 (5)
C1–C9	1.539 (5)	C10–C11	1.552 (5)
C1–C12	1.544 (5)	C11–C12	1.549 (5)
C1–C2–C7–C8	4.2 (4)	C9–C10–C11–C12	-24.9 (4)
O1–C1–C9–C10	150.3 (3)	O1–C1–C12–C11	-163.2 (3)
C12–C1–C9–C10	28.6 (4)	C9–C1–C12–C11	-43.7 (4)
C1–C9–C10–C11	-2.0 (4)	C10–C11–C12–C1	41.6 (3)
C21–C10–C11–C27	72.0 (4)		

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

D–H...A	D–H	H...A	D...A	D–H...A
O1–H1...O3 ⁱ	0.82 (5)	1.92 (5)	2.723 (5)	164 (5)
O2–H2...O1 ⁱⁱ	0.83 (5)	1.96 (5)	2.784 (4)	176 (5)

Symmetry codes: (i) x, -y + 1, z + ½; (ii) -x + ½, -y + ½, -z + 1.

The hydroxy H atoms were located in difference Fourier maps and refined isotropically. H atoms on C atoms were positioned geometrically and treated as riding on their parent C atoms, with C–H distances in the range 0.93–0.98 Å, and with U_{iso}(H) = 1.2U_{eq}(C), except for the methyl H atoms, for which U_{iso}(H) = 1.5U_{eq}(C).

Data collection: SMART (Bruker, 1998); cell refinement: SAINT (Bruker, 1999); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1999); software used to prepare material for publication: SHELXTL.

The authors thank the Foundation of the 'Surpassing Project' of Jiangsu Province, and the Natural Science Foundation of the Education Committee of Jiangsu Province (03 KJB150136), for financial support.

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