Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

2,9b-*trans*-3,9b-*cis*-2,3-Bis(4-bromophenyl)-2,3,3a,4,5,9b,1′,2′,3′,4′-decahydro-1*H*-benzo[e]indene-1-spiro-2′-naphthalene-1′,9b-diol acetone solvate

Daqing Shi,[a,b]* Chunling Shi,[a] Xiangshan Wang,[a] Liangce Rong[a] and Hongwen Hu[c]

[a]Department of Chemistry, Xuzhou Normal University, Xuzhou 221116, People's Republic of China, [b]The Key Laboratory of Biotechnology for Medical Plants of Jiangsu Province, Xuzhou 221116, People's Republic of Chiona, and [c]Department of Chemistry, Nanjing University, Nanjing 210093, People's Republic of China

Correspondence e-mail: dqshi@263.net

Received 10 September 2004
Accepted 20 September 2004
Online 30 September 2004

Key indicators

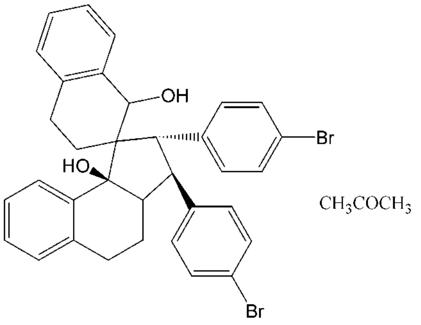
Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.005 Å
R factor = 0.036
wR factor = 0.045
Data-to-parameter ratio = 15.0

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

The title compound, $C_{34}H_{30}Br_2O_2.C_3H_6O$, was synthesized by the dimerization of 2-(4-bromobenzal)-1-tetralone, induced by a low-valent titanium reagent ($TiCl_4$/Zn). X-ray analysis reveals that the cyclohexane ring spiro-fused to the 5-membered ring adopts a boat conformation, while the other cyclohexane ring adopts a screw-boat conformation.

Comment

The spiro[4.5]decane skeleton has been found in many natural products (*e.g.* the sesquiterpene gleenol; Yatagai *et al.*, 1991; Barrero *et al.*, 1991). Compounds containing the spiro[4.5]-decane skeleton show the following biological activities: termiticidal, antihelmintic and growth regulation effects on plant seeds (Bozan *et al.*, 1999). 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 crystal structure of the title compound, (I).



(I)

In the title molecule, the cyclopentane ring (C1–C5) is the new ring formed by the dimerization of 2-(4-bromobenzal)-1-tetralone, induced by a low-valent titanium reagent. This ring adopts an envelope conformation; atoms C2, C3, C4 and C5 are coplanar, while atom C1 deviates from this plane by 0.720 (2) Å. There are two cyclohexane rings in the molecule; one (C5/C14–C16/C21/C22) adopts a boat conformation, with atoms C15 and C22 deviating from the plane defined by C5/C14/C16/C21 by 0.628 (2) and 0.479 (3) Å, respectively, and the other (C3/C4/C13/C8/C7/C6) adopts a screw-boat conformation, with C3 and C6 deviating from the plane defined by C7/C8/C13/C4 by 0.463 (2) and 0.920 (3) Å, respectively. The dihedral angle between the two *p*-bromophenyl rings is 78.9 (2)°. In the crystal structure, there are two hydrogen bonds involving the two hydroxyl groups and the ketone O atom of the acetone solvent molecule (Fig. 2 and Table 2).

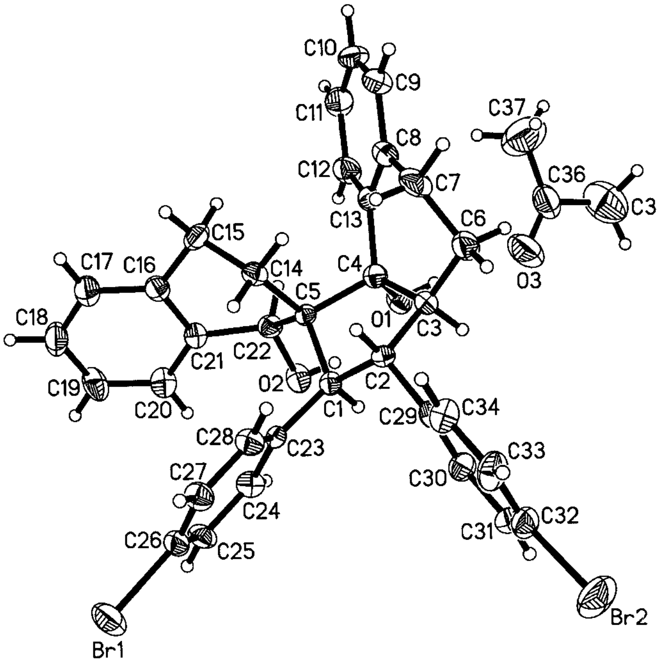


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme.

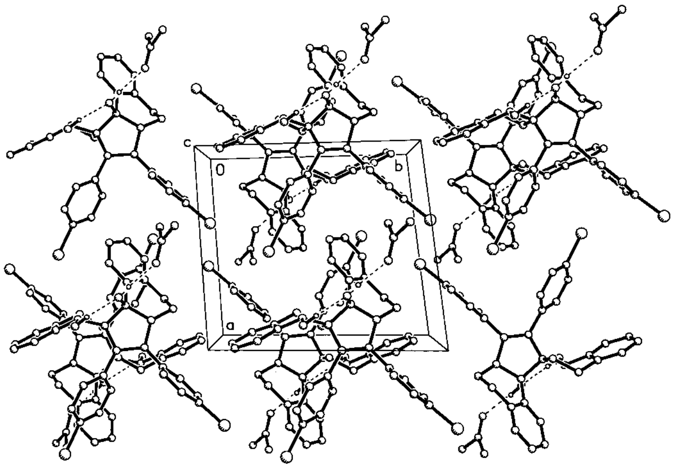


Figure 2
A packing diagram of the crystal structure of (I). Dashed lines indicate hydrogen bonds. H atoms not involved in hydrogen bonding have been omitted.

Experimental

The title compound, (I), was prepared by the dimerization of 2-(4-bromobenzal)-1-tetralone (1.56 g, 5 mmol), induced by a low-valent titanium reagent ($TiCl_4/Zn$) (yield 81%, mp. 428–429 K). IR: 3510 (OH), 3400 (OH), 1590, 1490, 1460, 850, 830, 760, 750 (phenyl ring). ^1H NMR: 1.08–1.11 (1H, *m*, C10—H), 1.27–1.34 (1H, *m*, C10—H), 1.62–1.65 (2H, *m*, C3′—H, C9—H), 1.78–1.88 (2H, *m*, C3′—H, C9—H), 2.17 (6H, *s*, 2CH$_3$), 2.50–2.53 (1H, *m*, C2—H), 2.75–2.79 (1H, *m*, C4′—H), 2.85–2.92 (1H, *m*, C4′—H), 3.32 (1H, *dd*, J_1 = 11.2, J_2 = 13.2 Hz, C3—H), 4.59 (1H, *d*, *J* = 13.2 Hz, C4—H), 5.45 (1H, *s*, C6—H), 6.49 (1H, *d*, *J* = 7.2 Hz, ArH), 6.84–6.88 (3H, *m*, ArH), 7.00–7.07 (3H, *m*, ArH), 7.19–7.26 (5H, *m*, ArH), 7.35 (2H, *d*, *J* = 8.4 Hz, ArH), 7.61 (1H, *d*, *J* = 7.6 Hz, ArH), 7.87 (1H, *d*, *J* = 5.6 Hz, ArH). Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a petroleum ether/acetone solution.

Crystal data

$C_{34}H_{30}Br_2O_2 \cdot C_3H_6O$
$M_r = 688.48$
Triclinic, $P\overline{1}$
$a = 11.427\ (1)$ Å
$b = 12.042\ (1)$ Å
$c = 12.992\ (2)$ Å
$\alpha = 77.87\ (1)^\circ$
$\beta = 67.73\ (1)^\circ$
$\gamma = 81.02\ (1)^\circ$
$V = 1611.8\ (4)$ Å^3

$Z = 2$
$D_x = 1.419$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 27 reflections
$\theta = 3.0–15.1^\circ$
$\mu = 2.55$ mm^{-1}
$T = 296\ (2)$ K
Block, colorless
0.36 × 0.36 × 0.14 mm

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: ψ scan (*XSCANS*; Siemens, 1994)
$T_{min} = 0.446$, $T_{max} = 0.700$
6445 measured reflections
5836 independent reflections
2436 reflections with $I > 2\sigma(I)$

$R_{int} = 0.028$
$\theta_{max} = 25.3^\circ$
$h = 0 \rightarrow 13$
$k = -14 \rightarrow 14$
$l = -14 \rightarrow 15$
3 standard reflections every 97 reflections
intensity decay: 7.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.045$
$S = 0.80$
5836 reflections
390 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.01P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.36$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0067 (2)

Table 1
Selected geometric parameters (Å, °).

O1—C4	1.442 (3)	C2—C3	1.540 (3)
O2—C22	1.425 (3)	C3—C6	1.528 (3)
C1—C2	1.541 (3)	C3—C4	1.558 (4)
C1—C5	1.553 (3)	C4—C5	1.579 (3)
C2—C29	1.516 (3)	C5—C22	1.561 (3)
C23—C1—C2	116.3 (2)	O1—C4—C5	105.8 (3)
C3—C2—C1	102.4 (2)	C3—C4—C5	105.1 (2)
C6—C3—C2	114.0 (2)	C1—C5—C4	101.3 (2)
C2—C3—C4	106.0 (2)	C15—C14—C5	114.9 (2)
O1—C4—C13	108.5 (3)		
C5—C1—C2—C3	−47.0 (3)	C3—C4—C5—C1	−27.7 (3)
C29—C2—C3—C6	−77.0 (3)	O1—C4—C5—C14	−155.1 (2)
C1—C2—C3—C6	158.1 (2)	O1—C4—C5—C22	−33.6 (3)
C1—C2—C3—C4	29.2 (3)	C2—C3—C6—C7	−81.9 (3)
C2—C3—C4—O1	−113.5 (3)	C4—C3—C6—C7	41.7 (4)
C2—C3—C4—C13	125.5 (3)	O1—C4—C13—C12	37.7 (4)
C2—C3—C4—C5	−0.7 (3)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2O···O1	0.815 (10)	1.963 (19)	2.681 (3)	147 (3)
O1—H1O···O3	0.810 (10)	2.036 (11)	2.842 (3)	174 (3)

H atoms attached to atoms O1 and O2 were refined isotropically, with the O—H bond lengths restrained to 0.81 (1) Å. Other H atoms were positioned geometrically and refined as riding, with C—H = 0.93–0.98 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

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Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Sheldrick, 1997); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; 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 (No. 03 KJB150136) for financial support.

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