

C13a—Sn2a—O2a'	84.2 (3)	C5'—Sn1'—O5b	79.6 (5)
C13a—Sn2a—O5a	90.8 (3)	C5'—Sn1'—O7b	84.0 (5)
O1a—Sn2a—O1a'	76.6 (2)	O1'—Sn1'—O2b	75.2 (3)
O1a—Sn2a—O2a'	134.7 (2)	O1'—Sn1'—O4b	142.8 (3)
O1a—Sn2a—O5a	70.6 (2)	O1'—Sn1'—O5b	68.5 (3)
O1a'—Sn2a—O2a'	58.9 (2)	O1'—Sn1'—O7b	140.7 (3)
O1a'—Sn2a—O5a	147.1 (2)	O2b—Sn1'—O4b	67.8 (2)
O2a'—Sn2a—O5a	154.0 (1)	O2b—Sn1'—O5b	139.8 (2)
Sn1a—O1a—Sn2a	123.2 (2)	O2b—Sn1'—O7b	143.8 (2)
Sn1a—O1a—Sn2a'	131.4 (2)	O4b—Sn1'—O5b	147.3 (2)
Sn2a—O1a—Sn2a'	103.4 (2)	O4b—Sn1'—O7b	76.5 (2)
C1b—Sn1b—C5b	168.3 (6)	O5b—Sn1'—O7b	73.0 (2)
C1b—Sn1b—O1b	92.7 (6)	C9'—Sn2'—C13'	133.3 (6)
C1b—Sn1b—O2b''	79.6 (6)	C9'—Sn2'—O1'	107.4 (6)
C1b—Sn1b—O4b''	86.1 (6)	C9'—Sn2'—O1b	115.9 (5)
C1b—Sn1b—O5b''	85.2 (6)	C9'—Sn2'—O2b	82.1 (4)
C1b—Sn1b—O7b''	85.6 (5)	C9'—Sn2'—O5b''	89.9 (5)
C5b—Sn1b—O1b	98.9 (5)	C13'—Sn2'—O1'	98.4 (5)
C5b—Sn1b—O2b''	105.1 (4)	C13'—Sn2'—O1b	107.6 (6)
C5b—Sn1b—O4b''	84.6 (4)	C13'—Sn2'—O2b	75.6 (5)
C5b—Sn1b—O5b''	97.4 (4)	C13'—Sn2'—O5b''	86.7 (4)
C5b—Sn1b—O7b''	85.2 (4)	O1'—Sn2'—O1b	76.2 (4)
O1b—Sn1b—O2b''	73.0 (3)	O1'—Sn2'—O2b	63.3 (3)
O1b—Sn1b—O4b''	149.1 (3)	O1'—Sn2'—O5b''	149.3 (3)
O1b—Sn1b—O5b''	70.3 (3)	O1b—Sn2'—O2b	139.3 (3)
O1b—Sn1b—O7b''	134.9 (3)	O1b—Sn2'—O5b''	73.4 (3)
O2b''—Sn1b—O4b''	76.4 (2)	O2b—Sn2'—O5b''	146.2 (2)
O2b''—Sn1b—O5b''	139.4 (2)	Sn1'—O1'—Sn2'	131.1 (5)
O2b''—Sn1b—O7b''	149.2 (2)	Sn1'—O1'—Sn2b	123.1 (5)
O4b''—Sn1b—O5b''	140.0 (2)	Sn2'—O1'—Sn2b	103.6 (4)
O4b''—Sn1b—O7b''	75.8 (2)		

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

The  $(C_4H_9)_2Sn$  portion of molecule *b* is ordered over a center of inversion and was refined as two  $[(C_4H_9)_2SnO]$  units, each of half site occupancy; their C atoms were refined isotropically. The pyridyl rings were refined as rigid hexagons. The C atoms of the butyl groups of the *a* and *b* molecules were refined subject to 1,2- and 1,3-related atom distances of  $1.54 \pm 0.01$  and  $2.52 \pm 0.02$  Å, respectively; restraints were imposed on the atoms of the chains. The final difference map had peaks of about  $1 e \text{ \AA}^{-3}$  near the Sn atoms.

Data collection: XSCANS (Siemens, 1990). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: ORTEPII (Johnson, 1976). Software used to prepare material for publication: SHELXL93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1060). Services for accessing these data are described at the back of the journal.

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## Racemic 1,1,6,6-Tetramethyl-1,6-distanna-tetranaphtho[2,1-*b*;1',2'-*d*;2'',1''-*g*;1''',2'''-*i*]-cyclodeca-2,4,7,9-tetraene

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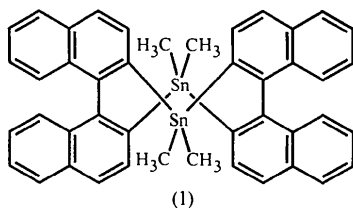
## Abstract

The title compound,  $[Sn_2(C_{20}H_{12})_2(CH_3)_4]$ , which is the first chiral tin-bridged cyclophane, was prepared from the reaction of racemic 2,2'-dilithio-1,1'-binaphthyl and dimethyltin dichloride. The molecule has approximate local  $D_2$  222 symmetry.

## Comment

An optically active compound containing the 1,1'-binaphthyl moiety is one of the potential target molecules for non-linear optical materials (Thorup, 1996). Much attention is being devoted to compounds containing a 2,2'-disubstituted 1,1'-biaryl group as efficient ligands of asymmetric catalysts or chiral reagents in asymmetric syntheses (Kagan, 1985; Takaya *et al.*, 1993; Noyori, 1994). As new examples of such chiral compounds, the authors and others have recently independently reported the preparation, structural analyses and properties of dinaphtho[2,1-*b*;1',2'-*d*]phosphole derivatives (Tani, Yamagata, & Tashiro, 1995; Tani, Tashiro *et al.*, 1995; Gladiali *et al.*, 1994) and their arsenic

analogues (Watson *et al.*, 1993). Although these compounds could be resolved by spontaneous resolution during crystallization and showed helical chirality in the solid state, they racemize easily in solution at ambient temperature due to their steric lability. Recently, 2,2'-bis(trimethylstannyl)-1,1'-binaphthyl has been prepared in good yield from the reaction of trimethyltin chloride and 2,2'-dilithio-1,1'-binaphthyl (Krishnamurti *et al.*, 1991). We therefore planned to prepare the tin analogue of the phosphole and to examine its properties. The title compound, (1), however, was obtained instead of the required phosphole analogue of tin by the reaction of 2,2'-dilithio-1,1'-binaphthyl with dimethyltin dichloride and its structure was determined by X-ray analysis.



The title compound forms a rigid framework comprised of a *cis*-cyclodecatetraene ring and no special strain is present in the molecule (Fig. 1). The naphthalene rings are planar and the dihedral angles between the two naphthalene rings of the binaphthyl moieties are 75.6(1) and 77.3(1)°, which lie between the corresponding angles found in [Rh{(R)-(+)-binap<sub>2</sub>}]<sub>2</sub>ClO<sub>4</sub> [72.9(3)°; Tani *et al.*, 1985] and (±)-1,1'-bi-2-naphthol [89.39(7)°; Gridunova *et al.*, 1982]. The Sn—C bond distances in (1) are normal (Table 1) and are not significantly different depending on whether tin is bonded

to a naphthalene ring or to a methyl group. The average bond angle, C—Sn—C for the bridged SnMe<sub>2</sub> groups, is 109.4°, which is expected for an *sp*<sup>3</sup> configuration, but that connecting naphthalene groups is slightly wider. The presence of these long Sn—C bonds within the ring may relieve some strain which might be present in the all-*cis* cyclodecatetraene ring. We want to emphasize here that the racemic stannacycloalkene (1) is a rare example of a molecule with pseudo-*D*<sub>2</sub> symmetry.

## Experimental

All reactions were carried out under an atmosphere of nitrogen by Schlenk tube techniques. (±)-2,2'-Dilithio-1,1'-binaphthyl was prepared from the reaction of (±)-2,2'-dibromo-1,1'-binaphthyl (331 mg, 0.80 mmol) with butyllithium/hexane (1.33 ml, 1.80 mmol) at 195 K. The yellow-green suspension of (±)-2,2'-dilithio-1,1'-binaphthyl was added to 15 ml of THF. To the resulting yellow-green slurry was added dropwise at 195 K over 10 min a solution of dimethyltin dichloride (211 mg, 0.96 mmol) in 15 ml of THF and the resulting mixture was stirred for a further 30 min at that temperature. The yellow-green colour of the slurry changed to yellow and the temperature was then allowed to increase to room temperature; the yellow slurry changed to a dark-yellow solution at about 253 K. After the solution was stirred overnight (12 h), the solvent was removed under reduced pressure and the residue was treated with a mixture of benzene and water. The organic layer was washed with brine, dried over MgSO<sub>4</sub> and concentrated *in vacuo*. The pale brown residual oil was purified by flash column chromatography using 2:1 hexane-ethyl acetate as an eluent and repeated recrystallizations of the first band from dichloromethane afforded (1) as colourless crystals (28 mg, 4%); m.p. >573 K. Analysis: C 66.02, H 5.16%; calculated for C<sub>44</sub>H<sub>36</sub>Sn<sub>2</sub> (802.15): C 65.88, H 4.52%. Mass (FD): *m/e* 786 (*M*—CH<sub>3</sub>—1)<sup>+</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ -0.78 [*s* with pairs of satellites, <sup>3</sup>*J*(<sup>119</sup>Sn—<sup>1</sup>H) = 50.6 Hz, 12H, Sn—CH<sub>3</sub>], 6.78 [*d* with pairs of satellites, *J* = 8.0 Hz, <sup>3</sup>*J*(<sup>119</sup>Sn—<sup>1</sup>H) = 45.0 Hz, 4H, 3-H of the naphthyl ring], 7.1–7.25 (*m*, 8H, aromatic H), 7.45 (*t*, *J* = 7.6 Hz, aromatic H), 7.71 (*d*, *J* = 8.0 Hz, 4H, aromatic H), 7.92 (*d*, *J* = 8.0 Hz, aromatic H). <sup>119</sup>Sn NMR (C<sub>6</sub>D<sub>6</sub>): δ -73.49 (*s*). UV (1,4-dioxane): λ<sub>max</sub> (log ε) 292.8 (4.1), 280.5 (4.1), 233.3 (5.0). A crystal suitable for X-ray analysis was fixed to the tip of a glass fibre with cyanoacrylate adhesive.

## Crystal data

[Sn<sub>2</sub>(C<sub>20</sub>H<sub>12</sub>)<sub>2</sub>(CH<sub>3</sub>)<sub>4</sub>]

*M<sub>r</sub>* = 802.15

Monoclinic

*P*2<sub>1</sub>/*n*

*a* = 17.789 (4) Å

*b* = 16.927 (5) Å

*c* = 11.751 (2) Å

β = 101.18 (2)°

*V* = 3471.2 (14) Å<sup>3</sup>

*Z* = 4

*D<sub>r</sub>* = 1.535 Mg m<sup>-3</sup>

*D<sub>m</sub>* not measured

Mo *K*α radiation

λ = 0.71069 Å

Cell parameters from 25

reflections

θ = 10–12°

μ = 1.469 mm<sup>-1</sup>

*T* = 293 (1) K

Plate

0.33 × 0.17 × 0.07 mm

Colourless

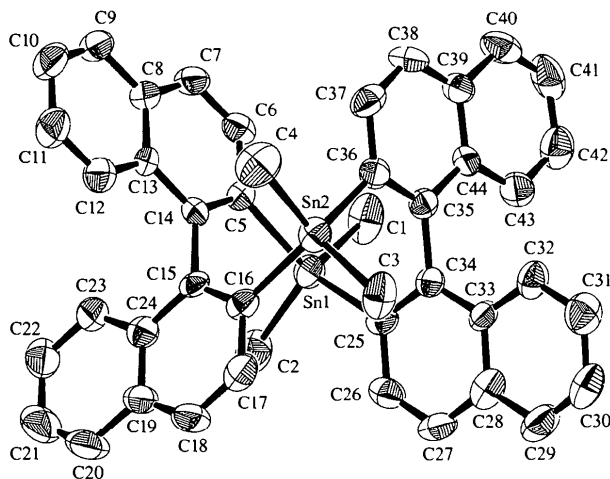


Fig. 1. The molecular structure of the title compound. Displacement ellipsoids are plotted at the 50% probability level (ORTEPII; Johnson, 1976).

**Data collection**

Rigaku AFC-4R diffractometer  
 $\omega$  scans  
 Absorption correction:  $\psi$  scan (North *et al.*, 1968)  
 $T_{\min} = 0.860$ ,  $T_{\max} = 0.898$   
 8640 measured reflections  
 7964 independent reflections

3558 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.023$   
 $\theta_{\max} = 27.5^\circ$   
 $h = 0 \rightarrow 25$   
 $k = 0 \rightarrow 23$   
 $l = -16 \rightarrow 16$   
 3 standard reflections every 150 reflections  
 intensity decay: none

**Refinement**

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.057$   
 $wR(F^2) = 0.086$   
 $S = 0.842$   
 6646 reflections  
 415 parameters  
 H-atom parameters constrained

$w = 1/\sigma^2(F_o^2)$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.398 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.429 \text{ e } \text{\AA}^{-3}$   
 Extinction correction: none  
 Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Sn1—Sn2	4.2793 (11)	Sn2—C3	2.138 (7)
Sn1—C1	2.135 (7)	Sn2—C4	2.138 (7)
Sn1—C2	2.117 (7)	Sn2—C16	2.153 (7)
Sn1—C5	2.151 (6)	Sn2—C36	2.149 (7)
Sn1—C25	2.150 (7)		
C2—Sn1—C1	107.9 (3)	C3—Sn2—C4	108.5 (3)
C1—Sn1—C5	106.8 (3)	C3—Sn2—C36	109.6 (3)
C1—Sn1—C25	105.9 (3)	C4—Sn2—C36	108.2 (3)
C2—Sn1—C5	109.4 (3)	C3—Sn2—C16	107.4 (3)
C2—Sn1—C25	107.4 (3)	C4—Sn2—C16	106.1 (3)
C25—Sn1—C5	118.9 (2)	C36—Sn2—C16	116.8 (3)

All H atoms were located at ideal positions with C—H = 0.96 ( $sp^3$ -hybridized geometry) or 0.93  $\text{\AA}$  ( $sp^2$ -hybridized geometry) and included in the refinement, but were restrained to ride on their bonded atoms. The isotropic displacement parameters of the H atoms were held fixed at  $1.2U_{\text{eq}}$  of their riding atoms.  $F_o$  data were collected and all calculations were carried out on an NEC EWS 4800/410 workstation at the Research Centre for Protein Engineering, Institute for Protein Research, Osaka University, Japan.

Data collection: Rigaku AFC-4R software. Cell refinement: Rigaku AFC-4R software. Data reduction: Rigaku AFC-4R software. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1135). Services for accessing these data are described at the back of the journal.

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## Bis[tris(2-aminoethyl)amine]cobalt(II) Bis[tetracarbonylcobaltate(1–)]

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**Abstract**

The title compound,  $[\text{Co}(\text{C}_6\text{H}_{18}\text{N}_4)_2][\text{Co}(\text{CO})_4]_2$ , comprises  $[\text{Co}(\text{N}_4\text{H}_{18}\text{C}_6)_2]^{2+}$  and  $[\text{Co}(\text{CO})_4]^-$  ions. The cation presents a distorted-octahedral arrangement of N atoms around the  $\text{Co}^{\text{II}}$  atom, while in the anion, four CO ligands are coordinated to the  $\text{Co}^{-\text{I}}$  atom in an approximately tetrahedral distribution. The anions and cations are linked in the crystal structure *via* hydrogen bonds of the type  $\text{Co}^{\text{II}}\text{—X—H}\cdots\text{OC—Co}^{-\text{I}}$  ( $\text{X} = \text{N}$  or  $\text{C}$ ), in which both donor and acceptor groups are influenced by the coordination to a metal center.

**Comment**

In recent years, we have been investigating hydrogen-bonding interactions involving organometallic species (Brammer *et al.*, 1991, 1992, 1995; Brammer & Zhao,