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Cyclohexane-Linked Indenyl Rings in 5,8-Bis(trimethylsilyl)-6,7,12b,12c-tetrahydro-indeno[2,1-*c*]fluorene

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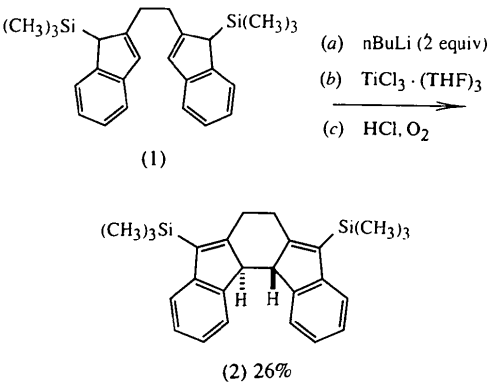
Abstract

A novel ring structure of formula $C_{26}H_{32}Si_2$ has been formed by oxidation of 1,2-bis(1-trimethylsilyl-2-indenyl)ethane during attempted $TiCl_3(thf)_3$ complexation. Two indenyl groups are linked by a cyclohexane ring having a chair conformation and the resulting dihedral angle between the planes of the indenyl groups is 10.6 (1)°.

Comment

ansa-Metallocenes based on Group 4 transition metals have drawn attention because of their role in reactions such as asymmetric hydrogenation (Willoughby & Buchwald, 1994) and asymmetric carbomagnesation (Hoveyda & Morken, 1993). Recently, we reported the synthesis of novel *ansa*-titanocenes based on 1,2-bis(2-indenyl)ethane (Hitchcock, Situ, Covel, Olmstead & Nantz, 1995). In the course of our studies, we encountered an *ansa* ligand, (1), that did not undergo facile $TiCl_3$ complexation. Rather, an unforeseen oxidative coupling process took place resulting in compound (2). This oxidative process was believed to occur as a result of the steric demands of the resident trimethylsilyl groups.



In the title compound, (2), short C1—C20 and C16—C17 bond distances of 1.356 (4) and 1.354 (3) Å, respectively, confirm the presence of indenyl double

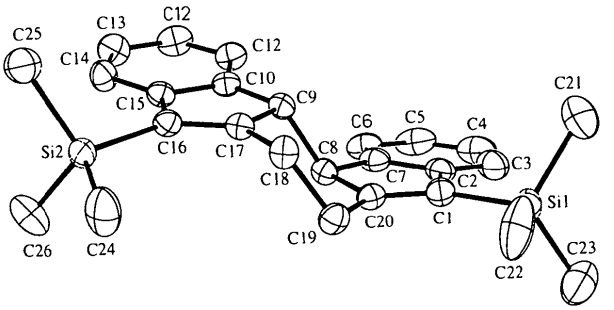


Fig. 1. The molecular structure of the title compound showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

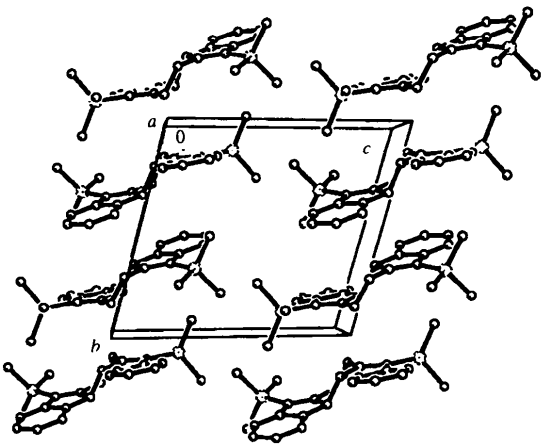


Fig. 2. A packing diagram of (2) showing the alignment of the indenyl rings. Si atoms are displayed as dotted spheres.

bonds, while the uniformity of the C—C bond lengths within the six-membered ring portions of the indenyl groups is in keeping with complete delocalization of the double bonds. The indenyl groups are flat, with mean plane deviations of 0.032 and 0.030 Å and an interplanar angle of 10.6 (1)°. The Si atoms are displaced slightly from their indenyl planes by 0.133 (3) and 0.114 (3) Å for Si1 and Si2, respectively. The connecting cyclohexyl group has a chair conformation, resulting in a chair-like shape for the molecule when viewed from the edge (Fig. 1). The molecular packing fits chairs onto chairs such that all the planar groups are essentially coplanar in the structure (Fig. 2). There are no unusually short intermolecular contacts. Refined C—H distances range from 0.92 (3) to 1.01 (3) Å.

Experimental

Crystal data

$C_{26}H_{32}Si_2$
$M_r = 400.71$
Triclinic
$P\bar{1}$
$a = 10.082\ (2)$ Å
$b = 10.912\ (2)$ Å
$c = 12.228\ (2)$ Å
$\alpha = 98.105\ (15)°$
$\beta = 108.339\ (14)°$
$\gamma = 106.541\ (15)°$
$V = 1184.1\ (4)$ Å^3
$Z = 2$
$D_x = 1.124$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 29 reflections
$\theta = 5.4$–$16.8°$
$\mu = 0.159$ mm^{-1}
$T = 130\ (2)$ K
Needle
0.60 × 0.22 × 0.12 mm
Yellow–orange dichroic

Data collection

Siemens *R3m/V* diffractometer
ω scans
Absorption correction: none
4186 measured reflections
4186 independent reflections
3267 observed reflections [$I > 2\sigma(I)$]

$\theta_{max} = 25.05°$
$h = 0 \rightarrow 12$
$k = -12 \rightarrow 12$
$l = -14 \rightarrow 13$
3 standard reflections monitored every 197 reflections
intensity decay: <0.6%

Refinement

Refinement on F^2
$R(F) = 0.0520$
$wR(F^2) = 0.1357$
$S = 1.034$
4186 reflections
301 parameters
Methyl H atoms treated as rigid groups, others refined; all displacement parameters fixed at 0.045 Å^2

$w = 1/[\sigma^2(F_o^2) + (0.0586P)^2 + 0.8448P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.236$
$\Delta\rho_{max} = 0.380$ e Å^{-3}
$\Delta\rho_{min} = -0.343$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$U_{eq} = (1/3)\sum_i\sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
Si1	−0.35554 (9)	0.31156 (8)	−0.28417 (7)	0.0386 (2)
Si2	0.02340 (8)	0.11531 (7)	0.32065 (6)	0.0286 (2)
C1	−0.1634 (3)	0.3369 (2)	−0.1777 (2)	0.0321 (6)
C2	−0.0275 (3)	0.3816 (2)	−0.2072 (2)	0.0338 (6)
C3	−0.0093 (4)	0.4278 (3)	−0.3038 (3)	0.0454 (8)
C4	0.1336 (5)	0.4722 (3)	−0.3058 (3)	0.0547 (9)
C5	0.2552 (4)	0.4718 (3)	−0.2146 (3)	0.0511 (9)
C6	0.2380 (4)	0.4260 (3)	−0.1175 (3)	0.0409 (7)
C7	0.0965 (3)	0.3796 (2)	−0.1147 (2)	0.0322 (6)
C8	0.0454 (3)	0.3307 (2)	−0.0204 (2)	0.0270 (5)
C9	0.0559 (3)	0.1949 (2)	−0.0008 (2)	0.0263 (5)
C10	0.2078 (3)	0.1929 (2)	0.0674 (2)	0.0275 (5)
C11	0.3312 (3)	0.2068 (3)	0.0362 (3)	0.0339 (6)
C12	0.4582 (3)	0.1966 (3)	0.1164 (3)	0.0407 (7)
C13	0.4609 (3)	0.1700 (3)	0.2232 (3)	0.0402 (7)
C14	0.3366 (3)	0.1523 (3)	0.2537 (3)	0.0344 (6)
C15	0.2099 (3)	0.1645 (2)	0.1760 (2)	0.0262 (5)
C16	0.0606 (3)	0.1439 (2)	0.1835 (2)	0.0258 (5)
C17	−0.0294 (3)	0.1542 (2)	0.0792 (2)	0.0260 (5)
C18	−0.1903 (3)	0.1412 (3)	0.0350 (2)	0.0296 (6)
C19	−0.2051 (3)	0.2710 (3)	0.0079 (3)	0.0323 (6)
C20	−0.1187 (3)	0.3148 (2)	−0.0678 (2)	0.0279 (6)
C21	−0.3898 (5)	0.1933 (4)	−0.4220 (3)	0.0846 (14)
C22	−0.5079 (4)	0.2392 (4)	−0.2306 (4)	0.0730 (12)
C23	−0.3702 (4)	0.4704 (3)	−0.3126 (3)	0.0612 (10)
C24	−0.1585 (4)	0.1242 (4)	0.3187 (3)	0.0534 (9)
C25	0.0299 (5)	−0.0491 (3)	0.3402 (3)	0.0578 (10)
C26	0.1692 (4)	0.2482 (3)	0.4503 (3)	0.0535 (9)

Table 2. *Selected geometric parameters (Å, °)*

Si1—C21	1.842 (4)	C7—C8	1.507 (3)
Si1—C23	1.853 (3)	C8—C20	1.519 (3)
Si1—C22	1.871 (4)	C8—C9	1.562 (3)
Si1—C1	1.879 (3)	C9—C10	1.504 (3)
Si2—C26	1.857 (3)	C9—C17	1.526 (3)
Si2—C24	1.857 (3)	C10—C11	1.387 (4)
Si2—C25	1.860 (3)	C10—C15	1.401 (3)
Si2—C16	1.878 (2)	C11—C12	1.391 (4)
C1—C20	1.356 (4)	C12—C13	1.371 (4)
C1—C2	1.492 (4)	C13—C14	1.387 (4)
C2—C3	1.392 (4)	C14—C15	1.386 (4)
C2—C7	1.405 (4)	C15—C16	1.492 (3)
C3—C4	1.392 (5)	C16—C17	1.354 (3)
C4—C5	1.375 (5)	C17—C18	1.496 (3)
C5—C6	1.391 (4)	C18—C19	1.536 (4)
C6—C7	1.385 (4)	C19—C20	1.497 (4)
C21—Si1—C23	111.5 (2)	C7—C8—C9	117.1 (2)
C21—Si1—C22	107.0 (2)	C20—C8—C9	107.7 (2)
C23—Si1—C22	106.4 (2)	C10—C9—C17	102.4 (2)
C21—Si1—C1	107.0 (2)	C10—C9—C8	117.2 (2)
C23—Si1—C1	110.80 (14)	C17—C9—C8	107.2 (2)
C22—Si1—C1	114.09 (14)	C11—C10—C15	120.3 (2)
C26—Si2—C24	106.3 (2)	C11—C10—C9	130.9 (2)
C26—Si2—C25	110.2 (2)	C15—C10—C9	108.7 (2)
C24—Si2—C25	108.8 (2)	C10—C11—C12	118.8 (3)
C26—Si2—C16	108.01 (13)	C13—C12—C11	120.9 (3)
C24—Si2—C16	113.76 (12)	C12—C13—C14	120.7 (3)
C25—Si2—C16	109.72 (13)	C15—C14—C13	119.3 (3)
C20—C1—C2	106.8 (2)	C14—C15—C10	120.0 (2)
C20—C1—Si1	130.1 (2)	C14—C15—C16	130.3 (2)
C2—C1—Si1	123.0 (2)	C10—C15—C16	109.6 (2)
C3—C2—C7	120.1 (3)	C17—C16—C15	107.1 (2)
C3—C2—C1	130.2 (3)	C17—C16—Si2	130.7 (2)
C7—C2—C1	109.6 (2)	C15—C16—Si2	122.2 (2)
C4—C3—C2	118.5 (3)	C16—C17—C18	131.3 (2)
C5—C4—C3	121.4 (3)	C16—C17—C9	111.8 (2)
C4—C5—C6	120.5 (3)	C18—C17—C9	116.7 (2)
C7—C6—C5	119.0 (3)	C17—C18—C19	109.7 (2)
C6—C7—C2	120.5 (3)	C20—C19—C18	109.8 (2)

C6—C7—C8	130.7 (3)	C1—C20—C19	130.9 (2)
C2—C7—C8	108.7 (2)	C1—C20—C8	112.3 (2)
C7—C8—C20	102.3 (2)	C19—C20—C8	116.8 (2)

Data collection: Siemens *P3* software. Cell refinement: Siemens *P3* software. Data reduction: *XDISK* (Siemens, 1991). Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL XP*. Software used to prepare material for publication: *SHELXTL XCIF*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1209). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Hemiasterlin Methyl Ester†

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Abstract

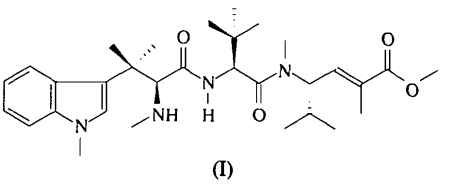
The structure of the tripeptide hemiasterlin methyl ester, $C_{31}H_{48}N_4O_4$, has been determined by X-ray analysis. The absolute configuration is based on the chiralities determined by other methods for two of the three chiral centers. Weak hydrogen bonding influences the solid-state conformation.

† IUPAC name: methyl 2,5-dimethyl-4-{2-[3-methyl-2-methylamino-3-(*N*-methylbenzo[*b*]pyrrol-3-yl)butanamido]-3,3-dimethyl-*N*-methylbutanamido}-2-hexenoate.

Comment

Marine sponges are a rich source of novel peptide metabolites that frequently exhibit potent biological activity (Fusetani & Matsunaga, 1993). We have recently reported the isolation of the tripeptides hemiasterlin, hemiasterlin A and hemiasterlin B, and the tetrapeptides criamide A and criamide B from the sponge *Cymbastela sp.* collected in Papua New Guinea (Coleman, de Silva, Kong, Andersen & Allen, 1996). One of these peptides, hemiasterlin, has been isolated previously from the marine sponge *Hemiasterella minor* collected in South Africa (Talpir, Benayahu, Kashman, Pannell & Schleyer, 1994) and a related compound, milnamide A, has been reported as being isolated from the sponge *Auletta c.f. constricta*, also collected in Papua New Guinea (Crews, Farias, Emrich & Keifer, 1994). The hemiasterlins and criamides exhibit potent *in vitro* inhibition of murine leukemia P388 and human solid-tumor cell lines and show promising *in vivo* activity against murine leukemia P388 in mice (Coleman *et al.*, 1995). Preliminary investigations indicate that the hemiasterlins are antimitotic agents that target cellular tubulin in a manner similar to the cytotoxic mechanisms of the well known anticancer drugs vincristine and taxol (Roberge, Anderson, Coleman & Andersen, 1995).

The cytotoxic properties of the hemiasterlins and criamides make them attractive targets for total synthesis. Any synthetic effort towards these cytotoxic peptides would benefit from knowledge of the absolute configurations of the component amino acids. Degradative analysis carried out as part of the structure elucidation of the hemiasterlins and criamides isolated from *Cymbastela sp.* showed that the *tert*-leucine, valine, *N*-methylhomovinylagous valine and arginine residues in these molecules all had the L configuration (Coleman *et al.*, 1995). Attempts to determine the configuration of the methylated tryptophan residues in the hemiasterlins and criamides by hydrolysis or circular dichorism analysis were unsuccessful. Fortunately, the methyl ester of hemiasterlin, (I), gave crystals suitable for X-ray diffraction analysis.



(I)

The results of this X-ray diffraction analysis, which are presented below, show that the tetramethylated tryptophan residue in hemiasterlin also has the L configuration. The molecular conformation in the solid state is stabilized by one weak hydrogen bond and several C—H···O interactions (Table 2). Two of the intramolecular C—H···O interactions [involving atoms H(34) and