

cis-2,2-Dimethyl-1,3-diphenyl-2,3-dihydro-1H-benzo[c]silole

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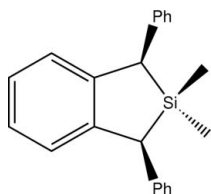
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Key indicators: single-crystal X-ray study; $T = 295$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.045; wR factor = 0.142; data-to-parameter ratio = 15.6.

The title compound, $\text{C}_{22}\text{H}_{22}\text{Si}$, is a benzosilacyclopentene in which the silacyclopentene ring assumes an envelope conformation. The Si atom is displaced by 0.722 (4) Å from the mean plane of the four C atoms, and is bonded to two methyl groups and to two Csp^3 atoms in the silacyclopentene ring. One phenyl ring is attached to each of these two C atoms in a *cis* configuration. The Si atom and the two methyl groups lie on a crystallographic mirror plane which relates the two halves of the molecule. The average Si—C_{methyl} bond distance is 1.852 (3) Å. The Si—C sp^3 bond distance is 1.886 (2) Å, and the corresponding C sp^3 —Si—C sp^3 angle is 93.0 (1)°. The displacement ellipsoids for the atoms in the fused benzene ring suggest a probable disorder, but no satisfactory disorder model could be found.

Related literature

This structure can be compared with one structure in the Cambridge Structural Database [Version 5.28; (Allen, 2002); *ConQuest*, Version 1.9 (Bruno *et al.*, 2002)] having the same fused ring system, 2,2-diphenyl-2-silaindane (Vidal & Falgueirettes, 1973), and with one recently published structure from this laboratory, *cis*-1,2,2,3-tetraphenyl-2,3-dihydro-1H-2-benzosilole (Duong *et al.*, 2006). See also: Bates *et al.* (1981); Mataka *et al.* (1981); Sato *et al.* (2001).



Experimental

Crystal data

$\text{C}_{22}\text{H}_{22}\text{Si}$	$V = 1837.6$ (4) Å ³
$M_r = 314.49$	$Z = 4$
Orthorhombic, <i>Pcmm</i>	Cu $K\alpha$ radiation
$a = 6.6298$ (7) Å	$\mu = 1.08$ mm ⁻¹
$b = 14.6001$ (18) Å	$T = 295$ (2) K
$c = 18.984$ (3) Å	$0.44 \times 0.37 \times 0.12$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer	1720 independent reflections
Absorption correction: analytical (Alcock, 1970)	1310 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.667$, $T_{\max} = 0.875$	3 standard reflections
1720 measured reflections	frequency: 60 min
	intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$	110 parameters
$wR(F^2) = 0.142$	H-atom parameters constrained
$S = 1.05$	$\Delta\rho_{\max} = 0.29$ e Å ⁻³
1720 reflections	$\Delta\rho_{\min} = -0.18$ e Å ⁻³

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2035).

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supplementary materials

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***cis*-2,2-Dimethyl-1,3-diphenyl-2,3-dihydro-1*H*-benzo[*c*]silole**

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Comment

The Si atom is bonded to two methyl groups and to two Csp^3 atoms in the silacyclopentene ring; one phenyl ring is attached to each of these two Csp^3 atoms in the *cis* configuration. The Si atom and the carbon atoms of the two methyl groups lie in a crystallographic mirror plane which relates the two halves of the structure. The average Si-methyl bond distance is 1.852 (3) Å. The Si— Csp^3 bond distance is 1.886 (2) Å, and the corresponding Csp^3 —Si— Csp^3 angle is 93.0 (1) °. The silacyclopentene ring assumes an envelope conformation, with the Si atom displaced 0.722 (4) Å from the mean plane of the four carbon atoms.

This structure can be compared to one structure in the Cambridge Structural Database (Version 5.28, ConQuest Version 1.9; Allen, 2002) having the same fused ring system, 2,2-Diphenyl-2-sila-indan (Vidal & Falgueirettes, 1973) and to one recently published structure from this laboratory, *cis*-1,2,2,3-tetraphenyl-2,3-dihydro-1*H*-benzo[*c*]silole (Duong *et al.*, 2006).

The 2,2-diphenyl-2-sila-indan has hydrogen atoms on the silacyclopentene ring where the title structure has phenyl rings, and has phenyl rings on the Si where the title structure has methyl groups. The average Si— Csp^3 distance is 1.886 Å, and the corresponding Csp^3 —Si— Csp^3 angle is 93.59°. The silacyclopentene ring assumes an envelope conformation, with the Si atom displaced 0.636 Å from the mean plane of the four carbon atoms.

The *cis*-1,2,2,3-tetraphenyl-2,3-dihydro-1*H*-benzo[*c*]silole has phenyl rings on the Si atom, where the title structure has methyl groups. The average Si— Csp^3 distance is 1.902 (2) Å, and the corresponding Csp^3 —Si— Csp^3 angle is 90.68 (7) Å. The silacyclopentene ring assumes an envelope conformation, with the Si atom displaced 0.953 (2) Å from the mean plane of the four carbon atoms.

Experimental

Compound (3) was prepared in a model reaction for the preparation of new phosphine ligands of similar structure *via* dicarbanions (Bates *et al.*, 1981). The two-step synthesis is outlined below.

The first step prepares the carbon diacid, (1), by Friedel–Crafts alkylation of benzene with α,α' -dichloro-*o*-xylene (Mataka *et al.*, 1981). The carbon acid is bislithiated using two equivalents of *n*-butyl lithium and tetramethylethylenediamine (TMEDA) to give the deep-red dicarbanion, (2) (Sato *et al.*, 2001), which, upon reaction with diphenyldichlorosilane, gives the title compound, (3). The major isomer is the crystalline *cis*-isomer. The compound has been also characterized by both 1H and ^{13}C NMR spectroscopy.

Compound (1), the precursor to the title compound, was prepared by charging a dry 250 ml two-necked round-bottomed flask, equipped with a stirrer bar, a reflux condenser and a gas inlet adapter, with α,α' -dichloro-*o*-xylene (50 mmol, 8.75 g), dry benzene (100 ml) and nitromethane (10 ml) under N_2 . Subsequently, $AlCl_3$ (20.0 g, 150 mmol) was added to the flask.

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The nitrogen line was removed and replaced with a drying tube, and the mixture was allowed to react for 30 min without external heating. External heat was then applied and the mixture was refluxed overnight. The reaction was then quenched with water and the phases separated. The organic layer was dried with Na₂SO₄. After solvent removal under a vacuum, the residue was purified by bulb–bulb distillation (393 K, 1 Pa). Further purification was accomplished by recrystallization from isooctane (11.2 g, 87% yield; m.p. 346–347 K).

For the preparation of (3), compound (1) (0.52 g, 2.0 mmol) was placed in an oven-dried vial equipped with a stirrer bar. After purging with N₂, a septum was attached. Dry degassed Et₂O (15 ml) was introduced via syringe. A positive pressure of N₂ gas was maintained as the vial was cooled to 273 K, and TMEDA (0.51 g, 4.4 mmol) followed by n-BuLi (1.61 ml, 2.74 M, solvent = hexanes, 4.4 mmol) were introduced *via* syringe. A deep-red color was observed almost immediately upon addition of the n-BuLi. The reaction was quenched after 30 min with dichlorodimethylsilane (0.28 g, 2.2 mmol). Saturated aqueous NH₄Cl was added 30 min later. The organic layer was separated and dried with Na₂SO₄. It was then reduced under vacuum and purified by bulb–bulb distillation (433 K, 1 Pa) to give 0.82 g of (3) (94% yield; m.p. 375–376 K). X-ray quality crystals of (3) were obtained by recrystallization from iso-octane.

Refinement

H atoms were constrained using a riding model. The aromatic C—H bond lengths were fixed at 0.93 Å, the methine C—H bond lengths at 0.98 Å, and the methyl C—H bond lengths at 0.96 Å, with $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{C})$. The orientation of the methyl groups was fixed by the location of the methyl carbons on a crystallographic mirror plane. The thermal ellipsoids for the atoms in the fused aromatic ring suggest a probable disorder, but no satisfactory disorder model could be found. Attempts to refine the structure in the equivalent non-centrosymmetric space group Pc2₁n gave results that were neither chemically nor crystallographically reasonable.

Figures

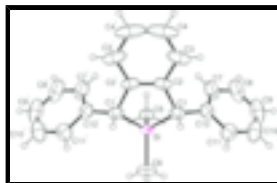


Fig. 1. View of (3) (30% probability displacement ellipsoids)

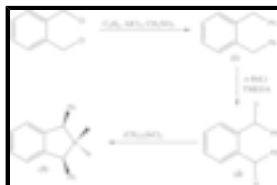


Fig. 2. The reaction scheme for the formation of (3)

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Crystal data

C₂₂H₂₂Si

$M_r = 314.49$

Orthorhombic, *Pcmm*

$F_{000} = 672$

$D_x = 1.137 \text{ Mg m}^{-3}$

Cu $K\alpha$ radiation

Hall symbol: -P 2n 2ac
 $a = 6.6298 (7) \text{ \AA}$
 $b = 14.6001 (18) \text{ \AA}$
 $c = 18.984 (3) \text{ \AA}$
 $V = 1837.6 (4) \text{ \AA}^3$
 $Z = 4$

$\lambda = 1.54184 \text{ \AA}$
 Cell parameters from 20 reflections
 $\theta = 11.5\text{--}18.5^\circ$
 $\mu = 1.08 \text{ mm}^{-1}$
 $T = 295 (2) \text{ K}$
 Prism, colorless
 $0.44 \times 0.37 \times 0.12 \text{ mm}$

Data collection

Enraf–Nonius CAD-4
 diffractometer
 non-profiled $\omega/2\theta$ scans
 Absorption correction: analytical
 (Alcock, 1970)
 $T_{\min} = 0.667, T_{\max} = 0.875$
 1720 measured reflections
 1720 independent reflections
 1310 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0$

$\theta_{\max} = 67.4^\circ$
 $\theta_{\min} = 4.7^\circ$
 $h = -7 \rightarrow 0$
 $k = -17 \rightarrow 0$
 $l = -22 \rightarrow 0$
 3 standard reflections
 every 60 min
 intensity decay: none

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.045$
 $wR(F^2) = 0.142$
 $S = 1.05$
 1720 reflections
 110 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0863P)^2 + 0.3313P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.29 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.18 \text{ e \AA}^{-3}$
 Extinction correction: SHELXL97,
 $F_c^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.0026 (6)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Si	1.00957 (10)	0.25	0.13620 (4)	0.0515 (3)	
C5	0.8661 (4)	0.25	0.21997 (15)	0.0645 (8)	
H5A	0.7241	0.25	0.21	0.097*	
H5B	0.8999	0.3037	0.2467	0.097*	0.5
H5C	0.8999	0.1963	0.2467	0.097*	0.5
C2	0.7492 (3)	0.20189 (16)	0.03756 (10)	0.0672 (6)	
C3	0.5952 (4)	0.1549 (3)	0.00241 (12)	0.1027 (11)	
H3	0.5936	0.0912	0.0022	0.123*	
C11	1.0430 (5)	-0.00202 (19)	0.10173 (13)	0.0865 (8)	
H11	1.1573	0.0101	0.0749	0.104*	
C1	0.9257 (3)	0.15629 (15)	0.07440 (10)	0.0622 (5)	
H1	1.0325	0.1493	0.0391	0.075*	

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C6	1.2841 (4)	0.25	0.15403 (18)	0.0797 (10)	
H6A	1.3565	0.25	0.1102	0.12*	
H6B	1.3191	0.1963	0.1806	0.12*	0.5
H6C	1.3191	0.3037	0.1806	0.12*	0.5
C12	0.8956 (4)	0.06378 (16)	0.10762 (11)	0.0712 (6)	
C8	0.7113 (7)	-0.0404 (2)	0.18266 (18)	0.1241 (14)	
H8	0.5994	-0.0529	0.2106	0.149*	
C9	0.8601 (8)	-0.1040 (2)	0.17542 (16)	0.1250 (15)	
H9	0.8491	-0.1602	0.1983	0.15*	
C7	0.7269 (5)	0.04360 (18)	0.14819 (16)	0.0995 (10)	
H7	0.6237	0.0864	0.1524	0.119*	
C10	1.0243 (6)	-0.0860 (2)	0.13505 (16)	0.1103 (12)	
H10	1.1244	-0.13	0.1298	0.132*	
C4	0.4468 (4)	0.2028 (3)	-0.03172 (13)	0.145 (2)	
H4	0.345	0.1712	-0.0551	0.174*	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Si	0.0357 (4)	0.0655 (5)	0.0534 (4)	0	0.0025 (3)	0
C5	0.0529 (16)	0.0787 (19)	0.0620 (16)	0	0.0082 (13)	0
C2	0.0436 (10)	0.1097 (15)	0.0484 (9)	-0.0059 (10)	0.0059 (8)	-0.0133 (10)
C3	0.0616 (14)	0.178 (3)	0.0687 (14)	-0.0240 (18)	0.0050 (12)	-0.0470 (17)
C11	0.100 (2)	0.0879 (17)	0.0718 (15)	0.0113 (15)	0.0050 (13)	-0.0105 (13)
C1	0.0487 (10)	0.0772 (13)	0.0607 (11)	-0.0013 (10)	0.0120 (8)	-0.0116 (10)
C6	0.0421 (15)	0.129 (3)	0.0677 (18)	0	-0.0002 (13)	0
C12	0.0781 (14)	0.0706 (13)	0.0648 (12)	-0.0078 (11)	0.0143 (11)	-0.0193 (10)
C8	0.175 (4)	0.0878 (19)	0.109 (2)	-0.052 (2)	0.050 (2)	-0.0214 (17)
C9	0.224 (5)	0.0742 (17)	0.0771 (17)	-0.025 (2)	0.005 (2)	-0.0094 (15)
C7	0.110 (2)	0.0760 (15)	0.113 (2)	-0.0233 (15)	0.0435 (18)	-0.0219 (15)
C10	0.165 (4)	0.0845 (19)	0.0815 (18)	0.020 (2)	-0.008 (2)	-0.0071 (15)
C4	0.0609 (14)	0.314 (8)	0.0594 (13)	-0.028 (2)	-0.0092 (10)	-0.036 (2)

Geometric parameters (\AA , $^\circ$)

Si—C6	1.851 (3)	C1—C12	1.504 (3)
Si—C5	1.853 (3)	C1—H1	0.98
Si—C1	1.886 (2)	C6—H6A	0.96
Si—C1 ⁱ	1.886 (2)	C6—H6B	0.96
C5—H5A	0.96	C6—H6C	0.96
C5—H5B	0.96	C12—C7	1.390 (3)
C5—H5C	0.96	C8—C9	1.362 (5)
C2—C3	1.400 (3)	C8—C7	1.394 (4)
C2—C2 ⁱ	1.405 (5)	C8—H8	0.93
C2—C1	1.517 (3)	C9—C10	1.357 (5)
C3—C4	1.370 (5)	C9—H9	0.93
C3—H3	0.93	C7—H7	0.93
C11—C12	1.375 (3)	C10—H10	0.93

C11—C10	1.385 (4)	C4—C4 ⁱ	1.380 (9)
C11—H11	0.93	C4—H4	0.93
C6—Si—C5	110.35 (15)	Si—C1—H1	106.7
C6—Si—C1	113.80 (9)	Si—C6—H6A	109.5
C5—Si—C1	112.48 (9)	Si—C6—H6B	109.5
C6—Si—C1 ⁱ	113.80 (9)	H6A—C6—H6B	109.5
C5—Si—C1 ⁱ	112.48 (9)	Si—C6—H6C	109.5
C1—Si—C1 ⁱ	93.00 (14)	H6A—C6—H6C	109.5
Si—C5—H5A	109.5	H6B—C6—H6C	109.5
Si—C5—H5B	109.5	C11—C12—C7	118.0 (2)
H5A—C5—H5B	109.5	C11—C12—C1	120.0 (2)
Si—C5—H5C	109.5	C7—C12—C1	122.0 (2)
H5A—C5—H5C	109.5	C9—C8—C7	119.9 (3)
H5B—C5—H5C	109.5	C9—C8—H8	120
C3—C2—C2 ⁱ	119.36 (19)	C7—C8—H8	120
C3—C2—C1	124.6 (3)	C10—C9—C8	120.3 (3)
C2 ⁱ —C2—C1	116.03 (12)	C10—C9—H9	119.8
C4—C3—C2	120.0 (4)	C8—C9—H9	119.8
C4—C3—H3	120	C12—C7—C8	120.4 (3)
C2—C3—H3	120	C12—C7—H7	119.8
C12—C11—C10	121.2 (3)	C8—C7—H7	119.8
C12—C11—H11	119.4	C9—C10—C11	120.1 (3)
C10—C11—H11	119.4	C9—C10—H10	119.9
C12—C1—C2	119.02 (18)	C11—C10—H10	119.9
C12—C1—Si	115.46 (14)	C3—C4—C4 ⁱ	120.7 (2)
C2—C1—Si	101.29 (14)	C3—C4—H4	119.7
C12—C1—H1	106.7	C4 ⁱ —C4—H4	119.7
C2—C1—H1	106.7		

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

Fig. 1

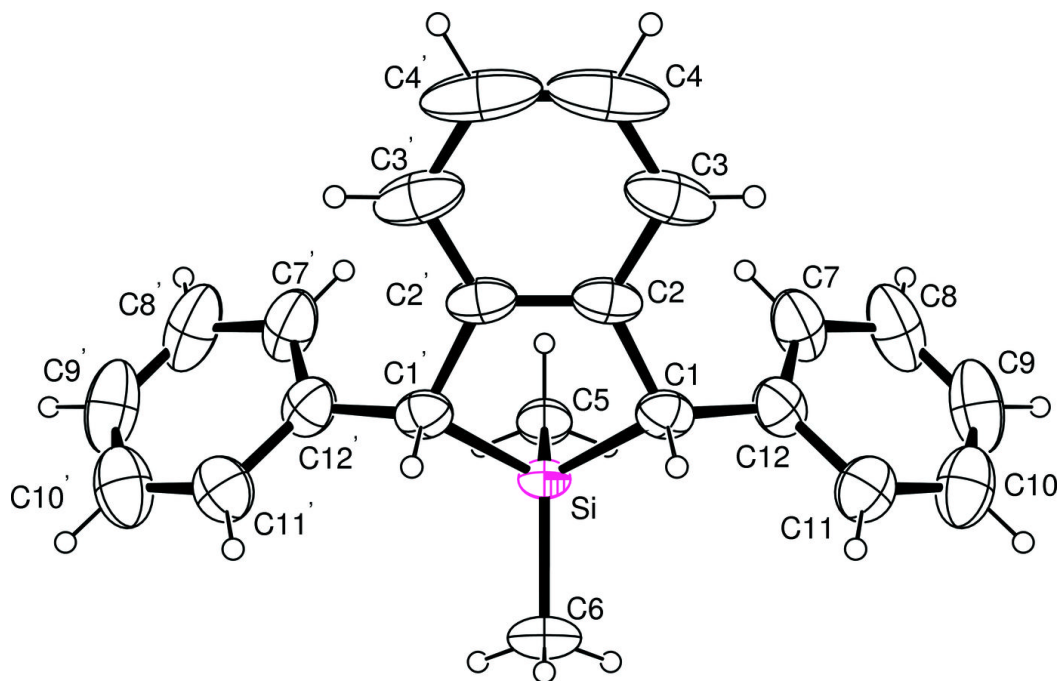


Fig. 2

