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13,13-Dimethyl-1,10-diphenyl-13-silatricyclo[8.2.1.$0^{2,9}$]trideca-2(9),11-diene, $C_{26}H_{30}Si$ (I), and 1,4-Dihydro-9,9-dimethyl-1,4-diphenyl-1,4-silanonaphthalene, $C_{24}H_{22}Si$ (II)

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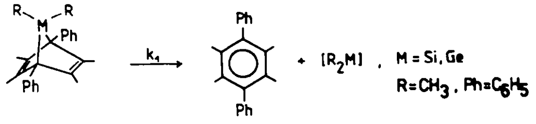
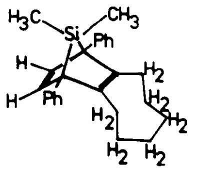
Abstract. (I), $M_r = 370{\cdot}6$, orthorhombic, *Pnma*, $a = 18{\cdot}825$ (15), $b = 15{\cdot}797$ (15), $c = 7{\cdot}219$ (5) Å, $U = 2147$ Å^3, $Z = 4$, $D_x = 1{\cdot}147$ Mg m^{-3}, $F(000) = 800$, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}105$ mm^{-1}, $T = 294$ (1) K. Final $R = 0{\cdot}087$ for 1535 unique X-ray diffractometer data [$F_o > 3\sigma(F_o)$]. Parts of the molecule show severe disorder in the crystal. (II), $M_r = 338{\cdot}5$, monoclinic, $C2/c$, $a = 13{\cdot}613$ (4), $b = 18{\cdot}900$ (4), $c = 16{\cdot}084$ (6) Å, $\beta = 114{\cdot}14$ (9)°, $U = 3776{\cdot}3$ Å^3, $Z = 8$, $D_x = 1{\cdot}191$ Mg m^{-3}, $F(000) = 1440$, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}109$ mm^{-1}, $T = 294$ (1) K. Final $R = 0{\cdot}071$ for 2402 unique diffractometer data [$F_o > 3\sigma(F_o)$]. The molecular structures have been elucidated.

Introduction. 7-Heterobicyclo[2.2.1]hept(adi)enes, hetero = R_2Si (Gilman, Cottis & Atwell, 1964), R_2Ge (Neumann & Schriewer, 1980), and R_2Sn (Neumann, Grugel & Schriewer, 1979), have been found to be, *via* a cycloelimination, thermal sources for the heavy carbene analogues, the silylenes R_2Si, germylenes R_2Ge, and stannylenes R_2Sn. These species have received growing interest during recent years. In the case of the Si and Ge derivatives we have found a strong dependence of the rate of the cycloelimination k_1 on the pattern of substitution around the basic ring:

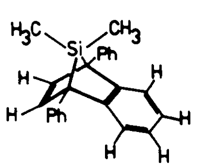


If the rotation of the two phenyl groups in 1,4-positions is unhindered and, therefore, a (nearly) coplanar conformation with the basic ring is possible, the stability of the strained bicyclic system is decreased, and k_1 is increased, *e.g.* for M = Si (Mayer & Neumann, 1980; Mayer, 1982).

We therefore chose the two R_2Si derivatives with the highest k_1 values for X-ray analysis, the Diels–Alder adducts of cyclooctyne (I) and of benzyne (II) to 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene (Mayer, 1982),* in order to elucidate whether the coplanar conformation mentioned above is possible, and to determine the bond lengths and angles of the strained C—Si—C bridge. Both molecules (I) and (II) are identified unequivocally by elemental analysis, ^{1}H NMR, ^{13}C NMR, and mass spectroscopy.



(I)



(II)

The present X-ray analysis is the first for this type of Si compound.*

Experimental. (I) has been recrystallized from *n*-hexane, then dissolved in refluxing *n*-nonane. The solution was allowed to stand for several days at room temperature giving appropriate colourless crystals. (II) has been obtained by recrystallization from CH_2Cl_2/MeOH (1:1). Data collection: crystal size $0{\cdot}78 \times 0{\cdot}43 \times 0{\cdot}33$mm (I), $0{\cdot}49 \times 0{\cdot}66 \times 0{\cdot}55$mm (II), $\omega/2\theta$ scans, scan speed 0·6° min^{-1} for (I) on a Hilger & Watts diffractometer, scan speed 3·33°–0·80° min^{-1} for (II) on a Nonius CAD-4, graphite-monochromated Mo $K\alpha$ radiation, lattice parameters: least-squares fit with 16 reflexions ($5{\cdot}6° \le \theta \le 15{\cdot}4°$) (I) and 25 reflexions ($6{\cdot}4° \le \theta \le 19{\cdot}3°$) (II); four standard reflexions every 2 h (I) and three standard reflexions every 2 h (II), only random deviations; 3024 reflexions ($1° \le \theta \le 25°$, $-1 \le h \le 9$, $-1 \le k \le 19$, $-1 \le l \le 22$) (I), 3671 reflexions ($1° \le \theta \le 25°$, $\pm h$, $+k$, $+l$) (II), after averaging 1535 (I) and 2404 (II) observed reflexions [$F_o > 3\sigma(F_o)$], Lorentz and polarization correction, no absorption correction; systematic absences: $0kl$ $k+l = 2n+1$ and $hk0$ $h = 2n+1$ for (I) conform to *Pnma* and $Pn2_1a$ and hkl $h+k = 2n+1$, $h0l$ $h = 2n+1$ and $l = 2n+1$ for (II) conform to $C2/c$ and Cc; structure solution in the centrosymmetric space groups *via* Patterson function and subsequent Fourier syntheses, full-matrix least-squares refinement (on F),

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* Earlier, (II) was reported to be unstable at room temperature (Barton, Nelson & Clardy, 1972). Meanwhile, (II) has been prepared independently by Sakurai, Sakaba & Nakadaira (1982).

* Former efforts with other derivatives of this type failed because of twin formation (Barton, Goure, Witiak & Wulff, 1982).

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unit weights, 138 (I) and 204 (II) refined parameters, $R = 0{\cdot}087$ (I) and 0·071 (II),* all non-H atoms anisotropic, complex neutral-atom scattering factors: Cromer & Liberman (1970), Cromer & Mann (1968), Cromer (1976, personal communication to G. M. Sheldrick), programs: *SHELX* (Sheldrick, 1976) *ORTEP*II (Johnson, 1976), *POP*1 (van de Waal, 1976), maximum/mean shift over error for all parameters during last refinement 0·7/0·06 (I) and 0·5/0·1 (II). All non-hydrogen atoms in (I) and (II) were refined independently except for the two phenyl rings in (II) which were refined as rigid bodies (C—C 1·395 Å, C—C—C 120°). H atoms were placed in geometrically calculated positions (C—H 1·08 Å, H—C—H 109·5°, C—C—H angles equal) and allowed to ride on the atoms to which they are attached. A common temperature factor for the H atoms in (I) refined to $U = 0{\cdot}137\,(9)$ Å^2. For the H atoms of the phenyl rings in (II) a common temperature factor refined to $U = 0{\cdot}084\,(5)$ Å^2 and for the remaining H atoms to $U = 0{\cdot}091\,(5)$ Å^2. The positions C(7), C(8) and C(9) in the disordered part of (I) were treated as normal C atoms during the refinement. Final ΔF syntheses showed maximum peak heights of 0·04 e Å^{-3} around Si in (I) and 0·2 e Å^{-3} in (II). No corrections for secondary extinction.

Discussion. The structures of the two title compounds are shown in Figs. 1 and 3 and stereoviews in Figs. 2 and 4. Positional parameters, equivalent values $B_{\rm eq}$ of the anisotropic temperature factors β_{ik} and anisotropic temperature factors for the disordered positions C(7), C(8) and C(9) of compound (I) are given in Table 1 and bond lengths and angles in Table 2. The asymmetric unit of compound (I) contains one half of the molecule and the molecule is halved by a mirror plane. Interestingly the angle C(4)—Si—C(4$^{\rm i}$) is very small [81·7 (2)°] and the bond lengths are in the normal range. Because of disorder only four atoms of the eight-membered ring could be located. Compound (II) contains one molecule in the asymmetric unit and the molecule has no symmetry. The molecular geometry of (II) deviates in the comparable parts of the molecule significantly from compound (I). In compound (I) the dihedral angle between the plane through a phenyl ring and the plane through the positions C(3), C(3$^{\rm i}$), C(5) and C(5$^{\rm i}$) is 29·0 (1)° whereas in compound (II) the dihedral angles between the planes through the phenyl rings with the atoms C(13) to C(18) and C(19) to C(24) and the plane through the positions C(4), C(5), C(7) and C(8) are 72·3 (1) and 20·8 (1)°, respectively. In each compound at least one phenyl ring deviates less than 30° from coplanarity. Because of steric hindrance this conformation is impossible in other hitherto existing much more stable compounds of this type (Mayer & Neumann, 1980) and our interpretation that this property is important for the thermal stability of these compounds is confirmed.

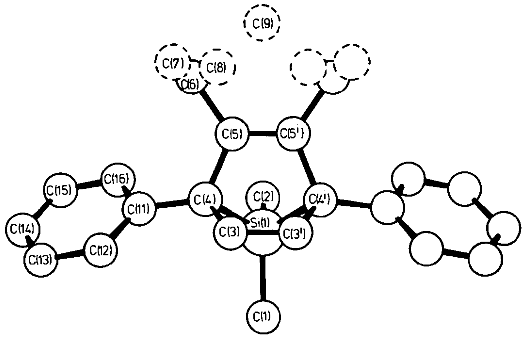

Fig. 1. General view of $C_{26}H_{30}Si$. Because of disorder the eight-membered ring could not be determined completely. The dotted circles show disordered positions. Symmetry code: (i) x, $\frac{1}{2}-y$, z.

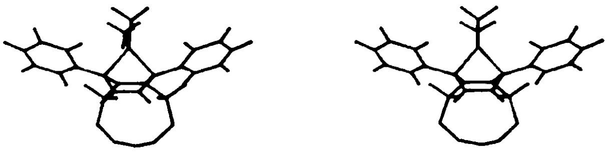

Fig. 2. Stereoscopic view of $C_{26}H_{30}Si$.

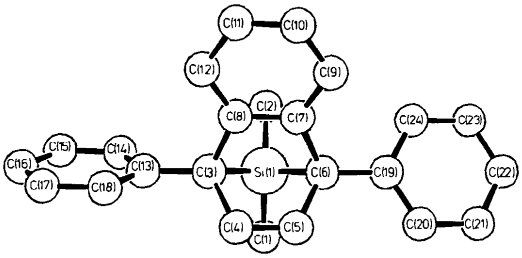

Fig. 3. General view of $C_{24}H_{22}Si$.

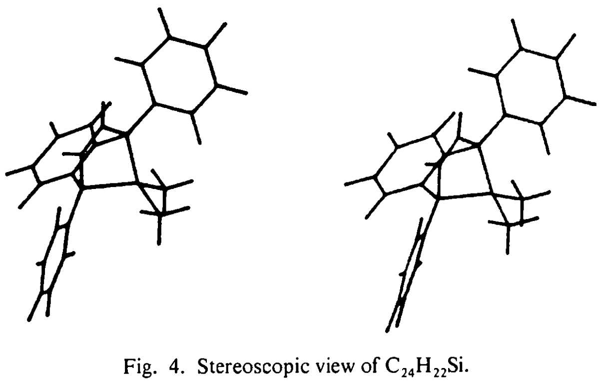

Fig. 4. Stereoscopic view of $C_{24}H_{22}Si$.

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* Lists of structure factors, thermal parameters and a complete list of atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38534 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates and* B_{eq} (Å^2) *for* $C_{26}H_{30}Si$ (I) *and* $C_{24}H_{22}Si$ (II) $\{B_{eq} = \frac{4}{3}(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{13}ac\cos\beta)\}$

Compound (I)

	x	y	z	B_{eq}
Si(1)	0·1758 (1)	0·25	0·1202 (3)	2·81 (4)
C(1)	0·2063 (5)	0·25	−0·128 (1)	4·0 (2)
C(2)	0·2551 (4)	0·25	0·274 (1)	4·1 (2)
C(3)	0·0484 (3)	0·2933 (4)	0·0451 (7)	3·1 (1)
C(4)	0·1025 (3)	0·3290 (4)	0·1782 (7)	2·8 (1)
C(5)	0·0849 (3)	0·2923 (4)	0·3707 (7)	2·8 (1)
C(6)	0·0580 (3)	0·3466 (4)	0·5270 (7)	3·6 (1)
C(7)	−0·0198 (4)	0·3687 (7)	0·509 (1)	7·4 (3)
C(8)	−0·0682 (7)	0·1892 (8)	0·458 (2)	12·8 (5)
C(9)	−0·0693 (7)	0·25	0·586 (2)	6·2 (3)
C(11)	0·1226 (3)	0·4210 (4)	0·1629 (8)	3·2 (1)
C(12)	0·0975 (3)	0·4724 (4)	0·0218 (9)	4·0 (1)
C(13)	0·1219 (4)	0·5553 (4)	0·005 (1)	4·9 (2)
C(14)	0·1714 (4)	0·5870 (4)	0·127 (1)	5·0 (2)
C(15)	0·1970 (4)	0·5365 (4)	0·268 (1)	4·9 (2)
C(16)	0·1731 (4)	0·4545 (4)	0·2848 (9)	4·1 (1)

$\beta_{ik}\times 10^3$ $\{\exp[-(\beta_{11}h^2+\cdots+\beta_{23}kl)]\}$ for the positions in the disordered part of the molecule $C_{26}H_{30}Si$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(7)	3·4 (3)	12·2 (8)	24 (2)	2·9 (8)	1 (1)	16 (2)
C(8)	7·6 (6)	12 (1)	72 (6)	−6 (1)	−15 (3)	18 (4)
C(9)	3·5 (4)	10·4 (9)	16 (2)	0	−3 (2)	0

Compound (II)

	x	y	z	B_{eq}
Si(1)	0·23846 (9)	0·09379 (7)	0·16898 (8)	3·44 (3)
C(1)	0·3651 (4)	0·0763 (3)	0·2719 (3)	4·7 (1)
C(2)	0·1227 (4)	0·0470 (3)	0·1777 (4)	5·0 (2)
C(3)	0·2156 (3)	0·1907 (2)	0·1311 (3)	3·4 (1)
C(4)	0·3181 (3)	0·1961 (2)	0·1124 (3)	3·7 (1)
C(5)	0·3366 (3)	0·1386 (3)	0·0734 (3)	3·8 (1)
C(6)	0·2513 (3)	0·0821 (2)	0·0534 (3)	3·4 (1)
C(7)	0·1434 (3)	0·1182 (2)	−0·0061 (3)	3·4 (1)
C(8)	0·1234 (3)	0·1771 (2)	0·0361 (3)	3·4 (1)
C(9)	0·0732 (3)	0·1007 (3)	−0·0946 (3)	3·9 (1)
C(10)	−0·0185 (4)	0·1422 (3)	−0·1370 (3)	4·5 (1)
C(11)	−0·0407 (4)	0·1979 (3)	−0·0943 (3)	4·6 (1)
C(12)	0·0302 (3)	0·2172 (3)	−0·0052 (3)	3·9 (1)
C(13)	0·1954 (3)	0·2502 (2)	0·1833 (2)	3·7 (1)
C(14)	0·1597 (3)	0·2362 (2)	0·2516 (2)	4·8 (2)
C(15)	0·1383 (3)	0·2920 (2)	0·2985 (2)	6·2 (2)
C(16)	0·1526 (3)	0·3617 (2)	0·2772 (2)	5·8 (2)
C(17)	0·1882 (3)	0·3757 (2)	0·2090 (2)	5·6 (2)
C(18)	0·2096 (3)	0·3199 (2)	0·1620 (2)	4·8 (1)
C(19)	0·2714 (2)	0·0081 (2)	0·0282 (2)	3·7 (1)
C(20)	0·3739 (2)	−0·0113 (2)	0·0367 (2)	4·4 (1)
C(21)	0·3927 (2)	−0·0799 (2)	0·0147 (2)	5·3 (2)
C(22)	0·3090 (2)	−0·1291 (2)	−0·0159 (2)	5·2 (2)
C(23)	0·2064 (2)	−0·1096 (2)	−0·0245 (2)	5·2 (2)
C(24)	0·1876 (2)	−0·0410 (2)	−0·0025 (2)	4·7 (1)

Table 2. *Bond lengths* (Å) *and angles* (°) *for crystals* (I) *and* (II)

Compound (I)

Si(1)–C(1)	1·885 (9)	C(5)–C(6)	1·505 (8)
Si(1)–C(2)	1·862 (9)	C(11)–C(12)	1·385 (8)
Si(1)–C(4)	1·907 (5)	C(12)–C(13)	1·392 (9)
C(3)–C(3$^{\mathrm{i}}$)	1·369 (8)	C(13)–C(14)	1·377 (10)
C(3)–C(4)	1·509 (7)	C(14)–C(15)	1·379 (10)
C(4)–C(5)	1·542 (7)	C(15)–C(16)	1·378 (9)
C(4)–C(11)	1·506 (8)	C(16)–C(11)	1·399 (9)
C(5)–C(5$^{\mathrm{i}}$)	1·335 (11)		
C(1)–Si(1)–C(2)	108·9 (4)	C(4)–C(5)–C(5$^{\mathrm{i}}$)	112·1 (4)
C(1)–Si(1)–C(4)	115·4 (3)	C(4)–C(5)–C(6)	122·3 (5)
C(2)–Si(1)–C(4)	116·7 (3)	C(6)–C(5)–C(5$^{\mathrm{i}}$)	124·7 (5)
C(4)–Si(1)–C(4$^{\mathrm{i}}$)	81·7 (2)	C(4)–C(11)–C(12)	122·3 (5)
Si(1)–C(4)–C(3)	96·0 (3)	C(4)–C(11)–C(16)	119·3 (5)
Si(1)–C(4)–C(5)	96·2 (3)	C(12)–C(11)–C(16)	118·2 (6)
Si(1)–C(4)–C(11)	115·7 (4)	C(11)–C(12)–C(13)	120·2 (6)
C(3)–C(4)–C(11)	118·9 (5)	C(12)–C(13)–C(14)	120·7 (7)
C(3)–C(4)–C(5)	106·7 (4)	C(13)–C(14)–C(15)	119·8 (7)
C(5)–C(4)–C(11)	118·9 (4)	C(14)–C(15)–C(16)	119·7 (7)
C(4)–C(3)–C(3$^{\mathrm{i}}$)	111·9 (5)	C(15)–C(16)–C(11)	121·5 (6)

Compound (II)

Si(1)–C(1)	1·868 (4)	C(6)–C(7)	1·546 (5)
Si(1)–C(2)	1·862 (6)	C(6)–C(19)	1·511 (5)
Si(1)–C(3)	1·916 (4)	C(7)–C(8)	1·387 (7)
Si(1)–C(6)	1·950 (5)	C(7)–C(9)	1·391 (5)
C(3)–C(4)	1·545 (7)	C(9)–C(10)	1·393 (6)
C(3)–C(8)	1·552 (5)	C(10)–C(11)	1·357 (8)
C(3)–C(13)	1·494 (6)	C(11)–C(12)	1·410 (6)
C(4)–C(5)	1·329 (7)	C(12)–C(8)	1·392 (6)
C(5)–C(6)	1·513 (6)		
C(1)–Si(1)–C(2)	110·6 (2)	C(5)–C(6)–C(7)	105·8 (3)
C(1)–Si(1)–C(3)	115·0 (2)	C(5)–C(6)–C(19)	120·2 (4)
C(1)–Si(1)–C(6)	114·5 (2)	C(7)–C(6)–C(19)	118·2 (3)
C(2)–Si(1)–C(3)	116·5 (2)	C(6)–C(7)–C(8)	112·2 (3)
C(2)–Si(1)–C(6)	115·2 (2)	C(6)–C(7)–C(9)	127·5 (4)
C(3)–Si(1)–C(6)	82·6 (2)	C(8)–C(7)–C(9)	120·1 (4)
Si(1)–C(3)–C(4)	94·8 (3)	C(3)–C(8)–C(7)	112·0 (3)
Si(1)–C(3)–C(8)	96·6 (3)	C(3)–C(8)–C(12)	126·3 (4)
Si(1)–C(3)–C(13)	125·7 (3)	C(7)–C(8)–C(12)	121·8 (4)
C(4)–C(3)–C(8)	104·5 (4)	C(7)–C(9)–C(10)	118·0 (4)
C(4)–C(3)–C(13)	116·7 (3)	C(9)–C(10)–C(11)	122·0 (4)
C(8)–C(3)–C(13)	114·7 (3)	C(10)–C(11)–C(12)	120·9 (4)
C(3)–C(4)–C(5)	113·5 (4)	C(11)–C(12)–C(8)	117·1 (4)
C(4)–C(5)–C(6)	113·6 (5)	C(3)–C(13)–C(14)	120·3 (3)
Si(1)–C(6)–C(5)	94·4 (3)	C(3)–C(13)–C(18)	119·7 (4)
Si(1)–C(6)–C(7)	96·2 (3)	C(6)–C(19)–C(20)	120·0 (3)
Si(1)–C(6)–C(19)	117·2 (3)	C(6)–C(19)–C(24)	119·9 (3)

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