Crystal structure of 1,1,4,4-tetramethyl-2,2,3,3-tetraphenyl-tetrasilane, $[(CH_3)_2(H)Si(C_6H_5)_2Si]_2$

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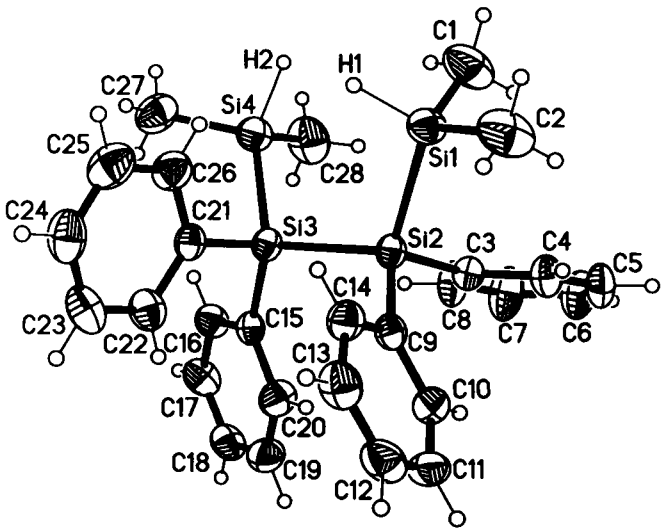

Abstract

$C_{28}H_{34}Si_4$, triclinic, $P\bar{1}$ (no. 2), $a = 10.149(2)$ Å, $b = 10.712(2)$ Å, $c = 15.148(3)$ Å, $\alpha = 85.51(1)°$, $\beta = 88.99(2)°$, $\gamma = 62.45(1)°$, $V = 1455.3$ Å^3, $Z = 2$, $R_{gt}(F) = 0.049$, $wR_{ref}(F^2) = 0.140$, $T = 293$ K.

Source of material

In the reaction of $(Me_3SiO)Ph_2SiCl$ or $(Me_3SiO)_2SiPh_2$ (Me = CH_3, Ph = C_6H_5) with lithium metal at –78 °C in tetrahydrofuran the silyllithium derivatives $Me_3SiO(Ph_2Si)_nLi$ (n = 1, 2), Me_3SiPh_2SiLi and $LiSiPh_2SiPh_2Li$ are formed, which are trapped with $Me_2(H)SiCl$ to give $Me_3SiO(Ph_2Si)_nSi(H)Me_2$, Me_3SiPh_2Si-$Si(H)Me_2$ and the tetrasilane $Me_2(H)SiSiPh_2SiPh_2Si(H)Me_2$ [1,2]. Purification of the mixture by distillation and crystallization from n-hexane give colorless single crystals of the tetrasilane.

Experimental details

The positions of the H atoms, which are bonded to Si1 and Si4 were determined from the electron density difference map. Because of the hydride character of H1 and H2, both atoms were refined freely using isotropic thermal parameters. The other hydrogen atom positions were refined using a riding model.

Discussion

The tetrasilane $[Me_2(H)Si$-$Ph_2Si]_2$ crystallizes with two molecules in the unit cell. The Si—Si bond distances (d(Si1—Si2) = 2.355(1) Å, d(Si2—Si3) = 2.369(1) Å, d(Si3—Si4) = 2.365(2) Å) are found within the typical range for disilanes and oligosilanes with relatively little steric strain (2.33 Å – 2.37 Å) [3-5] and are comparable to those in the tetrasilane $[Me_3Si$–$Ph_2Si]_2$ [6] (average Si—Si bond distance of 2.364 Å). In $[Me_3Si$–$Ph_2Si]_2$, the chain of silicon atoms shows a perfect staggered conformation. In contrast the chain of silicon atoms in $[Me_2(H)Si$–$Ph_2Si]_2$ is approximately gauche configurated (dihedral angle Si1–Si2–S3–Si4 of 43.39(7)°), due to the smaller steric effect of the $Me_2(H)Si$ in comparison to the Me_3Si group. The Si—C(Ph) bond distances (1.882(3) Å – 1.887(3) Å) are slightly longer than the Si—C(Me) bond distances (1.852(5) Å – 1.869(3) Å). The Si—H bond distances resulting from the free refinements are 1.45(4) Å for Si1—H1 and 1.54(3) Å for Si4—H2.

Table 1. Data collection and handling.

Crystal:	colorless prism, size 0.22 × 0.23 × 0.77 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	2.18 cm^{-1}
Diffractometer, scan mode:	Bruker P4, ω
$2\theta_{max}$:	44°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4311, 3568
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2727
$N(param)_{refined}$:	297
Programs:	SHELXS-97 [7], SHELXL-97 [8], DIAMOND [9]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1A)	2*i*	0.1377	0.3360	1.0178	0.171
H(1B)	2*i*	0.1335	0.2051	0.9810	0.171
H(1C)	2*i*	0.0185	0.3583	0.9455	0.171
H(2A)	2*i*	0.2435	0.5132	0.9071	0.165
H(2B)	2*i*	0.1250	0.5412	0.8330	0.165
H(2C)	2*i*	0.2935	0.4796	0.8096	0.165
H(4A)	2*i*	–0.0551	0.4841	0.7379	0.081
H(5A)	2*i*	–0.3079	0.5747	0.7399	0.100
H(6A)	2*i*	–0.4149	0.4262	0.7410	0.112
H(7A)	2*i*	–0.2657	0.1866	0.7422	0.124
H(8A)	2*i*	–0.0120	0.0950	0.7435	0.094
H(10A)	2*i*	0.0863	0.3520	0.5718	0.077
H(11A)	2*i*	0.1754	0.4309	0.4510	0.093
H(12A)	2*i*	0.4119	0.4082	0.4544	0.098
H(13A)	2*i*	0.5596	0.3058	0.5786	0.095
H(14A)	2*i*	0.4715	0.2286	0.7008	0.076
H(16A)	2*i*	0.3111	–0.2982	0.7443	0.078
H(17A)	2*i*	0.2343	–0.3920	0.6366	0.091
H(18A)	2*i*	0.1576	–0.2736	0.4999	0.088
H(19A)	2*i*	0.1554	–0.0594	0.4698	0.098
H(20A)	2*i*	0.2305	0.0365	0.5772	0.087
H(22A)	2*i*	0.5560	–0.1240	0.6177	0.083
H(23A)	2*i*	0.8006	–0.1697	0.5989	0.101

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Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(24A)	2*i*	0.9356	–0.1586	0.7154	0.106
H(25A)	2*i*	0.8267	–0.0992	0.8494	0.109
H(26A)	2*i*	0.5847	–0.0552	0.8697	0.087
H(27A)	2*i*	0.4635	–0.3580	0.9877	0.139
H(27B)	2*i*	0.5699	–0.3256	0.9247	0.139
H(27C)	2*i*	0.4669	–0.3824	0.8869	0.139
H(28A)	2*i*	0.1373	–0.1698	0.9822	0.167
H(28B)	2*i*	0.1223	–0.1824	0.8808	0.167
H(28C)	2*i*	0.0645	–0.0332	0.9171	0.167
H(1)	2*i*	0.399(4)	0.207(4)	0.911(2)	0.09(1)
H(2)	2*i*	0.341(4)	–0.056(4)	0.980(2)	0.08(1)

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Si(1)	2*i*	0.2487(1)	0.2974(1)	0.87821(7)	0.0828(8)	0.0611(6)	0.0637(7)	–0.0383(6)	–0.0019(6)	–0.0088(5)
Si(2)	2*i*	0.2049(1)	0.20813(9)	0.75090(6)	0.0466(6)	0.0413(5)	0.0592(6)	–0.0210(4)	0.0003(4)	–0.0038(4)
Si(3)	2*i*	0.3409(1)	–0.04160(9)	0.76229(6)	0.0502(6)	0.0420(5)	0.0591(6)	–0.0226(5)	–0.0013(5)	–0.0020(4)
Si(4)	2*i*	0.3250(1)	–0.1383(1)	0.90549(7)	0.0816(8)	0.0594(6)	0.0658(7)	–0.0351(6)	0.0026(6)	–0.0039(5)
C(1)	2*i*	0.1190(6)	0.2994(5)	0.9662(3)	0.177(6)	0.099(3)	0.081(3)	–0.076(4)	0.041(3)	–0.021(3)
C(2)	2*i*	0.2248(7)	0.4800(5)	0.8541(3)	0.177(6)	0.096(3)	0.100(3)	–0.098(4)	0.011(3)	–0.022(3)
C(3)	2*i*	–0.0024(4)	0.2773(3)	0.7429(2)	0.049(2)	0.051(2)	0.060(2)	–0.025(2)	0.001(2)	–0.003(2)
C(4)	2*i*	–0.0967(4)	0.4227(4)	0.7400(3)	0.060(3)	0.050(2)	0.091(3)	–0.024(2)	0.011(2)	–0.007(2)
C(5)	2*i*	–0.2484(5)	0.4776(4)	0.7403(3)	0.061(3)	0.056(2)	0.108(3)	–0.006(2)	0.012(2)	–0.010(2)
C(6)	2*i*	–0.3121(5)	0.3895(5)	0.7411(3)	0.046(2)	0.083(3)	0.140(4)	–0.021(3)	–0.001(3)	–0.005(3)
C(7)	2*i*	–0.2231(5)	0.2470(5)	0.7421(4)	0.056(3)	0.072(3)	0.182(5)	–0.031(3)	–0.006(3)	0.001(3)
C(8)	2*i*	–0.0705(4)	0.1923(4)	0.7429(3)	0.050(2)	0.054(2)	0.125(4)	–0.018(2)	–0.001(2)	–0.008(2)
C(9)	2*i*	0.2688(4)	0.2790(3)	0.6504(2)	0.054(2)	0.042(2)	0.060(2)	–0.023(2)	0.005(2)	–0.008(2)
C(10)	2*i*	0.1824(4)	0.3418(4)	0.5741(2)	0.062(2)	0.065(2)	0.064(2)	–0.026(2)	–0.003(2)	–0.005(2)
C(11)	2*i*	0.2355(6)	0.3895(4)	0.5014(3)	0.105(4)	0.068(3)	0.050(2)	–0.034(3)	0.001(2)	0.002(2)
C(12)	2*i*	0.3763(6)	0.3761(4)	0.5034(3)	0.100(4)	0.077(3)	0.074(3)	–0.046(3)	0.031(3)	–0.011(2)
C(13)	2*i*	0.4637(5)	0.3155(4)	0.5772(3)	0.071(3)	0.078(3)	0.091(3)	–0.038(2)	0.022(3)	–0.007(2)
C(14)	2*i*	0.4109(4)	0.2683(4)	0.6505(3)	0.063(3)	0.057(2)	0.070(2)	–0.028(2)	0.002(2)	–0.001(2)
C(15)	2*i*	0.2794(4)	–0.1190(3)	0.6737(2)	0.049(2)	0.041(2)	0.063(2)	–0.019(2)	0.004(2)	–0.007(2)
C(16)	2*i*	0.2795(4)	–0.2485(4)	0.6892(2)	0.076(3)	0.056(2)	0.066(2)	–0.033(2)	0.005(2)	–0.009(2)
C(17)	2*i*	0.2338(5)	–0.3053(4)	0.6245(3)	0.093(3)	0.066(2)	0.084(3)	–0.050(2)	0.017(2)	–0.020(2)
C(18)	2*i*	0.1880(4)	–0.2349(4)	0.5432(3)	0.069(3)	0.078(3)	0.083(3)	–0.038(2)	0.005(2)	–0.029(2)
C(19)	2*i*	0.1866(5)	–0.1077(4)	0.5253(3)	0.092(3)	0.076(3)	0.072(3)	–0.034(3)	–0.014(2)	–0.009(2)
C(20)	2*i*	0.2320(5)	–0.0504(4)	0.5902(3)	0.092(3)	0.054(2)	0.076(3)	–0.037(2)	–0.012(2)	–0.002(2)
C(21)	2*i*	0.5416(4)	–0.0840(3)	0.7458(2)	0.052(2)	0.038(2)	0.064(2)	–0.020(2)	0.002(2)	0.001(2)
C(22)	2*i*	0.6096(4)	–0.1189(4)	0.6653(3)	0.065(3)	0.065(2)	0.083(3)	–0.032(2)	0.008(2)	–0.015(2)
C(23)	2*i*	0.7570(5)	–0.1466(4)	0.6537(3)	0.077(3)	0.080(3)	0.101(3)	–0.039(3)	0.032(3)	–0.029(2)
C(24)	2*i*	0.8371(5)	–0.1396(5)	0.7228(4)	0.055(3)	0.085(3)	0.121(4)	–0.031(2)	0.017(3)	–0.002(3)
C(25)	2*i*	0.7724(5)	–0.1049(5)	0.8024(3)	0.069(3)	0.112(4)	0.097(4)	–0.050(3)	–0.014(3)	0.011(3)
C(26)	2*i*	0.6267(4)	–0.0780(4)	0.8144(3)	0.064(3)	0.082(3)	0.072(3)	–0.034(2)	–0.002(2)	0.000(2)
C(27)	2*i*	0.4745(5)	–0.3236(4)	0.9291(3)	0.109(4)	0.076(3)	0.090(3)	–0.044(3)	–0.018(3)	0.017(2)
C(28)	2*i*	0.1400(5)	–0.1299(5)	0.9236(3)	0.100(4)	0.115(4)	0.122(4)	–0.055(3)	0.040(3)	–0.009(3)

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