Acta Cryst. (1993). C**49**, 331–333

Structure of the Highly Crowded Alkyne Di[tris(trimethylsilyl)methyl]acetylene and the Octasilane Hexakis(trimethylsilyl)disilane

By Frank R. Fronczek

Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803-1804, *USA*

and Paul D. Lickiss

*Department of Chemistry and Applied Chemistry, University of Salford, Salford M*5 4*WT, England*

(*Received* 14 *October* 1991; *accepted* 2 *March* 1992)

Abstract. (I) 2,2,7,7-Tetramethyl-3,3,6,6-tetrakis-(trimethylsilyl)-2,7-disilaoct-4-yne, $C_{22}H_{54}Si_6$, $M_r = 487.2$, triclinic, $P\bar{1}$, $a = 9.0383\,(10)$, $b = 9.3596\,(9)$, $c = 11.855\,(3)$ Å, $\alpha = 68.207\,(13)$, $\beta = 74.837\,(14)$, $\gamma = 59.858\,(9)°$, $V = 801.8\,(2)$ Å^3, $Z = 1$, $D_x = 1.009$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 2.62$ cm^{-1}, $F(000) = 270$, $T = 297$ K, final $R = 0.035$ for 3484 unique observed reflections. The molecule is centrosymmetric. The two very bulky $(Me_3Si)_3C$ groups in the molecule have no unusually close methyl–methyl distances between them, the shortest such C···C distance being 4.043 (2) Å, *i.e.* approximately equal to the sum of the van der Waals radii for two methyl groups. The triple bond [1.199 (2) Å] is not significantly longer than expected for an alkyne. Si—C(methyl) distances range 1.860 (2)–1.873 (2) Å, while the C—Si distances of the CSi_3 group range 1.915 (1)–1.923 (2) Å. (II) 2,2,5,5-Tetramethyl-3,3,4,4-tetrakis(trimethylsilyl)-2,3,4,5-tetrasilahexane, $C_{18}H_{54}Si_8$, $M_r = 495.3$, trigonal, $R\bar{3}c$, hexagonal axes $a = 16.154\,(2)$, $c = 22.859\,(3)$ Å, $V = 5166.1\,(13)$ Å^3, $Z = 6$, $D_x = 0.955$ g cm^{-3}, $\lambda(\text{Cu } K\alpha) = 1.54184$ Å, $\mu = 30.11$ cm^{-1}, $F(000) = 1644$, $T = 296$ K, final $R = 0.042$ for 889 unique observed reflections. The molecule lies on a site of 32 symmetry. The effect of the six bulky Me_3Si groups is to lengthen the central Si—Si bond to 2.403 (2) Å, although the peripheral Si—Si bond lengths [2.3738 (9) Å] are not unusually long. The three Si—C distances range 1.855 (4)–1.876 (3) Å. The closest C···C distance between methyl groups in opposite halves of the molecule is 3.580 (5) Å, significantly shorter than the sum of the van der Waals radii.

Table 1. *Data collection and structure refinement parameters*

	(I)	(I)
Crystal size (mm)	0.38 × 0.43 × 0.50	0.30 × 0.38 × 0.38
Colour	Colourless	Colourless
Radiation	Mo *Kα*	Cu *Kα*
Reflections used for cell constants, θ range (°)	12–14	22–25
ω-scan width (°)	$0.80 + 0.35\tan\theta$	$0.70 + 0.14\tan\theta$
Scan speed (° min^{-1})	1.10–3.30	1.25–3.30
Maximum scan time per reflection (s)	60	60
Range for data collection		
θ (°)	1–30	2–75
h	0, 12	0, 20
k	−13, 13	−20, 20
l	−16, 16	−28, 28
Standard reflections	200, 030, 005	300, 030, 0,0,12
Intensity decay (%)	–	17.5
Empirical absorption correction, transmission coefficient		
Maximum	–	0.9990
Minimum	–	0.9184
Reflections measured		
Total	4670	7300
Unique	4670	1183
Observed [$I > 3\sigma(I)$]	3484	889
R_{int}	–	0.043
R, wR	0.035, 0.044	0.042, 0.045
Number of variables	236	40
Maximum shift/e.s.d. ratio (Δ/σ)	0.09	0.01
Minimum/maximum height in final ΔF (e Å^{-3})	−0.18 0.26	−0.19 0.25
Goodness of fit, S	2.264	1.281
Extinction parameter, g	1.3 (2) × 10^{-7}	–

Experimental. Compound (I) was kindly supplied by Professor J. Dunogues (University of Bordeaux) and compound (II) was prepared by addition of $BrCH_2CH_2Br$ to $(Me_3Si)_3SiLi$ according to the literature method (Gilman & Harrell, 1967). Crystals of (I) were obtained by slow evaporation of a chloroform solution, and of (II) by sublimation (373 K, 0.01 mm Hg).

Intensity data were collected on Enraf–Nonius CAD-4 diffractometers using graphite-monochromated Mo *Kα* radiation for (I) and Cu *Kα* for (II). Variable scan rates were employed in the ω–2θ scans, and a maximum was set on the time spent on a weak reflection. Cell dimensions were obtained from the setting angles of 25 reflections. Intensity standards were remeasured every 10000 s, and a linear decay correction was applied for (II). One hemisphere of data was collected for each crystal. Data reduction included corrections for background, Lorentz, polarization and absorption [for (II), based on ψ scans].

The space group for (I) was confirmed by successful refinement of a centrosymmetric model; the space

0108-2701/93/020331-03$06.00

Table 2. *Coordinates and equivalent isotropic thermal parameters* (Å^2)

$$B_{eq} = (8\pi^2/3)\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Compound (I)				
Si1	0.40973 (5)	0.64216 (5)	0.22215 (3)	3.581 (9)
Si2	0.65915 (5)	0.73653 (4)	0.29251 (4)	3.559 (9)
Si3	0.78498 (5)	0.35262 (5)	0.29180 (4)	3.77 (1)
C1	0.5263 (1)	0.5178 (1)	0.4473 (1)	2.47 (2)
C2	0.5923 (1)	0.5607 (1)	0.3179 (1)	2.68 (3)
C3	0.2008 (2)	0.7861 (2)	0.2900 (2)	5.57 (5)
C4	0.3768 (2)	0.4641 (2)	0.2147 (2)	5.68 (4)
C5	0.4489 (2)	0.7639 (2)	0.0612 (2)	5.79 (5)
C6	0.7650 (2)	0.6907 (2)	0.4255 (2)	5.47 (4)
C7	0.8093 (2)	0.7547 (2)	0.1514 (2)	5.87 (5)
C8	0.4713 (2)	0.9549 (2)	0.2771 (2)	5.33 (5)
C9	0.8422 (3)	0.3625 (2)	0.1263 (2)	6.70 (6)
C10	0.9818 (2)	0.3011 (2)	0.3531 (2)	5.99 (6)
C11	0.7379 (2)	0.1654 (2)	0.3731 (2)	5.58 (5)
Compound (II)				
Si1	0	0	0.19744 (5)	3.87 (2)
Si2	0.05750 (5)	0.15396 (5)	0.15601 (3)	6.15 (2)
C1	0.0882 (3)	0.1553 (3)	0.0767 (1)	13.9 (2)
C2	−0.0333 (2)	0.1922 (2)	0.1592 (2)	11.7 (1)
C3	0.1678 (2)	0.2508 (2)	0.1904 (2)	10.2 (1)

Table 3. *Bond distances* (Å), *bond angles* (°) *and selected torsion angles* (°)

Compound (I)			
Si1—C2	1.915 (1)	Si2—C8	1.869 (1)
Si1—C3	1.866 (2)	Si3—C2	1.919 (1)
Si1—C4	1.870 (2)	Si3—C9	1.873 (2)
Si1—C5	1.871 (2)	Si3—C10	1.865 (2)
Si2—C2	1.923 (2)	Si3—C11	1.860 (2)
Si2—C6	1.860 (2)	C1—C1^{i}	1.199 (2)
Si2—C7	1.871 (2)	C1—C2	1.475 (2)
C2—Si1—C3	110.73 (8)	C2—Si3—C10	112.49 (9)
C2—Si1—C4	112.88 (6)	C2—Si3—C11	110.25 (7)
C2—Si1—C5	111.94 (8)	C9—Si3—C10	107.2 (1)
C3—Si1—C4	105.55 (9)	C9—Si3—C11	108.2 (1)
C3—Si1—C5	108.46 (7)	C10—Si3—C11	105.90 (9)
C4—Si1—C5	107.0 (1)	C1^{i}—C1—C2	179.6 (1)
C2—Si2—C6	110.33 (7)	Si1—C2—Si2	111.70 (5)
C2—Si2—C7	112.27 (9)	Si1—C2—Si3	112.02 (8)
C2—Si2—C8	112.47 (8)	Si1—C2—C1	107.33 (9)
C6—Si2—C7	108.70 (9)	Si2—C2—Si3	111.78 (6)
C6—Si2—C8	106.07 (9)	Si2—C2—C1	106.9 (1)
C7—Si2—C8	106.70 (7)	Si3—C2—C1	106.73 (6)
C2—Si3—C9	112.49 (6)		
C1—C2—Si1—C4	−76.94 (10)		
C1—C2—Si2—C8	−78.49 (11)		
C1—C2—Si3—C10	−76.85 (12)		
Compound (II)			
Si1—Si1^{i}	2.403 (2)	Si1—Si2	2.3738 (9)
Si2—C1	1.876 (3)	Si2—C2	1.855 (4)
Si2—C3	1.858 (3)		
Si1^{i}—Si1—Si2	113.51 (3)	Si1—Si2—C1	111.1 (1)
Si1—Si2—C2	111.87 (9)	Si1—Si2—C3	114.9 (1)
Si2—Si1—Si2^{i}	105.15 (4)	C1—Si2—C2	106.4 (2)
C1—Si2—C3	105.2 (1)	C2—Si2—C3	106.7 (2)
Si1^{i}—Si1—Si2—C1	164.0 (2)		
Si1^{i}—Si1—Si2—C2	−77.22 (12)		
Si1^{i}—Si1—Si2—C3	44.72 (13)		
Si2^{iii}—Si1—Si2—C1	−71.4 (2)		
Si2^{iii}—Si1—Si2—C2	47.43 (13)		
Si2^{iii}—Si1—Si2—C3	169.36 (13)		
Si2^{iii}—Si1—Si1^{i}—Si2^{ii}	163.37 (3)		

Symmetry code: (i) $y, x, \frac{1}{2} - z$; (ii) $x - y, -y, \frac{1}{2} - z$; (iii) $-y, x - y, z$.

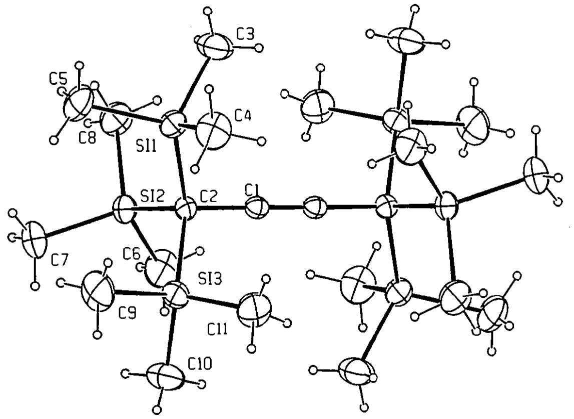

Fig. 1. The molecular structure of (I), with thermal ellipsoids drawn at the 30% probability level and H atoms represented by circles of arbitrary radius.

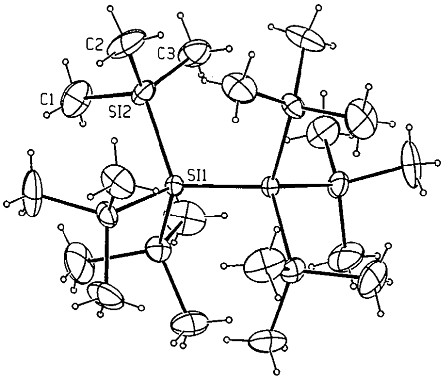

Fig. 2. The molecular structure of (II), with 20% probability ellipsoids.

group for (II) was determined by systematic absences hkl with $-h + k + l \neq 3n$ and $h\bar{h}l$ with l odd, and successful refinement of a centrosymmetric model. The structure of (I) is isomorphous with Mn[C(SiMe$_3$)$_3$]$_2$ (Buttrus, Eaborn, Hitchcock, Smith & Sullivan, 1985), the Si and C positions of which were used as a beginning refinement model, along with the alkynyl C atom, placed in a calculated position 0.6 Å from the inversion centre. The coordinates for the Mn compound were extracted from the Cambridge Structural Database (Allen, Kennard & Taylor, 1983). The structure of (II) was solved using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980).

Structures were refined by full-matrix least squares based on F with weights $w = 4F_o^2[\sigma^2(I) + (0.02F_o^2)^2]^{-1}$, using the Enraf–Nonius *SDP* (Frenz & Okaya, 1980), scattering factors of Cromer & Waber (1974), and anomalous coefficients of Cromer (1974). Non-H atoms were refined anisotropically, and H atoms were located by ΔF syntheses. H atoms were refined isotropically for (I), while for (II) they were included as fixed contributions with C—H distance 0.95 Å and $B = 1.3B_{eq}$ for the bonded atom. A secondary-extinction coefficient, g, was refined for (I) with the correction factor $(1 + gI_c)^{-1}$ applied to F_c.

Final values of the extinction coefficient, residual densities in final ΔF maps, R factors and other details of the refinements are given in Table 1.

Atomic parameters for non-H atoms are given in Table 1, the molecular structures are shown in Figs. 1 and 2, and selected bond distances, bond angles and torsion angles are given in Table 3.*

Related literature. Compound (I) is isomorphous with the organometallic species $[(Me_3Si)_3C]_2M$ where M = Hg (Glockling, Hosmane, Mahale, Magos & King, 1977), Mn (Buttrus, Eaborn, Hitchcock, Smith & Sullivan, 1985) and Mg (Al-Juaid, Eaborn, Hitchcock, McGeary & Smith, 1989), and is similar in structure to the anions in $[Li(thf)_4][\{(Me_3Si)_3C\}_2M]$ where M = Li (Eaborn, Hitchcock, Smith & Sullivan, 1983), Ag (Eaborn, Hitchcock, Smith & Sullivan, 1984*a*) or Cu (Eaborn, Hitchcock, Smith & Sullivan, 1984*b*). Compound (II) is similar in geometry to ${}^tBu_3SiSi{}^tBu_3$ (Wiberg, Schuster, Simon & Peters, 1986) which, however, has a significantly longer central Si—Si bond of 2.696 Å. The related compounds $[(Me_3Si)_3Si]_2M$ (M = Hg, Cd and Zn) have been prepared and the structure of the Zn compound determined (Arnold, Tilley, Rheingold & Geib, 1987).

---

* Lists of H-atom parameters, anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55265 (35 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HE0040]

References

Al-Juaid, S. S., Eaborn, C., Hitchcock, P. B., McGeary, C. A. & Smith, J. D. (1989). *J. Chem. Soc. Chem. Commun.* pp. 273–274.

Allen, F. H., Kennard, O. & Taylor, R. (1983). *Acc. Chem. Res.* **16**, 146–153.

Arnold, J., Tilley, T. D., Rheingold, A. L. & Geib, S. J. (1987). *Inorg. Chem.* **26**, 2106–2109.

Buttrus, N. H., Eaborn, C., Hitchcock, P. B., Smith, J. D. & Sullivan, A. C. (1985). *J. Chem. Soc. Chem. Commun.* pp. 1380–1381.

Cromer, D. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.3.1. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2B. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Eaborn, C., Hitchcock, P. B., Smith, J. D. & Sullivan, A. C. (1983). *J. Chem. Soc. Chem. Commun.* pp. 827–828.

Eaborn, C., Hitchcock, P. B., Smith, J. D. & Sullivan, A. C. (1984*a*). *J. Chem. Soc. Chem. Commun.* pp. 870–871.

Eaborn, C., Hitchcock, P. B., Smith, J. D. & Sullivan, A. C. (1984*b*). *J. Organomet. Chem.* **263**, C23–C25.

Frenz, B. A. & Okaya, Y. (1980). *Enraf–Nonius Structure Determination Package*. Enraf–Nonius, Delft, The Netherlands.

Gilman, H. & Harrell, R. L. (1967). *J. Organomet. Chem.* **9**, 67–76.

Glockling, F., Hosmane, N. S., Mahale, V. B., Magos, L. & King, T. J. (1977). *J. Chem. Res. (S)*, p. 116; *J. Chem. Res. (M)*, pp. 1201–1256.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

Wiberg, N., Schuster, H., Simon, A. & Peters, K. (1986). *Angew. Chem. Int. Ed. Engl.* **25**, 79–80.

Acta Cryst. (1993). C**49**, 333–336

Structures of Benzo[*a*]phenothiazine and Benzo[*c*]phenothiazine

By Sadamu Yoshida, Hidenori Matsuzawa,* Kozo Kozawa and Tokiko Uchida†

Department of Industrial and Engineering Chemistry, Faculty of Science and Technology, Science University of Tokyo, Noda, Chiba 278, Japan

(*Received* 18 *December* 1991; *accepted* 18 *May* 1992)

Abstract. Benzo[*a*]phenothiazine (I), $C_{16}H_{11}NS$, M_r = 249.3, monoclinic, $P2_1/a$, a = 25.269 (2), b = 23.347 (2), c = 8.306 (2) Å, β = 91.71 (1)°, V = 4898 (1) Å^3, Z = 16, D_m = 1.35, D_x = 1.35 Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, μ = 0.23 mm^{-1}, $F(000)$ = 2080, T = 293 K, R = 0.069 for 4248 observed reflections. Benzo[*c*]phenothiazine (II), $C_{16}H_{11}NS$, M_r = 249.3, monoclinic, $P2_1/a$, a = 19.703 (3), b = 5.365 (2), c = 11.523 (1) Å, β = 95.48 (1)°, V = 1212.5 (4) Å^3, Z = 4, D_m = 1.39, D_x = 1.37 Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, μ = 0.23 mm^{-1}, $F(000)$ = 520, T = 293 K, R = 0.047 for 2685 observed reflections. Four crystallographically independent molecules of (I) are essentially identical in bond distances and angles. The molecules of both (I) and (II) are bent at the N–S axis, and dihedral angles

---

* Present address: Department of Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi, Kohoku-ku, Yokohama 223, Japan.

† To whom correspondence should be addressed.

0108-2701/93/020333-04$06.00