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1,2,3,4,5,8-Hexakis(trimethylsilyl)-1,2,3,4,5,8-hexahydronaphthalene: the First Example of Double-*peri* Trimethylsilyl Substitution

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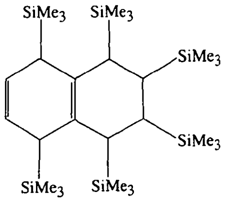
Abstract

The crystal structure determination of the title compound, $C_{28}H_{62}Si_6$, is the first reporting double-*peri* trimethylsilyl substitution. Four trimethyl groups are in axial positions, the remaining two groups are equatorial.

Comment

Polysilylation of naphthalene has been the subject of numerous works (Dunoguès, Calas, Biran & Duffaut, 1970; Birkofer & Ramadan, 1971; Yang, Liu & Liu, 1978; Laguerre, Dunoguès & Calas, 1981). In particular, it has been claimed (Dunoguès, Calas, Biran & Duffaut, 1970) that derivatives with two silicon groups in *peri* positions (*i.e.* 1,8 substitution of naphthalene) might be difficult to obtain due to exaggerated steric hindrance. On reinvestigation, we showed that some of the previous interpretations were wrong (Grignon-Dubois, Laguerre & Saux, 1995; Grignon-Dubois & Laguerre, 1995). This is well demonstrated by the isolation of 1,2,3,4,5,8-hexakis(trimethylsilyl)-1,2,3,4,5,8-hexahydronaphthalene, (I).



(I)

The geometry of the molecule is shown in Fig. 1. From a close examination of the structure, it appears that this molecule is less sterically hindered than expected. The distances between the *peri* Si atoms are essentially the same as the distance between two adjacent Si atoms (mean 4.34 Å for the five Si···Si distances). The C—Si bond lengths have standard values only for the Si atoms at the naphthalene positions 2 and 3 [C3—Si12 and C4—Si13 1.885 (4) and 1.889 (4) Å, respectively], but for the four Si atoms in the *peri* positions 1,8 and 4,5, the bond lengths are significantly longer than the standard value (mean of C2—Si11, C5—Si14, C7—Si15 and C10—Si16 1.931 Å). This behaviour may contribute to a noticeable lowering of the total steric hindrance. The three (Si)C—C(Si) bonds in the tetrasilylated ring (C2—C3, C3—C4, C4—C5) are longer than usual (1.560–1.574 Å), as found previously

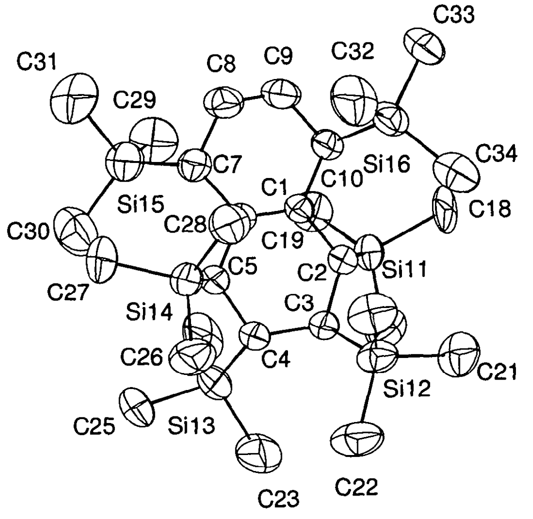


Fig. 1. Perspective view of the title molecule with the atomic numbering scheme. Displacement ellipsoids are plotted at the 50% probability level.

(Grignon-Dubois, Laguerre & Saux, 1995; Laguerre, Leger, Youhouvoulou N'Gabé, Biran & Dunoguès, 1986).

The intermolecular heavy-atom distances are all greater than 4 Å except for C32···C19($x, \frac{1}{2} - y, \frac{1}{2} + z$) 3.824 (8) and C19···C22($1 + x, y, z$) 3.915 (7) Å.

Experimental

Crystals of the title compound were obtained by slow evaporation of an ethanol solution.

Crystal data

$C_{28}H_{62}Si_6$
$M_r = 567.32$
Monoclinic
$P2_1/c$
$a = 10.233$ (2) Å
$b = 18.605$ (3) Å
$c = 19.900$ (3) Å
$\beta = 101.19$ (1)°
$V = 3717$ Å^3
$Z = 4$
$D_x = 1.01$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 25$–31°
$\mu = 2.1$ mm^{-1}
$T = 293$ K
Prism
0.3 × 0.2 × 0.2 mm
Transparent

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
6725 measured reflections
6296 independent reflections
4227 observed reflections [$I > 3\sigma(I)$]

$\theta_{\max} = 65°$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 21$
$l = -23 \rightarrow 23$
2 standard reflections frequency: 60 min intensity decay: 0.65%

Refinement

Refinement on F
$R = 0.051$
$wR = 0.072$
$S = 1.11$
4227 reflections
555 parameters
All H-atom parameters refined
Unit weights applied

$(\Delta/\sigma)_{\max} = 0.051$
$\Delta\rho_{\max} = 0.200$ e Å^{-3}
$\Delta\rho_{\min} = -0.195$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1)

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

$B_{eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	B_{eq}
C1	0.8164 (3)	0.2385 (2)	0.8977 (1)	3.4 (1)
C2	0.7303 (3)	0.1758 (2)	0.8680 (2)	3.7 (1)
C3	0.5788 (3)	0.1906 (2)	0.8423 (2)	3.9 (1)
C4	0.5381 (3)	0.2713 (2)	0.8263 (2)	4.1 (1)
C5	0.6367 (3)	0.3308 (2)	0.8605 (2)	3.9 (1)
C6	0.7792 (3)	0.3076 (2)	0.8877 (2)	3.6 (1)
C7	0.8767 (4)	0.3696 (2)	0.9060 (2)	4.6 (2)
C8	1.0111 (4)	0.3457 (2)	0.9424 (2)	5.4 (2)
C9	1.0462 (4)	0.2790 (2)	0.9530 (2)	5.2 (2)
C10	0.9538 (3)	0.2167 (2)	0.9362 (2)	4.2 (2)
Si11	0.8113 (1)	0.1233 (1)	0.8027 (1)	4.5 (1)
Si12	0.4750 (1)	0.1438 (1)	0.8976 (1)	5.1 (1)
Si13	0.4847 (1)	0.2901 (1)	0.7316 (1)	5.7 (1)
Si14	0.5707 (1)	0.3863 (1)	0.9289 (1)	5.3 (1)
Si15	0.9172 (1)	0.4308 (1)	0.8346 (1)	5.8 (1)
Si16	0.9696 (1)	0.1678 (1)	1.0228 (1)	5.0 (1)
C17	0.6843 (5)	0.0819 (2)	0.7335 (2)	6.5 (2)
C18	0.9107 (5)	0.0457 (2)	0.8465 (3)	7.0 (2)
C19	0.9252 (4)	0.1800 (3)	0.7620 (2)	6.1 (2)
C20	0.5070 (5)	0.1782 (3)	0.9872 (2)	7.0 (2)
C21	0.5105 (5)	0.0450 (2)	0.8983 (3)	7.1 (2)
C22	0.2932 (4)	0.1557 (3)	0.8598 (3)	7.6 (3)
C23	0.3596 (6)	0.2222 (3)	0.6892 (3)	8.9 (3)
C24	0.6290 (6)	0.2906 (3)	0.6876 (2)	7.9 (3)
C25	0.4012 (5)	0.3803 (3)	0.7214 (3)	7.2 (2)
C26	0.3862 (5)	0.3767 (3)	0.9199 (3)	8.1 (3)
C27	0.5977 (6)	0.4851 (3)	0.9155 (3)	7.9 (3)
C28	0.6511 (5)	0.3631 (3)	1.0189 (2)	6.5 (2)
C29	1.0212 (5)	0.3803 (3)	0.7839 (3)	7.8 (3)
C30	0.7758 (6)	0.4717 (3)	0.7720 (3)	8.9 (3)
C31	1.0144 (6)	0.5077 (3)	0.8801 (3)	9.1 (3)
C32	0.9456 (6)	0.2326 (3)	1.0904 (2)	8.6 (3)
C33	1.1439 (4)	0.1328 (3)	1.0421 (2)	6.8 (2)
C34	0.8594 (5)	0.0882 (3)	1.0270 (2)	7.3 (2)

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

C1—C2	1.511 (5)	Si11—C18	1.880 (5)
C1—C6	1.345 (5)	Si11—C19	1.869 (5)
C1—C10	1.520 (5)	Si12—C20	1.862 (5)
C2—C3	1.560 (5)	Si12—C21	1.874 (5)
C2—Si11	1.937 (3)	Si12—C22	1.880 (6)
C3—C4	1.574 (5)	Si13—C23	1.878 (6)
C3—Si12	1.885 (4)	Si13—C24	1.858 (6)
C4—C5	1.562 (5)	Si13—C25	1.887 (5)
C4—Si13	1.889 (4)	Si14—C26	1.870 (6)
C5—C6	1.516 (5)	Si14—C27	1.886 (6)
C5—Si14	1.932 (4)	Si14—C28	1.871 (5)
C6—C7	1.522 (5)	Si15—C29	1.857 (6)
C7—C8	1.492 (6)	Si15—C30	1.877 (6)
C7—Si15	1.928 (4)	Si15—C31	1.873 (7)
C8—C9	1.298 (6)	Si16—C32	1.858 (6)
C9—C10	1.492 (5)	Si16—C33	1.867 (5)
C10—Si16	1.928 (4)	Si16—C34	1.873 (5)
Si11—C17	1.866 (5)		
C2—C1—C6	123.6 (3)	C18—Si11—C19	107.9 (2)
C2—C1—C10	113.8 (3)	C3—Si12—C20	112.7 (2)
C6—C1—C10	122.5 (3)	C3—Si12—C21	109.1 (2)
C1—C2—C3	117.3 (3)	C3—Si12—C22	109.8 (2)
C1—C2—Si11	111.0 (2)	C20—Si12—C21	109.4 (2)
C3—C2—Si11	113.4 (2)	C20—Si12—C22	108.6 (2)
C2—C3—C4	116.2 (3)	C21—Si12—C22	107.1 (2)
C2—C3—Si12	111.3 (2)	C4—Si13—C23	111.3 (2)
C4—C3—Si12	113.7 (2)	C4—Si13—C24	111.6 (2)
C3—C4—C5	117.7 (3)	C4—Si13—C25	108.1 (2)
C3—C4—Si13	113.1 (2)	C23—Si13—C24	109.0 (3)
C5—C4—Si13	109.9 (2)	C23—Si13—C25	107.2 (3)
C4—C5—C6	116.7 (3)	C24—Si13—C25	109.3 (2)
C4—C5—Si14	113.6 (2)	C5—Si14—C26	111.5 (2)
C6—C5—Si14	110.1 (2)	C5—Si14—C27	109.9 (2)
C1—C6—C5	123.4 (3)	C5—Si14—C28	113.7 (2)
C1—C6—C7	122.4 (3)	C26—Si14—C27	104.6 (3)
C5—C6—C7	114.2 (3)	C26—Si14—C28	108.5 (2)
C6—C7—C8	112.9 (3)	C27—Si14—C28	108.1 (2)
C6—C7—Si15	119.7 (3)	C7—Si15—C29	109.2 (2)
C8—C7—Si15	102.9 (3)	C7—Si15—C30	118.7 (2)
C7—C8—C9	124.3 (4)	C7—Si15—C31	105.4 (2)
C8—C9—C10	124.3 (4)	C29—Si15—C30	107.1 (3)
C1—C10—C9	112.9 (3)	C29—Si15—C31	110.0 (3)
C1—C10—Si16	119.0 (2)	C30—Si15—C31	106.2 (3)
C9—C10—Si16	103.1 (3)	C10—Si16—C32	110.0 (2)
C2—Si11—C17	112.1 (2)	C10—Si16—C33	105.0 (2)
C2—Si11—C18	109.9 (2)	C10—Si16—C34	117.8 (2)
C2—Si11—C19	112.9 (2)	C32—Si16—C33	109.4 (2)
C17—Si11—C18	105.2 (2)	C32—Si16—C34	108.4 (3)
C17—Si11—C19	108.5 (2)	C33—Si16—C34	105.9 (2)

The stucture was solved by direct methods. An E map based on 320 reflections revealed the positions of all non-H atoms.

After refinement by least squares, H atoms were located from a difference synthesis. In the final cycles the heavier atoms were allowed to vibrate anisotropically.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Program(s) used to solve structure: *MULTAN*80 (Main *et al.*, 1980).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1172). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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α-(2,3,5,6-Tetrachlorophenyl)-α-(3-thienyl)-acetonitrile and α-(3-Methoxyphenyl)-α-(2,3,4,5,6-pentachlorophenyl)acetonitrile

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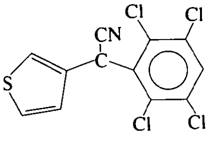
Abstract

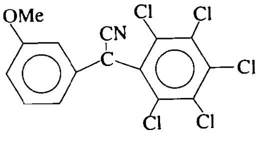
The C—Cl distances of the tetrachlorophenyl moiety in α-(2,3,5,6-tetrachlorophenyl)-α-(3-thienyl)acetonitrile, (1), $C_{12}H_5Cl_4NS$, are in the range 1.713 (3)–1.720 (3) Å, and those of the pentachlorophenyl moiety in α-(3-methoxyphenyl)-α-(2,3,4,5,6-pentachlorophenyl)acetonitrile, (2), $C_{15}H_8Cl_5NO$, are in the range 1.695 (9)–1.734 (8) Å. The thienyl ring of compound (1) is almost planar and the dihedral angle between the phenyl and thienyl rings is 78.8 (1)°, while that between the two phenyl planes of compound (2) is 88.6 (3)°.

Comment

As part of our synthetic and structural studies of the benzyne reaction, the structures of the title compounds, α-(2,3,5,6-tetrachlorophenyl)-α-(3-thienyl)acetonitrile, (1), and α-(3-methoxyphenyl)-α-(2,3,4,5,6-pentachlorophenyl)acetonitrile, (2), were determined by X-ray diffraction.



(1)



(2)

The present structure analysis reveals that compound (1) possesses an H atom in the *para* position of the tetrachlorophenyl moiety (Fig. 1). The C—Cl distances [1.713 (3)–1.720 (3) in (1) and 1.696 (9)–1.735 (8) Å in (2)] are comparable to the corresponding ranges of 1.725 (7)–1.799 (6) Å in $[Ir(C_6Cl_5)_4]^{2-}$ (Garcia, Jimenez, Oro, Lahoz, Tiripicchio & Tiripicchio, 1993), 1.673 (11)–1.738 (8) Å in perchlorotriphenylgermane (Fajari, Julia, Riera, Molins & Miravitlles, 1989) and 1.706 (11)–1.748 (11) Å in $[(PPh_3)(C_6Cl_5)BrPt(\mu\text{-}Br)Ag(PPh_3)]_2$ (Uson, Fornies, Tomas & Ara, 1991). Of the Cl atoms, Cl(5) of compound (1) and Cl(4) of compound (2) lie nearly in the plane of their respective phenyl rings, while the remaining eight Cl atoms are significantly displaced from their planes, the maximum deviation being 0.064 Å for Cl(2) in compound (1).

The orientations of the cyano groups with respect to the chlorophenyl rings are defined by the torsion

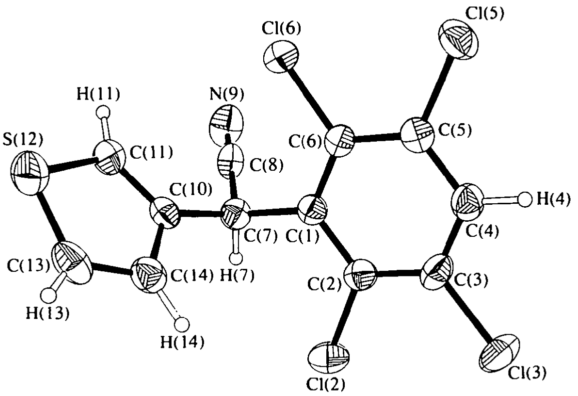


Fig. 1. The structure of compound (1) showing 50% probability displacement ellipsoids. For clarity, H atoms are drawn as small circles of arbitrary radii.

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