Hexasilylbenzene, $C_6(SiH_3)_6$

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The title compound was obtained in a four-step synthesis starting from (4-methoxyphenyl)silane. Owing to the presence of activating p-methoxy groups in the key intermediate hexakis[(4-methoxyphenyl)silyl]benzene (4), the peripheral aryl groups can be cleaved selectively from the silicon atoms with trifluoromethanesulfonic acid, leaving the Si−C bonds to the central benzene ring intact. LiAlH$_4$ reduction of the resulting hexakis[(trifluoromethylsulfonyloxy)silyl]benzene (5) finally leads to crystalline, sublimable, air-stable $C_6(SiH_3)_6$ (6), m.p. 165°C. In the crystals (triclinic, space group $P\bar{1}$) the structure of the centrosymmetrical molecules approaches very closely point group D_{3d}, as predicted from theoretical considerations.

We report on the synthesis of hexasilylbenzene, $C_6(SiH_3)_6$ (6). This molecule is of considerable interest regarding its structure and energy characteristics, but also as a precursor for cation and anion radicals, as an electron-rich ligand for organometallic compounds, as a multi-silicon-functional synthon, and as a single-component source of silicon and carbon for the deposition of silicon carbide. The compound is expected to suffer from very little, if any, sterical crowding as compared to the partially or fully methylated homologues $C_6(SiMe_2H)_6$ and $C_6(SiMe_3)_6$, which were shown to have extremely puckered benzene rings[1,2]. Though not prepared previously, the compound has been included in patents for chemical vapour deposition of surface coatings[3].

Recent attempts to synthesize $C_6(SiH_3)_6$ starting from phenyl- or (4-methylphenyl)silane were unsuccessful, since in the critical step (below) random cleavage by acid occurred with the key intermediates $C_6(SiH_2Ph)_6$ and $C_6(SiH_2C_6H_4-4-Me)_6$[4]. Therefore, in a new effort, aryl groups with more strongly activating substitutents were chosen for the protecting aryl groups, which were expected to favour peripheral cleavage over "central" cleavage.

Trichloro(4-methoxyphenyl)silane (1) is prepared and converted into (4-methoxyphenyl)silane (2) by LiAlH$_4$ reduction following literature methods[5]. Si−H cleavage by boron trichloride affords chloro(4-methoxyphenyl)silane (3), which undergoes a coupling reaction with hexabromobenzene and magnesium metal in boiling tetrahydrofuran [1,2,4,6] to give hexakis[(4-methoxyphenyl)silyl]benzene (4). Treatment of this crystalline intermediate with trifluoro-

methanesulfonic acid in toluene at low temperature leads to selective cleavage of the p-anisyl groups to yield hexakis[(trifluoromethylsulfonyloxy)silyl]benzene (5), and LiAlH$_4$ reduction of nonisolated 5 in toluene/diethyl ether gives hexasilylbenzene (6, Scheme 1).

Hexasilylbenzene is a crystalline solid, melting point 165°C. It is stable in air at room temperature and soluble in several of the common organic solvents. Solutions in C_6D_6 show a ^{1}H-NMR signal at $\delta = 4.4$ with satellites [$^1J(^{29}Si^{-1}H) = 204$ Hz]. The ^{13}C resonance appears at $\delta = 148.15$, the ^{29}Si resonance at $\delta = -65$ (q). The stoichiometry has been confirmed by elemental analysis and

Scheme 1

4-MeOC$_6$H$_4$−SiCl$_3$ **1**

LiAlH$_4$ ↓

4-MeOC$_6$H$_4$−SiH$_3$ **2**

BCl$_3$ ↓

4-MeOC$_6$H$_4$−SiH$_2$Cl   **3**

C$_6$Br$_6$/Mg ↓

[4-MeOC$_6$H$_4$−SiH$_2$]$_6$C$_6$ **4**

F$_3$CSO$_3$H ↓

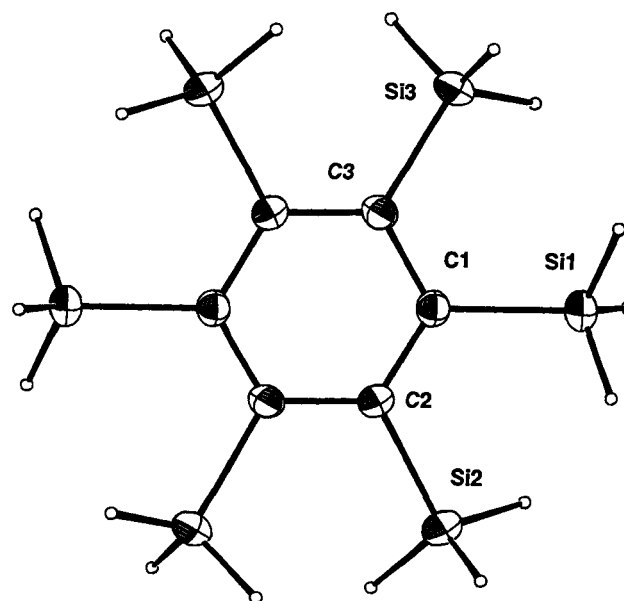[F$_3$CSO$_2$O−SiH$_2$]$_6$C$_6$ **5**

Figure 1. Molecular structure of hexasilylbenzene (6), projected down to the benzene plane, with atomic numbering. The molecule has a center of inversion (ORTEP, 50% probability ellipsoids for non-hydrogen atoms; arbitrary radii for hydrogen atoms). Selected distances [Å] and angles [°]: Si1−C1, Si2−C2, and Si3−C3 1.888(1), C1−C2 1.416(1), C1−C3 and C3−C2′ 1.414(1); Si1−C1−C2 119.3(1), Si1−C1−C3 and Si2−C2−C1 120.4(1), Si3−C3−C1 119.4(1), C2−C1−C3 119.9(1), C1−C3−C2′ 120.1(1), C1−C2−C3′ 120.0(1)
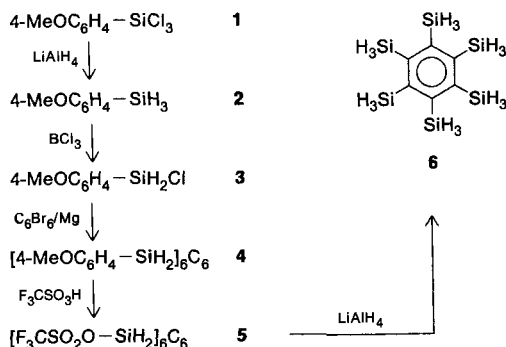
electron impact mass spectrometry (m/z = 258, M$^+$). The most prominent v(SiH) absorption appears in the IR spectrum at 2158 cm^{-1}.

Triclinic single crystals of C$_6$(SiH$_3$)$_6$ were grown from tetrahydrofuran (space group P$\bar{1}$, with one formula unit in the unit cell). The positions of all atoms of the molecule, including the hydrogen atoms, could be located and refined anisotropically. The individual molecules have a crystallographic center of inversion (point group C_i, Figure 1), but the overall molecular symmetry approaches quite closely point group D_{3d}.

The positions of the silicon atoms deviate slightly from the plane of the benzene ring (average 0.225 Å). The silyl groups are threefold rotors, with neighbouring groups minimizing intramolecular contacts by placing alternately one of the three hydrogen atoms up and down in planes perpendicular to the benzene ring plane (Figure 2). The deviation from this idealized position is small, with dihedral angles C−C−Si−H at an average of 93.5°. The bond distances and angles are not unusual (caption to Figure 1).

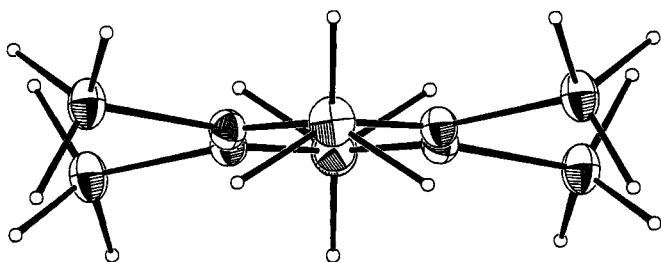
Figure 2. Projection of the molecular structure of hexasilylbenzene (6) approximately parallel to the benzene ring showing the up-and-down deviation of the silicon atoms from the molecular plane (ORTEP, 50% probability ellipsoids for C and Si, arbitrary radii for H). The center of inversion is obvious from the staggered conformation of trans-silyl threefold rotors

Crystalline hexasilylbenzene (6) is thus isotypical with the high-temperature form of hexamethylbenzene, the structure of which has been determined both by X-ray and neutron diffraction[7,8]. The conformation with slightly distorted D_{3d} symmetry appears to be a clear energy minimum as predicted from force field calculations[7]. The situation is not unlike the conformation in tetrahedral species with four threefold rotor substituents, as represented by molecules like neopentane, tetramethylsilane, or tetrasilylmethane[9], but also like the tetra-tert-butylphosphonium cation[10], where a conrotatory methyl, silyl, or tert-butyl "twist", respectively, lowers the symmetry
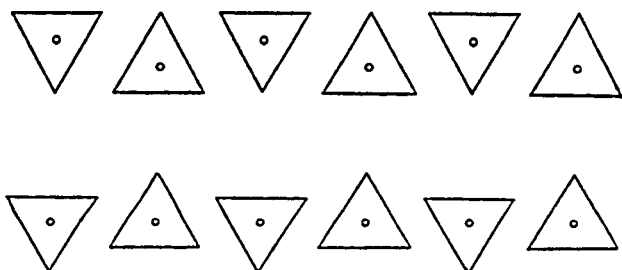

Figure 3. Conformational orientation of the peripheral silyl groups, a sequence of six threefold rotors drawn as equilateral triangles, (above) with the silicon atoms in the molecular plane (strained), and (below) with the displacement of the silicon atoms (up and down) from this plane (relaxed). In the experimentally confirmed structure there is a 3.5° twist of all silyl groups to further reduce the repulsive intramolecular interactions

from point group T_d to T. The deviation of the silicon positions in 6 away from the benzene plane is a direct consequence of the sequential ordering of the silyl threefold rotors with hydrogens (Figure 3). Studies of further structural details of 6 in the gas phase and at very low temperature are in progress. The energy characteristics and chemical behaviour are also under investigation.

Experimental

All experiments were carried out under pure, dry nitrogen. Solvents were purified, dried, and stored over molecular sieve under nitrogen. − NMR: Jeol GX 270 and 400. − IR: Nicolet FT 5 DX. − MS: Varian MAT 90 (EI, 70 eV).

Chloro(4-methoxyphenyl)silane (3): 4-(Methoxyphenyl)silane (2) (27.3 g, 0.20 mol) is dissolved in hexane (250 ml) and treated over a period of 8 h with a 1.44 M solution of boron trichloride in hexane (50 ml). After a total reaction time of 14 h at ambient temp. complete conversion is achieved (NMR). Volatile components are removed in vacuo at temperatures below 0°C. (Warning: At higher temperatures, strongly exothermic decomposition may occur with liberation of spontaneously inflammable silanes!) The residue is used without further purification. − ^{1}H NMR (C$_6$D$_6$): δ = 7.39 and 6.72, d each, J(H,H) = 8.67 Hz, C$_6$H$_4$; 5.12 s, SiH$_2$; 3.46 s, OMe. − ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ = 162.5, 136.3, 121.0, and 114.4, C$_6$H$_4$; 54.6, OMe. − ^{29}Si NMR (C$_6$D$_6$): δ = −18.1 t, J(Si,H) = 235.2 Hz. − MS: m/z (%) = 172 (100) [M$^+$].

Hexakis[(4-methoxyphenyl)silyl]benzene (4): A suspension of hexabromobenzene (12.0 g, 21.8 mmol) in tetrahydrofuran (300 ml) is added in small portions to a slurry of magnesium turnings (12.1 g, 0.5 g atom) in a boiling solution of 3 (34.0 g, 0.2 mol) in THF (250 ml) at such a rate, that the mixture continues to reflux in the condenser with reduced external heating. After complete addition and further refluxing for 10 h the mixture is poured onto crushed ice and neutralized with sodium hydrogen carbonate. 300 ml of ethyl acetate is added, the organic layer is separated, and the aqueous layer extracted with diethyl ether and chloroform (300 ml each). The combined organic extracts are dried with MgSO$_4$ and evaporated to leave a yellow solid, which is washed with hexane/diethyl ether (1:1) and crystallized from diethyl ether/chloroform. Yield 1.83 g (9.4%), m.p. 159°C. − ^{1}H NMR (CDCl$_3$): δ = 7.32 and 6.77, d each, J(H,H) = 8.57 Hz, C$_6$H$_4$; 5.08 s, SiH$_2$; 3.75 s, OMe. − ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 160.7, 150.9, 137.0, 122.3, C$_6$H$_4$; 54.9, OMe. − ^{29}Si NMR (CDCl$_3$): δ = −40.6 t, J(Si,H) = 198.0 Hz. − MS: m/z (%) = 894 (45) [M$^+$].

Hexakis[(trifluoromethylsulfonyloxy)silyl]benzene (5): A clear solution of 4 (0.40 g, 0.45 mmol) in toluene (25 ml) is cooled to −78°C and treated with trifluoromethanesulfonic acid (0.4 g, 2.67 mmol) with stirring. After 5 h the mixture is warmed to room temp. and cooled again to −18°C. Crystals of the product form, which are redissolved on warming. This solution is used for the preparation of 6. − ^{1}H NMR (CDCl$_3$): δ = 4.84 s, SiH$_2$. − ^{29}Si NMR (CDCl$_3$): δ = −17.5 t, J(Si,H) = 253.5 Hz.

Hexasilylbenzene (6): The solution of 5 (above) is slowly added to a suspension of LiAlH$_4$ (0.10 g, 2.64 mmol) in diethyl ether (25 ml). After completion of the addition the mixture is heated to reflux for 2 h and poured onto crushed ice mixed with sodium

hydrogen carbonate for neutralisation. The organic layer is separated and the aqueous phase extracted with hexane (100 ml) and diethyl ether (2 × 100 ml). The combined organic phases are dried with MgSO₄ and the solvents evaporated to leave a solid residue which is recrystallized from diethyl ether; yield 25 mg (22%), m.p. 165°C (subl.). − ¹H NMR (C₆D₆): δ = 4.40 s, SiH₃. − ¹³C NMR{¹H} (C₆D₆): δ = 148.15. − ²⁹Si NMR (C₆D₆): δ = −65.0 q, J(Si,H) = 204 Hz. − IR (KBr) [cm⁻¹]: 2158 s, 970, 942, 902 s, 702, 671, 694 s. − MS: m/z (%) = 258 [M⁺], 227 (100) [M⁺ − SiH₃].

C₆H₁₈Si₆ (258.7)   Calcd. C 27.36 H 6.97 Si 64.97
Found C 27.86 H 7.01 Si 65.13

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters for **6**; U(eq.) = $(U_1 \cdot U_2 \cdot U_3)^{1/3}$, where U_1, U_2, U_3 are the eigenvalues of the U_{ij} matrix (e.s.d.'s in parentheses)

ATOM	X/A	Y/B	Z/C	U(eq.)
Si1	0.15539(7)	0.25599(5)	0.87599(4)	0.024
C1	0.0537(2)	0.0994(2)	0.6619(1)	0.020
Si2	−0.28899(6)	0.35079(5)	0.63283(4)	0.025
C2	−0.1101(2)	0.1606(2)	0.5582(1)	0.020
Si3	0.34746(7)	−0.16450(6)	0.74183(4)	0.025
C3	0.1610(2)	−0.0630(2)	0.6034(1)	0.020

Crystal Data: C₆H₁₈Si₆, M_{rel} = 258.72, triclinic space group P1̄ (Nr. 2) with a = 5.822(1), b = 7.113(1), c = 9.553(1) Å, α = 108.40(1), β = 104.10(1), γ = 97.91(1)°, V = 354.04 Å³, Z = 1, d_{calc} = 1.213 gcm⁻³; μ(Mo-$K_α$) = 5.375 cm⁻¹, 1872 measured reflections, 1866 unique, 1774 observed with $F_o \geq 4\sigma F_o$, hkl range

±7, ±9, 13, sinϑ/λ_max = 0.6815 Å⁻¹; absorption correction, T (min/max) = 0.9939/0.999. Solution by direct methods (SHELXS 86). All atomic positions found and refined, 136 parameters (SHELX 76), R (R_w) = 0.022 (0.028). Δ_fin (max/min) 0.035/−0.23 eÅ⁻³. Supplementary material has been deposited and may be obtained on request from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-56307, the names of the authors, and the journal citation.

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