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Pericyclynosilanes: Single Crystal X-ray Structure of Dodecamethyl(6)pericyclynosilane, $(Me_2SiC\equiv C)_6$

ROBERTO BORTOLIN, SCOTT S. D. BROWN
and BHUKAN PARBHOO

*Dow Corning Research Group, School of Molecular Sciences,
University of Sussex, Brighton BN1 9QJ, U.K.*

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Pericyclynosilanes are cyclic compounds composed of alternating R_2Si and $C\equiv C$ units [1]. The X-ray structure of the pericyclynosilane 3,3,6,6,9,9,-12,12,15,15,18,18-dodecamethyl-3,6,9,12,15,18-hexasilacyclooctadeca-1,4,7,10,13,16-hexayne, which we report here, is the first for this class of organosilicon compounds. Experimental and theoretical investigations on the interaction between π-MOs of acetylene groups, separated by Me_2C units, have been reported and the importance of homoconjugation and heteroconjugation in pericyclynes has been assessed [2]. The presence of Me_2Si units between acetylene groups would provide additional bonding and structural aspects in novel cyclic non-conjugated systems.

Experimental

Preparation

The synthesis of $(Me_2SiC\equiv C)_n$ has already been reported [1]. Sublimation of $(Me_2SiC\equiv C)_n$ gives a mixture of $(Me_2SiC\equiv C)_{4,5,6}$. Slow evaporation of a THF–toluene solution of the sublimate affords clear colorless monoclinic crystals of dodecamethyl(6)-pericyclynosilane.

Crystallographic Data

X-ray diffraction data for $C_{24}H_{36}Si_6 \cdot 2C_4H_8$ are: $FW = 637.3$, space group $C2/m$; $a = 13.896(9)$, $b = 27.365(9)$, $c = 5.980(5)$ Å; $\beta = 103.37(6)°$, $U = 2212.4$ Å^3, $Z = 2$, $D_{calc} = 0.96$ g cm^{-3}. Data were collected using a crystal 2.0 × 0.1 × 0.15 mm on an Enraf-Nonius CAD4 diffractometer, using monochromated Mo Kα radiation ($\lambda = 0.71069$ Å, $\mu = 2.0$ cm^{-1}) in the θ–2θ mode with $\Delta\theta = (0.8 + 0.35\tan\theta)°$ and a maximum scan time of 1 min. A total of 1588 unique reflections were measured for $2 < \theta < 23°$ and $+h + h \pm l$, and 1118 reflections with $|F^2| > \sigma(F^2)$ were used in the refinement, where $\sigma(F^2) = \{\sigma^2(I) + (0.04I)^2\}^{0.5}/Lp$. There was no crystal decay and no absorption correction was made. The structure was solved by direct methods using MULTAN [3], revealing a molecule of $(Me_2SiC\equiv C)_6$ lying on a site of $2/m$ symmetry and a molecule of tetrahydrofuran lying on a two-fold rotation axis. Refinement of non-hydrogen atoms with anisotropic temperature factors was by full-matrix least-squares. A difference map revealed electron density up to 1.7e Å^{-3} near the tetrahydrofuran molecule, which was interpreted as partial occupancy of the solvent site by a toluene molecule. The methyl carbon atom of the toluene was included in the least-squares with a fixed B_{iso} of 8.0 Å^2 and a variable occupancy which refined to a value of 0.3. The other atoms of the toluene which lie close to those of the tetrahydrofuran were omitted. No hydrogen atoms could be located and all were omitted from the model. The weighting scheme was $w = 1/\sigma^2(F)$ and the final residues were $R = 0.085$ and $R = 0.125$, the rather high values reflecting the problems with the solvent disorder. Programs from the Enraf-Nonius SDP-Plus package were run on a MicroVase computer. Important bond lengths and angles are reported in Table 1.

Results and Discussion

The structure of $(Me_2SiC\equiv C)_6$ (Fig. 1) consists of an eighteen-membered ring of hexagonal geometry which adopts a chair conformation; it shows that the insertion of $C\equiv C$ units into adjacent Me_2Si groups of the cyclic $(Me_2Si)_6$ retains the overall geometry of the ring [4]. Figure 2 shows a computer-generated perspective drawing of the X-ray structure with some structural parameters of the molecule. The side Si(1)–Si(2) has a total length $a = 4.847(3)$ Å, which is slightly different from the side Si(2)–Si(2)′ with a length $b = 4.867(3)$ Å. The atoms Si(2)C(5)C(5)′-Si(2)′ and Si(2)″C(5)″C(5)‴Si(2)‴ lie on the same plane with a deviation of 0.003 Å. The valence angles at the silicon (Me)C–Si–C(Me) are larger than tetrahedral (110.9°–112.8°), but smaller for ≡C–Si–C≡ (107.5°–107.8°), while the (Me)-C–Si–C≡ are close to tetrahedral values (108.1°–109.2°). Because the angles at the ≡C–Si–C≡ are smaller than tetrahedral, the acetylene groups around the ring are slightly bent inward. This is evidenced by the transannular distance (Fig. 2) Si(2)″Si(2), $c = 8.039(3)$ Å, which is larger than the distance C(5)C(5)″, $d = 7.826(9)$ Å. The torsional angles Si(1)Si(2)Si(2)Si(1) and Si(2)Si(1)Si(2)Si(2) have values of 56.93° and −58.50° respectively, while the dihedral angle between the planes formed by Si(2)Si(2)′Si(2)″Si(2)‴ and Si(2)′Si(1)′Si(2)‴ is 53.5°. The torsion angle of the equatorial carbons C(6)Si(2)–Si(2)′C(6)′ has an average value of 46° while the torsion angle of the two axial carbons C(7)Si(2)–Si(2)′C(7)′ has an average value of 168°.

These values have a large deviation from the tetrahedral geometry at the carbons of a regular cyclohexane ring of 60° and 180°, but the same angular distortions have been observed at the silicon [4] in

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TABLE I. Intramolecular Distances (Å) and Angles (°) with Estimated Standard Deviations in Parentheses

(a) Bonds			
Si(1)–C(1)	1.808(7)	Si(1)–C(3)	1.857(13)
Si(1)–C(4)	1.821(12)	Si(2)–C(2)	1.829(7)
Si(2)–C(5)	1.826(7)	Si(2)–C(6)	1.865(8)
Si(2)–C(7)	1.837(7)	C(1)–C(2)	1.218(9)
C(5)–C(5)'	1.222(9)	C(9)–C(9)'''	1.568(13)
O–C(8)	1.435(12)	O–C(10)	1.58(2)
C(8)–C(9)	1.55(2)		
(b) Angles			
C(1)–Si(1)–C(1)''	107.5(3)	C(1)–Si(1)–C(3)	110.0(3)
C(1)–Si(1)–C(4)	109.2(3)	C(3)–Si(1)–C(4)	110.9(6)
C(2)–Si(2)–C(5)	107.8(3)	C(2)–Si(2)–C(6)	108.1(3)
C(2)–Si(2)–C(7)	110.4(3)	C(5)–Si(2)–C(6)	109.0(3)
C(5)–Si(2)–C(7)	108.6(3)	C(6)–Si(2)–C(7)	112.8(4)
Si(1)–C(1)–C(2)	174.8(5)	Si(2)–C(2)–C(1)	177.3(5)
Si(2)–C(5)–C(5)'	176.7(6)	C(8)–O–C(8)'''	113(1)
O–C(8)–C(9)	108.1(8)	C(8)–C(9)–C(9)'''	105.4(8)
C(8)–O–C(10)	123.5(6)		
(c) Torsion angles			
Si(1)–Si(2)–Si(2)–Si(1)	56.93(4)		
Si(2)–Si(1)–Si(2)–Si(2)	–58.50(6)		

$(Me_2Si)_6$ and α–α′-silaalkadiynes [5]. The range of values of bond lengths in $(Me_2SiC{\equiv}C)_6$ are: Si–C(Me), 1.821(12)–1.865(8) Å; Si–C≡, 1.808(7)–1.829(7) Å; and C≡C, 1.218(9)–1.222(9) Å. The Si–C(Me) bond lengths are within expected values. The equatorial carbons C(6) and C(3) are equivalent, the Si–C(eq-Me) bond length is in the range 1.857(3)–1.865(8) Å, while the axial carbons C(4) and C(7) are equivalent with a slightly shorter Si–C(ax-Me) distance of 1.821(12)–1.837(7) Å. The Si–C(acetylene) bond distances are shorter than in related cyclic compounds. In cyclic α,α′-silaalkadiynes [5] the average Si–C(acetylene) bond length is 1.843(1) Å and in 3,4,7,8-tetrasila-1,5-diyne [6] the Si–C(acetylene) distances are in the range 1.838–1.848 Å. The C≡C bond distances are within the range reported in α–α′-silaalkadiynes [5] (1.217(1) Å), but longer than in cyclic organic alkynes (1.18–1.19 Å) and in 3,4,7,8-tetrasila-1,5-diyne (1.182–1.183 Å) [6].

The X-ray analysis of $(Me_2SiC{\equiv}C)_6$ shows that the molecule is virtually free from angle and torsional strain and that homoconjugation has no consequence on the structure. Preliminary investigation on the reactivity of pericyclynosilanes shows an unusual stability of the C≡C towards electrophilic addition (no reaction with Br_2 and HBr) and the easy splitting of the Si–C≡ bond by attack of nucleophiles on the silicon. We are currently working on the isolation and identification of cyclic homologs with different ring sizes and substituents on the silicon, and are investigating reactivity, coordination chemistry and ring-opening polymerization of pericyclynosilanes.

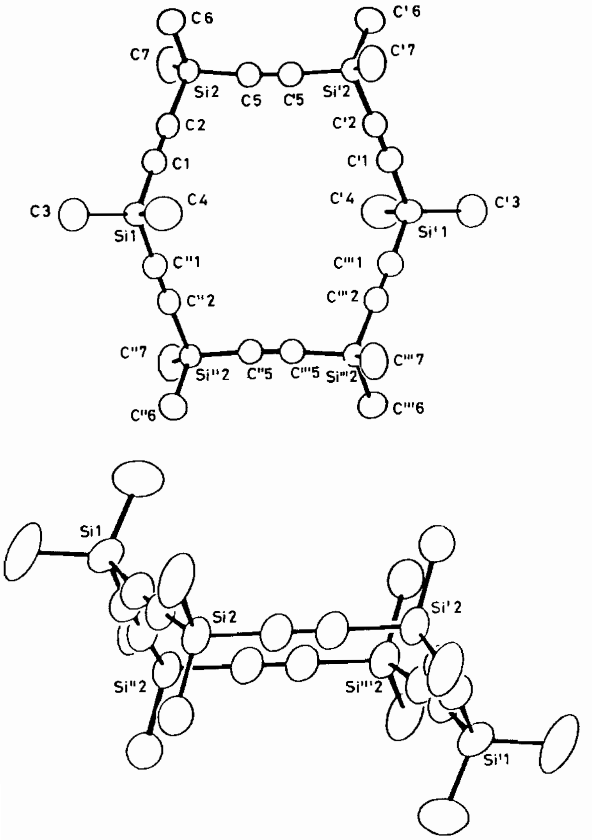

Fig. 1. ORTEP labeling diagram and perspective diagram for $(Me_2SiC{\equiv}C)_6$. The ellipsoids of thermal vibration are at 50% probability.

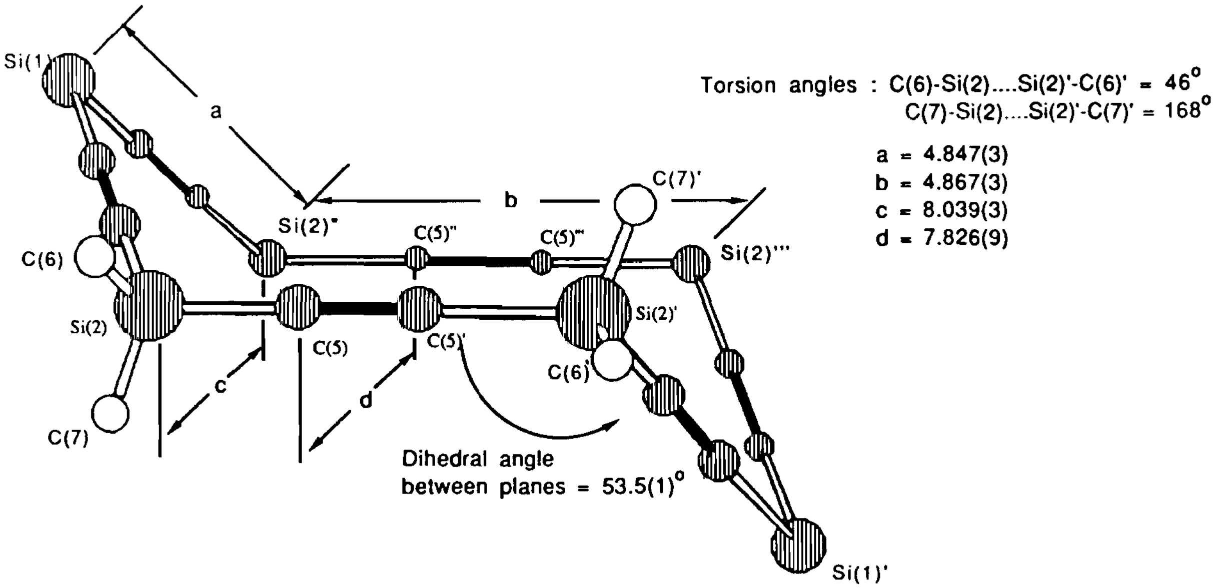

Fig. 2. Perspective drawing of the X-ray structure of $(Me_2SiC{\equiv}C)_6$ with some structural dimensions and angles.

Supplementary Material

Tables of crystal data, anisotropic temperature factors, fractional atomic coordinates and least-squares planes are available from the authors on request.

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