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SYNTHESIS AND STRUCTURE OF PENTASILACYCLOHEPTYNE

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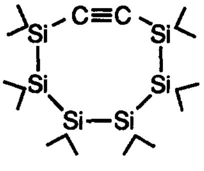
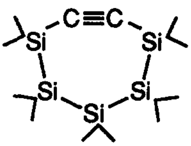
Abstract: Pentasilacycloheptyne 2 was synthesized by photolysis and thermolysis of hexasilacyclooctyne 1 which was obtained from the reaction of 1,6-dichlorododecamethylhexasilane with acetylene di-Grignard reagent. The molecular structure of 2 was determined by X-ray analysis.

Medium ring cycloalkynes have been the subject of considerable interest because there are bond-angle strains on the *sp* carbons.[1] Many strained cycloalkynes have been generated as the reactive intermediates and theoretically studied.[2] Heterocyclic alkynes were also studied.[3] However, few representatives of medium ring polysilacycloalkynes have been so far reported in the literature.[4] We will report here the synthesis of the first molecules of polysilacyclo-monoalkyne namely, hexasilacyclooctyne 1 and pentasilacycloheptyne 2, which are expected to be strain-free by a long Si-Si bond in comparison with the carbon analogue. We will also report the X-ray determined structure of 2.

A reaction of 1,6-dichlorododecamethylhexasilane with acetylene di-Grignard reagent under dilute conditions gave 3,3,4,4,5,5,6,6,7,7,8,8-dodecamethyl-3,4,5,6,7,8-hexasilacyclooctyne 1 in 46% yield. The cyclooctyne 1 was stable colorless liquid which showed a ^{13}C NMR signal of the acetylene carbons at 118ppm.[5] A preparative entry to 2 was accomplished by photofragmentation of 1. The photolysis of hexane solution of 1 with low-pressure mercury lamp in the presence of triethylsilane gave 3,3,4,4,5,5,6,6,7,7-decamethyl-3,4,5,6,7-pentasilacycloheptyne 2 in 22% yield after purification by silica gel chromatography. The cycloheptyne 2 thus obtained was colorless crystals (m.p. 43-45°C), which was stable even under atmospheric oxygen and moisture. The cycloheptyne 2 could be also obtained by thermolysis (550°C) in 18% yield. The spectral data of 2 are consistent with the proposed structure,[6] that is, the ultraviolet absorption maximum at 229 nm in hexane and the ^{13}C NMR signal of the acetylene carbons at 123ppm, which is lower than the corresponding carbons of 1. It may be attributable to decrease of the bond order of the triple bond due to the bond-angle strains of the acetylene carbons.


1


2

The molecular structure of 2 could be established by X-ray analysis shown in Figure 1.[7] The Si-Si, Si-C, and C≡C bond lengths are normal and ranged between 2.340-2.353, 1.80-1.84, and 1.22Å, respectively. However, there is interestingly an alternation in the bond angle around the polysilane chain; the bond angles of C(1)-C(2)-Si(1), C(2)-C(1)-Si(5), C(2)-Si(1)-Si(2), and C(1)-Si(5)-Si(4) are contracted, and those of

Si(1)-Si(2)-Si(3) and Si(3)-Si(4)-Si(5) are normal while those of Si(2)-Si(3)-Si(4) is considerably expanded from the normal bond angles. The most interesting point in the structure of **2** is of course the bending of the acetylene bond from linear geometry, which is represented by the bending angles θ_1 and θ_2. The bending angles of θ_1 and θ_2 of the compound **2** are 20.4 and 17.8°, respectively, which are comparable with those observed in the non-substituted cyclooctyne (θ = 21.5°)[8] and cyclononyne (θ = 19.8°)[9]. Apparently, the structure of **2** reveals that the magnitude of the bending in acetylene decreases, but the increase the deformation of polysilane chain is definitely noticeable. The observations are explained by high flexibility of the conformation in the polysilane chain.

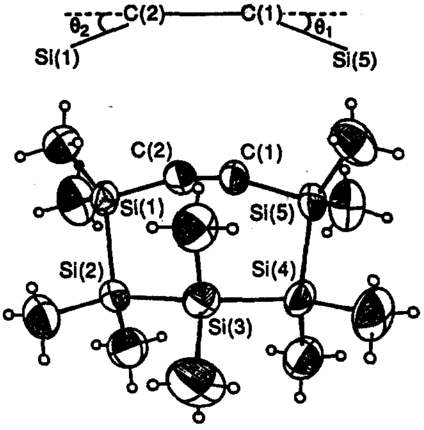


Figure 1. ORTEP plot of 2

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5. Spectral data of **1**: ^{1}H-NMR (500MHz, $CDCl_3$) δ 0.15 (12H,s), 0.17 (12H,s), 0.20 (12H,s). ^{13}C-NMR (125MHz, $CDCl_3$) δ –5.97, –4.88, –2.84, 117.98. ^{29}Si-NMR (18MHz, C_6D_6) δ -39.36, -38.61, -35.52. UV (hexane) λ_{max} 235 (ε 9720) nm. HRMS found: m/z 372.1426, calcd for $C_{14}H_{36}Si_6$: 372.1433.
6. Spectral data of **2**: ^{1}H-NMR (500MHz, $CDCl_3$) δ 0.17 (18H,s), 0.19 (12H,s). ^{13}C-MNR (125MHz, $CDCl_3$) δ -5.98, -5.86, -3.11, 123.24. ^{29}Si-NMR (18MHz, C_6D_6) δ -38.20, -34.29, -33.26. UV (hexane) λ_{max} 229 (ε 10200) nm. HRMS found: m/z 314.1186, calcd for $C_{12}H_{30}Si_5$: 314.1194.
7. A data set was collected at room temperature on an Enraf-Nonius CAD4 diffractometer. $C_{12}H_{30}Si_5$, fw = 314.80 are monoclinic with a = 7.902(4)Å, b = 12.723(4)Å, c = 10.700(6)Å, β = 101.27(4)°, V = 1054.8Å^3, space group P21, Z = 2, ρcal = 0.99 gcm^{-3}. Structure was solved by direct methods using 1431 unique reflections with $I > 3.0\sigma(I)$ and all non-hydrogen atoms were refined anisotropically to R = 0.077 and Rw = 0.095. Ideal position of hydrogen atoms were calculated and added to the refined structure shown in Figure 1. Selected bond lengths (Å) and angles (°) of **2**: C(1)-C(2) = 1.22(1), C(2)-Si(1) = 1.80(1), Si(1)-Si(2) = 2.340(4), Si(2)-Si(3) = 2.353(4), Si(3)-Si(4) = 2.342(5), Si(4)-Si(5) = 2.351(4), Si(5)-C(1) = 1.84(1), Si(5)-C(1)-C(2) = 159.6(9), C(1)-C(2)-Si(1) = 162.2(8), C(2)-Si(1)-Si(2) = 100.4(3), Si(1)-Si(2)-Si(3) = 108.7(1), Si(2)-Si(3)-Si(4) = 117.4(2), Si(3)-Si(4)-Si(5) = 109.9(2), Si(4)-Si(5)-C(1) = 101.7(4).
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