Short C–C Bonds

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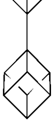
Hexakis(trimethylsilyl)tetrahedranyltetrahedrane**

*Masanobu Tanaka and Akira Sekiguchi**

The most important factor for bond shortening is the increase in s character of the bond orbital.[1] In 1988, Eaton and coworkers succeeded in the synthesis and structural characterization of cubylcubane (**1**).[2] The bond length between the two cubane units (1.458 Å) was significantly shorter than the usual carbon–carbon single-bond length (1.54 Å). This bond shortening was attributed to the high s character of the bond orbitals. Later, Ermer et al. synthesized coupled bicyclo[1.1.0]butane derivatives **2** and **3**,[3] in which the corresponding C–C bonds have higher s character than that in cubylcubane. As expected, the linking C–C bond lengths in these coupled bicyclo[1.1.0]butane derivatives are further shortened (1.445 and 1.440 Å). Tetrahedrane is the most strained cage compound with the highest degree of s character in the exocyclic bond. Therefore, the linking C–C bond length in tetrahedranyltetrahedrane (**4**) is expected to be even shorter. Indeed, theoretical studies suggest compound **4** as a candidate for the molecule with the shortest carbon–carbon single bond in a saturated hydrocarbon system.[4] However, treatment of substituted tetrahedranes is extremely difficult because of its high strain and, consequently, high reactivity.[5,6] Until now, no tetrahedranyltetrahedrane derivative has been synthesized.



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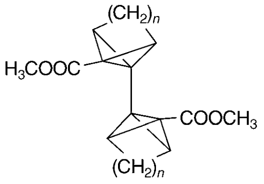
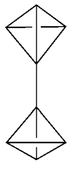


2: $n=2$
3: $n=3$



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Recently, we succeeded in the synthesis and characterization of trimethylsilyl-substituted tetrahedrane derivatives.[7,8] Electropositive silyl groups significantly release the inherent ring strain of the tetrahedrane skeleton. For

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[*] Dr. M. Tanaka, Prof. Dr. A. Sekiguchi
Department of Chemistry
Graduate School of Pure and Applied Sciences
University of Tsukuba
Tsukuba, Ibaraki 305-8571 (Japan)
Fax: (+81) 298-53-4314
E-mail: sekiguch@staff.chem.tsukuba.ac.jp

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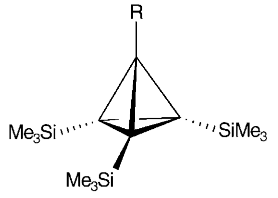
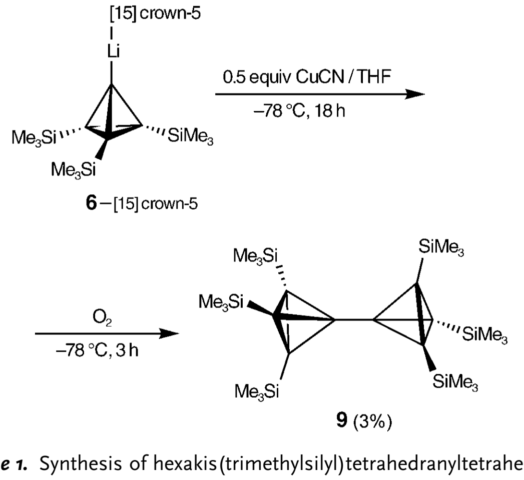


5: R = $SiMe_3$
6: R = Li
7: R = CH_3
8: R = H
9: R = $C_4(SiMe_3)_3$

example, tetrakis(trimethylsilyl)tetrahedrane (**5**) is stable in the presence of air and moisture at temperatures up to 300 °C. We also synthesized and isolated tetrahedranyllithium **6** as a thermally stable compound which is a good precursor for other tetrahedrane derivatives.[8] Indeed, we succeeded in the synthesis of methyl- and hydrogen-substituted tetrahedranes (**7** and **8**, respectively) from tetrahedranyllithium. Surprisingly, tetrahedranes with smaller substituents and hence a lower steric protection were stable in air and at temperatures up to 100 °C. In the ^{1}H NMR spectrum of hydrogen-substituted tetrahedrane **8**, a very large ring C–H coupling constant was observed which is comparable to that of acetylene. From the empirical correlation, we estimated the s character of the ring C–H bond to be 48 %.[8] These results indicate that the C–C link should also have high s character and a very short C–C bond in silyl-substituted tetrahedranyltetrahedrane. Herein, we report the synthesis of hexakis(trimethylsilyl)-tetrahedranyltetrahedrane (**9**) as well as the structural characterization by X-ray crystallography.

Tetrahedrane **9** was synthesized by the oxidative coupling of **6** via a cuprate complex (Scheme 1). First, tetrahedranyllithium **6** was prepared by the reaction of **5** with excess methyllithium in THF, and the ligand of **6** was changed from THF to [15]crown-5 to remove the remaining methyllithium completely. Reaction of **6** with CuCN (0.5 equiv) at −78 °C in THF gave the cuprate complex, which was subsequently oxidized with oxygen at −78 °C. The reaction mixture was purified consecutively by gel-permeation chromatography (toluene) and HPLC (MeOH/*t*BuOMe 1:1) equipped with a recycling system, and finally **9** was isolated as a colorless solid in 3 % yield in a pure form. Several other methods to synthesize **9** by the oxidation of **6** with various reagents such as dichlorodicyano-*p*-benzoquinone, tetracyano-*p*-benzoquinone, $NO^+PF_6^-$, and $(C_6F_5)_3B$ were performed; however, no trace amount of **9** was formed.



Scheme 1. Synthesis of hexakis(trimethylsilyl)tetrahedranyltetrahedrane (**9**).

Compound **9** was stable in air and up to 200 °C. The most important stabilizing factor can be attributed to the electronic effect of the trimethylsilyl groups, as found in **5**.[7] The ^{1}H, ^{29}Si, and ^{13}C NMR spectra of **9** in [D$_6$]benzene demonstrated its high symmetry. Only one signal was observed for the trimethylsilyl groups in the ^{1}H NMR ($\delta = 0.22$ ppm) and ^{29}Si NMR ($\delta = -2.5$ ppm) spectra, and three signals appeared at $\delta = -18.0$ (ring C–Si), −4.7 (linking ring C), and 0.07 ppm ($SiMe_3$) in the ^{13}C NMR spectrum. The large upfield shift of the ring C atom is typical for tetrahedrane.[7–10] The linking carbon atom shows a remarkably downfield shift relative to that of the silicon-substituted skeletal carbon atom because of the different electronegativities of the Si and C substituents and the high s character of the linking carbon atoms.

The molecular structure of tetrahedranyltetrahedrane **9** was determined by X-ray crystallographic analysis without disorder phenomena. X-ray-quality single crystals were obtained by crystallization from ethanol at 5 °C. As shown in Figure 1,[11] the bulky trimethylsilyl groups sterically

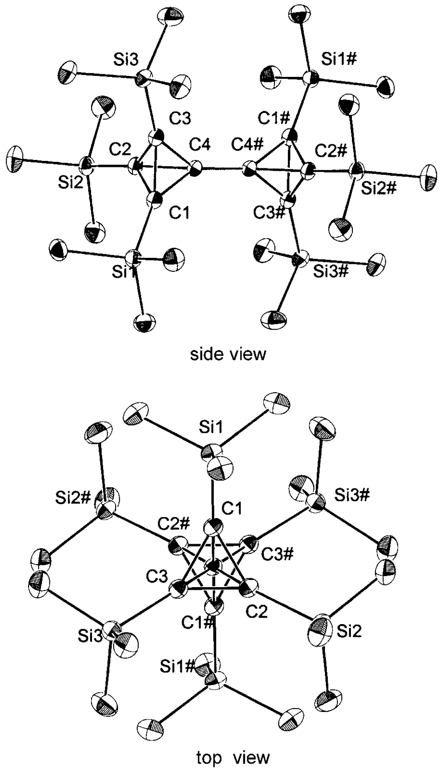


Figure 1. Structure of **9** (ORTEP plot; thermal ellipsoids set at 30 % probability; hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: C1–C2 1.523(2), C1–C3 1.528(2), C1–C4 1.483(2), C2–C3 1.511(2), C2–C4 1.484(2), C3–C4 1.484(2), C4–C4# 1.436(3), Si1–C1 1.8260(18), Si2–C2 1.8271(18), Si3–C3 1.8250(19); C4-C1-C2 59.13(11), C4-C1-C3 59.05(11), C2-C1-C3 59.39(11), C4-C1-Si1 153.45(14), C2-C1-Si1 140.76(13), C3-C1-Si1 140.42(14), C1-C4-C2 61.76(11), C1-C4-C3 61.97(11), C2-C4-C3 61.21(11), C4#-C4-C1 144.5(2), C4#-C4-C2 142.8(2), C4#-C4-C3 143.87(19).

protect the tetrahedranyltetrahedrane skeleton, and the two tetrahedrane units have a staggered conformation owing to steric repulsion.

As expected, the linking C–C bond length (1.436(3) Å) is shortened considerably, and this experimental value of the bond length is practically identical to the theoretical one.[4] To our knowledge, this is the shortest noncyclic (unbent) C–C single bond between saturated C atoms observed to date. The calculated s character of the linking C–C bond in **9** at the NBO/B3LYP/6-31G level is $sp^{1.53}$, which supports the suggestion that this shortening arises from the high s character of the bond. When the electronegativity increases (from Si to C), the s character of the exocyclic bond decreases. This electronic effect changes the structure of the tetrahedrane skeleton.[12] Whereas tetrahedrane **5** has a regular tetrahedral structure, the tetrahedrane units in **9** have a distorted tetrahedral structure. The endocyclic $C(C)-C(SiMe_3)$ bond lengths (C4–C1, C4–C2, C4–C3) in **9** range from 1.483(2) to 1.484(2) Å (average 1.484(2) Å), whereas the endocyclic $C(SiMe_3)-C(SiMe_3)$ bond lengths (C1–C2, C1–C3, C2–C3) range from 1.511(2) to 1.528(2) Å (average 1.521(2) Å), which are longer than those of C–C bond lengths of tetrahedrane **5** (average 1.501(4) Å). The endocyclic $C(SiMe_3)-C(SiMe_3)$ bond lengths of **9** (average 1.521(2) Å) are somewhat longer than those of **5** (average 1.501(4) Å) and $\mathbf{6}\cdot(\text{tmeda})_{1.5}$ (average 1.4986(15) Å).

It is interesting to compare the lengths of the endocyclic $C(SiMe_3)-C(R)$ bond: $R = Li$ for **6** (average 1.5425(15) Å), $R = SiMe_3$ for **5** (average 1.501(4) Å), $R = C_4(SiMe_3)_3$ for **9** (average 1.484(2) Å); certainly, the electronegativity of R affects the structural features of the tetrahedrane skeleton. In the case of the most electropositive Li atom the $C(SiMe_3)-C(Li)$ bond has a high p character, thus leading to the elongation of the C–C bond, whereas in the case of more-electronegative substituents (from $SiMe_3$ to $C_4(SiMe_3)_3$) the tendency is the opposite: increase in s character and shortening of the C–C bond.

Experimental Section

9: Tetrakis(trimethylsilyl)tetrahedrane (**5**)[7] (53 mg, 0.16 mmol) and a tenfold excess of methyllithium were placed in a reaction tube. Dry oxygen-free THF (3.0 mL) was introduced by vacuum transfer and stirred for 24 h. After the solvent was removed, dry oxygen-free hexane (5 mL) was introduced and the insoluble methyllithium in hexane was filtered through celite in a glove box. [15]Crown-5 (0.03 mL) was introduced as a solution in hexane, and the deposited methyllithium was filtered through celite in a glove box. The solvent was placed in a reaction tube and removed in vacuo. The colorless solid **6** was obtained. CuCN (4.5 mg, 0.05 mmol) was added to the reaction tube and dry oxygen-free THF (4 mL) was introduced by vacuum transfer and stirred at −78 °C for 18 h, and oxygen gas was bubbled in the solution at −78 °C. After the solvent was removed, the reaction mixture was purified by gel-permeation chromatography (toluene) and HPLC (MeOH/*t*BuOMe 1:1) equipped with a recycling system. The solvent was removed in vacuo and **9** was obtained as a colorless solid (2.5 mg, 3 %); m.p. 209–211 °C; ^1H NMR (400 MHz, $[D_6]$benzene, TMS): $\delta = 0.22$ ppm (s, 54 H, $SiMe_3$); $^{13}C\{^1H\}$ NMR (100 MHz, $[D_6]$benzene, TMS): $\delta = -18.0$ (C), -4.7 (C), 0.07 ppm ($SiMe_3$); $^{29}Si\{^1H\}$ NMR (80 MHz, $[D_6]$benzene, TMS): $\delta = -2.5$ ppm; MS (70 eV, EI): *m/z*: 534 [M^+], 461 [$M^+ - SiMe_3$], 73 ($SiMe_3$); HRMS: calcd for $C_{26}H_{54}Si_6$: 534.2841; found: 534.2806. The very low yield of **9** is due to the formation of tetrahedrane **5** and hydrogen-substituted tetrahedrane **8**, which were also produced under the reaction conditions together with **9**.

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[11] Crystal structure analysis of **9**: single crystals were grown from a solution in ethanol. A colorless crystal ($\approx 0.4 \times 0.3 \times 0.2$ mm^3) was used for X-ray diffraction data collection on a MacScience DIP2030 K Image Plate Diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71070$ Å). Crystal data for **9** at 120 K: $C_{26}H_{54}Si_6$, $M_r = 535.23$, triclinic, space group $= P\bar{1}$, $a = 9.5100(7)$, $b = 10.0500(9)$, $c = 11.6350$ (12) Å, $\alpha = 102.488(5)$, $\beta = 104.540(5)$, $\gamma = 114.754(5)°$, $V = 909.8(1)$ Å^3, $Z = 1$, $\rho_{calcd} = 0.997$ g cm^3, total reflections collected = 9434, unique reflections = 4051 ($R_{int} = 0.029$), $2\theta_{max} = 56.06$, completeness to $\theta = 91.9$ %, GOF = 1.042. The final *R* factor was 0.0471 ($R_W = 0.1367$ for all data) for 3325 reflections $I_o > 2\sigma(I_o)$. The structure was solved by direct methods and refined by the full-matrix least-squares method by using the SHELXL-97 program. CCDC-265873 contains the supplementary crystallographic data for **9**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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