Tetrakis(trimethylsilylbutadiynyl)ethene, $C_{18}(SiMe_3)_4$: An Extended Two-Dimensional π-Conjugated System Consisting of Eighteen Carbon Atoms

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Tetrakis(trimethylsilylbutadiynyl)ethene, $C_{18}(SiMe_3)_4$, containing an extended two-dimensional (2-D) π-conjugated carbon system has been prepared and characterized by spectroscopic and crystallographic methods.

Polycarbon systems associated with π-conjugated systems are expected to display unique physical properties, which are potentially applicable to materials science.[1] The studies on 1-D system (e.g. molecular wire) are followed by those on 2- and 3-D systems, which are relevant to carbon allotropes (e.g. graphite, diamond, and fullerenes) and would lead to more sophisticated systems such as molecular switch based on the higher dimensionality.[2] Ethene and benzene are two representative structural motifs 2-D of carbon systems (Chart 1) and their alkynylated derivatives with extended π-systems have been synthetic targets. Free polyethynylated species (R = H) are versatile precursors but, because of their potential detonative property, silyl derivatives ($R = SiR'_3$), which are readily deprotected in situ by treatment with F^- or base, are frequently employed as masked acetylenes. Tetraethynylethenes ($\mathbf{A^1}$) including silyl derivatives ($R = SiR'_3$) have been studied intensively by Diederich,[2b–d] and preparation of $\mathbf{B^{1,2}}$-derivatives was reported by Vollhardt.[3] Herein we wish to describe results of synthesis and characterization of tetrakis(trimethylsilylbutadiynyl)ethene **1** [$\mathbf{A^2}(R = SiMe_3)$].

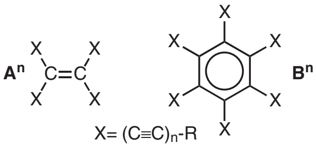
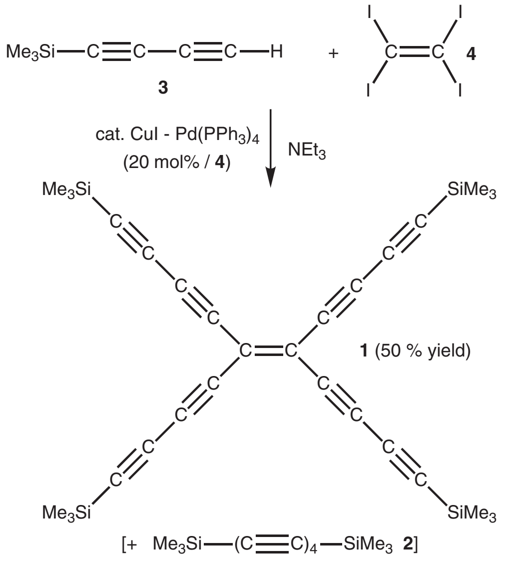


Chart 1.

Tetrakis(trimethylsilylethynyl)ethene $\mathbf{A^1}(R = SiMe_3)$, the ethynyl derivative of **1**, mentioned above was prepared via dehydrogenation of the tetraethynylethane derivative[2a] or a reaction sequence including Sonogashira coupling of $Me_3Si\text{-}C{\equiv}C\text{–}H$ with $Br_2C{=}C(C{\equiv}C\text{–}SiMe_3)_2$ at the final stage,[2b] but Low et al. recently reported short-cut, direct Sonogashira coupling between $Me_3Si\text{–}C{\equiv}C\text{–}H$ and tetrachloroethene.[4]

The title compound **1** [$A^2(R = SiMe_3)$] was prepared following the direct coupling method (Scheme 1). A NEt_3 solution of trimethylsilylbutadiyne **3**[5a] and tetraiodoethene **4** was stirred for 24 h at ambient temperature in the presence of a catalytic amount of $Pd(PPh_3)_4$ (20 mol % based on **4**) in the dark. The resultant mixture was evaporated, extracted with ether and filtered through a silica gel plug to remove salts. NMR analysis of the resultant filtrate revealed formation of two products, which were separated by silica gel column chromatography (eluted with pentane). The desired product **1** was eluted as the second band and isolated in 50% yield as yellow powders, and the by-product eluted first was 1,8-bis(trimethylsilyl)-1,3,5,7-octatetrayne **2** (the dehydrogenative oxidative-coupling product of **3**) as identified by comparison of its spectroscopic data with the reported one.[6] (**CAUTION!** Compound **1** could be purified by crystallization from THF–MeOH or pentane. However, while handling a crystallized sample, we experienced slow decomposition accompanying light emission, which formed black powders. The preparation, therefore, should be carried out in a small scale, with satisfactory protection, behind a safety shield, in a hood and with great caution. The chromatographic separation followed by evaporation gave a spectroscopically pure sample.) Use of tetrachloroethene instead of **4** did not give **1**.



Scheme 1.

The new compound **1** is readily characterized on the basis of its simple NMR features consistent with a D_{2h} symmetrical structure. A ^{1}H NMR spectrum of **1** contains a single singlet signal for the $SiMe_3$ groups [$\delta_H(CDCl_3)$ 0.23 (36H)]. In a ^{13}C NMR spectrum, four alkynyl carbon signals are located at δ_C 72.3, 85.9, 87.3, and 98.9 in addition to the olefinic carbon signal (δ_C 119.4) and the Me signal for the $SiMe_3$ group (δ_C −0.4). Although the olefinic signal is comparable to that for $\mathbf{A^1}(R = SiMe_3)$ (δ_C 118.8),[2b] the alkynyl carbon signals of **1** are slightly shielded compared with those of $\mathbf{A^1}(R = SiMe_3)$ (δ_C 101.0, 105.3) but appear in the range comparable to that for polyynyl compounds such as $X\text{–}(C{\equiv}C)_2\text{–}H$ [$X = SiMe_3$: δ_C 68.9, 69.2, 83.1, 88.7;[5a] $Fe(\eta^5\text{-}C_5Me_5)(CO)_2$: δ_C 53.5, 71.9, 92.8, 105.4][7] and $X\text{–}(C{\equiv}C)_4\text{–}X$ [$X = SiMe_3$ (**2**): δ_C 62.1, 68.0, 87.8, 88.0;[5a] $Fe(\eta^5\text{-}C_5Me_5)(CO)_2$: δ_C 51.4, 61.6, 94.8, 110.8].[7] $\nu_{C\equiv C}$ vibra-

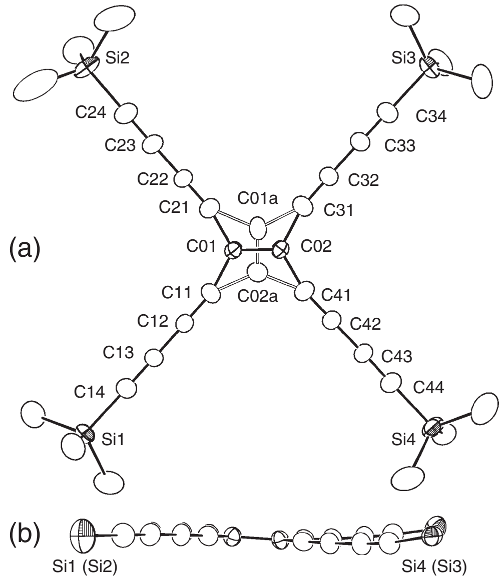


Figure 1. ORTEP views of **1** drawn with thermal ellipsoids at the 30% probability level. (a) an overview. C01a, C02a: minor components of the disordered structure.[8] (b) a side view of the core part.

tions (KBr pellet) are located at 2204 (w), 2180 (w), and 2095 cm^{-1} (vs), and a molecular ion peak ($m/z = 508$) is detected by FAB-MS.

Molecular structure of **1** is characterized by X-ray crystallography (Figure 1).[8] Because the molecule, in particular, the central olefinic part, is disordered with respect to the C_2 axis perpendicular to the olefinic plane, detailed discussion on the structural parameters cannot be made. But clear bond alternation for single, double and triple bonds is apparent [C(01)–C(02): 1.397(6), C(01, 02)–C(n1): 1.438–1.449(7), C(n1)–C(n2): 1.181–1.194(6), C(n2)–C(n3): 1.369–1.384(6), C(n3)–C(n4): 1.190–1.217(6), Si–C(n4): 1.821–1.852(5) Å (n = 1–4)] and therefore delocalization is not so significant. The molecule is essentially planar as can be seen from a side view (Figure 1b).[9] The dimension of the π-conjugated polycarbon system is as large as a square of the side of ca. 10 Å [Si1···Si2: 10.97, Si1···Si4: 10.17 Å] and the carbon chain consisting of ten carbon atoms spans two silicon atoms separated by the distances of 14.94 Å (Si1···Si3) and 14.95 Å (Si2···Si4).

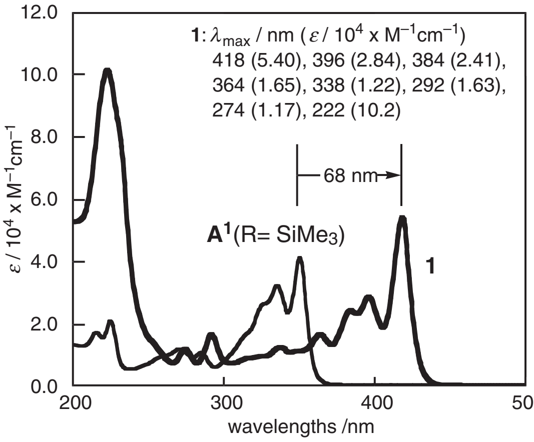


Figure 2. UV–vis spectra of **1** and $\mathbf{A^1}$(R = $\mathrm{SiMe_3}$) observed in hexane.

The characteristic UV–vis absorptions of $\mathbf{A^1}$(R = $\mathrm{SiMe_3}$)[2a,b] in longer wavelength region are shifted to lower energies by ca. 70 nm upon replacement of the C_2 linkers by the C_4 linkers (**1**) clearly indicating an extension of the π-conjugated system (Figure 2).

In summary, tetrakis(trimethylsilylbutadiynyl)ethene with an extended π-conjugated system consisting of 18 carbon atoms, **1** [$\mathbf{A^2}$(R = $\mathrm{SiMe_3}$)], is prepared and fully characterized.[10] Compound **1**, which can be readily functionalized, should serve as a component for architecture of higher order carbon networks.

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6 Low[4] suggested addition of several drops of HCl aq. upon crystallization of tetrakis(trimethylsilylethynyl)ethene, $\mathbf{A^1}$(R = $\mathrm{SiMe_3}$), to prevent base-catalyzed desilylation leading to explosive unprotected tetraethynylethene derivatives. But addition of HCl aq. to **1** caused its deterioration.

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8 Crystal data for **1** (at −60 °C): $\mathrm{C_{30}H_{36}Si_4}$, $M_r = 508.95$, triclinic, space group $P-1$, $a = 9.862(2)$ Å, $b = 12.051(4)$ Å, $c = 16.160(6)$ Å, $\alpha = 107.532(8)°$ $\beta = 97.40(2)°$, $\gamma = 102.16(2)°$, $V = 1757.2(10)$ Å^3, $Z = 2$, $D_{calcd} = 0.962\ \mathrm{g{\cdot}cm^{-3}}$, $R_1 = 0.086$ (refined on F^2) for 3493 data ($I > 2\sigma(I)$) and 329 parameters. The disordered olefinic part was refined taking into account a minor component [C(01,02):C(01a, 02a) = 0.753 : 0.247].

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