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Structure of a Cumulene Bearing Bulky Substituents. X-Ray Study of 1,1,4,4-Tetrakis(trimethylsilyl)butatriene

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Synopsis. The structure of cumulene bearing bulky substituents, 1,1,4,4-tetrakis(trimethylsilyl)butatriene, has been determined by an X-ray diffraction method. The molecule is centrosymmetric, and the variation in carbon-carbon double bonds has been observed. The distance of the central C=C bond is 1.276(8) Å, whereas that of the terminal C=C bond is 1.319(6) Å. These bond lengths are very similar to the unsubstituted butatrienes and the influence of bulky trimethylsilyl groups is not recognized in this context. Some distortions have been observed in the bond angles concerning the trimethylsilyl groups; the overcrowded environment of the central C=C bond seems to make this less reactive.

Cumulene is a very reactive molecule and it is important to know more details about the molecular structure in order to correlate its reactivety with structure. The trimethylsilyl group is an important substituent in synthetic chemistry because it gives an overcrowded environment to unsaturated compounds. Differences in the reactivity between 1,1,4,4-tetrakis(trimethylsilyl)butatriene (**1**) and other butatrienes have been reported. The hydrogenation of **1** with Rh-C or Pd-C gives $(Me_3Si)_2CH\text{-}CH{=}CH\text{-}CH(SiMe_3)_2$ and the hydrogenation of 1,4-diphenylbutatriene provides 1,4-diphenyl-1,3-butadiene.[1)] Here, we wish to describe the molecular structure of 1,1,4,4-tetrakis(trimethylsilyl)butatiiene and to discuss the effect of bulky substituents on the cumulene structure.

Experimental

A tetrahydrofuran solution of bis(trimethylsilyl)butadiyne (1.0 mmol) was added to a solution of $(Me_3Si)_3MnMgMe$ (2.0 mmol) at 0 °C.[2)] The resulting mixture was stirred at 0 °C for 1 h, then 30 min at 25 °C. A workup and purification by preparative thin-layer chromatography on silica gel gave 1,1,4,4-tetrakis(trimethylsilyl)butatriene (0.11 g)[3)] in 33% yield and was subjected to X-ray structure analysis. Pale-yellow crystals were obtained from a benzene solution. The specimen was sealed by immersion in collodion to prevent any sublimation. The unit cell parameters were determined from 25 Bragg angles, carefully measured on a Rigaku four-circle diffractometer. Graphite monochromatized Cu*Kα* radiation was used. Crystal data: $C_{16}H_{36}Si_4$, FW=340.78, crystal size 0.2×0.15×0.15 mm^3, triclinic, space group $P\bar{1}$; Z=1; a=11.075(2), b=12.035(2), c=6.501(1) Å, α=97.67(2), β=94.38(2), and γ=134.37(1)°. D_c=0.95 g cm^{-3}. μ(Cu*Kα*)=21.41 cm^{-1}. The intensity data were collected by a θ-2θ scan method at 24 °C. A total of 1727 reflections were obtained up to sin $\theta/\lambda<0.56$ Å^{-1}, of which 1613 reflections were non-zero and used for the subsequent structure analysis. No absorption correction was performed. The structure was solved by the direct method with use of the computer program MULTAN,[4)] and refined by block-diagonl least-squares method. Each weighting factor was assigned to twenty levels of the observed structure factors, divided according to their magnitude, in order to minimize any residuals in each region. Hydrogen atoms were located on a difference map and were included in the refinement. the final discrepancy indices, R and R_w, for 1613 non-zero reflections were 0.042 and 0.043, respectively. The calculation was carried out by a NEC PC-9801 computer using the UNICS computer program system[5)] modified by Profs. Y. Katsube and N. Tanaka. The atomic scattering factors were taken from Ref. 6. The final atomic parameteis are listed in Table 1, whereas the anisotropic thermal parameters and complete tables of the observed and calculated structure factors are kept as Document No. 8855 by the Editor of the Bulletin of the Chemical Society of Japan.

Results and Discussion

The molecular structure is shown in Fig. 1. A linear molecule lies on the center of symmetry in the crystal, and four trimethylsilyl groups are located in a staggered form. The effect of the bulkiness of the trimeth-

Table 1. Atomic Positional and Equivalent Isotropic Thermal Parameters of 1,1,4,4-Tetrakis(trimethylsilyl)butatriene

Atom	x	y	z	B_{eq}/B_{iso}
Si(1)	0.4395(1)	0.7272(1)	0.4142(1)	5.8
Si(2)	0.1633(1)	0.3403(1)	0.1487(2)	6.2
C(1)	0.3681(3)	0.5298(3)	0.3494(5)	5.5
C(2)	0.4587(4)	0.5123(3)	0.4537(5)	5.9
C(3)	0.6525(5)	0.8823(4)	0.6124(6)	8.4
C(4)	0.4638(5)	0.7977(5)	0.1709(6)	8.8
C(5)	0.2736(5)	0.7010(5)	0.5256(6)	8.7
C(6)	0.0433(6)	0.3726(5)	0.0075(9)	13.5
C(7)	0.2207(6)	0.2668(6)	−0.0438(7)	10.4
C(8)	0.0218(5)	0.1900(5)	0.3011(8)	11.3
H(31)	0.644(3)	0.847(3)	0.728(4)	3.1
H(32)	0.736(4)	0.896(3)	0.570(4)	4.7
H(33)	0.682(5)	0.977(4)	0.635(6)	9.2
H(41)	0.533(5)	0.809(4)	0.105(6)	9.0
H(42)	0.370(5)	0.736(4)	0.077(6)	8.9
H(43)	0.493(5)	0.883(5)	0.193(6)	9.6
H(51)	0.253(4)	0.659(4)	0.648(5)	6.9
H(52)	0.176(4)	0.635(4)	0.429(5)	7.7
H(53)	0.310(5)	0.790(5)	0.569(6)	10.6
H(61)	−0.035(5)	0.291(4)	−0.078(6)	8.1
H(62)	0.031(6)	0.416(6)	0.081(7)	13.5
H(63)	0.086(5)	0.430(5)	−0.094(7)	11.3
H(71)	0.292(5)	0.265(4)	0.013(6)	8.2
H(72)	0.131(6)	0.181(6)	−0.146(7)	13.3
H(73)	0.256(4)	0.336(4)	−0.122(5)	6.0
H(81)	0.077(6)	0.162(5)	0.360(7)	11.6
H(82)	−0.072(5)	0.095(4)	0.200(6)	8.6
H(83)	−0.022(6)	0.223(6)	0.348(7)	13.3

$B_{eq}=(4/3)(B_{11}a^2+B_{22}b^2+B_{33}c^2+B_{12}ab\cos(\gamma)+B_{13}ac\cos(\beta)+B_{23}bc\cos(\alpha))$.

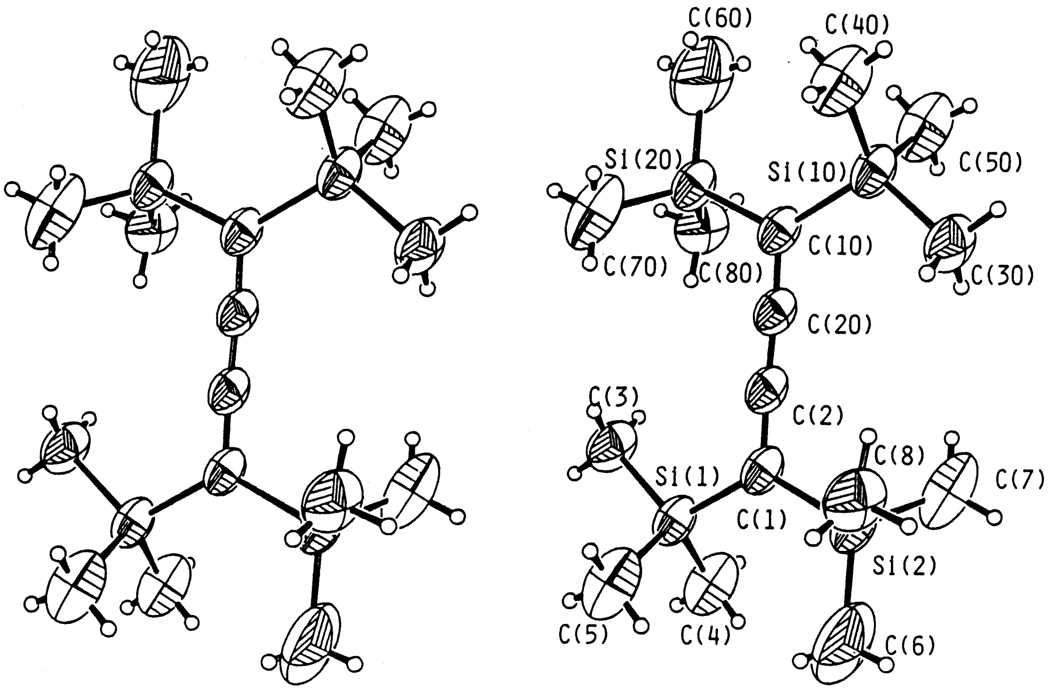


Fig. 1. Molecular structure (ORTEP drawing) of 1,1,4,4-tetrakis(trimethylsilyl)butatriene with atomic numbering scheme. The molecule is centrosymmetric. C(10) is related to C(1) by a center of symmetry and so on.

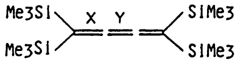
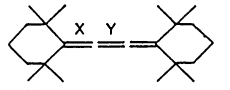
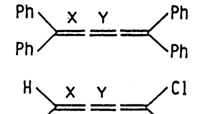
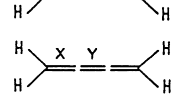
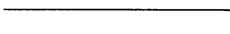
Table 2. Intramolecular Distances and Bond Angles in 1,1,4,4-Tetrakis(trimethylsilyl)butatriene

Intramolecular distances (l/Å)		Bond angles (θ/°)	
Si(1)-C(1)	1.872(4)	C(1)-Si(1)-C(3)	110.7(2)
Si(1)-C(3)	1.856(5)	C(1)-Si(1)-C(4)	110.1(3)
Si(1)-C(4)	1.844(6)	C(1)-Si(1)-C(5)	109.0(3)
Si(1)-C(5)	1.858(6)	C(3)-Si(1)-C(4)	108.1(3)
Si(2)-C(1)	1.889(4)	C(3)-Si(1)-C(5)	109.4(3)
Si(2)-C(6)	1.843(7)	C(4)-Si(1)-C(5)	109.5(3)
Si(2)-C(7)	1.834(7)	C(1)-Si(2)-C(6)	112.3(3)
Si(2)-C(8)	1.860(6)	C(1)-Si(2)-C(7)	109.1(3)
C(1)-C(2)	1.319(6)	C(1)-Si(2)-C(8)	106.9(3)
C(2)-C(20)	1.276(8)	C(6)-Si(2)-C(7)	110.1(4)
		C(6)-Si(2)-C(8)	108.1(3)
C(2)···C(3)	3.251(6)	C(7)-Si(2)-C(8)	110.3(3)
		Si(1)-C(1)-Si(2)	125.2(3)
		Si(1)-C(1)-C(2)	120.4(3)
		Si(2)-C(1)-C(2)	114.3(3)

ylsilyl groups is reflected on the bond angles around the C(1) atom. As can be seen from Table 2, which summarizes the interatomic distances and the angles in the molecule, the angle of C(2)-C(1)-Si(1) is larger than that of C(2)-C(1)-Si(2). This is due to the repulsion of C(2) and C(3), the latter being forced to lie on the plane through C(2), C(1), and Si(1) because of the overcrowded trimethylsilyl groups. The C(1)-C(2) double bond is seemingly buried by these groups and should be less reactive. The structure of tetrakis(trimethylsilyl)ethylene at −70 °C was reported by Sakurai and his co-workers.[7] The effect of bulky substituents has been observed on the molecular structure. The C=C bond length is 1.368(3) Å, significantly longer than the usual double bond. Furthermore, substituted ethylene is no longer planar, the dihedral angle between two Si-C-Si plane being 29.5°. It is reasonable that the effect of bulky trimethylsilyl groups on the present molecule is less remarkable than the tetrakis(trimethylsilyl)ethylene, because two bis(trimethylsilyl) groups are located at a greater distance in the former molecule than in the latter. In fact, a treatment of **1** with 1M HCl (1M=1 mol dm^{-3}) in THF at 25 °C provides $Me_3SiC{\equiv}C\text{-}CH{=}C(SiMe_3)_2$ quantitatively. Meanwhile, tetrakis(trimethylsilyl)ethylene was quite stable and was recovered unchanged under the same conditions.

The varieties observed in the C=C bond lengths in substituted cumelenes have been discussed by Irngartinger and his co-workers.[8] They recognized that a clear difference exists between cumulenes with

Table 3. The Variation in C=C Bond Lengths in Butatriene

Compound	X (l/Å)	Y (l/Å)	Technique	Ref.
	1.319(6)	1.276(8)	X-Ray	This work
	1.332	1.261	X-Ray	9
	1.345(3)	1.246(3)	X-Ray	10
	1.326(5)	1.260(10)	Electron diffraction	11
	1.318(5)	1.283(5)	Electron diffraction	12

an even number and those with an odd number of double bonds: that is, the terminal double bonds in the former are somewhat shorter than those in the latter. We summarize in Table 3 the C=C bond lentgths observed in substituted butatrienes. The longer terminal double bond in tetraphenylbutatriene may be attributed to conjugation with the phenyl group, whereas the bond lengths observed in the present molecule is very similar to those in unsubstituted butatriene.

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