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Molecular Structure of Tetrakis(2,6-diethylphenyl)disilene

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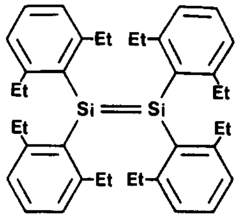
Summary: Tetrakis(2,6-diethylphenyl)disilene has been synthesized. A molecular analysis of this compound shows that (1) the Si═Si′ bond length is 2.140 Å, (2) each silicon atom and the three atoms directly attached to it are coplanar with a C–Si–C angle of 117.6° and C–Si–Si′ angles of 117.6 and 124.8°, and (3) the dihedral angle between the C–Si–C and C′–Si′–C′ planes is 10° (with a twisted Si═Si bond).

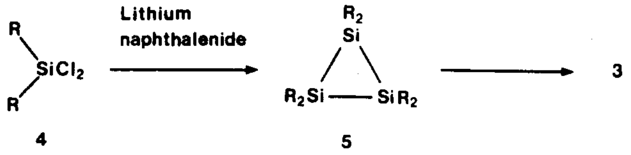
In this communication we describe the molecular structure of a disilene derivative. Two different approaches to the synthesis of stable disilenes independently conceived by West et al.[1] and by us[2] brought about in nately, however, compound 2 almost invariably crystallized in twin forms in our hands and thus complicated its X-ray crystallographic analysis.[4] This complication has now been circumvented by the use of the corresponding *tetrakis*(2,6-*diethylphenyl*) derivative (3) which forms untwinned crystals. The crystal structure outlined below reveals that (1) the silicon–silicon double bond (Si═Si 2.140 Å) is discernibly shorter than the corresponding single bond (2.331–2.425 Å)[5] and (2) the Si═Si bond is "twisted" by 10° in a manner similar to sterically crowded olefins (C═C)[6] but dissimilar to the distannene derivative (Sn═Sn).[7]

$R_2Si = SiR_2$

1 : R = mesityl
2 : R □ 2,6-dimethylphenyl



3



4 and 5 : R = 2,6-diethylphenyl

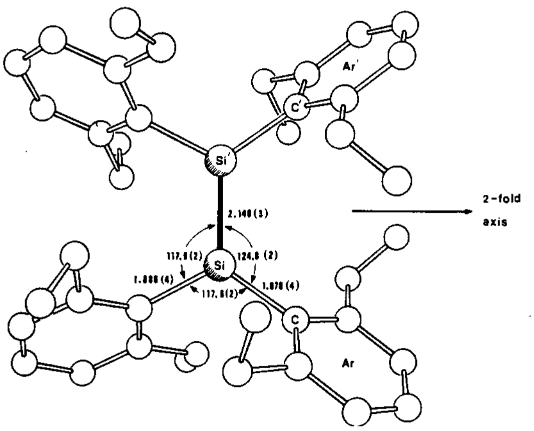


Figure 1. Molecular structure of 3.

Synthesis of 3. This synthesis follows the procedure described earlier for that of 2.[2] Thus, reaction of bis(2,6-diethylphenyl)dichlorosilane (4) with lithium naphthalenide provides hexakis(2,6-diethylphenyl)cyclotrisilane (5), mp 298–300 °C, in 16% yield.[8,9] A suspension of 5 (48 mg) in 3-methylpentane (2.9 mL) sealed in a Vycor tube is irradiated at ca. 100 °C with a low-pressure mercury lamp (spiral, 125-W output) for 25 min. During this photolysis all of 5 dissolves and the solution becomes intensely yellow. When the solution is left standing at room temperature, there appears yellow, crystalline precipitate that is chemically pure disilene 3 (>50% yield), as evidenced from its spectral data.[10] ^1H NMR spectra (270 MHz, toluene-d_8) are uniquely temperature dependent: two triplets (δ 0.86, 1.04) and two double quartets (δ 2.83, 3.04) and a multiplet (centering around δ 3.29) observed at –40 °C and assigned to the ethyl groups of 3 collapse

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(1) (a) West, R.; Fink, M. J.; Michl, J. *Science* (*Washington, D. C.*) **1981**, *214*, 1343. Also see: (b) *Chem. Eng. News* **1981**, Dec 21, 8. Also see footnote 1d of ref. 3a.

(2) Masamune, S.; Hanzawa, Y.; Murakami, S.; Bally, T.; Blount, J. F. *J. Am. Chem. Soc.* **1982**, *104*, 1150.

(3) For other disilene derivatives whose spectral properties have been recorded, see: (a) [tetra-*tert*-butyl]: Masamune, S.; Murakami, S.; Tobita, H. *Organometallics* **1983**, *2*, 1464. (b) [tetrakis(1-ethylpropyl)]: Masamune, S.; Tobita, H.; Murakami, S. *J. Am. Chem. Soc.* **1983**, *105*, 6524. (c) [tetraneopentyl]: Watanabe, H.; Okawa, T.; Kato, M.; Nagai, Y. *J. Chem. Soc., Chem. Commun.* **1983**, 781. For the digermene system, see: (d) Masamune, S.; Hanzawa, Y.; Williams, D. J. *J. Am. Chem. Soc.* **1982**, *104*, 6136.

(4) Dr. J. F. Blount informed us of this apparent twinning of 2 (Dec 1, 1981).

(5) The Si–Si bond lengths are 2.331 (3) Å in $(SiH_3)_2$ [(a) Beagley, B.; Conrad, A. R.; Freeman, J. M.; Monaghan, J. J.; Norton, B. G. *J. Mol. Struct.* **1972**, *11*, 371], 2.338 (4) Å in $(Me_2Si)_6$ [(b) Carrell, H. L.; Donohue, J. *Acta Crystallogr., Sect. B* **1972**, *B28*, 1566], 2.377 Å in $(t\text{-}BuMeSi)_4$ with the trans, trans, trans geometry [(c) Hurt, C. J.; Calabrese, J. C.; West, R. *J. Organomet. Chem.* **1975**, *91*, 273], 2.340 (9) Å in $Me_3SiSiMe_3$ [(d) Beagley, B.; Monaghan, J. J.; Hewis, T. G. *J. Mol. Struct.* **1971**, *8*, 401], 2.365 Å in $R_2HSi–SiHR_2$ (R = cyclohexyl) [(e) Baxter, S. G.; Dougherty, D.. A.; Hummel, J. P.; Blount, J. F.; Mislow, K. *J. Am. Chem. Soc.* **1978**, *100*, 7795 [also see: Baxter, S. G.; Mislow, K.; Blount, J. F. *Tetrahedron* **1980**, *36*, 605], 2.375, 2.422, and 2.425 Å in hexakis(2,6-dimethylphenyl)cyclotrisilane [(f) see ref 2], and 2.359 and 2.367 Å in $(Me_2Si)_4$ [(g) Kratky, C.; Schuster, H. G.; Hengge, E. *J. Organomet. Chem.* **1983**, *247*, 253]. The C–Si bond lengths are 1.935 (6) (equatorial) and 1.913 (4) Å (axial) in b, 1.918 (3) (axial) and 1.893 (4) Å (equatoral) in c, 1.877 (3) Å in d, and 1.886 Å in e.

(6) For reviews, see: (a) Liebman, J. F.; Greenberg, A. *Chem. Rev.* **1976**, *76*, 311. (b) Tidwell, T. T. *Tetrahedron* **1978**, *34*, 1855. For the most tortionally distorted olefin, see: (c) Sakurai, H.; Tobita, H.; Nakadaira, Y.; Kabuto, C. *J. Am. Chem. Soc.* **1982**, *104*, 4288.

(7) (a) Cotton,, J. D.; Davidson, P. J.; Lappert, M. F.; Donaldson, J. D.; Silver, J. *J. Chem. Soc., Dalton Trans.* **1976**, 2286. (b) Goldberg, D. E.; Harris, D. H.; Lappert, M. F.; Thomas, K. M. *J. Chem. Soc., Chem. Commun.* **1976**, 261.

(8) For further details of this experiment, see supplementary material.

(9) ^1H NMR (250 MHz, C_6D_6, temperature dependent): at room temperature δ 0.44 (t, J = 7 Hz, 18 H), 0.47 (t, J = 7 Hz, 18 H), 2.14 (dq, J = 16 and 7 Hz, 6 H), 2.61 (dq, J = 16 and 7 Hz, 6 H), 2.74 (dq, J = 14 and 7 Hz, 6 H), 2.82 (dq, J = 14 and 7 Hz, 6 H), 6.87 (d, J = 7.4 Hz, 6 H), 6.91 (d, J = 7.4 Hz, 6 H), 7.06 (t, J = 7.4 Hz, 6 H). IR ($CHCl_3$, cm^{-1}): 3050, 2965, 2930, 2865, 1450. UV (methylcyclohexane): λ_{max} 268 nm (ϵ 3.9×10^4), 271 (3.9×10^4), 353 (316), 387 (254). Mass spectrum (field desorption): found m/z 882.

(10) mp 201–204 °C with discoloration. UV (3-methylpentane): λ_{max} 273 nm (ϵ 1.1×10^4), 354 (9.2×10^3), 426 (1.6×10^4).

0276-7333/84/2303-0333$01.50/0

to one triplet (δ 0.93) and one quartet (δ 3.00) at 100 °C. The aromatic protons behave similarly and exhibit a typical A_2X signal (δ 6.91, 7.07) at 100 °C.

Crystallographic Analysis of 3. The crystals are orthorhombic with a = 9.787 (2) Å, b = 18.694 (3) Å, c = 19.289 (2) Å, U = 3529 Å^3, space group $Pcnb$, Z = 4, and D_{calcd} = 1.11 g cm^{-3}.[11] In view of the air and moisture sensitivity of **3**, a small single crystal surrounded by a small drop of mother liquor was sealed under argon in a Lindemann glass capillary tube. Data were measured on a Nicolet R3m diffractometer ($\theta \leq 50°$) with graphite-monochromated Cu Kα radiation and the ω scan measuring routine. The structure was solved by direct methods and refined anisotropically to a current R = 0.072 and R_w = 0.087[12] for 1575 independently observed reflections. Despite large thermal vibrations (or disorder) for the ethyl groups (and the consequent high R value), the definition of the Si=Si bond is good and of acceptable accuracy. The maximum residual electron density was 0.3 e Å^{-3} around the ethyl group and 0.14 e Å^{-3} in the region of the silicon atom.

The analysis shows (Figure 1) that there is a crystallographic twofold axis which bisects the Si=Si bond. Each silicon atom and the three atoms directly attached to it are coplanar with a C-Si-C angle of 117.6 (2)° and C-Si-Si′ angles of 117.6 (2)° and 124.8 (2)°. The Si=Si′ bond length is 2.140 (3) Å, and the Si-C bonds are 1.886 (4) and 1.878(4) Å, respectively. It is interesting to note that the presence of the silicon-silicon double bond does not result in any shortening of the silicon-aryl bond. All four Si-Ar bonds are not coplanar; the dihedral angle between the C-Si-C and C′-Si′-C′ planes is 10°. The planes of the phenyl rings are rotated by 62° and 64° from the C-Si-Si′ plane, respectively. This rotation and the twisting of the Si=Si bond are obviously brought about to minimize possible steric congestion due to the ethyl groups attached on the phenyl rings. The structure as a whole is loosely packed with short intermolecular contacts.

In recent years an extensive theoretical investigation of the Si_2H_4 potential surface has been performed. Although calculations at various levels lead to different results as to the relative stability of the silylsilylene and disilene ground states,[13] the former (in the singlet state) is 2-3 kcal/mol more stable than the latter (in the singlet state) at HF/6-31G level.[13a] Correlation energy corrections reverse this order, however. It appears that trans-bent disilene (C_{2h}) lies very slightly lower in energy than planar disilene (D_{2h}), but this C_{2h} conformation resides in a region of rather flat potential energy surface. The Si=Si bond distance is predicted to be between 2.13 and 2.17 Å.[13a] With the crystal structure of **3** described above a significant step has now been taken in solving this intriguing problem experimentally.[14]

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Registry No. 3, 88245-20-9; 4, 88245-21-0; 5, 88245-22-1.

Supplementary Material Available: Experimental details including the synthesis of **5** and detailed information of the X-ray crystal analysis of **3** (16 pages). Ordering information is given on any current masthead page.

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[11] The unit cell dimensions from least squares for 18 reflections centered on the diffractometer with Cu Kα radiation (θ between 20 and 40°). Positive and negative (hkl) values were used.

[12] Four reflections which had $[F_0| > |F_c]$ were suspected of being affected by extinction and were removed.

[13] (a) Krogh-Jespersen, K. *J. Phys. Chem.* **1982,** *86,* 1492. (b) Lischka, H.; Köhler, H.-J. *Chem. Phys. Lett.* **1982,** *85,* 467. (c) Poirier, R. A.; Goddard, J. D. *Ibid.* **1981,** *80,* 37. For earlier work, see: (d) Snyder, L. C.; Wasserman, Z. R. *J. Am. Chem. Soc.* **1979,** *101,* 5222. (e) Roelandt, F. F.; van de Vondel, D. F.; van der Kelen, G. P. *J. Organomet. Chem.* **1979,** *165,* 151. (f) Daudel, R.; Kari, R. E.; Poirier, R. A.; Goddard, J. D.; Csizmadia, I. G. *J. Mol. Struct.* **1978,** *50,* 115. (g) Dewar, M. J. S.; Lo, D. H.; Ramsden, C. A. *J. Am. Chem. Soc.* **1975,** *97,* 1311. (h) Curtis, M. D. *J. Organomet. Chem.* **1973,** *60,* 63. Also see for the Ge_2H_4 system: (i) Trinquier, G.; Malrieu, J.-P.; Rivière, P. *J. Am. Chem. Soc.* **1982,** *104,* 4529.

[14] After the submission of this manuscript, a report on the X-ray crystal structure of tetramesityldisilene appeared. Fink, J. F.; Michalczyk, M. J.; Haller, K. J.; West, R.; Michl, J. *J. Chem. Soc., Chem. Commun,* **1983,** 1010.

$[(C_5H_5)_2TiOCMo(CO)_2(C_5H_4CH_3)]_2$: A 12-Membered Organometallic Ring System Held Together by Ti-O-C-Mo Bridges

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Summary: The reaction between $(C_5H_5)_2Ti(CO)_2$ and $(C_5H_4CH_3)Mo(CO)_2{\equiv}Mo(CO)_2(C_5H_4CH_3)$ in toluene at room temperature leads to the formation of $[(C_5H_5)_2TiOCMo(CO)_2(C_5H_4CH_3)]_2$, **2a**. Complex **2a** was found to crystallize in the monoclinic space group $P2_1/n$ with two molecules in a unit cell of dimensions a = 13.510 (4) Å, b = 10.951 (2) Å, c = 13.361 (3) Å, β = 114.66 (2)°, V = 1797 (1) Å^3, and d_{calcd} = 1.616 g cm^{-3}. The core of **2a** consists of an unusual 12-membered ring: Ti-O-C-Mo-C-O-Ti-O-C-Mo-C-O. Each titanium atom is further bound by two η^5-C_5H_5 ligands while each molybdenum is further bound by one terminal carbonyl and one η^5-$C_5H_4CH_3$ ligand. Complex **2a** reacts with the donor tetrahydrofuran to form the known complex $(C_5H_5)_2Ti(THF)OCMo(CO)_2(C_5H_4CH_3)$, **1a**.

In recent years, a considerable effort has been directed toward the synthesis of early transition metal/later transition metal combination complexes with much of that effort focused on complexes of titanium, zirconium, and hafnium.[1] We became interested in building up complexes of the early transition elements by the reaction of a lower valent group 4B complex with metal dimers possessing metal-metal unsaturation. In a previous communication,[2] we reported on the synthesis and molecular structure of the Ti(III) complex $(C_5H_5)_2Ti(THF)OCMo(CO)_2(C_5H_5)$,

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[1] See: Casey, C. P; Jordan, R. F.; Rheingold, A. L. *J. Am. Chem. Soc.* **1983,** *105,* 665 and references therein.

[2] Merola, J. S.; Gentile, R. A.; Ansell, G. B.; Modrick, M. A.; Zentz, S. *Organometallics* **1982,** *1* (12), 1731.

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