Crystal Structures of Two Isomeric Cyclotrisilanes

John C. Dewan, Shu Murakami, James T. Snow, Scott Collins, and Satoru Masamune*

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, U.S.A.

The *X*-ray crystal structures of two isomeric cyclotrisilanes, *cis–cis-* and *cis–trans-*1,2,3-tri-t-butyl-1,2,3-trimesitylcyclotrisilanes (**1a**) and (**1b**), respectively, have been determined; the structure of (**1b**) reveals that one Si–Si bond is significantly longer than the other two in agreement with the recently reported chelotropy of photo-cleavage of (**1b**) to give *E*- and *Z*-1,2-di-t-butyl-1,2-dimesityldisilenes (**2a**) and (**2b**), respectively.

We recently reported the preparation of two isomeric cyclotrisilanes, *cis–cis-* and *cis–trans-*1,2,3-tri-t-butyl-1,2,3-trimesitylcyclotrisilanes (**1a**) and (**1b**).[1] Photolysis of compound (**1a**) or (**1b**) provided mixtures of *E*- and *Z*-1,2-di-t-butyl-1,2-dimesityldisilenes (**2a**) and (**2b**), the initial ratio of (**2a**) and (**2b**) in each case being different (Scheme 1). These results were consistent with the interpretation that cyclotrisilanes undergo photofragmentation with retention of configuration at silicon to provide disilenes. Furthermore, in the case of cyclotrisilane (**1b**), it was demonstrated that one (mode A, Scheme 1) of the two possible modes of cleavage of the three-membered ring was favoured over the other (mode B) by a factor of about four. This interesting result is apparently correlated with the ground-state geometry of (**1b**), which is recorded herein in comparison with that of (**1a**). Compounds (**1a**) and (**1b**) represent the first examples of isomeric cyclotrisilanes that have been structurally characterized, and thus reveal how the substituents affect the ring geometry.†

Crystal Data: Compound (**1a**); $C_{39}H_{60}Si_3$, $M = 613.18$, triclinic, space group $P\bar{1}$, a = 12.239(2), b = 12.339(3), c = 15.306(1) Å, α = 73.95(1), β = 85.89(1), γ = 69.15(1)°, U = 2075 Å^3, Z = 2, D_c = 0.981 g cm^{-3}; (**1b**); triclinic, space group $P\bar{1}$, a = 8.805(1), b = 12.602(3), c = 17.678(3) Å, α = 86.05(2), β = 75.86(1), γ = 77.51(2)°, U = 1857 Å^3, Z = 2, D_c = 1.097 g cm^{-3}. Data were collected on Enraf Nonius CAD4F-11 diffractometer using Mo-K_α radiation. The data collection, reduction, and refinement procedures used have been described in detail elsewhere.[2] The structures were determined from 5007 observed reflections for (**1a**) [$F_o > 6\sigma(F_O)$], and 3237 for (**1b**) [$F_O > 4\sigma(F_O)$] from a total of 7277 and 6540 reflections ($\pm h$, $\pm k$, $+l$) collected in the range $3 < 2\theta < 50°$ for (**1a**) and (**1b**), respectively. Both structures were refined by full-matrix least-squares techniques (382 variables) using SHELX-76. Final R and R' values are 0.060 and 0.092 for (**1a**) and 0.054 and 0.056 for (**1b**). In both cases, hydrogen atoms of the t-butyl groups and those on the mesityl rings were placed in geometrically calculated positions (C–H 1.08 Å) and constrained to ride on their respective carbon atoms. The methyl group hydrogen atoms of the mesityl rings were initially set up and refined as rigid groups, although in the final cycles of refinement they were included as invariants.‡ The molecular structures of cyclotrisilanes (**1a**) and (**1b**) are shown in Figures 1 and 2, respectively, along with selected bond lengths and angles and the atom numbering schemes.

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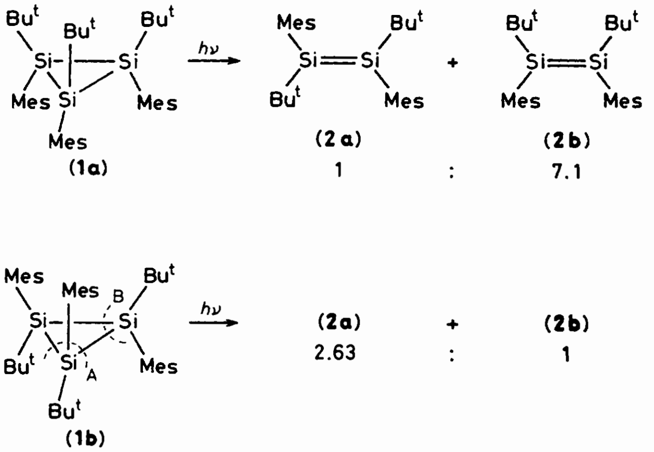
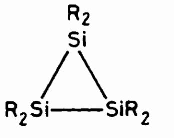
† Only the cyclotrisilanes (**1c**) and (**1d**) have thus far been crystallographically analysed.

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.



Mes = $2,4,6\text{-}Me_3C_6H_2$

Scheme 1



(**1c**) R= $2,6\text{-}Me_2C_6H_3$
(**1d**) R = Bu^t

In the case of the *cis–cis*-cyclotrisilane (**1a**), the structure shows approximate C_3 symmetry with Si–Si bond lengths of ~2.43 Å. They are not significantly different from the Si–Si bond lengths observed in the crystal structure of hexakis(2,6-dimethylphenyl)cyclotrisilane (**1c**) (Si–Si = 2.38—2.42 Å)[3] but are significantly shorter than the Si–Si bond length observed in the structure of hexa-t-butylcyclotrisilane (**1d**) [Si–Si = 2.511(3) Å].[4] Although the Si–C(mesityl) bond lengths are normal for aryl substituted cyclotrisilanes [1.92—1.93 Å; *cf.* 1.90—1.93° Å for (**1c**)] the Si–C(t-butyl) bonds are long (1.97 Å) and of equal length to those observed in cyclotrisilane (**1d**) [1.970(5) Å]. Evidently, vicinal steric repulsion between the t-butyl groups is partly responsible for the long Si–C bond lengths observed. This repulsion is also evident from the contraction in the C(mesityl)–Si–C(t-butyl) bond angles to 103—104° [*cf.* 105.7° for (**1d**) and 104—107° for (**1c**)].

The structure of cyclotrisilane (**1b**) (Figure 2) reveals several interesting and unexpected features. First *there is no element of symmetry in the molecule* (approximate or otherwise); however, in solution, the ^1H n.m.r. spectrum of (**1b**) indicates a plane of symmetry even at low temperatures. The Si(2)–Si(3) bond length of 2.441(2) Å is significantly longer than the other two [2.395(2) and 2.413(2) Å]. This result is consistent with the photokinetics of compound (**1b**) which suggested that this bond was cleaved preferentially in concert with either of the other two Si–Si bonds to provide a preponderance of *E*-1,2-di-t-butyl-1,2-dimesityldisilene (**2a**) (Scheme 1, mode A). While the Si(3)–C(61) bond length is apparently 'normal' [1.972(5) Å] for t-butyl substituted cyclotrisilanes, the other two Si–C(t-butyl) bonds are considerably shorter [1.930(5) and 1.945(5) Å for Si(1)–C(41) and Si(2)–C(51), respectively]. The Si–C(mesityl) bonds range between 1.92 and 1.94 Å and are not atypical by comparison with those observed in the structures of (**1a**) and (**1c**). The C(mesityl)–Si–C(t-butyl) angles lie in the range 103.6—

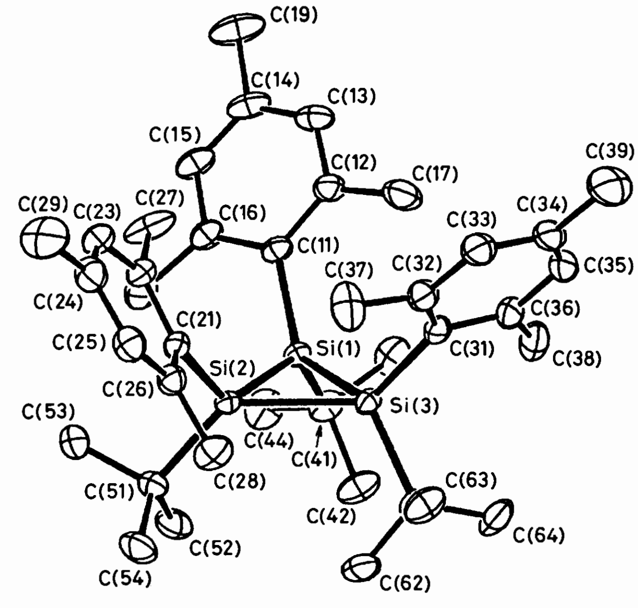


Figure 1. ORTEP diagram for cyclotrisilane (**1a**) showing the 30% probability thermal ellipsoids and atom numbering scheme. Selected interatomic distances (Å) with estimated standard deviations in parentheses: Si(1)Si(2), 2.425(2); Si(1)Si(3), 2.428(2); Si(2)Si(3), 2.431(2); Si(1)C(11), 1.932(5); Si(1)C(41), 1.968(6); Si(2)C(21), 1.924(6); Si(2)C(51), 1.968(6); Si(3)C(31), 1.920(6); Si(3)C(61), 1.970(6). Bond angles (°): Si(2)Si(1)Si(3), 60.1(1); Si(1)Si(2)Si(3), 60.0(1); Si(1)Si(3)Si(2), 59.9(1); C(11)Si(1)C(41), 102.6(2); C(21)Si(2)Si(51), 103.6(3); C(31)Si(3)C(61), 104.2(3); Si(2)Si(1)-C(11), 117.8(2); Si(2)Si(1)C(41), 130.6(2); Si(3)Si(1)C(11), 130.0(2); Si(3)Si(1)C(41), 113.6(2); Si(1)Si(2)C(21), 129.2(2); Si(1)Si(2)C(51), 113.4(2); Si(3)Si(2)C(21), 116.7(2); Si(3)Si(2)C(51), 131.1(2); Si(1)Si(3)C(31), 117.3(2); Si(1)Si(3)C(61), 130.1(2); Si(2)Si(3)C(31), 128.5(2); Si(2)Si(3)C(61), 113.5(2).

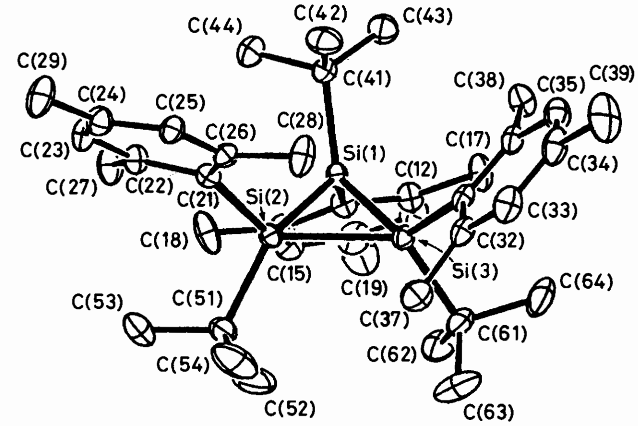


Figure 2. ORTEP diagram for cyclotrisilane (**1b**) showing the 30% probability thermal elipsoids and atom numbering scheme. Selected interatomic distances (Å) with estimated standard deviations in parentheses: Si(1)Si(2), 2.395(2); Si(1)Si(3), 2.413(2); Si(2)Si(3), 2.441(2); Si(1)C(11), 1.920(4); Si(1)C(41), 1.930(5); Si(2)C(21), 1.935(4); Si(2)C(51), 1.945(5); Si(3)C(31), 1.919(4); Si(3)C(61), 1.972(5). Bond angles (°): Si(2)Si(1)Si(3), 61.0(1); Si(1)Si(2)Si(3), 59.8(1); Si(1)Si(3)Si(2), 59.1(1); C(11)Si(1)C(41), 107.2(2); C(21)Si(2)C(51), 104.4(2); C(31)Si(3)C(61), 103.6(2); Si(2)Si(1)-C(11), 127.0(2); Si(2)Si(1)C(41), 112.7(1); Si(3)Si(1)C(11), 122.0(2); Si(3)Si(1)C(41), 121.1(1); Si(1)Si(2)C(21), 116.5(1); Si(1)Si(2)C(51), 130.1(2); Si(3)Si(2)C(21), 126.5(1); Si(3)Si(2)C(51), 115.8(2); Si(1)Si(3)C(31), 129.6(2); Si(1)Si(3)C(61), 113.9(2); Si(2)Si(3)C(31), 124.2(1); Si(2)Si(3)C(61), 122.3(2).

107.2°, there being a correlation between the length of the C(t-butyl)–Si bond and the degree of contraction observed (*i.e.*, a longer bond is accompanied by a smaller angle at silicon).

The reasons for the significant shortening of the Si(1)–C(41) and Si(2)–C(51) bonds in the structure of (**1b**) are not particularly evident. In the recently published structure of *E*-1,2-di-t-butyl-1,2-dimesityldisilene (**2a**)[5] the Si–C(t-butyl) bond length is 1.904 Å, the mesityl rings are nearly orthogonal (88°) to the Si–Si–C(mesityl) plane, and the Si–Si bond length is 2.143(1) Å. In the structure of compound (**1b**), the fragment containing Si(1) and Si(2) and their associated substituents resembles the structure of disilene (**2a**) more than the other two fragments do. The average deviation of Si(1) and Si(2) from the best plane defined by carbon atoms C(11), C(41), C(21), and C(51) is 0.57 Å [*cf.* 0.58 and 0.59 Å for Si(1), Si(3) and Si(2), Si(3) from their respective planes C(11),C(41),C(31),C(61) and C(21),C(51),C(61),C(31)] and the orientation of the mesityl rings, C(11)—C(16) and C(21)—C(26), is more closely orthogonal to this plane [16° average deviation from 90°, *cf.* 21° and 26° for rings C(11)—C(16), C(31)—C(36) and C(21)—C(26), C(31)—C(36) with respect to the best planes for C(11),C(41),C(31),C(61) and C(21),C(51),C(61),C(31)]. Thus the molecular structure of (**1b**) may be *loosely* interpreted as a molecule of disilene (**2a**) [comprising Si(1) and Si(2) and their respective substituents] perturbed by (bonded to) a molecule of t-butylmesitylsilylene [corresponding to Si(3)]. This view, although admittedly simplistic, is also consistent with the photochemical behaviour of compound (**1b**) described above.

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