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X-ray Crystallographic Analysis of a 3-Silacyclopropene with Electronegative Substituents on Silicon

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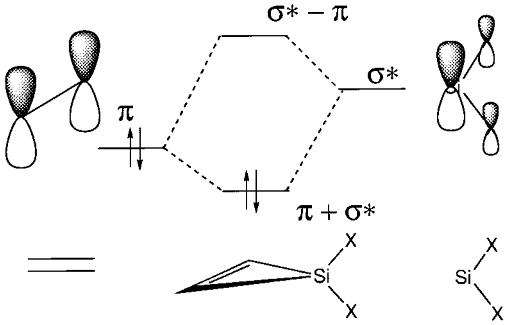
*Summary: X-ray crystallographic analysis of 3,3-bis-(diisopropylamino)-1,2-bis(trimethylsilyl)-3-silacyclopropene (**1**) gave the first experimental evidence for significant substituent effects on the ring structure deformation due to the interaction between the π-type σ^*-orbital of silicon−nitrogen bonds and the C═C π-bonding orbital. The degree of bond deformation in **1** was estimated by electron density distribution in the ring plane.*

Introduction

Although considerable interest has been focused on the chemistry of 3-silacyclopropenes, little is known about the substituent effects on the reactions and structural characteristics.[1,2] Recently, it has been shown by theoretical calculations that electronegative substituents on a silicon atom in 3-silacyclopropene stabilize the ring and modify the ring structure due to the effective $\sigma^*-\pi$ interaction (σ^*-aromaticity), as shown in Scheme 1;[3] lowering the energy level of the π-type σ^*-orbital on the silicon atom by introducing the electronegative substituents makes the $\sigma^*-\pi$ interaction more effective.

The ab initio theoretical study[3] has shown that electronegative substituents on silicon such as fluorine, hydroxy, and amino groups shorten the Si−C bonds and elongate the C−C bond in the 3-silacyclopropene ring, as a consequence of the stabilization due to the σ^*-aromaticity. Whereas X-ray structural analyses of a number of 3-silacyclopropene derivatives have been reported so far,[2] nothing is known about the structure of 3-silacyclopropenes with electronegative substituents on silicon. We wish herein to report the detailed structural analysis of 3,3-bis(diisopropylamino)-1,2-bis-(trimethylsilyl)-3-silacyclopropene (**1**),[4] as the first 3-silacyclopropene with heteroatom substituents on silicon. The results have not only confirmed the theoretically predicted substituent effects on the ring structure but also disclosed the bent-bond characteristics of the three-membered ring on the basis of the detailed analysis of the electron-density distribution.

Scheme 1. Schematic Representation of $\sigma^*-\pi$-Orbital Interaction in 3-Silacyclopropene



Experimental Section

Preparation and characterization of **1** were described in our previous paper.[4]

X-ray Structure Determination of 1. A yellow prismatic crystal (0.4 × 0.5 × 0.6 mm) was obtained by recrystallization from *n*-pentane. Crystal data: molecular formula $C_{20}H_{46}N_2Si_3$, MW = 398.85, monoclinic, space group *C*2/*c* (No. 15), $a = 16.649(1)$ Å, $b = 11.316(2)$ Å, $c = 15.762(2)$ Å, $\beta = 113.61(3)°$, $V = 2719.6(8)$ Å^3, $Z = 4$, $D_{\text{calcd}} = 0.974$ g cm^{-3}, $F(000) = 888$, $\mu = 1.80$ cm^{-1}. Data were collected at 200 K, because the intensity peaks were spread gradually at lower temperatures, using a Rigaku AFC5R diffractometer, graphite-monochromatized Mo Kα radiation ($\lambda = 0.710\,69$ Å), a rotating anode generator (50 kV, 200 mA), $2\theta-\omega$ scan mode, and a scan speed of 4°/min (in ω), up to $2\theta = 90.0°$ ((sin θ)/$\lambda = 0.995$ Å^{-1}), which is the limited angle for the effective observed intensities. A total of 10 959 unique reflections were corrected, of which 4586 observed reflections ($I > 3.0\sigma(I)$) were used in the refinement. The decay (2.84% decline) and empirical ψ scan (transmissn factor 0.8791−1.0) corrections were applied. The structure was solved by direct methods. In the final least-squares full-matrix refinement, Si, C, and N atoms were refined with anisotropic thermal displacement parameters. Hydrogen atoms (all located by a D-map) were refined isotropically. The final *R* value was 0.049 ($R_w = 0.048$). GOF = 2.62, $\Delta\rho_{\max} = 0.33$ e Å^{-3}, and $\Delta\rho_{\min} = -0.18$ e Å^{-3}. In addition, the bond lengths were corrected for the molecular rigid-body thermal motion using Busing and Levy's method,[5] which resulted in the lengthening of the bonds by 0.004−0.005 Å. The electron density distribution was calculated using low-order reflections ((sin θ)/$\lambda = 0.60$ Å^{-1}). All calculations except for the corrections of the rigid-

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[1] For reviews, see: (a) Barton, T. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 2, p 205. (b) Ayllett, B. J.; Sullivan, A. C. In *Comprehensive Organometallic Chemistry II*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1995; Vol. 2, p 45.

[2] X-ray crystallographic analysis of 3-silacyclopropenes: (a) Ando, W.; Shiba, T.; Hidaka, T.; Morihashi, K.; Kikuchi, O. *J. Am. Chem. Soc.* **1997**, *119*, 3629. (b) Hirotsu, K.; Higuchi, T.; Ishikawa, M.; Sugisawa, H.; Kumada, M. *J. Chem. Soc., Chem. Commun.* **1982**, 726. (c) Kunai, A.; Matsuo, Y.; Ohshita, J.; Ishikawa, M.; Aso, Y.; Otsubo, T.; Ogura, F. *Organometallics* **1995**, *14*, 1204. (d) Hojo, F.; Sekigawa, S.; Nakayama, N.; Shimizu, T.; Ando, W. *Organometallics* **1993**, *12*, 803. (e) Nefedov, O. M.; Egorov, M. P.; Kolesnikov, S. P.; Gal'minas, A. M.; Struchkow, T. Yu.; Antipin, M. Yu.; Sereda, S. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1986**, *7*, 1693. (f) Suzuki, H.; Tokitoh, N.; Okazaki, R. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 2471.

[3] Goller, A.; Heydt, H.; Clark, T. *J. Org. Chem.* **1996**, *61*, 5840.

[4] Sakamoto, K.; Tsutsui, S.; Sakurai, H.; Kira, M. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 253.

[5] Busing, W. R.; Levy, H. A. *Acta Crystallogr.* **1964**, *17*, 142.

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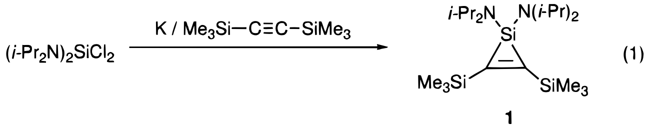
body thermal motions were carried out using the teXsan crystallographic software package on a Silicon Graphics IRIS Indigo workstation (Crystal Structure Analysis Package, Molecular Structure Corp., 1985 and 1992).

Results and Discussion

Compound **1** was prepared by the reduction of dichlorobis(diisopropylamino)silane with potassium in bis(trimethylsilyl)acetylene.[4] Recrystallization from pentane gave a single crystal of **1** suitable for the precise X-ray structural analysis involving determination of the electron-density distribution of the bent bonds in the molecule.

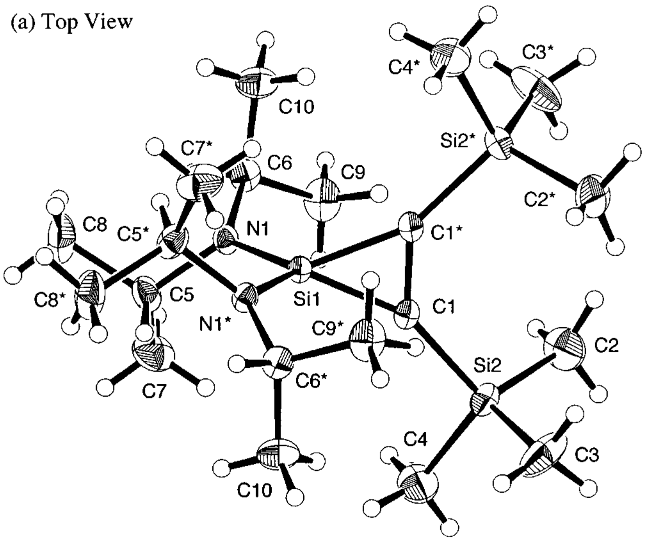


1

(1)

Figure 1 shows perspective views of the molecular structure of **1** with selected bond lengths and bond angles. The molecule has a crystallographic 2-fold axis through the Si(1) atom. The most intriguing structural feature is observed in the bond lengths in the silacyclopropene ring. The C(1)−C(1)* bond length of **1** is significantly longer but the Si(1)−C(1) bond lengths are shorter than those of the silacyclopropenes with carbon substituents on silicon (**3**−**7**; Chart 1), as shown in Table 1. The C=C and C−Si bond lengths of **1** are 1.371(2) [1.376(2)] and 1.806(1) [1.811(1)] Å, respectively (the bond lengths corrected for rigid-body thermal motion are in brackets); they are 1.342 and 1.827 Å as averaged values for **3**−**7**. The observed amino-substituent effects on the ring structure are in good agreement not only qualitatively but also quantitatively with those found by the ab initio MO calculations, regardless of the difference in the substituents on nitrogens and olefinic carbons; the differences in the experimental Si−C and C=C bond lengths for **1** from the corresponding theoretical values for 3,3-diamino-3-silacyclopropene (**8**) are only 0.004 and 0.002 Å, respectively (Table 1). The present results give the first experimental evidence for the σ^*-aromaticity in 3-silacyclopropene. The Si(2) and Si(2)* atoms do not lie precisely on the silacyclopropene plane but deviate by 0.148 Å; the Si(2)−C(1)−C(1)*−Si(2)* torsion angle is 13.5°. Corresponding to the twisting, the N(1)−Si(1)−N(1)* plane is not exactly orthogonal to the silacyclopropene ring but is slightly twisted, with a dihedral angle of 86.8°. The lengthening of the C(1)−C(1)* bond is not ascribed to the steric repulsion between two trimethylsilyl groups on the olefinic carbons, because the shortest H- - -H distance is 2.66(4) Å, longer than the sum of the van der Waals radii (2.4 Å).

(a) Top View



(b) Side View

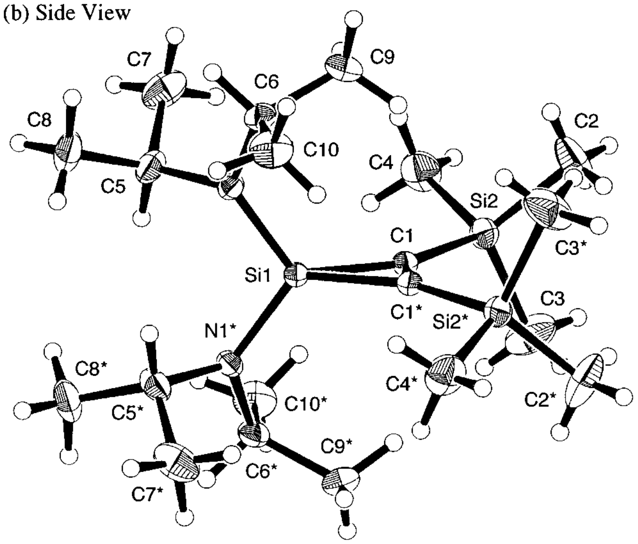


Figure 1. Top (a) and side ORTEP views (b) of **1**, showing the atom-numbering scheme. Asterisks indicate atoms related by symmetry. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) [corrected bond lengths for thermal motion]: C(1)−C(1)* = 1.371(2) [1.376(2)], C(1)−Si(1) = 1.806(1) [1.811(1)], C(1)−Si(2) = 1.859(1) [1.864(1)], N(1)−Si(1) = 1.714(1) [1.719(1)], Si(2)−C(2) = 1.857(2) [1.862(2)], Si(2)−C(3) = 1.869(2) [1.874(2)], Si(2)−C(4) = 1.858(2) [1.864(2)], N(1)−C(5) = 1.474(2) [1.479(2)], N(1)−C(6) = 1.477(2) [1.482(2)], C(methyl)−C(methyne) = 1.512(2)−1.532(2) [1.517(2)−1.537(2)]. Selected bond angles (deg): N(1)−Si(1)−N(1)* = 109.63(7), N(1)−Si(1)−C(1) = 123.37(5), N(1)−Si(1)−C(1)* = 121.08(8), C(1)−Si(1)−C(1)* = 44.60(7), Si(1)−C(1)−Si(2) = 154.38(7), Si(1)−C(1)−C(1)* = 67.70(4), Si(2)−C(1)−C(1)* = 137.33(6), Si(1)−N(1)−C(5) = 119.52(8), Si(1)−N(1)−C(6) = 123.55(8), C(5)−N(1)−C(6) = 115.3(1), C(methyl)−Si(2)−C(methyl) = 108.3(1)−110.0(2).

Although a number of studies on the electron density distribution obtained from the X-ray data have revealed the bending of the bonds in strained small-ring molecules,[6,7] no such investigation on 3-silacyclopropene derivatives has been reported so far. In **1**, the bond angles defined by inter-nucleus connection, C(1)−Si(1)−C(1)* and Si(1)−C(1)−C(1)*, are 44.60(7) and 67.70(4)°, respectively, indicating a considerably strained molecule. The electron densities in the bonds on the

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(6) Inter alia: (a) Irngartinger, H.; Goldmann, A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 775. (b) Irngartinger, H.; Jahn, R.; Maier, G.; Emrich, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 356. (c) Irngartinger, H.; Nixdorf, M. *Chem. Ber.* **1988**, *121*, 679. (d) Irngartinger, H.; Deuter, J. *Chem. Ber.* **1990**, *123*, 341. (e) Eisenstein, M.; Hirshfeld, F. L. *Acta Crystallogr.* **1983**, *B39*, 61.

(7) (a) Irngartinger, H.; Gries, S. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 565. (b) Bläser, D.; Boese, R.; Brett, W. A.; Rademacher, P.; Schwager, H.; Stanger, A.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 206.

Chart 1

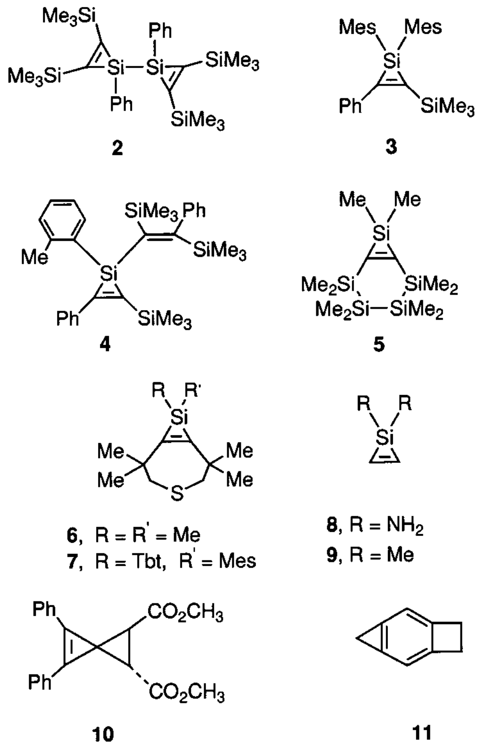

Table 1. Bond Lengths (Esd's) of Various 3-Silacyclopropene Derivatives

compd[a,b]	Si(ring)−C(ring)/Å	C(ring)−C(ring)/Å	ref
1	1.806(1)	1.371(2)	this work
2	1.80−1.84(1)	1.32(1), 1.33(1)	2a
3	1.800, 1.839(2)	1.349(3)	2b
4	1.801, 1.839(5)	1.352(7)	2c
5	1.83, 1.86(2)	1.35(2)	2d
6	1.810, 1.841(7)	1.332(7)	2e
7	1.813, 1.837(5)	1.326(5)	2f
8[c]	1.802	1.373	3
9[c]	1.822	1.354	3

[a] The structure is given in Scheme 2. [b] Unless otherwise noted, the structure was determined by X-ray crystallography. [c] The structure was optimized at the RMP2−FC/6-31G(d) level.

silacyclopropene ring of **1** have been determined at 200 K. The difference density map on the silacyclopropane plane is shown in Figure 2. The three density maxima denoted by P1, P2, and P3 lie almost in the same plane of the silacyclopropene ring. Point P1 is shifted by 0.27 Å from the center of the internucleus C(1)−Si(1) line, while P2 is shifted only by 0.16 Å from the C(1)−C(1)* line and P3 lies on the C(1)−Si(2) line. The angles of the electron density maximum−nucleus−electron density maximum connections at the saturated silicon and unsaturated carbons (substantial bond angles) in **1**, P1−Si(1)−P1* and P1−C(1)−P2, are 77.1 and 96.6°, respectively. Similar bond deformation has been observed in cyclopropene rings of a spiropentene (**10**) and a benzocyclopropene (**11**);[7] the corresponding substantial bond angles at the saturated and unsaturated carbons are ca. 85 and 95° in **10**, respectively, and 98 and 105° in **11**. The compression angles defined by the differences between the substantial and the apparent bond angles in **1** are comparable to those in **10** but much smaller than those in **11** with a highly strained cyclopropene ring; the compression angles in **1**, **10**, and **11** are 32.5, 31, and 42°, respectively, at the saturated silicon (or carbon) atom and 28.9, 32, and 45° at the olefinic carbons.

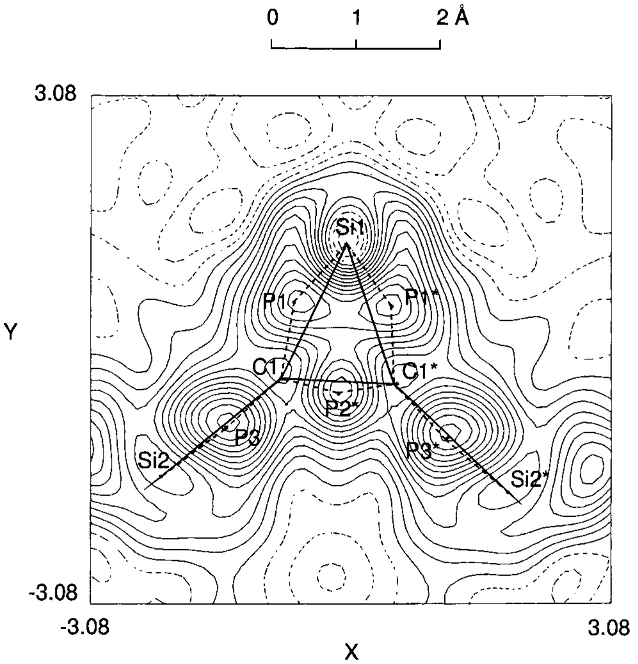

Figure 2. Electron density distribution in the bonds on the plane defined by C(1), C(1)*, and Si(1) atoms. The contour interval is 0.03 e Å^{-3}. The negative regions are shown by dashed lines. The electron densities at the maxima denoted by P1, P2, and P3 are 0.32, 0.30, and 0.33 e Å^{-3}, respectively.

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Supporting Information Available: Text and tables giving details of the X-ray structure analysis, atomic coordinates and isotropic thermal parameters, anisotropic displacement parameters, bond lengths, and bond angles for **1** (17 pages). Ordering information is given on any current masthead page.

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