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# Bonding in Cyclosilanes. Effect of Orbital Nonhybridization†

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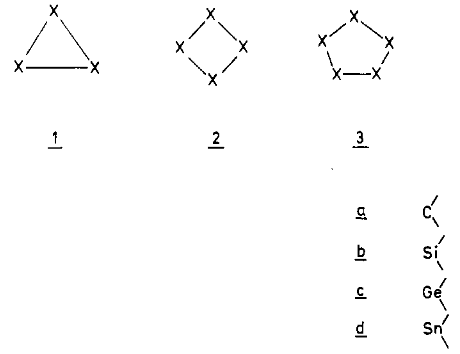
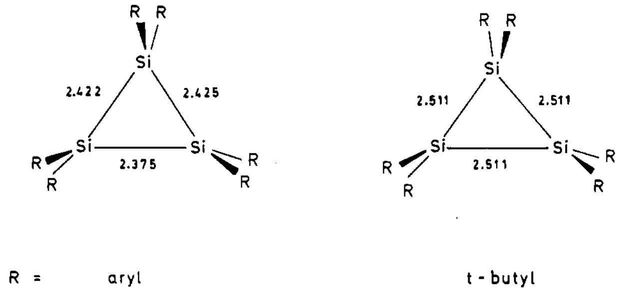
The bonding situation in cyclosilanes **1b**–**3b** is explored by quantum-chemical calculations at an ab initio SCF level. In silanes the silicon–silicon bonds are weaker than carbon–carbon bonds in alkanes, since the s valence orbitals can contribute less to the formation of strong hybrid orbitals. On this basis the resulting bonds are weak and the cyclic structures are stabilized by intramolecular perturbational orbital interaction. This is of importance for pronounced stabilization of four-membered ring structures. The ring strain is estimated from SCF calculations for isodesmic and homodesmic reaction energies.

## Introduction

The syntheses and structural elucidation of the inorganic ring systems **1b**–**d** are of current interest.[1] These supplement the larger ring systems **2b**–**d** and **3b**–**d**.[2] The recent structural investigations on **1b**–**d** reveal that the bond lengths between the heavy atoms (Si, Ge, Sn) are significantly longer compared to those in their open-chain analogues. Of the cyclotrisilane structures, two extreme cases are summarized here. In the structure reported by Masamune et al.[1a] all ring bonds (values are in angstroms) differ slightly from each other, but on the average they are longer than in disilane (2.33 Å[3]).





Compared to those in the structure reported by Weidenbruch et al.[1g] (R = *tert*-butyl), the Si–Si bonds are considerably elongated, all bonds being equal. In contrast, in the congener cyclopropane the C–C bonds are slightly shorter (1.512 Å[4]) than in ethane (1.526 Å[4]).

Here we report molecular orbital considerations on the series of cyclosilanes **1b**–**3b**. Some general features will be explored that reveal fundamental differences in bonding between ring systems constituted from the carbon series, $C_nH_{2n}$, vs. the silicon series, $Si_nH_{2n}$, or even the higher homologues of Ge and Sn. Our qualitative considerations are substantiated by ab initio SCF calculations of double-$\zeta$ quality for the cyclosilanes and cycloalkanes, including polarization functions at the heavy atoms.

In detail we will consider the following aspects: (a) ring strain, (b) hybridization of the ring bonds (banana-type bent bonds) and its relation to the Walsh model,[5] and (c) the effect of substituents on the distortion of the ring moiety. It will be shown that cyclotetrasilane (**2b**) possesses unusual bonding properties as compared with those of cyclobutane (**2a**).

For cyclopropane (**1a**) the effects of substituents on the distortion of the ring are well-understood,[6] but their role on the deformation of the parent cyclotrisilane (**1b**) has yet not been explored.

Silanes absorb light at longer wavelengths than alkanes,[2] because they possess energetically low-lying unoccupied molecular orbitals.[7] In addition, silicon is more electropositive than carbon.[8] An analysis of bonding in alkanes vs. that in silanes relates more s character to Si–Si bonds than to C–C bonds.[9] An important third factor may be summarized here. In silicon, the valence 3s orbital is more strongly contracted than its 3p valence orbital.[10] This trend increases from Si to Sn.[10] In fact, the valence s-orbital contraction is common for bonding for higher main-group elements. It is witnessed in some other important chemical phenomena as well, e.g. the occupancy of an oxidation state two below

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[2] West, R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 2.

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[5] Walsh, A. D. *Nature* (*London*) **1947**, *159*, 167, 712. Walsh, A. D. *Trans. Faraday Soc.* **1949**, *45*, 179. Sugden, T. M. *Nature* (*London*) **1947**, *160*, 367.

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[7] On this basis one can assign "metallic character" to silicon compounds. For a lucid discussion of metallic properties see: Albright, T. A.; Burdett, J. K.; Whangbo, M. H. *Orbital Interations in Chemistry*; Wiley: New York, 1985.

[8] Huheey, J. E. *Inorganic Chemistry*; Harper and Row: New York, 1983.

[9] Kovačevič, K.; Krmpotič, K.; Maksič, Z. B. *Inorg. Chem.* **1977**, *16*, 1421. Schoeller, W. W.; Dabisch, T. *J. Chem. Soc., Chem. Commun.* **1985**, 1706.

[10] (a) This is witnessed in the refined rules for the choice of orbital exponents of a Slater-type orbital wave function. Clementi, E.; Raimondi, D. L. *J. Chem. Phys.* **1963**, *38*, 2686. Burns, G. *J. Chem. Phys.* **1964**, *41*, 1521. (b) For further interpretations of the valence s-orbital contraction see: Pitzer, K. S. *Acc. Chem. Res.* **1979**, *12*, 271. Pykki, P.; Desclaux, J.-P. *Acc. Chem. Res.* **1979**, *12*, 276.

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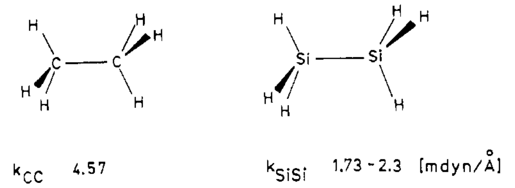
the group valence ("inert pair effect"[8]). Consequently, the valence s and p orbitals differ in space extension and overlap less to form strong hybrid orbitals.[11] In contrast, in carbon the valence s and p orbitals possess similar extensions in space and thus match perfectly for the formation of hybrid orbitals.

Hence, bonding in polyhedral $C_nH_{2n}$ molecules can be adequately described in terms of localized two-center-two-electron bonds.[12] Alternatively they have been classified as *electron-precise*[13] polyhedral molecules. In comparison to the situation in the silanes and the higher homologues the valence s and p orbitals cannot overlap perfectly for hybridization. Hence the two-center-two-electron bonds in silanes (and to a greater extent in the higher homologues Ge and Sn) suffer from orbital nonhybridization (denoted here as ONH).

As a consequence of the less "perfect" hybridization the bonds and deformation potentials in silanes are weaker than in alkanes; e.g., the force constant for the stretching vibration in ethane[14] is almost 3 times higher than in disilane.[15]



As we will see, in the absence of strong ("perfect") orbital hybridization, which causes a large HOMO-LUMO energy separation, the stabilities of the various structures are determined by the interaction of bonding molecular orbitals with energetically low-lying antibonding molecular orbitals of like symmetry (perturbational interaction[16]).

## Computational Procedure

Our qualitative analysis is based on the results of extended Hückel (EH)[17] calculations with the Wolfsberg-Helmholtz approximation,[18] the parameters given by Hinze and Jaffe,[19] and standard Slater exponents.[20] The bonding parameters for the EH calculations were chosen according to standard values.[8] The qualitative conclusions were supported by ab initio calculations at a double-ζ level and with inclusion of polarization functions at the heavy atoms C and Si. In detail the following basis sets were used:

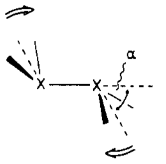
(1) Basis I refers to the ab initio STO 4/31G level.[21] If not stated otherwise, the geometries were optimized with this basis set. The optimizations of the geometries were performed at various levels of sophistication, e.g. cyclotetrasilane (**2b**) within $D_{4h}$ symmetry or alternatively without symmetry restriction. The results of these investigations are detailed in the text. The optimized geometries were then recomputed with basis II and basis III.

(2) Basis II consists of Gaussian lobe functions.[22] It is of double-ζ quality, constructed from the following Huzinaga[23] bases: Si, (11,7) in the contraction (5,6×1/4,3×1); C, (8,4) in the contraction (4,4×1/2,2×1); H, (3,1).

(3) Basis III is basis II augmented by one set of polarization functions at the heavy atoms C and Si: $\zeta_d(C) = 0.30$; $\zeta_d(Si) = 0.40$. Energy balances for the isodesmic and homodesmic reactions were obtained predominantly from basis II and basis III levels.

## Results and Discussion

**a. Disilyne.** The evaluation of the qualitative model begins with an analysis of bonding in the Si-Si double bond. Experimental and theoretical investigations[24] reveal for the (formal) π systems (**4**) antipyramidalization (as measured by the tilting angle α), which increases from Si to Sn.[24] According to EH calculations the molecular orbital system of disilyne ($D_{2h}$ symmetry) is



| X | α(°) |
|---|---|
| Si | 0. - 5. |
| Ge | 40. |
| Sn | 41. |

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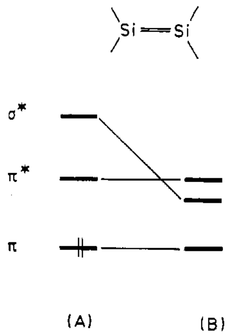

The EH calculations mimic two extreme bonding situations:

(A) The valence s and p orbitals possess equal orbital exponents; the bonding situation refers to the case of "perfect" orbital hybridization. A considerable energy difference between the HOMO (π) and the LUMO (π*) results.

(B) The valence s orbital is strongly contracted compared to the case for its valence p orbital. Hence, it can contribute less for hybridization to a $sp^3$ orbital (for the σ bonds). The situation refers to the case of orbital nonhybridization (ONH). Consequently, the σ* orbital becomes less antibonding and is considerably lowered in energy. Since the σ orbital and the π orbital possess different symmetry, they cannot interact. Interaction of both orbitals can only occur via symmetry breaking.[16] The mixing of the π orbital with the σ* orbital requires a vibration according to the direct product of the irreducible representations of the two orbitals (eq 1). The $b_{3g}$ distortion refers to induction of antipyramidalization at the Si atoms (**4**).

$$\Gamma_\pi \otimes \Gamma_{\sigma^*} = b_{1u} \otimes b_{2u} = b_{3g} \qquad (1)$$

A similar analysis on the Si-Si triple bond shows the distortion of a triple bond to a bridged structure[25] (**5**).

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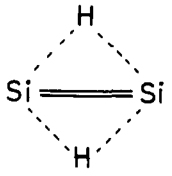

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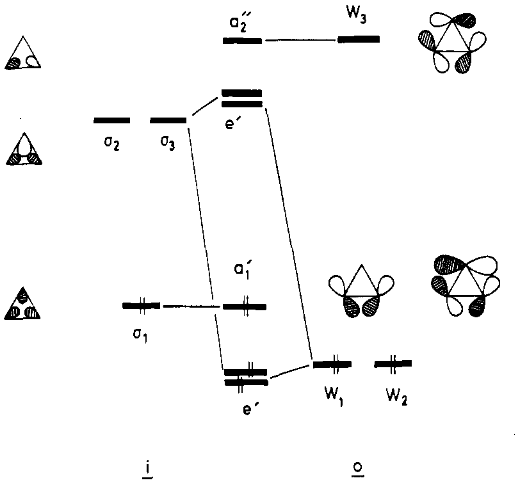
**b. Orbital Interactions in the Ring Systems.** Next we will apply this model to a qualitative analysis of bonding in the ring systems **1**–**3**. First, let us consider the familiar set of Walsh orbitals for cyclopropane:



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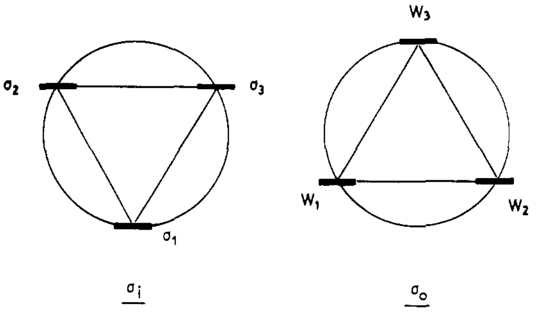
The orbital system consists of an inner set ($\sigma_1$–$\sigma_3$, **6i**) and an outer set ($W_1$–$W_3$, **6o**) of basis orbitals. In **6i** the degenerate e′ set is highest in energy while it is lowest for **6o**.

Qualitatively the eigenvalues for **6i** and **6o** are given by a triangle in a circle (Frost circle[26]) (**7**), with one vertex of the triangle placed either on the bottom (in **7**, $\sigma_i$) or the top (in **7**, $\sigma_o$) of the circle. It refers to the pattern of a Hückel (for **6i**) or Möbius (for **6o**) array of orbitals.[27] EH calculations on **1a** indicate that the mixing of the e′ (basis) sets of **6i** with those of **6o** is small, since the energy difference between the interacting orbitals is large.



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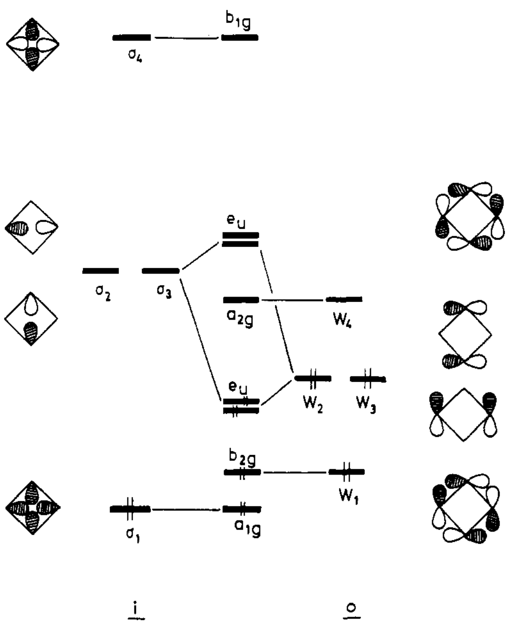

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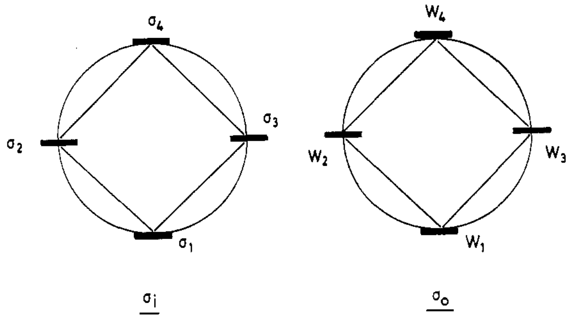
For cyclobutane (**2a**) one obtains the set of Walsh orbitals shown in **8**. Now the inner set, $\sigma_i$, as well as the outer set, $\sigma_o$, belong to a Hückel array[27] of orbitals. Within a Frost circle the eigenvalues are given by a square in a circle, with one vertex at the bottom as well as the top (**9**). These considerations indicate that the two degenerate sets of e′ orbitals are in closer proximity in the four-membered ring system as compared with the case for the three-membered ring system. It is also in accord with extended Hückel calculations, which reveal a stronger mixing of the e′ orbitals for **2a** than for **1a**.



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Consider finally the system of Walsh orbitals for the cyclosilanes, e.g. for **2b**, compared with that of the corresponding cycloalkanes (**2a**). Orbital nonhybridization lowers the antibonding $\sigma$ orbitals ($\sigma_2$, $\sigma_3$; **10**), which possess large s character (B vs. A). Since the $W_2$, $W_3$ orbitals are constituted from p

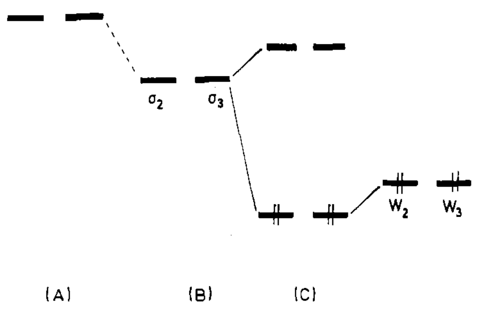

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**Table I.** Geometrical Parameters for Three- to Five-Membered Ring Systems and Open-Chain Congeners[a]

(A) Carbon Compounds

| structure | sym | CC | CH | $\angle$HCH | $\angle$CCC |
|---|---|---|---|---|---|
| $CH_4$[b] | $T_d$ | | 1.086 | 109.5 | |
| $C_2H_6$ | $D_{3d}$ | 1.526 | 1.088 | 107.4 | |
| *n*-$C_3H_8$ | $C_{2v}$ | 1.540 | 1.085[c]<br>1.084[d] | 106.1[c]<br>111.2 | 112.4 |
| c-$C_3H_6$[b] | $D_{3h}$ | 1.512 | 1.083 | 114.0 | 60.0 |
| c-$C_4H_8$ | $D_{4h}$ | 1.549[e] | 1.084 | 108.0 | 90.0 |
| c-$C_5H_{10}$ | $D_{5h}$ | 1.526[f] | 1.088 | 109.6 | 108.0 |

(B) Silicon Compounds

| structure | sym | SiSi | SiH | $\angle$HSiH | $\angle$SiSiSi |
|---|---|---|---|---|---|
| $SiH_4$ | $T_d$ | | 1.489 | 109.5 | |
| $Si_2H_6$ | $D_{3d}$ | 2.353 | 1.494 | 108.3 | |
| *n*-$Si_3H_8$ | $C_{2v}$ | 2.352 | 1.500[c]<br>1.492[d] | 106.6[c]<br>110.8[d] | 113.1 |
| c-$Si_3H_6$ | $D_{3h}$ | 2.334 | 1.494 | 112.4 | 60.0 |
| c-$Si_4H_8$ | $D_{4h}$ | 2.371 | 1.497 | 107.9 | 90.0 |
| c-$Si_5H_{10}$ | $D_{5h}$ | 2.380[f] | 1.490 | 112.0 | 108.0 |

[a] Energy optimization is at an ab initio basis I level, or values are taken from the literature. Bond distances are in angstroms and bond angles in degrees. [b] The geometrical parameters are according to: Gordon, M. S. *J. Am. Chem. Soc.* **1980**, *102*, 7419. Experimental geometries: Bastiansen, O.; Fritsch, F. N.; Hedberg, K. *Acta Crystallogr.* **1964**, *17*, 538. [c] $CH_2$ ($SiH_2$) group. [d] $CH_3$ ($SiH_3$) group. [e] Cremer, D. *J. Am. Chem. Soc.* **1977**, *99*, 1307. [f] Assumed; see also ref 35.

orbitals, they will not be affected. Hence, both degenerate sets come into closer proximity and they enhance their mutual interaction (C). It causes an overall stabilization of the occupied $W_2$, $W_3$ orbitals via orbital mixing with $\sigma_2$, $\sigma_3$. According to the previous considerations the mutual mixing of the degenerate sets will be larger in the four-membered ring system (**2b**) than in the three-membered ring system (**1b**). In fact, the SCF calculations that are reported in a later section of this publication evidence that in **2b** the orbitals $W_2$ and $W_3$ are already pushed below $W_1$.

It must be noted that symmetry breaking, as is observed for the case of **4**, does not take place here, since in the ring systems both degenerate orbital sets possess like symmetry. Hence, they can readily interact with each other without distortion of the structure to lower symmetry (the cross product analogous to eq 1 is e.g., for the case of **1**, $e' \otimes e' = a_1 + a_2 + e'$ and contains a total symmetric vibration with conservation of $D_{3h}$ symmetry).

In principle a similar analysis can be performed for cyclopentasilane (**3b**) as well as the other congeners disilane, trisilane, etc. These compounds do not possess energetically low-lying antibonding $\sigma^*$ orbitals which could considerably contribute via orbital mixing to bonding orbitals of like symmetry. Hence, intramolecular perturbational orbital mixing is not of essential importance for these structures. In other words an extra stabilization due to the effect of ONH is only of predominant importance for the four-membered ring system, **2b**. As we will see by the SCF calculations, this has two consequences: (a) the extreme low ring strain of **2b** and (b) the different sequences of frontier orbitals of **2b** vs. those of **2a**.

**c. Geometrical Parameters and Ring Strain.** In the quantitative assessment of bonding in **1**–**3** we will first report the bonding parameters of **1**–**3**. For the silanes (cyclosilanes) they were obtained from energy optimization at basis I level. For the carbon compounds they were chosen according to literature data. The resulting bonding parameters are collected in Table I and their corresponding SCF energies in Table II. In cyclotrisilane (**1b**) the ring bonds are almost equal in length as compared with those of their open-chain congeners disilane and trisilane. Thus, regarding the bond distances, the rings and disilane reveal analogous trends as in the corresponding carbon compounds. This is in variance to the experimental findings for **2b**.[1] The discrepancy will be discussed in a later part of our publication.

**Table II.** SCF Energies (Negative, in au) of Silane, Disilane, Trisilane, and Cyclotrisilane to Cyclopentasilane and Corresponding Carbon Analogues

| structure | basis I | basis II | basis III |
|---|---|---|---|
| $CH_4$ | 40.1398 | 40.1746 | 40.1753 |
| $C_2H_6$ | 79.1158 | 79.1886 | 79.1955 |
| *n*-$C_3H_8$ | 118.0879 | 118.1919 | 118.2162 |
| c-$C_3H_6$ | 116.8832 | 117.0008 | 117.0165 |
| c-$C_4H_6$ | 155.8660 | | 156.0416 |
| c-$C_5H_{10}$ | 194.8700 | | 195.0872 |
| $SiH_4$ | 290.8591 | 291.1752 | 291.2178 |
| $Si_2H_6$ | 580.5846 | 581.2072 | 581.2870 |
| *n*-$Si_3H_8$ | 870.3105 | | 871.3628 |
| *n*-$Si_4H_8$ | | | 1161.4366 |
| *n*-$Si_5H_{10}$ | | | 1451.5105 |
| c-$Si_3H_6$ | 869.0923 | 870.0466 | 870.1590 |
| c-$Si_4H_8$ | 1158.8720 | | 1160.2670 |
| c-$Si_5H_{10}$ | | | 1450.3570 |

**Table III.** Heats of Reaction for the Isodesmic and Homodesmic Reactions (1), at Various ab Initio Levels

| | | | reacn enthalpies, kcal/mol | | |
|---|---|---|---|---|---|
| X | *m* | *n* | basis I | basis II | basis III |
| C | 1 | 3 | 28.5 | 25.9 | 27.7 |
| | 1 | 4 | 24.4 | | 24.6 |
| | 1 | 5 | 6.9 | | 8.7 |
| | 2 | 3 | 20.6 | | 28.6 |
| | 2 | 4 | 13.8 | | 25.9 |
| | 2 | 5 | −6.3 | | 10.2 |
| Si | 1 | 3 | 52.7 | 31.1 | 30.5 |
| | 1 | 4 | 18.6 | | 6.2 |
| | 1 | 5 | | | −6.9 |
| | 2 | 3 | 53.6 | | 36.1[a] |
| | 2 | 4 | 19.8 | | 13.7 |
| | 2 | 5 | | | 2.5 |
| | 3 | 3 | | | 39.2 |
| | 3 | 4 | | | 17.7 |
| | 3 | 5 | | | 7.5 |
| | 4 | 3 | | | 39.3 |
| | 4 | 4 | | | 18.0 |
| | 4 | 5 | | | 7.8 |

[a] $C_{2v}$ symmetry of $Si_3H_8$.

Next we will estimate the ring strain in the parents (R = H) **1a** and **1b** by corresponding isodesmic ($m = 1$) and homodesmic[28] ($m > 1$) reactions (eq 2), for X = C, Si and $n = 3$–5. The reaction

$$X_nH_{2n} + nX_mH_{2m+2} \rightarrow nX_{m+1}H_{2m+4} \tag{2}$$

enthalpies (Table III) were calculated from the SCF energies (Table II) at various basis set levels. Most of the reactions are exothermic; i.e., the listed values are positive. For the carbon compounds the heats of formation are well-known and a comparison with experimental heats of formation is possible. A ring strain energy of 27.6 kcal/mol has been estimated,[29] which agrees well with our value, e.g., 28.6 kcal/mol for X = C, $n = 3$, $m = 2$, and basis III. In addition, it also agrees with a previous quantum-chemical study on cyclopropane.[30] In comparison, organosilicon chemistry lacks a large body of reliable and systematic thermochemical data,[31] and values for the cyclosilanes are not known.

For **1b**, the results for the calculations of ring strain (see Table III) by reaction 2 depend on the basis set. According to basis

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(28) Hehre, W. J.; Ditchfield, R.; Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 4796. George, P.; Trachtmann, M.; Brett, A. M.; Bock, C. W. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1036. George, P.; Trachtmann, M.; Bock, C. W.; Brett, A. M. *Tetrahedron* **1976**, *32*, 317.

(29) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley-Interscience: New York, 1976.

(30) 25.6 kcal/mol.[4]

(31) Experimental values (in kcal/mol) for the following silanes are known: $SiH_4$ −4.3 (Potzinger, P.; Lampe, F. W. *J. Phys. Chem.* **1970**, *74*, 719); $Si_2H_6$ −0.1, $Si_3H_8$ 0.1 (Wagman, D. D.; Evans, W. H.; Parker, V. B.; Halow, I.; Bailey, S. M.; Schumm, R. H. *NBS Tech. Note* (*U.S.*) **1968**, *No. 270-3*). Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246.

I the reaction energy is much larger than the results with basis II or basis III. It seems that the STO 4/31G basis overestimates the ring strain in **1b** since it is less flexible than basis II. Basis III differs from basis II in the inclusion of polarization functions at the heavy atoms. The results in Table III indicate that the addition of d functions does not alter the picture. In addition, we have tested the effect of additional polarization functions at the hydrogens.[32] For reaction 2 ($m = 1$, $n = 3$, X = Si) we obtained an energy difference of 29.7 kcal/mol, which is close to the estimate from basis III.

In the cyclosilane series, the result of the isodesmic reactions ($m = 1$) differ from those of the homodesmic ($m > 1$) reactions. The difference between both reactions ((eq 2, $m = 1$) − (eq 2, $m = 2$) results in the isomerization reaction given by eq 3 for $n = 1$. Reaction 3a is slightly endothermic and reaction 3b

$$SiH_4 + Si_3H_8 \rightarrow 2Si_2H_6 \quad -4.1 \text{ kcal/mol} \qquad (3a)$$

$$CH_4 + C_3H_8 \rightarrow 2C_2H_6 \quad -0.1 \text{ kcal/mol} \qquad (3b)$$

thermoneutral (values taken from Table III, basis III). With use of experimentally determined heats of formation, the energy balance for (3b) results to 2.3 kcal/mol.[29] Hence, the isomerization reaction (3) gives a quantitative estimate for the energy differences between isodesmic ($m = 1$) and homodesmic ($m > 1$) reactions.[33]

An ideal measure of strain would be in a comparison of the (strained) cyclic system with an infinite open-chain (strain-free) analogue. However, in reality this is not possible. Nevertheless, our investigations allow the study of the convergence limit of the series of homodesmic reactions, i.e. the effect of increasing $m$ on the resulting ring strain energies. The homodesmic reactions (see Table III) converge with increasing $m$ to an upper limit for the ring strain energies. The values for $m = 4$ are as follows (kcal/mol): **1b**, 39.3; **2b**, 18.0; **3b**, 7.8. However, the trend that the four-membered ring cyclotetrasilane takes up an exceptional position, i.e., it is extremely low in strain compared with that in cyclobutane, is paralleled by isodesmic and homodesmic reaction enthalpies. While cyclotetrasilane is much less strained than cyclobutane (table III, X = C, $m = 2$, 25.9 kcal/mol, basis III), it is at the same time more strained than cyclopropane (X = C, $m = 2$, 28.6 kcal/mol, basis III). Our findings may be contrasted with a recent analysis of ring strain in cyclotriphosphane and related compounds.[34] There the ring strain is negligibly small. In these systems s-electron density can be placed into the nonbonding lone pairs while the p electrons are used up for the ring bonds. It results in low strain for rings constituted of phosphorus.

**d. Bond Stretching in Cyclotrisilane.** While the calculated equilibrium Si–Si bond length for **1b** is 2.334 Å (see Table I), the experimentally determined bonds are in fact longer, ranging from 2.375[1a] to 2.511 Å.[1g] What is the reason for the apparent contradiction between experiment and theory?

In fact, the force constant for the Si–Si bond in disilane is much smaller than that of the C–C bond in ethane. This already indicates that stretching of the former bond costs less energy than stretching of a C–C bond. In order to quantify this argument, we performed SCF calculations on **1b** and disilane at various Si–Si bond lengths (keeping within $D_{3h}$ geometry the remainder constant). The resulting potential surface (at basis II) is extremely flat; e.g., some relative energies are as follows. (a) For disilane: Si–Si = 2.30 Å, 0.8 kcal/mol; Si–Si = 2.50 Å, 1.2 kcal/mol. (b) For parent cyclotrisilane: Si–Si = 2.35 Å, 0.4 kcal/mol; Si–Si = 2.51 Å, 3.9 kcal/mol. On this basis the bulky substituents introduced into the ring (in order to kinetically stabilize the structure) hinder each other sterically enough to stretch the Si–Si bonds.

**Table IV.** Valence Orbital Energies (Negative, in eV) of **1b** and **1a** (Basis III)

| MO's | c-$Si_3H_6$ | c-$C_3H_6$ |
|---|---|---|
| 1 | 9.2 (e′) | 11.4 (e′) |
| 2 | 9.2 (e′) | 11.4 (e′) |
| 3 | 13.1 (e″) ($\pi$) | 13.9 (e″) ($\pi$) |
| 4 | 13.1 (e″) ($\pi$) | 13.9 (e″) ($\pi$) |
| 5 | 13.5 ($a_1$′) | 17.1 ($a_1$′) |
| 6 | 14.0 ($a_2$″) ($\pi$) | 18.2 ($a_2$″) ($\pi$) |
| 7 | 17.9 (e′) | 22.3 (e′) |
| 8 | 17.9 (e′) | 22.3 (e′) |
| 9 | 21.7 ($a_1$′) | 30.3 ($a_1$′) |

**Table V.** Valence Orbital Energies (Negative, in eV) of **2b** and **2a** (Basis III)

| MO's | c-$Si_4H_8$ | c-$C_4H_8$ |
|---|---|---|
| 1 | 9.8 ($b_{2g}$) | 11.7 ($e_u$) |
| 2 | 10.4 ($e_u$) | 11.7 ($e_u$) |
| 3 | 10.4 ($e_u$) | 12.1 ($b_{2u}$) ($\pi$) |
| 4 | 12.6 ($b_{2u}$) ($\pi$) | 13.4 ($b_{2g}$) |
| 5 | 13.2 ($e_g$) ($\pi$) | 14.7 ($e_g$) ($\pi$) |
| 6 | 13.2 ($e_g$) ($\pi$) | 14.7 ($e_g$) ($\pi$) |
| 7 | 13.6 ($a_{1g}$) | 17.4 ($a_{1g}$) |
| 8 | 14.0 ($a_{2u}$) ($\pi$) | 17.8 ($a_{2u}$) ($\pi$) |
| 9 | 17.0 ($b_{1g}$) | 20.2 ($b_{1g}$) |
| 10 | 18.9 ($e_u$) | 24.5 ($e_u$) |
| 11 | 18.9 ($e_u$) | 24.5 ($e_u$) |
| 12 | 21.7 ($a_{1g}$) | 30.5 ($a_{1g}$) |

In addition, the structural investigations on cyclotetrasilane (**2b**) reveal slightly puckered ring systems.[2] We have studied in detail the puckering mode in **2b**. The resulting potential surface (not recorded here in detail) is extremely flat. However, the most stable geometry results in $D_{4h}$ symmetry, in agreement with previous investigations.[35] It should be kept in mind that the inversion barrier in cyclobutane is only 1.4 kcal/mol.[36] Puckering in the four-membered ring system is the consequence of relieving steric strain between eclipsed hydrogen atoms. Because the repulsive interaction between the eclipsed hydrogens in disilane is essentially smaller than in ethane, less tendency for folding the four-membered ring in unsubstituted **2b** as compared with that in **2a** is to be expected. Similar considerations hold for the equilibrium geometry of cyclopentasilane (**3b**).

It must be noted that in the optimization of the geometries d orbitals are not included in the basis set. This fact might cause an overestimation of planarity for the ring structures. Hence, the question of puckering of cyclotetrasilane and cyclopentasilane cannot be considered as definite at the present level of theory.

**e. Orbital Energies in Cyclosilanes.** Since in the present study we performed quantum-chemical calculations of rather good quality, we regard it worthwhile to report the orbital energies (Tables IV and V) of cyclotrisilane (**1b**) and cyclotetrasilane (**2b**). In view of Koopmans' theorem[37] they can be correlated with the experimental ionization potentials and they might be also useful for other purposes. Only the valence orbital energies are listed in the tables. For comparison the valence orbital energies of the corresponding **1a** (**2a**) are included. They agree well with the reported photoelectron spectra.[38] In the silicon case the lowest energy Walsh orbital, $\phi_5$, is closer to the upper Walsh orbitals, $\phi_1$ and $\phi_2$, than in carbon. Compared with the case for cyclobutane, **2b** reveals a reversed order of Walsh orbitals. The degenerate $e_u$ set is energetically below the $b_{2g}$ orbital, in accordance with the predications of our qualitative model.

**f. Hybridization and Bent-Bond Character.** In the Coulson–Moffitt picture[39] of bonding the ring bonds are bent (banana-like);

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(32) Basis III plus one set of p functions at each hydrogen; $\zeta_p(H) = 0.65$.

(33) As in the case of $CF_4$ (Benson, S. W. *Angew. Chem.* **1978**, *90*, 868; *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 812) $SiH_4$ gains extra stabilization due to the large difference in electronegativity between silicon and hydrogen. This results in an endothermic reaction balance for eq 3.

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**Table VI.** Mulliken Population Analysis (Gross Atomic Populations) of the Localized Orbitals in Cyclotrisilane to Cyclopentasilane, Carbon Analogues, and Open-Chain Congeners (Basis III)

(A) Carbon Structures

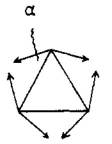
| structure | bond | atom | s | p | d | s/p/d ratio |
|---|---|---|---|---|---|---|
| $CH_4$ | C–H | C | 0.32 | 0.82 | 0.01 | 1/2.54/0.02 |
| | | H | 0.89 | | | |
| $C_2H_6$ | C–C | C | 0.28 | 0.74 | 0.02 | 1/2.64/0.05 |
| | C–H | C | 0.29 | 0.82 | 0.02 | 1/2.62/0.05 |
| | | H | 0.90 | | | |
| c-$C_3H_6$ | C–C | C | 0.21 | 0.81 | 0.02 | 1/3.78/0.08 |
| | C–H | C | 0.35 | 0.75 | 0.00 | 1/2.16/0.00 |
| | | H | 0.90 | | | |
| c-$C_4H_8$ | C–C | C | 0.26 | 0.77 | 0.02 | 1/2.96/0.08 |
| | C–H | C | 0.29 | 0.78 | 0.01 | 1/2.69/0.03 |
| | | H | 0.92 | | | |
| c-$C_5H_{10}$ | C–C | C | 0.26 | 0.75 | 0.02 | 1/2.88/0.08 |
| | C–H | C | 0.27 | 0.78 | 0.02 | 1/2.89/0.07 |
| | | H | 0.93 | | | |

(B) Silicon Structures

| structure | bond | atom | s | p | d | s/p/d ratio |
|---|---|---|---|---|---|---|
| $SiH_4$ | Si–H | Si | 0.32 | 0.54 | 0.05 | 1/1.67/0.15 |
| | | H | 1.13 | | | |
| $Si_2H_6$ | Si–Si | Si | 0.39 | 0.62 | 0.03 | 1/1.58/0.08 |
| | Si–H | Si | 0.31 | 0.56 | 0.05 | 1/1.81/0.12 |
| | | H | 1.12 | | | |
| *n*-$Si_3H_8$ | Si–Si | Si[a] | 0.39 | 0.65 | 0.00 | 1/1.65/0.00 |
| | | Si[c] | 0.37 | 0.61 | 0.00 | 1/1.65/0.00 |
| | Si–H[a] | Si | 0.30 | 0.59 | 0.04 | 1/1.93/0.14 |
| | | H | 1.10 | | | |
| | Si–H[b] | Si | 0.32 | 0.56 | 0.04 | 1/1.75/0.18 |
| | | H | 1.11 | | | |
| c-$Si_3H_6$ | Si–Si | Si | 0.35 | 0.69 | 0.03 | 1/1.97/0.09 |
| | Si–H | Si | 0.34 | 0.57 | 0.04 | 1/1.66/0.12 |
| | | H | 1.07 | | | |
| c-$Si_4H_8$ | Si–Si | Si | 0.38 | 0.64 | 0.03 | 1/1.68/0.08 |
| | Si–H | Si | 0.32 | 0.60 | 0.04 | 1/1.87/0.13 |
| | | H | 1.07 | | | |
| c-$Si_5H_{10}$ | Si–Si | Si | 0.37 | 0.64 | 0.03 | 1/1.73/0.13 |
| | Si–H | Si | 0.32 | 0.61 | 0.04 | 1/1.90/0.13 |
| | | H | 1.07 | | | |

[a] At the central atom. [b] Average of bonds at terminal atoms. [c] At the terminal atom.

i.e. the bonds point outward from the line connecting the ring atoms. Hence the angle $\alpha$ (here illustrated for **1**)



α [°]

| 1 | 2 | 3 | |
|---|---|---|---|
| 14.0 | 5.2 | 0.0 | a |
| 15.0 | 6.3 | 0.0 | b |

represents a measure of strain. We have calculated the banana-type bonds from the dipole moments of the localized orbitals. The angles between two ring bonds were calculated from the charge centers of this corresponding localized orbitals. In the cyclosilane series as well as the cycloalkane series the ring bonds are bent by approximately the same amount (basis III level). This indicates comparable bent banana bonds. For **1a** our result is in agreement with previous quantum-chemical investigations[40] as well as electron density measurements from crystallographic data.[41] It must be noted that a more refined analysis of the bent bond character in the ring systems is provided by the analysis of the electron density gradients.[42]

Finally, we complete our investigations by Mulliken population analyses of the localized orbitals of the silicon and carbon structures (Table VI). Since different basis sets were used for carbon vs. silicon, the population analyses amoung the two families of structures cannot strictly be compared to each other.[43] Nevertheless, some trends in bonding are obvious. First of all, the Si–H bonds are more polar than the C–H bonds, making the hydrogens accumulate more electron density. Second, in both cases the p character of the bonds between the heavy atoms (Si, C) increases from $Si_2H_6$ ($C_2H_6$) to $Si_3H_6$ ($C_3H_6$) at the expense of the s character. The larger ring systems, **2** and **3**, are intermediate cases.

For the carbon systems consistent data for comparison exist. As determined from maximum overlap calculations, the C–C bond in cyclopropane is described by an $sp^{3.86}$ hybrid orbital[44] and in ethane by a $sp^{3.21}$ hybrid orbital.[9] Thus, the p character in the ring bonds is larger than in the corresponding bonds of the open-chain congener. According to our investigations this observation also holds for bonding in the silane series. Hence, the essential difference in the ring bonds between **1a**–**3a** and **1b**–**3b** is the larger s character of the Si–Si bonds. In fact this also agrees with an analysis of the *J*(Si–H) spin–spin coupling constants on the basis of the maximum overlap approximation.[44,45]

## Conclusions

The results of our investigations can be summarized as follows: (1) The ring strain in cyclotrisilane is comparable to that in cyclopropane, as revealed by corresponding isodesmic reactions. However, they yield higher values with corresponding homodesmic reactions. (2) The ring bonds are bent similarly in both structures, as obtained from an analysis of localized orbitals. (3) The localized orbitals for the ring bonds in the parent (R = H) **1b** possess more s character than in the parent **1a**. This is in agreement with a previous analysis on silanes by the maximum overlap method. As in cyclopropane (**1a**) the bent ring bonds acquire more p character than the open-chain congeners disilane to pentasilane. (4) The potential surface for the Si–Si bond stretching in these ring systems is strongly influenced by relief of steric strain exerted by bulky substituents. (5) Cyclotetrasilane possesses an unusually low ring strain as compared with that in cyclobutane. Due to the topology of the ring orbitals (Hückel vs. Möbius systems) the mixing of antibonding with bonding orbitals is more facile in **2**.

Given the qualitative model, the stabilities of structures are strongly influenced by the "metallic character", which means a small energy separation between occupied and unoccupied molecular orbitals within these systems. This increases bonding via intramolecular orbital mixing. Our investigations, which have been detailed for **1b**–**3b**, should hold equally well for the higher homologues **1c,d**–**3c,d**. The atoms Ge and Sn are more electropositive than Si, and their "metallic character" is even more pronounced. Hence, on a qualitative basis our considerations are also valid for the higher congeners in the periodic table of elements.

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**Registry No.** c-$Si_3H_6$, 18548-76-0; c-$Si_4H_8$, 287-69-4; c-$Si_5H_{10}$, 289-22-5.

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