

Bond Stretch Isomerism in the Silicon Analogues of Bicyclo[1.1.0]butane and of [1.1.1]Propellane. Consequence of Orbital Nonhybridization¹

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Through-bond interactions in a polysilylene chain are different from those in a polymethylene chain. Hyperconjugative interactions are much stronger in the former due to (a) the presence of energetically low lying orbitals in silicon systems and (b) the electropositive character of silicon. As a consequence of orbital nonhybridization tetrasilabicyclo[1.1.0]butane and pentasilabicyclo[1.1.1]propellane suffer from an extremely facile bond-stretching isomerism. The lability of the central bond in these systems is also enforced by the relatively high ring strain in cyclotrisilane as compared with that in cyclotetrasilane. The theoretical analysis is supported by extended Hückel and ab initio SCF calculations at a double- ζ level. For tetrasilabicyclo[1.1.0]butane the preference for a closed or an open structure depends on the substituents at the silicon atoms.

Introduction

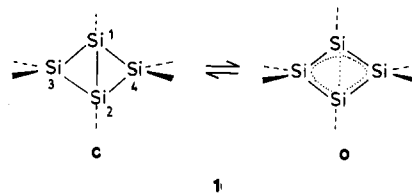
The concept of hybridization has proven to be one of the most powerful models for rationalizing repeated bonding in chemistry.² It is used to explain certain types of bonding, e.g. tetrahedral (sp^3), trigonal (sp^2), or digonal (sp) types of reiterated environments in molecules. The concept has its strength in carbon-hydrogen chemistry. There the bonding properties can be confined to localized bonds and the stability of a molecule, e.g. of an alkane, is proportional to the number of C-C bonds and C-H bonds. Additivity schemes have been constructed for the simple calculation of heats of formation of carbon-hydrogen bonds.³

An important requirement for hybridization of the valence s and p orbitals is similar extension in space. The resulting hybrid orbitals are more suitable for overlap. Consequently, the energy gain due to overlap of hybrid orbitals is larger than the promotion energy required for it.² This principle may not apply to the higher homologues in the periodic table of elements. There the valence s orbitals are more strongly contracted than the valence p orbitals. On this basis the s orbitals become more "inert", a rule that has been known for a long time in inorganic chemistry as the "inert electron pair effect".⁴

In this report we analyze the importance of this rule for certain aspects of bonding in cyclopolysilanes. We will investigate in detail the concept of through-space versus through-bond interactions of two nonbonding orbitals via a polysilylene chain and compare it with through-space versus through-bond interactions in the corresponding homologues of carbon-hydrogen chemistry. As a consequence of this concept it will be shown that bicyclopentasilane (**1**, Chart I) suffers from an easy bond-stretch isomerization of an open, **1o**, to a closed, **1c**, structure. Our theoretical analysis, which is based on the results of extended Hückel (EH) and ab initio SCF calculations, reveals substantial substituent effects on the preference of **1c** over **1o** (or vice versa). On this basis one should be able to synthesize bicyclic structures with an intact central bond, as in **1c**, or a strongly loosened Si-Si bond, as in **1o**. According to our analysis the latter corresponds to a nonclassical isomer of **1**.

From the viewpoint of experiment the central bond Si(1)-Si(2) in a derivative of **1** is extremely labile. A lower limit of 15 kcal/mol has been estimated for the energy of this central bond.^{5a}

Chart I



On the other hand, an X-ray investigation^{5b} on a derivative of **1** reveals a Si(1)-Si(2) bond length of 2.373 Å, quite typical for a Si-Si single bond (2.331 Å in disilane^{5c}). The lability of the central bond is supported by recent ab initio calculations¹ on the parent **1**, predicting a rather flat potential surface for bond stretching.

Computational Procedure

The EH calculations⁶ were carried out with the Wolfsberg-Helmholtz approximation,⁷ with the parameters given by Hinze and Jaffe,⁸ and with standard Slater exponents.⁹ The geometries for the EH calculations were chosen according to standard values⁶ or taken from the results of ab initio calculations.¹ To mimic the "inert electron pair" effect, we have chosen two extreme models for the EH calculations: model A with equal exponents for the Slater type valence (s, p) orbitals and model B with a strongly contracted s valence orbital. Details will be presented in the following discussion. The qualitative conclusions were supported by ab initio calculations at a double- ζ level with inclusion of polarization functions at silicon. The following basis sets were used:

(1) Basis I refers to the ab initio STO 4/31G level.¹⁰ The geometry of **1** was optimized with this basis set and then the energy recomputed with the better bases.

(2) Basis II consists of Gaussian lobe functions.¹¹ It is of double- ζ quality, constructed from the following Huzinaga¹² bases: Si, (11,7) in the contraction (5,6 \times 1/4,3 \times 1); C and F, (8,4) in the contraction (4,4 \times 1/2,2 \times 1); H, (3,1). One set of polarization functions was added to silicon, $\zeta_d(\text{Si}) = 0.40$.

(3) Basis III is basis II with one additional set of polarization functions for carbon, $\zeta_d(\text{C}) = 0.30$. It was used for the calculation of isodesmic and homodesmotic reactions of the carbon compounds.

(4) Basis IV is basis II augmented by two sets of polarization functions for silicon, $\zeta_d(\text{Si}) = 0.70, 0.20$. One set of polarization functions for hydrogen, $\zeta_p(\text{H}) = 0.433$, was included.

Results and Discussion

a. Orbital Nonhybridization in AH_2 and AH_3 Systems. We begin our discussion logically with an analysis of bonding in the smallest unit of a polysilylene chain, i.e. with silylene. Its familiar

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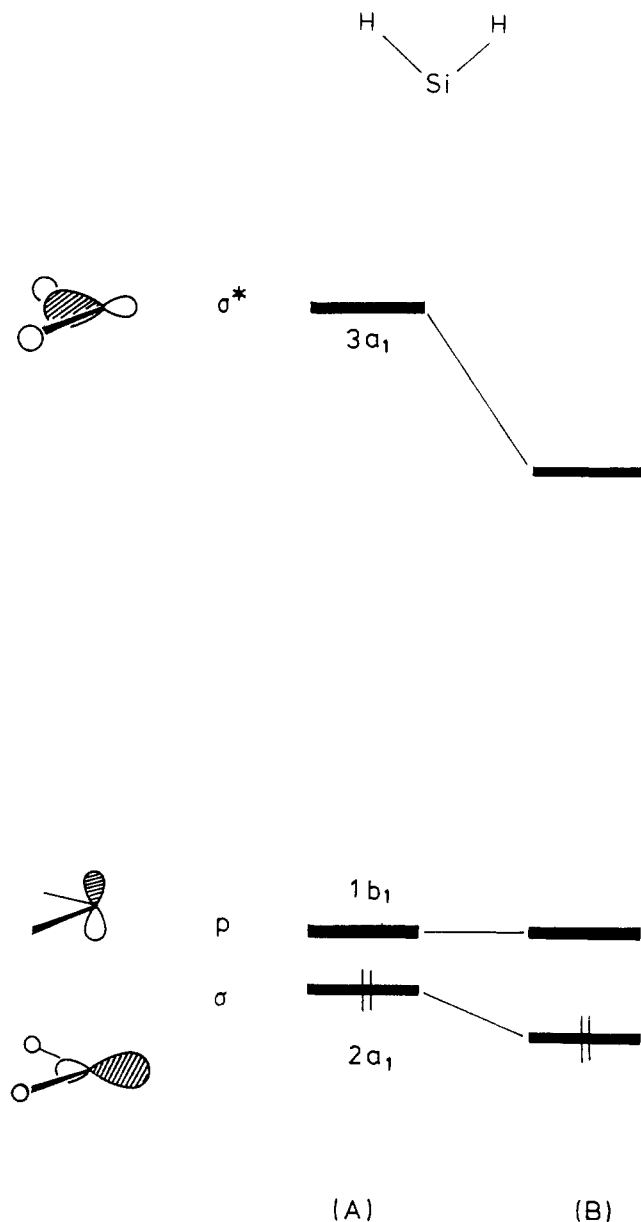


Figure 1. Molecular orbitals of SiH_2 (C_{2v} symmetry) before (A) and after (B) contraction of the 3s valence orbital at silicon.

orbital system¹³ is depicted in Figure 1. The orbitals that are of crucial importance for our discussion are σ and σ^* . They refer to an essentially nonbonding lone pair ($2a_1$) or an antibonding orbital ($3a_1$). Importantly, the orbitals σ and σ^* point in opposite directions. Part A in Figure 1 is derived from EH calculations by assuming equal Slater exponents for the valence 3s and 3p orbitals at Si. Hence, the orbitals perfectly match in their space extension for the formation of hybrid orbitals; it is the case of isovalent hybridization. In Figure 1B the 3s valence orbital at silicon is strongly contracted. For our model calculations we have chosen the s-orbital exponent for silicon as $\zeta'(s) = \zeta(s) + 1.0$. In other words, it mimics a bonding situation in which overlap of the 3s orbital with the 3p orbital is strongly diminished ("inert s orbital"). In the following discussion we will feature this fact as *orbital nonhybridization* (ONH).¹⁴

As a consequence of the 3s valence orbital contraction the σ^* orbital becomes less antibonding and is strongly lowered in energy. At the same time the nonbonding σ orbital increases its s character; e.g. model A results for $\sigma = 0.431 s(\text{Si}) + 0.834 p(\text{Si})$ and model

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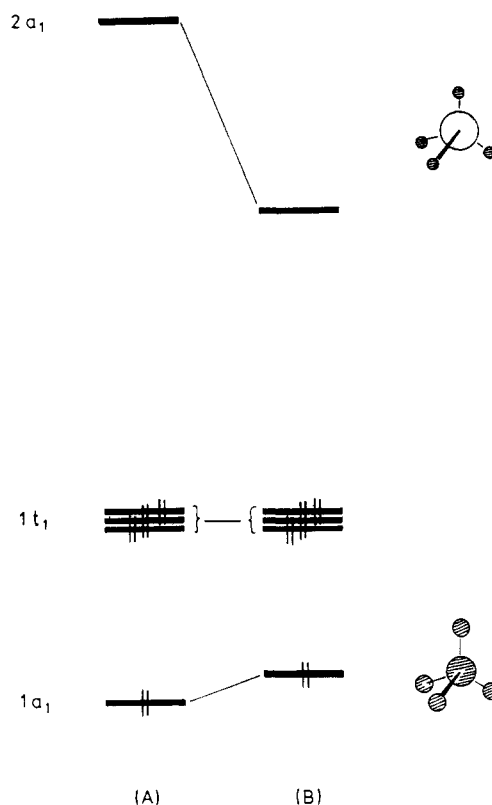


Figure 2. Molecular orbitals of SiH_4 (T_d symmetry) before (A) and after (B) contraction of the 3s valence orbital at silicon.

B for $\sigma = 0.537 s(\text{Si}) + 0.644 p(\text{Si})$. Hence, the energy splitting between the frontier orbitals HOMO ($2a_1$) and LUMO ($1b_1$) increases. In fact, a singlet ground state comes to the fore in the order $\text{CH}_2 < \text{SiH}_2 < \text{GeH}_2 < \text{SnH}_2$.¹⁵

	$E(S_0) - E(T_0)$	[kcal/M]
CH_2	10.5	
SiH_2	-18.6	
GeH_2	-19.0	
SnH_2	-19.0	

This sequence parallels the trend for an increase of s-valence-orbital contraction in the series $\text{Si} < \text{Ge} < \text{Sn}$.¹⁶

The bonding situation in AH_3 systems (NH_3 , PH_3 , AsH_3 , etc.) is related to that in the AH_2 cases. A lone pair at the central atom is present that increases its s character with increasing contraction of the ns valence orbital. Concomitantly, the inversion barrier in these systems increases in the same order.⁴ Similarly, silyl radicals adopt a nonplanar conformation^{17a} as do the higher ho-

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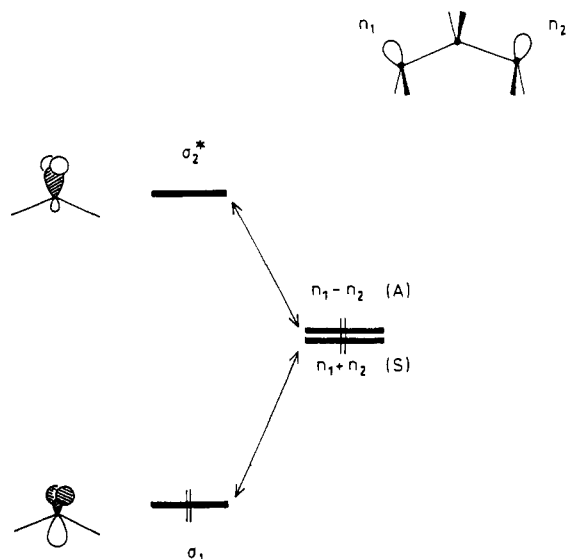
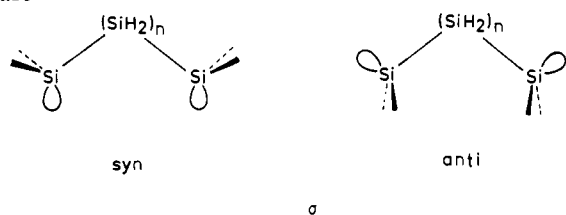


Figure 3. Hyperconjugative interactions in trisilylene, with σ orientation of the nonbonding orbitals.

Chart II



mologues, the germyl and stannyl radicals.^{17b,c}

b. A_nH_{2n+2} Systems. Next we will consider the effect of orbital nonhybridization (ONH) on bonding in the tetrahedral systems. For SiH_4 the corresponding correlation diagram is shown in Figure 2. 3s orbital contraction at Si causes a lowering of the $2a_1$ orbital while the $1a_1$ orbital is raised in energy. The t_1 set is not affected by these considerations since it does not contain s-orbital density at the central atom. As a net effect ONH causes an overall decrease in the total energy [ΔE (eV) = 2.07 for $\zeta(3s, Si) = \zeta(3s) + 1.0$]. In contrast, ONH results in a stabilization of silylene [ΔE (eV) = -0.65], due to the fact that the valence 3s orbital can separate as a nonbonding orbital ("inert electron pair").

Similarly, we have performed EH calculations for the higher homologues Si_nH_{2n+2} ($n = 2-6$). In all cases ONH causes a destabilization of these structures.

c. Through-Space versus Through-Bond Interactions. Silanes form radicals (anions) in which the nonbonding electron is strongly delocalized over the σ moiety.¹⁷ At the same time the radicals adopt a strongly pyramidalized conformation at the central atom. We will now generalize these findings for the electronic coupling of two nonbonding orbitals via through-space and through-bond interactions. It will be shown that the theoretical conclusions are at variance with the symmetry rules derived for carbon-hydrogen biradical systems.¹⁸

Of the manifold of conformations of a polysilylene chain we will consider in detail two principal structures. Our analysis begins with a study of the conformers with the nonbonding orbitals, $n_1 \pm n_2$, in plane with the silicon atoms, here denoted as σ conformers (Chart II). The terminal atoms are pyramidalized instead of being planar.¹⁹ The nonbonding orbitals are in a syn or anti

Table I. EH Calculations for the σ Conformers of Polysilylene Chains, at Times in an All-Trans Conformation^a

compd	HOMO, eV	LUMO, eV	ΔE , eV	
$n = 1$	anti (C_{2v})	-9.501 (S) ^b	-8.567 (A)	0.934
		-10.748 (S)	-8.528 (A)	2.220
$n = 2$	anti (C_{2h})	-9.372 (A)	-8.602 (S)	0.770
		-10.519 (A)	-8.748 (S)	1.771
$n = 3$	anti (C_{2v})	-9.166 (S)	-8.744 (A)	0.422
		-10.365 (S)	-8.826 (A)	1.532
$n = 4$	anti (C_{2h})	-9.083 (A)	-8.798 (S)	0.285
		-10.236 (A)	-8.941 (S)	1.295

^aSymmetry designations refer to a symmetric (S) or antisymmetric (A) combination of lone pairs. ^bFirst entry model A, second entry model B.

Chart III

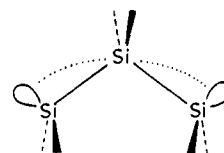
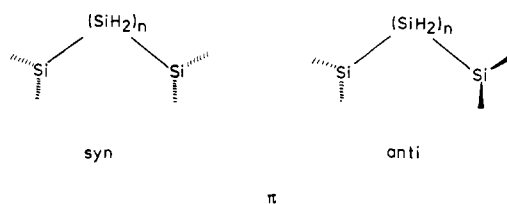


Chart IV



orientation to an intermediate (poly)silylene unit. For the simplest representative trisilylene the corresponding interaction diagram (anti conformation) is presented in Figure 3. The combination of nonbonding orbitals is either symmetric (S) or antisymmetric (A) with respect to a mirror plane (σ_v in C_{2v}).

For symmetry reasons the leveling of $n_1 \pm n_2$ is determined by two factors: (a) Through-space overlap places $n_1 + n_2$ (S) below $n_1 - n_2$ (A). (b) Through-bond interaction of $n_1 + n_2$ with the orbitals σ_1 and σ_2^* is superimposed on through-space overlap. (These orbitals refer to the $2a_1$ and $3a_1$ orbitals of a silylene system; see Figure 1.) Destabilization of $n_1 + n_2$ (S) via overlap with σ_1 is counteracted by stabilization with σ_2^* . ONH lowers σ_2^* ; i.e., it increases depression of the symmetric combination $n_1 + n_2$ below the antisymmetric combination $n_1 - n_2$. In other words, through-bond and through-space interactions become additive.

EH calculations on model systems¹⁹ confirm these qualitative considerations (Table I). Again we have chosen two models, one with equal Slater exponents (model A) and one with the conditions for ONH (model B). Noticeable ONH considerably increases the energy differences of the frontier orbitals without effecting their symmetry ordering. We have also studied the corresponding syn conformers of the polysilylene chains. They are always higher in energy and will not be reported here.

On this basis, for the anti conformers of a polysilylene chain for the operation of orbital nonhybridization, one arrives at the following conclusions:

With an odd number of silylene units between the nonbonding orbitals the symmetric level, $n_1 + n_2$, is placed below the antisymmetric level, $n_1 - n_2$. The opposite is true for an even number of silylene units between the nonbonding orbitals.

Tentatively for trisilylene the extremely facile hyperconjugative interaction may be viewed as shown in Chart III. The symmetric combination of nonbonding orbitals interacts via a two-electron-three-center bond with the central SiH_2 unit. It results from electron donation into the antibonding $3a_1$ orbital (see Figure 1) of the central SiH_2 unit.

It must be noted that the EH calculations cannot make accurate predictions about the biradical or closed-shell character of these structures. However, the assignment of the symmetry levels should

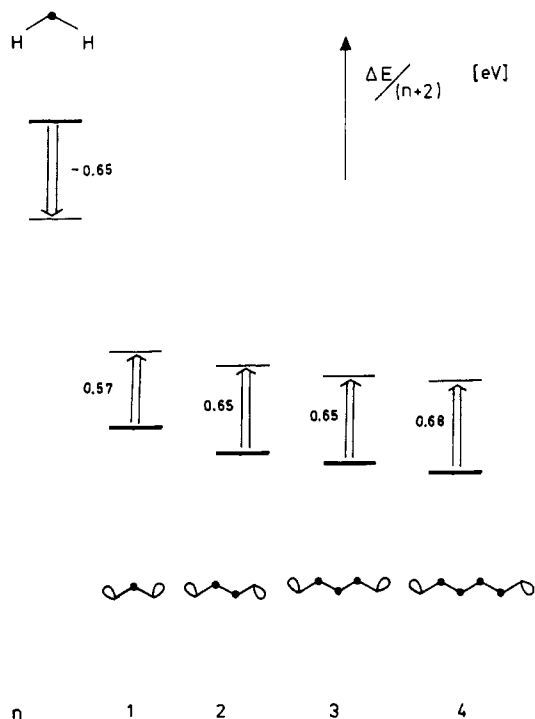
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(19) The bonding parameters for the model compounds are (bond lengths in angstroms, bond angles in degrees): Si-Si = 2.360, Si-H = 1.480, $\angle Si-Si-Si = 110.0$, $\angle H-Si-H = 109.5$; terminal Si atoms, $\angle H-Si-H = 100.0$, $\angle d-Si-Si = 150.0$ (d = dummy atom, bisecting the H-Si-H angle).

Table II. EH Calculations for the π Conformers of Polysilylene Chains, at Times in an All-Trans Conformation^a

compd		HOMO, eV	LUMO, eV	ΔE , eV
$n = 1$	syn (C_2)	-9.168 (A) ^b	-9.158 (S)	0.010
	anti (C_2)	-9.923 (S)	-9.360 (A)	0.563
$n = 2$	syn (C_2)	-9.189 (A)	-9.142 (S)	0.047
	anti (C_1)	-9.968 (S)	-9.335 (A)	0.633
$n = 3$	syn (C_2)	-9.213 (A)	-9.111 (S)	0.102
	anti (C_1)	-9.944 (A)	-9.317 (S)	0.627
$n = 4$	syn (C_2)	-9.196 (S)	-9.127 (A)	0.069
	anti (C_1)	-9.890 (A)	-9.388 (S)	0.502
$n = 3$	syn (C_2)	-9.175 (S)	-9.147 (A)	0.028
	anti (C_2)	-9.885 (S)	-9.365 (A)	0.520
$n = 4$	syn (C_2)	-9.161 ^c	-9.161	0.000
	anti (C_1)	-9.875 (S)	-9.376 (A)	0.499
$n = 4$	syn (C_2)	-9.164 (A)	-9.157 (A)	0.007
	anti (C_1)	-9.834 (A)	-9.396 (S)	0.438
$n = 4$	syn (C_2)	-9.166 (A)	-9.156 (S)	0.010
	anti (C_1)	-9.835 (A)	-9.395 (S)	0.440

^aSymmetry designations refer to a symmetric (S) or antisymmetric (A) combination of lone pairs. ^bFirst entry model A, second entry model B. ^cDegenerate frontier orbitals.

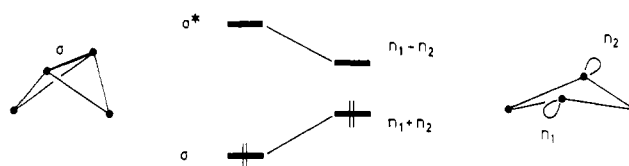
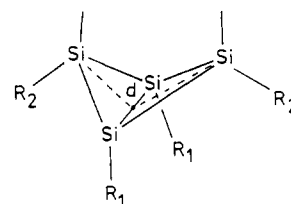
Chart V

be produced correctly. It is also clear that ONH tends to enhance the closed-shell character of the corresponding wave functions.

The rule that through-space and through-bond interactions are additive also holds true for the other structures, here denoted as π conformers (Chart IV). Corresponding EH calculations are presented in Table II.

Importantly, the results of this analysis are contrary to the expectations for the carbon analogues, e.g., trimethylene; there the A level is placed below the S level.¹⁸ The reversal of the symmetry ordering is just the consequence of the strong perturbational interaction of the nonbonding orbitals with the corresponding energetically low lying antibonding orbitals.

There is also another important aspect that must be discussed here. Orbital nonhybridization causes a stabilization of a silylene while it destabilizes a silane. For a polysilylene chain (all trans conformation assumed) the effect of orbital nonhybridization (per silylene unit) is as shown in Chart V. The levels (broad lines) indicate relative energies (model A) per silylene unit. ONH as simulated by model B (thin lines) causes stabilization (for SiH₂) or destabilization (for polysilylenes). Its effect on the energy per silylene unit is indicated by the arrows. Hence it facilitates

Chart VI**Chart VII**

fragmentation of a polysilylene chain into silylene units. It might be worthwhile to review some experimental facts. Silylenes have been considered in equilibrium with polysilylenes.²⁰ Similar considerations hold for stannylenes.²¹ The fragmentation tendency is larger in the latter compared with that in the former structures, which supports our analysis.

d. Symmetry-Allowed Bond-Stretch Isomerism in Bicyclic-tetrasilane. The very effective through-bond interaction in a polysilylene chain is the consequence of three aspects: (a) Silyl radicals adopt a pyramidal conformation at the central atom. Consequently, the nonbonding orbitals can interact with σ^* -type orbitals of the Si-Si and Si-H bonds. (b) Low-lying antibonding orbitals are evidently more important for the electronic coupling of the nonbonding orbitals, as compared with the situation for analogous carbon-hydrogen compounds (i.e. in a polymethylene biradical). (c) Silicon is more electropositive than hydrogen, which enhances the possibility for nucleophilic attack at the silicon atom.

Next we will analyze the bonding situation in bicyclic-tetrasilane. According to the previous analysis stretching the central bond in **1** is symmetry-allowed. The electrons of the central bond correlate with the symmetric combination, $n_1 + n_2$ (Chart VI), of nonbonding orbitals. From a thermodynamic viewpoint bond fission should be extremely facile. An estimation of the ring strain from SCF calculations for cyclotrisilane is 39.3 kcal/mol and for cyclotetrasilane is 18.0 kcal/mol.^{14,22} On the other hand, the Si-Si bond dissociation energy in disilane is 74 kcal/mol.²³ Thus, for the dissociation of the central bond in **1** one obtains an estimate of $74 - 2 \times 39.3 + 18 = 13.4$ kcal/mol (assuming that two three-membered rings are transformed into one four-membered ring system). This value is close to the estimate (15 kcal/mol) deduced from the experimental investigation²⁴ of the inversion process in a derivative of **1**. It must be noted that a similar estimate for the central bond in the carbon analogue, bicyclobutane, yields a much higher value.²⁴

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Table III. Relative Energy Differences ($E(1\mathbf{o}) - E(1\mathbf{c})$) between Various Substituted Bicyclobutrasilanes (C_{2v} Symmetry) at the ab Initio SCF Level

R ₁	R ₂	ΔE, kcal/mol	R ₁	R ₂	ΔE, kcal/mol
H	H	-9.86 ^a	F	H	-0.79 ^d
		-3.89 ^b	H	F	-6.87 ^d
		-2.94 ^c	CH ₃	H	+8.99 ^{d,e}

^aBasis II, without d functions at Si. ^bBasis II, $E_{\text{SCF}} = -1159.0517$ au (for $1\mathbf{o}$). ^cBasis IV, $E_{\text{SCF}} = -1159.0754$ au (for $1\mathbf{o}$). ^dBasis II. ^eMethyl hydrogens staggered with respect to the central bond.

Table IV. Mulliken Population Analysis of the LMO's of $1\mathbf{c}$

bond	atom	gross atomic population		
		s	p	d
Si(1)-Si(2)	Si(1)	0.199	0.737	0.051
	Si(3)	-0.025	-0.005	0.041
Si(1)-Si(3)	Si(1)	0.384	0.683	0.043
	Si(3)	0.249	0.636	0.052
Si(1)-H	Si(1)	0.346	0.451	0.032
	H	1.150	0.024	
Si(3)-H	Si(3)	0.300	0.464	0.042
	H _{ax}	1.195	0.023	
	Si(3)	0.318	0.471	0.040
	H _{eq}	1.168	0.023	

Since the bond stretching in 1 is orbital-symmetry-allowed and the delocalization of electron density via three-center bonding is very effective, the lability of the central bond should be considerable. In detail, the factors that contribute to an open, $1\mathbf{o}$, over a closed, $1\mathbf{c}$, structure are as follows: (1) Substituents that enhance through-bond interaction will stabilize $1\mathbf{o}$ over $1\mathbf{c}$. The interaction requires σ -electron-withdrawing substituents (e.g. F) at Si(3) (Si(4), etc.). (2) Electron-withdrawing substituents at the bridgehead positions decrease the p character of the central bond. Hence again they will preferentially stabilize $1\mathbf{o}$. Electron-donating substituents will do the opposite. (3) Bulky substituents at the bridgehead atoms (e.g. *tert*-butyl) exert mutual steric hindrance and enforce an increase of the angle $\angle\text{Si-Si-R}_1$. Hence, this effectively shortens the central bond since the interflap angle between the two three-membered-ring planes has to decrease for steric reasons. The last effect has already been recognized for the case of bicyclobutane.²⁵

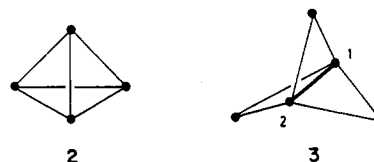
In order to quantify the electronic effects (factors 1 and 2), we performed ab initio calculations^{26a,b} on various substituted structures $1\mathbf{c}$ and $1\mathbf{o}$. The numerical results are collected in Table III, and the system is illustrated in Chart VII. At times the open, $1\mathbf{o}$, was compared with the closed, $1\mathbf{c}$, structure. A negative value for the energy differences is in favor of the open conformation. At all levels of sophistication, for the parent compound $1\mathbf{o}$ is preferred over $1\mathbf{c}$. In order to prove the existence of $1\mathbf{o}$ as a true minimum on the electronic hypersurface, we have in addition optimized $1\mathbf{o}$ and $1\mathbf{c}$ with a fairly large basis set that includes

(25) (a) A lucid discussion of this effect has been presented: Gassman, P. G.; Greenlee, M. L.; Dixon, D. A.; Richtsmeier, S.; Gougoutas, J. Z. *J. Am. Chem. Soc.* **1983**, *105*, 5865. (b) Woodward, R. B.; Dalrymple, D. L. *J. Am. Chem. Soc.* **1969**, *91*, 4612.

(26) (a) The bonding parameters were obtained from energy optimization at the basis I level or chosen according to the reported^{25b} structure. They are as follows (bond lengths in angstroms, bond angles in degrees) for $1\mathbf{c}$ (C_{2v} symmetry): Si(1)-Si(2) = 2.376, Si(1)-Si(3) = 2.320, Si(1)-H = 1.520, Si(2)-H_{ax,eq} = 1.490; $\angle\text{Si(3)-d-Si(4)} = 121.0$, $\angle\text{H-Si(1)-Si(2)} = 147.0$, $\angle\text{H-Si(2)-H} = 109.5$; d is the bisector of the Si(1)-Si(2) bond. For the geometry of $1\mathbf{o}$ see ref. 1. (b) Bonding parameters for the investigations of the substituent effects were chosen according to standard values⁴ (bond distances in angstroms, bond angles in degrees): Si-F = 1.703, Si-C = 1.890, C-H = 1.090; $\angle\text{HCSi} = 109.5$. (c) Basis II with additional polarization functions at the hydrogen atoms: $\zeta_p(\text{H}) = 0.433$. Compared with the results of basis I, the energy of $1\mathbf{o}$ drops on further optimization 2.8 kcal/mol within this basis. The recently reported^{26e} structure $1\mathbf{c}$ is 6.5 kcal/mol higher in energy at the extended basis II level. (d) Schleyer, P. v. R.; Sax, A. F.; Kalcher, J.; Janoschek, R. *Angew. Chem.* **1987**, *99*, 374; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 364. (e) Collins, S.; Dutler, R.; Rauk, A. *J. Am. Chem. Soc.* **1987**, *109*, 2564.}

Table V. Mulliken Population Analysis of the LMO's of $1\mathbf{o}$

bond	atom	gross atomic population		
		s	p	d
Si(1)-Si(2)	Si(1)	-0.053	0.709	0.031
	Si(3)	0.099	0.171	0.038
Si(1)-Si(3)	Si(1)	0.592	0.612	0.037
	Si(3)	0.207	0.516	0.049
Si(1)-H	Si(1)	0.310	0.509	0.037
	H	1.138	0.022	
Si(3)-H	Si(3)	0.297	0.488	0.041
	H _{ax}	1.172	0.023	
	Si(3)	0.295	0.491	0.039
	H _{eq}	1.169	0.023	

Chart VIII

polarization functions at all atoms.^{26c} Accordingly, both structures are separate energy minima, as evidenced by an inspection of the corresponding Hessian matrices and gradients. The optimum bonding parameters (bond lengths in angstroms, bond angles in degrees) at the extended basis II level are as follows for $1\mathbf{o}$ [$1\mathbf{c}$] (C_{2v}): Si(1)-Si(2), 2.784 [2.369]; Si(1)-Si(3), 2.327 [2.309]; $\angle\text{Si(4)-d-Si(3)}$, 141.7 [121.9]; $\angle\text{H-Si(1)-Si(2)}$, 95.8 [141.4]. The energy difference (in kcal/mol) $E(1\mathbf{o}) - E(1\mathbf{c})$ is -0.66. (Details of the structures are available on request.)

Our view is in agreement with a recent analysis,^{26d} while others^{26e} have identified only one isomer on the hypersurface.

In accordance with our qualitative analysis, fluorine, a typical σ -electron-withdrawing substituent, at the position Si(3) (Si(4)) strongly promotes $1\mathbf{o}$. The effect is minor for fluorine at the bridgehead atoms. On the other hand, methyl groups favor closure of the central bond. This agrees with thermochemical data,²⁷ which indicate that methyl groups strengthen the Si-Si bond rather than weaken it, in contrast with the case for the C-C single bond.²³

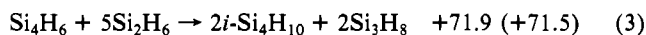
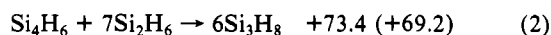
To put the analysis of bonding in 1 on firmer ground, we will now report the Mulliken population analysis of the localized molecular orbitals (LMO's) on the parent 1 (Tables IV and V). The results are based on calculations with the best basis (basis IV). In $1\mathbf{c}$ the central bond Si(1)-Si(2) is strongly localized; the sum of the gross atomic population at one bridgehead atom is 99% of the electron density, half of the localized orbital. The p character of the localized orbital Si(1)-Si(2) is slightly larger than that of the peripheral bond, Si(1)-Si(3). Stretching the central bond (see Table V) results in a different bonding picture. The p-electron density at the bridgehead atoms diminishes and appears at the peripheral silicon atoms; e.g., the ratio of p-electron density is Si(1)/Si(3) = 0.709/0.171 = 4.1. Approximately 24% of the p-electron density of the central bond is distributed to the peripheral silicon atoms. Most noticeable is the fact that the electron density in the open structure is only distributed among the silicon atoms. The contribution of s-electron density is fairly small. Thus, the population analysis is in support of the description of bicyclobutrasilane via the corresponding valence bond structures $1\mathbf{o}$ and $1\mathbf{c}$.

e. Ring Strain in Condensed Silicon Ring Systems. Our picture on bicyclobutrasilane will now be completed by a comparison of 1 with other condensed silicon ring systems (Chart VIII). The strain in $1-3$ is assigned by the isodesmic and homodesmic²⁸ reactions 1-3. They result as follows for $1\mathbf{o}$ (energies are in

(27) Davidson, I. M. T.; Howard, A. V. *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 69.

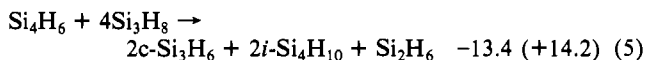
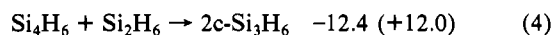
(28) Hehre, W. J.; Ditchfield, R.; Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 4796. George, P.; Trachtmann, M.; Brett, A. M.; Bock, C. W. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1036. George, P.; Trachtmann, M.; Bock, C. W.; Brett, A. M. *Tetrahedron* **1976**, *32*, 317.

kcal/mol obtained with basis III):



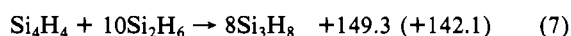
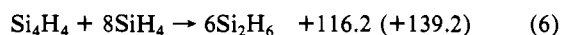
In parentheses are the corresponding values for the carbon analogue, bicyclobutane.¹ (For the geometries and energies of the silanes and alkanes, see ref 14.) Positive values (in kcal/mol) refer to an exothermic and negative values to an endothermic situation. On the basis of the homodesmic reactions 2 and 3 the enthalpies are comparable to those of the carbon case; i.e., the strains in bicyclobutane and its silicon analogue are equivalent.

Of greater interest are the ring separation energies (eq 4 and 5). The reaction enthalpies are endothermic for the silicon



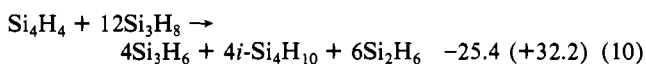
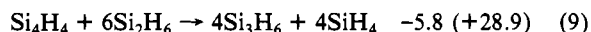
reaction enthalpies are endothermic for the silicon compound but exothermic for the analogous carbon compound. In other words, the fusion of rings stabilizes 1 to make it more stable than two cyclotrisilane units. In contrast, ring condensation introduces additional strain for bicyclobutane.

For comparison we include also tetrasilatetrahydrane (2). The geometrical parameters for this structure were obtained from optimization at basis I level.²⁹ Corresponding isodesmic and homodesmic reactions for an estimation of ring strain are given by eq 6–8. In parentheses are again the values computed from



corresponding reactions for the carbon analogue, tetrahedrane.³⁰ Our value (eq 7) of 149.3 kcal/mol for the ring strain compares with 140.9 kcal/mol reported recently.^{29b}

Again of considerable interest are the ring separation energies (eq 9 and 10). As before we observe the tendency that ring



condensation is exothermic for the silicon rings and endothermic for the carbon ring systems.

f. Sila[1.1.1]propellane. In the last section of our publication we analyze the bonding situation in pentasilatricyclopentane (3). According to our analysis we expect for this structure a very effective through-bond interaction. From a thermodynamic viewpoint the central bond should be even more labile than in 1. 3 possesses three three-membered rings, which result in three four-membered rings when the central bond is cleaved. Consequently, using the previous thermodynamic estimates, one arrives at an energy for the central bond of $74 - 3 \times 39.3 + 3 \times 18.0 = 10.1$ kcal/mol. On this basis the central bond should be extremely elongated. Figure 4 records corresponding EH calculations³¹ for stretching the central bond. Again the two models A and B were probed. The broken lines refer to the results of model A and the solid lines to model B. ONH results in a large energy separation between the orbitals σ and σ^* of the bridgehead bond.

(29) The optimized bonding parameters (T_d symmetry) are as follows: Si-Si = 2.295 Å, Si-H = 1.479 Å. These values are in good agreement with ab initio calculations of other research groups, which appeared in print during the completion of this publication. (a) Clabo, D. A., Jr.; Schaefer, H. F. *J. Am. Chem. Soc.* **1986**, *108*, 4344. (b) Nagase, S.; Nakano, M.; Kudo, T. *J. Chem. Soc., Chem. Commun.* **1987**, 60. (c) Nagase, S.; Kudo, T., personal communication.

(30) Bonding parameters for tetrahedrane (T_d symmetry, optimized with basis I): C-C = 1.482 Å, C-H = 1.054 Å.

(31) Bonding parameters: Si-Si = 2.360 Å, Si-H = 1.480 Å, $\angle\text{HSiH} = 120^\circ$.

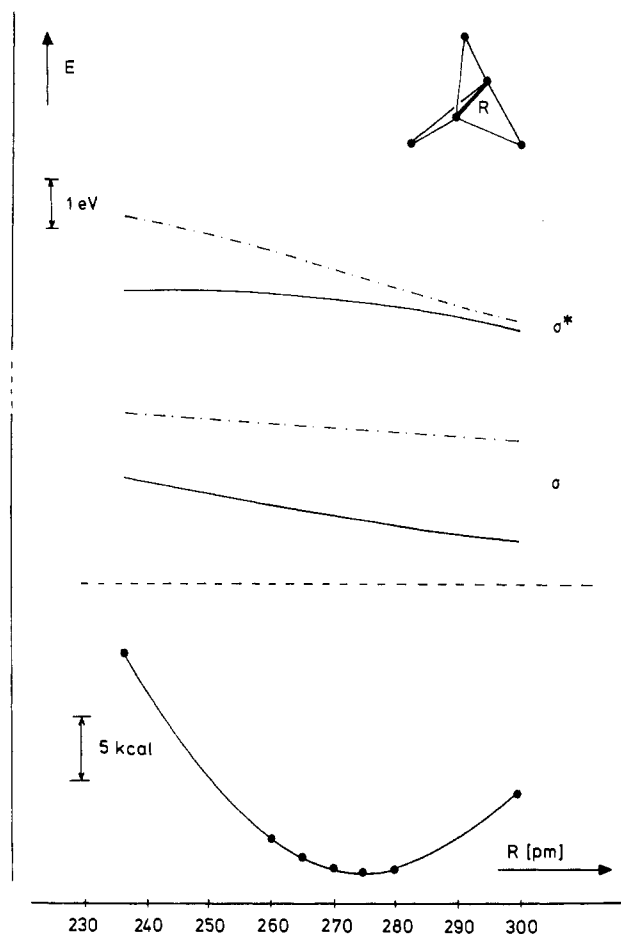


Figure 4. Bond-stretch isomerism in pentasila[1.1.1]propellane: (top) σ - and σ^* -orbital energies (in eV) of EH calculations from model A (broken line) and model B (solid line); (bottom) SCF-potential energy curve (basis II).

This indicates a very effective through-bond interaction mechanism.

The lower part of Figure 4 records the potential curve for bond stretching, obtained from ab initio calculations at the basis II level. For the computation of the hypersurface we assumed standard bond lengths for the peripheral bonds.³¹ Accordingly the central Si-Si bond is rather long (274 pm, estimated from extrapolation of the potential curve). It may be compared with a Si-Si distance of 272 pm as obtained from energy optimization at an ab initio STO-6/31 G* level.^{29c} Some relative energy values (in kcal/mol) of the potential curve are as follows (Si(1)-Si(2) distance of 272 pm as obtained from energy optimization at an ab initio STO-6/31 G* level.^{29c} Some relative energy values (in kcal/mol) of the potential curve are as follows (Si(1)-Si(2) bond lengths (pm) in parentheses): (280) 0.21; (274) 0; (270) 0.32; (265) 1.18. Hence, compared with a Si-Si single bond (2.360 Å) the central bond in 3 is elongated by ca. 14%. In the carbon analogue, i.e., [1.1.1]propellane,³² the central bond is only slightly longer than a normal C-C single bond.³³

Conclusions

In our study we have presented the first quantum-chemical investigations on through-bond isomerism in condensed ring systems containing three-membered silicon rings. Compared with the case for the analogous carbon systems, in tetrasilabicyclo[1.1.0]butane (1) and in pentasila[1.1.1]propellane (3) the central bond is extremely labile. This is a consequence of a very effective through-bond interaction in these systems and the relatively high

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(33) For theoretical considerations on strain energies of small ring propellanes, see: Wiberg, K. B. *J. Am. Chem. Soc.* **1983**, *105*, 1227. Wiberg, K. B. *Angew. Chem.* **1986**, *98*, 312; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 312.

strain of cyclotrisilane compared with that of cyclotetrasilane. The strong hyperconjugation mechanism is due to energetically low lying antibonding orbitals. In other words the quasi-metallic character¹⁴ in the cyclosilanes comes to the fore. A ring strain analysis of **1** and **2** via isodesmic and homodesmic reactions gives energies comparable to those of the carbon analogues. However, in contrast to the latter, ring condensation of silicon compounds is exothermic. The effect of through-bond interaction in fused four-membered ring systems remains to be established. According to our qualitative analysis one expects a rather strong central bond for persila[2.2.2]propellane. Detailed ab initio investigations on

the latter structure as well as persila[2.2.0]hexane are currently under investigation.

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Notes

Contribution from UA CEA/CNRS 331, IRDI/DESICP/DPC, CEA, CEN/SACLAY 91191, Gif S/Yvette, France, and Laboratoire de Chimie Moléculaire, UA CNRS 426, Parc Valrose, 06034 Nice, France

Pulse Radiolysis: A New Way To Study Molecular Oxygen Activation. Application to a Vanadium Complex, $\text{VCl}_3(4\text{-pic})_3$

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Biological oxygen carriers transport and store dioxygen in living systems. They are characterized by their ability to bind O_2 reversibly, generally through a low-valent metal atom such as iron(II) in hemoglobin or myoglobin¹ or vanadium(III) or -(IV) in haemovanadin² (a protein found in the 1.5–2 N H_2SO_4 solution existing in the vacuoles of Ascidiidae blood cells). In order to better understand the mechanism of this fundamental O_2 -carrying process, synthetic metal compounds able to add molecular oxygen reversibly were studied. This approach has given rise to a great deal of research,³ especially with group 9 and group 10 metal derivatives such as the Vaska complex $\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{Cl}$.⁴ Little has been done, however, with synthetic oxygen carriers containing early transition elements, although coordination of molecular oxygen, sometimes reversible, has been observed for some titanium(III),⁵ vanadium(III),⁶ and niobium(IV)⁷ adducts, with nitrogen donors, often porphyrines.

Investigating the radiolytic behavior of group 5 metal compounds (vanadium, niobium, tantalum) in nonaqueous solvents (acetonitrile, dichloromethane), as a route to low-valent derivatives,^{8–10} we noticed that after oxygenation of $\text{VCl}_3(4\text{-pic})_3$ (4-pic = 4- $\text{CH}_3\text{C}_6\text{H}_4\text{N}$), the initial vanadium(III) compound could be recovered by radiolysis in oxygen-free acetonitrile. The experimental data (IR, EPR, and absorption spectra and gas analysis), as well as the characteristics of the radiolytic experiments, led us to suggest the formation in solution of a dimeric vanadium-dioxygen adduct, with a coordinated superoxide like O_2^- . Nevertheless, the oxovanadium(IV) species $\text{VOCl}_2(4\text{-pic})_2$ represents the final and only isolable metallic species.

Experimental Section

All manipulations were performed under vacuum or dry argon, using Schlenk tube and vacuum-line techniques. Solvents and 4-picoline were purified by standard methods.¹¹ $\text{VCl}_3(4\text{-pic})_3$ was synthesized according to the literature.¹² This complex being very moisture-sensitive, its oxygenation reaction was carried out on a vacuum line by bubbling O_2 , previously dried over a P_2O_5 column, into its acetonitrile or dichloromethane solution.

The concentrations of the solutions (typically 2×10^{-3} mol-dm⁻³) were so chosen that, in radiolysis experiments, the solute modification occurs

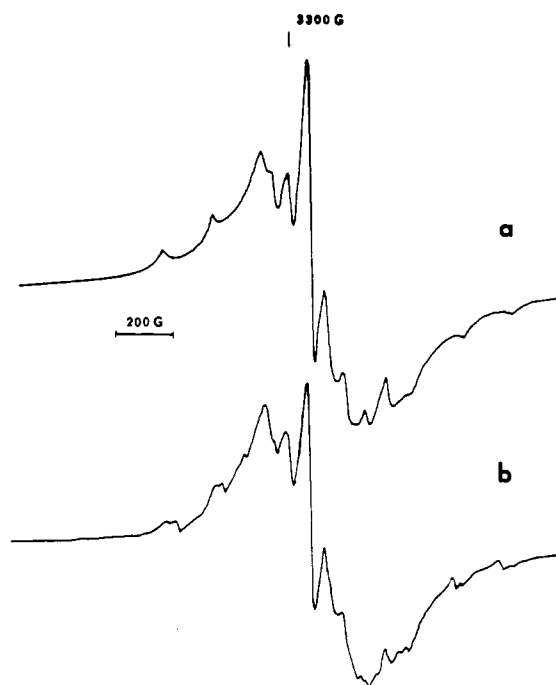


Figure 1. EPR spectra in frozen acetonitrile (173°K) of (a) $\text{VCl}_3(4\text{-pic})_3$; (b) $\text{VCl}_3(4\text{-pic})_3$ -dioxygen adduct.

by an indirect effect, i.e. by reaction with the transient species produced in the irradiated solvent.

Time-resolved experiments were performed with a Febetron 707 apparatus, delivering 1.8-MeV electron pulses of 30 ns base pulse duration and $(3\text{--}5) \times 10^{18}$ eV·g⁻¹ dose. The concentrations of the intermediates

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