Structure, Strain, and Degenerate Rearrangement of Tricyclo[2.1.0.0^{1,3}]pentasilane and Related Molecules

Kunihiro Takeuchi, Daijiro Uemura, and Satoshi Inagaki*

Department of Chemistry, Faculty of Engineering, Gifu University, 1-1 Yanagido, Gifu 501-1193, Japan

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We theoretically investigate a highly strained tricyclic silane (tricyclo[2.1.0.0^{1,3}]pentasilane (**4b**), an isomer of pentasila[1.1.1]propellane (**3b**)) composed of three fused three-membered rings. The central ring is distorted. One of the fusion bonds in the central ring is shorter than the normal Si−Si single bond (2.350 Å) whereas the other is as long as the fusion bonds in bicyclo[1.1.0]tetrasilane (**2b**) (2.860 Å) and **3b** (2.778 Å). The tricyclic silane is less strained than the carbon congener and more strained than the isomer **3b**. The electron delocalization between one of the fusion bonds and the geminal Si−Si ring bonds elongates the fusion bond and stabilizes the molecules to reduce the strain. The silanes composed of the fused three-membered rings are less strained than the carbon congener. A degenerate rearrangement of a three-membered ring is predicted. The enthalpy of activation of the rearrangement of the distorted central ring is low (7.2kcal/mol) for **4b**, but appreciable (22.3kcal/mol) for the germanium congener, tricyclo[2.1.0.0^{1,3}]pentagermane (**4c**). We investigate the effects of the substituents on the distortion of the central three-membered ring and the degenerate rearrangement.

Introduction

Highly strained molecules have been attracting much interest. Among them are silicon congeners (**1b**−**3b**) of mono-, bi-, and tricyclic alkanes (cyclopropane (**1a**), bicyclo[1.1.0]butane[1] (**2a**), and [1.1.1]propellane[2] (**3a**)). An interesting geometrical feature has been reported for the Si−Si single bonds in the three-membered rings of silanes. There are short (ca. 2.4 Å) and long (ca. 2.8 Å) bonds. The Si−Si fusion bond (2.373 Å) of a derivative of bicyclo[1.1.0]tetrasilane[3] (**2b**), i.e., 1,3-di-*tert*-butyl-2,2,4,4-tetrakis(2,6-diethylphenyl)tetrasilabicyclo[1.1.0]-butane, is as long as the Si−Si bonds (2.373−2.431 Å) of the derivatives[4] of cyclotrisilane **1b**. Schleyer[5] and Nagase[6] predicted another isomer with the long fusion Si−Si bond (2.731−2.775 Å). The fusion bond of pentasila[1.1.1]propellane (**3b**) is as long (2.719−2.885 Å).[7,8]

There is an interesting trend of the three-membered ring silanes in the strains, especially relative to those of the carbon congeners. The strain energy of the monocyclic silicon molecule **1b** (38.9 kcal/mol) is higher than that (28.7 kcal/mol) of cyclopropane (**1a**).[9] The bicyclic silicon molecule **2b** (65.2 kcal/mol) with the short fusion bond is strained as much as bicyclo[1.1.0]butane (**2a**) (68.9 kcal/mol).[6] The tricyclic silicon molecule **3b** (70.2−79.0 kcal/mol) is less strained than the carbon compound **3a** (104.3−110.6 kcal/mol).[7,10]

Tricyclo[2.1.0.0^{1,3}]pentane[11−13] (**4a**), an isomer of the propellane **3a**, is classified into a member of difusotricyclic geometry (Figure 1) according to Gund,[14] where the tricyclic systems share a common vertex (X_1) and the two fusion bonds. The geometry and strain of **4a** were theoretically investigated by Wiberg et al.[11,12] and by the present authors.[13] The unique geometry is expected to give new aspects of molecular structure, chemical bonding, and reaction. In this paper, we theoretically investigate tricyclo[2.1.0.0^{1,3}]pentasilane (**4b**), the silicon congener of **4a**, (1) to know whether the fusion bonds are long and/or short, (2) to know how much **4b** is strained, especially relative to the carbon congener, (3) to study origins of the long-bond isomers and the trend of the three-membered-ring strains relative to those of the carbon congener, (4) to show a degenerate rearrangement of a three-membered ring, and (5) to predict the substituent effect on the molecular geometry and the degenerate rearrangements.

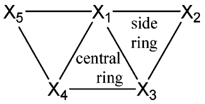
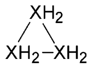
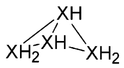
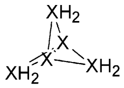
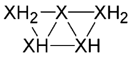


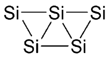
Figure 1. Difusotricyclic geometry.


1a: X=C
1b: X=Si


2a: X=C
2b: X=Si


3a: X=C
3b: X=Si


4a: X=C
4b: X=Si
4c: X=Ge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Method

The calculations were carried out by using the Gaussian program package.[15] The geometries were optimized at the B3LYP/6-31G* levels. The final energies of the B3LYP/6-31G* optimized structures were refined at the Gaussian-3 level in the case of second- or third-row elements, which has been recently proposed and proved to be very accurate and effective.[16] The strain energies were estimated by the homodesmotic reaction.[17]

We developed[18] and applied[10,19,20] the bond model method to analyze the electronic structures of molecules. The single

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* Address correspondence to this author. Phone: +81-58-293-2611. Fax: +81-58-230-1893. E-mail: inagaki@apchem.gifu-u.ac.jp.

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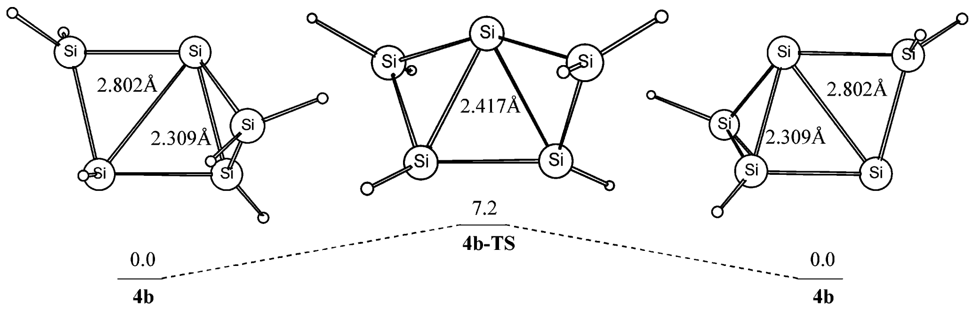
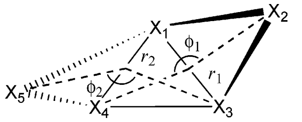


Figure 2. The structure (the fusion bond lengths) and the enthalpy of activation (kcal/mol) of the degenerate rearrangement of **4b** calculated at the G3B3//B3LYP/6-31G* level.

TABLE 1: Geometrical Parameters^{a} of 4−5



	r_1 (Å)	r_2 (Å)	ϕ_1 (deg)	ϕ_2 (deg)	$\theta_1{}^{b}$ (deg)	$\theta_2{}^{b}$ (deg)
4b	2.309	2.802	102.2	150.7	137.4	95.8
4b-TS	2.417	2.417	128.4	128.4	122.3	122.3
4c	2.403	3.049	97.2	155.3	140.2	89.7
4c-TS	2.617	2.617	106.0	106.0	142.1	142.1
5	2.499	2.844	151.9	97.1		
5-TS	2.593	2.593	115.7	115.7		

[a] Calculated at the B3LYP/6-31G* level. [b] θ_1 (X_1X_3H angle) and θ_2 (X_1X_4H angle).

Slater determinant Ψ for the electronic structure is expanded into electron configurations:

$$\Psi = C_G\Phi_G + \Sigma C_T\Phi_T + ...$$

In the ground configuration (Φ_G), a pair of electrons occupies a bonding orbital of a chemical bond (a nonbonding orbital of an unshared electron pair). Electron delocalization is expressed by mixing an electron-transferred configuration (Φ_T), where an electron shifts from a bonding orbital of one bond to an antibonding orbital of another. The bonding and antibonding orbitals ϕ_i and $\phi_i{}^*$ of the ith bond are linear combinations of hybrid atomic orbitals χ_{ia} and χ_{ib} on bonded atoms a and b:

$$\phi_i = c_{ia}\chi_{ia} + c_{ib}\chi_{ib}$$

$$\phi_i{}^* = c_{ia}{}^*\chi_{ia} + c_{ib}{}^*\chi_{ib}$$

We use the hybrid orbitals obtained by orthogonalizing the atomic basis functions on each atom. The bond orbitals are obtained by the diagonalization of the 2 × 2 Fock matrixes of the basis of the hybrid orbitals. The hybrid atomic orbitals and therefore the bond orbitals are optimized to give the maximum value of the coefficient (C_G) of the ground configuration. To estimate the interactions between the bond orbitals i and j, we used the interbond energy (IBE), which was defined as

$$\mathrm{IBE}_{ij} = P_{ij}(H_{ij} + F_{ij})$$

where P_{ij}, H_{ij}, and F_{ij} are the elements of the density, Fock, and core Hamiltonian matrixes, respectively.

Results and Discussion

Structure. The geometry of **4b** has C_1 symmetry (Figure 2). The geometrical parameters of **4b** are listed in Table 1. The fusion bonds are short (2.309 Å) and long (2.802 Å). No energy minima were located either for the difusotricyclic geometries with the fusion bonds both long or for those with the fusion bonds both short. The bicyclo[1.1.0]tetrasilane moiety containing the short fusion bond is puckered with the small interflap angle ϕ (102.2°) between the three-membered rings. The SiSiH angle θ is wide (137.4°) between the fusion bond and the Si−H bond. The bicyclic moiety with the long fusion bond has a large interflap angle ϕ (150.7°) and a small bond angle θ (95.8°). The two "isomers" of bicyclo[1.1.0]tetrasilane (**2b**) coexist in **4b**. Very recently, a stable derivative of tricyclo[2.1.0.0^{1,3}]pentasilane (**4b**) has been synthesized by Scheschkewitz.[21] The fusion bonds have similar distances (2.343, 2.337 Å). The disagreements with the results of the calculations will be discussed in the section on the degenerate rearrangement.

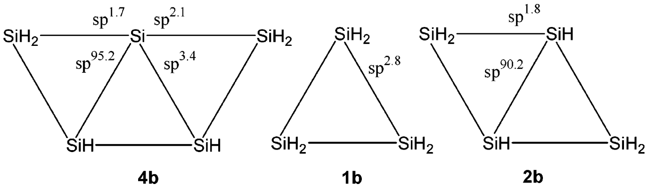
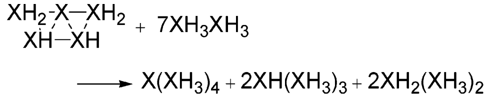


Figure 3. Hybridization diagrams.

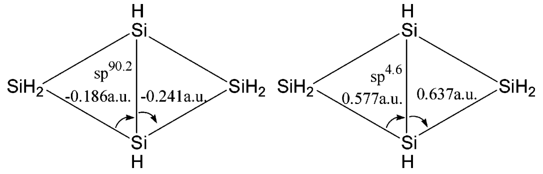
The unusual bonding character or hybridization of the vertex atom of the difusotricyclic silane **4b** is interesting. The hybrid orbital for the long fusion bond is almost of p-character (Figure 3) as is expected from the long bond distance (2.860 Å) and from the hybridization (sp$^{90.2}$) for the fusion bond of **2b**. The p-character of the hybrid orbital (sp$^{3.4}$) for the short fusion bond is naturally lower than that for the long bond and higher than that (sp$^{2.8}$) of less strained cyclotrisilane (**1b**). The hybrid orbitals of the two nonfusion bonds have high s-character (sp$^{1.7}$ and sp$^{2.1}$) close to that (sp$^{1.8}$) of the side bonds of the bicyclic silane **2b**, for the saturated silicon atoms. The nonfusion bonds (2.347, 2.367 Å) are as long as the side bonds (2.335 Å) in **2b**.

Strain. The strain energy (SE) was estimated by the homodesmotic reaction (eq 1).[17] The difusotricyclic silane **4b**

 (1)

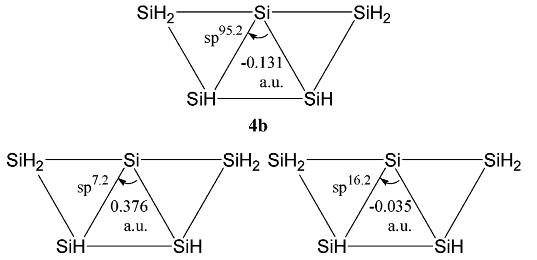
$$\mathrm{XH_2XXH_2XHXH} + 7\mathrm{XH_3XH_3} \longrightarrow \mathrm{X(XH_3)_4} + 2\mathrm{XH(XH_3)_3} + 2\mathrm{XH_2(XH_3)_2} \quad (1)$$

(SE = 86.4 kcal/mol) is more strained than the isomer of the [1.1.1]propellane frameworks (SE = 57.6 kcal/mol for **3b**), as the hydrocarbon **4a** (SE = 134.7 kcal/mol) is more strained than **3a** (SE = 100.4 kcal/mol). The difusotricyclic silane **4b** is less stained by 48.3 kcal/mol than the carbon congener **4a**, as the bi- and tricyclic silanes, **2b** and **3b**, are less strained than the alkanes, **2a** and **3a**, respectively. The value of the strain energy of **4b** is by 22.8 kcal/mol smaller than the sum of the strain energies (3 × 36.4 kcal/mol) of the component rings (cyclotrisilane). The value of the strain energy (134.7 kcal/mol) of **4a** is by 52.5 kcal/mol greater than the sum of the strain



2b **6**

Figure 4. The interbond energies (IBE) between the geminal σ and σ^* bond orbitals in **2b** and its hypothetical short-bond isomer **6**.



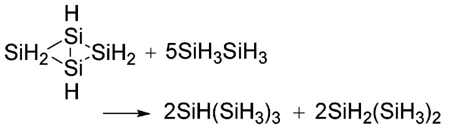
4b

7 **8**

Figure 5. Interbond energies (IBE) between the geminal σ and σ^* bond orbitals of **4b** and its hypothetical short- (**7**) and long-bond isomers (**8**).

energies of these cyclopropanes (3 × 27.4 kcal/mol). The difusotricyclic geometry gives the additional strain to the alkanes as is expected, but less strain to the silane.

The bicyclic geometry shows a similar effect on the strain as the difusotricyclic geometry. The value of the strain energy (53.7 kcal/mol) of the long bond (2.860 Å) isomer of the bicyclic silane **2b** estimated by the homodesmotic reaction (eq 2)[17] is



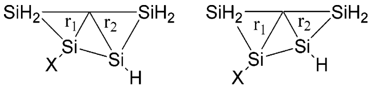
$$\mathrm{SiH_2(SiH)_2SiH_2} + 5\mathrm{SiH_3SiH_3} \longrightarrow 2\mathrm{SiH(SiH_3)_3} + 2\mathrm{SiH_2(SiH_3)_2} \quad (2)$$

by 19.1kcal/mol smaller than the sum of the strain energies (2 × 36.4 kcal/mol) of two cyclotrisilanes. The strain energy (66.2 kcal/mol) of the bicyclic alkane **2a** is by 11.4 kcal/mol greater than the sum of the strain energies (2 × 27.4 kcal/mol) of two cyclopropanes. The similar effect of the bicyclic and difusotricyclic geometries on the strain suggests that the bicyclic molecule **2b** should be a simple model to understand the effect of the difusotricyclic geometry on the fusion bond lengths and the strain of the silane.

The bond model analysis[10,18−20] of the bicyclic silane shows that the delocalization of electrons between the fusion bond (Si−Si) and the peripheral bonds significantly stabilizes the long-bond isomer or relaxes the ring strain (Figure 4). We compare the bicyclic silane **2b** with the hypothetical short-bond isomer **6** optimized for the fixed fusion bond length (2.345 Å: the bond length of **1b**). The geminal delocalization was previously predicted to reduce its antibonding property and to be finally bonding with the decrease in the s-character of the hybrid orbital for the geminal bonds involved in the delocalization.[19] The interbond energies (IBE) show that the $\sigma-\sigma^*$ interactions between the fusion bond and the peripheral bonds stabilize **2b** (IBE = −0.241, −0.186 au) whereas the geminal bond interactions destabilize **6** (IBE = 0.637, 0.577 au) (Figure 4). The differences result from the low s-character (sp$^{90.2}$ of Si$_1$ for $\sigma_{\mathrm{Si_1-Si_3}}$) of the hybrid orbitals for the Si$_1$−Si$_3$ fusion bond in **2b**, relative to that (sp$^{4.6}$ of Si$_1$ for $\sigma_{\mathrm{Si_1-Si_3}}$) in **6**.

The peculiar features of the interbond energies between geminal bonds were found in **4b** (Figure 5). We compared **4b** with the hypothetical short- and long-bond isomers (**7** and **8**) with the same lengths as the short and long fusion bonds in **4b**, respectively. The $\sigma-\sigma^*$ interaction from the short to long fusion bond was found to stabilize **4b** (IBE = −0.131 au) whereas the interaction destabilizes the short bond model, **7** (IBE = 0.376 au), and stabilize **8** (IBE = −0.035 au) to a lesser extent (Figure 5). The differences result from the low s-character (sp$^{95.2}$ of Si$_1$ for $\sigma_{\mathrm{Si_1-Si_3}}$) of the hybrid orbitals for the Si$_1$−Si$_3$ fusion bond in **4b**, relative to the s-character (sp$^{7.2}$, sp$^{16.2}$ of Si$_1$ for $\sigma_{\mathrm{Si_1-Si_3}}$) in **7** and **8**. The delocalization of σ-electrons between a pair of the short and long fusion bonds stabilizes **4b** to relax the ring strain. The significant effects of the geminal delocalization on the ring strain were previously[10] reported for [1.1.1]-propellane and its congeners. The effects are general.

TABLE 2: The Relative Stability of (ΔH) of 9 and 10 and the Fusion Bond Lengths

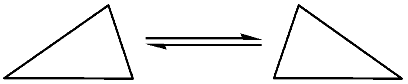


9 **10**

X	ΔH^a (kcal/mol)	**9** r_1 (Å)	**9** r_2 (Å)	**10** r_1 (Å)	**10** r_2 (Å)
Li	−5.1	2.323	2.667	2.828	2.373
CH$_3$	−3.1	2.307	2.789	2.812	2.329
NH$_2$	1.4	2.302	2.821	3.035	2.354
OH	1.3	2.293	2.805	2.947	2.341
F	1.5	2.279	2.804	2.890	2.326

[a] Calculated at the G3B3/B3LYP/6-31G* level. $\Delta H = H_9 - H_{10}$ where H_9 and H_{10} denote the energies of the most stable conformers of **9** and **10**, respectively.

Degenerate Rearrangement. The difusotricyclic silane **4b** undergoes a new type of degenerate rearrangement (Figure 2), where the distorted central three-membered rings are converted to each other as is represented by a generalized equation (eq 3). The structure optimized under the constraint of the C_2 symmetry was found to be a transition structure (**4b-TS**). An intrinsic reaction coordinate calculation shows that the difusotricyclic silane **4b** undergoes a degenerate rearrangement where the short fusion bond changes to the long one and vice versa. The enthalpy of activation is $\Delta H^\ddagger = 7.2$ kcal/mol (Figure 2). Wiberg et al.[12] located the transition structure of C_2 symmetry by 0.9 kcal/mol higher in energy than the local minimum of difusotricyclic alkane **4a** of C_1 symmetry. The low enthalpy of activation or the fast degenerate rearrangement can account for the similar distances of the two fusion bonds observed experimentaly.[21]



(3)

Substituent Effects. We investigate the effects of the substituent at the 3-position of the difusotricyclic silane **4b** on the relative stability of the two isomers, **9** and **10**, with the substituent on the silicon atom of the short and long fusion bonds, respectively (Table 2). The substituents (X) Li and CH$_3$ stabilize **9** more by 3.1−5.1 kcal/mol whereas the substituents (X) NH$_2$, OH, and F with lone pair(s) on the heteroatoms stabilize **10** more by 1.3−1.5 kcal/mol. The interaction of the lone pair on X with $\sigma^*_{\mathrm{Si-Si}}$ of the fusion bond results in the stabilization of **10** and the elongation of the fusion bond. In fact, a lone pair on X occupies the direction most favorable for the n−σ^* interaction or antiperiplanar to the fusion bond. The fusion bonds with the substituents (X) NH$_2$, OH, and F are longer than that of the parent with X = H. The fusion bond is

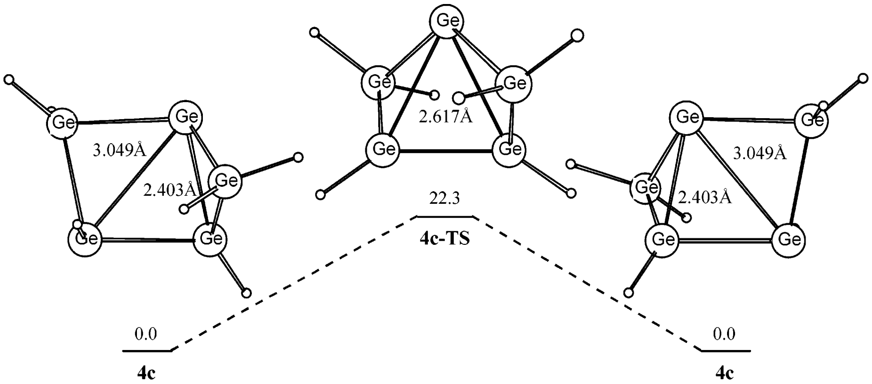
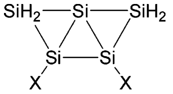


Figure 6. The structure (the fusion bond lengths) and the enthalpy of activation (kcal/mol) of the degenerate rearrangement of **4c** calculated at the B3LYP/6-31G* level.

TABLE 3: The Structure and the Enthalpy of Activation[a] ($\Delta H^{\ddagger}$) of the Degenerate Rearrangement of 11



11

X	r_s[b] (Å)	r_l[c] (Å)	Δr[d] (Å)	$\Delta H^{\ddagger}$[e] (kcal/mol)
Li	2.716	2.716		
CH_3	2.324	2.797	0.473	5.7
NH_2	2.338	3.029	0.691	8.5
OH	2.317	2.913	0.596	6.8
F	2.291	2.863	0.572	6.4

[a] Calculated at the G3B3//B3LYP/6-31G* level. [b] Short fusion bond. [c] Long fusion bond. [d] $\Delta r = r_l - r_s$. [e] The enthalpies of activation (kcal/mol) based on the most stable conformer of the reactants and transition states.

the longest for the amino substituent (X = NH_2) with the high electron-donating ability of the lone pairs.

The appreciable effects on the relative stability of the isomers of the monosubstituted difusotricyclic silanes prompted us to study the degenerate rearrangements of the 3,4-disubstituted silane **11** (Table 3). The difusotricyclic silane with a less electronegative substituent (X = Li) has the C_2 symmetry.[22] The central three-membered ring forms an isosceles. The fusion bond lengths are identical with each other. The difusotricyclic silanes with substituents (X) CH_3, NH_2, OH, and F have short (2.317−2.338 Å) and long (2.797−3.029 Å) fusion bonds. The central rings are distorted. The fusion bonds are long due to the lone pair on X in the antiperiplanar direction. The enthalpies of activation increase with the difference in the fusion bond length.

Related Species. There is low barrier in the degenerate rearrangement of the difusotricyclic silane **4b**. The rearrangement is rapid even at low temperatures. The distorted three-membered rings are difficult to observe experimentally. We investigated the difusotricyclic germane **4c**. The fusion bonds are short (2.403 Å) and long (3.049 Å) at the B3LYP/6-31G* level of the calculations (Figure 6). The germane **4c** (SE = 117.7 kcal/mol) is more strained than pentagerma[1.1.1]propellane (**3c**) (SE = 88.6 kcal/mol) at the B3LYP/6-31G*//B3LYP/6-31G* level of calculation. The value of the strain energy of **4c** is by 22.4 kcal/mol smaller than the sums of the strain energies (3 × 46.7 kcal/mol) of the cyclotrigermanes. The optimized structure of the C_2 symmetry is the transition structure (**4c-TS**) of the degenerate rearrangement.[23] The enthalpy of activation is appreciable ($\Delta H^{\ddagger} = 22.3$ kcal/mol) at the B3LYP/6-31G*//B3LYP/6-31G* level of calculation. The high enthalpy of activation of degenerate rearrangement suggests that the distortion of the central ring of **4c** can be observed in the isolated state.

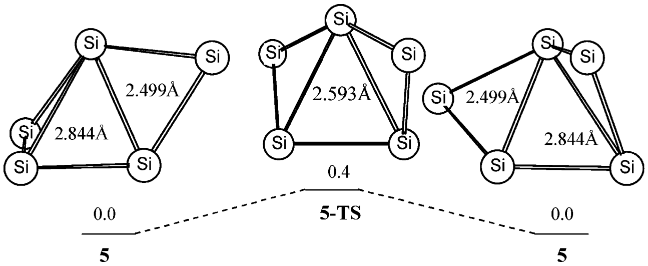


Figure 7. The structure (the fusion bond lengths) and the enthalpy of activation (kcal/mol) of the degenerate rearrangement of **5** calculated at the G3B3//B3LYP/6-31G* level.

Atomic clusters have attracted much attention in recent years due to their potential applications in many areas.[24] We investigate the degenerate rearrangement of the difusotricyclic Si_5 cluster. A difusotricyclic geometry **5** was located as a local energy minimum (Figure 7). The central three-membered ring is distorted with appreciably different fusion bond lengths (2.499, 2.844 Å). The optimized structure of the C_2 symmetry is the transition structure (**5-TS**) of the degenerate rearrangement. The low enthalpy of activation ($\Delta H^{\ddagger} = 0.4$ kcal/mol) suggests rapid interconversion of the isomers.

Conclusion

We theoretically investigated a highly strained tricyclic silane, tricyclo[2.1.0.0^{1,3}]pentasilane (**4b**), where the central three-membered ring is fused by the two three-membered side rings. One of the fusion bonds (2.309 Å) is shorter than the normal Si−Si single bond (2.350 Å) and cyclotrisilane (**1b**) (2.345 Å) whereas the other fusion bond (2.802 Å) is as long as those in bicyclo[1.1.0]tetrasilane (**2b**) (2.860 Å) and pentasila[1.1.1]propellane (**3b**) (2.778 Å). The significant difference in the fusion bond lengths indicates that the central silicon three-membered ring is distorted. The silane **4b** (86.4 kcal/mol) is less strained by 48.3 kcal/mol than the alkane tricyclo[2.1.0.0^{1,3}]pentane (**4a**) (134.7 kcal/mol), and more strained by 28.8 kcal/mol than the isomer, peantasila[1.1.1]propellane (**3b**) (57.6 kcal/mol). The strains of the silanes relative to the alkanes including those of the bicyclic silane, **2b** (53.7 kcal/mol) vs **2a** (66.2 kcal/mol), and the tricyclic molecules, **3b** vs **3a** (100.4 kcal/mol), suggest a general trend that the silanes composed of the fused three-membered rings are the less strained carbon congeners. The electron delocalization between the fusion bond and the geminal Si−Si ring bonds elongates the fusion bond and stabilizes the molecules to reduce the strain. Kira et al.[25] have prepared, isolated, and characterized the silicon congener of spiropentadiene of lower strain than the hydrocarbon, which has not been isolated as yet. A derivative of the silane **4b** was very recently isolated and characterized by Scheschkewitz[21] though the hydrocarbon **4a** has not been isolated. The difusotricyclic silane **4b** undergoes a new type of degenerate rearrangement where the distorted three-membered rings are converted to each other. The enthalpy of activation is 7.2 kcal/mol. The degenerate rearrangements were predicted to occur in the difusotricyclic Si_5 cluster **5** and tricyclo[2.1.0.0^{1,3}]-pentagermane (**4c**). The high enthalpy of activation ($\Delta H^{\ddagger} = 22.3$ kcal/mol) for the germanium congener encourages us to observe the distorted three-membered rings and the degenerate rearrangements.

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Supporting Information Available: Full description of the material. This material is available free of charge via the Internet at http://pubs.acs.org.

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(23) The nonfusion Ge_1-Ge_2 bonds (2.572 Å) are elongated in the transition structure **4c-TS**, whereas the Si_1-Si_2 bonds (2.302 Å) are shorted in **4b-TS**.

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