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REGULAR ARTICLE

Ab initio MO and DFT study for the isomerisation of bicyclo[1.1.0]tetrasilane and the germanium analogues

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Abstract The mechanism of the unimolecular isomerisation reaction of the silicon and germanium analogues of bicyclo[1.1.0]butane with various kinds of substituents (X_4R_6; X = Si and Ge, R=H, CH_3, *t*-Bu and SiH_3) to the corresponding cyclobutene analogues has been investigated by ab initio molecular orbital and DFT methods. Several reaction mechanisms were considered. They are roughly divided into two types; (1) skeletal rearrangement and (2) substituent migration. It was found that substituents (R) have the leading effect on the reaction mechanism but the partial or full replacement of the skeletal silicon atoms by germanium atoms has some important effects as well. Furthermore, the character of the bridge bond of the long-bond and short-bond isomers of these bicyclic compounds was investigated and discussed in comparison with the π bond in ethene and disilene by the CiLC analysis.

Keywords Bicyclo[1.1.0]tetrasilane analogue · Heavier group 14 elements · Isomerisation · Bridge bond

1 Introduction

Since a bicyclo[1.1.0]tetrasilane (Si_4R_6) was firstly synthesised and determined the X-ray structure [1–3], the compound and the related compounds have been intriguing research targets to both experimental and theoretical chemists because of the existence of two kinds of isomers with the different lengths of the bridge bond, which is not observed in the carbon analogue. Therefore, it is not a surprising thing that the character of the bridge bond has attracted considerable attention [4–8].

On the other hand, the properties of the heavier group 14 analogues such as Ge_4R_6, which has also been synthesised [9–12], are also an interesting topic in this area [8, 13]. Very recently, Yoshimura and Kyushin have succeeded in the synthesis of two kinds of the Si/Ge-mixed analogue of bicyclo[1.1.0]tetrasilane, Si_2Ge_2(*t*-Bu)$_6$, and the corresponding products of the isomerisation reactions, the Si/Ge-mixed analogues of cyclotetrasilene [14]. The mechanism of the unimolecular isomerisation between bicyclo[1.1.0]tetrasilane and cyclotetrasilene has been investigated vigorously [15–18] but that of the Si/Ge-mixed analogues has been unknown at present. In addition, they have proposed a new concept of chemical bond, 'π single bond', for the bridge bond of their compounds [14].

In the present study, therefore, we have tried to explore the reaction pathway connecting the two compounds on the ground electronic state in detail by ab initio molecular orbital and DFT calculations. Besides that, we have tried to obtain the general aspects for this type of reaction of the heavier group 14 analogues by comparing the result with those of the silicon analogue and related compounds with various kinds of substituent on the molecular skeletons. Furthermore, another concern of this study is to get the deeper knowledge for the character of the bridge bond

Dedicated to Professor Shigeru Nagase on the occasion of his 65th birthday and published as part of the Nagase Festschrift Issue.

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related to the concept of 'π single bond'. We have applied the CiLC analysis to this issue and compared the result with those of the typical compounds with a π bond, ethene, and the silicon analogue, disilene.

2 Computational methods

Geometry optimisations were performed for all molecules at the Hartree–Fock (HF) level of theory and the hybrid type of the HF and Density Functional Theory, B3LYP [19] method, with the 6-31G(d) [20] and 6-311G(d,p) basis sets [21, 22]. The effect of diffuse functions was also examined but it was found to be negligible both for the geometries and energetics of stationary points so only these two types of basis set were used in the current study. All optimised structures were characterised as minima or transition states by normal mode analyses. After that, the IRC [23, 24] calculations have been carried out to confirm the connectivity of the transition state and two minima, the reactant and product, for each reaction.

On the other hand, the CiLC analysis of Sakai et al. [25–27] is well known as a useful theoretical method to analyse the bond character of various molecules. The CiLC analysis is the representation of the electronic configurations for a bond on the basis of atomic-like orbitals and is performed through the configuration interaction (CI)/localised molecular orbital transformation (LMO)/CASSCF calculations. The electronic structures of bonds on the basis of the CiLC calculation were presented roughly as one singlet coupling term and two polarisation terms. The representation using these terms for one bond has been successful to explain the bond formation and bond extinction along a chemical reaction path. So, in order to understand the character of the bridge bond of the bicyclic isomers and other intermediates, the calculations of the CiLC analysis have been performed at the CASSCF(2,2) [28] level of theory where the two electrons and the two orbitals of the bridge bond are comprised in the active space.

All calculations were performed with the Gaussian 03 [29] and GAMESS programs [30].

3 Results and discussion

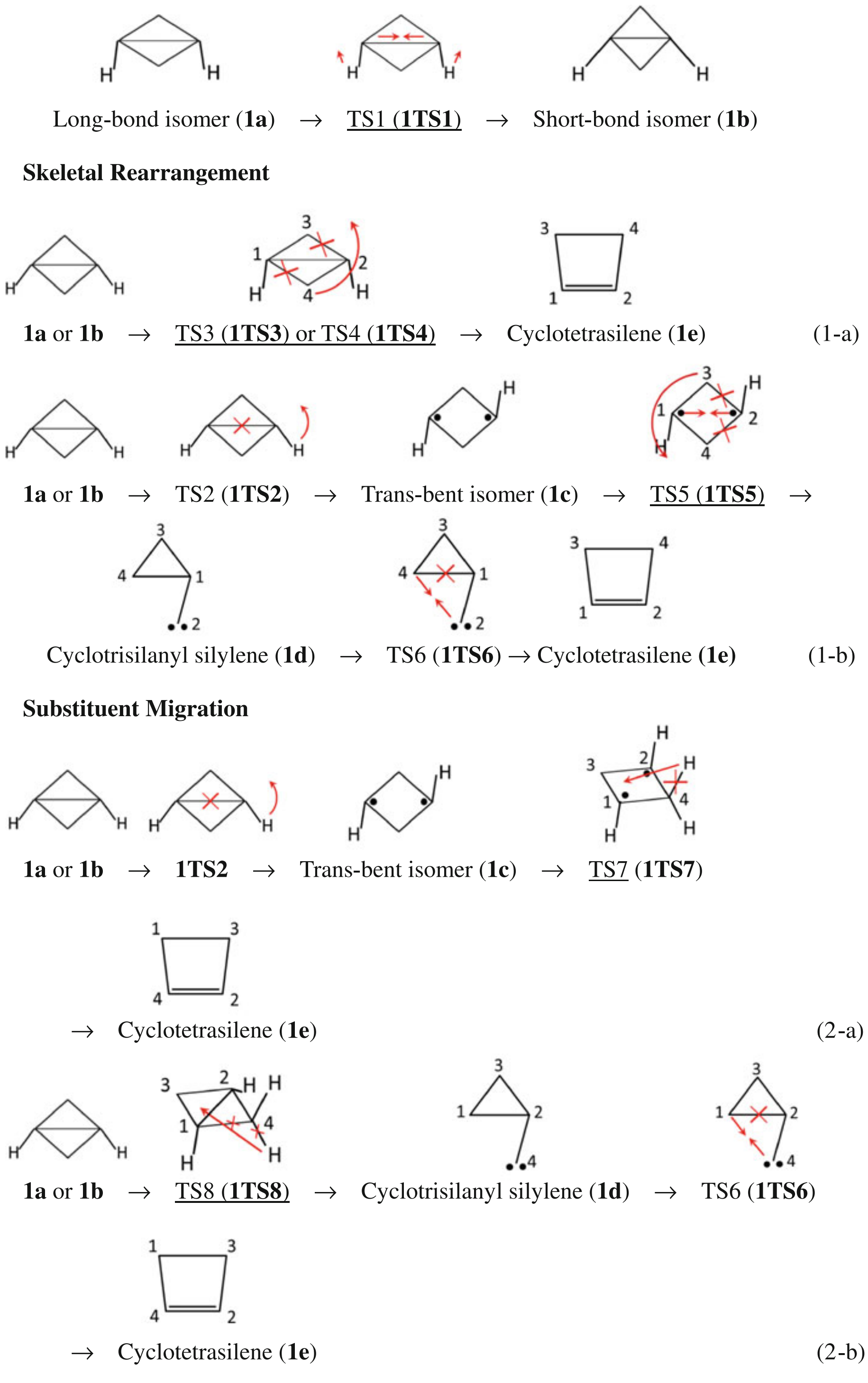
3.1 Isomerisation of bicyclo[1.1.0]tetrasilane (Si_4H_6, **1**)

First, we have investigated the mechanism of the isomerisation of bicyclo[1.1.0]tetrasilane to cyclotetrasilene, as the model system of the present study. The reaction mechanisms considered here are roughly divided into two types; (1) skeletal rearrangement and (2) substituent (a hydrogen atom in this case) migration (see Schemes 1 and 2). Furthermore, two kinds of reaction pathways (a and b) are obtained in each mechanism; (1-a) The bicyclic compounds isomerise directly to cyclotetrasilene via TS3 (**1TS3**) or TS4 (**1TS4**), the former being for the long-bond isomer whereas the latter being for the short-bond isomer, (1-b) The reaction occurs through two equilibrium structures (trans-bent isomer (**1c**) and a silylene compound (**1d**)) and three kinds of transition states, (2-a) The 1,2-hydrogen migration occurs on the same side of the four-membered ring of the trans-bent isomer (**1c**) in TS7(**1TS7**) after the trans-bent isomer is formed (end-H migration in Scheme 2), and (2-b) The 1,2-hydrogen transfer takes place across one of the peripheral Si–Si bonds of the short-bond isomer (**1b**) in TS8 (**1TS8**), which gives the cyclotrisilanyl silylene, Si_3H_5SiH (**1d**) (exo-H migration in Scheme 2). All mentioned above are summarised with the transition states connecting equilibrium structures in Scheme 1 in addition to the isomerisation of the long-bond (**1a)** and short-bond isomers (**1b**) of bicyclo[1.1.0]tetrasilane. The transition state underlined has the highest energy in each mechanism, corresponding to the rate determining step in the case of multi-step reaction.

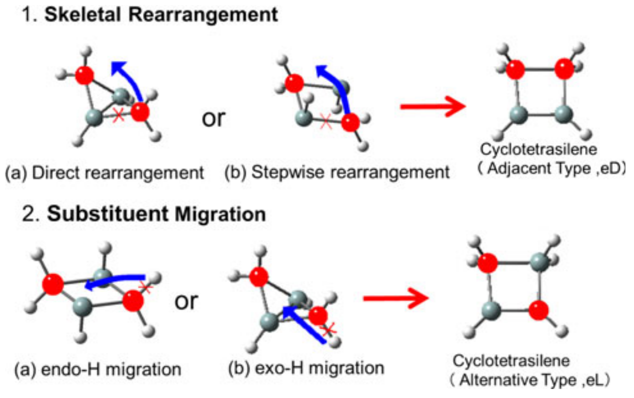
The optimised structures of all these stationary points considered here are displayed in Fig. 1.

As already mentioned, bicyclo[1.1.0]tetrasilane has two isomers (**1a** and **1b**), which is observed only in the heavier group 14 analogues and not in the corresponding carbon compound. As seen from Fig. 1 and Scheme 3, the name of two isomers originally comes from the difference of the bridge bond length (r) but the other geometrical parameters, θ and φ, are also significantly different between the two isomers. In addition, another isomer of these bicyclic compounds is trans-bent isomer (**1c**) with formally a further elongated bridge bond of **1a** and the hydrogen attached on the bridgehead atoms takes a trans position each other (The corresponding position is cis in **1a** and **1b**). The isomer **1c** has a planar four-membered ring and the diagonal distance is longest among the three isomers (**1a**, **1b** and **1c**). Here, it may be interesting to note the character of the peripheral Si–Si and Si–H bond from the viewpoint of the 3s-3p hybridisation. As seen from the Fig. 1, both the r(1–3) and r(1–5) increase in the order, **1b** < **1a** < **1c** at both levels of calculation. On the other hand, the angle around the bridgehead Si(1) atom (<315+<415+<314) decreases in the order, **1b** ($360° = sp^2$) > **1a** ($316.7° \sim sp^3$) > **1c** ($281.3° \sim 3 \times p =$ orthogonal) at the HF/6-31G(d) level. Therefore, the change of the peripheral Si–Si and Si–H bond distances from **1b** to **1c** can be explained from the amount of the contribution of the 3s orbital. Furthermore, as **1c** looks like a di-radical type of molecule with the broken central bond, we have performed the symmetry-broken

Scheme 1 All reaction mechanisms considered in the present study



UHF and UB3LYP levels of calculations for the geometry optimisation of trans-bent isomer in addition to the ordinary restricted HF (RHF) or B3LYP calculations but the obtained results did not change at all. Besides, according to the CASSCF(2,2)/6-31G(d) calculations, the coefficient of the adiabatic configuration is more than 0.9 and the occupation number of the HOMO and LUMO is 1.787 and 0.213, respectively, in the ground electronic state. From these results, this molecule is not considered to be a real di-radical so the application of the RHF and B3LYP methods seems to be appropriate. Trans-bent isomer (**1c**) is one of the important intermediates for the isomerisation



Scheme 2 Two types of reaction mechanisms in the Si/Ge-mixed molecules

reaction especially of the compound with bulky substituent such as the *t*-Bu group discussed later. The final product, cyclotetrasilene (**1e**), has also a planar four-membered structure with one silicon–silicon double bond. The Si=Si bond length obtained at the B3LYP/6-311G(d, p) level is 2.158 Å (2.141 Å at the HF/6-31G(d)) which is slightly shorter than 2.173 Å (2.133 Å at the HF/6-31G(d)) of disilene ($H_2Si{=}SiH_2$; trans-bent). The least stable equilibrium structure is a cyclotrisilanyl silylene (**1d**) appeared in the mechanism (1-b) and (2-b). In the former (1-b) mechanism, it is formed after the Si–Si bond alternation in **1c** via TS5 (**1TS5**) while in (2-b) the silylene is the product of the 1,2-H migration reaction from a silicon at the vertex of three-membered ring to another silicon at the bridgehead position in **1b**. As a consequence, one Si–Si bond of the triangle is significantly elongated as 2.511 Å at the B3LYP/6-311G(d,p) (same value at the HF/6-31G(d)). The <H–Si-Si_3H_5 bond angle obtained at the B3LYP/6-311G(d,p) is 92.3° (90.4° at the HF/6-31G(d)).

Now, consider the mechanism. What is the most favourable reaction pathway among such complicated and many candidates? The potential energy surfaces in Fig. 2 should give us the information about this issue. At the HF/6-31G(d) level (see Fig. 2a), **1a** is slightly more stable than **1b** and the energy barrier of direct isomerisation by skeletal rearrangement (1-a) from each isomer is 37.5 (**1TS3**, long-bond) and 49.3 (**1TS4**, short-bond) kcal/mol, respectively. For mechanism (1-b) via **1c** that is 13.7 kcal/mol unstable than **1a**, the energy barrier of the rate determining step (via **1TS5**) is 35.4 kcal/mol (21.7 kcal/mol from **1c**). On the other hand, the energy barrier of the two types of hydrogen migration mechanism, (2-a) and (2-b), is 42.3 (via **1TS7**) (28.6 from **1c**) and 40.2 (via **1TS8**) (37.5 from **1b**) kcal/mol, respectively. As a result, 1-b (skeletal rearrangement) is the most favourable mechanism at the HF/6-31G(d) level. However, the direct inter-conversion form **1a** to **1e** via **1TS3** (mechanism 1-a) may be another possible pathway since the energy barrier is not so high compared to that via **1TS5**.

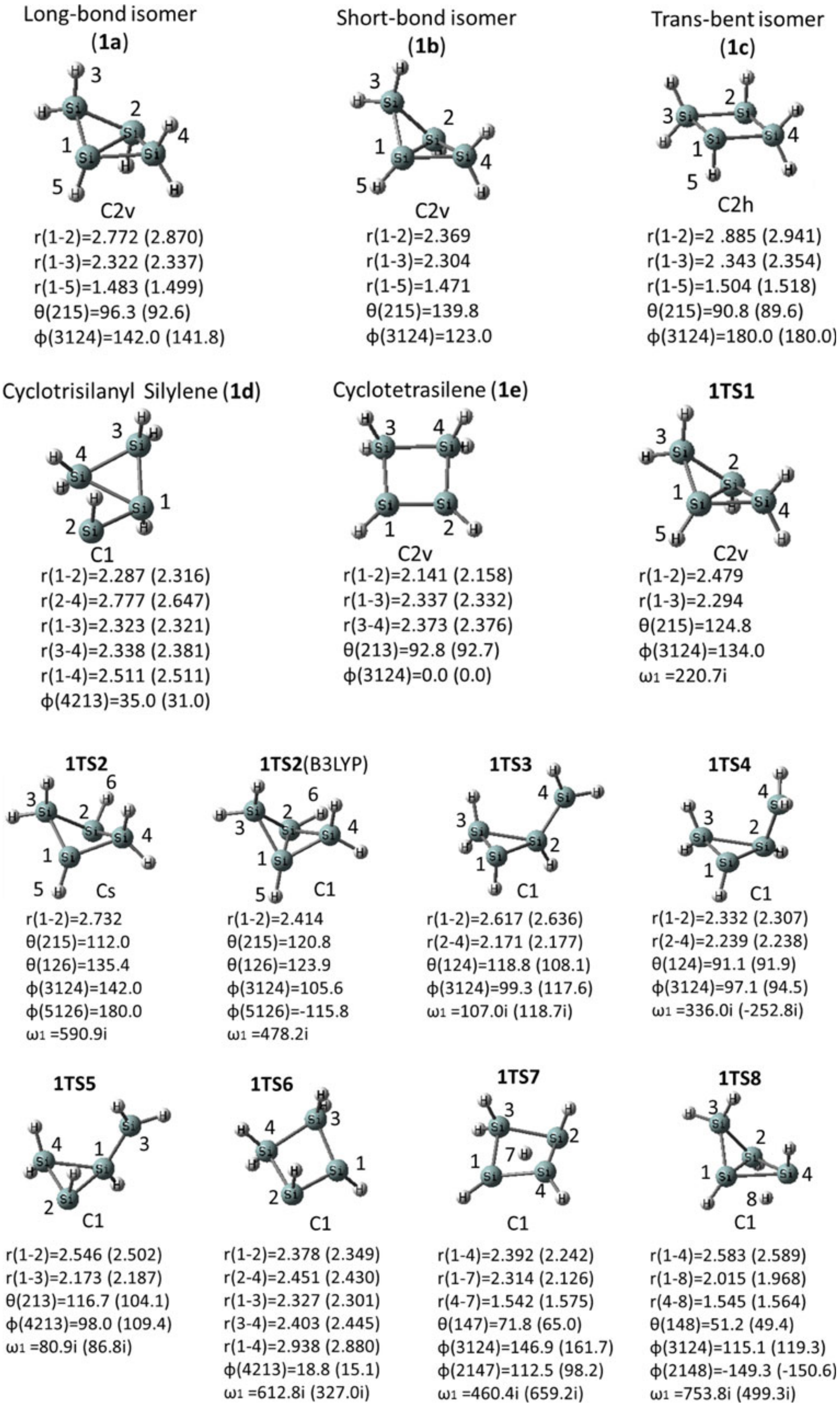
The landscape of the potential energy surface, however, was found to change considerably at the higher B3LYP/6-311G(d,p) level as shown in Fig. 2b. Most important difference is that **1b** and **1TS1** have disappeared. As a result, some transition states (**1TS2**, **1TS4** and **1TS8**) connected with **1b** are now directly connected with **1a**. This fragile existence of the short-bond isomer of Si_4H_6 may bring about the controversy in the early stage of the studies about this and the related compounds. Actually, as shown later, **1b** is located at the CASSCF(2,2)/6-31G(d) level and the stability relative to the long-bond isomer was found to change significantly depending on the substituent (R) or atomic element of the molecular skeleton. Furthermore, the stability of the final product (**1e**) relative to the reactant (**1a**) reversed as the energy difference was so small (3.6 kcal/mol) even at the HF level. Nevertheless, skeletal rearrangement (1-b) through **1TS5** is suggested still as the most favourable mechanism even at the higher level of calculations.

3.2 Isomerisations of 1,3-digerma-2,4-disilabicyclo[1.1.0]butane ($Si_2Ge_2H_6$-I, **2**), 1,3-disila-2,4-digermabicyclo[1.1.0]butane ($Si_2Ge_2H_6$-II, **3**) and bicyclo[1.1.0]tetragermane (Ge_4H_6, **4**)

On the basis of the results for Si_4H_6, we have investigated the same type of reaction of three analogous compounds where two or all silicon atoms in the molecular skeleton of Si_4H_6 are replaced by one of the heavier group 14 elements, germanium atoms. The structural formula of the molecular skeleton of the bicyclic isomer of $Si_2Ge_2H_6$-I, **2** and $Si_2Ge_2H_6$-II, **3** are shown in Scheme 4. As shown in Scheme 2, two kinds of cyclotetrasilene analogue, adjacent (**eD**)- and alternative (**eL**)-types, are possible to be formed in the isomerisation of the Si/Ge-mixed compounds depending on the reaction mechanism.

Figure 3 shows the optimised structures of the 5 equilibrium structures (the long-bond and short-bond isomers of bicyclo[1.1.0]tetrasilane analogue, the trans-bent isomer and silylene (germylene), and cyclotetrasilene analogue for each compound, $Si_2Ge_2H_6$-I (**2**), $Si_2Ge_2H_6$-II (**3**) and Ge_2H_6 (**4**). These minima of the Si/Ge-mixed compounds (**2** and **3**) are structural isomers each other and the relative stabilities are summarised in Table 1. As seen from the table, the **2a** is more stable than **3a** by 16.9 kcal/mol at the B3LYP/6-311G(d,p) level (22.3 kcal/mol at the HF/6-31G(d)) while the reaction product in the mechanism 1 (skeletal rearrangement) of the former, 3,4-disilacyclotetragermene (**2eD**), is more stable than that of the latter, 3,4-digermacyclotetrasilene (**3eD**), by 11.2 kcal/mol at the B3LYP/6-311G(d,p) level (16.9 kcal/mol at the HF/6-31G(d)). In addition, except for a few cases,

Fig. 1 The HF/6-31G(d) and B3LYP/6-311G(d,p) (in *parentheses*) optimised geometries of the stationary points on the potential energy surface of the isomerisation of Si_4H_6 (**1**) in Å and degrees



Long-bond isomer (**1a**)
C2v
r(1-2)=2.772 (2.870)
r(1-3)=2.322 (2.337)
r(1-5)=1.483 (1.499)
θ(215)=96.3 (92.6)
ϕ(3124)=142.0 (141.8)

Short-bond isomer (**1b**)
C2v
r(1-2)=2.369
r(1-3)=2.304
r(1-5)=1.471
θ(215)=139.8
ϕ(3124)=123.0

Trans-bent isomer (**1c**)
C2h
r(1-2)=2 .885 (2.941)
r(1-3)=2 .343 (2.354)
r(1-5)=1.504 (1.518)
θ(215)=90.8 (89.6)
ϕ(3124)=180.0 (180.0)

Cyclotrisilanyl Silylene (**1d**)
C1
r(1-2)=2.287 (2.316)
r(2-4)=2.777 (2.647)
r(1-3)=2.323 (2.321)
r(3-4)=2.338 (2.381)
r(1-4)=2.511 (2.511)
ϕ(4213)=35.0 (31.0)

Cyclotetrasilene (**1e**)
C2v
r(1-2)=2.141 (2.158)
r(1-3)=2.337 (2.332)
r(3-4)=2.373 (2.376)
θ(213)=92.8 (92.7)
ϕ(3124)=0.0 (0.0)

1TS1
C2v
r(1-2)=2.479
r(1-3)=2.294
θ(215)=124.8
ϕ(3124)=134.0
ω1 =220.7i

1TS2
Cs
r(1-2)=2.732
θ(215)=112.0
θ(126)=135.4
ϕ(3124)=142.0
ϕ(5126)=180.0
ω1 =590.9i

1TS2(B3LYP)
C1
r(1-2)=2.414
θ(215)=120.8
θ(126)=123.9
ϕ(3124)=105.6
ϕ(5126)=-115.8
ω1 =478.2i

1TS3
C1
r(1-2)=2.617 (2.636)
r(2-4)=2.171 (2.177)
θ(124)=118.8 (108.1)
ϕ(3124)=99.3 (117.6)
ω1 =107.0i (118.7i)

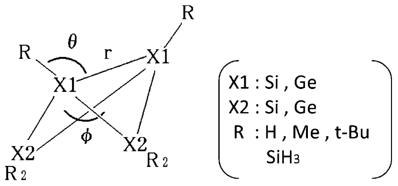
1TS4
C1
r(1-2)=2.332 (2.307)
r(2-4)=2.239 (2.238)
θ(124)=91.1 (91.9)
ϕ(3124)=97.1 (94.5)
ω1 =336.0i (-252.8i)

1TS5
C1
r(1-2)=2.546 (2.502)
r(1-3)=2.173 (2.187)
θ(213)=116.7 (104.1)
ϕ(4213)=98.0 (109.4)
ω1 =80.9i (86.8i)

1TS6
C1
r(1-2)=2.378 (2.349)
r(2-4)=2.451 (2.430)
r(1-3)=2.327 (2.301)
r(3-4)=2.403 (2.445)
r(1-4)=2.938 (2.880)
ϕ(4213)=18.8 (15.1)
ω1 =612.8i (327.0i)

1TS7
C1
r(1-4)=2.392 (2.242)
r(1-7)=2.314 (2.126)
r(4-7)=1.542 (1.575)
θ(147)=71.8 (65.0)
ϕ(3124)=146.9 (161.7)
ϕ(2147)=112.5 (98.2)
ω1 =460.4i (659.2i)

1TS8
C1
r(1-4)=2.583 (2.589)
r(1-8)=2.015 (1.968)
r(4-8)=1.545 (1.564)
θ(148)=51.2 (49.4)
ϕ(3124)=115.1 (119.3)
ϕ(2148)=-149.3 (-150.6)
ω1 =753.8i (499.3i)



	Long-bond isomer		Short-bond isomer
r	long	>	short
θ	small	<	large
ϕ	large	>	small

Scheme 3 The comparison of the geometrical character between the long-bond and short-bond isomers of various molecules considered here

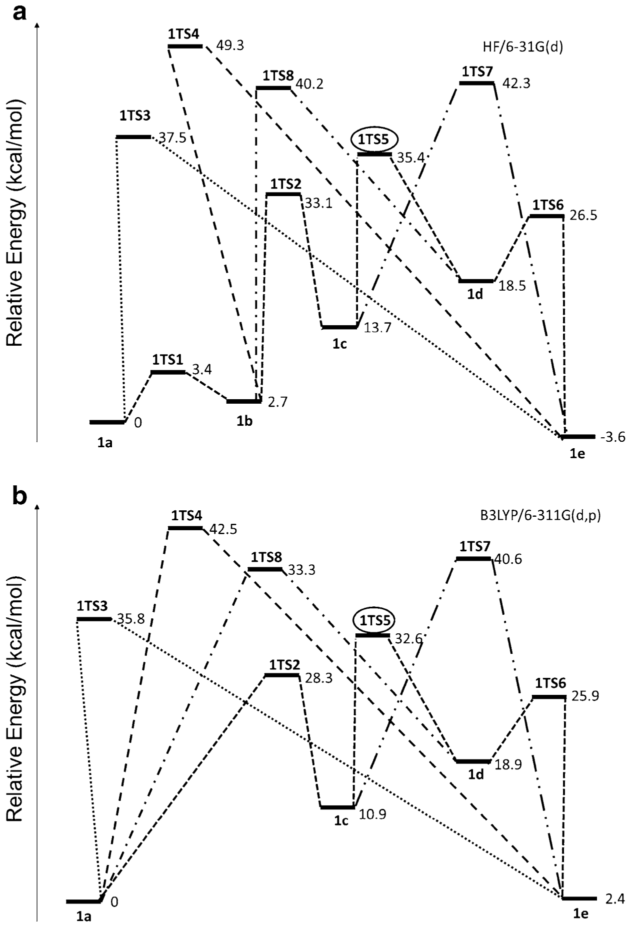
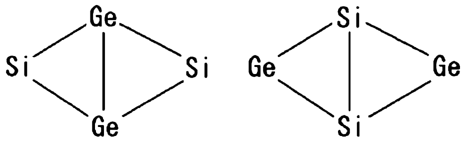


Fig. 2 The potential energy profiles for the isomerisation of Si_4H_6 at **a** the HF/6-31G(d) and **b** the B3LYP/6-311G(d,p) levels in kcal/mol



2 3

Scheme 4 The structural formula of the molecular skeleton of $Si_2Ge_2R_6$-I (**2**) and $Si_2Ge_2R_6$-II (**3**)

the other stationary points on the potential energy surface of the isomerisation of **2** are more stable than those of **3**. For silylenes and germylenes (**1d** analogues in Fig. 1) of the Si/Ge-mixed compounds, two kinds of structure are possible to exist depending on the reaction mechanism. $Si_2Ge_2H_6$-I (**2**) gives germylene (**2dD**) in the mechanism (1-b) while it gives silylene (**2dL**) in (2-b). On the other hand, $Si_2Ge_2H_6$-II (**3**) gives silylene (**3dD**) in the mechanism (1-b) while germylene (**3dL**) is obtained in (2-b). Incidentally, the **ndD** gives the adjacent type of product (**neD**) while the **ndL** gives the alternative type of product (**neL**). As seen in Table 1, germylenes are always more stable than the isomeric silylenes. Note that the reaction product in the mechanism 2 (substituent migration) of both reactants is the same alternative cyclic compound, **2eL** and **3eL**, as shown in Scheme 2. Therefore, for the Si/Ge-mixed compounds, the different product (cyclotetrasilene analogue) is obtained depending on the mechanism. In other words, we can estimate the reaction mechanism from the product in the synthetic experiment. The order of the stability of these three types of cyclic product is 3,4-disilacyclotetragermene (**2eD**) with a Ge=Ge bond > alternative compound (**2eL**, **3eL**) with a Ge=Si bond > 3,4-digermacyclotetrasilene (**3eD**) with a Si=Si bond, suggesting that the Ge doubly bonded structure tends to be more stable than that of the Si doubly bonded compound. In spite of this, Yoshimura et al. have obtained the hexa-*t*-Bu-3, 4-digermacyclotetrasilene as the isomerisation product of the $Si_2Ge_2(t\text{-Bu})_6$-II [14] suggesting substituent migration is hard to occur in the bulky *t*-butyl-substituted compound.

The relative energies of the stationary points on the potential energy surfaces of the isomerisation of these compounds at the HF/6-31G(d) and B3LYP/6-311G(d,p) levels are collected in Table 2 together with those of the parent Si_4H_6 for comparison. Among **1** to **4**, the short-bond isomer is located in all cases at the HF/6-31G(d) level but it has disappeared except for $Si_2Ge_2H_6$-II (**3**) at the B3LYP/6-311G(d,p) level. Furthermore, the HF/6-31G(d) level tends to prefer skeletal rearrangement via TS5 (1-b) in all cases and the same is true except for Ge_4H_6 (**4**) via TS8 (2-b) even at the higher level. Therefore, the disilene or digermene type of structures (**eD**) is expected to be the main product also for the Si/Ge-mixed compounds as discussed before.

The effect of the partial or full replacement of silicon in the molecular skeleton by germanium may be noteworthy. First, adjacent type (**eD**) of the cyclic product is largely destabilised relative to the bicyclic isomer except for $Si_2Ge_2H_6$-II (**3**). Second, the stability of intermediates such as the trans-bent isomer (**c**) and divalent species such as silylene or germylene (**dD**) slightly increases compared to

Fig. 3 The HF/6-31G(d) and B3LYP/6-311G(d,p) (in *parentheses*) optimised geometries of the isomers of $Si_2Ge_2H_6$-I (**2**), $Si_2Ge_2H_6$-II (**3**) and Ge_2H_6 (**4**) in Å and degrees

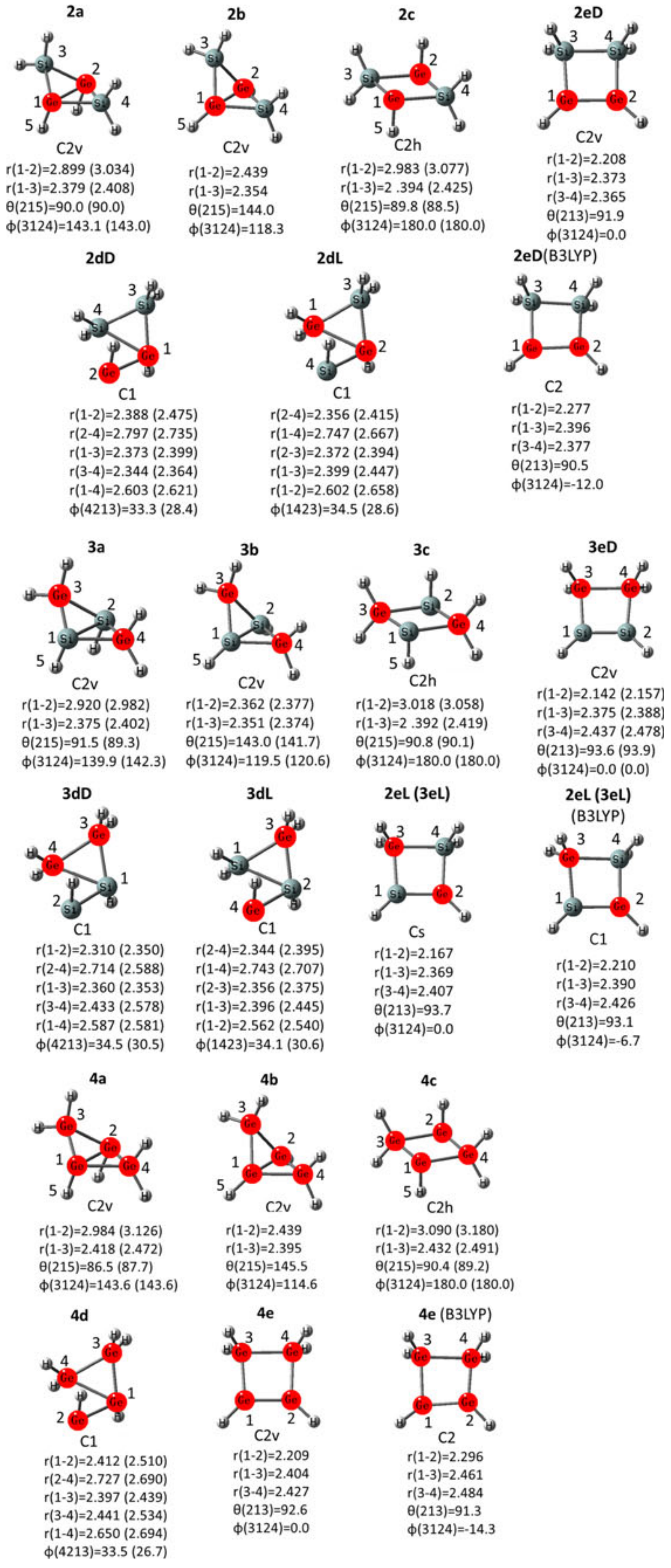


Table 1 The relative energies (kcal/mol) of equilibrium structures of $Si_2Ge_2H_6$-I (**2**) and $Si_2Ge_2H_6$-II(**3**) at the B3LYP/6-311G(d,p) and HF/6-31G(d)[a] levels

	2^c	3^c
a	0 (0)	16.9 (22.3)
b	(0)	(21.1)
c	0 (0)	17.8 (23.5)
dD^b	0 (0)	18.1 (18.8)
dL^b	12.3 (8.4)	6.8 (12.1)
eD^b	0 (0)	11.2 (16.9)
eL^b	5.7 (8.1)	5.7 (8.1)

[a] The values are in parentheses

[b] The 'D' is referred to the adjacent type of compounds while the 'L' is referred to the alternative type of compounds. Also, see Scheme 2 and the text

[c] The chemical structural formula of the bicyclic isomer of **2** and **3** are shown in Scheme 4

those of the silicon analogue. For the trans-bent isomer, the stability to the corresponding long-bond isomer is larger in the germanium analogues (**2c** or **4c**) than in the silicon analogues (**1c** or **3c**). Finally, the energy barriers for the skeletal rearrangement (via TS3/TS4 or TS5) of the Ge- and Si/Ge-mixed compounds are lower than those of the silicon analogue except for TS5 (**2TS5**) of $Si_2Ge_2H_6$-I (**2**). This may be explained from that the weaker Ge–Ge single bond compared to the Si–Si single bond is broken more easily. For the substituent migration (via TS7 and TS8), however, the order of barrier heights does not seem to change systematically. Otherwise, the reaction mechanisms and energetics do not change so largely.

3.3 The effect of substituents

Next, let us discuss the effect of the substituents attached on the bridgehead silicon or germanium atoms on the isomerisation reactions. The substituents investigated here are CH_3, *t*-Bu and SiH_3 groups; Si_4R_6 (R=CH_3 (**1_CH$_3$**), *t*-Bu (**1_tBu**) and SiH_3(**1_SiH$_3$**)), $Si_2Ge_2R_6$-I (R=SiH_3 (**2_SiH$_3$**) and $Si_2Ge_2R_6$-II (R=CH_3 (**3_CH$_3$**) and SiH_3 (**3_SiH$_3$**)). Table 2 also shows the relative energies of the stationary points on the potential energy surface of the unimolecular isomerisation for each compound except for $Si_4(t\text{-Bu})_6$ of which results will be discussed later.

In many cases, the short-bond isomer (**b**) does not exist at both levels of theory except for the methyl substituted analogues of **1_CH$_3$** and **3_CH$_3$**.

For the substituent migration in Si_4R_6, the silyl group tends to have the lower energy barrier whereas the opposite is true in the methyl group. This may be explained from the hypervalent character of the Si atom in the silyl group and the electron-donating behaviour to silicon atoms in the molecular skeleton. Also, it is in agreement with the findings of Kira et al. [15]. In the Si/Ge-mixed compounds,

Table 2 The relative energies (kcal/mol) of stationary points on the potential energy surfaces of the isomerisation of the compounds considered in the present study at the B3LYP/6-311G(d,p) and HF/6-31G(d)[a] levels

	1	2	3	4	1_Me	3_Me	1_SiH3[b]	2_SiH3	3_SiH3 I
a	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (–)	0	0
b	–(2.7)	–(6.4)	12.3 (5.3)	–(10.4)	3.0 (–1.9)	6.6 (–0.5)	–(0)	–	–
c	10.9 (13.7)	8.3 (10.1)	9.2 (11.3)	7.2 (8.5)	12.2 (16.6)	9.0 (12.3)	18.7 (26.5)	13.9	15.8
dD^c	18.9 (18.5)	16.0 (17.4)	17.2 (15.8)	15.8 (16.6)	22.2 (–)	18.4 (13.6)	20.3 (24.3)	16.3	16.5
dL^c		28.3 (25.9)	5.9 (7.2)			4.9 (16.3)		24.6	9.2
eD^c	2.4 (–3.6)	9.3 (–0.6)	3.5 (–5.9)	11.0 (–1.7)	–2.1 (–7.8)	–2.3 (–14.0)	–0.9 (–2.8)	4.0	–2.2
eL^c		15.0 (7.5)	–1.9 (–14.7)			–10.3 (–13.0)		6.0	–3.8
TS1	–(3.4)	–(8.0)	12.8 (7.4)	–(13.0)	3.3 (0.4)	8.0 (5.3)	–(–)	–	–
TS2	28.3 (33.1)	31.7 (31.3)	28.5 (30.5)	31.9 (31.5)	30.9 (33.6)	28.6 (30.8)	19.9 (27.0)	20.3	17.8
TS3	35.8 (37.5)	34.8 (35.6)	31.7 (35.5)	31.5 (35.2)	34.8 (37.4)	29.7 (39.9)	33.0 (40.4)	31.3	27.4
TS4	42.5 (49.3)	42.0 (50.4)	39.1 (45.9)	–(49.1)	37.5 (44.9)	33.0 (44.6)	36.5 (47.3)	40.3	31.3
TS5	32.6 (35.4)	33.2 (34.0)	28.4 (30.4)	29.8 (33.1)	32.7 (–)	28.0 (38.8)	30.2 (–)	30.7	24.7
$TS6D^c$	25.9 (26.5)	23.6 (25.4)	22.8 (22.8)	21.6 (22.8)	30.9 (–)	28.6 (20.2)	21.5 (27.0)	18.1	17.7
$TS6L^c$		33.0 (35.0)	14.4 (12.8)			10.7 (20.2)		25.0	12.1
TS7	40.6 (42.3)	38.7 (40.8)	36.8 (34.3)	34.9 (34.6)	45.2 (47.1)	38.8 (39.2)	31.7 (42.6)	31.0	28.7
TS8	33.3 (40.2)	33.6 (41.2)	28.9 (48.7)	28.6 (39.6)	54.8 (–)	42.5 (59.3)	33.8 (46.0)	38.1	26.3

[a] The values are in parentheses

[b] The HF/6-31G(d) energies are those relative to that of **1b_SiH$_3$**

[c] The 'D' is referred to the adjacent type of compounds while the 'L' is referred to the alternative type of compounds. Also, see Scheme 2 and the text

Table 3 The structural parameters (Å and degrees) and relative energies (kcal/mol) of some equilibrium structures of **1** and **1_tBu** at the B3LYP/6-311G(d,p)//B3LYP/6-31G(d) and B3LYP/6-31G(d)[a] levels

	Energy	r (1–2)	r (1–3)	r (3–4)	θ (215)
1a	0 (0)	(2.861)	(2.335)	–	(92.2)
1c	10.9 (10.8)	(2.934)	(2.351)	–	(89.8)
1e	2.4 (3.3)	(2.160)	(2.331)	(2.373)	–
1TS4	42.5 (43.7)	(2.632)	–	–	–
1a_tBu	0 (0)	(2.625)	(2.334)	–	(157.3)
Ib_tBu	−0.123 (−0.238)	(2.531)	(2.349)	–	(159.6)
1c_tBu	0.958 (1.035)	(2.802)	(2.326)	–	(174.7 and 177.2)
1e_tBu	0.564 (0.992)	(2.172)	(2.362)	(2.560)	–
1TS4_tBu	31.4 (31.2)	(2.258)	–	–	–

[a] The values are in parentheses

however, the trend is not always observed probably because of the participation of other factors. It is noteworthy that the stability of the product (cyclotetrasilene analogue, **eD**) relative to the reactant (the long-bond isomer) increases irrespective of substituent except for **2_SiH$_3$** suggesting that the substituted cyclotetrasilene analogues are more stable than expected despite of their unstable doubly bonded structures.

On the other hand, the structures of the stationary points and the landscape of the potential energy surface of the *t*-Bu substituted bicyclo[1.1.0]tetrasilane (**1_tBu**) are quite different with the other compounds probably because of the bulkiness of *t*-Bu group as shown in Table 3 and Fig. 4a. Table 3 shows selected geometric parameters and relative energies of the equilibrium structures of Si_4H_6 and the corresponding structures of the *t*-Bu substituted analogue obtained at the B3LYP/6-311G(d,p)//B3LYP/6-31G(d) and B3LYP/6-31G(d) levels. The **1b** was not located at the B3LYP/6-31G(d) level of calculation. For the bicyclic and the trans-bent isomers, the remarkable differences are seen in the bond angle and bridge bond length between **1** and **1_tBu**. In the *t*-butyl substituted compound, the bond angle (θ) is significantly widened because of the congestion, which makes the skeleton of the two isomers (**1a_tBu** and **1b_tBu**) less folded compared to those of Si_4H_6, as seen from Fig. 4a. The isomer **1a_tBu** seems to be less folded than **1b_tBu** as seen from the larger ψ(3124) in Fig. 4a. Incidentally, the label of the corresponding isomer of the Si/Ge-mixed analogue made by Yoshimura et al. is 'cis-bent' for the long-bond isomer while 'folded' for the short-bond isomer, respectively [14]. Furthermore, for **1c_tBu,** the conformation of the *t*-Bu groups on the bridgehead is not a trans-bent but almost planar or rather a cis-bent. However, the Si/Ge-mixed compound synthesised by Yoshimura et al. has kept a trans-bent conformation [14]. Therefore, 'planar' instead of 'trans-bent' seems to be appropriate for this isomer. The widening of the bond angle (θ) seems to strengthen the bridge bond of the long-bond and short-bond isomers and even the diagonal bond in the planar isomer probably because of larger overlap of the tail of the σ bonding orbital of C–Si bonds at the bridgehead Si atoms. In order to confirm this, the constrained geometry optimisation was carried out for the Si_4H_6 bicyclic compound with the bond angle (θ) as 180°which is close to that of **1a_tBu**. The bridge bond distance of the obtained structure is 2.651 Å that is quite similar to that of **1a_tBu**. As a result, the bridge bond distance decreases in the *t*-Bu compound compared with those in the H analogue. Furthermore, the peripheral bond length such as Si(1)-Si(3) is also shortened in the planar isomer (**1c_tBu**). In contrast, that in the bicyclic compounds does not change largely by the bulky substituent.

Also, for *t*-Bu substituted cyclotetrasilene (**1e_tBu**) with C_2 symmetry, the four-membered ring is not planar (the deviation is 5.7°) and the Si(3)-Si(4) single bond is significantly elongated (it is longer than **1e** by ca. 0.2 Å) because of the steric repulsion among total four *t*-Bu groups attached on both Si atoms.

The geometrical changes brought by the bulky substituent have made the trans-bent (**1c_tBu**, planar) or the short-bond isomer (**1b_tBu**, folded) markedly stable compared to the long-bond isomer (**1a_tBu**, cis-bent). Now, the stability between the long-bond and the short-bond isomers are reversed. Furthermore, **1c_tBu** is less stable than **1a_tBu** only by 0.96 kcal/mol at the B3LYP/6-311G(d,p)//B3LYP/6-31G(d) (1.0 kcal/mol at the B3LYP/6-31G(d)) level. Incidentally, the energy difference between **1c** and **1a** is large as 10.9 kcal/mol (10.8 kcal/mol) at the same level of theory. As a result, four isomers of $Si_4(t\text{-Bu})_6$ are found to have similar stability.

Figure 4b shows the potential energy surface of the isomerisation (by mechanism 1-a) of the long-bond isomer to cycltetrasilene analogue of $Si_4(t\text{-Bu})_6$ together with that of the corresponding H-compound calculated at the same levels of theory. The other mechanisms involving migration of substituent seem to be unfavourable for the bulky *t*-Bu

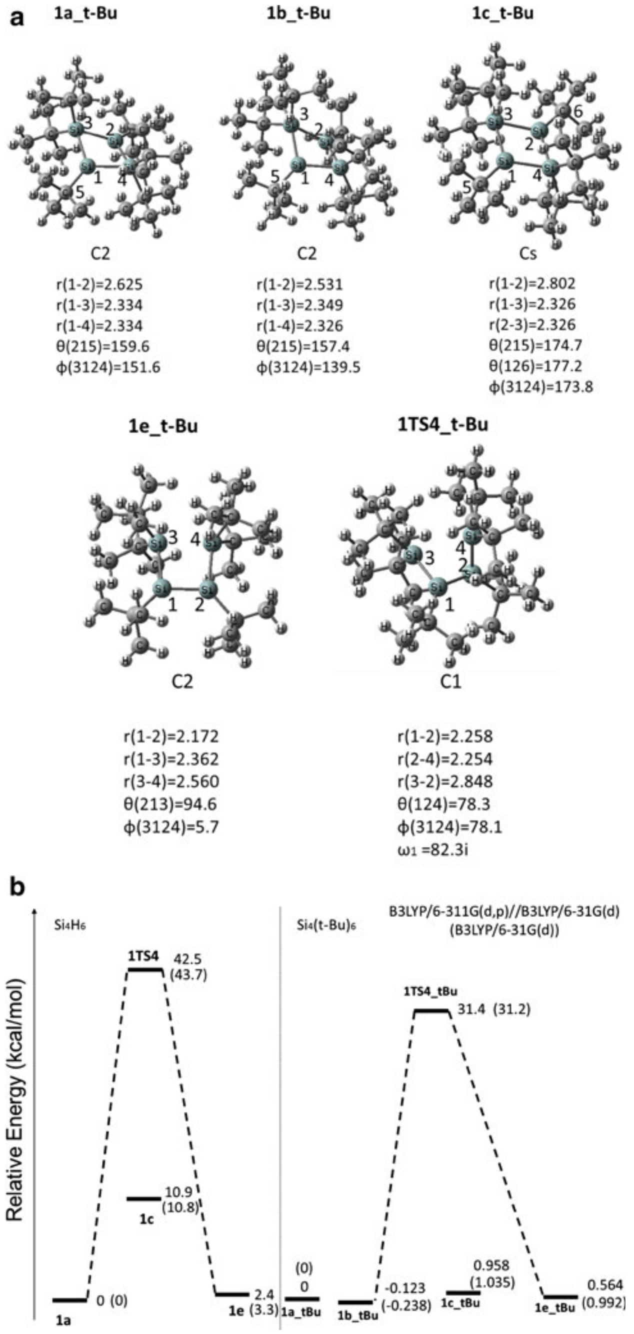


Fig. 4 **a** The B3LYP/6-31G(d) optimised geometries of some stationary points of $Si_4(t\text{-}Bu)_6$ (**1_tBu**). **b** The potential energy profiles for the isomerisation of Si_4H_6 (**1**) and $Si_4(t\text{-}Bu)_6$ (**1_tBu**) at the B3LYP/6-311G(d,p)//B3LYP/6-31G(d) and B3LYP/6-31G(d) (in *parentheses*) levels in kcal/mol

group, which is suggested by the fact that Yoshimura et al. have obtained the adjacent type of product in their experiment [14]. Therefore, the most plausible transition state connecting the two minima should be TS3 based on the results for the H analogue. However, the obtained structure by the transition state search was TS4 (**1TS4_tBu**) that connects the short-bond isomer and cyclotetrasilene for the H analogue. From the comparison of **1TS3** and **1TS4** in Fig. 1, it is apparent that the congestion caused by the bulky substituent on Si(3) and Si(4) is smaller in TS4 than in TS3. In addition, the short-bond isomer (folded, **1b_tBu**) was found to be slightly more stable than the long-bond isomer (cis-bent, **1a_tBu**) for the *t*-Bu analogue. Therefore, we have decided to focus on TS4 (**1TS4_tBu**) as the most important transition state for the reaction. As seen from the Fig. 4b, the energy barrier is large enough for the reactant and product to exist kinetically stably and this is in good agreement with the experiment for the *t*-Bu substituted Si/Ge-mixed analogue of bicyclo[1.1.0]tetrasilane [14]. Also, as both the long-bond isomer (cis-bent) and short-bond isomer (folded) were observed in the experiment for the Si/Ge-mixed compound, the considerable amount of energy barrier is expected to exist between **1a_tBu** and **1b_tBu** but it should be lower than that of the isomerisation between **1b_tBu** and **1e_tBu**. From these results, the bulky *t*-Bu substituent was found to make the isomerisation reaction easier compared to the case of the H analogue.

3.4 The character of the bridge bond

First, we have investigated the character of the bridge bond of two isomers of bicyclo[1.1.0]tetrasilane and the transition state (TS1) connecting both isomers by the CiLC analysis. The changes of (1) the weight of the electronic states of the bond, and (2) the ratio of polarisation to singlet coupling along the reaction pathways are shown in Fig. 5a, b. In these figures, the point 0 on the horizontal axis corresponds to the transition state. The ratio is larger than about 0.5 in the covalent bond. Apparently, the bridge bond in the long-bond isomer (**1a**) has large singlet coupling character while that in the short-bond isomer (**1b**) seems to be a normal covalent bond as expected from the bond distance. The interesting thing is that the character does not change smoothly along the reaction coordinate but the transition state (**1TS1**) is found to be an inflection point. The weights of the singlet coupling and polarisation terms almost do not change during the region from **1b** to the transition state and after the transition state the weights change dramatically. This means the electronic state of the bridge bond does not change much in the region between **1b** and the transition state, and this may bring about the very low or no energy barrier between **1a** and **1b**. On going from the transition state to **1a**, the conformation around the Si atoms on the bridgehead changes from the quasi-planar to the pyramidal like the folding of an umbrella as discussed for the 3s–3p hybridisation in the preceding section. This is supported by that the angle around the bridgehead Si atom (<315+<415+<314 in the long- and short-bond isomers in Fig. 1) is 359.7° for **1b**, 355.9° for **1TS** and 308.1° for **1a** at the CASSCF(2,2)/6-31G(d) level. This structural change makes outward part of the orbital of

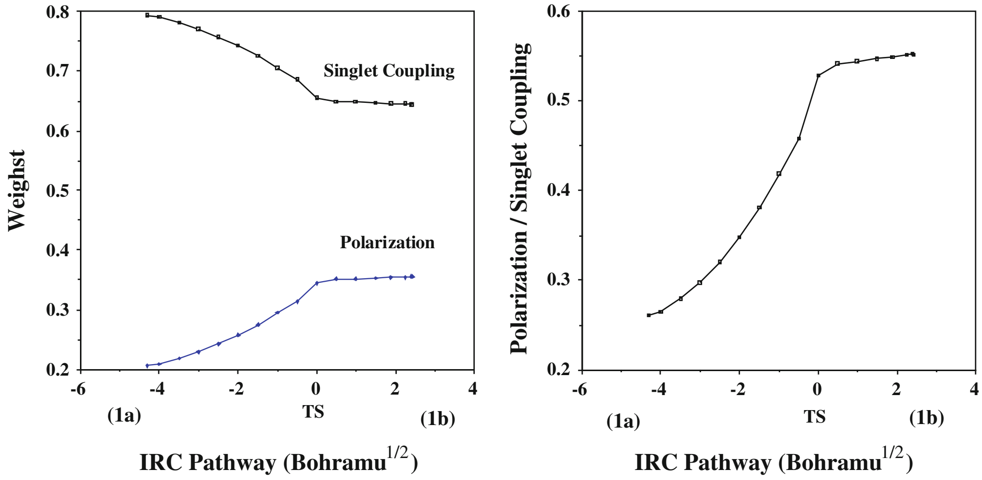


Fig. 5 The CiLC analysis along the IRC pathway of the isomerisation between **1a** and **1b**. Changes of **a** weights of singlet coupling and poralisation, and **b** ratio of polarisation/singlet coupling

Table 4 The relative energies (kcal/mol), bond lengths of bridge bond or diagonal bond (Å) and weights of the two electronic states by the CiLC analysis at the CASSCF(2,2)/6-31G(d) level

	Relative energy (kcal/mol)	Bond length (Å)	Singlet coupling	Polarisation
1a	0	2.952	0.794	0.206
1b	12.5	2.419	0.647	0.353
1c	12.6	3.018	0.809	0.191
1TS1	13.7	2.527	0.657	0.343
2a	0	3.070	0.781	0.219
2b				
2c	11.0	3.119	0.785	0.215
2TS1				
3a	0	3.040	0.800	0.200
3b	16.6	2.408	0.647	0.353
3c	11.4	3.130	0.813	0.187
3TS1	19.0	2.541	0.658	0.342
4a	0	3.150	0.782	0.218
4b				
4c	10.1	3.215	0.783	0.217
4TS1				
1a_Me	0	3.003	0.800	0.200
1b_Me	6.5	2.448	0.644	0.356
1c_Me	12.6	3.152	0.851	0.149
1TS1_Me	8.7	2.600	0.664	0.336
2^3a[a]	–	3.070	0.803	0.197
3^2a[a]	–	3.040	0.779	0.221

[a] **2^3a** is **2a** with the bridge bond length of **3a** while **3^2a** is **3a** with that of **2a**

the bridgehead Si atom larger than the inward part by mixing of the 3s orbital to the 3p orbital. Namely, the overlap of the orbital lobes between the Si atoms at the bridgeheads becomes small so the bridge bond is elongated and weakened. This corresponds to that the singlet coupling (di-radical) character increases considerably in **1a**. However, we have to remind the larger expanse of valence orbitals of Si atoms compared to those of C atoms. Therefore, the overlap of the orbitals may not be zero and some covalent bond character is expected to still remain in **1a**.

Next, the calculations of the CiLC analysis have been carried out for the bridge bond of the trans-bent isomer (**c**) as well as the two bicyclic isomers (**a** and **b**) and TS1 for various bicyclo[1.1.0]tetrasilane analogues. Table 4 summarises the results while the weight of the singlet coupling versus the bond distance is plotted in Fig. 6. For all compounds investigated here, trans-bent isomer (**c**) has the longest diagonal bond. Therefore, it is not surprising that the singlet coupling (di-radical in other word) character increases in the order, short-bond isomer < TS1 < long-bond isomer < trans-bent isomer. Furthermore, the singlet coupling character of the Ge compounds is found to be smaller than the Si analogues at the same bond length as shown in Fig. 6. This may be explained from that the larger overlap of the valence orbitals is expected in the Ge compounds compared with the case of the Si analogues.

Finally, we have tried to assess the π bond character in the *t*-Bu analogues (Si_4(*t*-Bu)$_6$) since Yoshimura and Kyushin called the bridge bond as an innovative 'π single bond' in their compounds, hexa-*t*-butyl-2,4-disilabicyclo[1.1.0]tetragermane (*t*-butyl substituted $Si_2Ge_2H_6$-II) [14]. For this purpose, the CiLC analysis has been carried out for the bridge bond of the long-bond (cis-bent in the *t*-Bu analogue), short-bond (folded) and trans-bent (planar) isomers of Si_4H_6 obtained by the constrained geometry optimisation in which the bridge bond length and the angle (r and θ in Scheme 3) are fixed as those of Si_4(*t*-Bu)$_6$. Then, as shown in Table 5, the results are compared with those for the π bond of ethene, disilene ($H_2Si{=}SiH_2$ with the C_{2h} symmetry) and cyclotetrasilene where the double bond length is same as that of the *t*-Bu analogue. From the table, it can be seen that the bridge bond in the long- and

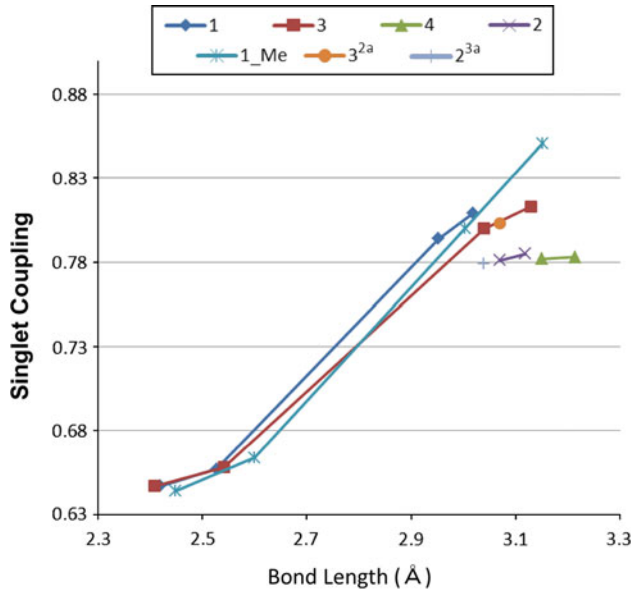


Fig. 6 The weight of singlet coupling versus bond length of the compounds in Table 4 by the CiLC analysis. The each line of **n(1-4)** and **1_Me** involves the data of the corresponding three isomers (**a**, **b** and **c**) and one TS (**TS1**)

Table 5 Selected structural parameters and relative weights of the two electronic states for ethene, disilene, and isomeric bicyclotetrasilanes, Si_4H_6 (**1a′**-**1e′**)[a] at the B3LYP/6-31G(d) level

	Bond length (Å)	θ (degress)[b]	Singlet coupling[c]	Polarisation[c]
Ethene	1.331	–	0.709	0.291
Disilene	2.179	–	0.806	0.194
1a′[a]	2.625	157.3	0.747	0.253
1b′[a]	2.531	159.6	0.703	0.297
1c′[a]	2.802	174.7 and 177.2	0.853	0.147
1e′[a]	2.172	–	0.737	0.263

[a] **1a′**-**1e′** are Si_4H_6 but with the same skeletal structural parameters (bond length and angle θ) as those of the $Sit_4(t\text{-Bu})_6$ (**1a_tBu**—**1e_tBu**). See Table 3

[b] <215 and <126

[c] Calculated using CiLC method at the CASSCF(2,2)/6-31G(d) level

short-bond isomers (especially for the latter) has the similar extent of covalent bond character to that of the π bond of ethene in spite of the large difference of the bond distance probably because of the larger overlap of the valence orbitals on the Si atoms. Also, the Si–Si π bond in cyclotetrasilene seems to have the similar extent of the covalent bond character to that of the long- or short-bond isomers. On the other hand, the covalent bond character of the diagonal bond of the trans-bent (planar) isomer is much smaller than that of bicyclic isomers and it is similar to that of the Si–Si π bond in disilene. As a result, from the similarity to the π bond of ethene or disilene for the covalent bond character, the name of 'π single bond' may be reasonable to describe the bridge or diagonal bond of these bicyclic compounds and the trans-bent (planar) isomer though the trans-bent (planar) isomer seems to have a significant singlet bi-radical character as indicated by the large weights of singlet coupling.

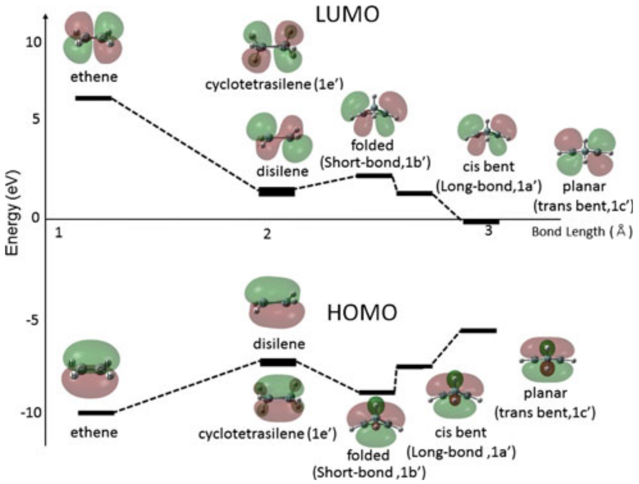


Fig. 7 The pictures and energy levels of the HOMO and LUMO of the compounds in Table 5. For Si_4H_6 (**1a′**-**1c′**), two kinds of labels are given; the upper is that for **1a_tBu—1c_tBu** while the lower in the parenthesis is that for **1a**-**1c**

In Fig. 7 shown are the energy levels and orbital pictures of the HOMO and LUMO of the compounds in Table 5. The frontier orbitals of the four isomers of $Si_4(t\text{-Bu})_6$ (Si_4H_6) resemble those of ethene and disilene very much though considerable extent of the σ bond character is seen in the orbitals of the long-bond (cis-bent) and short-bond (folded) isomers especially in the latter. However, energy levels between the bicylic compounds and the trans-bent (planar) isomer, and the compounds with a π bond (ethene, disilene and cyclotetrasilene), are intrinsically different as shown in Fig. 7. The former group has a strong correlation between the HOMO and LUMO levels and the bond distance. The Si=Si doubly bonded compounds; disilene and cyclotetrasilene, in the latter group have very similar energy levels of the HOMO and LUMO. Furthermore, the HOMO and LUMO levels of the long-bond (cis-bent) isomer considerably resemble to those of disilene and cyclotetrasilene, suggesting that the long-bond (cis-bent) isomer is expected to behave as an electron-donor and electron-acceptor by similar extent as disilene and cyclotetrasilene.

4 Concluding remarks

In the present study, the detailed reaction mechanisms of the unimolecular isomerisation between the various silicon, germanium and the Si/Ge-mixed analogues of bicyclo[1.1.0]butane and the corresponding cyclobutene analogues have been explored systematically.

It was found that the substituent on the molecular skeleton plays a very important role for the reaction mechanism. The silyl group makes substituent migration mechanism advantageous while the bulky t-butyl prefers skeletal rearrangement mechanism as expected.

Furthermore, the character of the bridge or diagonal bond of the bicyclic and trans-bent isomers of these compounds has been investigated by the CiLC analysis. The bridge bond of the long (cis-bent)- and short-bond isomers (folded) in the *t*-butyl substituted bicyclo[1.1.0]tetrasilane has considerable covalent bond character and the extent seems to be similar to that of the π bond in ethene. On the other hand, the covalent bond character of the diagonal bond in the trans-bent (planar) isomer is much less than that in the other isomers but it seems to have the similar extent to that of the π bond in disilene. So, in this sense, the name of 'π single bond' may be applicable to describe the bridge bond of this compound.

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