

Communication

## Re-examination of the photochemical reaction of octaisopropylcyclotetragermane

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### Abstract

The photochemistry of octaisopropylcyclotetragermane was studied by laser flash photolysis and trapping experiments. Upon irradiation of the cyclotetragermane, the main reaction was a ring opening to form octaisopropyltetragermane-1,4-diyl biradical ( $\lambda_{\max} = 310$  and 550 nm), but generations of diisopropylgermylene and tetraisopropyl digermene are negligible.

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### 1. Introduction

The photochemistry of cyclic oligosilanes has been studied extensively because these compounds are important sources for reactive intermediates such as silyl radicals, silylenes, and disilenes [1–7]. However, there are few reports on the photochemistry of the corresponding cyclic oligogermenes. In 1992, Mochida and Tokura proposed three pathways for the photochemical reaction of octaisopropylcyclotetragermane (**1**) (Scheme 1): a ring contraction to give diisopropylgermylene (**2**), a ring opening to form octaisopropyltetragermane-1,4-diyl biradical (**3**), and formation of tetraisopropyl digermene (**4**) [8]. Laser flash photolysis revealed an anomalous transient absorption peak at a  $\lambda_{\max}$  value of 560 nm with a lifetime of 56 ns. The peak was tentatively assigned to germylene **2** [8]. However, the absorption peaks of dialkylgermylenes are generally reported to fall in the 420–490 nm range, although a wide scatter of  $\lambda_{\max}$  values has been reported [9–16]. Thus,

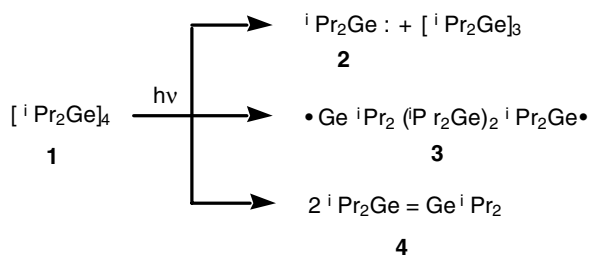
the assignment of the photochemical intermediate at 560 nm is still an open question.

To determine the reaction intermediates and primary photochemical process of **1**, we recently carried out laser flash photolysis and trapping experiments in the presence of various quenchers. In this paper, we report that ring opening to form octaisopropyltetragermane-1,4-diyl biradical **3** is the main reaction upon irradiation of **1** and that germylene **2** and digermene **4** are generated in minor or negligible quantities.

### 2. Results and discussion

Laser flash photolysis of **1** in deoxygenated cyclohexane was performed at 295 K in an apparatus that was essentially the same as the apparatus described elsewhere [17]. Using the fourth harmonic (266 nm) of a Nd:YAG laser as the exciting light source, we measured the time profiles of the transient absorption,  $A(t)$ , in the wavelength range of 300–700 nm. From the observed  $A(t)$  curves, transient absorption spectra at 10, 30, 50, and 100 ns after laser excitation were obtained and are shown in Fig. 1. Each

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Scheme 1.

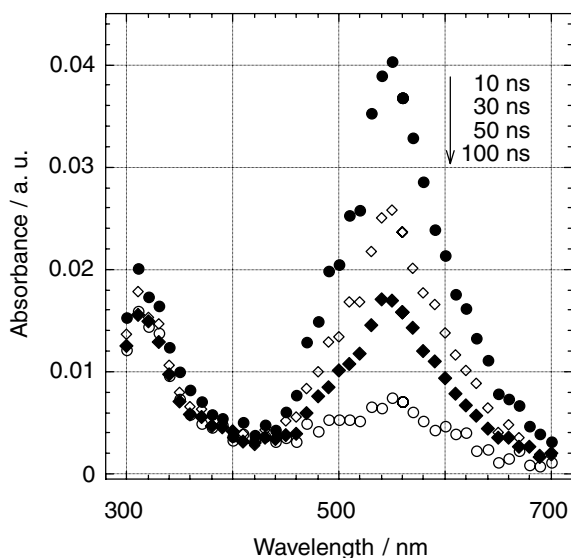
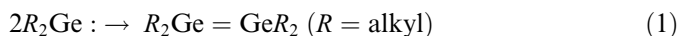


Fig. 1. Transient absorption spectra observed at 295 K at delay times of 10 ns (●), 30 ns (◇), 50 ns (◆), and 100 ns (○) after laser excitation of deoxygenated cyclohexane solution containing octaisopropylcyclotetragermane ( $1.7 \times 10^{-3} \text{ mol dm}^{-3}$ ).

spectrum has two transient absorption peaks, at 300–320 and 540–560 nm. The  $A(t)$  curve at 540 nm rapidly decayed with first-order kinetics as shown in Fig. 2. Its lifetime,  $\tau$ , was observed to be  $50 \pm 5$  ns. On the other hand, the  $A(t)$  curve at 310 nm has a fast decay component and a nearly constant component as shown in Fig. 3.

As mentioned previously, the peak at 540–560 nm has been tentatively assigned to diisopropylgermylene **2** [8], in spite of the fact that dialkylgermylenes are reported to absorb in the 420–490 nm range [9–16]. In addition, the lifetimes of dialkylgermylenes in inert solvents such as cyclohexane are usually as long as several microseconds, and the decay of dialkylgermylenes show second-order kinetics because dialkylgermylenes dimerize to form tetraalkyldigermenes [11–15].



In the present study, however, the transient absorption at 540 nm decayed rapidly with first-order kinetics. Moreover, in the presence of 2,3-dimethylbuta-1,3-diene ( $0.7 \text{ mol dm}^{-3}$ ), a well-known trapping agent of germylenes, no change in the  $A(t)$  curve was observed ( $\tau = 50 \pm 5$  ns). These results indicate that the transient absorption observed at 540–560 nm cannot be assigned to germylene **2**.

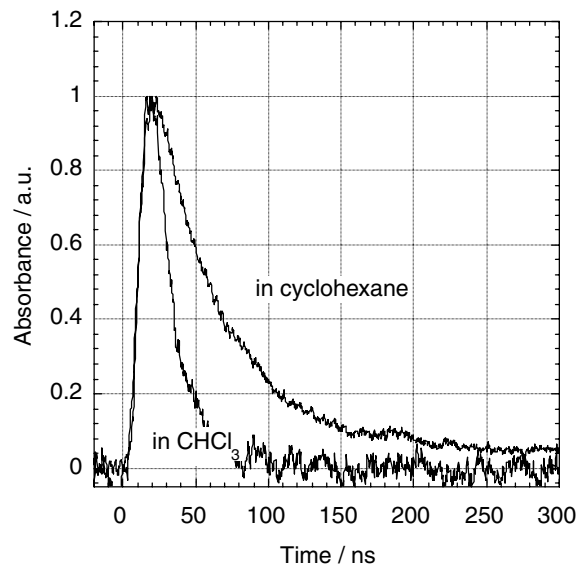


Fig. 2. The  $A(t)$  curves observed at 540 nm in cyclohexane and  $\text{CHCl}_3$  for deoxygenated solutions containing octaisopropylcyclotetragermane ( $1.7 \times 10^{-3} \text{ mol dm}^{-3}$ ).

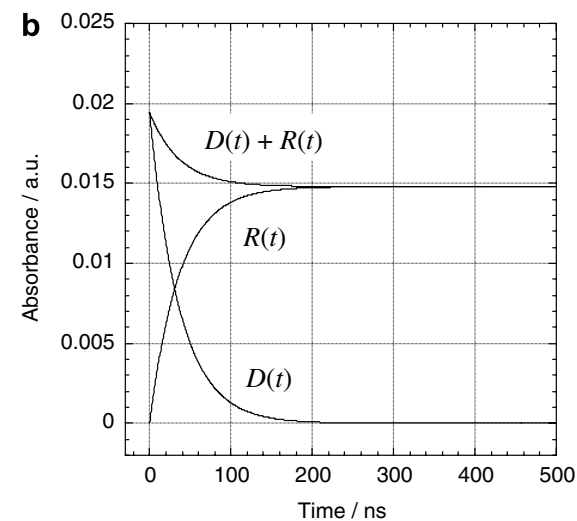
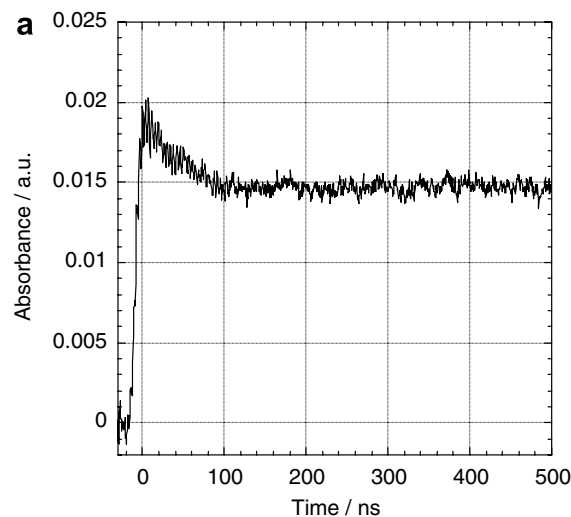


Fig. 3. (a)  $A(t)$  curve observed at 310 nm. (b)  $D(t) + R(t)$ ,  $D(t)$ , and  $R(t)$  curves calculated from with  $I_f = 0.0192$ ,  $I_c = 0.0148$ , and  $k = 2.05 \times 10^7 \text{ s}^{-1}$ .

Two other possible assignments for the absorption, digermene **4** and the excited state of **1** (e.g. triplet–triplet absorption), can be easily excluded. The transient absorption peaks of tetraalkyldigermenes are reported at 380–400 nm [11–15]. As shown in Fig. 1, however, no transient absorption peak was observed in this range. Therefore, digermene **4** was not formed by the primary photochemical process that occurred in the present reaction. Moreover, upon irradiation of **1** in a 3-methylpentane (3 MP) matrix at 77 K, a similar UV–Vis spectrum with an absorption peak at 550 nm was observed. Fig. 4 shows the spectrum observed at 10 min after irradiation of **1** in 3 MP at 77 K [18]. Because excited states do not usually have very long lifetimes, the peak cannot be assigned to an excited state and must instead correspond to a reaction intermediate.

To assign this transient absorption, we carried out laser flash photolysis in the presence of  $\text{CHCl}_3$  and  $\text{CCl}_4$ , which are well-known trapping agents of trialkylgermyl radicals. The typical  $A(t)$  curve observed at 540 nm in deoxygenated  $\text{CHCl}_3$  is shown in Fig. 2, along with the curve obtained in cyclohexane. The  $A(t)$  curve in  $\text{CHCl}_3$  decayed much faster than the curve in cyclohexane. The lifetimes observed in various solvents are listed in Table 1. Acceleration of the decay in the presence of halogenated hydrocarbons is ascribable to the chlorine abstraction by germyl radicals:

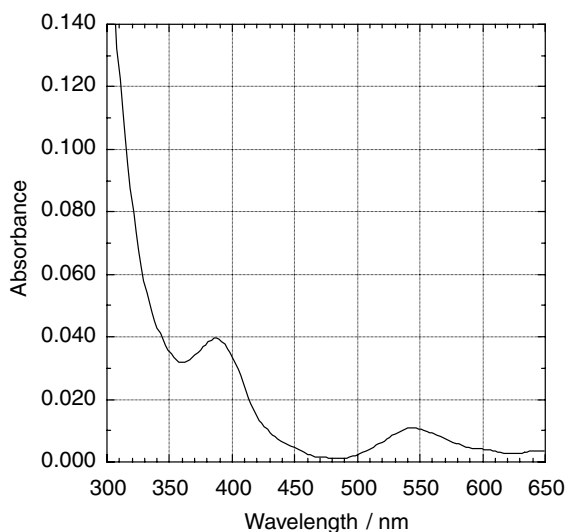
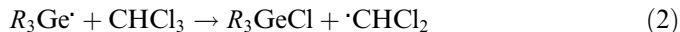


Fig. 4. UV–Vis spectrum observed at 10 min after irradiation of **1** ( $1.6 \times 10^{-3} \text{ mol dm}^{-3}$ ) in a 3-methylpentane matrix at 77 K.

Table 1  
Lifetimes of the transient absorption observed at 540 nm in various solvents

Solvent	Lifetime (ns)
Cyclohexane	50
Cyclohexane in the presence of DMB <sup>a</sup> ( $0.7 \text{ mol dm}^{-3}$ )	50
Cyclohexane in the presence of $\text{CHCl}_3$ ( $0.3 \text{ mol dm}^{-3}$ )	37
$\text{CHCl}_3$	15
$\text{CCl}_4$	19

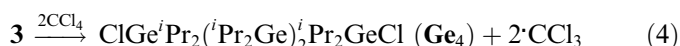
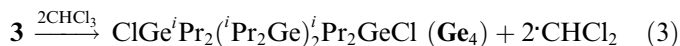
<sup>a</sup> 2,3-Dimethylbuta-1,3-diene.



Chlorine abstraction is a well-known reaction of silyl and germyl radicals with halogenated hydrocarbons. From these results, we concluded that the transient absorption at 540–560 nm was due to a radical-like reaction intermediate.

In addition to laser flash photolysis, we analyzed the products of the photochemical reactions of **1**. In the presence of various trapping agents, cyclohexane solutions containing **1** were irradiated with a 500-W Xe lamp. When EtOH and 2,3-dimethylbuta-1,3-diene were used as trapping agents, products resulting from the trapping of germylene **2** were observed, as has been reported previously [8]. However, it is noteworthy that germylene trapping products, for example, 1,1-diisopropyl-3,4-dimethyl-1-germacyclopent-3-ene, were not observed in the early stage of the photochemical reaction (that is, at irradiation time < 30 min). This result indicates that germylene **2** was not formed by the primary photochemical process.

Irradiation of **1** in  $\text{CHCl}_3$  led to the formation of diisopropylchlorogermene ( $\text{Ge}_1$ ) [19], tetraisopropylchlorodigermene ( $\text{Ge}_2$ ) [20], hexaisopropylchlorotrigermene ( $\text{Ge}_3$ ) [20], octaisopropylchlorotetragermene ( $\text{Ge}_4$ ) [21], and tetrachloroethane (TCE). The same dichlorogermenes and hexachloroethane (HCE) were observed when  $\text{CCl}_4$  was used as a trapping agent. Here,  $\text{Ge}_4$  can be regarded as a product of the trapping of octaisopropyltetragermene-1,4-diyl biradical **3**, and TCE and HCE can be regarded as products of coupling of dichloromethyl and trichloromethyl radicals, respectively:



The generation of  $\text{Ge}_4$  is consistent with the results of the quenching experiments by laser flash photolysis, in which the  $A(t)$  curve observed at 540 nm was effectively quenched by  $\text{CHCl}_3$  and  $\text{CCl}_4$ . Thus, the transient absorption can be assigned to octaisopropyltetragermene-1,4-diyl biradical **3**.

The yields of  $\text{Ge}_1$ – $\text{Ge}_4$  showed a marked time dependence. We carried out detailed quantitative analyses of the yields of  $\text{Ge}_1$ ,  $\text{Ge}_2$ ,  $\text{Ge}_3$ ,  $\text{Ge}_4$ , and TCE together with the consumption of **1**. The time dependence of the yields of products and TCE can be summarized as follows: (1)  $\text{Ge}_4$  formed quickly in the early stage of the reaction and then decreased; (2)  $\text{Ge}_3$  formed slowly and then decreased; (3)  $\text{Ge}_2$  also formed slowly but did not decrease during the period from 60 to 180 min [22]; (4)  $\text{Ge}_1$  was not observed initially, but the yield continually increased throughout the reaction period; and (5) formation of TCE started early in the reaction and continued after when **1** was almost completely consumed. Moreover, no transient absorption peak was observed at 380–400 nm, indicating that digermene **4** was not formed directly from **1**. Thus  $\text{Ge}_2$  cannot be regarded as a trapped product of digermene **4**. From these

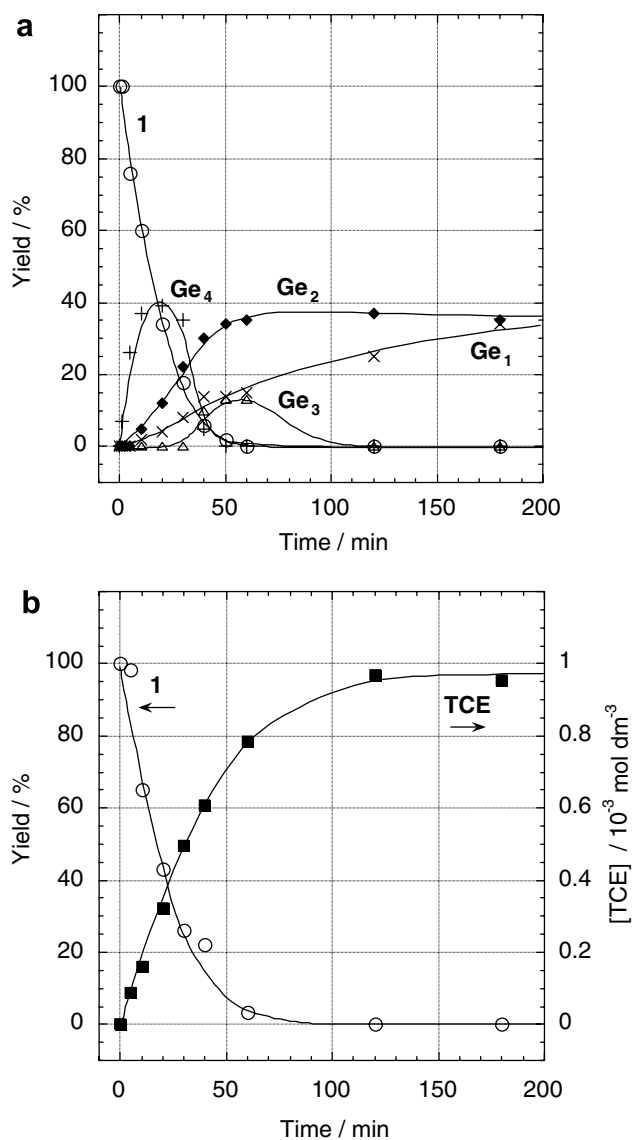
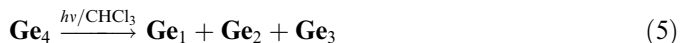


Fig. 5. (a) The time dependence of the consumption of octaisopropylcyclotetragermane ( $\circ$ , **1**) and the yields of the following dichlorooligogermynes: diisopropylchlorogermane ( $\times$ ,  $\text{Ge}_1$ ), tetraisopropylchlorogermane ( $\blacklozenge$ ,  $\text{Ge}_2$ ), hexaisopropylchlorotrigermane ( $\triangle$ ,  $\text{Ge}_3$ ), and octaisopropylchlorotetragermane ( $+$ ,  $\text{Ge}_4$ ), during the photolysis of **1** in  $\text{CHCl}_3$ . (b) The time dependence of the consumption of **1** ( $\circ$ ) and the yield of tetrachloroethane ( $\blacksquare$ , TCE) during the photolysis of **1** in  $\text{CHCl}_3$ .

results, we concluded that  $\text{Ge}_4$  was the primary photochemical product and that it decomposed to form  $\text{Ge}_3$ ,  $\text{Ge}_2$ , and  $\text{Ge}_1$ .

To study these secondary reactions of  $\text{Ge}_4$ , we carried out photochemical reaction of authentic  $\text{Ge}_4$  in  $\text{CHCl}_3$  under conditions similar to those used for the photolysis of **1**. Dichlorogermynes  $\text{Ge}_1$ – $\text{Ge}_3$  and TCE were generated in this reaction, and a clear time dependence of the yields was observed:



These results show that  $\text{Ge}_3$ ,  $\text{Ge}_2$ , and  $\text{Ge}_1$  are photochemical products from the secondary reactions of  $\text{Ge}_4$ .

Finally, let us consider the transient absorption spectrum of **3**. Because alkyl-substituted silyl, germyl, and stanlyl radicals usually have two absorption bands and their shorter wavelength bands appear at 300–320 nm [23–25], we measured the  $A(t)$  curves in the shorter wavelength range in detail. As seen in Fig. 3a, the  $A(t)$  curve observed at 310 nm has a fast decay component and a nearly constant component. The constant component,  $R(t)$ , may be due to the product generated from the fast decay component,  $D(t)$ . Because the rate constant,  $k$ , of the fast decay component is the same as the rate constant of the generation of the product, the observed  $A(t)$  curve was analyzed by the nonlinear least-squares method in terms of the following equations:

$$A(t) = D(t) + R(t) \quad (6)$$

$$D(t) = I_f \exp(-kt) \quad (7)$$

$$R(t) = I_c(1 - \exp(-kt)), \quad (8)$$

where  $I_f$  and  $I_c$  are the pre-exponential factors of the fast decay component and the nearly constant component, respectively. When the  $A(t)$  curve at 310 nm was analyzed in terms of Eqs. (6)–(8),  $I_f$ ,  $I_c$ , and  $k$  were determined to be 0.0192, 0.0148, and  $2.05 \times 10^7 \text{ s}^{-1}$ , respectively. Using these values, we calculated  $D(t) + R(t)$ ,  $D(t)$ , and  $R(t)$  and plotted them in Fig. 3b. As clearly seen in the figure, the  $A(t)$  curve at 310 nm can be reproduced from the calculated  $D(t)$  and  $R(t)$  curves. The lifetime ( $\tau = 1/k$ ) of the fast decay component was calculated to be  $49 \pm 10 \text{ ns}$ , which is similar to the lifetime of the absorption at 540–560 nm. These results indicate that the photochemical intermediate in the present reaction has two absorption bands, at 300–320 and 540–560 nm, and that the intermediate can be assigned as a germyl radical such as **3**.

However, the absorption peak in the longer wavelength range (540–560 nm) and the spectral pattern are somewhat different from those previously reported for trialkylgermyl radicals. These differences may be due to the through-bond interaction of two radicals in the 1,4-biradical. To predict the electronic spectrum of **3**, we carried out electronic structure calculations for **3** based on hybrid and non-hybrid density-functional calculations. Firstly, we have performed geometry optimization for **3** both in triplet and singlet states at the B3LYP/6-31G(d) level of theory. Fig. 6 shows optimized structures of **3** both in *cis*- and *trans*-forms in the triplet state. It was found that the *cis*-form is slightly stable than the *trans*-form by 2.6 kcal/mol at this level. In both cases, it is interesting to note that the Ge–Ge–Ge structures are significantly deformed from a planar structure. This may be due to the combination of strong repulsion between two unpaired electrons localized in the terminal Ge atoms and limited Ge–Ge–Ge angles. Notice that the Ge–Ge–Ge angles are in the range of about 90–110° and are smaller than the carbon analog. We have also performed geometry optimization of **3** in the singlet biradical state using the broken-symmetry prescription. Although we have succeeded in optimizing

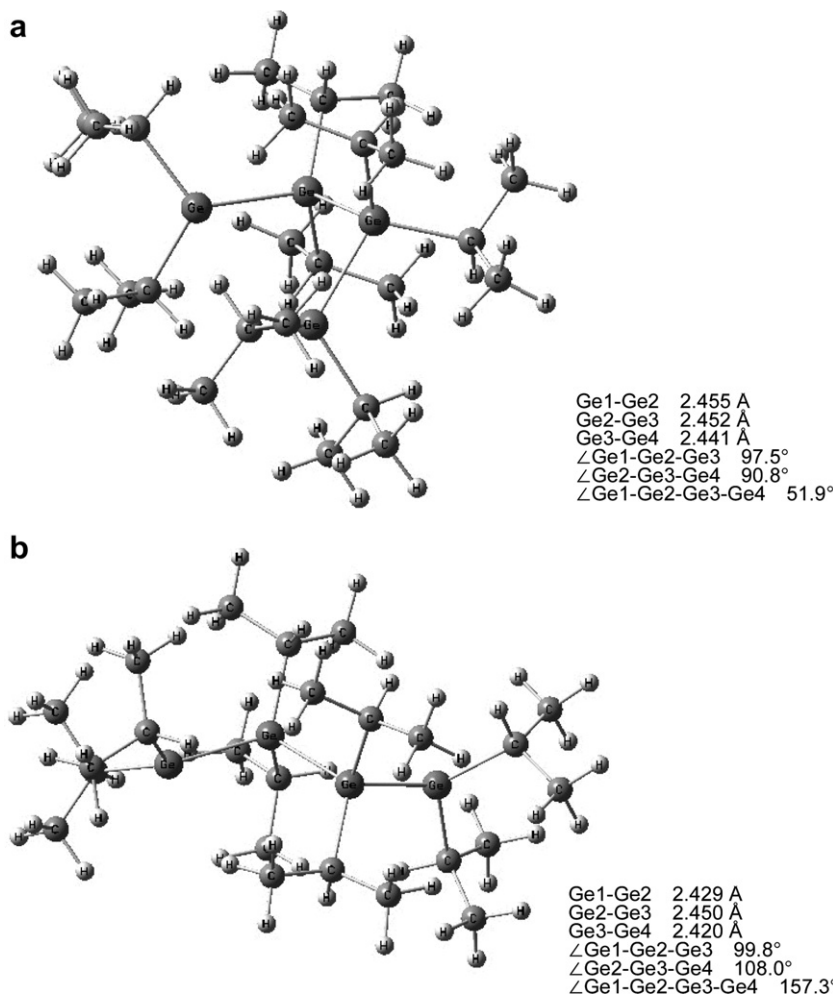


Fig. 6. The optimized structures of triplet biradical **3** (a) in *cis*-form and (b) *trans*-form obtained at the B3LYP/6-31G(d) level of theory.

the geometry in the *trans*-form, we have failed to obtain the optimized structure in the *cis*-form. It was found that the optimization of the *cis*-form always leads to the four-membered cyclic structure (**1**), which is the most stable conformer in this molecular system. This is not surprising since the electronic structure obtained by the broken-symmetry approach generally contains both triplet and singlet characters. However, it should be emphasized that the singlet optimized structure of **3** in the *trans*-form is essentially the same as the triplet optimized structure of **3**; the geometrical difference between them was found to be extremely small. This suggests that the biradical molecules in singlet and triplet states have a very similar structure. Presumably, the multi-configurational method such as a CASSCF approach would give a reliable geometry; however, such a method cannot be applied to the present complicated system.

Since the *cis*-form is stable than the *trans*-form, we have performed single-point time-dependent DFT (TD-DFT) calculations using the optimized geometry of the triplet biradical in the *cis*-form to obtain lowest electronic transitions [26]. First, we have examined the basis set dependence

for the B3LYP functionals with the 6-31G(d), 6-31G(d, p), 6-31+G(d,p), and 6-31++G(d,p) basis sets. It is found that the change of the basis set does not largely affect the transition energies. Then, we have carried out TD-DFT calculations with the PBE and BLYP functionals. Table 2 summarizes the computed results. The calculated values show that the triplet biradical **3** has the transient absorption bands at 460–560 nm. Since the singlet biradical **3** should be stabilized more than the triplet one by the through-bond interaction, the transient absorption bands of the singlet biradical **3** may appear at slightly higher wavelength. To clarify the spin multiplicity of the biradical, we are

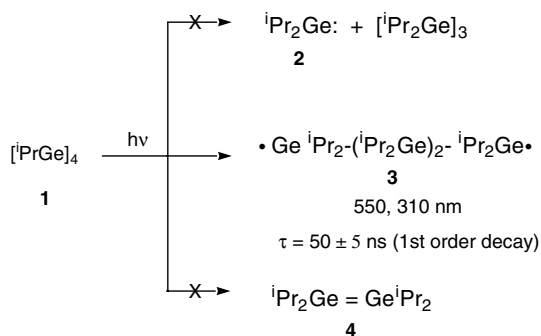
Table 2

The excitation wavelength (oscillator strength) of the triplet biradical **3** in the *cis*-form obtained from single-point time-dependent DFT calculations<sup>a</sup>

PBE	BLYP
539 nm (0.0002)	564 nm (0.0002)
474 nm (0.0029)	491 nm (0.0023)
456 nm (0.0016)	473 nm (0.0015)

<sup>a</sup> Calculated with 6-31G(d) basis set.





Scheme 2.

currently carrying out low-temperature (20 K) and time-resolved ESR measurements.

### 3. Conclusions

The results observed in the present study are best rationalized in terms of the reactions shown in Scheme 2. Upon irradiation, **1** undergoes a ring opening to form tetramer-1,4-diyl biradical **3** as the main reaction. The transient absorption at 550 nm can be assigned to biradical **3**, which has another transient absorption peak at 310 nm. TD-DFT calculations suggested triplet or singlet biradical **3** formation.

### 4. Experimental

Laser flash photolysis was performed on deoxygenated cyclohexane containing **1** ( $1.7 \times 10^{-3}$  mol dm<sup>-3</sup>) at 295 K using the fourth harmonic (266 nm, 7 ns) of a Quanta-Ray DCR-11 Nd:YAG laser as an exciting light source. The cyclohexane solution was deoxygenated by bubbling argon through it. To avoid secondary reactions, the solution was pumped through a quartz flow cell (1 mL/min).

The steady-state irradiation was carried out with a 500-W Xe lamp (Ushio UXL-500D). A deoxygenated cyclohexane solution containing **1** ( $2.7 \times 10^{-3}$  mol dm<sup>-3</sup>) was irradiated, and the photoproducts were analyzed by GC (Shimadzu GC-17A), GC-MS (Shimadzu QP5000, JEOL JMS700AM), and NMR (Bruker AM 300).

### Acknowledgements

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### References

- [1] R. West, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), *Comprehensive Organometallic Chemistry*, vol. 2, Pergamon Press, Oxford, New York, Toronto, Sydney, Frankfurt, 1982 (Chapter 9.4).
- [2] H. Sakurai, *Synthesis and Application of Organopolysilanes*, CMC, Tokyo, 1989.
- [3] R. West, *J. Organomet. Chem.* 300 (1986) 327, and references cited therein.
- [4] M. Ishikawa, M. Kumada, *Adv. Organomet. Chem.* 19 (1981) 51, and references cited therein.
- [5] H. Sakurai, *Yuki Gosei Kagaku Kyokaiishi* 47 (1989) 1051, and references cited therein.
- [6] R.D. Miller, J. Michl, *Chem. Rev.* 89 (1989) 1359.
- [7] H. Shizuka, K. Murata, Y. Arai, K. Tonokura, H. Tanaka, H. Matsumoto, Y. Nagai, G. Gillette, R. West, *J. Chem. Soc., Faraday Trans. 1* (85) (1989) 2369, and references cited therein.
- [8] K. Mochida, S. Tokura, *Organometallics* 11 (1992) 2752.
- [9] W. Ando, T. Tsumuraya, A. Sekiguchi, *Chem. Lett.* 2 (1987) 317.
- [10] S. Tomoda, M. Shimoda, Y. Takeuchi, Y. Kajii, K. Obi, I. Tanaka, K. Honda, *J. Chem. Soc., Chem. Commun.* (1988) 910.
- [11] K. Mochida, I. Yoneda, M. Wakasa, *J. Organomet. Chem.* 399 (1990) 53.
- [12] K. Mochida, N. Kanno, R. Kato, M. Kotani, S. Yamauchi, M. Wakasa, H. Hayashi, *J. Organomet. Chem.* 415 (1991) 191.
- [13] K. Mochida, S. Tokura, *Bull. Chem. Soc. Jpn.* 65 (1992) 1642.
- [14] W.J. Leigh, C.R. Harrington, I. Vargas-Baca, *J. Am. Chem. Soc.* 126 (2004) 16105.
- [15] W.J. Leigh, F. Lollmahomed, C.R. Harrington, *Organometallics* 25 (2006) 2055.
- [16] S.E. Boganov, M.P. Egorov, V.I. Faustov, O.M. Nefedov, in: Z. Rappoport (Ed.), *The Chemistry of Organic Germanium, Tin, and Lead Compounds*, vol. 2, John Wiley and Sons, New York, 2002, p. 749.
- [17] K. Mochida, T. Kayamori, M. Wakasa, H. Hayashi, M.P. Egorov, *Organometallics* 19 (2000) 3379.
- [18] An absorption peak at 390 nm was also observed and assigned to tetraisopropylidigermene **4**. Since the results of laser flash photolysis show that digermene **4** is not formed by the primary photochemical process, it may be generated from the secondary reactions of **3**.
- [19] H.H. Anderson, *J. Am. Chem. Soc.* 75 (1953) 814.
- [20] 1,2-Dichloro-1,1,2,2-tetraisopropylidigermene (**Ge<sub>2</sub>**) and 1,2-dichloro-1,1,2,2,3,3-hexaiso-propyltrigermene (**Ge<sub>3</sub>**) were characterized by <sup>1</sup>H NMR and HRGC-MS.
- [21] 1,4-Dichloro-1,1,2,2,3,3,4,4-octaisopropyltetragermene (**Ge<sub>4</sub>**) was synthesized by a method similar to that used to prepare dichlorooctaisopropyltetrasilane; H. Suzuki, K. Tanaka, B. Yoshizoe, T. Yamamoto, N. Kenmotsu, S. Matuura, T. Akabane, H. Watanabe, M. Goto, *Organometallics* 17 (1998) 5091.
- [22] Upon irradiation of **1** in CHCl<sub>3</sub> for an additional 60 min, the yield of **Ge<sub>2</sub>** decreased somewhat. This yield reduction may be due to nonphotochemical secondary reactions of **Ge<sub>2</sub>**.
- [23] K. Mochida, M. Wakasa, Y. Sakaguchi, H. Hayashi, *Nippon Kagaku Kaishi* 7 (1987) 1171.
- [24] J.S. Scaiano, *J. Am. Chem. Soc.* 102 (1980) 5400.
- [25] C. Chatgililoglu, K.U. Ingold, J. Luszyk, A.S. Narzran, J.S. Scaiano, *Organometallics* 2 (1983) 1332.
- [26] Although higher electronic transitions for the band at 310 nm can be calculated by TD-DFT, accuracy of the results is generally disputable.