

# Articles

## Theoretical Study of Germabutadienic Internal Rotations and $\pi$ -Conjugation

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Received April 4, 2008

The  $\pi$ -conjugational strength and the internal rotation barriers of germabutadienes are investigated at the level of B3LYP/6-311+G(d,p). The calculated potential energy surfaces (PES) for internal rotations of nine germabutadienes, which include mono-, di-, tri-, and tetragermabutadienes, are found to be similar to those of silabutadienes. For 1-germabutadiene, 2-germabutadiene, 1,3-digermabutadiene, 2,3-digermabutadiene, and 1,4-digermabutadiene, whose external double bonds belong to the Ge=C and C=C bond types, the *s-trans* (or twisted *s-trans*) conformations are the global minima for their internal rotational PESs. 1,2-Digermabutadiene, 1,2,3-trigermabutadiene, 1,2,4-trigermabutadiene, and tetragermabutadiene, which possess one and two *trans*-bent Ge=Ge double bonds, have two different *s-gauche* minima. The  $C_2$  *s-gauche* conformation ( $D(\text{GeGeGeGe}) = 74.4^\circ$ ) of tetragermabutadiene, which corresponds to the reported X-ray crystal structure, is found to be of comparable stability (higher by 0.63 kcal/mol) to  $C_i$  *s-trans*. The NBO second order perturbation analysis provides a direct insight into the  $\pi$ -conjugation strength for germabutadiene global minima. The  $\pi$ -conjugation strengths in mono-, di-, and trigermabutadienes groups follow the trend, 1-germabutadiene > 2-germabutadiene; 1,4-digermabutadiene > 1,3-digermabutadiene > 1,2-digermabutadiene > 2,3-digermabutadiene; and 1,2,4-trigermabutadiene > 1,2,3-trigermabutadiene. We found good linear correlation between the internal rotational barriers and the  $\pi$ -conjugation strengths of the studied germabutadienes. We conclude that the  $\pi$ -conjugations are the main factor dictating the internal rotational barrier, which is also supported by the calculated resonance energies using the stepwise hydrogenation approach.

### Introduction

After the first stable tetrasilabutadiene **1** was synthesized by Weidenbruch in 1997,<sup>1</sup> organic chemists continued to search for a heavier analogue compound with conjugated Ge=Ge double bonds. In 2000, Weidenbruch succeeded in synthesizing tetragermabutadiene **2** by following a similar approach.<sup>2</sup> X-ray crystallography showed that compound **2** adopted a *s-gauche* conformation, which had an approximate  $C_2$  symmetry, with the Ge<sub>4</sub> framework of a dihedral angle of 22.5°. Both external Ge=Ge bonds, whose lengths were 2.357 and 2.344 Å, were much longer than in digermene **3** (2.268 Å).<sup>3</sup> In addition, both Ge=Ge double bonds displayed a considerable *trans* bending away from the respective Ge=Ge vectors.<sup>2</sup>

Most of the theoretical research on germabutadienes came from the Trinquier group.<sup>4–6</sup> They had mainly studied the  $\pi$ -conjugation strength, the internal rotation, and electrocyclic ring closures of the symmetrical germabutadienes, 2,3-digermabutadiene, 1,4-digermabutadiene, and tetragermabutadiene, through ab initio calculations. Trinquier et al.<sup>4,5</sup> found that both 2,3-digermabutadiene and 1,4-digermabutadiene had a preferred planar *s-trans* conformation (the global minimum,  $C_{2h}$ ) on the potential energy surface (PES) of the internal rotation, 1,4-digermabutadiene had two equivalent *s-gauche* local minima ( $C_2$ ), and 2,3-digermabutadiene had only a *s-cis* local minima ( $C_{2v}$ ) because the longer Ge–Ge single bond of 2,3-digermabutadiene removed the steric hindrance. At the level of MP4/DZP//SCF/DZP, the bond separation energies calculated for the isodesmic reactions showed that the  $\pi$ -conjugation strengths in 2,3-digermabutadiene and 1,4-digermabutadiene were about half and one-and-a-half that in butadiene, respectively.<sup>4,5</sup> In 1999, Trinquier et al. examined the  $\pi$ -conjugation strength and the internal rotation PES of two kinds of tetragermabutadiene isomers whose GeH<sub>2</sub>=GeH- external double bonds always maintained a *trans*-bent arrangement.<sup>6</sup> The first kind of tet-

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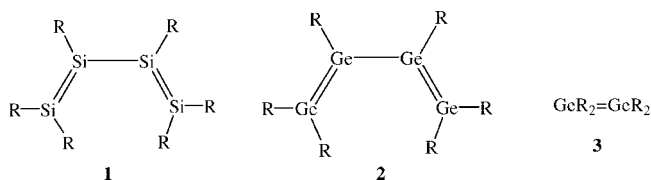
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Scheme 1<sup>a</sup>

<sup>a</sup> R = 2,4,6-*i*Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub> (tip).

ragermabutadiene with  $C_1$  rotamers in the course of internal rotation, denoted as the low-symmetric tetragermabutadiene, preferred the  $C_i$  *s-trans* conformation (see Schemes 1 and 2a), and its internal rotational PES was similar to those of 2,3-digermabutadiene and 1,4-digermabutadiene. The second kind of tetragermabutadiene kept the  $C_2$  symmetry in the course of internal rotation (denoted as the high-symmetric tetragermabutadiene) and had a  $C_2$  *s-gauche* global minimum (see Scheme 2b). The  $C_i$  *s-trans* conformation of the low-symmetric tetragermabutadiene, that is, the most stable linear conformer of tetragermabutadiene, is lower in potential energy than the  $C_2$  *s-gauche* minimum of the high-symmetric tetragermabutadiene by 0.5 kcal/mol. In 2005, Weidenbruch et al.<sup>7</sup> explored the structures and relative energies of Ge<sub>4</sub>R<sub>6</sub> (R = H, Me, Ph, or 2,6-dimethylphenyl) isomers using the B3LYP method and evaluated the merits of various Pople basis sets (the new 6-31G(d), 6-31+G(d), and triple- $\zeta$  6-311+G(d,p) basis sets). They found a significant dependency of the structures of Ge<sub>4</sub>R<sub>6</sub> on the substituents R.<sup>7</sup> The review of theoretical and experimental studies on germabutadienes had been given by Apeloig and Karni.<sup>8</sup> To the best of our knowledge, no theoretical studies of monogermabutadienes, asymmetric digermabutadienes, and trigermabutadienes have been reported.

In this article, we provide a systematic study of molecular structures, internal rotation barriers, and  $\pi$ -conjugation effects for all germabutadienes containing 1 to 4 Ge atoms (1-germabutadiene **4**, 2-germabutadiene **5**, 1,3-digermabutadiene **6**, 2,3-digermabutadiene **7**, 1,4-digermabutadiene **8**, 1,2-digermabutadiene **9**, 1,2,3-trigermabutadiene **10**, 1,2,4-trigermabutadiene **11**, and tetragermabutadiene **12**; see Scheme 3). First, the PESs of internal rotations around the central single bonds are obtained, and the geometries and relative energetics of local minima and transition states along these PESs are subsequently determined for **4–12**. Second, the extents of  $\pi$ -conjugation effects of the global minima of nine germabutadienes (**4–12**) are directly estimated on the basis of the NBO second order perturbation analysis<sup>9</sup> and indirectly based on the stepwise hydrogenation approach.<sup>10</sup> In conclusion, we will discuss the correlation between the internal rotation barriers and the extent of  $\pi$ -conjugation of germabutadienes. All results are also compared with the recent finding on silabutadienes.<sup>11</sup>

## Results and Discussion

**Internal Rotation PESs, Rational Barriers, and Molecular Structures of Local Minima. Germabutadienes 4–8.** The atom numberings in germabutadienes **4–12** shown in Scheme 3 are used throughout this article. The B3LYP/6-311+G(d,p) internal rotation PESs for **4–8** are shown in Figure 1. The relative energies and zero-point-correction energies (denote as

ZPE) of the twisted *s-trans*, *s-gauche*, and *s-cis* minima and transition states (TSs) for **4–8** molecules to the respective *s-trans* conformers are given in Table 1. The relative ZPEs of the *s-trans* and twisted *s-trans* minima of monogermabutadiene and digermabutadiene groups are also given in Table 1. Because the structure of **4–8** at a  $M_1=M_2-M_3=M_4$  (M = Ge or C) dihedral angle of  $-\theta$  is the mirror of their rotamer at a dihedral angle of  $\theta$ , the PES for  $\theta = 180^\circ$  to  $-180^\circ$  is symmetrical at  $\theta = 0^\circ$  (see Figure 1). For **5–7**, there exist two stable conformers, *s-trans* and *s-cis* minima, and transition states along the first half of the PESs (from  $180^\circ$  to  $0^\circ$ ). The *s-trans* conformers of **5–7** are the global minima of the whole PESs and the parts of PESs close to the *s-cis* appear almost planar (see Figure 1). Although the B3LYP calculations show that there is a twisted *s-cis* minimum for **5** ( $\theta = 14.9^\circ$ ) slightly less stable by 0.01 kcal/mol than the *s-cis* conformer, their ZPEs confirm that the *s-cis* conformer (lower in potential energy than the twist *s-cis* rotamer by 0.08 kcal/mol) is indeed the local minimum (see Tables 1 and 2). For **4** and **8**, two stable conformers are the *s-trans* (or twisted *s-trans*) and *s-gauche* minima, and their *s-cis* rotamers are TSs (see Figure 1). Their *s-gauche* minima are located at the  $\theta$  values of  $29.6^\circ$  (**4**) and  $39.4^\circ$  (**8**). The present B3LYP/6-311+G(d,p) calculations show that the twisted *s-trans* rotamer of GeH<sub>2</sub>=CH-CH=GeH<sub>2</sub> **8** ( $\theta = 170.5^\circ$ ) is the global minimum of internal rotation PES, which is comparable (only slightly more stable by 0.22 kcal/mol) with the *s-trans* rotamer (see Figure 1). The end GeH<sub>2</sub> groups of *s-trans* and twisted *s-trans* rotamers for **8** at the level of B3LYP are slightly pyramidal (the sums of  $A(\text{H}_{12}\text{Ge}_1\text{C}_1)$ ,  $A(\text{H}_{13}\text{Ge}_1\text{C}_1)$ , and  $A(\text{H}_{12}\text{Ge}_1\text{H}_{13})$  bond angles are  $352.8^\circ$  and  $351.9^\circ$ , respectively; see Table 2). The further MP2/6-311+G(d,p) optimization have different results: the MP2 global minimum of internal rotation PES is the planar *s-trans* conformation ( $C_{2v}$ ), and the end GeH<sub>2</sub> groups of rotamers are always planar. The difference comes from the considerably flat PES of internal rotation of 1,4-digermabutadiene **8** and lower pyramiding energy, for example, the MP2 energy at planar *s-trans* conformation is slightly lower than at B3LYP twisted *trans* conformation ( $170.5^\circ$ ) by 0.86 kcal/mol. For the consistency of energies, the subsequent discussion in this article is still based on the B3LYP/6-311+G(d,p) results. The TSs for **4–8** are located at the  $\theta$  values of  $101.1^\circ$  (**4**),  $98.7^\circ$  (**5**),  $97.9^\circ$  (**6**),  $99.2^\circ$  (**7**), and  $99.4^\circ$  (**8**).

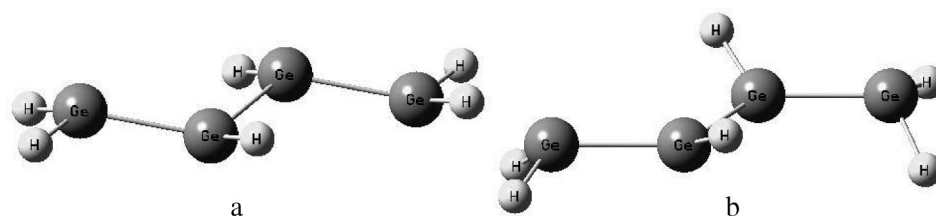
The ZPEs for **4–7** TSs relative to their *s-trans* minima, that is, the rotation barriers for the *s-trans*  $\rightarrow$  *s-cis* processes, are calculated to be 8.16, 3.50, 4.36, and 2.43 kcal/mol, respectively. The energies of the twisted *s-trans* minimum and TS of **8** relative to its *s-trans* minimum are  $-0.22$  and  $11.94$  kcal/mol, respectively. The internal rotation barrier for twisted *s-trans*  $\rightarrow$  *s-cis* processes of **8** is calculated to be 12.16 kcal/mol. The trend of internal rotation barriers for **4–8** is similar to those found for silabutadienes.<sup>11</sup> In general, **4** and **8** have higher rotation barriers than other germabutadienes. It is partially due to the fact that the Ge-Ge and Ge-C central single bonds in compounds **5–7** are relatively longer than the C-C bonds for **4** and **8** (see Table 2). We will discuss this in detail in the section  $\pi$ -Conjugation Stabilization Energies and Their Corresponding Internal Rotational Barriers.

The pertinent optimized geometric parameters for minima and TSs of germabutadienes **4–8** are given in Table 2. The external double bonds (CH<sub>2</sub>=CH-, GeH<sub>2</sub>=CH-, and CH<sub>2</sub>=GeH-) in germabutadienes **4–7** remain planar during the internal rotation. The Ge=C (ranging from 1.782 Å to 1.801 Å) and C=C bond lengths (1.336 Å and 1.347 Å) in the *s-trans* conformers of **4–7** are longer than those calculated for germene and ethene at the

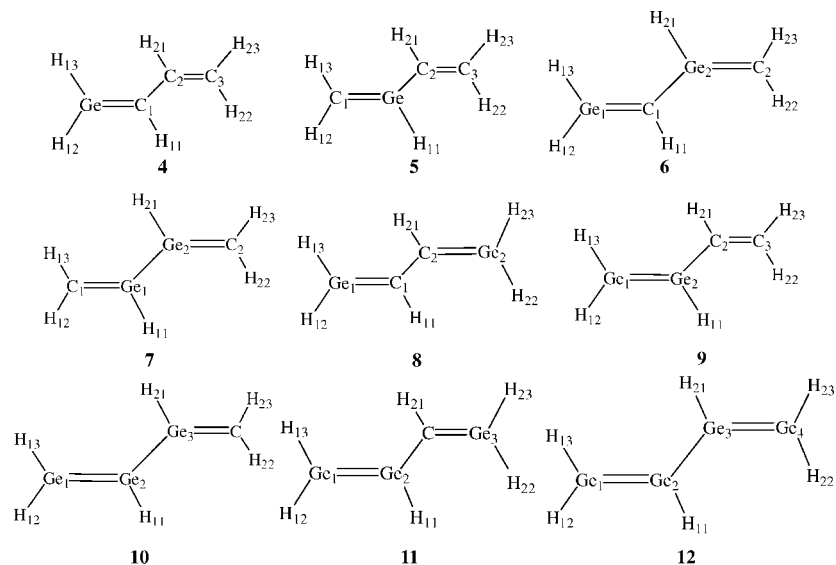
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Scheme 2



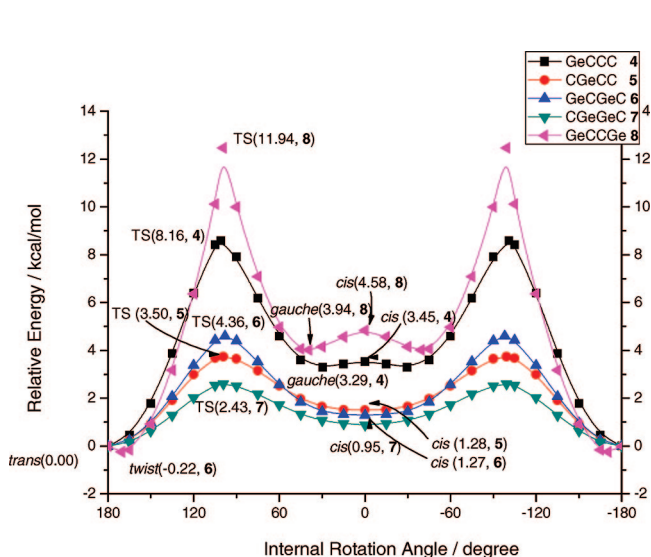
Scheme 3



**Table 1.** Relative Energies (in kcal/mol) of the Stationary Points along Internal Rotation Paths of Germabutadienes 4–8 with Respect to Their *s-trans* Conformers

molecules	<i>s-trans</i>	twist <i>trans</i>	TS	<i>s-gauche</i>	<i>s-cis</i>
GeH <sub>2</sub> =CH-CH=CH <sub>2</sub> (4)	0.0 (0.0) <sup>a</sup> [0.00] <sup>b</sup>		8.58 (8.16)	3.29 (3.29)	3.53 (3.45)
CH <sub>2</sub> =GeH-CH=CH <sub>2</sub> (5)	0.0 (0.0) [3.14] <sup>b</sup>		3.74 (3.50)	1.52 (1.36) <sup>c</sup>	1.51 (1.28)
GeH <sub>2</sub> =CH-GeH=CH <sub>2</sub> (6)	0.0 (0.0) [0.00] <sup>b</sup>		4.59 (4.36)		1.29 (1.27)
CH <sub>2</sub> =GeH-GeH=CH <sub>2</sub> (7)	0.0 (0.0) [-8.20] <sup>b</sup>		2.60 (2.43)		0.88 (0.95)
GeH <sub>2</sub> =CH-CH=GeH <sub>2</sub> (8)	0.0 (0.0) [-1.66] <sup>b</sup>	-0.25 (-0.22) [-1.88] <sup>d</sup>	12.46 (11.94)	4.02 (3.94)	4.84 (4.58)

<sup>a</sup> Values in parentheses are the relative energies corrected with zero-point energies. <sup>b</sup> The relative energies (with zero-point energy corrections) of *s-trans* conformers in every germabutadiene groups. The total energies of *s-trans* conformers of GeH<sub>2</sub>=CH-CH=CH<sub>2</sub> (4) and GeH<sub>2</sub>=CH-GeH=CH<sub>2</sub> (6) are -2194.82623 and -4233.698308 a. u., respectively. <sup>c</sup> The twisted *cis* rotamer, the torsion angle of C=Ge-C=C being 14.8°. <sup>d</sup> The relative energies (with zero-point energy corrections) of twisted *s-trans* minimum of GeH<sub>2</sub>=CH-CH=GeH<sub>2</sub> (8) to *s-trans* minimum of GeH<sub>2</sub>=CH-GeH=CH<sub>2</sub> (6).



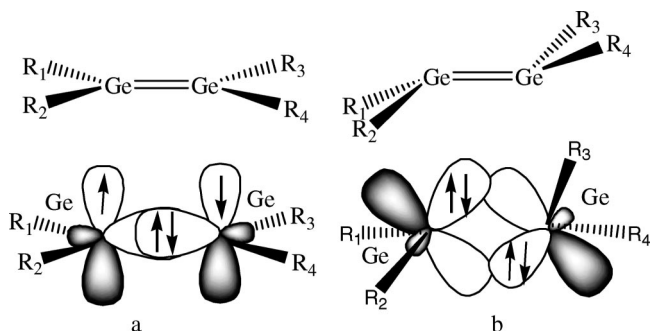
**Figure 1.** Internal rotation potential energy curves for 1-germabutadiene 4, 2-germabutadiene 5, 1,3-digermabutadiene 6, 2,3-digermabutadiene 7, and 1,4-digermabutadiene 8.

same level of theory (1.779 Å and 1.329 Å, respectively; see footnote b in Table 2). The Ge=C bond length of twisted *s-trans* minimum of 8 is slightly longer than its *s-trans* rotamer by 0.002 Å. It is also the longest bond length (1.839 Å) of external double bonds of all the rotamers of 4–8 (see Table 2). In contrast to the external double bond, the bond lengths of the C–C (1.440 and 1.402 Å for 4 and 8, respectively), Ge–C (1.925 and 1.898 Å for 5 and 6, respectively), and Ge–Ge (2.386 Å for 7) central single bonds in the *s-trans* (twisted *s-trans*) minima for 4–8 are considerably shorter than that of ethane (1.531 Å), germane (1.969 Å), and digermene (2.444 Å) (see footnote b in Table 2). The shorter central single bonds and longer external double bonds relative to those in small isolated molecules reflect a conjugation effect in 4–8. In addition, the GeH<sub>2</sub>=CH-CH=CH<sub>2</sub> 4 and GeH<sub>2</sub>=CH-CH=GeH<sub>2</sub> 8 who have higher internal rotation barriers diverge from their isolated molecules in M–N and M=N (M,N=C,Ge) bond lengths more than 5–7. The external bond lengths of other minima of 4–8 (the *s-gauche* and *s-cis* minima) are similar to their global minima, and the central single bond lengths are slightly longer than their global minima. The Ge=C (ranging from 1.780 Å to 1.796 Å) and C=C bond lengths (1.333 Å and 1.334 Å; see Table 2) in TSs of 4–8 are

**Table 2.** Calculated Geometric Parameters for the *s-trans* (twisted-*s-trans*), *s-gauche*, and *s-cis* (twisted *s-cis*) Minima, the Transition States, and the Values of Imaginary Frequencies of Transition States for Germabutadienes 4–8<sup>a,b</sup>

molecules	parameter	<i>s-trans</i>	twisted <i>s-trans</i>	TS	<i>s-gauche</i>	<i>s-cis</i>
GeH <sub>2</sub> =CH-CH=CH <sub>2</sub> (4) ( <i>C<sub>s</sub></i> , <i>C<sub>s</sub></i> , and <i>C<sub>1</sub></i> ) <sup>c</sup>	<i>D</i> (GeC <sub>1</sub> C <sub>2</sub> C <sub>3</sub> )	180.0		101.0	29.6	0.0
	<i>r</i> (GeC <sub>1</sub> )	1.801		1.789	1.800	1.801
	<i>r</i> (C <sub>1</sub> C <sub>2</sub> )	1.440		1.478	1.450	1.449
	<i>r</i> (C <sub>2</sub> C <sub>3</sub> )	1.347		1.334	1.344	1.345
	<i>r</i> (H <sub>11</sub> H <sub>21</sub> )	3.110		2.876	2.431	2.370
	<i>D</i> (H <sub>11</sub> C <sub>1</sub> C <sub>2</sub> H <sub>21</sub> )	180.0		99.1	23.4	0.0
	imaginary frequency <sup>d</sup>	no		-194.9	no	-89.8
CH <sub>2</sub> =GeH-CH=CH <sub>2</sub> (5) ( <i>C<sub>s</sub></i> , <i>C<sub>s</sub></i> , and <i>C<sub>1</sub></i> ) <sup>c</sup>	<i>D</i> (C <sub>1</sub> GeC <sub>2</sub> C <sub>3</sub> )	180.0		98.7	14.8 <sup>e</sup>	0.0
	<i>r</i> (C <sub>1</sub> Ge)	1.782		1.780	1.782	1.782
	<i>r</i> (GeC <sub>2</sub> )	1.925		1.947	1.933	1.933
	<i>r</i> (C <sub>2</sub> C <sub>3</sub> )	1.336		1.333	1.336	1.336
	<i>r</i> (H <sub>11</sub> H <sub>21</sub> )	3.847		3.561	3.066	3.049
	<i>D</i> (H <sub>11</sub> GeC <sub>2</sub> H <sub>21</sub> )	180.0		96.0	13.2	0.0
	imaginary frequency <sup>d</sup>	no		-108.3	no	-33.4
GeH <sub>2</sub> =CH-GeH=CH <sub>2</sub> (6) ( <i>C<sub>s</sub></i> , <i>C<sub>s</sub></i> , and <i>C<sub>1</sub></i> ) <sup>c</sup>	<i>D</i> (C <sub>1</sub> Ge <sub>1</sub> Ge <sub>2</sub> C <sub>2</sub> )	180.0		97.9		0.0
	<i>r</i> (Ge <sub>1</sub> C <sub>1</sub> )	1.792		1.785		1.792
	<i>r</i> (C <sub>1</sub> Ge <sub>2</sub> )	1.898		1.925		1.904
	<i>r</i> (Ge <sub>2</sub> C <sub>2</sub> )	1.786		1.782		1.786
	<i>r</i> (H <sub>11</sub> H <sub>21</sub> )	3.83		3.579		2.999
	<i>D</i> (H <sub>11</sub> C <sub>1</sub> Ge <sub>2</sub> H <sub>21</sub> )	180.0		99.6		0.2
	imaginary frequency <sup>d</sup>	no		-109.7		no
CH <sub>2</sub> =GeH-GeH=CH <sub>2</sub> (7) ( <i>C<sub>2h</sub></i> , <i>C<sub>2v</sub></i> , and <i>C<sub>2</sub></i> ) <sup>c</sup>	<i>D</i> (C <sub>1</sub> Ge <sub>1</sub> Ge <sub>2</sub> C <sub>2</sub> )	180.0		99.2		0.0
	<i>r</i> (C <sub>1</sub> Ge <sub>1</sub> )	1.789		1.786		1.788
	<i>r</i> (Ge <sub>1</sub> Ge <sub>2</sub> )	2.386		2.412		2.392
	<i>r</i> (H <sub>11</sub> H <sub>21</sub> )	4.650		4.313		3.716
	<i>D</i> (H <sub>11</sub> Ge <sub>1</sub> Ge <sub>2</sub> H <sub>21</sub> )	180.0		94.4		0.0
	imaginary frequency <sup>d</sup>	no		-77.5		no
GeH <sub>2</sub> =CH-CH=GeH <sub>2</sub> 8 ( <i>C<sub>2</sub></i> , <i>C<sub>2</sub></i> , and <i>C<sub>2</sub></i> ) <sup>c</sup>	<i>D</i> (Ge <sub>1</sub> C <sub>1</sub> C <sub>2</sub> Ge <sub>2</sub> )	180.0	170.5	99.4	39.4	0.0
	<i>r</i> (Ge <sub>1</sub> C <sub>1</sub> )	1.837	1.839	1.796	1.827	1.820
	<i>r</i> (C <sub>1</sub> C <sub>2</sub> )	1.402	1.402	1.465	1.418	1.421
	<i>r</i> (H <sub>11</sub> H <sub>21</sub> )	3.101	3.100	2.886	2.420	2.346
	<i>D</i> (H <sub>11</sub> C <sub>1</sub> Ge <sub>1</sub> H <sub>12</sub> )	-19.8	-22.6	-1.1	24.7	5.7
	<i>D</i> (H <sub>11</sub> C <sub>1</sub> Ge <sub>1</sub> H <sub>13</sub> )	-168.9	-169.9	179.4	-177.3	174.1
	<i>D</i> (H <sub>11</sub> C <sub>1</sub> C <sub>2</sub> H <sub>21</sub> )	-175.5	-176.8	97.8	14.2	-5.0
	∑α <sup>f</sup>	352.8 <sup>h</sup>	351.9 <sup>h</sup>	360.0	356.4	359.1
	imaginary frequency <sup>d</sup>	no	no	-238.0	no	-130.3

<sup>a</sup> For notations, see Introduction; bond distances (*r*) in Å and dihedral angles (*D*) in degrees. The C–H and Ge–H bond length values are omitted. The values of C–H range from 1.082 Å to 1.091 Å and the values of Ge–H from 1.522 Å to 1.532 Å. <sup>b</sup> The B3LYP/6-311+G(d,p) Ge=Ge, Ge=C, and C=C bond lengths of digermene, germene, and ethene molecules are 2.305, 1.779, and 1.329 Å, respectively, and the B3LYP/6-311+G(d,p) Ge–Ge, Ge–C, and C–C bond lengths of digermene, germane, and ethane molecules are 2.444, 1.969, and 1.531 Å, respectively. <sup>c</sup> The symmetry of the *s-trans* (the first), the *s-cis* (the second), and other rotamers (the third). <sup>d</sup> Imaginary frequencies of transition states on the PESs of 4–8, at cm<sup>-1</sup>. <sup>e</sup> For 2-germabutadiene (5), the part of PES which is close to its *s-cis* conformer is very flat, and there is only a *s-cis* conformer. <sup>f</sup> The sum of *A*(H<sub>12</sub>Ge<sub>1</sub>C<sub>1</sub>), *A*(H<sub>13</sub>Ge<sub>1</sub>C<sub>1</sub>), and *A*(H<sub>12</sub>Ge<sub>1</sub>H<sub>13</sub>) bond angle, in degrees. <sup>h</sup> At MP2, the end GeH<sub>2</sub> groups are planar, ∑α = 360.0°.



**Figure 2.** (a) Construction of planar  $R_2Ge=GeR_2$  from two triplet  $R_2Ge$  (high-energy path). (b) Construction of *trans*-bent  $R_2Ge=GeR_2$  from two singlet  $R_2Ge$  (low-energy path).

longer than those in small isolated molecules (1.779 Å and 1.329 Å; see footnote b of Table 2) and shorter than that in the *s-trans* or twisted *s-trans* minima (see Table 2). The central single bond lengths in TSs of 4–8 are also close to those in small isolated molecules. These indicate the weakening of  $\pi$ -conjugation in

the TS structures.

**Germabutadienes 9–12.** Compared with molecules 4–6, germabutadienes 9–12 incorporate at least a Ge=Ge double bond. From previous experimental reports<sup>3,12</sup> and theoretical studies,<sup>13–16</sup>  $R_2Ge=GeR_2$  favors a *trans*-bent structure. Trinquier<sup>13–16</sup> et al. consider that the  $R_2Ge=GeR_2$  molecule is formally composed of two singlet ground-state  $R_2Ge$ : units because of the relatively large singlet–triplet energy gap,  $\Delta E_{ST}$ . In order to dimerize to a planar  $R_2Ge=GeR_2$  molecule like ethylene, two germynes have to spend twice the amount of  $\Delta E_{ST}$  energy to excite the singlet  $R_2Ge$ : to its triplet state (see Figure 2a). The dimerization by two donor–acceptor interac-

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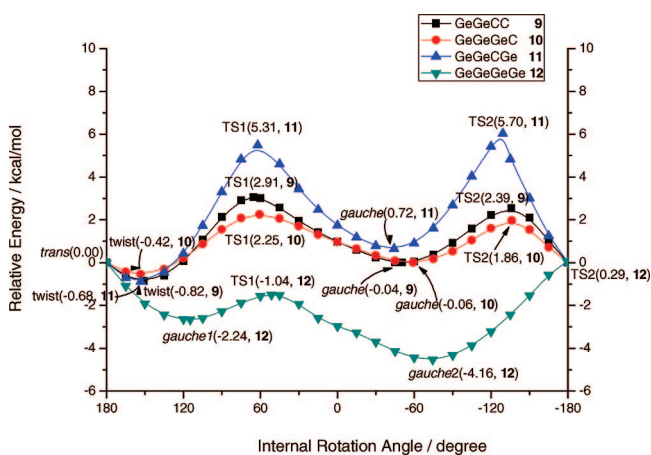


**Table 3.** Calculated Important Geometric Parameters of the *s-trans* Conformers, the *s-gauche* Minima, and the Transition States of Germabutadienes 9–12 and the Values of Imaginary Frequencies of Transition States for Germabutadienes 9–12<sup>a</sup>

molecules	parameter	<i>s-trans</i>	<i>s-gauche</i> 1	TS1	<i>s-gauche</i> 2	TS2
GeH <sub>2</sub> =GeHCH=CH <sub>2</sub> ( <b>9</b> ), (C <sub>s</sub> , C <sub>1</sub> ) <sup>b</sup>	$\theta$ (D(Ge <sub>1</sub> Ge <sub>2</sub> C <sub>1</sub> C <sub>2</sub> ))	180.0	151.0	65.4	-50.5	-135.8
	$r$ (Ge <sub>1</sub> Ge <sub>2</sub> )	2.316	2.322	2.312	2.326	2.314
	$r$ (Ge <sub>2</sub> C <sub>1</sub> )	1.943	1.944	1.967	1.952	1.965
	$r$ (C <sub>1</sub> C <sub>2</sub> )	1.338	1.338	1.334	1.337	1.333
	$r$ (H <sub>11</sub> H <sub>21</sub> )	3.773	3.782	3.579	2.964	3.441
	A(Ge <sub>1</sub> Ge <sub>2</sub> C <sub>1</sub> )	121.0	121.3	119.8	121.5	119.9
	A(Ge <sub>2</sub> C <sub>1</sub> C <sub>2</sub> )	123.3	123.1	125.4	123.1	123.6
	D(H <sub>11</sub> Ge <sub>2</sub> Ge <sub>1</sub> H <sub>12</sub> )	-52.1	-54.1	-52.3	-57.2	-52.1
	D(H <sub>21</sub> C <sub>1</sub> C <sub>2</sub> H <sub>23</sub> )	2.0	0.8	-0.3	-1.5	0.8
	$\Sigma\alpha^c$	327.8	329.3	334.4	329.1	335.1
	imaginary frequency <sup>d</sup>	no	no	-101.4	no	-95.4
GeH <sub>2</sub> =GeHGeH=CH <sub>2</sub> ( <b>10</b> ), (C <sub>s</sub> , C <sub>1</sub> ) <sup>b</sup>	$\theta$ (D(Ge <sub>1</sub> Ge <sub>2</sub> Ge <sub>3</sub> C))	180.0	153.3	60.5	-59.2	-136.1
	$r$ (Ge <sub>1</sub> Ge <sub>2</sub> )	2.312	2.317	2.311	2.320	2.311
	$r$ (Ge <sub>2</sub> Ge <sub>3</sub> )	2.413	2.411	2.445	2.419	2.440
	$r$ (Ge <sub>3</sub> C)	1.796	1.795	1.789	1.794	1.788
	$r$ (H <sub>11</sub> H <sub>21</sub> )	4.560	4.572	4.363	3.627	4.183
	A(Ge <sub>1</sub> Ge <sub>2</sub> Ge <sub>3</sub> )	117.1	117.3	114.7	117.6	115.8
	A(Ge <sub>2</sub> Ge <sub>3</sub> C)	122.4	122.7	125.9	122.5	121.2
	D(H <sub>11</sub> Ge <sub>2</sub> Ge <sub>1</sub> H <sub>12</sub> )	-50.3	-52.0	-50.2	-53.8	-49.3
	D(H <sub>21</sub> Ge <sub>3</sub> CH <sub>23</sub> )	12.0	7.4	-1.7	-7.9	3.6
	$\Sigma\alpha^c$	339.3	339.0	333.0	339.0	333.3
	imaginary frequency <sup>d</sup>	no	no	-54.0	no	-66.8
GeH <sub>2</sub> =GeHCH=GeH <sub>2</sub> ( <b>11</b> ), (C <sub>s</sub> , C <sub>1</sub> ) <sup>b</sup>	$\theta$ (D(Ge <sub>1</sub> Ge <sub>2</sub> CGe <sub>3</sub> ))	180.0	153.2	62.0	-44.2	-129.1
	$r$ (Ge <sub>1</sub> Ge <sub>2</sub> )	2.361	2.357	2.320	2.360	2.318
	$r$ (Ge <sub>2</sub> C)	1.907	1.909	1.940	1.917	1.941
	$r$ (CGe <sub>3</sub> )	1.799	1.798	1.787	1.797	1.786
	$r$ (H <sub>11</sub> H <sub>21</sub> )	3.759	3.760	3.578	2.911	3.429
	A(Ge <sub>1</sub> Ge <sub>2</sub> C)	124.6	124.1	120.7	125.5	120.7
	A(Ge <sub>2</sub> CGe <sub>3</sub> )	123.7	124.0	127.5	124.4	126.2
	D(H <sub>11</sub> Ge <sub>2</sub> Ge <sub>1</sub> H <sub>12</sub> )	-53.9	-57.0	-53.0	-61.3	-51.3
	D(H <sub>21</sub> CGe <sub>3</sub> H <sub>23</sub> )	1.8	-1.5	0.4	-4.0	2.8
	$\Sigma\alpha^c$	309.9	316.0	332.9	314.6	332.8
	imaginary frequency <sup>d</sup>	no	no	-104.9	no	-126.1
GeH <sub>2</sub> =GeHGeH=GeH <sub>2</sub> ( <b>12</b> ), (C <sub>2</sub> , C <sub>2</sub> ) <sup>b</sup>	$\theta$ (D(Ge <sub>1</sub> Ge <sub>2</sub> Ge <sub>3</sub> Ge <sub>4</sub> ))	180.0	114.7	51.4	-74.4	-179.0
	$r$ (Ge <sub>1</sub> Ge <sub>2</sub> )	2.306	2.312	2.317	2.327	2.309
	$r$ (Ge <sub>2</sub> Ge <sub>3</sub> )	2.428	2.432	2.480	2.443	2.477
	$r$ (H <sub>11</sub> H <sub>21</sub> )	4.397	4.506	4.506	3.527	4.057
	A(Ge <sub>1</sub> Ge <sub>2</sub> Ge <sub>3</sub> )	121.7	120.8	118.0	117.3	117.1
	D(H <sub>11</sub> Ge <sub>2</sub> Ge <sub>1</sub> H <sub>12</sub> )	-46.2	-49.0	-49.9	-51.6	-49.0
	$\Sigma\alpha^c$	337.2	339.6	342.7	340.4	340.7
	imaginary frequency <sup>d</sup>	-37.0	no	-24.9	no	-65.7

<sup>a</sup> For atom numberings, see Introduction. Bond distances ( $r$ ) in Å, bond angles ( $A$ ), and dihedral angles ( $D$ ) in degrees. The C–H and Ge–H bond length values are omitted. The values of C–H range from 1.082 Å to 1.089 Å and the values of Ge–H from 1.526 Å to 1.562 Å. <sup>b</sup> The symmetry of the *s-trans* rotamers (the first) and other rotamers (the second). <sup>c</sup> The sum of  $A(H_{12}Ge_1Ge_2)$ ,  $A(H_{13}Ge_1Ge_2)$ , and  $A(H_{12}Ge_1H_{13})$  bond angles. <sup>d</sup> The values of imaginary frequencies at cm<sup>-1</sup>.

tions, in which the lone-pair electron of a hybrid orbital of one

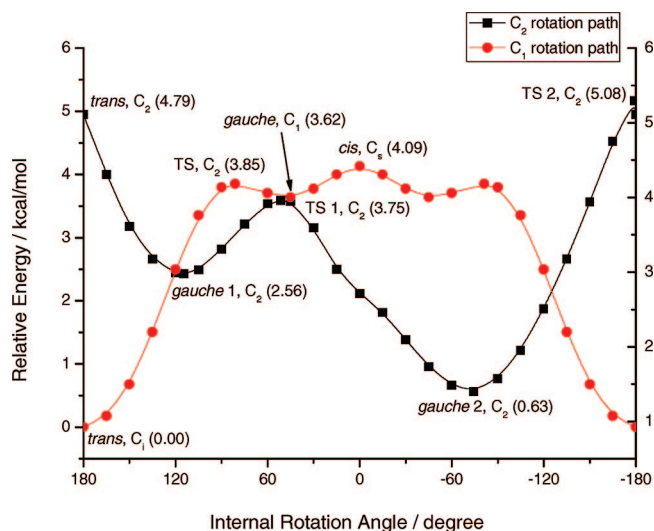


**Figure 3.** Internal rotation potential energy curves for the 1,2-digermbutadiene **9**, 1,2,3-trigermbutadiene **10**, 1,2,4-trigermbutadiene **11**, and tetragermabutadiene **12**.

R<sub>2</sub>Ge: enter into the empty 4p(Ge) orbit of another R<sub>2</sub>Ge:, is the lower energy path (see Figure 2b). Thus, R<sub>2</sub>Ge=GeR<sub>2</sub> takes the form of a *trans*-bent double bond structure by the low-energy dimerization path.

Our calculations support the previous experimental<sup>3,12</sup> and theoretical results.<sup>13–16</sup> The optimized geometries of the stationary points on the internal rotational PESs of **9–12** are given in Table 3. The sum of the angle around the terminal Ge<sub>1</sub> atoms (denoted as  $\Sigma\alpha$ ) in the minima and TSs of **8–12**, that is, the sum of  $A(H_{12}Ge_1Ge_2)$ ,  $A(H_{13}Ge_1Ge_2)$ , and  $A(H_{12}Ge_1H_{13})$  bond angles, range from 309.9° to 342.7° (see Table 3). The results show that the external Ge=Ge double bonds are pyramidal in the course of rotation. In contrast, the Ge=C double bonds of **8–11** are almost planar, whose  $D(H_{21}MNH_{23})$  ( $M, N = Ge, C$ ) dihedral angles range from 12.0° to -7.9° during the whole internal rotation of **9–11** (see Table 3).

The B3LYP/6-311+G(d,p) internal rotation PESs for **9–12** are shown in Figure 3. For tetragermabutadiene **12**, we selected the lower energetic internal rotation, that is, the rotation path of the C<sub>2</sub> high-symmetric rotamer (see Figure 4), as the research



**Figure 4.** Potential energy curves along the  $C_2$  high-symmetric and  $C_1$  low-symmetric rotation paths.

object. The skeletons of PESs for **9–12** are similar but differ from those of **4–8** because of the lack of symmetry for the rotamer. There are two different *s-gauche* minima and two different TSs along **9–12** PESs. The *s-trans* and *s-cis* conformations for **9–12** are now general rotamers (see Figure 3). Along the PES one *s-gauche* minimum (denoted as *s-gauche* 1) appears between the *s-trans* rotamer and the first TS (denoted as TS1), and another *s-gauche* minimum (denoted as *s-gauche* 2) locates between the *s-cis* rotamer and the second TS (denoted as TS2; see Figure 3). For **9–11**, the *s-gauche* 1 minimum is the global minimum of the internal rotation PES, and most rotamers of their PES are higher than the *s-trans* conformation. The *s-gauche* 2 minimum of **12** is more stable than the *s-gauche* 1 minimum by 1.92 kcal/mol. Most of the rotamers along the **12** PES skeleton are more stable than the *s-trans* conformation (see Figure 4). The *s-gauche* 1 minima of **9–12** are located at  $\theta$  values of  $151.0^\circ$  (**9**),  $153.3^\circ$  (**10**),  $153.2^\circ$  (**11**), and  $114.7^\circ$  (**12**), and the *s-gauche* 2 minima of **9–12** are located at the  $\theta$  values of  $-50.5^\circ$  (**9**),  $-59.2^\circ$  (**10**),  $-44.2^\circ$  (**11**), and  $-74.4^\circ$  (**12**) (see Table 3). Compounds **9–12** have the TS1 transition states at the  $\theta$  of  $65.4^\circ$  (**9**),  $60.5^\circ$  (**10**),  $62.0^\circ$  (**11**), and  $51.4^\circ$  (**12**), and have the TS2 at the  $\theta$  of  $-135.8^\circ$  (**9**),  $-136.1^\circ$  (**10**),  $-129.1^\circ$  (**11**), and  $-179.0^\circ$  (**12**) (see Table 3).

The relative energies and the ZPE of the *s-gauche* 1 and the *s-gauche* 2 minima, and TS1 and TS2 transition states for **9–12** molecules to their respective *s-trans* conformers are given in Table 4. Similar to **4–8**, the relative ZPEs of the *s-trans* and *s-gauche* 1 in every group of germabutadiene are also given in Table 4. The internal rotational barriers for **9–11** are denoted as the difference between the TS1 and global minimum (*s-gauche* 1) for the clockwise rotational process of *s-gauche* 1  $\rightarrow$  TS1 and the difference between the TS2 and global minimum (*s-gauche* 2) for tetragermabutadiene **12**. The barrier heights for **9–12** are evaluated to be 3.73, 2.67, 5.99, and 4.45 kcal/mol, respectively. For tetragermabutadiene **12**, the barrier height of the clockwise rotating from *s-gauche* 1 to TS1 is evaluated to be 1.20 kcal/mol.

For **9–11**, the lengths of the Ge–Ge and Ge–C central single bond of the two *s-gauche* minima (Ge–Ge, 2.411 Å and 2.419 Å; Ge–C, from 1.909 Å to 1.952 Å; see Table 3) are generally shorter than the respective bond lengths in  $\text{GeH}_3\text{–GeH}_3$  and  $\text{GeH}_3\text{–CH}_3$  (2.444 Å and 1.969 Å; see footnote b of Table 2) and the lengths of the Ge=Ge and Ge=C double bonds

(Ge=Ge, from 2.317 Å to 2.360 Å; Ge=C, from 1.794 Å to 1.798 Å; see Table 3) are longer than those of  $\text{GeH}_2\text{=GeH}_2$  or  $\text{GeH}_2\text{=CH}_2$  (2.305 and 1.779 Å; see footnote b of Table 2), implying a conjugation effect between the external double bonds. While rotating to their TS, the central single bonds were elongated by about 0.030 Å and the external double bonds shortened. These changes point to the weakening of  $\pi$ -conjugation through the central single bond in TSs.

Rotation of tetragermabutadiene **12** follows the trend of **9–11** (see Table 3). Both the present calculations, and those reported by Trinquier<sup>6</sup> found the Ge–Ge single bond of **12** longer than those of **7** and **10**, for example, single Ge–Ge bond lengths are 2.443 Å (B3LYP/6–311+g(d,p)) and 2.448 Å (Trinquier,<sup>6</sup> HF/DZP) in the *s-gauche* 2 global minima structure. They are close to the single bond length reported for its X-ray structure (2.458 Å)<sup>2</sup> and in the  $\text{GeH}_3\text{–GeH}_3$  molecule (2.444 Å; see footnote b of Table 2). The external Ge=Ge double bond length in the *s-gauche* 2 minimum of **12** (2.327 Å) is in good agreement with the average experimental values (2.350 Å) reported by Weidenbruch et al.<sup>2</sup> and is longer than digermene (by 0.022 Å). The GeGeGeGe torsional angle of the *s-gauche* 2 conformer of **12** is  $-74.4^\circ$ , similar to those reported by Trinquier ( $-80.4^\circ$ ),<sup>6</sup> and differ from the experimental values reported by Weidenbruch et al.<sup>2</sup> by  $22.5^\circ$ . The difference between the theoretical and experimental structures comes from the significant dependency of structures of  $\text{Ge}_4\text{R}_6$  on the substituents R.<sup>7</sup>

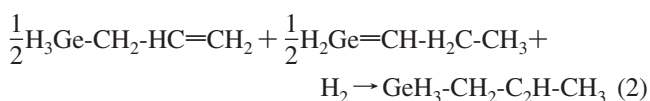
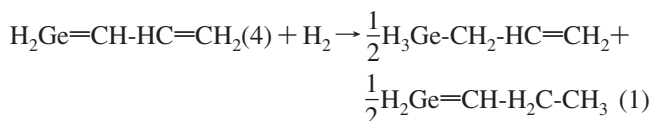
The relative energies and pertinent optimized geometry of the minima and important rotamers along the  $C_2$  high-symmetric and  $C_1$  low-symmetric internal rotation of tetragermabutadiene **12** are given in Table 5. The  $C_i$  *s-trans* arrangement along the  $C_1$  low-symmetric rotation is the most stable conformation among the linear tetragermabutadienes. The *s-gauche* 2 conformation along the  $C_2$  high-symmetric rotation path, which corresponds to the X-ray crystal structure, is slightly less stable than the  $C_i$  *s-trans* (0.63 kcal/mol). The energy comparison between the  $C_2$  group of rotamers and the  $C_1$  group shows that most of the rotamers in  $C_2$  PES are more stable than the corresponding points in  $C_1$  PES (see Figure 4). Because of the large energy gap between the pyramidal and planar structures, tetragermabutadiene **12** would likely adopt the pyramidal conformation (see Table 5).

Our present calculations show that the internal rotation barrier for germabutadiene, digermabutadiene, and trigermabutadiene groups from the global minima (the *s-trans*, the twisted *s-trans*, and the *s-gauche*) to TS follow the trend (kcal/mol) **4** (8.16) > **5** (3.50) (1 germanium atom), **8** (12.16) > **6** (4.36) > **9** (3.73) > **7** (2.43) (2 germanium atoms), and **11** (5.99) > **10** (2.67) (3 germanium atoms). The barrier heights of internal rotation of germabutadienes are similar to the corresponding silabutadienes, although germabutadienes (**5–7** and **9–12**) have longer central single bonds than silabutadienes by about 0.100 Å (for tetragermabutadiene, 0.154 Å).<sup>11</sup> This indicates that other factors besides the steric effect are also responsible for the internal rotation barriers of germabutadienes.

**$\pi$ -Conjugation Stability Energy.** Because germabutadienes **4–12** have two adjacent double bonds, their minima's conformation is energetically stabilized through the  $\pi$ -conjugation effect. Here, we employ two methods to evaluate the strength of  $\pi$ -conjugation of the global minima of the germabutadienes (for tetragermabutadiene **12**, including the  $C_i$  *s-trans* minimum of low-symmetric conformation): (a) indirect estimate of the  $\pi$ -conjugative stable energies (denoted as  $\pi$ -CSE) by stepwise hydrogenation reactions and (b) direct

estimation by the natural bond orbital (NBO) second order perturbation stabilization energies. We will also correlate the strength of the  $\pi$ -conjugation with the internal rotation barriers.

**Conjugative Stabilization by Stepwise Hydrogenation Heats.** On the basis of Kistiakowsky, the  $\pi$ -CSE of compounds containing two adjacent double bonds can be evaluated by calculating the difference of the reaction heats of two stepwise hydrogenation reactions.<sup>17</sup> For example, for the *s-trans* minimum of germabutadiene **4**, the hydrogenation heat of the first hydrogenation reaction from the germabutadiene to the germabutene [eq (1)] and the second from the germabutene to the germabutane [eq (2)] are  $-29.40$  and  $-35.42$  kcal/mol at the B3LYP/6-311+G level, respectively.

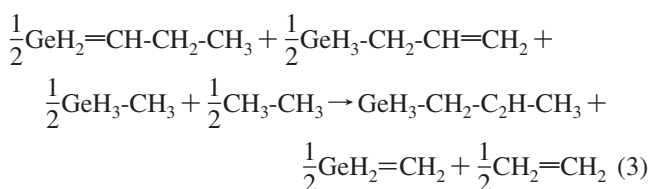


The reaction energy difference of eqs (1) and (2), 6.02 kcal/mol, indicates the stabilization energy via the  $\pi$ -conjugation of the *s-trans* conformation **4**.

The calculated hydrogenation heats and the heat differences from stepwise hydrogenation reactions are given in Table 6. For comparison with parent butadiene, we had also calculated butadienic hydrogenation heats and heat differences. However, we found that the heat differences of all the germabutadiene are less than the bond separation energies (denoted as BSE) by the isodesmic reactions:<sup>4-6</sup> the heat differences of **7** and **8** calculated by stepwise hydrogenation reactions are weaker than the BSEs<sup>4,5</sup> at the MP4//SCF level by 6.52

and 5.56 kcal/mol, respectively; the heat difference of **9** ( $-3.51$  kcal/mol) even produces the negative values, and the heat difference (2.34 kcal/mol) of **12** (*s-trans*,  $C_i$ ) is also far less than the BSEs of 11.7 kcal/mol<sup>6</sup> (at the MP4//SCF level).

It is the hyperconjugation of germabutienes, for example,  $\text{H}_3\text{Ge}-\text{CH}_2-\text{HC}=\text{CH}_2$ ,  $\text{H}_2\text{Ge}=\text{CH}-\text{H}_2\text{C}-\text{CH}_3$ , that causes the divergence between heat differences from the stepwise hydrogenation reactions and BSEs from the isodesmic reactions.<sup>10</sup> To remove the hyperconjugation effect, we estimated the strength of the hyperconjugation of the hydrogenated germabutienes by the isodesmic reactions. For example, we estimated the wholly hyperconjugation strength of two virtual intermediates of **4**,  $\text{H}_3\text{Ge}-\text{CH}_2-\text{HC}=\text{CH}_2$  and  $\text{H}_2\text{Ge}=\text{CH}-\text{H}_2\text{C}-\text{CH}_3$ , by eq (3).



All of the hyperconjugative stabilization energies of the hydrogenated germabutadienes of **4-12** are given in Table 7. Then, the hyperconjugative stabilization energies can be removed from the heats of hydrogenation reactions in eq (1) and added up to those in eq (2) (see Table 6). The CSEs are evaluated by the comparison between the new first and second hydrogenation heats corrected by the hyperconjugations. The  $\pi$ -CSEs of **7**, **8**, and **12** (*s-trans*,  $C_i$ ) are 5.71, 18.85, and 16.67 kcal/mol, respectively, which differ from the BSEs of the isodesmic reactions<sup>4-6</sup> by  $-1.29$ , 2.85, and 4.97 kcal/mol.

The conjugation strengths in the global minima (the *s-trans*, the twisted *s-trans*, and the *s-gauche* 1) of germabutadienes **4-11** will be discussed according to the number of germa-

**Table 4. Relative Energies (in kcal/mol) of the Stationary Points along the Rotation Paths of Germabutadienes 9-12 with Respect to Their *s-trans* Conformers**

molecules	<i>s-trans</i>	<i>s-gauche</i> 1	TS1	<i>s-cis</i>	<i>s-gauche</i> 2	TS2
$\text{GeH}_2=\text{GeH}-\text{CH}=\text{CH}_2$ ( <b>9</b> )	0.0 (0.0) <sup>a</sup> [-29.96] <sup>b</sup>	-0.86 (-0.82) [-30.78] <sup>b</sup>	3.05 (2.91)	0.98 (0.86)	0.0 (-0.04)	2.54 (2.39)
$\text{GeH}_2=\text{GeH}-\text{GeH}=\text{CH}_2$ ( <b>10</b> )	0.0 (0.0) [0.00] <sup>c</sup>	-0.54 (-0.42) [-0.42] <sup>c</sup>	2.25 (2.25)	0.97 (0.91)	0.00 (-0.06)	1.98 (1.86)
$\text{GeH}_2=\text{GeH}-\text{CH}=\text{GeH}_2$ ( <b>11</b> )	0.0 (0.0) [8.28] <sup>c</sup>	-0.88 (-0.68) [7.60] <sup>c</sup>	5.49 (5.31)	1.74 (1.72)	0.65 (0.72)	6.04 (5.70)
$\text{GeH}_2=\text{GeH}-\text{GeH}=\text{GeH}_2$ ( <b>12</b> )	0.0 (0.0)	-2.67 (-2.24)	-1.51 (-1.04)	2.98 (2.70)	-4.53 (-4.16)	0.07 (0.29)

<sup>a</sup> Values in parentheses are the relative energies corrected with zero-point energies. <sup>b</sup> The relative energies (with zero-point energy corrections) of *s-trans* and twisted *s-trans* conformers of  $\text{GeH}_2=\text{GeH}-\text{CH}=\text{CH}_2$  (**9**) to *s-trans* minimum of  $\text{GeH}_2=\text{CH}-\text{GeH}=\text{CH}_2$  (**6**). <sup>c</sup> The relative energies (with zero-point energy corrections) of *s-trans* and twisted *s-trans* conformers of **10** and **11** to *s-trans* minimum of  $\text{GeH}_2=\text{GeH}-\text{GeH}=\text{CH}_2$  (**10**). The total energies of  $\text{GeH}_2=\text{GeH}-\text{GeH}=\text{CH}_2$  (**10**) is  $-6272.639837$  a. u.

**Table 5. B3LYP Relative Energies and Optimized Geometry of the Minima and Some Important Rotamers of  $C_2$  and  $C_1$  Internal Rotation Paths of Tetragermabutadiene 12<sup>a</sup>**

	symmetry	relative energy <sup>b</sup>	$\text{Ge}_1\text{Ge}_2\text{Ge}_3\text{Ge}_4$	$\text{Ge}_1\text{Ge}_2\text{Ge}_3$	$\text{Ge}_1=\text{Ge}_2$	$\text{Ge}_2-\text{Ge}_3$	imaginary frequency <sup>c</sup>
<i>s-cis</i> (c) <sup>d</sup>	$C_{2v}$	10.51	0.0	127.1	2.242	2.372	$-307.4, -276.9$
<i>s-trans</i> (c) <sup>d</sup>	$C_{2h}$	9.22	180.0	123.6	2.243	2.364	$-319.8, -307.8$
TS 2 (a) <sup>d</sup>	$C_2$	5.08	-178.8	117.1	2.309	2.477	-65.7
<i>s-trans</i> (a) <sup>d</sup>	$C_2$	4.79	180.0	121.7	2.306	2.428	-37.0
<i>s-cis</i> (b) <sup>d</sup>	$C_s$	4.09	0.0	122.7	2.308	2.451	-34.0
TS (b) <sup>d</sup>	$C_1$	3.85	81.2	120.2 or 115.0	2.319 or 2.313	2.472,	-28.1
TS 1 (a) <sup>d</sup>	$C_2$	3.75	50.9	117.9	2.317	2.480	-25.2
<i>s-gauche</i> (b) <sup>d</sup>	$C_1$	3.62	45.2	115.7 or 121.5	2.303 or 2.320	2.455	no
<i>s-gauche</i> 1 (a) <sup>d</sup>	$C_2$	2.56	114.7	120.8	2.312	2.432	no
<i>s-cis</i> (a) <sup>d</sup>	$C_2$	2.09	0.0	114.6	2.322	2.462	-0.9
<i>s-gauche</i> 2 (a) <sup>d</sup>	$C_2$	0.63	-72.4	117.4	2.327	2.442	no
<i>s-trans</i> (b) <sup>d</sup>	$C_i$	0.00	180.0	115.32	2.324	2.439	no

<sup>a</sup> For atom numberings see Introduction. Bond distances are in Å and bond angles and dihedral angles in degree. <sup>b</sup> The zero-point correction energies. <sup>c</sup> The values of imaginary frequencies, at  $\text{cm}^{-1}$ . <sup>d</sup> a, b, and c denote three groups of tetragermabutadienes: the rotamers along the  $C_2$  and  $C_1$  internal rotation paths, and the planar structure.

**Table 6. Calculated Conjugative Energies of the Global Minima (the *s-trans* or *s-gauche* Conformations) and the Barrier Heights for Internal Rotation (the *s-trans* → *s-cis* or the Twisted *s-gauche* → *s-cis* Processes) of the Germabutadienes 4–12 at the Level of B3LYP/6-311+G(d,p)**

isodesmic equations of the germabutadienes	heat <sup>a,b</sup>	difference between (1) and (2) <sup>b</sup>	heat corrected by hyperconjugation <sup>b</sup>	conjugation stabilization <sup>b</sup>	rotational barrier <sup>b</sup>
CH <sub>2</sub> =CH-CH=CH <sub>2</sub>					
+H <sub>2</sub> →CH <sub>3</sub> -CH <sub>2</sub> -CH=CH <sub>2</sub> (1)	-22.70		-19.47		
+H <sub>2</sub> →CH <sub>3</sub> -CH <sub>2</sub> -C <sub>2</sub> H-CH <sub>3</sub> (2)	-26.89	4.19	-30.12	10.65	6.56
GeH <sub>2</sub> =CH-CH=CH <sub>2</sub> (4)					
+H <sub>2</sub> →1/2GeH <sub>3</sub> -CH <sub>2</sub> -CH=CH <sub>2</sub> +1/2GeH <sub>2</sub> =CH-CH <sub>2</sub> -CH <sub>3</sub> (1)	-29.40		-25.80		
+H <sub>2</sub> →GeH <sub>3</sub> -CH <sub>2</sub> -C <sub>2</sub> H-CH <sub>3</sub> (2)	-35.42	6.02	-39.03	13.23	8.16
CH <sub>2</sub> =GeH-CH=CH <sub>2</sub> (5)					
+H <sub>2</sub> →1/2CH <sub>3</sub> -GeH <sub>2</sub> -CH=CH <sub>2</sub> +1/2CH <sub>2</sub> =GeH-CH <sub>2</sub> -CH <sub>3</sub> (1)	-36.02		-34.84		
+H <sub>2</sub> →CH <sub>3</sub> -GeH <sub>2</sub> -C <sub>2</sub> H-CH <sub>3</sub> (2)	-37.86	1.84	-39.03	4.19	3.50
GeH <sub>2</sub> =CH-GeH=CH <sub>2</sub> (6)					
+H <sub>2</sub> →1/2GeH <sub>3</sub> -CH <sub>2</sub> -GeH=CH <sub>2</sub> +1/2GeH <sub>2</sub> =CH-GeH <sub>2</sub> -CH <sub>3</sub> (1)	-42.54		-40.24		
+H <sub>2</sub> →GeH <sub>3</sub> -CH <sub>2</sub> -GeH-CH <sub>2</sub> (2)	-45.64	3.10	-47.94	7.69	4.36
CH <sub>2</sub> =GeH-GeH=CH <sub>2</sub> (7)					
+H <sub>2</sub> →CH <sub>3</sub> -GeH <sub>2</sub> -GeH=CH <sub>2</sub> (1)	-44.84		-42.22		
+H <sub>2</sub> →CH <sub>3</sub> -GeH <sub>2</sub> -GeH <sub>2</sub> -CH <sub>3</sub> (2)	-45.32	0.48	-47.94	5.71	2.43
GeH <sub>2</sub> =CH-CH=GeH <sub>2</sub> (8)					
+H <sub>2</sub> →GeH <sub>3</sub> -CH-CH=GeH <sub>2</sub> (1)	-33.29		-29.09		
+H <sub>2</sub> →GeH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -GeH <sub>3</sub> (2)	-43.73	10.44	-47.94	18.85	12.16
GeH <sub>2</sub> =GeH-CH=CH <sub>2</sub> (9)					
+H <sub>2</sub> →1/2GeH <sub>3</sub> -GeH <sub>2</sub> -CH=CH <sub>2</sub> +1/2GeH <sub>2</sub> =GeH-CH <sub>2</sub> -CH <sub>3</sub> (1)	-31.72		-28.49		
+H <sub>2</sub> →GeH <sub>3</sub> -GeH <sub>2</sub> -CH <sub>2</sub> -CH <sub>3</sub> (2)	-28.21	-3.51	-31.44	2.95	3.73
GeH <sub>2</sub> =GeH-GeH=CH <sub>2</sub> (10)					
+H <sub>2</sub> →1/2GeH <sub>3</sub> -GeH <sub>2</sub> -GeH=CH <sub>2</sub> +1/2GeH <sub>2</sub> =GeH-GeH <sub>2</sub> -CH <sub>3</sub> (1)	-37.37		-33.20		
+H <sub>2</sub> →GeH <sub>3</sub> -GeH <sub>2</sub> -GeH <sub>2</sub> -CH <sub>3</sub> (2)	-38.86	1.49	-43.04	9.84	2.67
H <sub>2</sub> Ge=GeH-HC=GeH <sub>2</sub> (11)					
+H <sub>2</sub> →1/2GeH <sub>3</sub> -GeH <sub>2</sub> -CH=GeH <sub>2</sub> +1/2GeH <sub>2</sub> =GeH-CH <sub>2</sub> -GeH <sub>3</sub> (1)	-33.82		-28.93		
+H <sub>2</sub> →GeH <sub>3</sub> -GeH <sub>2</sub> -CH <sub>2</sub> -GeH <sub>3</sub> (2)	-38.14	4.32	-43.04	14.10	5.99
GeH <sub>2</sub> =GeH-GeH=GeH <sub>2</sub> (12, <i>s-gauche</i> 2, C <sub>2</sub> )					
+H <sub>2</sub> →GeH <sub>3</sub> -GeH <sub>2</sub> -GeH=GeH <sub>2</sub> (1)	-29.26		-22.09		
+H <sub>2</sub> →GeH <sub>3</sub> -GeH <sub>2</sub> -GeH <sub>2</sub> -GeH <sub>3</sub> (2)	-30.96	1.70	-38.13	16.04	4.45
GeH <sub>2</sub> =GeH-GeH=GeH <sub>2</sub> (12, <i>s-trans</i> , C <sub>i</sub> )					
+H <sub>2</sub> →GeH <sub>3</sub> -GeH <sub>2</sub> -GeH=GeH <sub>2</sub> (1)	-28.63		-21.46		
+H <sub>2</sub> →GeH <sub>3</sub> -GeH <sub>2</sub> -GeH <sub>2</sub> -GeH <sub>3</sub> (2)	-30.96	2.34	-38.13	16.67	3.85

<sup>a</sup>  $\sum(E + \text{ZPE energies})_{\text{products}} - \sum(E + \text{ZPE energies})_{\text{reactants}}$ , <sup>b</sup> In kcal/mol.

**Table 7. Calculated Hyperconjugative Stabilization Energy of Germabutene (Hydrogenated Germabutadienes 4–12) at the Level of B3LYP/6-311+G(d,p)**

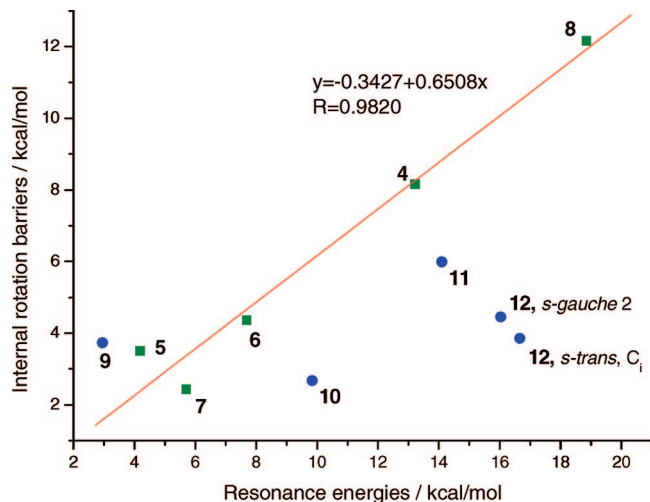
isodesmic equations of the germabutadienes	hyperconjugative stable energy <sup>a</sup>
CH <sub>2</sub> =CH-CH <sub>2</sub> -CH <sub>3</sub> + CH <sub>3</sub> -CH <sub>3</sub> → CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>3</sub> + CH <sub>2</sub> =CH <sub>2</sub>	3.23
1/2GeH <sub>2</sub> =CH-CH <sub>2</sub> -CH <sub>3</sub> + 1/2GeH <sub>3</sub> -CH <sub>2</sub> -CH=CH <sub>2</sub> + 1/2GeH <sub>3</sub> -CH <sub>3</sub> + 1/2CH <sub>3</sub> -CH <sub>3</sub> → GeH <sub>3</sub> -CH <sub>2</sub> -C <sub>2</sub> H-CH <sub>3</sub> + 1/2GeH <sub>2</sub> =CH <sub>2</sub> + 1/2CH <sub>2</sub> =CH <sub>2</sub>	3.60
1/2CH <sub>2</sub> =GeH-CH <sub>2</sub> -CH <sub>3</sub> + GeH <sub>3</sub> -CH <sub>2</sub> -CH=CH <sub>2</sub> + 1/2CH <sub>3</sub> -GeH <sub>3</sub> + 1/2CH <sub>3</sub> -CH <sub>3</sub> → CH <sub>3</sub> -GeH <sub>2</sub> -C <sub>2</sub> H-CH <sub>3</sub> + 1/2CH <sub>2</sub> =GeH <sub>2</sub> + 1/2CH <sub>2</sub> =CH <sub>2</sub>	1.17
1/2GeH <sub>2</sub> =CH-GeH <sub>2</sub> -CH <sub>3</sub> + 1/2GeH <sub>3</sub> -CH <sub>2</sub> -GeH=CH <sub>2</sub> + GeH <sub>3</sub> -CH <sub>3</sub> → GeH <sub>3</sub> -CH <sub>2</sub> -GeH-CH <sub>2</sub> + GeH <sub>2</sub> =CH <sub>2</sub>	2.30
CH <sub>2</sub> =GeH-GeH <sub>2</sub> -CH <sub>3</sub> + CH <sub>3</sub> -GeH <sub>3</sub> → CH <sub>3</sub> -GeH <sub>2</sub> -GeH <sub>2</sub> -CH <sub>3</sub> + CH <sub>2</sub> =GeH <sub>2</sub>	2.62
GeH <sub>2</sub> =CH-CH <sub>2</sub> -GeH <sub>3</sub> + GeH <sub>3</sub> -CH <sub>3</sub> → GeH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -GeH <sub>3</sub> + GeH <sub>2</sub> =CH <sub>2</sub>	4.21
1/2GeH <sub>2</sub> =GeH-CH <sub>2</sub> -CH <sub>3</sub> + 1/2GeH <sub>3</sub> -GeH <sub>2</sub> -CH=CH <sub>2</sub> + 1/2GeH <sub>3</sub> -GeH <sub>3</sub> + 1/2CH <sub>3</sub> -CH <sub>3</sub> → GeH <sub>3</sub> -GeH <sub>2</sub> -CH <sub>2</sub> -CH <sub>3</sub> + 1/2GeH <sub>2</sub> =GeH <sub>2</sub> + 1/2CH <sub>2</sub> =CH <sub>2</sub>	3.23
1/2GeH <sub>2</sub> =GeH-GeH <sub>2</sub> -CH <sub>3</sub> + 1/2GeH <sub>3</sub> -GeH <sub>2</sub> -GeH=CH <sub>2</sub> + 1/2GeH <sub>3</sub> -GeH <sub>3</sub> + 1/2GeH <sub>3</sub> -CH <sub>3</sub> → GeH <sub>3</sub> -GeH <sub>2</sub> -GeH <sub>2</sub> -CH <sub>3</sub> + GeH <sub>2</sub> =GeH <sub>2</sub> + GeH <sub>2</sub> =CH <sub>2</sub>	4.18
1/2GeH <sub>2</sub> =GeH-CH <sub>2</sub> -GeH <sub>3</sub> + 1/2GeH <sub>3</sub> -GeH <sub>2</sub> -CH=CH <sub>2</sub> + 1/2GeH <sub>3</sub> -GeH <sub>3</sub> + 1/2CH <sub>3</sub> -GeH <sub>3</sub> → GeH <sub>3</sub> -GeH <sub>2</sub> -CH <sub>2</sub> -GeH <sub>3</sub> + 1/2GeH <sub>2</sub> =GeH <sub>2</sub> + 1/2CH <sub>2</sub> =GeH <sub>2</sub>	4.89
GeH <sub>2</sub> =GeH-GeH <sub>2</sub> -GeH <sub>3</sub> + H <sub>3</sub> Ge-GeH <sub>3</sub> → GeH <sub>3</sub> -GeH <sub>2</sub> -GeH <sub>2</sub> -GeH <sub>3</sub> + GeH <sub>2</sub> =GeH <sub>2</sub>	7.17

<sup>a</sup>  $\sum(E + \text{ZPE energies})_{\text{products}} - \sum(E + \text{ZPE energies})_{\text{reactants}}$ , in kcal/mol.

nium atoms (monogermabutadiene, digermabutadiene, and trigermabutadiene groups). The conjugation strength of

1-germabutadienes **4** is significantly higher than 2-germabutadienes **5** by 9.04 kcal/mol in the monogermabutadiene





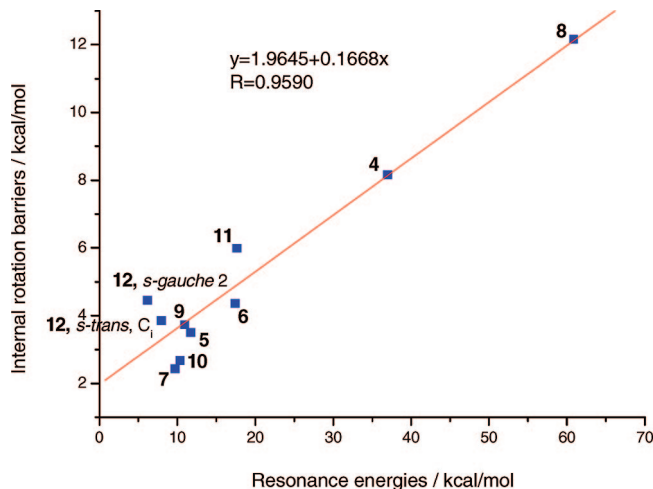
**Figure 5.** Correlation between the internal rotation barriers and the resonance energies calculated from the stepwise hydrogenation of the global minima of **4–8** (square symbols). There is no linear correlation for **9–12** (point symbols).

group, and in the trigermabutadiene group, the  $\pi$ -conjugation strength of **10** is lower than that of **11** by 4.26 kcal/mol. The conjugation stabilization in the digermabutadiene group follows the order: **8** > **6** > **7** > **9**. It is apparent that  $\pi$ -CSE of germabutadienes including such external double bond structures as  $\text{GeH}_2=\text{CH}-$  is higher than those of the  $\text{CH}_2=\text{GeH}-$ .

The  $\pi$ -conjugative strengths for germabutadienes **4–8** have a good linear correlation with their internal rotations barriers (square symbol,  $y = -0.3427 + 0.6508x$ , with linearly dependent coefficient of  $R = 0.9820$ ; see Figure 5). The results imply that  $\pi$ -conjugation is responsible for the internal rotation barrier in germabutadienes **4–8**. Germabutadienes **9–12** do not have a better linear correlation between  $\pi$ -conjugative stabilization energies and the barrier heights (see Figure 5). We also noted that the calculated CSEs for **9–12** are a little higher than that of the monogermabutadienes and digermabutadienes with the exception of **8**. For nonplanar **9–12** systems, there are no unequivocal  $\sigma$ - $\pi$  separations. The CSEs calculated by stepwise hydrogenation heats include other orbital coupling besides  $\pi$ -conjugation.<sup>6</sup> Thus, for **9–12** the estimated stabilization energies from stepwise hydrogenation heats are unable to predict the  $\pi$ -conjugation strength. Nevertheless, the orbital derived from the  $\pi$  system is still very informative for **9–12**.

**$\pi$ -Conjugation Stabilization Energies and Their Corresponding Internal Rotational Barriers.** Although we corrected the conjugative stabilization energies by considering the hyperconjugative effect of virtual intermediates, there are still some errors because the heats of hydrogenation reaction also include the steric and electronic effects. The directly estimated approach of  $\pi$ -conjugative stable energies based on NBO second order perturbation analysis will be very useful to study the  $\pi$ -conjugation strength of germabutadienes and their correlation with the rotational barriers.

We evaluate the  $\pi$ -conjugation stabilization strength by NBO donor–acceptor interaction energies.<sup>9</sup> The NBO donor–acceptor interaction energies are calculated on the foundation of Lewis- and Pauling-like localized structural and hybridization concepts and are presented with the classical  $\pi$ -conjugation concepts by a refinement of NBO analysis. For a characteristic conjugated  $\pi$ -bond network with two pairs of conjugated  $\pi$  bonds ( $\pi_a$  and  $\pi_b$ ; see Scheme 4), the delocalized molecular orbitals can be pictured using the



**Figure 6.** Correlation between the internal rotation barrier and the difference both the sum of the conjugative stabilization energies in the global minima and the sum in the TS of **4–12**.

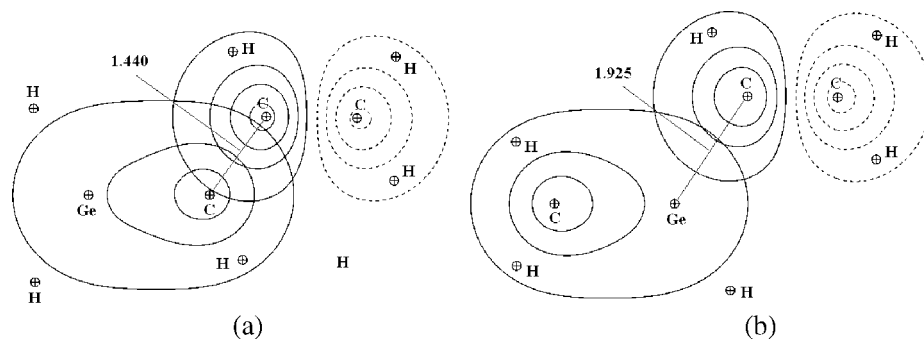
refined idealized Lewis structures by NBO donor–acceptor interaction of  $\pi_a \rightarrow \pi_b^*$  and  $\pi_b \rightarrow \pi_a^*$ . According to the perturbation theory, the lowering energy due to  $\pi_a \rightarrow \pi_b^*$  interaction, which is also referred to as the quantum-mechanical resonance energy (denoted as QMRE), is estimated as

$$\Delta E(\pi_a \rightarrow \pi_b^*) = -2 \frac{\langle \pi_a | \hat{F} | \pi_b^* \rangle^2}{\Delta \epsilon} \quad (4)$$

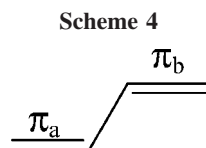
where  $\Delta \epsilon = \langle \pi_b^* | \hat{F} | \pi_b^* \rangle - \langle \pi_a^* | \hat{F} | \pi_a^* \rangle$  is the energy difference of interacting NBOs, and the matrix element  $\langle \pi_b | \hat{F} | \pi_b^* \rangle$  governs conjugative stability. The strength of  $\pi$ -type conjugation and its variations with rotation can be conveniently visualized in terms of the NBO second order perturbation stabilization energies  $\Delta E(\pi_a \rightarrow \pi_b^*)$  and the charge transfer from  $\pi_a$  to  $\pi_b^*$ .<sup>9</sup>

The QMREs ( $\pi_a \rightarrow \pi_b^*$  and  $\pi_b \rightarrow \pi_a^*$ ) of **4–12** (including their parent butadiene) are given in Supporting Information. The sum of stabilization energies, that is,  $\Delta E_{\pi_a \rightarrow \pi_b^*} + \Delta E_{\pi_b \rightarrow \pi_a^*}$  is chosen as an indicator of the degree of the  $\pi$ -conjugation. For mono-, di-, and trigermabutadienes groups, the sums of QMRE of their global minima follow the trend: **4** (40.31 kcal/mol) > **5** (12.18 kcal/mol), **8** (62.60 kcal/mol) > **6** (17.71 kcal/mol) > **9** (11.89 kcal/mol) > **7** (9.90 kcal/mol), and **11** (18.27 kcal/mol) > **10** (10.56 kcal/mol).

The QMRE sums of germabutadienes drastically decrease with the rotation from global minima (the *s-trans*, the twisted *s-trans*, and *s-gauche* conformation) to TS. The QMRE sums of the global minima of germabutadienes lie in the range from 9.90 to 62.60 kcal/mol, while the QMRE sums in the respective TSs are much smaller (from 0.29 to 3.34 kcal/mol) with the exception of tetragermabutadiene **12** [*s-gauche* minima ( $C_2$ ), 6.48 kcal/mol; *s-trans* ( $C_1$ ), 6.06 kcal/mol]. For the parent butadiene, we found the same trend that the sum of QMREs changes from 30.14 kcal/mol at the *s-trans* conformation to 2.16 kcal/mol at TS. To prove the reliability of QMRE as a criterion of  $\pi$ -conjugative strength, we studied the change of  $\pi$ -conjugation based on single and double bond lengths. The change in the central and external double bond lengths from global minima to TS ( $\Delta r(\text{TS}^-s\text{-trans})/r(s\text{-trans})$  or  $\Delta r(\text{TS}^-s\text{-gauche})/r(s\text{-gauche})$ ) and the charge occupancies of  $\pi_a$ ,  $\pi_b$ ,  $\pi_a^*$  and  $\pi_b^*$  are given in Supporting Information. The  $\Delta r$  values for the central single bonds are positive, and the  $\Delta r$  values for the external double bonds



**Figure 7.** Principal  $\pi$ -conjugative interaction shown in NBO contours: (a) the *s-trans* conformer of **4**; (b) the *s-trans* conformer of **5**.



are negative. The central single bond lengths of **4–12** molecules,  $r(M_2-M_3)$ , lengthen while rotating from global minima to TS and become similar to  $r(M-N)$  bond lengths in  $MH_3-NH_3$  ( $M, N=Ge, C$ ; see Tables 2 and 3). These facts suggest that most of the  $\pi$ -conjugations in germabutadienes minima vanish at TSs. The same trend between QMRE and  $\Delta r$  indicates that QMRE is a good criterion to estimate the  $\pi$ -conjugation for the global minima.

According to NBO donor–acceptor interaction theory,<sup>9</sup> the charge occupancy of the  $\pi^*$  NBO also indicates the strength of  $\pi$ -conjugation. The charge occupancy sums of the  $\pi_a^*$  and  $\pi_b^*$  NBO orbitals of the global minima of germabutadienes **4–12** locate at a range from 0.078 to 0.472 electrons, and those of TS are between 0.017 and 0.192 electrons. Because the larger  $\pi_a^*$  and  $\pi_b^*$  occupancies in minima correspond to the larger occupancy in the TSs, we come to the same conclusion as QMRE that the  $\pi$ -conjugation is almost removed at their TSs.

The NBO second order perturbation stabilization energies ( $\Delta E$ ) of germabutadienes **4–12** correlated well with the internal rotational barriers. For **4–12**, a good linear correlation coefficient ( $y = -0.3427 + 0.6508x$ ;  $R = 0.9590$ ) was found between the differences between the sum of the conjugative stabilization energies in the global conformer and the sum in the TSs and the rotational barriers in Figure 6. It is obvious that the  $\pi$ -conjugation effect is the main factor that dictates the internal rotation barriers.

The QMREs were found to depend sensitively on the connectivity pattern of the  $Ge=C$  external double bonds. The orientation in donor–acceptor interaction governs the degree of the  $\pi_a \rightarrow \pi_b^*$  ( $\pi_b \rightarrow \pi_a^*$ ) conjugation and consequently dictates the height of the rotation barriers, for example, the  $Ge=C$   $\pi$  bonding orbital in  $H_2Ge=CH-HC=CH_2$  **4** is polarized toward the central carbon atoms, with  $\pi_a$  orbital coefficients of 0.626 (Ge) and 0.780 (C); however, the  $\pi_a$  orbital coefficients in  $H_2C=GeH-HC=CH_2$  **5** are 0.802(C) and 0.597(Ge); all of the  $\pi_b^*$  orbital coefficients of  $C=C$  double bonds for **4–5** are about 0.700. The  $C-C$  central single bond length (1.440 Å) in **4** is shorter than the  $Ge-C$  bond length (1.925 Å) in **5** (see Table 2). Thus, both the polarity in NBO coefficients and central single bond length contribute significantly to the larger overlap between the  $\pi_a$  and the  $\pi_b^*$  orbital in **4** than in **5**, and a larger rotational barrier (see Figure 7). The factors governing the degree of

conjugation and rotational barrier of digermabutadiene and trigermabutadiene groups are similar. Therefore, we conclude that both the polarity in the  $\pi$  bond and the central single bond length govern the degree of  $\pi_a \rightarrow \pi_b^*$  ( $\pi_b \rightarrow \pi_a^*$ ) conjugation and the rotational barrier.

Similar to silabutadienes,<sup>11</sup> the total relative stability (E+ZPE) of the global minima in the monogermabutadiene, digermabutadiene, and trigermabutadiene groups follow the order **4** (0.0 kcal/mol, relative energy) > **5** (3.14 kcal/mol), **9** (0.0 kcal/mol, relative energy) > **7** (22.58 kcal/mol) > **8** (28.90 kcal/mol) > **6** (30.78 kcal/mol), and **10** (0.0 kcal/mol, relative energy) > **11** (8.02 kcal/mol). This trend is different from the  $\pi$ -conjugation stabilization trend because there are more differences among several set of bond energies, for example, the set of bond energy of 1-germabutadiene **4**, [( $Ge=C$ )+( $C=C$ )+( $C-C$ )+4( $C-H$ )+2( $Ge-H$ )], is estimated to be 44.05 kcal/mol in favor of 2-germabutadiene **5**, [( $Ge=C$ )+( $C=C$ )+( $Ge-C$ )+5( $C-H$ )+( $Ge-H$ )], at the B3LYP/6-311+G(d,p) level.

## Conclusions

In the present article, a systematic study of the internal rotations of all possible germabutadienes is reported. The B3LYP/6-311+G(d,p) calculations indicate that the PESs for germabutadienes **4–12** internal rotations have different characteristics. The PESs of **4–8**, which include  $C=Ge$  and  $C=C$  double bonds, have symmetric images about  $\theta = 0^\circ$ . The *s-trans* conformations of **4–7** are found to be the global minima on the rotational PES. In contrast to butadiene, the relatively long  $Ge-C$  and  $Ge-Ge$  central bonds of 2-germabutadiene **5**, 1,3-digermabutadiene **6**, and 2,3-digermabutadiene **7** remove the steric hindrance that causes germabutadienes to distort from the *s-cis* conformer to *s-gauche* so that they have two stable planar minima of *s-trans* and *s-cis* conformations. Along the rotation PESs of 1,2-digermabutadiene **9**, 1,2,3-trigermabutadiene **10**, 1,2,4-germabutadiene **11**, and tetragermabutadiene **12**, two different *s-gauche* minima were found. Their  $Ge=Ge$  double bonds have a strong propensity to pyramidalize in the whole course of the internal rotation. The optimized structure of the *s-gauche* 2 global minima of tetragermabutadiene **12** supports the recently reported X-ray crystal structure.

The nature of  $\pi$ -conjugation of germabutadienes were explored using the NBO second order perturbation approach, and the  $\pi$ -conjugative strength of their global minima (the *s-trans*, the twisted *s-trans*, and *s-gauche* conformation) were compared on the basis of the quantum-mechanical resonance energy. The stabilization due to  $\pi$ -conjugation follows the order **4** > **5**; **8** > **6** > **9** > **7**; and **11** > **10**, which is in line with the sequence of silabutadienes. A linear correlation was

found between the internal rotation barriers and the second order perturbation stabilization energies. The  $\pi$ -conjugations in germabutadienes are concluded to be the main factor governing the barrier height for internal rotation. The  $\pi$ -conjugative stabilization calculated by stepwise hydrogenation also supports the NBO second order perturbation conclusion.

### Computational Details

We have performed the calculations using density functional theory (DFT)<sup>18</sup> B3LYP (Becke's three-parameter hybrid function<sup>19</sup> with the nonlocal correlation of Lee–Yang–Parr<sup>20</sup> methods. On the basis of the reports by Weidenbruch<sup>7</sup> and Frenking,<sup>21</sup> the 6–311+G (d,p)<sup>22</sup> basis set is sufficient for our current purposes. All of the calculations were carried out using Gaussian 03.<sup>23</sup>

For the purpose of this study, the term internal rotation refers to the internal rotation around the central M–N (M, N=C, Ge) single bond. The internal rotational angle ( $\theta$ ) is defined as the  $M_1=M_2-M_3=M_4$  (M=C, Ge) torsion angle. The internal rotation PESs,  $E(\theta)$ , were obtained by performing anticlockwise rotations

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around the central single bond and geometry optimizations at a set of selected  $\theta$  values ranging from  $180^\circ$  to  $-180^\circ$ , which were kept constant, while all other geometric parameters were fully optimized. Frequency analyses were performed for the stationary point along the PESs, in order to determine these points to be either minima or TSs and also for the evaluation of the zero point energies (ZPEs) for correction to the relative energies. We had also calculated the NBO conjugation stabilization energies by the Natural Bond Orbital program (NBO 3.1),<sup>24</sup> which is implemented in Gaussian 03.

**Acknowledgment.** We are very grateful to Professor Y. Apeloig and Dr. M. Karni of Technion-Israel Institute of Technology for their enthusiastic scientific discussion. We also acknowledge the research funding from MOE/Acrf Tier 1, RG28/07 for financial support.

**Supporting Information Available:** Cartesian coordinates, total energies including zero-point-correction of all calculated species, conjugation stabilization energies, the occupancy charge in NBOs for global minima and TSs, the change in the central single bond lengths and external double bond lengths upon rotation from global minima to TS, and the polarization coefficients of the  $\pi$  and  $\pi^*$  bond. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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