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# Coupling Trans-Bent Double Bonds in Tetragermabutadiene

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The coupling of two trans-bent double bonds is examined theoretically through ab initio calculations on tetragermabutadiene $H_2Ge{=}HGe{-}GeH{=}GeH_2$. If a trans-bent arrangement is maintained for each $-GeH{=}GeH_2$ fragment, there are two ways of coupling two trans-bent units, starting from an s-trans conformation around the central bond. The first one preserves an all-trans arrangement of the four pyramidalized germanium atoms. Along the rotational pathway around the central bond, this configuration has no symmetry ($C_1$), except for dihedral angles of 0° ($C_s$) or 180° ($C_i$). As in butadiene, the potential curve along this coordinate is symmetrical with respect to 0° and 180°, with a preferred s-trans form, t-1 and two equivalent gauche forms, g-1, lying about 3 kcal/mol above in energy (MP4/DZP//SCF/DZP). The s-cis saddle point separating the two gauche forms is higher in energy than the barrier separating the s-trans and gauche forms. In the second coupling scheme, the molecule maintains a $C_2$ symmetry axis for any torsional angle, but the energy curve no longer exhibits any symmetry along the entire $[0-2\pi]$ rotational coordinate. As anticipated by simple overlap arguments within the pseudo $\pi$ orbital set, the two minima, reminiscent of s-trans and gauche arrangements, are both skewed. The gauche conformer, g-2, is now below the trans one, t-2, but still above t-1. The minima g-2 and t-2 are separated by two rotational barriers, depending on the direction of rotation. Interconversion between these coupling configurations proceeds through planar inversion at one $GeH{=}GeH_2$ unit. Two pathways are possible, linking either the two s-trans forms or the two gauche forms. The barrier along both the t-1→t-2 and g-2→g-1 pathways is calculated at 4 kcal/mol, in line with the barrier to planarity found in isolated digermene. In both coupling schemes, adiabatic singlet−triplet separations are calculated at 13 kcal/mol. Intramolecular cyclization of g-2 into the cyclobutene form proceeds with a slight activation barrier, and a large exothermicity of 27 kcal/mol. Alternatives in which one or both double bonds of the butadiene form are replaced by a double hydrogen bridge are not favored. By contrast, the two bond-stretch isomers of the bicyclobutane form are significantly lower in energy than the butadiene forms.

## Introduction

In previous theoretical studies, we addressed the substitution of two carbon atoms by two germanium atoms at positions 2,3 and 1,4 on the 1,3-butadiene frame.[1,2] It was shown how the central bond conjugation is reduced in 2,3-digermabutadiene $H_2C{=}HGe{-}GeH{=}CH_2$ but enhanced in 1,4-digermabutadiene $H_2Ge{=}HC{-}CH{=}GeH_2$. In the present paper, we wish to report a theoretical investigation, through quantum calculations, of tetragermabutadiene $H_2Ge{=}HGe{-}GeH{=}GeH_2$, the third of the symmetrically substituted germabutadienes. This compound constitutes the simplest way of coupling two trans-bent double bonds. These nonclassical double bonds have been found to be the preferred arrangements for disilene and digermene, and are local minima on the potential surface for all of the heavier analogues of ethylene, from $Si_2H_4$ to $Pb_2H_4$.[3−5] We note that interest in heavier analogues of 1,3-butadiene has recently been stimulated by the X-ray structure determination of a hexaaryl derivative of tetrasilabutadiene $R_2Si{=}SiR{-}RSi{=}SiR_2$ (R = 2,4,6-triisopropylphenyl), showing a cis-gauche conformation.[6]

The trans-bent organization of the Ge═Ge double bond is expected to give a nonplanar structure for $(H_2Ge{=}GeH{-})_2$, with various possible conformations around the central Ge−Ge bond. Of particular interest is the mixing that here is equivalent to the $\pi$ delocalization in planar butadiene or digermabutadienes and the extent of such “conjugation” effects, if any. As was done previously for 1,4-digermabutadiene, we shall also inspect the triplet state and we shall address the cyclization of tetragermabutadiene into tetragermacyclobutene. In addition, two types of alternatives will be examined and their relative stabilities with respect to the linear butadiene frame estimated. These are, first, the bicyclobutane derivative, expected to be a favorable competitor, and already studied by Nagase et al.[7,8] within the framework of bond-stretch isomerism occurring in group 14 bicyclobutanes.[9,15] Last, in the heavier group 14 analogues of ethylene, arrangements with a double hydrogen bridge have proved to be advantageous alternatives to double bonds.[3,4] We will therefore examine the coupling of two such systems, HGe−(HH)−Ge−Ge−(HH)−GeH, as well as the mixed coupling of such a double bridge with a Ge═Ge double bond, $HGe{-}(HH){-}GeH{=}GeH_2$. These alternatives to a butadiene frame are only a small fraction of the possible structural isomers for $Ge_4H_6$, which comprise various germylgermylenes and other ring derivatives.

Full geometry optimizations were carried out at the Hartree−Fock level, with double-zeta plus polarization (DZP) basis sets, using effective core potentials. At each stationary point so obtained, correlation effects were estimated through Möller−Plesset fourth-order perturbation theory (MP4), leading to refined energies that will be discussed throughout the paper. For the triplet states, and in a few other cases, additional calculations were performed using density functional theory

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(DFT). Technical details concerning the methods, basis sets, and procedures are given in the appendix. Since the current standard for geometry optimization is tending to DFT instead of SCF−HF, we have checked in the case of the parent digermene $Ge_2H_4$ that the two procedures lead to almost identical final relative energies for the various stationary points (see the second part of the appendix).

The following points will be addressed successively: (1) energies and structures; (2) the nature and extent of the interaction between the two $H_2Ge{=}GeH-$ subunits; (3) triplet states; (4) electrocyclization into tetragermacyclobutene; (5) bicyclobutane and double hydrogen-bridge alternatives; (6) concluding perspectives.

## Potential Surface

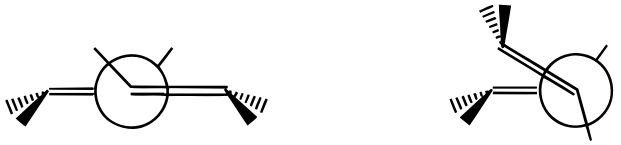
From butadiene to tetragermabutadiene, because of the pyramidalization of all germanium centers, there are two ways of building s-trans, s-cis, or gauche conformers along the central Ge−Ge rotational coordinate. Let us consider an s-trans arrangement at the central Ge−Ge bond. If we assume that each terminal fragment $-HGe{=}GeH_2$ essentially preserves its trans-bent character, their coupling can be made in two different ways according to whether the central junction is perfectly trans-bent or not. In the first case, we have an all-trans arrangement at all germaniums along the chain, resulting in a $C_i$ symmetrical system, **1a**.

t-1 g-1

**a** **b**

**1**

In the second case, the central $=HGe-GeH=$ junction is not in a trans-bent geometry nor a cis-bent one, but rather in a gauche arrangement, conferring a $C_2$ symmetry to the whole molecule, **2a**.



**a** **b**

**2**

In this case, the $C_2$ symmetry axis is maintained along the rotational pathway so that for this coupling scheme, the gauche or s-cis conformers keep a $C_2$ geometry. Such s-trans and gauche conformers, **2**, will be labeled t-2, and g-2 respectively, (“2” being here reminiscent of the $C_2$ symmetry whatever the GeGeGeGe dihedral angle). In the former coupling scheme, as soon as **1** departs from its perfect s-trans arrangement, there is no longer an element of symmetry and the entire rotational pathway along the central Ge−Ge bond corresponds to a $C_1$ symmetry, except for the perfect s-cis arrangement, where there is a $C_s$ symmetry. Owing to this essentially $C_1$ pathway, the s-trans and gauche conformers for this type of coupling will be labeled t-1 and g-1 respectively (“1” being reminiscent of $C_1$ symmetry).

Full exploration of the potential surface shows that these four structures are the only true minima on the tetragermabutadiene potential surface. Note that the existence of an s-cis true minimum, as observed for 2,3-digermabutadiene, no longer holds and we are back to the case of classical 1,3-butadiene, with only s-trans and gauche minima.

**TABLE 1: Relative Energies for Tetragermabutadiene and Intracyclization Products**[a]

| | | | SCF | MP4 | MP4 + ZPC |
|---|---|---|---|---|---|
| TS for cyclization | TC | $C_1$ | 3.9 | 1.9 | 1.6 |
| tetragermacyclobutene | (bridged) | $C_{2v}$ | −25.4 | −21.7 | −21.1 |
| tetragermacyclobutene | | $C_2$ | −31.1 | −26.4 | −24.8 |
| lowest triplet states $^3A$ | $^3$(g-2) | $C_1$ | | 13.5 | 13.0 |
| | $^3$(t-1) | $C_1$ | | 13.1 | 12.7 |
| inversional TS | TIg | $C_1$ | 3.0 | 4.7 | 4.7 |
| | TIt | $C_1$ | 2.4 | 4.1 | 4.1 |
| rotational TS | TR2gt | $C_2$ | 4.0 | 4.2 | 4.1 |
| | TR1gg | $C_s$ | 3.3 | 3.3 | 3.2 |
| | TR1tg | $C_1$ | 2.6 | 2.9 | 2.8 |
| | TR2tg | $C_2$ | 2.7 | 2.5 | 2.5 |
| true minima | g-1 | $C_1$ | 2.3 | 2.6 | 2.6 |
| | t-2 | $C_2$ | 1.4 | 1.9 | 1.9 |
| | g-2 | $C_2$ | 0.5 | 0.6 | 0.5 |
| | t-1 | $C_i$ | 0. | 0. | 0. |

[a] In kcal/mol. ZPC denotes zero-point energy correction. TS denotes transition state.

Conjugation through the central bond would be insufficient to force any germanium to planarity. The $C_{2h}$ s-trans planar form is calculated to lie 8.8 kcal/mol above the preferred $C_i$ form, which is about twice the barrier to planarity calculated in digermene under similar conditions (4.2 kcal/mol). With two imaginary vibrational frequencies (238i and 179i cm$^{-1}$), this planar form is not a transition state. The modes associated with these two imaginary frequencies correspond to relaxations toward t-1 and t-2, respectively. The $C_{2v}$ s-cis planar form is only 0.7 kcal/mol above the s-trans planar form, indicating a weak s-cis repulsion, as is the case for 2,3-digermabutadiene. Again, this planar structure is not a transition state but a saddle point of index three, the imaginary frequencies (225, 216, and 36 cm$^{-1}$) corresponding to relaxations toward g-1, g-2, and a rotational transition state, respectively. Whatever interaction exists between the two $-HGe{=}GeH_2$ fragments, it does not affect their trans-bent character, although it lowers the pyramidality of all germanium centers, as we shall detail later.

The relative energies of the four minima and other stationary points are given in Table 1, with the corresponding geometrical parameters listed in Table 2. The degree of pyramidalization at each germanium is further summarized in Table 3, and harmonic vibrational frequencies are collected in Table 4. As expected, the most symmetrical all-trans arrangement, t-1, is the most stable of the four minima. Next we find g-2, only 0.6 kcal/mol higher, then t-2, 1.9 kcal/mol higher, and finally g-1, 2.6 kcal/mol higher.

In t-1, the GeGeGeGe dihedral angle must be 180°; this is not the case in t-2, and the dihedral angle can deviate in two different ways, **3**. The actual shape of t-2 is **3a**. Similarly, g-2 can adopt two different forms, depending which side the terminal $GeH_2$ groups are tilted, **4**. The observed minimum for g-2 corresponds to **4b**. Note that the four possibilities in **3** and **4** reduce to two configurational possibilities, modulated only by the extent of the GeGeGeGe dihedral angle. Actually this torsional angle is calculated to be 118° in t-2 and 80° in g-2, a large value for a gauche form, which can be accounted for by the repulsion between two opposite terminal Ge−H bonds. The two remaining conformations **3b** and **4a** are expected to be associated with rotational barriers along the $C_2$ torsional pathways. In contrast, g-1 is unique in that its symmetrical alternative would be its mirror image, with strict equivalency

**TABLE 2: SCF Calculated Geometries**[a]

| | | | Ge=Ge | Ge−Ge | $H_1$−$Ge_1$ | $H_2$−$Ge_1$ | $Ge_2$−H | GeGeGe | $H_1Ge_1Ge_2$ | $H_2Ge_1Ge_2$ | HGeH | $Ge_1Ge_2H$ | GeGeGeGe |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $H_3Ge-GeH_3$ | | $D_{3d}$ | | 2.501 | 1.555 | | | | | | | | |
| $H_2Ge=GeH_2$ | | $C_{2h}$ | 2.327 | | 1.554 | | | | 117.3 | | 109.1 | | |
| $H_2Ge=GeH-HGe=GeH_2$ | | | | | | | | | | | | | |
| minima | t-1 | $C_i$ | 2.337 | 2.484 | 1.555 | 1.554 | 1.559 | 116.4 | 119.4 | 117.9 | 109.0 | 113.7 | 180. |
| | g-1 | $C_1$ | 2.334 | 2.491 | 1.557 | 1.555 | 1.558 | 120.8 | 118.6 | 117.0 | 109.1 | 114.5 | 56.4 |
| | | | 2.316 | | 1.552 | 1.551 | 1.556 | 115.9 | 120.9 | 119.0 | 110.0 | 115.2 | |
| | t-2 | $C_2$ | 2.326 | 2.478 | 1.554 | 1.553 | 1.555 | 120.4 | 119.3 | 117.5 | 109.6 | 116.0 | 117.8 |
| | g-2 | $C_2$ | 2.339 | 2.488 | 1.555 | 1.555 | 1.559 | 116.7 | 119.2 | 118.1 | 108.9 | 112.8 | 80.4 |
| transition states | TR1tg | $C_1$ | 2.331 | 2.504 | 1.556 | 1.554 | 1.559 | 119.6 | 119.9 | 118.6 | 109.0 | 112.9 | 94.5 |
| | | | 2.328 | | 1.554 | 1.554 | 1.557 | 115.8 | 120.1 | 118.5 | 109.1 | 113.2 | |
| | TR1gg | $C_s$ | 2.318 | 2.490 | 1.552 | 1.552 | 1.556 | 122.6 | 118.6 | 118.3 | 110.3 | 115.3 | 0. |
| | TR2tg | $C_2$ | 2.330 | 2.509 | 1.556 | 1.553 | 1.558 | 119.1 | 120.3 | 118.6 | 109.1 | 113.0 | 53.1 |
| | TR2gt | $C_2$ | 2.318 | 2.504 | 1.552 | 1.553 | 1.556 | 117.9 | 119.4 | 118.4 | 109.9 | 114.8 | 173.3 |
| | TIt | $C_1$ | 2.346 | 2.455 | 1.557 | 1.556 | 1.557 | 120.1 | 116.9 | 116.0 | 108.9 | 116.0 | 140.0 |
| | | | 2.267 | | 1.543 | 1.542 | 1.544 | 122.4 | 123.7 | 121.5 | 114.3 | 119.0 | |
| | TIg | $C_1$ | 2.345 | 2.463 | 1.557 | 1.556 | 1.558 | 119.1 | 117.5 | 116.5 | 108.7 | 114.8 | 63.1 |
| | | | 2.267 | | 1.543 | 1.542 | 1.546 | 120.2 | 123.7 | 121.8 | 114.1 | 118.6 | |

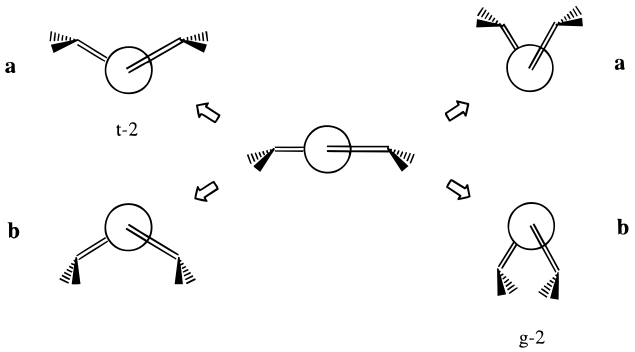
[a] Selected parameters, in angströms and degrees. For labeling, $H_1Ge_1=Ge_2H-$ corresponds to a cis arrangement.

**TABLE 3: Pyramidalization at each Germanium Center**[a]

| | | $Ge_1$ | $Ge_2$ | $Ge_3$ | $Ge_4$ |
|---|---|---|---|---|---|
| $sp^2$ | | 0 | | | |
| $sp^3$ | | 32 | | | |
| p | | 90 | | | |
| $\cdot GeH_3$ | | 28 | | | |
| $H_2Ge=GeH_2$ | | 16 | | | |
| $(H_2Ge=GeH)_2$ | t-1 | 14 | 20 | | |
| | g-1 | 15 | 15 | 14 | 10 |
| | t-2 | 14 | 13 | | |
| | g-2 | 14 | 20 | | |
| TR1tg | | 13 | 18 | 17 | 12 |
| TR1gg | | 13 | 12 | | |
| TR2tg | | 12 | 18 | | |
| TR2gt | | 12 | 14 | | |
| TIt | | 18 | 16 | 0 | 0 |
| TIg | | 17 | 18 | 0 | 0 |
| TC | | 12 | 20 | 55 | 6 |
| $^3$A triplet state | | 26 | 22 | 23 | 24 |
| tetragermacyclobutene | | 3 | | | |

[a] Defined as α(°) = 360 − Σ valence angles on Ge.

in energy. The dihedral angle in g-1 is calculated to be 56°. A schematic of these geometries is given in Figure 1.



**3** **4**

A subtle distinction deserves to be emphasized here. The $C_1$ torsional coordinate, **1**, is fully symmetrical with respect to GeGeGeGe dihedral angles of 0° and 180°. As in the cases of butadiene, 1,4-digermabutadiene, or 2,3−digermabutadiene, changes along the [0−π] interval are sufficient to describe the entire 2π torsional pathway. In contrast, along the $C_2$ rotational pathway, **2**−**4**, dihedral angles of 0° or 180° are no longer symmetrically singular points, so that the entire coordinate along the $C_2$ path is now unsymmetrical and requires a full exploration along the [0−2π] interval. In other words, the rotational coordinate for the $C_1$ *unsymmetrical* coupling scheme admits *symmetry* with respect to dihedral angles of 0° or 180°, whereas the rotational coordinate for the $C_2$ *symmetrical* coupling scheme is fully *unsymmetrical* along the [0−2π] period. This has consequences for the possible rotational barriers.

For the $C_1$ rotamers, again as in the case of butadiene, one expects two barriers: one, labeled TR1tg, roughly corresponding to an orthogonal arrangement, should connect the s-trans form to the gauche form; the other one, labeled TR1gg, corresponding to an s-cis type arrangement, should connect the two equivalent gauche forms. This is indeed what comes out from the calculations. In contrast to butadiene and digermabutadienes, however, the orthogonal barrier associated with TR1tg ($\theta = 94°$) is lower in energy than the $C_s$ s-cis barrier associated with TR1gg ($\theta = 0°$ necessarily). These two rotational transition states lie 2.9 and 3.3 kcal/mol, respectively, above the preferred $C_i$ s-trans minimum. For butadiene, the corresponding barriers were 5.8 and 3.5 kcal/mol, respectively. In Figure 2, the present $C_1$ rotational pathway is compared to those calculated under similar conditions for butadiene and for the two symmetrical digermabutadienes. Tetragermabutadiene has relative energies close to those of butadiene, except for the orthogonal transition state, whose barrier is half that calculated in butadiene. This effect probably originates in stronger hyperconjugation in an orthogonal pyramidalized form. On the other hand, despite the peculiar shapes of the two lower curves, no curve crossing is observed in Figure 2, which displays a nice regularity in the evolution of the curves.

For the $C_2$ coupling configuration, one could expect a distortion of the s-trans form into **3a** *or* **3b**, while both gauche forms **4a** and **4b** were a priori potential minima. An SCF exploration of the potential surface led to **3a** as the only s-trans conformer and **4b** as the only gauche conformer. Starting an optimization from **3b** leads to **4b**, while starting an optimization from **4a** leads to **3a**. As a further check, we explored a full 2π rotation around the central Ge−Ge in a rigid rotator model, starting from **3a** or **4b**, at both the SCF and MP4 levels. In all cases, one obtains a nonsymmetrical curve with only two minima.

In contrast to the $C_1$ coupling scheme and with butadiene and digermabutadienes, there is here only a single gauche form.

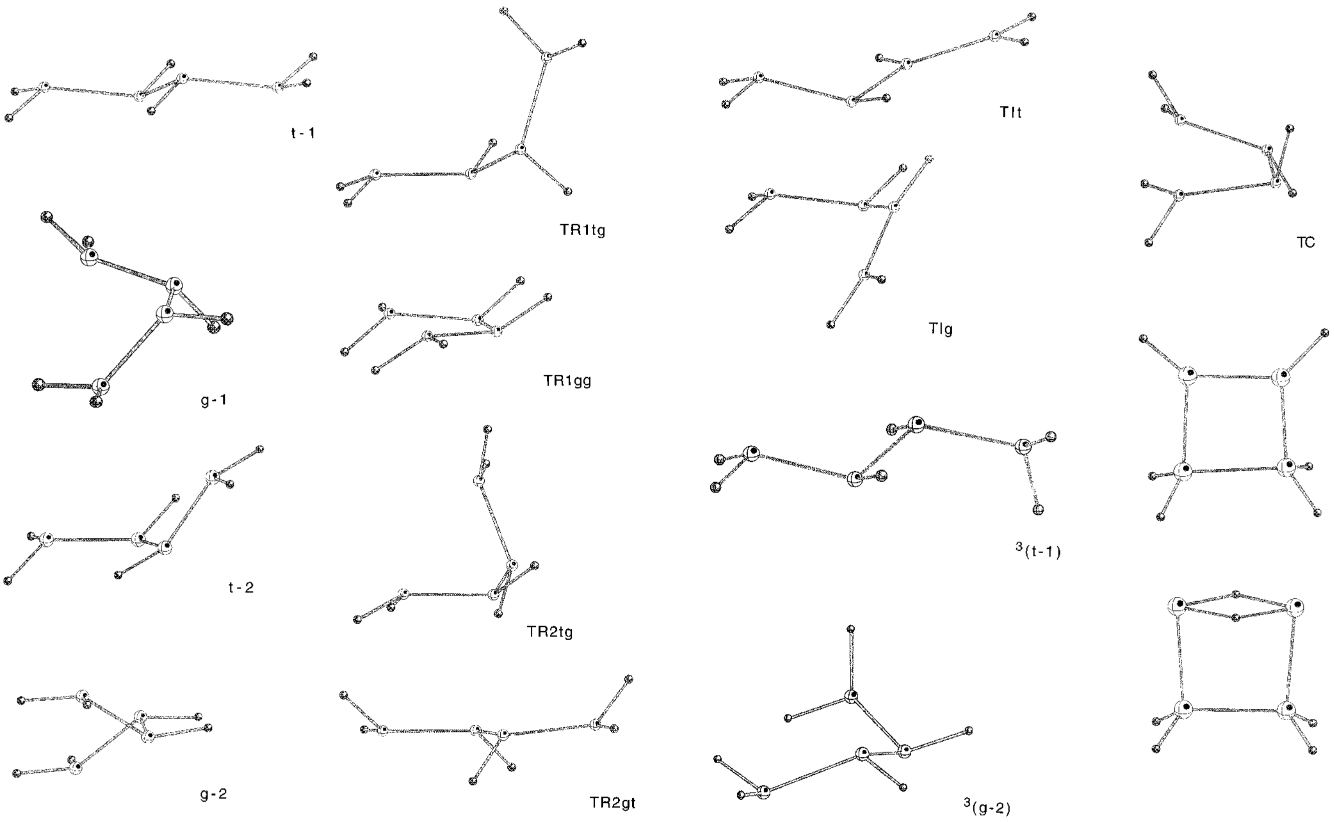


**Figure 1.** Geometries of stationary points.

**TABLE 4: Harmonic Vibrational Frequencies with Infrared Intensities and Vibrational Assignments**

| t-1 | | | g-1 | | | t-2 | | | g-2 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | freq (cm$^{-1}$) | ir int | | freq (cm$^{-1}$) | ir int | | freq (cm$^{-1}$) | ir int | | freq (cm$^{-1}$) | ir int | main assignment |
| 1a$_u$ | 24 | 0.0 | 1a | 26 | 0.0 | 1a | 28 | 0.0 | 1a | 27 | 0.0 | Ge−Ge torsion |
| 2a$_u$ | 41 | 0.1 | 2a | 51 | 0.0 | 1b | 54 | 0.2 | 2a | 56 | 0.0 | GeGeGe bend |
| 1a$_g$ | 80 | | 3a | 80 | 0.2 | 2a | 78 | 0.0 | 1b | 70 | 0.3 | GeGeGe bend |
| 2a$_g$ | 191 | | 4a | 168 | 0.1 | 2b | 184 | 0.2 | 3a | 194 | 0.0 | |
| 3a$_u$ | 223 | 0.7 | 5a | 213 | 0.1 | 3a | 193 | 0.0 | 2b | 202 | 0.1 | |
| 3a$_g$ | 247 | | 6a | 238 | 0.2 | 4a | 252 | 0.0 | 4a | 236 | 0.2 | Ge−Ge str |
| 4a$_u$ | 253 | 0.9 | 7a | 293 | 0.2 | 3b | 260 | 2.6 | 3b | 265 | 0.4 | Ge=Ge str |
| 4a$_g$ | 334 | | 8a | 331 | 0.1 | 5a | 327 | 0.0 | 5a | 326 | 0.0 | GeGe str |
| 5a$_u$ | 405 | 2.8 | 9a | 431 | 0.6 | 4b | 405 | 1.1 | 4b | 414 | 1.7 | Ge=Ge str |
| 6a$_u$ | 446 | 1.9 | 10a | 445 | 0.4 | 5b | 449 | 2.1 | 6a | 439 | 0.1 | GeGeH bend |
| 5a$_g$ | 464 | | 11a | 469 | 0.6 | 6a | 467 | 0.0 | 5b | 478 | 0.0 | |
| 6a$_g$ | 495 | | 12a | 476 | 0.2 | 6b | 490 | 1.2 | 7a | 488 | 0.9 | |
| 7a$_g$ | 508 | | 13a | 496 | 1.3 | 7a | 500 | 0.0 | 6b | 503 | 1.8 | |
| 7a$_u$ | 519 | 2.7 | 14a | 505 | 0.1 | 8a | 524 | 0.0 | 8a | 512 | 0.0 | |
| 8a$_u$ | 653 | 5.5 | 15a | 689 | 5.3 | 7b | 650 | 7.1 | 9a | 689 | 0.3 | GeGeH bend |
| 8a$_g$ | 770 | | 16a | 708 | 4.3 | 9a | 766 | 0.0 | 7b | 725 | 8.5 | Ge$_2$Ge$_3$H bend |
| 9a$_u$ | 929 | 7.2 | 17a | 929 | 4.2 | 8b | 929 | 9.2 | 8b | 931 | 3.0 | Ge$_2$Ge$_3$H bend |
| 9a$_g$ | 938 | | 18a | 932 | 2.4 | 10a | 930 | 0.0 | 10a | 938 | 3.1 | Ge$_2$Ge$_1$H bend |
| 10a$_u$ | 2172 | 2.8 | 19a | 2175 | 1.8 | 11a | 2184 | 0.3 | 9b | 2171 | 0.6 | GeH str |
| 10a$_g$ | 2173 | | 20a | 2177 | 5.1 | 9b | 2185 | 7.1 | 11a | 2174 | 3.9 | GeH str |
| 11a$_u$ | 2187 | 11.2 | 21a | 2189 | 6.6 | 10b | 2192 | 5.7 | 10b | 2183 | 7.5 | GeH str |
| 11a$_g$ | 2189 | | 22a | 2192 | 3.0 | 12a | 2195 | 0.1 | 12a | 2188 | 0.5 | GeH str |
| 12a$_g$ | 2194 | | 23a | 2203 | 4.2 | 13a | 2197 | 0.0 | 11b | 2189 | 4.8 | GeH str |
| 12a$_u$ | 2196 | 9.7 | 24a | 2213 | 3.3 | 11b | 2202 | 11.3 | 13a | 2191 | 7.2 | GeH str |

As a consequence, only two rotational transition states are expected along the full [0−2$\pi$] rotational interval, which should connect t-2 to g-2 in two possible ways, according to the chosen orientation of rotation. These two saddle points were determined and correspond to dihedral angles of −53° and 173°. In this case, because the gauche form g-2 is in fact close to orthogonal and the s-trans form t-2 is largely bowed, there is no s-cis transition state, they are both of TRtg type. Conventionally, we will label TR2tg the saddle point corresponding to $\theta = -53°$ and TR2gt that corresponding to $\theta = 173°$. TR2tg can be pictured as **4a** and lies 1.9 kcal/mol above the preferred g-2 form. TR2gt has a quasi s-trans arrangement like **2a** (see Figure 1) and is calculated to be 3.6 kcal/mol above g-2. With respect to t-2, these barriers reduce to 0.6 and 2.3 kcal/mol respectively, as summarized in the energy curve plotted in Figure 3. As there is no real symmetrical point on this curve, two turns have been drawn for convenience. Because there is a sense of rotation to be chosen, g-2 and t-2 have dihedral angles of opposite sign (recall **3a** and **4b**). In this figure, g-2 corresponds to 88° and t-2 to −118°. But the sense of rotation chosen is arbitrary, and we could have plotted the curve in an opposite orientation as

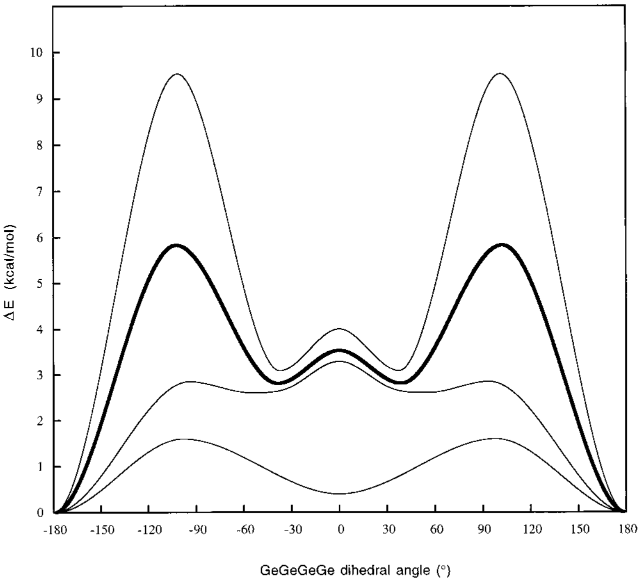


**Figure 2.** Conformational path along the central bond rotation in butadiene (bold), 1,4-digermabutadiene (bottom), 2,3-digermabutadiene (top), and tetragermabutadiene in the $C_1$ coupling scheme (middle).

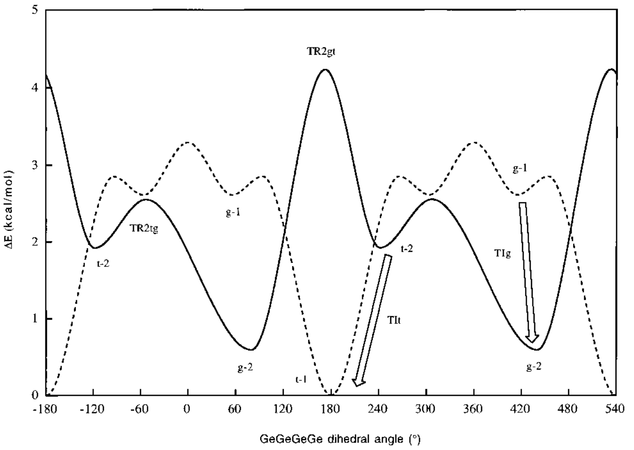


**Figure 3.** Conformational path along the central Ge−Ge bond rotation in tetragermabutadiene for the $C_2$ coupling scheme. For convenience, two revolutions are shown. The $C_1$ coupling curve is recalled in dashed line.

well, which would switch the curves with g-2 at −88° and t-2 at 118°, as illustrated in Figure 4.

Let us now try to rationalize the existence and the geometry of t-2 and g-2. One could be tempted to seek an explanation in the quasi anti arrangement of the two adjacent GeH−GeH bonds in **3a**, whereas they would be close to syn, a less favorable arrangement, in **3b**. **4a** could be just trapped by this minimum, which would leave **4b** for g-2. But in that case, why should this form, with its quasi orthogonal arrangement and its syn conformation at GeH-GeH, be so favored with respect to t-2, and why is it only 0.6 kcal/mol above t-1? The key to account for these data lies in simple one-electron arguments and overlap considerations from the pseudo $\pi$ orbital system.

Let us write the hybrid orbitals constituting this pseudo $\pi$ system in the simplest s-trans $C_1$ coupling scheme, t-1. These orbitals are sp$^3$-like hybrids derived from the $b_u/a_g$ set in digermene. They result from the deformation of the pure 4$p_z$ orbitals when all germanium atoms are pyramidalized. Their orientation in t-1 provides the best overlap because they are all parallel and coplanar two by two, in particular on the two middle germanium atoms, **5**. The s-cis $C_s$ arrangement in TR1gg would maintain this two-by−two coplanarity. In contrast, in the s-trans form of the $C_2$ coupling scheme, **2**, if nothing is changed in the relative arrangement of the hybrid orbitals within each terminal fragment $-HGe{=}GeH_2$, they have lost their coplanarity on the two middle germanium atoms, **6**. To recover the best overlap, a rotation about the central Ge−Ge bond is now necessary, and we understand easily why this rotation should occur as in **3a** rather than **3b**, and **4b** rather than **4a**. In the former cases coplanarity is recovered, **7**, **8**; in the latter cases, the overlap conditions would be worse. If such effects were the only driving forces, the corresponding rotational angles could be anticipated straightway from the tilt angle of the pseudo $\pi$ system. If $\alpha$ designates the deviation of the hybrid axis from perpendicularity to the Ge−Ge bond, the GeGeGeGe dihedral angles in t-2 and g-2 are estimated at 180-2$\alpha$ and 2$\alpha$, respectively.

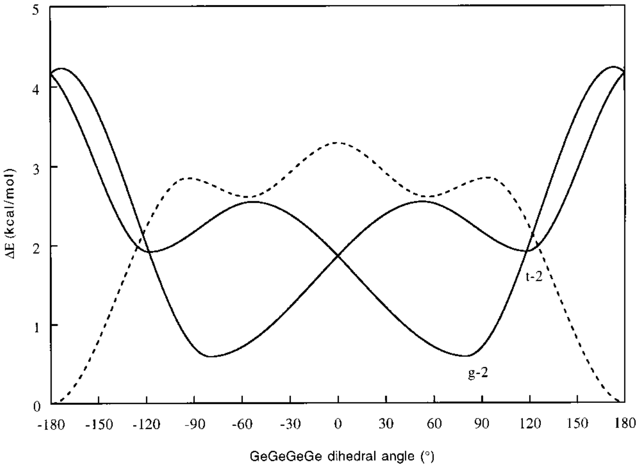
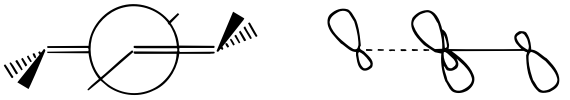
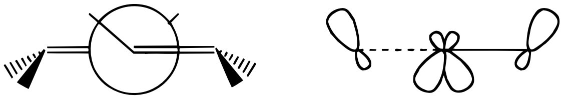
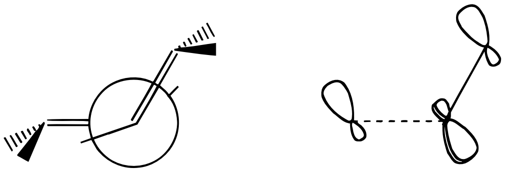
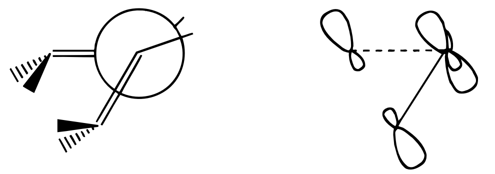


**Figure 4.** As Figure 3, with the $C_2$ coupling curve plotted along the [0−2$\pi$] interval in both clockwise and anticlockwise directions.


**5**

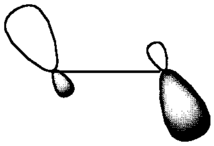

**6**


**7**

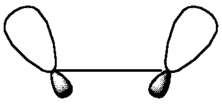

**8**

On a pure $sp^3$ atom, α would be about 20° (109.47−90). In our systems, one can measure this angle from the pseudo $C_3$ symmetry at each germanium in either digermene or tetragermabutadiene.[16] This gives values of 20−25°, which would imply at best dihedral angles of 130° in t-2 and 50° in g-2. The actual calculated values (118° and 80°, respectively) deviate significantly from these guesses, showing that the overlap effect is largely modulated by various mixing and repulsive effects. As there is no true $\pi$ symmetry, strong orbital mixing occurs within the a and b orbital sets in g-2 and t-2, and within the $a_g$ and $a_u$ sets in t-1. Actually, the $\pi$-type hybrids are not perfectly coplanar in g-2 and t-2 as can be seen in Figure 1 (the absence of real symmetry at $Ge_2$ and $Ge_3$ makes somewhat arbitrary the determination of their directions anyway). We think however that these overlap effects within the pseudo $\pi$ system catch the essence of the conformational driving force.

We would now like to understand why g-2 is favored over t-2. The overlap conditions at $Ge_2$−$Ge_3$ seem to be better in the latter arrangement, **7**, than in the former, **8**, but in fact this not so. In **8**, the coplanar hybrids are parallel to each other, with the large lobe of each hybrid pointing in trans directions with respect to the bond, **9**. In **7**, the coplanar hybrids are no longer parallel to each other and the large lobes of the hybrids are now in a cis position, on the same side of the bond, **10**.



**9**



**10**

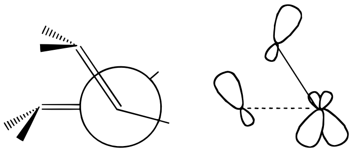
In such cases, the trans arrangement **9** is known to give a better overlap than the cis one **10**. This is a well-known and somewhat counterintuitive result, which has been illustrated, in particular, for the n+/n− lone pair splitting in hydrazine and diphosphine.[17] Therefore, g-2, **8**, is expected to be favored over t-2, **7**, in the same way that t-1, **5**, would be favored over a $C_s$ s-cis form, should that form be a minimum.

The stability of g-2 through the "conjugation" effects described above can be seen from other factors. Because of the orbital mixing, orbital energies associated with the two highest occupied molecular orbitals derived from the interacting $b_u/a_g$ sets of digermene are not accurate indicators and do not follow the relative stabilities of the four minima. Mulliken bond orders, on the other hand, reveal a stronger bonding in $Ge_2$−$Ge_3$ for g-2 and t-1, with a concomitant weakening of $Ge_1 = Ge_2$:

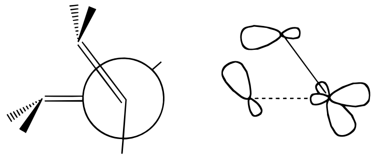
| | Ge=Ge | Ge−Ge |
|---|---|---|
| t-1 | 1.539 | 0.940 |
| g-1 | 1.565 | 0.932 |
| t-2 | 1.587 | 0.939 |
| g-2 | 1.537 | 0.942 |

From these trends, g-2 appears as the most "conjugated" of our isomers, although the effect is tiny. Repulsive effects between the terminal $GeH_2$ groups prevent the central Ge−Ge bond length from shortening in g-2, but its terminal Ge=Ge bond is the most lengthened of all the isomers (see Table 2). Another interesting geometrical feature is that in the preferred t-1 and g-2 structures, pyramidalization is enhanced in the inner atoms, not only with respect to the outer atoms but also with respect to digermene itself (see Table 3).

As can be seen in Figure 3, the full rotational $C_2$ path is mainly below that for the $C_1$, except near the s-trans zone. The rotational barrier at 173° is the highest one, and the phase opposition of both curves is quite manifest in this region. The second rotational barrier TR2tg occurs for a dihedral angle of 53°, which is quite close to that in the g-1 minimum (56°). Both singular points also have a very close energy, as can be seen in Table 1 and in Figure 3, where the two curves are nearly touching at this torsional coordinate. The reason these two configurations have comparable energy at this particular angle can be found, again, in the overlap matching between the two neighboring hybrids on $Ge_2$ and $Ge_3$. Their relative positions are nearly equivalent, as illustrated in **11**, **12**.

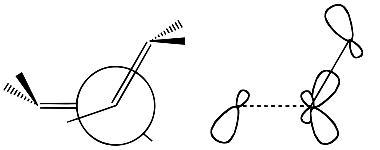


**11**

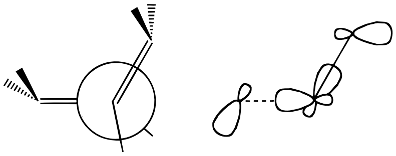


**12**

The crossing of the $C_1$ and $C_2$ curves near 120° may be accounted for by similar arguments, since at this torsional angle the relative orientations of the middle "$\pi$" orbitals are equivalent in both coupling configurations, **13**, **14**.



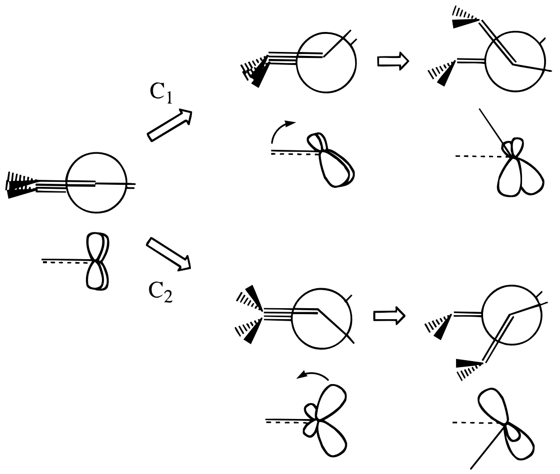
**13**



**14**

In the region of 0°, although $C_2$ coupling is obviously more favorable than $C_1$ coupling (because terminal $GeH_2$ groups are skewed in the former case, while eclipsed in the latter), the driving effects for leaving the s-cis arrangement are different in the two schemes. In the $C_1$ coupling, the rotation is basically induced by steric repulsion between the facing Ge−H bonds at the *terminal* germanium atoms. In the $C_2$ coupling, the rotation is induced by overlap improvement at the *middle* germanium atoms, to allow formation of the stable g-2 form, as schematized in **15**.

We now address the transition from one coupling scheme to the other; in other words, how can we jump from one curve to the other in Figure 3? Such interconversion will proceed through the inversion of one of the $HGe{=}GeH_2$ trans-bent fragments, thus constraining it to planarity. A priori, four channels for such inversion transition states are possible, namely t-1↔t-2, t-1↔g-2, g-1↔t-2, and g-1↔g-2. Two of these, t-1↔t-2, and g-1↔g-2, correspond to least motions and are therefore logically more likely. The search for all potential inversion transition states,

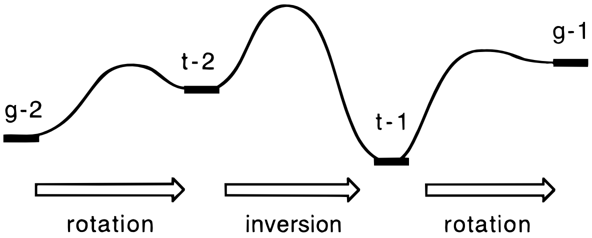


15

performed at the SCF−DZP level, actually led to only these two saddle points. We will label them TIt and TIg respectively, and the corresponding funnels are indicated by arrows in Figure 3.

As can be seen from Tables 2 and 3 and Figure 1, they exhibit a perfect planarity of one of the two $HGe{=}GeH_2$ fragments. Remarkably, the inversion barriers taken as the t-1→TIt and g-2→TIg energy promotions are calculated at 4.1 kcal/mol in both cases, which is almost identical with the barrier to planarity calculated in the parent digermene (4.2 kcal/mol). As can be checked in Table 2, the dihedral angles for these saddle points are intermediate between those of the end points. Taking this parameter as an indicator, the transition states occur at 64% of advancement along the reaction coordinate for the t-1→t-2 inversion, and at 72% along the g-2→g-1 pathway, in line with a Hammond-type behavior in both cases. The geometries of the planar fragments within TIt and TIg are quite close to those determined in planar digermene (GeGe = 2.251 Å, GeH = 1.539 Å, GeGeH = 122.2°, HGeH = 115.5°). In both cases, the central single bond is slightly strengthened.

The barrier to overcome to switch from one coupling configuration to the other is therefore 4.1 kcal/mol when starting from t-1 or g-2. This barrier reduces to 2.8 kcal/mol if one starts from t-2, or 1.5 kcal/mol if one starts from g-1. Any real molecule showing such effects would most likely bear bulky substituents and would presumably exist only in one of the s-trans forms. In this case, the inversion barriers should be sufficiently high to trap the system in one configuration. Finally, a walk through the *four* minima cannot avoid an inversion barrier, but it can elude the less favorable rotational barriers, as illustrated in the "least-effort" pathway **16**. We shall see below that the most kinetically favored route from g-2 is in fact the cyclization into tetragermacyclobutene.



16

## Bonding

We now consider the electronic structure, limiting our discussion to the preferred s-trans $C_i$ isomer. A closer look at its geometry (Table 2) reveals that the middle Ge−Ge bond is significantly shorter here than in digermane. However, the relative shortening is only of 0.7%, compared to 3.7% in butadiene.[18] Concurrently, the terminal Ge=Ge bonds are slightly longer than in digermene. To what extent can the present conjugation or delocalization effects be compared with those of butadiene? For orbital interactions, the main difference between ethylene and digermene, or between butadiene and tetragermabutadiene, is that in the carbon planar systems we have a unequivocal $\sigma-\pi$ separation, whereas this is no longer the case in their nonplanar heavier analogues. In butadiene, mixing within the $\pi$ system is therefore well separated from that in the $\sigma$ subset, and this is why we can analyze and measure the $\pi$ delocalization, or $\pi$ conjugation. This is no longer possible in the tetragerma analogue. Nevertheless, both in digermene and in tetragermabutadiene, the orbitals derived from the $\pi$ system still remain identifiable, although they mix within their symmetries. In the parent digermene, the mixing occurs within the $b_u$ and $a_g$ sets for "$\pi$" and "$\pi$*", respectively. In tetragermabutadiene, the mixing is even stronger, because there are only two overall orbital symmetries $a_g$ and $a_u$.

Because of this mixing, the four-electron four-orbital scheme is no longer valid as a quantitative one-electron picture. However, the splitting between the two highest occupied orbitals $5a_u$ and $6a_g$, $\pi_1$ and $\pi_2$ in the butadiene $\pi$ set, should still be an interesting indicator. This splitting is calculated to be 1.6 eV, which is less than half that calculated in butadiene. Of course, the lack of strict $\sigma-\pi$ separability prevents us from using any tools for selective localization of part of the wave function.

A more objective measure for conjugation or coupling effects can be obtained from the bond separation energy (BSE) given by the energy of the isodesmic reaction:

$$H_2Ge{=}GeH_2 + H_3Ge{-}GeH_3 + H_2Ge{=}GeH_2 \rightarrow H_2Ge{=}GeH{-}HGe{=}GeH_2 + 2\ GeH_4$$

The BSE is calculated to be 9.5 kcal/mol (SCF) and 11.7 kcal/mol (MP4). In contrast to the orbital splitting, this indicator gives a value which is now 90% as large as that in butadiene (10.6 and 12.5 kcal/mol at the SCF and MP4 levels, respectively), suggesting significant overall conjugation. Unlike in butadiene, where the $\sigma$ orbital set takes no part in the conjugation, the delocalization effects here occur via a mixing within both the $b_u$ and $a_g$ orbital sets of the trans-bent doubly bonded units. To discriminate and quantify these interactions, a valence−bond analysis would be required, which is beyond the scope of the present work. In summary, the coupling of two trans-bent double bonds brings significant stabilization through orbital mixing or delocalization. This mixing cannot be strictly compared to the $\pi$ conjugation in butadiene, but it appears to be of a similar extent when estimated from energy criteria. However, the expected bond length shortening is less marked than in a planar $\pi$−conjugated system.

## Triplet State

Triplet states have been examined, because they are known to be low lying states in unsaturated systems involving heavier analogues of carbon. The relaxed geometry of triplet digermene corresponds to a rotation around the trans-bent Ge=Ge double bond, in a $C_2$ arrangement, with one HGeGeH dihedral angle close to 180°.[19] Because the two coupling schemes correspond to real configurations, one expects to find two triplet states, one for each coupling scheme. These were indeed found, corresponding to the twisting of one terminal $GeH_2$ in t-1 or g-2. The two forms, labeled $^3$(t-1) and $^3$(g-2), are close in energy,

**TABLE 5: Geometrical Parameters and Harmonic Vibrational Frequencies for the Two Forms of Triplet Tetragermabutadiene**[a]

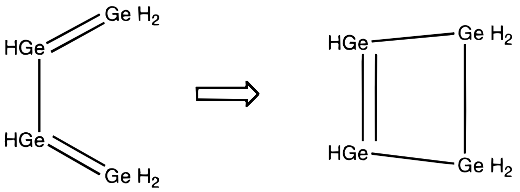
| | geometries | | | | vibrational frequencies | |
|---|---|---|---|---|---|---|
| | $H_2Ge{=}GeH_2$ | $^3$(t-1) | $^3$(g-2) | | $^3$(t-1) | $^3$(g-2) |
| $Ge_1{-}Ge_2$ | 2.500 | 2.506 | 2.504 | 1a | 29 | 31 |
| $Ge_3{-}Ge_4$ | | 2.459 | 2.459 | 2a | 42 | 56 |
| $Ge_2{-}Ge_3$ | | 2.450 | 2.449 | 3a | 79 | 82 |
| $Ge_1{-}H_1$ | 1.559 | 1.559 | 1.559 | 4a | 113 | 113 |
| $Ge_1{-}H_2$ | 1.561 | 1.561 | 1.561 | 5a | 171 | 167 |
| $Ge_2{-}H$ | | 1.562 | 1.563 | 6a | 210 | 206 |
| $Ge_3{-}H$ | | 1.563 | 1.564 | 7a | 258 | 255 |
| $Ge_4{-}H_1$ | | 1.559 | 1.559 | 8a | 294 | 295 |
| $Ge_4{-}H_2$ | | 1.558 | 1.558 | 9a | 376 | 367 |
| $Ge_1Ge_2Ge_3$ | | 117.8 | 118.3 | 10a | 444 | 430 |
| $Ge_2Ge_3Ge_4$ | | 116.9 | 117.0 | 11a | 458 | 473 |
| $Ge_2Ge_1H_1$ | 111.4 | 111.2 | 111.3 | 12a | 493 | 492 |
| $Ge_2Ge_1H_2$ | 114.3 | 114.2 | 114.2 | 13a | 529 | 524 |
| $Ge_1Ge_2H$ | | 109.3 | 109.1 | 14a | 555 | 551 |
| $Ge_4Ge_3H$ | | 110.0 | 109.8 | 15a | 673 | 689 |
| $Ge_3Ge_4H_1$ | | 113.7 | 113.4 | 16a | 751 | 707 |
| $Ge_3Ge_4H_2$ | | 113.6 | 113.7 | 17a | 912 | 911 |
| $HGe_1H$ | 108.8 | 108.6 | 108.6 | 18a | 918 | 920 |
| $HGe_4H$ | | 108.9 | 108.7 | 19a | 2151 | 2145 |
| $Ge_1Ge_2Ge_3Ge_4$ | | 177.1 | 57.2 | 20a | 2156 | 2153 |
| $Ge_3Ge_2Ge_1H_1$ | | −57.8 | −55.5 | 21a | 2159 | 2160 |
| $Ge_3Ge_2Ge_1H_2$ | | 65.5 | 68.0 | 22a | 2173 | 2172 |
| $H_1Ge_1Ge_2H$ | 179.4 | 174.5 | 177.1 | 23a | 2176 | 2176 |
| $HGe_3Ge_4H_1$ | | −50.7 | 50.7 | 24a | 2181 | 2180 |
| $Ge_2Ge_3Ge_4H_1$ | | 183.1 | 177.1 | | | |
| $Ge_2Ge_3Ge_4H_2$ | | 57.8 | −58.1 | | | |

[a] In angstroms and degrees for bond lengths and angles and cm$^{-1}$ for wavelengths. The geometry of the parent digermene is given for comparison.

separated by roughly the t-1/g-2 energy difference (0.4 kcal/mol). Geometrical parameters and harmonic vibrational frequencies are listed in Table 5, and geometries are drawn in Figure 1. The triplet extremities exhibit the same geometrical features as the parent triplet digermene. In both cases, one terminal $GeH_2$ group has been twisted by approximately 90°, the remaining germanium atoms maintaining a t-1 or g-2 arrangement, which corresponds to a pseudo allylic conjugation involving three adjacent hybrids instead of $p_z$ atomic orbitals. Interestingly, the GeGeGeGe dihedral angle in $^3$(g-2) has decreased from 80° to 57°, a value close to the 2α expectation mentioned above, and originating in the overlap of the middle hybrids. Because of the remaining pseudo allylic conjugation, the adiabatic singlet−triplet separation is expected to be lower in tetragermabutadiene than in the parent digermene. In the latter, the adiabatic transition is calculated to be 18.6 kcal/mol, while $^3$(t-1) is only 13.1 kcal/mol above t-1. The vertical singlet−triplet transition energies are calculated to be 32.5 kcal/mol in digermene and 23.3 kcal/mol in t-1. Twisting about Ge═Ge therefore brings relaxation energies of 12 kcal/mol in triplet digermene and 10 kcal/mol in triplet tetragermabutadiene, compared with relaxation energies calculated, under similar conditions, in triplet ethylene and butadiene of 35 and 25 kcal/mol, respectively. Clearly, real $\pi$ conjugation is stronger than pseudo $\pi$ mixing.

## Electrocyclic Ring Closure

Assuming that all single and double bonds keep their respective nature (in particular that the extent of trans bending is similar in linear and cyclic double bonds), the expected reaction energy for a ring closure such as the intramolecular rearrangement of tetragermabutadiene into tetragermacyclobutene, **17**, can be estimated as the sum of three components: (1) the differential $\sigma{-}\pi$ bond energy increment; (2) the conjugation energy in the butadiene form, and (3) the ring strain in the cyclobutene form.



**17**

These contributions can be estimated from mean bond energies for the first factor, and through various procedures, such as the use of isodesmic reactions, for the last two. For the butadiene-to-cyclobutene rearrangement, these contributions can be reasonably estimated at −20 kcal/mol for the differential $\sigma{-}\pi$ increment (≈ 63−83), +10 kcal/mol for the loss of $\pi$ conjugation, and +30 kcal/mol for the ring strain in the final product.[20] From such values, an endothermicity of about 20 kcal/mol is expected for the cyclization of butadiene into cyclobutene. The reaction is actually found to be endothermic, but the endothermicity is calculated or measured at only ≈10 kcal/mol.[21] For reaction **17**, taking a value of 45 kcal/mol for the mean bond energy of a Ge−Ge single bond,[22] and taking a $\pi$ increment of 25 kcal/mol,[19] one has, again, −20 kcal/mol for the $\sigma{-}\pi$ differential increment. Because the "conjugation" energy increment is about the same as that in butadiene (10 kcal/mol, see above), the main difference lies in the ring strain, expected to be much lower in tetragermacyclobutene than in cyclobutene, since the heavier analogues of carbon are generally more accommodating for small bond angles. Using the following isodesmic reaction

$$H_3X{-}XH{=}XH{-}XH_3 + 2\ H_3X{-}XH_2{-}XH_3 \rightarrow \text{cyclo-}X_4H_6 + 3\ H_3X{-}XH_3$$

Boatz and Gordon have calculated a ring strain of 30 kcal/mol in cyclobutene, in agreement with an experimental evaluation, and 11 kcal/mol in tetrasilacyclobutene.[20] Using the simpler reaction

$$H_2X{=}XH_2 + H_3X{-}XH_2{-}XH_2{-}XH_3 \rightarrow \text{cyclo-}X_4H_6 + 2\ XH_4$$

the ring strain is here calculated at 26 kcal/mol in cyclobutene and at 5 kcal/mol in tetragermacyclobutene. This reduction by one-fifth for germanium seems reasonable with regard to the one-third reduction mentioned above for silicon. The reaction energy for **17** is therefore estimated to be isergonic or weakly exothermic by 0−5 kcal/mol (≈ −20 + 10 +(5 ∼ 10)).

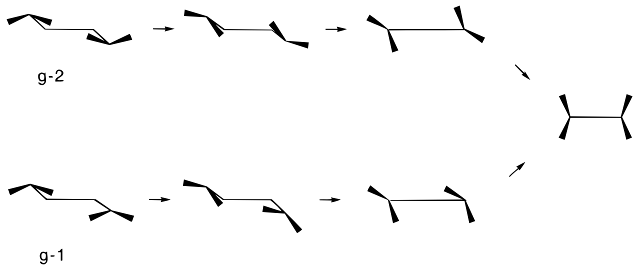
Reaction **17** is actually found to be strongly exothermic, since tetragermacyclobutene is calculated to lie 26 kcal/mol below its butadiene form t-1. Trying to understand such a discrepancy, we note that if the trans-bent Ge═Ge double bond were assigned the same bond energy as that of a standard Ge−Ge single bond, the energy changes due to bond increments in **17** would now be −45 kcal/mol. The ensuing net energy benefit for the reaction would in this case be expected to be −25 kcal/mol (≈ −45 + 10 + 10), in better agreement with the calculated value, and giving some support to a similar bond energy in single and trans−bent double GeGe bonds, as suggested earlier.[23]

**TABLE 6: Geometrical Parameters for Tetragermacyclobutene and the Transition State for Its Conrotatory Formation from Tetragermabutadiene**[a]

| TC transition state ($C_1$) | | | tetragermacyclobutene | | |
|---|---|---|---|---|---|
| | | | | double bonded ($C_2$) | double bridged ($C_{2v}$) |
| $Ge_1-Ge_2$ | 2.405 | 43 % | $Ge_1-Ge_2$ | 2.494 | 2.595 |
| $Ge_3-Ge_4$ | 2.352 | 8 % | | | |
| $Ge_2-Ge_3$ | 2.544 | −28 % | $Ge_2-Ge_3$ | 2.286 | 2.872 |
| $Ge_1-Ge_4$ | 3.933 | 50 % | $Ge_1-Ge_4$ | 2.525 | 2.508 |
| $Ge_1-H_1$ | 1.564 | | $Ge_1-H$ | 1.555 | 1.561 |
| $Ge_1-H_2$ | 1.556 | | | | |
| $Ge_4-H_1$ | 1.559 | | | | |
| $Ge_4-H_2$ | 1.557 | | | | |
| $Ge_2-H$ | 1.574 | | $Ge_2-H$ | 1.547 | 1.797 |
| $Ge_3-H$ | 1.563 | | | | |
| $Ge_1Ge_2Ge_3$ | 96.3 | 84 % | $Ge_1Ge_2Ge_3$ | 92.5 | 86.0 |
| $Ge_2Ge_3Ge_4$ | 116.6 | 0 % | | | |
| $Ge_2Ge_1Ge_4$ | 78.1 | 78 % | $Ge_2Ge_1Ge_4$ | 87.0 | 94.0 |
| $Ge_3Ge_4Ge_1$ | 66.5 | 49 % | | | |
| $Ge_2Ge_1H_1$ | 129.1 | | $Ge_2Ge_1H_1$ | 113.5 | 112.8 |
| $Ge_2Ge_1H_2$ | 119.0 | | $Ge_2Ge_1H_2$ | 116.9 | 112.8 |
| $Ge_3Ge_4H_1$ | 123.4 | | | | |
| $Ge_3Ge_4H_2$ | 116.1 | | | | |
| $Ge_1Ge_2H$ | 103.9 | | $Ge_1Ge_2H$ | 131.7 | 87.6 |
| $Ge_4Ge_3H$ | 111.6 | | | | |
| $HGe_1H$ | 106.1 | | $HGe_1H$ | 108.5 | 107.6 |
| $HGe_4H$ | 108.1 | | | | |
| $Ge_3Ge_2Ge_1H_1$ | −142.6 | 64 % | $Ge_3Ge_2Ge_1H_1$ | −123.3 | |
| $Ge_3Ge_2Ge_1H_2$ | 68.3 | 33 % | $Ge_3Ge_2Ge_1H_2$ | 109.2 | |
| $Ge_2Ge_3Ge_4H_1$ | −169.4 | 13 % | | | |
| $Ge_2Ge_3Ge_4H_2$ | 53.2 | 9 % | | | |
| $Ge_1Ge_2Ge_3Ge_4$ | 17.3 | 87 % | $Ge_1Ge_2Ge_3Ge_4$ | 7.9 | 0. |
| $HGe_2Ge_3H$ | 140.9 | | $HGe_2Ge_3H$ | 26.1 | 177.3 |

[a] In angstroms and degrees. The percentages indicate the proportion of parameter change along the reaction coordinate, starting from the g-2 gauche form.

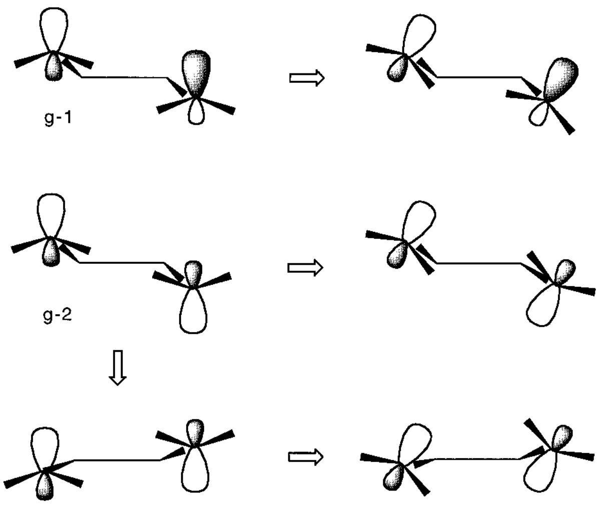
The conrotatory thermally allowed intramolecular cyclization may proceed from any of the two gauche forms, but reaction from g-2 should be favored over that from g-1 because in g-2 the terminal $GeH_2$ groups better anticipate the final product, **18**, exhibit a favorable combination of the lobes of the hybrids in the HOMO, **19**, and maintain a $C_2$ symmetry axis along the reaction.



**18**

Starting from g-2, the reaction energy for **17** is calculated at −27 kcal/mol, with a transition state only 1.3 kcal/mol above the reactant.

A search along the $C_2$ pathway actually led to a $C_1$ transition state (labeled TC). Relaxing TC actually led to g-2 or to the cyclic form, confirming that it is not the saddle point associated with the $C_1$ cyclization pathway from g-1. Since in the closure from g-2 both starting material and final product have $C_2$ symmetry, one would expect, as in the carbon series, a transition state of the same symmetry. To account for this unsymmetrical transition state, one must remember a particularity of g-2 with respect to g-1. Although it has a favored symmetry, g-2 is not well "prepared" for the conrotatory closure because in the HOMO the hybrids of the bond to be created are not well oriented. As illustrated in **19**, the overlap is facilitated if g-2 inverts its GeGeGeGe dihedral angle via an s-cis arrangement—a process requiring only ≈1 kcal/mol according to Figure 3.



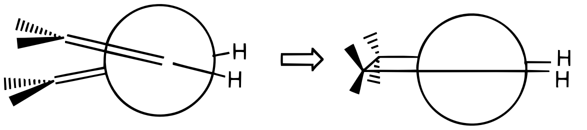
**19**

The geometry of the transition state TC actually corresponds to such an inversion in the dihedral angle (see Figure 1 and Table 6). Occurring in the early stage of the closure, this inversion of GeGeGeGe from 80° to −17° places the middle Ge−H bonds in a quasi *anti* situation, while in the final $C_2$ cyclic form, they will be in quasi *syn* arrangement, **21**. Because of the planarity at the carbon centers, such a change is much less important for the middle CH bonds of butadiene, **20**. The $C_1$ transition state and the ensuing non-least-motion character of the path simply arises from the pyramidalization at the germanium atoms. Detailed in Table 6, the geometry of TC reflects different degrees of advancement of the closure reaction,

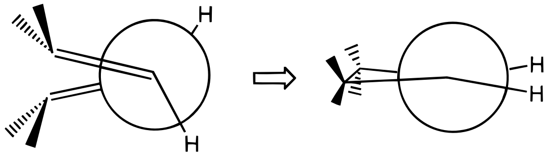
**TABLE 7: Harmonic Vibrational Frequencies for Tetragermacyclobutene**

| double-bonded form −HGe=GeH− ($C_2$) | | | double-bridged form −Ge(HH)Ge− ($C_{2v}$) | | |
|---|---|---|---|---|---|
| | freq (cm$^{-1}$) | ir int | | freq (cm$^{-1}$) | ir int |
| 1a | 40 | 0.0 | 1a$_2$ | 34 | |
| 1b | 166 | 0.0 | 1b$_1$ | 153 | 0.0 |
| 2a | 245 | 0.0 | 1a$_1$ | 226 | 0.0 |
| 3a | 253 | 0.0 | 2b$_1$ | 237 | 0.0 |
| 2b | 266 | 0.0 | 2a$_1$ | 240 | 0.1 |
| 4a | 280 | 0.1 | 3a$_1$ | 266 | 0.0 |
| 3b | 351 | 0.3 | 1b$_2$ | 314 | 0.9 |
| 5a | 370 | 0.0 | 2a$_2$ | 357 | |
| 4b | 458 | 0.4 | 3b$_1$ | 503 | 0.1 |
| 5b | 497 | 0.0 | 4b$_1$ | 581 | 0.3 |
| 6a | 497 | 0.0 | 4a$_1$ | 639 | 3.5 |
| 6b | 557 | 0.1 | 3a$_2$ | 663 | |
| 7a | 636 | 0.0 | 5a$_1$ | 734 | 0.1 |
| 8a | 648 | 0.1 | 5b$_1$ | 734 | 0.1 |
| 7b | 691 | 1.2 | 6b$_1$ | 922 | 4.1 |
| 9a | 721 | 4.2 | 6a$_1$ | 929 | 3.4 |
| 8b | 934 | 5.2 | 4a$_2$ | 989 | |
| 10a | 945 | 4.9 | 2b$_2$ | 1152 | 2.3 |
| 11a | 2174 | 0.4 | 7b$_1$ | 1263 | 47.0 |
| 9b | 2183 | 6.9 | 7a$_1$ | 1542 | 0.0 |
| 10b | 2193 | 5.2 | 5a$_2$ | 2145 | |
| 12a | 2197 | 8.6 | 8b$_1$ | 2152 | 6.2 |
| 11b | 2205 | 3.6 | 3b$_2$ | 2156 | 7.4 |
| 13a | 2215 | 1.0 | 8a$_1$ | 2159 | 6.2 |

depending on the parameter. Taking the Ge1⋯Ge4 distance as a criterion would correspond to a 50% advancement.



**20**



**21**

As expected, the ring strain in tetragermacyclobutene strongly perturbs the trans-bent arrangement of the intracyclic Ge=Ge double bond. Actually, a non-trans-bent planar form of $C_{2v}$ symmetry is only 0.4 kcal/mol above the $C_2$ preferred form. The trans bending is therefore small, as are the induced ring puckering and its associated vibrational frequency 1a shown in Table 7. This nearly planar arrangement at −HGe=GeH− makes the Ge=Ge bond length 0.04 Å shorter than that in the parent digermene, but still 0.04 Å longer than that in planar-constrained digermene. The intracyclic angles in tetragermacyclobutene are found to be close to those calculated in tetrasilacyclobutene,[20] these in turn being in good agreement with the experimental X-ray structure of the derivative bearing t-BuMe$_2$Si substituents at all positions.[24]

Hydrogen double bridges are a possible alternative to double bonds in the heavier analogues of ethylene. In tetragermacyclobutene, such an arrangement could be favored because the longer Ge⋯Ge distance of the Ge(HH)Ge bridge should release ring strain. Its calculated $C_{2v}$ structure shows that this lengthening, although significant (+0.6 Å), does not open drastically the two Ge−Ge−Ge valence angles of the square ring (see Table 6 and Figure 1) so that this form is found to lie 5 kcal/mol above the double-bonded form, as in the case of the parent digermene. Should such an arrangement be produced, it could be detected by the strong infrared band 7b1 corresponding to in-phase in-plane translation of the bridge hydrogens (see Table 7).

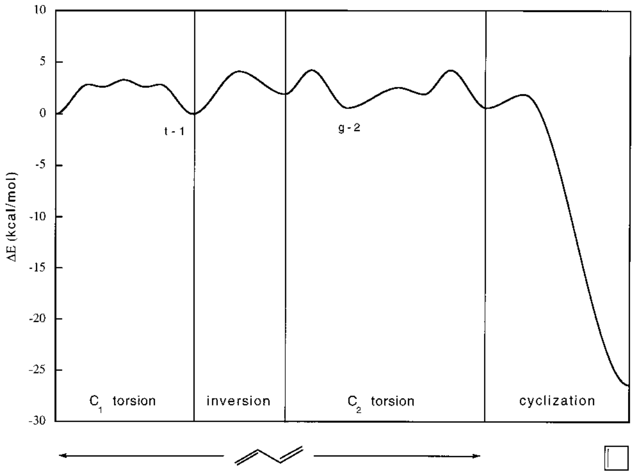


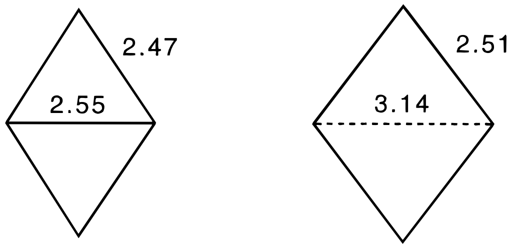
**Figure 5.** Schematic energy profile along the rotation, inversion, and cyclization coordinates.

Although TC is located above g-1 at the SCF level, it is found to lie below g-1 at the MP4 level (using SCF geometries). Presumably, there exists another transition state above g-1, but we failed to find it, and this may not deserve more attention as g-2 is significantly preferred over g-1.

Requiring only 1.3 kcal/mol of activation energy from g-2, the cyclization of tetragermabutadiene into tetragermacyclobutene is therefore an easy process, as it is also in 1-4 digermabutadiene. However, from the s-trans form t-1, a significant barrier has to be overcome to attain g-1 or g-2, so that in this case the molecule could be trapped in its butadiene form for a sufficient time to be detected. Finally, a synthetic view of the whole potential surface and its complexity can be schematized by the energy curves shown in Figure 5, corresponding to connected cross sections along the rotation, inversion, and cyclization coordinates.

## Bicyclobutane and Hydrogen-Bridged Isomers

Despite ring strain, the bicyclo[1.1.0]butane form may be expected to be thermodynamically favored over the butadiene form because it has formally five single bonds. In Si$_4$H$_6$, the bicyclobutane form was even found to be preferred to the cyclobutene isomer.[20] Such bicyclic structures give rise to a well-documented bond stretch isomerism.[7−15] Significant lengthening of the bridgehead bond stabilizes the structure by as much as 10 kcal/mol for Si, or 20 kcal/mol for Ge. Our calculations locate the normal (short-bonded) bicyclobutane form at 17.9 (SCF), 15.6 (MP4), or 11.9 (DFT) kcal/mol below the butadiene form t-1, and at 12.6 (SCF), 10.8 (MP4), or 11.2 (DFT) kcal/mol above the cyclobutene form. The stretched isomer is stabilized by 17.2 (SCF), 22.0 (MP4), or 21.9 (DFT) kcal/mol with respect to the normal short-bonded form, in agreement with previous calculations by Nagase et al.[7,8] This (overall preferred) isomer lies at 4.4 (SCF), 11.2 (MP4), or 10.7 (DFT) kcal/mol below the cyclobutene form, and 35.1 (SCF), 37.6 (MP4), or 33.8 (DFT) kcal/mol below the butadiene form. The geometrical parameters indicate a lengthening of the bridgehead bond by 0.6 Å, **22**. Our geometries are in agreement with those previously published by Nagase et al.[7,8] and we will not comment on them, further.

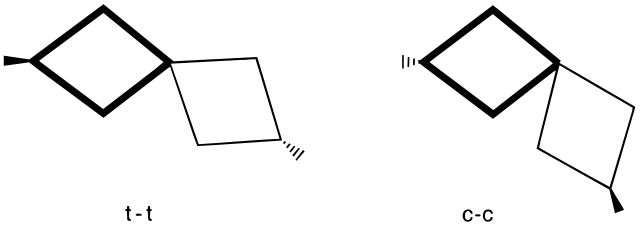


**22**

While the stretched isomer is below the cyclobutene form, the normal (short-bond) isomer lies about 10 kcal/mol *above* the cyclobutene form. For silicon, the normal bicyclobutane form was found to be *below* the cyclobutene form (by 3 kcal/mol).[20] Some explanation for this trend can be found in the ring strain analyses performed some years ago by Nagase and Nakano.[7] From various calculations, they came to the conclusion that “the difference in strain energy between four-membered rings and three-membered rings is significantly greater in germanium compounds than in silicon compounds”. This is in line with the greater stability of tetragermacyclobutene with respect to normal (short bond) tetragermabicyclobutane.

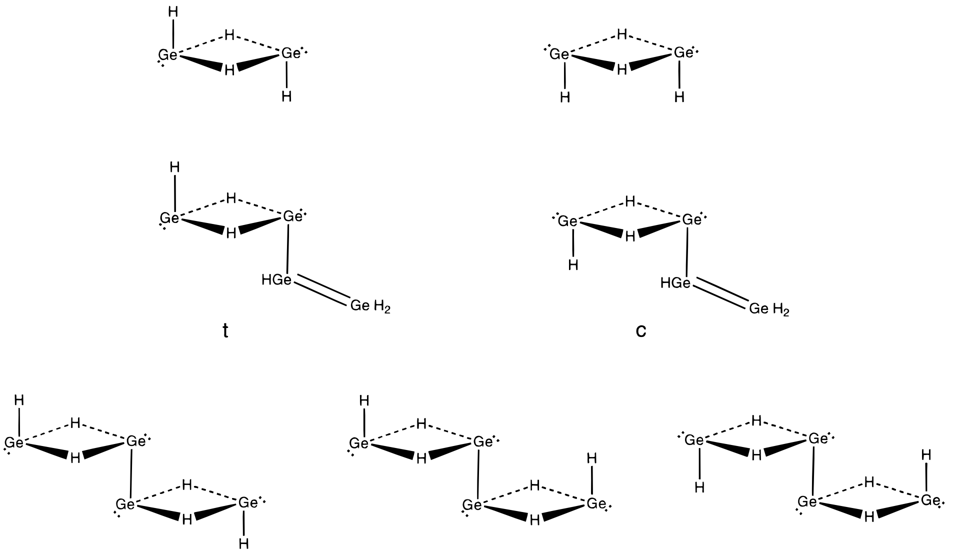
As a structural alternative to double bonds, the double hydrogen bridge corresponds to a real minimum on the potential surfaces of disilene, digermene, distannene, and diplumbene.[3,4,25] For $Ge_2H_4$ it lies about 5 kcal/mol above the double-bonded form, but it happens to be the preferred form for $Sn_2H_4$ and $Pb_2H_4$. We wanted to examine whether such a double hydrogen bridge arrangement could be favored here and which kind of interaction takes place when it is coupled with a double bond or with another such bridge. We thus studied both isomers and located their energies with respect to the butadiene form.

In the parent bridged digermene, the extracyclic Ge−H bonds can be in a cis or trans relative orientation, so that for HGe(HH)Ge−GeH═$GeH_2$ there are two possible isomers, trans and cis (labeled t and c), while three configurations are possible for HGe(HH)Ge−Ge(HH)GeH (t−t, t−c, and c−c), **23**. The five structures were optimized and all were found to be genuine minima on the potential surfaces. Because there is much to comment on in these coupled double bridges, a detailed analysis of their geometrical and electronic structures will be published elsewhere[26] and we will only report here the most salient features. Reflecting some structural and functional autonomy, all of the −Ge(HH)Ge− bridges in **23** exhibit a similar geometry. The rings are planar, or weakly puckered by only a few degrees, with the following geometrical parameter ranges: Ge-H: 1.75−1.83 Å; Ge···Ge: 2.81−2.83 Å; GeHGe: 104−105°; HGeH: 74−76°. The extracyclic Ge−Ge bond lengths are 2.63, 2.65, and 2.67 Å in c−c, t−c, and t−t, respectively, but only 2.55 Å in t and c. Note that this is longer than the central Ge−Ge bond lengths calculated in the butadiene forms (2.48−2.49 Å, see Table 2) and longer than the regular Ge−Ge single bond length calculated in digermane (1.50 Å). The GeGeGeGe dihedral angles are calculated to be 161° in t and 167° in c, making only small deviations (by 19° and 13°, respectively) from an exact s-trans orientation. In contrast, the coupling of two hydrogen double bridges gives rise to electrostatic interactions between the polarized atoms of the bridges and, on the other hand, possible repulsive effects between the germanium lone pairs and the extracyclic hydrogen atoms.[26] The ensuing interplay produces a significant rocking of the rings around the central Ge−Ge hinge, **24**, with GeGeGeGe dihedral angles of 146° in t−t, 116° in t−c, and 113° in c−c. In the latter case, this represents a departure from the s-trans arrangement of 67°. These effects are also responsible for the stability ordering given in Table 8, with c−c lying 2 kcal/mol below t−t.


t-t c-c

**24**

Not surprisingly, all of the bridged structural isomers **23** are found to be less stable than the butadiene forms. The trans isomer of the parent double-bridged digermene HGe(HH)GeH is 5.2 kcal/mol above the trans-bent double-bonded form $H_2Ge$═$GeH_2$. The cis isomer is 2.1 kcal/mol above the trans



t c
t-t t-c c-c

**23**

**TABLE 8: Relative Energies of the Hydrogen-Bridged and Bicyclic Isomers of Tetragermabutadiene**[a]

| | | | SCF | MP4 | MP4 + ZPC |
|---|---|---|---|---|---|
| $(HGe-(HH)-Ge-)_2$ | t-t | $C_2$ | 20.7 | 19.7 | 19.3 |
| | c-t | $C_1$ | 20.4 | 18.9 | 18.5 |
| | c-c | $C_2$ | 19.9 | 17.7 | 17.2 |
| $H_2Ge{=}GeH-Ge-(HH)-GeH$ | c | $C_1$ | 9.4 | 9.4 | 9.3 |
| | t | $C_1$ | 8.2 | 8.0 | 7.8 |
| $H_2Ge{=}GeH-GeH{=}GeH_2$ | t-1 | $C_i$ | 0. | 0. | 0. |
| tetragermabicyclo[1.1.0]butane | normal | $C_{2v}$ | −17.9 | −15.6 | −14.2 |
| | stretch | $C_{2v}$ | −35.1 | −37.6 | −36.3 |

[a] In kcal/mol. ZPC denotes zero-point energy correction.

form and thus 7.3 kcal/mol above the double-bonded form. Without interaction between the two double-bond or double-bridge functional groups, these increments place t 5.2 kcal/mol above t-1 and c−c 14.6 kcal/mol above t-1. As in the butadiene form, coupling effects between Ge(HH)Ge and Ge═Ge can again be appraised through bond separation energies (BSE) obtained from the isodesmic reactions:

$$HGe(HH)GeH + H_3Ge{-}GeH_3 + H_2Ge{=}GeH_2 \rightarrow HGe(HH)Ge{-}GeH{=}GeH_2 + 2\ GeH_4$$

$$HGe(HH)GeH + H_3Ge{-}GeH_3 + HGe(HH)GeH \rightarrow HGe(HH)Ge{-}Ge(HH)GeH + 2\ GeH_4$$

This procedure yields BSEs of 9.0 kcal/mol for $HGe(HH)Ge-GeH{=}GeH_2$ (t), and 8.9 kcal/mol for $(HGe(HH)Ge-)_2$ (c−c). These values are hardly lower than the BSE found in the butadiene form t-1 (11.7 kcal/mol). In the latter arrangement, the stabilization brought by the coupling arose from pseudoconjugation mainly originating in orbital mixing effects. In contrast, because the double hydrogen bridge is essentially ionic in nature,[27] the stabilization due to its coupling with the double bond or with another bridge mainly originates in electrostatic effects. Combining these differential BSEs of 2.7 and 2.8 kcal/mol with the double-bond/double-bridge increments in parent digermene would now place $HGe(HH)Ge-GeH{=}GeH_2$ (t) and $(HGe(HH)Ge-)_2$ (c−c) 7.9 and 17.4 kcal/mol, respectively, above $H_2Ge{=}GeH-GeH{=}GeH_2$ (t-1). As can be seen in Table 8, these values are quite close to the actual calculated relative energies.

Because the coupling effect involving double hydrogen bridges is not very different from that involving double bonds, the energy difference between double-bonded and double-bridged forms in any polyunsaturated entity is therefore mainly governed by that occurring in the parent compounds. Consequently, the outcome of the double-bond/double-bridge competition should presumably be predictable not only in hexagermahexatriene and the next conjugated polygermenes but also in any other group 14 analogues, providing the double-bond/double-bridge energy difference is known in the parent compound. Given the preference for hydrogen bridges in distannene and diplumbene, hydrogen-bridged forms should be preferred for $Sn_4H_6$ and $Pb_4H_6$, although butadiene forms should remain local minima on the corresponding potential surfaces.

Figure 6 summarizes the relative energies of the various minima on the $Ge_4H_6$ potential surface calculated in this work. The butadiene form appears to be midway between two particular types of rings: the favored stretched isomer of the bicyclobutane form and the unfavored structure bearing two double hydrogen bridges.

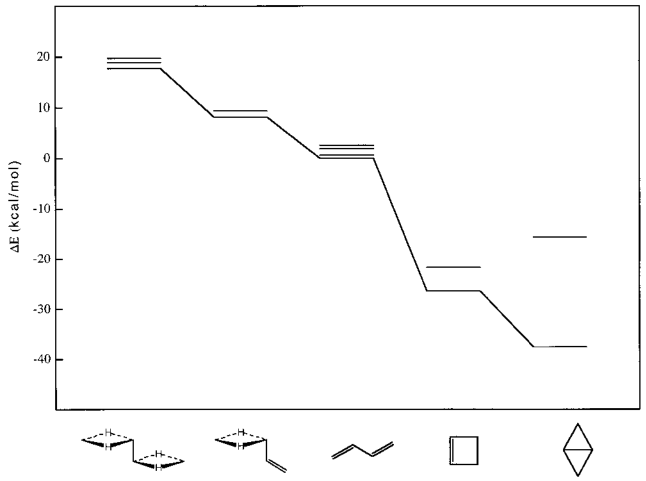


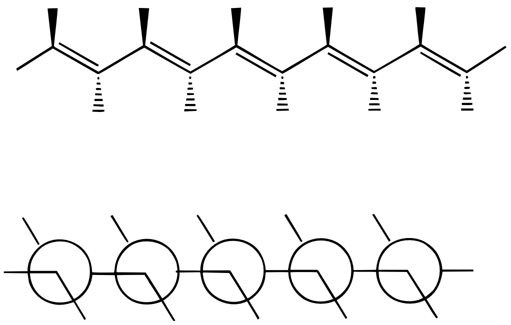
**Figure 6.** Relative energies for the $Ge_4H_6$ isomers studied in this work.

## Concluding Remarks

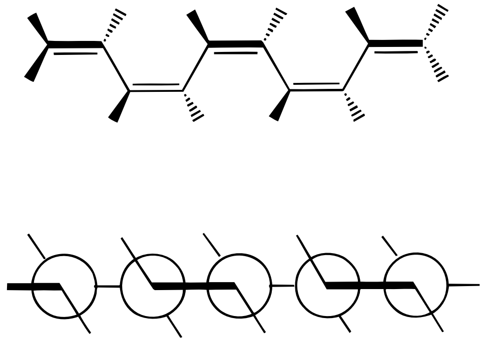
We have seen that the coupling of trans-bent double bonds can take place in two ways, each configuration giving s-trans and gauche type conformers as in butadiene. Of these four isomers, the s-trans arrangement t-1, of $C_i$ symmetry, with all pyramidal germanium atoms in a trans orientation, is the preferred form. Close in energy lies a cis-gauche conformation g-2, derived from the second $C_2$ coupling scheme. For the higher polyene homologues such as pergermahexatriene, one also expects the t-1 type extended structure to be preferred, with an all-trans arrangement along the pyramidal germanium chain. Despite the nonplanar germanium centers, these structures maintain a planar extended skeleton and overall $C_i$ symmetry, **25**. Other combinations of the two coupling schemes can also be formulated, such as the cis trans-like alternating sequence sketched in **26**. The ring isomers topologically close to tetragermabutadiene (tetragermacyclobutene and tetragermabicyclobutane) are both thermodynamically favored in our hydrogen-bearing model system. The existence of a stable tetragermabutadiene structure will depend on the magnitude of the barriers to overcome in an actual derivative, presumably bearing bulky substituents. The recent isolation of an hexaaryltetrasilabutadiene[6] suggests that tetragermabutadiene derivatives should also be tractable synthetic targets.

The thirteen isomers studied in this work are far from being the only possibilities for such an $X_4H_6$ system. The two unsaturations in $Ge_4H_6$ can be accommodated by any combination of the following permitted forms of unsaturation in germanium compounds: triple bond, double bond, three-membered ring, four-membered ring, germylene divalent form, and double hydrogen bridge. As tentatively sketched in Figure 7, this allows some thirty feasible structures. For heavier systems involving tin or lead atoms, one should add the single hydrogen bridge as a further possible form of unsaturation, expanding the structural diversity to some sixty conceivable minima. Once again, the increasing structural diversity down the group 14 column is illustrated, whereas carbon, with its propensity to give fewer minima, would largely favor multiple bonded arrangements, such as the butadiene and butyne forms.

**Acknowledgment.** The authors thank one referee and Prof. C. Marsden for improving the manuscript, and Dr. F. X. Gadéa for helpful discussions.



**25**



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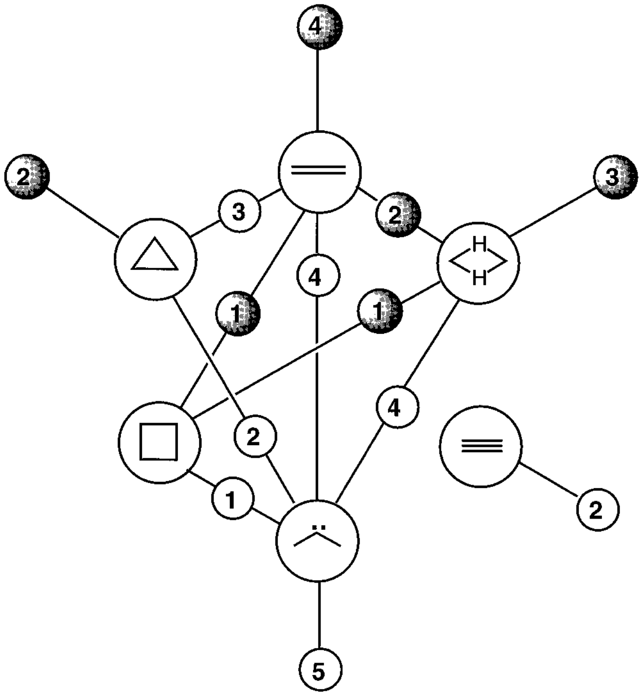

**Figure 7.** Number of reasonable $Ge_4H_6$ structures presumably obtained from combinations among the permitted forms of unsaturation: (clockwise from the top) double bond, double hydrogen bridge, triple bond, germylene divalent form, four-membered ring, and three-membered ring. Shaded insets refer to the thirteen isomers addressed in the present work.

## Appendix

Calculations were performed with the HONDO8 program from the MOTECC package,[28] and the GAUSSIAN92 program.[29] For germanium atoms, effective core potentials were used.[30] The DZP valence basis sets consist of four Gaussian functions contracted to double-$\zeta$ and augmented by a polarization function. The exponent for the d functions on germanium was taken 0.25, and that for the p functions on hydrogen was 0.90. Geometries were optimized at the RHF−SCF level for singlet species, and at the UHF−SCF level for triplet species, with final gradient Cartesian components less than $10^{-6}$. For each stationary point, the energy was recalculated at the MP4−SDTQ level (Möller−Plesset perturbation theory applied to the fourth order). In some cases, such as the open-shell triplet states, the final energy was also reevaluated from DFT calculations with the B3LYP functional.[31] As long as spin contamination is slight, as in the parent digermene, this gives a result quite similar to that of UMP4 after spin decontamination. For $^3$(g-2) and $^3$(t-1), because the UHF calculations give significant spin contamination, we consider the energy differences given by the DFT calculations to be more reliable.

The effect of reoptimizing the geometries at the DFT level on the final relative energies has been performed for three minima and the planar saddle point of digermene $Ge_2H_4$. As expected from a correlated treatment,[32] the DFT-calculated bond lengths are 0.01−0.03 Å (1%) longer, while the valence angles are here 1−2° (1%) smaller than the corresponding Hartree−Fock values. The final relative energies listed in the following table (kcal/mol), exhibit only slight differences.

| | MP4//SCF | DFT//DFT |
|---|---|---|
| $C_{2v}$ (double-bridged cis) | 2.1 | 1.9 |
| $C_{2h}$ (double-bridged trans) | 0. | 0. |
| | | |
| $C_{2h}$ (double-bridged trans) | 5.1 | 4.9 |
| $D_{2h}$ (double-bonded planar) | 4.2 | 4.5 |
| $C_{2h}$ (double-bonded trans-bent) | 0. | 0. |

Experimental geometries for trans-bent Ge═Ge double bonds are available in the Cambridge Structural Database.[33] Depending on the nature of the substituents in $Ge_2R_4$, the Ge═Ge bond lengths range from 2.27−2.35 Å with aliphatic ($SiR_3$) substituents, and 2.21−2.30 Å with aromatic substituents. These numbers are to be compared with the Ge═Ge bond length calculated in the trans-bent parent digermene: 2.33 Å (SCF) and 2.36 Å (DFT).

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