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# The Two Conformers of 2,3-Digermabutadiene

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**Abstract:** 1,3-Butadiene and its 2,3-digerma analogue $H_2C{=}HGe{-}GeH{=}CH_2$ are investigated through ab initio calculations. Geometries are determined at the SCF-DZP level, and energies are refined at the MP4 level. Substitution of carbon by germanium at positions 2,3 has two main effects. First, the central bond conjugation is significantly decreased. Second, the relatively long Ge–Ge central bond removes the steric hindrance that was causing the s-cis isomer of butadiene to distort into a nonplanar gauche form. Therefore, 2,3-digermabutadiene has two stable planar conformers, close in energy, corresponding to $C_{2h}$ s-trans and $C_{2v}$ s-cis forms. The s-cis isomer is unfavored by 0.4 kcal/mol. The rotational barrier from the trans isomer is calculated at 1.6 kcal/mol. Due to planar $\sigma$ repulsion, the coordinate corresponding to rotation around the central Ge–Ge bond in the s-cis isomer is very flat on the potential surface and is associated with a very low-frequency normal mode. Various approaches, based on geometry or energy criteria, are used to evaluate the extent of $\pi$ conjugation in butadiene and 2,3-digermabutadiene. They suggest that the $\pi$-conjugation in the latter is about half that in butadiene.

The rotational conformers of 1,3-butadiene are known to a good accuracy both from experimental and theoretical grounds.[1–6] Butadiene has a preferred $C_{2h}$ s-trans planar conformation. For obvious steric reasons, a planar $C_{2v}$ s-cis conformer is forbidden, and such form relaxes into a nonplanar $C_2$ gauche form in which the two $H_2C{=}CH{-}$ groups form a dihedral angle of *ca.* 38°.[1–3,5] According to the most refined calculations, this gauche conformer is lying at 2.7 kcal/mol above the preferred s-trans form, with a barrier from the trans form of about 5 kcal/mol.[3,5] The planar s-cis form is a saddle-point relating the two gauche forms and lies at 0.5 kcal/mol above these two equivalent minima. The problem of substituting one carbon atom by an heavier analogue such as silicon has been addressed some years ago. Theoretical calculations have shown that substitution of one carbon atom by one silicon atom perturbs the conjugated $\pi$ system in different ways and extent according to whether position 1 or 2 is considered.[7] Although derivatives of 1-silabutadiene,[8–13] 2-silabutadiene,[14–17] and 1,4-disilabutadiene[18] have been characterized by trapping reactions at low temperature, no heterodiene with one or two group 14 elements has yet been isolated. Because of recent progress accomplished in preparative techniques in organogermanium chemistry,[19–23] compounds such as digermabutadiene derivatives should now be attainable synthetic targets. This makes the knowledge of the electronic structure of heavier analogues of butadiene a current problem again.

We have undertaken the theoretical study of parent digerma- and tetragermabutadiene. The latter compound, $H_2Ge{=}HGe{-}GeH{=}GeH_2$, will be addressed in a subsequent work. It should give rise to very interesting structural properties since the $R_2Ge{=}GeR_2$ arrangement has a strong propensity to pyramidalize in a trans-bent way, and should therefore induce a somewhat flexible tetragerma skeleton. The first study in our series, which is the object of the present paper, is 2,3-digermabutadiene. This first compound was selected on several grounds. First, this arrangement should be more easily obtained in the preparative experiments.[24] Second, the location of the heavy atoms at positions 2,3 is expected to perturb the structure much more effectively than in position 1,4. Last, simple mean bond energies[25] suggest that 2,3-digermabutadiene should be more stable than 1,4-digermabutadiene, the sum of differential bond energies being

$$(\text{Ge–Ge} + 2\text{C–H}) - (\text{C–C} + 2\text{Ge–H}) \approx (45 + 2 \times 99) - (83 + 2 \times 68) \approx 24 \text{ kcal/mol}$$

For both butadiene and 2,3-digermabutadiene, the complete rotational space around the central bond will be explored at the SCF level, with basis sets of double-$\zeta$-plus polarization (DZP) quality, and making use of effective core potentials (ECP) for treating the effect of the core electrons on the valence shells. On

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**Table 1.** SCF-Calculated Geometries[a]

| | | | C—C | C=C | Ge—Ge | C=Ge | C—$H_1$ | Ge-$H_1$ | C—$H_3$ | C—$H_5$ | XXC | XXH | $XCH_3$ | $XCH_5$ | CXXC |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $H_2C{=}HC{-}CH{=}CH_2$ | s-trans | $C_{2h}$ | 1.470 | 1.328 | | | 1.086 | | 1.085 | 1.083 | 124.2 | 116.4 | 121.7 | 121.4 | 180.0 |
| | TS | $C_2$ | 1.493 | 1.324 | | | 1.087 | | 1.085 | 1.084 | 124.6 | 116.4 | 121.8 | 121.2 | 102.3 |
| | gauche | $C_2$ | 1.480 | 1.327 | | | 1.087 | | 1.084 | 1.083 | 125.6 | 115.6 | 121.9 | 121.1 | 38.6 |
| | s-cis | $C_{2v}$ | 1.482 | 1.327 | | | 1.085 | | 1.084 | 1.083 | 127.3 | 114.7 | 122.7 | 120.7 | 0.0 |
| $H_3C{-}CH_3$ | | | 1.527 | | | | 1.093 | | | | | | | | |
| $H_2C{=}CH_2$ | | | | 1.322 | | | 1.084 | | | | | | | | |
| $H_2C{=}HGe{-}GeH{=}CH_2$ | s-trans | $C_{2h}$ | | | 2.451 | 1.791 | | 1.544 | 1.083 | 1.084 | 122.4 | 116.3 | 121.8 | 122.1 | 180.0 |
| | TS | $C_2$ | | | 2.466 | 1.790 | | 1.545 | 1.083 | 1.084 | 122.4 | 117.2 | 121.9 | 122.0 | 98.1 |
| | s-cis | $C_{2v}$ | | | 2.456 | 1.791 | | 1.545 | 1.083 | 1.084 | 123.3 | 115.8 | 122.0 | 121.8 | 0.0 |
| $H_3Ge{-}GeH_3$ | | | | | 2.501 | | | 1.555 | | | | | | | |
| $H_2C{=}GeH_2$ | | | | | | 1.784 | 1.083 | 1.541 | | | | | | | |

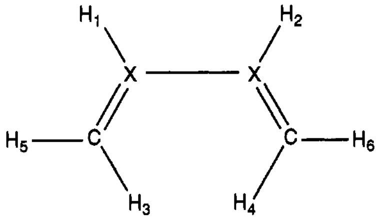
[a] Selected geometrical parameters, in Å and deg. See **1** for atom labeling. TS, standing for transition state, is the saddle point corresponding to the rotational barrier. The s-cis form of butadiene is a saddle point relating the two gauche forms.

each stationary point, energy is recalculated at the MP4 level, thus leading to relative energies taking into account part of the correlation effects. Theoretical details regarding the methods and basis sets are given in the Appendix. For the sake of consistency in our analyses, the simple molecules ethane, ethylene, digermane, and germaethylene will be recalculated in the same conditions as the butadiene systems.

## Structures

The SCF-determined geometries are given in Table 1, the corresponding harmonic vibrational frequencies and relative energies are listed in Tables 2 and 3, respectively. The effects of electronic correlation on the geometries—not taken into account here—are well-documented for butadiene. In most conformers, they shorten by 0.004 Å the central C–C bond length and lengthen by 0.01 Å the external C=C bonds, without significantly changing the remaining parameters, in particular the CCCC dihedral angle in the perpendicular and gauche forms.[3,5]

The potential surface of 1,3-butadiene is known to have three real minima: a planar s-trans form and two equivalent gauche forms. They are separated by three saddle points of index one: two equivalent perpendicular forms with a CCCC dihedral angle of 102° and a planar s-cis form. The present results are in good agreement with previous ones at the same level of theory.[5] In planar *s-cis*-butadiene, the main steric hindrance is due to the impeding between the inner hydrogen atoms ($H_3$, $H_4$) of the CH=CH groups, **1**. If unconstrained geometries of the $H_2C{=}CH{-}C$ arrangements were taken from the trans conformers, the $H_3{\cdots}H_4$ distance in the planar s-cis form would be only 2.03 Å. In the optimized $C_{2v}$-constrained s-cis isomer, the actual $H_3{\cdots}H_4$ distance is calculated at 2.35 Å. As soon as the planarity constrain is released, this $H_3{\cdots}H_4$ distance relaxes to 2.60 Å in the $C_2$ gauche form. In 2,3-digermabutadiene, since the Ge–Ge central bond is longer than the C–C one (from SCF calculations, the Ge–Ge bond in digermane is 0.97 Å longer than the C–C bond in ethane), the $H_3{\cdots}H_4$ distance in the planar s-cis form is expected to be longer than 3 Å, which definitely eliminates the $H_3{\cdots}H_4$ steric hindrance (the lengthening of the two Ge=C bonds enhances this trend, so that the actual such distance in the cis planar form is calculated at 3.52 Å). The planar s-cis conformer is therefore expected to be a real minimum on the potential surface of the 2,3-digermabutadiene, lying close in energy to the s-trans form. Actually, the rotational path for 2,3-digermabutadiene exhibits two real minima corresponding to the two planar $C_{2h}$ s-trans and $C_{2v}$ s-cis conformers. These minima are separated by a nonplanar saddle-point corresponding to the rotational barrier around the Ge–Ge bond. Energy curves along the complete rotational coordinate are given in Figures 1 and 2 for the SCF and MP4 potential surfaces, respectively.



**1**

The geometrical parameters for the s-trans and the s-cis planar isomers of 2,3-digermabutadiene are quite similar. In both cases, conjugation occurring through the central Ge–Ge bond is illustrated by both a 0.05-Å shortening of the Ge–Ge bond with respect to digermane and a 0.01-Å lengthening of the C=Ge bonds with respect to germaethylene. These length variations are close to those occurring in butadiene with respect to ethane and ethylene. The corresponding *relative* central bond contraction, however, is about twice smaller in the digerma derivative since the Ge–Ge central bond shortening from digermane is only 2%, whereas the C–C central bond shortening from ethane is closer to 4%. This indicates a weaker conjugation through the =Ge—Ge= bond, in line with the well-documented problem of $\pi$ bonding between heavier analogues of carbon in group 14. We shall address this point more quantitatively later on. If one takes the central bond in s-trans butane and 2,3-digermabutane as references for single bonds instead of ethane and digermane (see Table 4), the central bond shortening in our butadiene systems is further increased to 0.06 Å. Since the steric obstruction between hydrogens $H_3$ and $H_4$ no longer occurs in *s-cis*-2,3-digermabutadiene, the angular parameters for the $H_2C{=}GeH{-}$ groups are rather similar in both conformers.

The comparison between the trans conformer of butadiene and its digerma analogue indicates a complete similarity in C–H bond lengths and angular parameters of the $X{=}CH_2$ groups. The Ge—Ge=C valence angle is more closed than the C—C=C one by 2°. Due to the lower electronegativity of germanium, this trend is in agreement with Gillespie's rules.

In the transition state corresponding to the rotational barrier, the central bond is longer than that in the starting trans conformer but still shorter than a regular single bond. This trend, originated in hyperconjugation effects,[26] is observed in both butadiene and 2,3-digermabutadiene, but its relative extent is smaller in the latter. The CXXC dihedral angles correspond to orthogonal forms, slightly closer to the trans conformers: 102° and 98° for butadiene and 2,3-digermabutadiene, respectively. These values should be accounted for from the energy curves associated with the rotations about the central bond. Schematically, each curve can be seen as the sum of two other elementary curves. One, symmetrical, would correspond to the loss of $\pi$ conjugation and gain of hyperconjugation and would have its maximum for the orthogonal form at 90°. The second one would correspond to the variation in $\sigma$ repulsion when going from the trans form to the cis form. That curve, nonsymmetrical and nonmonotonous, should

**Table 2.** Harmonic Vibrational Frequencies (in cm$^{-1}$)

| butadiene | | | | | | | | | 2,3-digermabutadiene | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| s-trans | | | gauche | | | s-cis | | | s-trans | | | s-cis$^a$ | | | |
| $a_g$ | 1 | 542 | a | 1 | 184 | $a_1$ | 1 | 316 | $a_g$ | 1 | 177 | $a_1$ | 1 | 103 | 109 |
| | 2 | 947 | | 2 | 295 | | 2 | 922 | | 2 | 280 | | 2 | 272 | 274 |
| | 3 | 1304 | | 3 | 820 | | 3 | 1127 | | 3 | 704 | | 3 | 638 | 638 |
| | 4 | 1409 | | 4 | 930 | | 4 | 1456 | | 4 | 884 | | 4 | 882 | 884 |
| | 5 | 1575 | | 5 | 1056 | | 5 | 1569 | | 5 | 898 | | 5 | 897 | 899 |
| | 6 | 1880 | | 6 | 1101 | | 6 | 1836 | | 6 | 1500 | | 6 | 1503 | 1504 |
| | 7 | 3283 | | 7 | 1143 | | 7 | 3302 | | 7 | 2252 | | 7 | 2237 | 2242 |
| | 8 | 3322 | | 8 | 1436 | | 8 | 3322 | | 8 | 3285 | | 8 | 3298 | 3306 |
| | 9 | 3379 | | 9 | 1565 | | 9 | 3390 | | 9 | 3396 | | 9 | 3405 | 3408 |
| | | | | 10 | 1843 | | | | | | | | | | |
| $a_u$ | 1 | 169 | | 11 | 3293 | $a_2$ | 1 | 156i | $a_u$ | 1 | 54 | $a_2$ | 1 | 5 | 5 |
| | 2 | 576 | | 12 | 3311 | | 2 | 813 | | 2 | 274 | | 2 | 259 | 259 |
| | 3 | 1047 | | 13 | 3386 | | 3 | 1045 | | 3 | 668 | | 3 | 701 | 701 |
| | 4 | 1141 | | | | | 4 | 1121 | | 4 | 833 | | 4 | 836 | 836 |
| | | | b | 1 | 501 | | | | | | | | | | |
| $b_g$ | 1 | 841 | | 2 | 669 | $b_1$ | 1 | 601 | $b_g$ | 1 | 254 | $b_1$ | 1 | 181 | 183 |
| | 2 | 1046 | | 3 | 1057 | | 2 | 1193 | | 2 | 717 | | 2 | 694 | 692 |
| | 3 | 1094 | | 4 | 1122 | | 3 | 1409 | | 3 | 840 | | 3 | 830 | 835 |
| | | | | 5 | 1185 | | 4 | 1537 | | | | | 4 | 893 | 892 |
| $b_u$ | 1 | 312 | | 6 | 1402 | | 5 | 1849 | $b_u$ | 1 | 99 | | 5 | 1497 | 1498 |
| | 2 | 1070 | | 7 | 1533 | | 6 | 3287 | | 2 | 616 | | 6 | 2221 | 2230 |
| | 3 | 1408 | | 8 | 1841 | | 7 | 3311 | | 3 | 837 | | 7 | 3302 | 3306 |
| | 4 | 1517 | | 9 | 3281 | | 8 | 3391 | | 4 | 894 | | 8 | 3410 | 3408 |
| | 5 | 1794 | | 10 | 3305 | | | | | 5 | 1500 | | | | |
| | 6 | 3289 | | 11 | 3390 | $b_2$ | 1 | 556 | | 6 | 2244 | $b_2$ | 1 | 255 | 255 |
| | 7 | 3322 | | | | | 2 | 1053 | | 7 | 3290 | | 2 | 680 | 680 |
| | 8 | 3384 | | | | | 3 | 1126 | | 8 | 3397 | | 3 | 833 | 833 |

$^a$ The second column corresponds to a calculation with a two-points difference formula.

govern the resulting shape and the position of the barrier. Note that the transition state obeys Hammond's postulate in the case of butadiene (102° being closer to 39° than to 180°), whereas it does not in the case of 2,3-digermabutadiene (98° being closer to 180° than to 0°).

In both saddle points as well as in the gauche form of butadiene, the X—XH=$CH_2$ groups remain basically planar, with deviations from planarity associated with changes of less than 2° in the corresponding dihedral angles. Due to the propensity of germanium atoms to pyramidalize, one could have expected such an effect to occur in the rotational transition state of 2,3-digermabutadiene. Hyperconjugation is probably a sufficient driving force that prevents this deformation from occurring.

The force constants for bond lengths and bond angles are following the trends discussed above. Most f-matrix diagonal elements are smaller in the digerma derivative. In particular, the constants corresponding to rotation around the central bond are about twice as large in butadiene than in 2,3-digermabutadiene. In the cis conformer of 2,3-digermabutadiene, the harmonic vibrational frequency for the mode associated with nearly pure torsion around the central bond (1$a_2$) is calculated at 5 cm$^{-1}$ only. This value is confirmed when the harmonic force constants are calculated from a two-point difference formula. This very low frequency for such a mode can be rationalized from the repulsion between the Ge=C bonds occurring in the cis arrangement. A more direct illustration of this effect will be given in the next section. In the trans conformer, this torsional mode (1$a_u$) is still the lower mode in frequency, but it is lying significantly higher, at 54 cm$^{-1}$. In butadiene, the mode corresponding to rotation around the central bond is also the lowest mode, but, due to force constants and mass effects, its associated frequency is larger. As expected, it is higher in the gauche form (1a, 184 cm$^{-1}$) than in the trans form (1$a_u$, 169 cm$^{-1}$).

## Energies

Since the conjugation effects remain of the same extent in the two planar conformers, the s-cis isomer of 2,3-digermabutadiene is close in energy to the s-trans conformer: it lies only 0.4 kcal/mol above, in contrast with the second minimum of butadiene, the nonplanar gauche form, lying at 2.8 kcal/mol above the preferred s-trans form (see Table 3 and Figures 1 and 2). If the $\pi$-conjugation stabilization is of the same extent in both conformers

**Table 3.** Relative Energies$^a$

| | | | SCF | MP4 | MP4 + ZPC |
|---|---|---|---|---|---|
| $H_2C{=}HC{-}CH{=}CH_2$ | s-cis | $C_{2v}$ | 3.9 | 3.5 | 3.4 |
| | gauche | $C_2$ | 3.1 | 2.8 | 2.8 |
| | TS | $C_2$ | 6.1 | 5.8 | 5.5 |
| | s-trans | $C_{2h}$ | 0.0 | 0.0 | 0.0 |
| $H_2C{=}HGe{-}GeH{=}CH_2$ | s-cis | $C_{2v}$ | 0.8 | 0.4 | 0.3 |
| | TS | $C_2$ | 1.8 | 1.6 | 1.6 |
| | s-trans | $C_{2h}$ | 0.0 | 0.0 | 0.0 |

$^a$ In kcal/mol. ZPC stands for zero-point energy correction.

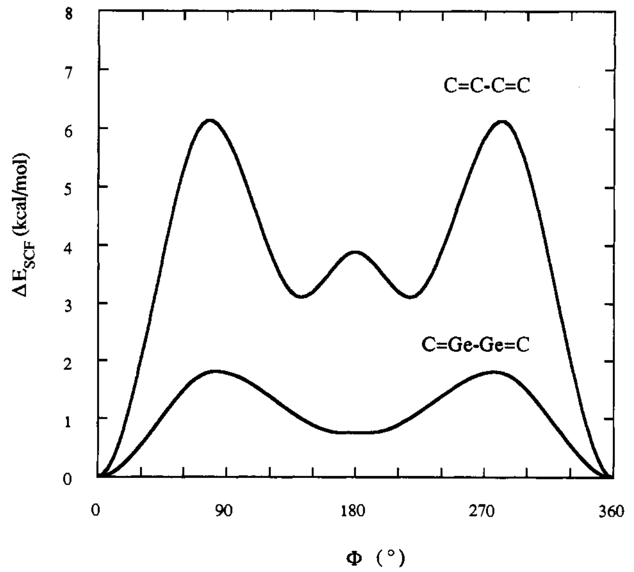


**Figure 1.** SCF-calculated conformational path along the central-bond rotation in butadiene and 2,3-digermabutadiene. The zero rotational angle corresponds to the s-trans form.

**Table 4.** SCF-Calculated Geometries and Relative Energies for *n*-Butane and 2,3-Digerma-*n*-butane[a]

| | | $X_2$–$X_3$ | $C_1$–$X_2$ | $X_2X_3C$ | $\Delta E_{SCF}$ | $\Delta E_{MP4}$ |
|---|---|---|---|---|---|---|
| $CH_3$—$CH_2$—$CH_2$—$CH_3$ | anti | 1.530 | 1.528 | 113.4 | 0.0 | 0.0 |
| | syn | 1.556 | 1.532 | 117.2 | 6.3 | 5.9 |
| | syn (eclipsed) | 1.567 | 1.547 | 120.7 | 16.0 | 15.4 |
| $CH_3$—$GeH_2$—$GeH_2$—$CH_3$ | anti | 2.506 | 1.990 | 112.1 | 0.0 | 0.0 |
| | syn | 2.516 | 1.991 | 111.8 | 0.8 | 0.7 |

[a] Main geometrical parameters, in Å and deg. Relative energies in kcal/mol.

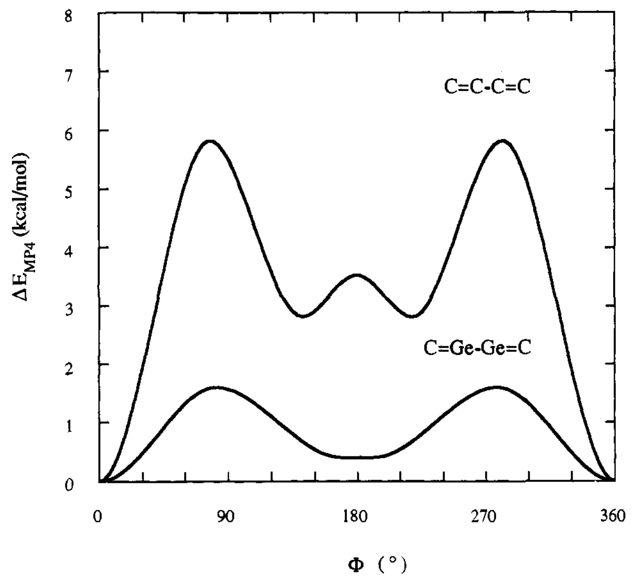


**Figure 2.** MP4-calculated conformational path along the central-bond rotation in butadiene and 2,3-digermabutadiene. The zero rotational angle corresponds to the s-trans form.

of the digerma compound, their difference in energy should mainly come from differences in the repulsion effects between the $\sigma$ bonds. Assuming these are mainly governed by the repulsion between the Ge=$CH_2$ bonds, the energy separation between the two planar conformers should roughly correspond to the energy separation between the syn (s-cis) and anti (s-trans) conformers of 2,3-digermabutane. This happens to be the case. After full geometry optimizations of $C_{2v}$ *syn* and $C_{2h}$ *anti*-2,3-digermabutane (see Table 4), the syn form is calculated to lie at 0.8 (SCF) and 0.7 kcal/mol (MP4) above the anti form, in line with the energy separation between the two rotamers of 2,3-digermabutadiene. The low rotational barrier obtained in the digerma derivative (1.6 kcal/mol) may be attributed to both a lower energy difference between the trans and cis arrangements and to the expected weaker resonance energy occurring in the planar forms.

The energy variation upon rotation around the central bond in the cis isomer happens to be very flat, as reflected by the low frequency associated with this mode (see above). The energy variations upon such a rotation in the trans and cis forms of 2,3-digermabutadiene are plotted in Figure 3, within the rigid rotator approximation (for now, ignore the dashed curves and the curves labeled $\sigma$). To understand the extreme ease for rotation in the cis isomer, one must remember that the s-cis conformation has an unfavored eclipsed arrangement of its $\sigma$ skeleton. As soon as it loses planarity by rotating around the central bond, two opposite effects take place: a *destabilizing* loss of $\pi$ conjugation and a *stabilizing* loss of $\sigma$ steric repulsion. In butadiene, the latter effect prevails, which induces a distortion of the $C_{2v}$ planar form into a $C_2$ gauche nonplanar form. In 2,3-digermabutadiene, because of the long Ge–Ge bond, the s-cis $\sigma$ repulsion is much less strong, so that the former effect prevails. The molecule remains planar, and the $\sigma$ effect makes the rotational coordinate very flat on the potential surface.

To illustrate more quantitatively these effects, let us start with the assumption that the $\sigma$ repulsion effects mainly originate in the repulsion between the Ge=$CH_2$ groups. In this case, there is no $\sigma$ repulsion effect when the s-trans conformer is rotated out of planarity, and, near planar equilibrium geometry, the energy loss can be considered to be due to the loss of $\pi$ conjugation only. The separate effect of $\sigma$ repulsion between the Ge=$CH_2$ groups in the s-cis isomer can be roughly estimated from the syn (s-cis) conformer of the corresponding saturated compound, namely 2,3-digerma-*n*-butane. After geometry optimization (see Table 4), energy benefit upon rotation around the central Ge–Ge bond in this syn conformer is plotted on the $\sigma_1$ curve in Figure 3. When this curve is added to the s-trans curve describing the pure $\pi$ effects, the resulting curve (upper dashed curve) is still significantly above the s-cis curve, which means the $\sigma$ effects have been underestimated. If we now take in the *syn*-digermabutane a central Ge–Ge bond length of 2.46 Å (as in 2,3-digermabutadiene) instead of 2.52 Å, the $\sigma$ effect is enhanced ($\sigma_2$ curve in Figure 3), so that the $\sigma + \pi$ resulting curve (lower dashed curve) is now quite close to the s-cis curve. The effect is even more spectacular when the energies are calculated at the MP4 level, as shown in Figure 4 (this time, the $\sigma$ effect seems slightly overestimated). This schematic discrimination of the two effects has therefore provided a satisfactory rationalization of the flat rotational coordinate in the s-cis isomer of 2,3-digermabutadiene.

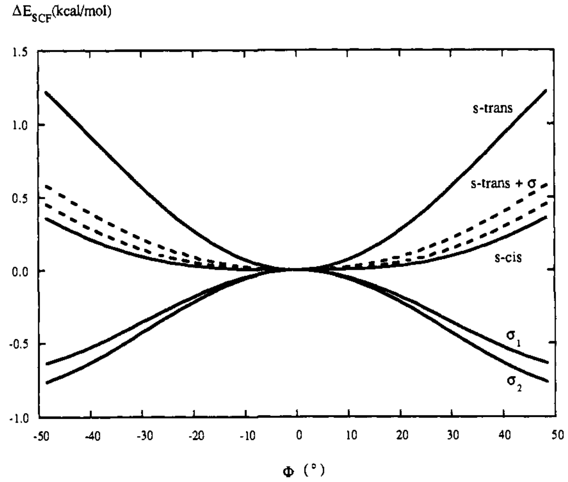


**Figure 3.** Limited rigid rotations around the central Ge–Ge bond in 2,3-digermabutadiene near planar equilibrium geometries. The top full curves correspond to the s-trans and s-cis conformers. The bottom curves labeled $\sigma$ correspond to the energy change upon rotation around the central Ge–Ge bond in *syn*-2,3-digermabutane. $\sigma_1$ corresponds to the optimized geometry of the syn isomer; $\sigma_2$ corresponds to a geometry in which the central Ge–Ge bond is ascribed a shorter value as in *s-cis*-2,3-digermabutadiene. The dashed curves, obtained by adding the s-trans curve to each $\sigma$ curve, illustrate the combination of $\sigma$ and $\pi$ separate effects. All curves are obtained from SCF-calculated energies.

Interestingly, applying such a treatment to *s-cis*-butadiene does lead to the distortion into the gauche form, as shown in Figure 5. To have a reasonable dihedral angle in the gauche form, one must take here also a "short" central C–C bond (1.48 Å, $\sigma_2$ curve) or a totally eclipsed arrangement ($\sigma_3$ curve).

## Discussion

Conjugation through the central bond can be appraised from structural grounds such as geometry, electronic structure, or from

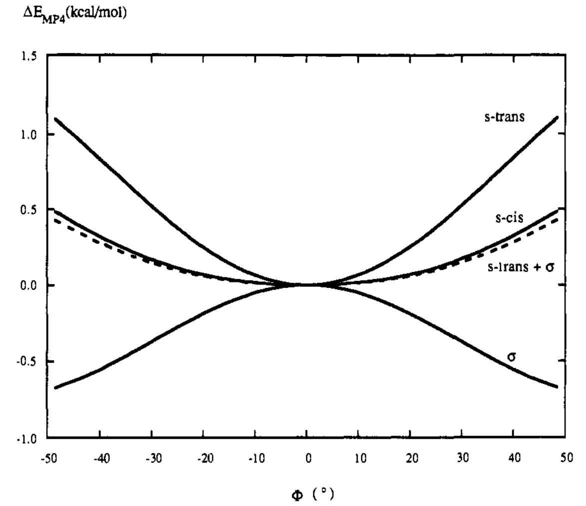


**Figure 4.** Same as Figure 3, from MP4-calculated energies. The $\sigma$ curve corresponds to the $\sigma_2$ case in which the central Ge–Ge bond of *syn*-2,3-digermabutane is arbitrarily shortened to its value in *s-cis*-2,3-digermabutadiene.

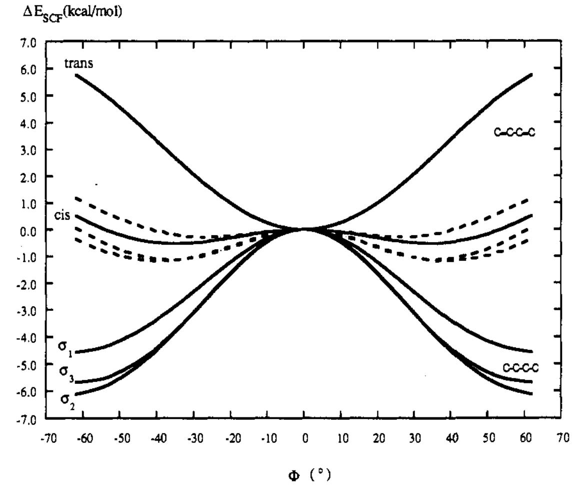


**Figure 5.** Limited rigid rotations around the central C–C bond in butadiene near planar geometries. The top full curves correspond to the s-trans and s-cis conformers. The bottom curves labeled $\sigma$ correspond to the energy change upon rotation around the central C–C bond in *syn-n*-butane. $\sigma_1$ corresponds to the optimized geometry of the syn form; $\sigma_2$ corresponds to a geometry in which the central C–C bond is ascribed a shorter value as in *s-cis*-butadiene; $\sigma_3$ corresponds to a totally eclipsed arrangement in *syn-n*-butane. As in Figure 3, the dashed curves, obtained by adding the s-trans curve to each $\sigma$ curve, illustrate the combination of $\sigma$ and $\pi$ separate effects. All curves are obtained from SCF-calculated energies.

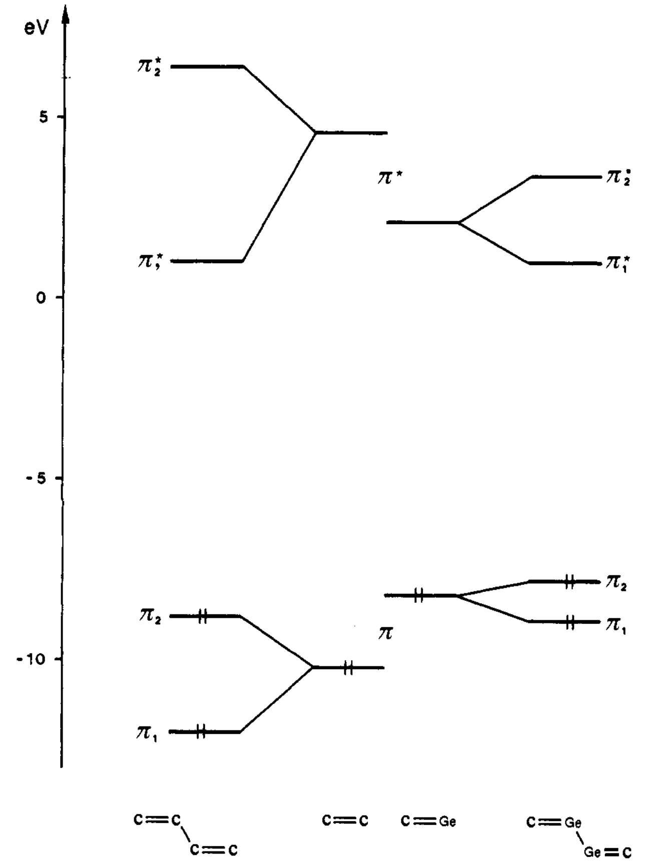


**Figure 6.** $\pi$ level diagram in ethylene, butadiene, germaethylene, and 2,3-digermabutadiene.

various—more or less sophisticated—energetic criteria. Let us try to examine all these criteria and to estimate the relative extent of $\pi$ conjugation in the s-trans forms of 2,3-digermabutadiene and butadiene.

As previously mentioned, the central-bond shortening occurring in the butadiene system with respect to a typical single bond is a first measure of the extent of delocalization between the two conjugated double bonds. Such relative contractions are calculated at -3.7% in butadiene and at -2.0% in 2,3-digermabutadiene, which would suggest that $\pi$ conjugation in the latter is only 54% of that in the former. Doing the same ratios from the relative increase in the stretching force constant of the central bond leads to a comparable result (60%, see Table 5). We next address an electronic structure parameter: the splitting between the two occupied $\pi$ energy levels. This splitting depends on the degree of mixing between the $\pi$ and $\pi^*$ orbitals of the two double bonds and therefore of the conjugation, inasmuch as butadiene can be seen as two interacting double bonds. The $\pi$ orbital interaction diagrams are drawn in Figure 6. The splittings of the occupied $\pi$ levels are listed in Table 5. As expected, it is significantly smaller in the 2,3-digerma derivative than in butadiene. According to this criterion, the conjugation in 2,3-digermabutadiene would be only 34% of that in butadiene.

A direct measure of conjugation in butadiene or any $\pi$-conjugated system has been proposed some time ago, which is grounded on a simple substitution in the Hartree–Fock determinant.[26,27] The procedure consists of calculating the difference between the energy associated with the SCF determinant $\Phi_0$, in which the $\pi_1$ and $\pi_2$ occupied orbitals are canonical delocalized orbitals, and the energy associated with a determinant $\Phi_{\pi\text{loc}}$ similar to $\Phi_0$ but in which the delocalized $\pi_1$ and $\pi_2$ orbitals are replaced by $\pi$ orbitals totally localized on each of the C=C bonds: $\pi_l$ and $\pi_r$ ($l$ and r standing for left and right)

$$\Delta E_\pi = \langle \Phi_{\pi\text{loc}}|H|\Phi_{\pi\text{loc}}\rangle - \langle \Phi_0|H|\Phi_0\rangle$$

$$\Phi_0 = |\sigma_1\bar{\sigma}_1\sigma_2\bar{\sigma}_2\cdots\sigma_n\bar{\sigma}_n\pi_1\bar{\pi}_1\pi_2\bar{\pi}_2|$$

$$\Phi_{\pi\text{loc}} = |\sigma_1\bar{\sigma}_1\sigma_2\bar{\sigma}_2\cdots\sigma_n\bar{\sigma}_n\pi_l\bar{\pi}_l\pi_r\bar{\sigma}_r|$$

This energy difference, also called *vertical resonance energy*,[27] is a direct estimate of the $\pi$ conjugation energy which is gained when two double bonds are coupled as in butadiene. Alternatively, it can be viewed as the $\pi$ localization energy, which is lost when the two $\pi$ bonds of butadiene are forced to be separate without any interaction. This $\pi$ localization energy is meaningful as long as the whole system is not too unsymmetrical or not too polarized, since the $\sigma$ orbitals are the same in $\Phi_0$ and $\Phi_{\pi\text{loc}}$, or, in other words, since the $\sigma$ skeleton is not allowed to repolarize or readapt to the new $\pi$-localized environment. This measure would not be therefore relevant in unsymmetrical monosubstituted systems such

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(26) Daudey, J. P.; Trinquier, G.; Barthelat, J. C.; Malrieu, J. P. *Tetrahedron* **1980**, *36*, 3399.

(27) Kollmar, H. *J. Am. Chem. Soc.* **1979**, *101*, 4832.

**Table 5.** Comparative Evaluation of π-Conjugation in Butadiene and 2,3-Digermabutadiene from Various Criteria

| criterion | parameter | butadiene | 2,3-digermabutadiene | digerma/butadiene |
|---|---|---|---|---|
| geometry[a] | relative central-bond shortening | −3.7% | −2.0% | 54% |
| | corresponding force-constant increase | +17% | +10% | 60% |
| energy[b] | occupied π-level splitting | 3.2 eV | 1.1 eV | 34% |
| | π localization energy | 10.4 kcal/mol | 3.9 kcal/mol | 37% |
| | bond separation energy SCF | 10.6 kcal/mol | 5.0 kcal/mol | 47% |
| | bond separation energy MP4 | 12.5 kcal/mol | 7.1 kcal/mol | 56% |

[a] Relative variations with respect to ethane or digermane. [b] See text for the definitions.

**Table 6.** Infrared Intensities and Vibrational Assignments for 2,3-Digermabutadiene

| s-trans | | | s-cis | | | |
|---|---|---|---|---|---|---|
| symmetry | frequency (cm$^{-1}$) | IR intensity | symmetry | frequency (cm$^{-1}$) | IR intensity | main assignment |
| $1a_u$ | 54 | 0.0 | $1a_2$ | 5 | | GeGe torsion |
| $1b_u$ | 99 | 0.2 | $1b_1$ | 181 | 0.4 | CGeGe in-plane bending antisym |
| $1a_g$ | 177 | | $1a_1$ | 103 | 0.1 | CGeGe in-plane bending sym |
| $1b_g$ | 254 | | $1b_2$ | 255 | 0.2 | out-of-plane bending |
| $2a_u$ | 274 | 0.2 | $2a_2$ | 259 | | out-of-plane bending |
| $2a_g$ | 280 | | $2a_1$ | 272 | 0.0 | GeGe str |
| $2b_u$ | 616 | 1.5 | $3a_1$ | 638 | 0.1 | HGeGe bending + HCGe bending |
| $3a_u$ | 668 | 1.5 | $2b_2$ | 680 | 1.4 | |
| $3a_g$ | 704 | | $2b_1$ | 694 | 0.7 | HGeGe bending + HCGe bending |
| $2b_g$ | 717 | | $3a_2$ | 701 | | |
| $4a_u$ | 833 | 1.8 | $3b_2$ | 833 | 1.8 | GeC str + in-plane bending |
| $3b_u$ | 837 | 5.9 | $3b_1$ | 830 | 5.8 | |
| $3b_g$ | 840 | | $4a_2$ | 836 | | |
| $4a_g$ | 884 | | $4a_1$ | 882 | 0.0 | GeC str sym |
| $4b_u$ | 894 | 0.5 | $4b_1$ | 893 | 0.5 | GeC str antisym |
| $5a_g$ | 898 | | $5a_1$ | 897 | 0.2 | GeC str + in-plane bending |
| $5b_u$ | 1500 | 0.2 | $5b_1$ | 1497 | 0.0 | HCH bending antisym |
| $6a_g$ | 1500 | | $6a_1$ | 1503 | 0.1 | HCH bending sym |
| $6b_u$ | 2244 | 5.6 | $6b_1$ | 2221 | 3.2 | GeH str antisym |
| $7a_g$ | 2252 | | $7a_1$ | 2237 | 3.5 | GeH str sym |
| $8a_g$ | 3285 | | $8a_1$ | 3298 | 0.1 | CH str |
| $7b_u$ | 3290 | 0.2 | $7b_1$ | 3302 | 0.1 | CH str |
| $9a_g$ | 3396 | | $9a_1$ | 3405 | 0.0 | CH str |
| $8b_u$ | 3397 | 0.0 | $8b_1$ | 3410 | 0.0 | CH str |

as 1-germabutadiene or 2-germabutadiene. In the present symmetrical case of 2,3-digermabutadiene, the procedure is quite valid since the whole system is not polar, and there is no resulting π electron transfer from one double bond to the other one. The procedure leads to a π localization increment of 10.4 kcal/mol for butadiene and 3.9 kcal/mol for 2,3-digermabutadiene. According to this criterion, the extent of conjugation in the digerma derivative would be only 37% of that in butadiene.

We now consider a last index which should be more rigorous. We will evaluate the *bond separation energies* as the energy of the following isodesmic reactions, in which the number of bonds of each type is conserved in both members of the equation

$$H_2C{=}CH{-}HC{=}CH_2 + 2CH_4 \rightarrow H_2C{=}CH_2 + H_3C{-}CH_3 + H_2C{=}CH_2$$

$$H_2C{=}GeH{-}HGe{=}CH_2 + 2GeH_4 \rightarrow H_2C{=}GeH_2 + H_3Ge{-}GeH_3 + H_2Ge{=}CH_2$$

This will measure the energy gain resulting from the coupling of two π bonds. Since each species is relaxed in its ground state, this index has an adiabatic character, whereas the previous one had a vertical character. It is encouraging to see that in butadiene, the bond separation energy is calculated at 10.6 kcal/mol, which differs from the π localization energy by only 0.2 kcal/mol. For 2,3-digermabutadiene, the bond separation energy is calculated 5.0 kcal/mol, which is 1.1-kcal/mol larger than the π localization index. According to these SCF bond separation energies, the extent of conjugation in the digerma derivative would be 47% of that in butadiene. Taking into account correlation effects through MP4 energy calculations favors the conjugated systems by 2 kcal in both cases, which increases our increments by a similar amount and enhances our ratio to 56% (see Table 5). Restraining any quest to further accuracy in this analysis, it seems sensible to conclude that the extent of π conjugation in 2,3-digermabutadiene is about *half* that in butadiene. This percentage is further confirmed by the ratio of the force constants for torsion around the central bond in the s-trans planar conformers of 2,3-digermabutadiene and butadiene (53%).

To help in the interpretation of possible spectroscopic data, the assignments and infrared intensities for the vibrational modes of 2,3-digermabutadiene are given in Table 6. The corresponding simulated infrared spectra for these parent compounds are given in Figure 7.

In conclusion, the present study has shown that the parent analogue of butadiene with germanium atoms at symmetrical positions 2 and 3, $H_2C{=}GeH{-}GeH{=}CH_2$, possesses two stable planar conformations, s-cis and s-trans, close in energy. Such a system undergoes a π conjugation through the germanium atoms, the extent of which can be estimated to be about half that occurring in butadiene. These points should be kept in mind when devising synthetic routes toward such a functional group, even if the real synthetic targets bear miscellaneous substituents. Among the other germanium analogues of butadiene under investigation, tetragermabutadiene is expected to have the most promising structural properties.

## Appendix

The calculations were performed with the HONDO8 program from the MOTECC package.[28] For carbon and germanium atoms, effective core potentials were used.[29] The DZP valence basis sets consist of four Gaussian functions contracted to a

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(28) Dupuis, M. MOTECC89; IBM Corporation, Center for Scientific and Engineering Computations: Kingston, NY 12401.

(29) Durand, Ph.; Barthelat, J.-C. *Theor. Chim. Acta* **1975**, *38*, 283.

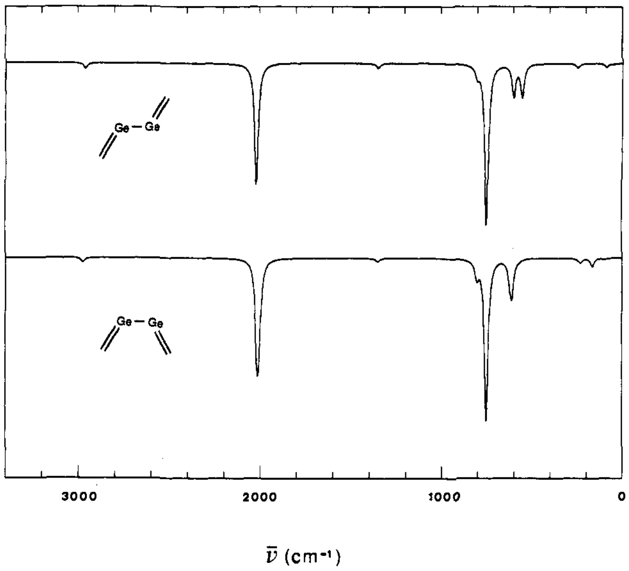

**Figure 7.** Simulated infrared spectra for the two conformers of 2,3-digermabutadiene. The SCF-calculated frequencies are scaled by a factor of 0.9.

double-$\zeta$ level and augmented by a polarization function. The exponents for the d functions are taken at 0.80 for carbon and 0.25 for germanium. The exponent for the p function on hydrogen is taken at 0.90. The geometries are optimized at the RHF-SCF level, the final gradient Cartesian components being better than $10^{-6}$. The harmonic vibrational frequencies are obtained from force constants calculated by finite differences of analytical first derivatives, using a single-point differencing formula (for *s-cis*-2,3-digermabutadiene, a two-point differencing formula was also tested, as reported in Table 2). The frequencies used for the zero-point energy corrections (ZPC) in Table 3 and in the spectra of Figure 7 were scaled by a factor of 0.9. On each stationary point, the energy is recalculated at the MP4 SDTQ level (Möller–Plesset perturbation theory applied to the fourth order). All energy curves upon rotation around planar equilibrium geometries reported in Figures 3–5 were obtained within a rigid rotator model from a set of angles ranging from 0° to 62° by steps of about 6° and were interpolated using cubic splines functions. The $\pi$-localized determinants used in the discussion were obtained as follows, according to the procedure defined in ref 26. In the SCF-converged wave function of the butadiene system, the delocalized $\pi_1$ and $\pi_2$ orbitals are replaced by two $\pi$ orbitals corresponding to the two isolated double bonds. In $\pi_1$ and $\pi_2$, the coefficients of each $p_z$ orbital on the *four* atoms are therefore replaced by coefficients of each $p_z$ orbital on the *two* atoms of the given double bond. These coefficients are taken as they come out from an SCF calculation on the isolated ethylenic system. Because of the use of polarization functions, the residual coefficient on one of the XH hydrogens in $H_2C{=}XH_2$ has to be transferred to the X vicinal atom in $H_2C{=}XH{-}HX{=}CH_2$. After properly splitting, this small coefficient of the $p_z$-type orbital on hydrogen is reinjected into the two $d_z$-type orbitals on the X atom. The so-altered wave function is then orthonormalized, and the energy of the associated determinant is given at iteration zero of a restarted SCF procedure.