3148 *Organometallics* **1997,** *16,* 3148−3157

Enhanced Conjugation in 1,4-Digermabutadiene

Claude Jouany and Georges Trinquier*

Laboratoire de Physique Quantique, IRSAMC-CNRS, Université Paul-Sabatier,
31062 Toulouse Cedex, France

Received March 4, 1997[⊗]

Due to the different strengths of the $Ge{=}C$ and $C{=}C$ π bonds, 1,4-digermabutadiene $H_2Ge{=}HC{-}CH{=}GeH_2$ is expected to exhibit stronger conjugation through its central $C{-}C$ bond than does butadiene. Ab initio calculations are used to investigate this effect. Like butadiene, 1,4-digermabutadiene has a preferred planar *s-trans* form, with two equivalent gauche conformers lying 3 kcal/mol higher in energy. As in butadiene, the *s-cis* planar form is a saddle point relating the two gauche forms, corresponding to a barrier of 1 kcal/mol. The perpendicular form associated with the rotational barrier around the central $C{-}C$ bond is found to be significantly higher in the 1,4-digerma derivative than in butadiene (10 vs 6 kcal/mol). Other indicators, based on geometry or energy criteria, actually suggest that π-conjugation in 1,4-digermabutadiene is about one-and-a-half that in butadiene. The ensuing enhanced weight of valence-bond forms reflecting electron arrangements like ${}^{\bullet}H_2Ge{-}HC{=}CH{-}GeH_2{}^{\bullet}$ is expected to favor 1,4-couplings, such as the intramolecular cyclization into 3,4-digermacyclobutene. In its conrotatory thermally-allowed pathway, this rearrangement is found to require a weak activation barrier of about 1 kcal/mol above the starting gauche form. The strong *exothermicity* of such an internal ring closure, calculated at 44 kcal/mol from the gauche conformer, is due to bond energies and geometrical features in the final four-membered frame, in contrast with the *endothermic* butadiene-to-cyclobutene rearrangement. The 1,4-diradical character of 1,4-digermabutadiene is further attested by a weak torsional barrier around the $Ge{=}C$ bond, estimated at less than 5 kcal/mol, and a low-lying triplet state, located at only 6 kcal/mol above the closed-shell singlet ground state.

The problem of substituting carbon atoms with heavier analogues in a 1,3-butadiene skeleton has attracted attention for many years. Attempts to synthesize such species have only yielded to transient species, verified by appropriate trapping reactions. Although active research is being developed on mono- and digermabutadiene derivatives,[1,2] to date only mono- and disilabutadiene derivatives have been the object of effective indirect evidence.[3−8]

In a previous theoretical study, we addressed the substitution of carbon by germanium at positions 2 and 3 on the 1,3-butadiene frame.[9] It was shown how the central bond conjugation is reduced in 2,3-digermabutadiene $H_2C{=}HGe{-}GeH{=}CH_2$ and why this compound possesses two nearly-degenerate planar conformers, *s-trans* and *s-cis*. We wish to report in the present paper a quantum chemical study on the other symmetrical alternative, the 1,4-digermabutadiene $H_2Ge{=}HC{-}CH{=}GeH_2$. We shall see that here, by contrast, the central bond conjugation is enhanced and that this has notable consequences on the chemical reactivity.

For the geometry optimization step, the ab initio calculations are carried out at the Hartree−Fock level, with double-zeta-plus-polarization basis sets, and using effective core potentials. On each stationary point so obtained, correlation effects are estimated through Möller−Plesset fourth-order perturbation calculations (MP4), leading to the refined energies that will be discussed in the paper. We shall start with energies and structures. Then, we will examine the extent of π conjugation. Next, the easy electrocyclic rearrangement into 3,4-digermacyclobutene will be studied. Last, a brief inspection of the first triplet state, unavoidable in view of the diradical character of our system, will precede the conclusion. Technical details concerning the methods and basis sets are given in the Appendix. As previously done,[9] and for the sake of consistency in the comparisons, the same treatments were also applied to the butadiene molecule.

Potential Energy Surface

From butadiene to 1,4-digermabutadiene, the central $C{-}C$ bond is unchanged while the $C{=}C$ and terminal $C{-}H$ bonds are changed into $C{=}Ge$ and $Ge{-}H$ bonds, respectively. As far as the $H_3 \cdots H_4$ repulsion in the *s-cis* form is concerned, **1**, the corresponding CC→ CGe and CH → GeH lengthenings work in opposite directions.

[⊗] Abstract published in *Advance ACS Abstracts,* June 1, 1997.

(1) Chaubon-Deredempt, M. A.; Escudié, J.; Couret, C. *J. Organomet. Chem.* **1994**, *467*, 37.

(2) Chaubon-Deredempt, M. A. Thesis. Université Paul-Sabatier, Toulouse, France, 1995.

(3) Ishikawa, M.; Sakamoto, H.; Tabuchi, T. *Organometallics* **1991**, *10*, 3173.

(4) Sakamoto, H.; Ishikawa, M. *J. Organomet. Chem.* **1992**, *427*, C26.

(5) Naka, A.; Okazaki, S.; Hayashi, M.; Ishikawa, M. *J. Organomet. Chem.* **1995**, *499*, 35.

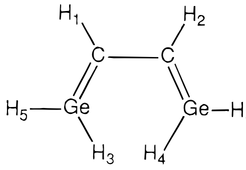
(6) Ando, W.; Sugiyama, M.; Suzuki, T.; Kato, C.; Arakawa, Y.; Kabe, Y. *J. Organomet. Chem.* **1995**, *499*, 99.

(7) Ishikawa, M.; Okazaki, S.; Naka, A. *Organometallics* **1995**, *14*, 114.

(8) Naka, A.; Hayashi, M.; Okazaki, S.; Kunai, A.; Ishikawa, M. *Organometallics* **1996**, *15*, 1101.

(9) Jouany, C.; Mathieu, S.; Chaubon-Deredempt, M. A.; Trinquier, G. *J. Am. Chem. Soc.* **1994**, *116*, 3973.

S0276-7333(97)00179-9 CCC: $14.00



1

Consequently, one expects that the shape of the potential energy surface for rotation around the central bond will be roughly similar to that occurring in butadiene, in which a rather short $H_3 \cdots H_4$ contact induces a distortion of the planar *s-cis* form into a nonplanar gauche form. An *s-cis* planar geometry obtained by rigid rotation of *s-trans*-1,4-digermabutadiene, thus preserving all its geometrical parameters but the GeCCGe dihedral angle, would put H_3 and H_4 only 2.50 Å apart, which should be short enough to induce the distortion.

The shape of the potential energy surface along the coordinate corresponding to the torsion around the central C−C bond is found to be similar to that of butadiene, indeed, with three minima and two saddle points. The preferred rotamer corresponds to the *s-trans* planar arrangement. Two equivalent nonplanar gauche forms, lying higher in energy, can be interconverted via the saddle point of the planar *s-cis* conformation. The gauche rotamer is separated from the preferred *s-trans* conformation by a saddle point corresponding to a quasi perpendicular conformation, in which the two $H_2Ge{=}CH$ sets are roughly orthogonal. In this form, corresponding to the rotational barrier, π conjugation cancels out and is replaced by hyperconjugation.

The relative energies for these stationary points are listed in Table 1. Except for the perpendicular rotational barrier, they happen to be close to those found in butadiene. The gauche form is lying 3.1 kcal/mol above the preferred *s-trans* planar form (vs 2.8 kcal/mol in butadiene). The planar *s-cis* barrier separating the two gauche forms is calculated at 0.9 kcal/mol (vs 0.7 kcal/mol in butadiene). The perpendicular saddle point corresponding to the rotational barrier is lying 9.5 kcal/mol above the *s-trans* form, which is significantly higher than the corresponding rotational barrier found in butadiene (5.8 kcal/mol). This significant energy difference already suggests there is more π conjugation through the central C−C bond in 1,4-digermabutadiene than in butadiene, an effect not compensated for by the differential hyperconjugation. The energy variation along the central bond rotational coordinate is plotted in Figures 1 and 2 for the SCF and MP4 levels of calculation, respectively. The barrier to overcome for the conversion of the gauche form into the preferred *s-trans* form, via the perpendicular form, is as high as 6.4 kcal/mol. This would suggest such a metastable form could have a sufficient lifetime to be trapped; in fact, we shall see there exists a more favorable channel from the gauche form.

Table 1. Relative Energies[a]

			SCF	MP4	MP4 + ZPC
cyclobutene		C_{2v}	14.5	10.9	11.9
$H_2C{=}CH{-}CH{=}CH_2$	TS	C_2	59.9	46.4	45.8
	s-cis	C_{2v}	3.9	3.5	3.4
	gauche	C_2	3.1	2.8	2.8
	perpendicular	C_2	6.1	5.8	5.5
	s-trans	C_{2h}	0	0	0
3,4-digermacyclobutene		C_{2v}	−54.3	−41.3	−39.7
$H_2Ge{=}CH{-}CH{=}GeH_2$	TS	C_2	6.2	4.0	3.7
	s-cis	C_{2v}	4.5	4.0	3.8
	gauche	C_2	3.9	3.1	3.0
	perpendicular	C_2	11.3	9.5	9.1
	s-trans	C_{2h}	0	0	0

[a] In kcal/mol. ZPC stands for zero-point energy correction. TS corresponds to the transition states for the conrotatory cyclizations.

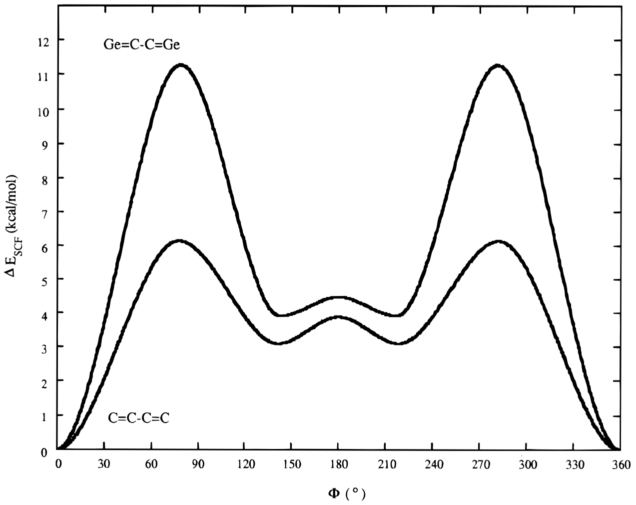


Figure 1. SCF-calculated conformational path along the central bond rotation in butadiene and 1,4-digermabutadiene. The zero rotational angle corresponds to the *s-trans* form.

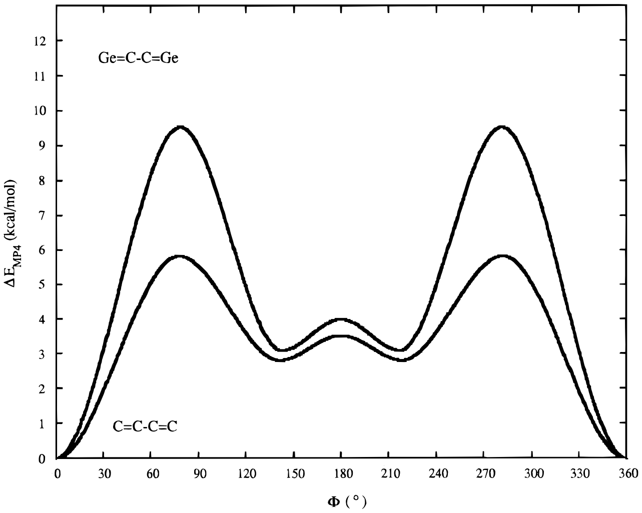


Figure 2. MP4-calculated conformational path along the central bond rotation in butadiene and 1,4-digermabutadiene. The zero rotational angle corresponds to the *s-trans* form.

The geometrical parameters, given in Table 2, all confirm the high π conjugation in 1,4-digermabutadiene. In the *s-trans* conformer, the C−C bond length is calculated at 1.43 Å, which represents a shortening of more than 6% with respect to ethane, while this shortening is less than 4% in butadiene. This effect is paralleled by the harmonic stretching force constants (diagonal elements of the *f* matrix) found to be 6.1 and 5.7 mdyn/Å, respectively. The enhanced partial double-bond character of the central −HC−CH− bond in $H_2Ge{=}CH{-}CH{=}GeH_2$ is of course concomitant with the decreased double-bond character of the $H_2Ge{=}CH{-}$ fragments. The GeC bond is 0.03 Å longer than in germaethylene, while it was only 0.01 Å longer in 2,3-

Table 2. SCF-Calculated Geometries[a]

			C−C	C=C	C=Ge	$C-H_1$	$X-H_3$	$X-H_5$	CCX	CCH_1	CXH_3	CXH_5	XCCX
$H_2C=HC-CH=CH_2$	*s-trans*	C_{2h}	1.470	1.328		1.086	1.085	1.083	124.2	116.4	121.7	121.4	180.
	perpendicular	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
$H_2Ge=HC-CH=GeH_2$	*s-trans*	C_{2h}	1.432		1.817	1.086	1.540	1.538	126.7	117.4	122.4	121.1	180.
	perpendicular	C_2	1.483		1.796	1.088	1.542	1.542	127.4	117.2	123.6	121.2	101.4
	gauche	C_2	1.441		1.815	1.088	1.541	1.540	129.1	115.9	122.9	120.5	37.2
	s-cis	C_{2v}	1.439		1.816	1.087	1.540	1.537	133.4	114.6	124.7	119.4	0
H_3C-CH_3		D_{3d}	1.527			1.093							
$H_2C=CH_2$		D_{2h}		1.322		1.084				121.7			
$H_2C=GeH_2$		C_{2v}			1.784	1.083	1.541				122.9		

[a] Selected geometrical parameters, in angströms and degrees. See **1** for atom labeling. The perpendicular form is the saddle point corresponding to the rotational barrier. The *s-cis* form is the saddle point relating the two gauche forms.

Table 3. Harmonic Vibrational Frequencies, with Infrared Intensities and Vibrational Assignments[a]

1,4-digermabutadiene *s-trans* (C_{2h})				1,4-digermabutadiene gauche (C_2)				3,4-digermacyclobutene (C_{2v})			
	ν (cm^{-1})	IR intensity	main assignment		ν (cm^{-1})	IR intensity	main assignment		ν (cm^{-1})	IR intensity	main assignment
$1a_u$	99	0.1	CC torsion	1a	88	0.0	GeCCGe str + CCGe bend.	$1a_2$	233		ring puckering
$1b_u$	154	0.1	CCGe bend.	2a	170	0.0	CC torsion + CC str	$1a_1$	274	0.0	GeGe str
$1a_g$	212		GeCCGe str+ CCGe bend.	1b	270	1.5	CGe torsion	$1b_2$	372	0.1	ring in-plane bend.
$2a_u$	253	0.0	HGeH pyram	3a	306	0.0	CGe torsion	$1b_1$	403	0.4	HGeH rock.
$1b_g$	293		HGeH pyram	2b	323	0.9	HGeH pyram	$2a_2$	538		HGeH rock.
$3a_u$	377	0.1	CGe torsion	3b	396	0.3	HGeH pyram.	$2b_1$	577	0.0	HGeH twist.
$2a_g$	505		GeCCGe str + HGeH rock.	4a	481	0.0	GeCCGe str	$2a_1$	627	0.4	ring in-plane bend.
$2b_g$	520		CGe torsion	5a	536	0.2	GeCCGe str + HGeH rock.	$2b_2$	654	3.5	HGeH wag.
$2b_u$	599	2.5	HGeH rock.	4b	657	1.1	GeC str + HGeH scis	$3a_2$	669		HGeH twist.
$3b_g$	847		CCH bend.	6a	731	0.7	GeC str	$3b_2$	723	0.8	ring in-plane bend.
$3a_g$	854		GeC str + CCGe bend.	5b	827	0.8	CC torsion + GeC str	$3a_1$	774	3.5	HGeH wag.
$3b_u$	869	0.2	GeC str	6b	866	0.2	GeC str + CCGe bend.	$3b_1$	813	4.2	CH out-of-plane bend.
$4b_u$	913	1.8	HGeH scis + GeC str	7a	891	0.1	GeCCGe torsions + CC str	$4b_2$	955	5.5	HGeH scis
$4a_g$	916		HGeH scis	8b	911	1.3	HGeH scis + GeC str	$4a_1$	960	1.9	HGeH scis
$4a_u$	971	0.9	CCH out-of-plane bend.	8a	915	1.3	HGeH scis	$4a_2$	1103		CH out-of-plane bend.
$5a_g$	1250		CC str	9a	1200	0.0	CC str + CCH bend.	$5a_1$	1152	0.3	CH in-plane bend.
$5b_u$	1282	1.0	CCH in-plane bend.	10a	1396	0.6	CC str + CCH bend.	$5b_2$	1376	0.2	CH in-plane bend.
$6a_g$	1504		CC str + CCH bend.	9b	1440	0.0	CCH bend. + CGe str	$6a_1$	1659	0.1	CC str
$7a_g$	2264		GeH str	11a	2257	0.4	GeH str	$5a_2$	2168		GeH str
$6b_u$	2267	5.2	GeH str	10b	2260	4.9	GeH str	$4b_1$	2177	8.7	GeH str
$7b_u$	2275	3.2	GeH str	11b	2268	0.8	GeH str	$6b_2$	2186	7.9	GeH str
$8a_g$	2277		GeH str	12a	2271	1.9	GeH str	$7a_1$	2195	2.0	GeH str
$9a_g$	3284		CH str	12b	3267	0.2	CH str	$7b_2$	3289	0.2	CH str
$8b_u$	3299	0.2	CH str	13a	3288	0.2	CH str	$8a_1$	3308	0.9	CH str

[a] Abbreviations used: str, stretching; bend., bending; pyram, pyramid; rock., rocking; scis, scissoring; twist., twisting; wag., wagging.

digermabutadiene. Note that this short CC bond is also observed in the planar *s-cis* saddle point (1.44, vs 1.48 Å in butadiene).

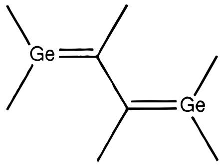
The harmonic vibrational frequencies of the two conformers of 1,4-digermabutadiene are listed in Table 3, together with the main assignments and infrared intensities. For the *s-trans* conformer, a comparison with the values of *s-trans* 2,3-digermabutadiene,[9] which has similar mass effects, illustrates the above-discussed effects. Typically, the central bond torsional mode occurs at a frequency of 54 cm^{-1} in 2,3-digermabutadiene (vs 99 cm^{-1} in 1,4-digermabutadiene), and the C=Ge stretching modes occur at 884 and 894 cm^{-1} (vs 854 and 869 cm^{-1}).

In the *s-trans* form, the Ge=C−C valence angle is calculated at 127°, which is larger than the corresponding C=C−C valence angle in butadiene (124°) and larger than the C=Ge−Ge valence angle found in 2,3-digermabutadiene (122°). Given the lower electronegativity of germanium, these trends are in agreement with a Gillespie model prediction. For the nonplanar stationary points, the X=C−C=X dihedral angle is remarkably similar in 1,4-digermabutadiene and butadiene. In the perpendicular forms, where this angle is calculated at 101° and 102°, respectively, this should occur for the structural reason of breaking the π conjugation. In the gauche form, the Ge=C−C=Ge dihedral angle is calculated at 37°, again close to the C=C−C=C dihedral angle found in butadiene (39°). This similarity, related with that of the corresponding gauche → *s-cis* barriers to planarity (0.9 and 0.7 kcal/mol, respectively), might seem more unexpected since these features reflect a compromise between the wanted loss of σ repulsion and the unwanted loss of π conjugation.

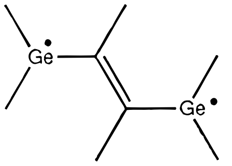
In the 1,4-digerma derivative, since the central bond conjugation is stronger, it must be compensated by a loss of σ repulsion. The reason why σ repulsion is stronger in 1,4-digermabutadiene lies more in bond polarities than in pure geometrical hindrance, since two facing $-C=Ge-H_3$ strong multipoles induce more repulsion than did two facing $-C=C-H_3$ weakly polar groups. This can be checked on the energy curve corresponding to the rotation around C−C in *syn* 1,4-digermabutane. As previously done on *n*-butane and 2,3-digermabutane,[9] this energy curve has been plotted both for the C_{2v} optimized geometry and after assigning to the central C−C bond the same short length as that occurring in *s-cis* planar 1,4-digermabutadiene. We could check, especially in the latter case, that the energy improvement upon C−C torsion in *syn* $H_3Ge-CH_2-CH_2-GeH_3$ is larger than that for the loss of π conjugation, as measured from the torsional curve of the unconstrained *s-trans* isomer. The sum of these two curves does lead to the gauche minimum appearing in Figures 1 and 2.

Bonding

Given what we know about the relative strengths of the C=C and Ge=C π bonds, the strong conjugation or delocalization in 1,4-digermabutadiene is not unexpected. The energy of a C=C π bond is about 63 kcal/mol while that of a Ge=C π bond is estimated around 30 kcal/mol,[10] which is *less than half*. Were the two π bonds strictly localized in 1,4-digermabutadiene, **2**, the π contribution to the binding energy would be about 60 kcal/mol (2 × 30). If the system was a true diradical with a genuine central C=C bond, **3**, the π energy would therefore contribute alike, formally.



2



3

In a valence-bond model, conjugation translates by the significant involvement, in the wavefunction, of forms reflecting **3**, besides the classical forms reflecting **2**.[11] In **2**, the four π electrons combine to form two π bonds localized on each Ge=C part. In **3**, they contribute to a localized C=C bond, the GeH_2 side groups remaining neutral, hence a diradical character. The involvement of structure **3**, therefore, suggests a 1,4-diradical behavior for 1,4-digermabutadiene, with facilitated 1,4-coupling reactions, and the existence of a low-lying competing triplet state.

The strong conjugation is reflected by the nature of the π orbitals and their one-electron energies. In *s-trans* 1,4-digermabutadiene, the lowest and highest π orbitals, π_1 and π_4, have large coefficients on the carbon atoms, prefiguring the π system of ethylene. The matching between π_1 and π_4 and the π and π^* levels in ethylene is further emphasized on an energy level diagram, as illustrated in Figure 3.

In the molecular-orbital approach, due to the symmetry, form **3** implies strict π neutrality along the Ge−C−C−Ge skeleton. Significant involvement of configurations like **3** in 1,4-digermabutadiene should therefore smooth the π net charges. This is verified from the π net charges given by the Mulliken population analysis. With respect to the π polarity of germaethylene, the Ge=C π polarity is significantly reduced in 1,4-digermaethylene while it is clearly less so in 2,3-digermabutadiene, **4**.

Incidentally, the total net charges (Ge, +0.40; C, −0.29) exhibit a reversal in the intensities with respect to those of 2,3-digermabutadiene (Ge, +0.29; C, −0.40).

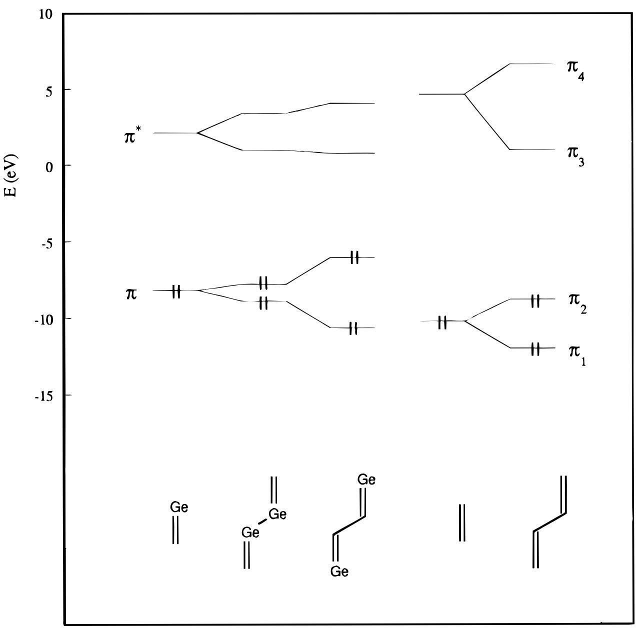
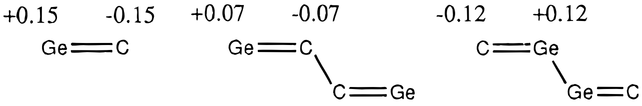


Figure 3. π Level diagram in germaethylene, digermabutadienes, ethylene, and butadiene.



4

As previously performed on 2,3-digermabutadiene,[9] more direct and objective estimates of the delocalization energy have been attempted. We first operated a simple substitution in the Hartree−Fock determinant. In this procedure,[12,13] the π conjugation energy is calculated as the difference between the energy associated with the SCF determinant ϕ_0, in which the π_1 and π_2 occupied orbitals are the canonical delocalized orbitals, and the energy associated with a determinant similar to ϕ_0 but in which the delocalized π_1 and π_2 orbitals are replaced by π orbitals totally localized on each Ge=C bond. In 1,4-digermabutadiene, this vertical resonance energy is calculated to be as large as 26 kcal/mol, which is more than twice that calculated in butadiene (10 kcal/mol). This value is overestimated because the procedure does not allow proper σ repolarization in the π-localized structure. Such σ polarity relaxation is probably important here, due to the presence of four polar Ge−H bonds (the σ net charges are calculated at +0.32 on Ge and −0.22 on C while they were +0.17 and −0.29, respectively, for 2,3-digermabutadiene).

A more reliable way for getting the resonance energy is to compute the energy required for separating the two Ge=C bonds by means of the isodesmic reaction

$$H_2Ge{=}CH{-}CH{=}GeH_2 + 2CH_4 \rightarrow H_2Ge{=}CH_2 + H_3C{-}CH_3 + H_2C{=}GeH_2$$

The calculated energy difference between both members

---

[10] (a) Purcell, K. F.; Kotz, J. C. *Inorganic Chemistry*; Saunders: Philadelphia, PA, 1977; p 270. (b) Dobbs, K. D.; Hehre, W. J. *Organometallics* **1986**, *5*, 2057. (c) Windus, T. L.; Gordon, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 9559.

[11] In valence-bond language, the difference between **2** and **3** lies in that **2** is associated with determinants corresponding to ionic arrangements at the Ge=C bonds (such as $Ge^+{-}C^-$ or $Ge^-{-}C^+$) while **3** is associated with determinants corresponding to ionic arrangements at the C=C bond ($C^+{-}C^-$ and $C^-{-}C^+$). Of course, both forms are also associated with the neutral determinants with one π electron at each center.

[12] (a) Daudey, J. P.; Trinquier, G.; Barthelat, J. C.; Malrieu, J. P. *Tetrahedron* **1980**, *36*, 3399. (b) Kollmar, H. *J. Am. Chem. Soc.* **1979**, *101*, 4832.

[13] For other measures of delocalization or resonance in butadiene and heterobutadienes, see: (a) Wiberg, K. B.; Rablen, P. R.; Marquez, M. *J. Am. Chem. Soc.* **1992**, *114*, 8654. (b) Mo, Y.; Wu, W.; Zhang, Q. *J. Phys. Chem.* **1994**, *98*, 10048. (c) Mo, Y.; Zhang, Q. *J. Mol. Struct. (Theochem)* **1995**, *357*, 171.

Table 4. Comparative Evaluation of π-Conjugation in Butadiene and 1,4-Digermabutadiene from Various Criteria

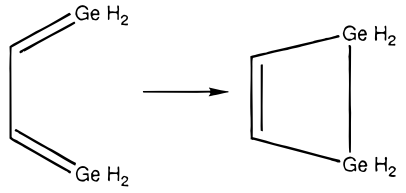
criterion	parameter	butadiene	1,4-digermabutadiene	digermabutadiene/ butadiene
geometry[a]	relative central-bond shortening	−3.7%	−6.2%	1.7
	corresponding force-constant increase	+17%	+24%	1.4
energy[b]	occupied π-level splitting	3.2 eV	4.6 eV	1.4
	π localization energy	10.4 kcal/mol	26.3 kcal/mol	2.5
	bond separation energy SCF	10.6 kcal/mol	12.2 kcal/mol	1.2
	bond separation energy MP4	12.5 kcal/mol	16.0 kcal/mol	1.3

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

of this equation gives a bond separation energy of 12.2 (SCF level) or 16.0 kcal/mol (MP4 level), which is significantly above that calculated under the same conditions in butadiene (10.6 and 12.5 kcal/mol, respectively). The splitting between the occupied π levels also indicates more π conjugation in 1,4-digermabutadiene than in butadiene. We have summarized both the geometry-grounded and energy-grounded indexes in Table 4. Putting aside the π-localization-energy criterion, these numbers suggest that the π conjugation energy in 1,4-digermabutadiene is about one-and-a-half that in butadiene. This is further supported by the ratio of the corresponding torsional force constants in the trans rotamers, calculated at 1.47. Given that the delocalization energy in 2,3-digermabutadiene was found to be around 50% of that in butadiene,[9] one will deduce that π conjugation is about 3 times stronger in 1,4-digermabutadiene, $H_2Ge{=}CH{-}CH{=}GeH_2$, than in 2,3-digermabutadiene, $H_2C{=}GeH{-}GeH{=}CH_2$.

Regardless of electronic π conjugation, the energy difference between the 1,4-digerma and 2,3-digerma isomers should arise from the difference between the two sets of bond energies, (C−C + 2Ge−H) and (Ge−Ge + 2C−H). From the mean bond energies, this difference is estimated at 24 kcal/mol in favor of 2,3-digermabutadiene. The actual energy difference is calculated at 9 kcal/mol (9.6 and 9.4 kcal/mol at SCF and MP4 levels, respectively). This additional 15 kcal/mol in favor of 1,4-digermabutadiene supports its stronger π conjugation and is in line with our estimate for the corresponding differential π conjugation energy (15−5 = 10 kcal/mol).

Electrocyclic Reaction



5

As mentioned, the gauche form of 1,4-digermabutadiene has two possible channels on the CC rotational coordinate: it can interconvert into the *s-trans* form with a barrier of 6 kcal/mol or it can isomerize into its gauche enantiomer with a barrier of 1 kcal/mol. Due to the 1,4-diradical character, one can presume that the ring closure into 3,4-digermacyclobutene, **5**, should also be a favorable pathway from the gauche form. Actually, for the thermally-allowed conrotatory process, the energy barrier to overcome is calculated at only 1.0 kcal/mol, similar to that separating the gauche form from the planar *s-cis* saddle point. The intramolecular rearrangement of 1,4-digermabutadiene into 3,4-digermacyclobutene is a favorable process for several reasons. First of all, the relative stability of the final product 3,4-digermacyclobutene is enhanced due to (1) the strong energy of its newly-created bonds π C═C and σ Ge−Ge and (2) the reduced strain energy in the GeGeCC four-membered ring, since the intrinsic geometry of the Ge−Ge bond, which is significantly longer than the C═C one (2.50 vs 1.34 Å), allows obtuse C═C−Ge angles at the C(sp^2) corners, hence the limited ring strain. The net balance between what is lost and what is created during this rearrangement deserves a closer look. For the butadiene-to-cyclobutene transformation, one C═C π bond is lost whereas one σ C−C bond is gained; in addition, a π conjugation energy is cancelled whereas a *strong* ring strain energy is demanded. For the 1,4-digermabutadiene-to-3,4-digermacyclobutene transformation, two Ge═C π bonds are lost whereas one C═C π bond and one Ge−Ge σ bond are gained. Similarly, π conjugation is destroyed while a *weak* ring strain energy is demanded. Using reasonable mean bond energies[10,14] and π conjugation energies obtained from the present calculations, one can estimate the net balance in terms of binding energies as follows (in kcal/mol):

	cyclobutene		3,4-digermacyclobutene	
lost	2 π C═C	−126 (2 × −63)	2 π Ge═C	−60 (2 × 30)
	π conjugation	−10	π conjugation	−15
gained	π C═C	+63	π C═C	+63
	C−C	+83	Ge−Ge	+45
net result		+10 (− strong strain)		+33 (− weak strain)

Given the large strain energy in cyclobutene, estimated around 30 kcal/mol,[15] and the much weaker strain energy in 3,4-digermacyclobutene, one therefore expects from these numbers a weak endothermicity for the gauche butadiene-to-cyclobutene rearrangement and a significant exothermicity for the gauche 1,4-digermabutadiene-to-3,4-digermacyclobutene rearrangement. The actual values are calculated at +8.1 kcal/mol in the former case (other correlated treatments give 6−8 kcal/mol,[16−19] while experimental values correspond to 9−11 kcal/mol)[20−23] and −44.3 kcal/mol in the latter case. As predicted, the intracyclization of 1,4-digermabutadiene

---

(14) Leroy, G.; Riffi Temsamani, D.; Wilante, C. *J. Mol. Struct. (Theochem)* **1994**, *306*, 21.

(15) Boatz, J. A.; Gordon, M. S. *J. Phys. Chem.* **1988**, *92*, 3037.

(16) Breulet, J.; Schaefer, H. F. *J. Am. Chem. Soc.* **1984**, *106*, 1221.

(17) Spellmeyer, D. C.; Houk, K. N. *J. Am. Chem. Soc.* **1988**, *110*, 1221.

(18) Yu, H.; Chan, W. T.; Goddard, J. D. *J. Am. Chem. Soc.* **1990**, *112*, 7529.

(19) Thomas, B. E.; Evanseck, J. D.; Houk, K. N. *J. Am. Chem. Soc.* **1993**, *115*, 4165.

(20) Wiberg, K. B.; Fenoglio, R. A. *J. Am. Chem. Soc.* **1968**, *90*, 3395.

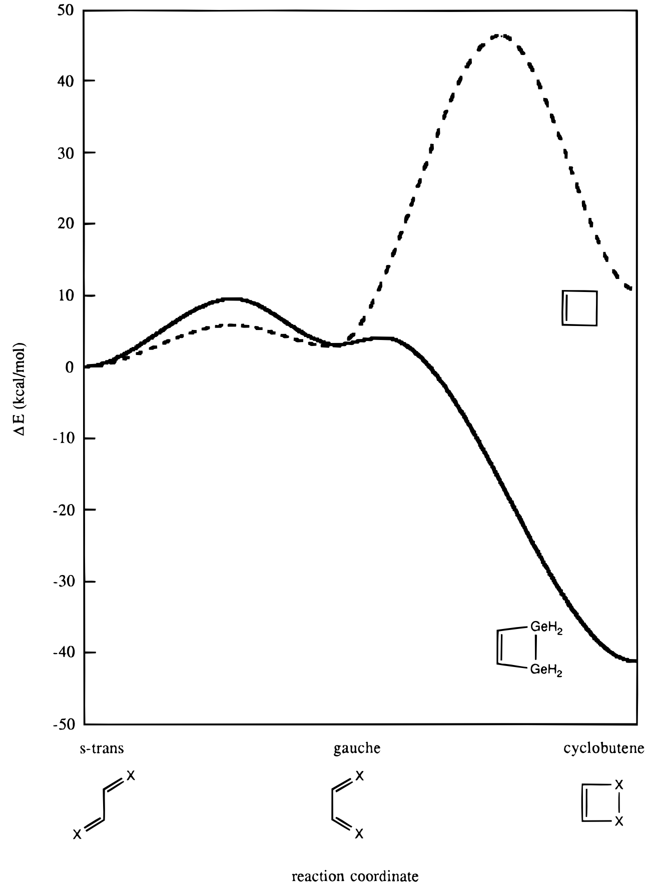


Figure 4. Schematic energy profiles across butadiene (dashed line) and 1,4-digermabutadiene (full line) potential surfaces. Left, from the *s-trans* conformer to the gauche conformer; right, conrotatory closure of the gauche conformer into cyclobutene or 3,4-digermacyclobutene.

into 3,4-digermacyclobutene is therefore found to be strongly exothermic. Besides this strong exothermicity, other arguments, also based on Hammond's postulate, further suggest that the energy barrier to overcome from the gauche 1,4-digermabutadiene should be weak. Because its central =C—C= bond has significant double-bond character and due to the involvement of valence-bond forms like **3**, the starting material anticipates the final product. Moreover, with its geometry of C_2 symmetry and its tilted =GeH_2 groups, it also anticipates the conrotatory motion itself. Actually, the barrier above the gauche conformer is calculated at only 1.0 kcal/mol and still survives at 0.7 kcal/mol once the zero-point energy difference is taken into account. As schematized in Figure 4, the contrast is sharp with butadiene, in which the corresponding barrier is calculated at 43.6 kcal/mol (other correlated treatments give 37−45 kcal/mol,[16−19] while the experimentally-observed barrier is 33 kcal/mol).[24]

The geometrical features of these saddle points are summarized in Table 5. For 1,4-digermabutadiene, all the geometrical parameters are clearly close to the starting material, corresponding to 20−30% reaction advancement versus 50−70% for butadiene. In particular, the =GeH_2 groups are substantially less inclined than the =CH_2 groups. Table 5 further illustrates how a concerted reaction does not necessarily imply a synchronous and regular variation of all the structural parameters.

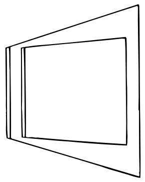
Table 5. Main Geometrical Parameters for the Transition States in the Conrotatory Ring Closures of Butadiene into Cyclobutene and 1,4-Digermabutadiene into 3,4-Digermacyclobutene[a]

	$H_2C{=}CH{-}CH{=}CH_2$		$H_2Ge{=}CH{-}CH{=}GeH_2$	
C—C	1.371	71%	1.413	29%
C=X	1.418	48%	1.843	16%
X···X	2.132	63%	3.483	26%
CCX	104.2	69%	122.4	30%
CXX	73.6	65%	55.1	28%
XCCX	8.6	78%	30.3	19%
$CCXH_3$	−61.3	52%	−34.7	29%
$CCXH_5$	145.6	53%	170.0	23%

[a] In angströms and degrees. See **1** for atom labeling. The percentages indicate the proportion of parameter change along the reaction coordinate, starting from the C_2 gauche forms.

The reason why the thermal conrotatory cyclization of butadiene into cyclobutene has a large barrier while being a formally allowed reaction lies in the physical correlation of the orbitals, before crossing avoidance, which relates occupied and virtual orbitals, as schematized in Figure 5a. Consequently, after the removal of the level crossings according to their symmetry, a barrier still remains and the reaction maintains some fundamental forbiddenness (Figure 5b). In the case of 1,4-digermabutadiene, the physical correlations exhibit less crossing (in particular π_1 and π_4 are very close in energy and nature to the π and π^* C=C orbital of the final product 3,4-digermacyclobutene) so that the process should no longer require a significant barrier (Figure 5c).

The optimized geometrical parameters for cyclobutene and 3,4-digermacyclobutene are given in Table 6. As mentioned, the trapezoidal versus rectangular shape, **6**, is the most striking difference between the two planar rings.[25] The C=C, C—C, and Ge—Ge bonds correspond to standard bond lengths, even if C=C is only 0.015 Å shorter in the digerma ring. Harmonic vibrational frequencies for 3,4-digermacyclobutene are listed in Table 3, together with the corresponding infrared intensities. As in cyclobutene, the lowest frequency mode corresponds to a puckering of the four-membered ring. The lowest frequencies of 3,4-digermacyclobutene are smaller than those of cyclobutene (the three lowest frequency of which are calculated at 349, 725, and 930 cm−1),[26] but one can see that digermacyclobutene is more rigid than its corresponding digermabutadiene.



6

---

(21) Pedley, J. B.; Rylance, J. *Sussex-N. P. L. Computer Analysed Thermochemical Data: Organic and Organometallic Compounds*; Sussex University: Brighton, England, 1977.

(22) Lipnick, R. L.; Garbisch, E. W. *J. Am. Chem. Soc.* **1973**, *95*, 6370.

(23) Furukawa, H.; Takeuchi, H.; Harada, I.; Tasumi, M. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 392.

(24) Cooper, W.; Walters, W. D. *J. Am. Chem. Soc.* **1958**, *80*, 4220. Carr, R. W.; Walters, W. D. *J. Phys. Chem.* **1965**, *69*, 1073.

(25) Similar contrast was previously noticed on 3,4-disilacyclobutene, the strain energy of which was predicted at about $^{2}/_{3}$ of that of cyclobutene (see ref 15).

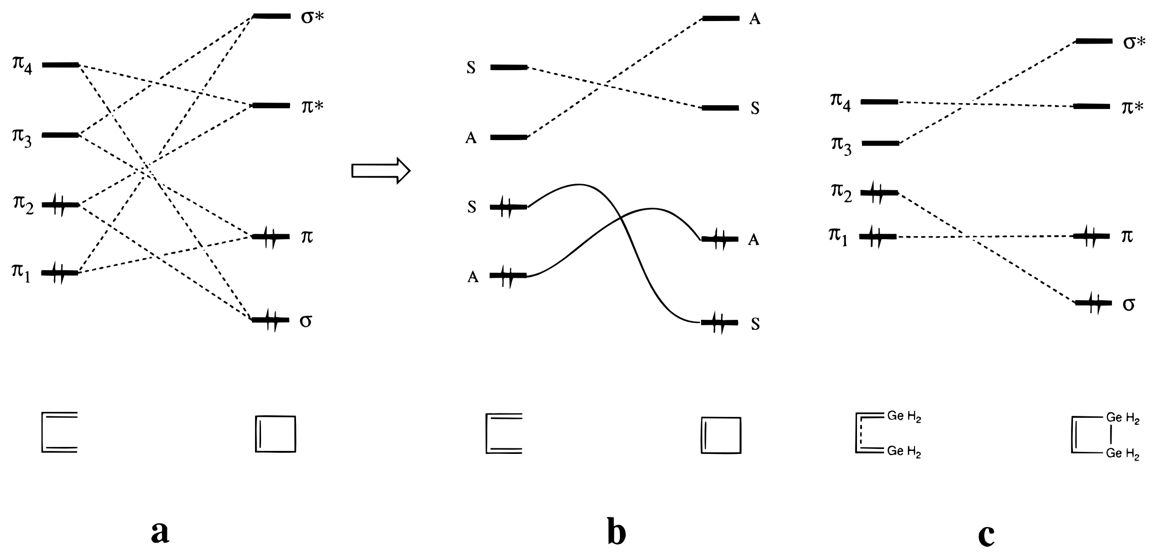


Figure 5. Level correlation diagrams for the conrotatory ring closure of butadiene into cyclobutene. (a) Physical correlation, without avoided crossing; (b) after crossing avoidance, the reaction becomes formally allowed but some barrier subsists due to level mixing; (c) simplified scheme for 1,4-digermabutadiene.

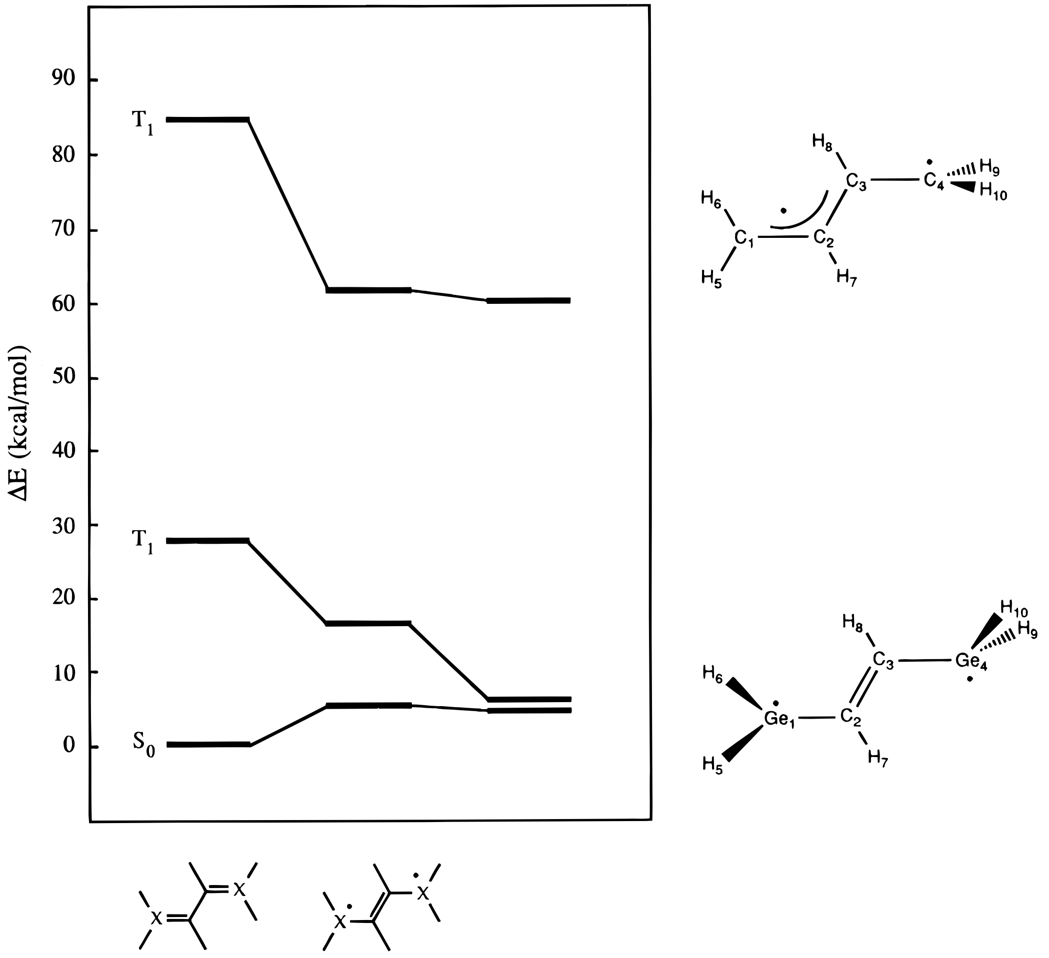


Figure 6. Relative energies of the singlet and triplet potential surfaces of 1,4-digermabutadiene at the singlet geometry (left), the planar-constrained triplet geometry (middle), and the triplet geometry (right). Triplet butadiene is reported on the upper curve for comparison.

The stability of the 3,4-digermacyclobutene structure is established experimentally since various derivatives of this type of digerma ring have been synthesized from the condensation of two germylenes (or of a digermene) with an acetylenic compound.[27-30] The above SCF geometry, calculated for the parent compound, is in good agreement with the X-ray structures available for such derivatives.[27-29]

---

(26) For a detailed study of the infrared spectrum of cyclobutene, see: Wiberg, K. B.; Rosenberg, R. E. *J. Phys. Chem.* **1992**, *96*, 8282.

(27) Espenbetov, A. A.; Struchkov, Y. T.; Kolesnikov, S. P.; Nefedov, O. M. *J. Organomet. Chem.* **1984**, *275*, 33.

Table 6. Calculated Geometrical Parameters (Å and deg) for C_{2v} Cyclobutene and 3,4-Digermacyclobutene

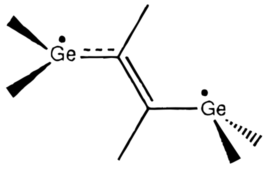
cyclobutene		3,4-digermacyclobutene	
C═C	1.327	C═C	1.342
C_2−C_3	1.517	C−Ge	1.994
C_3−C_4	1.563	Ge−Ge	2.494
C_1−H	1.084	C−H	1.088
C_3−H	1.093	Ge−H	1.556
$C_1C_2C_3$	94.5	CCGe	106.8
$C_2C_3C_4$	85.5	CGeGe	73.2
C_1C_2H	133.3	CCH	122.6
HC_3H	108.5	HGeH	108.1
$C_1C_2C_3H$	115.6	CCGeH	109.9

The favored 1,4-dipolar coupling reactions predicted on parent 1,4-digermabutadiene is in agreement with the observed chemical behavior of transient substituted 1,4-disilabutadienes. Ishikawa and co-workers have generated a transient benzodisilabutadiene (alternatively viewed as an *o*-quinodisilane) by pyrolysis of the corresponding benzodisilacyclobutene (as expected, the reaction is endothermic in this sense).[3−5,7,8,31] On this intermediate, both [4 + 1], [4 + 2], or [4 + 4] cycloadditions can be observed, as summarized in Scheme 1. Ando *et al.* have generated a disilyl 1,4-disilabutadiene intermediate which undergoes a Diels−Alder condensation with triazolinedione.[6]

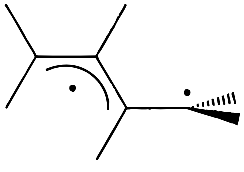
Discussion

Triplet State. Looking at 1,4-digermabutadiene as a diradical structure like **3** causes one to question the existence of a low-lying open-shell triplet state that could be in competition with the closed-shell planar form for the ground state. Exploration of the triplet potential energy surface has been carried out at the UHF level, refining energies at the MP4 level for the main interesting points.

At the planar singlet ground state geometry, the ^3B_u triplet state lies only 27.7 kcal/mol above the ground state. Planar relaxation brings about an energy lowering of 11.4 kcal/mol. Full relaxation of the geometry further brings about an additional 10.3 kcal/mol of energy stabilization through a torsion around one C═Ge bond and a pyramidalization of both GeH_2 groups. In its optimized unsymmetrical C_1 structure, **7**, the first triplet state is therefore located at only 6.0 kcal/mol above the ground state.[32] At the triplet geometry, the closed-shell singlet state is nearly degenerate in energy with the triplet state, but still lying *below* it, namely at 4.6 kcal/mol above the ground state in its optimal geometry. Such ordering is also observed with butadiene and is presumably due to the dynamic spin polarization of the σ bonds, an effect well-documented on ethylenic systems.[33] In the present case, this contributes to eliminating the potentiality for a triplet ground state.



7



8

On the triplet surface, the energy gained from the relaxed planar form to the dipyramidalized form is only 1 kcal/mol larger than twice the inversion barrier of the germyl radical.[34] This suggests that the remaining allylic H_2Ge−CH═CH− conjugation is weak and that twisting one GeH_2 group brings very little energy. Actually, the rotational barrier around Ge−C is small for both pyramidal groups, so that there is a quasi free rotation around the Ge−C bonds.[35]

The triplet state of butadiene is better known, both theoretically[36−46] and experimentally.[47−51] Due to the strong $2p_z-2p_z$ overlap and to the planar geometry of the methyl radical, the triplet relaxation proceeds through a rotation around one C═C bond without pyramidalization of any CH_2 group. One CH_2 group is involved in an allyl radical conjugation while the other one is twisted, virtually planar, and involved in hyperconjugation, resulting in a arrangement of C_s symmetry, **8**. The geometrical parameters for triplet butadiene and triplet 1,4-digermabutadiene are given in Table 7. These structures correspond to the true minima (all real frequencies) obtained at our UHF level of treatment.

The vertical excitation energy of butadiene is calculated at 84.5 kcal/mol. Several correlated treatments give a similar value.[42−46] The experimental value, 74 kcal/mol,[48,50] can be obtained from more elaborate treatments using properly extended basis sets.[42−46] The

---

(28) Krebs, A.; Jacobsen-Bauer, A.; Haupt, E.; Veith, M.; Huch, V. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 603.

(29) Weidenbruch, M.; Hagedorn, A.; Peters, K.; von Schnering, H. G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1085.

(30) Ohtaki, T.; Ando, W. *Organometallics* **1996**, *15*, 3103.

(31) Thermal interconversion between 3,4-disilacyclobutene and 1,4-disilabutadiene was proposed more than 20 years ago, see: Barton, T. J.; Kilgour, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 7150; *Ibid.* **1976**, *98*, 7746.

(32) Inclusion of zero-point vibrational energies reduces this number by 0.6 kcal/mol.

(33) Trinquier, G.; Malrieu, J. P. In *The Chemistry of Double-Bonded Functional Groups*; Patai, S., Ed.; Wiley Interscience: New York, 1989; Supplement A, Vol. 2.

(34) Both theory and experiment agree with a value of 4.3−4.5 kcal/mol for the inversion barrier of the germyl radical, see: Johson, R. D.; Tsai, B. P.; Hudgens, J. W. *J. Chem. Phys.* **1988**, *89*, 4558. Moc, J.; Rudzinski, J. M.; Ratajczak, H. *Z. Phys. D.* **1992**, *22*, 629. Bickelhaupt, F. M.; Ziegler, T.; Schleyer, P. v R. *Organometallics* **1996**, *15*, 1477.

(35) Determining which form is actually the lowest one in energy, among **7** and the isomers with both twisted GeH_2 groups (there are three of them since each GeH_2 can be *syn* or *anti* with respect to its neighboring C−H) would require an exploration of the potential surface at higher computational level.

(36) Ohmine, I.; Morokuma, J. *J. Chem. Phys.* **1980**, *73*, 1907.

(37) Ohmine, I.; Morokuma, J. *J. Chem. Phys.* **1981**, *74*, 564.

(38) Bonacic-Koutecky, V.; Persico, M.; Döhner, D.; Sevin, A. *J. Am. Chem. Soc.* **1982**, *104*, 6900.

(39) Aoyagi, M.; Osamura, Y.; Suehiro, I. *J. Chem. Phys.* **1985**, *83*, 1140.

(40) Aoyagi, M.; Osamura, Y. *J. Am. Chem. Soc.* **1989**, *111*, 470.

(41) Orlandi, G.; Zerbetto, F.; Zgierski, M. Z. *Chem. Rev.* **1991**, *91*, 867.

(42) Graham, R. L.; Freed, K. F. *J. Chem. Phys.* **1992**, *96*, 1304.

(43) Serrano-Andres, L.; Sanchez-Marin, J.; Nebot-Gil, I. *J. Chem. Phys.* **1992**, *97*, 7499.

(44) Serrano-Andres, L.; Merchan, M.; Nebot-Gil, I.; Lindh, R.; Roos, B. O. *J. Chem. Phys.* **1993**, *98*, 3151.

(45) Wiberg, K. B.; Hadad, C. M.; Ellison, G. B.; Foresman, J. B. *J. Phys. Chem.* **1993**, *97*, 13586.

(46) Minaev, B. F.; Jonsson, D.; Norman, P.; Ågren, H. *Chem. Phys.* **1995**, *194*, 19.

(47) Mosher, O. A.; Flicker, W. M.; Kuppermann, A. *J. Chem. Phys.* **1973**, *59*, 6502.

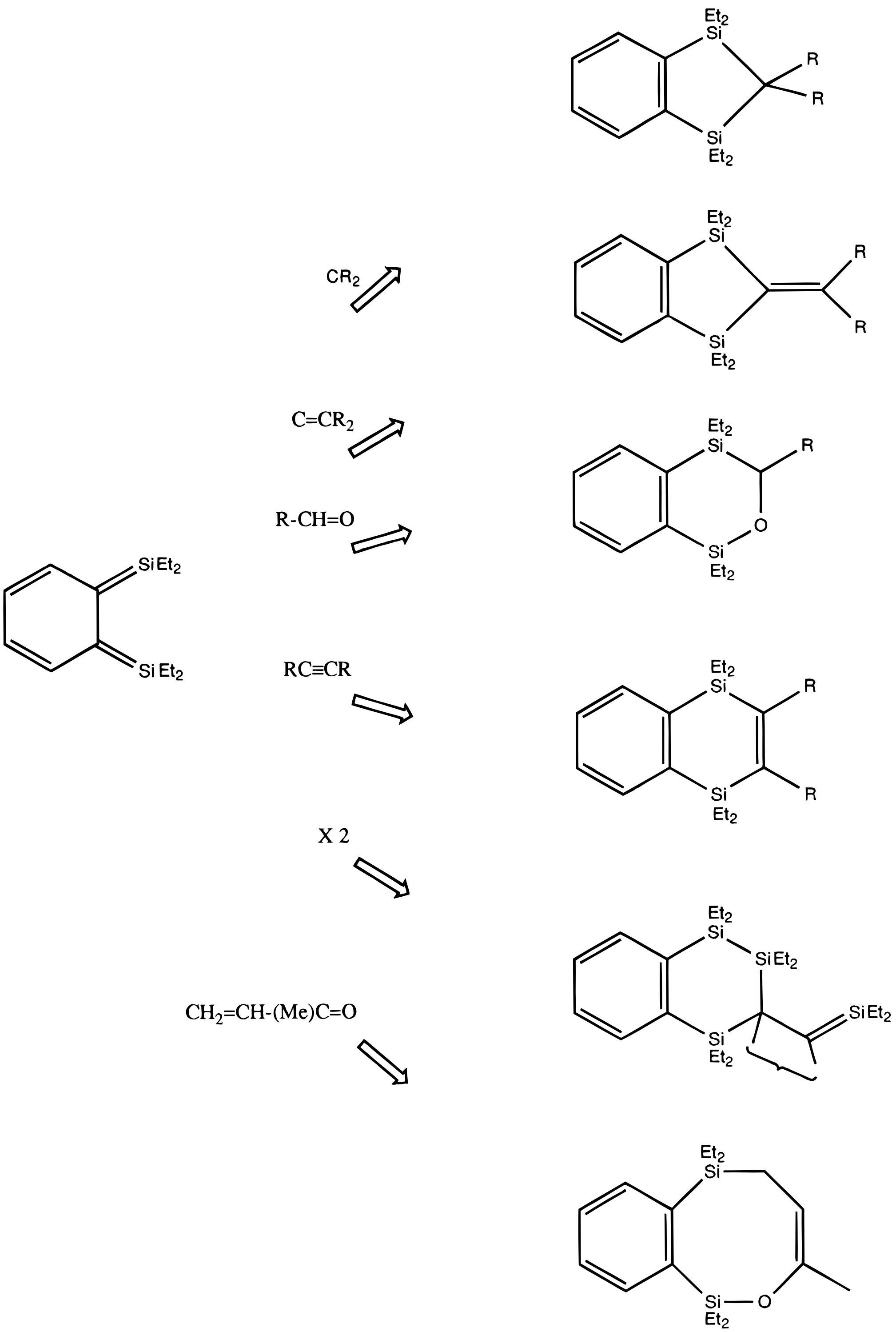
(48) Mosher, O. A.; Flicker, W. M.; Kuppermann, A. *Chem. Phys. Lett.* **1973**, *19*, 332.

(49) Flicker, W. M.; Mosher, O. A.; Kuppermann, A. *Chem. Phys.* **1978**, *30*, 307.

(50) Kellogg, R. E.; Simpson, W. T. *J. Am. Chem. Soc.* **1965**, *87*, 4230.

(51) Swiderek, P.; Michaud, M.; Sanche, L. *J. Chem. Phys.* **1993**, *98*, 8397.

Scheme 1



adiabatic or (0−0) energy difference is easier to obtain theoretically. We found this to be 60.2 kcal/mol, in agreement with the experimental data.[50,51] As shown in Figure 7, most of the vertical/adiabatic energy lowering here is due to the planar relaxation whereas for triplet 1,4-digermabutadiene it is equally distributed in planar and nonplanar relaxations, as discussed above.

Ge=C Torsional Barrier. On the ground-state singlet surface, the energy required to distort the relaxed planar form into the twisted optimal geometry of the triplet state practically represents the rotational barrier around a Ge=C bond (the right-hand-side one in **7**). Such a geometry change requires less than 5 kcal/mol, which is particularly low, about one-sixth of the rotational barrier in germaethylene, calculated at 31−32 kcal/mol.[10b,c] This effect is striking when compared with the C=C torsional barrier in butadiene, estimated to be only a few kcal/mol below that of ethylene (60 vs 65 kcal/mol). This low torsional barrier around Ge=C is an interesting consequence of the strongly conjugated character or 1,4-diradical character of 1,4-digermabutadiene. Bearing in mind that rotation around the central C−C bond requires, here, as much as 10 kcal/mol, a piquant feature of the potential surface for this system is that it undergoes easier rotation about its formally double Ge=C bond than about its formally single C−C bond. The sharp contrast with butadiene, is illustrated in Figure 7. In this figure, 2,3-digermabutadiene,

Table 7. Optimized Geometrical Parameters for the Lowest Triplet State of Butadiene and 1,4-Digermabutadiene[a]

butadiene (C_s)		1,4-digermabutadiene (C_1)	
C_1-C_2	1.394	Ge_1-C_2	1.956
C_2-C_3	1.397	C_2-C_3	1.357
C_3-C_4	1.480	C_3-Ge_4	1.984
C_1-H_5	1.083	Ge_1-H_5	1.556
C_1-H_6	1.084	Ge_1-H_6	1.556
C_2-H_7	1.087	C_2-H_7	1.089
C_3-H_8	1.089	C_3-H_8	1.090
C_4-H_9	1.086	Ge_4-H_9	1.560
		Ge_4-H_{10}	1.561
$C_1C_2C_3$	124.5	$Ge_1C_2C_3$	124.3
$C_2C_3C_4$	124.0	$C_2C_3Ge_4$	124.8
$C_2C_1H_5$	121.1	$C_2Ge_1H_5$	111.9
$C_2C_1H_6$	121.2	$C_2Ge_1H_6$	111.3
$C_1C_2H_7$	117.9	$Ge_1C_2H_7$	116.8
$C_4C_3H_8$	117.8	$Ge_4C_3H_8$	116.6
$C_3C_4H_9$	120.4	$C_3Ge_4H_9$	110.7
		$C_3Ge_4H_9$	110.8
		$Ge_1C_2C_3Ge_4$	176.7
		$C_3C_2Ge_1H_5$	149.0
		$C_3C_2Ge_1H_6$	23.4
		$Ge_4C_3C_2H_7$	2.0
		$Ge_1C_2C_3H_8$	−4.1
$C_2C_3C_4H_9$	92.0	$C_2C_3Ge_4H_9$	120.3
		$C_2C_3Ge_4H_{10}$	−119.0
		ΣGe_1	334.8
ΣC_4	357.8	ΣGe_4	330.3

[a] In angströms and degrees. See Figure 6 for atom labeling.

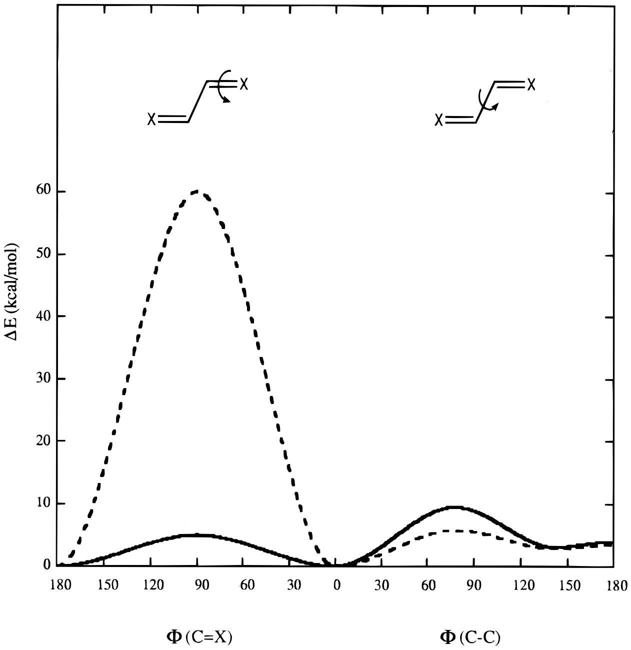


Figure 7. Energy profiles along C=X (left) and central C−C (right) torsional coordinates for 1,4-digermabutadiene (full curve) and butadiene (dashed curve).

$H_2C=GeH-GeH=CH_2$, would correspond to an intermediate curve on the left-hand side and to a lower curve on the right-hand side.

Conclusion. 1,4-Digermabutadiene undergoes a strong conjugation through its central CC bond. Except for the *s-trans*/gauche energy difference, which remains, as in butadiene, around 3 kcal/mol, this peculiarity clearly associated with the 1,4-diradical character has dramatic consequences on the structure and reactivity. It increases the rotational barrier correlating the *s-trans* conformer to the gauche one and decreases the torsional barrier around the Ge=C bonds, now lower than that around the middle C−C bond, a striking difference from butadiene. It also favors 1,4-coupling reactions, such as the electrocyclic rearrangement into 3,4-digermacyclobutene, which requires very little activation energy from the gauche form. More generally, it should favor any addition with radical intermediates and polymerization reactions.

The double substitution of carbon atoms by germanium atoms at positions 1 and 4 in butadiene has perturbative effects quite opposite to those resulting from the double substitution at positions 2 and 3. The C−Ge−Ge−C topology is responsible for less conjugation through the central bond in 2,3-digermabutadiene. While this can be achieved on other derivatives as well, the Ge−C−C−Ge order is unique in that only the conjunction of neighboring inner carbon atoms with terminal germanium atoms could confer 1,4-digermabutadiene its peculiar properties. Typically, these are no longer present in tetragermabutadiene. The substitution by germanium at positions 2 and 3 provided some flatness to the central-bond rotational coordinate. Substitution at positions 1 and 4 transfers it to the terminal Ge=C bonds. In a forthcoming paper that will end our trilogy on symmetrical germabutadienes we shall see that tetrasubstitution may bring another remarkable type of plasticity.

Acknowledgment. We thank Drs. Jean Escudié and Jean-Paul Malrieu for helpful discussions and Dr. Simon Mathieu for computational assistance.

Appendix. The calculations were performed with the HONDO8 program from the MOTECC package.[52] For carbon and germanium atoms, effective core potentials were used.[53] The DZP valence basis sets consist of four Gaussian functions contracted to a double-ζ level and augmented by a polarization function. The exponents for the d functions are 0.8 for carbon and 0.25 for germanium. The exponent for the p function on hydrogen is 0.90. The geometries are optimized at the RHF−SCF level for singlet species and at the UHF−SCF level for triplet species, with final gradient Cartesian components 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. On each stationary point, the energy is recalculated at the MP4 SDTQ level (Möller−Plesset perturbation theory applied to the fourth order). For open-shell systems, such an option is not available in the version of HONDO8 used so the open-shell triplet states were calculated by using the GAUSSIAN92 program.[54]

OM970179V

---

(52) Dupuis, M. *MOTECC89*; IBM Corporation, Center for Scientific and Engineering Computations: Kingston, NY, 1989.

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

(54) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92*, revision B; Gaussian Inc.: Pittsburgh, PA, 1992.