ratios (condition 2 described earlier).

It is interesting to note that the C_A/E_A ratio for the enthalpy of base adduct formation with phenol is 0.102 while the C_A^*/E_A^* ratio for the phenol adduct frequency shift is 0.149. Note that the C_A^*/E_A^* ratio is not a fundamental acceptor property of the acid but includes in it the response of the acid property being measured. It is possible to have two different properties of an acid obey the E and C equation but not give a straight line when plotted against each other if their C_A^*/E_A^* ratios are different. Since the C_A/E_A and C_A^*/E_A^* ratios are closer to each other than those for C_A^*/E_A^* and β (0.0287), a more general straight line plot of $\Delta\nu_{OH}$ vs. $-\Delta H$ is obtained which will be valid as long as bases with a C_B/E_B ratio of 1.5 to 6 are employed. Thus this analysis extends our earlier proposal that this correlation is of more general applicability than reported[19,20] and that the high polarizability of sulfur donors cause them to deviate from the $-\Delta H$ vs. $\Delta\nu_{OH}$ relation. We now clearly understand what the limitations of the $-\Delta H$ vs. $\Delta\nu_{OH}$ relation are, and when it can be used with confidence to predict enthalpies.

With this work we have provided a set of parameters to be used in conjunction with the equation:

$$\Delta X = \text{“}E_A\text{”}E_B + \text{“}C_A\text{”}C_B + SD^* \qquad (9)$$

Since in a new system, one does not know if the C_A/E_A ratio will be 0.0287, we feel it is first appropriate to determine if the observation, ΔX, is related to coordinate bond strengths and a relatively simple solvation model (eq 9). If the E, C, and D^* analysis indicates a C/E ratio close to 0.0287, the very extensive compilation of β parameters can be used with confidence for solvents for which E_B and C_B values are not determined. In interpreting deviations from an attempted fit of a data set to eq 9, one must remember that the parameters have been derived for dilute solutes undergoing specific and nonspecific interactions with varying solvents. As the observation that one is attempting to correlate, ΔX, becomes more complex and has more independent factors contributing to it, the chance diminishes for a successful correlation. Lack of a correlation does not mean that the model is incorrect but suggests that factors other than coordinate bond strength and this simple solvation model dominate the chemistry. Bulk solvation effects are a complex phenomenon coupled to the structure of the liquid state. Though a theoretical rationalization of the SD^* type of analysis has been provided,[20] a wider range of systems must be studied to determine the limitations of the treatment of this effect by the SD^* term.

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Registry No. 2-Nitroaniline, 88-74-4; *N*-methyl-2-nitroaniline, 612-28-2; *N*,*N*-dimethyl-2-nitroaniline, 610-17-3; *N*-ethyl-3-nitroaniline, 4319-19-1; 4-nitroaniline, 100-01-6; *N*-methyl-4-nitroaniline, 100-15-2; *N*,*N*-diethyl-4-nitroaniline, 100-23-2; 3-methyl-4-nitroaniline, 611-05-2; *N*-ethyl-3-methyl-4-nitroaniline, 52177-09-0; *N*,*N*-diethyl-3-methyl-4-nitroaniline, 52177-26-1; 3,5-dinitroaniline, 618-87-1; 2-nitro-*p*-toluidine, 89-62-3; *N*,*N*-dimethyl-2-nitro-*p*-toluidine, 52262-63-4; 2-nitro-*p*-anisidine, 96-96-8; *N*,*N*-dimethyl-2-nitro-*p*-anisidine, 60049-83-4; 4-nitrophenol, 100-02-7; 4-nitroanisole, 100-17-4; 4-aminobenzophenone, 1137-41-3; ethyl 4-aminobenzoate, 94-09-7; *N*-(4-nitrophenyl)aziridine, 30855-79-9; *N*-(4-nitrophenyl)pyrrolidine, 10220-22-1; *N*-(4-nitrophenyl)piperidine, 6574-15-8; 3-nitroaniline, 99-09-2; C_6H_{12}, 110-82-7; CCl_4, 56-23-5; C_2Cl_4, 127-18-4; C_5H_5N, 110-86-1; $(C_2H_5)_3N$, 121-44-8; $HCON(CH_3)_2$, 68-12-2; $CH_3CON(CH_3)_2$, 127-19-5; $CH_3COOC_2H_5$, 141-78-6; $(CH_3)_2CO$, 67-64-1; $(C_2H_5)_2O$, 60-29-7; $(CH_2)_4O$, 109-99-9; $(CH_2)_5O$, 142-68-7; $(CH_3)_2SO$, 67-68-5; $(C_2H_5O)_3PO$, 78-40-0.

Supplementary Material Available: Table M-1, spectroscopic data (bathochromic shifts from hexane) of a series of solutes (12 pages). Ordering information is given on any current masthead page.

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Unusual Bonding in Trans-Bent Digermene

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Abstract: Ab initio calculations using pseudopotentials have been carried out on the two singlet isomers of Ge_2H_4 at both SCF (double ζ + d basis set) and CI levels. Digermene ($H_2Ge{=}GeH_2$) is 5 kcal/mol more stable than germylgermylene ($H\ddot{G}e{-}GeH_3$). Its trans-bent geometry does not depend strongly on correlation effects; the wagging angle of the GeH_2 groups is 39° while the planar form stands 3–4 kcal/mol higher in energy. The type of bonding occurring in digermene can be described as two semipolar bent bonds between two singlet germylenes.

1. Introduction

Considerable interest arises from π-bonded silicon[2-10] and germanium[11-13] compounds. A recent extensive investigation of the Si_2H_4 potential surface[14] has confirmed (i) the singlet character of both disilene and silylsilylene ground states and (ii) the trans-bent geometry of singlet disilene. Although the organometallic chemistries of silicon and germanium are quite different, the available calculations on model compounds containing silicon or germanium atoms[11,12,15] do not show tremendous distinctions between the two series. Within our studies of π-bonded germanium compounds[11-13] we present here the study of the two Ge_2H_4 singlet isomers, namely, digermene ($H_2Ge{=}GeH_2$) and germylgermylene ($H\ddot{G}e{-}GeH_3$). In the light of the theoretical investigations on Si_2H_4[14] and on simple germylenes,[15] it can be

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stated that these two isomers are singlet in their ground state as soon as correlation is included. However, intermediates containing a >Ge-Ge< framework have a chemical behavior close to a diradical.[16-18] This paper reports results of ab initio calculations using double-ζ plus d-orbital basis sets and including correlation effects on the singlet ground state of $H_2Ge{=}GeH_2$ and $H\ddot{G}e{-}GeH_3$. The emphasis will be put on the electronic structure of the former species which strongly departs from planarity and therefore represents an unusual type of double bond.

2. Methods and Basis Sets

The SCF calculations were performed using the PSHONDO program[19] which introduces the pseudopotentials of Durand and Barthelat[20] in the HONDO program.[21] A pseudopotential technique makes it possible to treat explicitly only the germanium valence electrons by reproducing the interaction between valence and core electrons by a pseudopotential operator. This nonempirical pseudopotential is determined from the double-ζ atomic Hartree–Fock calculations of Clementi and Roetti.[22] Its analytical form is

$$W(r) = \sum_l W_l(r)P_l - (z/r)$$

where z is the number of valence electrons for the neutral atom (four for germanium), P_l is the projector on the lth subspace of the spherical harmonics, and W_l(r) has the following analytical form

$$W_l(r) = e^{-\alpha r^2} \sum_i \frac{C_i}{r^{n_i}}$$

The parameters α, C_i, n_i are determined to reproduce the valence Hartree–Fock energy levels and the outer part of the valence orbitals. They are obtained from the ($4s^24p^2$) ^3P ground state of the germanium atom for $l = 0$ and $l = 1$ (s and p components) and from the ($4s^24p4d$) ^3D atomic state for $l = 2$ (d components). These parameters have been given in ref 15. The s and p valence basis set was optimized in a pseudopotential SCF calculation of the atomic ground state using a quadruple ζ Gaussian basis set. These four Gaussian functions were contracted to the double-ζ level by means of a 3 + 1 procedure for the s basis set and a 2 + 2 procedure for the p basis set. A 4d Gaussian function was added as a polarization function ($\eta = 0.25$). This basis set for germanium is listed in ref 15. The double-ζ basis set for hydrogen is reported in ref 23.

The configuration interaction (CI) calculations were performed according to the CIPSI algorithm.[24,25] A variational zero-order wave function is built from an iterative selection of the most important determinants, the other ones being taken into account through a second-order Møller–Plesset perturbation. The determinants having a coefficient larger than 0.04 in the first-order wave function of the ground-state determinant have been included in the zero-order variational wave function at the final step; this makes 11 determinants for $H_2Ge{=}GeH_2$, 4 for $H\ddot{G}e{-}GeH_3$, and 6 for H_2Ge:. Single and double substitutions generated 97 353 determinants for $H_2Ge{=}GeH_2$, 79 965 for $H\ddot{G}e{-}GeH_3$, and 5 234 for H_2Ge:, which were treated perturbatively.

Table I. Energy Differences (kcal/mol) between $H\ddot{X}{-}XH_3$ and $H_2X{=}XH_2$[a]

X	SCF	CI
Si *b*	−0.1	+10.1
c	−8.2	
d	−2.1	
Ge (this work)	−8.4	+4.6

[a] A negative sign implies that $H\ddot{X}{-}XH_3$ is the most stable isomer. [b] 3-21 G basis set.[14] [c] 4-31 G basis set.[27] [d] 66-31 G basis set[14] which compares with our valence basis set.

Table II. GeGe Stretching Force Constant with Corresponding Uncoupled Vibrational Frequency and Wagging Force Constant in Trans-Bent Digermene

	SCF	CI
k wagging (mdyn/rd)	0.4	0.5
$k_{Ge\text{-}Ge}$ (mdyn/Å)	3.1	4.3
ν_{GeGe} (cm^{-1})	376	442

The geometrical parameters were optimized independently except for the GeGe distance and the φ bending angle in trans-bent digermene which are strongly dependent and which were optimized simultaneously.

3. Geometries

The SCF-optimized geometries of germylgermylene and digermene are reported in Figure 1 together with the SCF geometry of germylene (GeH_2)[15] and the CI geometry of digermene. The GeGe bond length in germylgermylene is 0.08 Å longer than the GeGe bond length calculated in digermane (2.49 Å),[26] and the valence angle on divalent germanium is smaller than it is in germylene. The same trends occur in silylsilylene with respect to disilane and silylene.[14] When a D_{2h} symmetry (i.e., a planar geometry) is imposed to digermene, its GeGe distance is calculated at 2.26 Å corresponding to a 9% shortening with respect to digermane. On planar disilene a similar shortening is obtained[14] while the C=C bond length in ethylene corresponds to a 13% shortening with respect to ethane. The HGeH valence angle is close to the HSiH angle in planar disilene (116.1°).[14] When totally relaxed, digermene takes up a C_{2h} trans-bent nonplanar geometry which was determined at both SCF and extended CI levels. At the SCF level, the GeGe distance has increased to 2.30 Å while the valence angle on germanium (111°) goes closer to the germylene value. The out-of-plane "flap" angle φ (34°) is greater than in disilene (13°,[27] 20°[14]). Starting from these SCF geometrical parameters, the GeGe distance and the bending angle φ were reoptimized at the CI level. As can be seen at the bottom of Figure 1, correlation effects not only lengthen the GeGe bond length but also increase the bending angle to 39°. Nevertheless, these changes induced by the CI are minor. The geometry of this molecule already suggests a digermylene entity. CI emphasizes this fact. Comparison with SCF disilene geometry[14] shows the stronger tendancy of germanium to dehybridization.

4. Energies

At the SCF level, germylgermylene lies 8.4 kcal/mol below trans-bent digermene while planar digermene is 1.85 kcal/mol above the trans-bent form. Table I shows that in the silicon series silylsilylene is also more stable than its disilene isomer at the SCF level. The relative energy which compares with our DZ + d basis

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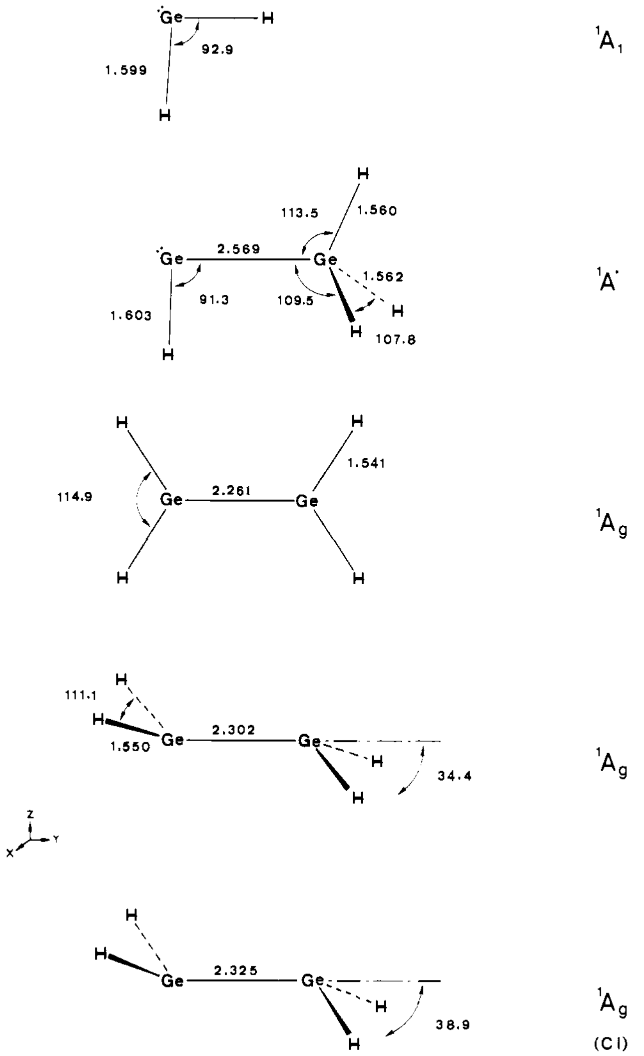


Figure 1. SCF optimized geometries (in angströms and degrees). From top to bottom: Germylene (from ref 15), germylgermylene, planar digermene, and trans-bent digermene. At the bottom CI optimized geometry of trans-bent digermene (GeH and ∠HGeH keeping their SCF values).

set value is that of Poirier and Goddard[14] using a 66-31G basis set, namely, −2.1 kcal/mol. One should point out that these authors criticize the value computed by Snyder and Wasserman[27] (−8.2 kcal/mol) as spurious due to a defect of their basis set.

Table III. Coefficient of the Main Doubly Excited Configurations in the CI Expansion for the Si_2H_4 Isomers (Ref 14) and the Ge_2H_4 Isomers (This Work)

$H_2Si{=}SiH_2$	$(\pi \rightarrow \pi^*)^2$	−0.16
$H\ddot{S}i{-}SiH_3$	$(n_\sigma \rightarrow p_\pi)^2$	−0.06
$H_2Ge{=}GeH_2$	$(\pi \rightarrow \pi^*)^2$ planar	−0.21
$H_2Ge{=}GeH_2$	$(2b_u \rightarrow 3a_g)^2$ trans-bent	−0.24
$H\ddot{G}e{-}GeH_3$	$(n_\sigma \rightarrow p_\pi)^2$	−0.09

Therefore, one can state that at the SCF level the energy difference $(H\ddot{X}{-}XH_3) - (H_2X{=}XH_2)$ in favor of the divalent species is larger when X = Ge than when X = Si. The planar form of digermene (i.e., the transition state to invert the trans-bent form) is 1.85 kcal/mol above the trans-bent form at the SCF level. In disilene, the planar form was calculated, at the SCF level, only 0.38[14] and 0.05 kcal/mol[27] above the trans-bent form. So digermene appears less flexible than disilene. It is interesting to measure the influence of the correlation effects on the relative energy of the planar form. Figure 2 provides the full curves of wagging and inversion of trans-bent digermene at both SCF and CI levels. At the CI level, the deepness of the trans-bent well is of 3.58 kcal/mol with respect to the planar form. This makes a fairly high barrier for the inversion of this trans-bent molecule. So, should such a model molecule be synthesized, it would be largely locked in one trans-bent form, even at room temperature. The effect of the CI is therefore to increase the "flap angle", the deepness, and the narrowness of the well as can be seen in Figure 2. Table II gives the force constants corresponding to stretching GeGe and wagging φ. Both are increased by the CI. The increase of the stretching force constant under correlation is rather unusual; $\partial^2 E_{corr}/\partial R^2$ is positive near the equilibrium distance for the bent geometry while it is negative, as for typical double bonds, in the planar geometry. This qualitative difference illustrates the strong specificity of the GeGe "double bond" in the trans-bent geometry.

Since the valence correlation energy is 93 kcal/mol for germylgermylene while 106 kcal/mol for trans-bent digermene, the latter is therefore the most stable isomer by 4.6 kcal/mol after the CI. Table I shows that the 13-kcal/mol energy difference brought by the CI in favor of $H_2Ge{=}GeH_2$ is quite comparable to the same quantity computed by Poirier and Goddard on planar disilene.[14] These authors assign the origin of this difference to the coefficients of the main excited configuration in the CI expansion, namely, $(\pi \rightarrow \pi^*)^2$ for $H_2Si{=}SiH_2$ and $(n_\sigma \rightarrow p_\pi)^2$ for $H\ddot{S}i{-}SiH_3$. We report these coefficients in Table III together with those of our variational CI expansion for $H\ddot{G}e{-}GeH_3$, planar $H_2Ge{=}GeH_2$, and trans-bent $H_2Ge{=}GeH_2$. The relative values of the coefficients are comparable for the two series; moreover, the coefficient corresponding to the "$\pi \rightarrow \pi^*$" diexcitation in trans-bent digermene is even more important and should be re-

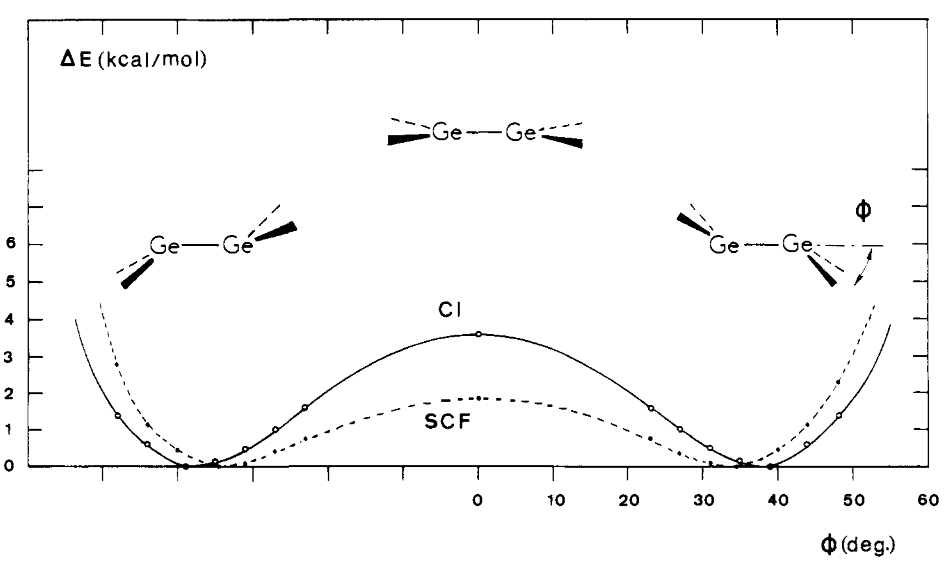


Figure 2. Potential curves corresponding to the C_{2h} wagging of digermene.

Table IV. Valence Molecular Orbital Energies (in eV) of Singlet Si_2H_4 [a] and Singlet Ge_2H_4 [b]

				planar			trans bent	
	$H\ddot{S}i-SiH_3$	$H\ddot{G}e-GeH_3$		$H_2Si=SiH_2$	$H_2Ge=GeH_2$		$H_2Si=SiH_2$	$H_2Ge=GeH_2$
2a'' (p_π)		−0.21	$1b_{2g}$ (π^*)		+1.13	$3a_g$		+0.46
5a' (n_σ)	−7.78	−8.52	$1b_{1u}$ (π)	−6.72	−7.22	$2b_u$	−6.83	−7.54
4a'	−10.39	−10.86	$1b_{1g}$	−11.81	−11.98	$2a_g$	−11.75	−11.69
1a''	−12.79	−12.67	$2a_g$	−12.52	−12.99	$1b_g$	−12.41	−12.77
3a'	−12.82	−12.70	$1b_{2u}$	−13.47	−13.70	$1a_u$	−13.36	−13.50
2a'	−16.57	−17.11	$1b_{3u}$	−17.12	−17.78	$1b_u$	−17.14	−17.71
1a'	−19.86	−19.88	$1a_g$	−20.16	−20.49	$1a_g$	−20.14	−20.39

[a] DZ basis set, ref 27. [b] DZ + d basis set, this work.

sponsible for its CI stabilization.

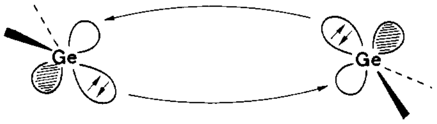
5. Valence Energy Levels and Charge Repartition

Table IV gives the valence molecular orbital levels for the Ge_2H_4 isomers together with those of the Si_2H_4 singlet isomers published by Snyder and Wasserman.[27] Although the basis set used by these authors does not include polarization functions, the comparison shows fairly comparable levels for the two series. For germylgermylene, one can notice a low p_π LUMO. The resulting weak $n_\sigma \rightarrow p_\pi$ (i.e., HOMO–LUMO) separation should induce a somewhat low triplet-state relative energy as in silylsilylene.[14] In digermene as in disilene an upward shift of the levels occurs from the planar form to the trans-bent form, except for the HOMO π level which is lowered in a $2b_u$ HOMO level. The overall lowering of the levels from Si to Ge should be due to the larger basis set used in our calculation.

The Mulliken population analyses show weakly polarized GeH bonds in digermene. The net charges on germanium atoms are +0.02 in planar digermene, +0.06 in trans-bent digermene, while +0.20 in germylene and +0.15 (both Ge^{II} and Ge^{IV}) in germylgermylene. For this latter compound a 0.45-D dipole moment results from the $H\ddot{G}e^{+}—^{-}GeH_3$ polarity. The d polarization orbitals remain weakly populated: 0.11 e in GeH_2, 0.14 e in planar and trans-bent digermene, and 0.12 e (Ge^{II}) and 0.18 e (Ge^{IV}) in $H\ddot{G}e—GeH_3$.

6. Bonding in Digermene

Since in singlet digermene and disilene the most stable form is nonplanar, a genuine π bond with an antisymmetry plane is not possible for these molecules.[28] On the other hand, it was noticed that in digermene, CI increases the GeGe bond length, the wagging angle, and their force constants, contrarily to what is usually expected from correlation effects.



The $2b_u$ highest occupied delocalized canonical molecular orbital indeed has strong components on $4p_z$ AO's of germanium atoms, but also components on 4s AO's of germanium atoms and 1s AO's of hydrogen atoms. Some isodensity curves of this orbital are drawn in Figure 3 exhibiting a center of symmetry (and the lack of π symmetry plane). The bonding in this nonplanar molecule cannot therefore be depicted by a classical $\sigma + \pi$ scheme. A more reasonable representation of the GeGe link consists of two donor–acceptor bent bonds between two singlet germylenes through the delocalization of the n_σ lone pair of one germanium atom into the p_π vacant orbital of the other germanium atom, and vice versa, according to the scheme below. The two resulting dative bonds are bent and unsymmetrical with respect to the GeGe axis; for this reason they are different from the "banana bonds" sometimes used to represent π system.[29] This picture

makes clear the peculiarity of the Ge═Ge bond while showing its double and unsaturated character; of course, it holds for trans-bent disilene also.[30]

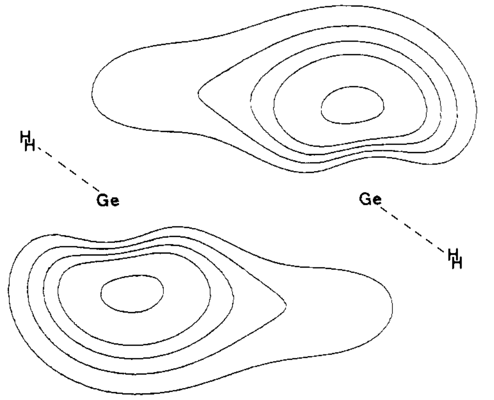


Figure 3. Isodensity contour map of the $2b_u$ HOMO of trans-bent digermene. The curves correspond to ψ^2 = 0.008, 0.012, 0.016, 0.02, and 0.03.

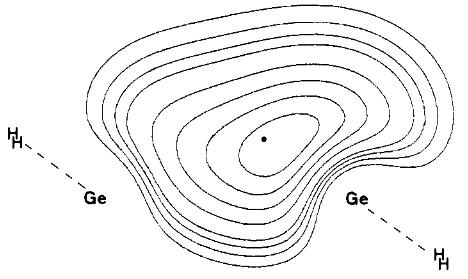


Figure 4. Isodensity contour map of one of the two orbitals localized on the GeGe bonds in trans-bent digermene. The curves correspond to ψ^2 = 0.008, 0.012, 0.016, 0.02, 0.03, 0.04, 0.05, and 0.06. The asterisk locates the charge centroid.

In order to visualize these two dative bent bonds, the SCF delocalized wave function of digermene was relocalized according to Boys' criterion.[31] Beside the four MO's localized on the four GeH bonds, the two bent bonds appear through two MO's, the charge centroids of which are located symmetrically to the inversion center of the molecule but not to the GeGe axis. The isodensity curves corresponding to one of these two localized molecular orbitals are drawn in Figure 4. They show a n_σ lone pair on one germanium atom delocalized into the p_π orbital of the other germanium atom. Both bonds are responsible for the cohesion between the two germylenes moieties. An estimate of the Ge═Ge bond energy in this molecule was computed through the enthalpy of the dissociating reaction

$$H_2Ge{=}GeH_2 \rightleftharpoons 2H_2Ge\colon \quad (^1A_1)$$

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(28) Some nonplanar π systems are reported, however; see, for instance, G. Wipff and K. Morokuma, *Tetrahedron Lett.*, **21**, 4445 (1980).

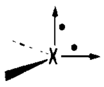
(29) For a review on this topic see, see: Ph. Millié, B. Lévy, and and G. Berthier, in "Localization and Delocalization in Quantum Chemistry", Vol. 1, O. Chalvet, R. Daudel, S. Diner, and J. P. Malrieu Eds., D. Reidel, Dordrecht, 1975, p 59.

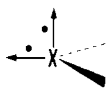
(30) In that case, the "di-silylene" description is supported by the recent synthesis of tetramesityldisilene from dimesitylsilylene: R. West, M. J. Fink, and J. Michl, Abstracts of the 6th International Symposium on Organosilicon Chemistry, Budapest, Aug 14th, 1981, p 122; *Science*, **214**, 1343 (1981).

(31) J. M. Foster and S. F. Boys, *Rev. Mod. Phys.* **32**, 300 (1960).

With a zero-point vibration energy difference assumed as $^1/_2h\nu_{GeGe}$, this dissociation energy is computed at 30 kcal/mol at the SCF level and at 45 kcal/mol at the CI level. The 2 SiH_2/Si_2H_4 energy difference was computed in disilene at 44 kcal/mol at the SCF level and at 57 kcal/mol at the CI level[14] (using a 3-21G basis set). The GeGe link would then be less strong than the SiSi link in such molecules. On the other hand, our calculated GeGe bond dissociation energy in trans-bent digermene is similar to what is usually admitted as a σ Ge–Ge single bond energy, namely, 45 kcal/mol.[32,33] The calculated SiSi bond dissociation energy in disilene (57 kcal/mol)[14] is also close to a σ Si–Si single bond energy (54 kcal/mol).[32]

The molecular bending may be related to the strong singlet → triplet separation in germylenes. The planar $\sigma + \pi$ bonding actually gives a dominant role to the instantaneous neutral open-shell structures in which the X atoms bear $n_\sigma p_\pi$ unpaired electrons.





The unsymmetrical banana (or "papaw") bonds give a dominant role to the germylene closed-shell singlet states.

The factors governing the bonding may be thought of in terms of intermolecular contributions and singlet → triplet separation.

(1) The short-range repulsions are specially important between the n_σ singlet lone pairs; bending favors their diminition.

(2) The electrostatic interactions between the parallel dipoles also tend to favor a bent geometry; they are larger for singlets partners because of their larger dipole moments.

(3) The delocalization factors are stronger for the planar ($\sigma + \pi$) bonding than for the the semipolar bent bonding.

(4) The singlet → triplet separation which favors the planar ($\sigma + \pi$) double bonding between methylenes ($\Delta E_{ST} \simeq -10$ kcal/mol) becomes the leading factor in favor of a bent geometry for large S → T separations as seen in germylenes ($\Delta E_{ST} \simeq 19$ kcal/mol).[15]

An illustration is given by the dimerization of singlet methylenes,[34,35] for which factors 1 and 2 lead to a nonplanar approach while factors 3 and 4 allow recovery of planarity for short C–C distances only.

If this interpretation is correct and despite the weakness of the "papaw" double bond (which is of the order of magnitude of a GeGe single bond), the chemical notation $>\dot{Ge}-\dot{Ge}<$ is not relevant for this singlet system since it would suggest a $n_\sigma p_\pi$ dominant occupation, which the bending actually tends to avoid.[36]

7. Conclusion

(1) Singlet digermene has a trans-bent nonplanar structure and is ≃5 kcal/mol more stable than its germylgermylene isomer. The first column of Table V shows that an important relative stabilization of $H\ddot{X}{-}XH_3$ with respect to $H_2X{=}XH_2$ occurs from carbon to silicon. This stabilization is even more pronounced for germanium.

Table V. Comparison of Some Computed Values in Group 4B Model Molecules

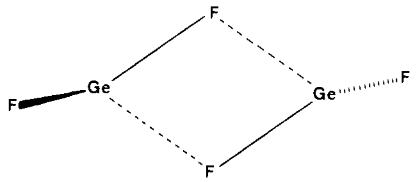
X	$H_2X{=}XH_2 \rightarrow H\ddot{X}{-}XH_3$ separation (kcal/mol)	bending angle in $H_2X{=}XH_2$ (deg)	singlet → triplet separation in H_2X: (kcal/mol)
C	77[a]	0 (planar)	−10
Si	10[b]	13[c]	11[b]
		20[d]	
Ge	5[e]	34[f]	19[g]

[a] 6-31 G basis set + Møller-Plesset third-order perturbation corrections.[37] [b] 3-21 G basis set + CI.[14] [c] 4-31 G basis set.[27] [d] 3-21 G basis set.[14] [e] DZ + d basis set + CI, this work. [f] DZ + d basis set, this work. [g] DZ + P basis set + CI.[15]

(2) The bonding in trans-bent digermene can be described as two $n_\sigma \rightarrow p_\pi$ semipolar "bent" bonds between two singlet germylenes. So digermene, which can be considered as these two interacting divalent species, should be better called "digermylene" instead of digermene.

(3) One should remember, however, that decreasing the wagging angle allows the "papaw" (i.e., semipolar bent) bonds to go *continuously* to the "banana" (i.e., $\sigma + \pi$) bonds. The later description, which is perfectly valid for ethylene becomes more and more irrelevant when going to disilene and digermene.

(4) The discussion of the various factors governing the geometry of the "double bond" (cf. section 6) suggests the leading role of the S → T separation in the bending; the larger the singlet → triplet splitting (in favor of the singlet) is in the monomer, the more bent is the dimer, as illustrated by the two last columns of Table V. GeF_2 appears as a limiting case which has a very large S → T separation (74 kcal/mol)[15] and which bears strongly polarized bonds. In this system the S → T separation factor and the electrostatic repulsion will both lead to an "overbent" structure. Actually, infrared and Raman spectroscopy studies[38] show a doubly bridged structure



As shown from SCF calculations by Olbrich,[39] the S → T splitting of stannylene should be rather close to that of germylene. As expected from electronegativities, SnH_2 should have a slightly larger dipole moment than GeH_2. The electrostatic factors should therefore induce a slightly more bent dimer.

Acknowledgment. We are grateful to Professor J. Satgé for helpful discussions.

Registry No. $H_2Ge{=}GeH_2$, 82323-93-1; $HGe{-}GeH_3$, 82323-94-2.

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(32) K. F. Purcell and J. C. Kotz, "Inorganic Chemistry", W. B. Saunders, Toronto, 1977, p 270.

(33) Discrepant values may be found: 38 kcal/mol for the GeGe bond dissociation energy in H_3GeGeH_3 (E.G. Rochow and E. W. Abel, "The Chemistry of Germanium, Tin and Lead", Pergamon Press, New York, 1975), 73 kcal/mol in $Me_3GeGeMe_3$ (R.A. Jackson, *J. Organomet. Chem.*, **166**, 17 (1979).

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(35) G. Trinquier and J. P. Malrieu, *Chem. Phys. Lett.*, **72**, 328 (1980).

(36) Note that in ref 16 the photolytically generated >Ge—Ge< system may be in a triplet state, for which the "papaw" bonding is no longer relevant.

(37) R. H. Nobes, L. Radom, and W. R. Rodwell, *Chem. Phys. Lett.*, **74**, 269 (1980).

(38) H. Huber, E. P. Kündig, G. A. Ozin, and A. Vander Voet, *Can. J. Chem.*, **52**, 95 (1974).

(39) G. Olbrich, *Chem. Phys. Lett.* 73, 110 (1980).