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Double Bonds vs. Carbene-Like Unsaturations in Germanium Intermediates

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Abstract: Germaethylene ($H_2Ge{=}CH_2$), germamimine ($H_2Ge{=}NH$), germanone ($H_2Ge{=}O$), and their respective germylene isomers (methylgermylene ($H\ddot{G}eCH_3$), aminogermylene ($H\ddot{G}eNH_2$), and hydroxygermylene ($H\ddot{G}eOH$)) are investigated through ab initio calculations with double-ζ (DZ) plus polarization basis sets. The geometries of the lowest singlet and triplet states of the doubly bonded molecules, as well as the geometries of the singlet germylenes, have been optimized at the SCF level of theory. Singlet $H_2Ge{=}X$ compounds possess planar structures while the corresponding triplets are both twisted and pyramidalized on germanium. $Ge{=}X$ bond lengths and stretching vibrational frequencies are refined including electron correlation. Germaethylene, germanimine, and germanone are predicted to have singlet ground states with their lowest triplet states 27, 30, and 44 kcal/mol (respectively) higher in energy as determined by CI calculations. For each case reported, singlet germylenes are calculated to be more stable than their π-bonded isomers by 15, 32, and 20 kcal/mol, respectively, at the CI level. Relative stabilizations of aminogermylene and hydroxygermylene are enhanced by delocalization of a π lone pair in the vacant germanium p_π orbital.

1. Introduction

In recent years there has been much interest in structures and reactivities of multiply bonded silicon and germanium intermediates.[2] Experimental evidence consistent with the transient existence of these species is now available, and a series of doubly bonded germanium compounds such as $>Ge{=}C<$, $>Ge{=}N{-}$, and $>Ge{=}O$ have been reported as reaction intermediates.[3]

A large number of extensive theoretical studies have been carried out in the field of π-bonded silicon compounds,[4] especially silaethylene[5-7] and silanone.[8] The general features of organosilicon unsaturated compounds have been clearly established, i.e., the thermodynamic instability of multiply bonded silicon systems with respect to cycles or silylene forms.[9]

However, very little is known concerning the corresponding germanium analogues. Only the germanium-carbon double bond has been the subject of a theoretical study by Gowenlock and Hunter[10] using a semiempirical CNDO scheme. As part of a series of investigations into unsaturated compounds containing silicon or germanium,[7,11-14] the present work is devoted to a study of the electronic structure and stability of model compounds involving three simple $Ge{=}X$ frameworks with X representing C, N, and O (respectively), namely, germaethylene, germanimine, and germanone. The relative stability with respect to the germylene isomers will be discussed carefully.

The most outstanding features of germanone have already been published.[15] Nevertheless recent complementary results justify the treatment of germanone again for the sake of comparison in the series.

2. Computational Details

All SCF calculations were carried out with a modified version of the HONDO program package[16] including pseudopotentials, the PSHONDO algorithm.[17] We used the pseudopotential method proposed by Durand and Barthelat.[18]

For each atom, the core electrons are taken into account through a nonempirical pseudopotential determined from the double-ζ atomic Hartree-Fock calculations of Clementi and Roetti.[19] Valence atomic basis sets are optimized in a pseudopotential SCF calculation of the ground state of the atom by using a quadruple-ζ Gaussian basis set. These four Gaussian functions are contracted to the double-ζ level (DZ) by means of a 3 + 1 procedure (except for the p basis set of Ge, where a 2 + 2 procedure was used). For germanium, a 4d Gaussian function was added as a polarization function ($\eta_{Ge} = 0.25$). Details of the pseudopotential parameters and optimized basis sets are available upon request.

Two separate basis sets were used in these calculations. Both have the DZ quality. The first one (noted basis A) has polarization functions only on germanium. Basis B is obtained from basis A by adding polarization functions on carbon ($\eta_C = 0.7$), nitrogen ($\eta_N = 0.95$), or oxygen ($\eta_O = 1.25$). All closed-shell geometry optimizations were performed by using basis A. Single-point calculations at the final geometries were then carried out by using basis B.

The SCF valence energies for the open-shell singlet and triplet states were obtained by calculating the mean value of the H operator between the wave functions determined from a Nesbet-type operator.[20] As a test case, the geometries of the $^1B_1$ and $^3B_1$ states of germylene (GeH_2) were optimized with this procedure. Excellent agreement was obtained by comparison with geometries optimized by using Roothaan's open-shell procedure.[21] Bond length and valence angle values differ by no more than 0.003 Å and 0.9°, respectively.

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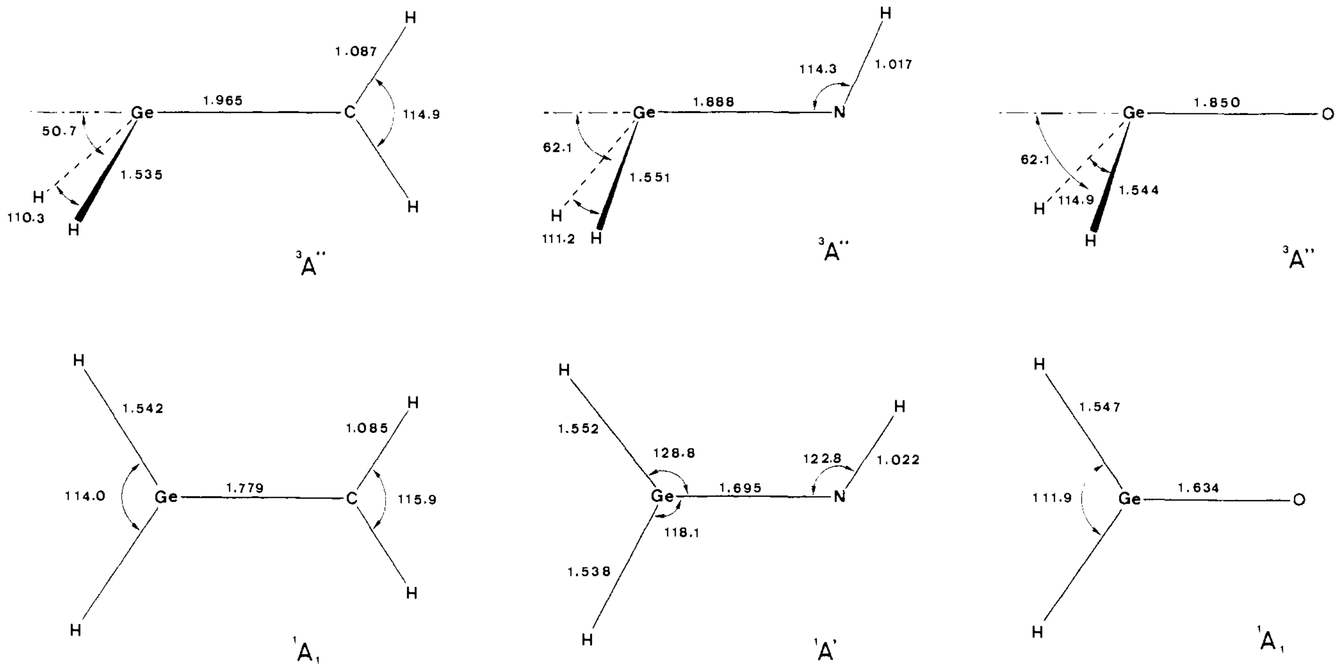

Figure 1. SCF optimized geometries (in angstroms and degrees) for the lowest singlet and triplet electronic states of germaethylene, germanimine, and germanone. The germanone singlet structure is that of ref 15.

Valence-shell configuration interaction (CI) calculations were performed according to an improved version[22] of the CIPSI algorithm,[23] which combines variation and perturbation techniques. A variational zeroth-order wave function ψ_m^0 is obtained by diagonalization of the Hamiltonian restricted to the subspace S of the n_S most important determinants selected from preliminary iterations of the process. Then ψ_m^0 is perturbed through a second-order Möller–Plesset scheme by its interactions with the determinants which do not belong to the subspace S. If a determinant D is involved in the first-order wave function ψ_m^1 with a coefficient larger than a given threshold (0.03), D is added to the S set and the process is repeated. As a typical example, for germanimine, 22 determinants were included in the variational wave function which was perturbed to the second order in energy, involving up to 3.2×10^5 determinants and bringing about 158 kcal/mol valence correlation energies.

Geometrical parameters were independently optimized except for strongly coupled parameters such as a Ge–X distance and a pyramidalization angle in excited states.

3. Equilibrium Geometries

Structures of Germaethylene, Germanimine, and Germanone. The SCF-predicted equilibrium geometries for the lowest singlet and triplet states of germaethylene, germanimine, and germanone are displayed in Figure 1. The closed-shell structures were optimized with basis A, and the open-shell excited ones with basis B.

We first established the planar geometry of $^1A_1$ germaethylene, $^1A'$ germanimine, and $^1A_1$ germanone. An out-of-plane deviation of the GeH_2 group by 5° leads to an increase of about 0.1–0.2 kcal/mol in the total energies. These planar singlet states will be shown to be the ground states in the following section.

The computed Ge=C bond length in $^1A_1$ germaethylene is 0.166 Å shorter than the corresponding single-bond length (1.945 Å) determined experimentally in methylgermane.[24] As expected, it is longer than the Si=C bond calculated in $^1A_1$ silaethylene (1.698 Å).[7] One can notice that the geometrical parameters of the CH_2 groups have very similar values for both molecules, 1.085 vs. 1.087 Å for the C—H bond length and 115.9° vs. 115.1° for the H-C-H angle.

Table I. Predicted Equilibrium Distances d_{GeX} (in angstroms), Force Constants k_{GeX} (in mdyn/Å), and Stretching Vibrational Frequencies ν_{GeX} (in cm^{-1}) for Ground-State π-Bonded Molecules Using Basis B

theoretical description	$H_2Ge{=}CH_2$			$H_2Ge{=}NH$			$H_2Ge{=}O$		
	d	k	ν	d	k	ν	d	k	ν
SCF	1.776	5.71	906	1.681	7.27	994	1.616	8.33	1036
CI	1.812	4.99	847	1.727	5.37	854	1.674	6.03	881

In the case of $^1A'$ germanimine, the Ge=N bond length is 0.141 Å shorter than the corresponding single-bond length (1.836 Å) measured experimentally in trigermylamine.[25] To our knowledge, no experimental or theoretical information is available concerning silanimine. However, the molecular structure of singlet methylenimine has been determined by microwave spectroscopy[26] and theoretically studied at the SCF level.[27] Both studies have shown that CH_2NH has a CH_2 tilt angle of about 3° in the direction opposite to the N-H bond. In the same way singlet GeH_2NH shows a GeH_2 tilt angle of about 5° away from the N-H bond. For this reason the Ge-H bonds are not equivalent, and the cis Ge-H bond length is 0.014 Å longer than the trans one.

The SCF geometrical parameters of singlet germanone have been discussed elsewhere[15] and only to a regular decrease in the H-Ge-H angle from germaethylene to germanone will be mentioned.

The structures of the lowest triplet states of germaethylene, germanimine, and germanone are also interesting since they are both twisted and pyramidalized. It should be noted that the XH_2 rocking angle has the same order of magnitude for triplet germaethylene (50.7°) and silaethylene (49.7°).[6] The H-Ge-H angle increases slowly on going from triplet germaethylene to triplet germanone. Moreover, as expected, the $^3A''$ Ge—X bond lengths

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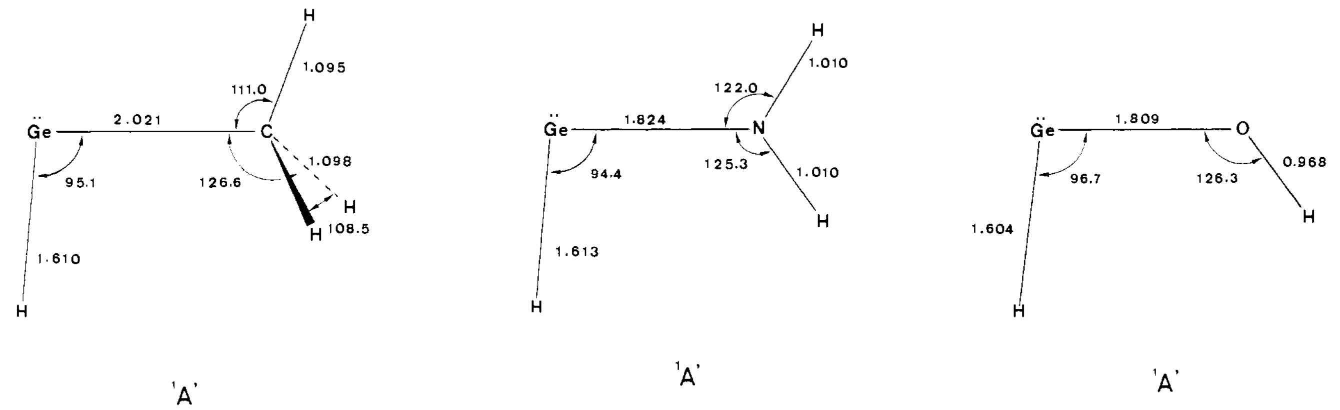

Figure 2. SCF optimized geometries (in angstroms and degrees) of methylgermylene, aminogermylene, and hydroxygermylene. The *s-cis*-hydroxygermylene structure is that of ref 15.

are longer than the corresponding ground-state ones. A more rigourous examination of these values shows a regular increase of the relative lengthening (10.5% for Ge—C, 12.3% for Ge—N, 14.5% for Ge—O) calculated by using basis B.

The open-shell singlet $^1A''$ states were found to have geometries very similar to their companions, the $^3A''$ states. For this reason, only triplet geometries will be used in both open-shell states for CI energy calculations.

The effects of the addition of d functions on carbon, nitrogen, or oxygen have been examined by reoptimizing the ground-state singlet Ge=X bond lengths by using basis B. The corresponding results are presented in Table I, together with the effects of electron correlation. With the addition of d polarization functions, the Ge=X equilibrium bond lengths are slightly shortened. It is interesting to note that this effect is more substantial for the Ge=N and Ge=O bond lengths (0.014 and 0.018 Å, respectively) than for that of Ge=C (0.003 Å).

Unlike the d polarization effect, the inclusion of electron correlation by extended CI calculations significantly lengthens the bond distances. It appears that the CI effects play a more crucial role for germanone (0.058 Å) than for germaethylene (0.036 Å). This may be connected to the decrease in size of the π bond on going from Ge=C to Ge=O.

Table I also contains Ge=X stretching harmonic force constants and vibrational frequencies at two levels of theory. These calculated values are obtained by assuming point XH_2 groups. As expected, the inclusion of electron correlation decreases the force constants and the vibrational frequencies relative to their SCF values. No experimental information is available concerning the model molecules. However, an observed transient frequency has been assigned to Ge=N stretching (~970 cm^{-1}) in F_2Ge=NPh and Ph_2Ge=NMe intermediates.[28] This experimental value differs by about 100 cm^{-1} from our predicted value, which may be attributed to substituent effects. It should in any case be noted that our calculated values are greater than the experimental Ge–X single-bond stretching frequencies.[29]

Finally, experimental values, when available, or CI calculated values of XC, XN, and XO single- and double-bond lengths are collected in Table II for X = C, Si, Ge. Once more, comparison of the relative bond distance shortenings on going from single to double bonds shows a very similar behavior in the silicon and germanium series in opposition to the carbon series.[32]

Structures of Methylgermylene, Aminogermylene, and Hydroxygermylene. SCF equilibrium geometries for the three corresponding germylene isomers assumed to be singlets in their ground state[12] are given in Figure 2.

Table II. Trends in Bond Length Shortening from σ to $\sigma + \pi$ Bonding[a]

X	H_3X-CH_3	H_2X=CH_2	Δ, %
C	1.534[c]	1.339[b]	12.7
Si	1.869[b]	1.722[d]	7.9
Ge	1.945[b]	1.812	6.8
X	$(H_3X)_3N$	H_2X=NH	Δ, %
C	1.451[b]	1.273[e]	12.3
Si	1.74[c]		
Ge	1.836[f]	1.727	5.9
X	$(H_3X)_2O$	H_2X=O	Δ, %
C	1.410[b]	1.206[g]	14.4
Si	1.633[c]	1.507[g]	7.7
Ge	1.77[h]	1.674	5.4

[a] Bond lengths are in angstroms. [b] Experimental value.[24] [c] Experimental value.[30] [d] CI caluclated value.[7] [e] Experimental value.[26] [f] Experimental value.[25] [g] CI calculated value.[8] [h] Experimental value.[31]

For each germylene, the Ge—X single bond is longer than the Ge=X double bond in the π-bonded isomers. Comparison with the GeX bond length in the $^3A''$ excited states shows lengthening by 0.056 Å for $H\ddot{G}eCH_3$ and shortening by 0.064 Å for $H\ddot{G}eNH_2$ and 0.041 Å for $H\ddot{G}eOH$. In the case of aminogermylene and hydroxygermylene this situation may be accounted for by delocalization of the nitrogen or oxygen lone pair into the germanium $4p_z$ vacant orbital (vide infra). This fact is also responsible for the preferred planar conformations of these two germylenes. For instance, an out-of-plane NH_2 rocking angle of 5° results in an energy increase of about 0.2 kcal/mol.

The singlet methylgermylene structure is similar to that of methylsilylene, especially as regards the methyl group. In both molecules, the C–H bond lying in the Ge (or Si) lone-pair plane is slightly shorter than the other two C–H bonds.[6] The H–Ge–C angle in singlet methylgermylene is predicted to be 95.1°, which is greater than the calculated angle in germylene (92.9°) and smaller than the C–Ge–C angle in dimethylgermylene (97.8°).[12] The regular opening of this angle during the substitution of hydrogen atoms by methyl groups may be attributed to a steric effect. Lastly, let us indicate that the methyl group in methylgermylene can rotate almost freely around the Ge–C bond. Indeed the eclipsed conformation lies 1.2 kcal/mol above the staggered one within the approximation of the rigid rotator.

For aminogermylene, note that the NH_2 group is tilted away from the Ge–H bond by about 1.6°. However, the two nonequivalent N–H bond lengths are not appreciably affected.

4. Energies

Low-Lying States of π-Bonded Systems. The total and relative energies of the two lowest states of H_2Ge=CH_2, H_2Ge=NH, and H_2Ge=O are given in Table III. Germaethylene, germanimine, and germanone are predicted to have singlet ground states with

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Table III. Total Valence Energies E and Adiabatic Separation Energies ΔE for Closed-Shell (π-Bonded) and Open-Shell (Diradical) Triplet and Singlet States of Germaethylene, Germanimine, and Germanone at CI Level[a]

H_2GeCH_2			H_2GeNH			H_2GeO		
electronic state	E, au	ΔE, kcal/mol	electronic state	E, au	ΔE, kcal/mol	electronic state	E, au	ΔE, kcal/mol
$^1A_1$	−11.582 34	0	$^1A'$	−15.232 74	0	$^1A_1$	−20.714 47	0
$^3A''$	−11.539 46	26.9	$^3A''$	−15.184 57	30.2	$^3A''$	−20.644 96	43.6
$^1A''$	−11.536 56	28.7[b]	$^1A''$	−15.176 63	35.2[b]	$^1A''$	−20.637 98	48.0

[a] $^1A''$ energies are obtained from CI calculations carried out at the corresponding $^3A''$ optimized geometries. [b] This state belongs to the ground-state surface. The corresponding ΔE therefore represents the rotational barrier around the double bond.

Table IV. Trends in Singlet–Triplet Adiabatic Energy Separations (in kcal/mol) for π-Bonded Systems, from CI Calculations

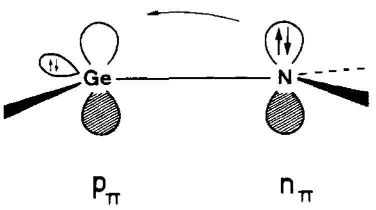
X	$H_2X{=}CH_2$	$H_2X{=}NH$	$H_2X{=}O$
C	64.3[a]	64.5[b]	69.5[c]
Si	34.7[d]		
Ge	26.9	30.2	43.6

[a] Extended basis set, CI.[33] [b] DZ + POL basis set, CI + Davidson corrections.[27] [c] DZ + POL basis set, CI + Davidson corrections.[34] [d] DZ + d(C,Si) basis set, CI + Davidson corrections.[6]

a singlet–triplet (S–T) energy separation ranging from 27 (germaethylene) to 44 (germanone) kcal/mol. It is now definitely established that the $H_2X{=}CH_2$ molecules have a singlet ground state when X = C, Si, or Ge. The available singlet–triplet separations for all parent valence isoelectronic molecules are collected in Table IV, which allows a double comparison. Firstly the S–T separation in germaethylene is ~8 kcal/mol smaller than in silaethylene. Both values are much lower than the S–T separation in ethylene. Secondly, the $H_2X{=}O$ molecules have a somewhat higher S–T separation than their $H_2X{=}NH$ or $H_2X{=}CH_2$ analogues although the S–T separations present a minor dispersion in the carbon series. Our computed S–T separations are therefore consistent.

The energy separation between the singlet ground state and the open-shell $^1A''$ singlet state represents the rotational barrier around the double bond, except for germanone.[35] Since in the open-shell situation no overlap is possible between π electrons, these rotational barriers can be considered as a reasonable measure of π-bond energies.[5] This point will be further discussed in section 5.

Germylenes vs. π-Bonded Germanium Compounds. The relative energies of germaethylene, germanimine, and germanone with respect to their germylene isomers are given in Table V at both SCF and CI levels. For each case reported the germylene isomers are more stable. As expected,[8] correlation effects relatively stabilize the π-bonded systems by 6, 9, and 12 kcal/mol from $H_2Ge{=}CH_2$ to $H_2Ge{=}O$, respectively. We can point out that in this series, in contrast with the silicon series, the SCF level already provides the correct order of stability. The germylenes are relatively stabilized when conjugation of a heteroatom lone pair is possible. This effect is especially reinforced with a nitrogen lone pair which possesses an important π donor character. This $n_\pi \rightarrow p_\pi$ delocalization which can be depicted for aminogermylene as



is also responsible for the planar geometries of aminogermylene and hydroxygermylene and for the somewhat high singlet–triplet separations which are to be expected from the n_σ–p_π energy

Table V. Energy Differences (in kcal/mol) between Singlet $H\ddot{G}e{-}XH$ and $H_2Ge{=}X$ at Two Levels of Theory[a]

X	SCF	CI
CH_2	21.0	15.0
NH	41.4	32.0
O	32.1	19.9

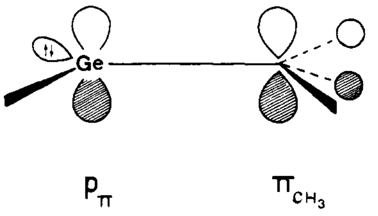
[a] In all cases germylene isomers are more stable.

Table VI. Trends in Relative Stabilities (in kcal/mol) between π-Bonded and Divalent Forms[a] from CI Calculations

X	$H_2X{=}CH_2$/ $H\ddot{X}{-}CH_3$	$H_2X{=}O$/ $H\ddot{X}{-}OH$
C	−77.2[b]	−52.6[c]
Si	−3.5[d]	
Ge	15.0	19.9

[a] A negative sign implies that the π-bonded form is more stable. [b] 6-31 G[2+] basis set + third-order Möller–Plesset perturbation corrections.[36] [c] DZ + d basis set + CI.[34] [d] DZ + d basis set + CI.[7]

difference (~10.2 eV) in these two germylenes (see section 5). Formally, an alkyl group does not bear a lone pair allowing a delocalization but it can give rise to hyperconjugation. In a methyl group, for instance, an occupied π_{CH_3} orbital has the appropriate symmetry to interact with the vacant germanium p_π orbital.



However, this interaction is weak because π_{CH_3} is low in energy and spatially remote from $p_{\pi Ge}$.

Table VI provides other available theoretical data on divalent/π-bonded competition of 4B-group elements. It is not surprising that germanium appears in this series as the most reluctant atom to form π-bonded structures. A great difference appears between the series of carbon and silicon. In the carbon series the π-bonded forms are always much more stable than the carbene isomers. We have calculated[7] silaethylene to be only 3 kcal/mol more stable than its silylene isomer while Goddard et al.[6] computed both isomers as degenerate in energy (methylsilylene 0.4 kcal/mol more stable than silaethylene). With germanium, the tendency to stabilize divalent forms is definitely established but, as regards this competition, the difference between carbon and silicon is more pronounced than the difference between silicon and germanium. Table VI also shows a more important stabilization of divalent forms on going from X–C to X–O bonds.

5. Discussion

Valence Energy Levels. In Table VII we report the most important energy levels for closed-shell compounds including available data on silicon and carbon analogues. The pattern of the occupied

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Table VII. Selected Orbital Energy Levels (in Electron Volts)

	π	π^*	
$H_2Ge=CH_2$	−8.23	+2.14	
$H_2Si=CH_2$	−8.54	+2.36	
$H_2C=CH_2$	−10.20	+4.45	
$H_2Ge=NH$	−9.69	+1.62	
$H_2C=NH$[a]	−12.24		
$H_2Ge=O$	−11.50	+0.93	
$H_2Si=O$[b]	−12.45		
$H_2C=O$	−14.31		
	n_σ	p_π	$n_\sigma \to p_\pi$
GeH_2	−9.06	+0.09	9.15
$Ge(CH_3)_2$	−8.12	+0.97	9.09
$HGe-CH_3$	−8.56	+0.53	9.09
$HGe-NH_2$	−8.81	+1.46	10.27
$HGe-OH$	−9.33	+0.82	10.15

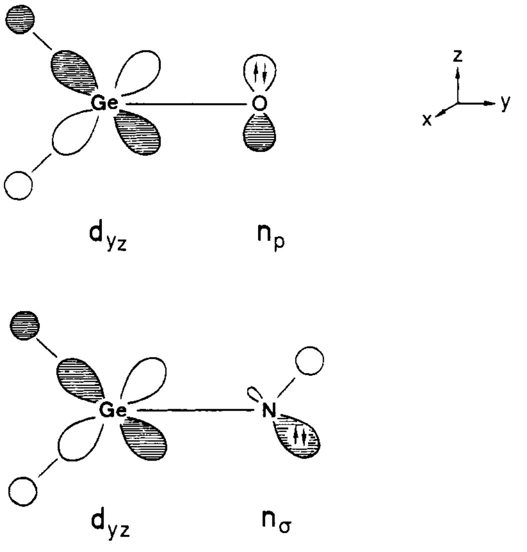
[a] DZ basis set.[37] [b] Extended basis set.[8]

Table VIII. d Atomic Populations on Germanium Atom and Calculated Dipole Moments

		d_{Ge}, $\bar{e}$	μ, D
$H_2Ge=CH_2$	$^1A_1$	0.19	0.89
$H_2Ge=NH$	$^1A'$	0.26	2.99
$H_2Ge=O$	$^1A_1$	0.30	4.66
$HGe-CH_3$	$^1A'$	0.12	0.76
$HGe-NH_2$	$^1A'$	0.15	1.46
$HGe-OH$	$^1A'$	0.13	1.52

valence MO's of germaethylene is shifted to 0.1–0.3 eV above that of silaethylene. The π and π^* levels in germaethylene can be contrasted with the corresponding levels computed with similar basis sets in ethylene and silaethylene. Along the series ethylene, silaethylene, and germaethylene, there is a trend for the π level to rise and the antibonding π^* level to fall. This effect is less marked between silaethylene and germaethylene. In the case of a double bond involving a heteroatom, the rise in the π level may result in an inversion between this level and the lone-pair level. Indeed, the HOMO level in germanimine is the $\pi_{Ge=N}$ level while the level corresponding to the n_σ nitrogen lone pair is just below at −10.63 eV. For methylenimine the reverse situation occurs: according to SCF calculations by Macaulay et al.,[37] the highest molecular orbital level is $n_\sigma(N)$ at −11.21 eV.

A similar n_p/π inversion has also been noticed in germanone[15] with respect to formaldehyde. In both cases the relative lowering of the nitrogen and oxygen lone pairs could be the consequence of their conjugation with a germanium $4d_{yz}$ orbital. For germanone the molecular orbital corresponding to the n_p oxygen lone pair involves a pure $2p_z$ oxygen atomic orbital and a germanium $4d_{yz}$ atomic orbital (together with hyperconjugation with hydrogen atoms). For this molecular orbital, the wave function shows a coefficient on the germanium $4d_{yz}$ AO of 0.13, which is the highest coefficient of d AO's in all occupied orbitals. In germanimine the nitrogen lone pair no longer has pure p character due to lack of C_{2v} symmetry; in this case, the coefficient of the germanium $4d_{yz}$ AO is only 0.09. Anyway, these two orbitals constitute the only examples of significant participation of germanium d orbitals in the electronic structures involved. The comparison of the total populations in germanium d orbitals given in Table VIII clearly supports our analysis.



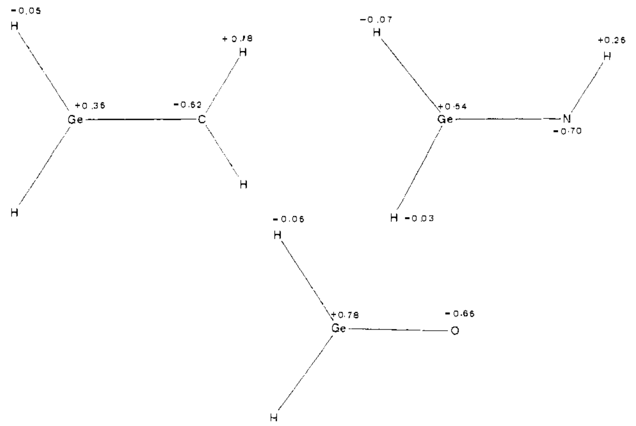


Figure 3. Net atomic charges in germaethylene, germanimine, and germanone from Mulliken population analyses (basis B).

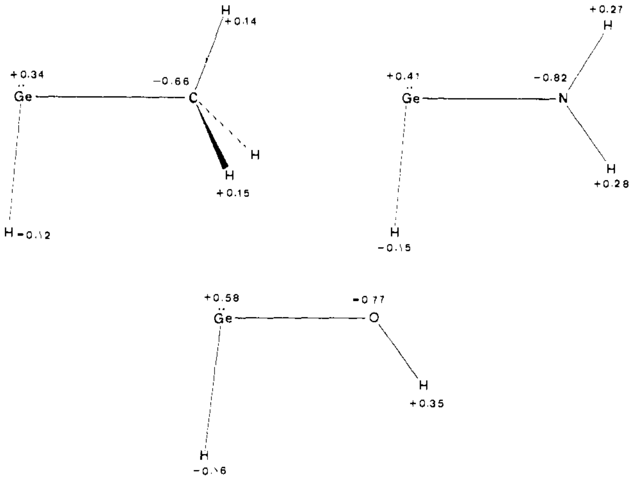


Figure 4. Net atomic charges in methylgermylene, aminogermylene, and hydroxygermylene from Mulliken population analyses (basis B).

The regular lowering of the π energy levels from $H_2Ge=CH_2$ to $H_2Ge=O$ parallels the ordering of the π levels in the series ethylene, methylenimine, and formaldehyde (Table VII).

The most important monoelectronic energy levels in germylenes are the germanium n_σ lone pair and the vacant germanium p_π orbital. Their separations can be related to singlet–triplet separation values. Although we did not directly compute these values, SCF estimates can be obtained by using the calculated[12] singlet–triplet separations in GeH_2, $Ge(CH_3)_2$, and GeF_2 and the n_σ–p_π orbital energy differences in the three germylenes studied here. Since the singlet stabilization due to the inclusion of electron correlation is most often about 8–10 kcal/mol in such systems,[6,12] we predict singlet–triplet separations of ~23 kcal/mol in methylgermylene and ~40 kcal/mol in aminogermylene and hydroxygermylene. As previously mentioned, the singlet stabilization in aminogermylene and hydroxygermylene is due to delocalization of the heteroatom lone pairs into the vacant germanium p_π orbital. This implies the relative rise of the p_π LUMO and the fall of the heteroatom lone pairs: $n_p(N) = -11.14$ eV, $n_p(O) = -13.30$ eV.

Charge Distributions. The net atomic charges derived from Mulliken population analyses in π-bonded compounds and in

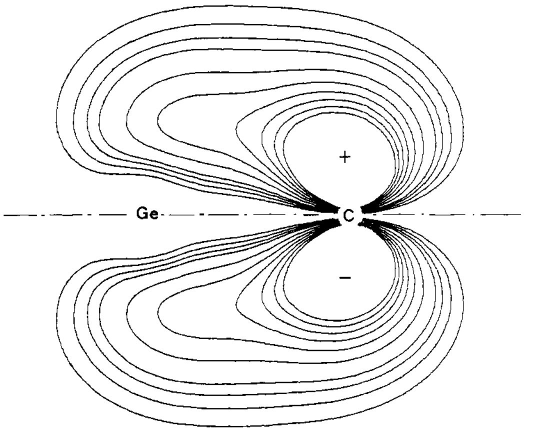


Figure 5. Isodensity contour map for the π MO in $H_2Ge{=}CH_2$. Lines plotted correspond to $\psi^2 = 0.004, 0.006, 0.008, 0.010, 0.015, 0.020, 0.025, 0.030, 0.035$, and 0.040 au (the germanium core region is not represented due to use of pseudopotentials).

germylenes are illustrated in Figures 3 and 4. The corresponding calculated dipole moments are given in Table VIII. The increase in the Ge=X bond polarity is regular from >Ge=C< to >Ge=O. When computed with comparable basis sets, silaethylene shows a more contrasted distribution (Si: +0.54; C: −0.71). The same observation can be made in methylsilylene (Si: + 0.47; C: −0.77) with respect to methylgermylene (see Figure 4) and also holds for the π charges

$$^{+0.18}Si{=}C^{-0.18} \qquad ^{+0.16}Ge{=}C^{-0.16}$$

This would suggest that our pseudopotentials follow the Allred–Rochow electronegativity scale. This might be fortuitous but we note that the depth of the radical s pseudopotential (which is related to electronegativity) also follows this scale from carbon to germanium. Figure 4 shows a regular increase of the Ge–X bond polarity in the germylenes $H\ddot{G}e{-}CH_3$, $H\ddot{G}e{-}NH_2$, and $H\ddot{G}e{-}OH$. The π-bonded compounds are however more polar than their germylene isomers. In particular, $H_2Ge{=}O$ appears to be the most polar of all the studied compounds and might be described as the following limiting form $H_2Ge\colon \rightarrow \overline{O}|$.[15]

The resulting dipole moments (Table VIII) illustrate these trends. Delocalization of the π heteroatom lone pair into the germanium p_π orbital in aminogermylene and hydroxygermylene can be measured by the π populations in these molecules; they show a migration of 0.23 electron from the nitrogen lone pair and of 0.16 electron from the oxygen lone pair. As an example, isodensity curves for the GeC π MO are presented in Figure 5. The $Ge^{+}{-}^{-}C$ polarity of this π bond appears clearly and the shape of the contour map is very similar to that of the Si=C π bond in silaethylene published by Ahlrichs and Heinzmann.[5] The d atomic populations in germanium remain weak (see Table VIII) although they are higher in the π-bonded isomers.

π Energy Contribution Estimates. One way to estimate a bond energy in a molecule is to dissociate it into the corresponding ground-state fragments, i.e., in our π-bonded compounds

$$H_2Ge{=}X \rightarrow H_2Ge\colon + X$$

With the type of basis set that we use, the correlation energy of the π-bonded molecule is generally underestimated so that even at the CI level the energy difference between all the fragments is less than the corresponding dissociation energy.[8,15] Without taking zero-point vibrational energies into account, the energy differences (at the CI level) between the fragments were computed in the three π-bonded compounds to be as follows:

$H_2Ge{=}O \rightarrow H_2Ge\ (^1A_1) + O\ (3P)$ 98 kcal/mol
$H_2Ge{=}NH \rightarrow H_2Ge\ (^1A_1) + NH\ (^3\Sigma^-)$ 77 kcal/mol
$H_2Ge{=}CH_2 \rightarrow H_2Ge\ (^1A_1) + CH_2\ (^3B_1)$ 88 kcal/mol

(Note that these direct dissociations are spin forbidden.) These values represent lower bounds for the Ge=X ($\sigma + \pi$) double-bond energies but the ordering that they display

$$E_{Ge=O} > E_{Ge=C} > E_{Ge=N}$$

(which is not expected to be modified by further refinements) is not very different from the carbon series results.[38]

$$E_{C=O} > E_{C=C} \simeq E_{C=N}$$

Even if one increases these values by a reasonable 10–15 kcal/mol correction term,[8,15,39] any attempt to separate the π contribution from the total bond energy is faced with discrepancies in available Ge–X single-bond energies:[29] Ge–O, 72–107 kcal/mol; Ge–N, 60–70 kcal/mol; Ge–C, 59–76 kcal/mol. Estimations for π bond energies can also be made through the closed-shell/open-shell singlet-state separations (Table III). Our calculated Ge=C π bond energy (29 kcal/mol) is, incidentally, similar to a recent estimation for the Si=C π bond energy (28 ± 8 kcal/mol).[40] For Ge=N this procedure gives 35 kcal/mol. It leads to a larger value for Ge=O (48 kcal/mol) which is of the same order of magnitude as an estimate of the π binding energy in $H_2Si{=}O$.[8]

6. Conclusion

The present study[41] shows the intrinsic preference of the germanium atom to carry one unsaturation as a germylene rather than a π-bonded compound, mainly when a heteroatom allows a lone pair → germanium p_π AO stabilizing conjugation. The structures of the germanium π-bonded compounds appear rather close to their silicon analogues; like the Si=X bonds, the Ge=X bonds are strongly polarized; this enhances their reactivity with respect to cycloaddition or polymerization reactions. Moreover the Ge=X π bond energies seem to be of the same order of magnitude as the Si=C π bond energies. However, the stability of divalent forms over their π-bonded isomers is significantly higher for germanium compounds than for silicon compounds.

Goddard et al.[6] computed a large barrier for the 1,2 hydrogen shift in silaethylene → methylsilylene isomerization (41 kcal/mol). In their case the two isomers were predicted to be degenerate in energy. In our case, methylgermylene is calculated as being 15 kcal/mol below its germaethylene isomer, so the barrier height from germaethylene to methylgermylene could be significantly reduced. However, it is likely that it remains sufficiently high to confer a certain kinetic stability to the germaethylene compound. Other factors such as stabilizing conjugation effects[7] or inhibition of reactivity by steric effects should be kept in mind in any attempts to isolate stable germanium π-bonded compounds.

Acknowledgment. We thank Dr. J. P. Malrieu for critical comments.

Registry No. $H_2Ge{=}CH_2$, 60188-36-5; $H_2Ge{=}NH$, 83025-94-9; $H_2Ge{=}O$, 78812-54-1; $H\ddot{G}eCH_3$, 78800-76-7; $H\ddot{G}eNH_2$, 83025-95-0; $H\ddot{G}eOH$, 81533-92-8.

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[39] Cheung, L. M.; Sunberg, K. R.; Ruedenberg, K. *J. Am. Chem. Soc.* **1978**, *100*, 8024.

[40] Gusel'nikov, L. E.; Nametkin, N. S. *J. Organomet. Chem.* **1979**, *169*, 155.

[41] After submission of this manuscript, recent all-electron SCF calculations on germaethylene and the corresponding closed-shell isomers have come to our attention (Kudo, T.; Nagase, S. *Chem. Phys. Lett.* **1981**, *84*, 375). Their results are in good agreement with ours at the SCF level, once again demonstrating the reliability of our nonempirical pseudopotential techniques.