J. Am. Chem. Soc. **1992**, *114*, 9559-9568 9559

initio quantum chemistry can provide by itself at present (a detailed investigation of reactions would require considerably larger efforts). Two medium-size phosphorus clusters, P_{12} (D_{3d}) and the P_8=P_8 structure of P_{16} (C_{2h}), have been established as particularly stable under appropriate conditions.

The calculated properties (equilibrium structures, IR and Raman spectra, and NMR shieldings) should allow experimentalists to positively identify some of the clusters or the structural units in red phosphorus. The expected range of error for calculated bond lengths is 3 pm, for bond angles 3°, for (stiff) vibrational frequencies 10–15% (systematically too high), and around 30 ppm for relative chemical shieldings. These estimates arise from comparison with experiment for P_4 and from the fact that SCF/TZDP geometries vary by only 1 pm from SCF/SVP for P_4 and P_{12}. Since the stable clusters form a relatively uniform class of compounds (PP single bond distances are between 220 and 231 pm throughout), it may be safely expected that trends in computed properties are reliably described.

After submission of this manuscript, a density functional study on phosphorus clusters P_9 to P_{11} was published.[22] The cluster P_{10} (C_{2v}), Figure 6a, which according to our study is the most stable P_{10} isomer, has not been found in ref 22.

Acknowledgment. We are indebted to Dr. F. Haase for performing the MP2 geometry optimization on P_{12} and to Professor M. Baudler for making unpublished material available to us. This work has been supported by the Fonds der Chemischen Industrie.

Supplementary Material Available: SCF/SVP vibrational frequencies for all molecules listed in Table III, if zero point vibrational energies are given, and NMR shielding constants σ and chemical shifts δ (in ppm) calculated with TZDP or DZP basis sets at the SCF/SVP geometries for the clusters depicted in Figures 1a, 1f, 1h, 3b, 3e, 4a, 5d, and 6a–6e (5 pages). Ordering information is given on any current masthead page.

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π-Bond Strengths of H_2X=YH_2: X = Ge or Sn, and Y = C, Si, Ge, or Sn

Theresa L. Windus[†] and Mark S. Gordon*[,†]

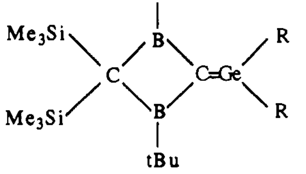
Contribution from the Department of Chemistry, North Dakota State University, Fargo, North Dakota 58105. *Received May 4, 1992*

Abstract: The molecular structures and π-bond strengths are determined using both MP2 and MCSCF + CI energies for a series of H_2X=YH_2 compounds, where X = Ge or Sn and Y = C, Si, Ge, or Sn. These strengths are estimated both by evaluating the rotation barriers and by investigating the appropriate thermochemical cycles. The results show that C > Si ~ Ge > Sn in their ability to form π-bonds.

I. Introduction

Recently there has been considerable interest in the molecular and electronic structure and the reactivity of compounds containing a double bond between group IVA elements. But, while the double bonds in ethylene, disilene, and silaethylene have been well-characterized by both experiment and theory (see, for instance, refs 1–5), the double bonds formed with germanium and tin have only recently been examined. Several reviews have been written on the subject of Ge and Sn double bonds.[6] Many of the species which contain double bonds to these elements are transient reactive intermediates. However, some have been isolated.

Through the use of large, bulky groups for steric and electronic stabilization, three germenes (R_2Ge=CR'_2) were isolated in 1987.[7,8] (Until then, germenes had been seen only as transient species.[9–12]) At that time, Berndt and co-workers[7] synthesized germenes **1a** and **1b**.



1a,b

a, R = $N(SiMe_3)_2$

b, R, R = $NtBu(SiMe_2)NtBu$

These stable germenes were characterized by both NMR and X-ray diffraction techniques. The Ge=C bond length was determined to be 1.827 Å, with an average twist angle of 36° about the GeC bond. In addition, the local structure about the Ge and

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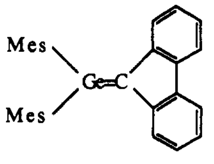
C atoms is nonplanar. Thus, the dihedrals at the Ge and C ends were determined to be 1.7 and 4.8°, respectively. The phenomenon of trans bending in heavier homologues of ethylene has been discussed by several authors.[13,14]

Couret and co-workers[8] synthesized the germene **2**. This molecule was characterized through selected reactions, as well



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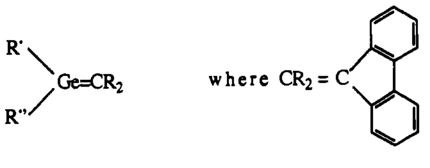
as by NMR and X-ray diffraction. The Ge═C bond length was determined to be 1.801 Å, with an average twist angle of 5.9° about the bond. However, the molecule was found to be essentially planar about Ge and C.

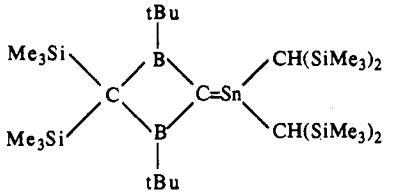
Recently four new germenes, **3a–d**, have been synthesized[15] and identified through the use of NMR.



3a, R'=R''=CHR$_2$; **3b**, R'=CHR$_2$, R''=tBu; **3c**, R'=R''=Bis; **3d**, R'=Bis,R''=Mes

The parent germene $H_2Ge{=}CH_2$, while not known experimentally, has been examined in several theoretical studies.[16-18] Both MNDO[16] and ab initio[17,18] calculations (at the self-consistent field (SCF) level using 3-21G*, pseudopotentials with double-ζ (DZ) valence, and DZ basis sets) predict germene to be planar, with a Ge–C bond distance of 1.717 Å predicted by MNDO and 1.71–1.81 Å calculated by the ab initio methods. Ab initio studies have also predicted methylgermylene to be more stable than germene by 22.7[17a] and 15.0[17b] kcal/mol. However, experience with Si[19] suggests that as the level of theory is improved, the double bond species will preferentially decrease in energy.

In 1987, the only isolated stannene **4** was synthesized.[7b,20] This stannene was thoroughly identified through NMR and X-ray diffraction studies. The Sn═C bond length was determined to be 2.025 Å, with an average twist angle of 61° about the bond. As in the case of GeC, the local structure at Sn and C is found to be nonplanar, with dihedrals at the Sn and C ends of 5° and 16°, respectively.



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Theoretical investigations of the stannenes are as scarce as experimental work. Dewar and co-workers[21] performed MNDO and UMNDO calculations on the lowest singlet and triplet states of stannene ($H_2Sn{=}CH_2$). Since the energy difference between these two states was determined to be small (the triplet being lower in energy than the singlet by 1.1 kcal/mol), they concluded that tin does not form π-bonds. This is in agreement with the conclusions of Pauling.[14] Dobbs and Hehre[18] performed calculations at the UHF/3-21G(d)[45] level and found stannene to be a planar structure with a weak π-bond of 19 kcal/mol and a Sn═C bond length of 1.982 Å. These authors determined the π-bond strength by calculating the rotation barrier (this method for finding the π-bond energy will be discussed in more detail later in the paper) and by calculating the energies of disproportionation of the products of hydrogen atom addition.

No germasilenes are known as stable species. However, Baines and Cooke[22] have found evidence of the tetramesitylgermasilene reactive intermediate.

The only theoretical study is that of Grev and co-workers[23] on germasilene ($H_2Ge{=}SiH_2$) at the configuration interaction with single and double excitations (CISD) level of theory using basis sets of DZ plus polarization (DZP) quality. This method predicts a Ge═Si bond length of 2.211 Å and out-of-plane bend angles of 31.2 and 33.5° at the Ge and Si, respectively. By calculating the rotation barrier, the authors predicted a π-bond energy of 25 kcal/mol. However, the twisted triplet state was used instead of the twisted singlet state and should lead to a π-bond energy that is too low. (Refer to section IV of this paper for more details of this method.) These authors also find silylgermylene, $H_3Si{-}GeH$, to be 7.5 kcal/mol more stable than germasilene.

To our knowledge, no stannasilenes are known as transient species or stable compounds.

Even though several transient digermenes have been identified (see, for instance, refs 24–27), only five stable digermenes have been reported. The parent digermene, $H_2Ge{=}GeH_2$, has been found in nitrogen and argon matrices at 5 K and has been studied using Raman and IR spectroscopy.[28] Three digermenes have been isolated in crystal form, (**5**,[29] **6**,[30] and **7**[31]) while another digermene (**8**[32]) has been found to be stable in solution.

Compound **5** was identified using Raman and X-ray spectra, **6** using X-ray spectra and chemical reactivity, **7** using X-ray and NMR spectra, and **8** using NMR, UV, and mass spectra and chemical reactivity. The X-ray structures show that **5** has a Ge═Ge bond length of 2.347 Å, a twist angle of 0° about the bond, and an out-of-plane angle of 32°. The corresponding data for **6** are 2.213 Å, 11°, and 15°, respectively, and for **7** are 2.313 Å, 7°, and 36°, respectively.

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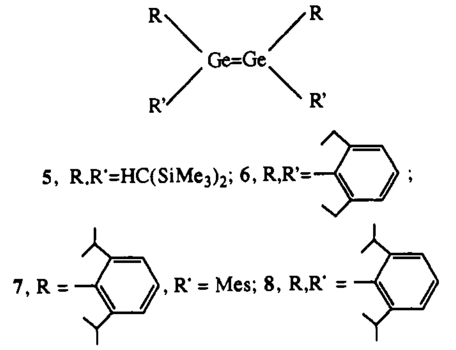
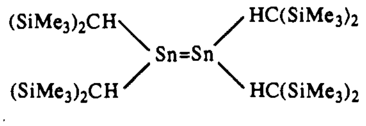


The parent digermene, $H_2Ge{=}GeH_2$, has been studied by several theoretical methods.[29c,33–38] The methods used included MNDO, RHF with pseudopotentials + DZ (and DZP) valence basis sets, all-electron DZ and DZP basis sets, and RHF plus CI with pseudopotentials + DZP valence basis set. The predicted Ge=Ge bond distances range from 2.259 to 2.325 Å, and the out-of-plane angle leading to a trans bent structure is predicted to be 34–40°. At the SCF with DZ basis set level of theory,[36] germylgermylene is predicted to be 9.5 kcal/mol more stable than digermene. However, when CI is used,[35] digermene is predicted to be 5 kcal/mol more stable than germylgermylene. Again, this suggests that as the level of theory is improved, the double-bond species will preferentially decrease in energy.

The only distannene isolated to date, **9**, is that synthesized by Lappert and co-workers.[29a,c,34,39] This molecule has been thoroughly identified through the use of X-ray diffraction and NMR studies. The X-ray structures show a Sn=Sn bond length of 2.768 Å, a twist angle of 0° about the bond, and an out-of-plane angle of 41°.



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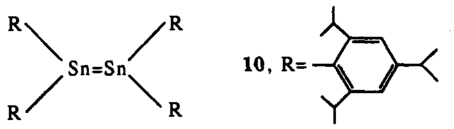
Another distannene (**10**) has been found to be stable in solution by Masamune and Sita.[40]



The parent distannene, $H_2Sn{=}SnH_2$, has been examined in several theoretical studies.[20,29c,34,37,38,41,42] The methods used included MNDO, RHF with pseudopotentials + DZ valence and all-electron DZ basis sets, MP2 with pseudopotentials + DZ valence basis set, and RHF plus CI with pseudopotentials + DZP valence basis set. These methods predict Sn=Sn bond distances ranging from 2.70 to 2.72 Å and an out-of-plane angle of 41–49°. Mārquez and co-workers[42] also predict stannylstannylene, SnH_3SnH, to be more stable than trans-bent $H_2Sn{=}SnH_2$ by 1.4 kcal/mol using energies at the two-reference single and double excitation CI (TRSDCI) level using pseudopotentials + DZP basis set.

Table I. MCSCF Natural Orbital Occupation Numbers for $H_2X{=}YH_2$

X	Y	σ	π	π^*	σ^*
C	C[a]	1.98	1.92	0.08	0.02
C	Si[a]	1.97	1.90	0.10	0.03
Ge	C	1.97	1.89	0.11	0.03
Si	Si[a]	1.98	1.84	0.16	0.02
Ge	Si	1.98	1.83	0.17	0.02
Ge	Ge	1.98	1.82	0.18	0.02
Sn	C	1.97	1.81	0.19	0.03
Sn	Si	1.98	1.79	0.21	0.02
Sn	Ge	1.98	1.80	0.20	0.02
Sn	Sn	1.98	1.78	0.22	0.02

[a] Reference 54.

No experimental or theoretical studies of germastannenes, $R_2Ge{=}SnR'_2$, have been reported to our knowledge.

Several methods have been used to determine π-bond strengths. One of these involves rotating one end of the molecule by 90°. Since this rotation breaks the π-bond, the π-bond strength, D_π, may be estimated as the energy difference between the rotated and the singlet ground-state forms. An alternative method for determining D_π involves using thermochemical cycles. One such method, presented by Schleyer and Kost,[43] uses isodesmic reactions and bond dissociation energies. All of these methods have been found to predict similar π-bond strengths for most compounds.[1,43,44] A different method based on hydrogenation will be used in this paper. Both the rotation and hydrogenation methods are described in further detail below. This paper is a continuation[1,44] of our interest in the structure, bonding, and π-bond strengths of unsaturated compounds containing group IV elements.

The remainder of this paper is organized in the following manner. The computational methods used are summarized in section II. Some preliminary considerations are discussed in section III. The results of the computations are presented in section IV. Section V contains a comprehensive discussion of the results, and the conclusions from this work are summarized in section VI.

II. Computational Methods

The 3-21G[45] basis set augmented by d functions on all heavy atoms is used throughout this work. The d polarization exponents used are C, 0.80; Si, 0.395; Ge, 0.246; and Sn, 0.183. Based on the level of agreement between experiment and theory in earlier work,[1] this basis set, together with methods that include electron correlation, should provide reliable structures. The tin isotope ^{120}Sn is used for all frequency calculations.

When planar or nearly planar π-bonded X=Y is rotated to a perpendicular form, the π-bond is broken and a biradical is produced, generally with singlet and triplet states that are very close in energy. A realistic[1,2] description of this rotational surface is provided by a four-electron, four-orbital full optimized reaction space (FORS)[46] MCSCF wavefunction. This wavefunction allows the four electrons in the X=Y bonds to be distributed in all possible ways among the σ, π, π^*, and σ^* orbitals and allows for breaking of the π-bond as well as correlation changes in the σ-bond due to its lengthening during the rotation. The resultant wavefunction consists of 20 electronic configurations. Geometry optimizations using analytical gradients and numerical energy second

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Table II. Primary Resonance Contributions from MC/LMO/CI for $H_2X{=}YH_2$[a]

config[b]	GeC	GeSi	GeGe	SnC	SnSi	SnGe	SnSn
$\|2020\rangle$	0.052	0.030	0.037	0.029	0.020	0.035	0.034
$\|1111\rangle$[c]	0.417	0.408	0.415	0.438	0.391	0.412	0.427
$\|0202\rangle$	0.049	0.040	0.037	0.040	0.030	0.030	0.034
$\|2110\rangle$	0.120	0.155	0.152	0.101	0.136	0.139	0.153
$\|1201\rangle$	0.062	0.061	0.053	0.046	0.038	0.040	0.044
$\|2200\rangle$	0.009	0.013	0.010	0.006	0.009	0.007	0.008
$\|0022\rangle$	0.023	0.010	0.010	0.016	0.008	0.010	0.008
$\|1021\rangle$	0.097	0.046	0.053	0.063	0.038	0.052	0.044
$\|0112\rangle$	0.171	0.141	0.152	0.188	0.134	0.158	0.153
neut[d]	0.518	0.478	0.489	0.507	0.441	0.477	0.495
elec[e]	0.191	0.229	0.215	0.153	0.183	0.186	0.205
nucl[f]	0.291	0.197	0.215	0.267	0.180	0.220	0.205
total[g]	1.000	0.904	0.919	0.927	0.804	0.883	0.905

[a] Values are the configuration coefficients squared. [b] Each configuration $|ijkl\rangle$ represents i electrons in a σ_X LMO, j electrons in a π_X LMO, k electrons in a π_Y LMO, and l electrons in a σ_Y LMO for an X=Y bond. [c] This configuration actually consists of two $|1111\rangle$ singlet configurations that differ in spin coupling. [d] Configurations $|2020\rangle + |1111\rangle + |0202\rangle$ correspond to a neutral charge distribution between center X and Y. [e] Configurations $|2110\rangle + |1201\rangle + |2200\rangle$ correspond to Y as an electrophilic center. [f] Configurations $|0022\rangle + |1021\rangle + |0112\rangle$ correspond to Y as a nucleophilic center. [g] Total of listed configurations.

derivative matrices at the optimized structures were calculated at the MCSCF level. Energies were determined using second-order CI (SOCI), in which all single and double excitations from the 20 MCSCF reference configurations into the MCSCF virtual orbitals are allowed.

The MC/LMO/CI analysis is used to gain qualitative understanding of the valence bond-like "resonance" structures (configurations) that contribute most to the wavefunction. This analysis has been described elsewhere,[44,46,47] so only a brief description of the three steps will be included here. The first step involves the MCSCF calculation described in the previous paragraph. In the second step, the MCSCF natural orbitals are localized using the technique developed by Pipek and Mezey.[48] In the final step, a CI calculation in C_1 symmetry using only the MCSCF active space is performed to generate all configurations that contribute to the double bond.

The MCSCF and SOCI calculations were performed using the Iowa State University version of the GAMESS[49] electronic structure package.

The thermochemical cycle, which will be discussed in more detail in section IV, requires the calculation of $H_2X{=}YH_2$ and H_3XYH_3 energies. Since these structures are closed shell, restricted SCF (RHF) and second-order Møller–Plesset perturbation theory (MP2)[50] wavefunctions were used to determine geometries and energy second derivatives. Final energies were determined at the full fourth-order Møller–Plesset perturbation theory level (MP4)[51] for all stationary points. Only the valence electrons (excluding inner ds for Ge and Sn) were correlated in the MP4 energy calculations. All calculations for this method were performed using the GAUSSIAN86[52] and GAUSSIAN88[53] programs.

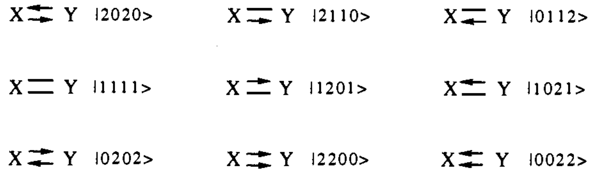

Figure 1. Primary resonance structures.

III. Preliminary Considerations

Before the details of the results are discussed, it is useful to consider some of the qualitative aspects of the π-bonds of these systems. The MCSCF natural orbital occupation numbers of the σ, π, π^*, and σ^* orbitals given in Table I provide some insight into the amount of biradical character in these molecules. The corresponding information for the C–C, C–Si, and Si–Si molecules are included for completeness. As will be discussed in section IV, the only π-bond structures that are planar are the C–C, C–Si, and C–Ge molecules. As may be seen in Table I, the σ and σ^* occupation numbers are nearly 2.0 and 0.0, respectively, so the σ-bond is well-described by a single configuration, Hartree–Fock wavefunction. There is more configurational mixing in the π space. In particular, the nonplanar molecules have a significantly higher π^* occupation number than the planar structures, suggesting that the nonplanar molecules have some biradical character.

The results of the MC/LMO/CI analysis are collected into Table II. The localization results in orbitals that resemble a p_z

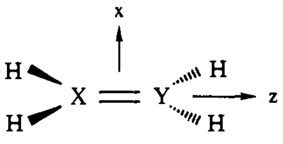

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Table III. Planar MCSCF Structures for XYH_4[a]

X	Y	X=Y	X-H	Y-H	X-Y-H	Y-X-H	H-X-H	H-Y-H	lowest frequency
Ge	C	1.814	1.536	1.076	121.4	122.9	114.3	117.2	266
Ge	Si	2.222	1.535	1.471	122.1	122.6	114.8	115.7	355*i*
Ge	Ge	2.270	1.534	1.534	122.4	122.4	115.3	115.3	390*i*
Sn	C	2.041	1.734	1.077	121.5	123.5	113.0	117.0	176*i*
Sn	Si	2.428	1.733	1.471	122.4	123.0	114.0	115.2	370*i*
Sn	Ge	2.466	1.732	1.536	122.7	123.0	114.1	114.7	390*i*
Sn	Sn	2.662	1.733	1.733	123.2	123.2	113.6	113.6	379*i*

[a] Bond lengths in angstroms and angles in degrees.

Table IV. MCSCF, RHF, and MP2 Structures for XYH_4[a]

X	Y	X=Y	X-H	Y-H	X-Y-H	Y-X-H	H-X-H	H-Y-H	X-Y-H-H	Y-X-H-H
Ge	C	1.814	1.536	1.076	121.4	122.9	114.3	117.2	0.0	0.0
		(1.761)	(1.536)	(1.077)	(121.9)	(123.1)	(113.8)	(116.3)	(0.0)	(0.0)
		[1.784]	[1.543]	[1.085]	[121.3]	[122.6]	[114.8]	[117.4]	[0.0]	[0.0]
Ge	Si	2.284	1.547	1.480	116.0	116.7	109.8	110.2	40.1	38.7
		(2.193)	(1.541)	(1.474)	(119.7)	(120.2)	(112.0)	(112.6)	(26.8)	(25.9)
		[2.208]	[1.550]	[1.484]	[118.0]	[118.4]	[111.6]	[112.3]	[32.4]	[32.1]
Ge	Ge	2.341	1.550	1.550	115.4	115.4	109.0	109.0	42.4	42.4
		(2.275)	(1.547)	(1.547)	(117.6)	(117.6)	(109.5)	(109.5)	(36.6)	(36.6)
		[2.270]	[1.554]	[1.554]	[116.9]	[116.9]	[110.4]	[110.4]	[37.5]	[37.5]
Sn	C	2.063	1.740	1.079	120.5	120.0	111.8	115.5	17.9	26.8
		(1.976)	(1.734)	(1.077)	(122.1)	(123.9)	(112.2)	(115.8)	(0.0)	(0.0)
		[2.007]	[1.741]	[1.085]	[121.5]	[123.3]	[113.4]	[117.1]	[0.0]	[0.0]
Sn	Si	2.511	1.749	1.482	114.5	115.9	107.7	108.4	44.7	42.2
		(2.436)	(1.747)	(1.481)	(116.5)	(118.9)	(107.8)	(108.9)	(39.9)	(34.9)
		[2.429]	[1.753]	[1.488]	[115.8]	[118.1]	[108.6]	[109.9]	[40.7]	[36.1]
Sn	Ge	2.555	1.752	1.554	114.1	115.3	107.4	107.5	46.3	43.7
		(2.504)	(1.751)	(1.555)	(114.8)	(117.6)	(106.0)	(106.8)	(45.3)	(39.7)
		[2.479]	[1.756]	[1.560]	[114.2]	[117.7]	[107.4]	[108.2]	[45.5]	[38.3]
Sn	Sn	2.769	1.754	1.754	114.1	114.1	106.2	106.2	47.1	47.1
		(2.728)	(1.756)	(1.756)	(115.4)	(115.4)	(104.7)	(104.7)	(45.4)	(45.4)
		[2.690]	[1.760]	[1.760]	[115.5]	[115.5]	[106.3]	[106.3]	[44.2]	[44.2]

[a] Bond lengths are in angstroms and angles in degrees. RHF structures are in parentheses. MP2 structures are in brackets.

(contributing to the σ-bond) and a p_y (contributing to the π-bond) on each end of the π-bond (referred to as σ_X, π_X, π_Y, and σ_Y, where X and Y are the heavy atoms in the molecule). Each configuration $|ijkl\rangle$ resulting from the CI represents i electrons in a σ_X LMO, j electrons in a π_X LMO, k electrons in a π_Y LMO, and l electrons in a σ_Y LMO. Only those configurations that are chemically sensible (i.e., configurations resulting in two electron bonds) are included in Table II, since the other contributions have vanishingly small coefficients. The following nomenclature is used in Figure 1. The lower line or arrow corresponds to the σ-bond, while the upper line or arrow corresponds to the π-bond. A line with no head means the bond is covalent, e.g., $|1jk1\rangle$ signifies a covalent σ-bond. An arrow (X→Y) signifies a dative bond in which X donates a pair of electrons to Y. In the case of $|1111\rangle$, there are two spin couplings which give a singlet state, so there are two such configurations. Figure 1 depicts the resonance structures that correlate with the major configurations with the $|2020\rangle$, $|1111\rangle$, and $|0202\rangle$ configurations (—, —, and —, respectively) representing a charge-balanced configuration, the $|2110\rangle$, $|1201\rangle$, and $|2200\rangle$ configurations (—, —, and —, respectively) representing an electrophilic Y, and the $|0112\rangle$, $|1021\rangle$, and $|0022\rangle$ configurations (—, —, and —, respectively) representing a nucleophilic Y.

The first noticeable trend in Table II is that the charge-balanced configurations (covalent, σ dative + π backbond, π dative + σ backbond) comprise the majority of the wavefunction for all species. Indeed, there are only minor variations in the contributions from the individual resonance structures, with the covalent contribution being approximately 50% in each case. This is qualitatively the same as the results obtained by Trinquier and Malrieu,[13c] who used their valence bond analysis. Also, as expected from electronegativity arguments, when carbon is part of the double bond, it is a nucleophilic center. The differences in the electrophilic contribution and the nucleophilic contribution for the other species are too small for any meaningful conclusions to be made. For most of the compounds, the configurations listed in Table II contribute 88% or more to the total wavefunction. The ten configurations omitted from Table II each contribute less than 5% to the total wavefunction in *all* cases. For H_2SnSiH_2, there are several of these excluded configurations that contribute approximately 5%. As a result, the primary configurations listed in Table II contribute only 80% to the total wavefunction.

IV. Results

Structures. Both planar and ground-state structures were examined for the XYH_4 species. The planar structures at the MCSCF/3-21G(d) level are given in Table III along with the lowest frequency associated with each species. The only planar structure that is a minimum on its surface is $GeCH_4$. It is particularly interesting that H_2SnCH_2 is not planar at the MCSCF level of computation. This is contrary to the SCF/3-21G(d) results of Dobbs and Hehre.[18] The imaginary frequency of the planar molecule is, however, only 176*i* (Table III), suggesting that the surface for this molecule is quite flat.

The fully optimized ground-state XYH_4 geometries at each level of theory are given in Table IV. It is interesting to note that the flap angles X-Y-H-H and Y-X-H-H are generally largest in the MCSCF geometry and smallest in the RHF geometry. Thus, RHF and MP2 predict $SnCH_4$ to be planar, whereas MCSCF predicts this compound to be trans bent. In general, the MP2 and RHF geometries agree to within 0.04 Å for bond lengths and 3° for bond angles. It is interesting that the MP2 X=Y distances are *not* consistently longer than those predicted at the RHF level. The predicted MCSCF X=Y bond lengths are generally longer than those predicted by either RHF or MP2. Also, the lengthening of R(X=Y) predicted by MCSCF upon relaxation of planarity is generally in the range of 0.07–0.10 Å. The difference in flap angles is less than 2.8° for all structures except for $GeSiH_4$, where the difference is 5.6° for GeSiHH and 6.2° for SiGeHH.

The geometries of the XYH_6 molecules at the RHF/3-21G(d) and MP2/3-21G(d) levels in the staggered configuration are given in Table V. Notice again that the RHF and MP2 geometries agree quite well: within 0.04 Å for bond lengths and 0.3° for angles. The major difference between the RHF and MP2 ge-

Table V. RHF and MP2 Structures for Staggered XYH_6[a]

X	Y	X-Y	X-H	Y-H	X-Y-H	Y-X-H	H-X-H	H-Y-H
Ge	C	1.976	1.551	1.087	110.5	110.4	108.5	108.5
		(1.966)	(1.556)	(1.092)	(110.2)	(110.5)	(108.4)	(108.7)
Ge	Si	2.400	1.550	1.481	110.2	110.5	108.4	108.7
		(2.374)	(1.555)	(1.488)	(110.2)	(110.6)	(108.4)	(108.8)
Ge	Ge	2.443	1.550	1.550	110.3	110.3	108.6	108.6
		(2.415)	(1.555)	(1.555)	(110.3)	(110.3)	(108.6)	(108.6)
Sn	C	2.188	1.750	1.087	110.5	110.3	108.6	108.4
		(2.178)	(1.756)	(1.092)	(110.3)	(110.4)	(108.5)	(108.6)
Sn	Si	2.610	1.748	1.481	110.4	110.5	108.4	108.5
		(2.585)	(1.754)	(1.488)	(110.4)	(110.5)	(108.4)	(108.6)
Sn	Ge	2.642	1.748	1.550	110.6	110.3	108.6	108.4
		(2.611)	(1.753)	(1.556)	(110.7)	(110.4)	(108.5)	(108.3)
Sn	Sn	2.845	1.748	1.748	110.6	110.6	108.3	108.3
		(2.813)	(1.754)	(1.754)	(110.7)	(110.7)	(108.2)	(108.2)

[a] Bond lengths are in angstroms and angles in degrees. MP2 structures are in parentheses.

Table VI. MCSCF, RHF, MP2, and Experimental X-Y Double and Single Bond Lengths in angstroms[a]

		X=Y		X-Y	
X	Y	theor	exptl	theor	exptl
Ge	C	1.814	1.80[b]		
		(1.761)	1.827[c]	(1.976)	1.945[h]
		[1.784]		[1.966]	
Ge	Si	2.284			
		(2.193)		(2.400)	2.357[i]
		[2.208]		[2.374]	
Ge	Ge	2.341	2.347[d]		
		(2.275)	2.213[e]	(2.443)	2.41[j]
		[2.270]		[2.415]	
Sn	C	2.063	2.025[f]		
		(1.976)		(2.188)	2.143[k]
		[2.007]		[2.178]	
Sn	Si	2.511			
		(2.436)		(2.188)	
		[2.429]		[2.585]	
Sn	Ge	2.555			
		(2.504)		(2.642)	
		[2.479]		[2.611]	
Sn	Sn	2.769	2.768[g]		
		(2.728)		(2.845)	2.823[l]
		[2.690]		[2.813]	

[a] RHF lengths are in parentheses. MP2 lengths are in brackets. [b] From **2**.[8] [c] From **1**[7] and **3**.[15] [d] From **5**.[29a] [e] From **6**.[30a] [f] From **4**.[7b] [g] From **8**.[29a] [h] From $GeCH_6$.[55] [i] From $GeSiH_6$.[56] [j] From Ge_2H_6.[57] [k] From $SnCH_6$.[58] [l] From Bz_6Sn_2.[59]

Table VII. RHF, MP2, MCSCF, and Experimental Frequencies (cm^{-1}) for X-Y Double and Single Bond Structures

	RHF	MP2	MCSCF	exptl
C-C	1046			995[a]
C=C	1853			1623[a]
Si-C	736			700[a]
Si=C	1080			985[b]
Si-Si	466			432[c]
Si=Si	653			630[d]
Ge-C	613	609		
Ge=C	904	827	785	988[e]
Ge-Si	377	379		320[f]
Ge=Si	526	497	371	
Ge-Ge	282	286		275[g]
Ge=Ge	272	311	285	404[g]
Sn-C	552	546		527[h]
Sn=C	755	737	660	
Sn-Si	323	324		
Sn=Si	295	378	314	
Sn-Ge	234	237		
Sn=Ge	222	259	233	
Sn-Sn	189	192		119[i]
Sn=Sn	172	204	184	

[a] From C_2H_6, C_2H_4, and $SiCH_6$.[60] [b] From $SiCH_6$.[61] [c] From Si_2H_6.[62] [d] From $Si_2(CH_3)_4$.[63] [e] From **2**.[8b] [f] From $GeSiH_6$.[64] [g] From $Ge_2(CH_3)_6$ and $Ge_2(CH_3)_4$.[28b] [h] From $SnCH_6$.[65] [i] From $I(tBu_2Sn)_4I$.[66]

ometries is the X-Y bond length, all other parameters being essentially the same for the two methods. Also, it is interesting to note that the X-Y-H and Y-X-H angles are approximately 110° for all X and Y. Likewise, the H-X-H and H-Y-H angles are all approximately 108°.

For ease of comparison, the double bond and single bond lengths for each X-Y are collected into Table VI. Known experimental values are also given in this table. The experimental bond lengths for the single bond structures are quoted for the fully hydrogenated compound, except for that of Sn-Sn, and are therefore directly comparable with experiment. The experimental bond lengths for compounds containing double bonds are those discussed in the Introduction.

The four experimental single bond distances are within 0.035 Å of the MP2/3-21G(d) values. The MP2 distances are consistently too long, suggesting that larger basis sets are needed to bring the theoretical values into closer agreement with experiment. The exception here is for the Sn-Sn bond, where the experimental value is from a substituted system.

For the double bond structures, the RHF distances, as expected, are shorter than experiment, varying from 0.04 to 0.07 Å from the first listed experimental values. In each case, the first experimental value quoted is the one that is least hindered by bulky substituents. However, where possible, a second experimental value is listed to illustrate the rather large variability that can occur in the bond length with change in substituents. Surprisingly, even the MP2 bond lengths are shorter than the experimental values. The error varies from 0.02 to 0.08 Å. The MCSCF values are within 0.04 Å, with the theoretical values being longer except in $GeCH_4$.

Generally, the calculated X=Y bond lengths are 0.12–0.21 Å shorter than the corresponding X-Y bond lengths. This difference tends to decrease as the participating group IVA elements become heavier, suggesting a weaker π interaction for those elements.

Frequencies. The frequencies for the X-Y stretches are listed in Table VII at all three theoretical levels. The values for C-C, Si-C, and Si-Si single and double bond structures are from ref 1. Also, experimental values are given when possible. It should be noted that several of the heavy atom (X = Ge or Sn) experimental frequencies are from heavily substituted molecules.

Note that four of the systems, Ge-Ge, Sn-Si, Sn-Ge, and Sn-Sn, have larger frequencies for the single bond structures than for the double bond structures at the RHF level. Comparison with the MP2 frequencies show that the double bond frequencies at the RHF level are significantly lower than the MP2 frequencies for these four species, whereas the single bond frequencies are nearly identical. This suggests that RHF frequencies for these four double bond species are unreliable.

The MP2 and MCSCF frequencies follow the generally expected trend. The heavier the elements involved in the X-Y stretch, the lower the associated stretching frequency. As an example, consider the sequence of the single bond stretches for the Ge-Y molecules at the MP2/3-21G(d) level: Ge-C (609 cm^{-1}) > Ge-Si (379 cm^{-1}) > Ge-Ge (286 cm^{-1}) > Ge-Sn (237 cm^{-1}).

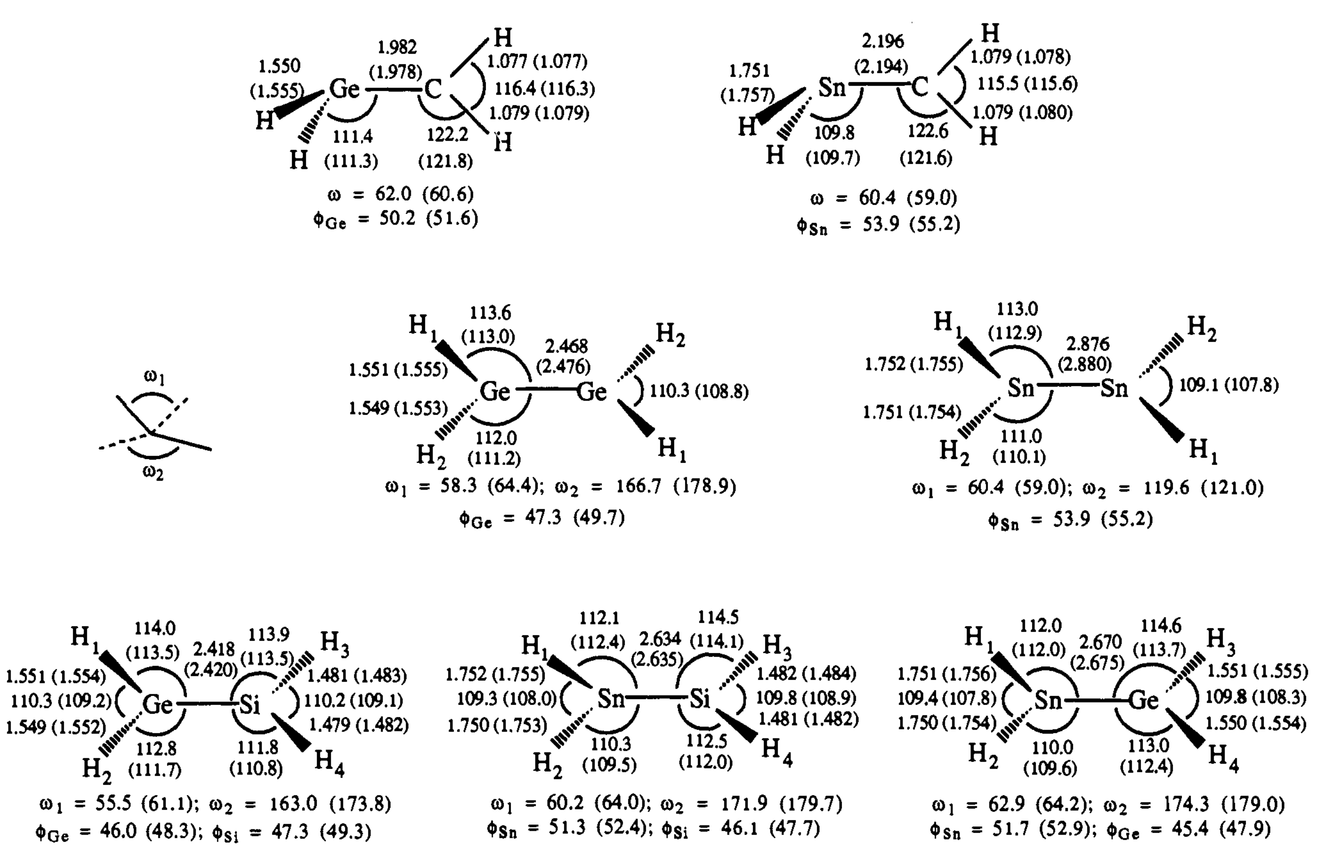
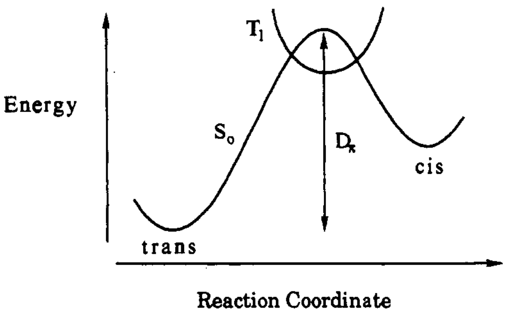


Figure 2. Twisted singlet and triplet structures. Bond lengths are in angstroms, and angles are in degrees. Triplet values are given in parentheses. ω is the dihedral angle HXYH, and ϕ_Y is the flap angle between bond XY and the plane YH_2 at pyramidal atom Y.

The experimentally known frequencies for the heavy atom single bond structures are lower than the MP2 frequencies by an amount ranging from 11 to 73 cm^{-1}. The two experimentally known frequencies for the heavy atom double bond structures are both larger than the MP2 frequencies, by 93 cm^{-1} for Ge=Ge and 161 cm^{-1} for Ge=C. This is reasonable agreement for the level of theory being used; however, larger basis sets would probably improve these results.

Torsional Barriers. This method of determining the π-bond strength involves the twisting of one end of the molecule by 90° to break the π-bond. The energy required to reach the perpendicular singlet transition state from the ground state is considered to be the energy D_π for breaking the π-bond. Of course, this is an approximation, because other factors are also involved, such as lengthening of the X-Y σ-bond. However, the D_π obtained in this manner corresponds to the most common experimental method for determining D_π. The triplet twisted biradical is a minimum on its surface, and its energy tends to be lower than that of the singlet. This leads to the following qualitative energy diagram.



Since the singlet and triplet twisted structures tend to have similar geometries, an efficient method for finding the singlet structure is to optimize the triplet structure and then perform the saddle point search for the singlet starting from the triplet geometry.

The structures of the singlet and triplet twisted molecules are given in Figure 2. The difference between the singlet and triplet geometries is small, differing by less than 0.01 Å for bond lengths and 2° for angles. The other structures required to evaluate the rotation barrier have already been given in Tables III and IV. Generally, the X-Y bond lengths in the twisted structures are similar to the single bond lengths listed in Table VI.

MCSCF and SOCI total energies of these molecules are given in Table VIII, and the relative energies are given in Table IX. As mentioned earlier, the $SnCH_4$ is rather floppy, requiring only 0.6 kcal/mol to become planar. The other molecules require 3.5–8.7 kcal/mol to make them planar.

Table IX also shows that the π-bond strengths (singlet excited-state energy relative to the ground-state energy) decrease in the following order: Ge–C > Ge–Si ~ Ge–Ge > Sn–C ~ Sn–Si ~ Sn–Ge > Sn–Sn. However, it should be noted that the last four species differ by only 2 kcal/mol. This general trend parallels that noted earlier for X=Y vs X-Y bond lengths.

In general, the twisted triplet minimum is, as expected, 2–3 kcal/mol lower in energy than the twisted singlet transition state. Contrary to the earlier MNDO predictions,[21] singlet stannene is predicted to be 19.1 kcal/mol *lower* in energy than the lowest triplet state.

Hydrogenation Reactions. An alternative method for determining D_π involves using the following thermochemical cycle:

$H_3X{-}YH_3$	→	$H_2\dot{X}{-}YH_3 + \dot{H}$	$D(X{-}H)$
$H_2\dot{X}{-}YH_3$	→	$H_2\dot{X}{-}\dot{Y}H_2 + \dot{H}$	$D(Y{-}H)$
$H_2\dot{X}{-}\dot{Y}H_2$	→	$H_2X{=}YH_2$	$-D\pi$
$2\dot{H}$	→	H_2	$-D(H{-}H)$
$H_3X{-}YH_3$	→	$H_2X{=}YH_2 + H_2$	$\Delta H°(0\ K)$

This allows D_π to be calculated by the equation

$$D_\pi = D(X{-}H) + D(Y{-}H) - D(H{-}H) - \Delta H°(0\ K) \quad (1)$$

$D(H{-}H)$ is known to be 103.3 kcal/mol.[67] With the exception

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(67) Huber, K. P.; Herzberg, G. *Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979.

Table VIII. Total Energies (hartrees) at the MCSCF/3-21G(d) Geometries[a]

molecule	ZPE MCSCF	total energies MCSCF	total energies SOCI
$H_2Ge{=}CH_2$			
gs	0.04022	−2105.50258	−2105.53125
sing	0.03779	−2105.44849	−2105.47745
trip	0.03840	−2105.45118	−2105.48065
$H_2Ge{=}SiH_2$			
gs	0.03171	−2355.28861	−2355.32016
pl	0.03109	−2355.28359	−2355.31395
sing	0.03094	−2355.24963	−2355.27847
trip	0.03157	−2355.25352	−2355.28317
$H_2Ge{=}GeH_2$			
gs	0.03018	−4133.34776	−4133.37773
pl	0.02967	−4133.34019	−4133.36878
sing	0.02913	−4133.30825	−4133.33618
trip	0.03017	−4133.31251	−4133.34132
$H_2Sn{=}CH_2$			
gs	0.03743	−6036.71807	−6036.74488
pl	0.03704	−6036.71752	−6036.74350
sing	0.03560	−6036.68273	−6036.70980
trip	0.03606	−6036.68570	−6036.71313
$H_2Sn{=}SiH_2$			
gs	0.02949	−6286.51939	−6286.54903
pl	0.02889	−6286.51152	−6286.53946
sing	0.02859	−6286.48710	−6286.51382
trip	0.02970	−6286.49117	−6286.51865
$H_2Sn{=}GeH_2$			
gs	0.02800	−8064.58155	−8064.60967
pl	0.02753	−8064.57140	−8064.59818
sing	0.02709	−8064.54789	−8064.57428
trip	0.02758	−8064.55223	−8064.57941
$H_2Sn{=}SnH_2$			
gs	0.02595	−11995.81786	−11995.84499
pl	0.02555	−11995.80578	−11995.83066
sing	0.02518	−11995.78815	−11995.81274
trip	0.02558	−11995.79257	−11995.81804

[a] gs = equilibrium ground-state structure; pl = planar structure; sing = singlet twisted structure; trip = triplet twisted structure.

Table IX. Relative Energies (kcal/mol) Using 3-21G(d) Basis Set[a]

molecule	relative enthalpies MCSCF	relative enthalpies SOCI
$H_2Ge{=}CH_2$		
gs	0.0	0.0
sing	32.4	32.2
trip	30.7	30.2
$H_2Ge{=}SiH_2$		
gs	0.0	0.0
pl	2.8	3.5
sing	24.0	25.7
trip	21.9	23.1
$H_2Ge{=}GeH_2$		
gs	0.0	0.0
pl	4.4	5.3
sing	24.1	25.4
trip	22.1	22.8
$H_2Sn{=}CH_2$		
gs	0.0	0.0
pl	0.1	0.6
sing	21.0	20.9
trip	19.5	19.1
$H_2Sn{=}SiH_2$		
gs	0.0	0.0
pl	4.6	5.6
sing	19.7	21.5
trip	17.8	19.2
$H_2Sn{=}GeH_2$		
gs	0.0	0.0
pl	6.1	6.9
sing	20.5	21.6
trip	18.1	18.7
$H_2Sn{=}SnH_2$		
gs	0.0	0.0
pl	7.3	8.7
sing	18.1	19.7
trip	15.6	16.7

[a] gs = equilibrium ground-state structure; pl = planar structure; sing = singlet twisted structure; trip = triplet twisted structure.

of D(Ge–H) in $CGeH_6$, the experimental values of D(X–H) and D(Y–H) are, unfortunately, not available for the compounds of interest. Therefore, estimates of the bond dissociation energies must be used instead. The values of the bond dissociation energies used for this paper can be found in the Appendix.

D_π could be determined entirely by experiment if the ΔH°(0 K) were known experimentally. Unfortunately, this is not the case, so computed values will be used in this paper. Combining experimental D(X–H) and D(H–H) with computed ΔH° affords a semitheoretical estimate of D_π from eq 1.

All of the necessary structures are given in Tables IV and V. The total energies along with the zero-point energies (ZPE) are given in Table X. RHF, MP2, and MP4 energies are given at both the RHF and MP2 geometries. The ΔH° values, which are determined by combining the MP4/3-21G(d)//MP2/3-21G(d) energies and the ZPEs from the MP2/3-21G(d) geometries, are given in Table XI. Also shown in this table are the D(X–H), the D(Y–H), and the calculated D_π values.

V. Discussion

The D_π energies from both methods are gathered into Table XII. Other theoretical values and two experimental values are also included for comparison. The thermochemical and rotational results from this work are in quite good agreement. The difference between the π-bond strengths obtained from the two methods is less than 1 kcal/mol in all cases except those of Ge–Ge (a difference of 2.6 kcal/mol) and Ge–Sn (a difference of 1.4 kcal/mol). This excellent agreement between the two methods is gratifying and lends some credibility to the calculated π-bond strengths. In addition, the agreement suggests that the configurational mixing presented in Table I does not have a significant effect on the thermochemical π-bond energies.

The calculated π-bond strengths presented in this work are in good agreement with the other theoretical values. The only exception to this is the value of the Ge–C π-bond energy of 26.9 kcal/mol obtained by Trinquier and co-workers.[17b] These workers used an SCF wavefunction to obtain geometries and CI energies. As mentioned earlier, the biradical nature of the excited singlet and triplet states require the use of MCSCF wavefunctions. This is believed to be the main cause of the discrepancy between their results and the results of this work.

The π-bond energies estimated from experiment are in disagreement with the rotationally determined values by 3.2 kcal/mol for Ge–Ge, 11 kcal/mol for Ge–C, and 24 kcal/mol for Sn–C. Part of the discrepancy for the last two experimental values could arise from the methyl substituents on the Ge and the Sn in the experimentally measured compounds. However, the experimentally determined numbers were, as noted by the authors, not consistent with the π-bond strengths in silicon compounds. The authors also comment that the values were not reliable as they were based on thermochemical data that was subject to large errors. It is likely that the calculated π-bond energies reported here are more accurate.

The data from Table XII also shows that Sn forms much weaker π-bonds than does Ge. This follows the generally accepted order of C > Si ~ Ge > Sn in effectiveness of forming π-bonds. Also of interest is the fact that the Sn molecules all have π-bond energies within 2 kcal/mol of each other. This reflects the in-

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(68) Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 4329–4332.

Table X. Energies (hartrees) at the RHF and MP2 Optimized Structures with Energies from the MP2 Structures in Parentheses

		total energies		
molecule	ZPE	RHF	MP2	MP4
$GeCH_6$	0.062 75	−2106.678 74	−2106.891 64	−2106.931 80
	(0.060 94)	(−2106.678 63)	(−2106.891 74)	(−2106.932 00)
$GeCH_4$	0.041 39	−2105.448 80	−2105.662 79	−2105.699 59
	(0.039 49)	(−2105.448 31)	(−2105.663 44)	(−2105.700 65)
$GeSiH_6$	0.050 58	−2356.464 29	−2356.628 65	−2356.673 24
	(0.048 97)	(−2356.464 08)	(−2356.628 76)	(−2356.673 46)
$GeSiH_4$	0.032 08	−2355.248 11	−2355.414 40	−2355.456 80
	(0.030 92)	(−2355.247 81)	(−2355.414 80)	(−2355.457 69)
Ge_2H_6	0.048 35	−4134.513 28	−4134.675 67	−4134.720 03
	(0.046 78)	(−4134.513 06)	(−4134.675 72)	(−4134.720 16)
Ge_2H_4	0.030 37	−4133.307 37	−4133.471 37	−4133.513 64
	(0.029 37)	(−4133.307 23)	(−4133.471 49)	(−4133.513 86)
$SnCH_6$	0.058 92	−6037.897 77	−6038.100 44	−6038.140 16
	(0.057 15)	(−6037.897 67)	(−6038.100 52)	(−6038.140 34)
$SnCH_4$	0.038 39	−6036.657 72	−6036.866 74	−6036.903 82
	(0.036 62)	(−6036.657 08)	(−6036.867 64)	(−6036.905 22)
$SnSiH_6$	0.047 18	−6287.687 47	−6287.840 71	−6287.884 98
	(0.045 61)	(−6287.687 28)	(−6287.840 80)	(−6287.885 18)
$SnSiH_4$	0.029 68	−6286.478 10	−6286.634 38	−6286.677 59
	(0.028 72)	(−6286.477 94)	(−6286.634 49)	(−6286.677 81)
$SnGeH_6$	0.044 97	−8065.738 81	−8065.890 31	−8065.934 37
	(0.043 44)	(−8065.738 59)	(−8065.890 34)	(−8065.934 50)
$SnGeH_4$	0.027 99	−8064.542 23	−8064.695 44	−8064.738 03
	(0.027 17)	(−8064.542 02)	(−8064.695 49)	(−8064.737 97)
Sn_2H_6	0.041 74	−11 996.965 98	−11 997.106 25	−11 997.150 05
	(0.040 23)	(−11 996.965 77)	(−11 997.106 26)	(−11 997.150 16)
Sn_2H_4	0.025 84	−11 995.780 69	−11 995.922 23	−11 995.964 88
	(0.025 11)	(−11 995.780 41)	(−11 995.922 30)	(−11 995.964 83)

Table XI. Thermochemical D_π for XYH_4[a]

X	Y	$\Delta H°$	D(X–H)	D(Y–H)	D_π
Ge	C	45.9	83	99	33
Ge	Si	38.3	82	86	26
Ge	Ge	32.7	82	82	28
Sn	C	48.9	74	99	21
Sn	Si	33.7	72	86	21
Sn	Ge	27.3	72	82	23
Sn	Sn	21.0	72	72	20

[a] Energies in kcal/mol.

Table XII. XYH_4 π-Bond Strengths[a]

X	Y	thermo cycle	rotation	other theor	exptl
Ge	C	33	32.2	31,[b] 26.9[c]	43[d]
Ge	Si	26	25.7	25[b]	
Ge	Ge	28	25.4	25[e]	22.2[f]
Sn	C	21	20.9	19[b]	45[d]
Sn	Si	21	21.5		
Sn	Ge	23	21.6		
Sn	Sn	20	19.7		

[a] Energies in kcal/mol. [b] Reference 18. [c] Reference 17b. [d] Reference 68. [e] Reference 24. [f] Reference 31.

efficiency of Sn in forming π-bonds, even with "good" π-bonding atoms such as carbon.

Another way to judge the π-bond capability of an atom is to define the π-bonding energy of atom X as

$$E_\pi(X) = (\tfrac{1}{2})D_\pi(X{=}X)$$

Using the D_π values from calculated rotation barriers and listed in Table XI, one obtains E_π of 12.7 kcal/mol for Ge and 9.9 kcal/mol for Sn. E_π for C and Si have previously been reported to be 32.5 and 12.5 kcal/mol, respectively.[1] For mixed bonds X=Y, one can evaluate which of the two atoms (X or Y) dominates the π-bond by using

$$E_\pi(X) = D_\pi(X{=}Y) - E_\pi(Y)$$

Averaging over the two different values (Y = Ge and Sn) gives 15.3 and 12.3 kcal/mol for C and Si, respectively. This again agrees with the order of C > Si ~ Ge > Sn. Note that while E_π(Si) is unchanged, E_π(C) is much lower than that reported by Schmidt and co-workers,[1] again reflecting the ineffectiveness of the heavier atoms to form π-bonds. This supports the notion expressed by others.[69]

VI. Conclusions

The results from this work show that the order of ability to form π-bonds is C > Si ~ Ge > Sn. Sn in particular seems to form compounds of approximately the same π-bond strength independent of the group IVA element to which it is bonded.

Interestingly, compounds containing Ge–Ge double bonds have been synthesized but compounds containing Ge–Si double bonds have not, even though these two are predicted to have approximately the same π-bond strength. The same can be said about the known Sn=Sn compounds and their as yet experimentally unknown Sn=Ge and Sn=Si analogues. This work suggests that the experimentally unknown compounds should be thermodynamically stable. All five of the aforementioned π-bonds have similar amounts of π diradical character (see Table I). At least by this measure, their kinetic stability should be similar as well, so the eventual synthesis of Ge=Si, Sn=Ge, and Sn=Si π-bond-containing compounds does not seem to be out of the question, unless these compounds are highly unstable to isomerizations.

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VII. Appendix

Only one of the necessary experimental D(A–H) BDEs is known. Therefore, the rest of the BDEs were estimated by finding the closest analogue to the system of interest and using that BDE for the calculations. This, of course, can be a major source of

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(69) Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 272–295.

error. The following gives the choices made for the BDEs.

CH. The CH BDEs of several molecules have been determined.[70] However, $Me_3Si{-}CH_3$[71] (BDE of 99.2 kcal/mol) is the most similar to the present systems. Therefore, the value of 99 kcal/mol is used for all CH BDEs.

SiH. The closest analogue to the systems of interest is the $H_3Si{-}SiH_3$ molecule, which has a BDE of 86.3 kcal/mol.[71] The value of 86 kcal/mol is used for all SiH BDEs.

GeH. The BDE of Ge–H for CH_3GeH_3 is 83 kcal/mol.[72] The BDE for GeH_4 is given as 84[73] and 89[72] kcal/mol by different experimental researchers. Also, a theoretical value of 84.8 kcal/mol has been determined by Binning and Curtiss.[74] The BDE for Me_3GeH has been determined to be 82 kcal/mol. The value of 82 kcal/mol is chosen for all Ge–H BDEs except for that of CH_3GeH_3, since the electronegativity of Si, Ge, and Sn should have similar effects as that of the bulky methyl groups of Me_3GeH.

SnH. The BDE of SnH_4 is 71.6 kcal/mol.[75] The value for $Me_3Sn{-}H$[76,77] and $Bu_3Sn{-}H$[78] is 74 kcal/mol. Therefore, the value of 74 kcal/mol is used for all Sn–H BDEs.

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Conformers of Gaseous Glycine

Attila G. Császár

Contribution from the Department of Theoretical Chemistry, Eötvös Loránd University, P.O. Box 32, H-1518 Budapest, Hungary. *Received May 11, 1992*

Abstract: Correlated level ab initio calculations (large basis set MP2, and MP4, CCSD, and CCSD(T) computations) have been performed for 13 conformers of neutral glycine, including all 8 possible conformers with planar heavy-atom arrangements. These calculations resulted in accurate geometric structures, relative energies, harmonic vibrational frequencies, and infrared intensities for all conformers. The structural results obtained support the rotational constants measured for the two lowest-energy forms of glycine, and their high accuracy should be profitable in the search for other conformers by rotational spectroscopy. Energetic, structural, and quadratic force field results indicate possible model improvements for an existing gas-phase electron-diffraction study of the lowest-energy conformer. Predictions, probably accurate to within about 100 cm^{-1}, are made for the order and relative energy of all conformers considered.

Introduction

The simplest amino acid, glycine, H_2NCH_2COOH, has three internal rotational degrees of freedom (ϕ, ψ, and θ, associated with bonds C–N, C–C, and C–O, respectively) in its neutral state, which leads to eight rotational isomers of C_s symmetry (see conformers Ip–VIIIp in Figure 1, where p refers to planar heavy-atom arrangement). In several of these rotamers intramolecular H-bonds, of different strengths, are formed stabilizing that particular form. On the other hand, steric strain and repulsion of lone electron pairs on the N and O atoms in some of the planar forms have a destabilizing effect that can be decreased by small torsional changes; thus, some planar forms might not correspond to local energy minima on the potential energy surface of glycine but rather to saddle points. As a result, rotational isomers of C_1 symmetry should also be considered in a conformational study of glycine (these are designated with the letter n, referring to nonplanar heavy-atom arrangement, in Figure 1). These conformational changes, resulting from the balance of steric and H-bond effects, are expected to be accompanied by very small changes in the total energy of the system. Indeed, theoretical calculations performed by Schäfer,[1-4] Pople,[5] and others[6-12] all indicate that several glycine isomers have relative energies less than 1000 cm^{-1} (the height of the rotational barrier of ethane) and that nonplanar forms are more stable for some low-energy isomers (specifically, for II and III of Figure 1) than the respective planar forms.

It is not surprising that prediction and/or reproduction of these small energy differences pose(s) a serious challenge to computational chemistry. In their comparative study using classical, semiempirical (extended Hückel, PCILO, CNDO), and non-empirical (STO-3G SCF) methods to map the rotational energy surface of glycine Palla et al.[7a] conclude that "if one compares numerical values of the relative depth of the potential holes and of the rotational barriers [of glycine], the accordance among the various methods vanishes almost completely". In a recent study

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