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Nonclassical Double Bonds in Ethylene Analogues: Influence of Pauli Repulsion on Trans Bending and π -Bond Strength. A Density Functional Study

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Abstract: The electronic and molecular structures of $H_2X=XH_2$ and $H_2C=XH_2$ systems for $X = C, Si, Ge, Sn, Pb$ have been studied by theoretical calculations. The calculations were based on approximate density functional theory within the local density approximation and augmented by nonlocal exchange and correlation corrections. A detailed bond analysis was performed, from which values for several intrinsic bond strengths have been extracted. The singlet-triplet splitting energies for XH_2 systems have been calculated in order to obtain accurate values for the preparation energy. The structures and bond energies are compared with the results for H_3X-XH_3 and H_3C-XH_3 systems. The peculiarities for the heavier homologues of ethylene, the trans-bent geometries and the essentially weak bond energy, are shown to be the consequences of enhanced interatomic as well as intraatomic Pauli repulsion.

1. Introduction

The ability of carbon to form multiple bonds with itself and other first row elements adds much to the richness and diversity of organic chemistry. Researchers tried for a long time to look for a similar diversity among other elements, and the quest for multiple bonds involving heavier main-group elements began early in this century.¹ However, the first attempts to synthesize compounds containing double-bonded silicon proved unsuccessful, leading to cyclic oligomers^{1b} and polymers^{1c} instead. On the theoretical side, Pitzer² and Mulliken³ were first to rationalize the weakness of multiple links involving heavier main-group

elements. It is interesting to note that Pitzer had already realized the importance of the inner-shell electrons for the chemical bonding of heavier elements. He pointed out that the so-called "inner-shell repulsion" between valence electrons of one atom and core electrons of its partner plays an important role in the equilibrium and stability of bonds formed by second and higher row atoms. Using overlap integrals as an index for bond strengths, Mulliken³ calculated that, on going from first row to higher row elements, the σ_{pp} interaction is getting stronger, whereas the π_{pp} bond strength decreases. These theoretical works, together with the experimental failures to form such multiple bonds, were brought to conclusion in the so-called "classical double bond rule" which states that elements having a principal quantum number greater than 2 should not be able to form π_{pp} bonds among themselves or with other elements.⁴ For the case of ethylene derivatives involving one or two heavier group 14 members, it became evident in the late 1960s and early 1970s that transient

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(2) Pitzer, K. S. *J. Am. Chem. Soc.* **1948**, 70, 2140.
(3) (a) Mulliken, R. S. *J. Am. Chem. Soc.* **1950**, 72, 4493. (b) Mulliken, R. S. *J. Am. Chem. Soc.* **1955**, 77, 884.

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species containing Si=C⁵ and Si=Si⁶ double bonds do indeed exist. It was about 10 years later, in 1981, that the isolation of stable compounds containing Si=C⁷ and Si=Si⁸ links completely overturned the classical double bond rule.

A lot of research interest was stimulated by the discovery of this new kind of double bonds, and, up to now, the structures of two silaethylenes, R₂Si=CR₂,⁹ five disilenes R₂Si=SiR₂,¹⁰ three germaethylenes, R₂Ge=CR₂,¹¹ three digermenes, R₂Ge=GeR₂,^{12,13} one stannaethylene, R₂Sn=CR₂,¹⁴ and one distannene, R₂Sn=SnR₂,¹² have been established by means of X-ray crystallography. The synthetic strategy toward all of these compounds involves the use of large, bulky substituents, for steric as well as electronic stabilization. Also recently, the first relatively stable gemasilene, R₂Ge=SiR₂,¹⁵ was reported. The parent-compounds XYH₄ are known as transient species for the silicon systems. Silaethylene, CSiH₄, has been trapped in argon matrices at 10 K and studied by vibrational spectroscopy.¹⁶ Disilene, Si₂H₄, prepared *in situ* by reaction of F atoms with Si₂H₆, has been studied by photoionization mass spectrometry.¹⁷

For the case of the disilenes, one finds a shortened Si=Si bond distance between 214 and 216 pm compared to known unstrained Si—Si single bonds (ca. 235 pm). All these compounds generally possess planar coordination around the silicon centers with a small or zero twist angle around the Si—Si bond. Only one of the disilenes,^{10a} Mes₂Si=SiMes₂ (Mes = 2,4,6-trimethylphenyl), exhibits a sizable fold angle around 10° and adapts a trans-bent structure with C_{2h} symmetry (Figure 1).

On going to the digermene and distannene compounds, the trans bending becomes more pronounced. R₂Ge=GeR₂ derivatives possess folding angles Φ , as defined in Figure 1, ranging from 12° to 32°; the distannene is trans-bent by 41°. It is remarkable that the experimental bond length of the distannene, 277 pm, comes close to a Sn—Sn single bond length (ca. 280 pm). The bond lengths of the digermenes range from 221 to 236 pm. A correspondence between folding angle and bond length is apparent; an increase in the degree of trans bending leads to

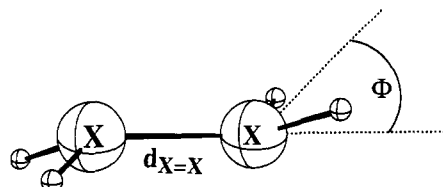


Figure 1. Trans-bent geometry of heavier ethylene homologues. Important structural parameters are the X—X bond length d_{X-X} as well as the fold or flap angle Φ .

an elongation of the Ge=Ge bond length. It should be noted that Lappert's distannene Sn₂[CH(SiMe₃)₂]₄, as well as the isostructural digermene Ge₂[CH(SiMe₃)₂]₄, exists as a dimer only in the crystalline form and dissociates to the corresponding monomeric unit in solution.^{12b} The existence of a corresponding plumblylene Pb[CH(SiMe₃)₂]₂ has also been established,^{12b} but no dimerization product has been observed.

For the mixed compounds, we find both planar and trans-bent structures. Silaethylene derivatives⁹ are generally planar around the silicon and carbon centers and typically possess nontwisted bonds with lengths of about 172 pm. The stannaethylene compound¹⁴ possesses nonplanar local structures around the tin and carbon centers with dihedrals of 5° and 16°, respectively. The Sn=C bond length was determined to be 203 pm with a twist angle of 61° around the bond. In between these two types of structures, we find the germaethylene derivatives as trans-bent molecules^{11a} with a bond length of 183 pm and a twist angle of 36° as well as planar units^{11b} with a C=Ge bond length of 180 pm and a slight twist by 6°. We refer the reader to several review articles on the subject of double bonding in heavier group 14 elements¹⁸ for further, more detailed information.

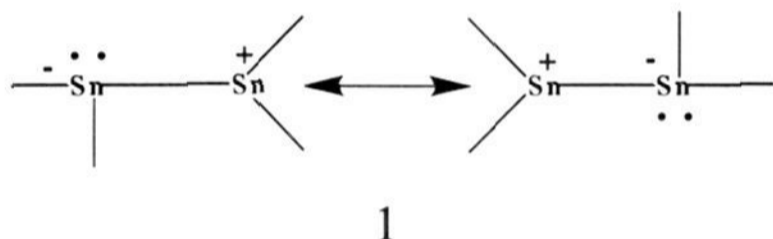
Various computational studies on different levels of theory have been performed for all parent molecules of the heavier

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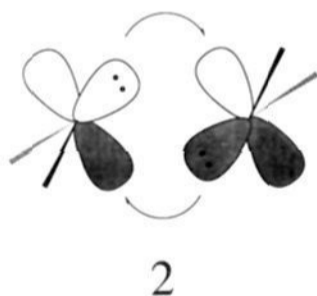
analogues of ethylene discussed above, that is, silaethylene, $\text{H}_2\text{Si}=\text{CH}_2$,¹⁹⁻²¹ disilene, $\text{H}_2\text{Si}=\text{SiH}_2$,²¹⁻²⁴ germaethylene, $\text{H}_2\text{Ge}=\text{CH}_2$,^{20,25,26} digermene, $\text{H}_2\text{Ge}=\text{GeH}_2$,^{12,23,24,26-28} stannaethylene, $\text{H}_2\text{Sn}=\text{CH}_2$,^{20,29} and distannene, $\text{H}_2\text{Sn}=\text{SnH}_2$,^{12,23,28,30} as well as germasilene, $\text{H}_2\text{Ge}=\text{SiH}_2$.^{24,31} Significant theoretical interest has been generated, especially with respect to the structural aspects of disilene. It has become clear that high-quality basis sets including polarization functions and a good treatment of electron correlation are necessary to satisfactorily describe the ground-state geometry of disilene. The most recent contribution to the study of heavier ethylene analogues is the work by Windhus and Gordon,³² who determined the structures and π -bond strengths for a series of $\text{H}_2\text{X}=\text{YH}_2$ compounds, using both MP2 and MCSCF+CI methods. This work includes the first calculations on stannasilene, $\text{H}_2\text{Sn}=\text{SiH}_2$, and stannagermene, $\text{H}_2\text{Sn}=\text{GeH}_2$. Plumbaethylene, $\text{H}_2\text{Pb}=\text{CH}_2$,³³ and diplumbene, $\text{H}_2\text{Pb}=\text{PbH}_2$,^{23,33,34} for which neither the parent molecules nor structural derivatives are known experimentally, have also been subject to a few theoretical studies.

The theoretical work on multiple bonding among the heavier analogues of ethylene focuses on various main themes. One of the general concerns is to develop a qualitative understanding of the nature of the nonclassical double bond. In the framework of valence bond theory, Pauling³⁵ describes the bonding in $\text{R}_2\text{-Sn}=\text{SnR}_2$ compounds as the resonance between two ionic configurations involving an unshared electron pair localized on one tin center:



The tin centers in **1** then exhibit different hybrid states. A similar explanation had been proposed several years earlier by Lappert and co-workers.^{12b}

Trinquier and Malrieu picture the bonding in $\text{H}_2\text{X}=\text{XH}_2$ systems by the interaction of two carbenic fragments,^{27a,36} in which the n_σ pair of one species partly delocalizes into the empty p_π orbital of its partner, as shown in **2**. This explanation takes into



account the fact that the higher homologues of carbene possess a singlet ground state rather than a triplet ground state. Structure

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2 may be regarded as a methylene derivative caught in the act of dimerizing.³⁷ Again, it was Lappert and co-workers^{12b} who had drawn a similar picture about 6 years earlier.

A third way to analyze this problem is to consider the orbital mixing under distortion from planar D_{2h} symmetry to the anti structure possessing C_{2h} symmetry. Under pyramidalization of the metal centers, the σ^* LUMO of the planar X_2H_4 system will mix into the π HOMO, leading to further stabilization of the latter orbital,³⁷ as shown in **3**.



Using either a valence bond model^{36a} or an elementary molecular orbital model,^{36b} Malrieu and Trinquier deduced a simple rule for the occurrence of trans-bent distortions at homopolar double bonds, considering $\sigma^*-\pi$ mixing. The domain of existence of a trans-bent double bond is then given as $1/4E_{\sigma+\pi} \leq \Delta E_{\text{ST}} < 1/2E_{\sigma+\pi}$, where ΔE_{ST} stands for the singlet-triplet energy splitting of the constituent carbenoid XH_2 , and $E_{\sigma+\pi}$ denotes the total $\text{X}=\text{X}$ bond energy.^{36b} Trinquier and Malrieu divide the different explanations for trans bending into two groups, according to whether the double bond is considered a four-electron set ($\sigma+\pi$ -bonds) or a two-electron set (π -bond).^{36c} They analyze these different explanations in terms of valence bond (VB) theory. As a two-electron problem, the double bond is governed by its neutral and ionic π VB components $\text{R}_2\text{X}^-\text{-}^+\text{XR}_2$, $\text{R}_2\text{X}^+\text{-}^-\text{XR}_2$, and $\text{R}_2\text{X}^-\text{-}^+\text{XR}_2$. As a four-electron problem, the double bond is analyzed as two carbenic fragments which each contribute two electrons and their two orbitals n_σ and p_π .^{36c}

Another qualitative description of double bonds involves bent bonds or banana bonds rather than a σ,π -bond representation.^{68,69} In this alternate bond description, two electrons are distributed above and the other two below the molecular plane. In a series of papers, Schultz and Messmer⁶⁹ carefully analyze the question of whether a banana bond or a σ,π -bond picture is capable of a more adequate description of double bonds. They conclude that a banana bond description is energetically superior to the symmetry-restricted σ,π -bond representation. An earlier investigation of Si_2H_4 also suggested⁷⁰ that for this molecule a banana bond description is favorable. However, neither of these representations can be proven to be "right" in an absolute sense;⁶⁹ both are legitimate as well as approximate descriptions. In the model of bent banana bonds, it is not obvious for what reasons certain molecules undergo a geometry distortion from a planar D_{2h} to a trans-bent C_{2h} structure. On the other hand, the σ,π -bond description provides an easier access to the solution of this kind of problems.

Recently, Lendvay determined fractional bond orders for the polarized banana bond or so called papaw bond in disilene, digermene, and distannene.³⁸ He calculated the bond orders for the trans-bent equilibrium structures to be larger than 1 but smaller than 2: $B_{\text{SiSi}} = 1.76$, $B_{\text{GeGe}} = 1.61$, and $B_{\text{SnSn}} = 1.46$. These structures can satisfactorily be described as a valence state between sp^3 and sp^2 , a description which refers back to the idea of a resonating electron pair, **2**.

A second major theme in the theoretical studies on nonclassical double bonds is the determination of the bond strength in $\text{H}_2\text{X}=\text{YH}_2$ systems and especially the contribution of π -bonding to the overall bond strength. Various methods have been used

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to assign π -bond strengths D_π . In the method of rotational barriers,^{20,32} one end of the molecule is twisted by 90°, and D_π is estimated as the energy difference between the rotated triplet state and the singlet ground state. However, this method may not be applicable in all cases of multiple bonding. Obviously, this concept cannot be transferred to triple bonds or bonds involving terminal atoms. But it also has been pointed out that "the low interconversion barriers measured and calculated for π -bonds between carbon and early transition metals probably do not accurately portrait their strength".²⁰ Alternative methods involve the use of thermodynamic cycles. The Benson analysis³⁹ defines the π -bond strength D_π as the negative of the energy of the disproportionation reaction of two XYH_2^\bullet radicals into $\text{H}_3\text{X}-\text{YH}_3$ and $\text{H}_2\text{X}=\text{YH}_2$. The π -bond energies for $\text{H}_2\text{X}=\text{CH}_2$ systems²⁰ as well as for ethylene and acetylene⁴⁰ have been determined by this method. Windhus and Gordon³² suggested the use of hydrogenation reactions of $\text{H}_2\text{X}=\text{YH}_2$ systems to derive values for the π -bond strength D_π .

The last important theme, which we will discuss only briefly, is the thorough exploration of the energy surfaces of the H_4XY systems. Silylsilylene, $\text{H}_3\text{Si}-\text{SiH}$, is a well-known minimum on the H_4Si_2 energy surface. Similar structures are known for the germanium and tin analogues. It is of interest to investigate the relative stability of such structural alternatives. Even more surprising geometries have been theoretically established for higher unsaturated systems⁴¹ containing multiple-bonded group 14 elements. Since we do not address this problem in our present work, we will not further elaborate on this interesting question, but we refer the reader to Trinquier's work on double-bonded and bridged arrangements on group 14 H_4X_2 potential surfaces^{23,42} for further information.

The goals of our present study are twofold. Up to now, no density functional studies have been reported for the heavier ethylene analogues. Since an appropriate treatment of electron correlation is important for a proper description of the ground-state geometry, it is interesting to investigate how well approximate density functional theory (DFT) can do as an alternative to *ab initio* methods. Over the last 10 years, DFT has evolved into a powerful tool for practical applications to molecular structures and energetics.⁴³ As this is especially true in the field of organo-transition-metal chemistry, there have been only a few applications of DFT to systems involving heavier main-group elements. This study is another contribution to the application of DFT in main-group chemistry.

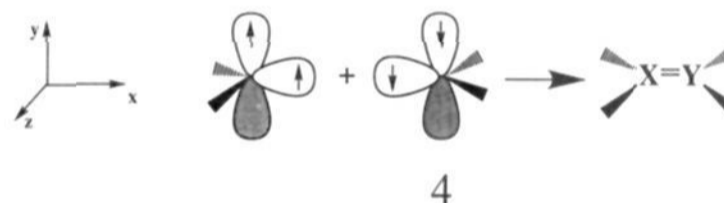
We will further present a detailed bonding analysis of $\text{H}_2\text{X}=\text{YH}_2$ systems. Use is made of the generalized transition-state method, which provides not only accurate calculations of total bonding energies⁴⁴ but also the possibility of a breakdown of the bonding energy into contributions due to steric as well as orbital interactions.⁴⁵ The importance of Pauli repulsion for the ground-state geometries is emphasized. We address the question of π -bond strength by performing a symmetry analysis of the orbital interaction energy. We hope to provide new insights into the phenomenon of trans bending and a better understanding of the chemical bonding in heavier ethylene analogues.

2. Computational Details

All calculations were performed utilizing the AMOL program package, developed by Baerends^{46a,b} et al. and vectorized by Ravenek.^{46c} The numerical integration was performed according to the procedure developed by teVelde^{46d} et al. The exchange factor, α_{ex} , was given the usual value of $2/3$. Electron correlation was treated within the local density approximation (LDA) in the parametrization of Vosko^{46e} et al. The final energies were determined by adding Becke's^{46f,g} nonlocal exchange correlation as well as Perdew's^{46h} inhomogeneous gradient corrections for correlation. A triple ζ -STO basis set,⁴⁶ⁱ augmented by two 3d-STO polarization function, was used for the *ns* and *np* shells of C, Si, Ge, Sn, and Pb. For H, the triple ζ -STO basis was extended by three 2p STO functions. Electrons in lower shells were considered as core and treated according to the procedure of Baerends^{46a} et al. An auxiliary set^{46j} of s, p, d, f, and g STO functions, centered on all nuclei, was used in order to fit the molecular density and present Coulomb and exchange potentials accurately in each SCF cycle. The geometry optimization procedure was based on the method of Versluis and Ziegler.^{46k} All geometries were optimized at the LDA level of theory (if not stated otherwise) without explicit treatment of relativistic effects. For the lead systems, the final electronic structures and energies were calculated by taking relativistic corrections into account according to the first-order perturbation scheme developed by Snijders^{46l,m} et al. Cartesian force constants and frequencies were calculated by numerical differentiation of the energy gradients.⁴⁶ⁿ

3. Results and Discussion

Methodology of the Energy Decomposition. We will begin our discussion with a brief outline of our energy decomposition scheme. In the following, we analyze the bonding in $\text{H}_2\text{X}=\text{YH}_2$ systems by the interaction of two fragments, XH_2 and YH_2 , which both possess the local equilibrium geometry of the final $\text{H}_2\text{X}=\text{YH}_2$ molecule and which both have an electronic structure suitable for covalent σ - as well as π -bonding. We therefore look at the interaction of two triplet $^3\text{B}_1$ -carbenoids, where the unpaired electrons of one fragment possess α -spin and the electrons on the other fragment are of β -spin. This process is shown in 4.



The total bond energy, ΔE_{TBE} , is made up of two major components (eq 1). The preparation energy, ΔE_{prep} , represents

$$\Delta E_{\text{TBE}} = \Delta E_{\text{snap}} - \Delta E_{\text{prep}} = \Delta E_{\text{snap}} - \Delta E_{\text{prep}}^{\text{g}} - \Delta E_{\text{prep}}^{\text{c}} \quad (1)$$

the energy which is required to make the ligand ready for the formation of the bond. This step involves deformation of the ligand framework to the geometry in the final molecule, $\Delta E_{\text{prep}}^{\text{g}}$, and, if required, the promotion energy from the electronic ground state to the electronic valence configuration, $\Delta E_{\text{prep}}^{\text{c}}$. The second component is the interaction energy, which is related to the process shown in 4, the so-called bond snapping energy, ΔE_{snap} . For the purpose of a detailed bond analysis, we break down ΔE_{snap} into several terms:⁴⁵

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$$\Delta E_{\text{snap}} = \Delta E^{\circ} + \Delta E_{\text{int}} = \Delta E_{\text{elstat}} + \Delta E_{\text{Pauli}} + \sum_{\Gamma} \Delta E_{\text{int}}^{\Gamma} \quad (2)$$

The steric repulsion⁴⁷ ΔE° consists of two components. ΔE_{elstat} is the electrostatic interaction of the nuclear charge and unmodified charge density of one fragment with the nuclear charge and unmodified charge density of the other fragment. ΔE_{elstat} usually stabilizes the bond between two fragments. The second component, ΔE_{Pauli} , which is called exchange repulsion⁴⁸ or Pauli repulsion, is due to the antisymmetry requirement of the total wave function. It may be understood as arising from the two-orbital three- or four-electron interactions between the occupied orbitals on both fragments. The larger the overlap between two occupied fragment orbitals, the stronger is the repulsive interaction. This point will be influential for the heavier main-group elements. The steric repulsion term ΔE° is usually repulsive at the equilibrium geometry, since the component ΔE_{Pauli} dominates.

In addition, there are attractive orbital interactions, ΔE_{int} . In our case, ΔE_{int} is mainly due to the interaction of the singly occupied orbitals of one fragment with the singly occupied orbitals of the other fragment (4). The stabilizing electronic interaction energy, ΔE_{int} , can be broken down into contributions from the orbital interactions within the various irreducible representations, Γ , of the overall symmetry group of the system.⁴⁷ We will make use of this analysis when assigning the π -bond energies of various systems.

Influence of Pauli Repulsion on Equilibrium Geometries. In order to understand the diversity in structure and bonding between ethylene and its heavier homologues, it is helpful to look at the differences between first and higher row elements. As Kutzelnigg⁴⁹ pointed out, the essential difference between the atoms of first and higher rows is that the cores of the former contain only s-orbitals whereas the cores of the latter include at least s- and p-orbitals. As a consequence, the s- and p-valence orbitals of first row atoms are localized in roughly the same region of space, whereas the p-valence orbitals of higher row atoms are much more extended in space. This again can be explained by the Pauli exclusion principle in the sense that the valence orbitals must be orthogonal to the core. We might call this effect an intraatomic Pauli repulsion, compared to the interatomic Pauli repulsion discussed above in connection with the term ΔE_{Pauli} .

In order to further elucidate the effect of steric repulsion on the bonding in ethylene analogues, we analyzed the bond snapping energy for ethylene and planar disilene as a function of C–C or Si–Si separation, respectively. This energy analysis is displayed in Figure 2. For ethylene (Figure 2a), we find that for C–C distances between 250 and 175 pm, the bond interaction energy resembles the electronic interaction energy. The influence of the steric repulsion term gets important for C–C separations $r_{\text{C-C}} < 150$ pm and dominates for $r_{\text{C-C}} < 120$ pm. At the equilibrium bond distance of ethylene, we find a well-defined minimum on the energy surface with respect to the C–C bond distance. A different situation is observed for disilene (Figure 2b). Due to the larger extent of the $3p_{\text{Si}}$ -orbitals compared to the $2p_{\text{C}}$ -orbitals, we find a significant bonding interaction for a Si–Si distance of 250 pm. However, the bond snapping energy ΔE_{snap} here is mainly influenced by steric interaction, which in turn is now determined by the two-orbital three-electron repulsive interaction between a 3p-valence orbital of one fragment with a 2p-core orbital of the other fragment. Under further contraction of the Si–Si bond, the stabilizing orbital interaction energy cannot anymore efficiently overturn the steric repulsion, as in the case for ethylene. The Pauli repulsion becomes dominant for atom–atom distances smaller than about 190 pm. This now has two major consequences. The first result is the well-known fact that X–X bonds for heavier

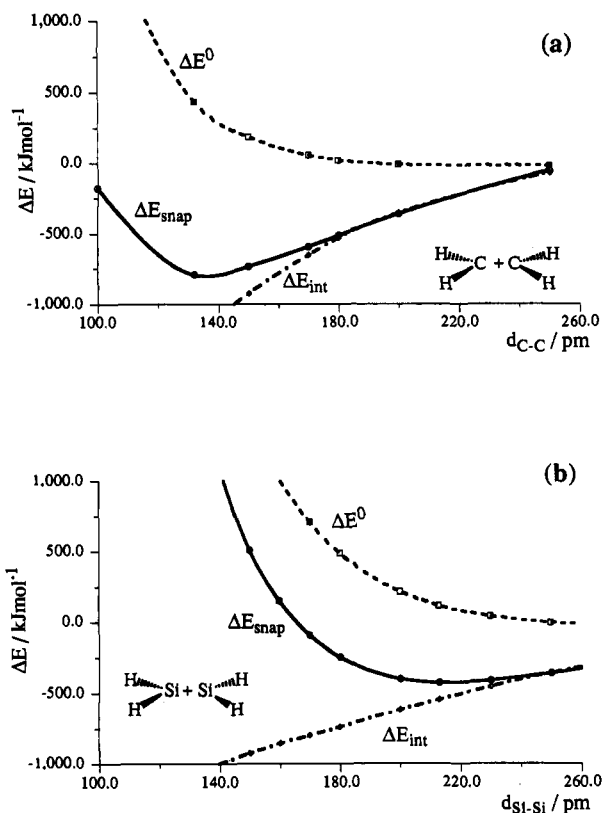


Figure 2. Orbital interaction energy ΔE_{int} , steric repulsion ΔE° , and bond snapping energy ΔE_{snap} for $\text{H}_2\text{X}=\text{XH}_2$ systems as a function of X–X separation. (a) Ethylene. (b) Disilene. Solid lines represent ΔE_{snap} , dashed lines represent ΔE° , and dashed-dotted lines represent ΔE_{int} .

group 14 elements are significantly longer than typical C–C bonds. Again, we like to point out that this is not to be explained by an argument employing maximum bonding overlap between the two σ -bonding 3p-orbitals but has to be reasoned in terms of steric interaction. Secondly, the potential energy surface around the equilibrium Si–Si distance becomes very shallow, and the energetic difference between the double-bonded equilibrium structure and a similar structure possessing a typical X–X single bond length is far smaller for disilene and other heavier ethylene analogues than it is for ethylene itself.

The longer bond distance in disilene and its heavier analogues now has further influence on the electronic as well as the geometric structure. In Figure 3, the well-known orbital energy diagram of ethylene is compared with the orbital energy diagram of planar disilene. Due to the longer bond distance in disilene, the energetic separation of the π_{pp} -bonding and antibonding orbitals decreases. This is true for orbitals that lie in the molecular plane as well as for those lying perpendicular to the molecular plane. As a consequence, the σ_{pp} -orbital of a_g symmetry energetically rises above the two in plane π_{pp} - and π_{pp}^* -orbitals of b_{1u} and b_{2g} symmetry. We should note that these orbitals are mainly of X–H bonding character. Thus it is possible that the π_{pp}^* -orbital is of lower energy than the σ_{pp} -orbital. At this point, we have to comment on the choice of our coordinate system. As usual, we chose the x-axis to be parallel to the X–Y bond in our $\text{H}_2\text{X}=\text{YH}_2$ systems. For the planar systems with D_{2h} symmetry, however, we chose the z-axis to lie in the plane of the molecule rather than to be perpendicular to it. Therefore, under geometric distortion from D_{2h} to C_{2h} symmetry, the coordinate system is preserved and the z-axis remains the main twofold axis.

Another important difference between C_2H_4 and Si_2H_4 is a dramatic decrease of the HOMO–LUMO gap. Compared to 5.7 eV in ethylene, we find the HOMO–LUMO gap in disilene to be only 2.5 eV. This corresponds to a wavelength around 500 nm, which indicates that these compounds absorb light in the

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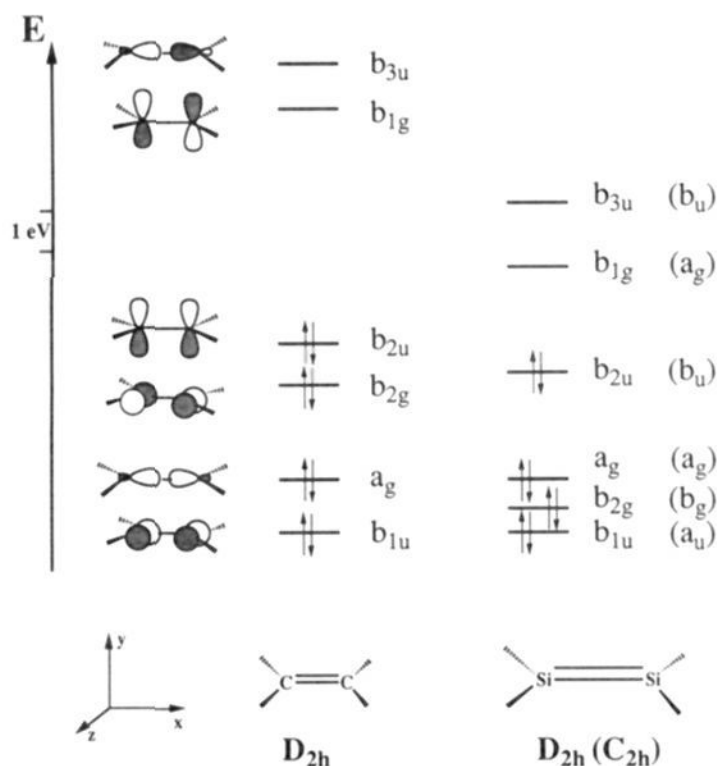
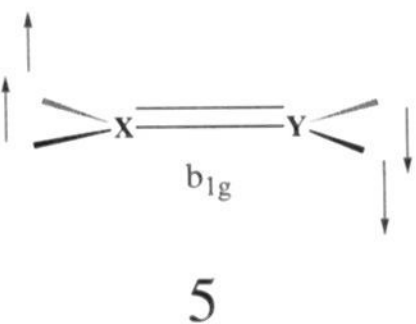


Figure 3. Partial orbital energy diagram for ethylene and planar disilene. The symmetry designations in parentheses refer to the trans-bent C_{2h} symmetry. The orbital diagrams are aligned at their b_{1u} energies.

blue-green region of the visible spectrum. This is in accordance with the observation that disilene compounds are of yellow and orange color^{18e,g} with electronic absorption bands between 400 and 470 nm. More significant is the fact that also the energetic difference between the b_{2u} HOMO and the lowest unoccupied orbital of b_{3u} symmetry significantly decreases. In D_{2h} symmetry, $\Gamma_{b_{2u}} \times \Gamma_{b_{3u}} = \Gamma_{b_{1g}}$, so a distortion mode of b_{1g} would allow these two orbitals to mix. The normal mode shown in **5** is indeed a b_{1g} distortion, which leads from the planar D_{2h} structure to the C_{2h} geometry. This orbital mixing maximizes the mutual HOMO-



5

LUMO interaction of the two dimerizing XH_2 and YH_2 units whenever they cannot undergo strong π_{pp} interactions due to a long $X-Y$ bond.

The small energy gap $\Delta E_{b_{2u}, b_{3u}}$ causes the heavier $H_2X=XH_2$ systems to be unstable with respect to a second-order Jahn-Teller distortion. The planar D_{2h} structure now corresponds to a transition state on the energy hypersurface, and the system undergoes spontaneously a geometric rearrangement toward the trans-bent structure. Figure 4 shows how for ethylene homologues $\Delta E_{b_{2u}, b_{3u}}$ decreases with increasing atomic number of X . This in turn will influence the folding angle Φ . As one might expect, the folding angle Φ will increase with increasing atomic number of X .

So far, we identified the $\pi_{pp}(b_{2u})/\sigma_{pp}^*(b_{3u})$ -orbital mixing as the driving force for a second-order Jahn-Teller distortion. Another mixing which becomes possible under a b_{1g} distortion is that of the $\sigma_{pp}(a_g)$ -orbital with the $\pi_{pp}^*(b_{1g})$ -orbital. However, we can neglect this interaction, since it has been pointed out that the a_g-b_{1g} separation is always larger than the $b_{2u}-b_{3u}$ one.^{36a,b}

We now return to a discussion of other relations between the Pauli repulsion and the equilibrium geometries. So far, we rationalized the possibility for trans bending in heavier ethylene homologues. Calculations further indicate that the folded structures should possess slightly longer $X-X$ bond distances than

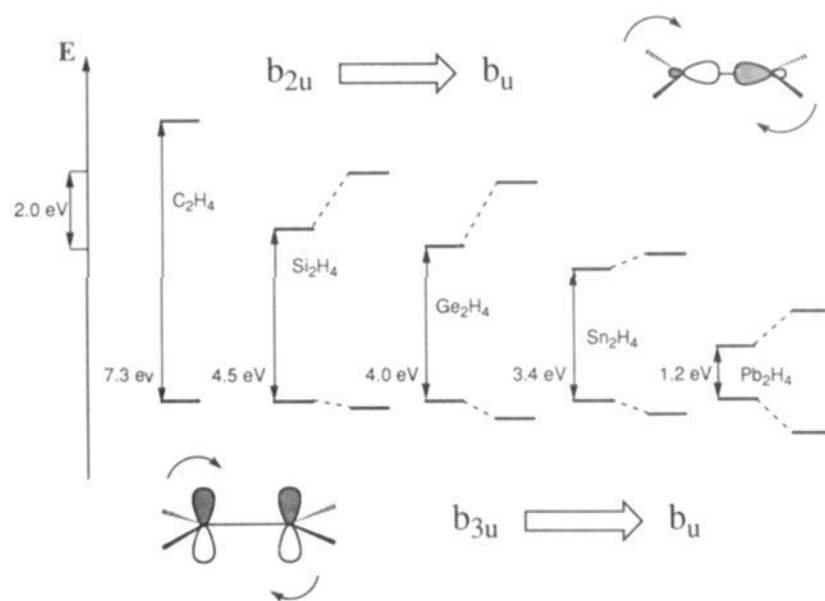


Figure 4. Energy separation and orbital mixing of the b_{2u} and b_{3u} orbitals for $H_2X=XH_2$ systems. A trans-bent distortion reduces the symmetry and transfers both orbitals into b_u types.

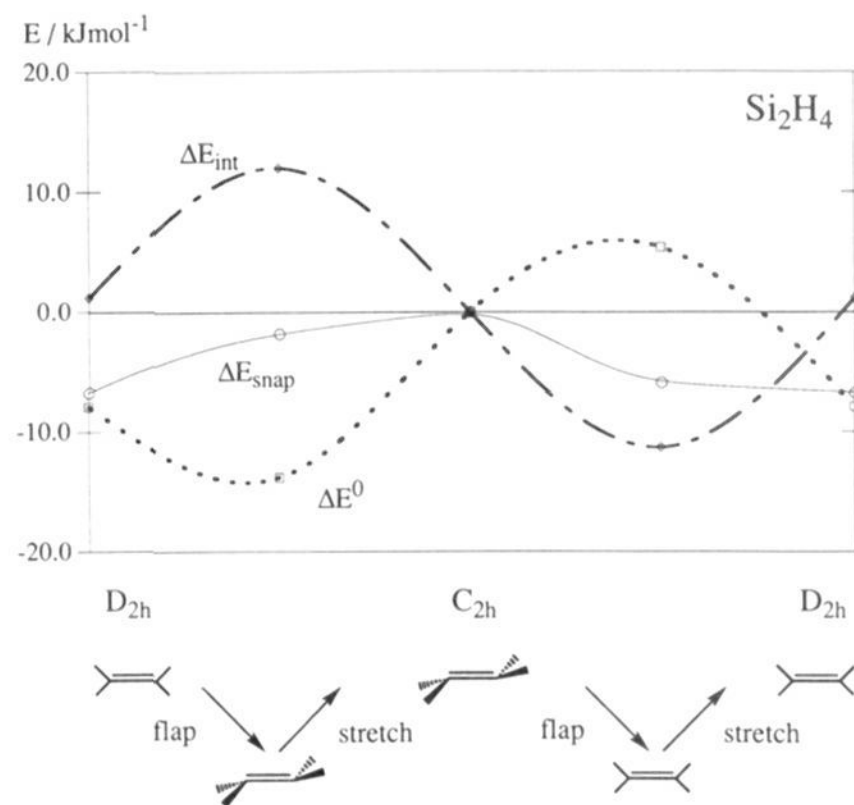


Figure 5. Change of bond snapping energy, steric repulsion, and orbital interaction under geometric distortion in the disilene system. The energy surface is traced along the coordinate for trans bending and long the coordinate for bond stretching. The solid line represents ΔE_{snap} , the dotted line represents ΔE^0 , and the dashed-dotted line represents ΔE_{int} . The energy components for the true ground state are set to zero. All energies refer to the changes in their absolute values.

their planar isomers. We therefore analyze the change in the bond snapping energy separately for the effect of trans bending and bond stretching (Figure 5). Again, we chose the disilene molecule as a representative example. We start out with planar disilene, which with respect to the bond snapping energy is 7 kJ/mol less stable than the trans-bent structure. We now follow the relaxation of the planar structure to the ground state along two different coordinates on the energy surface. First, we allow for trans bending but keep the bond distance fixed. We observe that the bond gets stronger due to ΔE_{int} but is weakened due to an increased steric interaction. The substituents on one silicon atom now undergo larger steric interaction with the other silicon center. This bending process makes up for 5 kJ/mol of the bond energy. We now follow the stretch of the $Si=Si$ bond length, which reduces the steric interaction and brings the system into its equilibrium geometry. However, the elongation of the $Si=Si$ bond is also accompanied with a decrease in ΔE_{int} . The bond stretch leads to a further stabilization of the bond by another 2 kJ/mol. We like to point out that the energy surface around the equilibrium structure is steeper for the bending coordinate than

Table 1. Bond Distances and Bond Angles for Various H₂X=YH₂ Systems

system	XYH ₄	symmetry	distances (pm)			angles (deg)				Φ (deg)
			X-Y	X-H	Y-H	H-X-H	H-Y-H	H-X-Y	H-Y-X	
I	C ₂ H ₄	D _{2h}	132.3	109.3		116.5		121.7		0.0
IIa	Si ₂ H ₄	C _{2h}	215.0	148.3		112.4		119.1		36.1
IIb	Si ₂ H ₄	D _{2h}	212.7	147.8		115.6		122.2		0.0
III	SiCH ₄	C _{2v}	168.7	148.0	109.2	114.7	115.5	122.6	122.2	0.0
IVa	Ge ₂ H ₄	C _{2h}	224.5	153.8		109.5		117.0		47.3
IVb	Ge ₂ H ₄	D _{2h}	220.5	152.1		116.9		121.5		0.0
V	GeCH ₄	C _{2v}	177.0	152.6	109.0	115.4	117.4	123.3	121.5	0.0
VIa	Sn ₂ H ₄	C _{2h}	256.9	172.7		105.8		117.9		51.0
VIb	Sn ₂ H ₄	D _{2h}	250.1	169.8		113.0		123.5		0.0
VII	SnCH ₄	C _{2v}	194.5	169.8	108.9	109.6	117.0	125.2	121.5	0.0
VIIIa	Pb ₂ H ₄	C _{2h}	281.9	179.4		107.7		115.2		53.6
VIIIb	Pb ₂ H ₄	D _{2h}	269.3	177.1		125.6		117.2		0.0
IX	PbCH ₄	C _{2v}	204.5	177.4	109.0	114.3	116.2	122.8	121.9	0.0

Table 2. Theoretical Bond Distances (*d*) and Fold Angles (∠) for H₂X=YH₂ Systems: A Comparison of DFT Geometries (This Work) and *ab Initio* Structures^a

H ₂ X=YH ₂ system	this work		Windhus and Gordon ^b		Trinquier ^c		Dobbs and Hehre ^d		others	
	<i>d</i>	∠	<i>d</i>	∠	<i>d</i>	∠	<i>d</i>	∠	<i>d</i>	∠
H ₂ Si=SiH ₂	215.0	36.1			211.7	0			212.5 ^e 216.4 ^f 216.5 ^g 216.9 ^h 219.2 ⁱ 222.4 ^j	11.4 29 ⁱ 25.7 29 ⁱ 38.5 38.6
H ₂ Si=CH ₂	168.7	0					169.1	0	170.3 ^k 171.8 ^l 174.3 ^m	0 0 0
H ₂ Ge=GeH ₂	224.5	47.3	234.1	42.4	231.5	36.5			227.0 ⁿ 227.2 ⁿ 230 ^o 230.7 ^p	34.6 36.2 40 38.1
H ₂ Ge=CH ₂	177.0	0	181.4	0			177.3	0	175.2 ^q 177.9 ^r	0 0
H ₂ Sn=SnH ₂	256.9	51.0	276.9	47.1	271.2	48.9			270.2 ^p 271 ^o 271.5 ^r	41.0 46 48.9
H ₂ Sn=CH ₂	194.5	0	206.3	17.9 26.8 ^u			198.2	0		
H ₂ Pb=PbH ₂	281.9	53.6			299.9	56.3				
H ₂ Pb=CH ₂	204.5	0								

^a Distances in picometers. Angles in degrees. ^b Reference 32 (MCSCF). ^c Reference 23 (SCF-DZP). ^d Reference 20 (SCF). ^e Reference 24 (SCF-DZP). ^f Reference 22p (G2). ^g Reference 22e (MP2). ^h Reference 22i (G1). ⁱ Reference 22h (SCF-TZP). ^j Reference 22m (GVB). ^k Reference 19h (SCF+D). ^l Reference 19e (SCF). ^m Reference 19i (GVB). ⁿ Reference 27b (SCF+D). ^o Reference 12e (RHF). ^p Reference 28 (SCF). ^q Reference 25c (SCF). ^r Reference 25b (SCF). ^s Reference 30 (RHF). ^t Reference 17. ^u The dihedral angles are SnCHH and CSnHH.

it is for the bond stretch. If we distort the equilibrium structure into a planar geometry, we destabilize the bond by 6 kJ/mol. The shortening of the bond required to establish the transition-state structure now amounts to only 1 kJ/mol. Further, it should be noticed that ΔE_{int} is comparable for both the D_{2h} and the C_{2h} structure. It is the change in ΔE° which makes the bond of the trans-bent structure the more stable one.

Structures of H₂X=YH₂ Systems. We have optimized the geometries of nine different H₂X=YH₂ systems. For the cases X = Y = Si, Ge, Sn, and Pb, calculations were performed in the planar D_{2h} geometry as well as for the trans-bent C_{2h} structure. For the mixed systems containing carbon and one heavier group 14 element, we optimized the structures in C_v symmetry. The geometries of these systems are given in Table 1.

For all H₂X=XH₂ systems, with the exception of ethylene, the D_{2h} structure has been identified to be a transition state on the LDA energy surface. The frequency calculations for all these molecules resulted in one imaginary frequency corresponding to the b_{1g} trans bending mode: b_{1g}(Si₂H₄) = 211 i cm⁻¹, b_{1g}(Ge₂H₄) = 391 i cm⁻¹, b_{1g}(Sn₂H₄) = 255 i cm⁻¹, and b_{1g}(Pb₂H₄) = 304 i cm⁻¹. The other systems are true minima on the LDA energy surface, possessing a spectrum of entirely real frequencies. For H₂X=XH₂ molecules, we observe a lengthening of the X=X bond on going from the planar to the trans-bent system and a

reduction of the angle ∠H-X-H, indicating pyramidalization of the X-center. The effect of bond shortening increases with increasing atomic number of X from about 2 pm for the silicon system up to 12 pm for the lead system. We also find that the fold angle Φ follows the same trend, ranging from 36° to 54°. These observations are in qualitative agreement with the trends as predicted above. In the following, we will elaborate on these two characteristic features, that is, the flap angle and the X=Y bond length, in more detail.

In Table 2, we compare our calculated X=Y bond lengths and fold angles Φ with the result of several recent *ab initio* calculations. It should be mentioned that we list only a representative selection of structures, and the reader is referred to the literature cited for further information. The case of ethylene is included in our calculations only for the sake of comparison, and we do not further comment on its structural features. The LDA C=C bond length in ethylene has already been reported⁵⁰ to be *d*_{C-C} = 132.1 pm

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and very recently⁵¹ to be $d_{C-C} = 132.3$ pm and is well in agreement with the experimental value⁵² of 133.9 pm.

We begin our discussion with the homonuclear $H_2X=XH_2$ systems. Our disilene bond length of 215.0 pm compares very well with the result of *ab initio* calculations. This Si=Si bond is about 2 pm shorter than the results obtained by MP2 methods. SCF-DZP calculations result in shorter bond lengths of about 212 pm, whereas the SCF-TZP bond length is slightly longer than the MP2 results. The GVB method results in a significantly longer Si=Si bond of 222 pm. The experimental bond length of disilene derivatives in the crystal state¹² ranges from 214 to 216 pm. Whereas most of the theoretical studies predict the trans-bent disilene to be the ground state, the disilene derivatives, for which crystal structures are known, are in general planar structures. As discussed above, the bending motion distorting planar D_{2h} Si₂H₄ to the C_{2h} geometry stabilizes the Si=Si bond due to orbital interaction but destabilizes it due to an increase in steric repulsion. As the steric bulk of the substituents is increased, the Pauli repulsion will drastically become larger compared to the orbital interaction. For most of the experimentally known, bulky substituted disilenes, the gain in orbital interaction cannot overcome the steric repulsion anymore, and these molecules adapt a planar ground-state geometry. If we compare the experimental structures^{10a} of Mes₂Si=SiMes₂ and (*E*)-^tBuMesSi=SiMes^tBu, we find that the former, trans-bent structure possesses a Si=Si bond length of 216.0 pm, whereas the latter, planar structure has the shorter bond length of 214.3 pm. This fact is in agreement with our previous discussion, and even more so as (*E*)-^tBuMesSi=SiMes^tBu is to be considered as the more sterically hindered disilene.^{10a} Our theoretical value of the lengthening of the Si=Si under bending distortion is 2.3 pm, very close to the experimental result of 1.7 pm.

For the parent molecule Si₂H₄, however, the experiment provides evidence for a trans-bent ground state.¹⁷ Our fold angle of 36° is 7° higher than those obtained from G1 and G2 calculations, and it comes close to the values for Φ obtained by GVB as well as SCF-TZP calculations.

If we proceed to digermene, we find that our Ge=Ge bond length is significantly shorter than those obtained by *ab initio* methods. Compared to the MCSCF calculations of Windhus and Gordon, we find a difference in bond length of about 10 pm. This difference goes down to 3 pm in comparison with other SCF calculations. However, experimental Ge=Ge bond lengths^{12,13} for substituted digermenes range from 221 to 235 pm, and our result is to be placed at the lower end of this spectrum of bond distances.

This situation becomes even more drastic if we consider the case of distannene. All *ab initio* calculations report a Sn=Sn bond length around 270 pm. The difference in d_{Sn-Sn} compared to the MCSCF calculation now amounts to 20 pm. The only experimentally known substituted distannene¹² possesses a Sn=Sn bond length of 277 pm, which is in good agreement with the result of Windhus and Gordon. However, one has to be careful here when comparing with experimental results. As already mentioned, Lappert's substituted distannene has been identified only in the crystal. In solution, one observes dissociation into two monomeric units. The same is true for the isostructural substituted digermene,¹² which with $d_{Ge-Ge} = 235$ pm marks the upper end of the scale of Ge=Ge bond lengths.

As we have demonstrated for the case of disilene, the energy surface for heavier ethylene analogues becomes very shallow with respect to the X=X separation. This was mainly due to the influence of steric repulsion. We expect this effect to become even more important for heavier systems involving Ge and Sn atoms. In the case of distannene, a distortion by 23 pm from our optimized bond length to the experimental value requires an energy of only 4 kJ/mol at the LDA level of the theory. The structures of heavier ethylene analogues, especially with respect to $d_{X=Y}$,

Table 3. Barriers to Planarity for Trans-Bent $H_2X=XH_2$ Systems^a

$H_2X=XH_2$ system	this work	Windhus and Gordon ^b	Tranquier ^c	others
H ₂ Si=SiH ₂	7			4, ^d 6, ^e 11 ^f
H ₂ Ge=GeH ₂	23	18	13	8, ^g 13 ^h
H ₂ Sn=SnH ₂	31	31	39	26, ^h 44 ⁱ
H ₂ Pb=PbH ₂	97		83	

^a Energies in kJ/mol. If necessary, literature values have been transformed and rounded. ^b Reference 32 (MCSCF). ^c Reference 23 (SCF-CI). ^d Reference 22e (MP2). ^e Reference 22m (GVB). ^f Reference 22h (SCF-TZP). ^g Reference 27b (SCF+D). ^h Reference 12e (RHF). ⁱ Reference 30 (RHF).

are very sensitive to the influence of Pauli repulsion and the steric demand of the substituents. This is demonstrated by the wide range possible for experimental Ge=Ge bond lengths among substituted digermenes. We expect the parent molecules H₂Ge=GeH₂ and H₂Sn=SnH₂ to have somewhat shorter metal-metal distances than those observed for the sterically demanding experimental structures.

Further, it has been shown that the LDA approximation in general underestimates bond distances.⁵⁰ Nonlocal corrections will become of importance in determining the true ground-state geometry. In this study, we have included nonlocal corrections only in the final energy calculation. If we compare the single point LDA/NL energies for distorted distannene at the experimental bond distance and for distannene at the LDA ground-state geometry, we find the latter to be more stable by only 1 kJ/mol. This again underlines the fact of the extremely flat energy surface along the X=X coordinate. We further can get an idea of the influence of the ground-state geometry on the bond energies. For the heavier systems, we estimate the error in LDA/NL energies for X=X bond dissociation due to an underestimated X=X bond length to be smaller than 5 kJ/mol.

To further support our argument, we optimized the geometries for Si₂H₄ and Sn₂H₄ including nonlocal corrections. For disilene, we find as the only significant difference in the geometry an elongated Si=Si bond of 217.4 pm. The fold angle stays within 35.9° essentially the same. For the case of distannene, the change in the X=X bond becomes more drastic. We now find an optimized Sn=Sn bond distance of 263.8 pm, which is 6.9 pm longer than in the LDA geometry. The Sn-H bond length increases slightly from 172.7 to 173.1 pm, and the angle $\angle H-Sn-H$ opens up about 1.7°. However, the fold angle was optimized to be 51.2° and thus does not significantly change when nonlocal corrections are included in the geometry optimization. For distannene, the LDA/NL ground state is about 8 kJ/mol more stable than the LDA geometry. This difference contains contributions due to both Sn-H bonds and the Sn=Sn bond. For disilene, this energy difference decreases to be even less than 1 kJ/mol.

In Table 3, the barriers to planarity are reported. We find that with increasing atomic number, the systems become more stable toward a trans-bent distortion. This trend was also analytically demonstrated.^{36b} Our values for the heavier systems are in good agreement with the results of the MCSCF calculations. Other SCF calculations give somewhat lower barriers for digermene and mostly higher values for distannene. We like to point out that our calculation and the work of Trinquier both result in high barriers for the diplumbene system. It seems that this molecule is particularly stabilized by trans bending and therefore by the $\sigma^*-\pi$ orbital mixing.

We now turn to a discussion of geometries for the $H_2X=CH_2$ systems. The structure of silaethylene from our DFT study compares well with other theoretical results. The Si=C bond length comes close to that determined by Dobbs and Hehre. All calculations listed in Table 2 satisfactorily represent the experimental Si=C bond length^{9c} of $d_{Si=C} = 171.2$ pm. Only the result of the GVB calculation gives rise to a slightly longer bond distance.

Table 4. Analysis of the Bond Dissociation Energies at 0 K for H₂X=YH₂ Systems^a

system	XYH ₄	symmetry	ΔE_{prep}			ΔE°	ΔE_{int}	ΔE_{snap}	ΔE_{ZPE}	ΔE_{TBE}^c
			geom.	elec.	tot.					
I	C ₂ H ₄	D _{2h}	13	0	13	-437	1230	794	42	739
IIa	Si ₂ H ₄	C _{2h}	8	148	156	-110	544	434	28	250
IIb	Si ₂ H ₄	D _{2h}				-119	546	427		
III	SiCH ₄	C _{2v}	17	74	91	-250	833	583	30	462
IVa	Ge ₂ H ₄	C _{2h}	8	192	200	-123	523	400	20	180
IVb	Ge ₂ H ₄	D _{2h}				-134	511	377		
V	GeCH ₄	C _{2v}	17	96	113	-234	731	497	27	357
VIa	Sn ₂ H ₄	C _{2h}	16	194	206	-82	424	342	15	121
VIb	Sn ₂ H ₄	D _{2h}				-103	414	311		
VII	SnCH ₄	C _{2v}	16	95	111	-207	628	421	26	280
VIIIa	Pb ₂ H ₄	C _{2h}	18	285	303	-73	431	358	13	42
VIIIb	Pb ₂ H ₄	D _{2h}				-84	346	262		
IX	PbCH ₄	C _{2v}	20	143	163	-172	548	376	22	191

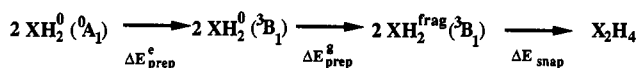
^a LDA/NL energies in kJ/mol. The complete analysis is presented only for the stable ground-state structures.

Our C=Ge bond length in germaethylene is comparable to that of Dobbs and Hehre but is 4 pm shorter than the MCSCF result of Windhus and Gordon. The difference between LDA and MCSCF bond lengths increases to 12 pm for the case of stannaethylene. The experimental bond lengths for substituted germaethylene and stannaethylene derivatives are 180–183 and 203 pm, respectively. For the case of stannaethylene, we again determined the geometry including nonlocal corrections. The major structural difference is an increase in the C=Sn distances up to $d_{\text{C-Sn}} = 197.7$ pm.

All our heteronuclear systems have a planar ground state. It is interesting to note that Gordon and Windhus found CSnH₄ to be bent at the MCSCF level of theory. The trans bending is enabled by a longer Sn–C separation, which reduces the increase of steric repulsion under trans bending. At shorter Sn–C distances we expect CSnH₄ derivatives to be planar. The experimental observations for germaethylene derivatives support our hypothesis. The germaethylene of Berndt and co-workers^{11a} possesses a Ge=C bond length of 182.7 pm and nonplanar structures around C and Ge, whereas the germaethylene of Couret and co-workers^{11b,c} is essentially planar, with a shorter bond length of 180.1 pm.

Little is known about H₂X=YH₂ systems containing lead atoms. The bond distance in diplumbene is about 20 pm shorter than that determined in an SCF calculation by Trinquier.²³ However, Trinquier finds a doubly bridged structure to be the true ground state for diplumbene.⁴² For plumbaethylene, we find a planar structure to be the ground state. This can be rationalized along lines similar to those given for stannaethylene. MNDO calculations³³ predict for both plumbaethylene and diplumbene a trans-bent structure. The MNDO bond lengths are C–Pb = 210 pm and Pb–Pb = 290 pm, about 5–8 pm longer than our results.

Bonding Analysis. As mentioned above, we analyze the bond in H₂X=YH₂ systems by the interaction of two appropriate prepared ³B₁ carbenoids. It is important to note that all the heavier carbene analogues have a singlet ground state rather than a triplet ground state as methylene itself. Thus the influence of the electronic preparation energy ΔE_{prep}^c will become of major importance for an assessment of the total bond energy. ΔE_{prep}^c can be identified with the sum of singlet–triplet splitting energy ΔE_{ST} of the carbenoid fragments. The importance of ΔE_{ST} on the bond strength has already been emphasized by Carter and Goddard.⁵³ Our bond analysis for X₂H₄ is once again shown in 6:



6

We further correct the total bond energy for the difference in

zero point energy of the final molecule and the constituting fragments:

$$\Delta E_{\text{TBE}}^c = \Delta E_{\text{TBE}} - \Delta E_{\text{ZPE}} \quad (3)$$

The results of our bond analysis are listed in Table 4.

As expected, the bond snapping energy and the total bond energy for ethylene are much higher than those for its heavier homologues. This is due to the long X–Y separation in the heavier systems. We also see the influence of the preparation energy, which is mainly responsible for the fact that double bonds between heavier group 14 elements are considerably weaker. For the planar systems, the orbital interaction decreases and the steric repulsion increases compared to the trans-bent analogues. This is in agreement with the previous discussion. An exception is the case of Si₂H₄, for which the orbital interaction in the planar geometry is somewhat higher than that in the trans-bent form. Of particular interest is the case of diplumbene. Here, the stabilization in the orbital interaction energy under trans bending is 85 kJ/mol, almost 3 times as high as that for the distannene system. A reason for this can be found in the small energy gap between the two mixing $\pi(b_{2u})$ and $\sigma^*(b_{3u})$ orbitals (see Figure 4). The relativistic inert pair effect energetically stabilizes the 6s_{pp}-orbital and destabilizes the $\sigma_{6s,6s}$ -bond. This in turn results in a energetically low-lying σ^* -orbital, which is readily available for stabilizing mixing with the π -HOMO. As a consequence, the total orbital interaction in trans-bent diplumbene is even higher than that in distannene. However, the same relativistic inert pair effect causes a large singlet–triplet splitting energy in the plumblyene fragment. The result is an electronic preparation energy for diplumbene which is almost 100 kJ/mol higher than that for distannene. The overall bonding energy is therefore 42 kJ/mol and significantly smaller for trans-bent diplumbene. The trend is that the overall bond strength for homonuclear systems decreases with increasing atomic number. All planar systems including those containing lead atoms further reflect the expected trend that also the orbital interaction energy should decrease with increasing atomic number of the heteroatom, due to a longer X–Y separation. The reason for this can be seen in the missing $\sigma_{\text{pp}}^*-\pi_{\text{pp}}$ orbital mixing in the planar systems.

In addition, we performed a bonding analysis for the LDA/NL geometry of trans-bent distannene. The bond snapping energy was found to be 345 kJ/mol, which is only 3 kJ/mol smaller than the value obtained for the LDA geometry. This justifies our previous estimate that the error in the bond snapping energy due to an underestimated bond length is smaller than 5 kJ/mol.

The total bond energy is identical to the bond dissociation energy for the process XYH₄ → XH₂ + YH₂. A comparison for

Table 5. LDA/NL Bond Dissociation Energies at 0 K for $H_2X=XH_2$ Systems^a

X_2H_4	this work	others	exptl
C_2H_4	739	717, ^b 735 ^c	719 ^d
Si_2H_4	250	218, ^e 246, ^e 267, ^f 273 ^g	265 ± 5 ⁱ
Ge_2H_4	180	154 ^d	
Sn_2H_4	121	119 ^h	54 ^k

^a Energies in kJ/mol. If necessary, literature values have been transformed and rounded. ^b Reference 54a (CASSCF/MRCI). ^c Reference 54b (G1). ^d Reference 24 (SCF-DZP). ^e Reference 22p (G2). ^f Reference 22o (MC-SCF/C1). ^g Reference 54c (MP4). ^h Reference 30 (RHF). ⁱ Calculated for 0 K from values given in ref 55. ^j Reference 17. ^k Reference 56 (value obtained in NMR studies on tetrakis[bis(trimethylsilyl)methyl]distannene).

ΔE_{TBE}^c with other theoretical studies and experimentally known values is given in Table 5.

The DFT bond energies satisfactorily describe the experimental results and compare very well with the data from *ab initio* studies. For ethylene, our value is comparable to the result of G1 calculations. Our C–C bond dissociation energy for ethylene is about 20 kJ/mol too high compared to the experiment. Recently, Ruscic and Berkowitz reported a value for the bond dissociation energy in disilene.¹⁷ DFT yields an energy which is about 15 kJ/mol too low compared to the experimental study. This again is comparable to the G2 value obtained by Curtiss^{22p} et al. For distannene, we should keep in mind that the comparison is made to a highly substituted system, and the experimental bond dissociation energy is obtained in solution. The range of the bonding energy is well estimated both in the DFT calculation and in the work of Marquez³⁰ et al.

On the basis of our bonding analysis, we now evaluate Trinquier and Malrieu's criterion for the existence of a double bond.³⁶ For the homopolar systems, it requires

$$2\Delta E_{ST} \leq E_{\sigma + \pi} \quad (4)$$

In most cases, the singlet–triplet splittings are seen to be the major components of our electronic preparation energy and may be identified with it (especially for the heavier carbenoids XH_2). The term $E_{\sigma + \pi}$ should not be taken as the total bond energy, since ΔE_{TBE} already includes contributions from the preparation energy and therefore from ΔE_{ST} . It should rather be identified with our snapping energy ΔE_{snap} . Equation 4 actually means that the bond snapping energy has to meet the requirements for preparing the fragments in order to form a stable double-bonded system. As long as the bond snapping energy is higher than the preparation energy, a double-bonded system is expected to be stable. This condition $\Delta E_{prep} \leq \Delta E_{snap}$ reduces to eq 4 if only the electronic terms are kept.

In order to obtain a value for the σ - and π -bond strengths, we further analyze the electronic interaction energy according to contributions from different symmetries. When analyzing the bonding in trans-bent systems, caution should be exercised using the terms σ and π . The characteristic feature of a π -bond or π -orbital is that it has one and only one nodal plane or nodal surface which contains the bond axis.⁶⁷ This definition certainly applies to the b_{2u} orbital for ethylene and its planar homologues (Figure 4) as well as to the isolobal b_{2u} orbital of the planar $H_2X=YH_2$ systems. In case of the trans-bent systems, however,

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Table 6. Intrinsic σ - and π -Bond Strengths in Planar $H_2X=YH_2$ Systems Compared with Intrinsic $a_g(\sigma)$ - and $b_u(\pi)$ -Bond Strengths in Trans-Bent $H_2X=XH_2$ Systems

system	XYH_4	symmetry	$D_{\sigma,el}$	$D_{\pi,el}$	σ/π	$D_{a_g,el}$	$D_{b_u,el}$	$a_g(\sigma)/b_u(\pi)$
I	C_2H_4	D_{2h}	875	315	2.78			
IIa	Si_2H_4	C_{2h}				373	158	2.36
III	$SiCH_4$	C_{2v}	578	228	2.56			
IVa	Ge_2H_4	C_{2h}				355	158	2.09
V	$GeCH_4$	C_{2v}	524	190	2.76			
VIa	Sn_2H_4	C_{2h}				281	134	2.10
VII	$SnCH_4$	C_{2v}	448	163	2.75			
VIIIa	Pb_2H_4	C_{2h}				250	177	1.41
IX	$PbCH_4$	C_{2v}	399	135	2.96			

^a $D_{\pi,el}$ and $D_{\sigma,el}$ values are extracted from LDA/NL ΔE_{int} values. Minor differences between the sum $D_{\pi,el} + D_{\sigma,el}$ and ΔE_{int} reported in Table 4 are due to neglected contributions to the electronic interaction energy (see text).

this strict classification does not hold for the HOMO of b_u symmetry. Due to the mixing of the $\sigma^*(b_{3u})$ - and $\pi(b_{2u})$ -orbitals, the resulting b_u orbital contains contributions from atomic s-type basis functions, which change the nodal characteristics of the orbital in a way that the X=X bond axis of the molecule no longer lies in the nodal plane of the orbital. Although this b_u orbital is still strongly dominated by p_y-type basis functions, it should not be considered as a π -orbital. We will classify this bond according to its symmetry as $b_u(\pi)$, where (π) points to the fact that this bonding interaction transforms to a real π -bond when going from the trans-bent geometry to the planar system. Similarly, we shall define the second major bonding interaction to represent an $a_g(\sigma)$ bond.

We analyze the interaction energy according to symmetry contributions to obtain a value for the π - or $b_u(\pi)$ -bond strength as well as for the σ - or $a_g(\sigma)$ -bond strength. For this purpose, we rotate our coordinate system so that the z-axis now corresponds to the main axis of the molecule. For the planar systems, we analyze the reaction $2XH_2 \rightarrow X_2H_4$ in C_{2v} symmetry. We can interpret the a_1 contribution of ΔE_{int} as the electronic interaction due to σ -bonding, $D_{\sigma,el}$, and the b_2 contribution as the electronic π -bond energy, $D_{\pi,el}$. Contributions from other irreducible representations are of minor importance and are not considered in our qualitative analysis. When we estimate the different bonding contributions in trans-bent molecules, we first perform a bond analysis for a planar system possessing the bond length of the trans-bent analogue. We assume that the change in electronic interaction energy between the elongated planar structure and trans-bent system is due only to an increase in $b_u(\pi)$ -bonding. Thus, by taking $D_{\sigma,el}$ and $D_{\pi,el}$ from the elongated planar structures and using the change of electronic interaction energy under trans bending, we can estimate values for $D_{a_g,el}$ and $D_{b_u,el}$, respectively. We call these bond strengths that are derived from the electronic interaction energy only the intrinsic π - or $b_u(\pi)$ - and the intrinsic σ - or $a_g(\sigma)$ -bond strengths. The results of our analysis are gathered into Table 6.

For the heavier ethylene homologues, both the $a_g(\sigma)$ - and the $b_u(\pi)$ -bonds are weaker than the corresponding σ - and π -bonds in ethylene itself. This is, as we already pointed out earlier, a consequence of the long X–Y separation which in turn was a result of the enhanced Pauli repulsion. The weak double bond is certainly not due to a reduced $b_u(\pi)$ interaction only. We are indeed dealing with real double bonds, in which both $a_g(\sigma)$ and $b_u(\pi)$ interactions are of importance. If we look at the ratio between the σ or $a_g(\sigma)$ and the π or $b_u(\pi)$ contributions, it is evident that systems involving the methylene unit possess a σ -bond that is roughly 2.75 times as strong as the π -bond. Exceptional are the cases of silaethylene, which possesses a somewhat stronger π -bond, and plumbaethylene, which has a weaker π -bond. The $a_g(\sigma)/b_u(\pi)$ ratio decreases significantly for the trans-bent systems. Here, the $a_g(\sigma)$ -bond is only twice as strong as the $b_u(\pi)$ -bond. This shows how the orbital mixing under trans

Table 7. π - and $b_u(\pi)$ -Bond Strengths in $H_2X=YH_2$ Systems: Intrinsic $D_{\pi,el}$ and $D_{b_u,el}$ Values (This Work) Compared with Results Obtained by Rotational Barriers

system	XYH_4	symmetry	this work	Windhus and Gordon ^b	Dobbs and Hehre ^c	others
I	C_2H_4	D_{2h}	315		268	274 ^d
IIa	Si_2H_4	C_{2h}	158			95, ^d 105 ^e
III	$SiCH_4$	C_{2v}	228		146	149 ^d
IVa	Ge_2H_4	C_{2h}	158	106		105 ^e
V	$GeCH_4$	C_{2v}	190	135	129	
VIa	Sn_2H_4	C_{2h}	134	82		
VII	$SnCH_4$	C_{2v}	163	87	79	
VIIIa	Pb_2H_4	C_{2h}	177			
IX	$PbCH_4$	C_{2v}	135			

^a Energies in kJ/mol. If necessary, literature values have been transformed and rounded. ^b Reference 32. ^c Reference 23. ^d Reference 57. ^e Reference 24.

bending strengthens the $b_u(\pi)$ -bond. On going from the silicon to the lead systems, we see that the $a_g(\sigma)/b_u(\pi)$ ratio decreases, indicating an increase in the relative $b_u(\pi)$ -bond strength. Significant is the drop in the $a_g(\sigma)/b_u(\pi)$ ratio between tin and lead. As we pointed out earlier, for diplumbene the orbital mixing becomes of major importance and strongly enhances the $b_u(\pi)$ -bond strength. The $b_u(\pi)$ -bond in diplumbene appears to be the strongest of all heavier homonuclear systems.

We can say that, with respect to the intrinsic bond strength values, the trans-bent systems possess even more double bond character than ethylene itself. However, the overall bond strength in these systems is mainly governed by the influence of Pauli repulsion and the preparation energy, which is the major cause for the weak link between the heavier atoms.

How do these intrinsic σ -, $a_g(\sigma)$ - and π -, $b_u(\pi)$ -bond strengths compare to results from other theoretical methods? In Table 7, π -bond strengths obtained from rotational barriers are collected together with our results.

We see that for all cases our value for the $b_u(\pi)$ -bond strength in homonuclear systems is about 50 kJ/mol higher than the values obtained by the rotational method. For the heteronuclear systems, the difference increases by 10–30 kJ/mol. If we twist the $H_2X=YH_2$ systems by 90°, we not only break the π -bond, but we also reduce the steric repulsion between the occupied p-orbitals at the X and Y centers, which form occupied bonding and occupied antibonding in-plane π_{pp} -orbitals (b_{1u} and b_{2g} in Figure 3). Whereas the first process destabilizes the $X=Y$ bond, the latter process, reducing the steric interaction, leads to a stabilization of the bond and lowers the energetic difference between the twisted and the planar structures. Since our analysis distinguishes between these different effects, we can extract our value for $D_{b_u,el}$ only from the orbital interaction. The difference between our intrinsic $b_u(\pi)$ -bond strength and the values obtained by rotational barriers is therefore due to the influence of the steric repulsion.

Grev and Schaefer²⁴ already pointed out the surprising fact that the $Si=Si$ π -bond energy and $Ge=Ge$ π -bond strengths are essentially the same. The results of other calculations are in agreement with this fact. Our analysis is consistent with this statement; our $D_{b_u,el}$ value for the $Si=Si$ bond is the same as that for $Ge=Ge$. On going to the tin–tin double bond, we observe a decrease in the $b_u(\pi)$ -bond strength by 24 kJ/mol. Windhus and Gordon³² obtain the same destabilization for the $Sn=Sn$ π -bond compared to the $Ge=Ge$ π -bond. We already pointed out that the $b_u(\pi)$ -bond in diplumbene is especially strengthened under trans bending. This was indicated by the high barrier to planarity as well as by the low σ/π ratio. We can rank the different $b_u(\pi)$ -bonds according to their strengths as $C=C \gg Pb=Pb > Si=Si \sim Ge=Ge > Sn=Sn$. This order is in accordance with the ability of forming π -bonds as classified by Windhus and Gordon:³² $C > Si \sim Ge > Sn$.

If we compare our results for the mixed systems, we find that our $X=Y$ π -bond strengths are about 80 kJ/mol higher than the results of Dobbs and Hehre.²⁴ The exception here is germaethylene, in which case the difference is about 20 kJ/mol smaller. What distinguishes our results from those determined by the rotational barrier method is the drop in π -bond strength. According to the results from the rotational barrier method, we would arrive at the following qualitative ranking for the π -bond strength: $Si=C \sim Ge=C \gg Sn=C$. Our intrinsic bond strengths, however, suggest a more equal ranking: $Si=C > Ge=C > Sn=C > Pb=C$. Similarly, an equal decrease in π -bond strength can also be observed for the planar $H_2X=XH_2$ systems: $(Si=Si)_{D_{2h}}$, 156 kJ/mol $>$ $(Ge=Ge)_{D_{2h}}$, 138 kJ/mol $>$ $(Sn=Sn)_{D_{2h}}$, 118 kJ/mol $>$ $(Pb=Pb)_{D_{2h}}$, 86 kJ/mol. It is the influence of trans bending which leads to the unusual ranking of the $b_u(\pi)$ -bond strengths.

In general, we can say that our analysis very well describes the trend in π - or $b_u(\pi)$ -bond strengths for ethylene analogues. The intrinsic bond strengths are a good measure for π -, $b_u(\pi)$ - and σ -, $a_g(\sigma)$ -binding capacity.

Having judged our method of the $\pi, b_u(\pi)$ -bond analysis, we now return to the second component of importance for an assessment of the overall bond strength, that is, the preparation energy. As we discussed above, our preparation energy is essentially influenced by the value of the singlet–triplet splitting energy. ΔE_{ST} is also one of the crucial terms in the bond analysis of Trinquier and Malrieu. Furthermore, the excitation energy $^1A_1-^3B_1$ is a sensitive test for gauging the efficiency of theoretical methods.⁵⁸ For the case of methylene itself, the prediction of its geometry as well as its electronic structure has been a paradigm for computational quantum chemistry and has been important for the establishment of credibility for new theories.⁵⁹ It seems to be worthwhile to discuss briefly our values for ΔE_{ST} in comparison with the result of other theoretical studies and experimental values available. These results are collected in Table 8.

Again, we present only a small selection of the data available, and for the cases of methylene and silylene we refer to a recent work of Grev and Schaefer^{60b} for a thorough discussion of the problem. For methylene itself, our absolute value for ΔE_{ST} is 27 kJ/mol too high compared to the experiment. This result, however, is comparable to the outcome of other density functional studies by Selmani and Salahub⁵⁸ as well as by Becke.^{60d} The best DFT value of Russo^{60f} and co-workers is –38 kJ/mol, in excellent agreement with experiment. Also for the heavier carbenoids silylene, germylene, and stannylene, our results compare very well with the results of Selmani and Salahub. Calculations including relativistic effects result in a slightly higher singlet–triplet splitting for stannylene. For plumbylene, we note that we obtain a value for ΔE_{ST} which is 42 kJ/mol higher than the value for SnH_2 . The relativistic calculations of Trinquier²³ and Balasubramanian^{60a} underline this trend. This again shows the special situation encountered in the lead systems: the very strong π -bond competes with a very high preparation energy.

The fact that methylene and its higher homologues have different electronic ground states can basically be rationalized by realizing that the valence s- and p-orbitals of the heavier systems are no longer localized in the same region of space.⁶² Thus, the

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Table 8. Singlet-Triplet Splitting Energies in XH₂ Systems for X = C, Si, Ge, Sn, Pb^a

XH ₂ system	this work	Trinquier ^b	Selmani and Salahub ^c	Balasubramanian ^d	others	exptl
CH ₂	-65	-53, -59	-63		-38, ^e -42, ^f -65, ^g -30, ^h -38 ⁱ	-38 ^j
SiH ₂	74	70	79		88, ^e 90, ^f 69 ^g	74, ^k 87 ^k
GeH ₂	96	91	94	96		
SnH ₂	97	104	98	104		
PbH ₂	143	146		154		

^a Energies in kJ/mol. If necessary, literature values have been transformed and rounded. ^b Reference 23. ^c Reference 58 (LSD-VWN). ^d Reference 60a (MCSCF/SOCI/RCI). The results listed are the ones obtained without spin-orbit coupling. ^e Reference 60b (CCSD(T)). ^f Reference 60c (DCCI-GVB). ^g Reference 60d (LSDA-Bx-PWc). ^h Reference 60e (LSD/NL). ⁱ Reference 60f (LSD/NLC). ^j Reference 61a. ^k Reference 61b.

Table 9. Calculated and Experimental X-Y Bond Lengths (*d*) in Single- and Double-Bonded Group XIV Systems^a

XYH _n system	this work			experimental ^b		
	<i>d</i> _d (X=Y), <i>n</i> = 4	<i>d</i> _s (X-Y), <i>n</i> = 6	<i>d</i> _d / <i>d</i> _s	<i>d</i> _d (X=Y) <i>n</i> = 4	<i>d</i> _s (X-Y), <i>n</i> = 6	<i>d</i> _d / <i>d</i> _s
C ₂ H _n	132.3	151.1	0.876	133.9	153.7 ⁱ	0.871
Si ₂ H _n	215.0	232.2	0.926	214.3–216.0 ^c	232.7	0.921–0.928
SiCH _n	168.7	184.7	0.913	170.2 ^d	186.9	0.911
Ge ₂ H _n	224.5	241.3	0.930	221.3–234.7 ^e	240.3 ^j	0.921–0.977
GeCH _n	177.0	192.4	0.920	180–182.7 ^f	194.3	0.926–0.940
Sn ₂ H _n	256.9	272.1	0.944	276.8 ^g	277.6 ^k	0.997
SnCH _n	194.5	212.7	0.914	202.5 ^h	214.3	0.945
Pb ₂ H _n	281.9	293.1	0.962		285.1 ^l	
PbCH _n	204.5	222.5	0.919			

^a Bond lengths in picometers. ^b Experimental bond lengths are taken from ref 52 if not stated otherwise. ^c Reference 10a. ^d Reference 9c. ^e References 12 and 13. ^f Reference 11. ^g Reference 12. ^h Reference 14. ⁱ Reference 63. ^j Reference 64a. ^k Reference 64b. ^l Reference 64c (from *p*-Tol₆Pb₂).

difference in the singlet-triplet splitting energies again is a consequence of the intraatomic Pauli repulsion.

Comparison with Single-Bonded Systems. We will finish our discussion with a brief comparison between the double-bonded systems H₂X=YH₂ and their single bonded analogues H₃X–YH₃. We will focus on two points, namely the difference in bond length for single versus double-bonded systems and the comparison of bond energies and intrinsic σ -bond strengths. We optimized the geometries of all single-bonded analogues for structures I to IX. In Table 9, we compare our values for single and double bond lengths with experimental data.

The LDA values calculated for the single bond lengths are in good agreement with experiment for the cases of disilane and digermene. The discrepancy here is only about 1 pm, with the exceptional case that the theoretical Ge–Ge bond length is slightly longer than the experimental result. For ethane and distannane, we find as expected the bond lengths to be too small by 3–5 pm compared to the experiment. The theoretical double bonds are in general between 15 and 19 pm shorter than the corresponding single bonds. Only for diplumbene, we find a bond contraction of only 11 pm.

To eliminate systematic errors, we will compare the theoretical and experimental double-to-single bond ratio. The general trend for the homonuclear systems is an increase of this ratio on going to heavier systems. This is reflected in the experimental ratios as well. However, the experimental data for some heavier systems give rise to a broad range of possible *d*_d/*d*_s ratios. For ethylene, disilene, digermene, and silaethylene, our *d*_d/*d*_s ratio is within the experimentally established range. For the heavier systems, we find that our ratio is generally to small compared with experiment. However, we have to keep in mind the fact that just a few of the heavier double-bonded systems are well described, which might represent only a few points out of a large range of possible X=Y distances.

We proceed with the bond analysis for the single-bonded systems, as shown in Table 10. The analysis is performed in a way similar to that for the double-bonded systems. However, the

Table 10. Analysis of the Bond Dissociation Energies at 0 K for H₃X–YH₃ Systems^a

XYH _n	ΔE_{prep}	ΔG°	ΔE_{int}	ΔE_{snap}	ΔE_{ZPe}	ΔE_{TBE}^c
C ₂ H ₆	80	-311	791	480	37	363
Si ₂ H ₆	2	-74	387	313	18	293
SiCH ₆	36	-196	604	408	31	341
Ge ₂ H ₆	6	-78	352	274	11	257
GeCH ₆	37	-160	504	344	22	285
Sn ₂ H ₆	4	-54	292	238	14	220
SnCH ₆	36	-146	451	305	30	239
Pb ₂ H ₆	6	-55	257	202	11	185
PbCH ₆	33	-112	386	274	20	221

^a LDA/NL energies in kJ/mol.

XH₃ fragments do not need any electronic preparation to undergo the bond snapping process.

The results of our analysis are not too surprising and follow the expected trends. If we look at the bond snapping energy for the homonuclear systems, we find that there is a significant drop on going from ethane to disilane. On going to the heavier systems, the bond snapping energy decreases steady by about 36–39 kJ/mol. For the mixed systems, we observe a similar trend. It is of interest that the Si–C bond energy comes close to the C–C bond energy. A reason can again be found in the preparation energy. Since the methyl radical possesses a planar ground state, 40 kJ/mol is needed to prepare a pyramidal CH₃ fragment ready for bonding interaction. All the other XH₃ fragments, however, possess a pyramidal ground state, and the preparation energy for the heavier fragments is evidently small. If we compare with the double-bonded systems, we find in all cases that the bond snapping energy for the double-bonded systems is higher than that for the single bonds. This clearly underlines the fact that the heavier XYH₄ systems have real double bonds. However, the overall bonding energies are smaller for the XYH₄ systems than for the XYH₆ systems. The well-known exceptions here are ethane and ethylene. In comparison with experimental values, we find that our C–C bond strength comes close to the experimental value of $D^\circ(\text{C–C}) = 367 \text{ kJ/mol}$,⁵⁵ whereas the theoretical values for the Si–Si, C–Si, and Ge–Ge bonds appear to be 20–30 kJ/mol too small ($D^\circ(\text{Si–Si}) = 321 \text{ kJ/mol}$,^{65a} $D^\circ(\text{Si–C}) = 376 \text{ kJ/mol}$,^{65a} and $D^\circ(\text{Ge–Ge}) = 276 \text{ kJ/mol}$ ^{65b}).

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Table 11. X—Y Stretching Frequencies ω and Harmonic Force Constants F for X—Y Single and Double Bonds^a

XYH _n	X=Y, n = 4		X—Y, n = 6	
	ω	F	ω	F
C ₂ H _n	1652 (1630 ^b)	9.658 (9.418 ^c)	1016 (995 ^d)	4.607 (5.276 ^e)
Si ₂ H _n	558 (630 ^d)	2.699	421 (434 ^b)	1.626 (1.71 ^b)
SiCH _n	987 (985 ^e)	5.517	710 (701 ^f)	3.031 (2.93 ^f)
Ge ₂ H _n	286 (404 ^f)	2.284	261 (268 ^g)	1.577 (1.63 ^g)
GeCH _n	842	4.876	583 (602 ^h)	2.556 (2.70 ^h)
Sn ₂ H _n	205	1.896	184 (190 ⁱ)	1.229 (1.40 ^m)
SnCH _n	766	4.309	543 (528 ⁿ)	2.358 (2.19 ⁿ)
Pb ₂ H _n	136	1.290	141	1.273
PbCH _n	712	3.814	499 (468 ^o)	2.137 (1.85 ^o)

^a Frequencies in cm⁻¹, force constants in mdyne/Å. Experimental values are given in parentheses. ^b Reference 66a. ^c Reference 66b. ^d Reference 66c (from Si₂Me₄). ^e Reference 16. ^f Reference 66d (from Ge₂Me₄). ^g Reference 66e. ^h Reference 66f. ⁱ Reference 66g. ^j Reference 66h. ^k Reference 66i. ^l Reference 66j (from Sn₂Me₆). ^m Reference 66h (extrapolated value). ⁿ Reference 66k. ^o Reference 66l (from PbMe₄).

We finally take a short look at the problem of double bonding from yet another view point. In Table 11, we report XY stretching frequencies and harmonic force constants for X—Y single as well as X=Y double bonds. The values for most of the single bonds have been well known experimentally for a long time. The drop in bond strength in going from ethane to heavier homonuclear systems indicates the relative weakness of the bond between heavier systems. This is even more significant for the double-bonded systems. The harmonic stretching frequency for disilene

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is about 3.5 times smaller than the one for ethylene. The value further decreases on going to heavier systems. This again shows that the energy surface around the equilibrium geometry is very flat with respect to the bond stretch. The X—Y separation is therefore a very sensitive structural parameter. We further note that for all our systems with the exception of diplumbene and diplumbane, the double-bonded systems have higher force constants and stretching frequencies than their single-bonded analogues. This indicates that the link between the heavier atoms, e.g., the bond snapping energy, is higher for the double-bonded systems than it is for the single bonds.

Compared to the experimentally known frequencies for the single-bonded XYH₆ systems, the error in our calculated frequencies ranges from -15 cm⁻¹ for methylgermane up to +21 cm⁻¹ for ethane. Thus, our unscaled stretching frequencies are in reasonable agreement with experiment.

4. Conclusion

Cowley^{18d} asked the question as to the nature of the multiple bonds between heavier main group elements: "Are they really double bonds?". As the result of our present study, we would answer the question with "Yes, indeed, they are." Our analysis of the intrinsic σ -, $a_g(\sigma)$ - and π -, $b_u(\pi)$ -bond strengths reveals that π -, $b_u(\pi)$ -bonding makes an important contribution to the overall bond strength of higher ethylene analogues. The influence of the $b_u(\pi)$ -bond becomes even stronger when the planar system undergoes a distortion toward a trans-bent geometry. The fact that for the heavier systems the dissociation energy is weaker for a double bonds than it is for a single bonds is due to a high preparation energy for the fragments possessing a singlet ground state. However, the bond snapping energy is still higher for double bonds than for single bonds. The influence of intraatomic as well as interatomic Pauli repulsion is mainly responsible for the changes in geometry and electronic structure as well as for the difference in bonding energy as observed in the systems containing heavier group 14 elements.

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