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# A theoretical approach to the molecular structure of vinylstannane and some structural isomers

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**Abstract**

A theoretical study of the electronic and molecular structure of vinylstannane $SnH_3CH{=}CH_2$ and structural isomers $CH_2{=}SnHCH_3$ and $SnH_2{=}CHCH_3$ has been carried out. Ab initio Hartree-Fock calculations were performed using an effective core potential to describe the core electrons of tin. Vinylstannane has a propene-like structure with a Sn–C bond similar to that of methylstannane. As in propene, the eclipsed rotamer is more stable than the bisected one. The molecular structures of $CH_2{=}SnHCH_3$ and $SnH_2{=}CHCH_3$ are planar according to the $\Delta E_{ST} - E(\sigma + \pi)$ model. The structures of allylic-type species $SnH_2CHCH_2$ and $CH_2SnHCH_2$ (cations, radicals and anions) have also been considered.

*Keywords:* Vinylstannane; Theoretical study; Ab-initio calculations; Hartree-Fock

## 1. Introduction

The molecular and electronic structure of organic derivatives of main group metals is now a topic of major interest. These organometallic compounds play a key role mainly in organic synthesis, both as precursors and as intermediates. Group 14 metal derivatives, in particular organotin compounds, are especially well suited for these purposes and their chemistry has been the subject of several reviews [1].

From a structural point of view, simple organotin(IV) compounds may be considered as hydrocarbons in which the central carbon atom has been replaced by tin. Therefore, their properties can be rationalized in terms of their carbon parents. However, care must be taken with these generalizations since they may no longer be valid when tin is involved in double bonds. For instance, the geometry of distannene $Sn_2H_4$ is not planar like its homologue, ethylene, but *trans*-bent as shown both from experiment [2,3] and from theoretical calculations [3–6]. This non-classical distortion of multiple bonds also features to a greater or lesser extent in the rest of the Group 14 metals and this topic has been the subject of recent theoretical work [6–10].

As part of our effort to elucidate the structural properties of simple organotin(IV) compounds, we present a theoretical study of the molecular and electronic structure of vinylstannane $SnH_3{-}CH{=}CH_2$ and related open-chain isomers, $SnH_2{=}CH{-}CH_3$ and $CH_2{=}SnH{-}CH_3$. Because of the multiple bond involving tin in the two latter compounds, we have also considered the molecular structure of $SnH_2{=}CH_2$, the simplest model with a tin–carbon double bond. The possibility that this compound might undergo non-classical distortions has been analyzed in terms of the singlet-triplet gap versus $\sigma + \pi$ energy model [6]. Finally, allyl-like species having the general formula $SnC_2H_5$ have also been considered.

## 2. Computational details

Ab initio Hartree-Fock calculations were undertaken using the relativistic pseudopotential approximation of Stevens et al. [11] to describe the tin core electrons. The valence basis set for tin was of double-zeta quality enlarged with d functions ($\zeta_d = 0.2$) [12]. For carbon and hydrogen the standard double-zeta

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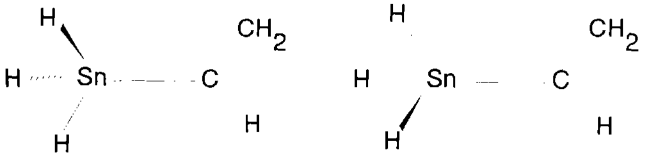
valence basis set of Dunning [13] was used. The Hartree-Fock calculations were of unrestricted type (UHF) for open-shell systems. Multiconfigurational SCF calculations for allylc-like compounds were of the CASSCF type [14], the active space being that formed by electrons and orbitals of the $\pi$-system. Stationary points on the potential energy hypersurface were obtained by analytical gradient techniques and characterized by computation and by further diagonalization of the force constant matrix. All calculations were carried out using the HONDO-8.4 program system [15].

## 3. Results and discussion

### 3.1. Vinylstannane $SnH_3CH{=}CH_2$

Rotational isomerism around the Sn–C single bond of vinylstannane (**1**) leads to two conformations, as classically assumed [16] for terminal alkenes, eclipsed and bisected.



In Table 1 and Fig. 1 the molecular structures, energies, and selected optimized structural parameters for these compounds are reported. In both rotamers the Sn–C and Sn–H bond distances computed at the HF-SCF level are close to those reported for methylstannane at the same level of calculation (2.108 and 1.716 Å, respectively) [17,18], showing that the carbon–carbon double bond has little effect.

Table 1
Selected structural parameters and energies of vinylstannane rotamers

| | Eclipsed | Bisected |
|---|---|---|
| $E$ [a] | −82.42541 | −82.42396 |
| $\Delta E$ [b] | 0.91 | |
| $r_{SnC}$ [c] | 2.1165 | 2.1210 |
| $r_{CC}$ [e] | 1.3404 | 1.3309 |
| < SnCC [d] | 123.8 | 124.6 |
| $r_{SnH}$ [c,e] | 1.7057<br>1.7068 | 1.7055<br>1.7064 |
| $f_{SnC}$ [f] | 2.635 | 2.620 |
| $f_{CC}$ [f] | 10.679 | 10.694 |
| $\omega_{SnC}$ [g] | 495 | 494 |
| $\omega_{CC}$ [g] | 1417 | 1418 |

[a] Hartree. [b] Rotational barrier (in kcal $mol^{-1}$) calculated as the energy difference between eclipsed and bisected isomers. [c] Interatomic distances (Å). [d] Bond angle (deg). [e] The first value corresponds to the on plane-hydrogen. [f] Force constants (mdyn Å). [g] Vibrational frequency ($cm^{-1}$).

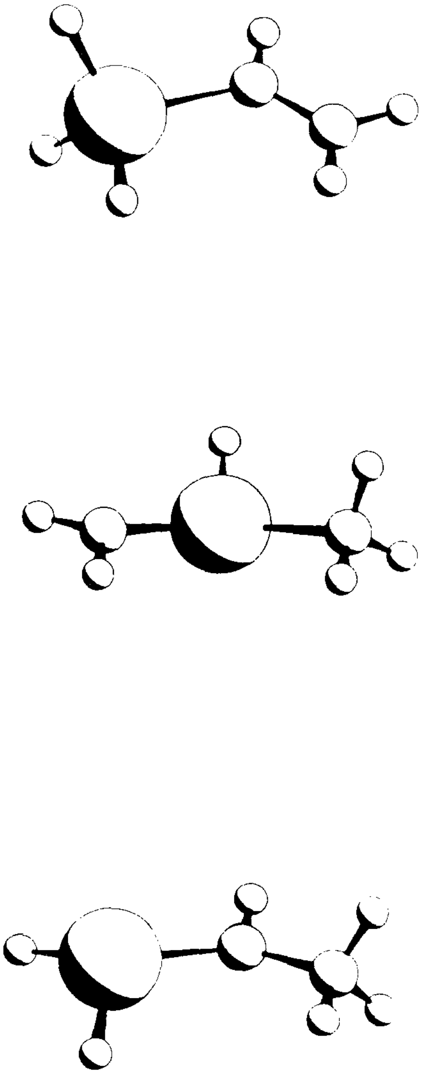


Fig. 1. HF-SCF optimized geometries of vinylstannane $SnH_3CH{=}CH_2$ (**1**), $CH_2{=}SnHCH_3$ (**2**) and $SnH_2{=}CHCH_3$ (**3**).

The eclipsed isomer appears to be slightly more stable than the bisected one, and structural characterization of the latter shows that it is not a minimum but a transition state with a low imaginary frequency associated with a rotation around the Sn–C axis. This higher stability of the eclipsed form has already been observed in the alkene series [16] and a hyperconjugative explanation in molecular orbital terms has been proposed [19].

The low rotational barrier, 0.91 kcal $mol^{-1}$ is slightly higher than that of methylstannane, 0.65 kcal $mol^{-1}$ [17], although this value is considerably lower than that of its homologue propene (about 2 kcal $mol^{-1}$), showing that the rotation around the Sn–C bond is less hindered than around the C–C, consistent with chemical intuition.

In Table 1, the $f_{Sn-C}$ and the $f_{C=C}$ stretching force constants and the associated vibrational frequencies are also reported. The value of $f_{Sn-C}$ is 2.635 mdyn

Table 2
Selected structural parameters and energies of $CH_2=SnHCH_3$ isomers

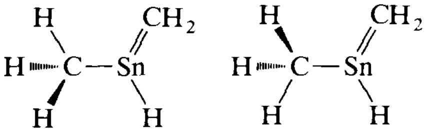
| | Eclipsed | Bisected |
|---|---|---|
| $E$ | −82.39931 | −82.39874 |
| $\Delta E$ | 0.36 | |
| $r_{Sr=C}$ | 1.9375 | 1.9377 |
| $r_{C-Sn}$ | 2.1327 | 2.1359 |
| $<CSnC$ | 125.0 | 124.9 |
| $f_{Sn=C}$ | 4.672 | 4.668 |
| $f_{C-Sn}$ | 2.444 | 2.438 |
| $\omega_{Sn=C}$ | 793 | 792 |
| $\omega_{C-Sn}$ | 553 | 552 |

For units, see footnotes to Table 1.

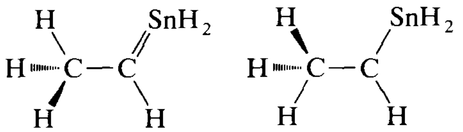
Å$^{-1}$, close to that computed for methylstannane (2.780 mdyn Å$^{-1}$) [18], and almost the same whatever rotamer is being considered.

### 3.2. $CH_2=SnHCH_3$ and $SnH_2=CHCH_3$ isomers

Interchanging the central carbon and tin atoms in vinylstannane gives methylene(methyl) stannane $CH_3=SnHCH_3$, (**2**) for which two structures are also expected, eclipsed and bisected:



However, a shift of one of the tin hydrogen atoms of vinylstannane to the terminal carbon leads to the ethylenic derivative of stannane $SnH_2=CHCH_3$ (**3**) also with two possible rotamers.



Optimized structural parameters for these compounds are reported in Table 2 and 3. As can be seen, eclipsed rotamers are also more stable than the bisected ones, the rotational barriers being 0.36 kcal mol$^{-1}$ for compound **2** and 2.16 kcal mol$^{-1}$ for compound **3**. The first value essentially corresponds to rotation around the Sn–C single bond and the second to rotation around a C–C bond, consistent with the value given above for propene. When the total energies of the eclipsed isomers of **1**, **2** and **3** are compared, it appears that vinylstannane (**1**) is by far the most stable, the relative energies of **2** and **3** being 16.4 and 26.5 kcal mol$^{-1}$.

Table 3
Selected structural parameters and energies of $SnH_2=CHCH_3$ isomers

| | Eclipsed | Bisected |
|---|---|---|
| $E$ | −82.38311 | −82.37967 |
| $\Delta E$ | 2.16 | |
| $r_{SnC}$ | 1.9436 | 1.9454 |
| $r_{CC}$ | 1.5182 | 1.5252 |
| $<SnCC$ | 127.7 | 129.1 |
| $f_{SnC}$ | 4.539 | 4.557 |
| $f_{CC}$ | 5.171 | 5.136 |
| $\omega_{SnC}$ | 695 | 692 |
| $\omega_{CC}$ | 1185 | 1169 |

For units, see footnotes to Table 1.

From a structural point of view, the most outstanding characteristic of compounds **2** and **3** is a tin–carbon double bond. As can be seen from Tables 2 and 3, the Sn–C distance is about 1.93–1.94 Å, i.e. 0.2 Å shorter than in vinylstannane, consistent with a strengthening of the tin–carbon bond. This effect is clearly observed in the diagonal force constants and associated vibrational frequencies. Thus, both the stretch force constant $f_{Sn=C}$ and the associated vibrational frequencies are considerably higher than those of vinylstannane (4.6–4.7 mdyn Å$^{-1}$ and 695–793 cm$^{-1}$).

The presence of a multiple bond involving tin is of prime interest because of its well-known tendency to undergo out-of-plane distortions. To rationalize this behaviour, a criterion that relates the existence of such distortions to the single–triplet separation $\Delta E_{ST}$ of its constituents and to the double bond energy $E(\sigma + \pi)$ has been proposed [6]. According to these models, the double bond in a compound such as $R_2X=YR'_2$ should distort *trans*-bent when the sum of the single–triplet gaps of $XR_2$ and $YR'_2$ fragments is larger than half the $\sigma + \pi$ X=Y bond energy. For the sake of simplicity, the model has been applied here to the simplest compound showing a tin–carbon double bond, $SnH_2CH_2$. Taking the values reported in Ref. [7], for the single–triplet separation of $CH_2$ and $SnH_2$ ($\Delta E_{ST}(CH_2) = -9$ kcal mol$^{-1}$ and $\Delta E_{ST}(SnH_2) = 23$ kcal mol$^{-1}$), i.e. $\Sigma \Delta E_{ST} = 12$ kcal mol$^{-1}$, and assuming that $E(\sigma + \pi)$ is only slightly lower than $GeH_2=CH_2$ (45–52 kcal mol$^{-1}$) [6], the model predicts a planar structure for the tin–carbon double bond. This prediction is fully confirmed by the calculations reported in Table 4 where results obtained from both SCF and correlated levels (CASSCF and second order Möller-Plesset perturbation, MP2) are given [20]. By these calculations, whatever the theoretical method the structure of $SnH_2CH_2$ is found to be planar. Since methylation of either $SnH_2$ or $CH_2$ is

Table 4
Selected structural parameters and energies of $SnH_2=CH_2$

| | RHF-SCF | CASSCF | MP2 |
|---|---|---|---|
| $E$ | −43.36339 | −43.39825 | −43.53415 |
| $r_{SnC}$ | 1.9359 | 1.9919 | 1.9856 |
| $f_{SnC}$ | 4.698 | 3.265 | 3.665 |
| $\omega_{SnC}$ | 802 | 681 | 693 |

For units, see footnotes to Table 1.

not expected to induce significant changes in the singlet–triplet separations, compounds **2** and **3** are expected to be planar, consistent with our results.

### 3.3. $SnH_2CHCH_2$ and $CH_2SnHCH_2$ allyl-like species

The elimination of a hydrogen atom from compounds **1** (or **3**) and **2** gives two structures closely related to the allyl system, $CH_2CHCH_2$, in which either the central or a terminal carbon atom has been replaced by a tin atom. Because such pseudo-allylic species may be intermediates in organic and organometallic synthesis, a theoretical analysis has been performed. In order to handle properly the problem associated with the well-known double instability of the allylic radical, a multiconfigurational wavefunction has been used in these calculations [21]. The configurations included were obtained by distributing the $\pi$-system electrons among the three low-lying $\pi$ orbitals: bonding, non-bonding and anti-bonding in all possible ways (CASSCF). The number of electrons was 2, 3 or 4 according to the nature of the pseudo-allyl species considered, cation, radical or anion.

In Tables 5 and 6, energies and selected structural parameters for these compounds are reported, and, in Fig. 2, the optimized geometries are drawn. Labels **1** or **2** refer to a species obtained from compound **1** or **2** (i.e. with a terminal or central tin atom). Labels **c**, **r**, and **a** refer to cation, radical and anion.

The cations **1c** and **2c** have their heavy atoms in a plane while both radicals and anions are distorted to some degree. The wagging angles $\delta_{Sn}$ are 55° and 83° for radical and anion of compound **1**, respectively. The addition of electrons to **1c** leads to a clear weakening of the bond between the tin and carbon atoms, as shown by the lowering of the bond order and the force constant $f_{Sn-C}$ and, the lengthening of the bond distance. Analysis of the wavefunction shows that on going from **1c** to **1a** there is a drop in s character in the tin–carbon bond consistent with the increase in $\delta_{Sn}$. In the anion **1a**, the tin bonds to the carbon atom through almost pure p orbitals. With these considerations, and taking into account that there is no significant distortion about the carbon bound to tin, these structures

Table 5
Selected structural parameters and energies of $SnH_2CHCH_2$ allyl-like species (cation, radical, and anion)

| | **1c** | **1r** | **1a** |
|---|---|---|---|
| $E$ | −81.62244 | −81.86041 | −81.86931 |
| Symmetry | $C_s$ | $C_1$ | $C_1$ |
| $r_{SnC}$ | 2.0609 | 2.1200 | 2.2409 |
| $r_{CC}$ | 1.3633 | 1.3615 | 1.3463 |
| $<$SnCC | 121.5 | 123.9 | 127.9 |
| $f_{SnC}$ | 2.9151 | 2.5241 | 1.5491 |
| $f_{CC}$ | 9.226 | 9.297 | 10.268 |
| $\omega_{SnC}$ | 617 | 499 | 411 |
| $\omega_{CC}$ | 1516 | 1396 | 1401 |
| $\delta(SnH_2)$ | 0 | 55.0 | 82.8 |
| $\delta$(CHC) | 0 | 1.3 | 3.6 |
| Bond order (SnC) | 1.029 | 0.877 | 0.666 |
| Bond order (CC) | 1.547 | 1.658 | 1.866 |

For units, see footnotes to Table 1.

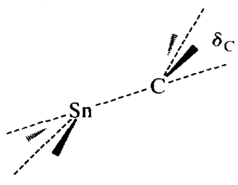


Table 6
Selected structural parameters and energies of $CH_2SnHCH_2$ allyl-like species (cation, radical, and anion)

| | **2c** | **2r** | **2a** |
|---|---|---|---|
| $E$ | −81.55533 | −81.80773 | −81.79114 |
| Symmetry | $C_{2v}$ | $C_s$ | $C_s$ |
| $r_{SnC}$ | 2.0408 | 2.0477 | 2.0089 |
| $<$SnCC | 117.8 | 118.1 | 133.5 |
| $f_{SnC}$ | 3.321 | 2.580 | 3.490 |
| $\omega_{SnC}$ | 647 | 586 | 686 |
| $\delta$(SnHC) | 0 | 35.3 | 19.3 |
| $\delta(CH_2)$ | 0 | 15.6 | 18.0 |
| Bond order (SnC) | 1.105 | 1.159 | 1.399 |

For units, see footnotes to Table 1.

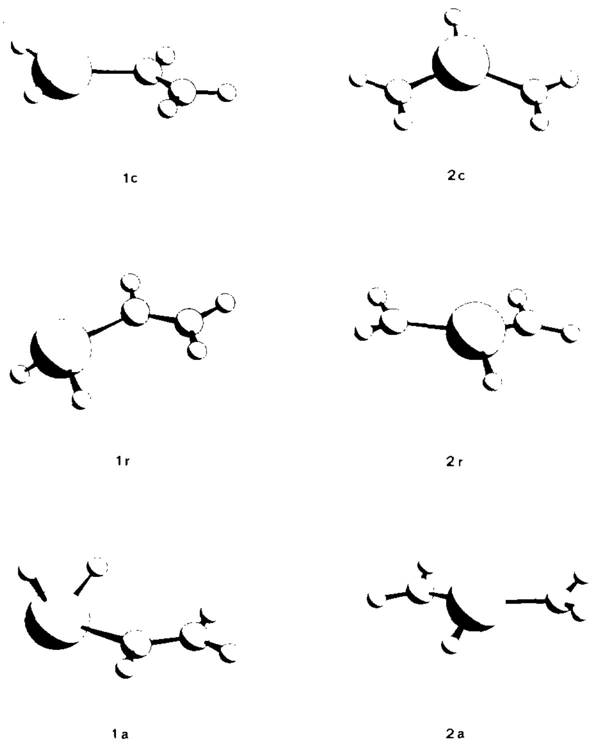


Fig. 2. MC-SCF optimized geometries of cation, radical and anion of allyl-like structures $SnH_2CHCH_2$ (**1c**, **1r**, **1a**) and $CH_2SnHCH_2$ (**2c**, **2r**, **2a**).

could be described more as a localized (vinyl)tin derivatives rather than ally-like delocalized structures.

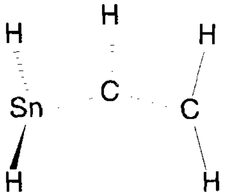
Concerning type **2** species, their behavior appears to be quite different, since on going from **2c** to **2r**, there is a significant distortion from planarity in both the tin and the carbon (35° and 16°, respectively). The force constant $f_{SnC}$ also drops considerably, although the Sn $\sim$ C distance lengthens only slightly. However, preliminary results for anion **2a** appeared surprising because the wavefunction of this compound shows a strong instability, which tends to localize a bond on one side of the molecule, thus leading to structures in which the two tin $\sim$ carbon bonds are inequivalent.

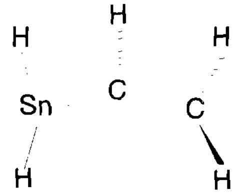
In order to analyze this problem more deeply, we summarize the results obtained for these compounds at the HF-SCF and the MC-SCF levels. Compounds **1c** and **2c** are planar at both levels of calculation. Planar compounds **1r** and **2r**, as well as **1a**, are first-order stationary points at both the HF-SCF and MC-SCF levels. The normal mode associated with the imaginary frequency corresponds to pyramidalization of tin. Optimization of these compounds without restrictions lends to distorted structures whatever is the level of calculation. The HF-SCF optimized geometries are close to those reported in Tables 5 and 6 and in Fig. 2. Compound **2a** in its planar form is a true minimum at the HF-SCF level. However, at the MC-SCF level two imaginary frequencies are found one corresponding to tin pyramidalization (268 cm$^{-1}$), and the other (1336 cm$^{-1}$) corresponding to distortion of Sn–C bond distances and H–Sn–C bond angles, making the two CH$_2$ groups non-equivalent. The calculations showed that the selected MC-SCF space was unstable with respect to substitution of one of the occupied $\pi$-orbitals by a $\sigma_{Sn-C}$ orbital.

This, produced by the analytical–numerical procedure used, leads a preferential localization of electronic density in one of the $\sigma_{Sn-C}$ bonds with additional stabilization. This instability can be overcome, either by introducing into the active space of the MC-SCF wavefunction the two occupied $\sigma_{Sn-C}$ orbitals as well as their antibonding partners, or by forcing the nature of the active space to remain unchanged. For the sake of comparison, the latter possibility seems to be preferable, and with this aim, computations for compound **2a** were performed with the First Order CAS-SCF (FOCAS) [15] technique with level shift that allowed us to retain the $\pi$-orbitals in the active space.

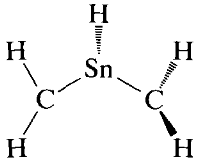
FOCAS-SCF calculations on the planar structure of compound **2a** showed it to be a first order stationary point, the imaginary frequency being 213 cm$^{-1}$ and effectively associated with a pyramidalization of the tin atom. When, a FOCAS-SCF geometry optimization of this compound is performed without $C_{2v}$ constraint, a true minimum of $C_s$ symmetry, moderately distorted, is found ($\delta_{Sn}$ = 19°, $\delta_c$ = 18°).

A final property of these pseudo-allyl compounds that was examined concerns the rotation barriers of the terminal XH$_2$ groups. Compounds of type **1** have two possibilities depending on whether the rotating group is CH$_2$ or SnH$_2$.





Compounds of type **2** have only one rotamer, corresponding to the rotation of a CH$_2$.



Since the interest of these rotations is the insight they give into the energetic cost owing to the loss of delocalization when the planar structure is broken, our analysis was limited to cations **1c** and **2c**. In compound **1c** the calculated barriers for rotation of CH$_2$ and SnH$_2$ are 63 and 8 kcal/mol$^{-1}$, respectively, while the rotation barrier in compound **2c** is 18 kcal mol$^{-1}$. For the allyl cation, this is reported to be about 35 kcal mol$^{-1}$ [22]. In the allylic system, rotation of a CH$_2$ leads to the loss of delocalization energy and half a $\pi$-bond but there is reinforcement of the remaining $\pi$-system. In compound **1c** there is a $\pi$-bond essentially localized on the vinyl group. In fact, as stated above, this structure can be described as a vinyl group bound to SnH$_2^+$. When SnH$_2$ group rotates there is only a small loss of delocalization energy. However, when CH$_2$ rotates, the C–C double bond is broken and there is no possibility of a significant stabilization by an enhancement of the Sn–C bond because this $\pi$-bond is intrinsically weak. On the other hand, in compound **2c**, there is no effect of a localized bond and this compound seems to be more similar to allyl cation although, of course, the Sn–C bond is less strong. Thus, rotation of CH$_2$ means breaking a weak bond and loss of a small delocalization energy as well as a reinforcement of a weak bond.

## 4. Conclusions

In this paper we have analyzed the structure of vinylstannane SnH$_3$CH=CH$_2$ and related isomers using ab initio HF-SCF calculations. Vinylstannane shows a propene-like structure with a tin–carbon bond strength close to that of methylstannane. Like propene, the eclipsed rotamer is more stable than the bisected one, although the energy difference is lower and of the same order as the rotational barrier connecting eclipsed and staggered forms of methylstannane.

As in vinylstannane, in the isomers $CH_3SnH{=}CH_2$ and $SnH_2{=}CHCH_3$, the eclipsed rotamers are also more stable than bisected ones. These structures are found to be undistorted, consistent with the $\Delta E_{ST}-E(\sigma + \pi)$ model.

Allyl-like species of structure $SnH_2CHCH_2$ and $CH_2SnHCH_2$ have also been analyzed. The cations of all these species are planar, whereas radicals and anions prefer distorted structures. In $SnH_2CHCH_2$ there is no distortion at the carbon atom, the ethylene group remains almost unchanged, suggesting that this compound would be better described as a localized, highly distorted vinyltin derivative.

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## Supplementary Material

Force constants in internal coordinates and vibrational frequencies as well as charge and bond orders for all compounds considered here are available from the authors on request.

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