Effects of Substituents on Arsenic−Tin Triple Bonds: A Theoretical Study

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The potential energy surface for the unimolecular rearrangement XSn≡As → TS → Sn═AsX was investigated using the B3LYP and QCISD methods. To explore electronic effects on the relative stability of XSn≡As and Sn═AsX, first-row substituents (X = H, Li, BeH, BH_2, CH_3, NH_2, OH, and F) have been used. Our theoretical findings suggest that the double bonded Sn═AsX species are always kinetically and thermodynamically more stable than the triply bonded XSn≡As isomers, regardless of the electronegativity of substituent X. Nevertheless, our model calculations based on the ONIOM(B3LYP/LANL2DZ:PM3) method indicate that an aryl group can, if sufficiently bulky, stabilize triply bonded XSn≡As molecules with respect to both isomerization and polymerization. That is to say, it is not electronic effects but steric effects that play a decisive role in stabilizing the Sn≡As triple bond.

I. Introduction

Our knowledge of molecular species exhibiting multiple bonds to tin has expanded greatly over the last 15 years because of both experimental progress and improvements in theoretical methods.[1] Above all, kinetic stabilization by bulky substituents on the tin atoms of >Sn═C< (stannene),[2] >Sn═Sn< (distannene),[3] and >Sn═P− (stannaphosphene)[4] has enabled the synthesis and isolation of numerous compounds that possess "formal" doubly bonded tin atoms. Nevertheless, in contrast to the extensive studies of doubly bonded tin chemistry, very little is known about triply bonded tin compounds. In addition, compounds that feature double bonds to arsenic are of current interest.[5] In the past decade, there have been some successful examples of the stabilization of arsethene (>C═As−)[6] and arsasilene (>Si═As−)[7] by taking advantage of steric protecting groups. However, the only evidence for triple bonds containing arsenic has recently been reported for arsaethyne (−C≡As).[8]

In this work, we therefore thought it might be of some interest to examine theoretically the existence and relative stabilities of arsenic−tin triply bonded systems. In view of the interest in stabilizing an arsenic−tin triple bond, it is important to consider the possibility of stabilizing this moiety using substituents. Indeed, it has been shown that in many of the multiply bonded systems the substituent attached to these compounds plays a prominent role in determining the nature of the resulting products in terms of the conformation, isomerization, and steric and electronic properties.[9,10] As a result, to gain new insight into the extent of double and triple bonds in compounds of arsenic and tin with elements of the second row, we have undertaken a theoretical investigation of an entire set of X−Sn≡As and Sn═As−X (X = H, Li, BeH, BH_2, CH_3, NH_2, OH, and F) molecules. All of these species are presently unknown but appear to offer good prospects for experimental observation. All details of the quantum chemical procedures employed in this study are given in the Theoretical Section at the end of this paper.

II. Results and Discussion

To investigate the relative stability of X−Sn≡As and Sn═As−X species, we have chosen the model reaction of eq 1:

$$XSn{\equiv}As \rightarrow TS \rightarrow Sn{=}AsX \qquad (1)$$

Selected geometrical parameters calculated at both the B3LYP/LANL2DZ and QCISD/LANL2DZ+dp levels of theory for the unimolecular isomerization reaction (eq 1) are collected in Table 1. The calculated vibrational frequencies, rotational constants, dipole moments, and net atomic charges of the above stationary points are listed in Table 2. Moreover, the results of our theoretical study of eq 1 are summarized in the reaction profiles in Scheme 1. As can be seen from Tables 1 and 2 and Scheme 1, the geometical parameters as well as the relative energies of the AsSnX isomers are quite similar at the different computational levels employed. Accordingly, unless otherwise noted, we shall use only the QCISD results in the following discussion for the sake of convenience.

As Table 1 shows, the structures of substituted Sn═As−X are strongly dependent on the substituent X. With electropositive substituents (e.g., X = Li, BeH, and BH_2), the Sn═As bond length is considerably shorter by 0.025−0.056 Å relative to that in the parent molecule (i.e., Sn═As−H). In contrast, electronegative substituents (e.g., X = CH_3, NH_2, OH, and F) result in a longer Sn═As bond. For instance, the results reported in Table 1 show that electronegative substituents elongate the Sn═As bond by 0.013−0.050 Å with respect to that of Sn═As−H. We attribute this effect to the inherent polarity of the bond. Namely, it is well known that arsenic ($y = 2.0$) is more electronegative than tin ($y = 1.8$).[11] The Sn═As bond is therefore expected to be polarized in the sense of $Sn^{\delta+}{=}As^{\delta-}$. Indeed, our QCISD calculations show that the arsenic atom of Sn═As−H carries a negative atomic change (−0.31), whereas the tin atom has a positive atomic charge (+0.30). As a result, substituents that increase the Sn═As bond polarization shorten this bond. Our model calculations confirm this prediction. As already shown above, the electron-donating substituents, in particular, Li, increase the negative charge on arsenic (indicated in Table 2 by the calculated net atomic charge) and thus the polarity of

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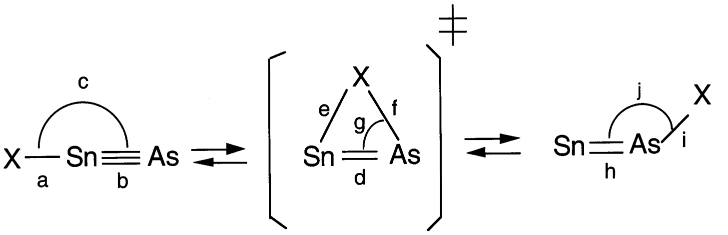
TABLE 1: Geometrical Parameters of Structures for Equation 1 at the QCISD/LANLADZ+dp and B3LYP/LANL2DZ[a] Levels of Theory[b]



(1)

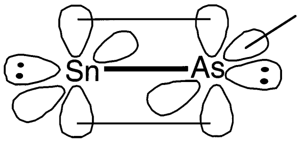
X	a	b	c	d	e	f	g	h	i	j
H	1.728	2.331	180.0	2.464	1.795	2.874	38.33	2.479	1.570	76.55
	(1.710)	(2.345)	(180.0)	(2.511)	(1.774)	(3.305)	(35.76)	(2.527)	(1.565)	(87.46)
Li	2.650	2.357	179.7	3.132	2.682	2.382	56.25	2.423	2.440	80.84
	(2.640)	(2.366)	(179.9)	(2.388)	(2.643)	(4.408)	(30.46)	(2.446)	(2.428)	(89.85)
BeH	2.378	2.342	180.0	2.412	2.389	3.866	36.16	2.445	2.119	82.75
	(2.360)	(2.346)	(180.0)	(2.318)	(2.387)	(3.741)	(37.96)	(2.471)	(2.123)	(92.56)
BH_2	2.243	2.342	179.9	2.425	2.313	2.995	49.14	2.454	2.020	102.1
	(2.213)	(2.357)	(179.2)	(2.458)	(2.315)	(3.013)	(48.77)	(2.460)	(2.004)	(115.6)
CH_3	2.148	2.343	178.1	2.470	2.299	3.201	45.62	2.492	2.036	115.8
	(2.147)	(2.343)	(180.0)	(2.523)	(2.282)	(3.299)	(43.68)	(2.492)	(2.036)	(115.8)
NH_2	1.998	2.471	112.0	2.608	2.058	3.173	40.23	2.529	1.838	111.8
	(1.983)	(2.532)	(111.5)	(2.678)	(2.025)	(3.272)	(38.18)	(2.574)	(1.849)	(112.7)
OH	1.937	2.339	178.4	2.619	1.991	3.032	40.43	2.506	2.010	60.16
	(1.900)	(2.369)	(169.2)	(2.708)	(1.944)	(3.357)	(35.39)	(2.562)	(2.079)	(54.94)
F	1.874	2.341	180.0	2.623	1.930	3.155	37.62	2.508	1.981	59.23
	(1.901)	(2.368)	(172.7)	(2.690)	(1.950)	(3.404)	(34.88)	(2.566)	(2.091)	(54.71)

[a] In parentheses. [b] Distance in Å, angles in degrees.

the Sn═As bond. Therefore, this bond is shorter than in Sn═As−H. By contrast, when an electronegative substituent is attached to the arsenic atom, the negative charge on this atom (see Table 2) decreases because of the electron-withdrawing effect of the substituent. This reduces the Sn═As bond polarity and thus lengthens this bond when compared to that of Sn═As−H. In any event, the Sn═As double-bond lengths were calculated to be in the range of 2.446−2.574 Å and 2.423−2.529 Å at the B3LYP/LANL2DZ and QCISD/LANL2DZ+dp levels of theory, respectively.

However, it is seen readily from Table 1 that the Sn≡As triple-bond length in X−Sn≡As is always longer than that in the parent H−Sn≡As molecule. Our B3LYP/LANL2DZ calculations estimate the Sn≡As triple-bond length to be in the range of 2.343−2.532 Å, whereas the QCISD/LANL2DZ+dp results are anticipated to be 2.331−2.471 Å.

The most noteworthy feature of the doubly bonded Sn═As−X molecules is the bond angle at arsenic. Our B3LYP and QCISD calculations reveal that the Sn═As−X compounds are strongly bent in their singlet states, whereas the X−Sn≡As species exist as stable linear molecules, as shown in Table 1. In the present study, all linear Sn═As−X molecules were found to be transition structures with two imaginary frequencies at both DFT and ab initio levels. The reason that the Sn═As−X doubly bonded compound favors a bent over a linear structure can be traced to the "orbital nonhybridization effect", also known as the "inert s-pair effect".[12] As is well known, arsenic (as well as tin) has a low tendency to form hybrid orbitals with high p character because of the size difference between the valence s and p atomic orbitals. Accordingly, whereas olefinic double bonds are considered to feature sp^2-hybridized carbon atoms, it would appear that in heavy main-group element chemistry a tendency toward sp hybridization occurs on going from carbon to arsenic (i.e., form **1** over form **2**). As mentioned above, this may reflect the emergence of an orbital nonhybridization effect on moving from carbon to arsenic, where sp hybridization is preferred to sp^2.[13−17]



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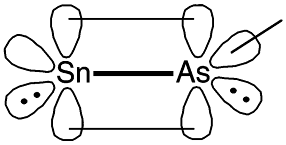

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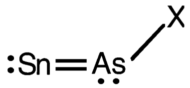
Furthermore, from a valence bond perspective, the formation of an sp^2-hybrid orbital is disfavored, and bent Sn═As−X (**3**) becomes considerably more stable than its linear structure (**4**). In fact, as mentioned previously, it is well established that the electronegativity of arsenic is larger than that of tin.[11] This makes it difficult for arsenic to donate a lone pair of electrons to tin, and thus the contribution from linear form **4** will be small. Considering the above results, we therefore conclude that the best representation of the Sn═As−X species should be the bent form, as shown in **3**.



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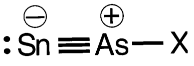

$:\overset{\ominus}{Sn}\equiv\overset{\oplus}{As}-X$

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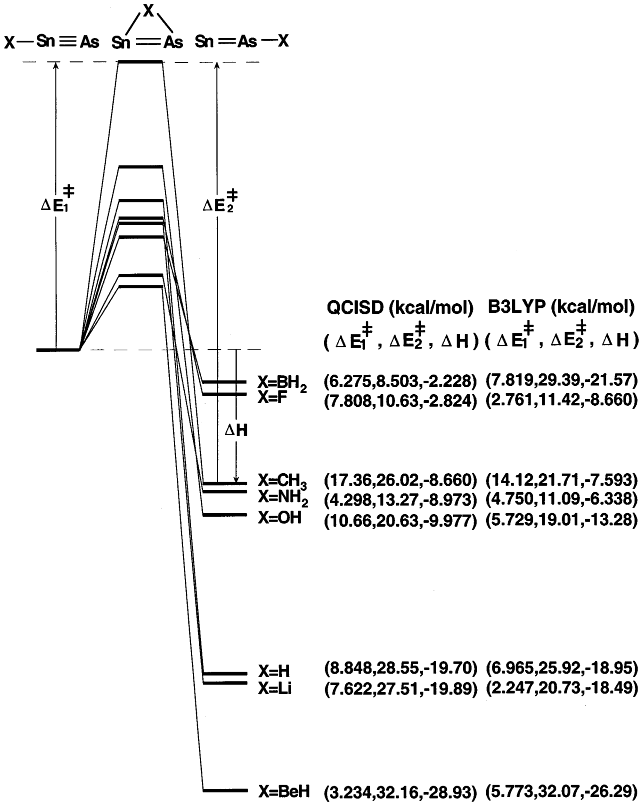
The other feature of interest concerns the relative stability of Sn═As−X doubly bonded and X−Sn≡As triply bonded spe-

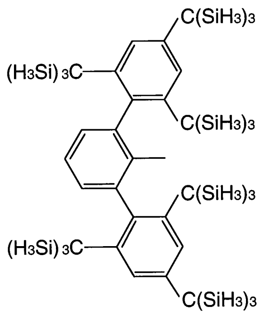
TABLE 2: Calculated Harmonic Vibrational Frequencies (cm^{-1}), IR Intensities (km/mol), Rotational Constants (GHz), Dipole Moments (Debye), and Net Atomic Charges of the Stationary Points in XSnAs Isomerization Reactions (Equation 1) at the QCISD/LANL2DZ+dp Level of Theory

species	frequencies (IR intensities)	rotational constants	dipole moments	*q*(Sn)	*q*(As)	*q*(X)	species	frequencies (IR intensities)	rotational constants	dipole moments	*q*(Sn)	*q*(As)	*q*(X)
$HSn\equiv As$	323 (3.6)	A. 1.97594	2.179	0.145	−0.157	0.011	$HSn\equiv As$	1921 (2.2)					
	472 (2.1)												
HSnAs-TS	281, 1689, 208i												
$Sn{=}AsH$	274 (3.0)	A. 207.77728	2.792	0.296	−0.309	0.013	$Sn{=}AsH$	2112 (61)	C. 1.70105				
	634 (13)	B. 1.71509											
$LiSn\equiv As$	106 (32)	A. 577374.38421	10.55	0.049	−0.280	0.231	$LiSn\equiv As$	420 (157)					
	314 (32)	B. 1.48443											
LiSnAs -TS	279, 473, 228i												
$Sn{=}AsLi$	159 (16)	A. 13.31159	5.907	0.063	−0.270	0.207	$Sn{=}AsLi$	458 (124)	C. 1.59709				
	307 (7.3)	B. 1.81483											
$HBeSn\equiv As$	139 (1.6)	A. 1.38629	2.591	0.042	−0.181	0.094(Be)	$HBeSn\equiv As$	677 (70)					
	324 (1.8)		1.976	0.190	−0.250	0.045(H)		681 (69)					
	504 (90)							2244 (54)					
HBeSnAs -TS	265, 460, 463, 469,												
	2144, 77i												
$Sn{=}AsBeH$	201 (7.3)	A. 10.86428				0.032(Be)	$Sn{=}AsBeH$	679 (53)					
	302 (5.6)	B. 1.73845				0.028(H)		689 (39)					
	583 (60)	C. 1.49864						2208 (57)					
$H_2BSn\equiv As$	142 (0.75)	A. 227.15686	2.659	0.161	−0.201	−0.149(B)	$H_2BSn\equiv As$	1023 (8.3)					
	155 (0.28)	B. 1.32982				0.095(H)		1151 (71)					
	322 (0.50)	C. 1.32208						2747 (80)					
	494 (20)							2842 (9.1)					
	787 (0.15)												
H_2BSnAs -TS	87, 281, 423, 562, 805,												
	1090, 2607, 2747, 107i						$Sn{=}AsBH_2$	801 (1.8)					
$Sn{=}AsBH_2$	178 (0.39)	A. 10.98924	1.710	0.195	−0.307	0.152(B)		1028 (8.6)					
	291 (3.6)	B. 1.51675				−0.020(H)		1217 (135)					
	593 (42)	C. 1.34840						2680 (2.6)					
	722 (0.20)							2770 (37)					
$H_3CSn\equiv As$	140 (0.52)	A. 153.35075	3.640	0.326	−0.203	−0.855(C)	$H_3CSn\equiv As$	1316 (0.51)					
	155 (0.52)	B. 1.29528				0.244(H)		1507 (4.4)					
	317 (0.85)	C. 1.29512						1508 (4.3)					
	530 (0.21)							3186 (322)					
	939 (2.5)							3293 (15)					
	940 (2.5)							3293 (15)					
H_3CSnAs -TS	285, 399, 575, 901, 912,												
	1265, 1497, 1511, 3188,						$Sn{=}AsCH_3$	1008 (1.6)					
	3298, 3305, 95i		2.180	0.225	0.162	−0.727(C)		1375 (2.8)					
$Sn{=}AsCH_3$	159 (0.96)	A. 8.67325				0.222(H)		1511 (1.4)					
	294 (0.93)	B. 1.57654						1529 (2.3)					
	540 (0.55)	C. 134557						3130 (69)					
	599 (0.12)							3241 (36)					
	983 (2.6)							3286 (8.0)					
$H_2NSn\equiv As$	170 (1.3)	A. 10.87079	2.374	0.513	−0.182	−1.057(N)	$H_2NSn\equiv As$	934 (3.3)					
	276 (0.09)	B. 1.51253				0.363(H)		1631 (19)					
	619 (22)	C. 1.32779						3735 (615)					
	645 (216)							3845 (101)					
	768 (5.2)												
H_2NSnAs -TS	146, 265, 365, 552, 664,												
	1618, 3507, 3626, 322i						$Sn{=}AsNH_2$	755 (0.78)					
$Sn{=}AsNH_2$	200 (7.3)	A. 13.79875	1.522	0.114	0.078	−0.911(N)		1043 (4.4)					
	268 (0.09)	B. 1.32972				0.360(H)		1654 (43)					
	505 (265)	C. 1.21285						3666 (140)					
	719 (46)							3853 (218)					
$HOSn\equiv As$	156 (6.1)	A. 601.69561	2.239	0.578	−0.181	−0.842(O)	$HOSn\equiv As$	611 (83)					
	316 (1.2)	B. 1.33213				0.445(H)		1081 (464)					
	322 (37)	C. 1.32929						3870 (182)					
HOSnAs -TS	115, 219, 538, 760, 3833,												
	139i						$Sn{=}AsOH$	1003 (47)					
$Sn{=}AsOH$	265 (3.9)	A. 10.32483	1.933	0.320	0.018	−0.779(O)		1144 (143)					
	296 (5.9)	B. 1.72155				0.441(H)		3840 (142)					
	505 (48)	C. 1.48143											
$FSn\equiv As$	152 (8.1)	A. 1.31218	0.422	0.697	−0.145	−0.552	$FSn\equiv As$	608 (97)					
	311 (2.5)												
FSnAs -TS	220, 529, 90i												
$Sn{=}AsF$	232 (0.59)	A. 10.28130	2.667	0.397	0.110	−0.508	$Sn{=}AsF$	496 (48)	C. 1.47348				
	290 (2.1)	B. 1.71998											

SCHEME 1



cies. As one can see in Scheme 1, Sn=As−X is estimated to be 2.2−29 kcal/mol below X−Sn≡As at the QCISD level. In addition, the barrier height ($\Delta E_2^{\ddagger}$; see Scheme 1) for the isomerization from Sn=As−X to X−Sn≡As is predicted to be roughly 8.5−32 kcal/mol at the same level of theory. Consequently, the doubly bonded molecule Sn=As−X is both thermodynamically and kinetically more stable than the corresponding X−Sn≡As triply bonded isomer, whatever the nature of substituent X. This shows that arsenic and tin are more reluctant to form triple bonds than double bonds. In other words, electronic effects do not play a role in stabilizing the X−Sn≡As triply bond species relative to its corresponding Sn=As−X isomer. It is therefore important to know whether the X−Sn≡As species are still synthetically accessible and isolatable as stable molecules when they bear sufficiently bulky substituents. Indeed, as stated in the Introduction, several molecules containing a multiply bonded arsenic or tin atom have been successfully synthesized and characterized by taking advantage of kinetic stabilization using bulky substituents.



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To provide a theoretical basis for stabilizing the arsenic−tin triple bond, the effects of bulky aryl groups such as Ar″ = C_6H_3-2,6-{C_6H_2−2,4,6-$C(SiH_3)_3$}$_2$ (see **5**) were investigated using the ONIOM(B3LYP/LANL2DZ:PM3) level of theory. The corresponding relative energies for Ar″AsSn isomers are given in Figure 1. As one can see, our ONIOM results predict that Ar″−Sn≡As is more stable than Sn=As−Ar″ by 25 kcal/mol. That is to say, with sufficiently bulky substituents, the relative stabilities of the doubly bonded Sn=As−X and triply bonded X−Sn≡As species can be dramatically reversed, and the X−Sn≡As → Sn=As−X isomerization becomes quite endothermic. Although we did not locate their isomerization transition states because of the size of the molecules, the fact that bulky substituent can strongly stabilize X−Sn≡As triply bonded species with respect to Sn=As−X doubly bonded species is quite encouraging.

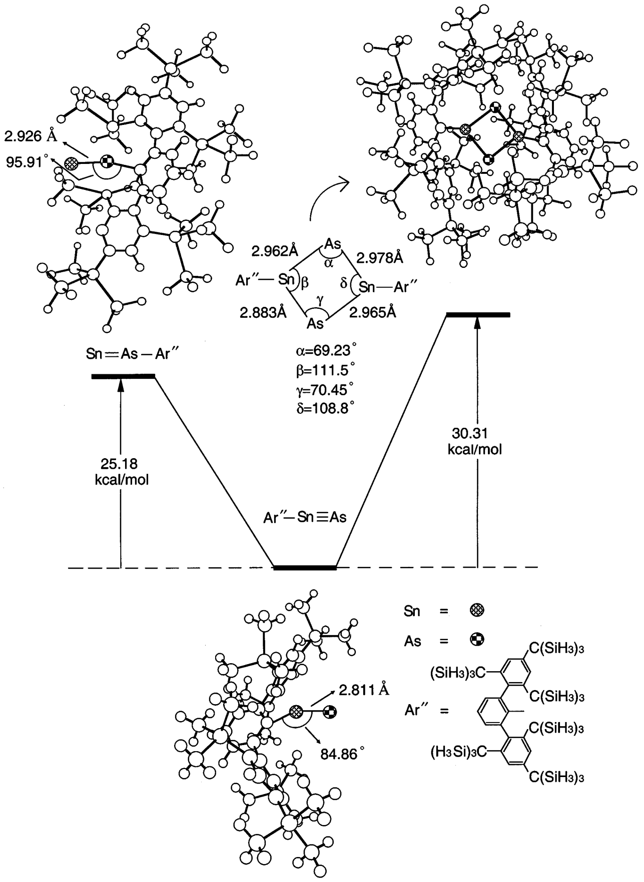

Figure 1. Optimized structures of Ar″Sn≡As (lowest), Sn=AsAr″ (left), and the four-membered-ring dimer (i.e., (Ar″Sn≡As)$_2$, right) at the ONIOM(B3LYP/LANL2DZ:PM3) level. Ar″ stands for C_6H_3-2,6-{C_6H_2-2,4,6-$C(SiH_3)_3$}$_2$.

It has been generally assumed in the past that the major difficulty in preparing molecules with triply bonded arsenic and tin atoms is facile polymerization. For instance, the dimerization of X−Sn≡As can easily lead to a four-membered ring dimer, which prevents the existence of X−Sn≡As as a monomer. To test whether Ar″−Sn≡As is stable with respect to dimerization, calculations were carried out using the ONIOM(B3LYP/LANL2DZ:PM3) method. These results are also illustrated in Figure 1. Calculations with the ONIOM method predict that the enthalpies of dimerization of both Ar″−Sn≡As species are endothermic by 30 kcal/mol. This strongly suggests that Ar″−Sn≡As is stable with respect to dimerization.

III. Conclusions

This work demonstrates how various kinds of substitution influence multiple-bonding preferences. Our model calculations strongly suggest that $\mathrm{Sn{=}As{-}X}$ itself lies at the minimum of the potential energy surface and is always kinetically and thermodynamically more stable than the triply bonded $\mathrm{X{-}Sn{\equiv}As}$ species, regardless of the electronegativity of substituent X. As a consequence, the experimental observation of these doubly bonded species as monomers should be possible either in a low-temperature inert matrix or in the low-pressure gas phase (e.g., as low as 10^{-4} Torr).

Furthermore, our theoretical findings indicate that only steric effects can play an important role in stabilizing the triply bonded $\mathrm{X{-}Sn{\equiv}As}$ with respect to the doubly bonded $\mathrm{Sn{=}As{-}X}$. That is to say, using a sufficiently bulky substituent is necessary both to overturn the intrinsic preference of $\mathrm{Sn{=}As{-}X}$ over $\mathrm{X{-}Sn{\equiv}As}$ and to avoid self-dimerization.

In short, molecules with a multiple bond containing both arsenic and tin are interesting synthetic targets worthy of experimental testing, irrespective of double or triple bonding, when they are appropriately substituted. It is therefore expected that these novel molecules will soon be synthesized in a stable form and open up a new area of both arsenic and tin chemistry.

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Theoretical Procedure

The geometries of all of the stationary points were initially optimized at the B3LYP[18] level of theory and then were fully optimized by using the QCISD(FC)[19] level with relativistic effective core potentials on As and Sn using double-ζ (DZ) basis sets[20] augmented by a set of d-type polarization functions (d exponents 0.303 and 0.180, respectively).[21] The DZ basis sets for the first-row elements[22] were augmented by a set of p-type polarization functions. Namely, the d exponents for Li, Be, B, C, N, O, and F are 0.20, 0.45, 0.70, 0.75, 0.80, 0.85, and 0.90, respectively. Accordingly, all of the B3LYP and QCISD(FC) calculations are denoted by B3LYP/LANL2DZ and QCISD/LANL2DZ+dp, respectively. All of the structures that were obtained were confirmed to be real minimal or transition states via frequency analysis, which was also used to calculate the zero-point energy (ZPE) without scaling. For all of the transition states, motion corresponding to the imaginary frequency was checked visually, and most structures were optimized visually to the minima that they connected after correspondingly perturbing the TS geometry.

The optimized structures for the large systems, such as $\mathrm{XSn{\equiv}As}$ and $\mathrm{Sn{=}AsX}$, and their corresponding four-membered-ring dimers ($\mathrm{X = Ar''}$) were obtained by a two-layered ONIOM approach.[23] The semiempirical PM3 method[24] and the hybrid density functional B3LYP method[18] were employed for the low-level and high-level treatments, respectively. The standard LANL2DZ basis set was used in conjunction with the B3LYP calculation. Geometry optimizations were performed within such an ONIOM(B3LYP/LANL2DZ:PM3) approach using the Gaussian 98 program.[25]

References and Notes

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(13) It is likely that some of the trends that are revealed are influenced by the relativistic contributions from the "heavy" species.[14] The major relativisitic effects for the As and Sn elements were incorporated into the ECPs we used.[20,21]. However, to examine the influence of the relativistic effects on a given molecular property, it is necessary to compare results of relativistic (R) and nonrelativistic (NR) calculatons on that property (e.g., ref 15). We believe that an analysis of this type provides more insight into the periodic trends revealed and discussed in this work. Examples of the comparative NR and R calculations on the group 15 compounds can be found in the recent literature (e.g., ref 16).

(14) The necessity of the relativistic effects for the elucidation of the As−Sn bond was suggested by a reviewer.

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