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Tin Analogues of Alkynes. Multiply Bonded Structures vs Singly Bonded Structures

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Summary: Unlike the recent proposal by Power and co-workers, theoretical calculations show that Ar′SnSnAr′ (Ar′ = C_6H_3*-2,6-(*C_6H_3*-2,6-iPr*$_2$*)*$_2$*) has a multiply bonded structure in solution; the same is also true for the related tin analogues of alkynes.*

Heavier group 14 element analogues of alkynes, REER (E = Si, Ge, Sn, Pb), have long attracted wide interest as challenging synthetic targets in main-group chemistry.[1] Bulky substituent groups play an important role in making REER synthetically accessible and isolable as stable compounds.[2] Thus, the Si,[3] Ge,[4,5] Sn,[6] and Pb[7] analogues of alkynes have been successfully synthesized and isolated by introducing bulky aryl and silyl groups. As verified by X-ray crystal analysis,[3−7] all of these compounds have a trans-bent core skeleton, unlike the alkyne case. Now that all group 14 element analogues have been isolated, it is of interest to characterize the E−E bonding and structures of REER.

A series of recent extensive reactivity studies has shown that Ar′SnSnAr′ (Ar′ = C_6H_3-2,6-(C_6H_3-2,6-*i*Pr$_2$)$_2$) is much less reactive than Ar′GeGeAr′.[8] We have suggested that two different bonding modes are possible for RSnSnR (Figure 1).[2d] Very recently, Power and co-workers have performed calculations for MeSnSnMe[9] and proposed that the lower reactivity of Ar′SnSnAr′ is due to the fact that Ar′SnSnAr′ has a singly bonded structure (S) with small biradical character in solution,[8f,9] though it has a less trans-bent, multiply bonded structure (M) in the X-ray crystal structure.[6]

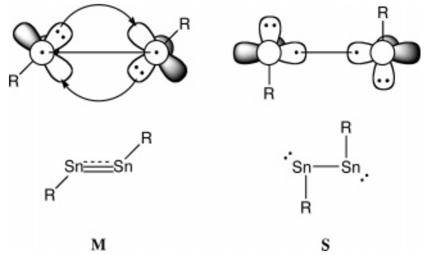

Figure 1. Two bonding modes of RSnSnR.

To confirm the proposal on the basis of the simplified model system (MeSnSnMe), we have carried out calculations for the real system, Ar′SnSnAr′. Geometries were fully optimized without symmetry constraint with hybrid density functional theory at the B3PW91 level[10] using the Gaussian 03 program.[11] The [4333111/433111/43] basis set augmented by two d polarization functions (d exponents 0.253 and 0.078) was used for Sn,[12] while the 6-31G(d) basis set was used for C and H.[13] To improve energies, single-point calculations were also performed using MP2, CCSD(T), and CASSCF(6,6)-MP2 methods available in the Gaussian 03 program.

For the multiply bonded structure (M) of Ar′SnSnAr′ in Figure 2, the orbital analysis shows that the central Sn−Sn bond consists of a somewhat distorted σ bond, a slipped in-plane π_{in} bond (due to the mixing of π_{in} and σ^*), and an unslipped out-of-plane π_{out} bond.[14] The optimized Sn−Sn distance and Sn−Sn−C trans-bent angle (θ) are 2.677 Å and 126.5°, respectively. These (as well as the arrangement of the aryl rings) agree very well with the X-ray crystal data of Sn−Sn = 2.668 Å and θ = 125.2°,[6] unlike our previous calculations at a lower level,[2d] suggesting that the present calculations are reliable. The core skeleton is almost planar, as indicated by the dihedral C−Sn−Sn−C angle (ω) of 179.7°.[15] When the HOMO (π_{out}) and LUMO (π_{in}^*) are switched, a singly bonded structure (S) is located as an energy minimum, as shown also in Figure 2. The distance and angles optimized for structure S are Sn−Sn = 3.100

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(1) For recent reviews, see: (a) Power, P. P. *Chem. Commun.* **2003**, 2091. (b) Weidenbruch, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 2222. (c) Weidenbruch, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 514.

(2) (a) Kobayashi, K.; Nagase, S. *Organometallics* **1997**, *16*, 2489. (b) Nagase, S.; Kobayashi, K.; Takagi, N. *J. Organomet. Chem.* **2000**, *611*, 264. (c) Kobayashi, K.; Takagi, N.; Nagase, S. *Organometallics* **2001**, *20*, 234. (d) Takagi, N.; Nagase, S. *Organometallics* **2001**, *20*, 5498. (e) Takagi, N.; Nagase, S. *Chem. Lett.* **2001**, 966. (f) Takagi, N.; Nagase, S. *Eur. J. Inorg. Chem.* **2002**, 2775. (g) Takagi, N.; Nagase, S. *J. Organomet. Chem.* **2007**, *692*, 217.

(3) Sekiguchi, A.; Kinjo, R.; Ichinohe, M. *Science* **2004**, *305*, 1755.

(4) Stender, M.; Phillips, A. D.; Wright, R. J.; Power, P. P. *Angew. Chem., Int. Ed.* **2002**, *41*, 1785.

(5) Sugiyama, Y.; Sasamori, T.; Hosoi, Y.; Furukawa, Y.; Takagi, N.; Nagase, S.; Tokitoh, N. *J. Am. Chem. Soc.* **2006**, *128*, 1023.

(6) Phillips, A. D.; Wright, R. J.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **2002**, *124*, 5930.

(7) Pu, L.; Twamley, B.; Power, P. P. *J. Am. Chem. Soc.* **2000**, *122*, 3524.

(8) (a) Stender, M.; Phillips, A. D.; Power, P. P. *Chem. Commun.* **2002**, 1312. (b) Cui, C.; Brynda, M.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **2004**, *126*, 6510. (c) Cui, C.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **2004**, *126*, 5062. (d) Spikes, G. H.; Fettinger, J. C.; Power, P. P. *J. Am. Chem. Soc.* **2005**, *127*, 12232. (e) Spikes, G. H.; Peng, Y.; Fettinger, J. C.; Steiner, J.; Power, P. P. *Chem. Commun.* **2005**, 6041. (f) Cui, C.; Olmstead, M. M.; Fettinger, J. C.; Spikes, G. H.; Power, P. P. *J. Am. Chem. Soc.* **2005**, *127*, 17530.

(9) Jung, Y.; Brynda, M.; Power, P. P.; Head-Gordon, M. *J. Am. Chem. Soc.* **2006**, *128*, 7185.

(10) (a) Becke, A. D. *Phys. Rev.* **1988**, *A38*, 3098. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (c) Perdew, J. P.; Wang, Y. *Phys. Rev.* **1992**, *B45*, 13244.

(11) *Gaussian 03*, Revision C.01; Gaussian, Inc.: Wallingford, CT, 2004.

(12) Huzinaga, S.; Andzelm, J.; Klobukowski, M.; Radzio-andzerm, E.; Sakai, Y.; Tatewaki, H. *Gaussian Basis Sets for Molecular Calculations*; Elsevier: Amsterdam, 1984.

(13) Francl, M. N.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; Defrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.

(14) In a donor−acceptor bond model (Figure 1), the Sn−Sn bond is regarded as consisting of two dative bonds and one π bond. For example, see refs 2a and 2b as well as recent papers: Lein, M.; Krapp, A.; Frenking, G. *J. Am. Chem. Soc.* **2005**, *127*, 6290. Landis, C. R.; Weinhold, F. *J. Am. Chem. Soc.* **2006**, *128*, 7335.

(15) An isoenergetic twisted form (Sn−Sn = 2.681Å, θ = 126.0°, ω = 163.8°) was also located as a minimum. However, it was calculated at the MP2 level[16] that the twisted form is 5.2 kcal/mol less stable than the planar form in Figure 2.

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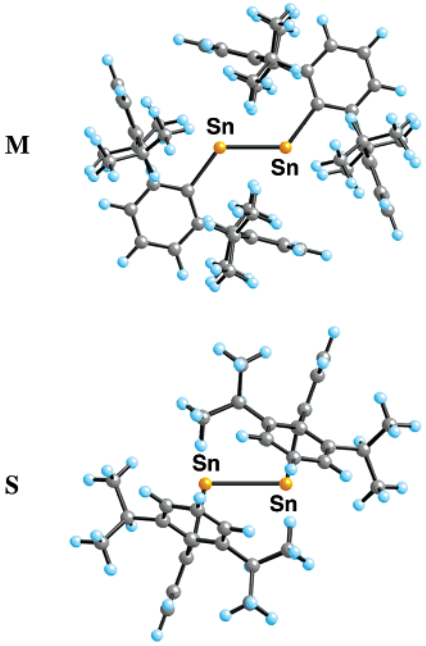

Figure 2. Multiply (M) and singly (S) bonded structures of Ar′SnSnAr′ optimized at the B3PW91 level.

Å, $\theta = 101.7^\circ$, and $\omega = 179.0^\circ$. It is noticeable that structure M is 5.3 kcal/mol more stable than structure S. This energy difference favoring structure M becomes 10.1 kcal/mol at the MP2 level.[16] These results suggest that Ar′SnSnAr′ keeps a multiply bonded structure (M) in solution.

We have also carried out calculations for the model system MeSnSnMe. Unlike the calculations by Power and co-workers,[9] the planar structure S (Sn−Sn = 3.060 Å, $\theta = 93.4^\circ$, and $\omega = 180.0^\circ$) of MeSnSnMe was not located as a minimum but has one imaginary frequency of 83*i* cm^{-1}.[17] In addition, the planar structure was calculated to be 5.6, 12.8, and 10.0 kcal/mol less stable than structure M (Sn−Sn = 2.605 Å, $\theta = 126.3^\circ$, and $\omega = 180.0^\circ$)[18] at the B3PW91, MP2, and CCSD(T) levels, respectively.[19] This trend was further enhanced at the higher CASSCF(6,6)-MP2 level, S being 16.6 kcal/mol less stable than M.[19] The energy differences of 5.6 (B3PW91) and 12.8 kcal/mol (MP2) for MeSnSnMe resemble those of 5.3 (B3PW91) and 10.1 kcal/mol (MP2) for Ar′SnSnAr′. This may allow us to infer that structure M is about 13−14 kcal/mol more stable than structure S for Ar′SnSnAr′ at high levels such as CASSCF-(6,6)-MP2.

UV−vis spectra provide important information (Table 1). For Ar′SnSnAr′, two strong absorptions have been observed at 410 and 597 nm in *n*-hexane solution,[6,20] as in the case of Ar′GeGeAr′ (371 and 501 nm).[4,20] For structure M, the two absorptions were calculated to be at 412 and 649 nm for Ar′SnSnAr′ and at 379 and 534 nm for Ar′GeGeAr′ at the TD-(time-dependent)-B3PW91 level, which are mainly assignable to $\pi_{in}-\pi_{in}^*$ and $\pi_{out}-\pi_{out}^*$ transitions, respectively.[21] For structure S, however, a strong $\pi_{in}^*-\sigma^*$ absorption was calculated to be at 414 nm for Ar′SnSnAr′ and 407 nm for Ar′GeGeAr′.[21] Obviously, these are consistent with the fact that Ar′SnSnAr′ has structure M in solution, as does Ar′GeGeAr′.

Table 1. UV−Vis Absorptions[a] of Ar′EEAr′ Calculated at the TD-B3PW91 Level

	exptl	structure M	structure S
Ar′GeGeAr′	501 (ϵ = 7500)	534 (*f* = 0.069)[b]	407 (*f* = 0.173)
	371 (ϵ = 34000)	379 (*f* = 0.403)	
Ar′SnSnAr′	597 (ϵ = 1700)	649 (*f* = 0.052)	414 (*f* = 0.283)
	410 (ϵ = 4300)	412 (*f* = 0.473)	

[a] Absorptions are given in nm; ϵ values are given in L mol^{-1} cm^{-1}. [b] *f* = oscillator strength.

Addition of one electron to structures M and S of Ar′SnSnAr′ leads to M$^-$ and S$^-$ anions. Key geometrical parameters optimized for the M$^-$ anion are Sn−Sn = 2.743 Å, $\theta = 113.6^\circ$, and $\omega = 177.6^\circ$, while those for the S$^-$ anion are Sn−Sn = 2.872 Å, $\theta = 102.3^\circ$, and $\omega = 180.0^\circ$. The small lengthening (0.066 Å) and large shortening (0.228 Å) of the Sn−Sn distance from 2.677 (M) to 2.743 Å (M$^-$) and from 3.100 (S) to 2.872 Å (S$^-$) reflect the fact that the LUMOs of M and S have small antibonding (slipped π_{in}^*) and large bonding (π_{out}) character between the Sn atoms, respectively. Unlike the neutral case, it was calculated that the S$^-$ anion is 3.3 kcal/mol more stable than the M$^-$ anion.[22] In this context, it is interesting that the distance and angle calculated for the S$^-$ anion are close to those of Sn−Sn = 2.808 Å and $\theta = 97.9^\circ$ in the X-ray crystal structure of the [Ar′SnSnAr′]$^-$[K(THF)$_6$]$^+$ salt.[23] In an attempt to rationalize that Ar′SnSnAr′ has structure S in solution, it has been discussed that the reduction of Ar′SnSnAr′ results in a Sn−Sn bond lengthening that is much larger than the corresponding Ge−Ge lengthening for Ar′GeGeAr′.[8f,9,20,23] This is now explained by the fact that the reduction of Ar′SnSnAr′ does not provide the M$^-$ anion but leads to the S$^-$ anion. Addition of one more electron to the S$^-$ anion of Ar′SnSnAr′ shortens the Sn−Sn distance, unlike the Ar′GeGeAr′ case, since the bonding π_{out} orbital is doubly occupied. This Sn−Sn shortening agrees with the experimental finding.[23]

Very recently, Power and co-workers have suggested that structure S is induced by modifying the Ar′ group.[24] As an interesting example, the X-ray crystal structure of 4-SiMe$_3$-Ar′SnSnAr′-4-SiMe$_3$ (Ar′-4-SiMe$_3$ = C$_6$H$_2$-2,6-(C$_6$H$_3$-2,6-*i*Pr$_2$)$_2$-4-SiMe$_3$) has been reported.[24] The distance and angle of Sn−Sn = 3.066 Å and $\theta = 99.3^\circ$ in the X-ray crystal structure correspond to those expected for structure S and agree reasonably well with the calculated values of Sn−Sn = 3.100 Å, $\theta = 101.6^\circ$, and $\omega = 180.0^\circ$.[25] As Figure 3 shows, however, structure M (Sn−Sn = 2.691 Å, $\theta = 124.9^\circ$, $\omega = 161.9^\circ$) was also located as a minimum. Structure M is 5.4 kcal/mol more stable than structure S. Therefore, it is not surprising that the UV−vis spectrum of 4-SiMe$_3$-Ar′SnSnAr′-4-SiMe$_3$ displays two

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(16) Because of the size of the molecules, the MP2 calculations were carried out using a high-speed parallel algorithm developed recently. For this algorithm and installation in the GAMESS program, see: Ishimura, K.; Pulay, P.; Nagase, S. *J. Comput. Chem.* **2006**, *27*, 407.

(17) This is not very surprising, since the planar structure S of RSnSnR corresponds to the transition state for the inversion of the doubly bridged structure when R is small. In this context, see: Chen, Y.; Hartmann, M.; Diedenhofen, M.; Frenking, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 2052. As is apparent from Figure 2 of ref 9, the planar structure S of MeSnSnMe is not the global minimum.

(18) In contrast, it seems that structure M was not considered by Power and coworkers in ref 9.

(19) Similar results were also obtained using relativistic effective core potentials.

(20) Power, P. P. *Appl. Organomet. Chem.* **2005**, *19*, 488.

(21) The [433111/43111/4] basis set augmented by two d polarization functions (d exponents 0.382 and 0.108) was used for Ge.[12] Geometrical parameters optimized for Ar′GeGeAr′ are Ge−Ge = 2.257 Å, $\theta = 129.4^\circ$, and $\omega = 172.9^\circ$ for structure M and Ge−Ge = 2.757 Å, $\theta = 105.2^\circ$, and $\omega = 171.7^\circ$ for structure S. For Ar′GeGeAr′, structure M is 14.7 kcal/mol more stable than structure S.

(22) For Ar′GeGeAr′, the S$^-$ anion was calculated to be 2.4 kcal/mol less stable than the M$^-$ anion.

(23) Pu, L.; Phillips, A. D.; Richards, A. F.; Stender, M.; Simons, R. S.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **2003**, *125*, 11626.

(24) Fischer, R. C.; Pu, L.; Fettinger, J. C.; Brynda, M. A.; Power, P. P. *J. Am. Chem. Soc.* **2006**, *128*, 11366.

(25) The 6-31G(d) basis set was used for Si.

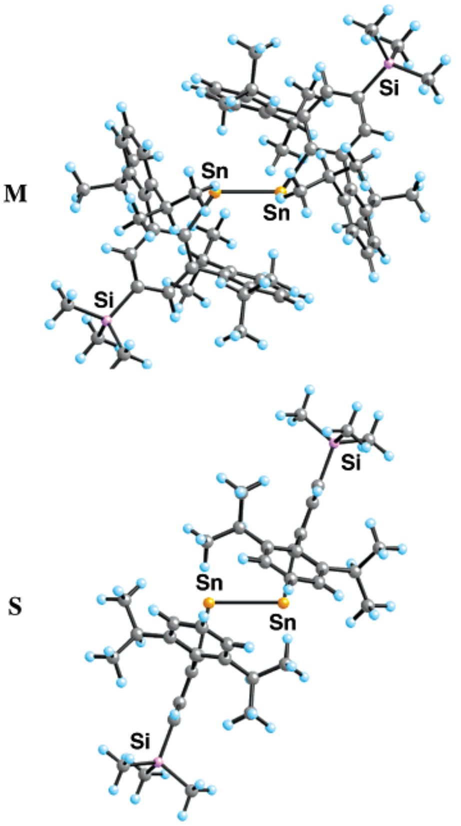

Figure 3. Multiply (M) and singly (S) bonded structures of 4-$SiMe_3$-Ar′SnSnAr′-4-$SiMe_3$ optimized at the B3PW91 level.

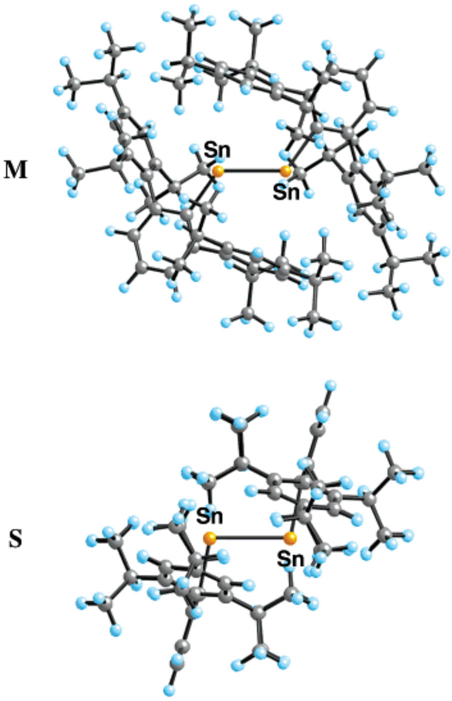

Figure 4. Multiply (M) and singly (S) bonded structures of Ar*SnSnAr* optimized at the B3PW91 level.

strong absorptions at 416 and 608 nm[24] that are very similar to those of Ar′SnSnAr′ (410 and 597 nm),[6] indicating that 4-$SiMe_3$-Ar′SnSnAr′-4-$SiMe_3$ takes structure M in solution.

Solid-state ^{119}Sn NMR and Mössbauer spectroscopic data[26] suggest that Ar*SnSnAr* (Ar* = C_6H_3-2,6-(C_6H_2-2,4,6-$i$$Pr_3$)$_2$) is more trans-bent and has a longer Sn−Sn distance than Ar′SnSnAr′. Although the X-ray crystal analysis of Ar*SnSnAr* is not yet successful because of poor diffraction,[23] the NMR and Mössbauer data agree with the geometrical parameters (Sn−Sn = 3.120 Å, θ = 100.8°, and ω = 177.3°) optimized for structure S. However, structure M (Sn−Sn = 2.705 Å, θ = 125.0°, and ω = 154.7°) in Figure 4 is 6.4 kcal/mol more stable than structure S. This indicates that Ar*SnSnAr* takes structure M in solution, as also supported by the almost identical UV−vis spectra of Ar*SnSnAr* (409 and 593 nm) and Ar′SnSnAr′ (410 and 597 nm).[6,23] The suggested structural differences of Ar*SnSnAr* and Ar′SnSnAr′ in the crystalline phase are ascribable to packing forces.[27]

In conclusion, RSnSnR (R = Ar′, Ar′-4-$SiMe_3$, Ar*) has a multiply bonded structure (M) in solution. The different structures for R = Ar′-4-$SiMe_3$, Ar* in solution and the crystal state are due to the fact that crystallization is significantly affected by the different spatial expanding of these groups and the Ar′ group.[28] A theoretical study of the lower reactivity of RSnSnR is in progress and will be published in due course. However, it is instructive to mention that, for example, the addition of MeSnSnMe (structure M) to $H_2C{=}CH_2$ is calculated to be 11 kcal/mol less exothermic than that of MeGeGeMe (structure M).

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(26) Spikes, G. H.; Giuliani, J. R.; Augustine, M. P.; Nowik, I.; Herber, R. H.; Power, P. P. *Inorg. Chem.* **2006**, *45*, 9132.

(27) For the effect of packing forces on the structures of Na_2[Ar*GaGaAr*] and Na_2[Ar′GaGaAr′], see ref 2g and Takagi, N.; Schmidt, M. W.; Nagase, S. *Organometallics* **2001**, *20*, 1646.

(28) The Ar* group has iPr at each para position of the flanking aryl rings, while the Ar′-4-$SiMe_3$ group has $SiMe_3$ at the para position of the central aryl ring. Despite this modification, it is interesting that the calculated structures of Ar*SnSnAr* and 4-$SiMe_3$-Ar′SnSnAr′-4-$SiMe_3$ resemble those of Ar′SnSnAr′, except that Ar*SnSnAr* (ω = 154.7°) is more twisted around the Sn−Sn bond than Ar′SnSnAr′ (ω = 179.7°) for structure M.