

Sandorfy Hückel Molecular Orbital Approximation for Modeling the Electronic Structures of Long-Chain Polystannanes[†]

Lawrence R. Sita,* Karl W. Terry,[‡] and Kazusato Shibata

Searle Chemistry Laboratory, Department of Chemistry
The University of Chicago, 5735 South Ellis Avenue
Chicago, Illinois 60637

Received May 1, 1995

Compounds with molecular frameworks composed of linear chains of σ -bonded group 14 heavy atoms, $R-(R_2M)_n-R$ ($M = Si, Ge, \text{ and } Sn$), have attracted considerable theoretical¹ and experimental² interest due to the observation of novel optical/electronic properties that are intrinsic to these polymetallane systems and that are lacking in their n -alkane organic counterparts. In this regard, the synthesis and characterization of discrete group 14 polymetallane oligomers have been instrumental in providing data that can be used to either refine existing theoretical models or develop new ones.^{1,2} Unfortunately, for the polystannanes (i.e., $M = Sn$), only short-chain oligomers for $n \leq 6$ have been obtained and characterized,^{2a,d,h} and thus, to date, it has not been possible to determine if the models developed previously for alkanes, and successfully applied to polysilanes, are still appropriate ones to use to describe the electronic structures of these heavier atom systems which are potentially more "metallic-like" in character.³ Herein, we now describe a novel route to a family of α,ω -difunctional polystannane oligomers represented by $X-(Bu_2Sn)_n-X$ ($X = 2$ -ethoxyethyl, $n = 3-15$) (**1**) and provide new experimental data which is used to show that, at the semiempirical level, the Sandorfy Hückel molecular orbital (HMO) approximation developed for saturated hydrocarbons⁴ appears, in fact, to still function well for describing the electronic structures of the heavier group 14 polymetallanes.

Recently, we reported a new strategy based on the hydrostannolysis reaction⁵ for the stepwise construction of homologically pure monofunctional polystannane oligomers of the type $Bu_3Sn-(Bu_2Sn)_n-X$ ($X = 2$ -ethoxyethyl),^{2h} and we have since extended this methodology to include the synthesis of the odd series of short-chain α,ω -difunctional polystannane oligomers, $X-(Bu_2Sn)_n-X$ ($X = 2$ -ethoxyethyl; $n = 3, 5, \text{ and } 7$), as well.⁶

[†] Performed in part at the California Institute of Technology (CIT).

[‡] CIT Postdoctoral Research Fellow 1993–1994.

(1) For some representative theoretical papers, see: (a) Pitt, C. G.; Jones, L. L.; Ramsey, B. G. *J. Am. Chem. Soc.* **1967**, *89*, 5471. (b) Pitt, C. G.; Bursey, M. M.; Rogerson, P. F. *Ibid.* **1970**, *92*, 519. (c) Boberski, W. G.; Allred, A. L. *J. Organomet. Chem.* **1975**, *88*, 65. (d) Herman, A.; Dreczewski, B.; Wojnowski, W. *Chem. Phys.* **1985**, *98*, 475. (e) Bigelow, R. W. *Chem. Phys. Lett.* **1986**, *126*, 63. (f) Balaji, V.; Michl, J. *Polyhedron* **1991**, *10*, 1265. (g) Ortiz, J. V. *Ibid.* **1991**, *10*, 1285. (h) Takeda, K.; Shiraishi, K.; Matsumoto, N. *J. Am. Chem. Soc.* **1990**, *112*, 5043. (i) Takeda, K.; Shiraishi, K. *Chem. Phys. Lett.* **1992**, *195*, 121.

(2) For some representative experimental papers, see: (a) Drenth, W.; Noltes, J. G.; Bulten, E. J.; Creemers, H. M. J. C. *J. Organomet. Chem.* **1969**, *17*, 173. (b) Kumada, M. *Adv. Organomet. Chem.* **1969**, *6*, 19. (c) Bock, H.; Ensslin, W.; Fehér, F.; Freund, R. *J. Am. Chem. Soc.* **1976**, *98*, 668. (d) Adams, S.; Dräger, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1255. (e) Maxka, J.; Huang, L.-M.; West, R. *Organometallics* **1991**, *10*, 656. (f) Sun, Y.-P.; Hamada, Y.; Huang, L.-M.; Maxka, J.; Hsiao, J.-S.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1992**, *114*, 6301. (g) Sun, Y.-P.; Michl, J. *Ibid.* **1992**, *114*, 8186. (h) Sita, L. R. *Organometallics* **1992**, *11*, 1442. (i) Zou, W. K.; Yang, N.-L. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1992**, *33*, 188. (j) Imori, T.; Tilley, T. D. *J. Chem. Soc., Chem. Commun.* **1993**, 1607.

(3) Relativistic effects are known to play an increasingly decisive role in governing the structures, stabilities, and properties of analogous sets of compounds as one moves down a group in the periodic table (see: Pyykkö, P.; Desclaux, J. P. *Acc. Chem. Res.* **1979**, *12*, 276).

(4) Sandorfy, C. *Can. J. Chem.* **1955**, *33*, 1337.

(5) Neumann, W. P. *The Organic Chemistry of Tin*; Wiley: New York, 1970.

(6) Sita, L. R.; Shibata, K. To be reported.

Due to practical limitations, however, the rational synthesis of long polystannane oligomers (i.e., $n \geq 8$) by either of these approaches was not possible, and accordingly, a new oligomerization procedure was sought which would provide direct access to these compounds. As Scheme 1 indicates, this was achieved through reaction of dibutyl(2-ethoxyethyl)stannane (**2**) with 0.2–0.3 equiv of lithium diisopropylamide (LDA) in tetrahydrofuran (THF) to presumably generate an intermediate family of hydride-terminated polystannane oligomers, which were then "end-capped" by the addition of dibutyl(dimethylamino)(2-ethoxyethyl)stannane (**3**) to finally provide **1**.⁷ The exact mechanism by which this oligomerization process occurs is still not known, but it is assumed that, upon deprotonation of **2**, the resulting tin-centered anion undergoes an α -elimination reaction to generate the highly reactive stannylene intermediate **4**, which then rapidly inserts into the Sn–H bonds of the growing polystannane oligomers.

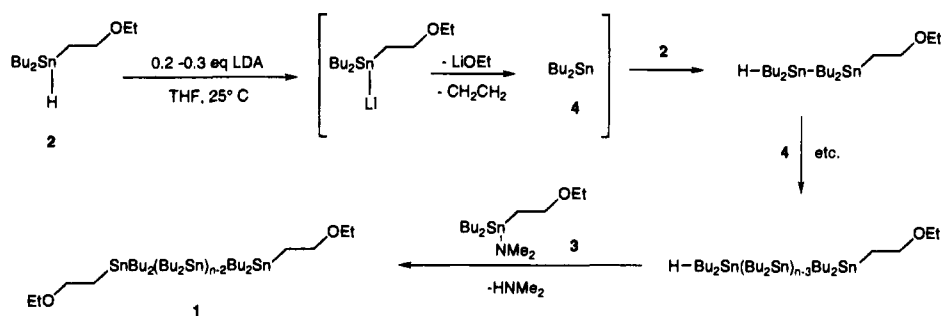
After separation of the small amount of cyclic oligomers⁸ via column chromatography on silica gel, analytic and spectroscopic analyses of the resulting, air-sensitive, near colorless product revealed its composition to be fully consistent with that of **1**.⁷ More importantly, it was discovered that the individual oligomeric components of **1** could be separated from one another via reverse-phase HPLC using a dichloromethane/acetonitrile solvent mixture gradient as shown in Figure 1. Thus, peak detection using a UV-vis diode array detector set at 254 nm revealed that short-chain oligomers with $n = 3, 4, \text{ and } 5$ predominate in **1**, although, by going to 322 nm, polystannane oligomers with chain lengths of at least 15 tin atoms could be easily detected (Figure 1).⁹ Since the diode array detector is capable of recording a full (200–600 nm) spectrum for each data point of the chromatograms shown in Figure 1, it was also possible to accurately obtain λ_{max} for the lowest energy transition in each of the oligomers of **1** for $n = 3-15$ (see Table 1).

Regarding the electronic structures of polystannanes, it has previously been claimed that HMO theory, as originally developed for conjugated organic systems, can be used to successfully correlate chain length with transition energy.^{2a} Unfortunately, this analysis was performed for polystannane oligomers with chain lengths of up to only six tin atoms, and an identical analysis using the full data set obtained for **1** now reveals that this model is actually a poor one to apply. However, it can be anticipated that more appropriate semiempirical methods to use to describe the valence and conduction bands of group 14 polymetallanes are the modified HMO theories first advanced by Sandorfy⁴ to model saturated hydrocarbons, and indeed, several groups have utilized this approach to successfully correlate the chain length dependent behavior of many of the physical properties of polysilane oligomers.^{1a-d,2c} Following the Sandorfy model C approximation, the polysilane backbone is represented as a linear chain of interacting sp^3 orbitals with two resonance integrals, β_{vic} and β_{gem} , now being introduced to describe, respectively, the strong (vicinal) interaction between two overlapping sp^3 orbitals on adjacent silicon atoms and the weaker (geminal) interaction between two sp^3 orbitals located on the same silicon atom. Furthermore, the ratio $\beta_{\text{gem}}/\beta_{\text{vic}}$ defines a parameter, m , which can be taken as a measure of the degree of delocalization of the backbone molecular orbitals. As can be seen in Figure 2, setting m to 0.75 produces a very high

(7) Detailed information is provided in the supporting information.

(8) Reverse-phase high-pressure liquid chromatography (HPLC) analysis reveals that this material consists chiefly of two compounds which are assigned as being $(Bu_2Sn)_5$ and $(Bu_2Sn)_6$ on the basis of ¹¹⁹Sn NMR spectral parameters which are identical to those previously reported; see: Jousseume, B.; Noiret, N.; Pereyre, M.; Saux, A.; Francés, J.-M. *Organometallics* **1994**, *13*, 1034.⁷

(9) The HPLC peak positions for the short-chain oligomers of **1** for $n = 3, 5, \text{ and } 7$ were found to be identical to those of authentic samples prepared by an alternative route.⁶

Scheme 1^a

^a LDA = lithium diisopropylamide; THF = tetrahydrofuran.

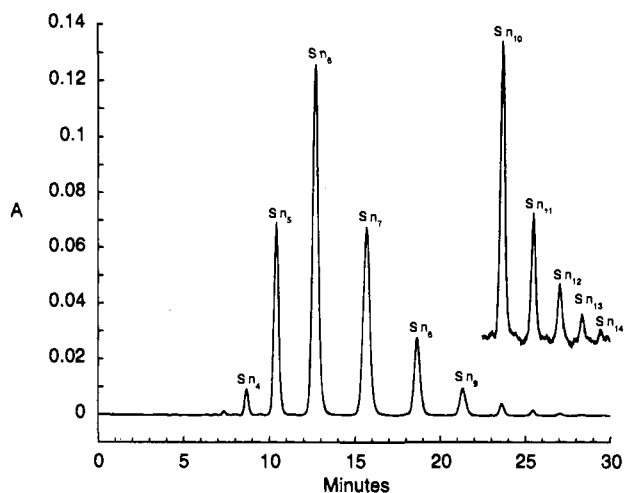


Figure 1. HPLC chromatogram for **1** (peak detection at 322 nm). Note: The oligomer of **1** for $n = 15$ is observable at higher sample concentrations.

Table 1. Lowest Energy Transitions of **1**

n	ν (cm^{-1})	λ_{max} (nm)
3	39 370	254
4	36 630	273
5	33 784	296
6	32 051	312
7	30 960	323
8	30 120	332
9	29 412	340
10	28 902	346
11	28 490	351
12	28 169	355
13	27 933	358
14	27 701	361
15	27 548	362

degree of correlation between the curve generated by the observed chain length behavior of the transition frequencies (cm^{-1}) of **1** and that determined by a plot of the calculated energy difference between the highest occupied molecular orbital (HOMO) and lowest unoccupied MO (LUMO), $\Delta\epsilon$, as a function of polystannane chain length.¹⁰ A similarly high value for m has previously been obtained for polysilanes,^{1d} thereby indicating, not surprisingly, that electrons in polystannanes are

(10) The pronounced deviation of the calculated curve for $n = 3$ is assumed to be due to "end-group" effects.

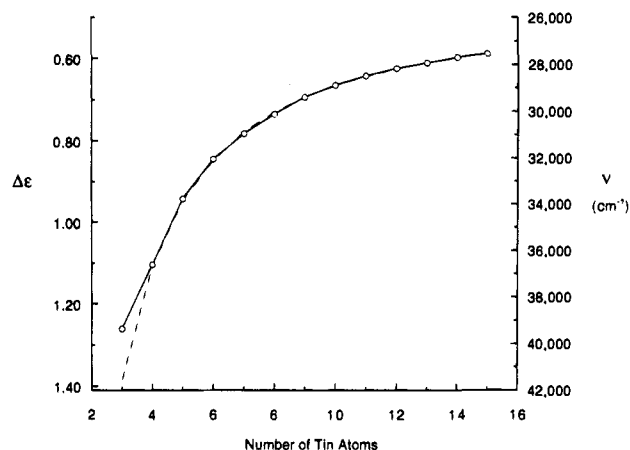


Figure 2. Curves for the calculated (Sandorfy model C) energy differences (LUMO-HOMO) (dashed line) and observed transition frequencies (circles and solid line) as a function of chain length.

anticipated to be highly delocalized along the σ -bonded backbones. The primary importance of the present analysis, however, is that the apparent ability of the Sandorfy HMO approximation to successfully model the electronic structures of long-chain polystannanes in a qualitative fashion implies that other recent additions and refinements to this theory as it applies to hydrocarbons and polysilanes can be extrapolated with some degree of confidence to include the heaviest group 14 polymetallanes as well. This, in turn, should prove crucial for helping to elucidate, at the next level of investigation, the role of various types of substituents (e.g., alkyl vs aryl) in defining the properties of different families of polystannane oligomers that are potentially accessible through the straightforward route shown in Scheme 1. Studies along these lines are now in progress.

Acknowledgment. We thank the National Science Foundation (CHE-9300022) for support of this work and Professor Jeremy Burdett for fruitful discussions.

Supporting Information Available: Detailed information concerning the synthesis and characterization of all new compounds (8 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA951391Y