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Supplementary Material Available: Tables of atomic coordinates, anisotropic thermal parameters, and bond distances and angles of all atoms (8 pages); listings of calculated and observed structure factors (10 pages). Ordering information is given on any current masthead page.

Isolation and Molecular Structure of the First Bicyclo[2.2.0]hexastannane

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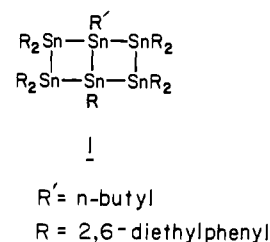
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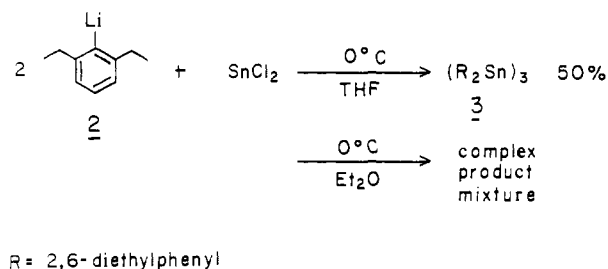
Recent advances in the area of group IVB polymetallanes has led to the isolation and characterization of a wide range of structurally unique polycyclic frameworks. These compounds represent not only challenging synthetic¹ and theoretical² "benchmarks" but also serve to provide insight for the design of new solid-state materials. With regard to polystannanes, linear³ and cyclic⁴ structures have been known for some time; however, report of a polycyclic polystannane has not yet been documented. Herein, we describe the isolation and molecular structure of the first bicyclo[2.2.0]hexastannane derivative, **1** (Scheme I).

Inherent in the quest for the synthesis of ring-strained polymetallanes is the judicious choice of an exocyclic ligand which can kinetically stabilize the final desired product as well as the proper selection of reaction conditions. For example, we find that slow addition of a solution of the aryllithium reagent, **2** [prepared from 10 g (47 mmol) of 1-bromo-2,6-diethylbenzene and 29 mL of *n*-butyllithium (1.8 M in hexane) in 50 mL of diethyl ether], to a solution of 3.65 g (24 mmol) of tin dichloride in 50 mL of tetrahydrofuran (THF) at 0 °C provides the known cyclotristannane **3**^{4a} in 50–55% yield after the usual workup and purification (Scheme II). By performing the same reaction with a suspension of SnCl₂ in diethyl ether at 0 °C, however, a deep red crude oil is obtained.⁵ From this mixture, compound **1** was

Scheme I



Scheme II



isolated in 1.5% yield in the form of orange-red single crystals by slow crystallization from a concentrated pentane solution at –20 °C.

A mass spectrum of **1** (field desorption) reveals an isotope cluster pattern, M⁺⁺ *m/z* (1958–1980), which is consistent with the molecular formula of C₉₄H₁₂₆Sn₆, and this implies that the organic ligands of **1** are comprised of one butyl (C₄H₉) and nine aryl (C₉₀H₁₁₇) groups.^{6,7} However, interpretation of both the ¹H NMR (300 MHz, toluene-*d*₆) and ¹³C{¹H} NMR (75 MHz, toluene-*d*₆) spectra is hampered by the number of resonances and complex multiplets (¹H NMR) arising from the aryl substituents which experience different chemical environments and restricted rotation up to 100 °C.⁶

Determination of a bicyclic framework for **1** was provided by crystallographic analysis which reveals several interesting structural features.⁶ As shown in Figure 1, the molecule is comprised of a cis fusion of two four-membered rings and overall possesses no axis or plane of symmetry. The angle between the mean planes formed by Sn₁–Sn₂–Sn₃–Sn₄ and Sn₁–Sn₂–Sn₅–Sn₆ is 131.9°, and each of the four-membered rings are puckered rather than planar as determined by the dihedral angle of 8.2° between the Sn₁–Sn₂–Sn₃ and Sn₂–Sn₃–Sn₄ planes and 4.5° between the Sn₁–Sn₂–Sn₅ and Sn₂–Sn₅–Sn₆ planes. The angles which construct the four-membered rings are in the range of 87.5–92.9° and are similar to those angles found for other cyclotetrastannanes.^{4c–e} It is interesting to note that due to steric interactions among the exocyclic ligands, the butyl group at Sn₁ adopts a gauche conformation with a dihedral angle of 55.7° for C_{1a}–C_{2a}–C_{3a}–C_{4a}.

The tin–tin bond lengths of 2.818 (1)–2.931 (1) Å for the bicyclohexastannane fall in the range commonly found for small cyclopolystannanes possessing sterically hindered ligands.⁴ Of particular interest, however, is that the shortest tin–tin bond length in the structure is between the central tin atoms (2.818 Å for Sn₁–Sn₂).⁸ This undoubtedly arises from a decrease in steric interactions between the ligands on Sn₁ and Sn₂ vs the steric interactions for the bonds of Sn₃–Sn₄ and Sn₅–Sn₆. Finally, all the tin–carbon bond lengths [2.214 (8)–2.230 (9) Å] are longer than normal and are indicative of strong steric interactions between the exocyclic ligands.

Compound **1**, which is surprisingly air-stable in crystalline form, exhibits unique optical properties, both in solution and in the solid

(1) (a) Masamune, S.; Kabe, Y.; Collins, S.; Williams, D. J.; Jones, R. J. *Am. Chem. Soc.* **1985**, *107*, 5552. (b) Matsumoto, H.; Miyamoto, H.; Kojima, N.; Nagai, Y. *J. Chem. Soc., Chem. Commun.* **1987**, 1316. (c) Matsumoto, H.; Higuchi, K.; Hoshino, Y.; Koike, H.; Naoi, Y.; Nagai, Y. *J. Chem. Soc., Chem. Commun.* **1988**, 1083. (d) Sekiguchi, A.; Kabuto, C.; Sakurai, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 55.

(2) (a) Clabo, D. A., Jr.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1986**, *108*, 4344. (b) Nagase, S.; Nakano, M.; Kudo, T. *J. Chem. Soc., Chem. Commun.* **1987**, 60.

(3) For crystallographic analysis of X-(R₂Sn)_n-X, see: (a) Adams, S.; Dräger, M. *J. Organomet. Chem.* **1985**, *288*, 295. (b) Adams, S.; Dräger, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1255.

(4) For crystallographic analysis of (R₂Sn)_n, *n* = 3: (a) Masamune, S.; Sita, L. R.; Williams, D. J. *J. Am. Chem. Soc.* **1983**, *105*, 630. *n* = 4: (b) Farrar, W. V.; Skinner, H. A. *J. Organomet. Chem.* **1964**, *1*, 434. (c) Belsky, V. K.; Zemlyansky, N. N.; Kolosova, N. D.; Borisova, I. V. *J. Organomet. Chem.* **1981**, *215*, 41. (d) Lappert, M. F.; Leung, W. P.; Raston, C. L.; Thorne, A. J.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1982**, *233*, C28. (e) Puff, H.; Bach, C.; Schuh, W.; Zimmer, R. *J. Organomet. Chem.* **1986**, *312*, 313. *n* = 6: (f) Dräger, M.; Mathiasch, B.; Ross, L.; Ross, M. *Z. Anorg. Allg. Chem.* **1983**, *506*, 99. (g) Puff, H.; Bach, C.; Reuter, H.; Schuh, W. *J. Organomet. Chem.* **1984**, *277*, 17.

(5) While efforts are in progress to characterize the main constituents of this reaction product, no cyclotristannane **3** is observed in freshly prepared material as determined by ¹¹⁹Sn{¹H} NMR (112 MHz).

(6) Detailed information is provided in the Supplementary Material.

(7) Mp 250 °C (dec), elemental Anal. Calcd for **1**: C, 57.34; H, 6.45. Found: C, 56.40; H, 6.23.

(8) In both the carbon and silicon analogues of **1**, the central bond of the ring is longer than the peripheral bonds, see: ref 1b and Andersen, B.; Srinivasan, R. *Acta Chem. Scand.* **1972**, *26*, 3468.

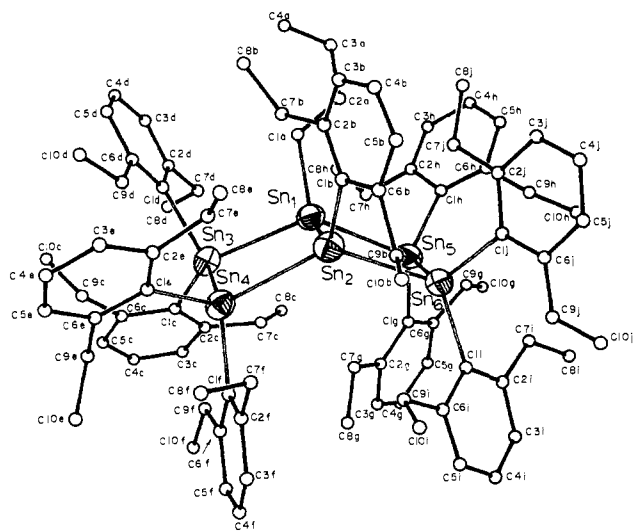


Figure 1. Crystal structure of **1**: Tin atoms are represented by thermal vibration ellipsoids drawn to encompass 50% of their electron density, and carbon atoms are represented by small spheres of arbitrary size for purposes of clarity. Butyl carbon atoms are labeled 1a–4a, and the aryl ligand carbons are each labeled with a number (from 1 to 10) with a literal subscript (b–j) identifying their particular ligand. Bond lengths (Å): Sn₁–Sn₂ 2.818 (1), Sn₁–Sn₃ 2.832 (1), Sn₁–Sn₅ 2.835 (1), Sn₂–Sn₄ 2.931 (1), Sn₂–Sn₆ 2.925 (1), Sn₃–Sn₄ 2.924 (1), Sn₅–Sn₆ 2.899 (1), Sn–C 2.214 (8)–2.230 (9). Bond angles (deg): Sn₃Sn₁Sn₂ 91.6 (1), Sn₁Sn₂Sn₄ 90.2 (1), Sn₂Sn₄Sn₃ 87.5 (1), Sn₄Sn₃Sn₁ 90.1 (1), Sn₂Sn₁Sn₃ 92.9 (1), Sn₁Sn₅Sn₆ 88.9 (1), Sn₅Sn₆Sn₂ 89.4 (1), Sn₆Sn₂Sn₁ 88.7 (1), Sn₃Sn₁Sn₅ 133.3 (1), Sn₄Sn₂Sn₆ 130.8 (1).

state, as demonstrated by its dramatic reversible thermochromic behavior, being pale yellow at –196 °C and orange-red at room temperature. In addition, the ultraviolet absorption maxima at 309 nm ($\epsilon_{\text{max}} = 37900$) and at 360 nm ($\epsilon_{\text{max}} = 13690$) in methylcyclohexane are similar to those attributed to σ -delocalization in short-chain linear polystannanes.^{3b} With regard to its mechanism of formation, it is likely that the aryllithium reagent, **2**, can serve to reductively remove either a chloro or aryl substituent to form a radical (or anionic) intermediate which can then react with the *n*-butyl bromide (produced from the reaction of the aryl bromide with *n*-butyllithium) to form **1**.⁹

In conclusion, the view provided by the structure of **1** will aid in identifying the steric features of the ligands which will be required for the successful development of new synthetic routes for the construction of polycyclic polystannane frameworks. Further studies concerning the physical properties of **1** and the synthesis of other derivatives are currently in progress.

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Supplementary Material Available: Detailed information concerning the spectroscopic and crystallographic analysis of **1**, including listings of atomic coordinates and temperature factors, bond lengths, bond angles, and anisotropic temperature factors and an ORTEP representation of **1** (23 pages). Ordering information is given on any current masthead page.

(9) Other *n*-butyltin derivatives have been isolated from the reaction of SnCl₄ with sterically hindered lithium reagents prepared from *n*-butyllithium, see: (a) Cardin, C. J.; Cardin, D. J.; Norton, R. J.; Parge, H. E.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1983**, 665. (b) Bigwood, M. P.; Corvan, P. J.; Zuckerman, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 7643.

Interactions between Amides in Solution and the Thermodynamics of Weak Binding

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Interactions between amides have been widely investigated owing to the connection to protein structure and stability.¹ Among classic studies,^{2,3} infrared work has revealed decreasing aggregation for secondary amides along the solvent series CCl₄ > C₆H₆ > CHCl₃, CH₂Cl₂ > dioxane >> water.³ In fact, Klotz and Franzen quantified the negligible self-affinity of *N*-methylacetamide (NMA) in water by measuring a free energy of association of +3.1 kcal/mol.^{3c} As reported here, modern theoretical methods have now been applied to obtain the first free energy profiles or “potentials of mean force” (pmf’s) for the association of amides and the corresponding predicted K_s ’s.

Monte Carlo statistical mechanics simulations were carried out for two NMA molecules plus 250 chloroform or 310 water molecules in periodic boxes in the NPT ensemble at 25 °C and 1 atm. The computational details are the same as for prior pmf determinations.^{4,5} In particular, statistical perturbation theory⁶ was used to obtain the free energy changes as the two solutes were perturbed apart in increments of 0.2 Å with the N...O distance as the reaction coordinate. The OPLS potential functions were used for NMA^{7,8} and chloroform⁹ along with the TIP4P model of water.¹⁰ Thus, all atoms are explicit except hydrogens on carbon, and Coulomb and Lennard–Jones interactions are included between the interaction sites. Feathered cutoffs were used to truncate the intermolecular interactions beyond 12 Å in chloroform and 8.5 Å in water.^{4,5} Bond lengths and bond angles were not varied, while the torsional motion about the central C–N bond of NMA was sampled.⁸ Otherwise, the motion of the solutes was unconstrained so all intermolecular arrangements were accessible at the set values of the reaction coordinate. Each of the 16 simulations then entailed equilibration for at least 6×10^5 configurations starting from equilibrated solvent boxes and the amides in a hydrogen-bonding orientation, followed by averaging for 2×10^6 configurations.

The resultant pmf’s are shown in Figure 1. In chloroform, a single free energy well is found with a depth of –3.5 kcal/mol for the minimum at $r(\text{N}\cdots\text{O}) = 2.8$ Å. Plots of configurations clearly show that the amides are hydrogen bonded (Figure 2, top). However, in water the amides exhibit no net attraction owing to the competition with hydrogen bonding to the solvent. In fact, plots of configurations reveal that at short separations the amides

(1) Schulz, G. E.; Schirmer, R. H. *Principles of Protein Structure*; Springer-Verlag: New York, 1979.

(2) (a) Schellman, J. A. *Compt. Rend. Trav. Lab Carlsberg, Ser. Chim.* **1955**, *29*, 223. (b) Davies, M.; Thomas, D. K. *J. Am. Chem. Soc.* **1955**, *60*, 763, 767. (c) Kauzmann, W. *Adv. Protein Chem.* **1959**, *14*, 1. (d) Nemethy, G.; Scheraga, H. A. *J. Phys. Chem.* **1962**, *66*, 1773. (e) Kresheck, G. C.; Klotz, I. M. *Biochemistry* **1969**, *8*, 8.

(3) (a) Klemperer, W.; Cronyn, M. W.; Maki, A. H.; Pimentel, G. C. *J. Am. Chem. Soc.* **1954**, *76*, 5846. (b) Tsuboi, M. *J. Chem. Soc. Jpn. Pure Chem. Sect.* **1955**, *76*, 376. (c) Klotz, I. M.; Franzen, J. S. *J. Am. Chem. Soc.* **1962**, *84*, 3461. (d) Susi, H.; Timasheff, S. N.; Ard, J. S. *J. Biol. Chem.* **1964**, *239*, 3051. (e) Spencer, J. N.; Garrett, R. C.; Mayer, F. J.; Merkle, J. E.; Powell, C. R.; Tran, M. T.; Berger, S. K. *Can. J. Chem.* **1980**, *58*, 1372. (f) Krikorian, S. E. *J. Phys. Chem.* **1982**, *86*, 1875.

(4) Jorgensen, W. L.; Buckner, J. K.; Huston, S. E.; Rossky, P. J. *J. Am. Chem. Soc.* **1987**, *109*, 1891.

(5) Buckner, J. K.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1989**, *111*, 2507.

(6) Zwanzig, R. W. *J. Chem. Phys.* **1954**, *22*, 1420.

(7) Jorgensen, W. L.; Tirado-Rives, J. *J. Am. Chem. Soc.* **1988**, *110*, 1657.

(8) Jorgensen, W. L.; Swenson, C. J. *J. Am. Chem. Soc.* **1985**, *107*, 569, 1489.

(9) Jorgensen, W. L.; Nguyen, T. B.; Boudon, S. *J. Am. Chem. Soc.* **1989**, *111*, 755.

(10) Jorgensen, W. L.; Chandrasekhar, J.; Madura, J. D.; Impey, R. W.; Klein, M. L. *J. Chem. Phys.* **1983**, *79*, 926.