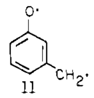
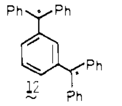


11

$|D/hc| = 0.032$ cm^{-1}



12

$|D/hc| = 0.08$ cm^{-1}

The spectrum generated by photolysis of bis(diazo) compound **8** obeys the simple form of the Curie law between 30 and 77 K at 0.01 mW.[16,17] The triplet is the ground state or within a few calories per mole of the ground state as predicted by theory.[2,3,5]

Finally, we have attempted to reproduce the experimental conditions of Migiridicyan and Baudet.[9] Photolysis of a 0.01 M solution of mesitylene in 3-methylpentane with 2537-Å light generated an ESR spectrum similar to that obtained from reaction of **7** at 77 K. The former spectrum is consistent with methyl-substituted **1**. Attempts to observe **1** by analogous irradition of *m*-xylene were unsuccessful.

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Registry No. 1, 32714-83-3; **7**, 25768-05-2; **8**, 18456-73-0; **10**, 626-15-3.

(15) Kothe, G.; Denkel, K. H.; Sümmermann, W. *Angew Chem., Int. Ed. Engl. 1970*, **9**, 906.
(16) Breslsow, R.; Chang, H.-W.; Hill, R.; Wasserman, E. *J. Am. Chem. Soc.* **1967**, *89*, 1112.
(17) At higher microwave power the ESR signal of **1** is saturated, which leads to apparent violations of the Curie law.

Cyclotristannoxane $(R_2SnO)_3$ and Cyclotristannane $(R_2Sn)_3$ Systems. Synthesis and Crystal Structures

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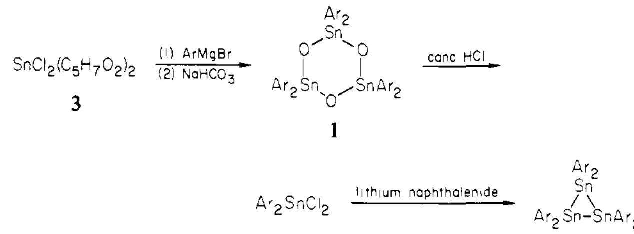
We describe herein the synthesis and crystal structures of two compounds, hexakis(2,6-diethylphenyl)cyclotristannoxane (**1**) and hexakis(2,6-diethylphenyl)cyclotristannane (**2**). The latter cyclotristannane system obviously constitutes the smallest cyclic framework made exclusively of tin atoms[1], while compound **1** is a rare crystalline diorgano tin oxide that possesses a discrete molecular structure with tetracoordinate tin atoms.[2] The alkaline hydrolysis of diorgano tin dihalides, the most common method of preparing the corresponding tin oxide, always in the past led to the formation of insoluble polymeric compounds exhibiting wide melting ranges as well as Mössbauer spectra indicative of pentacoordinate tin.[3] Crystallographic analyses of both **1** and **2** confirm the structural assignments of these compounds based on spectral data and further reveal several unique and intriguing structural features.

(1) Four-membered and larger ring systems have long been known. For reviews, see: (a) Gilman, H.; Atwell, W. H.; Cortledge, F. K. *Adv. Organomet. Chem.* **1964**, *4*, 1. (b) Armitage, D. A. "Inorganic Rings and Cages"; Edward Arnold: London, **1972**; Chapter 4. Also see references quoted in: (c) Neumann, W. P. *Rev. Silicon, Germanium, Tin, Lead Compd.* **1978**, *3*, 51. (d) Ishikawa, M.; Kumada, M. *Ibid.* **1979**, *4*, 7. (e) Neumann, W. P. *Nachr. Chem. Tech. Lab.* **1982**, *30*, 191.
(2) Di-*tert*-butyltin oxide postulated to exist as the trimer $(t\text{-}Bu_2SnO)_3$ in solution is the only other diorgano tin oxide with tetracoordinate tin atoms [(a) Chu, C. K.; Murray, J. D. *J. Chem. Soc. A* **1971**, 360]. For the crystal structure of this compound, see: (b) Puff, H.; Sievers, R.; Zimmer, R.; Schuh, W. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 591.
(3) This behavior is in sharp contrast with that of the analogous oxides of silicon and germanium, which readily form cyclotrisiloxanes and cyclotrigermoxane, respectively. See ref 1b and the following: Metlesics, W.; Zeiss, H. *J. Am. Chem. Soc.* **1960**, *82*, 3324.

Scheme I[a]



[a] Ar = 2,6-diethylphenyl.

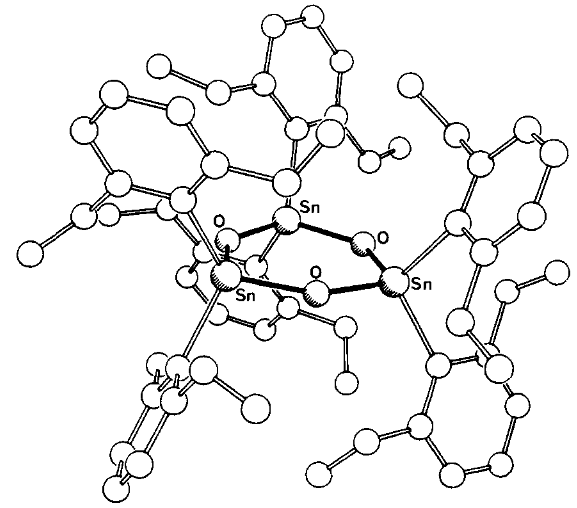


Figure 1. Crystal structure of **1**: Sn–O bond lengths 1.929 (6)–1.961 (6) Å; Sn–O–Sn bond angles 135.6 (3), 135.9 (3), and 137.1 (3)°; Sn–Ar bond lengths 2.138 (6)–2.169 (9) Å.

Synthesis of 1 and 2. The synthesis of **2** follows the approach previously adopted for that of the silicon analogue[4] as shown in Scheme I. Thus adding (2,6-diethylphenyl)magnesium bromide (47 mmol) in 1:5 benzene/ether (60 mL) to a solution of bis(2,4-pentanedionato)tin dichloride **3**[5] (23.5 mmol) in benzene (50 mL)[6] and then heating the reaction mixture at reflux for 2 h provide a crude product that, upon treatment with saturated aqueous sodium bicarbonate, gives rise to colorless crystals, mp >300 °C (33% yield, recrystallized from benzene). Spectral data of this compound are as follows: mass spectrum (field desorption), $M^{+\cdot}$ cluster m/z (1196–1211), in agreement with that calculated for the trimeric molecular formula $(C_{20}H_{26}OSn)_3$;[7] ^{119}Sn NMR (CCl_4) δ (ppm from Me_4Sn) −125.02;[8] IR ($CHCl_3$) ν_{SnOSn} 710 cm^{-1}; UV (cyclohexane) λ_{max} (log ϵ) 270 nm (3.64), 278 nm (3.61); ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.85 (t, 6 H), 2.84 (q, 4 H), 6.95 (d, 2 H), 7.19 (t, 1 H). Treatment of **1** with concentrated hydrochloric acid effects its quantitative conversion to **4**, mp 67.5–68.5 °C. After dropwise addition of **4** (900 mg, 2 mmol) in dimethoxyethane (DME, 10 mL) to a dark green solution of lithium naphthalenide at −78 °C [prepared from naphthalene (500 mg, 3.9 mmol) in DME (15 mL) and lithium wire (27 mg, 3.9 mmol)], the mixture is stirred at the same temperature for 15 min and at room temperature for 2 h, resulting in a bright yellow

(4) Masamune, S.; Hanzawa, Y.; Murakami, S.; Bally, T.; Blount, J. F. *J. Am. Chem. Soc.* **1982**, *104*, 1150. Also see: Masamune, S.; Hanzawa, Y.; Williams, D. J. *Ibid.* **1982**, *104*, 6136.
(5) Morgan, G. T.; Drew, H. D. K. *J. Chem. Soc.* **1924**, *125*, 372.
(6) Following the procedure developed by: Chandrasekaran, R. K.; Venkataraman, S.; Koola, J. D. *J. Organomet. Chem.* **1981**, *215*, C43.
(7) Detailed information is supplied in the supplementary material.
(8) The δ value of the ^{119}Sn signal of $(Me_2SnS)_3$ is −128: Davies, A. G.; Harrison, P. G.; Kennedy, J. D.; Mitchell, T. N.; Puddephatt, R. J.; McFarlane, W. *J. Chem. Soc. C* **1969**, 1136.

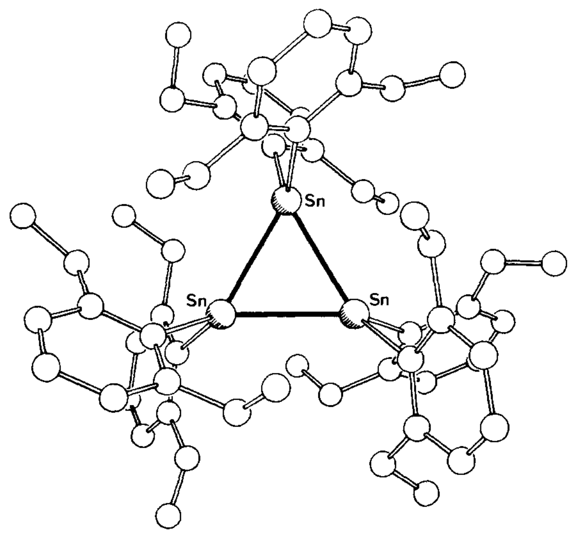


Figure 2. Crystal structure of **2**: Sn–Sn bond lengths 2.870 (1), 2.856 (1), and 2.854 (1) Å; Sn–Sn–Sn bond angles 59.8 (1), 59.9 (1), and 60.3 (1)°; C–Sn bond lengths 2.167 (10)–2.203 (9) Å.

coloration. The usual workup, including flash chromatography (5:1 petroleum ether/benzene), provides after recrystallization from benzene orange crystals, mp 175 °C with decomposition, in 53% yield, that exhibit physical properties fully consistent with the trimeric structure $(C_{20}H_{26}Sn)_3$: mass spectrum (field desorption) $M^{+\cdot}$ cluster m/z (1146–1164);[7] ^{119}Sn NMR (benzene) δ (ppm from Me_4Sn) −416.52. Resembling distannanes[9] and the silicon analogue,[4] compound **2** shows an ultraviolet absorption maximum at 295 nm (log ϵ 4.66, cyclohexane), and due to the expected slow rotation of the aryl rings along the tin and carbon bonds, the ^{1}H NMR spectra (250 MHz, toluene-d_8) of the ethyl groups are temperature dependent.[4] Thus, two triplets (δ 0.89 and 0.69) and a complex multiplet (centered at 2.83 ppm) observed at −20 °C collapse to one triplet (δ 0.77) and one quartet (δ 2.78) at 60 °C, respectively. Confirmation of the structures assigned above to **1** and **2** follows.

Crystallographic Analysis of 1. The crystal structure of **1** is shown in Figure 1.[10] The cyclotristannoxane ring is essentially planar with a maximum deviation from the least-squares plane of 0.02 Å[2b] and thus follows the trend of $(Ph_2MO)_3$ (M = Si, Ge) rings, which possess small torsional angles.[11] The Sn–O and Sn–Ar bond lengths are in the range of 1.929 (6)–1.961 (6)[12] and 2.138 (6)–2.169 (9) Å, respectively. The wide Sn–O–Sn angles of 135.6 (3), 135.9 (3), and 137.1 (3)° are characteristic for M–O–M (M = Si, Ge, Sn).[13] As outlined by Glidewell,[14] they can easily be attributed to nonbonded interactions rather than pπ–dπ bonding.[15]

Crystallographic Analysis of 2. As shown in Figure 2,[16] the three tin atoms of **2** form an isosceles triangle, as in the trisilicon analogue[4] with Sn–Sn bond lengths of 2.870 (1), 2.856 (1), and 2.854 (1) Å, respectively. The angles at the tin atoms are 59.8 (1), 59.9 (1), and 60.3 (1)°, respectively. The planes formed by each of the pairs of Sn–Ar bonds are all rotated in the same sense by between 7.9 and 8.8° from the normal to the plane of the three tin atoms. The Sn–Ar bonds are in the range of 2.167 (10)–2.203 (9) Å. The Sn–Sn bond lengths of **2** appear to be the longest ever found for a bond of this type.[17] The slow rotation of the phenyl rings along the C–Sn bonds shown above by ^{1}H NMR spectra is expected from the steric congestion created between several pairs of the ethyl groups.

Compound **2** in the crystalline form is air-stable but is converted to **1** upon standing in solution. **2** is also reactive toward chlorinated solvents. Of particular interest is obviously its thermal and photochemical behavior, which will be discussed in due course.

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Registry No. 1, 84143-91-9; **2**, 84143-92-0; **3**, 16919-46-3; **4**, 84143-93-1.

Supplementary Material Available: Listing of atom coordinates and temperature factors, bond lengths, bond angles, and anisotropic temperature factors as well as detailed information concerning the mass spectra, X-ray analyses, and other spectral data (15 pages). Ordering information is given on any current masthead page.

(9) Drenth, W.; Janssen, M. J.; Van Der Kerk, G. J. M.; Vliegenthart, J. A. *J. Organomet. Chem.* **1964**, *2*, 265.

(10) Crystals of **1** solvated with benzene $C_{60}H_{78}Sn_3O_3 \sim {}^1/_2C_6H_6$ are monoclinic with a = 21.219 (3) Å, b = 13.246 (2) Å, c = 21.372 (3) Å, β = 97.21 (1)°, U = 5959 Å^3, space group $P2/c$, Z = 4, μ(Cu Kα) = 105 cm^{-1}. Three-dimensional intensity data were collected on a Nicolet R3m diffractometer. The structure was solved by direct methods and refined by full-matrix least-squares calculations to R = 0.054 for 5263 observed reflections with $|F_0| > 3\sigma(|F_0|)$.[7]

(11) For $(Ph_2SiO)_3$: (a) Bokii, N. G.; Zakharova, G. N.; Struchkov, Yu. T. *J. Struct. Chem.* **1972**, *13*, 267. For $(Ph_2GeO)_3$: (b) Ross, L.; Dräger, M. *Chem. Ber.* **1982**, *115*, 616.

(12) The Sn–O bond lengths are 1.955 Å in $(Ph_3Sn)_2O$ [(a) Glidewell, C.; Liles, D. C. *Acta Crystallogr., Sect. B* **1978**, *B34*, 1693] and 1.940 Å in $(Me_3Sn)_2O$ [(b) Vilkov, L. V.; Tarasenko, N. A. *Zh. Strukt. Khim.* **1969**, *10*, 1102].

(13) For $(Ph_2SiO)_3$: Si–O–Si angle of 130–133°, ref 11a. For $(Ph_2GeO)_3$: Ge–O–Ge angle of 128–130°, ref 11b. For $(Ph_3Sn)_2O$: Sn–O–Sn angle of 137°, ref 12a.

(14) Glidewell, C. *Inorg. Chim. Acta* **1975**, *12*, 219.

(15) Replacement of oxygen by less electronegative sulfur reverts bond angles to the expected values rather than over more pronounced, i.e., $(Ph_2SnS)_3$, Sn–S–Sn angle of 104°: Schumann, H. *Z. Anorg. Allg. Chem.* **1967**, *354*, 192.

(16) Compound **2** solvated with benzene $(C_{60}H_{78}Sn_3\cdot{}^1/_2\,C_6H_6)$ crystallized in the monoclinic system, space group $P2/c$, with a = 20.920 (7) Å, b = 13.086 (4) Å, c = 21.155 (5) Å, β = 97.12 (2)°, U = 5747 Å^3, Z = 4, μ(Cu Kα) = 108 cm^{-1}. The structure was solved in the same manner as for **1**; R = 0.057 for 5216 observed reflections with $|F_0| > 3\sigma(|F_0|)$.[7]

(17) The Sn–Sn bond lengths are 2.78 Å in $(Ph_2Sn)_6$ [(a) Olson, D. H.; Rundle, R. E. *Inorg. Chem.* **1963**, *2*, 1310], 2.839 Å in $[(Me_3SiCH_2)_2Sn]_4$ [(b) Belsky, V. K.; Zemlyansky, N. N.; Kolosova, N. D.; Borisova, I. V. *J. Organomet. Chem.* **1981**, *215* 41], and 2.77 Å in Ph_6Sn_2 [(c) Preut, H.; Haupt, H. J.; Huber, F. *Z. Anorg. Allg. Chem.* **1973**, *396*, 81].

Isoquinolinium Cycloadditions: Total Synthesis of (±)-14-Epicorynoline and *O*-Methylarnottianamide

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Bradsher[1] and others[2] have established that polar cycloaddition of isoquinoline salts with electron-rich alkenes is virtually 100% regiospecific and, for easily polarizable, unsymmetrical alkenes, highly stereospecific. The overall process disrupts the aza aromatic ring, creating a tricyclic system with up to four new stereocenters and an immonium ion.[3] We have investigated the general use

(1) (a) Chen, T.-K.; Bradsher, C. K. *J. Org. Chem.* **1979**, *44*, 4680–4683. (b) Day, F. H.; Bradsher, C. K.; Chen, T.-K. *Ibid.* **1975**, *40*, 1195–1198. (c) Bradsher, C. K. *Adv. Heterocycl. Chem.* **1974**, *16*, 289–324.

(2) Intramolecular version: Gisby, G. P.; Sammes, P. G.; Watt, R. A. *J. Chem. Soc., Perkin Trans. 1* **1982**, 249–255.

(3) In this study, a fifth stereocenter is created by subsequent addition of a nucleophile to the immonium ion. Under these conditions we assume the addition leads to the kinetic product, although the stereochemistry at this center does not alter the overall synthesis (see ref 2).