

(1) (Table I), in spite of its proportion, is able to distort the normal equal probability¹⁴ for the left (M) and right (P) handed helical sequences among the *n*-hexyl isocyanate units. The $[\alpha]_D$ values of the copolymers in Table I allow a quantitative measure of this helical excess from the known $[\alpha]_D$ of poly(*n*-hexyl isocyanate) of a single helical sense.¹⁵ Thus, for example, sample I at -20 °C exists with a ratio of helical sense units of 56/44; sample E, 88/12.

A large literature⁴ describes poly(*n*-hexyl isocyanate), in contrast to most synthetic polymers,¹⁶ as adopting an extended helical conformation in which long stretches of one helix sense, M or P, are separated by higher energy helix reversal states.^{13,15,17} This conformational picture offers a simple explanation for the surprising influence (Table I) of the chiral comonomer. Since the units between two helix reversals are constrained to a single helical sense, they must all be influenced toward either the M or P state by the presence in their midst of one or more chiral monomer units. As a few sergeants can control the movements of large numbers of cooperative soldiers, so do the few chiral comonomers control the helix sense of the otherwise indifferent hexyl isocyanate units, the latter unable to escape this influence except through rarely occurring helix reversals. The strong temperature dependence (Table I, Figure 1), as in the previously observed¹³ phenomenologically related effect of deuterium stereogenicity, can be understood as arising from a diminishing number of helix reversal states as energy is withdrawn, causing more units to act in concert.

Significantly, the solvent dependent dimension of poly(*n*-hexyl isocyanate),¹⁸ known to depend on local conformational properties,^{15,18} shows an exactly parallel behavior to the observed $[\alpha]_D$ values (Figure 1). The intriguing steep change of $[\alpha]_D$ in *n*-hexane, under further investigation, could arise from aggregation, claimed for poly(alkyl isocyanates) in nonpolar solvents especially at low temperature.¹⁹⁻²¹

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Supplementary Material Available: The carbonyl regions in the 125-MHz NMR spectra of the cyclic trimers derived from samples C, J, and A (1 page). Ordering information is given on any current masthead page.

2,2,4,4,5,5-Hexakis(2,6-diethylphenyl)pentastanna-[1.1.1]propellane: Characterization and Molecular Structure

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[1.1.1]Propellane (**1**, M = C, R = H in Scheme I) is an intriguing molecule that has received considerable experimental¹ and theoretical² attention regarding the extent to which bonding occurs between the bridgehead carbon atoms (i.e. **1a** vs **1b**). While this issue is still being debated, support is growing for a bond order of greater than zero.^{2c} Recently, ab initio calculations applied to the same question concerning bonding in pentasila[1.1.1]propellane (**2**, M = Si, R = H in Scheme I) have shown that no minimum corresponding to a "classical" structure with a bond between the bridgehead atom exists, and instead, the preferred structure for **2** appears to be one that possesses significant singlet diradical character as in **2b**.³ To date, no derivatives of **2** have been reported; however, herein, we report the isolation, characterization, and molecular structure of a pentastanna[1.1.1]propellane derivative (**3**, M = Sn, R = 2,6-diethylphenyl in Scheme I), which provides the first insight concerning the nature of bonding for the tin analogue of **1**.

Isolation of 3. The formation of **3** was accomplished by the thermolysis of hexakis(2,6-diethylphenyl)cyclotristannane (**4**)⁴ in xylene at 200 °C and isolation was effected through the use of flash chromatography on silica gel to provide **3** as an air-sensitive, dark blue violet, microcrystalline material (13% yield) and hexakis(2,6-diethylphenyl)distannane (**5**) as a white crystalline co-product.⁵ Analytically pure **3** could be obtained through recrystallization from a 6:1 hexane/toluene mixture at -40 °C.

Characterization of 3.⁵ As shown in Figure 1, due to hindered rotation of the 2,6-diethylphenyl substituents, the ¹H NMR (300 MHz, toluene-*d*₈) spectrum of **3** at 20 °C (spectrum a) exhibits two equally intense ABX₃ patterns for the ethyl groups with resonances at δ (ppm from reference solvent peak at 2.09 ppm) 0.87 (3 H, t, $J_{ax} = 7.4$ Hz), 1.06 (3 H, t, $J_{ax} = 7.4$ Hz), 1.65 (1 H, dq, $J_{ax} = 7.4$ Hz, $J_{ab} = 15.3$ Hz), 2.69 (2 H, m, two overlapping methylenes), and 2.97 (1 H, dq, $J_{ax} = 7.4$ Hz, $J_{ab} = 14.5$ Hz). In addition, H₃ and H₅ of the aromatic ring are nonequivalent and appear at 6.76 (1 H, d, $J = 7.5$ Hz) and 6.86 (1 H, d, $J = 7.5$ Hz) ppm, both being equally coupled to H₄ [7.05 (1 H, t, $J = 7.5$ Hz) ppm]. However, at 100 °C (spectrum b in Figure 1), partial rotation of the aryl substituents occurs to remove the inequivalency of the methyl groups [0.94 (6 H, t, $J = 7.5$ Hz) ppm] and of H₃ and H₅ [6.78 (2 H, d, $J = 7.6$ Hz) ppm], but not that of the methylene protons. Strong support for the [1.1.1]propellane structure of **3** is provided by ¹¹⁹Sn NMR

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(20) The transition temperature (Figure 1) is unaffected by wide variation in concentration. Copolyisocyanates F, G, H, I (Table I) show parallel steep transitions. Hysteresis in moving to low temperature is observed, and at >5 mg/mL in sample F a thermally reversible gel appears to form. See: *Reversible Polymer Gels and Related Systems*; Russo, P. S., Ed.; ACS Symposium Series 350; American Chemical Society: Washington, DC, 1987. For related observations in other stiff polymers see: Rawiso, M.; Aime, J. P.; Fave, J. L.; Schott, M.; Müller, M. A.; Schmidt, M.; Baumgartl, H.; Wegner, G. *J. Phys. France* **1988**, *49*, 861.

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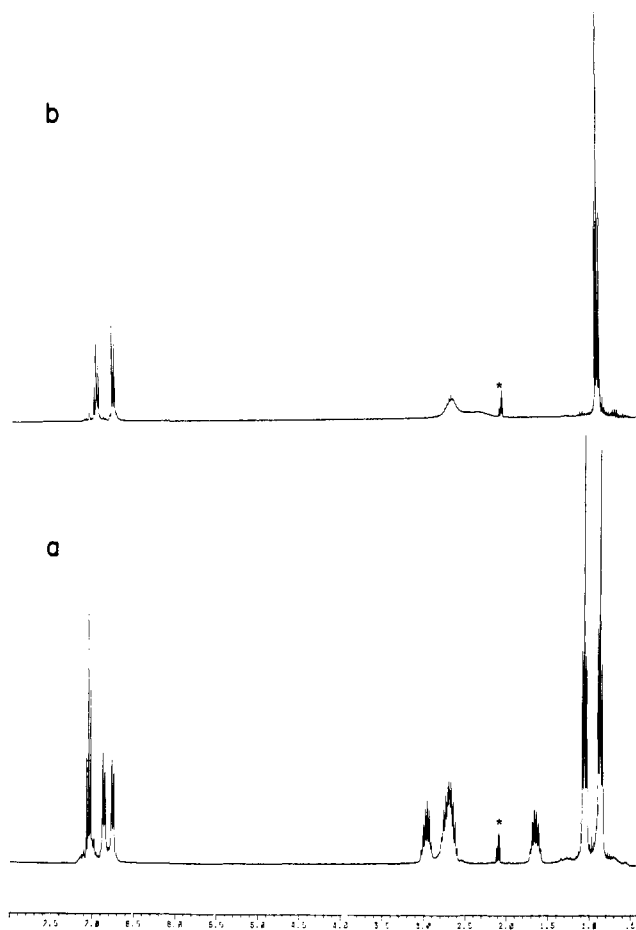
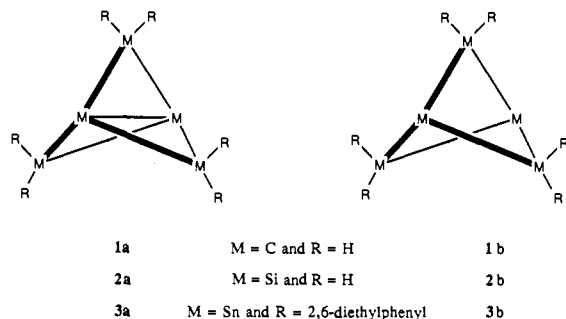


Figure 1. ^1H NMR (300 MHz, toluene- d_8) spectra of **3** taken at 20 °C (spectrum a) and at 100 °C (spectrum b). Solvent peaks are marked with an asterisk.

Scheme I



spectroscopy, which is a powerful tool for elucidating tin atom connectivity in polystannanes.⁶ Thus, a ^{119}Sn $\{^1\text{H}\}$ NMR (112 MHz, toluene- d_8 , δ relative to Me_4Sn) spectrum of **3** shows a resonance assigned to the equivalent bridging tin atoms (Sn_2 , Sn_4 , and Sn_5) at +356 ppm [$^1J(^{119}\text{Sn}-^{119}\text{Sn}) = 4159$ Hz (approximate relative intensity of each satellite signal to the parent peak, $I = 8\%$), $^1J(^{119}\text{Sn}-^{117}\text{Sn}) = 3975$ Hz ($I = 8\%$), and $^2J(^{119}\text{Sn}-^{117}\text{Sn}) = 262$ Hz ($I = 8\%$)] and a resonance for Sn_1 and Sn_3 at -1751 ppm [$^1J(^{119}\text{Sn}-^{119}\text{Sn}) = 4159$ Hz ($I = 14\%$), $^1J(^{119}\text{Sn}-^{117}\text{Sn}) = 3975$ Hz ($I = 14\%$)].⁷ It is important to note that in the 1D ^{119}Sn NMR spectrum of **3**, we do not observe a one-bond or two-bond coupling constant [$^nJ(^{119}\text{Sn}_{1,3}-^{117}\text{Sn}_{3,1})$ ($n = 1$ or 2)], which are expected for coupling between Sn_1 and Sn_3 in the structures of **3a** and **3b**, respectively.⁸ Neither the proton-coupled ^{119}Sn NMR

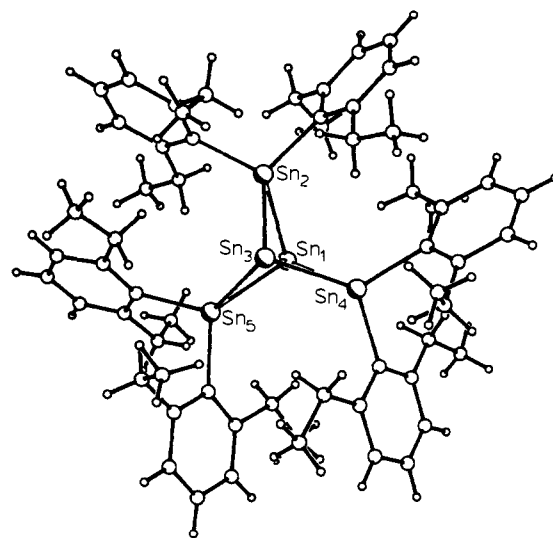


Figure 2. Crystal structure of **3**. Perspective of **3** viewed nearly perpendicular to the plane specified by Sn_2 , Sn_4 , and Sn_5 . Tin atoms are represented by large shaded spheres while carbon and hydrogen atoms are represented by medium and small open spheres, respectively. Bond lengths (\AA): Sn_1 - Sn_2 2.871 (1), Sn_1 - Sn_4 2.852 (1), Sn_1 - Sn_5 2.849 (1), Sn_3 - Sn_2 2.841 (1), Sn_3 - Sn_4 2.871 (1), Sn_3 - Sn_5 2.864 (1), Sn_1 - Sn_3 3.367 (1), $\text{Sn}-\text{C}$ 2.16 (1)-2.22 (1). Bond angles (deg): $\text{Sn}_2\text{Sn}_1\text{Sn}_3$ 53.5 (1), $\text{Sn}_3\text{Sn}_1\text{Sn}_4$ 54.2 (1), $\text{Sn}_3\text{Sn}_1\text{Sn}_5$ 54.1 (1), $\text{Sn}_1\text{Sn}_3\text{Sn}_2$ 54.3 (1), $\text{Sn}_1\text{Sn}_3\text{Sn}_4$ 53.7 (1), $\text{Sn}_1\text{Sn}_3\text{Sn}_5$ 53.7 (1), $\text{Sn}_1\text{Sn}_2\text{Sn}_3$ 72.2 (1), $\text{Sn}_1\text{Sn}_4\text{Sn}_3$ 72.2 (1), $\text{Sn}_1\text{Sn}_5\text{Sn}_3$ 72.2 (1), $\text{Sn}_2\text{Sn}_1\text{Sn}_4$ 88.4 (1), $\text{Sn}_2\text{Sn}_1\text{Sn}_5$ 88.2 (1), $\text{Sn}_4\text{Sn}_1\text{Sn}_5$ 89.9 (1), $\text{Sn}_2\text{Sn}_3\text{Sn}_4$ 88.6 (1), $\text{Sn}_2\text{Sn}_3\text{Sn}_5$ 88.5 (1), $\text{Sn}_4\text{Sn}_3\text{Sn}_5$ 89.3 (1).

nor the IR (Nujol) spectra show evidence for a directly bonded hydrogen atom at Sn_1 or Sn_3 (i.e. $\text{Sn}-\text{H}$),⁵ and at elevated temperatures up to 80 °C, the ^{119}Sn NMR spectra remain the same indicating that **3** does not undergo dynamic exchange with other species at these temperatures.

Solutions of **3** are intensely blue-violet in color, showing absorption maxima in pentane at 297 nm (ϵ_{max} 14500), 381 nm (ϵ_{max} 2600), 495 nm (ϵ_{max} 1000), and 558 nm (ϵ_{max} 1540) which extends beyond 700 nm (ϵ 628). A mass spectrum of **3** (field desorption) reveals an isotope cluster pattern $M^{+} m/z$ (1385-1400) which is consistent with the molecular formula of $\text{C}_{60}\text{H}_{78}\text{Sn}_5$.⁵ Finally, solutions of **3** in the presence of air decolorize over a period of minutes to produce hexakis(2,6-diethylphenyl)cyclotristannoxane (**6**).⁴

Crystallographic Analysis of 3.⁵ Attempts to grow suitable crystals of **3** for X-ray analysis failed in a variety of solvents at -40 °C. However, on several occasions we observed by ^1H NMR that **3** had a tendency to co-crystallize with the hexaaryldistannane **5** from hexane at -40 °C when **5** was present as an impurity. Dark purple crystals comprised of a 2:1 ratio of **3** and **5** proved to be suitable for crystallographic analysis.^{5,9} As shown in Figure 2, the tin-tin bond lengths between the bridging and bridgehead tin atoms of **3** are longer than normal being in the range of 2.841 (1) to 2.871 (1) \AA and this is to be expected for a ring-strained polystannane.¹⁰ Of particular interest is the distance of 3.367 (1) \AA between Sn_1 and Sn_3 . Prior to this investigation, the longest observed tin-tin bond length was on the order of 2.97 \AA ¹¹ and this has now been extended to 3.052 (1) \AA for the hexaaryldi-

(8) It is possible that the value of $^nJ(^{119}\text{Sn}_{1,3}-^{117}\text{Sn}_{3,1})$ is smaller than the line width of the parent peak ($w_{1/2} = 26$ Hz).

(9) The molecular structure of **5** is provided as part of the crystallographic analysis of **3** and while a detailed discussion of this compound will be made in a separate account, a crystal packing diagram shows no unusual intermolecular interactions between **3** and **5** (see Supplementary Material).

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(7) These unusual ^{119}Sn chemical shift values are in keeping with the observed downfield shift of the methylene carbon atoms and an upfield shift of the bridgehead carbon atoms in the ^{13}C NMR spectrum of **1** (see ref 1).

stannane, **5**.⁵ Thus, the distance of 3.367 Å falls well outside this new range which would appear to support significant singlet diradical character for the structure of **3** (i.e. **3b**), at least at 25 °C. The tin-carbon bond lengths are in the range of 2.16 (1)–2.22 (1) Å and the bond angles of the pentastanna[1.1.1]propellane framework follow from the geometry of this structure and the observed tin-tin bond lengths mentioned above (Figure 2).

In conclusion, the direct manner in which **3** can be prepared and isolated, together with its relatively high stability and the view provided by its molecular structure, will aid in future studies directed toward extending our knowledge concerning bonding within the Group IVB elements. Both experimental and theoretical investigations of the electronic structure and chemical reactivity of pentastanna[1.1.1]propellane derivatives are currently in progress and will be reported in due course.

Acknowledgment. We thank Dr. Cynthia Day of Crystallitics Co. for the structural analysis of **3** and **5** and the Office of Naval Research for financial support. The high-resolution mass spectrum of **3** was provided by Dr. Catherine Costello of the facility supported by the National Institutes of Health (Grant R-R-00317; principal investigator, Professor K. Biemann), from the Division of Research Resources.

Supplementary Material Available: Detailed information concerning the isolation and the spectroscopic and crystallographic analysis of **3**, including listings of atomic coordinates and temperature factors, bond lengths, bond angles, and anisotropic temperature factors and an ORTEP representation of **3** and **5** (24 pages). Ordering information is given on any current masthead page.

Structure of the Bicyclo[1.1.0]butane Radical Cation: An ESR Study

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Removal of an electron from bicyclo[1.1.0]butane (**1**) affects mainly the transannular C(1)–C(3) bond,¹ so that in the radical cation **1**^{•+} thus formed this bond is essentially due to one electron. The lengthening of the interatomic distance between the two bridgehead carbon atoms and the concomitant flattening of the four-membered ring upon ionization suggest that the geometry of **1**^{•+} should be intermediate between the buckled **1** (flap angle $\alpha = 121.7^\circ$)² and the planar cyclobutane-1,3-diyl (**2**^{••}) ($\alpha = 180^\circ$).³ Accordingly, the singly occupied orbital of **1**^{•+} should evolve from the HOMO of **1** toward that of **2**^{••}.

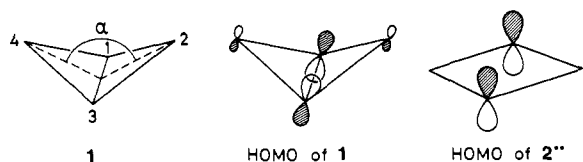


Figure 1. ESR spectra of **1**^{•+} (top) and **1-d**^{•+} (bottom) in a CFC1₃ matrix at 160 K ($g = 2.0030 \pm 0.0002$).

hyperfine data for **1**^{•+} are still unknown, although ESR spectroscopy is the most appropriate method to determine the structure of this radical cation. γ -Irradiation of **1**⁶ in a CFC1₃ matrix at 77 K (⁶⁰Co source) generates **1**^{•+}, which, at 160 K, gives rise to the spectrum shown at the top of Figure 1. This spectrum differs dramatically from that of the cyclobutene radical cation,⁷ to which **1** may rearrange upon electron removal. The well-defined hyperfine pattern of **1**^{•+} consists of a two-proton triplet spaced by 7.71 ± 0.05 mT, each component of the triplet being further split by 1.14 ± 0.05 mT into a four-proton quintet.

An unequivocal assignment of the coupling constants to sets of equivalent protons, and hence the crucial information about the structure of **1**^{•+}, has been provided by an ESR study of the radical cation **1-d**^{•+} generated from 1-deuteriobicyclo[1.1.0]butane (**1-d**) under the same conditions as **1**^{•+} from **1**. The labeled compound **1-d** was synthesized by lithiation of **1** at a bridgehead carbon atom with *n*-PrLi, followed by reaction of the Li derivative with D₂O. In the ESR spectrum of **1-d**^{•+} (Figure 1, bottom), the four-proton quintet is replaced by a three-proton quartet, as expected for the substitution of one bridgehead proton having a coupling constant of 1.14 mT by one deuteron. This finding requires the assignment of 1.14 mT to the two bridgehead protons (H_{br}) as well as to the two equatorial methylene protons (H_{eq}), while 7.71 mT represents the coupling constant of their two axial counterparts (H_{ax}). The apparent equality of the coupling constants observed for H_{br} and H_{eq} is presumably an artifact of a limited spectral resolution; even a difference as large as 0.2 mT would be obscured by the width of the hyperfine components. Also, as will be clarified by the arguments presented below, the equality or near-equality in question applies only to the absolute values of the coupling constants and not to their signs.

The strongly differing values of $a(\text{H}_{\text{eq}})$ and $a(\text{H}_{\text{ax}})$ point to a puckered geometry of **1**^{•+}. As no interchange between these coupling constants is observed at 160 K, the energy barrier to ring

Radical cations of **1** and its derivatives have been the subject of several theoretical and experimental studies.⁵ However, the

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