

CRYSTAL AND MOLECULAR STRUCTURE OF 1-AZA-5-STANNA-5-METHYLTRICYCLO[3.3.3.0^{1,5}]UNDECANE. EVIDENCE FOR A TRANSANNULAR DONOR–ACCEPTOR INTERACTION IN A TETRAORGANOTIN COMPOUND

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Summary

The compound 1-aza-5-stanna-5-methyltricyclo[3.3.3.0^{1,5}]undecane crystallizes in the space group $P2_1/c$. The unit cell, with a 7.700(1), b 9.289(3), c 16.296(5) Å, V 1159.4(5) Å³, β 95.89(2)°, contains four molecules. The structure was refined to a final R value of 0.042. The configuration of the tin atom is intermediate between a trigonal bipyramid and a tetrahedron. The intramolecular tin–nitrogen distance is 2.624 Å.

Introduction

We recently described the synthesis of 1-aza-5-stannatricyclo[3.3.3.0^{1,5}]undecanes from a trifunctional Grignard reagent [1]. The chloro-substituted derivative $\text{ClSn}(\text{CH}_2\text{CH}_2\text{CH}_2)_3\text{N}$ exhibits the expected slightly distorted trigonal bipyramidal geometry around the tin atom arising from a strong tin–nitrogen interaction associated with a distance of 2.372 Å [2]. For the methyl-substituted compound $\text{MeSn}(\text{CH}_2\text{CH}_2\text{CH}_2)_3\text{N}$, a tetraorganotin derivative, a pentacoordinated structure was indicated by the very small $^1J(^{119}\text{Sn}-^{13}\text{C})$ coupling constant in its ¹³C NMR spectrum [1]. In order to obtain more information concerning the strength of this tin–nitrogen dative bond in comparison with that in the chloro substituted derivative we carried out the X-ray diffraction study described here.

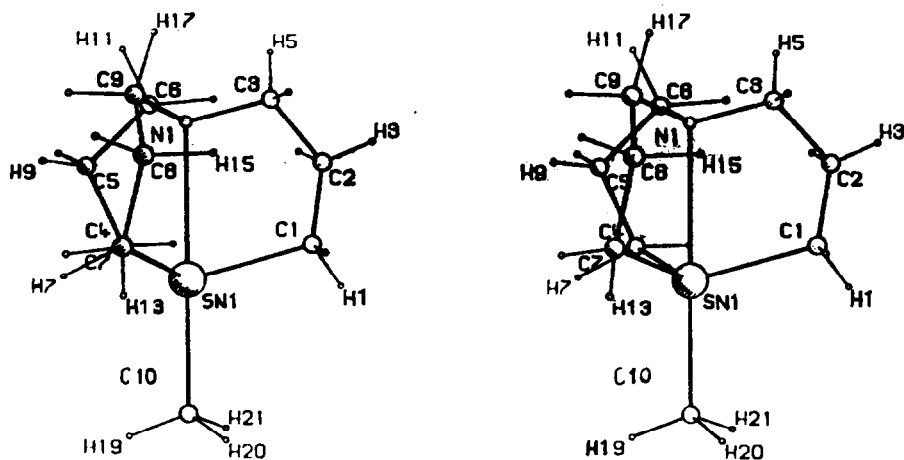


Fig. 1. Stereoscopic view of the molecular structure with atom numbering.

TABLE 1

FRACTIONAL ATOMIC COORDINATES ($\times 10^5$ for Sn, $\times 10^4$ for N and C, $\times 10^3$ for H atoms) AND B_{eq} VALUES

	x	y	z	B_{eq}
Sn(1)	19279(6)	8552(6)	38379(3)	3.15
N(1)	2031(8)	3678(9)	3853(4)	3.36
C(1)	-711(11)	1547(9)	3491(6)	3.99
C(2)	-1076(11)	3055(10)	3762(7)	4.29
C(3)	293(11)	4122(9)	3525(7)	3.81
C(4)	2875(15)	1427(11)	5099(6)	4.67
C(5)	3708(14)	2921(11)	5155(6)	4.86
C(6)	2471(16)	4063(9)	4725(7)	4.59
C(7)	3720(13)	1426(11)	2952(7)	4.49
C(8)	3446(13)	2964(10)	2636(6)	4.47
C(9)	3387(13)	4060(9)	3312(7)	4.33
C(10)	1821(14)	-1527(12)	3828(6)	5.14
H(1)	-155(0)	80(0)	375(0)	
H(2)	-68(11)	137(10)	291(6)	
H(3)	-213(11)	347(10)	363(5)	
H(4)	-92(10)	325(10)	444(6)	
H(5)	-1(11)	508(11)	383(5)	
H(6)	28(12)	412(9)	293(6)	
H(7)	415(12)	77(9)	536(6)	
H(8)	160(11)	140(10)	532(6)	
H(9)	468(12)	300(9)	489(5)	
H(10)	425(10)	326(10)	575(5)	
H(11)	309(0)	510(0)	478(0)	
H(12)	94(13)	420(8)	491(6)	
H(13)	382(13)	62(9)	248(6)	
H(14)	470(12)	123(10)	324(6)	
H(15)	222(0)	302(0)	224(0)	
H(16)	444(11)	327(10)	237(5)	
H(17)	310(0)	512(0)	306(0)	
H(18)	465(0)	409(0)	368(0)	
H(19)	307(0)	-198(0)	400(0)	
H(20)	132(0)	-190(0)	322(0)	
H(21)	79(11)	-184(10)	420(6)	

Experimental

Crystal data. $C_{10}H_{21}NSn$, M 274.0, monoclinic $P2_1/c$, a 7.700(1), b 9.289(3), c 16.296(5) Å, β 95.89(2)°, V 1159.4(5) Å³, $Z = 4$, $F(000) = 552$, $\mu(\text{Mo-}K_\alpha)$ 19.91 cm⁻¹.

The synthesis of $\text{MeSn}(\text{CH}_2\text{CH}_2\text{CH}_2)_3\text{N}$ has been described elsewhere [1]. Crystals suitable for X-ray analysis were obtained from a concentrated solution in diethyl ether. Unit-cell parameters and intensity data were measured on a Huber 424-511 automatic diffractometer in the next conditions:

Graphite-monochromatized Mo- K_α radiation

ω -Scan technique up to $2\theta = 50^\circ$

Cell dimensions refined by least-squares fitting values of 30 reflections.

2037 reflections measured, hkl range from $(-9,0,0)$ to $(9,11,18)$; 1985 with $I > 2.5\sigma(I)$ used in subsequent calculations

No absorption correction.

Structure determination. The positional parameters of the tin atoms obtained from a Patterson synthesis were used in the DIRDIF program [3] to find the position of the other 11 non-hydrogen atoms. Full-matrix least-squares refinement using F was carried out by the SHELX 76-program [4] with atomic scattering factors from International Tables for X-ray Crystallography [5].

14 H atoms were located from a difference-Fourier synthesis and refined with an overall isotropic temperature factor of 3.95 Å². Other H atoms were placed in calculated positions. Anisotropic thermal parameters were introduced for all non-hydrogen atoms. Weighting scheme is $w = 1/(\sigma^2 + 0.00007F^2)$. The final R value was 0.042, $R_w = 0.044$. A final ΔF map shows no regions of significant electron density. Final atomic coordinates are listed in Table 1 and the atom numbering is shown in Fig. 1. Lists of thermal parameters and structure factors are available from J.M.-P.

Results and discussion

The title molecule is illustrated in Fig. 1. The overall geometry of the present molecule is similar to that of $\text{ClSn}(\text{CH}_2\text{CH}_2\text{CH}_2)_3\text{N}$, even though the threefold axis is approximate in the present case. Furthermore the methyl substituted derivative is chiral, and the centrosymmetrical space group shows that equal amounts of the two enantiomers are present. The Sn-N distance of 2.624 Å is much longer than that in $\text{ClSn}(\text{CH}_2\text{CH}_2\text{CH}_2)_3\text{N}$ but considerably shorter than the sum of the Van der Waals radii of tin and nitrogen, and corresponds to a formal bond order of about 0.46 [6], for $\text{ClSn}(\text{CH}_2\text{CH}_2\text{CH}_2)_3\text{N}$ the corresponding formal bond order is about 0.71. Of the stannatranes [2], the present one shows the weakest intramolecular Sn-N interaction, and this is because of the absence of any electronegative atoms attached to the tin center. However, this interaction is not only a result of the atrane frame but also of some Lewis acidity of the tin atom. Very recently Reich and co-workers have demonstrated the existence of $R_5\text{Sn}^-$ species at low temperature [7]. For the tricyclic phosphatrane $\text{S}=\text{P}(\text{OCH}_2\text{CH}_2)_3\text{N}$ X-ray studies reveal a nearly planar arrangement of the nitrogen atom with a much weaker 1,5-interaction [8]. Furthermore manxine, $\text{HC}(\text{CH}_2\text{CH}_2\text{CH}_2)_3\text{N}$, is indicated by its chemical and spectroscopic properties to contain a planar nitrogen atom [9-11].

TABLE 2

BOND DISTANCES (Å) AND BOND ANGLES (°) WITH STANDARD DEVIATIONS

N(1)---Sn(1)	2.624(8)	C(1)–Sn(1)–N(1)	74.4(3)
C(1)---Sn(1)	2.151(8)	C(4)–Sn(1)–N(1)	74.9(3)
C(4)---Sn(1)	2.174(10)	C(4)–Sn(1)–C(1)	113.1(4)
C(7)---Sn(1)	2.163(9)	C(7)–Sn(1)–N(1)	74.9(3)
C(10)---Sn(1)	2.214(11)	C(7)–Sn(1)–C(1)	113.7(4)
C(3)---N(1)	1.449(11)	C(7)–Sn(1)–C(4)	113.3(4)
C(6)---N(1)	1.471(12)	C(10)–Sn(1)–N(1)	179.6(2)
C(9)---N(1)	1.478(10)	C(10)–Sn(1)–C(1)	105.3(4)
C(2)---C(1)	1.504(13)	C(10)–Sn(1)–C(4)	105.0(4)
C(3)---C(2)	1.524(11)	C(10)–Sn(1)–C(7)	105.4(4)
C(5)---C(4)	1.528(14)	C(3)–N(1)–Sn(1)	104.8(5)
C(6)---C(5)	1.545(15)	C(6)–N(1)–Sn(1)	104.8(5)
C(8)---C(7)	1.525(14)	C(6)–N(1)–C(3)	113.6(8)
C(9)---C(8)	1.504(13)	C(9)–N(1)–Sn(1)	104.9(5)
		C(9)–N(1)–C(3)	113.2(7)
		C(9)–N(1)–C(6)	114.3(8)
		C(2)–C(1)–Sn(1)	113.6(6)
		C(3)–C(2)–C(1)	112.1(7)
		C(2)–C(3)–N(1)	111.0(7)
		C(5)–C(4)–Sn(1)	112.1(6)
		C(6)–C(5)–C(4)	111.2(8)
		C(5)–C(6)–N(1)	110.0(7)
		C(8)–C(7)–Sn(1)	112.3(6)
		C(9)–C(8)–C(7)	113.6(8)
		C(8)–C(9)–N(1)	110.5(7)

As a result of the weakness of the Sn–N interaction the configuration of the tin atom is markedly distorted from the ideal trigonal bipyramidal, and must be more regarded as a monocapped tetrahedron. Indeed the equatorial angles (mean value 113.4° for C(1)–Sn(1)–C(4), C(1)–Sn(1)–C(7), C(4)–Sn(1)–C(7)) are closer to a tetrahedral angle than to 120°, and the apical angles (mean value 105.2° for C(10)–Sn(1)–C(1), C(10)–Sn(1)–C(4), C(10)–Sn(1)–C(7); Table 2) are not far from 109°. Thus, the difference between the sums of the equatorial and apical angles (a measure of the position of a given structure along the pathway tetrahedron → trigonal bipyramid [12]) is only 24.4°. The deviation of the tin atom from the plane defined by the carbon atoms C(1), C(4), C(7) is 0.569 Å, much greater than that for other stannatranes [2]. However, the deviation of the nitrogen atom from the plane defined by the three adjacent carbon atoms is 0.375 Å, in the range of the values cited in Table 3 of ref. [2]. The equatorial tin–carbon distances are not much different from those in other pentacoordinated organotin compounds [2,12–14], whereas the apical Sn(1)–C(10) bond distance exhibits the expected lengthening, and is to our knowledge the largest known for tetraorganotin compounds [15], and accounts for the high reactivity of this bond towards electrophiles such as Me₃SnBr [16]. The torsion angles listed in Table 3 show that the eight-membered rings have a boat-chair conformation which is comparable with that in the chloro-substituted derivative [2].

We believe that the structure described here represents the upper limit of a donor–acceptor interaction in stannatranes of the type RSn(CH₂CH₂CH₂)₃N. We

TABLE 3
TORSION ANGLES IN THE EIGHT-MEMBERED RINGS (°)

C(7)–Sn(1)–C(1)–C(2)	– 87.1
Sn(1)–C(1)–C(2)–C(3)	49.7
C(1)–C(2)–C(3)–N(1)	– 55.9
C(2)–C(3)–N(1)–C(9)	146.5
C(3)–N(1)–C(9)–C(8)	– 82.0
N(1)–C(9)–C(8)–C(7)	– 55.6
C(9)–C(8)–C(7)–Sn(1)	50.1
C(8)–C(7)–Sn(1)–C(1)	43.5
C(1)–Sn(1)–C(4)–C(5)	– 88.4
Sn(1)–C(4)–C(5)–C(6)	52.3
C(4)–C(5)–C(6)–N(1)	– 58.7
C(5)–C(6)–N(1)–C(3)	147.8
C(6)–N(1)–C(3)–C(2)	– 81.1
N(1)–C(3)–C(2)–C(1)	– 55.9
C(3)–C(2)–C(1)–Sn(1)	49.7
C(2)–C(1)–Sn(1)–C(4)	43.9
C(4)–Sn(1)–C(7)–C(8)	– 87.4
Sn(1)–C(7)–C(8)–C(9)	50.1
C(7)–C(8)–C(9)–N(1)	– 55.6
C(8)–C(9)–N(1)–C(6)	145.9
C(9)–N(1)–C(6)–C(5)	– 80.2
N(1)–C(6)–C(5)–C(4)	– 58.7
C(6)–C(5)–C(4)–Sn(1)	52.3
C(5)–C(4)–Sn(1)–C(7)	42.8

hope now to obtain single crystals of $[\text{Sn}(\text{CH}_2\text{CH}_2\text{CH}_2)_3\text{N}]^+ \text{BF}_4^-$ in which the strongest tin–nitrogen interaction should be observed.

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