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Molecular Structure of and Restricted Internal Rotation about the Tin–Tin Bond in $[ClSn(CH_2CH_2CH_2)_2NCH_3]_2$ and Solution Isomerism and Isomerizations in $[CH_3Sn(CH_2CH_2CH_2)_2NCH_3]_2$, Two Compounds with Five-Coordinate Tin Centers Bound to Each Other

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The crystal structure of $[ClSn(CH_2CH_2CH_2)_2NCH_3]_2$ (1) has been determined by an X-ray study. The crystal data are as follows: triclinic space group $P\bar{1}$, $a = 10.757$ (6), $b = 7.673$ (3), $c = 12.662$ (7) Å; $\alpha = 83.49$ (4), $\beta = 90.26$ (4), $\gamma = 72.48$ (4)°; $V = 989.4$ Å^3; $Z = 2$. The structure was refined to $R = 0.045$. The two five-coordinate tin moieties exhibit approximately trigonal-bipyramidal geometries with the chlorine and nitrogen atoms occupying apical positions and the tin–tin and tin–carbon bonds occupying equatorial positions and are twisted with respect to one another by about 120° along the tin–tin bond. The ^1H, ^{13}C, and ^{119}Sn NMR data indicate that in solution 1 exists as only one isomer having the same structure as in the solid state. At low temperature, the ^{13}C spectra reveal restricted internal rotation about the tin–tin bond with an activation barrier of about 11.5 ± 0.5 kcal/mol. In contrast, $[CH_3Sn(CH_2CH_2CH_2)_2NCH_3]_2$ (2) exists in solution as a mixture of at least three isomers, A, B, and C. NMR data on the major isomer A of 2 are explained in terms of a structure with the two methyl groups and the two intramolecularly coordinating nitrogen atoms in apical positions at each tin and the two ring carbon chains and the tin–tin bond in equatorial positions, in agreement with both the cyclic ligand structure and the polarity rule. For the medium and minor isomers of 2, B and C, respectively, no unambiguous structure can be proposed: B and C either have respectively only one and no methyl group in the apical position, with one and two tin atoms in the apical position, or have one and two four-coordinate tin centers, respectively. An analysis of the cross peaks of a two-dimensional EXSY ^{119}Sn NMR spectrum of 2 reveals that the isomers A and B interconvert through an uncorrelated rearrangement of one tin center at a time. No evidence could be found that the internal rotation about the tin–tin bond is restricted in 2 on the NMR time scale at temperatures at which it is in 1. The differences between the dynamic stereochemical behaviors of 1 and 2 are explained in terms of the apicophilicity differences between a methyl group and a chlorine atom.

Introduction

Although molecules with one or more tin–tin bonds have been known for a long time,[2] their chemistry has been studied especially in the last years. In this context, the structure of cyclic polystannanes,[3–5] the generation of divalent tin compounds starting from polystannanes or from substituted distannanes,[6] and the investigation of stannyl radicals[7] have received particular attention. On the other hand, it is well-known that especially when electronegative substituents are introduced at tin atoms, their coordination number can be increased by inter- or intramolecular donor ligands.[8–10]

Introducing 2D EXSY ^{119}Sn NMR spectroscopy, we demonstrated recently that in compound 3, $CH_2[SnPh(SCH_2CH_2)_2NCH_3]_2$, the isomerization of each tin center is not correlated to the other one.[11,12] The three possible isomers of 3 were shown to differ by the apical or equatorial position of their CH_2 bridge and their phenyl rings on the tin atom.

During our studies on transannular interactions in tin(II) and tin(IV) containing cyclooctanes,[11,13,14] we prepared 1-(1-chloro-5-methyl-5-aza-1-stanna[3.3.0^{1,5}]bicyclooctyl)-1-chloro-5-methyl-5-aza-1-stanna[3.3.0^{1,5}]bicyclooctane, $[ClSn(CH_2CH_2CH_2)_2NCH_3]_2$ (hereafter compound

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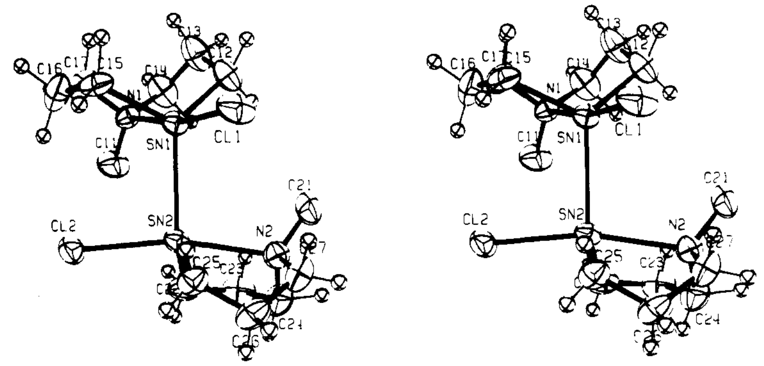

Figure 1. Stereoscopic ORTEP plot[47] of compound 1 with numbering scheme. H atoms are shown as spheres of 0.1-Å radius; the anisotropic ellipsoids enclose 50% probability.

Table I. Fractional Atomic Coordinates with Their Esd's in Parentheses (×10^5 for Sn Atoms, ×10^4 for all Other Non-H Atoms, ×10^3 for H Atoms)

atom	*x*	*y*	*z*
Sn(1)	33289 (6)	4703 (8)	32300 (4)
Sn(2)	13160 (6)	29929 (8)	18902 (4)
Cl(1)	2623 (3)	2414 (4)	4762 (2)
Cl(2)	2883 (2)	3841 (3)	567 (2)
N(1)	4324 (7)	-1765 (10)	2007 (6)
N(2)	-566 (8)	2752 (11)	2906 (6)
C(11)	3716 (12)	-1420 (17)	923 (8)
C(12)	3292 (13)	-2041 (14)	4142 (9)
C(13)	4271 (14)	-3689 (14)	3718 (9)
C(14)	4200 (14)	-3547 (16)	2536 (9)
C(15)	5196 (9)	970 (14)	3020 (8)
C(16)	5816 (11)	107 (16)	2071 (11)
C(17)	5677 (10)	-1750 (17)	2002 (11)
C(21)	-372 (12)	1095 (16)	3690 (9)
C(22)	182 (11)	2270 (18)	710 (9)
C(23)	-891 (13)	1585 (18)	1211 (10)
C(24)	-1543 (10)	2763 (18)	2053 (10)
C(25)	632 (10)	5709 (14)	2402 (10)
C(26)	-779 (10)	6110 (14)	2726 (10)
C(27)	-980 (12)	4469 (15)	3432 (10)
H(1)	241 (10)	-229 (13)	396 (7)
H(2)	359 (9)	-216 (12)	498 (8)
H(3)	409 (0)	-496 (0)	405 (0)
H(4)	525 (0)	-373 (0)	398 (0)
H(5)	473 (10)	-449 (14)	228 (8)
H(6)	309 (9)	-382 (13)	228 (7)
H(7)	584 (0)	36 (0)	371 (0)
H(8)	506 (0)	245 (0)	291 (0)
H(9)	682 (0)	6 (0)	206 (0)
H(10)	531 (0)	102 (0)	135 (0)
H(11)	626 (9)	-228 (13)	123 (8)
H(12)	632 (9)	-242 (13)	273 (8)
H(13)	70 (10)	116 (14)	38 (8)
H(14)	-17 (10)	292 (14)	22 (9)
H(15)	-45 (10)	38 (14)	159 (8)
H(16)	-157 (9)	163 (12)	66 (8)
H(17)	-185 (9)	411 (14)	175 (8)
H(18)	-223 (9)	229 (13)	262 (7)
H(19)	126 (10)	583 (13)	292 (8)
H(20)	59 (10)	659 ((14)	189 (8)
H(21)	-104 (0)	733 (0)	313 (0)
H(22)	-139 (0)	637 (0)	200 (0)
H(23)	-50 (10)	431 (13)	407 (9)
H(24)	-173 (11)	436 (14)	377 (8)

1), and its dimethyl analogue, 1-(1,5-dimethyl-5-aza-1-stanna[3.3.0^{1,5}]bicyclooctyl)-1,5-dimethyl-5-aza-1-stanna-[3.3.0^{1,5}]bicyclooctane, $[CH_3Sn(CH_2CH_2CH_2)_2NCH_3]_2$ (hereafter compound 2).

In analogy to compound 3 it seemed reasonable to expect similar interesting isomerism and isomerization phenomena for both compounds 1 and 2 because they also appeared likely to have their two tin atoms five-coordinated. However, unlike compound 3, the presence of a tin–tin bond in 1 and 2 let us presume that internal rotation about the tin–tin bond could eventually be observed.

Table II. Selected Interatomic Distances (Å) with Estimated Standard Deviations in Parentheses

Sn(1)–Cl(1)	2.560 (2)	Sn(2)–Cl(2)	2.552 (2)
Sn(1)–N(1)	2.448 (7)	Sn(2)–N(2)	2.446 (7)
Sn(1)–C(12)	2.143 (9)	Sn(2)–C(22)	2.147 (10)
Sn(1)–C(15)	2.167 (9)	Sn(2)–C(25)	2.166 (9)
	Sn(1)–Sn(2)	2.831 (1)	
C(11)–N(1)	1.478 (11)	C(21)–N(2)	1.483 (12)
C(14)–N(1)	1.497 (12)	C(24)–N(2)	1.500 (12)
C(17)–N(1)	1.458 (12)	C(27)–N(2)	1.492 (12)
C(12)–C(13)	1.534 (15)	C(22)–C(23)	1.520 (16)
C(13)–C(14)	1.488 (15)	C(23)–C(24)	1.513 (15)
C(15)–C(16)	1.500 (14)	C(25)–C(26)	1.523 (13)
C(16)–C(17)	1.489 (15)	C(26)–C(27)	1.530 (15)
	Shortest Cl···H Distances Intramolecular		
Cl(1)···H(19)	3.28	Cl(2)···H(10)	2.93
Cl(1)···H(23)	3.31		
	Intermolecular		
Cl(1)···H(7)	2.82	Cl(2)···H(11)	2.73
Cl(1)···H(3)	2.99	Cl(2)···H(6)	3.02
Cl(1)···H(21)	3.17	Cl(2)···H(17)	3.19
Cl(1)···H(24)	3.18		

This paper presents a study of the solid-state structure of compound 1 by X-ray analysis, its internal rotation about the tin-tin bond in solution by ^{13}C NMR spectroscopy, and the solution isomerism and isomerizations of compound 2 by multinuclear NMR comprising 2D EXSY ^{119}Sn NMR spectroscopy.[12]

Crystal and Molecular Structure of $[ClSn(CH_2CH_2CH_2)_2NCH_3]_2$ (1)

No comparative study of compounds 1 and 2 could be made in the solid state because no crystals suitable for X-ray analysis could be isolated for 2.

The molecular structure of compound 1 is shown in the ORTEP plot of Figure 1. Atomic coordinates, bond lengths, and bond angles are listed in Tables I, II, and III, respectively. The molecule is formed of two enantiomorphic units $[ClSn(CH_2CH_2CH_2)_2NCH_3]$ bound to one another by a tin–tin bond. Because of steric hindrance, the two five-coordinate moieties of the molecule are twisted by about 120° along the Sn–Sn vector: the dihedral angle between the planes Sn–Sn–Cl(1) and Sn–Sn–Cl(2) is 118.5°. Figure 2 shows that a rotation about the tin–tin bond, increasing the torsional angle ϕ, causes contacts of Cl(1) with C(21) and Cl(2) with C(11), whereas decreasing the torsional angle ϕ causes contacts of Cl(1) with C(25) and Cl(2) with C(15), respectively. As shown below, evidence for a hindered rotation was also found in solution.

Both tin atoms bound to each other exhibit a distorted trigonal-bipyramidal environment, with the nitrogen and

Table III. Bond Angles (deg) with Estimated Standard Deviations in Parentheses

N(1)-Sn(1)-Cl(1)	169.1 (2)	N(2)-Sn(2)-Cl(2)	166.7 (2)
C(12)-Sn(1)-Sn(2)	128.0 (3)	C(22)-Sn(2)-Sn(1)	125.3 (3)
C(12)-Sn(1)-C(15)	118.3 (4)	C(22)-Sn(2)-C(25)	119.1 (4)
C(15)-Sn(1)-Sn(2)	112.6 (2)	C(25)-Sn(2)-Sn(1)	113.9 (3)
Cl(1)-Sn(1)-Sn(2)	90.2 (1)	Cl(2)-Sn(2)-Sn(1)	94.1 (1)
N(1)-Sn(1)-Sn(2)	100.7 (2)	N(2)-Sn(2)-Sn(1)	99.1 (2)
C(12)-Sn(1)-Cl(1)	94.2 (3)	C(22)-Sn(2)-Cl(2)	94.5 (3)
C(12)-Sn(1)-N(1)	79.2 (3)	C(22)-Sn(2)-N(2)	79.0 (3)
C(15)-Sn(1)-Cl(1)	96.6 (3)	C(25)-Sn(2)-Cl(2)	94.3 (3)
C(15)-Sn(1)-N(1)	79.2 (3)	C(25)-Sn(2)-N(2)	79.0 (3)
C(11)-N(1)-Sn(1)	116.5 (6)	C(21)-N(2)-Sn(2)	117.1 (6)
C(11)-N(1)-C(14)	108.5 (8)	C(21)-N(2)-C(24)	109.4 (8)
C(11)-N(1)-C(17)	112.4 (8)	C(21)-N(2)-C(27)	111.2 (8)
C(14)-N(1)-Sn(1)	104.2 (6)	C(24)-N(2)-Sn(2)	102.7 (5)
C(14)-N(1)-C(17)	111.9 (8)	C(24)-N(2)-C(27)	111.4 (8)
C(17)-N(1)-Sn(1)	103.1 (6)	C(27)-N(2)-Sn(2)	104.6 (6)
C(13)-C(12)-Sn(1)	110.0 (7)	C(23)-C(22)-Sn(2)	111.2 (7)
C(12)-C(13)-C(14)	112.2 (9)	C(22)-C(23)-C(24)	110.8 (9)
C(13)-C(14)-N(1)	113.1 (8)	C(23)-C(24)-N(2)	110.7 (9)
C(16)-C(15)-Sn(1)	109.0 (6)	C(26)-C(25)-Sn(2)	110.0 (6)
C(15)-C(16)-C(17)	113.6 (9)	C(25)-C(26)-C(27)	111.2 (8)
C(16)-C(17)-N(1)	113.2 (9)	C(26)-C(27)-N(2)	111.7 (8)

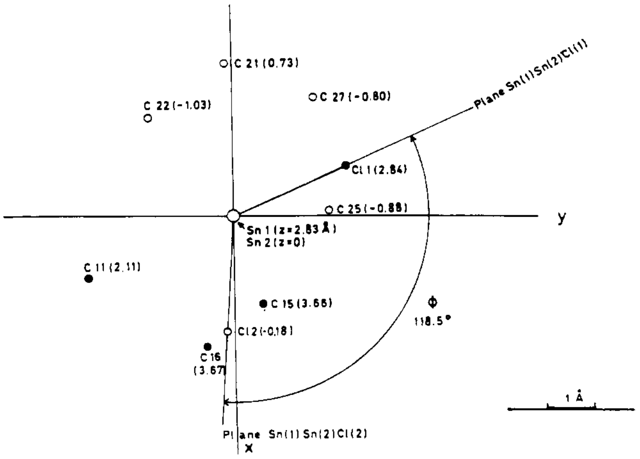

Figure 2. Projection along the Sn-Sn vector with the altitude of atoms in parentheses. Black circles represent atoms of the Sn(1) moiety and open circles those of the Sn(2) one.

Table IV. Torsion Angles (deg) in the Eight-Membered Rings

C(12)Sn(1)-C(15)C(16)	86.7	C(25)Sn(2)-C(22)C(23)	-84.6
Sn(1)C(15)-C(16)C(17)	-41.8	Sn(2)C(22)-C(23)-C(24)	42.3
C(15)C(16)-C(17)N(1)	55.9	C(22)C(23)-C(24)N(2)	-58.7
C(16)C(17)-N(1)C(14)	-147.8	C(23)C(24)-N(2)C(27)	153.2
C(17)N(1)-C(14)C(13)	78.6	C(24)N(2)-C(27)C(26)	-75.3
N(1)C(14)-C(13)C(12)	53.2	N(2)C(27)-C(26)C(25)	-55.9
C(14)C(13)-C(12)Sn(1)	-45.0	C(27)C(26)-C(25)Sn(2)	45.6
C(13)C(12)-Sn(1)C(15)	-52.1	C(26)C(25)-Sn(2)C(22)	51.7

Table V. Selection of ^1H NMR Data of Compounds 1 and 2[a]

resonance	1 (pyridine-d_5, 500 MHz, T = 298 K)	2 (toluene-d_8, 270 MHz) T = 298 K	T = 213 K
$SnCH_2$	1.51[b] (52)[d]	1.05-1.33[e]	1.05-1.35[c]
central CH_2	1.83[b] (112)[d]	1.72-1.92[e]	1.70-1.95[c]
NCH_2	2.32[b]	2.17-2.39[e]	2.15-2.40[c]
NCH_3	2.57	2.30	~2.25
$SnCH_3$		0.374 (14)[d] (35)[d]	0.404 (A)[f] (12)[d] (32)[d] 0.369 (B)[f] 0.548 (B′)[f] 0.270 (C)[f]

[a] Chemical shifts are in ppm toward TMS. [b] These values correspond to the chemical shift of the central signal of distorted multiplets. [c] Broad. [d] Unresolved $^2J(^{119/117}Sn-^1H)$ coupling in Hz. [e] Non-first-order patterns. [f] Signal labels, see Tables VI and VII and text.

chlorine atoms in apical positions and the ring carbon atoms C(12), C(15), C(22), and C(25) and the other tin atom in equatorial positions.

Differences between the bond angles around both tin atoms are in general slightly more marked where chlorine atoms are involved. This effect could be related to the weak intramolecular Cl(2)-H(10) interaction, since the distance of 2.93 Å between these atoms is shorter than the sum of the van der Waals radii.[15] The closest intramolecular contacts of the Cl(1) atom with the hydrogen atoms H(19) and H(23) were found to be only 3.28 and 3.31 Å, respectively, which is just at the limit of the sum of the van der Waals radii. The bond angles N(1)-Sn(1)-Cl(1) and N(2)-Sn(2)-Cl(2) are of the same order of magnitude as those of most stannaocanes studied previously;[11,16,17] they are however significantly smaller than the N-Sn-Cl angle of 176.8° in $Cl_2Sn(CH_2CH_2CH_2)_2NCH_3$, hereafter compound 4.[18] The Sn(1)-N(1) and Sn(2)-N(2) distances are comparable to those of other nitrogen-containing five-coordinate organotin compounds[16,19,20] and are even almost equal to the Sn-N bond length of 2.44 Å in 4.[18] This suggests the tin-nitrogen bonds of 1 and 4 to have similar bond energies. Both apical Sn-Cl bond distances of 1 exhibit the expected lengthenings caused by the intramolecular Sn-N interactions and are even longer than those in 4.[18] The Sn-C distances do not exhibit noteworthy differences with respect to those of other five-coordinate organotin compounds.[11,16-20]

The Sn-Sn bond length of 2.83 Å in 1 is significantly larger than that of other known molecules with tin-tin bonds,[3-5,21-25] although in the present case, this bond is equatorial in the trigonal-bipyramidal geometry at both tin atoms. However, this Sn-Sn distance is in the range of lengths found in compounds containing tin atoms with bulky substituents.[26,27]

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Table VI. ^{13}C NMR Data of Compounds 1 and 2 at 67.92 MHz[a]

	1 (CD_2Cl_2)			2 (toluene-d_8)		
signal	T = 290 K	T = 220 K	T_c	T = 343 K	T = 298 K	T = 213 K
$SnCH_2$	19.3 (400)[b] (382)[c] (64)[e]	19.1 18.0	[250]	12.9 (295)[b] (283)[c] (58)[e]	12.5 (301)[b] (288)[c] (53)[e]	12.6 (A) (315)[b] (304)[c] 12.3 (B) 11.8 (B′) 14.8 (C) 10.5 (D)?
central CH_2	24.0 (25)[b]	23.5 23.1	[235]	26.5 (29)[b]	26.0	26.2 (A) (26)[f] 26.4 (B) 24.9 (B′) 25.3 (C)
NCH_2	58.7 (39)[g]	58.1 57.3	[240]	60.1	59.5	58.9 (A) 60.0 58.4
NCH_3	45.3 (17)[h]	44.6		46.4	46.2 46.4	46.1 (A) 46.0
$SnCH_3$				–5.0 (162)[d]	–4.6[i]	–2.70 (A) (104)[d] (84)[e] –3.66 (B) –7.46 (B′) –7.68 (C) –4.69 (D)

[a] Chemical shifts are given in ppm toward TMS, used as external reference. In the case of 1, the TMS signal was located from the center of the CD_2Cl_2 multiplet taken to be 54.2 ppm. In the case of 2, the TMS signal was located from the center of the CD_3 multiplet of toluene-d_8 taken to be 21.3 ppm. Coupling constants are given in Hz between parentheses. T_c is the coalescence temperature, given between squared brackets in Kelvin. In the 220 K spectra of 1, the $SnCH_2$, NCH_2, and central CH_2 signals have pairwise identical intensities. No attempt was made to determine here the coupling constants to limit the number of scans in the temperature study. Capital letters in the 213 K spectra of 2, A, B, B′, C, and D, in parentheses are signal labels characterizing isomeric species A, B, C, and D respectively; see text. These spectra have always one dominant signals, A (≥70%), the signals B and B′ have roughly identical intensities, about twice that of unresolved $J(^{13}C-^{119/17}Sn)$ satellites, and signal C exceeds that of these satellites by a maximum of 50%, while signal D, when visible, has an intensity of the order of that of the satellites or slightly less. [b] $^1J(^{13}C-^{119}Sn)$. [c] $^1J(^{13}C-^{117}Sn)$. [d] Unresolved $^1J(^{13}C-^{119}Sn)$ and $^1J(^{13}C-^{117}Sn)$ splittings. [e] Unresolved $^2J(^{13}C-Sn-^{119}Sn)$ and $^2J(^{13}C-Sn-^{117}Sn)$ splittings. [f] Unresolved $^2J(^{13}C-C-^{119}Sn)$ and $^2J(^{13}C-C-^{117}Sn)$ splittings. [g] $^3J(^{13}C-C-C-^{119}Sn)$ and $^3J(^{13}C-C-C-^{117}Sn)$ splittings. [h] Poorly resolved, uncertain, as the satellites appear in the foot of the main NCH_3 signal. [i] Broad.

The torsional angles listed in Table IV indicate that both eight-membered rings adopt the boat–chair conformation observed for other tin compounds.[11,16,19] The conformation will be discussed in more detail in a comparative study on $Cl_2Sn(CH_2CH_2CH_2)_2E$ structures (E = NCH_3, O, S).[18]

NMR Results

^1H NMR Spectra. Similar to **3**,[11] compounds **1** and **2** were found to be monomeric in solution by osmometric and cryoscopic molar mass determinations in chloroform and in benzene, respectively.

Table V presents a selection of ^1H NMR data of compounds **1** and **2** in various solvents, at different temperatures and resonance frequencies. At room temperature, the 500-MHz ^1H spectrum of **1** in pyridine-d_5 exhibits distorted triplets at 1.51 and 2.32 ppm for the $SnCH_2$ and NCH_2 groups, respectively, a distorted quintet at 1.83 ppm for the central CH_2 group, and a singlet at 2.57 ppm for the NCH_3 group. Clear $^2J(^1H-C-^{119/117}Sn)$ and $^3J(^1H-C-^{119/117}Sn)$ coupling satellites of 52 and 112 Hz were found for the $SnCH_2$ and central CH_2 regions, respectively.

At 220 K, the spectrum of **1** roughly exhibits similar features. However all methylene signals undergo coalescence broadening, though the *N*-methyl signal remains sharp.

The 270-MHz ^1H NMR spectrum of compound **2** in toluene-d_8, at room temperature, exhibits non-first-order patterns in all three methylene regions. Thus the NCH_3 signal arises at 2.30 ppm in the middle of the NCH_2 region, that extends from 2.17 to 2.38 ppm. The $SnCH_2$ and central CH_2 regions extend from 1.05 to 1.33 ppm and from 1.72 to 1.92 ppm, respectively. Clear satellite images could be recognized only for the $SnCH_2$ resonances, corresponding roughly to a coupling constant of 70 Hz. The methyl group bound to tin gives rise to a unique sharp signal at 0.37 ppm, with $^2J(^1H-C-^{119/117}Sn)$ and $^3J(^1H-C-Sn-^{119/117}Sn)$ coupling satellites of 14 and 35 Hz, respectively.

At 213 K, the three methylene regions and the NCH_3 signal display roughly the same picture with broader signals. In the region of the tin methyl group the pattern is now composed of one intense signal A at 0.404 ppm, two smaller, equally intense signals B and B′ at 0.369 and 0.548 ppm with intensities only slightly larger than those of the satellites of A, and a unique, still smaller signal C at 0.270 ppm, the intensity of which does not exceed that of the satellites of A. The satellites of B, B′, and C are poorly defined as they overlap with the intense signals of A or interfere with its satellites and/or other unidentified very small signals.

^{13}C NMR Spectra. Table VI gives an overview of the most significant features of the ^1H broad-band-decoupled ^{13}C spectra at 67.92 MHz of compounds **1** and **2**.

The room-temperature spectrum of **1** in CD_2Cl_2 exhibits only one signal for each of the three methylene groups and the *N*-methyl group. However, at 220 K, two equally intense signals are observed for each of the Sn-bound, central, and N-bound methylene groups. They are separated by 75, 27, and 54 Hz and coalesce pairwise at 250, 235, and 240 K, respectively.

The NCH_3 signal remains unique and sharp throughout the whole temperature range studied. Satellites, with a coupling splitting of 17 Hz, are observed at room temperature. Although they overlap significantly with the foot of the parent signal, it is doubtful that these are spinning side bands, since the spinning rate was 13 Hz and no such bands were observed so close to the other main signals. To our knowledge, this would be the first observation of a

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direct coupling of the ^{13}C signal of a NCH$_3$ to $^{119/117}$Sn through a coordinating nitrogen-tin(IV) bond. In the tin(II)-containing heterocycle Sn(OCH$_2$CH$_2$)$_2$NCH$_3$, the ^2J(^{13}C-N-$^{119/117}$Sn) coupling is 56 Hz.[39e] No attempt was made to observe the coupling at low temperature, in order to limit the number of scans during the variable-temperature NMR study.

The room- and high-temperature spectra of **2** in toluene-d_8 exhibit roughly the same pattern as **1**, with an additional signal arising from the methyl groups bound to tin. This resonance is very broad, as a consequence of coalescence at 298 K, resulting in a unique signal that is still quite broad at 343 K.

These spectra were obscured by small impurity signals with intensities of the order of the satellites. Thus, in the central CH$_2$ region, two impurity signals are observed, slightly upfield from the main signal, in addition to the ^2J(^{13}C-C-$^{119/117}$Sn) coupling satellites that are clearly distinguished at high temperature. In the NCH$_3$ region, two such impurity signals appear also. They are not disposed symmetrically with respect to the main signal. Hence, in contrast to **1**, no ^2J(^{13}C-N-$^{119/117}$Sn) coupling is observed for **2**. In the NCH$_2$ region, no coupling satellites can be characterized since the two unequally intense impurity signals lie symmetrically with respect to the main signal and interfere probably with the coupling satellites. The SnCH$_2$ region exhibits only one impurity signal, upfield from the main signal with clearly defined ^1J(^{13}C-$^{119/117}$Sn) and ^2J(^{13}C-Sn-$^{119/117}$Sn) satellites. No impurity signal appears in the SnCH$_3$ region, as can be asserted from the fact that no narrow signal arises from the broadly coalescing methyl signals of **2**, over a quite broad temperature range. These unidentified impurities, which could not be discarded, are tin compounds since two impurity signals are also observed in the ^{119}Sn spectrum (see below).

Except for the SnCH$_2$ signal, no coupling satellites could be observed at room temperature because all signals were broader than in the high-temperature range.

As the temperature is lowered, the signals of **2** broaden and give rise, at 213 K, to additional small narrow signals. These do not arise from impurities, since they are coalesced away at higher temperatures. Roughly, each region is composed of a dominant signal A, with an intensity of at least 70%, and of a variable number of additional, less intense signals, two in the NCH$_2$ and the NCH$_3$ regions, three in the central CH$_2$ region, and four in the SnCH$_2$ and SnCH$_3$ regions. They are too close to one another or to the signal A to be identified in the NCH$_2$ and NCH$_3$ regions. In the SnCH$_2$, the SnCH$_3$, and the central CH$_2$ regions, however, two signals labeled B and B′ with identical intensities, about twice that of the J(^{13}C-$^{119/117}$Sn) satellites of A, and one signal labeled C, about 1.5 times as intense as these satellites, can be identified. Furthermore, in the SnCH$_2$ and SnCH$_3$ regions, an additional, still smaller but clearly recognizeable signal, labeled D appears. These signals D are clearly not associated with impurities, but we present their existence with some caution, as their intensity is even slightly less than that of the satellites.

Noteworthy are the exceptionally low values of the ^1J(^{13}C-$^{119/117}$Sn) coupling constant of the SnCH$_3$ signal: 104 Hz for signal A at low temperature. At high temperature, the coupling associated with the averaged SnCH$_3$ signal increases to 162 Hz. The coupling constants associated with SnCH$_2$ satellites vary only slightly with temperature. No coupling satellites could be observed for the additional signals B, B′, C, and D because of their low intensities.

^{119}Sn NMR Spectra. At room temperature, the 74.6-MHz proton broad-band-decoupled ^{119}Sn spectrum of **1** exhibits only one signal at −31.3 ppm in CD$_2$Cl$_2$ and −34.7 ppm in pyridine-d_5, toward Me$_4$Sn. The ^1J(^{119}Sn-^{117}Sn) satellites are clearly observable and display splitting values of 6814 and 6983 Hz in CD$_2$Cl$_2$ and pyridine-d_5, respectively. At 213 K, the ^{119}Sn spectrum of **1** still exhibits one single signal.

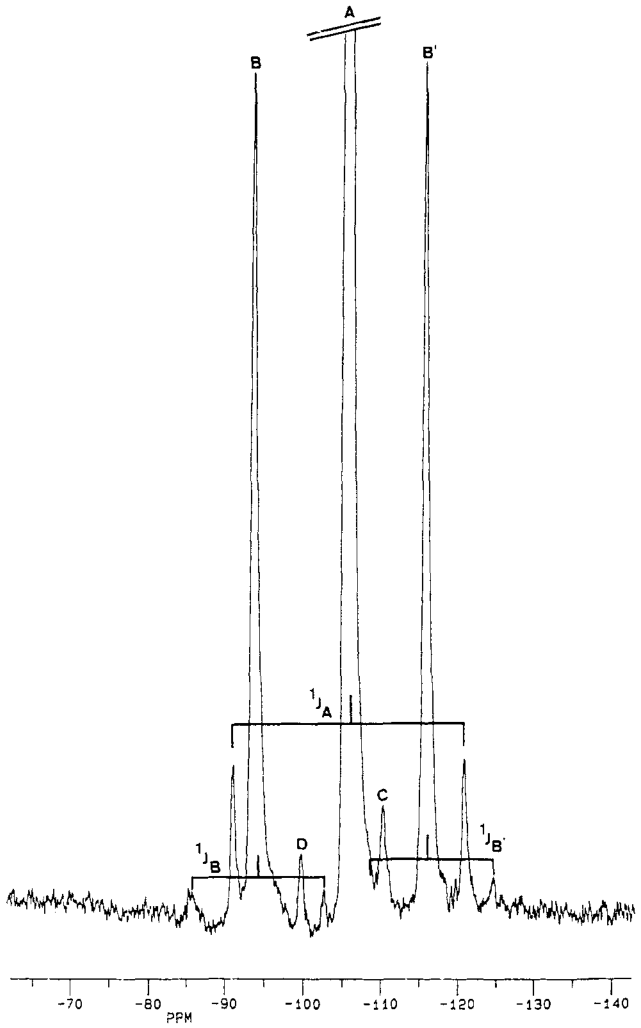

Figure 3. ^{119}Sn spectra of compound **2**, in toluene-d_8, at 186.5 MHz and 248 K.

The ^{119}Sn spectra of compound **2**, in toluene-d_8, at 74.6 and 186.5 MHz, are more complex. A data selection is given in Table VII. Figure 3 shows that the spectrum of compound **2** in toluene-d_8 at 248 K consists, in the chemical shift region of interest, of a very intense signal A (70%), with two satellites arising from the ^1J(^{119}Sn-^{117}Sn) coupling of 5521 Hz, two equally intense signals B and B′ (15% each with respect to A), with noisy satellites, and, accordingly, a less accurate, unresolved, averaged coupling of 3155 Hz. Furthermore, two very small signals C and D, the intensity of which does not exceed 2 and 1%, respectively, of the major signal A, are also observed. At room temperature all these signals coalesce to a unique, very broad averaged signal, that is of course sharper at lower resonance frequency and that further sharpens out a higher temperature. The ^{119}Sn spectral behavior, pattern, chemical shifts, and coupling constants of **2** in pyridine-d_5 are qualitatively the same as in toluene-d_8 at both low and room temperatures (see Table VII).

For completeness, it should be mentioned that, in the ^{119}Sn spectrum also, two impurity signals are observed, at 298 K, at −29.8 and −32.1 ppm, the latter being split into two subsignals at 248 K. They are not associated with

Table VII. ^{119}Sn NMR Data of Compound 2 in Toluene-d_8, Except the Last Series of Data Obtained in Pyridine-d_5

field frequency, MHz	temp, K	chem shift (ppm) vs TMT[a]	$^1J(^{119}$Sn–^{117}Sn),[n] Hz	molar fractn[h]
74.63	353	−101.9	4060	$x_A = 0.38$[i]
				$x_B = 0.62$[i]
74.63	305	−103.0	4543	$x_A = 0.59$[i]
				$x_B = 0.41$[i]
186.50	298	−104.3[b]	*c*	
186.50	248	A, −106.2	5521	$x_A = 0.70$[j]
		B, −94.2	3137[d]	$x_B = 0.30$[j]
		B′, −116.3	3174[d,e]	
		C, −110.5	*c*	*k*
		D, −99.9	*c*	*l*
74.63	238	A, −104.5	5546	$x_A = 0.72$[j]
		B, −93.1	3206[d,f]	$x_B = 0.28$[j]
		B′, −114.3	3164[d,g]	
		C, *m*	*c*	
		D, *c*	*c*	
74.63 (C_5D_5N)	233	A, −106.7	5613	$x_A = 0.72$[j]
		B, −95.0	3116[d]	$x_B = 0.28$[j]
		B′, −118.7	3106[d]	
		C, −109.8	*c*	
		D, −103.7	*c*	
	298	−105.0 (br)	*c*	

[a] TMT = tetramethyltin as external reference. [b] Broad; $\Delta\nu_{1/2} \approx$ 650 Hz. [c] Unobserved. [d] Unresolved $^1J(^{119}$Sn–^{119}Sn) and $^1J(^{119}$Sn–^{117}Sn) because the two tin atoms coupled are symmetry unequivalent. [e] Calculated from the high-field satellite alone, the low-field one being hidden in the foot of signal A. [f] Calculated from the low-field satellite alone, the high-field one being hidden in the foot of signal B′. [g] Calculated from the high-field satellite alone, the low-field one being hidden in the foot of signal B. [h] Molar fractions relative to the sum of the equilibrium populations of species A and B. [i] Calculated from the average $^1J(^{119}$Sn–^{117}Sn) and assuming $^1J(^{119}$Sn–^{117}Sn) = 5521 Hz for A and 3155 Hz for B. [j] Calculated from signal intensities, assuming identical spin–lattice relaxation times. [k] Intensity, maximum 2–4% of signal A. [l] Intensity, maximum 1–2% of signal A. [m] Visible as a small tail in the foot of signal A. [n] Estimated absolute error: ca. 20 Hz for A and ca. 40 Hz for B and B′.

compound 2 since they are not involved in the coalescences of the signals in the −100 ppm region, being sharp at room temperature, but indicate that the two small impurities already observed in the ^{13}C spectra contain tin.

Two-Dimensional (2D) ^{119}Sn EXSY Spectroscopy of Compound 2. In order to get a better insight into the dynamic processes responsible for the coalescences in the ^{1}H, ^{13}C, and ^{119}Sn NMR spectra of compound 2, we recorded two-dimensional (2D) ^{119}Sn EXSY (exchange spectroscopy) spectra.[12,35,36] The display presented in Figure 4 was obtained at 248 K and at 186.5 MHz, from a solution of 2 in toluene-d_8. It was symmetrized to avoid the important t_1 ridges and is given in the power mode.[35,36] The mixing time was 10 ms.[35]

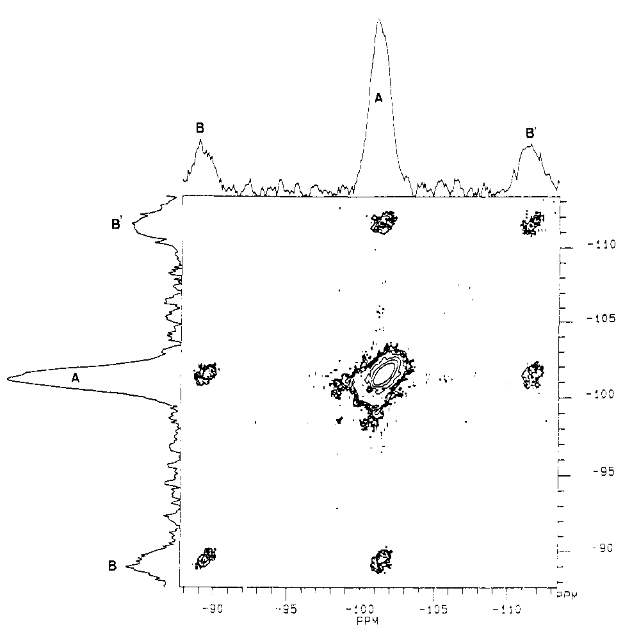

Figure 4. Two-dimensional (2D) ^{119}Sn EXSY (exchanging system) NMR spectrum of a solution of 2 in toluene-d_8 recorded at 248 K and at 186.5 MHz. The spectral window was chosen in such a way that the coupling satellites of signal A do not appear in the contour plot.

As expected, the resonances C and D can no longer be observed as they disappear in the very intense auto peak contour of resonance A. In contrast the autopeaks for B and B′ and the cross peaks are very clean. Importantly, cross-peak pairs are observed only between the resonances A and B and A and B′, but obviously not between B and B′. These observations clearly indicate that one-step transfers of magnetization[35,36n] under the stereochemical process do proceed only between the magnetic sites associated with A, on one hand, and B and B′, on the other hand, but that no transfer of magnetization is proceeding in one step between the two magnetic sites B and B′.

These findings are confirmed by another 2D EXSY spectrum obtained with a mixing time of 40 ms, where still no cross-peak pair between B and B′ appeared. The latter actually starts appearing only for a mixing time of 100 ms, a behavior that is characteristic for a two-step transfer of magnetization.[12,35,36]

Discussion

Static Stereochemistry of Compound 1 in Solution. The observations throughout the whole temperature range

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studied, of a unique resonance in the ^{119}Sn spectrum and a unique NCH_3 signal in the ^{1}H and ^{13}C spectra clearly indicate that no diastereoisomerism exists in compound 1 and that its two tin moieties are symmetry equivalent on the NMR time scale. All the NMR data at hand converge to the conclusion that the structure of 1 is identical with the one found in the solid state (see Figure 1). These NMR arguments can be summarized as follows.

The ^{119}Sn chemical shift value at −31.3 ppm in CD_2Cl_2 is characteristic for five-coordination at tin atoms,[29-34] $[ClSn(CH_3)_2]_2$ having chemical shifts in the range 70–120 ppm in nonligating solvents.[33] In addition, the absence of significant chemical shift modification when the nonligating dichloromethane is replaced by the ligating pyridine as a solvent and the fairly sure observation of the coupling satellite at the ^{13}C resonance of the *N*-methyl group indicate that intramolecular coordination by the ring nitrogen already exists and cannot be perturbed by external coordination with pyridine. Further, the value of the $^1J(^{119}Sn-^{13}C)$ coupling constant in 1 lies in the range generally observed for equatorial Sn–C bonds in five-coordinate tin compounds.[11,14] Finally, the value of 6814 Hz of the $^1J(^{119}Sn-^{117}Sn)$ coupling constant can be considered as characteristic for five-coordinate tin atoms since such couplings in ditin derivatives lie in the range 60–4500 Hz when the tin atoms are four-coordinate and in the range 7000–15000 Hz when they are five-coordinate.[9,29,33,34] However, the $^1J(^{119}Sn-^{117}Sn)$ coupling constants observed here for 1 are among the smallest ones ever observed for five-coordinate tin atoms bound to each other. This can be due either to a weak intramolecular coordination or to steric repulsion between the two tin moieties resulting in the lengthening of the tin–tin bond.

The fact that only one diastereomer is observed experimentally in solution indicates that the apicophilicity of the chlorine atom is well marked with respect to the other substituents at tin. However, the stabilizing electronic effect of this apicophilicity is probably attenuated by the steric repulsion, observed also in the solid state, between the *N*-methyl group and the CH_2 groups at one tin and the chlorine atom at the other in 1 with the quite long tin–tin bond and the low $^1J(^{119}Sn-^{117}Sn)$ value as consequences. The dynamic stereochemical behavior of 1 confirms actually the existence of such a repulsive steric interaction between the two tin moieties in 1.

Restricted Internal Rotation about the Tin–Tin Bond in Compound 1. Application of the equation of Gutowsky–Holm[41] to each coalescing pair of signals in the three methylene regions of the ^{13}C spectra of 1 (see Table VI) leads to $\Delta G^{*}_{250} = 11.6$, $\Delta G^{*}_{235} = 11.4$, and $\Delta G^{*}_{240} = 11.3$ kcal/mol as calculated free enthalpies of activation. Obviously these three values are due to a dynamic process with an activation barrier of roughly 11.5 ± 0.5 kcal/mol.

Since 1 exists also in solution as only one diastereomeric chiral species (see Figure 1), this process can only be a degenerate isomerization interconverting its enantiomers. Figure 5 illustrates that when the torsional angle ϕ between the two Cl–Sn–Sn planes of 1 is different from 0 or 180°, the molecule is chiral and exists as two enantiomeric rotamers with C_2 symmetry, the two tin moieties being homotopic.[43] Hence, when the internal rotation is frozen out on the NMR time scale, the methylene carbons C(15) (symmetry equivalent to C(25)) and C(12) (equivalent to C(22)) within the tin moiety 1 (equivalent to 2) are symmetry unequivalent (diastereotopic[43]) (see also Figure 1). The same holds for the other types of methylene groups. Therefore, each constitutional type of methylene group results into two equally intense ^{13}C resonances. When, at higher temperatures, the internal rotation becomes rapid on the NMR time scale, the diastereotopicity of these methylene groups is lost since the enantiomeric rotamers interconvert to an averaged achiral geometry having a symmetry identical with the transition state of the process. Since each tin moiety by itself has already a local achiral C_s symmetry,[43c] the only source of chirality in 1 is a torsional angle ϕ different from 0 or 180°. Hence, the internal rotation about the tin–tin bond is the only process in 1 that is able to release the symmetry unequivalence of the methylene groups, resulting in only one averaged ^{13}C signal for each type of them.

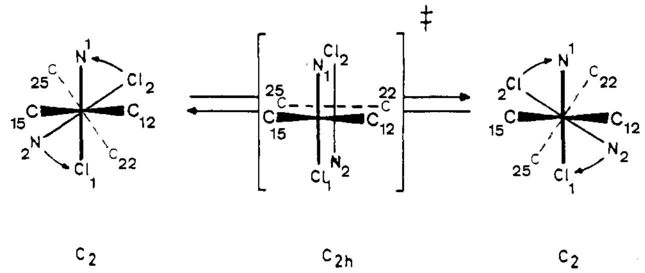

Figure 5. Newman projections, seen along the axis of the tin–tin bond, of the two C_2 enantiomeric rotamers of compound 1. The rotamers of 1 are chiral and can enantiomerize through internal rotation about the tin–tin bond.

To our knowledge, these data constitute the first evidence to observable restricted internal rotation about such a tin–tin bond. The achiral transition state of this process is believed to be the one presented in Figure 5 with C_{2h} symmetry, in which the chlorine atom of one tin moiety is eclipsed by the $N-CH_3$ of the other one, in a head-to-tail arrangement. The argumentation, presented above in connection to Figure 2, allows to understand why this transition state and, accordingly, the internal rotation are pretty hindered, since a repulsive interaction appears between the chlorine atom of one moiety and the NCH_3 group of the other one. It is probably the special steric interaction between the two NCH_3 groups pointing toward the neighboring tin moiety that is responsible for the quite large barrier of 11.5 kcal/mol. The other possible achiral transition state to the internal rotation, with C_{2v} symmetry, in which both NCH_3 groups and both chlorine atoms eclipse one another pairwise is likely to be even much more sterically hindered than the C_{2h} transition state because the methyl group of one NCH_3 moiety points closer toward the neighboring NCH_3 moiety than does the chlorine atom. NMR is unable to distinguish between the two possibilities. This argument suggests that the long equatorial tin–tin bond is indeed the result of the release of that steric repulsion between the two tin moieties.

Static Stereochemistry of Compound 2 in Solution. As analogous patterns were observable at low temperature in the $SnCH_3$ region of the ^{1}H spectra, in the $SnCH_3$, $SnCH_2$, and central CH_2 regions of the ^{13}C spectra, and in the ^{119}Sn spectra of compound 2, we assign the signals A, B, B′, C, and D (see Tables V–VII) to the species A, B, C, and, with much more care, D, that, on the NMR time scale,

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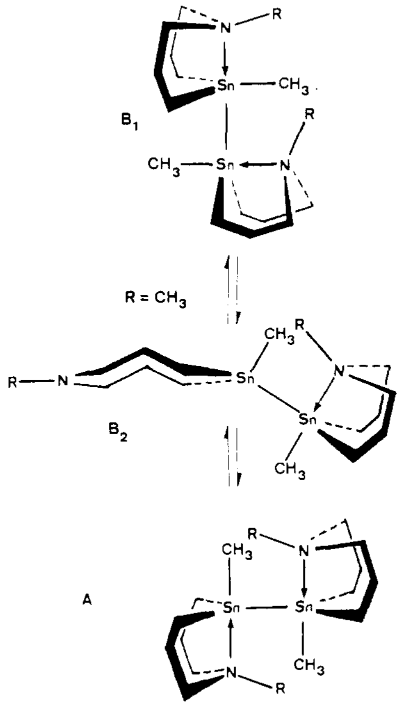

Figure 6. The structure of isomer A of 2, together with the two possible structures of B, compatible with the NMR data, B_1 and B_2. The uncorrelated isomerization pathway interconverting the isomers A and B of 2 is also presented. If the actual structure of B is B_2, then the structure B_1 should just be thought away. If, on the contrary, the actual structure of B is B_1, then B_2 is necessarily an intermediate complex or transition state of the pathway relating the isomers A and B_1 (see text).

are observable as separated diastereomers at low temperature but as a unique averaged one at higher temperatures. The existence of only one signal for A, C, and D indicates a twofold symmetry on the NMR time scale with respect to the tin–tin bond, i.e., symmetry equivalent tin moieties for these isomers. In contrast, the two tin moieties of isomer B are diastereotopic[43] since it gives two equally intense signals B and B′. As the accuracy of the NMR information available for the three isomers A, B, and C decreases in that order, we prefer to discuss the structure of each isomer separately.

The structure proposed for isomer A, given in Figure 6, is comparable to that of 1 (see Figure 1), with the tin–tin bond in equatorial positions at both tin moieties and both methyl groups in apical positions, the chlorine atoms of 1 being just replaced by methyl groups. The NMR data supporting this proposal are the following.

First, the exceptionally low value of 104 Hz of the $^1J(^{13}C-^{119}Sn)$ coupling constant associated with the ^{13}C $SnCH_3$ resonance in A is characteristic for apical methyl groups in five-coordinate tin compounds.[14] This argument results from the fact that apical couplings are smaller than equatorial ones, as a consequence of the lower contribution of s character in the orbitals of apical bonds than in those of equatorial ones.[11,14,37,39,40] The fact that among all isomers the CH_3Sn ^{13}C chemical shift of isomer A exhibits the highest deshielding at low temperatures is further in agreement with our conclusion and with previous observations in $Me_2Sn(CH_2CH_2CH_2)_2NCH_3$ and in $MeSn(CH_2CH_2CH_2)_3N$.[14]

Secondly, the value of 5521 Hz of the $^1J(^{119}Sn-^{117}Sn)$ coupling constant of A remains significantly higher than the maximum value of 4400 Hz of hexamethylditin found for all four-coordinate hexaorganoditin compounds. Of course it is smaller than the values of 7000–15000 Hz found for ditin derivatives with well-established five-coordination,[33,34] but only ca. 1300 Hz smaller than in compound 1, in which also the five-coordination suffers no doubt. Furthermore, it is normally expected that this coupling constant will be smaller in A than in 1 since it is also expected that the presumed equatorial tin–tin bond in A must be longer than in 1 because of the smaller electronegativity difference between the CH_3 group on tin and the neighboring tin atom in A than between the Cl atom and the neighboring tin in 1. Indeed, this smaller difference should result in a lower s character contribution to the equatorial tin–tin bond in A than in 1, with, accordingly, a smaller $^1J(^{119}Sn-^{117}Sn)$ coupling constant in A than in 1, as observed.

Finally, the absence of significant change in ^{119}Sn chemical shift, when changing the solvent from toluene-d_8 to pyridine-d_5, as in 1, suggests that five-coordination already exists. However, this argument cannot receive as much credit as in 1, since in the absence of strongly electronegative ligands bound to the tin atoms, the ligating power of pyridine toward tin in 2 is not expected to be high.

The favored apical position of the methyl group with respect to the neighboring tin moiety is in agreement with the well-known polarity rule,[39,40] favoring the more electronegative substituents into apical positions, carbon being more electronegative than tin. Actually, isomer A of 2 is not the first example of an organotin compound in which a donating ligand present in situ coordinates weakly the tin atom, even in the absence of other strongly electronegative substituents; compound 3[11,12] and the five-coordinate tetraorganotin derivatives $Me_2Sn(CH_2CH_2CH_2)_2NCH_3$ and $MeSn(CH_2CH_2CH_2)_3N$[14] are other such examples.

Though we conclude that isomer A of 2 has exactly the same structure as 1 itself, we believe however the donor–acceptor interaction between nitrogen and tin in A to be weaker than in 1 because it is well-known that tin atoms in organotin compounds are less electrophile in the absence than in the presence of electronegative substituents such as chlorines. Our ^{119}Sn chemical shift data confirm this. Thus, while isomer A has a ^{119}Sn shift of −106.2 ppm at 248 K, those of hexaorganoditin compounds with linear unbranched alkyl chains, that have undoubtedly four-coordinate tin atoms, lie between −60 and −109 ppm.[29,33,34] More precisely, within the series of $R_3SnSnR'_3$ compounds, a Me_3Sn moiety exhibits the most upfield chemical shift of −108 to −109 ppm, the Et_3Sn, Pr_3Sn, Bu_3Sn, and Oct_3Sn exhibit values of −60 to −66, −89, −82 to −83, and −84 ppm, respectively, and the chemical shift of the tin atom of the Me_2EtSn group in $Me_2EtSnSnMe_3$ is −92 ppm.[29,33,34]

Hence, the absence of a significantly large upfield shift of the ^{119}Sn chemical shift of the isomer A with respect to other hexaorganoditin compounds missing a potentially coordinating nitrogen atom in situ could eventually argue against five-coordination at the tin atoms of A. This conclusion is further supported by compound 3, $CH_2[PhSn(SCH_2CH_2)_2NCH_3]_2$, a diorganodithiolate tin compound, the three isomers of which exhibited ^{119}Sn chemical shifts between −4 and −32 ppm.[11,12] As for compound 1, these values are strongly upfield shifted with respect to diorganodithiolate tin compounds without coordinating ligands in noncoordinating solvents exhibiting chemical shift values of +25 to +80 ppm for $Ph_2Sn(SR)_2$ and of +75 to +230 ppm for $(Alk)_2Sn(SR)_2$ derivatives.[34] In view of the other NMR evidences at hand, we conclude that both tin atoms in A are five-coordinate, with a very weak intramolecular donor interaction from the ring nitrogen to the tin atom explaining the absence of significant ^{119}Sn chemical shift effect.

Because the two tin atoms of isomer B are diastereotopic[43] as evidenced by its two equally intense resonances in ^{13}C and ^{119}Sn spectra, we are tempted, in analogy to compound **3**, to propose for isomer B the structure B_1, given in Figure 6. In B_1, the two tin moieties are five-coordinate, with the tin methyl groups in apical and equatorial positions, with accordingly, the neighboring tin atom in equatorial and apical positions, respectively. As for A and for **1**, the absence of significant change in chemical shift at both tin atoms when toluene is replaced by the potentially ligating pyridine as solvent favors structure B_1. Thus, if B had structure B_2, also given in Figure 6, with one five-coordinate tin moiety, with the same structure as in isomer A, but the other tin moiety four-coordinate, pyridine ligation at the only four-coordinate tin atom left in B_2 would be expected to cause a significantly higher upfield shift at only one ^{119}Sn signal than at the other, an expectation that is not observed. Again, however, this argument should be relativated as for isomer A because of the overall low ligating power of pyridine in hexaorganoditin compounds and the absence of known dramatic upfield ^{119}Sn shifts due to pyridine in this type of compounds.

Because of this and of our experience that equilibria between four- and five-coordinate tin species were never observed,[11-14,18,37-39] we would in principle favor structure B_1. However, structure B_2 is not in contradiction with the remaining limited data on B:

(1) The quite different values of the $SnCH_3$ ^{13}C chemical shifts of B at low temperature (−3.66 and −7.46 ppm, table VI), in good agreement with those (−4.38 and −8.45 ppm) found in $Me_2Sn(CH_2CH_2CH_2)_2NCH_3$, a five-coordinate tin compound with one apical and one equatorial methyl group,[14,18] would in principle favor structure B_1. However, chemical shifts of methyl groups bound to four-coordinate tin atoms are found in a broad chemical shift range from +1 to −14 ppm,[44] indicating that the values found are not typical for five-coordination, so that structure B_2 is not excluded by this argument.

(2) The higher value of the $^1J(^{13}C-^{119}Sn)$ coupling constant associated with the $SnCH_3$ ^{13}C signal in the averaged high-temperature spectrum (162 Hz) than with the corresponding individual signal of isomer A at low temperature (104 Hz) undoubtedly indicates that the intrinsic value of at least one such a coupling constant in B, and probably also of both in C, must have a significantly higher value than in A; in this context, we regret of course that we could not observe these couplings directly; using nevertheless the roughly evaluated equilibrium populations, given in Table VII, and assuming a value of 104 Hz for the methyl group of B that is also in apical position, a value of 291 Hz, to be handled with much care, would be obtained for the other methyl groups; such a low value is not characteristic for five-coordination, since equatorial methyl groups give values of the order of magnitude of 400 Hz.[14,18]

(3) The $^1J(^{119}Sn-^{119/117}Sn)$ coupling constant of 3155 Hz found for B lies in the value range characteristic for tin–tin bonds between four-coordinate tin atoms[29,33,34] and would therefore favor structure B_2. However, as the tin–tin bond in apical position at one tin atom must normally be longer in B_1 than in A, the $^1J(^{119}Sn-^{119/117}Sn)$ coupling constant would be expected to be lower with respect to A in B_1 also.

(4) In view of the small differences in ^{119}Sn chemical shift values existing between four-coordinate hexaorganoditin compounds and the isomers of compound **2**,[29,33,34] the chemical shift difference of only 22 ppm between the two signals B and B′ is no longer in contradiction to one tin atom being four- and the other one being five-coordinate in isomer B.

As no coupling data could be obtained for isomer C, because of its too low population, we do not want to speculate too much on its possible structures. Logically, if the structure of B is B_1, then that of C should be one in which the two tin atoms are five-coordinate, with the tin–tin bond apical and the methyl groups equatorial at both tin atoms (C_1). If, on the contrary, the structure of B is B_2, then the structure of C must be one with two four-coordinate tin atoms (C_2).

Because of too restricted data, no reasonable proposal can be made for isomer D. It might be argued that if the isomers A, B, and C have all five-coordinate tin atoms, isomer D might possibly be one in which the ring nitrogen does not coordinate the tin atom of the ring it belongs to, but the neighboring tin.

Dynamic Stereochemistry. Isomerization Scheme of the Isomers A and B. The existence in the 2D ^{119}Sn EXSY spectrum of Figure 4 of the pairs of cross peaks [A, B] and [A, B′] is an unambiguous proof that the isomers A and B isomerize into one another through an uncorrelated rearrangement at a tin atom. This means that one tin center does not isomerize in concert with the other. We have previously[11,12] demonstrated on compound **3**, which is stereochemically correspondent[38] with **2** (aa in **3** = A in **2**; ae in **3** = B_1 or B_2 in **2**; ee in **3** = C_1 or C_2 in **2**) that a correlated rearrangement can never give rise to isomerizations interconverting isomers A and B, even through two-step rearrangements; indeed, when both tin centers rearrange simultaneously, only isomers A and C interconvert, while isomer B undergoes a degenerate isomerization, with exchange of its diastereotopic tin moieties. Hence, even when recorded with long mixing times, a purely correlated rearrangement can never give rise to pairs of cross peaks [A, B] and [A, B′]. The absence of first-order[12,35,36n] pairs of cross peaks [B, B′] in Figure 4 unambiguously excludes the existence of a correlated isomerization that would compete with the uncorrelated one. Clearly, this information would be very difficult to obtain without a 2D ^{119}Sn EXSY spectrum from the coalescence behavior alone; indeed, the average of signals B and B′ would be roughly superposed to the signal A or its average with C, since the position of resonances B and B′ is almost symmetric with respect to signal A.

Figure 6 gives a scheme for the interconversions of isomers A and B, the only isomerization directly observed. Actually this scheme applies whenever the structure of B is B_1 or B_2. Thus, if B is B_2, it suffices in the scheme of Figure 6 to think B_1 away. In contrast, if B is B_1, then B_2 must clearly be an intermediate complex or transition state on the isomerization pathway between A and B. In this pathway, the uncorrelated isomerization must obviously proceed through the dissociation–inversion mechanism previously presented for compound **3**[11,12] and other five-coordinate compounds with only one tin atom.[39]

For the uncorrelated isomerization from B to C, no cross-peak pairs [B, C] and [B′, C] could be observed because of the much too low intensity of signal C and its ^{119}Sn chemical shift value very close to that of signal A. However, the existence of this isomerization suffers no doubt from the coalescence of all signals A, B, B′, and C to a *unique* residual[38] signal. It can be understood easily in each scheme: either, opening of the second transannular structure in B_2 toward C_2 with its two four-coordinate tin

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[44] Mann, B. E.; Taylor, B. E. *^{13}C NMR Data for Organometallic Compounds*; Academic: London, 1981; pp 65–68.

centers or dissociation–inversion at the tin atom with the apical tin methyl group in B_1 toward the structure C_1 with its two equatorial methyl groups and, accordingly, its tin–tin bond apical at both tin atoms.

A Comment on Stereochemical Pitfalls. From a first preparation of 1 from compound 4, $Cl_2Sn(CH_2CH_2CH_2)_2NCH_3$, by reduction with lithium instead of sodium naphthalide (see Experimental Section), we obtained a sample of presumed 1, 1′, that gave satisfactory physicochemical characteristics and provided us even with the pure crystals we made the solid-state structure determination from. However, its ^{119}Sn NMR spectrum in pyridine-d_5, at room temperature, was quite different from the one described here, since, in addition to the signal of 1 at −31.3 ppm, noted A′ here, we found[45] two equally intense signals B″ and B‴ and two different minor signals C′ and D′. This signal pattern was very similar to that of compound 2. From a unique averaged ^1H resonance at 383 K, and a 2D EXSY ^{119}Sn spectrum at 313 K with pairs of cross peaks [A′, B″], [A′, B‴], [B″, B‴], [B″, C′], and [A′, D′], we concluded that 1′ existed as a mixture of four isomers A′, B′, C′, and D′. We found $^1J(^{119}Sn-^{117}Sn)$ satellites with couplings of 6555, 6290, and 3050 Hz for B′, C′, and D′ respectively and also the characteristic ^{13}C NMR behavior, allowing us to conclude the existence of internal rotation in B′. We assigned A′, B′, and C′, to isomers with respectively, two, one, and no chlorine atoms in apical positions, with accordingly, the tin–tin bond respectively twice, once, and not at all in equatorial positions.[45] Later, we assigned D′ to an isomer in which the ring nitrogen of each tin coordinated to the neighboring tin atom.

Because we remained suspicious toward the existence of isomers with equatorial chlorine atoms and toward the unusual high "isomerization" temperatures in 1′, we decided to resynthesize compound 1 by another method, with the results presented above. Although we were not able, neither to reproduce these preliminary results nor to synthesize the dihydroxylated analogue of compound 1, we think that 1′ was a mixture of Cl–Sn–Sn–Cl, Cl–Sn–Sn–OH, and HO–Sn–Sn–OH compounds, assignable to A′, B′, and C′, that interconvert through intermolecular exchange of the nucleophilic Cl and OH ligands. We have no idea of what D′ might be.

We felt this experience worth mentioning since it shows how suspicious one should be toward the stereochemical behavior of tin compounds, even (or especially?) when the latter is evidenced by 2D ^{119}Sn NMR EXSY experiments with their resulting pictorial stereochemical networks.

Conclusion

The static and dynamic stereochemistry of compounds 1 and 2 in solution are dramatically different, though they differ by only one substituent at each tin atom. Clearly the poorer apicophilicity of methyl groups with respect to chlorine atoms is responsible for the observed nonrigidity resulting in isomerism and isomerizations in 2 and for the stereochemical rigidity in 1. The existence in 1 of two apicophile substituents at each tin atom, the ring nitrogen and the chlorine atom, induces a high stereochemical rigidity because they match perfectly well the number of available apical sites at each tin center. According to the polarity rule,[39,40] these substituents are blocked in apical positions. Therefore, a maximum of s character of the orbitals is concentrated into the equatorial bonds, resulting in a tin–tin bond sufficiently shortened to cause restricted internal rotation about it on the NMR time scale. This is due to the *N*-methyl group of one tin moiety pointing strongly toward the atoms of the neighboring tin moiety.

In contrast, compound 2 is highly stereochemically nonrigid because it contains only one really apicophile ligand at each tin atom, the internally coordinating ring nitrogen atom. Its interaction as Lewis base with tin can be only moderate because the Lewis acidity of the latter is not enhanced by the presence of a second apicophile. This results in a more homogeneous distribution of s character over the five bond orbitals. A first consequence is the increased ability to break the probably very weak tin–nitrogen bond resulting in stereoisomerism and stereoisomerizations because returning to the four-coordinate state is easier and less destabilizing in 2 than in 1. A second consequence hereof is a more free internal rotation about the tin–tin bond that is likely to be longer in 2 than in 1. Note in this context that no pairwise splitting of the ^{13}C methylene signals at low temperatures, evidencing the restricted internal rotation about the tin–tin bond in 1, was observed in any isomer of 2. Thus while the restricted internal rotation in 1 is probably due to the repulsive interaction between a chlorine atom at one tin and the *N*-methyl group of the other, it seems that the tin–tin bond of 2 in A would be sufficiently longer for such an interaction to be much less stringent between the methyl group bound to one tin and the *N*-methyl group of the other, although chlorine atoms and methyl groups are well-known to have similar steric volumes.

Experimental Section

All synthetic manipulations were carried out under an atmosphere of dry argon.

Synthesis of 1. $Cl_2Sn(CH_2CH_2CH_2)_2NCH_3$ (4)[14] (4 g, 13.2 mmol) was dissolved in 150 mL of dry THF. At −70 °C, a solution of 14 mmol of sodium naphthalide in 30 mL of THF was added dropwise under magnetic stirring. After 2 h, the solvent was evaporated, and the residue was dissolved in methylene chloride. The mixture was filtered to remove the unreacted sodium naphthalide and the formed sodium chloride. Addition of diethyl ether caused precipitation of colorless crystals, which were recrystallized from methylene chloride/diethylether to yield 2.7 g of colorless crystals (76.5%), with a melting point of 263–265 °C. Anal. Calcd for $C_{14}H_{30}Cl_2N_2Sn_2$: C, 31.44; H, 5.61; N, 5.24; Cl, 13.27. Found: C, 31.41; H, 5.56; N, 5.16; Cl, 13.08.

Synthesis of 2. To a solution of 0.46 g (10.6 mmol) of sodium in 200 mL of liquid ammonia was added a solution of 6 g (21.3 mmol) of $CH_3ClSn(CH_2CH_2CH_2)_2NCH_3$[18] in 50 mL of THF added dropwise under magnetical stirring at −70 °C. The reaction mixture was stirred for 20 min at this temperature, and, then, the ammonia was evaporated. The THF solution left was filtered off to remove the formed sodium chloride, and the filtrate was evaporated. The residue was distilled to give 4.1 g (78%) of 2 as a colorless oil which slowly crystallized after cooling: bp 140 °C (0.1 mmHg); mp 66–70 °C. Anal. Calcd for $C_{16}H_{36}N_2Sn_2$: C, 38.91; H, 7.30; N, 5.67. Found: C, 38.56; H, 7.21; N, 5.41. It should be outlined that at the end of the distillation, decomposition under formation of elemental tin was observed.

Crystal Structure: Structure Determination and Refinement. $C_{14}H_{30}Cl_2N_2Sn_2$ crystallizes in colorless prisms in triclinic space group $P\bar{1}$. Lattices parameters were calculated by a least-squares fitting of 2θ values of 15 reflections (2θ from 10 to 25°): $a = 10.757$ (6), $b = 7.673$ (3), $c = 12.662$ (7) Å; $\alpha = 83.49$ (4), $\beta = 90.26$ (4), $\gamma = 72.48$ (4)°; $V = 989.4$ (9) Å^3; m/z 534.7; $\mu = 22.25$ cm^{-1}; $D_{calcd} = 1.79$ g cm^{-3} ($Z = 2$ dimensions). A suitable crystal with approximate dimension 0.18 × 0.20 × 0.25 mm was mounted for data collection. Intensity data were collected at ambient temperature of 21 °C with a Syntex $P2_1$ diffractometer using graphite-monochromatized Mo Kα radiation $\lambda = 0.71069$ Å), ω–2θ scan, $2\theta_{min}$ was 3°, $2\theta_{max}$ was 47° (index range h, 0/12,

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[45] (a) Jurkschat, K., Tzschach, A., Piret-Meunier, J., Van Meerssche, M., Van Binst, G., Wynants, C., Gielen, M., Willem, R. Proceedings of the XIIth International Conference on Organometallic Chemistry, Poster P279, 1985. (b) Jurkschat, K.; Tzschach, A. *Pure Appl. Chem.* **1986**, *58*, 639.

k, $-7/8$, l, $-13/14$); one standard reflection was measured after each batch of 50 reflections; no significant fluctuation was observed; of the 2934 reflections, 2447 (with $I > 2.5\sigma(I)$) were considered as observed; no absorption corrections were applied.

The structure was solved by heavy-atom method and refined by full-matrix least squares with SHELX76[46] using scattering factors included in the program. Sixteen H atoms were located on difference map; H(3), H(4), H(7), H(8), H(9), H(10), H(21), and H(22) are in calculated positions. Hydrogens of methyl groups are omitted.

All non-H atoms were refined anisotropically; H atoms were introduced in the refinement with isotropic thermal parameters. The weighting scheme is introduced in the final refinement cycles: $w = 0.0093/(\sigma^2(F) + 0.010(F)^2)$. Final R is 0.045; R_w is 0.050. The final difference map is featureless.

Mass Spectra. The monoisotopic EI mass spectrum of **1** shows the presence of the expected[42] fragment ions (m/z, intensity, structure): 120, 20, $Sn^{\bullet+}$; 121, 10, HSn^+; 155, 21, $ClSn^+$; 190, 22, $Cl_2Sn^{\bullet+}$; 233, 66, $CH_3N(CH_2CH_2CH_2)_2Sn^{\bullet+}$; 268, 100, $CH_3N(CH_2CH_2CH_2)_2SnCl^+$. The molecular ion was not observed, as is generally the case. A fragment at m/z 250 is also present and might be due to $CH_3N(CH_2CH_2CH_2)_2SnOH$; its intensity (2) is however very low.

The monoisotopic EI mass spectrum of **2** exhibits a (molecular ion + H) peak (3% of the base peak), which is rather surprising for a compound with a tin–tin bond, a (molecular ion minus CH_3) peak (1%), the expected $[CH_3Sn(CH_2CH_2CH_2)_2NCH_3]^+$ fragment ion (base peak), and also $[Sn(CH_2CH_2CH_2)_2NCH_3]^+$ (23%), CH_3Sn^+ (32%), HSn^+ (13%), and Sn^+ (15%).

Molar Mass Determinations. The molar mass determinations have been carried out by using a Knauer osmometer, in $CHCl_3$ solution at 40 °C for **1** and cryoscopically in C_6H_6 solution for **2**. Concentration: 0.02 mol/kg of solvent for **1** and 0.05 mol/kg of solvent for **2**. Molar masses (m/z): for **1**, found 520, calcd for $C_{14}H_{30}Cl_2N_2Sn_2$ 534.3; for **2**, found 510, calcd for $C_{16}H_{36}N_2Sn_2$ 493.4.

NMR Spectra. The ^1H ^{13}C, and ^{119}Sn spectra were recorded from CD_2Cl_2 and/or pyridine-d_5 (both from Aldrich) solutions of **1** and from toluene-d_8 (Isocommerz Leipzig) solutions of **2**, at various temperatures and at different magnetic field strengths (^1H, 270.13 and 500.13 MHz; ^{13}C, 67.92; MHz; ^{119}Sn, 74.62 and 186.49 MHz). All spectra of **1** in CD_2Cl_2 and of **2** in toluene-d_8 were recorded from samples in sealed tubes degassed by five cycles at 0.01 mmHg. All spectra were recorded with AM 500, AM 270, and WP 200 Bruker spectrometers, working in the FT mode, equipped with an Aspect 2000 (AM 270 and WP 200) and Aspect 3000 (AM 500) computers, and using the Bruker DISN841, DISN85, DISB84, DISB85, and DISR861 programs. The tetramethylsilane (TMS) signal was taken as external reference for the ^1H and ^{13}C spectra. Tetramethyltin was used as an external reference for the ^{119}Sn spectra. A Lorentz–Gauss transformation[28] was applied to the ^1H spectra in order to improve the resolution, with an exponential multiplication was necessary to improve the signal-to-noise ratio of the ^{13}C and ^{119}Sn spectra.

The 2D ^{119}Sn EXSY spectra were obtained with the standard EXSY pulse sequence introduced by Jeener and co-workers,[35a] preparation–90°–evolution–90°–mixing–90°–detection, with mixing times of t_m = 10, 40, and 100 ms at 248 K and with the usual 16-dimensional phase cycle program. The two-dimensional data matrices were submitted in both t_1 and t_2 dimensions to a Lorentz–Gauss transformation and twice zero-filled in the t_1 dimension prior to Fourier transformation ("power" spectrum calculation in all cases).

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Registry No. 1, 112021-16-6; 2, 112021-17-7; 4, 111004-38-7; $CH_3ClSn(CH_2CH_2CH_2)_2NCH_3$, 111004-39-8.

Supplementary Material Available: Crystal data, unit-cell drawing, and tables of bond distances and angles, anisotropic thermal parameters, and least-squares planes (7 pages); a listing of structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

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