Evidence for Hexacoordinate Tin Centers in Triorganotin Halides Containing Two 8-(Dimethylamino)-1-naphthyl Ligands

Johann T. B. H. Jastrzebski, Paul A. van der Schaaf, Jaap Boersma, and Gerard van Koten*

*Debye Research Institute, Department of Metal-Mediated Synthesis, University of Utrecht,
Padualaan 8, 3584 CH Utrecht, The Netherlands*

Dirk J. A. de Ridder and Dick Heijdenrijk

*Laboratory for Crystallography, University of Amsterdam, J. H. van't Hoff Instituut,
Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands*

A series of novel triorganotin halides, $SnX[1-C_{10}H_6NMe_2-8]_2R$, containing two potentially intramolecular-coordinating 8-(dimethylamino)-1-naphthyl groups has been synthesized and characterized. The compounds were prepared via oxidative addition of an alkyl halide RX (R = Me, X = I; R = Et, X = I; R = benzyl, X = Br) to bis[8-(dimethylamino)-1-naphthyl]tin(II). From one of these compounds (R = Me, X = I) the molecular structure in the solid state has been determined by X-ray diffraction methods: $C_{25}H_{27}IN_2Sn$, orthorhombic, space group *Pbca* with *a* = 19.212 (3) Å, *b* = 25.540 (8) Å, *c* = 9.482 (1) Å, and *Z* = 8, final *R* = 0.052 for 1798 observed reflections. The tin center has a distorted-octahedral coordination geometry with mutual trans positions of the two $C(1)_{naphthyl}$ atoms, one of the coordinating nitrogen atoms and the iodine atom, and the other coordinating nitrogen atom and the methyl group at tin. The length of the Sn–N bond trans to the iodine atom is in the normal range as expected for a Sn–N coordination bond (2.53 (1) Å) while the Sn–N bond trans to the methyl group is extremely long (3.10 (1) Å). ^1H, ^{13}C, and ^{119}Sn NMR spectra of these triorganotin halides show that, at low temperature in solution, these compounds exist in two geometrically different forms, one as found in the solid state and one with the two $C(1)_{naphthyl}$ atoms, the two coordinating nitrogen atoms, and the methyl group at tin and the iodine atom in cis position. At higher temperatures a process involving interconversion between these two isomers becomes fast on the NMR time scale.

Introduction

It is well-established that in triorganotin halides containing a C⌢Y chelating ligand (Y = heteroatom-containing substituent) Y–Sn coordination occurs, in the solid state and in solution. Representatives of this class are compounds of the type $SnR_2(C⌢Y)X$ (X = halide, Y = -P(= O)R,[1] -C(C=O)R,[2] =N—O—R,[3] or $-NR_2^{4-8}$) and compounds of the type $SnR(C⌢Y⌢C)X$ (X = halide, Y = NMe, O, or S).[9] As a result of intramolecular coordination the coordination geometry of the tin atom is trigonal-bipyramidal, with the more electronegative ligands X and Y at the axial sites and the three carbon ligands at the equatorial sites, as schematically shown in Figure 1.

Due to the increased Lewis acidity of the tin center in diorganotin dihalides, hexacoordination of the tin atom is often found in this type of compound when proper donor ligands are present.[10] Recently, we have shown that in diorganotin dihalides containing two potential C–N chelating ligands the tin center indeed is hexacoordinate, with the two carbon ligands in trans position and both halogen

atoms and coordinating nitrogen atoms in cis position.[11,12]

The only authentic example of hexacoordination at Sn in triorganotin compounds is [tris(pyrazolyl)borato]trimethyltin.[13] It would therefore be interesting to study triorganotin halides containing two potentially intramolecular-coordinating groups. The main questions to be answered are (i) are both coordinating groups involved in coordination to tin (i.e. is the Sn center hexacoordinate) and (ii) what is the behavior in solution of these compounds. In this context it must be noted that although tetraorganotin compounds were previously regarded as being unable to extend their coordination number beyond 4 because of the poor acceptor properties of the tin center,[14] recently a few examples of neutral tetraorganotin compounds, containing rigid C⌢Y chelating ligands, have been reported in which the tin center may be regarded as penta-[15-19] or even hexacoordinate[20] as a result of intramolecular Sn–Y coordination. Moreover, pentacoordination has been found for pentaorganotin anions, e.g. $SnMe_5^-$ and $SnPh_5^-$.[21] Recently, we reported a series

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Figure 1. Schematical representation of the pentacoordinate triorganotin halides of types $SnR_2(C\frown Y)X$ (A) and $SnR(C\frown Y\frown C)X$ (B).

of tetraorganotin compounds containing one 8-(dimethylamino)-1-naphthyl group. For one of these compounds, i.e. [8-(dimethylamino)-1-naphthyl]triphenyltin, a pentacoordinate tin center was unambiguously proven by an X-ray crystal structure determination.[22] It is interesting to note here that there is a great similarity in coordination chemistry between organotin and organosilicon compounds containing an 8-(dimethylamino)-1-naphthyl group.[23,24]

In this paper we report the synthesis and structural characterization of triorganotin halides containing two 8-(dimethylamino)-1-naphthyl groups which in principle could lead to hexacoordination at the tin center.

Results and Discussion

Synthesis of Bis[8-(dimethylamino)-1-naphthyl]methyltin Iodide (1), Bis[8-(dimethylamino)-1-naphthyl]ethyltin Iodide (2), and Bis[8-(dimethylamino)-1-naphthyl]benzyltin Bromide (3). Addition of methyl iodide, ethyl iodide, or benzyl bromide to a solution of bis[8-(dimethylamino)-1-naphthyl]tin(II)[25] in a 1:1 molar ratio in benzene affords in quantitative yield bis[8-(dimethylamino)-1-naphthyl]methyltin iodide (1), bis[8-(dimethylamino)-1-naphthyl]ethyltin iodide (2), and bis[8-(dimethylamino)-1-naphthyl]benzyltin bromide (3), respectively (eq 1). The novel triorganotin halides are

$$X = I, R = Me, \quad 1$$
$$X = I, R = Et, \quad 2$$
$$X = Br, R = benzyl, \quad 3$$
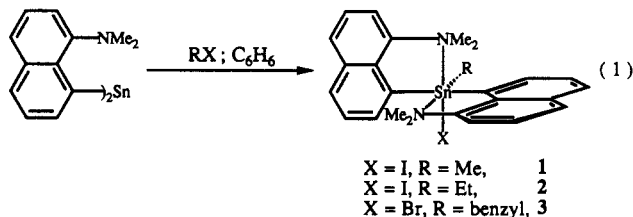
white crystalline solids that were characterized by their elemental analysis (see Experimental Part) and by ^1H, ^{13}C, and ^{119}Sn NMR spectroscopy. It appeared that the ^1H NMR spectra of these compounds are temperature dependent and rather complicated. In order to facilitate the interpretation of the NMR data the X-ray structure determination of one compound, i.e. bis[8-(dimethylamino)-1-naphthyl]methyltin iodide (1), was carried out.

Molecular Geometry and Crystal Structure of Bis[8-(dimethylamino)-1-naphthyl]methyltin Iodide (1). The crystal structure of 1 involves the packing of eight mononuclear molecules in the unit cell. The molecular geometry of 1 is shown in Figure 2, while selected data on the molecular geometry are given in Table I.

In our opinion the best way to describe the coordination geometry at tin in 1, is distorted octahedral with C(1) and
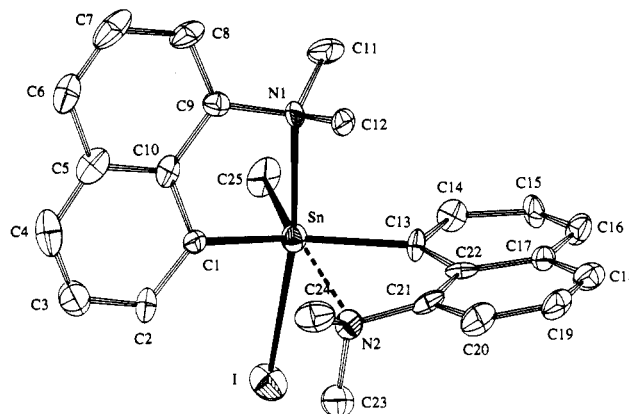

Figure 2. ORTEP drawing (30% probability level) of bis[8-(dimethylamino)-1-naphthyl]methyltin iodide (1).

Table I. Selected Geometrical Data for Bis[8-(dimethylamino)-1-naphthyl]methyltin Iodide (1) Compared with Those of Earlier Reported Bis[8-(dimethylamino)-1-naphthyl]tin Dibromide[12]

Distances (Å)			
Sn–C(1)	2.13 (1)	Sn–C(1)	2.12 (1)
Sn–C(13)	2.16 (1)	Sn–C(13)	2.13 (1)
Sn–N(1)	2.53 (1)	Sn–N(1)	2.62 (1)
Sn···N(2)	3.10 (1)	Sn–N(2)	2.64 (1)
Sn–I	2.950 (2)	Sn–Br(1)	2.623 (2)
Sn–C(25)	2.21 (1)	Sn–Br(2)	2.610 (2)
Angles (deg)			
N(1)–Sn–C(1)	75.3 (4)	N(1)–Sn–C(1)	75.4 (5)
N(1)–Sn–C(13)	89.8 (5)	N(1)–Sn–C(13)	87.7 (6)
N(1)–Sn–I	171.5 (2)	N(1)–Sn–Br(1)	174.6 (2)
N(1)–Sn–C(25)	91.1 (5)	N(1)–Sn–Br(2)	89.9 (3)
N(2)···Sn–N(1)	89.9 (3)	N(1)–Sn–N(2)	90.4 (5)
N(2)···Sn–C(1)	77.2 (5)	N(2)–Sn–C(1)	86.7 (5)
N(2)···Sn–C(13)	65.6 (4)	N(2)–Sn–C(13)	73.4 (6)
N(2)···Sn–I	92.4 (2)	N(2)–Sn–Br(1)	89.9 (3)
N(2)···Sn–C(25)	175.9 (5)	N(2)–Sn–Br(2)	174.0 (2)
I–Sn–C(1)	97.3 (3)	Br(1)–Sn–C(1)	99.2 (4)
I–Sn–C(13)	98.6 (4)	Br(1)–Sn–C(13)	97.6 (5)
I–Sn–C(25)	87.2 (5)	Br(1)–Sn–Br(2)	90.3 (1)
C(25)–Sn–C(1)	106.8 (6)	Br(2)–Sn–C(1)	99.2 (4)
C(25)–Sn–C(13)	110.4 (6)	Br(2)–Sn–C(13)	100.6 (5)
C(1)–Sn–C(13)	140.0 (5)	C(1)–Sn–C(13)	153.9 (5)

C(13), N(1) and I, and N(2) and C(25) in mutual trans positions. Although the Sn–N(2) distance of 3.10 (1) Å is extremely long for a Sn–N coordinate bond, this value is only slightly longer than one of the Sn–N bonds found in the diphenyltin dichloride pyrazine complex (2.965 (11) Å), the longest Sn–N bond so far, that has been ascribed to Sn–N coordination.[26] The difference in Sn–N distances correlate with the different character of the trans ligands, I to N(1) and C(25) to N(2).

The presence of a distorted-octahedral coordination geometry at tin in 1 becomes particularly clear when the bond angles around the tin atom in 1 are compared with those in bis[8-(dimethylamino)-1-naphthyl]tin dibromide (see Table I), for which an octahedral coordination geometry has been established unambiguously.[12] It is remarkable that the values in both compounds are so close, with

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Table II. Relevant ¹H NMR Data^a for the Triorganotin Halides 1–3

	H2(A)^b	H2'(A)^b	H2(B)^b	H2'(B)^b	NMe$_2$	H$_\alpha$(A)^c	H$_\alpha$(B)^c
1^e		8.48 (87)			2.03		1.35 (62)
1^f	9.35 (93)	8.05 (94)	9.65 (63)	7.85 (93)	2.90, 2.55, 2.33, 1.92^d 1.62, 1.30, 1.11, 0.88^d	1.33 (52)	1.38 (75)
2^e		8.42 (88)			2.23 and 2.02		1.94
2^f	9.25 (87)	7.98 (88)	9.60 (54)	7.80 (91)	2.60, 1.95, 1.40, 0.95 (A isomer) 2.90, 2.40, 2.05, 1.10 (B isomer)		g
3^e		8.30 (87)			2.21 and 2.03		3.27 (74)
3^f	8.88 (93)	8.20 (92)	9.05 (60)	7.90 (93)	2.95, 2.60, 2.45, 2.15^d 2.05, 1.39, 1.15, 0.85^d	3.58 (66)^g 3.08 (66)^g	3.45 (87)^h 3.30 (87)^h

^{a} All values are in δ relative to Me$_4$Si; toluene-d_8 solvent. ^{b} $^3J(^{119}$Sn$-^1$H) values in parentheses. ^{c} $^2J(^{119}$Sn$-^1$H) values in parentheses. ^{d} Because the ratio between the A and B isomers in compounds 1 and 3 is close to 1:1, we were unable to assign these resonances unambiguously to the A or B isomer. ^{e} At +100 °C. ^{f} At –50 °C. ^{g} Resonances masked by NMe resonances; see text. ^{h} AB pattern, ^2J(H–H) 14 Hz.

Table III. Relevant ¹³C^a and ¹¹⁹Sn^b NMR Data for the Triorganotin Halides 1–3

	¹³C			¹¹⁹Sn	
	C$_\alpha$(A)^c	C$_\alpha$(B)^c	NMe$_2$^{d}	A	B
1^e		10.2	49.5		–142.6
1^f	8.3 (433)	12.0 (664)	51.9, 51.8, 51.7, 50.4, 49.1, 47.9, 45.2, 43.3	–138.4	–141.4
2^e		19.3	50.1 and 48.3		–101.1
2^f	17.5 (428)	21.4 (674)	52.6, 50.6, 48.8, 45.4 (B isomer)^g	–98.1	–101.7
3^e		32.1	49.8 and 48.1		–142.2
3^f	30.6 (385)	32.4 (603)	51.9, 51.5, 51.1, 49.9, 48.9, 45.6, 45.3, 44.8	–148.0	–150.0

^{a} All values are in δ relative to Me$_4$Si. ^{b} All values are in δ relative to Me$_4$Sn. ^{c} $^1J(^{13}$C$-^{119}$Sn) values in parentheses. ^{d} Because the ratio between the A and B isomers in compounds 1 and 3 is close to 1:1, we were unable to assign these resonances unambiguously to the A or B isomer. ^{e} At +100 °C in toluene-d_8; due to some line broadening we were unable to detect the ^{119}Sn satellites. ^{f} At –50 °C in CDCl$_3$. ^{g} Resonances of the A isomer are partially masked by the resonances of isomer B.

the exception of the N(2)–Sn–C(1), N(2)–Sn–C(13), and C(1)–Sn–C(13) values. In 1 the N–Sn–C angles are about 8° smaller than those in bis[8-(dimethylamino)-1-naphthyl]tin dibromide. The latter is a logical consequence of the longer Sn–N(2) distance in 1 compared with that in bis[8-(dimethylamino)-1-naphthyl]tin dibromide. The C(1)–Sn–C(13) value of 140.0 (5)° in 1 deviates considerably from the ideal octahedral value of 180°. A similar deviation has been found in bis[8-(dimethylamino)-1-naphthyl]tin dibromide (153.9 (5)°), see Table I. Previously, Britton and Dunitz have correlated the structural features of SnC$_2$X$_2$Y$_2$ ensembles having a C,C-transoid arrangement.[27] It was shown that in such species the C–Sn–C angle is a function of the deviation of the C–X and C–Y distances from the theoretical values. The Sn–N(2) and Sn–C(25) distances in 1 do fit very well in the theoretically deduced curve; furthermore these distances predict a value of 141° for the C(1)–Sn–C(13) angle, which is very close to the value of 140.0 (5)° actually found for 1. Similarly, a value of 152° is predicted for the C(1)–Sn–C(13) angle in bis[8-(dimethylamino)-1-naphthyl]tin dibromide, which is also very close to the actual value found.

The influence of the trans position of N(2) relative to C(25) is reflected in an increase of the Sn–C(25) bond length to 2.21 (1) Å. Similar increases in Sn–C bond lengths have been found for the Sn–C bonds trans to a coordinating nitrogen atom in pentacoordinate tetraorganotin compounds in which an intramolecularly coordinating nitrogen atom is present, e.g. in [8-(dimethylamino)-1-naphthyl]triphenyltin (2.183 (4) Å)[22] and 1-aza-5-stanna-5-methyltricyclo[3.3.3.0^{1,5}]undecane (2.214 (11) Å).[15]

Accordingly, the coordination geometry at the tin atom in 1 can also be seen as trigonal bipyramidal, with C(1), C(13), and C(25) at the equatorial positions, which undergoes intramolecular nucleophilic attack by N(2) on the C(1)–C(15) equatorial edge (i.e. opposite to C(25)). It is

interesting to note that in bis[8-(dimethylamino)-1-naphthyl]silicon dihydrides, difluorides, and hydride fluorides the tetrahedral configuration at silicon is largely preserved. The hexacoordination at silicon can be best seen as that of a bicapped tetrahedron resulting from a 2-fold nucleophilic coordination.[24]

Solution Behavior of the Triorganotin Halides 1–3. The ¹H and ¹³C NMR spectra of the triorganotin halides 1–3, obtained at room temperature, show very broad resonances, indicating that a fluxional process is operative at this temperature. However, both at high (100 °C) and at low temperatures (below –25 °C) well-resolved ¹H and ¹³C NMR spectra were obtained (Tables II and III, respectively).

The ¹H and ¹³C NMR spectra of 1–3 at 100 °C show one resonance pattern for the two 8-(dimethylamino)-1-naphthyl groups present in these compounds. It should be noted, however, that for 1 only one NMe$_2$ resonance is observed, while for 2 and 3 two NMe$_2$ resonances are observed (Tables II and III). The latter may be the result of hindered rotation around the C$_{ipso}$–Sn bonds in the transition state, resulting in the observed high-temperature ¹H and ¹³C NMR spectra (vide infra).

It should be mentioned here that from the standpoint of structural assignment the resonances of H(2) of the naphthyl groups and those of the α-hydrogen atoms of the substituent at the tin atom are particularly informative. These resonances contain three- and two-bond ^{117}Sn and ^{119}Sn couplings, respectively, the values of which are sensitive measures of the state of hybridization at the tin atom in organotin compounds.[28-35]

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(A)   (B)

1, R = Me, X = I
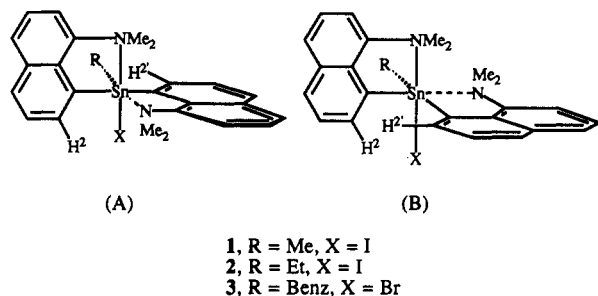2, R = Et, X = I
3, R = Benz, X = Br

Figure 3. Two different geometrical isomers of the triorganotin halides 1-3.

At low temperatures much more complicated ^{1}H NMR spectra are obtained for 1-3; see Table II. Below -25 °C the H(2)$_{naphthyl}$ resonance, which was observed at about 8.40 ppm in the high-temperature spectra, decoalesces into four signals, while the single resonance of the NMe$_2$ groups in 1 and the two resonances observed for the NMe$_2$ groups in 2 and 3 decoalesce into eight signals. Similarly, the low-temperature (-50 °C) ^{13}C NMR spectra of 1-3 showed the presence of eight resonances for the NMe$_2$ group (Table III).

These observations indicate that at these temperatures in solution two geometrically different isomers are present in which the two 8-(dimethylamino)-1-naphthyl groups are also inequivalent. The presence of two isomers was furthermore confirmed by the observation of two resonances for the Me–Sn group in 1 in the ^{1}H and ^{13}C NMR spectra and two AB patterns for the benzylic protons and two resonances for the benzylic carbon atom in 3. Also for 2 two resonances were observed for the α-carbon atom of the ethyl group bound to tin.

The presence of two isomers was also evident from the ^{119}Sn NMR spectra of 1-3. At low temperature (-50 °C) two resonances are present, while at high temperature these resonances coalesce into one line (Table III).

On the basis of the ^{1}H, ^{13}C, and ^{119}Sn NMR spectra at -50 °C of 1-3, we propose that at this temperature, in solution, the two isomers have structures A and B, which are schematically shown in Figure 3. The assignment of the specific ^{1}H and ^{13}C resonances to isomer A or B (see Tables II and III) is based on the $^2J(^{119}$Sn–^{1}H) and ^1J-(^{119}Sn–^{13}C) couplings. For 1 (R = Me) the A to B ratio is about 55:45, while for 2 (R = Et) this ratio is 10:90. Most likely this difference is a result of a larger difference in steric crowding around the tin atom between the two isomers of 2 as compared to 1. For 3 (R = benzyl) the A to B ratio is similar to that found for 1, i.e. 55:45. However, no conclusions can be drawn from this observation since in compound 3 also a different halogen atom is present (Br versus I in 1 and 2).

In both isomers the tin atom has a distorted-octahedral coordination geometry. In structure A the carbon atoms of the naphthyl groups bound to tin are in trans position, the two nitrogen atoms are in cis position, and the R group and the halogen atom X are consequently also in cis position. This is the structure that has been actually found for 1 in the solid state (vide supra). In structure B the carbon atoms of the naphthyl groups bound to tin are in cis position, while the R group is in trans position with respect to one of these carbon atoms and, consequently, both nitrogen atoms are in cis position. The observed

two-bond and three-bond tin–proton and one-bond tin–carbon couplings of 1-3 are in agreement with the proposed structures.

It is well-established that in diorganotin compounds in which the tin atom has an octahedral coordination geometry, the trans carbon atoms are bound to tin via sp-like orbitals at the tin center.[10] It is this enhanced s-electron participation in the tin–carbon bonds which causes larger two-bond and three-bond tin–proton and one-bond tin–carbon couplings in such compounds, compared to trigonal-bipyramidal and tetrahedral geometries, in which the carbon atoms are bound to tin via sp^2- and sp^3-like orbitals at tin, respectively.

In isomers A and B we therefore expect larger two-bond and three-bond tin–proton and one-bond tin–carbon couplings for the two groups that are in trans position, than for the third organic group that is in cis position with respect to the first two groups. Similarly, relatively large and small couplings have been found for equatorial and axial organic groups, respectively, in tetraorganotin compounds in which the tin atom has a trigonal-bipyramidal coordination geometry as a result of intramolecular coordination, e.g. for 1,5,5-trimethyl-1-aza-5-stannabicyclo-[3.3.0^{1,5}]octane: $^1J(^{119}$Sn–^{13}CH$_3$(eq)) 378 Hz, $^1J(^{119}$Sn–^{13}CH$_3$(ax)) 197 Hz, $^2J(^{119}$Sn–C^{1}H$_3$(eq)) 54.5 Hz, and ^2J-(^{119}Sn–C^{1}H$_3$(ax)) 40.1 Hz.[9,16] Indeed, the low-temperature (-50 °C) ^{1}H and ^{13}C NMR spectra of 1-3 showed relatively large $^1J(^{119}$Sn–^{13}C), $^2J(^{119}$Sn–^{1}H), and $^3J(^{119}$Sn–^{1}H) values for the two organic groups that are in trans position while for the third organic group, which is in cis position with respect to the first two groups, smaller values were observed (see Tables II and III). For 1 two sets of H(2)$_{naphthyl}$ resonances are found, one set at 9.35 and 8.05 ppm, both with a $^3J(^{119}$Sn–^{1}H) value of about 93 Hz, assigned to H(2) and H(2)', respectively, in isomer A (Figure 3), and one set at 9.35 ppm with a $^3J(^{119}$Sn–^{1}H) of 93 Hz and 7.85 ppm with a $^3J(^{119}$Sn–^{1}H) of 63 Hz, assigned to H(2) and (H2)', respectively, in isomer B (Figure 3). In our opinion the latter, smaller coupling constant is caused by the fact that the group on which this proton is present is in cis position with respect to the other two organic groups. According to the intensity ratios of the Me–Sn proton resonances, we could ascribe the signal at 1.33 ppm with the smaller ^2J-(^{119}Sn–^{1}H) coupling of 52 Hz to isomer A (Me group in cis position) and the signal at 1.38 ppm with the larger ^2J-(^{119}Sn–^{1}H) coupling of 75 Hz to isomer B (Me group trans). Unfortunately, we were unable to locate the ^{13}C(1)$_{naphthyl}$ resonances with their tin satellites due to the large number of aromatic resonances present in the ^{13}C NMR spectrum of 1. However, the ^{13}C NMR spectrum of 1 at -50 °C showed two Me–Sn resonances, one at 8.3 ppm with a $^1J(^{119}$Sn–^{13}C) of 433 Hz, assigned to isomer A (Me group in cis position), and one at 12.0 ppm with a $^1J(^{119}$Sn–^{13}C) of 664 Hz, assigned to isomer B (Me group in trans position).

For the triorganotin halides 2 and 3 similar observations were made, i.e. larger $^1J(^{119}$Sn–^{13}C), $^2J(^{119}$Sn–^{1}H), and ^3J-(^{119}Sn–^{1}H) values for the trans substituents and significantly smaller values for the substituent in cis position with respect to the first two substituents at the tin atom.

It has been well-established that the ^{119}Sn chemical shift is strongly dependent on the oxidation number of tin, the type of substituents present at the tin atom, the coordination number of the tin atom, and the geometric configuration at the tin center.[35,36] Although the ^{119}Sn NMR spectra of 1-3 nicely illustrates the presence of two species

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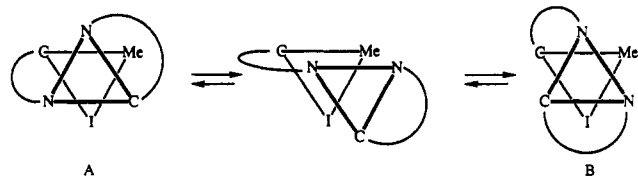
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Figure 4. Schematical representation (Bailar twist) of the interconversion between isomers A and B.

at low temperature, it is dangerous to draw conclusions concerning the structures of these compounds from the observed absolute chemical shift values. It has been shown that a large shift (normally over 100 ppm) to lower frequency is observed when the coordination number in pentacoordinate diorganotin dihalides is extended to 6, e.g. −141.4 ppm for pentacoordinate {2-[(dimethylamino)-methyl]phenyl}methyltin dibromide versus −293.8 ppm for its hexacoordinate pyridine adduct.[37] The [119]Sn chemical shift values found for 1–3 are in the range expected for pentacoordinate triorganotin halides.[37] On the other hand, we[22,37] and others[17] have shown that the [119]Sn chemical shift value is not or only slightly influenced when pentacoordinate tetraorganotin compounds are compared with their tetracoordinate analogues. Probably also the [119]Sn chemical shift value of hexacoordinate triorganotin halides only slightly differs from the pentacoordinate analogues.

As has been mentioned before, the high-temperature ^{1}H and ^{13}C NMR spectra of the triorganotin halides 1–3 are the result of a fluxional process which is fast on the NMR time scale at higher temperatures. Since at these temperatures only one resonance pattern is observed in both the ^{1}H and ^{13}C NMR spectra of 1–3 for both 8-(dimethylamino)-1-naphthyl groups, the following conclusions can be drawn: (i) both 8-(dimethylamino)-1-naphthyl groups bound to tin are equivalent on the NMR time scale, and (ii) isomer A and isomer B become equivalent on the NMR time scale. From the observed ^{1}H and ^{13}C NMR spectra no conclusions can be drawn about the mechanism resulting in the equivalence of all 8-(dimethylamino)-1-naphthyl groups. Preliminary ^{1}H, [1]H 2D EXSY[38] measurements of 1 point to a mechanism involving an exchange between isomers A and B. Such a rearrangement (Bailar twist), schematically shown in Figure 4, is known for octahedral arrangements and proceeds via a trigonal-prismatic transition state.[40]

However, a process involving Sn–N dissociation, with an infinite small population of the dissociated form may not a priori be excluded. If such a process is operative this would imply that also a fast exchange must occur between the coordinating and the noncoordinating NMe₂ groups. The geometry of the tin atom in the transition state for this process can be seen as tetrahedral with the two nitrogen atoms still in close proximity to the tin atom. The observation of two resonances for the NMe₂ group in the high-temperature ^{1}H and ^{13}C NMR spectra of 2 and 3 is the result of (i) blocked pyramidal inversion of the nitrogen atoms and (ii) hindered rotation around the C_{ipso}–Sn bonds. That for 1 only one NMe₂ resonance is observed at high temperature may be the result of less hindered rotation around the C_{ipso}–Sn bonds as a consequence of less steric crowding in this molecule. A process involving Sn–N dissociation/association of only one Sn–N bond, i.e. the

nitrogen atom trans to a carbon atom, would result in high-temperature ^{1}H and ^{13}C NMR spectra in which the two 8-(dimethylamino)-1-naphthyl groups are inequivalent (such an intermediate in fact is isostructural with pentacoordinate [8-(dimethylamino)-1-naphthyl]methylphenyltin bromide for which it was shown that both Sn–N dissociation/association and inversion of configuration at the tin center is inert on the NMR time scale, even at high temperature (+100 °C)).[22,41]

Concluding Remarks

Previously, we have reported the synthesis and characterization of triorganotin halides containing the monoanionic tridentate 2,6-bis[(dimethylamino)methyl]-phenyl group.[42] It appeared that this ligand promotes halogen displacement, giving rise to the formation of a triorganotin cation, both in the solid state and in solution. In this cation the tin atom has a trigonal-bipyramidal coordination geometry, with the organic groups at equatorial positions and both coordinating nitrogen atoms at axial positions.

In contrast, this study shows that the tin atom in triorganotin halides containing two 8-(dimethylamino)-1-naphthyl groups has a distorted-octahedral coordination geometry with one short and one long Sn–N coordination bond, as was established by an X-ray crystal structure determination of bis[8-(dimethylamino)-1-naphthyl]-methyltin iodide. The ^{1}H and ^{13}C NMR spectra of these compounds indicate that also in solution they have a hexacoordinate tin center. It is rather surprising that in these compounds the halogen atom is not displaced to give a pentacoordinate triorganotin cation, since it is known that the favored coordination number for triorganotin species is 5.

It appears that even in very polar solvents like alcohols no displacement of the halogen atom occurs, as shown by the ^{1}H and ^{13}C NMR spectra of 1 in MeOH-d_4, which are essentially the same over the whole temperature range studied as those in toluene-d_8. Preliminary experiments have shown that when the iodine atom in bis[8-(dimethylamino)-1-naphthyl]methyltin iodide is replaced by the extremely weakly coordinating ⁻O₃SCF₃ anion, indeed a triorganotin cation, 4, is formed[43] (eq 2); see Experimental Part.
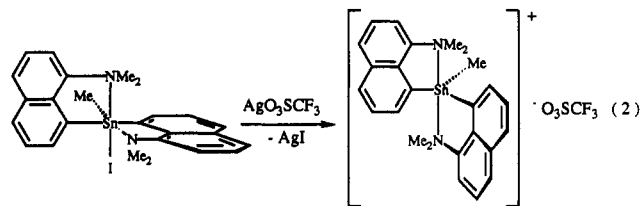
A possible explanation for the different coordination geometries at the tin atom in the triorganotin halides containing two 8-(dimethylamino)-1-naphthyl groups (distorted octahedral) and the triorganotin halides con-

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(43) The ^{1}H and ^{13}C NMR data of 4 (see Experimental Part) at 25 and 0 °C are in agreement with an ionic structure, as schematically shown in eq 2. However, at very low temperature (−70 °C), the ^{1}H NMR spectrum of 4 shows the presence of two isomers in a 90:10 ratio, in which the 8-(dimethylamino)-1-naphthyl groups are inequivalent. These observations suggest the occurrence of hexacoordinate tin centers, which may be the result of (i) formation of contact-ion pairs or (ii) additional coordination of a solvent molecule. The structural characterization in the solid state and in solution of this type of ionic organotin compound will be the subject of a forthcoming study.

Table IV. Final Coordinates and Equivalent Isotropic
Thermal Parameters and Their Esd's in Parentheses for
the Non-H Atoms of 1

atom	x	y	z	U_{eq},^{a} Å^2
Sn	0.38733 (6)	0.34873 (4)	0.3145 (1)	0.0389 (5)
I	0.51943 (6)	0.35518 (6)	0.4705 (1)	0.0687 (8)
C(1)	0.3194 (7)	0.3572 (6)	0.488 (1)	0.037 (8)
C(2)	0.3397 (8)	0.3719 (6)	0.623 (2)	0.046 (10)
C(3)	0.2939 (9)	0.3669 (7)	0.737 (2)	0.06 (1)
C(4)	0.2304 (9)	0.3482 (8)	0.723 (2)	0.06 (1)
C(5)	0.2045 (7)	0.3323 (6)	0.592 (2)	0.049 (10)
C(6)	0.1401 (8)	0.3075 (7)	0.572 (2)	0.06 (1)
C(7)	0.1170 (8)	0.2920 (7)	0.440 (2)	0.07 (1)
C(8)	0.1594 (7)	0.3000 (6)	0.321 (2)	0.05 (1)
C(9)	0.2246 (7)	0.3232 (5)	0.333 (2)	0.037 (8)
C(10)	0.2505 (9)	0.3374 (5)	0.472 (2)	0.042 (9)
C(11)	0.2660 (10)	0.2983 (7)	0.100 (2)	0.07 (1)
C(12)	0.2412 (9)	0.3889 (6)	0.156 (2)	0.05 (1)
C(13)	0.4187 (8)	0.3904 (5)	0.129 (1)	0.035 (8)
C(14)	0.4505 (8)	0.3569 (5)	0.035 (2)	0.044 (9)
C(15)	0.4722 (9)	0.3764 (5)	−0.099 (2)	0.046 (10)
C(16)	0.4593 (8)	0.4246 (6)	−0.144 (2)	0.047 (10)
C(17)	0.4256 (8)	0.4595 (5)	−0.051 (2)	0.036 (8)
C(18)	0.4092 (8)	0.5109 (6)	−0.096 (2)	0.048 (10)
C(19)	0.3760 (9)	0.5458 (6)	−0.009 (2)	0.05 (1)
C(20)	0.3620 (9)	0.5310 (6)	0.129 (2)	0.06 (1)
C(21)	0.3745 (6)	0.4815 (5)	0.183 (2)	0.038 (8)
C(22)	0.4061 (7)	0.4452 (5)	0.091 (2)	0.033 (8)
C(23)	0.4241 (9)	0.4821 (6)	0.411 (2)	0.06 (1)
C(24)	0.3039 (9)	0.4941 (7)	0.388 (2)	0.06 (1)
C(25)	0.408 (1)	0.2641 (5)	0.291 (2)	0.06 (1)
N(1)	0.2666 (7)	0.3379 (4)	0.214 (1)	0.040 (7)
N(2)	0.3650 (6)	0.4688 (5)	0.329 (1)	0.042 (7)

$^a U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*a_i{}\cdot a_j.$

taining the 2,6-bis[(dimethylamino)methyl]phenyl group (trigonal bipyramidal) may be as follows. In the former compounds the two coordinating nitrogen atoms have a cis arrangement and the halogen atom is in trans position with respect to one of these nitrogen atoms. In the latter compounds, however, the fixed geometry of the 2,6-bis-[(dimethylamino)methyl]phenyl group forces the two nitrogen atoms to occupy trans positions in an octahedral arrangement. As a result, the halogen atom is always in the less favorable trans position with respect to one of the tin–carbon bonds.[10] However, the exact factors that promote halogen displacement, i.e. the existence of nonionic or ionic structures, are not completely understood. Recently, it has been proposed that triorganotin compounds of the type $[CH_2(Me)NCH_2CH_2CH_2]_2SnXMe$ (X = Cl, Br, I), which in principle are isostructural with 1–3, i.e. two carbon atoms in trans position, the other carbon atom in cis position with respect to these two carbon atoms, and the two nitrogen atoms in cis position, also undergo halogen displacement giving rise to pentacoordinate triorganotin cations.[44] However, as these compounds are also soluble in apolar solvents like toluene, it cannot be excluded that in solution they exist as contact-ion pairs.

Experimental Part

Syntheses were carried out using standard Schlenk techniques under an atmosphere of purified nitrogen. The solvents were dried and distilled from sodium prior to use. ^{1}H, ^{13}C, and ^{119}Sn NMR spectra were recorded on a Bruker AC 200 spectrometer. Bis-[8-(dimethylamino)-1-naphthyl]tin(II) was prepared according to published methods.[25]

Synthesis of Bis[8-(dimethylamino)-1-naphthyl]methyltin Iodide (1), Bis[8-(dimethylamino)-1-naphthyl]ethyltin Iodide (2), and Bis[8-(dimethylamino)-1-naphthyl]benzyltin

Bromide (3). To a yellow solution of 5 mmol of bis[8-(dimethylamino)-1-naphthyl]tin(II) in 20 mL of benzene was added 5 mmol of methyl iodide, ethyl iodide, or benzyl bromide, resulting in immediate decoloration. The reaction mixture was stirred for 0.5 h, after which the solvent was removed in vacuo, leaving a white solid. This material was washed with pentane and dried in vacuo, giving bis[8-(dimethylamino)-1-naphthyl]methyltin iodide (1), bis[8-(dimethylamino)-1-naphthyl]ethyltin iodide (2), or bis[8-(dimethylamino)-1-naphthyl]benzyltin bromide (3) as white solids in quantitative yield. For analytical purposes the compounds were recrystallized from diethyl ether/pentane mixtures. Anal. Calcd for $C_{25}H_{27}IN_2Sn$ (1): C, 49.95; H, 4.53; N, 4.66; I, 21.11. Found: C, 49.57; H, 4.46; N, 4.40; I, 20.59. Anal. Calcd for $C_{26}H_{29}IN_2Sn$ (2): C, 50.77; H, 4.75; N, 4.55; I, 20.63. Found: C, 50.96; H, 4.76; N, 4.26; I, 20.38. Anal. Calcd for $C_{31}H_{31}BrN_2Sn$ (3): C, 59.08; H, 4.96; N, 4.45; Br, 12.68. Found: C, 57.99; H, 4.85; N, 4.42; Br, 13.41.

Synthesis of Bis[8-(dimethylamino)-1-naphthyl]methyltin Trifluoromethanesulfonate (4). To a solution of 2 mmol of bis[8-(dimethylamino)-1-naphthyl]methyltin iodide in 20 mL of methanol was added 2 mmol of silver trifluoromethanesulfonate, resulting in the immediate formation of a pale yellow precipitate (AgI). The reaction mixture was stirred for 0.5 h, after which the solid material was filtered off and the filtrate was concentrated in vacuo, leaving a white solid. This material was washed with pentane and dried in vacuo, giving bis[8-(dimethylamino)-1-naphthyl]methyltin trifluoromethanesulfonate (4) as a white solid in quantitative yield. Anal. Calcd for $C_{26}H_{27}F_3N_2O_3SSn$: C, 50.11; H, 4.37; N, 4.49. Found: C, 49.88; H, 4.53; N, 4.44. Relevant NMR data (^{1}H and ^{13}C δ relative to SiMe$_4$, in methanol-d_4, 25 °C): ^{1}H NMR δ 1.25 (SnCH$_3$, $^2J(^{119}$Sn–^{1}H) 66 Hz), 2.60 (NMe$_2$, broad, at 0 °C two resonances 2.25, 2.95), 8.05 (H(2)$_{naphthyl}$, $^3J(^{119}$Sn–^{1}H) ~15 Hz); ^{13}C NMR δ 2.3 (SnCH$_3$, $^1J(^{119}$Sn–^{13}C) 590 Hz), 49.2 (NMe$_2$, broad, at 0 °C two resonances 47.4, 51.0), 119.3, 127.2, 127.6, 127.8, 128.4, 131.4, 134.1, 136.0, 136.3, 151.0 (aromatics), 121.7 (CF$_3$SO$_3$, $^1J(^{19}$F–^{13}C) 318 Hz).

Crystal Structure Determination of 1. Transparent yellow crystals of 1, $C_{25}H_{27}IN_2Sn$, are orthorhombic, space group *Pbca* with eight molecules in a unit cell of dimensions a = 19.212 (3) Å, b = 25.540 (8) Å, and c = 9.482 (1) Å. A total of 4064 independent intensities (1.1 < θ < 25°, h 0–22, k 0–30, l 0–11) were measured on an Enraf-Nonius CAD4 diffractometer, at 25 °C, using graphite-monochromated Mo Kα radiation (λ(Mo Kα) = 0.710 69 Å); 2266 of these were below the 2.5$\sigma(I)$ level and were treated as unobserved.

The Sn and I positions were located by means of the symbolic addition program set SIMPEL.[45] The positions of the C and N atoms were obtained by standard difference Fourier techniques. After isotropic block-diagonal least-squares refinement, an empirical absorption correction (DIFABS[46]) was applied (crystal dimensions 0.25 × 0.10 × 0.08 mm; μ(Mo Kα) = 24.3 cm^{-1}). Hydrogen atoms were introduced at their calculated positions (for the calculation of the coordinates of the hydrogen atoms bound to C(25), one of the dihedral angles H–C–Sn–N(2) was taken as 0°). Continued refinement, anisotropic for Sn, I, C, and N (the thermal parameters of the H atoms were kept fixed at 0.038 Å^2) converged to R = 0.052 (R_w = 0.054). A weighting scheme w = $1/(4.64 + F_o + 0.032 F_o{}^2)$ was applied, and the anomalous dispersions of Sn and I were taken into account. Final coordinates of the non-hydrogen atoms are given in Table IV.

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