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**TRIORGANOTIN CATIONS STABILIZED BY INTRAMOLECULAR Sn–N
 COORDINATION; SYNTHESIS AND CHARACTERIZATION OF
 {C,N,N'-2,6-BIS[(DIMETHYLAMINO)METHYL] PHENYL } DIORGANOTIN**

BROMIDES R'R'' $\overline{\text{R-Sn}}^+ \text{Br}^-$ *

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Summary

The synthesis of {2,6-bis[(dimethylamino)methyl]phenyl} diorganotin bromides, 2,6-(Me₂NCH₂)₂C₆H₃SnRR'⁺ Br⁻ is described. The compounds in which R = R' = Me or Et and R = Me, R' = Ph are extremely soluble in water and other polar solvents and insoluble or slightly soluble (R = R' = Et) in apolar solvents. The diphenyl compound shows the opposite solubility behaviour. The dimethyl compound is completely dissociated in water into a triorganotin cation and bromide anion (mol. wt. and NMR) and has a molar conductance of 84.8 ohm⁻¹ cm⁻² mol⁻¹ (1/1 electrolyte). NMR spectroscopy reveals that the triorganotin cation has a TBP structure in which the N atoms occupy axial sites. Dynamic NMR spectra of the methylphenyl compound show that above -90°C rate-determining Sn–N dissociation occurs and that above 5°C a second process, involving rate-determining rotation of the substituted aryl group around the (N₂)C–Sn bond begins.

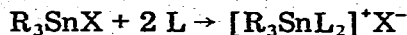
An X-ray investigation of single crystals of the dimethyl compound, which is unstable towards X-rays, establishes the ionic structure of the triorganotin halide in the solid (shortest Sn–Br 4.99 Å) as well as the molecular geometry of the triorganotin cation. Crystals are monoclinic, space group *P2₁/n* with *Z* = 4 in a unit cell of dimensions: *a* 11.13(1), *b* 16.73(2), *c* 10.10(1) Å and β 114.2(1)°.

* Data concerning the X-ray structure determination can be obtained on request from A.L.S.

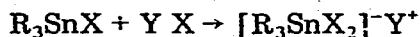
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Introduction

Among the various types of organotin compounds, triorganotin compounds R_3SnX are of particular interest because of the biocidal properties displayed by representatives of this group [1,2]. Several triorganotin compounds are now being produced on an industrial scale and used in a wide variety of applications [2,3]. In general, triorganotin compounds have low aqueous solubility. Because of the obvious utility of such compounds it is not surprising that attempts have been made to achieve the synthesis of water-soluble triorganotin biocides. So far, these attempts have met with remarkably little success. One possibility for achieving water solubility for triorganotin compounds is to incorporate the tin atom in either the anionic or cationic part of salt-like species of the type A or B:



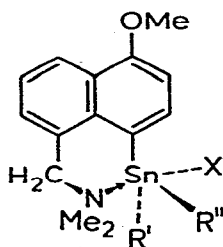
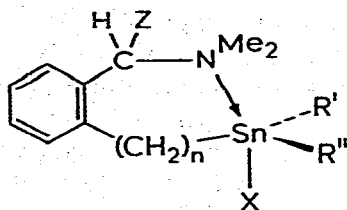
(A)



(B)

Examples of such compounds include $[Ph_3Sn(dmsO)_2]^+ BF_4^-$ [4] for type A, $[Ph_3SnCl_2]^- [Me_4N]^+$ [5] or $[Pr_3SnCl_2]^- [PhCH_2PPh_3]^+$ [6] for type B. Spectroscopic studies revealed that the tin atom in A and B is pentacoordinate and has a trigonal bipyramidal geometry [4,6,7]. Accordingly, these compounds have been formulated as ion-pairs. However, their solubility in water is very low (see e.g. ref. 6), which points to a low tendency for these salts to ionize into the respective ions.

Recently, we have reported the synthesis and characterization of triorganotin compounds $RR'R''SnX$ in which one of the organo groups (R) is a potentially bidentate ligand [8-12].



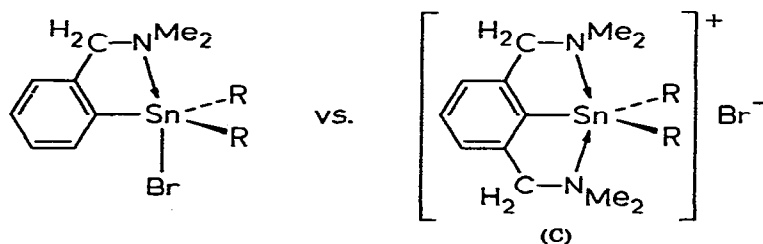
$\left\{ \begin{array}{l} Z = H \text{ or } Me; n = 0 \text{ or } 1 \\ R' \text{ and } R'' \text{ are Me or Ph} \end{array} \right.$

$R' \text{ and } R'' \text{ are Me or Ph}$

Preferential intramolecular coordination of the built-in ligand, $C(Z)HNMe_2$, with the tin atom which renders the tin atom pentacoordinate, appears to be a common structural feature of these compounds. X-ray structural determinations on 2- $Me_2NCH_2C_6H_4SnPh_2Br$ [9] and 2- $Me_2NCH(Me)C_6H_4SnMePhBr$ diastereomer [12] as well as spectroscopic studies [8,10,11] revealed that the Sn-C bonds are in the equatorial plane of a trigonal bipyramid, while the bromide and amino ligand occupy axial sites. The stabilizing effect of the built-in ligand on the stereochemical arrangement of the equatorial Sn-C₃ skeleton is demonstrated

by the configurational stability of the triorganotin halides $2\text{-Me}_2\text{NCH}(\text{Z})\text{C}_6\text{H}_4\text{SnMePhBr}$, in which the tin atom is a center of chirality [12]. Of decisive importance is the constraint imposed by the five-membered chelate ring (e.g. C-Sn-N angle of 72° ; two $sp^2\text{C}$ atoms) in these compounds which blocks stereoisomerization pathways involving either Sn-X dissociative steps or Berry pseudo-rotation processes taking place in the pentacoordinate conformer [12]. The importance of the latter factor is demonstrated by the rapid stereoisomerization of $2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{SnPhMeBr}$, which contains a less strained chelate ring [10,11]. Interaction of the pentacoordinate triorganotin halides $\text{RR}'\text{R}''\text{SnBr}$ (vide supra) with external Lewis bases does not occur for reasons discussed in ref. 12.

In the present paper we describe the results of a study of the influence of the introduction of a second (dimethylamino)methyl group at the 6 position of the aryl nucleus of $2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{SnR}_2\text{Br}$ on the aqueous solubility. This appeared to be of interest because a model had shown that the 2,6-bis[(dimethylamino)methyl]phenyl group could act as a terdentate ligand in triorganotin halides. Thus, the existence of pentacoordinate cationic species of type C might be envisaged:



The results of a biochemical and toxicological study of triorganotin compounds containing the 2-[(dimethylamino)methyl]phenyl and 2,6-bis[(dimethylamino)methyl]phenyl group will be published separately*.

Results and discussion

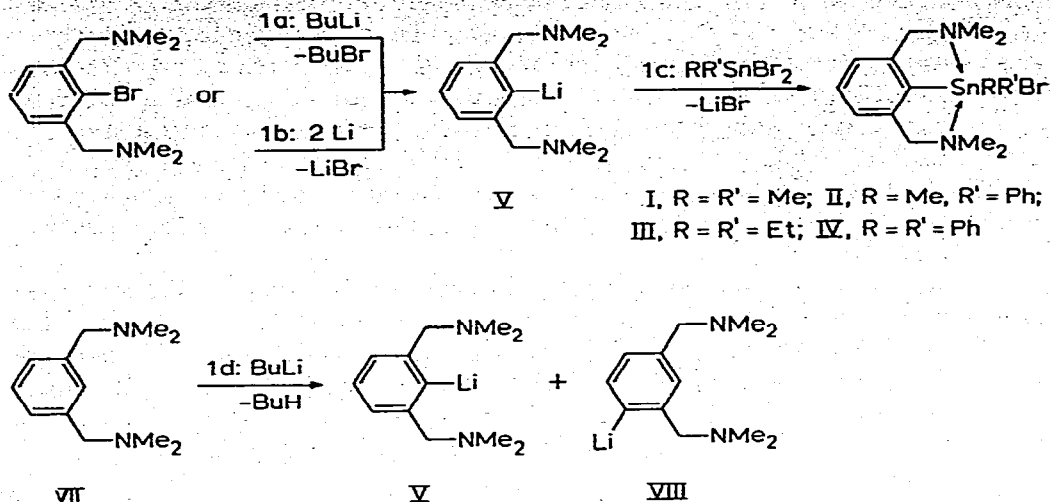
Synthesis of the triorganotin compounds I–IV

The 2,6-bis[(dimethylamino)methyl]phenyldiorganotin bromides I–IV are synthesized via the 1/1 reaction of the hitherto unreported organolithium compounds, 2,6-bis[(dimethylamino)methyl]phenyllithium (V) with the respective diorganotin bromides.

Two routes are available for the synthesis of the organolithium compound V. The Br/Li exchange reaction 1a in ether affords V and butyl bromide in quantitative yield (according to deuterolysis experiments as well as to NMR spectroscopic studies). V, which is extremely soluble in both polar and apolar solvents, is likewise formed in better than 90% yield in the 1/2 reaction of the bromide VI with metallic lithium (eq. 1b). The preparation of pure V via a direct metallation reaction (eq. 1d) of 1,3-bis[(dimethylamino)methyl]benzene (VII) with butyllithium in ether is not possible. Quantitative metallation does take place, but in addition to

* Preliminary results of this study were reported by Dr. W.N. Aldridge at the Second International Conference on the Organometallic and Coordination Chemistry of Germanium, Tin and Lead, Nottingham, England, 11–15 July 1977.

the 2,6-isomer (V; 86%) the 2,4-isomer VIII, which is readily detected by NMR (δ_{H} , 7.88 m ppm in diethyl ether) is formed in 14% yield*. Yields were established by



deuterolysis experiments and subsequent analysis of the amines by mass spectrometry and NMR spectroscopy.

The reactions of V with dimethyltin and methylphenyltin dibromide afford the respective organotin compounds I and II. Both compounds are extremely soluble in water and other polar solvents such as methanol and acetone, but are insoluble (like LiBr) in apolar solvents. As a result of the similar solubilities of LiBr and the organotin reaction product, I and II contamination with LiBr (cf. eq. 1c; up to a 1/1 molar ratio) cannot be avoided. Only in the case of the dimethyltin compound I could a solvent system be found which allowed purification of the crude material by recrystallization.

Interestingly, increase of the size of the organo groups on tin changes the aqueous solubility considerably. The diethyl compound III is moderately soluble in both polar (H₂O and MeOH) and apolar solvents, while the diphenyl compound IV is far more soluble in apolar solvents than in polar solvents, but is insoluble in water. This explains why III and IV have also been isolated in the pure state.

I has an apparent molecular weight of 216 (calcd. mol. wt. is 420) in water which indicates that in this solvent complete dissociation into a cationic 2,6-(Me₂NCH₂)₂C₆H₄SnMe₂⁺ moiety and Br⁻ takes place (cf. eq. 2a). NMR spectroscopy of a solution of I in water confirmed this conclusion. Only one resonance pattern (see Table 1) was observed for the SnMe, NMe and NCH₂ protons, thus excluding a dissociation of I according to eq. 2b.

The Sn-CH coupling constants have values which fall in the range for penta-coordinate triorganotin species [4,7,10-12]. This indicates that also the triorganotin cations have a trigonal bipyramidal structure, with the dimethylamino ligands in axial positions (see Structural Characterization).

* Trofimenko observed that palladation of the ethyl analogue of VII affords 1,3-dipalladio-4,6-bis[(diethylamino)methyl]benzene rather than 1-chloropalladio-2,6-bis[(diethylamino)methyl]benzene [13]. Recently, Shaw et al. showed that metallation of the corresponding diphosphine compound results in exclusive formation of the 2,6-disubstituted phenylpalladium isomer [14].

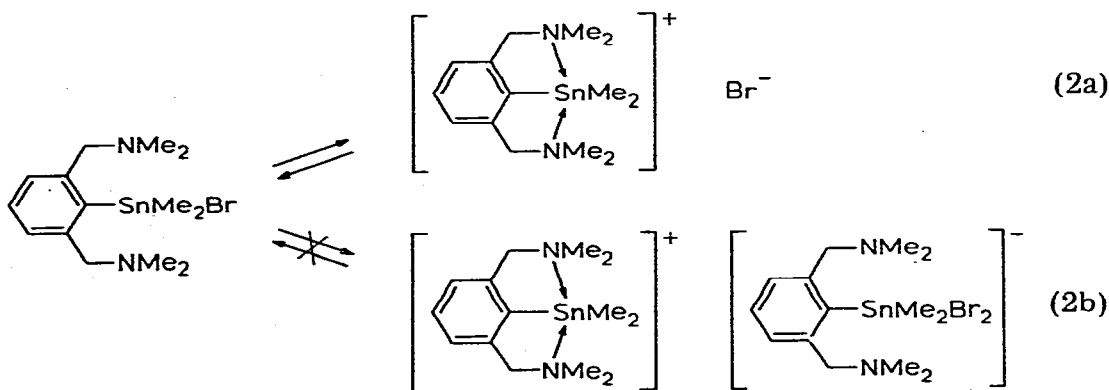
TABLE 1

NMR DATA (δ , ppm) FOR THE TRIORGANOTIN BROMIDES 2,6-(Me₂NCH₂)₂C₆H₃SnRR'Br I, II AND IV

Compound	Solvent	δ (Sn-Me) ^{a,b}	δ (NMe) ^a	δ (CH ₂) ^a	δ (ArH) ^a
I, R = R' = Me	D ₂ O ^c	0.85s (61.0/63.0)	2.52s	3.85s	7.1–7.6m
	DMSO-d ₆ ^c	0.82s (62.5/65.0)	^d	3.88s	
	MeOD-d ₃ ^c	0.86s	2.52s	3.89s	
	MeOD-d ₃ ^e	0.84s (60.6/63.5)	2.50s	3.84s	
II, R = Me, R' = Ph	D ₂ O ^f	1.18 (\approx 64)	2.33s	3.90s	
	Acetone-d ₆ ^f 25°C	1.23s (69/71)	2.24s	3.86br	7.0–7.9m ^g
	-30°C		2.35s	AB ^h (4.00; 10 Hz)	
	-45°C ⁱ		2.35br	br (4.05; —)	
	-90°C	1.50 (70)	2.25s 2.70s	AB (4.06 and 4.24; 18 Hz)	
IV, R = R' = Ph	MeOD-d ₃ ^e	—	2.21s	4.06s	7.3–8.2m

^a TMS internal. ^b $^2J(^{117,119}\text{Sn}-\text{CH})$ (Hz) between brackets. ^c Product composition RSnMe₂Br · 1.2 LiBr · 1.7 H₂O, cf. Experimental. ^d Masked by proton resonances of the solvent. ^e Pure product, i.e. without LiBr. ^f Product composition RSnMePhBr · LiBr, cf. Experimental. ^g Multiplets including the resonances of the phenyl group bound to tin. ^h Nature of the resonance pattern. The δ value at which the pattern is centered and the $\Delta\delta$ value are between brackets. At -5°C a broadened AB pattern ($\Delta\delta \approx 32$ Hz) is observed for the CH₂ protons. ⁱ Coalescence temperature of the NCH₃ resonances. The CH₂ proton resonances coalesce at 5°C.

Conductivity measurements of aqueous solutions of I in the concentration



range 0.2×10^{-3} to 20×10^{-3} M afford a molar conductance of $84.8 \text{ ohm}^{-1} \text{ cm}^{-2} \text{ mol}^{-1}$ corresponding to I being an 1/1 electrolyte. The organotin cation (cf. eq. 2a) has a very low limiting conductivity value of $6.4 \text{ ohm}^{-1} \text{ cm}^{-2} \text{ mol}^{-1}$ (based on $\lambda_{\text{Br}}^{\circ}$ 78.4, cf. ref. 15) which is in accord with the large size of the

cation. When I is recovered from aqueous solutions, several molecules of water are tenaciously retained (according to NMR spectroscopy).

Structural features

A. X-ray study of I. The structure in the solid of this novel type of triorganotin compound has been established by an X-ray investigation of crystals of I obtained by slow condensation of ether into a concentrated solution of I in butanol (1 g/4 ml). It appeared, however, that the crystals decompose upon exposure to X-rays. Because of the limited accuracy of the data set the refinement was stopped at $R = 0.24$. Although this precludes detailed discussion of bond distances and angles, the data provide a clear-cut overall picture of the crystal lattice, establishing the ionic structure of the triorganotin halide as well as the molecular geometry of the triorganotin cation.

The projection of the unit cell content on the x,y -plane is shown in Fig. 1. This projection shows discrete monomeric triorganotin cations $2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\text{SnMe}_2^+$. A projection of the Sn and Br atoms inside the unit cell on the y,z -plane (see Fig. 2) reveals that I has an ionic structure. The shortest Sn...Br distance in the lattice appears to be 4.99 Å.

The triorganotin cation consists of an almost planar Sn-C₃ arrangement, while the two intramolecular Me₂NCH₂ ligands occupy axial sites of a trigonal bipyramid. The two five-membered chelate rings are both puckered, resulting in a small angle between the plane through the phenyl ring and the plane bisecting the CH₃-Sn-CH₃ angle. In this respect the present structure and those of the previously reported 2-Me₂NCH(Z)C₆H₃SnR'PhBr (Z = Me, R' = Me [12] and

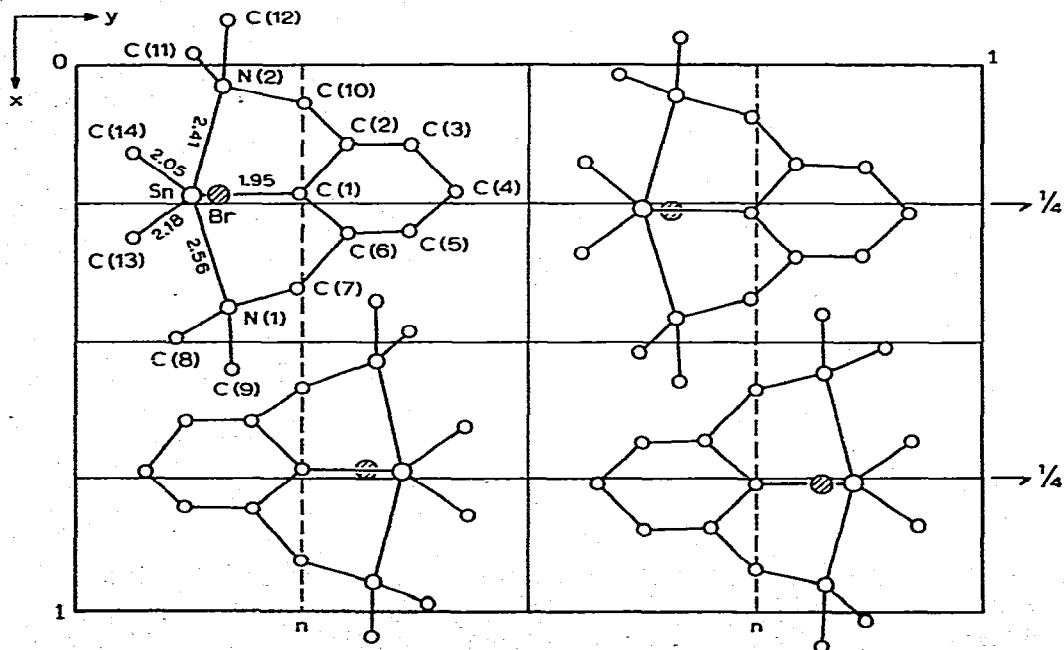


Fig. 1. Projection of the unit-cell content on the x,y -plane

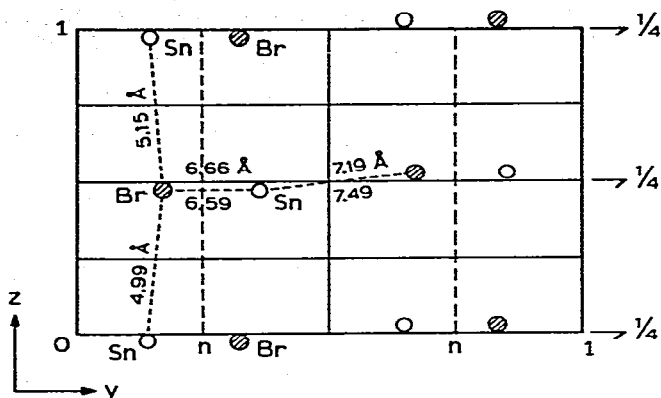
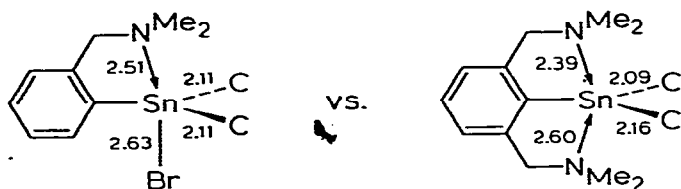


Fig. 2. Projection of the Sn and Br atoms inside the unit cell on the y, z -plane.

$Z = H$, $R' = Ph$ [6]) compounds have fully comparable structural features. The second intramolecular Me_2NCH_2 ligand in I resides at the same position as the bromine atom in the latter two triorganotin compounds.



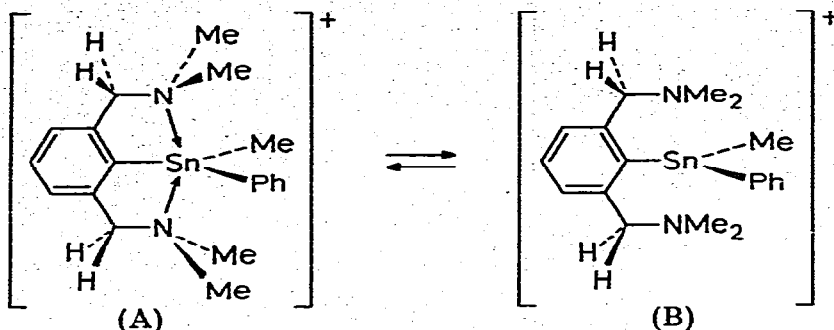
B. NMR spectroscopy. The structure in solution of these triorganotin bromide salts can be deduced from the results of a dynamic NMR study of the prochiral $2,6-(Me_2NCH_2)_2C_6H_3SnMe_2^+ Br^-$ (I) and chiral $2,6-(Me_2NCH_2)_2C_6H_3SnMePh^+ Br^-$ (II) compounds in polar solvents like D_2O , $DMSO-d_6$ and $MeOD-d_3$.

The complete dissociation of these compounds in water was demonstrated for I (vide supra). It was also shown that I and II can be dissolved in polar solvents without decomposition. With respect to an interpretation of the dynamic resonance patterns of I and II it is important to note that the presence of $LiBr$ in solutions of I, II or IV leaves the chemical shifts of the various protons unaffected.

Prochiral I has an apparent molecular symmetry plane in which both the tridentate NCN ligand and the tin atom reside. This is concluded from the observation of sharp singlet resonance patterns for the prochiral CH_2 and $SnMe_2$ groupings both at low and ambient temperatures. The NMR spectrum of I does not provide information about the existence of $Sn-N$ coordination. The observation of a singlet for the NMe protons can be explained either by rate determining $Sn-N$ coordination, which renders the NMe_2 grouping a stable prochiral assembly having enantiotopic Me groups, or by rapid pyramidal inversion at N in non-coordinated NMe_2 ligands.

A different situation exists in the case of II, in which the tin atom is a chiral center with respect to the configuration in the equatorial plane. In the penta-coordinate conformer A both the CH_2 protons and the NMe_2 protons are dia-

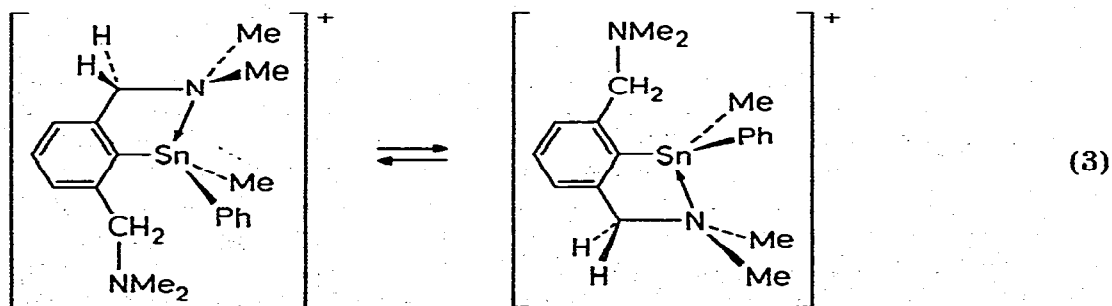
stereotopic*, and this is expected to result in an AB pattern for the first protons and two singlets for the latter set.



N—Sn bond dissociation affords conformer B for which on the basis of the chirality in the equatorial plane an AB pattern for the CH₂ protons is expected provided that the change of configuration at tin with respect to the plane through the C₆H₅ ring is slow on the NMR time scale. This is an important prerequisite, because the CH₂ protons become enantiotopic and thus isochronous by rapid rotation of the 2,6-(Me₂NCH₂)₂C₆H₅ group around the (N₂)C—Sn bond.

The actual dynamic NMR patterns of chiral II in acetone-*d*₆ are presented in Table 1.

At -90°C the spectrum shown in Fig. 3 was obtained. Two singlets for the NMe₂ protons and an AB pattern for the CH₂ protons are observed. This indicates that both intramolecular ligands are coordinated to the tin atom and, moreover, that Sn—N bond dissociation is slow on the NMR time scale. The anisochronous resonances coalesce at different rates (NMe₂, Δδ 45 Hz, -45°C; NCH₂, Δδ ≈ 30 Hz, +5°C). This points out that the respective protons become isochronous as a result of two different processes, i.e. the NMe₂ protons by a process which involves rate determining Sn—N dissociation followed by inversion at nitrogen, concomitant rotation around the (C(H₂))—N bond and reformation of the Sn—N bond, the CH₂ protons by a process which traverses Sn—N dissociation, followed by rate-determining rotation of the aryl group around the (N₂)C—Sn bond.



* Both the benzylic C atom and the N-atom in the N-coordinated situation lack relevant molecular symmetry planes bisecting the H—C—H and Me—N—Me angle, respectively. The two intramolecular CH₂NMe₂ ligands reside in enantiotopic environments with respect to the chiral equatorial plane, and thus in achiral solvents give rise to one resonance pattern only.

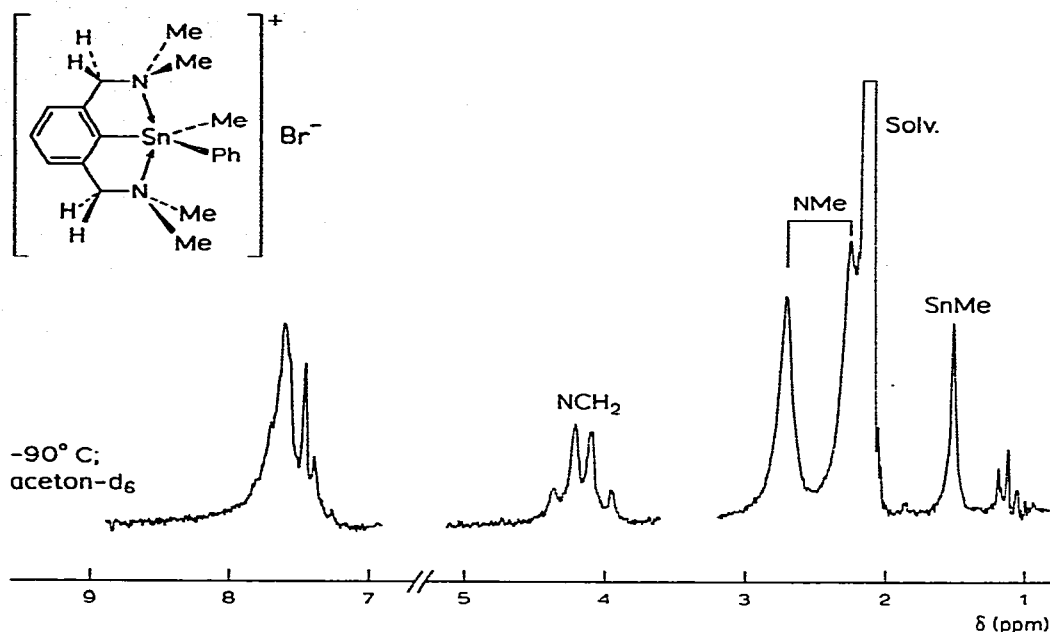
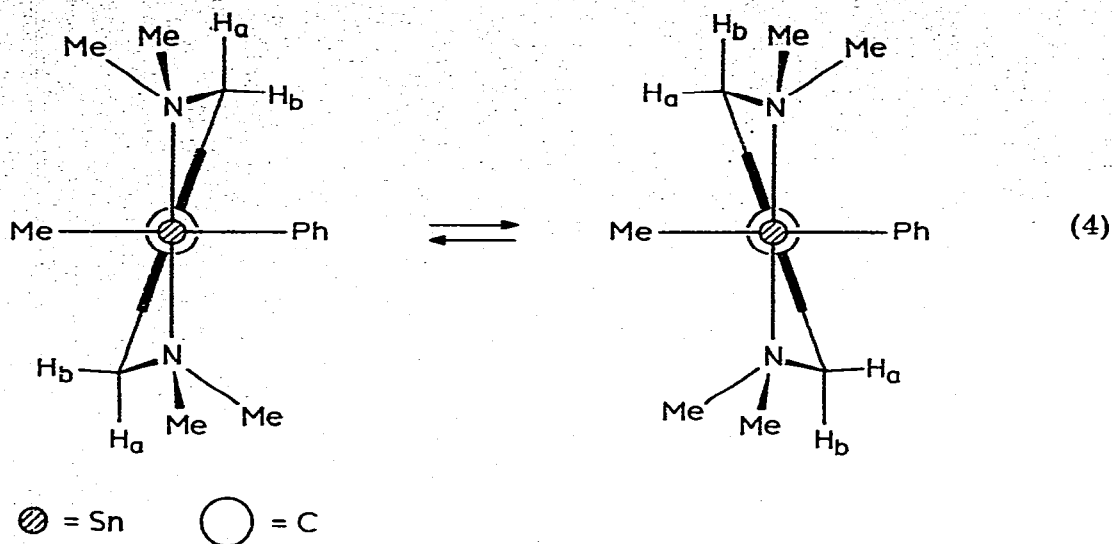


Fig. 3. NMR spectrum of II in acetone- d_6 recorded at -90°C .

An alternative process by which coalescence of the benzylic protons can be explained is shown in eq. 3. Dissociation of one Sn—N bond leads to a tetrahedral geometry around tin. Reformation of the Sn—N bond with simultaneous dissociation of the second Sn—N bond then develops the configuration at tin of the enantiomer. However, this process can be rejected on the basis of the steric requirements of the five-membered chelate ring (cf. ref. 10–12). The N—Sn—C (substituted phenyl) angle is 75° . Formation of the tetracoordinate enantiomers shown in eq. 3 would require opening of this angle to values greater than 90° (up to 109°) which represents a high energy route as compared to the process involving rate-determining rotation around the $(\text{N}_2)\text{C—Sn}$ bond.

The $\Delta\delta$ value of the diastereotopic benzylic protons shows a very complex temperature dependence. On raising the temperature the $\Delta\delta$ value decreases to about 10 Hz at -30°C , at which the NMe_2 proton signals coalesce, and then increase again to about 30 Hz at -5°C . Whether this $\Delta\delta$ change is caused by a change in individual chemical shift terms of the benzylic protons or results from alteration of conformer populations or from a complex interplay of these factors cannot be concluded from the data. However, it is obvious that the terdentate ligand, which has a very complex interaction with the SnC_2 unit, gives rise to a large number of different conformers. For example, as a result of the puckering in the five-membered chelate rings the conformations shown in eq. 4 are possible below -30°C .

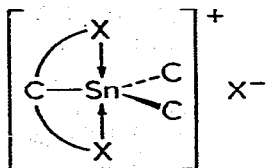
Wagging of the phenyl ring around the $(\text{N}_2)\text{C—Sn}$ axis will affect the environment of the benzylic protons, while the conformer populations will be affected by the asymmetry in the equatorial plane.



Conclusions

The structural features of the triorganotin compounds studied reveal some interesting aspects of the use of the 2,6-(Me₂NCH₂)₂C₆H₃ ligand. The steric requirements of this terdentate monoanion, which contains *sp*² hybridized C atoms adjacent to the C atom bound to the metal dictate an ax—eq—ax spanning in the trigonal bipyramid with the two N ligands occupying axial positions. This is the preferred arrangement in pentacoordinate R₃MX₂ molecules. This arrangement allows stabilization of the planar SnC₃ cation in the compounds studied, because the N ligands are positioned in such a way that they can donate electron density into the empty *p*-type orbital on tin which points to the axial sites of the TPB.

The results reported herein point to the possibility that other triorganotin species with aqueous solubility can be synthesized by using terdentate monoanionic ligands which are bound to tin via a covalent Sn—C-bond and two interactions with axially positioned hetero atoms. Moreover, this principle appears



also to be applicable to the synthesis of organotransition metal compounds. The interesting chemistry of transition metal complexes containing the terdentate 2,6-bis[(dimethylamino)methyl]phenyl ligand will be reported separately [15].

Experimental

All reactions were carried out under dry oxygen-free nitrogen. Solvents were carefully purified and distilled before use under nitrogen.

MePhSnBr_2 was synthesized by reaction of MePh_3Sn with two moles of Br_2 in CCl_4 .

^1H NMR spectra, which were run by Mrs. G.M. Bijlsma-Kreuger and Mrs. T. van Montfort-Volp, were recorded on a Varian Associates HA-100 NMR spectrometer. IR spectra were recorded on a Perkin-Elmer 577 Grating IR spectrometer. The molar conductance of I was determined on a Philips Model PW9501 conductometer, while the molecular weight data were measured by cryometry using a Knauer apparatus for temperature measurement.

Elemental analyses were carried out in the Analytical Department of the TNO Institute.

Synthesis of C,N,N'-{2,6-bis[(dimethylamino)methyl]phenyl}dimethyltin bromide (I)

A solution of butyllithium (22.14 mmol) in hexane (17 ml) was added at room temperature to a solution of 2,6-bis[(dimethylamino)methyl]phenyl bromide (22.14 mmol) in ether (125 ml). The resulting yellow solution was stirred for 0.5 h and then added dropwise to a solution of Me_2SnBr_2 (22.14 mmol) in ether. The colourless reaction mixture, containing a white precipitate, which was washed with Et_2O and with pentane and then dried in vacuo, appeared to be crude I contaminated with lithium bromide. Elemental analysis pointed to the composition $\text{RSnMe}_2\text{Br} \cdot 1.2 \text{LiBr} \cdot 1.7 \text{H}_2\text{O}$ (69% yield).

Purification of crude I involved dissolution in butanol (8 ml), filtration of the solution, and slow condensation of ether (200 ml) into the filtrate. Crystalline I was filtered off, washed with pentane and dried in vacuo (yield 40%). The absence of lithium was confirmed by a negative flame test. (Found: C, 39.2; H, 5.9; Br, 19.0; N, 6.7; Sn, 28.1. $\text{C}_{14}\text{H}_{25}\text{BrN}_2\text{Sn}$ calcd.: C, 40.03; H, 5.95; Br, 19.04; N, 6.67; Sn, 28.26%). M.p. 215°C . Mol.wt. in H_2O by cryoscopy; found 216; $\text{C}_{14}\text{H}_{25}\text{N}_2\text{SnBr}$ calcd. 419.6 ($\text{RMe}_2\text{Sn}^+ \text{Br}^-$ calcd. 209.8). Conductivity in H_2O ($25.00 \pm 0.01^\circ\text{C}$) Λ_0 84.8 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$; λ^{+0} 6.4 (based on λ^{-0} 78.4).

Preparation of single crystals of I

Crystals suitable for analysis by X-ray diffraction were obtained from a solution of 1 g of I in butanol (4 ml) into which 10 ml of ether was distilled under N_2 in about 72 h.

Synthesis of C,N,N'-{2,6-bis[(dimethylamino)methyl]phenyl}diphenyltin bromide (IV)

A clear solution of 2,6-bis[(dimethylamino)methyl]phenyllithium (from the reaction of the bromide (20 mmol) in ether (40 ml) with lithium (50 m-at)) in ether (100 ml) was added at room temperature to a solution of diphenyltin dibromide (20 mmol) in ether (50 ml). The suspension was stirred for 15 h and then filtered. The white solid was washed twice with ether (20 ml) and then suspended in water (100 ml; removal of LiBr). The insoluble white solid was filtered off, extracted with water (2×20 ml) and dried in vacuo over KOH. M.p. $200\text{--}201^\circ\text{C}$; 90% yield. (Found: C, 50.6; H, 5.3; Br, 14.2; N, 4.7, Sn, 20.2. $\text{C}_{24}\text{H}_{29}\text{N}_2\text{BrSn}$ calcd.: C, 52.97; H, 5.33; Br, 14.71; N, 5.15; Sn, 21.83%).

Synthesis of C,N,N'-(2,6-bis[(dimethylamino)methyl]phenyl)methylphenyllithium bromide (II)

A solution of 2,6-bis[(dimethylamino)methyl]phenyllithium (22.14 mmol) in ether (17 ml) was added to a solution of 22.14 mmol of MePhSnBr₂ in ether. The solution was stirred at room temperature for 2.5 h, then concentrated to about 50 ml, to give a crystalline precipitate, which was filtered off. This solid was washed with ether (2 × 5 ml) and pentane (2 × 50 ml), and then dried in vacuo at 65°C/1 mmHg. Elemental analysis indicated this solid to be II contaminated with LiBr. (Found: C, 37.2; H, 4.9; Br, 30.3; N, 4.9; Sn, 18.6. C₁₉H₂₇N₂SnBr · LiBr calcd.: C, 40.12; H, 4.78; Br, 28.09; N, 4.92; Sn, 20.86%).

X-ray data collection and structure determination

Crystals of I appear to be very unstable once they have been exposed to an X-ray source. A decay process which is approximately linear with time takes place. This process continues also when the irradiation is stopped. The actual decay times of the seven crystals that were examined on the diffractometer ranged from a few hours to a few days. The choice of Cu-K_α or Mo-K_α radiation appeared to have no major influence on this process. In contrast to the minor macroscopic changes of the crystals, only a slight colouration of the transparent colourless crystals was observed, the long-range ordering of the molecules appeared to be lost as a result of the decay process, resulting in an amorphous diffraction pattern.

Several partial data sets on different crystals were obtained and combined into a unique set of 1098 reflections with $I > \sigma(I)$. The data were collected on an Enraf-Nonius CAD3 diffractometer in the ω -scan mode up to $\theta = 60^\circ$. Cu-K_α radiation and the maximum possible scan speed were used in order to speed up the data collection. The crystals were not suitable to apply absorption correction.

The crystal data are: SnBrN₂C₁₄H₂₅, mol. wt. 420, monoclinic, space group P2₁/n, a 11.13(1), b 16.73(2), c 10.10(1) Å, β 114.2(1)°, V 1717 Å³, Z = 4, F_{000} 832, d_{obs} 1.63 g cm⁻³ (by flotation in CCl₄/C₂H₄Br₂), d_x 1.624 g cm⁻³, μ (Cu-K_α) 152 cm⁻¹.

The Sn and Br atoms were readily located from a Patterson synthesis. The R value at this point was 0.41. The other non-hydrogen atoms were found by standard Fourier techniques. Refinement of the positional and isotropic thermal parameters by least-square techniques [16] was stopped at $R = 0.24$. All parameters were stable at this point. Inspection of the difference Fourier map showed apart from the usual features around the heavy atoms some peaks in the area of the benzene ring, possibly indicating some disorder. In view of the limited quality of the data set this was not analyzed further.

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References

- 1 A.K. Sijpesteijn, J.G.A. Luijten and G.J.M. van der Kerk, in D.C. Torgeson (Ed.), *Fungicides*, Academic Press, N.Y., 1969.
- 2 A. Bokranz and H. Plum, *Fortschrit. Chem. Forsch.*, 16 (1971) 365.
- 3 G.J.M. van der Kerk, *Chem. Zeit.*, 99 (1975) 26; P.J. Smith and L. Smith, *Chem. Brit.*, 11 (1975) 208.
- 4 V.G. Kumar Das, *J. Inorg. Nucl. Chem.*, (1976) 1241.
- 5 R.V. Parish and R.H. Platt, *Inorg. Chim. Acta*, 4 (1970) 65.
- 6 A.J. Crowe and P.J. Smith, *Inorg. Chim. Acta*, 19 (1976) L7.
- 7 G.M. Bancroft, V.G. Kumar Das, T.K. Sham and M.G. Clark, *J. Chem. Soc., Dalton Trans.*, (1976) 643.
- 8 G. van Koten, C.A. Schaap and J.G. Noltes, *J. Organometal. Chem.*, 99 (1975) 157.
- 9 G. van Koten, J.G. Noltes and A.L. Spek, *J. Organometal. Chem.*, 118 (1976) 183.
- 10 G. van Koten and J.G. Noltes, *J. Amer. Chem. Soc.*, 98 (1976) 5393.
- 11 G. van Koten and J.G. Noltes, *Advan. Chem. Ser.*, 157 (1976) 275.
- 12 G. van Koten, J.T.B.H. Jastrzebski, J.G. Noltes, W.M.G.F. Pontenagel, J. Kroon and A.L. Spek, *J. Amer. Chem. Soc.*, in press.
- 13 S. Trofimenko, *J. Amer. Chem. Soc.*, 93 (1971) 1808.
- 14 C.J. Moulton and B.L. Shaw, *J. Chem. Soc. Dalton*, (1976) 1020.
- 15 G. van Koten, K. Timmer, J.G. Noltes and A.L. Spek, *J. Chem. Soc., Chem. Commun.*, in press.
- 16 J.M. Stewart, G.J. Kruger, H.L. Ammon, C. Dickinson and S.R. Hall, *XRAY-Sytem*, Technical Report TR-192. The Computer Science Center, University of Maryland, College Park, Maryland, 1972.