

Crystal and Molecular Structure of $\text{SnMePh}[\text{C}_{10}\text{H}_5(\text{OMe-5})(\text{CH}_2\text{NMe}_2\text{-8})]\text{Br}\dagger$ and Proton Nuclear Magnetic Resonance Study of the Puckering of the Chelate Ring in Five-co-ordinate Triorganotin Halides $\text{SnRR}'[\text{C}_{10}\text{H}_5(\text{OMe-5})(\text{CH}_2\text{NMe}_2\text{-8})]\text{X}$ and $\text{SnRR}'[\text{CH}_2\text{C}_6\text{H}_4(\text{CH}_2\text{NMe}_2\text{-2})]\text{X}$

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8-Dimethylaminomethyl-5-methoxynaphthyl- and 2-dimethylaminomethylbenzyl-diorganotin halides have been prepared *via* the organolithium-diorganotin dihalide route in 50–55% yield. The molecular structure of the title compound (3) has been determined by a single-crystal X-ray diffraction study using standard Patterson and Fourier techniques, and refined by block-diagonal least squares to $R = 0.024$ for 3 014 observed diffractometer data (Mo- $K\alpha$ radiation). Crystals are triclinic, space group $P\bar{1}$ with $Z = 2$ in a unit cell of dimensions $a = 7.795(5)$, $b = 11.178(2)$, $c = 12.159(1)$ Å, $\alpha = 106.20(2)$, $\beta = 91.75(3)$, and $\gamma = 100.83(3)^\circ$. The Sn co-ordination is pseudo-trigonal bipyramidal with N and Br in axial positions [Sn–N 2.401(4), Sn–Br 2.7391(7) Å]. Dynamic ^1H n.m.r. spectroscopy shows that the trigonal-bipyramidal structure is retained in solution. In the slow-exchange limit (3) exists in two diastereoisomeric forms as a result of the puckering of the chelate ring and the chirality at the Sn centre. On raising the temperature two different processes occur, the first of which involves interconversion between the two ring conformations. The second process (either Berry pseudo-rotation processes in the five-co-ordinate conformer, or Sn–N dissociation followed by combined pyramidal inversion at the N centre and rotation about the C–N bond) is difficult to define because of the coincident CH_2 and OMe resonances. Dynamic ^1H n.m.r. spectra of $\text{SnMePh}[\text{CH}_2\text{C}_6\text{H}_4(\text{CH}_2\text{NMe}_2\text{-2})]\text{Br}$ (5) reveal that the six-membered chelate ring containing two sp^3 -C atoms is very flexible compared with the five-membered ring in $\text{SnMePh}[\text{C}_6\text{H}_4(\text{CH}_2\text{NMe}_2\text{-2})]\text{Br}$. Accordingly stereoisomerization in the five-co-ordinate conformer of (5) could be detected.

In previous papers we described the single-step synthesis of a novel type of di- and tri-organotin halides $\text{SnR}_n\text{X}_{4-n}$ ($n = 2$ or 3)¹⁻³ in which at least one of the organo-groups is an aryl group containing in one or both *ortho* positions a built-in ligand. Examples having the CHZNMe_2 ($Z = \text{H}$ or Me) group as a built-in ligand are shown in Figure 1.

Intramolecular co-ordination of the built-in ligand with the tin centre, resulting in a co-ordination number of five in compounds of type (A) and (B) and six for compounds of type (C), is an important structural feature. The five-membered chelate rings formed are puckered at the CNSn part of the ring.^{3,4} The two ring conformers are of equal stability in $\text{SnR}_2[\text{C}_6\text{H}_4(\text{CHZNMe}_2\text{-2})]\text{X}$ ($Z = \text{H}$) but differ in the C-chiral compound with $Z = \text{Me}$. This can be ascribed to a difference in repulsive forces between the vicinal groups in the chelate rings of the respective conformers.³ Attempts to detect these conformers in solution at low temperature by ^1H n.m.r. spectroscopy failed, which points to a low activation barrier to interconversion.

We have been interested in the possibility of modifying the constraints of the chelate ring in this type of compound by introducing either sp^2 - or sp^3 -hybridized C atoms. For this purpose we have synthesized $\text{SnRR}'[\text{C}_{10}\text{H}_5(\text{OMe-5})(\text{CH}_2\text{NMe}_2\text{-8})]\text{X}$ and $\text{SnRR}'[\text{CH}_2\text{C}_6\text{H}_4(\text{CH}_2\text{NMe}_2\text{-2})]\text{X}$ and have studied the puckering of the chelate ring in these compounds by dynamic n.m.r.

† Bromo(8-dimethylaminomethyl-5-methoxynaphthyl- C^{1N})-methylphenyltin(IV).

methods. The results of this study together with the detailed stereochemistry of the six-membered chelate ring of the naphthyl compound with $R = \text{Me}$, $R' = \text{Ph}$, and $X = \text{Br}$, as determined by X-ray diffraction methods, are described in the present paper.

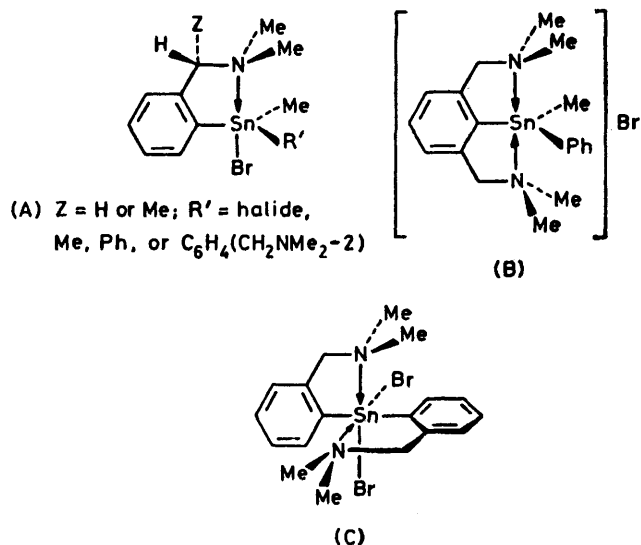


FIGURE 1 Tri- and di-organotin halides in which the tin centre has an increased co-ordination number by intramolecular co-ordination with built-in ligands

RESULTS

Synthesis.—The naphthyl- and benzyl-diorganotin halides (2), (3), and (5) were obtained in 50–55% yield from the

reaction of equimolar mixtures of the corresponding organolithium compounds (1)⁵ and (4) with the diorganotin

TABLE I

Bond distances (Å) and angles (°) involving non-hydrogen atoms, with estimated standard deviations in parentheses

Sn-Br	2.739 1(7)	C(16)-C(17)	1.383(6)
Sn-N	2.401(4)	C(17)-C(18)	1.397(7)
Sn-C(1)	2.147(4)	C(18)-C(19)	1.378(9)
Sn-C(15)	2.134(6)	C(19)-C(20)	1.367(7)
Sn-C(16)	2.141(4)	C(20)-C(21)	1.390(7)
C(1)-C(2)	1.378(7)	C(16)-C(21)	1.394(7)
C(2)-C(3)	1.390(7)	C(10)-C(1)	1.447(7)
C(3)-C(4)	1.354(7)	C(8)-C(11)	1.497(7)
C(4)-C(9)	1.422(7)	N-C(11)	1.489(5)
C(9)-C(5)	1.424(7)	N-C(12)	1.480(8)
C(5)-C(6)	1.369(7)	N-C(13)	1.481(7)
C(6)-C(7)	1.401(7)	O-C(5)	1.366(6)
C(7)-C(8)	1.367(7)	O-C(14)	1.428(8)
C(8)-C(10)	1.436(7)	N-Sn-C(1)	88.2(2)
C(9)-C(10)	1.429(6)	N-Sn-C(15)	89.4(2)
Br-Sn-N	174.32(8)	N-Sn-C(16)	87.3(2)
Br-Sn-C(1)	97.39(13)	N-C(11)-C(8)	114.9(4)
Br-Sn-C(15)	88.0(2)	Sn-N-C(11)	102.5(3)
Br-Sn-C(16)	89.83(13)	Sn-N-C(12)	113.8(3)
C(1)-Sn-C(15)	125.3(2)	Sn-N-C(13)	111.5(3)
C(1)-Sn-C(16)	112.0(2)	C(11)-N-C(12)	111.1(4)
C(15)-Sn-C(16)	122.4(2)	C(11)-N-C(13)	109.4(4)
Sn-C(1)-C(2)	115.5(3)	C(12)-N-C(13)	108.4(4)
Sn-C(1)-C(10)	125.8(3)	O-C(5)-C(6)	124.6(5)
C(2)-C(1)-C(10)	118.2(4)	O-C(5)-C(9)	114.8(4)
C(1)-C(2)-C(3)	123.2(5)	C(5)-O-C(14)	117.5(4)
C(2)-C(3)-C(4)	119.4(5)	Sn-C(16)-C(17)	121.6(4)
C(3)-C(4)-C(9)	121.4(4)	Sn-C(16)-C(21)	120.0(3)
C(6)-C(5)-C(9)	120.6(4)	C(17)-C(16)-C(21)	118.3(4)
C(5)-C(6)-C(7)	118.6(5)	C(16)-C(17)-C(18)	120.6(5)
C(6)-C(7)-C(8)	123.7(5)	C(17)-C(18)-C(19)	120.3(5)
C(7)-C(8)-C(10)	119.1(4)	C(18)-C(19)-C(20)	119.5(5)
C(4)-C(9)-C(5)	120.5(4)	C(19)-C(20)-C(21)	120.7(5)
C(4)-C(9)-C(10)	119.2(4)	C(16)-C(21)-C(20)	120.6(4)
C(5)-C(9)-C(10)	120.3(4)		
C(1)-C(10)-C(8)	124.0(4)		
C(1)-C(10)-C(9)	118.5(4)		
C(8)-C(10)-C(9)	117.6(4)		
C(7)-C(8)-C(11)	117.7(4)		
C(10)-C(8)-C(11)	123.1(4)		

naphthylcopper compound.⁵ However, separation of the resulting naphthyltin halides from the copper halide formed was difficult. The novel compounds (2), (3), and (5) are white solids which according to molecular-weight determinations are monomeric in solution.

Molecular Geometry.—The crystal structure of compound (3) contains two centrosymmetrically related enantiomers in the unit cell. The molecular geometry along with the atomic numbering scheme is shown in a thermal ellipsoid plot in Figure 2. Bond distances and angles are listed in Table I. The Sn co-ordination is pseudo-trigonal bi-

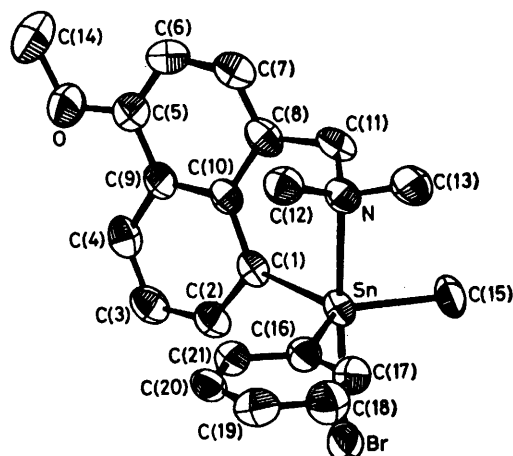
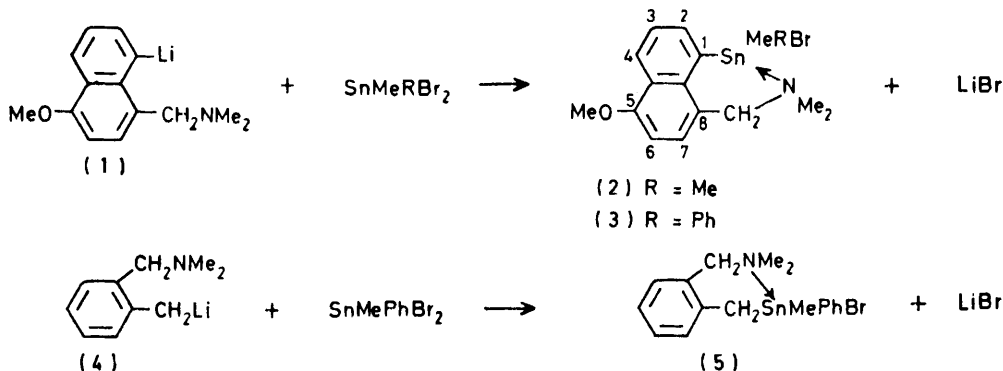


FIGURE 2 Molecular geometry of (3) and atomic numbering scheme. ORTEP drawing showing the 50% probability ellipsoids. Hydrogen atoms have been located but have not been included in the drawing

pyramidal with N and Br in axial positions. A comparison with the geometry of the related five-co-ordinate triorganotin halides $\text{SnPh}_2[\text{C}_6\text{H}_4(\text{CH}_2\text{NMe}_2)]\text{Br}$ ⁴ and the (*S*)_C(*S*)_{Sn} diastereoisomer of (*S*)- $\text{SnMePh}[\text{C}_6\text{H}_4(\text{CHMeNMe}_2)]\text{Br}$ ³ is given in Table 2. The sum of Sn-N and Sn-Br bonds appears to be remarkably constant, notwithstanding appreciable variations in the individual bond lengths. The Sn atom resides 0.06 Å below the equatorial plane on the side of the bromide atom; similar geometries are found in the related five-co-ordinate triorganotin halides (see Table 2). The N-Sn-Br configuration deviates from linearity with the Br atom bent away from H(2), still with a short distance of



dihalides. These reactions were only successful when the organolithium derivatives were added to the diorganotin halides (*cf.* ref. 1). The naphthyl derivatives (2) and (3) could also be prepared starting from the corresponding

2.76 Å. The five-co-ordinate structure is in full agreement with the predictions made on the basis of Sn Mössbauer data obtained for these compounds.⁶

No unusual short intermolecular distances are observed,

which points to the absence of any specific bonding between neighbouring molecular units in the crystal.

DISCUSSION

The ^1H n.m.r. data for the naphthyl- and benzyl-tin compounds (2), (3), and (5) reveal that in solution these

TABLE 2

Comparison of main structural features* of (i) $\text{SnMePh}[\text{C}_{10}\text{H}_5(\text{OMe}-5)(\text{CH}_2\text{NMe}_2-8)]\text{Br}$, (ii) $\text{SnPh}_2[\text{C}_6\text{H}_4(\text{CH}_2\text{NMe}_2-2)]\text{Br}$,⁴ and (iii) the $(S)_C(S)_{\text{Sn}}$ diastereoisomer of $\text{SnMePh}[\text{C}_6\text{H}_4(\text{CHMeNMe}_2-2)]\text{Br}$ ³

	(i)	(ii)	(iii)
N-Sn-Br/ $^\circ$	174.3(1)	171.0(1)	168.9(2)
Planarity of the SnC_3 unit [$\Sigma(\text{C-Sn-C})/^\circ$]	359.9(3)	357.7(7)	358.7(6)
Br-Sn-C/ $^\circ$	97.4(1)	96.2(3)	94.5(2)
	88.0(2)	96.3(3)	94.1(2)
	89.8(1)	92.7(3)	92.6(3)
Bite ($^\circ$) of ligand			
C-Sn-N	88.2(2)	75.3(4)	75.2(3)
C-N-Sn	102.5(3)	101.1(8)	105.3(5)
Sn-N/ Å	2.401(4)	2.511(12)	2.476(7)
Sn-Br/ Å	2.739(1)	2.630(2)	2.683(1)
Sum/ Å	5.140(4)	5.141(12)	5.159(7)

* Each of the compounds contains a five-co-ordinate Sn centre [type (A), Figure 1] but differs with respect to the number of atoms in the chelate ring [(i), six; (ii) and (iii), five].

compounds can be assigned a trigonal-bipyramidal structure (see Table 3). The $^2J(\text{Sn-H})$ values of *ca.*

The protons in the naphthalene nucleus could be assigned on the basis of the δ values as well as on proton-spin-decoupling experiments. The multiplet at 9.12 p.p.m. of (3) (*cf.* Figure 3) is accompanied by Sn satellites and is thus assigned to H(2). Irradiation at this doublet of doublets centred at 7.63 p.p.m. resulted in doublets at 9.12 (with Sn satellites) and 8.46 p.p.m. due to *meta* coupling. This allows unambiguous assignment of these resonances to H(2) and H(4), respectively (see Table 3). Although assignment of H(6) and H(7) remains uncertain the low-field doublet is suggested to arise from H(7).*

The dynamic ^1H n.m.r. spectra of (3) (Figure 4) are very complex as might be expected for a diastereoisomeric compound. Two elements of dissymmetry are present in (3): (i) a chiral tin centre (with either *S* or *R* configuration); and (ii) a puckered chelate ring which has either α or β conformation.† Figure 2 and Table 4 show that this puckering is not restricted to the C-N-Sn part of the chelate ring but that the non-coplanarity of the C(1)-Sn and C(8)-C(11) bonds with the naphthalene nucleus also contributes. Out-of-plane deformation of these two bonds in 1,8-disubstituted naphthalene skeletons is not uncommon (*cf.* ref. 8).

A Newman projection along the Sn-N bond in the actual diastereoisomer together with the computed projection along this bond in the diastereoisomer with

TABLE 3
Proton n.m.r. data of compounds (2), (3), and (5) (see diagram in text for numbering system)

Compound	$\theta_c/^\circ\text{C}$	$\delta/\text{p.p.m.}^a$								
		NMe ₂	NCH ₂	SnMe	OMe	SnCH ₂	H(2)	H(3)	H(4)	H(6,7)
(2)	<i>b</i>	2.25 (s)	4.05 (br)	1.05 (s) $^2J(\text{Sn-H})$ 63.6, 66.4	3.95 (s)		8.99 (m) ^c $^3J(\text{Sn-H})$ 78	7.55 (2d)	8.39 (m) ^d	6.68, 7.17 (2d)
	-45	2.09, 2.56 (2s)	3.49, 4.72 (2d) J_{AB} 14	1.01, 1.21 (2s)						
(3) ^e	<i>b</i>	1.93, 2.19 (2s, br)	4.00 (vbr)	1.28 (s) $^2J(\text{Sn-H})$ 65.5, 68.0	3.96 (s)		9.12 (m) ^{c,f} $^3J(\text{Sn-H})$ 80	7.63 (2d)	8.46 (m) ^{d,g}	6.70, 7.16 (2d)
	-25 ^g	1.65, 2.25 and 2.08, 2.35	4.70, 3.43, 3.18 ^h	1.22, 1.41 (2s)						
(5)	80 ⁱ	1.26 (s)	2.75 (s) ^j	0.59 (s) $^2J(\text{Sn-H})$ 58, 62		3.05 (s) ^j $^2J(\text{Sn-H})$ 86				
	-30	1.09 (s, br) ^k	2.51, 2.62 J_{AB} 11	0.59 (s)		2.93, 3.15 J_{AB} 13				

^a Relative to internal SiMe_4 ; coupling constants J in Hz. ^b In CDCl_3 at room temperature. ^c J_n 7, J_m 1.5 Hz. ^d J_n 8, J_m 1.5 Hz; irradiation at H(3) results in a doublet (J_m 1.5 Hz) with $^{117,119}\text{Sn}$ satellites and an estimated $J(\text{Sn-H})$ of 8 Hz. ^e Phenyl resonances: $\delta(\text{H}_m)$ 7.54, $^3J(\text{Sn-H})$ 62 Hz; $\delta(\text{H}_{\text{ortho}})$ 7.30 (m). ^f See text. ^g See also Figure 3. ^h Irradiation at 4.70 p.p.m. results in coalescence of the two doublets at 3.43 and 3.18 p.p.m., respectively, into two singlets. ⁱ In $[\text{D}_6]\text{toluene}$. Phenyl region shows multiplet resonances between 6.60 and 7.20 p.p.m. See also Figure 6 for the spectrum at 80 $^\circ\text{C}$. ^j Slightly broadened. ^k At -40 $^\circ\text{C}$ this peak has decoalesced into two broadened singlets at 0.90 and 1.20 p.p.m.

66 Hz observed for the MeSn protons are in the range found for five-co-ordinate triorganotin species shown in Figure 1 having the N and Br atoms in axial and the three C ligands in equatorial positions.

* For a complete assignment of the proton resonance pattern of 4-dimethylaminomethyl-1-methoxy- and 5-deuterio-4-dimethylaminomethyl-1-methoxy-naphthalene see ref. 5. Assignment of the resonance patterns of the products resulting from palladation of 1-dimethylaminomethylnaphthalene has been described in ref. 7.

reversed puckering of the chelate ring are shown in Figure 5. This Figure clearly reveals the relative arrangement of the various vicinal groups along the Sn-N bond in the two diastereoisomers which only differ with respect to the chelate-ring conformation, *i.e.* $\alpha(R)_{\text{Sn}}$ and $\beta(R)_{\text{Sn}}$.

Figure 3 shows that in the slow-exchange limit (below -30 $^\circ\text{C}$) two resonance patterns are observed for the

† The two ring conformations are arbitrarily denoted as α or β .

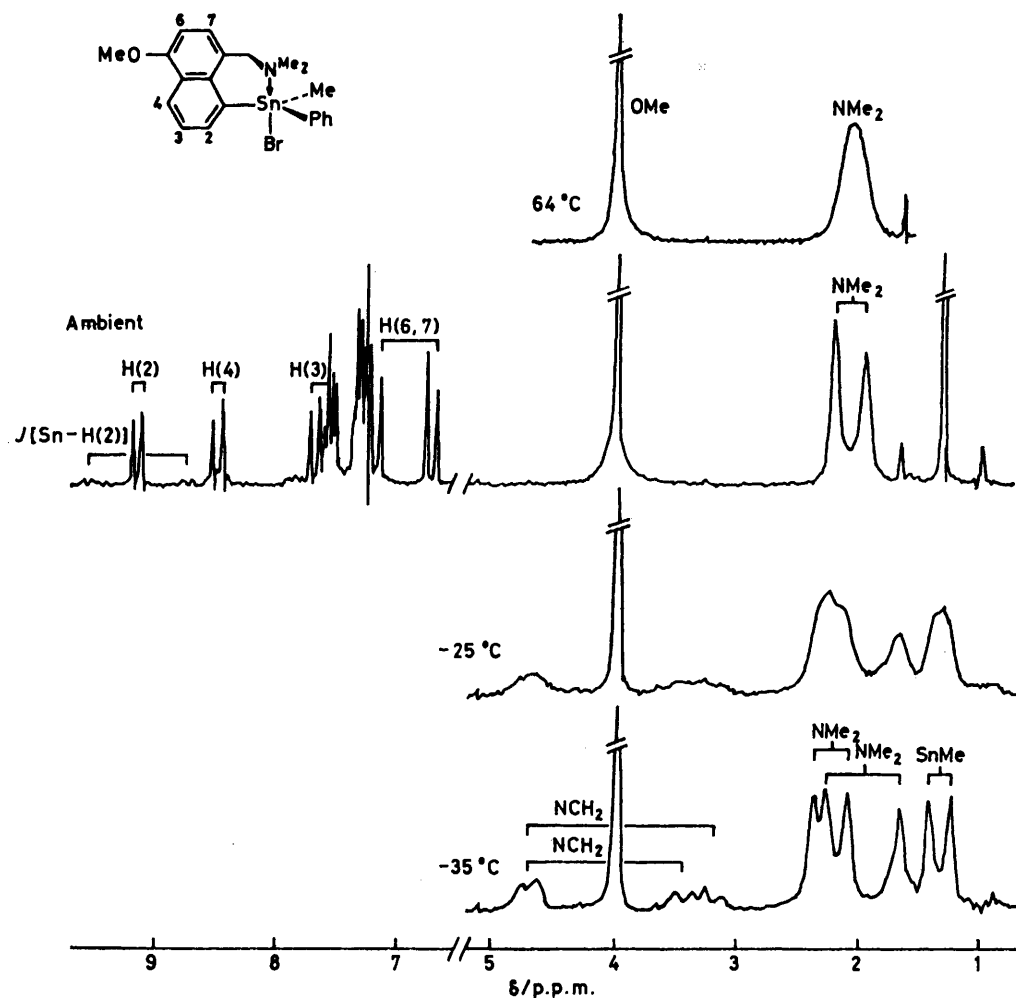


FIGURE 3 Proton n.m.r. spectra (100 MHz) of (3) in CDCl_3 at different temperatures (see also Table 3)

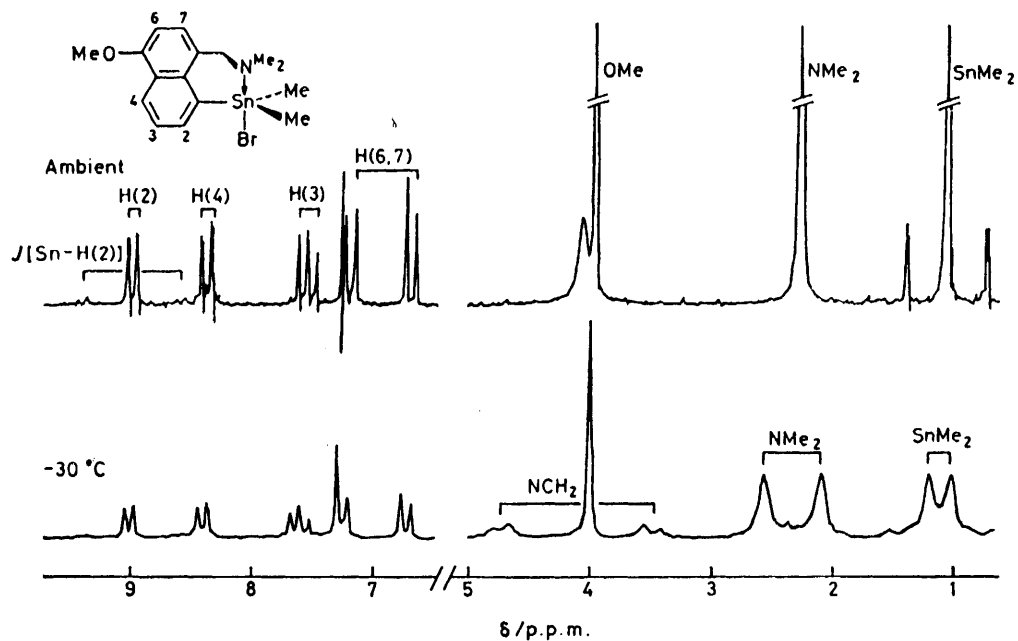


FIGURE 4 Proton n.m.r. spectra (100 MHz) of (2) in CDCl_3 at ambient temperature and $-30\text{ }^\circ\text{C}$ (see also Table 3)

diastereotopic NCH_2 protons (two AB patterns*), the NMe groups (two sets of two singlets), and for the SnMe group (two singlets). This is in accord with the presence in solution of the expected four diastereoisomers (*cf.*

TABLE 4

Stereochemistry of the chelate ring in (3) with estimated standard deviations in parentheses

(a) Torsion angles ($^\circ$) in the chelate ring ^a

N-Sn-C(1)-C(10)	28.(4)
Sn-C(1)-C(10)-C(8)	11.9(7)
C(1)-C(10)-C(8)-C(11)	5.0(7)
C(10)-C(8)-C(11)-N	-59.4(7)
C(8)-C(11)-N-Sn	75.1(5)
C(11)-N-Sn-C(1)	-45.3(3)

(b) Non-planarity of the chelate ring ^b

Atom	Distance (\AA)
Sn	-0.359 9(4)
N	-0.971(4)
C(11)	0.108(5)

Equation of plane: $2.533x + 9.628y - 4.732z - 1.839 = 0$

^a The torsion angle $\text{A}(1)-\text{A}(2)-\text{A}(3)-\text{A}(4)$ is viewed along $\text{A}(2)-\text{A}(3)$, with a clockwise rotation of $\text{A}(1)$ to $\text{A}(4)$ taken to be positive. ^b Distances from the plane through C(1), C(10), and C(8).

Scheme) of which the $\beta(R)_{\text{Sn}}$, $\alpha(S)_{\text{Sn}}$ and $\alpha(R)_{\text{Sn}}$, $\beta(S)_{\text{Sn}}$ pairs are n.m.r. distinguishable.

On raising the temperature the occurrence of two different processes can be recognized. The first process which starts to take place between -30 and -20 $^\circ\text{C}$

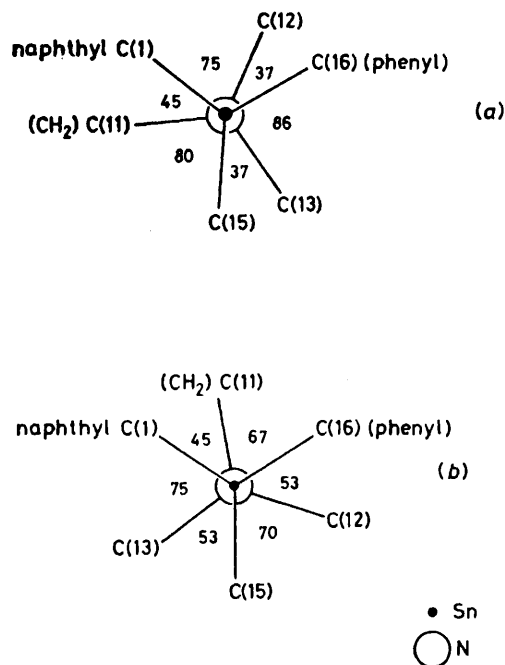
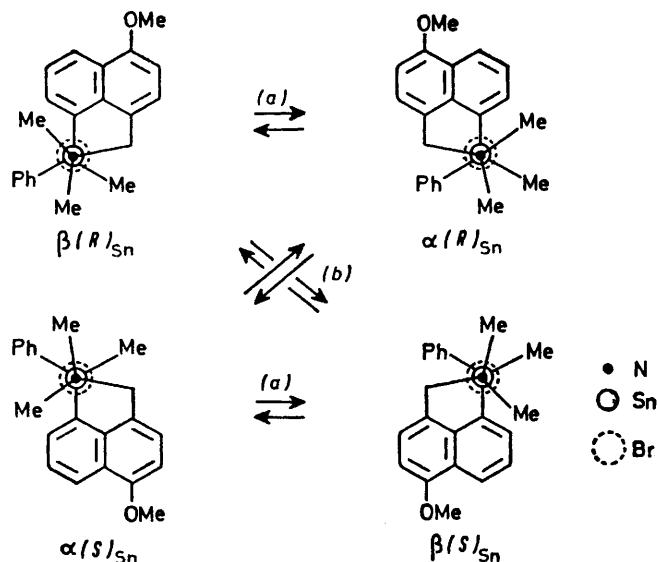


FIGURE 5 Newman plots along the Sn-N bond in (3). (a) Observed conformation; (b) calculated conformation with reversed puckering

involves coalescence of the two resonance patterns into one (*cf.* spectra in Figure 3 at -35 , -25 $^\circ\text{C}$, and ambient temperature). These changes are ascribed to the occurrence of rate-determining interconversion between the α and β ring conformations [*cf.* (a) in Scheme]. The observation that at ambient temperature the NMe

resonances are anisochronous (two singlets) indicates that, during the interconversion process up to the fast-exchange limit, the Sn-N co-ordination is inert on the n.m.r. time scale. It is only when co-ordinated that the MeN groups are diastereotopic as a result of the chirality at the tin centre (*cf.* ref. 3). In principle also, the benzylic protons are diastereotopic. This, however, cannot be concluded from the spectrum at ambient temperature because the CH_2 resonances coincide with the OMe resonance.

The dynamic spectra of compound (2) support the view that the first process involves interconversion between the α and β ring conformation. This compound contains three prochiral centres ($\text{Sn} \leftarrow \text{NMe}_2$,



SCHEME Routes for interconversion of the diastereoisomers of (3): (a) interconversion between ring conformers α and β ; (b) inversion of configuration at the Sn centre

CH_2N , and SnMe_2) while the ring puckering has remained as the only chiral element. Figure 4 shows that below -30 $^\circ\text{C}$ these groups are diastereotopic. On raising the temperature the anisochronous resonances coalesce at about the same rate into singlets ($\Delta\delta$, T_c : NCH_2 , 1.26, -20 ; NMe_2 , 0.45, -25 ; SnMe_2 , 0.18, -30 $^\circ\text{C}$).

The nature of the second process [*cf.* (b) in Scheme], which is responsible for the coalescence of the NMe singlets of (3) (see Figure 3, T_c 47 $^\circ\text{C}$), is difficult to define because of the coinciding CH_2 and OMe resonances.

In previous papers we have shown that on the basis of the dynamic resonance patterns of the CH_2N and Me_2N groups the stereochemistry at the tin centre could be followed.^{2,3,9} In the case of the related compound $\text{SnMePh}[\text{C}_6\text{H}_4(\text{CH}_2\text{NMe}_2)_2]\text{Br}$ (see Figure 1)⁹ we have shown that, in solution, inversion of configuration is in the slow-exchange limit on the n.m.r. time scale even at 123 $^\circ\text{C}$. This could be concluded from the AB pattern of the diastereotopic NCH_2 protons which remained un-

* See Table 3; irradiation at 4.70 p.p.m. results in coalescence of the respective doublets at 3.43 and 3.18 p.p.m. into two singlets.

changed over the whole temperature range. However, we have also shown for $\text{SnMePh}[\text{C}_6\text{H}_4(\text{CHMeNMe}_2\text{-2})\text{-}(S)]\text{Br}$ (see Figure 1)³ that inversion of configuration at five-co-ordinate tin centres (*i.e.* in the situation with inert Sn-N co-ordination) occurs on the laboratory time scale by an associative process. The fact that no stereoisomerizations by Berry pseudo-rotation processes take place in the five-co-ordinate species was ascribed to (i) site preference of the N and Br atoms in a trigonal-bipyramidal array for axial positions and (ii) the constraints of the five-membered chelate ring with a NSnC angle of 75° which dictates axial-equatorial spanning of the bidentate $\text{C}_6\text{H}_4(\text{CHMeNMe}_2\text{-2})$ ligand.

It is particularly the latter argument which does not seem to apply any longer for compounds (2) and (3). The crystal structure of (3) reveals an increased NSnC angle (88°) in the six-membered chelate ring. This makes more likely stereoisomerization processes passing through transition states having NSnC angles higher than 90° . Accordingly, coalescence of the NMe singlets of (3) can also be the result of a Berry pseudo-rotation process. This possibility cannot be excluded in the absence of information about the multiplicity of the resonance pattern arising from the CH_2N protons.

The influence of the magnitude of the NSnC angle and the puckering of the chelate ring on the stability of the configuration of the five-co-ordinate tin centre is demonstrated by the dynamic ^1H n.m.r. pattern of (5). In this compound intramolecular co-ordination leads to a six-membered chelate ring which contains two $sp^3\text{-C}$ atoms. The n.m.r. spectrum of (5) (see Figure 6) at 80°C shows isochronous resonances of the CH_2Sn protons (δ 4.07 p.p.m., $^2J(\text{Sn-H})$ (averaged) 86 Hz), the CH_2N protons (δ 3.91 p.p.m.), as well as the NMe protons (δ 1.41 p.p.m.). Upon cooling, the NMe groups ($T_c \approx -37^\circ\text{C}$; $\Delta\delta$ 38 Hz) and the CH_2Sn and CH_2N protons ($T_c \approx 0^\circ\text{C}$; $\Delta\delta$ 15 and 9 Hz, respectively) become diastereotopic at about the same rate. This indicates that stereoisomerization processes resulting in inversion of configuration at tin occur in the five-co-ordinate species, *i.e.* in the situation of inert Sn-N co-ordination. This result shows that by lowering the geometric constraint of the chelate ring, which in the case of (5) is very flexible due to the presence of two $sp^3\text{-C}$ atoms, the energy barrier to stereoisomerization in the five-co-ordinate species can be lowered sufficiently to make such processes feasible.

EXPERIMENTAL

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

Proton n.m.r. spectra were recorded on a Varian Associates HA-100 spectrometer, *i.e.* spectra on a Perkin-Elmer 577 grating infrared spectrometer. Elemental analyses were carried out in the Analytical Department of the TNO Institute.

Preparations.— (8-Dimethylaminomethyl-5-methoxynaphthyl)dimethyltin bromide (2). A suspension of purple

8-dimethylaminomethyl-5-methoxynaphthyl-lithium (38 mmol; from the 1:1 reaction of 1-dimethylaminomethyl-4-methoxynaphthalene with butyl-lithium⁵) in diethyl ether (120 cm^3) was added to a solution of SnMe_2Br_2 (38 mmol) in ether (130 cm^3). The resulting mixture, which consisted of a yellow precipitate and a light brown solution, was stirred at room temperature for 3 h. The precipitate was filtered off, extracted with diethyl ether ($3 \times 50\text{ cm}^3$), and subsequently dried *in vacuo*, affording almost white (2) in 50% yield. Recrystallization from hot toluene yielded white crystals, m.p. $185\text{--}187^\circ\text{C}$ (Found: C, 43.0; H, 4.9; Br, 17.9; N, 3.2; Sn, 26.4. Calc. for $\text{C}_{16}\text{H}_{22}\text{BrNOSn}$: C,

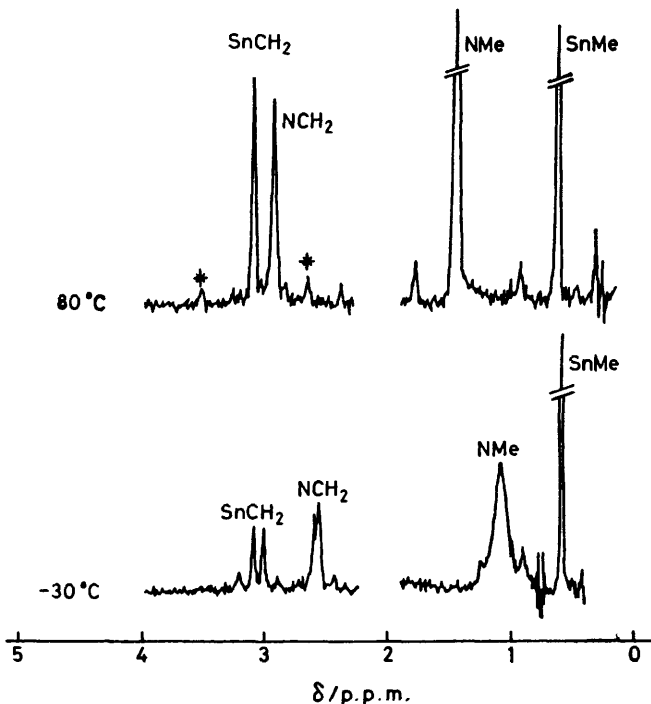


FIGURE 6 Proton n.m.r. spectra (100 MHz) of (5) in $[\text{2H}_6]$ toluene at different temperatures (see also Table 3). Peaks marked with an asterisk are the $^{117},^{119}\text{Sn}$ satellites of the SnCH_2 singlet

43.4; H, 5.00; Br, 18.05; N, 3.15; Sn, 26.8%). Molecular weight (osmometric in benzene): 454 (calc. 443). For n.m.r. spectrum see Table 3.

When CHCl_3 was used for the recrystallization of (2) an adduct with composition $\text{SnMe}_2\text{RBr}\cdot 0.4\text{CHCl}_3$ was obtained (Found: C, 40.1; H, 4.6; N, 2.9; O, 3.2; Sn, 24.1; total halogen, 25.8. Calc. for $\text{C}_{16.4}\text{H}_{22.4}\text{BrCl}_{1.2}\text{NOSn}$: C, 40.1; H, 4.55; N, 2.85; O, 3.25; Sn, 24.2; total halogen, 25.0%).

(8-Dimethylaminomethyl-5-methoxynaphthyl)methylphenylltin bromide (3). A suspension of $\text{Li}[\text{C}_{10}\text{H}_5(\text{OMe-5})(\text{CH}_2\text{NMe}_2\text{-8})]$ (27 mmol) in diethyl ether (120 cm^3) was added slowly to a solution of methylphenylltin dibromide (27 mmol) in ether (60 cm^3). The grey mixture was stirred for 3 h. The yellow precipitate was filtered off, washed with ether, and then dried in vacuum. The white solid was recrystallized from CHCl_3 yielding pure (3) in 55% yield, m.p. 202°C (Found: C, 49.7; H, 4.8; Br, 16.7; N, 2.9; O, 2.8; Sn, 23.4. Calc. for $\text{C}_{21}\text{H}_{24}\text{BrNOSn}$: C, 49.95; H, 4.75; Br, 15.85; N, 2.75; O, 3.15; Sn, 23.5%). Molecular weight (ebulliometric in CH_2Cl_2): 505 (calc. 504.7).

(2-Dimethylaminomethylbenzyl)methylphenylltin bromide

(5). A yellow solution of $\text{Li}[\text{CH}_2\text{C}_6\text{H}_4(\text{CH}_2\text{NMe}_2-2)]$ (40 mmol; from the 1:1 reaction of 2-Me₂NCH₂C₆H₄CH₃ with butyl-lithium) in ether (80 cm³) was slowly added to a solution of SnMePhBr₂ (40 mmol) in ether (100 cm³). The yellow solution was stirred for 1 h. The ether was then removed in vacuum and the oily residue dissolved in benzene. Filtration of the LiBr which precipitated followed by concentration of the filtrate again afforded an oily residue. Solid (5) was obtained by redissolving the residue in benzene (100 cm³) and slowly adding pentane (100 cm³). White crystalline (5) (50% yield) was filtered off, washed with pentane, and dried in vacuum, m.p. 152–160 °C (Found: C, 45.9; H, 5.3; Br, 18.6; N, 3.2; Sn, 25.8. Calc. for C₁₇H₂₂BrNSn: C, 46.5; H, 5.05; Br, 18.2; N, 3.20; Sn, 27.05%). Molecular weight (ebullimetric in benzene): 439 (calc. 438). For n.m.r. spectrum see Table 3.

TABLE 5

Atomic fractional co-ordinates for Sn and Br ($\times 10^5$) and for O, C, and N ($\times 10^4$) with estimated standard deviations in parentheses

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Sn	28 196(4)	20 456(3)	25 462(3)
Br	1 498(7)	30 960(5)	19 641(5)
O	5 758(5)	4 283(3)	8 242(3)
N	5 095(5)	972(3)	2 872(3)
C(1)	3 305(6)	3 162(4)	4 317(4)
C(2)	1 997(6)	3 784(4)	4 753(4)
C(3)	1 999(6)	4 431(4)	5 910(4)
C(4)	3 296(6)	4 415(4)	6 668(4)
C(5)	6 014(6)	3 745(4)	7 119(4)
C(6)	7 411(6)	3 200(5)	6 764(5)
C(7)	7 479(6)	2 646(5)	5 585(5)
C(8)	6 223(6)	2 613(4)	4 762(4)
C(9)	4 690(6)	3 783(4)	6 303(4)
C(10)	4 739(5)	3 173(4)	5 107(4)
C(11)	6 516(6)	2 044(5)	3 532(4)
C(12)	4 577(7)	47(5)	3 527(5)
C(13)	5 723(7)	302(5)	1 777(5)
C(14)	6 994(9)	4 216(6)	9 103(5)
C(15)	4 136(7)	2 505(5)	1 159(4)
C(16)	1 004(6)	285(4)	2 327(4)
C(17)	655(6)	−641(5)	1 277(4)
C(18)	−478(7)	−1 804(5)	1 165(5)
C(19)	−1 263(7)	−2 045(5)	2 104(5)
C(20)	−907(6)	−1 141(5)	3 149(4)
C(21)	216(6)	20(5)	3 270(4)

Determination and Refinement of the Crystal Structure of (3).—Crystals were obtained by slow distillation of pentane into a solution of (3) in CHCl₃.

Crystal Data. C₂₁H₂₄BrNOSn, *M* = 505, Triclinic, space group *P* $\bar{1}$ (no. 2, *C*₂^h), *a* = 7.795(5), *b* = 11.178(2), *c* = 12.159(3) Å, α = 106.20(2), β = 91.75(3), γ = 100.83(3)°, *U* = 995.38 Å³, *D*_c = 1.685 Mg m^{−3}, *F*(000) = 500, *Z* = 2, $\mu(\text{Mo-K}\alpha)$ = 35.8 cm^{−1}, λ = 0.710 7 Å, crystal dimensions 0.33 × 0.07 × 0.05 mm.

Cell dimensions were measured on a Nonius CAD 4 automatic diffractometer with zirconium-filtered Mo-*K* α radiation, and using a unit-weight least-squares adjustment in which the applied co-ordinates were the diffractometer co-ordinates for the Mo-*K* α maxima. Intensity measurements were made in an ω –2 θ scan mode to a $2\theta_{\text{max}}$ of 50° and with a scan angle $\Delta\omega$ of (0.60 + 0.35 tan θ)°. Two sets of symmetry-related reflections were measured with two reflections monitored as standards every 0.5 h of exposure

time to check crystal and instrument stability (their net count did not alter noticeably over the period of data collection). Standard Lorentz-polarization factors were applied and absorption corrections were made by a gaussian integration technique using a (8 × 5 × 5) grid. No extinction corrections were found to be necessary. After averaging redundant data, of the 3 513 unique reflections, 3 014 were considered to be significantly above background [$I \geq 2.5 \sigma(I)$] and were used for the subsequent analysis.

The structure was solved by Patterson and Fourier techniques and refined by block-diagonal least squares. Non-hydrogen atoms were refined anisotropically, whereas the parameter refinement for the H atoms (all located in a difference-Fourier map) was restricted to their co-ordinates with *B* fixed at 5.0 Å². Convergence was obtained at *R* = 0.024 (*R'* = 0.031). A final difference-Fourier synthesis showed no excursions of magnitudes greater than 0.3 e Å^{−3} apart from somewhat larger fluctuations in the neighbourhood of the Sn and Br atoms. Atomic scattering factors for the non-hydrogen atoms were taken from ref. 10, those for H from ref. 11. Anomalous scattering components¹² were included for Sn and Br. Most of the calculations were done with an extended version of the 'X-RAY '76' system.¹³

Thermal parameters for the non-hydrogen atoms, observed and calculated structure factors, atomic fractional co-ordinates for H, bond distances and angles involving hydrogen atoms, as well as a Figure containing the relevant numbering scheme are available as Supplementary Publication No SUP 22784 (34 pp.).* Table 5 displays the final fractional co-ordinates.

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

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