Synthesis, Spectroscopic Investigations, and Molecular Structures of 1-Elementa-5-stannabicyclo[3.3.0^{1,5}]octanes, $RR'Sn(CH_2CH_2CH_2)_2E$ (E = NMe, O, S)

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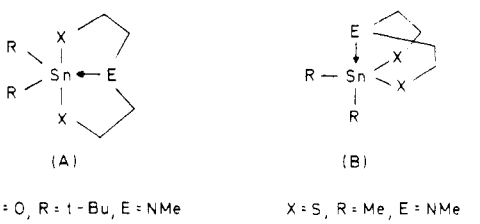
Received February 27, 1987

The 1-elementa-5-stannabicyclo[3.3.0^{1,5}]octanes $Cl_2Sn(CH_2CH_2CH_2)_2E$ (E = NMe, O, S), $Me(Cl)Sn(CH_2CH_2CH_2)_2E$ (E = NMe, O), $Me_2Sn(CH_2CH_2CH_2)_2E$ (E = NMe, O), and $t\text{-}Bu_2Sn(CH_2CH_2CH_2)_2NMe$ and the stannacyclooctane $Me_2Sn(CH_2CH_2CH_2)_2CH_2$ have been prepared by the reaction of the Grignard reagents $E(CH_2CH_2CH_2MgX)_2$ (X = Cl, Br) with tin tetrachloride or organotin halides. The molecular structures of $Cl_2Sn(CH_2CH_2CH_2)_2NMe$ (**1**), $Cl_2Sn(CH_2CH_2CH_2)_2O$ (**5**), and $Cl_2Sn(CH_2CH_2CH_2)_2S$ (**8**) were determined by X-ray analysis. **1** crystallizes in the monoclinic space group *Cc* ($Z = 4$) with $a = 13.987$ (5) Å, $b = 7.668$ (2) Å, $c = 11.213$ (3) Å, and $\beta = 112.68$ (2)°. The structure was refined to $R = 0.027$. **5** crystallizes in the monoclinic space group *C*2/*c* ($Z = 8$) with $a = 23.034$ (7) Å, $b = 7.153$ (2) Å, $c = 13.944$ (4) Å, and $\beta = 114.09$ (2)°. The structure was refined to $R = 0.163$. **8** crystallizes in the monoclinic space group $P2_1/a$ ($Z = 4$) with $a = 11.521$ (1) Å, $b = 13.869$ (3) Å, $c = 6.894$ (1) Å, and $\beta = 109.57$ (1)°. The structure was refined to $R = 0.072$. As a result of the Sn–N (2.441 Å), Sn–O (2.384 Å), and Sn–S (2.851 Å) interaction, respectively, the tin atoms in **1**, **5**, and **8** exhibit distorted trigonal-bipyramidal configurations with the heteroatom in apical position. ^1H, ^{13}C, and ^{119}Sn NMR studies in solution show conformational equilibria with dominating boat–chair (BC) and chair–chain (CC) conformations. The dynamic behavior of the compounds is interpreted in terms of a combined dissociation–inversion (DI) and ring inversion (RI) mechanism.

Introduction

Among the numerous pentacoordinated organotin compounds prepared so far,[1-13] the stannabicyclooctanes of the type $R_2Sn(XCH_2CH_2)_2E$ (X = O, S; E = O, S, NR, PR; R = halogen, alkyl, aryl) are the most systematically studied compounds. As shown by us[14,15] and others[16a,17] the two basic configurations A and B can be realized both in solution and in the solid state by introducing the appropriate ligands.



X = O, R = t-Bu, E = NMe X = S, R = Me, E = NMe

Furthermore, it has been demonstrated that the strength of the E–Sn donor–acceptor interaction determining the position of the tin atom along the pathway trigonal bipyramid ⇌ tetrahedron depends strongly on the electronegativity of the heteroatoms X and of the organic groups R and on the nature of the donor atom E.[1,14-19] This donor–acceptor interaction also determines the intramolecular dynamics observed in these compounds.[1,14,15,20,21]

In order to complete the stannocane family and to study transannular interactions in tetraorganotin compounds also, we present here the carba functional derivatives (X = CH_2) $R_2Sn(CH_2CH_2CH_2)_2E$ (E = NMe, O, S, CH_2). ^1H, ^{13}C, and ^{119}Sn NMR and X-ray studies provided a clear

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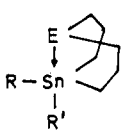
Table I. Physical Constants and Analytical Data for Compounds 1-9

compd	formula	mol wt found (calcd)	mp (bp), (°C)	anal. fouund (calcd) C	H	N	Cl
1	$C_7H_{15}Cl_2NSn$	310 (302.6)	160–162	27.61 (27.76)	4.92 (4.96)	4.52 (4.63)	23.12 (23.43)
1a	$C_{13}H_{33}Cl_2N_4OPSn$	(481.6)	79–81	32.57 (32.39)	7.03 (6.85)	12.01 (11.63)	
2	$C_8H_{18}ClNSn$	(282.15)	158–159	34.01 (34.02)	6.50 (6.38)	4.80 4.96)	12.26 (12.56)
3	$C_9H_{21}NSn$	268 (261.7)	(95–97 (10 mmHg))	41.11 (41.27)	7.95 (8.02)	5.27 (5.35)	
4	$C_{15}H_{33}NSn$	(345.7)	(125 (0.2 mmHg))	52.01 (52.07)	9.46 (9.55)	3.96 (4.05)	
5	$C_6H_{12}Cl_2OSn$	(289.6)	169–171	24.77 (24.86)	4.09 (4.14)	24.18 (24.48)	
6	$C_7H_{15}ClOSn$	(269.15)	80–82	31.15 (31.21)	5.49 (5.57)	12.98 (13.17)	
7	$C_8H_{18}OSn$	257 (248.7)	(75 (15 mmHg))	38.56 (38.60)	7.18 (7.24)		
8	$C_7H_{15}Cl_2SSn$	(320.6)	136	26.16 (26.20)	4.62 (4.68)		21.77 (22.14)
9	$C_9H_{20}Sn$	(246.7)	(80 (15 mmHg))	43.56 (43.78)	7.97 (8.11)		

insight into the molecular structure of these compounds in solution and in the solid state, respectively.



	R	R′	E
1	Cl	Cl	NMe
2	Me	Cl	NMe
3	Me	Me	NMe
4	*t*-Bu	*t*-Bu	NMe
5	Cl	Cl	O
6	Me	Cl	O
7	Me	Me	O
8	Cl	Cl	S
9[a]	Me	Me	CH_2

[a] For **9**, a transannular Sn–E interaction is not possible.

Experimental Section

Where necessary, the reactions were carried out under an atmosphere of dry argon. The solvents were dried by standard methods and freshly distilled before use. *N*-Methyl-bis(3-chloropropyl)amine, $MeN(CH_2CH_2CH_2Cl)_2$, bis(3-bromopropyl) ether, $O(CH_2CH_2CH_2Br)_2$, and bis(3-chloropropyl)sulfide, $S(CH_2CH_2CH_2Cl)_2$, have been prepared by halogenation of the corresponding alcohols using known procedures.[22-26] The ^1H, ^{13}C, and ^{119}Sn NMR spectra have been recorded on Varian HA 100, Bruker WP 90 and WP 200, and AM 500 spectrometers. The molecular weight determinations have been performed cryoscopically in benzene or by osmometry in chloroform at 40 °C (concentration = 0.02 mol/kg of solvent) using a Knauer osmometer. Physical constants and analytical data are summarized in Table I. Compounds **1** and **3** have been described elsewhere.[27] However, a slight modification of the procedure to prepare **1** increases the yield markedly.

Synthesis of 1-Methyl-5,5-dichloro-1-aza-5-stannabicyclo[3.3.0^{1,5}]octane (1). $MeN(CH_2CH_2CH_2MgCl)_2$ (0.1 mol), prepared from 18.5 g of $MeN(CH_2CH_2CH_2Cl)_2$ and 5 g of magnesium in 250 mL of THF at 40–50 °C, and 26 g (0.1 mol) of $SnCl_4$, dissolved in 250 mL of toluene, were added dropwise and synchronously under vigorous stirring into 2 L of toluene. The mixture was refluxed for 2 h, and 1 L of the solvent was distilled off. The hot reaction mixture was filtered off and evaporated in vacuo. The residue was recrystallized from methanol to give 18 g (59.5%) of **1**.

Synthesis of the HMPA Adduct of 1-Methyl-5,5-dichloro-1-aza-5-stannabicyclo[3.3.0^{1,5}]octane (1a). Equimolar quantities of HMPA and compound **1** were dissolved in methylene chloride and refluxed for 1 h. Slow evaporation of the solvent at −5 °C yields colorless crystals of **1a**.

Synthesis of 1,5-Dimethyl-5-chloro-1-aza-5-stannabicyclo[3.3.0^{1,5}]octane (2). $Me_2Sn(CH_2CH_2CH_2)_2NMe$ (13.08 g, 0.05 mol) and 9.96 g (0.05 mol) of Me_3SnCl were heated for 1 h at 120 °C. The tetramethyltin generated during the reaction was distilled off. The residue was recrystallized from CH_2Cl_2/hexane to yield 12.7 g of colorless crystals of **2**.

Synthesis of 1-Methyl-5,5-di-*tert*-butyl-1-aza-5-stannabicyclo[3.3.0^{1,5}]octane (4). A solution of 14 mmol of *t*-BuLi in 30 mL of pentane was added dropwise at −70 °C under magnetic stirring to a suspension of 2 g (6.6 mmol) of $Cl_2Sn(CH_2CH_2CH_2)_2NMe$ in 100 mL of diethyl ether. After 30 min the mixture was warmed up to room temperature and treated with 20 mL of water. The organic layer was separated and dried over Na_2SO_4. After the solvent was removed, the residue was distilled to give 1.5 g (66%) of a colorless oil.

Synthesis of 5,5-Dichloro-1-oxa-5-stannabicyclo[3.3.0^{1,5}]-octane (5). $O(CH_2CH_2CH_2MgBr)_2$ (0.05 mol), prepared from 13 g of $O(CH_2CH_2CH_2Br)_2$ and 2.4 g of Mg in 100 mL of THF, and 13 g (0.05 mol) of $SnCl_4$ in 100 mL of toluene were dropped synchronously under vigorous stirring into 2 L of toluene. The mixture was refluxed for 2 h, and 1 L of the solvent was distilled off. The hot reaction mixture was filtered off and evaporated until about 150 mL. Cooling of this solution yields 5 g (34.5%) of colorless crystals of **5**.

Synthesis of 5-Chloro-5-methyl-1-oxa-5-stannabicyclo-[3.3.0^{1,5}]octane (6). $Me_2Sn(CH_2CH_2CH_2)_2O$ (0.8 g, 3.2 mmol) and Me_3SnCl (0.65 g, 3.2 mmol) were heated for 1 h at 120 °C. After the tetramethyltin was removed, the residue was recrystallized from CH_2Cl_2/hexane to give 0.75 g (87%) of colorless crystals of **6**.

Synthesis of 5,5-Dimethyl-1-oxa-5-stannabicyclo-[3.3.0^{1,5}]octane (7). A solution of 22 mmol of LiMe in 50 mL of diethyl ether was added dropwise at −70 °C under stirring to a suspension of 3.2 g (11 mmol) of $Cl_2Sn(CH_2CH_2CH_2)_2O$ in 100 mL of diethyl ether. After 30 min the mixture was warmed up to room temperature and treated with 30 mL of water. The organic layer was separated and dried over Na_2SO_4. After the solvent was removed, the residue was fractionated to give 2.5 g (90%) of a colorless oil.

Synthesis of 5,5-Dichloro-1-thia-5-stannabicyclo-[3.3.0^{1,5}]octane (8). $S(CH_2CH_2CH_2MgCl)_2$ (0.05 mol), prepared from 9.5 g of $S(CH_2CH_2CH_2Cl)_2$ and 2.4 g of Mg in 150 mL of THF, and 13 g (0.05 mol) of $SnCl_4$ were dropped synchronously under vigorous stirring into 2 L of toluene. After the solution

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was stirred for a further two hours, the solvent was evaporated in vacuo at 50–60 °C. The residue was extracted with boiling benzene, from which 1.6 g (10%) of colorless crystals of **8** has been isolated by slow evaporation of the solvent. The major product was a mixture of oligomers that were not further separated.

Synthesis of 1,1-Dimethylstannacyclooctane (9). $CH_2(CH_2CH_2CH_2MgBr)_2$ (0.1 mol), prepared from 25.8 g (0.1 mol) of $CH_2(CH_2CH_2CH_2Br)_2$ and 4.8 g of Mg in 300 mL of THF, and 22 g (0.1 mol) of Me_2SnCl_2, dissolved in 300 mL of benzene, were dropped synchronously under vigorous stirring into 3 L of diethyl ether. The mixture was refluxed for 2 h, and 2 L of the solvent was distilled off. The mixture was hydrolyzed with an aqueous solution of NH_4Cl. The organic layer was separated and dried over Na_2SO_4. After the solvent was removed, the residue was distilled to give 1.5 g (6%) of a colorless liquid.

Preparative Aspects

The difunctional Grignard reagents $E(CH_2CH_2CH_2MgX)_2$ can be obtained from the method of Bickelhaupt and co-workers[26] described for the oxygen derivative (eq 1). The reaction of these reagents with tin

$$E(CH_2CH_2CH_2X)_2 + 2\ Mg \xrightarrow{\text{THF, 40–50 °C}} E(CH_2CH_2CH_2MgX)_2 \quad (1)$$

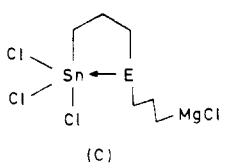
$$E = O, S, NMe;\ X = Cl, Br$$

tetrachloride leads under sufficient dilution to the eight-membered heterocycles **1**,[27] **5**, and **8**, respectively (eq 2).

$$E(CH_2CH_2CH_2MgX)_2 + SnCl_4 \xrightarrow[-MgClX]{\text{THF, toluene}} Cl_2Sn(CH_2CH_2CH_2)_2E \quad (2)$$

1, E = NMe
5, E = O
8, E = S

The yield drastically increases in the sequence S < O < NMe. As already pointed out for other stannaocanes[28] the critical step for the formation of the cycle is the ability of the heteroatom E to undergo a sufficiently strong donor–acceptor interaction with the formation of intermediate C along the reaction pathway. Replacing two chlorine



(C)

atoms in $SnCl_4$ by two methyl groups decreases the Lewis acidity at the metal and the yield of the eight-membered ring compound accordingly because the formation of intermediate C is much less favored. The same effect is observed by substituting the donor atom E by a methylene group (see below) or by replacing the tin atom by a phosphorus.[29] In such cases oligomeric species are the major products. Recently, we were able to isolate the 16-membered cycle *trans*-$[t\text{-}Bu_2Sn(CH_2CH_2)_2P(S)Ph]_2$ by the reaction of $t\text{-}Bu_2Sn(OMe)_2$ with $PhP(CH_2CH_2SH)_2$ followed by treatment with sulfur. However, the corresponding eight-membered ring could not be obtained.[30]

The tetraorganotin compounds **3**, **4**, and **7** can be obtained in a nearly quantitative yield from the reaction of

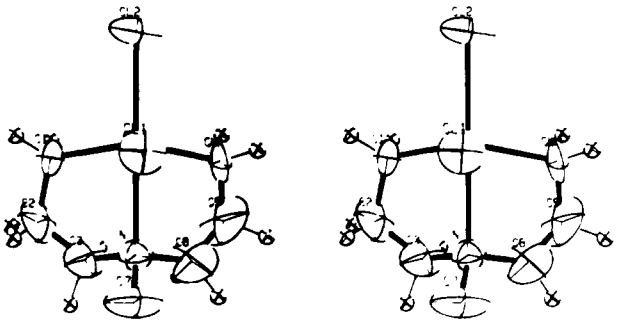


Figure 1. Stereoscopic view with atom numbering of the molecular structure of $Cl_2Sn(CH_2CH_2CH_2)_2NMe$ (**1**) (Program ORTEP (Johnson, C. K. ORTEP, Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1965).

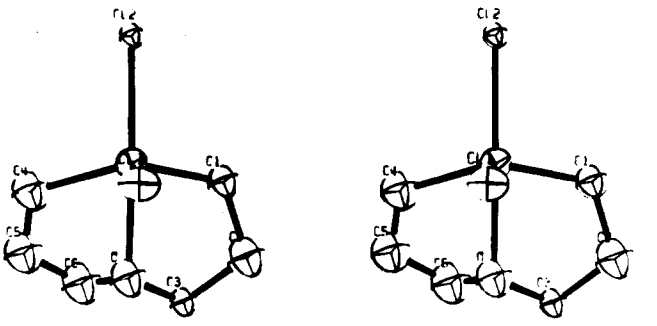


Figure 2. Stereoscopic view with atom numbering of the molecular structure of $Cl_2Sn(CH_2CH_2CH_2)_2O$ (**5**).

their dichloro precursors with organolithium reagents (eq 3). From **3** and **7**, respectively, one methyl group can

$$Cl_2Sn(CH_2CH_2CH_2)_2E + 2RLi \xrightarrow[-LiCl]{\text{ether, -70 °C}} R_2Sn(CH_2CH_2CH_2)_2E \quad (3)$$

3,[27] E =NMe, R = Me
4, E = NMe, R = *t*-Bu
7, E = O,R = Me

easily be cleaved by reaction with Me_3SnCl (eq 4). As a

$$Me_2Sn(CH_2CH_2CH_2)_2E + Me_3SnCl \xrightarrow[-Me_4Sn]{120\ °C} Me(Cl)Sn(CH_2CH_2CH_2)_2E \quad (4)$$

2, E =NMe
6, E = O

reference compound for **3** and **7** we prepared the stannacyclooctane **9** from the reaction of Me_2SnCl_2 with the Grignard reagent of 1,7-dibromoheptane (eq 5) because in

$$CH_2(CH_2CH_2CH_2MgBr)_2 + Me_2SnCl_2 \xrightarrow[-MgBrCl]{\text{THF, ether}} Me_2Sn(CH_2CH_2CH_2)_2CH_2 \quad (5)$$

9 no transannular donor–acceptor interaction is possible. Compounds **1**, **2**, **5**, **6**, and **8** are colorless, sharp melting crystals, soluble in polar organic solvents and, in the case of **1**, also in water to the extent that it can be recrystallized herefrom. Compounds **3**, **4**, **7**, and **9** are colorless liquids, stable under distillation.

Crystal and Molecular Structures

Crystals of compounds **1**, **5**, and **8** were mounted on a Syntex $P2_1$ automated four-circle diffractometer; data were collected at an ambient temperature of 21 °C. Crystal data and specific parameters relating to the collection of data sets are listed in Table II. The three structures were refined by full-matrix least squares with anisotropic thermal parameters for all non-hydrogen atoms in **1**, for Sn and Cl in **5**, and for Sn, Cl, and S in **8**. Twelve hy-

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Table II. Physical and Crystallographic Data, Data Collection, and Refinement Conditions for Compounds 1, 5, and 8

	1, $Cl_2Sn(CH_2CH_2CH_2)_2NMe$	5, $Cl_2Sn(CH_2CH_2CH_2)_2O$	8, $Cl_2Sn(CH_2CH_2CH_2)_2S$
formula unit	$C_7H_{15}Cl_2NSn$	$C_6H_{12}Cl_2OSn$	$C_6H_{12}Cl_2SSn$
system	monoclinic	monoclinic	monoclinic
space group	*Cc*	*C*2/*c*	$P2_1/a$
unit cell			
a/Å	13.987 (5)	23.034 (7)	11.521 (1)
b/Å	7.668 (2)	7.153 (2)	13.869 (3)
c/Å	11.213 (3)	13.944 (4)	6.894 (1)
β/deg	112.68 (2)	114.09 (2)	109.57 (1)
V/Å^3	1109.7 (6)	2097.4 (10)	1037.9 (3)
Z	4	8	4
D(calcd)/g·cm^{-3}	1.81	1.83	1.96
μ/cm^{-1} (Mo Kα)	25.32	26.81	28.90
cryst size	0.25 × 0.2 × 0.1	0.3 × 0.2 × 0.15	0.3 × 0.1 × 0.2
radiatn	Mo Kα	Mo Kα	Mo Kα
λ/Å	0.710 69	0.710 69	0.71069
monochromator	graphite	graphite	graphite
$2\theta_{max}$/deg	47	53	53
ω–2θ scan; scan width(θ, deg)	1.2	1.3	1.2
index range (h,k,l)	0/15,0/8,–12/11	–28/24,0/8,0/16	–14/13,0/17,0/8
independent reflctns			
measd	823	2178	2171
obsd ($I > 2.5\sigma(I)$)	792	1444	1698
resolutn	Patterson[a]	Patterson + Dirdif[b]	Patterson + Dirdif
refinement	SHELX[c]	SHELX76	SHELX76
final R (R_w)	0.027 (0.027)	0.163 (0.171)	0.072 (0.074)

[a] Patterson calculated with SHELX84: Sheldrick, G. M., personal communication 1984. [b] Beurskens, P. T.; Bosman, W. P.; Doesburg, H. M.; Gould, R. O.; van den Hark, Th. E. M.; Prick, P. A. J.; Noordik, J. H.; Beurskens, G.; Parthasarathi, V. DIRDIF, Technical Report 1981/2; Crystallography Laboratory: Toernooiveld, 6525 ED Nijmegen, The Netherlands, 1981. [c] Sheldrick, G. M. SHELX76, Program for Crystal Structure Determination: University of Cambridge, Cambridge, England, 1976.

Table III. Fractional Atomic Coordinates (×10^4) and B_{eq} Values for $Cl_2Sn(CH_2CH_2CH_2)_2NMe$ (1)

	x/*a*	*y*/*b*	*z*/*c*	*B*(eq), Å^2
Sn(1)	0	651 (1)	2500	3.32
Cl(1)	–38 (2)	1686 (4)	479 (2)	5.36
Cl(2)	–1258 (3)	–1686 (5)	1517 (3)	7.45
N(1)	1254 (7)	2923 (12)	3595 (9)	4.80
C(1)	–915 (8)	2234 (14)	3208 (11)	4.83
C(2)	–341 (14)	3853 (22)	3799 (20)	8.31
C(3)	758 (13)	3734 (25)	4415 (17)	7.81
C(4)	1390 (12)	–843 (15)	3422 (17)	5.80
C(5)	2203 (14)	257 (36)	4283 (41)	16.20
C(6)	2184 (13)	1852 (35)	4336 (26)	13.24
C(7)	1537 (16)	4215 (19)	2839 (19)	8.24

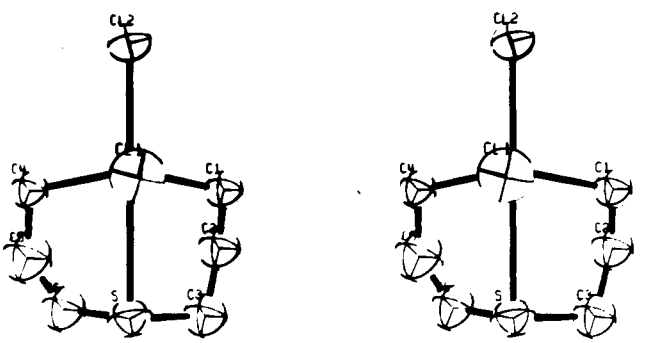

Figure 3. Stereoscopic view with atom numbering of the molecular structure of $Cl_2Sn(CH_2CH_2CH_2)_2S$ (8).

drogen atoms were calculated for 1; no H-atoms were included in 5 and 8. The final atomic coordinates are given in Tables III–V, and the Figures 1–3 show the molecular structures of 1, 5, and 8. The high value of R in 5 is due to the unsatisfactory quality of the crystal, involving a disadvantageous proportion of unobserved reflections (attempts at recrystallization were unsuccessfull). Bond lengths and bond angles are summarized in Tables VI and VII.

Because of the poor quality of the intensity data of 5 the details of its structure can be compared only with

Table IV. Fractional Atomic Coordinates (×10^4) and B_{eq} Values for $Cl_2Sn(CH_2CH_2CH_2)_2O$ (5)

	x/*a*	*y*/*b*	*z*/*c*	*B*(eq), Å^2
Sn(1)	3984 (1)	3216 (4)	4506 (2)	3.99
Cl(1)	3160 (3)	1209 (10)	3171 (5)	2.61
Cl(2)	4733 (3)	3524 (9)	3584 (5)	1.20
O(1)	3421 (18)	3186 (58)	5609 (30)	5.35
C(1)	3584 (16)	5882 (46)	4262 (26)	4.02
C(2)	2984 (59)	6138 (166)	4591 (95)	6.01
C(3)	3170 (57)	5129 (177)	5828 (92)	3.24
C(4)	4534 (19)	1398 (52)	5963 (30)	5.89
C(5)	4074 (26)	781 (79)	6216 (40)	5.90
C(6)	3799 (39)	2614 (124)	6477 (66)	6.95

Table V. Fractional Atomic Coordinates (×10^4) and B_{eq} Values for $Cl_2Sn(CH_2CH_2CH_2)_2S$ (8)

	x/*a*	*y*/*b*	*z*/*c*	*B*(eq), Å^2
Sn(1)	3226 (1)	129 (1)	1143 (1)	3.98
Cl(1)	2450 (3)	1295 (2)	2917 (5)	6.01
Cl(2)	4959 (3)	1165 (2)	1201 (5)	5.15
S(1)	1218 (3)	–1100 (2)	1017 (6)	5.76
C(1)	4167 (11)	–996 (8)	3161 (18)	4.96
C(2)	3556 (14)	–1986 (11)	2522 (23)	6.86
C(3)	2232 (15)	–2107 (12)	2435 (26)	6.73
C(4)	2176 (12)	138 (8)	–2093 (20)	4.82
C(5)	1346 (41)	–833 (24)	–2866 (67)	9.79
C(6)	911 (17)	–1330 (12)	–1634 (28)	7.43

Table VI. Bond Lengths (Å) for Compounds 1, 5, and 8 with Standard Deviations in Parentheses

	1, E = NMe	5, E = O	8, E = S
Cl(1)–Sn(1)	2.382 (2)	2.499 (6)	2.375 (3)
Cl(2)–Sn(1)	2.455 (3)	2.546 (7)	2.449 (3)
E–Sn(1)	2.441 (8)	2.384 (36)	2.851 (3)
C(1)–Sn(1)	2.127 (10)	2.084 (32)	2.130 (11)
C(4)–Sn(1)	2.147 (13)	2.308 (36)	2.152 (12)
C(3)–E	1.485 (16)	1.582 (114)	1.872 (16)
C(6)–E	1.489 (22)	1.236 (76)	1.770 (18)
C(7)–E	1.456 (18)		
C(1)–C(2)	1.488 (21)	1.635 (118)	1.539 (17)
C(2)–C(3)	1.423 (24)	1.754 (117)	1.516 (21)
C(4)–C(5)	1.449 (34)	1.322 (59)	1.634 (36)
C(5)–C(6)	1.228 (3)	1.563 (88)	1.317 (40)

Table VII. Bond Angles (deg) for Compounds 1, 5, and 8 with Standard Deviations in Parentheses

	1, E = NMe	5, E = O	8, E = S
Cl(1)-Sn(1)-Cl(2)	93.8 (1)	98.0 (2)	92.2 (1)
Cl(1)-Sn(1)-E	89.4 (2)	91.6 (9)	88.9 (1)
Cl(2)-Sn(1)-E	176.8 (2)	170.4 (9)	178.9 (1)
C(1)-Sn(1)-Cl(1)	111.7 (3)	104.7 (9)	111.1 (3)
C(1)-Sn(1)-Cl(2)	98.8 (3)	100.6 (9)	100.7 (3)
C(1)-Sn(1)-E	79.8 (4)	78.1 (13)	79.2 (3)
C(1)-Sn(1)-C(4)	133.5 (5)	135.0 (13)	131.9 (4)
C(4)-Sn(1)-Cl(1)	108.6 (4)	108.0 (9)	110.6 (3)
C(4)-Sn(1)-Cl(2)	100.7 (4)	104.5 (10)	100.7 (3)
C(4)-Sn(1)-E	78.3 (4)	71.0 (13)	78.6 (3)
C(3)-E-Sn(1)	101 (1)	117 (5)	94 (1)
C(3)-E-C(6)	114 (2)	106 (7)	106 (1)
C(3)-E-C(7)	112 (1)		
C(6)-E-C(7)	109 (2)		
C(7)-E-Sn(1)	120 (1)		
C(6)-E-Sn(1)	101 (1)	107 (4)	91 (1)
C(1)-C(2)-C(3)	117 (1)	110 (9)	118 (1)
C(2)-C(1)-Sn(1)	110 (1)	115 (5)	113 (1)
C(2)-C(3)-E	114 (1)	98 (8)	112 (1)
C(4)-C(5)-C(6)	126 (2)	103 (5)	122 (3)
C(5)-C(4)-Sn(1)	110 (1)	102 (3)	113 (2)
C(5)-C(6)-E	124 (2)	104 (6)	126 (2)

caution with those of **1** and **8**, although its rough structure is indisputable. As a result of the Sn–E donor–acceptor interaction, the configuration around the tin atom is that of a more or less distorted trigonal bipyramid in each of the three compounds **1**, **5**, and **8**. The donor atom E is axial while the chlorine atoms occupy the other axial and one equatorial position, respectively. A quantitative measure for the position of a given structure along the pathway trigonal bipyramid ⇌ tetrahedron is the difference between the sums of the equatorial and axial angles, respectively,[16] that is equal to 90° for the ideal trigonal bipyramid and tends to be 0° for the ideal tetrahedron. The classification of **1**, **5**, and **8** among known stannocanes is given in Table VIII. The whole area between both ideal structures is transversed by these stannocanes, with a satisfactory correlation between the donor–acceptor bond order[16a,43] and the bond angle difference despite some deviations, e.g. $Cl_2Sn(CH_2CH_2CH_2)_2O$ and $CH_2[PhSn(SCH_2CH_2)_2NMe]_2$. The tin–chlorine bond lengths in **1** and **8** are slightly longer than those in $Cl_2Sn(SCH_2CH_2)_2E$ (E = O, S)[32] and Me_2SnCl_2·salicylaldehyde[33] but exhibit the expected difference between the axial and equatorial chlorine atoms.

However, the lengthening of the axial Sn–Cl bond with respect to that of a tetracoordinated tin compound is less important in **1** than in $ClSn(CH_2CH_2CH_2)_3N$,[2] $Me_2ClSnCH_2CH_2CH_2PPh$-*t*-Bu,[5] $Me_2ClSnSCH_2CH_2NH_2$,[34] *p*-$Me_2NC_5H_4Ph_3SnCl$,[35] $Me_2ClSnCH_2CH(CO_2Et)NH_2$,[36] $(Ph_2ClSn)_2CH_2$·HMPA,[6] and $[Et_4N][(C_7H_6S_2)SnClPh_2]$[37] but is the same as in $Ph(Cl)Sn(SCH_2CH_2)_2S$[38] and Ph_2SnCl_2·benzthiazole.[39] The Sn–C bond distances have no particularity with respect to the structures above.

Dräger has investigated a number of stannabicyclooctanes of the type $RR'Sn(SCH_2CH_2)_2E$ (E = O, S, NMe).[16,18,19,32,40] These compounds adopt chair–chair (CC) and boat–chain conformations (BC) or intermediate structures along the interconversion pathway between these extreme conformations. Compound **1** exhibits a boat–chair conformation near the transition to the chair–chair conformation, with the boat part strongly flattened, similar to the transition between two different conformations already found for $Ph_2Sn(SCH_2CH_2)_2O$[41] and $CH_2[PhSn(SCH_2CH_2)_2NMe]_2$.[20] Substituting one chlorine atom in **1** for a tin moiety as in $[ClSn(CH_2CH_2CH_2)_2NMe]_2$,[31] the conformation of the eight-membered cycle shifts more to the boat–chair conformation although in both compounds the Sn–N distances are nearly equal. Compound **5** adopts an actually asymmetric chair–chair conformation comparable with that of $Cl_2Ge(SCH_2CH_2)_2O$.[42] For compound **8** an actually asymmetric boat–boat conformation is observed in which one boat part is again strongly flattened, as in **1**, which, once more, appears as a snapshot in the transition to the boat–chair conformation. Boat–boat conformations have already been observed for the tin(II)-containing stannabicyclooctanes $(CO)_5CrSn(SCH_2CH_2)_2N$-*t*-Bu[43] and $Sn(SCH_2CH_2)_2PPh$.[44]

Table VIII. Classification of Different Stannabicyclooctanes and Selected Pentacoordinated Organotin Compounds along the Pathway Tetrahedron ⇌ Trigonal Bipyramid[a]

compound	$\sum\theta_{eq} - \sum\theta_{ax}$, deg	formal bond order[43]
$[ClSn(CH_2CH_2CH_2)_2NMe]_2$[31]	77.9, 75.4	0.63
$Cl_2Sn(SCH_2CH_2)_2S$[16a]	70.1	0.66
$Cl_2Sn(SCH_2CH_2)_2O$[16a]	60.5	0.66
$Cl_2Sn(CH_2CH_2CH_2)_2NMe$ (**1**)	60.5	0.63
$Cl_2Sn(CH_2CH_2CH_2)_2S$ (**8**)	60.0	0.57
$CH_2[PhSn(SCH_2CH_2)_2NMe]_2$[20]	48.8, 56.4	0.43
$Me_2Sn(SCH_2CH_2)_2NMe$[16,17]	55.5	0.51
$Cl_2Sn(CH_2CH_2CH_2)_2O$ (**5**)	44.6	0.64
$Ph_2Sn(SCH_2CH_2)_2O$[16a]	35.7	0.36
$Ph_2Sn(SCH_2CH_2)_2S$[16a]	31.0	0.17
$Me_2Sn(SCH_2CH_2)_2O$[16b]	26.0	0.23
$Me_2Sn(SCH_2CH_2)_2S$[16b]	9.0	0.0

[a] $\sum\theta_{eq}$ and $\sum\theta_{ax}$ are the sums of the angles becoming equatorial and axial, respectively, during the transition of a tetrahedron to a trigonal bipyramid.[16a]

Spectroscopic Investigations

^{119}Sn NMR Spectra (Table IX). In noncoordinating solvents ($CDCl_3$, C_7D_8) all compounds exhibit a unique signal that is only slightly temperature-dependent. In comparison with **9** the signals of **1** to **8** are shifted to both high and low fields. The chemical shifts depend significantly on the substituents R and R′ and on the donor atom E. The transition from the dimethyl-substituted compounds **3** and **7** to the monochlorinated derivatives **2** and **6**, respectively, causes low-field shifts whereas for the dichloro-substituted stannabicyclooctanes **1** and **5** high-field shifts are observed. This result can be explained with the so-called U-shape dependence of $\delta(^{119}Sn)$ on the number of electronegative substituents bonded to the tin atom.[45] Thus, while this effect was quantitatively calculated for tetracoordinated species only, this dependence is obviously also valid for pentacoordinated tin compounds. The influence of the donor atom E on the chemical shift is more complex. Whereas in the series **1**, **5**, and **8** the oxygen

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Table IX. ^{13}C and ^{119}Sn NMR Data of Compounds 1–9, $RR'Sn^1(C^2H_2C^3H_2C^4H_2)_2E$

			chem shifts, δ ($J(^{119}Sn-^{13}C)$ coupling const (Hz))						
compd	solv	T, °C	R	R′	1	2	3	4	NMe
1	$CDCl_3$	32			−14.76	22.37 (612.4)	21.54 (35.0)	57.52 (78.6)	43.84
	pyridine-d_5	32			−32.70[a]				
	HMPA/CD_2Cl_2	32			−100.07[a]				
	CD_2Cl_2	−80			−15.23	22.69 (607.1)	21.47 (33.2)	57.06 (80.6)	44.17
1a	CD_2Cl_2	32			−19.99				
		−55			−35.09				
2	$CDCl_3$	32	−2.01 (428.0)		4.45	15.75 (509.0)	22.81 (30.0)	58.37 (43.4)	44.27
	toluene/CD_2Cl_2	−80	−0.48		−4.48	16.61 (512.7)	23.43 (*b*)	57.90 (42.7)	44.34
3	toluene-d_8	95	−7.26			11.02 (398.5)	24.32 (28.9)	59.08 (21.6)	44.95
	$CDCl_3$	32	−7.06[a]		−28.50	10.74 (418.3)	23.82 (21.2)	58.52 (21.9)	45.06
	toluene-d_8	−80	−8.45 (377.7)	−4.38 (196.9)	−29.00[c]	10.40 (420.3)	23.42 (27.6)	57.24 (20.7)	44.73
4	toluene-d_8	32	26.07[d]/31.62[e] (*b*)		−14.65	7.32 (313.4)	24.76 (24.1)	58.65 (12.9)	46.52
	toluene-d_8	−80	25.15[d] (285),[h] 31.07[e]	27.24[d] (382),[h] 32.78[e]	−14.62	7.08 (317.0)	24.66 (27.0)	58.18 (*b*)	47.01
5	$CDCl_3$	32			−28.46	23.25[a] (571.0[f])	25.84 (46.2)	70.85 (47.6)	
6	$CDCl_3$	32	−3.28 (405.7)		+45.02	14.10 (477.3)	25.23 (28.4)	71.47 (26.8)	
7	toluene-d_8	32	−8.60 (300.8)		−7.17	8.77 (393.2)	26.04 (28.3)	71.76 (17.6)	
	toluene-d_8	−70	−7.99 (301.5)			8.70 (391.8)	26.03 (27.7)	71.60 (17.4)	
8	toluene-d_8	32			19.76	24.36 (561.0)	23.00 (49.5)	34.41 (49.5)	
9	$CDCl_3$	32	−10.24 (297.3)		4.12	10.63 (349.4)	23.18 (24.5)	28.63	22.05[g]

[a] Broad [b] Not observed. [c] In CD_2Cl_2. [d] Quaternary carbon. [e] Methyl carbon. [f] Measured at 22.635 MHz. [g] Methylene carbon. [h] The well-resolved coupling is visible only at one side of the signal whereas the other one is superimposed with other signals.

derivative **5** exhibits the highest shift; in the methyl-substituted compounds **2** and **6** or **3** and **7**, respectively, the nitrogen-containing derivatives exhibit the higher shifts. In donor solvents like pyridine or HMPA compound **1** shows broad resonances at a higher field indicating equilibria between penta- and hexacoordinated, HMPA-containing, species. This is confirmed in the case of the HMPA adduct **1a** itself showing a temperature-dependent chemical shift.

^{13}C NMR Spectra (Table IX). The ^{13}C NMR spectra of **1–8** display one signal for each of the three methylene carbons at both ambient and low temperature. This means that the two rings are equivalent, in either a rigid BB or CC conformation but not in a rigid BC/CB one, in which the rings are diastereotopic (see Figure 5), or in any other intermediate one averaging out on the NMR time scale under partial ring inversion processes. All signals exhibit ^{119}Sn satellites. The chemical shifts of the tin-bonded methylene carbons are determined by the substituents on the tin atom. The introduction of chlorine atoms causes a low-field shift of these signals, whereas the donor atoms have no dramatic influence. The methylene carbons 3 are influenced only slightly by the number of chlorine atoms (~2 ppm) and by the donor atoms (~4 ppm). The position of the signals of the E–CH_2 carbons is primarily determined by the nature of E while the nature of the substituents R and R′ on tin has a small influence only (compare **1**, **2**, **3**, and **4**), although these determine the strength of the tin–nitrogen interaction. The same holds for the *N*-methyl signals.

The tin methyl and tin *tert*-butyl signals, respectively, of **3** and **4** exhibit a splitting into two resonances of equal intensities at low temperature. The $^1J(^{119}Sn-^{13}C)$ coupling constants of the two methyl signals of **3** are quite different. The spectrum of **7** displays only one signal for the Sn–CH_3 carbons, even at −70 °C.

^1H NMR Spectra (See Supplementary Material). The spectra have been recorded in different solvents, at various temperatures, and at two resonance frequencies, 200 and 500 MHz. In the 500-MHz spectra of **1** to **3** the three types of methylene protons $SnCH_2$, CH_2, and NCH_2 exhibit well-separated patterns. The increased number of chlorine atoms in the sequence **3**, **2**, and **1** causes a low-field shift of all methylene protons. Furthermore, the spectra of **1–4** differ by the chemical shifts of the protons within a given methylene group and by their temperature dependence. Whereas in **1** at −70 °C the NCH_2 protons (5, 6) are isochronous and the $SnCH_2$ protons (1, 2) exhibit a large chemical shift difference, the situation is reversed in the case of **3**. In the spectrum of **2** all methylene protons are nonequivalent. Therefore, the low-temperature spectra of **1**, **2**, and **3** can be considered as $(ABMNXY)_2$ spectra with an accidental isochrony between A and B in **1** and between X and Y in **3**. At 30 °C the NCH_2 protons of **1** display an AB system, confirming the equivalence of these protons to be an accidental one at −70 °C. When the temperature is raised to 150 °C, all methylene protons remain nonequivalent in both **1** and **2**. At 30 °C the spectrum of **3** displays a triplet for the $SnCH_2$ protons whereas the CH_2 protons and the $SnCH_2$ proton signals are still broad but sharpen out to a quintet and to a triplet also at 90 °C. At −70 °C the $SnCH_3$ protons of **3** exhibit two signals with equal intensities but with different $^2J(^{119}Sn-C-^1H)$ couplings. At 19 °C these signals coalesce to a unique broad signal that sharpens out at 90 °C. In contrast, the spectra of **5** (500 MHz) display at both −70 and 30 °C a triplet for the OCH_2 protons, a quintet for the CH_2 protons, and a broad signal for the $SnCH_2$ protons. In **6** (200 MHz, 30 °C) the OCH_2 and CH_2 protons are nonequivalent whereas the chemical shifts of the $SnCH_2$ protons are identical. The spectrum of **7** (500 MHz, −70 °C) exhibits again an unresolved broad pattern for the OCH_2 protons that sharpens out to a triplet at room temperature. The CH_2 protons and the $SnCH_2$ protons show a quintet and a triplet at low as well as at room temperature. A splitting of the $SnCH_3$ protons was not observed. The spectrum (500 MHz, −70 °C) of **8** looks similar to that of **3** under these conditions. At 30 °C the SCH_2 and CH_2 protons are just in the coalescence region. For the sake of illustration we present here the spectra of **3** at −40 and +30 °C in Figure 4.

Configuration of the Tin Atoms. As already shown by our X-ray investigations the tin atoms in **1**, **5**, and **8** adopt more or less distorted trigonal-bipyramidal configurations as a result of the donor–acceptor interactions. The NMR measurements answer the question whether these configurations remain unchanged or not in solution. Furthermore, we estimated the strength of the donor–acceptor interactions as a function of the substituents at the tin atoms, especially for those compounds for which X-ray

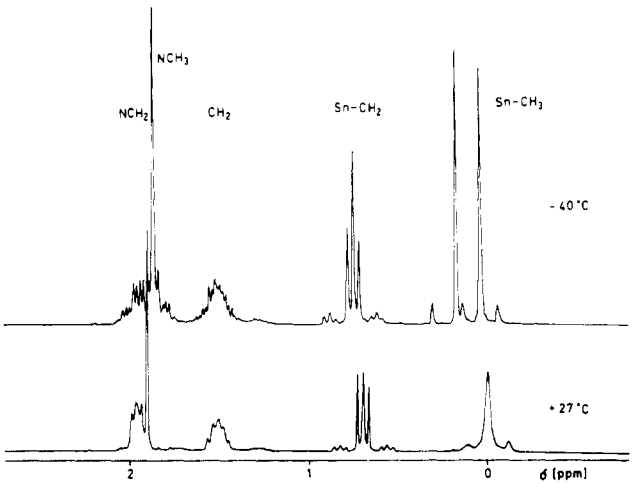

Figure 4. ^{1}H NMR (200-MHz) spectra of $Me_2Sn(CH_2CH_2CH_2)_2NMe$ (**3**) at −40 and +30 °C.

data are not available (i.e. **3**, **4**, **7**).

Usually, ^{119}Sn NMR spectroscopy is a powerful tool for the determination of the coordination number of tin atoms in organotin compounds.[46,47] Investigations on a large number of organotin derivatives have shown that increased coordination numbers cause high-field shifts of the NMR signals.[5,6,20,45-49] However, a comparison of the chemical shifts of different structures is only meaningful between compounds with similar substituents, i.e. Me_2SnX_2, coordination number four, and $Me_2SnX_2{\cdot}D$, coordination number five.[50] The dichloro-substituted derivatives **1**, **5**, and **8** exhibit considerable high-field shifts with respect to the tetracoordinated Bu_2SnCl_2 ($\delta(^{119}Sn)$ 123.0 ppm).[47] This confirms the existence of the transannular donor–acceptor interaction in these molecules in solution. The same holds for **2** and **6** when compared with Bu_3SnCl ($\delta(^{119}Sn)$ 141 ppm).[47] Further evidence for a B-type structure of **1**, **5**, **8** and **2**, **6** can be obtained from the ^{13}C NMR spectra, since the $^1J(^{119}Sn-^{13}C)$ coupling constants are unambiguously larger than those of Bu_2SnCl_2 and Bu_3SnCl respectively, a characteristic of equatorial carbon atoms.[51] The situation for the compounds **3** and **7** is more complicated. ^{119}Sn NMR alone does not give unambiguous evidence for the existence of a donor–acceptor interaction. Compound **7** exhibits a very small high-field shift of ca. 11 ppm with respect to the tetracoordinated derivative **9**, while this shift is more dramatic in **3** as it amounts ca. 30 ppm. Furthermore, the splitting of the methyl signal in both the ^{1}H and ^{13}C NMR spectra of **3** at low temperature is in agreement with a Sn–N contact; indeed the very different $^1J(^{119}Sn-^{13}C)$ and $^2J(^{119}Sn-^1H)$ coupling constants, respectively, are conclusive for a trigonal-bipyramidal tin with one apical and one equatorial methyl group. The high-field signal at −8.45 ppm with the large coupling of 377.7 Hz corresponds to the equatorial methyl group whereas the low-field signal at −4.38 ppm with the small coupling of 196.9 Hz can be assigned to the apical methyl group.

For $Me_2Sn(SCH_2CH_2)_2NMe$ the difference between both coupling constants is 131 Hz (^{13}C, −20 °C) whereas for $Me_2Sn(SCH_2CH_2)_2O$ this value amounts to 99 Hz (^{13}C, −95 °C). Thus, the difference of the direct coupling constants $^1J(^{119}Sn-^{13}C)$ of dimethyl-substituted stannocanes $Me_2Sn(XCH_2CH_2)_2E$ could be regarded as a quantitative measure for the transition tetrahedron ⇌ trigonal bipyramid in solution. Because of the temperature independence of the ^{119}Sn NMR chemical shift (Table IX) of **3** an equilibrium between penta- and tetracoordinated tin can be ruled out or, at least, the latter configuration is negligible. That the tin atom in tetraorganotin compounds is able to extend its coordination sphere has recently been shown by X-ray analysis of $MeSn(CH_2CH_2CH_2)_3N$[52] and bis[3-(2-pyridyl)thienyl]diphenyl(IV)[53] and by NMR on pentaorganostannate complexes.[54] A further argument supporting the Sn–N interaction in **3** is the slightly but significantly increased $^1J(^{119}Sn-^{13}CH_2)$ coupling constant with respect to the corresponding one in **9**. For **7** we have no evidence for a transannular Sn–O interaction because of the absence of the splitting of the tin methyl signals in the low-temperature ^{1}H and ^{13}C spectra. Obviously, the Sn–O contact is much weaker or even absent. The only indication favoring a Sn–O contact is again the increased $^1J(^{119}Sn-^{13}CH_2)$ coupling of 393.2 Hz compared with that of 349.4 Hz in **9**.

Ring Conformations. The solid-state investigations reveal the compounds **1**, **5**, and **8** to adopt a boat–chair (BC), a chair–chair (CC), and a boat–boat (BB) eight-membered ring conformation, respectively. However, in solution the situation is much more complicated because equilibria between these different conformations have to be considered, making comparisons with the solid-state structures difficult. Nevertheless, a number of investigations deal with the elucidation of conformational equilibria of eight-membered heterocycles.[55,56] With the assumption that transannular Sn–E interactions are retained, the CC, BB, and BC conformations (see Figure 5) have to be considered as the most energetically favored ones and must therefore be involved in the study of dynamic conformational equilibria in these systems. As a result of its chirality the BC conformation exists as two enantiomers (BC, CB), while the CC and BB conformations are achiral. Under retention of the Sn–E contact, a direct interconversion is possible between these conformations through an uncorrelated inversion of one ring at a time according to the scheme $\overline{BC-CC-CB-BB}$ (*uncorrelated partial ring inversion* = uPRI). A correlated inversion of the two rings simultaneously interconverts the pairs BC ⇌ CB and CC ⇌ BB (*correlated partial ring inversion* = cPRI) (Figure 5). The presence of only one ^{13}C signal for each type of methylene in **1** to **8** throughout the whole temperature range studied strongly suggests the symmetry equivalence of both five-membered rings, at least on the NMR time scale. The $J(^{119}Sn-^{13}C-E)$ coupling constants should provide information about the dihedral angles $\varphi_{Sn-C-C-E}$. However, this coupling is the sum of the values $^3J(^{119}Sn-C-C-^{13}C)$ and $^2J(^{119}Sn-E-^{13}C)$ for which a separation is not possible. Therefore, the use of the ^{13}C NMR data is irrelevant in the present conformational analysis because the second part of this coupling is sensitive to both the

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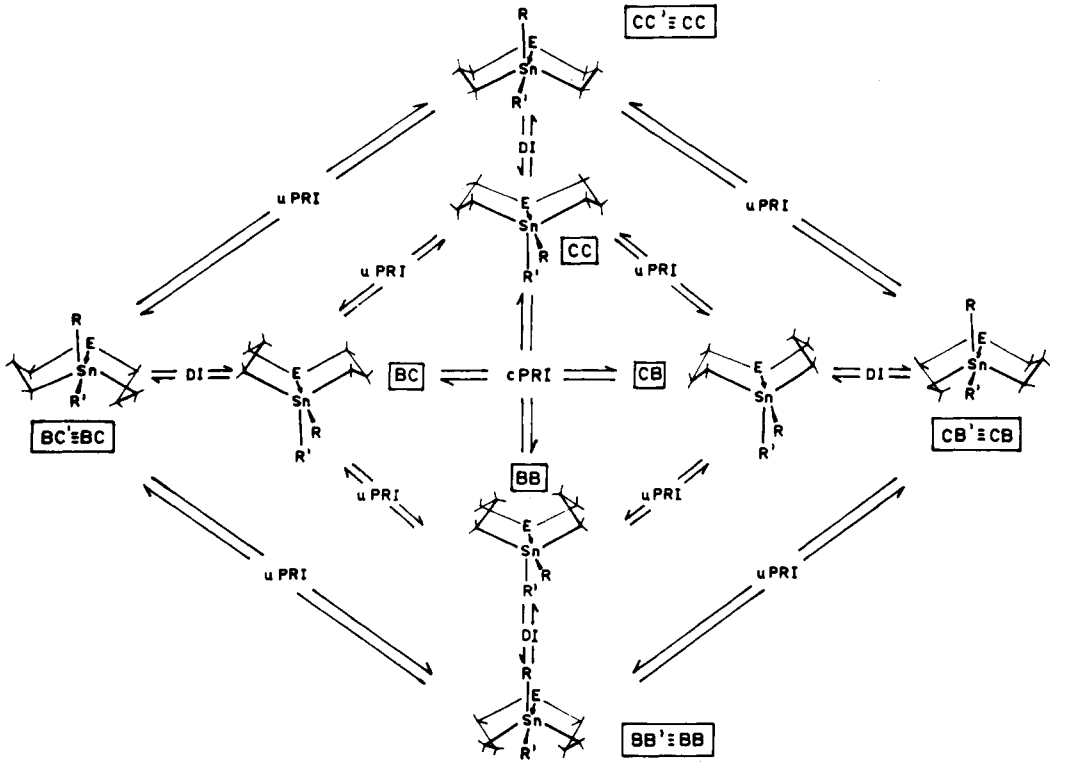

Figure 5. Conformational equilibria in the 1-element-5-stannacyclooctanes (uPRI = uncorrelated partial ring inversion; cPRI = correlated partial ring inversion; the substituents R and R′ are identical and are only labeled differently to show that they are permuted by the DI process, in contrast to the PRI processes. In the unprimed conformers the two apical bonds are Sn–E and Sn–R and in the primed ones are Sn–E and Sn–R′).

nature of E and the strength of the Sn–E interaction and also because comparable experimental data are not available. Fortunately, the method of Lambert[57] (*R* value method) based on ^{1}H couplings allows us to evaluate the torsion angles of the eight-membered rings with an accuracy of about 1°. The E–CH_2 methylene fragments were used for the estimation of these torsion angles because these spectral parts are best comparable with known data from the literature.[55] The following torsion angles $\varphi_{Sn\text{-}C\text{-}C\text{-}C\text{-}E}$ of 56° (1), 58° (2), 59.5° (3), and 59.0° (8) have been calculated. From these data the existence of conformational equilibria with the CC conformation dominating can be concluded for 2, 3, and 8. This means, especially for 8 with its flattened BB conformation in the solid state, that a conformational change takes place upon transition from the crystalline state to solution. This might be related to the weakening of the Sn–S interaction in solution because sulfur is known to be a weak donor toward tin(IV).[58] Conformation differences between solid state and solution have been discussed for other tin, germanium, and silicon heterocycles, too.[28,55] For 1 the smaller torsion angle indicates a preferred BC conformation in solution. However, an increased population of the BB conformation with respect to 2, 3, and 8 equilibrating rapidly with the BC conformation would lead to the same result. A comparison of the ^{1}H NMR spectra of 1 to 3 shows that a weakening of the Sn–N contact increases the dihedral angles $\varphi_{Sn\text{-}C\text{-}C\text{-}C\text{-}N}$. This effect was already observed for *t*-$Bu_2Sn(OCH_2CH_2)_2NMe$[59] and $Me_2Sn(SCH_2CH_2)_2NMe$.[59] The first compound exhibits a very short Sn–N interaction of 2.32 Å as a result of the equatorial attack of the nitrogen. The result is a strong flattening of the eight-membered ring with a small torsion angle of 47.6°.[59] The second compound with a much weaker Sn–N bond[16,17] exhibits a torsion angle of 60.6° comparable with those of 1 to 3 and 8.

The ^{1}H spectra, in the methylene region, of 1 to 8 show some of the conformational equilibria to be fast on the NMR time scale, even at −70 °C. Indeed, these spectra have either an $(A_2M_2X_2)_2$ (compounds 5 and 7) or an $(ABMNXY)_2$ pattern (compounds 1, 2, 3, and 8). In the latter case, they correspond to patterns that are averaged from the two $(ABMNXY)_2$ spectra of the BB and CC conformers and from the unique (ABMNXY)(CDPQVZ) spectrum of the pair of enantiomeric BC/CB conformers or eventually only from a part of these spectra. For this reason and in conjunction to the isomerization pathway snapshots obtained from the solid-state investigations in the present work, we suggest the conversions between the different conformers to proceed through monoplanar transition states, i.e.., through uncorrelated partial ring inversion (uPRI, see Figure 5). However, a diplanar transition state, i.e., an isomerization through correlated partial ring inversion (cPRI, see Figure 5) required for the direct interconversion BC ⇌ CB and BB ⇌ CC, cannot be excluded to compete with the uPRI: for PhClSn-$(SCH_2CH_2)_2O$, the latter one has been confirmed experimentally.[60]

The nonequivalence of the methylene protons, displayed in the ^{1}H-averaged $(ABMNXY)_2$ spectra of 3 and 8, disappears when the temperature is raised, since above the coalescence region, $(A_2M_2X_2)_2$, spectra result. For 4, 5, and 7 such patterns only were observed at the temperatures studied, even at −70 °C for the two last ones, while 1 displays coalescences at higher temperatures, but even at 130 °C and 200 MHz, the averaged $(A_2M_2X_2)_2$ spectrum

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Table X. Free Activation Enthalpies (kcal/mol) of the Dissociation–Inversion Mechanism in Selected Stannabicyclooctanes

compd	solv	ΔG^*, kcal/mol
$Me_2Sn(NMeCOCH_2)_2NMe$[63]	o-$C_6H_4Cl_2$	22.5[a]
t-$Bu_2Sn(NMeCOCH_2)_2NMe$[63]	o-$C_6H_4Cl_2$	20.9[a]
t-$Bu_2Sn(OCOCH_2)_2NMe$[62]	o-$C_6H_4Cl_2$	20.9[a]
$Cl_2Sn(CH_2CH_2CH_2)_2NMe$ (1)	$C_6H_5NO_2$	20.2[b]
$Me_2Sn(SCH_2CH_2)_2NMe$[15]	$CHCl_3$	15.6[a]
t-$Bu_2Sn(OCH_2CH_2)_2NMe$[14]	CH_2Cl_2	14.7[a]
$Me_2Sn(CH_2CH_2CH_2)_2NMe$ (3)	CD_2Cl_2	14.1[b]
$Cl_2Sn(CH_2CH_2CH_2)_2S$ (8)	$CDCl_3$	13.9[b]
t-$Bu_2Sn(SCH_2CH_2)_2NMe$[15]	CH_2Cl_2	11.6[a]
t-$Bu_2Sn(CH_2CH_2CH_2)_2NMe$ (4)	CD_2Cl_2	11.4[b]
$Me_2Sn(SCH_2CH_2)_2S$[50]	CD_2Cl_2	10.2[b]
$Me_2Sn(SCH_2CH_2)_2O$[64]	CD_2Cl_2	8.7[b]
$Cl_2Sn(CH_2CH_2CH_2)_2O$ (5)	CD_2Cl_2	<10.0
$Me_2Sn(CH_2CH_2CH_2)_2O$ (7)	CD_2Cl_2	<10.0

[a] Estimated by line-shape analysis. [b] Estimated by using approximative equations.

could not be obtained. In the case of **2** and **6**, where R ≠ R′, only $(ABMNXY)_2$ spectra are observed. Last but not least, in **3** and **4**, the singlet signals of the two identical but diastereotopic groups R and R′ also coalesce, while in **7**, only one averaged signal is observed, even at −70 °C. All these observations can be explained neither by uncorrelated nor by correlated partial ring inversions, as these do not exchange pairwise the protons within each methylene group or the diastereotopic groups R and R′ (see Figure 5). We suggest the process responsible for this high-temperature intramolecular mobility to be a combination of ring inversion and Sn–E dissociation, the so-called dissociation–inversion (DI) mechanism (see Figure 5), in which the transition state of the tin atom is tetracoordinated. In the case of **1–4**, the process is coupled to a nitrogen inversion, whereas in the oxygen- and sulfur-substituted derivatives, both lone pairs of the open intermediate can recoordinate the tin atom after the ring inversion. The dissociation–inversion mechanism has been discussed in the literature.[1,14,20,21] The dissociation is the rate-determining step. As this dissociation is very sensitive on both the tin substituent pattern and the nature of the donor E, it is quite normal to find very different temperature dependencies for the ^1H NMR spectra.

Table X documents the influence of the substituents on the tin atoms and of the donor E in several stannabicyclooctanes toward the free activation enthalpy. This free activation enthalpy reflects the unseparable contributions of the Sn–E dissociation and the ring inversion. Therefore, the values of Table X cannot be used to estimate the strength of the Sn–E interaction in different stannocanes, first, because the influence of exocyclic substituents and endocyclic heteroatoms on the barrier to ring inversions in cyclooctane derivatives is not fully understood[61] and, second, because systematic studies on tin heterocycles with or without Sn–E interactions are not yet reported. However, from the solid-state structure of $Me_2Sn(SCH_2CH_2)_2S$[16b] we know that there is no Sn–S interaction and, thus, the observed free activation enthalpy observed for this particular compound is representative for the ring inversion. Nevertheless, there is a clear tendency of increasing ΔG^* values upon substitution with electronegative atoms or atom groups in both exocyclic and endocyclic positions. A comparison of the dichloro-substituted derivatives **1**, **8**, and **5** shows decreasing ΔG^* values in this sequence, which is in agreement with the different donor strengths of nitrogen, sulfur, and oxygen toward tin(IV).[58] The same holds for $Me_2Sn(SCH_2CH_2)_2E$ (E = NMe, S, O), albeit to a much smaller extent.

In the nonsymmetrical substituted compounds **2** and **6**, the dissociation–inversion was not observed because the much larger apicophilicity of the chlorine atom with respect to the methyl group disfavors strongly the isomer with the latter in an apical position, so that, even if it does proceed, the isomerization cannot be detected anyhow.

Acknowledgment. We thank Mrs. A. Brassart for her assistance in the X-ray determination and Mrs. C. Mühlpfordt for recording several NMR spectra. We wish to express our gratitude to Mr. M. Desmet for having recorded the mass spectra. Financial support from the "Ministerie van Nationale opvoeding en Nederlandse Cultuur (Bestuur voor Internationale en Cultureele Betrekkingen)", the "Fonds voor Kollektief Fundamental Onderzoek" (FKFO), the "Nationaal Fonds voor Wetenschappelijk Onderzoek" (NFWO), and the "Nationale Raad voor Wetenschafsbeleid" is gratefully acknowledged by M.G. and R.W.

Registry No. **1** (cc entry), 111004-38-7; **1** (stannane entry), 93253-72-6; **1a**, 111004-45-6; **2** (cc entry), 111004-39-8; **2** (stannane entry), 110971-28-3; **3** (cc entry), 93083-33-1; **3** (stannane entry), 93253-74-8; **4** (cc entry), 111004-40-1; **4** (stannane entry), 110971-29-4; **5** (cc entry), 111004-41-2; **5** (stannane entry), 110971-30-7; **6** (cc entry), 111004-42-3; **6** (stannane entry), 110971-31-8; **7** (cc entry), 111004-43-4; **7** (stannane entry), 110971-32-9; **8** (cc entry), 111004-44-5; **8** (stannane entry), 110971-33-0; **9**, 110971-34-1; $MeN(CH_2CH_2CH_2MgCl)_2$, 99430-63-4; $O(CH_2CH_2CH_2MgBr)_2$, 40347-66-8; $S(CH_2CH_2CH_2MgCl)_2$, 110971-35-2; $CH_2(CH_2CH_2CH_2MgBr)_2$, 59321-71-0.

Supplementary Material Available: Tables of anisotropic thermal parameters of compound **1**, thermal parameters of compounds **5** and **8**, the torsion angles for compounds **1**, **5**, and **8**, the ^1H NMR data of compounds **1–9**, and selected mass spectra and the unit cell drawings of compounds **1**, **5**, and **8** (9 pages); listings of structure factors for **1**, **5**, and **8** (20 pages). Ordering information is given on any current masthead page.

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