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Influence of the steric effect on the conformation of stannocanes. The synthesis and X-ray structure of $X(CH_2CH_2S)_2Sn(n\text{-}Bu)Cl$ $(X = S, O)$

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Abstract

5-Chloro-5-*n*-butyl-1-oxa-4,6-dithia-5-stannocane (**1**) and 2-chloro-2-*n*-butyl-1,3,6-trithia-2-stannocane (**2**) have been prepared by reacting *n*-butyltin trichloride with 2-mercaptoethyl ether and 2-mercaptoethyl sulphide, respectively. Complexes **1** and **2** were characterised by elemental analyses, IR, EI MS, and multinuclear NMR (^1H, ^{13}C, ^{119}Sn). The molecular structures of **1** and **2** were determined by X-ray analyses. The eight-membered rings in both compounds are in the boat–chair conformation with a 1,5 transannular Sn···O (2.409(7) Å) or Sn···S (2.7855(16) Å) interaction. The coordination around the Sn atoms can be described as trigonal bipyramidal with Cl and X in the apical positions. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Metallocanes; Tin compounds; Ring conformation; X-ray structure

1. Introduction

Metallocanes [1] of the type $X(CH_2CH_2S)_2MRR'$ (M = Ge, Sn, Pb, As, Sb or Bi) (X = S, O, NMe) (RR′ = lone pair, halogen, alkyl or aryl) show a 1,5 transannular interaction between the X (donor group) and M, a situation that leads to an increase in the coordination number of M [2–13]. In addition to the intrinsically conformational interest of this type of metallocycles, they have been used recently by Dräger in the creation of a novel view about the bonding scheme in the main group hypervalency problem [14].

We have studied the influence of dithiolate ligands as RR′ groups, such as dithiophosphinates (S_2PR_2) [15–17], dithiophosphates [$S_2P(OR)_2$] [18] and dithiocarbamates (S_2CNR_2) [19], in the bond strength and the conformational preferences of the eight-membered ring of arsocanes and stibocanes. The trends observed, through structural determinations as well as NMR and IR spectroscopies, lead to the conclusion that there is a relationship between the strength of the transannular secondary bonding and the conformation of the metallocane ring. If the secondary bonding is sufficiently strong, the conformation becomes boat–boat, but if the bond strength decreases, the preferred conformation is boat–chair and then the chair–chair arrangement [20].

The hypervalence of the stannocanes of the type shown in Fig. 1 has been studied mainly through the use of vibrational spectroscopy and single-crystal X-ray diffraction [11,12]. Dräger has proposed that the ‘path’ of the nucleophilic attack from a tetrahedron to a trigonal bipyramid in metallocanes, is controlled by four electronic factors (donor strength of X, electronegativity of Hal*ax*, lone pair interaction of X Hal*ax*, type of equatorial ligands) and one steric factor (geometrical flexibility of X), and has been discussed in terms of the molecular orbitals of the three-centre, four-electron interaction X···Sn–Hal. In this work we report the synthesis and characterisation of two new stannocanes that

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contain a alkyl group, i.e. the 5-chloro-5-*n*-butyl-1-oxa-4,6-dithia-5-stannocane (**1**) and the 2-chloro-2-*n*-butyl-1,3,6-trithia-2-stannocane (**2**), in order to investigate the influence of the steric factor of the equatorial ligands (fourth electronic factor) on the conformational preferences of the stannocanes.

2. Experimental

All reagents were of commercial grade and were used as received. IR spectra were recorded in the region 4000–200 cm^{-1} as KBr pellets using a Perkin–Elmer 282-B spectrometer. Proton, carbon-13 and tin-119 magnetic resonance spectra were obtained on a Varian VXR-300 operating at 299.949, 75.3 and 111.86 MHz, respectively, using $CDCl_3$ as solvent The chemical shifts are relative to internal Me_4Si (^1H, ^{13}C) and external Me_4Sn (^{119}Sn) for the indicated nuclei. Mass spectra determinations were performed on a Hewlett–Packard MS/GS 598 instrument by electron impact at 70 eV. Elemental analyses (C, H) were carried out by Galbraith Laboratories Inc. (Knoxville, TN).

Single crystals of **1** and **2**, suitable for X-ray diffraction, were obtained by diffusion using a dichloromethane–*n*-hexane mixture. Crystallographic and structure solution data are summarised in Table 1. Data collections were carried out in a Siemens P4/PC diffractometer at room temperature, with graphite-monochromated Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å). In both cases corrections were applied for background and Lorentz polarisation effects. The structures were solved by direct methods and refined by full-matrix least-squares using SHELXTL program [21]. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were placed in idealised positions.

2.1. Synthesis of 5-chloro-5-n-butyl-1-oxa-4,6-dithia-5-stannocane (1)

A solution of $O(CH_2CH_2SH)_2$ (1.712 g, 12.4 mmol) in 50 ml of benzene was added dropwise under stirring to a solution of *n*-$BuSnCl_3$ (3.5 g, 12.4 mmol) in 50 ml of benzene. The mixture was refluxed for 10 h, and the resulting solid was filtered and recrystallised from a dichloromethane–*n*-hexane mixture. White crystals, stable on exposure to air, m.p. 39–40°C. Yield (3.8 g, 88%), Anal. Calc. for $C_8H_{17}OS_2ClSn$: C, 27.65; H, 4.93. Found: C, 27.55; H, 4.91%. EI MS (70 eV) m/z 291 ($M^+ - n$-Bu, 100%), 312 ($C_8H_{17}OS_2Sn^+$, < 10%), 231 ($C_2H_4OSClSn^+$, 15%), 195 ($C_2H_4OSSn^+$, 15%), 155 ($SnCl^+$, 33%), 151 (SnS^+, < 15%). IR (KBr) 2954s, 2918s, 2868s, 2849s (ν C–H), 1424s, 1146m (δ CH_2–S), 1060s, 980s ($\nu_{as,s}$ C–O–C), 880w, 840w, 660m ($\nu_{as,s}$ S–C–C), 380w, 355m cm^{-1} (ν Sn–S, Sn–Cl). ^1H-NMR ($CDCl_3$): δ 3.96 (ddd, $J = 3.6$, 5.1, 9.9 Hz, 2H), 3.6 (ddd, $J = 4.2$, 7.8 and 9.9 Hz, 2H) CH_2–O, 2.96 (m, 4H), CH_2–S, 1.75 (m, 4H), 1.50 (sext, $J = 7$ Hz, 2H), 0.95 (t, $J = 7$ Hz, 3H) *n*-Bu. ^{13}C-NMR ($CDCl_3$) δ 71.52 (CH_2–O), 27.67 (CH_2–S), 33.05, 27.40, 25.70, 13.52 (*n*-Bu). ^{119}Sn-NMR ($CDCl_3$) δ -10.93.

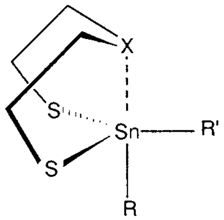


Fig. 1. Stannocanes of the type $X(CH_2CH_2S)_2SnRR'$ (X = S, O, NMe) (RR' = halogen, alkyl or aryl).

Table 1
Crystallographic and structure solution data for 5-chloro-5-*n*-butyl-1-oxa-4,6-dithia-5-stannocane **1** and 2-chloro-2-*n*-butyl-1,3,6-trithia-2-stannocane (**2**)

	1	**2**
Compound formula	$C_8H_{17}ClOS_2Sn$	$C_8H_{17}ClS_3Sn$
Formula weight	347.5	363.5
Crystal size (mm)	0.80 × 0.20 × 0.2	0.60 × 0.48 × 0.40
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbca*	$P2_1/c$
a (Å)	15.284(1)	7.9939(4)
b (Å)	9.223(1)	9.0165(4)
c (Å)	19.319(2)	19.643(1)
β (°)		101.626(5)
V (Å^3)	2723.3(4)	1386.78(13)
Z	8	4
D_{calc} (Mg m^{-3})	1.695	1.741
Absorption coefficient (mm^{-1})	2.346	2.448
F(000)	1376	720
Scan mode	ω	ω
Temperature (K)	293(2)	293
θ Range for data collection (°)	1.50–25.00	1.50–25.00
Index ranges	$-18 \leq h \leq 18$, $-10 \leq k \leq 10$, $-22 \leq l \leq 22$	$0 \leq h \leq 9$, $0 \leq k \leq 10$, $-23 \leq l \leq 22$
Reflections collected	4798	2641
Number of independent reflections	2399 [$R_{int} = 0.0502$]	2446 [$R_{int} = 0.0276$]
Max./min. transmission	0.7533 and 0.6136	0.4328 and 0.3329
Data/restraints/ parameters	2399/72/147	2446/0/119
Goodness-of-fit on F^2	0.996	1.055
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0553$, $wR_2 = 0.1135$	$R_1 = 0.0335$, $wR_2 = 0.0779$
Final indices (all data)	$R_1 = 0.1236$, $wR_2 = 0.1417$	$R_1 = 0.0466$, $wR_2 = 0.0841$
Extinction coefficient	0.0030(3)	0.0105(5)
Largest difference peak and hole (e Å^{-3})	0.747 and -0.420	0.651 and -0.507

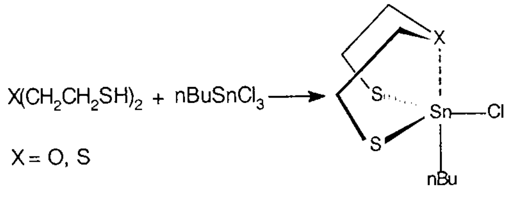
2.2. Synthesis of 2-chloro-2-n-butyl-1,3,6-trithia-2-stannocane (2)

This compound was obtained in a similar way as described above for **1** from $S(CH_2CH_2SH)_2$ (1.915 g, 12.4 mmol) and *n*-$BuSnCl_3$ (3.5 g, 12.4 mmol). Yield (4.1 g, 91%) of white crystals, m.p. 50–52°C. Anal. Calc. for $C_8H_{17}S_3ClSn$: C, 26.43; H, 4.71. Found: C, 26.48; H, 4.71%. EI MS (70 eV) m/z 307 ($M^+ - n$-Bu, 100%), 247 ($C_2H_4S_2ClSn^+$, 50%), 212 ($C_2H_4S_2Sn^+$, 30%), 155 ($SnCl^+$, 30%), 151 (SnS^+, 60%). IR (KBr) 2940s, 2920s, 2840s (ν C–H), 1420s, 1140m (δ CH_2–S), 850m, 840m, 680m ($\nu_{as,s}$ S–C–C), 660m (ν C–S–C), 350s, 330m cm^{-1} (ν Sn–S, Sn–Cl). ^{1}H-NMR ($CDCl_3$): δ 3.16 (m, 4H), 3.04 (m, 2H), 2.82 (m, 2H), CH_2–S, 2.09 (t, $J = 7$ Hz, 2H), 1.85 (q, 2H), 1.50 (sext, $J = 7$ Hz, 2H), 0.95 (t, $J = 7$ Hz, 3H) *n*-Bu. ^{13}C-NMR ($CDCl_3$) δ 39.32 (CH_2–S–Sn), 28.10 (CH_2–S), 31.70, 28.10, 25.67, 13.49 (*n*-Bu). ^{119}Sn-NMR ($CDCl_3$) δ −8.83.

3. Results and discussion

The reaction between *n*-butyltin trichloride and 2-mercaptoethyl ether or 2-mercaptoethyl sulphide in benzene gave the corresponding 5-chloro-5-*n*-butyl-1-oxa-4,6-dithia-5-stannocane (**1**) and 2-chloro-2-*n*-butyl-1,3,6-trithia-2-stannocane (**2**); both compounds are air-stable, colourless, crystalline solids. Experimental details, yields and melting points are given in Section 2. The compounds were characterised by IR, electron-impact (EI) mass spectrometry and multinuclear NMR (^{1}H, ^{13}C, ^{119}Sn) spectroscopy. The crystal and molecular structures were determined by single-crystal X-ray techniques (Scheme 1).

The IR spectra exhibit absorption bands characteristic of the symmetrical and asymmetrical C–X–C group in the stannocanes. The bands in the region 380–330 cm^{-1} are indicative of the Sn–Cl and Sn–S bonding. The absorption bands were assigned by comparison with the literature data [12]. EI mass spectra for **1** and **2** do not show the molecular ion, but as expected, the ion corresponding to $M - Bu^+$ is the base peak in both compounds; additionally present are fragments characteristic of the stanocanne rings, i.e. the $X(CH_2CH_2S)$-Sn^+ ($X = O$ or S).



Scheme 1.

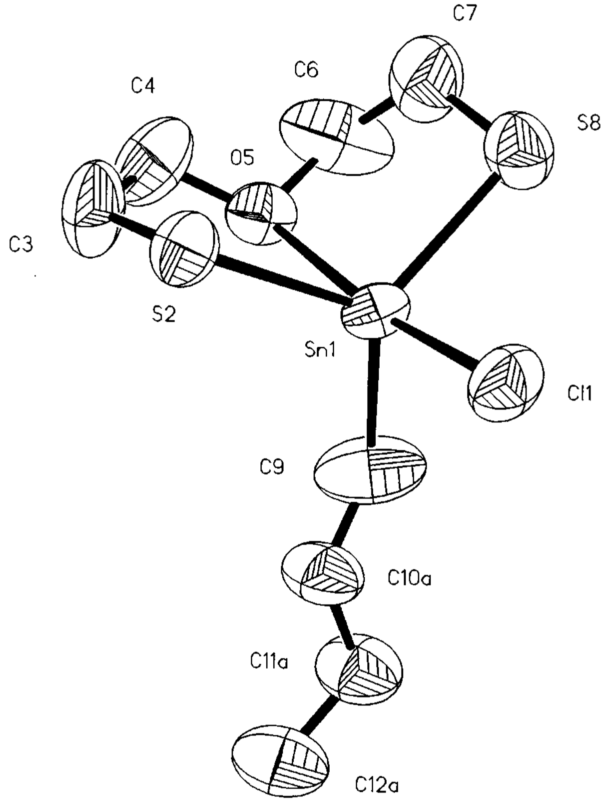


Fig. 2. ORTEP view of $O(CH_2CH_2S)_2Sn(n$-Bu)Cl.

The ^{1}H-NMR spectrum of **1** exhibits signals at low field typical of an ABCD spin system and these are ascribed to the $-SCH_2CH_2X-$ fragments of the eight-member heterocycle. It is interesting to note that both $O(CH_2CH_2S)_2SnCl_2$ [2e] and $O(CH_2CH_2S)_2Sn(CH_2CH_2CO_2CH_3)Cl$ [22] exhibit an AA′BB′ spin system with shifts of 3.88 and 3.8 ppm for $-O-CH_2-$, respectively. These values fall between those observed for **1** (3.96 and 3.6 ppm). The resonance for $-CH_2-S$ group exhibits an upfield shift of 0.28 ppm in comparison with the chlorine analogue. As expected, the ^{13}C-NMR spectra show the two singlets for the carbons of the eight-membered ring. The ^{119}Sn spectrum of **1** and **2** shows unique signals at δ −10.93 and −8.85, respectively. Such chemical shifts are outside the proposed ranges [23] for pentacoordinate tin (between ca. −90 and −330 ppm), but they are in agreement with values found in other pentacoordinated compounds such as $O(CH_2CH_2S)_2Sn(CH_2CH_2CO_2CH_3)Cl$ (−18.4 ppm) [22], and $O(CH_2CH_2S)_2SnBr_2$ (−40.9 ppm) [11].

The molecular structures of **1** and **2** are shown in Figs. 2 and 3, with the corresponding atom numbering scheme, while bond lengths and angles are in Table 2. Complexes **1** and **2** reveal a pentacoordinate tin and approaches a trigonal bipyramidal geometry with S(2), S(8) and C(9) of *n*-butyl in equatorial positions, Cl and X (X = O, S) in axial positions. The Sn···O transannular distance in **1** (2.409 Å) is slightly longer than in $O(CH_2CH_2S)_2SnCl_2$ (2.359 Å) [2,11], but shorter than in the dimethyl or diphenyl stannocanes, $O(CH_2CH_2S)_2SnRR'$ (2.774 and 2.66 Å, respectively). However, it is similar to that found in $O(CH_2CH_2S)_2SnPhCl$ (2.41 Å) [6] and $O(CH_2CH_2S)_2SnMeCl$ (2.42 Å) [12]. The $Sn\cdots S$ transannular distance in (**2**) (2.785 Å) is slightly shorter than that in $S(CH_2CH_2S)_2PhCl$ (2.806 Å) [10], but significantly shorter than that in $S(CH_2CH_2S)_2SnMeCl$ (2.863 Å) [12]. The structures of alkyl or aryl and dialkyl or diaryl substituted stannocanes lead to the assumption that the strength of the transannular $Sn\cdots X$ interaction decreases when the halogen atoms are replaced partially or totally. Also, it is observed that the $Sn–Cl_{ax}$ bond length slightly decreases in the alkyl or aryl substituted derivatives, in comparison with the dichlorostannocanes. The electronic factor proposed by Dräger for the 'path' from a tetrahedron to a trigonal bipyramid is described in terms of exponential Pauling-type bonds orders [24]. We calculated such values for **1** and **2** and in Table 3 there is a comparison with similar compounds. The steric 'path' proposed in terms of $\Delta\Sigma(\theta)$ shows that **1** and $O(CH_2CH_2S)_2SnPhCl$ present a lower deviation in comparison with the other analogues, while the value for the stannocane **2**, $\Delta\Sigma(\theta) = 80.9°$, corresponds to the closer observed value related to the ideal trigonal bipyramid structure.

The torsion angles (Table 4) of **1** and **2** are indicative of the boat–chair conformation of the eight-member rings. In both compounds, Sn(1)–S(2)–C(3)–C(4)–X(5) is the chair part while Sn(1)–S(8)–C(7)–C(6)–X(5) is the boat part. It is interesting to note that while mainly all stannocanes $O(CH_2CH_2S)_2SnHal_2/HalMe/Me_2$ [11,12] exhibit a chair–chair conformation of the eight-member ring, and the corresponding trithia compounds show the boat–chair, however, in $O(CH_2CH_2S)_2SnMeCl$ the chair–chair and boat–chair conformations are present in the same crystal, while the diplanar transition state is observed in $O(CH_2CH_2S)_2SnPhCl$ [6] as indicative of the transition between the two enantiomers of the boat–chair conformation. The $O(CH_2CH_2S)_2SnPh_2$ [5] shows the monoplanar transition conformation, which corresponds to the path between the chair–chair and boat–chair conformations.

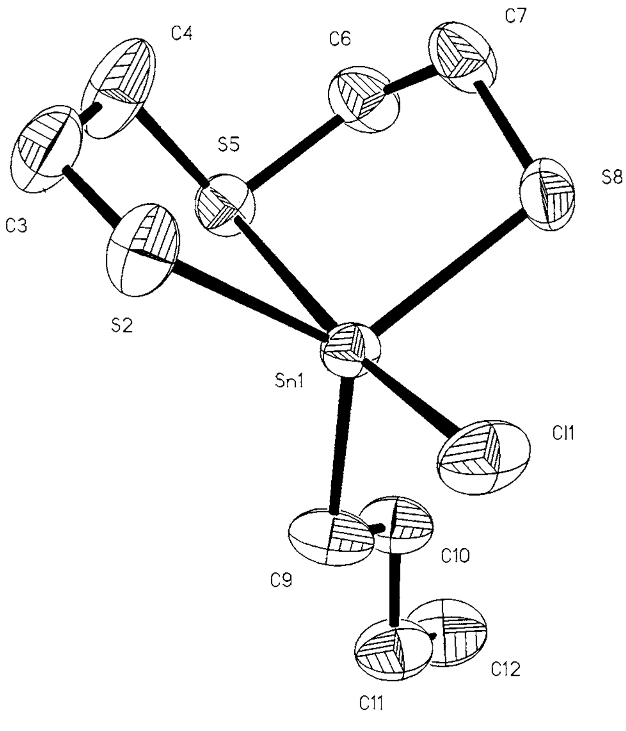


Fig. 3. ORTEP view of $S(CH_2CH_2S)_2Sn(n\text{-}Bu)Cl$.

Table 2

Bond distances (Å) and bond angles (°) in 5-chloro-5-*n*-butyl-1-oxa-4,6-dithia-5-stannocane (**1**) and 2-chloro-2-*n*-butyl-1,3,6-trithia-2-stannocane (**2**)

	1	**2**
Sn(1)–Cl(1)ax	2.407(3)	2.4458(15)
Sn(1)···X(5)ax	2.409(7)	2.7855(16)
Sn(1)–S(2)eq	2.381(4)	2.3984(18)
Sn(1)–S(8)eq	2.390(4)	2.3975(18)
Sn(1)–C(9)[*n*-Bu(eq)]	2.142(15)	2.128(6)
C(3)–C(4)	1.37(2)	1.407(10)
C(4)–X(5)	1.389(17)	1.797(8)
X(5)–C(6)	1.446(18)	1.812(7)
C(6)–C(7)	1.35(2)	1.480(9)
C(7)–S(8)	1.764(18)	1.782(7)
C(9)–C(10A)/C(9)–C(10B) [a]	1.28(3)/1.37(7)	1.493(9)
C(10)–C(11)A/B	1.59(3)/1.55(10)	1.517(8)
C(11)–C(12)A/B	1.36(4)/1.42(11)	1.459(10)
Cl(1)–Sn(1)···X(5)	169.70(2)	170.22(6)
S(2)–Sn(1)–S(8)	117.64(14)	117.97(8)
S(2)–Sn(1)–C(9)	119.5(6)	122.4(2)
S(8)–Sn(1)–C(9)	117.6(6)	117.90(2)
Cl(1)–Sn(1)–S(2)	95.25(11)	91.78(7)
Cl(1)–Sn(1)–S(8)	94.89(1)	92.75(7)
Cl(1)–Sn(1)–C(9)	102.6(5)	98.6(2)
X(5)···Sn(1)–S(2)	79.6(2)	82.88(6)
X(5)···Sn(1)–S(8)	79.9(2)	82.64(5)
X(5)···Sn(1)–C(9)	87.6(6)	91.2(2)
C(3)–S(2)–Sn(1)	99.0(7)	104.4(3)
C(4)–C(3)–S(2)	119.8(12)	123.4(6)
C(3)–C(4)–X(5)	116.6(14)	114.4(7)
C(4)–X(5)–C(6)	114.7(14)	101.6(5)
C(4)–X(5)–Sn(1)	113.1(8)	96.1(3)
C(6)–X(5)–Sn(1)	110.6(9)	98.2(2)
C(7)–C(6)–X(5)	116.6(14)	115.5(5)
C(6)–C(7)–S(8)	121.7(15)	118.0(5)
C(7)–S(8)–Sn(1)	100.3(6)	104.2(2)
C(10)–C(9)–Sn(1)A/B	125.2(15)/125(3)	115.2(4)
C(9)–C(10)–C(11)A/B	113(2)/126(7)	114.1(6)
C(12)–C(11)–C(10)A/B	109(3)/104(7)	114.3(7)
C(10A)–C(9)–C(10B)	42(3)	

[a] Disorder of *n*-Bu in **1**.

Table 3

Compounds	d(X···Sn)	Δd(X···Sn) [a]	d(Sn–Cl/R_{ax}), d(Sn–Cl/R_{ec})	Δd(Sn–Cl/R_{ax}), Δd(Sn–Cl/R_{ec})	BO(X···Sn) [b]	BO(Sn–Cl/R_{ax}) [b], BO(Sn–Cl/R_{ec})	$\Delta\Sigma(\theta)$ (°)	Conformations [c]	Angle$_{ax}$	Ref.
$O(CH_2CH_2S)_2SnCl_2$	2.359(6)	0.36	2.376(3), 2.346(3)	0.02, −0.014	0.31	0.94, 1.05	60.5	cc	170.9(2)	[3,11]
$O(CH_2CH_2S)_2$Sn*n*-BuCl (**1**)	2.409(7)	0.41	2.407(3), 2.142(15)	0.05, −0.008	0.26	0.85, 1.03	62	bc	169.7(2)	
$O(CH_2CH_2S)_2SnPhCl$	2.41(1)	0.41	2.420(5), 2.110(1)	0.06, −0.04	0.26	0.82, 1.14	62.7	Diplanar	167.3(4)	[6]
$O(CH_2CH_2S)_2SnMeCl$	2.42(2)	0.42	2.413(1), 2.170(4)	0.05, 0.02	0.26	0.85, 0.94	59.8	cc and bc	168.3(5)	[12]
$O(CH_2CH_2S)_2SnPh_2$	2.66(7)	0.66	2.147(7), 2.127(7)	−0.003, −0.023	0.12	1.0, 1.08	35.7	Monoplanar	168.8(3)	[5]
$O(CH_2CH_2S)_2SnMe_2$	2.774(5)	0.77	2.133(8), 2.119(7)	−0.02, −0.03	0.08	1.07, 1.10	25.5	cc	163.6(3)	[12]
$S(CH_2CH_2S)_2SnCl_2$	2.760(3)	0.36	2.392(3), 2.348(3)	0.03, −0.012	0.31	0.91, 1.04	70.1	bc	165.6(1)	[4,11]
$S(CH_2CH_2S)_2$Sn*n*-BuCl (**2**)	2.785(16)	0.38	2.446(15), 2.128(6)	0.09, −0.02	0.29	0.74, 1.07	80.9	bc	170.2(6)	
$S(CH_2CH_2S)_2SnPhCl$	2.806(2)	0.39	2.453(2), 2.129(5)	0.09, −0.02	0.28	0.74, 1.07	73.3	bc	174.2(1)	[10]
$S(CH_2CH_2S)_2SnMeCl$	2.863(1)	0.46	2.444(1), 2.122(3)	0.08, −0.03	0.22	0.77, 1.10	72	bc	168.6(3)	[12]
$S(CH_2CH_2S)_2SnPh_2$	3.24	0.83	2.156(3), 2.139(3)	0.006, −0.01	0.06	0.98, 1.03	31	bc	170.8(1)	[7]
$S(CH_2CH_2S)_2SnMe_2$ [d]	3.514(1)	1.11	2.147(3), 2.134(3)	−0.003, −0.016	0.03	1.0, 1.05	27	bc	169.3(1)	[12]

[a] Standard single-bond distances, d(Sn–O) = 2.00, d(Sn–S) = 2.40, d(Sn–Cl) = 2.36, d(Sn–C) = 2.15 Å.

[b] The Pauling orders were calculated according to $BO = 10^{-1.41(\Delta d)}$.

[c] c, chair; b, boat.

[d] This compound exhibits heptacoordinate tin due to two intermolecular coordinations.

Table 4
Torsion angles

	1	2
S(8)–Sn(1)–S(2)–C(3)	85.0(7)	78.7(4)
Sn(1)–S(2)–C(3)–C(4)	−33.5(19)	−30.6(10)
S(2)–C(3)–C(4)–X(5)	43(3)	53.9(12)
C(3)–C(4)–X(5)–C(6)	−153.9(16)	−140.2(8)
C(4)–X(5)–C(6)–C(7)	97.2(2)	69.5(7)
X(5)–C(6)–C(7)–S(8)	41(3)	55.1(8)
C(6)–C(7)–S(8)–Sn(1)	−24(2)	−48.5(7)
C(7)–S(8)–Sn(1)–S(2)	−68.9(8)	−58.0(3)

The anomalous situation observed in **1**, that is the boat–chair conformation instead of the chair–chair, may be due to steric effects of the *n*-butyl group. This steric effect is in agreement with the fact that the largest of the equatorial angles at tin is exocyclic, and it has been observed that in rings with a chair–chair conformation the endocyclic angle is the largest of the equatorial angles at tin. In compounds with a boat–chair ring, one of the *endo–exo* equatorial angles is the largest of the angles around tin.

In conclusion, it is possible to establish from the obtained results, that in addition to the four electronic factors mentioned by Dräger, a steric factor should be considered in controlling the proposed 'path' process. It is still not easy to predict the preferred conformation for the metallocane eight-membered rings, and it is necessary to add more experimental and theoretical research.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CSD-117981 for compound **1** and CSD-117982 for compound **2**.

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