Diorganotin(IV) compounds containing 2-(Et$_2$NCH$_2$)C$_6$H$_4$ moieties: Configurational stability in solution and solid state structures

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ABSTRACT

Hypercoordinated diorganotin(IV) dichloride, [2-(Et$_2$NCH$_2$)C$_6$H$_4$]$_2$SnCl$_2$ (**1**), was prepared by reacting [2-(Et$_2$NCH$_2$)C$_6$H$_4$]Li with SnCl$_4$. Halide-exchange reactions between **1** and the appropriate potassium halides gave [2-(Et$_2$NCH$_2$)C$_6$H$_4$]$_2$SnX$_2$ [X = F (**2**), Br (**3**), I (**4**)]. Reaction of **1** with excess of Na$_2$S gave the *cyclo*-[{2-(Et$_2$NCH$_2$)C$_6$H$_4$}$_2$SnS]$_2$ (**5**). The solution behavior of the title compounds in solution was investigated by multinuclear (^{1}H, ^{13}C, ^{19}F and ^{119}Sn) NMR spectroscopy, including variable temperature studies. Single-crystal X-ray diffraction analysis revealed for all compounds intramolecular N → Sn coordination thus resulting in distorted octahedral (C,N)$_2$SnX$_2$ configurations. Planar chirality is observed as result of the non-planarity of the SnC$_3$N rings; all compounds, however, crystallizing as racemates. The isomers are linked by extensive hydrogen bonds to give different supramolecular architectures in the crystals of compounds **1**, **3** and **4**.

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1. Introduction

Several diorganotin(IV) dihalides containing pendant arm ligands with nitrogen as donor atom, such as 2-(Me$_2$NCH$_2$)C$_6$H$_4$ [1–9] or related organic compounds [1,3,10–15], have been investigated so far both in solution and in the solid state. For all [2-(Me$_2$NCH$_2$)C$_6$H$_4$]$_2$SnX$_2$ (X = halogen) both nitrogen atoms of a molecular unit are strongly coordinated to the metal atom resulting in octahedral *cis*-X$_2$-*cis*-N$_2$-*trans*-C$_2$Sn configurations. By contrast, the related diorganotin(IV) dihalides [Me$_2$N(CH$_2$)$_3$]$_2$SnF$_2$ and [Me$_2$N(CH$_2$)$_2$CMe$_2$]$_2$SnCl$_2$ were found to exhibit octahedral *all-trans*-(C,N)$_2$SnX$_2$ configurations [13,15]. Protonation of one amine nitrogen atom provides ionic compounds of the type [{2-(Me$_2$N$^+$HCH$_2$)C$_6$H$_4$}{2-(Me$_2$NCH$_2$)C$_6$H$_4$}SnX$_2$][{2-(Me$_2$NCH$_2$)-C$_6$H$_4$}SnX$_4$] (X = Cl [16], Br [17]) [trigonal bipyramidal (C,N)CSnX$_2$ configuration for the cation], while hydrolysis can result in the mixed oxo-hydroxy species [{2-(Me$_2$NCH$_2$)C$_6$H$_4$}$_2$Sn(OH)]$_2$O [(C,N)$_2$SnO$_2$ core] [18]. Only a few organotin(IV) sulfides with 2-(Me$_2$NCH$_2$)C$_6$H$_4$ groups have been reported so far; they include the dimeric *cyclo*-[{2-(Me$_2$NCH$_2$)C$_6$H$_4$}BuSnS]$_2$ [(C,N)CSnS$_2$ core] and *cyclo*-[{2-(Me$_2$NCH$_2$)C$_6$H$_4$}$_2$SnS]$_2$ [(C,N)$_2$SnS$_2$ core] with planar Sn$_2$S$_2$ rings [8], and the unusual tetranuclear monoorganotin(IV) derivative, [{{[2-(Me$_2$NCH$_2$)C$_6$H$_4$]SnS}$_2$]$_2$S$_2$ [(C,N)SnS$_3$ core] [19]. Other related dinuclear cyclic sulfides, i.e. [MeN(CH$_2$CH$_2$CH$_2$)$_2$SnS]$_2$

[(C,N,C)SnS$_2$ core] [20], *trans*-[{Me$_2$N(CH$_2$)$_2$CMe$_2$}PhSnS]$_2$ [(C,N)-CSnS$_2$ core] [21], [{CH$_2$(Et)NCH$_2$CH$_2$CH$_2$}$_2$SnS]$_2$ [(C,N,N,C)SnS$_2$ core] [22], [{Me$_2$N(CH$_2$)$_3$}$_2$SnS]$_2$ [(C,N)$_2$SnS$_2$ core] [23], were also structurally characterized. They all exhibit planar Sn$_2$S$_2$ rings with the tin atoms being five- or six-coordinate. In some cases the identity of the organic ligand attached to the tin atom was found to produce structural changes, e.g. for [{8-NC$_9$H$_6$(Me$_3$Si)CH}$_2$SnS]$_2$ the bulkiness of the organic ligand prevents the coordination of both nitrogen atoms to the metal atom and the *trans* isomer with a (C,N)CSnS$_2$ core was isolated [24], while a dimer–trimer equilibrium in solution was observed for [MeN(CH$_2$CH$_2$CH$_2$)SnS]$_2$ [20].

Some transition metal derivatives containing the 2-(Et$_2$NCH$_2$)C$_6$H$_4$ group were previously reported [25–27] and we decided to use this moiety to investigate potential structural changes in main group organometallic compounds induced by the presence of different organic groups on the nitrogen atom. We report here on the synthesis and structural characterization of [2-(Et$_2$NCH$_2$)-C$_6$H$_4$]$_2$SnX$_2$ [X = Cl (**1**), F (**2**), Br (**3**), I (**4**)] as well as *cyclo*-[{2-(Et$_2$-NCH$_2$)C$_6$H$_4$}$_2$SnS]$_2$ (**5**).

2. Results and discussion

2.1. Preparation

The diorganotin(IV) dihalides, [2-(Et$_2$NCH$_2$)C$_6$H$_4$]$_2$SnX$_2$ [X = Cl (**1**), F (**2**), Br (**3**), I (**4**)], were prepared in good yields according to Scheme 1. The reaction between [2-(Et$_2$NCH$_2$)C$_6$H$_4$]Li and SnCl$_4$ in 2:1 molar ratio, under inert atmosphere, afforded

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NEt$_2$

Br

↓ BuLi

[2-(Et$_2$NCH$_2$)C$_6$H$_4$]Li

↓ SnCl$_4$

[2-(Et$_2$NCH$_2$)C$_6$H$_4$]$_2$SnCl$_2$
(1)

KX ↙   ↘ Na$_2$S

[2-(Et$_2$NCH$_2$)C$_6$H$_4$]$_2$SnX$_2$ [{2-(Et$_2$NCH$_2$)C$_6$H$_4$}$_2$SnS]$_2$
X = F (2), Br (3), I (4)   (5)

Scheme 1.
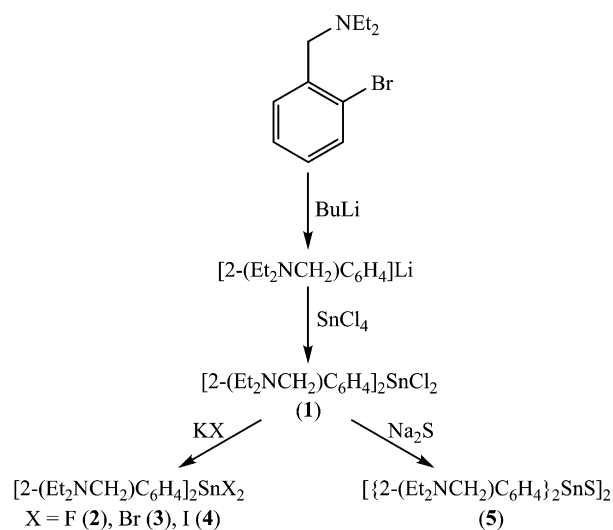
[2-(Et$_2$NCH$_2$)C$_6$H$_4$]$_2$SnCl$_2$ (**1**), which in turn was used in halide exchange reactions with the appropriate potassium halides, in a two-layer solvent system (H$_2$O/MeOH/CH$_2$Cl$_2$), to obtain the corresponding dihalides **2**–**4**. The reaction of **1** with excess of Na$_2$S, in H$_2$O/CH$_2$Cl$_2$ mixture provided of cyclo-[{2-(Et$_2$NCH$_2$)C$_6$H$_4$}$_2$SnS]$_2$ (**5**).

The compounds were obtained as air-stable, colorless (**1**–**3**, **5**) or yellow (**4**) crystalline solids by re-crystallization from CH$_2$Cl$_2$/n-hexane solvent mixture. They are soluble in organic solvents such as CH$_2$Cl$_2$, CHCl$_3$.

2.2. Crystal and molecular structure of [2-(Et$_2$NCH$_2$)C$_6$H$_4$]$_2$SnX$_2$ [X = Cl (1), F (2), Br (3), I (4)] and cyclo-[{2-(Et$_2$NCH$_2$)C$_6$H$_4$}$_2$SnS]$_2$ (5)

Single crystals suitable for X-ray diffraction studies were obtained from CH$_2$Cl$_2$/n-hexane solvent mixtures. Selected inter-atomic distances and angles are listed in Tables 1 and 2. The crystals of all five compounds each consist of discrete monomeric molecular units separated by normal van der Waals distances between heavy atoms. For compounds **1** and **3** two independent molecules (**1a**/**1b** and **3a**/**3b**, respectively) are present in the unit cell.

The molecular structures of compounds **1**–**5** feature some common patterns:

(i) In all cases, the organic groups are in trans and both nitrogen atoms of the diethylaminomethyl-substituents are strongly coordinated to the tin atom (c.f. Σr_{cov}(Sn,N) 2.1 Å; Σr_{vdW}(Sn,N) 3.74 Å [28]) in trans with respect to a halogen or a sulfur atom, thus resulting in hexacoordinated tin atoms;

(ii) The five-membered SnC$_3$N ring is not planar but folded along the Sn(1)···C$_{methylene}$ axis, a behavior which induces planar chirality [the aromatic ring and the nitrogen atom being the chiral plane and the pilot atom] [29], as described for related organotin compounds [7,8,17–19,30,31] and indeed all compounds reported here crystallize as racemates. The ORTEP diagrams for the isomers $S_{N1}S_{N1'}$-**1a**, $S_{N1}R_{N2}$-**2**, $R_{N1}R_{N1'}$-**3a**, $S_{N1}S_{N2}$-**4** and $S_{N1}S_{N2}/R_{N1'}R_{N2'}$-**5** are shown in Figs. 1 and 2.

The resulting distorted octahedral cis-X$_2$-cis-N$_2$-trans-C$_2$Sn configurations (X = halogen, sulfur; hypercoordinated 12-Sn-6 species, [32,33]) in compounds **1**–**5** are similar to those found for the analogous derivatives containing 2-(Me$_2$NCH$_2$)C$_6$H$_4$ moieties [7,8]. The main difference between the independent molecules in the crystal of **1** and **3** resides in different intramolecular N → Sn interactions, i.e. 2.771(4)/2.685(3) Å in **1a**/**1b** and 2.700(6)/2.788(7) Å in **3a**/**3b**, respectively. This difference is also reflected in the length of the corresponding trans Sn–halogen bonds, stronger N → Sn interaction corresponding to longer Sn–X bonds (Table 1). A similar effect is also noted within the molecule of the diiodide **4**, for which the two N → Sn interactions are non-equivalent (Table 1). A weakening of the N → Sn interactions is observed by replacing at nitrogen

Table 1
Selected interatomic distances (Å) and angles (°) in compounds **1**–**4**.

	1a, X = Cl[a]	**1b**, X = Cl[a]	**3a**, X = Br[a]	**3b**, X = Br[a]		**2**, X = F	**4**, X = I
Sn(1)–C(1)	2.116(4)		2.139(7)		Sn(1)–C(1)	2.117(4)	2.129(6)
Sn(2)–C(12)		2.131(4)		2.111(7)	Sn(1)–C(12)	2.111(4)	2.128(6)
Sn(1)–X(1)	2.4206(12)		2.6018(11)		Sn(1)–X(1)	1.994(2)	2.7734(8)
Sn(2)–X(2)		2.4529(12)		2.5536(11)	Sn(1)–X(2)	1.976(3)	2.7843(8)
Sn(1)–N(1)	2.771(4)		2.700(6)		Sn(1)–N(1)	2.673(3)	2.786(6)
Sn(2)–N(2)		2.685(3)		2.788(7)	Sn(1)–N(2)	2.655(3)	2.937(6)
C(1)–Sn(1)–C(1′)	151.7(2)		161.9(4)		C(1)–Sn(1)–C(12)	153.29(17)	144.5(2)
C(12)–Sn(2)–C(12″)		161.6(2)		151.9(4)			
N(1)–Sn(1)–X(1)	169.85(8)		167.04(12)		N(1)–Sn(1)–X(A)[b]	168.24(11)	170.08(13)
N(2)–Sn(2)–X(2)		167.72(8)		170.22(14)	N(2)–Sn(1)–X(B)[b]	164.32(10)	170.41(12)
C(1)–Sn(1)–X(1)	98.89(11)		95.51(19)		C(1)–Sn(1)–X(1)	97.42(15)	103.15(18)
C(1)–Sn(1)–X(1′)	100.98(10)		97.15(18)		C(1)–Sn(1)–X(2)	102.28(14)	100.33(19)
C(1)–Sn(1)–N(1)	72.02(11)		72.7(2)		C(1)–Sn(1)–N(1)	73.21(15)	72.3(2)
C(1)–Sn(1)–N(1′)	89.12(11)		95.5(2)		C(1)–Sn(1)–N(2)	90.26(15)	85.2(2)
C(12)–Sn(2)–X(2)		95.85(11)		100.83(18)	C(12)–Sn(1)–X(1)	99.98(14)	103.25(19)
C(12)–Sn(2)–X(2″)		96.92(11)		99.0(2)	C(12)–Sn(1)–X(2)	97.95(15)	102.43(18)
C(12)–Sn(2)–N(2)		73.15(12)		72.1(2)	C(12)–Sn(1)–N(1)	91.33(14)	87.2(2)
C(12)–Sn(2)–N(2″)		95.07(12)		88.9(2)	C(12)–Sn(1)–N(2)	73.37(14)	71.3(2)
X(1)–Sn(1)–N(1′)	87.12(8)		85.14(12)		X(A)–Sn(1)–N(2)[b]	79.30(10)	82.45(12)
N(1)–Sn(1)–N(1′)	97.01(10)		101.12(17)		N(2)–Sn(1)–N(1)	107.31(10)	103.11(18)
X(1)–Sn(1)–X(1′)	90.36(7)		91.08(6)		N(1)–Sn(1)–X(B)[b]	85.57(10)	84.19(13)
					X(1)–Sn(1)–X(2)	89.65(11)	91.26(2)
X(2)–Sn(2)–N(2″)		83.97(8)		88.09(14)			
N(2)–Sn(2)–N(2″)		102.11(10)		95.7(2)			
X(2)–Sn(2)–X(2″)		92.15(7)		89.58(6)			

[a] Symmetry equivalent positions (1 − x, y, 0.5 − z) and (−x, y, 0.5 − z) for **1**, and (−x, y, 1.5 − z) and (1 − x, y, 1.5 − z) for **3** are given by "prime" and "double prime", respectively.
[b] X(A) and X(B) are F(1) and F(2) for **2**, and I(2) and I(1) for **4**.

Table 2
Selected interatomic distances (Å) and angles (°) in compound **5**.[a]

Sn(1)–C(1)	2.126(3)	Sn(1)–C(12)	2.140(3)
Sn(1)–N(1)	2.932(4)	Sn(1)–N(2)	3.036(2)
Sn(1)–S(1)	2.4201(8)	Sn(1)–S(1′)	2.4376(8)
C(1)–Sn(1)–C(12)	123.87(11)		
N(1)–Sn(1)–S(1′)	166.58(9)	N(2)–Sn(1)–S(1)	165.28(5)
C(1)–Sn(1)–S(1)	114.98(8)	C(12)–Sn(1)–S(1)	106.56(8)
C(1)–Sn(1)–S(1′)	105.03(9)	C(12)–Sn(1)–S(1′)	110.03(8)
C(1)–Sn(1)–N(1)	68.77(12)	C(12)–Sn(1)–N(1)	82.89(13)
C(1)–Sn(1)–N(2)	78.54(9)	C(12)–Sn(1)–N(2)	67.31(8)
N(1)–Sn(1)–N(2)	110.52(9)	S(1)–Sn(1)–S(1′)	91.46(3)
N(1)–Sn(1)–S(1)	81.07(6)	N(2)–Sn(1)–S(1′)	78.82(8)
Sn(1)–S(1)–Sn(1′)	88.54(3)		

[a] Symmetry equivalent positions (0.5 − x, 0.5 − y, 1 − z) are given by "prime".

atom the methyl by ethyl substituents (c.f. [2-$(Me_2NCH_2)C_6H_4]_2SnX_2$: Sn–N 2.508(2)/2.606(2) Å, X = F; 2.620(2) Å, X = Cl [7]; 2.581(5)/2.600(5) Å, X = Br [6], and 2.572(5)/2.677(6) Å, X = I [7], with molecular parameters listed in Table 1). This behavior is due to combined electronic and steric effects induced by bulkier ethyl groups.

The molecular structure of the sulfide **5** is very similar to that of the related cyclo-[{2-$(Me_2NCH_2)C_6H_4]_2SnS]_2$ [8]. The two [2-$(Et_2NCH_2)C_6H_4]_2$Sn moieties are bridged by two sulfur atoms resulting in a planar four-membered Sn_2S_2 ring (Fig. 2). As in the case of the above diorganotin dihalides, the intramolecular N → Sn distances in **5** [2.932(4)/3.036(2) Å] are non-equivalent and considerably longer than in the methyl-substituted analogue [2.816(4)/2.855(6) Å] [8]. However, the Sn–S bonds are almost equivalent in **5** [Sn(1)–S(1) 2.4201(8) Å, Sn(1)–S(1′) 2.4376(8) Å]
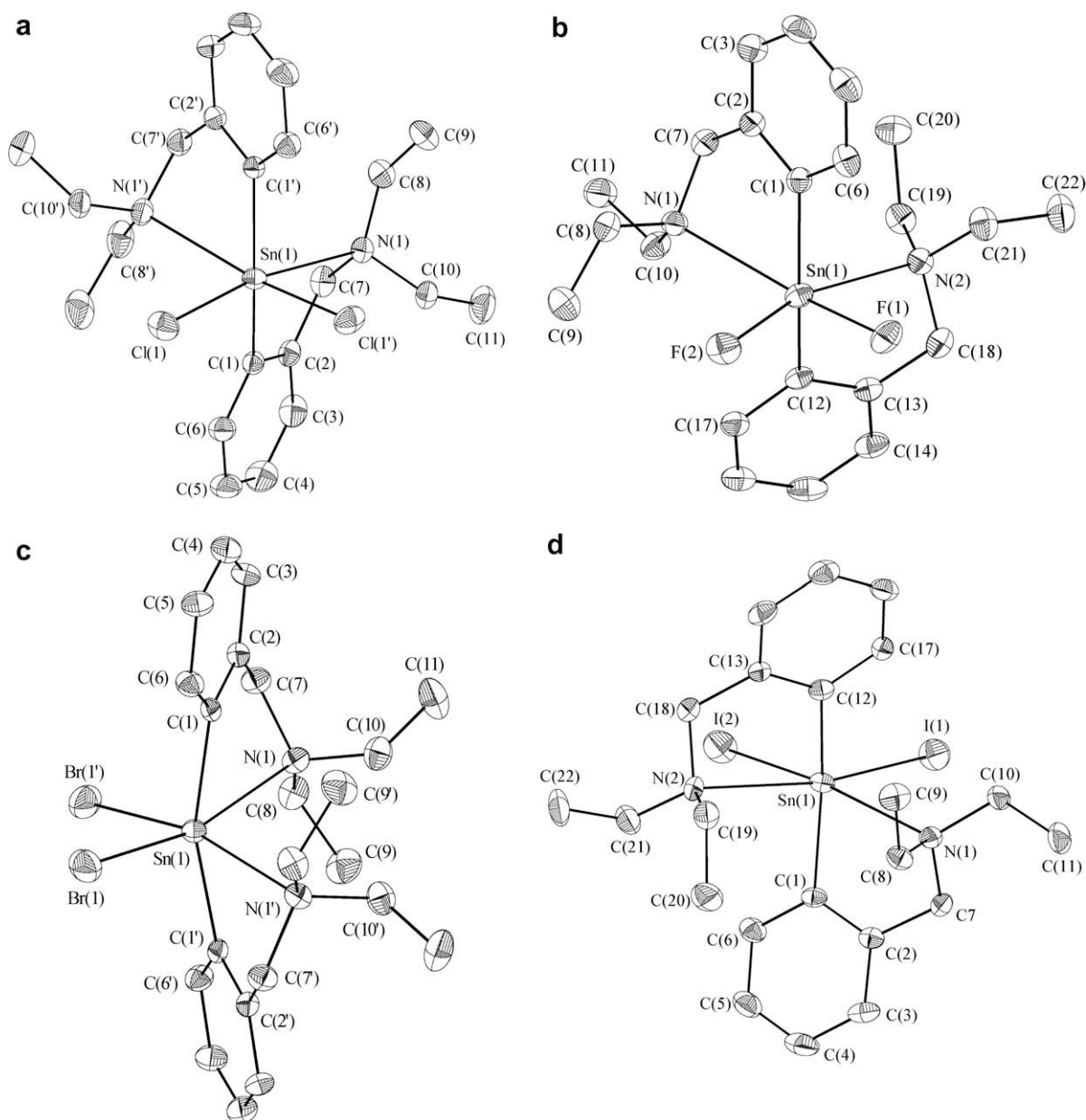

Fig. 1. ORTEP representation at 30% probability and atom numbering scheme for (a) the $S_{N1}S_{N1'}$-**1a** isomer; (b) the $S_{N1}R_{N2}$-**2** isomer; (c) the $R_{N1}R_{N1'}$-**3a** isomer; and (d) the $S_{N1}S_{N2}$-**4** isomer [symmetry equivalent atoms (1 − x, y, 0.5 − z) for **1a**, and (−x, y, 1.5 − z) for **3a** are given by "prime"; hydrogen atoms are omitted for clarity].
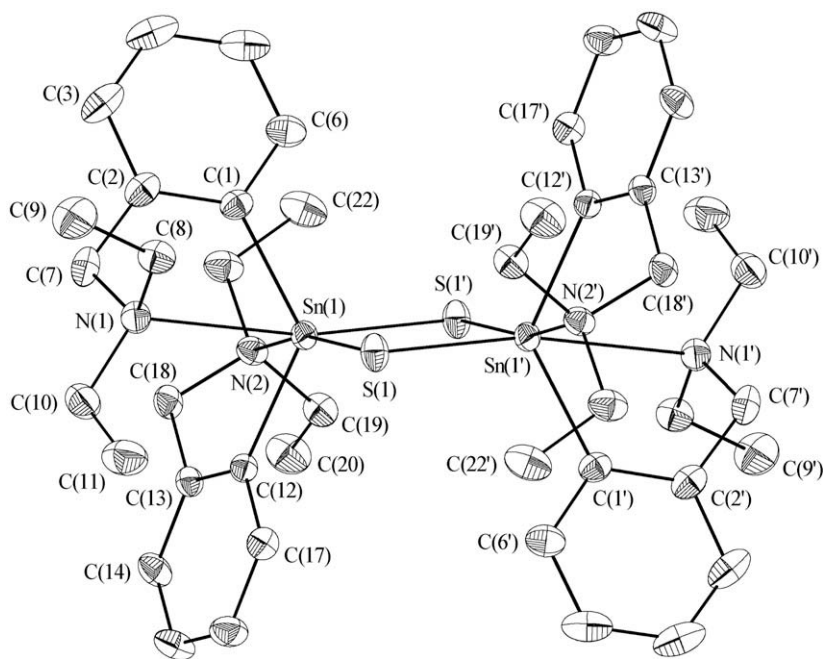
Fig. 2. ORTEP representation at 20% probability and atom numbering scheme for the $S_{N1}S_{N2}/R_{N1'}R_{N2'}$-**5** isomer [symmetry equivalent atoms $(0.5 − x, 0.5 − y, 1 − z)$ are given by "prime"; hydrogen atoms are omitted for clarity].

and only slightly shorter than in the methyl derivative [2.449(2)/ 2.466(2) Å] [8]. The octahedral $(C,N)_2SnS_2$ moiety in **5** is more distorted than in the methyl derivative, as reflected by the *trans* angles: C(1)–Sn(1)–C(12) 123.87(11)°, N(1)–Sn(1)–S(1′) 166.58(9)° and N(2)–Sn(1)–S(1) 165.28(5)° versus 133.4(2)°, 170.74(11)° and 170.18(11)° for the corresponding angles in *cyclo*-[{2-$(Me_2NCH_2)C_6H_4$}$_2SnS$]$_2$ [8].

A closer check of the crystal structures revealed that for the diorganotin difluoride **2** and the diorganotin sulfide **5** there are no intermolecular X···H distances shorter than the sum of van der Waals radii for the corresponding atoms (cf. $\Sigma r_{vdW}(F,H)$ ca. 2.55 Å; $\Sigma r_{vdW}(S,H)$ ca. 3.05 Å [28]). By contrast, different types of supramolecular architectures are built in the crystals of compounds **1**, **3** and **4** through weak intermolecular X···H contacts
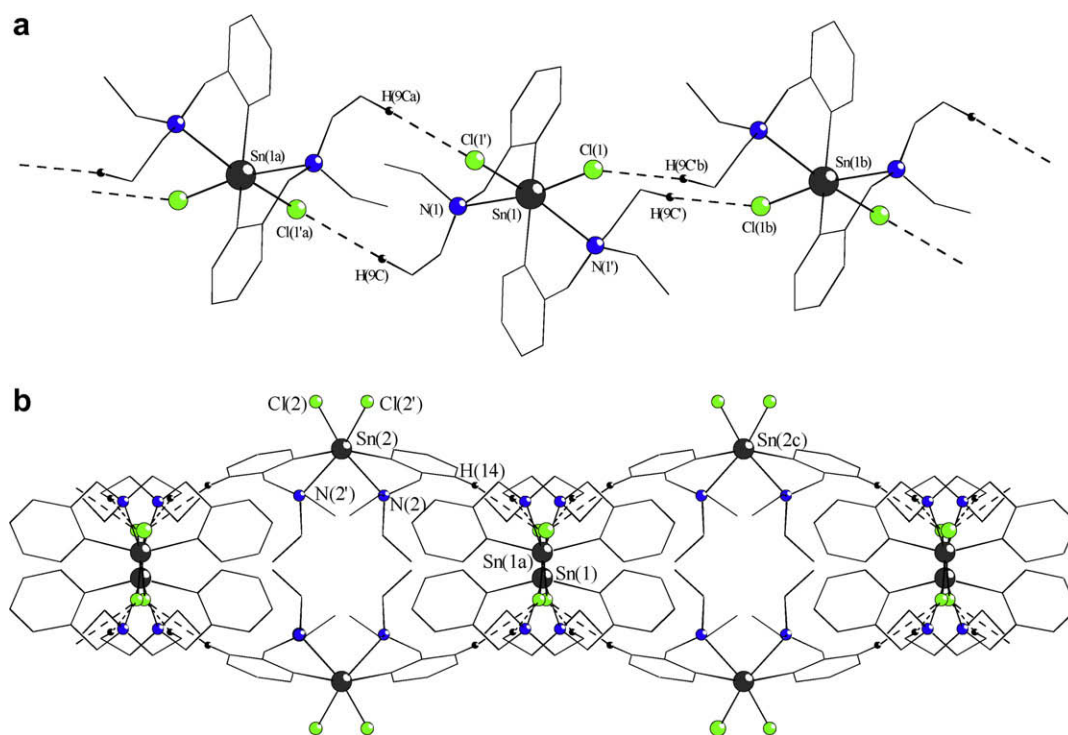

Fig. 3. (a) View of the chain polymer based on chlorine–hydrogen contacts between alternating $S_{N1}S_{N1'}$- and $R_{N1}R_{N1'}$-**1a** isomers; (b) view along *c*-axis of the layer based on chlorine–hydrogen contacts in the crystal of **1** [only hydrogens involved in intermolecular contacts are shown; symmetry equivalent atoms $(1 − x, 1 − y, 1 − z)$, $(1 − x, 1 − y, −z)$ and $(1 + x, y, z)$ are given by "a", "b" and "c", respectively].

between the molecular units (cf. Σr_{vdW}(Cl,H) ca. 3.0 Å; Σr_{vdW}(Br,H) ca. 3.15 Å; Σr_{vdW}(I,H) ca. 3.35 Å [28]). Thus, in the crystal of the diorganotin dichloride **1** polymeric chains are built from alternating $S_{N1}S_{N1'}$- and $R_{N1}R_{N1'}$-**1a** isomers doubly connected through Cl···H$_{methyl}$ contacts [Cl(1)···H(9Cb) 2.94 Å] (Fig. 3a). Parallel chains are further connected by alternating $S_{N2}S_{N2'}$- and $R_{N2}R_{N2'}$-**1b** isomers using aryl protons [Cl(1')···H(14) 2.95 Å], with the chlorine atoms of the **1b** molecules oriented on both sides of the resulting 2D layer network without being involved in any intermolecular interactions (Fig. 3b).

The isomorphous diorganotin dibromide **3** exhibit a similar array in the crystal, *i.e.* polymeric chains of a alternating $S_{N2}S_{N2'}$- and $R_{N2}R_{N2'}$-**3b** isomers [Br(2)···H(22A)$_{methyl}$ 2.98 Å] are connected into a layer by molecules **3a** [Br(2)···H(3)$_{aryl}$ 3.00 Å] (Fig. 4a), but in this case additional weak inter-layer Br(1)···H(11B)$_{methyl}$ contacts (3.13 Å) results in a 3D supramolecular architecture (Fig. 4a).

For the diorganotin diiodide **4** the crystal contains polymeric chains of alternating $S_{N1}S_{N2}$ and $R_{N1}R_{N2}$ isomers connected through weak contacts which involve only one halogen of the molecular unit and a hydrogen atom from the methylene group of a pendant
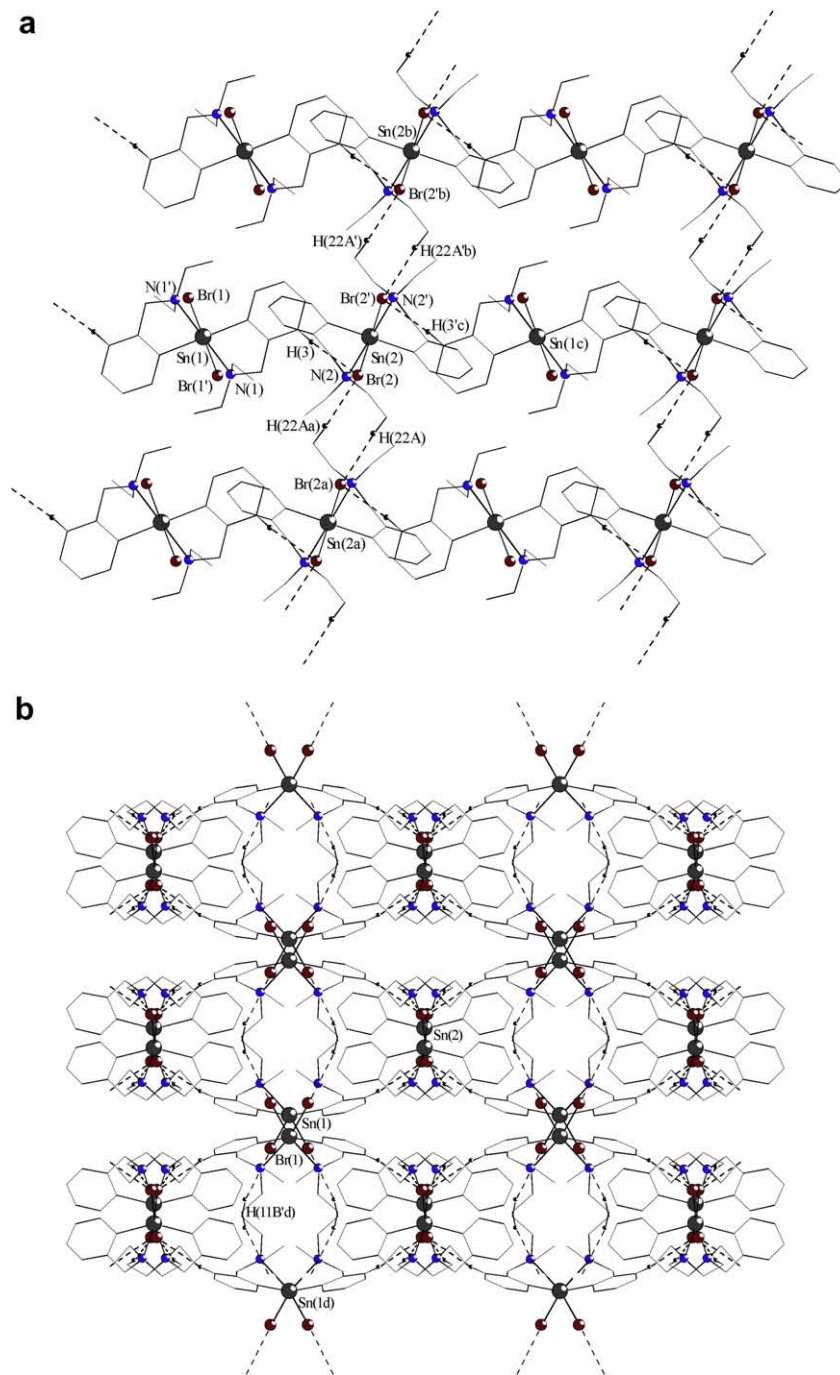

Fig. 4. (a) View along *b*-axis of the layer based on bromine–hydrogen contacts; (b) view along *c*-axis of the 3D architecture based on bromine–hydrogen contacts in the crystal of **3** [only hydrogens involved in intermolecular contacts are shown; symmetry equivalent atoms $(1 - x, 1 - y, 2 - z)$, $(1 - x, 1 - y, 1 - z)$, $(1 + x, y, z)$ and $(x, -1 + y, z)$ are given by "a", "b", "c" and "d", respectively].
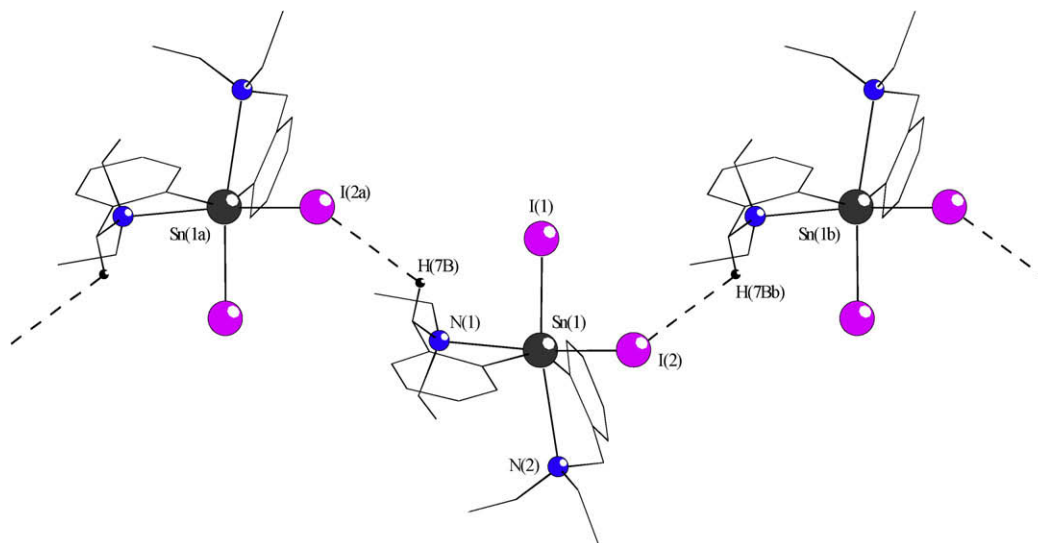
Fig. 5. View along *a*-axis of the chain polymer based on iodine–hydrogen contacts in the crystal of **4** [only hydrogens involved in intermolecular contacts are shown; symmetry equivalent atoms (*x*, 0.5 − *y*, 0.5 + *z*) and (*x*, 0.5 − *y*, −0.5 + *z*) are given by "a" and "b", respectively].

arm [I(2)···H(7Bb) 3.30 Å] (Fig. 5), with no further inter-chain interactions.

2.3. NMR spectra

The assignment of the resonances observed in ^1H and ^{13}C NMR spectra is based on 2D experiments and tin–carbon coupling constants. A numbering diagram is depicted in Scheme 2.

In solution, the tin atoms in compounds **1**–**5** show distorted *cis*-X_2-*cis*-N_2-*trans*-C_2Sn octahedral configurations similar to those observed in the solid state.

Notably, the configurational stability of the tin atoms depend on the identity of the halogen atoms, respectively, sulfur atoms attached, as it is indicated by the temperature-dependent ^1H NMR spectra. Thus, at −20 °C, the NCH_2 protons of all compounds exhibit well-resolved AB-type resonances indicating stereochemical rigidity on the ^1H NMR time-scale. On raising the temperature coalescence phenomena were observed, *i.e.* the AB-type resonances merged into singlet resonances. From the coalescence temperatures (**2**, 20 °C; **3**, 50 °C; **4**, 40 °C; **5**, −10 °C) the free activation energies $\Delta G^{\ddagger}$ [34] for the corresponding dynamic processes were calculated to amount to 14.2 (**2**), 15.1 (**3**), 14.8 (**4**), and 12.7 (**5**) kcal mol^{-1}. The ^{13}C NMR spectra of compounds **1**–**5** indicate, on the corresponding time scale, the equivalence of the organic groups attached to tin since only one set of resonances was observed.

The ^{119}Sn NMR spectra at room temperature of compounds each show single resonances at δ −217 (**1**), δ −364 (**2**), δ −304 (**4**) and δ −103 ppm (**5**) that are typical for hexacoordinated organotin(IV) compounds. They are downfield shifted compared to the related dimethylamino-substituted compounds (c.f. [2-$(Me_2NCH_2)C_6H_4]_2SnX_2$: δ_{Sn} −386.7 (t, $^1J_{SnF}$ 2663 Hz), −260.7, and
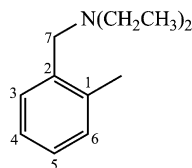
−346.9 ppm for X = F, Cl, and I [7]; *cyclo*-[{2-$(Me_2NCH_2)C_6H_4\}_2SnS]_2$]: δ_{Sn} −137.2 [8]).

The equivalence of the fluorine atoms in **2**, on the corresponding time scales, is reflected by a triplet ^{119}Sn resonance (δ −363.8 ppm, $^1J_{F,Sn}$ 2627 Hz) and a singlet ^{19}F resonance surrounded by tin satellites (δ −180.8 ppm, $^1J_{FSn}$ 2635 Hz).

3. Conclusions

New diorganotin(IV) dihalides, [2-$(Et_2NCH_2)C_6H_4]_2SnX_2$ [X = Cl (**1**), F (**2**), Br (**3**), I (**4**)], and the sulfide *cyclo*-[{2-$(Et_2NCH_2)C_6H_4\}_2SnS]_2$ (**5**) were prepared and characterized. The compounds exhibit similar structures in solution and in the solid state as the related hypercoordinated derivatives containing 2-$(Me_2NCH_2)C_6H_4$ moieties, the main difference being the weakening of the intramolecular N → Sn interactions due to combined electronic and steric effects of the ethyl groups on nitrogen. In the solid state, all compounds crystallize as racemates due to chiral planarity induced by the intramolecular N → Sn interactions. While no intermolecular interactions are established for **2** and **5**, in the crystals of **1**, **3** and **4** weak intermolecular halogen–hydrogen contacts result in different supramolecular architectures.

4. Experimental

4.1. Materials and procedures

All manipulations were carried out under an inert atmosphere of argon (Linde, 99.999%) by using Schlenk techniques. Solvents were dried by standard procedures and were freshly distilled prior to use. Starting materials such as $SnCl_4$, KF, KI, KBr, $Na_2S \cdot xH_2O$, 1-bromo-2-(bromomethyl)benzene, *N,N*-diethylamine and *n*-butyllithium were commercially available. (2-Bromobenzyl)diethylamine was prepared according to a published method [26]. Room-temperature ^1H and ^{13}C spectra were recorded in dried CDCl$_3$ with a Bruker Avance DRX 400 instrument for compound **1** (including 2D experiments) and with a Varian Gemini 300S instrument for compounds **2**–**5**, respectively. Variable-temperature ^1H spectra were recorded with a Varian Unity 300 instrument. ^{19}F and ^{119}Sn spectra were recorded in dried CDCl$_3$ with a Bruker DPX 300 instrument. The chemical shifts are reported in ppm relative to the residual peak of solvent [ref. CHCl$_3$: $\delta(^1H)$ 7.26, $\delta(^{13}C)$

Scheme 2.

77.0 ppm] for ^{1}H and ^{13}C NMR spectra, and relative to CFCl$_3$ for ^{19}F NMR and neat SnMe$_4$ for ^{119}Sn NMR spectra. Elemental analyses were performed by Facultatea de Farmacie, Universitatea de Medicina si Farmacie "Iuliu Hatieganu", Cluj-Napoca (Romania) on a VarioEL analyzer.

4.2. Synthesis of [2-(Et$_2$NCH$_2$)C$_6$H$_4$]$_2$SnCl$_2$ (1)

A solution of BuLi in hexane (20.86 ml, 1.6 M) was added dropwise to a stirred solution of (2-bromobenzyl)diethylamine (8.08 g, 16.69 mmol) in 150 ml anhydrous hexane, at room temperature, under argon. After the reaction mixture had been stirred for 24 h, a white precipitate deposited that was filtered and washed with 3×30 ml hexane. The solid [2-(Et$_2$NCH$_2$)C$_6$H$_4$]Li was suspended in 50 ml hexane and added dropwise, under stirring, to a cooled (−78 °C) solution of SnCl$_4$ (3.25 g, 12.47 mmol, 1.473 ml) in 200 ml hexane. After the addition had been completed, the reaction mixture was stirred for a further hour at −78 °C and was then slowly warmed to room temperature. The solvent was removed in vacuum to give a solid residue. After CH$_2$Cl$_2$ had been added to the latter and the resulting mixture had been stirred and filtered, the volume of the clear filtrate was concentrated and cooled at −20 °C to give the title compound as colorless crystals. Yield: 2.89 g (45%). M.p. 163 °C. Anal. Found: C, 51.16; H, 5.94; N, 5.27. Calc. for C$_{22}$H$_{32}$Cl$_2$N$_2$Sn: C, 51.40; H, 6.27; N, 5.45%. ^{1}H NMR (27 °C): δ 0.72t (12H, N–CH$_2$CH$_3$, $^3J_{HH}$ 7.1 Hz), 2.59 m (8H, N–CH$_2$CH$_3$), AB spin system with A at δ 3.58 and B at δ 3.92 ppm (4H, H_7, $^2J_{HH}$ 14.0 Hz), 7.19d (2H, H_3, $^3J_{HH}$ 6.9, $^4J_{SnH}$ 44.8 Hz), 7.40 m (4H, $H_{4,5}$), 8.27d (2H, H_6, $^3J_{HH}$ 6.9, $^3J_{SnH}$ 106.0 Hz). ^{13}C NMR (27 °C): δ 8.20 (N–CH$_2$CH$_3$), 44.82 (N–CH$_2$CH$_3$), 58.65 (C_7, $^2J_{SnC}$ 41.9 Hz), 128.24 ($^3J_{CSn}$ 102.8 Hz), 128.33 ($^3J_{CSn}$ 100.9 Hz) ($C_{3,5}$), 130.30 (C_4), 135.46 (C_6, $^2J_{CSn}$ 57.3 Hz), 141.03 (C_2, $^2J_{CSn}$ 79.2 Hz), 141.38 (C_1). ^{119}Sn NMR (20 °C): δ −217.

4.3. Synthesis of [2-(Et$_2$NCH$_2$)C$_6$H$_4$]$_2$SnF$_2$ (2)

The dichloride 1 (0.5 g, 0.97 mmol) was dissolved in CH$_2$Cl$_2$ (20 ml) and a saturated aqueous solution of KF was added in large excess. The obtained mixture was stirred for 2 h at room temperature. The organic layer was separated and the water one was washed with 3×5 ml CH$_2$Cl$_2$. The organic solution was dried over anhydrous Na$_2$SO$_4$, then the solvent was removed in vacuum. The obtained white residue was recrystallized from CH$_2$Cl$_2$/n-hexane (1:4, v/v) mixture to give the title compound as colorless crystals. Yield: 0.29 g (62%). M.p. 187 °C. Anal. Found: C, 54.56; H, 6.94; N, 5.47. Calc. for C$_{22}$H$_{32}$F$_2$N$_2$Sn: C, 54.91; H, 6.70; N, 5.82%. ^{1}H NMR (24 °C): δ 0.89t (12H, N–CH$_2$CH$_3$, $^3J_{HH}$ 6.8 Hz), 2.58s,br (8H, N–CH$_2$CH$_3$), 3.70s,br (4H, H_7), 7.16 m (2H, H_3, $^4J_{SnH}$ 40.0 Hz), 7.36 m (4H, $H_{4,5}$), 8.09 m (2H, H_6, $^3J_{SnH}$ 92.8 Hz). ^{1}H NMR (−40 °C): δ AB spin system with A at δ 3.49 and B at δ 3.70 ppm (H_7, $^2J_{HH}$ 14.2 Hz). ^{13}C NMR (26 °C): δ 8.51 (N–CH$_2$CH$_3$), 45.63 (N–CH$_2$CH$_3$), 59.17 (C_7, $^2J_{SnC}$ 48.7 Hz), 127.78 ($^3J_{CSn}$ 97.9 Hz), 127.99 ($^3J_{CSn}$ 96.6/100.7 Hz) ($C_{3,5}$), 130.01 (C_4, $^4J_{CSn}$ 17.6 Hz), 135.92 (C_6, $^2J_{CSn}$ 47.8 Hz), 140.14t (C_1, $^2J_{CF}$ 19.8 Hz), 141.24t (C_2, $^3J_{CF}$ 1.7, $^2J_{CSn}$ 68.8 Hz). ^{19}F NMR (20 °C): δ −180.8 ($^1J_{SnF}$ 2635 Hz). ^{119}Sn NMR (20 °C): δ −364t ($^1J_{SnF}$ 2627 Hz).

4.4. Synthesis of [2-(Et$_2$NCH$_2$)C$_6$H$_4$]$_2$SnBr$_2$ (3)

Prepared and worked up as for compound 2, from 1 (0.5 g, 0.97 mmol) and excess of a saturated aqueous solution of KBr. Yield: 0.29 g (49%). M.p. 172 °C. Anal. Found: C, 43.53; H, 5.64; N, 4.47. Calc. for C$_{22}$H$_{32}$Br$_2$N$_2$Sn: C, 43.82; H, 5.35; N, 4.65%. ^{1}H NMR (25 °C): δ 0.72s,br (12H, N–CH$_2$CH$_3$), 2.61s,br (8H, N–CH$_2$CH$_3$), AB spin system with A at δ 3.60 (s,br) and B at δ 3.93 (s,br) ppm (4H, H_7), 7.21s,br (2H, H_3), 7.41m (4H, $H_{4,5}$), 8.26s,br (2H, H_6, $^3J_{SnH}$ 104.9 Hz). ^{1}H NMR (40 °C): δ 3.81s,br (H_7). ^{1}H NMR

Table 3
X-ray crystal data and structure refinement for compounds 1–5.

	1	2	3	4	5
Empirical formula	C$_{22}$H$_{32}$Cl$_2$N$_2$Sn	C$_{22}$H$_{32}$F$_2$N$_2$Sn	C$_{22}$H$_{32}$Br$_2$N$_2$Sn	C$_{22}$H$_{32}$I$_2$N$_2$Sn	C$_{44}$H$_{64}$N$_4$S$_2$Sn$_2$
Formula weight	514.09	481.19	603.01	696.99	950.49
T (K)	297(2)	297(2)	297(2)	297(2)	297(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2/c$	$P2_1/n$	$P2/c$	$P2_1/c$	$C2/c$
Unit cell dimensions					
a (Å)	14.846(5)	9.0088(14)	14.9839(17)	9.9959(8)	24.3808(15)
b (Å)	9.440(3)	14.744(2)	9.5166(11)	15.3769(13)	14.3177(9)
c (Å)	16.879(5)	16.073(3)	17.049(2)	15.7448(13)	17.6297(11)
α (°)	90	90	90	90	90
β (°)	102.057(5)	94.183(3)	102.643(2)	93.446(2)	132.898(1)
γ (°)	90	90	90	90	90
Volume (Å^3)	2313.3(13)	2129.1(6)	2372.1(5)	2415.7(3)	4508.3(5)
Z	4	4	4	4	4
D_{calc} (g cm^{-3})	1.476	1.501	1.688	1.916	1.400
Absorption coefficient (mm^{-1})	1.345	1.226	4.455	3.623	1.234
$F(000)$	1048	984	1192	1336	1952
Crystal size (mm)	$0.32 \times 0.29 \times 0.22$	$0.19 \times 0.16 \times 0.12$	$0.28 \times 0.28 \times 0.19$	$0.25 \times 0.21 \times 0.15$	$0.30 \times 0.20 \times 0.15$
θ Range for data collection (°)	1.40–26.37	2.52–26.37	1.39–25.00	1.85–26.37	1.82–26.37
Reflections collected	17726	17005	16678	19218	23906
Independent reflections	4724 [R_{int} = 0.0358]	4349 [R_{int} = 0.0656]	4180 [R_{int} = 0.0344]	4946 [R_{int} = 0.0410]	4623 [R_{int} = 0.0351]
Data/restraints/parameters	4724/0/249	4349/0/248	4180/0/249	4946/0/248	4623/0/239
Goodness-of-fit on F^2	1.236	1.105	1.141	1.209	1.193
Final R indices[a]					
R_1	0.0486	0.0504	0.0604	0.0555	0.0362
wR_2	0.0925	0.0906	0.1583	0.1377	0.0759
R indices (all data)					
R_1	0.0553	0.0665	0.0677	0.0607	0.0409
wR_2	0.0953	0.0967	0.1631	0.1406	0.0779
Largest difference in peak and hole (e Å^{-3})	1.103 and −1.311	0.845 and −0.896	1.455 and −1.459	1.264 and −1.867	0.468 and −0.598

[a] $I > 2\sigma(I)$.

(−40 °C): δ AB spin system with A at 3.42 and B at 4.05 ppm (H_7, $^2J_{HH}$ 13.0 Hz). ^{13}C NMR (26 °C): δ 8.26 (N–CH$_2$CH$_3$), 44.87 (N–CH$_2$CH$_3$), 58.39 (C_7), 128.28 ($^3J_{CSn}$ 103.4 Hz), 128.54 ($^3J_{CSn}$ 93.6 Hz) ($C_{3,5}$), 130.43 (C_4), 135.80 (C_6), 141.05 (C_2, $^2J_{CSn}$ 59.8 Hz) (the resonance for the C_1 atom could not be identified).

4.5. Synthesis of [2-(Et$_2$NCH$_2$)C$_6$H$_4$]$_2$SnI$_2$ (**4**)

Prepared and worked up as for compound **2**, from **1** (0.5 g, 0.97 mmol) and excess of a saturated aqueous solution of KI. Yield: 0.43 g (64%). M.p. 156–157 °C. Anal. Found: C, 38.13; H, 4.44; N, 4.37. Calc. for C$_{22}$H$_{32}$I$_2$N$_2$Sn: C, 37.91; H, 4.63; N, 4.02%. ^{1}H NMR (24 °C): δ 0.83s,br (12H, N–CH$_2$CH$_3$), 2.65s,br (8H, N–CH$_2$CH$_3$), 3.88s,br (4H, H_7), 7.44s,br (6H, H_{3-5}), 8.15s,br (2H, H_6). ^{1}H NMR (−10 °C): δ AB spin system with A at 3.48 and B at 3.96 ppm (H_7, $^2J_{HH}$ 13.4 Hz). ^{13}C NMR (27 °C): δ 8.50 (N–CH$_2$CH$_3$), 45.33 (N–CH$_2$CH$_3$), 57.50 (C_7), 128.64, 129.24 ($C_{3,5}$), 130.97 (C_4), 136.26 (C_6), 139.40 (C_2) (the resonance for the C_1 atom could not be identified). ^{119}Sn NMR (20 °C): δ −304.

4.6. Synthesis of cyclo-[{2-(Et$_2$NCH$_2$)C$_6$H$_4$}$_2$SnS]$_2$ (**5**)

Prepared and worked up as for compound **2**, from **1** (0.5 g, 0.97 mmol) and excess of a saturated aqueous solution of Na$_2$S. Yield: 0.30 g (32%). M.p. 173–174 °C. Anal. Found: C, 55.23; H, 6.46; N, 5.53. Calc. for C$_{44}$H$_{64}$N$_4$S$_2$Sn$_2$: C, 55.60; H, 6.79; N, 5.89. ^{1}H NMR (24 °C): δ 0.74t (24H, N–CH$_2$CH$_3$, $^3J_{HH}$ 7.1 Hz), 2.25q (16H, N–CH$_2$CH$_3$, $^3J_{HH}$ 7.1 Hz), 3.49s (8H, H_7), 7.20 m (4H, H_3), 7.27 m (8H, $H_{4,5}$), 8.32 m (4H, H_6, $^3J_{SnH}$ 80.3 Hz). ^{1}H NMR (−50 °C): δ AB spin system with A at δ 3.42 and B at δ 3.61 ppm (H_7, $^2J_{HH}$ 13.5 Hz). ^{13}C NMR (27 °C): δ 8.95 (N–CH$_2$CH$_3$), 44.21 (N–CH$_2$CH$_3$), 59.23 (C_7, $^2J_{SnC}$ 33.0 Hz), 127.00 ($^3J_{CSn}$ 74.7/77.5 Hz), 127.58 ($^3J_{CSn}$ 64.7 Hz) ($C_{3,5}$), 128.62 (C_4, $^4J_{CSn}$ 14.8 Hz), 136.55 (C_6, $^2J_{CSn}$ 54.1 Hz), 143.58 (C_2, $^2J_{CSn}$ 47.0 Hz), 144.59 (C_1, $^1J_{CSn}$ 716.3/749.7 Hz). ^{119}Sn NMR (20 °C): δ −103.

4.7. X-ray structure determination

Colourless block crystals of [2-(Et$_2$NCH$_2$)C$_6$H$_4$]$_2$SnCl$_2$ (**1**), [2-(Et$_2$NCH$_2$)C$_6$H$_4$]$_2$SnF$_2$ (**2**), [2-(Et$_2$NCH$_2$)C$_6$H$_4$]$_2$SnBr$_2$ (**3**), cyclo-[{2-(Et$_2$NCH$_2$)C$_6$H$_4$}$_2$SnS]$_2$ (**5**) and yellow block crystal of [2-(Et$_2$NCH$_2$)C$_6$H$_4$]$_2$SnI$_2$ (**4**) were mounted on cryoloops. A hemisphere of data was collected on a Bruker APEX CCD diffractometer using a counting time of 10 s per frame. Data reduction was performed using the SAINT-plus [35] software and the data were corrected for absorption effects using the SADABS program [36]. Cell refinement gave cell constants corresponding to monoclinic cells whose dimensions are given in Table 3 along with other experimental parameters.

The structures were solved by direct methods and refined with SHELXTL versions of SHELX-97 [37]. All of the non-hydrogen atoms were treated anisotropically. All C-bound H atoms were placed in calculated positions (C–H = 0.93–0.97 Å) and treated using a riding model with U_{iso} = 1.5U_{eq}(C) for methyl and U_{iso} = 1.2U_{eq}(C) for aryl H atoms; the methyl groups were allowed to rotate but not to tip. The final cycle of full-matrix least-squares refinement converged (largest parameter shift was 0.001 times its esd). The drawings were created with the DIAMOND program [38].

Acknowledgements

Appendix A. Supplementary material

CCDC 688058, 688060, 688062, 688059 and 688061 contain the supplementary crystallographic data for compounds **1**, **2**, **3**, **4** and **5**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.12.023.

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