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Oxidative-addition reactions of molecular diiodine and dibromine to divalent organotin compounds. Crystal structures of bis[8-(dimethylamino)-1-naphthyl]tin(IV) dibromide and {2,6-[bis(dimethylamino)methyl]phenyl}-(4-tolyl)tin(IV) diiodide

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Abstract

The reactions of bis[8-(dimethylamino)-1-naphthyl]tin(II) with dibromine or diiodine afford bis[8-(dimethylamino)-1-naphthyl]tin(IV) dibromide (**1**) and bis[8-(dimethylamino)-1-naphthyl]tin(IV) diiodide (**2**), respectively. Reaction of {2,6-[bis(dimethylamino)methyl]phenyl}(4-tolyl)tin(II) with diiodine gives {2,6-[bis(dimethylamino)methyl]phenyl}(4-tolyl)tin(IV) diiodide (**3**) in quantitative yield. The crystal structures of **1** and **3** have been determined by X-ray diffraction methods. As a result of intramolecular coordination of the nitrogen atoms with the tin centers, the geometry about tin in both **1** and **3** is octahedral, while the carbon atoms bound to tin are in *trans* position. In **1** the two bromine atoms are *cis* to one another, as are the two nitrogen atoms, whereas in **3** the two iodine atoms, like the two nitrogen atoms, are *trans* to one another. ^1H , ^{13}C and ^{119}Sn solution NMR spectroscopic studies of **1**–**3** show that they retain the structures found in the solid state.

Introduction

It is well-known that the direct alkylation or arylation of tin(IV) halides to give organotin halides may be brought about by many organometallic reagents (RMgX , RLi , RNa , R_3Al , etc.), but that, even when precise reaction stoichiometries are used, a mixture of the three possible halides $\text{R}_n\text{SnX}_{4-n}$ is usually obtained [1]. However, if the organic group is fairly bulky, partial substitution of the tin(IV) halide may be achieved, to give good yields of the target organotin halide [2–6].

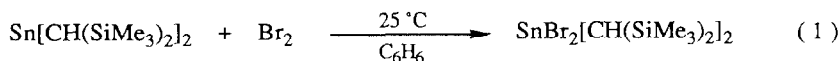
Another very important route to organotin halides is the reaction, discovered by

Kocheshkov [7], involving redistribution between tetraorganotin compounds and anhydrous tin(IV) halides [8,9]. These reactions are used industrially for the manufacture of triorganotin halides and diorganotin dihalides.

A third important route to triorganotin halides and diorganotin dihalides involves the selective tin-carbon bond cleavage in tetraorganotin compounds by dihalogens. By making use of the difference in ease of cleavage of various organic groups from tin ($\text{Ph} > \text{Bz} > \text{vinyl} > \text{Me} > \text{Et} > \text{Pr} > \text{Bu}$) [10] this route allows the synthesis of mixed triorganotin halides and mixed diorganotin dihalides from mixed tetraorganotin compounds [11,12].

In previous work we have shown that the reaction of arylcopper compounds with tin tetrahalides or diorganotin dihalides affords triorganotin halides [13] and diorganotin dihalides [14] selectively and in high yield.

Another potentially interesting approach to the one-step synthesis of diorganotin dihalides involves oxidative-addition of dihalogen to divalent diorganotin(II) compounds. Lappert et al. have described the reaction of bis[bis(trimethylsilyl)methyl]tin(II) with dibromine to give bis[bis(trimethylsilyl)methyl]tin(IV) dibromide in high yield (eq. 1) [15].

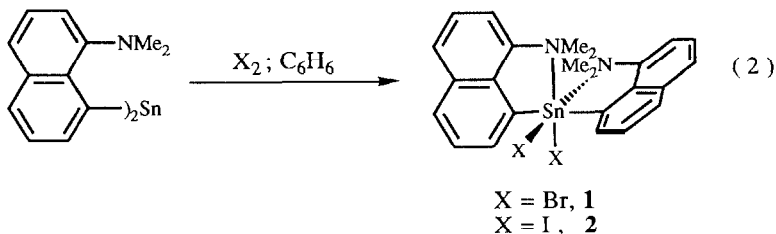


Although this route to diorganotin dihalides is promising, a major disadvantage is that the number of stable divalent organotin compounds is very limited. However, we recently reported the synthesis and structural characterization of some novel homo- [16] and hetero-leptic diorganotin compounds [17] that could be expected to be converted into diorganotin dihalides by direct halogenation. We now report on the synthesis and structural characterization of some bis[8-(dimethylamino)-1-naphthyl]tin(IV) dihalides, produced by oxidative-addition of dihalogens to the stable divalent organotin compound bis[8-(dimethylamino)-1-naphthyl]tin(II). The synthesis and structural characterization of the unique hexa-coordinate {2,6-bis[(dimethylamino)methyl]phenyl}(4-tolyl)tin(IV) diiodide is also described; this was made by reaction of {2,6-bis[(dimethylamino)methyl]phenyl}(4-tolyl)tin(II) with diiodine.

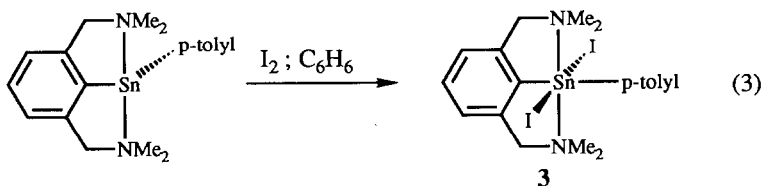
Results and discussion

Synthesis of bis[8-(dimethylamino)-1-naphthyl]tin dibromide (1), bis[8-(dimethylamino)-1-naphthyl]tin diiodide (2) and {2,6-bis[(dimethylamino)methyl]phenyl}(4-tolyl)tin diiodide (3)

Addition of a benzene solution of Br_2 or I_2 to a solution of bis[8-(dimethylamino)-1-naphthyl]tin(II) in a 1 : 1 molar ratio in benzene gives quantitative yields of bis[8-(dimethylamino)-1-naphthyl]tin dibromide (1) and bis[8-(dimethylamino)-1-naphthyl]tin diiodide (2) (eq. 2).



Similarly, reaction of a benzene solution of {2,6-[bis(dimethylamino)methyl]phenyl}(4-tolyl)tin(II) with diiodine in a 1:1 molar ratio quantitatively affords {2,6-[bis(dimethylamino)methyl]phenyl}(4-tolyl)tin diiodide (3), the structure of which is shown schematically in eq. 3.



The novel diorganotin dihalides are off-white crystalline solids that were characterized by elemental analyses and by ^1H , ^{13}C and ^{119}Sn NMR spectroscopy (see Experimental section). To gain insight into the type of bonding and the coordination geometry at tin in these type of compounds the X-ray structure determinations were carried out with both 1 and 3.

Solid state structure and molecular geometry of bis[8-(dimethylamino)-1-naphthyl]tin dibromide (1) and {2,6-[bis(dimethylamino)methyl]phenyl}(4-tolyl)tin diiodide (3)

The structure of $\text{SnBr}_2[8\text{-Me}_2\text{NC}_{10}\text{H}_6\text{-1}]_2$ (1) involves the packing of two discrete mononuclear molecules in the unit cell. The molecular geometry of 1 is shown in Figure 1, and selected data on the molecular geometry are listed in Table 1.

In 1 the tin atom is octahedrally coordinated as a result of the *C,N*-chelate bonding of two 8-(dimethylamino)-1-naphthyl groups and two Sn-Br bonds. As expected, the two organic groups are in a *trans* disposition [18], while both coordinating nitrogen atoms are *cis* to bromine atoms. The coordination geometry at tin is closely related to that found for bis(pyridine)dimethyltin dibromide [19],

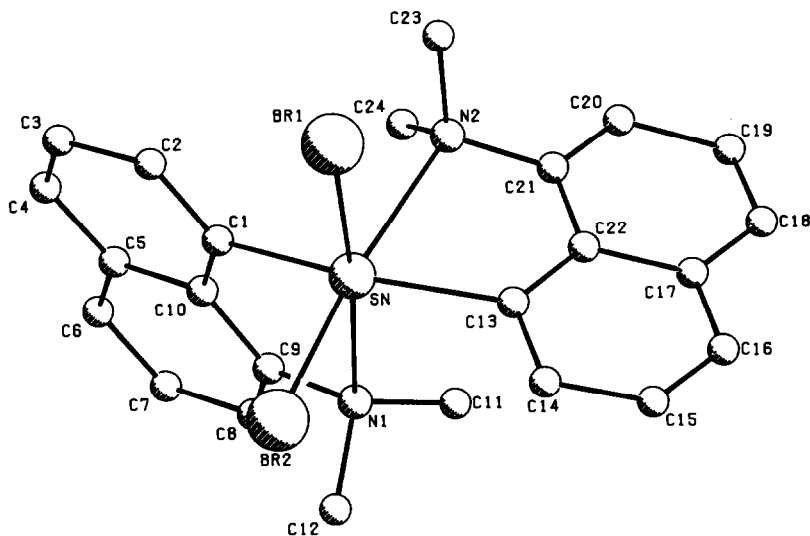


Fig. 1. PLUTO drawing of bis[8-(dimethylamino)-1-naphthyl]tin(IV) dibromide (1) with the adopted numbering scheme.

Table 1

Selected geometrical data for **1**

<i>Bond distances (Å)</i>			
Sn–C1	2.12(1)	Sn–N2	2.64(1)
Sn–C13	2.13(1)	Sn–Br1	2.623(2)
Sn–N1	2.62(1)	Sn–Br2	2.610(2)
<i>Bond angles (deg)</i>			
N1–Sn–C1	75.4(5)	N2–Sn–Br2	174.0(2)
N1–Sn–C13	87.7(6)	Br1–Sn–C1	99.2(4)
N1–Sn–Br1	174.6(2)	Br1–Sn–C13	97.6(5)
N1–Sn–Br2	89.9(3)	Br1–Sn–Br2	90.3(1)
N1–Sn–N2	90.4(5)	Br2–Sn–C1	99.2(4)
N2–Sn–C1	86.7(5)	Br2–Sn–C13	100.6(5)
N2–Sn–C13	73.4(6)	C1–Sn–C13	153.9(5)
N2–Sn–Br1	89.9(3)		

(2,2'-bipyridyl)diphenyltin dichloride [20] and (1,10-phenantroline)di-*n*-butyltin dichloride [21], although in the latter two complexes the *cis* geometry of the coordinating nitrogen atoms is dictated by the bidentate donor ligand.

In both five-membered chelate rings in **1** the N–Sn–C angles are 75.4(5) and 73.4(6)°, respectively, values which deviate considerably from the ideal 90°. This is not unexpected, since this angle is determined by the fairly inflexible values of the Sn–C and Sn–N bond lengths. This effect was also observed for trigonal bipyramidal arrays in which a bidentate ligand forms a five-membered chelate ring bridging an equatorial and an axial site (see refs. 22–24 and references cited therein). As a consequence, the C–Sn–C angle of 153.9(5)° also deviates considerably from the ideal value of 180°. Although the observed Sn–N distances in **1** are difficult to compare with known Sn–N distances in diorganotin compounds in which the tin atom is octahedrally coordinated (only complexes in which the coordinating nitrogen atoms are *sp*² hybridized have been reported [18]), these distances seem to be rather long (2.62(1) and 2.64(1) Å, respectively), when compared with those found in pentacoordinate triorganotin bromides (about 2.5 Å) [22–24]. On the other hand the observed Sn–Br distances (2.623(2) and 2.610(2) Å) seem to be rather short compared with those (2.719(5) Å) in bis(pyridine)dimethyltin dibromide [19]. In this respect it is noteworthy that Britton and Dunitz [25] have correlated the structural features of SnC₂X₂Y₂ ensembles having a *C,C* transoid arrangement, as they did for pentacoordinate structures. It is remarkable that the Sn–N and Sn–Br distances in **1** fit very well on the theoretically derived curve for these distances; furthermore, these correlations predict a value of 152° for the C–Sn–C angle, which is very close to the actual value of 153.9(5) Å found for **1**.

In the crystal structure of SnI₂[C₆H₃(CH₂NMe₂)₂-2,6](C₆H₄Me-4) (**3**) there are four discrete mononuclear molecules in the unit cell, which also contains four molecules of toluene (solvent of crystallization). It appears that the coordination geometry at tin in **3** is distorted octahedral with the organic groups, the two iodine atoms and the nitrogen atoms in *trans* dispositions. The molecular geometry of **3** is shown in Fig. 2, and selected geometric data are listed in Table 2. As has been noted previously, it is not surprising that the organic groups are in a *trans* disposition, since it is known that in octahedral diorganotin compounds R₂SnX₂L₂, the relative

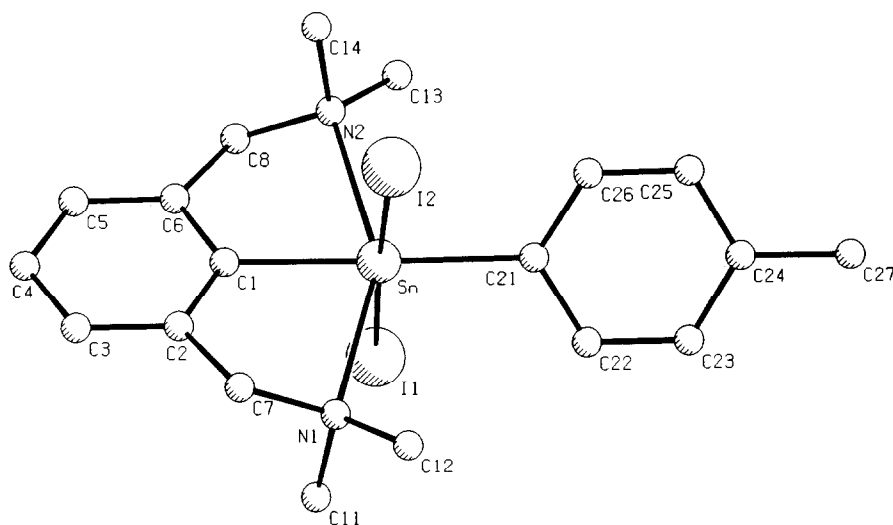


Fig. 2. PLUTO drawing of {2,6-[bis(dimethylamino)methyl]phenyl}(4-tolyl)tin(IV) diiodide (**3**) with the adopted numbering scheme.

positions of the groups X and L (*cis* or *trans*) are mainly controlled by steric factors [26]. Probably as a result of the rigid geometry of the 2,6-[bis(dimethylamino)methyl]phenyl group, the two coordinating nitrogen atoms are held in a *trans* disposition, thus giving a meridional coordination mode for the terdentate, monoanionic 2,6-[bis(dimethylamino)methyl]phenyl group. A similar situation was found in octahedral organometallic complexes of the late transition metals * containing the 2,6-[bis(dimethylamino)methyl]phenyl group [27–29].

The overall structural geometry at the tin center of **3** is closely related to that in diethyltin diiodide bis(triphenylphosphine oxide) [31] and diethyltin diiodide bis(HMPA) (HMPA = hexamethylphosphoric triamide) [31]. In these two complexes the tin center is again hexa-coordinate, with both ethyl groups, the two iodine atoms and the two other ligands all in *trans* dispositions. The Sn–I distances of 2.936, 3.101 and 3.016 Å in these compounds are very close to those in **3** (Table 2). As has been noted before, the presence of the five-membered chelate rings results in an decrease of the Cl–Sn–N angles to about 75°, and consequently the C21–Sn–N angles are increased to about 105°.

Structure in solution of the diorganotin dihalides **1**, **2** and **3**

On the basis of ^1H , ^{13}C and ^{119}Sn NMR spectra for **1** and **2** (see Experimental section) it can be concluded that the structure of **1** in the solid state is probably retained in solution. The observation of diastereotopic NMe_2 resonances in the ^1H as well as in the ^{13}C NMR spectra of **1** and **2** points to a *cis* arrangement for the coordinating nitrogen atoms. At higher temperatures (+110°C, the highest temper-

* Very recently we reported the X-ray structure of a tantalum alkylidene compound containing the terdentate monoanionic 2,6-[bis(dimethylamino)methyl]phenyl group, in which this group is facial *N,C,N*-bonded to the metal center [30].

Table 2

Selected geometrical data for **3**

<i>Bond distances (Å)</i>			
Sn–Cl	2.109(9)	Sn–N2	2.429(9)
Sn–C21	2.124(9)	Sn–I1	2.965(1)
Sn–N1	2.501(9)	Sn–I2	3.009(1)
<i>Bond angles (deg)</i>			
C1–Sn–C21	178.5(4)	C21–Sn–N2	104.3(3)
C1–Sn–I1	90.7(3)	I1–Sn–I2	177.26(3)
C1–Sn–I2	91.7(3)	I1–Sn–N1	93.5(2)
C1–Sn–N1	75.5(3)	I1–Sn–N2	87.1(2)
C1–Sn–N2	75.3(4)	I2–Sn–N1	85.8(2)
C21–Sn–I1	90.7(3)	I2–Sn–N2	94.8(2)
C21–Sn–I2	86.9(3)	N1–Sn–N2	150.7(3)
C21–Sn–N1	104.9(3)		

ature studied in toluene- d_8) no coalescence of the diastereotopic NMe_2 resonances was observed. This indicates that (i) the Sn–N coordination is inert on the NMR time-scale, and (ii) inversion of configuration at tin is either slow on the NMR time-scale or does not occur at all. Probably the rigid geometry of the 8-(dimethylamino)-1-naphthyl group holds the nitrogen atom close to the tin atom, thus preventing a process involving Sn–N dissociation and pyramidal inversion at nitrogen. A similar observation was made for triorganotin halides containing the 8-(dimethylamino)-1-naphthyl group [32]. The observed ^{119}Sn chemical shift values for **1** and **2** at relatively high field (-252.0 and -361.8 ppm, respectively) is indicative of a high coordination number at tin [33,34]. Furthermore the large $^1J(^{117,119}\text{Sn}-^{13}\text{C})$ values (1149 and 1204 Hz) in **1** are indicative of hexacoordination at tin [35].

From the standpoint of structural assignment the ^1H and ^{13}C NMR spectra obtained for **3** are not very informative (see Experimental section). In solution **3** must have a high symmetry, probably the same as that in the solid state. Moreover, the ^{119}Sn chemical shift value of -208.7 ppm is indicative of a high coordination number at tin [34].

Conclusions

It has been shown that oxidative addition of dihalogens to functionally substituted divalent organotin compounds affords diorganotin dihalides in quantitative yield. Although this single step reaction to diorganotin dihalides seems to be very attractive its scope is rather limited, since only a few divalent organotin compounds are known.

It appears that the tin atoms in these diorganotin dihalides, which contain two potentially intramolecular coordinating ligands, have octahedral coordination geometries, both in the solid state and in solution. Since the two organic groups are always in a *trans* disposition, only two geometrical isomers can exist: (i) one with the two halogen atoms and the two ligands in *cis* dispositions, and (ii) another with the two halogen atoms and the two coordinating ligands in *trans* dispositions. In compounds containing two *C,N*-chelating ligands, e.g. **1** and **2**, the two halogen

atoms adopt the *cis* geometry in the solid state as well in solution. In this respect it is noteworthy that oxidative-addition reactions at platinum in bis[8-(dimethylamino)-1-naphthyl]platinum may lead to different geometrical isomers, depending on the type of oxidant [36]. In the case of bis[8-(dimethylamino)-1-naphthyl]tin(II), however, the same product was always obtained*.

In {2,6-[bis(dimethylamino)methyl]phenyl}(4-tolyl)tin diiodide **3** the two halogen atoms are in a *trans* disposition. The formation of a *trans* oxidative-addition product in this case contrasts with the formation of a *cis* oxidative-addition product when diiodine reacts with {2,6-[bis-(dimethylamino)methyl]phenyl}(4-tolyl)-platinum(II). It has been argued that in the latter case *trans* oxidative-addition cannot take place for steric reasons [37]. However, the possibility cannot be excluded that in that case also the initial step in the oxidative-addition involves the formation of a *cis* oxidative-addition product, which rapidly rearranges to the more stable *trans* product. It seems very likely that steric factors control the geometry at tin in the final oxidative-addition products.

Experimental

Syntheses were carried out by standard Schlenk techniques under purified nitrogen. The solvents were dried and distilled from sodium prior to use. ^1H , ^{13}C and ^{119}Sn NMR spectra were recorded on a Bruker AC 200 spectrometer.

Synthesis of bis[8-(dimethylamino)-1-naphthyl]tin dibromide (**1**) and bis[8-(dimethylamino)-1-naphthyl]tin diiodide (**2**)

A solution of 2 mmol of Br_2 or I_2 in 10 mL of benzene was added during 15 min to a solution of 2 mmol of bis[8-(dimethylamino)-1-naphthyl]tin(II) in 20 mL of benzene, yielding a white precipitate in a colourless solution. The solid was filtered off, washed with two 15 mL portions of pentane, and dried *in vacuo*, to give pure **1** and **2** in almost quantitative yield (> 95%). **1**: Anal. Found: C, 46.20; H, 3.86; N, 4.33; Br, 26.20. $\text{C}_{24}\text{H}_{24}\text{Br}_2\text{N}_2\text{Sn}$ calcd.: C, 46.57; H, 3.91; N, 4.53; Br, 25.82%. ^1H NMR (CDCl_3 , 25 °C): δ 1.78 and 2.80 (NMe_2 , both s); 8.70 (H(2)). ^{13}C NMR (CDCl_3 , 25 °C): δ 47.8 and 53.4 (NMe_2); 131.5 (C(1), $^1J(^{117,119}\text{Sn}-^{13}\text{C})$ 1149 and 1204 Hz). ^{119}Sn NMR (C_6D_6 , 25 °C): δ -252.0. **2**: Anal. Found: C, 40.25; H, 3.38; N, 3.78; I, 35.37. $\text{C}_{24}\text{H}_{24}\text{I}_2\text{N}_2\text{Sn}$ calcd.: C, 40.43; H, 3.39; N, 3.93; I, 35.60%. ^1H NMR (CDCl_3 , 25 °C): δ 1.75 and 2.79 (NMe_2 , both s); 8.65 (H(2)). ^{13}C NMR (CDCl_3 , 25 °C): δ 48.0 and 55.3 (NMe_2). ^{119}Sn NMR (C_6D_6 , 25 °C): δ -361.8.

Crystal structure determination of **1** **

Transparent colorless crystals of **1**, $\text{C}_{24}\text{H}_{24}\text{Br}_2\text{N}_2\text{Sn}$ obtained by recrystallization from dichloromethane, are triclinic, space group $P\bar{1}$, with two molecules in a unit cell of dimensions $a = 10.830(3)$, $b = 12.764(3)$, $c = 8.658(3)$ Å, $\alpha = 96.07(3)$, $\beta = 104.25(3)$ and $\gamma = 77.77(3)^\circ$. 3953 Independent intensities were measured on a Nonius CAD4 diffractometer, at 25 °C, using graphite monochromated Mo- K_α

* Reaction of bis[8-(dimethylamino)-1-naphthyl]tin(II) with two equivalents of CuBr_2 gave **1** in quantitative yield.

** Complete tables of atomic coordinates, bond distances and angles, and lists of thermal parameters and structure factors can be obtained from the authors.

Table 3

Atomic fractional coordinates and equivalent isotropic thermal parameters (\AA^2) for **1**

Atom	x	y	z	U_{eq}^a
Sn	0.2498(1)	0.24948(9)	0.1866(1)	0.0316(5)
Br1	0.4710(2)	0.1837(2)	0.1011(3)	0.060(1)
Br2	0.1366(2)	0.3090(2)	-0.1017(2)	0.057(1)
C1	0.191(1)	0.100(1)	0.172(2)	0.030(8)
C2	0.264(2)	0.006(1)	0.129(2)	0.041(10)
C3	0.222(2)	-0.095(1)	0.123(2)	0.05(1)
C4	0.114(2)	-0.097(1)	0.175(2)	0.05(1)
C5	0.037(2)	-0.004(1)	0.228(2)	0.033(9)
C6	-0.077(2)	-0.006(2)	0.276(3)	0.06(1)
C7	-0.150(2)	0.086(2)	0.325(3)	0.07(1)
C8	-0.116(2)	0.186(2)	0.326(3)	0.07(1)
C9	-0.006(2)	0.191(1)	0.273(2)	0.05(1)
C10	0.075(1)	0.098(1)	0.224(2)	0.031(8)
C11	0.027(2)	0.363(2)	0.414(3)	0.06(1)
C12	-0.073(2)	0.358(1)	0.137(3)	0.07(1)
C13	0.288(2)	0.399(1)	0.303(2)	0.038(9)
C14	0.253(2)	0.490(1)	0.215(3)	0.06(1)
C15	0.275(2)	0.589(1)	0.293(3)	0.08(2)
C16	0.320(2)	0.597(1)	0.452(3)	0.07(1)
C17	0.351(2)	0.509(2)	0.547(2)	0.05(1)
C18	0.394(2)	0.514(2)	0.713(3)	0.07(1)
C19	0.419(2)	0.428(2)	0.803(2)	0.07(2)
C20	0.409(2)	0.323(2)	0.723(2)	0.06(1)
C21	0.371(2)	0.314(1)	0.566(2)	0.040(10)
C22	0.338(1)	0.405(1)	0.469(2)	0.032(9)
C23	0.502(2)	0.153(1)	0.489(2)	0.06(1)
C24	0.306(2)	0.144(1)	0.560(2)	0.05(1)
N1	0.025(1)	0.2966(9)	0.265(2)	0.039(8)
N2	0.369(1)	0.210(1)	0.486(2)	0.044(9)

$$^a U_{\text{eq}} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* (a_i \cdot a_j).$$

radiation ($\lambda(\text{Mo-K}\alpha) = 0.71069 \text{ \AA}$); 1936 of these were below the $2.5 \sigma(I)$ level and were treated as unobserved.

The Sn and Br positions were obtained from a Patterson synthesis. The other nonhydrogen atoms were found by standard difference Fourier techniques. After isotropic block-diagonal least-squares refinement an empirical absorption correction (DIFABS [38]) was applied (crystal dimensions $0.01 \times 0.1 \times 0.4 \text{ mm}$; $\mu(\text{Mo-K}\alpha) = 41.2 \text{ cm}^{-1}$). Hydrogen atoms were placed in calculated positions. Continued refinement, anisotropic for C, Br, N and Sn (the temperature factors of the hydrogen atoms were kept fixed at 0.045 \AA^2) converged to $R = 0.062$. Unit weights were used and the anomalous dispersion of Sn and Br was taken into account. Coordinates of the non-hydrogen atoms are given in Table 3.

Synthesis of {2,6-[bis(dimethylamino)methyl]phenyl}(4-tolyl)tin diiodide (**3**)

A solution of 2 mmol of I_2 in 10 mL of benzene was added during 15 min to a solution of 2 mmol of 2,6-[bis(dimethylamino)methyl]phenyl(4-tolyl)tin(II) in 10 mL of benzene. The resulting pale yellow solution was concentrated *in vacuo* to give

a pale yellow solid. The solid material was washed with two 10 mL portions of pentane and dried *in vacuo* to give pure **3** as a white solid in 80% yield. Anal. Found: C, 26.71; H, 3.74; N, 4.81. $C_{13}H_{22}I_2N_2Sn$ calcd.: C, 26.98, H, 3.83, N, 5.03%. 1H NMR (C_6D_6 , 25 °C): δ 2.12 (CH_3 , s); 2.52 (NMe_2 , s); 3.68 (CH_2N , s); 8.51 (H(2) tolyl, d, $^3J(HH) = 7$ Hz, $^3J(^1H-^{119}Sn) = 120$ Hz). ^{119}Sn NMR (C_6D_6 , 25 °C): $\delta - 208.7$.

Crystal structure determination of **3** *

Transparent colorless crystals of **3**, $C_{17}H_{26}I_2N_2Sn \cdot C_7H_8$, obtained by recrystallization from toluene, are monoclinic, space group $P2_1/c$, with four molecules in a unit cell of dimensions $a = 9.136(1)$, $b = 22.253(2)$, $c = 14.539(2)$ Å and $\beta =$

Table 4

Atomic fractional coordinates and equivalent isotropic thermal parameters (Å^2) for **3**

Atom	x	y	z	U_{eq}^a
I(1)	0.8839(1)	0.31473(4)	0.31741(6)	0.0524(3)
I(2)	0.43806(9)	0.30122(3)	0.54375(5)	0.0457(2)
Sn	0.66565(8)	0.31077(3)	0.43213(4)	0.0312(2)
N(1)	0.4419(9)	0.3428(4)	0.2931(6)	0.042(3)
N(2)	0.882(1)	0.3347(4)	0.5723(6)	0.043(3)
C(1)	0.666(1)	0.4054(4)	0.4405(7)	0.041(3)
C(2)	0.537(1)	0.4358(4)	0.3855(7)	0.041(3)
C(3)	0.541(2)	0.4987(5)	0.3896(9)	0.058(4)
C(4)	0.667(2)	0.5275(5)	0.4485(8)	0.058(5)
C(5)	0.796(2)	0.4953(5)	0.5027(9)	0.056(4)
C(6)	0.798(1)	0.4332(5)	0.4996(7)	0.045(4)
C(7)	0.394(1)	0.4010(5)	0.3298(8)	0.048(4)
C(8)	0.931(1)	0.3938(5)	0.5470(8)	0.045(3)
C(11)	0.489(2)	0.3571(5)	0.2064(7)	0.054(4)
C(12)	0.310(1)	0.3001(6)	0.267(1)	0.062(4)
C(13)	1.014(1)	0.2922(6)	0.595(1)	0.061(4)
C(14)	0.837(2)	0.3410(6)	0.6617(7)	0.061(5)
C(21)	0.663(1)	0.2154(4)	0.4268(6)	0.034(3)
C(22)	0.636(1)	0.1858(4)	0.3376(6)	0.034(3)
C(23)	0.620(1)	0.1236(4)	0.3346(6)	0.042(3)
C(24)	0.644(1)	0.0895(5)	0.4179(8)	0.048(4)
C(25)	0.674(1)	0.1180(5)	0.5056(7)	0.043(3)
C(26)	0.678(1)	0.1796(5)	0.5086(8)	0.049(4)
C(27)	0.632(2)	0.0223(5)	0.413(1)	0.068(5)
C(31)	0.149(2)	0.0047(9)	0.274(1)	0.118(8)
C(32)	0.050(2)	-0.005(1)	0.317(2)	0.17(1)
C(33)	0.027(2)	0.047(1)	0.384(1)	0.126(9)
C(34)	0.121(2)	0.0953(9)	0.390(1)	0.104(7)
C(35)	0.223(2)	0.101(1)	0.348(2)	0.118(9)
C(36)	0.234(2)	0.057(1)	0.290(1)	0.122(9)
C(37)	0.098(4)	0.148(2)	0.451(2)	0.23(2)

$$^a U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* (a_i \cdot a_j).$$

* Complete tables of atomic coordinates, bond distances and angles, and lists of thermal parameters and structure factors can be obtained from the authors.

107.72(1)°. 4917 Independent intensities were measured on a Nonius CAD4 diffractometer, at 25 °C, using graphite monochromated Mo- K_{α} radiation ($\lambda(\text{Mo-}K_{\alpha}) = 0.71069 \text{ \AA}$); 1822 of these were below the 2.5 $\sigma(I)$ level and were treated as unobserved.

The Sn and I positions were obtained from a Patterson synthesis. The other non-hydrogen atoms were found by standard difference Fourier techniques. It became apparent that per formula unit one molecule of toluene was present (solvent of crystallization). After isotropic block-diagonal least-squares refinement an empirical absorption correction (DIFABS [38]) was applied (crystal dimensions $0.15 \times 0.40 \times 0.45 \text{ mm}$; $\mu(\text{Mo-}K_{\alpha}) = 30.9 \text{ cm}^{-1}$). Hydrogen atoms were placed in calculated positions. Continued refinement, anisotropic for C, I, N and Sn (the temperature factors of the hydrogen atoms were kept fixed) converged to $R = 0.041$ ($R_w = 0.078$). A weighting scheme $w = 1/(6.4 + F_o + 0.018F_o^2)$ was applied and the anomalous dispersion of Sn and I were taken into account. Coordinates of the non-hydrogen atoms are given in Table 4.

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