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CRYSTAL AND MOLECULAR STRUCTURE OF *C,N*-{2-[(DIMETHYLAMINO)METHYL]PHENYL}DIPHENYLTIN BROMIDE

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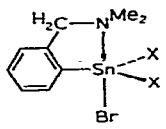
Summary

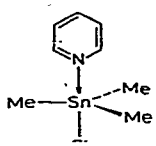
The crystal and molecular structure of *C,N*-{2-[(dimethylamino)methyl]-phenyl}diphenyltin bromide 2-$Me_2\vec{N}CH_2C_6H_4\overset{\leftarrow}{Sn}Ph_2Br$ have been determined by a single-crystal X-ray diffraction study. Crystals are monoclinic, space group $P2_1/c$ with $Z = 4$ in a unit cell of dimensions: $a = 8.609(1)$, $b = 15.470(2)$, $c = 17.149(4)$ Å and $\beta = 117.79(2)°$. The heavy atom positions were determined by direct methods while the other atoms were located by standard Fourier techniques. The structure was refined by block-diagonal least-squares techniques to a final R value of 0.060 for 2875 reflections. The tin atom has a distorted trigonal bipyramidal geometry, with the $Me_2NCH_2C_6H_4$ group spanning one equatorial and one axial site. The two phenyl groups reside in the two remaining equatorial positions while the bromine atom occupies an axial site. The axial bond lengths are: Sn—N(ax) 2.51 Å and Sn—Br(ax) 2.63 Å while the N—Sn—Br bond angle amounts to 171°. The acute C(13)—Sn—N bond angle in the five-membered chelate ring, which is puckered at the C(sp^3) N and Sn atoms, is 75.3°. The present structure provides the first example of a triorganotin halide containing a pentacoordinate tin atom as a result of intramolecular coordination with a built-in ligand.

Introduction

Recently we have reported the synthesis of triorganotin halides which contain as a potentially bidentate ligand the 2-$Me_2NCH_2C_6H_4$ group [1]. In view of the known tendency of triorganotin halides to form 1 : 1 complexes with Lewis bases [2], we proposed for this novel class of triorganotin compounds the trigonal bipyramidal structure I in which the tin atom is pentacoordinate as a result of intramolecular Sn—N bond formation [1].



(I)



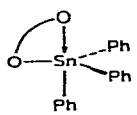
(II)

Ia, X = Ph; Ib, X = Me

The proposed arrangement of the ligands around tin is in accord with the well documented preference of the more electronegative groups for axial positions. A well-known example in organotin chemistry is the pentacoordinate structure (II) of the 1 : 1 complex of trimethyltin chloride with pyridine [3].

^{1}H NMR spectroscopy cannot confirm structure I because of the presence of relevant molecular symmetry planes through the prochiral carbon and the nitrogen center of the CH_2NMe_2 group. The observed singlet resonance for the benzylic as well as for the aminomethyl protons are compatible both with a tetracoordinate and with a pentacoordinate structure [1,4].

A number of crystal and molecular structures of pentacoordinate triorganotin compounds which are polymeric as a result of intermolecular coordination have been reported [5]. Very recently an X-ray study was reported for (1,3-diphenylpropane-1,3-dionato)triphenyltin(IV) which unambiguously established the occurrence of pentacoordination as a result of intramolecular coordination with the propane-1,3-dionato ligand spanning axial—equatorial sites [6].



O—O, 1,3-diphenylpropane-1,3-dionato

So far an X-ray structure of a triorganotin halide which contains a potentially bidentate ligand has not been reported although recently a few examples of this novel type of tin compounds have been synthesized, e.g. $Ph_2ClSn(CH_2)_3C(=NOH)Me$ [7], $Me_2ClSn(CH_2)_nC(=O)R$ [8].

In the present paper we report on the crystal structure and the molecular geometry of *C,N*-{2-[(dimethylamino)methyl]phenyl}diphenyltin bromide (Ia). Our interest in this compound stems from our recent finding that chiral triorganotin compounds, which contain the 2-[(dimethylamino)methyl]phenyl ligand, display exceptionally high optical stability [4].

Experimental

Colourless crystals of the title compound were grown from benzene. The intensity of 3974 independent reflections ($\theta < 26°$), of which 2875 reflections had intensities larger than 2.5 $\sigma(I)$, was collected with an Enraf—Nonius CAD-4 diffractometer using Zr-filtered Mo-K_α radiation (λ = 0.71069 Å).

The ω-scan technique was used. The data were corrected for Lorentz and polarization factors, but no absorption correction was applied. The crystal data

are as follows: $SnBrNC_{21}H_{22}$; mol.wt. 487.01; monoclinic; space group $P2_1/c$; $a = 8.609(1)$, $b = 15.470(2)$, $c = 17.149(4)$ Å; $\beta = 117.79(2)°$; $V = 2020.4$ Å; D_o (by flotation in CCl_4/1,2-dibromoethane) 1.605 g cm^{-3}, D_c 1.601 g cm^{-3}; $Z = 4$; μ(Mo-K_α) = 33.7 cm^{-1}; crystal dimensions 0.4 × 0.5 × 0.1 mm.

The heavy atom positions (Sn and Br) were easily determined by direct methods [9]. The other atoms were located using standard Fourier techniques. The positions of the hydrogen atoms were not investigated since they are not relevant to the aim of the study.

The structure was refined by block-diagonal least-squares techniques to a final R value of 0.060 for 2875 reflections ($R_{wF} = 0.069$). The final refined parameters are shown in Table 1. A final difference Fourier synthesis showed no significant features except for some peaks near the heavy atoms indicating uncorrected absorption effects.

Scattering factors are those of Cromer and Mann [10]. The applied corrections for the anomalous scattering for Sn are $\Delta f' = -0.81$, $\Delta f'' = 1.73$ and for Br $\Delta f' = -0.21$ and $\Delta f'' = 2.68$.

Most calculations were carried out with the Dutch version of the X-RAY SYSTEM [11].

Discussion

The adopted numbering scheme of the non-hydrogen atoms along with the thermal vibrational ellipsoids are shown in an ORTEP drawing [12] of the molecule, Fig. 1. Bond distances and angles are given in Tables 2 and 3.

The crystal structure of *C,N*-{2-[(dimethylamino)methyl]phenyl}diphenyltin bromide (Ia) consists of discrete monomeric molecular units, which are mutually separated by normal Van der Waals distances. The structure reveals a distorted

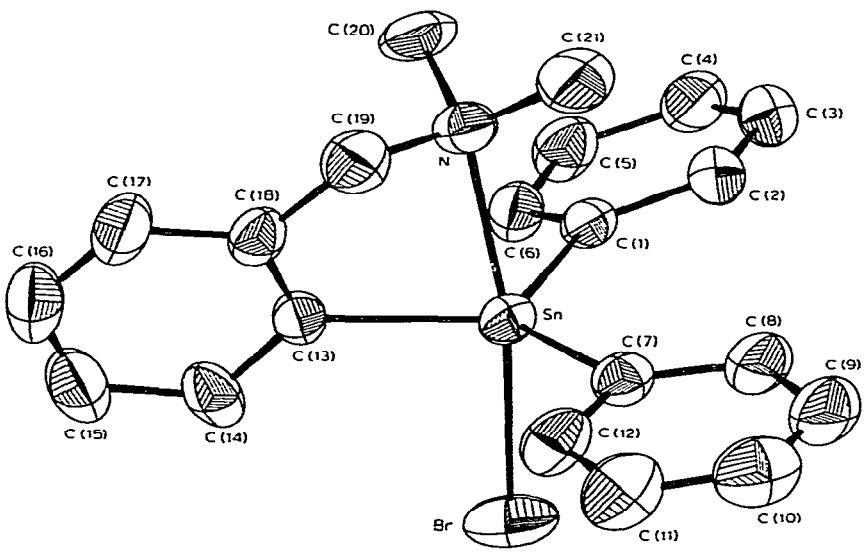


Fig. 1. Molecular geometry of *C,N*-{2-[(dimethylamino)methyl] phenyl}diphenyltin bromide (Ia) (vibrational ellipsoids scaled to include 40% probability).

TABLE 1

FINAL REFINED PARAMETERS [a] WITH STANDARD DEVIATIONS [b]. THE ANISOTROPIC TEMPERATURE FACTORS ARE OF THE FORM: $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2kl\beta_{23} + 2hl\beta_{13})]$

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	$2\beta_{12}$	$2\beta_{23}$	$2\beta_{13}$
Sn	0.5941(1)	0.0809(1)	0.2583(1)	173(1)	37(0)	33(0)	5(1)	7(1)	75(1)
Br	0.8236(2)	0.1793(1)	0.2396(1)	282(3)	71(1)	93(1)	−36(3)	46(2)	200(3)
N	0.3890(13)	−0.0004(6)	0.2985(6)	224(21)	48(5)	47(5)	−38(17)	3(8)	111(17)
C(1)	0.7650(14)	−0.0268(7)	0.2985(7)	189(21)	34(5)	39(5)	15(16)	7(8)	101(17)
C(2)	0.7354(16)	−0.1005(7)	0.2459(7)	249(26)	41(6)	44(5)	−5(19)	−8(9)	107(20)
C(3)	0.8550(18)	−0.1682(8)	0.2739(8)	298(31)	42(6)	55(7)	15(22)	−8(10)	148(24)
C(4)	1.0052(17)	−0.1644(8)	0.3543(8)	289(30)	53(7)	53(6)	42(23)	16(11)	153(24)
C(5)	1.0358(17)	−0.0917(8)	0.4073(8)	267(28)	57(7)	45(6)	65(23)	19(10)	108(21)
C(6)	0.9197(15)	−0.0230(8)	0.3785(7)	226(25)	48(6)	37(5)	22(20)	−6(9)	84(19)
C(7)	0.3902(14)	0.0946(7)	0.1270(7)	164(20)	46(6)	43(5)	−19(17)	3(9)	84(17)
C(8)	0.2868(16)	0.1689(9)	0.1092(8)	209(26)	73(8)	45(6)	55(24)	18(11)	85(20)
C(9)	0.1518(18)	0.1884(11)	0.0233(9)	223(29)	92(10)	56(7)	32(28)	18(14)	73(24)
C(10)	0.1230(18)	0.1294(11)	−0.0435(9)	233(30)	85(10)	58(7)	−14(28)	27(14)	52(24)
C(11)	0.2211(20)	0.0566(10)	−0.0288(8)	335(37)	84(10)	40(6)	−70(31)	−9(12)	81(25)
C(12)	0.3608(18)	0.0377(9)	0.0584(8)	305(33)	63(8)	39(6)	−44(26)	1(10)	92(23)
C(13)	0.5666(14)	0.1620(7)	0.3530(6)	184(21)	33(5)	33(5)	14(16)	3(7)	58(16)
C(14)	0.6808(17)	0.2300(7)	0.3960(7)	263(28)	34(5)	42(5)	47(20)	−1(9)	34(20)
C(15)	0.6517(20)	0.2782(9)	0.4581(9)	373(39)	45(7)	52(7)	53(26)	−15(11)	70(27)
C(16)	0.5142(21)	0.2575(10)	0.4751(8)	385(39)	64(8)	42(6)	97(29)	−13(11)	91(26)
C(17)	−0.3993(20)	0.1906(9)	0.4310(8)	394(40)	65(8)	48(6)	95(29)	8(12)	169(28)
C(18)	−0.4263(16)	0.1416(8)	0.3689(7)	257(27)	48(6)	37(5)	61(21)	13(9)	97(20)
C(19)	−0.2949(16)	0.0715(9)	0.3147(8)	236(26)	58(7)	65(7)	−4(24)	−1(12)	151(24)
C(20)	0.4942(19)	−0.0494(9)	0.3824(9)	349(36)	56(7)	59(7)	25(26)	44(11)	179(28)
C(21)	−0.2614(20)	−0.0575(10)	0.2288(9)	327(36)	83(10)	61(7)	−215(31)	−40(14)	139(28)

[a] The β_{ij} values have been multiplied by 10^4. [b] The standard deviations of the last significant figure are in parentheses.

TABLE 2

BOND DISTANCES (Å) WITH STANDARD DEVIATIONS IN PARENTHESES

Atoms	Å	Atoms	Å
Sn—Br	2.630(2)	C(13)—C(14)	1.394(15)
Sn—N(1)	2.511(12)	C(14)—C(15)	1.415(22)
Sn—C(1)	2.115(10)	C(15)—C(16)	1.384(27)
Sn—C(7)	2.124(9)	C(16)—C(17)	1.387(20)
Sn—C(13)	2.150(12)	C(17)—C(18)	1.411(22)
		C(18)—C(13)	1.393(20)
C(1)—C(2)	1.401(16)		
C(2)—C(3)	1.388(17)	C(18)—C(19)	1.529(16)
C(3)—C(4)	1.384(15)	C(19)—N(1)	1.477(19)
C(4)—C(5)	1.392(18)	C(20)—N(1)	1.500(15)
C(5)—C(6)	1.383(17)	C(21)—N(1)	1.480(16)
C(6)—C(1)	1.398(12)		
C(7)—C(8)	1.398(18)		
C(8)—C(9)	1.420(16)		
C(9)—C(10)	1.394(23)		
C(10)—C(11)	1.359(23)		
C(11)—C(12)	1.447(15)		
C(12)—C(7)	1.395(18)		

five-coordinate trigonal bipyramidal geometry about the tin atom and confirms the proposed arrangement (see I) of the three carbon ligands, the built-in ligand and the bromine atom in equatorial and apical positions, respectively.

The observed N—Sn—Br bond angle of 171° which is not far removed from the

TABLE 3

BOND ANGLES (°) WITH STANDARD DEVIATIONS IN PARENTHESES

Angle	(°)	Angle	(°)
Br—Sn—N(1)	171.0(1)	C(13)—C(14)—C(15)	117.8(14)
Br—Sn—C(1)	92.7(3)	C(14)—C(15)—C(16)	120.4(12)
Br—Sn—C(7)	96.3(3)	C(15)—C(16)—C(17)	121.3(15)
Br—Sn—C(13)	96.2(3)	C(16)—C(17)—C(18)	119.2(17)
		C(17)—C(18)—C(13)	119.2(11)
C(1)—Sn—C(13)	121.2(4)	C(17)—C(18)—C(19)	120.3(14)
C(1)—Sn—C(7)	122.0(4)		
C(7)—Sn—C(13)	114.5(4)	C(1)—C(2)—C(3)	120.5(9)
		C(2)—C(3)—C(4)	120.7(11)
Sn—C(1)—C(2)	122.7(6)	C(3)—C(4)—C(5)	119.3(12)
Sn—C(1)—C(6)	119.1(8)	C(4)—C(5)—C(6)	120.2(9)
Sn—C(7)—C(8)	116.1(8)	C(5)—C(6)—C(1)	121.1(10)
Sn—C(7)—C(12)	124.5(8)	C(6)—C(1)—C(2)	118.1(10)
Sn—C(13)—C(14)	122.7(10)		
Sn—C(13)—C(18)	115.2(7)	C(7)—C(8)—C(9)	122.1(13)
		C(8)—C(9)—C(10)	117.3(14)
C(13)—C(18)—C(19)	120.3(12)	C(9)—C(10)—C(11)	122.3(11)
C(18)—C(19)—N(1)	109.5(10)	C(10)—C(11)—C(12)	120.3(13)
		C(11)—C(12)—C(7)	118.7(13)
C(19)—N(1)—C(20)	109.8(11)	C(12)—C(7)—C(8)	119.3(9)
C(19)—N(1)—C(21)	109.6(10)		
C(20)—N(1)—C(21)	111.2(10)	N(1)—Sn—C(1)	89.3(4)
		N(1)—Sn—C(7)	90.1(4)
		N(1)—Sn—C(13)	75.3(4)

ideal value of 180°, presents clear evidence for the interaction of the intramolecular nitrogen ligand with the central tin atom. Moreover, an almost planar SnC_3 unit (ΣC—Sn—C 357.7°, see Table 3) is present in the structure, with the tin atom residing slightly below that plane on the side of the axial bromine atom. Accordingly, the value of the respective C—Sn—Br bond angles (92.7, 96.2 and 96.3°) exceed significantly the ideal value of 90°. The crystal and molecular structure of Ph_3SnBr, which can be considered to be the parent compound of Ia, has not been reported, but in Ph_3SnCl the C—Sn—Cl (106.4°) and mean C—Sn—C (112.3°) bond angles are close to the tetrahedral value [13].

Planarity of the equatorial SnC_3 units in pentacoordinate Ph_3Sn(IV) structures as well as the influence of the type of equatorial and axial ligands upon bond distances is well-documented [5,14]. The Sn—C bond distances (2.11—2.15 Å) in Ia fall within the range expected for triphenyltin(IV) structures. However, the axial bond lengths are significantly longer than expected. The Sn—Br bond distance of 2.63 Å is 0.1 Å longer than the covalent Sn—Br bond distances in, for example, tetrahedral Me_3SnBr (2.49 Å [15]) and in "pentacoordinate" $BrMe_2Sn(C_4Ph_4)Br$ (2.54 Å [16]). The Sn—N coordination bond (2.51 Å) is longer than that observed in, for example, *cis*-dimethyl-*cis*-(bis-oxinato)tin(IV) [17] where Sn—N bond lengths of 2.31 and 2.38 Å have been observed. Undoubtedly,

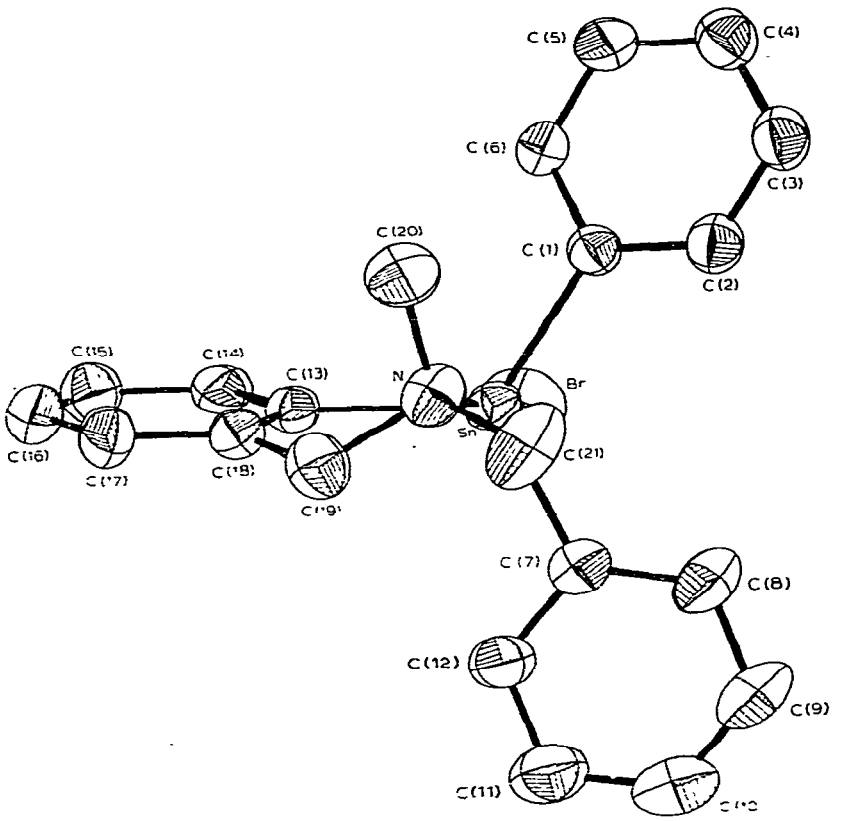


Fig. 2. Molecular structure of Ia viewed along the N—Sn—Br axis showing the puckering of the five-membered chelate ring (vibrational ellipsoids scaled to include 40% probability).

the actual Sn—N bond distance in Ia will be the result of a balance between the Sn—N bond strength which is determined by the Lewis basicity of the amine ligand and the amount of skeletal strain in the five-membered chelate ring. This chelate ring will be rather rigid as a result of the presence of two sp^2 carbon atoms and the restricted rotation around C(13)—C(18). Figure 2 shows that the Sn, C(13), C(18) and C(19) atoms are almost coplanar and that distinct puckering occurs at the C(19)NSn part of the five-membered ring. The bite of the *C,N*-bidentate benzylamine ligand is reflected in the C(13)—Sn—N angle of 75.3°. This value is somewhat smaller than the C—Mn—N angle of 80.2° observed in *C,N*-{2-[(dimethylamino)methyl]phenyl}tetracarbonylmanganese [18].

These features cause a significant deviation of the molecule from mirror symmetry, see Fig. 2. The deviations from the least-square plane through C(13), C(14), C(15), C(16), C(17) and C(18), which makes an angle of 12.5° with the mirror plane through the Ph_2SnBr part of the molecule, are respectively: C(19) 0.11; N —0.68; C(20) —2.14; C(21) —0.31; Sn —0.04 and Br 0.52 Å. Consequently, the distance between the *ortho*-hydrogen atom at C(14) and the bromine atom which is the only short non-bonding distance present in this structure, increases to 2.80 Å.

Acknowledgements

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