^{1}H NMR spectra of Ph_2SbX, $PhSbX_2$, and Ph_3SbX_2 (X = Cl, Br, I); ^{121}Sb Mössbauer spectra of $PhSbX_2$ and crystal structure of Ph_2SbI [1]

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Abstract

^{1}H NMR spectroscopic data of Ph_2SbX, $PhSbX_2$, and Ph_3SbX_2 (X = Cl, Br, I) have been determined by iterative simulation. ^{121}Sb Mössbauer spectra of $PhSbX_2$ (X = Cl, Br, I) have been measured. The synthesis of Ph_2SbI is achieved by reaction of Ph_2SbCl with NaI in ethanol. The crystal structure of Ph_2SbI consists of molecules with pyramidal C_2SbI units.

1. Introduction

Phenylantimony(III) chlorides and bromides are important starting materials for syntheses in organoantimony chemistry. Recently reported methods for the preparation of these halides are the phenyl halogen exchange reactions (1) and (2) between Ph_3Sb and $SbCl_3$ or $SbBr_3$ in the absence of solvent [1-3] or in CH_2Cl_2 [4] or diethylether [5].

$$Ph_3Sb + 2SbX_3 \rightarrow 3PhSbX_2 \qquad (1)$$

$$2Ph_3Sb + SbX_3 \rightarrow 3Ph_2SbX \qquad (2)$$
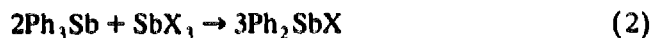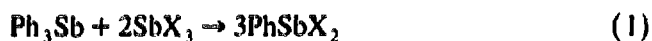
(X = Cl, Br)

Phenylantimony(III) iodides are obtained by the halide exchange reactions (3) and (4) between NaI and the corresponding chlorides in ethanol [6] or HCl [4].

$$Ph_2SbCl + NaI \rightarrow Ph_2SbI + NaCl \qquad (3)$$

$$PhSbCl_2 + 2NaI \rightarrow PhSbI_2 + 2NaCl \qquad (4)$$
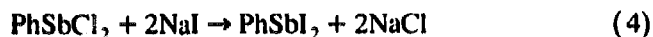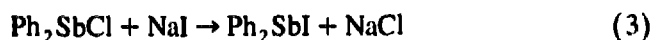
We felt that an analytical method for rapid control of the above reactions would be desirable and report here on the use of ^{1}H NMR spectroscopy in $CDCl_3$ at 360 MHz for this purpose. For reports on ^{1}H NMR data of $PhSbBr_2$ obtained at 60 MHz see Refs. [2,7].

Solid state structures of phenylantimony(III) halides have been investigated with respect to secondary bonding phenomena and the stereochemical role of the lone pair at the antimony atom. Considerable intermolecular interactions through halide bridges and Sb···C interactions have been observed for $PhSbX_2$ (X = Cl, Br, I) [4]. Reports on the crystal structures of diphenylantimony halides do not exhibit a continuous trend with respect to intermolecular interactions. Strong intermolecular fluorine bridges are characteristic for the solid state structure of Ph_2SbF [8]. Mere van der Waals contacts exist between the Ph_2SbCl molecules [9]. In the structure of Ph_2SbBr [3] there are no intermolecular antimony halide bridges but short Sb···C interactions (mean 343 pm).

For comparison with the other phenylantimony(III) halides we have synthesized and determined the structure of diphenylantimony iodide.

2. Results and discussion

2.1. Syntheses of $PhSbX_2$ and Ph_2SbX (X = Cl, Br, I)

For the syntheses of $PhSbX_2$ and Ph_2SbX (X = Cl, Br), the exchange reaction (1) or (2) between freshly sublimed $SbCl_3$ and $SbBr_3$ and commercially available Ph_3Sb in the absence of solvent in the appropriate molar ratio was used as described in Ref. [1]. We found

that the oils formed after several hours may contain mixtures of starting materials and products. Phenylantimony(III) halides that are sufficiently pure for many synthetic purposes were obtained when the products solidified after standing for several days at or below room temperature. Indeed, the lattice energy of the crystalline products could be the driving force for the completion of the distribution reactions. The purity of solid $PhSbCl_2$ or $PhSbBr_2$ judged by ^1H NMR was close to 100%. Solid samples of Ph_2SbCl or Ph_2SbBr contain ca. 5% of impurities (Ph_3SbX_2, Ph_2SbX, $PhSbX_2$). Further purification is achieved by crystallization from CH_2Cl_2.

Both $PhSbI_2$ and Ph_2SbI were obtained by the exchange reactions (3) and (4) in ethanol. Crystallisation of Ph_2SbI from a solution in n-heptane gave crystals suitable for X-ray analyses.

2.2. ^1H NMR spectra

The ^1H NMR parameters δ (chemical shift) and J (coupling constant) of Ph_3Sb, $PhSbX_2$, Ph_2SbX and Ph_3SbX_2 (X = Cl, Br, I) have been calculated for the phenyl protons by iterative simulation. As an example, the experimental and calculated spectra of Ph_2SbI are depicted in Fig. 1. The δ and J data are listed in Table 1. The parameter

$$\Delta\delta = \delta(\text{phenylantimony compound}) - \delta(\text{benzene})$$

demonstrates the effect of the different substituents. $\Delta\delta$ is given in brackets in Table 1 and is represented in Fig. 2. The parent compound Ph_3Sb shows that the substituent effect of an antimony atom is only very small. Larger substituent effects are observed when the phenyl groups are substituted by halogen atoms going from the Ph_3SbX to the $PhSbX_2$ type of compound. The nature of the halogen atom has inverse effects on *ortho* protons on the one hand and *meta* and *para* protons on the other hand. The $\Delta\delta$ values of the *ortho* protons increase with size of the halogen atom, whereas the $\Delta\delta$ parameters of the *meta* and *para* protons increase with electronegativity. It is probably a consequence of the
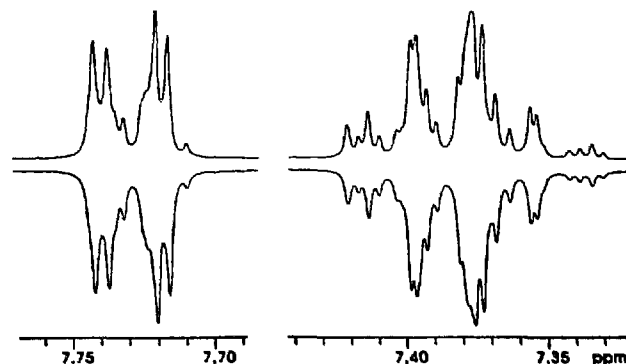

Fig. 1. Experimental (top) and calculated (bottom) ^1H NMR spectra (360 MHz) of Ph_2SbI.

inductive effect that the effects in the *para* positions are smaller than those in the *meta* positons. The largest substituent effects are observed in the case of antimony(V) compounds of the type Ph_3SbX_2, where inverse sterical and electronegative influences seem to add to the constant effect. The coupling constants J are in the region of literature data [10]. They vary only very little with the structure.

As a consequence of the substituent effects, even in mixtures containing compounds of the type $PhSbX_2$, Ph_2SbX and Ph_3SbX_2, there is no overlap of the *ortho* proton signals in the ^1H NMR spectra at 360 MHz and hence quantitative analyses are possible.

2.3. Crystal structure of Ph_2SbI

Bond distances and angles for Ph_2SbI are collected in Table 2. Table 3 contains the atomic coordinates and the equivalent isotropic displacement coefficients. The structure of the molecule and the numbering scheme are shown in Fig. 3. The unit cell is depicted in Fig. 4. The monomeric unit is pyramidal with bond angles between 93.6° and 98.7°. The Sb–C and Sb–I bond lengths are unremarkable. There are no intermolecular antimony iodine distances of less than 430 pm, the sum of van der Waals radii of antimony and iodine [11]. Weak inter-

Table 1

^1H NMR parameters δ and J of triphenylantimony and phenylantimony halides at 360 MHz in $CDCl_3$ ($\Delta\delta$ in brackets, see text)

|	Ph_3Sb	Ph_3SbCl	Ph_2SbBr	Ph_2SbI	$PhSbCl_2$	$PhSbBr_2$	$PhSbI_2$	Ph_3SbCl_2	Ph_3SbBr_2	Ph_3SbI_2
δ 1,5	7.453(0.19)	7.662(0.40)	7.686(0.43)	7.728(0.47)	7.883(0.62)	7.952(0.69)	8.041(0.78)	8.245(0.98)	8.183(0.92)	8.24(0.98)
δ 2,4	7.337(0.08)	7.458(0.20)	7.436(0.18)	7.394(0.13)	7.597(0.34)	7.565(0.31)	7.480(0.12)	7.572(0.31)	7.566(0.31)	7.55(0.29)
δ 3	7.347(0.09)	7.416(0.16)	7.396(0.14)	7.360(0.10)	7.517(0.26)	7.476(0.22)	7.387(0.03)	7.567(0.31)	7.553(0.29)	7.52(0.26)
J 1,2/4,5	7.35	7.61	7.51	7.64	7.64	7.58	7.77	7.99	8.01	8.0
J 1,3/3,5	1.42	1.24	1.28	1.30	1.26	1.25	1.27	1.01	1.00	1.0
J 1,4/2,5	0.64	0.56	0.64	0.54	0.54	0.64	0.44	0.55	0.61	0.5
J 1/5	1.31	1.37	1.47	1.37	1.32	1.27	1.64	1.70	1.74	1.7
J 2,3/3,4	7.54	7.50	7.48	7.50	7.50	7.45	7.47	7.50	7.43	7.5
J 2/4	1.39	1.57	1.44	1.44	1.37	1.27	1.34	1.68	1.62	1.7
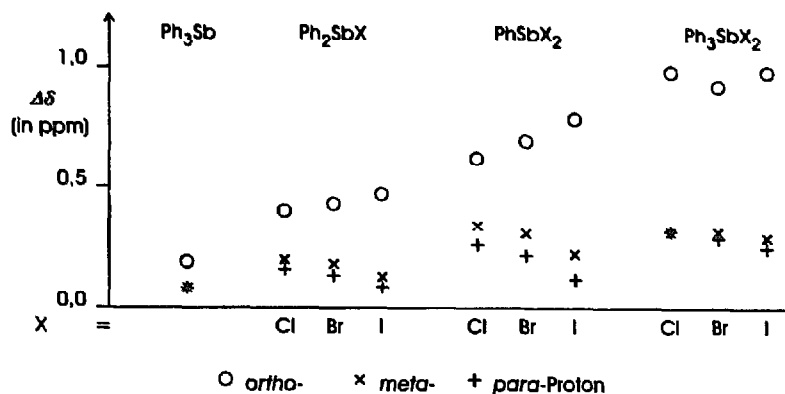
Fig. 2. ^{1}H NMR parameters $\Delta\delta = \delta$(phenylantimony compound) -δ(benzene).

molecular contacts (at 356 and 365 pm respectively) exist, however, between antimony and the C(3a) and C(4a) atoms of a phenyl group of a neighbouring molecule. The structure of Ph$_2$SbI is very similar to the structure of Ph$_2$SbBr [3], also with respect to inter-molecular interactions. Comparison with the structure of PhSbI$_2$ [4] shows that increasing phenyl substitution

leads to a reduction of the coordination at antimony as a consequence of a lower Lewis acidity.

3. Experimental section

For the ^{1}H NMR spectra a Bruker WH 360 spectrometer working at 360 MHz was used.

Table 2
Important bond distances (pm) and angles (°) in Ph$_2$SbI

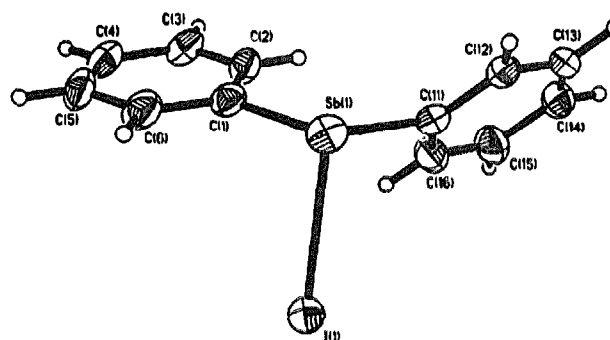| Bond distances			
I(1)–Sb(1)	277.1(1)		
Sb(1)–C(11)	213.6(6)		
Sb(1)–C(1)	213.9(6)		
Sb(1)···C(3a)	356.2		
Sb(1)···C(4a)	365.2		
Bond angles			
I(1)–Sb(1)–C(1)	93.6(2)	I(1)–Sb(1)–C(11)	95.8(2)
C(1)–Sb(1)–C(11)	98.7(2)	Sb(1)–C(1)–C(2)	124.0(4)
Sb(1)–C(1)–C(6)	117.5(4)	Sb(1)–C(11)–C(12)	117.6(4)
Sb(1)–C(11)–C(16)	123.5(4)		

Fig. 3. The molecular structure of Ph$_2$SbI.

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\times 10^4$ pm^2)

Atom	x	y	z	U_{eq} [a]
I(1)	1991(1)	4193(1)	−739(1)	36(1)
Sb(1)	2804(1)	1693(1)	410(1)	33(1)
C(1)	4265(5)	1631(7)	−666(5)	32(2)
C(2)	4462(5)	582(7)	−1571(5)	33(2)
C(3)	5455(5)	594(8)	−2221(6)	39(2)
C(4)	6239(5)	1649(8)	−1956(6)	42(2)
C(5)	6066(5)	2670(8)	−1024(7)	47(2)
C(6)	5086(5)	2643(8)	−395(6)	41(2)
C(11)	1832(4)	149(7)	−598(5)	32(2)
C(12)	1312(5)	−976(7)	45(6)	38(2)
C(13)	672(5)	−1999(7)	−573(7)	42(2)
C(14)	500(5)	−1927(7)	−1789(7)	46(2)
C(15)	1015(5)	−786(7)	−2454(6)	43(2)
C(16)	1680(5)	226(7)	−1859(5)	35(2)

[a] Equivalent isotropic U_{eq} defined as one third of the trace of the orthogonalized U_{ij} tensor.
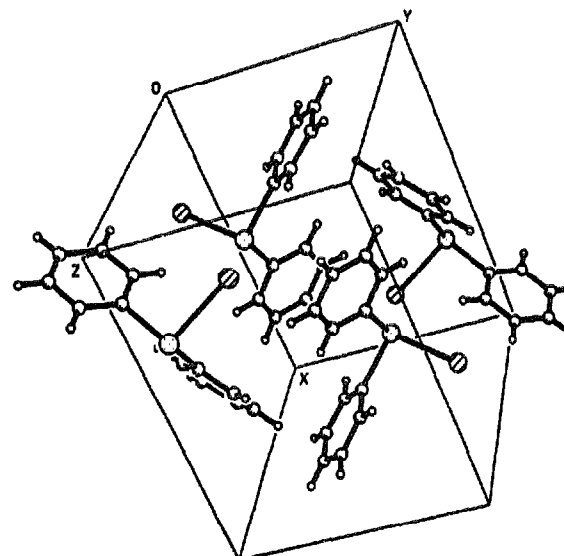

Fig. 4. Unit cell of Ph$_2$SbI.

3.1. Preparations

The compounds Ph$_2$SbCl, PhSbCl$_2$, Ph$_2$SbBr, and PhSbBr$_2$ were prepared by complete redistribution reactions between SbPh$_3$ and SbCl$_3$ or SbBr$_3$ in the appropriate molar ratio in the absence of solvent [1]. The iodides Ph$_2$SbI and PhSbI$_2$ were obtained by exchange reactions of Ph$_2$SbCl or PhSbCl$_2$ respectively with NaI in ethanol [6]. Single crystals of Ph$_2$SbI suitable for X-ray crystallography were obtained by recrystallization from n-heptane at -23°C. Oxidation of Ph$_3$Sb with SO$_2$Cl$_2$, Br$_2$ or I$_2$ gave Ph$_3$SbCl$_2$ [12], Ph$_3$SbBr$_2$ [13] and Ph$_3$SbI$_2$ [13] according to known methods.

3.2. Crystal structure determination

3.2.1. Crystal data

C$_{12}$H$_{10}$ISb; M = 402.9; monoclinic; a = 1213.9(2) pm, b = 904.5(2) pm, c = 1101.7(2) pm; β = 90.27(3)°; V = 1209.7(4) Å^3, Z = 4, D_c = 2.212 g cm^{-3}; μ = 4.870 mm^{-1}, $F(000)$ = 744; space group $P2_1/c$; crystal size 0.9 × 0.4 × 0.4 mm^3.

3.2.2. Structure determination

Data were collected on a Siemens P4 four-circle diffractometer at 173 K with Mo Kα radiation, λ = 0.71073 Å for 6539 reflections in the 2θ–ω mode, of which 2791 were independent reflections (R_{int} = 3.49%) and 2287 were used in the full-matrix least-squares refinement with SHELXTL (VMS) [14]. The structure was solved by direct methods for antimony and iodine and difference Fourier synthesis revealed the positions of the carbon atoms. Hydrogen atoms were calculated as a riding model with isotropic U thermal parameters. After an absorption correction was applied using the program DIFABS [15], the final R values were R_1 = 4.63% and wR = 5.63% (R_1 = 5.43% and wR = 6.43% for all data), with goodness of fit 1.30. Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the deposit number CSD 58925, the names of the authors and the journal citation.

3.3. Mössbauer spectra

The Mössbauer spectra were measured with both source Ca^{121}SnO$_3$ (nominal 0.5 mCi) and absorber at liquid nitrogen temperature using a glass cryostat. Absorbers, containing 15–20 mg of natural antimony per square centimetre, were prepared in a dry-nitrogen glove-box by mixing the appropriate amount of the compound and silicone grease. Lead holders with lucite

Table 4
^{121}Sb Mössbauer parameters of PhSbX$_2$

Compound	δ (mm s^{-1}) ($\pm$0.2))	eQV_{zz} (mm s^{-1}) ($\pm$0.5))	Γ (mm s^{-1}) ($\pm$0.1))
PhSbCl$_2$	-12.9	22.1	2.9
PhSbBr$_2$	-13.8	22.9	3.0
PhSbI$_2$	-14.0	22.8	2.7

windows, permitting sample diameters of 18 mm, were used. Spectra were computer fitted by a least-squares procedure to the sum of 12 Lorentzians. Detailed information on the experimental set-up and data reduction is given in a previous paper [16]. The obtained values of the spectroscopic parameters, the chemical isomer shift δ relative to the source, the ground state quadrupole coupling constant eQV_{zz}, and the full linewidth Γ are given in Table 4. The asymmetry parameter η was always found to be less than 0.1.

Acknowledgements

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