

Solid-state Structures of Triarylantimony Dihalides; the Isolation of Some Mixed-halide Species and Crystal Structures of Ph_3SbI_2 and $[\text{Ph}_4\text{Sb}]\text{I}_3$ †

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Fifteen compounds of stoichiometry R_3SbX_2 ($\text{R} = \text{Ph}$ or substituted aryl; $\text{X}_2 = \text{Br}_2, \text{I}_2$ or IBr) were synthesised and studied by Raman spectroscopy. The crystal structure of Ph_3SbI_2 has been determined, which shows it to be a distorted trigonal-bipyramidal molecule. The distortion from regular trigonal-bipyramidal geometry may be explained by a pseudorotation process towards a rectangular pyramid. Moreover, there are two independent molecules within the unit cell and its distorted structure is in direct contrast to the known Ph_3SbX_2 ($\text{X} = \text{Cl}$ or Br) which both adopt regular trigonal-bipyramidal geometry. The interhalogen compounds R_3SbI_2 also have trigonal-bipyramidal geometry. In direct contrast to the molecules Ph_3EI_2 ($\text{E} = \text{P}$ or As), which ionise in solution to form $[\text{Ph}_3\text{EI}]\text{I}$, Ph_3SbI_2 is chemically changed in acetonitrile solution and forms the ionic $[\text{Ph}_4\text{Sb}]\text{I}_3$, there being no evidence for $[\text{Ph}_3\text{SbI}]\text{I}$. The crystal structure of $[\text{Ph}_4\text{Sb}]\text{I}_3$ has also been determined.

Although the history of organostibine halogen compounds dates back to 1886, when Michaelis and Reese¹ first synthesised Ph_3SbCl_2 via the sodium condensation reaction, further progress in this area, in contrast to similar work in analogous phosphorus and arsenic chemistry, has been slow. There were few further reports until in 1938 Wells² published the crystal structures of three trimethylstibine dihalides, Me_3SbX_2 ($\text{X} = \text{Cl}, \text{Br}$ or I). He concluded that these crystalline compounds were best regarded as intermediate between the five-co-ordinate trigonal-bipyramidal (Me_3SbX_2) and the ionic ($[\text{Me}_3\text{Sb}]\text{X}_2$) structures.

Further progress has been slow: two isomers of $(\text{ClCH}=\text{CH})_3\text{SbCl}_2$ ^{3,4} and a reinvestigation of Ph_3SbCl_2 ⁵ showed trigonal-bipyramidal geometry by X-ray crystallographic methods, and low-temperature X-ray study of Me_3SbF_2 revealed the same stereochemistry.⁶

Subsequently, several other techniques have been employed to investigate the nature of R_3SbX_2 compounds. These include dipole⁷ and conductivity measurements,⁸⁻¹⁰ infrared and Raman spectroscopy,¹¹⁻¹⁵ NQR¹⁶ and Mössbauer techniques.¹⁷⁻¹⁹ These data point, almost overwhelmingly, to the conclusion that compounds of stoichiometry R_3SbX_2 are exclusively trigonal bipyramidal in the solid state.

Even more recently, the behaviour of some R_3SbX_2 compounds has been examined in solution upon the addition of one equivalent of SbX_3 or SbX_5 .^{20,21} Thus, when one mole equivalent of SbX_3 is added to R_3SbX_2 ($\text{R} = \text{Ph}$ or Me , $\text{X} = \text{Cl}$ or Br) a molecular adduct is formed,²⁰ whereas addition of SbX_5 to Ph_3SbX_2 results in the formation of $[\text{Ph}_3\text{SbX}][\text{SbX}_6]$ ($\text{X} = \text{Cl}$ or Br).²¹ These results indicate that the ionisation of R_3SbX_2 compounds is possible under certain conditions and, furthermore, the existence of ionic solid-state nitrates, e.g. $[\text{Me}_3\text{Sb}(\text{NO}_3)]\text{NO}_3$, has been postulated for a number of nitrate species.^{12,22}

However, the available data on R_3SbX_2 ($\text{X} = \text{Cl}, \text{Br}$ or I) compounds are predominantly for the dichlorides, and little has

been reported concerning the corresponding bromide and iodide derivatives. In fact, the communication by Wells² over fifty years ago, ambiguous as it was, represents the sole example of a crystal-structure determination of a diiodotriorganostibine compound. The crystal structure of Ph_3SbBr_2 has been published recently,²³ showing it to possess regular trigonal-bipyramidal geometry in accord with Ph_3SbCl_2 .⁵

Our own recent studies concerning compounds of stoichiometry R_3EX_2 ($\text{E} = \text{P}$ or As ; $\text{X}_2 = \text{Br}_2, \text{I}_2$ or IBr) have revealed that, as well as the generally accepted ionic $[\text{R}_3\text{EX}]\text{X}$ and trigonal-bipyramidal molecular, R_3EX_2 , forms, a third structural type exists. In this form the Group 15 element adopts a molecular four-co-ordinate geometry, onto which the dihalogen is bound as a linear 'spoke', $\text{Ph}_3\text{E}-\text{X}-\text{X}$. This structure has been established for Ph_3AsI_2 ²⁴ and R_3PX_2 [$\text{R}_3 = \text{Ph}_3$ ²⁵ or PhMe_2 ,²⁶ $\text{X} = \text{I}$; $\text{R}_3 = (\text{C}_6\text{H}_4\text{F}-p)_3$ ²⁷ or Ph_3 ,²⁸ $\text{X} = \text{Br}$] by single-crystal X-ray methods. Moreover, solid-state ³¹P-{H} magic angle spinning (MAS) NMR and Raman studies for a large number of R_3PX_2 compounds ($\text{X} = \text{Br}$ or I)^{27,29} indicate that this novel structure may be the preferred solid-state structure, rather than the ionic or trigonal-bipyramidal structures previously accepted by conventional wisdom.

In view of our unexpected results concerning $\text{Ph}_3\text{E}-\text{X}-\text{X}$ ($\text{E} = \text{P}$, $\text{X} = \text{Br}$ or I ; $\text{E} = \text{As}$, $\text{X} = \text{I}$) and the paucity of information regarding the analogous antimony compounds, we have investigated the solid-state structures of a large number of compounds of stoichiometry R_3SbX_2 ($\text{R} = \text{Ph}$ or substituted aryl; $\text{X}_2 = \text{Br}_2, \text{I}_2$ or IBr) the majority of which have not been described before. Additionally, no compound of stoichiometry R_3SbI_2 has previously been studied or even isolated in the solid state. Also we were intrigued to know that if R_3SbI_2 adopted the novel 'spoke' $\text{Ph}_3\text{E}-\text{X}-\text{X}$ structure, which halogen would be bound to the antimony atom.³⁰

We have also established that all compounds of stoichiometry R_3EI_2 ($\text{E} = \text{P}$ or As) ionise completely in solution to form $[\text{R}_3\text{PX}]\text{X}$.²⁵⁻²⁷ Previous workers^{20,21} have shown that R_3SbX_2 ($\text{X} = \text{Cl}$ or Br) ionise in solution under certain conditions and we were interested to know that if Ph_3SbI_2 ionised in solution, whether the familiar $[\text{Ph}_3\text{EI}]\text{I}$ species would

† Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii-xxviii.

result or whether perhaps Ph_3SbX_2 compounds ionise in a different way to produce a different ionised product.

Results and Discussion

All the complexes R_3SbX_2 ($\text{R}_3 = \text{Ph}$ or substituted aryl; $\text{X}_2 = \text{Br}_2, \text{I}_2$ or IBr) were synthesised under strictly anaerobic and anhydrous conditions by treating stoichiometric quantities of the tertiary stibine with the dihalogen or interhalogen in diethyl ether over *ca.* 5 d (see Experimental section). Characterisation data are contained in Table 1. All the compounds were obtained in quantitative yield and recrystallised from diethyl ether.

The crystal structure of Ph_3SbI_2 is illustrated in Fig. 1. Bond lengths and angles and atomic co-ordinates are shown in Tables 2 and 3 respectively. In contrast to the analogous compounds containing lighter Group 15 atoms, which adopt the unusual

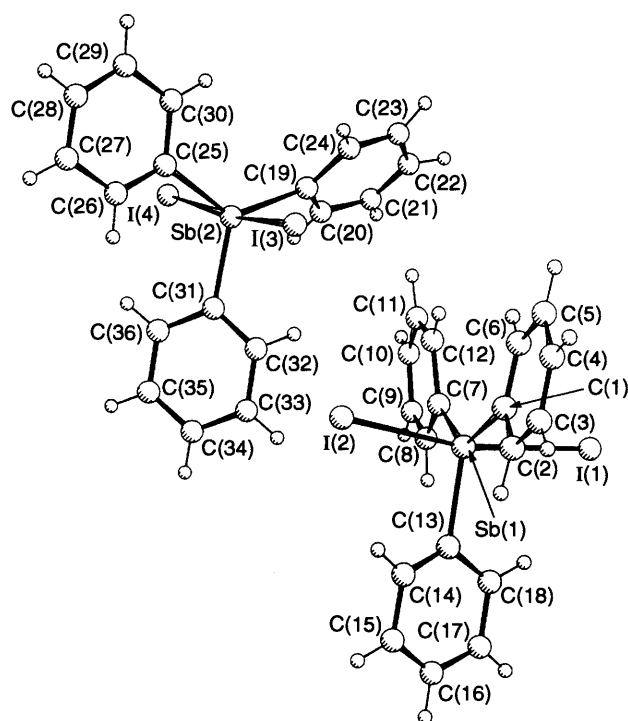


Fig. 1 Structure of Ph_3SbI_2 showing the two crystallographically different antimony sites within the unit cell

four-co-ordinate molecular 'spoke' structure, $\text{Ph}_3\text{E}-\text{I}-\text{I}$ ($\text{E} = \text{P}$ or As), Ph_3SbI_2 adopts a distorted trigonal-bipyramidal structure. These distortions mean that Ph_3SbI_2 contrasts with the regular trigonal-bipyramidal structure of both Ph_3SbCl_2 and Ph_3SbBr_2 . Additionally Ph_3SbI_2 contains two independent molecules within the unit cell, again differing from the regular structures of Ph_3SbX_2 ($\text{X} = \text{Cl}$ or Br). The exact nature of the distortions and the reason why they occur is difficult to assess but for Ph_3SbI_2 , both molecules clearly show evidence of Berry pseudorotation towards a rectangular pyramid with atom C(13) acting as the pivot for molecule 1 and C(31) for molecule 2 (see Table 2).

The Raman spectra of all the compounds studied clearly exhibit a band assignable to either $\nu(\text{Sb}-\text{Br})$, $\nu(\text{Sb}-\text{I})$ or both for the compounds R_3SbBr_2 , R_3SbI_2 and R_3SbIBr , respectively. In contrast to the compounds R_3PX_2 ($\text{R} = \text{aryl}$, alkyl or aryl/alkyl; $\text{X} = \text{Br}$ or I),^{27,29} the frequency of the $\text{E}-\text{X}$ band for the R_3SbX_2 compounds described here shows little variation upon changing the R groups on the tertiary stibine. All the compounds R_3SbIBr clearly show bands assignable to both $\nu(\text{Sb}-\text{Br})$ and $\nu(\text{Sb}-\text{I})$ thus indicating that they also adopt the trigonal-bipyramidal structure exemplified by Ph_3SbX_2 ($\text{X} = \text{Cl}$, Br or I). The low-frequency Raman spectra of the compounds Ph_3SbX_2 ($\text{X}_2 = \text{Br}_2, \text{I}_2$ or IBr) are compared in Fig. 2. Finally, to establish unequivocally Ph_3SbIBr as a genuine compound and not, for instance, a statistical mixture of Ph_3SbBr_2 and Ph_3SbI_2 , its X-ray powder diffraction pattern was recorded and compared to those of Ph_3SbX_2 ($\text{X} = \text{Br}$ or I).

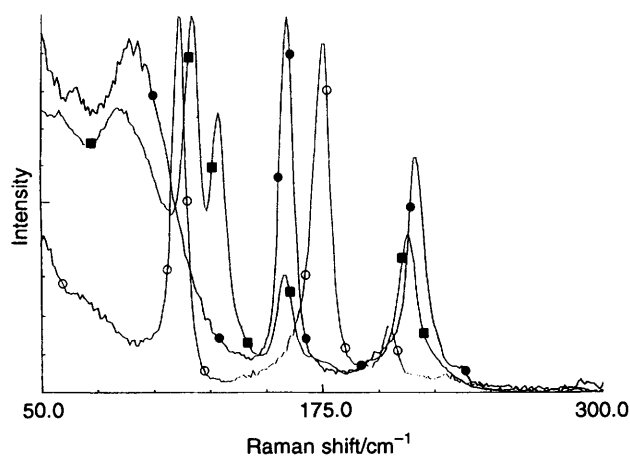


Fig. 2 The low-frequency Raman spectra of Ph_3SbBr_2 (●), Ph_3SbI_2 (○) and Ph_3SbIBr (■)

Table 1 Analytical and spectroscopic data for the compounds R_3SbX_2 ($\text{R} = \text{Ph}$ or substituted aryl; $\text{X}_2 = \text{I}_2, \text{Br}_2$ or IBr)

Compound	Analysis ^a (%)			$\tilde{\nu}(\text{Sb}-\text{Br})/\text{cm}^{-1}$	$\tilde{\nu}(\text{Sb}-\text{I})/\text{cm}^{-1}$
	C	H	X		
Ph_3SbBr_2	42.3 (42.1)	2.9 (2.9)	31.4 (31.2)	159	
<i>(o</i> - MeC_6H_4) ₃ SbBr_2	45.8 (45.4)	3.9 (3.8)	28.0 (28.8)	151	
<i>(m</i> - MeC_6H_4) ₃ SbBr_2	45.3 (45.4)	3.7 (3.8)	28.7 (28.8)	163	
<i>(p</i> - MeC_6H_4) ₃ SbBr_2	45.5 (45.4)	4.1 (3.8)	29.2 (28.8)	163	
<i>(p</i> - FC_6H_4) ₃ SbBr_2	38.4 (38.1)	2.3 (2.1)	27.9 (28.2)	160	
<i>(p</i> - MeOC_6H_4) ₃ SbBr_2	41.1 (41.8)	3.4 (3.5)	25.7 (26.5)	153	
Ph_3SbI_2	35.6 (35.6)	2.5 (2.5)	42.1 (42.1)		111
<i>(o</i> - MeC_6H_4) ₃ SbI_2	39.8 (38.8)	2.5 (2.5)	38.9 (39.1)		108
<i>(p</i> - MeC_6H_4) ₃ SbI_2	39.0 (38.8)	3.4 (3.2)	38.9 (39.1)		120
<i>(p</i> - FC_6H_4) ₃ SbI_2	32.7 (32.7)	1.7 (1.8)	38.3 (38.4)		113
<i>(p</i> - MeOC_6H_4) ₃ SbI_2	37.0 (36.2)	3.3 (3.0)	35.3 (36.4)		112
Ph_3SbIBr	38.8 (38.6)	2.6 (2.7)	22.8 (22.7), 14.5 (14.3)	158	117
<i>(o</i> - MeC_6H_4) ₃ SbIBr	42.0 (41.7)	3.5 (3.5)	20.4 (21.0), 12.6 (13.2)	<i>b</i>	<i>b</i>
<i>(m</i> - MeC_6H_4) ₃ SbIBr	41.0 (41.7)	3.4 (3.5)	21.0 (21.0), 13.2 (13.2)	163	123
<i>(p</i> - MeC_6H_4) ₃ SbIBr	42.0 (41.7)	3.4 (3.5)	21.5 (21.0), 12.8 (13.2)	163	122

^a Calculated values in parentheses. ^b Decomposes in the laser beam.

A comparison of the three powder patterns is illustrated in Fig. 3, from which it can be seen that each compound clearly has its own characteristic diffraction pattern, establishing Ph_3SbIBr as a genuine compound. Additionally the X-ray powder diffraction patterns of Ph_3SbBr_2 and Ph_3SbIBr suggest that these compounds may be isomorphous.

No compound of stoichiometry R_3SbIBr has ever been isolated in the solid state prior to the work presented here. The only previous report on a compound R_3SbIBr concerns the conductimetric studies of Harris and Ali¹⁰ on Ph_3SbIBr . These workers concluded that the compound is non-conducting (and thus molecular) in PhNO_2 solution, a result in agreement with the solid-state studies presented here.

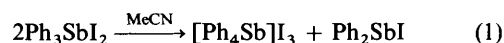
Table 2 Selected bond lengths (Å) and angles (°) for Ph_3SbI_2

I(1)–Sb(1)	2.903(2)	I(3)–Sb(2)	2.875(3)
I(2)–Sb(1)	2.853(2)	I(4)–Sb(2)	2.875(3)
Sb(1)–C(1)	2.09(2)	Sb(2)–C(19)	2.04(2)
Sb(1)–C(13)	2.15(2)	Sb(2)–C(31)	2.08(2)
I(1)–Sb(1)–I(2)	168.13(7)	I(3)–Sb(2)–I(4)	172.74(8)
I(1)–Sb(1)–C(13)	96.6(6)	I(3)–Sb(2)–C(31)	91.7(6)
I(2)–Sb(1)–C(13)	95.3(6)	I(4)–Sb(2)–C(31)	94.3(5)
C(1)–Sb(1)–C(7)	130.2(8)	C(19)–Sb(2)–C(25)	128.6(8)
C(1)–Sb(1)–C(13)	118.1(8)	C(19)–Sb(2)–C(31)	118.4(8)
C(7)–Sb(1)–C(13)	111.6(8)	C(25)–Sb(2)–C(31)	112.9(8)

Table 3 Fractional atomic coordinates for non-hydrogen atoms of Ph_3SbI_2

Atom	x	y	z
Sb(1)	0.4161(1)	0.3313(2)	0.2485(1)
Sb(2)	0.9043(1)	0.1913(2)	0.2643(1)
I(1)	0.3325(1)	0.6017(2)	0.1311(1)
I(2)	0.5234(1)	0.0670(2)	0.3254(1)
I(3)	0.7857(1)	0.0846(2)	0.1614(1)
I(4)	1.0399(1)	0.2783(2)	0.3512(1)
C(1)	0.396(1)	0.228(2)	0.128(1)
C(2)	0.330(2)	0.141(3)	0.148(2)
C(3)	0.317(2)	0.063(3)	0.070(2)
C(4)	0.371(2)	0.073(3)	–0.017(2)
C(5)	0.437(2)	0.153(3)	–0.043(2)
C(6)	0.450(1)	0.234(2)	0.035(2)
C(7)	0.514(1)	0.456(2)	0.256(2)
C(8)	0.506(2)	0.533(3)	0.333(2)
C(9)	0.571(2)	0.616(3)	0.337(2)
C(10)	0.641(2)	0.617(3)	0.266(2)
C(11)	0.652(2)	0.531(3)	0.193(2)
C(12)	0.590(2)	0.446(3)	0.182(2)
C(13)	0.324(1)	0.321(2)	0.388(2)
C(14)	0.319(1)	0.197(2)	0.455(2)
C(15)	0.261(2)	0.190(3)	0.548(2)
C(16)	0.206(2)	0.314(3)	0.563(2)
C(17)	0.207(1)	0.443(2)	0.494(2)
C(18)	0.266(2)	0.446(3)	0.401(2)
C(19)	0.897(1)	0.384(2)	0.157(1)
C(20)	0.889(1)	0.517(2)	0.192(2)
C(21)	0.878(2)	0.657(3)	0.128(2)
C(22)	0.871(2)	0.661(3)	0.027(2)
C(23)	0.885(1)	0.533(3)	–0.017(2)
C(24)	0.893(1)	0.397(2)	0.048(2)
C(25)	0.985(1)	–0.008(2)	0.253(2)
C(26)	0.977(1)	–0.126(2)	0.331(2)
C(27)	1.030(1)	–0.265(2)	0.325(2)
C(28)	1.084(1)	–0.271(2)	0.236(2)
C(29)	1.095(1)	–0.155(3)	0.156(2)
C(30)	1.044(1)	–0.020(2)	0.162(2)
C(31)	0.820(1)	0.181(2)	0.405(2)
C(32)	0.735(2)	0.226(2)	0.401(2)
C(33)	0.677(1)	0.225(2)	0.493(2)
C(34)	0.707(2)	0.175(3)	0.592(2)
C(35)	0.792(1)	0.128(2)	0.596(2)
C(36)	0.851(1)	0.130(2)	0.505(2)

We were interested to know if Ph_3SbI_2 could be ionised in solution and have previously reported that both Ph_3EI_2 (E = Ph or As) ionise completely in solution to form $[\text{Ph}_3\text{EI}]^+$.^{24,29} We thus set out to investigate whether the analogous antimony compound, $[\text{Ph}_3\text{SbI}]^+$, was the ionised species or whether ionisation occurs in a different way. Consequently, a sample of Ph_3SbI_2 was completely dissolved in acetonitrile and allowed to stand for ca. 3 d. During this time some brown crystals were deposited in the flask. A crystal suitable for single-crystal X-ray diffraction was selected. Surprisingly the ionised product was not the expected $[\text{Ph}_3\text{SbI}]^+$ but instead proved to be $[\text{Ph}_4\text{Sb}]^+$, Fig. 4. Thus for Ph_3SbI_2 , migration of a phenyl group occurs to produce the tetraphenylantimony cation. The charge is balanced by the triiodide anion which is presumably formed from free I_2 and I^- in solution. The only other antimony-containing species obtained from this reaction was a white crystalline substance, Ph_2SbI [Found (Calc.): C, 35.3 (35.7); H, 2.2 (2.5%)]. This transformation is therefore given by equation (1). This behaviour is in direct contrast to the compounds



Ph_3EI_2 (E = P or As) both of which ionise in solution to form $[\text{Ph}_3\text{EI}]^+$ quantitatively, and may be related to the weaker Sb–C bonds compared to E–C (E = P or As).^{24,29}

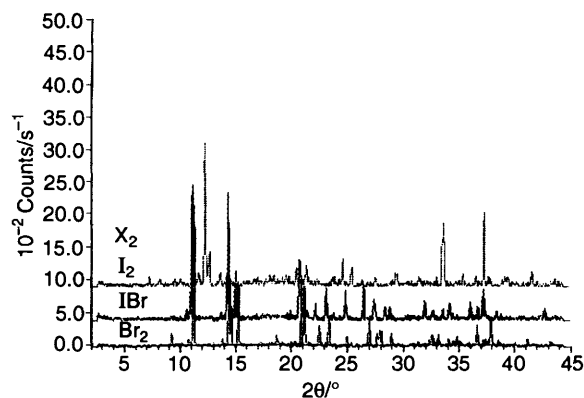


Fig. 3 The X-ray powder diffraction patterns of Ph_3SbX_2 ($\text{X}_2 = \text{Br}_2$, I_2 or IBr)

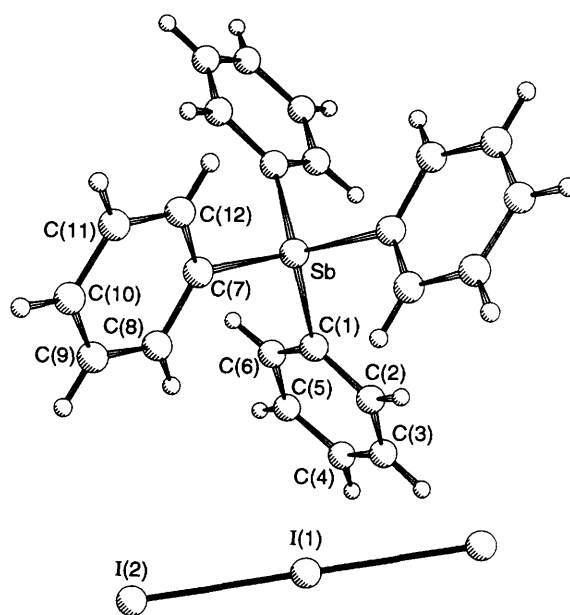


Fig. 4 Crystal structure of $[\text{Ph}_4\text{Sb}]^+\text{I}_3^-$

Table 4 Selected bond lengths (Å) and angles (°) for [Ph₄Sb]I₃

I(1)–I(2)	2.918(1)	Sb–C(7)	2.09(1)
Sb–C(1)	2.09(1)		
I(2)–I(1)–I(2)	177.33(8)	C(7)–Sb–C(7)	103.3(8)
I(1)–I(2)–Sb	156.25(5)	Sb–C(1)–C(2)	121(1)
I(2)–Sb–I(2)	148.38(5)	Sb–C(1)–C(6)	120(1)
C(1)–Sb–C(1)	103.7(8)	Sb–C(7)–C(8)	122(1)
C(1)–Sb–C(7)	112.7(5)	Sb–C(7)–C(12)	118(1)

Table 5 Fractional atomic coordinates for the non-hydrogen atoms of [Ph₄Sb]I₃

Atom	x	y	z
Sb	$\frac{3}{4}$	0.483 6(2)	$\frac{1}{4}$
I(1)	$\frac{1}{4}$	0.669 4(2)	$\frac{1}{4}$
I(2)	0.201 2(1)	0.677 7(2)	0.056 28(8)
C(1)	0.599(1)	0.325(2)	0.269 7(9)
C(2)	0.515(1)	0.359(2)	0.333(1)
C(3)	0.420(2)	0.247(2)	0.348(1)
C(4)	0.410(2)	0.106(2)	0.300(1)
C(5)	0.490(2)	0.074(2)	0.235(1)
C(6)	0.585(1)	0.186(2)	0.219(1)
C(7)	0.715(1)	0.643(2)	0.142 1(8)
C(8)	0.599(1)	0.644(2)	0.094(1)
C(9)	0.580(2)	0.762(3)	0.027(1)
C(10)	0.669(2)	0.873(2)	0.010(1)
C(11)	0.778(2)	0.876(2)	0.060(1)
C(12)	0.804(2)	0.762(2)	0.127(1)

Conclusion

All the compounds R₃SbX₂ (X₂ = Br₂, I or IBr) reported here are trigonal-bipyramidal molecules in the solid state. The authenticity of Ph₃SbIBr has been demonstrated from Raman spectroscopic studies and X-ray powder diffraction, the R₃SbIBr compounds being the first reported examples to be isolated in the solid state. In contrast to the molecules Ph₃SbX₂ (X = Cl or Br), Ph₃SbI₂ exhibits a distorted rather than a regular trigonal-bipyramidal structure, and contains two rather than one molecule in the unit cell. The distortion is towards a rectangular pyramid along the Berry coordinate. Although Ph₃SbI₂ ionises in solution it does not form the expected [Ph₃Sb]I, but rather phenyl migration occurs to produce the unpredicted [Ph₄Sb]I₃.

Experimental

All the compounds described decompose slowly in the presence of moisture, therefore strictly anaerobic and anhydrous conditions were observed for their synthesis. Any subsequent manipulations were carried out inside a Vacuum Atmospheres HE-493 glove-box. Diethyl ether (BDH) was dried by standing over sodium wire for ca. 1 d and subsequently refluxed over CaH₂ in an inert (N₂) atmosphere and distilled directly into the reaction vessel. Tertiary stibines were either synthesised by standard Grignard techniques or obtained commercially from Aldrich (SbPh₃). The purity of all the tertiary stibines was confirmed by elemental analysis (C, H, X) prior to use. Bromine, iodine and iodine monobromide were all obtained commercially from Aldrich and used as received. All the R₃SbX₂ compounds were prepared the same way, the synthesis of Ph₃SbI₂ being typical. Triphenylstibine (3.00 g, 8.50 mmol) was dissolved in diethyl ether (ca. 100 cm³) and subsequently diiodine (2.16 g, 8.50 mmol) was added. After ca. 4 d the resultant off-white solid was isolated using standard Schlenk techniques and dried *in vacuo*. It was then transferred to pre-dried argon-filled ampoules which were flame sealed.

Elemental analyses were performed by the analytical laboratory of this department and the results are presented in

Table 6 Crystal data and details of refinement for Ph₃SbI₂ and [Ph₄Sb]I₃

	Ph ₃ SbI ₂	[Ph ₄ Sb]I ₃
Formula	C ₁₈ H ₁₅ I ₂ Sb	C ₂₄ H ₂₀ I ₃ Sb
<i>M</i>	606.88	810.89
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> 1 (no. 2)	<i>P</i> 2/ <i>n</i> (no. 13)
<i>a</i> /Å	15.883(2)	10.622(4)
<i>b</i> /Å	9.341(2)	8.147(5)
<i>c</i> /Å	12.997(2)	14.966(4)
α /°	78.28(1), 80.54(1)	—
β /°	81.18(1)	93.12(3)
<i>U</i> /Å ³	1850(1)	1293(2)
<i>Z</i>	4	2
<i>D</i> _c /g cm ⁻³	2.178	2.082
<i>F</i> (000)	1120	748
μ /cm ⁻¹	47.96	46.25
Crystal size/mm	0.3 × 0.1 × 0.1	0.3 × 0.2 × 0.2
Total data measured	6349	2598
No. of unique reflections	6259	2460
No. of observed reflections	2355	1115
[<i>F</i> _o > 3σ(<i>F</i> _o)]		
No. of parameters	200	128
Minimum, maximum electron density/e Å ⁻³	−0.88, 0.83	−0.79, 0.77
Maximum least-squares shift to error ratio	0.01	0.04
Weighting scheme parameter <i>g</i> in $w = 1/[\sigma^2(F) + gF^2]$	0.03	0.03
Final <i>R</i> ^a	0.052	0.043
Final <i>R</i> ^b	0.037	0.051

$${}^a R = \sum |F_o| - |F_c| / \sum |F_o|, {}^b R' = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$$

Table 1. Raman spectra were recorded by the University of Manchester Raman Service using a Coherent Innova 90 5W argon-ion laser and a SPEX 1403 double monochromator (focal length 0.85 m) fitted with a BGCS microscope sampling attachment. The radiation was detected using a Hamamatsu R928 photomultiplier tube which was cooled to −30 °C in a Products for Research TE 177 RF-005 cooler housing. The data were processed on a SPEX DM1B data station. X-Ray powder diffraction patterns were recorded using a Scintag XRD2000 powder diffractometer using Cu-K α radiation of $\lambda = 1.5418$ Å.

Single-crystal X-Ray Studies.—Crystals of Ph₃SbI₂ were sealed under argon in thin-walled glass capillaries. The compound [Ph₄Sb]I₃ is air-stable and a suitable crystal was selected after examination under the microscope. Cell dimensions and intensity data were recorded as previously described²⁹ using a CAD4 diffractometer for Ph₃SbI₂ and a Rigaku AFC6S diffractometer for [Ph₄Sb]I₃. The structures were solved and developed by the heavy-atom method (SHELX 86)³¹ and refined by full-matrix least squares (TEXSAN)³². An absorption correction *via* the DIFABS³³ method was applied. The antimony and halide atoms were refined anisotropically and the carbons isotropically. Hydrogens were included in idealised positions. Crystal data and experimental details are given in Table 6. Bond lengths and angles and fractional atomic coordinates for [Ph₄Sb]I₃ are given in Tables 4 and 5 respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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